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# Atmospheric Chemistry of $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x=2$–$4$): Kinetics and Mechanisms of the Chlorine-Atom-Initiated Oxidation

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Smog chamber/FTIR techniques were used to measure $k(Cl+HCF_2O(CF_2CF_2O)_xCF_2H)=(5.3\pm1.5)\times10^{-17}\ cm^3\,molecule^{-1}\,s^{-1}$ in 700 Torr of $N_2/O_2$ diluent at $296\pm1$ K. The Cl-initiated atmospheric oxidation of $HCF_2O(CF_2CF_2O)_xCF_2H$, $x=2$,3 and 4, gave $COF_2$ in molar yields of $(593\pm41)$ %, $(758\pm71)$ % and $(939\pm73)$ %, respectively, with no other observable carbon-containing products (i.e., essentially complete conversion of the hydrofluoropolyethers into $COF_2$). Quantitative infrared spectra for $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x=2$–4) were recorded and used to estimate the radiative efficiencies of the title compounds (1.07, 1.33, and 1.36 $W\,m^{-2}\,ppb^{-1}$). Global warming potentials (100 year time horizon) of 3870, 4730 and 5060 were estimated for $HCF_2O(CF_2CF_2O)_xCF_2H$, $x=2$, 3 and 4, respectively. The results are discussed with respect to the atmospheric chemistry and environmental impact of hydrofluoropolyethers.

## 1. Introduction

Recognition of the adverse environmental consequences of the release of chlorofluorocarbons (CFCs) and Halon into the atmosphere[1,2] has led to an international effort to replace CFCs with environmentally acceptable alternatives. While safeguarding the ozone layer has been at the center of these efforts, concerns related to global climate change are becoming an increasingly important consideration in the choice of alternative compounds because of their significant atmospheric lifetime and radiative properties. Radiative forcing is the common metric used to compare the impacts of external drivers of climate change and is defined as the change in net irradiance ($W\,m^{-2}$) at the tropospause caused by a change in an external driver of the climate system. In the context of greenhouse gases, the change normally considered is a 1 ppb increase in the concentration of the gas in the troposphere and is termed *radiative efficiency* with units of $W\,m^{-2}\,ppb^{-1}$. The overall radiative forcing of a particular greenhouse gas is then the radiative efficiency of the compound multiplied by its atmospheric concentration. Radiative forcing values are useful in assessing the relative impacts on climate of long-lived greenhouse gases, such as fluorinated ethers. Perfluoropolyethers (PFPEs) and hydrofluoropolyethers (HFPEs) have been used as replacements for CFCs as heat transfer fluids and refrigeration working fluids. PFPEs and HFEs do not contain chlorine and therefore do not contribute to chlorine based catalytic destruction of stratospheric ozone. PFPEs do not contain hydrogen atoms and do not react in the lower atmosphere. The atmospheric lifetimes of PFPEs are determined by photolysis in the upper atmosphere and are expected to be long, probably $>800$ years.[3] The long lifetimes of PFPEs combined with their large radiative efficiencies result in these compounds having high global warming potentials (GWPs). HFPEs contain one or more carbon-hydrogen bonds and react with OH radicals in the troposphere. This reduces the atmospheric lifetime of HFPEs compared to PFPEs and CFCs and thus reduces their GWPs.

A new class of HFPEs, having the structure $HCF_2O(CF_2CF_2O)_xCF_2H$, has recently been developed. Atmospheric oxidation of $HCF_2O(CF_2CF_2O)_xCF_2H$ will be initiated by reaction with OH radicals [reaction (1)]:

$$HCF_2O(CF_2CF_2O)_xCF_2H + OH \rightarrow HCF_2O(CF_2CF_2O)_xCF_2 + H_2O \tag{1}$$

The alkyl radical produced in reaction (1) adds $O_2$ rapidly to give a peroxy radical, which we choose to abbreviate to $R_fOCF_2OO$ [reaction (2)]:

$$HCF_2O(CF_2CF_2O)_xCF_2 + O_2 + M \rightarrow R_fOCF_2OO + M \tag{2}$$

This peroxy radical will react with NO, $NO_2$, $HO_2$, or other peroxy radicals,[4–6] mainly $CH_3O_2$ under atmospheric conditions [reactions (3a)–(6b)]:

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$$R_fOCF_2OO + NO \rightarrow R_fOCF_2O + NO_2 \quad (3a)$$

$$R_fOCF_2OO + NO + M \rightarrow R_fOCF_2ONO_2 + M \quad (3b)$$

$$R_fOCF_2OO + NO_2 \rightarrow R_fOCF_2OONO_2 \quad (4)$$

$$R_fOCF_2OO + HO_2 \rightarrow R_fOCF_2OOH + O_2 \quad (5)$$

$$R_fOCF_2OO + CH_3O_2 \rightarrow R_fOCF_2O + CH_3O + O_2 \quad (6a)$$

$$R_fOCF_2OO + CH_3O_2 \rightarrow R_fOCF_2OH + HCHO + O_2 \quad (6b)$$

The importance of these reactions is determined by the relative abundances of NO, $NO_2$, $HO_2$, and $CH_3O_2$ and the rates of reactions (3–6).

Prior to their large-scale industrial use, an assessment of the atmospheric chemistry, and hence environmental impact, of HFPEs is needed. To improve our understanding of the atmospheric chemistry of HFPEs in general, and $HCF_2O(CF_2CF_2O)_xCF_2H$, in particular, samples of $HCF_2O(CF_2CF_2O)_2CF_2H$ (bp = 110 °C), $HCF_2O(CF_2CF_2O)_3CF_2H$ (bp = 133 °C) and $HCF_2O(CF_2CF_2O)_4CF_2H$ (bp = 160 °C) were prepared by 3M. Smog chamber/FTIR techniques were used to determine the kinetics and products of the chlorine atom initiated oxidation of $HCF_2O(CF_2CF_2O)_xCF_2H$. IR spectra were measured and used to determine the radiative efficiencies for the title compounds. The results are reported herein.

## Experimental Section

Experiments were performed in a 140 L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[7] The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. The loss of HFPEs and formation of products were monitored by FTIR spectroscopy. IR spectra were derived from 32 co-added interferograms with a spectral resolution of 0.25 $cm^{-1}$ and an analytical path length of 26.2 m.

Cl atoms were generated by the photolysis of molecular chlorine in air diluent [reaction (7)]:

$$Cl_2 + h\nu \rightarrow 2\,Cl \quad (7)$$

Samples of $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x = 2–4$) were obtained from the 3M Company. The stated purity of $HCF_2O(CF_2CF_2O)_xCF_2H$ was >99% ($x = 2$), >96% ($x = 3$) and 94% ($x = 4$). Sample impurities were various cyclic isomers with the same nominal formula as the parent compound minus 2 fluorine atoms. The samples of $HCF_2O(CF_2CF_2O)_xCF_2H$ were subjected to several freeze-pump-thaw cycles prior to use. All experiments were performed at 296 ± 1 K in 700 Torr total pressure of $N_2/O_2$ diluent. Analysis of the IR spectra was achieved through a process of spectral stripping in which small fractions of the reference spectrum were subtracted incrementally from the sample spectrum.

The decay of reactants and reference compounds and formation of products were monitored using their characteristic absorptions in the infrared over the following wavelength ranges (in $cm^{-1}$): $HCF_2O(CF_2CF_2O)_xCF_2H$, 1033 and 1368; $COF_2$, 773–775 and 1900–1980; $CF_2ClCH_3$, 850–950; and $CF_3CF_2H$, 710–730.

The relative rate method is a well-established technique for measuring the reactivity of Cl atoms with organic compounds.[8] Kinetic data were derived by monitoring the loss of HFPE relative to one or more reference compounds [reactions (8) and(9)]:

$$Cl + HFPE \rightarrow products \quad (8)$$

$$Cl + Reference \rightarrow products \quad (9)$$

Provided that the HFPE and the reference compound are lost only by reaction with chlorine atoms and neither HFPE nor the reference compounds are reformed in any process, then it can be shown that [Eq. (10)]:

$$\mathrm{Ln}\left(\frac{[\mathrm{HFPE}]\mathrm{to}}{[\mathrm{HFPE}]\mathrm{t}}\right) = \frac{k_{\mathrm{HFPE}}}{k_{\mathrm{Reference}}}\,\mathrm{Ln}\left(\frac{[\mathrm{Reference}]\mathrm{to}}{[\mathrm{Reference}]\mathrm{t}}\right) \quad (10)$$

where $[HFPE]_{t0}$, $[HFPE]_t$, $[Reference]_{t0}$, and $[Reference]_t$ are the concentrations of the HFPE and reference at times $t_0$ and $t$, and $k_{HFPE}$ and $k_{Reference}$ are the rate constants for reactions of the HFPE and the reference with Cl atoms. Plots of $Ln([HFPE]_{t0}/[HFPE]_t)$ versus $Ln([Reference]_{t0}/[Reference]_t)$ should be linear, pass through the origin and have a slope of $k_{HFPE}/k_{Reference}$. In smog chamber experiments unwanted loss of reactants and products via photolysis, dark chemistry and heterogeneous reactions have to be considered. Control experiments were performed in which mixtures of reactants (except $Cl_2$) in air were subjected to UV irradiation for 15 min and reactant/product mixtures obtained after the UV irradiation were allowed to stand in the dark in the chamber for 40 min. There was no observable loss (<1%) of reactants or reference compounds suggesting that photolysis, dark chemistry and heterogeneous reactions are not a significant complication over the time scale of the present experiments.

Quoted uncertainties are two standard deviations from the least-squares regressions (forced through zero) together with our estimated uncertainties (±1% of the initial concentration) associated with the IR spectral analysis of the relative reactant and reference concentrations.

## 2. Results and Discussion

### 2.1. Kinetics of the Reaction of Cl Atoms with HFPEs

Relative rate experiments were performed to investigate the kinetics of reaction (11) relative to reactions (12) and (13):

$$Cl + HCF_2O(CF_2CF_2O)_xCF_2H \quad (x = 2-4) \rightarrow products \quad (11)$$

$$Cl + CF_3CF_2H \rightarrow products \quad (12)$$

$$Cl + CF_2ClCH_3 \rightarrow products \quad (13)$$

The initial concentrations were 1.25–2.85 mTorr $HCF_2O(CF_2CF_2O)_xCF_2H$, 282–1387 mTorr $Cl_2$, and either 2.28–2.56 mTorr $CF_3CF_2H$ or 2.12–2.28 mTorr $CF_2ClCH_3$ in 700 Torr of either $N_2$ or air diluent. The observed loss of the $HCF_2O(CF_2CF_2O)_xCF_2H$ versus those of reference compounds are shown in Figure 1.

As seen from Figure 1, there was no discernable difference in the reactivity of the three HFPEs studied. Linear least squares analyses of the composite data sets in Figure 1 give $k_{11}/k_{12} = 0.206 \pm 0.016$ and $k_{11}/k_{13} = 0.138 \pm 0.011$ where the uncertainties include uncertainties in the IR analysis and two standard deviations from the regression analysis. Using literature values of $k_{12} = (2.5 \pm 0.6) \times 10^{-16}$[9] and $k_{13} = (3.90 \pm 0.52) \times$

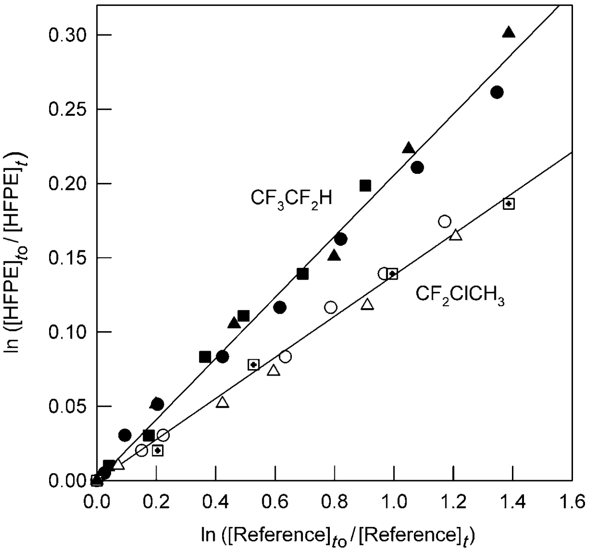

**Figure 1.** Decay of $HCF_2O(CF_2CF_2O)_2CF_2H$ (circles), $HCF_2O(CF_2CF_2O)_3CF_2H$ (triangles) and $HCF_2O(CF_2CF_2O)_4CF_2H$ (squares) versus $CF_3CF_2H$ (filled symbols) and $CF_2ClCH_3$ (open symbols) in the presence of Cl atoms in 700 Torr total pressure of either $N_2$ or air (cross-haired symbols). Separate experiments were conducted for each compound–reference combination.

$10^{-16}$[8] cm$^3$ molecule$^{-1}$ s$^{-1}$ (based on $k(Cl+CH_4) = 1.0\times10^{-13}$) gives $k_{11} = (5.15\pm1.30)\times10^{-17}$ and $(5.38\pm0.84)\times10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. The fact that consistent values of $k_{11}$ were derived from experiments using different reference compounds suggests the absence of significant systematic errors in the present work. 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, $k_{11} = (5.3\pm1.5)\times10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. There are no literature data for $k_{11}$ to compare with our results.

We find that $HCF_2O(CF_2CF_2O)_2CF_2H$, $HCF_2O(CF_2CF_2O)_3CF_2H$, and $HCF_2O(CF_2CF_2O)_4CF_2H$ have indistinguishable reactivities towards Cl atoms. This seems entirely reasonable based upon expectations that the $(CF_2CF_2O)$ groups will not react with Cl atoms, and that its influence on the reactivity of the -$CF_2H$ groups will not change markedly upon increasing "x" from two to four. Hence, the results presented herein can be generalized to $k_{11} = (5.3\pm1.5)\times10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for $x \geq 2$.

### 2.2. Products of Cl-Initiated Oxidation

The atmospheric degradation mechanism was studied using the UV irradiation of $HCF_2O(CF_2CF_2O)_xCF_2H(x{=}2–4)/Cl_2/O_2/N_2$ mixtures. Reaction mixtures consisted of 1.62–2.55 mTorr $HCF_2O(CF_2CF_2O)_xCF_2H$, 2.3–5.6 Torr $Cl_2$, and 14–73 Torr $O_2$ in 700 Torr $N_2$ diluent. Figure 2 shows IR spectra at 650–2100 cm$^{-1}$ obtained before (panel A) and after (panel B) subjecting a mixture containing 1.62 mTorr $HCF_2O(CF_2CF_2O)_4CF_2H$ and 3.4 Torr $Cl_2$ in 700 Torr of $N_2/O_2$ to UV irradiation for 33 min. Subtraction of the IR features attributed to $HCF_2O(CF_2CF_2O)_4CF_2H$ from panel B gives the product spectrum in panel C. Comparison of the product features in panel C with the reference spectrum in panel D shows the formation of

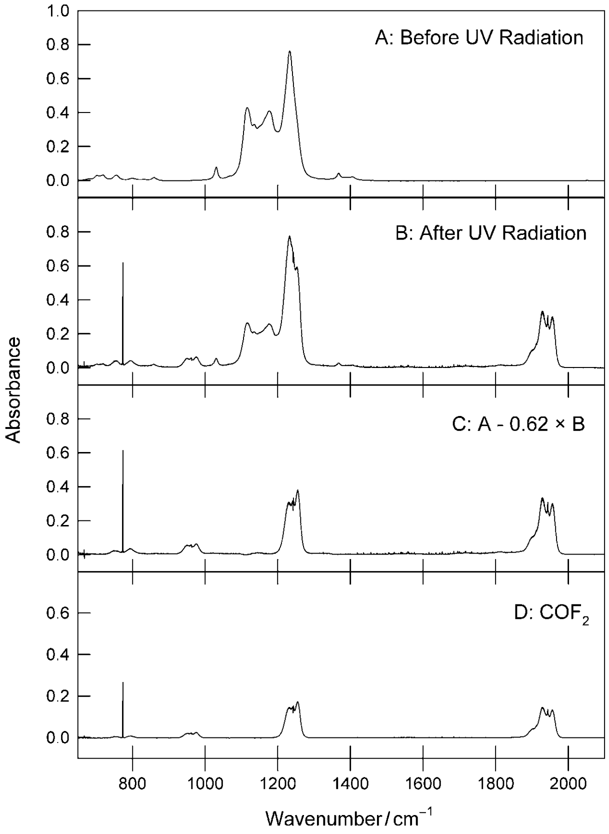

**Figure 2.** IR spectra obtained before (A) and after (B) a 33 min irradiation of a mixture containing 1.62 mTorr $HCF_2O(CF_2CF_2O)_4CF_2H$, 3.4 Torr $Cl_2$ and 15 Torr $O_2$ in 700 Torr of $N_2$ diluent. Subtraction of features attributable to $HCF_2O(CF_2CF_2O)_4CF_2H$ gives the product spectrum shown in panel C. A reference spectrum of $COF_2$ is shown in panel D.

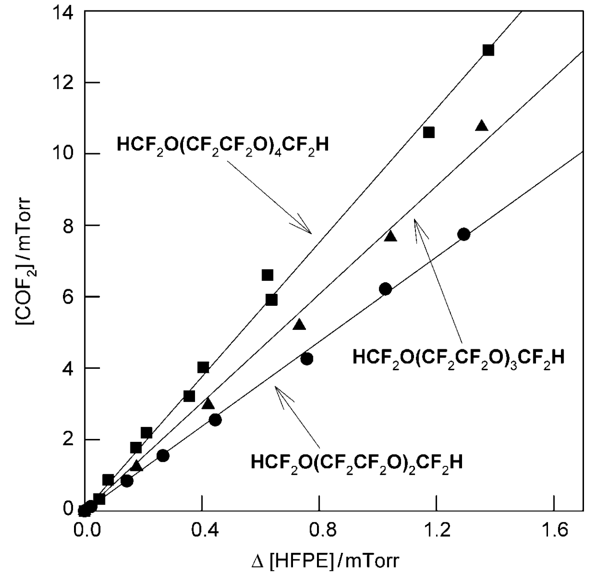

**Figure 3.** Formation of $COF_2$ following UV irradiation of mixtures of either $HCF_2O(CF_2CF_2O)_4CF_2H$ (two replicate experiments), $HCF_2O(CF_2CF_2O)_3CF_2H$ (one experiment) or $HCF_2O(CF_2CF_2O)_2CF_2H$ (one experiment), and $Cl_2$ in 700 Torr of $O_2/N_2$.

$COF_2$. Figure 3 shows a plot of the observed formation of $COF_2$ versus the loss of $HCF_2O(CF_2CF_2O)_2CF_2H$, $HCF_2O(CF_2CF_2O)_3CF_2H$ and $HCF_2O(CF_2CF_2O)_4CF_2H$.

As seen from Figure 3, the formation of $COF_2$ scaled linearly with the HFPE loss over the range studied (up to 61% consumption of the HFPEs). The linearity of the formation of $COF_2$ shown in Figure 3 suggests the absence of significant loss of $COF_2$ via secondary reactions in the chamber. There were no other carbon-containing products discernable in the IR spectra. The lines through the data in Figure 3 give molar yields of $COF_2$ of $(939\pm73)\%$, $(758\pm71)\%$ and $(593\pm41)\%$ for the oxidation of $HCF_2O(CF_2CF_2O)_4CF_2H$, $HCF_2O(CF_2CF_2O)_3CF_2H$ and $HCF_2O(CF_2CF_2O)_2CF_2H$, respectively.

Quoted uncertainties include two standard deviations from the regression analysis and 5% uncertainties in the calibration of $COF_2$ and HFPE spectra. Within the experimental uncertainties, the observed formation of $COF_2$ accounts for the entire loss of the $HCF_2O(CF_2CF_2O)_xCF_2H$. Given the absence of any other product features we also conclude that $COF_2$ accounts for the entire loss of $HCF_2O(CF_2CF_2O)_xCF_2H$, $x=2$–4.

### 2.3. IR Spectra and Radiative Efficiencies of $CHF_2O(CF_2CF_2O)_xCHF_2$ ($x=2$–4)

The IR spectra of $HCF_2O(CF_2CF_2O)_xCF_2H$ (x = 2–4) were recorded in 700 Torr of air diluent at $(295\pm2)$ K and are shown in Figure 4. The integrated cross-sections (650–1500 $cm^{-1}$) are $(9.25\pm0.46)\times10^{-16}$, $(8.52\pm0.43)\times10^{-16}$ and $(7.02\pm0.35)\times10^{-16}$ for $HCF_2O(CF_2CF_2O)_4CF_2H$, $HCF_2O(CF_2CF_2O)_3CF_2H$ and $HCF_2O(CF_2CF_2O)_2CF_2H$, respectively.

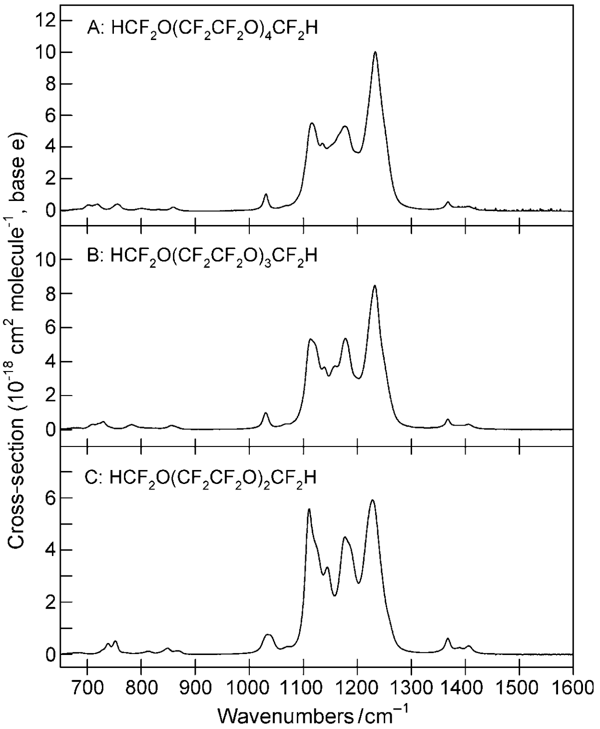

**Figure 4.** Infrared spectrum of $HCF_2O(CF_2CF_2O)_4CF_2H$ (A), $HCF_2O(CF_2CF_2O)_3CF_2H$ (B), and $HCF_2O(CF_2CF_2O)_2CF_2H$ (C) in 700 Torr of air, $295\pm2$ K (base e).

Compounds that absorb at wavelengths of 8–14 microns (700–1300 $cm^{-1}$) in the optically thin spectral region of the atmosphere, known as the "atmospheric window", hinder the escape of terrestrial radiation and increase the temperature at the surface of the Earth. Vibrational transitions associated with C–F bonds occur largely in the atmospheric window, and, consequently, highly fluorinated compounds tend to have high radiative efficiency values.

Using the method outlined by Pinnock et al.[10] and the IR spectra shown in Figure 4, we calculate radiative efficiencies for $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x=2,3,4$) of 1.07, 1.33, and 1.36 $W\,m^{-2}\,ppb^{-1}$, respectively. The trend in increasing *radiative efficiency* with increasing number of internal ($CF_2CF_2O$) units is consistent with the radiative efficiency in the latest Intergovernmental Panel on Climate Change (IPCC) report for $HCF_2O(CF_2CF_2O)CF_2H$ (HFE-338pcc13) of 0.87 $W\,m^{-2}\,ppbv^{-1}$.[12] Using the structure-activity relationship (SAR) derived by Young et al.,[11] to estimate radiative efficiencies of fluorinated ethers, we calculate 0.94, 1.20, and 1.45 $W\,m^{-2}\,ppb^{-1}$ for $HCF_2O(CF_2CF_2O)_2CF_2H$, $HCF_2O(CF_2CF_2O)_3CF_2H$ and $HCF_2O(CF_2CF_2O)_4CF_2H$, respectively. The radiative efficiency values predicted by SAR are in good agreement (within 15%) with our measurements. It is worth noting that the radiative efficiencies of $HCF_2O(CF_2CF_2O)_3CF_2H$ and $HCF_2O(CF_2CF_2O)_4CF_2H$, measured in this work, are larger than for any of the HPFEs considered in the latest Intergovernmental Panel on Climate Change (IPCC)[12] (the radiative efficiency $HCF_2OCF_2OCF_2CF_2OCF_2H$ is reported by the IPCC as 1.37 $W\,m^{-2}\,ppb^{-1}$, however, a recent study[13] has shown this value to be erroneously high, and a revised radiative efficiency of 1.02 $W\,m^{-2}\,ppb^{-1}$ was recommended).

### 2.4. Atmospheric Implications

The reaction of Cl atoms with $HCF_2O(CF_2CF_2O)_xCF_2H$ occurs via hydrogen abstraction from one of the terminal $-CF_2H$ groups [reaction (14)]:

$$Cl + HCF_2O(CF_2CF_2O)_xCF_2H \rightarrow CF_2O(CF_2CF_2O)_xCF_2H + HCl \tag{14a}$$

$$Cl + HCF_2O(CF_2CF_2O)_xCF_2H \rightarrow HCF_2O(CF_2CF_2O)_xCF_2 + HCl \tag{14b}$$

The radicals formed in reaction (14) will add $O_2$ to give peroxy radicals [reaction (2)], which will undergo self- or cross-reactions to produce the corresponding alkoxy radicals. The alkoxy radicals are expected to decompose via the elimination of a $COF_2$ molecule and initiate a sequence of reactions in which the radical "unzips" by shedding successive $COF_2$ molecules [reactions (15)–(19)]:

$$HCF_2O(CF_2CF_2O)_xCF_2O \rightarrow HCF_2O(CF_2CF_2O)_{x-1}CF_2CF_2O + COF_2 \tag{15}$$

$$HCF_2O(CF_2CF_2O)_{x-1}CF_2CF_2O \rightarrow HCF_2O(CF_2CF_2O)_{x-1}CF_2 + COF_2 \quad (16)$$

$$HCF_2O(CF_2CF_2O)_{x-1}CF_2 + O_2 \rightarrow HCF_2O(CF_2CF_2O)_{x-1}CF_2O_2 \quad (17)$$

$$\begin{aligned} &HCF_2O(CF_2CF_2O)_{x-1}CF_2O_2 + ROO \\ &\rightarrow HCF_2O(CF_2CF_2O)_{x-1}CF_2O + RO + O_2 \end{aligned} \quad (18)$$

$$HCF_2O(CF_2CF_2O)_{x-1}CF_2O \rightarrow HCF_2O(CF_2CF_2O)_{x-1} + COF_2 \quad (19)$$

Reactions (16) through (19) are repeated until only the terminal $HCF_2O$ group remains. This group undergoes final conversion into $COF_2$ [reaction (20)]:

$$HCF_2O + O_2 \rightarrow COF_2 + HO_2 \quad (20)$$

In contrast to the situation in the experimental chamber, the concentrations of fluorinated peroxy radicals in the atmosphere will be extremely small, and the self- and cross-reactions described above will not be of atmospheric significance. In the atmosphere the fate of the fluorinated peroxy radicals will be reaction with NO, $NO_2$, $HO_2$, or $CH_3O_2$ radicals [reactions (3)–(6)]. Reaction with NO gives the corresponding alkoxy radical and $NO_2$ as major products with the fluorinated organic nitrate as a minor product. Reaction with $NO_2$ gives a thermally unstable peroxynitrate whose fate is decomposition to reform $NO_2$ and the peroxy radical.[14,15] Reaction with $HO_2$ radicals gives a hydroperoxide which will be returned back to the fluorinated peroxy radical pool via reaction with OH radicals or photolysis.[16] Reaction with $CH_3O_2$ radicals is expected to proceed via two channels [reactions (6a) and (6b)], leading to the formation of alkoxy radicals [reaction (6a)] and a fluorinated alcohol and formaldehyde [reaction (6b)]. The atmospheric fate of the fluorinated alcohol is expected to be heterogeneous elimination of HF followed by hydrolysis of the acid fluoride to give a carboxylic acid; for example, from $HCF_2O(CF_2CF_2O)_xCF_2H$ one might expect the formation of $HCF_2O(CF_2CF_2O)_xC(O)OH$. The possibility that small amounts of fluorinated acidic compounds may be formed during the atmospheric oxidation of HFPEs is interesting and merits further study but is beyond the scope of the present work.

While to the best of our knowledge there are no previous studies of $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x = 2$–4), the results from the present work can be compared with those for similar HFPEs. Wallington et al.[17] reported a rate-constant ratio relative to $CF_3CF_2H$ for the reactions of chlorine atoms towards $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ of $k/k_{12} = 0.205 \pm 0.019$. Tuazon[6] studied the reactivity of chlorine atoms towards $HCF_2OCF_2OCF_2H$ and $HCF_2O(CF_2CF_2O)CF_2H$ and determined rate constant ratios of $k/k_{12} = 0.208 \pm 0.006$ and $0.188 \pm 0.004$, respectively. The reactivities reported by Tuazon and Wallington et al. are, within the experimental uncertainties, indistinguishable from that determined for the HFPEs in the present work ($k_{11}/k_{12} = 0.206 \pm 0.016$). Tuazon[6] also studied the reaction of Cl atoms with $HCF_2OCF_2OCF_2CF_2OCF_2H$, but for reasons which are unclear, reported a reactivity of $HCF_2OCF_2OCF_2CF_2OCF_2H$ which is approximately 25 % below those of the other HFPEs.

**Table 1.** Chlorine and OH kinetic data at 295 ± 5 K for selected HFEs and HFPEs.

| Compound | $k$(Cl) | $k$(OH) |
|---|---|---|
| $HCF_2OCF_2H$ | $(5.7 \pm 1.5) \times 10^{-14}$[20] | $(2.4 \pm 0.5) \times 10^{-15}$[21] |
| $HCF_2OCF_2OCF_2H$ | $(5.0 \pm 1.1) \times 10^{-17}$[6] | $(2.4 \pm 0.7) \times 10^{-15}$[22] |
| $HCF_2O(CF_2CF_2O)CF_2H$ | $(4.5 \pm 1.0) \times 10^{-17}$[6] | $(4.7 \pm 1.6) \times 10^{-15}$[20] |
| **$HCF_2O(CF_2CF_2O)_xCF_2H$ ($x \geq 2$)** | **$(5.3 \pm 1.5) \times 10^{-17}$[a]** | – |
| $HCF_2OCF_2OCF_2CF_2OCF_2H$ | $(5.0 \pm 1.4) \times 10^{-17}$[17] | $(4.6 \pm 1.6) \times 10^{-15}$[20] |
| $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ | $(5.0 \pm 1.4) \times 10^{-17}$[17] | – |
| $CF_3OCF_2H$ | $(2.3 \pm 0.3) \times 10^{-17}$[23] | $(4.9 \pm 1.0) \times 10^{-16}$[19] |

[a] Determined in this work.

Table 1 show kinetic data for the reactions of Cl atoms and OH radicals with selected HFEs and HFPEs. Given the similar chemical environment of the C–H bonds in $HCF_2OCF_2H$, $HCF_2OCF_2OCF_2H$, $HCF_2O(CF_2CF_2O)CF_2H$, $HCF_2O(CF_2CF_2O)_xCF_2H$, $HCF_2OCF_2OCF_2CF_2OCF_2H$ and $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$, it is not surprising that these compounds react with chlorine radicals at similar rates. As discussed by Sander et al.,[19] the reactivity of OH radicals towards $HCF_2OCF_2H$ has been studied by several groups using different experimental techniques and is well established. As with the reaction with chlorine atoms, we would expect the reactivity of $HCF_2OCF_2H$, $HCF_2OCF_2OCF_2H$, $CF_2O(CF_2CF_2O)CF_2H$, and $HCF_2OCF_2OCF_2CF_2OCF_2H$ towards OH radicals to be comparable. Consistent with this expectation, the reactivity reported by Cavalli et al.[20] for OH radicals towards $HCF_2OCF_2OCF_2H$ is indistinguishable from that recommended by Sander et al.[19] for $HCF_2OCF_2H$. Surprisingly, Cavalli et al.[20] reported that OH radicals react with $HCF_2O(CF_2CF_2O)CF_2H$ and $HCF_2OCF_2OCF_2CF_2OCF_2H$ at rates which are approximately a factor of 2 greater than for $HCF_2OCF_2H$ and $HCF_2OCF_2OCF_2H$. It is difficult to understand the reactivity trend reported by Cavalli et al.[20] Close inspection of the experimental data reveals that the magnitude of the consumptions of the HFEs in the investigation by Cavalli et al.[20] was rather small (< 7 %). The measurement of such small consumptions of compounds which have broad IR absorption features is challenging and we believe that the uncertainties reported by Cavalli et al. are probably underestimated. We proceed with the assumption that the reactivity of OH radicals towards the HFPEs studied in the present work will be similar to that of OH radicals towards $HCF_2OCF_2H$. This assumption needs to be investigated in further experimental work.

Wallington et al.[17] and Tuazon[6] reported the formation of $COF_2$ in a near-unit yield per carbon atom from the chlorine-atom-initiated oxidation of $HCF_2OCF_2OCF_2H$, $HCF_2O(CF_2CF_2O)CF_2H$, $HCF_2OCF_2OCF_2CF_2OCF_2H$ and $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ in 700–740 Torr of air/$N_2$/$O_2$ at 298 K. Cavalli et al.[20] conducted four experiments of the chlorine-atom-initiated oxidation of $HCF_2OCF_2OCF_2CF_2OCF_2H$ in 740 Torr of air and reported the formation of $COF_2$ in a molar yield of 300–485 %. The large range reported by Cavalli et al. presumably reflects difficulties in measuring the small amounts of $COF_2$ formed (0.16–0.74 mTorr) and HFPE lost (0.03–0.24 mTorr) in their experiments—approximately an order of magnitude smaller than those reported herein (see Figure 3). The molar

$COF_2$ yields measured in this work are consistent with expectations based on the previous work by Tuazon,[6] Cavalli et al.,[20] and Wallington et al.[17]

The atmospheric oxidation of HFPEs is initiated by reaction with OH radicals. Polyfluorinated compounds, such as HFPEs, are relatively unreactive in the troposphere, as the electron-withdrawing nature of fluorine reduces the probability of hydrogen abstraction by the hydroxyl radical. The presence of the ether bond generally increases the reactivity of organic compounds with hydroxyl radicals, yet atmospheric lifetimes for HFEs and HFPEs are still typically on the order of years. During the course of this work, experiments were performed to measure the kinetics of OH radicals towards $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x = 2$–4), using the methyl nitrite photolysis in the presence of NO as a source of OH radicals Photolysis of $CH_3ONO$ is a convenient source of OH radicals in relative rate studies, however, $CH_3ONO$ itself reacts with OH at a moderate rate (with a rate constant of approximately $3\times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$[18]), scavenges OH radicals, and makes loss of a less reactive compound (e.g., $HCF_2O(CF_2CF_2O)_xCF_2H$) small and difficult to measure. To circumvent this problem, we have in the past successfully employed a variation on the conventional relative rate method, in which the loss of the reactant is monitored indirectly by observing the formation of its oxidation products (e.g., $COF_2$).[19] Interestingly, we were unable to utilize this indirect method as we did not observe any formation of $COF_2$ (< 0.2 mTorr) in these experiments. The fact that $COF_2$ does not appear as a major product in these experiments suggests a competing different fate of the inital peroxy radical, $HCF_2O(CF_2CF_2O)_xCF_2O$, in the presence of large concentrations of $NO_x$ [reaction (21)]:

$$HCF_2O(CF_2CF_2O)_xCF_2O \rightarrow HCF_2O(CF_2CF_2O)_x + COF_2 \qquad (15)$$

$$HCF_2O(CF_2CF_2O)_xCF_2O + NO \rightarrow HCF_2O(CF_2CF_2O)_xC(O)F + FNO \qquad (21)$$

The experimental system at Ford used in the present study is not well suited to a determination of $k_1$ and further work using other techniques is needed.

Radiative efficiencies of 1.07–1.36 W m$^{-2}$ ppb$^{-1}$ were determined for $HCF_2O(CF_2CF_2O)_xCF_2O$ ($x = 2$–4). Radiative efficiency provides a measure of the instantaneous effect of a compound on climate; yet, this effect will only be realized if the compound is long-lived in the atmosphere. The potential of long-lived greenhouse gases to affect climate is assessed through the global warming potential (GWP), which is a function of both radiative efficiency and atmospheric lifetime of the forcing agent. Integrating the radiative efficiency over time gives the Absolute Global Warming Potential (AGWP) for time horizon $t'$ defined as [Eq. (22)]:[16]

$$\mathrm{AGWP}(x(t)) = \int_0^{\tau} F_x[x(t)]\mathrm{d}t \qquad (22)$$

where $F_x$ is the radiative forcing per unit mass of species $x$, $x(t)$ describes the decay with time of a unit pulse of compound $x$, and $t'$ is the time horizon considered. The AGWP has units of W m$^{-2}$ ppb$^{-1}$ yr and quantifies the future integrated radiative forcing to the time horizon of a unit mass pulse emission of a greenhouse gas.

The GWP for time horizon $t'$ can then be defined as [Eq. (23)]:

$$\mathrm{GWP}(x(t)) = \frac{\int_0^{t'} F_x \exp\left(-t/\tau_x\right)\mathrm{d}t}{\int_0^{t'} F_{CO_2} R(t)\mathrm{d}t} \qquad (23)$$

where $F_{CO2}$ is the radiative forcing of $CO_2$, $R$(t) is the response function that describes the decay of an instantaneous pulse of $CO_2$, and with the decay of the pulse of compound $x$ assuming it obeys a simple exponential decay curve determined by a response time of $\tau_x$. The denominator in Equation (23) is the absolute global warming potential (AGWP) for $CO_2$, which has been evaluated by the WMO as 0.676 W m$^{-2}$ ppm$^{-1}$ for a 100-year time horizon.[16] Thus, Equation (23) can be rewritten as [Eq. (24)]:

$$\mathrm{GWP}(x(t)) = \frac{\int_0^{t'} F_x \exp\left(-t/\tau_x\right)\mathrm{d}t}{0.676} \qquad (24)$$

Using the radiative efficiencies determined herein, and assuming a lifetime for $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x = 2$–4) similar to that of $HCF_2OCF_2H$ (26 years[12]), we estimate GWPs over a 100-year time horizon for $HCF_2O(CF_2CF_2O)_2CF_2H$, $HCF_2O(CF_2CF_2O)_3CF_2H$, and $HCF_2O(CF_2CF_2O)_4CF_2H$ of 3870, 4730 and 5060, respectively.

## 3. Conclusions

The goal of this work was to provide insight into the kinetics and mechanism of the atmospheric oxidation of the HFPEs, $HCF_2O(CF_2CF_2O)_xCF_2H$, $x = 2$,3 and 4. Chlorine atoms react with $HCF_2O(CF_2CF_2O)_xCF_2H$ with a rate constant of $(5.3\pm1.5)\times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The reactivity of chlorine atoms towards $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x = 2$–4) does not depend on the size of the central $(CF_2CF_2O)_x$ group. Hence, we are able to generalize our results for $x \geq 2$; $k(Cl+HCF_2O(CF_2CF_2O)_xCF_2H) = (5.3\pm1.5)\times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

The atmospheric oxidation of $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x = 2$–4) is initiated by reactions with OH radicals and gives carbonyl fluoride, $COF_2$, as the major product. $COF_2$ is removed from the troposphere via contact with water surfaces and hydrolysis to HF and $CO_2$ in rain/aerosol/cloud/sea water with a lifetime of approximately 5–10 days.[4]

$HCF_2O(CF_2CF_2O)_xCF_2H$ does not contain any chlorine and will not contribute to stratospheric ozone depletion via the well-established chlorine-based chemistry. As with all hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), and hydrofluoropolyethers (HFPEs), the ozone depletion of $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x = 2$–4) is, for all practical purposes, zero.

HFPEs absorb strongly in the optically thin spectral region of the atmosphere, known as the "atmospheric window". Using the radiative efficiencies determined herein, and assuming a lifetime for $HCF_2O(CF_2CF_2O)_xCF_2H$ ($x = 2–4$) similar to that of $HCF_2OCF_2H$, we estimate significant global warming potentials over a 100-year time horizon for $HCF_2O(CF_2CF_2O)_2CF_2H$, $HCF_2O(CF_2CF_2O)_3CF_2H$, and $HCF_2O(CF_2CF_2O)_4CF_2H$ of 3870, 4730 and 5060, respectively.

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