Kinetics and Products of Chlorine Atom Initiated Oxidation of HCF₂OCF₂OCF₂CF₂OCF₂H and HCF₂O(CF₂O)_n-(CF₂CF₂O)_mCF₂H

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ABSTRACT: Smog chamber/FTIR techniques were used to measure $k(Cl + HCF_2OCF_2OCF_2CF_2OCF_2H) = k(Cl + HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H) = (5.0 \pm 1.4) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in 700 Torr of N₂/O₂ diluent at 296 ± 1 K. The Cl-initiated atmospheric oxidation of HCF₂OCF₂OCF₂OCF₂CF₂OCF₂H and the sample of HCF₂O(CF₂O)_n(CF₂CF₂O)_mCF₂H used in this work gave COF₂ in molar yields of (476 ± 36)% and (859 ± 63)%, respectively, with no other observable carbon containing products (i.e., essentially complete conversion of both hydrofluoropolyethers into COF₂). The results are discussed with respect to the atmospheric chemistry and environmental impact of hydrofluoropolyethers of the general formula HCF₂O(CF₂O)_n(CF₂CF₂O)_mCF₂H. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 40: 819–825, 2008

INTRODUCTION

Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere [1,2] has led to an international effort to replace CFCs

with environmentally acceptable alternatives. 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 more than 800 years

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[3]. The long lifetimes of HFPEs combined with their large instantaneous forcings result in these compounds having high global warming potentials (GWPs). HF-PEs contain one or more carbon–hydrogen bonds and react with OH radicals in the troposphere. The reaction with OH radicals reduces the atmospheric lifetime of HFPEs compared to PFPEs and CFCs and thus reduces their GWPs.

$$\begin{aligned} &\text{HCF}_2\text{O}(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2\text{H} + \text{OH} \\ &\rightarrow \text{HCF}_2\text{O}(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2 + \text{H}_2\text{O} \quad (1a) \\ &\text{HCF}_2\text{O}(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2\text{H} + \text{OH} \\ &\rightarrow \text{CF}_2\text{O}(\text{CF}_2\text{O})_n(\text{CF}_2\text{CF}_2\text{O})_m\text{CF}_2\text{H} + \text{H}_2\text{O} \quad (1b) \end{aligned}$$

The alkyl radicals produced in reaction (1) add O_2 rapidly to give peroxy radicals,

$$HCF_{2}O(CF_{2}O)_{n}(CF_{2}CF_{2}O)_{m}CF_{2} + O_{2} + M$$

$$\rightarrow HCF_{2}O(CF_{2}O)_{n}(CF_{2}CF_{2}O)_{m}CF_{2}OO + M (2a)$$

$$CF_{2}O(CF_{2}O)_{n}(CF_{2}CF_{2}O)_{m}CF_{2}H + O_{2} + M$$

$$\rightarrow OOCF_{2}O(CF_{2}O)_{n}(CF_{2}CF_{2}O)_{m}CF_{2}H + M (2b)$$

The peroxy radicals will react with NO, NO₂, HO₂, or CH₃O₂ [4–6], for HCF₂O(CF₂O)_n-(CF₂CF₂O)_mCF₂OO radicals, which we abbreviate to R_fOCF₂OO:

$$R_f OCF_2 OO + NO \rightarrow R_f OCF_2 O + NO_2$$
 (3a)

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

$$R_{f}OCF_{2}OO + NO_{2} \rightarrow R_{f}OCF_{2}OONO_{2}$$
 (4)

 $R_f OCF_2 OO + HO_2 \rightarrow R_f OCF_2 OOH + O_2 \quad (5)$

$$R_f OCF_2 OO + CH_3 O_2$$

 $\rightarrow R_{\rm f} {\rm OCF}_2 {\rm O} + {\rm CH}_3 {\rm O} + {\rm O}_2 \tag{6a}$

$$R_f OCF_2 OO + CH_3 O_2$$

$$\rightarrow R_{\rm f} {\rm OCF}_2 {\rm OH} + {\rm HCHO} + {\rm O}_2 \tag{6b}$$

The importance of these reactions is determined by the relative abundances of NO, NO₂, HO₂, and CH₃O₂ and the rates of reactions (3)–(5). Alkyl peroxynitrates are thermally unstable and decompose rapidly to regenerate the peroxy radicals and NO₂ [7,8]. The hydroperoxide is returned to the peroxy radicals via reaction with OH or photolysis [9].

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 smog chamber/FTIR techniques were used to determine the kinetics and products of the chlorine atom initiated oxidation of $HCF_2OCF_2OCF_2CF_2OCF_2H$ and $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$. The results are reported herein.

EXPERIMENTAL

Experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer [10]. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. The loss of HFPE and formation of products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm⁻¹ and an analytical path length of 27.4 m.

Cl atoms were generated by the photolysis of molecular chlorine in air diluent,

$$Cl_2 + hv \rightarrow 2Cl$$
 (7)

 $HCF_2OCF_2OCF_2CF_2OCF_2H$ and $HCF_2O(CF_2O)_n$ - $(CF_2CF_2O)_m CF_2H$ were obtained from the Solvay Chemical Company (Brussels, Belgium). The stated purity of HCF2OCF2OCF2CF2OCF2H was more than 99%. HCF₂O(CF₂O)_n(CF₂CF₂O)_mCF₂H was supplied as a mixture with n values in the range 0-5 and m values in the range 0-7, the mixture had an average molecular weight of 572. A GC-MS analysis revealed the presence of nine major components of the $HCF_2O(CF_2O)_n$ - $(CF_2CF_2O)_mCF_2H$ mixture. The mass spectrum of each of the components had prominent m/z peaks at 51 (CHF₂⁺), 97 (C₂F₃O⁺), 100 (C₂F₄⁺), and 213 $(C_4F_7O_2^+)$, which are consistent with the general formula of $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ but do not allow a specific identification of the components. It is rather unusual in experimental studies such as the present to work with a reactant, which is a mixture of different compounds and this deserves some comment. In the present work, we used a sample that was a mixture of at least nine different compounds of the general formula $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$. It is well known that -CF2O- and -CF2CF2O- units are unreactive toward Cl atoms (and OH radicals, important in the atmosphere). The reactivity of $HCF_2O(CF_2O)_n$ - $(CF_2CF_2O)_mCF_2H$ is confined to the C-H bonds on either end of the molecule. The chemical environment of the C-H bonds is expected to be independent of the number of $-CF_2O-$ and $-CF_2CF_2O-$ units in the molecule. For the purposes of the present study, we

assume that we can treat the mixture as a simple compound, and the validity of this assumption is discussed in the discussion and atmospheric chemistry section. The samples of HCF₂O(CF₂O)_n(CF₂CF₂O)_mCF₂H and HCF₂OCF₂OCF₂CF₂OCF₂H were subjected to freeze–pump–thaw cycling prior to use. All experiments were performed at 296 ± 1 K in 700 Torr total pressure of N₂/O₂ diluent. The decay of the reactants and references were measured using their characteristic absorptions in the infrared over the following wavelength ranges (in cm⁻¹): HCF₂O-(CF₂O)_n(CF₂CF₂O)_mCF₂H/HCF₂OCF₂OCF₂CF₂OC-F₂H 1015–1045 and 1350–1435; COF₂ 773–775; CF₂CICH₃ 850–950; and CF₃CF₂H 710–730.

The relative rate method is a well-established technique for measuring the reactivity of Cl atoms with organic compounds. Kinetic data were derived by monitoring the loss of HFPE relative to one, or more, reference compounds. Providing that the HFPE and the reference are lost only by the reaction with chlorine atoms, and neither HFPE nor the reference compounds are reformed in any process then it can be shown that

$$\ln\left(\frac{[\text{HFPE}]_{t_0}}{[\text{HFPE}]_t}\right) = \frac{k_{\text{HFPE}}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_{t_0}}{[\text{reference}]_t}\right)$$

where $[HFPE]_{t_0}$, $[HFPE]_t$, $[reference]_{t_0}$, 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 $\ln([HFPE]_{t_0}/[HFPE]_t)$ versus $\ln([reference]_{t_0}/[reference]_t)$ should be linear, pass through the origin and have a slope of $k_{HFPE}/k_{reference}$. The uncertainties reported in this paper are two standard deviations unless stated otherwise.

RESULTS

Kinetics of the Reaction of Cl Atoms with HFPEs

Relative rate experiments were performed using the FTIR system to investigate the kinetics of reactions (8) and (9). The techniques used are described in detail elsewhere [11]. The rates of reactions (8) and (9) were measured relative to reactions (10) and (11):

$$Cl + HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H \rightarrow products$$
(8)

$$Cl + HCF_2OCF_2OCF_2CF_2OCF_2H \rightarrow products$$
 (9)



Figure 1 Decay of $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ (circles) and $HCF_2OCF_2OCF_2CF_2OCF_2H$ (triangles) versus CF_3CF_2H (open symbols) and CH_3CF_2CI (filled symbols) in the presence of Cl atoms in 700 Torr total pressure of air.

 $Cl + CF_3CF_2H \rightarrow products$ (10)

$$Cl + CH_3CFlCl \rightarrow products$$
 (11)

Reaction mixtures consisted of 7.0-12.2 mTorr HFPE, 433–497 mTorr Cl₂, and either 2.6–4.2 mTorr CF₃CF₂H or 3.2-6.1 mTorr CH₃CF₂Cl in 700 Torr of air diluent. The observed loss of the HFPEs versus those of reference compounds is shown in Fig. 1. As seen from Fig. 1, there was no discernible difference in the reactivity of the two HFPEs studied. Linear least-squares analyses of the composite data set in Fig. 1 give $k_8/k_{10} = k_9/k_{10} = 0.205 \pm 0.019$ and $k_8/k_{11} = k_9/k_{11} = 0.124 \pm 0.021$, where the uncertainties include uncertainties in the IR analysis and two standard deviations from the regression analysis. Using literature values of $k_{10} = (2.5 \pm 0.6) \times 10^{-16}$ [12] and $k_{11} = (3.90 \pm 0.52) \times 10^{-16}$ [11] (based on $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13}$ gives $k_8 = k_9 = (5.1 \pm 10^{-13})$ 1.3 × 10⁻¹⁷ and $k_8 = k_9 = (4.8 \pm 1.0) \times 10^{-17} \text{ cm}^3$ molecule $^{-1}$ s $^{-1}$, respectively. We choose to cite a final value, which is the average of the individual determinations together with error limits that encompass the extremes of the determinations, hence, $k_8 = k_9 = (5.0$ \pm 1.4) × 10⁻¹⁷ cm³ molecule⁻¹ s⁻¹.

Products of HFPE Oxidation

The atmospheric degradation mechanism was studied using the UV irradiation of $HCF_2O(CF_2O)_n$ - $(CF_2CF_2O)_mCF_2H/Cl_2/O_2/N_2$ mixtures. Reaction mixtures consisted of 0.79–3.89 mTorr HCF_2O -



Figure 2 IR spectra of a mixture consisting of 3.67 m Torr HCF₂OCF₂OCF₂CF₂OCF₂H and 4.11 Torr Cl₂ in 700 Torr total pressure of N₂/O₂ diluent before (A) and after (B) 23 min UV irradiation. Subtraction of features attributed to HCF₂OCF₂OCF₂CF₂OCF₂H from panel B gives the product spectra shown in panel C. A reference spectrum of COF₂ is shown in panel D. The small structured features at 1300– 1800 cm⁻¹ in panels B and C are attributable to the presence of small amounts of H₂O in the IR beam.

 $(CF_2O)_n(CF_2CF_2O)_mCF_2H$ or 3.7–7.5 mTorr HCF₂-OCF₂OCF₂CF₂OCF₂H, 4.1–5.1 Torr Cl₂, and 71–84 Torr of O₂ in 700 Torr of N₂ diluent. Figure 2 shows IR spectra at 800–2000 cm⁻¹ obtained before (panel A) and after (panel B) subjecting a mixture containing 3.7 mTorr HCF₂OCF₂OCF₂CF₂OCF₂H and 4.1 Torr Cl₂ in 700 Torr of N₂/O₂ to UV irradiation for 23 min. Subtraction of the IR features attributed to HCF₂OCF₂OCF₂CF₂OCF₂H 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 COF₂.

Figure 3 shows a plot of the observed formation of COF₂ versus the loss of HCF₂O(CF₂O)_n-(CF₂CF₂O)_mCF₂H and HCF₂OCF₂OCF₂CF₂OCF₂H. As seen from Fig. 3, the formation of COF₂ scaled linearly with the HFPE loss over the range studied (up to 71% consumption of HCF₂O(CF₂O)_n(CF₂CF₂O)_m-CF₂H and up to 40% consumption of HCF₂OCF₂-OCF₂CF₂OCF₂H). The linearity of the formation of COF₂ shown in Fig. 3 suggests the absence of significant loss of COF₂ via secondary reactions in the chamber. No other carbon-containing products were discernible in the IR spectra. The lines through the data in Fig. 3 give molar yields of COF₂ of (859 \pm 63)% for the oxidation of



Figure 3 Formation of COF_2 versus the loss of $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ (triangles) and $HCF_2OCF_2OCF_2CF_2OCF_2H$ (circles) observed following UV irradiation of mixtures consisting of 1.23–3.89 m Torr $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ and 4.44–4.75 Torr Cl_2 in 700 Torr total pressure of N_2/O_2 diluent at 296 ± 1 K and mixtures consisting of 1.94–7.46 mTorr $HCF_2OCF_2OCF_2CF_2OCF_2H$ and 4.06–4.24 Torr Cl_2 in 700 Torr total pressure of N_2/O_2 diluent.

 $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ and $(476 \pm 36)\%$ for the oxidation of $HCF_2OCF_2OCF_2CF_2OCF_2H$, 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 $HCF_2OCF_2OCF_2CF_2OCF_2H$. Given the absence of any other product features, we also conclude that COF_2 accounts for the entire loss of the $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$.

DISCUSSION AND ATMOSPHERIC CHEMISTRY

The reaction of Cl atoms with $HCF_2O(CF_2O)_n$ - $(CF_2CF_2O)_mCF_2H$ occurs via hydrogen abstraction from the terminal $-CF_2H$ groups:

$$Cl + HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$$

$$\rightarrow CF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H + HCl$$
(12a)
$$Cl + HCF_2O(CF_2O)_n(CF_2CF_2O)_nCF_2H$$

$$\rightarrow$$
 HCF₂O(CF₂O)_n(CF₂CF₂O)_mCF₂ + HCl

The radicals formed in reaction (12) 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 COF₂ molecule and initiate a sequence of reactions in which the radical "unzips" by shedding successive COF₂ molecules. 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, NO₂, HO₂, or CH₃O₂ radicals (reactions (3)–(6)). Reaction with NO gives the corresponding alkoxy radical and NO₂ as major products with the fluorinated organic nitrate as a minor product. Reaction with NO₂ gives a thermally unstable peroxynitrate whose fate is decomposition to reform NO₂ and the peroxy radical. Reaction with HO₂ radicals gives a hydroperoxide, which will be returned back to the fluorinated peroxy radical pool via reaction with OH radicals. Reaction with CH₃O₂ radicals is expected to proceed via two channels ((6a) and (6b)) leading to the formation of alkoxy radicals (6a) and a fluorinated alcohol and formaldehyde (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 HCF₂OCF₂OCF₂CF₂OCF₂H one might expect formation of HCF₂OCF₂OCF₂OCF₂OC(O)OH and HOC(O)OCF₂OCF₂CF₂OCF₂H. Long-chain perfluorocarboxylic acids, such as perfluorooctanoic acid $(C_7F_{15}C(O)OH)$, have no natural sources, are bioaccumulative, are found in fauna in remote locations, and are the subject of considerable current research interest. 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.

The results from the present work can be compared with those from the study by Tuazon [6] of the kinetics and products of the chlorine atom initiated oxidation of the hydrofluoropolyethers $HCF_2OCF_2OCF_2H$, $HCF_2OCF_2CF_2OCF_2H$, and $HCF_2OCF_2OCF_2CF_2OCF_2H$.

 $Cl + HCF_2OCF_2OCF_2H \rightarrow products$ (13)

$$Cl + HCF_2OCF_2CF_2OCF_2H \rightarrow products$$
 (14)

 $Cl + HCF_2OCF_2OCF_2CF_2OCF_2H \rightarrow products$

Tuazon used a relative rate method similar to that used in the present work and reported $k_{13}/k_{10} = 0.208 \pm$ 0.006, $k_{14}/k_{10} = 0.188 \pm 0.004$, and $k_{15}/k_{10} = 0.149 \pm$ 0.003. We can compare these results to the determination of $k_8/k_{10} = k_9/k_{10} = 0.205 \pm 0.019$ in the present work. The reactivities of HCF₂OCF₂OCF₂H and HCF₂OCF₂CF₂OCF₂H toward chlorine atoms reported by Tuazon are indistinguishable, within the experimental uncertainties, from those for the HFPEs studied in the present work. For reasons which are unclear, the reactivity of HCF₂OCF₂OCF₂CF₂OCF₂H reported by Tuazon is approximately 25% below those of the other HFPEs.

Tuazon reported the formation of COF₂ in a near unit yield per carbon atom from the chlorine atom initiated oxidation of HCF₂OCF₂OCF₂H, HCF₂OCF₂CF₂OCF₂H, and HCF₂OCF₂OCF₂CF₂-OCF₂H in 740 Torr of air at 298 K. Cavalli et al. [13] conducted four experiments of the chlorine atom initiated oxidation of HCF2OCF2OCF2CF2OCF2H in 740 Torr of air and reported the formation of COF₂ in a molar yield of 300%-485%. The large range reported by Cavalli et al. presumably reflects difficulties in measuring the small amounts of COF₂ formed (0.16-0.74 mTorr) and HFPE lost (0.03-0.24 mTorr) in their experiments; approximately an order of magnitude smaller than in the present work (see Fig. 3). The measurement of a molar COF_2 yields of 476 \pm 36% in the chlorine atom oxidation of HCF₂OCF₂OCF₂CF₂OCF₂H in the present work is consistent with expectations based on the previous work by Tuazon [6] and Cavalli et al. [13].

The atmospheric oxidation of HFPEs is initiated by reaction with OH radicals. The kinetic database for reactions of HFPEs with OH radicals is sparse. The reported kinetic data for reactions of Cl atoms and OH radicals with HFPEs can be compared to expectations based upon the correlation of the rates of abstraction of hydrogen atoms from hydrofluorocarbons and hydrofluorochlorocarbons reported by Sulbaek Andersen et al. [14]. The circles in Fig. 4 (adapted from Fig. 9 in Sulbaek Andersen et al. [14]) are the data used by Sulbaek Andersen et al. [14] to derive the relationship log $(k(OH)) = (0.412 \pm 0.049) \times \log(k(Cl)) (8.16 \pm 0.72)$, which is shown as the solid line. The dotted lines show variation from the solid line by a factor of 2. It can be seen from Fig. 4 that the reactivity of most saturated hydrofluorocarbons and hydrofluorochlorocarbons toward OH radicals can be predicted to within a factor of 2 from their reactivity toward chlorine atoms. The stars in Fig. 4 show the literature data for polyfluorinated HFEs and HFPEs (see Table I). From the very limited data, it appears that the trend of reactivity of HFEs/HFPEs toward OH radicals and Cl

Compound	k(OH)	Reference	k(Cl)	Reference
HCF ₂ OCF ₂ H	2.4×10^{-15}	[15]	5.73×10^{-14}	[16]
HCF ₂ OCF ₂ OCF ₂ H	2.4×10^{-15}	[13]	5.0×10^{-17}	[6]
HCF ₂ OCF ₂ OCF ₂ CF ₂ OCF ₂ H	4.6×10^{-15}	[13]	5.0×10^{-17}	This work
CF ₃ OCF ₂ H	4.9×10^{-16}	[15]	2.2×10^{-17}	[17]
CH ₃ OCF ₃	1.2×10^{-14}	[15]	1.36×10^{-14}	[18]
CH ₃ OC ₂ F ₅	1.1×10^{-14}	[15]	1.1×10^{-13}	[19]
CHF ₂ OCH ₂ CF ₃	1.2×10^{-14}	[15]	1.3×10^{-14a}	[20]
				[21]
				[22]
CH ₃ OCF ₂ CHF ₂	2.2×10^{-14}	[15]	2.49×10^{-13}	[23]

Table I Kinetic Data for HFEs and HFPEs

^a Average from available studies.



Figure 4 $\log(k(OH))$ versus $\log(k(CI))$ for saturated hydrofluoroethers and hydrofluoropolyethers (stars), and hydrofluorocarbons and hydrofluorocarbons (circles). The solid line is the expression reported by Sulbaek Andersen et al. [14], the dotted lines show variation by a factor of 2 from this expression. Data for hydrofluorocarbons, hydrofluorocarbons, CF₃OC(CF₃)₂H, CF₃CFHCF₂OCF₃, CF₃CFHCF₂OCF₂H, and CF₃OCF₂CF₂H were taken from Sulbaek Andersen et al. [14]. All other data were taken from Table I.

atoms is broadly similar to that for HFCs and HCFCs. However, there is substantial and somewhat surprising scatter of the HFE/HFPE data in Fig. 4. For example, CF₃OCF₂H and HCF₂OCF₂CF₂OCF₂H react with Cl atoms at similar rates but react with OH radicals at rates that differ by approximately an order of magnitude. HCF₂OCF₂OCF₂H and HCF₂OCF₂H react with OH radicals at rates that are indistinguishable, but HCF₂OCF₂OCF₂H reacts with Cl atoms approximately 1000 times slower than does HCF₂OCF₂H. Given that the mechanism of reaction of both Cl atoms and OH radicals with HFPEs is hydrogen atom abstraction, it is difficult to understand why the rates of these reactions are not better correlated. The scatter of the HFE/HFPE data in Fig. 4 suggests that perhaps there are differences in the mechanism of the OH and Cl reactions, or perhaps that there are errors in the kinetic database. Given the similar chemical environment of the C-H bond in HCF₂OCF₂H, HCF₂OCF₂OCF₂H, and HCF₂OCF₂CF₂OCF₂H, it is not surprising that these compounds react with OH radicals at similar rates, but it is puzzling that the reactivity of HCF₂OCF₂H toward chlorine atoms is a factor of 1000 times greater than for HCF₂OCF₂OCF₂H and HCF₂OCF₂CF₂OCF₂H. Further experimental and computational studies are needed to improve our limited understanding of the kinetics of the reactions of Cl atoms and OH radicals with HFPEs and hence the atmospheric lifetimes of these species.

The atmospheric oxidation of $HCF_2O(CF_2O)_n$ -(CF₂CF₂O)_mCF₂H and HCF₂OCF₂OCF₂CF₂OCF₂H gives carbonyl fluoride, COF₂, as the major product. COF₂ is removed from the troposphere via contact with water surfaces and hydrolysis to HF and CO₂ in rain/aerosol/cloud/sea water with a lifetime of approximately 5–10 days [4]. $HCF_2O(CF_2O)_n$ -(CF₂CF₂O)_mCF₂H and HCF₂OCF₂OCF₂CF₂OCF₂H do not contain any chlorine and will not contribute to stratospheric ozone depletion via the wellestablished chlorine-based chemistry. As with all hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), and hydrofluoropolyethers (HFPEs), the ozone depletion of $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$ and HCF₂OCF₂OCF₂CF₂OCF₂H is, for all practical purposes, zero.

Finally we return to discuss the validity of the assumption introduced in the experimental section that in the kinetic and mechanistic analysis, we can treat the HCF₂O(CF₂O)_n(CF₂CF₂O)_mCF₂H mixture as a single compound. In addition to chemical intuition, there are three pieces of information that support the assumption that the chemical environment of the C-H bonds is independent of the number of -CF₂O- and -CF₂CF₂Ounits in $HCF_2O(CF_2O)_n(CF_2CF_2O)_mCF_2H$: First, the fact that the reactivities of Cl atoms toward HCF₂OCF₂OCF₂H and HCF₂OCF₂CF₂OCF₂H measured by Tuazon et al. [6] are indistinguishable from that for HCF₂OCF₂OCF₂OCF₂OCF₂H measured herein; second, the linearity of the relative rate plots in Fig. 1, which show that the fractional loss of the different components during the course of the experiment are indistinguishable; and third, the linearity of the COF₂ formation versus HCF₂O(CF₂O)_n(CF₂CF₂O)_mCF₂H loss, shown in Fig. 3, which also indicates that the different components react at rates that are indistinguishable.

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