# Tropospheric Degradation Products of Novel Hydrofluoropolyethers

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The CI atom-initiated photooxidations of the hydrofluoropolyethers (HFPEs) HCF2OCF2OCF2CF2OCF2H, HCF2OCF2CF2-OCF<sub>2</sub>H, and HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H in air produced C(O)F<sub>2</sub> as the only carbon-containing product, with observed average C(O)F<sub>2</sub> molar formation yields of 4.73, 3.77, and 2.82, respectively. The C(0)F<sub>2</sub> molar formation yields during the early stages of the reactions were observed to be closer to the number of C atoms in each parent HFPE. On the basis of current knowledge concerning the degradation pathways of hydrofluorocarbons and hydrochlorofluorocarbons, it is expected that C(O)F<sub>2</sub> will also be produced with near unit yield per C atom from the above HFPEs in the troposphere, where loss processes would be initiated primarily by reaction with OH radicals. The rate constants for reaction with the CI atom at 298  $\pm$  2 K were determined for the HFPEs by a relative rate method that employed CF<sub>3</sub>CF<sub>2</sub>H as the reference compound  $[k(CI + CF_3CF_2H) = (2.4 \pm 0.5)]$  $\times$  10^{-16}  $cm^3$  molecule^{-1}  $s^{-1}],$  with measured values of (in units of 10<sup>-17</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>-OCF<sub>2</sub>H, 3.6  $\pm$  0.8; HCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H, 4.5  $\pm$  1.0; and HCF<sub>2</sub>- $OCF_2OCF_2H$ , 5.0 ± 1.1.

# Introduction

Perfluorinated polyethers (PFPEs) are among the organofluorine compounds that have found important industrial applications. They are being employed as solvents, lubricants in both delicate and heavy machinery, components of coatings and a variety of polymer formulations, and contact fluids for thermal testing of electronic components (1). However, in response to environmental issues that encompass industrial halocarbons in general, including their possible contributions to stratospheric ozone depletion and global warming, perfluorinated ethers are also being redesigned to enhance their degradability in the lower atmosphere. Thus, for example, the polyethers  $HCF_2O(CF_2CF_2O)_m(CF_2O)_nCF_2H$ , where m =0-7 and n = 0-5, represent a group of novel hydrofluoropolyethers (HFPEs) being developed by Ausimont (2) as replacements for the PFPEs as well as for chlorofluorocarbons (CFCs). As for the hydrofluorocarbon (HFC) and hydrochlorofluorocarbon (HCFC) substitutes for the CFCs (which have been phased out of production in industrialized nations), the presence of one or more carbon-hydrogen bonds in the molecule enables the abstraction of hydrogen atoms by the OH radical to be the initial step that facilitates the degradation of these replacement compounds in the troposphere, thus minimizing their transport into the stratosphere (3).

To assess the environmental impact that may result in the event of their widespread use, a knowledge of the identities and yields of products from the atmospheric degradation reactions of the HFPEs is required. In this work, experiments were carried out to study the products generated from the alkoxy radicals formed after the initial H atom abstraction step from  $HCF_2OCF_2OCF_2H$ ,  $HCF_2OCF_2OCF_2H$ , and  $HCF_2$ -

 $OCF_2OCF_2CF_2OCF_2H$ , since the predicted degradation pathway of this compound in the troposphere is by reaction with OH radicals. Because the rates of reaction of the OH radical with these halocarbons are generally very slow (*3, 4*), Cl atoms instead of OH radicals were employed for the initial H atom abstraction since they can be generated at higher concentration by Cl<sub>2</sub> photolysis. The rate constants for the reaction of Cl atoms with the above HFPEs were also measured in this work using a relative rate method.

# **Experimental Section**

The irradiation experiments were carried out in a 5800-L evacuable, thermostated, Teflon-coated chamber equipped with a solar simulator that provided radiation from a 24-kW xenon arc lamp (5). The chamber housed an *in situ* multiple-reflection optical system interfaced to a Nicolet 7199 Fourier transform infrared (FT-IR) absorption spectrometer equipped with a liquid nitrogen-cooled HgCdTe detector.

The partial pressures of the HFPEs were measured into calibrated 2-L Pyrex bulbs with a capacitance manometer (MKS Baratron, 100-Torr sensor) and introduced into the chamber filled with the diluent air by flushing with N<sub>2</sub> gas. Chlorine was measured and introduced into the chamber both by the above procedure and by direct injection into the chamber with the use of gas-tight, all-glass 100-mL syringes (the latter procedure being used for the lesser quantities of chlorine employed during the earlier experiments). The initial concentrations (in units of 10<sup>13</sup> molecule cm<sup>-3</sup>) employed were as follows: for the product studies, HFPEs, 4.8-7.2, and Cl<sub>2</sub>, 94-485; for the relative rate experiments, HFPEs, 4.8-6.0, CF<sub>3</sub>CF<sub>2</sub>H, 7.2, and Cl<sub>2</sub>, 360-480. An experiment for the infrared spectroscopic calibration of C(O)F<sub>2</sub> employed the photolysis in air of a mixture containing  $9.6 \times 10^{13}$  and 8.2 $\times$  10<sup>14</sup> molecule cm<sup>-3</sup>, respectively, of CHClF<sub>2</sub> and Cl<sub>2</sub>.

The experiments were conducted at 298  $\pm$  2 K and 740 Torr total pressure with irradiation times of 60–150 min. The reactants and products were monitored by FT-IR absorption spectroscopy, using a path length of 62.9 m and a full width at half-maximum resolution of 0.7 cm<sup>-1</sup>.

The samples of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H, HCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H, and HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H were supplied by Ausimont. Cl<sub>2</sub> (99.9% minimum) and CHClF<sub>2</sub> (99.8% minimum) were from Matheson, and CF<sub>3</sub>CF<sub>2</sub>H ( $\geq$ 99.5%) was from E. I. du Pont de Nemours and Co., Inc. The diluent gas was synthetic air (20% O<sub>2</sub> + 80% N<sub>2</sub>) made of M.O.S.-grade O<sub>2</sub> (99.995%, Liquid Carbonic) and head gas from liquid N<sub>2</sub> (Airco).

## Results

**Product Studies.**  $HCF_2OCF_2OCF_2CF_2OCF_2H$ . A quantitative vapor-phase spectrum (700–1700 cm<sup>-1</sup>) of the HCF<sub>2</sub>OCF<sub>2</sub>-OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H sample, along with those obtained for HCF<sub>2</sub>-OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H and HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H, is presented in Figure 1. The gas chromatographic analysis provided by Ausimont indicated a 95.24% purity for HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H, with the other sample constituents being 1.2% of a C<sub>4</sub> homolog and 3.4% of C<sub>6</sub> homologs. In the following, the concentrations and extent of reactions are reported first on the basis of a 100% pure C<sub>5</sub> sample and later discussed in terms of the above-measured composition.

Three irradiation experiments, each with  $4.8\times10^{13}$  molecule  $cm^{-3}$  initial concentration of the ether and  $2.0\times10^{15},\ 3.6\times10^{15},\ and\ 4.8\times10^{15}$  molecule  $cm^{-3}$  of  $Cl_2$  (runs EC-1628, EC-1629, and EC-1633, respectively), were carried out. The respective consumptions of HCF\_2OCF\_2OCF\_2CF\_2-OCF\_2H at the end of the experiments were 6.7% after 141 min (EC-1628), 11.8% after 147 min (EC-1629), and 10.6% after 138 min (EC-1633).



FIGURE 1. Quantitative vapor-phase infrared spectra of  $HCF_2OCF_2$ - $OCF_2CF_2OCF_2H$ ,  $HCF_2OCF_2CF_2OCF_2H$ , and  $HCF_2OCF_2OCF_2H$ .

Figure 2 shows the spectra of the initial HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>-CF2OCF2H-Cl2-air mixture and of the mixture after 138 min of irradiation during run EC-1633.  $C(O)F_2$ , HCl, and  $CO_2$  were the reaction products observed. CO<sub>2</sub> was primarily generated from the organic impurities of the diluent air, as confirmed by similar CO<sub>2</sub> levels ( $\sim 4 \times 10^{13}$  molecule cm<sup>-3</sup>) that were generated from a separate irradiation of a Cl<sub>2</sub>-air mixture. HCl was directly produced from H atom abstraction by Cl atoms from HCF2OCF2OCF2CF2OCF2H and the organic impurities.  $C(O)F_2$  was the only carbon-containing product observed from HCF2OCF2OCF2CF2OCF2H. An expanded plot of the product spectrum (Figure 2B) that focuses on the product  $C(O)F_2$  is presented in Figure 3A. Subtraction of the absorptions by the reactant ether results in the residual spectrum of Figure 3B, which shows the well-defined absorption bands of  $C(O)F_2$ .

The reference spectrum of C(O)F<sub>2</sub> shown in Figure 3C was obtained from the irradiation of a CHF<sub>2</sub>Cl–Cl<sub>2</sub>–air mixture (run EC-1630), since it has been demonstrated previously that the Cl atom-initiated photooxidation of CHF<sub>2</sub>Cl gave a 100% yield of C(O)F<sub>2</sub> ( $\delta$ ). An integrated absorption coefficient (base 10) of (2.94  $\pm$  0.01)  $\times$  10<sup>-17</sup> cm molecule<sup>-1</sup> for the carbonyl fluoride C=O stretch absorption band in the range 1870–1990 cm<sup>-1</sup> was obtained, with the error quoted being two times the least squares standard error. This absorption coefficient is 6.5% higher than the value measured previously ( $\delta$ ). The present value, which showed higher precision than



FIGURE 2. Infrared absorption spectra from an HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>-OCF<sub>2</sub>H–Cl<sub>2</sub>-air irradiation experiment (run EC-1633). (A) Initial HCF<sub>2</sub>-OCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H (4.8  $\times$  10<sup>13</sup> molecule cm<sup>-3</sup>). (B) Reaction mixture after 138 min of irradiation with 10.6% of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H consumed.



FIGURE 3. (A) Spectrum from run EC-1633 reaction mixture after 138 min of irradiation (same as Figure 2B). (B) From (A) after subtraction of absorptions by  $HCF_2OCF_2OCF_2OCF_2H$ . (C) C(0)F<sub>2</sub> reference spectrum. Numbers in parentheses are concentrations in molecule cm<sup>-3</sup>.

the earlier measurement and which was obtained under the same experimental conditions (e.g., radiation intensity, path length, use of the same manometers and calibrated glass bulbs) as those for the HFPEs, was employed in the calculation of the  $C(O)F_2$  product concentrations in this study.

By subtracting the reference spectrum (Figure 3C) from the product spectra (such as Figure 3B), it was verified that no other product species contributed any measurable signal to the C=O stretching region. Thus, from the known absorption coefficient and the integrated band areas (1870– 1990 cm<sup>-1</sup>range), the concentrations of C(O)F<sub>2</sub> formed during the HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H-Cl<sub>2</sub>-air irradiations were determined.



FIGURE 4.  $C(0)F_2$  yield data from CI atom-initiated photooxidation of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H (top plot), HCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H (middle plot), and HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H (bottom plot). Distinct symbols for each plot represent separate irradiation experiments.

The plots of  $C(O)F_2$  yields ( $[C(O)F_2]$  formed/ $[HCF_2OCF_2-OCF_2CF_2OCF_2H]$  reacted) vs amounts of ether consumed for the three experiments (EC-1628, EC-1629, and EC-1633) are presented in Figure 4 (top plot). An average  $C(O)F_2$  yield of 4.73 was calculated from the three experiments. However, yield values approaching 5.0 are suggested by the data for the earlier part of these irradiations.

The above yields have been provisionally reported on the basis of a 100% pure sample, since the infrared spectral features of the C4 and C6 constituents and their changes during the reactions could not be detected or distinguished from those of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H and since they are all expected to yield  $C(O)F_2$  as the sole or major carboncontaining product. As shown below, the rate constant for reaction of HCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H with the Cl atom is not vastly different from that of HCF2OCF2OCF2CF2OCF2H, and it is reasonable to assume that, by virtue of similar environments for the H atoms, the rate constants for the C<sub>6</sub> species are not too dissimilar also from that of the C<sub>5</sub> species. Hence, if all the carbon units of these compounds are converted to C(O)-F<sub>2</sub>, it is expected that '1 mol of the sample' with the  $C_4-C_6$ composition given above would yield 5.014 mol of  $C(O)F_{2}$ , with 95.0% contribution from HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H. The experimental data are consistent with these expected results.

 $HCF_2OCF_2CF_2OCF_2H$ . The sample of  $HCF_2OCF_2CF_2OCF_2H$ (infrared spectrum shown in Figure 1) had a cited analysis of 98.63%. The two irradiation experiments (EC-1632 and EC-1634) for  $HCF_2OCF_2CF_2OCF_2H$  each employed initial concentrations of  $4.80 \times 10^{13}$  molecule cm<sup>-3</sup> of the ether and  $4.8 \times 10^{15}$  molecule cm<sup>-3</sup> of Cl<sub>2</sub>, with 10–11% consumption of the ether being observed after ~120 min of photolysis. As in the case of the C<sub>5</sub> ether above, the infrared spectra of the reaction mixtures showed C(O)F<sub>2</sub> to be the only carboncontaining product from  $HCF_2OCF_2CF_2OCF_2H$ . The results of the above experiments, plotted in Figure 4 (middle plot), correspond to an average C(O)F<sub>2</sub> yield of 3.77, with yields closer to 4.0 being suggested by the data for the earlier part of each irradiation.

 $HCF_2OCF_2OCF_2H$ . The sample of  $HCF_2OCF_2OCF_2H$  (infrared spectrum shown in Figure 1) was quoted with a purity of 99.62%. The two of irradiation runs (EC-1631 and EC-1635) for  $HCF_2OCF_2OCF_2H$  each employed  $7.2 \times 10^{13}$  molecule



FIGURE 5. Plots of eq I for the reactions of CI atoms with HCF<sub>2</sub>-OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H, HCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H, and HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H with CF<sub>3</sub>-CF<sub>2</sub>H as reference. The ordinates of the plots for HCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H and HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H are offset by +0.05 and +0.10, respectively, for clarity.

TABLE 1. Relative Rate Data for Reactions of Hydrofluoropolyethers with Cl Atoms at 298  $\pm$  2 K

sample	ref	$(k_1/k_2)^a$	$\begin{array}{c} 10^{17} \times \textit{k}_1 \text{ (cm}^3 \\ \text{molecule}^{-1} \\ \text{s}^{-1} \text{)}^{\textit{b}} \end{array}$
HCF <sub>2</sub> OCF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> H HCF <sub>2</sub> OCF <sub>2</sub> CF <sub>2</sub> OCF <sub>2</sub> H HCF <sub>2</sub> OCF <sub>2</sub> OCF <sub>2</sub> H	$CF_3CF_2H$ $CF_3CF_2H$ $CF_3CF_2H$	$\begin{array}{c} 0.149 \pm 0.003 \\ 0.188 \pm 0.004 \\ 0.208 \pm 0.006 \end{array}$	$\begin{array}{c} 3.6 \pm 0.8 \\ 4.5 \pm 1.0 \\ 5.0 \pm 1.1 \end{array}$

<sup>*a*</sup> The random errors quoted for  $k_1/k_2$  are two times the least squares standard errors. The total of other possible errors (including systematic errors) is estimated to be  $\leq 5\%$ . <sup>*b*</sup> Placed on an absolute basis by use of a rate constant for reaction of the Cl atom with CF<sub>3</sub>CF<sub>2</sub>H of  $k_2 = (2.4 \pm 0.5) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 ± 2 K (7). The errors indicated include the uncertainty in  $k_2$ (CF<sub>3</sub>CF<sub>2</sub>H) and the total errors in  $k_1/k_2$ .

cm<sup>-3</sup> of the ether and  $3.6 \times 10^{15}$  (EC-1631) and  $4.8 \times 10^{15}$  (EC-1635) molecule cm<sup>-3</sup> of Cl<sub>2</sub>, with respective ether consumptions of 10.3% after 111 min and 11.3% after 138 min of irradiation. The infrared spectra of the reaction mixtures showed C(O)F<sub>2</sub> as the only carbon-bearing product from the reactant ether. An average C(O)F<sub>2</sub> yield of 2.82 was obtained, and the plot of the yield data is included in Figure 4 (bottom plot).

**Kinetic Studies.** On the assumption that the only important loss processes occurring for the sample (S) and reference (R) compounds are their reactions with Cl atoms

$$S + Cl \rightarrow products$$
 (1)

$$\mathbf{R} + \mathbf{Cl} \rightarrow \mathbf{products} \tag{2}$$

it can be shown that

$$\ln \{ [S]_{t} / [S]_{t} \} = (k_{1} / k_{2}) \ln \{ [R]_{t} / [R]_{t} \}$$
(I)

where  $[S]_t$  and  $[R]_t$  are the sample and reference compound concentrations, respectively, at time *t*;  $[S]_{t_0}$  and  $[R]_{t_0}$  are the concentrations of sample and reference at time  $t_0$ ; and  $k_1$  and  $k_2$  are the rate constants for reactions 1 and 2, respectively.

The plots of eq I for the irradiation of air mixtures containing  $Cl_2$ ,  $CF_3CF_2H$  as the reference compound, and each of the HFPEs HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CCF<sub>2</sub>OCF<sub>2</sub>H (runs EC-1642) and EC-1643), HCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H (run EC-1644), and HCF<sub>2</sub>-



FIGURE 6. Tropospheric degradation scheme for HCF2OCF2OCF2CF2OCF2H.

OCF<sub>2</sub>OCF<sub>2</sub>H (run EC-1645) are presented in Figure 5. The plots are seen to be straight lines with excellent linear regression statistics ( $r^2 \ge 0.998$ ). The slopes (which are equal to the rate constant ratios  $k_1/k_2$ ) of 0.208  $\pm$  0.006, 0.188  $\pm$  0.004, and 0.149  $\pm$  0.003 for the C<sub>3</sub>, C<sub>4</sub>, and C<sub>5</sub> HFPEs, respectively, indicate that these fluorinated ethers are even less reactive to Cl atoms than CF<sub>3</sub>CF<sub>2</sub>H is, the latter compound having the lowest rate constant for reaction with the Cl atom among a series of HCFCs and HFCs previously studied in this laboratory (7). The absolute values of the rate constants  $k_1$  for reaction of Cl atoms with the fluorinated ethers were calculated based on the value  $k_2 = (2.4 \pm 0.5) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for the CF<sub>3</sub>CF<sub>2</sub>H + Cl reaction (7) and are summarized in Table 1.

# Discussion

The results described above for the Cl atom-initiated photooxidations of the HFPEs are consistent with the generally accepted reactions of hydrocarbons and halogenated hydrocarbons that follow the initial H atom abstraction step (3, 4). The series of equations involved in the HFPE laboratory reaction systems is illustrated for HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H:

 $\begin{array}{c} HCF_2OCF_2OCF_2CF_2OCF_2H + \\ \dot{C}l \rightarrow HCF_2OCF_2OCF_2CF_2O\dot{C}F_2 + HCl \ (3) \end{array}$ 

$$\begin{array}{c} HCF_2OCF_2OCF_2CF_2O\dot{C}F_2 + \\ O_2 \rightarrow HCF_2OCF_2OCF_2CF_2O\dot{C}F_2O\dot{O} \end{array} (4) \end{array}$$

$$\begin{array}{c} 2HCF_2OCF_2OCF_2OCF_2O\dot{O} \rightarrow \\ 2HCF_2OCF_2OCF_2OCF_2OCF_2\dot{O} + O_2 \end{array} (5) \end{array}$$

$$HCF_{2}OCF_{2}OCF_{2}CF_{2}OCF_{2}\dot{O} \xrightarrow{-C(O)F_{2}} HCF_{2}OCF_{2}OCF_{2}CF_{2}\dot{O} \xrightarrow{-C(O)F_{2}} HCF_{2}OCF_{2}O\dot{C}F_{2}\dot{O} \xrightarrow{-C(O)F_{2}} HCF_{2}OCF_{2}\dot{O} \xrightarrow{-C(O)F_{2}} HCF_{2}OCF_{2}\dot{O} \xrightarrow{-C(O)F_{2}} HCF_{2}\dot{O} \xrightarrow{-C$$

Reaction with Cl atoms yields HCl and the halogenated radical, which then reacts with  $O_2$  to give the peroxy radical ( $\dot{RO}_2$ ). Under the laboratory conditions employed, the major fate of the  $\dot{RO}_2$  radical is self-reaction to produce the corresponding alkoxy radical ( $\dot{RO}$ ). The  $\dot{RO}$  radical then undergoes a sequence of decomposition steps and reaction with  $O_2$ , as depicted in eq 6, to give the theoretical yield of 5 molecules of  $C(O)F_2$  per molecule of  $HCF_2OCF_2OCF_2CF_2$ -OCF<sub>2</sub>H reacted.

Although the  $RO_2 + RO_2$  reaction (eq 5) is expected to predominantly yield RO radicals, the occurrence of minor channels yielding other products, such as those enumerated below, cannot be totally ruled out in the present reaction systems:

$$\begin{array}{l} HCF_2OCF_2OCF_2CF_2OCF_2OOO + \\ HO_2 \rightarrow HCF_2OCF_2OCF_2OCF_2OOH + O_2 \end{array} (9) \end{array}$$

$$\begin{array}{c} HCF_2OCF_2OCF_2O\dot{O} + H\dot{O}_2 \rightarrow \\ HCF_2OCF_2OCF_2OOH + O_2 \end{array} (10) \end{array}$$

It is to be noted that HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>OO is an intermediate peroxy radical formed during the decomposition of the C<sub>5</sub> alkoxy radical in eq 6. Minor amounts of these peroxide products that could form via eqs 7-10 would not be detectable beneath the strong absorption bands of the parent ether. The formation of small yields of these peroxides under laboratory conditions could have contributed to the observation of C(O)-F<sub>2</sub> yields that were slightly lower than the theoretical 5.0 molar yield for the HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>H reaction. The same reasoning applies to the cases of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>H and HCF<sub>2</sub>- $OCF_2CF_2OCF_2H$ , where reactions analogous to those for the  $C_5$  homolog can be written and where the observed  $C(O)F_2$ yields were also slightly lower than the respective 3.0 and 4.0 theoretical yields. However, the peroxidic bond is susceptible to UV photolysis, such that the above-mentioned peroxide products, if formed in the atmosphere, are expected to yield back alkoxy radicals.

As in the case of the HFCs and HCFCs, the dominant loss process for the HFPEs in the troposphere is expected to be reaction with the OH radical, leading to the formation of RO<sub>2</sub> radicals. Unlike in the laboratory reaction systems, however, the prevailing RO<sub>2</sub> radical concentrations will be much lower in the atmosphere such that self-reaction (eq 5) will be unimportant. Instead, the fate of peroxy radicals will be reactions with NO, NO<sub>2</sub>, and HO<sub>2</sub> radicals. A tropospheric degradation scheme for HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF<sub>2</sub>Ĥ, which is heavily based on current knowledge of the degradation pathways of HFCs and HCFCs (3, 4), is presented in Figure 6. Both the RO<sub>2</sub> reactions with NO and NO<sub>2</sub> will be fairly rapid, with the NO reaction leading to the alkoxy radical and the sequence of bond scissions producing the main product  $C(O)F_2$ . The reaction with NO<sub>2</sub> is an equilibrium leading to the production of a thermally unstable peroxynitrate. The rate of reaction with HO2 radicals is relatively more uncertain (8), but the resulting hydroperoxide product is expected to

undergo photolysis and reaction with OH radicals. As illustrated in Figure 6, these reactions of the hydroperoxide and the thermal decomposition of the peroxynitrate largely return the  $C_5$  fragment to the  $RO_x$  pool. Hence, in time, the OH radical-initiated decomposition of HCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>-OCF<sub>2</sub>H in the atmosphere will produce C(O)F<sub>2</sub> with the expected molar yield of 5.0.

The values of the rate constants for reaction of the  $C_3-C_5$ HFPEs with Cl atoms measured in this work indicate that the terminal C–H bonds of these compounds are stronger than that of the highly fluorinated CF<sub>3</sub>CF<sub>2</sub>H with respect to H atom abstraction by the Cl atom. However, for the more atmospherically relevant reactions with the OH radical, the tentative range of OH rate constants for these  $C_3-C_5$  HFPEs appear to be comparable or higher than the OH rate constant for CF<sub>3</sub>-CF<sub>2</sub>H (*9, 10*). A quantitative assessment of the atmospheric lifetimes of the above HFPEs is still ongoing (*9*).

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