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Atmospheric Chemistry of Hydrofluoroethers: Reaction of a Series of Hydrofluoroethers with OH Radicals and Cl Atoms, Atmospheric Lifetimes, and Global Warming Potentials

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The kinetics of the OH radical and Cl atom reactions with nine fluorinated ethers have been studied by the relative rate method at 298 K and 1013 hPa using gas chromatography−mass spectroscopy (GC−MS) detection: $k(OH + CH_3CH_2OCF_3) = (1.55 \pm 0.25) \times 10^{-13}$, $k(OH + CF_3CH_2OCH_3) = (5.7 \pm 0.8) \times 10^{-13}$, $k(OH + CF_3CH_2OCHF_2) = (9.1 \pm 1.1) \times 10^{-15}$, $k(OH + CF_3CHFOCHF_2) = (6.5 \pm 0.8) \times 10^{-15}$, $k(OH + CHF_2CHFOCF_3) = (6.8 \pm 1.1) \times 10^{-15}$, $k(OH + CF_3CHFOCF_3) < 1 \times 10^{-15}$, $k(OH + CF_3CHFCF_2OCHF_2) = (1.69 \pm 0.26) \times 10^{-14}$, $k(OH + CF_3CHFCF_2OCH_2CH_3) = (1.47 \pm 0.13) \times 10^{-13}$, $k(OH + CF_3CF_2CF_2OCHFCF_3) < 1 \times 10^{-15}$, $k(Cl + CH_3CH_2OCF_3) = (2.2 \pm 0.8) \times 10^{-12}$, $k(Cl + CF_3CH_2OCH_3) = (1.8 \pm 0.9) \times 10^{-11}$, $k(Cl + CF_3CH_2OCHF_2) = (1.5 \pm 0.4) \times 10^{-14}$, $k(Cl + CF_3CHFOCHF_2) = (1.1 \pm 1.9) \times 10^{-15}$, $k(Cl + CHF_2CHFOCF_3) = (1.2 \pm 2.0) \times 10^{-15}$, $k(Cl + CF_3CHFOCF_3) < 3 \times 10^{-15}$, $k(Cl + CF_3CHFCF_2OCHF_2) < 6 \times 10^{-16}$, $k(Cl + CF_3CHFCF_2OCH_2CH_3) = (3.1 \pm 1.1) \times 10^{-12}$, and $k(Cl + CF_3CF_2CF_2OCHFCF_3) < 3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. The error limits include three standard deviations (3σ) from the statistical data analyses, as well as the errors in the rate coefficients of the reference compounds that are used. Infrared absorption cross sections and estimates of the trophospheric lifetimes and the global warming potentials of the fluorinated ethers are presented. The atmospheric degradation of the compounds is discussed.

1. Introduction

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs) have been important classes of chemical compounds in the industrial society for years. They are used in a variety of applications, including refrigeration, cleaning of critical electronic and precision mechanical components, air conditioning, medical products, and energy-efficient insulation. Unfortunately, they are greenhouse gases—some of them have considerable global warming potentials—and are becoming ever more important, relative to other greenhouse gases (e.g., CO_2, CH_4), whose effects are growing more slowly. CFCs and HCFCs are also able to destroy stratospheric ozone. The identification of suitable industrial alternatives to these compounds remains a challenge, because of the complex combination of performance, safety, and environmental properties required. Hydrofluoroethers (HFEs) have been suggested as substituents for HFCs in applications such as the cleaning of electronic components, refrigeration, and carrier compounds for lubricants. HFEs have zero ozone depletion potentials; however, they are potential greenhouse gases and their atmospheric degradation products may not be benign to the environment. Removal of HFEs from the troposphere will mainly be initiated by reaction with OH radicals. To ascertain the environmental impact of HFEs released into the troposphere, their atmospheric lifetimes, with respect to reaction with OH radicals, and the nature and fate of the resulting oxidation products are therefore required.

As part of ongoing work in our laboratory concerning the environmental impact of industrial replacement compounds, we have measured the infrared absorption cross sections and studied the reactions of OH radicals and Cl atoms with nine HFEs, for which few data are available in the literature: $CH_3CH_2OCF_3$ (R−E 143a), $CF_3CH_2OCH_3$, $CF_3CH_2OCHF_2$ (HFC-E 245; HFE 245fa2; R−E 245fa1), $CF_3CHFOCHF_2$ (Desflurane, Suprane, HFE 236; I 653; R−E 236ea1), $CHF_2CHFOCF_3$, $CF_3CHFOCF_3$ (HFE 227), $CF_3CHFCF_2OCHF_2$, $CF_3CHFCF_2OCH_2CH_3$ and $CF_3CF_2CF_2OCHFCF_3$ (Du Pont E 1; Freon E 1). Kinetic data have previously been reported for the OH reactions of $CF_3CHFOCHF_2$,[1] $CF_3CH_2OCHF_2$,[2−5] $CF_3CHFOCF_3$,[6,7] and $CF_3CH_2OCH_3$,[3,5] whereas rate coefficients are available for the Cl atom reactions of $CF_3CH_2OCH_3$,[8] $CF_3CH_2OCHF_2$,[2,8−10] and $CF_3CHFOCF_3$.[6,11] Infrared (IR) absorption cross sections have been published for $CF_3CH_2OCHF_2$,[12,13] $CF_3CHFOCF_3$,[7,14,15] $CF_3CH_2OCH_3$,[15] and $CF_3CHFOCHF_2$.[15]

2. Experimental Section

2.1. Relative Rate Measurements. The HFE rate coefficients for reaction with OH radicals and Cl atoms were determined by the relative rate (RR) method:

$$S + X \xrightarrow{k_S} Prod \qquad (1)$$

$$R + X \xrightarrow{k_R} Prod \qquad (2)$$

where S is the substrate of interest, R is the reference compound, X is the radical, and k_S and k_R are the reaction rate coefficients. Assuming that the reactant and reference compounds are lost solely via reaction with the radical species of interest and that they are not reformed in any process, the RR coefficient (k_{rel}) can be obtained by the following relation:

$$\ln\left\{\frac{[S]_0}{[S]_t}\right\} = k_{rel} \ln\left\{\frac{[R]_0}{[R]_t}\right\} \qquad \left(k_{rel} = \frac{k_S}{k_R}\right) \qquad (3)$$

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in which $[S]_0$, $[R]_0$, $[S]_t$, and $[R]_t$ denote the concentrations of S and R at time zero and time t, respectively. A plot of $\ln\{[S]_0/[S]_t\}$ vs $\ln\{[R]_0/[R]_t\}$ will give k_{rel} as the slope. Data from independent experiments were analyzed jointly, according to eq 3, using a weighted least-squares procedure including uncertainties in both reactant concentrations;[16] the uncertainties in the reactant concentrations were taken as the variance in three consecutive measurements but were not <1%. The analyses were conducted in two steps: (i) all data were fitted to a straight line with no constraints imposed. If there were no statistical significance to the nonzero intercept, the first data point ($t = 0$) was taken out and the remaining ($n - 1$) data points were then fitted to a straight line forced through the origin. If a dataset showed a statistically significant nonzero intercept, the dataset was disregarded (the experiment was repeated).

The measurements were performed at 1013 ± 15 hPa and 298 ± 2 K in synthetic air in a 250-L smog chamber of electropolished stainless steel. The temperature was monitored on the outside of the chamber, and it remained constant for the duration of the experiments. In situ air analyses were obtained with an Agilent model 6890/5973 gas chromatography−mass spectroscopy (GC−MS) system, using chemical ionization (CI). The gas chromatograph was operated under isothermal conditions at 40 °C. A constant overpressure of ca. 5 hPa was applied to the reactor to ensure a steady flow of ca. 20 mL/min through a 0.5-mL GC sampling loop, the content of which was injected into the gas chromatograph in a 1:50 split mode, using helium as the carrier gas; there was a 2-min time delay between turning off the photolysis lamps and starting the GC/MS scans. The column used for the separation was DB−Waxetr with a length of 30 m, an internal diameter of 0.25 mm, and a film coating of 0.25 μm. The DB−Waxetr column was coated with a poly(ethylene glycol). The inlet and the sample loop temperatures were kept constant at 100 °C. An inert tracer (perfluoro-1,2-dimethylcyclohexane) was added in initial experiments to monitor the dilution of the reactants, because of the constant reactor in-flow/out-flow—the dilution during an experiment was so small that corrections to eq 3 were negligible. The positive chemical ionization (PCI) mode, using CH_5^+ as the ionizing gas, was applied, because it is a soft method of ionization with little fragmentation. As a first step, the full-scan mode was selected to obtain complete mass spectra to identify the reactants and the reaction products in the gas chromatograms. The compounds studied, the reference compounds, and the reaction products all had unique mass peaks, which made it possible to operate the mass spectrometer in the selected ion mode (SIM), in which only chosen m/z numbers are followed. The SIM mode was then used for the quantification of the individual compounds, the advantage being reduced background noise and the elimination of overlap in cases of incomplete GC separation. The relative concentrations of HFEs were determined from the m/z signals at MH^+ and/or from their daughter ions at $[M-20]H^+$ resulting from elimination of HF. As an example, the PCI−MS spectrum of $CH_3CH_2OCF_3$ is shown in Figure 1. The following m/z signals were used to determine the relative concentrations of the reference compounds: $C_4F_9CH_2CH_3$ (245), $C_4F_9OCH_3$ (231), CHF_2CH_2F (65), CH_2ClCH_2Cl (63), CH_3CN (42), CH_3CCl_3 (97), CH_3COCH_3 (59), $CHCl_3$ (83), CH_3CH_2Cl (65), and CH_2Cl_2 (49).

2.2. Chemicals. Hydroxyl radicals were generated by the photolysis of ozone/H_2 mixtures. Typical volume fractions of H_2 and ozone were 2×10^3 ppm and 300 ppm, respectively. Ozone was produced from oxygen, using a TRI−OX model T-200 ozone generator that converts ~2% of the oxygen gas flow to ozone. The photo dissociation of ozone was accomplished through the use of two Philips TUV 30W lamps ($\lambda_{max} \approx 253.7$ nm) that were mounted in a quartz tube in the smog chamber; photolysis was conducted in time intervals of 1−20 min.

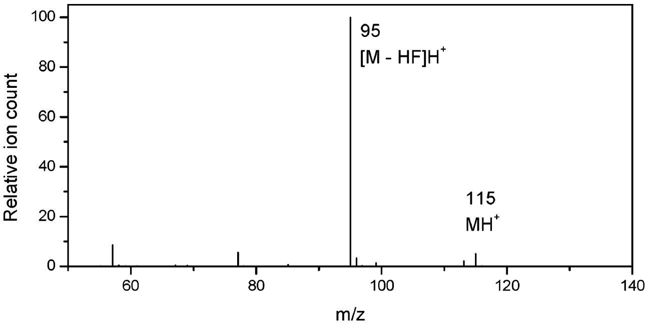

Figure 1. Positive chemical ionization−mass spectroscopy (PCI−MS) spectrum of $CH_3CH_2OCF_3$.

$$O_3 + h\nu\ (\lambda \approx 310\text{ nm}) \rightarrow O(^1D) + O_2 \tag{4}$$

$$O(^1D) + H_2 \rightarrow OH + H \tag{5}$$

$$H + O_3 \rightarrow OH + O_2 \tag{6}$$

The Cl atom source in the chamber was the photolysis of Cl_2, using Philips TLD-08 fluorescence lamps ($\lambda_{max} \approx 370$ nm), leading to the production of ground-state Cl atoms. Synthetic air (CO + NO_x content of <100 ppb, C_nH_m content of <1 ppm), ethane (99.0% purity), and oxygen gas (99.95% purity) were delivered from AGA. The purity of the HFEs, as checked by GC−MS, was, in all cases, >97%: $CH_3CH_2OCF_3$ (Oakwood products); $CF_3CH_2OCH_3$ and $CF_3CH_2OCHF_2$ (from Fluorochem, Ltd.); $CF_3CHFOCHF_2$, $CH_2FCF_2OCF_3$, $CF_3CHFOCF_3$ (from Apollo Scientific, Ltd.); and CF_3CHFCF_2OCHF2, $CF_3CHFCF_2OCH_2CH_3$, and $CF_3CF_2CF_2OCHFCF_3$ (from the Oceanchemical group). Traces of CF_2O in the HFEs were removed by single-plate vacuum distillation at −78 °C before use. Reference compounds included $C_4F_9CH_2CH_3$ (3M, technical grade), $C_4F_9OCH_3$ (3M, technical grade), CHF_2CH_2F (PCR, Inc.), whereas CH_2ClCH_2Cl, CH_3CN, CH_3CCl_3, CH_3COCH_3, $CHCl_3$, CH_3CH_2Cl, and CH_2Cl_2 were standard commercial chemicals with purities of >98%.

The volume fractions of the organic compounds were typically 2−6 ppm. The rate coefficients of the OH and Cl reactions with the fluorinated ethers were determined, relative to various reference compounds, as shown in Tables 1 and 2. The organic compounds did not undergo photolysis under our experimental conditions, and the reaction mixtures were chemically stable in the reaction chamber when the photolysis lamps were turned off. As a standard practice in our laboratory, the reaction mixtures are left in the chamber for ~1 h before the starting the kinetic experiments. If a loss of >2% of the initial substrate or reference was observed during this period, the experiment was discarded and the experimental conditions changed.

2.3. Measurements of IR Absorption Cross Sections. Our experimental procedure for measuring IR absorption cross sections has been reported recently,[17,18] and only a brief description will be given here. The absorption cross section of a compound J at a specific wavenumber $\tilde{\nu}$ is given by the Beer−Lambert law by $\sigma(\tilde{\nu}) = A_e(\tilde{\nu})/(n_J l)$, where $A_e(\tilde{\nu}) = -\ln \tau(\tilde{\nu})$ is the Naperian absorbance, τ the transmittance, n_J the number density of J, and l the path length over which the absorption

TABLE 1: Rate Coefficients at 298 K for the Reaction of OH Radicals with a Series of Fluorinated Ethers

reference compound[a]	k_{rel}(298 K)	k_{abs}(298 K)[b] (cm^3 molecule^{-1} s^{-1})	method[c]
		$CH_3CH_2OCF_3$	
$CHCl_3$	1.55 ± 0.09	$(1.55 \pm 0.25) \times 10^{-13}$	RR-GC/MS
		$CF_3CH_2OCH_3$	
$CHCl_3$	5.94 ± 0.31	$(5.9 \pm 0.9) \times 10^{-13}$	RR-GC/MS
$CH_3C(O)CH_3$	2.87 ± 0.30	$(5.2 \pm 1.4) \times 10^{-13}$	RR-GC/MS
		$(5.7 \pm 0.8) \times 10^{-13}$	weighted average
		$(6.24 \pm 0.67) \times 10^{-13}$	FP−RF[3]
		$(6.4 \pm 0.5) \times 10^{-13}$	RR-GC[5]
		$CF_3CH_2OCHF_2$	
CH_3CCl_3	0.928 ± 0.032	$(9.3 \pm 1.4) \times 10^{-15}$	RR-GC/MS
CHF_2CH_2F	0.520 ± 0.024	$(8.8 \pm 1.8) \times 10^{-15}$	RR-GC/MS
		$(9.1 \pm 1.1) \times 10^{-15}$	weighted average
		$(1.7 \pm 0.1) \times 10^{-14}$	DF−RF[2]
		$(1.22 \pm 0.09) \times 10^{-14}$	FP−RF[3]
		$(1.18 \pm 0.08) \times 10^{-14}$	FP−RF[4]
		$(1.10 \pm 0.03) \times 10^{-14}$	RR-GC[5]
		$CF_3CHFOCHF_2$	
CH_3CCl_3	0.670 ± 0.024	$(6.7 \pm 1.0) \times 10^{-15}$	RR-GC/MS
CHF_2CH_2F	0.36 ± 0.04	$(6.1 \pm 1.4) \times 10^{-15}$	RR-GC/MS
		$(6.5 \pm 0.8) \times 10^{-15}$	weighted average
		$(4.4 \pm 0.84) \times 10^{-15}$	FP-LLPA[1]
		$CHF_2CHFOCF_3$	
CH_3CCl_3	0.69 ± 0.07	$(6.9 \pm 1.3) \times 10^{-15}$	RR-GC/MS
CH_3CN	0.229 ± 0.027	$(5.3 \pm 2.7) \times 10^{-15}$	RR-GC/MS
CHF_2CH_2F	0.487 ± 0.19	$(8.3 \pm 3.6) \times 10^{-15}$	RR-GC/MS
		$(6.8 \pm 1.1) \times 10^{-15}$	weighted average
		$CF_3CHFOCF_3$	
CHF_2CH_2F	<0.05 ± 0.01	$<1 \times 10^{-15}$	RR-GC/MS
		$(1.4 \pm 0.3) \times 10^{-15}$	RR−FTIR[7]
		$(4.98 \pm 1.64) \times 10^{-15}$	DF-MS, DF−RF[6]
		$CF_3CHFCF_2OCHF_2$	
CH_3CN	0.91 ± 0.08	$(2.1 \pm 1.0) \times 10^{-14}$	RR-GC/MS
$C_4F_9OCH_3$	1.10 ± 0.07	$(1.66 \pm 0.26) \times 10^{-14}$	RR-GC/MS
		$(1.69 \pm 0.26) \times 10^{-14}$	weighted average
		$CF_3CHFCF_2OCH_2CH_3$	
$CHCl_3$	1.69 ± 0.11	$(1.69 \pm 0.28) \times 10^{-13}$	RR-GC/MS
$C_4F_9OC_2H_5$	1.69 ± 0.07	$(1.40 \pm 0.15) \times 10^{-13}$	RR-GC/MS
		$(1.47 \pm 0.13) \times 10^{-13}$	weighted average
		$CF_3CF_2CF_2OCHFCF_3$	
CHF_2CH_2F	<0.05 ± 0.01	$<1 \times 10^{-15}$	RR-GC/MS

[a] Reaction rate coefficients of reference compounds (in units of cm^3 molecule^{-1} s^{-1}): $k(OH + CHCl_3) = (1.00 \pm 0.15) \times 10^{-13}$, $k(OH + CH_3C(O)CH_3) = (1.80 \pm 0.45) \times 10^{-13}$, $k(OH+CH_3CCl_3) = (1.00 \pm 0.15) \times 10^{-14}$, $k(OH+CHF_2CH_2F) = (1.70 \pm 0.34) \times 10^{-14}$, and $k(OH+CH_3CN) = (2.30 \pm 1.15) \times 10^{-14}$ (all taken from ref 19); $k(OH+C_4F_9OCH_3) = (1.51 \pm 0.22) \times 10^{-14}$ (taken from ref 20); and $k(OH+C_4F_9OCH_2CH_3) = (8.3 \pm 0.8) \times 10^{-14}$ (taken from refs 20 and 21). [b] The absolute errors quoted in the present results include the three-standard-deviation (3σ) error from the statistical data analysis and the uncertainty factor in the reaction rate coefficient of the reference compound assigned in the latest JPL evaluation.[19] [c] Abbreviations in this column of data are as follows: RR, relative rate; GC, gas chromatography; MS, mass spectrometry; FP, flash photolysis; RF, resonance−fluorescence; DF, discharge flow; LLPA, laser long-path absorption technique.

occurs. The integrated absorption cross section (S_{int}) is given as the integral of $\sigma(\tilde{\nu})$ over the absorption band, or, as shown here, over regions of overlapping bands:

$$S_{int} = \int_{band} \sigma(\tilde{\nu})\, d\tilde{\nu} \qquad (7)$$

Infrared spectra of the pure gases at 298 ± 2 K were recorded in the region of 4000−400 cm^{-1}, using a Bruker IFS 113v FTIR spectrometer with a nominal resolution of 1.0 cm^{-1} and Blackman-Harris 3-Term apodization of the interferograms (the linewidth of rovibrational bands in the IR region at 1 bar is ∼0.1 cm^{-1}; none of the compounds showed rotational fine structure at this instrumental resolution, and none of the compounds showed a discernible dependency in their absorption cross section by the addition of N_2 to atmospheric pressure). A Ge/KBr beam splitter was used to cover the spectral region. To ensure optical linearity, only deuterated triglycine sulfate (DTGS) detectors were used. Eight single-channel spectra, each recorded with 32 scans, were averaged to yield one background or sample spectrum. A gas cell of 2.34 ± 0.02 cm equipped with KBr windows was used. The partial pressures of the gases in the cell were in the range of 1−16 hPa and were measured using a MKS Baratron Type 122A pressure transducer with a stated accuracy of ±0.15%. The absorption cross sections were obtained from the absorbance spectra, assuming that the gas was ideal and applying a baseline correction. The baseline correction was performed by subtracting a polynomial function, which was obtained by fitting the regions of the spectrum where no absorptions were expected.

3. Results

3.1. Relative Rate Measurements. The OH reaction with $CF_3CHFCF_2OCH_2CH_3$ was studied, using $CHCl_3$ and $C_4F_9OC_2H_5$ (HFE-7200) as reference compounds. Figure 2 shows a plot of $\ln\{[CF_3CHFCF_2OCH_2CH_3]_0/[CF_3CHFCF_2OCH_2CH_3]_t\}$ vs $\ln\{[CHCl_3]_0/[CHCl_3]_t\}$ during the reaction with OH radicals;

TABLE 2: Rate Coefficients at 298 K for the Reaction of Cl Atoms with a Series of Fluorinated Ethers

reference compound[a]	k_{rel}(298 K)	k_{abs}(298 K) (cm^3 $molecule^{-1}$ s^{-1})	method[b]
		$CH_3CH_2OCF_3$	
CH_2ClCH_2Cl	1.44 ± 0.17	$(1.9 \pm 1.0) \times 10^{-12}$	RR-GC/MS
CH_3CH_2Cl	0.38 ± 0.06	$(2.8 \pm 1.4) \times 10^{-12}$	RR-GC/MS
		$(2.2 \pm 0.8) \times 10^{-12}$	weighted average
		$CF_3CH_2OCH_3$	
$C_4F_9OC_2H_5$	6.6 ± 0.4	$(1.8 \pm 0.9) \times 10^{-11}$	RR-GC/MS
		$(2.31 \pm 0.11) \times 10^{-11}$	VLPR[8]
		$CF_3CH_2OCHF_2$	
$CHCl_3$	0.153 ± 0.006	$(1.5 \pm 0.4) \times 10^{-14}$	RR-GC/MS
CHF_2CH_2F	0.449 ± 0.004	$(2 \pm 6) \times 10^{-14}$	RR-GC/MS
		$(1.5 \pm 0.4) \times 10^{-14}$	weighted average
		$(3.11 \pm 0.14) \times 10^{-14}$	VLPR[8]
		$(1.1 \pm 0.1) \times 10^{-14}$	DF− RF[2]
		$(1.2 \pm 0.1) \times 10^{-14}$	RR−FTIR[9]
		$(1.2 \pm 0.2) \times 10^{-14}$	RR−FTIR[10]
		$CF_3CHFOCHF_2$	
CH_3CCl_3	0.1426 ± 0.0031	$(1.0 \pm 2.0) \times 10^{-15}$	RR-GC/MS
CHF_2CH_2F	0.046 ± 0.004	$(2 \pm 7) \times 10^{-15}$	RR-GC/MS
		$(1.1 \pm 1.9) \times 10^{-15}$	weighted average
		$CHF_2CHFOCF_3$	
CH_3CCl_3	0.152 ± 0.008	$(1.1 \pm 2.1) \times 10^{-15}$	RR-GC/MS
CHF_2CH_2F	0.050 ± 0.007	$(2 \pm 7) \times 10^{-15}$	RR-GC/MS
		$(1.2 \pm 2.0) \times 10^{-15}$	weighted average
		$CF_3CHFOCF_3$	
CHF_2CH_2F	$<0.05 \pm 0.01$	$<3 \times 10^{-15}$	RR-GC/MS
		$(3.1 \pm 2.5) \times 10^{-14}$	RR−FP−FTIR[6]
		$(6.0 \pm 0.8) \times 10^{-17}$	RR−FTIR[11]
		$CF_3CHFCF_2OCHF_2$	
CH_3CN	$<0.05 \pm 0.01$	$<6 \times 10^{-16}$	RR-GC/MS
		$CF_3CHFCF_2OCH_2CH_3$	
CH_2ClCH_2Cl	2.62 ± 0.04	$(3.4 \pm 1.7) \times 10^{-12}$	RR-GC/MS
CH_2Cl_2	8.9 ± 0.4	$(2.9 \pm 1.5) \times 10^{-12}$	RR-GC/MS
		$(3.1 \pm 1.1) \times 10^{-12}$	weighted average
		$CF_3CF_2CF_2OCHFCF_3$	
CHF_2CH_2F	$<0.05 \pm 0.01$	$<3 \times 10^{-15}$	RR-GC/MS

[a] Reaction rate coefficients, k, and uncertainty factors from the JPL evaluation, f, of reference compounds (in units of cm^3 $molecule^{-1}$ s^{-1}) are as follows: $k(Cl + CH_2ClCH_2Cl) = 1.3 \times 10^{-12}$, $f = 1.5$ (taken from ref 22); $k(Cl + CH_3CH_2Cl) = 7.3 \times 10^{-12}$, $f = 1.5$ (taken from ref 47); $k(Cl + C_4F_9OC_2H_5) = 2.7 \times 10^{-12}$, $f = 1.5$ (taken from ref 21); $k(Cl + CHCl_3) = 9.6 \times 10^{-14}$, $f = 1.3$ (taken from ref 19); $k(Cl + CHF_2CH_2F) = 4.9 \times 10^{-14}$, $f = 3$ (taken from ref 19); $k(Cl+CH_3CCl_3) = 7.0 \times 10^{-15}$, $f = 2$ (taken from ref 19); $k(Cl+CH_3CN) = 1.2 \times 10^{-14}$, $f = 2$ (taken from ref 19); and $k(Cl+CH_2Cl_2) = 3.3 \times 10^{-13}$, $f = 1.5$ (taken from ref 19). [b] Abbreviations in this column of data are as follows: RR, relative rate; FP, flash photolysis; FTIR, Fourier transform infrared spectroscopy; GC, gas chromatography; and MS, mass spectrometry.

analysis of data from two independent experiments according to eq 3 gives $k(OH + CF_3CHFCF_2OCH_2CH_3)/k(OH + CHCl_3) = 1.69 \pm 0.11$, where the error quoted in the relative rate corresponds to the 3σ error of the statistical analysis only. The latest JPL data evaluation[19] has recommended a rate coefficient of $(1.00 \pm 0.15) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction between OH and $CHCl_3$ at 298 K, and, hence, the derived absolute OH reaction rate coefficient for $CF_3CHFCF_2OCH_2CH_3$ is $(1.69 \pm 0.28) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, where the error limit includes the error in the absolute reaction rate coefficient of the reference compound. The experimental data from an RR study using HFE-7200 as the reference compound is shown in Figure S12 (see Supporting Information) and gives a relative rate of $k(OH + CF_3CHFCF_2OCH_2CH_3)/k(OH + \text{HFE-7200}) = 1.69 \pm 0.07$. Using the average of the reported rate coefficients for the reaction between OH and HFE-7200 $(8.3 \pm 0.8) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K[20,21] places the OH rate coefficient of $CF_3CHFCF_2OCH_2CH_3$ at $(1.40 \pm 0.15) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. The weighted average of the two results give $k(OH + CF_3CHFCF_2OCH_2CH_3) = (1.47 \pm 0.13) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

Figure 3 summarizes the results from four independent RR experiments of the OH reaction with $CF_3CHFOCHF_2$, using CH_3CCl_3 as the reference compound. The relative rate obtained, $k(OH + CF_3CHFOCHF_2)/k(OH + CH_3CCl_3) = 0.670 \pm 0.24$, combined with the recommended value of $k(OH + CH_3CCl_3) = (1.00 \pm 0.15) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K[19] places the derived absolute OH reaction rate coefficient for $CF_3CHFOCHF_2$ at $(6.7 \pm 1.0) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. Experiments using CHF_2CH_2F as the reference (see Figure S6 in the Supporting Information) places the absolute OH reaction rate coefficient for $CF_3CHFOCHF_2$ at $(6.1 \pm 1.4) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} and the weighted average at $(6.5 \pm 0.8) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (see Table 1).

The results from the analyses of the data for the other OH reactions with the HFEs are included in Table 1 (the data are presented in the form of $\ln\{[HFE]_0/[(HFE]_t\}$ vs $\ln\{[REF]_0/[REF]_t\}$ in Figures S1−S12 in the Supporting Information). For the HFEs $CF_3CHFOCF_3$ and $CF_3CF_2CF_2OCHFCF_3$, we were not able to detect reaction with OH radicals, whereas the reference compound CHF_2CH_2F in both cases was observed to react readily. Because we are able to register relative rates of 1:20 with an estimated uncertainty of 20%, a conservative estimate places the OH rate coefficients of $CF_3CHFOCF_3$ and $CF_3CF_2CF_2OCHFCF_3$ as $<{}^1/_{20}$ of that of CHF_2CH_2F, that is, $<1 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (see Table 1).

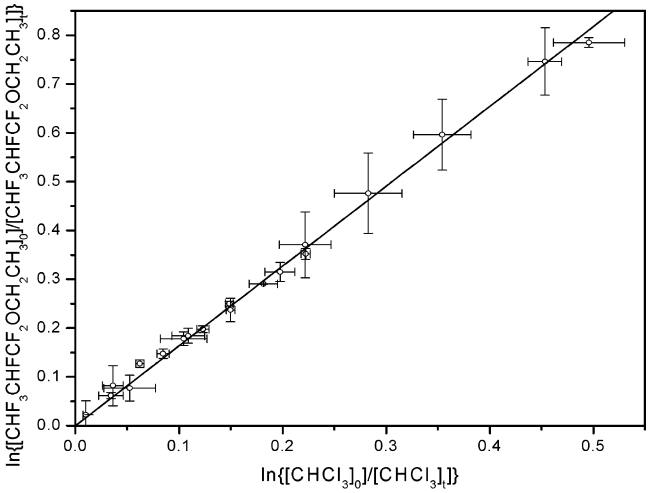

Figure 2. Decay of $CF_3CHFCF_2OCH_2CH_3$ versus $CHCl_3$ in the presence of OH radicals at 298(2) K. Nineteen data points from two independent experiments give a relative reaction rate of $k_{rel} = 1.69 \pm 0.11$. The error bars represent the variance in three consecutive measurements. The quoted error in k_{rel} corresponds to three standard deviations (3σ) from the statistical analysis.

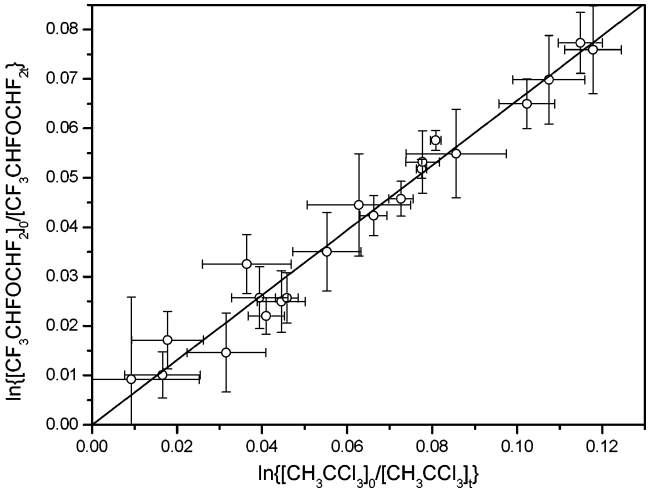

Figure 3. Decay of $CF_3CHFOCHF_2$ versus CH_3CCl_3 in the presence of OH radicals at 298(2) K. Twenty nine data points from four independent experiments give a relative reaction rate of $k_{rel} = 0.670 \pm 0.024$. The error bars represent the variance in three consecutive measurements. The quoted error in k_{rel} corresponds to 3σ from the statistical analysis.

Currently, there is a lack of compounds with well-determined Cl atom reaction rate coefficients suitable for the GC/PCI–MS method. Hydrocarbons cannot be used (CH_5^+ is the ionizing agent and causes signals corresponding to all the lower alkanes), and other reference compounds may have mass peaks masked by the fragmentation of the other reactants or products present if the GC separation is not complete—the choice of reference compounds is, in each case, a result of compromises. Of the eight different reference compounds used in our study of the Cl atom reactions, only five are included in the latest JPL evaluation,[19] and the assigned uncertainty factors are rather large: $CHCl_3$ (1.3), CH_2Cl_2 (1.5), CH_3CN (2.0), CH_3CCl_3 (2.0), and CHF_2CH_2F (3.0). The reference compounds that were not included in the JPL evaluation (CH_2ClCH_2Cl, CH_3CH_2Cl, C_4F_9-OC_2H_5) were all assigned an uncertainty factor of 1.5.

The Cl atom reaction with $CF_3CHFCF_2OCH_2CH_3$ was studied using CH_2ClCH_2Cl and CH_2Cl_2 as reference compounds. The results of the study with CH_2ClCH_2Cl as the reference compound are shown in Figure 4. The data from three independent experiments give $k(Cl + CF_3CHFCF_2OCH_2CH_3)/k(Cl + CH_2ClCH_2Cl) = 2.62 \pm 0.04$. Using a rate coefficient of 1.3×10^{-13} cm^3 molecule^{-1} s^{-1} for the reaction between Cl and CH_2ClCH_2Cl at 298 K[22] places the derived absolute Cl reaction rate coefficient for $CF_3CHFCF_2OCH_2CH_3$ at $(3.4 \pm 1.7) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. The data from the experiment using CH_2Cl_2 as the reference compound are shown in Figure S22 in the Supporting Information and gives a relative rate of $k(Cl + CF_3CHFCF_2OCH_2CH_3)/k(Cl + CH_2Cl_2) = 8.9 \pm 0.4$. The latest JPL data evaluation[19] recommends a value of $(3.3 \pm 1.6) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for the reaction of Cl with CH_2Cl_2 at 298 K, which places the value of $k(Cl + CF_3CHFCF_2OCH_2CH_3)$ at $(2.9 \pm 1.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. As was the case for the OH reactions, we were not able to detect reaction of Cl atoms with the HFEs $CF_3CHFOCF_3$ and $CF_3CF_2CF_2OCHFCF_3$, whereas the reference compound, which, again, was CHF_2CH_2F, was observed to react readily. Therefore, we place the Cl rate coefficients of $CF_3CHFOCF_3$ and $CF_3CF_2CF_2OCHFCF_3$ as $<{}^1/_{20}$ of that of CHF_2CH_2F ($<3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K) (see Table 2). The results from the analyses of the data for the other Cl atom reactions with the HFEs are included in Table 2 (the data are presented in the form of $\ln\{[HFE]_0/[(HFE]_t\}$ vs $\ln\{[REF]_0/[REF]_t\}$ in Figures S13–S22 in the Supporting Information).

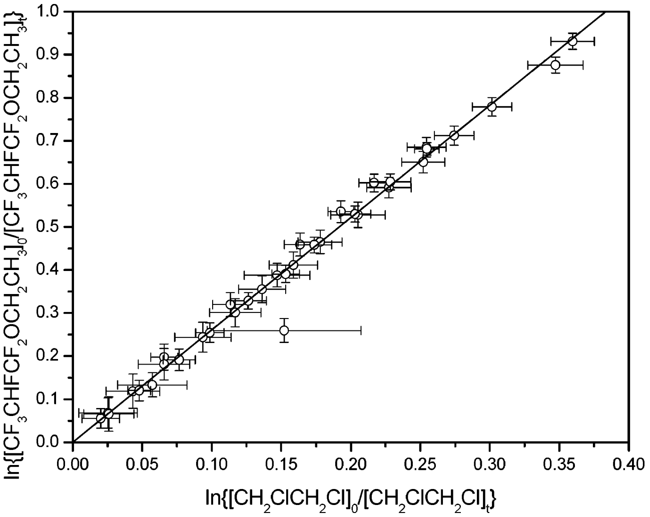

Figure 4. Decay of $CF_3CHFCF_2OCH_2CH_3$ versus CH_2ClCH_2Cl in the presence of Cl atoms at 298(2) K. Thirty five data points from three independent experiments give a relative reaction rate of $k_{rel} = 2.62 \pm 0.04$. The error bars represent the variance in three consecutive measurements. The quoted error in k_{rel} corresponds to 3σ from the statistical analysis.

3.2. IR Absorption Cross Sections. The integrated cross sections of the absorption bands of the HFEs under study were determined by plotting the integrated absorbance against the product of the number density and the path length. None of the regression lines had a y-intercept that was significantly different from zero. Therefore, a least-squares method that forced the regression line through zero was used to determine the absorption intensities. Quantified systematic errors are as follows: 0.15% for pressure measurements, 0.90% for path-length measurements, and 0.67% for temperature measurements.

The absorption cross sections (base e) of $CF_3CH_2OCH_3$ in the 3200–400 cm^{-1} region are shown in Figure 5 (the spectra of the other HFEs are given in Figures S23–S30 in the Supporting Information), and the integrated absorption cross sections are summarized in Table 3. We routinely use the absorption cross section of HCFC-22, which has been critically evaluated by Ballard et al.,[23] as a benchmark. Our measurements

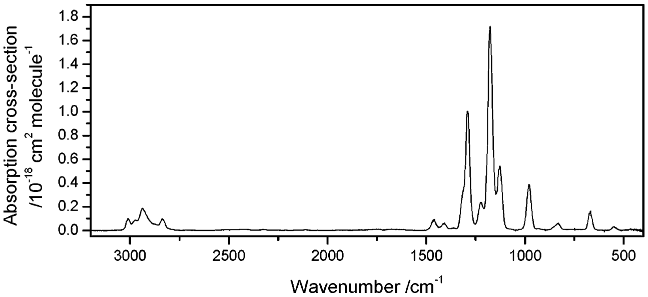

Figure 5. Infrared absorption cross section 3200−400 cm^{-1} (base e) of pure $CF_3CH_2OCH_3$ vapor at 298(2) K.

of HCFC-22 are constantly within 5% of the absorption intensities reported by Ballard and co-workers. Caveat: from our measurements of HCFC-22, we have experienced that the integrated absorption cross sections may be overestimated by as much as 20% if a standard mercury cadmium telluride (MCT) detector is used uncritically instead of a linear DTGS detector. As can be observed in Table 3, the estimated uncertainty in the integrated absorption cross section of the HFEs is, at most, 5%, which includes the error from the least-squares fit and the aforementioned systematic errors. One may also notice the excellent agreement with previous results of the absorption cross sections. In a recent work,[18] we also documented excellent agreement with two previous studies of the IR absorption cross section of $CF_3CH_2OCH_2CF_3$.[13,24] Therefore, we suggest that our measurements of the HFEs are not affected by any large systematic errors.

4. Discussion

4.1. Relative Rates of Reaction. The oxidation of HFEs such as $CF_3CH_2OCHF_2$ results in the generation of CF_3 and, thereby, CF_3O radicals. It is known that CF_3O reacts with halogenated compounds, such as CH_2FCl[25] and CF_3CH_2F,[26] with rate coefficients of 1.2×10^{-14} and 1.1×10^{-15} cm^3 molecule^{-1} s^{-1}, respectively, and we anticipate a rate coefficient of $<1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} for its reaction with the substrate and reference compounds in the present experiments. A conservative estimate of the CF_3O rate coefficient for reaction with H_2 is 2×10^{-14} cm^3 molecule^{-1} s^{-1}.[17] Because the concentration of H_2, which was used as the OH source by reaction with O(^{1}D), is ∼3 orders of magnitude larger than those of the substrate and reference compounds in our experiments, we suggest that the large concentrations of H_2 in the system will act as a scavenger for CF_3O radicals and that our results are not seriously affected by the reactions of the CF_3O radicals in the reactor. In the cases where chlorine-containing reference compounds were used in the OH reaction experiments, H_2 will also act as a scavenger for the possible Cl atoms that are released ($k(Cl + H_2) = 1.65 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K[19]).

Table 1 summarizes the results from our studies of the OH reaction with the nine fluorinated ethers. In the cases where we report results from experiments with more than one reference compound, the derived absolute rate coefficients are in agreement within the error limits, which are dominated by the uncertainties in the absolute values of the reaction rate coefficients of the reference compounds. For $CF_3CH_2OCH_3$ our weighted average result of $k(OH + CF_3CH_2OCH_3) = (5.7 \pm 0.8) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} compares well with previous results from an absolute rate study by Zhang and co-workers,[3] and with the preliminary results from an RR study by Nolan et al.[5] Also, for $CF_3CH_2OCHF_2$, our value of $k(OH + CF_3CH_2OCHF_2) = (9.1 \pm 1.1) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} agrees with the previous results from both the RR and absolute rate experiments.[2−5] For both $CHF_2CHFOCF_3$ and $CF_3CH_2OCHF_2$, the present results for their OH reaction rate coefficients are ∼15% *lower* than those from the absolute rate experiments. For $CF_3CHFOCHF_2$, however, our result of $k(OH + CF_3CHFOCHF_2) = (6.5 \pm 0.8) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} is ∼50% *higher* than that from the absolute rate study of Langbein et al.[1] It is difficult to offer an explanation for this discrepancy, because the documentation in the study by Langbein et al. is inadequate. We note that the results for the OH reaction rate coefficients of the other four compounds presented in the same study of Langbein et al.[1] all are 20%−75% lower than those determined by Brown and co-workers.[27,28] Furthermore, we note that our reference compound—in this case, CH_3CCl_3—has one of the best-known OH reaction rate coefficients in the literature, and our result is based on 29 data points from four independent experiments (see Figure 3).

As mentioned, we were not able to detect the reaction of OH radicals with $CF_3CHFOCF_3$ and we can only place an upper limit of 1×10^{-15} cm^3 molecule^{-1} s^{-1} for this reaction at 298 K. This is obviously in conflict with the results of Li et al.,[6] who reported a value of $(4.98 \pm 1.64) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. Takahashi et al.[7] has recently performed an RR study using FTIR detection, in which they monitored the formation of the oxidation product of the OH reaction, $FC(O)OCF_3$, versus the loss of their reference compounds (HCCH and H_2CCH_2), and thereby indirectly determined a value of $k(OH + CF_3CHFOCF_3) = (1.4 \pm 0.3) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (the uncertainty quoted by Takahashi et al.[7] only reflects the accuracy of their measurements). Taking the errors in the reaction rate coefficients of the reference compounds into consideration, the present upper limit for the OH reaction rate coefficient of $CF_3CHFOCF_3$ is in agreement with the result of Takahashi et al.[7] We further note that the corrections for wall loss and radial diffusion of OH radicals in the experiments of Li et al.[6] are of the same magnitude as that derived in their pseudo-first-order rate constants, and that rejecting obvious outliers from the pseudo-first-order rate constants will reduce the derived absolute reaction rate coefficient by almost a factor of 2. Finally, we agree with the suggestion of Takahashi et al.[7] that the absolute rate experiment of Li et al.[6] most likely is affected by their sample having a small amount of a more reactive impurity: given an OH reaction rate coefficient of 10^{-15} cm^3 molecule^{-1} s^{-1}, a 0.01% impurity with a rate constant of $k_{OH} = 10^{-12}$ cm^3 molecule^{-1} s^{-1} would affect the absolute rate measurements by 10%.

There are no previous kinetic results for the OH reaction with $CHF_2CHFOCF_3$, $CF_3CHFCF_2OCHF_2$, $CF_3CHFCF_2OCH_2CH_3$, and $CF_3CF_2CF_2OCHFCF_3$. For the latter HFE, we can only place an upper limit of 1×10^{-15} cm^3 molecule^{-1} s^{-1} for its reaction rate coefficient with OH. For the other three HFEs, our weighted averages from experiments with several reference compounds, and including errors in the absolute value of the reaction rate coefficients of the reference compounds, are as follows: $k(OH + CHF_2CHFOCF_3) = (6.8 \pm 1.1) \times 10^{-15}$, $k(OH + CF_3CHFCF_2OCHF_2) = (1.69 \pm 0.26) \times 10^{-14}$, and $k(OH + CF_3CHFCF_2OCH_2CH_3) = (1.72 \pm 0.13) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K.

The results from the various studies of the Cl atom reactions with the HFEs are compared in Table 2. As can be seen, the derived absolute values for the Cl atom reaction rate coefficients, obtained using different reference compounds, sometimes differ by more than the combined statistical errors. We attribute this phenomenon mainly to errors in the values of the reference

TABLE 3: Integrated Absorption Cross Sections (S_{int}) in the Mid-infrared Region of a Series of HFEs and Estimated Global Warming Potentials *GWP*(t) for 20-Year and 100-Year Time Horizons, Relative to CFC-11

compound	spectral region (cm^{-1})	integrated cross section (x 10^{-17} cm $molecule^{-1}$)	k_{OH} (cm^3 $molecule^{-1}$ s^{-1})	τ_{OH} (yr)[a]	*IF* (W m^{-2} $ppbv^{-1}$)[b]	$HGWP_{20}$[c]	$HGWP_{100}$[c]
$CH_3CH_2OCF_3$	1550−550	22.0 ± 0.3	1.55×10^{-13}	0.431	0.210	0.025	0.010
$CF_3CH_2OCH_3$	1525−500	15.3 ± 0.7	5.7×10^{-13}	0.117	0.190	0.006	0.002
	2000−500	16.1 ± 0.4[d]					
$CF_3CH_2OCHF_2$	1550−470	26.5 ± 0.3	9.1×10^{-15}	7.348	0.374	0.550 (2749)	0.224 (897)
		26.0 ± 1.3[e]		4.4[e]	0.384[e]	0.31[e]	0.12[e]
		26.31[f]					
$CHF_2CHFOCF_3$	1600−465	28.2 ± 0.4	6.8×10^{-15}	9.834	0.349	0.630 (3152)	0.276 (1106)
$CF_3CHFOCHF_2$	1530−485	30.3 ± 0.7	6.5×10^{-15}	10.288	0.447	0.753 (3766)	0.335 (1341)
	2000−500	30.8 ± 0.8[d]					
$CF_3CHFOCF_3$	1600−485	37.0 ± 0.4	$<1 \times 10^{-15}$	>67	0.402	>1.199 (>5995)	>1.372 (>5488)
	1460−645	33.3 ± 3.4[g]		40	0.36	1.04	0.97
	1500−700	41 ± 2[h]					
	2000−500	38.4 ± 1.0[d]					
$CF_3CHFCF_2OCHF_2$	1450−620	34.2 ± 1.1	1.69×10^{-14}	3.957	0.485	0.303 (1513)	0.116 (465)
$CF_3CHFCF_2OCH_2CH_3$	1450−675	27.4 ± 0.3	1.72×10^{-13}	0.389	0.331	0.021	0.008
$CF_3CF_2CF_2OCHFCF_3$	1450−500	43.7 ± 0.8	$<1 \times 10^{-15}$	>67	0.563	>1.092 (>5461)	>1.250 (>5000)
CFC-11				50.00[i]	0.26[i]	1.000 (5000)	1.000 (4000)

[a] The atmospheric lifetimes (τ_{OH}) were calculated from a global average OH concentration of 9.4 × 10^5 radicals/cm^3.[33] [b] The instantaneous cloudy-sky radiative forcing (*IF*) values for a 1 ppbV increase in atmospheric concentrations were calculated according to the procedure given by Pinnock et al.[41] [c] Global warming potential for the HFEs, relative to CFC-11. Value in parentheses denotes the corresponding global warming potential, relative to CO_2. [d] From ref 15. [e] From ref 12. [f] From ref 13. [g] From ref 7. [h] From ref 14. [i] From IPCC 2001.[48]

reaction rate coefficients (see previous discussion) and stress again that the error limits presented here for the Cl reaction rate coefficients of the HFEs only reflect the precision of the experiments. For $CF_3CH_2OCH_3$, our result of (1.8 ± 1.1) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the Cl reaction at 298 K compares with the value of (2.31 ± 0.11) × 10^{-11} obtained by an absolute method at very low pressure (VLPR).[8] For $CF_3CH_2OCHF_2$, two RR studies [9,10] agree with an absolute rate study[2] on a value of (1.2 ± 0.2) × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} for the Cl rate coefficient at 298 K—our result of (1.5 ± 0.4) × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} from experiments using $CHCl_3$ as a reference matches, considering the uncertainty factor of 1.3 in $k(Cl + CHCl_3)$.[19] The corresponding result from experiments with CHF_2CH_2F as a reference is almost 50% larger, and the result from a VLPR study by Kambanis et al.[8] of (3.11 ± 0.14) × 10^{-14} cm^3 $molecule^{-1}$ s^{-1} is another 50% higher. Although we cannot completely disregard CF_3O radical reactions as a potential source of error, we suggest that the difference between our results using $CHCl_3$ and CHF_2CH_2F as a reference is mainly attributable to errors in the reaction rate coefficients of the reference compounds.

For $CF_3CHFOCF_3$ and $CF_3CF_2CF_2OCHFCF_3$, we could only determine an upper limit for the Cl atom reaction rate coefficient of 3 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} at 298 K. Previous results for the former C_3−HFE are obviously in conflict. Li et al.[6] reported a value of $k(Cl + CF_3CHFOCF_3) = (3.1 \pm 2.5) \times 10^{-14}$, whereas Takahashi et al.[11] reported a value of 6 × 10^{-17} cm^3 $molecule^{-1}$ s^{-1}. Our upper limit for this reaction rate coefficient supports the results of Takahashi and co-workers. All three studies are RR studies; both Li et al. and Takahashi et al. used FTIR detection, whereas we have used GC−MS detection. However, the major difference between the experimental conditions in the study by Li et al. and those of the present and the Takahashi et al. study is observed in the concentration of the reactants. In the present study and in the Takahashi et al.[11] study, the reactant concentration is ~5 ppm in air or N_2, whereas in the study of Li et al.,[6] the reaction gas mixture consists of 0.5−1 Torr of $CF_3CHFOCF_3$, 2−5 Torr of the reference compound (CH_3F or CH_2F_2), 5−10 Torr Cl_2, and 5 Torr O_2. A closer inspection of the Li et al.[6] results, which are given as plots of $\ln\{[REF]_0/[REF]_t\}$ vs $\ln\{[HFE]_0/[(HFE]_t\}$, reveals that their data points show a clear curvature toward the reference compound axis. That is, there are obviously some additional reactions occurring in their system and the underlying assumption in their RR study—that the reactant and reference compounds are lost solely via reaction with the radical species of interest and that they are not reformed in any process—is not fulfilled. As CF_3 radicals are generated in the oxidation of $CF_3CHFOCF_3$ (see previous discussion), we suggest that their RR results reflect the reactions of CF_3O radicals rather than those of the Cl atoms.

The Cl reaction rate coefficient of $CF_3CHFCF_2OCHF_2$ is poorly determined in the present study, and we only quote an upper limit of 6.0 × 10^{-16} cm^3 $molecule^{-1}$ s^{-1} at 298 K for this reaction. For the other HFEs, we currently prefer to quote the weighted average values $k(Cl + CH_3CH_2OCF_3) = (2.2 \pm 0.8) \times 10^{-12}$, $k(Cl + CF_3CHFOCHF_2) = (1.1 \pm 1.9) \times 10^{-15}$, and $k(Cl + CHF_2CHFOCF_3) = (1.2 \pm 2.0) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K; the error limits given are essentially determined by the uncertainties in the reaction rate coefficients of the reference compounds and do not reflect the precision of the experiments.

The reference compound CHF_2CH_2F is, from a chemical point of view, ideal as a reference compound in the present study of HFEs. Unfortunately, its reaction rate coefficient with Cl atoms is inadequately determined and, as mentioned previously, the assigned uncertainty factor in the latest JPL evaluation is 3.[19] We may derive $k(Cl + CHF_2CH_2F)$ from the experiments where we used other reference compounds in addition to CHF_2CH_2F: that is, in the experiments with $CF_3CH_2OCHF_2$, where $CHCl_3$ also was used, and in the experiments with $CF_3CHFOCHF_2$ and $CHF_2CHFOCF_3$, where CH_3CCl_3 also was used. From these data, we extract $k(Cl + CHF_2CH_2F)/k(Cl + CHCl_3) = 0.341 \pm 0.013$, $k(Cl + CHF_2CH_2F)/k(Cl + CH_3CCl_3) = 3.10 \pm 0.28$ and 3.0 ± 0.5. Taking $k(Cl + CHCl_3) = 9.6 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} and $k(Cl + CH_3CCl_3) = 7.0 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, with uncertainty factors of 1.3 and 2, respectively,[19] places the weighted average of $k(Cl + CHF_2CH_2F) = (3.2 \pm 0.9) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K, where the error limit includes the three-standard-deviation (3σ) statistical errors from the data analyses, as well as the assigned error limits in the reaction rate coefficients of the reference compounds. Thus, the present data suggest that the Cl reaction rate coefficient

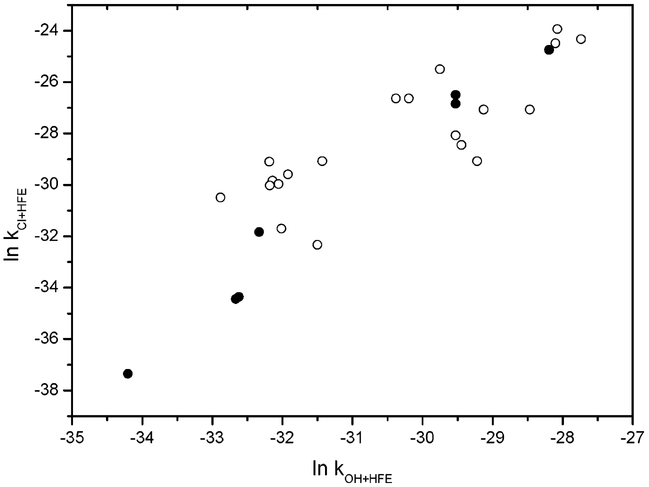

Figure 6. Correlation between ln{$k_{\mathrm{OH+HFE}}$} and ln{$k_{\mathrm{Cl+HFE}}$}: (○) literature data collected in ref 30 and (●) this work.

of CHF_2CH_2F is 35% lower than that reported by Tschuikow-Roux et al. from RR studies.[29]

There is a clear correlation between the logarithms of the OH and the Cl rate coefficients at 298 K with the same substrate, suggesting that the preferred site of reaction may be the same for the two radicals. Figure 6 shows the present as well as other available data in the literature.[18,30] The correlation may, in part, be rationalized in terms of the quite-different C−H bond dissociation enthalpy (BDE_{C-H}) values of the >CH−, $-CH_2-$, and $-CH_3$ groups in the HFEs, for which an empirical, and easy-to-use, interpolation/estimation method of BDE_{C-H} (based on density functional theory (DFT) calculations and an Arrhenius-type relation between BDE and ln k_{OH}) was recently presented[31] (see later discussion). The correlation coefficient between the predicted and calculated ln k_{OH} values for the present HFEs is ca. 0.9. Generally, however, the method apparently underestimates the OH reaction rate coefficients by a factor of 2.

4.2. Atmospheric Lifetimes and Global Warming Potentials. The atmospheric lifetimes of the HFEs due to removal by reaction with OH radicals (τ_{OH}) may be estimated from the data obtained in this study. Assuming that the HFEs studied here will have the same atmospheric distribution as CH_3CCl_3, their atmospheric lifetimes ($\tau_{\mathrm{HFE}}^{\mathrm{OH}}$) may be calculated, relative to that of CH_3CCl_3, from[32]

$$\tau_{\mathrm{HFE}}^{\mathrm{OH}} = \frac{k_{\mathrm{OH+CH_3CCl_3}}(272\ \mathrm{K})}{k_{\mathrm{OH+HFE}}(272\ \mathrm{K})} \times \tau_{\mathrm{CH_3CCl_3}}^{\mathrm{OH}} \qquad (8)$$

where $\tau_{\mathrm{CH_3CCl_3}}^{\mathrm{OH}}$ is the atmospheric lifetime of CH_3CCl_3, with respect to reaction with OH ($\tau_{\mathrm{CH_3CCl_3}}^{\mathrm{OH}} = 5.99$ years[33]), and the scaling temperature of 272 K is chosen to compensate for the tropospheric OH distribution.[34] To estimate the reaction rate coefficients at 272 K, we assume an Arrhenius behavior of the OH + HFE reactions and have taken $E_a/R = 1500$ as an average of the available energies of activation for the OH reaction with HFEs.[2,24,35−40] Using the value of $k_{\mathrm{OH+CH_3CCl_3}}(272\ \mathrm{K}) = 6.0 \times 10^{-15}$ $\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ from the latest JPL evaluation,[19] the following lifetimes in the gas phase are observed: $\tau_{OH}(CH_3CH_2OCF_3) \approx 160$ days, $\tau_{OH}(CF_3CH_2OCH_3) \approx 43$ days, $\tau_{OH}(CF_3CH_2OCHF_2) \approx 7.4$ years, $\tau_{OH}(CHF_2CHFOCF_3) \approx 9.8$ years, $\tau_{OH}(CF_3CHFOCHF_2) \approx 10.3$ years, $\tau_{OH}(CF_3CHFOCF_3) > 67$ years, $\tau_{OH}(CF_3CHFCF_2OCH_2CH_3) \approx 142$ days, $\tau_{OH}(CF_3CHFCF_2OCHF_2) \approx 4.0$ years, and $\tau_{OH}(CF_3CF_2CF_2OCHFCF_3) > 67$ years. The contribution from other radicals to the removal of the studied HFEs in the atmosphere is insignificant, except for the short-lived species $CH_3CH_2OCF_3$, $CF_3CH_2OCH_3$, and $CF_3CHFCF_2OCHF_2$, where as much as 30% may be removed by Cl atoms.

Pinnock et al.[41] provided a simple method for estimating the instantaneous cloudy-sky radiative forcing (*IF*) directly from a molecule's absorption cross sections. Global warming potentials for the HFEs, relative to CFC-11 (*HGWP*(*t*)), can then be calculated from the following expression:[42]

$$HGWP(t) = \left(\frac{IF_{\mathrm{HFE}}}{IF_{\mathrm{CFC-11}}}\right)\left(\frac{\tau_{\mathrm{HFE}}}{\tau_{\mathrm{CFC-11}}}\right)\left(\frac{M_{\mathrm{HFE}}}{M_{\mathrm{CFC-11}}}\right) \times \left[\frac{1-\exp(-t/\tau_{\mathrm{HFE}})}{1-\exp(-t/\tau_{\mathrm{CFC-11}})}\right] \qquad (9)$$

where *M* is the molecular mass and *t* is the time horizon over which the instantaneous forcing is integrated. Instantaneous forcings and global warming potentials for a time horizon of 20 and 100 years for the HFEs are included in Table 3. The data for CFC-11 were taken from the work of Pinnock et al.[41] For the HFEs with atmospheric lifetimes longer than 1 year, the global warming potentials, relative to CO_2 (*GWP*(*t*)), were estimated from that of CFC-11, referenced to CO_2:[43]

$$GWP_{\mathrm{HFE}}(t) = HGWP_{\mathrm{HFE}}(t) \times GWP_{\mathrm{CFC-11}}(t) \qquad (10)$$

The instantaneous forcings of the HFEs are relatively large, compared to that of CFC-11, and the global warming potential of the long-lived HFEs $CF_3CHFOCF_3$ and $CF_3CF_2CF_2OCHFCF_3$ is considerable. For the other HFEs studied, the global warming potentials are moderate, because of their relatively short lifetimes.

Pinnock et al.[41] reported that the model generally overestimates the real forcing when calculating the instantaneous radiative forcing directly from the absorption cross sections. Therefore, it is likely that the present results provide upper estimates for the global warming potentials of the four HFEs studied. With the exception of $CF_3CHFOCF_3$ and $CF_3CF_2CF_2OCHFCF_3$, the atmospheric lifetimes of the HFEs studied are sufficiently short, such that their global warming potentials are much smaller than those of the compounds they are meant to replace.

4.3. Atmospheric Fate of the Hydrofluoroethers (HFEs). HFEs have a very slow rate of dissolution in water, with their uptake coefficients ranging from 10^{-6} to 10^{-8}.[44] Therefore, uptake in rainwater or cloud droplets is not an important atmospheric sink for HFEs and the major fate of the HFEs in the troposphere is reaction with OH. Takahashi and co-workers reported CF_2O and CF_3OCFO to be the sole products in the oxidation of $CF_3CHFOCF_3$ and interpreted this in terms of a higher activation barrier to breaking the C−O bond than that necessary to break the $C-CF_3$ bond.[11]

Nolan et al. studied the atmospheric fate of $CF_3CH_2OCH_3$ and reported the formation of ~90% CF_3CH_2OCHO and ~10% CF_2O (originating from CF_3 radicals) in the Cl initiated oxidation.[5] Although we have not quantified the yield of CF_2O, our results also suggest CF_3CH_2OCHO to be the main product (84% ± 5% of the ester formation); however, in addition, we find that $CF_3C(O)OCH_3$ may account for as much as 16% of the ester formation in the oxidation. That is, the two routes (eqs 9 and 10) of the alkoxy-radical, eventually resulting from

H-abstraction from the methylene group in $CF_3CH_2OCH_3$, are equally important:

$$CF_3CH(\dot{O})OCH_3 \xrightarrow{O_2} CF_3C(O)OCH_3 + HO_2 \quad (11)$$

$$\xrightarrow{\Delta} CF_3 + CH(O)OCH_3 \quad (12)$$

The product distribution derived from combining results from the present work and that of Nolan et al.[5] (~75% CF_3CH_2OCHO, ~15% $CF_3C(O)OCH_3$, ~10% $CF_2O + CH_3OCHO$) is apparently not in complete agreement with the predicted C−H bond dissociation enthalpies[31]—$BDE_{C-H}(CF_3C\mathbf{H}_2OCH_3) \approx 398$ kJ/mol and $BDE_{C-H}(CF_3CH_2OC\mathbf{H}_3) \approx 406$ kJ/mol—although the statistical factor of 3:2 compensates for some of the discrepancy.

In $CF_3CF_2CF_2OCHFCF_3$, there is only one possible site of oxidation, leading either to $CF_3 + CF_3CF_2CF_2OCFO$ or to $CF_3CFO + 3CF_2O$. We could only identify CF_2O among the products. In $CHF_2CHFOCF_3$, the two C−H BDEs are predicted to have approximately the same value: $BDE_{C-H}(C\mathbf{H}F_2CHFOCF_3) \approx 425$ kJ/mol and $BDE_{C-H}(CHF_2C\mathbf{H}FOCF_3) \approx 425$ kJ/mol. However, both routes will lead to the same oxidation products:

$$CHF_2CHFOCF_3 \xrightarrow{Ox} CF_2O + CF_3OCFO$$

We have recently presented results from a study of the products formed in the oxidation of $(CF_3)_2CHOCH_3$, $CF_3CH_2OCH_2CF_3$, $CF_3CF_2CH_2OCH_3$, and $CHF_2CF_2CH_2OCH_3$ and found a clear correspondence between the estimated BDE_{C-H} and the main site of reaction.[18] The differences in BDEs are so large (>10 kJ/mol) in the other HFEs studied here that only one major site of the initial radical attack is expected. Thus, the atmospheric oxidation of $CH_3CH_2OCF_3$ will result in $CH_3C(O)OCF_3$ as the main product: $BDE_{C-H}(C\mathbf{H}_3CH_2OCF_3) \approx 430$ kJ/mol and $BDE_{C-H}(CH_3C\mathbf{H}_2OCF_3) \approx 405$ kJ/mol. The H-abstraction in $CF_3CH_2OCHF_2$ will occur at the CH_2 group, and the alkoxy-radical eventually formed will undergo C−C bond scission to form CF_3 radicals and CHF_2OCHO: $BDE_{C-H}(CF_3C\mathbf{H}_2OCHF_2) \approx 410$ kJ/mol and $BDE_{C-H}(CF_3CH_2OC\mathbf{H}F_2) \approx 428$ kJ/mol. In $CF_3CHFOCHF_2$, with $BDE_{C-H}(CF_3C\mathbf{H}FOCHF_2) \approx 422$ kJ/mol and $BDE_{C-H}(CF_3CHFOC\mathbf{H}F_2) \approx 432$ kJ/mol, the main route will lead to $CF_3 + CHF_2OCFO$, whereas in $CF_3CHFCF_2OCHF_2$ the products expected are $CF_3 + CHF_2OCF_2CFO$, $BDE_{C-H}(CF_3C\mathbf{H}FCF_2OCHF_2) \approx 423$ kJ/mol and $BDE_{C-H}(CF_3CHFCF_2OC\mathbf{H}F_2) \approx 434$ kJ/mol. Finally, the atmospheric oxidation of $CF_3CHFCF_2OCH_2CH_3$ should exclusively result in $CF_3CHFCF_2OC(O)CH_3$, as $BDE_{C-H}(CF_3C\mathbf{H}FCF_2OCH_2CH_3) \approx 422$ kJ/mol, $BDE_{C-H}(CF_3CHFCF_2OC\mathbf{H}_2CH_3) \approx 407$ kJ/mol, and $BDE_{C-H}(CF_3CHFCF_2OCH_2C\mathbf{H}_3) \approx 430$ kJ/mol.

Previous studies have shown that the esters originating from the HFEs are all less reactive toward gas-phase oxidants than their parent HFEs.[18,45,46] They may likely dissolve in droplets and aerosols, hydrolyze, and undergo further oxidation in the liquid phase. The fluoroformates (R−O−CFO) and the carbonylfluorides (R−CFO) are also likely to be incorporated in droplets and aerosols, hydrolyze, and undergo further oxidation. That is, of the nine HFEs studied, only $CF_3CH_2OCH_3$, $CF_3CHFCF_2OCH_2CH_3$, and $CF_3CHFCF_2OCHF_2$ will contribute to the environmental burden of trifluoroacetic acid. The other HFEs studied will eventually become HF and CO_2.

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Supporting Information Available: Kinetic data for OH and Cl reactions in the form of $\ln\{[HFE]_0/[(HFE]_t\}$ vs $\ln\{[REF]_0/[REF]_t\}$ and infrared absorption cross sections (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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