Atmospheric Chemistry of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$: Reaction with Cl Atoms and OH Radicals, Degradation Mechanism, and Global Warming Potentials

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Fourier transform infrared (FTIR) smog chamber techniques were used to measure $k(Cl + CF_3CFHCF_2OCF_3) = (4.09 \pm 0.42) \times 10^{-17}$, $k(OH + CF_3CFHCF_2OCF_3) = (1.43 \pm 0.28) \times 10^{-15}$, $k(Cl + CF_3CFHCF_2OCF_2H) = (6.89 \pm 1.29) \times 10^{-17}$, and $k(OH + CF_3CFHCF_2OCF_2H) = (1.79 \pm 0.34) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} in 700 Torr of N_2/O_2 diluent at 296 K. The atmospheric lifetimes of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ are approximately 40 and 32 years, respectively. Chlorine atom-initiated oxidation of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ gives $CF_3C(O)F$ in molar yields of 82 ± 5% and 96 ± 6%, respectively. The 100-year time horizon global warming potentials of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ relative to CO_2 are 4530 and 4340. Results are discussed with respect to the atmospheric chemistry of hydrofluoroethers.

1. Introduction

Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) and halon release into the atmosphere[1,2] has led to an international effort to replace these compounds with environmentally acceptable alternatives. Hydrofluoroethers (HFEs) are a class of compounds which have been developed to replace CFCs and halons in applications such as the cleaning of electronic equipment, heat transfer, carrier fluids for lubricant deposition, and fire suppression. Prior to their large-scale industrial use, an assessment of the atmospheric chemistry, and hence environmental impact, of HFEs is needed. To address this need, the atmospheric chemistry of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ was investigated. Smog chamber/FTIR techniques were used to determine the following parameters for these compounds: (i) kinetics of reactions with chlorine atoms, (ii) kinetics of reactions with hydroxyl radicals, (iii) infrared spectra, (iv) atmospheric lifetimes, and (v) global warming potentials. Results are reported herein.

2. Experimental Section

All experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[3] The reactor was surrounded by 22 fluorescent blacklamps (GE F40BLB) which were used to photochemically initiate the experiments.

Cl atoms were generated by the photolysis of Cl_2

$$Cl_2 + h\nu \rightarrow 2Cl \tag{1}$$

OH radicals were generated by UV irradiation of CH_3ONO/NO/air mixtures

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{2}$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \tag{3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{4}$$

Reactant and product concentrations were monitored using in situ FTIR. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 m. Reference spectra were acquired by expanding known volumes of reference compounds into the chamber.

Experiments were performed at 296 ± 2 K in 700 Torr of N_2/O_2 diluent. All reagents except CH_3ONO were obtained from commercial sources at purities greater than 99%. The samples of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ were supplied by Great Lakes Chemical Corporation. Ultrahigh purity nitrogen, oxygen, and synthetic air diluent gases were used as received. CH_3ONO was prepared by the dropwise addition of concentrated H_2SO_4 to a saturated solution of $NaNO_2$ in methanol and was devoid of any detectable impurities using FTIR analysis.

In smog chamber experiments, the unwanted loss of reactants, reference compounds and products via photolysis, chemistry occurring in the dark, and heterogeneous reactions have to be considered. The reactant and reference compounds used in the present work ($CF_3CFHCF_2OCF_3$, $CF_3CFHCF_2OCF_2H$, C_2H_4, C_2H_2, CF_3CF_2H, and CF_3CH_3) do not absorb at wavelengths above the Pyrex cutoff (>300 nm). Photolytic loss of these compounds will not be a complication in the present work. Control experiments were performed in which reactant and product mixtures obtained after UV irradiation were allowed to stand in the dark in the chamber for 30 min. There was no observable (<2%) loss of reactants or products, showing that heterogeneous reactions are not a significant complication in the present experiments. Analysis of the IR spectra was achieved through a process of spectral stripping, in which small fractions of the reference spectrum were subtracted incrementally from

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the sample spectrum. The concentration of reactant and reference compounds could be determined with a precision of ±1% of their initial concentrations.

The relative rate method is a well-established and widely used procedure for measuring the reactivity of Cl atoms and OH radicals with organic compounds.[4] Kinetic data are derived by monitoring the loss of a reactant compound ($CF_3CFHCF_2OCF_3$ or $CF_3CFHCF_2OCF_2H$ in the present work) relative to one or more reference compounds. The decays of the reactant and reference are then plotted using the following expression

$$Ln\left(\frac{[\text{Reactant}]_{t_0}}{[\text{Reactant}]_t}\right) = \frac{k_{\text{Reactant}}}{k_{\text{Reference}}} Ln\left(\frac{[\text{Reference}]_{t_0}}{[\text{Reference}]_t}\right)$$

where $[\text{Reactant}]_{t_0}$, $[\text{Reactant}]_t$, $[\text{Reference}]_{t_0}$, and $[\text{Reference}]_t$ are the concentrations of reactant and reference at times t_0 and t, and k_{Reactant} and $k_{\text{Reference}}$ are the rate constants for the reactions of Cl atoms or OH radicals with the reactant and reference.

The photolysis of CH_3ONO is the most convenient and widely used source of OH radicals in relative rate studies. CH_3ONO itself reacts with OH at a moderate rate (approximately 3×10^{-13} cm^3 $molecule^{-1}$ s^{-1}[5]), scavenges OH radicals, and makes the loss of a less reactive compound (e.g., $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$) small and difficult to measure. In the present work, we have employed a variation on the typical relative rate method in which the loss of the reactant ($CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$) was monitored indirectly by observing the formation of its oxidation product ($CF_3C(O)F$). Large initial concentrations of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ (0.74−2.18 Torr) were used to facilitate monitoring of the $CF_3C(O)F$ product resulting from small (<0.2%) consumptions of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$. It should be stressed that an accurate determination of the initial reactant concentrations is vital to this variation of the relative rate method.

3. Results

3.1. Cl Atom Kinetics. Relative rate experiments were performed to measure the rates of reaction of Cl atoms with $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$. The results are shown in Figure 1. Linear least-squares analyses of the data in Figure 1 give $k_5/k_7 = 0.163 \pm 0.010$, $k_5/k_8 = 1.14 \pm 0.09$, $k_6/k_7 = 0.253 \pm 0.019$, and $k_6/k_8 = 2.07 \pm 0.17$. Using literature values of $k_7 = (2.5 \pm 0.2) \times 10^{-16}$[6] and $k_8 = (3.6 \pm 0.2) \times 10^{-17}$[7] gives the following values: $k_5 = (4.08 \pm 0.41) \times 10^{-17}$ and $(4.10 \pm 0.39) \times 10^{-17}$ and $k_6 = (6.33 \pm 0.69) \times 10^{-17}$ and $(7.45 \pm 0.73) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}. The fact that experiments using different references give indistinguishable results provides confidence in our results. We choose to quote final values of $k_5 = (4.09 \pm 0.42) \times 10^{-17}$ and $k_6 = (6.89 \pm 1.29) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}, which are the averages of the individual determinations with error limits which encompass the extremes of the individual determinations.

$$Cl + CF_3CFHCF_2OCF_3 \rightarrow \text{products} \quad (5)$$

$$Cl + CF_3CFHCF_2OCF_2H \rightarrow \text{products} \quad (6)$$

$$Cl + CF_3CF_2H \rightarrow \text{products} \quad (7)$$

$$Cl + CF_3CH_3 \rightarrow \text{products} \quad (8)$$

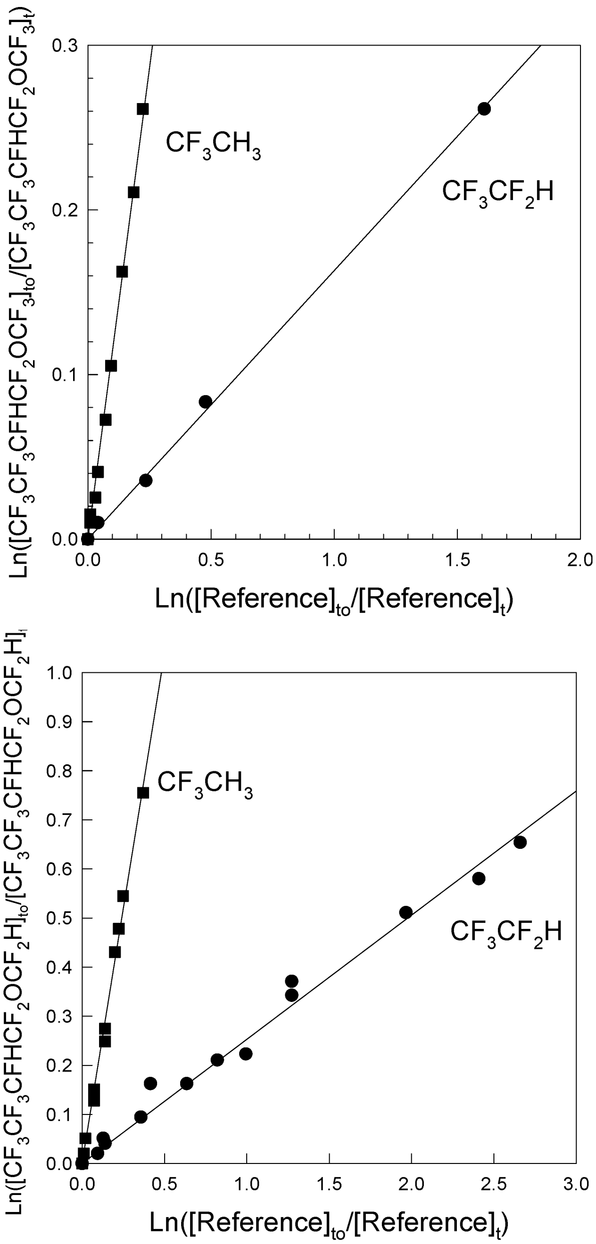

Figure 1. Kinetic data for reactions of Cl atoms with $CF_3CFHCF_2OCF_3$ (top) and $CF_3CFHCF_2OCF_2H$ (bottom).

The value of $k_5 = (4.09 \pm 0.42) \times 10^{-17}$ measured in the present work is consistent with the upper limit of $k_5 < 7 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} reported by Oyaro et al.[8] There are no literature data for k_6 to compare with our results. The reactivity of Cl atoms toward $CF_3CFHCF_2OCF_3$ is indistinguishable, within the experimental uncertainties, from that toward CF_3CFHCF_3 ($k_{Cl+CF3CFHCF3} = (4.5 \pm 1.2) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}[9]). Interestingly, the reactivity of Cl atoms toward $CF_3CFHCF_2OCF_2H$ measured in the present work is indistinguishable, within the experimental uncertainties, from that of the sum of CF_3CFHCF_3 and CF_3OCF_2H: $(4.5 \pm 1.2) \times 10^{-17} + (2.3 \pm 0.3) \times 10^{-17} = (6.8 \pm 1.5) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}.[9,10] The simplest explanation for the experimental observations is that the reactivities of the two C−H bonds in $CF_3CFHCF_2OCF_2H$ are independent and additive. The simple kinetic arguments presented here would suggest that approximately 30% of the reaction of Cl atoms with $CF_3CFHCF_2OCF_2H$ proceeds via attack on the terminal C−H bond with the remaining approximately 70% of the reaction occurring at the secondary site.

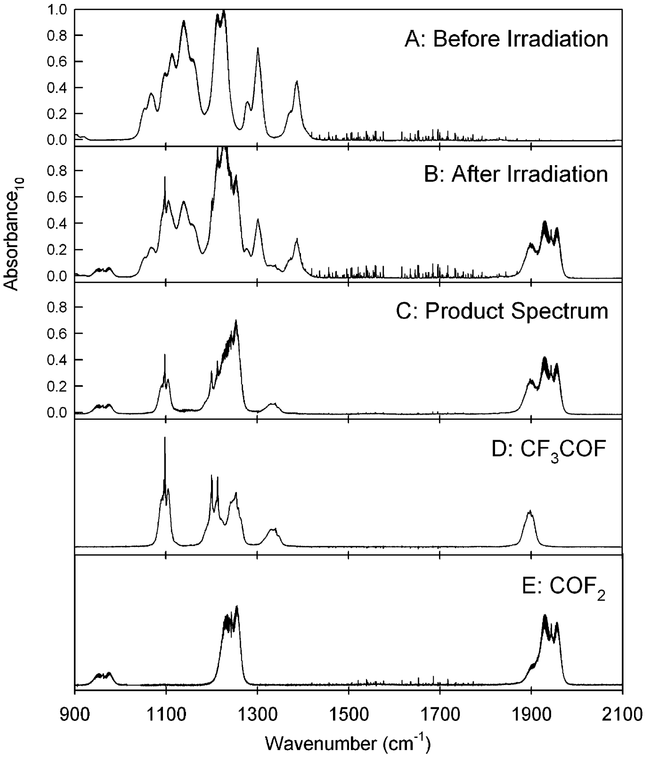

Figure 2. IR spectra obtained before (panel A) and after (panel B) a 12-min irradiation of a mixture containing 10.7 mTorr $CF_3CFHCF_2OCF_2H$, 8.4 Torr Cl_2, and 21 Torr O_2 in 700 Torr of N_2 diluent. Subtraction of features attributable to $CF_3CFHCF_2OCF_2H$ gives the product spectrum shown in panel C. Reference spectra of CF_3COF and COF_2 are shown in panels D and E.

3.2. Products of Cl Atom-Initiated Oxidation. To elucidate the atmospheric oxidation mechanism of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$, experiments were performed using mixtures of 10 mTorr of either $CF_3CFHCF_2OCF_3$ or $CF_3CFHCF_2OCF_2H$, 0.5−8.4 Torr of Cl_2, and 21 Torr of O_2 in 700 Torr of N_2 diluent. As shown in Figure 2, $CF_3C(O)F$ and COF_2 were observed as major oxidation products in these experiments. Figure 3 shows plots of the observed formation of $CF_3C(O)F$ versus the loss of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$. Variation of $[Cl_2]$ over a factor of 20 had no observable effect on the $CF_3C(O)F$ yield, suggesting that the present work is free from complications arising from the reaction of Cl_2 with radical species in the system. The lines through the data in Figure 3 give molar yields of $CF_3C(O)F$ of 82 ± 5 and 96 ± 6% in the oxidation of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$, respectively. A molar yield of COF_2 of 192 ± 15% in the oxidation of $CF_3CFHCF_2OCF_2H$ was also determined, while significant curvature in the COF_2 yield was found in the oxidation of $CF_3CFHCF_2OCF_3$. IR product features consistent with the formation of CF_3OOCF_3 were observed in the $CF_3CFHCF_2OCF_3$ experiments, but not in the $CF_3CFHCF_2OCF_2H$ experiments. Finally, there was evidence in the IR product spectra and small amounts of a trioxide product in the $CF_3CFHCF_2OCF_3$ experiments, but not in experiments involving $CF_3CFHCF_2OCF_2H$.

The simplest mechanism which explains the experimental observations is given immediately following for $CF_3CFHCF_2OCF_3$ (the • symbol indicates the position of the radical center):

$$Cl + CF_3CFHCF_2OCF_3 \rightarrow CF_3CF(\bullet)CF_2OCF_3 + HCl$$

$$CF_3CF(\bullet)CF_2OCF_3 + O_2 \rightarrow CF_3CF(OO\bullet)CF_2OCF_3$$

$$2CF_3CF(OO\bullet)CF_2OCF_3 \rightarrow 2CF_3CF(O\bullet)CF_2OCF_3 + O_2$$

$$CF_3CF(O\bullet)CF_2OCF_3 \rightarrow CF_3C(O)F + CF_3OCF_2(\bullet)$$

$$CF_3OCF_2(\bullet) + O_2 \rightarrow CF_3OCF_2OO(\bullet)$$

$$2CF_3OCF_2OO(\bullet) \rightarrow 2CF_3OCF_2O(\bullet) + O_2$$

$$CF_3OCF_2O(\bullet) \rightarrow CF_3O(\bullet) + COF_2$$

$$CF_3O(\bullet) + CF_3O(\bullet) \rightarrow CF_3OOCF_3$$

$CF_3CFHCF_2OCF_2H$ will follow a similar mechanism except that the penultimate step gives a CHF_2O radical instead of a CF_3O radical. In contrast to the behavior of CF_3O radicals, CHF_2O radicals react rapidly with O_2. Hence, there is no possibility of the formation of dioxides (ROOR) or trioxides (ROOOR) in the $CF_3CFHCF_2OCF_2H$ system. Abstraction of the secondary hydrogen in $CF_3CFHCF_2OCF_2H$ will result in the formation of one molecule of $CF_3C(O)F$ by the reactions outlined here. Abstraction of the primary hydrogen will lead to the formation of CF_3CFHO radicals, 97% of which under the present experimental conditions (21 Torr O_2) will decompose via C−C

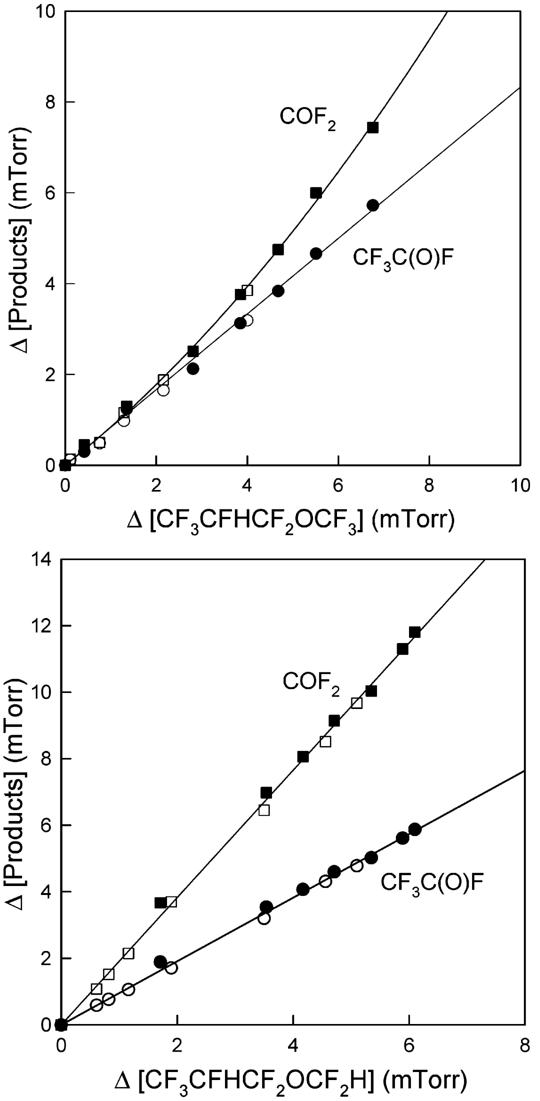

Figure 3. Formation of COF_2 (squares) and $CF_3C(O)F$ (circles) following UV irradiation of mixtures of 10 mTorr of either $CF_3CFHCF_2OCF_3$ or $CF_3CFHCF_2OCF_2H$, 0.5 Torr (open symbols) or 8.4 Torr (filled symbols) of Cl_2, and 21 Torr of O_2, in 700 Torr of N_2.

bond scission and will not form $CF_3C(O)F$.[11] The fact that the yield of $CF_3C(O)F$ observed following the Cl atom-initiated oxidation of $CF_3CFHCF_2OCF_2H$ is 96 ± 6% shows that the branching ratio of abstraction of the secondary hydrogen in the reaction of Cl atoms with $CF_3CFHCF_2OCF_2H$ is less than 10%. This result is at odds with the conclusion based upon kinetic arguments at the end of section 3.1. Such a disagreement highlights the difficulty in drawing quantitative mechanistic conclusions from such kinetic arguments.

It is interesting to note that $CF_3C(O)F$ and COF_2 are formed in the $CF_3CFHCF_2OCF_2H$ system in yields which are indistinguishable from 100 and 200%, respectively, whereas in the $CF_3CFHCF_2OCF_3$ experiments, the yields are both slightly less than 100%. The most likely explanation of this observation lies in the formation of small amounts of the trioxide $CF_3CF(OOOCF_3)CF_2OCF_3$ from the reaction of CF_3O radicals with the $CF_3CF(OO\bullet)CF_2OCF_3$ peroxy radical. No such possibility exists in the experiments involving $CF_3CFHCF_2OCF_2H$. The observed curvature in the COF_2 yield in the $CF_3CFHCF_2OCF_3$ system, evident in Figure 3A, can be explained by the heterogeneous decomposition of CF_3OH to give COF_2 and HF. CF_3O radicals formed during the oxidation of $CF_3CFHCF_2OCF_3$ can abstract an H-atom from hydrogen-containing species (e.g., $CF_3CFHCF_2OCF_3$, HO_2) to give CF_3OH. IR features attributable to CF_3OH were observed in the product spectra. CF_3OH decomposes slowly in the chamber to give COF_2 and HF. The decomposition of CF_3OH augments the formation of COF_2 in the system leading to the curvature in the COF_2 yield plot.

The experiments described in the preceding paragraph were performed in the absence of NO. A limited number of experiments were performed with added NO in the system. Unfortunately, the loss of $CF_3CFHCF_2OCF_3$ in such experiments was too small (because of the competing reaction of Cl atoms with NO) to enable a reliable determination of the $CF_3C(O)F$ yield.

3.3. OH Radical Kinetics. For the purposes of quality control, a measurement of $k(OH + CF_3CFHCF_3)$ was performed prior to the study of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$. Relative rate experiments were performed to measure $k(OH + CF_3CFHCF_3)$ using $CF_3CFHCF_3/CH_3ONO/C_2H_4$ and $CF_3CFHCF_3/CH_3ONO/C_2H_2$ mixtures in 700 Torr of air diluent at 296 K. UV irradiation of CH_3ONO is a convenient source of OH radicals in the laboratory. After their formation in the chamber, the OH radicals will react with either the reactant (CF_3CFHCF_3) or the reference (C_2H_4 or C_2H_2).

$$OH + CF_3CFHCF_3 \rightarrow \text{products} \tag{9}$$

$$OH + C_2H_4 \rightarrow \text{products} \tag{10}$$

$$OH + C_2H_2 \rightarrow \text{products} \tag{11}$$

Loss of the reference compounds was monitored directly using their characteristic features in the IR region at 700−900 cm^{-1}. The loss of CF_3CFHCF_3 was measured indirectly by monitoring the formation of its oxidation product, $CF_3C(O)F$. It has been established previously that oxidation of CF_3CFHCF_3 gives $CF_3C(O)F$ in 100% yield.[9] Figure 4A shows the loss of CF_3CFHCF_3 versus those of C_2H_4 and C_2H_2 observed in our experiments. The lines through the data are linear least-squares fits which give $k_9/k_{10} = (1.88 \pm 0.16) \times 10^{-4}$ and $k_9/k_{11} = (2.20 \pm 0.18) \times 10^{-3}$. These relative rate data can be placed upon an absolute basis using literature values of $k_{10} = (8.66 \pm 0.38) \times 10^{-12}$ [12] and $k_{11} = (8.5 \pm 1.0) \times 10^{-13}$ [13] to give independent determinations of $k_9 = (1.62 \pm 0.16) \times 10^{-15}$ and $(1.87 \pm 0.27) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. We choose to quote a final value which is the average of the individual determinations with error limits which encompass the extremes of the individual determinations. Hence, $k(OH + CF_3CFHCF_3) = (1.75 \pm 0.39) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}. This result is in good agreement with the recommended[14] literature value of $k(OH + CF_3CFHCF_3) = (1.7 \pm 0.2) \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}, providing confidence in the experimental methodology.

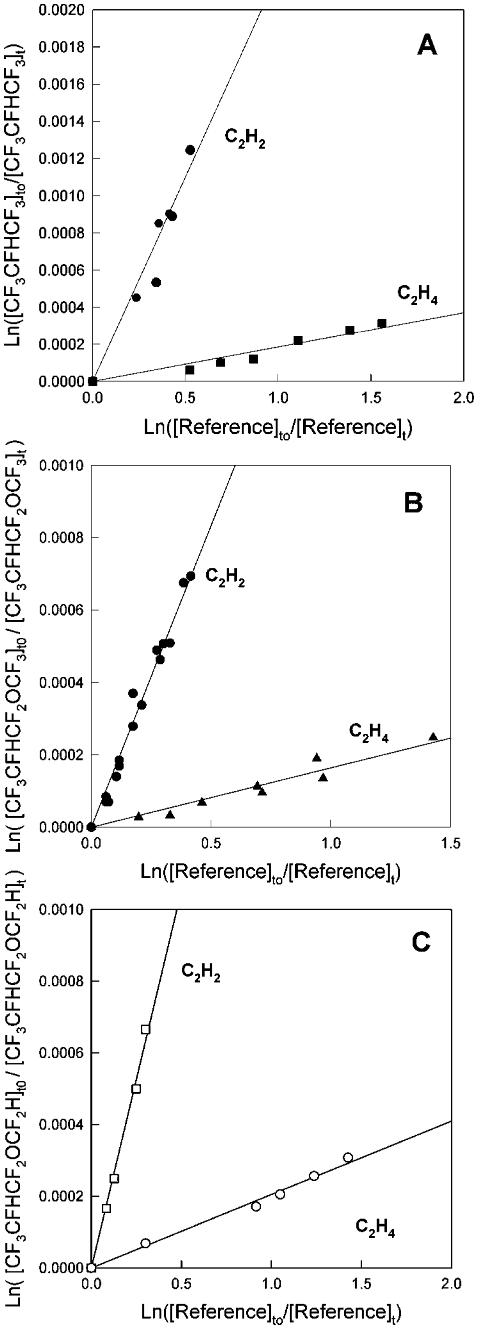

Figure 4. Kinetic data for reaction of OH radicals with CF_3CFHCF_3 (panel A), $CF_3CFHCF_2OCF_3$ (panel B), and $CF_3CFHCF_2OCF_2H$ (panel C).

The kinetics of the reactions of OH radicals with $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ were studied using the method described in the preceding paragraph. The results are shown in Figure 4B,C. The loss of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ was inferred from the observed formation of $CF_3C(O)F$. As discussed in section 3.2, the Cl atom-initiated oxidation of $CF_3CFHCF_2OCF_3$ gives $CF_3C(O)F$ in a yield of 82 ± 5%. The reactions of Cl atoms and OH radicals with CF_3CFHCF_2-

OCF_3 proceed via the same mechanism: hydrogen atom abstraction. It is reasonable to expect that the products of Cl atom-initiated oxidation of $CF_3CFHCF_2OCF_3$ will be identical to those of OH radical-initiated oxidation. Consequently, the $CF_3CFHCF_2OCF_3$ loss in the OH kinetic experiments can be estimated using the $CF_3C(O)F$ yield data given in section 3.2. There is one difference between the Cl atom and OH radical experiments which deserves discussion. The experiments described in section 3.2 were performed in the absence of NO, while the OH kinetic experiments were performed in the presence of NO. When NO is present, the fate of CF_3O radicals will be a reaction with NO to give COF_2 and FNO.[15] Formation of trioxide via the addition of CF_3O to $CF_3CF(OO\bullet)CF_2OCF_3$ radicals will not occur. Hence, the yield of $CF_3C(O)F$ is expected to increase to 100%. Consistent with this expectation, we chose to assume a $CF_3C(O)F$ yield from the OH radical-initiated oxidation of $CF_3CFHCF_2OCF_3$ of 100%. The data for $CF_3CFHCF_2OCF_2H$ shown in Figure 4C were determined using a molar yield of $CF_3C(O)F$ of 100% (consistent with the results reported in section 3.2).

$$\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_3} \rightarrow \text{products} \qquad (12)$$

$$\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_2H} \rightarrow \text{products} \qquad (13)$$

The lines through the data in Figure 4B,C are linear least-squares fits which give $k_{12}/k_{10} = (1.65 \pm 0.32) \times 10^{-4}$, $k_{12}/k_{11} = (1.67 \pm 0.24) \times 10^{-3}$, $k_{13}/k_{10} = (2.05 \pm 0.30) \times 10^{-4}$, and $k_{13}/k_{11} = (2.11 \pm 0.32) \times 10^{-3}$. These relative rate data can be placed upon an absolute basis using literature values of $k_{10} = (8.66 \pm 0.38) \times 10^{-12}$ [12] and $k_{11} = (8.5 \pm 1.0) \times 10^{-13}$ [13] to give independent determinations of $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_3}) = (1.43 \pm 0.28) \times 10^{-15}$ and $(1.42 \pm 0.26) \times 10^{-15}$ and $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_2H}) = (1.78 \pm 0.27) \times 10^{-15}$ and $(1.79 \pm 0.34) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. We choose to quote final values which are averages of the individual determinations with error limits which encompass the extremes of the individual determinations. Hence, $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_3}) = (1.43 \pm 0.28) \times 10^{-15}$ and $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_2H}) = (1.79 \pm 0.34) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

We can compare our determination of $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_2H}) = (1.79 \pm 0.34) \times 10^{-15}$ with the measurement of $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_2H}) = (1.69 \pm 0.26) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} by Oyaro et al.[8] For reasons which are unclear, Oyaro et al.[8] report a rate constant which is a factor of 9 greater than that observed in the present work.

In section 3.1, we concluded that the reactivity of Cl atoms toward the two C−H bonds in $CF_3CFHCF_2OCF_2H$ is independent and additive. If one assumes that the reactivity toward OH radicals displays similar behavior, the literature values of $k(\mathrm{OH} + \mathrm{CF_3CFHCF_3}) = (1.7 \pm 0.2) \times 10^{-15}$ and $k(\mathrm{OH} + \mathrm{CF_3OCF_2H}) = (4.9 \pm 1.0) \times 10^{-16}$ [14] can be used to estimate $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_2H}) \approx k(\mathrm{OH} + \mathrm{CF_3CFHCF_3}) + k(\mathrm{OH} + \mathrm{CF_3OCF_2H}) \approx (2.2 \pm 0.3) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. Our value of $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_2H}) = (1.79 \pm 0.34) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} is consistent with this estimation, providing confidence in the present methodology.

3.4. Atmospheric Lifetimes. The values of $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_3})$ and $k(\mathrm{OH} + \mathrm{CF_3CFHCF_2OCF_2H})$ can be used to provide estimates of the atmospheric lifetimes of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$. Assuming an atmospheric lifetime for CH_3CCl_3 with respect to the reaction with OH radicals of 5.7 years[16] and a rate constant for the CH_3CCl_3 + OH reaction of 1.0×10^{-14} cm^3 molecule^{-1} s^{-1} [14] leads to estimates of the atmospheric lifetimes of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ of 40 and 32 years, respectively. The optimal temperature for such a scaling analysis is 272 K[17] (rather than 295 K used here), but we do not have any data for k_1 at 272 K. By analogy to other HFEs, the temperature dependence of reaction 1 is expected to be similar to that for the reaction of OH radicals with CH_3CCl_3. Hence, the use of 295 K rather than 272 K is not expected to have any material impact on the estimated atmospheric lifetime.

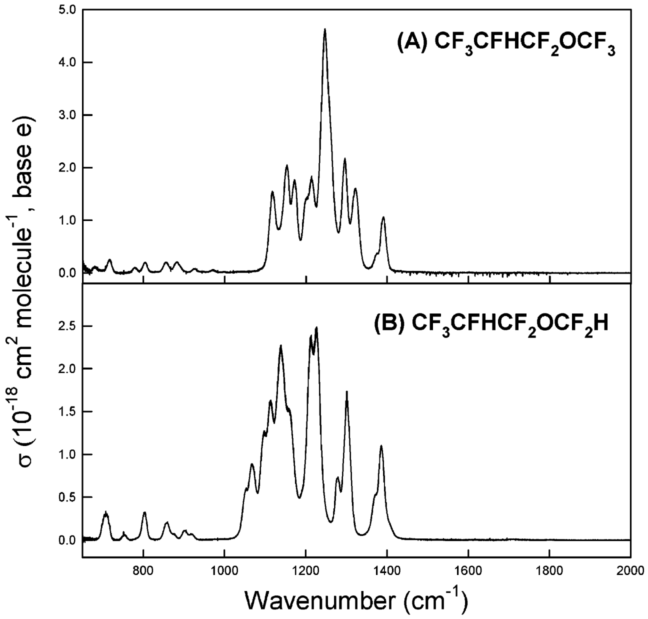

Figure 5. IR spectra of $CF_3CFHCF_2OCF_3$ (panel A) and $CF_3CFHCF_2OCF_2H$ (panel B).

3.5. IR Spectra and Global Warming Potentials. The IR spectra of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ recorded in 700 Torr of air diluent at 296 K are shown in Figure 5. The integrated cross-sections (650−1500 cm^{-1}) are $(4.28 \pm 0.22) \times 10^{-16}$ and $(3.64 \pm 0.19) \times 10^{-16}$ cm^2 molecule^{-1} cm^{-1} for $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$, respectively. Our measured intensity for the $CF_3CFHCF_2OCF_2H$ spectrum is in good agreement with the value of 3.42×10^{-16} cm^2 molecule^{-1} cm^{-1} (620−1450 cm^{-1}) reported by Oyaro et al.[8] There are no literature data for $CF_3CFHCF_2OCF_3$ to compare with our result.

Using the method outlined by Pinnock et al.,[18] the IR spectra of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ shown in Figure 5, and the IR spectrum of CFC-11 reported elsewhere,[19] we calculate instantaneous forcings for $CF_3CFHCF_2OCF_3$, $CF_3CFHCF_2OCF_2H$, and CFC-11 of 0.48, 0.51, and 0.26 W m^{-2} ppb^{-1}, respectively. It is of interest to note that, while the integrated absorption intensity of $CF_3CFHCF_2OCF_3$ is 18% greater than that of $CF_3CFHCF_2OCF_2H$, the instantaneous forcing of $CF_3CFHCF_2OCF_3$ is 6% less than that of $CF_3CFHCF_2OCF_2H$. This is explained by the fact that a greater proportion (72%) of the absorption by $CF_3CFHCF_2OCF_2H$ lies in the atmospheric window region (approximately 8−12 μm, 800−1250 cm^{-1}). This same region only accounts for 55% of the absorption by $CF_3CFHCF_2OCF_3$. Values of the GWP (global warming potential) for $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ (relative to CFC-11) can then be estimated using the expression[20]

$$\mathrm{GWP_{HFE}} = \left(\frac{\mathrm{IF_{HFE}}}{\mathrm{IF_{CFC-11}}}\right)\left(\frac{\tau_{\mathrm{HFE}} M_{\mathrm{CFC-11}}}{\tau_{\mathrm{CFC-11}} M_{\mathrm{HFE}}}\right)\left(\frac{1 - \exp(-t/\tau_{\mathrm{HFE}})}{1 - \exp(-t/\tau_{\mathrm{CFC-11}})}\right)$$

where IF_{HFE}, IF_{CFC-11}, M_{HFE}, M_{CFC-11}, τ_{HPE}, and τ_{CFC-11} are the instantaneous forcings, molecular weights, and atmospheric lifetimes of HFE and CFC-11 and t is the time horizon over which the forcing is integrated. Using $\tau(CF_3CFHCF_2OCF_3) =$ 40 years, $\tau(CF_3CFHCF_2OCF_2H) =$ 32 years, and τ(CFC-11) = 45 years,[21] we estimate that the GWPs of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ (relative to CFC-11) are 1.05 and 1.14 for a 20-year horizon and 0.98 and 0.94 for a 100-year time horizon, respectively. Relative to CO_2, the GWPs of CFC-11 on 20- and 100-year time horizon are 6300 and 4600.[21] Hence, relative to CO_2, the GWPs of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ are 6600 and 7180 for a 20-year horizon and 4530 and 4340 for a 100-year time horizon, respectively.

4. Discussion

A large body of self-consistent data concerning the atmospheric chemistry of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ is presented. The kinetic arguments advanced in section 3.3 suggest that under ambient conditions OH radicals abstract hydrogen from CF_3CFHCF_2- and $-CF_2OCF_2H$ moeities in HFEs and HFCs with rate constants of approximately 1.7×10^{-15} and 4.9×10^{-16} cm^3 molecule^{-1} s^{-1}, respectively. As with all other saturated HFEs,[22] the atmospheric lifetime of these compounds is determined by the reaction with OH radicals and is approximately 40 years for $CF_3CFHCF_2OCF_3$ and 32 years for $CF_3CFHCF_2OCF_2H$. $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ have global warming potentials (relative to CO_2) of 4530 and 4340 (100-year time horizon), respectively. Atmospheric oxidation of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ gives $CF_3C(O)F$ in a molar yield which is indistinguishable from 100%. The atmospheric fate of $CF_3C(O)F$ is hydrolysis to produce trifluoroacetic acid. The remaining molecular fragments will be oxidized to CO_2 and HF.[15,22] At the levels anticipated in the environment, the atmospheric oxidation products of $CF_3CFHCF_2OCF_3$ and $CF_3CFHCF_2OCF_2H$ are not of concern.

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