Atmospheric Chemistry of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$: Reaction with Cl Atoms and OH Radicals, Degradation Mechanism, Global Warming Potentials, and Empirical Relationship between k(OH) and k(Cl) for Organic Compounds

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Using FTIR smog chamber techniques, $k(Cl + CF_3OCF_2CF_2H) = (2.70 \pm 0.52) \times 10^{-16}$, $k(OH + CF_3OCF_2CF_2H) = (2.26 \pm 0.18) \times 10^{-15}$, $k(Cl + CF_3OC(CF_3)_2H) = (1.58 \pm 0.27) \times 10^{-18}$ and $k(OH + CF_3OC(CF_3)_2H) = (3.26 \pm 0.95) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} were measured. The atmospheric lifetimes of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ are estimated to be 27 and 216 years, respectively. Chlorine atom initiated oxidation of $CF_3OCF_2CF_2H$ in 700 Torr of air in the presence of NO_x gives $CF_3OC(O)F$ in a molar yield of 36 ± 5% and COF_2 in a molar yield of 174 ± 9%, whereas oxidation of $CF_3OC(CF_3)_2H$ gives $CF_3OC(O)CF_3$ and COF_2 in molar yields that are indistinguishable from 100%. Quantitative infrared spectra were recorded and used to estimate global warming potentials of 3690 and 8230 (100 year time horizon, relative to CO_2) for $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$, respectively. All experiments were performed in 700 Torr of N_2/O_2 diluent at 296 ± 2 K. An empirical relationship can be used to estimate the preexponential factor, which can be combined with k(298 K) to give the temperature dependence of reactions of OH radicals with organic compounds proceeding via H-atom abstraction: $\log(A/n) = (0.239 \pm 0.027) \log(k(OH)/n) - (8.69 \pm 0.372)$, k(OH) is the rate constant at 298 K and n is the number of H atoms. The rates of H-atom abstraction by OH radicals and Cl atoms at 298 K from organic compounds are related by the expression $\log(k(OH)) = (0.412 \pm 0.049) \log(k(Cl)) - (8.16 \pm 0.72)$. The utility of these expressions and the atmospheric chemistry of the title hydrofluoroethers are discussed.

1. Introduction

Recognition of the detrimental 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 that have been suggested and used as possible CFC and Halon replacements in applications such as the cleaning of electronic equipment, heat transfer, lubricant deposition, and fire suppression.

HFEs do not contain chlorine and therefore do not contribute to chlorine based catalytic destruction of stratospheric ozone. Prior to large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact, of HFEs is needed. Prompted by this need, we have conducted a study of the atmospheric chemistry of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$. 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.

A substantial kinetics database exists for hydrogen atom abstraction reactions of OH radicals and Cl atoms with a wide range of organic compounds.[3−5] Examination of these data provides useful relationships for testing new results for consistency with previous measurements on related compounds, and for the prediction and extrapolation of data where no measurements exist. Two predictions can be made with reasonable reliability for the kinetics of H-atom abstraction reactions by OH radicals. First, the value of k(298 K) can be estimated by comparison with related compounds using structure activity relationships.[6] However, that method is not presently useful for fluoroethers, owing mainly to the lack of sufficient data for calibration of group effects. Second, if only k(298 K) is known, estimates of the temperature dependence can be obtained quite reliably on the basis of a relationship between k(298 K) and the preexponential factor.[7] Correlations can be demonstrated between the rate constants of H-atom abstraction from organic compounds by OH radicals and Cl atoms. These correlations can be used to test new OH and Cl data for consistency, and to estimate Cl reaction rates in cases where only OH data are available (and vice versa). The kinetics data for reactions of Cl and OH with $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ measured herein were used to refine and extend these correlations.

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2. Experimental Section

All experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer.[8] The reactor was surrounded by 22 fluorescent blacklamps (GE F40BLB) that were used to photochemically initiate the experiments.

Cl atoms were generated by photolysis of Cl_2:

$$Cl_2 \xrightarrow{h\nu} 2Cl \tag{1}$$

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

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

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

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

Reactant and product concentrations were monitored using in situ Fourier transform infrared spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm^{-1} and an analytical path length of 27.1 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 >99%. Samples of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ were supplied by Great Lakes Chemical Corp. 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 unwanted loss of reactants, reference compounds and products via photolysis and heterogeneous reactions need to be considered. The reactant and reference compounds used in the present work ($CF_3OCF_2CF_2H$, $CF_3OC(CF_3)_2H$, C_2H_4, C_2H_2, CF_3CF_2H, $CHClF_2$, 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. To test for the presence of heterogeneous reactions, 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, suggesting 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 a reference spectrum were subtracted incrementally from the sample spectrum.

The relative rate method is a well-established technique for measuring the reactivity of Cl atoms and OH radicals with organic compounds.[9] Kinetics data are derived by monitoring the loss of a reactant compound ($CF_3OCF_2CF_2H$ or $CF_3OC(CF_3)_2H$ in the present work) relative to one or more reference compounds. The decays of the reactant and reference are then plotted using the expression

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

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 reactions of Cl atoms or OH radicals with the reactant and reference.

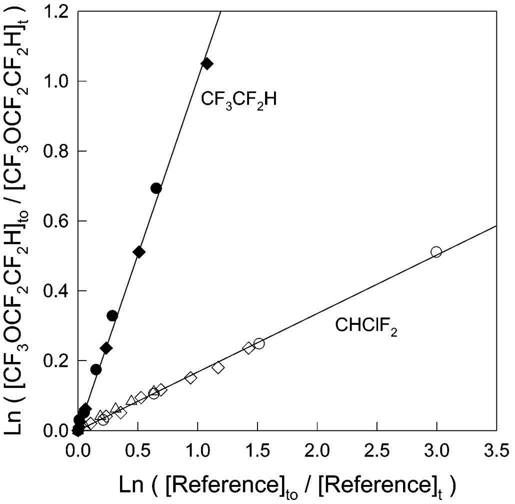

Figure 1. Decay of $CF_3OCF_2CF_2H$ versus CF_3CF_2H (solid symbols) and $CHClF_2$ (open symbols) in the presence of Cl atoms in 700 Torr air (circles), air + NO_x (triangles), or N_2 (diamonds), diluent at 296 ± 2 K.

Photolysis of CH_3ONO is a convenient source of OH radicals in relative rate studies. However, CH_3ONO itself reacts with OH at a moderate rate (with a rate constant of approximately 3×10^{-13} cm^3 $molecule^{-1}$ s^{-1} [10]), scavenges OH radicals, and makes loss of a less reactive compound (e.g., $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$) small and difficult to measure. In the present work we used a variation on the conventional relative rate method in which the loss of the reactant ($CF_3OCF_2CF_2H$ or $CF_3OC(CF_3)_2H$) was monitored indirectly by observing the formation of its oxidation products ($CF_3OC(O)F$ and/or COF_2). High initial concentrations of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ (595−2401 mTorr) were used to facilitate monitoring the oxidation products resulting from small (<0.1%) consumptions of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$. Unless stated otherwise, all uncertainties are 2 standard deviations from the linear regressions. Molar yields specified in this work are defined as mole of product formed per mole of substrate degraded.

3. Results

3.1. Relative Rate Study of $k(Cl+CF_3OCF_2CF_2H)$ and $k(Cl+CF_3OC(CF_3)_2H)$. Experiments were performed to measure the kinetics of reactions 5 and 6 relative to reactions 7−9:

$$CF_3OCF_2CF_2H + Cl \rightarrow CF_3OCF_2C(\bullet)F_2 + HCl \tag{5}$$

$$CF_3OC(CF_3)_2H + Cl \rightarrow CF_3OC(\bullet)(CF_3)_2 + HCl \tag{6}$$

$$CF_3CF_2H + Cl \rightarrow \text{products} \tag{7}$$

$$CHClF_2 + Cl \rightarrow \text{products} \tag{8}$$

$$CF_3CH_3 + Cl \rightarrow \text{products} \tag{9}$$

The initial concentrations were 3.3−13 mTorr $CF_3OCF_2CF_2H$ or $CF_3OC(CF_3)_2H$, 0−20 mTorr NO, 0.1−3.8 Torr Cl_2 and 3.1−7.6 mTorr of one of the three references in 700 Torr air, or N_2, diluent at 296 K. The observed losses of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ are plotted versus those of the reference compounds in Figures 1 and 2. As seen from Figure 1, there was no discernible effect of diluent or presence of NO on the

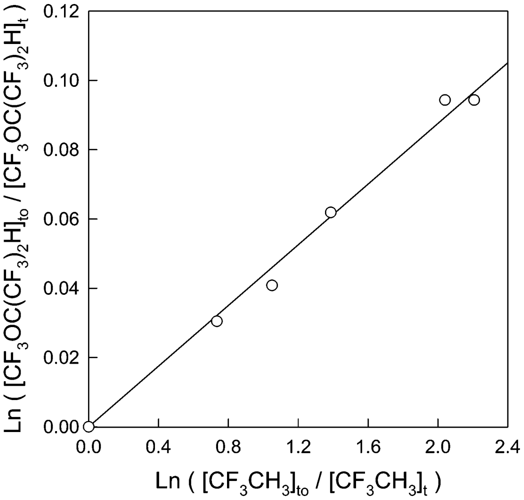

Figure 2. Decay of $CF_3OC(CF_3)_2H$ versus CF_3CH_3 in the presence of Cl atoms in 700 Torr air diluent at 296 ± 2 K.

reactivity of Cl atoms toward $CF_3OCF_2CF_2H$. We expect the same in the case of $CF_3OC(CF_3)_2H$.

Linear least squares analyses of the data in Figures 1 and 2 give $k_5/k_7 = 1.01 \pm 0.12$, $k_5/k_8 = 0.168 \pm 0.021$, and $k_6/k_9 = (4.38 \pm 0.75) \times 10^{-2}$. Using literature values of $k_7 = 2.5 \times 10^{-16}$ [11] and $k_8 = 1.70 \times 10^{-15}$ [4] gives $k_5 = (2.53 \pm 0.30) \times 10^{-16}$ and $(2.86 \pm 0.36) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. Using $k_9 = 3.6 \times 10^{-17}$ [12] gives $k_6 = (1.58 \pm 0.27) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}. We choose to quote a final value for k_5 that is the average of the individual determinations together with uncertainties that encompass the extremes of the individual determinations. Hence, $k_5 = (2.70 \pm 0.52) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

The reactivity of Cl atoms toward $CF_3OCF_2CF_2H$ is indistinguishable, within the experimental uncertainties, from that toward CF_3CF_2H ($k_7 = 2.5 \times 10^{-16}$ [11]). This seems reasonable based upon expectations that Cl atoms will not react with CF_3OCF_2 and CF_3 groups, and that the influence of these groups on the reactivity of the CF_2H group will be similar

3.2. Products of Cl Atom Initiated Oxidation of $CF_3OCF_2CF_2H$ in the Presence of NO_x in Air Diluent. To elucidate the atmospheric oxidation mechanism of $CF_3OCF_2CF_2H$ experiments were performed using mixtures of 9.7−210 mTorr $CF_3OCF_2CF_2H$, 500 mTorr Cl_2, and 9.7−50 mTorr NO in 700 Torr of air diluent. When low to moderate amounts of $CF_3OCF_2CF_2H$ were used the quantity of oxidation products formed within the typical experimental time scale (1−3 h) was too small for reliable quantification. When large amounts of $CF_3OCF_2CF_2H$ were used the products could be readily quantified but the IR features of $CF_3OCF_2CF_2H$ were saturated and it was not possible to measure the consumption of $CF_3OCF_2CF_2H$ directly. A Cl atom tracer compound, $CHCl_2F$ (5 mTorr), was added to the reaction mixtures to provide an indirect measure of the $CF_3OCF_2CF_2H$ consumption. Consumption of $CHCl_2F$ was measured directly via FTIR spectroscopy and the ratio $k_5/k_{Cl+CHCl2F} = 2.70 \times 10^{-16}/2.09 \times 10^{-14}$ [13] $= 0.0129$ was used to calculate the consumption of $CF_3OCF_2CF_2H$.

Figure 3 shows IR spectra acquired before (A) and after (B) a 105-min irradiation of a mixture containing 204 mTorr $CF_3OCF_2CF_2H$, 50 mTorr NO, 4.7 mTorr $CHCl_2F$ and 0.5 Torr Cl_2 in 700 Torr of air diluent. The consumption of $CHCl_2F$ was 60%. Comparison of the IR features shown in Panel C with reference spectra of $CHCl_2F$, $CF_3OC(O)F$, and COF_2 shown in panels D, E, and F shows the loss of $CHCl_2F$, and the formation of $CF_3OC(O)F$ and COF_2. Figure 4 shows plots of the observed formation of $CF_3OC(O)F$ and COF_2 versus the calculated loss of $CF_3OCF_2CF_2H$. The concentration of NO was varied by a factor of 5 with no discernible effect on the product yields. The lines through the data in Figure 4 are linear least-squares fits that give molar yields of $CF_3OC(O)F$ and COF_2 of 36 ± 5% and 174 ± 9%, respectively. The observed formation of COF_2 and $CF_3OC(O)F$ accounts for 82 ± 7% of the reacted $CF_3OCF_2CF_2H$. We estimate that uncertainties in the rate constant ratio $k_5/k_{Cl+CHCl2F}$ contribute an additional 20% uncertainty to the

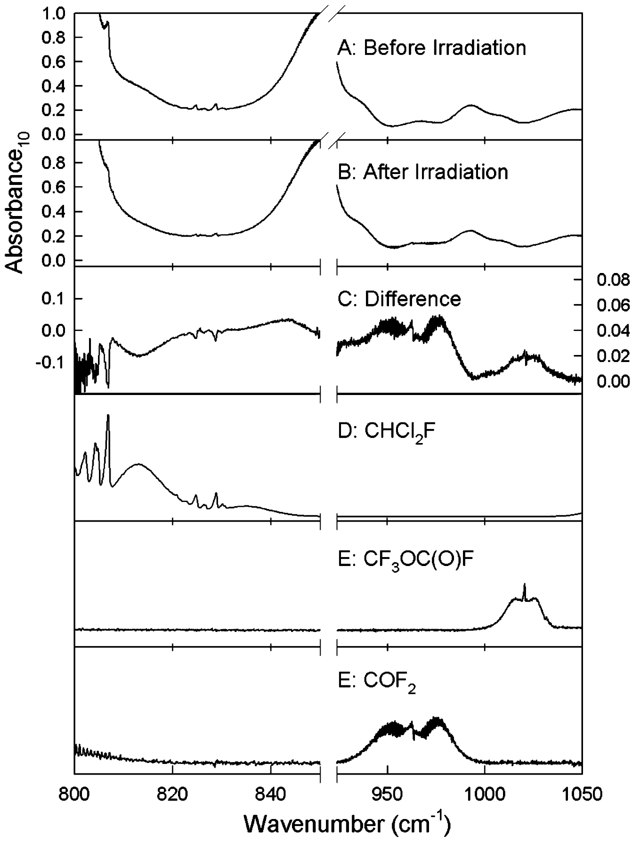

Figure 3. IR spectra obtained before (A) and after (B) a 105 min irradiation of a mixture containing 204 mTorr $CF_3OCF_2CF_2H$, 50 mTorr NO, 4.7 mTorr $CHCl_2F$ and 0.5 Torr Cl_2 in 700 Torr of air diluent. Panel C shows the difference between panels A and B. Reference spectra of $CHCl_2F$, $CF_3OC(O)F$ and COF_2 are shown in panels D−F.

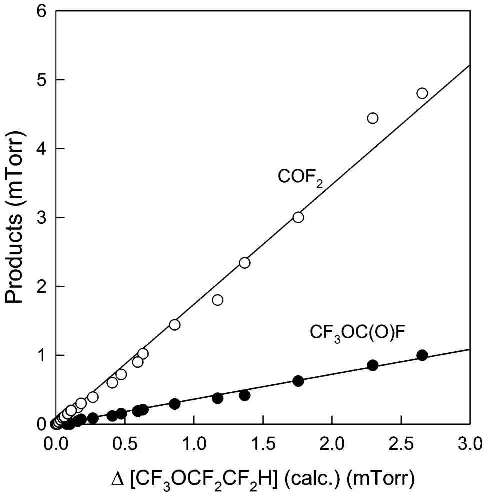

Figure 4. Yield of COF_2 and $CF_3OC(O)F$ from the reaction of Cl atoms with $CF_3OCF_2CF_2H$ in the presence of NO_x in 700 Torr of air diluent at 296 ± 2 K.

product yields. Hence, within the combined uncertainties we can account for 100% of the loss of $CF_3OCF_2CF_2H$.

The simplest mechanism that explains the experimental observations is given below:

$$Cl + CF_3OCF_2CF_2H \rightarrow CF_3OCF_2CF_2(\bullet) + HCl \tag{5}$$

$$CF_3OCF_2CF_2(\bullet) + O_2 \rightarrow CF_3OCF_2CF_2OO(\bullet) \tag{10}$$

$$CF_3OCF_2CF_2OO(\bullet) + NO \rightarrow CF_3OCF_2CF_2O(\bullet) + NO_2 \tag{11}$$

$$CF_3OCF_2CF_2O(\bullet) \rightarrow COF_2 + CF_3OCF_2(\bullet) \tag{12}$$

$$CF_3OCF_2(\bullet) + O_2 \rightarrow CF_3OCF_2OO(\bullet) \tag{13}$$

$$CF_3OCF_2OO(\bullet) + NO \rightarrow CF_3OCF_2O(\bullet) + NO_2 \tag{14}$$

$$CF_3OCF_2O(\bullet) \rightarrow CF_3O(\bullet) + COF_2 \tag{15}$$

When NO is present, the fate of CF_3O radicals will be reaction with NO to give COF_2 and FNO:[14]

$$CF_3O(\bullet) + NO \rightarrow COF_2 + FNO \tag{16}$$

It is interesting that $CF_3OC(O)F$ is a product in the oxidation of $CF_3OCF_2CF_2H$. By analogy to the behavior of CF_3O, the source of $CF_3OC(O)F$ is probably the reaction of CF_3OCF_2O radicals with NO:

$$CF_3OCF_2O(\bullet) + NO \rightarrow CF_3OC(O)F + FNO \tag{17}$$

Although reaction with NO is an important loss mechanism for $CF_3OCF_2O(\bullet)$ in the present smog chamber studies, this reaction is not likely to be of importance in the atmosphere where the concentration of NO is much lower. The unimolecular reaction (15) is likely to be the predominant loss mechanism for $CF_3OCF_2O(\bullet)$ radicals at atmospherically relevant NO concentrations. It is interesting to note that though we have strong evidence for two different competing fates for $CF_3OCF_2O(\bullet)$ radicals (reactions 15 and 17) there was no observable effect on NO concentration on the relative yields of COF_2 and $CF_3OC(O)F$. The simplest explanation for this observation is that a significant fraction of the $CF_3OCF_2O(\bullet)$ radicals produced in reaction 14 are formed with sufficient internal excitation to undergo prompt decomposition and are not available to react with NO.

A possible explanation for the somewhat low carbon balance in these experiments is the formation of $CF_3OCF_2C(O)F$ via reaction of NO with the $CF_3OCF_2CF_2O$ radical:

$$CF_3OCF_2CF_2O(\bullet) + NO \rightarrow CF_3OCF_2C(O)F + FNO \tag{18}$$

$CF_3OCF_2C(O)F$ is not commercially available and we do not have an IR spectrum for this species. After subtraction of features attributable to COF_2 and $CF_3COC(O)F$, there were no residual features in the carbonyl stretching region at 1800–2000 cm^{-1}. It seems reasonable to believe that the IR spectrum of $CF_3OCF_2C(O)F$ will have a carbonyl feature that is similar in magnitude, but shifted somewhat in frequency, from that in $CF_3OC(O)F$. Using the absorption cross section of $CF_3C(O)F$ as a guide, we estimate an upper limit of ≤10% for the $CF_3OCF_2C(O)F$ yield.

3.3. Products of Cl Atom Initiated Oxidation of $CF_3OC(CF_3)_2H$ in the Presence of NO_x in N_2/O_2 Diluent. Figure 5 shows IR spectra acquired before (A) and after (B) a 138 min irradiation of 1.2 Torr $CF_3OC(CF_3)_2H$, 7.3 mTorr NO, 1 Torr Cl_2 and 5 Torr O_2 in 700 Torr of N_2 diluent. Panel C shows the difference between panels A and B. The IR features in panel C can be compared with the IR spectra of $CF_3OC(O)CF_3$ and COF_2, shown in panels D and E. Features attributable to ClNO have been subtracted from panel C for clarity. $CF_3OC(O)CF_3$ and COF_2 were observed as major oxidation products in these experiments. As shown in section 3.1, $CF_3OC(CF_3)_2H$ reacts slowly with Cl atoms. When using moderate amounts (10–100 mTorr) of $CF_3OC(CF_3)_2H$ it was not possible to measure its oxidation products within an acceptable experimental time span (<3 h). By using large amounts of $CF_3OC(CF_3)_2H$, the absolute concentration of products increased sufficiently to become detectable. However, under these conditions saturation of the IR spectra makes it impossible to measure the consumption of $CF_3OC(CF_3)_2H$ directly. The loss of $CF_3OC(CF_3)_2H$ was monitored indirectly by following the loss of a more reactive tracer compound: $CHClF_2$. Consumption of $CHClF_2$ was measured via FTIR spectroscopy and combined with $k_6/k_8 = 1.58 \times 10^{-18}/1.70 \times 10^{-15} = 9.24 \times 10^{-4}$ to calculate the consumption of $CF_3OC(CF_3)_2H$.

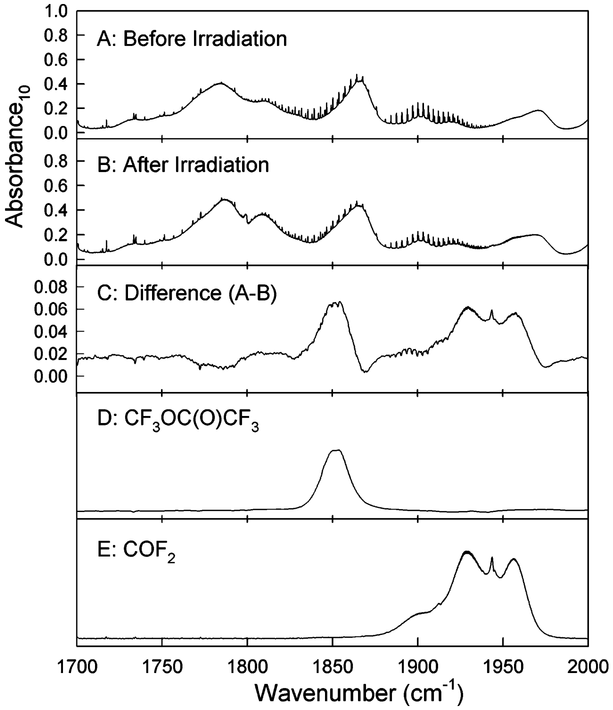

Figure 5. IR spectra obtained before (A) and after (B) a 138 min irradiation of a mixture containing 1.2 Torr $CF_3OC(CF_3)_2H$, 7.3 mTorr NO, 1 Torr Cl_2, and 5 Torr O_2 in 700 Torr of N_2 diluent. Panel C shows the difference between panels A and B. Features attributable to ClNO have been subtracted from panel C for clarity. Reference spectra of $CF_3OC(O)CF_3$ and COF_2 are shown in panels D and E.

Experiments were performed using mixtures of 1.2 Torr of $CF_3OC(CF_3)_2H$, 1 Torr of Cl_2, 3.7–15 mTorr NO, and 5 Torr of O_2 in 700 Torr of N_2 diluent. Figure 6 shows plots of the observed formation of COF_2 and $CF_3OC(O)CF_3$ versus the calculated loss of $CF_3OC(CF_3)_2H$. The lines through the data in Figures 6 give molar yields of 95 ± 6% for $CF_3OC(O)CF_3$ and 83 ± 7% for COF_2 in the Cl atom initiated oxidation of $CF_3OC(CF_3)_2H$ in the presence of NO. The data were corrected for COF_2 formation from the reaction of Cl atoms with $CHClF_2$. We estimate that uncertainties in the rate constant ratio k_6/k_8 contribute an additional 20% uncertainty to the product yields. Within the experimental uncertainties we can account for 100% of the loss of $CF_3OC(CF_3)_2H$.

The simplest explanation for the experimental observations is reaction 6 followed by reactions 19−23:

$$CF_3OC(CF_3)_2H + Cl \rightarrow CF_3OC(CF_3)_2(\bullet) + HCl \tag{6}$$

$$CF_3OC(CF_3)_2(\bullet) + O_2 \rightarrow CF_3OC(CF_3)_2OO(\bullet) \tag{19}$$

$$CF_3OC(CF_3)_2OO(\bullet) + NO \rightarrow CF_3OC(CF_3)_2O(\bullet) + NO_2 \tag{20}$$

$$CF_3OC(CF_3)_2O(\bullet) \rightarrow CF_3(\bullet) + CF_3OC(O)CF_3 \tag{21}$$

$$CF_3(\bullet) + O_2 \rightarrow CF_3OO(\bullet) \tag{22}$$

$$CF_3OO(\bullet) + NO \rightarrow CF_3O(\bullet) + NO_2 \tag{23}$$

As discussed in section 3.2, the fate of CF_3O radicals is reaction with NO to give COF_2 and FNO:[14]

$$CF_3O(\bullet) + NO \rightarrow COF_2 + FNO \tag{16}$$

In the mechanism given above the sole fate of the $CF_3OC(CF_3)_2O(\bullet)$ alkoxy radical is elimination of a CF_3 radical (reaction 21). An additional possible fate of $CF_3OC(CF_3)_2O(\bullet)$ radicals is elimination of a CF_3O radical to give $CF_3C(O)CF_3$. IR features of $CF_3C(O)CF_3$ were sought but not found. An upper limit for the yield of $CF_3C(O)CF_3$ of 5% was established. It is possible that small amounts of CF_3ONO_2 are formed via

$$CF_3O + NO_2 + M \rightarrow CF_3ONO_2 + M \tag{24}$$

Evidence for CF_3ONO_2 was sought in the product spectra but not found. An upper limit of 5% was established for the CF_3ONO_2 molar yield.

3.4. Relative Rate Study of the OH + $CF_3OCF_2CF_2H$ and the OH + $CF_3OC(CF_3)_2H$ Reaction in 700 Torr of Air. The kinetics of reactions 25 and 26 were measured relative to reactions 27 and 28:

$$CF_3OCF_2CF_2H + OH \rightarrow \text{products} \tag{25}$$

$$CF_3OC(CF_3)_2H + OH \rightarrow \text{products} \tag{26}$$

$$C_2H_4 + OH \rightarrow \text{products} \tag{27}$$

$$C_2H_2 + OH \rightarrow \text{products} \tag{28}$$

Experiments were performed using mixtures of 1.0−1.2 Torr $CF_3OCF_2CF_2H$ or $CF_3OC(CF_3)_2H$, 9−12 mTorr NO, 97−140 mTorr CH_3ONO and 3.0−7.4 mTorr of one of the reference compounds in 700 Torr air diluent at 296 ± 2 K. As mentioned in section 2, the loss of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ was inferred from the formation of their oxidation products: $CF_3OC(O)F$ and COF_2 for $CF_3OCF_2CF_2H$, and COF_2 for $CF_3OC(CF_3)_2H$. As discussed in sections 3.2 and 3.3, the Cl atom initiated oxidation of $CF_3OCF_2CF_2H$ in the presence of NO_x gives $CF_3OC(O)F$ and COF_2 in molar yields of 36 ± 5% and 174 ± 9%, whereas the Cl atom initiated oxidation of $CF_3OC(CF_3)_2H$ in the presence of NO_x gives $CF_3OC(O)CF_3$ and COF_2 both in a yield that is indistinguishable from 100%. The reactions of Cl atoms and OH radicals with $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ proceed via the same mechanism; hydrogen atom abstraction. It is reasonable to expect that the products of the Cl atom initiated oxidation of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ will be the same as those of the OH radical initiated oxidation. Consequently, the $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ loss in the OH kinetics experiments can be estimated using the product yields determined in sections 3.2 and 3.3. Hence, the data for $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ shown in Figure 7

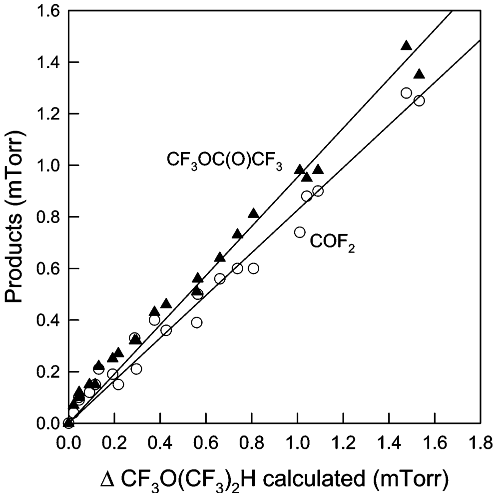

Figure 6. Formation of $CF_3OC(O)OCF_3$ (triangles) and COF_2 (circles) following Cl atom initiated oxidation of $CF_3OC(CF_3)_2H$ in the presence of NO in 700 Torr of N_2/O_2 diluent at 296 K.

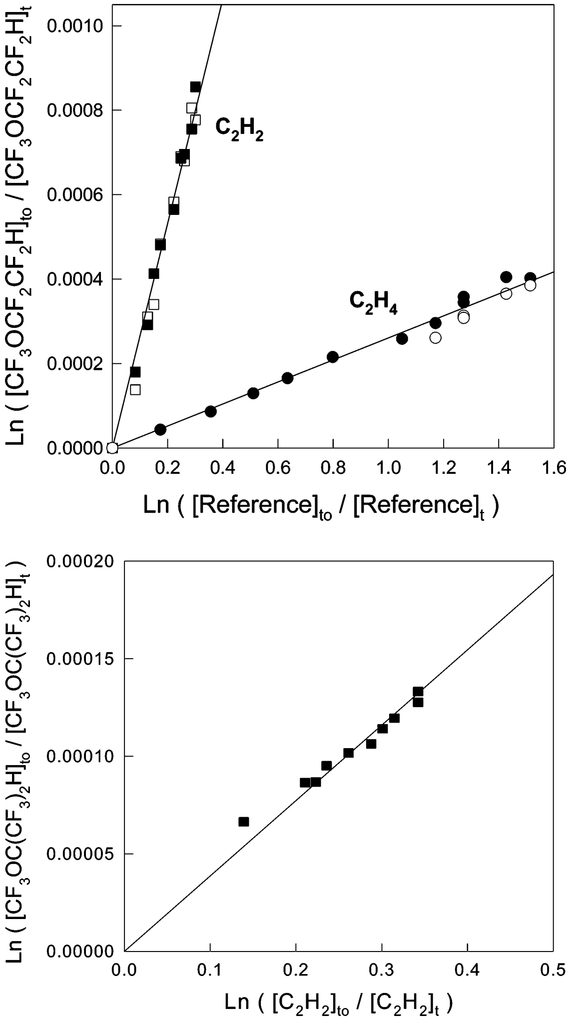

Figure 7. Loss of $CF_3OCF_2CF_2H$ and $CF_3O(CF_2)_2H$ versus C_2H_4 (circles) and C_2H_2 (squares) following exposure to OH radicals in 700 Torr air at 296 K. The loss of $CF_3OCF_2CF_2H$ was calculated from the formation of either $CF_3OC(O)F$ (open symbols) or COF_2 (solid symbols). The loss of $CF_3O(CF_2)_2H$ was calculated from the formation of COF_2.

TABLE 1: Comparison of k(298 K) for OH Abstraction Reactions from Selected Fluorocarbons and the Corresponding Fluoroethers in Which a F Atom Has Been Replaced by a CF_3O Group

compound	k(298 K) (cm^3 molecule^{-1} s^{-1})	source
CH_3F	2.0×10^{-14}	JPL 97-4[3]
CH_3OCF_3	1.2×10^{-14}	JPL 97-4[3]
CF_3H	2.8×10^{-16}	JPL 97-4[3]
CF_3OCF_2H	4.1×10^{-16}	JPL 97-4[3]
CF_3CF_2H	1.9×10^{-15}	JPL 97-4[3]
$CF_3OCF_2CF_2H$	2.3×10^{-15}	this work
CF_3CHFCF_3	1.7×10^{-15}	JPL 97-4[3]
$CF_3OC(CF_3)_2H$	3.3×10^{-16}	this work

were determined using molar yields of 36% $CF_3OC(O)F$ and 174% COF_2 for $CF_3OCF_2CF_2H$ and 100% COF_2 for $CF_3OC(CF_3)_2H$. Overlapping spectral features obscured the detection of $CF_3OC(O)CF_3$, and hence only the formation of COF_2 was used to calculate the consumption of $CF_3OC(CF_3)_2H$.

The lines through the data in Figure 7 are linear least-squares fits that give $k_{25}/k_{27} = (2.61 \pm 0.19) \times 10^{-4}$, $k_{25}/k_{28} = (2.66 \pm 0.20) \times 10^{-3}$, and $k_{26}/k_{28} = (3.86 \pm 1.12) \times 10^{-4}$. Quoted uncertainties are two standard deviations from the linear regressions together with our estimate of the uncertainty associated with the product determination. As seen from Figure 7 (top), the use of either $CF_3OC(O)F$ or COF_2 as markers for the consumption of $CF_3OCF_2CF_2H$ produces indistinguishable results. The relative rate data can be placed upon an absolute basis using literature values of $k_{27} = 8.66 \times 10^{-12}$ [15] and $k_{28} = 8.45 \times 10^{-13}$ [16] to give $k_{25} = (2.26 \pm 0.16) \times 10^{-15}$ and $(2.25 \pm 0.17) \times 10^{-15}$, and $k_{26} = (3.26 \pm 0.95) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. We choose to quote final values that are averages of the individual determinations with error limits that encompass the extremes of the individual determinations. Hence, $k_{25} = (2.26 \pm 0.18) \times 10^{-15}$ and $k_{26} = (3.26 \pm 0.95) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}.

3.5. Estimates and Correlations for the OH and Cl Abstraction Reactions. 3.5.1. OH Reactions. As shown previously,[17] the CF_3O group has an effect on OH abstraction rate constants similar to that of the F atom. In particular, the CF_3OCF_2 group has an effect similar to the CF_3 group, and therefore predictions for compounds containing the CF_3OCF_2 group can often be made by comparison with the analogous compound containing the CF_3 group. Some examples of these relationships are shown in Table 1, including the present results. The $CF_3OCF_2CF_2H$ rate constant is, as expected, similar to that of CF_3CHF_2. However, the $CF_3OC(CF_3)_2H$ rate constant is surprisingly slow, and CF_3CHFCF_3 is only an approximate model for estimating the rate constant of that compound.

When k(298 K) is known, reliable values of the Arrhenius parameters can be obtained by taking advantage of correlations between k(298 K) and the preexponential factors of the reactions.[7] Table 2 lists A-factors and k(298 K) values from JPL 97-4[3] for H-atom abstraction by OH radicals from a variety of substrates containing a single type of C−H bond. The latter restriction avoids any ambiguity resulting from different A-factors at different reaction sites. The cycloalkane data are from DeMore and Bayes.[18] These data, normalized to a per-hydrogen basis, are plotted logarithmically in Figure 8. In a previous publication[7] the data were based on relative rate measurements taken in the JPL laboratory. Those data, being self-consistent, showed somewhat less scatter but otherwise do not differ significantly from the present. The relationship between A-factor and k(298 K) can be expressed as follows

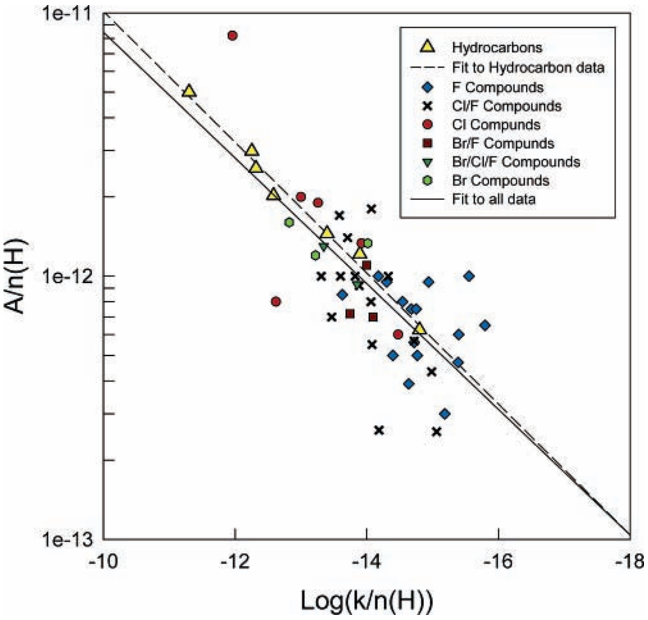

Figure 8. Logarithmic plot of k(OH) data from Table 2, showing the dependence of A-factors on the magnitude of k(298 K).

$$\log(A/n) = (0.239 \pm 0.027) \log(k/n) - (8.69 \pm 0.372) \quad \text{(II)}$$

The quantity n is the number of H atoms. Activation temperatures can then be calculated from the equation

$$E/R = -298 \ln(k/A) \quad \text{(III)}$$

Predictions of the A-factor using eq II are normally accurate to within a factor of 1.5, corresponding to an uncertainty in E/R of about 100 K. Thus the reliability of these estimates is comparable to that of most experimental data, provided that k(298 K) is known accurately. Table 3 lists the calculated Arrhenius parameters for $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$.

Two important conclusions can be reached on the basis of Figure 8. First, it is clear that there is a dependence of A-factor on the magnitude of the rate constant, with faster reactions having larger A-factors. Second, there is no dependence of A-factor on the nature or degree of halogenation of the molecules; C−H bonds in halogen compounds show the same A-factor behavior as C−H bonds in hydrocarbons. The large deviation of some of the halogen compound data points from the fitted line in Figure 8 is probably attributable to experimental uncertainties (particularly in the A-factor). The hydrocarbon data show much less scatter.

3.5.2. Cl Reactions. Although the database for Cl abstraction reactions is less extensive than that for OH, sufficient data are available in JPL 97-4 to derive an equation similar to (II) for Cl abstraction reactions for the purpose of estimating the Arrhenius parameters. However, the uncertainties are about twice as large, which will be reflected in larger uncertainties for the calculated E/R parameters.

$$\log(A/n) = (0.209 \pm 0.052) \log(k/n) - (8.52 \pm 0.707) \quad \text{(IV)}$$

The resulting Arrhenius parameters for the Cl reactions with $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ are shown in Table 4.

TABLE 2: *A*-Factors and *k*(298 K) Values for H-Atom Abstraction Reactions of OH Radicals with Compounds Containing Only One Type of C−H Bond, Taken Mainly from JPL 97-4[3] (See Text and Figure 8)

	compound	*A*-factor (cm^3 $molecule^{-1}$ s^{-1})	*k*(298 K) (cm^3 $molecule^{-1}$ s^{-1})
F compounds	CH_3F	3.00×10^{-12}	2.00×10^{-14}
	CH_2F_2	1.90×10^{-12}	1.00×10^{-14}
	CHF_3	1.00×10^{-12}	2.80×10^{-16}
	CH_2FCH_2F	3.40×10^{-12}	9.40×10^{-14}
	CF_3CH_3	1.80×10^{-12}	1.20×10^{-15}
	CF_3CH_2F	1.50×10^{-12}	4.20×10^{-15}
	CHF_2CHF_2	1.60×10^{-12}	5.70×10^{-15}
	CF_3CHF_2	5.60×10^{-13}	1.90×10^{-15}
	CF_3OCH_3	1.50×10^{-12}	1.20×10^{-14}
	CF_2HOCF_2H	1.90×10^{-12}	2.30×10^{-15}
	CF_3OCHF_2	4.70×10^{-13}	4.10×10^{-16}
	$CF_3CF_2CH_2F$	1.50×10^{-12}	4.20×10^{-15}
	$CF_3CH_2CF_3$	1.30×10^{-12}	3.20×10^{-16}
	CF_3CHFCF_3	5.00×10^{-13}	1.70×10^{-15}
	$CF_3CH_2CH_2CF_3$	3.00×10^{-12}	7.10×10^{-15}
	$CHF_2CF_2CF_2CF_2H$	7.80×10^{-13}	4.60×10^{-15}
	$CF_3CH_2CF_2CH_2CF_3$	1.20×10^{-12}	2.60×10^{-15}
Cl/F compounds	CH_2ClF	2.80×10^{-12}	3.90×10^{-14}
	$CHFCl_2$	1.70×10^{-12}	2.60×10^{-14}
	CHF_2Cl	1.00×10^{-12}	4.70×10^{-15}
	CH_3CFCl_2	1.70×10^{-12}	5.70×10^{-15}
	CH_3CF_2Cl	1.30×10^{-12}	3.10×10^{-15}
	CH_2ClCF_2Cl	3.60×10^{-12}	1.70×10^{-14}
	$CHCl_2CF_2Cl$	1.00×10^{-12}	4.90×10^{-14}
	$CHFClCFCl_2$	1.00×10^{-12}	1.50×10^{-14}
	CH_2ClCF_3	5.20×10^{-13}	1.30×10^{-14}
	$CHCl_2CF_3$	7.00×10^{-13}	3.40×10^{-14}
	$CHFClCF_2Cl$	9.20×10^{-13}	1.30×10^{-14}
	$CHFClCF_3$	8.00×10^{-13}	8.60×10^{-15}
	$CH_3CF_2CFCl_2$	7.70×10^{-13}	2.60×10^{-15}
	$CF_3CF_2CHCl_2$	1.00×10^{-12}	2.50×10^{-14}
	CF_2ClCF_2CHFCl	5.50×10^{-13}	8.30×10^{-15}
Cl compounds	CH_3Cl	4.00×10^{-12}	3.60×10^{-14}
	CH_2Cl_2	3.80×10^{-12}	1.10×10^{-13}
	$CHCl_3$	2.00×10^{-12}	1.00×10^{-13}
	CH_3OCl	2.40×10^{-12}	7.20×10^{-13}
	CH_3CCl_3	1.80×10^{-12}	1.00×10^{-14}
	CCl_3CHO	8.20×10^{-12}	1.10×10^{-12}
Br/F compounds	CHF_2Br	1.10×10^{-12}	1.00×10^{-14}
	CH_2BrCF_3	1.40×10^{-12}	1.60×10^{-14}
	$CHFBrCF_3$	7.20×10^{-13}	1.80×10^{-14}
Br/Cl/F compounds	$CHClBrCF_3$	1.30×10^{-12}	4.50×10^{-14}
	$CHFClCF_2Br$	9.30×10^{-13}	1.40×10^{-14}
Br compounds	CH_3Br	4.00×10^{-12}	2.90×10^{-14}
	CH_2Br_2	2.40×10^{-12}	1.20×10^{-13}
	$CHBr_3$	1.60×10^{-12}	1.50×10^{-13}
hydrocarbons	CH_4	2.50×10^{-12}	6.30×10^{-15}
	H_2CO	1.00×10^{-11}	1.00×10^{-11}
	C_2H_6	8.70×10^{-12}	2.40×10^{-13}
	c-C_3H_6	7.28×10^{-12}	7.64×10^{-14}
	c-C_4H_8	1.62×10^{-11}	2.08×10^{-12}
	c-C_5H_{10}	2.57×10^{-11}	4.83×10^{-12}
	c-C_6H_{12}	3.58×10^{-11}	6.69×10^{-12}

TABLE 3: Predicted Arrhenius Parameters for Reaction of OH Radicals with $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$, Based on the Observed Correlation between *A*-Factors and *k*(298 K)

fluoroether	observed *k*(298 K) (cm^3 $molecule^{-1}$ s^{-1})	predicted *A*-factor (cm^3 $molecule^{-1}$ s^{-1})	predicted *E*/*R* (K)
$CF_3OCF_2CF_2H$	2.26×10^{-15}	6.5×10^{-13}	1685
$CF_3OC(CF_3)_2H$	3.26×10^{-16}	4.1×10^{-13}	2124

Useful estimates of *k*(298 K) can often be made by taking advantage of the correlation between *k*(OH) and *k*(Cl), shown in Figure 9 (data taken from JPL 97-4 and the present work). The line through the data in Figure 9 is a least-squares fit that gives

$$\log(k(\mathrm{OH})) = (0.412\pm0.049)\log(k(\mathrm{Cl})) - (8.16\pm0.72) \quad \mathrm{(V)}$$

TABLE 4: Predicted Arrhenius Parameters for the Reaction of Cl Atoms with $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$, Based on the Observed Correlation between *A*-Factors and *k*(298 K)

fluoroether	observed *k*(298 K) (cm^3 $molecule^{-1}$ s^{-1})	predicted *A*-factor (cm^3 $molecule^{-}$ s^{-1})	predicted *E*/*R* (K)
$CF_3OCF_2CF_2H$	2.70×10^{-16}	1.7×10^{-12}	2604
$CF_3OC(CF_3)_2H$	1.58×10^{-18}	5.8×10^{-13}	3816

The correlation is more exact for the slower reactions, in which the rate constants are dominated largely by the effects of strong C−H bond energies. Other effects evidently come into play for the faster reactions, because the scatter is larger than can be explained by experimental error. As seen from Figure 9, the relative reactivities of Cl atoms and OH radicals with the HFEs studied in the present work are consistent with expectations based upon the existing database.

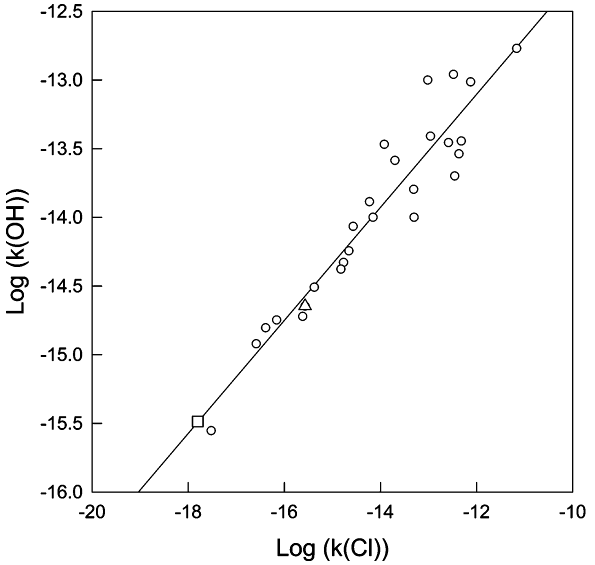

Figure 9. Plot of log(*k*(OH)) vs log(*k*(Cl)): circles, data from JPL 97-4[3] for saturated hydrofluorocarbons, hydrochlorofluorocarbons, hydrofluoroethers, and chloroalkanes; triangle, $CF_3OCF_2CF_2H$ (this work); square, $CF_3OC(CF_3)_2H$ (this work).

3.6. Atmospheric Lifetimes. The *k*(OH) Arrhenius parameters derived in section 3.5 and given in Table 3 can be used to provide estimates of the atmospheric lifetimes of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$. The atmospheric lifetime of CH_3CCl_3 with respect to reaction with OH radicals is 6 years.[19] The rate constant for reaction of OH radicals with CH_3CCl_3 is $k = 1.6 \times 10^{-12} \exp(-1520/T)$ cm^3 $molecule^{-1}$ s^{-1}.[4] Scaling the reactivity of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ to that of CH_3CCl_3 provides an estimate of the atmospheric lifetimes for these compounds. The optimal temperature for such a scaling analysis is 272 K.[20] From the data given in Table 3 and the expression for $k(OH + CH_3CCl_3)$ given above we estimate atmospheric lifetimes for $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ of 27 and 216 years, respectively.

3.7. IR Spectra and Global Warming Potentials of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$. IR spectra of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ recorded in 700 Torr of air diluent at 296 K are shown in Figure 10. The integrated cross section (650−1500 cm^{-1}) values are $(3.63 \pm 0.18) \times 10^{-16}$ and $(4.36 \pm 0.22) \times 10^{-16}$ cm^2 $molecule^{-1}$ cm^{-1} for $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$, respectively. There are no literature data for either $CF_3OCF_2CF_2H$ or $CF_3OC(CF_3)_2H$ to compare with the results from the present work. The integrated IR absorption cross section (650−1500 cm^{-1}) of $CF_3OCF_2CF_2H$ can be compared to that of the corresponding HFC, $CF_3CF_2CF_2H$, 2.1×10^{-16} cm^2 $molecule^{-1}$.[21] As noted previously,[22] the IR absorption by HFEs appears to be substantially greater than that of analogous HFCs. The fundamental cause of this effect is not clear and would be an interesting subject for future research.

Using the method of Pinnock et al.,[23] the IR spectra of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ shown in Figures 10, and the IR spectrum of CFC-11 reported elsewhere,[24] we calculate instantaneous forcings for $CF_3OCF_2CF_2H$, $CF_3OC(CF_3)_2H$, and CFC-11 of 0.43, 0.40, and 0.26 W m^{-2} ppb^{-1}, respectively. It is of interest to note that though the integrated absorption intensity of $CF_3OCF_2CF_2H$ is 17% smaller than that of $CF_3OC(CF_3)_2H$, the instantaneous forcing of $CF_3OCF_2CF_2H$ is 8% greater than that of $CF_3OC(CF_3)_2H$. This is explained by the fact that a greater proportion (65%) of the absorption by $CF_3OCF_2CF_2H$ lies in the atmospheric window region (approximately 8−12 μm, i.e., 800−1250 cm^{-1}). This same region only accounts for 46% of the absorption by $CF_3OC(CF_3)_2H$.

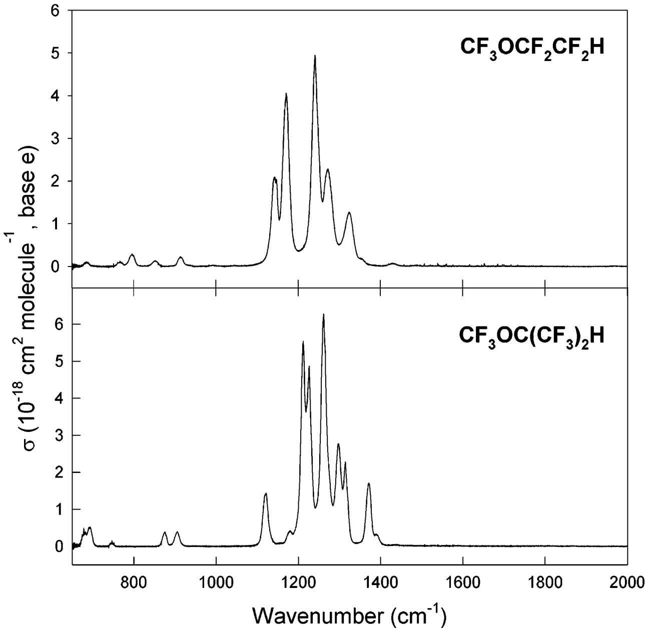

Figure 10. IR spectra of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ in 700 Torr air diluent at 296 ± 2 K.

Values of the HGWP (Halocarbon Global Warming Potential) for $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ (relative to CFC-11) can be estimated using the expression[25]

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

where $\mathrm{IF_{HFE}}$, $\mathrm{IF_{CFC-11}}$, M_{HFE}, $M_{\mathrm{CFC-11}}$, τ_{HFE}, and $\tau_{\mathrm{CFC-11}}$ are the instantaneous forcings, molecular weights, and atmospheric lifetimes of the HFE and CFC-11, and t is the time horizon over which the forcing is integrated. Using $\tau(CF_3OCF_2CF_2H) = 27$ years, $\tau(CF_3OC(CF_3)_2H) = 216$ years, and $\tau(\mathrm{CFC\text{-}11}) = 45$ years,[26] we estimate that the HGWPs of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ (relative to CFC-11) are 1.07 and 1.06 for a 20 year horizon and 0.80 and 1.79 for a 100 year horizon, respectively.

Relative to CO_2, the GWPs of CFC-11 on 20 and 100 year time horizons are 6300 and 4600.[26] Hence, relative to CO_2, the GWPs of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ are 6740 and 6680 for a 20 year horizon and 3690 and 8230 for a 100 year time horizon, respectively.

4. Implications for Atmospheric Chemistry

We present here a large quantity of self-consistent kinetics and mechanistic data concerning the atmospheric chemistry of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$. As with all saturated HFEs,[27] the atmospheric lifetime of these compounds is determined by the reaction with OH radicals and is approximately 27 and 216 years for $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$, respectively.

In addition to reaction with OH radicals, organic compounds are removed from the atmosphere via photolysis, wet deposition, dry deposition, and reaction with NO_3 radicals, Cl atoms, and O_3. For saturated compounds such as $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ reaction with NO_3 radicals and O_3 are typically too slow to be of importance. The average concentration of Cl atoms in the troposphere is several orders of magnitude less than that of OH radicals.[28] In the present study we observe that OH radicals are 8 and 206 times more reactive than Cl atoms toward $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$, respectively. Reaction with Cl atoms will not be a significant atmospheric loss mechanism for either $CF_3OCF_2CF_2H$, or $CF_3OC(CF_3)_2H$. Ethers do not absorb at UV wavelengths > 190 nm[29] and fluorination shifts the absorption further into the vacuum UV region. Photolysis will not be a major fate of either $CF_3OCF_2CF_2H$ or $CF_3OC(CF_3)_2H$. Highly fluorinated molecules such as $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ are hydrophobic and wet deposition is unlikely to be of importance. Finally, the volatility of these compounds will render dry deposition an unlikely removal mechanism. In conclusion, the atmospheric lifetime of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ is determined by reaction with OH radicals.

With regard to the environmental impact of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ we can make the following statements. First, $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ do not contain any chlorine and will not contribute to stratospheric ozone depletion via the well-established chlorine based chemistry. As with all hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs), the ozone depletion potential of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ is for all practical purposes zero.[30,31] Second, the atmospheric lifetime of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ is approximately 27 and 216 years, respectively, and consequently these compounds have relatively large GWPs (see section 3.7). Third, atmospheric oxidation of $CF_3OCF_2CF_2H$ gives COF_2, whereas $CF_3OC(CF_3)_2H$ gives $CF_3OC(O)CF_3$ and COF_2. The atmospheric fate of COF_2 and $CF_3OC(O)CF_3$ is likely uptake into rain, cloud, and ocean water, followed by hydrolysis to produce CO_2 and HF from COF_2, and $CF_3C(O)OH$ and HF from $CF_3OC(O)CF_3$.[14] At the levels anticipated in the environment, the atmospheric oxidation products of $CF_3OCF_2CF_2H$ and $CF_3OC(CF_3)_2H$ are not of concern.

A method to estimate Arrhenius parameters for reactions of OH radicals and Cl atoms with saturated organic compounds is presented and discussed. The method is based on the correlation of preexponential factors with k(298 K). Finally, a correlation between the rate constants for reactions of OH radicals and Cl atoms with saturated hydrofluorocarbons, hydrochlorofluorocarbons, hydrofluoroethers, and chloroalkanes is presented (see Figure 9). This correlation has two uses: first, for testing the consistency of kinetic data where k(OH) *and* k(Cl) are available; second, for estimating k(Cl) or k(OH) when only k(OH) *or* k(Cl) is available.

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Correction after ASAP Publication. This article was published on Articles ASAP on April 12, 2005, with a lowercase letter “c” in the second chemical formula in the title. The corrected article was posted April 18, 2005.

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