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Atmospheric Chemistry of HFC-236cb: Fate of the Alkoxy Radical CF_3CF_2CFHO

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An FTIR/environmental chamber technique was used to study the fate of the alkoxy radical CF_3CF_2CFHO formed in the atmospheric degradation of HFC-236cb ($CF_3CF_2CFH_2$). Experiments were performed over the temperature range 228−296 K at 7.8−1000 Torr total pressure. Two reaction pathways are possible for CF_3CF_2CFHO radicals: reaction with oxygen, $CF_3CF_2CFHO + O_2 \rightarrow CF_3CF_2C(O)F + HO_2$ (k_{O2}) and decomposition via C−C bond scission, $CF_3CF_2CFHO \rightarrow CF_3CF_2 + HC(O)F$ (k_d). CF_3CF_2CFHO radicals were produced by two reactions: the $CF_3CF_2CFHO_2$ self-reaction and the $CF_3CF_2CFHO_2 + NO$ reaction. In the absence of NO at 800 Torr total pressure the rate constant ratio k_d/k_{O2} was determined to be $(6.6^{+16.3}_{-4.7}) \times 10^{25} \exp(-(3560 \pm 295)/T)$ molecules cm^{-3}. The pressure dependence of k_d/k_{O2} was studied at 238 K and was well described by a Troe type expression using $k_{d,0}/k_{O2} = 30.8 \pm 6.9$ and $k_{d,\infty}/k_{O2} = (2.31 \pm 0.12) \times 10^{19}$ molecules cm^{-3} where $k_{d,0}$ and $k_{d,\infty}$ are the second- and first-order rate constants for decomposition in the low- and high-pressure limits, respectively. CF_3CF_2CFHO radicals formed in the $CF_3CF_2CFHO_2 + NO$ reaction undergo more C−C bond scission than those generated in the $CF_3CF_2CFHO_2$ self-reaction. This is consistent with a significant fraction (67^{+19}_{-22}%) of the alkoxy radicals being formed with sufficient internal energy to undergo prompt decomposition. Overall, we calculate that less than 1% of the $CF_3CF_2CFH_2$ (HFC-236cb) released to the atmosphere degrades to form $CF_3CF_2C(O)F$ while >99% gives CF_3CF_2 radicals and HC(O)F.

1. Introduction

Recognition of the adverse impact of chlorofluorocarbons, CFCs, on the stratospheric ozone layer has led to an international effort to phase out these compounds. Hydrofluorocarbons, HFCs, are an important class of CFC substitutes, and HFC-236cb ($CF_3CF_2CFH_2$) is one such potential CFC replacement. The atmospheric chemistry of HFC-236cb is of interest for two reasons. First, it is necessary to establish the atmospheric fate of HFC-236cb to determine its environmental impact. Second, HFC-236cb has structural similarities to HFC-134a (CF_3CFH_2), which is widely used in vehicle air conditioning and domestic refrigeration units, and a study of HFC-236cb may shed light on the atmospheric degradation of HFC-134a. We have recently studied the oxidation of HFC-134a and found evidence for a "hot alkoxy radical" effect in a study of the CF_3CFHO radical.[1,2] It was found that 60 ± 15% of CF_3CFHO radicals produced in the exothermic reaction of CF_3CFHO_2 with NO have sufficient internal energy to decompose immediately. The remaining alkoxy radicals undergo collisional stabilization to give thermalized radicals that then undergo both reaction with O_2 or thermal decomposition via C−C bond scission.[1] The alkoxy radicals derived from HFC-134a and HFC-236cb have a similar molecular structure, and it seems likely that a "hot alkoxy radical" effect may also be operative in the atmospheric chemistry of HFC-236cb.

After release into the atmosphere HFC-236cb is expected to undergo reaction with OH radicals.

$$CF_3CF_2CFH_2 + OH \rightarrow CF_3CF_2CFH + H_2O \qquad (1)$$

The atmospheric lifetime of HFC-236cb is assumed to be approximately 15 years.[3] CF_3CF_2CFH radicals produced in reaction 1 will rapidly (within 1 μs) add O_2 to form a peroxy radical:[4]

$$CF_3CF_2CFH + O_2 + M \rightarrow CF_3CF_2CFHO_2 + M \qquad (2)$$

The peroxy radical will then react with NO, NO_2, HO_2, or other peroxy radicals, RO_2, in the atmosphere:

$$CF_3CF_2CFHO_2 + NO \rightarrow CF_3CF_2CFHO + NO_2 \qquad (3a)$$

$$CF_3CF_2CFHO_2 + NO + M \rightarrow CF_3CF_2CFHONO_2 + M \qquad (3b)$$

$$CF_3CF_2CFHO_2 + NO_2 + M \leftrightarrows CF_3CF_2CFHO_2NO_2 + M \qquad (4,-4)$$

$$CF_3CF_2CFHO_2 + HO_2 \rightarrow \text{products} \qquad (5)$$

$$CF_3CF_2CFHO_2 + RO_2 \rightarrow \text{products} \qquad (6)$$

The atmospheric fate of $CF_3CF_2CFHO_2NO_2$ is expected to be thermal decomposition via reaction (−4). The atmospheric fate of $CF_3CF_2CFHOOH$ produced in reaction 5 is expected to be either photolysis to CF_3CF_2CFHO and OH radicals or reaction with OH radicals to regenerate the $CF_3CF_2CFHO_2$ radical.[5]

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Aqueous uptake may also be a possible sink for $CF_3CF_2CFHOOH$.[5]

To understand the ultimate products and, hence, the environmental impact of HFC-236cb, data concerning the atmospheric chemistry of the CF_3CF_2CFHO radical are needed. A previous study has shown that reactions 7 and 8 compete for CF_3CF_2CFHO radicals under atmospheric conditions:

$$\mathrm{CF_3CF_2CFHO + O_2 \rightarrow CF_3CF_2C(O)F + HO_2} \tag{7}$$

$$\mathrm{CF_3CF_2CFHO + M \rightarrow CF_3CF_2 + HC(O)F + M} \tag{8}$$

At 700 Torr total pressure and 296 K, the rate constant ratio $k_8/k_7 = k_d/k_{O2}$ was found to be 3×10^{20} molecule cm^{-3}.[4] However, the effect of temperature and total pressure on k_d/k_{O2} is unknown.

In the previous study of reactions 7 and 8 we employed the self-reaction of $CF_3CF_2CFHO_2$ radicals as a source for CF_3CF_2CFHO radicals. The self-reaction of peroxy radicals is a convenient source of alkoxy radicals for laboratory studies. However, in the atmosphere the main source of CF_3CF_2CFHO radicals is not the self-reaction of $CF_3CF_2CFHO_2$ radicals but rather the reaction of $CF_3CF_2CFHO_2$ radicals with NO.

$$\mathrm{CF_3CF_2CFHO_2 + CF_3CF_2CFHO_2 \rightarrow CF_3CF_2CFHO + CF_3CF_2CFHO + O_2} \tag{9a}$$

$$\mathrm{CF_3CF_2CFHO_2 + CF_3CF_2CFHO_2 \rightarrow CF_3CF_2C(O)F + CF_3CF_2CFHOH + O_2} \tag{9b}$$

$$\mathrm{CF_3CF_2CFHO_2 + NO \rightarrow CF_3CF_2CFHO + NO_2} \tag{3a}$$

The aim of the present work is twofold: first, to extend our previous study of k_d/k_{O2} to temperatures other than 295K and pressures other than 700 Torr; second, to investigate the possibility of a “hot alkoxy radical” effect in the presence of NO in the oxidation of HFC-236cb.

2. Experimental Section

The system consists of a Fourier transform infrared (FTIR) spectrometer coupled to a temperature-regulated reaction vessel. The system has been described previously[6,7] and will only be described briefly here. The reaction vessel, which has a volume of 47 L, was operated at temperatures between 228 and 296 K and pressures from 7.8 to 1000 Torr. Hanst type optics to multipass the IR beam were mounted inside the cell.

The spectrometer, a BOMEM DA3.01, was coupled to the cell via evacuable transfer optics. The total path length of the analyzing IR beam was 32.6 m, and a spectral resolution of 1 cm^{-1} was used. For each spectrum 100−500 interferograms were acquired. The UV photolysis light was provided by a xenon arc lamp situated at the end of the reaction cell. The light was filtered by a Corning 7-54 glass filter that transmits light between 240 and 400 nm.

Gases were expanded from known volumes and flushed into the reaction chamber with N_2 or O_2. The gas mixtures were allowed to stand for 5 min to reach temperature equilibrium prior to each experiment. Gas mixtures were subjected to three to five successive UV irradiations each of a duration of 5−20 min, and IR spectra were acquired after each irradiation. The loss of reactants and the formation of products were quantified by comparison to calibrated reference spectra. Reference spectra of $C(O)F_2$ and $CF_3CF_2CFH_2$ were acquired by expanding known volumes into the cell. Reference spectra of HC(O)F and $CF_3CF_2C(O)F$ were taken from the library at Ford Motor Company.[4] HC(O)F concentrations were quantified using an absorption cross section of 1.0×10^{-18} cm^2 molecule^{-1} at 1849 cm^{-1} at room temperature. The absorption cross section for HC(O)F was corrected for temperature dependence by adding 5% at 269 and 250 K and 10% at 238 and 228 K by analogy with the behavior of HC(O)Cl.[8] For $CF_3CF_2C(O)F$ the integrated absorption over the range 1850−1920 cm^{-1}, $\sigma_{int} = 2.47 \times 10^{-17}$ cm^2 molecule^{-1}, was used assuming the integrated cross section is independent of temperature.

Two chemical sources of CF_3CF_2CFHO radicals were used: either the $CF_3CF_2CFHO_2$ self-reaction 9a or the $CF_3CF_2CFHO_2$ + NO reaction 3a. $CF_3CF_2CFHO_2$ radicals were prepared by reaction of Cl atoms with HFC-236cb in the presence of O_2. Molecular chlorine was used as the source of Cl atoms.

$$\mathrm{Cl_2} + h\nu \rightarrow \mathrm{2Cl} \tag{10}$$

$$\mathrm{CF_3CF_2CFH_2 + Cl \rightarrow CF_3CF_2CFH + HCl} \tag{11}$$

$$\mathrm{CF_3CF_2CFH + O_2 + M \rightarrow CF_3CF_2CFHO_2 + M} \tag{2}$$

Mixtures of $CF_3CF_2CFH_2/O_2/Cl_2/N_2$ and $CF_3CF_2CFH_2/O_2/Cl_2/N_2/NO$ were irradiated with UV light, and the yields of HC(O)F and $CF_3CF_2C(O)F$ were followed by FTIR spectroscopy. At 295 K, Cl atoms react with $CF_3CF_2CFH_2$ with a rate constant of $k_{11} = (1.5 \pm 0.3) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} [4] and with HC(O)F with a rate constant of 2.0×10^{-15} cm^3 molecule^{-1} s^{-1}.[9] Loss of HC(O)F via reaction with Cl is important at large conversions of HFC-236cb. Therefore, only small conversions of HFC-236cb (<10%) were used. The temperature dependence of the Cl + HC(O)F reaction was recently measured by Bednarek et al.[10] They find the activation temperature for Cl + HC(O)F to be $E_a/R = 1130$ K. Since we expect the activation energy for the Cl + HFC-236cb to be similar to that for the Cl + HFC-134a reaction ($E_a/R = 1700$) and since we use small conversions of HFC-236cb, we expect that loss of HC(O)F via reaction with Cl will be neglible in the present work at low temperatures as well. In addition, no evidence for any heterogeneous loss or photolysis of HC(O)F was observed. Two factors complicate the use of absolute HC(O)F and $CF_3CF_2C(O)F$ yields to determine the fate of CF_3CF_2CFHO radicals. First, the use of small conversions of HFC-236cb imposes large uncertainties in the measurements of the loss of $CF_3CF_2CFH_2$ compared to the uncertainties in the quantification of the formation of HC(O)F and $CF_3CF_2C(O)F$ yields. Second, the combined yields of HC(O)F and $CF_3CF_2C(O)F$ are expected to fall below 100% compared to the HFC-236cb loss, due to the formation of trioxides and peroxynitrates, as discussed in ref 11. Therefore, instead of measuring the absolute yields of $CF_3CF_2C(O)F$ and HC(O)F as a function of loss of HFC-236cb, we chose to monitor the relative yields of HC(O)F and $CF_3CF_2C(O)F$ normalized to a combined yield of HC(O)F + $CF_3CF_2C(O)F$ = 100%.

Three sets of experiments were performed. First, to determine the effect of temperature on the rate constant ratio k_d/k_{O2} for CF_3CF_2CFHO radicals from the self-reaction of $CF_3CF_2CFHO_2$ radicals, mixtures of $CF_3CF_2CFH_2/O_2/Cl_2$ with N_2 added to a total pressure of 800 Torr were irradiated at 296, 278, 269, 250, 238, and 228 K. Second, to determine the effect of total pressure on k_d/k_{O2} for CF_3CF_2CFHO radicals from the self-reaction of $CF_3CF_2CFHO_2$ radicals at 238 K, mixtures of $CF_3CF_2CFH_2/Cl_2/O_2/N_2$ with the total pressure varied between 7.8 and 1000 Torr were subject to UV irradiation. Finally, to

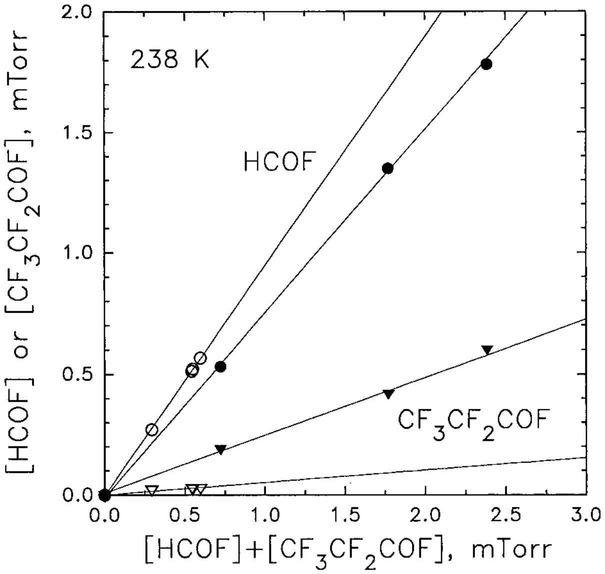

Figure 1. Yields of HC(O)F (●) and $CF_3CF_2C(O)F$ (▼) plotted versus the combined yield of these species observed following irradiation of mixtures of 44 mTorr of $CF_3CF_2CFH_2$, 660 mTorr of Cl_2, and 100 Torr of O_2 in 800 Torr total pressure of N_2 diluent at 238 K. The yields of HC(O)F and $CF_3CF_2C(O)F$ were 76% and 24%, respectively. The hollow symbols are data taken under the same conditions but with 7.7 mTorr of NO present. The yields of HC(O)F and $CF_3CF_2C(O)F$ were 95% and 5%, respectively.

determine the potential effect of internal excitation of CF_3CF_2CFHO radicals formed in the $CF_3CF_2CFHO_2$ + NO reaction, mixtures of $CF_3CF_2CFH_2/O_2/Cl_2/NO$ with N_2 added to 800 Torr were irradiated at 269, 250, 238, and 228 K.

3. Results

3.1. Fate of CF_3CF_2CFHO Radicals Formed in the Self-Reaction of $CF_3CF_2CFHO_2$ Radicals. Effect of Temperature on k_d/k_{O2}. To study the competition between reactions 7 and 8, mixtures of 44 mTorr of $CF_3CF_2CFH_2$, 660 mTorr of Cl_2, and 2−800 Torr of O_2 with N_2 added to give 800 Torr total pressure were subject to UV irradiation. CF_3CF_2CFHO radicals were generated via reactions 2 and 9−11:

$$Cl_2 + h\nu \rightarrow 2Cl \tag{10}$$

$$CF_3CF_2CFH_2 + Cl \rightarrow CF_3CF_2CFH + HCl \tag{11}$$

$$CF_3CF_2CFH + O_2 + M \rightarrow CF_3CF_2CFHO_2 + M \tag{2}$$

$$CF_3CF_2CFHO_2 + CF_3CF_2CFHO_2 \rightarrow CF_3CF_2CFHO + CF_3CF_2CFHO + O_2 \tag{9a}$$

$$CF_3CF_2CFHO_2 + CF_3CF_2CFHO_2 \rightarrow CF_3CF_2CFHOH + CF_3CF_2C(O)F + O_2 \tag{9b}$$

The filled symbols in Figure 1 show the observed formation of HC(O)F and $CF_3CF_2C(O)F$ following the irradiation of a mixture containing 100 Torr of O_2 at 238 K. When normalized to a combined yield of HC(O)F + $CF_3CF_2C(O)F$ = 100%, the yields of HC(O)F and $CF_3CF_2C(O)F$ were 76% and 24%.

In Figure 2 the HC(O)F and $CF_3CF_2C(O)F$ yields obtained at six different temperatures are plotted as a function of the oxygen concentration. The yield of $CF_3CF_2C(O)F$ increases at the expense of the HC(O)F yield at higher oxygen concentrations, reflecting the competition between reactions 7 and 8:

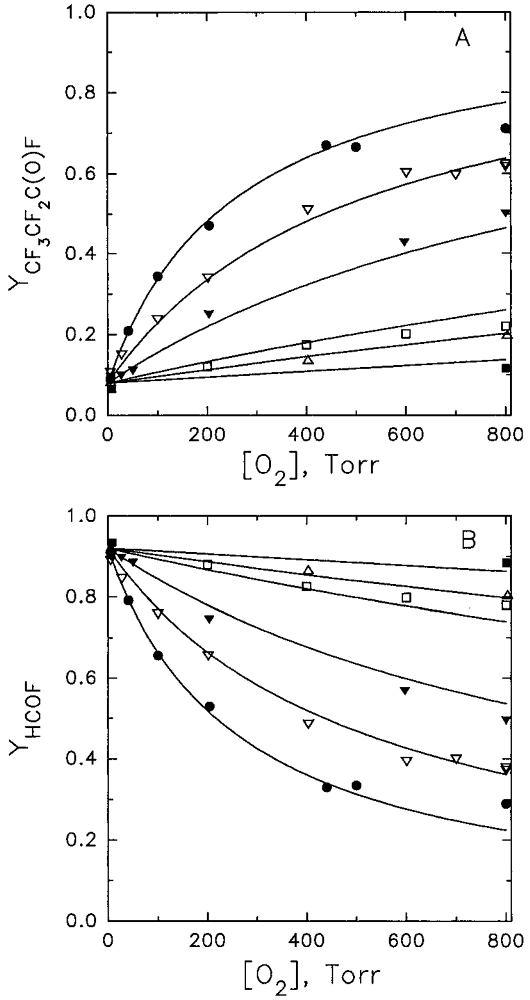

Figure 2. Relative yields of $CF_3CF_2C(O)F$ (A) and HC(O)F (B) at 296 (■), 278 (△), 269 (□), 250 (▼), 238 (▽), and 228 K (●) observed following irradiation of HFC-236cb/$Cl_2/O_2/N_2$ mixtures as a function of oxygen partial pressure. All experiments were performed at 800 Torr total pressure. The smooth lines are a fit to the data. See text for details.

$$CF_3CF_2CFHO + O_2 \rightarrow CF_3CF_2C(O)F + HO_2 \tag{7}$$

$$CF_3CF_2CFHO + M \rightarrow CF_3CF_2 + HC(O)F + M \tag{8}$$

However, a yield of approximately 8% of $CF_3CF_2C(O)F$ was observed even at very low oxygen pressures, which can be explained by formation of $CF_3CF_2C(O)F$ via reaction 9b. Furthermore, by analogy with the Cl atom-initiated oxidation of CH_3OH,[12] we expect that $CF_3CF_2C(O)F$ may also be formed from CF_3CF_2CFHOH via the following reactions:

$$CF_3CF_2CFHOH + Cl \rightarrow CF_3CF_2CFOH + HCl \tag{12}$$

$$CF_3CF_2CFOH + O_2 \rightarrow CF_3CF_2C(O)F + HO_2 \tag{13}$$

Assuming that the formation of $CF_3CF_2C(O)F$ in the system is described solely by reactions 2 and 7−13, then we can describe the yield of $CF_3CF_2C(O)F$ by the following equation:

$$Y_{CF3CF2C(O)F} = y_0 + (1 - y_0)\Gamma \tag{I}$$

where y_0 is the yield of $CF_3CF_2C(O)F$ in the limit of zero oxygen pressure and Γ is $1/(1 + k_d/(k_{O2}[O_2]))$. Expression I was fitted

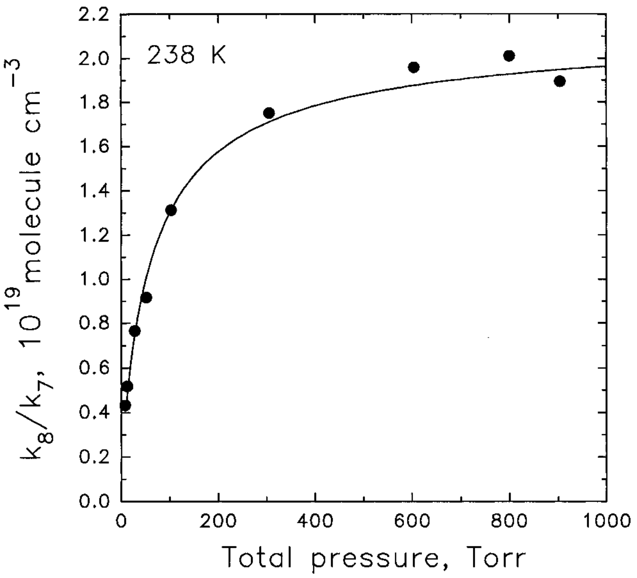

Figure 3. k_d/k_{O2} plotted as a function of total pressure at 238 K. The smooth line is a fit to the data. See text for details.

simultaneously to all six data sets in Figure 2. Since the value of k_d/k_{O2} is expected to vary strongly with temperature, we parametrized the ratio as $k_d/k_{O2} = A \exp(-E_a/(RT))$. To fit the yield of $CF_3CF_2C(O)F$ at different temperatures, three parameters were varied simultaneously: y_0, A, and E_a/R. The best fit was obtained with $y_0 = 0.08 \pm 0.01$, $A = (6.6^{+16.3}_{-4.7}) \times 10^{25}$ molecules cm^{-3}, and $E_a = (3558 \pm 295)$ K. The fits are shown in Figure 2 as smooth curves.

The fraction of the self-reaction of $CF_3CF_2CFHO_2$ radicals that proceeds via reaction 9b, y_0, did not display any discernible temperature dependence. Although there are no literature studies to compare with our result, there have been several product studies of the analogous molecule CF_3CFH_2 (HFC-134a). The comparable y_0 values for HFC-134a are the $CF_3C(O)F$ yields extrapolated to the limit of zero oxygen pressure. As discussed by Wallington et al.[1] and Bednarek et al.,[10] the values of y_0 for HFC-134a obtained in the literature vary considerably with temperature. In contrast, as shown by the y-axis intercept in Figure 2, there is little or no effect of temperature on y_0 in the HFC-236cb system.

In a previous study of HFC-236cb, Møgelberg et al.[4] reported a value of $k_d/k_{O2} = (3 \pm 1) \times 10^{20}$ molecule cm^{-3} at 295 K. Using the values of A and E_a/R derived here, we arrive at $k_d/k_{O2} = 4.0 \times 10^{20}$ molecule cm^{-3} for 295 K, in good agreement with results from our previous work. The expression $k_d/k_{O2} = (6.6^{+16.3}_{-4.7}) \times 10^{25} \exp((-3560 \pm 295)/T)$ molecules cm^{-3} can be compared to the analogous rate constant ratio $k_{CF3CFHO \rightarrow CF3+HC(O)F}/k_{CF3CFHO+O2} = (4.8^{+2.9}_{-2.0}) \times 10^{24} \exp((-3625 \pm 140)/T)$ molecule cm^{-3},[1] which describes the atmospheric fate of the alkoxy radical CF_3CFHO from HFC-134a. The values of E_a/R for CF_3CFHO and CF_3CF_2CFHO radicals are, within the experimental uncertainties, indistinguishable. The values of A differ by a factor of 10, accounting for the more rapid decomposition of CF_3CF_2CFHO radicals.

3.2. Pressure Dependence of k_d/k_{O2}. To investigate the pressure dependence of k_d/k_{O2}, experiments were performed in which mixtures of 44 mTorr of HFC-236cb, 600 mTorr of Cl_2, 7.8−105 Torr of O_2, and 0−900 Torr of N_2 at 238 K were irradiated and the yields of HC(O)F and $CF_3CF_2C(O)F$ were determined. These yields were used to calculate k_d/k_{O2} using eq I. As depicted in Figure 3, k_d/k_{O2} increases with increasing total pressure, since reaction 8 is a unimolecular decomposition whose rate will increase with increasing pressure, while k_{O2} is independent of total pressure. The solid line in Figure 3 is a fit to the data using a Troe type expression:

$$k(M) = k_0[M]/(1 + k_0[M]/k_\infty)F_c^{(1+(\log[k0[M]/k\infty])2)-1} \quad \text{(II)}$$

where M is the concentration of the third body, i.e., N_2 and O_2, $k_0 = (k_{d,0}/k_{O2})$ is the value of the rate constant ratio k_d/k_{O2} in the low-pressure limit, and $k_\infty = (k_{d,\infty}/k_{O2})$ is the value of k_d/k_{O2} in the high-pressure limit. F_c was kept constant at 0.6 as recommended by DeMore et al.[3] $(k_{d,0}/k_{O2})$ and $(k_{d,\infty}/k_{O2})$ were varied simultaneously to obtain the best fit to the experimental data. The best fit was obtained using $(k_{d,0}/k_{O2}) = 30.8 \pm 6.9$ and $(k_{d,\infty}/k_{O2}) = (2.31 \pm 0.12) \times 10^{19}$ molecules cm^{-3}.

3.3. Fate of CF_3CF_2CFHO Radicals Formed in the $CF_3CF_2CFHO_2$ + NO Reaction. Mixtures of 7.7 mTorr of NO, 219 mTorr of $CF_3CF_2CFH_2$, 660 mTorr of Cl_2, 100−600 Torr of O_2, and N_2 added to a total pressure of 800 Torr were irradiated to determine the fate of CF_3CF_2CFHO radicals formed from the reaction of $CF_3CF_2CFHO_2$ with NO:

$$CF_3CF_2CFHO_2 + NO \rightarrow CF_3CF_2CFHO + NO_2 \quad \text{(3a)}$$

Experiments performed at 269 ($[O_2]$ = 600 Torr), 250 ($[O_2]$ = 200 Torr), 238 ($[O_2]$ = 100 Torr), and 228 K ($[O_2]$ = 100 Torr) gave yields of $CF_3CF_2C(O)F$ of 5.0, 8.4, 5.1, and 4.0%, respectively. For comparison the $CF_3CF_2C(O)F$ yields predicted by eq I at 269, 250, 238, and 228 K are 15, 15, 16, and 28%, respectively, for the corresponding O_2 partial pressures (in this calculation y_0 was set to zero, since in the presence of NO reaction 9 is of no importance). Clearly, the observed yields fall well below those predicted by eq I. CF_3CF_2CFHO radicals formed via reaction of $CF_3CF_2CFHO_2$ radicals with NO (reaction 3a) behave differently from those formed from reaction 9a. We have recently reported a similar effect for CF_3CFHO radicals:[1]

$$CF_3CFHO_2 + NO \rightarrow CF_3CFHO + NO_2 \quad (14)$$

$$CF_3CFHO_2 + CF_3CFHO_2 \rightarrow CF_3CFHO + CF_3CFHO + O_2 \quad (15)$$

In the study of CF_3CFHO radicals formed from reaction 14 it was shown that 60% of the CF_3CFHO radicals are produced with sufficient internal energy to decompose immediately and 40% are thermalized.[1] The thermalized CF_3CFHO radicals decompose or react with O_2 in the same way as those formed from reaction 15. In the present study it was not possible to study the behavior of thermalized CF_3CF_2CFHO radicals from the reaction of $CF_3CF_2CFHO_2$ reaction with NO because of the very low yields of $CF_3CF_2C(O)F$ in the presence of NO. There was no discernible effect of temperature or oxygen partial pressure on the $CF_3CF_2C(O)F$ yield. Therefore, we assume in the following that a certain fraction, α, of the CF_3CF_2CHFO radicals formed by reaction 3a are thermalized and behave in a manner that can be predicted using the rate constant ratio k_d/k_{O2} derived in section 3.1 and that a fraction, (1 − α), decomposes promptly. Estimates of α can be derived by comparing the measured yields of $CF_3CF_2C(O)F$ in the presence of NO with the yields of $CF_3CF_2C(O)F$ assuming no prompt decomposition. The fraction of CF_3CF_2CFHO radicals that is thermalized, α, can be calculated from

$$\alpha = \frac{Y_{CF3CF2C(O)F} \text{ with NO}}{\Gamma}$$

The values for α are 0.325, 0.548, 0.316, and 0.144 at 269, 250, 238, and 228 K, respectively. The scatter in the values of α is attributable to experimental difficulties in measuring the small yields of $CF_3CF_2C(O)F$. Within the experimental uncertainties, there is no discernible dependence of α on temperature. We therefore quote a value for α that is an average of the four values above with an uncertainty that encompasses the extremes, i.e., $\alpha = 0.33^{+0.22}_{-0.19}$. This value is similar to that of $\alpha = 40 \pm 15\%$ for the CF_3CFHO radicals formed from the $CF_3CFHO_2 + NO$ reaction.[1] In our previous study of CF_3CFHO radicals, we were unable to discern any effect of temperature on α.[1]

4. Discussion

In the present work the fate of the alkoxy radical CF_3CF_2CFHO was studied. Alkoxy radicals were formed either via the self-reaction of $CF_3CF_2CFHO_2$ radicals (reaction 9a) or via the reaction of $CF_3CF_2CFHO_2$ radicals with NO (reaction 3a). A significant decrease in the $CF_3CF_2C(O)F$ yield was observed when CF_3CF_2CFHO radicals were formed via reaction 3a as compared to reaction 9a at 298 K. The simplest explanation for this observation is to postulate that $67^{+19}_{-22}\%$ of the CF_3CF_2CFHO radicals formed via reaction 3a undergo prompt decomposition. This behavior is analogous to that observed for CF_3CFHO radicals[1] where $60 \pm 15\%$ of those formed in the presence of NO decomposed promptly.

It has previously been reported that in the atmosphere 98% of CF_3CF_2CFHO radicals undergo C−C bond scission and only 2% react with O_2.[4] The result was based on one value of k_d/k_{O2} at 296 K and 700 Torr. A new calculation of the relative importance of C−C bond scission and reaction with O_2 for CF_3CF_2CFHO radicals in the atmosphere was performed using the temperature and pressure dependence of k_d/k_{O2} measured in this work. In making the calculation the following assumptions were made. HFC-236cb is well mixed in the troposphere, i.e., its concentration scales with atmospheric density, and HFC-236cb reacts with OH at a rate equal to the rate at which HFC-134a reacts. Vertical profiles of OH, O_2, density, and temperature in the atmosphere were taken from Brasseur and Solomon.[13] It was assumed that in the atmosphere all CF_3CF_2CFHO radicals are formed via reaction with NO, reaction 3a, and that 67% decompose immediately after formation. The atmospheric yield of $CF_3CF_2C(O)F$ was found to be <1%. By analogy to the behavior of $CF_3C(O)F$, the atmospheric fate of $CF_3CF_2C(O)F$ is expected to be incorporation into rain-cloud sea water followed by hydrolysis to give $CF_3CF_2C(O)OH$. Since the yield of $CF_3CF_2C(O)OH$ in the atmospheric degradation of HFC-236cb is so small (<1%) and since HFC-236cb is expected to be produced and released in small quantities, formation of $CF_3CF_2C(O)OH$ in the atmospheric degradation of HFC-236cb is not anticipated to have any practical environmental impact. As discussed elsewhere,[4] C_2F_5 radicals will be degraded into COF_2, which is of no environmental concern. Finally, the fate of HC(O)F is dominated by hydrolysis to give HCOOH and HF. The atmospheric degradation products of HFC-236cb thus appear to be benign.

References and Notes

(1) Wallington, T. J.; Hurley, M. D.; Fracheboud, J. M.; Orlando, J. J.; Tyndall, G. S.; Sehested, J.; Møgelberg, T. E.; Nielsen, O. J. *J. Phys. Chem.* **1996**, *100*, 18116.

(2) Wallington, T. J.; Schneider, W.; Barker, J. *J. Phys. Chem.*, in press.

(3) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *JPL Publ.* **1994**, *94-26*.

(4) Møgelberg, T. E.; Feilberg, A.; Giessing, A. M. B.; Sehested, J.; Bilde, M.; Wallington, T. J.; Nielsen, O. J. *J. Phys. Chem.* **1995**, *99*, 17386.

(5) Atkinson, R. Scientific Assessment of Stratospheric Ozone. World Meteorological Organization Global Ozone Research and Monitoring Project, Report No. 20; World Meteorological Organization: Geneva, 1989; Vol. II, p 167.

(6) Shetter, R. E.; Davidson, J. A.; Cantrell, C. A; Calvert, J. G. *Rev. Sci. Instrum.* **1987**, *58*, 1427.

(7) Staffelbach, T. A.; Orlando, J. J.; Tyndall, G. S.; Calvert, J. G. *J. Geophys. Res.* **1995**, *100*, 14189.

(8) Wallington, T. J.; Orlando, J. J; Tyndall, G. S. *J. Phys. Chem.* **1995**, *99*, 9437.

(9) Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Kaiser, E. W. *Environ. Sci. Technol.* **1992**, *26*, 1318.

(10) Bednarek, G.; Breil, M.; Hoffmann, A.; Kohlmann, J. P.; Mors, V.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1996**, *100*, 528.

(11) Sehested, J.; Ellermann, T.; Nielsen, O. J.; Wallington, T. J.; Hurley, M. D. *Int. J. Chem. Kinet.* **1993**, *25*, 701.

(12) Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F. *NIST Chemical Kinetics Database*, Version 6.0; NIST Standard Reference Data; National Institute of Standards and Technology: Gaitersburg, MD, 1994.

(13) Brasseur, G. S.; Solomon, S. *Aeronomy of the Middle Atmosphere*; Reidel: Dordrect, 1986.