

Role of Excited CF₃CFHO Radicals in the Atmospheric Chemistry of HFC-134a

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The atmospheric degradation of HFC-134a (CF₃CFH₂) proceeds via the formation of CF₃CFHO radicals. Long path length FTIR environmental chamber techniques were used to study the atmospheric fate of CF₃CFHO radicals. Two competing reaction pathways were identified for CF₃CFHO radicals: reaction with O₂, CF₃CFHO + O₂ → CF₃C(O)F + HO₂, and decomposition via C–C bond scission, CF₃CFHO + M → CF₃ + HC(O)F + M. CF₃CFHO radicals were produced by two different reactions: either via the self-reaction of CF₃CFHO₂ radicals or via the CF₃CFHO₂ + NO reaction. It was found that decomposition was much more important when CF₃CFHO radicals were produced via the CF₃CFHO₂ + NO reaction than when they were produced via the self-reaction of CF₃CFHO₂ radicals. We ascribe this observation to the formation of vibrationally excited CF₃CFHO* radicals in the CF₃CFHO₂ + NO reaction. Rapid decomposition of CF₃CFHO* radicals limits the formation of CF₃C(O)F and hence CF₃COOH in the atmospheric degradation of HFC-134a. We estimate that the CF₃COOH yield from atmospheric oxidation of HFC-134a is 7–20%. Vibrationally excited alkoxy radicals may play an important role in the atmospheric chemistry of other organic compounds.

Introduction

Recognition of the adverse effect of chlorofluorocarbon (CFC) release into the atmosphere^{1,2} has led to an international effort to replace CFCs with environmentally acceptable alternatives.³ Hydrofluorocarbon 134a (1,1,1,2-tetrafluoroethane) is an important CFC replacement used in automotive air conditioning and domestic refrigeration systems. The current global production of HFC-134a is 1.5 × 10⁵ t yr⁻¹ and is anticipated to double in the next 25 years.⁴ The HFC-134a concentration in the remote atmosphere is 1.5 ppt and is increasing exponentially at a rate of approximately 100% yr⁻¹.⁵

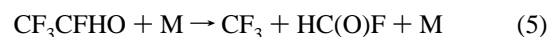
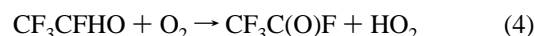
HFC-134a has no impact on stratospheric ozone^{6,7} and has a modest global warming potential.⁸ The atmospheric oxidation of HFC-134a is initiated by reaction with the OH radical.⁹ The alkyl radical formed in reaction 1 adds molecular oxygen to give the peroxy radical CF₃CFHO₂.



Reaction with NO is an important fate of CF₃CFHO₂ radicals in the atmosphere,^{10–12} leading to the formation of the alkoxy radical CF₃CFHO.^{10,11}



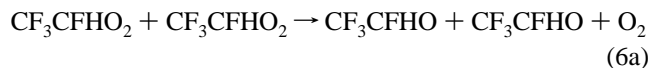
In the atmosphere, CF₃CFHO radicals either react with O₂ or decompose:



Decomposition gives a CF₃ radical and HC(O)F which are of no environmental concern.¹³ Reaction with O₂ produces CF₃C(O)F which is incorporated into rain–cloud–sea water and hydrolyzed to CF₃COOH,¹⁴ which is mildly phytotoxic.¹⁵ Concern has been expressed that in seasonal wetlands CF₃COOH could accumulate over several decades to levels where ecological impacts may be felt.¹⁶ The impact of CF₃COOH on the global environment is uncertain.^{16,17}

Assessment of the ecological impact of CF₃COOH requires accurate knowledge of its source, i.e., an understanding of the efficiency by which CF₃CFHO radicals formed in reaction 3 are converted into CF₃C(O)F, and hence CF₃COOH. Six experimental studies of the atmospheric fate of CF₃CFHO have reported results which are in broad agreement.^{18–23} Current assessments of the yield of CF₃C(O)F, and hence CF₃COOH, from the atmospheric oxidation of HFC-134a are based upon the results of experiments in which the self-reaction of CF₃CFHO₂ radicals was used as a source of CF₃CFHO radicals.

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Reaction 6a is close to thermoneutral, $\Delta H = -6 \text{ kcal mol}^{-1}$,²⁴ and the CF₃CFHO radicals formed possess little excess internal energy. In contrast, reaction 3 is exothermic by 17 kcal mol⁻¹.²⁴ By analogy to the reaction of other peroxy radicals with NO, reaction 3 is expected to proceed via the formation of a complex which decomposes into products.²⁵ CF₃CFHO radicals formed in reaction 3 could possess excess internal energy which is comparable to, or greater than, the barrier to C–C bond scission in the CF₃CFHO radical of 7.5–9 kcal mol⁻¹. Hence, it is conceivable that unlike their counterparts formed in reaction 6a, some fraction of the CF₃CFHO radicals produced in reaction 3 might undergo immediate decomposition before collisional relaxation occurs. If this is the case, then experiments employing reaction 6a as a source of CF₃CFHO radicals might not provide a reliable description of the atmospheric fate of CF₃CFHO radicals formed in reaction 3. An experimental study using the FTIR–smog chamber facilities at Ford and NCAR was undertaken to investigate this possibility.

Experimental Section

The experimental systems at Ford²⁶ and NCAR²⁷ have been described previously and are only discussed briefly here. In both systems chemical analysis was performed using FTIR spectroscopy. Experiments were conducted over the temperature range 238–295 K. The system at Ford Motor Co. consists of a 140 L Pyrex chamber surrounded by 22 UV fluorescent lamps interfaced to a Mattson Instruments Inc. Sirius 100 FT-IR spectrometer. The system at NCAR consists of a 47 L stainless steel reactor fitted with a quartz window at one end to allow photolysis using a filtered xenon arc lamp. A Bomem DA 3.01 FTIR spectrometer was interfaced to a Hanst-type optical arrangement²⁷ mounted within the reaction cell. The path lengths for the analyzing infrared beam were 26.6 m (Ford) and 33 m (NCAR), and the spectral resolutions were 0.25 cm⁻¹ (Ford) and 1 cm⁻¹ (NCAR); infrared spectra were derived from 32 (Ford) and 100–200 (NCAR) coadded interferograms.

Initial concentrations (and purities) of the gas mixtures used were 15–400 mTorr of HFC-134a (>99.9%), 0.05–0.4 Torr of chlorine (>99%), 0–30 mTorr of NO (>99%), and 50–800 Torr of O₂ (>99.999%) in N₂ (99.999%) diluent. Products were quantified by fitting reference spectra of the pure compounds obtained at appropriate total pressures to the observed product spectra using integrated absorption features. HFC-134a, NO, COF₂, CF₃C(O)F, and HC(O)F were identified and quantified using features over the following wavelength ranges: 800–1500, 1850–1950, 700–800 and 1850–2000, 1000–1200 and 1800–1950, and 950–1150 and 1800–1900 cm⁻¹, respectively. With the exception of HC(O)F, all reagent and reference compounds were obtained from commercial sources. The spectrum of HC(O)F was taken from the reference library at Ford¹⁸ with $\sigma(1850 \text{ cm}^{-1}) = 9.5 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$.

Two different chemical systems were used to make CF₃CFHO radicals: the self-reaction of CF₃CFHO₂ radicals and the reaction of CF₃CFHO₂ with NO. The first chemical system has been used previously^{18,28} and served as a check of our experimental technique. Reaction 6 proceeds via two channels with $k_{6a}/(k_{6a} + k_{6b}) \approx 90\%$.^{18,20,23}

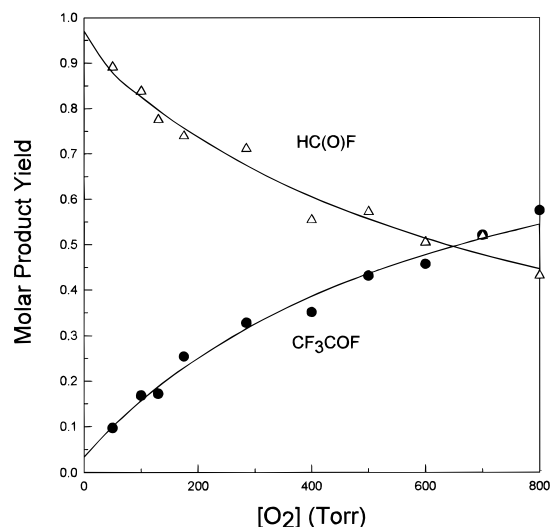
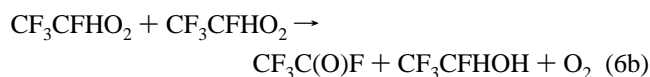
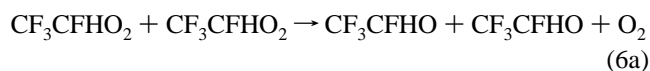
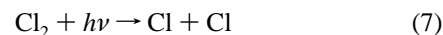


Figure 1. Yield of HC(O)F (Δ) and CF₃C(O)F (●) observed following the UV irradiation of mixtures of 15 mTorr of HFC-134a, 100 mTorr of Cl₂, and 50–800 Torr of O₂ in 800 Torr total pressure with N₂ at 295 K. The curves are fits to the data using expressions I and II; see text for details.

Experiments were performed by irradiating mixtures of 16–100 mTorr of HFC-134a, 50–100 mTorr of Cl₂, and 10–800 Torr of O₂ with N₂ diluent added as appropriate to 20–800 Torr total pressure. CF₃CFHO₂ radicals are formed by the following reactions:



In the second chemical system 7–30 mTorr of NO was added to the HFC-134a/Cl₂/O₂/N₂ mixtures described above, and reaction 3 was used to prepare the CF₃CFHO radicals.

Results

Measurement of k_4/k_5 in the Absence of NO. Following irradiation of mixtures of HFC-134a, Cl₂, and O₂, the observed products were CF₃C(O)F, HC(O)F, COF₂, CF₃O₃CF₃, CF₃OH, and HCl. The chemical reactions occurring in this system have been the subject of numerous studies, and the origin of the observed products is well understood.^{18–23} In the present study we need only consider two products to obtain k_4/k_5 : CF₃C(O)F and HC(O)F. Figure 1 shows the molar yields of CF₃C(O)F and HC(O)F (defined as moles of product formed per mole of HFC-134a consumed) observed in a series of experiments in which mixtures of 15 mTorr of HFC-134a, 100 mTorr of Cl₂, and 50–800 Torr of O₂ in 800 Torr total pressure of N₂ diluent were subject to UV irradiation. The HC(O)F yields shown in Figure 1 have been corrected for loss via Cl atom attack,¹⁸ and corrections were in the range 1–10%.

As seen from Figure 1, the yields of HC(O)F and CF₃C(O)F are sensitive to the oxygen partial pressure reflecting competition between reactions 4 and 5 for the CF₃CFHO radicals.

The simplest chemical mechanism that explains the observed dependence of the CF₃C(O)F and HC(O)F product yields on the O₂ partial pressure consists of reactions 6a, 6b, 4, and 5.¹⁸ This mechanism predicts that the CF₃C(O)F and HC(O)F yields depend on the O₂ partial pressure according to expressions I and II:

$$\text{CF}_3\text{C(O)F yield} = Y_0 + (1 - 2Y_0) \left\{ \frac{(k_4/k_5)[\text{O}_2]}{1 + (k_4/k_5)[\text{O}_2]} \right\} \quad (\text{I})$$

$$\text{HC(O)F yield} = (1 - 2Y_0) \left(1 - \frac{(k_4/k_5)[\text{O}_2]}{1 + (k_4/k_5)[\text{O}_2]} \right) \quad (\text{II})$$

where Y_0 is the $\text{CF}_3\text{C(O)F}$ yield from reaction 6, k_4 is the bimolecular rate constant for reaction 4, k_5 is the unimolecular rate constant for reaction 5, and $[\text{O}_2]$ is the partial pressure of oxygen. The solid lines shown in Figure 1 are fits of expressions I and II to the observed $\text{CF}_3\text{C(O)F}$ and HC(O)F yields. The dependence of these yields on $[\text{O}_2]$ is well described by expressions I and II. A least-squares fit to the $\text{CF}_3\text{C(O)F}$ data gives $Y_0 = 0.03 \pm 0.03$ and $k_4/k_5 = (4.6 \pm 0.3) \times 10^{-20}$ molecule $^{-1}$ cm 3 , while a fit to the HC(O)F data gives $Y_0 = 0.03 \pm 0.03$ and $k_4/k_5 = (4.3 \pm 0.3) \times 10^{-20}$ molecule $^{-1}$ cm 3 . Unless specified otherwise, quoted errors are 2 standard deviations throughout this paper. It is gratifying to note that the $\text{CF}_3\text{C(O)F}$ and HC(O)F yields are described by indistinguishable parameters.

Reaction 5 is a unimolecular decomposition whose rate should decrease as the total pressure is lowered. To examine the effect of total pressure, experiments were performed in which the HC(O)F and $\text{CF}_3\text{C(O)F}$ product yields were measured as a function of total pressure over the range 22–1100 Torr. The rate constant ratio k_5/k_4 was then calculated from individual experiments using the expression

$$\frac{k_5}{k_4} = \frac{(\text{yield of HC(O)F, corrected for Cl atom attack}) \times [\text{O}_2]}{(\text{observed CF}_3\text{C(O)F yield}) - Y_0}$$

As seen from Figure 2, the results from the present work at Ford (filled circles) and NCAR (triangles) are consistent with those reported previously by Wallington et al.¹⁸ (open circles). The solid curve in Figure 2 is a least-squares fit of the three-parameter expression proposed by Troe and co-workers:^{29,30}

$$k(M) = k_0[M]/(1 + (k_0[M]/k_\infty) \times 0.6^{\{1 + [\log(k_0[M]/k_\infty)]^2\}})^{-1}$$

to all the data in Figure 2 which gives $k_0 = 10.2 \pm 2.5$ and $k_\infty = (3.45 \pm 0.28) \times 10^{19}$ molecule cm $^{-3}$, where $k_0 = k_{5,0}/k_4$ and $k_\infty = k_{5,\infty}/k_4$. These results are in agreement with values of $k_0 = 12.3$ and $k_\infty = 3.0 \times 10^{19}$ molecule cm $^{-3}$ evaluated at 296 K from the temperature-dependent expressions given by Meller et al.²³

The ratio k_4/k_5 was also measured at temperatures of 269 and 238 K. Reference spectra for COF_2 and CF_3COF were taken under the appropriate conditions to ensure reliable spectral stripping. Since no low-temperature reference spectra of HC(O)F were available, its Q-branch was assumed to get sharper by approximately 10% between the maximum and minimum temperatures used, by analogy with HC(O)Cl and HC(O)Br .^{31,32} A correction for the reaction of Cl with HC(O)F was made, as at room temperature. Bednarek et al. very recently measured the temperature dependence of this reaction²¹ and found an activation temperature $E_a/R = 1130$ K. Since the reaction of Cl atoms with HFC-134a is expected to have a comparable activation energy ($E_a/R \approx 1700$ K), at the small extents of conversion used here the error introduced by using the room temperature rate coefficients will not be too large. At each temperature the yields of $\text{CF}_3\text{C(O)F}$ and HC(O)F were fit using expressions I and II and values of Y_0 and k_4/k_5 derived. The values of Y_0 and k_4/k_5 obtained at 269 and 238 K were 0.05 ± 0.02 and $(2.1 \pm 0.7) \times 10^{-19}$ molecule $^{-1}$ cm 3 and 0.10 ± 0.05 and $(9.5 \pm 1.4) \times 10^{-19}$, respectively. The trend of increasing

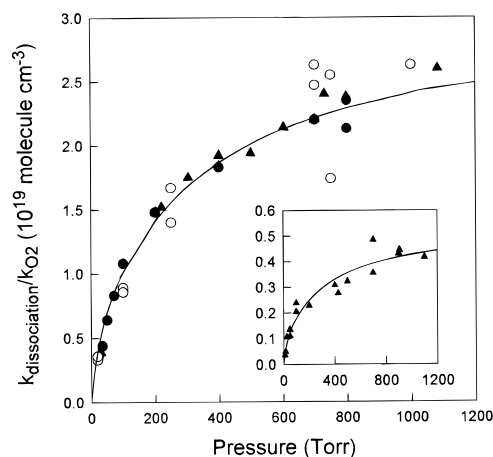


Figure 2. Plot of k_5/k_4 as a function of total pressure of N_2 diluent at 295 K derived from experiments conducted at Ford (●) and NCAR (▲). Data reported previously from our laboratory¹⁸ are shown by the open circles. The solid line is a fit of the Troe expression to the combined data set from ref 18 and this work. The insert shows data obtained at 269 K (axes have the same units as for the 295 K data); the solid curve is a fit to the Troe expression.

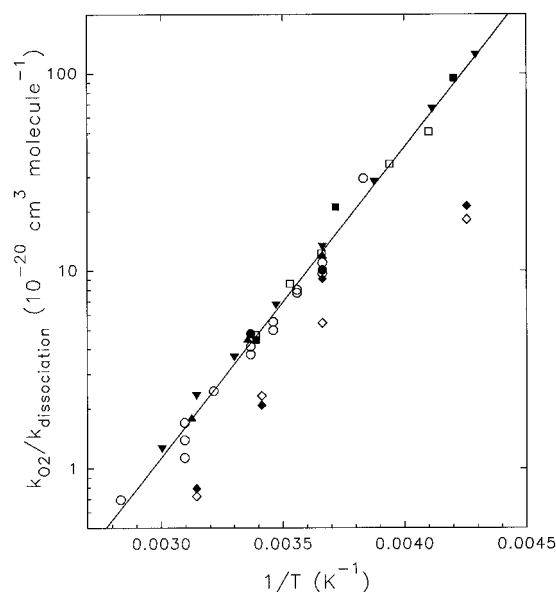


Figure 3. Plot of k_4/k_5 versus $1/T$. Data have been normalized to an effective total pressure of 760 Torr (see text for details). The source of the data, pressure at which they were measured, and scaling factors applied to convert to 760 Torr were the following: Wallington et al.,¹⁸ 1520 Torr, multiplied by a factor of 1.15 (○); Wallington et al.,¹⁸ 700 Torr, multiplied by a factor of 0.98 (●); Tuazon and Atkinson,²⁰ 740 Torr, multiplied by a factor of 0.995 (▲); Rattigan et al.,²² 760 Torr (◆, ◇ depending upon analysis method); Meller et al.,²³ 760 Torr (▼); Bednarek et al.,²¹ 760 Torr (□); this work, 760 Torr (■).

intercept Y_0 at lower temperatures is in accord with other studies,^{16,18,21} but the absolute values do differ from study to study. This may reflect the difficulties in abstracting values of Y_0 from experiments not specifically designed to measure them or may be related to the differing extents of Cl atom reaction with RO_2 versus $\text{RO}_2 + \text{RO}_2$ occurring in the different systems (see discussion by Bednarek et al.²¹).

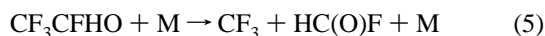
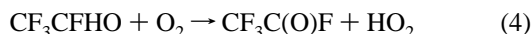
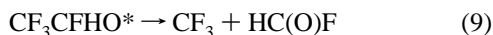
The values of k_4/k_5 obtained in all the available studies are plotted in Arrhenius form in Figure 3. As discussed above, the rate constant ratio k_4/k_5 varies with total pressure. Different research groups have employed a variety of total pressures in their studies of the effect of temperature on k_4/k_5 . To facilitate comparison of results from the different laboratories, we have normalized all results to 760 Torr total pressure using the pressure dependence of k_4/k_5 at 295 K measured above. The

scaling factors applied to the literature data are small, ranging from 0.995 to 1.15, and slight changes in the form of the pressure dependence with temperature are not expected to influence the comparison significantly. As seen from Figure 3, with the exception of the data from Rattigan et al.,²² there is excellent agreement between the various studies. The line in Figure 3 is a least-squares fit through all the data (except those of Rattigan et al.²²), giving

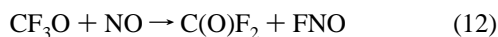
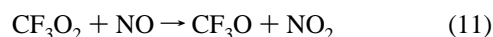
$$k_4/k_5 = 2.1_{-0.8}^{+1.4} \times 10^{-25} \exp(3625 \pm 140/T) \text{ cm}^3 \text{ molecule}^{-1}$$

The pressure dependence of k_5/k_4 was also studied at 269 K. The results are shown in the insert in Figure 2. Using a value for F_c of 0.6, the fitted values of the low- and high-pressure limits for the ratio were 1.6 ± 0.8 and $(6.1 \pm 1.4) \times 10^{18}$ molecule cm⁻³. These results can be compared to values of $k_0 = 3.5$ and $k_\infty = 7.9 \times 10^{18}$ molecule cm⁻³ evaluated at 269 K from the temperature-dependent expressions given by Meller et al.²³ Our high-pressure limit is consistent with that reported by Meller et al.,²³ while our low-pressure limit is approximately a factor of 2 lower than that of Meller et al.²³ The likely cause of this discrepancy lies in the experimental pressure range used. At the lowest pressure employed by Meller et al. (50 Torr) the reaction is still far from the low-pressure limit. In the present work the reaction was studied down to 10 Torr pressure, and hence our determination of k_0 should be more accurate.

Fate of CF₃CFHO Radicals Produced in the CF₃CFHO₂ + NO Reaction at 295 K. The atmospheric fate of CF₃CFHO radicals produced in the CF₃CFHO₂ + NO reaction was investigated by monitoring the formation of CF₃C(O)F and HC(O)F following UV irradiation of HFC-134a/Cl₂/O₂/NO/N₂ mixtures. The reactions occurring in this system are



CF₃ radicals, formed by the decomposition of CF₃CFHO, add O₂ to give CF₃O₂ radicals which react as follows:³³



Consistent with the above reactions, three carbon-containing products were observed: HC(O)F, CF₃C(O)F, and COF₂. In all cases the yields of HC(O)F and COF₂ were, within the experimental uncertainties, indistinguishable. This observation is important as it shows that reaction 5 is the only significant source of HC(O)F. Figure 4 shows typical spectra acquired before (A) and after (B) a 4 min irradiation of a mixture of 224 mTorr of HFC-134a, 366 mTorr of Cl₂, 9.6 mTorr of NO, and 713 Torr of O₂, made up to 800 Torr total pressure with N₂. Spectrum C is the result of subtracting IR features attributable

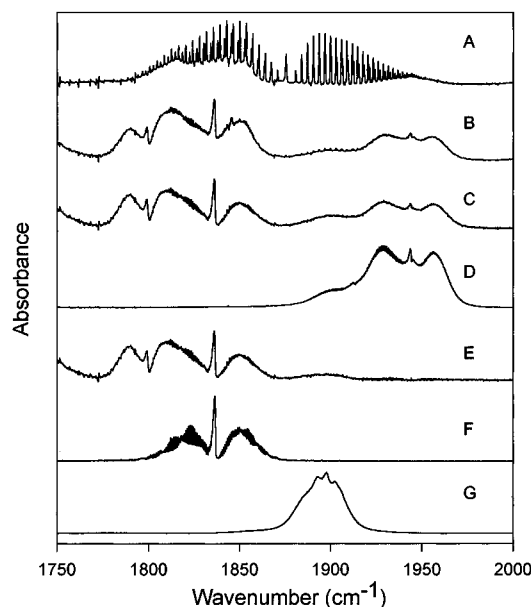


Figure 4. Spectra obtained before (A) and after (B) a 4 min irradiation of a mixture of 224 mTorr of HFC-134a, 366 mTorr of Cl₂, 9.6 mTorr of NO, and 713 Torr of O₂ in 800 Torr total pressure of N₂ diluent. Spectrum C is the result of subtracting IR features attributable to HFC-134a and NO from (B). Reference spectra of COF₂, HC(O)F, and CF₃C(O)F are shown in panels D, F, and G, respectively. Panel E is the result of stripping COF₂ features from (C).

to HFC-134a and NO from B. Reference spectra of COF₂, HC(O)F, and CF₃C(O)F are shown in spectra D, F, and G, respectively. Panel E shows the result of stripping features attributable to COF₂ from the product spectrum C. By comparison with the reference spectra, it was determined that 0.96 mTorr of COF₂, 1.03 mTorr of HC(O)F, and 0.24 mTorr of CF₃C(O)F were formed in this experiment.

The product feature at 1799 cm⁻¹ in Figure 4E is attributable to CINO formed in the reaction of Cl atoms with NO. At 800 Torr total pressure, Cl atoms react 1660 ($2.3 \times 10^{-12}/1.4 \times 10^{-15}$)^{9,34} times faster with NO than with HFC-134a. CINO reacts rapidly with Cl atoms to give Cl₂ and re-form NO, $k(\text{Cl}+\text{CINO}) = 9.6 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹,³⁵ and so CINO/NO acts as an effective scavenger for Cl atoms in the system. As a consequence of the reactivity of Cl atoms toward CINO/NO, it was necessary to use relatively high concentrations of HFC-134a (0.2–0.4 Torr). With such large HFC-134a concentrations it is not possible to quantify the small losses (1–2 mTorr) of HFC-134a. In the previous section molar yields of HC(O)F and CF₃C(O)F were obtained by comparing the observed formation of these products with the observed loss of HFC-134a. In the bulk of the experiments with NO this was not possible, and yields of HC(O)F and CF₃C(O)F were obtained relative to the combined yields of these two species. Control experiments performed in the absence of NO confirmed that the yields of HC(O)F and CF₃C(O)F were independent of the initial HFC-134a concentration over the range used in this study.

In all experiments in which NO was present, the observed product ratio [HC(O)F]/[CF₃C(O)F] was substantially larger than expected based upon the results obtained from experiments without NO. For example, in the experiment shown in Figure 4 the observed ratio [HC(O)F]/[CF₃C(O)F] was $1.03/0.24 = 4.3$. The partial pressure of oxygen used in this experiment was 713 Torr, and using the value of $k_4/k_5 = (1.5 \pm 0.1) \times 10^{-3}$ Torr⁻¹ derived in the previous section, the expected [HC(O)F]/[CF₃C(O)F] ratio is 1.1, which is substantially lower than that observed.

When compared to their counterparts formed in CF₃CFHO₂ self-reaction, CF₃CFHO radicals formed in the CF₃CFHO₂ +

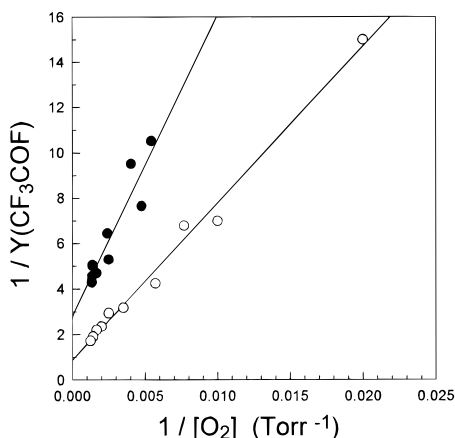


Figure 5. Plots of $1/Y(\text{CF}_3\text{C}(\text{O})\text{F})$ versus $1/[\text{O}_2]$ for experiments using HFC-134a/ $\text{Cl}_2/\text{O}_2/\text{N}_2$ mixtures with (filled symbols) and without (open symbols) added NO at 800 Torr total pressure. Data were obtained at Ford and NCAR.

NO reaction show a distinct tendency toward decomposition rather than reaction with O_2 . Such behavior is perhaps not too surprising when the energetics of the C–C bond scission (reaction 5) are considered. From Figure 3 it can be seen that the activation energy for C–C bond scission is ≈ 7 kcal mol $^{-1}$ greater than that for reaction of the alkoxy radicals with O_2 . Reactions of alkoxy radicals with O_2 typically have activation barriers of 0.5–2.0 kcal mol $^{-1}$.^{9,36} Hence, the activation barrier for C–C bond scission is expected to be ≈ 7.5 –9.0 kcal mol $^{-1}$. Reaction 3 is exothermic by 17 kcal mol $^{-1}$,²⁴ and it does not seem unreasonable to postulate that some fraction of the $\text{CF}_3\text{-CFHO}^*$ radicals formed will possess internal energy exceeding that necessary to overcome the barrier to decomposition. At this point we will interpret our data using a simple mechanism in which reaction 3 gives two types of CF_3CFHO^* radicals; those with internal excitation energies above the barrier for C–C bond scission which decompose promptly and those with energies below the barrier which are collisionally equilibrated to give thermalized CF_3CFHO radicals. Thermalized CF_3CFHO radicals can either undergo thermal decomposition or reaction with O_2 . The validity of this procedure is discussed in later sections. If α is the fraction of CF_3CFHO^* radicals which become thermalized, then

$$Y(\text{CF}_3\text{C}(\text{O})\text{F}) = \alpha \left(\frac{k_4[\text{O}_2]}{(k_4[\text{O}_2] + k_5)} \right)$$

and

$$\frac{1}{Y(\text{CF}_3\text{C}(\text{O})\text{F})} = \frac{1}{\alpha} \frac{k_5}{k_4} \frac{1}{[\text{O}_2]} + \frac{1}{\alpha} \quad (\text{III})$$

where k_4 and k_5 are rate constants for reactions 4 and 5 and $Y(\text{CF}_3\text{C}(\text{O})\text{F})$ is the molar yield of $\text{CF}_3\text{C}(\text{O})\text{F}$.

Figure 5 shows a plot of $1/Y(\text{CF}_3\text{C}(\text{O})\text{F})$ versus $1/[\text{O}_2]$ for the data obtained in this work in which reaction 3 was used as a source of CF_3CFHO radicals (filled symbols). The intercept of this plot gives $1/\alpha = 2.8 \pm 1.1$ ($\alpha = 0.36^{+0.23}_{-0.12}$) while the slope gives $(1/\alpha)(k_5/k_4) = 1330 \pm 360$ Torr and hence $k_5/k_4 = 475 \pm 227$ Torr. Quoted errors in k_5/k_4 include uncertainties in both the slope and intercept of the data in Figure 5 combined using standard error propagation analysis. Within the admittedly large experimental uncertainties, the value of k_5/k_4 determined using this approach is indistinguishable from the value of $k_5/k_4 = 667 \pm 44$ Torr obtained in the previous section. The y-axis intercept is distinctly greater than unity, which shows that a substantial fraction of the alkoxy radicals formed in reaction 3

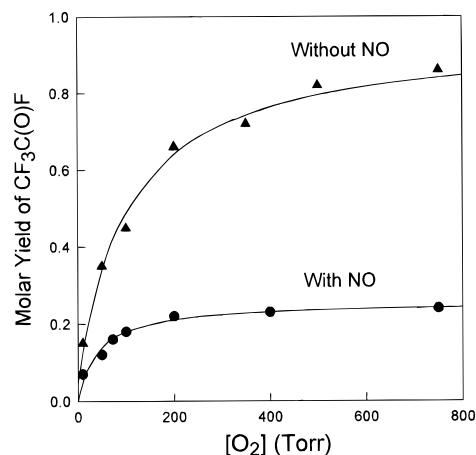


Figure 6. Yield of $\text{CF}_3\text{C}(\text{O})\text{F}$ observed during the photolysis of HFC-134a/ $\text{Cl}_2/\text{O}_2/\text{N}_2$ mixtures at 269 K and 800 Torr total pressure as a function of the O_2 partial pressure with (●) and without (▲) added NO.

decompose immediately. From the intercept in Figure 5 we conclude that at 295 K and 800 Torr total pressure collisions with the diluent gas thermalize approximately 36% of the $\text{CF}_3\text{-CFHO}^*$ radicals.

To investigate the possibility that some fraction of the $\text{CF}_3\text{-CFHO}$ radicals formed in the self-reaction of CF_3CFHO_2 have sufficient energy to decompose promptly, the data from Figure 1 were reanalyzed using expression III which recognizes the possibility of prompt CF_3CFHO^* decomposition. The result is given as the open symbols in Figure 5. In plotting the data in this fashion, we have to make a correction to the measured $\text{CF}_3\text{C}(\text{O})\text{F}$ yield. As shown in Figure 1, there is a small yield (3.5%) of $\text{CF}_3\text{C}(\text{O})\text{F}$ that is attributable to the molecular channel of reaction 6. In replotting the data from Figure 1, we have corrected the $\text{CF}_3\text{C}(\text{O})\text{F}$ yield using the expression corrected yield = (observed yield – 0.035)/0.93. As seen from Figure 5, replotting the $\text{CF}_3\text{C}(\text{O})\text{F}$ data from Figure 1 according to expression III results in a linear plot which, in contrast to the data obtained in the presence of NO, has an intercept of 0.88 ± 0.40 and a slope of 691 ± 52 Torr. Within the experimental uncertainties, the y-axis intercept is unity, demonstrating the absence of any discernible effect of internal excitation of the CF_3CFHO radical formed in reaction 6a. From the slope and intercept we can derive $k_5/k_4 = 785 \pm 362$ Torr, consistent with that derived in section 3.1.

Fate of CF_3CFHO Radicals Produced in the $\text{CF}_3\text{CFHO}_2 + \text{NO}$ Reaction over the Temperature Range 238–263 K.

Addition of NO at lower temperature led to observations similar to those at room temperature. The yield of $\text{CF}_3\text{C}(\text{O})\text{F}$ was reduced significantly in experiments conducted with NO added compared to those conducted without NO. Representative data obtained at 269 ± 2 K are shown in Figure 6. The rate of conversion of HFC-134a was much slower than at room temperature since the addition reactions of Cl with NO and NO_2 have negative temperature dependencies, while the abstraction reaction of Cl atoms with HFC-134a would be expected to slow down by about a factor of 4. Further, the formation of $\text{RO}_2\text{-NO}_2$, which is reversible at room temperature, is essentially a termination step below about 250 K, so not all RO_2 are converted into alkoxy radicals. In fact, bands were observed in the infrared spectra which could be assigned to RO_2NO_2 from a previous study of the $\text{RO}_2 + \text{NO}_2$ reaction.³⁷ Qualitatively, it was observed that at 238 K roughly the same proportion of alkoxy radicals decomposed promptly as at room temperature, while the proportion of stabilized radicals that reacted with O_2 was much higher. Thus, it was possible to add enough O_2 to scavenge greater than 90% of the stabilized radicals and measure

α directly. Experiments carried out with 800 Torr of O₂ led to values of α of 0.41 ± 0.05 at 263 K and 0.43 ± 0.05 at 243 K. At lower O₂ partial pressures the competition between O₂ reaction and decomposition for thermalized radicals was found to be consistent with that observed in the absence of NO.

If the alkoxy radicals formed above the barrier have a lifetime of the order of 1 ns, then some quenching by the bath gases N₂ or O₂ may be expected, and α may display a pressure and/or temperature dependence. Within the experimental uncertainties, there was no discernible dependence of α on temperature over the range 243–296 K. To search for an effect of total pressure on α , experiments were carried out at 263 and 243 K in the presence of NO with 110 Torr of O₂ (sufficient to scavenge 50–75% of the thermalized RO radicals), while the total pressure was varied between 120 and 1100 Torr by addition of N₂. After correcting for the known pressure dependence of k_5/k_4 there was a small dependence of the CF₃C(O)F yield on the total pressure. This observation is consistent with a small fraction (0–15%) of the nascent alkoxy radicals being just above the dissociation barrier and able to be quenched by collisions.

Discussion

Experiments without NO. The experiments carried out in the absence of NO are in good overall agreement with previous studies carried out using FTIR analysis, all of which were also carried out in the absence of NO. As seen in Figure 3, the experiments of Rattigan et al. give values for k_4/k_5 which are significantly lower than results of the FTIR experiments reported in refs 18, 20, 21, and 23. The experiments reported by Rattigan et al. were carried out using the less sensitive technique of UV absorption and only monitored one product, HC(O)F, the yield of which was calculated from the loss of Cl₂. It seems that this approach suffers from systematic uncertainties associated with not measuring CF₃C(O)F, or the loss of HFC-134a, directly.

The FTIR experiments also allow values for the apparent branching fraction k_{6a}/k_6 to be obtained. The values from the different studies all exhibit a negative temperature dependence, but the absolute values differ somewhat. Bednarek et al.²¹ pointed out that in most chamber studies Cl atoms should build up to considerable levels and that Cl + RO₂ may in fact be a major loss process for the peroxy radicals, along with CF₃O₂ + RO₂. The use of differing starting conditions, leading to differing relative contributions of the reaction between RO₂ and Cl atoms, could account for the quantitative differences between the various experimental systems.

Experiments with NO. The experiments described in the present paper are the first to be carried out in a static photolysis system in the presence of NO, and it is clear that the results differ both qualitatively and quantitatively from studies carried out in the absence of NO. The CF₃CHFO radicals formed in the reaction of NO with CF₃CHFO₂ have a much higher propensity toward decomposition than those formed in the absence of NO. The results of all the experiments can be described by a mechanism in which the reaction of RO₂ with NO leads to the formation of RO radicals with a wide spread of energies. Some of these ($\approx 60\%$) are formed above the dissociation barrier leading to the prompt dissociation of that fraction. The rapid dissociation of such molecules gives a pressure- and temperature-independent yield of CF₃ + HC(O)F. The remaining molecules are produced below the dissociation barrier and undergo stabilizing collisions. Even though these radicals will presumably also be produced with excess internal energy, the predominant effect of collisions will be to deactivate them until a thermal distribution is reached. Reactions of alkoxy radicals with O₂ typically have A factors no greater than 10^{-13} cm³ molecule⁻¹ s⁻¹; thus, collisions with O₂ are more likely to

lead to stabilization than reaction. The stabilized radicals then undergo the same competition between O₂ reaction and thermal dissociation as those produced in the absence of NO; thus, dissociation and reaction both occur from the tail of a thermalized distribution, not from a chemically activated distribution.

At present, neither the lifetime of hot or cold radicals nor the rate coefficient for the reaction of cold radicals with O₂ is known with any certainty. Depending on their exact lifetime, the alkoxy radicals produced just above the barrier may also undergo collisions. The fraction of excited molecules that are deactivated depends on the distribution of internal energies produced by the RO₂ + NO reaction, the lifetimes of molecules above the barrier, and the average energy removed per collision. RRKM calculations by Barker³⁸ suggest that some of the chemically activated alkoxy radicals may indeed live long enough to undergo several collisions and that α could actually depend on pressure. The experiments at 243 and 263 K suggest that α may increase slightly with increasing pressure, consistent with a broad thermal distribution of the excited molecules. Molecules formed a long way ($> kT$) above the barrier will dissociate before sufficient collisions occur to deactivate them, while molecules formed well below the barrier will be deactivated and react from essentially a Boltzmann distribution of internal energies.

The remaining consideration is whether the dynamics of reaction 3 is appropriate to form approximately two-thirds of the molecules above the dissociation barrier. The exothermicity of reaction 3 is estimated to be about 17 kcal mol⁻¹, and the barrier to C–C bond scission is ≈ 7.5 –8.5 kcal mol⁻¹. It is known from the study of the oxidation of simple hydrocarbons that a small fraction of RO₂ + NO reactions lead to stabilization of the RONO₂ species.²⁵ This implies that the collision complex must have a lifetime of the order of 0.1–1.0 ns, i.e., the duration of a few collisions. This is sufficient time for the excess energy to be redistributed statistically between the vibrational modes of the complex, and it is therefore plausible that most of the energy ultimately resides in the larger alkoxy fragment.

The behavior of the alkoxy radicals formed in reaction 3 can be contrasted with those formed by the photolysis of alkyl nitrites. In the latter case, much more energy is available (40 kcal mol⁻¹ at 360 nm).⁹ However, molecular beam studies show that only about one-third of the available energy goes into internal excitation of the products and that this is shared between the photofragments.^{39,40} Thus, only about 7 kcal mol⁻¹ ends up in the vibrational modes of the alkoxy radical. Since the dissociation barriers of aliphatic alkoxy radicals are typically 15 kcal mol⁻¹, these radicals are not subject to prompt dissociation and are rapidly thermalized by collisions.

In the flash photolysis study of Bednarek et al.,²¹ NO was used to react with peroxy radicals, ultimately forming OH radicals, which were detected by CW laser absorption. The experiments should thus be comparable to the present ones. Bednarek et al. analyzed their results in terms of a single distribution of RO radicals, assumed to be thermalized. Their value for k_4/k_5 is consistent with those from FTIR studies (see Figure 3). The results obtained by Bednarek et al. are sensitive not only to the value of k_4/k_5 but also to the value of the rate constant for RO + NO, since many of the cold RO radicals would be expected to react with NO. In the absence of a reliable value for the rate coefficient for that reaction, it is not possible to reanalyze the data reported by Bednarek et al.,²¹ however, ACUCHEM simulations suggest that a value of around 0.5 for α , along with the ratio k_5/k_4 measured at 40 Torr in the present study, would lead to indistinguishable traces from those presented by Bednarek et al.²¹

While the study by Bednarek et al.²¹ was most sensitive to

the ratio k_5/k_4 , absolute values for the rate constants could also be derived (although with much less certainty). Bednarek et al.²¹ quote values of $k_4 = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_5 = 1.8 \times 10^4 \text{ s}^{-1}$ in 38 Torr of O_2 at 296 K. The ratio of these values ($k_5/k_4 = 6.7 \times 10^{18} \text{ molecule cm}^{-3}$) is in excellent agreement with the results from the present work shown in Figure 2. While there have been no other direct studies of k_4 , Wu and Carr³⁶ derived a rate constant of approximately 1×10^{-16} for the analogous reaction of $\text{CFCl}_2\text{CH}_2\text{O}$ with O_2 at 298 K. It appears that reactions of fluorinated ethoxy radicals with O_2 proceed with rate constants which are 1–2 orders of magnitude slower than the $\text{C}_2\text{H}_5\text{O} + \text{O}_2$ reaction, which has a rate constant of 1×10^{-14} at 298 K.⁹

In the flash photolysis study of Maricq and Szente,⁴¹ a transient absorption due to RO radicals was tentatively identified, and its time dependence was used to derive a value for k_5 . For reasons which are unknown, the temperature dependence of k_5 derived by Maricq and Szente is inconsistent with the results from the chamber studies.

Finally, the thermochemistry of the decomposition reaction 5 can be related to other alkoxy radicals. Atkinson and Carter⁴² have developed a formulation for the expected behavior of organic alkoxy radicals in air at ambient temperature, relating the tendency to decompose to the difference in enthalpy between the O_2 reaction and the decomposition reaction. According to the latest calculations of Schneider,⁴³ the decomposition reaction is approximately thermoneutral, while the O_2 reaction is exothermic by approximately 35–40 kcal mol⁻¹. Thus, the alkoxy radical from HFC-134a would be expected to exhibit competition between O_2 reaction and decomposition at room temperature, as observed in all studies.

Implications for Atmospheric Chemistry. All previous assessments of the $\text{CF}_3\text{C}(\text{O})\text{F}$, and hence CF_3COOH , yields in the atmospheric degradation of HFC-134a are based upon the assumption that reaction 3 produces CF_3CFHO radicals which are rapidly thermalized. In contrast, our experimental data show that a substantial fraction of the CF_3CFHO radicals formed in reaction 3 undergo prompt decomposition and are not thermalized. The fraction of CF_3CFHO radicals which are thermalized in the atmosphere, α , is 0.40 ± 0.15 . Current assessments of CF_3COOH formation are too high by a factor of $1/\alpha = 1.8$ –4.0. Kanakidou et al.⁴⁴ have recently reported the results of a three-dimensional global modeling of HFC-134a chemistry and find the CF_3COOH yield from the atmospheric oxidation of HFC-134a to be 29–36%. Incorporation of the results from the present work revises this range downward to 7–20%. The current consensus in the scientific community is that it is unlikely that formation of CF_3COOH is a significant environmental problem.^{18,44} The results from the present work provide further justification for this view.

To the best of our knowledge, this is the first instance where it has been demonstrated that chemical activation of an alkoxy radical plays an important role in its atmospheric fate. The atmospheric oxidation of all organic compounds proceeds via the formation of peroxy radicals. Chemical activation of alkoxy radicals formed in reactions of peroxy radicals with NO may be an important consideration in the degradation mechanism of other organic compounds where two competing channels exist for the alkoxy radical (e.g., for alkenes).

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