Kinetic and Mechanistic Studies for Reactions of $CF_3CH_2CHF_2$ (HFC-245fa) Initiated by H-Atom Abstraction Using Atomic Chlorine

Junyi Chen,[†] **Valerie Young,**[‡] **and Hiromi Niki**[§]

Centre for Atmospheric Chemistry and Department of Chemistry, York University, 4700 Keele Street, North York, Ontario, Canada M3J 1P3

Hillel Magid*

Buffalo Research Laboratory, AlliedSignal, Inc., 20 Peabody Street, Buffalo, New York 14210

Received: November 8, 1996; In Final Form: January 28, 1997[⊗]

Kinetics and mechanisms of Cl atom initiated oxidation reactions of $CF_3CH_2CHF_2$ (HFC-245fa) were investigated by long-path FTIR spectroscopic methods at 297 ± 2 K. The Cl atoms initiated the reaction mainly via H-atom abstraction from the terminal carbon ($\geq$95%) to produce a $CF_3CH_2CF_2$ radical. Subsequent reactions in 700 Torr of air produced CF_3CHO and CF_2O as the primary products. Secondary reactions of CF_3CHO with Cl atoms led to the formation of $CF_3C(O)OH$, CF_3OH, CO_2, and CF_3OOOCF_3 in the experimental system. However, under atmospheric conditions, CF_3CHO would undergo a series of rapid oxidation and decomposition reactions ultimately leading to HF and CO_2, and no long-lived organic decomposition products would be produced.

Introduction

Destruction of stratospheric ozone by chlorofluorocarbons (CFCs)[1] has led to an international agreement to replace CFCs with atmospherically acceptable alternatives. Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) have been developed as CFC alternatives because they can, to a large extent, be removed by tropospheric OH radicals. Thus, the alternatives have shorter lifetimes in the troposphere as well as lower ozone depletion potential (ODP) and global warming potential (GWP) values than those of CFCs. However, the tropospheric degradation of the alternatives, after initial hydrogen abstraction by OH radicals, will lead to new halogen-containing products, the atmospheric behavior of which may not be well-known. Thus, to assess the atmospheric acceptability of the alternatives, we need to understand their degradation mechanisms and product distributions.

There have been many studies of the atmospheric reaction mechanisms of HCFCs and HFCs after initial abstraction of hydrogen atoms.[2−5] However, most of the studies were concerned with the degradation of HCFCs and HFCs containing one or two carbons. There are few experimental data available for larger HCFCs and HFCs. Presented here is the long-path FTIR spectroscopic kinetic and mechanistic study of the Cl atom initiated oxidation of $CF_3CH_2CHF_2$ (HFC-245fa) at 297 ± 2K in 700 Torr of He, N_2, and air diluents. This molecule is being considered as a potential non-ozone-depleting replacement for CH_3CCl_2F (HCFC-141b) as a blowing agent for foam applications.[6a−c]

Experimental Section

The details of the experimental facility and procedures have been described in our previous publications.[7] In brief, a Pyrex glass cylinder (5 cm diameter, 50 cm long, 100 cm path length) surrounded by 6 UV fluorescent lamps (GE F30T8/BLB; 300 nm < λ < 400 nm) was used as the IR cell and photochemical reactor for experiments carried out in He and N_2; another Pyrex glass cylinder (30 cm diameter, 2 m long, 92 m path length) surrounded by 26 UV fluorescent lamps (GE F40T12/BLB; 300 nm < λ < 400 nm) was used as the IR cell and photochemical reactor for experiments carried out in the presence of O_2. Spectra were collected over the frequency range 500−4000 cm^{-1} in 70 s at 0.125 cm^{-1} resolution by co-adding 16 scans, using a Mattson FTIR spectrometer (Galaxy 4326C) with a KBr beamsplitter and a liquid N_2 cooled Hg−Cd−Te detector.

Cl atoms were generated by the UV irradiation (300 nm < λ < 400 nm) of Cl_2 (Aldrich, 99+%). N_2 (O_2 < 3 ppm, total hydrocarbon < 1 ppm), He (O_2 < 0.5 ppm) and synthetic air (total hydrocarbon < 0.1 ppm) were obtained from Liquid Carbonic Inc. Reactant ($CF_3CH_2CHF_2$, 99%) was supplied by the Buffalo Research Laboratory of AlliedSignal. No IR peaks of impurities were observed in the reactant. CF_3CHO was synthesized by hydrolyzing $CF_3CH(OH)OCH_3$ (PCR, 99%) in a mixture of H_2SO_4 (Aldrich, 95.5%)/P_2O_5 (Aldrich, 97%). $CF_3C(O)OH$ (99.9%) and $CF_3CH_2CClF_2$ (97%) were obtained from PCR and the Buffalo Research Laboratory of AlliedSignal, respectively.

Reactant and product species reported in this work, unless otherwise specified, were identified and quantified by reference to quantitative IR spectra of pure compounds previously collected in our laboratory. The concentration uncertainties of these reference spectra are estimated to be less than 5%, except for $CF_3C(O)OH$. Because of the formation of the dimer, $(CF_3C(O)OH)_2$, and because the necessity of separating the dimer adds uncertainty to the reference spectrum, the concentration uncertainty of the reference spectrum of $CF_3C(O)OH$ is estimated to be 10%.

Results and Discussion

1. Kinetic Study. The rate constant for the reaction of Cl atom with $CF_3CH_2CHF_2$ was determined from the decay rates

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* Corresponding author. E-mail: hillel.magid@alliedsignal.com.

[†] Present address: NU-Pharm Inc, 380 Elgin Mills East, Richmond Hill, Ontario, L4C 5H2, Canada.

[‡] Present address: Department of Chemical Engineering, Ohio University, 179 Stocker Center, Athens, OH 45701.

[§] Deceased.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

S1089-5639(96)03735-8 CCC: $14.00 © 1997 American Chemical Society

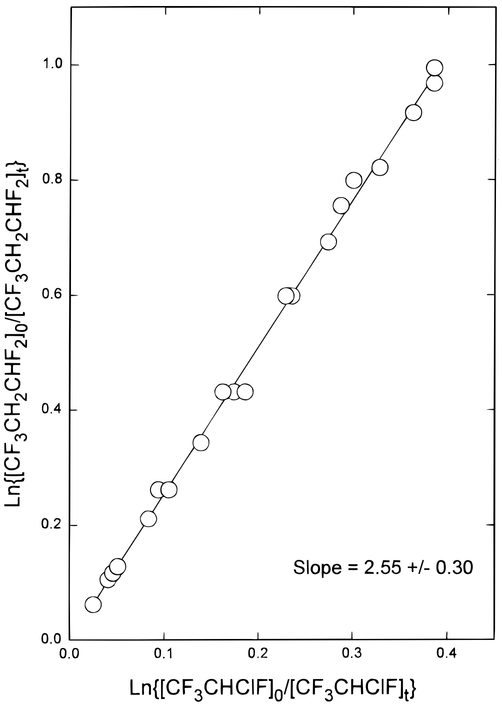

Figure 1. Plot of ln{$[CF_3CH_2CHF_2]_0/[CF_3CH_2CHF_2]_t$} against ln{$[CF_3CHClF]_0/[CF_3CHClF]_t$}, in which the slope gives the rate constant ratio $k(CF_3CH_2CHF_2+Cl)/k(CF_3CHClF+Cl) = 2.55 \pm 0.30$.

of $CF_3CH_2CHF_2$ and a reference compound, CF_3CHClF (HCFC-124), in the UV photolysis of mixtures containing these two compounds and Cl_2 at 297 ± K, and using the integrated relative rate equation:

$$\frac{\mathrm{Ln}\{[CF_3CH_2CHF_2]_0/[CF_3CH_2CHF_2]_t\}}{\mathrm{Ln}\{[CF_3CHClF]_0/[CF_3CHClF]_t\}} = \frac{k[CF_3CH_2CHF_2 + Cl]}{k[CF_3CHClF + Cl]}$$

In the presence of O_2, CF_3O radicals may be produced in the reaction system as an important intermediate product. These CF_3O radicals may initiate reactions in competition with the Cl atoms and confound the rate constant measurement. To avoid the possible side reactions of $CF_3CH_2CHF_2$ and CF_3CHClF with CF_3O radicals,[8] the experiments were carried out in 700 Torr of N_2, using reactant mixtures containing $CF_3CH_2CHF_2$ (0.4−0.5 Torr), CF_3CHClF (0.4−0.5 Torr) and Cl_2 (2−3 Torr). A relative rate constant, $k[CF_3CH_2CHF_2 + Cl]/k[CF_3CHClF + Cl]$, was derived to be 2.55 ± 0.30 (2σ) by linear regression of Ln{$[CF_3CH_2CHF_2]_0/[CF_3CH_2CHF_2]_t$} against Ln{$[CF_3CHClF]_0/[CF_3CHClF]_t$}, as presented in Figure 1. Placed on an absolute basis, the rate constant is $k[CF_3CH_2CHF_2 + Cl] = (6.9 \pm 0.8) \times 10^{-15}$ (2σ) cm^3 $molecule^{-1}$ s^{-1}, using $k[CF_3CHClF + Cl] = 2.7 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} as the reference.[9] The uncertainty reported above refers only to experimental error.

2. Reactions in He. The Cl atom abstracts an H atom from $CF_3CH_2CHF_2$, leaving a radical site. In the absence of O_2, this radical site will be chlorinated by reaction with Cl_2. To establish the relative importance of central vs terminal H-atom abstraction for Cl + $CF_3CH_2CHF_2$ reactions, spectra were collected after UV irradiation of mixtures containing $CF_3CH_2CHF_2$ (0.4−0.7 Torr) and Cl_2 (3−4 Torr) diluted in He to 700 Torr. The absorbance spectra recorded in a typical run are illustrated in Figure 2. Parts A and B of Figure 2 correspond to the spectra recorded before and after 25 s photolysis of a mixture initially containing $CF_3CH_2CHF_2$ (0.5 Torr) and Cl_2 (3.4 Torr) in 700 Torr of He; Figure 2C is the difference spectrum [2B −2A], with the absorbance scale expanded by a factor of 3 for clarity. The identified products after irradiation of the mixtures were $CF_3CH_2CClF_2$ and HCl. The observed yield of $CF_3CH_2CClF_2$ is plotted as a function of the reactant conversion in Figure 3. The slope gives the percentage yield of $CF_3CH_2CClF_2$ to be 95%. The observation of $CF_3CH_2CClF_2$ as the predominant product is consistent with the occurrence of reaction 1a, H-atom

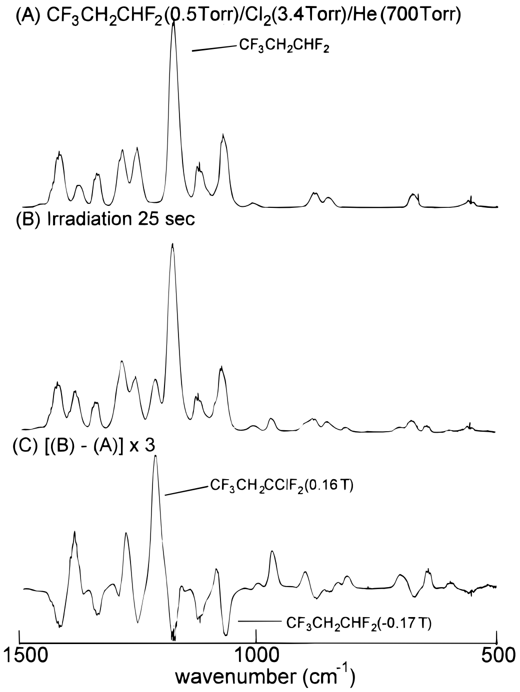

Figure 2. Spectral data in the frequency region 500−1500 cm^{-1} obtained from the photolysis of a mixture containing $CF_3CH_2CHF_2$ (0.5 Torr) and Cl_2 (3.4 Torr) in 700 Torr of He: (A) before irradiation; (B) after 25 s irradiation; (C) difference spectrum = [(B) − (A)] × 3.

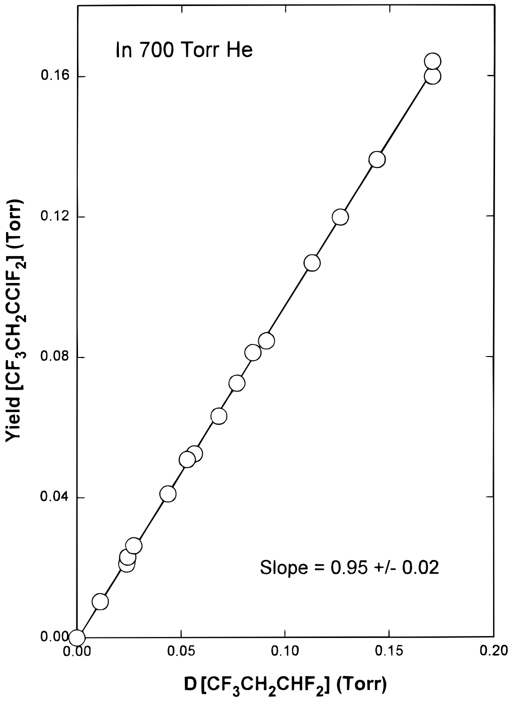

Figure 3. Plot of the $CF_3CH_2CClF_2$ yield against the $CF_3CH_2CHF_2$ conversion observed in 700 Torr of He. The slope gives the observed yield of $CF_3CH_2CClF_2$ to be 95% based on the conversion of $CF_3CH_2CHF_2$.

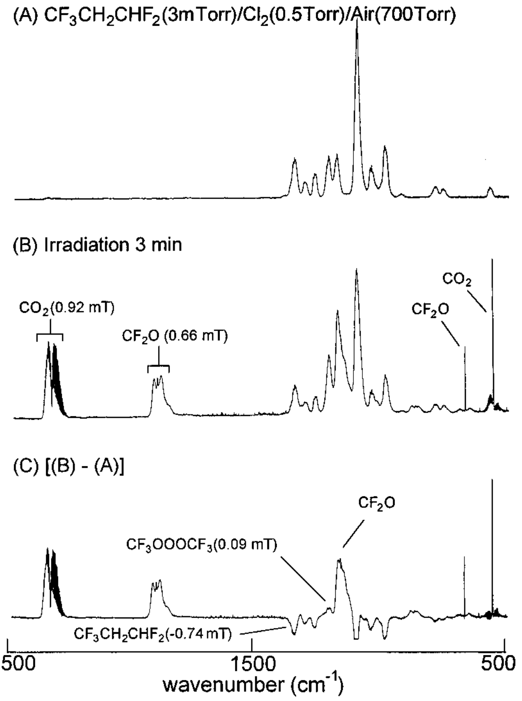

Figure 4. Spectral data in the frequency region 500−2500 cm^{-1} obtained from the photolysis of a mixture containing $CF_3CH_2CHF_2$ (3 mTorr) and Cl_2 (0.5 Torr) in 700 Torr of air: (A) before irradiation; (B) after 3 min irradiation; (C) difference spectrum = [(B) − (A)].

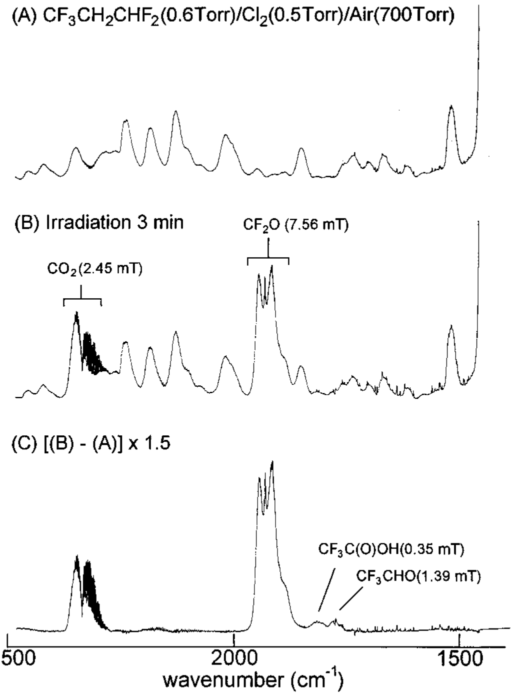

Figure 5. Spectral data in the frequency region 1500−2500 cm^{-1} obtained from the photolysis of a mixture containing $CF_3CH_2CHF_2$ (0.6 Torr) and Cl_2 (0.5 Torr) in 700 Torr of air: (A) before irradiation; (B) after 3 min irradiation; (C) difference spectrum = [(B) − (A)] × 1.5.

abstraction from the terminal carbon producing $CF_3CH_2CF_2$ radical, followed by reaction with Cl_2 molecule, reaction 2.

$$CF_3CH_2CHF_2 + Cl \rightarrow CF_3CH_2CF_2 + HCl \quad (1a)$$

$$CF_3CH_2CHF_2 + Cl \rightarrow CF_3CHCHF_2 + HCl \quad (1b)$$

$$CF_3CH_2CF_2 + Cl_2 \rightarrow CF_3CH_2CClF_2 + Cl \quad (2)$$

It is to be noted that $CF_3CHClCHF_2$ would be formed by a central H-atom abstraction producing CF_3CHCHF_2 radical, reaction 1b, followed by reaction 3.

$$CF_3CHCHF_2 + Cl_2 \rightarrow CF_3CHClCHF_2 + Cl \quad (3)$$

After subtracting $CF_3CH_2CClF_2$ and HCl from Figure 2C, the residual spectrum showed IR peaks at 1281, 1217, and 1182 cm^{-1}, which are in the C−F stretching frequency range. If all the residual spectra are assigned to $CF_3CHClCHF_2$, a lower limit for the yield of $CF_3CH_2CClF_2$ and a higher limit for the yield of $CF_3CHClCHF_2$ are estimated to be 95% and 5%, respectively. In other words, at least 95% of the $CF_3CH_2CHF_2$ + Cl reactions proceed via terminal H-atom abstraction. Reactions via central H-atom abstraction, if they occur, account for no more than 5% of the total.

3. Reactions in Air. To determine the subsequent reaction pathways for $CF_3CH_2CF_2$ radical in the presence of O_2, experiments were carried out in 700 Torr of air. Parts A and B of Figure 4 correspond to the spectra recorded before and after 3 min irradiation of a mixture initially containing $CF_3CH_2CHF_2$ (3 mTorr) and Cl_2 (500 mTorr) in 700 Torr of air; Figure 4C is the difference spectrum [4B − 4A]. As shown in Figure 4, the identified carbon-containing products were CO_2, CF_2O, and CF_3OOOCF_3 (1290, 1252, and 1169 cm^{-1}).[10] As reported by Wallington et al.,[10] CF_3OOOCF_3 may be formed from the reaction of CF_3O and CF_3OO radicals. However, CF_3OOOCF_3 is unlikely to form in the troposphere since the concentrations of the CF_3O and CF_3OO would be very low. Under the experimental conditions, no H-containing products, except inorganic HCl and HF, were identified. Because of the slow reaction rate of $CF_3CH_2CHF_2$ + Cl ($k = 6.9 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1}), it is quite possible that some active H-containing intermediate products were formed in the system and then scavenged by the faster secondary reactions with Cl atoms. For example, CF_3CHO is a possible product and its reaction rate with Cl atoms ($k = 2.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1})[11] is more than 400 times faster than that of $CF_3CH_2CHF_2$ with Cl.

To limit the possible secondary reactions of the intermediate products with Cl atoms, the experiments were also carried out with high reactant concentrations and at low reactant conversions. That is, the initial concentrations of $CF_3CH_2CHF_2$ and Cl_2 were both 500−1000 mTorr, and the conversions of $CF_3CH_2CHF_2$ were a few percent. Parts A and B of Figure 5 correspond to the spectra recorded before and after 3 min irradiation of a mixture initially containing $CF_3CH_2CHF_2$ (600 mTorr) and Cl_2 (500 mTorr) in 700 Torr of air; Figure 5C is the difference spectrum [5B − 5A]. As shown in Figure 5, no $CF_3CH_2CClF_2$ was identified above the detection limit (0.02 mTorr). Thus, in 700 Torr of air, the Cl_2 reaction with the initially formed $CF_3CH_2CF_2$ radicals, reaction 2, was negligible, while O_2 addition, reaction 4, is the predominant channel.

$$CF_3CH_2CF_2 + O_2\,(+M) \rightarrow CF_3CH_2CF_2OO\,(+M) \quad (4)$$

The identified carbon-containing products were CF_2O (1944, 1243, and 774 cm^{-1}), CO_2, CF_3CHO (2864, 1787, and 706 cm^{-1}),[12,13] $CF_3C(O)OH$ (3584 and 1827 cm^{-1}),[14] CF_3OH (3664 cm^{-1}),[8,15] and a trace amount of CO. The product yields are plotted as a function of the conversion of $CF_3CH_2CHF_2$ in Figure 6. Since the initial concentration of $CF_3CH_2CHF_2$ was very high, all the IR peaks of fundamentals were saturated, and those of overtones and combinations were too weak to be sensitive enough to a few percent change of the reactant. Thus, the reactant conversions in Figure 6 were estimated from the observed yields of total products. The concentrations of

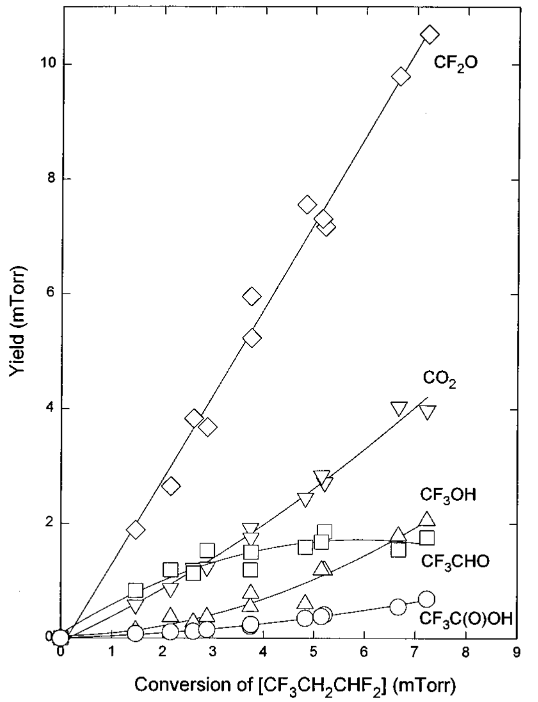

Figure 6. Plots of product yields against conversion of $CF_3CH_2CHF_2$. Data were obtained from experiments carried out by the photolysis of mixtures initially containing $CF_3CH_2CHF_2$ and Cl_2 (500−1000 mTorr) in 700 Torr of air.

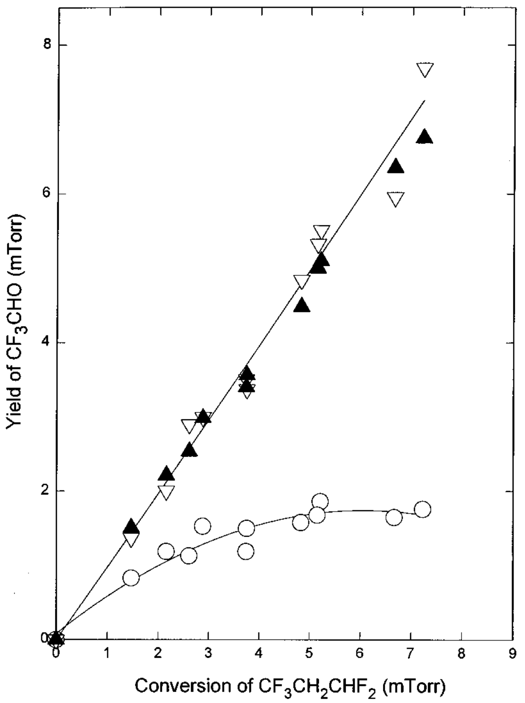

Figure 7. Yields of CF_3CHO against conversion of $CF_3CH_2CHF_2$. Symbols ○, ▽, and ▲ express yields of CF_3CHO observed from experiments, corrected for the secondary reaction with Cl atoms and derived from the sum of observed percentage yields of CF_3CHO, CO_2, and $CF_3C(O)OH$, respectively.

CF_3OH were calculated from the IR absorbance σ (3664 cm^{-1}) $= 2.4 \times 10^{-3}$ $mTorr^{-1}$ M^{-1}.[8]

A small IR peak was observed at 3628 cm^{-1}, which could be the O−H stretching of a ROOH type molecule produced by an $ROO + HOO \rightarrow ROOH + O_2$ reaction. By comparison with the IR absorbance of the O−H stretching of CH_3OOH and C_2H_5OOH, acquired previously in our laboratory, the yield of this ROOH type product is estimated to be less than 2%.

As shown in Figure 6, the yield of observed CF_3CHO (55−25%) decreased with increasing $CF_3CH_2CHF_2$ conversion, indicating that loss of CF_3CHO to secondary reactions is important. The main secondary reaction of CF_3CHO was expected to be with Cl atoms, so the observed yield of CF_3CHO could be corrected by the method suggested by Atkinson et al.,[16] using the rate constants $k(CF_3CH_2CHF_2 + Cl)$ and $k(CF_3CHO + Cl)$ noted above. The yields of CF_3CHO before and after correcting for the secondary reaction with Cl atoms are plotted against the conversion of $CF_3CH_2CHF_2$ in Figure 7. The plot after correction is linear, with a slope of 0.97 ± 0.05, which strongly suggests that CF_3CHO was a main primary product and that degradation of $CF_3CH_2CF_2OO$ radicals produced a stoichometric amount of CF_3CHO. This result is consistent with reactions 5−9 following reaction 4.

$$2CF_3CH_2CF_2OO \rightarrow 2CF_3CH_2CF_2O + O_2 \qquad (5)$$

$$CF_3CH_2CF_2O\ (+M) \rightarrow CF_3CH_2 + CF_2O\ (+M) \qquad (6)$$

$$CF_3CH_2 + O_2\ (+M) \rightarrow CF_3CH_2OO\ (+M) \qquad (7)$$

$$2CF_3CH_2OO \rightarrow 2CF_3CH_2O + O_2 \qquad (8)$$

$$CF_3CH_2O + O_2 \rightarrow CF_3CHO + HOO \qquad (9)$$

The self-reactions of CF_3CH_2OO radicals may proceed via two possible channels, reactions 8 and 10. The absence of IR peaks assignable to CF_3CH_2OH suggests that reaction 10 is of minor importance and reaction 8 is the main degradation channel for CF_3CH_2OO radicals.

$$2CF_3CH_2OO \rightarrow CF_3CH_2OH + CF_3CHO + O_2 \qquad (10)$$

Unimolecular dissociation producing CF_3 radicals and CH_2O was expected to be a degradation channel for CF_3CH_2O radicals. However, no CH_2O was observed; our detection limit for CH_2O is about 0.01 mTorr. The unimolecular dissociation, reaction 11, was thus negligible.

$$CF_3CH_2O\ (+M) \rightarrow CF_3 + CH_2O\ (+M) \qquad (11)$$

Atkinson and Carter summarized the thermodynamic and kinetic properties of a series of alkoxy radicals and introduced an empirical method for assessing the relative importance of reactions 9 and 11 under atmospheric conditions.[17] This method utilizes the differences in the enthalpies of reactions, $\Delta(\Delta H) = (\Delta H_{11} - \Delta H_9)$, where ΔH_{11} and ΔH_9 refer to enthalpies of reactions 11 and 9, respectively. For $\Delta(\Delta H) < 40$ kcal/mol, the unimolecular dissociation (11) dominates over O_2 reaction, reaction 9, while the opposite is true for $\Delta(\Delta H) > 43$ kcal/mol, at room temperature and atmospheric pressure. $\Delta(\Delta H)$ is calculated to be 47.2 kcal/mol for CF_3CH_2O radical. In the calculation, the value for the enthalpy of formation of CF_3CHO was estimated to be −187.5 kcal/mol by using the empirical AM1 method,[18] while those for other products of reactions 9 and 11 were found from the literature.[19] This estimation supports that the O_2 reaction with the CF_3CH_2O radicals producing CF_3CHO and HOO radicals, reaction 9, dominates over the unimolecular dissociation, reaction 11, and is consistent with the previous report by Nielsen et al. that >99.3% of the CF_3CH_2O radicals react with O_2 to produce CF_3CHO.[20] Another possible decomposition channel for CF_3CH_2O radical is elimination of a hydrogen atom, reaction 12.[21] Because the HOO radical is about 50 kcal/mol more stable than the H atom,[19] reaction 9 must be thermodynamically favored over reaction

12. Thus, CF_3CH_2O radical mainly degrades via reaction 9 under atmospheric conditions.

$$CF_3CH_2O\ (+M) \rightarrow CF_3CHO + H\ (+M) \tag{12}$$

Based on the above-discussed reaction mechanism, the yield of CF_2O should be equal to that of CF_3CHO. Actually, the observed percentage yield of CF_2O was about 30−60% higher than that of CF_3CHO and increased with the reactant conversion. Thus, part of the observed CF_2O was probably produced by reactions subsequent to the CF_3CHO + Cl reaction. The reaction of CF_3CHO with Cl has been studied by several groups[11,22] and is expected to produce CF_3CO radicals, reaction 13.

$$CF_3CHO + Cl \rightarrow CF_3CO + HCl \tag{13}$$

The unimolecular dissociation of CF_3CO radicals leading to CO and CF_3 radicals was confirmed to be a minor channel by the result that less than 2% yield of CO was identified under the experimental conditions. Wallington et al.[22] studied the degradation mechanism of CF_3CO radicals in the presence of 27 mTorr of O_2 and reported that 84% of the CF_3CO radicals reacted with O_2 forming $CF_3C(O)OO$ radicals, reaction 14, and 16% decomposed to give CO and CF_3 radicals. Because of the presence of 140 Torr of O_2, reaction 14 is the most likely fate of CF_3CO radicals at our experimental conditions, and thus at atmospheric conditions.

$$CF_3CO + O_2\ (+M) \rightarrow CF_3C(O)OO + (+M) \tag{14}$$

The identified product yields of CO_2 (40−60%), $CF_3C(O)OH$ (5−8%), CF_3OH (10−30%) changed with the reactant conversion. They and part of the CF_2O were formed via a series of reactions which follow reaction 14.

$$2CF_3C(O)OO \rightarrow 2CF_3C(O)O + O_2 \tag{15}$$

$$CF_3C(O)O\ (+M) \rightarrow CF_3 + CO_2\ (+M) \tag{16}$$

$$CF_3C(O)O + HOO \rightarrow CF_3C(O)OH + O_2 \tag{17}$$

$$CF_3 + O_2\ (+M) \rightarrow CF_3OO\ (+M) \tag{18}$$

$$2CF_3OO \rightarrow 2CF_3O + O_2 \tag{19}$$

$$CF_3O + HOO \rightarrow CF_3OH + O_2 \tag{20}$$

$$CF_3O + RH \rightarrow CF_3OH + R \tag{21}$$

$$CF_3OH + \text{wall} \rightarrow CF_2O + HF + \text{wall} \tag{22}$$

Scollard et al. studied the degradation mechanisms of a series $CX_3C(O)O$ radicals (X = Cl and F) and reported that the radicals mainly dissociate to give CO_2 and CX_3 radicals.[11] In the present experiments, the observed yield of CO_2 was about 8 times larger than that of $CF_3C(O)OH$. Thus, the unimolecular dissociation of $CF_3C(O)O$ radicals leading to CO_2 and CF_3 radicals, reaction 16, dominates over the reaction with HOO radicals, reaction 17. The sum of observed percentage yields of CF_3CHO, CO_2, and $CF_3C(O)OH$ is very similar to the yield of CF_3CHO after correcting for the secondary reaction with Cl atoms, as shown in Figure 7. This result is consistent with the above reaction mechanism. Since the lifetime for the unimolecular decomposition for $CF_3C(O)O$ is 8.3×10^{-6} s as determined by Wallington et al. at 760 Torr,[23] under atmospheric conditions, the rate for reaction 17 forming $CF_3C(O)OH$ (trifluoroacetic acid) would be negligible compared to reaction 16. Using a global averaged value for HO_2 concentration of 10^9 molecule cm^{-3} [24] and assuming that the rate constant for reaction 17 was gas kinetic, the rate of unimolecular decomposition, reaction 16, would be at 5 orders of magnitude faster than the formation of trifluoroacetic acid, reaction 17. Therefore, the trifluoroacetic acid formed in these experiments resulted from reactions subsequent to the secondary reaction of Cl atoms with CF_3CHO, reaction 13, and would not be an expected product from the atmospheric degradation of 1,1,3,3-pentafluoropropane, HFC-245fa.

In this study, the CF_3CH_2O radicals were produced by the self-reaction of two CF_3CH_2OO radicals, reaction 15, which is a nearly thermoneutral process. Recent work by Wallington et. al. indicated that when a similar alkoxy radical, CF_3CFHO, was generated by a more exothermic reaction between CF_3CFHOO and NO (reaction 23), a "hot" CF_3CFHO radical was produced, and compared to the thermalized radical (reaction 27), the extent of unimolecular decomposition (reaction 24) was increased over the competing hydrogen abstraction reaction (reaction 25).[25]

$$CF_3CHFOO + NO \rightarrow CF_3CHFO^* + NO_2 \tag{23}$$

$$CF_3CHFO^* + (M) \rightarrow CF_3 + CH(O)F + (M) \tag{24}$$

$$CF_3CHFO + HOO \rightarrow CF_3C(O)F + O_2 \tag{25}$$

$$CF_3CHFO^*\ (+M) \rightarrow CF_3CHFO + (M) \tag{26}$$

$$CF_3CHFO\ (+M) \rightarrow CF_3 + CH(O)F + (M) \tag{27}$$

Bevilacqua et al.[26] and Pultau et al.[27] have also studied the reaction of NO with fluoroperoxy radicals. Comparing the reactivity of the fluoroalkoxy radicals produced by the reaction of NO with the precursor fluoroperoxy radicals, the results indicated that the CF_3CHFO radical did undergo further carbon−carbon bond cleavage which is not inconsistent with the results of Wallington et al.,[25] whereas the CF_3CH_2O did not undergo further decomposition. Therefore, based on results from these two studies, it is unlikely that there would have been any significant unimolecular decomposition of CF_3CH_2O, reaction 11, even if the CF_3CH_2O radicals were produced in this study by the reaction of NO with the peroxy radical, CF_3CH_2OO.

Conclusion

Our investigation of Cl atom initiated oxidation of $CF_3CH_2CHF_2$ (HFC-245fa) in 700 Torr of air suggests that terminal H abstraction producing $CF_3CH_2CF_2$ radicals will be the predominant channel during the tropospheric oxidation of $CF_3CH_2CHF_2$ by OH radicals. At atmospheric conditions, self-reactions (reactions 5, 8, 15, and 19) of the peroxy radicals produced via the subsequent reactions of $CF_3CH_2CF_2$ radicals are negligible. By analogy to the behavior of other peroxy radicals,[9] it is expected that the rate constants of NO with the peroxy radicals involved in this study are larger than 5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. With an estimated background tropospheric NO concentration of about 1×10^9 molecule cm^{-3},[28,29] the lifetimes of these peroxy radicals with respect to NO reactions are estimated to be 2−3 min. Thus, at atmospheric conditions, reactions with NO producing the corresponding alkoxy radicals are likely to be the main degradation channels for these peroxy radicals. The present study has shown that the fate of $CF_3CH_2CF_2O$ radicals is unimolecular dissociation leading to CF_2O and CF_3CH_2 radicals. The observation of CF_3CHO as a main primary product and the absence of CH_2O suggest that the atmospheric fate of CF_3CH_2O radicals is to react with O_2 producing CF_3-CHO and HOO radicals, while the unimolecular dissociation leading to CF_3 and CH_2O is negligible. The atmospheric degradation of CF_3CHO will produce CO_2 and CF_3 radicals as the main products.

The atmospheric fate of CF_3 radicals has been well studied.[5,30] The main terminating processes will be reaction with NO and CH_4 which produce, respectively, CF_2O and CF_3OH.[8,31,32] The most probable fate for both CF_2O and CF_3OH would be uptake by cloud, rain, or ocean water to yield CO_2 and HF.[33] Consequently, no long-term decomposition products such as trifluoroacetic acid (TFA) are expected to result from the atmospheric degradation of $CF_3CH_2CHF_2$(HFC-245fa).

Acknowledgment. We thank AlliedSignal and British Gas/Consumers Gas for financial support. The late H. Niki was the holder of the British Gas/Consumers Gas/AES Industrial Research Chair in Atmospheric Chemistry. We also thank Dr. M. Van Der Puy from the Buffalo Research Laboratory of AlliedSignal for synthesizing $CF_3CH_2CC1F_2$, and Drs. O. Melo and G. Harris for critical review of the manuscript.

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