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Atmospheric Chemistry of $CF_3CF{=}CF_2$: Kinetics and Mechanism of Its Reactions with OH Radicals, Cl Atoms, and Ozone

M. Mashino, Y. Ninomiya, and M. Kawasaki

Department of Molecular Engineering, Kyoto University, Kyoto 606-8501, Japan

T. J. Wallington* and M. D. Hurley

Ford Research Laboratory, SRL-3083, Ford Motor Company, P.O. Box 2053, Dearborn, Michigan 48121-2053

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Smog chamber/FTIR techniques were used to study the OH radical, the Cl atom, and ozone initiated oxidation of $CF_3CF{=}CF_2$ in 700 Torr of air at 296 K. Relative rate methods were used to measure $k(OH + CF_3CF{=}CF_2) = (2.4 \pm 0.3) \times 10^{-12}$ and $k(Cl + CF_3CF{=}CF_2) = (2.7 \pm 0.3) \times 10^{-11}$; absolute techniques were used to derive an upper limit of $k(O_3 + CF_3CF{=}CF_2) < 3 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}. OH radical and Cl atom-initiated atmospheric oxidation of $CF_3CF{=}CF_2$ gives COF_2 and $CF_3C(O)F$ in molar yields of 100%. The atmospheric lifetime of $CF_3CF{=}CF_2$ is approximately 9 days with degradation proceeding via reaction with OH radicals to give trifluoroacetic acid in a molar yield of 100%. Results are discussed with respect to previous measurements of $k(OH + CF_3CF{=}CF_2)$ and $k(O_3 + CF_3CF{=}CF_2)$ and the potential importance of $CF_3CF{=}CF_2$ as a source of trifluoroacetic acid.

1. Introduction

Trifluoroacetic acid, CF_3COOH, has been detected in surface waters (oceans, rivers, and lakes) and in fog, snow, and rainwater samples around the globe[1−5] and is a ubiquitous component of the hydrosphere. Interestingly, while it is clearly established that there is a substantial environmental burden of $CF_3C(O)OH$ (estimated as 10^7−10^8 tonnes[6]), the sources of this compound are unclear. No significant natural sources of trifluoroacetic acid have been identified. Several man-made compounds, that is, the anesthetics isoflurane ($CF_3CHClOCHF_2$) and halothane ($CF_3CHClBr$) and the CFC replacements HFC-134a (CF_3CFH_2) and HCFC-123 (CF_3CHCl_2), are emitted into the environment and produce $CF_3C(O)OH$. However, the magnitude of these industrial sources is several orders of magnitude too small to account for the levels of $CF_3C(O)OH$ observed in the environment.[6] At the present time, there is a significant research effort to identify possible additional industrial and natural sources of $CF_3C(O)OH$ and its precursors in the environment.

Perfluorinated polymers are used widely in plastics, elastomers, and water repellants. The global annual production of these polymers was 40,000 tonnes in 1988.[3] As noted by Jordan and Frank,[3] hexafluoropropene ($CF_3CF{=}CF_2$) is a pyrolysis product of perfluoroalkyl ethers,[7] polytetrafluoroethene (PTFE),[8] and polyperfluoroethenepropene (FEP).[8] It has been suggested that incineration of municipal waste containing perfluorinated polymers may result in the emission of $CF_3CF{=}CF_2$ into the atmosphere and that this $CF_3CF{=}CF_2$ may undergo atmospheric oxidation to give $CF_3C(O)OH$.[3]

Studies of the atmospheric oxidation mechanism of $CF_3OCF{=}CF_2$ have shown that HF elimination from the initially formed excited $[CF_3OCF(\bullet)CF_2OH]^*$ adduct is significant,[9,10] leading to formation of oxalyl fluoride (FC(O)C(O)F). In light of the obvious structural similarities between $CF_3OCF{=}CF_2$ and $CF_3CF{=}CF_2$, it seems reasonable to speculate that a similar mechanism may be operative for $CF_3CF{=}CF_2$. If so, the atmospheric oxidation of $CF_3CF{=}CF_2$ would yield oxalyl fluoride (FC(O)C(O)F) instead of $CF_3C(O)OH$. In the absence of an experimental study of the atmospheric oxidation mechanism of $CF_3CF{=}CF_2$, it is difficult to assess its potential contribution to the global $CF_3C(O)OH$ budget.

At the present time, the atmospheric oxidation mechanism of $CF_3CF{=}CF_2$ is unclear. To remedy this situation, we have used FTIR−smog chamber techniques to study the kinetics and products of reactions 1, 2, and 3 at total pressures of 10−700 Torr of air diluent:

$$OH + CF_3CF{=}CF_2 \rightarrow \text{products} \quad (1)$$

$$Cl + CF_3CF{=}CF_2 \rightarrow \text{products} \quad (2)$$

$$O_3 + CF_3CF{=}CF_2 \rightarrow \text{products} \quad (3)$$

2. Experimental Section

All experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[11] The optical path length of the infrared beam was 27.7 m. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL), which were used to photochemically initiate the experiments. The oxidation of $CF_3CF{=}CF_2$ was initiated by reaction with either OH radicals, Cl atoms, or O_3 in 700 Torr total pressure of O_2/N_2 diluent at 295 ± 2 K. Hydroxyl radicals were generated by the UV irradiation of methylnitrite/NO/air mixtures:

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

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* Corresponding author. Email: twalling@ford.com.

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Chlorine atoms were generated by the photolysis of molecular chlorine:

$$Cl_2 + h\nu \rightarrow 2Cl$$

Loss of $CF_3CF{=}CF_2$ and the formation of products were measured by FT-IR spectroscopy at a resolution of 0.25 cm^{-1}. IR spectra were derived from 32 co-added interferograms. Reference spectra were acquired by expanding known volumes of authentic reference compounds into the chamber. All reagents except CH_3ONO were obtained from commercial sources at purities >99%. Ultrahigh purity synthetic air was used as the diluent gas in all experiments. CH_3ONO was prepared by dropwise addition of concentrated H_2SO_4 to a saturated solution of $NaNO_2$ in methanol and was devoid of any detectable impurities using FTIR analysis. Reference spectra of $CF_3CF{=}CF_2$, COF_2, and $CF_3C(O)F$ were obtained by expansion of calibrated volumes containing authentic samples of these compounds into the reaction chamber. Unless otherwise stated, all uncertainties quoted in the present manuscript are 2 standard deviations from regression analyses.

In smog chamber experiments, unwanted loss of reactants and products via photolysis, dark chemistry, and wall reactions have to be considered. Control experiments were performed to check for such unwanted losses of $CF_3CF{=}CF_2$, COF_2, and $CF_3C(O)F$ in the chamber; none were observed.

Three sets of experiments were performed. First, relative rate techniques were used to determine rate constants for the reactions of OH radicals and Cl atoms with $CF_3CF{=}CF_2$, using C_2H_4, C_2H_2, and C_2H_5Cl as reference gases. Second, the products of the OH radical- and Cl atom-initiated oxidation of $CF_3CF{=}CF_2$ in 700 Torr of air were identified and quantified. Third, the kinetics of the reaction of O_3 with $CF_3CF{=}CF_2$ was studied using an absolute technique.

3. Results

3.1. Relative Rate Study of $k(Cl + CF_3CF{=}CF_2)$. The kinetics of reaction 2 were measured relative to reactions 4 and 5:

$$CF_3CF{=}CF_2 + Cl \rightarrow \text{products} \tag{2}$$

$$C_2H_4 + Cl \rightarrow \text{products} \tag{4}$$

$$C_2H_5Cl + Cl \rightarrow \text{products} \tag{5}$$

Reaction mixtures consisted of 6.4−9.8 mTorr of $CF_3CF{=}CF_2$, 73−83 mTorr of Cl_2, and 3.4−76 mTorr of either C_2H_4 or C_2H_5Cl in 700 Torr of air or N_2 diluent. The rate constant k_2 was derived by observing the relative loss rates of $CF_3CF{=}CF_2$ and the reference compounds; results are shown in the top panel of Figure 1.

Linear least-squares analysis of the data in Figure 1 gives $k_2/k_4 = 0.29 \pm 0.02$ and $k_2/k_5 = 3.26 \pm 0.25$. Using $k_4 = 9.29 \times 10^{-11}$,[12] and $k_5 = 8.04 \times 10^{-12}$,[13] we derive $k_2 = (2.69 \pm 0.19) \times 10^{-11}$ and $(2.62 \pm 0.20) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. We estimate that potential systematic errors associated with uncertainties in the reference rate constants contribute an additional 10% uncertainty to k_2. Propagating this additional uncertainty gives $k_2 = (2.69 \pm 0.32) \times 10^{-11}$ and $(2.62 \pm 0.33) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. We choose to cite a final value for k_2 that is the average of those determined using the two different reference compounds together with error limits that encompass the extremes of the individual determinations. Hence, $k_2 = (2.7 \pm 0.3) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}; the quoted uncertainty reflects the accuracy of the measurements. There are no literature data for k_2 to compare with our results.

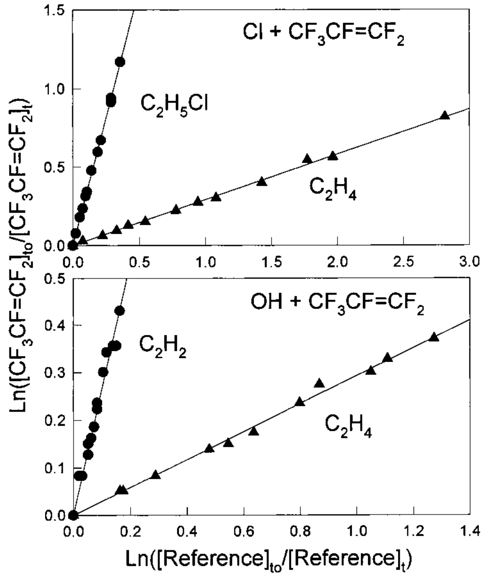

Figure 1. Loss of $CF_3CF{=}CF_2$ versus the reference compounds C_2H_5Cl, C_2H_2, and C_2H_4 in the presence of either Cl atoms (top panel) or OH radicals (bottom panel). Experiments were performed at 296 K in 700 Torr of either air or N_2 diluent.

3.2. Relative Rate Study of $k(OH{+}CF_3CF{=}CF_2)$. The kinetics of reaction 1 were measured relative to reactions 6 and 7:

$$CF_3CF{=}CF_2 + OH \rightarrow \text{products} \tag{1}$$

$$C_2H_4 + OH \rightarrow \text{products} \tag{6}$$

$$C_2H_2 + OH \rightarrow \text{products} \tag{7}$$

Initial concentrations were 6.9−10.4 mTorr of $CF_3CF{=}CF_2$, 50−102 mTorr of CH_3ONO, 7.4−15 mTorr of NO, and 4.4−10.1 mTorr of either C_2H_4 or C_2H_2 in 700 Torr of air or N_2 diluent. The observed loss of $CF_3CF{=}CF_2$ versus those of reference compounds in the presence of OH radicals is shown in the bottom panel of Figure 1. Linear least-squares analysis of the data gives $k_1/k_6 = 0.29 \pm 0.02$ and $k_1/k_7 = 2.65 \pm 0.15$. Using $k_6 = 8.53 \times 10^{-12}$ and $k_7 = 8.70 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1},[14] we derive $k_1 = (2.47 \pm 0.17) \times 10^{-12}$ and $(2.31 \pm 0.13) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. We estimate that potential systematic errors associated with uncertainties in the reference rate constants contribute an additional 10% uncertainty range to k_1. Propagating this additional uncertainty gives $k_1 = (2.47 \pm 0.30) \times 10^{-12}$ and $(2.31 \pm 0.27) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. We choose to cite a final value for k_1 that is the average of those determined using the two different reference compounds together with error limits that encompass the extremes of the individual determinations. Hence, $k_1 = (2.4 \pm 0.3) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. Quoted error reflects the accuracy of the measurements. This result is in excellent agreement with the previous measurements at 298 K of $k_1 = (2.3 \pm 0.1) \times 10^{-12}$ by McIlroy and Tully,[15] $k_1 = (2.2 \pm 0.1) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} by Orkin et al.,[16] and $k_1 = (2.1 \pm 0.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} by Dubey et al.[17]

3.3. Products and Mechanism of Cl Atom Initiated Oxidation of $CF_3CF{=}CF_2$. To investigate the products and mechanism of the reaction of Cl atoms with $CF_3CF{=}CF_2$, reaction mixtures consisting of 6.8 mTorr $CF_3CF{=}CF_2$, 7.5 mTorr Cl_2, and 0−15 mTorr NO in 700 Torr air were introduced

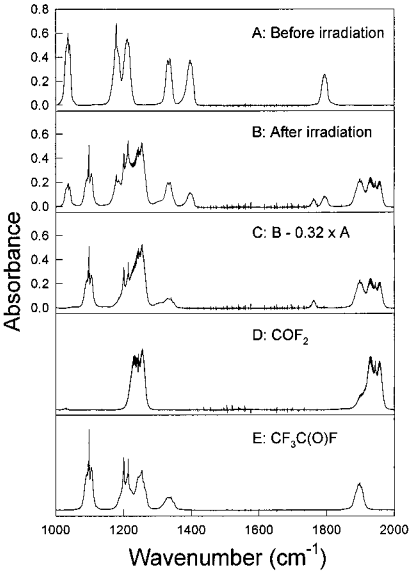

Figure 2. Infrared spectra acquired before (A) and after (B) a 60-s irradiation (using 22 fluorescent lamps) of a mixture of 6.8 mTorr of $CF_3CF{=}CF_2$ and 7.5 mTorr of Cl_2 in 700 Torr of air. Panel (C) shows the product spectrum obtained after subtracting features attributable to $CF_3CF{=}CF_2$ (32% of the original amount) from panel (B). Panels (D) and (E) are reference spectra of COF_2 and $CF_3C(O)F$.

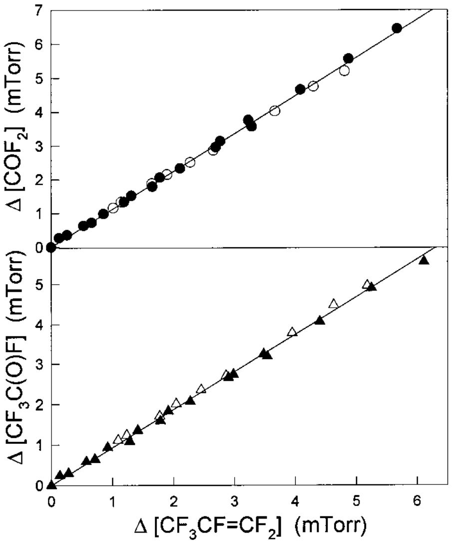

Figure 3. Formation of COF_2 (circles) and $CF_3C(O)F$ (triangles) versus loss of $CF_3CF{=}CF_2$ following UV irradiation of $CF_3CF{=}CF_2/Cl_2$/air mixtures in the presence (filled symbols) and absence (open symbols) of NO.

into the reaction chamber and subjected to UV irradiation. Typical consumptions of $CF_3CF{=}CF_2$ were in the range 5−90%. Figure 2 shows typical spectra acquired before (A) and after (B) a 60-s irradiation (using 22 fluorescent lamps) of a mixture containing 6.8 mTorr of $CF_3CF{=}CF_2$ and 7.5 mTorr of Cl_2 in 700 Torr of air. Subtraction of IR features attributable to $CF_3CF{=}CF_2$ from (B) gives the product spectrum shown in (C). Comparison of the IR features in panel (C) with reference spectra of COF_2 and $CF_3C(O)F$ shown in panels (D) and (E) shows the formation of these compounds. After subtraction of features attributable to COF_2 and $CF_3C(O)F$, residual IR features at 788, 964, 1240, 1302, and 1763 cm^{-1} were observed due to one or more unidentified additional products.

Figure 3 shows a plot of the observed formation of COF_2 and $CF_3C(O)F$ versus loss of $CF_3CF{=}CF_2$ following irradiation of $CF_3CF{=}CF_2/Cl_2$ air mixtures in the presence (filled symbols) or absence (open symbols) of NO. As seen from Figure 3, there was no discernible difference in the COF_2 and $CF_3C(O)F$ yields between experiments performed with and without added NO. Linear least-squares analysis of the composite data sets gives molar yields of COF_2 and $CF_3C(O)F$ of 104 ± 7% and 94 ± 6%, respectively.

The reaction of Cl atoms with $CF_3CF{=}CF_2$ proceeds via addition to give two different substituted alkyl radicals which, in air, are expected to add O_2 rapidly (within 1 μs) to give the corresponding peroxy radicals:

$$Cl\bullet + CF_3CF{=}CF_2 \rightarrow CF_3C(Cl)FCF_2\bullet \qquad (2a)$$

$$Cl\bullet + CF_3CF{=}CF_2 \rightarrow CF_3C(\bullet)FCF_2Cl \qquad (2b)$$

$$CF_3C(Cl)FCF_2\bullet + O_2 \rightarrow CF_3C(Cl)FCF_2O_2\bullet$$

$$CF_3C(\bullet)FCF_2Cl + O_2 \rightarrow CF_3C(O_2\bullet)FCF_2Cl$$

There is no available information concerning the branching ratio k_{2a}/k_{2b}, and we will proceed on the assumption that both radicals are formed. Peroxy radicals react rapidly with NO,[18] and for those experiments where NO was present, the sole fate of the peroxy radicals will be reaction with NO. Such reactions proceed via two channels, giving alkoxy radicals as major products and alkyl nitrates as minor products, that is,

$$CF_3C(O_2\bullet)FCF_2Cl + NO \rightarrow CF_3C(O\bullet)FCF_2Cl + NO_2 \qquad (8a)$$

$$CF_3C(O_2\bullet)FCF_2Cl + NO \rightarrow CF_3C(ONO_2)FCF_2Cl \qquad (8b)$$

In the present work, there was no evidence of nitrate formation showing that channel (8b) is of minor importance. This observation is consistent with previous studies of halogenated alkyl peroxy radicals that produce low nitrate yields in their reactions with NO.[18] Whether by peroxy radical self- or cross-reactions or by peroxy radical and NO reactions, two alkoxy radicals are produced: $CF_3C(Cl)FCF_2O\bullet$ and $CF_3C(O\bullet)FCF_2Cl$. From the fact that the observed COF_2 and $CF_3C(O)F$ products account for 100% of the loss of $CF_3CF{=}CF_2$, we conclude that the fate of $CF_3C(Cl)FCF_2O\bullet$ and $CF_3C(O\bullet)FCF_2Cl$ radicals is decomposition via C−C bond scission, giving $CF_3C(Cl)F\bullet$ radicals and CF_2O, and $CF_3C(O)F$ and $\bullet CF_2Cl$ radicals, respectively. The atmospheric fate of $CF_3C(Cl)F\bullet$ and $\bullet CF_2Cl$ radicals is addition of O_2 to give a peroxy radical, reaction with NO to give an alkoxy radical, and elimination of a Cl atom to give either $CF_3C(O)F$ or COF_2.[19]

3.4. Products and Mechanism of OH Radical-Initiated Oxidation of $CF_3CF{=}CF_2$. To investigate the products and mechanism of the reaction of OH radicals with $CF_3CF{=}CF_2$, reaction mixtures consisting of 7.0−8.0 mTorr $CF_3CF{=}CF_2$, 50−114 mTorr CH_3ONO, and 7.5−10.4 mTorr NO in either 10 or 700 Torr air were introduced into the reaction chamber and subjected to UV irradiation. Typical consumptions of $CF_3CF{=}CF_2$ were in the range 5−55%. Figure 4 shows typical spectra acquired before (A) and after (B) 22-min irradiation (using 22 fluorescent lamps) of a mixture containing 7.3 mTorr of $CF_3CF{=}CF_2$, 51 mTorr of CH_3ONO, and 7.5 mTorr of NO in 700 Torr of air. Subtraction of IR features attributable to $CF_3CF{=}CF_2$ and NO from (B) gives the product spectrum shown in (C). Comparison with reference spectra of COF_2 and $CF_3C(O)F$ given in panels (D) and (E) shows these compounds are products. There were no other carbon-containing products detected. An upper limit of 5% was established for the molar

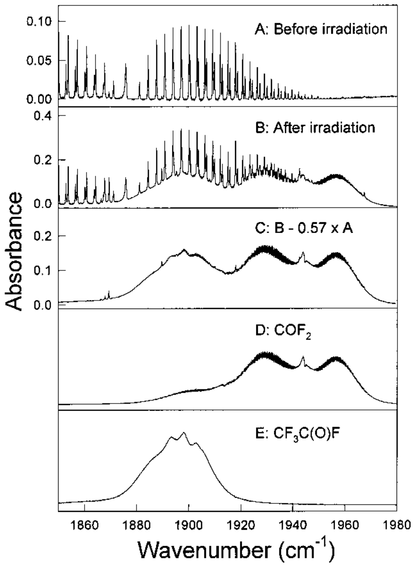

Figure 4. Infrared spectra acquired before (A) and after (B) a 22-min irradiation of a mixture of 7.7 mTorr of $CF_3CF{=}CF_2$, 51 mTorr of CH_3ONO, and 7.5 mTorr of NO in 700 Torr of air. Panel (C) shows the product spectrum obtained after subtracting features attributable to $CF_3CF{=}CF_2$ and NO (57% of the original amount) from panel (B). Panels (D) and (E) are reference spectra of COF_2 and $CF_3OC(O)F$.

yield of oxalyl fluoride, showing that the OH-initiated atmospheric oxidation of $CF_3CF{=}CF_2$ does not proceed via the same mechanism as $CF_3OCF{=}CF_2$.[10]

The observed yields of COF_2 (circles) and $CF_3C(O)F$ (triangles) are plotted versus the loss of $CF_3CF{=}CF_2$ in Figure 5 for experiments conducted in either 700 (open symbols) or 10 (filled symbols) Torr of air diluent. As seen from Figure 5, there was no discernible effect of total pressure on the observed product yields. Linear least-squares analysis of the composite data set gives molar yields of COF_2 and $CF_3C(O)F$ of 98 ± 7% and 90 ± 6%. Quoted errors represent statistical uncertainties (2 standard deviations); we estimate that systematic uncertainties associated with calibration of the reference spectra contribute an additional 10% uncertainty.

The reaction of OH radicals with $CF_3CF{=}CF_2$ proceeds via addition to give two different substituted alkyl radicals which, in air, will add O_2 rapidly (within 1 μs) to give the corresponding peroxy radicals:

$$OH\bullet + CF_3CF{=}CF_2 \rightarrow CF_3C(OH)FCF_2\bullet \tag{1a}$$

$$OH\bullet + CF_3CF{=}CF_2 \rightarrow CF_3C(\bullet)FCF_2OH \tag{1b}$$

$$CF_3C(OH)FCF_2\bullet + O_2 \rightarrow CF_3C(OH)FCF_2O_2\bullet$$

$$CF_3C(\bullet)FCF_2OH + O_2 \rightarrow CF_3C(O_2\bullet)FCF_2OH$$

There is no available information concerning the branching ratio k_{1a}/k_{1b}, and we will proceed on the assumption that both radicals are formed. Peroxy radicals react rapidly with NO,[18] and for those experiments where NO was present, the sole fate of the peroxy radicals will be reaction with NO. Such reactions generally proceed via two channels, giving alkoxy radicals as major products and alkyl nitrates as minor products, that is,

$$CF_3C(O_2\bullet)FCF_2OH + NO \rightarrow CF_3C(O\bullet)FCF_2OH + NO_2 \tag{9a}$$

$$CF_3C(O_2\bullet)FCF_2OH + NO \rightarrow CF_3C(ONO_2)FCF_2OH \tag{9b}$$

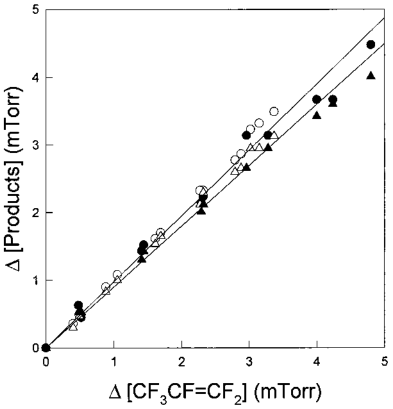

Figure 5. Formation of COF_2 (circles) and $CF_3C(O)F$ (triangles) versus loss of $CF_3CF{=}CF_2$ following the UV irradiation of $CF_3CF{=}CF_2/CH_3ONO/NO$ in 700 (open symbols) or 10 (filled symbols) Torr of air diluent at 296 K.

In the present work, there was no evidence of nitrate formation, showing that channel (9b) is of minor importance. This observation is consistent with previous studies of fluorinated alkyl peroxy radicals that produce low nitrate yields in their reactions with NO.[18] By peroxy radical and NO reaction, two alkoxy radicals are produced: $CF_3C(OH)FCF_2O\bullet$ and $CF_3C(O\bullet)FCF_2OH$. The observed COF_2 and $CF_3C(O)F$ products account for 100% of the loss of $CF_3CF{=}CF_2$; the fate of both alkoxy radicals is decomposition via C−C bond scission. The resulting α-hydroxy alkyl radicals react rapidly with O_2 to give the corresponding carbonyl and an HO_2 radical:

$$CF_3C(\bullet)(OH)F + O_2 \rightarrow CF_3C(O)F + HO_2$$

$$\bullet CF_2OH + O_2 \rightarrow COF_2 + HO_2$$

3.5. Study of $k(O_3 + CF_3CF{=}CF_2)$. The kinetics of reaction 3 were investigated by filling the smog chamber with 700 Torr of ozonized O_2 containing 899−963 mTorr of O_3, then adding 1.5−8.1 mTorr of $CF_3CF{=}CF_2$ and monitoring the decay of $CF_3CF{=}CF_2$ and O_3 for 60−70 min:

$$CF_3CF{=}CF_2 + O_3 \rightarrow \text{products} \tag{3}$$

During the 60−70 min of each experiment, there was a slow but discernible loss of ozone in the chamber, corresponding to a loss of approximately 2% in 60 min. We attribute the slow loss of ozone mainly to loss via decomposition on the chamber walls. Loss of ozone via reaction 3 is of minor importance because ozone is present in great excess compared to $CF_3CF{=}CF_2$.

Figure 6 shows the observed decay of $CF_3CF{=}CF_2$ as a function of time when $CF_3CF{=}CF_2/O_3/O_2$ mixtures were allowed to stand in the dark in the chamber. Control experiments using $CF_3CF{=}CF_2/O_2$ mixtures established that $CF_3CF{=}CF_2$ loss was negligible (<2% in 60 min) in the absence of O_3. We conclude that the $CF_3CF{=}CF_2$ loss shown in Figure 6 is caused by reaction with ozone. It is interesting to note that whereas the initial ozone concentrations used in the experiments shown in Figure 6 varied by less than 7%, the rates of decay of $CF_3CF{=}CF_2$ varied by 36% (pseudo first-order rates of 0.9−1.4 × 10^{-4} s^{-1}). Furthermore, close inspection of the data in Figure 6 reveals a systematic increase in the pseudo first-order $CF_3CF{=}CF_2$ loss rate with the initial concentration of $CF_3CF{=}CF_2$. The simplest interpretation of this observation is that there is a complication in the system caused by radicals formed from the $O_3 + CF_3CF{=}CF_2$ reaction that react with

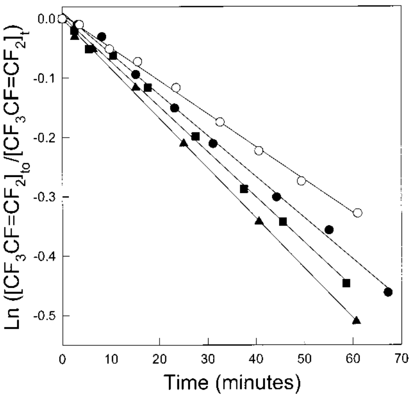

Figure 6. Decay of $CF_3CF=CF_2$ in experiments employing mixtures of 1.5 mTorr $CF_3CF=CF_2$ and 927 mTorr O_3 (open circles), 2.8 mTorr $CF_3CF=CF_2$ and 963 mTorr O_3 (filled circles), 4.3 mTorr $CF_3CF=CF_2$ and 899 mTorr O_3 (filled squares), and 8.1 mTorr $CF_3CF=CF_2$ and 920 mTorr O_3 (filled triangles) in 700 Torr of O_2 diluent at 296 K.

$CF_3CF=CF_2$, leading to an enhanced loss of $CF_3CF=CF_2$. This effect will be more important at higher initial concentrations of $CF_3CF=CF_2$, leading to the observed behavior. Our conclusion is that the lowest value of $k(CF_3CF=CF_2 + O_3)$ derived from the data in Figure 6 should be treated as an upper limit. Hence, we report $k(CF_3CF=CF_2 + O_3) < 3 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}. This result is approximately 10^4 times lower than the value of $k(CF_3CF=CF_2 + O_3) = 2.2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} reported by Heicklen.[20] The initial concentrations of $CF_3CF=CF_2$ used in the study by Heicklen were 100−1000 times greater than those used herein. It seems reasonable to suspect that secondary loss of $CF_3CF=CF_2$ was a major problem in the previous work and that the value of k_3 reported by Heicklen[20] is erroneously large.

4. Conclusions

The motivation behind the present study was 2-fold; first, to provide an understanding of the atmospheric chemistry of $CF_3CF=CF_2$ and second, to assess its potential contribution to the environmental burden of trifluoroacetic acid.

With regard to the first aim, we present a substantial body of kinetic and mechanistic data pertaining to the atmospheric chemistry of $CF_3CF=CF_2$. The atmospheric lifetime of $CF_3CF=CF_2$ with respect to reaction with OH can be estimated using three pieces of information: the value of $k_1 = 2.4 \times 10^{-12}$ measured herein, $k(OH + CCl_3CH_3) = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K,[21] and the atmospheric lifetime of CCl_3CH_3 with respect to reaction with OH of 5.9 years.[22] This approach gives an atmospheric lifetime of $CF_3CF=CF_2$ with respect to reaction with OH of 9 days. The atmospheric lifetime of $CF_3CF=CF_2$ with respect to reaction with ozone can be estimated by combining a typical tropospheric ozone concentration of 50 ppb with $k_3 < 3 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}, giving a lower limit for the lifetime of $CF_3CF=CF_2$ with respect to reaction with ozone of 8 years. Current estimates suggest that typical marine boundary layer levels of Cl atoms are around 10^4 cm^{-3},[23−25] with lower levels over continental areas. Using $[Cl] = 10^4$ cm^{-3} in conjunction with the value $k_2 = 2.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} reported in this study gives a lifetime of 43 days for $CF_3CF=CF_2$ via reaction with Cl atoms. As for other alkenes, photolysis of $CF_3CF=CF_2$ in the atmosphere will not be of any significance.[26] The atmospheric loss of $CF_3CF=CF_2$ is dominated by reaction with OH radicals, giving COF_2 and $CF_3C(O)F$ in molar yields of 100%. The atmospheric fate of COF_2 and $CF_3C(O)F$ is incorporation into water droplets (within 5−15 days) followed by hydrolysis to give either CO_2 and HF or $CF_3C(O)OH$ and HF.[19]

With regard to the second aim, we show that, following release into the atmosphere, $CF_3CF=CF_2$ is converted within a week or two into $CF_3C(O)OH$. There are two atmospheric fates of $CF_3C(O)OH$; rainout and reaction with OH. Reaction with OH is slow; approximately 95% of the $CF_3C(O)OH$ produced from the atmospheric oxidation of $CF_3CF=CF_2$ will be rained out and will enter the hydrosphere.[27] To assess the importance of $CF_3CF=CF_2$ as a source of $CF_3C(O)OH$, we need to compare it with other sources and with the environmental burden of $CF_3C(O)OH$. Table 1 provides a list of the known sources of $CF_3C(O)OH$ in the atmosphere. We have shown that any $CF_3CF=CF_2$ that is emitted into the atmosphere is converted into $CF_3C(O)OH$. The importance of $CF_3CF=CF_2$ as a $CF_3C(O)OH$ source depends on the amount of $CF_3CF=CF_2$ emitted. There are no published data concerning the global industrial production of $CF_3CF=CF_2$. However, based upon the published fluoropolymer production in 1997, it has been estimated that the global industrial production of $CF_3CF=CF_2$ lies in the range 10−15 ktonnes/year.[28] It is reasonable to expect that essentially all of this $CF_3CF=CF_2$ will be incorporated into chemical products and that direct emission of $CF_3CF=CF_2$ from the point of production will be minimal. It is possible that $CF_3CF=CF_2$ is released during incineration of fluoropolymers. The global production of fluoropolymers is large (40,000 tonnes in 1988); if even a small fraction is converted into $CF_3CF=CF_2$, this would be significant. To the best of our knowledge, there have been no measurements of $CF_3CF=CF_2$ emissions from incineration plants. Jordan and Frank[3] assume that 2500 tonnes/yr of fluoropolymer waste is incinerated in Europe and that 10% of the fluoropolymer is released to the atmosphere as $CF_3CF=CF_2$. Emission measurements are required to determine if this assumption is reasonable and to provide a clearer picture of the importance of this potential source of $CF_3CF=CF_2$.

At this point, we should contrast the environmental burden of $CF_3C(O)OH$, which has been estimated at $10^7 - 10^8$ tonnes,[6] with the potential source from atmospheric oxidation of $CF_3CF=CF_2$, which has been estimated at 250 tonnes.[3] There is a very large difference between the environmental burden of $CF_3C(O)OH$ and its potential source from $CF_3CF=CF_2$. It is possible that atmospheric oxidation of $CF_3CF=CF_2$ may

TABLE 1: Compounds Known to Produce CF_3COOH in the Atmosphere

compound	common name	molar CF_3COOH yield	atmospheric lifetime	estimated TFA flux (tonne/yr)
$CF_3CHClBr$	Halothane	0.6	1.2 years	520
$CF_3CHClOCHF_2$	Isoflurane	0.6	5 years	280
CF_3CHCl_2	HCFC-123	0.6	1.5 years	<760
CF_3CHFCl	HCFC-124	1.0	6.0 years	<320
CF_3CH_2F	HFC-134a	0.13	14.6 years	1200[a]
$CF_3CF=CF_2$	hexafluoropropene	1.0	9 days	250?[b]

[a] Assuming [HFC-134a] = 10 pptv and 5 pptv in N. and S. hemispheres, respectively.[29−31] [b] Estimate from ref 3.

constitute a significant fraction of the *man-made* $CF_3C(O)OH$ in the environment, but it does not appear to contribute a significant fraction of the levels of $CF_3C(O)OH$ observed in the global environment.

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