J. Phys. Chem. A **2000,** *104,* 2925−2930 **2925**

Atmospheric Degradation of $CF_3OCF{=}CF_2$: Kinetics and Mechanism of Its Reaction with OH Radicals and Cl Atoms

M. Mashino 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

Received: November 30, 1999; In Final Form: January 31, 2000

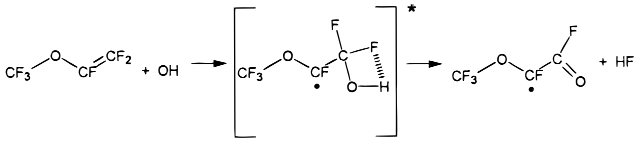
Smog chamber/FTIR techniques were used to study the OH radical and Cl atom initiated oxidation of $CF_3OCF{=}CF_2$ in 700 Torr of air at 296 K. Using relative rate techniques it was determined that $k(OH + CF_3OCF{=}CF_2) = (2.6 \pm 0.3) \times 10^{-12}$ and $k(Cl + CF_3OCF{=}CF_2) = (3.0 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Cl atom initiated atmospheric oxidation of $CF_3OCF{=}CF_2$ gives COF_2 and $CF_3OC(O)F$ in molar yields of 100%. OH radical initiated atmospheric oxidation of $CF_3OCF{=}CF_2$ in 700 Torr of air at 295 K gives COF_2, $CF_3OC(O)F$, and FC(O)C(O)F in molar yields of 90, 53, and 40%. The results are discussed with respect to the atmospheric degradation mechanism of $CF_3OCF{=}CF_2$ and other ethers.

1. 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. Hydrofluoroethers (HFEs) are a class of compounds which have been developed to replace CFCs in applications such as the cleaning of electronic equipment, heat transfer agents in refrigeration systems, and carrier fluids for lubricant deposition.[3] $CF_3OCF{=}CF_2$ (HFE-216, trifluoromethyl trifluorovinyl ether) has been proposed as an environmentally friendly replacement for the perfluorocarbons currently used as plasma etching gas.[4] $CF_3OCF{=}CF_2$ is a volatile gas and may be released into the atmosphere during its use. Atmospheric oxidation of $CF_3OCF{=}CF_2$ is initiated by reaction with OH radicals.

$$OH + CF_3OCF{=}CF_2 \rightarrow \text{products} \qquad (1)$$

The kinetics and mechanism of the reaction of OH with $CF_3OCF{=}CF_2$ have been studied by Li et al.[5] in 1 Torr of helium diluent. Li et al.[5] report $k_1 = 8.24 \times 10^{-11} \exp(-964/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 253−348 K ($k_1 = 3.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K). Li et al.[5] observed, but did not quantify, the formation of HF and $CF_3OC(\bullet)FC(O)F$ as products of reaction 1. The observation of HF as a product of reaction 1 is interesting and novel. Under atmospheric conditions, the reaction of OH radicals with alkenes proceeds essentially exclusively via addition to the double bond to give a β-hydroxy alkyl radical. The sole atmospheric fate of β-hydroxy alkyl radicals is addition of O_2 to give the corresponding peroxy radicals which then react with NO, NO_2, HO_2, or other peroxy radicals in the atmosphere to give a variety of products.[6] Direct production of HF from reaction 1 is not expected from the database for reactions of OH radicals with other alkenes. The mechanism proposed by Li et al.[5] for HF formation was



Under atmospheric conditions in the presence of 760 Torr of air collisional stabilization of the excited intermediate $[CF_3OC(\bullet)FCF_2OH]^*$ radical may be significant and thus the mechanism proposed by Li et al. may not be relevant to the atmospheric chemistry of $CF_3OCF{=}CF_2$. To provide further insight into the mechanism of reaction 1 and the atmospheric oxidation mechanism of $CF_3OCF{=}CF_2$ we have used FTIR−smog chamber techniques to study the kinetics and products of reactions 1 and 2 at total pressures of 10−700 Torr of air diluent.

$$Cl + CF_3OCF{=}CF_2 \rightarrow \text{products} \qquad (2)$$

2. Experimental Section

All experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[7] 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 $CF_3OCF{=}CF_2$ was initiated by reaction with OH radicals or Cl atoms which were generated by the photolysis of methylnitrite, or molecular chlorine, in 700 Torr total pressure of O_2/N_2 diluent at 295 ± 2 K, respectively,

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

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

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

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

$$X + CF_3OCF{=}CF_2 \rightarrow CF_3OCF(X)CF_2\bullet$$

$$X + CF_3OCF{=}CF_2 \rightarrow CF_3OC(\bullet)FCF_2X$$

---

* Author to whom correspondence should be addressed. E-mail: twalling@ford.com.

10.1021/jp9942264 CCC: $19.00

where X = Cl or OH. Loss of $CF_3OCF{=}CF_2$ and the formation of products were measured by FTIR spectroscopy at a resolution of 0.25 cm^{-1}. IR spectra were derived from 32 coadded 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 the dropwise addition of concentrated H_2SO_4 to a saturated solution of $NaNO_2$ in methanol and was devoid of any detectable impurities using FTIR analysis. Reference spectra of $CF_3OCF{=}CF_2$, COF_2, and FC(O)C(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 $CF_3OCF{=}CF_2$, COF_2, $CF_3OC(O)F$, and FC(O)C(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 $CF_3OCF{=}CF_2$, using C_2H_4, C_2H_2, and C_2H_5Cl as reference gases. Second, the products of the Cl atom initiated oxidation of $CF_3OCF{=}CF_2$ in 700 Torr of air in the presence and absence of NO were identified and quantified. Third, the products of the OH radical initiated oxidation of $CF_3OCF{=}CF_2$ in the presence of NO were measured.

3. Results

3.1. Relative Rate Study of *k*(Cl + $CF_3OCF{=}CF_2$) and k(OH+$CF_3OCF{=}CF_2$).

The kinetics of reaction 2 were measured relative to reactions 3 and 4.

$$CF_3OCF{=}CF_2 + Cl \rightarrow \text{products} \tag{2}$$

$$C_2H_4 + Cl \rightarrow \text{products} \tag{3}$$

$$C_2H_5Cl + Cl \rightarrow \text{products} \tag{4}$$

Reaction mixtures consisted of 3.0 mTorr of $CF_3OCF{=}CF_2$, 15−75 mTorr of Cl_2, and 7.7−76 mTorr of either C_2H_4, or C_2H_5Cl, in 700 Torr of either air or N_2 diluent. The rate constant k_2 was derived by observing the relative loss rates of $CF_3OCF{=}CF_2$ 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 $k_2/k_3 = 0.32 \pm 0.02$ and $k_2/k_4 = 3.71 \pm 0.25$. Using $k_3 = 9.29 \times 10^{-11}$ [8] and $k_4 = 8.04 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1},[9] we derive $k_2 = (2.97 \pm 0.19) \times 10^{-11}$ and $(2.98 \pm 0.20) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. We estimate that potential systematic errors associated with uncertainties in the reference rate constants add a 10% uncertainty range for k_2. Propagating this additional uncertainty gives $k_2 = (2.97 \pm 0.35) \times 10^{-11}$ and $(2.98 \pm 0.36) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. We choose to cite a final value for k_3 which is the average of those determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k_2 = (3.0 \pm 0.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, the quoted uncertainty reflects the accuracy of the measurements.

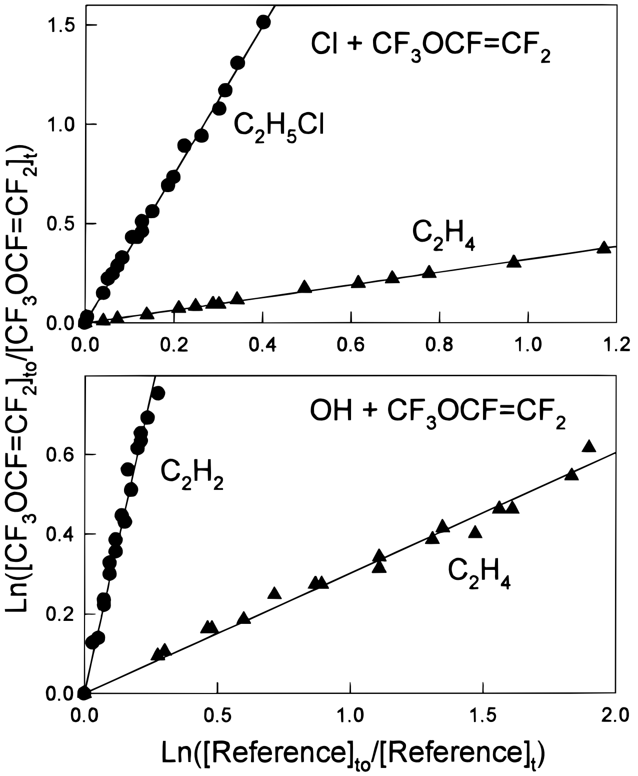


Figure 1. Loss of $CF_3OCF{=}CF_2$ versus the reference compounds C_2H_5Cl, C_2H_2, and C_2H_4 in the presence of either Cl atoms (top panel) or OH radicals (bottom panel). Experiments were performed at 296 K in 700 Torr of air.

The kinetics of reaction 1 were measured relative to reactions 5 and 6.

$$CF_3OCF{=}CF_2 + OH \rightarrow \text{products} \tag{1}$$

$$C_2H_4 + OH \rightarrow \text{products} \tag{5}$$

$$C_2H_2 + OH \rightarrow \text{products} \tag{6}$$

Initial concentrations were 2.2−3.7 mTorr $CF_3OCF{=}CF_2$, 100 mTorr CH_3ONO, 10 mTorr NO, and 6.8−19 mTorr of either C_2H_4, or C_2H_2, in 700 Torr of air diluent. The observed loss of $CF_3OCF{=}CF_2$ 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 $k_1/k_5 = 0.29 \pm 0.02$ and $k_1/k_6 = 2.89 \pm 0.25$. Using $k_5 = 8.53 \times 10^{-12}$, and $k_6 = 8.70 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [10] we derive $k_1 = (2.47 \pm 0.17) \times 10^{-12}$ and $(2.64 \pm 0.22) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. We estimate that potential systematic errors associated with uncertainties in the reference rate constants add a 10% uncertainty range for k_1. Propagating this additional uncertainty gives $k_1 = (2.47 \pm 0.30) \times 10^{-12}$ and $(2.64 \pm 0.34) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. We choose to cite a final value for k_1 which is the average of those determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k_1 = (2.6 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. Quoted error reflects the accuracy of the measurements. This result is indistinguishable from the value of $k_1 = (3.22 \pm 0.51) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} measured at 298 K in 1 Torr of helium diluent by Li et al.[5] Clearly reaction 1 does not display any pressure dependence over the range 1 Torr of helium to 700 Torr of air.

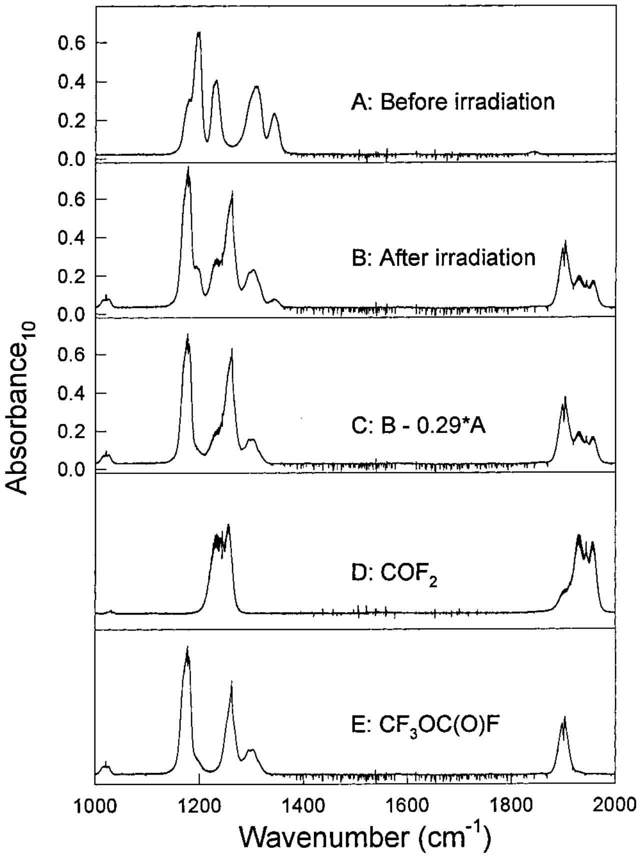


Figure 2. Infrared spectra acquired before (A) and after (B) a 40 s irradiation (using 2 fluorescent lamps) of a mixture of 3.7 mTorr of $CF_3OCF{=}CF_2$ and 14.8 mTorr of Cl_2 in 700 Torr of air. Panel (C) shows the product spectrum obtained after subtracting features attributable to $CF_3OCF{=}CF_2$ from panel (B). Panel (D) is a reference spectrum of COF_2. Subtraction of features attributable to COF_2 from panel (C) gives panel (E) where all the features are attributed to $CF_3OC(O)F$.

3.2. Products and Mechanism of Cl Atom Initiated Oxidation of $CF_3OCF{=}CF_2$. To investigate the products and mechanism of the reaction of Cl atoms with $CF_3OCF{=}CF_2$ reaction mixtures consisting of 3.7 mTorr $CF_3OCF{=}CF_2$, 14.8 mTorr of Cl_2, and 0−10.4 mTorr of NO in 700 Torr of air were introduced into the reaction chamber and subjected to UV irradiation. Figure 2 shows typical spectra acquired before (A) and after (B) a 40 s irradiation (using two fluorescent lamps) of a mixture containing 3.7 mTorr of $CF_3OCF{=}CF_2$ and 14.8 mTorr of Cl_2 in 700 Torr of air. Subtraction of IR features attributable to $CF_3OCF{=}CF_2$ from (B) gives the product spectrum shown in (C). Subtraction of IR product features attributable to COF_2 from panel C gives a residual spectrum with IR features at 1176, 1262, and 1900 cm^{-1}. These residual features match in size and shape those of the IR spectrum of $CF_3OC(O)F$ reported by Johnston et al.[11] Quantification of $CF_3OC(O)F$ was achieved using σ_e (1299 cm^{-1}) = 1.09×10^{-18} cm^2 molecule^{-1}.[11] Panel E shows our reference spectrum of $CF_3OC(O)F$ obtained by subtracting features attributable to COF_2 from panel (C). COF_2 and $CF_3OC(O)F$ were the only carbon-containing products observed.

Figure 3 shows a plot of the observed yields of COF_2 and $CF_3OC(O)F$ versus loss of $CF_3OCF{=}CF_2$ following irradiation of $CF_3OCF{=}CF_2/Cl_2$/air mixtures with (open symbols) and without (filled symbols) added NO. There was no discernible difference in the product yields between experiments conducted in the presence and absence of NO. Linear least-squares analysis of the composite data set (with and without NO present) gives molar yield of COF_2 and $CF_3OC(O)F$ of 103 ± 5% and 102 ± 4%.

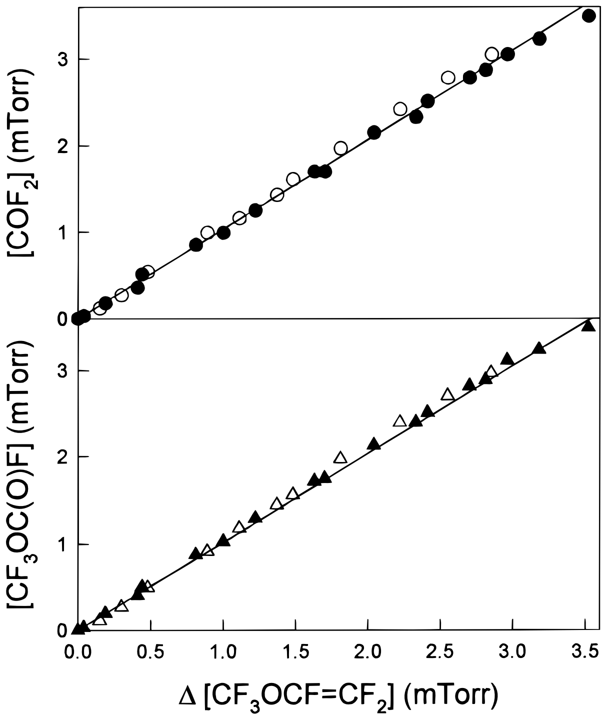


Figure 3. Formation of COF_2 (top panel) and $CF_3OC(O)F$ (bottom panel) versus loss of $CF_3OCF{=}CF_2$ following UV irradiation of $CF_3OCF{=}CF_2/Cl_2$/air mixtures in the presence (filled symbols) and absence (open symbols) of added NO.

The reaction of Cl atoms with $CF_3OCF{=}CF_2$ 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.

$$Cl\bullet + CF_3OCF{=}CF_2 \rightarrow CF_3OC(Cl)FCF_2\bullet \qquad (2a)$$

$$Cl\bullet + CF_3OCF{=}CF_2 \rightarrow CF_3OC(\bullet)FCF_2Cl \qquad (2b)$$

$$CF_3OC(Cl)FCF_2\bullet + O_2 + M \rightarrow CF_3OC(Cl)FCF_2O_2\bullet + M$$

$$CF_3OC(\bullet)FCF_2Cl + O_2 + M \rightarrow CF_3OC(O_2\bullet)FCF_2Cl + M$$

While there is no available information concerning the branching ratio k_{2a}/k_{2b}, when the strong inductive effect of fluorine atom substituents and the mesomeric effect of the oxygen atom are considered it seems likely that channel 2b will dominate. In the absence of definitive information concerning k_{2a}/k_{2b} in the following discussion we will assume that both radicals are formed. In the absence of NO, the two peroxy radicals undergo self- and cross-reactions which will generate alkoxy radicals, e.g.,

$$CF_3OC(O_2\bullet)FCF_2Cl + RO_2 \rightarrow CF_3OC(O\bullet)FCF_2Cl + RO + O_2$$

All peroxy radicals react rapidly with NO[12] 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, e.g.,

$$CF_3OC(O_2\bullet)FCF_2Cl + NO \rightarrow CF_3OC(O\bullet)FCF_2Cl + NO_2 \quad (7b)$$

In the present work there was no evidence of nitrate formation

$$CF_3OC(O_2\bullet)FCF_2Cl + NO \rightarrow CF_3OC(ONO_2)FCF_2Cl \quad (7b)$$

showing that channel 7b is of minor importance. This observation is consistent with previous studies of halogenated alkyl peroxy radicals which appear to produce little or no nitrate in their reactions with NO.[12] Whether by peroxy radical self- or cross-reactions, or by peroxy radical and NO reactions, two alkoxy radicals are produced; $CF_3OC(Cl)FCF_2O\bullet$ and $CF_3OC(O\bullet)FCF_2Cl$. From the fact that the observed COF_2 and $CF_3OC(O)F$ products account for 100% of the loss of $CF_3OCF{=}CF_2$, we conclude that both alkoxy radicals decompose via C−C bond scission; see the reaction mechanism given in Figure 4.

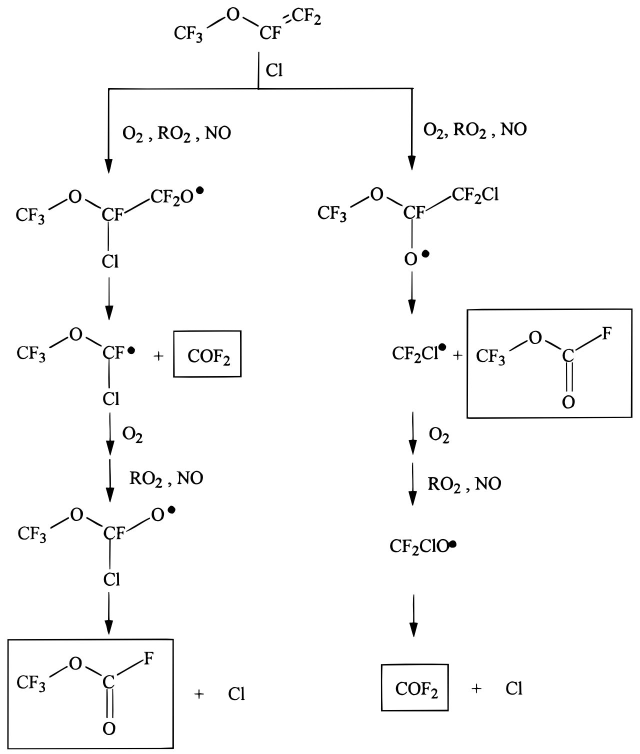


Figure 4. Degradation mechanism for Cl atom initiated oxidation of $CF_3OCF{=}CF_2$.

3.3. Products and Mechanism of OH Radical Initiated Oxidation of $CF_3OCF{=}CF_2$. To investigate the mechanism of reaction 6, mixtures of 3.7 mTorr of $CF_3OCF{=}CF_2$, 28−51 mTorr of CH_3ONO, and 5.3−10 mTorr of NO in either 10 or 700 Torr of air were introduced into the reaction chamber and irradiated using the UV fluorescent lamps. Figure 5 shows typical spectra acquired before (A) and after (B) a 6 min irradiation (using 22 fluorescent lamps) of a mixture containing 7.4 mTorr of $CF_3OCF{=}CF_2$, 50 mTorr of CH_3ONO, and 10 mTorr of NO, in 700 Torr of air. Subtraction of IR features attribute to $CF_3OCF{=}CF_2$ and NO from panel (B) gives the product spectrum shown in panel (C). By comparison with the reference spectra of COF_2, $CF_3OC(O)F$, and $FC(O)C(O)F$ shown in panels D, E, and F it can be seen that these compounds are formed as products. There were no other carbon-containing products detected.

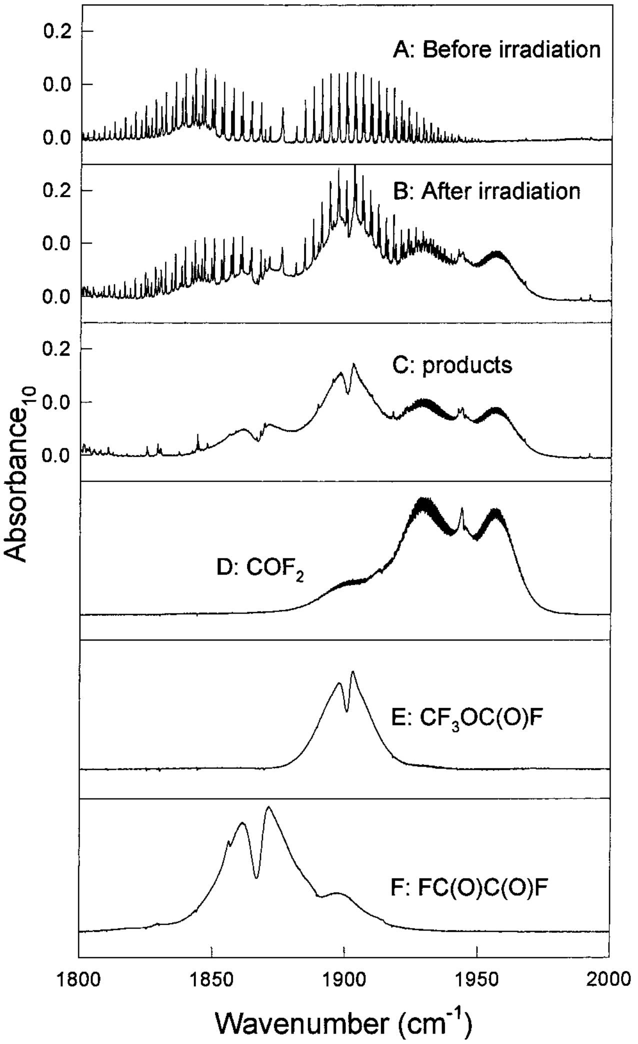
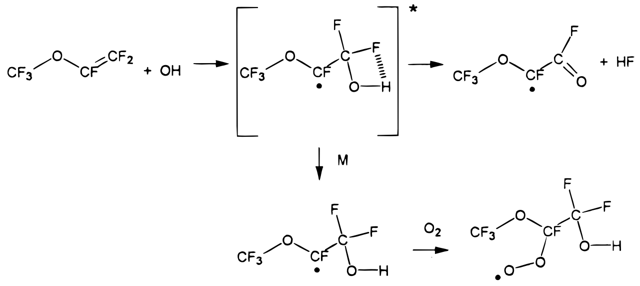


Figure 5. Infrared spectra acquired before (A) and after (B) a 6 min irradiation of a mixture of 7.4 mTorr of $CF_3OCF{=}CF_2$, 50 mTorr of CH_3ONO, and 10 mTorr of NO in 700 Torr of air. Panel (C) shows the product spectrum obtained after subtracting features attributable to $CF_3OCF{=}CF_2$ and NO from panel (B). Panels (D), (E), and (F) are reference spectra of COF_2, $CF_3OC(O)F$, and $FC(O)C(O)F$, respectively.

The products following the OH-initiated oxidation of $CF_3OCF{=}CF_2$ were investigated in either 700 or 10 Torr of air diluent. The observed yields of COF_2 (circles), $CF_3OC(O)F$ (triangles), and $FC(O)C(O)F$ (squares) are plotted versus the loss of $CF_3OCF{=}CF_2$ in Figure 6 for experiments conducted in either 700 or 10 Torr of air diluent (top and bottom panels, respectively). Linear least-squares analysis gives molar yields of COF_2, $CF_3OC(O)F$, and $FC(O)C(O)F$ of 90 ± 5%, 53 ± 4%, and 40 ± 3%, and 104 ± 6%, 8 ± 2%, and 69 ± 8%, for experiments conducted in 700 and 10 Torr of air diluent, respectively. The combined yields of COF_2, $CF_3OC(O)F$, and $FC(O)C(O)F$ account for 93 ± 5% and 86 ± 7% of the $CF_3OCF{=}CF_2$ loss observed at 700 and 10 Torr total pressure, respectively.

It should be noted that the initial reagent concentrations, irradiation times, and fractional conversions of $CF_3OCF{=}CF_2$ were essentially identical for the two sets of experiments shown in Figure 6; the only significant difference was the total pressure of diluent gas (700 or 10 Torr). It is clear from inspection of Figure 6 that the $CF_3OC(O)F$ and $FC(O)C(O)F$ product yields are dependent upon the total pressure. Decrease in total pressure favors $FC(O)C(O)F$ at the expense of $CF_3OC(O)F$. This observation can be rationalized in terms of a competition between decomposition via HF elimination and collisional stabilization for the excited $[CF_3OC(\bullet)FCF_2OH]^*$ intermediate.



Formation of FC(O)C(O)F after HF elimination from $[CF_3OC(\bullet)FCF_2OH]^*$ radicals is explained by the following reactions:

$$CF_3OC(\bullet)FCF_2OH \rightarrow CF_3OC(\bullet)FC(O)F + HF$$

$$CF_3OC(\bullet)FC(O)F + O_2 + M \rightarrow CF_3OC(O_2\bullet)FC(O)F + M$$

$$CF_3OC(O_2\bullet)FC(O)F + NO \rightarrow CF_3OC(O\bullet)FC(O)F + NO_2$$

$$CF_3OC(O\bullet)FC(O)F \rightarrow CF_3O\bullet + FC(O)C(O)F$$

$CF_3O\bullet$ radicals react rapidly with NO to give COF_2.[13]

$$CF_3O\bullet + NO \rightarrow COF_2 + FNO$$

Formation of $CF_3OC(O)F$ after collisional stabilization of $[CF_3OC(\bullet)FCF_2OH]^*$ radicals is explained by the following reactions:

$$CF_3OC(\bullet)FCF_2OH + O_2 + M \rightarrow CF_3OC(O_2\bullet)FCF_2OH + M$$

$$CF_3OC(O_2\bullet)FCF_2OH + NO \rightarrow CF_3OC(O\bullet)FCF_2OH + NO_2$$

$$CF_3OC(O\bullet)FCF_2OH \rightarrow CF_3OC(O)F + \bullet CF_2OH$$

$\bullet CF_2OH$ radicals react with O_2 to give COF_2.[13]

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

Our observation of an increased yield of FC(O)C(O)F with decreased total pressure is entirely consistent with the observation of HF and $CF_3OC(\bullet)FC(O)F$ products by Li et al.[5] in 1 Torr of helium.

In the discussion thus far we have considered only the fate of the radical following OH addition of the terminal carbon atom. The formation of FC(O)C(O)F product can only be ascribed to chemistry following OH addition at the $=CF_2$ group, the 69 ± 8% yield of FC(O)C(O)F at low pressure provides a lower limit for the fraction of OH attack that occurs at the $=CF_2$ group. Li et al.[5] searched for evidence of products expected from OH addition to the $-CF=$ position but none were found. As seen from Figure 6, the COF_2 yield in experiments conducted at 10 Torr total pressure was slightly greater than that at 700 Torr total pressure. This difference may be an indication of the importance of a minor channel involving OH addition to the $-CF=$ position followed by HF elimination which is expected to produce two molecules of COF_2 and one of CO_2:

$$OH + CF_3OCF{=}CF_2 \rightarrow [CF_3OCF(OH)CF_2\bullet]^*$$

$$[CF_3OCF(OH)CF_2\bullet]^* \rightarrow CF_3OC(O)CF_2\bullet + HF$$

$$CF_3OC(O)CF_2\bullet + O_2 + M \rightarrow CF_3OC(O)CF_2OO\bullet + M$$

$$CF_3OC(O)CF_2OO\bullet + NO \rightarrow CF_3OC(O)CF_2O\bullet + NO_2$$

$$CF_3OC(O)CF_2O\bullet \rightarrow CF_3OC(O)\bullet + COF_2$$

$$CF_3OC(O)\bullet + O_2 + M \rightarrow CF_3OC(O)OO\bullet + M$$

$$CF_3OC(O)OO\bullet + NO \rightarrow CF_3OC(O)O\bullet + NO_2$$

$$CF_3OC(O)O\bullet \rightarrow CF_3O\bullet + CO_2$$

Small amounts of CO_2 were formed in the smog chamber following irradiation of $CF_3OCF{=}CF_2/CH_3ONO/NO$/air mixtures. However, the formation of CO_2 from secondary reactions following CH_3ONO photolysis precludes any estimate of the CO_2 yield from $CF_3OCF{=}CF_2$ oxidation. While we are not able to exclude a minor channel of reaction 1 occurring via addition on the middle carbon atom, it is clear that the majority of the reaction proceeds via attack on the terminal carbon atom.

The simplest way to account for the observed products in the present study and that of Li et al.[5] is to assume that essentially all of the OH reaction with $CF_3OCF{=}CF_2$ occurs via addition to the terminal carbon atom to give an excited adduct which either eliminates HF, or undergoes collisional stabilization. As discussed above, the chemistry following elimination of HF leads to the formation of FC(O)C(O)F and COF_2 while that after collisional stabilization leads to $CF_3OC(O)F$ and COF_2.

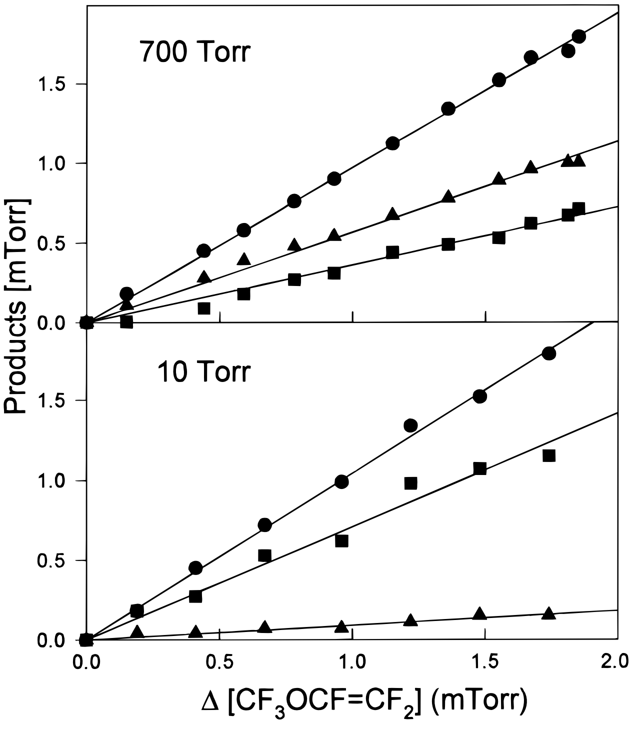


Figure 6. Formation of COF_2 (circles), $CF_3OC(O)F$ (triangles), and FC(O)C(O)F (squares) versus loss of $CF_3OCF{=}CF_2$ following the UV irradiation of $CF_3OCF{=}CF_2/CH_3ONO/NO$ at 296 K in either 700 (top panel) or 11 Torr (bottom panel) of air diluent.

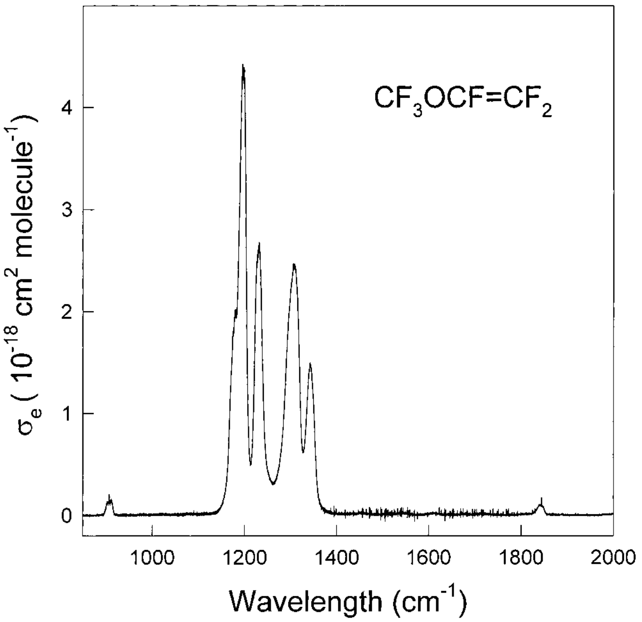


Figure 7. Infrared spectrum of $CF_3OCF{=}CF_2$.

4. Implications for Atmospheric Chemistry

We present herein a substantial body of kinetic and mechanism data pertaining to the atmospheric chemistry of $CF_3OCF{=}CF_2$ (HFE-216). The atmospheric lifetime of HFE-216 is determined by its reaction with OH radicals which occurs with a rate constant of $k_1 = (2.6 \pm 0.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 296 K in 700 Torr of air. The atmospheric lifetime of $CF_3OCF{=}CF_2$ with respect to reaction with OH can be estimated using three pieces of information: the value of k_1 given above, $k(OH + CCl_3CH_3) = 1.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K,[8] and the atmospheric lifetime of CCl_3CH_3 with respect to reaction with OH = 5.9 years.[14] This approach gives an atmospheric lifetime of $CF_3OCF{=}CF_2$ with respect to reaction with OH of 0.023 years (8 days).

The OH radical initiated atmospheric oxidation of $CF_3OCF{=}CF_2$ gives COF_2, $CF_3OC(O)F$, and $FC(O)C(O)F$ in molar yields of 90, 53, and 40%. As with other fluorinated carbonyl compounds the atmospheric fate of COF_2, $CF_3OC(O)F$, and $FC(O)C(O)F$ is expected to be incorporation into water droplets within a time frame of 5−15 days followed by hydrolysis to give HF and CO_2.[13] The atmospheric degradation of HFEs produces the same fluorinated radical species as formed during the degradation of HFCs. HFCs do not impact stratospheric ozone[15] and the same conclusion applies to HFEs; $CF_3OCF{=}CF_2$ has an ozone depletion potential of zero.

Finally, we need to consider the potential for $CF_3OCF{=}CF_2$ to impact the radiative balance in the atmosphere. The infrared spectrum of $CF_3OCF{=}CF_2$ is shown in Figure 7. The absorption cross section for $CF_3OCF{=}CF_2$ integrated over the range 1100−1200 cm^{-1} is $(2.67 \pm 0.30) \times 10^{-16}$ cm molecule^{-1} (base e), quoted errors reflect our estimate of the total accuracy of the measurement, and is consistent with the previous determination of 2.48×10^{-16} cm molecule^{-1}.[5] The method of Pinnock et al.[16] was used to calculate the instantaneously cloudy-sky radiative forcing of $CF_3OCF{=}CF_2$, from the measured absorption cross section. The instantaneous radiative forcings of $CF_3OCF{=}CF_2$ and CFC-11 were calculated to be 0.28 W/m^2 and 0.26 W/m^2, respectively. The global warming potential (GWP) was estimated using the expression

$$\mathrm{GWP}_t = \frac{\mathrm{IF}_{CF_3OCF{=}CF_2}}{\mathrm{IF}_{CFC-11}} \frac{\tau_{CF_3OCF{=}CF_2}}{\tau_{CFC-11}} \frac{M_{CFC-11}}{M_{CF_3OCF{=}CF_2}} \times \frac{1 - \exp\left(-\frac{t}{\tau_{CF_3OCF{=}CF_2}}\right)}{1 - \exp\left(-\frac{t}{\tau_{CFC-11}}\right)}$$

where IF, τ, and M are the radiative forcing, lifetime, and molecular weight of the two compounds and t is the time horizon over which the forcing is integrated. Using $\tau_{CF_3OCF{=}CF_2} = 8$ days and $\tau_{CFC-11} = 50$ years we estimate that the GWP of $CF_3OCF{=}CF_2$ is $\approx 1.20 \times 10^{-3}$ for a 20 year horizon and $\approx 4.57 \times 10^{-4}$ for a 100 year time horizon. The GWP of $CF_3OCF{=}CF_2$ is negligible. A similar conclusion was been reached by Li et al.[5]

Acknowledgment. We thank the Japanese Government for a NEDO grant which made this collaborative research project possible.

References and Notes

(1) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.

(2) Farman, J. D.; Gardiner, B. G.; Shanklin, J. D. *Nature* **1985**, *315*, 207.

(3) Product information sheet from 3M Specialty Chemicals Division, 1996.

(4) Sekiya, A.; Takagaki, T.; Morikawa, S.; Yamashita, S.; Takaichi, A.; Hibino, Y.; Furutaka, Y.; Otsuka, N. *Jpn. Kokai Tokkyo Koho*, 1999.

(5) Li, Z.; Tao, Z.; Naik, V.; Good, D. A.; Hansen, J.; Jeong, G. R.; Francisco, J. S.; Jain, A.; Wuebbles, D. J. *J. Geophys. Res.*, in press.

(6) Calvert, J. G.; Atkinson, R.; Kerr, J. A.; Madronich, S.; Moortgat, G. K.; Wallington, T. J.; Yarwood, G. *Mechanisms of the Atmospheric Oxidation of the Alkenes*; Oxford University Press: New York, 1999.

(7) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.

(8) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Jet Propulsion Laboratory Publication 97-4*, Pasadena, CA, 1997.

(9) Wine, P. H.; Semmes, D. H. *J. Phys. Chem.* **1983**, *87*, 3572.

(10) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521.

(11) Johnston, T.; Heicklen, J.; Stuckey, W. *Can. J. Chem.* **1968**, *46*, 332.

(12) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. *Chem. Rev.* **1992**, *92*, 667.

(13) Wallington, T. J.; Schneider, W. F.; Worsnop, D. R.; Nielsen, O. J.; Sehested, J.; DeBruyn, W.; Shorter, J. A. *Environ. Sci. Technol.* **1994**, *28*, 320A.

(14) Intergovernmental Panel on Climate Change (IPCC), The Science of Climate Change, Cambridge University Press: New York, 1995.

(15) Wallington, T. J.; Schneider, W. F.; Sehested, J.; Nielsen, O. J. *J. Chem. Soc., Faraday Discuss.* **1995**, *100*, 55.

(16) Pinnock, S.; Hurley, M. D.; Shine, K. P.; Wallington, T. J.; Smyth, T. J. *J. Geophys. Res.* **1995**, *100*, 23227.