J. Phys. Chem. A **2002,** *106,* 8391−8398

Atmospheric Chemistry of $CF_3CH_2OCHF_2$ and $CF_3CHClOCHF_2$: Kinetics and Mechanisms of Reaction with Cl Atoms and OH Radicals and Atmospheric Fate of $CF_3C(O\bullet)HOCHF_2$ and $CF_3C(O\bullet)ClOCHF_2$ Radicals†

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

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

V. Fedotov

Institute of Chemical Physics, Russian Academy of Sciences, Moscow V-94, Russia

C. Morrell and G. Hancock

Department of Physical Chemistry, Oxford University, Oxford OX1 3QZ, U.K.

Received: January 9, 2002; In Final Form: April 26, 2002

Relative rate techniques were used to measure $k(\mathrm{Cl} + CF_3CH_2OCHF_2) = (1.2 \pm 0.1) \times 10^{-14}$, $k(\mathrm{Cl} + CF_3CHClOCHF_2) = (5.4 \pm 0.5) \times 10^{-15}$, $k(\mathrm{Cl} + HC(O)OCHF_2) = (2.0 \pm 0.2) \times 10^{-14}$, and $k(\mathrm{Cl} + CF_3C(O)OCHF_2) < 4 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 295 K. Cl atoms react with $CF_3CHClOCHF_2$ (isoflurane, HCFE-235da2) via H-atom abstraction to give $CF_3C(\bullet)ClOCHF_2$ and $CF_3CHClOC(\bullet)F_2$ radicals in yields of 92% and 8%. OH radicals react with $CF_3CHClOCHF_2$ via H-atom abstraction to give $CF_3C(\bullet)ClOCHF_2$ and $CF_3CHClOC(\bullet)F_2$ radicals in yields of 95% and 5%. $CF_3C(\bullet)ClOCHF_2$ and $CF_3CHClOC(\bullet)F_2$ add O_2 to give peroxy radicals which react with NO to give the alkoxy radicals $CF_3C(O\bullet)ClOCHF_2$ and $CF_3CHClOC(O\bullet)F_2$. The atmospheric fate of $CF_3C(O\bullet)ClOCHF_2$ radicals is decomposition via elimination of a Cl atom to give $CF_3C(O)OCHF_2$ and is unaffected by the method used to generate the $CF_3C(O\bullet)ClOCHF_2$ radicals. Reaction of Cl atoms with $CF_3CH_2OCHF_2$ (HFE-245fa2) proceeds via H-atom abstraction to give $CF_3C(\bullet)HOCHF_2$ radicals in a yield which is indistinguishable from 100%. The fate of the alkoxy radical $CF_3C(O\bullet)HOCHF_2$ is affected by the method in which it is generated. There are two competing fates for $CF_3C(O\bullet)HOCHF_2$ radicals formed by the reaction of $CF_3C(OO\bullet)HOCHF_2$ with other peroxy radicals; bimolecular reaction with O_2 to give $CF_3C(O)OCHF_2$ and unimolecular decomposition via C−C bond scission to give a CF_3 radical and $HC(O)OCHF_2$. In contrast, decomposition is the only observable fate of $CF_3C(O\bullet)HOCHF_2$ produced via the $CF_3C(OO\bullet)HOCHF_2$ + NO reaction. We ascribe this observation to the formation of vibrationally excited $CF_3C(O\bullet)HOCHF_2$ radicals in the $CF_3C(OO\bullet)HOCHF_2$ + NO reaction. IR spectra of $CF_3C(O)OCHF_2$ and $HC(O)OCHF_2$ are presented. The results are discussed with respect to the atmospheric chemistry of $CF_3CHClOCHF_2$ and other ethers.

1. Introduction

Trifluoroacetic acid, $CF_3C(O)OH$, has been detected in surface waters (oceans, rivers, and lakes) and in fog, snow, and rainwater samples around the globe[1−4] and is a ubiquitous component of the hydrosphere. No significant natural sources of trifluoroacetic acid have been identified,[5] and it is believed that trifluoroacetic acid is *not* a natural component of the freshwater environment.[6] There is a significant research effort focused on the identification and quantification of anthropogenic $CF_3C(O)OH$ sources. The atmospheric degradation of the anesthetic halothane ($CF_3CHClBr$) and the CFC replacement HFC-134a (CF_3CFH_2) gives $CF_3C(O)OH$ fluxes of approximately 520 and 1200 metric tons year^{-1}.[7,8] Pyrolysis of fluoropolymers also appears to be a significant source of $CF_3C(O)OH$.[3,9] While the global production of fluoropolymers is substantial (40 000 metric tons year^{-1} in 1988[3]), it is unclear what fraction undergoes pyrolysis and conversion to $CF_3C(O)OH$.

Isoflurane ($CF_3CHClOCHF_2$) is an anesthetic and is emitted into the atmosphere at a rate of approximately 750 metric tons year^{-1}.[5] The atmospheric oxidation of $CF_3CHClOCHF_2$ is initiated by reaction with OH radicals which is expected to proceed predominantly via H-atom abstraction to give the $CF_3C(\bullet)ClOCHF_2$ radical.[10] In the atmosphere this radical will add O_2 rapidly to give the corresponding peroxy radical.

$$CF_3CHClOCHF_2 + OH \rightarrow CF_3C(\bullet)ClOCHF_2 + H_2O \quad (1a)$$

$$CF_3C(\bullet)ClOCHF_2 + O_2 + M \rightarrow CF_3C(OO\bullet)ClOCHF_2 + M \quad (2)$$

It is expected that $CF_3C(OO\bullet)ClOCHF_2$ radicals will react with NO to give the corresponding alkoxy radical and possibly the nitrate $CF_3C(ONO_2)ClOCHF_2$.[7]

$$CF_3C(OO\bullet)ClOCHF_2 + NO \rightarrow CF_3C(O\bullet)ClOCHF_2 + NO_2 \quad (3a)$$

$$CF_3C(OO\bullet)ClOCHF_2 + NO + M \rightarrow CF_3C(ONO_2)ClOCHF_2 + M \quad (3b)$$

---

† Part of the special issue “Donald Setser Festschrift”.

10.1021/jp020017z CCC: \$22.00

There are three possible fates of the $CF_3C(O\bullet)ClOCHF_2$ radical: elimination of a Cl atom, CHF_2O radical, or CF_3 radical.

$$CF_3C(O\bullet)ClOCHF_2 \rightarrow Cl\bullet + CF_3C(O)OCHF_2 \quad (4)$$

$$CF_3C(O\bullet)ClOCHF_2 \rightarrow CF_3C(O)Cl + \bullet OCHF_2 \quad (5)$$

$$CF_3C(O\bullet)ClOCHF_2 \rightarrow CF_3\bullet + ClC(O)OCHF_2 \quad (6)$$

The first two possible fates lead to species ($CF_3C(O)OCHF_2$ and $CF_3C(O)Cl$) that will undergo hydrolysis to give $CF_3C(O)OH$. In process 6 the C−C bond is broken and there will be no formation of $CF_3C(O)OH$. There is no available information concerning the relative importance of processes 4−6 in the atmospheric chemistry of isoflurane. To assess the contribution of isoflurane to the $CF_3C(O)OH$ budget, we have conducted an experimental study of the atmospheric oxidation products of isoflurane. For completeness, the oxidation mechanism of the related compound $CF_3CH_2OCHF_2$ (HFE-245fa2) was also studied. Results are reported herein.

2. Experimental Section

All experiments were performed using a 140-L Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer described in detail elsewhere.[11] The reactor was surrounded by 22 fluorescent blacklamps which were used to photochemically initiate the experiments. The oxidation of $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$ was initiated by reaction with Cl atoms or OH radicals in 700 Torr of N_2/O_2 diluent at 295 ± 2 K. The loss of $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$ and the formation of products were monitored by Fourier transform infrared spectroscopy using an infrared path length of 27 m and a spectral resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms.

Three sets of experiments were performed. First, relative rate techniques were used to study the kinetics of the reactions of Cl atoms with $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$. Second, the products of the Cl atom initiated oxidation of $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$ were investigated by irradiating $CF_3CHClOCHF_2/Cl_2/O_2/N_2$ and $CF_3CH_2OCHF_2/Cl_2/O_2/N_2$ mixtures. Third, the products of the OH radical initiated oxidation of $CF_3CHClOCHF_2$ were determined by irradiating mixtures containing $CF_3CHClOCHF_2$, CH_3ONO, and NO in air.

Initial concentrations of the gas mixtures for the relative rate experiments were 4−6 mTorr of reactant ($CF_3CHClOCHF_2$ or $CF_3CH_2OCHF_2$), 12−28 mTorr of reference (CH_4 or CD_4), and 296−701 mTorr of Cl_2 in 700 Torr of air diluent. In the Cl atom initiated product studies, reaction mixtures contained 4−6 mTorr reactant ($CF_3CHClOCHF_2$ or $CF_3CH_2OCHF_2$), 111−1820 mTorr Cl_2, and 0−700 Torr O_2 in 700 Torr of N_2 diluent. For the OH-initiated experiments, the reaction mixtures contained 438−672 mTorr of $CF_3CHClOCHF_2$, 157−216 mTorr of CH_3ONO, 4−5 mTorr of C_2H_4, and 5−6 mTorr of NO in 700 Torr of air diluent. All experiments were performed at 295 K. The samples of $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$ used in this work were supplied by the Solvay Chemical Company at stated purities of >99.99% and were subjected to repeated freeze−pump−thaw cycling before use. The uncertainties reported in this paper are two standard deviations unless otherwise stated. Standard error propagation methods were used to combine uncertainties where appropriate.

3. Results

3.1. Relative Rate Studies of the Reactions of Cl with $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$.

Prior to investigating the atmospheric fate of alkoxy radicals, relative rate experiments were performed to investigate the kinetics of reactions 8 and 9. The techniques used are described in detail elsewhere.[12] Cl atoms were generated by photolysis of molecular chlorine.

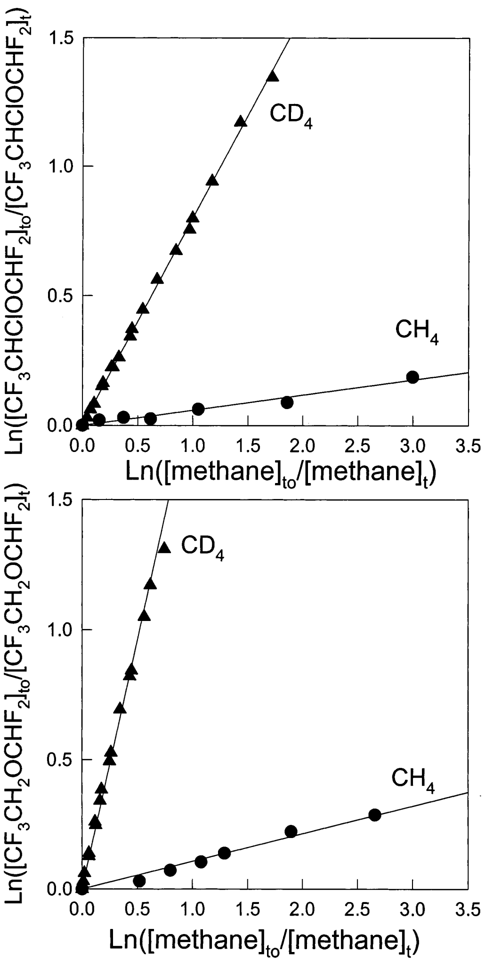

Figure 1. Decay of $CF_3CHClOCHF_2$ (top panel) and $CF_3CH_2OCHF_2$ (bottom panel) versus CD_4 (triangles) and CH_4 (circles) in the presence of Cl atoms in 700 Torr of air at 295 K.

$$Cl_2 + h\nu \rightarrow 2Cl \quad (7)$$

The kinetics of reactions 8 and 9 were measured relative to reactions 10 and 11.

$$Cl + CF_3CHClOCHF_2 \rightarrow products \quad (8)$$

$$Cl + CF_3CH_2OCHF_2 \rightarrow products \quad (9)$$

$$Cl + CH_4 \rightarrow products \quad (10)$$

$$Cl + CD_4 \rightarrow products \quad (11)$$

The observed losses of $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$ versus those of reference compounds in the presence of Cl atoms are shown in Figure 1. Linear least-squares analysis of the data in Figure 1 gives $k_8/k_{10} = 0.06 \pm 0.01$, $k_8/k_{11} = 0.80 \pm 0.07$, $k_9/k_{10} = 0.12 \pm 0.01$, and $k_9/k_{11} = 1.90 \pm 0.10$. Multiplication of these ratios by literature values for k_{10} and k_{11} provides two independent determinations of k_8 and k_9. Using $k_{10} = 1.0 \times 10^{-13}$[13] and $k_{11} = 6.1 \times 10^{-15}$[12] gives $k_8 = (6.0 \pm 1.0) \times 10^{-15}$, $k_8 = (4.9 \pm 0.5) \times 10^{-15}$, $k_9 = (1.20 \pm 0.10) \times 10^{-14}$, and $k_9 = (1.16 \pm 0.06) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. We

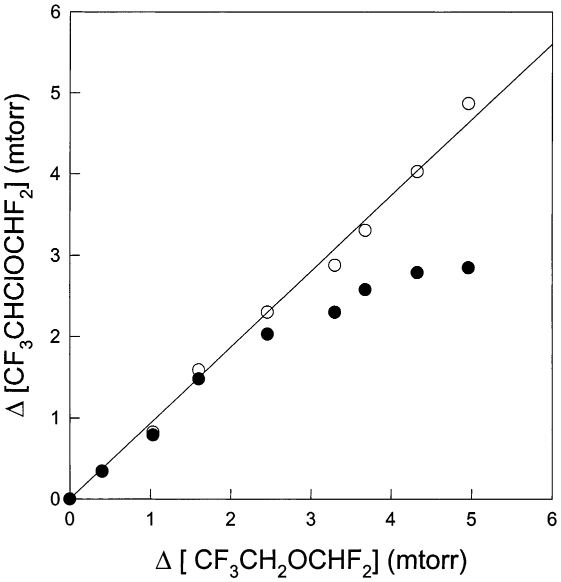

Figure 2. Formation of isoflurane $CF_3CHClOCHF_2$ versus loss of $CF_3CH_2OCHF_2$ following irradiation of mixtures of 5 mTorr of $CF_3CH_2OCHF_2$ and 1.5 Torr of Cl_2 in 700 Torr of N_2 diluent. Filled symbols are the observed data; open symbols have been corrected for secondary reaction with Cl atoms; see text for details.

estimate that potential systematic errors associated with uncertainties in the reference rate constants contribute an additional 10% uncertainty range for k_8 and k_9. Propagating this additional uncertainty gives $k_8 = (6.0 \pm 1.2) \times 10^{-15}$, $k_8 = (4.9 \pm 0.7) \times 10^{-15}$, $k_9 = (1.20 \pm 0.16) \times 10^{-14}$, and $k_9 = (1.16 \pm 0.13) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. We choose to cite final values of k_8 and k_9 which are averages of those determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k_8 = (5.5 \pm 1.7) \times 10^{-15}$ and $k_9 = (1.2 \pm 0.2) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}.

There have been three previous studies of k_8 and k_9. Kambanis et al.[14] used a very low pressure reactor to measure k_9 in helium diluent (the total pressure was not specified but was probably a few millitorr) and reported $k_9 = (3.11 \pm 0.14) \times 10^{-14}$ at 303 K. Hickson and Smith[15] used relative rate methods in 700 Torr of N_2/O_2 diluent and reported $k_8 = (4.3 \pm 0.7) \times 10^{-15}$ and $k_9 = (1.2 \pm 0.2) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 295 K. Beach et al.[16] employed a discharge flow resonance fluorescence technique in 2.0−3.4 Torr of helium diluent and measured $k_8 = (5.9 \pm 0.5) \times 10^{-15}$ at 294 K and $k_9 = (1.1 \pm 0.1) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 318 K. The results from the present work and the previous studies of Hickson and Smith[15] and Beach et al.[16] are indistinguishable within the experimental uncertainties, while the value of k_9 reported by Kambanis et al.[14] is approximately a factor of 2.5 times larger.

3.2. Mechanism of the Reaction of Cl Atoms with $CF_3CH_2OCHF_2$ and $CF_3CHClOCHF_2$. Experiments were conducted using $CF_3CH_2OCHF_2/Cl_2/N_2$ mixtures to provide information on the mechanism of the reaction of Cl atoms with $CF_3CH_2OCHF_2$. $CF_3CHClOCHF_2$ was the only product observed in these experiments. Figure 2 shows a plot of $CF_3CHClOCHF_2$ formed versus $CF_3CH_2OCHF_2$ consumed following UV irradiation of mixtures containing 5 mTorr of $CF_3CH_2OCHF_2$ and 1.5 Torr of Cl_2 in 700 Torr of N_2 diluent. The filled symbols are the observed data. The open symbols show the result of correction for secondary loss of $CF_3CHClOCHF_2$ via reaction with Cl atoms. Corrections were computed using values of k_8 and k_9 reported in section 3.1.[17] Linear least-squares analysis of the corrected data in Figure 2 gives a molar yield of $CF_3CHClOCHF_2$ of 95 ± 8%. The UV irradiation of $CF_3CH_2OCHF_2/Cl_2/N_2$ mixtures produces $CF_3CHClOCHF_2$ in a yield which is indistinguishable, within the experimental uncertainties, from 100%. We conclude that the reaction of Cl atoms with $CF_3CH_2OCHF_2$ proceeds essentially exclusively via attack at the $-CH_2-$ site to give $CF_3C(\bullet)HOCHF_2$ radicals which then react with molecular chlorine to give $CF_3CHClOCHF_2$.

Using $k_8/k_{10} = 0.06 \pm 0.01$, $k_8/k_{11} = 0.80 \pm 0.07$, $k_9/k_{10} = 0.12 \pm 0.01$, and $k_9/k_{11} = 1.90 \pm 0.10$ (reported in section 3.1), we can derive two independent determinations of $k_8/k_9 = 0.50 \pm 0.09$ and $k_8/k_9 = 0.42 \pm 0.05$. Substitution of one of the two hydrogens at the $-CH_2-$ site by a chlorine atom (i.e., $CF_3CH_2OCHF_2 \rightarrow CF_3CHClOCHF_2$) leads to a reduction in reactivity of the molecule of approximately a factor of 2. It seems reasonable to speculate that the majority of the reaction of Cl atoms with $CF_3CHClOCHF_2$ occurs at the secondary carbon atom. It would appear that the $-CHF_2$ group makes a minor contribution to the overall reactivity of $CF_3CH_2OCHF_2$ and $CF_3CHClOCHF_2$.

3.3. Atmospheric Fate of the Alkoxy Radical $CF_3C(O\bullet)ClOCHF_2$. The reaction of Cl atoms with $CF_3CHClOCHF_2$ generates $CF_3C(\bullet)ClOCHF_2$ radicals. $CF_3C(\bullet)ClOCHF_2$ radicals are expected to react rapidly with O_2 to give peroxy radicals. The peroxy radicals will undergo self-reaction to give the alkoxy radical, $CF_3C(O\bullet)ClOCHF_2$. The Cl atom initiated oxidation of $CF_3CHClOCHF_2$ in air provides a convenient method to study the atmospheric fate of $CF_3C(O\bullet)ClOCHF_2$ radicals.

Figure 3 shows spectra acquired before (A) and after (B) a 3 min UV irradiation of a mixture of 6 mTorr of $CF_3CHClOCHF_2$, 207 mTorr of Cl_2, and 10 Torr of O_2 in 700 Torr of N_2 diluent. Panel C in Figure 3 shows the product spectrum obtained by subtracting features attributable to $CF_3CHClOCHF_2$ from panel A. By comparison of the 1900−2000 cm^{-1} region in panel C with the reference spectrum of COF_2 (panel D), it was determined that COF_2 is a product. IR features attributable to $CF_3C(O)Cl$ and $CF_3O_3CF_3$ (product expected if CF_3 radicals are formed in chamber[7]) were sought but not found. Upper limits of 3% and 5% were derived for the molar yields of $CF_3C(O)Cl$ and $CF_3O_3CF_3$, respectively.

There are three possible fates of the $CF_3CCl(O\bullet)OCHF_2$ radical: elimination of either a Cl atom, CHF_2O radical, or CF_3 radical.

$$CF_3C(O\bullet)ClOCHF_2 \rightarrow Cl\bullet + CF_3C(O)OCHF_2 \quad (4)$$

$$CF_3C(O\bullet)ClOCHF_2 \rightarrow CF_3C(O)Cl + \bullet OCHF_2 \quad (5)$$

$$CF_3C(O\bullet)ClOCHF_2 \rightarrow CF_3\bullet + ClC(O)OCHF_2 \quad (6)$$

The absence of any observable $CF_3C(O)Cl$ or $CF_3O_3CF_3$ shows that pathways 5 and 6 are of minor importance. By a process of elimination, we conclude that pathway 4 is the major fate of $CF_3C(O\bullet)ClOCHF_2$ radicals.

Subtraction of IR features attributed to COF_2 from panel C in Figure 3 gives the residual spectrum shown in panel E. The features in panel E scaled linearly in all experiments suggesting, but not proving, that they are attributable to one product. We assign the spectrum in panel E to $CF_3C(O)OCHF_2$ formed in reaction 4. The IR features at 1050, 1117, 1200, 1250, and 1827 cm^{-1} can be assigned to $\nu(C-F)$, $\nu(C_O-O)$, $\nu(C_F-O)$, $\nu(F-C_O)$, and $\nu(C=O)$ stretches, respectively.[18]

Experiments were conducted using $CF_3CHClOCHF_2/Cl_2/O_2/N_2$ mixtures with the oxygen partial pressure varied over the

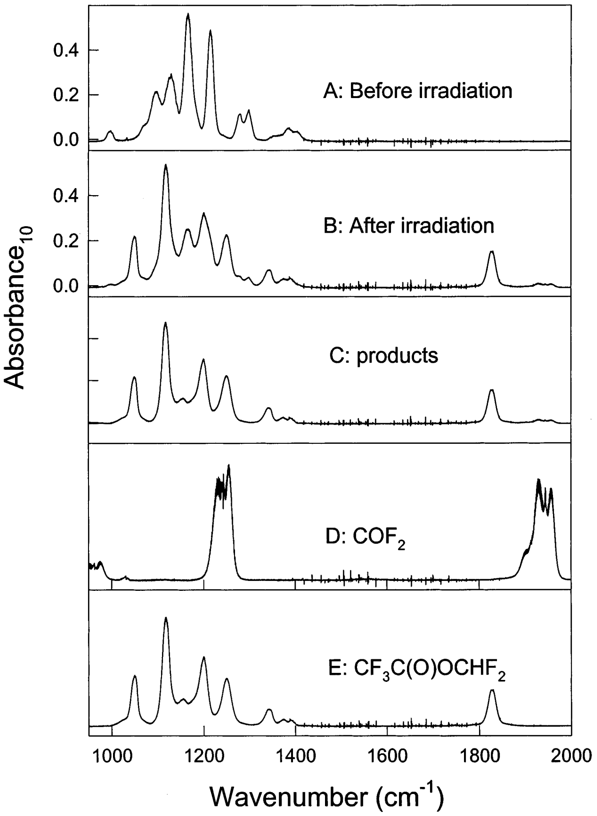

Figure 3. IR spectra of a mixture of 6 mTorr of $CF_3CHClOCHF_2$, 207 mTorr of Cl_2, and 10 Torr of O_2 in 700 Torr of N_2 before (A) and after (B) 3 min UV irradiation. Panel C is the product spectrum obtained by subtracting features attributable to $CF_3CHClOCHF_2$ from panel B ($C = B - 0.28A$). Panel D shows a COF_2 reference spectrum. Subtraction of COF_2 features from panel C gives the features shown in panel E which we assign to $CF_3C(O)OCHF_2$.

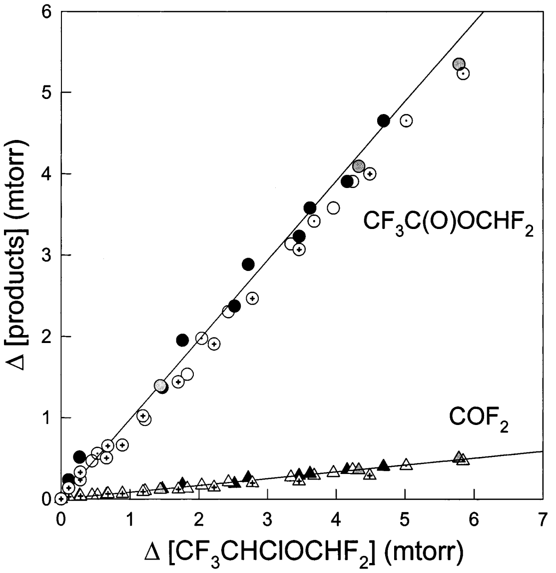

Figure 4. Formation of $CF_3C(O)OCHF_2$ (circles) and COF_2 (triangles) versus loss of $CF_3CHClOCHF_2$ following UV irradiation of $CF_3CHClOCHF_2/Cl_2$ mixtures in 700 Torr of N_2/O_2 diluent with $[O_2]$ = 700 (open symbols), 147 (filled symbols), 10 (light gray symbols), or 3 Torr (dotted symbols). Results from experiments conducted using $CF_3CHClOCHF_2/Cl_2$/NO/air mixtures are indicated by the open symbols with crosses.

range 3−700 Torr. As shown in Figure 4, there was no discernible effect of $[O_2]$ on the observed COF_2 and $CF_3C(O)OCHF_2$ yield. Linear least-squares analysis of the COF_2 data gives a molar yield of 8.2 ± 0.6%. There are two possible mechanisms by which COF_2 can be formed following the UV irradiation of $CF_3CHClOCHF_2/Cl_2/O_2/N_2$ mixtures. The first possibility is that $CF_3C(O\bullet)ClOCHF_2$ radicals decompose via reaction 5 to generate $\bullet OCHF_2$ radicals which will react with O_2 to give COF_2:

$$\bullet OCHF_2 + O_2 \rightarrow COF_2 + HO_2 \qquad (12)$$

If reaction 5 followed by reaction 12 were the source of the COF_2, we would observe $CF_3C(O)Cl$ in a molar yield indistinguishable from that of COF_2 (i.e., 8.2 ± 0.6%). The second possibility is that a small fraction (e.g., 8%) of the reaction of Cl atoms with $CF_3CHClOCHF_2$ proceeds via attack at the $-OCHF_2$ moiety leading to the formation of $CF_3CHClOCF_2O(\bullet)$ radicals which then decompose:

$$CF_3CHClOCF_2O(\bullet) \rightarrow CF_3CHClO(\bullet) + CF_2O \qquad (13)$$

$CF_3CHClO(\bullet)$ radicals formed in reaction 13 undergo unimolecular decomposition (via either C−C bond scission, Cl atom elimination, or three center HCl elimination[19]) and bimolecular reaction with O_2.

$$CF_3CHClO(\bullet) \rightarrow \text{decomposition products} \qquad (14)$$

$$CF_3CHClO(\bullet) + O_2 \rightarrow CF_3C(O)Cl + HO_2(\bullet) \qquad (15)$$

While the relative importance of reactions 14 and 15 for $CF_3CHClO(\bullet)$ radicals produced in reaction 13 is unknown, it is clear that if reaction 13 were the source of COF_2 we would observe $CF_3C(O)Cl$ formation in a molar yield less than, or equal to, that of COF_2 (i.e., <8.2%). As noted above, $CF_3C(O)Cl$ was not an observed product in the experiments. The upper limit for the molar yield of $CF_3C(O)Cl$ (<3%) is inconsistent with the first possible mechanism for COF_2 formation but is consistent with the second. The simplest explanation of the observed formation of COF_2 is that reaction 8 proceeds via two channels with $k_{8b}/(k_{8a} + k_{8b}) = 0.082 \pm 0.006$ and that reaction 13 is the source of COF_2

$$Cl + CF_3CHClOCHF_2 \rightarrow CF_3CCl(\bullet)OCHF_2 + HCl \qquad (8a)$$

$$Cl + CF_3CHClOCHF_2 \rightarrow CF_3CHClOC(\bullet)F_2 + HCl \qquad (8b)$$

Calibration of the $CF_3C(O)OCHF_2$ reference spectrum was achieved by assuming that $CF_3C(O)OCHF_2$ was formed in a yield $= k_{8a}/(k_{8a} + k_{8b}) = 0.918$. The integrated absorption cross section of the carbonyl stretch of $CF_3C(O)OCHF_2$ at 1800−1855 cm^{-1} was $(2.1 \pm 0.4) \times 10^{-17}$ cm molecule^{-1}. The quoted uncertainty reflects an assessment of the accuracy (±20%) of the measurement. As seen from Figure 4, the concentration of $CF_3C(O)OCHF_2$ increased linearly with the loss of $CF_3CHClOCHF_2$. This linearity suggests that the reactivity of Cl atoms toward $CF_3C(O)OCHF_2$ is substantially lower than that toward $CF_3CHClOCHF_2$. The reactivity of Cl atoms toward $CF_3C(O)OCHF_2$ was quantified by irradiating $CF_3CHClOCHF_2/Cl_2$/air mixtures until all (>98%) of the $CF_3CHClOCHF_2$ was consumed, adding CD_4, resuming UV irradiation, and monitoring the subsequent loss of $CF_3C(O)OCHF_2$ and CD_4. In such experiments there was no observable loss (<2%) of $CF_3C(O)OCHF_2$ while there was up to 96% consumption of CD_4. Using $k(Cl + CD_4) = 6.1 \times 10^{-15}$,[12] an upper limit of $k(Cl + CF_3C(O)OCHF_2) < 4 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} is derived.

Alkoxy radicals formed in the reaction of peroxy radicals with NO possess vibrational excitation which may influence the importance of decomposition pathways.[20] To check for such effects, experiments were performed using the irradiation of $CF_3CHClOCHF_2/Cl_2/NO$ mixtures in 700 Torr of N_2/O_2. As seen from Figure 4, the $CF_3C(O)OCHF_2$ yield in the presence of NO was indistinguishable, within experimental uncertainties, from that in the absence of NO. We conclude that the atmospheric fate of $CF_3C(O\bullet)ClOCHF_2$ radicals is decomposition via elimination of a Cl atom to give CF_3 $C(O)OCHF_2$ and is unaffected by the method used to generate the $CF_3C(O\bullet)ClOCHF_2$ radicals (reaction of $CF_3C(OO\bullet)ClOCHF_2$ with either NO or with other peroxy radicals).

$$CF_3C(OO\bullet)ClOCHF_2 + RO_2 \rightarrow CF_3C(O\bullet)ClOCHF_2 + RO + O_2 \quad (16)$$

$$CF_3C(OO\bullet)ClOCHF_2 + NO \rightarrow CF_3C(O\bullet)ClOCHF_2 + NO_2 \quad (3a)$$

From Figure 4 it can be seen that the yields of COF_2 observed in experiments conducted in the presence and absence of NO are indistinguishable. This observation is surprising, as it would be expected that in the presence of NO the $CF_3CHClO(\bullet)$ radicals produced in reaction 13 would be converted into COF_2[7]

$$CF_3CHClO(\bullet) \rightarrow CF_3(\bullet) + HC(O)Cl$$

$$CF_3(\bullet) + O_2 + M \rightarrow CF_3OO(\bullet) + M$$

$$CF_3OO(\bullet) + NO \rightarrow CF_3O(\bullet) + NO_2$$

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

while in the absence of NO the there would be no such conversion.

$$CF_3CHClO(\bullet) \rightarrow CF_3(\bullet) + HC(O)Cl$$

$$CF_3(\bullet) + O_2 + M \rightarrow CF_3OO(\bullet) + M$$

$$CF_3OO(\bullet) + CF_3OO(\bullet) \rightarrow CF_3O^{(\bullet)} + CF_3O(\bullet) + O_2$$

$$CF_3OO(\bullet) + CF_3O(\bullet) \rightarrow CF_3OOOCF_3$$

Hence, we would expect the COF_2 yield in the presence of NO to be twice that in the absence of NO. It appears that $CF_3CHClO(\bullet)$ radicals are not converted effectively into COF_2 in the present experiments. A possible explanation for this observation is that $CF_3CHClO(\bullet)$ radicals are converted into $CF_3CO(\bullet)$ (either by intramolecular HCl elimination or via Cl atom elimination followed by secondary reaction of CF_3CHO with Cl atoms) and that these radicals add O_2 and then NO_2 to give the relatively stable peroxy nitrate $CF_3C(O)OONO_2$, thereby preventing further COF_2 formation. At the concentrations expected in the present experiments (<0.5 mTorr), $CF_3C(O)OONO_2$ would escape detection by FTIR analysis.

3.4. Atmospheric Fate of the Alkoxy Radical $CF_3C(O\bullet)HOCHF_2$. To investigate the atmospheric fate of $CF_3C(O\bullet)HOCHF_2$ radicals, $CF_3CH_2OCHF_2/Cl_2/N_2/O_2$ mixtures were introduced into the chamber and subjected to UV irradiation. The Cl atom initiated oxidation of $CF_3CH_2OCHF_2$ generated four carbon-containing products: COF_2, $CF_3O_3CF_3$, $CF_3C(O)OCHF_2$, and an unknown compound. Figure 5 shows IR spectra acquired before (A) and after (B) a 1 min UV irradiation of a mixture of 5.6 mTorr of $CF_3CH_2OCHF_2$ and 140 mTorr of Cl_2 in 700 Torr of O_2. The product feature at 1900−2000 cm^{-1} in panel B is attributable to COF_2 (see panel D in Figure 3). Subtraction of IR features attributable to $CF_3CH_2OCHF_2$ and COF_2 from panel B gives panel C (note change of *y*-axis scale). Comparison of panel C with a spectrum of $CF_3C(O)OCHF_2$ (panel D) demonstrates the formation of this species.

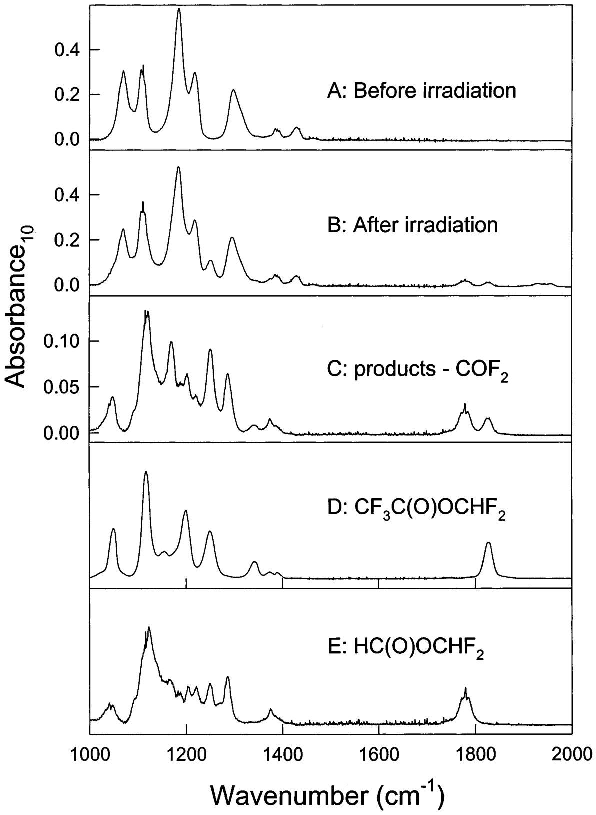

Figure 5. IR spectra of a mixture of 5.6 mTorr of $CF_3CH_2OCHF_2$ and 140 mTorr of Cl_2 in 700 Torr of O_2 before (A) and after (B) 1 min UV irradiation. Subtraction of IR features of $CF_3CH_2OCHF_2$ and COF_2 from panel B gives panel C. Subtraction of IR features of $CF_3C(O)OCHF_2$ (see panel D) and $CF_3O_3CF_3$ from panel C gives the residual spectrum shown in panel E which we attribute to $HC(O)OCHF_2$.

Experiments were performed using O_2 partial pressures varied over the range 50−700 Torr. Figure 6 shows the formation of $CF_3C(O)OCHF_2$ versus loss of $CF_3CH_2OCHF_2$ for experiments conducted using $[O_2]$ = 50, 105, 200, 415, and 700 Torr. Increasing O_2 partial pressure led to an increase in the $CF_3C(O)OCHF_2$ yield and a corresponding decrease in the yield of the unknown product. The simplest explanation of the experimental observations is that reactions 15 and 16 compete for the available $CF_3C(O\bullet)HOCHF_2$ radicals and that the unknown is $HC(O)OCHF_2$.

$$CF_3C(O\bullet)HOCHF_2 \rightarrow CF_3 + HC(O)OCHF_2 \quad (17)$$

$$CF_3C(O\bullet)HOCHF_2 + O_2 \rightarrow HO_2 + CF_3C(O)OCHF_2 \quad (18)$$

Subtraction of features attributable to $CF_3C(O)OCHF_2$ and $CF_3O_3CF_3$ from panel D in Figure 5 gives the residual spectrum shown in panel E in Figure 5 which we assign to $HC(O)OCHF_2$. By analogy to the published spectrum of $HC(O)OCF_3$,[18] the IR features at 1043, 1123, 1248, 1285, 1375, and 1780 cm^{-1} can be assigned to ν(C−F), ν(C_O−O), ν(F−C_O), ν(F−C_O), ν(H−C_H−O), and ν(C=O) stretches, respectively. The 1750−1810 cm^{-1} band in $HC(O)OCHF_2$ has an integrated absorption cross

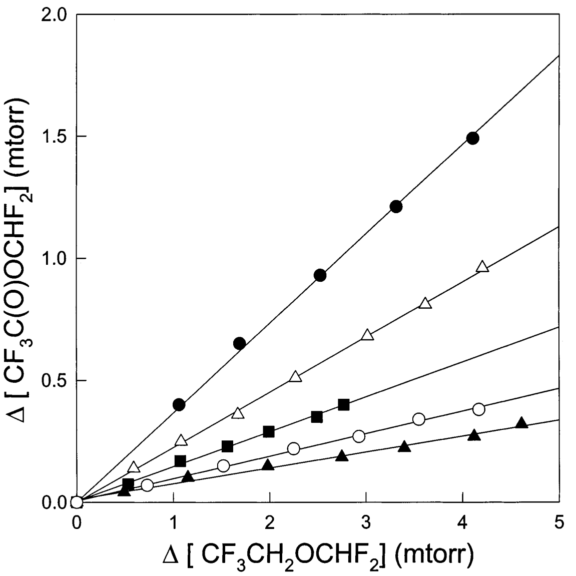

Figure 6. Formation of $CF_3C(O)OCHF_2$ versus loss of $CF_3CH_2OCHF_2$ following UV irradiation of $CF_3CH_2OCHF_2/Cl_2/O_2$ mixtures in 700 Torr of N_2 diluent with $[O_2] = 50$ (filled triangles), 105 (open circles), 200 (filled squares), 415 (open triangles), or 700 Torr (filled circles). Lines indicate linear least-squares fits to the data which give molar yields of 0.06 ± 0.01, 0.09 ± 0.01, 0.14 ± 0.01, 0.22 ± 0.02, and 0.36 ± 0.02.

section (base e) = $(2.3 \pm 0.7) \times 10^{-17}$ cm molecule^{-1} which is similar to the absorption strength of the 1770−1860 cm^{-1} band in $HC(O)OCF_3$: $(3.1 \pm 0.4) \times 10^{-17}$ cm molecule^{-1}.[18]

Figure 7A shows the observed formation of $HC(O)OCHF_2$, $CF_3C(O)OCHF_2$, and COF_2 following successive UV irradiations of the mixture of 6 mTorr of $CF_3CH_2OCHF_2$, 740 mTorr of Cl_2, and 400 Torr of O_2 in 700 Torr total pressure of N_2 diluent. As seen from Figure 7A, the formation of $CF_3C(O)OCHF_2$ increased linearly with the $CF_3CH_2OCHF_2$ loss. In contrast to the behavior of $CF_3C(O)OCHF_2$, the data plots for $HC(O)OCHF_2$ and COF_2 in Figure 7A are distinctly curved. This behavior suggests that $HC(O)OCHF_2$ is consumed and COF_2 is formed via secondary reactions involving Cl atoms.

$$HC(O)OCHF_2 + Cl \rightarrow (\bullet)C(O)OCHF_2 + HCl \quad (19)$$

$$(\bullet)C(O)OCHF_2 + O_2 + M \rightarrow (\bullet)OOC(O)OCHF_2 + M \quad (20)$$

$$(\bullet)OOC(O)OCHF_2 + (\bullet)OOC(O)OCHF_2 \rightarrow (\bullet)OC(O)OCHF_2 + (\bullet)OC(O)OCHF_2 + O_2 \quad (21)$$

$$(\bullet)OC(O)OCHF_2 \rightarrow (\bullet)OCHF_2 + CO_2 \quad (22)$$

$$(\bullet)OCHF_2 + O_2 \rightarrow COF_2 + HO_2 \quad (12)$$

Figure 8 shows a plot of the yield of $HC(O)OCHF_2$ (expressed as a fraction of the initial $CF_3CH_2OCHF_2$ concentration) versus $CF_3CH_2OCHF_2$ consumption following UV irradiation of $CF_3CH_2OCHF_2/Cl_2$/air mixtures. The curvature of the data plot in Figure 8 is related to the rate constant ratio k_{19}/k_9 by the expression[17]

$$[HC(O)OCHF_2]/[CF_3CH_2OCHF_2]_0 = \alpha(k_{19}/k_9 - 1)^{-1}(1 - x)[(1 - x)^{(k_{19}/k_9 - 1)} - 1] \quad (I)$$

where α is the molar yield of $HC(O)OCHF_2$ following reaction 9, $[CF_3CH_2OCHF_2]_0$ is the initial concentration of $CF_3CH_2OCHF_2$, and x is the fractional loss of $CF_3CH_2OCHF_2$ at time t ($x = \Delta[CF_3CH_2OCHF_2]/[CF_3CH_2OCHF_2]_0$). The curve in

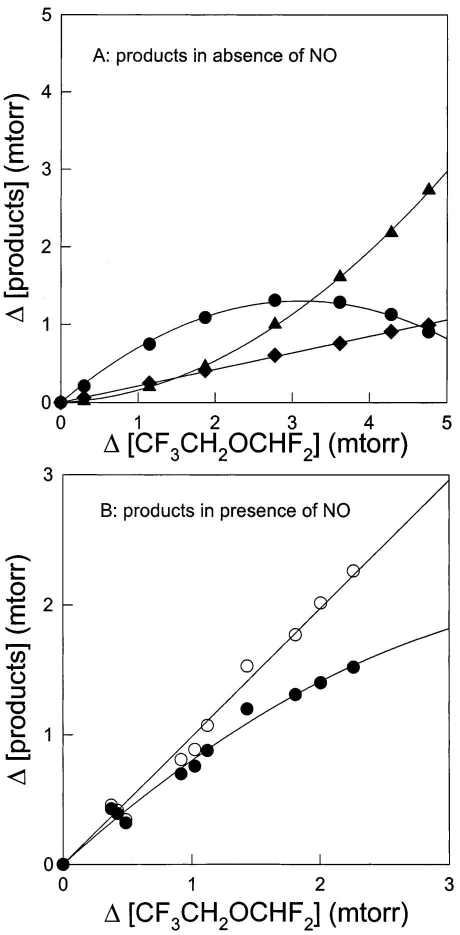

Figure 7. Formation of COF_2 (triangles), $HC(O)OCHF_2$ (circles), and $CF_3C(O)OCHF_2$ (diamonds) versus loss of $CF_3CH_2OCHF_2$ following irradiation of mixtures of 6 mTorr of $CF_3CH_2OCHF_2$, 740 mTorr of Cl_2, 400 Torr of O_2, and either 0 (top panel) or 16 mTorr (bottom panel) of NO in 700 Torr total pressure of N_2 diluent. The open symbols in the lower panel show the result of correction for secondary reactions involving Cl atoms; see text for details.

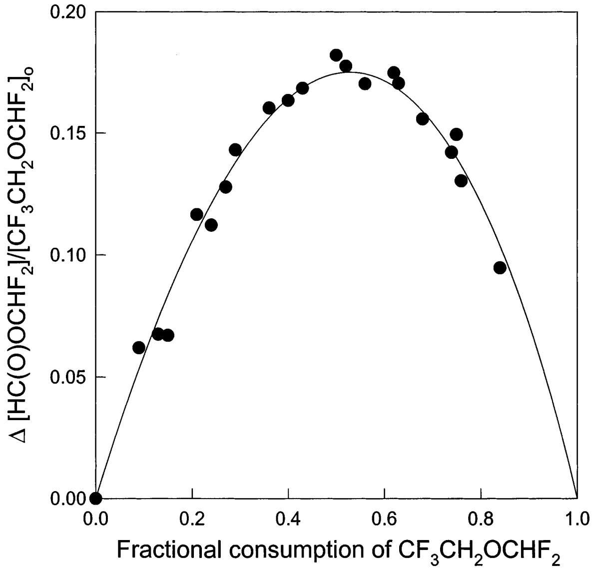

Figure 8. Concentration of $HC(O)OCHF_2$ normalized to the initial concentration of $CF_3CH_2OCHF_2$ versus the fractional consumption of $CF_3CH_2OCHF_2$ following irradiation of $CF_3CH_2OCHF_2/Cl_2$/air mixtures. The curve is a fit to the data (see text for details).

Figure 8 shows a fit of expression I to the data which yields $k_{19}/k_9 = 1.67 \pm 0.14$. Combining $k_{19}/k_9 = 1.67 \pm 0.14$ with $k_9 = (1.2 \pm 0.2) \times 10^{-14}$ gives $k_{19} = (2.0 \pm 0.4) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. This result can be compared to k(Cl + HC(O)OCH$_3$) = $(1.4 \pm 0.1) \times 10^{-12}$,[21] k(Cl + HC(O)OCF$_3$) = $(9.8 \pm 1.2) \times 10^{-15}$,[18] k(Cl + HC(O)OC$_3F_7$) = $(8.2 \pm 2.2) \times 10^{-15}$,[22] and k(Cl + HC(O)OC$_4F_9$) = $(1.6 \pm 0.7) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[23] Fluorination leads to a substantial decrease in the reactivity of formates toward Cl atoms. The reactivity of HC(O)OCHF$_2$ is comparable to that reported for similar fluoroformates.

As in the case of the decomposition pathway of $CF_3C(O\bullet)ClOCHF_2$ described above, the effect of vibrational excitation on the decomposition pathway of the $CF_3C(O\bullet)HOCHF_2$ alkoxy radical needs to be considered. To check for such effects, experiments were performed using the irradiation of the same mixture used for the experiments reported in Figure 7A but with the addition of 16 mTorr of NO. Following UV irradiation two products were observed: HC(O)OCHF$_2$ and COF$_2$. There was no observable formation of CF$_3$C(O)OCHF$_2$ (<5% yield). Figure 7B shows a plot of the formation of HC(O)OCHF$_2$ versus loss of CF$_3$CH$_2$OCHF$_2$ in the presence of NO. The filled symbols are the observed data; the open symbols have been corrected for loss of HC(O)OCHF$_2$ via reaction with Cl atoms. The straight line in Figure 7B is a linear least-squares fit to the corrected data which gives a molar HC(O)OCHF$_2$ yield of 99 ± 6%. Clearly, within the experimental uncertainties, the yield of HC(O)OCHF$_2$ accounts for 100% of the loss of CF$_3$CH$_2$OCHF$_2$. The presence of NO has a major impact on the product distribution. We conclude that chemical activation is an important factor in the fate of $CF_3C(O\bullet)HOCHF_2$ radicals. Alkoxy radicals formed via the self-reaction of peroxy radicals have little, if any, internal excitation while alkoxy radicals formed via reaction of peroxy radicals with NO can possess significant internal excitation.[20] The experimental results suggest that reaction of $CF_3C(OO\bullet)HOCHF_2$ radicals with NO produces vibrationally excited $CF_3C(O\bullet)HOCHF_2$ radicals that possess internal energy exceeding that necessary to overcome the barrier for C−C bond scission. The mechanism can be written as

$$CF_3CH(OO\bullet)OCHF_2 + NO \rightarrow CF_3CH(O\bullet)OCHF_2{}^* + NO_2$$

$$CF_3CH(O\bullet)OCHF_2{}^* \rightarrow CF_3 + HC(O)OCHF_3$$

Similar chemical activation effects have been reported for a variety of other alkoxy radicals (e.g., $CF_3CFHO\bullet$,[20] $HOCH_2CH_2O\bullet$,[24] and $CH_2ClO\bullet$ [25]).

3.5. Products of the OH Radical Initiated Oxidation of CF$_3$CHClOCHF$_2$. To provide insight into the mechanism of the reaction of OH radicals with CF$_3$CHClOCHF$_2$, the products of the OH radical initiated oxidation of CF$_3$CHClOCHF$_2$ in air in the presence of NO were determined. OH radicals were generated by the photolysis of methyl nitrite in 700 Torr total pressure of air diluent at 295 ± 2 K.

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

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

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

While photolysis of CH$_3$ONO is a convenient source of OH radicals, it is not well suited to the study of less reactive compounds because CH$_3$ONO itself reacts with OH at a moderate rate (approximately 3×10^{-13} cm^3 molecule^{-1} s^{-1} [26]), scavenges OH radicals, and makes loss of a less reactive compound (e.g., CF$_3$CHClOCHF$_2$) small and difficult to measure. In the present work the loss of the reactant (CF$_3$CHClOCHF$_2$) was monitored indirectly by observing the loss of a more reactive tracer compound (C$_2$H$_4$). In 700 Torr of air diluent OH radicals react with C$_2$H$_4$ with a rate constant $k_{23} = 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[27]

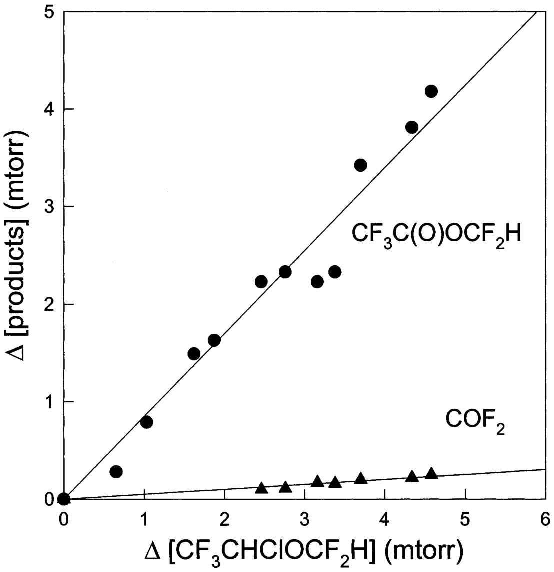

Figure 9. Formation of CF$_3$C(O)OCHF$_2$ (circles) and COF$_2$ (triangles) versus loss of CF$_3$CHClOCHF$_2$ (inferred from measured C$_2$H$_4$ loss) following UV irradiation of CF$_3$CHClOCHF$_2$/C$_2$H$_4$/CH$_3$ONO/NO mixtures in 700 Torr of air.

$$C_2H_4 + OH \rightarrow \text{products} \qquad (23)$$

The kinetics of the reaction of OH radicals with CF$_3$CHClOCHF$_2$ have been studied by Brown et al.,[28] Tokuhashi et al.,[29] and Beach et al.[16] As discussed by Beach et al.,[16] the results from the three studies are in good agreement. Taking a value of $k_1 = (1.9 \pm 0.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} from Beach et al.,[16] it follows that $k_{23}/k_1 = 450$. The loss of CF$_3$CHClOCHF$_2$ can be calculated from the consumption of C$_2$H$_4$. Experiments were performed using mixtures of 4−5 mTorr of C$_2$H$_4$, 438−672 mTorr of CF$_3$CHClOCHF$_2$, 157−216 mTorr of CH$_3$ONO, and 5−6 mTorr of NO in 700 Torr of air diluent. UV irradiation for periods of 0.5−30 min leads to consumption of 30−95% of the C$_2$H$_4$ with corresponding (calculated) CF$_3$CHClOCHF$_2$ consumptions of 0.079−0.66%. Two carbon-containing products were observed: CF$_3$C(O)OCHF$_2$ and COF$_2$. Figure 9 shows a plot of the observed formation of CF$_3$C(O)OCHF$_2$ and COF$_2$ versus CF$_3$CHClOCHF$_2$ loss in these experiments. As seen from Figure 9, CF$_3$C(O)OCHF$_2$ and COF$_2$ increased linearly with CF$_3$CHClOCHF$_2$ loss. Linear least-squares analysis of the data in Figure 9 gives molar yields of 85 ± 10% for CF$_3$C(O)OCHF$_2$ and 5 ± 1% for COF$_2$. The formation of CF$_3$C(O)OCHF$_2$ in reaction 4 is accompanied by the production of Cl atoms which can react with CF$_3$CHClOCHF$_2$ and raises the question, "to what extent does Cl atom initiated oxidation of CF$_3$CHClOCHF$_2$ contribute to the observed CF$_3$C(O)OCHF$_2$ and COF$_2$ product yields shown in Figure 9?" Using k(Cl + CF$_3$CHClOCHF$_2$) = 5.4×10^{-15}, k(Cl + C$_2$H$_4$) = 9.3×10^{-11},[13] k(Cl + CH$_3$ONO) = 2.1×10^{-12} [30] cm^3 molecule^{-1} s^{-1}, and the average initial experimental conditions given above, it can be calculated that only 0.2% of the Cl atoms generated in the system will react with CF$_3$CHClOCHF$_2$. Cl atom initiated oxidation of CF$_3$CHClOCHF$_2$ is of negligible importance.

The yields of CF$_3$C(O)OCHF$_2$ and COF$_2$ provide information concerning the relative importance of reaction pathways

1a and 1b.

$$CF_3CHClOCHF_2 + OH \rightarrow CF_3C(\bullet)ClOCHF_2 + H_2O \quad (1a)$$

$$CF_3CHClOCHF_2 + OH \rightarrow CF_3CHClOC(\bullet)F_2 + H_2O \quad (1b)$$

$CF_3C(\bullet)ClOCHF_2$ radicals formed in reaction 1a are converted into $CF_3C(O)OCHF_2$, while $CF_3CHClOC(\bullet)F_2$ radicals are converted into COF_2. From the yields of $CF_3C(O)OCHF_2$ and COF_2 observed from the OH radical initiated oxidation of $CF_3CHClOCHF_2$ and assuming that in the presence of NO each $CF_3CHClOC(\bullet)F_2$ radical is converted into either one or two molecules of COF_2 (see section 3.3), we derive $k_{1a}/(k_{1a} + k_{1b}) = 0.95 \pm 0.03$ and $k_{1b}/(k_{1a} + k_{1b}) = 0.05 \pm 0.03$.

4. Discussion

The aim of the present work was to provide a better understanding of the atmospheric chemistry of isoflurane. A substantial body of data concerning the atmospheric chemistry of isoflurane is presented herein. The results from this work taken together with those from previous studies provide a reasonably complete picture of the atmospheric chemistry of isoflurane. The atmospheric oxidation of $CF_3CHClOCHF_2$ is initiated by reaction with OH radicals which proceeds with a rate constant $k_1 = (1.9 \pm 0.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.[16] Assuming an atmospheric lifetime for methane of 8.9 years [31] and a rate constant for the CH_4 + OH reaction of 6.3×10^{-15} cm^3 molecule^{-1} s^{-1} leads to an estimate of the atmospheric lifetime of isoflurane with respect to reaction with OH radicals of approximately 3 years. The reaction of OH radicals with $CF_3CHClOCHF_2$ proceeds via H-atom abstraction with $k_{1a}/(k_{1a} + k_{1b}) = 0.95 \pm 0.03$.

$$CF_3CHClOCHF_2 + OH \rightarrow CF_3C^{(\bullet)}ClOCHF_2 + H_2O \quad (1a)$$

$$CF_3CHClOCHF_2 + OH \rightarrow CF_3CHClOC^{(\bullet)}F_2 + H_2O \quad (1b)$$

In the atmosphere $CF_3C(\bullet)ClOCHF_2$ radicals will add O_2 rapidly to give $CF_3C(OO\bullet)ClOCHF_2$ which will be converted by reaction with NO into $CF_3C(O\bullet)ClOCHF_2$ radicals. The sole fate of $CF_3C(O\bullet)ClOCHF_2$ radicals is decomposition via Cl-atom elimination to give the ester $CF_3C(O)OCHF_2$ which is relatively unreactive toward further gas-phase chemistry. By analogy to similar fluoroesters, $CF_3C(O)OCHF_2$ is expected to be removed from the atmosphere by incorporation into cloud-rain-fog water followed by hydrolysis to give $CF_3C(O)OH$, CO_2, and HF.[32] The atmospheric oxidation of isoflurane gives trifluoroacetic acid in a molar yield of 95 ± 3%. Isoflurane is emitted into the atmosphere at a rate of approximately 750 metric tons year^{-1},[5] and its contribution to the global trifluoroacetic acid budget is $750 \times 0.95 \times (114/184.5) = 440$ metric tons year^{-1}.

With an atmospheric lifetime of approximately 3 years, isoflurane will be well mixed in the atmosphere. To provide an estimate for the contribution of isoflurane oxidation to trifluoroacetic acid levels in rainwater, we can combine the 440 metric tons year^{-1} flux with the annual global rainfall of 4.9×10^{17} L [33] to arrive at approximately 1 ng L^{-1}. This value can be compared to the levels of trifluoroacetic acid that are observed in rainwater which are typically of the order of 10−100 ng L^{-1}.[2,34−36] Isoflurane oxidation makes a small, but nonnegligible, contribution to trifluoroacetic acid observed in precipitation.

Acknowledgment. We thank James Franklin (Solvay Chemical Co.) for supplying the ether samples, Mads Sulbaek Andersen for help with the experiments described in section 3.5, Masahiro Kawasaki (Kyoto University) for helpful discussions, and the Japanese Government for a NEDO grant which made this collaborative research project possible.

References and Notes

(1) Zehavi, D.; Seiber, J. N. *Anal. Chem.* **1996**, *68*, 3450.
(2) Frank, H.; Klein, A.; Renschen, D. *Nature* **1996**, *382*, 34.
(3) Jordan, A.; Frank, H. *Environ. Sci. Technol.* **1999**, *33*, 522.
(4) Wujcik, C. E.; Zehavi, D.; Seiber, J. N. *Chemosphere* **1998**, *36*, 1233.
(5) Boutonnet, J. C.; Bingham, P.; Calamari, D.; De Rooij, C.; Franklin, J.; Kawano, T.; Libre, J.-M.; McCulloch, A.; Malinverno, G.; Odom, J. M.; Rusch, G. M.; Smythe, K.; Sobolev, I.; Thompson, R.; Tiedje, J. M. *Hum. Ecol. Risk Assess.* **1999**, *5*, 59.
(6) Nielsen, O. J.; Scott, B. F.; Spencer, C.; Wallington, T. J.; Ball, J. C. *Atmos. Environ.* **2001**, *35*, 2799.
(7) Wallington, T. J.; Schneider, W. F.; Worsnop, D. R.; Nielsen, O. J.; Sehested, J.; Debruyn, W. J.; Shorter, J. A. *Environ. Sci. Technol.* **1994**, *28*, 320.
(8) Mashino, M., Ninomiya, Y.; Kawasaki, M.; Wallington, T. J.; Hurley, M. D. *J. Phys. Chem. A* **2000**, *104*, 7255.
(9) Ellis, D. A.; Mabury, S. A.; Martin, J.; Muir, D. C. G. *Nature* **2001**, *412*, 321.
(10) Kwok, E. S. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685−1695.
(11) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.
(12) Wallington, T. J.; Hurley, M. D. *Chem. Phys. Lett.* **1992**, *189*, 437.
(13) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. JPL Publication No. 94-26; NASA Jet Propulsion Lab.: Pasadena, CA, 1997.
(14) Kambanis, K. G.; Lazarou, Y. G.; Papagiannakopoulos, P. *J. Phys. Chem. A* **1998**, *102*, 8620.
(15) Hickson, K. M.; Smith, I. W. M. *Int. J. Chem. Kinet.* **2001**, *33*, 165.
(16) Beach, S. D.; Hickson, K. M.; Smith, I. W. M.; Tuckett, R. P. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3064.
(17) Meagher, R. J.; McIntosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet.* **1997**, *29*, 619.
(18) Christensen, L. K.; Wallington, T. J.; Guschin, A.; Hurley, M. D. *J. Phys. Chem. A* **1999**, *103*, 4202.
(19) Møgelberg, T. E.; Nielsen, O. J.; Sehested, J.; Wallington, *J. Phys. Chem.* **1995**, *99*, 13437.
(20) Wallington, T. J.; Hurley, M. D.; Fracheboud, J. M.; Orlando, J. J.; Tyndall, G. S.; Sehested, J.; Møgelberg, T. E.; Nielsen, O. J. *J. Phys. Chem.* **1996**, *100*, 18116.
(21) Wallington, T. J.; Hurley, M. D.; Ball, J. C. *Chem. Phys. Lett.* **1993**, *211*, 41.
(22) Ninomiya, Y.; Kawasaki, M.; Guschin, A.; Molina, L. T.; Molina, M. J.; Wallington, T. J. *Environ. Sci. Technol.* **2000**, *34*, 2973−2978.
(23) Wallington, T. J.; Schneider, W. F.; Sehested, J.; Bilde, M.; Platz, J.; Nielsen, O. J.; Christensen L. K.; Molina, M. J.; Molina, L. T.; Wooldridge, P. W. *J. Phys. Chem. A* **1997**, *101*, 8264.
(24) Orlando, J. J.; Tyndall, G. S.; Bilde, M.; Ferronato, C.; Wallington, T. J.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **1998**, *102*, 8116.
(25) Bilde, M.; Orlando, J. J.; Tyndall, G. S.; Wallington, T. J.; Hurley, M. D.; Kaiser, E. W. *J. Phys. Chem. A* **1999**, *103*, 3963.
(26) Nielsen, O. J.; Sidebottom, H. W.; Donlon, M.; Treacy, J. *Int. J. Chem. Kinet.* **1991**, *23*, 1095.
(27) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, Jr., R. F.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data.* **1997**, *26*, 521.
(28) Brown, A. C.; Canosa-Mas, C. E.; Parr, A. D.; Pierce, J. M. T.; Wayne, R. P. *Atmos. Environ., Part A* **1990**, *24*, 2499.
(29) Tokuhashi, K.; Takahashi, A.; Kaise, M.; Kondo, S. *J. Geophys. Res. D* **1999**, *104*, 18681.
(30) Sokolov, O.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Nelsen, W.; Barnes, I.; Becker, K. H. *Int. J. Chem. Kinet.* **1999**, *31*, 357.
(31) Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang, J.; Alyea, F. N.; Cunnold, D. M.; Fraser, P. J.; Hartley, D. E.; Simmonds, P. G. *Science* **1995**, *269*, 187.
(32) Nohara, K.; Toma, M.; Kutsuna, S.; Takeuchi, K.; Ibusuki, T. *Environ. Sci. Technol.* **2001**, *35*, 114.
(33) Erchel, E. *World water balance*; Elsevier: New York, 1975.
(34) Berg, M.; Müller, S. R.; Mühlemann, Wiedmer, A.; Schwarzenbach, R. P. *Environ. Sci. Technol.* **2000**, *34*, 2675.
(35) Scott, B. F.; Mactavish, D.; Spencer, C.; Strachan, W. M. J.; Muir, D. C. G. *Environ. Sci. Technol.* **2000**, *34*, 4266.
(36) Römpp, A.; Klemm, O.; Fricke, W.; Frank, H. *Environ. Sci. Technol.* **2001**, *35*, 1294.