J. Phys. Chem. A **2006,** *110,* 12845−12851

Kinetics and Mechanisms of $CF_3CHFOCH_3$, $CF_3CHFOC(O)H$, and $FC(O)OCH_3$ Reactions with OH Radicals

L. Chen,* S. Kutsuna, K. Tokuhashi, and A. Sekiya

National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

Received: August 1, 2006; In Final Form: September 28, 2006

The kinetics and mechanism of oxidation of $CF_3CHFOCH_3$ was studied using an 11.5-dm^3 environmental reaction chamber. OH radicals were produced by UV photolysis of an O_3−H_2O−He mixture at an initial pressure of 200 Torr in the chamber. The rate constant of the reaction of $CF_3CHFOCH_3$ with OH radicals (k_1) was determined to be $(1.77 \pm 0.69) \times 10^{-12} \exp[(-720 \pm 110)/T]$ cm^3 molecule^{-1} s^{-1} by means of a relative rate method at 253−328 K. The mechanism of the reaction was investigated by FT-IR spectroscopy at 298 K. $CF_3CHFOC(O)H$, $FC(O)OCH_3$, and COF_2 were determined to be the major products. The branching ratio (k_{1a}/k_{1b}) for the reactions $CF_3CHFOCH_3 + OH \rightarrow CF_3CHFOCH_2^{\bullet} + H_2O$ (k_{1a}) and $CF_3CHFOCH_3 + OH \rightarrow CF_3CF^{\bullet}OCH_3 + H_2O$ (k_{1b}) was estimated to be 4.2:1 at 298 K from the yields of $CF_3CHFOC(O)H$, $FC(O)OCH_3$, and COF_2. The rate constants of the reactions of $CF_3CHFOC(O)H$ (k_2) and $FC(O)OCH_3$ (k_3) with OH radicals were determined to be $(9.14 \pm 2.78) \times 10^{-13} \exp[(-1190 \pm 90)/T]$ and $(2.10 \pm 0.65) \times 10^{-13} \exp[(-630 \pm 90)/T]$ cm^3 molecule^{-1} s^{-1}, respectively, by means of a relative rate method at 253−328 K. The rate constants at 298 K were as follows: $k_1 = (1.56 \pm 0.06) \times 10^{-13}$, $k_2 = (1.67 \pm 0.05) \times 10^{-14}$, and $k_3 = (2.53 \pm 0.07) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The tropospheric lifetimes of $CF_3CHFOCH_3$, $CF_3CHFOC(O)H$, and $FC(O)OCH_3$ with respect to reaction with OH radicals were estimated to be 0.29, 3.2, and 1.8 years, respectively.

1. Introduction

Hydrofluoroethers (HFEs) are being investigated as alternatives to chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons (HFCs).[1,2] Because HFEs do not contain Cl atoms, their stratospheric ozone depletion potential is zero. However, HFEs are potential greenhouse gases because of their strong absorption at 1000−3000 cm^{-1}.[2,3] 1,2,2,2-Tetrafluoroethyl methyl ether, $CF_3CHFOCH_3$, is one of the HFEs being developed, and it has a boiling point of 309 K at 760 Torr.[4] Because $CF_3CHFOCH_3$ will be released into the atmosphere during use, its atmospheric chemistry should be assessed. In the atmosphere, $CF_3CHFOCH_3$ will be removed by reaction with OH radicals:

$$CF_3CHFOCH_3 + OH \rightarrow \text{products}, \qquad k_1 \qquad (1)$$

$CF_3CHFOCH_3$ is expected to have a short atmospheric lifetime because its molecular structure is analogous to that of $(CF_3)_2CHOCH_3$, which is reported to have a very short atmospheric lifetime (2.0 months).[5] However, there are no experimental data on the atmospheric chemistry of $CF_3CHFOCH_3$.

We measured the kinetics for the reaction of $CF_3CHFOCH_3$ with OH radicals by means of a relative rate method at 253−328 K and investigated the mechanism of the reaction using FT-IR spectroscopy at 298 K. COF_2 was observed to be the major product of the reaction. Also, $CF_3CHFOC(O)H$, and $FC(O)OCH_3$ were identified by density functional theory calculations. $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ are potential greenhouse gases because of their strong absorption at 1000−3000 cm^{-1}. $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ are expected to be removed from the atmosphere by reaction with OH radicals, rain washout, dissolution into the ocean,[6] and photolysis by sunlight owing to their C=O groups:

$$CF_3CHFOC(O)H + OH \rightarrow \text{products}, \qquad k_2 \qquad (2)$$

$$FC(O)OCH_3 + OH \rightarrow \text{products}, \quad k_3 \qquad (3)$$

$$CF_3CHFOC(O)H + h\nu\ (\text{sunlight}) \rightarrow \text{products} \qquad (4)$$

$$FC(O)OCH_3 + h\nu\ (\text{sunlight}) \rightarrow \text{products} \qquad (5)$$

In this study, k_2 and k_3 were determined by means of a relative rate method at 253−328 K.

2. Experimental Methods

2.1. Apparatus and OH Generation. All experiments were carried out in an 11.5-dm^3 cylindrical quartz chamber (diameter, 10 cm; length, 146 cm) with an external jacket.[7] The OH radicals were produced by UV photolysis of O_3 in the presence of water vapor (reactions 6 and 7) at an initial He pressure of 200 Torr, and the O_3/O_2 (3% O_3) gas mixture was continuously introduced into the reaction chamber at a flow rate of 1−3 cm^3 min^{-1} STP during the UV irradiation period:[7]

$$O_3 + h\nu\ (254\ \text{nm}) \rightarrow O(^1D) + O_2 \qquad (6)$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad (7)$$

The O_3/O_2 gas mixture was generated from pure O_2 with a silent-discharge ozone generator (ECEA-1000, Ebarajitsugyo, Japan). The temperature in the reaction chamber was controlled by

---

* To whom correspondence should be addressed. E-mail: l-chen@aist.go.jp.

10.1021/jp064917h CCC: \$33.50

circulating coolant or heated water through the external jacket. Ten 40-W low-pressure Hg lamps (254 ± 8 nm) (GL-40, National Co., Japan) were used to generate the UV light. A greaseless vacuum line was used in preparing the reaction gas mixtures.

2.2. Relative Rate Method. The rate constants were determined from the relative disappearance rate of the sample with respect to the disappearance rate of a reference compound in the presence of OH radicals.[8,9]

$$\text{sample} + \text{OH} \rightarrow \text{products}, \qquad k_s \tag{8}$$

$$\text{reference} + \text{OH} \rightarrow \text{products}, \qquad k_r \tag{9}$$

For the measurements of k_1, typical initial concentrations (in molecules cm^{-3}) were 1.0×10^{15} ($CF_3CHFOCH_3$), 1.0×10^{15} (reference compound), and 5.6×10^{17} (H_2O) in He at 200 Torr. However, the concentrations of H_2O were lower than 5.6×10^{17} molecules cm^{-3} at reaction temperatures lower than 298 K, because the vapor pressure of H_2O decreased with decreasing temperature; the concentration of H_2O at 253 K was 3.6×10^{16} molecules cm^{-3}. C_2H_6 and CH_3CHF_2 were used as reference compounds. The disappearance of both the sample and reference compound was monitored by flame ionization detector (FID) gas chromatography (GC) (Shimadzu 14A, Japan). By means of an automatic sampling system with a sampling loop (0.5 cm^3), samples were extracted from the reaction chamber with a pressure the same as that in the chamber and transferred to a wide-bore capillary column (Rtx-1; length, 30 m; i.d., 0.53 mm) held at 278 K.[7] In each sampling, the gas mixture residing in the line between the sampling loop and the chamber was drawn and discarded, and then the sample was charged in to the sampling loop and transferred to the GC-FID. The mass of reactants decreased by 0.2% with each GC-FID analysis. Even though the mixing ratio of reactants was diluted by the addition of O_3/O_2 gas mixture in the chamber, the mass of reactants in the chamber and sampling loop did not decrease. The decay rate of reactants was determined from the peak areas measured by GC-FID; therefore, the measurements of the rate constants were not interfered by the addition of O_3/O_2 gas mixture. The concentrations (molecule cm^{-3}) of the reactants decreased due to reaction with OH radicals by up to 50−80% ($CF_3CHFOCH_3$), 70% (C_2H_6), and 30% (CH_3CHF_2) during the 100- to 120-min irradiation at 298 K. Uncertainties in the concentrations of samples and reference compounds measured by GC-FID were <2% and were generally in the range of 0.5−1.5%. Taking into account the reduction of reactant concentration (0.2%) with each GC-FID analysis step,[7] we used eq I to evaluate the rate constant ratios, k_s/k_r:

$$\ln\left(\frac{[\text{sample}]_0}{[\text{sample}]_t}\right) + D_n = \frac{k_s}{k_r}\left[\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) + D_n\right] \tag{I}$$

where $[\text{sample}]_0$ and $[\text{reference}]_0$ represent the initial concentrations of the sample ($CF_3CHFOCH_3$) and the reference compound; $[\text{sample}]_t$ and $[\text{reference}]_t$ represent the concentrations of the sample and reference compound at reaction time t; D_n is a parameter that corrects for the nonreactive decay of the reactant concentration (0.2%) as reactants were removed for GC-FID analysis ($D_n = n \ln(0.998)$, where n is the sample number in the GC-FID analysis);[7] and k_s and k_r are the rate constants for reactions 8 and 9, respectively.

2.3. Product Analysis. The mechanism of the reaction of $CF_3CHFOCH_3$ with OH radicals was investigated at 298 K using FT-IR spectroscopy (JIR-6500, JEOL, Japan) at a resolution of 0.5 cm^{-1} with an aluminum multipass White cell (coated on the inside with nickel; 375 cm^3; optical path length, 3 m), which was connected to the circulation line of the reaction chamber.[7] Experiments were performed at initial concentrations (in molecules cm^{-3}) of 6.0×10^{15} ($CF_3CHFOCH_3$) and 5.6×10^{17} (H_2O) in He at 200 Torr, and the O_3/O_2 (3% O_3) gas mixture was continuously introduced into the reaction chamber at a flow rate of 1 cm^3 min^{-1} STP during the UV irradiation. The sample in the reaction chamber was continuously circulated through the White cell by a magnetically driven glass pump at a flow rate of 850 cm^3 min^{-1} during UV irradiation. The products of the reaction of $CF_3CHFOCH_3$ with OH radicals were identified and quantified by IR spectroscopy.

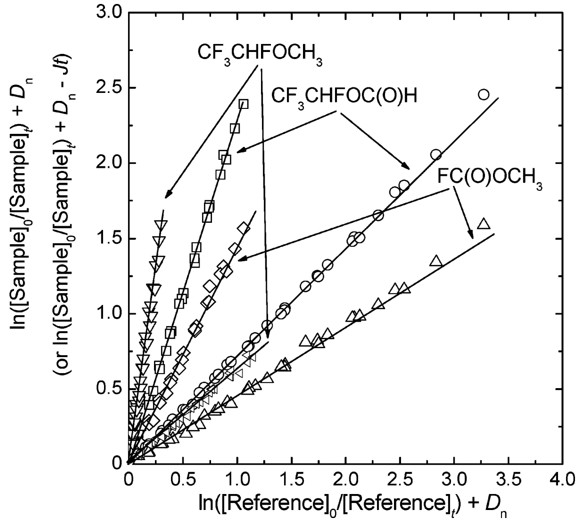

Figure 1. Loss of $CF_3CHFOCH_3$, $CF_3CHFOC(O)H$, and $FC(O)OCH_3$ versus reference compounds in the presence of OH radicals at 298 K under 200 Torr of He. An O_3/O_2 (3% O_3) gas mixture was introduced into the chamber at flow rate of 3 cm^3 min^{-1} STP. For $CF_3CHFOCH_3$, C_2H_6 (left triangle), CH_3CHF_2 (▽); for $CF_3CHFOC(O)H$, CH_2F_2 (◇), CH_3CHF_2 (△); for $FC(O)OCH_3$, CH_2F_2 (□), CH_3CHF_2 (○).

The reagents used were $CF_3CHFOCH_3$ (99% pure) and CH_3CHF_2 (99% pure) (SynQuest Labs., USA), C_2H_6 (99.5% pure, GL Sciences, Japan), CH_2F_2 (99.7% pure, Sigma-Aldrich Co., USA), O_2 (99.5% pure, Nihon Sanso Corp., Japan), and COF_2/N_2 standard (85% pure, Takachiho Chemical Industry Co., Japan).

3. Results and Discussion

3.1. Kinetics of $CF_3CHFOCH_3$ (k_1) Reactions with OH Radicals. The values of k_1 at 298 K were derived from the data presented in Figure 1 on the basis of data for the reference compounds C_2H_6 and CH_3CHF_2. The plots of $\ln([\text{sample}]_0/[\text{sample}]_t) + D_n$ versus $\ln([\text{reference}]_0/[\text{reference}]_t) + D_n$ gave straight lines, with slopes k_1/k_r, that intersected the origin. Linear least-squares analysis of the data shown in Figure 1 after three runs gave k_1/k_r values of 0.632 ± 0.045 (C_2H_6) and 4.88 ± 0.35 (CH_3CHF_2). The errors reported are 2 standard deviations and represent precision only. Using these k_1/k_r values and $k_{298K}(C_2H_6) = 2.4 \times 10^{-13}$ and $k_{298K}(CH_3CHF_2) = 3.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1},[10] we estimated the following values for k_1: $k_1(298\text{ K}) = (1.52 \pm 0.11) \times 10^{-13}$ (C_2H_6) and $(1.65 \pm 0.12) \times 10^{-13}$ (CH_3CHF_2). The two values were the same, within experimental uncertainty.

Table 1 lists the values of k_1 determined over the temperature range 253−328 K from the measured k_1/k_r ratios and $k(C_2H_6) = 8.7 \times 10^{-12} \exp(-1070/T)$ and $k(CH_3CHF_2) = 9.4 \times 10^{-13} \exp(-990/T)$ cm^3 molecule^{-1} s^{-1}.[10] The temperature dependence

TABLE 1: Measured Values of k_i/k_r and k_i (i = 1, 2, 3) over Temperature Range 253−328 K[a]

compounds	references	T (K)	k_i/k_r	$10^{14} \times k_i$ (cm^3 molecule^{-1} s^{-1})
$CF_3CHFOCH_3$	C_2H_6	253	0.764 ± 0.030	9.68 ± 0.38
		268	0.688 ± 0.022	11.1 ± 0.4
		283	0.651 ± 0.010	12.9 ± 0.2
		298	0.632 ± 0.045	15.2 ± 1.1
		313	0.599 ± 0.044	17.1 ± 1.3
		328	0.549 ± 0.024	18.3 ± 0.8
	CH_3CHF_2	253	5.72 ± 0.45	10.7 ± 0.9
		268	5.54 ± 0.53	12.9 ± 1.2
		283	5.05 ± 0.86	14.4 ± 2.5
		298	4.88 ± 0.35	16.5 ± 1.2
		313	4.67 ± 0.31	18.6 ± 1.2
		328	4.43 ± 0.62	20.3 ± 2.8
$CF_3CHFOC(O)H$	CH_2F_2	253	1.83 ± 0.11	0.826 ± 0.050
		268	1.58 ± 0.07	0.826 ± 0.050
		283	1.51 ± 0.06	1.28 ± 0.05
		298	1.50 ± 0.03	1.66 ± 0.03
		313	1.48 ± 0.06	2.10 ± 0.08
		328	1.45 ± 0.05	2.55 ± 0.09
	CH_3CHF_2	253	0.469 ± 0.011	0.881 ± 0.021
		268	0.469 ± 0.041	1.10 ± 0.10
		283	0.476 ± 0.014	1.35 ± 0.04
		298	0.471 ± 0.017	1.60 ± 0.06
		313	0.498 ± 0.005	2.00 ± 0.02
		328	0.512 ± 0.013	2.39 ± 0.06
$FC(O)OCH_3$	CH_2F_2	253	3.84 ± 0.16	1.74 ± 0.07
		268	2.97 ± 0.23	1.74 ± 0.15
		283	2.54 ± 0.09	2.15 ± 0.08
		298	2.29 ± 0.05	2.54 ± 0.05
		313	2.02 ± 0.08	2.85 ± 0.11
		328	1.89 ± 0.05	3.32 ± 0.09
	CH_3CHF_2	253	1.00 ± 0.03	1.88 ± 0.06
		268	0.876 ± 0.043	2.05 ± 0.10
		283	0.782 ± 0.009	2.22 ± 0.03
		298	0.726 ± 0.027	2.46 ± 0.09
		313	0.688 ± 0.007	2.74 ± 0.03
		328	0.658 ± 0.039	3.03 ± 0.18

[a] The quoted errors are 2 standard deviations.

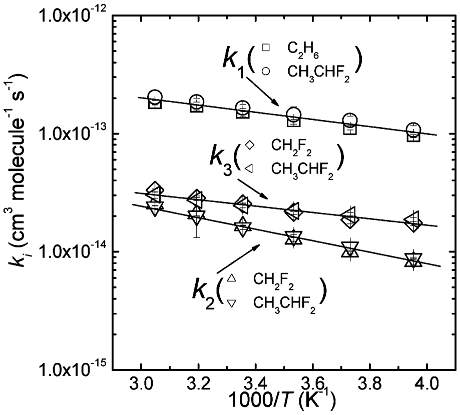

Figure 2. Arrhenius plot of kinetic data obtained by a relative rate method for reactions of $CF_3CHFOCH_3$, $CF_3CHFOC(O)H$, and $FC(O)OCH_3$ with OH radicals at 253−328 K. for $CF_3CHFOCH_3$ (k_1), C_2H_6 (□), CH_3CHF_2 (○); for $CF_3CHFOC(O)H$ (k_2), CH_2F_2 (△), CH_3CHF_2 (▽); for $FC(O)OCH_3$ (k_3), CH_2F_2 (◇), CH_3CHF_2 (left triangle).

of k_1 is illustrated in Figure 2. Using the Arrhenius equation, $k = A\ e^{-E/(RT)}$, we determined the Arrhenius rate parameters (A and E/R) by nonlinear least-squares analyses of the data presented in Table 1. The Arrhenius rate parameters and the values of k_1 at 298 K calculated from the Arrhenius expressions are listed in Table 2.

TABLE 2: The Rate Constants at 298 K and Arrhenius Rate Parameters for $CF_3CHFOCH_3$, $CF_3CHFOC(O)H$, and $FC(O)OCH_3$ Reaction with OH Radicals over the Temperature Range 253−328 K[a]

compounds	$10^{13} \times k$(298 K) (cm^3 molecule^{-1} s^{-1})	$10^{12} \times A$ (cm^3 molecule^{-1} s^{-1})	E/R (K)
$CF_3CHFOCH_3$	1.56 ± 0.06	1.77 ± 0.69	720 ± 110
$CF_3CHFOC(O)H$	0.167 ± 0.005	0.914 ± 0.278	1190 ± 90
$FC(O)OCH_3$	0.253 ± 0.007	0.210 ± 0.065	630 ± 90

[a] The quoted errors are 2 standard deviations.

Loss processes for samples and reference compounds other than reaction with OH radicals must be accounted for in any estimate of the rate constants. In this reaction system, UV photolysis and reactions with O_3, H_2O, and $O(^1D)$ represent the potential losses for samples and reference compounds. $CF_3CHFOCH_3$ and reference compounds were photolyzed by UV irradiation in separate experiments for 5 h, and the decays of the concentrations of these reactants were found to be lower than the GC-FID analysis uncertainties (2%). The dark reactions of these reactants with either O_3 or H_2O were also examined for 5 h in this study, and losses due to dark reactions were lower than the GC-FID analysis uncertainties (2%). In this reaction system, the disappearance rates of $CF_3CHFOCH_3$ by the reaction with OH or $O(^1D)$ are compared. The concentration of OH radicals at reaction time t, $[OH]_t$, was estimated from the decay of $CF_3CHFOCH_3$ using eq II:

$$[OH]_t = \frac{-1}{k_1[CF_3CHFOCH_3]_t}\frac{d[CF_3CHFOCH_3]}{dt} \qquad (II)$$

The average concentration of OH radicals was obtained to be 3.3×10^9 radicals cm^{-3}. The concentration of $O(^1D)$ was estimated from the average concentrations of $CF_3CHFOCH_3$ and C_2H_6 using eq III:

$$[(O^1D)] = (k_1[CF_3CHFOCH_3] + k_{C_2H_6}[C_2H_6] + k_{O_3}[O_3])[OH]/(2k_7[H_2O]) \qquad (III)$$

The losses of reactants in reaction with $O(^1D)$ might be considerable at 253 K because the concentration of H_2O (3.6×10^{16} molecules cm^{-3}) at 253 K was lowest during the measurements. In the measurement at 253 K, the values of k_1, $k_{C_2H_6}$, k_{O_3} (for reaction $O_3 + OH \rightarrow$ products), and k_7 were 1.03×10^{-13}, 1.27×10^{-13}, 4.1×10^{-14}, and 2.1×10^{-10} cm^3 molecule^{-1} s^{-1}, respectively.[10] The average concentrations of $CF_3CHFOCH_3$, C_2H_6, and O_3 (obtained from FTIR analysis) were 6.1×10^{14}, 5.4×10^{14}, and 1.0×10^{14} molecules cm^{-3}, respectively. The concentration of $O(^1D)$ was obtained to be 2.3×10^4 radicals cm^{-3}. The rate constant of reaction $O(^1D) + CF_3CHFOCH_3 \rightarrow$ products was assumed to be 2×10^{-10} cm^3 molecule^{-1} s^{-1}. The disappearance rates of $CF_3CHFOCH_3$ by the reaction with OH or $O(^1D)$ were obtained to be 3.4×10^{-4} s^{-1} and 4.6×10^{-6} s^{-1}, respectively. The loss of $CF_3CHFOCH_3$ due to reaction with $O(^1D)$ was about 1.4% of that with OH radicals. We assumed that the rate constant of reaction $O(^1D) + C_2H_6 \rightarrow$ products at 253 K is equal to that at 300 K (6.29×10^{-10} cm^3 molecule^{-1} s^{-1}).[11] The loss of C_2H_6 due to reaction with $O(^1D)$ was estimated to be about 3.5% of that with OH radicals. Therefore, the losses of the reactants with $O(^1D)$ were considered to be insignificant in this system.

We confirmed that the measurement errors were insignificant in the measurements of k_1 with C_2H_6 and CH_3CHF_2 as reference compounds. However, the values of k_1 obtained relative to CH$_3$-

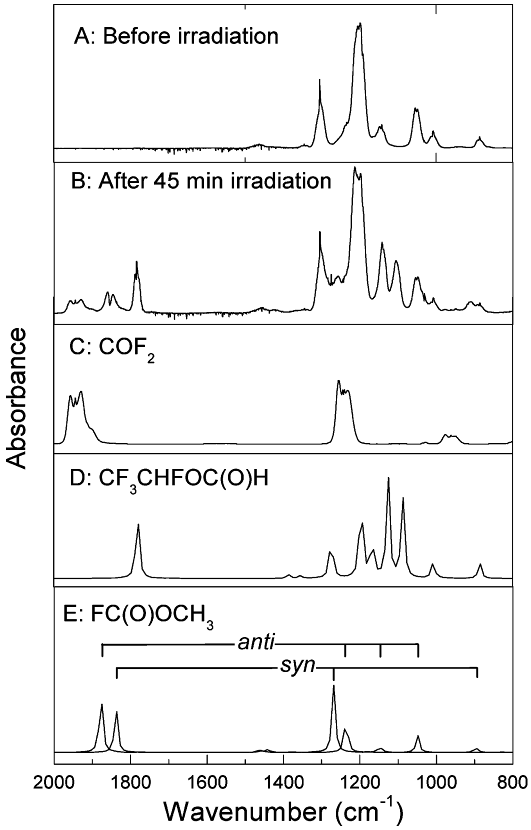

Figure 3. IR spectra observed before (A) and after (B) a 45-min irradiation of a gas mixture of $CF_3CHFOCH_3$ (6.0×10^{15} molecules cm^{-3}) and H_2O (5.6×10^{17} molecules cm^{-3}) at 298 K under 200 Torr of He. An O_3/O_2 (3% O_3) gas mixture was introduced into the chamber at a flow rate of 1 cm^3 min^{-1}. The following reference spectra are shown: (C) spectrum of COF_2; calculated spectra of (D) $CF_3CHFOC(O)H$ and (E) *anti*-$FC(O)OCH_3$ and *syn*-$FC(O)OCH_3$ (DFT, B3LYP/6-31G(d) level).

CHF_2 are consistently about 10% higher than those relative to C_2H_6. In our previous study, the errors of $k((CF_3)_2CHOCH_3 + OH)$ obtained from the reference compounds of C_2H_6 and CH_2Cl_2 were less than 6%.[5] This fact supports that the measurement errors were insignificant in this measurement system with C_2H_6 as reference compound. Therefore, the higher data of k_1 from CH_3CHF_2 might suggest that the recommended value of $k(CH_3CHF_2)$ is slightly too high.

3.2. Mechanism of the Reaction of $CF_3CHFOCH_3$ with OH Radicals. The infrared spectra of the $CF_3CHFOCH_3-O_3-H_2O-O_2$ gas mixture before and after 45 min of UV irradiation are shown in Figure 3, panels A and B, respectively. Comparison of the latter spectrum with the IR spectrum of a COF_2 standard (Figure 3C) indicated that the band at 1928 cm^{-1} belongs to COF_2. The three unknown IR bands at 1788, 1845, and 1860 cm^{-1} in Figure 3B indicate the presence of C=O groups. By analogy with the mechanism of the reaction of $(CF_3)_2CHOCH_3$ with OH radicals,[5] $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ might be produced from the OH radical-initiated reaction of $CF_3CHFOCH_3$. However, we had no standard samples of $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ for identification and quantification of these two products. Therefore, we calculated the theoretical IR spectra of $CF_3CHFOC(O)H$, *syn*-$FC(O)OCH_3$, and *anti*-$FC(O)OCH_3$ by means of density functional theory at the B3LYP/6-31G(d) level (*Gaussian 03*, revision C.02; Figure 3, panels D and E).[12] The calculated wavenumbers were scaled by a factor of 0.9613.[13] The calculated absorptions at 1788 cm^{-1} ($CF_3CHFOC(O)H$), 1845 cm^{-1} (*syn*-$FC(O)OCH_3$), and 1860 cm^{-1} (*anti*-$FC(O)OCH_3$) were consistent with the observed IR bands at 1788, 1845, and 1860 cm^{-1} in Figure 3B. This fact shows that $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ could be formed in this reaction system.

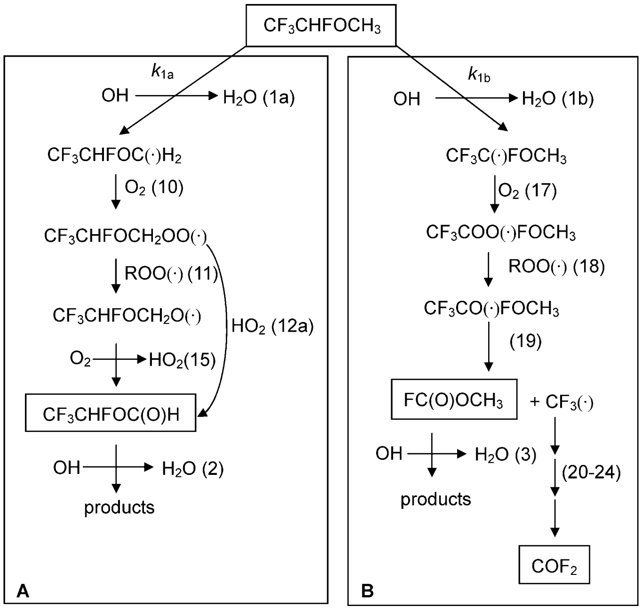

Figure 4. Proposed mechanism for degradation of $CF_3CHFOCH_3$ initiated by OH radicals at 298 K.

A proposed mechanism for the reaction of $CF_3CHFOCH_3$ with OH radicals is shown in Figure 4. The mechanism for the formation of $CF_3CHFOC(O)H$ from the $CF_3CHFOC^{\bullet}H_2$ radical is shown in Figure 4A. The peroxyl radical $CF_3CHFOCH_2OO^{\bullet}$ formed by the reaction of $CF_3CHFOC^{\bullet}H_2$ with O_2 (reaction 10) reacts with the $ROO^{\bullet}$ radical ($R = CF_3CHFOCH_2, CF_3CFOCH_3$) and with HO_2 (reactions 11 and 12a). Theoretically, $CF_3CHFOCH_2OO^{\bullet}$ could also react with HO_2 to form $CF_3CHFOCH_2OOH$ (reaction 12b), but the formation of this product could not be determined unequivocally in this study.

$$CF_3CHFOCH_2OO^{\bullet} + HO_2 \rightarrow CF_3CHFOCH_2OOH + O_2 \tag{12b}$$

Hydroperoxides are generally very reactive toward OH radicals (for example, $k(OH + CH_3OOH) = 7.4 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K),[10] although the presence of fluorine is expected to reduce the reactivity of $CF_3CHFOCH_2OOH$. Even if $CF_3CHFOCH_2OOH$ was formed in this study, it would react with OH radicals and undergo photolysis by UV irradiation to regenerate the $CF_3CHFOCH_2OO^{\bullet}$ and $CF_3CHFOCH_2O^{\bullet}$ radicals by means of reactions 13 and 14:

$$CF_3CHFOCH_2OOH + OH \rightarrow CF_3CHFOCH_2OO^{\bullet} + H_2O \tag{13}$$

$$CF_3CHFOCH_2OOH + h\nu \rightarrow CF_3CHFOCH_2O^{\bullet} + OH \tag{14}$$

The $CF_3CHFOCH_2O^{\bullet}$ radical produced by reaction 11 (see Figure 4) can react with O_2 (reaction 15) or undergo unimolecular dissociation (reaction 16):

$$CF_3CHFOCH_2O^{\bullet} + M \rightarrow CF_3CHFO^{\bullet} + HC(O)H + M \tag{16}$$

However, HC(O)H was not observed in this reaction system. HC(O)H might also have been removed by reaction with OH radicals, toward which it is highly reactive: $k(OH + HC(O)H) = 8.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.[10] Previous studies reported that for $C_nF_{2n+1}OCH_2O^•$ radicals ($n = 1-4$), the reaction with O_2 predominates over unimolecular dissociation.[14-16] Therefore, the reaction of $CF_3CHFOCH_2O^•$ with O_2 (reaction 15) could be considered to predominate over the unimolecular dissociation (reaction 16) in our reaction system. Comparison of our reaction conditions with tropospheric reaction conditions provides confirmation that reaction 15 likely predominated in troposphere. A previous study showed that the decomposition rate constants at 37.5 Torr are about $^1/_5$ those at 760 Torr for $RO^•$ radicals (2-butoxy, 3-pentoxy, and isomerization 1-butoxy),[17] and therefore, the rate of reaction 16 is likely to increase by less than a factor of 5 in going from our reaction pressure of 200 Torr to tropospheric pressure. In addition, the O_2 concentration (5.17×10^{18} molecule cm^{-3}) in the troposphere is 63 times larger than the O_2 concentration (8.2×10^{16} molecule cm^{-3}) in our reaction system, which increases the likelihood that the reaction of $CF_3CHFOCH_2O^•$ with O_2 will predominate over unimolecular dissociation under tropospheric conditions.

The proposed mechanism for the formation of FC(O)OCH$_3$ and COF_2 from the $CF_3C^•FOCH_3$ radical is shown in reactions 1b and 17−24 (Figure 4B). The peroxyl radical $CF_3CFOO^•OCH_3$ formed by reaction of $CF_3C^•FOCH_3$ with O_2 (reaction 17) can react with $ROO^•$ (R = $CF_3CHFOCH_2$, CF_3CFOCH_3) to produce $CF_3CO^•FOCH_3$ (reaction 18). Like $CF_3CHFOCH_2OO^•$, the $CF_3CFOO^•OCH_3$ radical can also react with HO_2 radicals, as discussed above. The discussion of $CF_3CFOO^•OCH_3$ radical reaction with HO_2 radicals was omitted. FC(O)OCH$_3$ and the $CF_3^•$ radical are formed by unimolecular dissociation of the $CF_3CO^•FOCH_3$ radical (reaction 19). $CF_3^•$ radicals can produce COF_2 by means of reactions 20−24:[18-20]

$$CF_3^• + O_2 + M \rightarrow CF_3OO^• + M \qquad (20)$$

$$2CF_3OO^• \rightarrow 2CF_3O^• + O_2 \qquad (21)$$

$$CF_3O^• + HO_2 \rightarrow CF_3OH + O_2 \qquad (22)$$

$$CF_3O^• + RH \rightarrow CF_3OH + R^• \qquad (23)$$

$$CF_3OH + \text{wall} \rightarrow COF_2 + HF + \text{wall} \qquad (24)$$

The mechanism illustrated in Figure 4 shows that $CF_3CHFOC(O)H$, FC(O)OCH$_3$, and COF_2 are the main products of the reaction of $CF_3CHFOCH_3$ with OH radicals.

$CF_3CHFOC(O)H$, FC(O)OCH$_3$, and COF_2 were the only products that contained both carbon and fluorine (Figure 4), and both FC(O)OCH$_3$ and COF_2 were formed only in reaction 19. Therefore, we can use eqs IV and V to calculate the IR absorption cross-sections (ϵ) of $CF_3CHFOC(O)H$ and FC(O)OCH$_3$ from the concentration of $CF_3CHFOCH_3$ consumed and the concentration of COF_2 formed during the initial 12-min reaction period to minimize the effects of any secondary reactions of the product species:

$$[CF_3CHFOC(O)H]_t = \Delta[CF_3CHFOCH_3]_t - [COF_2]_t \qquad (IV)$$

$$[FC(O)OCH_3]_t = [COF_2]_t \qquad (V)$$

where $\Delta[CF_3CHFOCH_3]_t = ([CF_3CHFOCH_3]_0 - [CF_3CHFOCH_3]_t)$, $[CF_3CHFOCH_3]_0$ represents the initial concentration of $CF_3CHFOCH_3$, and $[CF_3CHFOCH_3]_t$, $[CF_3CHFOC(O)H]_t$, $[FC(O)OCH_3]_t$, and $[COF_2]_t$ represent the concentrations of $CF_3CHFOCH_3$, $CF_3CHFOC(O)H$, FC(O)OCH$_3$, and COF_2, respectively, at reaction time t. The concentrations of $CF_3CHFOCH_3$ consumed and COF_2 formed were determined from the IR absorption cross-sections (ϵ; cm^2 molecule^{-1}; base 10) of $CF_3CHFOCH_3$ (2.60×10^{-20} at 3000 cm^{-1}) and COF_2 (6.3×10^{-19} at 1928 cm^{-1}), which were calculated from the IR spectra of He mixtures of known concentration [$(0.3-3.0) \times 10^{15}$ molecules cm^{-3})] at a total pressure of 200 Torr at 298 K. The ϵ values determined for $CF_3CHFOC(O)H$ and FC(O)OCH$_3$ were $(3.8 \pm 0.3) \times 10^{-19}$ and $(1.0 \pm 0.2) \times 10^{-18}$ cm^2 molecule^{-1} (base 10) at 1788 and 1860 cm^{-1}, respectively, from the results of four experiments. In Figure 5, the concentrations of $CF_3CHFOC(O)H$, FC(O)OCH$_3$, and COF_2 formed during a 24-min UV irradiation period are plotted against the concentration of $CF_3CHFOCH_3$ consumed. The plots in Figure 5 gave straight lines that intersected the origin. They show that losses of $CF_3CHFOC(O)H$, FC(O)OCH$_3$, and COF_2 due to reaction with OH radicals, photolysis by UV irradiation, and wall reaction are minor at most during a 24-min UV irradiation period. Therefore, the error due to the secondary reactions of the product species was minimal in the calculation of ϵ for $CF_3CHFOC(O)H$ and FC(O)OCH$_3$ using the data obtained during the initial 12-min UV irradiation period from eqs IV and V. The slopes of these plots gave initial values of $\alpha(CF_3CHFOC(O)H)$, $\alpha(FC(O)OCH_3)$, and $\alpha(COF_2)$ as 0.83 ± 0.11, 0.19 ± 0.02, and 0.20 ± 0.02, respectively. The values k_{1a}/k_1 and k_{1b}/k_1 for $CF_3CHFOCH_2^•$ and $CF_3C^•FOCH_3$ radicals were equal to the values of $\alpha(CF_3CHFOC(O)H)$ (0.83 ± 0.11) and $\alpha(COF_2)$ (0.20 ± 0.02), respectively. The branching ratio k_{1a}/k_{1b} was estimated to be 4.2:1, and because there are three H atoms in the $-CH_3$ group (k_{1a}), the reactivity of the terminal H atoms was 1.4 times that of the central H atom in OH-radical H-atom abstraction reactions.

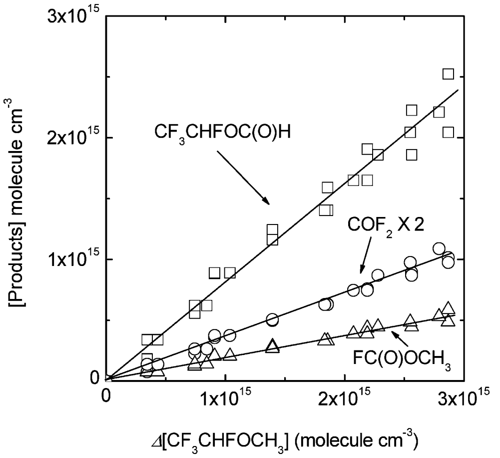

Figure 5. Plots of the concentrations of the products against the concentration of $CF_3CHFOCH_3$ consumed: $CF_3CHFOC(O)H$ (□), FC(O)OCH$_3$ (△), and COF_2 (○). Data were obtained from the experiment illustrated in Figure 3.

The values of k_{1a} and k_{1b} at 298 K were estimated to be 1.26×10^{-13} and 3.0×10^{-14} cm^3 molecule^{-1} s^{-1}, respectively, from k_{1a}/k_{1b} and k_1. The reactivity of the $-CH_3$ group in $CF_3CHFOCH_3$ is 10 times that of the $-CH_3$ group in $CF_3CF_2OCH_3$ (1.21×10^{-14} cm^3 molecule^{-1} s^{-1}).[21] Similar behavior has been observed for $(CF_3)_2CHOCH_3$ [$k(-CH_3) = 1.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}] and $(CF_3)_2CFOCH_3$ [$k(-CH_3) = 1.52 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}].[5,21] The OH radical reactivity of $-CH_3$ in the $-OCH_3$ group was increased by replacement of $-F$ with $-H$ in the $-CF_2O-$ group of $CF_3CHFOCH_3$. The value of k_{1b} at 298 K was 6 times that of $CF_3OCHFCF_3$ (4.98×10^{-15} cm^3 molecule^{-1} s^{-1}),[22] which indicates that replacing $-OCF_3$ with $-OCH_3$ increased the OH radical reactivity of the H atom in the $-OCHFCF_3$ group.

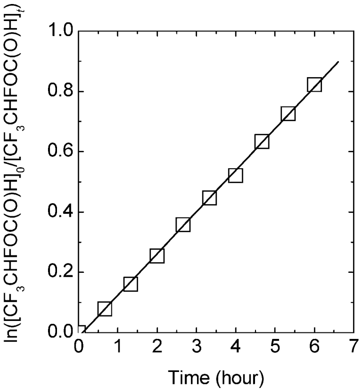

Figure 6. Photolysis of $CF_3CHFOC(O)H$ by UV irradiation at 298 K in a gas mixture of $CF_3CHFOC(O)H$ and $FC(O)OCH_3$, which was produced by irradiation of a $CF_3CHFOCH_3-H_2O-O_3-O_2-He$ mixture at 200−230 Torr.

3.3. Kinetics of $CF_3CHFOC(O)H$ (k_2) and $FC(O)OCH_3$ (k_3) Reactions with OH Radicals. The rate constants k_2 and k_3 were measured by means of a relative rate method with CH_2F_2 and CH_3CHF_2 as reference compounds. $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ were produced by irradiation of a mixture of $CF_3CHFOCH_3$ (6.0×10^{15} molecules cm^{-3}), H_2O (5.6×10^{17} molecules cm^{-3}), and He (200 Torr) in the presence of a O_3/O_2 (3% O_3) gas mixture that was continuously introduced into the reaction chamber at a flow rate of 1 cm^3 min^{-1} STP. After $CF_3CHFOCH_3$ was completely consumed by reaction with OH radicals, the flow of O_3/O_2 into the chamber was stopped. $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ remaining in the chamber were photolyzed by UV irradiation. The concentrations of $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ were monitored both by FT-IR and by GC-FID, the latter being a more precise method for determining the concentrations. FT-IR measurements indicated that photolysis of $CF_3CHFOC(O)H$ occurred and that there was no change in the concentration of $FC(O)OCH_3$:

$$CF_3CHFOC(O)H + h\nu\ (254\ \text{nm}) \rightarrow \text{products} \qquad (25)$$

This same pattern was evident in GC-FID analysis and was used to identify the GC peaks corresponding to $CF_3CHFOC(O)H$ and $FC(O)OCH_3$. The photolysis rate (J) for reaction 25 was estimated to be $(3.83 \pm 0.04) \times 10^{-5}$ s^{-1} based on the time-dependent decrease of the $CF_3CHFOC(O)H$ concentration observed by GC-FID (Figure 6). The average reaction rate of $CF_3CHFOC(O)H$ with OH radicals at 298K was estimated to be 3.7×10^{-4} s^{-1}. The photolysis of $CF_3CHFOC(O)H$ was about 10% compared with its reaction with OH radicals. Taking into account the decay of the $CF_3CHFOC(O)H$ concentration by photolysis, we used the modified eq VI to evaluate k_2/k_r:

$$\ln\left(\frac{[\text{sample}]_0}{[\text{sample}]_t}\right) + D_n - Jt = \frac{k_2}{k_r}\left[\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) + D_n\right] \qquad \text{(VI)}$$

where J is the photolysis rate of $CF_3CHFOC(O)H$ by UV irradiation in this reaction system. The decays of $CF_3CHFOC(O)H$, $FC(O)OCH_3$, and a reference compound were determined after the GC peak for $CF_3CHFOCH_3$ had disappeared completely. The plots of $\ln([\text{sample}]_0/[\text{sample}]_t) + D_n - Jt$ (or $\ln([\text{sample}]_0/[\text{sample}]_t) + D_n$) versus $\ln([\text{reference}]_0/[\text{reference}]_t) + D_n$ gave straight lines, with slopes k_2/k_r and k_3/k_r, that intersected the origin (Figure 1). The values of k_2/k_r and k_3/k_r were also determined over the temperature range 253−328 K. Values of k_2 and k_3 were determined from the measured k_2/k_r and k_3/k_r ratios and $k(CH_2F_2) = 1.7 \times 10^{-12} \exp(-1500/T)$ and $k(CH_3CHF_2) = 9.4 \times 10^{-13} \exp(-990/T)$ cm^3 molecule^{-1} s^{-1} (Table 1).[10] The temperature dependencies of k_2 and k_3 are plotted in Figure 2. Using the Arrhenius equation, $k = A\,e^{-E/(RT)}$, we determined the Arrhenius rate parameters (A and E/R) by nonlinear least-squares analyses of the data presented in Table 1. The Arrhenius rate parameters and the values of k_2 and k_3 at 298 K calculated from the Arrhenius expressions are listed in Table 2 with the data for k_1.

The value of k_2 [$(1.67 \pm 0.05) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}] at 298 K is similar to the reported rate constants for reactions of $CF_3OC(O)H$ [$(1.65 \pm 0.13) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}] and $C_2F_5OC(O)H$ [$(1.48 \pm 0.06) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}] with OH radicals.[23,24] This similarity indicates that the OH radical reactivity of the H in the $-OC(O)H$ group is larger than that of the H in the CF_3CHFO- group. The value for k_3 [$(2.53 \pm 0.07) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}] at 298 K is twice the reported value for $k(CF_3C(O)OCH_3)$ (5.38×10^{-14} cm^3 molecule^{-1} s^{-1}) at 298 K,[25] which implies that replacing $-F$ with $-CF_3$ in the $FC(O)O-$ group increased the OH radical reactivity of $-CH_3$ in $FC(O)OCH_3$.

4. Atmospheric Implications

We determined the rate constant of the reaction of $CF_3CHFOCH_3$ with OH radicals, $k_1(T)$, to be $(1.77 \pm 0.69) \times 10^{-12} \exp[(-720 \pm 110)/T]$ cm^3 molecule^{-1} s^{-1}. The tropospheric lifetime of $CF_3CHFOCH_3$ (τ_1) with respect to its reaction with OH radicals was estimated to be 0.29 years by scaling the lifetime of CH_3CCl_3:

$$\tau_1 = \frac{k_{CH_3CCl_3}(272\ \text{K})}{k_1(272\ \text{K})} \times \tau_{CH_3CCl_3} \qquad \text{(VII)}$$

where k_1(272 K) and $k_{CH_3CCl_3}$(272 K) represent the rate constants for the reactions of $CF_3CHFOCH_3$ and CH_3CCl_3 with OH radicals at 272 K, respectively, and $\tau_{CH_3CCl_3}$ represents the tropospheric lifetime of CH_3CCl_3 with respect to reaction with OH radicals. The k_1 value at 272 K was calculated to be 1.25×10^{-13} cm^3 molecule^{-1} s^{-1} from the Arrhenius expression for k_1. The recommended value of $k_{CH_3CCl_3}$ at 272 K is 6.1×10^{-15} cm^3 molecule^{-1} s^{-1}.[10] The $\tau_{CH_3CCl_3}$ value has been estimated to be 6.0 years.[26] $CF_3CHFOCH_3$ is expected to have less impact on global warming than HCFCs and HFCs because it is more rapidly removed from the atmosphere.[2] However, in this study, we found that two esters, $CF_3CHFOC(O)H$ and $FC(O)OCH_3$, can be produced from the OH radical-initiated reaction of $CF_3CHFOCH_3$. These esters are also potential greenhouse gases, owing to their strong absorption at 1000−3000 cm^{-1}. We measured the rate constants of the reactions of $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ with OH radicals, $k_2(T)$ and $k_3(T)$, respectively, to be $(9.14 \pm 2.78) \times 10^{-13} \exp[(-1190 \pm 90)/T]$ and $(2.10 \pm 0.65) \times 10^{-13} \exp[(-630 \pm 90)/T]$ cm^3 molecule^{-1} s^{-1}. The tropospheric lifetimes of $CF_3CHFOC(O)H$ (3.2 years) and $FC(O)OCH_3$ (1.8 years) with respect to their reactions with OH radicals were obtained from the k_2 (1.15×10^{-14} cm^3 molecule^{-1} s^{-1}) and k_3 (2.07×10^{-14} cm^3 molecule^{-1} s^{-1}) at 272 K by scaling the lifetime of CH_3CCl_3 using eq VII. The lifetimes of $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ are longer than that of $CF_3CHFOCH_3$. However, $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ may also be removed from the atmosphere by rain washout, dissolution into the ocean, and photolysis; therefore, further investigation of the final fate of $CF_3CHFOC(O)H$ and $FC(O)OCH_3$ in the atmosphere is needed.

References and Notes

(1) Sekiya, A.; Misaki, S. *CHEMTECH* **1996**, *26*, 44.

(2) Houghton, J. T.; Ding Y.; Griggs, D. J.; Noguer, M.; van der Linden, P. J.; Dai, X.; Maskell, K.; Johnson, C. A. *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*; Intergovernmental Panel on Climate Change (IPCC): Geneva, Switzerland, 2001.

(3) Imasu, R.; Suga, A.; Matsuno T. *J. Meteorol. Soc. Jpn.* **1995**, *73*, 1123.

(4) Zapevalov, A. Ya.; Filyakova, T. I.; Peschanskii, N. V.; Kodess, M. I.; Kolenko, I. P. *J. Org. Chem. U.S.S.R. (Engl. Transl.)* **1989**, *25*, 441.

(5) Chen, L.; Kutsuna, S.; Tokuhashi, K.; Sekiya, A.; Tamai, R.; Hibino, Y. *J. Phys. Chem. A* **2005**, *109*, 4766.

(6) Kutsuna, S.; Chen, L.; Abe, T.; Mizukado, J.; Uchimaru, T.; Tokuhashi, K.; Sekiya, A. *Atmos. Environ.* **2005**, *39*, 5884.

(7) Chen, L.; Kutsuna, S.; Tokuhashi, K.; Sekiya, A. *Int. J. Chem. Kinet.* **2003**, *35*, 317.

(8) Atkinson, R. *Chem. Rev.* **1986**, *86*, 69.

(9) Finlayson-Pitts, B. J.; Hernandez, S. K.; Berko, H. N. *J. Phys. Chem.* **1993**, *97*, 1172.

(10) Sander, S. P.; Friedl, R. R.; Golden, D. M.; Kurylo, M. J.; Moortgat, G. K.; Keller-Rudek, H.; Wine P. H.; Ravishankara, A. R.; Kolb C. E.; Molina, M. J.; Finlayson-Pitts, B. J.; Huie, R. E.; Orkin V. L. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*; Evaluation No. 15, JPL Publication 06-2; National Aeronautics and Space Administration, Jet Propulsion Laboratory, California Institute of Technology: Pasadena, CA.

(11) Matsumi, Y.; Tonokura, K.; Inagaki, Y.; Kawasaki, M. *J. Phys. Chem.* **1993**, *97*, 6816.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(13) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391.

(14) Christensen, L. K.; Wallington, T. J.; Guschin, A.; Hurley, M. D. *J. Phys. Chem. A* **1999**, *103*, 4202.

(15) Nohara, K.; Toma, M.; Kutsuna, S.; Takeuchi, K.; Ibusuki, T. *Environ. Sci. Technol.* **2001**, *35*, 114.

(16) Chen, L.; Kutsuna, S.; Nohara, K.; Takeuchi, K.; Ibusuki, T. *J. Phys. Chem. A* **2001**, *105*, 10854.

(17) Atkinson, R.; Arey J. *Chem. Rev.* **2003**, *103*, 4605.

(18) Sehested, J.; Wallington, T. J. *Environ. Sci. Technol.* **1993**, *27*, 146.

(19) Wallington, T. J.; Schneider, W. F. *Environ. Sci. Technol.* **1994**, *28*, 1198.

(20) Turnipseed, A. A.; Barone, S. B.; Jensen, N. R.; Hanson, D. R.; Howard, C. J.; Ravishankara, A. R. *J. Phys. Chem.* **1995**, *99*, 6000.

(21) Tokuhashi, K.; Takahashi, A.; Kaise, M.; Kondo, S.; Sekiya, A.; Yamashita, S.; Ito, H. *Int. J. Chem. Kinet.* **1999**, *31*, 846.

(22) Li, Z.; Jeong, G. R.; Hansen, J. C.; Good, D. A.; Francisco, J. S. *Chem. Phys. Lett.* **2000**, *320*, 70.

(23) Chen, L.; Kutsuna, S.; Tokuhashi, K.; Sekiya, A. *Int. J. Chem. Kinet.* **2004**, *36*, 337.

(24) Chen, L.; Kutsuna, S.; Tokuhashi, K.; Sekiya, A. *Chem. Phys. Lett.* **2004**, *400*, 563.

(25) Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 177.

(26) Prinn, R. G.; Huang, J.; Weiss, R. F.; Cunnold, D. M.; Fraser, P. J.; Simmonds, P. G.; McCulloch, A.; Harth, C.; Salameh, P.; O'Doherty, S.; Wang, R. H. J.; Porter, L.; Miller, B. R. *Science* **2001**, *292*, 1882.