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Kinetics and Mechanisms for the Reactions of CF_3OCH_3 and $CF_3OC(O)H$ with OH Radicals Using an Environmental Reaction Chamber

L. Chen,[†] S. Kutsuna,*[,†] K. Nohara,[‡] K. Takeuchi,[†] and T. Ibusuki[†]

National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan, and Research Institute of Innovative Technology for the Earth, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

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The atmospheric chemistry of CF_3OCH_3, a possible HCFCs/HFCs substitute was studied using a smog chamber/FTIR technique. The ether was reacted with OH radicals prepared by photolysis of ozone in 100 Torr of an $H_2O/O_2/He$ gas mixture in a 1 m^3 temperature-controlled chamber. Using a relative rate method, $k(OH + CF_3OCH_3) = (4.22 \pm 0.84) \times 10^{-12} \exp[(-1750 \pm 350)/T]$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 268−308 K. The rate constant at 298 K was $(1.19 \pm 0.14) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. The products of the OH radical initiated degradation of CF_3OCH_3 were investigated in 100−230 Torr of an O_2/He gas mixture at 298 K using in situ FTIR spectroscopy. $k(OH + CF_3OC(O)H) = (1.68 \pm 0.20) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K was determined. The major products of the oxidation of $CF_3OC(O)H$ were COF_2 and CO_2. These results are discussed with respect to the atmospheric chemistry of CF_3OCH_3 and $CF_3OC(O)H$.

Introduction

Hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) have been used as substitutes for chlorofluorocarbons (CFCs) because they react with OH radicals in the troposphere and have shorter atmospheric lifetimes than CFCs. However, HCFCs have finite ozone depletion potentials because they contain chlorine atoms. HCFCs and HFCs have strong absorption bands in the terrestrial infrared radiation range and, thus, contribute to global warming.[1]

CF_3OCH_3 is one of the hydrofluoroethers (HFEs) that has been developed to replace HCFCs/HFCs in such applications as refrigerant and cleaning agents. Because the boiling point of CF_3OCH_3 is 249.1 K and the vapor pressure is 4328 Torr at 298 K, it will be released into the atmosphere when used. As with other fluorinated species, CF_3OCH_3 has been shown to have little impact on stratospheric ozone and only has less impact on global warming if it and its products are more rapidly removed than HCFCs and HFCs.[2]

CF_3OCH_3 will be removed from the atmosphere by a reaction with OH radicals as reaction 1:

$$CF_3OCH_3 + OH \rightarrow CF_3OCH_2 + H_2O \qquad (1)$$

The rate constant for the reaction of CF_3OCH_3 with OH radicals, k_1, has been measured by several researchers[2−4] at ≥ 296 K. Values of k_1 at room temperature and below are needed to evaluate the atmospheric lifetime of CF_3OCH_3. Although it is possible to derive rate constants k_1 below 296 K from extrapolation of higher temperature data using the Arrhenius expression, it is more reliable to make measurement at lower temperature.[4]

The chlorine atoms initiated oxidation of CF_3OCH_3 has been investigated by Wallington et al.[5] From their results of the chlorine initiated oxidation, trifluoromethyl formate, $CF_3OC(O)H$, will be a major primary product from the oxidation of CF_3OCH_3 by OH radicals in the atmosphere. $CF_3OC(O)H$ has a strong absorption in the wavenumber region of 1000−1300 cm^{-1},[5] which overlaps the atmospheric window of 770−1430 cm^{-1}.[6] Therefore, $CF_3OC(O)H$ has the potential to be a greenhouse gas, and it is necessary to investigate the atmospheric chemistry of $CF_3OC(O)H$. An upper limit for the rate constant $k(CF_3OC(O)H + OH)$ was estimated to be around 9.8×10^{-15} cm^3 $molecule^{-1}$ s^{-1} based on the rate constant, $k(CF_3OC(O)H + Cl) = 9.8 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1};[5] however, some fluorinated organic compounds react faster with OH radicals than with Cl atoms such as CHF_2CF_3 (HFC-125) and CH_2FCF_3 (HFC-134a).[7]

In this study, we employed a relative rate method to measure k_1 in the ambient temperature range of 268−308 K, which can be used without extrapolation to estimate the atmospheric lifetime of CF_3OCH_3 by scaling to a CH_3CCl_3 lifetime at 272 K.[8] We monitored the concentration−time profiles of CF_3OCH_3 and its products in the reaction with OH radicals quantitatively using in situ FTIR spectroscopy at 298 K. $k(CF_3OC(O)H + OH)$ at 298 K was determined according to a reported method by Meagher et al.[9] The products of the reaction of CF_3OCH_3 with OH radicals observed in this experiment were also compared with the products reported by Wallington et al.[5] from the reaction of CF_3OCH_3 with Cl atoms.

Experimental Section

All experiments were performed by using a 1 m^3 stainless steel cylindrical chamber with an inner diameter of 1.0 m interfaced to a Bomem DA8 FTIR spectroscope with a White-optical multiple refection mirror system. The optical path length of the infrared beam was 54 m. The inside wall of the chamber was coated with Teflon to minimize the wall effects in the reactions. Two 1 kW Xe short-arc lamps (USHIO Co., Japan) were positioned on the top of the chamber to initiate the photochemical experiments. The UV light was cut by an optical filter (>260 nm; SHIMA QUARTZ, Co., Japan). The illuminated part of the chamber was 18% in volume. The gas mixtures

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* To whom correspondence should be addressed.

[†] National Institute of Advanced Industrial Science and Technology.

[‡] Research Institute of Innovative Technology for the Earth.

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were continuously stirred using a fan with an diameter of 15 cm and a speed of 200 rpm, which was attached to the inside of the chamber. The chemicals were separately added to the chamber and pumped away after each complete experiment. The chamber temperature can be controlled over the range 233−308 K to ±1 K using a temperature-control system that consists of two refrigerators, a heater, and a coolant flow controlling system.

OH radicals were produced by UV photolysis of O_3 in the presence of water vapor in 100 Torr of He as illustrated in the following reaction sequence:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad (2)$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad (3)$$

An O_3/O_2 (5%) gas mixture, which was generated from pure O_2 with a silent-discharge ozone generator (ECEA-1000, EBARA JITSUGYO, Japan) was used in the experiments. The concentration of OH radicals produced in the chamber was estimated to be the order of $(1-10) \times 10^{10}$ molecule cm^{-3} from the decay of the concentration of CH_4 because of reaction with OH radicals in the chamber.

The kinetics of the reaction of CF_3OCH_3 with OH radicals was measured using the relative rate method, which has been described in several previous publications.[10,11] Absolute rate constants for the reaction of CH_4 and CH_3CCl_3 have been measured accurately, and the values of these two rate constants are comparable to that of CF_3OCH_3.[7] Therefore, CH_4 and CH_3CCl_3 were used as the reference compounds in this study. Cl and CF_3O radicals are produced in the reaction of OH with CH_3CCl_3 and OH with $CF_3OC(O)H$, respectively. Both of these species may contribute to the loss of CF_3OCH_3, CH_3CCl_3, and CH_4, but the relative rate plots obtained in this work are quite linear suggesting that Cl and CF_3O formed in secondary reactions do not complicate the kinetic studies.

All experiments were performed in the temperature range of 268−308 K in 100 Torr He. The typical initial concentrations of CF_3OCH_3, CH_4 (or CH_3CCl_3), H_2O, O_3 , and O_2 were 1.3×10^{14}, 2.5×10^{14} (or 1.2×10^{14}), 1.3×10^{17}, 1.2×10^{16}, and 2.4×10^{17} molecule cm^{-3} in 100 Torr of He, respectively. Each experiment was performed with either CH_4 or CH_3CCl_3 as the reference compounds. The loss of CF_3OCH_3, CH_4, and CH_3CCl_3 was measured with the FTIR spectrometer at a resolution of 0.5 cm^{-1}. The concentrations of CF_3OCH_3, CH_4, and CH_3CCl_3 were determined with their absorption cross sections (base 10) of 1.11×10^{-18}, 2.04×10^{-20}, and 6.17×10^{-19} cm^2 $molecule^{-1}$ at 1167, 3149, and 728 cm^{-1}, respectively.

Under various combinations of gas mixtures and with or without irradiation, the concentration of CF_3OCH_3, CH_4, and CH_3CCl_3 were monitored for 6 h. A linear least-squares analysis of the concentrations of CF_3OCH_3, CH_4, and CH_3CCl_3 gives <2% changes of these compounds with irradiation condition at 308 K. The changes in concentrations of CF_3OCH_3, CH_4, and CH_3CCl_3 were obtained to be <2% in the presence of ozone with or without irradiation conditions for 6 h at 308 K, respectively. The heterogeneous reactions of CF_3OCH_3, CH_4, and CH_3CCl_3 with H_2O were not observed in the presence of H_2O without irradiation conditions at 298 K. Therefore, the losses of CF_3OCH_3, CH_4, and CH_3CCl_3 via photolysis or dark chemistry were confirmed to be insignificant in this chamber.

Estimation of the rate constant for the reaction of $CF_3OC(O)H$ with OH radicals was performed in three runs. The initial concentrations were CF_3OCH_3 (2.5×10^{14} molecule cm^{-3})/H_2O (1.3×10^{17} molecule cm^{-3}) at 298 K in 100 Torr of He. In these runs, an O_3/O_2 (5%) gas mixture was continuously added to the system at a flow rate of 0.3−0.5 mL min^{-1} to maintain a concentration of O_3 between 2×10^{15} and 3×10^{15} molecule cm^{-3} during the UV irradiation. The UV irradiation was continued for 50−70 h and the total pressure increased to 160−230 Torr at the end of the runs. The fractional loss of CF_3OCH_3 was 90% for a 50−70 h photolysis. The primary oxidation product $CF_3OC(O)H$ increased initially with time and was subsequently removed in secondary reactions forming COF_2 which was identified and quantified by IR spectra. The absorption cross section, ϵ_{COF2}, of 6.3×10^{-19} cm^2 $molecule^{-1}$ at 1928 cm^{-1} was obtained from an artificial COF_2/N_2 standard.

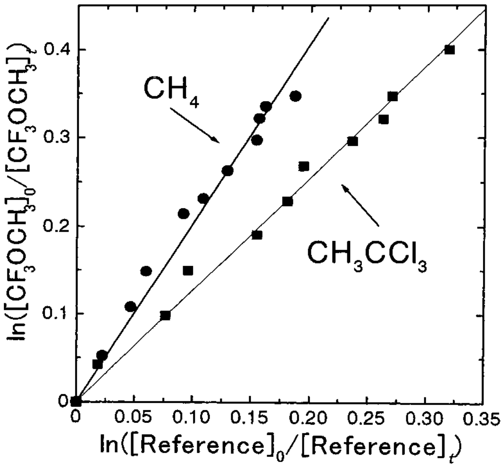

Figure 1. Loss of CF_3OCH_3 versus the reference compounds of CH_4 and CH_3CCl_3 in the presence of OH radicals. Experiments were performed at 298 K in 100 Torr of He.

The reagents used were CH_4 (99.7%) and CH_3CCl_3 (99%; both from GL Science, Japan), COF_2/N_2 standard (85%) and He (99.99995%; both from Takachiho Chemical Industry, Co., Japan), and pure O_2 (99.99%, Nippon Sanso, Corp., Japan). CF_3OCH_3 (99%) was obtained from the Research Institute of Innovative Technology for the Earth (RITE).

Results and Discussion

Kinetics of the Reaction of CF_3OCH_3 with OH Radicals. The results obtained at 298 K based on the two reference compounds of CH_4 and CH_3CCl_3 are shown in Figure 1, and eq 4 is used to determine the rate constant:[10,11]

$$\ln\left(\frac{[CF_3OCH_3]_0}{[CF_3OCH_3]_t}\right) = \frac{k_1}{k_r}\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \qquad (4)$$

where $[CF_3OCH_3]_0$ and $[\text{reference}]_0$ represent the initial concentrations of the reactant and reference compounds, $[CF_3OCH_3]_t$ and $[\text{reference}]_t$ represent the concentrations of reactant and reference compounds at the reaction time t, and k_1 and k_r are the rate constants for the reaction of OH radicals with CF_3OCH_3 and reference compounds, respectively. The plots of $\ln([CF_3OCH_3]_0/[CF_3OCH_3]_t)$ versus $\ln([\text{Reference}]_0/[\text{Reference}]_t)$ gave straight lines, which intersected the origin for the two references of CH_4 and CH_3CCl_3. The slopes from the linear least-squares analysis of the data in Figure 1 give $k_1/k_r = 1.91 \pm 0.12$ and 1.18 ± 0.08 for CH_4 and CH_3CCl_3, respectively. The errors reported are ±2 standard deviation and represent precision only. The k_1 (298 K) values were estimated to be $(1.20 \pm 0.14) \times 10^{-14}$ and $(1.18 \pm 0.12) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} from the rate constants of the reactions of CH_4 and CH_3-

TABLE 1: Measured Rate Constant, k_1/k_r and k_1, as a Function of Temperature

	k_1/k_r		k_1[a]	
T (K)	CH4	CH3CCl3	CH4	CH3CCl3
268		1.07 ± 0.12		0.593±0.07
278	1.85 ± 0.23		0.764±0.10	
281		1.22 ± 0.07		0.875±0.05
288	2.08 ± 0.17		1.07±0.09	
290		1.30 ± 0.26		1.12±0.22
298	1.91 ± 0.12	1.18 ± 0.08	1.20±.0.08	1.18±0.08
308	2.01 ± 0.28	1.11 ± 0.06	1.55±0.22	1.30±0.07

[a] The unit is 10^{-14} cm^3 molecule^{-1} s^{-1}.

CCl_3 with OH radicals at 298 K, 6.3×10^{-15} and 1.0×10^{-14}, respectively,[7] and the ratio of k_1/k_r were determined using eq 4. The values of k_1 (298 K) obtained using CH_4 and CH_3CCl_3 as reference compounds were the same within experimental uncertainty. We estimate that the potential systematic errors associated with uncertainties in the reference rate constants add a further 10% uncertainty in the values of k_1. The values at 298 K of k_1 of 1.30×10^{-14} and $(1.0 \pm 0.07) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} reported by Orkin et al.[3] and DeMore et al.,[4] respectively, are in agreement with the data obtained in this study within experimental uncertainty. The absolute rate measurement value at 296 K of k_1 of $(2.14 \pm 0.15) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} measured at a total pressure of 35 Torr by Zhang et al.[2] is a factor of about 2 higher than the present measurement, possibly because the presence of impurities in the sample.

The values of k_1 at different temperatures were estimated from k_1/k_r and the rate constant of $k(CH_4) = 2.45 \times 10^{-12} \exp[-(1775 \pm 100)/T]$ and $k(CH_3CCl_3) = 1.8 \times 10^{-12} \exp[-(1550 \pm 150)/T]$ cm^3 molecule^{-1} s^{-1}.[7] The result of k_1 obtained are summarized in Table 1. The temperature dependence of k_1 is shown in Figure 2. The rate constant Arrhenius expression of k_1 was derived to be $(4.22 \pm 0.84) \times 10^{-12} \exp[-(1750 \pm 350)/T]$ cm^3 molecule^{-1} s^{-1} from a linear least-squares fits to the data in Figure 2. The uncertainty in the Arrhenius expression was calculated by considering the random errors of k_1.

The value of k_1 calculated at 272 K, the average troposphere temperature,[8] from the Arrhenius expression is used to estimate the atmospheric lifetime and GWP of CF_3OCH_3. The atmospheric lifetime of CF_3OCH_3 with respect to loss by reaction with OH radicals was estimated from eq 5 to be 4.9 years:

$$\tau_{CF_3OCH_3} = \frac{k_{CH_3CCl_3}}{k_{CF_3OCH_3}} \tau_{CH_3CCl_3}, \qquad (5)$$

where $\tau_{CF3OCH3}$ and $\tau_{CH3CCl3}$ represent the tropospheric lifetime of CF_3OCH_3 and CH_3CCl_3 through the reaction with OH radicals. $\tau_{CH3CCl3}$ was estimated to be 5.5 years by Spivakovaky et al.[8] $k_{CF3OCH3} = 6.8 \times 10^{-15}$ and $k_{CH3CCl3} = 6.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} represent the reaction rate constants for the reactions of CF_3OCH_3 and CH_3CCl_3 with OH radicals at 272 K.

Estimate of the Kinetics of the Reaction of $CF_3OC(O)H$ with OH Radicals. Figure 3 shows IR spectra obtained from the experiment of the OH radicals initiated photooxidation of CF_3OCH_3.

The observed products of the reaction were $CF_3OC(O)H$, COF_2, CO_2, and traces of CO. $CF_3OC(O)H$ was identified from its reported spectrum.[5] Therefore, making the reasonable assumption that $CF_3OC(O)H$ and COF_2 account for all of the reaction products containing both carbon and fluorine, then the absorption cross-section of $CF_3OC(O)H$, $\epsilon_{CF3OC(O)H}$, was determined from the material balance $\Delta CF_3OC(O)H]_t = \Delta[CF_3OCH_3]_t - [COF_2]_t$, where $\Delta[CF_3OCH_3]_t$ is $([CF_3OCH_3]_0 - [CF_3OCH_3]_t)$, in the initial 4.2 h period. On the basis of a blank experiment of COF_2 in the system, about 12% of the COF_2 will be lost from the chamber by wall reaction in the initial 4.2 h period. Because the yield of COF_2 after a 4.2 h photolysis experiment is only around 10%, the error in the calculation of

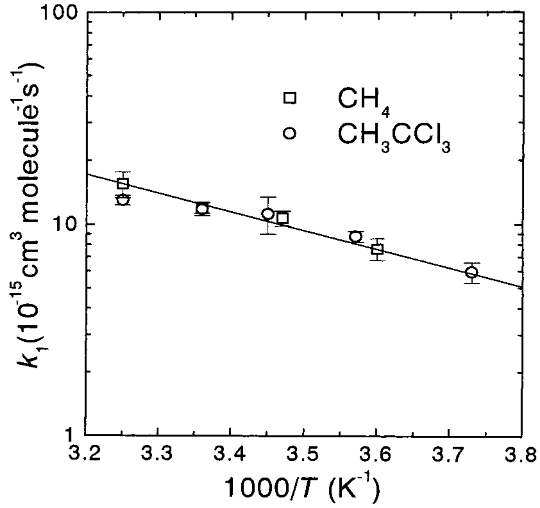

Figure 2. Arrhenius plot of kinetics data obtained by a relative rate method for CF_3OCH_3 reaction with OH radicals.

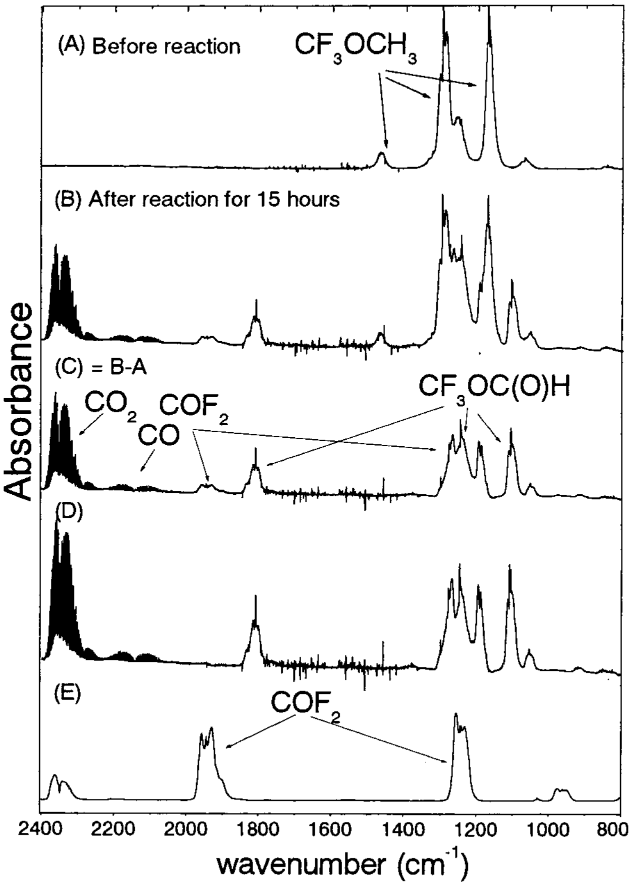

Figure 3. IR spectra observed before (A) and after (B) 15 h irradiation of a gas mixture of CF_3OCH_3 (2.5×10^{14})/H_2O (2.5×10^{17} molecule cm^{-3}) at 298 K in 100 Torr of He. O_3/O_2 (5%) gas mixture was introduced into the chamber at a flow of 0.5 mL/min continuously during the UV irradiation. (C) A spectrum of B after subtraction of unreacted CF_3OCH_3, (D) a spectrum of C after subtraction of COF_2, and (E) a reference spectrum of COF_2.

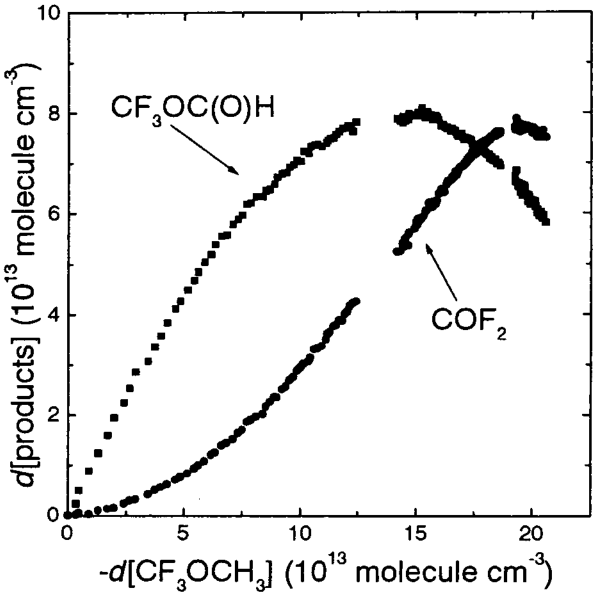

Figure 4. Plot of the $[CF_3OC(O)H]_t$ and $[COF_2]_t$ versus $\Delta[CF_3OCH_3]_t$. The data were obtained from the experiment presented in Figure 3.

$\epsilon_{CF3OC(O)H}$ due to correction for wall loss of COF_2 will be minimal. A value for $\epsilon_{CF3OC(O)H}$ was obtained $= 4.0 \times 10^{-19}$ cm^2 molecule^{-1} at the absorption band of 1814 cm^{-1} with an estimated error of 2%.

Plots of the $[CF_3OC(O)H]_t$ and $[COF_2]_t$ against loss of CF_3OCH_3 in Figure 4 indicate that $CF_3OC(O)H$ and COF_2 are the primary and secondary products against loss of CF_3OCH_3, respectively. $CF_3OC(O)H$ is an intermediate in the consecutive reactions 1 and 6:

$$CF_3OCH_3 + OH \rightarrow\rightarrow \alpha CF_3OC(O)H + \text{products} \quad (1)$$

$$CF_3OC(O)H + OH \rightarrow \text{products} \quad (6)$$

The parameter α is the yield of $CF_3OC(O)H$ from CF_3OCH_3 ($0 \le \alpha \le 1$). The following eq 7 can be derived:[9]

$$y = \frac{\alpha}{1 - \frac{k_6}{k_1}}(1 - x)[(1 - x)^{\{k_6/k_1 - 1\}} - 1] \quad (7)$$

$$x = \frac{\Delta[CF_3OCH_3]_t}{[CF_3OCH_3]_0}$$

$$y = \frac{[CF_3OC(O)H]_t}{[CF_3OCH_3]_0}$$

where x and y are the ratio of CF_3OCH_3 reacted and $CF_3OC(O)H$ formed to the initial concentration of CF_3OCH_3 at reaction time t and k_1 and k_6 are the reaction rate constants of reactions 1 and 6, respectively. A fit of the eq 7 to the data in Figure 5 of $[CF_3OC(O)H]_t/[CF_3OCH_3]_0$ versus $\Delta[CF_3OCH_3]_t/[CF_3OCH_3]_0$ gives the values of α and k_6/k_1. The obtained values of α and k_6/k_1 were 1.04 ± 0.01 and 1.40 ± 0.04, respectively, as the simple average of three runs. A value of $\alpha = 1$ shows that the yield of $CF_3OC(O)H$ is close to unity for the reaction of CF_3OCH_3 with OH radicals. Using k_1 (298 K) $= (1.2 \pm 0.14) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} from this work, k_6 (298 K) was estimated to be $(1.68 \pm 0.20) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. We estimate that potential systematic errors associated with uncertainties in k_1 add a further 20% uncertainty range for k_6. Thus, $CF_3OC(O)H$ reacts faster with OH radicals than with Cl atoms by a factor 1.7 at 298 K.[5]

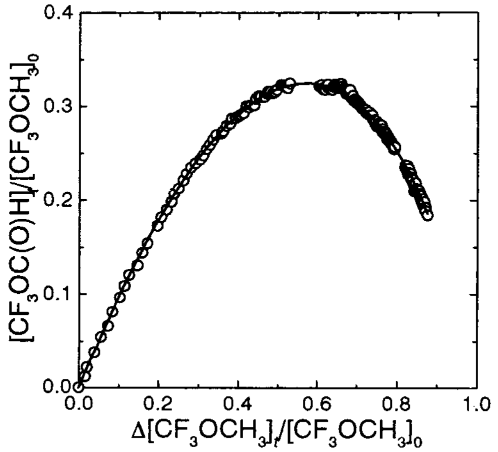

Figure 5. Plot of $[CF_3OC(O)H]_t/[CF_3OCH_3]_0$ versus $[CF_3OCH_3]_t/[CF_3OCH_3]_0$. The curve is a fit of eq 7 in the text to the data of $[CF_3OC(O)H]_t/[CF_3OCH_3]_0$.

Long period photoillumination (50−70 h) was carried out in which the primary product $CF_3OC(O)H$ was reacted in secondary reaction. These conditions were needed to determine the parameters α and k_6/k_1 accurately by fitting the plot of $[CF_3OC(O)H]_t/[CF_3OCH_3]_0$ versus $\Delta[CF_3OCH_3]_t/[CF_3OCH_3]_0$. Because such relatively long photolysis reactions might be accompanied by some artifact reactions, the dark reactions of $CF_3OC(O)H$ and COF_2 were examined in the experimental system. Irradiation of CF_3OCH_3 (2.5×10^{14})/O_3 (1.25×10^{16})/O_2 (2.4×10^{17})/H_2O (1.3×10^{17} molecule cm^{-3}) mixtures was carried out at 298 K in 100 Torr total pressure of He. After $CF_3OC(O)H$ and COF_2 were produced by UV irradiation for 6 h, the gas mixture was stored in the chamber for 24 h without further UV irradiation. The decays of $CF_3OC(O)H$ and COF_2 were monitored and have apparent first-order rate constants of $(5.1 \pm 1.0) \times 10^{-7}$ and $(7.8 \pm 0.2) \times 10^{-6}$ s^{-1}, respectively. The dark reaction of $CF_3OC(O)H$ was considered to be insignificant in the kinetic experiments, in which small amounts of COF_2 were shown to react with water on the wall of the chamber heterogeneously. In addition, photolysis of $CF_3OC(O)H$ because of UV irradiation (>260 nm) was also shown to be negligible.

Because $CF_3OC(O)H$ reacts with OH radicals via H abstraction from the −OC(O)H group, the value of k_6 should decrease with a decrease in temperature. A lower limit for the lifetime of $CF_3OC(O)H$ of 2.0 years can be estimated from k_6 (298 K) using eq 5. This lifetime is long enough for $CF_3OC(O)H$ to contribute to global warming because $CF_3OC(O)H$ shows a strong absorption in the wavenumber region 1000−1300 cm^{-1}. However, $CF_3OC(O)H$ is expected to hydrolyze easily by analogy with esters reference. Further study on dissolution into clouds and wet deposition of $CF_3OC(O)H$ is important in order to evaluate the contribution of CF_3OCH_3 to global warming.

Mechanism of the Reaction of CF_3OCH_3 with OH Radicals. According to the product distribution yields, the following mechanism is proposed for the reaction of CF_3OCH_3 with OH radicals under the conditions of the present studies:

$$CF_3OCH_3 + OH \rightarrow CF_3OCH_2 + H_2O \quad (1)$$

$$CF_3OCH_2 + O_2 + M \rightarrow CF_3OCH_2O_2 + M \quad (8)$$

The peroxy radical formed in reaction 8 can react with HO_2 and itself:[5,3,14]

$$CF_3OCH_2O_2 + HO_2 \rightarrow CF_3OCH_2OOH + O_2 \quad (9a)$$

$$CF_3OCH_2O_2 + HO_2 \rightarrow CF_3OC(O)H + H_2O + O_2 \quad (9b)$$

$$2CF_3OCH_2O_2 \rightarrow 2CF_3OCH_2O + O_2 \quad (10a)$$

$$2CF_3OCH_2O_2 \rightarrow CF_3OC(O)H + CF_3OCH_2OH + O_2 \quad (10b)$$

However, CF_3OCH_2OOH and CF_3OCH_2OH were not observed. The absence of CF_3OCH_2OOH was supported by the measurement of $k_{9a}/(k_{9a} + k_{9b}) = 0.2$ by Wallington et al.[5] In addition, hydroperoxides and alcohols are generally very reactive toward OH radicals, $k(OH + CH_3OOH) = 7.4 \times 10^{-12}$, $k(OH + CH_3OH) = 8.9 \times 10^{-13}$, and $k(OH + C_2H_5OH) = 3.18 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K,[7] although the presence of fluorine in CF_3OCH_2OOH and CF_3OCH_2OH would be expected to reduce their reactivity. Therefore, it is possible that CF_3OCH_2OOH and CF_3OCH_2OH would react with OH radicals to regenerate $CF_3OCH_2O_2$ and CF_3OCH_2O radicals in the chamber.

The CF_3OCH_2O radical produced in reaction 10a can react with O_2 or decompose by carbon−oxygen bond fission:

$$CF_3OCH_2O + O_2 \rightarrow CF_3OC(O)H + HO_2 \quad (11a)$$

$$CF_3OCH_2O + M \rightarrow CF_3O + HC(O)H + M \quad (11b)$$

Because the yield of $CF_3OC(O)H$ is close to unity, decomposition via reaction 11b was considered to be insignificant in this reaction system. This result is consistent with the measurement by Wallington et al.,[5] who reported the yield of $CF_3OC(O)H$ as unity over the partial pressure range 6−700 Torr of O_2.[5] Variation of the pressure in this work from 100 to 230 Torr by adding O_3/O_2 to the gas mixtures did not impact the yield of $CF_3OC(O)H$ supporting this observation.

$CF_3OC(O)H$ formed can react with OH radicals in the chamber in reaction 6:

$$CF_3OC(O)H + OH \rightarrow CF_3OC(O) + H_2O \quad (6)$$

$CF_3OC(O)$ radicals will rapidly react with O_2 to produce $CF_3OC(O)O_2$ radicals, which will produce $CF_3OC(O)O$ radicals via reaction with peroxy radicals (RO_2):

$$CF_3OC(O) + O_2 + M \rightarrow CF_3OC(O)O_2 + M \quad (12)$$

$$CF_3OC(O)O_2 + RO_2 \rightarrow CF_3OC(O)O + RO + O_2 \quad (13)$$

The small amounts of CO seen in the IR spectra of the products in Figure 3 shows that $CF_3OC(O)$ radicals also will decompose to CF_3O radicals and CO in competition with reaction 12:

$$CF_3OC(O) \rightarrow CF_3O + CO \quad (14)$$

The $CF_3OC(O)O$ radical may decompose to CF_3O radical and CO_2:[15]

$$CF_3OC(O)O + M \rightarrow CF_3O + CO_2 \quad (15)$$

A CF_3O radical is expected to react with CF_3OCH_3, $CF_3OC(O)H$, or H_2O to produce CF_3OH as in eqs 16−18 in the gas phase or on the chamber walls:[16−18]

$$CF_3O + CF_3OCH_3 \rightarrow CF_3OH + OH \quad (16)$$

$$CF_3O + CF_3OC(O)H \rightarrow CF_3OH + OH \quad (17)$$

$$CF_3O + H_2O \rightarrow CF_3OH + OH \quad (18)$$

Because of the high concentration of H_2O of 1.3×10^{17} molecule cm^{-3} in the chamber, the fate of CF_3O radicals is considered to react with H_2O in this reaction system. CF_3OH formed from a reactions (16−18) can rapidly decompose heterogeneously to COF_2 and HF on the chamber walls:[16,19,20]

$$CF_3OH \rightarrow COF_2 + HF \quad (19)$$

COF_2 is a secondary product of the reaction of CF_3OCH_3 with OH radicals via $CF_3OC(O)H$ and CF_3OH. This mechanism is consistent with the observation of COF_2 in Figure 4.

Summary

The rate constant of the reaction of CF_3OCH_3 with OH radicals is $k_1(T) = (4.22 \pm 0.84) \times 10^{-12} \exp[(-1750 \pm 350)/T]$ cm^3 $molecule^{-1}$ s^{-1}, and the atmospheric lifetime is estimated to be 4.9 years using the rate constant at 272 K. The rate constant of the reaction of $CF_3OC(O)H$ with OH radicals at 298 K is $(1.68 \pm 0.20) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, and the lower limit for the lifetime of $CF_3OC(O)H$ is estimated to be 2.0 years in this study. CF_3OCH_3 has less impact on global warming because it and its oxidation products are more rapidly removed from the atmosphere than typical refrigerants of HCFC-22 and HFC-134a.[7]

In the atmosphere, the CF_3OCH_2 radical produced in the reaction of CF_3OCH_3 with OH radicals will rapidly react with O_2 to form the peroxy radical $CF_3OCH_2O_2$. The $CF_3OCH_2O_2$ radicals will react with HO_2, NO_2, NO, and other peroxy radicals. The reaction of the $CF_3OCH_2O_2$ radical with HO_2 has been known to produce $CF_3OC(O)H$ within a yield of 80 ± 11%.[5] $CF_3OCH_2O_2NO_2$ formed from the reaction of $CF_3OCH_2O_2$ with NO_2 will decompose to $CF_3OCH_2O_2$ and NO_2 due to its thermally instability. The reaction of $CF_3OCH_2O_2$ with NO will produce the CF_3OCH_2O radical. The fate of the CF_3OCH_2O radical has been shown to form $CF_3OC(O)H$ by reaction with O_2. $CF_3OC(O)H$ will also be oxidized by OH radicals in the atmosphere. The $CF_3OC(O)$ radical produced from the reaction of $CF_3OC(O)H$ with OH radicals is known to react with O_2 to form $CF_3OC(O)O_2$ or decompose to the CF_3O radical and CO in this study. The formation of the $CF_3OC(O)O_2$ radical is likely to be the main processes in the atmospheric condition. As with other peroxy radicals, the $CF_3OC(O)O_2$ radicals also will react with HO_2, NO_2, NO, and other peroxy radicals in the atmosphere, but the atmospheric chemistry of the $CF_3OC(O)O_2$ radicals has not been known, it is necessary to study these reactions in detail. On the other hand, $CF_3OC(O)H$ is predicted to be hydrolyze easily; therefore, it is important to investigate the removal of $CF_3OC(O)H$ from the atmosphere by dissolution into clouds and wet deposition.

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References and Notes

(1) UNEP/WMO. Global Ozone Research and Monitoring Project; *Scientific Assessment of Ozone Depletion*; Report No. 37; 1994.

(2) Zhang, Z.; Saini, R. D.; Kuryol, M. J.; Huie, R. E. *J. Phys. Chem*. **1992**, *96*, 9301.

(3) Orkin, W. L.; Khamaganov, V. G.; Guschin, A. G.; Huie, R. E.; Kurylo, M. J. *The 13th International Symposium on Gas Kinetics*; The University College, Dublin: Dublin, Ireland, 1994.

(4) Hsu, K.-J.; DeMore, W. B. *J. Phys. Chem*. **1995**, *99*, 11141.

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

(6) Hanel, R. A.; Conrath, B. J.; Kunde, V. G.; Prabhakara, C.; Revah, I.; Salomonson, V. V.; Wolford, G. *J. Geophys. Res*. **1972**, *77*, 2629.

(7) 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 Publ.* **1997**, *97−4*.

(8) Spivakovsky, C. M.; Logan, J. A.; Montzka, S. A.; Balkanski, Y. J.; Foreman-Fowler, M.; Jones, D. B. A.; Horowitz, L. W.; Fusco, A. C.; Brenninkmeijer, C. A. M.; Prather, M. J.; Wofsy, S. C.; McElroy, M. B. *J. Geophys. Res*. **2000**, *105*, 8931.

(9) Meagher, R. J.; Mcintosh, M. E.; Hurley, M. D.; Wallington, T. J. *Int. J. Chem. Kinet*. **1997**, *29*, 619.

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

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

(12) Ko, M.; Shia, R.-L.; Sze, N.-D.; Magid, H.; Bray, R. G. *J. Geophys. Res*. **1999**, *104*, 8173.

(13) Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. *Atmos. Environ*. **1992**, *26A*, 1085.

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

(15) Atkinson, R. *J. Phys. Chem. Ref. Data* **1994**, *20*, 459.

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

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

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

(19) Huey, L. G.; Hanson, D. R.; Lovejoy, E. R. *J. Geophys. Res*. **1995**, *100*, 18771.

(20) Lovejoy, E. R.; Huey, L. G.; Hanson, D. R. *J. Geophys. Res*. **1995**, *100*, 18775.