

Kinetics and Mechanisms for the Reactions of CF₃OCH₃ and CF₃OC(O)H with OH Radicals Using an Environmental Reaction Chamber

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The atmospheric chemistry of CF₃OCH₃, 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 H₂O/O₂/He gas mixture in a 1 m³ temperature-controlled chamber. Using a relative rate method, $k(\text{OH} + \text{CF}_3\text{OCH}_3) = (4.22 \pm 0.84) \times 10^{-12} \exp[(-1750 \pm 350)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 268–308 K. The rate constant at 298 K was $(1.19 \pm 0.14) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The products of the OH radical initiated degradation of CF₃OCH₃ were investigated in 100–230 Torr of an O₂/He gas mixture at 298 K using in situ FTIR spectroscopy. $k(\text{OH} + \text{CF}_3\text{OC(O)H}) = (1.68 \pm 0.20) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K was determined. The major products of the oxidation of CF₃OC(O)H were COF₂ and CO₂. These results are discussed with respect to the atmospheric chemistry of CF₃OCH₃ and CF₃OC(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

CF₃OCH₃ 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 CF₃OCH₃ 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, CF₃OCH₃ 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

CF₃OCH₃ will be removed from the atmosphere by a reaction with OH radicals as reaction 1:



The rate constant for the reaction of CF₃OCH₃ 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 CF₃OCH₃. 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 CF₃OCH₃ has been investigated by Wallington et al.⁵ From their results of the chlorine initiated oxidation, trifluoromethyl formate, CF₃OC(O)H, will be a major primary product from the oxidation of CF₃-

OCH₃ by OH radicals in the atmosphere. CF₃OC(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, CF₃OC(O)H has the potential to be a greenhouse gas, and it is necessary to investigate the atmospheric chemistry of CF₃OC(O)H. An upper limit for the rate constant $k(\text{CF}_3\text{OC(O)H} + \text{OH})$ was estimated to be around $9.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on the rate constant, $k(\text{CF}_3\text{OC(O)H} + \text{Cl}) = 9.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁵ however, some fluorinated organic compounds react faster with OH radicals than with Cl atoms such as CHF₂CF₃ (HFC-125) and CH₂FCF₃ (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 CF₃OCH₃ by scaling to a CH₃CCl₃ lifetime at 272 K.⁸ We monitored the concentration–time profiles of CF₃OCH₃ and its products in the reaction with OH radicals quantitatively using in situ FTIR spectroscopy at 298 K. $k(\text{CF}_3\text{OC(O)H} + \text{OH})$ at 298 K was determined according to a reported method by Meagher et al.⁹ The products of the reaction of CF₃OCH₃ with OH radicals observed in this experiment were also compared with the products reported by Wallington et al.⁵ from the reaction of CF₃OCH₃ with Cl atoms.

Experimental Section

All experiments were performed by using a 1 m³ stainless steel cylindrical chamber with an inner diameter of 1.0 m interfaced to a Bomem DA8 FTIR spectroscope with a White-optical multiple reflection 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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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 O₃ in the presence of water vapor in 100 Torr of He as illustrated in the following reaction sequence:



An O₃/O₂ (5%) gas mixture, which was generated from pure O₂ 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 CH₄ because of reaction with OH radicals in the chamber.

The kinetics of the reaction of CF₃OCH₃ 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 CH₄ and CH₃CCl₃ have been measured accurately, and the values of these two rate constants are comparable to that of CF₃OCH₃.⁷ Therefore, CH₄ and CH₃CCl₃ were used as the reference compounds in this study. Cl and CF₃O radicals are produced in the reaction of OH with CH₃CCl₃ and OH with CF₃OC(O)H, respectively. Both of these species may contribute to the loss of CF₃OCH₃, CH₃CCl₃, and CH₄, but the relative rate plots obtained in this work are quite linear suggesting that Cl and CF₃O 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 CF₃OCH₃, CH₄ (or CH₃CCl₃), H₂O, O₃, and O₂ 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 CH₄ or CH₃CCl₃ as the reference compounds. The loss of CF₃OCH₃, CH₄, and CH₃CCl₃ was measured with the FTIR spectrometer at a resolution of 0.5 cm⁻¹. The concentrations of CF₃OCH₃, CH₄, and CH₃CCl₃ were determined with their absorption cross sections (base 10) of 1.11×10^{-18} , 2.04×10^{-20} , and 6.17×10^{-19} cm² molecule⁻¹ at 1167, 3149, and 728 cm⁻¹, respectively.

Under various combinations of gas mixtures and with or without irradiation, the concentration of CF₃OCH₃, CH₄, and CH₃CCl₃ were monitored for 6 h. A linear least-squares analysis of the concentrations of CF₃OCH₃, CH₄, and CH₃CCl₃ gives <2% changes of these compounds with irradiation condition at 308 K. The changes in concentrations of CF₃OCH₃, CH₄, and CH₃CCl₃ 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 CF₃OCH₃, CH₄, and CH₃CCl₃ with H₂O were not observed in the presence of H₂O without irradiation conditions at 298 K. Therefore, the losses of CF₃OCH₃, CH₄, and CH₃CCl₃ via photolysis or dark chemistry were confirmed to be insignificant in this chamber.

Estimation of the rate constant for the reaction of CF₃OC(O)H with OH radicals was performed in three runs. The initial concentrations were CF₃OCH₃ (2.5×10^{14} molecule cm⁻³)/

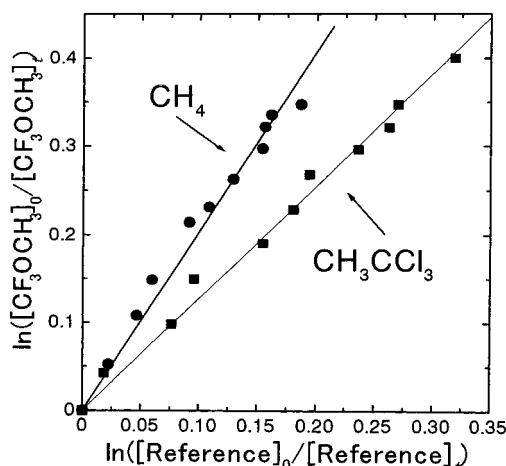


Figure 1. Loss of CF₃OCH₃ versus the reference compounds of CH₄ and CH₃CCl₃ in the presence of OH radicals. Experiments were performed at 298 K in 100 Torr of He.

H₂O (1.3×10^{17} molecule cm⁻³) at 298 K in 100 Torr of He. In these runs, an O₃/O₂ (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 O₃ 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 CF₃OCH₃ was 90% for a 50–70 h photolysis. The primary oxidation product CF₃OC(O)H increased initially with time and was subsequently removed in secondary reactions forming COF₂ which was identified and quantified by IR spectra. The absorption cross section, ϵ_{COF_2} , of 6.3×10^{-19} cm² molecule⁻¹ at 1928 cm⁻¹ was obtained from an artificial COF₂/N₂ standard.

The reagents used were CH₄ (99.7%) and CH₃CCl₃ (99%; both from GL Science, Japan), COF₂/N₂ standard (85%) and He (99.99995%; both from Takachiho Chemical Industry, Co., Japan), and pure O₂ (99.99%, Nippon Sanso, Corp., Japan). CF₃OCH₃ (99%) was obtained from the Research Institute of Innovative Technology for the Earth (RITE).

Results and Discussion

Kinetics of the Reaction of CF₃OCH₃ with OH Radicals.

The results obtained at 298 K based on the two reference compounds of CH₄ and CH₃CCl₃ are shown in Figure 1, and eq 4 is used to determine the rate constant:^{10,11}

$$\ln\left(\frac{[\text{CF}_3\text{OCH}_3]_0}{[\text{CF}_3\text{OCH}_3]_t}\right) = \frac{k_1}{k_r} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \quad (4)$$

where [CF₃OCH₃]₀ and [reference]₀ represent the initial concentrations of the reactant and reference compounds, [CF₃OCH₃]_t and [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 CF₃OCH₃ and reference compounds, respectively. The plots of ln([CF₃OCH₃]₀/[CF₃OCH₃]_t) versus ln([reference]₀/[reference]_t) gave straight lines, which intersected the origin for the two references of CH₄ and CH₃CCl₃. The slopes from the linear least-squares analysis of the data in Figure 1 give *k*₁/*k*_r = 1.91 ± 0.12 and 1.18 ± 0.08 for CH₄ and CH₃CCl₃, 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 $(1.18 \pm 0.12) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ from the rate constants of the reactions of CH₄ and CH₃-

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

T (K)	k_1/k_r		k_1^a	
	CH ₄	CH ₃ CCl ₃	CH ₄	CH ₃ CCl ₃
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} cm³ molecule⁻¹ s⁻¹.

CCl₃ 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 CH₄ and CH₃CCl₃ 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 $(1.0 \pm 0.07) \times 10^{-14}$ cm³ 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 $(2.14 \pm 0.15) \times 10^{-14}$ cm³ 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 $k(\text{CH}_4) = 2.45 \times 10^{-12} \exp[-(1775 \pm 100)/T]$ and $k(\text{CH}_3\text{CCl}_3) = 1.8 \times 10^{-12} \exp[-(1550 \pm 150)/T]$ cm³ 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 $(4.22 \pm 0.84) \times 10^{-12} \exp[-(1750 \pm 350)/T]$ cm³ 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 CF₃OCH₃. The atmospheric lifetime of CF₃OCH₃ with respect to loss by reaction with OH radicals was estimated from eq 5 to be 4.9 years:

$$\tau_{\text{CF}_3\text{OCH}_3} = \frac{k_{\text{CH}_3\text{CCl}_3}}{k_{\text{CF}_3\text{OCH}_3}} \tau_{\text{CH}_3\text{CCl}_3}, \quad (5)$$

where $\tau_{\text{CF}_3\text{OCH}_3}$ and $\tau_{\text{CH}_3\text{CCl}_3}$ represent the tropospheric lifetime of CF₃OCH₃ and CH₃CCl₃ through the reaction with OH radicals. $\tau_{\text{CH}_3\text{CCl}_3}$ was estimated to be 5.5 years by Spivakovsky et al.⁸ $k_{\text{CF}_3\text{OCH}_3} = 6.8 \times 10^{-15}$ and $k_{\text{CH}_3\text{CCl}_3} = 6.0 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ represent the reaction rate constants for the reactions of CF₃OCH₃ and CH₃CCl₃ with OH radicals at 272 K.

Estimate of the Kinetics of the Reaction of CF₃OC(O)H with OH Radicals. Figure 3 shows IR spectra obtained from the experiment of the OH radicals initiated photooxidation of CF₃OCH₃.

The observed products of the reaction were CF₃OC(O)H, COF₂, CO₂, and traces of CO. CF₃OC(O)H was identified from its reported spectrum.⁵ Therefore, making the reasonable assumption that CF₃OC(O)H and COF₂ account for all of the reaction products containing both carbon and fluorine, then the absorption cross-section of CF₃OC(O)H, $\epsilon_{\text{CF}_3\text{OC(O)H}}$, was deter-

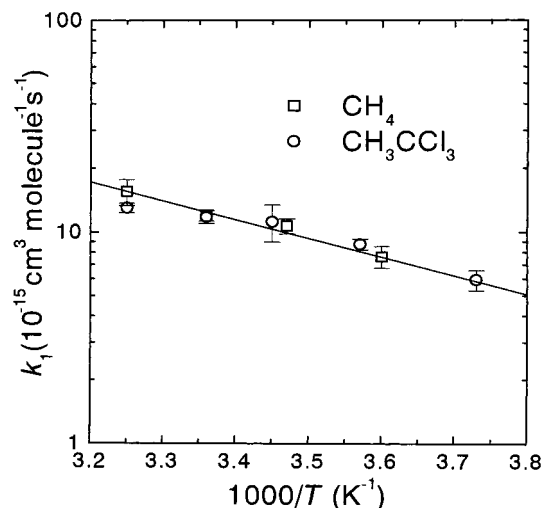


Figure 2. Arrhenius plot of kinetics data obtained by a relative rate method for CF₃OCH₃ reaction with OH radicals.

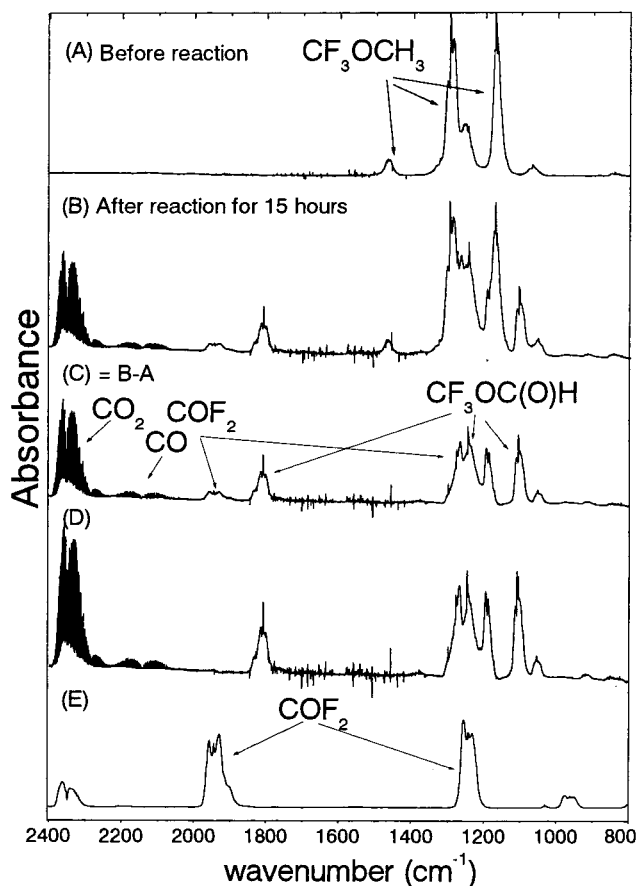


Figure 3. IR spectra observed before (A) and after (B) 15 h irradiation of a gas mixture of CF₃OCH₃ (2.5×10^{14})/H₂O (2.5×10^{17} molecule cm⁻³) at 298 K in 100 Torr of He. O₃/O₂ (5%) gas mixture was introduced into the chamber at a flow of 0.5 mL/min continuously during the UV irradiation. (C) A spectrum of B after subtraction of unreacted CF₃OCH₃, (D) a spectrum of C after subtraction of COF₂, and (E) a reference spectrum of COF₂.

mined from the material balance $\Delta\text{CF}_3\text{OC(O)H}_t = \Delta[\text{CF}_3\text{OCH}_3]_t - [\text{COF}_2]_t$, where $\Delta[\text{CF}_3\text{OCH}_3]_t$ is $([\text{CF}_3\text{OCH}_3]_0 - [\text{CF}_3\text{OCH}_3]_t)$, in the initial 4.2 h period. On the basis of a blank experiment of COF₂ in the system, about 12% of the COF₂ will be lost from the chamber by wall reaction in the initial 4.2 h period. Because the yield of COF₂ after a 4.2 h photolysis experiment is only around 10%, the error in the calculation of

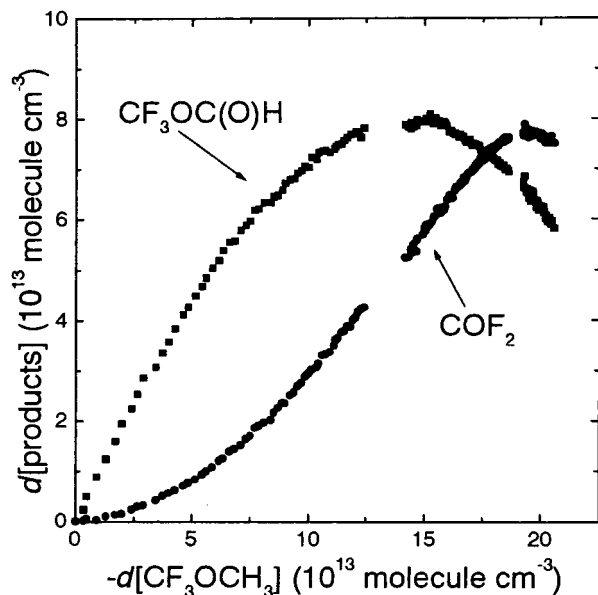
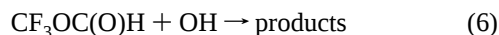


Figure 4. Plot of the [CF₃OC(O)H]_t and [COF₂]_t versus Δ[CF₃OCH₃]_t. The data were obtained from the experiment presented in Figure 3.

ε_{CF₃OC(O)H} due to correction for wall loss of COF₂ will be minimal. A value for ε_{CF₃OC(O)H} was obtained = 4.0 × 10⁻¹⁹ cm² molecule⁻¹ at the absorption band of 1814 cm⁻¹ with an estimated error of 2%.

Plots of the [CF₃OC(O)H]_t and [COF₂]_t against loss of CF₃OCH₃ in Figure 4 indicate that CF₃OC(O)H and COF₂ are the primary and secondary products against loss of CF₃OCH₃, respectively. CF₃OC(O)H is an intermediate in the consecutive reactions 1 and 6:



The parameter α is the yield of CF₃OC(O)H from CF₃OCH₃ (0 ≤ α ≤ 1). The following eq 7 can be derived:⁹

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

$$x = \frac{\Delta[\text{CF}_3\text{OCH}_3]_t}{[\text{CF}_3\text{OCH}_3]_0}$$

$$y = \frac{[\text{CF}_3\text{OC(O)H}]_t}{[\text{CF}_3\text{OCH}_3]_0}$$

where x and y are the ratio of CF₃OCH₃ reacted and CF₃OC(O)H formed to the initial concentration of CF₃OCH₃ at reaction time t and k₁ and k₆ are the reaction rate constants of reactions 1 and 6, respectively. A fit of the eq 7 to the data in Figure 5 of [CF₃OC(O)H]_t/[CF₃OCH₃]₀ versus Δ[CF₃OCH₃]_t/[CF₃OCH₃]₀ gives the values of α and k₆/k₁. The obtained values of α and k₆/k₁ were 1.04 ± 0.01 and 1.40 ± 0.04, respectively, as the simple average of three runs. A value of α = 1 shows that the yield of CF₃OC(O)H is close to unity for the reaction of CF₃OCH₃ with OH radicals. Using k₁ (298 K) = (1.2 ± 0.14) × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ from this work, k₆ (298 K) was estimated to be (1.68 ± 0.20) × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹. We estimate that potential systematic errors associated with uncer-

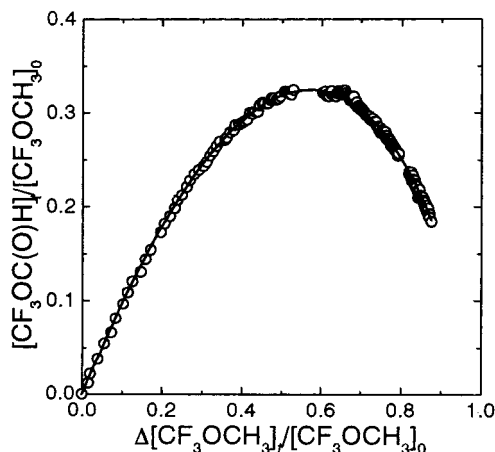


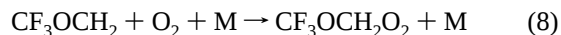
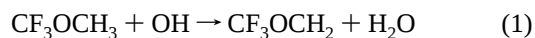
Figure 5. Plot of [CF₃OC(O)H]_t/[CF₃OCH₃]₀ versus Δ[CF₃OCH₃]_t/[CF₃OCH₃]₀. The curve is a fit of eq 7 in the text to the data of [CF₃OC(O)H]_t/[CF₃OCH₃]₀.

tainties in k₁ add a further 20% uncertainty range for k₆. Thus, CF₃OC(O)H reacts faster with OH radicals than with Cl atoms by a factor 1.7 at 298 K.⁵

Long period photoillumination (50–70 h) was carried out in which the primary product CF₃OC(O)H was reacted in secondary reaction. These conditions were needed to determine the parameters α and k₆/k₁ accurately by fitting the plot of [CF₃OC(O)H]_t/[CF₃OCH₃]₀ versus Δ[CF₃OCH₃]_t/[CF₃OCH₃]₀. Because such relatively long photolysis reactions might be accompanied by some artifact reactions, the dark reactions of CF₃OC(O)H and COF₂ were examined in the experimental system. Irradiation of CF₃OCH₃ (2.5 × 10¹⁴)/O₃ (1.25 × 10¹⁶)/O₂ (2.4 × 10¹⁷)/H₂O (1.3 × 10¹⁷ molecule cm⁻³) mixtures was carried out at 298 K in 100 Torr total pressure of He. After CF₃OC(O)H and COF₂ 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 CF₃OC(O)H and COF₂ were monitored and have apparent first-order rate constants of (5.1 ± 1.0) × 10⁻⁷ and (7.8 ± 0.2) × 10⁻⁶ s⁻¹, respectively. The dark reaction of CF₃OC(O)H was considered to be insignificant in the kinetic experiments, in which small amounts of COF₂ were shown to react with water on the wall of the chamber heterogeneously. In addition, photolysis of CF₃OC(O)H because of UV irradiation (>260 nm) was also shown to be negligible.

Because CF₃OC(O)H reacts with OH radicals via H abstraction from the -OC(O)H group, the value of k₆ should decrease with a decrease in temperature. A lower limit for the lifetime of CF₃OC(O)H of 2.0 years can be estimated from k₆ (298 K) using eq 5. This lifetime is long enough for CF₃OC(O)H to contribute to global warming because CF₃OC(O)H shows a strong absorption in the wavenumber region 1000–1300 cm⁻¹. However, CF₃OC(O)H is expected to hydrolyze easily by analogy with esters reference. Further study on dissolution into clouds and wet deposition of CF₃OC(O)H is important in order to evaluate the contribution of CF₃OCH₃ to global warming.

Mechanism of the Reaction of CF₃OCH₃ with OH Radicals. According to the product distribution yields, the following mechanism is proposed for the reaction of CF₃OCH₃ with OH radicals under the conditions of the present studies:

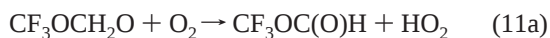


The peroxy radical formed in reaction 8 can react with HO₂ and itself:^{5,3,14}



However, CF₃OCH₂OOH and CF₃OCH₂OH were not observed. The absence of CF₃OCH₂OOH 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, $k(\text{OH} + \text{CH}_3\text{OOH}) = 7.4 \times 10^{-12}$, $k(\text{OH} + \text{CH}_3\text{OH}) = 8.9 \times 10^{-13}$, and $k(\text{OH} + \text{C}_2\text{H}_5\text{OH}) = 3.18 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K,⁷ although the presence of fluorine in CF₃OCH₂OOH and CF₃OCH₂OH would be expected to reduce their reactivity. Therefore, it is possible that CF₃OCH₂OOH and CF₃OCH₂OH would react with OH radicals to regenerate CF₃OCH₂O₂ and CF₃OCH₂O radicals in the chamber.

The CF₃OCH₂O radical produced in reaction 10a can react with O₂ or decompose by carbon–oxygen bond fission:

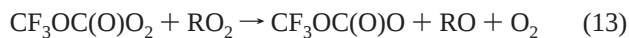
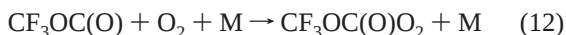


Because the yield of CF₃OC(O)H is close to unity, decomposition via reaction 11b was considered to be insignificant in this reaction system. This result is consistent with the measurement by Wallington et al.,⁵ who reported the yield of CF₃OC(O)H as unity over the partial pressure range 6–700 Torr of O₂.⁵ Variation of the pressure in this work from 100 to 230 Torr by adding O₃/O₂ to the gas mixtures did not impact the yield of CF₃OC(O)H supporting this observation.

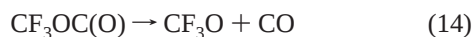
CF₃OC(O)H formed can react with OH radicals in the chamber in reaction 6:



CF₃OC(O) radicals will rapidly react with O₂ to produce CF₃OC(O)O₂ radicals, which will produce CF₃OC(O)O radicals via reaction with peroxy radicals (RO₂):



The small amounts of CO seen in the IR spectra of the products in Figure 3 shows that CF₃OC(O) radicals also will decompose to CF₃O radicals and CO in competition with reaction 12:

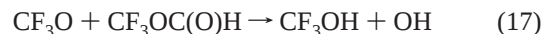


The CF₃OC(O)O radical may decompose to CF₃O radical and CO₂.¹⁵



A CF₃O radical is expected to react with CF₃OCH₃, CF₃OC(O)H,

or H₂O to produce CF₃OH as in eqs 16–18 in the gas phase or on the chamber walls:^{16–18}



Because of the high concentration of H₂O of 1.3×10^{17} molecule cm⁻³ in the chamber, the fate of CF₃O radicals is considered to react with H₂O in this reaction system. CF₃OH formed from a reactions (16–18) can rapidly decompose heterogeneously to COF₂ and HF on the chamber walls:^{16,19,20}



COF₂ is a secondary product of the reaction of CF₃OCH₃ with OH radicals via CF₃OC(O)H and CF₃OH. This mechanism is consistent with the observation of COF₂ in Figure 4.

Summary

The rate constant of the reaction of CF₃OCH₃ with OH radicals is $k_1(T) = (4.22 \pm 0.84) \times 10^{-12} \exp[(-1750 \pm 350)/T]$ cm³ 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 CF₃OC(O)H with OH radicals at 298 K is $(1.68 \pm 0.20) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, and the lower limit for the lifetime of CF₃OC(O)H is estimated to be 2.0 years in this study. CF₃OCH₃ 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 CF₃OCH₂ radical produced in the reaction of CF₃OCH₃ with OH radicals will rapidly react with O₂ to form the peroxy radical CF₃OCH₂O₂. The CF₃OCH₂O₂ radicals will react with HO₂, NO₂, NO, and other peroxy radicals. The reaction of the CF₃OCH₂O₂ radical with HO₂ has been known to produce CF₃OC(O)H within a yield of $80 \pm 11\%$.⁵ CF₃OCH₂O₂NO₂ formed from the reaction of CF₃OCH₂O₂ with NO₂ will decompose to CF₃OCH₂O₂ and NO₂ due to its thermally instability. The reaction of CF₃OCH₂O₂ with NO will produce the CF₃OCH₂O radical. The fate of the CF₃OCH₂O radical has been shown to form CF₃OC(O)H by reaction with O₂. CF₃OC(O)H will also be oxidized by OH radicals in the atmosphere. The CF₃OC(O) radical produced from the reaction of CF₃OC(O)H with OH radicals is known to react with O₂ to form CF₃OC(O)O₂ or decompose to the CF₃O radical and CO in this study. The formation of the CF₃OC(O)O₂ radical is likely to be the main processes in the atmospheric condition. As with other peroxy radicals, the CF₃OC(O)O₂ radicals also will react with HO₂, NO₂, NO, and other peroxy radicals in the atmosphere, but the atmospheric chemistry of the CF₃OC(O)O₂ radicals has not been known, it is necessary to study these reactions in detail. On the other hand, CF₃OC(O)H is predicted to be hydrolyze easily; therefore, it is important to investigate the removal of CF₃OC(O)H from the atmosphere by dissolution into clouds and wet deposition.

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