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Kinetics and mechanism of gas-phase reactions of n-$C_4F_9OCH_3$, i-$C_4F_9OCH_3$, n-$C_4F_9OC(O)H$, and i-$C_4F_9OC(O)H$ with OH radicals in an environmental reaction chamber at 253–328 K

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ABSTRACT

The rate constants of the reactions of n-$C_4F_9OCH_3$ (k_1), i-$C_4F_9OCH_3$ (k_2), n-$C_4F_9OC(O)H$ (k_3), and i-$C_4F_9OC(O)H$ (k_4) with OH radicals were studied in an 11.5-dm^3 environmental reaction chamber. k_1 and k_2 were determined to be $(1.44 \pm 0.33) \times 10^{-12}$ exp[–(1450 ± 70)/T] and $(1.59 \pm 0.41) \times 10^{-12}$ exp[–(1470 ± 80)/T] cm^3 molecule^{-1} s^{-1} at 253–328 K. At 298 K, k_3 and k_4 were deduced to be $(1.71 \pm 0.32) \times 10^{-14}$ and $(1.67 \pm 0.19) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The observed products of the reaction of n-$C_4F_9OCH_3$ with OH radicals were n-$C_4F_9OC(O)H$, $CF_3CF_2CF_2C(O)F$, and COF_2, and those for the reaction of i-$C_4F_9OCH_3$ were i-$C_4F_9OC(O)H$, $(CF_3)_2CFC(O)F$, $CF_3C(O)F$, and COF_2.

1. Introduction

Hydrofluoroethers (HFEs), which do not contain Cl and thus have zero stratospheric ozone depletion potential, are being investigated as alternatives to chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons [1]. For example, HFE-7100, which is a mixture of $CF_3CF_2CF_2CF_2OCH_3$ (n-$C_4F_9OCH_3$) and $(CF_3)_2CFCF_2OCH_3$ (i-$C_4F_9OCH_3$), is a commercial cleaning agent. Although n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ have no ozone depletion potential, they are potential greenhouse gases because their C–F bonds absorb in the terrestrial infrared radiation region of 800–1200 cm^{-1} [2]. Therefore, the rate constant for the reaction of HFE-7100 ($k_{\text{HFE-7100}}$) with OH radicals has been investigated by Wallington et al. [3] and Cavalli et al. [4].

However, these investigators measured $k_{\text{HFE-7100}}$ at 295 K using two different HFE-7100 samples: one consisting of 95% n-$C_4F_9OCH_3$ and 5% i-$C_4F_9OCH_3$ [3] and the other consisting of 25% n-$C_4F_9OCH_3$ and 75% i-$C_4F_9OCH_3$ [4]. In addition, neither the rate constants (k_1 and k_2) for the separate reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals (Eqs. 1 and 2) nor the temperature dependencies of k_1 and k_2 have been reported:

$$n\text{-}C_4F_9OCH_3 + OH \rightarrow \text{products} \quad k_1 \tag{1}$$

$$i\text{-}C_4F_9OCH_3 + OH \rightarrow \text{products} \quad k_2 \tag{2}$$

$CF_3CF_2CF_2CF_2OC(O)H$ (n-$C_4F_9OC(O)H$) and $(CF_3)_2CFCF_2OC(O)H$ (i-$C_4F_9OC(O)H$) are reported to be intermediate products of the reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals, respectively [3]. These intermediates might be removed from the atmosphere by reaction with OH radicals like $CF_3OC(O)H$, $C_2F_5C(O)H$, and n-$C_3F_7OC(O)H$ (Eqs. 3 and 4) [5,6]:

$$n\text{-}C_4F_9OC(O)H + OH \rightarrow \text{products} \quad k_3 \tag{3}$$

$$i\text{-}C_4F_9OC(O)H + OH \rightarrow \text{products} \quad k_4 \tag{4}$$

However, the kinetics of these reactions have not been reported.

In this study, we used a relative rate method to determine k_1 and k_2 in an 11.5-dm^3 environmental reaction chamber at 253–328 K [7,8]. The values of k_3 and k_4 at 298 K were deduced from the time profiles of the concentrations of n/i-$C_4F_9OC(O)H$ and n/i-$C_4F_9OCH_3$ at 298 K [5]. The products of the reactions of n/i-$C_4F_9OCH_3$ with OH radicals were studied by means of FT-IR at 298 K [9]. We estimated the tropospheric lifetimes of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with respect to reaction with OH radicals by scaling from the tropospheric lifetime of CH_3CCl_3 using k_1 and k_2 at 272 K.

2. Experimental

A sample of HFE-7100 (36% n-$C_4F_9OCH_3$ and 64% i-$C_4F_9OCH_3$, >99% pure) was obtained from DuPont–Mitsui Fluorochemicals Co. (Tokyo, Japan). Experiments were performed in an 11.5-dm^3 cylindrical quartz chamber (10 cm diameter, 146 cm long) with an external jacket [10]. The temperature in the reaction chamber was controlled by circulation of heated or cooled water, or a coolant (PF–5070, Sumitomo 3M, Tokyo, Japan), through the external jacket. The variation of the temperature distribution in the reaction chamber was monitored and found to be ±1 K over the

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temperature range of 253–328 K by means of two thermocouples, one attached to each side of the reaction chamber.

Hydroxyl radicals were produced by UV photolysis of O_3, which was generated from pure O_2 (99.5% pure; Nihon Sanso Corp., Japan) with a silent-discharge ozone generator (ECEA-1000, Ebara Jitsugyo Co., Japan) in the presence of water vapor at an initial He pressure of 200 Torr (99.995% pure; Iwatani International Corp., Osaka, Japan) [10]:

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad (5)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (6)$$

Ten 40-W low-pressure Hg lamps (254 ± 8 nm) surrounding the reaction chamber were used as the UV light sources for the determination of k_1 and k_2; and two lamps were used for the measurement of the products of the reactions of n/i-$C_4F_9OCH_3$ with OH radicals and rate constants k_3 and k_4. An O_3/O_2 (3%, O_3) gas mixture was continuously introduced at a flow rate of 1–2 $cm^3\ min^{-1}$ at STP into the reaction chamber during the UV irradiation period. A greaseless vacuum line was used for preparation of the reaction gas mixtures.

For the determination of k_1 and k_2, n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ were each analyzed relative to a reference compound, CF_3OCH_3 or $CF_3CF_2OCH_3$. CF_3OCH_3 (99% pure) and $CF_3CF_2OCH_3$ (99% pure) were obtained from Research Institute of Innovative Technology for the Earth (Kyoto, Japan). Because n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ were used as a mixture, the data for k_1 and k_2 were simultaneously measured in a single experiment. The initial concentrations (molecules cm^{-3}) were 4.7×10^{14} (n-$C_4F_9OCH_3$), 8.3×10^{14} (i-$C_4F_9OCH_3$), 1.0×10^{15} (reference compound), and $(0.36–5.8) \times 10^{17}$ (H_2O) in 200 Torr of He. The absolute concentrations of n-$C_4F_9OCH_3$, i-$C_4F_9OCH_3$, and the reference compounds were determined with a gas chromatograph (GC) with a flame ionization detector (FID) (GC-14A-FID; Shimadzu, Tokyo, Japan) equipped with a stainless steel column (3 mm i.d., 1 m long) packed with KRYTOX 143AC (GL Sciences Inc., Tokyo Japan). The column oven was set at a constant temperature of 393 K for the measurements of k_1 and k_2. A sample of the gas mixture (0.5 cm^3) was extracted from the chamber and transferred to the GC-FID by an automatic sampling system at 6-min intervals. In each sampling cycle, the gas mixture residing in the line between the sampling loop and the chamber was withdrawn and discarded, and then the gas mixture was charged into the sampling loop and transferred to the GC-FID. The mass of reactants decreased by 0.2% with each GC-FID analysis. The uncertainties in the measured concentrations of reactants were <2% for n-$C_4F_9OCH_3$, i-$C_4F_9OCH_3$, CF_3OCH_3, and $CF_3CF_2OCH_3$. The reactant percent decays after 90 min of irradiation at 298 K were 70–80%.

The values of k_1 and k_2 were obtained by measuring the disappearance rate of the sample relative to that of the reference compound in the presence of OH radicals (k_r):

$$\text{Reference} + OH \rightarrow \text{products} \quad k_r \quad (7)$$

Taking into account the nonreactive decay (0.2%) due to removal of the sample and reference compound for each GC-FID analysis, we used Eq. (I) to evaluate k_1/k_r and k_2/k_r [10]:

$$\ln\left(\frac{[\text{Sample}]_0}{[\text{Sample}]_t}\right) + D_n = \frac{k_i}{k_r}\left[\ln\left(\frac{[\text{Reference}]_0}{[\text{Reference}]_t}\right) + D_n\right] \quad k_i\ (i = 1\ or\ 2) \quad (I)$$

where $[\text{Sample}]_0$ and $[\text{Reference}]_0$ represent the initial concentrations of the sample (n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$) and the reference compound (CF_3OCH_3 or $CF_3CF_2OCH_3$); $[\text{Sample}]_t$ and $[\text{Reference}]_t$ represent the concentrations of the sample and the reference compound at reaction time t; and D_n is a parameter correcting for the nonreactive decay (0.2%) due to removal of the sample and reference compound for each GC-FID analysis ($D_n = n$ ln 0.998, where n is the sampling number of the GC-FID analysis [10]).

For determination of k_3 and k_4, samples of pure n-$C_4F_9OCH_3$ (98.5% pure) and pure i-$C_4F_9OCH_3$ (99.99% pure) were purified from the HFE-7100 sample with a gas chromatograph equipped with a stainless steel column (9.6 mm i.d., 1.2 m long) packed with KRYTOX 143AC. The apparatus and procedure for the purification of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ have been described in detail previously [11]. The typical initial concentrations (in molecules cm^{-3}) were 1.0×10^{15} (n/i-$C_4F_9OCH_3$) and 5.6×10^{17} (H_2O) in He at 200 Torr. The decay of the reactant was ~75% over a 100-min irradiation period at 298 K. The loss of n/i-$C_4F_9OCH_3$ and the formation of n/i-$C_4F_9OC(O)H$ and other products were monitored with an FT-IR spectrometer (JIR-6500, JEOL, Japan) with a nickel-coated aluminum multiple-reflection IR cell (375 cm^3; optical path length 3 m) at a resolution of 0.5 cm^{-1}. The sample in the reaction chamber was continuously circulated through the IR cell by a magnetically driven glass circulating pump at a flow rate of 850 $cm^3\ min^{-1}$ during UV irradiation. The concentrations of n-$C_4F_9OCH_3$, i-$C_4F_9OCH_3$, $CF_3CF_2CF_2C(O)F$, $(CF_3)_2CFC(O)F$, $CF_3C(O)F$, and COF_2 were quantified from the IR absorptions at 1460, 1460, 1888, 1889, 1902, and 1928 cm^{-1}, respectively, of their He mixtures of known concentration at a total pressure of 200 Torr at 298 K. $CF_3CF_2CF_2C(O)F$ (99% pure), $(CF_3)_2CFC(O)F$ (99% pure), and $CF_3C(O)F$ (99% pure) were obtained from Asahi Glass Co. (Japan), and COF_2 (95% pure) was purchased from SynQuest (Alachua, FL, USA).

n-$C_4F_9OCH_3$ or i-$C_4F_9OCH_3$ served as both a reference compound and a precursor for n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$, which not only react with OH radicals but also undergo photolysis under UV irradiation. Therefore, n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ are the intermediates in the following consecutive reactions:

$$n/i\text{-}C_4F_9OCH_3 + OH \rightarrow \alpha n/i\text{-}C_4F_9OC(O)H + \text{other products} \quad (8)$$

$$n/i\text{-}C_4F_9OC(O)H + OH \rightarrow \text{products} \quad (k_3, k_4) \quad (9)$$

$$n/i\text{-}C_4F_9OC(O)H + h\nu(254\ \text{nm}) \rightarrow \text{products} \quad (J_3, J_4) \quad (10)$$

The parameter α is the yield of n/i-$C_4F_9OC(O)H$ from the reaction of n/i-$C_4F_9OCH_3$ with OH radicals (α = 0–1). The values of α and k_3 and k_4 can be determined from Eq. (II) [5]:

$$y = \frac{\alpha}{1 - \left[\frac{k_{i+2}}{k_i}\left(1 + \frac{J_{i+2}}{k_{i+2}[OH]_{av}}\right)\right]}(1-x)\left[(1-x)^{\left\{\frac{k_{i+2}}{k_i}\left(1+\frac{J_{i+2}}{k_{i+2}[OH]_{av}}\right)-1\right\}} - 1\right] \quad (i = 1, 2) \quad (II)$$

$$x = \frac{\Delta[n/i - C_4F_9OCH_3]_t}{[n/i - C_4F_9OCH_3]_0}$$

$$y = \frac{[n/i - C_4F_9OC(O)H]_t}{[n/i - C_4F_9OCH_3]_0}$$

where J_3 and J_4 are the rates of photolysis of n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ (J_3 and J_4 were determined to be $(1.76 \pm 0.04) \times 10^{-5}$ and $(1.88 \pm 0.10) \times 10^{-5}\ s^{-1}$, respectively, for two 40 W lamps using the same method reported in our previously study [5,6]); $[OH]_{av}$ is the average concentration of OH radicals in the reaction chamber; and $\Delta[n/i$-$C_4F_9OCH_3]_t$, $[n/i$-$C_4F_9OC(O)H]_t$, and $[n/i$-$C_4F_9OCH_3]_0$ are, respectively, the concentration of n/i-$C_4F_9OCH_3$ consumed, the concentration of n/i-$C_4F_9OC(O)H$ at reaction time t, and the initial concentration of n/i-$C_4F_9OCH_3$. However, Eq. (II) is based on the presupposition that the concentration of OH radicals is approximately constant during measurement [5]. In this study, a nearly constant

OH radical concentration was produced by means of continuous addition of the O_3/O_2 gas mixture into the chamber during irradiation.

3. Results and discussion

3.1. Rate constants for reaction of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals

The rate constants for the reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals (k_1 and k_2) were measured in a single experiment because a mixture of HFE-7100 (36% n-$C_4F_9OCH_3$ and 64% i-$C_4F_9OCH_3$) was used as the reactant. Relative rate constants were derived from the fit to the data presented in Figure 1, in which $\ln([Sample]_0/[Sample]_t) + D_n$ is plotted versus $\ln([Reference]_0/[Reference]_t) + D_n$. These measurements were obtained in triplicate, and the results were consistent with each other. Linear least-squares analysis of the data presented in Figure 1 gave k_1/k_r and k_2/k_r (Table 1). The errors reported are 2 standard deviations; the errors were lower than 10% and represent precision only. Using the experimental data obtained for k_1/k_r and k_2/k_r along with the literature values $k_{298K}(CF_3OCH_3) = 1.2 \times 10^{-14}$ (±10%, one standard error) [12] and $k_{298K}(CF_3CF_2OCH_3) = 1.21 \times 10^{-14}$ (±7%, 2 standard errors) [13], we estimated k_1(298 K) and k_2(298 K) (Table 1). A possible systematic uncertainty could add an additional 10% (one standard error) to the values of k_1 and k_2 with due consideration of possible errors in the rate constants for the reference data. The values of k_1 and k_2 at 298 K obtained from the two reference compounds were the same within experimental uncertainty.

We investigated the potential loss of samples and reference compounds by means of UV photolysis, reactions with $O(^1D)$, and dark reactions with O_3 or H_2O. The losses of samples and reference compounds were less than the measurement errors (<2%) after 5 h of direct UV photolysis. In a previous study, we determined that $O(^1D)$ reactions do not occur to an appreciable extent in this reaction system [9]. The effects of $O(^1D)$ reactions on the measurements of k_1 and k_2 should be insignificant because H_2O is present at a >36-fold excess relative to the samples and reference compounds. The insignificance of $O(^1D)$ reactions was addressed in our previous study [9], which utilized virtually identical reaction conditions. Dark reactions of samples and reference compounds with either O_3 or H_2O were also found to be insignificant: the loss of reactants observed after 5 h was less than the loss due to concentration measurement errors (<2%).

The values of k_1/k_r and k_2/k_r were determined over the temperature range 253–328 K. The plots of $\ln([Sample]_0/[Sample]_t) + D_n$ versus $\ln([Reference]_0/[Reference]_t) + D_n$ obtained over this temperature range were similar to those shown in Figure 1. Table 1 lists the values of k_1 and k_2 determined from the measured k_1/k_r and k_2/k_r ratios, under the assumption that $k(CF_3OCH_3) = 1.84 \times 10^{-12} \exp(-1500/T)$ [12] and that $k(CF_3CF_2OCH_3) = 1.9 \times 10^{-12} \exp(-1510/T)$ cm^3 molecule^{-1} s^{-1} [13].

Using plots of the temperature dependences of k_1 and k_2 (Figure 2) and the Arrhenius expression, $k_i = A_i e^{-Ei/RT}$, we determined the Arrhenius rate parameters (A_i and E_i/R, where $i = 1, 2$) by nonlinear least-squares analysis and then calculated the values of k_1 and k_2 at 298 K (Table 2; $k_{HFE\text{-}7100}$ values from the literature are also listed in the table). The rate constants at 298 K, the pre-exponential factors, and activation energies obtained in this study were similar to each other. Because k_1 is equal to k_2, we can expect $k_{HFE\text{-}7100}$ not to vary with the molar ratio of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$. Our values for k_1 and k_2 at 298 K were similar to the value of $\sim 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} obtained at 295 K by Wallington et al. [3] and were about 67% higher than the value of $(0.72 \pm 0.16) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} obtained by Cavalli et al. [4]. In addition, our values of k_1 and k_2 at 298 K were similar to the values of 1.0×10^{-14} (CF_3OCH_3 [14]), $(1.21 \pm 0.09) \times 10^{-14}$ ($CF_3CF_2OCH_3$ [13]), and $(1.18 \pm 0.05) \times 10^{-14}$ ($CF_3CF_2CF_2OCH_3$ [13]) cm^3 molecule^{-1} s^{-1}. This similarity is consistent with the fact that the replacement of CF_3– with CF_3CF_2–, $CF_3CF_2CF_2$–, $CF_3CF_2CF_2CF_2$–, or $(CF_3)_2CFCF_2$– does not impact the OH radical reactivity of –OCH_3 [13].

The tropospheric lifetimes of n-$C_4F_9OCH_3$ (5.2 years) and i-$C_4F_9OCH_3$ (5.1 years) with respect to reaction with OH radicals were estimated by scaling to CH_3CCl_3 [9,15,16]. Because lifetimes of the two compounds were estimated to be almost same, the tropospheric lifetime of HFE-7100 can also be expected to 5.2 years.

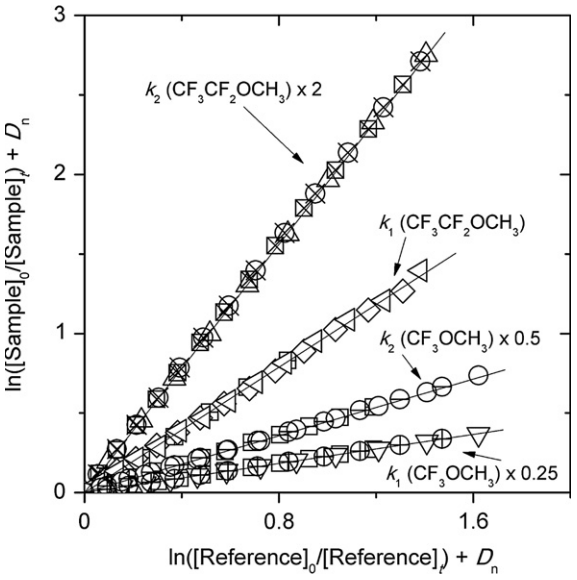

Figure 1. Loss of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ versus loss of reference compounds CF_3OCH_3 and $CF_3CF_2OCH_3$ in the presence of OH radicals at 298 K under an initial He pressure of 200 Torr. n-$C_4F_9OCH_3$ obtained from 3 runs: CF_3OCH_3 (□, ⊕, ▽) × 0.25, $CF_3CF_2OCH_3$ (◁, ◇, ⊞); i-$C_4F_9OCH_3$:CF_3OCH_3 (○, ⊖, ⊟) × 0.5; $CF_3CF_2OCH_3$ (Δ, ⊗, ⊠) × 2.

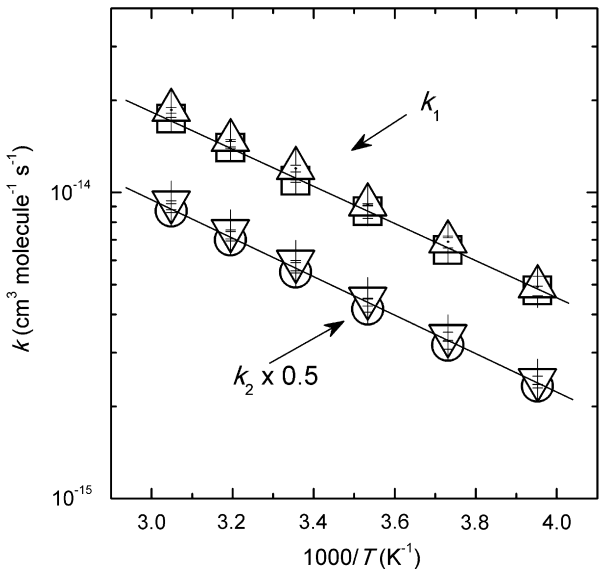

Figure 2. Arrhenius plots of kinetic data obtained by the relative rate method for reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals at 253–328 K. n-$C_4F_9OCH_3$:CF_3OCH_3 (□), $CF_3CF_2OCH_3$ (Δ); i-$C_4F_9OCH_3$:CF_3OCH_3 (○) × 0.5; $CF_3CF_2OCH_3$ (▽) × 0.5.

Table 1
Measured values of k_i/k_r and k_i (i = 1,2) over the temperature range 253–328 K.

Compounds	T	k_i/k_r		$10^{14} \times k_i$	
	K			cm^3 $molecule^{-1}$ s^{-1}	
		CF_3OCH_3	$CF_3CF_2OCH_3$	CF_3OCH_3	$CF_3CF_2OCH_3$
n-$C_4F_9OCH_3$	253	0.976 ± 0.035	1.01 ± 0.08	0.478 ± 0.017	0.493 ± 0.039
	268	0.950 ± 0.093	1.02 ± 0.05	0.648 ± 0.064	0.690 ± 0.031
	283	0.945 ± 0.048	0.997 ± 0.009	0.867 ± 0.044	0.912 ± 0.008
	298	0.905 ± 0.008	0.989 ± 0.026	1.09 ± 0.01	1.20 ± 0.03
	313	0.919 ± 0.009	0.973 ± 0.003	1.40 ± 0.01	1.48 ± 0.01
	328	0.915 ± 0.010	0.979 ± 0.023	1.74 ± 0.02	1.86 ± 0.04
i-$C_4F_9OCH_3$	253	0.952 ± 0.013	1.00 ± 0.03	0.466 ± 0.006	0.488 ± 0.015
	268	0.929 ± 0.027	1.00 ± 0.03	0.634 ± 0.019	0.681 ± 0.021
	283	0.906 ± 0.021	0.986 ± 0.002	0.832 ± 0.019	0.902 ± 0.002
	298	0.913 ± 0.012	0.981 ± 0.002	1.10 ± 0.01	1.19 ± 0.01
	313	0.915 ± 0.009	0.982 ± 0.009	1.40 ± 0.01	1.50 ± 0.01
	328	0.917 ± 0.012	0.976 ± 0.011	1.74 ± 0.02	1.86 ± 0.02

The quoted errors are 2 standard deviations.

Table 2
Arrhenius rate parameters of k_i (i = 1–4) over the temperature range 253–328 K.

Compounds	$10^{14} \times k_i$(298 K) cm^3 $molecule^{-1}$ s^{-1}	$10^{12} \times A_i$[a] cm^3 $molecule^{-1}$ s^{-1}	E_i/R[a] K	Temp. range K	Reference
n-$C_4F_9OCH_3$	1.15 ± 0.12[b]	1.44 ± 0.33	1450 ± 70	253–328	This work
i-$C_4F_9OCH_3$	1.14 ± 0.12[b]	1.59 ± 0.41	1470 ± 80	253–328	This work
95% n-$C_4F_9OCH_3$/5% i-$C_4F_9OCH_3$	~1.2			295	[3]
25% n-$C_4F_9OCH_3$/75% i-$C_4F_9OCH_3$	0.72 ± 016			295	[4]
n-$C_4F_9OC(O)H$	1.71 ± 032[a]			298	This work
i-$C_4F_9OC(O)H$	1.67 ± 019[a]			298	This work

[a] The quoted errors are two standard deviations.
[b] The quoted errors are one standard deviation and added an additional systematic error of 10% (one standard deviation).

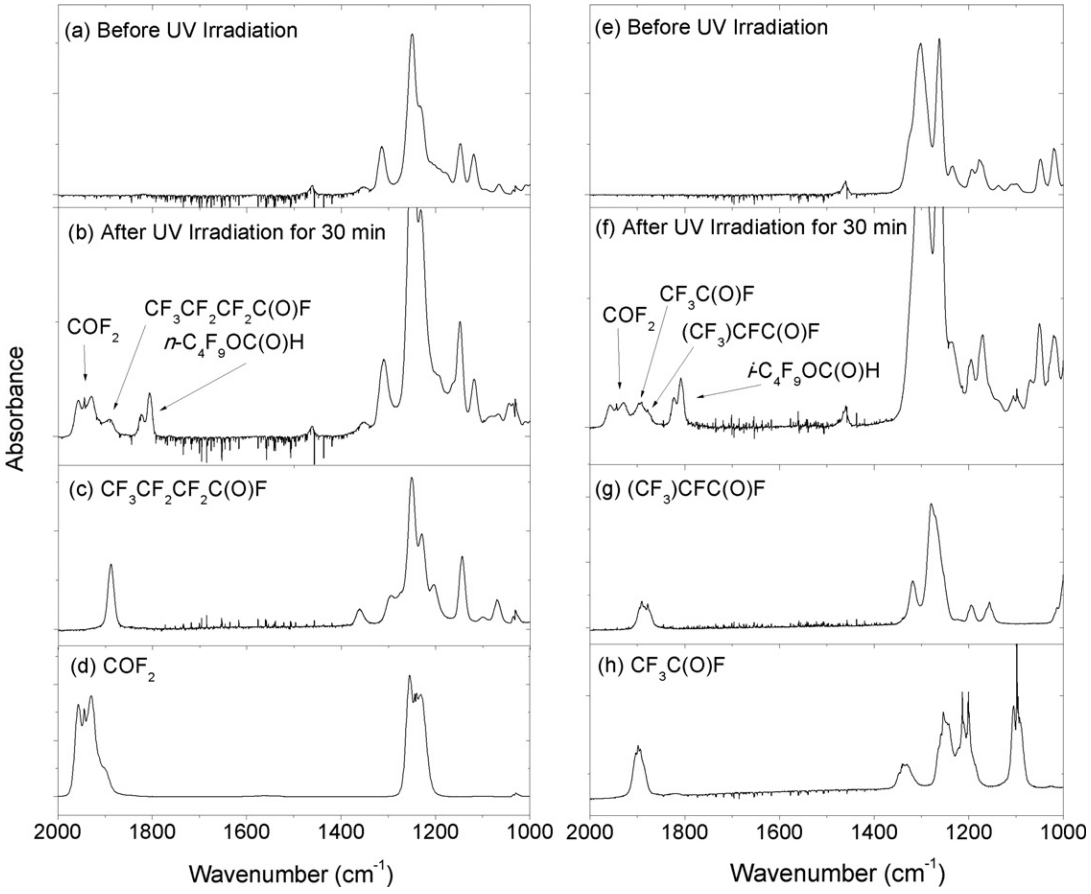

Figure 3. IR spectra observed before and after 30-min irradiation of n-$C_4F_9OCH_3$ (1.0×10^{15})/H_2O (5.6×10^{17}) (a and b) and i-$C_4F_9OCH_3$ (1.0×10^{15})/H_2O (5.6×10^{17}) (e and f) at 298 K in 200 Torr of He; reference spectra of $CF_3CF_2CF_2CF_2C(O)F$ (c), COF_2 (d), $(CF_3)_2CFC(O)F$ (g), and $CF_3C(O)F$ (h).

3.2. Mechanism of the reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals

The observed products of the OH radical–initiated oxidation of n-$C_4F_9OCH_3$ were n-$C_4F_9OC(O)H$, $CF_3CF_2CF_2C(O)F$, and COF_2, and those for i-$C_4F_9OCH_3$ were i-$C_4F_9OC(O)H$, $(CF_3)_2CFC(O)F$, $CF_3C(O)F$, and COF_2 (Figure 3). We did not determine CO_2 in this study. n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ were identified from their reported spectra [3].

On the basis of our results, we proposed the following mechanism for the reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals (Figure 4). n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ are formed as primary products of the reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals, which is consistent with the measurement of the reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals by Wallington et al. [3]. n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ subsequently react with OH radicals to form n-$C_4F_9OC(O)$ and i-$C_4F_9OC(O)$ radicals. n-$C_4F_9OC(O)$ and i-$C_4F_9OC(O)$ radicals undergo O_2 addition and subsequent reaction with HO_2 or RO_2 radicals ($R = n$-$C_4F_9OCH_2O_2$, n-$C_4F_9OC(O)O_2$, and n-$C_nF_{2n+1}O_2$, where $n = 1$–4; or i-$C_4F_9OCH_2O_2$, i-$C_4F_9OC(O)O_2$, $(CF_3)_2CFO_2$, and CF_3O_2) to produce n-$C_4F_9OC(O)O$ and i-$C_4F_9OC(O)O$ radicals, which decompose to n-C_4F_9O and i-C_4F_9O radicals and CO_2. n-C_4F_9O and i-C_4F_9O radicals should decompose quickly to $CF_3CF_2CF_2$ and COF_2, and $(CF_3)_2CF$ and COF_2, respectively, as pathways (a) and (b). However, it is interesting that $CF_3CF_2CF_2C(O)F$ and $(CF_3)_2CFC(O)F$ were observed in the reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals, respectively; these products likely formed by pathways (c) and (d), respectively. According to the mechanism proposed, the yield of COF_2 from the loss of n-$C_4F_9OC(O)H$ was estimated to be

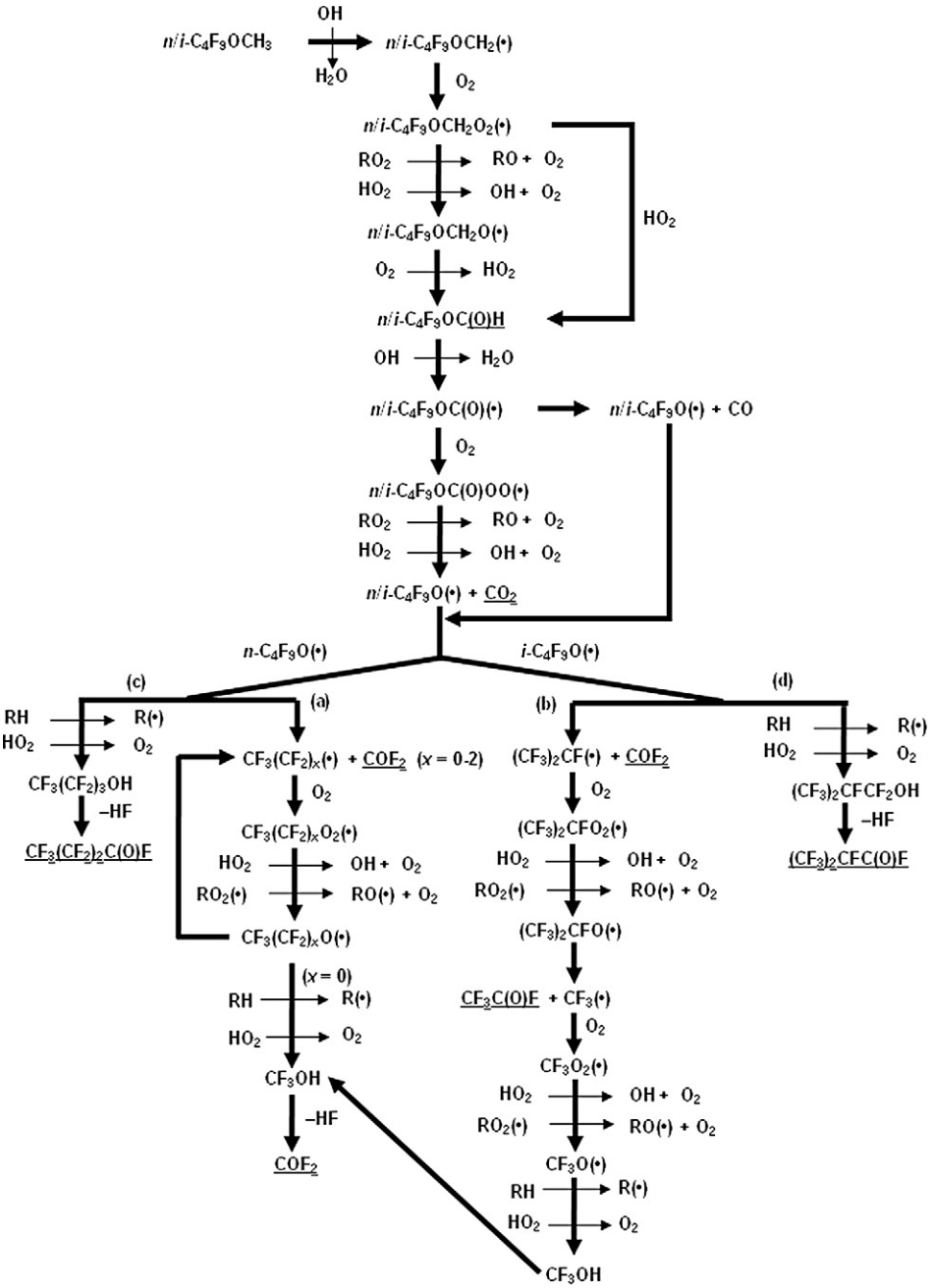

Figure 4. Mechanism of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ degradation initiated by OH radicals at 298 K.

2.0 ± 0.2 from $[COF_2]_t/([CF_3CF_2CF_2C(O)F]_t + [COF_2]_t/4)$, and the yield of COF_2 from the loss of i-$C_4F_9OC(O)H$ was estimated to be 1.0 ± 0.1 from $[COF_2]_t/([(CF_3)_2CFC(O)F]_t + [COF_2]_t/2)$. The branching ratio k_a/k_c was estimated to be 1.0 ± 0.2 from $([COF_2]_t/4)/[CF_3CF_2CF_2C(O)F]_t$, and k_b/k_d was estimated to be 1.2 ± 0.1 from $([COF_2]_t/2)/[(CF_3)_2CFC(O)F]_t$. A possible systematic uncertainty could add an additional 50% to the values of yield of COF_2, k_a/k_c, and k_b/k_d with due consideration of possible errors in the concentrations of $CF_3CF_2CF_2C(O)F$, $(CF_3)_2CFC(O)F$, and COF_2. The values of k_a/k_c and k_b/k_d obtained shows that pathways (c) and (d) are comparable with pathways (a) and (b). However, the pathways (a) and (b) are expected to be very fast ($k = 5 \times 10^6$ s^{-1} for C_2F_5O) [17] compared with reactions of (c) and (d). This inconsistence might be resulted from the fact that n-C_4F_9O and i-C_4F_9O in this study are formed by unimolecular decomposition of n/i-$C_4F_9OC(O)O$ radicals, while $C_xF_{2x+1}O$ observed in other studies are formed by collision reaction of $C_xF_{2x+1}O_2$ radicals [17–19]. To clarify this inconsistence, further study is needed. $CF_3CF_2CF_2$ and $(CF_3)_2CF$ radicals are expected to add O_2 to produce $CF_3CF_2CF_2O_2$ and $(CF_3)_2CFO_2$ radicals, which react with HO_2 or RO_2 to form $CF_3CF_2CF_2O$ and $(CF_3)_2CFO$ radicals. Finally, CF_3CF_2 and CF_3 radicals produced from the decomposition of $CF_3CF_2CF_2O$ and $(CF_3)_2CFO$ will produce the product of COF_2 (Figure 4).

3.3. Rate constants for the reactions of n-C4F9OC(O)H and i-C4F9OC(O)H with OH radicals

In the reaction of n-$C_4F_9OCH_3$ by the mechanism shown in Figure 4, n-$C_4F_9OC(O)H$, $CF_3CF_2CF_2C(O)F$, and COF_2 were the only products containing both carbon and fluorine, and therefore we determined the absorption cross-section (ε) for n-$C_4F_9OC(O)H$ to be $(4.2 \pm 0.3) \times 10^{-19}$ cm^2 molecule^{-1} (base 10) at 1808 cm^{-1} from the material balance equation $\Delta[n\text{-}C_4F_9OC(O)H]_t = \Delta[n\text{-}C_4F_9OCH_3]_t - [CF_3CF_2CF_2OC(O)F]_t - [COF_2]_t/4$, where $\Delta[n\text{-}C_4F_9OCH_3]_t = ([n\text{-}C_4F_9OCH_3]_0 - [n\text{-}C_4F_9OCH_3]_t)$ for the initial 18-min period. The ε value for i-$C_4F_9OC(O)H$ was determined to be $(4.3 \pm 0.3) \times 10^{-19}$ cm^2 molecule^{-1} (base 10) at 1808 cm^{-1} from the material balance equation $\Delta[i\text{-}C_4F_9OC(O)H]_t = \Delta[i\text{-}C_4F_9OCH_3]_t - [(CF_3)_2CFC(O)F]_t - [CF_3C(O)F]_t - [COF_2]_t/2$, where $\Delta[i\text{-}C_4F_9OCH_3]_t = ([i\text{-}C_4F_9OCH_3]_0 - [i\text{-}C_4F_9OCH_3]_t)$ for the initial 18-min period. Although a blank experiment indicated that the concentrations of $CF_3CF_2CF_2C(O)F$, $(CF_3)_2CFC(O)F$, $CF_3C(O)F$, and COF_2 were reduced by photolysis and wall reaction in this system, the losses of $CF_3CF_2CF_2C(O)F$, $(CF_3)_2CFC(O)F$, $CF_3C(O)F$, and COF_2 were all <2% in the initial 18-min period. Therefore, calculation of the ε values for n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ from the data during the initial 18-min period was not affected by these losses.

The concentration of OH radicals in the reaction chamber was estimated from the decay rate of n/i-$C_4F_9OCH_3$ by means of Eq. (III).

$$[OH]_t = \frac{-1}{k_i[n/i-C_4F_9OCH_3]_t}\frac{d[n/i-C_4F_9OCH_3]}{dt} \quad k_i(i=1,2) \qquad \text{(III)}$$

where $[OH]_t$ and $[n/i\text{-}C_4F_9OCH_3]_t$ are the concentrations of OH radicals and n/i-$C_4F_9OCH_3$ at reaction time t, and k_i (i = 1, 2) are the rate constants for reactions (1) and (2). To derive the value of $d[n\text{-}C_4F_9OCH_3]/dt$ at time t, we fitted the $[n\text{-}C_4F_9OCH_3]$ versus time data to a third-order polynomial and differentiated the resulting function to obtain $d[n\text{-}C_4F_9OCH_3]/dt$. The plot of OH radical concentration versus irradiation time was similar to that in our previously study [5,6]. The OH radical concentration was nearly constant during irradiation. The average OH radical concentration was $(2.3 \pm 0.4) \times 10^{10}$ radicals cm^{-3} for the measurement of k_3, and the average OH radical concentration was $(2.7 \pm 0.2) \times 10^{10}$ radicals cm^{-3} for the measurement of k_4.

Figure 5 shows a plot of $[n/i\text{-}C_4F_9OC(O)H]_t/[n/i\text{-}C_4F_9OCH_3]_0$ versus $\Delta[n/i\text{-}C_4F_9OCH_3]_t/[n/i\text{-}C_4F_9OCH_3]_0$ for n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ at 298 K. Fitting the data for n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ in Figure 5 to Eq. (II) by means of a nonlinear least-squares analysis gave values of $\alpha = (1.00 \pm 0.01)$ and $k_3 = (1.57 \pm 0.02) \times 10^{-14}$, and $\alpha = (1.04 \pm 0.04)$ and $k_4 = (1.70 \pm 0.05) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} using k_1 (298 K) = 1.15×10^{-14} and k_2 (298 K) = 1.14×10^{-14} cm^3 molecule^{-1} s^{-1} obtained in this study.

Whether, and to what extent, n-$C_4F_9OCH_3$, i-$C_4F_9OCH_3$, n-$C_4F_9OC(O)H$, and i-$C_4F_9OC(O)H$ were consumed in processes other than reaction with OH radicals and photolysis of n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ must be determined. In Section 3.1 we indicated that no change in n-$C_4F_9OCH_3$ or i-$C_4F_9OCH_3$ concentration was observed by direct UV photolysis and the dark reaction and that $O(^1D)$ reactions were insignificant in this reaction system. Possible routes for loss of n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ were direct UV photolysis, reactions with $O(^1D)$ produced by the photolysis of O_3, and the dark reaction. The photolyses of n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ (J_3 and J_4) were measured as described in Section 2. The effects of $O(^1D)$ reactions on the measurements of k_3 and k_4 should be insignificant, as discussed in the Section 3.1. The dark reactions of n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ were investigated over a period of 5–6 h in the presence of water vapor at the same concentration used in the measurement. The decay rates of n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ were estimated to be less than 3% for a 2-h irradiation period. Therefore, losses due to dark reactions of n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ were negligible.

The values of α and k_i (i = 3, 4) were measured in three runs at 298 K. Average values of $\alpha = (1.02 \pm 0.05)$ and $k_3 = (1.71 \pm 0.32) \times 10^{-14}$, and $\alpha = (1.03 \pm 0.03)$ and $k_4 = (1.67 \pm 0.19) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (Table 2) were obtained. The errors reported are ±2 standard deviations, which are random errors and represent precision only. The α values for n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ indicated that the yields of n-$C_4F_9OC(O)H$ and i-$C_4F_9OC(O)H$ were unity for the reactions of n-$C_4F_9OCH_3$ and i-$C_4F_9OCH_3$ with OH radicals. This result is consistent with the results of previous studies [5,6]. The values of k_3 and k_4 were comparable to the values for the rate constants of the following reactions: $CF_3OC(O)H + OH$ (298 K), $(1.65 \pm 0.13) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} [5]; $CF_3CF_2OC(O)H + OH$ (298 K), $(1.48 \pm 0.06) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} [6];

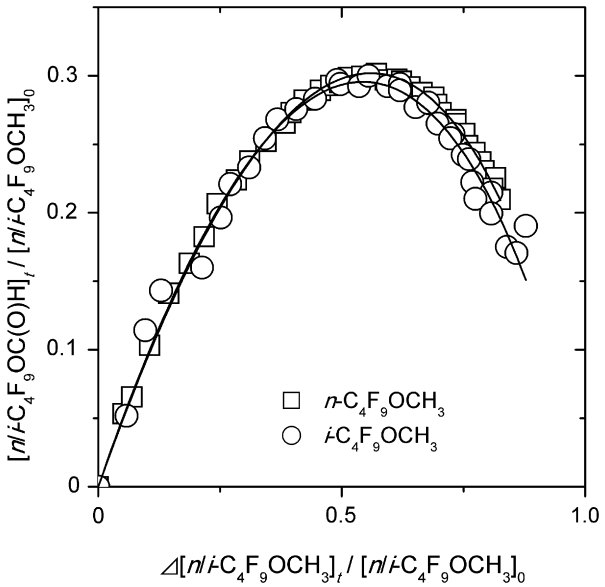

Figure 5. Plot of $[n/i\text{-}C_4F_9OC(O)H]_t/[n/i\text{-}C_4F_9OCH_3]_0$ versus $\Delta[n/i\text{-}C_4F_9OCH_3]_t/[n/i\text{-}C_4F_9OCH_3]_0$. The data were obtained from the experiment shown in Figure 3. The curve is a fit of Eq. (II) to the data for $[n/i\text{-}C_4F_9OC(O)H]_t/[n/i\text{-}C_4F_9OCH_3]_0$ versus $\Delta[n/i\text{-}C_4F_9OCH_3]_t/[n/i\text{-}C_4F_9OCH_3]_0$; n-$C_4F_9OCH_3$ (□), i-$C_4F_9OCH_3$ (○).

and $CF_3CF_2CF_2OC(O)H + OH$ (298 K), $(2.04 \pm 0.04) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} [6].

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