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# Kinetics study of the gas-phase reactions of $C_2F_5OC(O)H$ and *n*- $C_3F_7OC(O)H$ with OH radicals at 253–328 K

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#### Abstract

The rate constants,  $k_1$  and  $k_2$  for the reactions of  $C_2F_5OC(O)H$  and  $n-C_3F_7OC(O)H$  with OH radicals were measured using an FT-IR technique at 253–328 K.  $k_1$  and  $k_2$  were determined as  $(9.24 \pm 1.33) \times 10^{-13} \exp[-(1230 \pm 40)/T]$  and  $(1.41 \pm 0.26) \times 10^{-12} \exp[-(1260 \pm 50)/T]$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The random errors reported are  $\pm 2 \sigma$ , and potential systematic errors of 10% could add to the  $k_1$  and  $k_2$ . The atmospheric lifetimes of  $C_2F_5OC(O)H$  and  $n-C_3F_7OC(O)H$  with respect to reaction with OH radicals were estimated at 3.6 and 2.6 years, respectively.

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#### 1. Introduction

Two hydrofluoroethers (HFEs), C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> and  $n-C_3F_7OCH_3$ , have been developed to replace hydrochlorofluorocarbons and hydrofluorocarbons [1,2]. These HFEs have stratospheric-ozone depletion potentials of zero because they do not contain Cl atoms. However, they have been reported to have relative short atmospheric lifetimes of 4.9 and 5.0 years, respectively, which were estimated from the rate constants of their OH radical reactions at 272 K by scaling from the lifetime of CH<sub>3</sub>CCl<sub>3</sub> (6 years) [3]. Two perfluoroalkyl formates,  $C_2F_5OC(O)H$  and  $n-C_3F_7OC(O)H$ , are major primary products of the oxidation of C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> and  $n-C_3F_7OCH_3$  by OH radicals in the atmosphere [4,5]. These perfluoroalkyl formates are potential greenhouse gases owing to their strong absorption at 1000-1300 cm<sup>-1</sup>, and thus an assessment of their atmospheric chemistry is needed [4,5]. In the atmosphere, they can be removed by reaction with OH radicals:

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 $C_2F_5OC(O)H + OH \rightarrow \text{products} \quad k_1$  (1)

$$n-C_3F_7OC(O)H + OH \rightarrow \text{products} \quad k_2$$
 (2)

Therefore, the rate constants for OH radical reaction,  $k_1$  and  $k_2$ , are important factors in the atmospheric chemistry of these compounds. An upper limit of  $8.2 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for  $k_2$  has been estimated on the basis of the rate constant  $k(n-C_3F_7O)$ C(O)H + Cl), which is  $(8.2 \pm 2.2) \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 295 K [4]. However,  $k_1$  and  $k_2$  have not been measured. In this study, we determined  $k_1$  and  $k_2$ by using a Fourier transform infrared spectroscopic technique in an 11.5-dm<sup>3</sup> reaction chamber at 253–328 K. The atmospheric lifetimes of C<sub>2</sub>F<sub>5</sub>OC(O)H and  $n-C_3F_7OC(O)H$  with respect to reaction with OH radicals were estimated from the data for  $k_1$  and  $k_2$  at 272 K.

#### 2. Experimental

The  $C_2F_5OCH_3$  and  $n-C_3F_7OCH_3$  samples (99% pure) used in this study were provided by the Research Institute of Innovative Technology for the Earth (RITE). Measurements were carried out in an

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11.5-dm<sup>3</sup> cylindrical quartz chamber (diameter, 10 cm; length, 146 cm) with an external jacket [6]. The temperature in the reaction chamber was controlled by circulating heated water or a coolant through the external jacket. One or Two 40-W low-pressure Hg lamps (254  $\pm$  8 nm) (GL-40, National Co., Japan) were used as the UV light source.

The OH radicals were generated by UV photolysis of  $O_3$  in the presence of water vapor at an initial pressure of 200 Torr of He, as illustrated in Eqs. (3) and (4):

$$O_3 + hv \to O(^1D) + O_2 \tag{3}$$

$$O(^{1}D) + H_{2}O \rightarrow 2OH \tag{4}$$

He was used as a diluent because of its low quenching efficiency for  $O(^{1}D)$ . The  $O_{3}/O_{2}$  (3%) gas mixture was generated from pure  $O_{2}$  with a silent-discharge ozone generator (ECEA-1000, EBARAJITSUGYO, Japan). The  $O_{3}/O_{2}$  gas mixture was continuously introduced into the chamber at a flow rate of 6–20 cm<sup>3</sup> min<sup>-1</sup> during the UV irradiation period [6].

In the measurement of the rate constants,  $n-C_nF_{2n+1}OCH_3$  (n = 2 and 3) served as both a reference compound and a precursor for  $n-C_nF_{2n+1}OC(O)H$ .  $n-C_nF_{2n+1}OC(O)H$  not only reacts with OH radicals but also undergoes photolysis under UV irradiation. Therefore,  $n-C_nF_{2n+1}OC(O)H$  is the intermediate in the consecutive reactions illustrated in Eqs. (5)–(7)

$$n - C_n F_{2n+1} OCH_3 + OH \rightarrow \alpha n - C_n F_{2n+1} OC(O)H + other products$$
(5)

 $n-C_nF_{2n+1}OC(O)H + OH \rightarrow \text{products}$  (6)

 $n-C_nF_{2n+1}OC(O)H + hv(254 \text{ nm}) \rightarrow \text{products}$  (7)

The parameter  $\alpha$  is the yield of n-C<sub>n</sub>F<sub>2n+1</sub>OC(O)H from the reaction of n-C<sub>n</sub>F<sub>2n+1</sub>OC(O)H<sub>3</sub> with OH radicals ( $\alpha = 0 - 1$ ). The values of  $\alpha$  and  $k_6$  can be determined from Eq. (I) [7]

$$y = \frac{\alpha}{1 - \left[\frac{k_{6}}{k_{5}}\left(1 + \frac{J}{k_{6}[OH]_{av}}\right)\right]} \times (1 - x) \left[\left(1 - x\right)^{\left\{\frac{k_{6}}{k_{5}}\left(1 + \frac{J}{k_{6}[OH]_{av}}\right)^{-1}\right\}} - 1\right],$$
(I)

$$x = \frac{\Delta [n - C_n F_{2n+1} OCH_3]_t}{[n - C_n F_{2n+1} OCH_3]_0},$$
  
$$y = -\frac{[n - C_n F_{2n+1} OC(O)H]_t}{[n - C_n F_{2n+1} OCH_3]_0},$$

where  $k_5$  and  $k_6$  are the rate constants for the reactions in Eqs. (5) and (6); *J* is the rate of photolysis of n-C<sub>n</sub>F<sub>2n+1</sub>O C(O)H (the *J* values of C<sub>2</sub>F<sub>5</sub>OC(O)H and n-C<sub>3</sub>F<sub>7</sub>O C(O)H were determined to be  $(1.88 \pm 0.10) \times 10^{-5}$  (two

lamps) and  $(1.24 \pm 0.13) \times 10^{-5} \text{ s}^{-1}$  (one lamp), respectively);  $[OH]_{av}$  is the average concentration of OH radicals in the reaction chamber;  $\Delta[n-C_nF_{2n+1}OCH_3]_t$ ,  $[n-C_nF_{2n+1}OC(O)H]_t$  and  $[n-C_nF_{2n+1}OCH_3]_0$  are, respectively, the concentration of  $n-C_nF_{2n+1}OCH_3$  consumed, the concentration of  $n-C_nF_{2n+1}OCH_3$ . However, Eq. (I) is based on the presupposition that the concentration of OH radicals is approximately constant during measurement [7]. In this study, a nearly constant OH radical concentration were produced by means of continuous addition of the O<sub>3</sub>/O<sub>2</sub> gas mixture into the chamber during irradiation.

The typical initial concentrations (in molecules cm<sup>-3</sup>) were  $1.0 \times 10^{15}$  (C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> or *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub>) and  $5.6 \times 10^{17}$  (H<sub>2</sub>O) in He at 200 Torr. The decay of reactant was ~90% over a 60-min irradiation period at 298 K.

The loss of  $n-C_nF_{2n+1}OCH_3$  and the formation of  $n-C_nF_{2n+1}OC(O)H_3$  were monitored with an FT-IR spectrometer (JIR-6500, JEOL Ltd., Japan) with a nickel-coated aluminum multiple-reflection IR cell (375 cm<sup>3</sup>; optical path length, 3 m) at a resolution of  $0.5 \text{ cm}^{-1}$ . 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 absorption cross-sections ( $\epsilon$ ) (cm<sup>2</sup> molecule<sup>-1</sup> (base 10)) of C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> (8.08 × 10<sup>-20</sup> at 1461 cm<sup>-1</sup>), *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub> (9.73 × 10<sup>-20</sup> at 1461 cm<sup>-1</sup>), CF<sub>3</sub>C(O)F (1.72 × 10<sup>-19</sup>) at 1883 cm<sup>-1</sup>),  $C_2F_5C(O)F$  (2.96×10<sup>-19</sup> at 1883 cm<sup>-1</sup>), and COF<sub>2</sub> ( $6.3 \times 10^{-19}$  at 1928 cm<sup>-1</sup>) were calculated from the IR spectra of their He mixtures of known concentration. The following reagents were used:  $CF_3C(O)F$  (99%, RITE);  $C_2F_5C(O)F$  (97%, PCR Inc.); COF<sub>2</sub>/N<sub>2</sub> standard (85%); He (99.99995%, Takachiho Chemical Industry Co., Japan); and pure O<sub>2</sub> (99.99%, Nihon Sanso Corp., Japan).

#### 3. Results and discussion

### 3.1. Absorption cross-section of $n-C_nF_{2n+1}OC(O)H$

The observed products of the OH radical-initiated oxidation of C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> were C<sub>2</sub>F<sub>5</sub>OC(O)H, CF<sub>3</sub>C(O)F, and COF<sub>2</sub>, and those for *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub> were *n*-C<sub>3</sub>F<sub>7</sub>O C(O)H, C<sub>2</sub>F<sub>5</sub>C(O)F, and COF<sub>2</sub> (Fig. 1). We did not determine CO<sub>2</sub> in this study. C<sub>2</sub>F<sub>5</sub>OC(O)H and *n*-C<sub>3</sub>F<sub>7</sub>O C(O)H were identified from their reported spectra [4,5]. For the reaction of C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub>, because C<sub>2</sub>F<sub>5</sub>OC(O)H, CF<sub>3</sub>C(O)F, and COF<sub>2</sub> were the only products that contained both carbon and fluorine, we determined the  $\varepsilon$ value for C<sub>2</sub>F<sub>5</sub>OC(O)H to be (5.20 ± 0.50) × 10<sup>-19</sup> cm<sup>2</sup> molecule<sup>-1</sup> (base 10) at 1803 cm<sup>-1</sup> from the material balance equation  $\Delta$ [C<sub>2</sub>F<sub>5</sub>OC(O)H]<sub>t</sub> =  $\Delta$ [C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub>]<sub>t</sub> – [CF<sub>3</sub>C(O)F]<sub>t</sub> – [COF<sub>2</sub>]<sub>t</sub>, where  $\Delta$ [C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub>]<sub>t</sub> = ([C<sub>2</sub>F<sub>5</sub>



Fig. 1. IR spectra observed before and after 30-min irradiation of  $C_2F_3OCH_3$   $(1.01 \times 10^{15})/H_2 O(5.6 \times 10^{17})$  (a) and (b), and *n*- $C_3F_7OCH_3$   $(1.01 \times 10^{15})/H_2O(5.6 \times 10^{17})$  (d) and (e) at 298 K in 200 Torr of He; reference spectra of  $CF_3C(O)F$  (c) and  $C_2F_3C(O)F$  (f).

OCH<sub>3</sub>]<sub>0</sub> –  $[C_2F_5OCH_3]_t$ ) for the initial 18-min period. The  $\varepsilon$  value for n-C<sub>3</sub>F<sub>7</sub>OC(O)H was determined to be  $(5.47 \pm 0.57) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$  (base 10) at 1803 cm<sup>-1</sup> by the same method.

Although a blank experiment indicated that the concentrations of CF<sub>3</sub>C(O)F, C<sub>2</sub>F<sub>5</sub>C(O)F, and COF<sub>2</sub> were reduced by photolysis and wall reaction in this system, the losses of CF<sub>3</sub>C(O)F, C<sub>2</sub>F<sub>5</sub>C(O)F, and COF<sub>2</sub> were <2%, <2%, and 2%, respectively, in the initial 18-min period. Therefore, calculation of the  $\varepsilon$  values for C<sub>2</sub>F<sub>5</sub>O-C(O)H and *n*-C<sub>3</sub>F<sub>7</sub>OC(O)H from the data during the initial 18-min period was not affected by these losses. Therefore, calculation of the  $\varepsilon$  values for C<sub>2</sub>F<sub>5</sub>OC(O)H and *n*-C<sub>3</sub>F<sub>7</sub>OC(O)H from the data during the initial 18-min period was not affected by these losses.

#### 3.2. Estimate of OH radical concentration

The concentration of OH radicals in the reaction chamber was estimated from the decay rate of  $n-C_nF_{2n+1}OCH_3$  by means of Eq. (II).

$$[OH]_{t} = \frac{-1}{k_{5}[n-C_{n}F_{2n+1}OCH_{3}]_{t}} \frac{d[n-C_{n}F_{2n+1}OCH_{3}]}{dt},$$
(II)

where  $[OH]_t$  and  $[n-C_nF_{2n+1}OCH_3]_t$  are the concentrations of OH radicals and  $n-C_nF_{2n+1}OCH_3$  at reaction time t, and  $k_5$  is the rate constant for reaction (5). Fig. 2 shows the plots of  $C_2F_5OCH_3$  and OH radical concentration versus irradiation time. To derive the value of  $d[C_2F_5OCH_3]/dt$  at time t, the  $[C_2F_5OCH_3]$ vs. time data were fitted to a third-order polynomial, and the function thus obtained was differentiated to obtain  $d[C_2F_5OCH_3]/dt$ . The OH radical concentration was nearly constant during irradiation. The average OH radical concentration was  $(4.1 \pm 0.8) \times 10^{10}$  radicals  $cm^{-3}$ . Over all the measurements of C<sub>2</sub>F<sub>5</sub>OC(O)H and  $n-C_3F_7OC(O)H$ , the average OH radical concentration range was  $(2.41-5.41) \times 10^{10}$  radicals cm<sup>-3</sup>. The variation of OH radical concentration was less than 30% for each measurement.



Fig. 2. Plots of  $C_2F_5OCH_3$  and OH radical concentrations versus irradiation time. The data were obtained from the experiment in Fig. 1. The curves were obtained by fitting the data to a third-order polynomial.

## 3.3. Rate constants for the reaction of $n-C_nF_{2n+1}OC(O)H$ with OH radicals

Fig. 3 shows a plot of  $[C_2F_5OC(O)H]_t/[C_2F_5OCH_3]_0$ versus  $\Delta[C_2F_5OCH_3]_t/[C_2F_5OCH_3]_0$  at 298 K. Fitting the data for  $C_2F_5OCH_3$  and  $C_2F_5OCH_3$  in Fig. 3 to Eq. (I) by means of a nonlinear least-squares analysis gave  $\alpha$  and  $k_1$  values of  $(0.98 \pm 0.03)$  and  $(1.60 \pm 0.06)$  $\times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> using k (C\_2F\_5O-



Fig. 3. Plot of  $[n-C_nF_{2n+1}OC(O)H]/[n-C_nF_{2n+1}OCH_3]_0$  versus  $\Delta[n-C_nF_{2n+1}OCH_3]_{/}[n-C_nF_{2n+1}OCH_3]_0$ . The data were obtained from the experiment in Fig. 1. The curve is a fit of Eq. (I) to the data for  $[n-C_nF_{2n+1}OC(O)H]_{/}[n-C_nF_{2n+1}OCH_3]_0$  and  $\Delta[n-C_nF_{2n+1}OCH_3]_{/}[n-C_nF_{2n+1}OCH_3]_0$ .

CH<sub>3</sub> + OH) (298 K) =  $1.21 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K [3],  $J = 1.88 \times 10^{-5} \text{ s}^{-1}$ , and  $[\text{OH}]_{\text{av}} = 4.1 \times 10^{10}$ radicals cm<sup>-3</sup>. Average  $\alpha$  and  $k_1$  values of (0.99 ± 0.12) and  $(1.50 \pm 0.11) \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively, were obtained from four runs. The plot of [n- $C_3F_7OC(O)H_1/[n-C_3F_7OCH_3]_0$  versus  $\Delta[n-C_3F_7OCH_3]_1/$ [n-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub>]<sub>0</sub> at 298 K obtained was also shown in Fig. 3. The values of  $\alpha$  and  $k_2$  were determined to be  $(0.99 \pm 0.06)$  and  $(2.04 \pm 0.14) \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The errors reported are ±2 SD, which are random errors and represent precision only. Potential systematic errors to the  $k_1$  and  $k_2$  values might be from the errors in the values of J, the average OH radical concentration, the values of the absorption cross-sections ( $\varepsilon$ ) for  $n-C_nF_{2n+1}OC(O)H_3$ , and the values of the rate constants for  $n-C_nF_{2n+1}OCH_3$  with OH radicals. The loss of  $n-C_nF_{2n+1}OC(O)H$  by photolysis was actually only less than 5% of the loss by the OH reaction. The errors for  $k_1$  and  $k_2$  due to the errors in the values of J (10%) and the average OH radical concentration (30%) were examined to be less than 3%. We examined the influence of the errors in the  $\varepsilon$  of n-C<sub>n</sub>F<sub>2n+1</sub>OC(O)H to the values of  $k_1$ ,  $k_2$ , and,  $\alpha$  in this method. The same values of  $k_1$ and  $k_2$ , 10% change of  $\alpha$  value, were obtained by varying the value of  $\varepsilon$  of *n*-C<sub>*n*</sub>F<sub>2*n*+1</sub>OC(O)H with 10%. Thus, the errors in the  $\varepsilon$  of n-C<sub>n</sub>F<sub>2n+1</sub>OC(O)H were not considered to affect the values of  $k_1$  and  $k_2$ . Finally, potential systematic errors could add an additional 10% to the  $k_1$ and  $k_2$  values with due consideration for the errors in the rate constants of  $n-C_nF_{2n+1}OCH_3$  with OH radicals. The  $\alpha$  values for C<sub>2</sub>F<sub>5</sub>OC(O)H and *n*-C<sub>3</sub>F<sub>7</sub>OC(O)H showed that the yields of  $C_2F_5OC(O)H$  and  $n-C_3F_7O$ -C(O)H were unity for the reactions of  $C_2F_5OCH_3$  and  $n-C_3F_7OCH_3$  with OH radicals, a result that is consistent with the results of previous studies [4,5].

It is necessary to examine whether, and to what extent,  $C_2F_5OCH_3$ ,  $n-C_3F_7OCH_3$ ,  $C_2F_5OC(O)H$ , and  $n-C_3F_7OC(O)H$  are consumed in processes other than reaction with OH radicals and photolysis of  $C_2F_5O-C(O)H$  and  $n-C_3F_7OC(O)H$ . Possible routes for loss of these species are direct UV photolysis of  $C_2F_5OCH_3$  and  $n-C_3F_7OCH_3$ , reactions with  $O(^1D)$  produced by the photolysis of  $O_3$ , and the dark reaction.

When C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> or *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub> was directly photolyzed by irradiation of a C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> (or *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub>)/He gas mixture at 298 K for 5 h, no change in C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> or *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub> concentration was observed. The rate constants for reactions of organic compounds with O(<sup>1</sup>D) range from 10<sup>-10</sup> to 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [8]. By assuming that the upper limit for the rate constants of the reactions of reactants with O(<sup>1</sup>D) was  $2 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, we can estimate the reaction rate to be  $<2 \times 10^5$  s<sup>-1</sup>, which is 1/500 times the reaction rate of H<sub>2</sub>O and O<sub>2</sub> (>1.27 × 10<sup>8</sup> s<sup>-1</sup>) in this system. Therefore, reactions of the HFEs with O(<sup>1</sup>D) were insignificant. The dark reactions of C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub>, *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>OC(O)H, and *n*-C<sub>3</sub>F<sub>7</sub>OC(O)H were investigated over a period of 5–6 h in the presence of the same concentration of water vapor as that used in the measurement. No changes in C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub> and *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub> concentrations were observed, and the decay rates of C<sub>2</sub>F<sub>5</sub>OC(O)H and *n*-C<sub>3</sub>F<sub>7</sub>OC(O)H were determined to be  $(3.1 \pm 0.6) \times 10^{-6}$  and  $(3.3 \pm 0.6) \times 10^{-6}$  s<sup>-1</sup>, respectively. In the measurement, the irradiation time was less than 2 h, and the decays of C<sub>2</sub>F<sub>5</sub>OC(O)H and *n*-C<sub>3</sub>F<sub>7</sub> OC(O)H were estimated to be less than 3% for a 2-h irradiation period. Therefore, losses due to the dark reactions of C<sub>2</sub>F<sub>5</sub>OCH<sub>3</sub>, *n*-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub>, C<sub>2</sub>F<sub>5</sub>OC(O)H, and *n*-C<sub>3</sub>F<sub>7</sub>OC(O)H were negligible.

The  $\alpha$ ,  $k_1$  and  $k_2$  values were measured over the temperature range 253–328 K. Plots of  $[n-C_nF_{2n+1}OC(0)H]_t/[n-C_nF_{2n+1}OCH_3]_0$  versus  $\Delta[n-C_nF_{2n+1}OCH_3]_t$ / $[n-C_nF_{2n+1}OCH_3]_0$  could be fitted by Eq. (I), as could the plot shown in Fig. 3. Values of  $\alpha$ ,  $k_1$  and  $k_2$  at various temperatures are summarized in Table 1. Arrhenius plots for  $k_1$  and  $k_2$  are shown in Fig. 4. Using  $k = Ae^{-E_a/RT}$ , we estimated the temperature dependences of  $k_1$  and  $k_2$  as  $(9.24 \pm 1.33) \times 10^{-13} \exp[(-1230 \pm 40)/T]$  and  $(1.41 \pm 0.26) \times 10^{-12} \exp[(-1260 \pm 50)/T]$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> from the nonlinear weighted least-squares analysis of the data in Fig. 4. The Arrhenius parameters and the values of  $k_1$  and  $k_2$  at 298 K are listed in Table 2.

Table 1 Observed values of  $\alpha$ ,  $k_1$  and  $k_2$  at the temperature range of 253–328 K



Fig. 4. Arrhenius plots for the reactions of  $C_2F_5OC(O)H$  and  $n-C_3F_7OC(O)H$  with OH radicals.

# 3.4. Atmospheric lifetime of $n-C_nF_{2n+1}OC(O)H$ with respect to reaction with OH radicals

We estimated the atmospheric lifetimes of  $C_2F_5O$  C(O)H and *n*-C<sub>3</sub>F<sub>7</sub>OC(O)H with respect to reaction

observed values of a, x1 and x2 at the emperature range of 255 526 K							
Compound	Temp. (K)	$[OH]_{av}$ range $(10^{10} \text{ molecule cm}^{-3})$	$k_{\rm r}$ (10 <sup>-14</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>	α <sup>b</sup>	$k_{\rm s}$ (10 <sup>-14</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup>		
C <sub>2</sub> F <sub>5</sub> OC(O)H	328	3.19-3.28	1.90	$1.00 \pm 0.03$	$2.11 \pm 0.11$		
	313	2.76-4.20	1.53	$1.00 \pm 0.02$	$1.82 \pm 0.07$		
	298	3.60-4.11	1.21	$0.99 \pm 0.12$	$1.50 \pm 0.11$		
	283	2.41-2.78	0.915	$1.00 \pm 0.02$	$1.19 \pm 0.06$		
	268	3.37-3.71	0.679	$0.98 \pm 0.02$	$0.911 \pm 0.052$		
	253	3.08-3.90	0.486	$0.96\pm0.04$	$0.712 \pm 0.033$		
n-C <sub>3</sub> F <sub>7</sub> OC(O)H	328	2.94-3.10	1.88	$0.99 \pm 0.04$	$2.95 \pm 0.26$		
	313	3.64-3.83	1.50	$0.99 \pm 0.06$	$2.51 \pm 0.12$		
	298	4.31-5.41	1.17	$0.99 \pm 0.06$	$2.04 \pm 0.14$		
	283	3.91-4.61	0.892	$1.03 \pm 0.04$	$1.66 \pm 0.16$		
	268	3.47-4.92	0.658	$1.00 \pm 0.03$	$1.20 \pm 0.13$		
	253	3.98-5.13	0.468	$0.99\pm0.04$	$0.965 \pm 0.053$		

<sup>a</sup> Ref. [3].

<sup>b</sup> The errors reported are  $\pm 2$  SD. Potential systematic errors could add an additional 10% to the  $k_1$  and  $k_2$  values with due consideration for the errors in the rate constants of n- $_n$ F<sub>2n+1</sub>OCH<sub>3</sub> with OH radicals.

Table 2 Arrhenius rate constant parameters for the OH radical reaction of  $C_2F_5OC(O)H$  and  $n-C_3F_7OC(O)H$ 

	*			
Compound	$k_1$ (298 K) (10 <sup>-14</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>a</sup>	$A (10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^a$	E <sup>a</sup> /R (K) <sup>a</sup>	Temp. range (K)
C <sub>2</sub> F <sub>5</sub> OC(O)H n-C <sub>3</sub> F <sub>7</sub> OC(O)H	$1.48 \pm 0.06$ $2.04 \pm 0.04$	$0.924 \pm 0.133$ $1.41 \pm 0.26$	$1230 \pm 40$ $1260 \pm 50$	253–328 253–328

<sup>a</sup> The errors reported are  $\pm 2$  SD. Potential systematic errors could add an additional 10% to the  $k_1$  and  $k_2$  values with due consideration for the errors in the rate constants of  $n-C_nF_{2n+1}OCH_3$  with OH radicals.

with OH radicals to be 3.6 and 2.6 years, respectively, by using Eq. (III) [9]

$$\tau_i = \frac{k_{\text{CH}_3\text{CCl}_3}}{k_i} \times \tau_{\text{CH}_3\text{CCl}_3},\tag{III}$$

where  $\tau_i$  and  $\tau_{CH_3CCl_3}$  (6.0 years [10]) represent the atmospheric lifetimes of n- $C_n$ F<sub>2n+1</sub>OC(O)H and CH<sub>3</sub>CCl<sub>3</sub> with respect to reaction with OH radicals, and  $k_i$  and  $k_{CH_3CCl_3}$  (6.0 × 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [8]) represent the rate constants for the reactions of n- $C_n$ F<sub>2n+1</sub>OC(O)H and CH<sub>3</sub>CCl<sub>3</sub> with OH radicals at 272 K. The  $k_1$  and  $k_2$  values at 272 K were estimated to be  $1.00 \times 10^{-14}$  and  $1.37 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively.

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