

# Reaction Processes of O(<sup>1</sup>D) with Fluoroethane Compounds

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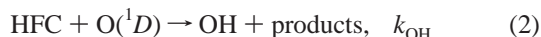
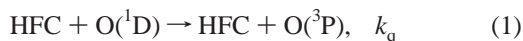
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Product branching ratios and rate constants for the O(<sup>3</sup>P) atom and OH radical formation processes in the reaction of electronically excited oxygen O(<sup>1</sup>D) atoms with fluoroethanes were measured at room temperature. The reactions of CHF<sub>2</sub>–CF<sub>3</sub> (HFC-125), CH<sub>2</sub>F–CF<sub>3</sub> (HFC-134a), CHF<sub>2</sub>–CHF<sub>2</sub> (HFC-134), CH<sub>3</sub>–CF<sub>3</sub> (HFC-143a), CH<sub>2</sub>F–CHF<sub>2</sub> (HFC-143), and CH<sub>3</sub>–CHF<sub>2</sub> (HFC-152a) were studied. Laser-induced fluorescence techniques using vacuum and near-ultraviolet lasers are applied to the detection of O(<sup>1</sup>D, <sup>3</sup>P<sub>2</sub>) atoms and OH radicals, respectively. The results are compared with previous investigations, and reaction mechanisms are discussed on the basis of the present results. The rate constants for the OH radical production were proportional to the total number of H atoms included in the fluoroethane reactants, and those for the reaction processes are interpreted with the molecular structures of fluoroethane reactants.

## 1. Introduction

Hydrofluorocarbon (HFC) compounds are used as substitutes for the ozone-destroying chlorofluorocarbon (CFC) compounds.<sup>1–7</sup> However, they still have the potential to be greenhouse gases, because their radiative forcing, i.e., absorption of the infrared radiation from the earth, is significant.<sup>7,8</sup> Therefore, the reaction rate coefficient of HFC with O(<sup>1</sup>D) atoms  $k_r$ , as well as that with OH radicals, plays the important role of controlling the atmospheric lifetime of the HFCs.<sup>9,10</sup> The interaction between O(<sup>1</sup>D) and HFC is considered to lead to



where  $k_q$ ,  $k_{\text{OH}}$ , and  $k_{\text{other}}$  are the rate constants for the physical quenching of O(<sup>1</sup>D) to O(<sup>3</sup>P), the chemical reactions producing OH(X <sup>2</sup>Π), and the chemical reaction pathway(s) other than the quenching and OH formation, respectively. The total decomposition rate of an HFC is  $k_r = k_{\text{OH}} + k_{\text{other}} = k_{\text{total}} - k_q$ .

The total  $k_{\text{total}}$  and quenching  $k_q$  rate constants of the reaction between O(<sup>1</sup>D) and the fluoromethane compounds (CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, and CH<sub>3</sub>F) were measured in our previous study.<sup>11</sup> The values of  $k_{\text{total}} - k_q$  which we determined in the reaction with CHF<sub>3</sub>, CH<sub>2</sub>F<sub>2</sub>, and CH<sub>3</sub>F were  $0.026 \pm 0.013$ ,  $0.15 \pm 0.08$ , and  $1.2 \pm 0.1$  in units of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. This indicates that the reaction rate constants are unambiguously related to the probability of the attack of O(<sup>1</sup>D) atom on the C–H bonds. However, the reaction system between O(<sup>1</sup>D) and larger HFC molecules is more complicated, i.e., (i) there are many feasible reaction pathways and (ii) the reactivity of fluoroethane probably depends on its molecular structure.

In the present study, we report the  $k_q$ ,  $k_{\text{OH}}$ , and  $k_{\text{other}}$  values in the reaction of O(<sup>1</sup>D) with the fluoroethane compounds by measuring the total rate coefficients for the removal of O(<sup>1</sup>D),  $k_{\text{total}} = k_q + k_{\text{OH}} + k_{\text{other}}$ , and the quantum yields for the production of O(<sup>3</sup>P),  $\phi_q$ , and OH(X),  $\phi_{\text{OH}}$ . These values are defined as

$$k_q = \phi_q k_{\text{total}} \quad (4)$$

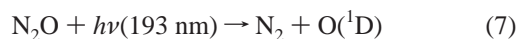
$$k_{\text{OH}} = \phi_{\text{OH}} k_{\text{total}} \quad (5)$$

$$k_{\text{other}} = (1 - \phi_q - \phi_{\text{OH}}) k_{\text{total}} \quad (6)$$

In the present experiment, the decay of O(<sup>1</sup>D) and rise of O(<sup>3</sup>P) were monitored to determine the  $k_{\text{total}}$  values. To measure the concentration of O(<sup>1</sup>D) and O(<sup>3</sup>P) produced by the physical quenching process (reaction 1), we applied the technique of time-resolved laser-induced fluorescence (LIF) detection using a vacuum UV (vuv) laser. The vuv laser wavelengths was tuned at the atomic resonance lines of the  $3s \text{ } ^1\text{D}^\circ \leftarrow 2p \text{ } ^1\text{D}$  and  $3s \text{ } ^3\text{S}^\circ \leftarrow 2p \text{ } ^3\text{P}_2$  transitions which were located at 115.22 and 130.22 nm, respectively. The OH(X) products are also detected by LIF using the OH(A<sup>2</sup>Σ<sup>+</sup>–X <sup>2</sup>Π; 1–0) transition around 282 nm.

## 2. Experimental Section

The HFC compounds studied were CHF<sub>2</sub>–CF<sub>3</sub> (HFC-125), CH<sub>2</sub>F–CF<sub>3</sub> (HFC-134a), CHF<sub>2</sub>–CHF<sub>2</sub> (HFC-134), CH<sub>3</sub>–CF<sub>3</sub> (HFC-143a), CH<sub>2</sub>F–CHF<sub>2</sub> (HFC-143), and CH<sub>3</sub>–CHF<sub>2</sub> (HFC-152a). The photolysis of N<sub>2</sub>O by an ArF excimer laser (Lambda Physik, Compex) generating 193 nm radiation was used to produce O(<sup>1</sup>D),<sup>12,13</sup>

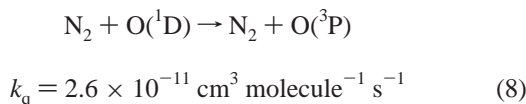


For each HFC reactant, the quenching quantum yield  $\phi_q$  was obtained by measuring the relative intensity of the asymptotic

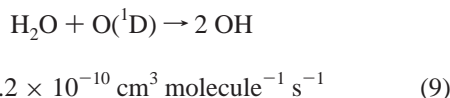
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O(<sup>3</sup>P) signal to that produced in the interaction between O(<sup>1</sup>D) and N<sub>2</sub>,



where the quenching quantum yield is  $\phi_q = 1$ .<sup>14</sup> The quantum yield for OH production  $\phi_{\text{OH}}$  was obtained by measuring the relative intensity of the asymptotic OH signal to that produced in the reaction between O(<sup>1</sup>D) and H<sub>2</sub>O,

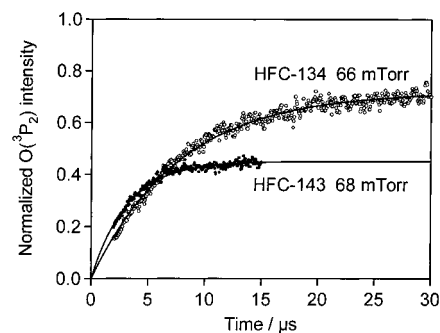


where the OH formation quantum yield is  $\phi_{\text{OH}} = 2$ .<sup>14</sup> The value of  $k_{\text{total}}$  was determined by the measurement of the temporal profiles of O(<sup>3</sup>P) and O(<sup>1</sup>D), where the signal intensity was plotted as a function of the delay between the photolysis and LIF laser pulses.

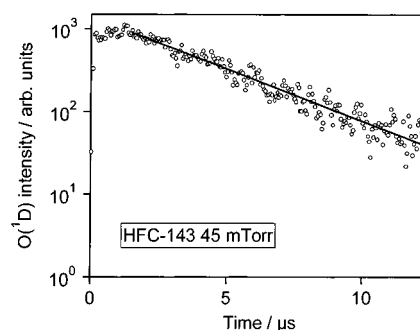
The experimental setup was essentially the same as that in the previous study.<sup>15</sup> The reaction cell (60 × 60 × 60 mm<sup>3</sup>) was evacuated by a rotary pump through a liquid N<sub>2</sub> trap. Sample gas mixtures containing N<sub>2</sub>O as the O(<sup>1</sup>D) source, HFC or N<sub>2</sub> as the reactant, and He as a buffer were flowed (~100 Torr cm<sup>3</sup> s<sup>-1</sup>) through the reaction cell where the pressure was measured by a capacitance pressure gauge. The HFC, N<sub>2</sub>O, N<sub>2</sub>, and He gases were obtained commercially and used without further purification. The H<sub>2</sub>O vapor was obtained from degassed, distilled water at room temperature. The O(<sup>1</sup>D) was generated in the reaction cell by the photolysis of N<sub>2</sub>O at 193 nm. Since the translationally hot O(<sup>1</sup>D) atom is quickly thermalized by the collisions with buffer gas on a time scale of less than a microsecond under our experimental conditions, hot atom effects can be ignored.<sup>16</sup> The probe laser beam for the detection of O(<sup>1</sup>D) or reaction products was also introduced into the reaction cell after a time delay. The reaction time is defined as this delay time,  $t$ , between the photolysis and probe laser pulses, which was controlled by a pulse delay generator (Stanford Research, model DG535).

The O(<sup>1</sup>D) and O(<sup>3</sup>P<sub>2</sub>) atoms were detected by LIF at 115.22 and 130.22 nm, respectively. The VUV laser light at 115.22 nm was generated by frequency tripling (3 $\omega$ ) of a dye laser (Lambda Physik, model FL3002) at 345.6 nm in Xe gas. The vuv laser light at 130.22 nm was generated by four-wave difference mixing (2 $\omega_1 - \omega_2$ ) using two dye lasers (Lambda Physik, model FL3002 and Scanmate) in Kr gas. The dye laser output was frequency doubled by a BBO crystal for the  $\omega_1$  light of 212.56 nm, which was two-photon resonant with Kr 5p[<sup>1</sup>/<sub>2</sub>]<sub>0</sub>. The two dye lasers were pumped by a XeCl excimer laser (Lambda Physik, model Lextra-50). The wavelength of  $\omega_2$  was tuned around 578.1 nm. The laser beams were focused into a Xe or Kr gas cell with a lens with a focal length of 200 mm. The vuv laser light generated in the Xe or Kr gas cell was introduced into the reaction cell through a LiF window in a direction orthogonal to the photolysis laser direction. The intensity of the vuv light was monitored by the measurements in a photocurrent cell which contained nitric oxide (NO) gas. The photocurrent cell was located behind the reaction region. The LIF emission was detected by a photomultiplier tube (EMR, model 547 J-08-17) at right angles to the both photolysis and probe laser beams.

The OH(X <sup>2</sup>I) radical was also detected by LIF around 282 nm using the dye laser pumped by the XeCl excimer laser. This



**Figure 1.** Temporal profiles of the O(<sup>3</sup>P<sub>2</sub>) signal produced from CHF<sub>2</sub>-CHF<sub>2</sub> (HFC-134) + O(<sup>1</sup>D) and CH<sub>2</sub>FCHF<sub>2</sub> (HFC-143) + O(<sup>1</sup>D). The signal intensities are normalized by the asymptotic signal intensity of O(<sup>3</sup>P<sub>2</sub>) produced from N<sub>2</sub> + O(<sup>1</sup>D). The O(<sup>1</sup>D) atoms are produced from the photodissociation of N<sub>2</sub>O by 193 nm laser pulse at  $t = 0$ . The partial pressure of N<sub>2</sub>O is kept constant (ca. 1 mTorr) in the reactions of HFC-134, HFC-143, and N<sub>2</sub>. Helium gas is added (ca. 500 mTorr) as a buffer.



**Figure 2.** Temporal profile of O(<sup>1</sup>D) produced from the photodissociation of N<sub>2</sub>O at 193 nm under the presence of 45 mTorr of CH<sub>2</sub>FCHF<sub>2</sub> (HFC-143). The N<sub>2</sub>O pressure is ca. 1 mTorr. Helium gas is added (ca. 500 mTorr) as a buffer.

laser beam was introduced into the reaction cell in a direction counterpropagated to the photolysis laser beam. The intensity of the beam was monitored by a photodiode. The LIF signals of OH(A–X) transition around 309 nm were separated by an interference filter (BARR Associates, Inc.; bandwidth = 12 nm) and detected by a dynode-gated photomultiplier tube (Hamamatsu, models 1P28 and C1392-56) with a high-speed amplifier (Hamamatsu, model C5594) to separate the resonance fluorescence and the strong laser scattering. The signal from the photomultipliers for the detection of O(<sup>1</sup>D), O(<sup>3</sup>P), and OH(X) was averaged by gated integrators (Stanford Research, SR250). The fluorescence decay curve of OH(A–X) was measured by using a digital oscilloscope (Tektronix, model TDS380P).

### 3. Results

**3.1. Total Rate Constants for the Removal of O(<sup>1</sup>D).** Typical results of the temporal profiles of O(<sup>3</sup>P) and O(<sup>1</sup>D) are shown in Figures 1 and 2, respectively. Because the quenching rate of O(<sup>1</sup>D) by the He gas used as a buffer gas is extremely slow ( $< 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ),<sup>17</sup> the quenching process of O(<sup>1</sup>D) by He can be neglected here. The rise and decay rates  $k$ , obtained by a least-squares fit, were measured at different pressures in the reaction cell, because they are the function of reactant concentrations, i.e.,

$$k = k_{\text{HFC}}[\text{HFC}] + k_{\text{N}_2\text{O}}[\text{N}_2\text{O}] + k_{\text{diff}} \quad (10)$$

where  $k_{\text{N}_2\text{O}}$  and  $k_{\text{HFC}}$  are the second-order rate constants for the removal of O(<sup>1</sup>D) by the reactants N<sub>2</sub>O and HFC, respec-

**TABLE 1: Rate Constants in the Reaction of O(<sup>1</sup>D) with HFC (Units in 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>)**

reactant	$k_{\text{total}}$		$k_q$	$k_{\text{OH}}$	$k_{\text{other}}$	ref
	O( <sup>1</sup> D) decay <sup>a</sup>	O( <sup>3</sup> P) rise <sup>b</sup>				
CF <sub>3</sub> -CF <sub>3</sub> (CFC-116)	0.015 (±0.003)	—	0.013 (±0.003)			25
CHF <sub>2</sub> -CF <sub>3</sub> (HFC-125)	—	1 (+1/-0.5)	0.2 (+0.2/-0.1)	0.6 (+0.6/-0.3)	0.2(±0.2)	this work
	12.3 (±0.6)	—	—	$k_{\text{OH}} + k_{\text{other}} = 1.8(+2.8/-1.8)$		10
CH <sub>2</sub> F-CF <sub>3</sub> (HFC-134a)	4.9(±0.5)	—	3.2(±0.5)	1.2(±0.3)	0.5(±0.3)	this work
	4.85(±0.25)	—	—	$k_{\text{OH}} + k_{\text{other}} = 4.6(±1.2)^c$		18
CHF <sub>2</sub> -CHF <sub>2</sub> (HFC-134)	3.9(±0.4)	4 (±1)	2.8(±0.5)	1.0(±0.3)	0.1 (+0.3/-0.1)	this work
CH <sub>3</sub> -CF <sub>3</sub> (HFC-143a)	4.0 (±0.5)	5 (±1)	0.7(±0.2)	1.5(±0.3)	1.8(±0.4)	this work
	—	—	—	$k_{\text{OH}} + k_{\text{other}} = 10(±2)^c$		18
CH <sub>2</sub> F-CHF <sub>2</sub> (HFC-143)	11 (±1)	12 (±2)	5.0(±0.8)	2.0(±0.5)	4.1(±0.9)	this work
CH <sub>3</sub> -CHF <sub>2</sub> (HFC-152a)	—	15 (±2)	5.1 (±1.1)	2.3(±0.5)	7.6(±1.4)	this work
	20.2(±1.5)	—	—	$k_{\text{OH}} + k_{\text{other}} = 9.3(±1.6)$		10

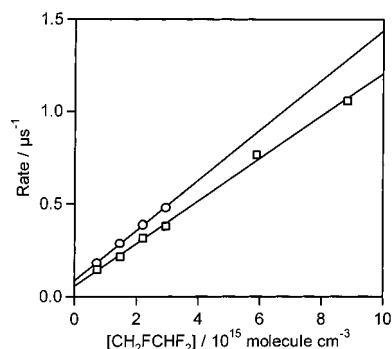
<sup>a</sup> Determined from the decay curve of O(<sup>1</sup>D) signal. <sup>b</sup> Determined from the rise curve of O(<sup>3</sup>P) signal. <sup>c</sup> Using the currently recommended value of the rate constant for O(<sup>1</sup>D) + N<sub>2</sub>O of  $1.16 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>14</sup>

**TABLE 2: Branching Ratios in the Reaction of O(<sup>1</sup>D) with HFC**

reactant	$\phi_q$	$\phi_{\text{OH}}$	$\phi_{\text{other}}$	ref
CF <sub>3</sub> -CF <sub>3</sub> (CFC-116)	0.85(±0.15)	—	0.15(±0.15)	25
CHF <sub>2</sub> -CF <sub>3</sub> (HFC-125)	0.24(±0.04)	0.6(±0.1)	0.2(±0.1)	this work
	0.85(+0.15/-0.22)	—	—	10
CH <sub>2</sub> F-CF <sub>3</sub> (HFC-134a)	0.65(±0.06)	0.24(±0.04)	0.11(±0.07)	this work
	0.94(+0.06/-0.10)	—	—	10
CHF <sub>2</sub> -CHF <sub>2</sub> (HFC-134)	0.72(±0.10)	0.25(±0.06)	0.03 (-0.03/+0.12)	this work
CH <sub>3</sub> -CF <sub>3</sub> (HFC-143a)	0.18(±0.04)	0.38(±0.06)	0.44(±0.07)	this work
CH <sub>2</sub> F-CHF <sub>2</sub> (HFC-143)	0.45(±0.06)	0.18(±0.04)	0.37(±0.07)	this work
CH <sub>3</sub> -CHF <sub>2</sub> (HFC-152a)	0.34(±0.06)	0.15(±0.02)	0.51(±0.06)	this work
	0.54(±0.07)	—	—	10

tively, [N<sub>2</sub>O] and [HFC] are the concentrations of N<sub>2</sub>O and HFC, respectively, and  $k_{\text{diff}}$  corresponds to effects of the diffusion from the viewing zone for the reactants and products. The plots of the O(<sup>1</sup>D) decay rates and the O(<sup>3</sup>P) rise rates vs the HFC-143 concentration are shown in Figure 3. The rate constant obtained from the slope of the O(<sup>1</sup>D) decay rate plots is  $(1.2 \pm 0.2) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, while that from the O(<sup>3</sup>P) rise rate plots is  $(1.1 \pm 0.1) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The relatively large intercepts of both plots for the O(<sup>1</sup>D) decay and O(<sup>3</sup>P) rise rates in Figure 3 are mainly due to the diffusion, that is,  $k_{\text{diff}}$  in eq 10. The diameters of the photolysis and probe laser beams were both ca. 1 mm. The escape time out of the overlap region of these laser beams is estimated to be about  $\sim 10^{-6}$  s with these beam diameters. The rate constants of O(<sup>1</sup>D) with the various HFC reactants obtained in this study from the plots of O(<sup>1</sup>D) decay and/or O(<sup>3</sup>P) rise rates are listed in Table 1. For HFC-134, HFC-143a, and HFC143, the total reaction rate constants were obtained by measuring both O(<sup>1</sup>D) decay and O(<sup>3</sup>P) rise. The values determined by the two different methods are in agreement with each other within their experimental uncertainties for all of the three compounds.

**3.2. Quantum Yields for the O(<sup>3</sup>P) Production.** The temporal profiles of O(<sup>3</sup>P<sub>2</sub>) formed in the reaction of O(<sup>1</sup>D) with HFC were measured. Since the intramultiplet relaxation rate by collision is fast enough,<sup>15</sup> the distributions among the spin-orbit states  $j = 2, 1,$  and  $0$  of O(<sup>3</sup>P<sub>*j*</sub>) should be completely thermalized in a time scale of less than a micro-second under our experimental conditions.<sup>15</sup> The thermal population at room temperature is [O(<sup>3</sup>P<sub>2</sub>)]:[O(<sup>3</sup>P<sub>1</sub>)]:[O(<sup>3</sup>P<sub>0</sub>)] = 1:0.282:0.068. Therefore, the measured O(<sup>3</sup>P<sub>2</sub>) signal intensity is proportional to the total concentration of spin-orbit states of O(<sup>3</sup>P). When the delay time is long enough to quench O(<sup>1</sup>D) completely, the signal intensity of O(<sup>3</sup>P) approaches an asymptotic value. Since N<sub>2</sub> quenches O(<sup>1</sup>D) to O(<sup>3</sup>P) with unit efficiency, the asymptotic signal intensity measured in the reaction HFC + O(<sup>1</sup>D) is compared with that in the reaction N<sub>2</sub> + O(<sup>1</sup>D) keeping the

**Figure 3.** Plots of the measured decay rates of O(<sup>1</sup>D) (circles) and rise rates of O(<sup>3</sup>P) (squares) as a function of the concentration of CH<sub>2</sub>FCHF<sub>2</sub> (HFC-143).

initial O(<sup>1</sup>D) concentration constant. The ratio obtained by this comparison is the quantum yield,  $\phi_q$ , for the electronic quenching of O(<sup>1</sup>D). The removal by the reaction of O(<sup>1</sup>D) with N<sub>2</sub>O was estimated according to the concentrations and the reported rate constant of  $k_{\text{N}_2\text{O}} = 1.16 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>14</sup> In the present experiments, the ratio of  $k_{\text{N}_2\text{O}}[\text{N}_2\text{O}]$  to  $k_{\text{HFC}}[\text{HFC}]$  in eq 10 was kept less than 10% and was taken into account in the calculations of  $\phi_q$ . The values of  $\phi_q$  thus measured are listed in Table 2 with literature values for C<sub>2</sub>F<sub>6</sub>. The values of the rate constant  $k_q$  for the quenching path calculated with expression (4) are summarized in Table 1.

**3.3. Quantum Yields for the OH Production.** In the reactions between O(<sup>1</sup>D) and HFCs, OH radicals are generated. For the determination of the quantum yield for OH radicals produced in the reactions of O(<sup>1</sup>D) with HFCs, the temporal profile of the OH signal was also observed in the present study with the exciting laser wavelength fixed at the Q<sub>1</sub>(2) line of the A-X 1-0 transition. The signal intensity of OH approached an asymptotic value. This asymptotic OH signal was also normalized by the method similar to that used in the quantum

yield measurements of O(<sup>3</sup>P) production. Since the reaction rates of O(<sup>1</sup>D) with HFCs are over 10<sup>3</sup> times larger than those of OH + HFCs,<sup>14</sup> the decay of OH radicals due to the secondary reactions can be ignored. However, the quenching of OH(A) radicals excited by the LIF laser must be considered. Actually, the fluorescence lifetimes of OH(A–X) observed in the present study were shorter (300–600 ns) than the natural radiation lifetime (≈700 ns) of OH(A). The fluorescence quantum yield of OH(A)  $\phi_f$  is given by

$$\phi_f = \frac{\tau_f}{\tau_0} \quad (11)$$

where  $\tau_f$  and  $\tau_0$  are the observed fluorescence and the natural radiation lifetimes, respectively. Therefore, the quantum yield for the OH production is given by

$$\phi_{\text{OH}} = 2 \frac{I_{\text{asy}}^{\text{HFC}} \tau_f^{\text{H}_2\text{O}}}{I_{\text{asy}}^{\text{H}_2\text{O}} \tau_f^{\text{HFC}}} \quad (12)$$

where  $I_{\text{asy}}^{\text{HFC}}$  and  $I_{\text{asy}}^{\text{H}_2\text{O}}$  are the observed asymptotic intensities of the OH signal formed in the reaction HFC + O(<sup>1</sup>D) and that of the OH signal formed in the reaction H<sub>2</sub>O + O(<sup>1</sup>D), respectively.  $\tau_f^{\text{H}_2\text{O}}$  and  $\tau_f^{\text{HFC}}$  are the fluorescence lifetimes measured under the experimental condition of the reaction H<sub>2</sub>O + O(<sup>1</sup>D) and HFC + O(<sup>1</sup>D), respectively. The values of  $\phi_{\text{OH}}$ , and  $\phi_{\text{other}} (= 1 - \phi_q - \phi_{\text{OH}})$  obtained in this study are summarized in Table 2 with the literature values for C<sub>2</sub>F<sub>6</sub>. The values of the rate constants,  $k_{\text{OH}}$  and  $k_{\text{other}}$ , calculated with expressions (5) and (6) are summarized in Table 1.

#### 4. Discussion

Warren et al.<sup>10</sup> measured the  $k_{\text{total}}$  values with HFCs using time-resolved vuv atomic resonance fluorescence detection of O(<sup>3</sup>P) with an oxygen lamp after the photolysis of O<sub>3</sub> by a KrF laser pulse (248 nm), and obtained the  $\phi_q$  values by measuring the ratios of the asymptotic fluorescence signal level between the HFCs and N<sub>2</sub>. The results reported by Warren et al.<sup>10</sup> are also listed in Tables 1 and 2. The total rate constants obtained in this study are in good agreement with those reported by Warren et al. for CH<sub>2</sub>FCF<sub>3</sub> (HFC-134a) and CH<sub>3</sub>CHF<sub>2</sub> (HFC-152a) (Table 1). However, for O(<sup>1</sup>D) + CHF<sub>2</sub>CF<sub>3</sub> (HFC-125), our value of the total rate constant is about 10 times smaller than their value. The reason for the difference is not clear. The rate constant reported by Warren et al. for CHF<sub>2</sub>CF<sub>3</sub> (HFC-125) is even 2 times larger than that for CH<sub>2</sub>FCF<sub>3</sub> (HFC-134a). It is more likely that the rate constant for CHF<sub>2</sub>CF<sub>3</sub> (HFC-125) which has one H atom is smaller than that for CH<sub>2</sub>FCF<sub>3</sub> (HFC-134a) which has two H atoms, since C<sub>2</sub>F<sub>6</sub> is almost nonreactive with O(<sup>1</sup>D) (Table 1). The  $\phi_q$  value of 0.24 ± 0.02 for HFC-125 in this study is much smaller than the value of 0.85 + 0.15/–0.22 reported by Warren et al.<sup>10</sup> (Table 2). The OH formation quantum yield of 0.6 ± 0.1 for O(<sup>1</sup>D) + HFC-125 measured in this study indicates that the  $\phi_q$  value for HFC-125 should be less than 0.4. Our small  $\phi_q$  value of 0.24 for HFC-125 is consistent with the measured  $\phi_{\text{OH}}$  value. The  $\phi_q$  values for HFC-134a and HFC-152a are a little smaller than those reported by Warren et al.<sup>10</sup> (Table 2). The  $\phi_{\text{OH}}$  value of 0.24 ± 0.02 measured in this study supports our  $\phi_q$  value of 0.65 and indicates that the value of 0.94 by Warren et al.<sup>10</sup> is too large.

Green and Wayne<sup>18</sup> measured the loss rate of the HFC reactants relative to loss rate of N<sub>2</sub>O by O(<sup>1</sup>D) atoms from N<sub>2</sub>O with irradiation of a continuous cadmium lamp (229 nm),

detecting the infrared absorption intensities of the HFC and N<sub>2</sub>O as a function of time. Table 2 also lists the  $k_{\text{OH}} + k_{\text{other}}$  values which are calculated from the results reported by them, using the currently recommended value of the rate constant for O(<sup>1</sup>D) + N<sub>2</sub>O of 1.16 × 10<sup>–10</sup> cm<sup>3</sup> molecule<sup>–1</sup> s<sup>–1</sup>.<sup>14</sup> The values of  $k_{\text{OH}} + k_{\text{other}}$  calculated from their results for HFC-125 and HFC-143a are several times larger than our values of  $k_{\text{OH}} + k_{\text{other}}$  and even larger than the total rate constants obtained in this study.

Note that the  $k_{\text{OH}}$  values are proportional to the total number of H atoms included in the HFC molecule. This means that the attack of O(<sup>1</sup>D) on the C–H bond of HFC gives rise to the chemical reaction to produce the OH radical. That is consistent with other numerous other studies<sup>19–43</sup> where the mechanisms of H atom abstraction by O(<sup>1</sup>D) and of O(<sup>1</sup>D) atom insertion into a C–H bond have been suggested. Luntz<sup>19</sup> concluded that the insertion dominates for small hydrocarbons while the abstraction becomes an increasingly important source of OH as the size of the hydrocarbon increases.

The C–H bond fission, C–C bond fission, and HF molecule elimination accompanied by C–O bond formation are expected as the reaction pathway(s) for  $k_{\text{other}} (= k_{\text{total}} - k_{\text{OH}} - k_q)$  in the reactions of HFCs + O(<sup>1</sup>D). The reaction mechanism of C<sub>2</sub>H<sub>6</sub> + O(<sup>1</sup>D) has been investigated,<sup>19–22</sup> in which the C–C bond cleavage have been suggested to be a dominant reaction pathway. Park and Wiesenfeld<sup>22</sup> reported that the quantum yield for the OH formation in the reaction of C<sub>2</sub>H<sub>6</sub> + O(<sup>1</sup>D) was 0.033, while it was near unity in the reaction of CH<sub>4</sub> + O(<sup>1</sup>D). Analogous to the discussion on the C<sub>2</sub>H<sub>6</sub> + O(<sup>1</sup>D) reaction, the C–C bond fission process is the most feasible as the reaction pathway for  $k_{\text{other}}$  in the reactions of HFCs + O(<sup>1</sup>D).

Another possibility of the main reaction pathway which is responsible for  $k_{\text{other}}$  is the HF formation process, since the infrared emissions from the vibrationally excited HF molecules were observed in the reaction of O(<sup>1</sup>D) with CHF<sub>3</sub> and CH<sub>3</sub>F.<sup>23,24</sup> However, we have not succeeded in explaining the trend of  $k_{\text{other}}$  by counting the numbers of adjacent H–F combinations in the HFC reactants. Anyway, further experiments are required to identify the reaction pathway(s) for  $k_{\text{other}}$  and to understand the dependence of  $k_{\text{other}}$  on the HFC reactants.

Since C<sub>2</sub>F<sub>6</sub> is quite inert to the quenching of O(<sup>1</sup>D) (Table 1), the interaction of O(<sup>1</sup>D) on the H site of HFCs seems to affect the physical quenching as well as the OH formation. The quenching rate constants, however, seem to depend neither on the number of included H atoms nor on the molecular structure. Probably, the position and shape at the seam of the singlet and triplet potential energy surfaces of the intermediate complex in the HFCs + O(<sup>1</sup>D) reaction may affect the  $k_q$  values. These factors may not be simply related to the structure of the HFC reactants.

If the intermediate complex formed in the reaction process of HFC + O(<sup>1</sup>D) is decomposed statistically, the product branching ratios to the OH formation, the C–C bond fission, and HF formation can be predicted by statistical theories such as RRKM calculations. However, we did not perform the estimation of the reaction branching using the RRKM theory, because the many parameters, e.g., bond energies and normal-mode frequencies of the complexes, which were required in the RRKM calculations were not available for the reaction systems of HFCs + O(<sup>1</sup>D). In the reaction of C<sub>2</sub>H<sub>6</sub> + O(<sup>1</sup>D), Luntz<sup>19</sup> measured the vibrational and rotational distributions of OH products and found that the distributions were different from the predictions by the statistical theory. This suggests that the

statistical calculations may not be effective in the HFCs + O(<sup>1</sup>D) reaction systems.

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