

Kinetics and Mechanism of (CF₃)₂CHOCH₃ Reaction with OH Radicals in an Environmental Reaction Chamber

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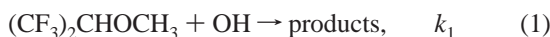
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The atmospheric chemistry of (CF₃)₂CHOCH₃, a possible HCFC/HFC alternative, was studied using a smog chamber/FT-IR technique. OH radicals were prepared by the photolysis of ozone in a 200-Torr H₂O/O₃/O₂ gas mixture held in an 11.5-dm³ temperature-controlled chamber. The rate constant, *k*₁, for the reaction of (CF₃)₂CHOCH₃ with OH radicals was determined to be $(1.40 \pm 0.28) \times 10^{-12} \exp[(-550 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by means of a relative rate method at 253–328 K. The value of *k*₁ at 298 K was $(2.25 \pm 0.04) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The random errors are reported with ± 2 standard deviations, and potential systematic errors of 15% could increase *k*₁. In considering OH-radical reactions, we estimated the tropospheric lifetime of (CF₃)₂CHOCH₃ to be 2.0 months using the rate constant at 288 K. The degradation mechanism of (CF₃)₂CHOCH₃ initiated by OH radicals was also investigated using FT-IR spectroscopy at 298 K. Products (CF₃)₂CHOC(O)H, CF₃C(OH)₂CF₃, CF₃C(O)OCH₃, and COF₂ were identified and quantified. The branching ratio, *k*_{1a}/*k*_{1b}, was estimated to be 2.1:1 for reactions (CF₃)₂CHOCH₃ + OH → (CF₃)₂CHOCH₂• + H₂O (*k*_{1a}) and (CF₃)₂CHOCH₃ + OH → (CF₃)₂C•OCH₃ + H₂O (*k*_{1b}).

Introduction

Hydrofluoroethers (HFEs) have been developed to replace hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC).¹ HFEs have stratospheric ozone depletion potentials of zero because they do not contain Cl atoms, and they have been reported to have relatively short atmospheric lifetimes.^{1,2} The atmospheric lifetime of one HFE, (CF₃)₂CHOCH₃, was estimated from theoretical calculations of the rate constant to be 0.25 years, which is very short in comparison to other HFEs.³



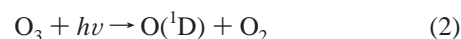
The value of *k*₁ reported ($2.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K) was estimated on the basis of highest occupied molecular orbital (HOMO) energies.³ In this study, we determined *k*₁ by means of a relative rate method at 253–328 K. In addition to the high OH-radical reactivity with (CF₃)₂CHOCH₃, the degradation mechanism of (CF₃)₂CHOCH₃ initiated by OH radicals was also investigated using FT-IR spectroscopy at 298 K. The branching ratio of *k*_{1a}/*k*_{1b} was estimated for (CF₃)₂CHOCH₃ + OH → (CF₃)₂CHOCH₂• + H₂O (*k*_{1a}) and (CF₃)₂CHOCH₃ + OH → (CF₃)₂C•OCH₃ + H₂O (*k*_{1b}). The observed kinetics and mechanism data are discussed with respect to the atmospheric chemistry of (CF₃)₂CHOCH₃.

Experimental Section

We obtained the (CF₃)₂CHOCH₃ sample (99.99% pure) used in this study from Central Glass Co., Ltd. (Japan). All of the experiments were carried out in an 11.5-dm³ cylindrical quartz

chamber (diameter, 10 cm; length, 146 cm) with an external jacket.⁴ The temperature in the reaction chamber was controlled by circulating coolant or heated water through the external jacket. A 40-W low-pressure Hg lamp (254 ± 8 nm) (GL-40, National Co., Japan) was used as the UV light source. Aluminum foil (thickness, 12 μm) was used to block out 80% of the lamp's light intensity in order to control the reaction rate of (CF₃)₂CHOCH₃ with OH radicals.

OH radicals were generated by the UV photolysis of O₃ in the presence of water vapor in an O₃/O₂ (3% O₃) gas mixture at an initial pressure of 200 Torr (reactions 2 and 3)



The O₃/O₂ (3% O₃) gas mixture was generated from pure O₂ with a silent-discharge ozone generator (ECEA-1000, Ebara-jitsugyo Ltd., Japan).

A greaseless vacuum line was used in preparing the reaction gas mixtures. C₂H₆ and CH₂Cl₂ were used as reference compounds in this study. Typical initial concentrations (in molecules cm⁻³) were 1.0×10^{15} ((CF₃)₂CHOCH₃), 1.0×10^{15} (reference compound), and 5.6×10^{17} (H₂O) in the O₃/O₂ (3%) gas mixture at 200 Torr. The sample was continuously circulated by a magnetically driven glass pump at a flow rate of 850 cm³ min⁻¹ during UV irradiation in order to mix the sample in the reaction chamber. Concentrations of (CF₃)₂CHOCH₃ and reference compounds were determined with a GC-14A-FID gas chromatograph (Shimadzu, Japan) equipped with a wide-bore capillary column (Rtx-1, 30 m in length, 0.53-mm i.d.). The column oven temperature was set at a constant temperature (293 K). The sample (0.5 cm³) was extracted from the reaction chamber and transferred to the GC-FID by the automatic

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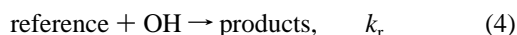
[‡] Central Glass Co., Ltd.

sampling system at 6-min intervals. The partial pressure of the reactants decreased by 0.2% with each GC-FID analysis. The uncertainties in the measured concentrations of (CF₃)₂CHOCH₃ and the reference compounds were <2% and were generally in the range of 0.5–1.5%. The reactants decayed up to 95% ((CF₃)₂CHOCH₃ and C₂H₆) and 75% (CH₂Cl₂) during the 54-min irradiation at 298 K.

The rate constants for the reaction of (CF₃)₂CHOCH₃ with OH radicals were measured using a relative rate method. The key step in this method is that of determining the relative disappearance rates of (CF₃)₂CHOCH₃ and the reference compound (C₂H₆ or CH₂Cl₂) in the presence of OH radicals. Taking into account the decay of the reactants (0.2%) with each GC-FID analysis step, we used eq 1 to evaluate the rate constant ratio, k_1/k_r^{4-6}

$$\ln\left(\frac{[(CF_3)_2CHOCH_3]_0}{[(CF_3)_2CHOCH_3]_t} + D_n\right) = \frac{k_1}{k_r} \left[\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t} + D_n\right) \right] \quad (1)$$

where [(CF₃)₂CHOCH₃]₀ and [reference]₀ represent the initial concentrations of (CF₃)₂CHOCH₃ and the reference compound and [(CF₃)₂CHOCH₃]_t and [reference]_t represent the concentrations of (CF₃)₂CHOCH₃ and the reference compound at reaction time *t*; *D_n* is a parameter that corrects for the nonreactive decay of 0.2% of the reactants because they were removed for GC-FID analysis during the sampling process ($D_n = n \ln(0.998)$, where *n* is the sample number in the GC-FID analysis);⁴ *k₁* and *k_r* are the rate constants for reactions 1 and 4, respectively.



Photolysis by UV irradiation and reactions with O(¹D), Cl atom, O₃, and H₂O represent the potential losses of (CF₃)₂CHOCH₃, C₂H₆, and CH₂Cl₂ due to non-OH-radical reactions in this reaction system. The direct photolysis of (CF₃)₂CHOCH₃, C₂H₆, and CH₂Cl₂ was conducted in separate experiments for 5 h, and the decays of (CF₃)₂CHOCH₃, C₂H₆, and CH₂Cl₂ were lower than the GC-FID analysis uncertainties (2%). Reactions of the reactants with O(¹D) are insignificant in this reaction system because of the 10,000-fold excesses of H₂O and O₂ over the reactants. The rate constants for the reactions of organic compounds with O(¹D) range from 10⁻¹⁰ to 10⁻¹³ cm³ molecule⁻¹ s⁻¹,⁷ and we assumed the upper limit of the rate constants of the reactions of (CF₃)₂CHOCH₃, C₂H₆, and CH₂Cl₂ with O(¹D) to be 2 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. The reaction rates with O(¹D) were estimated to be <2 × 10⁵ s⁻¹, which is more than 4500 times smaller than the reaction rates with H₂O and O₂ (>9 × 10⁸ s⁻¹). Cl atoms, which would be formed only when using CH₂Cl₂ as the reference compound, are rapidly scavenged by O₃ at 10¹⁶–10¹⁷ molecules cm⁻³, with a reaction rate constant of 1.2 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹,⁷ and the reactivity of the resultant ClO with (CF₃)₂CHOCH₃, C₂H₆, and CH₂Cl₂ is expected to be low compared to the reactivity with OH radicals because CH₄ reacts with ClO with a rate constant of <4.0 × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹.⁷ The dark reactions of (CF₃)₂CHOCH₃, C₂H₆, and CH₂Cl₂ with either O₃ or H₂O were also examined for 5 h in this study, and losses of (CF₃)₂CHOCH₃, C₂H₆, and CH₂Cl₂ were lower than the GC-FID analysis uncertainties (2%).

The mechanisms for the reaction of (CF₃)₂CHOCH₃ with OH radicals were investigated at 298 K using FT-IR spectroscopy with a nickel-coated aluminum multiple-reflection IR cell (375 cm²; optical path length, 3 m), which connected to the circulation line of the 11.5-dm³ reaction chamber used for the kinetic

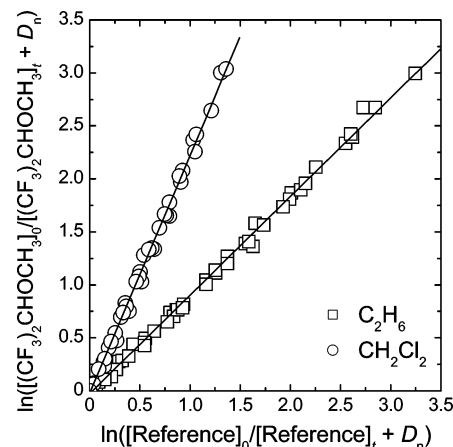
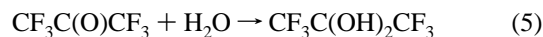


Figure 1. Loss of (CF₃)₂CHOCH₃ versus reference compounds C₂H₆ and CH₂Cl₂ in the presence of OH radicals. Experiments were performed at 298 K in an O₃/O₂ (3%) gas mixture at 200 Torr.

studies.⁴ The experiments were performed at initial concentrations (in molecules cm⁻³) of 0.5 × 10¹⁵ ((CF₃)₂CHOCH₃) and 5.6 × 10¹⁷ (H₂O) in an O₃/O₂ (3%) gas mixture at 200 Torr. The loss of (CF₃)₂CHOCH₃ and the formation of products were monitored with an FT-IR spectrometer (JIR-6500, JEOL Ltd., Japan) 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 pump at a flow rate of 850 cm³ min⁻¹ during UV irradiation. Absorption cross sections (ϵ) (cm² molecule⁻¹ (base 10)) of (CF₃)₂CHOCH₃ (2.16 × 10⁻¹⁹ at 879 cm⁻¹), CF₃C(O)OCH₃ (9.56 × 10⁻¹⁹ at 1804 cm⁻¹), and COF₂ (6.3 × 10⁻¹⁹ at 1928 cm⁻¹) were calculated from the IR spectra of their He mixtures of known concentration at a total pressure of 200 Torr at 298 K. The ϵ values (cm² molecule⁻¹ (base 10)) of CF₃C(OH)₂CF₃ (2.76 × 10⁻¹⁹ at 3632 cm⁻¹) were calculated from known concentrations of CF₃C(O)CF₃. CF₃C(OH)₂CF₃ was prepared by a gas-phase reaction of CF₃C(O)CF₃ with H₂O (5.6 × 10¹⁷ molecules cm⁻³) in 200 Torr of He at 298 K



The observed IR spectrum of CF₃C(OH)₂CF₃ is consistent with that reported by Kivinen et al.⁸ All of the CF₃C(O)CF₃ was assumed to convert to CF₃C(OH)₂CF₃ in this reaction system because the CF₃C(O)CF₃ peaks at 1809 and 970 cm⁻¹ disappeared completely. The CF₃C(OH)₂CF₃ sample was shown to be stable in this reaction system. The reagents used were C₂H₆ (99.5% pure, GL Sciences, Inc., Japan), CH₂Cl₂ (99% pure, Nacalai Tesque Inc., Kyoto, Japan), O₂ (99.5% pure, Nihon Sanso Corp., Japan), CF₃C(O)CF₃ (97% pure) and CF₃C(O)OCH₃ (>99% pure, SynQuest Labs, Inc., Alachua, FL), and COF₂/N₂ standard (85% pure, Takachiho Chemical Industry, Co., Japan).

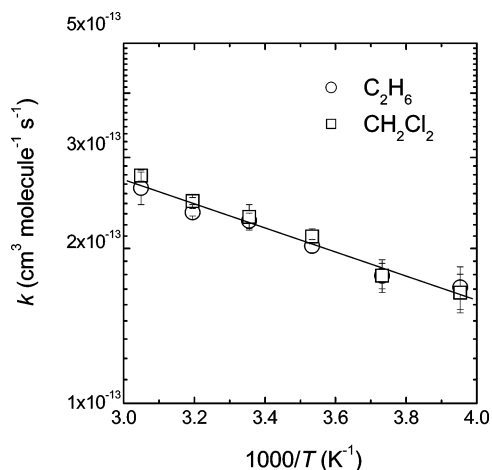
Results and Discussion

Kinetics of the Reaction of (CF₃)₂CHOCH₃ with OH Radicals. The rate constants for the reaction of (CF₃)₂CHOCH₃ with OH radicals at 298 K were derived from the plots of reference compounds C₂H₆ and CH₂Cl₂ (Figure 1). For both reference compounds, the plots of ln([(CF₃)₂CHOCH₃]₀/[(CF₃)₂CHOCH₃]_t + *D_n*) versus ln([reference]₀/[reference]_t + *D_n*) gave straight lines with slopes *k₁/k_r* that intersected the origin. Linear least-squares analysis of the data (Figure 1) gave *k₁/k_r* = 0.940 ± 0.034 for C₂H₆ and *k₁/k_r* = 2.23 ± 0.13 for CH₂Cl₂ after 5–7 runs. The errors reported are ±2 standard deviations and

TABLE 1: Measured Values of k_1/k_r and k_1 over the Temperature Range 253–328 K

T (K)	k/k_r^a		$10^{13} \times k_1^{a,b}$, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
	C_2H_6	CH_2Cl_2	C_2H_6	CH_2Cl_2
253	1.32 ± 0.13	2.69 ± 0.23	1.68 ± 0.16	1.64 ± 0.14
268	1.10 ± 0.06	2.40 ± 0.17	1.77 ± 0.10	1.77 ± 0.13
283	1.02 ± 0.03	2.40 ± 0.08	2.02 ± 0.06	2.11 ± 0.07
298	0.940 ± 0.034	2.23 ± 0.13	2.26 ± 0.08	2.30 ± 0.13
313	0.825 ± 0.013	2.09 ± 0.03	2.35 ± 0.04	2.47 ± 0.04
328	0.786 ± 0.058	2.07 ± 0.05	2.62 ± 0.19	2.77 ± 0.07

^a Values shown are ± 2 standard deviations. ^b Rate constants of $k(\text{C}_2\text{H}_6) = 8.7 \times 10^{-12} \exp(-1070/T)$ and $k(\text{CH}_2\text{Cl}_2) = 1.9 \times 10^{-12} \exp(-870/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

**Figure 2.** Arrhenius plot of kinetics data obtained by a relative rate method for the reaction of $(\text{CF}_3)_2\text{CHOCH}_3$ with OH radicals at 253–328 K.

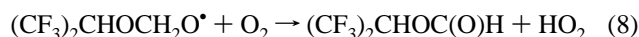
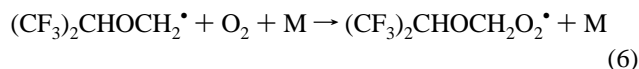
represent precision only. Using eq 1, $k_{298\text{K}}(\text{C}_2\text{H}_6) = 2.4 \times 10^{-13} (\pm 10\%) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{298\text{K}}(\text{CH}_2\text{Cl}_2) = 1.0 \times 10^{-13} (\pm 15\%) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁷ the $k_1(298 \text{ K})$ values were estimated to be $(2.26 \pm 0.08) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (C_2H_6 reference) and $(2.30 \pm 0.13) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (CH_2Cl_2 reference). The random errors are reported with ± 2 standard deviations. Systematic uncertainty may also add an additional 15% to the k_1 value. The $k_1(298 \text{ K})$ values obtained from the two reference compounds were the same within experimental uncertainty.

The k_1/k_r ratios were determined with C_2H_6 and CH_2Cl_2 as reference compounds over the temperature range 253–328 K. The plots of $\ln([\text{CF}_3)_2\text{CHOCH}_3]_0/[\text{CF}_3)_2\text{CHOCH}_3]_t + D_n$ versus $\ln([\text{reference}]_0/[\text{reference}]_t) + D_n$ (not shown) were similar to those in Figure 1. The k_1 values determined from the measured k_1/k_r ratios and the rate constants of C_2H_6 and CH_2Cl_2 are listed in Table 1.⁷ The Arrhenius plots obtained for k_1 are shown in Figure 2. The Arrhenius expression of $k_1 = (1.40 \pm 0.28) \times 10^{-12} \exp[(-550 \pm 60)/T]$ was derived from nonlinear least-squares analyses of the plots in Figure 2. The value of $k_1 = (2.25 \pm 0.04) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K was obtained from the Arrhenius rate parameters of k_1 . The theoretically calculated value of k_1 ($2.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at 296 K is consistent with our measurements.³ We compared the data of k_1 to the rate constants of $\text{CF}_3\text{CH}_2\text{OCH}_3$ and CHF_2OCH_3 . The value of k_1 is lower than that of $\text{CF}_3\text{CH}_2\text{OCH}_3$ ($(5.7 \pm 0.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁹ and higher than that of CHF_2OCH_3 ($3.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁷ at 298 K. According to the substituent factors reported by Kwok et al.,¹⁰ the same value of the substituent factors of $-\text{OCH}_2\text{CF}_3$ (0.44) and $-\text{OCH}(\text{CF}_3)_2$ (0.44) shows that the $-\text{OCH}_3$ group in both $\text{CF}_3\text{CH}_2\text{OCH}_3$ and $(\text{CF}_3)_2\text{CHOCH}_3$ have

similar reactivities. The group rate constants of $-\text{CH}_2-$ ($0.934 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), $-\text{CH}<$ ($1.94 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and the substituent factor of $-\text{CF}_3$ (0.071) show that the reactivity of $-\text{CH}_2-$ in $\text{CF}_3\text{CH}_2\text{OCH}_3$ is higher than that of $-\text{CH}<$ in $(\text{CF}_3)_2\text{CHOCH}_3$. These facts imply that a value of k_1 lower than that of $\text{CF}_3\text{CH}_2\text{OCH}_3$ is reasonable. The values of $-\text{OHF}_2$ (0.17) and $-\text{OCH}(\text{CF}_3)_2$ (0.44) show that the $-\text{OCH}_3$ group in $(\text{CF}_3)_2\text{CHOCH}_3$ is higher than that in CHF_2OCH_3 . This fact shows that a value of k_1 higher than that of CHF_2OCH_3 is reasonable. The value of A ($(1.40 \pm 0.28) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for k_1 shows a slightly lower value comparable with those reported for other HFEs, such as CH_3OCF_3 ,⁷ $\text{CH}_3\text{-OCF}_2\text{CF}_3$, and $\text{CH}_3\text{OCF}(\text{CF}_3)_2$,¹¹ because there are four H atoms in $(\text{CF}_3)_2\text{CHOCH}_3$. It might be caused from the narrow measurement temperature range of this study.

By using $\tau = (k_1(288 \text{ K}) \times [\text{OH}])^{-1}$, we obtained an atmospheric lifetime (τ) of 2.0 months for $(\text{CF}_3)_2\text{CHOCH}_3$ with respect to reaction with OH radicals, considering a global mean value for the OH radicals concentration ($9.4 \times 10^5 \text{ cm}^{-3}$)¹² and the $k_1(288 \text{ K})$ value of $2.07 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ calculated from the Arrhenius expression of k_1 .

Mechanism of the Reaction of $(\text{CF}_3)_2\text{CHOCH}_3$ with OH Radicals. (a) *Identified and Quantified Products.* The infrared spectra of the $(\text{CF}_3)_2\text{CHOCH}_3-\text{O}_3-\text{H}_2\text{O}-\text{O}_2$ gas mixture before irradiation and after 24 min of irradiation are shown (Figure 3A,B). The standard IR spectra of $\text{CF}_3\text{C}(\text{OH})_2\text{CF}_3$, $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$, $\text{CF}_3\text{C}(\text{O})\text{CF}_3$, and COF_2 are also shown (Figure 3C–F). Compared with the standard IR spectra (Figure 3C–F), the IR bands at 3632, 1804, and 1928 cm^{-1} (Figure 3B) were considered to belong to $\text{CF}_3\text{C}(\text{OH})_2\text{CF}_3$, $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$, and COF_2 , respectively. Therefore, $\text{CF}_3\text{C}(\text{OH})_2\text{CF}_3$, $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$, and COF_2 were formed from the UV irradiation of a gas mixture of $(\text{CF}_3)_2\text{CHOCH}_3-\text{O}_3-\text{H}_2\text{O}-\text{O}_2$. $\text{CF}_3\text{C}(\text{OH})_2\text{CF}_3$ was presumably formed from $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ as in reaction 5, and there must be some $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ present up through at least 80 min of irradiation time. However, the IR band at 970 cm^{-1} of $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ (Figure 3E) was not observed during UV irradiation (Figure 3B,I). The presence of $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ was negligible in this study. It is possible that the hydrolysis rate of $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ (reaction 5) was significantly higher than the generation rate of $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ in this reaction system. We did not determine CO_2 in this study. There are three unknown IR bands at 1778, 1386, and 1362 cm^{-1} (Figure 3B,H,I). The IR band at 1778 cm^{-1} indicated the presence of a C=O group, but we assumed that the possible product was $(\text{CF}_3)_2\text{CHOC}(\text{O})\text{H}$, which could be produced by a $(\text{CF}_3)_2\text{CHOCH}_2^\bullet$ radical with O_2 , as in reactions 6–8



The IR spectrum of $(\text{CF}_3)_2\text{CHOC}(\text{O})\text{H}$ was calculated by means of DFT (at the B3LYP/6-31G(d) level using Gaussian 98; Figure 3G).¹³ The calculated wavenumber was scaled by a factor of 0.9613.¹⁴ The calculated absorptions at 1776, 1370, and 1336 cm^{-1} were consistent with the observed unknown IR bands (Figure 3B,G,H,I), and we determined that $(\text{CF}_3)_2\text{CHOC}(\text{O})\text{H}$ was produced from the reaction of $(\text{CF}_3)_2\text{CHOCH}_3$ with OH radicals.

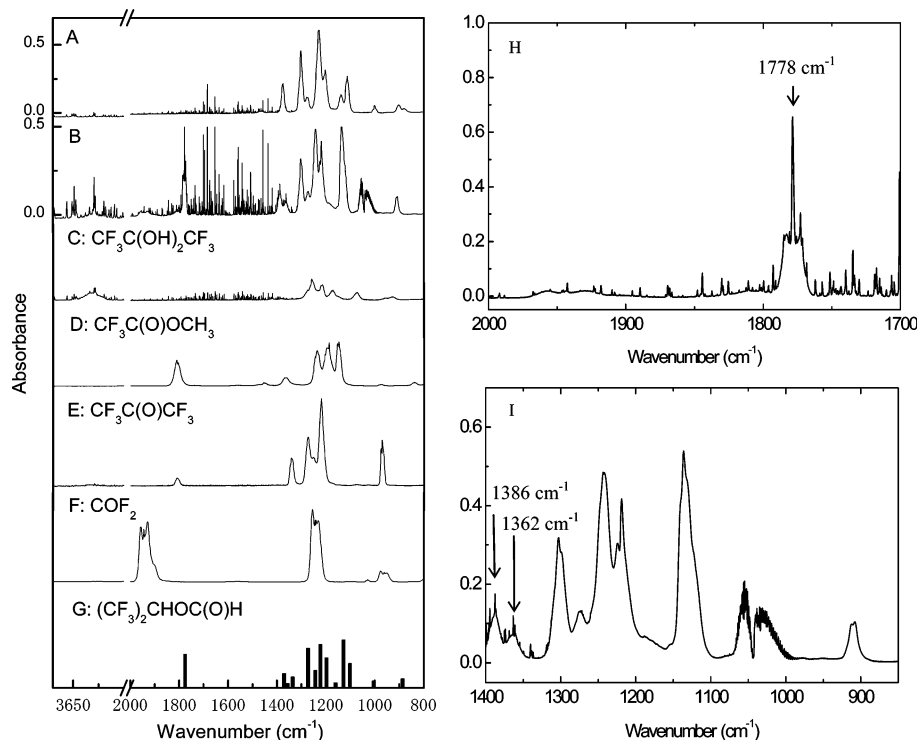


Figure 3. IR spectra observed before (A) and after (B) a 24-min irradiation of a gas mixture of (CF₃)₂CHOCH₃ (0.5×10^{15} molecules cm⁻³), H₂O (5.6×10^{17} molecules cm⁻³), and O₃/O₂ (3%) at 298 K and 200 Torr. Reference spectra of (C) CF₃C(OH)₂CF₃, (D) CF₃C(O)OCH₃, (E) CF₃C(O)CF₃, and (F) COF₂. (G) Spectrum of (CF₃)₂CHOC(O)H calculated by DFT (at the B3LYP/6-31G(d) level), (H) 1700–2000 cm⁻¹ region spectrum of B, (I) 950–1400 cm⁻¹ region spectrum of B.

The concentrations of CF₃C(OH)₂CF₃, CF₃C(O)OCH₃, and COF₂ were calculated by their IR absorption cross sections (ϵ). Because CF₃C(O)CF₃ was not observed during UV irradiation, (CF₃)₂CHOC(O)H, CF₃C(OH)₂CF₃, CF₃C(O)OCH₃, and COF₂ were the only products that contained both carbon and fluorine. However, both CF₃C(O)OCH₃ and COF₂ were formed in a single reaction event, and CF₃C(O)OCH₃ underwent a subsequent reaction, whereas COF₂ was relatively stable in this reaction system. Therefore, we determined the ϵ value for (CF₃)₂CHOC(O)H to be $(3.1 \pm 0.9) \times 10^{-18}$ cm² molecule⁻¹ (base 10) at 1778 cm⁻¹ from the material balance eq II from four experiments

$$[(\text{CF}_3)_2\text{CHOC(O)H}]_t = \Delta[(\text{CF}_3)_2\text{CHOCH}_3]_t - ([\text{CF}_3\text{C(OH)}_2\text{CF}_3]_t - [\text{COF}_2]_t) \quad (\text{II})$$

where

$$\Delta[(\text{CF}_3)_2\text{CHOCH}_3]_t = [(\text{CF}_3)_2\text{CHOCH}_3]_0 - [(\text{CF}_3)_2\text{CHOCH}_3]_t$$

Although a blank experiment indicated that the concentrations of COF₂ were reduced by photolysis and wall reactions in this system, losses of COF₂ were <2% in the initial 18-min period. Therefore, calculation of ϵ values for (CF₃)₂CHOC(O)H from the data during the initial 18-min period was not affected by these losses.

(b) *Mechanism of the OH Radical-Initiated Oxidation of (CF₃)₂CHOCH₃.* The concentration–radiation time profiles for the concentrations of (CF₃)₂CHOCH₃, (CF₃)₂CHOC(O)H, CF₃C(OH)₂CF₃, CF₃C(O)OCH₃, and COF₂ are shown in Figure 4. The concentration–radiation time behavior shows that (CF₃)₂CHOC(O)H, CF₃C(O)OCH₃, and COF₂ are the primary products and that CF₃C(OH)₂CF₃ is a secondary product. A mechanism

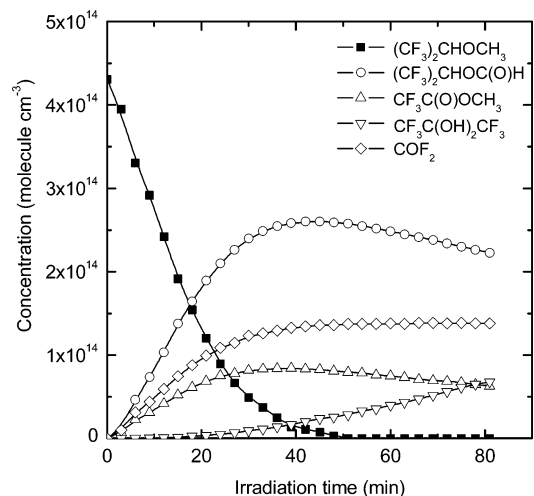
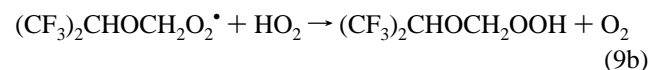


Figure 4. Concentration–radiation time profiles for (CF₃)₂CHOCH₃ (■), (CF₃)₂CHOC(O)H (○), CF₃C(OH)₂CF₃ (▽), CF₃C(O)OCH₃ (△), and COF₂ (◇); data were obtained from the experiment described in Figure 3.

(Figure 5) is proposed for the reaction of (CF₃)₂CHOCH₃ with OH radicals.

The formation mechanisms of (CF₃)₂CHOC(O)H and CF₃C(OH)₂CF₃ from the (CF₃)₂CHOCH₂* radical are shown in Figure 5A. The peroxy radical of (CF₃)₂CHOCH₂O₂* formed in reaction 6 can then react with the RO₂ radical (R = (CF₃)₂CHOCH₂, (CF₃)₂COCH₃) and HO₂ (reactions 7–9a).

However, the (CF₃)₂CHOCH₂OOH theoretically formed in reaction 9b could not be determined unequivocally in this study.



The IR band at 3628 cm⁻¹ was of an ROOH-type molecule,¹⁵ and it overlapped the 3632 cm⁻¹ band of CF₃C(OH)₂CF₃.

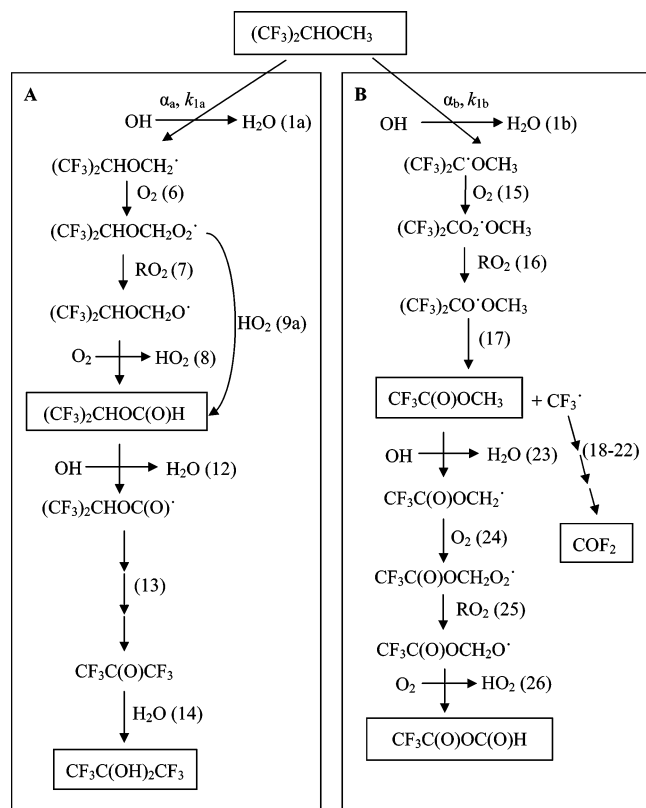
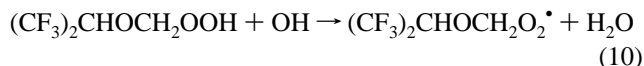
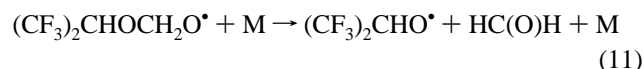


Figure 5. Degradation mechanism of $(\text{CF}_3)_2\text{CHOCH}_3$ initiated by OH radicals at 298 K.

Hydroperoxides are generally very reactive toward OH radicals, $k(\text{OH} + \text{CH}_3\text{OOH}) = 7.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K,⁷ although the presence of fluorine in $(\text{CF}_3)_2\text{CHOCH}_2\text{OOH}$ would be expected to reduce their reactivity. Even if $(\text{CF}_3)_2\text{CHOCH}_2\text{OOH}$ was formed in this study, it would react with OH radicals to regenerate the $(\text{CF}_3)_2\text{CHOCH}_2\text{O}_2^\bullet$ radical in the chamber, as in reaction 10.



The $(\text{CF}_3)_2\text{CHOCH}_2\text{O}^\bullet$ radical produced in reaction 7 can undergo a reaction with O_2 in reaction 8 (Figure 5A) or unimolecular dissociation as in reaction 11.



However, the HC(O)H that formed theoretically in reaction 11 was not observed in this reaction system. It is possible that the unimolecular dissociation of reaction 11 was negligible in this reaction system. HC(O)H might also be removed by reaction with OH radicals because HC(O)H reacts with OH radicals with high reactivities, $k(\text{OH} + \text{HC(O)H}) = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.⁷ Previous studies reported that the reaction with O_2 dominates the unimolecular dissociation for $\text{C}_n\text{F}_{2n+1}\text{OCH}_2\text{O}^\bullet$ radicals ($n = 1-4$).¹⁶⁻¹⁸ Considering the high concentration of O_2 ($6.29 \times 10^{18} \text{ molecules cm}^{-3}$) in the chamber, we assumed that $(\text{CF}_3)_2\text{CHOCH}_2\text{O}^\bullet$ with O_2 (reaction 8) would dominate the unimolecular dissociation (reaction 11) in this reaction system.

The $(\text{CF}_3)_2\text{CHOC(O)H}$ produced in reactions 8 and 9a can react with OH radicals and produce $\text{CF}_3\text{C(OH)}_2\text{CF}_3$, as in reactions 12–14 (Figure 5A).

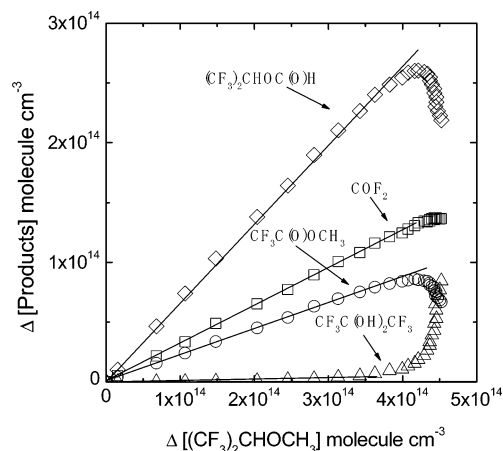
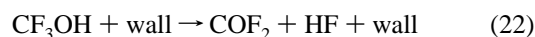
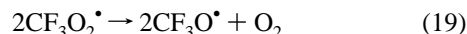
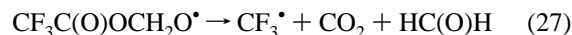


Figure 6. Plots of the concentrations of the products observed against the concentration of $(\text{CF}_3)_2\text{CHOCH}_3$ reacted. $(\text{CF}_3)_2\text{CHOC(O)H}$ (\diamond), $\text{CF}_3\text{C(OH)}_2\text{CF}_3$ (\triangle), $\text{CF}_3\text{C(O)OCH}_3$ (\circ), and COF_2 (\square); data were obtained from the experiment described in Figure 3.

The formation mechanism of $\text{CF}_3\text{C(O)CH}_3$ and COF_2 from the $(\text{CF}_3)_2\text{C}^\bullet\text{OCH}_3$ radical is the same as that in reactions 1b and 15–17 (Figure 5B). The peroxy radical of $(\text{CF}_3)_2\text{CO}_2^\bullet\text{OCH}_3$ formed in reaction 15 can react with RO_2 ($\text{R} = (\text{CF}_3)_2\text{CHOCH}_2$, $(\text{CF}_3)_2\text{COCH}_3$), as in reactions 16 and 17. The CF_3^\bullet radical formed in reaction 17 can produce COF_2 via a series of steps, as in reactions 18–22.¹⁹⁻²¹



Because decay of $\text{CF}_3\text{C(O)OCH}_3$ was observed in this study, reaction of $\text{CF}_3\text{C(O)OCH}_3$ with OH radicals was considered to occur in this reaction system, as in reactions 23–27 (Figure 5B). The unimolecular dissociation of $\text{CF}_3\text{C(O)OCH}_2\text{O}^\bullet$ might occur in this reaction system as in reaction 27. The CF_3^\bullet radical formed in reaction 27 can produce COF_2 in a series of steps (reactions 18–22).



However, the concentration of COF_2 did not increase with the decay of $\text{CF}_3\text{C(O)OCH}_3$ after a radiation time of 40 min, and the reaction of $\text{CF}_3\text{C(O)OCH}_2\text{O}^\bullet$ with O_2 (reaction 26) was considered to dominate the unimolecular dissociation (reaction 27) in this reaction system. However, we failed to observe the formation of $\text{CF}_3\text{C(O)OC(O)H}$.

Figure 6 shows the concentrations of the products observed against the concentration of $(\text{CF}_3)_2\text{CHOCH}_3$ reacted. The initial formation yields of $\alpha((\text{CF}_3)_2\text{CHOC(O)H})$, $\alpha(\text{CF}_3\text{C(OH)}_2\text{CF}_3)$, $\alpha(\text{CF}_3\text{C(O)OCH}_3)$, and $\alpha(\text{COF}_2)$ were obtained from the slopes of these plots at the first stage in Figure 6 for $(\text{CF}_3)_2\text{CHOC(O)H}$, $\text{CF}_3\text{C(OH)}_2\text{CF}_3$, $\text{CF}_3\text{C(O)OCH}_3$, and COF_2 , respectively. The values of $\alpha((\text{CF}_3)_2\text{CHOC(O)H})$, $\alpha(\text{CF}_3\text{C(OH)}_2\text{CF}_3)$, $\alpha(\text{CF}_3\text{C(O)OCH}_3)$, and $\alpha(\text{COF}_2)$ were obtained to be (0.66 ± 0.11) , (0.04 ± 0.05) , (0.22 ± 0.02) , and (0.33 ± 0.02) , respectively, from four experiments. According to the reaction

mechanism shown in Figure 5, it is clear that (CF₃)₂CHOC(O)H and CF₃C(OH)₂CF₃ were produced from (CF₃)₂CHOCH₂* radicals and that CF₃C(O)OCH₃ and COF₂ were produced from (CF₃)₂C*OCH₃ radicals. However, CF₃C(O)OCH₃ underwent a subsequent reaction 23, whereas COF₂ was relative stable in this reaction system. Therefore, values k_{1a}/k_1 and k_{1b}/k_1 for (CF₃)₂CHOCH₂* and (CF₃)₂C*OCH₃ radicals could be calculated from the data of $\alpha((CF_3)_2CHOC(O)H)$, $\alpha(CF_3C(OH)_2CF_3)$, and $\alpha(COF_2)$ using equations III and IV

$$k_{1a}/k_1 = \alpha((CF_3)_2CHOC(O)H) + \alpha(CF_3C(OH)_2CF_3) \quad (III)$$

$$k_{1b}/k_1 = \alpha(COF_2) \quad (IV)$$

The values of k_{1a}/k_1 and k_{1b}/k_1 were obtained to be 0.70 ± 0.11 and 0.33 ± 0.02 , respectively. The branching ratio of k_{1a}/k_{1b} was 2.1:1, and there are three H atoms in the -CH₃ group (k_{1a}), therefore, the central H atoms have reactivities 1.4 times as high as the terminal H atoms in OH-radical H-atom abstraction reactions. The value of k_{1a} at 298 K was estimated to be $1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, from k_{1a}/k_{1b} and k_1 at 298 K. The -CH₃ group in (CF₃)₂CHOCH₃ has a reactivity 10 times as high as that in (CF₃)₂CFOCH₃ ($1.52 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).¹¹ The changes for CH₃CHF₂ ($3.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁷ to CH₃CF₃ ($1.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁷ and CH₂-FCH₂F ($9.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁷ to CH₂FCHF₂ ($1.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁷ show a similar tendency when an H atom is replaced by an F atom.

Atmospheric Implications. The rate constant of the reaction of (CF₃)₂CHOCH₃ with OH radicals is $k_1(T) = (1.40 \pm 0.28) \times 10^{-12} \exp[(-550 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the atmospheric lifetime is estimated to be 2.0 months using the rate constant at 288 K. (CF₃)₂CHOCH₃ is expected to have less impact on global warming because it is more rapidly removed from the atmosphere than HCFCs and HFCs.^{2,7}

In the atmosphere, the reaction of (CF₃)₂CHOCH₃ with OH radicals will produce (CF₃)₂CHOCH₂* and (CF₃)₂C*OCH₃ radicals with a branching ratio of 2.1:1 at 298 K. The (CF₃)₂CHOCH₂* and (CF₃)₂C*OCH₃ radicals formed can rapidly react with O₂ to produce the peroxy radicals, (CF₃)₂CHOCH₂O₂* and (CF₃)₂CO₂*OCH₃. These peroxy radicals will react with HO₂, NO₂, NO, and other peroxy radicals. It is not obvious that the reactions of the peroxy radicals, (CF₃)₂CHOCH₂O₂* and (CF₃)₂CO₂*OCH₃, with HO₂ lead to (CF₃)₂CHOC(O)H and CF₃C(O)OCH₃, respectively, in the present work. In the atmosphere, it is possible that (CF₃)₂CHOC(O)H and CF₃C(O)OCH₃ are produced from (CF₃)₂CHOCH₂O₂* and (CF₃)₂CO₂*OCH₃ radical reaction with HO₂. (CF₃)₂CHOCH₂O₂NO₂ and (CF₃)₂C(O₂NO₂)OCH₃, formed from the reactions of (CF₃)₂CHOCH₂O₂* and (CF₃)₂CO₂*OCH₃ with NO₂, decompose to (CF₃)₂CHOCH₂O₂*, (CF₃)₂CO₂*OCH₃, and NO₂ due to their thermal instability. Reactions of (CF₃)₂CHOCH₂O₂* and (CF₃)₂CO₂*OCH₃ with NO produce (CF₃)₂CHOCH₂O* and (CF₃)₂CO*OCH₃ radicals. The fate of (CF₃)₂CHOCH₂O* and (CF₃)₂CO*OCH₃ radicals is shown in this study to form (CF₃)₂CHOC(O)H and CF₃C(O)OCH₃ by reaction with O₂ and decomposition, respectively. OH radicals also oxidize (CF₃)₂CHOC(O)H in the atmosphere. In this study, the OH-radical oxidation of (CF₃)₂CHOC(O)H is observed to

produce CF₃C(O)CF₃. CF₃C(O)CF₃ is then likely to form CF₃C(OH)₂CF₃ by reaction with H₂O in atmospheric conditions. However, because the atmospheric chemistry of CF₃C(OH)₂CF₃ is not yet known, further investigation of CF₃C(OH)₂CF₃ is required. CF₃C(O)OCH₃ can be oxidized by OH radicals in the atmosphere, with the final products likely to include COF₂. CF₃C(O)OCH₃ may also be removed from the atmosphere by dissolution into the ocean.²²

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