



Kinetics and mechanism of gas-phase reaction of $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$ with OH radicals in an environmental reaction chamber at 253–328 K

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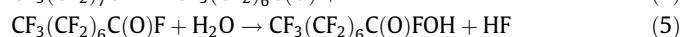
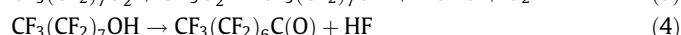
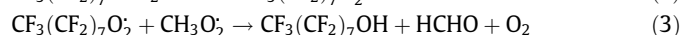
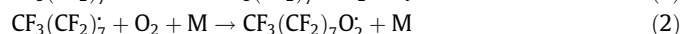
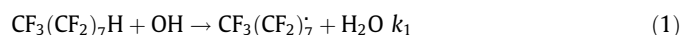
ABSTRACT

The atmospheric chemistry of $\text{CF}_3(\text{CF}_2)_7\text{H}$ was studied in an 11.5-dm³ environmental reaction chamber by means of Fourier transform infrared spectroscopy. Using a relative rate method, we determined the Arrhenius expression for the rate constant of the reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals to be $(4.32 \pm 1.87) \times 10^{-13} \exp[-(1540 \pm 130)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 253–328 K. At 298 K, COF_2 was a sole product in a molar yield of (1.02 ± 0.11) in terms of carbon.

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1. Introduction

Chemicals with the formula $\text{CF}_3(\text{CF}_2)_x\text{H}$ ($x \geq 0$) are by-products of the manufacture for various fluorine compounds and are contained in such compounds as trace impurities. Therefore, $\text{CF}_3(\text{CF}_2)_x\text{H}$ can be expected to be released into the atmosphere during the manufacture and use of such fluorine compounds. $\text{CF}_3(\text{CF}_2)_7\text{H}$ is a typical long-chain example of $\text{CF}_3(\text{CF}_2)_x\text{H}$. $\text{CF}_3(\text{CF}_2)_7\text{H}$ may be oxidized to perfluorooctanoic acid (PFOA) in the atmosphere [1]:



PFOA is persistent, bioaccumulative, and potentially toxic [2]. Although, like other hydrofluorocarbons, $\text{CF}_3(\text{CF}_2)_7\text{H}$ has no ozone depletion potential because it does not contain Cl or Br atoms, it is a potential greenhouse gas because its C–F bonds absorb in the terrestrial infrared radiation region of 800–1200 cm^{-1} [3,4]. For these reasons, an investigation of the atmospheric chemistry of $\text{CF}_3(\text{CF}_2)_7\text{H}$ is needed. However, the kinetics and the mechanism of the reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals have not been reported.

In this study, we used a relative rate method to determine the rate constant (k_1) for the reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals at 253–328 K [5,6]. The tropospheric lifetime of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with respect to reaction with OH radicals was estimated by scaling from the tropospheric lifetime of CH_2Cl_2 , by using k_1 at 272 K. The

product of the OH radical-initiated reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ was determined in an 11.5-dm³ environmental reaction chamber by means of Fourier transform infrared spectroscopy at 298 K. On the basis of our results, we propose a mechanism for the degradation of $\text{CF}_3(\text{CF}_2)_7\text{H}$ by means of reaction with OH radicals.

2. Experimental

A sample of $\text{CF}_3(\text{CF}_2)_7\text{H}$ (>99% pure) was obtained from Asahi Glass Co., (Japan). Experiments were performed in an 11.5-dm³ cylindrical quartz chamber (diameter: 10 cm; length: 146 cm) with an external jacket [7]. The temperature in the reaction chamber was controlled by circulation of heated or cooled water, or a coolant (PF-5070, Sumitomo 3 M, Japan), through the external jacket and was monitored with an accuracy of ± 1 K over the temperature range 253–328 K by means of two thermocouples, one attached to each side of the reaction chamber.

For the determination of k_1 and the reaction mechanism, OH radicals were produced by ultraviolet (UV) photolysis of O_3 , which was generated from pure O_2 (99.5% purity; 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) [7]:



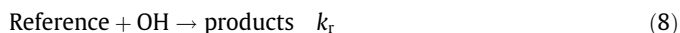
Ten 40-W low-pressure Hg lamps (254 ± 8 nm) surrounding the reaction chamber were used as the UV light sources. An O_3/O_2 (3% O_3) gas mixture was continuously introduced at a flow rate of 5–10 $\text{cm}^3 \text{ min}^{-1}$ at STP into the reaction chamber during the UV irradiation period. A greaseless vacuum line was used for preparation of the reaction gas mixtures.

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For the determination of k_1 , the reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ was analyzed relative to the reactions of two reference compounds, CHF_2CF_3 and CH_2FCF_3 . CHF_2CF_3 (99% pure) was obtained from Showa Denko Co., (Tokyo, Japan), and CH_2FCF_3 (99% pure) was purchased from SynQuest (Alachua, FL, USA). The initial concentrations (in molecules cm^{-3}) of the reactants were 1.0×10^{15} ($\text{CF}_3(\text{CF}_2)_7\text{H}$), 1.0×10^{15} (reference compound), $(0.36\text{--}5.8) \times 10^{17}$ (H_2O), and 3.2×10^{18} (O_2) in 200 Torr of He. The concentrations of $\text{CF}_3(\text{CF}_2)_7\text{H}$ and the reference compounds were determined with a GC-14A gas chromatograph with a flame ionization detector (GC-FID; Shimadzu, Tokyo, Japan) equipped with a wide-bore capillary column (Rtx-1, 30-m length, 0.53-mm i.d.). The column oven was set at a constant temperature of 313 K for the determination of k_1 . A 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 the reactants were <2% for $\text{CF}_3(\text{CF}_2)_7\text{H}$ and the reference compounds. The percentage decays after 72 min of irradiation at 298 K were 70% ($\text{CF}_3(\text{CF}_2)_7\text{H}$), 55% (CHF_2CF_3), and 85% (CH_2FCF_3).

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



Taking into account the nonreactive decay (0.2%) due to removal of the sample and reference compound for each GC-FID analysis, we used the following equation to evaluate k_1/k_r [7]:

$$\ln \left(\frac{[\text{CF}_3(\text{CF}_2)_7\text{H}]_0}{[\text{CF}_3(\text{CF}_2)_7\text{H}]_t} \right) + D_n = \frac{k_1}{k_r} \left[\ln \left(\frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right) \right] + D_n \quad (1)$$

where $[\text{CF}_3(\text{CF}_2)_7\text{H}]_0$ and $[\text{Reference}]_0$ represent the initial concentrations of the sample ($\text{CF}_3(\text{CF}_2)_7\text{H}$) and the reference compound (CHF_2CF_3 or CH_2FCF_3); $[\text{CF}_3(\text{CF}_2)_7\text{H}]_t$ and $[\text{Reference}]_t$ represent the concentrations of the $\text{CF}_3(\text{CF}_2)_7\text{H}$ 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 [7].

For determination of the mechanism, the reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals was investigated at 298 K by means of FT-IR spectroscopy with a nickel-coated aluminum multiple-reflection IR cell (375 cm^3 ; optical path length, 3 m), which was connected to the circulation line of the 11.5-dm^3 reaction chamber used for the kinetic studies [7]. Experiments were performed at initial concentrations (in molecules cm^{-3}) of 5.0×10^{14} ($\text{CF}_3(\text{CF}_2)_7\text{H}$) and 5.6×10^{17} (H_2O) in an O_3/O_2 (3%) gas mixture at 200 Torr. Loss of $\text{CF}_3(\text{CF}_2)_7\text{H}$ and formation of products were monitored with an FT-IR spectrometer (JIR-6500, JEOL, 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 $850 \text{ cm}^3 \text{ min}^{-1}$ during UV irradiation. The concentrations of $\text{CF}_3(\text{CF}_2)_7\text{H}$ and COF_2 were quantified from the IR absorptions at 1156 and 1928 cm^{-1} , respectively, of He mixtures of known concentration at a total pressure of 200 Torr at 298 K. COF_2 (95% pure) was purchased from SynQuest (Alachua, FL, USA).

3. Results and discussion

3.1. Rate constants for reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals

The k_1 values were derived from Figure 1, in which $\ln([\text{CF}_3(\text{CF}_2)_7\text{H}]_0/[\text{CF}_3(\text{CF}_2)_7\text{H}]_t) + D_n$ is plotted against $\ln([\text{Reference}]_0/[\text{Reference}]_t) + D_n$. These data were obtained in triplicate, and the results of each replicate were consistent with each other. Linear least-squares analysis of the data in Figure 1 gave $k_1/k_r = 1.38 \pm 0.16$ (CHF_2CF_3) and 0.578 ± 0.007 (CH_2FCF_3). The errors reported represent 2 standard deviations in the data for k_1/k_r ; the errors were lower than 12% and represent precision only. Using the experimental data for k_1/k_r along with reference values of $k_{298 \text{ K}}(\text{CHF}_2\text{CF}_3) = 1.9 \times 10^{-15}$ ($\pm 20\%$) and $k_{298 \text{ K}}(\text{CH}_2\text{FCF}_3) = 4.6 \times 10^{-15}$ ($\pm 20\%$) $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [8], we estimated the values of $k_1(298 \text{ K})$ to be $(2.62 \pm 0.30) \times 10^{-15}$ (CHF_2CF_3) and $(2.66 \pm 0.03) \times 10^{-15}$ (CH_2FCF_3) $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A possible systematic uncertainty could add an additional 10–20% to the values of k_1 with due consideration of possible errors in the rate constant data for the two reference compounds. The values of k_1 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 $\text{O}(^1\text{D})$, and dark reactions with O_3 or H_2O . The losses of sample and reference compound were less than the measurement errors (<2%) after 5 h of direct UV photolysis. In a previous study, we determined that $\text{O}(^1\text{D})$ reactions do not occur to an appreciable extent in this reaction system [9]. The effects of $\text{O}(^1\text{D})$ 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 $\text{O}(^1\text{D})$ reactions has been discussed 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 owing to concentration measurement errors (<2%).

Values of k_1 were determined over the temperature range 253–328 K. The plots of $\ln([\text{CF}_3(\text{CF}_2)_7\text{H}]_0/[\text{CF}_3(\text{CF}_2)_7\text{H}]_t) + D_n$ versus $\ln([\text{Reference}]_0/[\text{Reference}]_t) + D_n$ obtained over this temperature range were similar to those shown in Figure 1. Table 1 lists the values of k_1 determined from the measured k_1/k_r ratios, under the assumption that $k(\text{CHF}_2\text{CF}_3) = 4.4 \times 10^{-13} \exp(-1630/T)$ and that $k(\text{CH}_2\text{FCF}_3) = 4.9 \times 10^{-13} \exp(-1395/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [8].

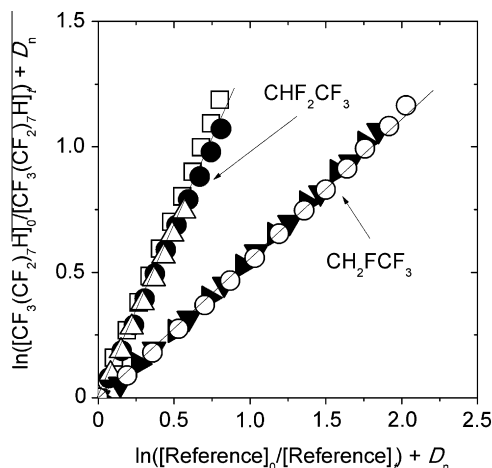


Figure 1. Loss of $\text{CF}_3(\text{CF}_2)_7\text{H}$ versus loss of reference compounds CHF_2CF_3 (\square , \bullet , \blacktriangle) and CH_2FCF_3 (\circ , \blacktriangleright , \blacktriangleleft) in the presence of OH radicals at 298 K under an initial He pressure of 200 Torr (data are averages of 3 runs).

Table 1
Measured values of k_1/k_r and k_1 over the temperature range 253–328 K.

T (K)	k_1/k_r		$10^{15} \times k_1$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	
	CHF_2CF_3	CH_2FCF_3	CHF_2CF_3	CH_2FCF_3
253	1.34 ± 0.04	0.547 ± 0.025	0.941 ± 0.029	1.08 ± 0.05
268	1.24 ± 0.05	0.560 ± 0.017	1.25 ± 0.05	1.51 ± 0.05
283	1.30 ± 0.12	0.563 ± 0.016	1.80 ± 0.17	2.00 ± 0.06
298	1.38 ± 0.16	0.578 ± 0.007	2.62 ± 0.30	2.66 ± 0.03
313	1.34 ± 0.06	0.558 ± 0.008	3.24 ± 0.15	3.17 ± 0.05
328	1.29 ± 0.02	0.547 ± 0.002	3.94 ± 0.06	3.81 ± 0.02

The quoted errors are 2 standard deviations.

From a plot of the temperature dependencies of k_1 (Figure 2) and the Arrhenius expression, $k_1 = Ae^{-E/RT}$, we determined the Arrhenius rate parameters (A and E/R) by nonlinear least-squares analyses of the data in Figure 2. The Arrhenius expression for k_1 was determined to be $(4.32 \pm 1.87) \times 10^{-13} \exp[-(1540 \pm 130)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the value of k_1 at 298 K of $(2.49 \pm 0.10) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was calculated from the Arrhenius expression. This value is comparable to previously reported values for $k(\text{CHF}_2\text{CF}_3)$ ($1.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [8] and $k(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H})$ ($1.89 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [10,11]. The E/R value for k_1 is slight smaller than the values for $k(\text{CHF}_2\text{CF}_3)$ (1700 K) and $k(\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H})$ (1690 K). Therefore, the OH radical reactivities of CHF_2CF_3 , $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$, and $\text{CF}_3(\text{CF}_2)_7\text{H}$ were similar. This result indicates that the substituent effect of $-\text{CF}_2-$ was similar to that of $-\text{CF}_3$, as discussed in our previous paper [10]. The ratio of $k(\text{CH}_2\text{FCF}_3)/k(\text{CHF}_2\text{CF}_3)$ of 2.38, which was calculated from the data of $k_1/k_r = 1.38 \pm 0.16$ (CHF_2CF_3) and 0.578 ± 0.007 (CH_2FCF_3) measured in this study, is good agreement with the ratio of 2.42 obtained from recommended rate constants ($k_{298\text{K}}(\text{CHF}_2\text{CF}_3) = 1.9 \times 10^{-15}$ and $k_{298\text{K}}(\text{CH}_2\text{FCF}_3) = 4.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) reviewed by Atkinson et al. [8]. The ratio of $k(\text{CH}_2\text{FCF}_3)/k(\text{CHF}_2\text{CF}_3)$ of 2.2 obtained from the values ($k_{298\text{K}}(\text{CHF}_2\text{CF}_3) = 2.0 \times 10^{-15}$ ($\pm 20\%$) and $k_{298\text{K}}(\text{CH}_2\text{FCF}_3) = 4.4 \times 10^{-15}$ ($\pm 10\%$) $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the NASA report is slightly lower [12].

The tropospheric lifetimes of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with respect to reaction with OH radicals were estimated from Eq. (II) [13]:

$$\tau_1 = \frac{k_{\text{CH}_3\text{CCl}_3}}{k_1} \times \tau_{\text{CH}_3\text{CCl}_3} \quad (\text{II})$$

where τ_1 and $\tau_{\text{CH}_3\text{CCl}_3}$ represent the tropospheric lifetimes of $\text{CF}_3(\text{CF}_2)_7\text{H}$ and CH_3CCl_3 , respectively, with respect to reaction with OH radicals; and k_1 and $k_{\text{CH}_3\text{CCl}_3}$ represent rate constants for the reactions of $\text{CF}_3(\text{CF}_2)_7\text{H}$ and of CH_3CCl_3 , respectively, with OH radi-

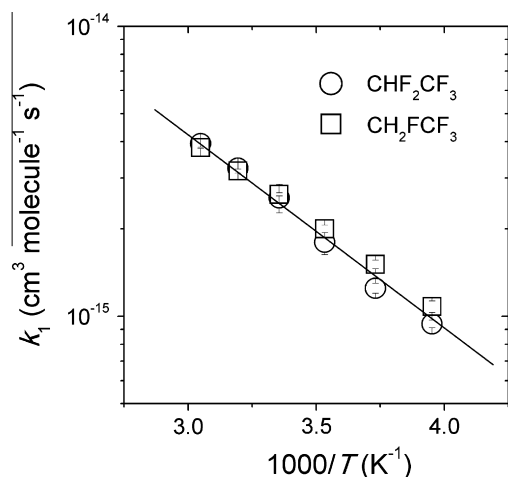


Figure 2. Arrhenius plots obtained by the relative rate method for reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals at 253–328 K.

cals at 272 K. Prinn et al. [14] estimated a $\tau_{\text{CH}_3\text{CCl}_3}$ value of 6.0 years. The k_1 value at 272 K was calculated to be $1.50 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and the literature value for $k_{\text{CH}_3\text{CCl}_3}$ at 272 K is $6.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [12]. Therefore, we estimated the tropospheric lifetime of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with respect to reaction with OH radicals to be 24 years.

3.2. Mechanism for reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals

We obtained the infrared spectra of the $\text{CF}_3(\text{CF}_2)_7\text{H}/\text{O}_3/\text{H}_2\text{O}/\text{O}_2$ gas mixture before irradiation and after 40 min of irradiation (Figure 3A,B). The concentration of $\text{CF}_3(\text{CF}_2)_7\text{H}$ decreased to 72% of the original value after 40 min of irradiation. Comparison with the IR spectrum of the COF_2 standard (Figure 3C) suggests that the IR bands at 1928 cm^{-1} (Figure 3B) belong to COF_2 , and we identified COF_2 to be a sole product. In this study, we did not determine CO_2 concentration, owing to interference from atmospheric CO_2 in the laboratory. The concentrations of $\text{CF}_3(\text{CF}_2)_7\text{H}$ and COF_2 were calculated from their IR absorptions at 1156 and 1928 cm^{-1} , respectively, using the calibration curve method. We plotted the concentration of produced COF_2 (divided by 8) versus $d[\text{CF}_3(\text{CF}_2)_7\text{H}]$ due to reaction with OH radicals (two runs; Figure 4). Because COF_2 was consumed by hydrolysis on the wall of the reaction chamber, we estimated the yield of COF_2 from the data observed during the initial 24 min of irradiation, to minimize interference of the hydrolysis reaction with our estimation of the yield of COF_2 from the reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals. The concentration of $\text{CF}_3(\text{CF}_2)_7\text{H}$ decreased by about 11% during the initial 24-min irradiation. The data for the initial 24-min irradiation were fitted to a quadratic function (solid line, Figure 4), which was then differentiated to give a differential function. The slope of the differential function at the origin gave a COF_2 yield of (1.02 ± 0.11) in terms of carbon. This yield implies that COF_2 was a sole product of the reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals, which was consistent with the conclusion obtained from IR spectroscopy.

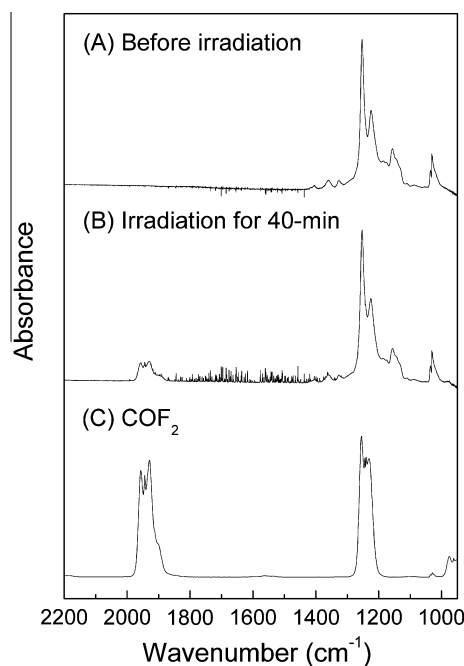


Figure 3. IR spectra observed before (A) and after (B) 40-min UV irradiation of a gas mixture of $\text{CF}_3(\text{CF}_2)_7\text{H}$ in the presence of OH radicals at 298 K under an initial He pressure of 200 Torr. An O_3/O_2 (3%) gas mixture was introduced continuously into the chamber at a flow rate of 3 ml/min during the irradiation. (C) A reference spectrum of COF_2 .

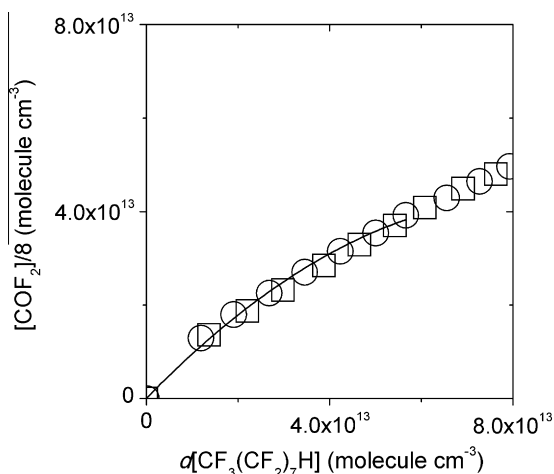


Figure 4. Plots of $[\text{COF}_2]/8$ versus $d[\text{CF}_3(\text{CF}_2)_7\text{H}]$ due to reaction with OH radicals (2 runs). The curve was obtained by fitting data obtained during the initial 24 min of irradiation to a quadratic function.

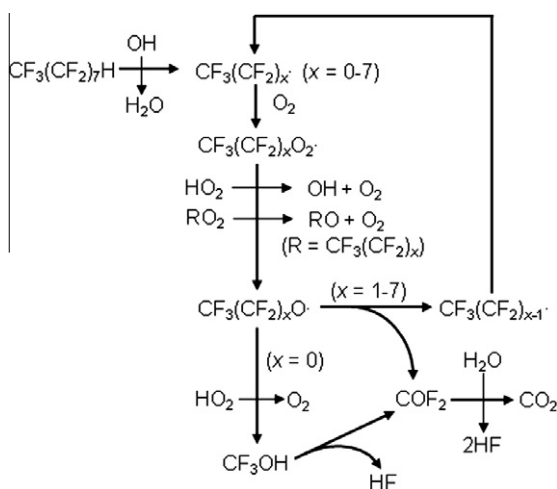
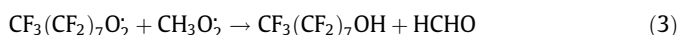
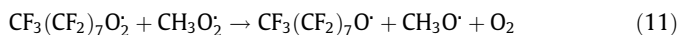
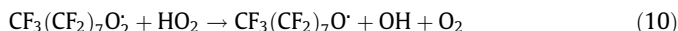
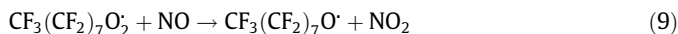


Figure 5. Proposed mechanism for degradation of $\text{CF}_3(\text{CF}_2)_7\text{H}$ by OH radicals during irradiation of the $\text{CF}_3(\text{CF}_2)_7\text{H}/\text{O}_3/\text{H}_2\text{O}/\text{O}_2$ gas mixture at 298 K.

The observed product suggest the following mechanism for reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals (Figure 5). $\text{CF}_3(\text{CF}_2)_7\cdot$ radicals formed by the reaction of $\text{CF}_3(\text{CF}_2)_7\text{H}$ with OH radicals reacted rapidly with O_2 to produce $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ radicals; reaction of $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ radicals with HO_2 and $\text{RO}_2\cdot$ ($\text{R} = \text{CF}_3(\text{CF}_2)_x$, $x = 0-7$) formed $\text{CF}_3(\text{CF}_2)_7\text{O}\cdot$ radical, which decomposed to $\text{CF}_3(\text{CF}_2)_6\cdot$ radicals and COF_2 . This reaction sequence was repeated for $\text{CF}_3(\text{CF}_2)_x\cdot$ ($x = 0-6$) radicals to produce $\text{CF}_3(\text{CF}_2)_x\cdot$ ($x = 0-5$) radicals and COF_2 . Finally, $\text{CF}_3\text{O}\cdot$ radicals reacted with HO_2 to form CF_3OH , which decomposed rapidly to COF_2 and HF.

Several possible competing side reactions must be considered. $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ radicals formed by the oxidation of $\text{CF}_3(\text{CF}_2)_7\text{H}$ will react with NO, HO_2 , and $\text{CH}_3\text{O}_2\cdot$ in the atmosphere [3]:



The $\text{CF}_3(\text{CF}_2)_7\text{OH}$ produced by reaction (3) will decompose to $\text{CF}_3(\text{CF}_2)_6\text{C}(\text{O})\text{F}$ and HF (reaction (4)), and then $\text{CF}_3(\text{CF}_2)_6\text{C}(\text{O})\text{F}$ can be hydrolyzed to PFOA.

Because the reactions of $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ with HO_2 and NO compete with the reaction with $\text{CH}_3\text{O}_2\cdot$, the yield of PFOA from $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ radicals can be estimated from the concentrations of HO_2 , NO, and $\text{CH}_3\text{O}_2\cdot$ and the rate constants for their respective reactions with $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ radicals. Wallington et al. reported that PFOA can be formed by atmospheric oxidation of 8:2 fluorotelomer alcohol ($\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$) [3]. Because the atmospheric lifetime of $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$ is about 10–20 days, the molar yields of PFOA depend on the emission location and the season. By using a three-dimensional model for chemistry and transport (IMPACT), these investigators estimated the molar yield for PFOA from $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ radicals to be 0.04–0.08 in the Northern Hemisphere and 0.10–0.16 in the Southern Hemisphere. In this study, we estimated the atmospheric lifetime of $\text{CF}_3(\text{CF}_2)_7\text{H}$ to be 24 years, and it can be expected to be ubiquitous in the atmosphere. Therefore, the molar yield of PFOA produced by the oxidation of $\text{CF}_3(\text{CF}_2)_7\text{H}$ does not depend on emission location and season. The mechanism that we propose in this study suggests that $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ radicals were produced in 100% yield by the oxidation of $\text{CF}_3(\text{CF}_2)_7\text{H}$. We estimated the molar yield of PFOA from the oxidation of $\text{CF}_3(\text{CF}_2)_7\text{H}$ to be 0.07–0.12, by using an average of the molar yields for PFOA from $\text{CF}_3(\text{CF}_2)_7\text{O}_2\cdot$ radicals in the Northern and Southern Hemispheres (0.04–0.08 and 0.10–0.16, respectively, as reported by Wallington et al. [3]).

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