

Cl Atom-Initiated Oxidation of Three Homologous Methyl Perfluoroalkyl Ethers

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Chlorine atom-initiated photooxidations of three homologous methyl perfluoroalkyl ethers (HFEs), $n\text{-C}_n\text{F}_{2n+1}\text{OCH}_3$ ($n = 2, 3, \text{ and } 5$), in air in the absence of NO_x were investigated with a long path FTIR/photochemical reaction system to elucidate the degradation mechanisms. The environmental removal processes of these three ethers in the troposphere were estimated. For oxidation of the three ethers, perfluoroalkyl formates ($\text{C}_n\text{F}_{2n+1}\text{OCHO}$; $n = 2, 3$ and 5) as relatively stable intermediates were produced at unity of the production ratio, which was independent of the perfluoroalkyl length. The rate constants for the reaction of Cl atoms with $\text{C}_2\text{F}_5\text{OCHO}$, $\text{C}_3\text{F}_7\text{OCHO}$, and $\text{C}_5\text{F}_{11}\text{OCHO}$ were $(1.2 \pm 0.5) \times 10^{-14}$, $(1.2 \pm 0.5) \times 10^{-14}$, and $(1.8 \pm 0.7) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The rate constants of the reaction of Cl with produced perfluoroalkyl formates were larger than those of perfluoroalkyl ethers. The formyl group of the perfluoroalkyl formates was finally converted to carbon dioxide. The $-\text{CF}_2-$ of the perfluoroalkyl groups for the three ethers was mainly converted to COF_2 through the C–C cleavage; the conversion ratios from the carbons of the perfluoroalkyl group to COF_2 were 48 ± 10 , 76 ± 10 , and $60 \pm 10\%$ for $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, respectively. Sixteen percent of the perfluoroalkyl group for $n\text{-C}_3\text{F}_7\text{OCH}_3$ was converted to $\text{C}_2\text{F}_5\text{COF}$. Similarly, the perfluoroalkyl group of $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ was converted to $\text{C}_n\text{F}_{2n+1}\text{COF}$ ($n = 2, 3, \text{ and/or } 4$) with the yield of 15–30%, while for $\text{C}_2\text{F}_5\text{OCH}_3$, the formation of CF_3COF was not confirmed. As an oxidation product of the terminal CF_3- group, 20, 22, and 16% of the CF_3 group for $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, respectively, were converted to $\text{CF}_3\text{OOOCF}_3$.

Introduction

Development of alternatives to hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) has been extensively conducted throughout the world, because HFCs and HCFCs will be regulated due to their global warming potentials (GWPs) and/or stratospheric ozone depletion potentials (ODPs) (1, 2). Hydrofluorinated ether compounds (HFEs) (3, 4) are considered to be promising materials as new alterna-

tives. Their ODP is zero, because they contain no chlorine atoms. RITE (Research Institute of Innovative Technology for the Earth) has been developing three homologous methyl perfluoroalkyl ethers ($n\text{-C}_n\text{F}_{2n+1}\text{OCH}_3$; $n = 2, 3, 5$) (5) as refrigerants and/or blowing agents. The rate constants for $\text{C}_2\text{F}_5\text{OCH}_3$ and $n\text{-C}_3\text{F}_7\text{OCH}_3$ for the reaction with the OH radical at 273 K are $0.819 \pm 0.025 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $0.741 \pm 0.023 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (6) which were measured by the laser induced fluorescence technique (LIF). Their tropospheric lifetimes estimated by using the $7.5 \times 10^5 \text{ molecule cm}^{-3}$ of the concentration of $[\text{OH}]$ (7) is thus less than 6 years. If they are degraded in the troposphere to form relatively stable byproducts, it would induce the environmental impacts in addition to global warming. The research of degradation processes for HFEs in troposphere is important for the environmental assessment of HFEs.

In this study, the oxidations of the three ethers were initiated by Cl atoms. The changes in the concentration of the ethers and their degradation products were monitored by an FTIR spectrometer. It was revealed that the perfluoroalkyl formate was formed as a major intermediate in the reaction. The final products observed were CO_2 (produced from CH_3 group), COF_2 , $\text{CF}_3\text{OOOCF}_3$, and $\text{C}_n\text{F}_{2n+1}\text{COF}$ ($n = 2, 3, \text{ and/or } 4$) which were produced from the perfluoroalkyl group. The concentrations of all the final products were determined, to check the mass balance of the reactions and to elucidate the reaction mechanisms. The kind and distribution of the products from the perfluoroalkyl groups were found to be dependent on the chain length. The fate of the degradation products in the environment was discussed in connection with their environmental impact.

Experimental Section

The experimental apparatus used here has been previously described in detail (8). Experiments were carried out using a 25-L evacuable quartz cylinder (14 cm in diameter, 150 cm long), surrounded with four 40-W black lamps, equipped with an in situ multiple reflection optical system (30-m path length) interfaced to a JEOL JIR100 FTIR spectrometer. The IR spectra of the reactants and products were measured over the frequency range from 700 to 3500 cm^{-1} at 0.5 cm^{-1} resolution by 50 scans/interferograms. Liquid fluorinated ethers were injected into the chamber with a microsyringe. The prescribed amount of Cl_2 ($2.46 \times 10^{14} \text{ molecule cm}^{-3}$) was taken in a gas cell and then introduced into the reaction chamber. Each of the HFEs– Cl_2 mixtures was diluted to atmospheric pressure ($1.01 \times 10^5 \text{ Pa}$) with synthetic air (80% $\text{N}_2 + 20\% \text{O}_2$) at $298 \pm 3 \text{ K}$. The initial concentrations of HFEs was 1.65×10^{14} , 1.23×10^{14} , and $2.16 \times 10^{14} \text{ molecule cm}^{-3}$ for $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, respectively. The oxidation of HFEs was initiated by Cl atoms, which were generated by photolysis of Cl_2 .

Three kinds of methyl perfluoroalkyl ethers ($\text{C}_2\text{F}_5\text{OCH}_3$, 99.9%; $n\text{-C}_3\text{F}_7\text{OCH}_3$, 99.8%; $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, 99.8%) were supplied from RITE and used without further purification.

Results and Discussion

The Identification of the Degradation Products by the IR Spectra. IR spectra of $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ ($2.16 \times 10^{14} \text{ molecule cm}^{-3}$) and Cl_2 ($2.46 \times 10^{14} \text{ molecule cm}^{-3}$) in $1.01 \times 10^5 \text{ Pa}$ of air are shown in Figure 1(a) (before irradiation) and (b) (after 30 min irradiation). Figure 1(c) is the subtracted spectrum (1(b) – 1(a)). After 30-min irradiation, the peaks in the range of $1875\text{--}1978 \text{ cm}^{-1}$ and split peaks about 2300 cm^{-1} appeared, which were attributed to COF_2 and CO_2 ,

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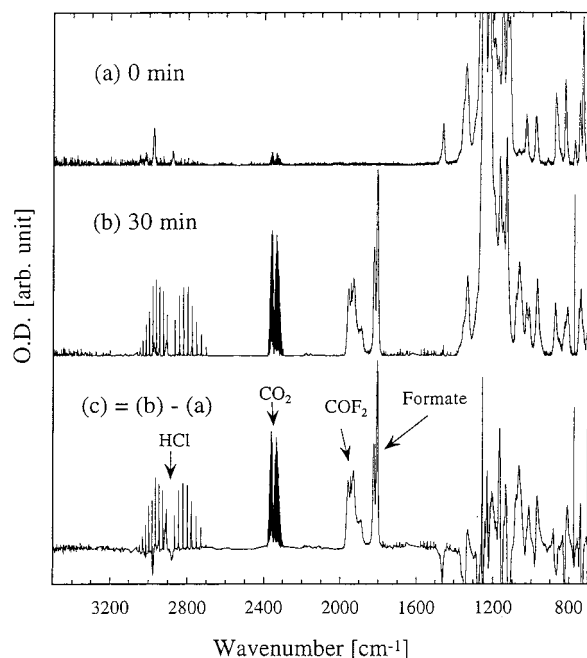


FIGURE 1. IR spectra in the frequency region of 700–3500 cm^{-1} obtained from the photolysis of a mixture containing $\text{C}_5\text{F}_{11}\text{OCH}_3$ (2.16×10^{14} molecule cm^{-3}) and Cl_2 (2.46×10^{14} molecule cm^{-3}) in 1.01×10^5 Pa of air: (a) before irradiation; (b) after 30-min irradiation; and (c) differential spectrum.

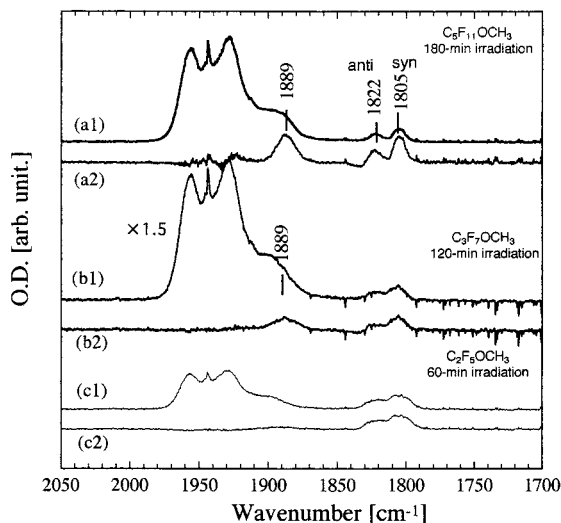


FIGURE 2. Comparison with the three subtracted IR features (1700–2100 cm^{-1}) obtained from the photolysis of the gas mixture: (a1) $\text{C}_5\text{F}_{11}\text{OCH}_3$ (2.16×10^{14} molecule cm^{-3}) after 180-min irradiation, (b1) $\text{C}_3\text{F}_7\text{OCH}_3$ (1.23×10^{14} molecule cm^{-3}) after 120-min irradiation, and (c1) $\text{C}_2\text{F}_5\text{OCH}_3$ (1.65×10^{14} molecule cm^{-3}) after 60-min irradiation with Cl_2 (2.46×10^{14} molecule cm^{-3}) in 1.01×10^5 Pa of air. (a2), (b2), and (c2) are the subtracted IR features from each of the (a1), (b1), and (c1) from the IR spectra of COF_2 .

respectively. Carbon monoxide was not detected in this experiment. The absorption bands of HCl were observed from 2726 to 3014 cm^{-1} . The IR absorption of intermediates appeared at 1805 and 1822 cm^{-1} .

Similar experiments were conducted for $\text{C}_2\text{F}_5\text{OCH}_3$ (1.65×10^{14} molecule cm^{-3}) or $\text{C}_3\text{F}_7\text{OCH}_3$ (1.23×10^{14} molecule cm^{-3}) mixed with Cl_2 (2.46×10^{14} molecule cm^{-3}). IR spectrum of $\text{C}_5\text{F}_{11}\text{OCH}_3$ in the range of 1700 to 2050 cm^{-1} at 180 min illumination, that of $\text{C}_3\text{F}_7\text{OCH}_3$ after 120-min, and that of $\text{C}_2\text{F}_5\text{OCH}_3$ after 60-min irradiation are shown in Figure 2 [parts (a1), (b1), and (c1), respectively]. The peaks in the

TABLE 1. Comparison of Calculated and Observed Frequencies (cm^{-1}) for the IR Spectrum of Perfluoroalkyl Formates

		$\nu_{\text{CH=O}}$ (calcd) ^a	$\nu_{\text{CH=O}}$ (exptl)
$\text{C}_2\text{F}_5\text{OCHO}$	anti	1827.4	1822
	syn	1806.0	1805
$\text{C}_3\text{F}_7\text{OCHO}$	anti	1827.0	1822
	syn	1805.0	1805
$\text{C}_5\text{F}_{11}\text{OCHO}$	anti	1827.3	1822
	syn	1805.0	1805

^a Ab initio MO calculation with RHF/6-31G(d, p) frequencies in cm^{-1} , scaled by 0.873.

range of 1875–1978 cm^{-1} for COF_2 were detected as the final product. Two IR peaks at 1805 and 1822 cm^{-1} for intermediates also appeared for the oxidation of both $\text{C}_2\text{F}_5\text{OCH}_3$ and $n\text{-C}_3\text{F}_7\text{OCH}_3$, as similarly to $n\text{-C}_5\text{F}_{11}\text{OCH}_3$. The absorption bands of the intermediates other than these two peaks were not observed in the oxidation of three ethers.

Wallington et al. (7) calculated the vibrational frequencies of syn and anti structures of CF_3OCHO by ab initio molecular orbital calculation with RHF/6-31G(d,p) to confirm the carbonyl stretching bands ($\text{C}_\text{H}=\text{O}$) at 1800 cm^{-1} and 1823 cm^{-1} for syn and anti structures, respectively. Therefore, the observed two peaks at 1805 cm^{-1} and 1822 cm^{-1} in the oxidation of three ethers can be attributed to the perfluoroalkyl formates. To estimate the vibrational frequencies of the carbonyl stretching bands ($\text{C}_\text{H}=\text{O}$) for the three perfluoroalkyl formates ($\text{C}_2\text{F}_5\text{OCHO}$, $\text{C}_3\text{F}_7\text{OCHO}$, and $\text{C}_5\text{F}_{11}\text{OCHO}$), the syn and anti structures of these three perfluoroalkyl formates were calculated by the ab initio molecular orbital calculation with restricted Hartree–Fock (RHF), basis set of 6-31G-(d,p), by using the Gaussian 94 program. The calculated spectra are corrected by the scale factor of 0.873 which has been proposed for CH_3OCHO (7). The results of this calculation are summarized in Table 1. Calculated spectra for the $\text{C}_\text{H}=\text{O}$ vibrational stretching bands for syn and anti of the three kinds of perfluoroalkyl formates show the frequencies similar to the experimental ones. The vibrational frequencies of $\text{C}_\text{H}=\text{O}$ for syn and anti of three perfluoroalkyl formates are almost same. For the oxidation of $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, the observed spectra at 1805 and 1822 cm^{-1} are thus attributed to the $\text{C}_\text{H}=\text{O}$ bands of syn and anti of $\text{C}_2\text{F}_5\text{OCHO}$, $\text{C}_3\text{F}_7\text{OCHO}$, and $\text{C}_5\text{F}_{11}\text{OCHO}$, respectively.

Parts (a2), (b2), and (c2) of Figure 2 are obtained by subtracting the spectrum around 1900 cm^{-1} of COF_2 from each of the IR spectra of (a1), (b1), and (c1). An absorption at 1889 cm^{-1} was confirmed for both $n\text{-C}_3\text{F}_7\text{OCH}_3$ and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ degradation. The peak at 1889 cm^{-1} was the $\text{C}=\text{O}$ stretching band of $\text{C}_2\text{F}_5\text{COF}$, which was confirmed by using the authentic sample. Although the $\text{C}=\text{O}$ stretching band of CF_3COF has been reported to appear at 1898 cm^{-1} (9), the absorption at 1898 cm^{-1} (CF_3COF) was not detected in Figure 2 [parts (a2), (b2), and (c2)]. The absorption at 1889 cm^{-1} for $n\text{-C}_3\text{F}_7\text{OCH}_3$ can be attributed to $\text{C}_2\text{F}_5\text{COF}$. The peak at 1889 cm^{-1} for $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ may be attributed to $\text{C}_2\text{F}_5\text{COF}$, $\text{C}_3\text{F}_7\text{COF}$, and/or $\text{C}_4\text{F}_9\text{COF}$, taking into account the degradation processes as described later, if the $\text{C}=\text{O}$ stretching band of $\text{C}_n\text{F}_{2n+1}\text{COF}$ ($n \geq 2$) is independent of the perfluoroalkyl length.

The Quantification of the Intermediates and Final Products. The products other than the perfluoroalkyl formate were not observed at the initial reaction period for the oxidation of the three ethers. Assuming that CO_2 is produced from the oxidation of $-\text{CHO}$ group for the perfluoroalkyl formates, the values which are derived by subtracting the CO_2 concentration formed from the loss of $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ ($\Delta[\text{HFes}]-[\text{CO}_2]$) would be same as the concentration of the

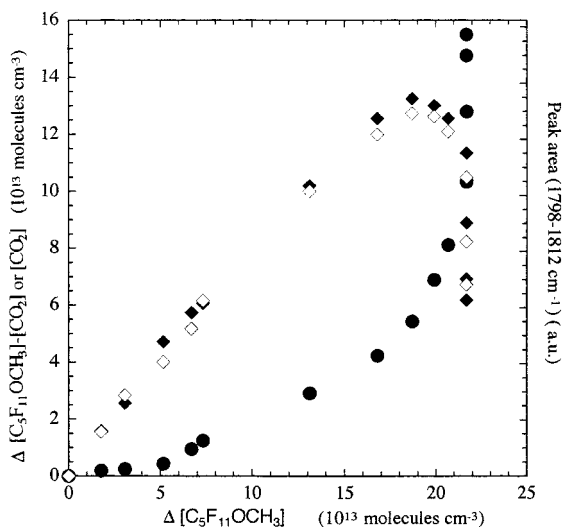


FIGURE 3. The plots of IR peak area in the range of 1798–1812 cm^{-1} for syn- $\text{C}_5\text{F}_{11}\text{OCHO}$ (◇) at arbitrary unit and the concentration of $\Delta[\text{C}_5\text{F}_{11}\text{OCH}_3] - [\text{CO}_2]$ (●), and the concentration of CO_2 (●) versus the loss of $\text{C}_5\text{F}_{11}\text{OCH}_3$ in the photolysis of the gas mixture of $\text{C}_5\text{F}_{11}\text{OCH}_3$ ($2.16 \times 10^{14} \text{ molecule cm}^{-3}$) with Cl_2 ($2.46 \times 10^{14} \text{ molecule cm}^{-3}$) in $1.01 \times 10^5 \text{ Pa}$ of air.

perfluoroalkyl formates. For the oxidation of $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, the concentrations of $(\Delta[n\text{-C}_5\text{F}_{11}\text{OCH}_3] - [\text{CO}_2])$ are plotted against the loss of $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ in Figure 3. Since the absorption coefficient of the perfluoroalkyl formate has not been reported and evaluated, the concentration of the perfluoroalkyl formate cannot be calculated. Therefore, the peak area in the range of 1798–1812 cm^{-1} which has been assigned as the $\text{C}_\text{H}=\text{O}$ stretching band of syn- $\text{C}_5\text{F}_{11}\text{OCHO}$ is also plotted against the $\Delta[n\text{-C}_5\text{F}_{11}\text{OCH}_3]$ in Figure 3. The plots of the peak area at an arbitrary unit could be adjusted to those of $(\Delta[\text{HFEs}] - [\text{CO}_2])$. The profile of plots of $\Delta[n\text{-C}_5\text{F}_{11}\text{OCH}_3] - [\text{CO}_2]$ is in good agreement with that of the peak area in the range of 1798–1812 cm^{-1} . For the oxidation of both $\text{C}_2\text{F}_5\text{OCH}_3$ and $n\text{-C}_3\text{F}_7\text{OCH}_3$, the profile of plots of $\Delta[\text{HFEs}] - [\text{CO}_2]$ were also similar to that of the peak area in the range of 1798–1812 cm^{-1} . This result supports that the perfluoroalkyl formate is the sole primary intermediate for the oxidation of the three ethers, and the CO_2 is quantitatively produced by the degradation of methyl perfluoroalkyl ether.

It has been reported that syn- CF_3OCHO is more stable than anti by about 1 kcal which implies the relative population of 80% syn and 20% anti (7). The $\text{C}_5\text{F}_{11}\text{OCHO}$ may exist at the relative population of 80% syn and 20% anti on the basis of reference about CF_3OCHO . Given that the 80% of $(\Delta[n\text{-C}_5\text{F}_{11}\text{OCH}_3] - [\text{CO}_2])$ corresponds to the concentration of syn- $\text{C}_5\text{F}_{11}\text{OCHO}$, the absorption coefficient of IR absorption band in the range of 1798–1812 cm^{-1} for the $\text{C}_\text{H}=\text{O}$ stretching band of syn- $\text{C}_5\text{F}_{11}\text{OCHO}$ is calculated to be $\sigma\text{-(base e)} = 3.9 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. To confirm whether this absorption coefficient is reasonable for the $\text{C}_\text{H}=\text{O}$ vibration band of syn- $\text{C}_5\text{F}_{11}\text{OCHO}$, the infrared absorption coefficient in the range of 1798–1812 cm^{-1} was estimated by the following steps. IR absorption coefficient in the range of 1680–1820 cm^{-1} for $\text{C}_\text{H}=\text{O}$ vibration band of CH_3OCHO was measured as $\sigma\text{-(base e)} = 4.97 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ (a). The IR intensity for $\text{C}=\text{O}$ vibration band of CH_3OCHO calculated by using the ab initio MO calculation with RHF/6-31G-(d,p) was 452 km/mol (b). The ratio of (a)/(b), the experimental IR absorption coefficient to the calculated IR intensity for CH_3OCHO , was utilized to evaluate the IR absorption coefficient of syn- $\text{C}_5\text{F}_{11}\text{OCHO}$ as follows; the IR intensity for the $\text{C}_\text{H}=\text{O}$ vibration band (1798–1812 cm^{-1}) of syn- $\text{C}_5\text{F}_{11}\text{OCHO}$ calculated with the ab initio MO was multiplied by (a)/(b). The calculated IR absorption coefficient for syn- $\text{C}_5\text{F}_{11}\text{OCHO}$ was obtained

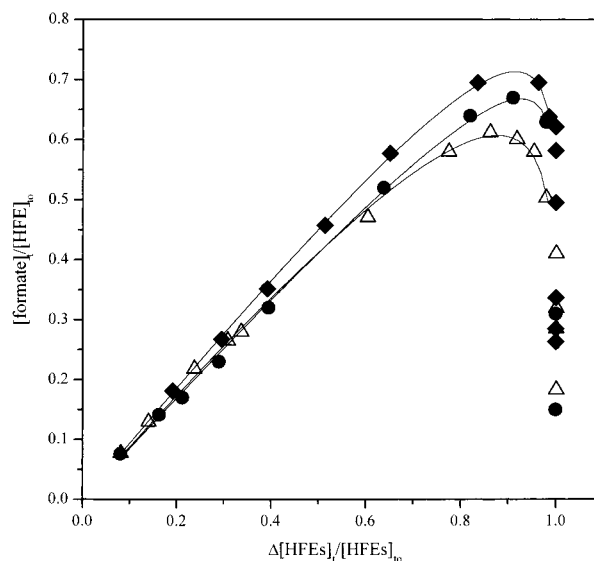


FIGURE 4. Change in the ratio of the concentrations of $\text{C}_n\text{F}_{2n+1}\text{OCHO}$ (2, 3, and 5) to the initial HFEs concentrations versus the fractional loss of $\text{C}_n\text{F}_{2n+1}\text{OCH}_3$ (2, 3, and 5) in the photolysis of HFEs with Cl_2 ($2.46 \times 10^{14} \text{ molecule cm}^{-3}$) in $1.01 \times 10^5 \text{ Pa}$ of air: ●, $\text{C}_2\text{F}_5\text{OCH}_3$, ●, $\text{C}_3\text{F}_7\text{OCH}_3$ and △, $\text{C}_5\text{F}_{11}\text{OCH}_3$. The initial concentrations of $\text{C}_2\text{F}_5\text{OCH}_3$, $\text{C}_3\text{F}_7\text{OCH}_3$, and $\text{C}_5\text{F}_{11}\text{OCH}_3$ are 1.65×10^{14} , 1.23×10^{14} , and $2.16 \times 10^{14} \text{ molecule cm}^{-3}$, respectively.

to be $\sigma\text{-(base e)} = 3.1 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, which is not so different from the experimental derived value of $\sigma\text{-(base e)} = 3.9 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$.

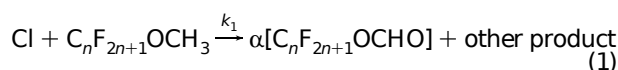
The rate constants of the perfluoroalkyl formates with the Cl atom can be evaluated using eq 1 (10)

$$[\text{formate}]_t / [\text{HFE}]_{t_0} = \frac{[\alpha / (1 - k_2/k_1)](1 - x)[(1 - x)^{(k_2/k_1 - 1)} - 1]}{(1 - x)^{(k_2/k_1 - 1)} - 1} \quad (\text{I})$$

$$x = 1 - [\text{HFE}]_t / [\text{HFE}]_{t_0} \quad (\text{II})$$

where α is the yield of formate from perfluoroalkyl methyl ether ($0 \leq \alpha \leq 1$), and k_1 and k_2 are the secondary rate constants of reactions 1 and 2, respectively.

The relevant reactions are



Ratios of the concentration of $\text{C}_n\text{F}_{2n+1}\text{OCHO}$ ($n = 2, 3$, and 5), which are used by the value of $\Delta[\text{C}_n\text{F}_{2n+1}\text{OCH}_3] - [\text{CO}_2]$ ($n = 2, 3$, and 5), to the initial HFEs concentration are plotted against the fractional loss of HFEs in Figure 4. Each rate constant (k_1) of the H abstractions for the $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ by Cl atom was measured by the method of relative rate constant study (11). The kinetics of $(\text{HFEs} + \text{Cl})$ were measured relative to reaction $(\text{CH}_4 + \text{Cl})$. The initial concentrations were $1.2\text{--}2.2 \times 10^{14} \text{ molecule cm}^{-3}$ of the three ethers, $3.2\text{--}4.5 \times 10^{14} \text{ molecule cm}^{-3}$ of Cl, and $4.9 \times 10^{14} \text{ molecule cm}^{-3}$ of CH_4 in the $1.01 \times 10^5 \text{ Pa}$ of air diluent. The observed loss of three ethers versus those of reference compounds in the presence of Cl atoms is shown in Figure 5. Absorption bands used were at 1462.2 cm^{-1} for $\text{C}_2\text{F}_5\text{OCH}_3$, 1461.7 cm^{-1} for $n\text{-C}_3\text{F}_7\text{OCH}_3$, 1462.0 cm^{-1} for $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, and 3017 cm^{-1} for CH_4 . The k_1 values for three ethers were obtained by linear least-squares analysis of the data in Figure 5. Using the rate constant for $\text{CH}_4 + \text{Cl}$ as $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (12), these k_1 for $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$ and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ are $(11.0 \pm 1.4) \times 10^{-14} \text{ cm}^3$

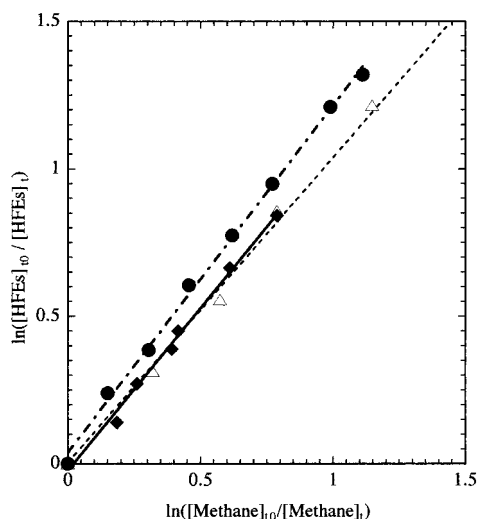


FIGURE 5. The loss of three ethers, $\text{C}_2\text{F}_5\text{OCH}_3$ ($\blacklozenge$), $\text{C}_3\text{F}_7\text{OCH}_3$ ($\bullet$), and $\text{C}_5\text{F}_{11}\text{OCH}_3$ ($\triangle$), versus the loss of CH_4 compounds in the presence of Cl atoms in the 1.01×10^5 Pa of air diluent.

TABLE 2. k_2/k_1 , k_1 , and k_2 Values for the Degradation of the Three Ethers

	CF_3OCH_3	$\text{C}_2\text{F}_5\text{OCH}_3$	$\text{C}_3\text{F}_7\text{OCH}_3$	$(\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	
				$\text{C}_4\text{F}_9\text{OCH}_3$	$\text{C}_5\text{F}_{11}\text{OCH}_3$
k_2/k_1		0.11 ± 0.02	0.10 ± 0.02	0.17 ± 0.07^c	0.17 ± 0.06
			0.09 ± 0.02^b		
k_1	14 ± 0.2^a	11.0 ± 1.4	11.8 ± 1.4	9.7 ± 1.4^c	10.3 ± 1.4
			9.1 ± 1.3^b		
k_2	0.98 ± 0.12^a	1.2 ± 0.5	1.2 ± 0.5	1.6 ± 0.7^c	1.8 ± 0.7
			0.82 ± 0.22^b		

^a The data for the Cl atom initiated oxidation of CF_3OCH_3 by L. K. Christensen et al. (11). ^b The data for the Cl atom initiated oxidation of $\text{C}_3\text{F}_7\text{OCH}_3$ by Y. Ninomiya et al. (13). ^c The data for the Cl atom initiated oxidation of $\text{C}_4\text{F}_9\text{OCH}_3$ by T. J. Wallington et al. (7).

$\text{molecule}^{-1} \text{ s}^{-1}$, $(11.8 \pm 1.4) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $(10.3 \pm 1.4) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (see Table 2), respectively.

The data in Figure 4 were fitted nonlinearly by eq 1 to obtain the k_2/k_1 which are summarized in Table 2. Using k_1 values which was obtained in our experiments, the rate constants (k_2) for reaction of Cl atoms with the formates $\text{C}_2\text{F}_5\text{OCHO}$, $\text{C}_3\text{F}_7\text{OCHO}$, and $\text{C}_5\text{F}_{11}\text{OCHO}$ were calculated to be $(1.2 \pm 0.5) \times 10^{-14}$, $(1.2 \pm 0.5) \times 10^{-14}$, and $(1.8 \pm 0.7) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively (see Table 2). The rate constants of the reaction of Cl with produced perfluoroalkyl formates were larger than these of perfluoroalkyl ethers. The k_2/k_1 , k_1 , and k_2 for the Cl atom initiated degradations of CF_3OCH_3 (11), $n\text{-C}_4\text{F}_9\text{OCH}_3$ (7), and $n\text{-C}_3\text{F}_7\text{OCH}_3$ (13) which have been reported by other groups were also depicted in Table 2. Measured k_1 values for three ethers were similar to that of $n\text{-C}_4\text{F}_9\text{OCH}_3$. The values of k_2 (Cl + $\text{C}_5\text{F}_{11}\text{OCHO}$) were also similar to that of k_2 (Cl + $\text{C}_4\text{F}_9\text{OCHO}$) and were larger than that of k_2 (Cl + $\text{C}_2\text{F}_5\text{OCHO}$) and k_2 (Cl + $\text{C}_3\text{F}_7\text{OCHO}$). The value of k_2 (Cl + $\text{C}_3\text{F}_7\text{OCHO}$) observed in our experiment indicated the similar value of k_2 (Cl + $\text{C}_3\text{F}_7\text{OCHO}$) which was reported by Ninomiya et al. in the range of experimental error.

Figure 6(a),(b) shows the change in the concentration of CO_2 and perfluoroacetyl fluoride, respectively, with the loss of HFEs (ΔHFEs) for the degradation of $\text{C}_2\text{F}_5\text{OCH}_3$ ($1.65 \times 10^{14} \text{ molecule cm}^{-3}$), $n\text{-C}_3\text{F}_7\text{OCH}_3$ ($1.23 \times 10^{14} \text{ molecule cm}^{-3}$), and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ ($2.16 \times 10^{14} \text{ molecule cm}^{-3}$) under the same conditions as in Figure 3. For the oxidation of three ethers,

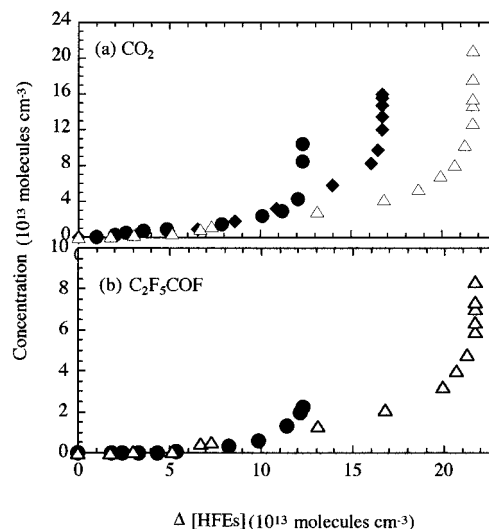


FIGURE 6. The plots of the production yields of CO_2 (a) and perfluoroalkylacetyl fluoride (b) versus the fractional loss of HFEs (ΔHFEs) for the photolysis of $\text{C}_2\text{F}_5\text{OCH}_3$ ($\blacklozenge$), $\text{C}_3\text{F}_7\text{OCH}_3$ ($\bullet$), and $\text{C}_5\text{F}_{11}\text{OCH}_3$ ($\triangle$). The initial concentrations of $\text{C}_2\text{F}_5\text{OCH}_3$, $\text{C}_3\text{F}_7\text{OCH}_3$, and $\text{C}_5\text{F}_{11}\text{OCH}_3$ are 1.65×10^{14} , 1.23×10^{14} , and $2.16 \times 10^{14} \text{ molecule cm}^{-3}$, respectively.

the formations of CO_2 were not observed in the initial loss of HFEs. CO_2 was produced after approximately 20% loss of HFEs. When the loss of HFEs reached 100%, the production of CO_2 continues to increase. The final concentration of CO_2 for $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ were $1.59 \times 10^{14} \text{ molecule cm}^{-3}$, $1.18 \times 10^{14} \text{ molecule cm}^{-3}$, and $2.10 \times 10^{14} \text{ molecule cm}^{-3}$, respectively, which was the same as the initial concentration of each ether. The production of perfluoroalkylacetyl fluoride was not observed at the initial reaction period. For $n\text{-C}_3\text{F}_7\text{OCH}_3$, perfluoroalkyl acetyl fluoride appeared after a 60% loss of $n\text{-C}_3\text{F}_7\text{OCH}_3$. Concerning $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, perfluoroalkyl acetyl fluoride began to be produced after a 32% loss of $n\text{-C}_5\text{F}_{11}\text{OCH}_3$. The final concentrations of perfluoroalkyl acetyl fluoride for $n\text{-C}_3\text{F}_7\text{OCH}_3$ and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ were $2.16 \times 10^{13} \text{ molecule cm}^{-3}$ and $8.11 \times 10^{13} \text{ molecule cm}^{-3}$, respectively.

For the degradation of $n\text{-C}_3\text{F}_7\text{OCH}_3$, only $\text{C}_2\text{F}_5\text{COF}$ is produced as a perfluoroalkyl acetyl fluoride. The conversion ratio of the perfluoroalkyl group to $\text{C}_2\text{F}_5\text{COF}$ was 11.7%. For $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, the produced perfluoro acetyl fluoride may be $\text{C}_2\text{F}_5\text{COF}$, $\text{C}_3\text{F}_7\text{COF}$, and/or $\text{C}_4\text{F}_9\text{COF}$ as mentioned in the previous section. The actual conversion ratio cannot be calculated, but the conversion ratio would be 15%, if only $\text{C}_2\text{F}_5\text{COF}$ would be produced. Similarly, given that only $\text{C}_4\text{F}_9\text{COF}$ was produced, the ratio would be 30%. Therefore, the conversion ratio is estimated to be in the range of 15–30%.

Figure 7(a),(b) plots the COF_2 and bis(trifluoromethyl)trioxide ($\text{CF}_3\text{OOOCF}_3$) formed, respectively, as a function of the loss of HFEs (ΔHFEs) for the degradation of $\text{C}_2\text{F}_5\text{OCH}_3$ ($1.65 \times 10^{14} \text{ molecule cm}^{-3}$), $n\text{-C}_3\text{F}_7\text{OCH}_3$ ($1.23 \times 10^{14} \text{ molecule cm}^{-3}$), and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$ ($2.16 \times 10^{14} \text{ molecule cm}^{-3}$) under the same conditions as in Figure 3. The subtracted IR feature ($700\text{--}1400 \text{ cm}^{-1}$) for the reaction gas mixture of $\text{C}_2\text{F}_5\text{OCH}_3$ degraded after 90 min is shown in Figure 8. The absorption of $\text{CF}_3\text{OOOCF}_3$ appeared at 1292, 1252, and 1169 cm^{-1} (14, 15). The concentration of $\text{CF}_3\text{OOOCF}_3$ was calculated by using the absorption coefficient at 1292 cm^{-1} (σ (base e) = $4.1 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$) (16). For the oxidation of three ethers, the formation of COF_2 seems to have the same induction periods. The production of COF_2 occurred after the approximately 50–60% loss of HFEs. The concentration of COF_2 reached a constant value at 1.77×10^{14} , 2.77×10^{14} , and $6.81 \times 10^{14} \text{ molecule cm}^{-3}$ for $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, respectively.

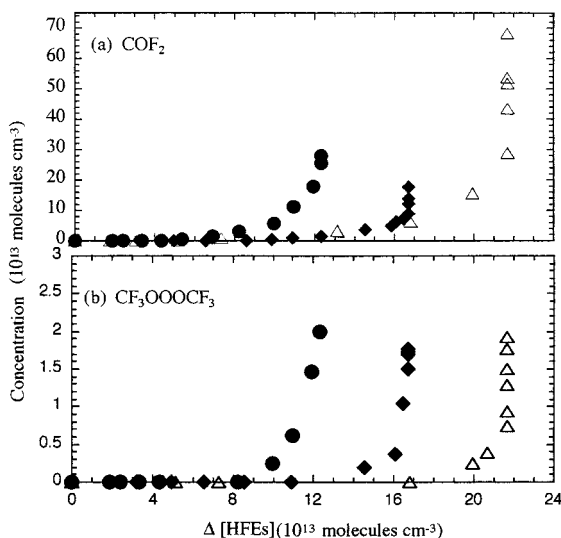


FIGURE 7. The plots of the concentrations of COF_2 (a) and $\text{CF}_3\text{OOOCF}_3$ (b) versus the fractional loss of HFEs (ΔHFEs) obtained from the photolysis of $\text{C}_2\text{F}_5\text{OCH}_3$ ($\blacklozenge$), $\text{C}_3\text{F}_7\text{OCH}_3$ ($\bullet$), and $\text{C}_5\text{F}_{11}\text{OCH}_3$ ($\triangle$). The initial concentrations of $\text{C}_2\text{F}_5\text{OCH}_3$, $\text{C}_3\text{F}_7\text{OCH}_3$, and $\text{C}_5\text{F}_{11}\text{OCH}_3$ are 1.65×10^{14} , 1.23×10^{14} , and 2.16×10^{14} molecule cm^{-3} , respectively.

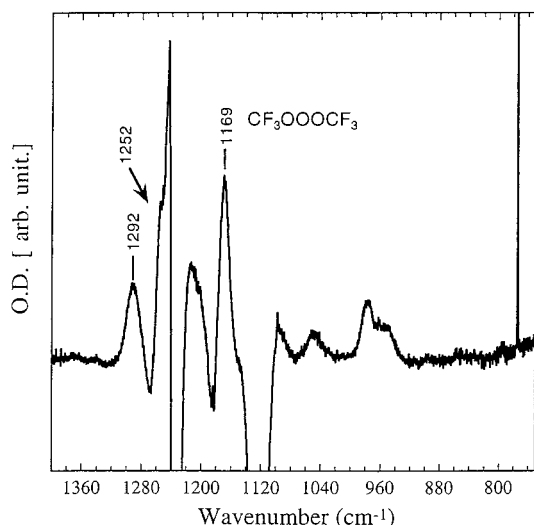


FIGURE 8. The subtracted IR feature ($700\text{--}1400\text{ cm}^{-1}$) of the gas mixture of $\text{C}_2\text{F}_5\text{OCH}_3$ degraded after 60-min irradiation.

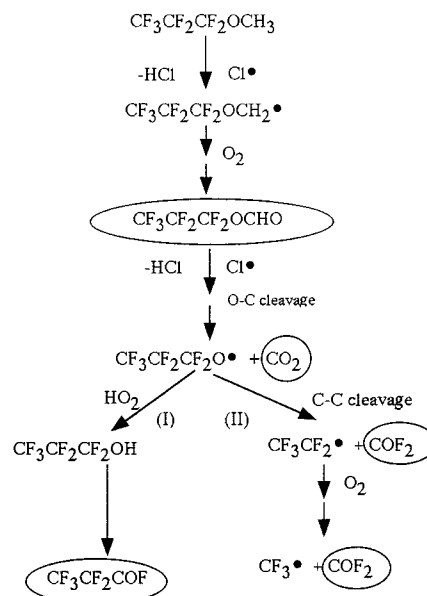
OCH_3 , and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, respectively. On the other hand, the production of $\text{CF}_3\text{OOOCF}_3$ was observed after approximately 90% loss of HFEs. The final concentrations of $\text{CF}_3\text{OOOCF}_3$ were 1.69×10^{13} , 1.99×10^{13} , and 1.92×10^{13} molecule cm^{-3} for $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, respectively. Concerning $\text{C}_2\text{F}_5\text{OCH}_3$, the molar conversion for the carbon of the perfluoroalkyl group to COF_2 was $48 \pm 10\%$, meaning that the $-\text{CF}_2$ group was completely converted to COF_2 , while the $-\text{CF}_3$ group was not oxidized to COF_2 . For the degradation of $n\text{-C}_3\text{F}_7\text{OCH}_3$, the conversion from the perfluoroalkyl group to COF_2 was $76 \pm 10\%$. For the degradation of $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, the conversion from C_5F_{11} to COF_2 was $60 \pm 10\%$. Probably, a part of the CF_3 moiety is transformed into the $\text{CF}_3\text{OOOCF}_3$. The conversion ratios from CF_3 group to $\text{CF}_3\text{OOOCF}_3$ were estimated as 20%, 22%, and 16% for $\text{C}_2\text{F}_5\text{OCH}_3$, $n\text{-C}_3\text{F}_7\text{OCH}_3$, and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$, in that order. The conversion ratios of the perfluoroalkyl group for the ethers to COF_2 , perfluoroalkyl acetyl fluoride, and $\text{CF}_3\text{OOOCF}_3$ after 100% loss of the perfluoroalkyl formates are summarized in Table 3. For $n\text{-C}_3\text{F}_7\text{OCH}_3$ and $n\text{-C}_5\text{F}_{11}\text{OCH}_3$,

TABLE 3. Molar Conversion Ratio of the Perfluoroalkyl Group in the Ethers to the Products

	COF_2 (%)	$\text{C}_n\text{F}_{2n+1}\text{COF}^a$ (%)	$\text{CF}_3\text{OOOCF}_3$ (%)	total conversion
$\text{C}_2\text{F}_5\text{OCH}_3$	48 ± 10	0	20	68 ± 10
$\text{C}_3\text{F}_7\text{OCH}_3$	76 ± 10	12	22	110 ± 10
$\text{C}_5\text{F}_{11}\text{OCH}_3$	60 ± 10	15–30	16	$91 \pm 10\text{--}106 \pm 10$

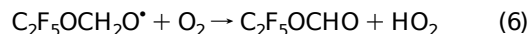
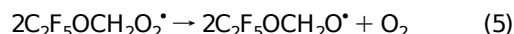
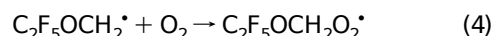
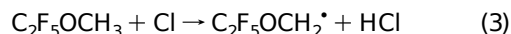
^a CF_3COF for $\text{C}_2\text{F}_5\text{OCH}_3$, $\text{C}_2\text{F}_5\text{COF}$ for $\text{C}_3\text{F}_7\text{OCH}_3$, $\text{C}_n\text{F}_{2n+1}\text{COF}$ ($n = 2, 3$, and/or 4) for $\text{C}_5\text{F}_{11}\text{OCH}_3$.

SCHEME 1



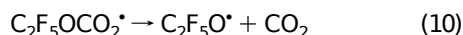
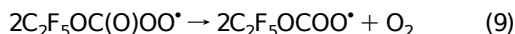
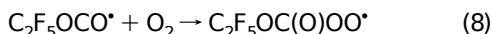
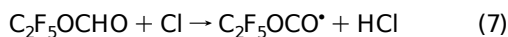
the mass balance of the degradation of the perfluoroalkyl group is about 100%. Scheme 1 of the Cl -initiated reaction of the methyl perfluoroalkyl ether ($n\text{-CF}_3\text{CF}_2\text{CF}_2\text{OCH}_3$) is estimated from the identified degradation products. The perfluoroalkyl ether is completely converted to perfluoroalkyl formate ($n\text{-CF}_3\text{CF}_2\text{CF}_2\text{OCHO}$). The $\text{O}\text{--}\text{C}$ bond cleavage of perfluoroalkyl formate takes place to produce the CO_2 and perfluoroalkoxy radical ($\text{CF}_3\text{CF}_2\text{CF}_2\text{O}^\bullet$). The degradation of perfluoroalkoxy radical proceeds through the two different pathways to mainly produce the COF_2 and has the minor production of the perfluoroacetyl fluoride ($\text{CF}_3\text{CF}_2\text{COF}$).

Degradation Mechanism of the Methyl Perfluoroalkyl Ethers. The initial stages of oxidation are considered as follows: H -abstraction with a Cl atom from the methyl group occurs to produce the alkyl radical (17), and, then, the alkoxy radical is formed via O_2 addition and radical–radical reactions 3–5. Actually, the detection of $\text{C}_4\text{F}_9\text{OCH}_2^\bullet$ and $\text{C}_4\text{F}_9\text{OCH}_2\text{O}_2^\bullet$ radicals for the degradation of HFE-7100 ($\text{C}_4\text{F}_9\text{OCH}_3$) was reported (7).

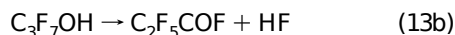
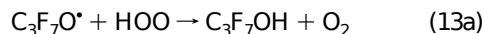
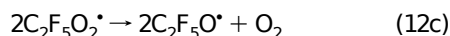
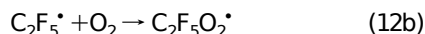


Hydrogen of $\text{C}_2\text{F}_5\text{OCH}_2\text{O}^\bullet$ is abstracted by O_2 to produce pentafluoroethyl formate ($\text{C}_2\text{F}_5\text{OCHO}$) as reaction 6. Relatively stable $\text{C}_2\text{F}_5\text{OCHO}$ is oxidized through reactions 7–10 to give $\text{C}_2\text{F}_5\text{O}^\bullet$. The $\text{C}\text{--}\text{C}$ cleavage of $\text{C}_2\text{F}_5\text{O}^\bullet$ leads to formation of the CF_3 radical and COF_2 . For $\text{C}_3\text{F}_7\text{OCH}_3$ and $\text{C}_5\text{F}_{11}\text{OCH}_3$,

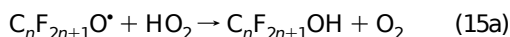
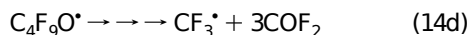
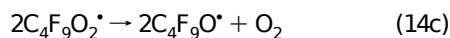
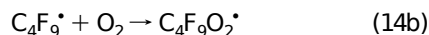
$C_3F_7O^*$, and $C_5F_{11}O^*$ are produced by a route analogous to the degradation processes of $C_2F_5OCH_3$. Subsequently, the cleavage of C–C bond occurs to form $C_2F_5^*$ and $C_4F_9^*$ along with COF_2 . The C–C bond cleavage of $C_2F_5^*$ and $C_4F_9^*$ occurs gradually through such reactions as 12a–d and 14a–d, and the $(n-1)COF_2$ ($n = 3$ and 5) and CF_3^* were produced finally. In another pathway, the perfluoro acetyl fluoride is produced. The possible process of formation of it is that $C_3F_7O^*$ may react with HO_2 (18) to produce C_3F_7OH , which is thermally transformed to C_2F_5COF (19). $C_nF_{2n+1}O^*$ ($n = 5, 4$, and 3) also may react with HO_2 to produce $C_{n-1}F_{2n-1}COF$ ($n = 5, 4$, and 3) as 15a–b. However, the processes of formation of the perfluoroacetyl fluoride have not been revealed. Further discussion of these formation processes will be needed.



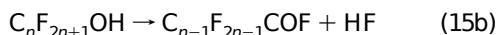
In the case of $C_3F_7OCH_3$



In the case of $C_5F_{11}OCH_3$



($n = 5, 4$, and 3)



CF_3 radicals react with oxygen to produce the CF_3O_2 radicals (20) as shown in reaction 16, and, subsequently, the bimolecular reaction of CF_3O_2 (reaction 17) takes place to produce the CF_3O^* (21–23). The CF_3O radical reacts with CF_3O_2 to produce CF_3OOOCF_3 as shown in reaction 18.

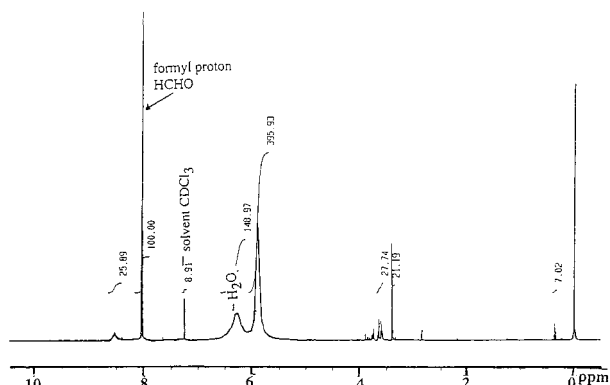
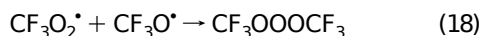
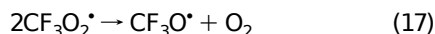
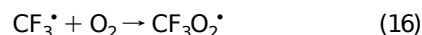


FIGURE 9. 1H NMR spectrum of the photolysis mixture of $C_5F_{11}OCH_3$ (12.3×10^{14} molecule cm^{-3}) and Cl_2 (49.2×10^{14} molecule cm^{-3}) in 1.01×10^5 Pa of air sampled in $CDCl_3$ after 30-min irradiation.

Estimation of Environmental Impacts of the Degradation Products. Formation of various kinds of relatively stable intermediates and degradation products has been confirmed in this study. The Cl-initiated oxidation of three methyl perfluoroalkyl ethers (n - $C_nF_{2n+1}OCH_3$; $n = 2, 3$, and 5) produces the corresponding perfluoroalkyl formates (n - $C_nF_{2n+1}OCHO$; $n = 2, 3$, and 5) as the sole product. This formation process of the perfluoroalkyl formates is insensitive to the difference in the perfluoroalkyl length of the compounds. In general, the reaction rate of organic compounds with Cl atoms is faster than that with OH radicals (12). Therefore, the lifetime of the perfluoroalkyl formates in the troposphere was estimated by assuming the k_2 values in Table 2 as an upper limit of the reaction rate constant of $OH + C_nF_{2n+1}OCHO$. Using the average tropospheric OH concentration of 7.5×10^5 molecules cm^{-3} (7), the corresponding lifetimes were calculated to be longer than 3.5 ± 0.10 , 3.6 ± 0.10 , and 2.4 ± 0.3 years for C_2F_5OCHO , C_3F_7OCHO , and $C_5F_{11}OCHO$, respectively, assuming a temperature of 298 K. Since the lifetimes of the formates seem to be relatively long with respect to reaction with OH radicals, tropospheric removal processes by water droplets such as clouds and/or rain will be important. A reaction gas mixture of n - $C_5F_{11}OCH_3$ (1.23×10^{15} molecules cm^{-3})/ Cl_2 (4.92×10^{15} molecules cm^{-3})/air (1.01×10^5 Pa) which was irradiated for 30 min was taken by a stainless steel cylinder cooled at 203 K. The collected sample was transferred to $CDCl_3$ solution in a NMR sample tube and was analyzed by a 1H and ^{19}F -NMR spectrometer. The spectrum of 1H NMR shows that water is present in the sample (see Figure 9). In the 1H NMR spectrum, the peak of the formyl proton appeared at 8.03 ppm. The peak at 119 ppm in ^{19}F NMR was assigned as F atom of $-CF_2COOH$. It is thus implied that the $C_5F_{11}OCHO$ produced in the gas-phase reaction is hydrolyzed to $CF_3(CF_2)_4OH$ and formic acid in the water which contained HCl in the steel cylinder. No NMR peaks which could be assigned to $CF_3(CF_2)_4OH$ were observed. $CF_3(CF_2)_4OH$, which is unstable (23), may be readily converted to $CF_3(CF_2)_3COF$, which may be further hydrolyzed to produce a perfluoro carboxylic acid. Further studies on an uptake and a chemical reaction of the perfluoroalkyl formates by water will be desired to estimate their environmental impacts including their GWP values.

The formyl group of perfluoroalkyl formate is oxidized to CO_2 via C–C cleavage in the presence of oxygen. The perfluoroalkyl group mainly reacts with O_2 to produce $R_FCF_2O^*$, followed by C–C bond cleavage to form COF_2 . However, when the carbon number of the perfluoroalkyl group is larger than 2, e.g. n - C_3F_7 - and n - C_5F_{11} -, their corresponding a few perfluoro alkoxy radicals are converted to perfluoroacetyl fluorides. The terminal CF_3 - group is oxidized to produce CF_3OOOCF_3 through the CF_3O^* in the chamber experiment. However, CF_3OOOCF_3 is unlikely to

form in the troposphere because the concentration of the $\text{CF}_3\text{O}^\bullet$ and CF_3O_2 is considered to be very low.

As has been reported, the COF_2 and CF_3COF have the values larger than 0.5 of Hk , where H is the Henry's law constant and k is the hydrolysis rate constant and their tropospheric lifetimes by clouds/rain are estimated less than 30 days (24). For the perfluoroalkyl halides ($\text{C}_n\text{F}_{2n+1}\text{COF}$, $n > 2$), the values of Hk have not been determined but may be similar to those for COF_2 and CF_3COF . It is thus inferred that the perfluoroalkyl halides may not contribute to the global warming, because their short lifetimes will be estimated. However, it is to be noted that the perfluoroalkyl halides will be converted to perfluoroalkyl carboxylic acids and HF, which are suspected to cause ecological impacts.

In summary, we have the potential degradation products of the three ethers in troposphere. All the products except CO_2 are likely to be removed by clouds/rainwater, taking into account the rates of their gas-phase reactions estimated. The products themselves may not cause human health and ecological systems, but more attention should be paid to perfluoroalkyl carboxylic acids and HF.

Acknowledgments

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