3 August 2001

ELSEVIER

Chemical Physics Letters 343 (2001) 296–302

CHEMICAL
PHYSICS
LETTERS

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Atmospheric degradation mechanism of CF_3OCF_2H

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Received 27 January 2001; in final form 5 June 2001

Abstract

Smog chamber/FTIR techniques were used to study the Cl atom initiated oxidation of CF_3OCF_2H in 700 Torr of N_2/O_2 at 295 ± 2 K. Atmospheric oxidation of CF_3OCF_2H proceeds via the formation of CF_3OCF_2 radicals. The atmospheric fate of CF_3OCF_2 radicals is addition of O_2 to give $CF_3OCF_2O_2$ radicals. In the atmosphere $CF_3OCF_2O_2$ radicals are converted via COF_2 and CF_3OH into CO_2 and HF. Relative rate techniques were used to measure $k(\mathrm{Cl} + CF_3OCF_2H) = (2.3 \pm 0.3) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. The results are discussed with respect to the atmospheric degradation and environmental impact of CF_3OCF_2H. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

It is now well established that the release of chlorofluorocarbons (CFCs) into the atmosphere leads to stratospheric ozone loss [1,2]. Hydrofluoroethers (HFEs) are a class of compounds which have been developed to replace CFCs. HFEs do not contain chlorine and do not contribute to stratospheric ozone loss via the well established chlorine based catalytic cycles. CF_3OCF_2H is under consideration for use as a CFC replacement. Prior to its large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact of this compound is needed.

The atmospheric oxidation of CF_3OCF_2H is initiated by reaction with OH radicals:

$$CF_3OCF_2H + OH \rightarrow CF_3OCF_2 + H_2O. \quad (1)$$

From measurements of the kinetics of reaction (1) [3,4] the atmospheric lifetime of CF_3OCF_2H has been estimated to be 165 years. CF_3OCF_2H has a global warming potential which is 14 000 times that of CO_2 [5]. Reaction (1) proceeds via H-atom abstraction to give the CF_3OCF_2 radical. Computational and experimental data suggest that addition of O_2 and decomposition via C–O bond fission are competing atmospheric fates of the CF_3OCF_2 radical [6]:

$$CF_3OCF_2 + O_2 + M \rightarrow CF_3OCF_2O_2 + M, \quad (2)$$

$$CF_3OCF_2 + M \rightarrow CF_3 + COF_2 + M. \quad (3)$$

It is highly unusual for the atmospheric fate of an alkyl radical to be anything other than reaction with O_2. The competition between reactions (2) and (3) deserves further study.

By analogy to other peroxy radicals [7], $CF_3OCF_2O_2$ radicals are expected to react with NO, NO_2, HO_2, and other peroxy radicals in the atmosphere:

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PII: S0009-2614(01)00698-4

$$CF_3OCF_2O_2 + NO \rightarrow CF_3OCF_2O + NO_2, \quad (4)$$

$$CF_3OCF_2O_2 + NO_2 + M \rightarrow CF_3OCF_2O_2NO_2 + M, \quad (5)$$

$$CF_3OCF_2O_2 + HO_2 \rightarrow \text{products}, \quad (6)$$

$$CF_3OCF_2O_2 + R'O_2 \rightarrow \text{products}. \quad (7)$$

We have conducted an experimental study of the atmospheric fate of CF_3OCF_2 and $CF_3OCF_2O_2$ radicals. No evidence for reaction (3) was observed and we conclude that the atmospheric fate of CF_3OCF_2 radicals is addition of O_2 to give $CF_3OCF_2O_2$ radicals. $CF_3OCF_2O_2$ radicals are observed to be converted into COF_2. The results are discussed with respect to the atmospheric chemistry and environmental impact of CF_3OCF_2H.

2. Experimental

With one exception (see Section 3.2) all experiments were performed in a 140 l Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer [8]. The optical path length of the infrared beam was 27 m. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. The oxidation of CF_3OCF_2H was initiated by reaction with Cl atoms in 700 Torr total pressure at 295 ± 2 K:

$$Cl_2 + h\nu \rightarrow 2Cl, \quad (8)$$

$$Cl + CF_3OCF_2H \rightarrow CF_3OCF_2 + HCl, \quad (9)$$

$$CF_3OCF_2 + O_2 + M \rightarrow CF_3OCF_2O_2 + M. \quad (2)$$

The loss of CF_3OCF_2H and the formation of products were monitored by FTIR spectrometry at a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms. Reference spectra were acquired by expanding known volumes of authentic reference compounds into the chamber. All reagents were obtained from commercial sources at purities >99%. In smog chamber experiments, unwanted loss of reactants and products via photolysis, dark chemistry, and wall reactions have to be considered. Control experiments were performed to check for such unwanted losses of CF_3OCF_2H and COF_2 in the chamber; none were observed.

Three sets of experiments were performed. First, relative rate techniques were used to determine the rate constant for the reaction of Cl atoms with CF_3OCF_2H, using CF_3CH_3 and CF_2ClCH_3 as references. Second, the fate of CF_3OCF_2 radical was investigated by irradiating CF_3OCF_2H/Cl_2 mixtures. Third, the products of the Cl atom initiated atmospheric oxidation of CF_3OCF_2H were determined.

3. Results and discussion

3.1. Relative rate studies of the reactions of Cl with CF_3OCF_2H

The kinetics of reaction (9) were measured relative to reaction (10) and (11):

$$CF_3OCF_2H + Cl \rightarrow \text{products}, \quad (9)$$

$$CF_3CH_3 + Cl \rightarrow \text{products}, \quad (10)$$

$$CF_2ClCH_3 + Cl \rightarrow \text{products}. \quad (11)$$

Reaction mixtures consisted of 7.3–8.6 mTorr of CF_3OCF_2H, 0.74–0.90 Torr of Cl_2, and 15 mTorr of CH_3CF_3 or 3.0–4.3 mTorr of CF_2ClCH_3 in 700 Torr of N_2 or air diluent. UV irradiation for 1 h typically led to approximately 30% loss of the reactants. The rate constant k_9 was determined by observing the relative loss rates of CF_3OCF_2H and the reference compounds; results are shown in Fig. 1. Linear least squares analysis gives $k_9/k_{10} = 0.63 \pm 0.004$ and $k_9/k_{11} = 0.056 \pm 0.002$. Using $k_{10} = 3.6 \times 10^{-17}$ [9] and $k_{11} = 3.8 \times 10^{-16}$ (average of [10] and [11]) gives $k_9 = (2.3 \pm 0.01) \times 10^{-17}$ and $k_9 = (2.1 \pm 0.08) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. We estimate that potential systematic errors associated with uncertainties in the reference rate constants could add an additional 10% uncertainty range for k_9. Propagating this additional uncertainty gives $k_9 = (2.3 \pm 0.2) \times 10^{-17}$ and $k_9 = (2.1 \pm 0.2) \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}.

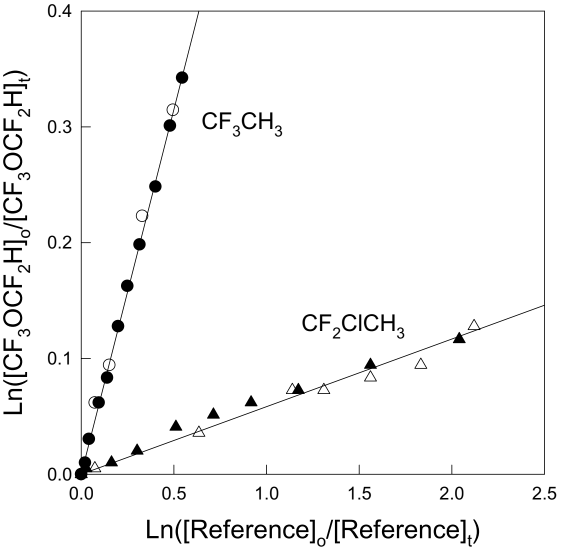

Fig. 1. Decay of CF_3OCF_2H versus CF_2ClCH_3 (triangles) and CF_3CH_3 (circles) in the presence of Cl atoms. Experiments were performed at 295 ± 2 K in 700 Torr of N_2 (open symbols) or air (filled symbols).

We choose to cite a final value of k_9, which is an average of those determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations; hence, $k_9 = (2.2 \pm 0.4) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}.

This result can be compared to $k(\mathrm{Cl} + CF_3OCH_3) = (1.4 \pm 0.2) \times 10^{-13}$ [12] and $k(\mathrm{Cl} + CH_3OCH_3) = (1.9 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} [13]. Fluorination leads to a dramatic decrease in reactivity towards Cl atoms presumably reflecting an increase in C–H bond strength in the fluorinated species. Reported C–H bond dissociation energies from quantum chemical calculations are 95.7 kcal mol^{-1} for CH_3OCH_3, 100.7 kcal mol^{-1} for CF_3OCH_3 and 103.5 kcal mol^{-1} for CF_3OCF_2H [14].

3.2. Atmospheric fate of CF_3OCF_2 radicals

As discussed by Good et al. [6] there are two possible atmospheric fates of CF_3OCF_2 radicals: addition of O_2 and unimolecular decomposition:

$$CF_3OCF_2 + O_2 + M \rightarrow CF_3OCF_2O_2 + M, \quad (2)$$

$$CF_3OCF_2 + M \rightarrow CF_3 + COF_2 + M. \quad (3)$$

In principle there is a straightforward test for the existence of reaction (3). Experiments can be performed using the UV irradiation of $CF_3OCF_2H/Cl_2/He$ in the absence of O_2. Under such conditions the chain chlorination of CF_3OCF_2H should lead to the formation of CF_3OCF_2Cl and, if reaction (3) is important, COF_2 and CF_3Cl:

$$Cl + CF_3OCF_2H \rightarrow CF_3OCF_2 + HCl, \quad (9)$$

$$CF_3OCF_2 + Cl_2 \rightarrow CF_3OCF_2Cl + Cl, \quad (12)$$

$$CF_3OCF_2 + M \rightarrow CF_3 + COF_2 + M, \quad (3)$$

$$CF_3 + Cl_2 \rightarrow CF_3Cl + Cl. \quad (13)$$

The formation of COF_2 in such experiments was one of two pieces of experimental evidence cited by Good et al. [6] for the importance of reaction (3). However, there is a potential problem associated with this approach. Namely, that fluorinated alkyl radical reacts slowly with Cl_2 and rapidly with O_2. For example, in atmosphere pressure at 298 K, $k(CF_3 + Cl_2)/k(CF_3 + O_2) = 0.00929$ [15]. It seems reasonable to assume that CF_3OCF_2 radicals will behave similarly to CF_3 radicals. If so, then the observation of COF_2 following UV irradiation of $CF_3OCF_2H/Cl_2/He$ in the absence of O_2 may reflect the reaction of CF_3OCF_2 radicals with trace amounts of O_2 in the system, rather than the existence of reaction (3). For the experimental conditions employed by Good et al. [6] (1 Torr CF_3OCF_2H, 1–2 Torr of Cl_2 in 100 Torr He) even a small O_2 contamination would lead to CF_3OCF_2 radicals reacting with O_2 (and hence giving COF_2) rather than reacting with Cl_2.

To minimize problems associated with O_2 contamination in the present work we performed experiments using CF_3OCF_2H/Cl_2 mixtures with high concentrations of both CF_3OCF_2H and Cl_2 without added diluent. These experiments were conducted in a 150 cm^3 Pyrex reactor equipped with BaF_2 windows to enable in-situ FTIR analysis. Fig. 2 shows IR spectra obtained before and after a 30 min UV irradiation of a mixture of 1.3 Torr of CF_3OCF_2H and 100 Torr of Cl_2. Panel (C) in Fig. 2 shows the result of subtracting features

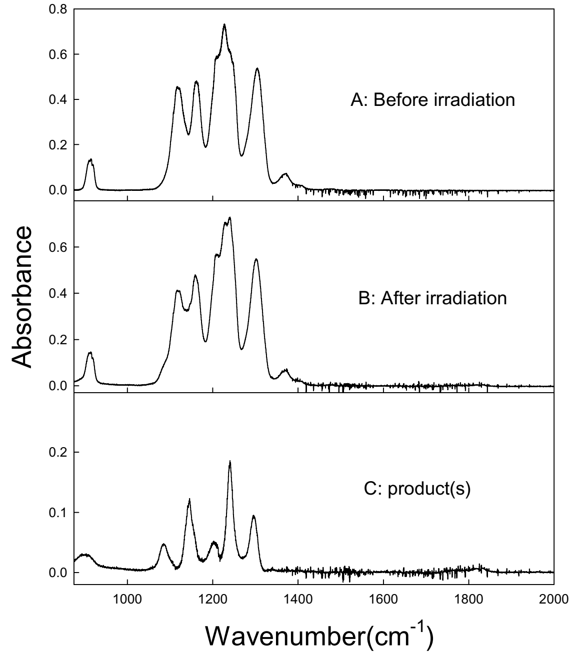

Fig. 2. IR spectra acquired before (A) and after (B) a 30 min irradiation of a mixture of 1.3 Torr of CF_3OCF_2H and 100 Torr Cl_2 using a short cell reactor. Panel (C) shows the result of subtracting features attributable to CF_3OCF_2H from (B).

attributable to CF_3OCF_2H from panel (B). COF_2 has an intense characteristic IR absorption feature at 1950 cm^{-1}. There was no evidence for the formation of COF_2 (<1% yield). The IR product features at 1085, 1146, 1240, and 1296 cm^{-1} in Fig. 2 increased linearly with the consumption of CF_3OCF_2H and are presumably attributable to CF_3OCF_2Cl formed in reaction (12). While the absence of any observable COF_2 product following the UV irradiation of CF_3OCF_2H/Cl_2 mixtures proves that reaction (3) is not important in such systems it does not provide any information concerning the role of reaction (3) in the atmosphere. To provide such information we need to conduct a study of the relative rates of reactions (2) and (3) under atmospheric conditions.

Reaction (3) generates CF_3 radicals. The competition between reactions (13) and (14) is well characterized [15] and can be used to measure the yield of CF_3 radicals and hence the importance of reaction (3) in the presence of O_2:

$$CF_3 + Cl_2 \rightarrow CF_3Cl + Cl, \tag{13}$$

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M. \tag{14}$$

As a preliminary exercise, control experiments were performed using $CF_3I/Cl_2/O_2/N_2$ mixtures to study the fate of CF_3 radicals using the 140 l reactor. Reaction of Cl atoms with CF_3I provides a convenient source of CF_3 radicals.

$$CF_3I + Cl \rightarrow CF_3 + ICl. \tag{15}$$

Reaction mixtures consisted of 16.3 mTorr of CF_3I, 3.7 Torr of Cl_2, and 0.42 Torr O_2 in 700 Torr of N_2. CF_3Cl and COF_2 were the only carbon-containing products observed. COF_2 formation has been proposed to result from reaction of CF_3O_2 radicals with I atoms to give CF_3OOI which then decomposes to give COF_2 and IOF [16]. Iodine atoms will be formed via the rapid reaction of Cl atoms with ICl [17]. The absence of CF_3OOOCF_3 and CF_3OOCF_3 products shows that reactions (16)–(18) are of negligible importance:

$$CF_3O_2 + CF_3O_2 \rightarrow 2CF_3O + O_2. \tag{16}$$

$$CF_3O + CF_3O \rightarrow CF_3OOCF_3. \tag{17}$$

$$CF_3O + CF_3O_2 \rightarrow CF_3OOOCF_3. \tag{18}$$

The observed yields of CF_3Cl (triangles) and COF_2 (circles) are plotted versus the loss of CF_3I in Fig. 3. Linear least-squares analysis gives molar yields of CF_3Cl and COF_2 of $7.5 \pm 0.6\%$ and $91 \pm 5\%$. Within the experimental uncertainties, the combined yield of COF_2 and CF_3Cl accounts for 100% of the loss of CF_3I. The proposed mechanism by which COF_2 is formed during the irradiation of $CF_3I/Cl_2/N_2/O_2$ mixtures can explain our results. The detailed discussion about the mechanism is interesting but beyond the scope of the present work and was not pursued further. The observed CF_3Cl yield can be compared to that expected based upon the following expression.

$$Y_{CF_3Cl} = 1/\{1 + k_{14}[O_2]/(k_{13}[Cl_2])\}. \tag{E1}$$

Using $k_{13}/k_{14} = 0.00929$ [15], $[Cl_2] = 3.7$ Torr, and $[O_2] = 0.42$ Torr the expected CF_3Cl yield is 7.6%. The observed CF_3Cl yield is consistent with

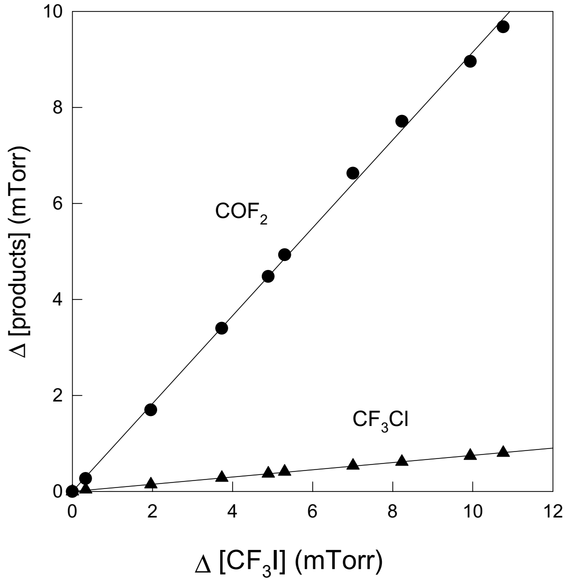

Fig. 3. Formation of COF_2 (circles) and CF_3Cl (triangles) versus loss of CF_3I following the UV irradiation of $CF_3I/Cl_2/O_2$ at 295 ± 2 K in 700 Torr of N_2 diluent.

expectations based upon the literature data for k_{13} and k_{14}.

To investigate the fate of CF_3OCF_2 radicals mixtures consisting of 17.6 mTorr CF_3OCF_2H, 0.41 Torr O_2, 4.2 Torr Cl_2 in 700 Torr N_2 diluent were introduced into the reaction chamber and subjected to UV irradiation. No evidence for the formation of CF_3Cl was observed. After 87 min of irradiation the molar yield of CF_3Cl was less than 2%. If reaction (3) was the sole fate of CF_3OCF_2 radicals we would expect a 9% molar yield of CF_3Cl based on the above equation. There was no evidence for the formation of CF_3OCF_2Cl, indicating that reaction (12) does not compete effectively with reactions (2) and (3) under these experimental conditions and that $k_2/k_{12} > k_{14}/k_{13}$. We conclude that in the presence of 0.41 Torr of O_2, $k_3/(k_3 + k_2[O_2]) < 2/9$ or 0.22 and therefore in one atmosphere of air ($[O_2] = 160$ Torr) $k_3/(k_3 + k_2[O_2]) < 0.0007$. In contrast to the previous findings of Good et al. [6], we find that the sole (>99.93%) atmospheric fate of CF_3OCF_2 radicals is reaction with O_2 to give $CF_3OCF_2O_2$ radicals.

3.3. Products of Cl atom initiated oxidation of CF_3OCF_2H in the presence of O_2

To investigate the products of the Cl atom initiated oxidation of CF_3OCF_2H mixtures containing 7.1–8.1 mTorr CF_3OCF_2H, 2.1–4.4 Torr Cl_2, and 12–147 Torr of O_2 in 700 Torr total pressure of N_2 diluent at 295 ± 2 K were irradiated using the output of the UV fluorescent blacklamps. Fig. 4 shows spectra acquired before (A) and after (B) a 30 min irradiation of a mixture containing 8.14 mTorr CF_3OCF_2H, 4.4 Torr Cl_2, and 12 Torr O_2 in 700 Torr of N_2 diluent. Comparison of panel (B) with the reference spectrum of COF_2 given in panel (C) shows the formation of this product. The observed formation of COF_2 is plotted versus the loss of CF_3OCF_2H in Fig. 5. There was no discernable effect of variation of O_2 partial pressure over the range 12–147 Torr. Linear least squares analysis of the data in Fig. 5 gives a COF_2 yield of 132 ± 15%. This yield is similar to that reported by

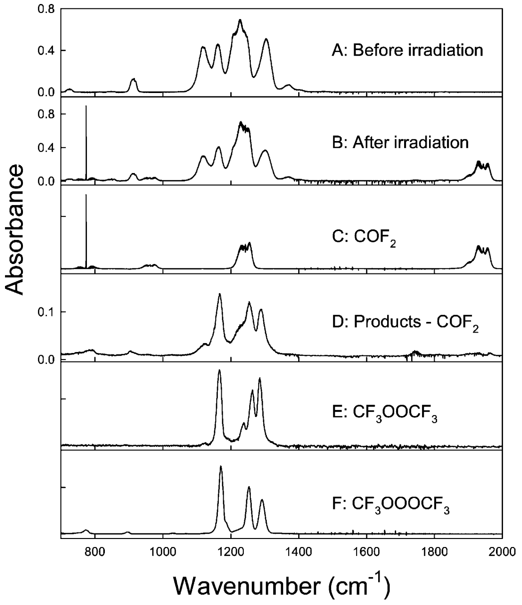

Fig. 4. IR spectra acquired before (A) and after (B) a 30 min irradiation (using 22 fluorescent lamps) of a mixture of 8.1 mTorr of CF_3OCF_2H, 4.4 Torr Cl_2 and 12 Torr O_2 in 700 Torr of N_2. Panel (C) shows a reference spectrum of COF_2. Panel (D) is the result of subtracting features attributable to CF_3OCF_2H and COF_2 from (B). Panels (E) and (F) are reference spectra of CF_3OOCF_3 and CF_3OOOCF_3.

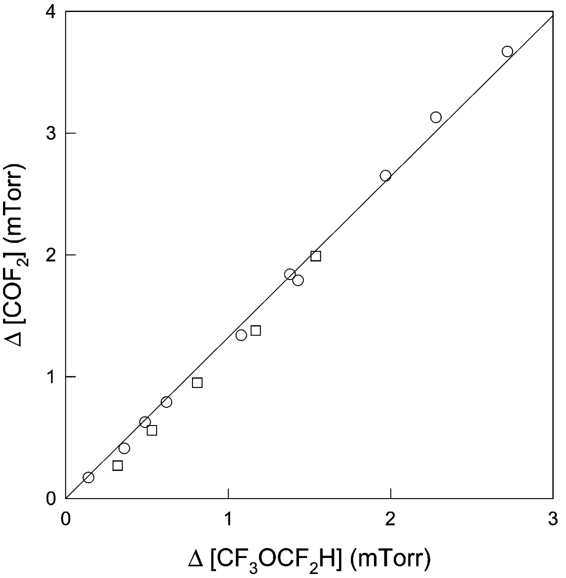

Fig. 5. Formation of COF_2 versus loss of CF_3OCF_2H following irradiation of mixtures of 7.1–8.1 mTorr CF_3OCF_2H, 2.1–4.4 Torr Cl_2 and either 12 Torr (squares), 147 Torr (circles) of O_2 in 700 Torr total pressure of N_2 diluent at 295 ± 2 K.

Good et al. [6] ($152 \pm 13\%$) following irradiation of CF_3OCF_2H/Cl_2 mixtures in a large excess of O_2.

As discussed in the preceding section, the reaction of Cl atoms with CF_3OCF_2H in the presence of O_2 generates $CF_3OCF_2O_2$ radicals. In the present system these $CF_3OCF_2O_2$ radicals will undergo self-reaction and reaction with Cl atoms to generate CF_3OCF_2O radicals. The observation of a substantial yield of COF_2 shows that the fate of CF_3OCF_2O radicals is decomposition via C–O bond scission:

$$CF_3OCF_2O_2 + CF_3OCF_2O_2 \rightarrow CF_3OCF_2O + CF_3OCF_2O + O_2, \quad (19)$$

$$CF_3OCF_2O_2 + Cl \rightarrow CF_3OCF_2O + ClO, \quad (20)$$

$$CF_3OCF_2O \rightarrow CF_3O + COF_2. \quad (21)$$

CF_3O radicals formed in reaction (21) react with hydrogen-containing compounds (for example HCl) in the system to give CF_3OH, which decomposes to give COF_2 and HF. The fact that the observed yield of COF_2 ($132 \pm 15\%$) is significantly less than 200% indicates the existence of other competing process for loss of CF_3O radicals, $CF_3OCF_2O_2$ radicals, or both. Possibilities include reaction (17) and reaction with $CF_3OCF_2O_2$ radicals to give $CF_3OCF_2OOOCF_3$:

$$CF_3O + CF_3OCF_2O_2 \rightarrow CF_3OCF_2OOOCF_3. \quad (22)$$

Subtraction of IR features attributable to CF_3OCF_2H and COF_2 from panel (B) in Fig. 4 gives the residual spectrum shown in panel (D) with prominent features at 1167, 1254, and 1289 cm^{-1}. Comparison of the IR features in panel (D) of Fig. 4 with reference spectra of CF_3OOCF_3 and CF_3OOOCF_3 in panels (E) and (F) shows that the residual features are similar, but not identical, to those of CF_3OOCF_3 and CF_3OOOCF_3. The present IR features in panel (D) cannot be described as a combination of CF_3OOCF_3 and CF_3OOOCF_3 (the molar yield of CF_3OOOCF_3 was <6%). We believe that the residual features in panel (D) are attributable to $CF_3OCF_2OOOCF_3$ formed in reaction (22) with a possible contribution by CF_3OOCF_3 formed in reaction (17). Good et al. [6] observed a residual spectrum with features at 1174, 1257, and 1294 cm^{-1} and assigned this to CF_3OOOCF_3. The identification of CF_3OOOCF_3 was the second of two pieces of experimental evidence which led Good et al. [6] to conclude that CF_3OCF_2 radicals undergo decomposition to give CF_3 radicals (which then can form CF_3OOOCF_3). However, the relative intensities of the features reported by Good et al. [6] do not match those reported for authentic samples of CF_3OOOCF_3 [18–20].

It should be noted that exotic compounds such as $CF_3OCF_2OOOCF_3$ will not be formed in the real atmosphere where the CF_3O and $CF_3OCF_2O_2$ radical concentrations are much lower than in the reaction chamber. The exact identification of the residual product(s) responsible for the spectral features in panel (D) is not relevant in understanding the atmospheric oxidation mechanism of CF_3OCF_2H and was not pursued further. The important point is that the fate of CF_3OCF_2O radicals is decomposition via reaction (21) into CF_3O radicals and COF_2.

4. Implications for atmospheric chemistry

Atmospheric oxidation of CF_3OCF_2H is initiated by reaction with OH radicals to give CF_3OCF_2 radicals. We show herein that the atmospheric fate of CF_3OCF_2 radicals is addition of O_2. By analogy with other peroxy radicals, $CF_3OCF_2O_2$ radicals will react with NO to produce CF_3OCF_2O radicals that decompose to give CF_3O radicals and COF_2. It is well established that CF_3O radicals react with NO and hydrocarbons:

$$CF_3OCF_2O_2 + NO \rightarrow CF_3OCF_2O + NO_2, \quad (23)$$

$$CF_3OCF_2O \rightarrow CF_3O + COF_2, \quad (21)$$

$$CF_3O + NO \rightarrow COF_2 + FNO, \quad (24)$$

$$CF_3O + CH_4 \rightarrow CF_3OH + CH_3. \quad (25)$$

Reaction with NO yields COF_2 while reaction with hydrocarbons such as CH_4 produces CF_3OH. CF_3OH is not attacked by any trace atmospheric radical [21] and is not photolyzed [22,23]. CF_3OH undergoes heterogeneous decomposition on surfaces to give COF_2 and HF and reaction with atmospheric water droplets to give CO_2 and HF [24,25]. COF_2 does not react with any gas phase trace atmospheric species and its photolysis is slow [26]. COF_2 is removed from the atmosphere by incorporation into water droplets and hydrolysis to give CO_2 and HF. The atmospheric oxidation of CF_3OCF_2H gives CO_2 and HF as the ultimate products. At the levels expected in the atmosphere, none of the intermediate or final products pose any environmental threat.

Acknowledgements

We thank the Japanese Government for a NEDO grant that made this collaborative research project possible. M.K. thanks the Ministry of Education for a Grant-in-Aid in Scientific Field.

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