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Kinetics and products formation of the gas-phase reactions of tetrafluoroethylene with OH and NO_3 radicals and ozone

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Abstract

Fourier-transformed infrared spectroscopy (FT-IR) was used to determine the rate constants and products for the reactions of tetrafluoroethylene (C_2F_4) with OH, NO_3 and O_3 at 298 ± 4 K and 740 ± 5 Torr. The rate constants (k) measured were: $k_{CF2CF2+OH} = (1.13 \pm 0.33) \times 10^{-11}$, $k_{CF2CF2+NO3} < 3 \times 10^{-15}$ and $k_{CF2CF2+O3} = (4.80 \pm 0.62) \times 10^{-21}$ (in cm^3 molecule^{-1} s^{-1} and all values are with 2σ overall uncertainties). CF_2O was the only oxidation end-product identified from the above reactions. The results obtained indicate a chemical lifetime of tetrafluoroethylene of about 1 day in the troposphere. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The kinetics of saturated perfluoro compounds like CF_4, C_2F_6 and SF_6 have been investigated and it is well understood that they are very stable with atmospheric lifetimes of more than 3000 years [1]. Only very limited kinetic information is available about unsaturated perfluoro compounds, like C_2F_4, and their atmospheric lifetimes are not known. In this investigation, we have determined the rate coefficients and the products for the reactions of C_2F_4 with the radicals OH and NO_3 and with O_3 in order to estimate the chemical lifetime and the fate of this compound in the atmosphere.

For unsaturated perfluoro compounds like C_2F_4, global annual production has been estimated to be around 50×10^9 g year^{-1} in 1998 [2], but the amount emitted into the atmosphere is unknown. This could be compared, for example, with the global annual production and emissions of saturated perfluoro compounds like CF_4, C_2F_6 and SF_6, which have been estimated to be about 27×10^9, 27×10^9 and 5×10^9 g year^{-1}, respectively, by the end of the 1980s and the early 1990s (assuming that all is emitted to the atmosphere) [3,4].

Three previous studies dealing with the gas-phase degradation of C_2F_4 have been published: Heicklen [5] used infrared spectroscopy to study the gas-phase reaction between C_2F_4 and O_3 at room temperature and at 1–24 Torr total pressure. He measured the rate constant for the reaction between C_2F_4 and O_3 to be 4.98×10^{-19} cm^3 molecule^{-1} s^{-1} and he found carbonyl fluoride, CF_2O, as the only product. Toby and Toby [6] also studied the gas-phase reaction between C_2F_4 and O_3 in the temperature range from 273 to 383 K and in the pressure range from 0.3 to

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15 Torr by using gas chromatography. They obtained a value of 2.84×10^{-20} cm^3 molecule^{-1} s^{-1} for the rate constant of this reaction. Because of the above discrepancy, we decided to investigate this reaction. Gozzo and Camaggi [7] used gas chromatography to study the products of the reaction between C_2F_4 and ozone at 273 K and at 1 atm. They observed CF_2O and tetrafluoroethylene epoxide, CF_2CF_2O, as products. To our knowledge, kinetics or products of the reactions of C_2F_4 with OH and NO_3 have not been determined.

2. Experimental

All the experiments were performed in purified air at 740 ± 5 Torr total pressure and at 298 ± 4 K in a 480 l Teflon-coated reaction chamber. The chamber is surrounded by UV/VIS lamps (black lamps, $\lambda \geqslant 300$ nm) and equipped with a multiple reflection mirror system for on-line Fourier transform infrared spectroscopy (FT-IR) with a total optical pathlength of 81.23 m. A detailed description of the experimental system has been published previously [8]. The spectra were obtained with a Bruker IFS 113v at a nominal resolution of 1 cm^{-1} by co-adding 20–50 scans.

Hydroxyl radicals were generated from in-situ photolysis of methylnitrite (CH_3ONO) in the presence of NO by using UV/VIS lamps ($\lambda \geqslant 300$ nm). NO_3 radicals were produced by mixing O_3 with an excess of NO_2, to establish equilibrium between NO_3, NO_2 and N_2O_5. Ozone was prepared by silent discharge of pure oxygen. CH_3ONO was synthesized by adding H_2SO_4 (50 wt% aqueous solution) to sodium nitrite dissolved in a methanol/water mixture as described in detail elsewhere [9].

Table 1
Rate constants k determined in this and other investigations at room temperature. All k values from this investigation are given in units of cm^3 molecule^{-1} s^{-1} and with 2σ overall uncertainty

Compound	CF_2CF_2	Reference
OH	$1.13 \pm 0.33 \times 10^{-11}$ [a]	This work.
NO_3	$< 3 \times 10^{-15}$ [b]	This work.
O_3	$4.80 \pm 0.62 \times 10^{-21}$ [c]	This work.
O_3	4.98×10^{-19}	Heicklen [5]
O_3	2.84×10^{-20}	Toby and Toby [6]

[a] Measured relative to propene and cyclohexane using $k_{\mathrm{OH+propene}} = (3.0 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, where a rate constant ratio of (0.375 ± 0.118) was found, and $k_{\mathrm{OH+cyclohexane}} = (7.2 \pm 1.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [11,12], where a rate constant ratio of (1.566 ± 0.226) was found.

[b] Measured relative to propene using $k_{\mathrm{NO3+C3H6}} = (9.4 \pm 5.5) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} [13].

[c] Determined by pseudo-first-order method.

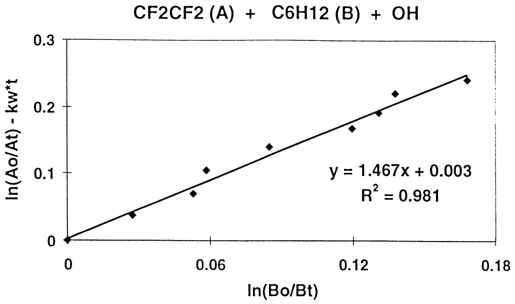

Fig. 1. Plot of $\ln\{[CF_2CF_2]_0/[CF_2CF_2]_t\}$ corrected for wall losses and photolysis versus $\ln[\text{cyclohexane}]_0/[\{[\text{cyclohexane}]_t\}$ for the decay of CF_2CF_2 and cyclohexane during the photolysis of methylnitrite producing OH radicals. k_w = losses on the wall and/or photolysis.

The OH and NO_3 reaction rate constants were determined with the ‘relative rate’ method and the O_3 reaction rate constant was measured under ‘pseudo-first-order’ conditions on C_2F_4. Both methods have been previously described in detail [10]. Reference compounds used in the ‘relative rate’ method were propene and cyclohexane. The reference compounds used for each reaction are listed in the footnote of Table 1. By the ‘relative rate’ method, the ratio of the rate constants k_A/k_B is found as the slope of a plot of $\ln(A_0/A_t) - k_w t$ versus $\ln(B_0/B_t) - k_w t$, where A_0 and B_0 are the initial concentrations, A_t and B_t are the concentrations at time t and $k_w t$ is an additional first-order loss process, if any additional loss process is present, described by the rate constant k_w for A and B, respectively (see, e.g., Fig. 1). The pseudo-first-order method has also been described elsewhere [10]. Loss of C_2F_4 in an excess of O_3 was measured to obtain a pseudo-first-order decay $k' (= k[O_3])$ from the plot of $\ln[CF_2CF_2]_t$ versus time t. A plot of measured k' values versus $[O_3]$ yielded the rate constant k as the slope (see, e.g., Fig. 3). It should be mentioned that for the O_3 reaction a large amount of cyclohexane (50–90 ppmV) was added to scavenge OH radicals and other radicals that may be formed by secondary chemistry (1 ppmV $= 2.46 \times 10^{13}$ molecules cm^{-3} at 298 K and 760 Torr).

In purified air, CF_2CF_2 showed a first-order decay in our reaction chamber with the UV/VIS lamps turned on ($\lambda \geqslant 300$ nm), but without the presence of CH_3ONO; this additional loss process was attributed to wall loss and losses due to photolytical generation of radicals with $k_w = (4.7 \pm 0.3) \times 10^{-6}$ s^{-1}. In the case of loss rate coefficients for the reference compound propene, a value of $k_w = (1.1 \pm 0.2) \times 10^{-5}$ s^{-1} was obtained. The reference compound cyclohexane did not show any loss process, and a value of $< 2 \times 10^{-6}$ s^{-1} were assumed for k_w, which means that no data adjustment is needed for this compound. Without lamps on, none of the compounds showed any significant loss and a value $< 2 \times 10^{-6}$ s^{-1} were assumed for k_w, which again means that no data adjustment is needed for the compounds in this investigation. It should be mentioned that these additional losses are relatively small, because duration of an experiment is normally between 10 and 60 min. The additional loss process (wall loss + photolysis) was always below 10% of the overall decay coefficients during an experiment for all of the experiments performed in this investigation.

The following IR bands were used for spectral subtraction: 1163–1201 and 1265–1370 cm^{-1} for CF_2CF_2, 907–915 cm^{-1} for propene and 2840–2895 cm^{-1} for cyclohexane.

Typical initial experimental conditions: 2 ppmV $< [C_2F_4] <$ 4 ppmV, 8 ppmV $<$ [reference compound] $<$ 50 ppmV, 10 ppmV $< [CH_3ONO] <$ 30 ppmV, 8 ppmV $<$ [NO] $<$ 15 ppmV, 10 ppmV $< [N_2O_5] <$ 100 ppmV and 25 ppmV $< [O_3] <$ 600 ppmV.

CF_2CF_2 was calibrated by the normal monometric method.

The value of the OH reaction rate constant and its uncertainty were obtained as follows. First, rate constants and σ values were obtained from four individual experiments for each of the reference compounds, then the uncertainty of the rate constant of the reference compound were incorporated by using standard propagation of error, i.e., $(a^2 + b^2)^{0.5}$. Two reference compounds were used, so the value of the rate constant was calculated as the mean of the two values weighted by their standard deviations. The uncertainty is given as 2σ, where σ is the weighted average of the standard deviation obtained in the two series of experiments. The uncertainty of the O_3 rate constant was obtained by taking to 2σ of the slope shown in Fig. 3.

The compounds used in this investigation had the following purity: CF_2CF_2 ($>$ 99.9% pure, Ausimont), propene (Ucar, $>$ 99.5% pure), cyclohexane (99.5% pure, Carlo Erba), (99.9% pure, Ucar, CF_2O (97% pure, Matheson), synthetic air (80% N_2 and 20% O_2: $\geqslant$ 99.95% pure, SIO) and O_2 ($\geqslant$ 99.9% pure, SIO).

3. Results and discussion

The reactions of CF_2CF_2 with the radicals OH and NO_3, and with O_3 have been investigated and the results from the kinetics study are summarised in Table 1.

The reaction between CF_2CF_2 and the OH radical:

$$CF_2CF_2 + OH \rightarrow \text{products} \tag{1}$$

Fig. 1 shows the relative loss rates of CF_2CF_2 and cyclohexane in the presence of OH radicals. As shown in Table 1, a value of $k_1 = (1.13 \pm 0.33) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was determined. To our knowledge, this rate constant has not been determined before, but one can compare it to the rate coefficients of the reactions of CH_2CH_2, CH_2CF_2 and CCl_2CCl_2 with the OH radical: $k_{\mathrm{CH2CH2+OH}} = (9.0 \pm 4.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [11], $k_{\mathrm{CH2CF2+OH}} = (4.0 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [13] and $k_{\mathrm{CCl2CCl2+OH}} = (1.7 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [14]. As can be seen, our value is similar to the ethene and CH_2CF_2 reactions but very different from the CCl_2CCl_2 reaction. For reaction 1, carbonyl fluoride was the only end-product identified with a product yield of 40–45% (carbon in product compared to the reacted carbon). Spectral features at 793, 1302 and 1718 cm^{-1} were observed in the product spectrum indicating the presence of a peroxynitrate compounds [15]. We have tentatively attributed these bands to the compound CF_2-(OH)$CF_2O_2NO_2$. This peroxynitrate compound is not commercial available and therefore we do not know how much of this compound is produced by the reaction between C_2F_4 and the OH radical, but some of the missing carbon in the carbon balance is within that product.

Fig. 2 shows the loss rates of CF_2CF_2 due to its reaction with NO_3,

$$CF_2CF_2 + NO_3 \rightarrow \text{products} \qquad (2)$$

relative to that for propene in the presence of NO_3 radicals. As shown in Table 1, a value of $k_2 < 3 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} was determined. Due to the relatively large random error on the individual experiments and due to the large uncertainty for the rate constant for the reference compound, we prefer to present here the value as an upper limit. To our knowledge, this parameter has not been determined before, but it can be compared with the rate coefficient for reactions of CH_2CH_2 with the NO_3 radicals: $k_{CH2CH2+NO3} = (2.09 \pm 0.40) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} [11]. As can be seen, both of these reactions are relatively slow. For reaction 2, carbonyl fluoride, CF_2O, was the only identified product and it had a yield of 55-80% (also here on a carbon basis). In contrast to reaction 1, no spectral features for either peroxynitrates or nitrates were observed in the product spectrum, possibly indicating that $CF_2(ONO_2)CF_2O_2NO_2$ is very unstable.

This rate constant, k_3, for the reaction between CF_2CF_2 and O_3:

$$CF_2CF_2 + O_3 \rightarrow \text{products} \qquad (3)$$

was determined using first-order conditions and a plot of k' versus $[O_3]$ can be found in Fig. 3. As can be seen in Table 1, a value of $k_3 = (4.80 \pm 0.62) \times 10^{-21}$ cm^3 $molecule^{-1}$ s^{-1} was determined. This value is significantly lower than the other values available in the literature, as shown in see Table 1. It should be mentioned, that when we performed our experiment in absence of cyclohexane (added to scavenge OH and other radicals), we obtained a value about a factor of 10 larger, indicating that secondary chemistry may have contributed to the loss of C_2F_4 reported in two previous investigations. CF_2O was determined as the only identified oxidation end-product and it had a product yield of 92–98% (again on a carbon basis). Our yield of CF_2O agrees with those reported previously [5,7].

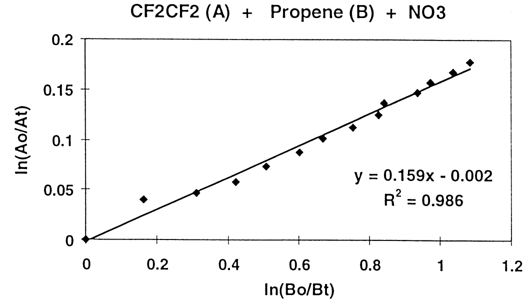

Fig. 2. Plot of $\ln\{[CF_2CF_2]_0/[CF_2CF_2]_t\}$ versus $\ln\{[propene]_0/[\{[propene]_t\}$ for the decay of CF_2CF_2 and propene during the reaction with NO_3 radicals.

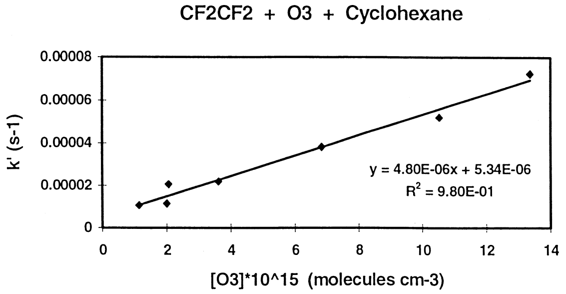

Fig. 3. Plot of k' versus $[O_3]$ for the reaction between CF_2CF_2 and O_3 in the presence of cyclohexane.

4. Atmospheric implications

Table 2 shows a rough estimate of the tropospheric chemical lifetime of CF_2CF_2 with respect to reactions with OH, NO_3 and ozone. As can be seen a very short atmospheric lifetime of about 1 day for CF_2CF_2 could be estimated with respect to its reaction with the OH radical. Therefore the lifetime will strongly depend on local and seasonal conditions, but it does indicate a negligible global warming potential (GWP) from this compound compared to GWP for

Table 2
Estimate of the tropospheric chemical lifetime τ of tetrafluoroethylene with respect to the reaction with OH, NO_3 and ozone

Compound	OH [a]	NO_3 [b]	O_3 [c]
C_2F_4	1 day	> 156 days	9 years

[a] Assuming an [OH] of 1×10^6 molecules cm^{-3} [16].
[b] NO_3 is assumed to be 2.5×10^7 molecules cm^{-3} (1 pptV) [17,18].
[c] The concentration given for O_3 is a 24-h average [19].

CFC-11, which has been estimated to have an overall atmospheric lifetime of about 50 years [20]. Compared to atmospheric lifetimes of saturated perfluoro compounds like CF_4, CF_3CF_3 and SF_6, which have been estimated to be more than 3000 years [1], the lifetime of C_2F_4 of about 1 day is negligibly small.

The main atmospheric degradation product from CF_2CF_2 has been identified in this investigation to be CF_2O, which is rapidly (within a few days) incorporated into raindrops/aerosols [21] and eventually converted to HF and CO_2 [22].

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