Rate Constants for Reactions of $O(^1D)$ with Partially Fluorinated Ethers, E143A (CH_3OCF_3), E134 (CHF_2OCHF_2), and E125 (CHF_2OCF_3)

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The rate constants for the reaction of $O(^1D)$ with CH_3OCF_3 (E143a), CHF_2OCHF_2 (E134), and CHF_2OCF_3 (E125) have been measured at 298 K using the relative rate method relative to CH_4, CH_3F, and CH_2F_2. The results are discussed with respect to previous literature data. For E143a, E134, and E125 the 298 K rate constants have been determined to be $(1.0 \pm 0.3) \times 10^{-10}$, $(2.4 \pm 0.7) \times 10^{-11}$ and $(1.5 \pm 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, respectively. We find that reaction with $O(^1D)$ may be a significant loss mechanism for E125 and E134 in the atmosphere.

I. Introduction

Fluorinated ethers, such as E143a (CH_3OCF_3), E134 (CHF_2OCHF_2), and E125 (CHF_2OCF_3), are one class of compounds that has received attention as possible third generation alternative chlorofluorocarbons (CFCs). An important issue to address is the atmospheric fate of these species. Generally, three main pathways lead to the destruction of organic molecules in the atmosphere, reaction with OH radicals, UV photolysis, and reaction with $O(^1D)$. Recent work has shown that the more highly fluorinated ethers, such as E125, are slow to react with tropospheric hydroxyl radical.[1−3] A consequence of this slow reaction rate is a long atmospheric lifetime and the possible infiltration of these ethers into the stratosphere. In the case of most nonchlorinated hydrocarbons, UV photolysis does not play a significant role since these molecules do not absorb at wavelengths greater than 145 nm.[4,5] In the stratosphere, reactions of electronically excited oxygen atoms, $O(^1D)$, play an important role in establishing the chemical composition.[6,7] The interaction between $O(^1D)$ and atmospheric organics can lead to the chemical removal of the reactant or result in quenching the $O(^1D)$ to $O(^3P)$, leaving the reactant intact.

$$O(^1D) + \text{reactant} \rightarrow \text{products} \tag{1}$$

$$O(^1D) + \text{reactant} \rightarrow O(^3P) + \text{reactant} \tag{2}$$

Reaction 1 is a chemical reaction resulting in loss of the reactant, while reaction 2 is referred to as a quenching process. In the atmosphere, the quantity of interest is the rate of removal of the atmospheric organic rather than the removal of $O(^1D)$. In most cases, chemical reaction is found to dominate physical quenching, except for molecules such as CF_4 and CHF_3.

To correctly model the effects fluorinated ethers have on the atmosphere, it is necessary to know the rate of reaction between $O(^1D)$ and each ether. $O(^1D)$ reactions are typically very fast and do not exhibit significant temperature dependence.[8] The aim of this work is to determine the 298 K rate constant for reaction of $O(^1D)$ with E143a, E134, and E125.

II. Experimental Methods

The experiment consists of a Matteson Instruments Galaxy Series FTIR spectrometer operating at 1.0 cm^{-1} resolution in which 64 scans are coadded. The spectrometer is interfaced to a 512 cm^3 Teflon reaction vessel. Perpendicular to the infrared probe axis is a Lambda Physik Compex 102, using ArF to generate 60 mJ of 193 nm radiation at 10 Hz; 193 nm radiation and nitrous oxide were used to produce electronically excited oxygen atoms, as shown in reaction 3.

$$N_2O + h\nu = 193\ \text{nm} \rightarrow N_2 + O(^1D) \tag{3}$$

Reaction mixtures as monitored by their pressures using MKS capacitance manometers were introduced into the chamber and allowed to equilibrate for ca. 1 h. Typical concentrations include 1 Torr of both the ether and a reference gas along with 5 Torr of N_2O. After photolysis initiation, the reaction was monitored by following the selected nonoverlapping absorption features of the ether and reference gases. In the presence of oxygen atoms the ether and reference species decay via reactions 4 and 5.

$$\text{reference} + O(^1D) \rightarrow \text{products} \tag{4}$$

$$\text{ether} + O(^1D) \rightarrow \text{products} \tag{5}$$

Providing that both ether and reference organics decay only by reactions 4 and 5, it can be shown that

$$\ln\left(\frac{\text{reference}_{to}}{\text{reference}_t}\right) = \frac{k_4}{k_5}\ln\left(\frac{\text{ether}_{to}}{\text{ether}_t}\right) \tag{6}$$

where k_4 and k_5 are the rate constants of reactions 4 and 5, respectively. Prior to the addition of N_2O, it was demonstrated that neither the ethers nor the reference species photolyze at 193 nm to any appreciable extent. Three different reference gases were used, CH_4, CH_3F, and CH_2F_2. Ultrahigh purity methane (99.97%) is obtained from Matheson Gas Products. Nitrous oxide and difluoromethane are obtained from Aldrich Chemical Co., with a manufacturer's stated purity of 99.0 and 99.7%, respectively. Fluoromethane (98.0%) is obtained from Lancaster, while E134 (1,1,2,2-tetrafluorodimethyl ether, 97.0%) is obtained from Oakwood Products. E125 and E143a were obtained from DuPont Inc.; no impurities were detected using GC/MS. All reagents were used without further purification.

III. Results and Discussion

To test the methodology, all three combinations of reference gases CH_4, CH_3F, and CH_2F_2 were measured using the relative rate technique. CH_3F and CH_2F_2 were reacted simultaneously

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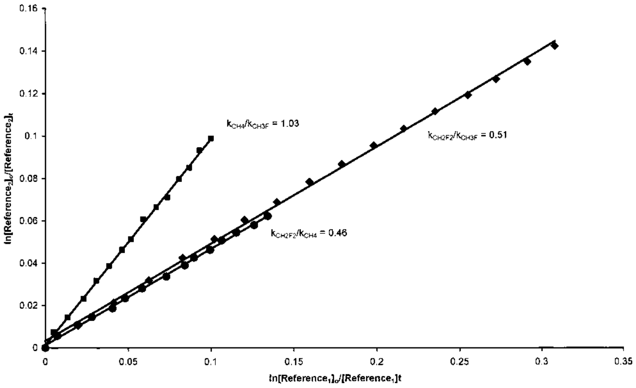

Figure 1. Relative rate for reference species in the presence of O(^{1}D).

in the presence of O(^{1}D), and their relative rates were measured. The results are illustrated in Figure 1. A relative rate of $k_{CH_2F_2}/k_{CH_3F} = 0.51 \pm 0.03$ is measured. CH_4 and CH_2F_2 were also reacted simultaneously in the presence of O(^{1}D). A relative rate of $k_{CH_2F_2}/k_{CH_4} = 0.46 \pm 0.01$ is measured. The previous two measurements can be used to infer the relative rate of $k_{CH_4}/k_{CH_3F} = 0.51/0.46 = 1.11 \pm 0.03$. Our experimentally determined value is found to be $k_{CH_4}/k_{CH_3F} = 1.03 \pm 0.07$. A deviation on the order of 7.0% exists.

The 1997 JPL publication *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*,[9] recommends the reaction between CH_4 and O(^{1}D) to be $(1.5 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This value includes both the rate of chemical reaction and the rate of physical quenching.[9] Matsumi reports the O(^{3}P) yield to be <5%,[10] Wine and Ravishankara report the O(^{3}P) yield to be <4.3%,[11] and Takashi et al. report the O(^{3}P) yield to be less than 1%.[12] The JPL publication recommends the O(^{3}P) yield as 5 ± 5%. The root sum of squares of the relative errors in the measured rate constant and quenching fraction yield a chemical reaction of $(1.43 \pm 0.29) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. This is the rate of chemical reaction between CH_4 and O(^{1}D) that will be used throughout this work.

For CH_3F, the rate constant is recommended to be 1.5×10^{-10} cm^3 molecule^{-1} s^{-1} by the JPL publication.[9] The recommendation is based on the work of Force and Wiesenfeld et al.[6] and Schmoltner et al.[4] and is the total of both chemical reaction and physical quenching. Force and Wiesenfeld found the O(^{3}P) yield to be 25 ± 3%. Schmoltner found the O(^{3}P) yield to be 11 ± 5%, and Takahashi reports a yield of 19 ± 5%.[4,12] Thus, the rate of chemical reaction between CH_3F and O(^{1}D) ranges from 1.1×10^{-10} to 1.3×10^{-10} cm^3 molecule^{-1} s^{-1}. Atkinson et al. recommends a value of 1.42×10^{-10} cm^3 molecule^{-1} s^{-1}.[13] The weighted mean and weighted deviation were computed using the following equations:

$$\mathrm{av} = \frac{\sum_{i=1}^{n} \frac{x_i}{(s_i)^2}}{\sum_{i=1}^{n} \frac{1}{(s_i)^2}} \qquad \mathrm{std\ dev} = \left[\sum_{i=1}^{n} \frac{1}{(s_i)^2}\right]^{-1/2} \tag{7}$$

where x_i and s_i are the individual measurements and deviations, respectively. The analysis yields a value of $(1.19 \pm 0.27) \times 10^{-1}$ cm^3 molecule^{-1} s^{-1}, which will be used for the reaction between CH_3F and O(^{1}D).

TABLE 1: Relative Rates of Reference Compounds to Ethers, Expressed as k_4/k_5[a]

ref	CH_3OCF_3	CHF_2OCHF_2	CHF_2OCF_3
CH_4	1.4 ± 0.1	5.9 ± 0.2	9.5 ± 0.3
CH_3F	1.09 ± 0.01	5.3 ± 0.6	7.7 ± 0.4
CH_2F_2	0.51 ± 0.02	1.7 ± 0.2	3.0 ± 0.2

[a] All values at 298 K.

The probabilities that these measurements would have been obtained by these trials, based on χ^2, were over 90% in each case. The reported uncertainty on this and subsequent values represents one standard deviation from the average. From these experimental rate constants, the ratio k_{CH_4}/k_{CH_3F} is found to vary between 1.00 and 1.30, having an average value of 1.13. Our experimentally determined values are within this range. The indirectly determined value of $k_{CH_4}/k_{CH_3F} = 1.11 \pm 0.03$ agrees well with the average literature value, while the direct determination of $k_{CH_4}/k_{CH_3F} = 1.03 \pm 0.07$ is roughly 9% lower than the average literature value. One possible explanation for this is interference from the OH radical. The reaction between O(^{1}D) and one of the reference species is expected to produce OH radical, which can further react with the reference species. CH_4 is reported to have a reaction rate of 6.3×10^{-15} cm^3 molecule^{-1} s^{-1}, while CH_3F reacts 3 times faster with a rate of 2.0×10^{-14} cm^3 molecules^{-1} s^{-1}.[9] Because CH_3F reacts faster with OH than does CH_4, the relative decay of CH_4/CH_3F would appear too low and the relative rate, k_{CH_4}/k_{CH_3F}, would, as a result, be low. This effect is small, as our determinations are in reasonable agreement with the literature values. In addition, further reaction of OH radicals with either the reference or ether species would result in the production of water, which absorbs very strongly in the infrared. In our investigations, no evidence for the formation of water was detected.

For CH_2F_2 the recommended reaction rate with O(^{1}D) is 5.1×10^{-11} cm^3 molecule^{-1} s^{-1} based on the work of Schmoltner et al., who found the O(^{3}P) yield to be 70 ± 11%.[4] The rate of chemical reaction is then inferred to be 1.5×10^{-11} cm^3 molecule^{-1} s^{-1}. Green and Wayne also measured the loss of CH_2F_2 relative to the loss of N_2O, and a relative rate of 0.4 ± 0.2 was determined.[14] The total rate of reaction of N_2O with O(^{1}D) is calculated from reactions 7 and 8 to be 1.16×10^{-10} cm^3 molecule^{-1} s^{-1}.

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \qquad k = 4.9 \times 10^{-11} \tag{8}$$

$$N_2O + O(^1D) \rightarrow NO + NO \qquad k = 6.7 \times 10^{-11} \tag{9}$$

Thus, the rate for the CH_2F_2 with O(^{1}D) reaction is determined to be $(4.6 \pm 2.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. This value is approximately 3 times faster than the Schmoltner value. Our measured value of $k_{CH_2F_2}/k_{CH_4} = 0.46$ suggests a CH_2F_2 + O(^{1}D) reaction rate of 6.6×10^{-11} cm^3 molecule^{-1} s^{-1}. $k_{CH_2F_2}/k_{CH_3F} = 0.51$ suggests a reaction rate of 6.1×10^{-11} cm^3 molecule^{-1} s^{-1}. Both values are within the large error bars of Green et al.[14] but are about 4 times faster than the Schmoltner value.[4] Further investigation of the CH_2F_2 reaction with O(^{1}D) is needed to resolve this apparent discrepancy. In this work, we will use the Green and Wayne rate constant of 4.6×10^{-11} cm^3 molecule^{-1} s^{-1}. The values for the CH_4, CH_3F, and CH_2F_2 rate constants for chemical reaction with O(^{1}D) are $(1.43 \pm 0.29) \times 10^{-10}$, $(1.19 \pm 0.27) \times 10^{-10}$, and $(4.6 \pm 2.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.

Table 1 tabulates the relative rate of reaction of each reference gas relative to each ether, while Figure 2 illustrates example reactions. Close inspection of the relative rates listed in Table 1 reveals an apparent discrepancy in the method. The data in Table 1 lead to the following rate constant ratios: k_{CH_3F}/k_{CH_4}

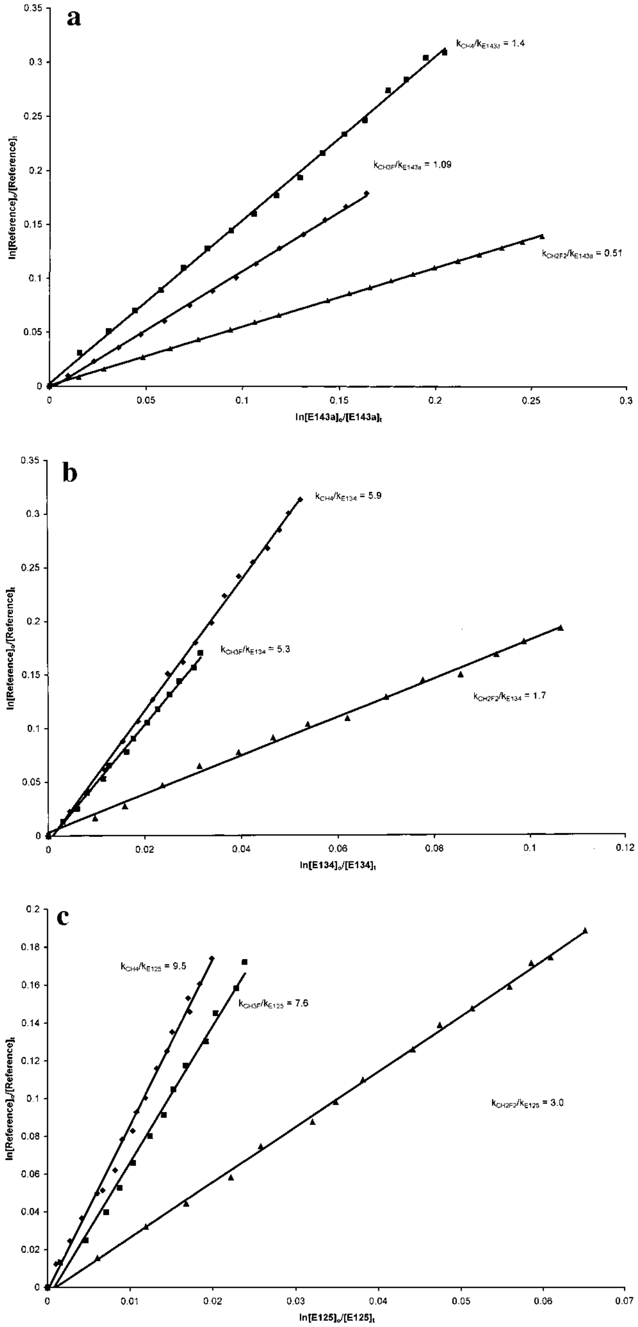

Figure 2. Relative rates for CH_4, CH_3F, and CH_2F_2 reaction with O(^{1}D) relative to each ether: (a) reference compound relative to E143a; (b) reference compound relative to E134; (c) reference compound relative to E125.

= 0.788 ± 0.06, 0.90 ± 0.11, and 0.81 ± 0.05 from the experiments with E143a, E134, and E125, respectively. Only the second determination is within the experimental error of the direct measurement of 0.97 ± 0.07. Similarly for $k_{CH_2F_2}/k_{CH_4}$ the relative rate ratios are 0.36 ± 0.03, 0.29 ± 0.04, and 0.32 ± 0.03 from the experiments with E143, E134, and E125, respectively. These values are each much lower than the direct measurement of 0.46 ± 0.01. On average, the direct measurements are a factor of 1.3 higher than the indirect measurements. One possible reason for this discrepancy is band interference. CH_4, CH_3F, and CH_2F_2 are structurally similar and, as a result, their absorption bands are convolved to a large extent; i.e., the CH stretches and bends of CH_4 overlap with the CH bends and stretches of CH_2F_2 and CH_3F. This fact casts suspicion on the direct measurements. For the ethers, the CO stretching modes (especially the lower energy symmetric stretch) are fairly isolated from the features of CH_4, CH_3F, and CH_2F_2. In addition, the CH stretching features of these ethers are fairly weak and unstructured, thus allowing measurement of the CH stretching features of CH_4, CH_3F, and CH_2F_2. These two facts allow for the simultaneous measurement of IR features from the ether and reference, while reference vs reference measurements were hindered by band congestion.

The ratios in Table 1 can be combined with the literature values for CH_3F and CH_4 listed in the text to infer a CH_2F_2/O(^{1}D) rate constant. The six values are 5.2×10^{-11}, 4.1×10^{-11}, 4.5×10^{-11}, 5.6×10^{-11}, 3.8×10^{-11}, and 4.6×10^{-11}. The average value of 4.63×10^{-11} agrees very well with the value from Green et al.

Table 2 lists the rate constants for each ether reacting with O(^{1}D). The average values in Table 2 have an error larger than would be expected from the individual determinations in Table 2. This is a reflection of the fact that direct measurements of reference ratios were, on average, 1.3 times larger than the indirect determinations.

As expected, as the number of hydrogens decrease so, too, do the rates of reaction. E143a is found to have a rate of reaction with O(^{1}D) of $(1.0 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. E134 reacts 4 times slower with O(^{1}D) than does E143a. E134 has a reaction rate of $(2.4 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. E125 reacts 6.7 times slower with O(^{1}D) than does E143a and 1.6 slower than E134. E125 has a reaction rate of $(1.5 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

IV. Atmospheric Significance

The lifetime of each ether with respect to reaction with the hydroxyl radical has been determined previously.[2] For E134 and E125, significantly long atmospheric lifetimes have been found. Thus, the possibility exists that photolysis or reaction with O(^{1}D) may compete with the hydroxyl radical. Using a simple relation, that the lifetime is equal to the concentration of the ether divided by its loss rate, the following expression can be derived:

$$\tau = \frac{[\text{ether}]}{k_{OH}[\text{ether}_t][OH] + k_{O(^1D)}[\text{ether}_s][O(^1D)]} \qquad (10)$$

where k_{OH}[ether][OH] represents the rate of removal by OH in the troposphere and $k_{O(^1D)}$[ether][O(^{1}D)]] represents the rate of removal by O(^{1}D) in the stratosphere. In the troposphere, the concentration of OH is on the order of 10^6 molecules cm^{-3}, while in the stratosphere at a height of about 30 km, the O(^{1}D)

TABLE 2: Rate Constants for Chemical Reaction of O(^{1}D) with Fluorinated Ethers at 298 K[a]

ref	CH_3OCF_3	CHF_2OCHF_2	CHF_2OCF_3
CH_4	$(1.02 \pm 0.22) \times 10^{-10}$	$(2.42 \pm 0.50) \times 10^{-11}$	$(1.50 \pm 0.31) \times 10^{-11}$
CH_3F	$(1.09 \pm 0.25) \times 10^{-10}$	$(2.24 \pm 0.57) \times 10^{-11}$	$(1.55 \pm 0.36) \times 10^{-11}$
CH_2F_2	$(0.90 \pm 0.45) \times 10^{-10}$	$(2.71 \pm 1.39) \times 10^{-11}$	$(1.53 \pm 0.77) \times 10^{-11}$
av	$(1.0 \pm 0.3) \times 10^{-10}$	$(2.4 \pm 0.7) \times 10^{-11}$	$(1.5 \pm 0.6) \times 10^{-11}$

[a] All values in cm^3 molecule^{-1} s^{-1}.

concentration is on the order of 100 molecules cm^{-3}. For an altitude of 30 km, the concentration of a well-mixed species is 1 order of magnitude lower than at ground level. This can be estimated using the hydrostatic equation for air and then using the mixing ratios for each ether as modeled by Good et al.[2] Using these parameters, the lifetime of E125 with respect to loss from reaction with both OH and O(^{1}D) is estimated to be about 70 years. This value is substantially shorter than the 165 year lifetime due to loss only from hydroxyl. Using the same procedure, E134 is estimated to have a lifetime with respect to reaction with OH and O(^{1}D) of 20 years as compared to a 29.7 year lifetime with respect to loss from OH. This implies that reaction with OH is dominant, but both will contribute to the total loss of the ether. For E143a, a lifetime with respect to loss from OH and O(^{1}D) of 4.3 years is determined. This can be compared to a lifetime of 5.7 years with reaction with OH. Loss of E143a from the atmosphere will be primarily from reaction with tropospheric OH.

We find that reaction of E125 and E134 with O(^{1}D) may be a significant loss mechanism for these fluorinated ethers in the atmosphere.

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