Temperature Dependence of the Gas Phase Reactions of CF₃O with CH₄ and NO

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A temperature-regulated flow tube reactor coupled to a chemical ionization mass spectrometer (CIMS) was used to investigate reactions of CF₃O with CH₄ and NO. The reaction rate constant for the CF₃O + CH₄ reaction was measured in the temperature range 231-385 K and found to be $k_3(T) = (3.1 \pm 0.5) \times 10^{-12} \exp[(-1470 \pm 250) \text{ K}/T] \text{ cm}^3$ molecule⁻¹ s⁻¹, with $k_3(298 \text{ K}) = (2.2 \pm 0.4) \times 10^{-14} \text{ cm}^3$ molecule⁻¹ s⁻¹ (where the uncertainties represent our estimated accuracy at the 95% confidence level). The latter is in good agreement with recently reported measurements at room temperature. The reaction rate constant for the CF₃O + NO reaction was measured in the temperature range 231-393 K and found to be $k_4(T) = (4.1 \pm 0.6) \times 10^{-11} \exp[(60 \pm 100) \text{ K}/T]$, with $k_4(298 \text{ K}) = (5.0 \pm 1.0) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹. The value at room temperature disagrees with two previously reported values by a factor of about 2.5 but is in good agreement with three recently reported values. The results reported in this study are important in establishing the fate of the CF₃O_x radicals produced as degradation products from hydrofluorocarbons (HFC's) in the atmosphere.

Introduction

Chlorofluorocarbons (CFC's) are known to be responsible for ozone depletion in the stratosphere via chlorine liberated during their photochemical destruction as well as for contributing directly to the greenhouse effect.¹ An international agreement has been established to phase out the use of CFC's in certain countries by the end of 1995.² The primary replacements for the CFC's are hydrofluorocarbons (HFC's) and hydrochlorofluorocarbons (HCFC's).² An advantage of replacing the CFC's with HFC's and HCFC's is that the latter are hydrogenated, which allows OH abstraction of hydrogen, thereby reducing their lifetime in the atmosphere.³ Another advantage of the HFC's is that they contain no Cl, and therefore their ozone depletion potentials (ODP) are thought to be zero.³

Many of the HFC's contain a CF_3 group, and laboratory studies have shown that CF_3 is a degradation product from these compounds.⁴⁻⁸ In the atmosphere CF_3 reacts with O_2 , and frequently this is followed by the reaction with NO:⁹⁻¹¹

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M$$
 (1)

$$CF_3O_2 + NO \rightarrow CF_3O + NO_2$$
 (2)

Thus there are the two species CF_3O and CF_3O_2 , which we collectively designate as CF_3O_x , that are of interest in atmospheric chemistry.

When this investigation was started, the atmospheric fate of CF_3O was uncertain, because only very limited data for this radical were available and because most of the data were based on indirect measurements. In earlier studies it was shown that CF_3O reacts with organic compounds by abstracting a hydrogen atom.^{11,12} Several laboratories have recently studied the reaction between CF_3O and CH_4 at room temperature:¹³⁻¹⁸

$$CF_3O + CH_4 \rightarrow CF_3OH + CH_3$$
 (3)

In the present investigation we have performed a direct measurement of reaction 3 over the temperature range 231-385 K.

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It has also recently been shown that the CF₃O radical reacts rapidly with NO, but the results are not in good agreement with the reported room temperature rate coefficients in the range $(2-6) \times 10^{-11}$ cm³ molecule⁻¹ s^{-1;11,19-22}

$$CF_3O + NO \rightarrow CF_2O + FNO$$
 (4)

In this study we have performed a direct measurement of reaction 4 over the temperature range 231-393 K.

An interesting aspect of the CF_3O_x chemistry that has been analyzed recently is the suggestion that CF_3O_x from HFC's/ HCFC's could be involved in catalytic cycles, which destroy ozone.²³ One key cycle is shown by reactions 5 and 6:

$$CF_3O_2 + O_3 \rightarrow CF_3O + 2O_2 \tag{5}$$

$$CF_3O + O_3 \rightarrow CF_3O_2 + O_2 \tag{6}$$

$$2O_3 \rightarrow 3O_2$$
 net (5) + (6)

The purpose of this investigation was to clarify the fate of the CF_3O radical in the atmosphere by determining the importance of the reactions of CF_3O with CH_4 and NO, which both terminate the ozone destruction cycle described above.

Experimental Section

The experimental setup with a flow tube reactor and CIMS detection has been described previously.^{24,25} For this study, a variable temperature flow tube was installed to cover the range from 210 to 420 K using a temperature-regulated circulating bath ($\Delta T \le \pm 0.3$ K). Below 295 K, methanol was used as a cooling fluid, and above 295 K, ethylene glycol was used as a heating agent.

The glass flow tube has a 2.47 cm i.d. and an overall length of about 150 cm. To minimize heterogeneous effects, the tube was fitted with a Teflon sleeve of 2.30 cm i.d. which spanned from a point 2 cm upstream of the radical inlet to 10 cm from the downstream end of the flow tube. Helium at flow rates of 5-7 STP cm³ s⁻¹ (STP = 273 K and 1 atm pressure) was used as a carrier gas and entered the flow tube 50 cm upstream of the radical inlet port. The kinetics studies were carried out with carrier flow velocities of 600–1200 cm s⁻¹ at flow tube pressures of 1.3–1.7 Torr and at temperatures between 231 and 393 K.

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Gas Phase Reactions of CF₃O with CH₄ and NO

CF₃O radicals were generated by pyrolysis of CF₃OOCF₃ at 815 ± 30 K in a quartz sidearm reactor. The quartz reactor was connected to the main flow tube about 50 cm below the He carrier gas inlet. The precursor was diluted in a stream of He (~0.5 STP cm³ s⁻¹).

The reactant NO was used as a mixture of 2.01% NO in He. The reactant CH₄ was used directly from the compressed gas cylinder. The NO and CH₄ were diluted in a He carrier stream $(0.2-0.5 \text{ STP cm}^3 \text{ s}^{-1})$ before they entered the moveable injector for addition to the flow tube.

 SF_6^- was used as the ionizing reagent for the CIMS detection of CF_3O , CF_3O_2 , and CF_3OH . SF_6^- is known to react with NO_2 by charge transfer:²⁶

$$SF_6^- + NO_2^- + SF_6$$
 (7)

 $k_7 = (1.3 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

As we have found previously, ¹¹ SF₆⁻ reacts with CF₃O₂ and CF₃O by charge transfer and rapidly with CF₃OH by fluoride transfer. In this work we estimated the following values for k_8 , k_9 , and k_{10} :

$$SF_6^- + CF_3O_2 \rightarrow CF_3O_2^-SF_6$$
 (8)

 $k_8 = (7 \pm 3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

$$SF_6^- + CF_3OH \rightarrow CF_3O^- HF + SF_5$$
 (9)

 $k_9 = (7 \pm 4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

$$SF_6^- + CF_3O \rightarrow CF_3O^- + SF_6 \tag{10}$$

$$k_{10} = (2 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The estimates of k_8 , k_9 , and k_{10} and the calibration for [CF₃O] were obtained using a procedure involving several steps. In the first step the CF₃O₂ radical signal was calibrated relative to the NO₂ signal using reactions 11, 1, and 2. As is shown in reaction 2, the destruction of one CF₃O₂ was assumed to lead to the production of one NO₂.

$$CF_3I \xrightarrow{\Delta} CF_3 + I$$
 (11)

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \tag{1}$$

$$CF_3O_2 + NO \rightarrow CF_3O + NO_2$$
 (2)

Thus a value of k_8 relative to k_7 was obtained. The decrease of CF₃O₂ and the increase of NO₂ were measured simultaneously using SF₆⁻ as the ionizing reagent. In the second step CF₃OH was calibrated relative to CF₃O₂ by adding large amounts of isobutane to the system, which converts CF₃O rapidly to CF₃OH via reaction 12:^{11,18}

$$CF_3O + (CH_3)_3CH \rightarrow CF_3OH + (CH_3)_3C$$
 (12)

$$k_{12} = (7 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

It was assumed that the destruction of one CF_3O_2 produced one CF_3OH ; thus a value for k_9 relative to k_8 was obtained. The ratio [isobutane]/[NO] was about 1000, which assured that the CF_3O product of reaction 2 reacts predominately via reaction 12 and not via reaction 4. In the last step CF_3O was calibrated relative to CF_3OH in a system described by reactions 12 and 13. It was assumed that one CF_3O produced one CF_3OH via reaction 12.

$$CFOOCF_3 \xrightarrow{\Delta} 2CF_3O \tag{13}$$

$$CF_3O + (CH_3)_3CH \rightarrow CF_3OH + (CH_3)_3C$$
 (12)

Thus a value of k_{10} relative to k_9 was obtained.

 SF_6^- is known to react with CF_2O by fluoride transfer (reaction 14):^{27,28}

$$SF_6^- + CF_2O \rightarrow CF_3O^- + SF_5$$
 (14)

$$k_{14} = (2 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{ref } 28)$$

CF₃O is detected a m/e = 85 amu, as is CF₂O. Reaction 14 is slow and found to be a factor of about 10 slower than reaction 10, and therefore only a small correction to the decay plots of CF₃O is required. A background signal of about 10% of the initial signal at m/e = 85 amu was indeed observed while reaction 4 was investigated. This was measured by adding an excess of NO to ensure that all CF₃O was removed. CF₂O is believed to be the major product from reaction 4,29 and when this background signal was attributed to reaction 14, one obtains that k_{10} should be a factor of about 10 larger than k_{14} , which is consistent with the above estimate of k_{10} . The uncertainties in the ion-neutral reaction rate coefficients (k_8-k_{10}) are rather large. We have not accounted for possible wall reactions of the radical reactants, which we know can be significant for CF_3O . Also, we previously encountered¹¹ a large uncertainty in the stoichiometry of reaction 4, when O_2^+ ions were used to detect the NO reactant and NO_2 product. Our objective here was to derive an estimate of the concentrations of those species in our reactor and not an accurate determination of the ion-neutral rate coefficients.

The $[CF_3O]_0$ in the flow tube was typically 3×10^{10} molecule cm⁻³ and always $<5 \times 10^{10}$ molecule cm⁻³. Therefore, to ensure pseudo-first-order decay of the radicals, the [reactants] was in the range 2×10^{11} to 2×10^{15} molecule cm⁻³ in the flow tube. The detection limit for CF₃O was estimated to be 5×10^8 molecule cm⁻³ for a 2 s integration period.

The radical reaction rate coefficients were determined as follows. For the reaction

$$CF_3O + CH_4 \xrightarrow{k_3} CF_3OH + CH_3$$
 (3)

under pseudo-first-order conditions one obtains an expression for $[CF_3O]$:

$$[CF_{3}O]_{t} = [CF_{3}O]_{0} \exp\{-k_{3}[CH_{4}]t\}$$
(15)

The standard procedure for obtaining k_3 , the bimolecular rate coefficient, using the flow tube movable inlet method 11 is to vary the inlet position with a constant [CH4] to measure the pseudofirst-order rate coefficient, k. Then a set of these k's are plotted versus $[CH_4]$ to determine k_3 . Due to loss of CF₃O radicals on the outer wall of the injector, however, unacceptable long periods of time were required for the $[CF_3O]$ to stabilize each time the injector had been moved. Therefore, k_3 was determined in a different manner. The inlet position was fixed, while the [CH₄] was varied. We plot $\ln[CF_3O]$ vs $[CH_4]$ and obtain $-k' = -k_3t$ as the slope. To obtain different reaction times, t, the inlet was moved, [CF₃O] was allowed to stabilize, and again [CF₃O] was monitored as a function of $[CH_4]$. We then plot these data, k'vs t, to obtain k_3 as the slope. The flow tube time t is the relative reaction time based upon the relation t = z/v, where z is the distance from the inlet tip to the end of the flow tube (cm) and v is the average gas flow velocity in the flow tube (cm s⁻¹). We do not need to know the "absolute" reaction time t in this analysis. The small intercepts on Figures 2 and 5 reflect the uncertainty in our knowledge of the absolute time scale.



Figure 1. Variation of CF₃O⁻ signal with [CH₄] at different reactions times (t): P = 1.57 Torr, v = 811 cm s⁻¹, and T = 293 K; (O) t = 0.112 s, (\bullet) t = 0.0859 s, (∇) t = 0.0603 s.

Chemicals used in this study had the following purities: CF_3 -OOCF₃ (>95% pure), CH_4 (>99.9% pure and >99.99% pure), and He (>99.999% pure). NO (>99%) was purified by passing it through a trap filled with silica gel cooled to 195 K. The [NO] in the He mixture was determined using a capacitance manometer in preparing the mixture.

A propagation of random error analysis of a rate coefficient derived from the measurement of the gas flow rates $(\pm 3\%)$, temperature $(\pm 1\%)$, pressure $(\pm 1\%)$, flow tube radius $(\pm 3\%)$, and the slope of the decay plots $(\pm 4\%)$ gives an estimated value of about $\pm 9\%$ for the uncertainty in a rate coefficient measurement at the 95% confidence level. To this we add a factor of 10% for possible systematic error, which gives an overall uncertainty of $\pm 19\%$ for our kinetic measurements.

Results

CF₃O + CH₄ → CF₃OH + CH₃. The reaction rate coefficient for the CF₃O + CH₄ reaction was determined using the methods described in the previous section. The SF₆⁻CIMS ionizing reagent was used to detect the CF₃O reactant and the CF₃OH product. Figure 1 shows a typical example for the dependence of [CF₃O] (detected as CF₃O⁻, m/e = 85) as a function of [CH₄] at three fixed injector positions (reaction times t) at T = 293 K. The decay in CF₃O indicates that a reaction between the radical and CH₄ occurs. The data in Figure 1 were used to determine decay coefficients k' for three reaction times.

In Figure 2 the decay coefficients, k' are plotted as a function of relative reaction time, t, in the flow tube. The line is a linear least-squares fit to the experimental data, and the slope is equal to the reaction rate coefficient k_3 . The fit in Figure 2 gives k_3 = $(1.98 \pm 0.06) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ (where the uncertainty is the standard error of the fit). Our estimated overall uncertainty, as described above, gives a value of $(1.98 \pm 0.38) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

In Table 1 the reaction rate constants for reaction 3 measured at nine different temperatures from 231 to 385 K are listed. Figure 3 is an Arrhenius plot of the values listed in Table 1 showing the temperature dependence of reaction 3. The line in the figure is a least-squares fit to the experimental data. The slope of the line in Figure 3 yields a value for $k_3(T)$ of $(3.07 \pm 0.77) \times 10^{-12}$ $\exp[(-1468 \pm 59) \text{ K}/T] \text{ cm}^3$ molecule⁻¹ s⁻¹, where th uncertainties are the standard errors of the fit. Our recommended expression is $k_3(T) = (3.1 \pm 0.5) \times 10^{-12} \exp[(-1470 \pm 250) \text{ K}/T]$ cm³ molecule⁻¹ s⁻¹, which incorporates our estimated accuracy over the temperature range of the measurements.

 $CF_3O + NO \rightarrow CF_2O + FNO$. These measurements were



Figure 2. Decay constants, k', as a function of relative reaction time for the reaction between CF₃O and CH₄ at T = 293 K. The error bars, which represent one standard deviation derived from the fits in Figure 1, are smaller than the size of the symbols. The line in the figure is a linear least-square fit to the experimental data, and the slope is the reaction rate constant k_3 . The fit yields a value for k_3 of $(1.98 \pm 0.06) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ (where the uncertainty is the standard error of the fit).

TABLE 1: Reaction Rate Constants, k_3 , Obtained for the Reaction between CF₃O and CH₄ in the Temperature Range 231-385 K

T (K)	k_{3}^{a} (cm ³ molecule ⁻¹ s ⁻¹)	T (K)	k_3^a (cm ³ molecule ⁻¹ s ⁻¹)
231.3 250.8 272.4 293.0 314.8	$\begin{array}{c} (6.02 \pm 0.92) \times 10^{-15} \\ (8.09 \pm 1.21) \times 10^{-15} \\ (1.26 \pm 0.18) \times 10^{-14} \\ (1.98 \pm 0.32) \times 10^{-14} \\ (3.37 \pm 0.64) \times 10^{-14} \end{array}$	332.5 350.3 367.8 385.4	$\begin{array}{c} (3.63 \pm 0.72) \times 10^{-14} \\ (5.33 \pm 1.36) \times 10^{-14} \\ (5.45 \pm 0.71) \times 10^{-14} \\ (7.09 \pm 1.64) \times 10^{-14} \end{array}$
	(

Note: The error bars represent an error of 10% + 2 times the standard error of the fit. These error bars were used in weighting the values in the least-square fit (see Figure 3).



Figure 3. Arrhenius plot for k_3 data for the reaction of CF₃O with CH₄. The error bars are described in Table 1.

performed in the same way as the $CF_3O + CH_4$ reaction measurements described above. Figure 4 shows typical examples of the dependence of $[CF_3O]$ as a function of [NO] at three fixed injector positions at T = 295 K. Figure 4 shows that, upon addition of NO through the injector, a loss of the CF_3O radical occurs.

In Figure 5 the decay coefficients, k', are plotted as a function of relative reaction time, t, in the flow tube. The line in the figure is a linear least-squares fit to the experimental data and yields a value for k_4 of $(5.09 \pm 0.24) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (where the uncertainty is the standard error of the fit). Our estimated



Figure 4. Variation of CF₃O⁻ signal with [NO] at different reaction times (t): P = 1.55 Torr, v = 753 cm s⁻¹, and T = 295 K; (O) t = 0.102 s, (\bullet) t = 0.0624 s, (∇) t = 0.0491 s.



Relative reaction time t (s)

Figure 5. Decay constants, k', as a function of relative reaction times for the reaction between CF₃O and NO at T = 295 K. The error bars represent one standard deviation derived from the fits in Figure 4. The line is a linear least-square fit to the experimental data, and the slope is equal to the reaction rate constant k_4 . The fit gives $k_4 = (5.09 \pm 0.24) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (where the uncertainty is the standard error of the fit).

TABLE 2: Reaction Rate Constants, k_4 , Obtained for the Reaction between CF₃O and NO in the Temperature Range 231–393 K

T (K)	k_4^a (cm ³ molecule ⁻¹ s ⁻¹)	<i>T</i> (K)	k_4^a (cm ³ molecule ⁻¹ s ⁻¹)
231.4	$(5.19 \pm 0.90) \times 10^{-11}$	315.3	$(5.04 \pm 0.94) \times 10^{-11}$
250.8	$(5.04 \pm 0.99) \times 10^{-11}$	344.1	$(5.16 \pm 1.18) \times 10^{-11}$
270.8	$(4.92 \pm 1.02) \times 10^{-11}$	369.7	$(4.16 \pm 0.92) \times 10^{-11}$
294.9	$(5.09 \pm 0.98) \times 10^{-11}$	393.0	$(4.76 \pm 0.65) \times 10^{-11}$

^a Note: The error bars represent an error of 10% + 2 times the standard error of the fit. These error bars were used in weighting the values in the least-square fit (see Figure 6).

overall uncertainty, as described above, gives a value of $(5.09 \pm 0.97) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

In Table 2 the reaction rate constants for reaction 4 at eight different temperatures are listed. Figure 6 shows an Arrhenius plot for our reaction 4 data for the temperature range 231-393 K. The line in the figure is a least-square fit to the experimental data giving $k_4(T) = (4.09 \pm 0.48) \times 10^{-11} \exp[(57 \pm 31) \text{ K}/T] \text{ cm}^3$ molecule⁻¹ s⁻¹. Our recommended expression is $k_4(T) = (4.1 \pm 0.6) \times 10^{-11} \exp[(60 \pm 100) \text{ K}/T] \text{ cm}^3$ molecule⁻¹ s⁻¹, which incorporates our estimated accuracy over the temperature range of the measurements.



Figure 6. Arrhenius plot for k_4 data for the reaction of CF₃O with NO. The error bars are described in Table 2.

TABLE 3: Comparison of Reaction Rate Coefficients for Reaction 3: $CF_3O + CH_4 \rightarrow Product (k_3(T) cm^3 molecule^{-1} s^{-1})$

Arrhenius expression					
$k_3(T)^a$ (10 ⁻¹⁴)	Т (К)	A (10 ⁻¹²)	<i>E/R</i> (K)	T range (K)	ref
$2.2 \pm 0.4 <0.2b1.2 \pm 0.1 2.2 \pm 0.2 3 \pm 2 2.7 \pm 0.2 1.9 \pm 0.1$	298 298 295 298 297 298 298 298	3.1 ± 0.5 3.3 ± 0.8 1.9 ± 0.3	1470 ± 250 1430 ± 150 1370 ± 85	231–385 235–401 247–360	this work Chen et al. ¹³ Kelly et al. ¹⁴ Saathoff and Zellner ¹⁵ Bevilacqua et al. ¹⁶ Bednarek et al. ¹⁷ Barone et al. ¹⁸

 $^{a}k_{3}$ (298 K) was calculated from the Arrhenius plot when possible. b See discussion section.

Discussion

 $CF_3O + CH_4 \rightarrow CF_3OH + CH_3$. The results from our study are compared with those of seven other studies of the reaction between CF_3O and CH_4 in Table 3. As can be seen, there is generally good agreement at room temperature, where all of the values are near $k_3 = 2 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, except for the investigations by Chen et al.¹³ and Kelly et al.¹⁴ Both of these studies used relative rate methods with long-path FTIR detection. Chen et al.¹³ searched for the formation of the CH₂O product resulting from oxidation of CH₄ initiated by reaction 3 vs the formation rates of CF_2O and FNO products of reaction 4. They failed to see any evidence of reaction 3 upon the addition of up to 1000 ppm of CH₄ and concluded that reaction 3 was very slow. Their reported value $k_3 < 2 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹ was based upon the previous measurement of k_4 from our laboratory,¹¹ which is in error as discussed below. Although this error accounts for some of the discrepancy, about a factor of 4 difference remains. A reinvestigation of the reaction by Niki and co-workers³⁰ gives better agreement with the other values in Table 3. The reason for the discrepancy is not known but may be due to a lack of sensitivity to the CH₂O product or some unaccounted for loss of CH_2O . Interestingly, the reaction rate coefficient reported by Chen et al.¹³ for the $CF_3O + C_2H_6$ reaction yields good agreement with other studies, 18 while their measurement for the CF₃O + C_3H_8 reaction is about a factor of 2 low using the present result for k_4 , their reference reaction rate coefficient. Their studies of the C_2H_6 and C_3H_8 reactions employed a different product detection scheme, observing the formation of the CF₂O product of reaction 4 vs the CF₃OH product of the CF₃O + RH reaction.

The study reported by Kelly et al.¹⁴ used CF_3OOCF_3 photolysis to produce CF_3O radicals. They measured the temporal loss of

TABLE 4: Comparison of Reaction Rate Coefficients for reaction 4: CF₃O + NO \rightarrow Products ($k_4(T)$ cm³ molecule⁻¹ s-1)

Arrhenius expression					
k4(T)ª (10 ⁻¹¹)	Т (К)	A (10 ⁻¹¹)	<i>E/R</i> (K)	T range (K)	ref
$5.0 \pm 1.0 \\ 2.5 \pm 0.4 \\ 2 \pm 1 \\ 5.2 \pm 2.7 \\ 4.8 \pm 1.0 \\ 5.6 \pm 0.7 \\ 1.0 \\ 1.$	298 298 297 295 298 298	4.1 ± 0.6 3.3 ± 0.7	-60 ± 100 -160 ± 45	231–393 233–360	this work Zellner and Saathoff ¹⁹ Bevilacqua et al. ¹¹ Sehested and Nielsen ²⁰ Zellner ²¹ Turnipseed et al. ²²

^a $k_4(298 \text{ K})$ was calculated from the Arrhenius plot when possible.

 CH_4 relative to the loss of C_2H_6 , obtaining 0.010 ± 0.001 for the rate coefficient ratio. Using $k(CF_3O + C_2H_6) = 1.2 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹, they obtained $k_3 = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is about 40% lower than the present result. Their similarly measured ratios for the reactions of CF_3O with C_3H_6 and $(CH_3)_3$ -CH are in good agreement with the absolute values reported by Barone et al.¹⁸ It is not clear what could cause the discrepancy found in their CH₄ data, although this reaction is much slower than the others.

Two concurrent studies have dealt with the temperature dependence of reaction 3: Bednarek et al.¹⁷ used a combined pulsed laser photolysis/LIF technique to study the temperature dependence of the $CF_3O + CH_4$ reaction in the temperature range 235-401 K. The result from Bednarek et al. is 23% higher than our value at 298 K, but the measurements overlap within the combined uncertainties. The other investigation is from this laboratory by Barone et al.,18 who also used a pulsed laser photolysis/pulsed laser induced fluorescence technique in the temperature range 247-360 K. As can be seen in Table 3, the value from our investigation of the temperature dependence is in good agreement with the two others, and they all show a strong temperature dependence.

With CIMS detection the formation of the product CF₃OH was observed to correlate with the loss of the CF₃O reactant. Hydrogen abstraction by the CF₃O radical appears to be the only reasonable route for the reaction. The CF₃O radical is found to be behave very similarly to OH in its reactivity with organic molecules.^{13,14,18} Abstraction of H from saturated molecules and addition to unsaturated molecules such as ethylene have been observed.14 The relative reactivity of CF₃O toward organics follow the trends observed for OH.13,14,18

 $CF_3O + NO \rightarrow CF_2O + FNO$. The results from our study of reaction 4 are compared with the results from five other studies in Table 4. As can be seen, there is generally good agreement at room temperature, where all of the numbers are about 5 \times 10^{-11} cm³ molecule⁻¹ s⁻¹, except for the early investigations by Zellner and Saathoff,¹⁹ who used a LIF technique to study the reaction and by Bevilacqua et al.¹¹ in a earlier paper from our laboratory, who found a number about a factor of 2.5 lower. The low result of Zellner and Saathoff¹⁹ is superseded by the value from Zellner,²¹ which is in good agreement with the other recent investigations.

In our previous study, Bevilacqua et al.¹¹ used the same apparatus to obtain an estimate of $k_4 = (2 \pm 1) \ 10^{-11} \ \mathrm{cm}^3$ molecule⁻¹ s⁻¹. No kinetic source of CF₃O weas available for that work, so the estimate was derived using a computer model to fit [CF₃O] vs time profiles at different [NO]. This method has a large uncertainty, as reflected in the large error bars. The reaction sequence began with the CF₃O₂ radical, which was converted to CF₃O via reaction 2. The CF₃O₂ and CF₃O radicals were also lost to wall reactions. A reexamination of that study has failed to reveal the reason for the factor of 2.5 discrepancy with the present result. We have not attempted to repeat those indirect measurements because the present result, using a wellcharacterized source of CF₃O, provides much more reliable results.

The other indirect result from our previous study¹¹ was an estimate of the rate coefficient for the CF_3O + isobutane reaction, k = $(5 \pm 3) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, which is reasonably close to the direct measurement value $6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Barone et al.¹⁸ The other direct measurements reported earlier,¹¹ e.g., for $CF_3O_2 + NO$, are reliable.

Very small temperature dependencies of reaction 4 are reported here and in a concurrent paper by Turnipseed et al.²² from our laboratory. Turnipseed et al. used a pulsed laser photolysis/ pulsed laser induced fluorescence technique to study the temperature dependence of the $CF_3O + NO$ reaction in the temperature range 233-360 K. As can be seen in Table 4, the two values are in good agreement, and they both show a very small negative temperature dependence. A weak negative temperature coefficient is commonly observed in radical-radical reactions of this type which occur on attractive "recombination" types of reaction surfaces. CF_2O and FNO are found to be the only products from reaction 4 by Bevilacqua et al.¹¹ and Chen et al.²⁹ The latter discuss the mechanism in terms of a radicalradical recombination scheme. The possibility that CF₃ONO is formed to a small extent at high pressures has not been ruled out, but the facile formation of CF_2O + FNO implies that this compound may not be very stable.

Conclusions and Atmospheric Implications

Tables 3 and 4 show that there is now excellent agreement among several investigators on the two important atmospheric reactions of CF₃O radicals. Different techniques operating at low and high pressures indicate no significant pressure effects.

Recent model studies of the stratospheric ozone depletion effects of CF_3O_x radicals by Ravishankara et al.³¹ and Ko et al.²³ demonstrate the importance of reactions 3 and 4 in determining the stratospheric role of CF₃ containing halocarbons. Both reactions remove CF_3O_x radicals from the ozone depletion scheme. The reaction of CF₃O with CH₄ forms CF₃OH which is inert,³² although a small amount may be recycled back into CF_3O_x via photolysis or abstraction of H. On the other hand, the reaction of CF₃O with NO results in the irreversible destruction of CF₃O_r and terminates the chain (from the results obtained by Chen et al.²⁹ of the $CF_3O + NO$ reaction at 700 Torr total pressure and 298 K, it was concluded that it is highly unlikely that CF₃ONO is an important product of that reaction in the atmosphere). Further studies are underway to examine the chemistry of CF_3O_x as well as the fate of the CF₃OH molecule in the atmosphere.

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