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Atmospheric chemistry of CF_3O radicals: reaction with O_3

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Abstract

A relative rate technique has been used to study the title reaction over the pressure range 100-700 Torr of air at 296 \pm 2 K. Four different reference compounds (¹³CO, CH₄, CH₂FCl, and CD₄) were used. Using $k(CF_3O + CH_4) = (2.2 \pm 0.2) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ a rate constant of $k(CF_3O + O_3) = (1.5 \pm 0.5) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ was derived, quoted errors reflect statistical and potential systematic errors. There was no observable effect of diluent pressure over the range 100-700 Torr. As part of the present work the rate constant for reaction of CF₃O radicals with CH₂FCl was determined to be $(1.2 \pm 0.2) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. Implications for the atmospheric chemistry of CF₃O radicals are discussed.

1. Introduction

Recognition of the adverse effect of chlorofluorocarbon (CFC) release into the atmosphere has led to an international effort to replace CFCs with environmentally acceptable alternatives. Hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) are under consideration as CFC substitutes. For example, HFC-134a is a replacement for CFC-12 in automotive air conditioning systems. With their large scale industrial use, the environmental consequence of release of HFCs and HCFCs into the atmosphere has come under scrutiny.

 CF_3 radicals are produced during the oxidation of HFC-134a, HFC-125, HFC-23, and HCFC-123 [1]. In the atmosphere, CF_3 radicals react with O_2 to give

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 CF_3O_2 radicals which, in turn, react rapidly with NO to form CF_3O radicals [2,3],

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

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

The atmospheric chemistry of CF_3O radicals has received considerable attention recently. Interest in CF_3O chemistry stems from speculation regarding the ability of this radical to participate in catalytic ozone destruction cycles [4]. Quantification of the potential impact of CF_3O radicals on stratospheric ozone requires accurate rate data for the following reaction:

$$CF_3O + O_3 \rightarrow \text{products.}$$
 (3)

Measurements of k_3 have an interesting history. Biggs et al. [5] were the first to study k_3 and reported $k_3 = 1 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Realization of the potential importance of reaction (3) in stratospheric chemistry led to many other studies of

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this reaction. Reported values of k_3 are (in units of cm³ molecule⁻¹ s⁻¹): Nielsen and Sehested [6], <1 × 10⁻¹³; Wallington et al. [7], <3 × 10⁻¹⁴; Maricq and Szente [8], <5 × 10⁻¹⁴; Ravishankara et al. [9], <4 × 10⁻¹⁴; Fockenberg et al. [10], <2 × 10⁻¹⁵; Turnipseed et al. [11], (2.5^{+0.7}_{-1.5}) × 10⁻¹⁴; and Meller et al. [12], (2.7 ± 0.2) × 10⁻¹⁵.

There is now general agreement that the value of k_3 reported by Biggs et al. [5] is erroneously large and that reaction (3) does not play any significant role in atmospheric chemistry. However, it is interesting to note the significant difference in results reported by Turnipseed et al. [11], Fockenberg et al. [10], and Meller et al. [12]. It is particularly puzzling to consider the difference between the observations of Turnipseed et al. [11] and Fockenberg et al. [10]. Both groups used a pulsed laser photolysis/laser-induced fluorescence technique and both have studied the kinetics of other important reactions involving CF₃O radicals (for example, with CH₄ and C₂H₆) and report results which are in excellent agreement [13,14].

To improve our understanding of the $CF_3O + O_3$ reaction we have used a relative rate method to study k_3 . CF_3O radicals were generated by the photolysis of hexafluoroazomethane, $CF_3N_2CF_3$, in air diluent as described recently [15].

2. Experimental details

The experimental setup used has been described previously [16] and consists of a Mattson Instruments Inc. Sirius 100 FT-IR spectrometer interfaced to a 140 l, 2 m long evacuable pyrex chamber. White type multiple reflection optics were mounted in the reaction chamber to provide a total path length of 26.6 m for the IR analysis beam. The spectrometer was operated at a resolution of 0.25 cm⁻¹. Infrared spectra were derived from 32 co-added interferograms. CF₃O radicals were generated by the photolysis of CF₃N₂CF₃ using the output of 22 UV fluorescent lamps (GTE F40BLB),

$$CF_3N_2CF_3 + h\nu(\lambda > 300 \text{ nm}) \rightarrow 2CF_3 + N_2, \quad (4)$$

followed by reaction (1) and

$$CF_3O_2 + CF_3O_2 \rightarrow CF_3O + CF_3O + O_2.$$
 (5)

Reaction mixtures consisting of the reactant and reference compounds and $CF_3N_2CF_3$ diluted in air were admitted to the reaction chamber. In the presence of CF_3O radicals the reactant and reference compounds decay via

 $CF_3O + reactant \rightarrow products,$ (6)

$$CF_3O + reference \rightarrow products.$$
 (7)

Provided that the reactant and reference are lost solely by reactions (6) and (7) and that neither is reformed in any process, it can be shown that

$$\ln\left(\frac{[\text{reactant}]_{t}}{[\text{reactant}]_{t_0}}\right) = \frac{k_6}{k_7} \ln\left(\frac{[\text{reference}]_{t}}{[\text{reference}]_{t_0}}\right)$$

where $[reactant]_{t_0}$ and $[reference]_{t_0}$, and $[reactant]_{t_0}$ and [reference], are the concentrations of the reactant and reference compounds at times t_0 and t respectively, and k_6 and k_7 are the rate constants of reactions (6) and (7), respectively. The loss of reference and reactant compounds were monitored using their characteristic infrared features over the following wavenumber ranges: CH₄, 1180-1400 and 2850-3150; CD₄, 950-1050; CH₂FCl, 700-800 and 1040-1080; ¹³CO, 2000-2200; and O₃, 980-1070 cm⁻¹. Reaction mixtures consisted of 50–150 mTorr CF₃N₂CF₃ and 1-14 mTorr of the reference and reactant compounds diluted in either 100 or 700 Torr of ultra pure synthetic air. The temperature was 296 ± 2 K in all experiments. With the exception of $CF_3N_2CF_3$ and O_3 , all reactants were purchased from commercial sources at purities > 99% and were used as received.

CF₃N₂CF₃ was synthesized by passing cyanogen chloride, diluted with nitrogen or helium, over a bed of silver fluoride (AgF₂) and collecting the product in a cold trap (pentane/liquid nitrogen or liquid nitrogen) [17]. CF₃N₂CF₃ (b.p. -31° C) is easily separated from its impurities (unreacted CNCl, b.p. 13° C; SiF₄, b.p. -86° C; CF₃NO, b.p. -81° C) based on their relative vapor pressures. Cyanogen chloride was prepared by passing chlorine diluted with nitrogen through a solution of zinc sulfate and potassium cyanide and collecting the product in a CO₂/acetone bath [18]. Condensed chlorine (b.p. -35° C) was removed from cyanogen chloride (m.p. -6° C; b.p. 13° C) by passing nitrogen through the sample cooled to -23° C using a CCl₄/CO₂ bath. O₃ was prepared by flowing ultra high purity O_2 through a silent electrical discharge.

3. Results

The relative rate technique relies on the assumption that both the reactant and reference compounds are removed solely by reaction with CF₃O radicals. Possible complications could arise in the present work if there were significant loss of either reference or reactant compounds by heterogeneous processes, reaction with CF₃N₂CF₃, photolysis, or reaction with radical species other than CF₃O. These potential complications are addressed below.

To check for heterogeneous loss and reaction with $CF_3N_2CF_3$, mixtures of $CF_3N_2CF_3$ with the reference and reactant compounds were prepared and allowed to stand in the dark for 20 min. No loss (<1%) of reactant or reference compounds was observed. To test for photolysis, mixtures of the reactants in nitrogen, in the absence of $CF_3N_2CF_3$, were irradiated using the output of all the UV lamps surrounding the chamber for 20 min. No photolysis was observed.

Photolysis of CF₃N₂CF₃ gives CF₃ radicals. The formation of other radical species such as F atoms, even in a small yield, would complicate the data analysis. The pyrex reaction chamber blocks UV radiation with $\lambda < 300$ nm. The energy of a 300 nm photon is 95.3 kcal mol⁻¹. The C–F bond strength in CF₃N₂CF₃ has not been measured but it is reasonable to assume that it is similar to other C-F bonds in alkanes which have strengths of 105-110 kcal mol^{-1} [19]. The formation of F atoms in the present work is unlikely. CF₃ radicals formed by photolysis of CF₃N₂CF₃ react rapidly with O₂, $k_1 = 8.5 \times$ 10^{-12} cm³ molecule⁻¹ s⁻¹ [2,3,20]. In all experiments the O₂ concentration was at least 2100 times greater than that of the reactant and reference organics. Hence, secondary reactions involving CF₃ radicals are not expected to be a significant complication. The reaction of CF₃ radicals with O₂ gives CF₃O₂ radicals. CF₃O₂ radicals are expected to behave like typical alkylperoxy radicals which do not react with any of the reference or reactant species considered here [2,3]. It has been shown previously that CF_3O_2 radicals do not react significantly with ¹³CO under the present experimental conditions [15]. Possible reaction of CF_3O_2 with O_3 will be considered later in this section.

Figs. 1 and 2 show plots of $\ln([reactant]_{t_0}/[reactant]_t)$ versus $\ln([reference]_{t_0}/[reference]_t)$ obtained in this work. All plots are linear with intercepts at the origin suggesting the absence of complications due to secondary chemistry. Linear least-squares analysis of the data in Figs. 1 and 2 gives the rate constant ratios listed in Table 1. Quoted errors in Table 1 are 2 standard deviations from the linear regression analyses.

In the present work, the reactivity of CF₃O radicals towards CH₂FCl was measured relative to that of CH₄ and CD₄. CH₂FCl was found to be $0.56 \pm$ 0.06 times as reactive as CH₄, and 2.45 ± 0.28 times as reactive as CD₄. These two rate constant ratios provide an indirect measure of $k_8/k_9 = 0.23 \pm 0.04$ (errors were propagated using conventional techniques),

$$CF_3O + CD_4 \rightarrow CF_3OD + CD_3,$$
 (8)

$$CF_3O + CH_4 \rightarrow CF_3OH + CH_3.$$
(9)

This indirect determination is in agreement with our recent direct relative rate measurement of $k_8/k_9 = 0.23 \pm 0.02$ [15], and with the ratio $k_8/k_9 = (5.2 \pm 0.3) \times 10^{-15}/(1.93 \pm 0.11) \times 10^{-14} = 0.27 \pm 0.02$ derived from an absolute rate study [14]. This agreement lends confidence to the present experimental technique.

The rate constant ratios presented in Table 1 provide four chemically independent methods to determine k_3/k_9 . The experiments where CH₄ was used as a reference provide a direct measurement of $k_3/k_9 = 0.75 \pm 0.07$. Experiments involving ¹³CO, CH₂FCl, and CD₄ provide indirect measurements of $k_3/k_9 = 0.56 \pm 0.10$ (700 Torr data) and 0.71 ± 0.07 (100 Torr data), 0.78 ± 0.11 , and 0.60 ± 0.07 , respectively. Quoted errors are either taken directly from Table 1, or, if the reactivity was calculated from two or more measured relative rates, were calculated using conventional error propagation analysis. We choose to quote a final value of $k_3/k_9 =$ 0.68 ± 0.22 which covers the extremes of the determinations above.

There have been five absolute rate studies of the reactivity of CF₃O radicals towards CH₄ at 296 \pm 2



Fig. 1. Plot of $\ln([O_3]_{t_0}/[O_3]_t)$ versus $\ln([reference]_{t_0}/[reference]_t)$ for the following references: (\blacktriangle) ¹³CO (at 700 Torr); (\bigtriangledown) ¹³CO (at 100 Torr); (\blacklozenge) CH₄; (\bigcirc) CH₂FCl and (\blacklozenge) CD₄ at 296±2 K. Solid lines are first-order fits to the data.

K, values of k_9 reported are (in units of cm³ molecule⁻¹ s⁻¹): $(2.2 \pm 0.2) \times 10^{-14}$, Saathoff and Zellner [13]; $(3 \pm 2) \times 10^{-14}$, Bevilacqua et al. [21]; $(2.7 \pm 0.2) \times 10^{-14}$, Bednarek et al. [22]; $(1.9 \pm 0.1) \times 10^{-14}$, Barone et al. [14]; and $(2.2 \pm 0.4) \times 10^{-14}$,



Fig. 2. Plot of $\ln([CH_2FCI]_{t_0}/[CH_2FCI]_t)$ versus $\ln([reference]_{t_0}/[reference]_t)$ using (\bigoplus) CH₄, (\blacktriangle) CD₄, and (\bigcirc) ¹³CO references. Solid lines are first-order fits to the data.

Table 1

Rate constant ratios, $k_{reactant} / k_{reference}^{a}$, measured during the present work in 700 Torr of air diluent at 296 K

Reactant	Reference			
	¹³ CO	CH ₄	CH ₂ FCl	CD ₄
0 ₃	0.17 ± 0.03 0.34 ± 0.03 ^b	0.75 ± 0.07	1.39±0.12	2.62 ± 0.20
CH ₂ FCl ¹³ CO	0.16 ± 0.02	0.56 ± 0.06 3.29 ± 0.13^{c} $2.09 \pm 0.12^{b,c}$		2.45 ± 0.28
CD ₄		0.23 ± 0.02 ^c		

^a Quoted errors are 2σ .

^b At 100 Torr total pressure of air diluent.

^c From Ref. [15].

Jensen et al. [23]. With the exception of the result from Bevilacqua et al. [21], which is superseded by the study of Jensen et al. [23], there is no obvious reason to prefer any of these studies. Thus, we choose to place the relative rate data on an absolute basis by using an average of the above studies (Ref. [21] excluded) of $k_3 = (2.2 \pm 0.2) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, the quoted uncertainty reflects our estimate of a 10% uncertainty in k_9 based upon the close agreement of the absolute rate data. Hence, a final value of $k_3 = (1.5 \pm 0.5) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ is derived.

At this point is it appropriate to consider possible, complications caused by secondary reactions involving CF₃O₂ and HO₂ radicals in the present work. CF₃O₂ radicals are precursors to CF₃O radicals via reaction (5) and must be considered as possible complications in all experiments. HO₂ (or DO₂) radicals are formed during the oxidation of CH₄, CH₂FCl, and CD₄ and need to be considered in experiments involving these compounds. Reactions of CF₃O₂ and HO₂ radicals with CH₄, CH₂FCl, and CD₄ are thermodynamically unfavorable [19,24] and need no further consideration.

It is well known that HO_2 radicals react with O_3 , albeit slowly [20], to give OH radicals which will in turn react with O_3 to regenerate HO_2 radicals,

$$HO_{2} + O_{3} \rightarrow OH + 2O_{2},$$

$$k = 2.0 \times 10^{-15} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} [20], \quad (10)$$

$$OH + O_{3} \rightarrow HO_{2} + O_{2},$$

$$k = 6.8 \times 10^{-14} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1} [20]. \quad (11)$$

Reactions (10) and (11) constitute a chain mechanism for the loss of O_3 and clearly have the potential to be a major complication in our experiments. Fortunately, other loss mechanisms for HO₂ and OH radicals exist in the chamber. For example, reaction with CF₃O₂, CF₃O, and RO₂ radicals (R=CH₃, CHFCl, or CD₃) might reasonably be expected to proceed with rate constants in the $10^{-12}-10^{-10}$ cm³ molecule⁻¹ s⁻¹ range, i.e. orders of magnitude faster than for reactions of HO_x with O₃. Let us consider one possible competition, that between reactions (10) and the following reaction for HO₂ radicals:

$$CF_3O + HO_2 \rightarrow CF_3OH + O_2.$$
(12)

The steady-state CF₃O concentration in the present experiments, as calculated from the rate of loss of CH_4 , CH_2FCl , and CD_4 , was in the range (2-4) × 10^{10} cm⁻³. The O₃ concentrations used were in the range 32-46 mTorr $(1.0-1.5) \times 10^{15}$ cm⁻³. The rate constant for reaction (12) has not been measured. The analogous reaction of OH radicals with HO₂ radicals proceeds with a rate constant of 1.1×10^{-10} cm³ molecule⁻¹ s⁻¹ [20]. CF₃O radicals are generally more reactive than OH radicals in H-atom abstraction reactions and it seems reasonable to suppose that $k_{12} > 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The rate constant ratio k_{12}/k_{10} is then > 55000 and it follows that for an average O3 concentration used in the present work $(1.25 \times 10^{15} \text{ cm}^{-3}) \text{ CF}_3\text{O}$ radicals will scavenge HO₂ radicals more effectively than O₃ so long as the CF₃O steady-state concentration is $> 2.3 \times 10^{10}$ cm³ (which is at the low extreme of the range of CF₃O concentrations employed herein). It appears that the chain mechanism involving HO, radicals will not be very efficient in removing O_3 in our experiments.

In light of the potential problems caused by HO₂ radicals in experiments using CH₄, CH₂FCl, and CD₄ references, experiments were performed with O₃ in large excess. Initial concentration ratios employed were: $[O_3]/[CH_4] = 9.2-30$; $[O_3]/[CH_2FCl] = 22.4$; and $[O_3]/[CD_4] = 2.5-27$. With O₃ in large excess, any impact of HO₂ radicals on the O₃ concentration is minimized. There are two pieces of experimental evidence that suggest that under the present experimental conditions the formation of HO₂ radicals does not complicate the kinetic analysis. First, as seen from Fig. 1, variation of the initial

 $[O_3]/[CH_4]$ and $[O_3]/[CD_4]$ concentration ratios by factors of 3 and 11 did not produce any discernable effect on the O_3 decay. A decrease in the initial $[O_3]/[methane]$ concentration ratio leads to a proportionate increase in the amount of HO₂ radicals produced in the system for a given O₃ loss. Second, as discussed above, ratios of k_3/k_9 determined from experiments employing CH₄, CH₂FCl, and CD₄ references gave consistent results. The oxidation of CH_4 (CD_4) produces two HO_2 (DO_2) radicals, whereas the oxidation of CH₂FCl gives one HO₂ radical. If HO₂ radicals were responsible for significant O₃ loss then one might expect the value of k_3/k_9 derived from experiments involving a given initial $[CH_2FCI]/[O_3]$ concentration ratio to be lower than those from a comparable experiment employing CH_4 as reference. No such effect was observed. The experimental observations suggest that the formation of HO₂ radicals in the present experiments does not complicate the kinetic analysis.

 CF_3O_2 radicals are present in the chamber and their possible reaction with O_3 must be considered. Upper limits of $(0.5-1.0) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ have been reported for the rate constant of the reaction of CF_3O_2 radicals with O_3 [6,8,11]. As mentioned above, reaction of CF_3O_2 radicals with CH_4 , CH_2FCl , and CD_4 is ruled out by thermodynamical considerations. It has been shown that reaction of CF_3O_2 radicals with ¹³CO does not occur to any measurable extent under the present experimental conditions [15]. To gain insight into the chemistry occurring in the chamber, the system was modelled using a chemical mechanism consisting of reactions (4), (1), (5), (3), (7), and

$$CF_3O + CF_3O_2 \rightarrow CF_3OOOCF_3, \tag{13}$$

$$CF_3O + CF_3O \rightarrow CF_3OOCF_3.$$
 (14)

Kinetic data used were (in units of cm³ molecule⁻¹ s⁻¹): $k_1 = 8.5 \times 10^{-12}$ [20]; $k_3 = 1.5 \times 10^{-14}$ (this work); $k_5 = 1.8 \times 10^{-12}$ [25]; $k_7 =$ as appropriate for ¹³CO or CD₄ references (see above); $k_{13} = k_{14} =$ 2.5×10^{-11} [25]; $k_4 = 8 \times 10^{-5}$ s⁻¹, estimated from the initial rate of loss of C₂H₆ in experiments using 30 mTorr of C₂H₆. The Acuchem program [26] was used to model the system. The experimentally observed rates of decay of O₃ and the reference compounds were well simulated using the above mechanism. In the simulations the concentration of CF_3O_2 radicals was 10-30 times greater than the concentration of CF₃O radicals. To assess the impact of reaction of CF₃O₂ radicals with O₃ this reaction was added to the mechanism with a rate constant of 1.0×10^{-15} cm³ molecule⁻¹ s⁻¹ and reaction (3) was removed. The new mechanism simulates a worst case scenario where ozone is lost solely by reaction with CF_3O_2 radicals. With the new mechanism three observations were made: (i) the ratio of the decay of O_3 versus that of CD_4 varied by a factor of almost 2 as the initial $[O_3]/[CD_4]$ concentration ratio was varied over the range used in the experiments, (ii) plots of the decay of 13 CO versus that of O₃ were distinctly curved, and (iii) the rate constant ratios derived from the initial slopes of the simulated ¹³CO and CD4 data did not scale with the ratio of the reactivity of CF₃O radicals with these two references. These three observations run counter to the experimental observations. We conclude that CF_3O_2 radicals do not cause any major complications in the present work.

4. Discussion

A value of $k_3 = (1.5 \pm 0.5) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ at 296 ± 2 K independent of total pressure over the range 100–700 Torr of air diluent is reported herein. This result is consistent with the recent determination by Turnipseed et al. [11] of $k_3 = (2.5^{+0.7}_{-1.5}) \times 10^{-14}$ but is inconsistent with the upper limit of $k_3 < 2 \times 10^{-15}$ reported by Fockenberg et al. [10] and the value of $k_3 = (2.7 \pm 0.2) \times 10^{-15}$ given by Meller et al. [12].

In the study of Fockenberg et al. [10] pulsed laser photolysis of CF₃OCl was used as a source of CF₃O radicals. Cl atoms released from CF₃OCl react rapidly with O₃ to give ClO radicals. ClO radicals undergo a variety of reactions with the various radical species present (e.g with CF₃O, CF₃O₂, and other ClO radicals). Fockenberg et al. [10] recognized the importance of such secondary reactions and used a 23 reaction mechanism to simulate their experimental observations and derive a value of k_3 . It seems reasonable to speculate that uncertainties in the complex chemical system employed may have led Fockenberg et al. [10] to underestimate k_3 . Meller et al. [12] derived a value of k_3 by observing the rate of O₃ loss following the 254 nm irradiation of O₃/O₂ and CF₃OOCF₃/O₃/O₂ mixtures and ascribing the difference to CF₃O_x chemistry. As with the study of Fockenberg et al. [10] a complex chemical mechanism was employed to model the system and derive a value for k_3 . Again, it seems possible that complexities in the chemical mechanism used to extract a value for k_3 could explain the discrepancy between our results and those of Meller et al. [12].

At this point it is worthwhile to underscore the simplicity and strength of the present relative rate study. In our work the loss of O_3 was measured relative to four reference compounds which react with CF_3O via two different mechanisms. Loss of O_3 and reference compounds was observed only when these species were irradiated in the presence of $CF_3N_2CF_3$. UV irradiation of $CF_3N_2CF_3$ is a well-known source of CF_3 radicals [27]. CF_3 radicals react rapidly with O_2 to give CF_3O_2 radicals [20] which undergo self-reaction to give CF_3O radicals [25]. The kinetic analysis employed in the relative rate method assumes that the reactant and reference compounds are only lost by the reaction of interest and are not reformed in any process. It is difficult to



Fig. 3. Pseudo first-order constants for the loss of CF_3O radicals with respect to reaction with CH_4 , O_3 , and NO as a function of altitude.

imagine how O₃ or the reference compounds employed could be regenerated in the chamber. Experimental tests were made to establish the absence of any significant secondary loss processes. The four different reference compounds all gave consistent values of k_3/k_9 . Finally, when ¹³CO was used as a reference the measured rate constant ratio was found to depend upon total pressure in a manner consistent with that expected from the known pressure dependence of the reaction of CF₃O radicals with ¹³CO. It is not easy to understand how the measured value of $k_3/k_9 = 0.68 \pm 0.22$ could be in error. As discussed above, the reference value of $k_9 = 2.2 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ is well established. Thus, $k_3 = (1.5 \pm 0.5) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

5. Implications for atmospheric chemistry

In the stratosphere, reaction (3) will compete with reactions (9) and

$$CF_3O + NO \rightarrow COF_2 + FNO$$
 (15)

for the available CF₃O radicals. Kinetic data for reactions (9) and (15) as a function of temperature are available in the literature. The temperature dependence of reaction (3) has yet to be studied. The value of k_3 measured herein $(1.5 \times 10^{-14} \text{ cm}^3)$ molecule⁻¹ s⁻¹) was obtained at 296 K. To obtain an estimate of k_3 at typical stratospheric temperatures (220-260 K) we shall assume that reaction (3)displays the same temperature dependence as the analogous reaction of OH radicals with O₃ (which slows down by a factor of 3 as the temperature is lowered from 296 to 220 K [20]). Fig. 3 shows the result of multiplying the rate constants for k_3 , k_9 , and k_{15} by the altitude profiles for O₃, CH₄, and NO given by the NASA data panel [20]. Temperature-dependent rate expressions for k_9 and k_{15} were taken from Refs. [14,11], respectively.

As seen from Fig. 3, at all altitudes reaction with O_3 is a minor loss for CF₃O radicals. CF₃O radicals react with NO and (at low altitudes) CH₄ in preference to reaction with O_3 . Reaction of CF₃O with NO gives COF₂, thereby destroying the CF₃ group [28]. Reaction of CF₃O with CH₄ gives CF₃OH which is essentially inert in the stratosphere [29]. CF₃OH is removed by heterogeneous decomposition and physi-

cal transport to the lower atmosphere followed by incorporation into rain-cloud-sea water and hydrolysis. For CF_3O_x radicals to have an appreciable impact on stratospheric ozone they would have to participate in catalytic ozone destruction cycles with chain lengths of the order of 10^3-10^6 . For comparison the Cl/ClO chain length is of the order of 10^3-10^4 . From the data displayed in Fig. 3 it is clear that there is no possibility of catalytic removal of stratospheric O₃ by CF₃O_x radicals.

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Note added

A recent study of k_3 has been conducted by Howard Sidebottom (University College Dublin) and Richard Wayne (Oxford University) and co-workers employing photolysis of CF₃OOCF₃ at 193 nm in the presence of O₃. The resulting loss of O₃ was used to derive $k_3 = (3 \pm 2) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. This result is consistent with that reported herein.

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