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Kinetics of the Reactions of CF_3O_x Radicals with NO, O_3, and O_2

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The technique of pulsed laser photolysis/pulsed laser-induced fluorescence detection of CF_3O was used to study the stratospherically important reactions of CF_3O radicals with NO (k_5), O_3 (k_4), and O_2 (k_6) and that of CF_3-OO with NO (k_2) and O_3 (k_3). Over the temperature range 233–360, K, $k_5(T) = (3.34 \pm 0.68) \times 10^{-11} \exp[(160 \pm 45)/T]$ cm^3 molecule^{-1} s^{-1}. At 298 K, $k_2 = (1.57 \pm 0.38) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} in agreement with past work. The reactions of CF_3O and CF_3OO with O_3 were found to be slow with rate coefficients at 298 K of $k_4 = (2.5^{+0.7}_{-1.5}) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $k_3 \leq 7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, respectively. No reaction of CF_3O with O_2 was observed at 298 or 373 K, leading to an upper limit of $k_6 \leq 4 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 373 K. The implications of these results to the chemistry of CF_3O_x radicals and O_3 in the stratosphere are discussed.

Introduction

It is now established that the chlorine and bromine contained in chlorofluorocarbons (CFCs) and halons catalytically destroy ozone in the polar stratosphere.[1] These compounds are also implicated in the midlatitude O_3 loss observed over the past decade.[2,3] Therefore, production of CFCs and halons are being phased out,[4] and compounds which are removed significantly in the troposphere or do not contain any chlorine or bromine are being considered as possible substitutes. Two classes of such compounds are the hydrofluorocarbons (HFCs) and the hydrochlorofluorocarbons (HCFCs). It has been assumed that HFCs, even if they reach the stratosphere, do not destroy ozone.[3] In the case of HCFCs, only those which carry very little chlorine to the stratosphere are deemed acceptable on a temporary basis. They are considered as only interim replacements to be eventually phased out of production.[4]

There is a growing body of evidence from end-product studies[5–8] for the release of the CF_3 group during the atmospheric degradation of CF_3-containing HFCs and HCFCs. Once released into the atmosphere, the CF_3 radicals are quickly converted into CF_3O and CF_3OO through the reactions

$$CF_3 + O_2 + M \rightarrow CF_3OO + M \qquad (1)$$

$$CF_3OO + NO \rightarrow CF_3O + NO_2 \qquad (2)$$

Recent studies have shown that CF_3O radicals are similar to OH radicals in their reactivity towards hydrocarbons and alkenes,[9–11] with the CF_3O reactions appearing to be faster at 298 K in most cases. Of chief concern, therefore, is the reactivity of CF_3O radicals toward ozone. It has been suggested[12] that CF_3O and CF_3OO can participate in a catalytic ozone destruction cycle via

$$CF_3OO + O_3 \rightarrow CF_3O + 2O_2 \qquad (3)$$

$$CF_3O + O_3 \rightarrow CF_3OO + O_2 \qquad (4)$$

analogous to the HO_x cycle involving HO_2 and HO. If this is an efficient cycle in the atmosphere, the ozone depletion potential (ODP ≡ a measure of how efficiently a compound destroys stratospheric ozone relative to CFC-11, $CFCl_3$, on a unit weight basis) for many HFC compounds would not be negligible, and their suitability as CFC substitutes would be questionable.

The efficiency of the above cycle is also determined by other reactions of CF_3O and CF_3OO which can terminate the catalytic cycle. One such reaction is that of CF_3O with NO, which has been observed to be a rapid bimolecular reaction:[9,11b,13]

$$CF_3O + NO \rightarrow CF_2O + FNO \qquad (5)$$

To determine the ODP of CF_3-containing compounds, the rate coefficients for reactions 3 and 4, as well as the rate coefficients for all competing loss processes (such as reaction 5) must be accurately known. Therefore, we have initiated a series of studies aimed at evaluating the CF_3O_x radical chemistry. Since this work was initiated, and part of it reported, other indirect studies of reactions 3 and 4 have appeared in the literature.[14–16] They will be quoted and discussed in the Discussion section.

In this study, the technique of pulsed laser photolysis/pulsed laser-induced fluorescence, for direct detection of the CF_3O radicals, was used to study the reactions In addition, information

$$CF_3O + NO \rightarrow CF_2O + FNO \qquad (5)$$

$$CF_3O + O_3 \rightarrow \text{products} \qquad (4)$$

$$CF_3O + O_2 \rightarrow CF_2O + FO_2 \qquad (6)$$

on the rate coefficients for the reactionswere also obtained. We

$$CF_3OO + NO \rightarrow NO_2 + CF_3O \qquad (2)$$

$$CF_3OO + O_3 \rightarrow CF_3O + 2\,O_2 \qquad (3)$$

$$O(^3P) + CF_3O \rightarrow \text{products} \qquad (7)$$

recently reported our assessment of the ODP of several HFCs due to the reactions of CF_3O_x radicals.[17] In this report, the details of the methodology employed to obtain the rate coefficients used in our assessment are given. Furthermore, our previous assessment was based on mostly data at 298 K. We have extended these studies to include a measure of the temperature dependence of the CF_3O reaction rate coefficients. In the accompanying paper[18] the reaction rate coefficients of CF_3O with hydrocarbons, the

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major reactive pathways for CF_3O radical loss in the troposphere, are reported.

Experimental Section

A detailed description of the experimental apparatus, photolytic generation of CF_3O, and the methodology for its detection by LIF is given in the accompanying paper.[18] Therefore, only a brief description will be given here. CF_3O radicals were generated by 193-nm photolysis of either bis(trifluoromethyl) peroxide (CF_3OOCF_3) or a mixture of $CF_3Br/O_2/NO$ using an excimer laser (0.1–6.0 mJ pulse^{-1} cm^{-2}, ~20 ns wide, 5–10 Hz). CF_3O concentrations were probed by exciting the $\tilde{A}(^2A_1) \leftarrow \tilde{X}(^2E)$ (0–0 band) electronic transition at 350.33 nm[10,18,19] using a XeCl excimer laser-pumped dye laser (0.4–4 mJ pulse^{-1} cm^{-2}, ~8 ns wide, 5–10 Hz). The red-shifted fluorescence was collected orthogonal to the photolysis and probe beams by a 5-cm focal length lens, passed through an aperture and a bandpass filter (λ = 365 ± 6 nm), and imaged onto a slit in front of a photomultiplier tube. The signal from the photomultiplier tube was fed into a gated charge integrator and to a microcomputer for data analysis. The delay time between the photolysis and the probe beam was varied between 10 μs and 50 ms, to construct the temporal profile of CF_3O. The energy of the photolysis and the probe beams were monitored by disk calorimeters to check the stability of their fluence.

All experiments were carried out in a large excess of He (Bureau of Mines, ≥99.9997%) under slow gas flow conditions (linear velocity of 2–10 cm s^{-1}) with the gas flow being orthogonal to the photolysis laser axis. CF_3Br (Great Lakes Chem. Corp., >99%), N_2 (Scott Gases, ≥99.9995%), O_2 (Scott Gases, ≥99.99%), and CH_4 (Scott Gases, >99.99%) were added above the reaction cell to the main flow of He via calibrated mass flow meters. NO (Scientific Gases, 99.0%) was passed through a silica gel trap at dry ice temperatures into a 12-L glass bulb and diluted with He (≈0.5–2.0%); the concentrations of NO in these mixtures were determined manometrically. NO was added to the main flow just at the entrance to the reactor to reduce any possible reactions with other constituents in the main flow. The concentrations of these gases in the reactor were calculated from the individual mass flow rates and the cell pressure, which was measured by a capacitance manometer. CF_3OOCF_3 was synthesized by Prof. Darryl DesMarteau of Clemson University and had a stated purity of 99% with the major impurity being CF_3OCF_3 (<1% by FTIR). It was added to a 4-L stainless steel cylinder and diluted with He to generate ≈1–4% mixtures. This mixture was added to the main flow just upstream of the reaction cell. Its concentration in the gas mixture flowing through the cell was measured on-line by absorption at 184.9 nm ($\sigma = 1.07 \times 10^{-19}$ cm^2 molecule^{-1}, measured during this work) after exiting the reactor. Ozone was purified as described previously[20] and diluted with He (1–2.5%) in a blackened 12-L bulb. About 20 Torr of O_2 was usually added to help stabilize the O_3 in the mixture. The concentrations of O_3 in the gas mixture flowing through the reactor were measured by UV absorption at 253.7 nm ($\sigma = 1.15 \times 10^{-17}$ cm^2 molecule^{-1}).[21]

The reactor temperature was regulated by flowing cooled methanol or heated ethylene glycol from temperature-regulated baths through its jacket. The temperature across the reaction volume (the intersection of the photolysis and probe lasers) was measured by a calibrated thermocouple inserted through a movable injector opposite the photomultiplier tube under gas flow conditions identical to those in the experiments. The temperature across the reaction volume was constant and is accurate to ±0.5 K.

Results

The details of the chemistry and data analysis were different for the various reactions. Therefore, for ease of presentation, we will discuss the reactions individually.

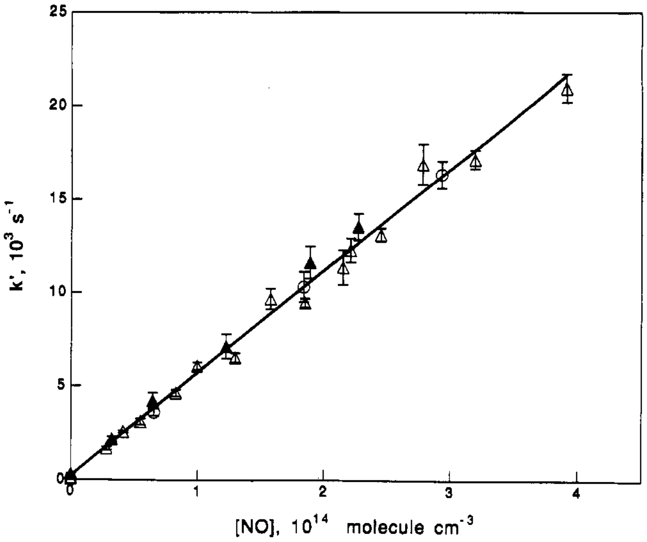

Figure 1. Plot of k' vs [NO] at T = 298 K. Δ, P = 100 Torr of He; ○, 35 Torr of He; ▲, 20 Torr of He. The line is the linear least-squares fit to all of the data.

TABLE 1: Rate Coefficients for the Reaction of CF_3O With NO

T, K	pressure He, Torr	[NO], 10^{14} molecule cm^{-3}	$[CF_3O]_0$,[a] 10^{11} molecule cm^{-3}	($k_5 \pm 2\sigma$),[b] 10^{-11} cm^3 molecule^{-1} s^{-1}
360	100	0.20–3.30	5.0	5.18 ± 0.16
327	100	0.20–3.30	5.0	5.66 ± 0.18
298	70[c]	0.40–16.0	*d*	5.46 ± 0.40
	20	0.30–2.30	4.0	5.80 ± 0.16
	35	0.60–3.00	4.0	5.54 ± 0.15
	98	0.28–2.80	5.0	5.69 ± 0.24
	108	0.40–4.00	1.0–5.0	5.43 ± 0.30
			av at 298 K	5.62 ± 0.48
279	100	0.24–3.10	7.0	5.93 ± 0.48
260	100	0.25–3.50	7.0	5.97 ± 0.34
247	100	0.35–3.10	7.0	6.46 ± 0.18
233	100	0.24–3.40	4.0	6.73 ± 0.34

[a] $[CF_3O]_0$ is calculated assuming a CF_3O quantum yield from CF_3OOCF_3 photolysis at 193 nm of 2 and an absorption cross section of ~6×10^{-20} cm^2 molecule^{-1}. [b] σ is obtained from the precision of a linear least-squares fit of the k' vs [NO] data. [c] This experiment employed the 193-nm photolysis of $CF_3Br/O_2/NO$ as the source of CF_3O; all other experiments used CF_3OOCF_3 photolysis at 193 nm. [d] In this system CF_3O is generated not directly but via the CF_3OO + NO reaction. The initial CF_3 concentrations (which were converted rapidly to CF_3OO) were approximately (2–7) × 10^{12} molecules cm^{-3}.

CF_3O + NO (k_5). The CF_3O + NO reaction was studied by 193-nm photolysis of CF_3OOCF_3 (~8×10^{14} molecules cm^{-3}) to generate CF_3O in an excess of NO ({2–40} × 10^{13} molecules cm^{-3}) and buffer gas (20–108 Torr of He). The CF_3O temporal profile was governed by the reactions

$$CF_3OOCF_3 + h\nu \rightarrow 2CF_3O \tag{8a}$$

$$CF_3OOCF_3 + h\nu \rightarrow \text{other photoproducts} \tag{8b}$$

$$CF_3O + NO \rightarrow \text{products} \tag{5}$$

$$CF_3O \rightarrow \text{loss} \tag{9}$$

where reaction 9 represents diffusive loss of CF_3O out of the reaction zone (the intersection of the two laser beams) as well as loss due to reactions with the CF_3OOCF_3 precursor, other photolytically produced radicals, and possible impurities. In an excess of [NO], the CF_3O loss rate obeys pseudo-first-order kinetics. The temporal profile of CF_3O can be described by

$$[CF_3O]_t = [CF_3O]_0 \exp(-k't) \tag{I}$$

where $k' = k_5[NO] + k_9$. In the absence of [NO], the CF_3O

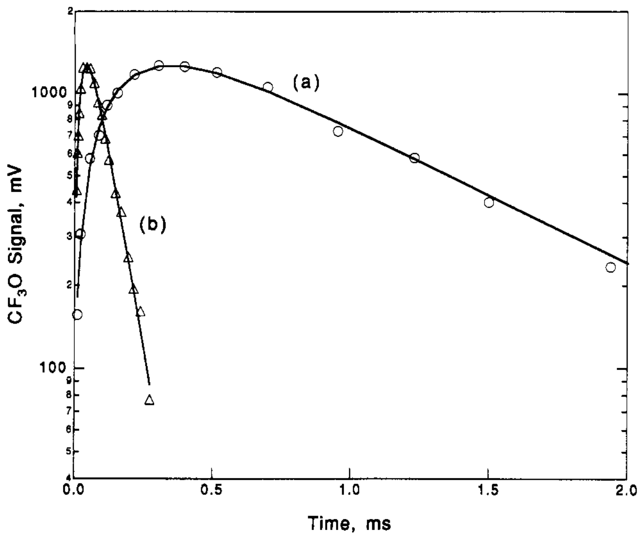

Figure 2. CF$_3$O temporal profiles following the 193-nm photolysis of CF$_3$Br (1.1×10^{16} molecules cm^{-3}), O$_2$ (5 Torr) and NO: curves are (a) [NO] = 9.2×10^{13} molecules cm^{-3} and (b) [NO] = 2.23×10^{14} molecules cm^{-3}. The lines are fits to eq III.

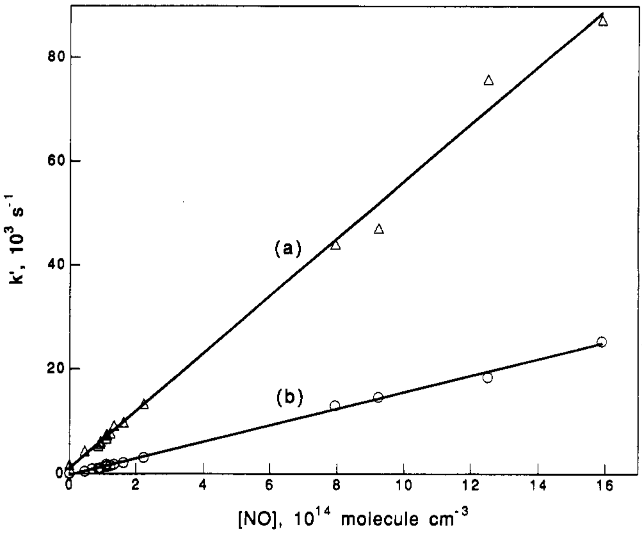

Figure 3. Plots of (a) k'_a and (b) k'_d vs [NO] obtained from the photolysis of CF$_3$Br (1.1×10^{16} molecules cm^{-3}), O$_2$ (5 Torr) and NO. See text for description of k'_a and k'_d. These lines are linear least-squares fits.

decays were exponential with a time constant of $k_9 \approx 50$–80 s^{-1}. Profiles of CF$_3$O were strictly exponential under all conditions. The rate coefficients for reaction 5 were obtained from the slopes of plots of k' vs [NO] (Figure 1). Table 1 shows a summary of the obtained rate coefficients and the experimental conditions employed to measure them. At room temperature, the measured rate coefficient was found to be independent of total He pressure (20–108 Torr), photolysis fluence (1–5.5 mJ pulse^{-1} cm^{-2}), and addition of 5 Torr of O$_2$.

At 298 K, a second source of CF$_3$O was also used to check for possible systematic errors. Here CF$_3$Br (1.1×10^{16} molecules cm^{-3}) was photolyzed at 193 nm in an excess of O$_2$ (5–15 Torr), NO ({0.4–16} $\times 10^{14}$ molecules cm^{-3}) and buffer gas (70 Torr of He). The temporal profile of CF$_3$O was observed to be a double exponential (Figure 2), rising from $[\mathrm{CF_3O}]_0 = 0$ to a maximum and then exponentially decaying away. The major reactions occurring in this system are thought to be

$$\mathrm{CF_3Br} + h\nu \rightarrow \mathrm{CF_3} + \mathrm{Br} \qquad (10)$$

$$\mathrm{CF_3} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{CF_3OO} + \mathrm{M} \qquad (1)$$

$$\mathrm{CF_3OO} + \mathrm{NO} \rightarrow \mathrm{CF_3O} + \mathrm{NO_2} \qquad (2)$$

$$\mathrm{CF_3O} + \mathrm{NO} \rightarrow \text{products} \qquad (5)$$

$$\mathrm{CF_3O} \rightarrow \text{loss} \qquad (9)$$

$$\mathrm{CF_3OO} \rightarrow \text{loss} \qquad (11)$$

$$\mathrm{CF_3OO} \rightarrow \mathrm{CF_3O} \qquad (12)$$

Reaction 12 is any process other than reaction 2 that produces CF$_3$O from CF$_3$OO and is assumed to be first order in CF$_3$OO. In the above mechanism, the CF$_3$O temporal profile should be described by the equation

$$[\mathrm{CF_3O}]_t = \frac{(k_2[\mathrm{NO}] + k_{12})[\mathrm{CF_3OO}]_0}{k'_a - k'_d}[e^{-k'_d t} - e^{-k'_a t}] \qquad (\mathrm{II})$$

where $k'_a = k_5[\mathrm{NO}] + k_9$ and $k'_d = k_2[\mathrm{NO}] + k_{11} + k_{12}$. When NO is present, k'_a should be larger than k'_d (using the accepted value[21] for k_2 and our measured value for k_5). In this case the CF$_3$O rise is governed by k'_a and the decay by k'_d. The profiles were fit by a nonlinear least-squares fitting routine to the equation

$$[\mathrm{CF_3O}]_t = A \exp(-k'_a t) + B \exp(-k'_d t) \qquad (\mathrm{III})$$

where k'_a is the pseudo-first-order appearance rate coefficient and k'_d is the pseudo-first-order decay rate coefficient of CF$_3$O. Plots of k'_a and k'_d vs [NO] were linear (see Figure 3), with slopes of $k_5 = (5.46 \pm 0.40) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k_2 = (1.57 \pm 0.35) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.

When CF$_3$Br/O$_2$ was photolyzed, a production of CF$_3$O was also observed even in the absence of NO ($k' \sim 500$–1200 s^{-1}). At long times this CF$_3$O decayed with a loss rate coefficient comparable to that measured for CF$_3$O alone in He (k_9). The appearance rate of CF$_3$O and the magnitude of the signal varied with both photolysis laser fluence and CF$_3$Br concentration, suggesting that CF$_3$O is formed via reactions of photolysis products such as

$$2\mathrm{CF_3OO} \rightarrow 2\mathrm{CF_3O} + \mathrm{O_2} \qquad \Delta^\circ H = -16 \text{ kcal mol}^{-1} \qquad (13)$$

$$\mathrm{Br} + \mathrm{CF_3OO} \rightarrow \mathrm{BrO} + \mathrm{CF_3O} \qquad \Delta^\circ H = -6 \text{ kcal mol}^{-1} \qquad (14)$$

In the absence of NO, $k_{11} + k_{12}$ is larger than k_9. Therefore, the appearance rate of CF$_3$O is governed by k'_d and the decay by k'_a in this case. The intercept of the k'_a vs [NO] plot was approximately equal to the appearance rate coefficient in the absence of NO; therefore, we feel that CF$_3$O production from these reactions is adequately accounted for by assuming reaction 12. This will be further discussed in the next section.

The variation of k_5 with temperature is shown in Figure 4 and is described by the expression $k_5(T) = (3.34 \pm 0.68) \times 10^{-11} \exp[\{160 \pm 45\}/T]$ cm^3 molecule^{-1} s^{-1} over the temperature range 233–360 K. The errors reported are 2σ (precision and an estimated systematic uncertainty of ±10% in [NO] and ±1% in T). The value at $T = 298$ K is $k_5(298\text{ K}) = (5.62 \pm 0.74) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} where the error bars are the 95% confidence limits and include the error in [NO]. Both NASA/JPL[21] and IUPAC/CODATA[22] panels have adopted the following format for representing the uncertainties in the parameters which describe the error limits of a given rate coefficient at temperature T:

$$f(T) = f(298)\{\exp|(\Delta E/R)(1/T - 1/298)|\} \qquad (\mathrm{IV})$$

where $f(298)$ and $f(T)$ are the uncertainties in the rate coefficient at 298 K and at temperature T, respectively, and $\Delta E/R$ is the uncertainty in the activation energy. For reaction 5, $f(298) = 1.2$ and $\Delta E/R = \pm 50$ at the 95% confidence level.

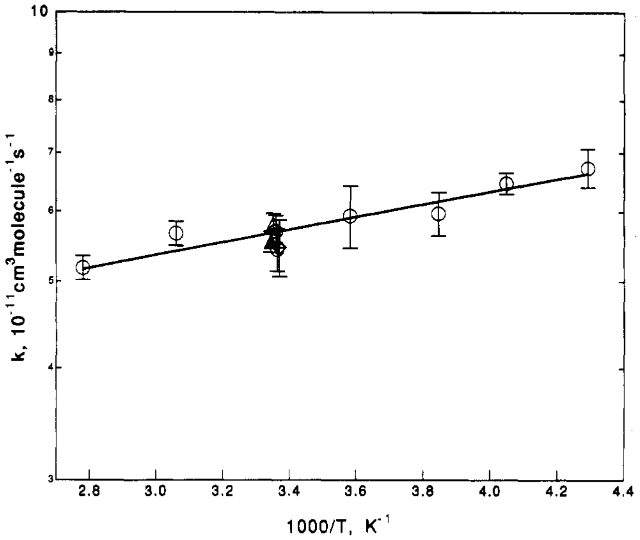

Figure 4. Observed rate coefficients for k_5 vs 1000/T. ○, P = 98 and 108 Torr of He; ▲, P = 35 Torr of He; △, 20 Torr of He; ◇, P = 70 Torr of He and CF_3O produced by $CF_3Br/O_2/NO$ photolysis. The line is the least-squares fit to the data. Error bars are 2σ and include only the experimental precision.

$CF_3O + O_3$ (k_4). In the study of the reaction

$$CF_3O + O_3 \rightarrow \text{products} \tag{4}$$

only CF_3OOCF_3 photolysis could be used as the CF_3O radical source. Even here, the photolysis of O_3 by the 193-nm radiation used to generate CF_3O could cause complications. At laser fluences of 1.0–4.5 mJ pulse^{-1} cm^{-2}, where concentrations of O atoms reached (1.5–7.0) × 10^{12} cm^{-3}, the CF_3O temporal profiles were nonexponential (Figure 5c). Initially, CF_3O decayed rapidly ($k' \approx$ 100–500 s^{-1}) and then, at longer reaction times, exhibited a slower exponential decay (50–80 s^{-1}). This initial fast decay rate coefficient increased with increasing photolysis laser fluence. Addition of N_2 or O_2 (5 Torr) did not influence the observed profile. We attribute the initial fast decay to the reaction of $O(^3P)$ atoms with CF_3O:

$$O(^3P) + CF_3O \rightarrow O_2 + CF_3 \qquad \Delta°H = -14 \text{ kcal mol}^{-1} \tag{7a}$$

$$\rightarrow CF_2O + FO \qquad \Delta°H = -30 \text{ kcal mol}^{-1} \tag{7b}$$

$$\rightarrow CF_3OO\,(+M) \qquad \Delta°H = -50 \text{ kcal mol}^{-1} \tag{7c}$$

To reduce the effects of the O + CF_3O radical chemistry, the extent of O_3 photolysis was suppressed by using low photolysis fluences (≤0.3 mJ pulse^{-1} cm^{-2}) and high [CF_3OOCF_3] (~5 × 10^{15} molecules cm^{-3}). This combination allowed for the generation of $[CF_3O]_0 \approx 2 \times 10^{11}$ molecules cm^{-3} ($\sigma_{193} \approx 6 \times 10^{-20}$ cm^2 molecule^{-1}) while generating <7 × 10^{11} cm^{-3} of O atoms. Under these conditions, the temporal profiles of CF_3O were exponential (Figure 5b) and the pseudo-first-order rate coefficient, $k' = k_4[O_3] + k_9$, varied linearly with O_3 concentration ($[O_3]$ = (0.5–3.2) × 10^{15} molecule cm^{-3}) as shown in Figure 6. (Note that the fraction of O_3 photolyzed was always ~1 × 10^{-4} and hence [$O(^3P)$] scaled with [O_3].) As seen in Figure 6, addition of 13 Torr of O_2 to the reaction mixture did not affect the observed CF_3O decay rate coefficients. Addition of O_2 scavenges any CF_3 radicals (produced either photolytically or by subsequent reactions) and suppresses the reaction

$$CF_3 + O_3 \rightarrow CF_3O + O_2 \tag{15}$$

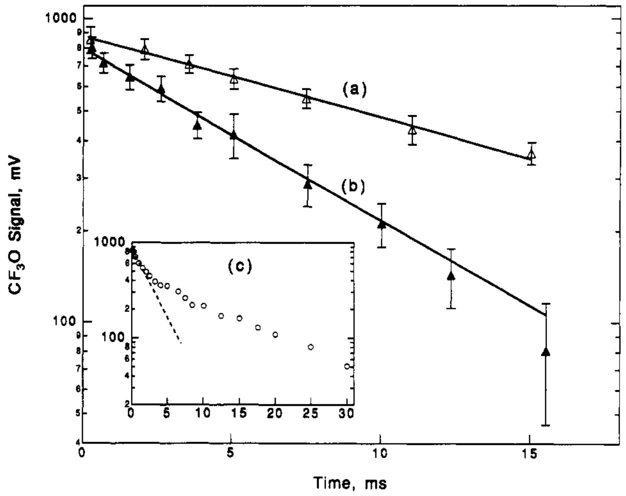

Figure 5. CF_3O temporal profiles following the 193-nm photolysis of CF_3OOCF_3 and O_3. Curves are (a) $[O_3]$ = 0, E = 0.27 mJ pulse^{-1} cm^{-2}; (b) $[O_3]$ = 1.94 × 10^{15} molecules cm^{-3}, E = 0.27 mJ pulse^{-1} cm^{-2}; and (c) $[O_3]$ = 1.20 × 10^{15} molecules cm^{-3}, E = 4.5 mJ pulse^{-1} cm^{-2}. Lines on curves (a) and (b) are fits to eq I. Error bars are the 2σ precision of the experimental data. The dashed line on curve (c) is a fit of the short time data to eq (I) and is used to estimate k_7 (the $CF_3O + O(^3P)$ reaction).

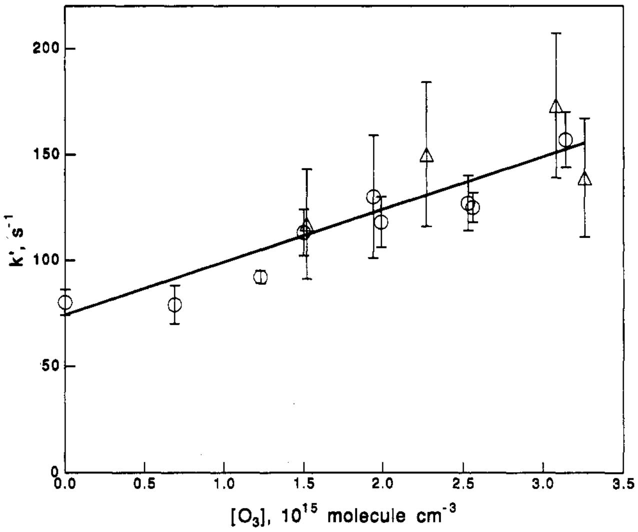

Figure 6. Plot of k'vs $[O_3]$ at T = 298 K. Conditions are [CF_3OOCF_3] = 5 × 10^{15} molecule cm^{-3}; E = 0.27 mJ pulse^{-1} cm^{-2}. ○, P = 100 Torr of He; △, P = 100 of He with 13 Torr of O_2 added.

which could regenerate CF_3O and cause an underestimation of the CF_3O loss rate. From the slope of the weighted linear least-squares fit to the data, a rate coefficient of k_4 = (2.50 ± 0.66) × 10^{-14} cm^3 molecule^{-1} s^{-1} was obtained, where the reported error is 2σ and includes only the precision of the slope. The contributions due to possible systematic error in the measurement of k_4 along with other possible complications from the reactions of photoproducts are discussed in the next section.

We also studied this rate coefficient at 373 K. At these high temperatures and conditions needed to suppress the O atom production (high [CF_3OOCF_3] and low photolysis fluence, as described earlier), a reaction between CF_3O and CF_3OOCF_3 (or an impurity in the CF_3OOCF_3) became significantly fast and made it difficult to observe small changes in the measured decay rates with [O_3]. Yet, we did obtain a value of k_4 = (3.7 ± 1.5) × 10^{-14} cm^3 molecule^{-1} s^{-1} with rather large error bars. Even though this value is, within the stated uncertainty, the same as that at 298 K, it may indicate that k_4 increases with temperature. But it does suggest that the reaction is not much faster at the lower temperatures characteristic of the stratosphere.

$CF_3OO + O_3$ (k_3). The only radical species that we were monitoring during the present study is CF_3O. Yet, by observing

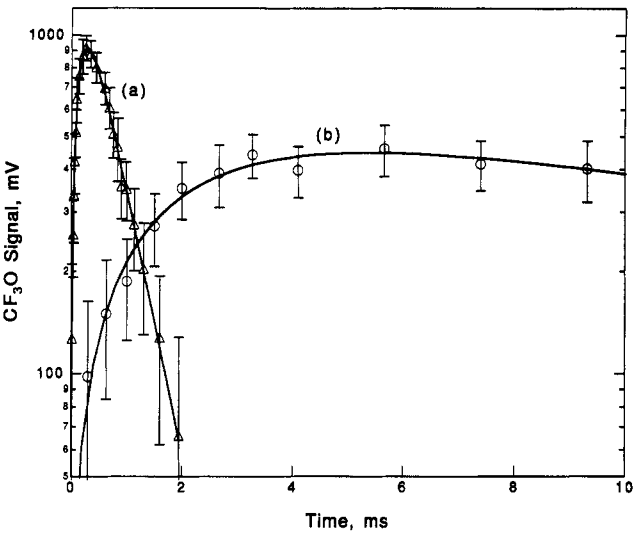

Figure 7. Back-to-back CF_3O temporal profiles from the 193-nm photolysis of CF_3Br (1.1×10^{16} molecules cm^{-3}) and O_2 (5 Torr) with (a) [NO] = 1.04×10^{14} molecules cm^{-3} and (b) $[O_3] = 1.22 \times 10^{15}$ molecules cm^{-3}. Laser fluence was 0.6 mJ pulse^{-1} cm^{-2}. The lines are nonlinear least-squares fit to eq III.

the production of CF_3O from reaction 3, we can get a rough value for k_3. Reaction 3 is most likely the rate-limiting step in the catalytic cycle described in the introduction, and an estimation of k_3 is very useful.

Using $CF_3Br/O_2/NO$ photolysis as a reference system, we measured the ratio of k_4/k_3 by comparing the CF_3O signal when NO was replaced with O_3 in back-to-back runs. These experiments also employed the use of low photolysis fluence ($E < 0.7$ mJ pulse^{-1} cm^{-2}) to reduce the photolysis of O_3. Typically the NO concentration was maintained at $\approx 1 \times 10^{14}$ molecules cm^{-3}, while the O_3 concentration was varied in the range $(1.0–4.0) \times 10^{15}$ molecules cm^{-3}.

Initially, $CF_3Br/O_2/NO$ was photolyzed and the CF_3O temporal profile was measured and fitted to eq III. The preexponential factor (A in eq III) is

$$A = k'_d[CF_3OO]_0/\{k'_a - k'_d\} \qquad (V)$$

when $k_2[NO] + k_{12} \gg k_{11}$ (which is the case in the present experiments). A signal proportional to $[CF_3OO]_0$ was calculated from the coefficients obtained in the fit. NO was then replaced by O_3 and a second temporal profile was measured (see Figure 7). CF_3O was observed to rise to a maximum ($k'_a \approx 500–700$ s^{-1}) and then slowly decay ($k'_d \approx 50–80$ s^{-1}). If we assume that only reactions 3 and 4 govern the CF_3O temporal profile, the CF_3O signal should reach a steady state concentration governed by

$$[CF_3OO]_{ss}/[CF_3O]_{ss} = k_4/k_3 \qquad (VI)$$

The observed CF_3O concentrations would not be constant because both CF_3OO and CF_3O are removed by loss processes other than reactions 3 and 4 such as diffusion. If we assume these losses to be small, by mass balance, $[CF_3OO]_{ss} = [CF_3OO]_0 - [CF_3O]_{ss}$. Then, the ratio of k_4/k_3 can be determined by using the maximum CF_3O signal in the run with O_3 present ($[CF_3O]_{ss} \approx [CF_3O]_{max}$) and the signal calculated for $[CF_3OO]_0$ in the NO run. For eight back-to-back runs, a value of $k_4/k_3 = 7.5 \pm 2.5$ (2σ, precision only) was measured.

There are several complications in these experiments which suggest that the CF_3O temporal profile is not governed solely by reactions 4 and 3. The appearance rate coefficient, k'_a, did not vary with $[O_3]$ within the uncertainty of our nonlinear least-squares fits and was much faster than expected from our measured value for k_4. As mentioned in the last section, photolysis of the CF_3Br/O_2 mixture (without NO) also led to a production of CF_3O. The temporal profile of CF_3O in the absence of O_3 was very similar to that when O_3 is present. Therefore, it is difficult to make definite conclusions about the photochemistry involved upon O_3 addition. However, the most probable reactions of the various radicals generated in this experiment (CF_3OO, Br, BrO, $O(^3P)$) all will likely produce CF_3O:

$$BrO + CF_3OO \rightarrow Br + O_2 + CF_3O$$
$$\Delta°H = -12 \text{ kcal mol}^{-1} \qquad (16)$$

$$O(^3P) + CF_3OO \rightarrow O_2 + CF_3O$$
$$\Delta°H = -69 \text{ kcal mol}^{-1} \qquad (17)$$

$$O(^3P) + CF_3Br \rightarrow Br + CF_3O$$
$$\Delta°H = -36 \text{ kcal mol}^{-1} \qquad (18)$$

These production reactions are in addition to reactions 13 and 14 and only add to the maximum CF_3O signal. Therefore, our measurement of k_4/k_3 is likely a lower limit for this ratio. Therefore, we feel confident that $k_4/k_3 \geq 5$. Using the measured value of k_4, we calculate $k_3 \leq 7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}.

$CF_3O + O_2$ (k_6). The reaction

$$CF_3O + O_2 \rightarrow FO_2 + CF_2O \qquad \Delta H° = +10 \text{ kcal mol}^{-1} \qquad (6)$$

was studied by photolyzing CF_3OOCF_3 ($\sim 1 \times 10^{15}$ molecules cm^{-3}) at 193 nm in an excess of O_2 ($\{1–6\} \times 10^{17}$ molecules cm^{-3}). No evidence for production of O atoms from O_2 photolysis was observed. Previous work in our lab has shown that the ≈ 1.5-m path length of the 193-nm photolysis laser through the laboratory to the reactor cell is sufficient to remove any laser light that can photodissociate O_2. Any effects of O_2 on the diffusional loss of CF_3O was accounted for by substituting N_2 for the added O_2. At 298 K, no reaction was observed and an upper limit of $k_6 \leq 2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} was obtained. However, due to the overwhelming abundance of O_2 relative to other reactants in the atmosphere, even such a slow reaction could completely dominate the CF_3O loss. Since the barrier to reaction is estimated by thermochemistry[23] to be at least 10 kcal mol^{-1}, it may be measurable at higher temperatures. Therefore, we attempted to measure this rate coefficient at 373 K. Again, no reaction again could be observed at 373 K upon addition of 19 Torr of O_2. Within the 2σ error bars of the measured decay slopes, we estimate that $k'_6 \leq 20$ s^{-1}. This leads to an upper limit of $k_6 \leq 4 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 373 K. When O_2 was added, CF_3O could possibly be regenerated via the sequence

$$CF_3O + O_2 \rightarrow FO_2 + CF_2O \qquad \Delta H° = +10 \text{ kcal mol}^{-1} \qquad (6)$$

$$FO_2 + M \rightleftharpoons F + O_2 + M \qquad \Delta H° = +13 \text{ kcal mol}^{-1} \qquad (19)$$

$$F + CF_3OOCF_3 \rightarrow CF_3OF + CF_3O$$
$$\Delta H° = +2 \text{ kcal mol}^{-1} \qquad (20)$$

obscuring any CF_3O loss. Even though reaction 20 is endothermic, it may be significant at elevated temperatures. To test this possibility, a small amount of CH_4 ($[CH_4] = 5 \times 10^{13}$ molecules cm^{-3}) was added to the reaction cell. This amount of CH_4 was small enough not to cause any observable change in k' due to $CF_3O + CH_4$ reaction ($k_{CH_4}(373\text{ K}) = 4.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}),[18] but it was easily enough to scavenge any F atoms produced via photolysis or reaction 19 due to the rapid reaction[21,22]

$$F + CH_4 \rightarrow HF + CH_3 \qquad (21)$$

Note that reaction 20 is endothermic and, hence, much slower than the collision frequency. Upon addition of the CH_4 with 19

Torr of O_2, no increase in the CF_3O decay was observed, and we conclude that CF_3O is not being regenerated by this mechanism in our system. Some preliminary experiments have shown that the 248-nm photolysis of CF_3OOCF_3 produces a small amount of F atoms. We do not, however, observe an increase in CF_3O at short reaction times when only CF_3OOCF_3 is photolyzed; thus, reaction 20 is an unlikely source of CF_3O in the above experiments.

Discussion

CF_3O + NO (k_5). The rate coefficient for the reaction of CF_3O with NO has been reported to be $k_5 = (2.0 \pm 1.0) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K from an earlier study by our colleagues Bevilacqua *et al.* in the NOAA laboratory.[9] This value is nearly a factor of 3 lower than the value reported here. In the present study, CF_3O was generated directly and not via the CF_3OO radical, and heterogeneous wall loss of CF_3O was absent. Bevilacqua *et al.* produced CF_3O via the CF_3OO + NO reaction (similar to our $CF_3Br/O_2/NO$ photolysis system) and monitored its rise and decay. By independently measuring the rate coefficient for the CF_3OO + NO reaction, they estimated the CF_3O + NO rate coefficient using computer simulations of the measured CF_3O temporal profiles.[9] A subsequent study by Jensen *et al.*[24] using the same apparatus but a direct source of CF_3O (unlike the indirect CF_3OO + NO source used by Bevilaqua *et al.*) yielded a rate coefficient of $k_5(295\text{ K}) = (5.1 \pm 1.1) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, in good agreement with our value obtained using the PLP/PLIF system. Jensen *et al.*[24] have discussed the possible reasons for the lower value measured by Bevilacqua *et al.* and the new value supersedes that of Bevilacqua *et al.* The value published recently by Sehested and Nielsen[13] of $k_5(295\text{ K}) = (5.2 \pm 2.7) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} is also in good agreement with the measurement reported here.

Since the quantum yield for CF_3O production from the 193-nm photolysis of CF_3OOCF_3 is not known, it was necessary to determine if reactions of any other photoproducts could be affecting the observed CF_3O temporal profiles. Three likely photodissociation products (in addition to CF_3O) are F atoms and CF_3 or CF_3OO radicals. If F atoms were produced, regeneration of CF_3O is possible via reaction 20. However, if this reaction were significantly fast, a time-dependent production of CF_3O should be observed when no reactants were present. The CF_3O temporal profiles measured with only CF_3OOCF_3 and He were strictly exponential with a time constant of $\approx$50–80 s^{-1} in the absence of any reactant. Therefore, if reaction 20 occurs, its effects are negligible on the observed CF_3O temporal profiles. If photolysis of CF_3OOCF_3 yields CF_3OO radicals, then a slow production of CF_3O via reaction 2 could occur and lead to an underestimate of k_5. Computer simulations of reactions 2, 5, 9, and 11 suggest that nonexponential CF_3O temporal profiles (exhibiting a regeneration of CF_3O at along times) should be observed in our data if CF_3OO was produced with a significant quantum yield ($\Phi(CF_3OO) \geq 0.35$). However, our observed CF_3O temporal profiles were strictly exponential until >95% of the CF_3O had reacted away. To test for the presence of CF_3 radicals, 5–10 Torr of O_2 was added. In the presence of O_2, any CF_3 should be converted to CF_3OO. Generation of CF_3O should then be observed as discussed for the case of CF_3OO. Addition of O_2 had no effect on the CF_3O temporal profiles. Furthermore, if reactions between two radicals were influencing the measurement of k_5, the measured rate coefficient we obtained should depend upon laser fluence. However, the measured value of k_5 was independent of the laser fluence. These observations suggest that photolytic production of CF_3 and CF_3OO is small enough not to influence our measured rate coefficients.

A second photolytic system ($CF_3Br/O_2/NO$) at 298 K was also used to further check for possible systematic errors. CF_3Br photolysis at 193 nm is known to generate Br (along with CF_3) with unit quantum yield.[25] Upon addition of 5 Torr of O_2, reaction 1 should go to completion within a few microseconds ($k_1(100\text{ Torr}) \approx 4.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}).[21] The temporal profile of CF_3O should then be primarily governed by the consecutive reactions 2 and 5. When the production rate is faster that the loss rate in a series of consecutive reactions, the rate of appearance of the intermediate species (here, CF_3O) is governed by the faster removal process and the loss by the slower formation process. From the appearance of CF_3O, a rate coefficient for reaction 5 was measured to be in excellent agreement with that obtained using CF_3OOCF_3 photolysis. From the disappearance of CF_3O a value for the rate coefficient of the reaction

$$NO + CF_3OO \rightarrow NO_2 + CF_3O \tag{2}$$

was found to be $k_2 = (1.57 \pm 0.38) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} (the quoted uncertainty is at the 95% confidence level including a ±10% uncertainty in [NO]). This is in excellent agreement with the recommended value[21] and provides a confirmation of the photochemistry assumed here.

As briefly discussed in the results section, photolysis of only CF_3Br/O_2 at 193 nm showed a production of CF_3O. The dependence of the appearance rate coefficient upon laser fluence and $[CF_3Br]$ suggested that this CF_3O is produced by photolytically generated radicals reacting with each other or with a stable precursor. Since initial radical concentrations were relatively high ($[CF_3]_0 = [Br]_0 \approx (2\text{–}7) \times 10^{12}$ molecules cm^{-3}), radical-radical reactions are likely. Reaction 13 and 14 are the most likely candidates to explain the observed CF_3O profiles. The rate coefficient for reaction 13 has been measured to be $k_{13} = 1.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} by both Nielsen *et al.*[26] and Maricq and Szente.[27] Reaction 14 has not been studied to our knowledge. For the production of $[CF_3]_0 = [Br]_0 \approx 7 \times 10^{12}$ molecules cm^{-3}, the observed appearance rate (from the fit to eq III which assumes first-order kinetics) was $\sim$1500 s^{-1}, suggesting that reaction 14 may be quite rapid. If reaction 14 is responsible for the CF_3O production, then addition of NO will not have a significant effect upon this CF_3O production, since the combination of halogens with NO is relatively slow[28] compared to reactions 2 and 5. The fitted appearance rate coefficient in the absence of NO was within the 1σ error bars of the intercept of the k'_a vs [NO] plot, suggesting that the chemistry generating CF_3O in the absence of NO is not significantly altered when NO was added. Therefore, we feel that this system does provide a reliable measurement of the rate coefficient of reaction 5.

The rate coefficient for reaction 5, shown in Figure 4, exhibits a slight negative temperature dependence. Jensen *et al.* also observe a weak negative temperature dependence.[24] This is not unexpected for a fast radical–radical reaction. It may occur via a short-lived intermediate:

$$CF_3O + NO \rightleftharpoons [CF_3ONO]^* \rightarrow CF_2O + FNO$$

which rapidly decomposes to products. The low-pressure flow tube studies of Jensen et al.[23] yields the same rate coefficient as that measured here at higher pressures and suggests that k_5 is independent of pressure (from 1 to 100 Torr of He). The value of k_5 reported by Sehested and Nielson (which is in good agreement with that reported here) was measured in 900 mbar of SF_6,[13] supporting the conclusion that k_5 is pressure independent. Thus, the $[CF_3ONO]^*$ intermediate, if formed, decomposes very rapidly and is not stabilized by collisions. Our data do not rule out, however, the possibility that a small fraction of the intermediates could be stabilized under atmospheric conditions. Niki and coworkers[11b] have observed quantitative conversion of CF_3O to FNO and CF_2O in reaction 5 and observed no evidence for the formation of CF_3ONO or other products in an atmosphere of air.

$CF_3O + O_3$ (k_4). Indications of unwanted photochemistry were apparent in our system at high photolysis laser fluences, as described in the last section. Since the absorption cross section of O_3 at 193 nm is approximately a factor of 7 larger than that of CF_3OOCF_3, significant amounts of O_3 were photolyzed. Addition of N_2 did not alter the observed CF_3O profiles, suggesting that $O(^1D)$ produced by O_3 photolysis ($\Phi\{O(^1D)\} = 0.5$)[20] was not the cause of the observed secondary chemistry. Furthermore, at the high concentrations of O_3 used, $O(^1D)$ would be consumed on a much shorter time scale ($\tau < 20\ \mu s$) than the time scales for CF_3O observations. Addition of O_2 also did not affect the observed CF_3O temporal profiles, suggesting CF_3 radicals, which would be converted to CF_3OO upon O_2 addition, was negligible. However, reactions of $O(^3P)$ atoms ($\{1.5–7.0\} \times 10^{12}$ cm^{-3}) could not be ruled out. $O(^3P)$ was generated both by direct photolysis of O_3 and via the reactions of $O(^1D)$ and $O_2(^1\Sigma)$, the other photoproducts of O_3 photolysis at 193 nm,[20] with O_3:

$$O(^1D) + O_3 \rightarrow O(^3P) + O(^3P) + O_2 \qquad (22a)$$

$$\rightarrow 2O_2 \qquad (22b)$$

$$O_2(^1\Sigma) + O_3 \rightarrow O(^3P) + 2O_2 \qquad (23)$$

By calculating the total concentrations of $O(^3P)$ produced by the above processes and fitting the initial CF_3O decay to eq I, we estimate that the reaction of $O(^3P)$ with CF_3O occurs with a rate coefficient of $k_7 \approx 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Such a fast rate coefficient is to be expected for an exothermic radical–radical reaction.

At low laser fluences the photolysis of O_3 was minimized to make $[O]_0 \leq 7 \times 10^{11}$ cm^{-3}. Under these conditions exponential decays of CF_3O were observed. These low fluence decays of CF_3O were still not affected by addition of 13 Torr of O_2. As described in the previous section, the addition of O_2 suppresses the possible reaction

$$CF_3 + O_3 \rightarrow CF_3O + O_2 \qquad (15)$$

Such a reaction could obscure the CF_3O decay or slow it down. If F atoms were photolytically produced, then the large concentrations of O_3 used in these experiments would rapidly set up a steady state of F and FO radicals:

$$F + O_3 \rightarrow FO + O_2 \qquad (24)$$

$$FO + O_3 \rightarrow F + 2O_2 \qquad (25)$$

There is some controversy whether reaction 25 is rapid or not[21] which would affect both $[F]_{ss}$ and $[FO]_{ss}$. However, F atoms could regenerate CF_3O only via reaction 20, which, as described previously, was not observed to be important. FO could generate CF_3O via the reaction

$$FO + CF_3OOCF_3 \rightarrow CF_3OOF + CF_3O \qquad (26)$$

To our knowledge the heat of formation of CF_3OOF is not known, but by assuming the O–O bond energy in CF_3OOF is the same as in CF_3OOH ($\Delta^\circ H_f = -196$ kcal mol^{-1}),[23] we estimate that $\Delta^\circ H_f$ (CF_3OOF) ≈ -179 kcal mol^{-1}. This makes reaction 26 exothermic by 2 kcal mol^{-1} and a possible source of interference. Reaction 26 can be ruled out to a large extent since it will be independent of $[O_3]$. If reaction 26 were very important, a production of CF_3O should have been observed at low ozone concentrations. However, only exponential decays of CF_3O were observed, even at low $[O_3]$.

Another secondary reaction which may interfere with the measurement of k_4 is

$$O(^3P) + CF_3OOCF_3 \rightarrow CF_3O + CF_3OO \qquad \Delta^\circ H = -2 \text{ kcal mol}^{-1} \quad (27)$$

This possibility, which could generate CF_3O, was investigated by photolyzing CF_3OOCF_3/O_3 mixtures at 248 nm in 100 Torr of N_2. At 248 nm, the O_3 cross section is $\approx$5000 times larger than that of CF_3OOCF_3.[21,29] Low concentrations of O_3 ($\sim 5 \times 10^{13}$ molecules cm^{-3}) and high CF_3OOCF_3 (3×10^{15} molecules cm^{-3}) were used to generate $O(^3P)$ concentrations on the order of $(1.0–2.0) \times 10^{12}$ cm^{-3} while not generating a measurable amount of CF_3O from CF_3OOCF_3 photolysis. Under these conditions, production of CF_3O was not observed even out to 40 ms. Thus, we can place an upper limit for $k_{27} \leq 5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. Since this reaction is slow, it cannot contribute to lowering the value of k_4.

At 298 K, we report a rate coefficient of $k_4 = (2.5^{+0.7}_{-1.5}) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The error bars are chosen to include the observed experimental error, as well as taking into account the uncertainties in $[O_3]$ ($\pm 5\%$) and contribution from reaction 7 to the measured decays of CF_3O. The latter uncertainty was estimated via computer simulations of the sequence of reactions 4, 7, 9, 11, 22, and 23 using the known laser fluence and $[O_3]$ to calculate the initial radical concentrations. The rate coefficient for reaction 7 was set at 5×10^{-11} cm^3 molecule^{-1} s^{-1} (since this estimation was also based on a similar calculation of the oxygen atom concentration), while k_4 was varied in the range $(0.15–2.5) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

Our measured value of k_4 is much slower than the earlier estimate of Biggs *et al.*[12] These investigators estimated at 298 K value of $\sim 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} from experiments where O_3 loss was observed following CF_3Cl photolysis. The rapid O_3 loss observed in such experiments may be due to the presence of other free radicals. Our measured low value is consistent with the directly measured value of $k_4 \leq 4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} of our colleagues, Jensen *et al.*[24] It is also consistent with several recent indirect studies of the $CF_3O + O_3$ reaction which were reported during the completion of this work. Upper limits of ≤ 10, 5, and 3×10^{-14} cm^3 molecule^{-1} s^{-1} were reported by Nielsen and Sehested,[14] Maricq and Szente,[16] and Wallington *et al.*,[15] respectively. This rate coefficient is also consistent with the growing body of evidence suggesting that the reactivity of CF_3O is similar to that of OH.[11,18] The OH + O_3 reaction has a similar rate coefficient of 6.8×10^{-14} cm^3 molecule^{-1} s^{-1} at 298 K.[21] As stated in the last section, it appears that k_4 increases with increasing temperature, but the uncertainty of the data is too large to conclusively ascertain the temperature dependence. The rate coefficient for reaction 4 would be expected to exhibit a positive temperature dependence based on analogy with the OH + O_3 reaction, which has an activation energy of 1880 cal mol^{-1}.[21] Therefore, it is very unlikely to be faster at stratospheric temperatures than the value reported at 298 K.

$CF_3OO + O_3$ (k_3). To fully evaluate the role of CF_3O_x in possible stratospheric ozone depletion, the rate coefficients and products of the reaction of $CF_3OO + O_3$ must also be well characterized. If rapid, reaction 3 may also act to regenerate CF_3O on a fast time scale, thereby causing an underestimate of the $CF_3O + O_3$ rate coefficient in this study. To get a measure of the k_3 relative to k_4, we photolyzed CF_3Br/O_2 mixtures to generate CF_3OO. By monitoring the production of CF_3O when either NO or O_3 was present, we could obtain k_4/k_3. As described in the previous section, we measured $k_4/k_3 = 7.5 \pm 2.5$, and the production of CF_3O from the photolysis of CF_3Br/O_2 alone appeared quite similar to the temporal profile when O_3 was added. In several runs it was even difficult to observe the difference between the two profiles. We were unable to gain an unequivocal explanation for the chemistry which produced CF_3O in this system. However, as explained earlier, nearly all the possible secondary reactions that could be taking place produce CF_3O. The only exception is reaction 7. This reaction consumes CF_3O (lowering $[CF_3O]_{max}$) and possibly produces CF_3OO (via formation of CF_3 in channel 7a). Under our experimental conditions, the most likely fate for $O(^3P)$ atoms are its reactions with CF_3OO and BrO radicals which are present at much higher concentrations than CF_3O ($[CF_3OO] \approx [BrO] = 3 \times 10^{12}$ molecules cm^{-3}, $[CF_3O]_{max} \leq 2 \times 10^{11}$ molecules cm^{-3}). The measured $[CF_3O]_{max}$ was also independent of $[O_3]$ (the photolytic source of O atoms), suggesting that reaction 7a could not have been significant. Therefore, we report our ratio as a lower limit, $k_4/k_3 \geq 5$, yielding an upper limit for reaction 3, $k_3 \leq 7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. This is consistent with $k_3 \leq 3 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, measured by Jensen *et al.*, who monitored CF_3OO directly in an excess of O_3 and the presence of a CF_3O scavenger.[24] The studies of Nielsen and Sehested[14] and Maricq and Szente[16] (both of whom monitored CF_3OO directly by UV absorption) report upper limits for reaction 3 of $\leq 5 \times 10^{-14}$ and $\leq 1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, respectively, which is consistent with the limit reported here.

$CF_3O + O_2$. No reaction could be observed between CF_3O and O_2 at both 298 and 373 K. At 373 K, we report an upper limit of $k_6 \leq 4 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}. No complications due to the possible formation of F atoms could be observed. Assuming that the endothermicity of the reaction ($\Delta^\circ H = +10$ kcal mol^{-1}) is the minimum barrier to the reaction, the upper limit at 373 K leads to calculated value at 298 K of $k_6 \leq 1.5 \times 10^{-18}$ cm^3 molecule^{-1} s^{-1}. At the lower stratospheric temperatures (≈ 220 K), this rate coefficient should be $< 5 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1}. End product analysis studies carried out by Chen *et al.*[11b] also observe no evidence for reaction 6 at 298 K in an atmosphere of air.

Implications for the Stratosphere. The rate coefficients measured here have recently been used in both a 2-D dynamical–photochemical model and a semiempirical estimation to determine the ODP of several important CF_3-containing HFCs.[17] Those calculations indicated that the competition between the $CF_3O + O_3$ reaction and the chain termination reaction of CF_3O + NO primarily determines the ODP for these compounds. In addition, the reaction of CF_3O with CH_4 (reported in the accompanying paper)[18] could also be a termination step depending upon the fate of the CF_3OH product. At all altitudes in the stratosphere, reaction 5 is the major sink for CF_3O, and the CH_4 reaction becomes important at low altitudes (10–20 km). CF_3O_x radicals were found to be at least a factor of 1000 less effective at catalytically destroying ozone relative to Cl-catalyzed reactions. For calculations involving HFC 134a (lifetime of 15 years)[17] and HFC 23 (lifetime between 270 and 405 years),[17,30] all possible scenarios led to ODPs of $< 5 \times 10^{-4}$. The best estimate of the ODP for HFC 134a was $(1–2) \times 10^{-5}$.[17] Our present findings essentially substantiate those in our previous paper.

Our previous calculations did not consider the reaction of $CF_3O + O_2$ as a possible loss; however, at temperature characteristic of the lower stratosphere (where CF_3O_x reactions are the most important with regard to ozone depletion),[17] $k_6 < 5 \times 10^{-21}$ cm^3 molecule^{-1} s^{-1} as mentioned earlier and should play a negligible role. Reaction 7 has been discussed by Li and Francisco[31] as possibly being involved in a catalytic ozone depletion cycle.[32] Their *ab initio* study concluded that reaction 7 either proceeded through channel 7a or produced an excited CF_3OO molecule. Our estimate of $k_7 \approx 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} is the same magnitude of the rate coefficient for reaction 5. Since NO concentrations in the stratosphere up to 40 km are at least an order of magnitude greater than that of $O(^3P)$ atoms, catalytic ozone depletion due to reaction 7 cannot be significant. It should be noted that Li and Francisco did not consider that the excited CF_3OO could rearrange and eliminate FO and CF_2O (reaction 7b). This would be analogous to the elimination of FNO and CF_2O from a short lived CF_3ONO complex which is possibly formed in reaction 5. Such a channel for $CF_3O + O(^3P)$ would make this reaction a chain termination step in the stratosphere. Although not necessary for understanding the atmospheric chemistry of CF_3O_x, it would be of interest to clarify both the rate coefficient and product channels for reaction 7.

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