Kinetics and Mechanism of the Reaction of CF₃ Radicals with NO₂

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ABSTRACT

The reaction of CF₃ with NO₂ was studied at 296 ± 2K using two different absolute techniques. Absolute rate constants of $(1.6 \pm 0.3) \times 10^{-11}$ and $(2.1_{-0.3}^{+0.7}) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ were derived by IR fluorescence and UV absorption spectroscopy, respectively. The reaction proceeds via two reaction channels: CF₃ + NO₂ \rightarrow CF₂O + FNO, (70 ± 12)% and CF₃ + NO₂ \rightarrow CF₃O + NO, (30 ± 12)%. An upper limit of 11% for formation of other reaction products was determined. The overall rate constant was within the uncertainty independent of total pressure between 0.4 to 760 torr. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

It is now well established the CFCs (Chlorofluorocarbons) deplete the earths stratospheric ozone layer and that the release of CFCs is the reason for the ozone hole over Antarctica [1]. This has lead to an internationally agreed production stop of CFCs by the end of year 1995. HCFCs (Hydrochlorofluorocarbons) and HFCs (Hydrofluorocarbons) are substitutes for CFCs in air conditioning and refrigeration units, e.g., CF_3CFH_2 (HFC-134a) is used as refrigerant in automotive air conditioning units and CF_3CCl_2H (HCFC-123) is used for other cooling purposes. Both compounds contain CF3 groups. It has been shown that 70% of the CF₃ groups in HFC-134a are released into the atmosphere as CF₃ radicals in the degradation of this compound [2]. Within the last three years a great deal of scientific interest has been given to the impact of CF₃, CF₃O, and CF₃O₂ radicals on the stratospheric ozone layer through reaction (1) and (2):

$$CF_3O + O_3 \longrightarrow CF_3O_2 + O_2$$
 (1)

$$CF_3O_2 + O/O_3 \longrightarrow CF_3O + O_2/2O_2$$
 (2)

It is known that this catalytic cycle is not important due to the loss processes of CF_3O in the atmosphere [3,4]:

Received August 16, 1995; accepted January 16, 1996

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International Journal of Chemical Kinetics, Vol. 28, 579-588 (1996)

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 CCC 0538-8066/96/080579-10

$$CF_3O + NO \longrightarrow CF_2O + FNO$$
 (3)

$$CF_{3}O + CH_{4} \longrightarrow CF_{3}OH + CH_{3}$$
 (4)

Reaction (3) is the most important loss process for CF_3O radicals in the stratosphere. The rate of reaction (3) is almost independent of temperature [3] and is therefore expected to proceed via a $(CF_3ONO)^*$ complex.

In this work we have studied the reaction of CF_3 radicals with NO₂. This reaction is of no importance in the atmosphere since the fate of CF_3 radicals in the atmosphere is entirely reaction with O₂. However, the $CF_3 + NO_2$ reaction is expected to form the $(CF_3ONO)^*$ complex also formed in reaction (3). This work is a fundamental study of the kinetics and mechanism of the reaction of CF_3 radicals with NO₂.

Four studies of this reaction have been reported previously in the literature [5-8]. The reported rate constants for the reaction of CF3 radicals with NO2 are $(2.7 \pm 0.5) \times 10^{-12}$ [5], $(2.5 \pm 0.3) \times 10^{-11}$ [6], and $(2.5 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ [7]. Clearly, the value obtained by Rossi et al. [5] is not in agreement with the two recent studies. There could be two reasons for this discrepancy. The value of $(2.7 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ was derived}$ by fitting a kinetic mechanism to a product distribution and several assumptions were made to determine the rate constant. This procedure could lead to an incorrect value of the rate constant. The rate constant could be pressure dependent under 4 torr total pressure. The pressure in the experimental system used by Rossi et al. [5] were less than 5 mtorr while the pressures in the two more recent studies were 5-20 torr [6] and 4-12 torr [7], respectively. It is interesting to note that a preliminary study by Bevilacqua et al. [8] gave a rate constant of $(1.0 \pm 0.7) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at a total pressure of Helium of 0.8-2.0 torr. This low value indicates that the reaction could indeed be pressure dependent. However, no firm conclusions about the pressure dependence of the reaction between CF₃ and NO₂ could be drawn. To solve this problem, experiments conducted at low pressures (< 1 torr) should be performed. This was not possible with the equipment available in our present study.

The reaction of CF_3 radicals and NO_2 may proceed through four reaction channels:

$$CF_3 + NO_2 \longrightarrow CF_2O + FNO$$
 (5a)

$$\longrightarrow CF_3O + NO$$
 (5b)

$$+ M \longrightarrow CF_{3}ONO + M \qquad (5c)$$

$$+ M \longrightarrow CF_3NO_2 + M$$
 (5d)

Rossi et al. [5] assumed that reaction (5) produces CF_3O and NO while Sugawara et al. [6] report FNO and CF_2O as the only products. However, Sugawara et al. cannot exclude other less important reaction channels. Francisco and Li [7] also report CF_2O as the major product but they also observe NO as a product of reaction (5). Bevilacqua et al. [8] observe all reaction channels with channel (5a) as the most important. Here we present a study using two techniques, IR multiphoton dissociation coupled with IR fluorescence and pulse radiolysis UV absorption spectroscopy, to study the kinetics and mechanism of the reaction of CF_3 radicals with NO₂.

EXPERIMENTAL

IR Fluorescence

NO₂ was obtained by thermal decomposition of Pb(NO₃)₂ and its purity was controlled by IR spectroscopy and gas chromatography. CF3 radicals were generated by IR multiphoton dissociation (IRMPD) of CF₁I (PCR, Research Chemicals, purity > 97%). The CO₂ laser was tuned at the R14 line (1074 cm^{-1}) resonant with the ν_1 mode of CF₃I and a fluence of 0.6 J cm⁻² was used to generate the radicals. The initial pressure of CF₃I was always 0.1 torr whereas the pressure of NO₂ was varied from 0.27 to 0.76 torr. Experiments were carried out in the presence of Ar or N₂ as added inert gases. The pressure of these gases was varied between 0 and 15 torr. The fraction of CF₃I dissociated per pulse in the irradiated zone was approximately 0.03, producing approximately 1014 molecules cm⁻³ CF₃ radicals in the fundamental vibrational state.

The experimental set-up is shown in Figure 1. A SbIn detector (Infrared Associated) with a matched preamplifier was used for the detection of IR fluorescence. The optical path-length was 25 cm. The output signal from the preamplifier was fed to a Tektronik 7633 oscilloscope and was digitized and averaged by a DSA 524 Thurlby Thandar digital storage adaptor. Typically, 40-100 pulses were averaged in each experiment at a repetition rate of 1 Hz.

Since the irradiated volume was only about 10% of the total volume (707 cm³) of the reaction cell and only about 3% of the CF₃I was dissociated in the irradiated zone, the fraction of CF₃I dissociated during the experiments was negligible. To eliminate a radio frequency pick-up by the detector, it was shielded with a Faraday cage made of copper with a small orifice to allow for the IRF entrance. The complete IRF



Figure 1 Scheme diagram of the experimental set-up for the IRF experiment: (1) PC IBM Compatible Computer; (2) DSA (Digital Store Adaptor); (3) Oscilloscope; (4) Detector of SbIn; (5) Gas Filter; (6) Lens f = 7 cm; (7) Galilean telescope; and (8) Fluorescence cell.

detection system was tested for its rise-time, using the scattered light from a Nd:YAG laser with pulses of 10 ns. The rise-time of the detection system was found to be approximately 1 μ s.

To isolate the v_1 and $2v_2$ bands of CF₂O, a band pass filter was used. A typical signal acquired with this set-up is shown in Figure 2 for several pressures of added N₂ buffer.

A Nicolet 55X Fourier Transform infrared spectrometer was used to study the products formed in the reaction cell. Uncertainties are given as two standard deviations if nothing else is stated.

Pulse Radiolysis

The experimental system has been described in detail previously [9,10] and will only be discussed briefly here.

 CF_3 radicals were generated by pulse radiolysis of $SF_6/CF_3H/NO_2$ gas mixtures in a one liter stainless steel reactor with a 30 ns pulse of 2 MeV electrons from a Febetron 705B field emission accelerator. SF_6 was always in great excess and was used to generate fluorine atoms:

$$SF_6 + \xrightarrow{2MeVe^-} F + products$$
 (6)



Figure 2 IR intensity of CF_2O from experiment with 0.1 torr of CF_3I and 0.57 torr of NO_2 at different pressure of added N_2 . The buffer pressure are 0, 4.0, 6.3, and 12.2 torr from the top to the bottom, respectively.

$$F + CF_3H \longrightarrow CF_3 + HF$$
 (7)

The radiolysis dose could be varied by insertions of stainless steel attenuators between the electron accelerator and the reaction cell. The radiolysis dose is given relative to full dose in the following.

To monitor the transient UV absorbance, the output of a pulsed 150 Watt Xenon arc lamp was multipassed through the reaction cell using internal White cell optics (40, 80, and 120 cm path-length). A McPherson grating monochromator, a Hamamatsu R 955 photomultiplier, and a Biomation 8100 waveform digitizer were used to detect and record the light intensity at the desired wavelength. The spectral resolution used was 0.8 nm.

Reagent concentrations used were; SF₆, 899–1000 mbar; CF₃H, 0–100 mbar: NO₂, 0–1 mbar. All experiments were performed at an ambient temperature of 296 \pm 2 K. High purity NO₂ (>98%) was supplied by Linde Techniche Gase and SF₆ (99.9%) by Gerling and Holz. CF₃H (>99.7%) was provided by Fluorochem. All reagents were used as received without further purification.

Two sets of experiments were performed using the pulse radiolysis system. First, the amount of NO_2 lost by reaction (5) and the subsequent reactions and the kinetics of NO_2 was determined from the transient absorbance of NO_2 at 400 nm. Second, the yield of FNO formed was determined at 310.5 nm.

RESULTS

IR Fluorescence

Determination of k_5 . The reactions following the CO₂ laser pulse are:

$$CF_3I + nh\nu \longrightarrow CF_3I^* \longrightarrow CF_3 + I$$
 (8)

$$CF_3 + NO_2 \longrightarrow CF_2O^* + FNO$$
 (5a)

$$CF_2O^* + M \longrightarrow CF_2O + M$$
 (9)

$$CF_3 + NO_2 \longrightarrow Products$$
 (5b-d)

where $M = NO_2$, N_2 , and Ar, and Products represents all reaction products from reaction (5) other than those of channel (5a).

From the above reaction scheme, the concentration of CF_3 radicals is given by:

$$[CF_{3}] = [CF_{3}]_{0} exp(-k_{5}[NO_{2}]t)$$
(I)

and the concentration of vibrationally excited CF_2O is:

$$[CF_{2}O^{*}] = (k_{5a}[NO_{2}][CF_{3}]_{0}/(k_{9}[M] - k_{5}[NO_{2}])) \times (exp(-k_{5}[NO_{2}]t) - exp(-k_{9}[M]t))$$
(II)

Since the IRF signal is proportional to the concentration of CF_2O^* , its temporal evolution is given by the following equation:

$$I(t) = A[\exp(-k_5't) - \exp(-k_9't)]$$
(III)

where k_5' and k_9' are pseudo-first-order rate constants for the total rate of disappearance of CF₃ radicals and for the collisional relaxation of CF₂O^{*}.

The experimental profile of the IRF signal was fitted by eq. (III) using a nonlinear least-squares method, from which the value of k_5' and k_9' were calculated. A plot of k_5' against the pressure of NO₂ is shown in Figure 3. From a linear regression, k_5 was determined to be $(1.6 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

Figure 3 shows the value of k_5 as a function of NO₂ pressure for experiments with the addition of Ar and N₂ buffer gases. The pressures were varied between 2 and 10 torr for N₂ and 2-8 torr for Ar. It can be seen that reaction rate constants are independent of the pressure of the buffer gases within the pressure range used.

Relaxation Processes. The relaxation processes of CF_2O^* in this system are:

$$CF_2O^* + N_2 \longrightarrow CF_2O + N_2$$
 (10)

$$CF_2O^* + NO_2 \longrightarrow CF_2O + NO_2$$
 (11)

$$CF_2O^* + Ar \longrightarrow CF_2O + Ar$$
 (12)

In N_2 buffer gas the overall decay constant is given by:

$$k_{9}' = k_{10}[N_{2}] + k_{11}[NO_{2}]$$
 (IV)

and in Ar buffer gas k_0' is given by:

$$k_{9}' = k_{12}[\text{Ar}] + k_{11}[\text{NO}_2]$$
 (V)

In order to obtain the value of the relaxation rate constant for CF_2O^* with N_2 as the bath gas, k_{10} , experiments were made varying the N_2 pressure from 2 to 10 torr while keeping the pressure of NO_2 constant. The experimental results are shown in Figure 4 for different pressures of NO_2 . The same procedure was used to determine the relaxation rate constant with Ar as buffer gas, k_{12} (see Fig. 5). The slopes of



Figure 3 Reaction rate for disappearance of CF_3 radicals as obtained from the appearance of IRF of CF_2O , as a function of NO_2 pressure, with the addition of $N_2(\bullet)$ and $Ar(\Box)$.

these plots provide the values of k_{10} and k_{12} of $(2.3 \pm 1.4) \times 10^{-13}$ and $(2.6 \pm 1.0) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹, respectively. The ordinates in Figures 4 and 5 correspond to $k_{11}[NO_2]$. The values of $k_{11}[NO_2]$ are plotted as a function of the NO₂ pressure in Figure 6. A straight line obtained by a linear least-squares fit of the experimental data is observed in the figure. The slope of this plot yields a value of k_{11} of $(3.0 \pm 0.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. It is apparent from these results that the most important relaxation process is the relaxation of the excited

 CF_2O by NO_2 , e.g., reaction (11). Therefore, this process must be taken into account for the analysis of relaxation processes.

Reaction Products from IR Fluorescence Experiments. According to previous work [7], the fluorescent species is CF_2O^* . In order to verify this, several experiments were performed to characterize the emitting species. A combination of cold gas filter with a band pass filter was used to isolate the ν_1 and $2\nu_2$ emission bands of CF_2O . When the filter was filled with 400 torr of CF_2O , the amplitude of the signal de-



Figure 4 Relaxation rate of CF_2O^* as a function of N_2 buffer pressure at different initial pressures of NO_2 . For clarity, only three pressures of NO_2 were included in the figure: (\bigcirc) 0.2 torr; (\triangle) 0.4 torr; and (\blacksquare) 0.5 torr of NO_2 . The lines indicate the least-square fits.



Figure 5 Relaxation rate of CF_2O^* as a function of Ar buffer pressure at different initial pressures of NO_2 : (\Box) 0.272 torr and (\odot) 0.57 torr of NO_2 . The lines indicate the least-square fit.

creased to 70%. This confirms that the emission arises mainly from CF_2O .

Finally, 1 torr of CF_3I was photolyzed with the CO_2 laser in presence of 4 torr for NO_2 , using FTIR spectroscopy to characterize the reaction products. The main product observed was CF_2O and a small, but not quantified, amount of CF_3NO_2 . Under these conditions no detectable amounts of FNO or NO were found. When the same reaction mixture was photolyzed in the presence of 760 torr N_2 , the same reaction products were obtained. The reason for the

missing FNO and NO could be wall-reactions in the reaction cell.

Pulse Radiolysis

 CF_3 radicals were produced by pulse radiolysis of gas mixtures of 100 mbar CF_3H , 0.5 mbar NO_2 , and 900 mbar SF_6 :

$$SF_6 + \xrightarrow{2MeV e^-} F + products$$
 (6)

$$F + CF_3H \longrightarrow CF_3 + HF$$
 (7)



Figure 6 Relaxation rate of CF_2O^* as a function of the NO₂ pressure. (•) N₂ buffer and (\Box) Ar buffer. The line indicates the least-square fit.



Figure 7 NO₂ transients at 400 nm using full dose (A) and dose 0.527 (B). The smooth lines are simulations of the experimental transients using the chemical mechanism in Table I with $k_5 = 2.8, 2.2, 2.0, 1.8 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (A) and $k_5 = 2.8, 2.1, 1.8 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (B). $k_{5a}/(k_{5a} + k_{5b}) = 0.7$ and $k_{5b}/(k_{5a} + k_{5b}) = 0.3$ was kept constant.

The transient absorption observed at 400 nm using full and half dose are shown in Figure 7(A) and 7(B), respectively. No transient absorbance was observed upon radiolysis of reaction mixtures that did not contain NO_2 . It therefore seems reasonable to ascribe the loss of absorbance in Figure 7 to a loss of NO_2 . NO_2 is consumed by three different reactions in this system:

$$CF_3 + NO_2 \longrightarrow Products$$
 (5)

$$F + NO_2 + M \longrightarrow FNO_2 + M$$
 (13)

$$CF_3O + NO_2 + M \longrightarrow CF_3ONO_2 + M$$
 (14)

The importance of reaction (13) can be determined from the values of k_7 , k_{13} , $[CF_3H]_0$, and $[NO_2]_0$. k_7 has been determined previously to be $(1.2 - 1.4) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ [11-13]. We choose to use $k_7 = (1.3 \pm 0.2) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ in the following. k_{13} has been determined at our laboratory as $(9.9 \pm 0.6) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ [14]. Using $[CF_3H]_0 = 100$ mbar and $[NO_2]_0 = 0.5$ mbar we derive that $(72.4 \pm 3.9)\%$ of the initially formed F atoms react with CF₃H and $(27.6 \pm 3.9)\%$ react with NO₂. This result will be used in the following.

To determine the importance of reaction (14) in our kinetic system and thereby reaction channel (5b) three different reaction mixtures were radiolysed and the transient absorbance was measured as a function of the dose (see Fig. 8): (i) 0.5 mbar NO₂ and 1000 mbar SF₆ ($\mathbf{\nabla}$); (ii) 0.5 mbar NO₂ and 100 mbar CF₃H (\bigcirc); and (iii) 100 mbar CF₃H, 0.5 mbar NO₂, and 900 mbar SF₆ ($\mathbf{\Theta}$). For all three sets of experiments, the loss of absorbance at 400 nm is proportional to the dose. This indicates that radical-radical reactions are unimportant under these experimental conditions.

In the first set of experiments, F atoms are only lost by reaction with NO_2 :

$$F + NO_2 + M \longrightarrow FNO_2 + M$$
 (13)

The loss of NO₂ therefore equals the amount of F atoms produced by radiolysis of 1000 mbar of SF₆. The slope of the straight line through the filled triangles in Figure 8 is determined by linear regression to be (0.0774 \pm 0.0026). Using this slope and the literature value for the absorption cross section of NO₂ at 400 nm and 296 K, (6.0 \pm 0.6) \times 10⁻¹⁹ cm² [15], we calculate an initial F atom concentration of



Figure 8 Transient absorbance (1 = 120 cm) at 400 nm after all reactions in the reaction system have ceased following pulse radiolysis of 0.5 mbar NO₂ and 1000 mbar SF₆ ($\mathbf{\nabla}$); 0.5 mbar NO₂ and 100 mbar CF₃H (\bigcirc); 100 mbar CF₃H, 0.5 mbar NO₂ and 900 mbar SF₆ ($\mathbf{\Theta}$); and 100 mbar CF₃H, 0.5 mbar NO₂ and 900 mbar SF₆ ($\mathbf{\Theta}$); and 100 mbar CF₃H, 0.5 mbar NO₂ and 900 mbar SF₆ ($\mathbf{\Theta}$) with detection at 310.5 nm. See text for details.

 $(2.47 \pm 0.26) \times 10^{15}$ molecule cm⁻³. This is consistent with recent determinations of the F atom yield determined from the literature value for σ (CH₃O₂) at 260 nm of $(2.77 \pm 0.30) \times 10^{15}$ molecule cm⁻³ [16].

The loss of NO₂ following pulse radiolysis of 100 mbar CF₃H, 0.5 mbar NO₂, and 900 mbar of SF₆ can be determined from the slope of a straight line through the filled dots in Figure 8. The slope found by a linear regression of the filled circles is (0.0927 ± 0.0031) . Before we can determine the loss of NO₂ from this slope, three corrections need to be made. First, we need to correct for the loss of NO, by the CF₃ radicals produced from the direct radiolysis of the 100 mbar of CF₃H. The hollow circles in Figure 8 show the loss of absorbance following pulse radiolysis of 100 mbar CF₃H and 0.5 mbar NO₂. The slope of the straight line through the hollow circles is (0.00785 ± 0.00043) . The corrected slope is then $(0.0927 \pm 0.0031) - (0.00785 \pm 0.00043) =$ (0.0849 ± 0.0053) . Second, we have to divide this slope by 0.9 because we radiolysed only 900 mbar of SF₆ in experiment (ii) compared to experiment (i). This correction gives a slope of (0.0943 ± 0.0059) . Third, a correction need to be made for the fact that not all F atoms react with CF, H. As derived above, only 72.4% of the F atoms react with CF₃H giving CF₃ radicals. The final corrected value of the slope is $(0.1007 \pm 0.0084).$

The NO₂ yield in the system can then be calculated to be $(0.1007 \pm 0.0084)/(0.07739 \pm 0.0026) =$ (1.301 ± 0.117) . This means that the actual NO₂ loss is $(30 \pm 12)\%$ larger than the initial F atom yield. Therefore 30% of the reactions of CF₃ radicals with NO₂ give a radical species that consume another NO₂. The only radical species that can be formed from reaction (5) is CF₃O. This species is known to react with NO₂ to give CF₃ONO₂ [17]. It therefore seems reasonable to attribute the more than 100% consumption of NO₂ to the formation of $(30 \pm 12)\%$ CF₃O radicals from reaction (5).

Another prominent product channel of reaction (5) is formation of FNO and CF₂O. CF₂O cannot be detected with the present experimental system due to its weak absorption in the UV at wavelengths above 220 nm. However, FNO has a sharp absorption peak at 310.5 nm with an absorption cross section of $(4.7 \pm 0.7) \times 10^{-19}$ cm² molecule⁻¹ [18]. The maximum transient absorption at 310.5 nm following the radiolysis of 100 mbar of CF₃H, 0.5 mbar of NO₂, and 900 mbar of SF₆ is approximately 0.025 absorbance units greater than at 317 nm. This compares well with the absorption of FNO which is three times weaker at 317 nm than at 310.5 nm [19]. The maximum transient absorbance at 310.5 nm as a function

of the dose is shown with filled squares in Figure 8. The maximum transient absorption is proportional to the dose indicating the absence of any interfering radical-radical reactions in the system as discussed previously. The slope of the straight line through the data is (0.0115 ± 0.0020) . This absorbance needs to be corrected for absorption due to other absorbing species in the system. NO₂ is known to absorb at 310.5 nm. The loss of NO₂ has been determined previously at 400 nm. The FNO yield is determined from the absorption at 310.5 nm plus the absorbance loss at 400 nm times the ratio between the absorbance cross sections of NO₂ at 310.5 nm and 400 nm: $A_{FNO}(310.5 \text{ nm}) = A_{FNO} + (0.0927 \pm$ $(0.0030)\sigma_{NO2}(310.5 \text{ nm})/\sigma_{NO2}(400 \text{ nm}) = 0.01146 \pm$ $0.00195 + (0.0927 \pm 0.0030) \times (18.55/60.007) =$ 0.0401 ± 0.0026 . From the absorbance cross section of FNO at 310.5 nm we arrive with a FNO yield of $(1.63 \pm 0.25) \times 10^{15}$ molecules cm⁻³. This yield has to be corrected for the fact that only 900 mbar of SF₆ was used in the system and that only 72.4% of the F atoms react with CF₃H, the rest of the F atoms react directly with NO2. The corrected FNO concentration is $(1.626 \pm 0.250) \times 10^{15}/(0.724 \times 0.9) = (2.496 \pm 0.250)$ $(0.407) \times 10^{15}$ molecules cm⁻³. This gives a FNO yield of $(101 \pm 20)\%$ in terms of the initial F atom concentration. We choose to add an extra 10% uncertainty due to FNO formed by direct radiolysis of CF₁H and hence we arrive with a FNO yield of $(101 \pm 30)\%$.

The conclusion from the absorption measurements at 400 nm and 310.5 nm is: (i) The yield of CF₃O and NO from reaction (5) is $(30 \pm 12)\%$. The FNO yield is $(101 \pm 30)\%$. These two product yields are consistent. They allow for 11% of the reaction products of reaction (5) to be CF₃ONO and/or CF₃NO₂. Since the product yield determined from NO₂ is more precise than that determined from FNO, we choose to report a product yield of $(30 \pm 12)\%$ of CF₃O and NO and $(70 \pm 12)\%$ CF₂O and FNO.

From the NO₂ decay monitored at 400 nm and the reaction scheme seen in Table I the overall rate constant for reaction (5) can be derived. In Figure 7 two experimental transients obtained at 400 nm following pulse radiolysis of 0.5 mbar NO₂, 100 mbar CF₃H, and 900 mbar SF₆ are shown. For the transient in Figure 7(A) full dose was used while dose 0.527 was used for the transient in Figure 7(B). The smooth lines in Figure 7 are numerical simulations of the experimental transients using the kinetic data from Table I and CHEMSIMUL numerical integration program [20]. k_5 was varied between 1.8 and 2.8×10^{-11} cm³ molecule⁻¹ s⁻¹. As seen from the figure the best fit was obtained with $k_5 =$

Rate Constant (cm ³ molecule ^{-1} s ^{-1})	Reference
1.3×10^{-13}	[21]
0.99×10^{-11}	[14]
varied	This work
varied	This work
0.9×10^{-11}	[17]
	Rate Constant $(cm^3 molecule^{-1} s^{-1})$ 1.3×10^{-13} 0.99×10^{-11} varied $varied$ 0.9×10^{-11}

Table I Reaction Mechanism

 $(2.1_{...03}^{+0.7}) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. This is consistent with the $(1.6 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

DISCUSSION

To check the values of the rate constants obtained in this work, the following reaction scheme was used to simulate the fluorescence signal following the CO_2 laser pulse of a mixture of 0.10 torr of CF_3I , 0.57 torr of NO_2 , and 4 torr of N_2 :

$$CF_3I + nh\nu \longrightarrow CF_3 + I$$
 (8)

$$CF_3 + NO_2 \longrightarrow CF_2O^* + FNO$$
 (5a)

$$CF_3 + NO_2 \longrightarrow CF_3O + NO$$
 (5b)

$$CF_3O + NO_2 \longrightarrow CF_3ONO_2 + M$$
 (14)

$$CF_2O^* + NO_2/N_2 \longrightarrow CF_2O + NO_2/N_2$$
 (11,10)

In order to carry out the calculations, the rate equa-

tions for the above reaction scheme were numerical integrated. The following values of the rate constants, in cm³ molecule⁻¹ s⁻¹ were used: $k_{5a} = 1.12 \times 10^{-11}$ and $k_{5b} = 0.48 \times 10^{-11}$ are estimated from this work, $k_{14} = 0.9 \times 10^{-11}$ [17], $k_{11} = 3.0 \times 10^{-12}$ [this work], and $k_{10} = 2.3 \times 10^{-13}$ [this work]. The fluorescence signal were simulated using a numerical integration program. The experimental data and the simulated data are shown in Figure 9. As seen from the figure, the simulated data fit the fluorescence signal quite well.

The value for k_5 obtained in the present work by pulse radiolysis, $(2.1_{-0.3}^{+0.7}) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ is in agreement with the value for k_5 reported by Sugawara et al. [6] of $(2.5 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and the value reported by Francisco and Li [7] of $(2.5 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. However, the value of $k_5 = (1.6 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ obtained by IR fluorescence is in better agreement with the k_5 reported by Bevilacqua et al. [8] of $(1.0 \pm 0.7) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. This could be due to a pressure de-



Figure 9 Typical experimental IRF signal for 0.100 torr of CF_3I , 0.57 torr of NO_2 , and 4 torr of N_2 . The dashed line indicated the signal calculated by a numerically solved rate equations system.

pendence of k_5 . However, the value of $(1.6 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ obtained in the present work is determined at similar pressures (1-16 torr) as the values of Sugawara et al. [6] and Francisco and Li [7], and it is still significantly lower than those values. The reason for this discrepancy is unknown. As stated earlier the value of k_5 obtained by Rossi et al. [5] is much lower than the more recent determinations of k_5 .

The present work does indicate a pressure dependence of k_5 , but since we cannot work at pressures (<0.5 mbar) necessary to detect the potential pressure dependence we cannot present any conclusive experiments at this point.

The product distribution of reaction (5) determined here are 30% CF₃O and NO, 70% FNO and CF₂O, and less than 10% other products. The products of reaction (5) reported in the literature are: (i) Rossi et al. [5] assumed that reaction (5) is producing CF₃O and NO; (ii) Sugawara et al. [6] report FNO and CF₂O as the only products. However, they cannot exclude other less important reaction channels; (iii) Francisco and Li [7] report CF₂O as the major product but they also observe NO as a product of reaction (5); and (iv) Bevilacqua et al. [8] observe all reaction channels with channel (5a) as the most important. As seen from the above list of products, the product distribution obtained in this work is consistent with the literature data.

Finally, we want to compare the (CF₃ONO)* complex from the reaction of CF₃ radicals with NO₂ and the $(CF_3ONO)^*$ complex from the reaction of CF_3O with NO. The reaction of CF₃O with NO is known to give FNO and CF₂O in 100% yield at room temperature and this channel is known also to be important at low temperatures. The formation of a (CF₃ONO)* complex by the reaction of CF₃ radicals and NO₂ still needs to be confirmed. A study of the temperature dependence of k_5 would show whether reaction (5) goes via a complex. However, it is likely that such a complex is formed. As shown above the reaction of CF₃ radicals with NO_2 give 30% CF_3O and NO. This could be a product of a direct abstraction channel and the 70% FNO and CF₂O could originate from the (CF₃ONO)* complex. Product studies at different temperatures are needed to elucidate this question.

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