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The $CF_3 + NO_2$ rate constant measured between 1.5 and 110 Torr and between 251 and 295 K by time resolved infrared emission

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The rate constant k_1 for reaction of CF₃ with NO₂ was investigated over the pressure range 1.5–110 Torr Ar or N₂ and at temperatures between 251 and 295 K. Time resolved emission from vibrationally excited CF₂O and FNO products was used as a detection method for CF₃ removal. The rate constant at room temperature shows no marked variation with pressure, with an average value of $k_1 = (1.75 \pm 0.26) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, where the errors are 2σ , but a small reduction at the lowest pressure indicates the possible contribution from a third body recombination process. We conclude that this process is minor, and if it is treated as a separate reaction channel it results in a limiting high pressure branching ratio of $13 \pm 7\%$, which drops to half that value at 10 Torr. As the limiting high and low pressure rate constants are within the 2σ error bars of k_1 , we recommend the average value as applying over the full pressure range. Combination with previous results shows that of the possible bimolecular channels, formation of CF₂O + FNO dominates (*ca.* 95%). No temperature dependence is seen, within experimental error. Pitfalls in the extraction of rate constants from the analysis of time resolved product emission are discussed, and a method is described to assign rate constants unambiguously to reactive formation and collisional quenching. CF₃ radicals were formed from the 248 nm photolysis of CF₃I, and observations of emission from the radical show previously unobserved excitation in the asymmetric C–F stretching mode v₃.

Introduction

Atmospheric degradation of a number of fluorocarbon species leads to the formation of the CF₃ radical,¹ and its subsequent chemistry has been the subject of a number of experimental investigations. The radical's major atmospheric fate is recombination with molecular oxygen, and we have recently investigated the rate constant for this reaction by using time resolved infrared (IR) emission as a marker for the decay of the radical in the presence of O₂ and NO₂.² The emission results from vibrationally excited products formed from the fast reaction of CF₃ with NO₂, and one of the requirements of the study of the competition between removal by NO₂ and O₂ has been a thorough understanding of the CF₃ + NO₂ reaction. Here we describe measurements which provide values of the CF₃ + NO₂ rate constant between 1.5 and 110 Torr total pressure and between 251 and 295 K and which illustrate potential pitfalls in using kinetic observations of products for rate constant measurements.

Although the $CF_3 + NO_2$ reaction is only of minor atmospheric importance, its rate constant has received a great deal of experimental attention, and the results of eight previous studies are shown in Table 1.³⁻¹⁰ At first sight, these data seem to indicate a trend of increasing rate constant with increase in total pressure, but closer inspection shows that this interpretation depends crucially on the accuracy of the two lowest pressure studies. The very low pressure photolysis measurement of Rossi *et al.*³ was carried out under conditions which have been suggested as leading to an overestimation of the low pressure of NO_2 ,⁴ and hence to a low value of the rate constant. Bevilacqua *et al.*⁶ reported only a brief investigation of the reaction in the course of a study in which the major aim was to observe the kinetics of CF_3O_2 and CF_3O species, and their value has correspondingly large error bars.

Table 1	Measurements of k_1	
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Study	Pressure range/Torr	Rate constant/ 10^{-11} cm ³ molecule ⁻¹ s ⁻¹
Rossi et al. ³ Bevilacqua et al. ⁶	0.005 0.8 2 (He)	0.27 ± 0.05 10 + 0.7
Schested <i>et al.</i> ^{8 <i>a</i>}	$2-10 (Ar/N_2)$	1.0 ± 0.7 1.6 ± 0.3
Pagsberg et al. ¹⁰	3–17 (Ar)	1.5 ± 0.2
Francisco and Li ³	4-5 (He/Ar) 5 (Ar)	2.5 ± 0.3 2.4 + 0.5
Sugawara <i>et al.</i> ⁴	4-20 (Ar)	2.4 ± 0.3 2.5 ± 0.3
Vahktin ⁹	300-600 (He)	3.2 ± 0.7
Sehested <i>et al.</i> ⁸	$760 (SF_6)$	$2.10^{+0.7}_{-0.3}$
This work	$1.5-110 (Ar/N_2)$	1.75 ± 0.26
IR fluorescence. ^b Pulse radiolysis.		

Furthermore, a pressure dependent reaction which from the data of Table 1 would appear to have reached its limiting high pressure value at around 5 Torr would need an unrealistically high value of its third body recombination rate constant to reproduce the apparent fall-off behaviour. A series of consistent measurements over a wider pressure range than provided by the individual studies in Table 1 would therefore appear warranted. Furthermore, no measurements have been reported at temperatures other than close to 295 K.

Several product channels have been suggested for the CF_3 + NO_2 reaction:

$$CF_2 + NO_2 \rightarrow CF_2O + FNO_2$$

 $\Delta H_{298}^{\circ} = -270 \text{ kJ mol}^{-1}$ (1a)

$$\rightarrow \mathrm{CF}_2\mathrm{O} + \mathrm{F} + \mathrm{NO}$$

$$\Delta H_{298}^\circ = -31 \ \mathrm{kJ} \ \mathrm{mol}^{-1} \quad (1\mathrm{b})$$

$$\rightarrow CF_3O + NO$$

 $\Delta H_{298}^{\circ} = -226 \text{ kJ mol}^{-1} \quad (1c)$

$$\rightarrow CF_3NO_2(CF_3ONO)$$

$$\Delta H_{298}^{\circ} = -247(-314) \text{ kJ mol}^{-1} \quad (1d)$$

and the data of Table 1 have been obtained by observations of the kinetic behaviour of both reactants,^{3,4,6,8-10} and products.^{4,5,7,8} Time resolved observations of CF₂O and FNO have shown them to be directly formed by reaction (1), ^{4,5,7,8,10} and product analyses have shown that this channel dominates.^{6,8–11} A branching ratio of $k_{1a}/k_{1d} \approx 3$ has been inferred by the long time observation of stable addition products following the reaction at high pressures (>300 Torr),^{9,11} but quantitative observations of CF3 loss and CF2O production by time resolved diode laser absorption at low pressures (<17 Torr) have concluded that $95 \pm 4\%$ of the reaction proceeds through channel (1a), with no stable adduct observable on the time-scale of the CF₃ decay.¹⁰ As the formation of CF₃NO₂ may be affected by long time heterogeneous processes, a study over a larger pressure range than employed in the individual measurements shown in Table 1 will help to clarify the importance of the recombination channel (1d).

The interpretation of reactant loss data in terms of the overall rate constant for process (1) is straightforward, but that of product formation can be ambiguous if the observed product itself is also subject to removal processes. This is the case in the present experiments (and in previous studies^{5,7,8}), where time resolved IR emissions from the CF₂O and FNO products are observed. For a reaction sequence (1a) producing vibrationally excited CF₂O[‡] followed by the quenching process

$$CF_2O^{\ddagger} + M \rightarrow CF_2O + M$$
 (2)

the time dependent concentration of CF_2O^{\ddagger} (and hence the time dependence of the observed signal) will take the form

$$[CF_2O^{\ddagger}] = \left(\frac{k_1[CF_3]_0[NO_2]}{k_1[NO_2] - k_2[M]}\right) (e^{-k_2[M]t} - e^{-k_1[NO_2]t}) \quad (3)$$

leading to a double exponential rise and fall behaviour where the rising rate will always be the faster of the two rates $k_1[NO_2]$ and $k_2[M]$. Additional evidence therefore needs to be found to decide which of the rising or falling rates should be associated with reaction, and in only one of the previous IR emission studies⁷ has this been explicitly provided. We note that expression (3) clearly cannot apply when the rates of processes (1) and (2) are equal, and we discuss the practical problems associated with fitting the data when this condition is approached.

In this study, we used time resolved IR emission to measure the rate of process (1) under conditions such that quenching is at least a factor of five faster than reaction, and so that the fall of the emission signal corresponds to process (1). In this way we were able to measure the rate constant over the pressure range 1.5-110 Torr and between 251 and 295 K, and conclude that within experimental error a single value of the rate constant is appropriate under all conditions.

Experimental

CF₃ radicals were formed by the 248 nm pulsed photolysis of CF₃I. For experiments at room temperature the radiation from an excimer laser (Lambda Physik Compex 102, 250 mJ per pulse, 10 Hz) was multipassed (13 times) into a stainless steel reaction vessel. IR radiation was collected with Welsh optics and directed either into an FTIR spectrometer (Bruker IFS/66) or through an interference filter and observed with either an InSb (Graseby IS2) or HgCdTe (Kolmar D317) detector. The interferometer was operated in step scan mode¹² and the time resolution of the detectors and associated electronics was set to ~2 μ s. Signals were digitised at 1 μ s channel width and averaged for a pre-set number of laser shots. A reaction vessel without multipass or Welsh collection optics was used for experiments at lower temperatures.

 NO_2 (BOC, >99.5%) was purified by reaction with excess O_2 with the O_2 then being removed by freeze-thaw cycling. Ar (BOC, >99.999%), N_2O (BOC, >99.997%), N_2 (BOC, >99.998%) and CF_3I (Fluorochem, >99%) were used without further purification. A slow flow of gases was used to replenish photolysed molecules and to remove products, with reagent partial pressures calculated from measured total pressures and reagent flows.

Results

(a) Emission from 248 nm irradiation of separate samples of CF_3I and NO_2

The 248 nm irradiation of CF₃I results in prompt IR emission from CF₃, and a delayed feature which is from the parent molecules formed vibrationally excited by energy transfer. The strongest prompt feature is between 1200 and 1270 cm^{-1} and is assigned to $\Delta v_3 = -1$ transitions in CF₃, shifting with time to higher wavenumbers as vibrational relaxation takes place. Fig. 1 shows a contour plot of the spectral intensities around 1200 cm^{-1} as a function of time. At higher wavenumbers (and at a factor 20 lower intensity) similar behaviour was seen for bands near 2300 and 2500 cm⁻¹, assigned as the combination band $\Delta v_3 = \Delta v_1 = -1$ and the overtone band $\Delta v_3 = -2$, respectively. Previous experimental studies at this wavelength have either identified¹³ or assumed¹⁴ excitation in the symmetric modes of CF₃ (the umbrella v_2 and the stretch v_1), with the time-of-flight measurements of Felder showing the clearest evidence of v_2 excitation.¹³ In contrast to the behaviour of the asymmetric v_3 mode, we did not detect emission on the $\Delta v_2 = -2$ overtone near 1400 cm⁻¹, presumably because of low Einstein A factors for this transition. Our data are not sufficient to determine the extent of vibrational partitioning into the observed modes, but our observations of the $\Delta v_3 =$ -2 overtone implies excitation of v₃ at least equal to 2, and suggests that the vibrational distribution in the CF₃ fragment is more complex than previously considered. Finally in this section, a band at 1185 cm⁻¹ was seen to peak at a delay from the prompt CF₃ emission, and was removed by a cell containing CF_3I as a cold gas filter (1.8 Torr, 8 cm pathlength). The band is identified as the antisymmetric CF stretching mode, $\Delta v_4 = -1$, in CF₃I formed by energy transfer from the nascent CF₃. A sample of NO₂ also showed emission features when irradiated at 248 nm, and these will be described in a separate publication.² Fortunately for this study, the absorption of NO₂ is at a minimum at 248 nm (with an absorption



Fig. 1 Contour plot of the emission from 248 nm irradiated CF₃I (51 mTorr in 1.8 Torr Ar) as a function of time and wavenumber. The feature near 1250 cm⁻¹ appears promptly and shifts to higher wavenumber with time, and is assigned to the $\Delta v_3 = -1$ transition in the CF₃ radical. The band at 1185 cm⁻¹ reaches its maximum at later times, and is assigned to the $\Delta v_4 = -1$ transition in the parent CF₃I, formed by energy transfer from CF₃. Resolution 4 cm⁻¹.

cross-section a factor of 20 lower than that of CF₃I), but bands corresponding to fundamental and first overtone transitions in NO(v) produced by photolysis are clearly seen for levels v = 1-8 between 1700 and 1900 cm⁻¹ and between 3400 and 3700 cm⁻¹, respectively. Emission from NO₂ (0,0,1-0,0,0)at 1600 cm⁻¹ results from excited molecules formed by energy transfer processes, and at higher pressures and lower temperatures emission from NO₂ produced by photolysis of the N_2O_4 dimer can be seen at 1450 and 2750 cm⁻¹, and is assigned to highly vibrationally excited NO2 emitting in the $\Delta v_3 = -1$ and $\Delta v_3 = \Delta v_1 = -1$ bands, respectively. Although, as will be shown, the bands from NO₂ irradiation are weak in comparison with those from the products of the $CF_3 + NO_2$ reaction, an understanding of their identification and behaviour is crucial as they interfere kinetically with the data.

(b) Emission from $CF_3 + NO_2$

Fig. 2 shows time resolved spectra in the region 1100-2100 cm^{-1} arising from the photolysis of a mixture of CF₃I and NO₂. Additional features are seen, particularly near 1900 cm^{-1} , which are absent in the irradiation of the separate species, and are identical with those seen in our previous study of the reaction when the CF₃ reagent was formed from infrared multiple photon dissociation of CF₃I.⁷ Fig. 3 shows a time integrated spectrum between 1700 and 2100 cm⁻¹, where the emission is identified as CF_2O emitting in the $\Delta v_1 = -1$ band (the C-O stretch) near 1930 cm⁻¹ and from FNO emitting in the $\Delta v_1 = -1$ band, showing the double peak expected at this resolution from the P and R branches of the $(1,0,0 \rightarrow 0,$ 0,0) band centred at 1844 cm⁻¹. The superior resolution and wavenumber accuracy of the present instrument compared with our previous laboratory-made step scan interferometer is illustrated in the spectra observed in Fig. 3 and shown in Fig. 4 of our previous work.⁷ In the latter study, a small wavenumber shift had led to our assignment of the two peaks near 1844 cm^{-1} as arising from FNO and another reaction product, and the isomeric FON was suggested as a possibility. This now seems not to be the case; the present spectrum is entirely consistent with the double peaked carrier near 1844 cm⁻¹ being



Fig. 2 Plots of the emission spectra between 1100 and 2100 cm⁻¹ as a function of time after the irradiation of a mixture of CF₃I (9 mTorr), NO₂ (63 mTorr) and Ar (1.8 Torr). Spectra are summed in 20 µs intervals between 20 and 200 µs at a resolution of 6 cm⁻¹. Features near 1900 cm⁻¹ are assigned as the $\Delta v_1 = -1$ bands of CF₂O (near 1900 cm⁻¹ and shifting to higher wavenumbers with time) and the $\Delta v_1 = -1$ bands of FNO (showing the double peaked P and R branches centred at 1844 cm⁻¹). Between 1170 and 1280 cm⁻¹ the emission seen in the absence of NO₂ (Fig. 1) is augmented by emission from the $\Delta v_4 = -1$ bands of CF₂O near 1250 cm⁻¹.

FNO. In principle, time resolved data at specific wavenumbers, characteristic of particular species, can be extracted from the spectra of Fig. 2 and 3. Fig. 4(a) shows decay curves for two different wavenumber regions, and illustrates a potential pitfall in the observations of unresolved IR emission. Emission summed between 1850 and 1910 cm⁻¹ peaks at earlier times than that at higher wavenumbers, 1920-1970 cm⁻¹, and this is because the emission from CF₂O shifts to higher wavenumber with time because of vibrational cascade from the nascent vibrationally excited levels. Careful inspection of the time resolved spectra shows that in the region $1700-2100 \text{ cm}^{-1}$ in Fig. 3 the FNO emission does not show a high wavenumber shift, and thus for kinetics to reflect the true time dependence of the nascent products of process (1) emission should be viewed in a region that encompasses FNO or the highest vibrational levels (i.e., the lowest wavenumber) of CF₂O. Fig. 3 shows the transmission of an interference filter in such a region, 1850-1910 cm⁻¹, and Fig. 4(b) illustrates the time



Fig. 3 Time integrated spectrum from the data in Fig. 2 between 0 and 400 μ s. Marked on the spectrum are the positions of the absorption bands of CF₂O and FNO, where long time emission from the products of reaction would be expected. Also shown as a dashed line is the transmission curve of the filter used in kinetic experiments.



Fig. 4 (a) Time dependences of the emission summed between 1920 and 1970 cm⁻¹ (upper trace) and 1850 and 1910 cm⁻¹ (lower trace) taken from the data in Fig. 2. It can be seen that the emission at the higher wavenumber peaks at a later time, indicative of vibrational cascade. (b) Time dependences of the emission following irradiation of a mixture of CF₃I (47 mTorr), NO₂ (150 mTorr) and Ar (6.8 Torr). The lower trace shows emission measured through the interference filter whose spectrum is shown in Fig. 3. The upper trace is from time resolved spectra of the kind shown in Fig. 2, summed over the wavenumber range corresponding to the filter transmission. The two traces have been separated in vertical scale, as they are indistinguishable, apart from the clear improvement in S/N ratio in the filter data.

resolved behaviour in this region obtained from the interferometer traces compared with that from the filter. The time dependences are identical, but the enhanced S/N ratio of the filter data allows a far more comprehensive evaluation of the kinetics, and was used in all further kinetic measurements.

As described above, there is an additional emitting species in the region of the filter, namely that from vibrationally excited NO formed from the 248 nm photolysis of NO₂. Although there is very little nascent NO formed in the levels viewed by the filter (v = 1, 2 and 3),^{2,15} vibrational cascade will lead to these levels being populated at longer times and thus interfere with the extraction of k_1 . The small effect can be seen at long times in the low noise filter trace of Fig. 4(b), where the signal does not fall exponentially to zero at the rate expected from the earlier time behaviour. Traces were taken with and without CF₃I present and subtracted to eliminate this effect. This procedure is valid only if CF₃I has no effect on the NO(v) kinetics, and this was proved from measurements of the behaviour of the NO(1-0) emission with and without CF₃I present. A cold gas filter was placed in front of the detector under conditions such that emission from NO(1-0) was absorbed, but non-resonant emission (from other species and from higher levels of NO) was unaffected. The kinetic behaviour of the NO(1-0) emission was identical in the two cases, showing that CF₃I at the pressures used had a negligible effect on the vibrational cascade of NO.

Data such as those of Fig. 4(b), corrected for NO emission, were found to fit the double exponential expression (3), and rising and falling rates were linear functions of $[NO_2]$ as shown in Fig. 5. The extracted rising and falling rate constants are shown as a function of Ar pressure in Fig. 6. At first sight the data could be interpreted in the following way. The falling rate constant corresponds to process (1), as it shows a dependence on total pressure which can only be explained by a third body recombination effect [process (1d)], and which would not be expected for simple quenching. There is in addi-



Fig. 5 Results of fitting the double exponential expression (3) to emission data taken through the interference filter and corrected for the small amount of emission from NO as explained in the text. The upper panel shows the rising rates and the lower panel the falling rates, each as a function of NO₂ pressure for a range of total pressures of Ar. $P(Ar) = (\clubsuit) 2.8$, $(\blacksquare) 7.8$, $(\times) 12.8$, $(\diamondsuit) 17.8$, $(\blacktriangle) 21.8$ and $(\bigcirc) 25.3$ Torr.

tion a low pressure bimolecular component [processes (1a–c)] of *ca*. 2×10^{-12} cm³ molecule⁻¹ s⁻¹, slower than previously observed. The rising rate constant is for quenching of the emitting species by NO₂ and experimental error is invoked to



Fig. 6 Slopes of the plots of rising rates (upper panel) and falling rates (lower panel) against NO_2 pressure shown in Fig. 5 as a function of total pressure of Ar. The data appear to be consistent with a pressure dependent falling rate constant, which could be interpreted as that for reaction (1) having a dominant third body component, process (1d). This explanation, as explained in the text, is erroneous, and illustrates the pitfalls of attempting to fit expression (3) to data even as good as the example shown in Fig. 4(b) when rising and falling rates are similar.

account for its variation with Ar pressure. There are, however, several problems with this interpretation. First, the marked intercept of the falling rate at zero NO₂ pressure (Fig. 5) remains unexplained, and second, the noticeable downward trend in rising rate constant with increasing total pressure (Fig. 6) has been ignored. The interpretation turns out to be incorrect, and is illustrated here to emphasise the pitfalls of analysing data even of such high quality as shown in Fig. 4(b). The problem arises through the relative magnitudes of the rising and falling rates. At low Ar pressure, reaction is faster than quenching, but the reverse is true at high Ar pressure. This means that identification of each of the rising and falling rate constants of Fig. 6 with a single process is incorrect except in the limits of high and low Ar pressures. The trends in Fig. 6 illustrate this qualitatively, in that similar rate constants are returned from the analysis of for example the rising rates at low [Ar] and the falling rates at high [Ar], which now would be associated dominantly with the reactive component. Simulations of reaction (1) and quenching (2) under these conditions were fitted by the double exponential expression (3) (taking great care over the fitting when the rates approached equality), and the extracted rate constants showed the same behaviour as seen in Fig. 6. At some combination of Ar and NO₂ concentrations this means that the true reaction and quenching rates will become equal, and these processes would produce a time dependent behaviour that cannot be analysed by eqn. (3). We still find, however, very good fits to the experimental data but which return different rates under conditions where we would expect similarity.

We believe that there are two reasons for this. We have made no allowance for the behaviour of vibrationally excited CF₃, undoubtedly produced but in an unknown fraction by the photolysis of CF₃I. Vibrational cascade and/or changed reactivity with vibrational excitation could affect the returned rates. In addition, there is secondary chemistry occurring in the system, and the time dependent behaviour will not be precisely described by a simple reaction scheme which incorporates only processes (1) and (2). O atoms are formed from NO_2 photolysis and, although their main fate will be the reaction with NO₂, they can regenerate CF₃ radicals by reaction with CF₃I, thus leading to an underestimate of the rate of process (1). In addition, F atoms, formed both as a minor product in reaction (1b) (estimated as $1.5\%^7$) and from the O + CF₃ reaction, react rapidly with CF₃I to regenerate CF₃. A FACSIMILE¹⁶ fit to the data including the reactions listed in Table 2 was carried out, and produced values of k_1 which showed a less marked trend with total pressure than the falling rate constants shown in Fig. 6, but which exhibited non-systematic variations, which were unexpected given the high quality of the raw data.

We conclude that when rates of formation and quenching are of similar magnitudes, when secondary chemistry occurs and when the influence of vibrationally excited CF_3 is neglected, it is difficult to extract meaningful data from the emission traces. We chose to solve these problems by increasing the ratio of falling and rising rates by adding an efficient

Table 2 Rate constants used in the FACSIMILE fits

Process	Rate constant/ cm^3 molecule ⁻¹ s ⁻¹	Ref.
$\begin{array}{c} CF_3 + NO_2 \rightarrow CF_2O^{\ddagger} + FNO\\ CF_3 + NO_2 \rightarrow CF_2O^{\ddagger} + F + NO\\ CF_2O^{\ddagger} + M \rightarrow CF_2O + M\\ O + NO_2 \rightarrow O_2 + NO\\ O + CF_3I \rightarrow CF_3 + IO\\ O + CF_3 \rightarrow CF_2O + F\\ F + CF_3I \rightarrow CF_3 + IF\\ CF_3 + CF_3 \rightarrow C_2F_6 \end{array}$	$\begin{array}{c} 0.98 \ k_1 \\ 0.02 \ k_1 \\ k_2 \\ (9.7 \pm 1.0) \times 10^{-12} \\ (3.6 \ ^{+1.5}_{-1.0}) \times 10^{-12} \\ (3.1 \pm 0.8) \times 10^{-11} \\ (1.2 \pm 0.6) \times 10^{-10} \\ (3.9 \pm 1.3) \times 10^{-12} \end{array}$	17 18 19 20 21

quencher, which does not react with CF₃, so that quenching is always the faster process and the falling rate then becomes the true rate of reaction. Fig. 7 shows the effect of adding 1 Torr N₂O as the chosen quencher. The rising rate is now markedly increased, but at the expense of a reduced signal, and one of the consequences of this is that the emission from NO becomes proportionally larger. Fig. 8 shows the emission signals with and without CF₃I present together with the subtracted data which now can be analysed to extract k_1 . In contrast to the data shown in Fig. 4(a), spectra taken with N_2O present now showed no marked difference in the time behaviour summed over the same spectral windows as before, illustrating the added advantage of removal of the effect of vibrational cascade by addition of N2O. Furthermore, observation of the effect of N₂O on CF₃ emission showed that the vibrationally excited reactant was quenched on a time scale faster than that of reaction, thus removing the potential problem of CF₃ relaxation.

Emission traces in the presence of N_2O were analysed by the FACSIMILE model including the reactions in Table 2, and an example of the fit is shown in Fig. 8. The returned rate constants k_1 are shown as a function of total pressure (both Ar and N_2) between 1.5 and 37 Torr in Fig. 9. The straight dashed line is the unweighted average of the values of k_1 returned from 67 measurements at a variety of NO₂ pressures



Fig. 7 Kinetic behaviour observed through the filter with and without N_2O (1 Torr) present. The upper curve shows the emission accompanying irradiation of CF₃I (19 mTorr), NO₂ (110 mTorr) and Ar (4.8 Torr), and the lower curve illustrates the reduction of emission and the increase in its rising rate when N_2O is added.



Fig. 8 Emission signals observed through the interference filter with and without CF₃I (9 mTorr) for irradiation of NO₂ (104 mTorr), Ar (5.1 Torr) and N₂O (1.4 Torr). With CF₃I absent the emission shows a sharp rise, a slow increase and slower decrease resulting from vibrationally excited NO formed from photolysis of NO₂ and relaxing through the spectral window of the filter. With CF₃I present additional emission from CF₂O and FNO is seen. The difference is shown in the inset together with a kinetic fit (virtually indistinguishable from the data) as described in the text.



Fig. 9 Rate constants k_1 obtained from the fits to data such as in Fig. 8 as a function of Ar (\bullet) and N₂ (O). The horizontal straight line shows the weighted average of all the data, yielding a value of $(1.75 \pm 0.26) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for reaction (1). The dotted line shows a fit to the data assuming that the high pressure limit is reached at 40 Torr, with fall-off parameters identical with those extracted from Vahkin.⁹ As can be seen, the dotted line does not fit the data well, and predicts an unrealistic limiting low pressure rate constant as explained in the text. The solid curve is a fit to the data including a contribution from a third body dependent association reaction, as explained in the text.

(25–160 mTorr) and total pressures (1.5–37 Torr), $k_1 = (1.75 \pm 0.26) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, where the errors are 2σ . The percentage errors of the individual fits to the data such as that shown in Fig. 8 were far lower than the 2σ error limits quoted for the mean value, and we attribute the latter predominantly to random errors in the measured concentrations of the flowing reagents.

Although it is clear that there is no marked variation in k_1 with total pressure or identity of buffer gas (Ar or N_2), the data show hints of a small reduction in value below about 6 Torr. We return to this point later. Extensive checks were made on the data. First, the effect of secondary chemistry involving F atoms was assessed by adding H₂ to the system so that they were removed dominantly by the $F + H_2$ reaction. FACSIMILE fitting with and without H₂ produced the same values of k_1 . Laser fluences were varied to alter the extent of radical-radical reactions, and again produced no change in the returned values of k_1 . A sensitivity analysis of the fitting procedures was carried out by altering values of the rate constants in Table 2 by their error limits, by changing the branching ratio of eqn. (1b) between 0 and 5% and by altering other parameters such as absorption cross-sections by 10%. Percentage changes in the returned k_1 values were considerably less than the statistical errors quoted above. Variation of gas residence time between shots showed that the effect of reagent depletion was negligible, and CF₃I precursor variation between 3 and 20 mTorr produced the same value of k_1 .

Fig. 10 shows the falling rate obtained from fits of the data to eqn. (3) with N_2O present as a function of NO_2 concentration, *i.e.*, without the inclusion of secondary chemistry in order to illustrate the magnitude of the effect. The slope of the line vields a rate constant of 1.5×10^{-11} cm³ molecule⁻¹ s⁻¹. 14% lower than from the FACSIMILE fits because of the effect of neglecting the secondary chemistry which can re-form CF₃. The falling rate is independent of Ar or N₂ pressure and, in contrast to the data in Fig. 5, now passes sensibly through zero. Also shown in Fig. 10 are data for N₂ pressures up to 110 Torr. At pressures above 37 Torr the reduction in the overall signal made adequate fits from the FACSIMILE modelling difficult because of the rapid signal rise compared with the associated detector and amplifier response. Double exponential rise and fall fits, however, were still possible, and the invariance of the falling rate with N_2 pressure up to this value, as shown in Fig. 10, indicates that we can conclude that



Fig. 10 Plot of the falling rate as extracted from double exponential fits to data such as shown in Fig. 8 as a function of NO₂ pressure for total pressures of Ar or N₂ between 1.5 and 110 Torr. The line now passes sensibly through zero (in contrast to the data in Fig. 5 taken without N₂O present), and the slope has a value of $(1.52 \pm 0.06) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (2 σ error limits), *ca.* 14% lower than the value obtained from the full fits. The data, however, show that there is no marked difference in rate constant as a function of pressure over the range 1.5–110 Torr.

between 37 and 110 Torr there is no significant change in the value of k_1 .

Temperature dependent measurements of the reaction were carried out in a single pass cell, and Fig. 11 shows examples of data taken at 288 and 251 K compared with the traces at room temperature. Although the lower temperature S/N ratio is far worse in comparison with the data taken under conditions of multipass irradiation and Welsh collection optics, it can be seen that the falling rates are very similar in all cases. Data were taken at two Ar pressures, 5 and 19 Torr, with again no measurable effect of third body concentration. Analysis of the decays was carried out in the same way as before, with rate constants in the simulation modified from their values in Table 2 to account for the lower temperatures. As N_2O_4 is necessarily present in the NO₂ sample and its proportion increases as the temperature is lowered, its photolysis behaviour needs to be considered. We observe signals from vibrationally excited NO formed from N₂O₄, either by direct photolysis or by secondary dissociation of the dominant NO₂ product during the laser pulse.² At lower temperatures the effect is to increase the NO background signal seen



Fig. 11 Comparison of data taken at three temperatures for the same reactant concentrations, showing no variation of the time dependence within experimental error. The clear advantage of data taken at room temperature with the multipass excitation and collection optics is evident. Rate constants extracted from lower temperature data such as these are listed in Table 3.

through the interference filter, and this can be allowed for by subtraction in the same way as before. Additional O atoms are formed which could affect the secondary chemistry, but fitting routines in which the extremes of a quantum yield of unity or zero for O atoms produced from N_2O_4 yielded no difference in the returned values of k_1 within experimental error as shown in Table 3. The rate constants at four different temperatures between 215 and 295 K are shown in Table 3. Although the error bars at the lower temperatures are considerably larger than at room temperature (reflecting the poorer quality of the low temperature data as shown in Fig. 11), there is seen to be no noticeable change in the rate constant in this pressure range 295–251 K.

Discussion

We first comment on the values of the rate constant in comparison with other studies shown in Table 1, and consider first the previous measurements from time resolved IR emission.^{5,7,8} Previous data from our group were taken at relatively low Ar pressures (5 Torr) and we identified the rising rate as corresponding to reaction and the falling rate to quenching because of the effect of adding up to 2.5 Torr of N_2 or O2. The rising rate was unchanged with N2, but increased with O2, as expected for reactive removal, and the falling rate increased with both gases, as expected for quenching. Although the rising and falling rates extracted from the fits of eqn. (3) appeared to be well behaved, it is also clear that under these conditions (5 Torr Ar) they were sufficiently close to one another to render the data treatment unreliable, particularly given the lower S/N ratio of the earlier experiments which did not have the advantage of Welsh cell collection optics. Although our present data agree with the previous work within the error bars, the agreement is probably fortuitous. In the two other reported IR emission experiments the S/N ratios were considerably lower than those in the present experiments, and the problems of data analysis alluded to above were not addressed. The rate constants obtained in these seemingly identical studies, $(2.5 \pm 0.4) \times 10^{-11}$ (ref. 5) and $(1.6 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (ref. 8), are sufficiently different to indicate problems with such data analysis, and the agreement of one of them⁸ with the present result is again probably fortuitous.

Rates of removal of reactants should in principle provide unambiguous kinetic data, and as Table 1 shows our results agree well with the most recent determinations from loss of $CF_3^{6,10}$ and NO_2 ,⁸ but are outside the error limits of an earlier CF_3 loss measurement.⁴ Our results, however, are almost a factor of two lower than the higher pressure (300 and 600 Torr He) measurements of Vakhtin,⁹ which were carried out by relative rate constant measurements of process (1) compared with the recombination of CF_3 with NO, with the rate constant for the latter process taken from the literature.²² As these high pressure rate constants are considerably faster than those in the present study and as this study⁹ was one of two^{9,11} in which CF_3NO_2 was detected as a significant end product, we need to consider carefully the total pressure dependence of the reaction.

Although the present data show that between 1.5 and 110 Torr the value of k_1 is $(1.75 \pm 0.26) \times 10^{-11}$ cm³ molecule⁻¹

 s^{-1} , there is an indication that the lowest pressure measurements (<6 Torr) cluster below the horizontal straight dashed line shown in Fig. 9, and a possible explanation is that there is a small third body effect underlying a dominant bimolecular component. We first note that if this is so, any extrapolation from our present data to reach the value of 3.2×10^{-11} cm³ molecule⁻¹ s⁻¹ at 300 Torr as reported by Vakhtin⁹ is impossible. Vakhtin measured the branching ratio (1d)/(1a) by end product analysis of CF₂O and CF₃NO₂ as 30-35% at three pressures, 150, 300 and 600 Torr He, dropping slightly to 25% at 4 Torr, and from these data he modelled a fall-off curve. If we model a similar branching ratio, but constrain the high pressure limiting rate constant to give a value of $k_1 = 1.75$ $\times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, we produce the curve shown as a dotted line in Fig. 9. As can be seen, this is an unsatisfactory fit to the data, and it also results in a low pressure limiting rate constant for the association reaction (1d) as 4.3×10^{-28} cm^6 molecule⁻² s⁻¹, which is over an order of magnitude larger than other recombination reactions involving CF₃ with NO^{23} and $O_2^{2,17}$ and CF_3O_2 with NO_2^{17} .

We now examine the evidence for the formation of a stable addition product in other studies. Substantial (ca. 30%) formation of CF₃NO₂ has been seen in some end product analyses^{9,11} whereas in others only small $(<11\%^8)$ or negligible⁵ amounts were observed. Real time observation of the species would remove the uncertainty of wall reactions which can affect such analyses. In the chemical ionisation measurements of Bevilacqua et al.,6 evidence for formation CF_3NO_2 (or CF_3ONO) is described, but not quantified, with formation of CF₂O simply stated as being predominant. Most recently, however, Pagsberg et al.¹⁰ measured the yield of CF₂O from reaction (1) as 95% over the pressure range 3-17 Torr by observing both CF₃ loss and CF₂O formation quantitatively by IR absorption, but were unable to observe CF_3NO_2 formation with the same technique. We shall now examine whether our data can be fitted with any confidence to a model which incorporates both bimolecular and third body processes, and we first address the problem with reactions formulated in eqn. (1), namely with two separate and independent channels leading to bimolecular [reactions (1a-c)] and recombination [reaction (1d)] products. To do this we would have several adjustable parameters, namely the true bimolecular component of reaction (1), incorporating processes (1a-c), and the fall-off behaviour of process (1d), so that many potential fits would be possible. As we can conclude from Fig. 9 that bimolecular kinetics dominate, we simplify the fitting by fixing the value for the low pressure limiting rate constant for reaction (1d). We choose a low pressure value which is identical with that for the $CF_3 + O_2$ recombination reaction, namely $(2.5 \pm 0.3) \times 10^{-29}$ cm⁶ molecule⁻² s^{-1.2} This value is similar to those reported for CF₃ recombination with NO²³ and CF_3O with NO_2 .¹⁷ We use the Troe expression for the fall-off behaviour,²⁴ with the broadening factor $F_{\rm c} = 0.6$ as found for the $CF_3 + O_2$ reaction.² Fig. 9 shows the resultant best fit to the data with two adjustable parameters, namely the bimolecular value of k_1 [the sum of processes (1a–c)] and the high pressure limiting value of process (1d). At low pressure k_1 now becomes $(1.61 \pm 0.04) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, with the limiting high pressure value of $k_{1d} = (0.21 \pm 0.11) \times 10^{-11}$ cm³ molecule⁻¹ \hat{s}^{-1} . Our low and high pressure values of k_1

 Table 3
 Rate constant determination at low temperatures

Temperature/K	No. determinations	$k_1/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1a}$
288	6	(a) 1.75 ± 0.34 (b) 1.74 ± 0.34
251	6	(a) 2.00 ± 1.0 (b) 1.80 ± 0.90
256	12	(a) 2.00 ± 1.0 (b) 1.80 ± 0.60

^{*a*} The data marked as (a) and (b) are for quantum yields of one and zero O atoms produced in the photolysis of N_2O_4 . No difference is seen in the returned values of k_1 within experimental error.

are thus $(1.61 \pm 0.04) \times 10^{-11}$ and $(1.82 \pm 0.15) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, and can be seen to lie well within the error limits of the average value quoted above.

A second and intuitively more satisfactory route to the production of a stabilised adduct would be the formation of an energised complex which either decomposes (possibly after rearrangement) or is collisionally stabilised, *i.e.*, both bimolecular and third body processes originate from a common precursor rather than separate steps indicated by reaction (1). If formation of the adduct is the rate determining step then the rate constant will show no pressure dependence, but the yield of stabilised product will rise with pressure, and hence the emission yield of process (1a) will fall. We measured emission intensities between 3 and 25 Torr Ar, corrected these for the measured quenching rates and found that the resultant emission yields showed no variation within experimental error $(\pm 10\%)$. This indicates that over this pressure range the formation of a stabilised adduct in competition with decomposition to form products is of minor importance. The data therefore seem to favour separation of bimolecular and termolecular processes, but it should be emphasised that there is a need for direct observation of stabilised products at higher pressures under conditions such that heterogeneous formation can be eliminated.

The present data provide no further evidence of channels other than process (1a), but taken with our previous estimates of a yield of 1.5% of channel (1b),⁷ and the most recent time resolved observations of a branching ratio of NO from the sum of processes (1b) and (1c) to be only 1%.¹⁰ we conclude that reaction (1a) is the dominant bimolecular step, and we concur with the estimate of Pagsberg et al.¹⁰ of a bimolecular branching ratio of $95 \pm 4\%$ at low pressures (<17 Torr). The fitting of the data in Fig. 9 yields a limiting high pressure yield of $13 \pm 7\%$ for process (1d) if it is treated as a separate independent step, the relative errors being large because of its small contribution, and we note that it has reached 50% of its limiting value at a pressure of 10 Torr with a fitted value of 1.72×10^{-11} cm³ molecule⁻¹ s⁻¹. Although parameterisation of the contributions from processes (1a-c) and (1d) will yield the various values of the rate constants and quantum yields, we present a simple result which fits in with our error bars. We recommend a value of k_1 which applies over all pressures of $(1.75 \pm 0.26) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (2 σ error limits), and recommend that if CF₃NO₂ (CF₃ONO) is formed in a separate third body association step, it has a limiting yield of $13 \pm 7\%$ which drops to $6 \pm 3\%$ at 10 Torr. If this is so, our results suggests that previous end product observations of a 30% quantum yield for process (1d) at pressures above 300 Torr^{9,11} are overestimates, but we are in good agreement with the more recent quantum yield data of Pagsberg et al.¹⁰ which show the dominance of process (1a).

Finally, we consider our observed lack of a temperature dependence. The bimolecular reaction is rapid and only small temperature effects would be expected, but a decrease in temperature would be expected to increase the recombination rate constant in the fall-off regime. Again we make a comparison with the $CF_3 + O_2$ recombination reaction, where the measured temperature dependence in the pressure range near 6 Torr would indicate a 60% increase in the rate constant when the temperature decreases from 295 to 256 K.²⁵ For a contribution of <10% for process (1d) at room temperature and 6 Torr, this increase would again not be noticeable within the large error bars associated with the lower temperature measurements.

Conclusions

The reaction between CF_3 and NO_2 shows no pressure or temperature dependence within the random errors of our measurements between 1.5 and 110 Torr and between 251 and

295 K, and we recommend a value of $(1.75 \pm 0.26) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ as encompassing all pressure conditions and the temperature range measured. There is evidence of falloff behaviour at the lowest pressures studied, and at room temperature if this is considered to indicate a separate reaction channel, we recommend a high pressure limiting branching ratio of the CF₃NO₂ (or CF₃ONO) product as $13 \pm 7\%$, dropping to half this value at 10 Torr. Bimolecular reaction is dominant, and the evidence points clearly to CF₂O and FNO being the overwhelmingly dominant bimolecular component. Our results highlight the difficulties in drawing kinetic conclusions from time resolved product observations when rates of formation and removal of an observed species are of the same magnitude.

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