Investigation into the Kinetics and Mechanism of the Reaction of NO, with CH, and CH,O at 298 K between 0.6 and 8.5 Torr: Is there a Chain Decomposition Mechanism in Operation?

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The reactions CH, +NO, + products (1), and CHO, +NO, - products (2), have been studied using a flow system at T = 298 K and at pressures between 0.6 and 8.5 Torr. The laser-induced fluorescence (LIF) technique was used to detect CHO and multi-pass optical absorption to detect NO. The chemical systems were studied as a pair of consecutive reactions; however, a simple analytical treatment was not sufficient to describe them because CH302was formed as one of the products in the major channel of reaction (2). This species also reacts with NO, regenerating CHO. Use of a numerical model to correct for this regeneration process allowed rate parameters of $k_r = (3.5t_1.10) \times 10^{-11}$ cm3 molecule-' s-' and $k_r = (2.3 \& 0.7) \times 10^{-1}$, cm3 molecule-' s-' to be determined at 2.4 Torr. There is no pressure dependence observed for reaction (1) between 1 and 2.4 Torr, but the possibility of a slight pressure dependence for reaction (2) exists. These pressure effects are examined using the semi-empirical quantum RRK method.

The importance of the nitrate radical (NO,) as a night-time oxidant in the troposphere has become apparent in recent years.' Although the two reactions

CH, + NO, -, products (1)

CH,O + NO, + products (2)

would not be expected to be significant sinks for methyl and methoxyl radicals in the troposphere, where reactions with molecular oxygen

$$CH, +O, +M + CH,O, +M$$
 (3)

are by far the most important reaction pathways, they are nevertheless worthy of study. First, they are examples of radical-radical reactions where the possibility of more than one product channel exists. Secondly, a knowledge of the product channels and rate parameters for these reactions is essential in the interpretation of our laboratory studies of the interactions of the nitrate radical with CH,O,, which may itself be involved in atmospheric chemistry (see following paper)., No kinetic results have been reported previously for either reaction (1) or reaction (2).

Experimental

The apparatus is shown in Fig. 1. It is similar to that described in detail elsewhere., A conventional discharge-flow apparatus is used with a double sliding-injector arrangement, coupled to a fluorescence cell. An optical multi-pass absorption cell (12 passes, base path 10 cm) and a quadrupole mass spectrometer were incorporated in the flow tube downstream of the LIF cell. Nitrate radicals were prepared by the reaction of fluorine atoms with dry nitric acid

$$F + HNO, + HF + NO,$$
 (5)

and detected by optical absorption at $l_t = 662 \text{ nm.4}$ An effective absorption cross-section was determined experimentally for NO, [$o = (1.1 \& 0.1) \times 10^{-11}$ molecule cm-,] *via* the titration of NO, with NO

NO,
$$+ NO - 2NO$$
, (6)

from which absolute concentrations of NO, could be assigned. The minimum detectable [NO,] for a signal-to-noise ratio of unity with a 10 s integration time was *ca.* **10**" molecule cm-,. Experiments were performed at T = 298 K and between 0.6 and **8.5** Torr total pressure, with helium as the carrier gas. The NO, was maintained in excess over the other reactants. Initial concentrations of NO, were typically in the range (**0.5–3.5**) x lo', molecule cm-, and the organic radicals were present initially at concentrations of (**0.3–5**) x lo', molecule e**T**-,. For the investigation of reactions (**1**) and (2), methyl radicals were prepared by the reaction of F atoms with CH, . Methyl radicals reacted rapidly with NO, forming CH,O (see later) in the reaction

$$CH, + NO, - CH, O + NO,$$
 (14)

The methoxyl radicals so produced could further react with NO, to form products

$$CH,O + NO, \rightarrow products$$
 (2)

and a consecutive reaction sequence was established in a similar fashion to that observed when NO, reacts with methyl radicals., Thus, by monitoring the concentration-time profile of the methoxyl radical by the LIF technique, the rate coefficients k, and k, could be determined. The details of the LIF detection of the methoxyl radical are described elsewhere.,

For calibration purposes, and in some kinetic experiments, we generated CH,O directly in the sliding injector *via* the reaction **of** fluorine atoms with methyl nitrite'

$$F + CH,ONO + CH,O + FNO$$
 (7)

and used this system to study reaction (2). Mass spectrometric analysis showed that the signal from the species FNO at m/e = 49 remained essentially constant while CH,O decayed, indicating that FNO chemistry does not interfere.

Materials

Nitric acid (BDH, **99.9%**) was dehydrated by sulfuric acid (BDH, **99.5%**) in a 1:2 volume-to-volume mixture and held at *ca.* **258 K.** Helium (BOC) was passed through two traps held at **77 K** containing molecular sieve **4A** (BDH) to remove water and an OXISORB cartridge (Messer Griesheim) to remove oxygen. Methane (BOC) and fluorine (**5%** in He)



Fig. 1 Experimental arrangement of the flow tube and detection system. Sources of radicals are indicated in the table.

were used without further purification. For the experiments using deuteriated reagents, the chemicals used were: helium (Messer Griesheim), CD₄ (MSD isotopes, 99% D) and fluorine (5% in He). Methyl nitrite (CH₃ONO) was synthesised by the dropwise addition of sulfuric acid (33% in H₂O, 150 ml) onto a 1:1 mixture of water and methanol (20 ml each) and sodium nitrite (25 g, Aldrich) at 273 K. The brown methyl nitrite gas produced was pumped through two traps, the first containing CaCO₃ powder (Aldrich) and the second containing KOH pellets (Aldrich) to remove any residual acid. The gas was then trapped in a cold finger held at 196 K. The resulting yellow liquid was stored in the dark at this temperature until required. As will appear later, it is essential to minimise residual methanol in the methyl nitrite. To purify the CH₃ONO, it was vacuum distilled from 196 K to 77 K several times (typically three) until the CH₃OH impurity, as determined mass spectrometrically, was less than 5%.

Results and Their Analysis

Reaction of CH_3O with NO_3 using CH_3ONO as the Source of CH_3O

A preliminary investigation of the kinetics of reaction (2) was performed in which CH₃O was generated via the reaction of fluorine atoms with methyl nitrite⁵ in reaction (7). At first sight, this method seemed to be successful and a good combined second-order plot was obtained at 1.6 Torr total pressure (see Fig. 2), which gives the result $k_2 = 1.6 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. However, we observed anomalous effects when NO₃ concentrations were lower than 8×10^{12} molecule cm⁻³. For these concentrations, rather than a drop in CH₃O signal following addition of NO₃, an increase occurred. We attributed this effect to the presence of the hydroxymethyl radical (CH₂OH) and its reaction with NO_3 . The source of CH₂OH was the reaction^{6,7}

$$F + CH_3OH \rightarrow CH_2OH + HF$$
 (8)

the methanol being an impurity in the methyl nitrite samples. When methanol alone was used as a source of CH_3O , these anomalous effects were more pronounced, confirming our hypothesis. NO₃ may react with CH_2OH to form CH_3O directly, or the removal of CH_3O in reaction with CH_2OH may be suppressed. It is inappropriate to speculate further about this phenomenon, but the value obtained for k_2 at 1.6 Torr should only be treated as approximate, and an alternative source of CH_3O was sought.



Fig. 2 Plot of $\ln([CH_3O]_0/[CH_3O])/[NO_3]_0$ as a function of time. P = 1.6 Torr.

Reactions of CH_3 and CH_3O with NO_3 using the Reaction between CH_3 and NO_3 as the Source of CH_3O

We discovered an excellent alternative source for the generation of methoxyl radicals, which was a branch of reaction (1) itself

$$CH_3 + NO_3 \rightarrow CH_3O + NO_2$$
 (1a)

Using this source, reactions (1) and (2) were studied as a pair of consecutive reactions. With NO₃ in excess, both processes (1) and (2) could be treated as first order. It was assumed that, for both methyl and methoxyl radicals, some first-order losses independent of NO₃ could occur, *e.g.* on the walls. With these rate coefficients for losses identified as k'_{CH_3} and k'_{CH_3O} , the total first-order loss can be written

$$k'_1 = k'_{\rm CH_3} + k_1 [\rm NO_3]$$
 (I)

$$k'_2 = k'_{\rm CH_{3}O} + k_2[\rm NO_3]$$
 (II)

The concentration-time profile for CH_3O can therefore be expressed as

$$[CH_{3}O]_{t} = \frac{k'_{1a}[CH_{3}]_{0}}{k'_{1} - k'_{2}} [exp(-k'_{2}t) - exp(-k'_{1}t)]$$
(III)

where $k'_{1a}(=k_{1a}[NO_3])$ denotes the specific channel forming methoxyl radicals and [CH₃]₀ is the initial methyl radical concentration. Eqn. (III) could then be used to fit the experimentally derived LIF signal from CH₃O as a function of time. We use this equation as the basis for analytical methods of obtaining the rate constants, but, as we shall show shortly, a numerical correction procedure had to be adopted because of complications in the reaction system. A non-linear least-squares fitting procedure was applied, with k'_{1a} [CH₃]₀, k'_{1} and k'_{2} being the three parameters optimised. Fig. 3 shows a set of typical profiles for [CH₃O] and the results of the three-parameter fit. Note that the absolute scale for [CH₃O] emerges only as an outcome of the modelling procedures to be presented later, but has no bearing on the three-parameter fit, which can use arbitrary units for the calculations. The expected rise and decay indicative of consecutive processes is evident. Values of k'_1 and k'_2 obtained from the fitting procedure were plotted against [NO₃]₀ to yield the second-order rate constants k_1 and k_2 . There is no ambiguity about which rate constant is the larger, since we already have



Fig. 3 Concentration-time profiles for $[CH_3O]$ showing the results of the three-parameter fitting in the $CH_3 + NO_3$ system. P = 2.4 Torr. (\blacklozenge) $[NO_3]_0 = 4.6 \times 10^{12}$ molecule cm⁻³; (\bigtriangledown) $[NO_3]_0 = 1.2 \times 10^{13}$ molecule cm⁻³; (\blacksquare) $[NO_3]_0 = 1.7 \times 10^{13}$ molecule cm⁻³. The results obtained from numerical modelling are almost identical (see text).

an approximate value for k_2 obtained from the experiments with CH₃ONO.

An alternative method employed to analyse the CH₃O concentration-time profiles was to use just the decay part of the curve to determine k'_2 . Provided that k'_1 is much larger than k'_2 , and at a sufficiently long time t, eqn. (III) can be rewritten

$$\ln[CH_{3}O]_{t} = \ln\left(\frac{k'_{1a}[CH_{3}]_{0}}{k'_{1}}\right) - k'_{2}t$$
 (IV)

and k'_2 can be determined. Then a two-parameter $(k'_{1a}[CH_3]_0)$ and k'_1) fit of the data using the calculated k'_2 could be performed to determine k'_1 . The two methods yielded essentially the same rate constants for k'_1 and k'_2 . However, for some experiments where there were not enough points in the decay part of the curve, the first method was used exclusively. In those experiments where the shortest contact time had already exceeded the time for the maximum [CH₃O] to be reached, the second method was used. At a pressure of 2.4 Torr, the three-parameter fit could always be used. This pressure is particularly important to us, because it is the same as that used in the experiments described in the next paper² and in support of which the present work was a necessary precursor. We shall show in the subsequent paragraphs that the rate constants must be corrected. In this discussion, several modifications to the pseudo-first-order rate constants, k'_1 and k'_2 , will be needed. We shall adopt a superscript 'exp' to indicate uncorrected experimental rate coefficients; other superscripts for rate constants corrected for secondary reactions or diffusion, or extracted by numerical modelling, are defined in the footnote to Table 1. The table presents the uncorrected rate coefficients for k_1^{exp} and k_2^{exp} derived at 2.4 Torr (columns 4 and 7). This type of approach has been employed previously³ to good effect for the reactions of NO₂ with CH₃ and CH₃O. There were, however, two important differences between the NO₂ and the NO₃ systems. First, the maximum concentration which could be attained for NO3 was an order of magnitude less than for NO₂ ([NO₃]_{max} = 3.5×10^{13} molecule cm^{-3}); thus, in the NO₃ case, methyl radical loss via its self reaction could not be neglected. Secondly, at long contact times in the NO₂ system, the LIF signal for CH₃O decayed to zero, whereas in the NO₃ experiments there was a distinct CH₃O signal still present even at contact times as long as 120 ms. In fact, this signal was virtually constant after 80 ms. This second phenomenon is demonstrated in Fig. 4, which shows a typical experimental concentration-time profile for CH₃O together with a fit from a numerical model (see later). It is evident that some process is in operation that regenerates CH_3O . A probable explanation for this regeneration is that the products of reaction (2) are predominantly CH_3O_2 and NO_2

$$CH_3O + NO_3 \rightarrow CH_3O_2 + NO_2$$
 (2a)

and that CH₃O₂ itself reacts with NO₃ reforming CH₃O

$$CH_3O_2 + NO_3 \rightarrow CH_3O + NO_2 + O_2 \tag{9}$$

The regeneration process appears to be efficient, as demonstrated by the very small decay of CH_3O seen at long contact times, which itself points strongly to reactions (2*a*) and (9) being the major channels in the reaction of CH_3O and CH_3O_2 with NO₃. Model calculations show that the fraction of CH_3O radicals passing through the reactions that regenerate these radicals is between 0.6 and 0.7 for t > 60 ms. To test the hypothesis that CH_3O was regenerated, a set of experiments was performed to look specifically for CH_3O_2 as a product, as we shall discuss later. Regeneration of CH_3O makes simple application of the three-parameter fitting

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| Table 1 | Values of k'_1 | and k'_2 at | P = 2.4 | Torr |
|---------|------------------|---------------|---------|------|
|---------|------------------|---------------|---------|------|

| P/Torr | $[NO_3]_0/10^{13}$ molecule cm ⁻³ | Δ[NO ₃]/[NO ₃] ₀ | $k_1^{\prime exp}/s^{-1}$ | $k_1^{\prime m corr}/ m s^{-1}$ | $k_1^{\prime num}/s^{-1}$ | $k_2^{\prime \exp}/{ m s}^{-1}$ | $k_2^{\prime \mathrm{diff}}/\mathrm{s}^{-1}$ |
|--------|--|---|---------------------------|----------------------------------|---------------------------|---------------------------------|--|
| 2 37 | 0.81 | 0.18 | 595 | 368 | 324 | 69 | 72 |
| 2.40 | 0.46 | 0.20 | 364 | 212 | 189 | 60 | 62 |
| 2.40 | 0.58 | 0.14 | 370 | 252 | 220 | 61 | 63 |
| 2.40 | 0.83 | 0.14 | 442 | 303 | 307 | 74 | 77 |
| 2.40 | 0.80 | 0.14 | 366 | 250 | 240 | 78 | 81 |
| 2.40 | 1 24 | 0.12 | 593 | 440 | 397 | 74 | 77 |
| 2.40 | 1.24 | 0.09 | 856 | 675 | 656 | 69 | 71 |
| 2.40 | 2 27 | 0.02 | 000 | 0,0 | 863 | 88 | 92 |
| 2.40 | 1.20 | 0.14 | 496 | 341 | 336 | 74 | 77 |
| 2.51 | 1.20 | 0.17 | 1047 | 766 | 730 | 103 | 108 |
| 2.31 | 1.92 | 0.12 | 622 | 482 | 383 | 82 | 86 |
| 2.31 | 1.42 | 0.10 | 520 | 304 | 329 | 68 | 71 |
| 2.38 | 0.94 | 0.12 | 320 | 256 | 323 | 87 | 86 |
| 2.38 | 1.23 | 0.12 | 460 | 530 | 352 | 02 71 | 72 |
| 2.38 | 1.53 | 0.10 | /1/ | 547 | 439 | /1 | 100 |
| 2.47 | 2.28 | 0.06 | | | | 95 | 100 |
| 2.39 | 1.21 | 0.12 | 570 | 412 | 424 | 71 | /4 |
| 2.39 | 0.63 | 0.16 | 293 | 192 | 189 | 54 | 56 |
| 2.43 | 1.67 | 0.13 | 719 | 508 | 451 | 83 | 87 |
| 2.40 | 1.97 | 0.14 | | | | 89 | 93 |
| 2.40 | 1.28 | 0.16 | 592 | 391 | 384 | 64 | 66 |
| 2.38 | 1.35 | 0.13 | 567 | 400 | 378 | 69 | 72 |
| 2.38 | 0.68 | 0.15 | 364 | 246 | 204 | 54 | 55 |

Column 3 displays the values of Δ [NO₃]/[NO₃]₀ averaged over all contact times. Column 4 shows the values of k'_1 derived from applying the three-parameter fitting method to the experimental data. In column 5 are the corrected values of k'_1 (see text). In column 6 are the values of k'_1 derived from application of the numerical model to the experimental data. Column 7 shows the values of k'_2 derived from application of the numerical model to the experimental data. Column 7 shows the values of k'_2 derived from application of the three-parameter fitting method. Column 8 shows the values of k'_2 corrected for axial diffusion and radial concentration gradients.

method as used previously for the NO₂ system subject to error.³ We therefore adopted a correction procedure in which a numerical model was used to refine the results of the threeparameter fit in an iterative way. We prefer this procedure to straight fitting to a numerical model. Preliminary trials indicated that there was no advantage in using such a model to fit the data from our experiments at relatively short contact times (t < 25 ms). It is not possible either to distinguish between the reaction of CH₃O with NO₃ to form CH₃O₂ and other losses of CH₃O, or to define a value for the rate coefficient for reaction between CH₃O₂ and NO₃. The numerical integrations for the model were performed using a program written in BASIC that employed a second-order single-step backward-differentiation method.



Fig. 4 Experimental (CH₃O) and modelled (CH₃O, CH₃O₂) concentration-time profiles for long contact times in the CH₃ + NO₃ system. P = 0.6 Torr; [NO₃]₀ = 2.5×10^{13} molecule cm⁻³. (**II**) Experimental [CH₃O]; (---) modelled [CH₃O]; (---) modelled [CH₃O₂].

Correction Procedures

Data for the numerical model are given in Table 2. Fitting was achieved largely by eye, assisted by examination of mean-square deviations. The approximate values of k_1 , k_2 and k_9 so derived are then used as the starting point for a correction procedure based on the numerical model. This procedure consisted of first generating simulated concentration-time profiles of [CH₃O] for a variety of starting conditions, including input values of k'_1 and k'_2 , called here $k_1^{\prime in}$ and $k_2^{\prime in}$. We then ran the three-parameter fit on these generated data to recover the values of k_1^{out} and k_2^{out} . In all experimental runs, we observed a drop in [NO₃] on addition of methyl radicals to the system (Table 1). This drop, identified as Δ [NO₃], was usually about 10–15% of the $[NO_3]$ in the absence of CH₃ ($[NO_3]_0$). A simple empirical relating $R = k_1^{\prime in}/k_1^{\prime out}$ relationship was found to $\Delta[NO_3]/[NO_3]_0$. This relation is

$$R = (0.97 \pm 0.02) - (1.86 \pm 0.12) \times \Delta[\text{NO}_3]/[\text{NO}_3]_0 \text{ (V)}$$

R was used to modify the values of $k_1^{(exp)}$, obtained from the three-parameter fit to the experimental data. The modified values for k'_1 (termed $k'_1^{(corr)}$) at 2.4 Torr are shown in Table 1, column 5. Fig. 5 shows $k'_1^{(corr)} (=R \times k'_1^{(exp)})$ plotted as a function of $[NO_3]_0$. Although there are generally few points on the rise portions of the concentration-time profiles, the time dependence of the maximum of the $[CH_3O]$ provides a good definition of k'_1 , as indicated by the relatively small scatter in Fig. 5. Indeed, the statistical error on the slope of this figure is $\pm 0.24 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ (95% confidence limits), but an additional error arises from uncertainty in the zero of time that is itself due to mixing effects and axial diffusion. We therefore quote k_1 as $(3.5 \pm 1.0) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The intercept in Fig. 5 is zero, the reason for which is that the correction procedure corrects for any first-order losses that are independent of $[NO_3]$.

Correction of the rate constant for reaction (2) proceeds in a similar manner, but here there appears to be no simple factor to be applied to the pseudo-first-order rate coefficient

 Table 2
 Rate parameters used in the numerical model

| reaction | k/cm^3 molecule ⁻¹ s ⁻¹ | number | ref. |
|---|--|---------------|-----------|
| $CH_3 + NO_3 \rightarrow CH_3O + NO_2$ | 3.3×10^{-11} | (1 <i>a</i>) | a |
| $CH_3 + CH_3 \rightarrow CH_3CH_3$ | 4×10^{-11} | (10) | 8 |
| $CH_3O + CH_3O \rightarrow products$ | 1.0×10^{-11} | άň | 9 |
| $CH_3 + CH_3O \rightarrow products$ | 4×10^{-11} | (12) | 6 |
| $CH_3O \rightarrow products$ | $25-50 \text{ s}^{-1}$ | (13) | see text |
| $CH_3O + NO_3 \rightarrow CH_3O_2 + NO_2$ | $2-3 \times 10^{-12}$ | (2a) | see text |
| $CH_{3}O_{2} + NO_{3} \rightarrow CH_{3}O + NO_{2} + O_{2}$ | 1×10^{-12} | (9) | see text |
| $CH_3 + NO_2 \rightarrow CH_3O + NO$ | 2.3×10^{-11} | (14) | 3. 10 |
| $CH_3O + NO_2 \rightarrow products$ | 2.0×10^{-12} | (15) | 3, 11, 12 |
| $CH_3O + NO \rightarrow products$ | 5.0×10^{-12} | (16) | 13 |
| $NO_3 + NO_2 + M \rightarrow N_2O_5 + M$ | 4.0×10^{-14} | (17) | 14 |
| $NO_3 + NO \rightarrow 2NO_2$ | 3.0×10^{-11} | (6) | 15 |

^a The numerical model yields a value $k_1 = (3.3 \pm 0.9) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹; the corresponding first-order rate constants are listed in Table 1. ^b For reaction (12) the rate constant was estimated to be twice the geometric mean of k_{10} and k_{11} .

 k'_2 . Instead, we plot the values of k'_2^{out} (generated by application of the three-parameter fit to the simulated data) against $[NO_3]$ to obtain a predicted value of the second-order rate constant, k_2^{out} , and compare k_2^{in} with this value to provide the correction. The relation is $k_2^{in} = 1.1 \times k_2^{out}$. Values of k'_2^{exp} were obtained from the three-parameter method or from direct logarithmic analysis at relatively long contact times. These values were corrected for radial and axial diffusion using the standard methods of Walker,¹⁶ Brown¹⁷ and Keyser¹⁸ to yield the rate constant k'_2^{diff} . Fig. 6 is a plot of k'_2^{diff} against $[NO_3]_0$ for three pressures, and is the source of the uncorrected value of k_2 . Table 3 collects the uncorrected and final corrected values for k_2 at each pressure. At the lowest pressure (0.6 Torr), the available linear flow velocity was not sufficient to give a range of contact times suitable for



Fig. 5 Corrected pseudo-first-order rate coefficient (see text) for the reaction $CH_3 + NO_3$, plotted as a function of $[NO_3]_0$. (\triangledown) 1.0; (\triangle) 1.4 and (\square) 2.4 Torr.

the evaluation of the rate constant k'_2 by the analytical method. The only way of extracting kinetic parameters from these data was to use the numerical model. It was possible to distinguish clearly between the numerical fits to the experimental data at these long contact times (up to 120 ms), for values of k_2 in the range $(1.5-2.5) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Similar calculations were carried out for the experiments at 1.01 and 1.40 Torr. For the higher pressures, 2.4-8.5 Torr, the numerical model produced very good fits to the experimental data using the values of k_2 shown in Table 3 (column 4). In making this fit, k_9 is used as an adjustable parameter and a value for this rate constant can therefore also be derived. The value obtained for k_9 is $(1.0^{+1.0}_{-0.5}) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. The error limits indicate the highest and lowest possible rate coefficients that could be used to fit the



Fig. 6 Pseudo-first-order rate coefficient (derived from the threeparameter method) for the reaction $CH_3O + NO_3$, plotted as a function of $[NO_3]_0$. (∇) 1.0; (\Box) 2.4 and (\blacksquare) 5.4 Torr.

Table 3 Summary of the values obtained for k_2 at various pressures

| pressure/Torr | no. of experiments | $k_2/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹ | $k_2/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹ | $k_2/10^{-12}$ cm ³ molecule ⁻¹ s ⁻¹ |
|---------------|-----------------------|--|--|--|
| 0.60 | 6 | | | 2.2 ± 0.5 |
| 1.01 | 9 | 1.6 + 0.3 | 1.7 ± 0.3 | 2.1 ± 0.6 |
| 1.40 | 6 | 1.8 ± 0.6 | 2.0 ± 0.6 | 2.1 ± 0.6 |
| 2.40 | 22 | 2.1 + 0.7 | 2.3 ± 0.7 | |
| 5.44 | 10 | 3.0 + 1.2 | 3.3 ± 1.2 | |
| 8.50 | 6 | 3.3 ± 1.5 | 3.6 ± 1.5 | |

Column 3 shows the values of k_2 derived from the three-parameter fit corrected for axial diffusion and radial concentration gradients. Column 4 shows the values of k_2 from column 3 corrected by the numerical method. Column 5 shows the values derived for k_2 by fitting to the numerical model.



Fig. 7 Mass-spectrometric determination of the relative concentration of CD_3O_2 in the reaction of CD_3 with NO_3 . (\blacksquare) Experimental points; (——) a fit using the numerical model (see text).

experimental data. However, the fits using these limiting values are not as good as those employing the centre value, requiring values of k_9/k_2 which are incompatible with the experiments presented in the next paper.²

Identification of CH₃O₂

We cannot detect CH_3O_2 directly in our system. In experiments where CH_3O_2 is produced directly (see subsequent paper),² titration with NO

$$CH_{3}O_{2} + NO \rightarrow CH_{3}O + NO_{2}$$
(18)

can be used as an indirect method of monitoring the peroxy radical. However, in the present studies the NO would react mainly with NO₃ and CH₃O so that the method is not satisfactory. An alternative series of experiments was used to demonstrate the occurrence of reaction (2a). A discharge-flow system at the University of Kiel (Germany) equipped with a quadrupole mass spectrometer that had a high sensitivity towards the peroxy radical CH₃O₂ (1 × 10¹⁰ molecule cm⁻³) was used for this purpose. In these experiments, CD₄ was substituted for CH₄. Unambiguous assignment of CD₃O₂ at its parent ion (m/e = 50) was possible, whereas the CH₃O₂ peak (m/e = 47) suffered from strong interferences from secondary peaks of other species in the system. The deuteriated peroxy radical was indeed identified; it arises from the reaction sequence

$$F + CD_4 \rightarrow CD_3 + DF \tag{19}$$

$$CD_3 + NO_3 \rightarrow CD_3O + NO_2$$
 (20)

$$CD_3O + NO_3 \rightarrow CD_3O_2 + NO_2$$
(21)

A typical experimental run showing the build up of CD_3O_2 , together with the calculated $[CD_3O_2]$ from the numerical model, is shown in Fig. 7. We are confident, therefore, that the inclusion of reaction (2*a*) in the numerical model is justified.

Discussion

Reaction between CH₃ and NO₃

It is clear that the reaction between CH_3 and NO_3 is fast; the major channel appears to be process (1*a*). It is also evident that the reaction does not show a significant pressure dependence, at least over the range 1.0-2.4 Torr (see Fig. 5). In a previous study,³ we investigated the pressure dependence of the reaction of NO_2 with CH_3 and CH_3O and used the semi-

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empirical quantum RRK (QRRK) method¹⁹ to rationalise our observations. If the same approach is adopted here, we must first look at the possible products which arise from the formation of the [CH₃-ONO₂]* energised complex. There are four possible channels, illustrated by the energy diagram for this reaction system in Fig. 8; simple bond fission of the complex can either regenerate the reactants or yield CH₃O $+ NO_2$ depending on whether the C-ON or CO-N bond breaks. Similarly, the energised complex can undergo extensive bond rearrangement and fission to form HCHO and HONO; and finally, the complex can be stabilised to form an adduct, which in this system is likely to be CH₃ONO₂. The **ORRK** method allows the calculation of the microcanonical rate constants for each particular channel for a given total internal energy of the energised complex. The data required for this calculation are the high-pressure Arrhenius preexponential factor (A^i_{∞}) and the activation energy (E^i) for each process i; the parameters employed are summarised in Table 4. No information exists for the dissociation of CH₃ONO₂ to CH₃ and NO₃. The activation energy was therefore taken to be the difference between the heat of formation of CH₃ONO₂ and the combined heat of formation of CH_3 and NO_3 ; the A factor was estimated from A factors for similar simple bond fission reactions.²⁰ Table 5 shows the partitioning of the four channels at four pressures. It is clear that channel (1a) should dominate at pressures up to 10 atm and that the stabilised adduct (CH₃ONO₂) would only become a significant channel beyond this pressure. This result is consistent with our experimental conclusion that channel (1a) is the only branch of reaction (1) in our system and indicates that a pressure dependence is not expected.

Reaction between CH₃O and NO₃

As in the case of reaction (1), several possible channels

$$CH_3O + NO_3 \rightarrow CH_3O_2 + NO_2$$
 (2a)

$$CH_3O + NO_3 \rightarrow HCHO + HNO_3$$
 (2b)

$$CH_3O + NO_3 + M \rightarrow CH_3O_2NO_2 + M \qquad (2c)$$

exist for reaction (2). As pointed out earlier, the extent to which CH_3O is regenerated in the pair of reactions (2) and (9)



Fig. 8 Energy diagram for the reaction between CH_3 and NO_3 . The energies on which this diagram is based, and the justifications for their adoption, are presented in Table 4.

Table 4 Parameters used in the QRRK calculation for reaction (1)

| reaction | A/s^{-1} | $E/kJ mol^{-1}$ | $\langle v \rangle_{g}/cm^{-1}$ | m | ref. |
|--------------------------------------|----------------------|-----------------|---------------------------------|----|------|
| $CH_3ONO_2 \rightarrow CH_3 + NO_3$ | 1.0×10^{16} | 337.0 | 972.4 | 29 | a |
| $CH_3ONO_2 \rightarrow CH_3O + NO_2$ | 3.2×10^{15} | 166.5 | 972.4 | 15 | 22 |
| $CH_3ONO_2 \rightarrow HCHO + HONO$ | 3.3×10^{13} | 151.0 | 972.4 | 13 | 23 |

^a The A factor was estimated²⁰ and E was calculated¹⁵ from $\Delta_t H(CH_3) + \Delta_t H(NO_3) - \Delta_t H(CH_3ONO_2)$. $\langle v \rangle_g$ is the geometric mean frequency for CH₃ONO₂, estimated from the vibrational data of Bock *et al.*²¹ *m* is the critical number of quanta required for reaction, *i.e.* $E/hv + 1 \ge m \ge E/hv$; here the lower bound is stated. The number of oscillators, for CH₃ONO₂ is 18.

Table 5 Fractional contributions of different channels obtained in the QRRK calculations on the $CH_3 + NO_3$ system

| | P/atm | | | | | |
|---|---------------|-------|-------|-------|--|--|
| process | 0 | 1 | 10 | 100 | | |
| $CH_3 + NO_3$ | ca. 0 | ca. 0 | ca. 0 | ca. 0 | | |
| $CH_{3}O + NO_{2}$ | 0.96 | 0.95 | 0.90 | 0.58 | | |
| HCHO + HONO | 0.04 | 0.04 | 0.04 | 0.03 | | |
| CH ₃ ONO ₂ (stabilised) | <i>ca</i> . 0 | 0.01 | 0.06 | 0.39 | | |

indicates an overall efficiency of 0.6 to 0.7, and thus the lower limit for the fractional contribution of reaction (2*a*) is also in this range.

An interesting feature of reaction (2) is the possible weak pressure dependence observed up to 8.5 Torr (Table 3). By analogy with the corresponding reactions of NO_2

$$CH_3O + NO_2 \rightarrow HCHO + HONO$$
 (19a)

$$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$$
 (19b)

where the pressure-dependent channel (19b) dominates^{3,11,12} above a pressure of 1 Torr, we might expect reaction (2) to show the same characteristics. In addition, the peroxynitrate $(CH_3O_2NO_2)$ formed in reaction (2c) has three more vibrational modes than the corresponding alkyl nitrate (CH_3ONO_2) formed in reaction (19b), so that, for a given fractional excess internal energy and pressure of the bath gas, the stabilisation of a peroxynitrate energised complex relative to redissociation would be expected to be greater than that for the alkylnitrate. Once again, the QRRK method was used to investigate this hypothesis. The data relevant to the calculation are summarised in Table 6. There were no data in the literature for the high-pressure dissociation of methyl peroxynitrate to form either $CH_3O + NO_3$ or HCHO + HONO₂; the A factor was therefore estimated from the kinetics of similar reactions.²⁰ The activation energy for the first of these channels was estimated from heats of formation,¹⁵ and for the second an estimate was made based on the dissociation of CH₃ONO₂ to HCHO + HONO.²³ The QRRK calculations show that complex bond fission of the energised complex leading to HCHO + HONO₂ is negligible, even when the largest possible A factor is used (Table 7). The calculations show that the relative importance of stabilisation of the energised complex is also small. The redissociation channel reforming reactants is negligible even

when the assumed A factor is some ten times greater than that for channel (2a). A measurable pressure dependence of rate of reaction is only expected if changes in bath-gas concentration alter the relative rates of reaction into the various channels as a consequence of the redistribution of the internal energy. As Table 7 shows, no channel other than (2a) appears to contribute in the pressure range of our experiments. No dependence of k_2 on pressure is thus expected. We note that if we use the smallest possible activation energy for redissociation (i.e. the minimum possible energy difference as dictated by the error limits quoted for the heats of formation), we find that at zero pressure a fraction of 0.1 of the energised complexes formed do redissociate to reactants and 0.9 form $CH_3O_2 + NO_2$. There is then the possibility of a small pressure effect. Although there is some tendency for k_2 to increase with pressure (Table 3), we believe that the experimental uncertainties in the individual rate constants do not allow us to be more dogmatic at present. The real problem is that the QRRK method cannot be applied in cases where the energy difference between different possible product channels is small enough to make the predicted differences in rate coefficients comparable with the inherent errors in the calculation of those coefficients introduced by the approximations. This problem is compounded where there are uncertainties in the thermochemical data.

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Table 7 Fractional contributions of different channels obtained in the QRRK calculations on the $CH_3O + NO_3$ system

| P/Torr | | | | | |
|---------------|-------------------------------------|---|--|--|--|
| 0 | 1 | 10 | 760 | | |
| <i>ca</i> . 0 | ca. 0 | <i>ca.</i> 0 | <i>ca</i> . 0 | | |
| 0.98 | 0.98 | 0.95 | 0.80 | | |
| 0.02 | 0.02 | 0.02 | 0.01 | | |
| <i>ca</i> . 0 | <i>ca.</i> 0 | 0.03 | 0.19 | | |
| | 0 ca. 0 0.98 0.02 ca. 0 | P/T 0 1 ca. 0 ca. 0 0.98 0.98 0.02 0.02 ca. 0 ca. 0 | P/Torr 0 1 10 ca. 0 ca. 0 ca. 0 0.98 0.98 0.95 0.02 0.02 0.02 ca. 0 ca. 0 0.03 | | |

Table 6 Parameters used in the QRRK calculation for reaction (2)

| reaction | A/s ⁻¹ | $E/kJ \text{ mol}^{-1}$ | $\langle v \rangle_{g}/cm^{-1}$ | m | ref. |
|--|----------------------|-------------------------|---------------------------------|----|------|
| $CH_3O_2NO_2 \rightarrow CH_3O + NO_3$ | 1×10^{17} | 130.0 | 724 | 15 | a |
| $CH_3O_2NO_2 \rightarrow HCHO + HONO_2$ | 1×10^{15} | 100.0 | 724 | 12 | ь |
| $CH_3O_2NO_2 \rightarrow CH_3O_2 + NO_2$ | 1.1×10^{16} | 87.8 | 724 | 11 | 24 |

^a The A factor was estimated²⁰ and E was calculated¹⁵ from $\Delta_f H(CH_3O) + \Delta_f H(NO_3) - \Delta_f H(CH_3O_2NO_2)$. ^b The A factor was estimated²⁰ and the energy barrier was estimated by comparison with the reaction²³ CH₃ONO₂ \rightarrow HCHO + HONO. $\langle v \rangle_g$ is the geometric mean frequency for CH₃O₂NO₂, calculated from the vibrational data of Zabel *et al.*²⁴

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