Investigation into the Pressure Dependence between 1 and 10 Torr of the Reactions of NO_2 with CH_3 and CH_3O

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The kinetics and pressure dependence of the reactions of NO₂ with CH₃ and CH₃O have been investigated in the gas phase at 298 K, at pressures from 1 to 10 Torr. A low-pressure discharge-flow laser-induced fluorescence (LIF) technique was used. In a consecutive process, CH₃ reacted with NO₂ to form CH₃O, CH₃ + NO₂ \rightarrow CH₃O + NO (1), which further reacted with NO₂ to form products, CH₃O + NO₂ \rightarrow products (2). Reaction (1) displayed no discernible pressure dependence over the pressure range 1–7 Torr, and k_1 was calculated to be $(2.3 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Reaction (2) displayed a strong pressure dependence and an RRKM analysis yielded the following limiting low- and high-pressure rate constants in He, $k_0 = 5.9 \times 10^{-29}$ cm⁶ molecule⁻² s⁻¹ and $k_{\infty} = 2.1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. It is unrealistic to quote errors for this type of analysis. Parametrisation in the standard Troe form with $F_c = 0.6$ yielded $k_0 = (5.3 \pm 0.2) \times 10^{-29}$ cm⁶ molecule⁻² s⁻¹ and $k_{\infty} = (1.4 \pm 0.1) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Atmospheric implications and possible reaction mechanisms are discussed.

Methane is the simplest and most abundant hydrocarbon in the Earth's atmosphere. Both methyl (CH₃) and methoxyl (CH₃O) radicals are key intermediates in the oxidation of methane in the atmosphere and also in combustion systems.¹ In the atmosphere, the fate of methyl and methoxyl radicals is thought to be predominantly reaction with molecular oxygen. However, it has been suggested that in a polluted troposphere, where NO_x (NO and NO₂) levels are elevated, the reactions of CH₃ and CH₃O with NO_x may become important.² These systems are also interesting examples of radical-radical reactions where the possibility of more than one product channel exists.³

In this paper, we report kinetic measurements of the reactions of CH_3 and CH_3O with NO_2

$$CH_3 + NO_2 \rightarrow products$$
 (1)

$$CH_3O + NO_2 \rightarrow products$$
 (2)

at 298 K over a pressure range of 1–10 Torr. Only one previous direct study of reaction (1) has been reported (Gutman and co-workers⁴). These workers followed the decay of CH₃ in the presence of excess NO₂ by mass spectrometry, using a discharge-flow apparatus at 1 Torr total pressure and at room temperature. They observed NO as a product but were unable to detect CH₃O, although they inferred it as the complementary product to NO, and calculated the rate constant k_1 to be $(2.5 \pm 0.5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Other more indirect studies by Glänzer and Troe⁵ and Phillips and Shaw⁶ are also in broad agreement with the value of Gutman and co-workers for k_1 , although the values are a little higher. In the present study, we investigated the pressure dependence of the reaction and confirmed that CH₃O is a reaction product. Possible channels for reaction (2) are

$$CH_3O + NO_2 + M \rightarrow CH_3ONO_2 + M$$
 (2a)

$$CH_3O + NO_2 \rightarrow CH_2O + HONO$$
 (2b)

Several studies of the reaction have been reported; most have used indirect methods,⁷⁻¹¹ but since the discovery by Inoue *et al.*¹² that CH₃O can be detected with great sensitivity by laser-induced fluorescence (LIF), two direct investigations

employing the LIF technique have been undertaken. McCaulley *et al.*² have carried out a low-pressure (1-4 Torr) study using the discharge-flow technique, whilst Frost and Smith¹³ have performed a flash-photolysis LIF experiment to examine the reaction at higher pressures (30-100 Torr). We have extended the range of the low-pressure data. Atmospheric implications of the rate data are discussed.

Experimental

A conventional discharge-flow apparatus was used (Fig. 1) with a double-sliding injector arrangement, consisting of two concentric movable inlets. The flow tube was coupled to a metal fluorescence cell which was blackened inside, and had short baffle arms (30 cm) with Brewster angled windows. The flow tube was made of Pyrex and had an inner diameter of 26.8 mm, while the inner diameters of the concentric injectors were 8.8 mm and 2 mm, respectively. The surface of the flow tube was coated with halocarbon wax (KMZ Chemicals Ltd) and the carrier gas used throughout was helium (BOC); typical flow speeds for the pressures investigated are shown in Table 1.

Methyl radicals were prepared in the sliding injector by the reaction of methane (BOC) with fluorine atoms generated by



Fig. 1 Schematic diagram of apparatus

linear flow velocity/cm s ⁻¹	
1100	
1200	
2000	
2500	
1470	
1000	
700	

a microwave discharge passed through a mixture of F_2 in He, in the reaction

$$F + CH_4 \rightarrow HF + CH_3 \tag{3}$$

By flowing methane through the innermost sliding injector and fluorine atoms through the outermost one, the relative distances between the tips of these two injectors could be adjusted so that a constant concentration of methyl radicals emerged from the tip of the whole sliding injector assembly. At the same time, it was possible to ensure that no fluorine atoms were introduced into the main flow tube. The methyl radicals so produced were allowed to react with an excess of NO_2 , added to the main flow either via a fixed injector (Fig. 1: inlet marked $NO_2^{(b)}$) or directly into the side arm (Fig. 1: inlet marked $NO_2^{(a)}$). Methoxyl radicals were produced and they could further react with NO2. This is a consecutive reaction system of the type $A \rightarrow B \rightarrow C$, where A is CH_3 , B is CH₃O and C is the product. Thus, by monitoring the temporal profile of the CH₃O, both k_1 and k_2 could be determined. Methoxyl radicals were detected by the LIF technique. Note that some early experiments were performed in a system in which the methane was introduced via a single injector into a flow of fluorine atoms and nitrogen dioxide. The results obtained from these early studies were reproducible using the double-sliding injector arrangement. The spectrum obtained for the methoxyl radical (Fig. 2) was in good agreement with the literature spectrum.¹² The excitation wavelengths 298.8 nm $(v'_3 = 3 \leftarrow v''_3 = 0)$ and 292.4 nm $(v'_3 = 4 \leftarrow v''_3 = 0)$ of the $\tilde{A}^2A_1 \leftarrow X^2E_1$ electronic transition were used, although in the vast majority of experiments the shorter wavelength was preferred because of the higher laser power achieved with the dye employed and also because of the reduction in scattered light afforded by our filter combination (see later). The exciting radiation was generated by frequency doubling the output from an excimer (Questek 2000, 308 nm) pumped dye laser (Lambda Physik FL2002) using Rhodamine 6G (Lambda Physik) as the dye medium. The excimer laser was



Fig. 2 LIF excitation spectrum for CH_3O (bars). The dotted line is a spectrum from the literature,¹² normalised to our intensity at 292.4 nm.

Table 2 Compilation of data for reaction (2a) with M = He at 298 K

P/Torr	$NO_2/10^{13}$ molecule cm ⁻³	$k_{2a}/10^{-12} \text{ cm}^3$ molecule ⁻¹ s ⁻¹	ref.
1.04 1.17 2.00 2.98 ^a 3.00 4.95 7.24	1.8-10.5 $1.4-9.2$ $1.6-7.8$ $0.7-4.9$ $1.3-7.5$ $1.9-7.9$ $1.0-5.6$ $1.0-5.6$	1.07 ± 0.27 0.9 ± 0.04 2.28 ± 0.15 2.64 ± 0.63 2.68 ± 0.73 3.31 ± 0.23 4.02 ± 0.99	this work
0.74 1.29 4.04	0.6–20.0	$\begin{array}{c} 4.37 \pm 0.36 \\ 0.64 \pm 0.16 \\ 1.30 \pm 0.19 \\ 2.98 \pm 0.49 \end{array}$	2
30.0 60.0 90.0	67–323 52–146 52–275	7.7 ± 1.6 9.6 ± 1.35 10.2 ± 1.3	13

Errors quoted are one standard deviation (this work), one standard deviation plus 10% experimental error (ref. 2) and two standard deviations (ref. 13). " Refers to experiments performed using just a single sliding injector (see Experimental).

run at a pulse repetition rate of 10 Hz, and approximately 0.1 mJ per pulse of frequency-doubled radiation was obtained. The experimental arrangement was one where the flow tube, excitation beam and photomultiplier (EMI 9893QB/350) were mutually orthogonal. The excitation beam was collimated with a series of baffles. The fluorescence was collected with a quartz lens and detected with the photomultiplier equipped with a filter combination (Schott UG11 $\lambda = 270-380$ nm bandpass filter and Andover Corporation $\lambda \ge 305$ nm long pass filter). The transmission of the filter system is compared with the published fluorescence emission spectrum¹² in Fig. 3. A pulse generator triggered both the excimer laser and a boxcar integrator (EG & G 162). The delay was optimised (*ca.* 2 μ s) to give maximum rejection of the scattered light from the laser and of electrical interference, and the gate width (*ca.* 6 μ s) was chosen to give maximum



Fig. 3 Fluorescence spectrum¹² (solid line) compared with transmission of the filter combination UG11 + 305 nm cut-off (dotted line)



Fig. 4 Typical profile showing variation of $[CH_3O]$ with time of contact with NO₂, P = 2 Torr, flow velocity = 2000 cm s⁻¹; $[NO_2]_0 = 1.65 \times 10^{13}$ molecule cm⁻³

signal-to-noise ratio for the chosen integration time (usually 1 s), by encompassing the fluorescence emission time but not extending beyond it. The integrated signal was displayed on a chart recorder. With this system, a typical sensitivity of $(0.5-1.0) \times 10^{10}$ molecule cm⁻³ was achieved for the methoxyl radical for a signal-to-noise ratio of unity, a 1 s time constant for the boxcar and a 20 s total integration time. All gas mixtures were prepared in a conventional Pyrex vacuum system and stored in bulbs until used. The flow rates were determined by ball flowmeters (Jencons RS1 Type) which were



Fig. 5 Second-order plot for the reaction of CH₃ with NO₂. $P = (\bigcirc) 1.1, (\bigcirc) 2.0, (\square) 3.0, (\bigcirc) 5.0, (\triangle) 7.2 \text{ and } (\blacktriangle) 10.3 \text{ Torr.}$



Fig. 6 Second-order plot for the reaction of CH₃O with NO₂. Data are corrected for diffusion effects. $P = (\blacksquare) 1.0, (\diamondsuit) 2.00, (\Box) 4.95$ and $(\bigtriangledown) 10.30$ Torr.

individually calibrated. The pressure in the flow tube was measured (Edwards differential capacitance manometer Type 600AD) just before the fluorescence cell. Nitrogen dioxide (Matheson) was purified by repeated freeze-pump-thaw cycles at 77 K, and corrections were made for the N_2O_4 - NO_2 equilibrium when calculating the NO_2 concentration in the system from its flow rate. Helium was passed through an 'Oxisorb' cartridge (Messer Griesheim) to remove molecular oxygen, and through two traps held at 77 K containing molecular sieve 4A (BDH Chemicals Ltd) to remove water vapour. Methane (BOC) and fluorine (BOC, 5% in He) were used without further purification.

Results

Reactions (1) and (2) were studied under pseudo-first-order conditions, with at least a ten-fold excess in the concentration of NO₂ over both CH₃ and CH₃O in all experiments. The CH₃O radical concentration never exceeded 8×10^{11} molecule cm⁻³. Conventional analysis¹⁴ of a consecutive reaction scheme yields an expression

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

for the temporal profile of [CH₃O]. Here, k'_1 (= k_1 [NO₂]) and k'_2 (= k_2 [NO₂]) are the pseudo-first-order rate constants, and $[CH_3]_0$ is the initial methyl radical concentration; we know that $[CH_3O]_0 = 0$. This equation was used to fit the observed CH₃O LIF signal as a function of reaction time. A three-parameter fit of the data then yielded k'_1 , k'_2 and $[CH_3]_0$, and hence the true rate constants k_1 and k_2 could be obtained. A typical CH₃O profile is shown in Fig. 4; as expected, we see a rise and decay of [CH₃O] with reaction time, confirming the consecutive reaction scheme. At 10 Torr, the available flow velocity was too small for the rise part of the profile to be observed. In this case, where we observe only the decay of CH_3O in the presence of excess NO_2 , a semilogarithmic plot of ln(CH₃O) vs. reaction time yielded just the pseudo-first order rate constant k'_2 . All values of k'_1 and k'_2 were calculated initially assuming plug-flow. Corrections were then made for axial and radial diffusion by integration of the continuity equation following the methods of Walker¹¹ and Brown,¹⁶ together with the modifications of Keyser,¹⁷ where the fraction of wall collisions that remove radicals (γ) is assumed to be 0.005. Using this value for γ , the wall loss rate constant for CH₃O is 51.5 s⁻¹ at 1 Torr and 23 s⁻¹ at 10 Torr, in agreement with the experimental results of Bérces and co-workers.¹⁸ The pseudo-first-order rate constants were converted into bimolecular rate constants k_1 and k_2 from the known NO₂ concentrations or were obtained from plots of k'_1 and k'_2 vs. [NO₂]. Fig. 5 shows the second-order plot for reaction (1). For reaction (2), there was a clear pressure dependence over the range 1-3 Torr. However, it was only after corrections for diffusion that the higher-pressure data (5-10 Torr) displayed any significant further increase in rate with pressure. This result follows because radial corrections increase with increasing pressure and dominate at the higher pressures. Fig. 6 shows the second-order plots obtained at various pressures, corrected for diffusion effects.

Discussion

Over the pressure range of 1-7 Torr, there is no discernible pressure dependence for reaction (1), and the rate constant obtained in this study was

$$k_1 = (2.3 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Table 3 Structural parameters used for RRKM (columns 2 and 3) and QRRK calculations (column 4); $\langle v \rangle_g$ is the geometric mean frequency (see text)

species	vibrational frequency/cm ⁻¹	rotational constants/cm ⁻¹	$\langle v \rangle_{g}/cm^{-1}$	ref.
CH ₃ ONO ₂	3029 3029 2967 1656 1465 1440 1434 1291 1177 1150 1004 763 858 662 610 361 202 131	A: 0.3934 B: 0.157 C: 0.1147	972.4	20, 21
CH ₃ O	2840 2774 1487 1362 1047 653	A: 5.169 B: 0.932	not used	22, 23
NO ₂	1616.0 1322.5 749.7	A: 8.002 B: 0.434	not used	24, 25
cis-CH ₃ ONO	3040 1411 623 1140 2957 1171 377 249 1620 991 3000 186 1450 836 1446	not used	1029.9	26
trans-CH ₃ ONO	3040 1423 567 1156 2943 1208 340 213 1678 1048 3000 150 1460 812 1446	not used	999.4	26
CH ₃ NO ₂	3065 1586 1397 1087 605 3065 1482 1377 918 477 2972 1443 1100 658 145	not used	1123	27
Lennard-Jones parameters	$\sigma(CH_3ONO_2) = 4.76 \text{ Å} \epsilon/k(CH_3O)$ $\sigma(He) = 2.55 \text{ Å} \epsilon/k(He)$	$(NO_2) = 490 \text{ K}$ = 10.22 K		28

which is in good agreement with the value quoted by Gutman and co-workers⁴ (2.5×10^{-11} cm³ molecule⁻¹ s⁻¹). It is reasonable to assume that three possible channels could exist for reaction (1),

 $CH_3 + NO_2 + M \rightarrow CH_3NO_2 + M$ (1a)

$$CH_3 + NO_2 + M \rightarrow CH_3ONO + M$$
 (1b)

$$CH_3 + NO_2 \rightarrow CH_3O + NO$$
 (1c)

viz two pressure-dependent ones, (1a) and (1b), and a pressure-independent one, (1c).



Fig. 7 Corrected second-order rate constant, k_{2a} , for the reaction $CH_{3}O + NO_{2}$ plotted as a function of pressure in logarithmic 'fall-off' form. The solid curve is the result of an RRKM calculation. (\bigcirc) This work, (\bigcirc) McCaulley *et al.*,² (\blacksquare) Frost and Smith.¹³

From the work of Glänzer and Troe⁵ we would expect channel (1c) to dominate at low pressures. We would therefore conclude that, within the limits of our errors, our rate constant refers exclusively to channel (1c) at 298 K and low pressure.

The analysis of the data for reaction (2) is a little more complicated. Here it is apparent that the pressure-dependent channel is important. Smith³ has suggested that reactions of this type can proceed via an energised complex that may be collisionally stabilised to give an adduct or that may fall apart to give back reactants or products other than the stabilised adduct. Competing with this process is a straightforward bimolecular channel. The scheme thus contains the elements

$$\begin{array}{c} \mathbf{R}_1 + \mathbf{R}_2 \rightleftarrows [\mathbf{R}_1 \mathbf{R}_2]^* & \xrightarrow{[\mathbf{M}]} & \mathbf{R}_1 \mathbf{R}_2 \\ \searrow & \downarrow & \\ & \mathbf{R}_3 + \mathbf{R}_4 \end{array}$$

$$(4)$$

From their temperature dependence study, McCaulley et al.² have calculated a value for k_{2b} of $1 \times 10^{-11} \exp(-1150/T)$ cm³ molecule⁻¹ s⁻¹, yielding a value at 298 K of 2×10^{-13} cm³ molecule⁻¹ s⁻¹. We, like Frost and Smith,¹³ have used this value and subtracted it from the total measured values of k_2 (corrected for diffusion) to give k_{2a} . All three data sets for k_{2a} (this work, McCaulley et al.² and Frost and Smith¹³) are compiled in Table 2 and were used in an RRKM analysis. The RRKM calculation was performed using the program FALLOFF written by Forst;¹⁹ a detailed list of the parameters used in that calculation are shown in Table 3. The calculations were first performed for the reverse dissociation of CH₃ONO₂, and microcanonical rate coefficients for the forward process of reaction (2a) were then evaluated by using

 Table 4
 Comparison of limiting rate constants for reaction (2a) at 298 K

$k_0/10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	$k_{\infty}/10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	ref.
$5.9 5.3 \pm 0.2 5.2 2.6 \pm 0.7$	$2.1 \\ 1.4 \pm 0.1 \\ 2.1 \pm 0.6$	this work: RRKM this work: Troe; $F_{c} = 0.6$ 29 2

the data set and pressure range used in their calculation were rather limited. Reactions (1) and (2) display very different characteristics. For reaction (1), the pressure-dependent recombination channel is minor, while for reaction (2) the opposite behaviour is observed, with the pressure-dependent channel dominating above 1 Torr. Some understanding of this behaviour can be obtained by considering the fate of the energised complex in each case. Fig. 8 and 9 are energy diagrams for the two systems, the energy scales being constructed from a combination of experimental enthalpies of reaction and activation energies. Two points of difference between the two

paper. The value of k_0 from McCaulley et al.² is lower, but



Fig. 8 Energy diagram for the system $CH_3 + NO_2$, data taken from ref. 30, 31 and 34



Fig. 9 Energy diagram for the system $CH_3O + NO_2$, data taken from ref. 30, 35 and 36

reaction systems are evident. First, CH₃ONO is less complex that CH₃ONO₂, so that, for a given internal energy of the reactant, and at a given pressure of bath gas, redissociation is relatively more probable than stabilisation. Secondly, as reference to the two figures will show, there are two exit channels in addition to redissociation for the energised CH₃ONO, but only one for CH_3ONO_2 . One further consideration in the case of the $CH_3 + NO_2$ reaction is that there is also the possibility of forming energised CH₃NO₂, but, as we shall show later, isomerisation from CH₃ONO is severely retarded and stabilisation is again slow compared with redissociation. As an alternative to a full RRKM calculation of the rates of the possible processes (the feasibility of which is not, in any case, assured), it is possible to obtain a semi-quantitative view of the relative reactivities by using a quantum RRK (QRRK) method, as suggested by Dean.³² In this approach, the limiting high-pressure Arrhenius pre-exponential factor (A^i_{∞}) for the particular reaction i is used to stand in place of the transition-state information of the RRKM formulation; the critical threshold energy E_i for reaction *i* is taken either as the dissociation energy of the appropriate (stabilised) complex, or as the measured activation barrier for the formation of new products. The energy-dependent rate constants are then written in Kassel form

$$k_i(E) = A_{\infty}^i \frac{n!(n-m_i+s-1)!}{(n-m_i)!(n+s-1)!}$$
(II)

where s is the number of vibrational degrees of freedom of the adduct, m_i is the number of quanta corresponding to the threshold energy for reaction $i (m_i = E_i/hv)$ and the value of v is taken as the geometric mean of the vibrational frequencies of the adduct $\langle v \rangle_{g}$, as suggested by Thiele *et al.*³³ The total number, n, of quanta of energy available (n = E/hv) must start equal to m_i , and the calculations are performed for this value and successive quantum states. Overall rate coefficients are then determined by summing the values of $k_i(E)$ weighted by the appropriate population factor. In reality, only the first two or three quantum states above m_i make any significant contribution. The two energy diagrams suggest that six reactions should be considered, four for reaction (1) and two for reaction (2); the relevant data used are summarised in Table 5. For reaction (1) between CH_3 and NO_2 , the calculations indicate that channel (1c) to form $CH_3O + NO$ accounts for a fraction 0.975 of the energised CH₃ONO at zero pressure, and that this fraction drops only to 0.723 by 10 atm. The relative rate of formation of (a) $CH_3O + NO$ and (b) HCHO + HNO is 50:1 at $E = 240 \text{ kJ mol}^{-1} (E_{CH_3 + NO_2})$ - $E_{CH_{3}ONO}$). The channel reforming reactants is over 100 times slower than either of these two channels. As noted earlier, the reaction system is rendered more complex by the existence of both methyl nitrite (CH₃ONO) and nitromethane (CH_3NO_2) as possible complexes in the reaction. However, isomerisation between the two is severely hindered by a high energy barrier and a transition state of restricted ('tight') geometry.³⁷ Thus conversion from CH₃ONO to CH₃NO₂ is unlikely to occur. Either redissociation or stabilisation of the CH₃NO₂ complex are possible, but at the low

Table 5 Data compiled for QRRK calculation

reaction	A/s^{-1}	$E/kJ \text{ mol}^{-1}$	$\langle v \rangle_{g}/cm^{-1}$	m	ref.
$CH_3ONO \rightarrow CH_3O + NO$	6.3×10^{15}	172.3	1029.9	14	34
$CH_3ONO \rightarrow CH_2O + HNO$	4.0×10^{13}	161.0	1029.9	13	34
$CH_{3}ONO \rightarrow CH_{3} + NO_{2}$	1.0×10^{16}	240.0	1029.9	16	30ª
$CH_3NO_2 \rightarrow CH_3 + NO_2$	1.8×10^{16}	244.7	1123.0	19	5
$CH_3ONO_2 \rightarrow CH_3O + NO_2$	3.2×10^{15}	166.5	972.4	15	36
$CH_3ONO_2 \rightarrow CH_2O + HONO$	3.3×10^{13}	151.0	972.4	13	35

^a The activation energy was estimated from the thermodynamic data contained in ref. 30; the A factor was also estimated.

Table 6 Fractional contribution of different channels obtained in the QRRK calculations on the $CH_3O + NO_2$ system

process			P/Torr		
	0	1	5	10	100
HCHO + HONO	0.146	0.114	0.064	0.042	0.007
CH ₃ ONO ₂ (stabilised)	0	0.203	0.535	0.678	0.937
$CH_{3}O + NO_{2}$	0.854	0.683	0.401	0.280	0.056

pressures employed in our system very little nitromethane will be formed, as confirmed by the QRRK calculations. We can therefore conclude that CH_3O formation and not adduct formation is to be expected, and that HCHO production will be only a minor channel in our low-pressure system. Mass spectrometric studies^{4,36} have been made of system (1), but neither HCHO nor CH_3ONO were detected as products. Evidence for some CH_3NO_2 formation has been reported.³⁶

Reaction system (2), $CH_3O + NO_2$, is relatively simpler than the $CH_3 + NO_2$ system, since there is only one exit channel in addition to stabilisation and redissociation. Table 6 shows the result of the QRRK calculations in the form of the fractional contribution of the different channels to loss of the energised complex CH₃ONO₂. We note that the absolute pseudo-first-order rate constant for stabilisation ($\beta Z_{11}[M]$; $\beta = 0.2$) is 3.6 × 10⁶ s⁻¹ at a pressure of 1 Torr. According to Table 6, the chemical reaction channel to form HCHO + HONO is always a very minor one at all the pressures above 1 Torr, so that it is justified to analyse the data in terms of a simple Lindemann mechanism in which the excited adduct either redissociates or is stabilised. Since the redissociation in this case corresponds exactly to the process for which we have already carried out the full RRKM analysis, it is instructive to compare the microcanonical rate coefficients k(E) provided by the RRKM calculation with those obtained using the QRRK calculation for the same energies. In general, the microcanonical calculations return rate coefficients a factor of two to four larger than the QRRK values. This agreement is rather satisfactory in view of the assumptions made in the QRRK method, and lends confidence in the use of the approximation, at least for assessing the relative importance of different channels where the predicted rate coefficients differ by factors of several orders of magnitude.

Atmospheric Implications

From a simple pseudo-first-order loss calculation for CH₃, taking³⁸ [NO₂]_{max} to be 3.5×10^{12} molecule cm⁻³, $k_{(CH_3+NO_2)}$ as 2.3×10^{-11} cm³ molecule⁻¹ s⁻¹ and³⁰ $k_{(CH_3+O_2)}$ as 1.8×10^{-12} cm³ molecule⁻¹ s⁻¹ (high-pressure limit), the first-order loss rate constants in reaction with NO₂ and O₂ are 80 s⁻¹ and 9×10^6 s⁻¹ respectively. For CH₃O, taking $k_{(CH_3O+NO_2)}$ as 2.11×10^{-11} cm³ molecule⁻¹ s⁻¹ (high-pressure limit) and³⁰ $k_{(CH_3O+O_2)}$ as 1.9×10^{-15} cm³ molecule⁻¹ s⁻¹, the first-order loss rate constant in reaction with NO₂ is 74 s⁻¹ and approximately 9000 s⁻¹ with O₂. We can therefore conclude that reaction with nitrogen dioxide is not a major loss process for either CH₃ or CH₃O, even when NO₂ concentrations are elevated.

In tabulations of data for use in atmospheric modelling, it has become common practice to use the formalism developed by Troe,³⁹ using a value for the quantity F_c of 0.6. Although this value is probably unrealistic for a system of the kind discussed here, the rate coefficients obtained by this method are included in Table 4 and the fit of the data displayed in Fig. 10.



Fig. 10 Corrected second-order rate constant, k_{2a} , for the reaction CH₃O + NO₂ plotted as a function of pressure. Using the standard Troe formalism³⁹ the solid curve was generated to fit the data. (\blacksquare) This work, (\triangle) McCaulley *et al.*,² (\bigcirc) Frost and Smith.¹³

$$k_{2a} = \frac{k_0[\mathbf{M}]}{1 + \frac{k_0[\mathbf{M}]}{k}} F^{[1 + (\log k_0[\mathbf{M}]/k_{\infty})^2]^{-1}}$$

with F = 0.6, $k_0 = (5.3 \pm 0.2) \times 10^{-29}$ cm⁶ molecule⁻² s⁻¹ and $k_{\infty} = (1.43 \pm 0.03) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

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