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NO₂ Kinetic Studies using Laser-induced Fluorescence

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A laser-induced fluorescence technique has been used to monitor NO₂ in kinetic studies involving this species. Rate-constant values of 2.0, 6.4, 6.8, 11.3 and 22.5×10^{-11} cm³ molecule⁻¹ s⁻¹ have been measured at 300 K for the quenching of NO₂ fluorescence (excitation wavelength 447.9 nm) by Ar, NO₂, CH₂O, CH₃OH and methoxyethyl nitrate, respectively; the rate constants for quenching by Ar and NO₂ are essentially unchanged when the temperature is raised to 590 K. A preliminary study of the reaction of NO₂ with CH₃OH in the temperature range $639 \le T/K \le 713$ has yielded 6.1×10^{-13} cm³ molecule⁻¹ s⁻¹ and 21.4 kcal mol⁻¹ for the pre-exponential factor and activation energy, respectively.

Organic nitrate additives are known to improve the ignition properties of alcohols when the latter are used as diesel fuels.¹ Their action is probably associated with fast thermal decomposition, leading to a variety of radical intermediates that promote the branchedchain oxidation process. Little kinetic information exists on the primary decomposition step, where one of the products is NO₂, or on the subsequent reactions involving either this species or hydrocarbon-derived radicals. We have begun studies on the kinetics of NO₂ in the presence of alcohols, in the gas phase and at elevated temperatures, using laser-induced fluorescence to monitor this species. Our studies have included the characterisation of the NO₂ fluorescence under a variety of pressure and temperature conditions, and a determination of rate constants for several quenching agents. This has been followed by a preliminary kinetic study on the reaction of NO₂ with CH₃OH.

Experimental

The experimental method relies on the use of pulsed laser-induced fluorescence of NO_2 to follow the kinetic behaviour of this species in the presence of an excess of quenching agents or reactants. The experimental design is simple (fig. 1). Light from a nitrogenpumped dye laser is focussed to a point inside a quartz cell and fluorescence is observed through a window at right-angles to the laser beam. Two lenses are used to collect the fluorescence, while spectral discrimination is achieved *via* a high-throughput Bausch and Lomb monochromator. The signal from a high-gain photomultiplier (EMI 9810QB) placed at the exit slit of the monochromator is fed directly into a 50 Ω terminator at the input of a boxcar averager (EG and G model 162) fitted with a digital storage option; this instrument is triggered by a photodiode, which responds to light within the dye-laser cavity. The averaged signal is either read off the meter or fed directly to a chart recorder.

The cell complex is shown in fig. 2. It consists of a quartz tube (3.3 cm diameter) with vacuum ends to limit heat losses *via* conduction; the reaction vessel occupies the middle third of the tube (*ca.* 10 cm long). The vacuum ends contain carbon baffles to improve the quality of the laser beam and limit scattered light. A small Woods horn opposite the observation window also helps to reduce the scattered-light interference.

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Fig. 1. Experimental arrangement for the NO₂ studies using the laser-induced fluorescence technique.



Fig. 2. The cell complex used in the NO_2 studies.

Glass inserts with thermocouples inserted at either end of the reaction vessel, and away from the laser light train, allow continuous monitoring of the gas temperature. Two quartz rods with wire windings along their length, and mounted on glass pillars, heat the cell by radiation.

The cell complex was placed inside a box constructed of 1 cm insulating material (Sindanyo) with openings for the laser beam and observation window and blackened on the inside (Novamet 150) to limit stray light. A second box surrounds the first, separated by 3 cm of ceramic fibre (Kawool). At 700 K the temperature difference along the cell did not exceed 10 K.

The laser has been described before.² Briefly, a N₂ laser (Molectron UV 24) provides 337 nm radiation and stimulates laser action in a dye-laser cavity; the dye (Coumarin 2) gave tunable radiation in the 430-465 nm range with a peak output of *ca*. 700 μ J at 10 Hz repetition rate.

The experiments were conducted in a non-resonant fashion, *i.e.* the laser excitation was in the 450 nm range, while fluorescence was observed in a band *ca.* 48 nm wide



Fig. 3. The excitation spectrum of NO₂ in the region 434-456 nm ($[NO_2] = 1.5 \times 10^{16}$ and $[argon] = 3.2 \times 10^{17}$ molecule cm⁻³; T = 300 K). The experimental spectrum (---) was divided by the laser power (\Box) to give a corrected spectrum (----).

centred at 550 nm; any residual stray laser light was eliminated by monitoring the fluorescence signal beyond the narrow laser excitation radiation using the aperture delay on the boxcar averager (whereas the fluorescence signal was hundreds of ns long, the 'stray light' pulse was only 30 ns long).

The measurements were conducted on static mixtures; samples containing the required gas components were metered into the reaction vessel from prepared mixtures.

Materials

Methanol (BDH) was thoroughly outgassed before use, while formaldehyde was prepared and stored as before.³ The methoxyethyl nitrate preparation was based on the method of Desseigne⁴ and was thoroughly outgassed before use. NO₂ was taken directly from a cylinder (Matheson) and outgassed at 196 K. Oxygen-free argon (BOC) was obtained by passing the gas through an Oxy-Trap (Phase Separation Ltd).

Results

NO₂ Excitation Spectrum

Fig. 3 shows an excitation spectrum for NO₂ monitored at 550 nm obtained by scanning the laser in the 450 nm region on a point-by-point basis, and consists of a series of poorly resolved bands; the true relative intensities of these bands is also shown and was determined by taking the measured laser output profile into account. Much effort has gone into the study of NO₂, which has proved to be a complex molecule spectroscopically. It is difficult to assign the individual bands since there are believed to be contributions from both the ${}^{2}B_{1}-{}^{2}A_{1}$ and ${}^{2}B_{2}-{}^{2}A_{1}$ transitions.⁵ For the purposes of our kinetic measurements the band chosen to monitor NO₂ for optimum signal coincided with the peak of the laser output, *i.e.* the band centred at 447.9 nm.

NO₂^{*} Quenching Rate Constants

Fig. 4(a) shows the NO₂ fluorescence profile as a function of time, the fluorescence promoted by laser excitation at 447.9 nm and monitored at 550 nm. Increased quenching



Fig. 4. NO₂ fluorescence signal as a function of time for various argon concentrations: \Box , 6.4, \bigcirc , 33.7, \triangle , 93.6×10¹⁶ molecule cm⁻³ argon; (---) $\lambda_{\text{excite}} = 447.9 \text{ nm}$; (---) $\lambda_{\text{excite}} = 435.8 \text{ nm}$; $\lambda_{\text{monitor}} = 550 \text{ nm}$.



Fig. 5. First-order quenching rate constant as a function of argon concentration ($[NO_2] = 7.4 \times 10^{16}$ molecule cm⁻³; T = 300 K).

is observed as the concentration of argon is increased from, e.g. $(6.4-94.0) \times 10^{16}$ molecule cm⁻³ at a constant NO₂ concentration of 7.4×10^{14} molecule cm⁻³. For each argon concentration a plot of ln (fluorescence signal) vs. time [fig. 4(b)] is a straight line whose gradient is the first-order rate constant k_{1st} (or $1/\tau$, where τ is the measured lifetime). Similarly a plot of k_{1st} vs. argon concentration is a straight line (fig. 5) whose gradient is the quenching rate constant $k_{Ar} = 2.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The zero intercept suggests quenching by NO₂ to be negligible in this case and that the natural radiative lifetime is not measurable on this timescale.

Fig. 4 also shows the fluorescence profile observed when the laser excitation wavelength is changed from 447.9 to 435.8 nm; within experimental error, the rate constants derived are the same.



Fig. 6. First-order quenching rate constant as a function of NO₂ (\bigcirc) and MEN concentration (\Box) ([NO₂] = 1.6×10¹⁶ molecule cm⁻³) at T = 300 K.

Fig. 6 and 7 show the results when the same procedure is conducted for NO₂, HCHO, CH₃OH and methoxyethyl nitrate (MEN), respectively. The intercepts observed in fig. 7 are the contributions of the bath gas (argon) to the first-order decay constant; the magnitudes of these intercepts are consistent with the observations in fig. 5. Table 1 summarises the quenching rate constants derived in this manner, with argon and MEN being the least and most effective quenching agents, respectively. Table 1 also compares the results obtained for argon and NO₂ at 300 and 590 K; within experimental error, the results are unchanged.

Reaction of NO₂ with CH₃OH

Fig. 8(a) shows the NO₂ fluorescence signal in the presence of argon at 682 K. The gas mixture is introduced into the hot cell and the averager response is steady after *ca.* 12 s, remaining constant over a 200 s period. On repeating this exercise with methanol replacing argon, quenching of the NO₂ fluorescence is more severe, the signal-to-noise ratio is lower and the NO₂ signal decays to zero in *ca.* 120 s [fig. 8(b)]. A plot of 1n (fluorescence signal) vs. time is a straight line consistent with pseudo-first-order removal of NO₂, although a small deviation appears at long times (fig. 9). This deviation is attributed to a breakdown of the proposed mechanism outlined below; the effect is minimised by considering the early part of the decay curve, with the gradient attributed to a pseudo-first-order rate constant k_{1st} .

The following reactions must be considered when a mixture of NO_2 in excess of CH₃OH is introduced into the reaction vessel at elevated temperatures:

$$NO_2 + CH_3OH \rightarrow HNO_2 + CH_2OH \tag{1}$$

$$NO_2 + CH_2OH \rightarrow HNO_2 + CH_2O.$$
 (2)



 $[CH_2O, CH_3OH]/10^{16}$ molecule cm⁻³

Fig. 7. First-order quenching rate constant as a function of CH_2O (\Box , $NO_2 = 3.1 \times 10^{14}$ molecule cm⁻³) and CH_3OH concentration (\bigcirc) ($NO_2 = 9.7 \times 10^{14}$ molecule cm⁻³) at T = 300 K.

quenching gas	quenching rate constant/ 10^{-11} cm ³ molecule ⁻¹ s ⁻¹		
	300 K	590 K	300 K ^a
Ar	2.0	2.2	2.1
NO_2	6.4	6.2	7.0
CH ₂ O	6.8		
CH₃ÕH	11.3		_
MĔN	22.5	_	_

Table 1. Quenching rate constants for NO_2 excitation at 447.9 nmwith fluorescence monitored at 550 nm

^a From ref. (12); NO₂ excitation at 435.8 nm (see text).

The unimolecular reaction

$$CH_2OH + M \rightarrow CH_2O + H + M$$

where M refers to the diluent gas, is too slow to compete with reaction (2) in the removal



Fig. 8. NO₂ fluorescence signal in the absence (a) and presence (b) of CH₃OH. (a) $[NO_2] = 2.2 \times 10^{16}$ and $[argon] = 1.1 \times 10^{17}$ molecule cm⁻³; (b) $[NO_2] = 2.2 \times 10^{16}$ and $[CH_3OH] = 1.1 \times 10^{17}$ molecule cm⁻³, T = 682 K.



Fig. 9. NO₂ fluorescence signal as a function of time ([NO₂] = 2.2×10^{16} and [CH₃OH] = 1.1×10^{17} molecule cm⁻³; T = 682 K).

of CH₂OH.⁶ The behaviour of NO₂ and CH₂OH with time is given by $d[NO_2]/dt = -k_1[NO_2][CH_3OH] - k_2[NO_2][CH_2OH]$ $d[CH_2OH]/dt = k_1[NO_2][CH_3OH] - k_2[NO_2][CH_2OH]$

where k_1 and k_2 are the rate constants for reactions (1) and (2), respectively, and square

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	$k_1/10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		
T/K	а	b	[CH ₃ OH]/[NO ₂]
639	7.2	3.6	4.9
647	6.4	3.2	5.0
663	8.5	4.3	5.2
680	15.0	7.5	5.0
682	14.0	7.0	5.0
686	17.3	8.7	5.1
693	20.0	10.0	4.6
693	21.2	10.6	5.0
698	20.9	10.5	5.1
702	26.3	13.2	5.0
713	42.5	21.3	5.2

Table 2. Bimolecular rate constants for the reaction of NO2 with
CH3OH in the temperature range 639-713 K

^a Derived from: $k_1 = k_{1st}/2$ [CH₃OH]. ^b Derived from: $k_1 = k_{1st}/4$ [CH₃OH].

brackets denote concentrations. Assuming steady-state behaviour for CH₂OH leads to

$$k_1[NO_2][CH_3OH] = k_2[NO_2][CH_2OH]$$

and

$$d[NO_2]/dt = -2k_1[NO_2][CH_3OH].$$
 (I)

In excess of CH₃OH this expression becomes

$$d[NO_2]/dt = -k_{1st}[NO_2]$$

where $k_1 = k_{1st}/2$ [CH₃OH], *i.e.* pseudo-first-order removal of NO₂ characterised by the pseudo-first-order rate constant k_{1st} . The methanol concentration is known and k_1 is calculated using eqn (I); in the case illustrated by fig. 9, $k_1 = 1.4 \times 10^{-19}$ cm³ molecule⁻¹ s⁻¹ at 682 K. Table 2 summarises the results obtained when this procedure is conducted on measurements carried out at various temperatures in the range 639-713 K.

The role of the product CH_2O must also be considered since this may lead to additional removal of NO_2 via

$$NO_2 + CH_2O \rightarrow HNO_2 + CHO$$
 (3)

followed by

$$NO_2 + CHO \rightarrow HNO_2 + CO.$$
 (4)

Once again, the unimolecular reaction

$$CHO(+M) \rightarrow CO+H(+M)$$

is too slow to compete with reaction (4) in the removal of CHO.⁶ Pollard and Wyatt⁷ reported an activation energy of 15.1 kcal mol⁻¹ and a pre-exponential factor of 2.1×10^{-14} cm³ molecule⁻¹ s⁻¹ for reaction (3). However, the pre-exponential factor is very much lower than that suggested by Koda and Tanaka⁸ for the reaction of NO₂ with CH₃OH or the value that is derived from the rate constants measured in the present study (*q.v.*). This is surprising when the nature of the two species is considered, it is likely that the pre-exponential factors are similar and that the activation energy reported by Pollard and Wyatt⁷ is more reliable than the pre-exponential factor because of possible

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Fig. 10. Arrhenius plot for the reaction of NO₂ with CH₃OH (where $k_1 = k_{1st}/4$ [CH₃OH]).

heterogeneous reactions. If this is the case the removal of NO_2 by reaction with CH_2O in the present system would be considerable. Applying a steady-state analysis for CH_2O and CHO, in addition to CH_2OH , leads to

$$d[NO_2]/dt = -4k_1[NO_2][CH_3OH]$$
 (II)

where $k_1 = k_{1st}/4$ [CH₃OH], *i.e.* the rate constants derived from the simple analysis above are reduced by a factor of two. The corrected rate constants are given in table 2, while fig. 10 displays these values as a function of temperature in an Arrhenius form; this plot yields an activation energy of 21.4 kcal mol⁻¹ and a pre-exponential factor of 6.1×10^{-13} cm³ molecule⁻¹ s⁻¹.

A possible source of error lies in the fate of HNO₂. The unimolecular decomposition

$$HNO_2 + M \rightarrow HO + NO + M$$
 (5)

yields hydroxyl radicals which would regenerate CH_2OH by reaction with CH_3OH ; the homogeneous decomposition is too slow to play a role at these temperatures,⁹ but heterogenous decomposition of HNO_2 at the reactor walls may contribute to the chemistry. The effect of this process is assumed to remain constant over the small temperature range considered in this study, causing error in the pre-exponential factor but not the activation energy.

The kinetic information available on the self-reaction of HNO₂,

$$2HNO_2 \rightarrow NO_2 + NO + H_2O \tag{6}$$

is both limited and confusing. The reaction is thought to be largely heterogeneous in nature with an upper limit of $k_6 < 1 \times 10^{-20}$ cm³ molecule⁻¹ s⁻¹ for the homogeneous reaction at room temperature.¹⁰

There has been only one study of reaction (6) at temperature close to those used in this study. Asquith and Tyler¹¹ measured a half-life of 10 min for HNO_2 produced in

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the relatively fast reaction of H_2O_2 with NO; the concentration of HNO_2 was similar to the total generated in the reaction of NO₂ with CH₃OH outlined in the present work. The half-life is less than an order of magnitude lower than that expected by using the upper limit for k_6 measured at room temperature; it is unlikely then, that this process is sufficiently fast at 700 K to compromise the analysis used in this work. Nevertheless, the effect of a fast biomolecular reaction (6) can be determined by applying a steady-state analysis for HNO₂ in addition to those species outlined above; this yields expression (I), *i.e.* the rate constants are increased by a factor of two with the same change in the pre-exponential factor.

Discussion

The quenching rate constants for NO₂ and argon at 300 K derived in this study are in good agreement with those given by Myers *et al.*,¹² as shown in table 1. There are no quenching constants for CH₂O, CH₃OH and methoxyethyl nitrate reported in the literature.

Koda and Tanaka⁸ have studied the effect of NO₂ addition to the ignition characteristics of methanol-air mixtures and derived an Arrhenius expression $k_1 = 3.3 \times 10^{-13} \exp(-22.6 \text{ kcal mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the range 900-1100 K for the reaction of NO₂ with methanol. The activation energy is in very good agreement with that measured in the present work, while the pre-exponential factor is lower by a factor of two; however, bearing in mind the experimental techniques and the temperature regimes are different, the agreement is fair.

It is also interesting to compare the activation energy for this reaction with the corresponding reactions involving CH_2O and CH_3CHO . The values reported are 15.1 kcal mol⁻¹⁷ in the CH_2O case and 12.6⁹ and 16¹³ kcal mol⁻¹ in the CH_3CHO case; all three measurements are lower than the value of 21.4 measured in the present study for CH_3OH , a trend consistent with the bond energies and with other abstraction reactions involving these reactants.

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