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Pulsed Laser Photolysis-Laser-induced Fluorescence Measurements on the Kinetics of CN($v = 0$) and CN($v = 1$) with O_2, NH_3 and NO between 294 and 761 K

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Time-resolved laser-induced fluorescence (LIF) measurements have been carried out on the kinetics of CN($v = 0$) and CN($v = 1$) radicals with O_2, NH_3 and NO at temperatures between 294 and 761 K. The radicals were generated by pulsed laser photolysis of NCNO at 532 nm, and the decays of concentration were monitored using a dye laser tuned to lines in either the (0, 0) or (0, 1) band of the CN($B\,^2\Sigma^+$-$X\,^2\Sigma^+$) system. The observed rate constants all decrease with temperature, and accurate values have been determined for the parameters which decribe these variations (see table 4). With O_2 and NH_3, the rate constants for CN($v = 1$) are slightly larger (*e.g.* 23 and 56% at 295 K) than for CN($v = 0$). It appears that the reactions (CN + O_2 and CN + NH_3) must occur over potential-energy surfaces which are initially attractive. With NO, CN($v = 1$) is removed very rapidly [$k_{295} = (7.6 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}], almost certainly because of vibrational relaxation in collisions in which a complex forms and then redissociates. For CN($v = 0$) + NO the rate constant is pressure-dependent and has been investigated only in a limited range. However, at a total pressure of 30 Torr† the rate constant shows a strong negative temperature dependence. The results are consistent with reaction by a radical association mechanism, with no evidence for the channel leading to CO + N_2.

Although reactions of the CN radical are important in a variety of environments,[1-4] there have until recently been rather few efforts to measure their rate constants in direct experiments. In the last few years, however, three research groups, including our own, have taken advantage of the ease with which CN can be observed by laser-induced fluorescence (LIF) to perform kinetic measurements on CN radical reactions in experiments which combine time-resolved LIF detection with generation of the radicals by pulsed laser photolysis of some suitable precursor.[5-9] In addition to these LIF studies, there has been an investigation in which tunable diode lasers have been used to follow loss of CN and formation of HCN by time-resolved infrared absorption.[10]

Although in some of the previous laser-based studies on CN + O_2, NH_3 and NO,[6,7,10] the kinetics of CN($v = 1$), as well as of CN($v = 0$), were investigated, in all of them (and in most of the even earlier work)[11-17] measurements were only carried out at room temperature. The present paper reports one of the first direct measurements on elementary processes involving the CN radical in which the rates have been measured over an extended range of temperatures. As in previous experiments from our laboratory,[9] CN radicals are generated by photolysis of NCNO[18] using the frequency-doubled output of a Nd : YAG laser (λ = 532 nm), and relative concentrations of CN($v = 0$) or CN($v = 1$) are measured at various delays after the photolysis pulse, by measuring the LIF signals

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† 1 Torr = 101 325/760 Pa.

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generated by tuning a pulsed dye laser to a line in the (0, 0) or (0, 1) band of the $B\,^2\Sigma^+$-$X\,^2\Sigma^+$ system of CN.

Here we report rate constants for removal of CN($v = 0$) and CN($v = 1$) by O_2, NH_3 and NO. The reaction of CN with O_2 has now been studied several times at room temperature, but information about its temperature dependence is scarce and contradictory.[11] The reaction of CN with NH_3 has previously been studied at two temperatures (300 and 375 K) in pulsed radiolysis experiments[15] and at room temperature by de Juan *et al.*[8] The rate of reaction of CN with NO is pressure-dependent, and, at least at room temperature, the main reaction channel appears to be association to yield NCNO,[6,16,17] although there is some evidence for a bimolecular route to $N_2 + CO$.[6,17] The rates of these competing reactions would be expected to depend differently on temperature, as well as on total pressure. Li *et al.*[5,6] have measured rates for the removal of CN($v = 1$) by O_2 and NO. In our work, as in theirs, the measured rates are for the sum of the reactive and non-reactive relaxation processes.

Experimental

The apparatus and procedures used in our current experiments are similar to, but modified from, those described by de Juan *et al.*[8,9] Here we shall emphasise the modifications from the earlier experiments.

Reaction is initiated by pulsed laser photolysis of NCNO in the central section of a 1.5 m long flowtube. The laser beams used for generating and detecting CN radicals propagate in opposite directions along the axis of the tube. The centre of the flowtube is enclosed in an oven constructed from refractory fire bricks. Heating is provided by four 1 kW heating elements which are mounted parallel to the flowtube and *ca.* 2 cm from it. At the centre of the furnace, a mineral-insulated type K thermocouple rests on the outer surface of the flowtube. The heating elements are wired in parallel and connected *via* a thyristor (Eurotherm, 425 SSC) to a 20 A, 240 V supply. The power switching is accomplished by a 5-10 V d.c. logic signal from a temperature controller (Eurotherm 810) which is connected to the thermocouple.

At right angles to the hole which takes the thermocouple, there is a $1\frac{1}{4}$ in† diameter horizontal aperture in which is mounted a 1 in diameter, 2 in focal length quartz lens. This gathers any fluorescence from CN and directs it through an appropriate interference filter [for (0, 1) fluorescence, $\lambda_{peak} = 420$ nm; f.w.h.m. = 10 nm; for (0, 0) fluorescence, $\lambda_{peak} = 390$ nm, f.w.h.m. = 10 nm] onto the cathode of a photomultiplier tube (EMI, type 9659 QAM). The whole oven assembly is *ca.* 33 cm long and is enclosed in a stainless-steel box.

The lasers are the same as those used in the experiments of de Juan *et al.*[8,9] Except in some 'test' experiments (see below), NCNO was photolysed by the frequency-doubled output of the Nd:YAG laser ($\lambda = 532$ nm) which provides pulses of *ca.* 100 mJ energy at 10 Hz. This laser is directed through the baffles with the help of a 2 m focal length lens. The home-built dye laser used to detect CN is pumped by a N_2 laser. It is tuned to one of the rotational lines in the B-X (0, 0) band to observe CN($v = 0$) *via* (0, 1) fluorescence and to a line in the (0, 1) band to monitor CN($v = 1$) *via* (0, 0) fluorescence.

A microcomputer (BBC Torch system) is used to control the delays between photolysis and probe laser pulses, to provide the electrical pulses for firing the lasers and to store the LIF signals. The time delays are provided by the internal timer of a 6522 VIA (versatile interface adaptor) chip using interrupt processing to achieve the required 1 μs time resolution. Checks carried out using a commercial pulse delay generator indicated an accuracy in timing of better than 0.1%. The way in which the sequence of pulses to fire the lasers is generated is described in detail in ref. (8).

† 1 in = 2.54 cm.

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Signals from the photomultiplier tube are digitised in a purpose-built gated integrator. A voltage follower is used with a load resistor providing an overall time response of 2-3 μs close to the selected gate width of 4 μs. Digitised signals are accumulated in the microcomputer but are fitted on the University of Birmingham mainframe computer, using a non-linear least-squares procedure to match both the single exponential decay and the baseline of the signals. This procedure takes account of the fact that the residuals depend on the magnitude of the signals, since the main source of variation is the amplitude variation in the output of the probe laser. Signal is recorded at 128 time delays. Usually, 7 signals are accumulated at each delay for measurements on CN($v = 0$); 10 signals per point for measurements on CN($v = 1$).

The total pressure in the flowtube is measured with a calibrated capacitance manometer (MKS Baratron, model 222B), and is kept constant throughout each series of experiments (usually at 15 or 30 Torr), by adjusting a needle valve downstream from the flowtube as different additions of reagent gas plus diluent are made. The total flowrate is such that the lasers fire only once before any sample of gas reaches the observation zone, and it should be remembered that the photolysis laser illuminates $\leq 5\%$ of the cross-section of the flowtube.

In the present experiments, all the gas flows are controlled by mass flow controllers (A.S.M. and Hi-Tec) which have been carefully calibrated by measurements of pressure drop in known volumes. The NCNO, diluted to $<3\%$ in argon, is mixed with the molecular reagent and the main argon diluent in the side-arm leading to the main flowtube. A separate, approximately equal flow of argon is passed into the baffle arm on the upstream side of the reaction zone in order to avoid any accumulation of reaction products.

In order to check how the temperatures of flowing gas in the centre of the flowtube relate to those measured by the thermocouple at the outer surface of the tube, a separate set of experiments was performed. A thermocouple was enclosed in a thin Pyrex tube mounted on a Pyrex end-plate and was then inserted through the baffles on the downstream side of the reaction zone until it reached the point in the flowtube from which fluroescence is normally observed. A normal flow of argon was then set up and the readings of the two thermocouples were compared for several temperature settings. For the flow rates used in most of the kinetic experiments, the temperature in the tube was found to be between 12 and 16 K lower than that measured externally, and this correction was allowed for when recording the temperatures of the kinetic measurements. It is estimated that corrected temperatures should be accurate to ±2 K.

The preparation of NCNO has been described elsewhere.[8] The other gases were obtained commercially: O_2 (B.O.C. standard grade) was passed through a coil immersed in liquid air; NH_3 (B.D.H., laboratory reagent, 99.98% pure) was used without further purification: NO (Cambrain Gases, CP grade, 99% pure) was distilled twice between pentane slush and liquid N_2 traps; Ar (B.O.C. zero grade, $O_2 < 1$ vppm, 99.998% pure) was used directly from the cylinder.

Results

The experiments reported here yield rate data of unusually high precision. In addition, we have made every effort to eliminate sources of systematic error. The time resolution of our method is limited not by the width of the photolysis and probe laser pulses but by the timing equipment. The first-order rate constants that have been measured are in the range *ca.* 10^4-2×10^5 s^{-1}. Using the estimated fluence of the photolysis laser in the reaction zone, the concentration of NCNO in the reaction mixture, and the known absorption cross-section of NCNO at 532 nm,[18] it is possible to estimate that the initial concentration of CN radicals was $[CN]_0 < 4\times10^{11}$ cm^{-3} in experiments on CN($v = 1$)

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and $<1\times10^{11}$ cm^{-3} in measurements on CN($v=0$). This combination of good time resolution and high detection sensitivity was quite sufficient to ensure negligible removal of CN by side and secondary reactions.[19]

To obtain second-order rate constants (k) for removal of CN($v=0$) or CN($v=1$) by a particular reagent, R, a series of experiments was performed with the reagent concentration, [R], being varied systematically whilst the temperature and total pressure were kept constant. During the course of preliminary experiments on the kinetics of CN($v=0$) with O_2 and NH_3, it appeared that the rate constants k for each of these reactions was 10-15% larger at a total pressure of 5 Torr than at 30 Torr. It was eventaully discovered that this systematic discrepancy arose because a first-order constant (k°_{1st}) for decay of the radical concentration in the absence of $R+O_2$ or NH_3 had been included in the plots of k_{1st} *vs.* [R] from which values of k were deduced. In the absence of added reagent and at low total pressure, the observed loss of radicals results mainly from their diffusion out of the region illuminated by the photolysis and probe lasers. This loss process does not necessarily give rise to a single exponential decay. So if a rate constant k°_{1st} derived on the basis of exponential decay is included in the analysis it may affect the gradient of the k_{1st} *vs.* [R] plot and lead to a systematic error in k unless the importance of k°_{1st} is minimised by including at least several values of k_{1st} which are much greater than k°_{1st}. In practice, having discovered this effect, it could be guarded against by: (*a*) generally carrying out experiments at sufficient total pressure to ensure that diffusion was slow, and (*b*) including, in the plots of k_{1st} *vs.* [R], only values of k_{1st} that were at least three times the background rate, k°_{1st}.

Whilst searching for the cause of the discrepancy just described, and subsequently, a number of checks were made on the reliability and reproducibility of the kinetic data. These tests included changing the total pressure, the total flow rate and the partitioning of the argon diluent flow between the main inlet and the inlet to the upstream baffle arm. The rate of the reaction between CN($v=0$) and NO depends on total pressure (see below), but otherwise these changes had no effect on the derived rates. In addition, changes were made to the pulse energy of the photolysis laser, to the wavelength of the photolysis laser (by changing from the frequency-doubled Nd:YAG laser to a dye laser pumped by that laser), to the diameter of the photolysing laser beam, and to the concentration of the NCNO included in the gas mixture as precursor of the CN radicals. Once more the kinetic decays were unaffected. The constancy of the results obtained as these changes were made to the experimental conditions increases confidence in the accuracy of the results.

Tables 1-3 summarise the conditions used in our experiments to determine second-order rate constants for the removal of CN($v=0$) and CN($v=1$) by O_2, NH_3 and NO. Values of k were found from the gradients of plots of k_{1st} *vs.* [R] using a procedure which allows for errors in both quantities. Samples of these plots for CN($v=0$) and CN($v=1$) with O_2 at the extreme ends of the temperature range are given in fig. 1 and 2. The standard deviations in the values of k_{1st} were provided by the non-linear least-squares program that was used to fit the exponential decays of LIF signals. In addition, we estimated the possible random and systematic errors in [R] to be 1.5% each. Allowance for the random error was made in computing the gradient of k_{1st} *vs.* [R] and its standard deviation. A further 1.5% was added to allow for systematic error and the result was then doubled to yield the estimates of uncertainty included in the last columns of tables 1-3.

It has been proposed that CN radicals react in two ways with NO: (i) by pressure-dependent association to give NCNO, and (ii) to yield $CO+N_2$. We find NO to remove CN($v=1$) extremely rapidly. The rate constant was shown to be independent of pressure at 295 K and to decrease with temperature in a similar way to the rate constants for removal of CN($v=0$) and CN($v=1$) by O_2 and NH_3. In the case of CN($v=1$)+NO, we believe (for further discussion, see below) that the dominant process is vibrational

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Table 1. Summary of the experiments and the rate constants derived for the kinetics of CN($v=0$) and CN($v=1$) with O_2[a]

T/K	no. of measurements	range of $[O_2]$ $/10^{15}$ molecule cm^{-3}	$k/10^{-11}$ cm^3 molecule^{-1} s^{-1}
		CN($v=0$)	
294	9	0.6-4.2	2.45±0.10[b]
294	10	0.6-4.7	
359	8	0.5-5.2	2.32±0.12
437	8	0.4-4.3	2.06±0.12
560	8	0.6-4.3	1.89±0.14
761	8	0.45-3.2	1.60±0.07
		CN($v=1$)	
295	5	0.65-2.8	3.01±0.24
359	6	0.5-2.45	2.68±0.26
437	8	0.4-3.7	2.53±0.16
560	8	0.6-3.7	2.40±0.16
761	8	0.45-2.7	2.23±0.20

[a] All experiments were performed at 15 Torr total pressure. [b] Errors equivalent to two standard deviations and including an estimate of systematic error (see text).

Table 2. Summary of the experiments and the rate constants derived for the kinetics of CN($v=0$) and CN($v=1$) with NH_3[a]

T/K	no. of measurements	range of $[NH_3]$ $/10^{15}$ molecule cm^{-3}	$k/10^{-11}$ cm^3 molecule^{-1} s^{-1}
		CN($v=0$)	
295	7	1.0-7.4	2.85±0.14[b]
359	8	0.8-7.7	2.36±0.16
437	8	0.7-6.3	2.21±0.14
560	8	0.9-6.9	1.99±0.14
761	8	0.7-5.1	2.05±0.14
		CN($v=1$)	
295	10	0.6-4.5	4.45±0.30
294	7	1.0-5.4	
348	9	0.5-3.8	3.80±0.30
359	8	0.8-5.0	3.74±0.22
437	10	0.65-5.0	3.18±0.24
560	10	0.8-5.9	2.57±0.14
560	8	0.5-5.8	
761	8	0.7-5.1	2.42±0.14
761	8	0.4-4.3	

[a] All experiments were performed at 30 Torr total pressure. [b] Errors equivalent to two standard deviations and including an estimate of systematic error (see text).

relaxation which is facilitated by the formation of strongly bound NCNO complexes in collisions over an attractive potential-energy surface.

In the present work we have made no attempt to investigate fully the pressure dependence of the reaction between CN($v=0$) and NO, although the results given in table 3 do demonstrate that the rate constants measured for this system at 295±1 K are

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Table 3. Summary of the experiments and the rate constants derived for the kinetics of CN($v = 0$) and CN($v = 1$) with NO

T/K	no. of measurements	range of [NO] /10^{15} molecule cm^{-3}	total pressure /Torr	$k/10^{-11}$ cm^3 molecule^{-1} s^{-1}
		CN($v=0$)		
294.5	7	0.6-2.5	30	0.147 ± 0.018[a]
294.5	9	4.2-30.5	30	0.142 ± 0.010
295.5	7	3.7-10.1	10	0.060 ± 0.004
450	8	12.4-59.8	30	0.038 ± 0.004
		CN($v=1$)		
296	8	0.06-0.45	10	7.5 ± 0.6
294	8	0.2-1.2	30	7.7 ± 0.4
359	9	0.15-1.1	30	7.1 ± 0.5
437	9	0.13-0.91	30	6.7 ± 0.3
560	8	0.10-0.71	30	6.45 ± 0.4
761	9	0.07-0.52	30	5.7 ± 0.4

[a] Errors equivalent to two standard deviations and including an estimate of systematic error (see text).

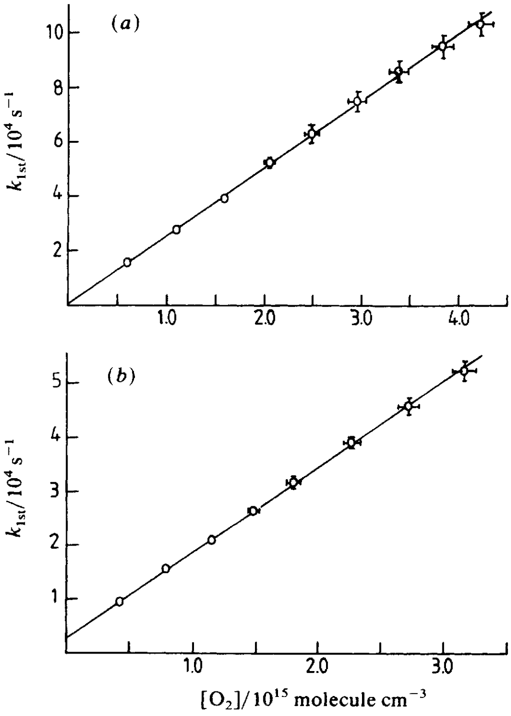

Fig. 1. First-order decay constants for CN($v = 0$) in the presence of O_2 at (a) 294 and (b) 761 K. Error limits are shown where these exceed the size of the symbols: those in the values of k_{1st} are derived from the non-linear least-squares fit to the exponential decays; those in the concentrations correspond to 0.03 [O_2] (see text).

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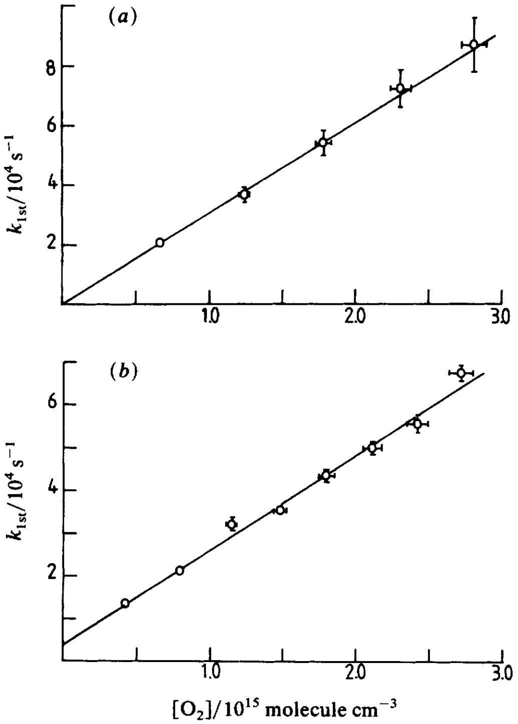

Fig. 2. First-order decay constants for CN($v = 1$) in the presence of O_2 at (a) 295 and (b) 761 K. See fig. 1 for an explanation of the error bars.

much smaller than that for CN($v = 1$)+NO and do depend on total pressure. Table 3 also records the result of measurements at 450 K and 30 Torr; the observed rate constant is 3.8×10^{-13} cm^3 molecule^{-1} s^{-1}, a factor of 3.8 lower than the rate constant at 295 K and 30 Torr. The strong negative temperature dependence of this reaction rate constant was confirmed by measurements at the same total pressure, but at 771 K. Now the rate of removal of CN($v = 0$) by reaction with NO was only comparable to that arising from diffusion, and consequently it was only possible with the present apparatus to estimate a rough value: $k = (5 \pm 3) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Nevertheless, this result further demonstrates the strong negative temperature dependence of the rate constant in this regime of total pressure: the observed reduction of a factor of *ca.* 30 from 295 to 771 K is much greater than in any other system which was studied in the present work.

For all the processes which have been studied in this work, the rate constants decrease with temperature. For all but CN($v = 0$)+NO, this variation of k with T has been fitted to two expressions, the Arrhenius equation

$$k = A \exp(-E_{act}/RT)$$

and a power dependence:

$$k = C(T/298)^n.$$

The derived values of A, E_{act}, C and n are given in table 4 along with their associated uncertainties.

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Table 4. Parameters describing the temperature dependence of the kinetics of CN($v=0$) and CN($v=1$) with O_2, NH_3 and NO

	$k = A \exp(-E_{act}/RT)$		$k = C(T/298)^n$	
process	$A/10^{-11}$ cm^3 molecule^{-1} s^{-1}	E_{act}/kJ mol^{-1}	$C/10^{-11}$ cm^3 molecule^{-1} s^{-1}	n
CN($v=0$)+O_2	1.25 ± 0.16^a	-1.7 ± 0.4	2.47 ± 0.07^a	-0.45 ± 0.04
CN($v=1$)+O_2	1.86 ± 0.08	-1.15 ± 0.15	2.90 ± 0.13	-0.30 ± 0.08
CN($v=0$)+NH_3	1.52 ± 0.23	-1.5 ± 0.6	2.7 ± 0.3	-0.4 ± 0.2
CN($v=1$)+NH_3	1.55 ± 0.15	-2.6 ± 0.4	4.2 ± 0.3	-0.6 ± 0.2
CN($v=1$)+NO	4.95 ± 0.2	-1.09 ± 0.22	7.6 ± 0.2	-0.30 ± 0.04

[a] Errors correspond to two standard deviations (*i.e.* 2σ) calculated according to the formula: $\sigma = \{\Sigma[k(T)_{obs} - k(T)_{calc}]^2/m\}^{1/2}$, where m is the number of individual values of $k(T)$.

Discussion

The reaction of CN with O_2 is the most widely studied reaction of the CN radical. It plays some role in the formation of nitrogen oxides during the combustion of hydrocarbons in air. The reaction almost certainly proceeds according to the equation:

$$CN + O_2 \rightarrow NCO + O; \qquad \Delta H^\circ_{298} \approx -27 \text{ kJ mol}^{-1}.^{20}$$

Its rapid rate and the decrease in the rate constant with increased temperature suggest strongly[21] that the reaction occurs *via* the initial formation of a transient NCOO radical along a reaction path potential which is initially entirely attractive.[22] Clary[22] has reported theoretical calculations which agree with our experimental results in regard to the gentle decrease in the rate constant for reaction above room temperature. The absolute values which he gives for the rate constants are larger than those which we measure. However, no allowance was made in the calculations for the fact that CN($^2\Sigma^+$) and $O_2(^3\Sigma_g^-)$ correlate with two potential surfaces, one doublet and one quartet. If reaction only proceeds *via* the lowest doublet state of NCOO, then the calculated rate has to be reduced by multiplying it by (2/6), yielding rate constants *ca.* 20% lower than the experimental values.

The comparisons which are made in table 5 demonstrate that there is good agreement between our result for the CN($v=0$)+O_2 rate constant at room temperature and the values derived in other, recent, room-temperature measurements using the technique of pulsed laser photolysis-laser-induced fluorescence.[5-9,14] However, fig. 3 shows clearly that our data provide the first accurate and extensive study of the temperature dependence of this reaction, and that our results are considerably at variance with the recommendation made by Baulch and coworkers in 1981.[11] This could have significant effects in any high-temperature modelling calculations which include this reaction.

The rate constant for loss of CN($v=1$) in collisions with O_2 at room temperature has been measured in three previous studies.[5,14,16] Our finding that the ratio of rate constants for CN($v=1$) and CN($v=0$), *i.e.* $k_{v=1}/k_{v=0}$, is equal to 1.23 ± 0.1 is in excellent agreement with the result of Li *et al.*,[5] $(k_{v=1}/k_{v=0}) = 1.2 \pm 0.14$, although the absolute values which they determined for each of the rate constants were slightly lower (*ca.* 20%) than those which we find (see table 5). From the results of two even earlier studies[14,16] it was concluded that the rate constant for CN($v=1$) is slightly less than that for CN($v=0$). However, both these investigations gave rate-constant values which are only *ca.* half those determined in all the most recent work,[5,7,8] including our own.

Although the change in rate constant when CN is excited from $v=0$ to $v=1$ is small, it is statistically significant. It seems very unlikely that this increase results from

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Table 5. Comparison of rate constants obtained in recent pulsed laser photolysis-laser-induced fluorescence studies of the kinetics of CN($v=0$) and CN($v=1$) with O_2 at room temperature

	$k/10^{-11}$ cm^3 molecule^{-1} s^{-1}	source of CN	ref.
CN($v=0$)	1.38 ± 0.13	C_2N_2	14[a]
CN($v=1$)	1.25 ± 0.26	C_2N_2	14[a]
CN($v=0$)	2.0 ± 0.1	C_2N_2	5[a]
CN($v=1$)	2.4 ± 0.1	C_2N_2	5[a]
CN($v=0$)	2.4 ± 0.2	ICN	7[a]
CN($v=0$)	2.6 ± 0.2	ICN	7[b]
CN($v=0$)	1.86 ± 0.2	NCNO	8[a]
CN($v=0$)	2.45 ± 0.10	NCNO	this work[a]
CN($v=1$)	3.01 ± 0.24	NCNO	this work[a]

[a] CN detected using LIF on the *B*–*X* system. [b] CN detected using LIF on the *A*–*X* system.

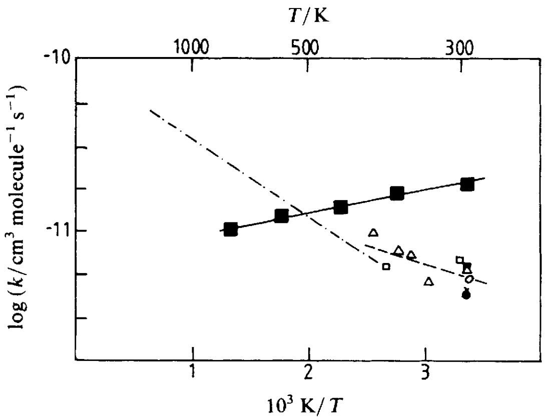

Fig. 3. Arrhenius plot of the rate constants for reaction of CN($v=0$) with O_2. Our data (—■—) are superimposed on those included in the 1981 evaluation of Baulch *et al.*[11] (- - -) More recent room-temperature results for this reaction are listed in table 5.

non-reactive vibrational relaxation by what might be termed the usual mechanisms, since the relaxation of CO($v=1$) by O_2, where the vibrational frequencies and atomic masses are very similar, is much slower[23] than would be required in the present system to give an observable effect. Given that the CN + O_2 reaction gives every sign of occurring *via* a transient NCOO complex, a second possibility is that some complexes redissociate to O_2 + CN rather than separating to the products NCO + O. Such complex formation followed by redissociation can provide a highly efficient mechanism for relaxation.[24,25] Although it is difficult to rule out this possibility entirely, it would seem likely that the dissociation to NCO + O would be strongly favoured over redissociation to CN + O_2 for complexes formed from CN($v=0$) + O_2. The reasons for this are the exothermicity of the overall reaction to products and the likelihood that there is no potential-energy barrier obstructing the dissociation of NCOO to NCO + O, since it is a simple bond-breaking process yielding two free radicals.[21]

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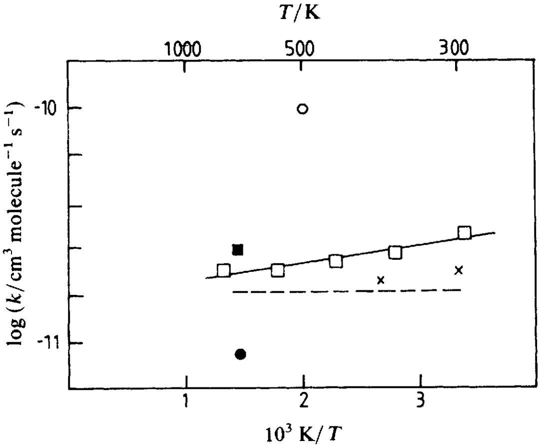

Fig. 4. Arrhenius plot of the rate constants for reaction of CN($v=0$) with NH_3. Our data (—□—) are superimposed on those included in the 1981 evaluation of Baulch *et al.*[11] (- - -).

A final possibility is that as CN and O_2 approach the formation of a bond between the reagents lowers the vibrational frequency of the CN stretching motion. Then the vibrationally adiabatic curves leading from the separated reagents to the transition-state region will not be exactly parallel. Consequently, the flux of reagents through the transition-state region may be slightly greater for the case of CN($v=1$)+O_2 than for CN($v=0$)+O_2. This seems to be the most likely explanation for the slight effect of vibrational excitation on the kinetics of CN(v) with O_2.

It would seem that the only possible channel for reaction between CN radicals and NH_3 is H-atom transfer:

$$CN + NH_3 \rightarrow HCN + NH_2; \qquad \Delta H^\circ_{298} = -69 \text{ kJ mol}^{-1}$$

(although formation of HNC may also be thermodynamically possible[26]). The remarkable thing about our rate data for this radical-molecule system is that they show all the characteristics usually associated with a radical-radical reaction:[21] namely, a rate constant which is within a small factor of the collisional rate and which decreases with increasing temperature (see fig. 4). This reaction goes orders of magnitude faster than the reactions of CN with other H-atom-containing small molecules like H_2, CH_4 and HCl,[5-9] where the H—X bond strength is less than in NH_3.

De Juan *et al.*[8] briefly considered the possible influence of the attractive dipole-dipole forces in reactions involving CN and OH radicals. Both CN and NH_3 have large permanent dipoles of 1.47 D,[27] but it is not immediately obvious either that the forces between these dipoles will orient the species favourably for reaction or that one can consider these forces dominant at those reagent separations which influence the overall kinetics of reaction.

Although our experiments on the kinetics of CN($v=0$)+NO are limited with regard to the ranges of temperature and pressure which they cover, they and our results for CN($v=1$)+NO do provide important information about the nature of the reaction between these two free radicals. The detailed studies of the photodissociation of NCNO by Nadler *et al.*[18] have established that for the ground state of this molecule, the dissociation limit is $D_0 = 203.3$ kJ mol^{-1}. Moreover, there is no potential barrier on the surface leading from CN($^2\Sigma^+$)+NO($^2\Pi$) to the $^1A'$ electronic ground state of NCNO,[18,28,29] as is to be expected for a simple radical association.[21] In other systems,

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such as OH + NO and OH + NO_2, where this situation prevails, it has been shown[21,24] that rapid vibrational relaxation of one radical by the other can occur in bimolecular collisions in which a strongly bound complex forms. The rate constant for relaxation then corresponds closely to that for formation of the collision complex and hence, since this rate is unlikely to depend at all strongly on the initial vibrational states of the colliding radicals, to the rate constant for the radical association reaction in the limit of high pressure.[21,24]

In addition to the NCNO ground state, $^1A''$ and $^3A''$ states arising from an $n \rightarrow \pi^*$ excitation of an oxygen lone-pair electron are bound and correlate adiabatically to ground-state CN + NO. However, the photodissociation[18] and the theoretical calculations[28,29] indicate the presence of barriers on these surfaces arising from avoided curve crossings. If this is correct, the CN + NO reaction would be dominated by association into the $\tilde{X}\ ^1A'$ state of NCNO. The very large rate constant found for relaxation of CN($v = 1$) by NO casts some doubt on this interpretation, since the fraction of collisions between CN($^2\Sigma^+$) and NO($^2\Pi$) occurring on the $\tilde{X}\ ^1A'$ surface would be only $1/f_{\text{el,CN}}f_{\text{el,NO}}$, where f_{el} is the electronic partition function for the specified diatomic. At 295 K, this ratio is equal to 0.16. The rate constant for relaxation of CN($v = 1$) by NO in those collisions which occur on the ground-state surface would then be 4.7×10^{-10} cm^3 molecule^{-1} s^{-1}, which seems unexpectedly large.

The rate constant which we have determined for the removal of CN($v = 1$) by NO at room temperature is, like those for CN($v = 0$) and CN($v = 1$) with O_2, larger (in this case, 36%) than the value reported by Li *et al.*[6] From earlier LIF measurements on the CN + NO system, Lam *et al.*[17] claimed rather similar kinetics for CN($v = 1$) as for CN($v = 0$). If true, this would be very surprising, since the extra energy present in $(NCNO)^\dagger$ complexes formed from CN($v = 1$) + NO should reduce the three-body association rate considerably. Li *et al.*[6] have given what appears to be a valid criticism of the experiments of Lam *et al.*[17] The dye laser used by Lam had a bandwidth of 6-7 cm^{-1}. To monitor the kinetics of CN($v = 1$), the laser frequency was centred on the R9 line of the (1, 1) band of the B-X system. However, the laser output was sufficiently broad that it would then have overlapped the R22 and R23 lines of the (0, 0) band. If, as now seems established by our results and those of Li *et al.*,[6] the concentration of CN($v = 1$) decays much more rapidly than that of CN($v = 0$), then at the delay times used by Lam *et al.* (>50 μs) the LIF signals would be determined entirely by [CN($v = 0$)]. However, there is no difficulty with near-coincident transitions if one observes [CN($v = 1$)] by exciting lines in the (0, 1) band, as in our own work.

The role of the non-associative reaction yielding CO + N_2 from CN(v) + NO is still questionable. From discharge-flow experiments at 687 K, Boden and Thrush[30] concluded that at this temperature CN is removed by NO predominantly through this reaction with a rate constant of $(5 \pm 3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Both Lam *et al.*[17] and Li *et al.*[6] claim that their experiments demonstrate the occurrence of this reaction at room temperature and they reported rate constants of $(1.2 \pm 0.6) \times 10^{-13}$ and $(1.6 \pm 0.3) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, respectively. In both cases the evidence came from the fact that plots of the second-order rate constants against total gas pressure gave finite intercepts when extrapolated to zero pressure, even after allowance had been made for diffusion-controlled loss of radicals. It has to be emphasised, however, that in reaching this conclusion both groups assumed that the kinetics of the association reaction, CN + NO (+M) → NCNO (+M), are fully in the third-order regime at total pressures (diluent gas, Ar) between 5 and 35 Torr. This is not the case for other associative reactions, such as OH + NO, which are of similar exothermicity and involve radicals of the same size and which have been studied extensively both experimentally and theoretically.[21] Consequently, the second- and third-order rate constants for reaction between NO + CN which have been derived on the basis of this assumption should be viewed with some suspicion.

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Further doubt is cast on the importance of the non-associative reaction by our results on the temperature dependence of the rate of reaction between CN($v=0$) and NO, limited as our data are at the present time. The rate constants which we have measured (at a total pressure of 30 Torr) at 295 and 450 K, and the preliminary result at 771 K, are consistent with a temperature dependence of the form: $k = C(T/298)^n$ with $n \approx -3$.† Such a large, negative temperature dependence is consistent with what is found for radical association reactions at or close to their third-order kinetic regime,[21] but it is very difficult to reconcile with the kinetics of bimolecular, non-associative reaction, even if it occurs *via* a transitory collision complex. In addition, note that our preliminary value for the rate constant of the overall reaction of CN($v=0$) with NO at 771 K, $(5\pm3)\times10^{-14}$ cm^3 molecule^{-1} s^{-1}, is an order-of-magnitude smaller than that deduced by Boden and Thrush[28] for 687 K and 3-4 times smaller than the values reported for room temperature by Lam *et al.*[17] and by Li *et al.*[6]

The lack of any evidence in our results for the reaction, CN($v=0$) + NO → CO + N_2, also leads us to question whether the removal of CN($v=1$) by NO occurs, at approximately equal rates, by reaction to CO + N_2 and by non-reactive relaxation, as has been suggested by Li *et al.*[6] This conclusion was based on measurements of the magnitude and time-dependence of changes in the concentration of CN($v=0$) during the short time period through which CN in higher vibrational levels was removed. However, the conclusions of Li *et al.*[6] regarding the kinetics of the non-associative reaction between CN and NO imply that its rate is increased by a factor of *ca.* 200 when the vibrational state of CN is raised from $v=0$ to $v=1$. This seems improbable if the reaction proceeds, as Li *et al.* suggest, *via* a strongly bound collision complex, since energy is likely to be randomised during the lifetime of this complex. Moreover, we note that at the highest temperature used in our experiments *ca.* 2% of a thermal distribution of CN radicals are in $v=1$. Under the conditions of our measurements on the kinetics of CN($v=0$) + NO, relaxation are rapid enough to maintain the thermal distribution of CN radicals over vibrational states, so that a rate enhancement of the magnitude reported by Li *et al.*[6] should alone increase the overall rate of the non-associative reaction by a factor of *ca.* 5 from its room-temperature value. We find no such acceleration in the overall rate.

In conclusion, we believe that our results raise serious doubts about the existence of the non-associative channel yielding CO + N_2 in the reaction between CN radicals and NO. A careful and extensive examination of the temperature and pressure dependence of this reaction is required, perhaps coupled with direct measurements on the reaction products.

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† Note that n is derived from experiments at constant pressure not at constant total gas concentration.

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