J. Chem. Soc., Faraday Trans. 2, 1988, **84**(1), 9-15

Reaction of CN Radicals with CH_4 and O_2

Christopher Anastasi*† and Denise U. Hancock
Shell Research Ltd, Thornton Research Centre, P.O. Box 1, Chester CH1 3SH

A flash-photolysis laser-induced fluorescence technique has been used to study CN radical kinetics at 300 K. A radiative lifetime of 66.70 ± 4.60 ns has been measured for the $B\,^2\Sigma^+$ state of this radical. Rate constants for the reaction of the CN radical with CH_4 and O_2 have been measured to be $(1.14 \pm 0.06) \times 10^{-12}$ and $(18.2 \pm 1.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.

CN species are of interest and importance since their chemistry produces the pollutant NO from fuel nitrogen.[1] However, the flame environment makes experimental studies of important individual reactions difficult. In the past, kinetic information on the reaction of CN has been derived using flash photolysis[2,3] and pulse radiolysis,[4] usually of cyanogen, to produce the radical species and absorption to monitor its kinetic behaviour in the presence of reactants. More recently, broad band photolysis has given way to laser photolysis[5,6] of suitable precursors followed by the more sensitive laser-induced fluorescence detection of CN.

In the present study a flash-photolysis laser-induced fluorescence technique has been used to study CN kinetics at 300 K. The radioactive lifetime for the $B\,^2\Sigma^+$ state has been measured and rate constants for the reaction of CN with CH_4 and O_2 have been determined.

Experimental

The experimental design used in this study is shown in fig. 1. Light from a N_2-pumped dye laser is focussed to a point inside a 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-intensity 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 to either a fast oscilloscope (Tektronix 7033) or a Boxcar averager (E G and G model 162) fitted with a digital storage option.

The fluorescence cell consists of a Pyrex sphere with two arms along the axis of the laser beam. The arms contain nine equally spaced blackened (Fluon One-Coat) aluminium baffles; they have gas ports to allow a flow of reaction mixture through the cell and Spectrosil windows at the ends inclined at the Brewster angle. There are two Woods horns, one opposite a Spectrosil window through which fluorescence is observed and one opposite a calcium fluoride window (transmission > 125 nm) which separates the reaction vessel from the flash lamp.

The flash lamp consists of a Pyrex T-piece with small steel hemispherical ball electrodes on tungsten rods. N_2 flows through the lamp at low pressures (*ca.* 50 Torr) and across the calcium fluoride window to help restrict accumulation of 'blow-off' deposits from the electrodes. A flash energy of 22 J was provided by charging a 2.2 μF capacitor to 4.5 kV. A blackened Pyrex baffle sits on the calcium fluoride window and restricts flash lamp radiation to a central cone in the fluorescence cell and into a Woods horn.

---

† Present address: Department of Chemistry, University of York, Heslington, York YO1 5DD.

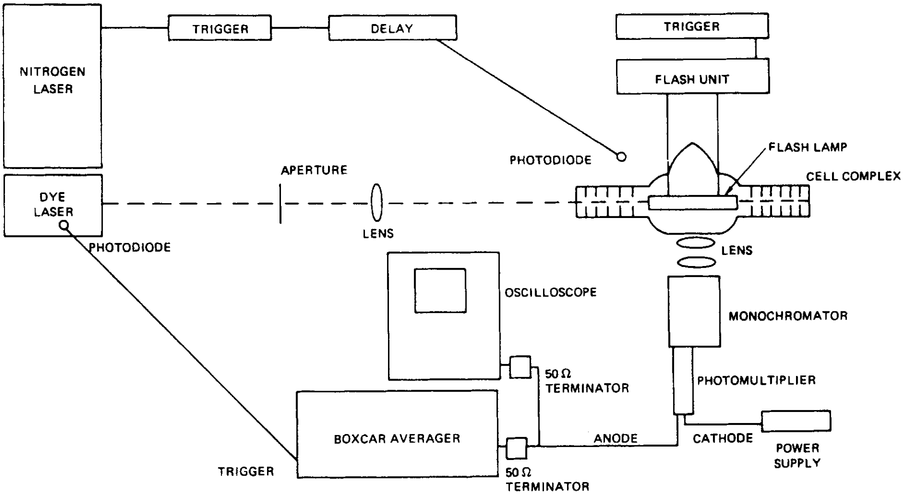

Fig. 1. The experimental arrangement for the CN studies using the flash photolysis/laser-induced fluorescence technique.

Scattered laser radiation in the cell is restricted by the blackened baffles and a Woods horn while scattered flash lamp radiation is restricted by the Pyrex aperture and Woods horn combination. In addition to these methods for minimising scattered light, the cell complex was painted black.

The laser has been described previously.[7] Briefly, an N_2 laser (Molectron UV 24) provides 337 nm radiation and stimulates laser action in a dye laser cavity; the dye (BBQ) gives tunable radiation in the 373–399 nm range.

Trigger pulses were used to fire both the flash lamp and laser while a delay unit allowed the time between the two to be altered at ease. A photodiode, the response of which is in the visible, is placed close to the flash lamp to ensure the delay is reproducible in time. Another photodiode responds to the light within the dye laser cavity and supplies a trigger pulse to the oscilloscope or Boxcar averager.

The repetition rate of the experiment was governed by the flash lamp electronics and in particular the charging rate of the 2.2 μF capacitor. In our experiments a repetition rate of *ca.* 0.2 Hz was used with the digital storage facility of the Boxcar averager for signal processing. The experiments were conducted in a flow mode. Gases taken from cylinders in prescribed concentrations passed through oxy-trap units (phase separations) at controlled flow rates (ASM mass flow controllers) and were mixed in a 0.5 dm^3 bulb before flowing into the reaction vessel.

Materials

C_2N_2, O_2, argon and N_2 (B.O.C.) in prescribed concentrations were taken directly from the cylinders.

Results

In the present series of experiments, CN radicals were produced in the $X\,^2\Sigma$ and $A\,^2\Pi$ states by the flash photolysis of a flowing stream of C_2N_2 in Argon.

$$C_2N_2 + h\nu(\lambda = 150\text{–}180\ \text{nm}) \rightarrow 2CN(X\,^2\Sigma^+) \quad (1)$$

$$\rightarrow CN(X\,^2\Sigma^+) + CN(A\,^2\Pi). \quad (2)$$

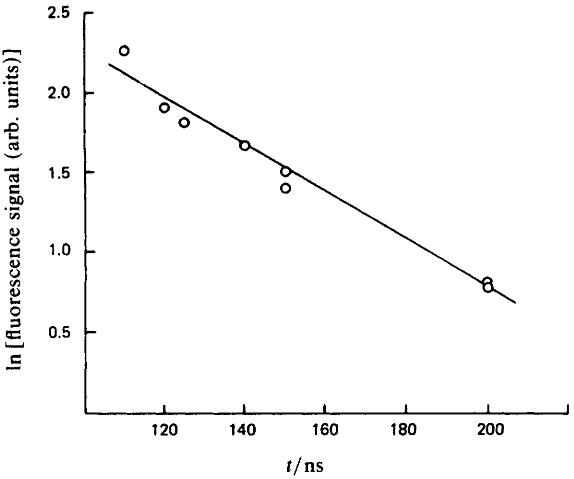

Fig. 2. CN fluorescence intensity as a function of time ($C_2N_2 = 6 \times 10^{14}$ and argon $= 6.5 \times 10^{17}$ molecule cm^{-3}; $T = 300$ K).

A minimum 10 μs delay between the flash lamp and laser allows the *A* state to decay radiatively or be quenched to the *X* state; it also ensures that the photomultiplier has recovered from any flash lamp derived scattered light. Radiation (388 nm) from the laser excites the *X* state radicals to the *B* state:

$$CN(X\,^2\Sigma^+) + h\nu(\lambda = 388\text{ nm}) \rightarrow CN(B\,^2\Sigma^+). \tag{3}$$

These can radiate or be quenched by collision with the parent molecules or bath gas (M):

$$CN(B\,^2\Sigma^+) \rightarrow CN(X\,^2\Sigma^+) + h\nu \tag{4}$$

$$CN(B\,^2\Sigma^+) + C_2N_2 \rightarrow CN(X\,^2\Sigma^+) + C_2N_2 \tag{5}$$

$$CN(B\,^2\Sigma^+) + M \rightarrow CN(X\,^2\Sigma^+) + M. \tag{6}$$

The fluorescence signal can be used to obtain the radiative lifetime for the CN radical and to study reactions involving this species.

The excitation spectrum for the radical, obtained by monitoring the fluorescent signal as a function of laser wavelength, was the same as that reported in the literature.[8] In this study the spectrum consisted of a poorly resolved band centred at 388 nm, corresponding to the P-branch of the CN violet transition.

CN Radical Radiative Lifetime

By varying the position of the boxcar gate the fluorescence signal was seen to decay to zero after *ca.* 250 ns. Since $k_5 = 2.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and the concentration of C_2N_2 was 6.5×10^{14} {quenching by the bath gas Argon [eqn (6)] can be ignored[9]} the lifetime of CN ($B\,^2\Sigma^+$) due to reaction (5) can be calculated to be 7.7 μs. This is very much longer than that observed and confirms radiative decay to be the only process removing excited radicals.

The time dependence of the fluorescence is given by

$$\text{fluorescence}_{(t=t)} = \text{fluorescence}_{(t=0)} \times \exp(-t/\tau)$$

where t is the time and τ is the radiative lifetime of the radical. A plot of ln (fluorescence) *vs.* time is shown in fig. 2 with each point an average of 40 events; the gradient leads to a value of 66.7 ± 4.6 ns for τ.

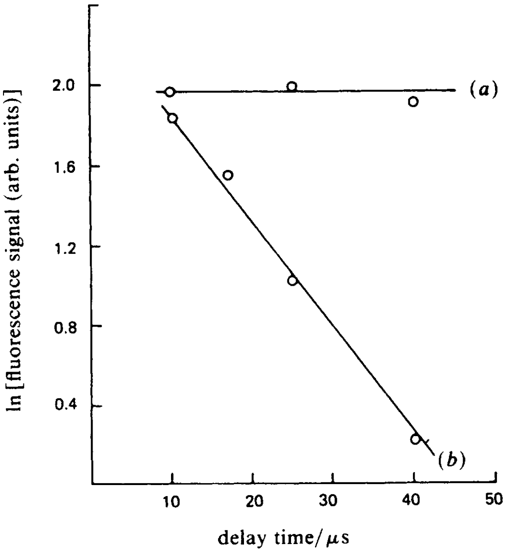

Fig. 3. ln(CN fluorescence intensity) as a function of delay time between flash lamp and laser. [$C_2N_2 = 6.5 \times 10^4$, argon $= 6.5\ 10^7$; (*a*) $O_2 = 0.0$; (*b*) $O_2 = 2.7 \times 10^{15}$ molecule cm^{-3}; $T = 300$ K].

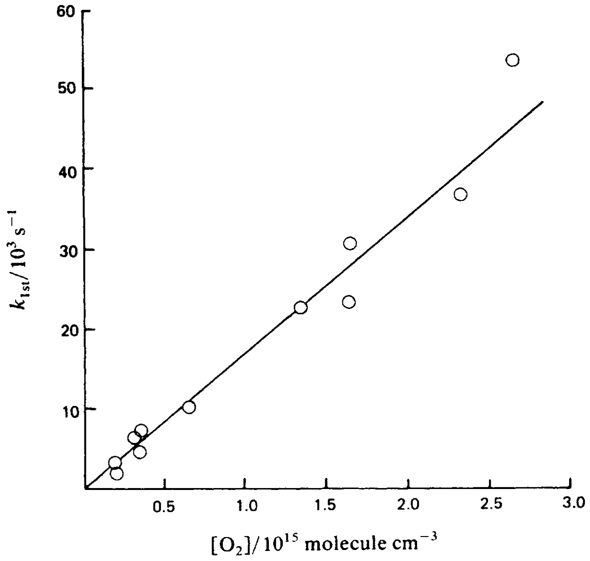

Fig. 4. First-order rate constant as a function of O_2 concentration ($C_2N_2 = 6.5 \times 10^{14}$ and argon 6.5×10^7 molecule cm^{-3}; $T = 300$ K).

CN Radical Reaction with O_2 and CH_4

Fig. 3 shows a plot of ln(fluorescence) as a function of delay time between the flash lamp and laser for the reaction of CN with O_2

$$CN + O_2 \rightarrow NCO + O \tag{7}$$

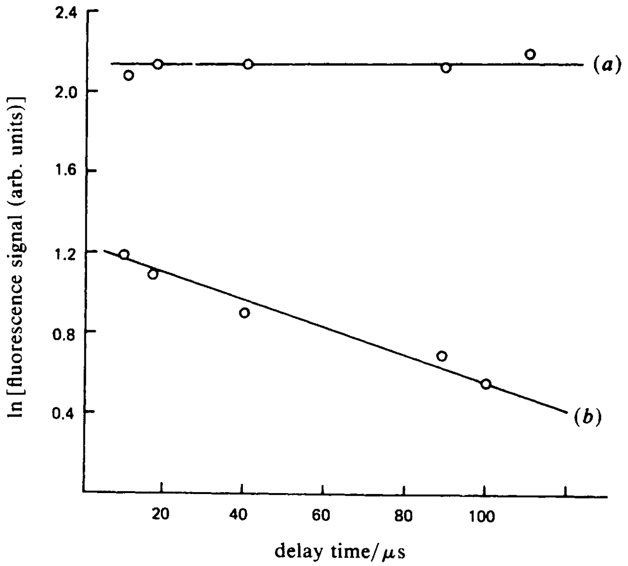

Fig. 5. ln(CN fluorescence intensity) as a function of delay time between flash lamp and laser [$C_2N_2 = 6.5 \times 10^{14}$, argon $= 6.5 \times 10^{17}$; (*a*) $CH_4 = 0.0$; (*b*) $CH_4 = 6.9 \times 10^{15}$ molecule cm^{-3}; $T = 300$ K].

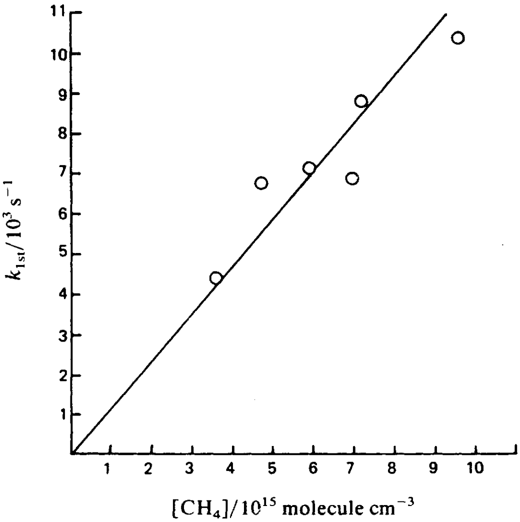

Fig. 6. First-order rate constant as a function of CH_4 concentration ($C_2N_2 = 6.5 \times 10^{14}$ and argon 6.5×10^{17} molecule cm^{-3}; $T = 300$ K).

This figure also shows the radical signal to be essentially constant in the absence of O_2 over the same timescale. A pseudo-first-order decay constant (k_{1st}) is derived from the gradient and varies as the oxygen density is changed. A plot of k_{1st} *vs.* O_2 concentration is shown in fig. 4 to be a straight line through zero and whose gradient is the bimolecular rate constant $k_7 = (1.82 \pm 0.12) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

Table 1. Radiative lifetime of the CN ($B\,^2\Sigma^+$) radical

ref.	ns
11	64.0
12	65.6
9	60.8
10	39.4
	66.7 ± 4.6

Table 2. Summary of rate constants for the reaction of CN with O_2 at room temperature

ref.	technique	$k_7/10^{-11}$ cm^3 molecule^{-1} s^{-1}
2	FP/KA	0.76
4	PR/KA[a]	1.13
3	FP/KA[b]	1.00
5	LFP/LIF	1.35
6	LFP/LIF[c]	2.00
	FP/LIF[d]	1.82

[a] Pulse radiolysis/kinetic absorption spectroscopy.
[b] Flash photolysis/kinetic absorption spectroscopy.
[c] Laser flash photolysis/laser-induced fluorescence.
[d] Flash photolysis/laser-induced fluorescence.

Table 3. Summary of rate constants for the reaction of CN with CH_4 at room temperature

ref.	technique	$k_8/10^{-12}$ cm^3 molecule^{-1} s^{-1}
13	PR/KA[a]	0.75
6	LFP/LIF[b]	0.56
	FP/LIF[c]	1.14

[a] Pulse radiolysis/kinetic absorption spectroscopy.
[b] Laser flash photolysis/laser-induced fluorescence.
[c] Flash photolysis/laser-induced fluorescence.

Fig. 5 and 6 show the above procedure applied to the reaction of CN with CH_4.

$$CN + CH_4 \rightarrow HCN + CH_3 \qquad (8)$$

The plot of k_{1st} *vs.* CH_4 concentration leads to $k_8 = (1.14 \pm 0.06) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Discussion

Table 1 compares the radiative lifetime measured in the present study with those reported in the literature. Of the four values reported elsewhere, one (39.4 ns[10]) is considerably lower than the other three (64.0,[11] 65.6[12] and 60.8 ns[9]); our measurement is in very good agreement with the higher values.

There have been five studies of the reaction of O_2 with rate constant values ranging from 0.76[2] to 2.00×10^{-11} cm^3 $molecule^{-1}$ s^{-1};[6] table 2 shows our value to agree with the more recent measurements where laser-induced fluorescence (LIF) has been used to monitor the kinetic behaviour of CN. Interestingly, all the studies have used C_2N_2 as the precursor for the radical removing one possible source of discrepancy. The difference between the recent LIF studies and the earlier, lower rate constant values measured when absorption techniques have been used, may lie in the larger densities necessary for the latter, thus increasing the possibility of secondary reactions.

There are only two other measurements reported for the reaction of CN with CH_4 and these along with the result from the present study are given in table 3; bearing in mind the different techniques used in producing and monitoring the radical, the agreement is good.

References

1 C. Morley, *18th Symposium (International) on Combustion*, 1981, 23.
2 N. Basco, *Proc. R. Soc. London, Ser. A*, 1965, **283**, 302.
3 E. A. Albers, K. Hoyerman, H. Schacke, K. J. Schmatjko, H. G. Wagner and J. Wolfrum, *15th Symposium (International) on Combustion*, 1975, 765.
4 G. E. Bullock and R. Cooper, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 2175.
5 A. R. Whyte and L. F. Phillips, *Chem. Phys. Lett.*, 1983, **98**, 590.
6 W. M. Jackson, *J. Chem. Phys.*, 1984, **81**, 833.
7 C. Morley, *Combust. Flame*, 1982, **47**, 67.
8 W. M. Jackson, *J. Chem. Phys.*, 1973, **59**, 960.
9 C. K. Luk and R. Bersohm, *J. Chem. Phys.*, 1973, **58**, 2153.
10 T. J. Cook and D. H. Levy, *J. Chem. Phys.*, 1972, **57**, 5059.
11 D. I. Duric, R. Erman and M. Larsson, *Phys. Scr.*, 1978, **18**, 39.
12 W. M. Jackson, *J. Chem. Phys.*, 1974, **61**, 4177.
13 G. E. Bullock and R. Cooper, *Trans. Faraday Soc.*, 1971, **67**, 3258.

Paper 6/2434; *Received* 17*th December*, 1986