KINETIC STUDIES OF THE REACTION OF CN WITH H_2O FROM 518 TO 1027 K

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Absolute rate coefficients for the reaction $CN+H_2O \rightarrow OH+HCN$ were measured from 518 to 1027 K in a flow reactor using laser photolysis–laser-induced fluorescence techniques. The data fit the expression $k_1(T) = (8.0 \pm 0.8) \times 10^{12} \exp[-(31.2 \pm 0.6)$ kJ$/RT]$ cm^3 mol^{-1} s^{-1}.

1. Introduction

The chemistry of the CN radical is crucial to understanding the complex nature of NO_x formation, especially in fuel-rich flames and coal combustion [1–4]. The reaction of HCN with the OH radical is one important step in this reaction sequence. Besides the addition product HCNOH, water and CN, and, through an exchange reaction, HNCO and H, are possible reaction products. The importance of these different reaction channels and the rate parameters under various conditions are not clear. The aim of the present work was to investigate the reaction of the CN radical with water. The predominant pathway should lead to OH+HCN, although there are some indications that HOCN+H will be favoured at temperatures around 2000 K [3]:

$$CN+H_2O \rightarrow OH+HCN\,, \quad \Delta H^0_{298} = -6.28 \text{ kJ/mol}\,, \tag{1}$$

$$CN+H_2O \rightarrow HOCN+H\,, \quad \Delta H^0_{298} = -63.2 \text{ kJ/mol}\,. \tag{2}$$

Together with the thermodynamic properties, the rate constant of the reverse reaction (k_{-1}) can be evaluated. As mentioned above, kinetic data concerning this abstraction channel are of great importance for describing nitrogen turnover in flames. In addition, information is obtained about the importance of this channel at lower temperatures where the addition reaction is reported to be predominant [5].

2. Experimental technique

All experiments were performed using the laser photolysis–laser-induced fluorescence (LIF) technique. An ArF excimer laser (Lambda Physik EMG 501) delivered the photolysis beam. A circular diaphragm shaped a homogeneously irradiated beam of 4 mm diameter and of typically 2–3 mJ. A frequency-doubled pulsed dye laser (Lambda Physik FL 2002 EC, grating version) pumped by a XeCl excimer laser and working with sulforhodamine B emitted light in the 305–320 nm region was used to excite OH radicals from the X $^2\Pi$ ground state to the A $^2\Sigma$ state. A second dye laser (Lambda Physik FL 2002, tuning range 370–400 nm) excited the CN radicals from the X $^2\Sigma$ ground state to the B $^2\Sigma$ state (violet band). To work in the linear region we attenuated both probe lasers and expanded the beam profiles with a telescope by 15:1. The emitted fluorescence was collected by a lens ($f=D=50$ mm) perpendicular to the laser beam directions. We took precautions to suppress stray light and furnace radiation, which would interfere with our measurements. This was done by inserting light baffels and UV filters (Schott, UG11 or BG23) between the fluorescence imaging lens and the photomultiplier (EMI 9781B).

The heart of the apparatus was a microcomputer (HP 9816) which controlled the measurements via the data-acquisition and control unit (HP 3497A). The two laser systems and the boxcar were triggered by a software-initiated pulse, distributed by a delay

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generator. The computer normalized the fluorescence signal to both laser energies.

The quartz reactor was fitted in a 60 cm long silver tube to ensure a homogeneous temperature profile (fig. 1). The whole system was heated by means of an accurately thermostatted furnace. The temperature gradient along the quartz tube was determined to be less than 1% at temperatures up to 1100 K. The gas temperature in the reaction zone was measured with a retractable Ni/CrNi thermocouple. Heatable gas intake and outlet conduits and a thermostatted evaporator made it possible to take measurements over a wide partial pressure range of water (up to 60 Torr). All gas flows were regulated by Tylan mass flow controllers and the pressure was measured by a MKS Baratron. The gases used in our experiment had purities: $N_2 \geqslant 99.996\%$ (Messer Griesheim), $C_2N_2 \geqslant 98.5\%$ (Matheson), and NO $\geqslant 99.8\%$ (Messer Griesheim).

We carried out all experiments under slow-flow conditions, such that each photolysis pulse initiated the reaction within a locally fresh gas mixture. This procedure eliminates kinetic complications caused by unwanted accumulation of photolysis or reaction products.

3. Results and discussion

ArF laser photolysis of cyanogen produced the initial CN concentrations. Although there are benefits using pulsed laser photolysis in reaction-kinetic studies, the fact that the fragments produced are nonthermal causes some problems. C_2N_2 photolysis at 193 nm produces vibrationally excited CN radicals. Experimental results concerning the $[CN(v=1)]/[CN(v=0)]$ ratio are conflicting. Eres et al. reported a value of 0.15 [6], while Jackson and Halpern obtained 0.35 [7]. CN radicals in higher excited vibrational states were not found [6]. The influence of the $CN(v=1)$ radicals on the reaction kinetics is discussed later. At 193 nm the excess energy produces only CN fragments in the electronic ground state [6]. Generation of electronically excited CN by two-photon processes could be ruled out because our photolysis photon densities did not exceed 10^{17} cm^{-2} [8].

Shock tube measurements [9] indicate that the rate constant k_1 is low between 500 and 1100 K compared with the rapid radical–radical reaction $OH+CN \rightarrow OCN+H$ ($k_3=3.2\times10^{13}$ cm^3 mol^{-1} s^{-1}, $E_a=0$ [3]). In order to suppress the influence of this

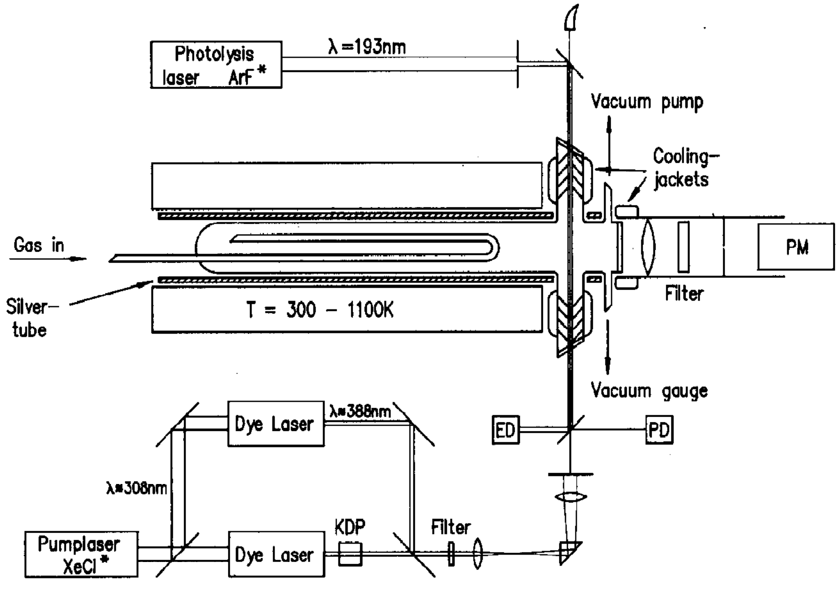

Fig. 1. Experimental apparatus. PM, photomultiplier; ED, energy detector; PD, photodiode.

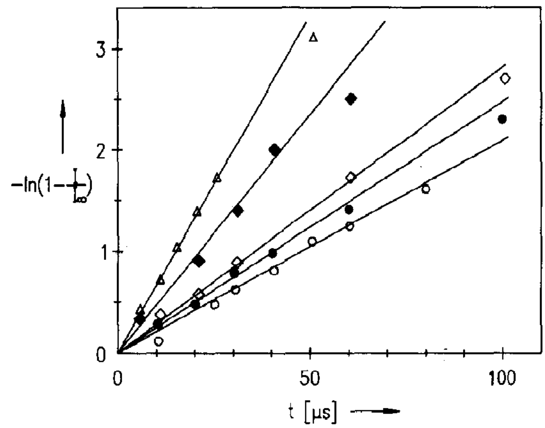

Fig. 2. Semilogarithmic plot of the OH (A→X) LIF signal I (arbitrary units) versus delay of probe after photolysis. $T=804$ K; ○, $p(H_2O)=13$ Torr, ●, $p(H_2O)=16$ Torr; ◇, $p(H_2O)=18$ Torr; ◆, $p(H_2O)=27$ Torr; △, $p(H_2O)=50$ Torr.

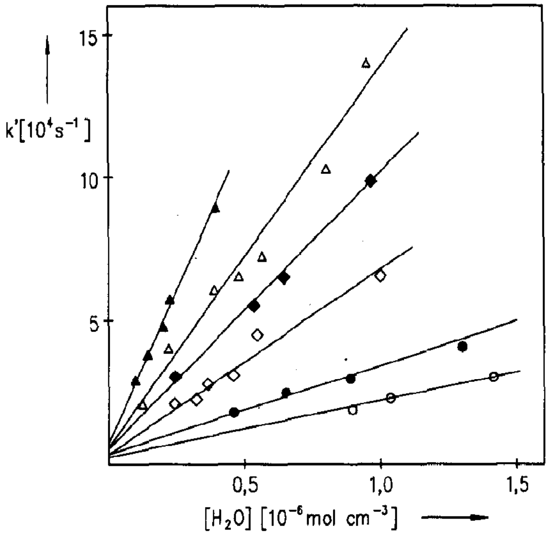

Fig. 3. Plots of pseudo-first-order reaction rates at different temperatures. Probed via OH(A→X) LIF. ○, $T=588$ K; ●, $T=678$ K; ◇, $T=804$ K; ◆, $T=844$ K; △, $T=927$ K; ▲, $T=1027$ K.

competing reaction we worked with relatively high H_2O partial pressures (10–60 Torr). Because of the strong fluorescence quenching behaviour of water, which diminished the CN and OH detection sensitivity (10^{-15}–10^{-16} mol cm^{-3}) by at least two orders of magnitude, and the low absorption coefficient of C_2N_2 at 193 nm ($\sigma \approx 10^{-19}$ cm^2 [7]), we needed cyanogen pressures around 0.3 Torr to obtain sufficient fluorescence intensities. Small OH fluorescence signals were observed as a result of water photolysis at 193 nm. We recorded the time history of these background signals (obtained by pure water photolysis at a certain H_2O pressure) and subtracted these values from the fluorescence signals obtained with the reaction mixture under the same working conditions.

We used laser-induced fluorescence (LIF) from pumping the $Q_1(4)(v'=0, v''=0)$ rotational line of the OH radical at 308.3278 nm and the $R_{10}(v'=0, v''=0)$ rotational line of the CN radical at 386.871 nm, respectively, to determine the rate constants. All experiments were performed under pseudo-first-order conditions ($[H_2O] \gg [CN]$). [OH] rises and [CN] decays were observed to be exponential for at least two 1/e periods as typified by the data shown in fig. 2. The observation of single exponential behaviour validates the existence of first-order conditions, hence k' is the pseudo-first-order rate constant. At each temperature time-resolved measurements were taken at several fixed reactant concentrations. The bimolecular rate constant was obtained from the slope of k' versus reactant concentration plots (fig. 3). Increasing the N_2 buffer gas pressure from 0 to 160 Torr (H_2O partial pressure: 15 Torr) had no influence on the rate constant. The results of these experiments are given in table 1, where the uncertainties represent 95% confidence intervals. The data show that the rate constant extracted from the $[CN(v=0)]$ decay plots coincide within the margin of error with the [OH] rise measurements, although they tend to

Table 1
k_1 as a function of temperature

T (K)	k_1 (10^{10} cm^3 mol^{-1} s^{-1})	Probed species
518	0.45 ± 0.06	CN
588	1.7 ± 0.3	OH
588	1.5 ± 0.3	CN
678	3.0 ± 0.4	OH
763	5.1 ± 0.6	OH
804	6.5 ± 1	OH
804	5.7 ± 1	CN
844	11 ± 2	OH
927	14 ± 2	OH
927	12 ± 2	CN
1027	20 ± 3	OH

be slightly lower (by 5–15%). We observed an increase in [CN(v=0)] at early reaction times, due to vibrational relaxation of the CN(v=1) fragments. At longer times we observed exponential CN(v=0) decay due to reaction (1). These results indicate that the initial non-thermal vibrational distribution of the CN radicals does not interfere with the determination of k_1 via OH detection. In order to clarify this more accurately, we added NO (0.17–0.33 Torr) to the reaction mixture. NO is a pronounced CN(v=1) quencher ($k_{\mathrm{qNO}} = 1.8 \times 10^{13}$ cm^3 mol^{-1} s^{-1}) but reacts quite slowly with CN(v=0) ($k_{\mathrm{NO}} = 9.6 \times 10^{10}$ cm^3 mol^{-1} s^{-1}) [10]. Under our working conditions vibrational relaxation is complete in the first few microseconds. The observed OH rise rates were identical to those produced in experiments done without NO. We estimate $k(\mathrm{CN}(v=1)+\mathrm{H_2O}) \leqslant 2k_1$ (provided that the photolysis delivered a $[\mathrm{CN}(v=1)]/[\mathrm{CN}(v=0)]$ ratio of 0.15, according to ref. [6]). No data concerning $k(\mathrm{CN}(v=1)+\mathrm{H_2O})$ could be found in the literature. However, extensive measurements performed by Schacke et al. [11] and Jackson and co-workers [12], showed a similar vibrational energy effect on reaction rates of CN(v=1) with several other reactants. From the observed CN(v=1) history as a function of the water pressure (probed line: $P_{10}(v'=1, v''=1)$, 386.887 nm) in the range from 518 to 927 K a temperature-independent coefficient k_q of $(4.6 \pm 0.5) \times 10^{11}$ cm^3 mol^{-1} s^{-1} was determined. According to our conclusions outlined above, we believe this value predominantly describes vibrational relaxation of CN(v=1) by water.

Fig. 4 shows a plot of log k_1(cm^3 mol^{-1} s^{-1}) versus 1000/K. The Arrhenius plot is linear and yields the rate coefficient expression

$$k_1 = (8.0 \pm 0.8) \times 10^{12}$$
$$\times \exp[-(31.2 \pm 0.6)\ \mathrm{kJ}/RT]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}\ .$$

The quoted errors are 95% confidence intervals. The results of Szekely et al. [9] are also included. These data points give a good fit to our Arrhenius expression, although Szekely et al. evaluated different Arrhenius parameters ($k_1 = 2.3 \times 10^{13} \exp(-55.7$ kJ/RT) cm^3 mol^{-1} s^{-1}). Very little is known about the second possible product channel (2). However, there is evidence [13] that this rate constant was overestimated by Haynes [3] and should have a larger energy barrier than channel (2). From thermodynamical considerations [14] we evaluated the following Arrhenius expression for the reverse reaction (−1):

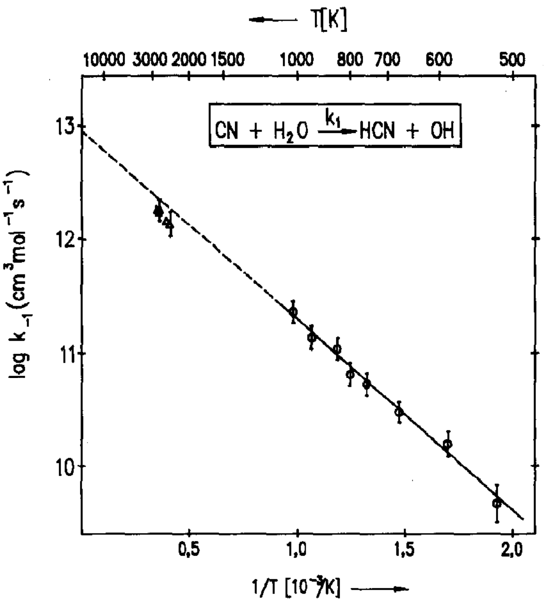

Fig. 4. Arrhenius plot for reaction (1). ○, this work; △, ref. [9].

$$k_{-1} = (7.7 \pm 1) \times 10^{12}$$
$$\times \exp[-(34.6 \pm 1)\ \mathrm{kJ}/RT]\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}\ .$$

The error limits reflect the uncertainty in both k_1 and the equilibrium constant K_1. In particular, the heat of formation of CN is subject to some uncertainty [15]. The result agrees with the suggestion of Fritz et al. [5] and shows the preference for the abstraction channel as the main high-temperature pathway for reaction (−1).

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