## KINETICS OF CN(X $^{2}\Sigma^{+}$ ) RADICAL REACTIONS WITH HCN, BrCN AND CH<sub>3</sub>CN \*

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Absolute rate constants were obtained for CN(X  ${}^{2}\Sigma^{+}$ ) radical reactions with HCN, BrCN and CH<sub>3</sub>CN. The CN radical relative concentration was followed by laser-induced fluorescence (LIF) with a cw ring dye laser on the A  ${}^{2}\Pi$ -X  ${}^{2}\Sigma^{+}$  (4, 0) band at 621.5 nm. CN radicals were generated by laser photolysis of ICN at 266 nm. The following Arrhenius parameters were obtained over the temperature range 296-578 K: CN+HCN,  $k \pm 10^{-11.41 \pm 0.15} \exp[-(670 \pm 100)/T]$  cm<sup>3</sup> s<sup>-1</sup>; CN+BrCN,  $k \pm 10^{-10.7 \pm 0.4} \times \exp[-(1340 \pm 330)/T]$  cm<sup>3</sup> s<sup>-1</sup>; CN+CH<sub>3</sub>CN,  $k \pm 10^{-10.19 \pm 0.10} \exp[-(1190 \pm 70)/T]$  cm<sup>3</sup> s<sup>-1</sup>. The rates measured here and that of Szekely et al. for CN+HCN could be well fitted by the form,  $k = 10^{-16.20}T^{1.57} \exp(-50/T)$  cm<sup>3</sup> s<sup>-1</sup> over the temperature range 300-3000 K, allowing extrapolation to the combustion temperature regime. The measured rates and those of Kayes and Levitt and Clark et al. for the CN+BrCN reaction could be fitted by the form,  $k = 10^{-14.18}T^{1.16} \exp(-940/T)$  cm<sup>3</sup> s<sup>-1</sup>, over the temperature range 300-3000 K. In addition, the non-linearity of these data over a wide range of temperature could be satisfactorily accounted for by transition-state theory calculations for both of these reactions.

# 1. Introduction

The CN radical has been proposed to be an important intermediate in a variety of reactive systems including flames [1], planetary atmospheres [2], comets [3] and chemical lasers [4]. Until recently, there have been very few direct measurements of rate constants for CN radical reactions [5–9], and only in the last few years has temperature-dependent rate constant information been obtained [10–12]. As it is amenable to study by laser-induced fluorescence techniques, a series of direct measurements have recently been performed for the reaction of CN with molecules that are important in combustion and in planetary atmospheres [5,6,7,9,12].

The reaction of HCN with CN is potentially important as a pathway for removal of HCN and formation of  $C_2N_2$  in combustion systems. Szekely et al.

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[11] have measured the rate constant for the reaction,  $CN+HCN\rightarrow C_2N_2+H$ , by following CN absorption in a shock tube. They obtained the rate constant  $k=1.7\times10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> over the temperature range 2720-3070 K. Thielen and Roth [13] have incorporated this reaction into their modeling of shock heated mixtures of HCN and O<sub>2</sub>. Melius [14] has implicated the reaction in the first stage ignition of cyclic nitramines. Also, Fifer and Holmes [15] have used this reaction in their modeling of the  $HCN/NO_2$ chemistry in shock waves. Most recently, Miller and Bowman [16] have included the reaction in their modeling of nitrogen in combustion. It is apparant that more direct rate constant measurements are needed for this reaction. In addition, knowledge of how the CN radical reacts with the entire class of CNcontaining molecules, including those relevant to planetary atmospheres, would provide modelers in different fields with much needed mechanistic information. In order to further these goals, we have performed the first temperature-dependent laser photol-

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ysis/LIF rate constant measurements for the reaction of the ground state of CN with HCN, BrCN and  $CH_3CN$ .

## 2. Experimental

The experimental apparatus is similar to previous laser photolysis/LIF experiments performed at NRL and will only be described briefly [17,18]. Photodissociation of ICN by the quadrupled output at 266 nm of a Nd<sup>3+</sup>: YAG laser (Quanta-Ray DCR-1A) was utilized to generate ground state  $CN(X^{2}\Sigma^{+})$  radicals. The photolysis laser beam of  $\approx 6$  to 10 mJ/pulse was collimated and directed down one arm of the reaction cell. The photolysis laser was operated at 10 Hz. The CN radicals were probed by laser-induced fluorescence generated by a cw ring dye laser (Coherent 699-29) using a mixture of rhodamine 6G and rhodamine 640 (200-400 mW) laser dyes on the  $Q_1(5)$  transition of the A  ${}^2\Pi$ -X  ${}^2\Sigma^+$  (4, 0) band at 621.5 nm (16085.87 cm $^{-1}$ ). This probe laser beam was focused with a 25 cm lens and directed counterpropagating down the opposing arm of the reaction cell. The ring laser was pumped by a Spectra Physics model 171 Ar<sup>+</sup> laser (6-8 W "all lines").

Fluorescence at wavelengths greater than 620 nm was collected with a two-lens system, filtered with Corning 2-62, 2-61 and Hoya UV-36 color filters and directed to an RCA 7265 photomultiplier tube (S-20 photocathode) chosen for its sensitivity in the red. The output of the PMT was sent to a Nicolet 1174 signal averager where profiles  $(0-300 \ \mu s)$  obtained for 500 laser shots were averaged and digitized. The data were then transferred via a serial interface to a personal computer where data analysis was performed. Excitation spectra were obtained by scanning the ring laser with the Coherent Autoscan unit with wavemeter. The PMT output was sent to a PAR 162/164 boxcar averager. The boxcar output was then digitized and plotted by the Autoscan Apple IIe computer.

The reaction cell was constructed of pyrex and was resistively heated. A thermocouple placed within 5 mm of the reaction zone was employed to monitor the reaction temperature with accuracy of  $\pm 1$  K. Pressures were monitored with Baratron capacitance manometers. ICN, obtained from Kodak and Eastman, was vacuum sublimed and pumped on prior to use to remove most of the  $I_2$  impurity. The ICN was placed on a fritted surface and a flow of argon gas was passed through the crystals thus entraining a flow of ICN vapor that was directed into the reaction cell. The reactants BrCN and CH<sub>3</sub>CN, obtained from Eastman, were vacuum distilled prior to use and stored in glass bulbs in the dark. HCN was synthesized by the reaction of NaCN with HCl and also distilled and stored in the dark. Argon (99.995% purity) was obtained from Matheson and used without further purification.

#### 3. Results

The present work differs from the previous LIF rate constant measurements in that a cw ring dye laser is incorporated for the probe laser. The cw laser provides certain advantages over a pulsed laser system. It enables one to obtain the entire relative concentration profile of the CN radical in a single shot of the pulsed photolysis laser. Therefore, many shots can be averaged to generate a relatively noise-free profile. Unfortunately, there are also inherent disadvantages to this experiment, mostly with respect to utilizing the A  ${}^{2}\Pi$  state for probing. The A  ${}^{2}\Pi$  of CN is relatively low lying and has a fluorescence lifetime of 7 us. Its use as a kinetic probe thus results in complications due to its long fluorescence lifetime and its large quenching cross section. As a result, at relatively high pressures the fluorescence is strongly quenched and the signal level is therefore quite low, and at relatively low pressures the signal is strong but the long fluorescence lifetime makes the study of fast reactions prohibitive.

The B  ${}^{2}\Sigma^{+}$  state of CN is much more attractive for use as a kinetic probe. It has a short fluorescence lifetime (61 ns) and has a relatively small quenching cross section [19]. Unfortunately, the B state was not accessible with our Ar<sup>+</sup>-ring dye laser system. Recent work by Tully and Durant [20] has demonstrated that the CN B state is accessible with a ring dye laser system that employs a new experimental laser dye.

The use of the A state thus limited the range of data that could be taken. All experiments were performed at 20 Torr total pressure, mostly argon. This was necessary because higher pressures of argon resulted in much reduced LIF signal intensity due to rapid quenching. It was also necessary to average 500 shots in order to obtain an adequate signal-to-noise ratio. At relatively large reactant concentrations we were limited by low signal intensity due to quenching and/ or by rapid decays which approached the fluorescence lifetime of the A state. Fortunately, at large reactant concentrations the quenching usually shortened the fluorescence lifetime to the extent that short reactive lifetimes ( $\approx 10 \, \mu$ s) could still be measured.

The experimental rate constant measurements were limited to temperatures below 578 K. It was found that at temperatures approaching 550 K the ICN precursor began to decompose. This decomposition manifested itself as a reduction in the LIF signal due to ICN photolysis and a rise in the dc signal from the PMT. This dc component was due to production of  $I_2$  upon thermal decomposition of ICN as demonstrated by scanning the dye laser and observation of the characteristic  $I_2$  spectrum. The  $Q_1(5)$  transition was chosen for kinetic probing because it is a particularly strong line under our conditions and it does not overlap with any of the  $I_2$  transitions.

All runs were performed under pseudo-first-order conditions. A constant concentration of ICN was photolyzed and varying amounts of reactant were added. Argon buffer gas was added to a total pressure of 20 Torr. The LIF signal was taken as a relative measure of the ground state CN radical concentration. In all cases the CN radical decay could be fitted to a single exponential decay. The data were leastsquares fitted by the equation

$$I=A\exp(-k_1t)+B,$$

where I is the measured LIF intensity,  $k_1$  is the pseudo-first-order decay rate constant due to all removal processes, and t is the time following the photolysis laser pulse. The parameters A, B and  $k_1$  are obtained from the non-linear least-squares fit. These  $k_1$  values are then obtained at various reactant concentrations and fitted by the equation

$$k_1 = k_0 + k_2[\mathbf{R}]$$
,

where  $k_2$  is the bimolecular rate constant for the reaction of CN with R, [R] is the reactant concentration or number density, and  $k_0$  is the removal rate constant for CN due to all other loss processes. Fig. 1



Fig. 1. Plot of  $k_1$  versus HCN number density for the CN+HCN reaction at 478 K. Slope of plot yields bimolecular rate constant,  $k = (8.74 \pm 0.43) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

Table 1 Rate constants for the reaction of CN radicals with HCN, BrCN and CH<sub>3</sub>CN  $^{a)}$ 

Reactant	Temperature (K)	Rate constant $(10^{-13} \text{ cm}^3 \text{ s}^{-1})$
HCN	296	4.10±0.50
	478	$8.74 \pm 0.43$
	567	$12.8 \pm 1.1$
BrCN	302	$2.89 \pm 0.77$
	372	$3.36 \pm 0.59$
	477	$10.3 \pm 0.4$
	578	$23.2 \pm 1.2$
CH <sub>3</sub> CN	297	$11.2 \pm 3.0$
	380	$29.7 \pm 2.6$
	578	$79.1 \pm 3.5$

<sup>a)</sup> All rate constants obtained at 20 Torr total pressure (mostly argon).

demonstrates a plot of  $k_1$  versus the HCN number density for the reaction of CN with HCN at 478 K. The slope yields the bimolecular rate constant,  $k_2 = (8.74 \pm 0.43) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

Table 1 lists the bimolecular rate constants obtained for the reaction of CN with HCN, BrCN, and CH<sub>3</sub>CN over the temperature range 296–578 K. The listed uncertainties are due to the statistical precision of the least-squares fits only. An overall uncertainty of 50% is estimated for the absolute accuracy of the rate constant measurements. The data are plotted in Arrhenius form in fig. 2. It is apparent that each of the reactions has a positive activation energy. The data were fitted to the simple Arrhenius form, k=



Fig. 2. Arrhenius plots of data for CN radical reactions: ( $\bullet$ ) CH<sub>3</sub>CN, ( $\blacksquare$ ) HCN, ( $\blacktriangle$ ) BrCN.

 $A \exp(-E_a/RT)$ . The following Arrhenius parameters are obtained:

CN+HCN,

 $k = 10^{-11.41 \pm 0.15} \exp[-(670 \pm 100)/T] \text{ cm}^3 \text{ s}^{-1};$ 

CN+BrCN,

 $k = 10^{-10.7 \pm 0.4} \exp[-(1340 \pm 330)/T] \text{ cm}^3 \text{ s}^{-1};$ 

 $CN+CH_3CN$ ,

$$k = 10^{-10.19 \pm 0.10} \exp[-(1190 \pm 70)/T] \text{ cm}^3 \text{ s}^{-1}$$
.

## 4. Discussion

Fig. 2 demonstrates that each of these reactions occurs with similar activation energies. Also, the HCN and BrCN reactions have very similar rate constants, while the CH<sub>3</sub>CN rate constants are a factor of five to ten faster. The energetically possible reaction pathways and their exothermicities are

 $CN + HCN \rightarrow (CN)_{2} + H \qquad \Delta H = -27.0 \text{ kcal/mole},$   $CN + BrCN \rightarrow (CN)_{2} + Br \qquad \Delta H = -63.4 \text{ kcal/mole},$   $CN + CH_{3}CN \qquad \rightarrow (CN)_{2} + CH_{3} \qquad \Delta H = -31.5 \text{ kcal/mole},$ 

 $\rightarrow$  HCN+CH<sub>2</sub>CN  $\Delta H = -28.7$  kcal/mole.

The only available exothermic reaction pathways for both the HCN and BrCN reactions involve production of cyanogen,  $(CN)_2$ . The similar rate constants obtained for these two reactions also lend credence to their having similar reaction mechanisms. For the case of HCN one could think of the reaction occurring via addition of the radical to the carbon atom of HCN followed by elimination of H via

$$CN + HCN \rightarrow H - C = N' \rightarrow (CN)_2 + H$$

An analogous reaction mechanism is possible for the BrCN reaction. The difference in activation energies between these two reactions, 1.3 and 2.7 kcal/mole, may be due to the large scatter and small number of temperatures at which the rate constants have been measured. If we compare the data for these two reactions at 480 and 300 K in fig. 2, it is apparent that at these temperatures the reactions have equal rate constants and that these reactions may indeed have similar activation energies.

The only measurement of the HCN rate constant reported in the literature is that of Szekely et al. [11], who measured the rate constant over the temperature range 2720–3070 K by following CN absorption in a shock tube. They obtained a rate of  $1.7 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> independent of temperature. Extrapolating our result to 3000 K with the Arrhenius parameters determined here results in a rate that is a factor of five or six lower. A transition-state theory extrapolation would provide a more reasonable comparison of these measurements.

There are three literature determinations of the rate constant for the BrCN reaction [21–24]; these measurements have been evaluated by Baulch et al. [25]. Each of the determinations is from a computer fit to complex mechanisms in shock waves. These measurements vary by as much as three orders of magnitude and Baulch et al. were unable to recommend preferred rate coefficients. It would be valuable to be able to extrapolate our directly measured rate constants into the high temperature regime.

Therefore, in order to better understand the Arrhenius behavior of these reactions and also to be able to allow extrapolation of these relatively low temperature rate constants to the combustion regime we have performed transition-state theory calculations (TST) for the HCN and BrCN reactions. The calculation requires estimation of the geometry and vibrational frequencies of the transition state. For these reactions, we have assumed very simple geometries and vibrational frequencies are estimated by analogy with known compounds and the compiled estimates of Benson [26]. We have also included a free internal rotation about the forming bond; this moment of inertia was calculated by the methods of Hershbach et al. [27]. The single remaining vibrational frequency, created due to the formation of the new bond, and the barrier of the potential energy surface are varied by a non-linear least-squares fitting routine to match the measured rate constants and temperature dependence. Comparison of the calculated result over a broad temperature range with the measured rates allows us to discount "unreasonable" transition state configurations and reaction mechanisms. It also permits better extrapolation to the combustion regime than a simple Arrhenius extrapolation as it has been found that very few reactions exhibit simple Arrhenius behavior over such a wide temperature range.

Table 2 contains the parameters incorporated in the TST calculations for the HCN and BrCN reactions. The geometry assumed for both reactions is

$$C-N$$
  
 $X-C-N$ ,

Table 2Parameters used in transition-state theory calculations

	Transition state	
	CN-HCN	CN-BrCN
moments of inertia (amu Å <sup>2</sup> )	11.3	122.3
	144.6	289.7
	155.9	412.0
	4.98 <sup>a)</sup>	10.3 <sup>a)</sup>
vibrational frequencies (cm <sup>-1</sup> )	3311	2100
• • • • •	2100	2069
	2069	635
	1150	560
	713	360
	635	350
	1095 <sup>b)</sup>	204 <sup>ь)</sup>
barrier height (kcal/mole)	1.42	
• • • •	1.89	

<sup>a)</sup> Moment of inertia of free internal rotation about the forming bond.

b) This frequency is obtained from the TST fitting.

where X is either a hydrogen atom or a bromine atom. For the HCN reaction the bond lengths are assumed to be those of separated CN and HCN. The X–C–C and C–C–N bond angles are 90°, while the transition states are assumed to be linear. For the BrCN reaction the assumed bond lengths are: 1.94 Å for Br–C, and 1.5 Å for C–N (on the BrCN part of the transition state). Both transition states have C–C bond lengths of 2.5 Å.

The result of the calculation over the temperature range 300-3000 K is demonstrated in fig. 3 for the HCN reaction along with the measured rate constants from this work and that of Szekely et al. [11]. It is apparent from fig. 3 that the calculation predicts that the rate constant turns upward with increasing temperature. The calculation does an excellent job of reproducing the measured temperature dependence of this work and the high-temperature work of Szekely et al. The result of the calculation can be represented by the equation,  $k = 10^{-16.46} T^{1.66} \exp(-70/T) \text{ cm}^3$  $s^{-1}$ . Also shown in fig. 3 is the result of a non-linear least-squares fit of the present measured rate constants and that of Szekely et al. by the three-parameter form,  $k = AT^B \exp(-C/T)$ . This results in the equation,  $k=10^{-16.20}T^{1.57} \exp(-50/T)$  cm<sup>3</sup> s<sup>-1</sup>. Fig. 3 demonstrates that the two curves are in excellent agreement.

Fig. 4 demonstrates the result of the TST calculation for the BrCN reaction. As for the HCN reaction, the calculation predicts a significant upward curva-



Fig. 3. Arrhenius plots for the CN+HCN reaction; ( $\bigcirc$ ) measured rate constants of the present work, ( $\square$ ) measured rate of Szekely et al. [11]. Dashed curve is transition-state theory calculation, solid curve is non-linear fit to measured rate constants of the present work and that of Szekely et al.



Fig. 4. Arrhenius plots for the CN+BrCN reaction; ( $\bullet$ ) measured rate constants of the present work, ( $\bigcirc$ ) Clark et al., ( $\square$ ) Tabayashi et al., ( $\blacksquare$ ) Kayes and Levitt. Dashed curve is TST calculation, solid curve is non-linear fit to measured rate constants of the present work and that of Kayes and Levitt [22,23] and Clark et al. [21].

ture of the rate with increasing temperature. Also shown in the figure are the data of Clark et al. [21], Kayes and Levitt [22,23], and Tabayashi et al. [24]. The measurements of Clark et al. and Kayes and Levitt are somewhat lower than the TST extrapolation, while the data of Tabayashi et al. are two orders of magnitude lower than the other measurements. The TST calculation can be represented by the form,  $k=10^{-17.91}T^{2.34} \exp(-380/T) \text{ cm}^3 \text{ s}^{-1}$ . Also shown in fig. 4 is the result of fitting our measured rate constants and those of Kayes and Levitt [22,23] and Clark et al. [21] by the abovementioned three-parameter form. The resulting equation is,  $k=10^{-14.18}T^{1.16} \exp(-940/T) \text{ cm}^3 \text{ s}^{-1}$ .

The CH<sub>3</sub>CN reaction has two reaction pathways with very similar exothermicities. The first is analogous to the above reactions with HCN and BrCN; CN can add to the carbon atom and then eliminate a methyl radical thereby producing  $(CN)_2$ . The second pathway may occur by an abstraction mechanism, where CN abstracts a hydrogen atom from CH<sub>3</sub>CN. The present data do not yield direct evidence to allow us to differentiate between the two mechanisms. If we assume that the  $(CN)_2$  producing pathway has similar rate constants to the analogous reactions with HCN and BrCN, then the abstraction pathway appears to be the dominant mechanism. Lichtin and Lin [6] have concluded that an abstraction mechanism is dominant for the reaction of CN with  $H_2$ ,  $CH_4$  and  $C_2H_6$ . In addition, their measured room temperature rate constant for  $CH_4$  is equal to our measured  $CH_3CN$  rate. This evidence supports the dominance of the abstraction pathway. More work needs to be performed to further elucidate the exact reaction mechanisms.

Unfortunately, the rapid quenching of the A state of CN precluded the measurement of the pressure effect on the rate constant. Previous work at NRL had demonstrated that measuring the rate constant over a broad pressure range is extremely informative mechanistically. It is recommended that future work on these reactions include measurements over a significant range of pressures. This should be quite possible by employing the B state for probing the concentration of CN. B-state probing should also allow much more precise rate coefficients to be determined. This will help differentiate between the different possible mechanisms and allow more precise determination of Arrhenius parameters.

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