#### KINETICS OF CN RADICAL REACTIONS WITH SELECTED MOLECULES AT ROOM TEMPERATURE

# D.A. LICHTIN<sup>1</sup> and M.C. LIN

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The two-laser photoinitiation probe technique has been used to obtain room-temperature second-order rate constants for the reaction of CN radicals with compounds key to atmospheric and combustion chemistry. CN was generated by 266 nm photolysis of ICN. Laser-induced fluorescence probing via both CN(A  $\leftarrow$  X) and CN(B  $\leftarrow$  X) has been utilized. Values reported are:  $k(H_2) = (4.9 \pm 0.4) \times 10^{-14}$ ,  $k(CH_4) = (1.1 \pm 0.1) \times 10^{-12}$ ,  $k(C_2H_6) = (2.9 \pm 0.1) \times 10^{-11}$ ,  $k(C_2H_2) = (2.3 \pm 0.1) \times 10^{-10}$ ,  $k(C_2H_4) = (2.7 \pm 0.1) \times 10^{-10}$ ,  $k(C_3H_6) = (2.3 \pm 0.3) \times 10^{-10}$ , and  $k(O_2) = (2.5 \pm 0.2) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. A comparison with available literature data is made and mechanisms are discussed.

#### 1. Introduction

The chemistry of the CN radical is crucial to understanding the complex nature of NO, formation in a hydrocarbon flame and the nitrogen balance in atmospheres of several key planets in our solar system. To date most studies of CN reaction kinetics utilized the flash photolysis/ UV-absorption technique [1-12], which, albeit useful for measuring the slower reaction rates, is not appropriate for very fast processes. Accordingly, only a limited amount of kinetic data on CN reactions exists in the literature.

We have recently employed the two-laser pump-probe technique to study the kinetics and mechanisms of very fast processes involving CH radicals over a broad range of temperature and pressure [13-16]. By utilizing the very sensitive laser-induced fluorescence (LIF) detection method and a judicious choice of radical precursors, rate constant values were determined readily and reliably up to the gas-kinetic limit. In this work, we have employed the same approach to studying

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kinetics of several CN reactions relevant to combustion and planetary atmospheric chemistry. Room temperature rate constants measured for some of these reactions will be compared with those available in the literature.

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### 2. Experimental

The two-laser photoinitiation/probe apparatus used in the experiment is similar to that employed for CH kinetic studies [13-16]. It consisted of five major components: a flow-through reaction cell, two lasers (one for CN radical generation, one for LIF probing), detectors with associated optics, and electronics to control laser firing as well as collect and process LIF data.

The reaction cells used were basically six-way pyrex crosses with one baffled horizontal axis for the two collinearly propagating laser beams, the other for fluorescence detection and the vertical axis for reactant flow. Molecular reactant, premixed with Ar, was introduced into the system through a fritted glass filter on which purified solid ICN (the CN radical precursor) was placed. This mixture was further diluted with Ar to achieve the desired concentrations and total pressure. System pressures were measured with calibrated MKS

Baratrons situated immediately downstream from the cross.

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The photolysis light at 266 nm was provided by a quadrupled Nd : YAG laser (Quanta-Ray DCR-IA). After prismatic separation of the dissociation beam from the Nd : YAG fundamental- and second-harmonic frequencies, it was directed through the baffled axis of the reaction cell with the aid of a mildly focusing 1 m focal length lens. To avoid multiphoton processes generating excited CN radicals, the 266 nm output energy of the laser was maintained at  $\approx 50 \mu J$ .

For LIF probing two different lasers were used. A flashlamp pumped dye laser (Chromatix CMX-4) operating at 619 nm was used to monitor CN via the  $A^2\Pi(v'=4)-X^2\Sigma^+(v''=0)$  transition. Data obtained from these experiments suffered relatively large uncertainties due to this laser's erratic output power and the weakness of  $A \rightarrow X$  fluorescences. The latter problem was exasperated by the need to filter out the direct LIF (at 619 nm) because of excessive dispersion of the probe beam. Finally, the long fluorescence lifetime of the A state, = 7 µs [17] \* makes this transition inappropriate under our conditions for monitoring the near gas-kinetic reactions. The second probe used in our experiments was a XeCl-excimer laserpumped dye laser system (Lambda Physics) operated at 388 nm, monitoring the CN concentration decay via the  $B^2\Sigma^+ - X^2\Sigma^+$  transition. Because of the short radiative lifetime of the B state (61 ns [19]), our ability to monitor LIF directly at 388 nm and the laser power pulse-to-pulse stability (10% fluctuation), kinetic data obtained from B-state probing experiments were less scattered and more reproducible.

The detection part of the apparatus consisted of appropriate filters, collection optics and an RCA C31024 photomultiplier tube. This particular PMT was chosen for its high sensitivity up to 800 nm, allowing detection of both  $A \rightarrow X$  and  $B \rightarrow X$ emissions. During all experiments an SnCl<sub>2</sub> (0.5 N in 3 : 2 HCl : H<sub>2</sub>O) solution filter (T = 50% at 345 nm) was used in the detection train (before any

This value is incorrectly transcribed by Huber and Herzberg [18] who (using the same source) quote 0.7  $\mu$ s.

any glass filters) to block scattered light at shorter wavelengths, particularly that from the photodissociation source.

Signal averaging and data acquisition were accomplished with gated integrators used in conjunction with a laboratory computer (D.E.C. MINC-11/23). In the initial  $A \leftarrow X$  LIF probing experiments a two-channel gated integrator constructed from Evans circuit boards was utilized. In subsequent experiments with  $B \leftarrow X$  probing, a two-channel SRS (Stanford Research Systems) boxcar averager was employed in "last sample" mode. The rate of CN radical disappearances was measured by following the decrease in LIF intensity with increasing delay times between firing the



Fig. 1. Semilog plot of the CN( $B \rightarrow X$ ) LIF signal versus delay of probe after photolysis, for 295 K (room temperature)  $C_2H_2$ reaction with CN. Shown are points for four  $C_2H_2$  partial pressures: x = 0.00 Torr,  $\Phi = 3.3 \times 10^{-4}$  Torr,  $O = 9.6 \times 10^{-3}$ Torr,  $+ = 2.06 \times 10^{-2}$  Torr with total pressure of  $45.8 \pm 0.5$ (mainly Ar). Error bars indicate  $\pm 1\sigma$  for the 48 individual laser firings used to obtain each point. Baseline value " $I_{bkg}$ " from fitting the raw data to  $I = I_{bkg} + C \exp(-k_1 t)$  has been subtracted from the value plotted and the fits are the remaining  $I' = C \exp(-k_1 t)$ .





photodissociation and the probe lasers. The increments in delay time, ranging from 1 to 10  $\mu$ s, and delay limits, ranging from -5 to +400  $\mu$ s, were chosen to guarantee that 2-3 reactive lifetimes were covered.

In all measurements, shot-by-shot normalization was done with probe-laser power measurements made with a photodiode, utilizing one gated integrator. Normalization and averaging of the normalized signal for each delay time was performed in the computer. Initially fifty data points were taken at each delay. Data points where the reference (i.e. photodiode) signal varied by more than one standard deviation from the average reference value for that delay were discarded. The routine was designed to eliminate erroneous data caused by temporal and energy jitter of the probe



Fig. 4. Plots of pseudo-first-order rate constants versus molecular pressure for the reaction of CN (v = 0) with O<sub>2</sub> at 294 K, in Ar. ( $\bullet$ ):  $k_2 \pm 2\sigma = (2.6 \pm 0.2) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, CN(A  $\leftarrow$  X) LIF probe, total pressure =  $18 \pm 1$  Torr. (O)  $k_2 \pm 2\sigma = (2.4 \pm 0.1) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, CN(B  $\leftarrow$  X) LIF probe, total pressure =  $16 \pm 1$  Torr. Similar, but noisier, results were obtained at = 50 Torr total pressure (i.e.  $(2.5 \pm 0.4) \times 10^{-11}$  and  $(2.2 \pm 0.2) \times 10^{-11}$ , respectively, for A and B state probing). Error bars indicate  $2\sigma$  for fits used to generate the data point.

laser. A non-linear least-squares regression was used to determine pseudo-first-order decay rate constants for each run carried out at a fixed molecular reactant pressure.

All gases used in this study were obtained from Matheson Gas Products. Before use, all condensible gases were purified by trap-to-trap distillation. ICN (Eastman Organic) was purified via vacuum sublimation. Reaction mixtures were prepared in large storage bulbs at high pressures (typically 1-5 atm) with UHP grade Ar.

### 3. Results

The intensity of the LIF signal from both  $CN(A^2\Pi \leftarrow X^2\Sigma^+)$  and  $(B^2\Sigma^+ \leftarrow X^2\Sigma^+)$  transitions was taken as a measure of the ground state CN radical relative concentration. The LIF intensity, *I*, was found to decay exponentially as a function of time, *t*, after the photolysis laser pulse. The signal was fitted by means of the least-squares method to the equation

$$I = I_{\rm bkg} + C \exp(-k_1 t),$$

where  $k_1$  is the pseudo-first-order rate constant for net CN removal due to all processes (i.e. chemical reactions and diffusion out of the probed region) under the condition [molecular reactant]  $\gg$  [CN]. Typical pseudo-first-order plots of CN decay, with various molecular-reactant concentrations are presented (with  $I_{bkg}$  subtracted) in fig.1 for the reaction with  $C_2H_2$ .

To obtain second-order constants  $(k_2)$  for the reactions

# $CN + R \rightarrow products$ ,

the concentration of reactant R was varied while the total pressure of the system was held constant. The pseudo-first-order rate constants obtained at a particular total pressure and temperature for a number of molecular-reactant concentrations were then least-squares fitted (with weighing by the  $k_1$ standard deviation) to the equation

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

where  $k_0$  is the loss rate constant for CN due to diffusion and/or reaction in the absence of R. Typical plots of  $k_1$  versus [R] for the reaction of CN with H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and  $O_2$  are shown in figs. 2-4. The total pressure of the system was maintained constant at  $\approx 45$ Torr (except for  $O_2$ , see fig. 4) using Ar as the buffer gas. The reaction temperature was mea-

Reactant	<i>T</i> (K)	This work b)	Literature values	Ref.
H <sub>2</sub>	294	$(4.9\pm0.4)\times10^{-14}$ (A)	والمرجعة والمحمد والمحم	an a
	300		$(1.4\pm0.5)\times10^{-14}$	[10]
	297		$<(8\pm3)\times10^{-14}, v=1$	[10]
	300		$(1.6\pm0.3)\times10^{-14}$	[20]
	300		$(3.0\pm0.4)\times10^{-14}, v=1$	[20]
CH4	294	$(1.13 \pm 0.06) \times 10^{-12}$ (A)		
	293		$(5\pm3)\times10^{-13}$	[10]
	293		$(1.2\pm0.3)\times10^{-12}, v=1$	[10]
	300		$(7.4 \pm 0.2) \times 10^{-13}$	[4]
	300		$(83+03)\times 10^{-13}$ $n=4$	[-] [4]
	300		$(5.5 \pm 0.3) \times 10^{-13}$	[7]
	300		$(8.4\pm0.3)\times10^{-13}, v=1$	[20]
C-H	70.1	$(29\pm31)\times10^{-11}$ (B)		• •
C7116	200	(=)=0.1)×10 (B)	(2.41 + 0.17)+10-11	
			$(2.41 \pm 0.17) \times 10^{-10}$	[4]
C <sub>2</sub> H <sub>2</sub>	294	$(2.28 \pm 0.06) \times 10^{-10}$ (B)		
	259-396		$(5.0 \pm 1.7) \times 10^{-11}$	[10]
	293		$2.5 \times 10^{-10}$ , $v = 1$	ion
	300		$(2.2\pm0.2)\times10^{-10}$	[21]
С.н.	294	$(2.68 \pm 0.07) \times 10^{-10}$ (B)		
	300	((2)	$(19+07)\times 10^{-10}$	[4]
	300		$(7.7 \pm 0.3) \times 10^{-10} = 4$	[ <sup>-</sup> ]
	259-396		$(50+08)\times 10^{-11}$	1101
	293		$11 \times 10^{-10} n = 1$	[10]
	300		$(1.6 \pm 0.2) \times 10^{-10}$	[2]]
	300		$(7.3+0.7)\times10^{-10}$ n=1	[21]
				[-1]
C <sub>3</sub> H <sub>6</sub>	294	(2.3±0.3)×10 <sup>-10</sup> (B)		
	300		$(2.6 \pm 0.3) \times 10^{-10}$	[4]
0,	294	$(2.6\pm0.2)\times10^{-11}$ (A)		the second second
e Registra interna	294	$(2.4\pm0.1)\times10^{-11}$ (B)		
			$7.7 \times 10^{-12}$	[2]
and the second second	303		$(1.12 \pm 0.03) \times 10^{-11}$	isi
	303		$(1.3+0.03)\times 10^{-11}$ , $v=1$	[5]
	298		$1.1 \times 10^{-11}$	nn
	293		$9 \times 10^{-12}$ , $r = 1$	m
	300		$(1.35 \pm 0.13) \times 10^{-11}$	[22]
	300		$(1.25+0.26)\times 10^{-11}$ n = 1	[22]
			$9.1 \times 10^{-12}$	[23]
	300		$(2.0+0.2)\times10^{-11}$	(20)
	300		$(74+01)\times10^{-11}$ n=1	[70]

Rate constants for CN reactions at room temperature<sup>2)</sup>

<sup>a)</sup> All rate constants given, unless otherwise specified, are for the ground vibrational state (v = 0) reactions, in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

<sup>b)</sup> (A) and (B) represent results obtained from  $A \leftarrow X$  and  $B \leftarrow X$  LIF probing.

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Table 1

sured to be  $294 \pm 1$  K throughout the experiments. The values of  $k_2$  determined for the aforementioned reactants are tabulated, alongside those from other investigators' studies in table 1.

### 4. Discussion

The observed second-order rate constants for the seven reactions studied vary from a low value of  $5 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for CN + H<sub>2</sub> to the near gas-kinetic values of  $(2-3) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for CN + unsaturated hydrocarbons. As will be detailed below this significant variation in rate constants reflects the difference in the operative mechanisms among these reactions.

For comparison with previous measurements our values are listed in table 1 together with literature data for the corresponding reactions. In table 2 we also compare the measured rate constants for the CN reaction from this study (excluding CN +  $C_3H_6$ ) and those of O(<sup>3</sup>P), OH(X<sup>2</sup>II), and CH(X<sup>2</sup>II) with the same reactants.

In the following sections we will discuss the kinetics and mechanisms of the reactions studied, in three different groups, with emphasis on ground vibrational state (v = 0) reactions.

### 4.1. $CN + H_2$ , $CH_4$ , and $C_2H_6$

The reaction of CN with  $H_2$  and alkanes (fig. 2) most likely occurs by direct H-atom abstraction:

$$CN + HX \rightarrow HCN + X$$
,  $X = H$  and alkyls.

The rate constant values determined in this work for reactions with H2 and CH4 are higher than the literature values by a factor of 2-3 (cf. table 1) and that for the reaction with C2H6 is in reasonably good agreement with the values reported by Bullock and Cooper [6]. The reason for the discrepancy in the cases of H, and CH<sub>4</sub> is not clear. Almost all previous studies on these reactions were made using  $B \leftarrow X$  probing either by absorption [1,2,4-6,8,10,11,25] or LIF [20,22,26] while we employed  $A \leftarrow X$  LIF for these two reactions. Due to the long radiative lifetime of the A state there was concern; however, one would expect any discrepancy to be towards lower k values. Subsequent study of the O, reaction (see table 1) shows that  $B \leftarrow X$  and  $A \leftarrow X$  LIF probings yield values which are in close agreement.

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The trend of rate constants for CN reactions with H<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> appear to be qualitatively consistent with other abstraction reactions, e.g., those of O and OH, as shown in table 2. However, the increase by a factor of 20 from H<sub>2</sub> to CH<sub>4</sub> is entirely out of line with the fact that  $D(H-H) = D(CH_3-H)$ . This is kinetically a rather interesting finding. The rate constants for these abstraction reactions are much smaller than those for their near gas-kinetic CH counterparts. The latter reactions have been shown to occur entirely via the insertion or addition mechanism [13-16].

We have investigated the possible relation between the reported rate constants herein and those for other CN reactions, with the ionization potentials (IP) of the molecular reactants. The resulting correlation is shown in fig. 5. Interestingly, despite

Table 2

Comparison of	room tempe	erature second-order ra	te constants with	those for O(	°P), OF	$H(X^{-}\Pi)$ and	CH(X-11)
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Reactant CN *	$k_2$ (cm <sup>3</sup> molecul	$e^{-1} s^{-1}$ )	
	0)	OH p)	СН
H <sub>2</sub> 4.9×10 <sup>-14</sup>	2.9×10 <sup>-18</sup>	7.0×10 <sup>-15</sup>	$2 \times 10^{-10}$ c)
CH. 1.1×10 <sup>-12</sup>	4.8×10 <sup>-18</sup>	8.2×10 <sup>-15</sup>	$1.0 \times 10^{-10}$ d)
C <sub>5</sub> H <sub>6</sub> 2.9×10 <sup>-11</sup>	9.8×10 <sup>-16</sup>	$2.6 \times 10^{-13}$	$2.7 \times 10^{-10}$ d)
C,H, 2.3×10 <sup>-10</sup>	$1.4 \times 10^{-13}$	7.4×10 <sup>-13</sup>	4.2×10 <sup>-10 c)</sup>
C <sub>1</sub> H <sub>4</sub> 2.7×10 <sup>-10</sup>	$7.6 \times 10^{-13}$	$2.9 \times 10^{-12}$	4.2×10 <sup>-10 c)</sup>
0 <sub>2</sub> 25×10 <sup>-11</sup>	이 흔들어야 요구 ^^	· · · · · · · · · · · · · · · · · · ·	5.1×10 <sup>-11</sup> 9

<sup>a)</sup> This work: <sup>b)</sup> Combustion kinetic data survey [24]. <sup>c)</sup> Ref. [16]; extrapolated to high-pressure limit. <sup>d)</sup> Ref. [15]. <sup>c)</sup> Ref. [14]. <sup>0</sup> Ref. [13]. the expected difference in the mechanisms of these reactions, including CN + HCN [20] and  $CO_2$  [20], the rates of these reactions are seen to correlate nicely with ionization potentials of molecular reactants. The majority of OH radical reactions listed in table 2 also show a similar parallel correlation. The only reactions which appear to deviate significantly from the linearity of these two simple correlations involve  $H_2$  as the reactant. In these cases dynamic constraints due to mass effect (e.g. tunnelling) may play an important role in the abstraction reactions.

## 4.2. $CN + C_2H_2$ , $C_2H_4$ and $C_3H_6$

The reactions of CN with unsaturated hydrocarbons (fig. 3) appear to be very fast and have near gas-kinetic rate constants as indicated by the data summarized in table 1.



Fig. 5. Semilog plot of second-order reaction rates versus ionization potentials (IP) of several molecular reactants, [i.e.  $H_2(\Delta)$ ,  $CH_4(Q)$ ,  $C_2H_6(Q)$ ,  $C_2H_2(Q)$ ,  $C_2H_4(D)$ ,  $O_2(Q)$ , HCN (+) and CO<sub>2</sub> (×)], for reactions with CN and OH (filled symbols) radicals at room temperature. The dashed lines have been drawn parallel to emphasize the similarity in these two radical reactions. See text for discussion.

These CN reactions probably take place mainly by addition into unsaturated  $\pi$ -bonds, followed by ejection of H-atoms from excited adducts. For example the CN + C<sub>2</sub>H<sub>2</sub> reaction mechanism can be described by

$$CN + C_2H_2 \rightarrow HC = CHCN^{\dagger} \rightarrow HC = C - CN + H$$
,

which is exothermic overall by  $\approx 18$  kcal/mole. Only this mechanism can reasonably account for the similar magnitudes of the measured rate constants for the three unsaturated hydrocarbons which have C-H bond energies varying from 90 kcal/mole in C<sub>3</sub>H<sub>6</sub> to 127 kcal/mole in C<sub>2</sub>H<sub>2</sub>. Direct abstraction of H atoms from these three compounds with comparable near gas-kinetic rates is thus improbable. In the future it would be useful to examine the mechanisms of these reactions more thoroughly, covering a wide range of temperature and pressure.

The observed large rate constants for these unsaturated hydrocarbon reactions also appear to be in accord with the low ionization potentials of these compounds as indicated by the good correlation shown in fig. 5 between k and IP. A similar linear correlation also exists for the OH reactions with the same saturated and unsaturated hydrocarbons, despite the gross differences in their reaction mechanism.

4.3.  $CN + O_{7}$ 

The reaction of the CN radical with O<sub>2</sub> has been studied by a number of workers [1,3,5,7,8, 11.25,27,28]. The reaction is pertinent to NO, formation kinetics in hydrocarbon-air combustion reactions. Earlier studies of this reaction were carried out primarily with flash photolysis [1.3,7,8.11] or pulse radiolysis [5], followed by kinetic UV-absorption spectroscopy using the  $B \leftarrow X$  transition. Rate constant values obtained from these earlier experiments are smaller by a factor of 2-3 than our result (fig. 4) of  $2.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup>  $s^{-1}$ . The latter value is based on both A  $\leftarrow$  X and  $B \leftarrow X$  diagnostics, as given in table 1. Our rate constant is in good agreement with the high value of  $2.0 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> recently reported by Jackson and co-workers [20].

The  $CN + O_2$  reaction probably takes place effectively by abstraction as follows:

 $CN + O_7 \rightarrow OCN + O.$ 

The reaction is exothermic by  $\approx 4$  kcal/mole with neeligible activation energy [7]. The simultaneous formation of CO and NO via the very exothermic four-centered route ( $\Delta H^0 = -106$  kcal/mole) is most likely unimportant. Previously it was found, in our study of CO stimulated emission from the  $O(^{3}P)$  + CN reaction, that addition of a small amount of O<sub>2</sub> to such a laser system drastically diminished the laser output [29]. This quenching effect was assumed to be caused by removal of the CN radical by rapid reaction with O<sub>2</sub>, as given above, followed by reactions involving OCN<sup>•</sup> to produce vibrationally cold CO molecules. Production of vibrationally excited CO directly via the exothermic four-centered process, if it did occur to any significant extent, would have enhanced rather than diminished the CO laser output. An unequivocal test for the mechanism of this reaction can be made by directly probing for OCN and NO or CO formation. This can be achieved by either time-resolved LIF or resonance absorption utilizing UV or IR lasers.

## 5. Concluding remarks

We have determined the rate constants for the reactions of the ground state CN radical, CN  $(X^2\Sigma^+, v=0)$  generated by the photodissociation of ICN at 266 nm [30], with H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and O<sub>2</sub>, at room temperature by varied delay laser-induced fluorescence. The magnitudes of these rate constants range from a low value of  $5 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for CN + H<sub>2</sub> to near gas-kinetic values of  $(2-3) \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for reactions with unsaturated hydrocarbons. The trend correlates inversely with the ionization potentials of the molecular reactants, paralleling what is observed for the reaction of OH radicals with these same compounds.

In this paper our discussion centers on reactions of the CN(v=0) radical. The kinetics for disappearance of the vibrationally excited radical CN(v=1) have been investigated previously by several workers [4,10,20]. For cases where abstraction reactions can occur (e.g.,  $CN + H_2$  or  $CO_2$ ), the rates of disappearance for CN(v=1) appear to be about twice as fast as those for CN(v=0)according to recent data of Jackson and coworkers. In the case of  $CN + O_2$ , for which vibrational excitation was earlier reported [11,22] to have a retarding effect, such excitation has now been shown to have negligible effect [20].

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To clarify these discrepancies, a systematic study of some of these fundamentally important processes (such as  $CN + H_2$ ,  $O_2$ ,  $C_2H_2$  and  $C_2H_4$ ) should be made over a broad range of temperature and pressure to establish more firmly their kinetics as well as the operative mechanisms. Take  $CN + O_2$ , for example; in addition to the direct mechanism discussed earlier it also may take place, in principle, via the long-lived adduct CN-OO [20]. If this is the case, a careful study of the reaction over a wide range of temperature and pressure may reveal the importance of this additional channel.

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