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Laser measurements of the effects of vibrational energy on the reactions of CN

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Pulsed laser photolysis of C_2N_2 at 193 nm has been used as a source of CN radicals in both the $v'' = 0$ and $v'' = 1$ levels. Individual rovibronic levels of these radicals were measured as a function of time with a tunable dye laser. From these measurements the rate constants for the reaction of each of these vibrational levels with H_2, O_2, CO, CO_2, N_2, HCN, C_2N_2, and CH_4 have been determined. Some enhancement in the rate constant with vibrational energy which could not be ascribed to quenching was observed for O_2, CH_4, and H_2. Only vibrational quenching was observed for HCN, N_2, CO_2, CO, and C_2N_2. In the CO case the vibrational quenching rate appears to be significantly enhanced by complex formation during the quenching process.

INTRODUCTION

The rates of CN reactions are important in the chemical processes that occur in flames,[1] comets,[2] lasers,[3] and planetary atmospheres.[4] In each of the above systems the overall conditions vary over a wide range of temperature and pressures. Often it is not possible to determine the laboratory rate constants under conditions that are equivalent to the conditions in the above systems. Thus, it is desirable to investigate the effects of internal energy on the rate constants of CN so that with the information that one obtains better models for these complex systems can be developed.

Most of the earlier work[5–11] that has been reported on CN reactions used broadband flash lamps[5,6,8,10] and a pulse radiolysis apparatus.[7] In these studies the radical concentrations were generally monitored by absorption spectroscopy which, because of its insensitivity, required high radical concentrations to obtain accurate measurements of the rate constants. These high concentrations can result in complicated reaction mechanism making it difficult to be sure that the real rate constant has been measured. The broadband flash lamps can also produce the unstable radical species in more than one electronic state[12–14] which in turn makes it difficult to observe state to state reaction rate constants. Laser sources for the production of the radical species are ideal for reaction kinetics if the intensity is low enough so that multiphoton effects are unimportant[15] and if the photochemical reaction mechanism is completely understood.[16]

In the present study, experiments will be described which use a low intensity ArF laser to photolyze cyanogen to produce a known concentration of CN radicals in the $v'' = 0$ and $v'' = 1$ levels. The concentrations of individual rovibronic states of the radical are then followed as a function of time using a high resolution (~ 1 cm^{-1}), tunable dye laser. From the observed time dependence, the pseudo-first order rate constants for the reactions of each of the above vibrational levels can be measured. These pseudo-first order rate constants are then used to determine the appropriate rate constants by measuring its variation with reactant gas pressure.

EXPERIMENTAL

A schematic diagram of the apparatus used for these experiments is shown in Fig. 1. The Math Sciences Northwest ArF Laser (XL-401) that was used produces a 1 mJ beam of 193 nm photons with a pulse repetition rate of 20 Hz. The area of the laser beam is about 0.5 cm^2 and it has a pulse width of 5 ns. The laser enters the stainless steel cell through a CaF_2 window and is collimated by internal baffles to reduce the amount of scattered light that is produced when the laser strikes the window leading to the cell. This scattered light occurs with all windows and may indicate some kind of surface fluorescence. After the laser passes through the cell it is attenuated with an interference filter that is centered at 160 nm with a 55 nm bandwidth. This filter eliminates the fluorescence background from the laser and insures that the signals that are measured are associated with the laser and are linear over the complete range of laser intensities. The light after passing through the filter is further attenuated by a slit and is allowed to strike the backwall of the photomultiplier housing. Some of the light that strikes the backwall eventually finds its way to the photocathode of the PM tube where it is converted to electrons, amplified, and put into the "B" channel of a dual channel boxcar integrator (PAR 162/164).

A Molectron UV 12 nitrogen laser is used to pump a Molectron DL II dye laser which generates narrow band (~ 1 cm^{-1}) tunable radiation that covers the wavelength

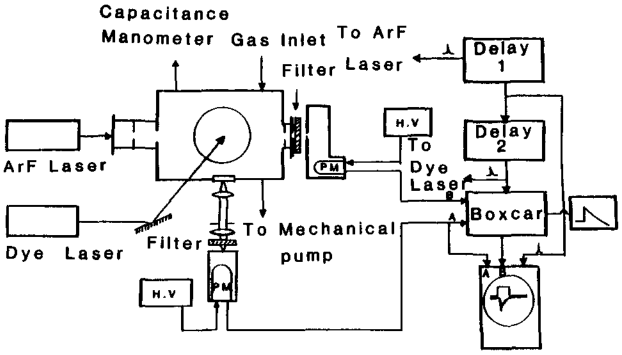

FIG. 1. Schematic diagram of the experimental apparatus.

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range of the ($B\,^2\Sigma \rightarrow X\,^2\Sigma$) band of CN. The light from the tunable dye laser enters the cell through long baffle arms that are at right angles to the path of the ArF laser. The emission that is excited by the dye laser was then measured at right angles to both the dye laser and the ArF laser by first collecting it with a lens, then collimating it with another lens before passing it through an interference filter with a central wavelength of 420 nm into a (EMI, 9789QB) photomultiplier tube. The signal from the PM tube is processed by the "A" channel of the boxcar integrator and then divided by the signal from the "B" channel.

High purity C_2N_2 was obtained from Matheson and was purified with pump and thaw cycles between room and liquid nitrogen temperatures. The purity of the reactant gases were 99.995% for CO_2, 99.95% for CH_4, 99.999% for H_2, 99.8% for O_2, 99.995% for N_2, 99.99% for CO, and 99.999% for argon. The HCN was prepared by dropping concentrated sulfuric acid on potassium cyanide and dried over P_2O_5. The HCN was further purified by pump and thaw cycles between liquid nitrogen and liquid ethanol baths.

Argon was the major component of all of the reaction mixtures. It was added to the mixture to reduce the rate of diffusion of the radicals out of the viewing zone. Three component mixtures were made which consisted of 20 to 100 mTorr C_2N_2, 200 to 800 mTorr of the reactant gas, and 5 to 25 Torr of an argon. In the nitrogen and carbon monoxide experiments, no Ar was used. To insure that the sample was thoroughly mixed it was allowed to mix for several hours. The premixed sample was then stored in a 10 ℓ storage vessel and was slowly leaked into the fluorescence chamber through a Granville–Phillips leak. The total pressure in the fluorescence chamber was monitored using a MKS baratron capacitance manometer. The residual leak rate into the fluorescence chamber was 1.2×10^{-6} Torr ℓ/s and it could be pumped to an ultimate pressure of less than 10^{-5} Torr.

Our primary interest in these experiments was to determine the effects of vibrational excitation on the rate constants for CN reactions, thus, it is important that the other degrees of freedom are in thermal equilibrium. Collisions of CN radicals[12] with a buffer gas should result in rapid rotational equilibration. To insure that rotational equilibration occurs in all of the experiments, a laser excitation spectra was run at the shortest delay time and lowest total pressure used in a series of experimental runs. A typical example of such a spectra is shown in Fig. 2 where it is clear that the CN radical is rotationally relaxed.

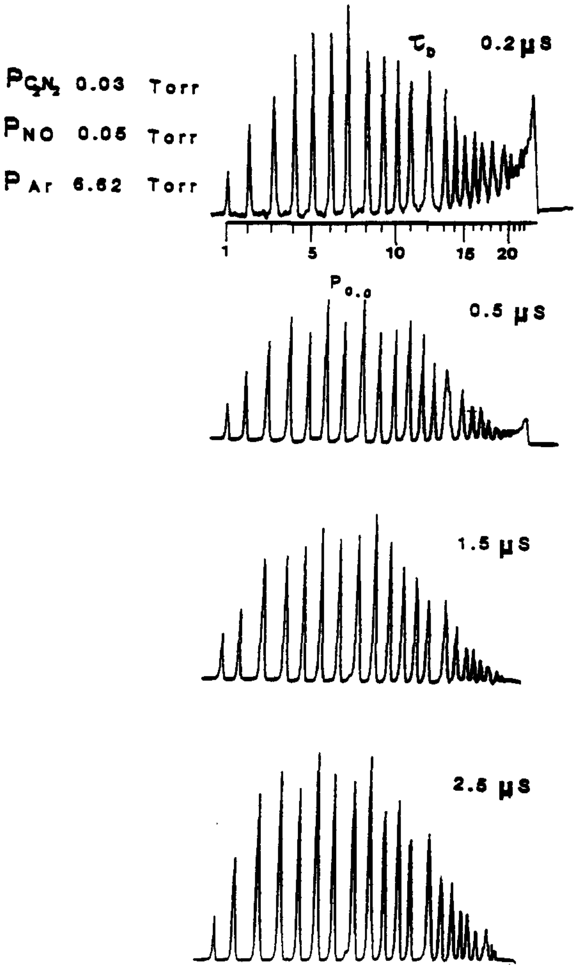


FIG. 2. The rotational relaxation of CN($v''=0$) radical observed from the $P_{0,0}$ branch of $B\,^2\Sigma$–$X\,^2\Sigma$.

Pseudo-first order decay constants were obtained by determining the intensity of a given rotational line as a function of delay time between the ArF and probe lasers. The dye laser was tuned to the wavelength of a rotational line, usually the $P_{0,0}(8)$ line for CN ($v''=0$) and the $R_{1,1}(8)$ for CN($v''=1$). The intensities of these rotational lines which are proportional to the concentration of a particular vibrational level were recorded for a minimum of 300 laser shots on a strip chart recorder. A decay curve was developed by manually averaging these intensities and combining them with the appropriate delay times that are determined on a Tektronix 7603 oscilloscope. A typical plot of the decay curves that were obtained are shown in Fig. 3. The slope of this plot is described by the following equation:

$$\text{Slope} = 1/\tau = k_{C_2N_2}[C_2N_2] + k_R[R] + k_D\,. \qquad (1)$$

In this equation, k_R is the rate constant for the reaction of CN radicals in a particular vibrational level with the particular reactant, k_D is a diffusion term, and $k_{C_2N_2}$ is the rate for the particular vibrational level with C_2N_2. By plotting the slope vs the pressure of the reactant gas, one should obtain a

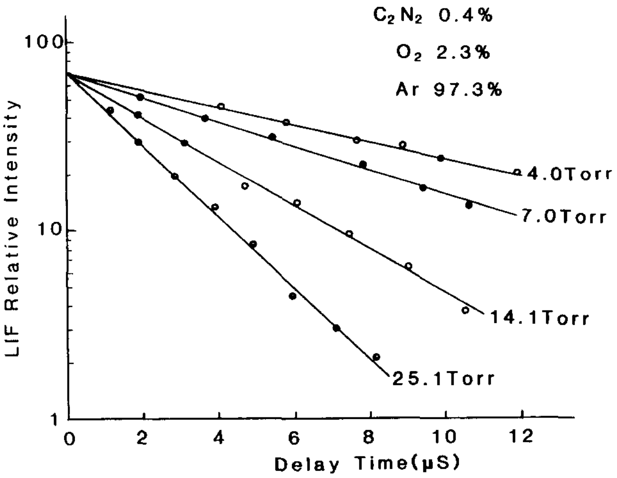


FIG. 3. Typical semilogarithmic decay plots for CN($v''=0$) in O_2.

straight line whose slope is the bimolecular rate constant k_R. The intercept is the sum of the rate of diffusion out of the observation zone and the residual reaction rate with the C_2N_2 molecule.

RESULTS AND DISCUSSION

Argon

Argon was the major component of all the reaction mixtures, because it is not very effective in vibrationally quenching the $v'' = 1$ level of CN. Our measurements of this rate constant indicates that it is below 10^{-16} cm^3/s. This low quenching rate is to be expected since the only mode for vibrational relaxation is via V-T transfer. This type of transfer has also been observed to be slow for quenching of CO by inert gases.[17] The vibrational frequency of CN is only 100 cm^{-1} smaller than that of carbon monoxide, therefore, the quenching rate via V-T transfer by argon for both molecules should be similar. Yardley[17] has reported that the probability for this type of transfer for CO is 10^{-6} which is in agreement with our observations for CN.

Nitrogen, carbon monoxide, cyanogen, and hydrogen cyanide

The k_R that can be measured using Eq. (1) is a composite rate constant for vibrationally excited CN radicals. It is the sum of the rate constants for quenching and chemical reactions with the reactant R. In general, it is difficult to separate the effects of quenching from chemical reaction. Arguments are often presented, based upon the energy gap law, which suggest that quenching is slow unless the reactant has a vibrational frequency close to that of the excited species under investigation.[17] It is then concluded that quenching is slow when this is not the case and that any enhancement that is observed in the rate constant is due to the effect of vibrational energy on the rate constant. We will use a similar argument but in our case when the $v'' = 0$ level reacts with the reactant it's rate of reaction will be subtracted from the observed decay rate of the $v'' = 1$ level. The quenching rate of the reactant is then compared with what one would expect from the energy gap law. If it agrees with this law, then we will conclude that no enhancement of the chemical reaction occurs with vibrational excitation.

The four reactant molecules N_2, CO, C_2N_2, and HCN that will be discussed in this section all have vibrational frequencies that are larger than the CN radical by 291,100,89, and 28 cm^{-1}, respectively.[18] The pseudo-first order rate constant plots for these four gases are shown in Fig. 4 which illustrates that they all exhibit the expected linear behavior. Neither nitrogen nor carbon monoxide react with the $v'' = 0$ level of CN so that no plot is shown for this vibrational level with these molecules. The figure does show that there is a small but measurable reaction between HCN and CN($v'' = 0$) radicals. The reaction rate of CN($v'' = 0$) + C_2N_2 has been reported by Paul *et al.* as 3.5×10^{-5} cm^{-3}/s at 301 K.[19]

The rate constant that can be derived from the pseudo-first order plots for nitrogen reacting with the $v'' = 1$ level are given in Table I. They were obtained by using a least squares program to fit the data points. The error that is

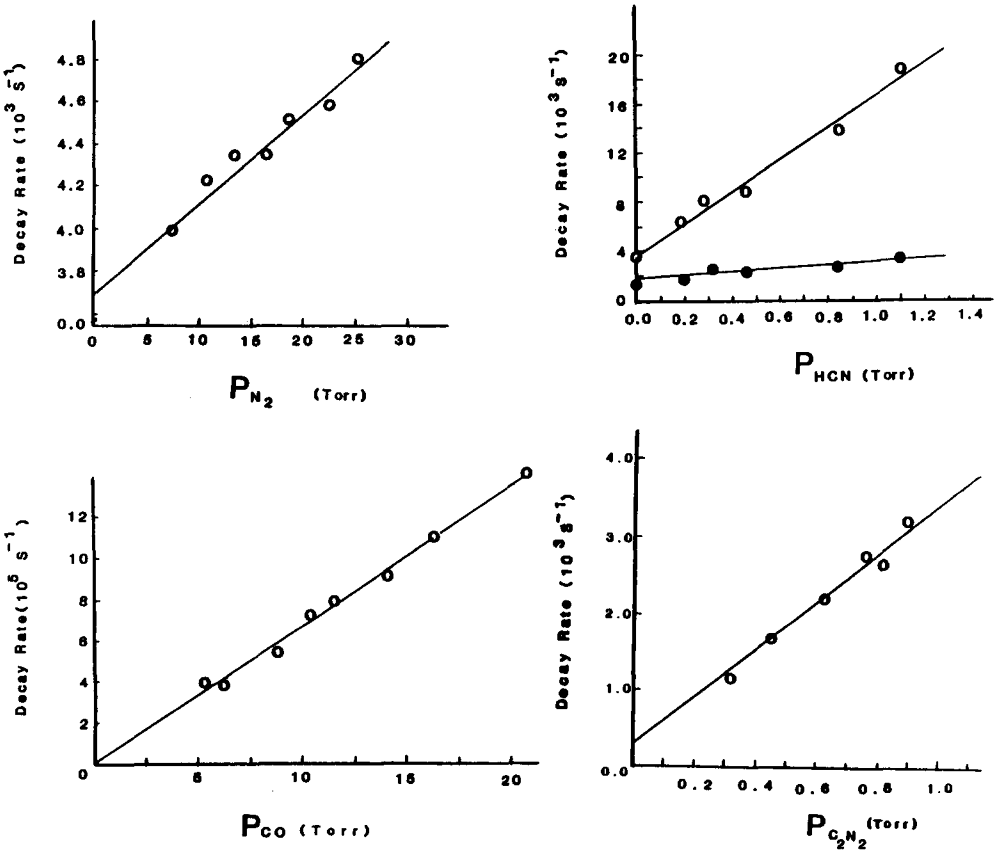


FIG. 4. A plot of first-order decay constants for CN(($v'' = 0$ and/or 1) radicals vs the pressure of N_2, CO, C_2N_2, and HCN. The open circles are for radicals in the $v'' = 1$ level while the filled circles are for the $v'' = 0$ level.

TABLE I. Second-order bimolecular rate constants for the reaction of $CN(v''=0,1) + M \xrightarrow{K}$ products.

		K (cm^3 $molecule^{-1}$ s^{-1})				
M	Vibrational level	This work (300 K)	Literature		Method	References
O_2	$v''=0$	$(2.0\pm0.1)\times10^{-11}$	$(1.12\pm0.03)\times10^{-11}$	(303 K)	Absorption	7
			1.1×10^{-11}	(298 K)	Absorption	8
			1.38×10^{-11}	(300 K)	LIF	11(b)
	$v''=1$	$(2.4\pm0.1)\times10^{-11}$	$(1.30\pm0.03)\times10^{-11}$	(303 K)	Absorption	7
			9×10^{-12}	(298 K)	Absorption	8
			1.25×10^{-11}	(300 K)	LIF	11(b)
CH_4	$v''=0$	$(5.6\pm0.3)\times10^{-13}$	$(5\pm3)\times10^{-13}$	(293 K)	Absorption	10
			$(7.4\pm0.2)\times10^{-13}$	(300 K)	Absorption	7
	$v''=1$	$(8.4\pm0.3)\times10^{-13}$	$(8.4\pm0.3)\times10^{-13a}$	(300 K)	Absorption	7
			$(1.12\pm0.3)\times10^{-12}$	(293 K)	Absorption	10
CO_2	$v''=0$	$(2.3\pm0.4)\times10^{-14}$	$(6.2\pm0.7)\times10^{-12}$	(1830–2400 K)	Flame	9
	$v''=1$	$(4.0\pm0.4)\times10^{-14}$				
H_2	$v''=0$	$(1.6\pm0.3)\times10^{-14}$	$(1.4\pm0.5)\times10^{-14}$	(300 K)	Absorption	10
	$v''=1$	$(3.0\pm0.4)\times10^{-14}$	$(1.7\pm0.5)\times10^{-13}$	(297 K)	Absorption	10
N_2	$v''=0$	No reaction				
	$v''=1$	$(1.5\pm0.6)\times10^{-15}$				
CO	$v''=0$	No reaction				
	$v''=1$	$(1.3\pm0.4)\times10^{-12}$				
HCN	$v''=0$	$(1.8\pm0.6)\times10^{-14}$	$1.7(+1.7-0.9)\times10^{-11}$	(2720–3070 K)	Shock tube	24
	$v''=1$	$(4.0\pm0.5)\times10^{-13}$				
C_2N_2	$v''=0$		$(3.5\pm0.4)\times10^{-15}$	(301 K)	Absorption	19
	$v''=1$	$(1.1\pm0.1)\times10^{-13}$				

[a] $v''=4$.

quoted in this table corresponds to 1σ sd. The experimentally determined rate constant for the quenching of $CN(X\,^2\Sigma, v''=1)$ by N_2 is $1.5\pm0.6\times10^{-15}$ cm^3/s and using the principle of detailed balancing one can calculate a rate constant for the reverse reaction of 4.5×10^{-15} cm^3/s. The reverse reaction is exothermic and can be compared with other exothermic quenching reactions using SSH theory.[17] The results of this comparison is shown in Fig. 5 which shows that there is reasonable agreement between the predicted probability for quenching and the experimental results. This agreement between theory and experiment suggests that quenching occurs via an impulsive collision rather than any long lived complex formation.

The pseudo-first order rate constant for the quenching of CN by CO is much faster than the comparable rate constant for nitrogen. Despite the fact that the energy difference for the quenching reaction is only 100 cm^{-1} the results are at least an order of magnitude faster than theory would predict. The experimentally determined rate constant is $1.3\pm0.4\times10^{-12}$ cm^3/s for the quenching of CN $v''=1$ by CO, and detailed balancing leads to a rate constant for the quenching of CO $(v''=1)$ by CN of 2.1×10^{-12} cm^3/s. Figure 5 shows that SSH theory would predict that the rate constant of this reaction should be about an order of magnitude lower than the rate that was observed. Somehow the quenching rate is being enhanced over and above what would be expected due to the small energy difference for the reaction.

A clue to why this reaction rate constant is so much larger in this case may be found by comparing the CO–CN system with the NO–NO system.[20] In the latter case two vibrationally excited NO molecules pool their energy to produce one ground state NO and one NO molecule with two quanta of vibrational energy. The rate constant for this reaction is also enhanced by an order of magnitude. This enhancement is thought to be due to the formation of a $[(NO)_2]$ complex which increase the quenching rate constant.[21] As Fig. 5 shows the rate constant in the CN–CO system is enhanced by about the same amount as observed in the NO–NO system. We feel that this is evidence for the formation of a [CNCO] complex. That such a complex should be formed is not surprising because the CN radical has a high electron affinity so that it is often called a superhalogen. Chlorine atoms are known to form a ClCO complex[22] during the photolysis of Cl_2 in the presence of CO so that CN should also form a similar complex. Thus, we conclude that the vibrationally excited CN radical is quenched via complex formation, i.e.,

$$CN(v''=1)+CO(v''=0) \rightleftarrows NCCO^* \rightarrow CN(v''=0)+CO(v''=1)+\Delta E = -100\ cm^{-1}. \tag{2}$$

In addition, it is also possible that the enhanced vibrational relaxation in the CN–CO system could be due to a long-range attractive interaction. This type of interaction is important for near-resonant energy transfer.[23]

It is generally accepted[24] that CN reacts with HCN via

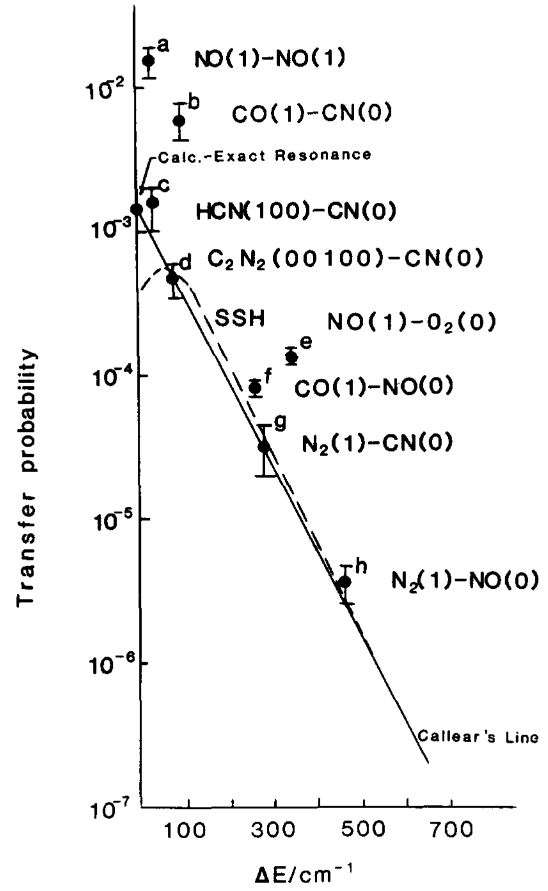


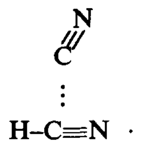
FIG. 5. The plot of V–V transfer probabilities on a logarithmic scale vs the energy gaps ΔE. a—From Ref. 20. b—Calculated from the present result for CN(1) + CO(0) according to the principle of detailed balance. c—Calculated from the present result for CN(1) + HCN(000) according to the principle of detailed balance. d—Calculated from the present result for CN(1) + C_2N_2 (00000) according to the principle of detailed balance. e—From R. P. Fernando and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2 77, 459 (1981). f—From Ref. 20. g—Calculated from the present result for CN(1) + N_2(0) according to the principle of detailed balance. h—From Ref. 32. The transfer probability $P = k/k_{\rm kin}$, where k is the rate constant in s^{-1} Torr^{-1}, the collision rate $k_{\rm kin} = 4.32\times 10^7 d_{AB}^2 T^{-1/2} \mu^{-1/2}$ s^{-1} Torr^{-1}, $d_{AB} = 1/2(d_A + d_B)$ in Å, μ is the reduced mass in amu. Hard sphere collision diameters used in calculation are the following: NO:3.5; CO:3.6; C_2N_2:4.4; O_2:3.4; and N_2:3.7 in Å taken from Ref. 33. 3.5 and 3.8 Å were used for CN and HCN, respectively. The calculations of exact resonant point and SSH line were taken from Ref. 17, p. 140.

the similar reaction depicted as follows:

$$CN(v''=0) + HCN \rightarrow C_2N_2 + H,$$
$$\Delta H = -8 \text{ kcal/mol.} \quad (3)$$

Reaction (3) has been studied in a shock tube and the rate constant has been reported to be 1.7×10^{-11} cm³/s.[24] Combining this rate constant with the rate constant reported in Table I, which was measured at room temperature, one can estimate that the activation energy for this reaction is approximately 3.8 kcal/mol. This is a reasonable value for an activation energy of an exothermic abstraction reaction.[25]

The measurement rate constant for reaction (3) of 1.8×10^{-14} cm³/s at 300 K along with the above activation energy suggests that the preexponential factor for this reaction is about 1×10^{-11} cm³/s. A large preexponential factor for an abstraction reaction requires a nonlinear activated complex. This is entirely reasonable because it would suggest that the CN radical attacks the carbon atom yielding a transition state of the type



Using simple transition state theory,[26] and allowing free rotation of HCN about the C–C bond along with a $r_{C\text{-}C}$ of 2 Å one can estimate a preexponential factor of 5×10^{-12} cm³/s for this type of nonlinear complex. This is in surprisingly good agreement with the experimental value considering the crude nature of the calculation.

Both Fig. 4 and Table I show that vibrationally excited CN radicals react much faster with HCN than those in the ground vibrational state. An explanation of this behavior is a quenching reaction for vibrationally excited CN of the following type:

$$CN(v''=1) + HCN(000) + CN(v''=0)$$
$$+ HCN(100) + \Delta E = -28 \text{ cm}^{-1}. \quad (4)$$

The principle of detailed balancing can be used to calculate the rate constant for the reverse reaction using the measured rate constant reported in Table I. This quenching probability is compared with other exothermic quenching probabilities in Fig. 5, which show that in all likelihood the observed increase in the rate of $v''=1$ CN radicals is almost entirely due to impulsive V–V transfer.

The rate constant that was measured for vibrational quenching of CN($v''=1$) radicals by N_2 molecules has been used with the principle of detailed balancing to calculate the rate of the reverse reaction. This rate is compared with similar type of quenching reactions in Fig. 5. The results indicate that the energy gap law fits all of the results including the quenching reaction of HCN(100) + CN(0). At first the latter result was surprising, but upon reflection, it seems reasonable if one considers that the hydrogen atom acts as a spectator during the quenching process. Since the ν_1 vibration of HCN is similar to that in N_2, this agreement is readily explained.[27]

Carbon dioxide

The plot in Fig. 6 shows that the CN ($v''=0$) radical reacts with CO_2 even at room temperature. The most plausible exothermic reaction that can be used to explain these results is depicted in Eq. (5).

$$CN(v''=0) + CO_2 \rightarrow NCO + CO,$$
$$\Delta H = -3.7 \text{ kcal/mol.} \quad (5)$$

This reaction is mildly exothermic at room temperature and leads to a radical product NCO, which may be important in combustion. The rate constant for this reaction that can be obtained from the plots is $2.3 \pm 0.4\times 10^{-14}$ cm³/s. This can be compared with a result of $6.2 \pm 0.7\times 10^{-12}$ cm³/s that was obtained in a flame with a temperature that was reported to be between 1830 and 2400 K.[9] Using these two results, a crude but reasonable estimate of 3 kcal/mol is obtained for

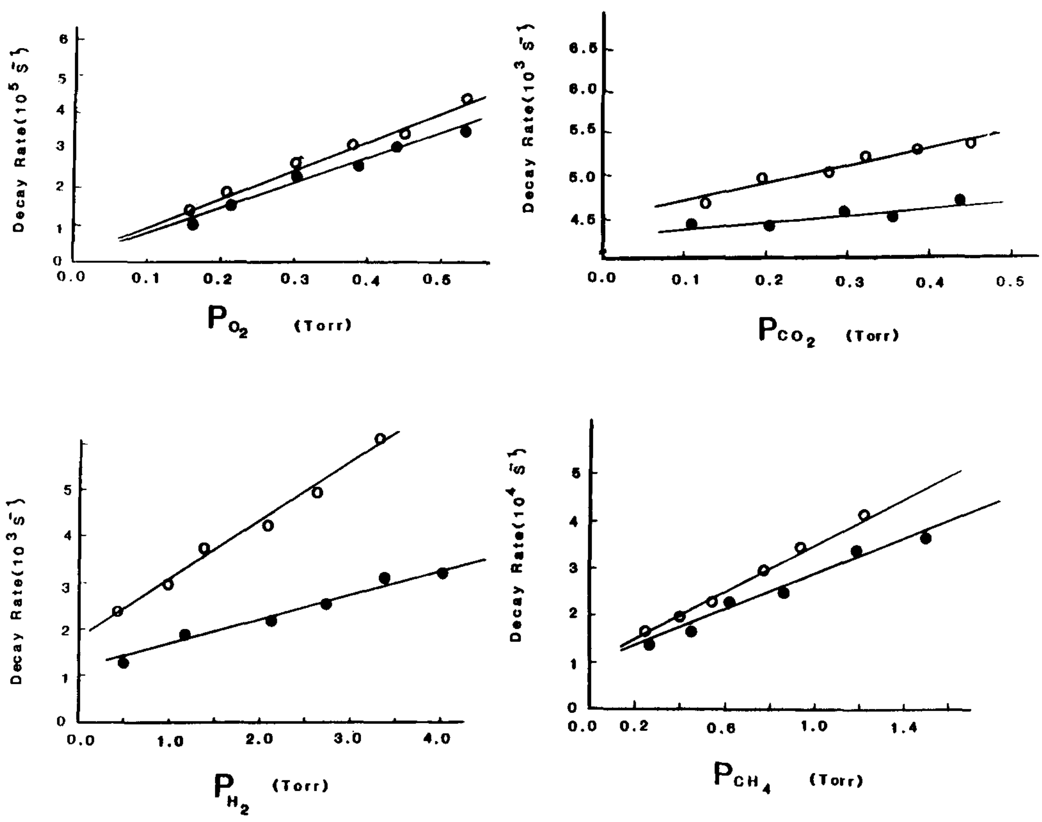


FIG. 6. A plot of first-order decay constants for CN($v'' = 0,1$) radicals vs the pressures of CO_2, O_2, H_2, and CH_4. The open circles are for radicals in the $v'' = 1$ level while the filled circles are for the $v'' = 0$ level.

the activation energy for this reaction.

Carbon dioxide can quench vibrationally excited CN($v'' = 1$) level radicals via the following reaction:

$$\mathrm{CN}(v''=1) + \mathrm{CO_2}(000) \rightarrow \mathrm{CN}(v''=0) + \mathrm{CO_2}(001) + \Delta E = -280\ \mathrm{cm}^{-1}. \quad (6)$$

This reaction is endothermic by little more than the mean thermal energy at 300 K so that most species might be expected to have enough energy to undergo this reaction. The rate constant derived from the data in Fig. 6 is $4.0\times \pm 0.4\times 10^{-14}$ cm^3/s, which is a factor of 2 greater than the rate constant for CN($v'' = 0$) and could be the result of significant vibrational enhancement of the rate constant. A comparison in Fig. 7 of the CN($v'' = 1$) quenching probability, calculated by assuming that the reaction rate was the same as the $v'' = 0$ level, with the quenching probability of vibrationally excited CO^{20} and NO^{20} by carbon dioxide indicates that this is not the case. The observed probability (point c) is very close to the probability that one would predict on the basis of the energy gap law using both of these rate constants as guides.

Oxygen, hydrogen, and methane

There have been previous studies of the reactions of all of these molecules with both $v'' = 0$ and the $v'' = 1$ levels of CN.[7,8,10] The present results given in Fig. 6 show that the $v'' = 0$ level of CN reacts at an appreciable rate with each of these molecules and that a significant increase rate is also observed with the $v'' = 1$ level.

From the data given in Fig. 6, one can derive the rate constants for the overall reaction of both $v'' = 0$ and $v'' = 1$ CN radicals with O_2, CH_4, and H_2. The results are given in Table I along with previous measurements reported in the literature. Given the large differences in the method for obtaining these rate constants, the agreement is quite good. Where there are discrepancies in the results, they are gener-

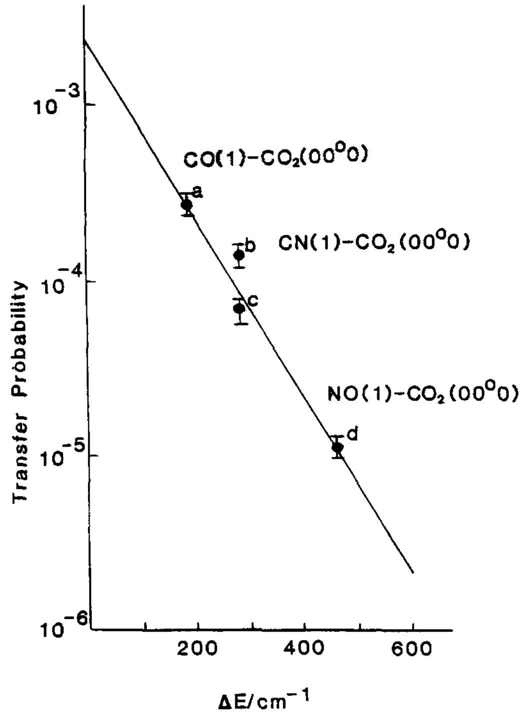


FIG. 7. The plot of V–V transfer probabilities on a logarithmic scale vs the energy gaps ΔE. a—From Ref. 20. b—The total decay rate of CN(1) by CO_2 obtained in the study. c—The quenching rate of CN(1) (see the text). d—From Ref. 20. The hard sphere collision diameter for CO_2 used in calculation is 4.0 Å.

ally in the direction one would expect if there were secondary reactions that produced the radicals. This is not the case, however, for the CN($v''=1$) reaction with H_2. The literature value is almost a factor of 6 higher than the present measurements. It is even more disturbing because our results agree with the author's measurement of the rate constant for CN radicals in the $v''=0$ level with hydrogen. We do, however, believe that the present measurements are to be preferred because our experimental system is simpler and is therefore less prone to errors.

The rate of reaction of oxygen with CN is very fast, occurring in one in every 15 collisions. The products are known to be NCO and O atoms and the reaction is exothermic by 4.4 ± 0.3 kcal/mol. Because the reaction is so fast at room temperature, the activation energy must be low. Assuming that the only hindrance to the reaction is the activation energy, one can estimate an activation energy of the order of 1.4 kcal/mol. This is in agreement with a recent measurement by Albers *et al.*[28] of 1.0 ± 0.3 kcal/mol and suggests that the steric factor is ~ 1.

It might be thought that vibrational energy would not play an important role in an exothermic reaction with a low energy barrier but the present results indicate that there is a measurable increase in the rate constant with increasing vibrational energy. To explain the observed increase in rate constants it will first be assumed that vibrational energy is not responsible for this enhancement. All of the increase in the $v''=1$ rate constant would then be due to vibrational quenching by O_2. Using this assumption along with the data in Table I, one would estimate a quenching rate constant of approximately 4×10^{-12} cm^3/s. This is three orders of magnitude greater than one would predict on the basis of the energy gap law. So that one can conclude that simple V–V transfer does not explain the observed results.

The factor of thousand could be the result of the formation of an intermediate complex, e.g., CNOO, during the quenching process. A similar intermediate complex ClOO is known[29] which in light of the halogen-like character of CN means that it may also occur here. The formation of a [CNOO] complex would then increase the quenching probability. The observed quenching probability should lie in Fig. 5 on the same energy gap straight line with the other quenching reactions which involve complex formation. In fact, the quenching rate is still two orders of magnitude higher than one would predict on the basis of such an analysis. Thus, we are forced to conclude that, despite the low activation energy for the process, vibrational energy does appear to enhance the chemical reaction. Though the results indicate that there is some enhancement, the vibrational energy does not completely negate the presence of the barrier despite the fact that it is four to six times greater than the barrier height. In terms of the dynamics of the motion on the potential energy surface this suggests that the reaction has an early barrier so that the vibrational energy is not as effective as translational energy in enhancing the reaction.

The rate constant derived from the data in Fig. 6 and reported in Table I for the reaction of CN($v''=1$) radicals with H_2 is about a factor of 2 higher than it is for those in the $v''=0$ level. It was pointed out earlier that the rate for the $v''=1$ level does not agree with the value reported in the literature even though the $v''=0$ level does. The lower rate constant in the present study cannot be accounted for by cascade processes from excited electronic or vibrational levels since earlier work[16] has shown that at 193 nm the single photon photolysis yields only X state radicals in the $v''=0$ and 1 levels. The rate constant that has been measured in the present work must represent an upper limit for the observed rate constant.

One can estimate the rate constant for vibrational quenching of CN($v''=1$) by hydrogen from the overall rate constant by assuming that the rate of chemical reaction is the same as it is for the $v''=0$ level. The quenching rate constant would then be 1.4×10^{-14} cm^3/s. This is much too high for a quenching reaction with an energy gap of 2332 cm^{-1} between the vibrational levels of hydrogen and CN.

Vibrational to rotational energy transfer by collisions between *para* hydrogen and CN($v''=1$) is also an unlikely explanation for the rapid quenching that is observed since it requires a large change in angular momentum of p-H_2 of the order of $\Delta J = 4$. Millikan *et al.*[30] obtained a quenching rate of a similar molecule, CO($v''=1$), by p-H_2 of only 6.3×10^{-16} cm^3/s and 3.8×10^{-16} cm^3/s by n-H_2. Both are almost two orders of magnitude lower than 1.4×10^{-14} cm^3/s which was calculated in present study from the experimental data using the previously quoted assumption. Thus we are forced to conclude that vibrational energy does enhance the rate of this chemical reaction.

Despite the fact that vibrational energy increases the rate of this reaction, it does not do it as efficiently as translational energy. It has been reported that the abstraction reactions given below:

$$\mathrm{CN}(v''=0) + H_2 \rightarrow \mathrm{HCN} + \mathrm{H}, \quad \Delta H = -16\ \mathrm{kcal/mol} \tag{7}$$

has an activation energy of more than 5.3 kcal/mol[10] so that if vibrational energy was equally as effective as translational energy then the rate constant would have been about 3×10^{-11} cm^3/s. This, is in agreement with *ab initio* calculations,[31] that suggests that reaction (7) has an early barrier and would mean that vibrational energy was not as effective as translational energy in surmounting this barrier.

The plot of the decay rates vs methane pressure is given in Fig. 6. The linearity of the plot shows that this reaction obeys second order kinetics. The following reactions can occur in our system between methane and CN radicals in the $v''=0$ and 1 levels.

$$\mathrm{CN}(v''=1) + \mathrm{CH}_4(000) \rightarrow \mathrm{CN}(v''=0) + \mathrm{CH}_4(0100) + \Delta E = 535\ \mathrm{cm}^{-1}, \tag{8}$$

$$\rightarrow \mathrm{CN}(v''=0) + \mathrm{CH}_4(0001) + \Delta E = 763\ \mathrm{cm}^{-1}, \tag{9}$$

$$\rightarrow \mathrm{HCN} + \mathrm{CH}_3, \quad \Delta H = -22.5\ \mathrm{kcal/mol}, \tag{10}$$

$$\mathrm{CN}(v''=0) + \mathrm{CH}_4 \rightarrow \mathrm{HCN} + \mathrm{CH}_3, \quad \Delta H = -16.5\ \mathrm{kcal/mol}. \tag{11}$$

If the chemical reaction rates for CN($v''=0$) and CN($v''=1$) with CH_4 are comparable, then the quenching rate for CN($v''=1$) is $2.8 \pm 0.3 \times 10^{-13}$ cm^3/s. This is still higher than the value $1.9 \pm 0.2 \times 10^{-13}$ cm^3/s obtained in the study of the quenching of NO ($v''=1$) by methane.[32] The ground states for both NO and CN are doublet so that one should not expect that the electronic configuration would substantially alter this quenching probability. The energy gap for NO–CH_4 is 165 cm^{-1} smaller than it is for CN–CH_4 and the energy gap law would suggest that the quenching rate of CN($v''=1$) in CH_4 should be even slower than it is in the NO–CH_4 system. We, therefore, conclude that vibrational energy does enhance the rate of chemical reaction of CN($v''=1$) with methane.

CONCLUSION

The laser induced fluorescence technique as been combined with excimer laser photolysis to determine the rate constants for the reaction of CN radicals in the $v''=1$ and/or $v''=0$ levels with H_2, O_2, CO, CO_2, N_2, HCN, C_2N_2, and CH_4. The well-defined nature of the system permits accurate measurements of these rate constants. Where the rate constants have been measured before there is reasonable agreement between the results of this study and those previous measurements. In most cases the disagreement between the present results and previous measurements can be accounted for on the basis of cascade processes being present in the earlier measurements.

The effects of quenching have been separated from chemical reaction by careful application of the energy gap law. Purely impulsive quenching, i.e., no complex formation, has been identified in the case of the reactions N_2, HCN, C_2N_2, and CO_2 with CN($v''=1$). Whereas, complex formation has been found to be important in the quenching by CO. Vibrational enhancement occurs in the reactions of CN with O_2, H_2, and CH_4.

Analysis of the magnitude of the rate constant for the reaction of CN with HCN suggest that this reaction proceeds through a nonlinear activated complex with free rotation about the C–C bond.

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