J. Chem. Soc., Faraday Trans. 2, 1989, **85**(7), 915–923

Kinetics of CN($v = 0$) and CN($v = 1$) with HCL, HBr and HI between 295 and 764 K

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Time-resolved laser-induced fluorescence (LIF) measurements have been carried out on the kinetics of CN($v = 0$) and CN($v = 1$) radicals with HCl, HBr and HI at temperatures between 295 and 764 K. The radicals were generated by pulsed laser photolysis of NCNO at 532 nm, and the decays of concentration were monitored using a dye laser tuned to lines in either the (0, 0) or (0, 1) band of the CN(B $^2\Sigma^+$–X $^2\Sigma^+$) system. The rate constants for reaction of CN($v = 0$) at 295 K are: (k/cm^3 molecule^{-1} s^{-1}) = $(5.9 \pm 0.3) \times 10^{-15}$ for HCl; $(9.1 \pm 0.6) \times 10^{-13}$ for HBr; and $(7.0 \pm 0.4) \times 10^{-11}$ for HI. The temperature dependences of the three reaction rates are also markedly different: they yield approximate activation energies (the Arrhenius plots show some curvature) of 18.0 ± 0.8, 7.7 ± 0.7 and −0.3 ± 0.3 kJ mol^{-1}, respectively. The rate constants for removal (reaction *plus* relaxation) of CN($v = 1$) only exceeds that for reaction of CN($v = 0$) in the case of HCl in the lower part of the temperature range. This is attributed to the occurrence of vibrational relaxation. The lack of any significant enhancement of the reaction rates on vibrational excitation of CN is consistent with the predictions of vibrationally adiabatic transition-state theory.

Kinetic and dynamical studies of reactions of the CN radical are currently being performed by a number of research groups. In part, this activity reflects the importance of these reactions in a number of environments, especially in combustion systems,[1] but it is also a consequence of the ease with which the CN radical can be observed in small concentrations using laser-induced fluorescence (LIF). As a result, direct and accurate rate measurements can be made in experiments which combine time-resolved LIF detection with generation of CN radicals by pulsed laser photolysis of some suitable, molecular precursor. The photolysis may produce CN in vibrationally excited levels, as well as in ($v = 0$). This can be a source of extra information, but care must be taken to ensure that measurements on the kinetics of CN in any particular vibrational level are not affected by relaxation into or through that level from higher states.

The present paper is the latest in a series from our laboratory[2-6] in which we measure and compare the kinetics of CN($v = 0$) and CN($v = 1$) in collision with various, potentially reactive partners. CN radicals are generated by photolysis of NCNO using the frequency-doubled output of a Nd:YAG laser ($\lambda = 532$ nm) and relative concentrations of CN($v = 0$) and CN($v = 1$) are observed at variable delays after the photolysis pulse, by measuring the LIF signals which are generated by tuning a pulsed dye laser to a line in the (0, 0) or (0, 1) band of the B $^2\Sigma^+$–X $^2\Sigma^+$ system of CN. The photolysis of NCNO at 532 nm produces only a small fraction of the CN radicals in vibrational levels above $v = 0$. Consequently, the kinetic decays derived for CN($v = 0$) are not significantly affected by any relaxation of molecules from higher levels.

Here, we report the first kinetic studies of the reactions of CN with the hydrogen halides at temperatures other than room temperature. The three reactions

$$\mathrm{CN + HCl \rightarrow HCN + Cl}; \qquad \Delta H^\circ_{298} = -86.4 \text{ kJ mol}^{-1}$$

$$\mathrm{CN + HBr \rightarrow HCN + Br}; \qquad \Delta H^\circ_{298} = -151.8 \text{ kJ mol}^{-1}$$

$$\mathrm{CN + HI \rightarrow HCN + I}; \qquad \Delta H^\circ_{298} = -219.6 \text{ kJ mol}^{-1}$$

provide a sequence of reactions of increasing exothermicity. It is interesting to compare their rates and temperature dependences both with one another and also with the data for related reactions of hydrogen halides with halogen atoms and hydroxyl radicals. *Ab initio* data on the potential-energy surface for the CN + HCl system are available,[7] and we intend to study how the rate of this reaction is enhanced by vibrational excitation of the HCl reagent. The only previous kinetic examination of these reactions, and of the relative rates for CN($v = 0$) and CN($v = 1$), were carried out at room temperature only by de Juan *et al.*[2,3] The room-temperature rate constant for the endothermic, fourth member of the series, CN + HF → HCN + F, $\Delta H^\circ_{298} = 54.3$ kJ mol^{-1}, can be evaluated by applying detailed balance to the rate constant measured by Frost *et al.*[8] for the reverse exothermic reaction.

Experimental

Our apparatus and the experimental and analytical procedures used in the measurements have been described in detail elsewhere.[4] Briefly, reaction was initiated by photolysing NCNO in a gas mixture flowing through a cylindrical tube enclosed in a high-temperature oven. The photolysis source was a frequency-doubled Nd:YAG laser operated at 10 Hz. Decays in the concentration of CN($v = 0$) or CN($v = 1$) were observed by exciting LIF using a home-built dye laser pumped by an N_2 laser. 'Off-resonance' detection was used: the probe laser being tuned to the B-X(0, 0) band to observe CN($v = 0$) *via* (0, 1) fluorescence or to the (0, 1) band to observe CN($v = 1$) by (0, 0) fluorescence, appropriate filters being employed to isolate the emission bands. The time delays between the photolysis and probe laser pulses were controlled by a microcomputer, which also accumulated the LIF signals.

Total pressures in the reaction cell were measured with a calibrated capacitance manometer (MKS Baratron, model 222B) and gas flows were governed by mass-flow controllers (ASM and Hi-Tec). Temperatures were measured at the surface of the flow tube and corrected for the observed difference between this temperature and that in the centre of the flowing gas.[4] The corrected temperatures are estimated to be accurate to ±3 K.

NCNO was prepared as before[2] and the argon diluent was used directly from a cylinder (BOC zero grade, $O_2 < 1$ ppm, 99.998% pure). The rapid rate of reaction of CN radicals with O_2[4,6] and with some hydrocarbons[9,10] means that particular care must be taken over the purity of any gases, such as HCl, which do not themselves react rapidly with CN. Consequently electronic grade HCl (BDH) was used in our experiments. It has a nominal purity of 99.99% with a typical analysis showing only 6 ppm of O_2/Ar and 5 ppm of total hydrocarbons. This gas was used after several freeze-pump-thaw cycles. HBr (Cambrian, CP grade, 99.8%) was purified by distillation through an ethanol-acetone slush at *ca.* −100 °C to remove Br_2, and was then subjected to several freeze-pump-thaw cycles. HI was prepared by the action of excess tetrahydronaphthalene on I_2,[11] using a procedure that has been described elsewhere.[2,12] After several freeze-pump-thaw cycles, a suitable solution (4.3%) of HI in high-purity argon (BDH, research grade, 99.9995%) was prepared and used before substantial decomposition could occur.

Results

The first-order rate constants that have been measured in the present work are in the range *ca.* 4×10^2–4×10^4 s^{-1}. The ultimate time resolution of our experiments is limited not by the width of the photolysis and probe-laser pulses but by the timing equipment.

Table 1. Summary of the experiments and the rate constants derived for the kinetics of CN($v=0$) and CN($v=1$) with HCl[a]

T/K	no. of measurements	[HCl]/10^{16} molecule cm^{-3}	k/10^{-14} cm^3 molecule^{-1} s^{-1}
		CN($v=0$)	
295*	7	4.5-22.8	
295.5*	8	3.1-22.7	0.59 ± 0.08[b]
364*	8	3.7-18.4	2.27 ± 0.36
444	8	1.2-9.1	5.30 ± 0.48
566	7	1.0-6.1	17.1 ± 1.1
761	7	0.4-2.5	51.7 ± 5.4
		CN($v=1$)	
297	7	1.8-11.6	2.7 ± 0.4
298.3	7	1.8-13.5	
364	8	1.5-11.0	3.5 ± 0.7
444	8	1.2-9.0	7.9 ± 0.7
444	7	1.2-6.9	
566	8	1.0-6.1	20.6 ± 2.0
566	7	1.0-4.5	
761	8	0.4-2.5	48.0 ± 5.0

[a] Experiments were performed at 30 Torr total pressure, except those runs marked with an asterisk which were carried out at 50 Torr total pressure; *b* Errors equivalent to two standard deviations and including an estimate of systematic error (see text).

In practice, in the present series of investigations, an upper limit to the decay constant was set, at least for HCl and HBr, by the need to limit the amount of reagent gas added in order to avoid considerable quenching of the CN fluorescence. Nevertheless, the combination of the time resolution and the high detection sensitivity for CN[4] was sufficient to ensure negligible removal of the radicals by side and secondary reactions.

Some reduction in the LIF signals was observed in the experiments with HCl and HBr and could be attributed to efficient fluorescence quenching by these gases. Despite this effect, measurements of rate constants were relatively straightforward even with HCl, although particular care was needed to obtain reliable results for the slowest rates, *i.e.* those at room temperature. Addition of HI, especially at the higher temperatures, also brought about appreciable reduction in the LIF signals. In view of the short radiative lifetime[13] of CN B $^2\Sigma^+$ and the small concentrations of HI involved, it seems unlikely that this was caused by fluorescence quenching. A more likely explanation is the occurrence of some dark, possibly surface-catalysed, reaction between NCNO and HI. As the initial concentration of NCNO is much less than that of HI, this would reduce the concentration of CN produced but not significantly change its decay rate, since the HI concentration would remain virtually unaltered.

To obtain second-order rate constants (k) for removal of CN($v=0$) or CN($v=1$) by a particular reagent, R, a series of experiments was performed with the concentration [R] being varied systematically whilst the temperature and total pressure were kept constant. Tables 1-3 summarise the conditions used in these experiments on the removal of CN($v=0$) and CN($v=1$) by HCl, HBr and HI. Values of k were determined from the gradients of plots of the individual, first-order decay constants (k_{1st}) against [R]. Examples of such plots for CN($v=0$) and CN($v=1$) with R = HBr are given in fig. 1. The standard deviations in the values of k_{1st} were provided by the non-linear least-squares program that was used to fit the exponential decays of LIF signals in each experiment. In addition, we estimated the possible random and systematic errors in [R] to be 1.5%

Table 2. Summary of the experiments and the rate constants derived for the kinetics of CN($v = 0$) and CN($v = 1$) with HBr[a]

T/K	no. of measurements	[HBr]/10^{15} molecule cm^{-3}	$k/10^{-12}$ cm^3 molecule^{-1} s^{-1}
		CN($v = 0$)	
296	8	2.3-14.3	0.92 ± 0.06^b
364	8	1.9-11.6	1.43 ± 0.14
444	7	1.6-9.5	2.17 ± 0.18
566	8	1.2-7.4	3.75 ± 0.34
764	8	0.9-5.5	7.0 ± 0.7
		(CN($v = 1$)	
295.5	8	2.2-17.8	0.88 ± 0.08
364	8	1.9-11.5	1.44 ± 0.12
444	7	1.6-9.5	2.39 ± 0.26
566	7	2.2-14.3	4.16 ± 0.34
764	8	1.6-10.6	6.8 ± 0.6

[a] All experiments were performed at 30 Torr total pressure. [b] Errors equivalent to two standard deviations and including an estimate of systematic error (see text).

Table 3. Summary of the experiments and the rate constants derived for the kinetics of CN($v = 0$) and CN($v = 1$) with HI

T/K	no. of measurements	P/Torr	range of [HI] /10^{13} molecule cm^{-3}	$k/10^{-11}$ cm^3 molecule^{-1} s^{-1}
			CN($v = 0$)	
295.5	8	10	4.4-28.0	7.0 ± 0.4^a
359	7	10	6.7-23.0	7.2 ± 0.9
437	8	30	4.9-30.9	6.3 ± 0.7
437	7	10	5.5-22.0	6.5 ± 0.6
560	7	30	3.8-24.0	6.1 ± 0.7
560	7	10	6.1-17.1	7.1 ± 1.4
761	8	30	2.8-17.7	6.8 ± 1.2
761	7	10	4.5-12.6	7.6 ± 1.6
			CN($v = 1$)	
295.5	8	10	4.4-27.8	8.0 ± 0.8
359	8	10	6.7-26.6	7.6 ± 0.7
437	8	10	5.5-22.0	7.4 ± 1.0
560	7	15	6.5-25.8	7.7 ± 1.1
761	8	15	4.8-19.0	7.5 ± 0.5

[a] Errors equivalent to two standard deviations and including an estimate of systematic error (see text).

each. Allowance for the random error was made in computing the gradient of k_{1st} *vs.* [R] and its standard deviation. A further 1.5% was added to allow for systematic error and the result was then doubled to yield the estimates of uncertainty in k, which are included in the last columns of tables 1-3.

For all the processes studied in the present work, the rate constants were found to be independent of total pressure. The dependence of several of the rate constants on temperature is displayed in the usual Arrhenius representation in fig. 2 and 3. The rate constants for removal of CN($v = 1$) by HBr and by HI are very similar to those for the

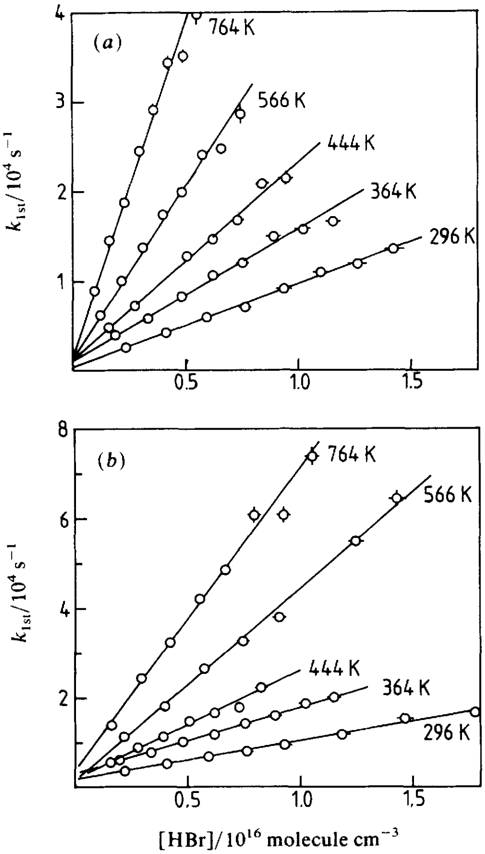

Fig. 1. First-order decay constants for (*a*) CN($v=0$) and (*b*) CN($v=1$) in the presence of HBr at different temperatures. Error limits are shown where they exceed the size of the symbols: those in the values of k_{1st} are derived from the non-linear least-squares fit to the exponential decays; those in the concentrations correspond to 0.03 [HBr] (see text).

reaction of CN($v=0$) with these gases and are not shown. Table 4 lists parameters derived from the normal Arrhenius equation:

$$k = A \exp(-E_{act}/RT).$$

The plots for CN($v=0$) with HCl and HBr show evidence of curvature. However, in contrast to the cases of CN($v=0$)+H_2, D_2,[5] we feel that the accuracy of our data is insufficient in these cases to justify its fitting to the extended Arrhenius equation:

$$k = A'(T/298)^n \exp(\theta/T).$$

Reasons for the strong curvature in the Arrhenius plot for CN($v=1$)+HCl are discussed below.

Discussion

The rate constants determined in the present work for the reasons of CN($v=0$) with HI and HBr at room temperature are in good agreement with the values obtained previously by de Juan *et al.*[2,3] They reported two different values for the rate constant

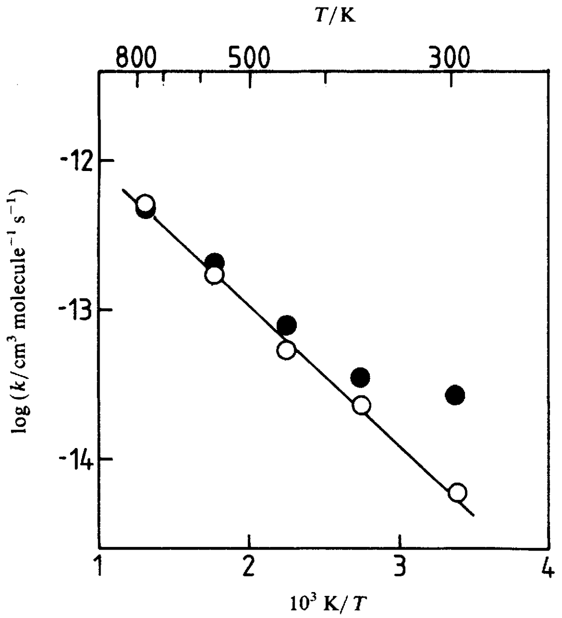

Fig. 2. Arrhenius plot of the rate constants for reaction of CN($v = 0$) (○) and removal (reaction plus relaxation) of CN($v = 1$) (●) by HCl.

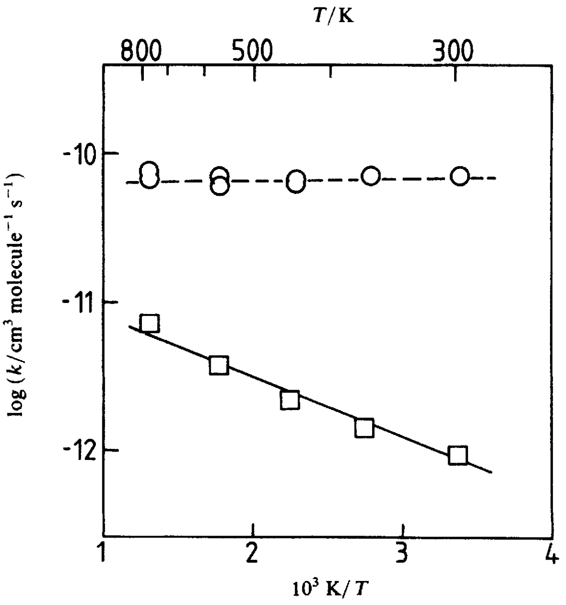

Fig. 3. Arrhenius plots for the reactions of CN($v = 0$) with HBr (□) and with HI (○).

Table 4. Activation energies and A factors for the kinetics of CN($v=0$) and CN($v=1$) with HCl, HBr and HI

	E_a/kJ mol^{-1}	$A/10^{-11}$ cm^3 molecule^{-1} s^{-1}
CN($v=0$)+HCl	18.0 ± 0.8^a	0.78 ± 0.17
CN($v=1$)+HCl	15.8 ± 0.4	0.58 ± 0.06
CN($v=0$)+HBr	7.7 ± 0.7	2.0 ± 0.4
CN($v=1$)+HBr	8.3 ± 0.4	2.4 ± 0.3
CN($v=0$)+HI	-0.3 ± 0.3	6.1 ± 0.6
CN($v=1$)+HI	-0.2 ± 0.1	7.2 ± 0.2

[a] Errors equivalent to $\pm1\sigma$ random error.

Table 5. Comparison of rate constants (k/cm^3 molecule^{-1} s^{-1}) at 295 K and activation energies ([E_{act}/R]/K) for reactions of radicals with H_2 and hydrogen halides

[D_0^X(H—X)/kJ mol^{-1}]: [D_0^Y(H—Y)/kJ mol^{-1}]	F (566.6)	CN (516)	OH (493.7)	Cl 427.8)
H_2	$2.8\,(-11)^{a,14}$	$2.5\,(-14)^5$	$6.7\,(-15)^{17}$	$1.6\,(-14)^{17}$
(432.1)	570	2070	2100	2300
HCl	$7.0\,(-12)^{15,16}$	$5.9\,(-15)^c$	$8.1\,(-13)^{18}$	$4.1\,(-15)^{19}$
(427.8)	curv.^{b}	2165	330	1300
HBr	$6.2\,(-11)^{15,16}$	$9.2\,(-13)^c$	$1.1\,(-11)^{18}$	$1.0\,(-11)^{20\text{-}22}$
(362.5)	curv.	930	0	450
HI	$5.6\,(-11)^{15,16}$	$7.0\,(-11)^c$	$1.3\,(-11)^{14}$	$1.6\,(-10)^{20\text{-}22}$
(294.7)	curv.	0	—	curv.

[a] Upper entry is the rate constant, $2.8\,(-11)\equiv2.8\times10^{-11}$, lower entry is [$E_{act}/R$]/K. [b] curv. indicates that the Arrhenius plot is markedly curved. [c] This work.

for reaction of CN($v=0$) with HCl at room temperature: $(6\pm4)\times10^{-15}$ and $(13.7\pm2.5)\times10^{-15}$ cm^3 molecule^{-1} s^{-1}. Our result is in better agreement with the earlier, less precise value.[2] Possibly, despite the care taken, the later measurements were affected by impurity in the HCl. The present work is the first to obtain data for these reactions over a range of temperatures.

Largely because of its high electron affinity (3.82 eV[23]), the CN radical is often referred to as a pseudo-halogen or super-halogen.[24] It is interesting, therefore, to compare rate data for its reactions to those for reactions of halogen atoms, especially F and Cl (for which the electron affinity, at 3.60 eV,[23] is very similar to that for CN) and also to data for reactions of OH, which might also be expected to behave like a halogen atom. Table 5 compares rate constants at room temperature and activation energies for the reactions of F, Cl, CN and OH with H_2 and the hydrogen halides. The same general trend is observed for the reactions of each radical: namely, similar rates of reaction with H_2 and HCl (which have very similar bond strengths) and then an increase in rate on passing to HBr and then to HI. However, the gradations in the rates as one passes down the sequence of reactions differ markedly for different reactions. In particular, the exothermic reactions of CN with HCl and HBr are much slower, and have much higher activation energies, than the corresponding reactions of F atoms (which are more exothermic) and of OH radicals (which are less exothermic).

The relatively slow rates of reaction of CN with HCl and HBr may be connected with the nautre of the dipole-dipole forces. In collisions between OH and a hydrogen halide, these forces will tend to orient the molecules favourably for reaction, that is

Table 6. Ratio of rate constants for removal of CN($v=1$) and CN($v=0$) by HCl, HBr and HI

T_{approx}/K	HCl	HBr	HI
296	4.5 ± 0.7[a]	0.96 ± 0.06	1.15 ± 0.26
364	1.53 ± 0.32	1.01 ± 0.09	1.06 ± 0.31
444	1.48 ± 0.13	1.10 ± 0.10	1.15 ± 0.35
566	1.20 ± 0.09	1.11 ± 0.09	1.22 ± 0.44
761	0.93 ± 0.10	0.97 ± 0.09	1.05 ± 0.33

[a] Rate constant for CN($v=1$) divided by that for CN($v=0$); errors equivalent to $\pm 2\sigma$ random error.

with the O-atom end of the radical towards the H-atom end of the hydrogen halide. In the case of CN, however, the dipole-dipole forces will act to bring the N atom close to the H atom and hence to hinder reaction leading to production of HCN (although the same effect would encourage the formation of HNC, but in a less exothermic reaction). It is noticeable, in this respect, that the reactions of CN and OH with non-polar H_2 have very similar activation energies, whereas those of CN and OH with polar HCl have very different activation energies. However, the suggestion that dipole-dipole forces are important is speculative, *ab initio* calculations on systems of the complexity of those reviewed in table 5 are now possible and should considerably aid our understanding of the variations in kinetic parameters that have been measured for these reactions.

Table 6 lists the ratio of rate constants for removal of CN($v=1$) by HCl, HBr and HI by reaction plus relaxation to the rate constants for reaction of CN($v=0$) with the same hydrogen halide. For HBr and HI, these ratios do not differ significantly from one. These findings are consistent with the predictions of vibrationally adiabatic transition-state theory,[25] if, as seems likely, the CN bond-stretching vibrational frequency remains essentially the same throughout a reactive collision.

The situation is different for CN + HCl, in that the rate constants for removal of $v=1$ at lower temperatures are significantly greater than those for reaction of the vibrationally unexcited radical. Since the observed rate for CN($v=1$) can include contributions from reaction and from vibrational relaxation, the interpretation of these results is not entirely clear. A rough estimate for the rate of relaxation of CN($v=1$) by HCl can be made by analogy with the rate of relaxation of CO($v=1$) by HCl, since the vibrational frequencies, rotational constants and atomic masses of CN and CO are very similar. An accurate measurement of the latter rate has not been made, but the measurements of Chen and Moore[26] and of Braithwaite and Smith[27] suggest a value of *ca.* 5×10^{-15} cm^3 molecule^{-1} s^{-1}. A rate constant only four times larger than this would explain the difference between the observed rate constants associated with removal of CN($v=1$) and CN($v=0$) in collisions with HCl.

Our feeling that vibrational relaxation is responsible for the difference between $k(v=1)$ and $k(v=0)$ with HCl is strengthened by the observed temperature dependence of this difference. If the observed increase in rate constant for CN($v=1$) at low temperatures was due to enhancement of the reaction rate, the increase in $k(v=1)$ with temperature would be only slightly less steep than that of $k(v=0)$, so that the ratio $k(v=1)/k(v=0)$ would fall but still be appreciably greater than unity at the highest temperatures in our experiments. On the other hand, if vibrational relaxation is dominant (probably by a combination of vibrational-vibrational energy exchange and vibrational-rotational, translational energy transfer) the change in $k(v=1)$ with temperature would be markedly different than that for $k(v=0)$, and in all probability much less steep. This is what is observed.

The conclusiton that relaxation, not reaction, causes $k(v=1)$ to be larger with HCl than $k(v=0)$ is further supported by *ab initio* calculations on the NCHCl system by Segal.[7b] These calculations indicate a slight increase of the vibrational frequency ($88\ \text{cm}^{-1}$) of the CN bond-stretching mode at the transition state for this reaction. On the basis of vibrationally adiabatic transition-state theory, this would suggest that reaction of CN($v=1$) with HCl should occur at a rate only *ca.* 65% of the rate of CN($v=0$) with HCl. Further details of these calculations and their predictions regarding the effects of reagent vibrational excitation on the rate of the CN + HCl reaction will be published in a later paper.

We thank the S.E.R.C. and Shell Research for support of this work, including the provision by the S.E.R.C. of a research studentship (I.R.S.). We are grateful to Professor G. A. Segal for useful discussions and permission to quote some of the results of his theoretical calculations.

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Paper 9/00738K; *Received* 20*th February*, 1989