

Infrared chemiluminescence studies of H+BrCN and H abstraction by CN reactions. Importance of the HNC channel

E. Arunan¹, G. Manke II and D.W. Setser²

Department of Chemistry, Kansas State University, Manhattan, KS 66506, USA

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The H+BrCN reaction and the H abstraction reactions from HI, H₂S, PH₃, SiH₄, CH₃OCH₃, *c*-C₃H₁₀ and C(CH₃)₄ by CN were studied by infrared chemiluminescence in a fast flow reactor. From the dependence of the HCN and HNC emission intensities on temperature, activation energies of 5.2 ± 0.4 and 7.5 ± 0.8 kcal mol⁻¹ were assigned for the HCN and HNC channels from the H+BrCN reaction. The anharmonicity constant, $X_{3,3}$ for HNC, was determined to be 66 cm⁻¹. All reactions yielded HCN with an inverted vibrational distribution in ν_3 along with ν_2 excitation and $\langle f_{\nu} \rangle = 0.4-0.5$. The abstraction reactions from PH₃ and HI produced HNC($\nu_3, \geq 1$) with HNC/HCN ratios of ≥ 0.02 and ≥ 0.43 , respectively.

1. Introduction

We previously reported the HCN infrared chemiluminescence (IRCL) from the H+ICN reaction and derived the vibrational distribution [1]. The branching fraction for the HNC channel was estimated to be ≈ 0.01 . Recently Jackson and co-workers reported time-resolved infrared emission studies from CN reactions with hydrocarbons [2]. They came to a similar conclusion for the CN+C₃H₈ reaction, noting that the HNC channel roughly accounted for 1% of the reaction. Marciq et al. [3] studied the CN⁻ reactions with HCl, HBr, HI and H₂; they observed HNC from only the CN⁻+HI reaction with a HNC(0, 0, 1)/HCN($\nu_3=1-4$) ratio of ≈ 0.2 . In this work we wish to report three reactions that are moderately strong sources of HNC emission; these are H+BrCN, CN+HI and CN+PH₃. We will also discuss the HNC and HCN vibrational distributions.

Unlike the alkyl isonitriles (R-NC), which are relatively stable and well characterized, the simplest

member of the family, HNC, remains poorly understood. HNC was first identified in an Ar matrix following photolysis of HCN [4]. In 1971 Snyder and Buhl [5] observed the $J=0 \leftarrow 1$ rotational transition in the interstellar medium. At room temperature the HNC concentration in HCN sample is insignificant [6], but at ≈ 1000 K both infrared [7] and microwave [8] spectra of HNC were obtained from HCN samples. Infrared [9,10] and microwave [11,12] data for HNC have also been obtained from reactions of active nitrogen with CH₃Br/CH₃I [9,12], C₂H₂, C₂H₄ and CH₃CN [9] or from a dc discharge through mixtures of N₂ with C₂H₂, H₂ with C₂N₂ or C₂H₂ with C₂N₂ [11]. Only the ground and first vibrationally excited (NH stretch, ν_3) states have been reported.

There are numerous studies of H abstraction reactions by CN using the first-order loss of CN to measure the rate constants. Balla et al. [13] concluded that HCN was the dominant product at 295 K for CN+CH₄, C₂H₆ and C₃H₈ from diode laser absorption. Atakan and Wolfrum studied the temperature dependence of these reactions and suggested that one explanation for the curvature of the Arrhenius plots could be two product channels [14]. Yang et al. [15] also studied the temperature de-

¹ Present address: Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA.

² Author to whom correspondence should be addressed.

pendence of these reactions, as well as the *i*-C₄H₁₀, neo-C₃H₁₂ and C₈H₁₈ (2,2,3,3-tetramethylbutane) reactions, and observed non-linear Arrhenius plots. However, the relative yields of HCN and HNC have not been systematically determined. Infrared chemiluminescence can be used to determine the relative importance of HCN and HNC because the Einstein coefficients are favorable; the $A_{1,0}$ values for $\Delta v_3 = -1$ are 77 and 385 s⁻¹ for HCN [16] and HNC [17], respectively. We report here the results from our IRCL studies of H+BrCN and CN+HI, H₂S, PH₃, SiH₄, CH₃OCH₃, C(CH₃)₄ and *c*-C₅H₁₀. Results from the H+ICN reaction [1] will be included for comparison. Emission from HCN was observed from all these reactions, but HNC emission was observed only from H+BrCN and from the CN+HI and PH₃ reactions. The H+BrCN reaction gave emission from $v_3 = 1$ and 2 of HNC from which the anharmonicity constant was determined.

Our laboratory has previously studied the H abstraction reactions from the molecules given above by F, Cl and O atoms [18]. These reactions gave inverted vibrational distributions and in most cases the vibrational ground state population was negligible. There is a strong similarity in the energy disposal to HCN(v_3) for H abstraction by CN radicals.

2. Experimental methods

The IRCL flowing-afterglow technique has been well documented [18,19], and we will only describe the changes made for the specific experiments reported here. The H atom concentration, produced by passing a H₂/Ar mixture through a microwave discharge, was $(1-5) \times 10^{13}$ molecule cm⁻³. The reagents were added just in front of the observation window; the distance from the reagent inlet to the center of the window was ≈ 3 cm. The BrCN was carried to the reactor by flowing Ar carrier gas over the solid sample; the concentration was $(5-20) \times 10^{13}$ molecule cm⁻³. The H+BrCN reaction is slow at room temperature and a heated reactor was necessary. The distance between the inlets for the H atom and the main Ar flow and the observation window was 50 cm, and this section could be heated to 600 K by varying the voltage delivered to the heating tapes. The gas temperature was measured just after

the observation window with a type-K thermometer. The background emission increased with temperature, and the gain was reduced for the In/Sb detector and a quartz filter was placed before the detector to block thermal background below ≈ 2300 cm⁻¹. The Ar pressure was 1.0 Torr for a pumping speed of 60 m s⁻¹, which corresponds to a reaction time of 0.4 ms. Attempts to observe HCN/HNC emission at the highest pumping speed, corresponding to a reaction time of 0.2 ms, were unsuccessful.

The CN radicals were produced by passing C₂N₂ in He or Ne carrier through a dc electrical discharge; the cathode was made from rolled Ta foil and the anode was a tungsten wire. The discharge was operated at a voltage of ≈ 400 V. Better signals were obtained by adding C₂N₂ to the flow before the discharge for Ne carrier and after the discharge with He carrier. Reduced pumping speed (≤ 45 m s⁻¹) was required with He to obtain acceptable emission intensity, but larger pumping speeds (≤ 80 m s⁻¹) were possible with Ne carrier. The observation region was located ≈ 10 cm beyond the discharge zone; the reagents were added to the reactor just before the observation window. The CN reacts with C₂N₂, and the walls of the reactor were coated with a dark brown polymer after a few days of operation.

3. Results

3.1. Spectral simulation

Due to the small rotational constants for HCN and HNC (≈ 1.5 cm⁻¹) relative to our resolution (2-4 cm⁻¹), the $\Delta v_3 = -1$ emission spectra were observed as broad bands. Spectral simulation was used to determine the relative vibrational populations by trial and error comparison with the experimental spectra. Representative emission spectra and the simulations of those spectra, which were used to obtain the vibrational distributions from the H+BrCN, CN+HI and CN+PH₃ reactions, are shown in fig. 1. All the HCN spectroscopic constants are known and the simulation is straightforward [1]. The rotational constants for $v_3 = 0$ and 1 of HNC are known [7,9,10] and these were extrapolated to determine rotational constants for $v_3 = 2$. The anharmonicity constant for HNC was determined to be 66 cm⁻¹, from the band

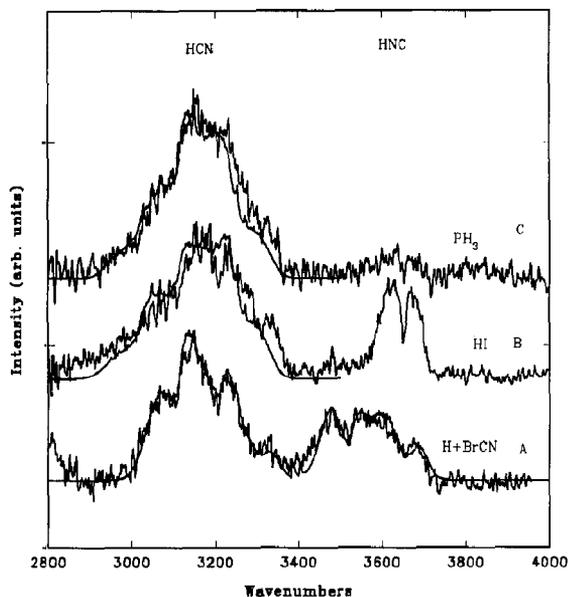


Fig. 1. Comparison of simulated and observed HCN and HNC emission ($\Delta v_3 = -1$) spectra (4 cm^{-1} resolution) from (A) H+BrCN (475 K), (B) CN+HI (300 K) and (C) CN+PH₃ (300 K). The C₂N₂ concentration was $\approx 3 \times 10^{13}$, the HI and PH₃ concentrations were 7×10^{13} molecule cm^{-3} , with $\Delta t = 0.9$ ms and 1.5 Torr of Ne. For the BrCN reaction, [H₂] was 6×10^{13} , [BrCN] was 6×10^{14} with 1.4 Torr of Ar and $\Delta t = 0.6$ ms. All rotational distributions were Boltzmann for the simulated spectra. The distributions used in the simulation are as follows (population in $v_3 = 1, 2, 3$, and 4 are given with the v_2 distribution in square brackets): (A) HCN 30[5, 4, 3, 2, 1]:45[4, 3, 2, 1]:25[3, 2, 1] and HNC 78[4, 2, 1]:22[5, 3]; (B) HCN 35[1, 2, 3, 2, 1]:40[2, 3, 2, 1]:20[2, 3, 2, 1]:5[4, 3, 2, 1]; (C) HCN 35[1, 2, 3, 2, 1]:40[1, 2, 2, 1]:20[2, 2, 1, 1]:5[2, 1, 1]. The entries in table 1 for HI and BrCN are based upon spectra for shorter reaction times than those in fig. 1.

centers of the $v_3 = 1 \rightarrow 0$ and $2 \rightarrow 1$ emission from the H+BrCN reaction, see fig. 1. The Einstein coefficients for transitions with $v_2 > 0$ were assumed to be the same as those for transitions with $v_2 = 0$, i.e. $(0, 1, 1) \rightarrow (0, 1, 0)$ has the same Einstein coefficient as $(0, 0, 1) \rightarrow (0, 0, 0)$. The HCN Einstein coefficients have been calculated for $\Delta v_3 = -1$, $1 \leq v_3 \leq 4$ [16]. Only the Einstein coefficient for the $v_3 = 1 \rightarrow 0$ transition of HNC is known; the $v_3 = 2 \rightarrow 1$ Einstein coefficient was estimated using the harmonic approximation [3]. In principle, matching experimental and simulated spectra can give vibrational distribution in all three HCN or HNC modes. But, because of the overlap between the emissions from certain combinations of v_1 , v_2 and v_3 populations, the distribution

obtained by simulation may not be unique. We assumed that the CN stretch mode had no population, because this mode is expected to be virtually adiabatic [1], and assigned distributions to v_2 and v_3 to fit the spectra. The experimental spectra can unambiguously indicate whether or not there is some bending excitation. Without bending excitation the $\Delta v_3 = 1$ band centers for the different v_3 levels show a clear dip in the spectrum for a resolution of 2 or 4 cm^{-1} . If the v_2 excitation is low, a specific distribution can be assigned even for our resolution. If the v_2 excitation is high, then other criteria must be used to distinguish between v_2 and v_3 excitation. For example, the $(0, 5, 2) \rightarrow (0, 5, 1)$ and $(0, 0, 3) \rightarrow (0, 0, 2)$ transitions have the same band centers. Ref. [1] gave simulated spectra with different combinations of vibrational excitation in HCN. We previously used collisional relaxation rates to aid in distinguishing between v_2 and v_3 excitation.

3.2. The HCN/HNC vibrational distributions

Table 1 gives the enthalpies of reaction (kcal mol^{-1}) and the product vibrational distributions for the HCN/HNC channels. The total available energy, $\langle E \rangle$, is the sum of the ΔH_0^0 , the activation energy, E_a , and the thermal energy of the reactants. The energy difference ($15.2 \text{ kcal mol}^{-1}$) between HCN and HNC was taken from experimental results of Pau and Hehre [20]. Although all of these reactions are exergic for HNC formation, the $(\text{CH}_3)_4\text{C}$ reaction does not have enough energy to form HNC ($v_3 = 1$), which needs 3650 cm^{-1} ($\approx 10.4 \text{ kcal mol}^{-1}$). The E_a for the H+ICN and BrCN reactions were assigned from plots of the logarithm of the emission intensities as a function of temperature from 298–475 K; see fig. 2. From the slope of these plots, the E_a for the H+BrCN reaction were determined to be 5.2 ± 0.4 and $7.5 \pm 0.8 \text{ kcal mol}^{-1}$ for the HCN and HNC channels, respectively. The activation energy for the HCN channel from H+ICN was only $0.8 \pm 0.2 \text{ kcal mol}^{-1}$. We did not attempt variable temperature experiments for the CN abstraction reactions. The E_a for the CN+HI [21] and $\text{C}(\text{CH}_3)_4$ [3] reactions are negligible and by comparison with similar systems [3,13–15], the activation energies for $c\text{-C}_5\text{H}_{10}$, CH_3OCH_3 , SiH_4 and PH_3 should also be small. The CN+H₂S reaction might have a significant E_a , as it

Table 1
Thermochemistry and vibrational distributions for the H+BrCN and CN abstraction reactions

Reagent	E_a (kcal/mol)	$\Delta H_0^{\circ a)}$ (kcal/mol)	$P_v^b)$				$\langle f_v \rangle^c)$
			1	2	3	4	
(CH ₃) ₄ C	0.0	24.4	65	35	–	–	0.47 (0.40)
<i>c</i> -C ₃ H ₁₀	d)	29.9	45	45	10	–	0.51 (0.43)
CH ₃ OCH ₃	d)	31.4	55	40	5	–	0.45 (0.37)
H ₂ S ^{e)}	f)	34.8	35	45	20	–	0.43
SiH ₄ ^{e)}	d)	34.1	25	45	30	–	0.53
PH ₃	d)	48.3	30	45	20	5	0.40 (0.33)
	g)	33.1 ^{b)}	100	–	–	–	–
HI	0.0	52.9	25	40	28	7	0.40 (0.34)
	g)	37.7 ^{b)}	90	≈ 10	–	–	–
BrCN ⁱ⁾	5.2	37.1	20	40	30	10	0.47 (0.42)
	7.5	21.9 ^{b)}	67.0	33	–	–	0.38 (0.35)
			2.3, 1.5, 1.0	2.6, 1.6, 1.0			

^{a)} Enthalpy of reaction. The total available energy is $-\Delta H_0^{\circ} + E_a +$ thermal energy ($\frac{3}{2}RT$) of the reactants.

^{b)} All these reactions required several quanta in ν_2 in order to fit the experimental spectrum. The second line for each reaction shows the distribution for $\nu_2=0, 1, 2, 3, 4$.

^{c)} $\langle f_v \rangle$ calculated assuming $P_0 \approx 0.5P_1$. The distribution in ν_2 for $\nu_3=0$ was assumed to be the same as for $\nu_3=1$. The value in parentheses shows the $\langle f_v \rangle$ for excitation in ν_3 only with $P_0 = \frac{1}{2}P_1$.

^{d)} Activation energy is expected to be negligible.

^{e)} The experiments with H₂S and SiH₄ were done in He carrier gas for variable pressure and extrapolated to zero pressure; the ν_2 distribution was 3:2:1 for each ν_3 level. Comparison to other experiments done in both He and Ne carrier gas showed that the extrapolation in He gave similar results as in experiments 1.0 Torr of Ne. All other data are for 1.0 Torr of Ne carrier and a reaction time of <0.6 ms, except for PH₃, which had a reaction time of 0.9 ms and 1.5 Torr of Ne.

^{f)} Activation energy could be of the order of 2 kcal mol⁻¹.

^{g)} Activation energy could be higher than that for the HCN channel.

^{h)} Corresponds to the HNC channel.

ⁱ⁾ These BrCN data were taken at 475 K; all other data were collected at 300 K.

gave very weak emission. This reaction could be comparable to CN+HBr for which the E_a is ≈ 2 kcal mol⁻¹ [21].

Since CN⁻ ion is known to react with HI to form HCN and HNC [3] and since CN⁻ might be present from the discharge, some reagents (e.g. H₂S) were chosen that could only react with CN radicals to form HCN or HNC. The CN⁻+H₂S reaction is endoergic, whereas the CN radical reaction is exoergic. Experiments were also done with some reagents (HBr, HCOOH and CF₃COOH) that react with CN⁻ to give HCN, but these did not give any emission. The observed HCN vibrational distributions are consistent only with the CN radical thermochemis-

try, which is given in table 1. We conclude that the observed HNC and HCN emission in the abstraction experiments arises from only CN radical reactions.

The H+BrCN reaction was studied in Ar carrier and the HCN($\nu_1\nu_2\nu_3$) vibrational relaxation rates should be the same as for the H+ICN experiments [1]. Based upon the former work, the ν_3 distribution should be close to nascent, but the ν_2 distribution could be partly relaxed. The degree of HCN($\nu_1\nu_2\nu_3$) relaxation for the CN reactions in He and Ne carrier is more difficult to estimate. Experiments were first done with variable He pressure and these distributions showed evidence for ν_3 relaxation. Most reactions were repeated in Ne carrier at 1 Torr with an

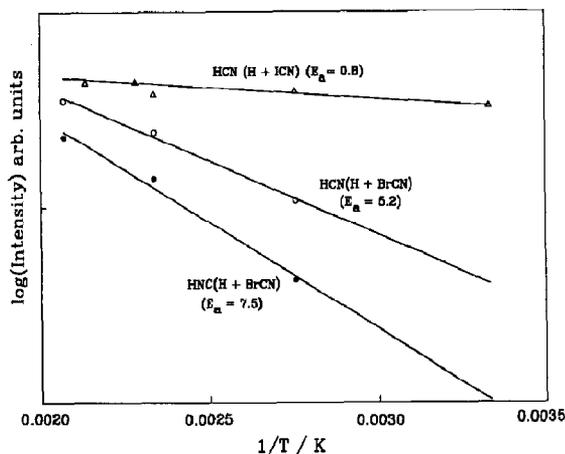


Fig. 2. Arrhenius plot for the emission intensities from the H+BrCN and H+ICN reactions. The HCN and HNC channels are both shown for H+BrCN. Only the HCN channel is important for H+ICN. The E_a values are in kcal mol⁻¹.

observation time of 0.6 ms. The latter data gave HCN(ν_3) distributions that closely resembled the results from extrapolation of the He data to zero pressure. A full discussion of these CN abstraction reactions will be presented at a later time. The population assignments in table 1, at worst, will be close lower limits to the nascent vibrational distribution.

The abstraction reactions tend to give inverted vibrational distributions in HCN(ν_3) with excitation close to the thermochemical limit. The ν_2 distributions assigned to the ν_3 levels given in table 1 certainly suggest an importance for bending excitation, as well as H-CN stretching excitation. The partial relaxation of the ν_2 population cannot be excluded for the present data. As already noted, we have assumed that ν_3 is not excited. In order to estimate $\langle f_v \rangle$, the fraction of the total available energy released as HCN vibrational energy, we assumed $P_0 = 0.5P_1$, with a ν_2 distribution in $\nu_3 = 0$ the same as for $\nu_3 = 1$. The $\langle f_v \rangle$ for the reactions in table 1 vary between 0.40 and 0.53. Only for the CN+C(CH₃)₄ reaction are vibrational distributions available from another laboratory. Based upon an approximate analysis, Copeland et al. [2] reported P_1/P_2 to be 0.8 with no excitation in ν_2 . Our experimental spectrum clearly indicates a modest level of bending excitation. As pointed out in the spectral simulation section, some of the (0, m , 1) and (0, 0, 2) emission bands overlap. In other words, part of the intensity

observed in the (0, 0, 2) → (0, 0, 1) emission band is due to (0, m , 1) states. The actual spectrum published by Copeland [2] is similar to our experimental spectrum. If the ν_2 excitation is included in the simulation, a distribution similar to that in table 1 can fit their spectrum. The lack of strong emission from HNC($\nu_3 = 2$ and 3) from CH+HI is puzzling. Either the relaxation rates are more rapid than for HCN(ν_3) or the dynamics are different from those for HCN formation. Given the uncertainty in the relaxation and the population in $\nu_3 = 0$, the $\langle f_v(\text{HNC}) \rangle$ for the HI and PH₃ reactions was not assigned.

The BrCN reaction produced HCN and HNC in vibrational states that extended to the thermochemical limit. The $\langle f_v \rangle$ for the HCN channel was 0.47 and 0.55 for the H+BrCN and H+ICN [1] reactions, respectively. The HNC distribution from H+BrCN was $P_1:P_2 = 67:33$, and $\langle f_v \rangle$ is 0.38, if P_0 is assigned as $\frac{1}{2}P_1$. These experiments were done in Ar carrier and by analogy to the more extensive H+ICN data, the HCN(ν_3) distribution should not be relaxed. However, the HNC(ν_3) distribution varied somewhat with change of reaction time and the nascent HNC($\nu_2\nu_3$) distribution may be more excited than the one in table 1 (for 475 K).

3.3. HCN/HNC branching ratio

The HCN and HNC relative intensities were corrected for instrumental response and then divided by their Einstein coefficients to obtain the $[\text{HNC}(0, m, \nu_3 \geq 1)]/[\text{HCN}(0, m, \nu_3 \geq 1)]$ ratio, which was 3:1 in favor of HCN for the H+BrCN reaction at 475 K. Including the $\nu_3 = 0$ population for HCN and HNC would make the branching ratio even higher for HNC. The H+ICN reaction, which is more exothermic than the H+BrCN reaction, gave ≈ 0.01 as the branching fraction for HNC [1]. For the CN+HI reaction, the signal-to-noise for the HNC spectrum was very poor for the data at ≤ 1.5 Torr of Ne. However, the estimate for the $[\text{HNC}(0, m, \nu_3 = 1)]/[\text{HCN}(0, m, \nu_3 \geq 1)]$ ratio was ≈ 0.43 at 2.0 Torr of Ne (see fig. 1). The $\langle f_v \rangle$ for the HCN distribution at this pressure was 0.35 compared to 0.4 obtained at 1.0 Torr. If adjustments are made for the $\nu_3 = 0$ contributions, the [HNC] would be further enhanced. The HNC emission was barely observable from the CN+PH₃ reaction, and the $[\text{HNC}(\nu_3 =$

1)]/[HCN($\nu_3 \geq 1$)] was estimated to be ≈ 0.02 . The vibrational relaxation of HNC probably is more rapid than for HCN, and our measurements are lower limits to the true HNC($\nu_3 \geq 1$) yields for the abstraction reactions.

4. Discussion and conclusions

The isomerization between HCN-HNC must be considered before discussing the relative importance of the two channels. Until recently, the Murrell, Carter and Halonen [22] surface for the HCN-HNC system with an isomerization barrier of 34.8 kcal mol⁻¹ above the HCN minimum has been widely accepted. However, recent stimulated emission pumping [23]^{#1} and vibrational overtone excitation [25] experiments suggest a significantly higher barrier and ab initio calculations [26] estimate the barrier to be 44.6 ± 1.0 kcal mol⁻¹. Given the $\langle f_v \rangle$ values, the HCN formed in the reaction of table 1 cannot rearrange to HNC. The branching ratios, HNC(0, m , $\nu_3 \geq 1$)/HCN(0, m , $\nu_3 \geq 0$), for the CN+HI and H+BrCN reactions are 0.43 and 0.33, respectively, and these reactions could be used as chemical sources for HNC. The H+BrCN reaction gives both HCN and HNC, and $\langle E \rangle$ is less than the barrier, i.e. the HNC formation must be direct. The attack of H at the N end or at the C center of BrCN must lead to HNC and HCN, respectively. The H+ICN reaction with an $\langle E \rangle$ comparable to CN+HI did not give significant HNC formation. It is likely that H attack on the bulky I atom followed by migration to C dominates the dynamics of the H+ICN reaction, as for the H+IF reaction [27,28]. Another possibility is that the trajectories which initially attack the N end of ICN have enough energy to migrate to C before the I atom and CNH molecule can dissociate. The anharmonicity constant, $\omega_{3,3}$, for HNC was assigned as 66 ± 4 cm⁻¹.

To explain the large difference in rate constants between the CN+HI and HBr reactions, Sims and Smith [21] suggested that, due to the polarity of CN, the N end may preferentially orient towards the H of HI/HBr, thus hindering the formation of HCN and favoring HNC. As HNC formation is energeti-

cally less favored than HCN, the H abstraction rates are slower than for analogous reactions with non polar H atom donors. Our results show that $\geq 40\%$ of the CN+HI reaction events do go through the HNC channel. The slow rate of the CN+H₂S reaction could arise from a polar effect. The only other abstraction reaction giving observable HNC($\nu_3 \geq 1$) for our conditions was PH₃; the yield was low but there may have been some relaxation. Formation of HNC($\nu_3 \geq 1$) by CN abstraction reactions does not appear to be important except for reactions with large exoergicity. However, the HNC channel may have a small vibrational energy release and/or rapid relaxation, and direct observation of HNC($\nu_3 = 0$) is needed for the PH₃ and SiH₄ reactions to be certain about the HNC channel.

The product vibrational distributions from both H+XCN and H abstraction by CN radical reactions are inverted in ν_3 with concomitant ν_2 excitation. The energy disposal to HCN(ν_3) by H abstraction reactions resembles the established pattern for analogous reactions with halogen and oxygen atoms [18], except that HNC can also be formed from molecules with weak H-R bonds. The inverted HCN(ν_3) distributions are expected for mixed energy release associated with transfer of the light H atom between two heavy atoms on a repulsive potential surface. However, the apparent inverse correlation between the vibrational energy in ν_3 and ν_2 suggests that new information can be learned about the dynamics. More complete analysis and discussion of the HCN($\nu_1 = 0$, ν_2 , ν_3) distributions will be given in the near future.

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