Reaction of Cyanomethylene with Nitric Oxide and Oxygen at 298 K: HCCN + NO, O_2

J. D. Adamson, J. D. DeSain, R. F. Curl,* and G. P. Glass*
*Department of Chemistry and Rice Quantum Institute Rice University, 6100 S. Main Street,
Houston, Texas 77005*

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The reactions of the cyanomethylene (HCCN) radical with nitric oxide (NO) and with molecular oxygen (O_2) have been investigated using infrared kinetic spectroscopy. The overall second-order rate constant for each reaction has been determined using pseudo-first-order methods yielding $(3.5 \pm 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction with NO and $(1.8 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction with O_2. For each reaction, several products were observed, but none were quantified. Hydrogen cyanide (HCN) and fulminic acid (HCNO) were observed as products of the reaction with NO. For the reaction with O_2, HCN, hydrogen isocyanide (HNC), and carbon dioxide (CO_2) were observed. Species searched for but not detected from either reaction include isocyanic acid (HNCO), cyanic acid (HOCN), formyl (HCO) radical, isofulminic acid (HONC), hydroxyl radical (OH), and ethynyl radical (C_2H). In addition, NO was searched for, but not observed, as a product of the O_2 reaction. On the time scale of our experiments, no reaction between HCCN and any of the following species was observed ($k < 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}): methane (CH_4), CO_2, acetylene (C_2H_2), ethylene (C_2H_4), carbon monoxide (CO), and hydrogen (H_2).

Introduction

The combustion of coal-derived liquids (CDLs), used as a source of energy in many power plants, results in the formation of various oxides of nitrogen, the production of which ultimately leads to such environmental hazards as acid rain and smog. A number of strategies to reduce the formation of these products have been used, including the methods of thermal deNOx[1] or RAPRENOx,[2] as well as combustion modification techniques such as NO reburning. Unfortunately, none of these is totally successful, in part because the complete mechanism involved in CDL combustion is still unknown. CDLs consist of a complex mixture of aromatic hydrocarbons and heterocyclic aromatic compounds containing nitrogen, oxygen and sulfur.[3] To avoid the complications involved in the study of such complex mixtures, a number of simpler "model" compounds have been used in many previous investigations. In the case of nitrogen-containing heterocyclic aromatics, pyridine[3] has proved to be a suitable model compound. A recent matrix isolation study investigating the thermal decomposition of pyridine[3] found that HCCN is a major product. Since reactions of HCCN with species normally present in combustion systems have not been previously studied and since a method for producing and observing the HCCN radical has been recently developed,[4] a program to study such reactions has been initiated in this laboratory. In this paper, we present the overall rate constants for the reactions of HCCN with NO and O_2 along with the results of a search for potential reaction products.

Experimental Section

The infrared kinetic spectrometer has been previously described.[5,6] Briefly, the unfocused beam of an excimer laser is overlapped with an IR color center laser probe beam in a multipass (White) flow cell. The HCCN radical was produced by photolysis of dibromoacetonitrile (Argos) at 193 nm using an ArF excimer laser operated at 10 Hz:

$$Br_2HCCN + 193\ \text{nm} \rightarrow HCCN + 2Br \qquad \text{(R1a)}$$

The dibromoacetonitrile was introduced into the flow cell through the use of a helium (99.999%) carrier gas. Helium was also used as a buffer gas. Nitric oxide (99.0%), oxygen (99.8%), methane (99.0%), carbon dioxide (99.5%), ethylene (99.5%), sulfur hexafluoride (99.8%), carbon monoxide (99.3%), and hydrogen (99.999%) were used without further purification. Acetone was removed from acetylene (99.6%) by passage through a copper coil immersed in a dry ice/acetone bath. Nitric oxide was similarly treated to remove residual NO_2. Total pressures in the flow cell ranged from 6 to 30 Torr. Flow rates for NO and O_2 were measured and controlled using an MKS 20 sccm flow meter and an MKS 200 sccm flow controller, respectively. The HCCN radical was monitored at the P(14) transition of the ν_1 CH stretch[4] at 3236.2322 cm^{-1}; HCN was monitored[7] at 3328.7753 cm^{-1}, R(5) of the 100−000 band; HNC was monitored[8] at 3611.8171 cm^{-1}, P(13) of the 100−000 band; and CO_2 was monitored[9] at 3611.278 cm^{-1}, P(2) of the 02^01-00^00 combination band.

Rate Constants

Figure 1 shows HCCN time profiles obtained without added reagent, with added NO and also with added O_2. The HCCN decay in the presence of the added NO and O_2 can be well fitted with a negative exponential yielding a first-order decay constant, k_{eff}, which is consistent with pseudo-first-order kinetics. The HCCN decay in the absence of added reagent qualitatively appears to follow a second-order kinetics law:

$$[\text{HCCN}] = \frac{[\text{HCCN}]_0}{1 + 2k[\text{HCCN}]_0 t} \qquad (1)$$

Because there is no convenient way to determine the HCCN absorption cross-section needed to convert the infrared absorbance into a concentration of HCCN, we have not attempted to determine k in eq 1. Furthermore, k does not have to reflect the reaction of HCCN with itself as there are other species likely to be created by the photolysis such as CHBrCN which might be reacting with HCCN. The HCCN decay profile should still be approximately second order if other species created by the flash are reacting only with HCCN and other photolysis products, as it is extremely difficult to distinguish the resulting

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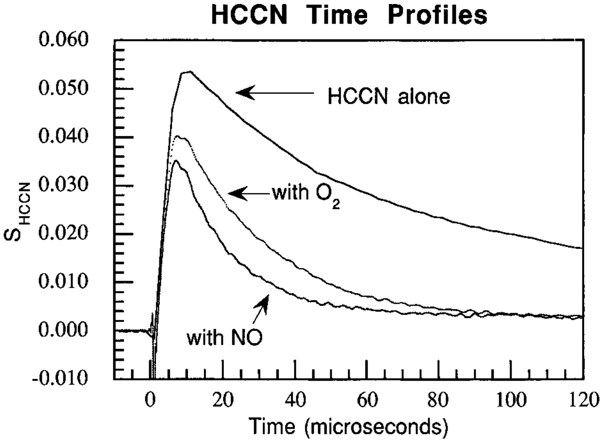

Figure 1. Time profiles of HCCN with no reagents added, with 50 mTorr of NO added and with 0.7 Torr O_2 added. Total pressure = 11.6 Torr. The ordinate scale is in base e absorbance units.

decay curves from a true second-order decay. Thus, we cannot be certain that the observed decay in the absence of added reagent is uncontaminated by reaction with other photolysis products.

When excess NO or O_2 is added, there are two limiting cases: the substance created by the flash photolysis of HCCN that reacts with HCCN does not react with the added reagent or it reacts rapidly with the added reagent. Neither case causes a serious problem in the data analysis. The HCCN decay in the presence of added reagent was always dominated by reaction with the added reagent and could be fitted with negative exponentials even at the lowest concentration of either added reagent used. Therefore, as long as we keep the precursor dibromoacetonitrile pressure and the flash energy constant, a plot of k_{eff} vs [NO] (or [O_2]) will result in straight line with a slope equal the reaction rate constant but not necessarily with a zero intercept. In the first case given above, the intercept is expected to be nonzero; in the second, the intercept should be zero. Usually, the intercepts are positive, but in some NO datasets quite close to zero. Since we would like to reduce the sensitivity of the analysis to flash energy and precursor pressure and we would like to be able to combine data sets with different flash energies and precursor pressures, we have chosen to perform the data analysis by representing the zero added reagent contribution to HCCN decay as a reaction of HCCN with itself. Then the relevant reaction systems are

$$\mathrm{HCCN} + \mathrm{NO} \rightarrow \mathrm{products} \tag{R2}$$

$$\mathrm{HCCN} + \mathrm{O_2} \rightarrow \mathrm{products} \tag{R3}$$

$$\mathrm{HCCN} + \mathrm{HCCN} \rightarrow \mathrm{products} \tag{R4}$$

There are no significant differences in the rate constants obtained by this method as compared with a fit of the exponential decay constants with a floating intercept.

In all the experiments reported here, NO and O_2 were added to the reaction system in sufficiently large excess that their concentrations were not sensibly decreased by reaction with HCCN.

Under these conditions, the overall rate equation for HCCN can be written as a sum of two terms, one first order and the other second order in HCCN:

$$-\mathrm{d[HCCN]/d}t = k_{\mathrm{eff}}[\mathrm{HCCN}] + 2k_4\,[\mathrm{HCCN}]^2 \tag{2}$$

Here k_{eff} is equal to either k_2[NO] or k_3[O_2]. This well-known differential equation was long ago solved yielding:

$$\ln\left[\frac{[\mathrm{HCCN}](2k_4[\mathrm{HCCN}]_0 + k_{\mathrm{eff}})}{[\mathrm{HCCN}]_0(2k_4[\mathrm{HCCN}] + k_{\mathrm{eff}})}\right] = -k_{\mathrm{eff}}t \tag{3}$$

However, the infrared absorption cross section for HCCN is unknown, and therefore the absolute concentration of HCCN cannot be determined from the measured absorption signals. Instead the observed base e absorbance is proportional to the concentration of the absorbing molecule through the Beer–Lambert law:

$$A = \sigma_0 L[\mathrm{HCCN}] \tag{4}$$

where the peak infrared absorption cross section, σ_0, is unknown, as is for that matter the path length L, which is determined by a complex overlap of the excimer and the IR probe beams. Letting $C = \sigma_0 L$, after substitution and some rearrangement, eq 3 transforms to

$$A = \frac{A_0 \exp(-k_{\mathrm{eff}}t)}{1 + \left(\dfrac{2k_4}{Ck_{\mathrm{eff}}}\right)A_0(1 - \exp(-k_{\mathrm{eff}}t))} \tag{5}$$

In practice, the data representing the observed time dependence of the absorbance was not accurate enough to obtain simultaneously "best-fit" values of the variables, k_4/C and k_{eff}. Therefore, at the beginning of each series of experiments, k_4/C was determined independently by making a number of rate measurements in the absence of NO (or O_2). Using the substitution introduced previously, eq 1, the rate equation for second-order reaction, transforms to

$$A = \frac{A_0}{1 + (2k_4/C)A_0 t} \tag{6}$$

Values of k_4/C thus determined in the absence of added reagent by using eq 6 with an added baseline parameter using a commercial fitting program[10] were then used in the series of subsequent experiments performed in the presence of NO (or O_2).

With k_4/C fixed in this manner, for each decay curve corresponding to a given concentration of added reagent, A_0 and k_{eff} of eq 5 plus an added baseline parameter were determined by fitting.[10] Figure 2 illustrates the quality of the fit that was obtained for an experiment in which the addition of 50 mTorr of NO reduced the half-life for HCCN decay from 65 μs to less than 10 μs. In this figure, the even spread of the residuals about the zero line shows that the data is adequately represented by eq 5. Plots of similar quality were obtained when using O_2 as a reactant.

To determine whether either of the rate constants, k_2 or k_3, varied as the overall pressure was changed, experiments were performed at a total pressure of 6.2, 18, and 30 Torr. The rate constants measured at these pressures are compared in Table 1. As can be seen, no systematic variation with pressure of either rate constant was observed. In particular, no increase of rate with pressure is found. Such an increase would be expected if redissociation back to reactants of an adduct formed between HCCN and the added reagent were competing solely with adduct stabilization.

Since no significant pressure dependence of the reaction rate was observed, the data at all three pressures was combined to determine the overall rate constants. As an illustration of the results obtained, Figure 3 shows the plot of k_{eff} vs [O_2] used to determine the rate constant for that reactant. The overall rate constant, k_2, for reaction with NO which resulted is (3.5 ± 0.6)

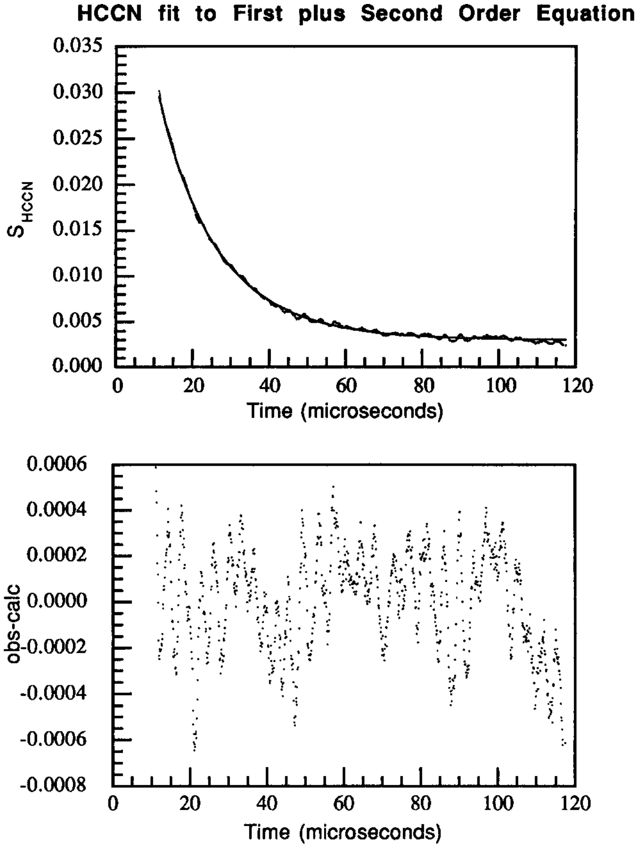

Figure 2. Typical fit of HCCN with first plus second-order equation (eq 5); with 50 mTorr of NO and total pressure of 6.2 Torr; residuals are show below the plot. The ordinate scale is in base e absorbance units.

TABLE 1: Rate Constants at Varying Pressures[a]

total pressure (Torr)	rate constant for HCCN + NO (cm^3 molecule^{-1} s^{-1})	rate constant for HCCN + O_2 (cm^3 molecule^{-1} s^{-1})
6	$4.0(2) \times 10^{-11}$	$2.1(1) \times 10^{-12}$
18	$3.3(11) \times 10^{-11}$	$1.3(3) \times 10^{-12}$
30	$3.6(5) \times 10^{-11}$	$1.6(1) \times 10^{-12}$

[a] The numbers in parentheses are 3 standard deviations of the fit in units of last digit reported for the rate. The real uncertainties taking into account possible systematic errror are probably ±30%.

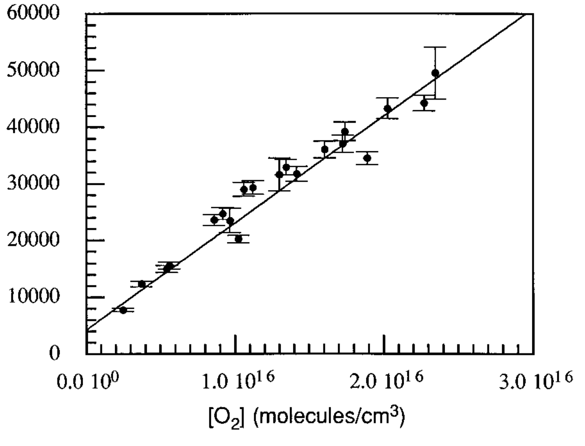

Figure 3. k_{eff} vs [O_2] plot for HCCN + NO. The data shown combine the results at all three pressures, 6, 18, and 30 Torr.

$\times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and k_3, the rate constant for reaction with O_2, is found to be $(1.8 \pm 0.4) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. No significant reactivity was observed when any of the following molecules were added to HCCN at pressures in excess of 1 Torr: CH_4, CO_2, C_2H_2, C_2H_4, CO, and H_2. Therefore, the overall second-order rate constants for reaction of any of these molecules with HCCN must be less than 10^{-13} cm^3 molecule^{-1} s^{-1}.

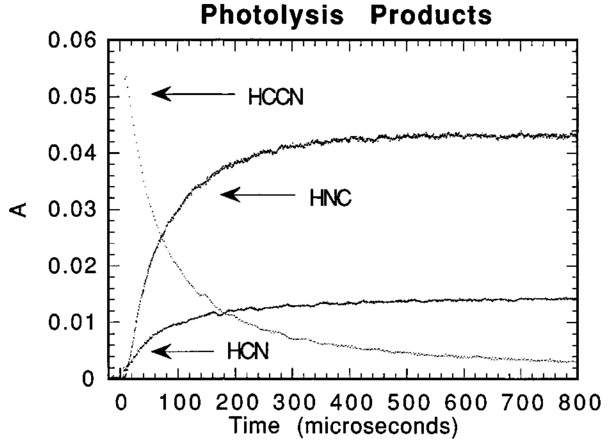

Figure 4. Time profiles of HCCN, HCN, and HNC with no reagents added. The ordinate scale is in base e absorbance units.

Identification of Reaction Products

Photolysis Products. The photolysis channels of dibromoacetonitrile at 193 nm have not been determined. Potential channels may include not only that producing HCCN (R1a), but also

$$Br_2HCCN + 193\ nm \rightarrow BrHCCN + Br \qquad (R1b)$$

$$\rightarrow Br_2HC + CN \qquad (R1c)$$

A search was made for products from the photolysis of dibromoacetonitrile with no other reagents in the flow cell, and HCCN, HCN, and HNC were identified. Figure 4 shows the time profiles of infrared absorptions arising from the ground vibrational state of these products. The rapid rise of the HCCN signal after the flash indicates that it is a direct result of photolysis. The HCN and HNC signals rise much more slowly. The early time behaviors within the first few microseconds after the flash of the HCN and HNC signals are different: HCN exhibits a small rapid initial rise followed by a slower rise; HNC shows a definite induction period of about 10 μs duration. This indicates that a small fraction of the HCN is produced directly in the ground state by the photolysis by a fourth photolysis channel but that ground-state HNC is not produced by the photolysis. The bulk of the HCN and HNC are produced during the first 200 μs: their concentrations can be represented as in a $(1 - \exp(k_g t))$ form with the same rate constant, k_g, within experimental error. However, between 300 and the 700 μs limit of the data there is a small additional growth in both cases which is rather more pronounced for HCN. In other words, the growth seems biexponential. The most plausible explanation for the similar growth of HCN and HNC between 20 and 200 μs is that they are both produced by reactions of a common intermediate. A plausible hypothesis for these secondary reactions is hydrogen atom abstraction from the dibromoacetonitrile precursor by CN radical produced by R1c. The rate of H atom abstraction by CN from ethane and propane at room temperature have been measured[11] as 2.7×10^{-11} and 8.3×10^{-11} molecules^{-1} cm^3 s^{-1}, respectively, so that abstraction from dibromoacetonitrile is plausible. In the product searches to be described, methane was frequently added as a vibrational relaxant. For reference, the rate of H atom abstraction by CN from CH_4 is[12] 8.3×10^{-13} molecules^{-1} cm^3 s^{-1} at 296 K.

Products from HCCN + NO. By permuting the atoms in the system, a number of potential reaction products can be listed for the reaction of HCCN with NO. Many of these are shown below, together with heats of reaction calculated from the relevant heats of formation:[13]

$$\mathrm{HCCN + NO \rightarrow HCN + NCO} \qquad \Delta H = -71 \text{ kcal/mol} \tag{R2a}$$

$$\mathrm{\rightarrow HNC + NCO} \qquad \Delta H = -58 \text{ kcal/mol} \tag{R2b}$$

$$\mathrm{\rightarrow HNCO + CN} \qquad \Delta H = -56 \text{ kcal/mol} \tag{R2c}$$

$$\mathrm{\rightarrow OH + NCCN} \qquad \Delta H = -49 \text{ kcal/mol} \tag{R2d}$$

$$\mathrm{\rightarrow HOCN + CN} \qquad \Delta H = -34 \text{ kcal/mol} \tag{R2e}$$

$$\mathrm{\rightarrow HCN + CNO} \qquad \Delta H = -6 \text{ kcal/mol} \tag{R2f}$$

$$\mathrm{\rightarrow HCO + CNN} \qquad \Delta H = 14 \text{ kcal/mol} \tag{R2g}$$

$$\mathrm{\rightarrow C_2H + N_2O} \qquad \Delta H = 16 \text{ kcal/mol} \tag{R2h}$$

$$\mathrm{\rightarrow HCNO + CN} \qquad \Delta H = 16 \text{ kcal/mol} \tag{R2i}$$

$$\mathrm{\rightarrow HONC + CN} \qquad \Delta H = 29 \text{ kcal/mol} \tag{R2j}$$

Six of the above channels are exothermic. Even given the uncertainties (conservatively estimated[13] to be as high as ±10 kcal/mol for channels 2f−j) that arise from the fact that the heats of formation of HCCN and the various HCNO isomers result from theoretical calculations and not from experiment, it is clear that at room temperature, none of the channels (2g−j) can possibly contribute to the overall reaction process.

Scanning the appropriate regions of the infrared for products of the six exothermic channels, we observed HCN, which, in the presence of NO, was formed in an amount roughly a factor of 3 greater than that produced by photolysis alone. We did not see OH[14] or HNCO.[15] Nor were signals observed in the OH stretch region of HOCN which has been seen in matrix isolation.[16] Unfortunately, the fundamental frequencies of CN, NCO, CNO, and NCCN, the other species produced in these exothermic channels, are not in a region of the spectrum accessible to the color-center laser.

In addition, we observed that HNC, which was formed in small amounts in the absence of NO by photolysis, was suppressed when NO was added to the reaction system. As the concentration of added NO increased, the HNC absorption monotonically decreased, and the HNC signal rose and leveled off more rapidly. Since HNC does not react with NO, this observation suggests that it is formed from the photolytic process by a secondary reaction of dibromoacetonitrile with a species that reacts preferentially with NO. We postulated earlier that CN radicals from R1c are the source of HCN and HNC in the photolysis. At room temperature, the only open reaction channel between CN and NO[17] is one in which CN combines with NO to form ONCN via third-body stabilization. This reaction has been extensively studied with Ar and N_2 as the third body but not with He or CH_4. At 10 Torr of Ar, the effective bimolecular rate constant is[17] approximately 1.5×10^{-12} molecules^{-1} cm^3 s^{-1}. Thus it is plausible that NO competes with dibromoacetonitrile for CN.

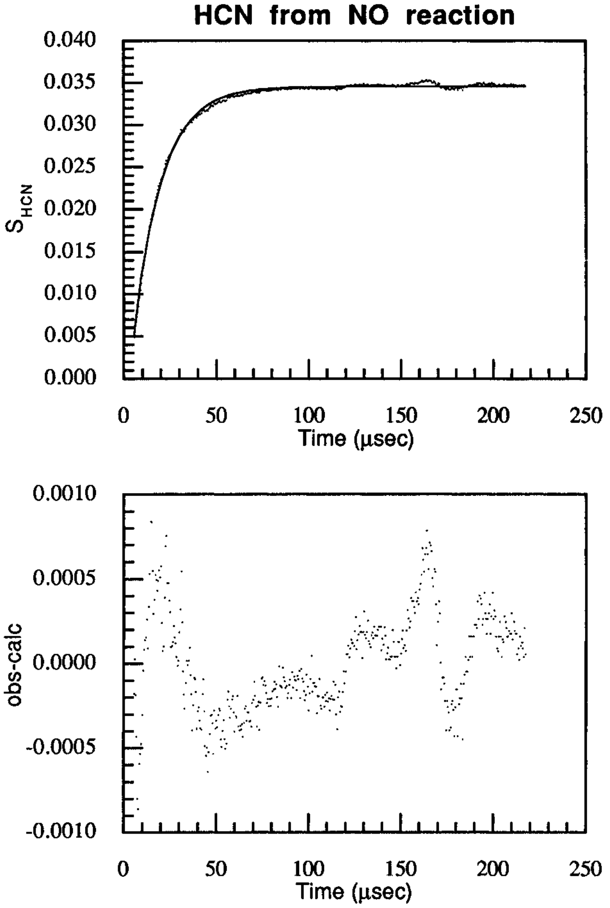

Figure 5. HCN from reaction of HCCN with NO fit with equation for product of first-order reaction, $S_{HCN} = S_0(1 - \exp(-bt))$; 70 mTorr NO; 11.6 Torr total pressure; residuals are shown under the plot. The ordinate scale is in base e absorbance units.

A search for the products of some of the endothermic channels (R2g−R2j) was also made. Neither C_2H,[18] which has a very large absorption cross section due to the vibronic nature of its infrared transition, nor HONC, whose low-resolution spectra has been recorded by using matrix isolation techniques,[16] were detected. However, we did observe a small absorption from HCNO.[19] As direct production of HCNO through the endothermic channel 2h seems impossible, HCNO must be a secondary product.

To determine whether HCN was formed directly by reaction R2a, its time dependence was measured. If HCN is formed in its vibrational ground state in a single step, its formation should mirror the destruction of HCCN, and its concentration should grow according to the equation

$$[\mathrm{HCN}] = [\mathrm{HCN}]_f[1 - \exp(-k_{\mathrm{eff}}t)] \tag{7}$$

where the subscript f denotes the final (or longtime) value of the concentration and k_{eff} is the effective rate of disappearance of HCCN, which is approximately equal to k_2[NO]. Accordingly the measured HCN time profile was fitted to an equation of the form $[\mathrm{HCN}] = [\mathrm{HCN}]_f[1 - \exp(-bt)]$, and the constant b adjusted to give a best fit to the experimental data. Figure 5 shows the fit obtained. For the experiment shown, b was estimated to be 6.5×10^4 s^{-1}; k_2[NO] was calculated, using the newly measured rate constant, to be 8.6×10^4 s^{-1}. Considering that the HCN profile appears to be slightly biexponential with a long-term component contaminating the fit, these numbers can be considered to be in reasonable agreement.

Unfortunately attempts to perform similar experiments for HCNO were inconclusive because the S/N ratio obtained for this species was too small to allow reliable time profiles to be obtained.

HCCN + O_2. A number of reaction products can be listed for the reaction of HCCN with O_2. Many of these are shown below, together with heats of reaction calculated from the relevant heats of formation:[13]

$$HCCN + O_2 \rightarrow HCN + CO_2 \qquad \Delta H = -176 \text{ kcal/mol} \qquad \text{(R3a)}$$

$$\rightarrow HNCO + CO \qquad \Delta H = -171 \text{ kcal/mol} \qquad \text{(R3b)}$$

$$\rightarrow HNC + CO_2 \qquad \Delta H = -164 \text{ kcal/mol} \qquad \text{(R3c)}$$

$$\rightarrow HOCN + CO \qquad \Delta H = -146 \text{ kcal/mol} \qquad \text{(R3d)}$$

$$\rightarrow HCNO + CO \qquad \Delta H = -100 \text{ kcal/mol} \qquad \text{(R3e)}$$

$$\rightarrow HCO + NCO \qquad \Delta H = -72 \text{ kcal/mol} \qquad \text{(R3f)}$$

$$\rightarrow HCCO + NO \qquad \Delta H = -47 \text{ kcal/mol} \qquad \text{(R3g)}$$

$$\rightarrow OH + CO + CN \qquad \Delta H = -34 \text{ kcal/mol} \qquad \text{(R3h)}$$

$$\rightarrow HCO + CNO \qquad \Delta H = -7 \text{ kcal/mol} \qquad \text{(R3i)}$$

$$\rightarrow HNO + CCO \qquad \Delta H = 2 \text{ kcal/mol} \qquad \text{(R3j)}$$

$$\rightarrow C_2H + NO_2 \qquad \Delta H = 26 \text{ kcal/mol} \qquad \text{(R3k)}$$

This reaction is somewhat more complicated since there are nine exothermic channels plus a thermoneutral one as opposed to six exothermic channels for the NO reaction. However, many of the products listed are observable in the infrared wavelength region of the color center laser. High-resolution spectra have been reported for HCN,[7] HNCO,[15] HNC,[8] CO_2,[9] HCNO,[19] and NO.[20] A low-resolution spectrum of HOCN,[16] measured in a matrix, has also been recorded. In addition, HCO, which is a product of two of the three channels that do not produce species with observable IR fundamentals (with frequencies greater than 2950 cm^{-1}), is rapidly converted by O_2 to HO_2, which has a well-known[21] fundamental near 3320 cm^{-1}.

A search for all of the molecules listed above was made. However, only HCN, HNC, and CO_2 were positively identified as products. No absorptions were observed corresponding to HNCO, HCNO, HOCN, C_2H, NO, or HO_2. Time profiles for all of the observed molecules are shown in Figure 6. As can be seen, the largest signal was obtained for HNC. The HNC and the HCN signals were at least 5 times larger in the presence of O_2 than in its absence. If the HCN and HNC signals produced by photolysis in the absence of O_2 are, as postulated, formed from H atom abstraction by CN, they should be completely suppressed upon addition of O_2 as a result of the rapid reaction between CN and O_2. The rate constant for this reaction, which produces NCO + O is[12] 2.4×10^{-11} $molecules^{-1}$ cm^3 s^{-1} at 296 K.

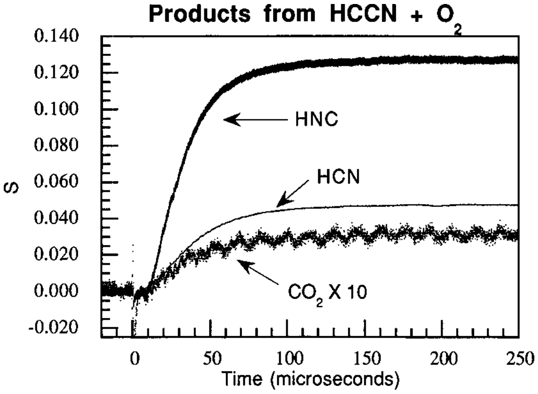

Figure 6. Time profiles of products of HCCN + O_2: HCN, HNC, and CO_2; with 0.7 Torr of O_2; total pressure of 11.6 Torr. The ordinate scale is in base e absorbance units.

Analysis of the HCN signal resulting from the addition of O_2 revealed that it was produced more slowly than HCCN was removed. The production rate increased upon the addition of excess methane, which is an efficient relaxer of vibrational excited HCN, but still the rate of growth of the HCN signal was smaller than the rate of removal of HCCN. When an attempt was made to estimate the first-order rate constant for the production of HCN from the reaction of HCCN with O_2 by using eq 8 in a manner identical with that used for the reaction with NO, a good fit to the data could not be obtained, because the early growth is too slow as compared with the later growth. This kind of behavior is characteristically seen when a species is produced through one or more intermediate steps. When a fit was forced, the resulting rate constant for the production of HCN was 40% of that for removal of HCCN. A similar situation was encountered when an attempt was made to fit the time profiles of HNC and CO_2. The rate constant obtained from a forced fit of the CO_2 data was about the same as that from HCN; the rate constant from a forced fit of the HNC rise was about 35% faster. Close examination of early time behavior revealed that there is an induction period of about 10 μs in all three cases before the signals from these species start to rise. SF_6 should be reasonably effective in relaxing CO_2. We found that the rise time of the CO_2 signal decreased somewhat upon addition of SF_6. The rise time of HNC was not affected significantly by the addition of either CH_4 or SF_6.

Discussion

In the reaction between HCCN and NO, chemical intuition suggests that the first step is the formation of an adduct between the two species, and it seems likely that the adduct bond will be between the terminal carbon of HCCN and the N of NO. Maclagan[22] has begun ab initio calculations on this system and finds a ΔE(298 K) of −63 kcal/mol for the formation of the *cis* form of this adduct with a *trans* form less stable by about 1 kcal/mol. A crude RRKM calculation of the unimolecular redissociation rate back to reactants of the adduct formed from room-temperature reactants gives a rate constant of 2×10^7 s^{-1}.

The magnitude of this rate indicates that re-dissociation will compete with collisional stabilization at pressures of a few Torr. Therefore if no rearrangement or decomposition channels were accessible, one might expect that the rate of reaction (to the adduct) would increase as the pressure is raised from 6 to 30 Torr.

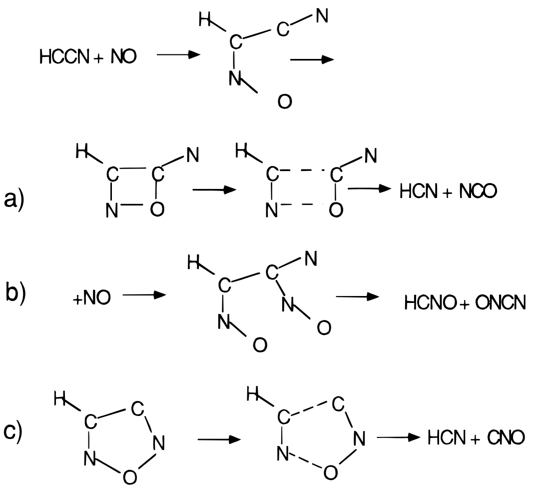

Figure 7. Possible geometries for HCCN + NO reaction channels. See text for discussion of these three channels.

However, Maclagan's initial calculations indicate that cyclization of the *cis* adduct for the cyclic structure shown in Figure 7a is feasible and that the energy of the transition state for this rearrangement is approximately 15 kcal/mol below the energy of the reactants. A crude RRKM calculation indicates that the rate of such a cyclization is at least 2 orders of magnitude faster than redissociation to reactants. Therefore, if it proves to be energetically possible for the cyclic structure to break up as shown in Figure 7a, this pathway would seem a plausible route to HCN. The completion of Maclagan's calculations should provide a clearer picture of what can be taking place.

Guided by theoretical work[23] on the HCCO + NO system, which in many ways is similar to that investigated here, an isomerization/fragmentation pathway leading to the exothermic reaction product, HCN, is shown in Figure 7a. This pathway mirrors one of the energetically favorable rearrangements identified by Nguyen et al.[23] as having accessible entrance channels. In the present study HCN was observed as a major product, formed at a rate equal to that at which HCCN was destroyed. Therefore, it is reasonable to assume that it is formed directly as indicated in Figure 7a, although formation from a secondary reaction with NO or the photolyte cannot be entirely ruled out.

If the mechanism is that of Figure 7a, which is analogous to the pathway proposed by Nguyen *et al.*,[23] our failure to observe HNCO formed by H atom abstraction by NCO from dibromoacetonitrile is easily explained by the rapid reaction[17] between NCO and NO which has[24] two roughly equal channels:

$$\mathrm{NCO} + \mathrm{NO} \rightarrow \mathrm{N_2O} + \mathrm{CO} \qquad 44\% \qquad \text{(R5a)}$$

$$\rightarrow \mathrm{CO_2} + \mathrm{N_2} \qquad 56\% \qquad \text{(R5b)}$$

and a rate constant of 3.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 296 K. However, no CO_2 could be observed as a product in the NO system.

The observation of HCNO as a reaction product in the HCCN + NO reaction cannot be explained by the endoergic channel 2i. A second reaction must be occurring. The observation of HCNO could be interpreted as evidence that at least some HCCN·NO collision complexes are stable enough to survive to a collision with a second NO when they could react to form HCNO + ONCN as illustrated in Figure 7b. Alternatively, CNO could be produced by channel 2f through a five-membered ring intermediate as depicted in Figure 7c (such a five-membered ring intermediate was not proposed by Nguyen et al.). This CNO could abstract H from the precursor to make HCNO. Both H atom abstraction channels to make HCNO and to make HONC are exothermic.[13] There appear to be no measurements of any CNO H-atom abstraction rates or of the reaction rate between CNO and NO.

While there are a multitude of plausible exothermic channels associated with the reaction of HCCN with molecular oxygen, most can be eliminated because at least one of the resulting products is not observed. Only HNC, HCN, and CO_2 were observed as products. Since the ground vibrational states of these species were formed more slowly than HCCN was destroyed, we cannot tell whether they were formed by the highly exothermic direct reactions (3a and 3c) into vibrationally excited states, some of which were indeed observed or were created via secondary processes.

No CHNO isomers were detected, although a lack of knowledge of the strengths of their infrared absorptions prevents us from being sure that none were present. We can, however, be certain that virtually no C_2H or HCO was formed. Previously we have been able to detect C_2H at a concentration estimated[25] to be less than 10^{12} molecule cm^{-3}. Therefore, although this species is quite reactive, it should have been detectable at short reaction times if it had been formed in significant amounts. Also we should have been able to detect HO_2, which is formed from HCO, since it has been observed in the past[26] with good S/N.

An ab initio investigation of the potential energy surfaces involved in the reaction of HCCN with O_2 seems highly desirable. Without guidance from such a calculation, we feel it is pointless to speculate about the pathway of this reaction, especially in view of our doubts that any of the observed products are produced directly by the reaction.

Conclusions

The overall rate constants for reaction of HCCN with O_2 and NO have been determined using pseudo-first-order methods. These rates have been found to be $(3.5 \pm 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for reaction with NO and $(1.8 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} for reaction with O_2. Several products for these reactions were identified. From reaction with NO, HCN, and HCNO were found, and HCN could be a primary product. From reaction with O_2, HCN, HNC, and CO_2 were observed. None of these species are believed to be produced directly by the reaction.

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