in HI of  $G(H)_{HI} = 11.6$ . Using literature data on W and M/N values of hydrogen halides as cited in ref 25 one can estimate  $G(\mathbf{H})_{\mathrm{HI}}$  as  $12.5 \pm 1.5$ .

Rate Constants. In addition to the information on product vields, our measurements allowed us to derive a number of rate constants for elementary reactions. Table II summarizes these results and compares them with literature data as far as available. The agreement between these data, obtained by different experimental techniques, is very good.

Acknowledgment. We are grateful to Dr. P. B. Pagsberg for suggesting this investigation. The authors thank P. L. Genske, A. Nielsen, and J. Nielsen for technical assistance.

# Kinetics of the HCN + NO<sub>2</sub> Reaction behind Shock Waves<sup>†</sup>

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The kinetics of the HCN + NO<sub>2</sub> reaction has been studied behind incident shock waves (T = 1329-1846 K, P = 1.7-12.6 atm) by using dilute mixtures of the reactants in argon. The rate of reaction was measured by monitoring the disappearance of NO<sub>2</sub> absorption at 450 nm. The time-dependent emissions due to NO\*, OH\*, and NO<sub>2</sub>\* were also followed at 237, 307.2, and 427.5 nm, respectively. The 427.5-nm emission was due primarily to the chemiluminescent recombination reaction  $O + NO (+M) \rightarrow NO_2^*$  (+M) and provided a qualitative indication of oxygen-atom concentration during the reaction. The products of the reaction were determined by chemical analysis of samples heated by reflected shock waves and gas dynamically quenched. The reaction rate was independent of HCN concentration within experimental error:  $-d(NO_2)/dt = 4.90 \times 10^{11}$  $\exp(-43300/RT)(Ar)^{1.03}(HCN)^{-0.03}(NO_{2})^{0.65}$  mol cm<sup>-3</sup> s<sup>-1</sup>. The results indicate that the reaction proceeds by a nonbranching chain process initiated by NO<sub>2</sub> unimolecular dissociation, NO<sub>2</sub> + M  $\rightarrow$  NO + O + M, enabling an upper limit to be placed on the rate constant for any direct reaction between HCN and NO<sub>2</sub>. The emission measurements showed that there is a sudden increase in O atoms and electronically excited NO and OH at that point in the reaction when the NO<sub>2</sub> is almost depleted, signaling the onset of a second stage of the reaction. Modeling calculations have been carried out to simulate the course to the reaction using elementary reactions and available rate data. The calculations suggest that the chain carriers in the HCN +  $NO_2$  reaction are O, OH, CN, and NCO, that significant amounts of  $O_2$  and HCN remain at the end of the first stage of reaction, and that the second stage begins because of NO<sub>2</sub> depletion when the reaction  $O + NO_2 \rightarrow O_2 + NO$  can no longer suppress the O atoms being generated by the reaction  $CN + O_2 \rightarrow NCO + O$ .

# Introduction

Interest in the high-temperature reactions of HCN has grown in recent years following the discovery by Fenimore<sup>1</sup> of "prompt NO" in the early portion of the reaction zone of fuel-rich hydrocarbon flames. This NO apparently could not be accounted for by the well-known Zeldovich mechanism<sup>2</sup> involving atmospheric nitrogen:

$$0 + N_2 \rightarrow NO + N \tag{A}$$

$$N + O_2 \rightarrow NO + O \tag{B}$$

Fenimore suggested that prompt NO arose through cyanide intermediates formed from hydrocarbon radicals, e.g.

$$CH + N_2 \rightarrow HCN + N$$
 (C)

More recently, other investigators have measured HCN in the hydrocarbon flames,<sup>3-7</sup> and it now appears that HCN is the dominant nitrogenous species (other than  $N_2$ ) leaving the primary reaction zone of hydrocarbon flames, regardless of whether the nitrogen comes from atmospheric or fuel nitrogen. Although the reactions responsible for the formation and the subsequent destruction of HCN are not certain, there is considerable evidence that the oxidation of HCN leads to the formation of NO. Thus, it is im-

portant to know the rates and pathways of reactions of HCN (and CN radicals) with  $O_2$ , the nitrogen oxides (NO,  $N_2O$ ,  $NO_2$ ), and other species. Merryman and Levy<sup>8</sup> have recently observed appreciable amounts of  $NO_2$  in the early reaction zone of methane flames, indicating that it too is somehow involved in the complex sequence of events leading to NO formation in flames.

Our interest in the HCN +  $NO_2$  reaction arises from the fact that these two species (as well as NO, HCHO, and  $N_2O$ ) are produced in the thermal decomposition of RDX (cyclotrimethylenetrinitramine) and other nitramines (compounds with  $>N-NO_2$  groups) used as propellants and explosives. Thus, the HCN +  $NO_2$  reaction may play a role in the primary flame zone of burning nitramine propellants, and it is of interest to know how the kinetics of this reaction compares with that of the very fast HCHO + NO<sub>2</sub> reaction.<sup>9</sup>

Very little is known about the reaction of HCN and CN with the nitrogen oxides. Drummond<sup>10</sup> has measured ig-

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nition delays for HCN +  $N_2O$  and  $C_2N_2$  +  $N_2O$  from 1500 to 2000 K. Boden and Thrush<sup>11</sup> and Mulvihill and Phillips<sup>12</sup> have reported rate constants for the CN + NO  $\rightarrow$  $N_2$  + CO reaction (in cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, 3 × 10<sup>11</sup> at 687 K and  $7.3 \times 10^{12}$  at 1500 K, respectively). It is not known whether HCN reacts directly with NO, NO<sub>2</sub>, or  $N_2O$  (and if so by what pathway), and there are no rate data for the possible reactions of CN with NO2 and N2O. With regard to HCN + NO<sub>2</sub>, the preferred pathway would be one of the following:

 $HCN + NO_2 \rightarrow CN + HONO$  $\Delta H = 45.0 \text{ kcal/mol}$ (D)

> $\rightarrow$  HNO + NCO  $\Delta H = 21.7 \text{ kcal/mol}$ (E)

The first is analogous to other known reactions involving H abstraction by NO<sub>2</sub> to form nitrous acid, while the second involves more complex bond rearrangements and might therefore be expected to have an activation energy  $(E_{s})$  considerably higher than the endothermicity of the reaction. Either pathway could be faster than unimolecular dissociation of NO<sub>2</sub>

 $NO_2 + M \rightarrow NO + O + M$  $\Delta H = 73.3 \text{ kcal/mol} (1)$ 

for which  $E_a = 65.6 \text{ kcal/mol.}^{13}$  The results of this study suggest that this is not so-that at high temperatures and for low concentrations NO<sub>2</sub> dissociation is, in fact, faster than any direct reaction between fuel and oxidizer.

# **Experimental Section**

The experiments were carried out in a 5.3-cm i.d. stainless-steel shock tube described elsewhere.<sup>14</sup> Most shocks were driven by helium. Temperature and pressure of the shocked gas  $(T_2 \text{ and } P_2, \text{ respectively})$  were varied independently from run to run by using various combinations of initial sample pressure  $(P_1)$  and diaphragmbursting pressure  $(P_4)$ . For the rate measurements, the  $P_1$  values were varied from 60 to 600 torr. Diaphragms were soft aluminum, 0.508, 0.635, or 1.016 mm in thickness, scored to burst reproducibly at pressure differences of roughly 14, 20, and 38 atm, respectively. In order to further extend the range of pressures, some shocks at the highest bursting pressures were driven by hydrogen. For these the sample pressures for the same shock temperatures were approximately twice as high as those for the shocks driven by helium.

For each experiment, the initial incident shock temperature  $T_2$ , pressure  $P_2$ , and density  $\rho_2$  were computed from the known initial temperature  $T_1$  and pressure  $P_1$  and the measured shock velocity  $u_1$  at the window location, assuming ideal gas behavior, equilibration of rotational and vibrational energies, and no reaction. The density ratio across the shock wave,  $\rho_2/\rho_1$ , was also calculated for each shock and used to convert all measured times or rates from laboratory to gas-particle coordinates. The NASA-Lewis CEC 71 program<sup>15</sup> was used for the calculations, in conjunction with JANAF thermochemical data.<sup>16</sup> Based on

past experience, corrections to the temperatures, densities, and measured reaction times for the effects of boundary layer formation and shock deceleration would be unimportant because of the high pressures and the short measurement times employed in this study. Effects due to heat of reaction would probably be somewhat larger but were nevertheless neglected because of uncertainty as to the heat of reaction and the proper way to make a correction when measuring rates by the "initial-slope" method. Presumably, heat of reaction effects would be fairly small for mixtures as highly diluted as in this study ( $\sim 99\%$  inert gas).

The hydrogen cyanide was obtained as an 8% mixture (in helium) from Matheson. It was removed from the helium by cryogenic trapping, subjected to two bulb-tobulb vacuum distillations, and stored in liquid nitrogen until needed. The nitrogen dioxide was Matheson (minimum 99.5%) and was distilled once before use. The argon was Matheson ultrahigh purity (minimum 99.999%). The mixtures were prepared in 35-L stainless-steel tanks to a pressure of 750 torr and allowed to mix for several hours. Since the  $NO_2$  content never exceeded 1%, its partial pressure ( $\leq 7.5$  torr) was sufficiently low that the 2NO<sub>2</sub> =  $N_2O_4$  equilibrium did not have to be taken into account in preparing the mixtures. The composition and the purity of the mixtures were checked by infrared spectroscopy. For reflected-shock experiments (product analysis, emission spectra), helium (Matheson ultrahigh purity, minimum 99.999%) was used as the reactant diluent instead of argon. This made it possible to obtain reflected-shock temperatures that fell in the same temperature range as the incident-shock experiments, without having to change to very low bursting pressure diaphragms.

The rate of the HCN +  $NO_2$  reaction was measured by monitoring the disappearance of NO<sub>2</sub> absorption at 450 nm. Light from a high-intensity dc tungsten lamp was focused at the center of the shock tube through a 2.5-mm vertical slit placed near the first window. The light emerging from the opposite window passed through a second 2.5-mm slit and was focused onto the entrance slit of a 0.25-m grating monochromator (Jarrel Ash 82-410) set to 450 nm. Entrance and exit slits were 2 mm wide, and the grating dispersion was 3.3 nm/mm, giving a 6.6-nm band-pass (half-width). The light was detected by a RCA 1P28 photomultiplier, and the resulting signal recorded photographically from a Tektronix 7603 oscilloscope operated in the dc mode, generally at a 50  $\mu$ s cm<sup>-1</sup> sweep speed. The rise time of the electronics was  $2-3 \mu s$ , while that defined by the optics (window slit width divided by shock velocity (~1.1-1.4 mm  $\mu$ s<sup>-1</sup>)) was between 1.8 and  $2.3 \ \mu s$  for most experiments. Experiments were carried out with the light source turned off to confirm that the 450-nm absorption traces were not affected by light emission from the reacting gases.

The optical setup for the separate emission measurements was essentially the same as for the absorption measurements at 450 nm, with the exception that the tungsten light was not used, and the gain of the photomultiplier was increased by a couple of orders of magnitude by increasing its supply voltage. Experiments were carried out at a large number of wavelengths where likely reaction intermediates might be expected to emit. In the final series of experiments to be described here, emission intensity, I, vs. time was measured for the  $A^2B_1-X^2A_1$  system of NO<sub>2</sub> at 570.0 and 427.5 nm, the  $\nu' = 0$ ,  $\nu'' = 1$  band of the

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 $A^2\Sigma^+-X^2\Pi$  system of NO at 237.0 nm, and the  $\nu'=0, \nu''$ = 0 band of the  $A^2\Sigma^+ - X^2\Pi$  system of OH at 307.2 nm. For the measurements at 237.0 and 307.2 nm, the 1.6 nm/mm low blaze wavelength grating of the monochromator was used, and the slits were reduced from 2 to 1 mm to reduce the band-pass to 1.6 nm.

The identity of species emitting in the different spectral regions for reacting HCN/NO<sub>2</sub> mixtures was determined by several techniques. In the visible region (400-700 nm) emission spectra were obtained for reflected-shock-heated samples; the amount of light collected was increased manyfold by measuring the light emitted in the direction of the axis of the shock tube. For these experiments, the standard end plate of the shock tube was replaced with another having a large (>53 mm) quartz window. The exit slit of the monochromator was replaced with a Polaroid film pack containing ASA 3000 speed black and white film. Although the focal zone of the monochromator was not flat, the spectra were quite good over the roughly 100-nm range made possible by the opening in the monochromator housing. Diffuse spectra were more easily obtained with a 0.5- or 1.0-mm entrance slits; a 0.1-mm entrance slit was generally used for spectra with discrete lines. Mercury lines were superimposed on the spectra for calibration purposes. Despite the use of fast film and end-on viewing, the short exposure time made it necessary also to use more concentrated mixtures (1% HCN + 2% NO<sub>2</sub> and 3% HCN +6% NO<sub>2</sub> in helium) than those used for the rate measurements, as well as higher temperatures (e.g.,  $T_5 =$ 2000-2200 K), although some spectra of NO<sub>2</sub> were obtained at temperatures as low as 1600 K. The second technique involved use of a Princeton Applied Research series 1200 optical multichannel analyzer (OMA) with the 0.25-m monochromator. The high gain of the OMA made it possible to obtain side-view spectra behind incident shock waves using lower temperatures and more dilute mixtures, but only about 30 nm could be covered in one experiment because of the size of the sensing element of the OMA. The third technique was used in the UV region. It involved time-resolved measurements using photomultiplier detection, as described in the previous paragraph. The UV spectrum was first "scanned" at low resolution (band-pass  $\sim 10$  nm) by making a series of near-identical shocks, the measuring wavelength being changed for each successive shock. In regions where emission was observed, additional shocks were made with higher resolution (band-pass  $\sim 1$ nm) in order to further define the position of the emission bands. Although somewhat tedious, this technique was quite effective and provided unambiguous identification of the NO and OH bands.

For the product-analysis experiments, a valve connected to a small hole in the end plate of the shock tube was manually opened immediately after initiating the shock, and a 25-cm<sup>3</sup> stainless-steel cell having silver chloride windows and an 8-cm path length was filled with reacted gas to a pressure of 6.8 atm, and the infrared spectrum run on a PE-421 spectrometer. The observed absorptions were converted to component partial pressures by using calibration spectra obtained with known partial pressures of the observed species at the same 6.8-atm total pressure. No techniques were used to increase the quenching rate, minimize secondary shocks, or prevent mixing of the shocked gas with driver gas, as in "single-pulse" shock tube techniques.<sup>17</sup> This was adequate, however, since no attempt was made to derive kinetic data from the measured products, and since ratios of products are relatively in-



Figure 1. Absorption traces at 450 nm. 0.25% HCN + 1.00% NO2. Top: T = 1397 K, P = 5.97 atm. Bottom: T = 1684 K, P = 5.01atm.

sensitive to variations in temperature and pressure.

### Results

The rate of the HCN +  $NO_2$  reaction—and its dependence on temperature, density, and mixture composition—was determined by following the rate of  $NO_2$ consumption at 450 nm, over the temperature range 1329–1846 K and the pressure range 1.7–12.6 atm. A total of 47 experiments were carried out, using four reaction mixtures: (A) 1.00% HCN + 1.00% NO<sub>2</sub>; (B) 1.00% HCN + 0.40% NO<sub>2</sub>; (C) 0.50% HCN + 1.00% NO<sub>2</sub>; and (D) 0.25% HCN + 1.00% NO<sub>2</sub>, the remainder being argon.

Figure 1 shows the appearance of the  $NO_2$  absorption traces at 450 nm for two experiments. Arrival of the shock wave at the window position compresses (and heats) the mixture, resulting in an increase in NO<sub>2</sub> absorption. This absorption then decreases because of consumption of the NO<sub>2</sub>. The 100% (full transmission) and 0% (zero transmission) base lines are recorded before the experiment with the shock tube evacuated and the light beam blocked, respectively. Note that, even for a  $4:1 \text{ NO}_2/\text{HCN}$  ratio, all of the  $NO_2$  is consumed by reaction during the measurement time at the higher temperatures. This suggests extensive formation of NO and/or  $O_2$  in the reaction. The decadic extinction coefficient,  $\epsilon$ , of NO<sub>2</sub> was measured for each experiment from the calculated postshock NO<sub>2</sub> concentration and the measured absorption at  $t = t_i$  (i.e., after shock compression but before any significant amount of  $NO_2$  decomposition has occurred). It was found to decrease from about 110 L mol<sup>-1</sup> cm<sup>-1</sup> at 1300 K to 65 L mol<sup>-1</sup> cm<sup>-1</sup> at 1900 K and, based on least-squares analysis for 47 experiments, could be represented by

$$\epsilon(T) = 205.9 - 0.0739T \tag{I}$$

A negative temperature coefficient ( $\epsilon(T) = 140.1 - 0.0274T$ ) was also found in a previous study involving shock-heated  $NO_2$  at somewhat lower temperatures (850–1600 K).<sup>14</sup>

For each experiment, the rate of NO<sub>2</sub> consumption was determined from the initial slope of the absorption trace by using the relation

$$\frac{-d(NO_2)}{dt} = \frac{0.4343S(NO_2)_i}{C(\rho_2/\rho_1)I_i \log (I_0/I_i)} \text{ mol } \text{cm}^{-3} \text{ s}^{-1}$$
(II)

where  $(NO_2)_i$  is the initial concentration of  $NO_2$  in the shocked mixture, S is the initial slope, C is the seconds per unit horizontal distance on the trace,  $I_i$  is the distance between the 0% base line and the trace at  $t = t_i$ ,  $I_0$  is the



Figure 2. Arrhenius plot for  $NO_2$  disappearance in HCN +  $NO_2$  reaction, eq III.

distance between the 0% and 100% base lines, and the density ratio across the shock wave  $(\rho_2/\rho_1)$  corrects for the flow velocity of the shocked gas past the observation windows, i.e., converts from laboratory to gas coordinates. The slope S was measured by using a line drawn through that portion of the trace corresponding to the first few percent of reaction.

The measured rates were used to determine the partial reactant orders, the preexponential factor, and the "activation energy" (overall temperature dependence) of the reaction. An iterative computational procedure was used, the best-fit parameters being those that produced the lowest standard deviation for the activation energy and the preexponential factor, A, in the least-squares analysis for the resulting Arrhenius plot. Best fit was obtained with

$$\frac{-d(NO_2)}{dt} = 4.90 \times 10^{11} \exp(-43300/RT) \times (Ar)^{1.03} (HCN)^{-0.03} (NO_2)^{0.65} \text{ mol cm}^{-3} \text{ s}^{-1} (III)$$

The standard deviations for log A and  $E_a$  are 0.117 and 830, respectively. The corresponding Arrhenius plot is shown in Figure 2. It can be seen that the rate depends strongly on the concentrations of NO<sub>2</sub> and inert gas but is independent, within experimental error, of the HCN concentration. (If the HCN order is held at zero in the calculations, the resulting  $A, E_a$ , and orders for argon and NO<sub>2</sub> are  $6.75 \times 10^{11}$ , 43 300, 0.97, and 0.69, respectively). The activation energy is about 43 kcal/mol, and the total order is 1.65.

Equation III suggests the importance of NO<sub>2</sub> dissociation in the HCN +  $NO_2$  reaction. In fact, for typical experimental conditions, the rate of NO2 disappearance is only a little greater than that for NO<sub>2</sub> dissociating in the absence of HCN. Consequently, an attempt was made to fit the data to a second-order rate expression (first order in Ar and NO<sub>2</sub>). The resulting rate constant is  $k = 2.7 \times 10^{14}$  $\exp(-46300/RT)$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, but the fit is much worse than that shown in Figure 2, the points for mixtures A and B (equimolar and HCN-rich, respectively) being too high, and those for mixtures C and D  $(NO_2$ -rich) being too low. For  $NO_2$  unimolecular dissociation in the second-order region,  $k = 1.1 \times 10^{16} \exp(-65600/RT)$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>,<sup>13</sup> the activation energy being 22 kcal/mol greater than for the  $HCN + NO_2$  reaction. The implication of these results is that the HCN +  $NO_2$  reaction proceeds via a chain mechanism initiated by NO<sub>2</sub> unimolecular dissociation, the steps after initiation lowering the apparent activation energy and NO<sub>2</sub> order. The rate of reaction, relative to



**TRANSMITTANCE** 

**Figure 3.** Infrared spectrum of sample heated by reflected shock and quenched. 3% HCN + 3% NO<sub>2</sub> + 94% He,  $T_5 = 1702$  K,  $P_5 = 3.08$  atm. Sample pressure, 6.8 atm in 8-cm cell.

500

2000

WAVENUMBER, CM-I

that of  $NO_2$  dissociation, indicates that the chain length is relatively short, especially at the higher temperatures. The shape of the absorption traces (Figure 1) indicates a linear, or nonbranching, type process.

The results for the 47 experiments at 450 nm are given in Table I, which gives for each the initial temperature  $(T_1)$ and pressure  $(P_1)$ , the measured shock velocity  $(u_1)$ , the calculated shock temperature  $(T_2)$ , the density ratio  $(\rho_2/\rho_1)$ , the total postshock density [M], the initial postshock concentrations of HCN and NO<sub>2</sub>, the extinction coefficient  $(\epsilon)$  of the shocked NO<sub>2</sub>, the measured rate of NO<sub>2</sub> disappearance (eq II), and log k based on eq III.

Figure 3 shows the infrared spectrum of a sample extracted from the end of the shock tube after reflectedshock heating and gas dynamic quenching. In addition to reaction products, the spectrum shows the presence of unreacted HCN and NO<sub>2</sub>. This is due to extensive postshock mixing and the fact that the gas originally located near the diaphragm is not reacted since the shock wave requires a certain distance to form from the coalescing pressure waves produced during diaphragm rupture. Consequently, only ratios of infrared-active products can be determined with any degree of certainty. The products observed, and the frequencies  $(cm^{-1})$  at which they were measured, are as follows: CO (2130), CO<sub>2</sub> (620, 670, 3720), NO (1900), and  $N_2O$  (1290, 2240). In addition, some  $H_2O$ and  $N_2$  are undoubtedly formed; the  $H_2O$  peaks were too small to measure accurately, however, and  $N_2$  is, of course, not infrared active.

The results of six experiments with an equimolar mixture, and an  $NO_2$ -rich mixture, are given in Table II, along with the calculated reflected-shock temperature and pressure (these are approximate for reasons discussed in the Experimental Section). The temperatures and the pressures were such that the reaction undoubtedly went to "completion" before quenching began. Completion, for this reaction, does not correspond to thermodynamic equilibrium; consequently, useful information about the course of the reaction can be obtained from the measured reaction products.

The formation of large amounts of NO is not surprising for a reaction involving  $NO_2$ , since  $NO_2$  is frequently only reduced as far as NO at moderately high temperatures and pressures. On the other hand, the formation of small amounts of  $N_2O$  might not have been anticipated. For both mixtures, the NO yield decreases with increasing temperature, indicating increased  $N_2$  formation at the higher temperatures (the concomitant pressure changes are assumed to have much less effect on the product dis-

TABLE I: Experimental Parameters, Absorption Measurements at 450 nm

						10 <sup>5</sup> ×	10" ×	107 ×		104 ×	
						[M].	[HCN].	[NO,].	$\epsilon$ , L	(rate),	
		P.,	$U_1, mm$			mol	mol	mol	mol <sup>-1</sup>	mol	log k-
expt	$T_1$ , K	torr	$\mu s^{-1}$	$T_{2}, K$	$\rho_2/\rho_1$	cm <sup>-3</sup>	cm - 3	cm <sup>-3</sup>	cm <sup>-1</sup>	cm <sup>-3</sup> s <sup>-1</sup>	(eq III)
A1	299	175	1.112	1347	3.284	3.08	3.08	3.08	114	0.946	4.70
A2	299	150	1.174	1472	3.357	2.70	2.70	2.70	106	2.81	5.26
A3	299	125	1.259	1653	3.444	2.31	2.31	2.31	88.3	9.98	5.93
$\mathbf{A4}$	299	105	1.310	1768	3.491	1.97	1.97	1.97	79.3	19.6	6.34
A5	299	200	1.273	1684	3.458	3.71	3.71	3.71	87.8	30.9	6.08
A6	299	250	1.207	1541	3.392	4.55	4.55	4.55	97.4	12.1	5.52
A7	299	300	1.127	1377	3.302	5.31	5.31	5.31	104	3.81	4.91
$A8^a$	299	440	1.241	1614	3.427	8.09	8.09	8.09	84.5	90.4	5.98
A9	300	225	1.226	1583	3.408	4.11	4.11	4.11	99.3	15.6	5.71
A10	300	80	1.203	1533	3.385	1.45	1.45	1.45	121	1.43	5.42
A11	300	65	1.284	1710	3.465	1.21	1.21	1.21	82.9	5.36	6.12
$B1^a$	299	500	1.195	1522	3.350	8.98	8.98	3.59	76.5	16.4	5.43
$B2^a$	299	570	1.153	1435	3.305	10.1	10.1	4.04	98.7	8.11	5.03
$B3^a$	299	425	1.255	1652	3.410	7.77	7.77	3.11	71.4	45.9	5.98
B4	300	275	1.154	1438	3.301	4.85	4.85	1.94	84.9	2.71	5.09
B5	301	300	1.134	1398	3.277	5.25	5.25	2.10	87.6	2.23	4.94
<b>B</b> 6	301	200	1.273	1695	3.421	3.64	3.64	1.46	57.8	20.0	6.16
B7	301	230	1.217	1571	3.367	4.13	4.13	1.65	76.8	7.69	5.66
<b>B</b> 8	301	158	1.293	1740	3.439	2.89	2.89	1.16	56.6	18.6	6.29
$C1^a$	300	575	1.181	1496	3.339	10.3	5.13	10.3	97.7	33.3	5.37
$C2^{a}$	300	500	1.210	1557	3.369	9.00	4.50	9.00	90.8	42.7	5.57
C3	300	300	1.159	1450	3.315	5.32	2.66	5.32	103	5.42	5.05
C4	299	250	1.203	1541	3.366	4.51	2.26	4.51	95.7	10.1	5.44
C5	299	307	1.144	1418	3.302	5.44	2.72	5.44	104	5.43	5.04
C6	299	200	1.264	1674	3.426	3.67	1.84	3.67	87.0	21.8	5.92
C7	299	160	1.341	1851	3.492	3.00	1.50	3.00	61.1	75.3	6.61
C8	299	160	1.159	1449	3.319	2.85	1.42	2.85	103	1.98	5.06
C9	301	170	1.126	1384	3.275	2.97	1.49	2.97	108 ·	1.26	4.83
C10	300	140	1.203	1542	3.362	2.52	1.26	2.52	101	4.69	5.53
C11	301	118	1.249	1642	3.407	2.15	1.07	2.15	96.7	11.6	6.03
C12	301	95	1.30 <del>9</del>	1779	3.460	1.75	0.876	1.75	76.7	15.8	6.31
C13	301	70	1.281	1715	3.435	1.28	0.640	1.28	91.7	6.55	6.16
C14	301	60	1.338	1846	3.484	1.11	0.557	1.11	77.2	10.3	6.45
$D1^a$	302	582	1.125	1387	3.261	10.1	2.52	10.1	98.3	10.6	4.87
$\mathrm{D}2^a$	302	430	1.210	1563	3.354	7.66	1.91	7.66	89.9	41.9	5.66
D3	302	300	1.130	1397	3.267	5.20	1.30	5.20	96.9	3.51	4.87
D4	302	250	1.191	1520	3.333	4.42	1.11	4.42	95.1	9.25	5.40
D5	302	200	1.265	1684	3.408	3.62	0.906	3.62	80.8	38.5	6.17
D6	302	<b>225</b>	1.210	1561	3.353	4.01	1.00	4.01	88.8	11.1	5.55
D7	302	175	1.280	1718	3.421	3.18	0.795	3.18	78.3	34.4	<b>6.2</b> 1
D8	302	170	1.124	1384	3.261	2.95	0.737	2.95	101	1.19	4.81
D9	302	140	1.178	1495	3.322	2.47	0.618	2.47	97.7	2.87	5.31
D10	302	110	1.242	1633	3.386	1.98	0.494	1.98	85.7	9.02	5.97
D11	302	85	1.332	1839	3.465	1.56	0.391	1.56	68.7	27.1	6.62
D12	302	120	1.096	1329	3.226	2.06	0.515	2.07	101	0.645	4.80
D13	301	95	1.195	1530	3.341	1.69	0.423	1.69	93.4	2.00	5.43
D14	302	70	1.303	1770	3.442	1.28	0.320	1.28	70.9	11.6	6.39

<sup>a</sup> Shocks driven with hydrogen instead of helium.

TABLE II: Product Analysis forReflected-Shock-Heated Samples<sup>a</sup>

mixture <sup>b</sup>	$T_{\mathfrak{s}}, \mathbf{K}$	P₅, atm	со	CO2	NO	N <sub>2</sub> O
2% HCN + 4% NO <sub>2</sub>	1603 1735 1976	$3.73 \\ 3.18 \\ 2.25$	1 1 1	5.1 6.0 5.1	3.8 3.9 1.3	0.12 0.11 0.06
3% HCN + 3% NO <sub>2</sub>	$1574 \\ 1755 \\ 2000$	3.87 2.95 1.99	1 1 1	$1.3 \\ 1.1 \\ 1.2$	$1.05 \\ 0.74 \\ 0.61$	0.02 0.02 0.01

 $^a$  Pressure or moles relative to CO, IR-active species only.  $^b$  Helium diluent.

tribution). More NO is formed, relative to CO, for the  $NO_2$ -rich mixture. The  $CO_2/CO$  ratio varies strongly with oxidizer/fuel ratio but does not seem to be a function of temperature. This type of data is as valuable as the real time measurements when validating a reaction mechanism.

An extensive effort was made to identify other UV or visible absorptions or emissions that could be used to further characterize the pathway of the  $HCN + NO_2$  reaction. These experiments were unsuccessful in that no absorptions or emissions were found which could be quantitatively related to ground-state radical or molecule concentrations. Qualitative information, however, was obtained regarding the time-dependent concentration of ground-state O atoms, as well as of electronically excited NO and OH.

Attempts were made to measure a number of species by UV absorption. The species and the central wavelengths investigated are as follows:  $N_2O$  (210, 215, 220 nm), NO (226.5, 237 nm), OH (283, 307.8, 313 nm), CH (315 nm), and CN (388.2 nm). No OH, CH, or CN absorptions were observed in experiments in which the light source was a continuous deuterium lamp, an acetylene oxygen flame (OH, CH), or a capillary discharge lamp<sup>18</sup> containing either water (for OH) or HCN (for CN). Some NO absorption

<sup>(18)</sup> S. H. Bauer, N. C. Rol, and J. H. Kiefer, *Planet. Space Sci.*, 3, 118 (1961).

TABLE III: Mixture and Temperature Dependence of the Maximum Second-Stage Emission Intensity<sup>a</sup>

$\lambda$ , nm	species	temp, K	no. of expts	$E_{a},$ kcal/mol	x	У	z	
427.5 ± 3.3	[0][N0]	1491-1879	15	51.6	0.12	0	0.47	
				51.5	0	0.08	0.51	
$307.2 \pm 0.8$	OH*	1581-1930	14	49.3	-1.09	0	1.70	
				49.4	0	-0.66	1.28	
$237.0 \pm 0.8$	NO*	1497-1893	15	55.5	-1.41	0	2.13	
				55.5	0	-0.86	1.58	

<sup>a</sup>  $I_{\max} \propto \exp(-E_a/RT)(Ar)^x (HCN)^y (NO_2)^z$ . Based on measurements with two mixturs: 0.5% HCN + 1.0% NO<sub>2</sub> + 98.5% Ar and 0.91% HCN + 0.40% NO<sub>2</sub> + 98.6% Ar; assuming either zero HCN dependence or zero Ar dependence.

was observed, but it was too weak relative to the rather high noise level ( $D_2$  lamp) to be of use. No  $N_2O$  was observed; this is consistent with the low yields shown in Table II.

Visible emission spectra recorded photographically through the end plate (reflected shock), or through the side windows using the OMA (incident shock), showed diffuse  $NO_2$  emission ( $A^2B_1-X^2A_1$  system) extending from the violet to about 650 nm, but most easily recorded between 550 and 650 nm. Some weak maxima at about 590, 606, 610, 613, 616, and 624 nm were presumably also due to  $NO_2$ . The spectra also showed an intense line at 589.6 nm due to the sodium doublet, a series of well-defined lines and band heads between 430 and 516 nm due to aluminum oxide (AIO),<sup>19</sup> and an unidentified line at 424 nm.

Using the side window photomultiplier tube scanning technique with incident-shock heating of argon-diluted mixtures containing 0.5% HCN + 1% NO<sub>2</sub>, we observed emission from both the (0,0) and 0,1) transitions of the  $A^2\Sigma^+-X^2\Pi$  system of NO at about 227 and 237 nm, respectively. The appearance of the NO emission traces is described below. Similarly, emission from the  $A^2\Sigma^+-X^2\Pi$  system of OH was observed in the vicinity of both the (0,0) bands (above 306 nm) and the (1,0) bands (above 281 nm).

Experiments were carried out to define the dependence of the emission at four wavelengths (237, 307.2, 427.5, and 570 nm) on temperature, pressure, and oxidizer/fuel ratio. At each wavelength, approximately 15 experiments were run, using two argon-diluted mixtures: 0.5% HCN + 1.0%NO<sub>2</sub> and 0.9% HCN + 0.4% NO<sub>2</sub>. All emissions were very temperature dependent and required several changes in the vertical sensitivity of the oscilloscope in going from the lowest to the highest temperature. Experimental data for emission experiments at 237, 307.2, and 427.5 nm are provided as supplementary material. (See paragraph at end of text regarding supplementary material.)

Measurements were made at 570 nm since at this wavelength the NO<sub>2</sub> emission is very strong and less influenced by self-absorption than at lower wavelengths. The recorded traces show emission rising rapidly to a maximum just after shock passage, and then decaying on the same time scale as the absorption at 450 nm, suggesting that the thermal-rather emission is due to than chemiluminescent-excitation of NO2. This was further confirmed by plotting log  $[I_{max}/(NO_2)_i]$  vs.  $1/T_2$ . The points fell along a straight line with a slope corresponding to  $E_{\rm a} \sim 45$  kcal/mol (50.1 kcal/mol would be expected for 570 nm ignoring possible pressure effects). For shocks in a mixture containing  $NO_2$  only, the measured peak intensities fell on the same line. Since all evidence pointed to a thermal excitation process, it was apparent that no information could be obtained from the 570-nm emission that had not already been obtained from the NO<sub>2</sub> absorption measurements.



**Figure 4.** Emission traces at 427.5 nm. 0.5% HCN + 1.0% NO<sub>2</sub>. Top: T = 1732 K, P = 2.61 atm. Bottom: T = 1879 K, P = 1.29 atm.

Measurements were also made of NO<sub>2</sub> emission at 427.5 nm, since emission might not be thermal when from the higher vibrational levels of the excited state. This wavelength was chosen as the lowest at which acceptable signal/noise ratios resulted. The emission traces are quite different from those at 570 nm, as shown in Figure 4, and show the existence of two reaction stages in the HCN +  $NO_2$  reaction. During the first stage, the emission is due largely to  $NO_2$  thermal excitation, as at 570 nm. During the second stage, the emission is almost entirely due to O + NO (+M)  $\rightarrow$  NO<sub>2</sub>\* (+M) recombination chemiluminescence with  $I(t) \propto (NO)(O)$ . Careful comparison of these emission traces with 450-nm absorption (or 570-nm emission) traces at the same temperature shows that the second stage begins when the  $NO_2$  is almost gone. The concentration of ground-state NO probably reaches a near-constant level by the end of the first-stage reaction. The traces therefore suggest that there is a sudden increase in the concentration of oxygen atoms at that point in the reaction. The maximum emission intensity,  $I_{max}$ , (i.e., millivolts on the oscilloscope) in the second stage was measured for each experiment. It was found to be higher for the NO<sub>2</sub>-rich mixture. The  $I_{max}$  values were fitted to an empirical equation, assuming a zero dependence on argon, or alternatively HCN, concentration (data from two mixtures are insufficient to determine three species orders). The results are shown in Table III below. An activation energy (O-atom temperature dependence) of 51.5 kcal/mol was found.

The appearance of the OH\* emission traces at 307.2 nm is shown in Figure 5. Some emission is observed during the first stage of reaction at the higher temperatures. As at 427.5 nm, there is a rapid increase in emission at the point where the NO<sub>2</sub> has almost disappeared, indicating a sudden growth in OH\*. The measured second-stage  $I_{max}$  values were even more strongly dependent on NO<sub>2</sub> con-

<sup>(19)</sup> R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra", 4th ed., Wiley, New York, 1976, and references therein.



**Figure 5.** Emission traces at 307.2 nm. 0.5% HCN + 1.0% NO<sub>2</sub>. Top: T = 1722 K, P = 2.61 atm. Bottom: T = 1824 K, P = 2.22 atm.



Figure 6. Emission traces at 237 nm. 0.5% HCN + 1.0% NO<sub>2</sub>. Top: T = 1722 K, P = 2.59 atm. Bottom: T = 1840 K, P = 4.28 atm.

centration or oxidizer/fuel ratio than for  $NO_2^*$  at 427.5 nm. The results are summarized in Table III.

The emission traces at 237 nm (see Figure 6) were very similar in appearance to those at 307.2 nm, indicating that NO\* also increases during the second stage of reaction. The mixture and temperature dependencies of the second-stage  $I_{\rm max}$  are similar to those for OH\*, as shown in Table III.

The duration of the second-stage emission is a measure of the second-stage reaction time. The dependence of the emission duration on temperature, pressure, and concentration therefore provides clues concerning the kinetics of the second-stage reaction. Therefore, the peak widths (i.e., time) at half-height  $(t^1)$  were measured for each experiment. Within experimental error, they were the same at all three wavelengths. Therefore, the measured widths for 41 traces at 237, 307.2, and 427.5 nm were used to obtain the expressions

$$\frac{1}{t^{1}(\rho_{2}/\rho_{1})} = \frac{1}{1.13 \times 10^{-3} \exp(-10930/RT)(Ar)^{-0.74}(NO_{2})^{1.09} s^{-1}}$$
 (IV)

$$\frac{1}{t^1(\rho_2/\rho_1)} =$$

 $2.75 \times 10^{-5} \exp(-10970/RT)(\text{HCN})^{-0.46}(\text{NO}_2)^{0.8} \text{ s}^{-1}$  (V)

Very similar expressions were obtained if only the righthand side of the peak (less influenced by overlap with first-state emission) was used. It can be seen that, with an activation nergy of about 11 kcal/mol and a total order of only 0.34-0.35, the second-stage reaction is not very dependent on either temperature or pressure.

## Discussion

The rate measurements, as summarized by eq III, strongly suggest that the HCN +  $NO_2$  reaction is initiated by unimolecular dissociation of  $NO_2$ 

$$NO_2 + M \rightarrow NO + O + M$$
  $\Delta H = 73.3 \text{ kcal/mol} (1)$ 

rather than by a direct bimolecular exchange reaction like HCN + NO<sub>2</sub>  $\rightarrow$  CN + HONO  $\Delta H = 45.0$  kcal/mol (D)

$$\rightarrow$$
 HNO + NCO  $\Delta H = 21.7 \text{ kcal/mol}$  (E)

This makes it possible to set an upper limit to  $k_{\rm D}$  and  $k_{\rm E}$ . Thus, for example,  $k_{\rm D} < k_1({\rm M})/({\rm HCN})_i$ . In the rate measurement described above, the lowest  $({\rm M})/({\rm HCN})_i$  was 100 (see Table I), which gives for  $k_{\rm D}$  and  $k_{\rm E}$  an upper limit of 10<sup>7</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at 1300 K, and 10<sup>10</sup> cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at 1800 K.

The kinetics of the HCN +  $NO_2$  reaction has been modeled by using a mechanism consisting of 18 species (plus inert gas) and 24 reversible elementary reactions. These reactions are listed in Table IV, along with the literature or estimated rate constants used in the computations. Following the customary procedure for a system about which not much is known, we included in the model only species in ground electronic states. Reactions involving two intermediates (e.g., NCO + O, H, OH) were generally not included since their rates would be low because of the low product of concentrations; this concentration factor is especially low early in the reaction. For the most part, we have attempted to model only the first stage of reaction, since for the second-stage reaction the only ground-state species profile measured was for O atoms, and it was never quantified by calibration. As will be seen, however, information has been obtained about the reactions responsible for the onset of the second-stage reaction.

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<sup>(20)</sup> P. B. Davies and B. A. Thrush, Trans. Faraday Soc., 64, 1836 (1968).

<sup>(21)</sup> M. A. A. Clyne and P. B. Monkhouse, J. Chem. Soc., Faraday Trans. 2, 73, 298 (1977).

<sup>(22)</sup> L. F. Phillips, Chem. Phys. Lett., 57, 538 (1978), showed that this reaction is pressure dependent at low temperatures, with  $k \sim 3 \times 10^8$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at 398 K and the highest pressure investigated (20 torr). The rate expression in Table IV is based on this value, and an assumed  $E_a$  of 5 kcal/mol.

<sup>(23)</sup> A fit to the values of ref 24 ( $3 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 687 K) and ref 12 (7.3  $\times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 1500 K).

<sup>(24)</sup> W. E. Wilson, J. Phys. Chem. Ref. Data, 1, 535 (1972).

TAB	LE I	V:	Reaction	Mechanism	and	Kinetic	Data <sup>a</sup>
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	forward reaction						reverse reaction				
reaction	$\Delta H$	log A	Ea	log k <sub>1500</sub>	ref	$\log A$	Ea	log k <sub>1500</sub>	ref		
(1) NO <sub>2</sub> + Ar $\neq$ NO + O + Ar	73.3	16.04	65.6	6.5	13	15.04	1.87	14.8	13		
$(2)$ O + NO, $\neq$ O, + NO	-45.9	13.0	0.60	12.9	13	12.23	46.5	5.5	13		
(3a) O + HCN ⋜ NCO + H	-1.7	12.72	8.1	11.5	<b>20</b>	13.38	9.53	12.0	с		
$(3b)$ O + HCN $\rightleftharpoons$ CN + OH	21.6	14.0	22.0	10.8	d	12.87	0.50	12.8	с		
$(4)$ H + NO, $\neq$ OH + NO	-28.9	14.46	0.81	14.3	21	12.64	30.4	8.2	с		
$(5a)$ HCN + $O_{3} \gtrsim$ NCO + OH	15.3	13.0	20.0	10.1	d	12.31	4.15	11.7	с		
(6) $OH + HCN \neq H_2O + CN$	4.4	11.22	5.0	10.5	<b>22</b>	11.12	0.87	11.0	с		
$(7a) \mathbb{C}N + NO_2 \rightleftharpoons NCO + NO$	-52.2	13.7	0	13.7	d	13.33	51.1	5.9	с		
$(8a)$ CN + NO $\rightleftharpoons$ CO + N <sub>2</sub>	-152	14.03	8.04	12.9	23	15.40	160	-8.0	с		
$(9a)$ NCO + NO <sub>2</sub> $\neq$ 2NO + CO	-29.2	13.0	0	13.0	d	10.98	33.0	6.2	с		
$(10a) \text{ NCO} + \text{NO} \neq \text{N}_2\text{O} + \text{CO}$	-66.5	12.0	0	12.0	d	13.48	66.9	3.7	с		
(11) $OH + CO \gtrsim CO_2 + H$	-25.0	11.49	0.60	11.4	<b>24</b>	13.86	24.7	10.3	с		
$(12a) CN + O_2 \rightleftarrows NCO + O$	-6.3	13.51	1.00	13.4	26	13.84	6.44	12.9	с		
$(13)$ H + O <sub>2</sub> $\rightleftharpoons$ OH + O	17.0	14.34	16.8	11.9	25	13.18	0.42	13.1	с		
$(14) O + H_2 \rightleftharpoons OH + H$	2.0	10.25	8.90 <sup>b</sup>	12.1	<b>25</b>	9.92	6.95 <sup>b</sup>	12.1	<b>25</b>		
$(15)$ H + HCN $\rightleftharpoons$ H <sub>2</sub> + CN	19.6	14.43	24.4	10.9	с	13.78	5.30	13.0	26		
(16) $CN + HCN \rightleftharpoons \tilde{C}_2N_2 + H$	-10.3	12.31	3.15	11.9	с	13.70	10.0	12.2	d		
$(17) C_2 N_2 + Ar \neq 2CN + Ar$	134.1	16.82	98.64	2.5	<b>27</b>	14.79	-26.6	18.7	с		
$(18a) \overline{CN} + O \rightleftharpoons CO + N$	-77.0	13.78	2.40	13.4	11	14.15	78.7	2.7	с		
$(19) \text{ HCN} + \text{Ar} \rightleftarrows \text{H} + \text{CN} + \text{Ar}$	123.8	16.76	117.1	-0.3	28	15.72	-4.87	16.4	с		
$(20) \operatorname{NO}_2 + \operatorname{NO}_2 \rightleftarrows \operatorname{NO}_3 + \operatorname{NO}_3$	22.8	11.59	23.9	8.1	29	12.09	-0.21	12.0	с		
$(21) \operatorname{NO}_3 + \operatorname{Ar} \rightleftharpoons \operatorname{NO}_2 + \operatorname{O} + \operatorname{Ar}$	50.5	17.93	44.8	11.4	30	15.54	-3.15	16.0	с		
$(22) \operatorname{NO}_2 + \operatorname{NO}_2 \rightleftarrows 2\operatorname{NO} + \operatorname{O}_2$	27.3	12.30	26.9	8.4	13	9.78	1.48	9.6	С		
$(23) \operatorname{NO}_3 + \operatorname{NO}_2 \rightleftarrows \operatorname{NO}_2 + \operatorname{O}_2 + \operatorname{NO}_2$	4.6	11.28	3.95	10.7	31	8.34	2.65	8.0	с		

<sup>a</sup>  $k = A \exp(-E_a/RT)$ , units cm, K, mol, s;  $E_a$  and  $\Delta H$  in kcal/mol. <sup>b</sup>  $AT \exp(-E_a/RT)$ . <sup>c</sup> From rate constant for forward (reverse) reaction and equilibrium constant. <sup>d</sup> Estimate.

At a typical temperature (i.e., 1700 K), reactions 1-12a in Table IV are found to be the most important, and the mechanism proceeds as follows. Most of the O atoms that are formed in reaction 1 react rapidly with  $NO_2$  (reaction 2) to form  $O_2$  which tends to build up as a stable intermediate. Some of the O atoms react with HCN (reaction 3a) to form the NCO radical and H atoms; the H atoms are quickly converted to OH by reaction 4 as long as NO<sub>2</sub> is present. As the concentration of  $O_2$  increases, reactions 5a and 6 quickly replace reaction 3 as the major HCNremoving steps, producing more NCO and OH and forming the CN radical. The CN is removed mainly by reaction 7a—at least if  $k_{7a}$  is high, as estimated— and to a lesser extent by reaction 16 (early) or 12a (later). The NCO is removed by reactions 9a and 10a;  $k_{9a}$  was made larger than  $k_{10a}$  so that N<sub>2</sub>O would be a minor product, as observed experimentally (see Table II). Late in the first-stage reaction,  $CO_2$  begins to be formed via reaction 11. Note that in this scheme there is no chain branching and that the chain length for  $NO_2$  is short, as observed experimentally by comparing the rate of NO<sub>2</sub> consumption with and without HCN. At the lower temperatures (e.g., below 1500 K) bimolecular  $NO_2$  decomposition (reaction 20) begins to compete with reaction 1. This, along with the chain steps, contributes to the low activation energy of the overall reaction compared to that of reaction 1.

Reaction 3b represents an alternative pathway for the O + HCN reaction. The tabulated rate constant (more or less an upper limit) for reaction 3b, compared to that for reaction 3a, indicates that the rates for the two pathways may be similar at the highest temperatures employed for the rate measurements (~1850 K). Pathway 3b does not change the course of the reaction, however, since reactions 3b and 7a produce the same products as reactions 3a and 4.

When this mechanism is used, the calculated rate of  $NO_2$ consumption is in satisfactory agreement with that predicted by eq III. At 1700 K, it is approximately 2.5–3 times faster than that calculated for  $NO_2$  alone under the same conditions (this ratio is larger at lower temperatures and decreases to less than 2.0 at 1900 K). The hydrogen cyanide disappears much more slowly than the NO<sub>2</sub>; however, this depends strongly on the value chosen for  $k_{5a}$ . The NO yield is high, as observed. The calculated CO<sub>2</sub>/CO ratio is small early in the reaction but subsequently increases in a way that suggests that much of the CO<sub>2</sub> must be formed in the second stage of reaction. In the calculations, OH builds up to quite high levels—concentrations that should have been observable in absorption. Actually, as discussed below, there are so many uncertainties in the elementary reaction pathways and rate constants for the proposed mechanism that detailed comparisons with experiment, sensitivity analyses, and "fitting" of rate constants is totally unwarranted at the present time for this system.

There are few or no rate data available for most of the important reactions involving HCN, CN, and NCO in the proposed mechanism. In particular, no data are available for reactions 5a, 7a, 9a and 10a, no measurements have been made of the temperature dependence of reaction 8a, and  $k_6$  has not been measured above 600 K. The value of  $k_{5a}$  largely determines how fast HCN is consumed. This was not measured experimentally in this study; consequently, it is not known how much of the HCN reacts during the first stage of the HCN + NO<sub>2</sub> reaction. Surprisingly, no studies of HCN oxidation by O<sub>2</sub> have been reported, although there has been a study of the C<sub>2</sub>N<sub>2</sub>/O<sub>2</sub> reaction.<sup>32</sup>

Moreover, there is some uncertainty as to the pathways for certain of the reactions in the proposed mechanism. For example, for reaction 3, the following low-energy possibilities exist:

 $\rightarrow$  OH + CN  $\Delta H = 21.6 \text{ kcal/mol}$  (3b)

 $\rightarrow$  CO + NH  $\Delta H = 28.1 \text{ kcal/mol}$  (3c)

<sup>(32)</sup> A. Lifshitz and M. Frenklach, Int. J. Chem. Kinet., 12, 159 (1980), and ref 1 therein.

Davies and Thrush<sup>20</sup> found evidence for pathway 3a but could not rule out reaction 3c on the basis of their data. For reaction 5 there are two low-energy pathways:

$$HCN + O_2 \rightarrow NCO + OH$$
  $\Delta H = 15.3 \text{ kcal/mol}$ 
(5a)

$$\rightarrow$$
 CHO + NO  $\Delta H = -0.3 \text{ kcal/mol}$  (5b)

We chose the first pathway by analogy with reaction 3, but this requires an activation energy of at least 15 kcal/mol, so some argument could be made for the second pathway. For reaction 12

 $CN + O_2 \rightarrow NCO + O$   $\Delta H = -6.3 \text{ kcal/mol}$  (12a)

$$\rightarrow$$
 CO + NO  $\Delta H = -108.8 \text{ kcal/mol}$  (12b)

Boden and Thrush<sup>11</sup> considered the first pathway to be the correct one. Basco<sup>33</sup> suggested that up to 15% might proceed by the second pathway, and Schmatjko and Wolfrum<sup>34</sup> report 6% under their experimental conditions. For reaction 18 the reaction takes place mainly by the first

$$CN + O \rightarrow CO + N$$
  $\Delta H = -77.0 \text{ kcal/mol}$  (18a)

$$\rightarrow$$
 NO + C  $\Delta H = 28.9 \text{ kcal/mol}$  (18b)

pathway,<sup>34-36</sup> although two electronic states of N can form exothermically<sup>37</sup> and it has been suggested<sup>35</sup> that the increase in rate for CN ( $\nu'' = 7$ ) may indicate the participation of the endothermic pathway 18b. This might be expected to occur at high temperatures as well, since at high temperatures higher vibrational levels are populated. For the reactions of CN and NCO with NO<sub>2</sub> and NO (reactions 7a-10a),

$$CN + NO_2 \rightarrow NCO + NO$$
  $\Delta H = -52.2 \text{ kcal/mol}$ 
(7a)

$$\rightarrow$$
 N<sub>2</sub>O + CO  $\Delta H = -118.7 \text{ kcal/mol}$  (7b)

 $CN + NO \rightarrow CO + N_2$   $\Delta H = -152.0 \text{ kcal/mol}$  (8a)

$$\rightarrow$$
 NCO + N  $\Delta H = 25.5 \text{ kcal/mol}$  (8b)

$$\rightarrow$$
 N<sub>2</sub>O + C  $\Delta H = 64.9 \text{ kcal/mol}$  (8c)

 $NCO + NO_2 \rightarrow 2NO + CO$   $\Delta H = -29.2 \text{ kcal/mol}$ (9a)

 $\rightarrow$  N + CO<sub>2</sub> + NO  $\Delta H = -5.4 \text{ kcal/mol}$  (9b)

$$\rightarrow N_2O + CO_2$$
  $\Delta H = 120.4 \text{ kcal/mol}$  (9c)

 $NCO + NO \rightarrow N_2O + CO$   $\Delta H = -66.5 \text{ kcal/mol}$ (10a)

$$\rightarrow$$
 NO<sub>2</sub> + CN  $\Delta H = 52.2 \text{ kcal/mol}$  (10b)

$$\rightarrow CO_2 + N_2$$
  $\Delta H = -34.4 \text{ kcal/mol}$  (10c)

there are also alternate pathways to those written in Table IV. Finally, there is the question of NCO dissociation

$$NCO + M \rightarrow N + CO + M$$
  $\Delta H = 48.5 \text{ kcal/mol}$ 
(24)

about which nothing is known. It could play a role at the higher temperatures, especially if reactions like reactions 9 and 10 are not as fast as estimated.



**Figure 7.** (A) Numerical simulation, major species. 0.5% HCN + 1.0% NO<sub>2</sub> + 98.5% Ar at T = 1800 K, P = 2 atm. (B) Numerical simulation, minor species. 0.5% HCN + 1.0% NO<sub>2</sub> + 98.5% Ar at T = 1800, K, P = 2 atm.

Despite all of these uncertainties concerning rate constants and pathways, the modeling calculations have provided insight into the types of elementary reactions occurring in the HCN +  $NO_2$  system. This is illustrated by Figure 7, A and B, which shows the computed profiles for 0.5% HCN + 1.0% NO<sub>2</sub> + 98.5% Ar at  $T_2 = 1800$  K,  $P_2 = 2$  atm. At about 500  $\mu$ s into the reaction, there is an accelerated growth in the concentrations of O, H, and H<sub>2</sub>, as well as a decrease in OH. The  $NO_2$  is almost gone at this point in the reaction. This would appear to correspond to the second-stage reaction, since the 427.5-nm emission indicates a rapid increase in O atoms to "superequilibrium" levels beginning just before the NO<sub>2</sub> disappears. An analysis of the computed results shows that the increase in O atoms is due to a decrease in importance of reaction 2 as the NO<sub>2</sub> is depleted. That is, while the NO<sub>2</sub> concentration is high, O atoms are mainly produced and removed by  $NO_2$  (reactions 1 and 2, respectively), with reaction 12a also contributing heavily to O-atom formation once the CN and  $O_2$  concentrations become high. As long as the  $NO_2$ concentration is high, the O atom concentration remains low. As the  $NO_2$  is depleted, reaction 2 becomes ineffective in removing O atoms. Reaction 1 slows also, but O atoms continue to be produced rapidly by reaction 12a (and to a small extent by reaction -14). As reaction 2 loses effectiveness, reaction -13 (and to a smaller extent reactions 3 and 18) are left as the O-atom removal steps; these, however, are much slower than reaction 2 had been, and consequently the O-atom concentration rises rapidly,

<sup>(33)</sup> N. Basco, Proc. R. Soc. London, Ser. A, 305, 107 (1968).

<sup>(34)</sup> K. J. Schmatjko and J. Wolfrum, Ber. Bunsenges. Phys. Chem.,
82, 419 (1978).
(35) H. Schacke, K. J. Schmatjko, and J. Wolfrum, Ber. Bunsenges.

<sup>(35)</sup> H. Schacke, K. J. Schmatjko, and J. Wolfrum, Ber. Bunsenges.
Phys. Chem., 77, 248 (1973).
(36) K. J. Schmatjko and J. Wolfrum, Symp. (Int.) Combust., [Proc.],

 <sup>(36)</sup> K. J. Schmatjko and J. Wolfrum, Symp. (Int.) Combust., [Proc.],
 16, 819 (1977).
 (37) R. G. Shortridge and M. C. Lin, J. Phys. Chem., 78, 1451 (1974).

precipitating the second-stage reaction which presumably eventually consumes the remainder of the  $O_2$  and HCN.

In the numerical model, the calculated time from shock heating to rapid radical growth (i.e., to the second stage of reaction) increases rapidly with decreasing temperature, as observed experimentally. However, this time, like the rate of NO<sub>2</sub> disappearance, is relatively insensitive to all rate constants except that of reaction 1. This is because the second-stage reaction begins when the NO<sub>2</sub> is almost depleted, while the rate of NO<sub>2</sub> disappearance is only a little higher than that for NO<sub>2</sub> decomposing in the absence of HCN. Thus, although the theoretical prediction of the second-stage reaction indicates that the proposed mechanism includes certain essential features of the reaction, no additional information concerning unknown rate constants and pathways can be derived by detailed comparisons between computed and experimental results.

The reactions responsible for the emissions at 307.2 and 237 nm cannot, of course, be deduced from the proposed mechanism. Excitation of OH\* and NO\* requires 93 and 120 kcal/mol, respectively, so very exothermic reactions are involved. One possibility is atom combination:

$$H + O \rightarrow OH^* \rightarrow OH + h\nu \qquad \Delta H = -102 \text{ kcal/mol}$$
(25)  

$$N + O \rightarrow NO^* \rightarrow NO + h\nu \qquad \Delta H = -151 \text{ kcal/mol}$$
(26)

This would be consistent with the observed and predicted increase in O-atom concentration in the second-stage reaction. Another, less likely, possibility is that OH and NO are excited by participation as third bodies in some highly exothermic combination reaction, e.g.

$$O + O + M \rightarrow O_2 + M \qquad \Delta H = -120 \text{ kcal/mol} \quad (27)$$
  
H + CN + M \rightarrow HCN + M \quad \Delta H = -124 \text{ kcal/mol} (27)  
(-19)

$$CN + CN + M \rightarrow C_2N_2 + M$$
  $\Delta H = -134 \text{ kcal/mol}$ 
(-17)

where M is OH or NO. In either case, a negative dependence of the peak emission intensity on inert gas concentration would be expected because of quenching and/or competition effects.

In the case of OH (but not NO), it could be argued that the emission is thermal rather than chemiluminescent in origin and therefore, at a given temperature, is proportional to the time-dependent concentration of ground-state OH during reaction. Although a thermal excitation process cannot be completely ruled out for OH\*, the close similarity of the OH\* and NO\* emission traces, the low temperature dependence for the OH\* emission (Table III, 49 kcal/mol) relative to that expected for thermal excitation (93 kcal/mol if OH concentration is temperature independent), and the fact that the predicted ground-state OH concentration actually decreases during the second-stage reaction (Figure 7B) all suggest a nonthermal excitation process.

In conclusion, although much has been learned in this first study of the HCN + NO<sub>2</sub> reaction, additional species measurements, and more rate and pathway data on contributing elementary reactions, will be required before the mechanism of the reaction can be truly established. Measurements of HCN and O<sub>2</sub> concentrations during the reaction would be especially valuable, as would also an independent study of the HCN/O<sub>2</sub> reaction. Successful measurement of reaction intermediates (H, OH, CN, NCO, etc.) during reaction would undoubtedly help determine the mechanism. Elementary reactions that need to be studied either experimentally or theoretically include the reaction of HCN with O<sub>2</sub>, the dissociation of NCO, and the reactions of CN and NCO with NO and NO<sub>2</sub>.

Supplementary Material Available: Experimental data for emission experiments at three wavelengths, including peak intensities used to derive expressions in Table III, and peak widths used to derive eq IV and V (1 page). Ordering information is given on any current masthead page.