Oxidation of Hydrogen Cyanide in Shock Waves. Formation of Nitrogen Monoxide¹

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The oxidation of HCN by O_2 or $O_2 + NO_2$ has been studied in shock waves over the temperature range 1450–2600 K and the pressure range 0.75-2.0 atm. The kinetics of the oxidation was monitored by following IR emission at 5.34 μ m and UV emission at 306.7 nm, simultaneously. Induction times τ_{IR} and τ_{OH} were defined as the time that the intensities of the IR and UV emissions began to rapidly increase, respectively. The induction time τ_{IR} for the HCN-O₂-Ar system could be represented by $\tau_{IR} = 10^{-12.45} \exp(90.1 \text{ kJ}/RT)[\text{HCN}]^{-0.66}$. [O₂]^{-0.01}[Ar]^{-0.26} s. When NO₂ was added to the HCN-O₂-Ar system, the induction time τ_{OH} became longer than that without NO_2 at temperatures below 2000 K. The experimental profiles of the IR and UV emissions and the dependences on temperature and on concentrations of reactants of $\tau_{\rm IR}$ and $\tau_{\rm OH}$ were well reproduced by computer simulation by using 46 elementary reactions. A proper mechanism for the oxidation and the resulting formation of NO is proposed.

Introduction

There have been many attempts to clarify the mechanism of NO formation during combustion of hydrocarbons. For example, in order to shed light on the mechanism of formation of prompt NO, Miyauchi et al.¹ have measured the concentrations of O, H, NO, O_2 , HCN, etc. in a premixed methane-oxygen-nitrogen flame. They suggested that the main route for the formation of prompt NO is as follows:

$$CH_2 + N_2 \rightarrow HCN + NH \xrightarrow{\text{oxidation}} NO$$

Fenimore² has studied the formation and destruction of NO in a fuel-rich flame in which the fuel nitrogen was added as ammonia or pyridine. By measuring the concentrations of HCN and NH_3 in addition to NO, he found that at first HCN is produced and then NH_3 and NO are produced, and suggested the following scheme:

Thus, it has been concluded that HCN plays an important role as an intermediate for the formation of NO during the combustion of hydrocarbons.

There have been some studies to explain the role of CN species in the formation and destruction of NO. For example, Mulvihill and Phillips³ have studied the breakdown of C_2N_2 in fuel-rich $H_2-N_2-O_2$ flames. They found that the following reactions are important:

$$CN + O_2 = NCO + O$$

 $NCO + O = NO + CO$
 $NCO + H = CO + NH$
 $NH + NO = products$

By using an atomic resonance absorption method, Roth et al.⁴ have measured the concentration changes of H and O atoms in shock-heated mixtures of HCN and N₂O which were highly diluted with Ar. The main reaction that they found is

HCN + O = NCO + H

Then, they determined the rate constant for the reaction to be $10^{13.86} \exp(-62.4 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. More recently, when we were preparing this paper, Fifer and Holmes⁵ reported the reaction of HCN + NO_2 in shock waves. They found that this reaction takes place in two stages; the first stage proceeds by a nonbranching chain process initiated by NO₂ unimolecular dissociation, and the second stage begins when NO_2 is almost depleted and is accompanied by a sudden increase in O atoms and electronically excited NO and OH.

In the present study, in order to clarify the detailed mechanism for the formation of NO from HCN, we studied the reactions HCN + O_2 and HCN + O_2 + NO₂ in shock waves by monitoring the IR emission at 5.34 μ m and the UV emission at 306.7 nm, and derived a reasonable mechanism to explain the experimental results for the three systems, $HCN + O_2$, $HCN + O_2 + NO_2$, and HCN+ NO_2 , studied by Fifer and Holmes.

Experimental Section

The shock tube used was made of stainless steel with a 9.4 cm i.d. It was described in a previous paper.⁶ All experiments were performed behind reflected shock waves. The initial sample pressure was kept at 15 or 30 torr and the pressure of driver gas (H_2) was varied. The compositions of the reaction mixtures were as follows: (A) 2% HCN-2% O₂-96% Ar; (B) 1% HCN-1% O₂-98% Ar; (C) 1% HCN-2% O₂-97% Ar; (D) 2% HCN-1.75% O₂-0.5% NO₂-95.75% Ar.

Hydrogen cyanide was generated by pouring a 50% sulfuric acid aqueous solution onto potassium cyanide, and dried by passing through calcium chloride and phosphorus pentoxide. The gas thus obtained was purified by trap-

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Figure 1. Typical experimental profiles of the UV (upper trace) and the IR (lower trace) emissions: (a) 2% HCN-2% O₂-96% Ar mixture, $\rho_5 = 9.807 \times 10^{-6}$ mol cm⁻³, $T_5 = 1847$ K; (b) 2% HCN-1.75% O₂-0.5% NO₂-95.75% Ar mixture, $\rho_5 = 9.775 \times 10^{-6}$ mol cm⁻³, $T_5 = 1728$ K.

to-trap distillations. Commercial high-purity oxygen, nitrogen monoxide, and argon were used without further purifications.

The kinetics of the HCN + O_2 and HCN + O_2 + NO_2 reactions were monitored by following emission intensities at 306.7 nm and 5.34 μ m. The UV emission was detected by a photomultiplier after passing through a grating monochromator (half-width = 3.3 nm). The IR emission was detected by an InSb detector through an interference filter (half-width = 0.4 μ m). The output signals were fed to a preamplifier and then to a digital recorder connected to an oscilloscope and a pen recorder.

Typical examples of the output signals are shown in Figure 1 (a is for the 2% HCN-2% O_2 -96% Ar mixture and b is for the 2% HCN-1.75% O₂-0.5% NO₂-95.75% Ar mixture). The UV emission at 306.7 nm is due to OH* (electronically excited OH). The IR emission at 5.34 μ m is mainly due to NO, but some contributions from the symmetric stretching band of HCN and the bending band of H_2O are observed (see Figure 4). So that the experimental profile of the IR emission can be compared with the calculated one, it is necessary to obtain the emission intensities per unit concentrations of NO, HCN, and H₂O. Those of NO and H₂O were determined by shock heating 2% NO-98% Ar and 1% H₂-1% O₂-98% Ar mixtures, respectively. As emission just behind the shock front in the case of shock heating the HCN-O₂-Ar mixture is due to HCN (see Figure 1a), the emission intensity per unit concentration of HCN was determined from this intensity.

Results

For the $HCN-O_2-Ar$ system, both the UV and the IR emission intensities increase rapidly after some time lag, as seen in Figure 1a. Then, induction times τ_{OH} (the time elapsed between reflected shock arrival and the onset of the rapid increase in the UV emission) and τ_{IR} (the time elapsed between reflected shock arrival and the onset of the rapid increase in the IR emission) were defined as shown in Figure 1. It is assumed that τ_{OH} corresponds to the time for the product of O and H atom concentrations to increase rapidly. This is confirmed later by the simulation using elementary reactions listed in Table I, that is, OH* is mainly produced by the reaction H + O + Ar = OH* + Ar. τ_{IR} corresponds mainly to the time until NO begins to be produced rapidly (see Figure 4).

In general, it is known that when NO₂ is added to oxidation systems the oxidation is accelerated. Therefore, the influence of NO₂ addition on the HCN-O₂-Ar system was also examined in this study. As Figure 1b shows, the UV



Figure 2. Observed and simulated induction time $\tau_{\rm IR}$ as a function of reciprocal temperature. Solid lines represent the simulated induction time using the 46 elementary reactions listed in Table I.

emission behavior of the HCN-O₂-NO₂ system is the same as that of the HCN– O_2 system, although, at temperatures lower than 2000 K, τ_{OH} becomes longer than for mixtures without NO_2 . When NO_2 is present, the UV emission is always observed just behind the shock front. This may be due to the thermal emission of NO_2 . This emission decreases with time, suggesting that the NO_2 reacts during the induction time. The IR emission behavior of the $HCN-O_2-NO_2-Ar$ mixture is very different from that of the mixture without NO_2 . That is, the IR emission begins to increase from the shock front and after some time lag a second stage increase is observed. The onset of this second stage increase corresponds to the onset of the increase in the UV emission. At higher temperatures, however, the first and second stage increases of the IR emission become undistinguishable. Two reaction stages were also observed by Fifer and Holmes⁵ for the HCN-NO₂ system.

Figure 2 shows the Arrhenius plot of τ_{IR} . It is recognized that the induction time is strongly influenced by the concentration of HCN but not by the concentrations of O_2 and Ar. This induction time is expressed by a least-squares analysis as

$$\tau_{\rm IR} = 10^{-12.45} \exp(90.1 \text{ kJ mol}^{-1}/RT) \times [\text{HCN}]^{-0.66} [\text{O}_2]^{-0.01} [\text{Ar}]^{-0.26} \text{ s}$$

In all the oxidation systems studied so far, except for the oxidation of cyanogen studied by Lifshitz et al.,⁷ a very strong dependence on the oxygen concentration has always been reported.

Figure 3 shows the Arrhenius plot of τ_{OH} . It is seen that the temperature dependence of τ_{OH} for the HCN-O₂-NO₂ system is greater than that for the HCN-O₂ system. For the HCN-O₂ system, this induction time is expressed by a least-squares analysis as

$$\tau_{\rm OH} = 10^{-13.42} \exp(101.6 \text{ kJ mol}^{-1}/RT) \times [\text{HCN}]^{-0.44} [\text{O}_2]^{-0.17} [\text{Ar}]^{-0.52} \text{ s}$$

It is possible to elucidate the mechanism of HCN oxidation by simulating the characteristic features of the UV and the IR emission behaviors and the dependences on the temperature and the reactants concentrations of $\tau_{\rm OH}$ and $\tau_{\rm IR}$. Elementary reactions and their rate constants used for the simulation are listed in Table I.

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Figure 3. Observed and simulated induction time $\tau_{\rm OH}$ as a function of reciprocal temperature. Solid lines represent the simulated induction time using the 46 elementary reactions listed in Table I.



Figure 4. Comparisons of the observed profiles (O, \bullet) of UV and IR emissions with calculated ones (solid lines) for four runs. Broken lines indicate calculated emission intensities of HCN, H₂O, and NO₂ for A and C: (A) 2% HCN-2% O₂-96% Ar, $\rho_5 = 9.849 \times 10^{-6}$ mol cm⁻³, $T_5 = 1743$ K; (B) 2% HCN-1.75% O₂-0.5% NO₂-95.75% Ar, $\rho_5 = 9.807 \times 10^{-6}$ mol cm⁻³, $T_5 = 1728$ K; (C) 2% HCN-2% O₂-96% Ar, $\rho_5 = 9.807 \times 10^{-6}$ mol cm⁻³, $T_5 = 1847$ K; (D) 2% HCN-1.75% O₂-0.5% NO₂-95.75% Ar, $\rho_5 = 9.812 \times 10^{-6}$ mol cm⁻³, $T_5 = 1851$ K.

Figure 4 shows comparisons of the experimental profiles of the UV and the IR emissions with calculated ones for the 2% HCN-2% O_2 -96% Ar and 2% HCN-1.75% O_2 -0.5% NO₂-95.75% Ar mixtures. As this figure shows, the characteristic features of the UV and the IR emissions for the mixtures with and without NO₂ are well simulated by using the elementary reactions listed in Table I.

The dependences on the temperature and the reactants concentrations of the induction times, τ_{IR} and τ_{OH} , are also well reproduced by the simulation. (The simulated induction times are shown by solid lines in Figures 2 and 3.)

Figures 5 and 6 show the changes with time of reactant and product concentrations for the mixtures of 2% HCN-2% O_2 -96% Ar and 2% HCN-1.75% O_2 -0.5% NO₂-95.75% Ar. The reaction conditions of Figures 5 and 6 are much the same except for the presence or absence of NO₂. The main products are NO, CO, H₂O, CO₂, and N₂ and the yields of these species are almost the same for both the systems. When NO₂ is present, the reaction is retarded and the concentrations of the reactants, HCN and O₂, begin to decrease rapidly after NO₂ is almost completely consumed.

It is very useful to test whether or not the reaction HCN + NO_2 studied by Fifer and Holmes⁵ is simulated by using the elementary reactions listed in Table I. Figure 7 shows the concentration changes of reactants and products calculated by using our mechanism for the same conditions of Fifer and Holmes' simulation (Figure 7 in Fifer and Holmes' paper). The calculated results of Fifer and Holmes and ours are the same for the rate of NO_2 disappearance and for the onset time of the rapid increase in the concentrations of O and H atoms. Thus the mechanism proposed to explain the reactions $HCN + O_2$ and $HCN + O_2 + NO_2$ is also able to explain the HCN + NO_2 reaction.

As shown in Figures 2, 3, 4, and 7, the experimental results for the HCN + O_2 , HCN + O_2 + NO_2 , and HCN + NO_2 reactions are reasonably reproduced from the elementary reactions listed in Table I. In order to clarify which elementary reactions play important roles for the formation of NO, we calculated at 10- μ s intervals the formation and destruction rates of each chemical species.

Figure 8 shows examples of these calculations for the mixture without NO₂. From Figure 8a, it is known that the main reactions for the formation of NO are reactions 12 and 26. It also becomes apparent from this figure that about 70% of the NO is produced by reaction 12. The NO thus produced is mainly converted to N₂ by reactions 16 and 25. The NCO, which is converted to NO by reaction 12, to N by reaction 13, and to NH by reaction 15, is



Figure 5. Time-dependent concentration changes of chemical species for 2% HCN-2% O_2 -96% Ar mixture. $\rho_5 = 9.849 \times 10^{-6}$ mol cm⁻³, $T_5 = 1743$ K.



Figure 6. Time-dependent concentration changes of the chemical species for 2% HCN-1.75% O₂-0.5% NO₂-95.75% Ar mixture. ρ_5 = 9.775 × 10⁻⁶ mol cm⁻³, T_5 = 1728 K.



Figure 7. Concentration changes calculated by using the elementary reactions listed in Table I for 0.5% HCN-1% NO₂-98.5% Ar mixture. $\rho = 1.355 \times 10^{-5}$ mol cm⁻³, T = 1800 K (the same conditions as those of Figure 7 in Fifer and Holmes' paper).

mainly produced by reactions 6 and 10, as shown in Figure 8b. The CN radical, which is converted to NCO by reaction 10, is mainly produced by reactions 5 and 7; O atoms are produced by reactions 10 and 19 and are converted to OH, NCO, and NO through reactions 5, 6, and 12, respectively.

Figure 9 shows examples of the rate calculations for the $HCN-O_2-NO_2$ system. As shown in this figure, the main reactions to produce NO from HCN do not change between the mixtures with and without NO_2 . It is seen, however, by comparing Figures 8 and 9, that the rate of each elementary reaction is retarded as long as NO_2 is present. This is explained as follows. In an early stage of reaction, significant amounts of O atoms produced by reactions 31 and 10 are converted by reaction 32 to O_2 and the rates of the reactions to produce important intermediates CN (reaction 5), NCO (reaction 6), etc. are retarded.

Figure 10 shows the schematic mechanism for the oxidation of HCN and the formation of NO. This mechanism was derived from the estimations of the rate of formation of each chemical species as described in part above.

Figure 11 shows the effects of reactions 12 and 13 on the rate of reaction (a is for the $HCN-O_2$ system and b is for



Figure 8. Calculated formation rates of NO and NCO for the $HCN-O_2$ system. Conditions are the same as those of Figure 4C. The numbers in the parentheses are the reaction numbers indicated in Table I.



Figure 9. Calculated formation rates of NO and NCO for the HCN– O_2 -NO₂ system. Conditions are the same as those of Figure 4D. The numbers in the parentheses are the reaction numbers indicated in Table I.

the $HCN-O_2-NO_2$ system). These two reactions have not yet been characterized well, and in our mechanism the rate

TABLE I: Elementary Reactions and Their Rate Constants

	reaction	rate constant ^a	ref	
(1)	HCN + Ar = H + CN + Ar	$10^{16.1} \exp(-417.1/RT)$	в	
(2)	$C_1N_1 + Ar = 2CN + Ar$	$10^{16.62} \exp(-412.7/RT)$	с	
(3)	$\dot{CN} + HCN = H + C_2N_2$	$10^{12.77} \exp(-6.44/RT)$	b	
(4)	$CN + H_2 = HCN + \dot{H}$	$10^{13.78} \exp(-22.2/RT)$	d	
(5)	$HCN + \hat{O} = CN + OH$	$10^{13.64} \exp(-62.0/RT)$	4	
(6)	HCN + O = NCO + H	$10^{13.86} \exp(-62.0/RT)$	4	
(7)	$HCN + OH = CN + H_2O$	$10^{13.30} \exp(-62.8/RT)$	е	
(8)	$C_2N_2 + O = NCO + CN$	$10^{13.4} \exp(-46.0/RT)$	f	
(9)	CN + O = CO + N	$10^{13.08}$	d	
(10)	$CN + O_2 = NCO + O$	$10^{13.31} \exp(-4.2/RT)$	d	
(11)	CN + OH = NCO + H	$10^{13.20}$	4	
(12)	NCO + O = CO + NO	$10^{15.00}$	est	
(13)	NCO + Ar = N + CO + Ar	$10^{13.0} \exp(-195.0/RT)$	est	
(14)	$NCO + N = N_2 + CO$	1 0 13.26	1	
(10)	NO + N = V + O	1013.19	4	
(10)	NO + N - NO + O	$10^{9.99}T^{1.0} \text{ orm}(-97.7/BT)$	8 a	
(17)	N + OH - NO + H	$10^{10} \exp(-27.7/101)$	B k	
(10)	H + O = OH + O	$10^{14.35} \exp(-70.3/RT)$	σ	
(20)	$O + H^2 = OH + O$	$10^{10.26}T^{1.0} \exp(-32.3/RT)$	h	
(20)	$H_{1} + OH = H + H_{1}O$	$10^{13.34} \exp(-21.5/RT)$	h	
(22)	$O + H_0 = 2OH$	$10^{13.83} \exp(-26.8/RT)$	h	
(23)	$NH + O_2 = NO + OH$	10 ^{10.0}	ĩ	
$(\overline{24})$	NH + O = NO + H	$10^{11.7}T^{0.5} \exp(-20.9/RT)$	l	
(25)	$\mathbf{NH} + \mathbf{NO} = \mathbf{N}_2 + \mathbf{O} + \mathbf{H}$	10 ^{12.19}	п	
(26)	$NH + OH = NO + H_2$	$10^{12.2}T^{0.56} \exp(-6.3/RT)$	m	
(27)	$CO + O_2 = CO_2 + O$	$10^{11.95} \exp(-180.9/RT)$	g	
(28)	$CO + OH = CO_2 + H$	$\log k = 10.83 + 3.94 \times 10^{-4} T$	i	
(29)	$N + CO_2 = NO + CO$	$10^{14.30}$	j	
(30)	$\mathbf{NH} + \mathbf{O} = \mathbf{N} + \mathbf{OH}$	$10^{12.0}T^{0.5} \exp(-0.4/RT)$	l	
(31)	$NO_2 + Ar = NO + O + Ar$	$10^{16.04} \exp(-272.0/RT)$	0	
(32)	$NO_2 + O = NO + O_2$	$10^{12.88} \exp(-1.8/RT)$	g	
(33)	$H + NO_2 = NO + OH$	$10^{14.43} \exp(-6.2/RT)$	0	
(34)	$2NO_2 = 2NO + O_2$	$10^{12.50} \exp(-112.6/RT)$	0	
(35)	$N + NO_2 = 2NO$	1012.67	8	
(36)	$N + NO_2 = O + N_2O$	10^{14} , $\frac{49}{10}$ arm (-8.0 / BT)	8 h	
(37)	$H + HO_2 = 2OH$	$10^{15.32} \exp(-3.0/RT)$	n h	
(30)	$HO_2 + HO_2 + HO_2 + HO_2$	$10^{13} e^{4} \exp(-191.3/RT)$	h	
(39)	$H + HO_2 - H_2 + O_2$ O + HO - OH + O	$10^{13.68} \exp(-4.9/RT)$	n	
(40)	$O + HO_2 = OH + O_2$ OH + HO = H O + O	$10^{13} exp(-4.2/RT)$	p n	
(41)	H + OH + Ar = HO + Ar	$10^{19.20}T^{-0.864}$	Р ø	
(43)	$H + O + Ar = OH^* + Ar$	$10^{13.08} \exp(-29.0/RT)$	a	
(44)	$OH^* + Ar = OH + Ar$	$10^{10.7}T^{0.5}$	a	
(45)	$OH* + H_0 = OH + H_0$	$10^{12.93}T^{0.5}$	q	
(46)	$\mathbf{OH*} = \mathbf{OH} + h\nu$	106.15	\hat{q}	
			-	

⁽⁴⁰⁾ ⁽



Figure 10. Schematic diagram of the mechanis of NO formation from HCN. The reaction numbers indicated in Table I are shown in parentheses.

constants of these reactions were estimated. It is seen that the rate of reaction is very sensitive to these reactions. If reaction 13 was eliminated from the mechanism, the reaction became very slow.

Discussion

There is no doubt that HCN is an intermediate for the formation of NO and is mainly produced by the reactions

$$CH + N_2 = HCN + N$$
$$CH_2 + N_2 = HCN + NH$$

On the other hand, for the conversion of HCN to NO, the following three routes have been postulated:

route 1HCN \rightarrow CN $\xrightarrow{O_2}$ CO + NOroute 2HCN \rightarrow NCO \xrightarrow{O} CO + NOroute 3HCN \rightarrow NCO(HNCO) \rightarrow NH_i $\xrightarrow{O,OH}$ NO



Figure 11. Time histories of HCN, NO, and NO₂ calculated with various values of k_{12} and k_{13} : NCO + O = CO + NO (12), $k_{12} = 10^{13.6}$ cm³ mol⁻¹ s⁻¹; NCO + Ar = N + CO + Ar (13) $k_{13} = 10^{15.0}$ exp(-195.0 kJ/*RT*) cm³ mol⁻¹ s⁻¹. (a) 2% HCN-2% O₂-96% Ar, conditions are the same as those of Figure 5. (b) 2% HCN-1.75% O₂-0.5% NO₂-95.75% Ar, conditions are the same as those of Figure 6.

For example, Miyauchi et al.¹ postulated route 1 and gave the rate constant for the reaction

$$CN + O_2 = CO + NO \tag{47}$$

as $10^{14.0}$ cm³ mol⁻¹ s⁻¹. Fifer and Holmes⁵ postulated the reaction

$$NCO + NO_2 = 2NO + CO \tag{48}$$

(corresponding to route 2). On the other hand, Fenimore² and Takagi et al.⁸ took into account route 3 but not routes 1 and 2. Mulvihill and Phillips³ considered routes 2 and 3 for the conversion of HCN to NO. As Figure 10 shows, our mechanism corresponds to that of Mulvihill and Phillips.

In a preliminary simulation, route 1 was included in the mechanism. In this case, the disappearance rates of reactants and the resulting formation rate of NO became very slow. This phenomenon can be easily explained by Figures 8b and 10. That is, by including reaction 47, the CN radical produced by reactions 4, 5, and 7 is smoothly converted by reaction 47 to the inert species CO and NO, and the formations of the important chain carrier species O and NCO by reaction 10 is retarded. The rate of NO formation becomes equal to the rate of CN formation and the contributions of reactions proceeding through NCO to the formation of NO become very small.

Although Fenimore² and Takagi et al.⁸ have not considered reaction 12 (route 2) as a reaction to produce NO, as Figure 8a shows, by taking into account reaction 12, this reaction becomes one of the main reactions for the formation of NO. As shown in Figure 11, even if reaction 12 was eliminated from the mechanism, NO was produced, although the rate of reaction became very fast. In this case, of course, NO is mainly produced by reactions 24 and 26 (route 3). Therefore, one may consider that reaction 12 is not so important. With regard to this problem, we have studied the oxidation of BrCN and the resulting formation of NO in shock waves.⁹ The BrCN molecule does not contain an H atom. Therefore during oxidation, NH_i species are not produced and reactions 24 and 26 cannot occur. For the mixture with $[BrCN]/[O_2] = 1$, the conversion of BrCN to NO was about 50%. To explain the mechanism for the formation of NO it was necessary to include reaction 12. The importance of this reaction has also been mentioned by Lifshitz and Frenklach⁷ in their study of C_2N_2 oxidation.

As has already been mentioned, for the $HCN-NO_2$ system the rate of NO_2 disappearance and the onset time of the second stage reaction are explained by the mechanism either of Fifer and Holmes or of ours. This is because the first stage reaction is mainly controlled by the dissociation of NO_2 (reaction 31). The main differences between Fifer and Holmes' mechanism and ours are as follows. They considered the reactions

$$NCO + NO_2 = 2NO + CO \tag{48}$$

$$k_{48} = 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

CN + NO₂ = NCO + NO (49)
$$k_{49} = 10^{13.7} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for the consumption of the NCO and CN species, reactions which were not taken into account in our mechanism. On the other hand, Fifer and Holmes did not consider the reaction

$$NCO + O = CO + NO$$
(12)

because of the low product of the concentrations of NCO and O. In our mechanism, reactions 10 and 12 are important for the formation of NO from HCN. Even if reactions 48 and 49 were added to our mechanism, the rate of NO₂ disappearance and the onset time of the second stage reaction did not change much. In this case, however, reaction 48 becomes one of the main reactions for the formation of NO, and reactions 10 and 12 are largely retarded as long as NO₂ is present.

Registry No. Hydrogen cyanide, 74-90-8; nitrogen monoxide, 10102-43-9.

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