Mixtures of cyanogen and nitrous oxide diluted in argon were shock heated to measure the ratio of the rate constants for

\[ \text{NCO} + \text{O} \rightarrow \text{CO} + \text{NO} \]  

(3)

and

\[ \text{NCO} + \text{M} \rightarrow \text{N} + \text{CO} + \text{M}. \]  

(4)

The diagnostic was narrow-line absorption of NCO at 440.479 nm using a remotely located cw ring dye laser source. By varying the mole fraction of nitrous oxide in the initial mixture and conducting otherwise identical experiments, we inferred at 2240°K

\[ k_3 / k_4 = 10^{3.54(0.34, -0.37)}. \]

Utilizing a recent determination of \( k_3 \) and previous measurements of the ratio \( k_3 / k_4 \), we recommend over the temperature range 2150 ≤ \( T \) ≤ 2400°K

\[ k_4 = 10^{16.8T^{-0.5} \exp[-24000/T]} \text{ cm}^3/\text{mole/s} \times 2.3, \times 0.4. \]

An additional mixture of cyanogen, oxygen, hydrogen, and nitrous oxide diluted in argon was shock heated and NCO was monitored to infer the rate constant for

\[ \text{NCO} + \text{H} \rightarrow \text{CO} + \text{NH} \]  

(5)

and the ratio \( k_6 / k_7 \):

\[ \text{C}_2\text{N}_2 + \text{H} \rightarrow \text{CN} + \text{H} \text{CN}. \]  

(6)

\[ \text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}. \]  

(7)

We found near 1490°K

\[ k_5 = 10^{13.7(0.42, -0.37)} \text{ cm}^3/\text{mole/s}, \]

and

\[ k_6 / k_7 = 0.81(0.89, -0.47). \]

These experiments also led to an estimate of the rate constant for

\[ \text{NCO} + \text{H}_2 \rightarrow \text{HNCO} + \text{H}, \]  

(8)

with the result, near 1490°K,

\[ k_8 = 10^{12.4(0.4, -0.7)} \text{ cm}^3/\text{mole/s}. \]
INTRODUCTION

NCO plays an important role in the mechanism of nitric oxide formation from nitrogen-containing fuels. In an earlier paper on cyanogen oxidation kinetics [1], we utilized measurements of CN, CO, and NO to examine the formation of NCO from C_2N_2 and CN. Subsequently, we developed a novel laser absorption diagnostic of NCO [2], and we used this technique to study NCO removal in an oxidizing medium [3]. In the present study, the NCO diagnostic was used again to measure other reactions involving NCO at high temperatures.

Mixtures of C_2N_2 and N_2O diluted in argon were shock heated to measure the ratio of the rate constants of reactions (3) and (4) at 2240°C, the rate constants for the other reactions significant at early times, reactions (1) and (2), being already well established [1]:

\[
\begin{align*}
\text{N}_2\text{O} + \text{M} & \rightarrow \text{N}_2 + \text{O} + \text{M}, \\
\text{C}_2\text{N}_2 + \text{O} & \rightarrow \text{CN} + \text{NCO}, \\
\text{NCO} + \text{O} & \rightarrow \text{CO} + \text{NO}, \\
\text{NCO} + \text{M} & \rightarrow \text{N} + \text{CO} + \text{M}.
\end{align*}
\]

Another mixture containing C_2N_2, O_2, H_2, and N_2O diluted in argon was shock heated at 1490°C to measure the rate constant of

\[
\text{NCO} + \text{H} \rightarrow \text{CO} + \text{NH},
\]

and the ratio \(k_6/k_7\):

\[
\begin{align*}
\text{C}_2\text{N}_2 + \text{H} & \rightarrow \text{CN} + \text{HCN}, \\
\text{CN} + \text{H}_2 & \rightarrow \text{H} + \text{HCN}.
\end{align*}
\]

In addition this mixture led to an estimate for the rate constant of

\[
\text{NCO} + \text{H}_2 \rightarrow \text{HNCO} + \text{H}.
\]

Previous work to establish \(k_3\) and \(k_4\) is limited primarily to our own shock tube work in which we determined the ratio \(k_3/k_4\) at 2150 and 2400°C from measurements of NO and CN [1], and \(k_1\) by monitoring NCO using laser absorption [3]. There are no previous data for \(k_5\) and \(k_6\); the limited data for \(k_6\) and \(k_7\) have been reviewed by Baulch et al. [4]. In addition, we note the recent shock tube work in our laboratory by Szekely, Hanson, and Bowman, who measured \(k_7\) in the range 2700 ≤ T ≤ 3500°C [5], and the reverse rate of reaction (6) in the range 2720 ≤ T ≤ 3070°C [6].

In this paper, the experimental facility and optical technique will be briefly described; then the data reduction and results for each of the mixtures will be presented.

EXPERIMENTAL

The experiments were conducted in a 15.24 cm internal diameter stainless-steel pressure-driven shock tube [7]. Shock speeds varied between 1.2 and 1.5 mm/μs with attenuation of 0.3%/m or less. Typical leak plus outgassing rates were 3–5 \(\times 10^{-5}\) Torr/min. Gases were taken directly from commercial cylinders (Matheson) with the following purities: O_2, H_2, and N_2O (>99.9%); C_2N_2 (1.01% diluted in argon; HCN and CNCI < 50 ppmv, O_2 < 20 ppmv, CO_2 < 20 ppmv).

The shock tube test section and laser absorption system for NCO are shown schematically in Fig. 1. The absorption from the \(P_2 + \text{P}_Q_{12}\) band head of the [A^2Σ^+(OO'OO') \leftarrow X^2Π([OO'OO'])] band of NCO at 440.479 nm (vac.) was used to monitor NCO. This system was described in detail elsewhere [3]. It consisted of an Ar^+ -pumped ring dye laser with a typical output power of 60 mW (single-mode) at 440.5 nm. After amplitude stabilization, the output was transported 65 m via a 200 μm optical fiber to the shock tube facility, where it was double-passed through the shock tube test section. The incident and return beams were filtered (FWHM: 40 nm, center at 450 nm) and monitored on separate detectors. The signals were electronically balanced prior to each experiment using small dc offset and gain adjustments on one of the differential amplifiers. The difference \((i_0 - i)\) and reference \((i_0)\) signals were recorded on two separate channels of a digital oscilloscope (Nicolet Explorer III, dc-coupled through a 100 kHz upper frequency cutoff filter). The data were subsequently transferred to a computer for analysis.
Six runs were conducted behind incident shock waves with the following mixtures and conditions: \( x_{\text{C}_2\text{N}_2} = 0.41\% \), \( 0.10 \leq x_{\text{N}_2\text{O}} \leq 0.42\% \), \( T_2 = 2240^\circ\text{K} \), \( p_2 = 0.65\text{ atm} \), and \( \rho_{21} = 3.57 \). (\( \rho_{21} \) is the density ratio across the shock and also the ratio of particle time to laboratory time.) The temperature of the experiments was set by considerations of growing interferences on the NCO absorption system from spontaneous emission at higher temperatures and by insufficient rates of NCO removal from reaction (4) at lower temperatures:

\[
\text{NCO} + \text{M} \rightarrow \text{N} + \text{CO} + \text{M}. \tag{4}
\]

An additional mixture of \( \text{H}_2 \), \( \text{O}_2 \), \( \text{N}_2\text{O} \), \( \text{C}_2\text{N}_2 \), and argon was shock heated with \( x_{\text{H}_2} = 0.58\% \), \( x_{\text{O}_2} = 0.09\% \), \( x_{\text{N}_2\text{O}} = 0.41\% \), \( x_{\text{C}_2\text{N}_2} = 0.40\% \), \( T_2 = 1490^\circ\text{K} \), \( p_2 = 0.63\text{ atm} \), and \( \rho_{21} = 3.34 \). Here, the temperature was set by considerations of growing interferences on NCO removal by reaction (4) at higher temperatures and diminishing confidence in the rate of reaction (1) at lower temperatures. Vibrational equilibrium of NCO was assumed in all experiments [3].

The transmission of the laser system is related to the level of NCO through the Lambert–Beer law,

\[
i/i_0 = \exp[-\beta(T)p_{\text{NCO}}L],
\]

where \( i/i_0 \) is the fractional transmission, \( \beta(T) \) is the absorption coefficient at 440.479 nm and the temperature \( T \), \( p_{\text{NCO}} \) is the partial pressure of NCO, and \( L \) is the path length (30.5 cm). \( \beta(T) \) has been experimentally determined in our laboratory at 1450°K [2] and can be extrapolated to other temperatures using a spectroscopic model [2].

### N\(_2\)O/C\(_2\)N\(_2\)/Ar Mixtures—Analysis and Results

#### a. Simplified Reaction Mechanism

A complete mechanism that encompasses 17 reactions in the C/N/O system was used in the data reduction (see Table 1), but a simplified description, useful in guiding the actual data interpretation, can be given as follows. \( \text{N}_2\text{O} \) decomposes exponentially to provide O-atoms, which rapidly reach a steady-state concentration; \( \text{C}_2\text{N}_2 \) then reacts to form NCO, which in turn is removed either by O-atoms or by dissociation:

\[
\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O} + \text{M}, \tag{1}
\]

\[
\text{C}_2\text{N}_2 + \text{O} \rightarrow \text{NCO} + \text{CN}, \tag{2}
\]

\[
\text{NCO} + \text{O} \rightarrow \text{CO} + \text{NO}, \tag{3}
\]

\[
\text{NCO} + \text{M} \rightarrow \text{N} + \text{CO} + \text{M}. \tag{4}
\]
TABLE 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH°</th>
<th>Equilibrium Constant</th>
<th>log10 A</th>
<th>m</th>
<th>θ(°K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N₂O + M → N₂ + O + M</td>
<td>+40</td>
<td>-2.1</td>
<td>23.89</td>
<td>-2.5</td>
<td>32,710</td>
<td>[16]</td>
</tr>
<tr>
<td>2 C₂N₂ + O → CN + NCO</td>
<td>+3</td>
<td>0.5</td>
<td>12.66</td>
<td>0</td>
<td>4440</td>
<td>[1]</td>
</tr>
<tr>
<td>3 NCO + O → CO + NO</td>
<td>-106</td>
<td>10.5</td>
<td>13.75</td>
<td>0</td>
<td>0</td>
<td>[3]</td>
</tr>
<tr>
<td>4 NCO + M → N + CO + M</td>
<td>+48</td>
<td>-3.7</td>
<td>16.80</td>
<td>-0.5</td>
<td>24,000</td>
<td>This study</td>
</tr>
<tr>
<td>9 CN + O₂ → NCO + O</td>
<td>-1</td>
<td>0.1</td>
<td>12.75</td>
<td>0</td>
<td>0</td>
<td>[1]</td>
</tr>
<tr>
<td>10 CN + O → CO + N</td>
<td>-75</td>
<td>6.7</td>
<td>13.31</td>
<td>0</td>
<td>210</td>
<td>[1]</td>
</tr>
<tr>
<td>11 N₂O + O → NO + NO</td>
<td>-39</td>
<td>5.3</td>
<td>13.84</td>
<td>0</td>
<td>13,040</td>
<td>[16]</td>
</tr>
<tr>
<td>12 N₂O + O → N₂ + O₂</td>
<td>-83</td>
<td>8.3</td>
<td>14.00</td>
<td>0</td>
<td>14,100</td>
<td>[16]</td>
</tr>
<tr>
<td>13 N₂ + O → N + NO</td>
<td>+75</td>
<td>-6.8</td>
<td>14.26</td>
<td>0</td>
<td>38,370</td>
<td>[16]</td>
</tr>
<tr>
<td>14 NO + O → N + O₂</td>
<td>+32</td>
<td>-3.8</td>
<td>9.58</td>
<td>1.0</td>
<td>20,820</td>
<td>[16]</td>
</tr>
<tr>
<td>15 NCO + N → N₂ + CO</td>
<td>-182</td>
<td>17.3</td>
<td>13.30</td>
<td>0</td>
<td>0</td>
<td>[18]</td>
</tr>
<tr>
<td>16 NCO + N → CN + NO</td>
<td>-31</td>
<td>3.7</td>
<td>14.66</td>
<td>0</td>
<td>5530</td>
<td>[19]</td>
</tr>
<tr>
<td>17 NCO + C → CN + CO</td>
<td>-137</td>
<td>13.3</td>
<td>14.00</td>
<td>0</td>
<td>0</td>
<td>estimate</td>
</tr>
<tr>
<td>33 CN + N → C + N₂</td>
<td>-44</td>
<td>4.0</td>
<td>14.64</td>
<td>0</td>
<td>4530</td>
<td>[20]</td>
</tr>
<tr>
<td>34 N₂O + CN → NCN + NO</td>
<td>+4</td>
<td>0.8</td>
<td>4.60</td>
<td>2.5</td>
<td>6080</td>
<td>[21]</td>
</tr>
<tr>
<td>35 NCN + O → CN + NO</td>
<td>-43</td>
<td>4.5</td>
<td>10.20</td>
<td>1.1</td>
<td>1160</td>
<td>[21]</td>
</tr>
<tr>
<td>36 NCN + N → CN + N₂</td>
<td>-119</td>
<td>11.3</td>
<td>10.50</td>
<td>0.9</td>
<td>0</td>
<td>[21]</td>
</tr>
<tr>
<td>37 C₂N₂ + M → CN + CN + M</td>
<td>+126</td>
<td>-10.0</td>
<td>34.46</td>
<td>-4.5</td>
<td>63,150</td>
<td>[17]</td>
</tr>
</tbody>
</table>

* Heat of reaction at 2200*K (kcal/mole) [10]. Thermochemical data were taken from the JANAF tables for all species [10], except for CN, where we used ΔH°CN = 101.2 kcal/mole, an average of the values of JANAF [10] and Colket [27].

# log10(k_forward/k_backward) at 2200*K [10].

Using the notation k = AT^n exp(-θ/T) (cm³/mole/s).

Colket measured k_backward = 10^14 exp(-21900/T) (cm³/mole/s); we assumed k/k_b = 4.54 exp(15660/T).

At the peak of the NCO concentration, we have

\[ \frac{d[NCO]}{dt} = k_2 [C_2N_2][O] - k_3[NCO][O] - k_4[NCO][M] = 0, \]

and hence

\[ \frac{[C_2N_2]}{[NCO]_{peak}} = \frac{k_3}{k_2} + \frac{k_4}{k_2} \times \frac{[M]}{[O]}. \]

The mole fraction of O-atoms at steady-state is proportional to the initial N₂O mole fraction, and we have [O]/[M] ≈ (N₂O)₀. If [C₂N₂] is nearly constant throughout the time scale of interest, measurements of the peak NCO concentration for different values of the initial N₂O mole fraction can be plotted as a straight line on a graph showing [C₂N₂]/[NCO]ₚₑᵃᵏ as a function of 1/(N₂O)₀. In the case of this simple model, the intercept and the slope are proportional to, respectively, the ratios k₃/k₂ and k₄/k₂. Furthermore, the ratio of the intercept and the slope yields k₃/k₄.

b. Results and Discussion

A numerical routine derived from the NASA-Lewis general chemical kinetics program [8], and incorporating the mechanism in Table 1, was used for the actual data interpretation. Thermochemical data were taken from the JANAF tables for all species [10], except for...
HIGH TEMPERATURE KINETICS OF NCO

Fig. 2. A typical experimental trace in N2O/C2N2/Ar mixtures with T2 = 2210°K, p2 = 0.64 atm, N2O : C2N2 : Ar = 2 : 4 : 994, and p2, = 3.56. The initial spike corresponds to a shock-generated Schlieren effect. The dashed line is an estimate of the unperturbed NCO profile at early times. The peak absorption of 1.9% corresponds to \( X_{\text{NCO}} = 57 \text{ ppmv} \), with \( (2210^\circ \text{K}) \) = 17 cm\(^{-1}\) atm\(^{-1}\) [2].

CN, where we used \( \Delta H^*_f = 101.2 \text{ kcal/mole} \), an average of the values of JANAF [10] and Colket [27]. Figure 2 shows a typical experimental trace, converted to NCO mole fraction. The initial spike results from a Schlieren effect, which is useful in determining the shock arrival time. The NCO mole fraction at the peak (\( t = 14\mu s \)) was used in the data reduction. Values for \( k_3/k_2 \) and \( k_4/k_2 \) were inferred by varying these quantities in the detailed kinetic mechanism until least-squares agreement was found between the experimental and computer-generated results for \( [\text{C}_2\text{N}_2]/[\text{NCO}]_{\text{peak}} \) versus \( 1/(X_{\text{N}_2\text{O}})_{t=0} \) (see Fig. 3). Finally, the ratio \( k_3/k_4 \) was computed from the ratio of the inferred values of \( k_3/k_2 \) and \( k_4/k_2 \).

Computer calculations confirmed that the ratio \( k_3/k_4 \) inferred by this procedure is reasonably insensitive to the value of \( k_2 \) employed in the detailed model (see Fig. 3); hence the value \( k_3/k_4 \) reported is nearly independent of the substantial uncertainties associated with both \( k_2 \) [1] and the absorption coefficient \( \beta(T = 2240^\circ \text{K}) \) [2].

Residual uncertainties in \( k_3/k_4 \) result primarily from the uncertain knowledge of other rate constants in the mechanism [\( \times 1.7, \times 0.6 \)], and the 95% confidence interval on the fit to the data in Fig. 3 [\( \times 1.8, \times 0.5 \)] [9]. These two uncorrelated uncertainties can be combined to give an overall uncertainty in \( k_3/k_4 \) of [\( \times 2.2, \times 0.43 \)], which means that the ratio \( k_3/k_4 \) is bounded by values 2.2 times and 0.43 times the reported value. No significant uncertainty in \( k_3/k_4 \) resulted from uncertain heats of reaction (e.g., for CN or NCO) since most reactions proceeded in the forward direction. Figure 4 shows computer-generated profiles of reactants and intermediate species using the values of \( k_3/k_2 \) and \( k_4/k_2 \) inferred from Fig. 3 and other rates reported in the detailed mechanism of Table 1.

Our result \( k_3/k_4 = 10^{3.54(±0.34,−0.27)} \) at 2240^°K is plotted in Arrhenius form along with our earlier determinations at 2150 and 2400°K (Fig. 5), which were obtained in two independent experiments based on measurements of NO and CN [1]. Reasonable agreement is found among the three independent measurements within the size of their individual error bars. Because of these error bars and the narrow range of temperatures studied, it is difficult to estimate a correct temperature dependence of the ratio. For the purpose of reporting a single expression,
we assumed for $k_4$ an activation energy equal to the NCO dissociation energy, i.e., 47.3 kcal/mol [10], and a number of effective degrees of freedom $s = 2$ [11]. [The latter assumption implies a temperature exponent in the preexponential factor of Ar4 equal to $m = 3/2 - s = -1/2$.] In addition, we assumed no temperature dependence for $k_3$ in the range $2150 < T < 2400^\circ$K. Using a least-squares-fit expression based on the three experimental data points, we found $k_3/k_4 = 10^{-3}T^{0.5} \exp\left[ \frac{-24000}{T} \right]$ [×2.0, ×0.5] for $2150 \leq T \leq 2400^\circ$K.

No experimental measurement of $k_3$ has been performed above 1500°K. However, it is reasonable to assume that $k_3$ is nearly constant over a large temperature range. Using our earlier measurement of $k_3 = 10^{13.75}$ cm$^3$/mole/sec [×1.60, ×0.55] at 1450°K [3] and combining the corresponding uncertainties in $k_3$ and $k_3/k_4$, we recommend $k_4 = 10^{16.8}T^{-0.5} \exp\left[ -24000/T \right]$ [×2.3, ×0.4] over the range $2150 \leq T \leq 2400^\circ$K. There are no previous data for $k_4$ available for comparison.

**N$_2$O/O$_2$/Ar MIXTURE—ANALYSIS AND RESULTS**

The mechanism shown in Table 2 was used in the data reduction, but a simplified model based on the following reactions is helpful in understanding the influence of $k_3$ and $k_6/k_7$ on the measured NCO profile. As before, N$_2$O decomposes first to provide O-atoms. The influx of O-atoms is sufficient to trigger reactions in the O/H system that lead to partial equilibrium concentrations of H, O, and OH. Because of the relative proportions of O$_2$ and H$_2$ in the initial mixture, H is the dominant species in the O/H system [12] and reaction (6) becomes the major sink of C$_2$N$_2$:

$$C_2N_2 + H \rightarrow CN + HCN.$$  \hspace{1cm} (6)

The CN radicals formed by reaction (6) can in turn react with H$_2$ via reaction (7),

$$CN + H_2 \rightarrow HCN + H,$$  \hspace{1cm} (7)

or react with O$_2$ to form NCO via reaction (9),

$$CN + O_2 \rightarrow NCO + O.$$  \hspace{1cm} (9)

Finally, NCO is removed by H-atoms via reaction (5),

$$NCO + H \rightarrow NH + CO.$$  \hspace{1cm} (5)

For the purpose of this simplified mechanism, we can assume that CN has reached steady-state (ss) between reactions (6) and (7), and hence

$$\frac{[CN]^{ss}}{[C_2N_2]} = \frac{k_6}{k_3} \frac{[H]^{pe}}{[H_2]}.$$  \hspace{1cm} (pe = partial equilibrium). Further, the rate of
### TABLE 2
Reaction Mechanism—N$_2$O/O$_2$/H$_2$/C$_2$N$_2$/Ar Mixture

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^*$ (kcal/mole)</th>
<th>$\log_{10} A$</th>
<th>$m$</th>
<th>$\theta$ (°K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N$_2$O + M $\rightarrow$ N$_2$ + O + M</td>
<td>+40</td>
<td>-3.8</td>
<td>23.89</td>
<td>-2.5</td>
<td>32,710</td>
</tr>
<tr>
<td>2 C$_2$N$_2$ + O $\rightarrow$ CN + NCO</td>
<td>+4</td>
<td>0.3</td>
<td>12.66</td>
<td>0</td>
<td>4440</td>
</tr>
<tr>
<td>3 NCO + O $\rightarrow$ NO + CO</td>
<td>-105</td>
<td>15.4</td>
<td>13.75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4 NCO + M $\rightarrow$ N + CO + M</td>
<td>+48</td>
<td>-5.8</td>
<td>16.80</td>
<td>-0.5</td>
<td>24,000</td>
</tr>
<tr>
<td>5 NCO + H $\rightarrow$ CO + NH</td>
<td>-39</td>
<td>6.0</td>
<td>14.02</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>6 C$_2$N$_2$ + H $\rightarrow$ CN + HCN</td>
<td>+4</td>
<td>0.7</td>
<td>14.50</td>
<td>0</td>
<td>4030</td>
</tr>
<tr>
<td>7 CN + H$_2$ $\rightarrow$ HCN + H</td>
<td>-16</td>
<td>1.8</td>
<td>11.74</td>
<td>0.7</td>
<td>2460</td>
</tr>
<tr>
<td>8 NCO + H$_2$ $\rightarrow$ (HNCO) + H</td>
<td>-10</td>
<td>1.0</td>
<td>13.23</td>
<td>0</td>
<td>4000</td>
</tr>
<tr>
<td>9 CN + O$_2$ $\rightarrow$ NCO + O</td>
<td>-2</td>
<td>0.1</td>
<td>12.75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10 CN + O $\rightarrow$ CO + N</td>
<td>-75</td>
<td>10.2</td>
<td>13.31</td>
<td>0</td>
<td>210</td>
</tr>
<tr>
<td>11 N$_2$O + O $\rightarrow$ NO + NO</td>
<td>-38</td>
<td>19.2</td>
<td>13.84</td>
<td>0</td>
<td>13,400</td>
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<tr>
<td>12 N$_2$O + O $\rightarrow$ N$_2$ + O$_2$</td>
<td>-81</td>
<td>12.1</td>
<td>14.00</td>
<td>0</td>
<td>14,100</td>
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<tr>
<td>13 N$_2$ + O $\rightarrow$ N + O$_2$</td>
<td>+75</td>
<td>-10.3</td>
<td>14.26</td>
<td>0</td>
<td>38,370</td>
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</tr>
<tr>
<td>15 NCO + N $\rightarrow$ N$_2$ + CO</td>
<td>-180</td>
<td>25.7</td>
<td>13.30</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16 NCO + N $\rightarrow$ CN + NO</td>
<td>-30</td>
<td>5.2</td>
<td>14.66</td>
<td>0</td>
<td>5530</td>
</tr>
<tr>
<td>17 N$_2$O + H $\rightarrow$ N$_2$ + OH</td>
<td>-65</td>
<td>10.8</td>
<td>13.88</td>
<td>0</td>
<td>7600</td>
</tr>
<tr>
<td>18 NH + NO $\rightarrow$ N$_2$O + H</td>
<td>-28</td>
<td>2.3</td>
<td>12.03</td>
<td>0</td>
<td>230</td>
</tr>
<tr>
<td>19 NO + H $\rightarrow$ N + OH</td>
<td>+48</td>
<td>-6.6</td>
<td>14.23</td>
<td>0</td>
<td>24,560</td>
</tr>
<tr>
<td>20 O$_2$ + H $\rightarrow$ OH + O</td>
<td>+16</td>
<td>-1.2</td>
<td>17.57</td>
<td>-1.0</td>
<td>8810</td>
</tr>
<tr>
<td>21 H$_2$ + O $\rightarrow$ OH + OH</td>
<td>+2</td>
<td>+0.1</td>
<td>10.26</td>
<td>1.0</td>
<td>4480</td>
</tr>
<tr>
<td>22 H$_2$O + O $\rightarrow$ OH + OH</td>
<td>+17</td>
<td>-1.5</td>
<td>9.66</td>
<td>1.3</td>
<td>8605</td>
</tr>
<tr>
<td>23 OH + H$_2$ $\rightarrow$ H + H$_2$O</td>
<td>-15</td>
<td>1.6</td>
<td>9.07</td>
<td>1.3</td>
<td>1825</td>
</tr>
<tr>
<td>24 HCN + O $\rightarrow$ NCO + H</td>
<td>0</td>
<td>-0.4</td>
<td>8.24</td>
<td>1.47</td>
<td>3775</td>
</tr>
<tr>
<td>25 HCN + O $\rightarrow$ NH + CO</td>
<td>-39</td>
<td>5.6</td>
<td>8.73</td>
<td>1.2</td>
<td>3820</td>
</tr>
<tr>
<td>26 HCN + OH $\rightarrow$ H$_2$O + CN</td>
<td>+1</td>
<td>-0.2</td>
<td>12.64</td>
<td>0</td>
<td>4530</td>
</tr>
<tr>
<td>27 CN + OH $\rightarrow$ NCO + H</td>
<td>-18</td>
<td>1.4</td>
<td>13.75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>28 C$_2$N$_2$ + OH $\rightarrow$ HNCO + CN</td>
<td>-8</td>
<td>1.3</td>
<td>11.27</td>
<td>0</td>
<td>1450</td>
</tr>
<tr>
<td>29 HNCO + H $\rightarrow$ NH$_2$ + CO</td>
<td>-17</td>
<td>2.8</td>
<td>14.00</td>
<td>0</td>
<td>4280</td>
</tr>
<tr>
<td>30 NH + H $\rightarrow$ N + H$_2$</td>
<td>-20</td>
<td>2.7</td>
<td>13.70</td>
<td>0</td>
<td>1000</td>
</tr>
<tr>
<td>31 NH$_2$ + H $\rightarrow$ NH + H$_2$</td>
<td>-11</td>
<td>2.2</td>
<td>13.28</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$ Heat of reaction at 1500°K (kcal/mole) [10]; we used $\Delta H_{CN}^\circ$ (CN) = 101.2 kcal/mole [10, 27].

$^b$ $\log_{10}(k_{forward}/k_{backward})$ at 1500°K [10].

$^c$ Using the notation $k = AT^m \exp[\theta/T]$ (cm$^3$/mole/s).

$^d$ We estimated an activation energy of 2 kcal/mole for this reaction.

$^e$ We estimated an activation energy of 8 kcal/mole for this reaction. The form of the product (HNCO) is uncertain.

$^f$ Colket measured $k_{forward} = 10^{14} \exp(-21190/T)$ (cm$^3$/mole/s); we assumed $k_r/k_a = 4.54 \exp[15660/T]$.

$^g$ The products of this slow reaction are uncertain.

The change of NCO concentration is given by

$$\frac{d[NCO]}{dt} = k_5[CN][O_2] - k_3[NCO][H].$$

If C$_2$N$_2$, O$_2$, and H$_2$ are nearly constant throughout the period of interest, the NCO profile peaks at a value ($d[NCO]/dt = 0$) where, after substituting the above relations for [CN]$_{eq}$, we obtain

$$\frac{[NCO]_{peak}}{[C_2N_2]} = \frac{k_5}{k_3} \times \frac{k_7[H_2]}{[O_2]}.$$
For this simplified model, the relative NCO profile (using the peak as a reference) depends primarily on the rate of reaction (5), since (after substituting the relation for \([CN]_{SS}\) in the NCO rate equation)

\[
d\frac{[NCO]}{[NCO]^\text{peak}} dt = k_5[H][1
- \frac{[NCO]}{[NCO]^\text{peak}}].
\]

The NCO peak concentration thus depends primarily on \((k_6/k_7) \times (k_6/k_7)\) and the relative time behavior depends on \(k_5\). A record of NCO is therefore sufficient to infer \(k_5\); using the established value of \(k_6 [1]\) and the measured NCO peak concentration [2], the ratio \(k_6/k_7\) can also be inferred.

Despite the apparent simplicity of this model, we found it necessary to use a computer fitting technique to explain further the influence of key rate parameters on the NCO profile. In particular, we found that, despite the small value of \(k_8\), the experimental time histories cannot be adequately fitted without accounting for reaction (8),

\[
\text{NCO} + \text{H}_2 \rightarrow \text{HNCO} + \text{H},
\]

because of the large quantities of \(\text{H}_2\) present in the mixture. We assumed that the products of reaction (8) are \(\text{HNCO} + \text{H}\) \((\Delta H = -10 \text{ kcal/mole at } 1500^\circ \text{K})\), rather than the thermodynamically favored \(\text{NH}_2 + \text{CO}\) \((\Delta H = -27 \text{ kcal/mole at } 1500^\circ \text{K})\), because the path to \(\text{NH}_2 + \text{CO}\) requires a complex rearrangement of the molecular bonds. Using computer calculations based on the mechanism of Table 2, we identified three features of the NCO profile which could be simultaneously fitted to yield the three rate parameters of interest, namely \(k_5\), \(k_6/k_7\), and \(k_8\). These three features are the absolute peak NCO concentration, the relative initial slope, and the relative decay of the NCO profile (using the peak as a reference). Figure 6 shows a best computer fit to the experimental trace. The computed effects of variations in \(k_5\), \(k_6/k_7\) and \(k_8\) on the three features are illustrated in Table 3. For example, this table shows that an increase (↑) in \(k_6/k_7\) would result in increases (↑) in relative initial slope and absolute peak concentration, and to a faster relative decay of the NCO profile.

Figure 7 illustrates the effect of \(k_6/k_7\) on the relative NCO profile. Note from Table 3 that \(k_5\) and \(k_8\) both have similar effects (↓) on the absolute peak concentration, but opposite effects on the relative initial slope; further, \(k_5\) and \(k_8\) do not substantially influence the relative decay. It therefore appears possible to determine \(k_5\), \(k_6/k_7\), and \(k_8\) by fitting the NCO trace alone.

A unique value for \(k_6/k_7\) can fit the relative

**TABLE 3**

NCO Profile Sensitivity*

<table>
<thead>
<tr>
<th>Characteristic Features</th>
<th>Rates</th>
<th>Relative Slope</th>
<th>Peak Concentration</th>
<th>Relative Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_5) ↑ (× 2)</td>
<td>↑</td>
<td>↓ (× 0.64)</td>
<td>←</td>
<td></td>
</tr>
<tr>
<td>((k_6/k_7)) ↑ (× 2)</td>
<td>↑</td>
<td>↑ (× 1.42)</td>
<td>↑</td>
<td></td>
</tr>
<tr>
<td>(k_8) ↑ (× 2)</td>
<td>↓</td>
<td>↓ (× 0.82)</td>
<td>←</td>
<td></td>
</tr>
</tbody>
</table>

* Legend: ↑, increasing value; ↓, decreasing value; ←, no variation.
HIGH TEMPERATURE KINETICS OF NCO

Fig. 7. Effect of the ratio $k_6/k_7$ on the relative NCO time history. The dotted line corresponds to $(k_6/k_7) \times 2.0$ and the dashed line to $(k_6/k_7) \times 0.5$.

Decay, and a unique set of values for $k_5$ and $k_8$ can simultaneously fit the relative initial slope and the absolute peak concentration. Figure 8 illustrates the effect of $k_5$ on the relative NCO profile.

On the basis of this analysis, we found $k_5 = 10^{13.73(\pm0.42,-0.27)}$ cm$^2$/mole/s, $k_6/k_7 = 0.81\ (\pm0.89,-0.47)$ and $k_8 = 10^{12.14(\pm0.4,0.7)}$ cm$^3$/mole/s. Uncertainties in $k_5$ result from the uncertain knowledge of other reactions in the mechanism $[\times1.7, \times0.57]$ and the uncertainty in the measured NCO peak concentration resulting in uncertainty factors in $k_5$ of $[\times2.1, \times0.75]$ [2]. Uncertainties in $k_6/k_7$ are attributed primarily to the uncertain knowledge of other rates $[\times2.1, \times0.42]$, because no absolute knowledge of the NCO concentration was required to fit the relative decay slope to $k_6/k_7$. Uncertainties in $k_8$ are fairly large $[\times2.5, \times0.2]$ and can be attributed mostly to the uncertainty in the absolute peak NCO concentration. A significant reduction in the overall uncertainty of $k_5$ and $k_8$ could be achieved if a more precise value of $\beta(1490^\circ\text{K})$ were available. No significant uncertainty resulted from uncertain heats of formation (e.g., for CN, NCO, or NH) since most reactions proceeded in the forward direction.

There are no previous data of $k_5$ and $k_8$ available for comparison. Miller et al. [13] recently calculated an expression for $k_7$, based on the measurements of Szekely et al. [5] in the range $2700 \leq T \leq 3500^\circ\text{K}$ and Albers et al. [14] at lower temperatures: $k_7 = 10^{11.74(T^{0.7}) \exp[-2460/T]}$ cm$^3$/mole/s. Judging from the error bars attached to the high and low temperature data, we believe the above expression should be valid within a factor of two at $1490^\circ\text{K}$. By using our measurement of $k_6/k_7$, this expression leads to $k_6 = 10^{13.5\pm0.5}$ cm$^3$/mole/s at $1490^\circ\text{K}$. Another estimate of $k_6$ can be obtained from the reverse rate $k_{-6}$ measured by Szekely et al. [6] at high temperatures, with the result $k_6 = 10^{14.7\pm0.5}$ cm$^3$/mole/s at the average temperature of $2900^\circ\text{K}$ [15]. Figure 9 is an Arrhenius plot of $k_6$. By using the two values of $k_6$ at $2900$ and $1490^\circ\text{K}$, a straight Arrhenius fit would lead to $k_6 = 10^{15.1\exp[-6700/T]}$ cm$^3$/mole/s. However, the corresponding activation energy and preexponential factor of the fit

Fig. 8. Effect of $k_5$ on the relative NCO time history. The dotted line corresponds to $k_5 \times 0.5$ and the dashed line to $k_5 \times 2.0$.

Fig. 9. Arrhenius plot for $k_6$.
appear too high for this mildly endothermic reaction ($\Delta H_R < 5.3$ kcal/mole at 2000°K [10, 27]). A more realistic activation energy of 8 kcal/mole leads to the expression $k_6 = 10^{14.3} \exp[-4030/7] \text{cm}^3/\text{mole/s}$, which we recommend within factors of $\times 3.2$, $\times 0.32$ over the range $1490 \leq T \leq 3070^\circ\text{K}$.

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