

SHOCK TUBE STUDY OF NCO KINETICS

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Mixtures of cyanogen, oxygen and nitrous oxide diluted in argon were shock-heated to measure the rate constant of:



The primary diagnostic was narrow-line absorption of NCO at 440.479 nm using a remotely located cw ring dye laser source. A detailed kinetic analysis of the experiments near 1450° K led to:

$$k_3 = 10^{13.73(-0.28, +0.20)} \text{cm}^3/\text{mole}/\text{sec}.$$

Additional experiments, in mixtures of hydrogen cyanide, oxygen and nitrous oxide diluted in argon, enabled a determination of the ratio k_4/k_2 :

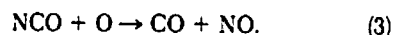
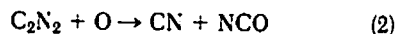
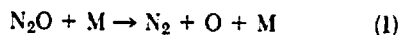


We found (at 1440° K): $k_4/k_2 = 2.4(-0.9, +2.4)$. Utilizing a recent determination of k_2 , we infer $k_4 = 10^{11.70(-0.35, -0.40)} \text{cm}^3/\text{mole}/\text{sec}$.

Introduction

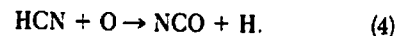
Cyano species such as CN and NCO are known to play a key role in fuel-nitrogen chemistry¹ and the formation of combustion-generated nitric oxide. In an earlier paper on cyanogen oxidation kinetics,² we examined the conversion of C_2N_2 to these cyano radicals. In this study, a novel laser absorption diagnostic was used to probe NCO time-histories in high temperature shock tube experiments aimed at determining rate constants for important NCO formation and removal reactions.

Mixtures of C_2N_2 , N_2O and O_2 diluted in argon were shock-heated to determine the rate constant of reaction (3) at 1450° K, the rate constants for (1) and (2) being already well established.²



In other experiments, C_2N_2 was replaced by HCN and a comparison of the NCO time-histories in the

C_2N_2 and HCN mixtures was used to establish a value for the rate of reaction (4) at 1440° K:



There are no previous data for k_3 , and data for k_4 are limited. Roth *et al.*³ measured k_4 by shock heating $\text{HCN}/\text{N}_2\text{O}/\text{Ar}$ mixtures in the range $1800 \leq T \leq 2500^\circ \text{K}$ and monitoring the H- and O-atom concentrations using an ARAS technique. Davies and Thrush⁴ conducted a discharge flow study to find k_4 in the range $469 \leq T \leq 574^\circ \text{K}$. Recently, Perry and Melius⁵ obtained k_4 in the range $540 \leq T \leq 900^\circ \text{K}$ by monitoring NCO using a laser photolysis—laser induced fluorescence technique.

In this paper, the experimental facility and optical technique will first be 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.⁶ Shock speeds varied between 1.14 and 1.17 mm/ μ sec, with attenuation of 1.5%/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 and N_2O (>99.9%); C_2N_2 (1.01% diluted in argon; HCN and CNCl < 50 ppmv, O_2 < 20 ppmv, CO_2 < 20 ppmv); HCN (Airco, 7.4% diluted in argon; H_2O , SO_2 , O_2 and $CO_2 \leq 1$ ppmv). The mole fraction of HCN in the cylinder was checked against known C_2N_2 and HCN mixtures using high-temperature CN emission tests since HCN may slowly decompose in high pressure cylinders.

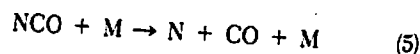
The shock tube test section and laser absorption system for NCO are shown schematically in Fig. 1. The signal obtained from the double-pass NCO diagnostic was recorded on a digital oscilloscope (Nicolet Explorer III, dc-coupled through a 100 kHz upper frequency cut-off filter) and stored on tape for subsequent data reduction.

The absorption from the $P_2 + {}^PQ_{12}$ band head of the $[A^2\Sigma^+(00^0) \leftarrow X^2\Pi_i(00^10)]$ band of NCO at 440.479 nm (vac.) was used to monitor NCO. The laser system consisted of a UV-enhanced Ar^+ laser (Spectra Physics model 171-18) and a standard Spectra Physics 380A ring dye laser. The available Ar^+ UV power (1.9 W all lines) was sufficient to excite the stilbene S3 dye above threshold, providing a typical dye laser output power of 60 mW. The nominal laser wavelength was varied using a standard 3-plate birefringent filter; fine tuning was achieved with an uncoated 5 mm-thick fused silica etalon in a temperature-controlled oven. Single mode output of the laser was verified using a confocal interferometer (Spectra Physics model 470, free spectral range 2 GHz). An amplitude stabilizer (Coherent Associates model 307) was employed to improve the signal quality. The component of the laser power

rejected by the amplitude stabilizer was sufficient to drive the wavemeter (Burleigh model WA-10) used for setting the laser wavelength. It was necessary to correct the displayed wavelength for the change in the index of refraction of air between the He-Ne reference wavelength at 632.991 nm and our blue wavelength at 440.479 nm (correction = actual - displayed wavelength = +0.002 nm).

The laser light was coupled into a 200 μ m fused silica optical fiber for transport to the shock tube facility⁷ (length: 65 m). The output from the optical fiber was double-passed through the shock tube test section as shown in Fig. 1. The incident and return beams were monitored on two separate detectors D_1 and D_2 (EG&G UV 100B silicon photodiodes mounted in an amplifier/filter package with a 240 kHz (-3dB) cutoff frequency). Neutral density filters (transmission: 10^{-1}) were used to reduce the incident power of 1 mW below the saturation limit of the detectors while proportionally reducing the spontaneous emission from the test gas. Narrow bandpass filters (FWHM: 40 nm, centered at 450 nm) were used to discriminate against other sources (primarily room lights). The signal from each detector was passed through a differential amplifier (Tektronix model AM 502, dc-1MHz bandwidth). Prior to each experiment, the laser light was chopped to balance (i.e., equalize) the reference signal (i_0) and the return signal (i) using small dc offset and gain adjustments on one of the differential amplifiers. The difference ($i_0 - i$) and the reference signal (i_0) were recorded on two separate oscilloscope channels, thereby providing a direct measurement of the fractional absorption through the system.

Three runs were conducted with the following mixtures and conditions: $N_2O:O_2:C_2N_2:Ar \approx 4:1:4:991$, $T_2 = 1450 \pm 10^\circ K$, $P_2 \approx 0.60$ atm, and $\rho_{21} \approx 3.31$ (ρ_{21} is the density ratio across the shock and also the ratio of particle time to laboratory time). Nine additional runs were conducted with HCN mixtures: $N_2O:O_2:HCN:Ar \approx 8:1:8:983$, $T_2 = 1430 \pm 20^\circ K$, $P_2 \approx 0.60$ atm, and $\rho_{21} \approx 3.32$. The temperature of the experiments was set by considerations of growing interference on NCO removal by reaction (5) at higher temperatures,



and diminishing confidence in the rate of reaction (1) at lower temperatures. In addition, a few tests were conducted with the laser blocked to monitor possible spontaneous emission interferences from the test gas. These emission levels were found to be insignificant.

The transmission of the laser system is related to the level of NCO through the Lambert-Beer law:

$$\frac{i}{i_0} = \exp[-\beta(\lambda) p_{NCO} L]$$

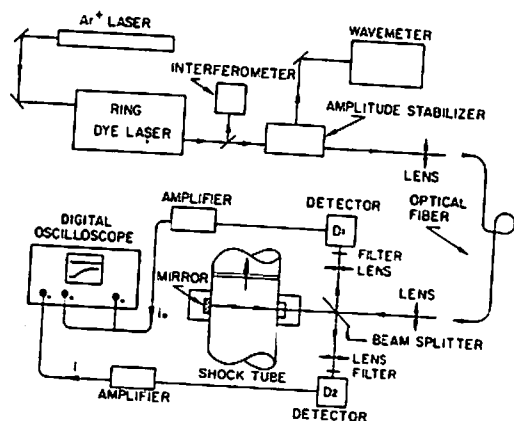


FIG. 1. Shock tube NCO laser absorption diagnostic.

where i/i_0 is the fractional transmission, $\beta(\lambda)$ is the absorption coefficient at wavelength λ , p_{NCO} is the partial pressure of NCO and L is the optical path length (30.5 cm). The data reduction procedure was based on relative profiles of NCO concentrations and hence did not require knowledge of β ; however, β has been determined recently in our laboratory.⁸

In order to establish the optimum wavelength for NCO detection, the relative absorption coefficient was measured as a function of wavelength by conducting nine nearly identical HCN experiments (see above), each at a different laser wavelength. The relative absorption coefficient (corrected for small excursions in the shock wave conditions) is plotted along with a computer-predicted profile in Fig. 2. The peak of the absorption coefficient was measured to be near 440.479 nm, in good agreement with our expectations and the value quoted by Dixon.⁹

$\text{N}_2\text{O}/\text{O}_2/\text{C}_2\text{N}_2/\text{Ar}$ Mixtures—Analysis and Results

a) Reaction Mechanism:

A complete reaction mechanism was utilized in the data reduction (see Table I), but a simplified description can be given as follows. At early times, N_2O rapidly decomposes to provide O-atoms; C_2N_2 then reacts to form NCO, which in turn is removed by O-atoms:

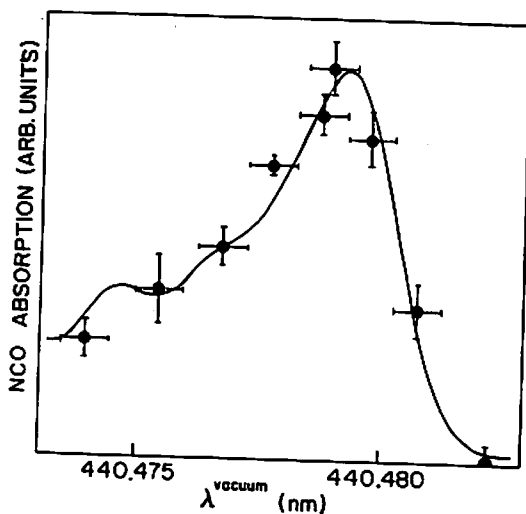
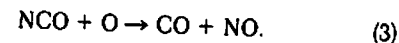
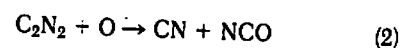
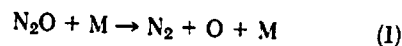
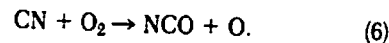


FIG. 2. NCO absorption spectrum around 440.479 nm. The horizontal error bars on the experimental data correspond to the wavemeter resolution. The solid line is based on a spectroscopic model, including 30 lines near the $P_2 + {}^PQ_{12}$ band head and assuming a Voigt "a" parameter of 0.1.⁸



The presence of molecular oxygen converts the CN into additional NCO and replenishes the O-atom pool via reaction (6):



Assuming a steady-state of [CN] between reaction (2) and (6), the rate of change of NCO concentration is given by:

$$\frac{d[\text{NCO}]}{dt} = 2k_2[\text{C}_2\text{N}_2][\text{O}] - k_3[\text{NCO}][\text{O}].$$

Since O and C_2N_2 are nearly constant throughout the process (see Fig. 3), the NCO profile eventually reaches a plateau ($d[\text{NCO}]/dt = 0$) where

$$\frac{[\text{NCO}]^{\text{plateau}}}{[\text{C}_2\text{N}_2]} = \frac{2k_2}{k_3}$$

It follows that the relative NCO profile (using the plateau as a reference) depends primarily on the rate of reaction (3), since (for this simplified model):

$$\begin{aligned} \frac{d[\text{NCO}]/[\text{NCO}]^{\text{plateau}}}{dt} &= k_3[\text{O}](1 - [\text{NCO}]/[\text{NCO}]^{\text{plateau}}). \end{aligned}$$

The NCO plateau concentration thus depends primarily on the ratio k_2/k_3 and the relative time behavior depends on k_3 . An absorption record of NCO is therefore sufficient to infer k_3 and, using the established value of k_2 ,² the absolute value for the NCO plateau concentration. This approach for the establishment of a known level of NCO was utilized in a recent study of NCO spectroscopy.⁸

Vibrational equilibrium of NCO was assumed, even though there is some evidence for NCO production in excited vibrational states from reaction (6) at lower temperatures.¹⁰

b) Results and Discussion:

A numerical routine derived from the NASA-Lewis general chemical kinetics program,¹⁹ and incorporating the mechanism in Table I, was used for the kinetics calculations. Values for k_3 were inferred from best fits to the measured relative NCO concentration profiles. Figure 4 shows such a best fit (solid line) to the relative NCO trace and the influence of varying k_3 using factors of 0.67 and 1.50

TABLE I
 Reaction mechanism

Reactions	ΔH°	equil. const. ^b	rate constants ^c			Source (Ref #)
			$\log_{10}A$	m	$\theta^\circ(K)$	
1 $N_2O + M \rightarrow N_2 + O + M$	+40	-3.8	23.89	-2.5	32710	[11]
2 $C_2N_2 + O \rightarrow CN + NCO$	+4	0.3	12.66	0	4440	[2]
3 $NCO + O \rightarrow NO + CO$	-105	15.4	13.75	0	0	This study
4 $HCN + O \rightarrow NCO + H$	0	-0.4	8.24	1.47	3775	This study
5 $NCO + M \rightarrow N + CO + M$	+48	-5.8	16.80	-0.5	24000	[12]
6 $CN + O_2 \rightarrow NCO + O$	-2	0.1	12.75	0	0	[2]
7 $CN + O \rightarrow CO (\nu = 1) + N$	-69	9.2	13.31	0	210	[2]
8 $NCO + H \rightarrow CO + NH$	-39	6.0	14.02	0	1000	[12]
9 $HCN + O \rightarrow NH + CO$	-39	5.6	8.73	1.21	3825	[5]
10 $HCN + OH \rightarrow H_2O + CN$	+1	-0.2	12.64	0	4530	[13]
11 $N_2O + O \rightarrow NO + NO$	-38	7.1	13.84	0	13400	[11]
12 $N_2O + O \rightarrow N_2 + O_2$	-81	12.1	14.00	0	14100	[11]
13 $N_2 + O \rightarrow N + NO$	+75	-10.3	14.26	0	38370	[11]
14 $NO + O \rightarrow N + O_2$	+32	-5.3	9.58	1.0	20820	[11]
15 $NCO + N \rightarrow N_2 + CO$	-180	25.7	13.30	0	0	[14]
16 $NCO + N \rightarrow CN + NO$	-30	5.2	14.66	0	5530	[15] ^d
17 $NCO + OH \rightarrow HNCO + O$	-12	0.9	13.30	0	0	estimate
18 $N_2O + H \rightarrow N_2 + OH$	-65	10.8	13.88	0	7600	[11]
19 $O_2 + H \rightarrow OH + O$	+16	-1.2	17.57	-1.0	8810	[16]
20 $H_2 + O \rightarrow H + OH$	+2	+0.1	10.26	1.0	4480	[16]
21 $H_2O + O \rightarrow OH + OH$	+17	-1.5	9.66	1.3	8605	[16]
22 $OH + H_2 \rightarrow H + H_2O$	-15	1.6	9.07	1.3	1825	[17]
23 $CN + H_2 \rightarrow HCN + H$	-16	1.8	11.74	0.7	2460	[13]
24 $CN + HCN \rightarrow C_2N_2 + H$	-4	-0.7	13.30	0	2140	[12] ^e
25 $NH + O \rightarrow NO + H$	-66	9.4	11.80	0.5	0	[11]
26 $NH + H \rightarrow N + H_2$	-20	2.7	13.70	0	1000	[11]

^aHeat of reaction at 1500° K (kcal/mole).¹⁸ We used $\Delta H_f^\circ(CN) = 101$ kcal/mole, an average of the values of Janaf¹⁸ and Colket.²¹

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

^cUsing the notation $k = A T^m \exp[-\theta/T]$ (cm³/mole/sec).

^dColket measured $k_{backward} = 10^{14} \exp[-21190/T]$ (cm³/mole/sec); we assumed $k_f/k_b = 4.54 \exp[15660/T]$.

^eWe measured $k_{backward} = 10^{14.5} \exp[-4030/T]$ (cm³/mole/sec); we assumed $k_f/k_b = 0.058 \exp[1890/T]$.

(dashed lines). The modified curves clearly fail to fit the data. We conservatively estimate the range of possible values for an acceptable fit to be [$\times 0.74$, $\times 1.35$] around the reported rate. Additional uncertainties in k_3 may result from uncertain knowledge of other rates of reactions present in the mechanism. In order to estimate these uncertainties, individual rates (Table I) were adjusted by reasonable factors (based on current literature or our judgment); k_3 was subsequently modified to ensure the return to an optimum fit. We found the resulting uncertainty in k_3 to be approximately [$\times 0.60$, $\times 1.42$]. The two uncorrelated uncertainties mentioned above may be combined to give a global uncertainty of $[\Sigma(\text{uncertainty})^2]^{1/2} = [\times 0.55, \times 1.60]$.

On the basis of this analysis, we recommend at temperatures near 1450° K:

$$k_3 = 10^{13.75(-0.26, +0.20)} \text{ cm}^3/\text{mole/sec.}$$

There are no previous data available for comparison.

From the computer-predicted NCO plateau and the corresponding experimental absorption, we can infer a value for β , the absorption coefficient at the peak wavelength. Uncertainties in β include experimental scatter, uncertainty in the Voigt parameter "a," and the uncertain knowledge of some reaction rates, including k_2 and k_3 . For a typical experiment, with an absorption plateau of 5% and

Source (Ref #)	
0	[11]
10	[2]
0	This study
75	This study
100	[12]
0	[2]
210	[2]
000	[12]
925	[5]
530	[13]
100	[11]
100	[11]
370	[11]
320	[11]
0	[14]
330	[15] ^d
0	estimate
100	[11]
10	[16]
80	[16]
05	[16]
25	[17]
60	[13]
40	[12] ^e
0	[11]
30	[11]

an average of the

$$= 4.54 \exp[15660/$$

$$= 0.058 \exp[1890/$$

we recommend at

³/mole/sec.

uitable for compari-

NCO plateau and absorption, we can a coefficient at the in β include ex- the Voigt param- ledge of some re- k_3 . For a typical plateau of 5% and

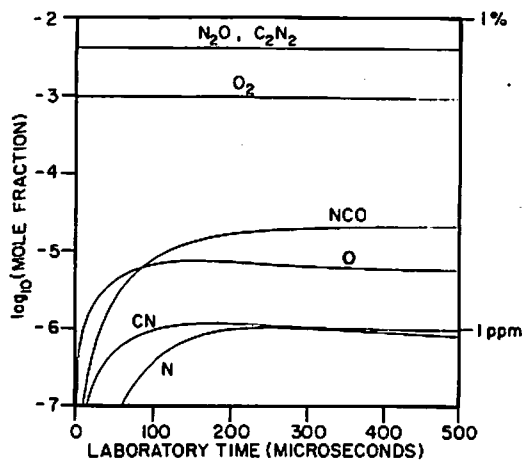


FIG. 3. Computer-generated profiles of N_2O , C_2N_2 , O_2 , NCO, O, CN and N mole fractions using the rates shown in Table I. Conditions: $T_2 = 1440^\circ K$, $p_2 = 0.60$ atm, $N_2O:O_2:C_2N_2:Ar = 4:1:4:991$ and $p_{21} = 3.31$.

$$p_{NCO} = 0.012 \text{ torr } (p_{NCO}/p = 26 \text{ ppmv}), \text{ we have:}^8$$

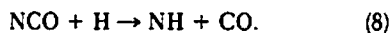
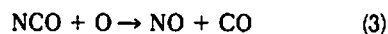
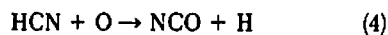
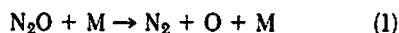
$$\beta(1450^\circ K) = 110 (-50, +130) \text{ cm}^{-1} \text{ atm}^{-1}$$

at 440.479 nm.

The signal-to-noise ratio achieved in these experiments was about 30, so that the detection limit of NCO ($S/N = 1$) using this scheme is about 1 ppmv.

$N_2O/O_2/HCN/Ar$ Mixtures—Analysis and Results

Data from these experiments were reduced using the complete kinetic mechanism in Table I, but a simplified model based on the following reactions is helpful in appreciating the similarity between the C_2N_2 and HCN experiments:



As with the C_2N_2 mixtures, the relative NCO trace depends on the rate of NCO removal $k_3[O] + k_8[H]$, and the plateau NCO concentration (normalized by the concentration of the NCO source, i.e. $[HCN]$) is given approximately by the ratio of the rate constants for the formation and removal steps:

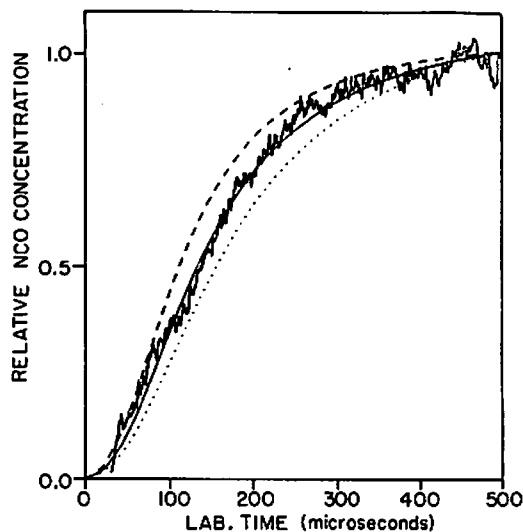


FIG. 4. Best computer fit to a typical experimental trace. Conditions: $T_2 = 1440^\circ K$, $p_2 = 0.60$ atm and $N_2O:O_2:C_2N_2:Ar = 4:1:4:991$. Abscissa: Laboratory time (microseconds). Absorption at 500 $\mu\text{sec} = 4.6\%$. Solid line: best computer fit using $k_3 = 10^{13.73} \text{ cm}^3/\text{mole}/\text{sec}$ and other rates shown in Table I. Dotted lines: Computer-generated profile using best rates, except: — $k_3 [\times 1.50]$ and - - - $k_3 [\times 0.67]$.

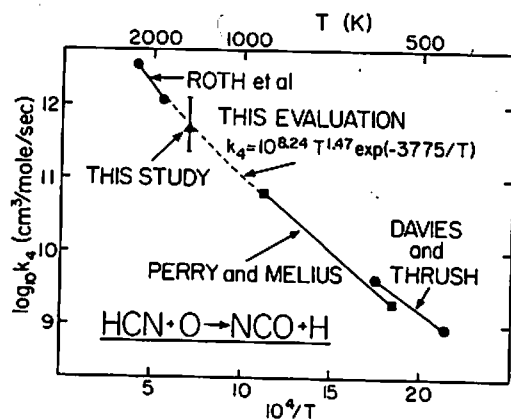
$$\frac{[NCO]_{\text{plateau}}}{[HCN]} \approx \frac{k_4}{k_3 + k_8 \frac{[H]}{[O]}}$$

Values of the steady-state concentrations of H- and O-atoms can be computed using the complete mechanism in Table I. Under typical conditions for the HCN mixtures, we have $[H]/[O] \approx 1.6$.

By conducting HCN and C_2N_2 experiments under similar conditions of temperature and pressure, it is therefore possible to infer the ratio k_4/k_2 by comparing the respective NCO absorption plateaus. We have:

$$\frac{[NCO]_{\text{plateau}}/[HCN]}{[NCO]_{\text{plateau}}/[C_2N_2]} = \frac{k_4}{2k_2} \times \frac{1}{1 + \frac{k_8}{k_3} \times \frac{[H]}{[O]}}$$

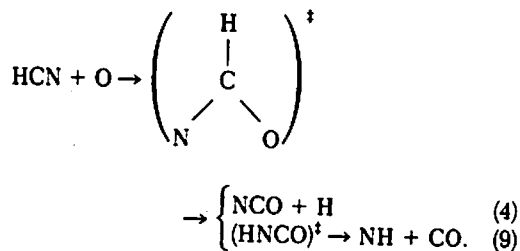
This approach makes the measurement of k_4/k_2 independent of the uncertainties associated with β that we reported above. However, the uncertain knowledge of some reaction rates in the mechanism (including k_3 and k_8) introduces an uncertainty of $[\times 0.6, \times 2.0]$ in the ratio. (Note that the rate of reaction (8) has been recently determined at $1490^\circ K$ in our laboratory.¹²) A reduction of the overall un-

FIG. 5. Arrhenius plot for k_4 .

certainty in k_4/k_2 could be achieved with further optimization of reactant mixtures.

We found at temperatures near 1440° K: $k_4/k_2 = 2.4 (-0.9, +2.4)$. Using our previously reported value² for $k_2 = 10^{12.66} \exp[-4440/T] \text{ cm}^3/\text{mole}/\text{sec}$ [$\times 0.54, \times 1.86$], we calculate $k_4 = 10^{11.70(-0.35, +0.40)} \text{ cm}^3/\text{mole}/\text{sec}$ at 1440° K. This determination of k_4 is plotted in Fig. 5 along with the earlier results of Roth *et al.*³ and Davies and Thrush,⁴ and the recent data of Perry and Melius.⁵

Melius and Binkley²⁰ recently showed that the reaction of HCN with O atoms follows two major paths:



Using transition state theory, and the results of Melius and Binkley,²⁰ Perry and Melius⁵ calculated the temperature dependence of k_4 :

$$k_4 \propto T^{1.47} \exp[-3775/T].$$

This temperature dependence is in excellent agreement with the three independent studies of Roth, *et al.*,³ Perry and Melius,⁵ and this study. For the purpose of providing a single expression for use over the temperature range $540 \leq T \leq 2500^\circ \text{ K}$, we have assumed the temperature dependence calculated by Perry and Melius⁵ and computed a least-squares fit expression based on the two end points of Roth *et al.*, the two end points of Perry and Melius, and one point from this study. On the basis of

this analysis, we recommend $k_4 = 10^{8.24} T^{1.47} \exp[-3775/T] \text{ cm}^3/\text{mole}/\text{sec}$ ($\pm 30\%$) in the range $540 \leq T \leq 2500^\circ \text{ K}$.

It should be noted that this expression does not extrapolate well into the temperature range studied by Davies and Thrush.⁴ Our recommended expression is lower than their value by about 50%. However, the value reported by Davies and Thrush should be interpreted as a total reaction rate ($k_4 + k_9$) (despite their assumption that NCO and H are the most likely products of this reaction), since they did not treat reaction (4) as a specific path for the (HCN + O) reaction. Thus, the results of Davies and Thrush are in excellent agreement with the total rate ($k_4 + k_9$) of Perry and Melius, who found $k_9/k_4 = 0.5$.⁵

Acknowledgments

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end $k_4 \approx 10^{8.24} T^{1.47}$
c ($\pm 30\%$) in the range

this expression does
temperature range stud-
Our recommended ex-
r value by about 50%.
orted by Davies and
d as a total reaction rate
umption that NCO and
ts of this reaction), since
(4) as a specific path for
hus, the results of Dav-
ent agreement with the
and Melius, who found

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l by the Environmental
ntract R-810019 and the
fic Research under con-
; assistance of E. C. Rea
laboratory in operating
acknowledged. The au-
woman for useful advice

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COMMENTS

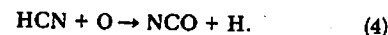
W. J. McLean, Sandia National Laboratories, USA.
Your results are affected by uncertainties in rate
constants used in the model as well as by experi-
mental uncertainties. Are you able to ascertain the
contributions of such rate constant uncertainties to
your overall uncertainty?

Authors' Reply. Uncertainties in the rate mea-
surements do result from the uncertain knowledge
of other rates of reactions present in the mecha-
nism. In order to estimate these uncertainties, in-
dividual rates (Table 1) were adjusted by reasonable
factors (based on current literature or our judg-
ment); values of the rate measurements were sub-
sequently modified to ensure the return to an op-
timal fit. Using a linear statistical analysis of these
uncorrelated individual uncertainties, we estimated
the total uncertainty on a rate measurement to be
given by

$$\text{total uncertainty} = [\sum(\text{uncertainty})^2]^{1/2}.$$

D. M. Golden, SRI International, USA. What evi-
dence is there that the reaction $O + HCN$ is pres-
sure independent? If the experiments do show
pressure independence, is this what would be ex-
pected from the Melius surface and an RRKM life-
time calculation?

Authors' Reply. The pressure range of our ex-
periments is too narrow to assess the effect of pres-
sure on the rate of reaction (4)



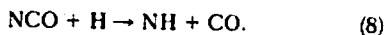
Please refer to Robert Perry's question for addi-
tional comments about this reaction.

R. A. Perry, Sandia National Laboratories, USA.
In the analysis of the kinetics of the reaction of $O(^1P)$
 $+ HCN \rightarrow NCO + H$ a detailed knowledge of the
relative concentrations of H and O atoms is re-
quired. How sensitive is your calculated rate coef-
ficient to the calculated H and O atom concentra-
tions? What are the estimated concentrations as-
sociated with these estimates?

In response to David Golden's questions, a simi-
lar question was asked by Van Tiggelen to myself
about my paper at this symposium. While the cal-
culations did not address this question directly the
fact that the energy barriers for rearrangement to
form $NH + CO$ and simple bond fission to form
 $NCO + H$ are nearly equivalent argues against a
major pressure dependence on the products. Also,
no pressure dependence is observed for the total
rate from low pressures torr to 200 torr total pres-
sure.

Authors' Reply. As indicated in the text, the ratio
 k_4/k_2 was inferred by comparing the steady-state
NCO concentrations in the HCN and C_2N_2 mix-
tures. The data reduction was performed on the
computer using a multi-reaction model based on the
mechanism of Table 1. However, a simplified model
is helpful in understanding the data reduction. pro-

cedure and the sensitivity of the present measurement of k_4/k_2 to the rate of reaction (8),



Using this simplified model,

$$\frac{[\text{NCO}]^{\text{plateau}}/[\text{HCN}]}{[\text{NCO}]^{\text{plateau}}/[\text{C}_2\text{N}_2]} = \frac{k_4}{2k_2} \times \frac{1}{1 + \frac{k_6[\text{H}]}{k_3[\text{O}]}}$$

Thus, the extraction of k_4/k_2 from the experimental ratio of NCO concentrations requires the knowledge of $[\text{H}]/[\text{O}]$ and k_6/k_3 . Values of the steady-state H- and O-atoms concentrations can be computed using the complete mechanism in Table 1. Under the present conditions $[\text{H}]/[\text{O}] \approx 1.6$. In addition, k_3 and k_6 have been measured in our laboratory, with the results $k_3 = 10^{13.75} \text{ cm}^3/\text{mole}/\text{sec}$ at 1450° K and $k_6 = 10^{13.73} \text{ cm}^3/\text{mole}/\text{sec}$ at 1490° K .¹² Note that the uncertainty analysis reported in the present paper was based on the complete mechanism of Table 1; the sensitivity of k_4/k_2 to uncertainties in $[\text{H}]$, $[\text{O}]$, k_3 , k_6 and other rates was estimated using this mechanism.

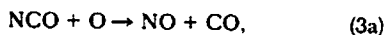
Thank you for your comments regarding Dr. Golden's question.

C. F. Melius, Sandia National Laboratories, USA. Have you considered the branching ratio of O + NCO to form N + CO₂ compared to NO + CO and could it be important in the formation of N atoms from fuel-bound nitrogen?

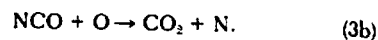
Authors' Reply. In these experiments, the direct measurement of NCO makes the determination of the rate of the reaction



fairly insensitive to the composition of the products. Nevertheless, we have assumed in the data reduction that the products of reaction (3) are NO + CO,



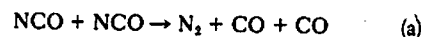
rather than N + CO₂,



If reaction (3b) proves a significant branching of reaction (3), then the NCO → NH → N sequence of the fuel-nitrogen mechanism may be partially bypassed by reaction (3b). Thus, further theoretical or experimental work is needed to assess the magnitude of the possible branching ratios of reaction (3).

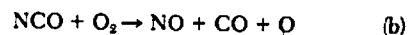
A. Lifshitz, Hebrew University of Jerusalem, Israel. Did you consider the termination reaction: $2\text{NCO} \rightarrow \text{N}_2 + 2\text{CO}$? Also, did you consider the reaction: $\text{NCO} + \text{O}_2 \rightarrow \text{NO} + \text{CO} + \text{O}$? Without the NCO + O₂ reaction we could not fit our computed ignition delay times to the experimental ones in shock heated mixtures of C₂N₂ + O₂ + Ar and C₂N₂ + O₂ + H₂ + Ar. We believe that this reaction does exist. The rate constant that we have assigned to this reaction is: $1.6 \times 10^{13} \exp(-19000/\text{RT}) \text{ cc mole}^{-1}\text{sec}^{-1}$.

Authors' Reply. Despite its high exothermicity ($\Delta H_R \approx -137 \text{ kcal/mole}$ at 1500° K), the reaction

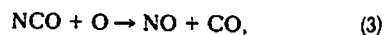


was not considered in the present data reduction, because the path to N₂ + 2CO requires a complex rearrangement of molecular bonds, with a presumably low transition probability.

Using similar arguments, the endothermic reaction



can be omitted from the present study of dilute C₂N₂/O₂/N₂O/argon mixtures ($\Delta H_R \approx +16 \text{ kcal/mole}$ at 1500° K). In addition, according to your evaluation $k_b = 1.6 \cdot 10^{13} \exp[-19000/\text{RT}] \text{ cm}^3/\text{mole}/\text{sec}$, the rate of reaction (b) is about seven times slower than the rate of reaction (3)



under the present experimental conditions ($T = 1500^\circ \text{ K}$). Thus, reaction (b) constitutes only a minor interference to the data reduction leading to k_4 .