

O- and N-Atom Measurements in High Temperature $C_2N_2 + O$ Kinetics

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The reaction of O-atoms with cyanogen was studied behind reflected shock waves using mixtures of nitrous oxide and cyanogen dilute in argon (10/100, 15/150, and 30/300 ppm N_2O /ppm C_2N_2), with temperatures in the range $1780 \leq T \leq 2285K$ and pressures of about 1.9 bar. Generation of O-atoms was achieved by the thermal decomposition of N_2O , and the reaction with C_2N_2 was monitored using resonance absorption measurements of the atomic species O and N (ARAS). The rate of disappearance of O-atoms by the reaction



was found to be

$$k_2 = 2.14 \times 10^{-10} \exp(-7130/T) \text{ cm}^3 \text{ s}^{-1} (\pm 20\%).$$

Measured N-atom concentration profiles confirm the reaction products $CN + NCO$ and the rate of reaction (2a) measured by Louge and Hanson [4], but a comparison of O- and N-atom profiles suggests, one or more additional channels to reaction (2).



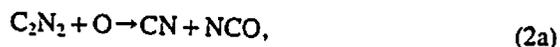
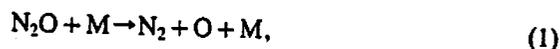
Computer simulations based on a proposed kinetic mechanism further substantiate the existence of additional channel(s) to reaction (2).

1. INTRODUCTION

Cyano species such as CN, C_2N_2 , and NCO have been shown to play an important role in the kinetics of fuel-nitrogen chemistry [1-3]. Unfortunately, direct measurements of their individual reaction rates are limited at high temperatures. In several recent papers, Louge and

Hanson [4-6] studied the oxidation of C_2N_2 , CN, and NCO behind incident shock waves. Generation of O-atoms was achieved primarily by the thermal decomposition of nitrous oxide, and the behavior of radical intermediates (CN, NCO) and reaction products (CO, NO) was monitored at high temperatures using several laser and conventional absorption techniques.

Louge and Hanson analyzed the data using a model comprising 17 reactions, and proposed a simplified description based on reactions (1)–(5),



Infrared laser absorption measurements of CO established that reaction (3) produces CO in excited vibrational states, and the direct narrow-line absorption of NCO using a cw ring dye laser confirmed the production of NCO by reaction (2a). Assuming that CN and NCO are the only products of reaction (2), a detailed kinetic analysis of the experiments led to

$$k_{2a} = 5.0 \times 10^{11} \text{ cm}^3/\text{mol s},$$

$$k_3 = 1.8 \times 10^{13} \text{ cm}^3/\text{mol s} \quad \text{near } 2000\text{K},$$

$$k_4 = 5.6 \times 10^{13} \text{ cm}^3/\text{mol s} \quad \text{near } 1450\text{K},$$

and a best-fit expression of k_5 in the range $2150 \leq T \leq 2400\text{K}$, $0.6 \leq p \leq 0.7$ bar,

$$k_5 = 6.3 \times 10^{16} T^{-0.5}$$

$$\times \exp[-24,000/T] \quad (\pm 90\%) \text{ cm}^3/\text{mol s}.$$

The value of k_{2a} measured by Louge and Hanson falls below the extrapolated expression determined by Boden and Thrush [7], who monitored the disappearance of O-atoms in $\text{C}_2\text{N}_2 + \text{O}$ systems at lower temperatures ($570 \leq T \leq 687\text{K}$), namely,

$$k_2 = 2.5 \times 10^{13} \exp[-5500/T] \text{ cm}^3/\text{mol s}.$$

Other measurements of cyano species rate constants are limited at flame temperatures [8]. However, many authors have studied k_3 at lower temperatures. Their results have been extensively reviewed by Baulch et al. [9].

From the above reaction mechanism, it is clear that O- and N-atoms play a key role in the

high temperature reactions of cyano species. In earlier shock tube studies, it was shown that atomic resonance absorption spectroscopy (ARAS) is a very sensitive and powerful technique for measuring these atomic species under conditions of high temperature and low reactant concentrations [10–12]. In the present paper, mixtures of C_2N_2 and N_2O highly dilute in argon were shock heated and O- and N-atoms were monitored behind reflected shock waves to determine the rate of



in the range $1780 \leq T \leq 2285\text{K}$. Further, O- and N-atom measurements established the existence of channels for reaction (2) other than (2a).

2. EXPERIMENTAL

The experiments were conducted behind reflected waves in a 79 mm internal diameter stainless-steel pressure-driven shock tube [10]. The tube could be heated during evacuation to a pressure of about 10^{-8} mbar. Typical leak-plus-outgassing rates were 8×10^{-7} mbar/min.

The reactant gases were carefully mixed in a special stainless steel storage cylinder which could be heated and evacuated using a secondary pumping unit. Commercial argon was used as a diluent (Messer-Griesheim, certified purity: 99.9999%, N_2 being the main impurity). N_2O (99.0%, impurity not specified) was utilized in very low concentrations, and served as a fast and clean source of O-atoms. C_2N_2 (1% dilute in argon, C_2N_2 impurity not specified) was taken from commercial Messer-Griesheim cylinders.

The optical diagnostic for measuring O- and N-atom concentrations was based on a line emission-line absorption technique. The optical arrangement [10, 11] consisted of a microwave discharge lamp, two thin LiF windows mounted flush on both shock tube walls, a 1 m McPherson vacuum uv monochromator, and a special solar blind photomultiplier. The O- and N-atom spectral lines (OI and NI, respectively) were excited using mixtures of 1% O_2 or N_2 dilute in helium, passing through the lamp at a pressure of 6 mbar. The rise time of the detection system

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was 25 μ s for a signal-to-noise ratio of about 15.

The mean temperature behind the reflected shock was computed from the measured incident shock speed using one-dimensional gasdynamic theory. The optical windows were located 15 mm from the end plate of the shock tube. Under these conditions, cooling of the reaction volume by heat transfer in the temperature boundary layer was negligible. In addition, boundary layer effects resulting in small time-dependent temperature fluctuations were ignored in this analysis.

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3. CALIBRATION PROCEDURE

The ARAS measurement technique is applied to measure O-atom concentrations at $\lambda = 130.5$ nm and N-atoms at $\lambda = 119.9$ nm. Spectral shapes of the lines emitted by the resonance lamp are not known precisely as a result of self-absorption or perhaps self-reversal. Thus, a calibration procedure is necessary to relate the measured resonance absorption to the corresponding O- and N-atom concentrations. The resulting relations are given elsewhere [12]. For typical conditions ($T \approx 2000$ K and $p \approx 1.9$ bar), $A_{OI} = 0.5$ for $[O] = 1.5 \times 10^{13}$ cm⁻³ and $A_{NI} = 0.5$ for $[N] = 4.3 \times 10^{12}$ cm⁻³. Note that these values depend also on the experimental conditions under which the light sources are operated [12].

In addition, possible absorption of atomic resonance radiation by the initial reactants must be taken into account in the data interpretation. Such interference absorption is negligible for N₂O, which is present under very low initial concentrations. On the other hand, interference absorption of both OI and NI radiation by C₂N₂ was found to be significant. Thus, the interference was characterized in three series of experiments, where mixtures of 100, 150, and 300 ppm C₂N₂ dilute in argon were shock heated to temperatures in the range $1870 \leq T \leq 2200$ K. Corresponding absorption cross-sections are shown in Fig. 1, with the results

$$\sigma_{OI}(C_2N_2) = 5.1 \times 10^{-17} \text{ cm}^2,$$

$$\sigma_{NI}(C_2N_2) = 1.5 \times 10^{-16} \exp[-1520/T] \text{ cm}^2.$$

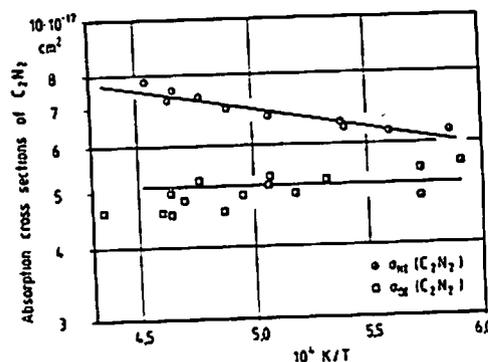


Fig. 1. Measured absorption cross-sections of C₂N₂ for OI and NI radiation.

In the case of short lived molecular intermediates, interference absorption was assumed to be negligible as a result of insufficient concentration levels. This assumption is made plausible by the observation of higher absorption cross-sections for O- and N-atoms than typical cross-sections for molecules.

4. EXPERIMENTAL RESULTS

The mixtures of initial reactants used in the present experiments were chosen to optimize the sensitivities and detection limits of the spectroscopic diagnostics, given an expected value of the rate coefficient k_2 . Several runs were conducted with 30/300, 15/150, and 10/100 ppm N₂O/ppm C₂N₂ dilute in argon. Temperatures behind the reflected shock waves were in the range $1780 \leq T \leq 2285$ K, with pressures of about 1.9 bar. Typical experimental traces of OI and NI resonance radiation are shown in Fig. 2. Rapid decrease in the transmission interference associated with C₂N₂ was observed immediately behind the incident and reflected shocks. Absorption of uv radiation by O-atoms generated in the decomposition of N₂O was observed behind the shock ($t > 0$, upper trace). O-atoms then reacted with C₂N₂ and the measured absorption signals reached a maximum value. Later, consumption of N₂O resulted in a decrease of O-atom concentrations. On the other hand, the

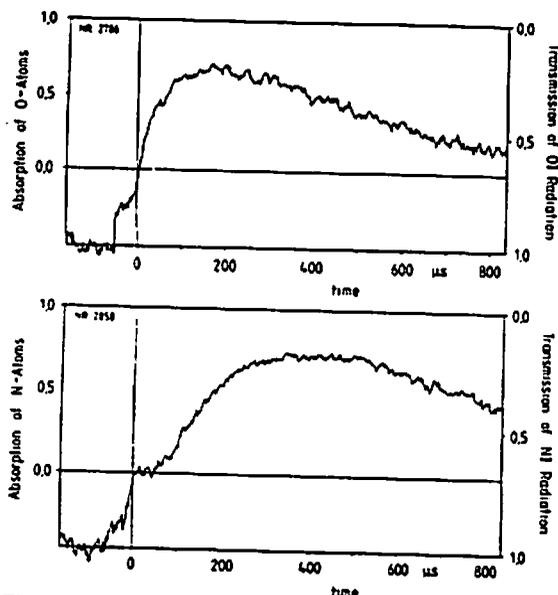


Fig. 2. Upper trace: typical absorption of O-atoms at $\lambda = 130.5$ nm, with the conditions: $T_1 = 1973$ K, $[\text{Ar}] = 6.9 \times 10^{18} \text{ cm}^{-3}$, $[\text{C}_2\text{N}_2]_0 = 150$ ppm, $[\text{N}_2\text{O}]_0 = 15$ ppm. Lower trace: typical absorption of N-atoms, with the conditions: $T_1 = 2095$ K, $[\text{Ar}] = 6.75 \times 10^{18} \text{ cm}^{-3}$, $[\text{C}_2\text{N}_2]_0 = 100$ ppm, $[\text{N}_2\text{O}]_0 = 10$ ppm.

absorption by N-atoms (lower trace) followed a distinct induction time, indicating that N-atoms are not among primary reaction products. In most N-atom traces, a maximum value was observed, which occurred at later times than comparable O-atom absorption maxima (Fig. 2).

Nearly 20 individual experiments were conducted under different experimental conditions. Typical examples of O- and N-atom concentrations measured behind reflected shock waves in $\text{N}_2\text{O}/\text{C}_2\text{N}_2/\text{Ar}$ mixtures are shown in Fig. 3. Both concentration profiles show a characteristic maximum. O-atom concentrations increase rapidly after the shock arrival and reach a maximum value of $[\text{O}]_m = 2.9 \times 10^{13} \text{ cm}^{-3}$, whereas N-atom concentrations increase more slowly and reach a much smaller value, $[\text{N}]_m = 6.2 \times 10^{12} \text{ cm}^{-3}$. Tables I and II summarize the experimental data. For each experiment, temperature and initial concentrations are given together with concentration maxima and as many as two additional points in a relative time

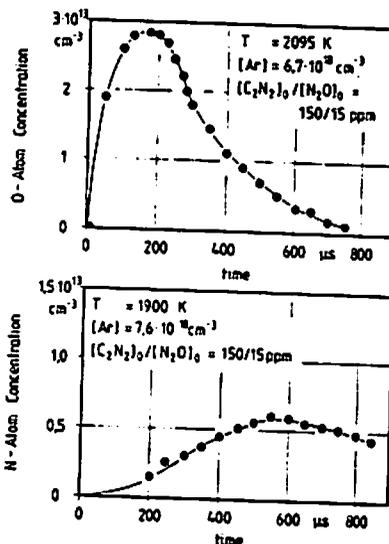
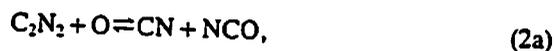
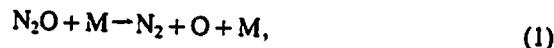


Fig. 3. Typical measurements of O- and N-atom concentrations behind shock waves.

scale. Experimental uncertainties in O- and N-atom concentrations are of the order of $\pm 20\%$.

5. ANALYSIS AND DISCUSSION

The direct measurement of atomic concentrations and the low amounts of reactants used in the present experiments greatly simplify the data interpretation. A simplified kinetic analysis following Louge and Hanson [5] is useful in guiding the data reduction, as follows: O-atoms produced by the well-established and rapid decomposition of N_2O react with C_2N_2 . Unlike the earlier interpretation of Louge and Hanson [5], an additional channel of reaction (2) has been postulated here without specifying reaction products,



Rates of secondary reactions of CN and NCO with O-atoms [reactions (3) and (4)], and the rate of NCO decomposition [reaction (5)] have been studied by Louge and Hanson [5]. However, in the present experiments, these reactions

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TABLE I

Experimental Data of Measured O-Atom Concentrations in N₂O/C₂N₂/Ar Mixtures

T (K)	[Ar] × 10 ⁻¹⁸ (cm ⁻³)	[N ₂ O]/ [C ₂ N ₂] ₀ (ppm/ppm)	t _m (μs)	[O] × 10 ⁻¹³ cm ⁻³			
				t _{m/2}	t _m	2t _m	3t _m
1780	7.38	30/300	300	0.95	1.15	1.00	—
1978	6.96	30/300	150	2.80	3.20	1.90	1.0
2150	6.40	30/300	75	—	5.30	3.75	1.50
1840	7.13	15/150	320	1.10	1.40	1.10	—
1920	7.50	15/150	225	1.80	2.30	1.42	0.85
1973	6.90	15/150	190	2.15	2.65	1.70	0.90
2085	6.35	15/150	150	2.70	3.60	2.00	0.8
2115	6.76	15/150	115	2.90	3.70	2.65	1.2
2120	6.57	15/150	120	2.90	3.70	2.25	1.1
1840	7.56	10/100	450	1.20	1.45	—	—
1970	7.06	10/100	230	1.90	2.35	1.50	—
2090	6.73	10/100	165	2.40	2.90	1.70	0.8
2170	6.41	10/100	120	3.00	3.60	2.25	1.0

TABLE II

Experimental Data of Measured N-Atom Concentrations in N₂O/C₂N₂/Ar Mixtures

T (K)	[Ar] × 10 ⁻¹⁸ (cm ⁻³)	[N ₂ O]/ [C ₂ N ₂] ₀ (ppm/ppm)	t _m (μs)	[N] × 10 ⁻¹² cm ⁻³			
				t _{m/4}	t _{m/2}	t _m	2t _m
1900	7.60	15/150	600	—	3.1	6.2	—
1910	7.28	15/150	550	1.0	3.6	6.3	—
2000	6.82	15/150	400	1.0	4.5	9.0	4.5
2030	7.07	15/150	400	1.6	5.5	9.3	2.0
2060	6.69	15/150	350	1.5	6.4	11.8	4.0
2165	6.43	15/150	260	1.5	6.2	12.4	4.2
1845	7.53	10/100	>800	—	—	2.4 ^a	5.0 ^b
1890	7.20	10/100	>800	—	—	2.0 ^a	5.2 ^b
2005	7.02	10/100	525	1.1	5.0	8.8	—
2095	6.75	10/100	400	0.8	5.0	10.0	4.0
2150	6.91	10/100	320	1.0	6.8	14.0	4.2
2280	5.75	10/100	260	<1.0	9.0	13.5	3.2
2285	6.20	10/100	250	<1.0	8.0	13.8	4.2

^a Reaction time t = 400 μs.^b Reaction time t = 800 μs.

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do not influence O-atom profiles significantly, especially at times leading to the peak. On the other hand, these reactions are more important for the understanding of the measured N-atom concentrations,



Secondary reactions such as (3), (4), and (5) are deduced from the known products of primary reactions such as (1) and (2). However, a set of secondary reactions is necessarily incomplete in the present case, because reactions involving the unknown products of (2b) have been omitted. As a result, the reaction behavior of the system becomes increasingly speculative at times long past the shock. On the other hand, the simplified reaction model presented above can hardly describe the measured peak of N-atom concentrations. Thus, a third group of reactions is postulated which involves known primary products and consumes N-atoms. The relatively high concentrations of C_2N_2 and the high reactivity of CN [13] make both species likely reaction partners of N-atoms, i.e.,



Possible products of reaction (7) include CN + NCN.

A simplified analysis of the measured O-atom profiles has been based on the above reaction mechanism. In this case, the rate of change of O-atom concentrations can be written

$$\frac{d[\text{O}]}{dt} = k_1[\text{N}_2\text{O}][\text{Ar}] - k_2[\text{C}_2\text{N}_2][\text{O}] - k_3[\text{CN}][\text{O}] - k_4[\text{NCO}][\text{O}].$$

At time $t = t_m$, the O-atom peak concentration is reached and $d[\text{O}]/dt = 0$. Note that C_2N_2 concentrations are nearly constant and equal to their initial value throughout the period of interest. At the peak, the above equation can be

rearranged, as follows:

$$k_2 = \frac{k_1[\text{N}_2\text{O}]_m[\text{Ar}]}{[\text{C}_2\text{N}_2]_0[\text{O}]_m} - k_3 \frac{[\text{CN}]_m}{[\text{C}_2\text{N}_2]_0} - k_4 \frac{[\text{NCO}]_m}{[\text{C}_2\text{N}_2]_0},$$

where

$$\frac{[\text{N}_2\text{O}]_m}{[\text{N}_2\text{O}]_0} = \exp(-k_1[\text{Ar}]t_m).$$

Note that k_1 , the rate coefficient for N_2O decomposition, is well established [14, 15]. In addition, since the decomposition of NCO is fast under the present conditions of pressure and temperature, the concentration of NCO at the peak ($[\text{NCO}]_m$) is much smaller than the concentration of CN at the peak ($[\text{CN}]_m$). Thus, the last term in the equation giving k_2 can be ignored. Finally, the contribution of reaction (3) to the O-atom balance is smaller than 15% at any time before the peak. Thus, the rate of disappearance of O-atoms is controlled by reactions with C_2N_2 , and the following simplified expression gives the rate of reaction (2):

$$k_2 = \frac{k_1[\text{Ar}][\text{N}_2\text{O}]_0 \exp(-k_1[\text{Ar}]t_m)}{[\text{C}_2\text{N}_2]_0[\text{O}]_m}.$$

(Note that k_2 is the sum of k_{2a} and k_{2b} .) Thus, k_2 can be determined from the measured concentrations $[\text{O}]_m$ at times t_m and the known levels of initial reactants. Results corresponding to the data of Table I are summarized in Table III. The approximate values of k_2 show an Arrhenius behavior which can be fitted using the least-squares expression

$$k_2 = 2.14 \times 10^{-10} \exp[-7130/T]$$

$$\text{cm}^3 \text{ s}^{-1} (\pm 20\%)$$

in the range $1780 \leq T \leq 2170\text{K}$. This value of k_2 is slightly above the value extrapolated from the low temperature results of Boden and Thrush [7] (Fig. 4) and a factor of 7 higher than the value of k_{2a} determined by Louge and Hanson [4]. From the earlier results of Louge and Hanson and the present experiments, it is clear that an additional reaction channel (2b) becomes important for the high temperature reaction of

$\text{C}_2\text{N}_2 + \text{O} \rightarrow \text{KJ}$

Rate

T (K)

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1978
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Rate coefficients
 k_2, k_{2a}

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TABLE III

Rate Coefficient k_2 Determined from the Data in Table I and Assuming a Simple Reaction Model

T (K)	$[Ar] \times 10^{-18}$ (cm ⁻³)	t_m (μ s)	$[O]_m \times 10^{-13}$ (cm ⁻³)	$[N_2O]_0 / [C_2N_2]_0$	$[N_2O]_m / [N_2O]_0$	$k_2 \cong k_1 [Ar] / ([O]_m [N_2O]_0 / [C_2N_2]_0)$ $[N_2O]_m / [N_2O]_0$ (cm ³ s ⁻¹)
1780	7.38	300	1.15	0.1	0.85	4.0 10 ⁻¹²
1978	6.96	150	3.20	0.1	0.65	5.8 10 ⁻¹²
2150	6.40	75	5.30	0.1	0.50	8.7 10 ⁻¹²
1840	7.13	320	1.40	0.1	0.75	4.9 10 ⁻¹²
1920	7.50	225	2.30	0.1	0.65	5.5 10 ⁻¹²
1973	6.90	190	2.65	0.1	0.59	6.1 10 ⁻¹²
2085	6.35	150	3.60	0.1	0.42	6.8 10 ⁻¹²
2115	6.76	115	3.70	0.1	0.41	8.5 10 ⁻¹²
2120	6.57	120	3.80	0.1	0.40	8.0 10 ⁻¹²
1840	7.56	450	1.45	0.1	0.64	4.3 10 ⁻¹²
1970	7.06	230	2.35	0.1	0.53	6.2 10 ⁻¹²
2090	6.73	165	2.90	0.1	0.35	7.7 10 ⁻¹²
2170	6.41	120	3.60	0.1	0.33	8.5 10 ⁻¹²

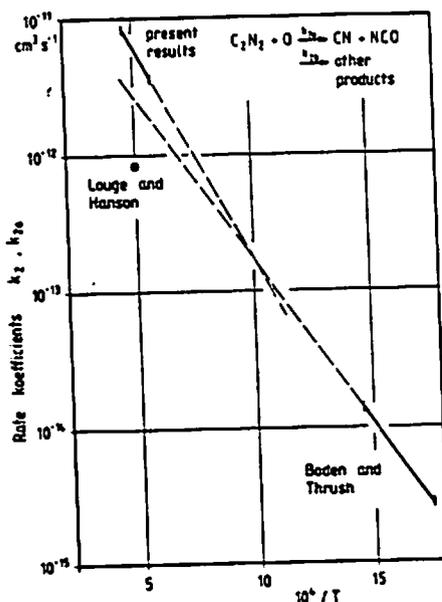
O-atoms with C₂N₂. Unfortunately, the present lack of knowledge on the products of reaction (2b) makes a more detailed computer analysis of our experimental O-atom traces somewhat speculative.

A tentative simplified analysis of the mea-

sured N-atom profiles is based on reactions (1), (2a), (2b), and (5). The resulting differential equations describing the time-dependent concentrations of N₂O, O, and N can be linearized and solved analytically assuming that reaction (5) is very fast, the concentration of C₂N₂ is nearly constant, and the unknown products of reaction (2b) do not decompose rapidly to form N-atoms. Among these conditions, the first two are satisfied for the early period of N-atoms generation. Reactions (1), (2a), (2b), and (5) can then be described using a system of linear differential equations. The corresponding solution for the time-dependent N-atom concentrations can be written

$$\frac{[N]}{[N_2O]_0} = \frac{c}{a-b} \left[\frac{a-b}{b} + \exp(-at) - \frac{a}{b} \exp(-bt) \right],$$

where $a = k_1[Ar]$, $b = k_2[C_2N_2]_0$, and $c = k_{2a}[C_2N_2]_0$. This approximate solution depends on three parameters, namely, a , b , and c . Note that if channel (2a) were the only channel for reaction (2), the above solution would still apply using $c = b$.

Fig. 4. Arrhenius diagram for k_2 and k_{2a} .

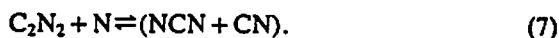
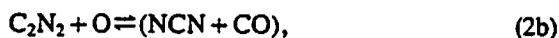
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A comparison between measured and computed N-atom profiles is given in Fig. 5. It appears that the analytical solution using $c = k_{2a}[C_2N_2]_0$ and k_{2a} from Louge and Hanson [4] fits the early stages of N-atom formation quite well, whereas the approximate solution using $c = b$ is much too high. This observation together with the O-atom measurements reported above underlines the existence of two or more channels for the reaction of $C_2N_2 + O$ and confirms the value of k_{2a} measured by Louge and Hanson [4] around 2000K.

At this point of the analysis, results have been fairly independent of the exact nature of the unspecified products of reactions (2b) and (7). However, additional insight may be gained by making further assumptions concerning the products of these reactions. As discussed in the literature [7, 9], the NCN radical is a plausible product, which we will assume in further kinetic modeling,



Accordingly, a simple reaction mechanism is

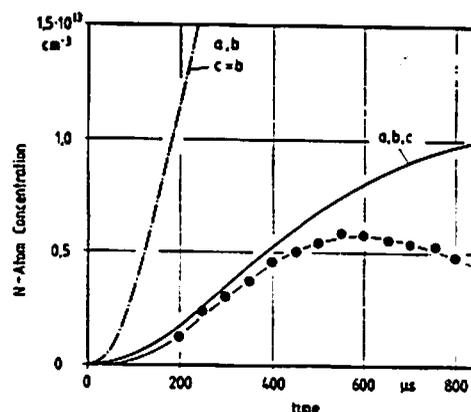


Fig. 5. Comparison of a typical time-dependent N-atom concentration measurement with various simple analytical solutions for the N-atom profiles. The experimental conditions are $T_1 = 1900K$, $[Ar] = 7.6 \times 10^{18} \text{ cm}^{-3}$, $[C_2N_2]_0 = 150 \text{ ppm}$, $[N_2O]_0 = 15 \text{ ppm}$.

developed, which can be divided in three groups, as shown in Table IV.

In the first group, reaction rates seem well established and, apart from reaction channel (2b), products are well defined. These reactions are most important to describe early time-histories of O- and N-atoms, except reaction (4),

TABLE IV

Proposed Reaction Mechanism for the High Temperature $C_2N_2/N_2O/Ar$ System with Low N_2O Concentrations

	Reaction	Rate Coefficient $\text{cm}^3 \text{ s}^{-1}$	Ref.
1	$N_2O + M = N_2 + O + M$	$1.55 \times 10^{-9} \exp(-29830/T)$	[14, 15]
2a	$C_2N_2 + O = CN + NCO$	$7.60 \times 10^{-12} \exp(-4440/T)$	[4]
2b	$= (CO + NCN)$	$2.30 \times 10^{-10} \exp(-7540/T)$	See text
3	$CN + O = CO + N$	3.00×10^{-11}	[4, 16]
4	$NCO + O = CO + NO$	9.33×10^{-11}	[6]
5	$NCO + M = CO + N + M$	$1.05 \times 10^{-10} \exp(-24000/T) \times T^{-0.5}$	[5]
6	$CN + N = C + N_2$	$7.30 \times 10^{-10} \exp(-4530/T)$	[13]
7	$C_2N_2 + N = CN + NCN$	k_{2a}	Estimated
8	$NCN + O = CN + NO$	k_{12}	Estimated
9	$= NCO + N$		Estimated
10	$NCN + N = CN + N_2$		Estimated
11	$NCN + M = CN + N + M$	$1.00 \times 10^{-10} \exp(-45000/T) \times T^{-0.5}$	Estimated
12	$NO + N = N_2 + O$	4.00×10^{-11}	[17]
13	$CN + C = C_2 + N$	$5.00 \times 10^{-10} \exp(-18,120/T)$	[13]
14	$C_2N_2 + M = CN + CN + M$	$1.05 \times 10^{-7} \exp(-50040/T)$	[18, 19]

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which is overshadowed by a fast thermal decomposition of NCO. Reactions of the NCN radical are gathered in a more speculative second group, where uncertain rate coefficients are merely estimated. Because of a predictably slower thermal decomposition of NCN, it is reckoned that, unlike NCO, bimolecular reactions of NCN with O and N should be significant. In addition, the well-established reaction (12) can influence the N- and O-atom profiles marginally, given the levels of NO produced by (8). Finally, reactions (13) and (14) are of minor importance under the relatively low temperatures of the present experiments.

In this study, it is not an intention to fit all rate coefficients by matching computed and measured atomic profiles, because of the uncertain nature of reactions (7)–(11). However, the computer model based on Table IV is useful in appreciating general tendencies of the kinetic mechanism. Figure 6 illustrates the computer analysis.

O-atom profiles are nearly independent of

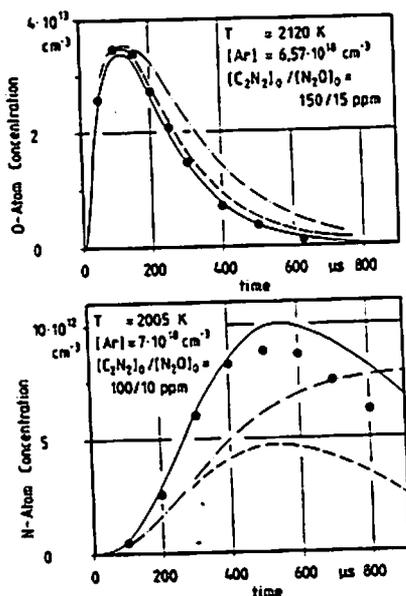


Fig. 6. Comparison of typical O- and N-atom profiles with computer simulations based on the mechanism in Table IV. The solid line (—) corresponds to the complete mechanism; the dash-dotted line (-·-) assumes k_7 to $k_{11} = 0$, and the dashed line (- -) $k_9 = 0$.

reactions (7)–(11), but a better fit is obtained by including these reactions in the model (solid line). The value of k_2 based on our simplified interpretation above is thus confirmed by detailed modeling, although computed O-atom maxima fall slightly below measurements, indicating a value of k_2 perhaps smaller than reported above.

By contrast, N-atom profiles are strongly dependent on reactions involving NCN. Ignoring reactions (7)–(11) leads to erroneous fits (Fig. 6, dash-dotted line). Further, reaction (9) is particularly important to the N-atom time-history, because it gives rise to two N-atoms (one directly, and another through rapid NCO decomposition); the dashed line in Fig. 6 corresponds to $k_9 = 0$, and clearly fails to reproduce the data. In general, it should be possible to fit measured N-atom profiles over a considerable time range by introducing individual rates for reactions (8)–(10). In the present study, we have merely assumed $k_8 = k_9 = k_{10} = k_{12}$ (Table IV). Despite occasional deviations toward later times, this approximate mechanism reproduces well the early behavior of N-atom profiles.

Thus, computer modelling corroborates our measurements for k_2 and the value for k_{2a} reported by Louge and Hanson [4]. In addition, it emphasizes the role of NCN as an intermediate in the oxidation of cyanogen at high temperatures.

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