

Chemical Kinetic Data Base for Propellant Combustion. II. Reactions Involving CN, NCO, and HNCO

Cite as: Journal of Physical and Chemical Reference Data **21**, 753 (1992); <https://doi.org/10.1063/1.555914>
Submitted: 19 June 1991 . Published Online: 15 October 2009

Wing Tsang



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Chemical Kinetic Data Base for Propellant Combustion I. Reactions Involving NO, NO₂, HNO, HNO₂, HCN and N₂O](#)

Journal of Physical and Chemical Reference Data **20**, 609 (1991); <https://doi.org/10.1063/1.555890>

[Chemical Kinetic Data Base for Combustion Chemistry. Part I. Methane and Related Compounds](#)

Journal of Physical and Chemical Reference Data **15**, 1087 (1986); <https://doi.org/10.1063/1.555759>

[Evaluated Kinetic Data for Combustion Modelling](#)

Journal of Physical and Chemical Reference Data **21**, 411 (1992); <https://doi.org/10.1063/1.555908>



Where in the **world** is AIP Publishing?
Find out where we are exhibiting next



Chemical Kinetic Data Base for Propellant Combustion

II: Reactions Involving CN, NCO, and HNCO

Wing Tsang

Chemical Kinetics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Received June 19, 1991; revised manuscript received December 18, 1991

This paper contains evaluated chemical kinetic data on single step elementary reactions involving small polyatomic molecules which are of importance in propellant combustion. The work consists of the collection and evaluation of mechanistic and rate information and the use of various methods for the extrapolation and estimation of rate data where information does not exist. The conditions covered range from 500–2500 K and 10^{17} – 10^{22} particles cm^{-3} . The results of the second year's effort add to the existing data base reactions involving CN, NCO and HNCO with each other and the following species: H, H_2 , H_2O , O, OH, HCHO, CHO, CO, NO, NO_2 , HNO, HNO_2 , HCN, and N_2O .

Key words: CN; combustion; HNCO; kinetic; NCO; propellant.

Contents

1. Preface.....	753	1.6. Acknowledgements.....	756
1.1. Scope.....	753	1.7. References to the Preface.....	756
1.2. Organization.....	754	2. Index of Reactions and Summary of Recommended Rate expressions.....	756
1.3. Guide to Summary Table.....	754	3. Chemical Kinetic Data Tables.....	759
1.4. Guide to Chemical Kinetic Data Tables...	754	4. Thermodynamic Data Tables.....	791
1.5. Guide to Thermodynamic and Transport Tables.....	756	5. Transport Properties Table.....	791

1. Preface

1.1. Scope

This is the second¹ of a series of papers designed to provide information for the quantitative understanding of the chemical kinetic aspects of propellant, or more specifically, nitramine combustion. The general approach is to start with the simplest possible subsystems and build to increasingly complex situations. Thus our earlier efforts in hydrocarbon combustion² have generated data dealing with formaldehyde pyrolysis and combustion. This also contains as subsets data pertaining to the H_2 – O_2 –CO combustion system. The first of this series of papers brings into the picture contributions from nitrogenated oxidants such as NO_2 and N_2O . In this paper we are concerned with two important and highly reactive intermediates formed in the course of nitramine decomposition CN, NCO and the more stable HNCO species. Together with earlier data dealing with HCN, we have, in

principle at least, the capability of simulating HCN pyrolysis and combustion either by itself or in the presence of formaldehyde. The species that are considered are important players in NO_x formation and decomposition processes. Thus there has been a considerable amount of past work in these contexts. An important objective in this work is to extend the existing data into conditions that may be prevalent in propellant combustion systems. This presents a number of challenges which will be discussed in the course of this work.

Our approach is to be as inclusive as possible. Having decided on the important species that should be considered we constructed a reaction grid and examined all possible reactions of these species. In the absence of information a best possible estimate is given. Where information on a particular reaction is not given, the implication is that under the reaction conditions covered in this evaluation the rate constant is sufficiently small so that it can be safely ignored. Thus for example we assume that CO will not react with NCO. The reaction grid containing all the reactions that have been considered can be found in Figure 1. They represent the past (A and B) present (C) and next set of reactions to be covered (D). In all cases we give recommended rate expressions over

©1992 by the U.S. Secretary of Commerce on behalf of the United States. This copyright is assigned to the American Institute of Physics and the American Chemical Society.

Reprints available from ACS; see Reprints List at back of issue.

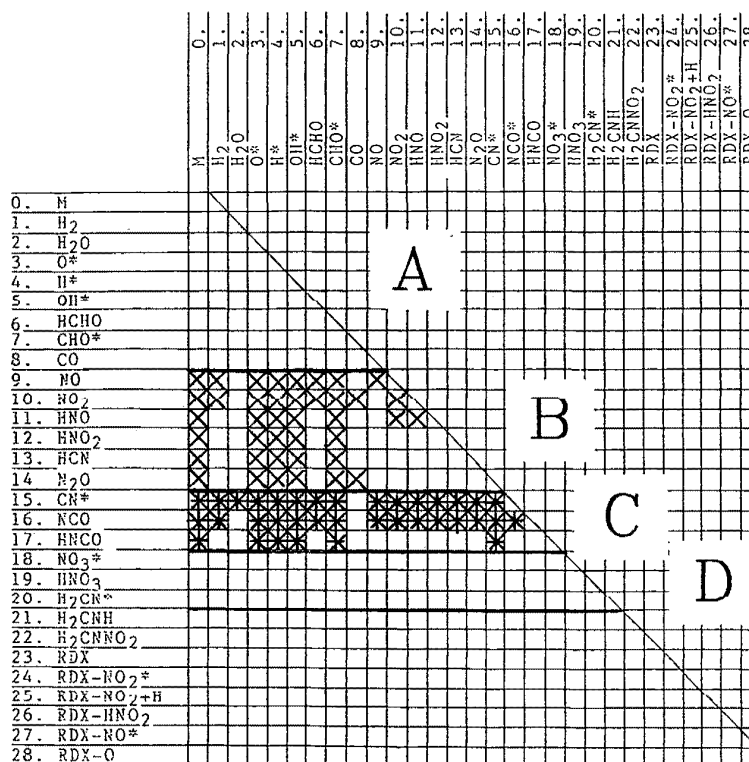


FIG. 1. Reaction grid for RDX decomposition
 X: Reactions Covered in Ref. 1
 +: Reactions evaluated in current study

the temperature range of 500–2500 K and the particle density range of 10^{17} – 10^{22} molecules/cm³.

1.2. Organization

The data are presented in the same fashion as in the earlier evaluations^{1,2}. It is expected that the data presented here will be used in conjunction with those given in the previous publications. A more detailed discussion of many important general issues and justification of procedures used can be found in our earlier publication¹. In the following, we provide information necessary for the use of the present data.

The data are presented in three different portions of the manuscript. The first contains a summary of the recommended rate expressions, the estimated error limits and the page where a discussion can be found. The second contains additional information on the individual reactions. It includes a summary of past work and the justification for the recommendations. The last contains relevant thermodynamic and transport property data.

1.3. Guide to Summary Table

The summary table contains all the recommended rate expressions, the uncertainty limits and the page where a more detailed discussion can be found. In the case of unimolecular processes or the reverse we give results in

terms of the high pressure limit and closed expressions for k/k_∞ for N₂ and CO₂. The latter is intended to approximate the situation with respect to collisional efficiencies in propellant decomposition contexts.

1.4. Guide to Chemical Kinetic Data Tables

The information in these tables contains a summary of past work, our analysis of this literature and recommendations on rate expressions and uncertainty limits. We retain the numbering system that we use in our first contribution and to the 14 species, labelled 1–14, add labels 15, 16, and 17 for CN, NCO and HNCO. The number 0 is reserved for the collision partner (M) in unimolecular decompositions. It does not take part in the reaction. Since pairs of these numbers form a particular reaction, we now consider reactions of these three compounds with all lower numbered species and with themselves. These sequence numbers are at the top left hand corner of all the data tables. This is followed by a statement of the elementary reaction and, if applicable, the appropriate equilibrium constant.

In the next row is a synopsis of all previous work. It begins with a listing of the author(s) and the year of publication. In the case of a review, a note is made to this effect and in many cases this is used as a starting point for our efforts. This is followed by a synopsis of the reaction conditions, the derived rate expressions and the uncer-

tainty limits. The latter are either given by the author or estimated by the reviewer on the basis of similar experiments. Most of the reactions are bimolecular and the units are $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For unimolecular and bimolecular reactions the units are s^{-1} and $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, respectively. As an aid to the user in those cases where there are an extensive experimental data or for other reasons we also include a plot in the Arrhenius form of the data and our recommendations.

The next section contains the justification for the recommended expression. In the case of unimolecular reactions (or the reverse bimolecular process) there are also two tables. This is due to the pressure dependence of the rate constants under certain conditions. The first table contains the ratio of rate constants at a particular pressure and the pressure independent value at sufficiently high pressure assuming strong collisions (deactivation on every collision) and with the molecule itself as the collision partner. The second table contains values for the collision efficiency as a function of the step size down and the reaction temperature. The tabulated results are based on the relation of Troe³. At the present time there is uncertainty regarding the magnitude and temperature dependence of the step sizes. No exact predictions can be made and therefore it can be treated as an adjustable parameter. However, in the course of the work on hydrocarbons², some general trends have been observed. We have cast our calculations in this form so that users can utilize their own step sizes. In order to convert these values to those for an arbitrary collider we follow the approach of Troe⁶ and derive a correction factor, $\beta(c) = C^2 W/R^{0.5}$ where C is the ratio of collision diameters, W is the ratio of collision integrals and R the ratio of reduced masses. In each case we compare collisions of the target molecule with itself and with the bath molecule. Having now corrected for the collisional effects we then multiply this factor with the collision efficiency derived on the basis of the step size down and arrive at the total collision efficiency $\beta(t) = \beta(e) \times \beta(c)$. $\beta(t)$ is then used to scale the reaction pressure to a value that can be read from the Table. It is necessary to present the data in this form because no one has yet found a closed form relation for the rate constants of unimolecular reaction that is applicable at all temperatures, pressures and collisional partners.

In the following we carry out a sample calculation. It involves the combination of CN radicals at 1100 K in N_2 and 1 atm pressure (data sheet 15,15). We begin by calculating the quantities discussed earlier;

- Ratio of reduced masses (R); $18.2/26 = 0.7$; where the systems under consideration are $\text{C}_2\text{N}_2\text{-N}_2$ and $\text{C}_2\text{N}_2\text{-C}_2\text{N}_2$.
- Ratio of collision diameters (C); $4.361 + 3.798/2 \times 4.361 = 0.935$; where 4.361 is the collision diameter for C_2N_2 and 3.798 is that for N_2 (in Angstroms).
- Ratio of collision integrals (W); since ϵ/k for C_2N_2 and N_2 are 348.6 K and 71.4 K respectively and $\epsilon/k(\text{C}_2\text{N}_2\text{-N}_2) = [\epsilon/k(\text{C}_2\text{N}_2\text{-C}_2\text{N}_2) \times \epsilon/k(\text{N}_2\text{-N}_2)]^{0.5}$, the substitution into the relation recommended by Troe

for the collisional integral $(0.697 + 0.5185 \log(T/\epsilon(\text{gas}_1 - \text{gas}_2)/k))^{-1}$ leads to values of 1.046 and 0.882 for $\text{C}_2\text{N}_2\text{-C}_2\text{N}_2$ and $\text{C}_2\text{N}_2\text{-N}_2$ collisions respectively. The ratio of the two number is then 0.842. This then leads to a value for $\beta(c)$ of 0.881 for collisions between C_2N_2 and N_2 . If we now take a step size down of 440 cm^{-1} we find from Table 2, $\beta(e) = 0.11$. The total collision efficiency is thus 0.097. The number density at 1 atm and 1100 K is $6.7 \times 10^{18} \text{ molecules/cm}^3$. When multiplied by the collision efficiency of 0.097 we arrive at an equivalent density of $6.5 \times 10^{17} \text{ molecules/cm}^3$. Then from Table 1 we find $\log_{10}[k/k_\infty] = -0.59$ or 0.26 of the limiting high pressure value. Note that the transport properties are from Ref. 7.

If one specifies the collision partner Troe³ has found a means of writing a closed form expression. The general relations are

$$k = \{k_0 k_\infty / [k_0 + (k_\infty / M)]\} \times F$$

$$\log F = \log F_c / \{1 + [\log(k_0 \times M / k_\infty)]^2\}$$

where k_0 is the second(or third) order rate constant and k_∞ is the first(or second) order rate constant, M is the concentration of the collision partner and F_c is a correction term called the broadening factor. Although Troe gives methods for calculating F_c on the basis of transition state considerations, we have found it much simpler to derive F_c by comparing the k/k_∞ derived from the RRKM calculations with the Lindemann expression $[k_0 k_\infty / (k_0 + k_\infty / M)]$ and determining at each temperature the appropriate broadening factor. We find the broadening factor F_c determined in this fashion can be easily expressed as a linear function of the temperature with an uncertainty of no more than a factor of about 1.20. This is well within experimental error. Thus we also present closed expressions for N_2 and CO_2 as the collisional partner. We suspect that for most applications this can be used directly. Results with CO_2 as a collision partner are presented because unlike hydrocarbon combustion systems, where reactions are carried out in a background of N_2 , propellants carry their own oxidizers. Therefore, the reactive background is a more complex mixture of polyatomic gases. We have chosen CO_2 as a gas with properties that will be representative of such mixtures. We do not believe that this will cause serious errors except at the lowest temperatures where the presence of water may have very serious effects. In the case of $\text{C}_2\text{N}_2 - \text{N}_2$ at 1100 K given above, we find with $F_c = 0.5$, $k_\infty = 9.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_0(\text{N}_2) = 9.4 \times 10^{-23} (1/T)^{2.61}$, then $\log_{10}(k/k_\infty) = -0.63$, in close approximation to the number derived from Tables 1 and 2 given above.

The final section contains the references, the person who carried out the analysis and the date. Hopefully, all the literature on this reaction previous to this date has been reviewed. We will be most grateful to readers who will bring to our attention publications that have

been omitted. We will also welcome any and all kineticists who would like to prepare data sheets for inclusion in these evaluations.

1.5. Guide to Thermodynamic and Transport Tables

This section contains thermodynamic and transport properties for the molecules of concern. Inasmuch as the values used here are extracted from the JANAF⁶ compilation we summarize the results in terms of a polynomial expression for $\log[K_p]$. For the CN radical we have chosen to use a heat of formation of 415.1 kJ/mol. This is the value selected by Colket⁵. This is about 17 kJ/mol lower than the JANAF⁶ recommendation. The latter is based on the average of high values near 456 kJ/mol and low values clustering about 415 kJ/mol. In the course of this work we found that the data for cyanogen decomposition in shock tubes, the reverse of CN combination (see 15,15), could not be fitted with the JANAF recommended value. Note that in this instance any discrepancy in the heat of formation of CN is doubled. As a result a 37 kJ/mol higher reaction threshold would have forced the use of a compensating collisional efficiency a factor of 10 higher to match the experimental results, if the decomposition process is still in the second order region. Indeed, it was found that such a large collisional efficiency brings the high temperature shock tube decomposition reaction into the pressure dependent region. As a result a match of the experimental result could never be made. For an even larger value of the heat of formation of CN the situation

will be made worse. With the present number a step size down in argon of about 500–1000 cm⁻¹ was required to fit the data. This is very much in line with other high temperature decomposition reactions². Finally for unimolecular decomposition we also include a table of transport properties⁷. It should be noted that in the cases where such data does not exist we have made estimates using as a basis the closest comparable molecule.

1.6. Acknowledgement

This work was carried out with the support of the Air Force Office of Scientific Research, the Office of Naval Research and the Hercules Aerospace Company. We wish to thank Dr. John T. Herron for a careful reading of the manuscript.

1.7. References to Preface

- ¹Tsang, W., "Chemical Kinetic Data Base for Propellant Combustion: I: Reactions Involving NO, NO₂, HNO, HNO₂, HCN, N₂O", J. Phys. Chem. Ref. Data., **20**, 609, (1991).
- ²Tsang, W. and Hampson, R. F., J. Phys. Chem. Ref. Data, **15**, 1087, (1986).
- ³Troe, J., J. Chem. Phys., **66**, 4725, 4758, (1977); R. C. Gilbert, K. Luther and J. Troe, Ber. Bunsenges. Phys. Chem., **87**, 169, (1983).
- ⁴Tsang, W., Comb. and Fuel, **78**, 71, (1989).
- ⁵Colket, M. B., J. Quant. Spectros. Radiat. Transfer **31**, 7, (1984).
- ⁶Chase, M. W., Davies, C. A., Downey, J. R., Frurip, D. J., MacDonald, D. R., and Syverud, A. N. J. Phys. Chem. Ref. Data, **14**, (1985).
- ⁷Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids" McGraw-Hill Book Company, New York, (1987).

2. Index of Reactions and Summary of Rate Expressions

Reactions	Rate expressions cm ³ molecule ⁻¹ s ⁻¹	Uncertainties	Page
15,0 CN + M → C + N + M	4.2 × 10 ⁻¹⁰ exp(-71000/T) Ar 6.3 × 10 ⁻¹⁰ exp(-71000/T) N ₂ 1 × 10 ⁻⁹ exp(-71000/T) CO ₂	2 at 6000 K	759
15,1 CN + H ₂ → H + HCN	6 × 10 ⁻¹⁶ T ^{1.55} exp(-1510/T)	1.6	759
15,2 CN + H ₂ O → HCN + OH	1.3 × 10 ⁻¹¹ exp(-3755/T)	1.2 at 750 K 3 at 2500 K	761
15,3 CN + O → CO + N	3.4 × 10 ⁻¹¹ exp(-210/T)	2	762
15,4 CN + H + M → HCN + M	$k_{\infty} = 2.99 \times 10^{-9}(1/T)^5$ $k(0, N_2) = 2.4 \times 10^{-24}(1/T)^{2.2}$ $\exp(-567/T)$ cm ⁶ molecule ⁻² s ⁻¹ $F_c(N_2) = 0.95 - 10^{-4}T$ $k(0, CO_2) = 8.3 \times 10^{-25}(1/T)^2$ $\exp(-521/T)$ cm ⁶ molecule ⁻² s ⁻¹ $F_c(CO_2) = 0.875 - 0.5 \times 10^{-4}T$	3 above 1000 K increasing to 10 at lower temp. and pressures	763
15,5 CN + OH → HCN + O	(a) $k_a = 1 \times 10^{-11}$	5	764
→ NCO + H	(b) $k_b = 7 \times 10^{-11}$	3	
→ NH + CO	(c)		
→ HNCO	(d)		
15,6 CN + HCHO → HCN + HCO	7 × 10 ⁻¹¹	2	765
15,7 CN + HCO → HCN + CO	1 × 10 ⁻¹⁰	2	765

2. Index of Reactions and Summary of Rate Expressions — Continued

Reactions		Rate expressions $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainties	Page
15,9 $\text{CN} + \text{NO} \rightarrow \text{ONCN}$	(a)	$k_{\infty} = 6.6 \times 10^{-11}$ $k_a(0, \text{N}_2) = 4.3 \times 10^{-12}(1/T)^{6.2}$ $\exp(-2455/T) \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c(\text{N}_2) = 0.65$	3 1.5	766
	(b)	$k_a(0, \text{CO}_2) = 3.1 \times 10^{-14}(1/T)^{5.4}$ $\exp(-2213/T) \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c(\text{CO}_2) = 0.65$	3	
$\rightarrow \text{NCO} + \text{N}$	(b)	$k_b = 1.6 \times 10^{-10} \exp(-21200/T)$	2	
$\rightarrow \text{CO} + \text{N}_2$	(c)			
15,10 $\text{CN} + \text{NO}_2 \rightarrow \text{NCO} + \text{NO}$		$4 \times 10^{-11} \exp(186/T)$	1.5	769
15,11 $\text{CN} + \text{HNO} \rightarrow \text{HCN} + \text{NO}$		3×10^{-11}	3	770
15,12 $\text{CN} + \text{HNO}_2 \rightarrow \text{HCN} + \text{NO}_2$		2×10^{-11}	3	770
15,13 $\text{CN} + \text{HCN} \rightarrow \text{H} + \text{C}_2\text{N}_2$		$2.5 \times 10^{-17} T^{1.71} \exp(-770/T)$	1.5 300–740 up to 4 at 3000 K	770
15,14 $\text{CN} + \text{N}_2\text{O} \rightarrow \text{NCN} + \text{NO}$		$6.4 \times 10^{-21} T^{2.6} \exp(-1860/T)$	2	772
15,15 $\text{CN} + \text{CN} \rightarrow \text{C}_2\text{N}_2$		$k_{\infty} = 9.4 \times 10^{-12} \text{s}^{-1}$ $k(0, \text{N}_2) = 9.44 \times 10^{-23}(1/T)^{2.61}$ $\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c = 0.5$ $k(0, \text{CO}_2) = 1.5 \times 10^{-22}(1/T)^{2.62}$ $F_c = 0.5$	3 $\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$	772
16,0 $\text{NCO} + \text{M} \rightarrow \text{N} + \text{CO} + \text{M}$		$k(0, \text{N}_2) = 1.9 \times 10^{-1}(1/T)^{1.95}$ $\exp(-30160/T)$ $k(0, \text{CO}_2) = 0.21(1/T)^{1.91}$ $\exp(-30114/T)$	3 1800–2500 K	774
16,1 $\text{NCO} + \text{H}_2 \rightarrow \text{HNCO} + \text{H}$		$3.44 \times 10^{-18} T^2 \exp(-3030/T)$	1.3 400–1000 K 2 at 1500	776
16,2 $\text{NCO} + \text{H}_2\text{O} \rightarrow \text{HNCO} + \text{OH}$		$3.9 \times 10^{-19} T^{2.17} \exp(-3046/T)$	5 at 2000 K increasing to a factor of 20 at 1000 K	777
16,3 $\text{NCO} + \text{O} \rightarrow \text{CO} + \text{NO}$	(a)	$k_a = 7.5 \times 10^{-11}$	2	777
$\rightarrow \text{CN} + \text{O}_2$	(b)	$k_b = 1.4 \times 10^{-6} T^{-1.43} \exp(-3501/T)$	5 at 2000 K increasing to a factor of 20 at 1000 K	
16,4 $\text{NCO} + \text{H} \rightarrow \text{NH} + \text{CO}$	(a)	$k_a = 8.9 \times 10^{-11}$	2.5	779
$\rightarrow \text{HNCO}$	(b)	see text		
$\rightarrow \text{O} + \text{HCN}$ (c)	(c)	$k_c = 1.1 \times 10^{-13} T^{0.9} \exp(-2923/T)$	> 3 at 500 K larger at lower temperatures	
16,5 $\text{NCO} + \text{OH} \rightarrow \text{HNCO} + \text{O}$	(a)	$k_a = 1.3 \times 10^{-10} T^{2.27} \exp(497/T)$	5 above 1000 K, larger at at lower temperatures	779
$\rightarrow \text{HONCO}$	(b)	$k_{b\infty} = 1.7 \times 10^{-11}$ $k(0, \text{N}_2) = 1.75 \times 10^{-12}(1/T)^{5.96}$ $\exp(-1785/T) \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c = 0.5$ $k(0, \text{CO}_2) = 8.1 \times 10^{-13}(1/T)^{5.77}$ $\exp(-1665/T) \text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c = 0.5$	2 3 3	

2. Index of Reactions and Summary of Rate Expressions — Continued

Reactions		Rate expressions $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainties	Page
16,6 $\text{NCO} + \text{HCHO} \rightarrow \text{HNCO} + \text{HCO}$		1×10^{-11}	3	781
16,7: $\text{NCO} + \text{HCO} \rightarrow \text{HNCO} + \text{CO}$		6×10^{-11}	2	782
16,9 $\text{NCO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{CO}$ $\rightarrow \text{CO}_2 + \text{N}_2$ $\rightarrow \text{CO} + \text{N}_2 + \text{O}$	(a) (b) (c)	$k_{a+b+c} = 1.7 \times 10^{-11} \exp(196/T)$ $k_a/k_{a+b+c} = 0.33$ $k_b/k_{a+b+c} = 0.44$ $k_c/k_{a+b+c} = 0.23$	1.1 to 1000 K 2 at 2000 K 1.2 1.2 1.4	782
16,10 $\text{NCO} + \text{NO}_2 \rightarrow \text{CO} + 2\text{NO}$ $\rightarrow \text{CO}_2 + \text{N}_2\text{O}$	(a) (b)	$k_{a+b} = 3 \times 10^{-11}$ $k_b/k_a = 0.3$	3 3	783
16,11 $\text{NCO} + \text{HNO} \rightarrow \text{HNCO} + \text{NO}$		3×10^{-11}	3	783
16,12 $\text{NCO} + \text{HNO}_2 \rightarrow \text{HNCO} + \text{NO}_2$		6×10^{-12}	3	783
16,13 $\text{NCO} + \text{HCN} \rightarrow \text{HNCO} + \text{CN}$		$2 \times 10^{-11} \exp(-4456/T)$	10 at 2500 K larger at lower temperatures	784
16,14 $\text{NCO} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{NO} + \text{CO}$		$< 1.5 \times 10^{-10} \exp(-14000/T)$		784
16,15 $\text{NCO} + \text{CN} \rightarrow \text{NCN} + \text{CO}$		3×10^{-11}	3	784
16,16 $\text{NCO} + \text{NCO} \rightarrow \text{N}_2 + 2\text{CO}$		3×10^{-11}	2.5	785
17,0 $\text{HNCO} \rightarrow \text{NH} + \text{CO}$	(a)	$k(0, \text{N}_2) = 3.6 \times 10^4 (1/T)^{3.1} \exp(-51280/T)$ $k(0, \text{CO}_2) = 5.13 \times 10^4 (1/T)^{3.06} \exp(-51240/T)$ $k_\infty = 6 \times 10^{13} \exp(-50228/T) \text{ s}^{-1}$ $F_c = 0.9 - 2 \times 10^{-4} T$ for CO_2 and N_2	2	785
17,3 $\text{HNCO} + \text{O} \rightarrow \text{CO}_2 + \text{NH}$ $\rightarrow \text{OH} + \text{NCO}$	(a) (b)	$k_a = 1.6 \times 10^{-16} T^{1.41} \exp(-4290/T)$ $k_b = 3.7 \times 10^{-18} T^{2.11} \exp(-5750/T)$	1.5 at 600 K 2.5 at 2500 K	787
17,4 $\text{HNCO} + \text{H} \rightarrow \text{NH}_2 + \text{CO}$ $\rightarrow \text{H}_2 + \text{CN}$	(a) (b)	$k_a = 5 \times 10^{-11} \exp(-2300/T)$ $k_b = 4.8 \times 10^{-17} T^{1.81} \exp(-8332/T)$	3 > 1000 K 10 at 1000 K larger at lower temperatures	788
17,5 $\text{HNCO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NCO}$		$1.06 \times 10^{-18} T^2 \exp(-1290/T)$	2	789
17,7 $\text{HNCO} + \text{HCO} \rightarrow \text{NCO} + \text{H}_2\text{CO}$		$5 \times 10^{-12} \exp(-13100/T)$	10	790
17,15 $\text{HNCO} + \text{CN} \rightarrow \text{HCN} + \text{NCO}$		2.5×10^{-11}	3	790
17,17 $\text{HNCO} + \text{HNCO} \rightarrow \text{CO}_2 + \text{HNCNH}$		$1.1 \times 10^{-13} \exp(-21240/T)$	2 800–1300 K increasing to 5 at 500 K 3 at 2000 K	791

3. Chemical Kinetic Data Tables



Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Mozzhukhin <i>et al.</i> (1989)	4060–6060	5–25 ppm C ₂ N ₂ 0–200 ppm N ₂ 1–4 × 10 ¹⁸ Ar. Shock tube study using ARAS detection of C and N	4.2 × 10 ⁻¹⁰ exp(–71000/T)	1.5
Baulch, D. L. <i>et al.</i> (1981)	5000–12000		3.3 × 10 ⁻¹⁰ exp(–75000/T)	1.7
Recommendation			4.2 × 10 ⁻¹⁰ exp(–71000/T) Ar 6.3 × 10 ⁻¹⁰ exp(–71000/T) N ₂ 1 × 10 ⁻⁹ exp(–71000/T) CO ₂	2 at 6000 K

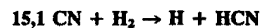
Comments

The latest experimental results of Mozhukhin *et al.* are about a factor of 3 larger than the recommendations of Baulch *et al.* We favor the latest measurements on the basis of the use of the well established ARAS method for the direct detection of C and N in highly dilute cyanogen mixtures. Our recommendations for N₂ are based on the assumption that N₂ and CO₂ are more efficient by factors of 1.5 and 2.4 in comparison to argon. These results show that the thermal decomposition of CN cannot be an important process under any conditions.

References

Mozhukhin, E., Burmeister, M. and Roth, P. "High Temperature Dissociation of CN", *Ber. Bunsenges Phys. Chem.*, **93**, 70, 1989.
Baulch, D. L., Duxbury, J. Grant, S. J. and Montague, D. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 4", *J. Phys. Chem. Ref. Data* **10**, Supp. 1, 1981.

W. Tsang
September, 1989



Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Sun <i>et al.</i> (1990)	209–740	<7 × 10 ¹⁶ Ar. CN from 248 nm laser photolysis of ICN. Detection of CN via LiF.	2.23 × 10 ⁻²¹ (T) ^{3.31} exp(–756/T)	1.10
Sims and Smith (1988)	298–768	1–18 × 10 ¹⁶ H ₂ in 2 × 10 ¹⁸ Ar. CN from laser photolysis of ONCN. Detection via LiF.	2.4 × 10 ⁻¹² (T/298) ^{1.6} exp(–1340/T) from CN(ν = 0)	1.2
Natarajan, K and Roth, P. (1988)	2050–2590	50–200 ppm C ₂ N ₂ 2.5–40 ppm H ₂ in 5–7 × 10 ¹⁸ Ar Shock tube with H-atom detection via ARAS.	3 × 10 ⁻¹⁰ exp(–4000/T)	2
Balla and Pasternack (1987)	294–300	3–650 × 10 ¹⁶ N ₂ , He or Ar. 0–30 × 10 ¹⁶ H ₂ and 0.16–1 × 10 ¹⁶ C ₂ N ₂ . CN from photolysis of C ₂ N ₂ . Detected by diode laser absorption. Also HCN detection.	2.6 × 10 ⁻¹⁴	1.15

15,1 CN + H₂ → H + HCN – Continued

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
de Juan <i>et al.</i> (1987)	298	0–9 × 10 ¹⁶ H ₂ and 3–10 × 10 ¹⁷ Ar. CN from laser photolysis of ONCN. LiF detection of CN	2.5 × 10 ⁻¹⁴	1.2
Lichtin and Lin (1985)	294	0–4 × 10 ¹⁷ H ₂ in 1.7 × 10 ¹⁸ Ar total pressure CN from ICN photolysis at 266nm. Detected via LiF at 388nm.	4.9 × 10 ⁻¹⁴	1.1
Li <i>et al.</i> (1984)	298	0.6–3.3 × 10 ¹⁵ C ₂ N ₂ , 6.6–26 × 10 ¹⁵ H ₂ , 1.7–9 × 10 ¹⁷ Ar. CN from laser photolysis of C ₂ N ₂ . Detection by absorption.	1.6 × 10 ⁻¹⁴ (<i>v</i> = 0) 3.0 × 10 ⁻¹⁴ (<i>v</i> = 1)	1.2
Szekely <i>et al.</i> (1983)	2700–3500	110–600 ppm C ₂ N ₂ 370–2580 ppm H ₂ 5.6–15 × 10 ¹⁷ Ar Shock tube with resonance absorption detection of CN	1.4 × 10 ⁻¹⁰	1.5
Baulch <i>et al.</i> (1981) review	300–1000		1.1 × 10 ⁻¹⁰ exp(–2700/ <i>T</i>)	3
Schacke <i>et al.</i> (1977)	259–396	1–2 × 10 ¹⁷ H ₂ in 1.6 × 10 ¹⁸ Ar. CN from flash photolysis of C ₂ N ₂ . Detection via resonance absorption.	1 × 10 ⁻¹⁰ exp(–2672/ <i>T</i>)	1.3
Albers <i>et al.</i> (1975)	295–398	Flash photolysis of dilute C ₂ N ₂ in 6–30 × 10 ¹⁶ H ₂ . CN detection by resonance absorption at 388.3 nm	1 × 10 ⁻¹⁰ exp(–2672/ <i>T</i>)	
Recommendation:			6 × 10 ⁻¹⁶ <i>T</i> ^{1.55} exp(–1510/ <i>T</i>)	1.6

Comments

There is surprisingly large scatter in the data at room temperature. It is probably not accidental that all the results leading to lower rate constants are from uv absorption, while with one exception the higher rate constants are from LiF detection of CN. The present preference is for the results with the higher rate constants and the assumption that the results of Lichtin and Lin have now been superseded by those of Sun *et al.* We have fitted all the existing data on the basis of the rate expression.

$$k = 6 \times 10^{-16} T^{1.55} \exp(-1510/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 1.6. The temperature dependence of the pre-exponential factor is reasonable. A plot of the results can be found in Figure 1. Our recommendation is in reasonable accord with that of Baulch except that we have factored into our analysis the more recent lower temperature results.

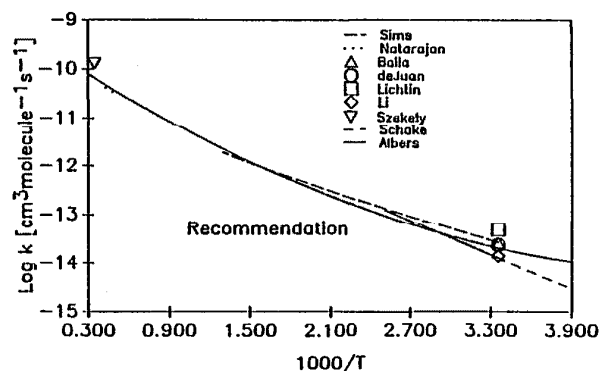


FIG. 1. experimental results and recommendations for the rate constants of the reaction CN + H₂ → HCN + H.

References

- Albers, E. A., Hoyeremann, K., Schake, H., Schmatjko, K. J. Wagner, H. Gg., and Wolfrum, J., "Absolute Rate Coefficients for the Reaction of H-atoms with N₂O and some Reactions of CN Radicals" 15th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 765, 1975.
- Balla, J. and Pasternack, L., "Kinetics of Gas Phase CN by Diode Laser Absorption", J. Phys. Chem., **91**, 73, 1987.
- Baulch, D. L., Duxbury, J., Grant, S. J. and Montague, D. C., "Evaluated Kinetic Data for High Temperature Reactions Vol. 4 Homogeneous Gas Phase Reactions of Halogen and Cyanide Containing Species" J. Phys. Chem. Ref. Data., **10**, 1981 Supp. 1.
- de Juan, J., Smith, I. W. M., Veyret, B., "Pulsed Photolysis-Laser Induced Fluorescence Measurement of the Rate Constants for the Reactions of CN Radical with H₂, O₂, NH₃, HCl, HBr, and HI," J. Phys. Chem., 1987, **91**, 69.
- Li, X., Sayah, N. and Jackson, W., "Laser Measurement on the Effect of Vibrational Energy on the Reactions of CN" J. Chem. Phys., 1984, **81**, 833.
- Lichten, D. A. and Lin, M. C., "Kinetics of CN Radical Reactions with Selected Molecules at Room Temperature" Chem. Phys., 1985, **96**, 473.
- Natarajan, K. and Roth, P., "A Shock Tube Investigation of CN Radical Reactions with H₂ and NO Verified by H, N, and O Atom Measurements", 21st. Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, Pa., 729, 1986.
- Schacke, H., Wagner, H. Gg. and Wolfrum, J., "Reaktionen von Molekulan in definierten Scheinungszuständen (IV). Reaktionene schwingungsaneregter Cyan-Radikale mit Wasserstoff und einfachen Kohlenwasserstoffen", Ber. Bunsenges Phys. Chem., 1977, **81**, 670.
- Sims, I. R. and Smith, I. W. M., "Rate Constants for the Reactions CN($\nu = 1$) + H₂, HCN, DCN + H, D between 298 and 760 and Comparison with Transition State Theory Calculations" Chem. Phys. Lett., **149**, 565, 1988.
- Sun, Q., Yang, D. L., Wang, N. S., Bowman, J. M. and Lin, M. C., "experimental and Reduced Dimensionality Quantum Rate Coefficients for H₂(D₂) + CN \rightarrow H(D)CN + H(D)", J. Chem. Phys., 1990, **93**, 4730.
- Szekely, A., Hanson, R. K., and Bowman, C. T., "High Temperature Determination of the Rate Coefficient for the Reaction H₂ + CN \rightarrow H + HCN." Int. J. Chem. Kin., **15**, 915, 1983.

W. Tsang
December, 1991

15.2 CN + H₂O \rightarrow HCN + OH

Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Jacobs <i>et al.</i> (1988)	518–1027	0.2–1 $\times 10^{18}$ H ₂ O in 0–3 $\times 10^{18}$ N ₂ . CN from ArF laser photolysis of C ₂ N ₂ . Detection of CN and OH via LiF.	$1.3 \times 10^{-11} \exp(-3755/T)$	1.2
Szekely <i>et al.</i> (1984)	2460–2840	83–450 ppm C ₂ N ₂ 603–2320 ppm H ₂ O in 1.7×10^{18} Ar. Shock tube study CN detected via absorption at 388.3 nm OH detected via absorption at 306.67 nm	$3.8 \times 10^{-11} \exp(-6700/T)$	1.5
Recommendation:			$1.3 \times 10^{-11} \exp(-3755/T)$	1.2 at 750 K 3 at 2500 K

Comments

Both of the experimental studies involve real time measurements of OH and CN. In the case of the flow tube experiments the rate constants determined from both radicals are in good agreement. This is very strong evidence for the reliability of the work. For the shock tube studies, the rate of initial OH increase is directly related to the process of interest and mechanistic difficulties should not be important. It is somewhat surprising that the extrapolated results of Jacobs *et al.* run into those of Szekely *et al.* One would have expected some degree of positive curvature. If one use the results of Jacobs *et al.* as a base then a T² dependence for the A-factor will re-

sult in a rate constant that is a factor of 2.5 higher than that from the shock tube study. Indeed, the activation energy determined by Szekely *et al.* is consistent with such an interpretation. For the present purposes we recommend the rate expression given by Jacobs *et al.* over the entire temperature range or:

$$k(\text{CN} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{CN}) = 1.3 \times 10^{-11} \exp(-3755/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

However, we assign an uncertainty that range from a factor of 1.2 at 750 K to 3 at 2500 K.

Jacobs, A., Wahl, M., Weller, R. and Wolfrum J., "Kinetic Studies of the Reactions of CN with H₂O from 518–1027", Chem. Phys. Lett., 144, 203, 1988.

Szekely, A., Hanson, R. K. and Bowman, C. T. "High Temperature Determination of the Rate Coefficient for the Reaction H₂O + CN → HCN + OH" Int. J. Chem. Kin., 16, 1609, 1984.

W. Tsang

August, 1989

15,3 CN + O → CO + N

Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Louge and Hanson(1984)	2000	1.2% N ₂ O; 0.3% C ₂ N ₂ CN detection at 388.8nm CO detection at 306.3nm shock tube experiments	3 × 10 ⁻¹¹ 3.4 × 10 ⁻¹¹ exp(-210/T) (combination of low and high temperature data)	2in 2.6 × 10 ¹⁸ Ar
Schmatjko and Wolfrum (1981)	295	2–3.8 × 10 ¹⁵ C ₂ N ₂ and 0.8–4.8 × 10 ¹⁵ O in 8 × 10 ¹⁶ He in discharge flow reactor. CN from flash photolysis of C ₂ N ₂ O from microwave discharge. CO(v) from ir. N from vuv absorption	1.8 × 10 ⁻¹¹	1.5
Baulch <i>et al.</i> (review)	298		1.7 × 10 ⁻¹¹	1.5
Recommendation:			3.4 × 10 ⁻¹¹ exp(-210/T)	2

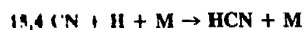
Comments

The measured rate constants are large and are in accord with a combination reaction and the rapid decomposition of the hot molecule. The results of Schmatjko and Wolfrum show that the main channel is the production of N atom in the ²D state as opposed to the ground ⁴S state. The CO is also produced with vibrational excitation. It is expected that these excited states will be quenched in high pressure systems. We accept the recommendation of Louge and Hanson for the rate expression and estimate an uncertainty of a factor of 2.

References

- Baulch, D. L., Duxbury, J., Grant, S. J. and Montague, D. C., "Evaluated Kinetic Data for High Temperature Reactions, Vol. 4, Homogeneous Gas Phase Reactions of Halogen and Cyanide Containing Species" J. Phys. Chem. Ref. Data., 10, 1981, Supp. 1.
 Louge, M. Y. and Hanson, R. K., "Shock Tube Study of Cyanogen Oxidation Kinetics", Int. J. Chem. Kin., 16, 231, 1984.
 Schmatjko, K. J., and Wolfrum, J., "Direct Determination of the Product Distribution in the Reaction of O atoms with CN" 18th Symposium (Int.) on Combustion, 819, 1981.

W. Tsang
 September, 1989



Reaction/reference	Conditions <i>T</i> range/K [<i>M</i>] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:		$k_{\infty} = 2.99 \times 10^{-9} (1/T)^5$ $k(0, \text{N}_2) = 2.4 \times 10^{-24} (1/T)^{22}$ $\exp(-567/T) \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$ $F_c(\text{N}_2) = 0.95 - 10^{-4} T$ $k(0, \text{CO}_2) = 8.3 \times 10^{-25} (1/T)^2$ $\exp(-521/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c(\text{CO}_2) = 0.875 - 0.5 \times 10^{-4} T$	3 > 1000 K 10 at lower temps and pressures

Comments

There are no measurements on the rate constants for this reaction. Our recommendation is based on our analysis of the reverse reaction (13,0). Pressure effects assuming strong collisions are summarized in Table 1. The collision efficiencies as a function of temperature and step size down are given in Table 2. For pressure effects in the presence of CO₂ and N₂ see

$$F_c(\text{N}_2) = 0.95 - 10^{-4} T$$

$$F_c(\text{CO}_2) = 0.875 - 0.5 \times 10^{-4} T$$

The uncertainty is a factor of 3 at temperatures above 1000 K and increasing to a factor of 10 at lower temperatures and pressures where the contributions from possible errors in the heat of formation of CN and collision efficiencies becomes more important.

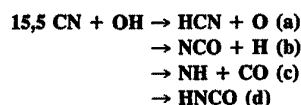
TABLE 1. $\log(k/k(0))$ for the reaction $\text{CN} + \text{H} + \text{HCN} \rightarrow \text{HCN} + \text{HCN}$ as a function of temperature and pressure assuming strong collisions

<i>T</i> (K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
$\log(\text{density})$											
17											
17.5	-0.01	-0.01	-0.01	-0.01	-0.01						
18	-0.02	-0.02	-0.02	-0.02	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
18.5	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.03
19	-0.11	-0.11	-0.10	-0.10	-0.10	-0.09	-0.09	-0.09	-0.09	-0.08	-0.08
19.5	-0.24	-0.23	-0.22	-0.21	-0.21	-0.20	-0.19	-0.19	-0.19	-0.18	-0.18
20	-0.46	-0.44	-0.43	-0.41	-0.40	-0.39	-0.38	-0.37	-0.36	-0.35	-0.35
20.5	-0.79	-0.76	-0.74	-0.72	-0.70	-0.68	-0.66	-0.65	-0.63	-0.62	-0.61
21	-1.21	-1.17	-1.14	-1.11	-1.09	-1.06	-1.04	-1.02	-1.00	-0.98	-0.96
21.5	-1.67	-1.63	-1.60	-1.57	-1.54	-1.51	-1.48	-1.46	-1.43	-1.41	-1.39
22	-2.16	-2.12	-2.08	-2.05	-2.02	-1.99	-1.96	-1.93	-1.90	-1.88	-1.86

TABLE 2. Collision efficiency as a function of temperature and step size down for $\text{H} + \text{NO} + \text{M} = \text{HNO} + \text{M}$

Step size (cm ⁻¹)	200	400	800	1600	3200
Temp(K)					
500	1.2×10^{-1}	2.7×10^{-1}	4.7×10^{-1}	6.6×10^{-1}	8.0×10^{-1}
700	7.8×10^{-2}	1.9×10^{-1}	3.7×10^{-1}	5.7×10^{-1}	7.4×10^{-1}
900	5.4×10^{-2}	1.4×10^{-1}	3.0×10^{-1}	5.0×10^{-1}	6.9×10^{-1}
1100	3.9×10^{-2}	1.1×10^{-1}	2.5×10^{-1}	4.4×10^{-1}	6.4×10^{-1}
1300	2.9×10^{-2}	8.5×10^{-2}	2.0×10^{-1}	3.9×10^{-1}	5.9×10^{-1}
1500	2.3×10^{-2}	6.8×10^{-2}	1.7×10^{-1}	3.4×10^{-1}	5.5×10^{-1}
1700	1.8×10^{-2}	5.6×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	5.1×10^{-1}
1900	1.5×10^{-2}	4.7×10^{-2}	1.3×10^{-1}	2.7×10^{-1}	4.7×10^{-1}
2100	1.2×10^{-2}	3.9×10^{-2}	1.1×10^{-1}	2.5×10^{-1}	4.4×10^{-1}
2300	1.0×10^{-1}	3.3×10^{-2}	9.5×10^{-2}	2.2×10^{-1}	4.1×10^{-1}
2500	8.7×10^{-3}	2.9×10^{-2}	8.4×10^{-2}	2.0×10^{-1}	3.8×10^{-1}

W. Tsang
September, 1989



Reaction/reference	<i>T</i> range/K	Conditions	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Morley (1976)	2300–2560	Fuel rich atmospheric hydrocarbon flames. Sampling of HCN, NO and NH ₃ via mass spectrometry of appropriate ions in flames.		$k_{\text{total}} < 1 \times 10^{-10}$	2
Haynes (1977)	1950–2380	Post flame region of rich hydrocarbon flames with added fuel nitrogen in the form of pyridine ammonia or NO. Conc. adjusted for 2000 ppm unburnt N species. HCN and NH ₃ (cyanates also) from probe samples. NO from NDIR.		$k_{\text{total}} < 9.3 \times 10^{-11}$	2
Szekely <i>et al.</i> (1984)	2460–2840	83–450 ppm C ₂ N ₂ 603–2320 ppm H ₂ O in 1.7×10^{18} Ar. Shock tube study CN detected via absorption at 388.3 nm OH detected via absorption at 306.67 nm		$k < 1 \times 10^{-10}$	1.5
Recommendation:				$k_a = 1 \times 10^{-11} \exp(-1000/T)$ $k_b = 7 \times 10^{-11}$ see text for other possibilities	5 3

Comments

There are no direct measurements on the rate constants for these reactions. The work of Morley and Haynes is based on the observation of the rate of loss of HCN in flames and depends on an assumed mechanism. We believe that these values are most probably upper limits. Szekely *et al.*, give their rates as an upper limit since all loss of CN is attributed to this channel. There are two possible reaction channels, (a) abstraction of the OH hydrogen by CN, a very exothermic process or (b-d) a radical combination reaction followed by decomposition of the hot adduct. We have also included the possibility of the hot HOCN isomerizing to HNCO and this can then lead to channel(c) or the production of NH and CO.

Despite its exothermicity, the abstraction channel is probably not the most important process. On the basis of reactions such as $\text{CN} + \text{HCl}$ and $\text{CN} + \text{NH}_3$ we suggest a rate expression of the form

$$\begin{aligned}
 k(\text{CN} + \text{OH} \rightarrow \text{HCN} + \text{O}) = \\
 1 \times 10^{-11} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
 \end{aligned}$$

with an uncertainty of a factor of 5. Note that this channel will not make any contribution to the rate constant deduced by Haynes or Morley. The important channel is undoubtedly that of combination. We suggest a rate constant of

$$7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 3. The main problem is the relative contributions from the three possible channels. At high temperatures and ambient pressures the hydrogen ejection channel is probably the most important. We therefore recommend that we associate the recommended rate constant with this process. This is due to the exothermic nature of the process $\text{OH} + \text{CN} \rightarrow \text{NCO} + \text{H}$. However, the energetics of the HOCN will determine whether some of it may be stabilized. In the absence of high pressure unimolecular data, estimates cannot be made. In addition there is also the possibility of isomerization of HOCN to HNCO and the decomposition of the latter. Here again the absence of thermal data prevent estimates. Finally, if HNCO is formed the decomposition channel to NH and CO must be considered. The present recommendation must therefore be used with great caution.

References

Haynes, B. S., "The Oxidation of Hydrogen Cyanide in Fuel Rich Flames" *Combustion and Flame*, **28**, 113-121, 1977.
 Morley, C., "The Formation and Destruction of Hydrogen Cyanide from Atmospheric and Fuel Nitrogen in Rich Atmospheric-Pressure Flames", *Combustion and Flame*, **27**, 189, 1976.

Szekely, A., Hanson, R. K., and Bowman C. T., "High Temperature Determination of the Rate Coefficient for the Reaction $\text{H}_2\text{O} + \text{CN} \rightarrow \text{HCN} + \text{OH}$ ", *Int. J. Chem. Kin.*, **16**, 1609, 1984.

W. Tsang
 January, 1991

15,6 $\text{CN} + \text{HCHO} \rightarrow \text{HCN} + \text{HCO}$

Reaction/reference	T range/K	Conditions	[M] range/cm ³	Reaction rate constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty
Recommendation:				7×10^{-11}	2

Comments

There have not been any measurements on the rate constants for this reaction. This is a very exothermic process. Our estimate is based on the recent measurement of Hess, Durant and Tully (*J. Phys. Chem.*, **93**, 6402, 1989)

on the rate expression for the abstraction of secondary H-atoms from propane to be $3.3 \times 10^{-13} T^{0.56} \exp(649/T)$ $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$. This is certainly a lower limit.

W. Tsang
 September, 1989

15,7: $\text{CN} + \text{HCO} \rightarrow \text{HCN} + \text{CO}$

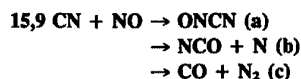
Reaction/reference	T range/K	Conditions	[M] range/cm ³	Reaction rate constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty
Recommendation:				1×10^{-10}	2

Comments

There are no kinetic data on this reaction. The overall reaction is extremely exothermic. It is highly likely that either abstraction or combination followed by rapid decomposition of the hot adduct will ultimately lead to the

same products. The recommended rate constant is a reflection of the latter and the usually large rate constants for such reactions with formyl.

W. Tsang
 March, 1990



Reaction/reference	T range/K	Conditions [M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Wang <i>et al.</i> (1989)	297–740	1–17 × 10 ¹⁸ Ar with 0.7–18 × 10 ¹⁵ NO. CN from laser photolysis of ICN. Detection via LiF.	$k_a(298, 1 \times 10^{18}) = 1.4 \times 10^{-12}$ $k_a(298, 1.7 \times 10^{18}) = 2.0 \times 10^{-12}$ $k_a(298, 3.3 \times 10^{18}) = 3.5 \times 10^{-12}$ $k_a(298, 1 \times 10^{19}) = 7.6 \times 10^{-12}$ $k_a(298, 1.7 \times 10^{19}) = 1.1 \times 10^{-11}$ $k_a(353, 2.8 \times 10^{18}) = 2.5 \times 10^{-12}$ $k_a(430, 2.3 \times 10^{18}) = 1.3 \times 10^{-12}$ $k_a(555, 1.8 \times 10^{18}) = 7.5 \times 10^{-13}$ $k_a(740, 1.3 \times 10^{18}) = 2.6 \times 10^{-13}$ $k_a(740, 2.6 \times 10^{18}) = 4.4 \times 10^{-13}$ $k_a(740, 4.6 \times 10^{18}) = 6.6 \times 10^{-13}$ $k_a(740, 6.5 \times 10^{18}) = 1.0 \times 10^{-12}$	1.2
		1.7–4 × 10 ¹⁸ N ₂ . Similar conditions and methods as above.	$k_a(297, 4 \times 10^{18}) = 5.3 \times 10^{-12}$ $k_a(425, 2.8 \times 10^{18}) = 2.0 \times 10^{-12}$ $k_a(740, 1.7 \times 10^{18}) = 4.1 \times 10^{-13}$	
Sims and Smith (1988)	294–761	< .3% NOCN in 3–6 × 10 ¹⁷ Ar with 0.6–60 × 10 ¹⁵ NO CN(<i>v</i> = 0 and 1) via pulse laser photolysis. Detection with LiF	$k_a(295, 1 \times 10^{18}) = 1.5 \times 10^{-12}$ $k_a(450, 6.6 \times 10^{17}) = 0.38 \times 10^{-12}$ $k_a(295, 3.3 \times 10^{17}) = 0.6 \times 10^{-12}$ $k_a(771, 3.8 \times 10^{17}) = 5 \times 10^{-14}$	1.2 1.6
Natarajan and Roth (1986)	2480–3160	100 ppm C ₂ N ₂ 100–700 ppm NO in 3.4 × 5.4 × 10 ¹⁸ Ar in shock tube experiments N and O detection via ARAS.	$k_b = 1.6 \times 10^{-10} \exp(-21200/T)$	2
Colket(1984)	2240–2955	0.1–0.5% C ₂ N ₂ and 0.8– 7% NO in 1.1–2.7 × 10 ¹⁸ Ar in shock tube experiments. Reaction followed from CN absorption behind incident shock	$k_c = 4 \times 10^{-14}$ $k_b = 1.7 \times 10^{-10} \exp(-21190/T)$	3
Li <i>et al.</i> (1985)	298	2–12 × 10 ¹⁶ NO, 2 × 10 ¹⁶ C ₂ N ₂ in 3–10 ¹⁸ Ar. CN from laser photolysis of C ₂ N ₂ . Detection via LiF	$k_c = 1.6 \times 10^{-13}$ $k_a(\text{Ar}) = 6 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k_a(\text{NO}) = 3 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	1.2 1.1 1.1
Lam <i>et al.</i> (1978)	298	1.6–8 × 10 ¹⁷ Ar; 6.5–13 × 10 ¹⁵ C ₂ N ₂ and 2–16 × 10 ¹⁵ NO. CN from flash photolysis of C ₂ N ₂ . Detection via LiF.	$k_c = 1.2 \times 10^{-13}$ $k_a(\text{Ar}) = 7.7 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	1.5 1.2
Mulvihill and Phillips (1975)	1500	5 × 10 ¹⁸ total density from 4.5/8/1 H ₂ /N ₂ /O ₂ flame. Mass spectrometric detection of HCN	$k_c(1500) = 1.2 \times 10^{-11}$	1.5
Boden and Thrush (1968)	578–687	2 × 10 ¹⁶ N ₂ , 1 × 10 ¹⁵ C ₂ N ₂ 3.4 × 10 ¹² O, in flow system CN from O + C ₂ N ₂ CN detection via absorption	$k_a = 5 \times 10^{-13}$	2
Setser and Thrush (1965)	673	2–10 × 10 ¹⁶ N ₂ , 2.5 × 10 ¹⁴ C ₂ N ₂ , 2.5 × 10 ¹³ O in flow system. CN from O + C ₂ N ₂ . CN monitored via emission	$k_a/k(\text{CN} + \text{O}_2) = 3.7$	2

15,9 CN + NO → ONCN (a) — Continued
 → NCO + N (b)
 → CO + N₂ (c)

Reaction/reference	T range/K	Conditions [M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Basco and Norrish (1965)	298	8–17 × 10 ¹⁸ N ₂ ; 0.04–3.2 × 10 ¹⁷ NO; 2–8 × 10 ¹⁷ C ₂ N ₂ ; CN from flash photolysis. CN detection via absorption.	$k_a = 3.3 \times 10^{-12}$	2
Recommendations			$k_{a\infty} = 6.6 \times 10^{-11}$	3
			$k_a(0, N_2) = 4.3 \times 10^{-12} (1/T)^{6.2}$ $\exp(-2455/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c(N_2) = 0.65$	1.5
			$k_a(0, CO_2) = 3.1 \times 10^{-14} (1/T)^{5.4}$ $\exp(-2213/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c(CO_2) = 0.65$	3
			$k_b = 1.6 \times 10^{-10} \exp(-21200/T)$	2

Comments

The earlier results involving studies on complex systems postulated a very rapid exothermic CN + NO reaction proceeding through a 4-centered transition state and the formation of CO and N₂, (*k_c*: Setser and Thrush, Boden and Thrush, Mulvihill and Phillips). More recent investigations on better characterized systems have failed to reproduce the very large rate constants and demonstrated a pressure dependence that is inconsistent with a straightforward bimolecular reaction. Mechanistically, the high temperature shock tube studies have shown that the interaction of CN and NO leads to the formation of O and N atoms that destroy the CN. All of this cast seri-

ous doubts on the earlier interpretation. The present analysis based on the results of Sims and Smith and Wang *et al.* and implies that all the lower temperature results have determined rate constants for combination.

Although Colket and Natarajan and Roth assign a rate expression for *k_c*, it appears that their measurements are not particularly sensitive to this process. All that can probably be said is that the rate constant they give is probably an upper limit. Indeed it is possible to question whether the four-center process occur at all. Certainly the value given by Colket invalidates the interpretation of the lower temperature measurements on CN disappearance as derived from this process.

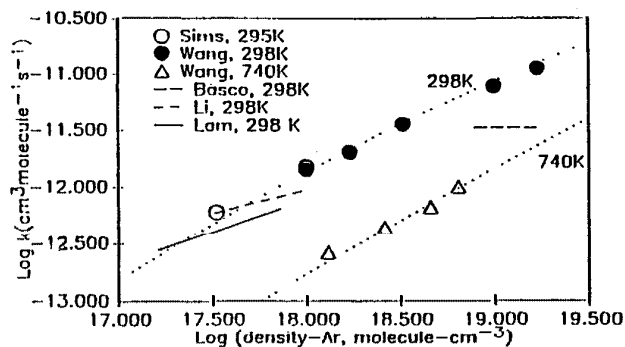


FIG. 1. Fit of experimental results for the reaction NO + CN at 298 K in argon as a function of pressure.

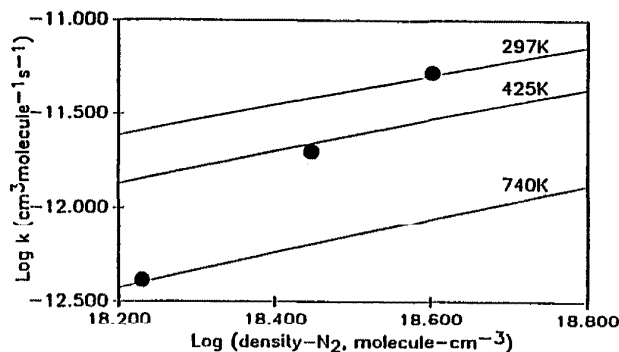


FIG. 2. Fit of experimental results over the temperature range 298–740 K as a function of nitrogen pressure.

We have carried out RRKM calculation assuming the formation of ONCN, using as a basis the results of Sims and Smith and Wang *et al.* Most of these studies are carried out in the presence of argon. The work of Wang *et al.* in the presence of N₂ is however particularly valuable since it leads directly to the present recommendations.

Following the suggestion of Sims and Smith we have chosen to convert the reported rate constants of Li *et al.* and Lam *et al.* to solely bimolecular rate constants for k_a . This is in contrast to their interpretation of the process as a combination of the bimolecular k_c and termolecular k_a . A summary of relevant experimental results and our RRKM fit of the results are plotted in Figs. 1 and 2. We are unable to fit the results of Mulvihill and Philipps, Setter and Thrush and Boden and Thrush within this framework.

The measured rate constants are quite large for a combination process involving such small species and forming only a 200 kJ/mol bond. In order to fit this result a very large high pressure rate constant as well as very large step size for reaction at room temperature in argon is required. The latter situation is contrary to most other sys-

tems that we have fitted. It is however very reminiscent of that with OH + NO and Sims and Smith have discussed the possibility of multiple reaction channels in the combination process. In order to fit the temperature dependence observed by Sims and Smith and Wang *et al.* it is necessary to assume that the step-size down is decreasing with temperature. This is also contrary to other systems. The present results must therefore be regarded as an empirical fit of the data. Fortunately, the direct measurements in N₂ mean that the recommendations of rate constants in the presence of N₂ are probably of high reliability and the estimated uncertainty is a factor of 1.5. However the values in the presence of CO₂ may be subject to larger errors and an uncertainty of a factor of 3 is assigned.

The results of the RRKM calculations using the high pressure rate expression;

$$k_{a\infty} = 6.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 3 are given in Tables 1 and 2.

TABLE 1. $\log(k/k_{\infty})$ for the reaction $\text{NO} + \text{CN} \rightarrow \text{NOCN}$ as a function of temperature and pressure assuming strong collisions

$T(\text{K})$	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
$\log(\text{density})$											
17	-2.74	-2.98	-3.18	-3.34	-3.48	-3.61	-3.72	-3.82	-3.91	-4.00	-4.08
17.5	-2.26	-2.50	-2.69	-2.85	-2.99	-3.12	-3.23	-3.33	-3.42	-3.50	-3.58
18	-1.80	-2.03	-2.22	-2.37	-2.51	-2.63	-2.74	-2.84	-2.93	-3.01	-3.09
18.5	-1.37	-1.58	-1.76	-1.91	-2.04	-2.16	-2.26	-2.36	-2.45	-2.53	-2.60
19	-0.98	-1.17	-1.33	-1.46	-1.59	-1.70	-1.80	-1.89	-1.98	-2.05	-2.13
19.5	-0.64	-0.80	-0.93	-1.06	-1.17	-1.27	-1.36	-1.45	-1.53	-1.60	-1.67
20	-0.37	-0.49	-0.60	-0.70	-0.80	-0.89	-0.97	-1.04	-1.11	-1.18	-1.24
20.5	-0.18	-0.26	-0.34	-0.42	-0.49	-0.56	-0.63	-0.69	-0.75	-0.80	-0.86
21	-0.08	-0.12	-0.17	-0.22	-0.27	-0.32	-0.36				
-0.41	-0.45	-0.49	-0.53								
21.5	-0.03	-0.05	-0.07	-0.10	-0.12	-0.15	-0.18	-0.21	-0.24	-0.26	-0.29
22	-0.01	-0.02	-0.03	-0.04	-0.05	-0.06	-0.08	-0.09	-0.10	-0.12	-0.13

TABLE 2. Collision efficiency as a function of temperature and step size down for $\text{CN} + \text{NO} + \text{M} \rightarrow \text{NOCN} + \text{M}$

Step size (cm^{-1})	200	400	800	1600	3200
Temp(K)					
500	1.2×10^{-1}	2.6×10^{-1}	4.5×10^{-1}	6.5×10^{-1}	8.0×10^{-1}
700	6.8×10^{-2}	1.7×10^{-1}	3.4×10^{-1}	5.5×10^{-1}	7.2×10^{-1}
900	4.4×10^{-2}	1.2×10^{-1}	2.6×10^{-1}	4.6×10^{-1}	6.5×10^{-1}
1100	3.0×10^{-2}	8.6×10^{-2}	2.1×10^{-1}	3.9×10^{-1}	5.9×10^{-1}
1300	2.1×10^{-2}	6.3×10^{-2}	1.6×10^{-1}	3.3×10^{-1}	5.3×10^{-1}
1500	1.5×10^{-2}	4.8×10^{-2}	1.3×10^{-1}	2.8×10^{-1}	4.8×10^{-1}
1700	1.1×10^{-2}	3.6×10^{-2}	1.0×10^{-1}	2.4×10^{-1}	4.3×10^{-1}
1900	8.3×10^{-3}	2.8×10^{-2}	8.2×10^{-2}	2.0×10^{-1}	3.8×10^{-1}
2100	6.3×10^{-3}	2.2×10^{-2}	6.6×10^{-2}	1.7×10^{-1}	3.4×10^{-1}
2300	4.9×10^{-3}	1.7×10^{-2}	5.4×10^{-2}	1.4×10^{-1}	3.0×10^{-1}
2500	3.8×10^{-3}	1.4×10^{-2}	4.4×10^{-2}	1.2×10^{-1}	2.6×10^{-1}

Near 1500 K there is a shock tube measurement (Dorko, E. A., Flynn, P. H., Grimm, U., Scheller, K., and Mueller, G. H., *J. Phys. Chem.*, **81**, 811, 1977) of ONCN decomposition. Unfortunately experimental problems related to the handling of ONCN led to data of large scatter and uncertain quality. In addition, and probably more serious, the analytical method involving infra-red emissions suffer from interferences. The results are therefore not consistent with any reasonable extrapolation of the step sizes down in argon that we have used at lower temperatures.

For reactions in the presence of N₂ and CO₂ we recommend the following rate expressions;

$$k_a(0, \text{N}_2) = 4.3 \times 10^{-12} (1/T)^{6.2} \exp(-2455/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$F_c(\text{N}_2) = 0.65$$

$$k_a(0, \text{CO}_2) = 3.1 \times 10^{-14} (1/T)^{5.4} \exp(-2213/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$F_c(\text{CO}_2) = 0.65$$

where the F_c values in combination with the high pressure rate expression permits derivation of the rate constant for all pressures. For channel b, we recommend the rate expression given by Natarajan and Roth

$$k_b = 1.6 \times 10^{-10} \exp(-21200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 2 at the higher temperatures and lower pressures where it is applicable. Under

other situations the combination process will be predominant. We do not assign an expression for channel(c). There is really no direct evidence for its occurrence.

References

- Basco, N. and Norrish, R. G. W., "The Reaction of Cyanogen Radical with Nitric Oxide", *Proc. Roy. Soc.*, **283**, 291, 1965.
- Colket, M. B. "Cyanogen Pyrolysis and the CN + NO Reaction behind Incident Shock Waves", *Int. J. Chem. Kin.*, **18**, 353-369 1984.
- Lam, L., Dugan, C. H. and Sadowski, C. M., "The Gas Phase Reaction of CN and NO", *J. Chem. Phys.*, **69**, 2788, 1978.
- Li, X., Sayah, N., and Jackson, W. M., "A Large Vibrational Enhancement in the Reaction of CN($\nu = 1, 2$) + NO", *J. Chem. Phys.*, **83**, 616, 1985.
- Mulvihill J. N. and L. F. Phillips, "Breakdown of Cyanogen in Fuel-Rich H₂/N₂/O₂ Flames", 15th Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1113, 1975.
- Natarajan, K. and Roth, P., "A Shock Tube Investigation of CN Radical Reactions with H₂ and NO Verified by H, N, and O Atom Measurements", Twenty-first Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 729, 1986.
- Sims, I. R. and Smith, I. W. M., "Pulse Laser Photolysis - Laser Induced Fluorescence Measurements on the Kinetics of CN($\nu = 0$) and CN($\nu = 1$) with O₂, NH₃ and NO Between 294-761 K", *J. Chem. Soc., Faraday Trans. 2*, **84**, 527, 1988.
- Wang, N. S., Yang, D. L. and Lin, M. C., "Kinetics of CN Radical Reactions with NO_x Between 297 and 740 K", *Chem. Phys. Lett.*, **163**, 480, 1989.

W. Tsang
December, 1991

15,10 CN + NO₂ → NCO + NO

Reaction/reference	Conditions		Reaction rate constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty
	T range/K	$[M]$ range/ cm^3		
Wang <i>et al.</i> (1989)	297-740		$4 \times 10^{-11} \exp(186/T)$	1.1
Recommendations			$4 \times 10^{-11} \exp(186/T)$	1.5

Comments

The recent work of Wang *et al.* leads to rate constants that are in the expected range for a radical combination reaction. The chief uncertainty is whether it is possible to form the stable adduct O₂NCN. No such compound has ever been detected and it is expected that the N-C bond will be very weak. If it is formed in this reaction a pressure dependence would have been expected. The independence of the rate constant with respect to pressure leads to the conclusion that a rearrangement must occur. The most likely products are as given above. The recommendation is the rate expression of Wang *et al.* or

$$k(\text{CN} + \text{NO}_2 \rightarrow \text{NCO} + \text{NO}) = 4 \times 10^{-11} \exp(186/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 1.5.

References

- Wang, N. S., Yang, D. L. and Lin, M. C., "Kinetics of CN Radical Reactions with NO_x Between 297 and 740 K", *Chem. Phys. Lett.*, **163**, 480, 1989.

W. Tsang
December, 1991

15,11 CN + HNO → HCN + NO

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation			3×10^{-11}	3

Comments

There have been no measurements on the mechanism and rate constant for this reaction. In view of the exothermicity it must be a very rapid abstraction process. We therefore recommend

$$k(\text{CN} + \text{HNO} \rightarrow \text{HCN} + \text{NO}) = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 3.

W. Tsang
December, 1990

15,12 CN + HNO₂ → HCN + NO₂

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendations			2×10^{-11}	3

Comments

There have been no measurements on the mechanism and rate constant for this reaction. CN abstraction reactions being very exothermic are very fast and the present recommendation of

$$k(\text{CN} + \text{HNO}_2 \rightarrow \text{HCN} + \text{NO}_2) = 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 3 is based on this premise.

W. Tsang
Nov. 1990

15,13 CN + HCN → H + C₂N₂

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Yang <i>et al.</i> (1991)	300–740	CN from laser photolysis of ICN in presence of HCN $1.3\text{--}2.3 \times 10^{19}$ Ar. CN detection via LiF	$2.5 \times 10^{-17} T^{1.71} \exp(-770/T)$ (include high temp. results)	1.2
Zabarnick and Lin (1989)	296–578	CN from laser photolysis of ICN in $0\text{--}10 \times 10^{16}$ HCN in 4×10^{17} Ar. CN detection via LiF	$3.9 \times 10^{-12} \exp(-670/T)$	1.25
Li <i>et al.</i>	298	CN from laser photolysis of $0.7\text{--}3.5 \times 10^{15}$ C ₂ N ₂ in $7\text{--}2.8 \times 10^{16}$ HCN and $1.6\text{--}8 \times 10^{17}$ Ar	1.8×10^{-14}	1.4
Szekely <i>et al.</i> (1983)	2720–3070	Shock tube study 0–39 ppm C ₂ N ₂ , 76–572 ppm HCN in 1.4×10^{18} Ar. CN detection via broad band absorption at 388.3 nm	1.7×10^{-11}	2

$\text{CN} + \text{HCN} \rightarrow \text{H} + \text{C}_2\text{N}_2$ — Continued

Reaction/reference	Conditions T range/K [M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation		$2.5 \times 10^{-17} T^{1.71} \exp(-770/T)$	1.5 300–740 K increasing to 4 at 3000 K

Comments

The mechanism of this process involves the formation of a hot adduct and then its decomposition. Yang *et al.* have used the BAC-MP4 method to estimate the thermodynamic properties of the adduct and deduced that it is stable with respect to the reactants and products by 159 and 121 kJ/mol respectively. The general situation is therefore similar to the chemically activated decomposition of olefins by hydrogen atom. Under most higher temperature conditions the adduct lifetime will be sufficiently short so that it need not be considered in any reaction scheme. The experimental data show larger than expected scatter. Presumably the results of Yang *et al.* supersede that of Zabarnik *et al.* Nevertheless the data of the former is still about a factor of 1.8 higher than that of Li *et al.* The general situation is striking similar to that for $\text{CN} + \text{H}_2$ (15,2). Our recommendation is the rate expression given by Yang *et al.*

$$k = 2.5 \times 10^{-17} T^{1.71} \exp(-770/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

This is based on a transition state fit of their data and that of Szekely *et al.* and thus covers the range of 300–3000 K. The uncertainty is estimated to be a factor of 1.5 over the temperature range of 300–740 and up to a factor of 4 at 3000 K. The uncertainty at this point arises from combining the results of Szekely *et al.* with the very careful work of Natarajan and Roth on $\text{H} + \text{C}_2\text{N}_2$ (21st Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, Pa., 729, 1986) leading to a heat of formation of CN of 455 kJ/mol. This is 40 kJ/mol higher than the recommended value used in the course of the present analysis and is equivalent to a factor of 4 in the rate constant. A summary of the experimental situation can be found in Fig. 1.

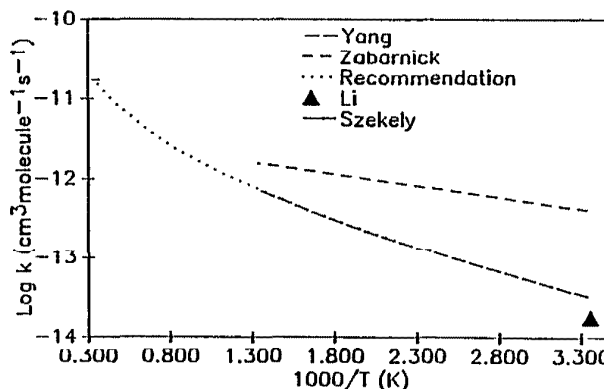


FIG. 1. Summary of experimental data for the reaction $\text{CN} + \text{HCN} \rightarrow \text{H} + \text{C}_2\text{N}_2$.

References

- Li, X., Syah, N. and Jackson, W. M., "Laser Measurements of the Effects of Vibrational Energy on the Reactions of CN" *J. Chem. Phys.*, **81**, 833, 1984.
- Szekely, A., Hanson, R. K., and Bowman, C. T., "Shock Tube Determination of the Rate Coefficient for the Reaction $\text{CN} + \text{HCN} \rightarrow \text{H} + \text{C}_2\text{N}_2 + \text{H}$ ", *Int. J. Chem. Kin.*, **15**, 1237–1241, 1983.
- Yang, D. L., Yu, T., Lin, M. C., Melius, C. F., "Kinetics of CN Reactions with HCN and C_2N_2 " *Chem. and Phys. Proc. in Comb.*, 1991, Fall Meeting, Eastern States Sec. of the Combustion Institute.
- Zabarnick, S. and Lin, M. C., "Kinetics of CN ($X^2\Sigma^+$) Radical Reaction with HCN, BrCN and CH_3CN ", *Chemical Physics*, **134**, 185, 1989.

W. Tsang
November, 1991

15,14 CN + N₂O → NCN + NO

Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Wang <i>et al.</i>	500–740 K	1–6 × 10 ¹⁸ Ar, small amount of N ₂ O. Slow flow system CN from laser photolysis of ICN. Detected via LiF.	$6.4 \times 10^{-21} T^{2.6} \exp(-1860/T)$	1.2
Recommendation			$6.4 \times 10^{-21} T^{2.6} \exp(-1860/T)$	2

Comments

The work of Wang *et al.* is a measurement of CN disappearance in the presence of N₂O. The mechanism was derived on the basis of BAC-MP4 calculations and favors a NCNNO intermediate breaking up into NCN and NO. We recommend their determination of

$$k(\text{CN} + \text{N}_2\text{O} \rightarrow \text{NCN} + \text{NO}) = 6.4 \times 10^{-21} T^{2.6} \exp(-1860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 2 over the entire temperature range.

References

Wang, N. S., Yang, D. L., M. C. Lin and Melius, C. F., "Kinetics of CN Reactions with N₂O and CO₂", *Int. J. Chem. Kin.*, **23**, 151, 1991.

W. Tsang
September, 1990

15,15 CN + CN + M → C₂N₂ + M

Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Basco <i>et al.</i>	300	7–7000 × 10 ¹⁴ CNR R = (CN, Br, I) in 1.1 × 10 ¹⁹ N ₂ . CN from flash photolysis. Detected via absorption	1 × 10 ⁻¹²	3
Recommendation			$k_{\infty} = 9.4 \times 10^{-12}$ $k(0, \text{N}_2) = 9.44 \times 10^{-23} (1/T)^{2.61}$ $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c = 0.5$ $k(0, \text{CO}_2) = 1.5 \times 10^{-22} (1/T)^{2.62}$ $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c = 0.5$	3

Comment

The only measurement on the rate constant for this reaction is that of Basco *et al.* On the basis of our RRKM calculations the reaction must be very close to the high pressure limit at room temperature. However, the reported rate constant is very small for a radical combination reaction near the high pressure limit. This is probably due to errors in calibrating the second order decay of CN in this system. We believe that a more likely number will be an order of magnitude larger. Note that although C₂N₂ is a small molecule the large bond energy moves the fall-off region into much lower pressures. There are extensive high temperature data on C₂N₂ decomposition in argon. Results are summarized in Fig. 1.

Rate constants for the reverse can be calculated through the equilibrium constant. There is, unfortunately, considerable uncertainty about the value of the heat of formation of CN. We have not been able to satisfactorily fit the decomposition data on the basis of the recommended heat of formation of CN (Stull and Prophet, "JANAF Thermochemical Tables", NSRDS-NBS 37, US Government Printing Office, Washington, DC 20402). Instead we have used a number that is 17 kJ/mol smaller as deduced more recently by Colket (*Int. J. Chem. Kin.*, **18**, 353, 1984). The results of RRKM calculations for strong colliders can be found in Table 1. Collision efficiencies as a function of temperature and step-size down can be found in Table 2.

For N_2 and CO_2 as the third bodies we recommend the following rate expressions with an uncertainty of a factor of 3

$$k_{\infty} = 9.4 \times 10^{-12}$$

$$k(0, N_2) = 9.44 \times 10^{-23} (1/T)^{2.61} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$F_c = 0.5$$

$$k(0, CO_2) = 1.5e \times 10^{-22} (1/T)^{2.62} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$F_c = 0.5$$

The estimated uncertainties are a factor of 3. Note that these recommendations are based on the fits of the high temperature decomposition data for C_2N_2 in argon and then scaled appropriately for N_2 and CO_2 .

TABLE 1. $\log(k/k_{\infty})$ for the reaction $CN + CN \rightarrow C_2N_2$ as a function of temperature and pressure assuming strong collisions

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
log(density)											
17	-0.58	-0.78	-0.96	-1.12	-1.28	-1.42	-1.54	-1.67	-1.78	-1.88	-1.98
17.5	-0.33	-0.48	-0.63	-0.77	-0.90	-1.02	-1.14	-1.25	-1.36	-1.46	-1.55
18	-0.16	-0.26	-0.37	-0.48	-0.59	-0.69	-0.79	-0.89	-0.98	-1.07	-1.15
18.5	-0.07	-0.12	-0.19	-0.27	-0.34	-0.43	-0.50	-0.58	-0.66	-0.73	-0.81
19	-0.02	-0.05	-0.09	-0.13	-0.18	-0.23	-0.29	-0.35	-0.41	-0.46	-0.52
19.5	-0.01	-0.02	-0.03	-0.06	-0.08	-0.11	-0.15	-0.18	-0.22	-0.26	-0.30
20		-0.01	-0.01	-0.02	-0.03	-0.05	-0.06	-0.08	-0.10	-0.13	-0.15
20.5				-0.01	-0.01	-0.02	-0.02	-0.03	-0.04	-0.05	-0.06
21						-0.01	-0.01	-0.01	-0.01	-0.02	-0.02
21.5										-0.01	-0.01
22											

TABLE 2. Collision efficiency as a function of temperature and step size down for $CN + CN + M = C_2N_2 + M$

Step size (cm^{-1})	200	400	800	1600	3200
Temp(K)					
500	1.2×10^{-1}	2.7×10^{-1}	4.6×10^{-1}	6.6×10^{-1}	8.0×10^{-1}
700	7.5×10^{-2}	1.8×10^{-1}	3.6×10^{-1}	5.6×10^{-1}	7.4×10^{-1}
900	5.0×10^{-2}	1.3×10^{-1}	2.9×10^{-1}	4.9×10^{-1}	6.8×10^{-1}
1100	3.6×10^{-2}	1.0×10^{-1}	2.3×10^{-1}	4.2×10^{-1}	6.2×10^{-1}
1300	2.6×10^{-2}	7.8×10^{-2}	1.9×10^{-1}	3.7×10^{-1}	5.7×10^{-1}
1500	2.0×10^{-2}	6.2×10^{-2}	1.6×10^{-1}	3.2×10^{-1}	5.3×10^{-1}
1700	1.6×10^{-2}	4.9×10^{-2}	1.3×10^{-1}	2.9×10^{-1}	4.8×10^{-1}
1900	1.2×10^{-2}	4.0×10^{-2}	1.1×10^{-1}	2.5×10^{-1}	4.5×10^{-1}
2100	1.0×10^{-2}	3.3×10^{-2}	9.5×10^{-2}	2.2×10^{-1}	4.1×10^{-1}
2300	8.2×10^{-3}	2.8×10^{-2}	8.1×10^{-2}	2.0×10^{-1}	3.8×10^{-1}
2500	6.8×10^{-3}	2.3×10^{-2}	7.0×10^{-2}	1.8×10^{-1}	3.5×10^{-1}

Reference

Basco, N., Nicholas, J. E., Norrish, R. G. W. and Vickers, W. H. J., "Vibrationally Excited Cyanogen Radicals Produced in the Flash Photolysis of Cyanogen and Cyanogen Halides" *Proc. Roy. Soc.*, **272**, 147, 1963.

W. Tsang
December 1990

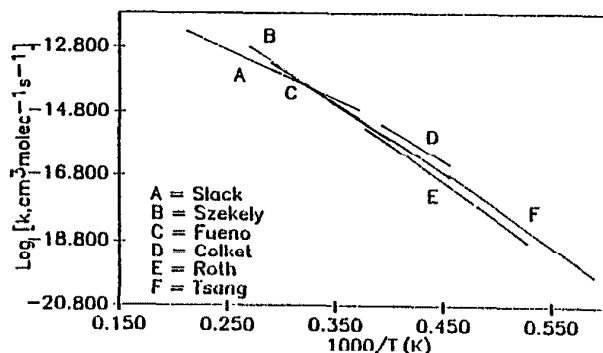
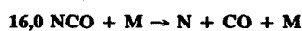


FIG. 1. Summary of data on C_2N_2 Decomposition and Fit of the data. Names refer to: Slack, M. W., Fishburne, E. S. and Johnson, A. R., *J. Chem. Phys.*, **77**, 575, 1973; Szekely, A. Hanson, R. K. and Bowman, C. T., *J. Phys. Chem.*, **80**, 4982, 1984; Fueno, T., Tabayashi, K., and Kajimoto, O., *J. Phys. Chem.*, **77**, 575, 1973; Colket, M. B., *J. Quant. Spectrosc. Radiat. Transfer*, **31**, 7, 1984; Natarajan, K., Thielen, K., Hermanns, H. D., and Roth, P., *Ber. Bunsenges. Phys. Chem.*, **90**, 533, 1986.



Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Higashihara <i>et al.</i> (1985)	1450–2600	0.02:02:96 0.01:01:98 0.02:04:95 0.01:02:97 BrCN:O ₂ :Ar at 6–12 × 10 ¹⁸ NO by IR emission at 5.34 microns	$k(\text{NCO} + \text{O})/k = 0.5$ $\exp(19130/T)$	2
Louge and Hanson (1984a)	2240	0.41% C ₂ N ₂ ; 0.1–0.42% N ₂ O in 2 × 10 ¹⁸ Ar in shock tube. NCO detection via narrow line laser absorption	$k(\text{NCO} + \text{O})/k = 3467$	2
Louge and Hanson (1984b)	2150 and 2400	1.2% N ₂ O, 0.3% C ₂ N ₂ in in Argon at 1.6 × 10 ¹⁸ near 2150 K, 0.6% O ₂ , 0.6% C ₂ N ₂ in Argon at 1.3 × 10 ¹⁸ near 2400 K CN in absorption at 388 nm. CO and NO IR absorption.	$k(\text{NCO} + \text{O})/k = 2300$ (2150) $k(\text{NCO} + \text{O})/k = 490$ (2400)	2 2
Recommendations			$k(\text{O}, \text{N}_2) = 1.9 \times 10^{-1}(1/T)^{1.95}$ $\exp(-30160/T)$ $k(\text{O}, \text{CO}_2) = 0.21(1/T)^{1.91}$ $\exp(-30114/T)$	3 at 1800– 2500

Comments

There are no direct measurements on the rate constants for this reaction. Nevertheless the rate constants derived from modeling experiments employing different diagnostics are not in gross disagreement. In all the experiments the quantity that is determined is the ratio $k(\text{NCO} + \text{O})/k$. The results are summarized in Fig. 1. We have converted this ratio into the desired rate constants through use of our recommendation for $k(\text{O} + \text{NCO})$. Thus there are small differences between the numbers given here and those actually published.

The rate expression for this process is highly uncertain. The activation energy determined by Higashihara *et al.* cannot be correct since it is below the lowest possible reaction barrier (even after taking into account the fact that the decomposition process is at the low pressure limit). For the present analysis we have weighted the two studies equally and derived the best fit through these points. The result is the rate expression:

$$\begin{aligned} k(\text{O} + \text{NCO})/k &= \exp(24836/T)/36 \quad \text{or} \\ k &= 2.7 \times 10^{-9} \exp(-24836/T) \\ &\quad \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1} \quad (\text{in Argon}) \end{aligned}$$

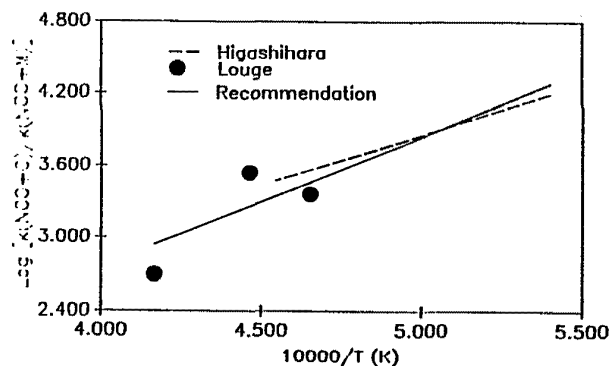


Fig. 1. $k(\text{O} + \text{NCO})/k$ as a function of temperature.

However, as can be seen from Fig. 1 the data has a large scatter and there is a statistical uncertainty of 40 kJ/mol

in the activation energy. Thus large uncertainties are expected if the data is extrapolated over large temperature ranges.

If this rate expression is accepted at face value then it is possible through RRKM calculations to determine the reaction threshold and the step size down. For the former we find a reaction threshold of 244 kJ/mol. The implication is that the reverse $\text{N}(\text{S})$ addition reaction with CO has a barrier of 39 kJ/mol. This is compatible with the spin forbidden nature of the reaction. On this basis and assuming that the effect of N_2 and CO_2 substitution are similar to that found for N_2O (14,0) in this temperature range, we recommend the following limiting low pressure rate expression with these colliding partner:

$$\begin{aligned} k(\text{O}, \text{N}_2) &= 1.9 \times 10^{-1} (1/T)^{1.95} \exp(-30160/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \\ k(\text{O}, \text{CO}_2) &= 0.21 (1/T)^{1.91} \exp(-30114/T) \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1} \end{aligned}$$

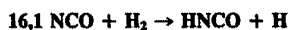
with an uncertainty of a factor of 2 in the temperature range of 1800–2400 K and increasing to an order of magnitude at 1000 K.

An important question is the range of applicability of these limiting “low pressure” rate expressions. Unfortunately, there are no data on the high pressure rate expression and thus it is not possible to assign pressure dependence in a concrete manner. We have carried out RRKM calculations assuming a “normal” transition state with an A -factor in the $3 \times 10^{13} \text{ s}^{-1}$ range. It appears that within the constraints set by the uncertainties given above the expressions can be used at pressures up to 10–300 atms in the temperature range of 1000–2500 K.

References

- Higashihara, T., Kuroda, K., Saito, K. and Murakami, I., “Oxidation of BrCN in Shock Waves and Formation of NO”, *Comb. and Flame*, **61**, 167, 1985.
- Louge, M. Y. and Hanson, R. K., “High Temperature Kinetics of NCO”, *Comb. and Flame* **58**, 291, 1984.
- Louge, M. Y. and Hanson, R. K., “Shock Tube Study of Cyanogen Oxidation Kinetics”, *Int. J. Chem. Kin.*, **16**, 231, 1984.

W. Tsang
September, 1990



Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Perry (1985)	592-913	NCO from the fluorine excimer laser photolysis of trace quantities of HNCO in $0-4 \times 10^{16}$ H ₂ in $2.7-17 \times 10^{17}$ Ar. LiF detection of NCO	$1.43 \times 10^{-11} \exp(-4530/T)$	1.2
Louge and Hanson (1984)	1490	0.58% H ₂ , 0.09% O ₂ , 0.41% N ₂ O, 0.4% C ₂ N ₂ in 3.1×10^{18} Ar in shock tube with detection of NCO via narrow line absorption at 440.479 nm. Rate constant from modeling of complex decomposition process	2×10^{-12}	5
Recommendation:			$3.44 \times 10^{-18} T^2 \exp(-3030/T)$	1.3 at 400-1000 2 at 1500

Comments

The recommendation is based on the direct measurements of Perry. The technique is well established and the *A*-factor is in the expected range. The results of Louge and Hanson suggest a strongly curved Arrhenius plot. In view of the large estimated uncertainty we have assumed a T^2 dependence for the *A*-factor and derived the rate expression

$$k(\text{H}_2 + \text{NCO} \rightarrow \text{HNCO} + \text{H}) = 3.44 \times 10^{-18} T^2 \exp(-3030/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of 1.3 from 400 to 1000 K and increasing to a factor of 2 at 1500 K.

A plot of experiments and recommendation can be found in Fig. 1.

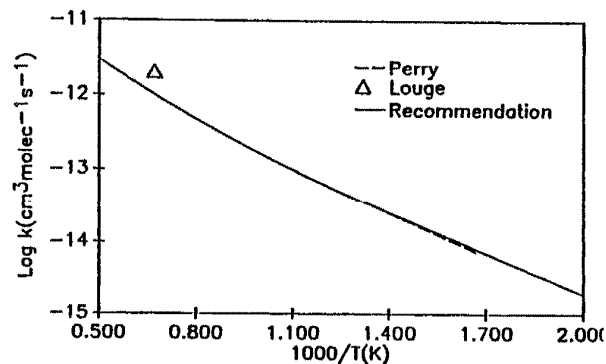
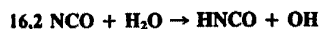


FIG. 1. Experimental data and recommendations for the reaction $\text{H}_2 + \text{NCO} \rightarrow \text{HNCO} + \text{H}$.

References

- Perry, R. A., "Kinetics of the Reactions of NCO radicals with H₂ and NO Using Laser Photolysis and Laser Induced Fluorescence", *Chem. Phys.*, **82**, 5485-5488, 1985.
 Louge, M. Y. and Hanson, R. K., "High Temperature Kinetics NCO", *Combust. Flame* **58**, 291, 1984.

W. Tsang
 July, 1989



Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
$\log_{10} K_p = 0.1970 - 1.1938 \times 10^3/T + 4.1562 \times 10^4/T^2 - 4.1555 \times 10^6/T^3$				
Recommendation			$3.9 \times 10^{-19} T^{2.17} \exp(-3046/T)$	5 at 2000 K increasing to a factor of 20 at 1000 K

Comments

There are no measurements on the rate constants for this reaction. However on the basis of our recommendation for the reverse reaction (17,3) $1.1 \times 10^{-18} T^2 \exp(-1290/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ and the equilibrium constant for this reaction we calculate

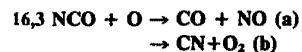
$$k(\text{NCO} + \text{H}_2\text{O} \rightarrow \text{HNCO} + \text{OH}) = 3.9 \times 10^{-19} T^{2.17} \exp(-3046/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

Unfortunately there are uncertainties of 10 kJ/mol in the heat of formation of HNCO and NCO. This means

that there can be errors in the rate constant may be as large as a factor of 20 at 1000 K, but decreasing to a factor of 5 at 2000 K.

The reaction is likely to be of consequence only at the higher temperatures.

W. Tsang
August, 1990



Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
$\log_{10} K_p(\text{b}) = 0.0041 - 4.807 \times 10^2/T - 3.7222 \times 10^5/T^2 + 5.0634 \times 10^7/T^3$				
Higashihara <i>et al.</i> (1985)	1450–2600	0.02:02:96 0.01:01:98 0.02:04:95 0.01:02:97 BrCN:O ₂ :Ar at $6\text{--}12 \times 10^{18}$ NO by IR emission at 5.34	6.6×10^{-11}	3
Louge and Hanson (1984)	1450	0.4% N ₂ O, 1% O ₂ , 4% 2C ₂ N ₂ in argon at 3×10^{18} . NCO detection via narrow line absorption	9.3×10^{-11}	

16,3 NCO + O → CO + NO (a) – Continued
→ CN+O₂ (b)

Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Higashihara <i>et al.</i> (1983)	1680–2250	0.02:02:96 0.01:01:98 0.01:02:97 HCN:O ₂ :Ar 0.02:0175:005:9575 HCN:O ₂ :NO ₂ :Ar OH from UV emission at 306.7 nm and IR emission at 5.34 (mostly NO)	6.6 × 10 ⁻¹¹	3
Recommendation:			$k_a = 7.5 \times 10^{-11}$ $k_b = 1.4 \times 10^{-6} T^{-1.43} \exp(-3501/T)$	2 5 at 2000 K increasing to 20 at 1000 K

Comments

There are two possible channels for this reaction. The first channel must involve combination followed by the rapid decomposition of the adduct. One expects a very large rate constant and the experimental measurements, although none of them are truly direct, are commensurate with our estimate. We therefore recommend

$$k_a = 7.5 \times 10^{-11} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

with an uncertainty of a factor of 2. From much more complex systems, Lifshitz and Frenklach (Int. J. Chem. Kin., 12, 159, 1980) and Mulvihill and Phillips (15th Symp. (Int.) on Combustion 1113, 1975), have estimated rate constants of 3.3×10^{-11} and 1.7×10^{-11} cm³molecule⁻¹s⁻¹, respectively. This can be considered to be satisfactory agreement.

There is also the possibility for the formation of CN and O₂, channel (b). In this case, the rate expression for the reverse reaction is well established at 2.5×10^{-11} (298/T)⁵ cm³molecule⁻¹s⁻¹ (Sims and Smith, Chem. Phys. Lett. 151, 481, 1988). Then, through the equilibrium constant, we obtain:

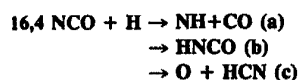
$$k_b = 1.4 \times 10^{-6} T^{-1.43} \exp(-3501/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

with an uncertainty of a factor of 5 at temperatures in excess of 2000 K and increasing to a factor of 20 at 1000 K. The magnitude of these values is dictated by that of the thermochemistry. On the basis of these values it is clear that $k_a > 15k_b$, where the equality is most closely approached as the temperature is increased.

References

- Higashihara, T., Kuroda, K., Saito, K. and Murakami, I., "Oxidation of BrCN in Shock Waves and Formation of NO", Comb. and Flame, 61, 167, 1985.
- Higashihara, T., Saito, K., and Murakami, I., "Oxidation of Hydrogen Cyanide in Shock Waves. Formation of Nitrogen Monoxide", J. Phys. Chem., 87, 3702, 1983.
- Louge, M. Y. and Hanson, R. K., "Shock Tube Studies of NCO Kinetics", 20th Symposium on Combustion, The Combustion Institute Pittsburgh Pa., 665–672, 1984.

W. Tsang
September, 1990



Reaction/reference	Conditions T range/K [M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
$\log_{10} K_p(c) = 0.3535 + 1.8959 \times 10^2/T - 2.1931 \times 10^5/T^2 + 2.000 \times 10^8/T^3$			
Louge and Hanson (1984)	1490 0.58% H ₂ , 0.09% O ₂ 0.41% N ₂ O, 0.4% C ₂ N ₂ in 3.1×10^{18} Ar in shock tube with detection of NCO via narrow line absorption at 440.479 nm. Rate constant from modelling of complex decomposition process	$k_a = 8.9 \times 10^{-11}$	2.5
Recommendation:		$k_a = 8.9 \times 10^{-11}$ $k_c = 1.1 \times 10^{-13} T^{0.9} \exp(-2923/T)$	2.5

Comments

The main process involves the addition of a hydrogen atom to the NCO radical and then the decomposition of the chemically activated HNCO. The large rate constant determined by Louge and Hanson is indicative of this process. There is also the possibility the the hot HNCO radical can be stabilized at sufficiently high pressures. Unfortunately, there are no high pressure data on the decomposition of HNCO to HN and CO. Furthermore, the reaction is spin forbidden. There is very little basis for prediction. For the present purposes we have made rough RRKM calculations assuming a variety of transition states. On a strong collision basis it would appear that at 500 K stabilization effects may be important at pressures in excess of 5 atms. At 2500 K the limit is about 100 atm. Since these are strong collision values it appears that at temperatures above 1500 K stabilization cannot be important under any conditions.

A third process involves the displacement of the O atom. This is readily calculated from the recommended

rate expression for oxygen addition to HCN and the appropriate equilibrium constant. This leads to the rate expression

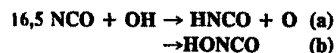
$$k(\text{H} + \text{NCO} \rightarrow \text{HCN} + \text{O}) = 1.1 \times 10^{-13} T^{0.9} \exp(-2923/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an estimated uncertainty of a factor of 3 at 2500 K and larger at lower temperatures. Note however that while this process has a rate constant that is about one-third that of (a) at 2500 K it becomes much less important as the temperature is lowered.

References

Louge, M. Y. and Hanson, R. K., "High Temperature Kinetics of NCO", *Combust. Flame* **58**, 291, 1984.

W. Tsang
September, 1990



Reaction/reference	Conditions T range/K [M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
$\log_{10} K_p(a) = -0.7924 + 2.4936 \times 10^3/T + 1.0441 \times 10^5/T^2 - 1.6532 \times 10^7/T^3$			
Recommendation:		$k_a = 1.3 \times 10^{-19} T^{2.27} \exp(497/T)$	5 above 1000 K
		$k_{b,\infty} = 1.7 \times 10^{-11}$	2
		$k(0, \text{N}_2) = 1.75 \times 10^{-12} (1/T)^{5.96} \exp(-1785/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	3
		$F_c = 0.5$	
		$k(0, \text{CO}_2) = 8.1 \times 10^{-13} (1/T)^{5.77} \exp(-1665/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	3
		$F_c = 0.5$	

Comments

There are no data on the mechanism and rate constants for the interaction between the NCO radical and OH. Undoubtedly the combination of the two radicals is an important process and we expect that a typical oxime N-OH type bond will be formed with an energy of about 220 kJ/mol. Miller *et al.* (20th Symp. (Int.) on Combustion, 673, 1984) have postulated that this will be followed by a rapid 1,3 hydrogen shift leading to the formation of H₂CO and NO. We do not believe that this is a likely possibility. Saito *et al.* (J. Phys. Chem., **92**, 4371, 1988) have found that the preferred direction for formaldoxime decomposition is to form H₂O and HCN with an activation energy of about 200 kJ/mol and that there is no evidence

for a 1,3 shift to form CH₃NO (analogous, but more exothermic, to the HCONO in this case). They also presented theoretical results that show that the barrier to this process is of the order of 300 kJ/mol. Equally important, from studies on the reaction between HCO and NO, Langford and Moore (J. Chem. Phys. **80**, 4204, 1984) have convincingly demonstrated that the most likely decomposition products of the HCONO complex are CO + HNO.

On this basis we suspect that a stable HONCO moiety is formed, we estimate that the high pressure rate constant will be 1.7×10^{-11} cm³molecule⁻¹s⁻¹ with an uncertainty of a factor of 2. RRKM calculations have been carried out to determine the pressure dependence and these can be found in Tables 1 and 2.

TABLE 1. $\log(k/k_\infty)$ for the reaction OH+NCO→HONCO as a function of temperature and pressure assuming strong collisions

T(K) log (density)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
17	-0.93	-1.28	-1.60	-1.88	-2.14	-2.37	-2.58	-2.77	-2.95	-3.11	-3.26
17.5	-0.62	-0.93	-1.22	-1.48	-1.72	-1.93	-2.13	-2.32	-2.49	-2.64	-2.79
18	-0.38	-0.63	-0.88	-1.11	-1.33	-1.53	-1.71	-1.89	-2.05	-2.19	-2.33
18.5	-0.21	-0.40	-0.59	-0.79	-0.98	-1.16	-1.32	-1.48	-1.63	-1.77	-1.90
19	-0.10	-0.22	-0.37	-0.52	-0.68	-0.83	-0.97	-1.11	-1.24	-1.37	-1.48
19.5	-0.04	-0.11	-0.21	-0.31	-0.43	-0.55	-0.67	-0.78	-0.89	-1.00	-1.10
20	-0.02	-0.05	-0.10	-0.17	-0.25	-0.33	-0.42	-0.51	-0.59	-0.68	-0.76
20.5	-0.01	-0.02	-0.04	-0.08	-0.12	-0.18	-0.23	-0.29	-0.36	-0.42	-0.48
21		-0.01	-0.02	-0.03	-0.05	-0.08	-0.11	-0.15	-0.19	-0.23	-0.27
21.5			-0.01	-0.01	-0.02	-0.03	-0.05	-0.06	-0.08	-0.10	-0.13
22					-0.01	-0.01	-0.02	-0.02	-0.03	-0.04	-0.05

TABLE 2. Collision efficiency as a function of temperature and step size down for OH+NCO+M=HONCO+M

Step size (cm ⁻¹) Temp(K)	200	400	800	1600	3200
500	1.1×10^{-1}	2.4×10^{-1}	4.4×10^{-1}	6.3×10^{-1}	7.9×10^{-1}
700	6.2×10^{-2}	1.6×10^{-1}	3.3×10^{-1}	5.3×10^{-1}	7.1×10^{-1}
900	3.9×10^{-2}	1.1×10^{-1}	2.5×10^{-1}	4.4×10^{-1}	6.4×10^{-1}
1100	2.5×10^{-2}	7.5×10^{-2}	1.9×10^{-1}	3.6×10^{-1}	5.7×10^{-1}
1300	1.7×10^{-2}	5.4×10^{-2}	1.4×10^{-1}	3.0×10^{-1}	5.0×10^{-1}
1500	1.2×10^{-2}	3.9×10^{-2}	1.1×10^{-1}	2.5×10^{-1}	4.4×10^{-1}
1700	8.4×10^{-3}	2.8×10^{-2}	8.3×10^{-2}	2.0×10^{-1}	3.8×10^{-1}
1900	6.0×10^{-3}	2.1×10^{-2}	6.3×10^{-2}	1.6×10^{-1}	3.3×10^{-1}
2100	4.4×10^{-3}	1.5×10^{-2}	4.9×10^{-2}	1.3×10^{-1}	2.8×10^{-1}
2300	3.2×10^{-3}	1.2×10^{-2}	3.7×10^{-2}	1.1×10^{-1}	2.4×10^{-1}
2500	2.4×10^{-3}	8.6×10^{-3}	2.9×10^{-2}	8.4×10^{-2}	2.0×10^{-1}

For N_2 and CO_2 as the third bodies we recommend the following limiting rate expressions with an uncertainty of a factor of 3

$$k(O, N_2) = 1.75 \times 10^{-12} (1/T)^{5.96} \exp(-1785/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$F_c = 0.5$$

$$k(O, CO_2) = 8.1 \times 10^{-13} (1/T)^{5.77} \exp(-1665/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$F_c = 0.5$$

Channel(a) is an exothermic abstraction process. The recommended rate expression is based on the recommendation for the reverse reaction (17,3) and through the equilibrium constant. This leads to

$$k_a = 1.3 \times 10^{-19} T^{2.27} \exp(497/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Due to the large uncertainties in the heats of formation of NCO and HNCO there are possibilities of large uncertainties. However a rough lower limit can be set by the rate constants for the reaction $NH_2 + OH \rightarrow NH_3 + O$ which can be derived from the very reliable values of the reverse reaction ($OH + NH_3$, Cohen, Int. J. Chem. Kin., 1987, 19, 319) and the equilibrium constant. This leads to the following rate expression.

$$k(OH + NH_2 \rightarrow O + NH_3) = 7 \times 10^{-21} T^{2.42} \exp(818/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

A plot of these results can be found in Fig. 1. On the basis of the smaller exothermicity it is tempting to consider this as a lower limit. The overall uncertainty is a factor of 5 at temperatures in excess of 1000 K. This value can be expected to be larger at lower temperatures, where fortunately the combination reaction will be more important.

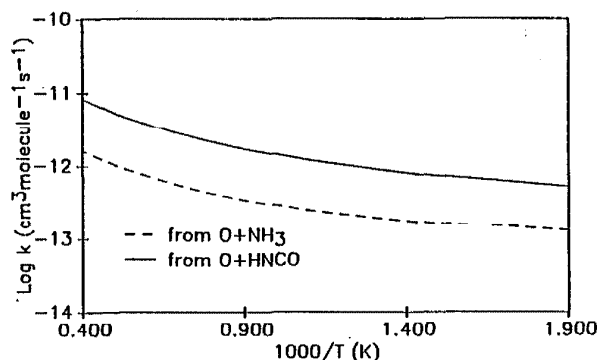


FIG. 1. Rate constants for $OH + NH_2 \rightarrow NH_3 + O$ and recommended values for $OH + NCO \rightarrow HNCO + O$

W. Tsang
January, 1991



Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:			1×10^{-11}	3

Comments

There are no measurements on the rate constant for this process. This is, however, a very exothermic reaction. We therefore recommend a large rate constant appropriate for an abstraction process with negligible barrier.

$$k(NCO + HCHO \rightarrow HNCO + HCO) = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 3.

W. Tsang
September, 1989

16,7: $\text{NCO} + \text{HCO} \rightarrow \text{HNCO} + \text{CO}$

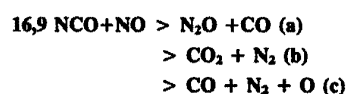
Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:			6×10^{-11}	2

Comments

There are no data on the mechanism and rate constant for this reaction. In view of the extremely weak H-CO bond and the corresponding tendency for disproportionation of radical reactions with HCO, it is suggested that

the same process occurs in this case. The rate constant is slightly reduced from that of $\text{CN} + \text{HCO}$ to reflect effects arising from the more complex NCO structure and smaller exothermicity.

W. Tsang
September 1990



Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction Rate Constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Cooper and Hershberger (1992)	298	1×10^{16} NO, O ₂ 1.6×10^{15} ICN and 1×10^{17} SF ₆ . NCO from CN + O ₂ reaction where CN from 266 nm photolysis of ICN. CO ₂ , CO and NO detected via infrared diode laser absorption	$k_a/k_{a+b+c} = 0.33$ $k_b/k_{a+b+c} = 0.44$ $k_c/k_{a+b+c} = 0.23$	0.06 0.06 0.09
Hancock and McKendrick (1986)	295	0.8×10^{15} PhNCO $3.3\text{--}33 \times 10^{15}$ NO and 1.6×10^{17} N ₂ O NCO from IRMPD of PhNCO. NCO via LiF.	$k_{a+b+c} = 3.4 \times 10^{-11}$	1.1
Perry (1985)	294–538	NCO from the fluorine excimer laser photolysis of trace quantities of HNCO in $0\text{--}4 \times 10^{16}$ H ₂ in $2.7\text{--}17 \times 10^{17}$ Ar. LiF detection of NCO	$k_{a+b+c} = 1.7 \times 10^{-11} \exp(196/T)$	1.1
Recommendation:			$k_{a+b+c} = 1.7 \times 10^{-11} \exp(196/T)$ 2 at 2000K $k_a/k_{a+b+c} = 0.33$ $k_b/k_{a+b+c} = 0.44$ $k_c/k_{a+b+c} = 0.23$	1.1 to 1000K 1.2 1.2 1.4

Comments

The recent measurements of Cooper and Hershberger are somewhat unexpected. Nevertheless the experiments appear to be clearcut. We recommend their branching ratio and the absolute rate constant for the total process as determined by Perry. The latter is good agreement with the determination of Hancock and McKendrick.

with an uncertainty of 1.1 up to 1000 K and increasing to a factor of 2 at 2000 K.

and

$$\begin{aligned} k_a/k_{a+b+c} &= 0.33 \pm 0.06 \\ k_b/k_{a+b+c} &= 0.44 \pm 0.06 \\ k_c/k_{a+b+c} &= 0.23 \pm 0.09 \end{aligned}$$

$$k_{a+b+c} = 1.7 \times 10^{-11} \exp(196/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

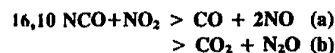
independent of temperature. The mechanism must involve the combination of the two radicals followed by the decomposition of the hot adduct.

References

- Cooper, W. F., and Hershberger, J. F., "Measurement of Product Branching Ratios of the NCO + NO Reaction", J. Phys. Chem., 96, 771, 1992
- Hancock, G. and McKendrick, K. G., "Vibrational Relaxation of NCO(X) by Rare Gases and Rate Constant Measurement of the NCO + NO Reaction" Chem. Phys. Lett., 127, 125, 1986.

Perry, R. A., "Kinetics of the Reactions of NCO radicals with H₂ and NO Using Laser Photolysis and-Laser Induced Fluorescence, J. Chem. Phys., 82, 5485-5488, 1985.

W. Tsang
September, 1990



Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction Rate Constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:			$k_{a+b} = 3 \times 10^{-11}$ $k_o/k_a = 0.2$	3 3

Comments

There are no data on the rate constant and mechanism of this reaction.

The estimated rate constant is based on the assumption of a radical combination process followed by the decomposition of the hot molecule. The main reaction involves combination to form the N-N bond, and a rapid 1,3 shift of the oxygen atom to the carbon as appears to be the case for ONNCO (see 16,9). In the case of the decomposition of nitro-organics there are always contributions from an isomerization channel to form the nitrite.

In the present case this will lead to channel (b).
The recommendations are therefore

$$k_{a+b} = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_b/k_a = 0.3$$

with an uncertainty of a factor of 3 for both values.

There have been no reports on the synthesis of the O₂NNCO molecule.

W. Tsang
March, 1992



Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:			3×10^{-11}	3

Comments

There have been no measurements on the mechanism and rate constant for this reaction. In view of the exothermicity of the abstraction channel and the possibility that the same results may arise from an addition and decomposition pathway, the rate constant must be very large and we recommend

$$k(\text{NCO} + \text{HNO} \rightarrow \text{HNCO} + \text{NO}) = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 3.

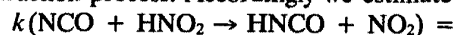
W. Tsang
January, 1991



Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:			6×10^{-12}	3

Comments

There are no measurements on the rate constant for this reaction. The reaction is undoubtedly an exothermic [although less so than the reaction with HNO (16,11)] abstraction process. Accordingly we estimate



with an uncertainty of a factor of 3.

W. Tsang
January, 1991

16,13 NCO + HCN → HNCO + CN

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
$\log_{10} K_p = -0.08192 - 1.4951 \times 10^3/T - 2.2566 \times 10^5/T^2 + 3.1086 \times 10^7/T^3$				
Recommendation:			$2 \times 10^{-11} \exp(-4456/T)$	10 at 2500 K

Comments

There are no measurements on the rate constant and mechanism for this reaction. We have derived the following rate expression,

$$k(\text{NCO} + \text{HCN} \rightarrow \text{HNCO} + \text{CN}) = 2 \times 10^{-11} \exp(-4456/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

on the basis of our estimated rate expression for the reverse process. Due to the uncertainty in the heat of formation of NCO we estimate a possible error of 10 at 2500 K and even larger as the temperature is lowered.

W. Tsang
Janaury, 1991

16,14 NCO + N₂O → N₂ + NO + CO

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:			$< 1.5 \times 10^{-10} \exp(-14000/T)$	

Comments

There are no measurements on the rate constant and mechanism of this reaction. This cannot be a fast reaction. Hancock and Mckendrick (Chem. Phys. Lett., 127, 125, 1986) used N₂O to deactivate vibrationally excited NCO and studied its reaction with NO in the presence of 1.7×10^{17} molecule cm⁻³ N₂O. This sets an upper limit of

1×10^{-14} cm³ molecule⁻¹s⁻¹ at 295. Radical attack (OH, for example) on N₂O are generally speaking very slow. The upper limit given here is for O + N₂O and should certainly be larger than any conceivable reaction with NCO.

W. Tsang
January, 1991

16,15 NCO + CN → NCN + CO

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:			3×10^{-11}	3

Comments

There are no data on the mechanism and rate constant for this reaction. The main process is probably combination of the two radicals with a rate constant of,

$$k(\text{NC} + \text{NCO} \rightarrow \text{NCNCO}) = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 3. Although NCNCO has been synthesized (Mayer, Monatsh Chem., 101, 834, 1970) and there are structural (Hocking and Gerry, J. C. S., Chem. Comm., 47, 1973) and vibrational frequency (Devore, J. Mol. Spec., 162, 287, 1987) data, none of the

more important thermochemical information is available. Thus we are unable to estimate the conditions where NCNCO may be stabilized. From the preparative procedure one would estimate that the NC-NCO bond energy exceeds 220 kJ/mol. The reaction as written above is exothermic by 215 kJ/mol. Thus the decomposition of the hot molecule is very likely under high temperature and ordinary pressure conditions. However at lower temperatures and especially high pressures, consideration must be given to the possibility of the stabilization of the adduct.

W. Tsang
June, 1990

16,16 $\text{NCO} + \text{NCO} \rightarrow \text{N}_2 + 2\text{CO}$

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Recommendation:			3×10^{-11}	2.5

Comments

There are no measurements on the mechanism and rate constant for this process. If we assume that this is a standard radical combination processes, then there can be little doubt that the newly formed adduct will rapidly decompose to form nitrogen and carbon monoxide. We therefore recommend

$$k(\text{NCO} + \text{NCO} \rightarrow \text{N}_2 + 2\text{CO}) = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 2.5.

W. Tsang
Jan, 1991

17,0 $\text{HNCO} + \text{M} \rightarrow \text{NH} + \text{CO} + \text{M}$ (a)
 $\rightarrow \text{H} + \text{NCO}$ (b)

Reaction/reference	Conditions <i>T</i> range/K	[M] range/cm ³	Reaction rate constant <i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
Wu <i>et al.</i> (1990)	2120–2570	0.01–0.5% HNCO Argon. CO-laser absorption and H-atom ARAS detection in separate shock tube experiments.	$4.3 \times 10^{-9} \exp(-39800/T)$	3 in $1-2 \times 10^{18}$
Mertens <i>et al.</i> (1989)	1830–3340	0.01–2.5% HNCO in $6-9 \times 10^{18}$ Argon NH detection via laser absorption at 336 nm	$1.6 \times 10^{-8} \exp(-43000/T)$ $5.4 \times 10^{11} (1/T)^{5.11} \exp(-55300/T)$	2
Kajimoto <i>et al.</i> (1985)	2100–2500	0.1–2% HNCO in $2.5-7 \times 10^{18}$ Argon HNCO disappearance at 206 nm and NH production at 336 nm	$2.8 \times 10^{-7} \exp(-48379/T)$	3
Recommendation:			$k(0, \text{N}_2) = 3.6 \times 10^4 (1/T)^{3.1} \exp(-51280/T)$ $k(0, \text{CO}_2) = 5.13 \times 10^4 (1/T)^{3.06} \exp(-51240/T)$ $k_\infty = 6 \times 10^{13} \exp(-50228/T) \text{ s}^{-1}$ $F_c = 0.9-2 \times 10^{-4} T$ for CO_2 and N_2	2

Comments

The three different experiments using completely different diagnostics are in excellent agreement. The results are plotted in Fig. 1.

Wu *et al.* using ARAS detection of H-atoms also detected a minor hydrogen atom channel. For most purposes this is probably not very important. Since their branching ratio originated from totally different experiments we are uncertain of the accuracy. A serious problem in extrapolating these results to a wide range of pressures is the lack of any knowledge regarding the high

pressure rate expression. This is compounded by the main reaction channel being a spin forbidden process. In our first attempts at modeling these reactions we found that with reasonable step sizes and a high pressure *A*-factor near that for N_2O there should be a marked pressure dependence. Since the work of Mertens *et al.* covered a considerable pressure range and no pressure dependence was observed it would appear that a higher *A*-factor may be more appropriate. In the present analysis we have chosen a value sufficiently large so that within the experimental spread of the results of Mertens *et al.* no pressure effect would have been discerned and adjusted other

parameters to reproduce their rate expression. The results of our RRKM calculations can be found in Tables 1 and 2.

It should be noted that we will in fact be over predicting any pressure effect. Therefore the tables are given merely for cautionary purposes. For most purposes it will be sufficient to use the limiting low pressure rate expression. Due to the high activation energy of this process decomposition can be important only at high temperatures.

Assuming that at these temperatures rate constants for N_2 and CO_2 are factors of 1.6 and 3.2 larger than that for argon leads to the following rate expressions:

$$k(0, N_2) = 3.6 \times 10^4 (1/T)^{3.1} \exp(-51280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(0, CO_2) = 5.13 \times 10^4 (1/T)^{3.06} \exp(-51240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 2. The assumed high pressure rate expression is;

$$k_\infty = 6 \times 10^{13} \exp(-50228/T) \text{ s}^{-1}$$

and the corresponding F_c values are

$$F_c = 0.9 - 2 \times 10^{-4} T$$

for both N_2 and CO_2 . The reader is warned again that the predicted pressure effects are rough limits and that pressure dependences may not occur until much higher pressures.

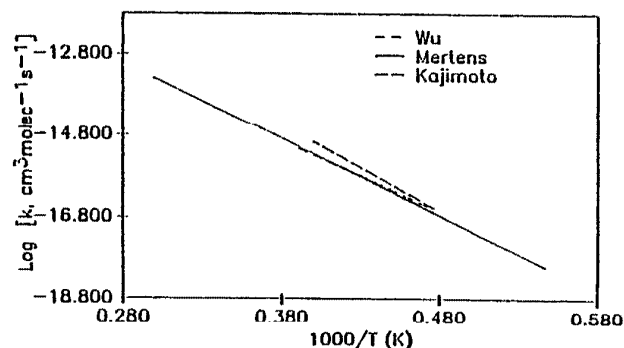


FIG. 1. Summary of data on HNCO Decomposition.

TABLE 1. $\log(k/k_\infty)$ for the reaction $HNCO \rightarrow NH + CO$ as a function of temperature and pressure assuming strong collisions

$T(K)$ log (density)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
17	-0.67	-0.83	-0.98	-1.13	-1.26	-1.39	-1.51	-1.63	-1.74	-1.84	-1.93
17.5	-0.38	-0.51	-0.65	-0.77	-0.90	-1.02	-1.13	-1.23	-1.33	-1.43	-1.52
18	-0.19	-0.29	-0.39	-0.49	-0.60	-0.70	-0.79	-0.89	-0.97	-1.06	-1.14
18.5	-0.08	-0.14	-0.21	-0.29	-0.36	-0.44	-0.52	-0.60	-0.67	-0.74	-0.81
19	-0.03	-0.06	-0.10	-0.15	-0.20	-0.25	-0.31	-0.37	-0.43	-0.48	-0.54
19.5	-0.01	-0.02	-0.04	-0.07	-0.10	-0.13	-0.17	-0.20	-0.24	-0.28	-0.32
20		-0.01	-0.02	-0.03	-0.04	-0.06	-0.08	-0.10	-0.12	-0.15	-0.17
20.5			-0.01	-0.01	-0.01	-0.02	-0.03	-0.04	-0.05	-0.07	-0.08
21						-0.01	-0.01	-0.02	-0.02	-0.03	-0.03
21.5									-0.01	-0.01	-0.01
22											

TABLE 2. Collision efficiency as a function of temperature and step size down for $\text{HNCO} + \text{M} \rightarrow \text{HN} + \text{CO} + \text{M}$

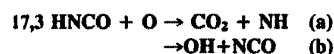
Step size (cm^{-1}) Temp(K)	200	400	800	1600	3200
500	1.2×10^{-1}	2.7×10^{-1}	4.6×10^{-1}	6.5×10^{-1}	8.0×10^{-1}
700	7.4×10^{-2}	1.8×10^{-1}	3.6×10^{-1}	5.6×10^{-1}	7.4×10^{-1}
900	5.0×10^{-2}	1.3×10^{-1}	2.9×10^{-1}	4.9×10^{-1}	6.8×10^{-1}
1100	3.6×10^{-2}	1.0×10^{-1}	2.3×10^{-1}	4.2×10^{-1}	6.2×10^{-1}
1300	2.6×10^{-2}	7.8×10^{-2}	1.9×10^{-1}	3.7×10^{-1}	5.7×10^{-1}
1500	2.0×10^{-2}	6.2×10^{-2}	1.6×10^{-1}	3.2×10^{-1}	5.3×10^{-1}
1700	1.6×10^{-2}	4.9×10^{-2}	1.3×10^{-1}	2.8×10^{-1}	4.8×10^{-1}
1900	1.2×10^{-2}	4.0×10^{-2}	1.1×10^{-1}	2.5×10^{-1}	4.5×10^{-1}
2100	1.0×10^{-2}	3.3×10^{-2}	9.5×10^{-2}	2.2×10^{-1}	4.1×10^{-1}
2300	8.2×10^{-3}	2.8×10^{-2}	8.1×10^{-2}	2.0×10^{-2}	3.8×10^{-1}
2500	6.8×10^{-3}	2.3×10^{-2}	7.0×10^{-2}	1.8×10^{-2}	3.5×10^{-1}

References

Wu, C. H., Wang, H. T., Lin, M. C. and Fifer, R. A., "Kinetics of CO and H-atom Production from the Decomposition of HNCO in Shock Waves" *J. Phys. Chem.*, **94**, 3344, 1990.
 Mertens, J. D., Chang, A. Y., Hanson, R. K., Bowman, C. T., "Reaction Kinetics of NH in the Shock Tube Pyrolysis of HNCO", *Int. J. Chem. Kin.*, **21**, 1049-1067, 1989.

Kajimoto, O., Kondo, O., Okada, K., Fujikane, J. and Fueno, F., "Kinetic Study of the Thermal Decomposition of Isocyanic Acid in Shock Waves", *Bull. Chem. Soc. Japan*, **58**, 3469-73, 1985.

W. Tsang
 September, 1990

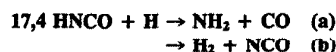


Reaction/reference	Conditions T range/K	[M] range/ cm^3	Reaction rate constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty
He <i>et al.</i> (1991)	1400-2500	HNCO:NO ₂ :Ar 0.001:0.002:997 0.001:0.001:998 0.002:0.001, 997 in $1-1.3 \times 10^{18}$ total pressure in shock tube. NO, CO and H ₂ O by IR laser absorption	$k_a = 1.6 \times 10^{-16} T^{1.41} \exp(-4290/T)$ $k_b = 3.7 \times 10^{-18} T^{2.11} \exp(-5750/T)$	2.5
Mertens <i>et al.</i> (1991)	2120-3190	0.05-0.5% HNCO and 0.074-0.253% N ₂ O in $0.7-3.5 \times 10^{18}$ Ar in shock tube experiments. Reactions followed by thin line laser absorption at 336 nm (NH) and 307 nm (OH). Rate constants from kinetic modeling.	$k_a = 3.2 \times 10^{-11} \exp(-7150/T)$ $k_b = 2.3 \times 10^{-10} \exp(-10300/T)$	1.6
Tully <i>et al.</i> (1985)	679-741	O ₂ (or N ₂ O), NO and HNCO in $6.6-26$ $\times 10^{17}$ Ar. O from 157 nm photolysis of O ₂ and NO or 192 nm photolysis of N ₂ O O(¹ D) quenched by Ar O detected by chemiluminescence from O + NO	$k_{a+b} = 5.4 \times 10^{-12} \exp(-5200/T)$	1.2
Recommendation:			$k_a = 1.6 \times 10^{-16} T^{1.41} \exp(-4290/T)$ $k_b = 3.7 \times 10^{-18} T^{2.11} \exp(-5750/T)$	1.5 at 600 K 2.5 at 2500 K

Comments

The recent results on these reactions have led to a unambiguous determination of mechanisms and rate constants. The experiments involve the simultaneous detection of reaction products. Particularly important is the work of Mertens *et al.* since the NH and OH which they monitored are initial products. The work of He *et al.* is less clear cut since the compounds they monitored are more in the nature of secondary products. The earlier work of Tully *et al.* represents a highly accurate determination of the total rate constants for both channels. He *et al.* has performed a valuable service in correlating all the data within the framework of transition state theory and the recommended rate expressions are as given by these authors or

$$k_a = 1.6 \times 10^{-16} T^{1.41} \exp(-4290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
$\text{Log}_{10} K_p(\text{b}) = 0.43282 - 2.0351 \times 10^3/T - 1.2095 \times 10^5/T^2 + 1.9367 \times 10^7/T^3$				
Recommendation:			$k_a = 5 \times 10^{-11} \exp(-2300/T)$ $k_b = 4.8 \times 10^{-17} T^{1.81} \exp(-8332/T)$ larger at lower temperatures	3 > 1000 10 at 1000 K

Comments

There are no direct studies on the rate and mechanism for this reaction. There are essentially two processes, addition, followed by decomposition of the hot H₂NCO radical, and abstraction of the hydrogen.

For the former, Miller *et al.* (20th Symp. (Int.) on Combustion, 673, 1984) have given an estimate for the temperature range 1100–1400 K of $3.33 \times 10^{-11} \exp(-1510/T) \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and used it, along with many other reactions, to model a low pressure H₂-O₂ flame. The results do not appear to be particularly sensitive to this process. The rate expression is close to that for H+ketene ($1.9 \times 10^{-11} \exp(-1715/T)$; Michael *et al.*, J. Chem. Phys., 70, 5222, 1979) and H+HN₃ ($2.6 \times 10^{-11} \exp(-2300/T)$; LeBras and Combourieu, Int. J. Chem. Kin., 5, 559, 1973). Our recommendation is very close to these values or,

$$k(\text{H} + \text{NHCO} \rightarrow \text{NH}_2 + \text{CO}, \text{NH}_2\text{CO}) = 5 \times 10^{-11} \exp(-2300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty is a factor of 3 for temperatures greater than 1000 K. However at lower temperatures the

$$k_b = 3.7 \times 10^{-18} T^{2.11} \exp(-5750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 1.5 at the lower temperatures and increasing to a factor of 2.5 at 2500 K.

References

- He, Y., Lin, M. C., Wu, C. H. and Melius, C. F. "The Reaction of HNCO with NO₂ in Shock Waves" 24th Symp. (Int'l) on Combustion, submitted.
 Mertens, J. D., Chang, A. Y., Hanson, R. K., and Bowman, C. T., "A Shock Tube Study of Reactions of Atomic Oxygen with Isocyanic Acid", Int. J. Chem. Kin., submitted.
 Tully, F. P., Perry, R. A., Thome, L. R. and Allendorf, M. D., "Free Radical Oxidation of Isocyanic Acid" 22nd Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1101–1106, 1988.

W. Tsang
November, 1991

uncertainties in the activation energy can lead to very large uncertainties in the rate constants. At room temperature this may be as much as 2 orders of magnitude.

Under high pressure conditions and sufficiently low temperatures the H₂NCO radical can be stabilized. We have carried out RRKM calculations in order to arrive at some estimate of the relative importance of these two channels. These calculations are based on the reverse of the rate expression given above or $k(\text{NH}_2\text{CO} \rightarrow \text{H} + \text{HNCO}) = 5 \times 10^{12} \exp(-20500/T) \text{ s}^{-1}$ and $k(\text{NH}_2\text{CC} \rightarrow \text{NH}_2 + \text{CO}) = 10^{13} \exp(-16000/T) \text{ s}^{-1}$. The latter is different from the rate expression $k(\text{NH}_2\text{CO} \rightarrow \text{NH} + \text{CO}) = 5.9 \times 10^{12} \exp(-12500/T) \text{ s}^{-1}$ reported by Yokota and Back, (Int. J. Chem. Kin., 5, 37, 1973) and was derived from a very complex experimental situation and implies through the thermochemistry that the NH addition reaction with CO proceeds with no activation energy. We have assigned an activation energy for this process that is of the same order as CH₃+CO. The results of RRKM calculations assuming strong collision can be found in Table 1. It should be noted that the stabilization reaction is only important at lower temperature since at higher temperatures the stabilized molecule will rapidly decompose. Due to the uncertainties in the rat

TABLE 1. $\log(k(\text{dec})/(k(\text{dec})+k(\text{stab})))$ for the reaction $\text{H} + \text{HNCO} \rightarrow \text{NH}_2 + \text{CO}$ (decomposition) and $\text{H} + \text{HNCO} \rightarrow \text{NH}_2\text{CO}$ as a function of temperature and pressure assuming strong collisions

$T(\text{K})$ $\log(\text{density})$	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
17											
17.5											
18											
18.5	-0.02	-0.01	-0.01	-0.01	-0.01	-0.01					
19	-0.05	-0.04	-0.03	-0.03	-0.02	-0.02	-0.01	-0.01	-0.01	-0.01	-0.01
19.5	-0.13	-0.11	-0.09	-0.07	-0.06	-0.05	-0.04	-0.04	-0.03	-0.03	-0.03
20	-0.32	-0.27	-0.23	-0.19	-0.16	-0.14	-0.12	-0.10	-0.09	-0.08	-0.07
20.5	-0.64	-0.56	-0.48	-0.41	-0.36	-0.31	-0.27	-0.24	-0.21	-0.19	-0.17
21	-1.05	-0.95	-0.84	-0.75	-0.66	-0.59	-0.54	-0.49	-0.44	-0.41	-0.38
21.5	-1.52	-1.40	-1.28	-1.17	-1.07	-0.98	-0.90	-0.84	-0.78	-0.73	-0.69
22	-2.01	-1.89	-1.76	-1.64	-1.53	-1.43	-1.35	-1.27	-1.21	-1.15	-1.09

expressions used in these calculation we present only the strong collision values. They can serve as a basis for estimating when stabilization may be important. Note that this is a maximum pressure with respect to stabilization, and the actual pressure where stabilization can occur is probably higher. For most purposes the recommended rate expression refers to the decomposition process.

There is also the possibility of direct abstraction. This can be derived on the basis of the recommendations for the reverse reaction and leads to the rate expression,

$$k(\text{H} + \text{HNCO} \rightarrow \text{H}_2 + \text{NCO}) = 4.8 \times 10^{-17} T^{1.81} \exp(-8332/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

The estimated uncertainties are a factor of 10 at 1000 K and much larger at lower temperatures and is largely due to the uncertainties in the thermodynamics.

W. Tsang
September, 1990

17.5 $\text{HNCO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NCO}$

Reaction/reference	Conditions T range/K	[M] range/ cm^3	Reaction rate constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Uncertainty
Mertens <i>et al.</i> (1991)	2120–2500	500–1000 ppm HNCO; 739–2380 ppm N_2O in shock tube experiments with narrow line laser absorption detection of NH (336nm) and OH (307nm).	$< 2.5 \times 10^{-12}$	
Tully <i>et al.</i>	624–875	OH from the photolysis of N_2O and the reaction of O^1D with H_2O or HNCO OH detection by LiF 0.6×10^{15} HNCO in 1×10^{19} He	$4.4 \times 10^{-12} \exp(-2790/T)$	1.5
Recommendation:			$1.06 \times 10^{-18} T^2 \exp(-1290/T)$	2

Comments

The main uncertainty is the mechanism for this reaction. On the basis of determination of the isotope effect from OH interaction with DNCO, Tully *et al.* suggest that the abstraction process is the main reaction. We base our recommendations on the work of Tully *et al.* and extend the range of applicability by assuming the standard T^2 dependence of the pre-exponential factor for OH reactions and obtain

$$k(\text{OH} + \text{HNCO} \rightarrow \text{H}_2\text{O} + \text{NCO}) = 1.06 \times 10^{-18} T^2 \exp(-1290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 2 over the entire range. At 2200 K this leads to $2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ or in excellent agreement with the upper limit of Mertens *et al.*

References

- Tully, F. P., Perry, R. A., Thorne, L. R. and Allendorf, M. D., "Free Radical Oxidation of Isocyanic Acid" 22nd Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1101-1106, 1988.
Mertens, J. D., Chang, A. Y., Hanson, R. K., and Bowman, C. T., "A Shock Tube Study of Reactions of Atomic Oxygen with Isocyanic Acid", Int. J. Chem. Kin., submitted.

W. Tsang
September, 1990

17,7: $\text{HNCO} + \text{HCO} \rightarrow \text{NCO} + \text{H}_2\text{CO}$

Reaction/reference	Conditions T range/K	[M] range/ cm^3	Reaction rate constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty
$\log_{10} K_p = -0.5466 - 5.9376 \times 10^3/T + 1.8784 \times 10^5/T^2 - 3.1487 \times 10^7/T^3$ Recommendation:			$5 \times 10^{-12} \exp(-13100/T)$	10

Comments

There are no data on the mechanism and rate constant for this reaction. From our estimated rate expression for the reverse reaction we find

$$k(\text{HNCO} + \text{HCO} \rightarrow \text{NCO} + \text{H}_2\text{CO}) = 5 \times 10^{-12} \exp(-13100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The large activation energy is reflective of the endothermicity of the reaction. When this is coupled with the instability of the formyl radical, it is unlikely that this reaction will be of importance in any application. We assign an uncertainty of a factor of 10 for temperatures in excess of 600 K.

W. Tsang
January, 1991

17,15 $\text{HNCO} + \text{CN} \rightarrow \text{HCN} + \text{NCO}$

Reaction/reference	Conditions T range/K	[M] range/ cm^3	Reaction rate constant $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Uncertainty
Recommendation:			2.5×10^{-11}	3

Comments

There are no data on the rate constant for this reaction. Considering the exothermicity of the reaction the rate constants must be large. A lower limit is set by the less exothermic reaction of

$$k(\text{CN} + \text{NH}_3) = 3 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

(Sims and Smith, J. Chem. Soc., Faraday Trans. 2, 84, 527, 1988. After taking into consideration the three available hydrogens in ammonia, we recommend

$$k(\text{CN} + \text{HNCO} \rightarrow \text{HCN} + \text{NCO}) = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 3.

W. Tsang
January, 1991

17,17 HNCO + HNCO → CO₂ + HNCNH

Reaction/reference	Conditions T range/K	[M] range/cm ³	Reaction rate constant k/cm ³ molecule ⁻¹ s ⁻¹	Uncertainty
He <i>et al.</i> (1991)	873–1220	0.15, 60, 90% in 7.5 × 10 ¹⁸ Ar. Static reactor. Final products CO, CO ₂ , HCN, NH ₃ and HNCO by FTIR	1.1 × 10 ⁻¹³ exp(-21240/T)	2
Recommendation:			1.1 × 10 ⁻¹³ exp(-21240/T) increasing to 5 at 500 K and 3 at 2000 K	2800–1300

Comments

The recent work of He *et al.* provides striking evidence for a bimolecular channel for HNCO decomposition. Since CO₂ is the initial product and it is not formed via any of the subsequent processes, the derived rate expression should be quite accurate.

References

He, Y., Liu, X. P., Lin, M. C. and Melius, C. F., "The Thermal Reaction of HNCO at Moderate Temperatures", *Int. J. Chem. Kin.*, in press.

W. Tsang
September, 1991

4. Thermodynamic Data

$$\log_{10}[K_p, \text{CN}] = 5.0873 - 2.12995 \times 10^4/T - 2.33218 \times 10^5/T^2 + 3.66103 \times 10^7/T^3$$

$$\log_{10}[K_p, \text{NCO}] = 1.57379 - 8.3795 \times 10^3/T - 4.9539 \times 10^2/T^2 + 2.1012 \times 10^6/T^3$$

$$\log_{10}[K_p, \text{HNCO}] = -2.01827 + 5.6649 \times 10^3/T - 1.15892 \times 10^5/T^2 + 1.33608 \times 10^7/T^3$$

5. Transport Properties
(Lennard-Jones Potential)
for Unimolecular Reactions

Substance	σ (Angstroms)	ϵ/k K
Argon	3.542	93.3
Helium	2.551	10.22
Krypton	3.655	178.9
Neon	2.82	32.8
Air	3.711	78.6
Carbon Monoxide	3.690	91.7
Carbon Dioxide	3.941	195.2
Hydrogen(H ₂)	2.827	59.7
Nitrogen(N ₂)	3.798	71.1
Oxygen(O ₂)	3.467	106.7
Water	2.641	804.1
Cyanogen	4.361	348.6
NCO(estimated)	4.0	300
HNCO(estimated)	4.15	320

Reid, R. C., Prausnitz, J. M. and Poling, B. E., "The Properties of Gases and Liquids" McGraw-Hill Book Company, New York, 1987 except estimated values.