

# Chemical Kinetic Data Base for Propellant Combustion I. Reactions Involving NO, NO<sub>2</sub>, HNO, HNO<sub>2</sub>, HCN and N<sub>2</sub>O

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# Chemical Kinetic Data Base for Propellant Combustion

## I. Reactions Involving NO, NO<sub>2</sub>, HNO, HNO<sub>2</sub>, HCN and N<sub>2</sub>O

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This publication contains evaluated chemical kinetic data on a number of single step elementary reactions involving small polyatomic molecules which are of importance in propellant combustion. The work involves 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<sup>17</sup>–10<sup>22</sup> particles/cm<sup>3</sup>. The results of the first years effort lead to coverage of all pertinent reactions of the following species; H, H<sub>2</sub>, H<sub>2</sub>O, O, OH, HCHO, CHO, CO, NO, NO<sub>2</sub>, HNO, HNO<sub>2</sub>, HCN, and N<sub>2</sub>O.

Key words: combustion, elementary reactions, kinetics, nitrogen oxides, propellants.

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## 1. Preface

### 1.1. Introduction

Quantitative understanding of the detailed chemical kinetics of propellant combustion can have important impacts on the formulation of such mixtures, the optimization of current systems and the design of new combustors. A complicating factor has been the scores of rate expressions of elementary reactions that are needed to give a complete description of the process. For many years the necessary experimental tools and theoretical understanding were not available for the development of such a chemical kinetic information base. In addition, there is also a need to identify key reactions and develop simple mechanisms. This is not an easy task. With these two major impediments, it is not surprising that as far as the chemistry is concerned much work in this area has been empirical. This implies the necessity of a great deal of physical testing. The expense of such efforts is a severe limitation on innovative efforts in this area.

In recent years a number of exciting technological developments have made it worthwhile to look anew into the possibility of developing a basic understanding of the chemistry that underlies propellant combustion. These include:

a) Rapid progress in computational capabilities, so that the simulation of increasingly realistic physico-chemical systems are or will be well within our capabilities. Thus, the information in a chemical kinetic data base can be used immediately. Indeed, a major impetus for this work was furnished by the successful efforts of Melius<sup>1</sup> in reproducing through computer simulation a number of the observations on the properties of RDX flames.

b) Development of experimental and theoretical capabilities in chemical kinetics, so that the needed rate constants can be measured or estimated.

c) Extensive applications of powerful modern diagnostic techniques to laboratory systems, so that we are developing much better pictures of the micro-structure of combustion processes. However, the interpretation and the projection of such results to real systems is crucially dependent on the existence of a *correct* detailed model. Given the large number of parameters one can always "fit" a particular experimental observation. Only the model with the *correct* inputs can be expected to project results to real systems.

This paper contains the results of work recently initiated at the National Institute of Standards and Technology and with the support of DOD. We begin with a description of its scope and give reasons for the reactions considered. The procedures used in the evaluation work will be discussed. The major part of the paper will be a series of data sheets reporting on our evaluation of existing data or our estimates on the rate expressions for individual reactions. We will conclude with some general comments on the lessons that can be derived from our

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work, indicate future directions, and describe needs with respect to additional experimental and theoretical work.

## 1.2. Scope and Approach

This is the first of series of papers aimed at covering all gas phase reactions pertinent to the decomposition of RDX as shown in Fig. 1.

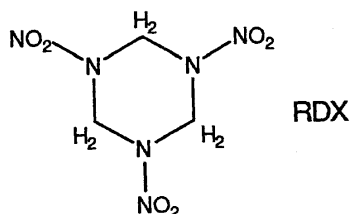


Fig. 1. Structural formula for RDX.

It represents the starting point of what may be a more ambitious project to cover propellants and binders in general. RDX is a widely used propellant and is the most volatile of the nitramine propellants. There is good reason to believe that a significant amount of the decomposition process occurs in the gas phase and it will thus be possible to gauge the usefulness of the work. Our approach is in terms of elementary single step thermal reactions. This may be considered the first transferable bit of chemical kinetic information. Thus, many of the reactions to be considered will actually be components of data bases dealing with other propellants. The physical conditions to be covered are 500–2500 K in temperature and  $10^{17} - 10^{22}$  particles/cm<sup>3</sup> in density. The lower temperature limit is slightly lower than the boiling point of RDX.

The compounds that we will consider are listed in the reaction grid in Fig. 2. Justification for the inclusion of the various compounds is given below. There can be little question regarding the inclusion of the small species (4 atoms or less). They include practically all the possible compounds. Many of these species have been detected in experiments involving RDX. Others are natural precursors or products of these compounds. The selection of the larger fragments is more speculative. Most of these have not been detected and the possibilities are considerably larger than the number of species that we have chosen. Mechanistic considerations enter into the selection. We postulate that detrimerization occurs at a very early stage in the decomposition and that all linear species larger than the monomeric methylene nitramine are so unstable that they need not be considered. No claim is made that we have the correct mechanism. We regard this program as merely a first cut and that the compounds listed are a minimal listing. As new data are accumulated additional species can be added to cover a wider range of situations.

We now review our evaluation procedure. There is at present no standard method for carrying out data evaluation in chemical kinetics. Our experience in these matters

has led to the following procedure. First preference is given to experimental determinations where the mechanism is clear-cut. Frequently, this is from direct determinations of the rate of disappearance or appearance of reactants or intermediate products in real time. We have also found that in complex (or apparently complex) situations, careful modeling of the temporal history of products and intermediates can lead to accurate results. In many cases, these may not be individual rate constants, but accurate ratios of rate constants. In this manner, we are able to generate accurate networks of reactions. Note that it is our judgement that the most accurate of modern day kinetic results still have uncertainties in the 10 to 20% range. In the absence of kinetic data, thermodynamic considerations in the form of detailed balance are used. For the substances under consideration in the current review the thermodynamics are all well established<sup>2</sup>. In other cases, rate constants are assigned on the basis of analogy or thermokinetic information. In all cases, we assign an uncertainty value to our recommendations. This is a subjective number. It is based on the intercomparison of data sets, considerations imposed by related reaction mechanisms, and the constraints imposed by thermodynamics and theory. Quantitatively, it means that the user of the data should feel free to adjust the rate constant in his models within these limits.

Unimolecular reactions in the broadest sense, including not only decompositions and isomerizations but also combination and chemical activation processes, are rendered more complex than true bimolecular reactions, for example metathesis, by their dependence not only on temperature but also on the nature and pressure of the bath gas. There is at present a fully developed calculational method, the RRKM procedure<sup>3</sup>, which provides a framework for projecting data over all relevant pressure and temperature ranges. We have applied this technique for a large number of reactions involving hydrocarbons<sup>4</sup>. The results have proven to be very satisfactory in correlating a wide variety of data. The consistencies in the collisional efficiencies that we have derived have led us to use the general method for predictive purposes.

## 1.3. Organization

The reaction grid in Fig. 2 is divided into a number of blocks. Block A consists of the reactions involved with formaldehyde oxidation. We have already prepared data sheets for these reactions in the context of hydrocarbon combustion<sup>4</sup>. Block B contains reactions involving the smaller nitrogenated species. They are covered in the current work. With its completion it should be possible to model HCHO—NO<sub>2</sub> combustion systems. Other blocks will be covered in the future. Thus validation of the data base can begin at the subsystem level. It is expected that the overall process will involve continuous iteration between data evaluators, modelers and experimentalists. A similar procedure has worked with marked success for the stratospheric ozone problem<sup>5</sup>.

	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.	24.	25.	26.	27.	28.	
0.	M																													
1.	H <sub>2</sub>																													
2.	H <sub>2</sub> O																													
3.	O*																													
4.	H*																													
5.	OH*																													
6.	HCHO																													
7.	CHO*																													
8.	CO																													
9.	NO																													
10.	NO <sub>2</sub>	X																												
11.	HNO	X	X																											
12.	HNO <sub>2</sub>	X	X	X																										
13.	HCN	X	X	X	X																									
14.	N <sub>2</sub> O	X	X	X	X	X																								
15.	CN*	X	X	X	X	X	X																							
16.	NCO	X	X	X	X	X	X	X																						
17.	HNCO	X	X	X	X	X	X	X	X																					
18.	NO <sub>3</sub> *	X	X	X	X	X	X	X	X	X																				
19.	HNO <sub>3</sub>	X	X	X	X	X	X	X	X	X	X																			
20.	H <sub>2</sub> CN*	X	X	X	X	X	X	X	X	X	X	X																		
21.	H <sub>2</sub> CNH	X	X	X	X	X	X	X	X	X	X	X	X																	
22.	H <sub>2</sub> CNNO <sub>2</sub>	X	X	X	X	X	X	X	X	X	X	X	X	X																
23.	RDX	X	X	X	X	X	X	X	X	X	X	X	X	X	X															
24.	RDX-NO <sub>2</sub> *	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X														
25.	RDX-NO <sub>2</sub> +H	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X													
26.	RDX-HNO <sub>2</sub>	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X												
27.	RDX-NO*	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X											
28.	RDX-O	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X										

FIG. 2. Reaction grid of possible processes X reactions considered in present text; A, B, C subsets of reactions.

Each of the compounds in the data base is assigned a number. The array of two numbers represent a particular reaction. Unimolecular reactions are designated by a number followed by a zero. The ordering of reactions begins with a reactant that is associated with a particular number and then considers all reactions with compounds designated with lower numbers. The absence of a reaction signifies that the rate constant is considered to be too slow to be of consequence for the present application.

This paper is divided into five sections. The first section contains the preface. Quantitative information can be found in the next four sections. Section 2 contains a summary of all our recommendations, the estimated uncertainties and the page where more detailed discussions can be found. Section 3 contains the individual data sheets and represents the bulk of our efforts. It is divided into a number of subsections. These will be described in detail. Thermodynamic data are summarized in Sec. 4. This contains a polynomial fit to the  $\log_{10}K_p$  values for the species contained in this study. They are based on the values given in the JANAF Tables. Note that in this analysis we have accepted all the JANAF thermochemical data. Section 5 contains a summary of transport properties that

are used in the calculation of unimolecular processes in the pressure dependent region.

The basic product from this work is the data sheet. It begins with the two numbers that have assigned to the reactants and is followed by a statement of the reaction(s). This is followed by summaries of previous investigations. It includes a description of the experimental conditions and methods, the results of the experiments in the form of the rate expressions and estimated errors. The latter is usually based on the author's estimates. Also included in this data block are the recommendations from earlier reviews. In many cases, we use these as the starting point for our work. The final entry gives our recommendations and the estimated uncertainties. Since most of the reactions are bimolecular the usual units are  $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . In certain cases they may be unimolecular or ter-molecular. For these cases the units,  $\text{s}^{-1}$  and  $\text{cm}^6\text{molecule}^{-1}\text{s}^{-1}$ , respectively, are given with the rate expression.

The next sub-section (in Sec. 3) contains the justification for the recommended expression. In the case of unimolecular reactions 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 Troe<sup>6</sup>. At the present time, there is uncertainty regarding the magnitude and temperature dependence of the step sizes. It is not predictable and must be determined experimentally for each case. 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 Troe<sup>6</sup> and derive a correction factor,  $\beta(c) = C^2W/R^{0.5}$  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 nitric acid formation from  $\text{OH} + \text{NO}_2$  at 1100 K in  $\text{N}_2$  and 1 atm pressure. We begin by calculating the quantities discussed earlier: a) Ratio of reduced masses ( $R$ ),  $19.4/31.5 = 0.62$ ; b) Ratio of collision diameters ( $C$ ),  $4.02 \times 10^{-8}/4.24 \times 10^{-8} = 0.95$ ; c) Ratio of collision integrals ( $W$ ),  $\epsilon/k$  for  $\text{HNO}_3$  and  $\text{N}_2$  are 390 K and 71.4 K respectively. Substitution into the relation recommended by Troe for the collisional integral  $(0.697 + 0.5185 \log(kT/\epsilon))^{-1}$  leads to values of 1.075 and 0.891 for  $\text{HNO}_3\text{—HNO}_3$  and  $\text{HNO}_3\text{—N}_2$  collisions respectively. The ratio of the two numbers is then 0.826.

This then leads to a value for  $\beta(c)$  of 0.947 for collisions between  $\text{OH} + \text{NO}_2$  and  $\text{N}_2$ . If we now take a step size down of  $275 \text{ cm}^{-1}$  we find from Table 2,  $\beta(e) = 0.04$ . The total collision efficiency is thus 0.038. The number density at 1 atm and 1100 K is  $6.7 \times 10^{18}$  molecules/ $\text{cm}^3$ . When multiplied by the collision efficiency of 0.031 we arrive at an equivalent density of  $2.5 \times 10^{17}$  molecules/ $\text{cm}^3$ . Then from Table 1 we find  $\log_{10} [k/k_\infty] = -2.76$  or 0.17% of the limiting high pressure value.

As an additional aid to the user we also give closed formed expressions that permit the calculation of  $k/k_\infty$  for  $\text{N}_2$  and  $\text{CO}_2$ . The procedure is due to Troe<sup>7</sup>. The general relations are;

$$k = [k_0 k_\infty / (k_0 + k_\infty / M)] * F$$

and

$$\log F = \log F_c / (1 + (\log k_0 \times M / k_\infty)^2),$$

where  $k_0$  is the second(or third) order rate constant and  $k_\infty$  is the first(or second) order rate constant,  $M$  is 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  $k/k_\infty$  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 20%. This is well within experimental error. In the case of  $\text{HNO}_3\text{—N}_2$  given above we find for example  $\log_{10}(k/k_\infty) = -2.73$ .

We present estimated results with  $\text{CO}_2$  as a collision partner because unlike hydrocarbon combustion systems, where reactions are carried out in a background of  $\text{N}_2$ , propellants carry their own oxidizers. Therefore, the reactive background is a more complex mixture of polyatomic gases. We have, perhaps arbitrarily, chosen  $\text{CO}_2$  (triatomic and likely to be a more efficient collision partner than  $\text{N}_2$ ) as a gas with properties that will be representative of such mixtures. It leads to somewhat larger limiting low pressure rate constants than argon or nitrogen. It may well be that an even more efficient collision partner is more appropriate. This is particularly the case at the lowest temperatures where the presence of water may have very serious effects.

The final subsection (Sec. 3) contains the references, the person who carried out the analysis and the date. Hopefully, all the literature on this reaction previous to this date have 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.

#### 1.4. Discussion

The work described here has benefited from the intensive research effort aimed at understanding  $\text{NO}_x$  formation and destruction at high temperatures and stratospheric ozone depletion in the low temperature regime. The careful reviews of Hanson and Salimian<sup>8</sup>, Baulch *et al.*<sup>9</sup> and Atkinson *et al.*<sup>5</sup> have provided a firm basis for our work. The focus of this work has been the extension of the data to cover the intermediate region between the high and low temperatures and pressures to ranges and collision partners more in line with propellant applications. Some of the extrapolations are very long and the estimates are usually based on analogies. There is thus a great need for high quality experimental work. The excellent reproducibility of all the data that we have used, particularly the shock tube results, demonstrate that such efforts are well within the state of the art.

There are, however, a number of uncertainties that may become even more important in the future as we deal with reactions that are more closely associated with

the nitramines. For most bond breaking and/or bond forming reactions, there are few conceptual problems. In the case of  $O + NO$  the formation of  $NO_2$  in a variety of electronic states leading to much higher rate constants than expected and represents a new range of phenomena which may have serious consequences. An analogous situation occurs for the  $N_2O$  decomposition. Here the process is spin forbidden and therefore one obtains an unusually low pre-exponential factor for unimolecular decomposition. Fortunately in both cases there are sufficient experimental data so that there is no need to make estimates. We have serious doubts that present day theory can make accurate predictions on these effects. This is also the case for complex rearrangements. For example the rate expression for the reaction  $HNO + HNO \rightarrow H_2O + N_2O$  has now been determined by Lin and coworkers<sup>10</sup>. They believe that the results are consistent with passage through a hot adduct. RRKM calculations provide a formalism for extrapolating these results. The important parameters involve the properties of the adduct and the nature of the transition states for its formation and destruction. At the present time these can only be deduced theoretically and we are not sure of the accuracy of such estimates. The general problem of adduct formation becomes particularly serious as the pressure is increased. It could mean that more species must be added to the data base. Clearly, there is the need for more experimental work at the higher pressures and tests of theoretical predictions.

Our plans for the next year involve expansion of the data base to cover the reactions listed in Block C. This will involve the reactions of CN, NCO, HNCO with the species that have been covered so far and with each other. Completion of the work on the first three radicals should permit us to model  $HCN-NO_2$  flames and thus

provide us with another test of the correctness of the data base. Due to the fact that these three species are in the chain of reactions of importance to the oxidation of fuel nitrogen there exists considerable information on their kinetic behavior. Nevertheless, some of the problems that we have mentioned before will become increasingly important as we evaluate the data and attempt to make estimates.

### 1.5. Acknowledgement

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## 2. Index of Reactions and Summary of Rate Expressions

No.	Reactions	Rate expressions ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ unless otherwise stated)	Uncertainties	Page
9,0	$NO + M \rightarrow N + O + M$	$1.6 \times 10^{-9} \exp(-74700/T)$ $2.4 \times 10^{-9} \exp(-74700/T)[N_2]$ $4.0 \times 10^{-9} \exp(-74700/T)[CO_2]$	2	616
9,1	$NO + H_2 \rightarrow HNO + H$	$2.3 \times 10^{-11} \exp(-28450/T)$	3	617
9,3	$NO + O + M \rightarrow NO_2 + M$ (a) $NO + O \rightarrow O_2 + N$ (b)	$k_{a\infty} = 2.16 \times 10^{-9} (1/T)^{0.75}$ $k_a(0, N_2) = 1.3 \times 10^{-23} (1/T)^{2.87}$ $\exp(-781/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ $F_c(N_2) = 0.95 - 10^{-4} T$ $k_a(0, CO_2) = 1.13 \times 10^{-25} (1/T)^{2.16}$ $\exp(-529/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ $F_c(CO_2) = 0.95 - 10^{-4} T$ $k_b = 3 \times 10^{-13} T \exp(-19500/T)$	3 1.3 at 300 K 3 at 2500 K 1.5 at 300 K 3 at 2500 K 1.5	618
9,4	$NO + H + M \rightarrow HNO + M$ (a) $\rightarrow N + OH$ (b)	$k_{a\infty} = 2.53 \times 10^{-9} (1/T)^{0.41}$ $k_a(0, N_2) = 2.47 \times 10^{-28} T^{-1.32}$ $\exp(-370/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ $F_c(0, N_2) = 0.82$ $k_a(0, CO_2) = 9.56 \times 10^{-29} T^{-1.17}$ $\exp(-212/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ $F_c(0, CO_2) = 0.82$	4 1.5 up to 700 K 3 at 2500 K	622

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

No.	Reactions	Rate expressions ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ unless otherwise stated)	Uncertainties	Page
9,5	$\text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M}$	$k_\infty = 3.3 \times 10^{-12} (1/T)^{0.05} \exp(363/T)$ $k(0, \text{sc}) = 2 \times 10^{-25} (1/T)^{2.13}$ $\exp(185/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $k(0, \text{N}_2) = 1.4 \times 10^{-24} (1/T)^{2.51}$ $\exp(34/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c(\text{N}_2) = 0.62$ $k(0, \text{CO}_2) = 4.7 \times 10^{-25} (1/T)^{2.3}$ $\exp(124/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c(\text{CO}_2) = 0.62$	1.4 at 300 K 3 at 2500 K  1.5 at 300 K 4 at 2500 K  2 at 300 K 10 at 2500 K	625
9,6	$\text{NO} + \text{HCHO} \rightarrow \text{HNO} + \text{HCO}$	$1.7 \times 10^{-11} \exp(-20540/T)$	10	628
9,7	$\text{NO} + \text{HCO} \rightarrow \text{HNO} + \text{CO}$	$1.2 \times 10^{-11}$	1.4	628
9,9	$\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O} + \text{O}$	$6.0 \times 10^{-12} \exp(-32900/T)$	2	629
10,0	$\text{NO}_2 + \text{M} \rightarrow \text{NO} + \text{O} + \text{M}$	$k_\infty = 7.6 \times 10^{18} T^{-1.27}$ $\exp(-36883/T) \text{ s}^{-1}$ $k(0, \text{CO}_2) = 359 T^{-2.66}$ $\exp(-37392/T)$ $F_c(\text{CO}_2) = 0.95 - 10^{-4} T$ $k(0, \text{N}_2) = 4.1 \times 10^4 T^{-3.37}$ $\exp(-37644/T)$ $F_c(\text{N}_2) = 0.95 - 10^{-4} T$	3  2  2	630
10,1	$\text{NO}_2 + \text{H}_2 \rightarrow \text{HONO} + \text{H}$	$4 \times 10^{-11} \exp(-14500/T)$	5	631
10,3	$\text{NO}_2 + \text{O} \rightarrow \text{O}_2 + \text{NO}$ (a) $\rightarrow \text{NO}_3$ (b)	$k_a = 6.5 \times 10^{-12} \exp(120/T)$ $k_{b\infty} = 2.2 \times 10^{-11}$ $k_b(0, \text{N}_2) = 4.1 \times 10^{-20} T^{-4.08}$ $\exp(-1242/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c(\text{N}_2) = 0.79 - 1.8 \times 10^{-4} T$ $k_b(0, \text{CO}_2) = 3.7 \times 10^{-20} T^{-3.94}$ $\exp(-1146/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c(\text{CO}_2) = 0.775 - 1.5 \times 10^{-4} T$	1.2 2 1.3 at 300 K 5 at 2500 K	632
10,4	$\text{NO}_2 + \text{H} \rightarrow \text{NO} + \text{OH}$	$1.4 \times 10^{-10}$	1.3	634
10,5	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$ (a) $\rightarrow \text{HO}_2 + \text{NO}$ (b)	$k_{a\infty} = 4 \times 10^{-11}$ $k_a(\text{N}_2, \text{O}) = 1.77 \times 10^{-15} (1/T)^{5.49}$ $\exp(-1183/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $k_a(\text{CO}_2, \text{O}) = 1.6 \times 10^{-15} (1/T)^{5.4}$ $\exp(-1100/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$ $F_c(\text{N}_2) = 0.725 - 2.5 \times 10^{-4} T$ $F_c(\text{CO}_2) = 0.725 - 2.5 \times 10^{-4} T$ $k_b = 3 \times 10^{-11} \exp(-3360/T)$	1.2 at 300 K  2.5 at 1200 K  1.2	635
10,6	$\text{NO}_2 + \text{HCHO} \rightarrow \text{HNO}_2 + \text{CHO}$	$1.3 \times 10^{-21} T^{2.77} \exp(-6910/T)$	2	641
10,7	$\text{NO}_2 + \text{CHO} \rightarrow \text{CO} + \text{HNO}_2$ (a) $\rightarrow \text{H} + \text{CO}_2 + \text{NO}$ (b)	$k_a = 2.1 \times (1/T)^{-3.29} \exp(-1185/T)$ $k_b = 1.4 \times 10^{-8} (1/T)^{0.75} \exp(-970/T)$	2	641
10,8	$\text{NO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}$	$1.5 \times 10^{-10} \exp(-17000/T)$	2.5	642
10,10	$\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ (a) $\rightarrow 2\text{NO} + \text{N}_2$ (b)	$k_a = 1.6 \times 10^{-14} T^{-0.73} \exp(-10530/T)$ $k_b = 2.7 \times 10^{-12} \exp(-13147/T)$	2 at 300–600 K 5 at 2500 K 1.5 at 300–1000 K 2 at 2500 K	643

## 2. Index of Reactions and Summary of Rate Expressions – Continued

No.	Reactions	Rate expressions ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ unless otherwise stated)	Uncertainties	Page
11,0	$\text{HNO} + \text{M} \rightarrow \text{H} + \text{NO} + \text{M}$	$k_\infty = 1.2 \times 10^{16} T^{-0.43}$ $\exp(-24922/T) \text{s}^{-1}$ $k(0, \text{N}_2) = 0.01 T^{-1.61}$ $\exp(-25585/T)$ $F_c = 0.83$ $k(0, \text{CO}_2) = 6.4 \times 10^{-4} T^{-1.24}$ $\exp(-25172/T)$ $F_c = 0.83$	4 1.5 up to 700 K 3 at 2500 K	643
11,3	$\text{HNO} + \text{O} \rightarrow \text{OH} + \text{NO}$	$3 \times 10^{-11}$	3	644
11,4	$\text{H} + \text{HNO} \rightarrow \text{H}_2 + \text{NO}$	$3 \times 10^{-11} \exp(-500/T)$	4	645
11,5	$\text{OH} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{NO}$ > 10 at 300 K	$8 \times 10^{-11} \exp(-500/T)$	3 at 2000 K	645
11,7	$\text{HNO} + \text{CHO} \rightarrow \text{HCHO} + \text{NO}$	$1 \times 10^{-12} \exp(-1000/T)$	5	646
11,10	$\text{HNO} + \text{NO}_2 \rightarrow \text{HNO}_2 + \text{NO}$	$1 \times 10^{-12} \exp(-1000/T)$	5	646
11,11	$\text{HNO} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{N}_2\text{O}$	$1.4 \times 10^{-15} \exp(-1561/T)$	2 at 500 K 10 at 1000 K (see text)	646
12,0	$\text{HNO}_2 + \text{M} \rightarrow \text{OH} + \text{NO} + \text{M}$	$k_\infty = 1.2 \times 10^{19} (1/T)^{1.23}$ $\exp(-25010/T) \text{s}^{-1}$ $k(0, \text{sc}) = 7.3 \times 10^5 (1/T)^{3.42}$ $\exp(-25200/T)$ $k(0, \text{N}_2) = 5 \times 10^6 (1/T)^{3.8}$ $\exp(-25340/T)$ $F_c(\text{N}_2) = 0.62$ $k(0, \text{CO}_2) = 1.7 \times 10^6 (1/T)^{3.59}$ $\exp(-25250/T)$ $F_c(\text{CO}_2) = 0.62$	1.4 at 300 K 5 at 2500 K	647
12,3	$\text{HNO}_2 + \text{O} \rightarrow \text{OH} + \text{NO}_2$	$2 \times 10^{-11} \exp(-3000/T)$	10	648
12,4	$\text{HNO}_2 + \text{H} \rightarrow \text{H}_2 + \text{NO}_2$	$2 \times 10^{-11} \exp(-3700/T)$	20	649
12,5	$\text{HNO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	$2.1 \times 10^{-14} T \exp(-68/T)$ 5 (1000–2500 K)	2 at 300 K, 1000 K	649
12,7	$\text{HNO}_2 + \text{CHO} \rightarrow \text{H}_2\text{CO} + \text{NO}_2$	$2 \times 10^{-21} T^{2.37} \exp(-1940/T)$	2 at 400–500 K 5 at 300, 1000 K	650
13,0	$\text{HCN} + \text{M} \rightarrow \text{H} + \text{CN} + \text{M}$	$k_\infty = 8.3 \times 10^{17} (1/T)^{0.93}$ $\exp(-62294/T) \text{s}^{-1}$ $k(0, \text{N}_2) = 5.93 \times 10^2 (1/T)^{0.6}$ $\exp(-62845/T)$ $F_c(\text{N}_2) = 0.95 - 10^{-4} T$ $k(0, \text{CO}_2) = 2.1 \times 10^2 (1/T)^{2.4}$ $\exp(-62800/T)$ $F_c(\text{CO}_2) = 0.875 - 0.5 \times 10^{-4} T$	1.5	651
13,3	$\text{HCN} + \text{O} \rightarrow \text{CN} + \text{OH}(\text{a})$ $\rightarrow \text{NH} + \text{CO}(\text{b})$ $\rightarrow \text{NCO} + \text{H}(\text{c})$	$k_a = 3.3 \times 10^{-16} T^{1.47} \exp(-3800/T)$ $k_b = 9.0 \times 10^{-16} T^{1.21} \exp(-3850/T)$ $k_c = 4.5 \times 10^{-15} T^{1.58} \exp(-13400/T)$	2	653
13,4	$\text{H} + \text{HCN} \rightarrow \text{H}_2 + \text{CN}(\text{a})$ $+ \text{M} \rightarrow \text{H}_2\text{CN} + \text{M}(\text{b})$	$k_a = 6.2 \times 10^{-10} \exp(-12507/T)$ $k_{b\infty} = 5.5 \times 10^{-11} \exp(-2438/T)$ $k_{b1}(0, \text{N}_2) = 4.4 \times 10^{-24} (1/T)^{0.73}$ $\exp(-3855/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ $k_{b2}(0, \text{CO}_2) = 4.3 \times 10^{-24} (1/T)^{2.63}$ $\exp(-3791/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$ $F_c = 0.95 - 10^{-4} T$ ( $\text{CO}_2, \text{N}_2$ )	100 at 500 K 3 at 2500 K 100 at 500 K 10 at 1200 K and above	654



## 2. Index of Reactions and Summary of Rate Expressions – Continued

No.	Reactions	Rate expressions ( $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ unless otherwise stated)	Uncertainties	Page
13,5	HCN+OH $\rightarrow$ H <sub>2</sub> O+CN (a) $\rightarrow$ H+HOCN (b) $\rightarrow$ H+HNCO (c)	$k_a = 3.6 \times 10^{-17} T^{1.5} \exp(-3887/T)$ $k_b = 5.3 \times 10^{-20} T^{2.45} \exp(-6100)$ $k_c = 9.3 \times 10^{-30} T^{4.71} \exp(248/T)$	1.5 at 2500 K 3 at 1000 K 5 at 2000 K	656
13,7	HCN+CHO $\rightarrow$ HCHO+CN	$4 \times 10^{-12} \exp(-17200/T)$	3	657
14,0	N <sub>2</sub> O $\rightarrow$ N <sub>2</sub> + O	$k_\infty = 1.3 \times 10^{11} \exp(-30000/T)$ $k(0, \text{N}_2) = 1.2 \times 10^{-6} T^{-0.73} \exp(-31600/T)$ $F_c(\text{N}_2) = 1.167 - 1.25 \times 10^{-4} T$ $k(0, \text{CO}_2) = 2 \times 10^{-6} T^{-0.67} \exp(-31300/T)$ $F_c(\text{CO}_2) = 1.167 - 1.25 \times 10^{-4} T$	2	657
14,3	N <sub>2</sub> O+O $\rightarrow$ O <sub>2</sub> +N <sub>2</sub> (a) $\rightarrow$ NO+NO (b)	$k_a = 1.7 \times 10^{-10} \exp(-14100/T)$ $k_b = 1.1 \times 10^{-10} \exp(-13400/T)$	2	659
14,4	N <sub>2</sub> O+H $\rightarrow$ N <sub>2</sub> +OH	$1.6 \times 10^{-10} \exp(-7600/T)$	1.7	660
14,5	N <sub>2</sub> O+OH $\rightarrow$ HO <sub>2</sub> +N <sub>2</sub>	$< 1.4 \times 10^{-11} \exp(-5000/T)$		661
14,8	N <sub>2</sub> O+CO $\rightarrow$ N <sub>2</sub> +CO <sub>2</sub>	$5.3 \times 10^{-13} \exp(-10230/T)$	2	662

## 3. Chemical Kinetic Data Tables

9,0 NO + M  $\rightarrow$  N + O + M

Reference	Conditions		Reaction rate constants	Uncertainties
	T range/K	[M] range/cm <sup>3</sup>	$k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	
Thielen and Roth (1984)	2400–6200	Shock tube study in $1-5 \times 10^{18}$ Ar 10–10000ppm NO with atomic resonance absorption detection of N and O-atoms	$1.6 \times 10^{-9} \exp(-74700/T)$	1.4
Koshi <i>et al.</i> (1979)	4000–7500	Shock tube study with 1.0–5.0% NO in $3-15 \times 10^{17}$ Ar. NO concentration via i-r emission	$8.6 \times 10^{-9} \exp(-76030/T)$	3
Myerson (1973)	2600–6300	Shock tube study with 0.1–1.0% NO in $2-20 \times 10^{17}$ Ar. atomic resonance absorption detection of O	$2.3 \times 10^{-10} \exp(-74700/T)$	2
Baulch <i>et al.</i> (1973) review	3000–5000		$3.8 \times 10^{-7} T^{-0.5} \exp(-74900/T)$	
Wray and Teare (1962)	4180–6580	0.5% NO in $1.5 \times 10^{18}$ Ar. NO concentration followed by UV absorption at 1270 Å	$6.6 \times 10^{-4} T^{-1.5} \exp(-75500/T)$	3
Recommendation			$1.6 \times 10^{-9} \exp(-74700/T)$ $2.4 \times 10^{-9} \exp(-74700/T) \{ \text{N}_2 \}$ $4.0 \times 10^{-9} \exp(-74700/T) \{ \text{CO}_2 \}$	2

## Comments

The experimental work shows considerable scatter (see Fig. 1). The recent work of Thielen and Roth, involving direct measurements of the N and O concentration with ppm levels of NO must be preferred. We therefore recommend their rate expression for reaction in argon. This is the expression quoted by Baulch and coworkers (based on an earlier review and is also in agreement with the earlier work of Wray and Teare. It is nevertheless disturbing that the results of Meyerson, which also used ARAS detection of O, should be so much lower than those of Thielen and Roth. The uncertainty is a factor of 2. For other colliders we suggest increases of factors of 1.5 and 2.5 for N<sub>2</sub> and CO<sub>2</sub> respectively. This reaction is not expected to be important except at the highest temperatures.

## References

- Baulch D. L., Drysdale, D. D. and Horne, D. G. "Evaluated Kinetic Data for High Temperature Reactions Vol. 2, Homogeneous Gas Phase Reactions of the H<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> System", Butterworths, London, 1973.
- Koshi, M., Bando, S., Saito, M., and Asaba, T., "Dissociation of Nitric Oxide in Shock Waves" 17th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 553, 1979.
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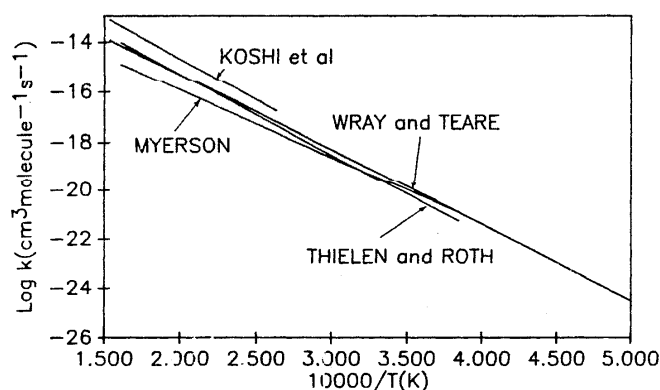


FIG. 1. Summary of experimental work on the reaction NO + Ar  
→ N + O + Ar.

9,1 NO + H<sub>2</sub> → HNO + H

Reference	Conditions T range/K	[M] range/cm <sup>3</sup>	Reaction rate constant k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty
Ando and Asaba (1976) (also review of much previous work)	2020-3250	7-230 × 10 <sup>15</sup> NO 6-180 × 10 <sup>15</sup> H <sub>2</sub> in 8-54 × 10 <sup>17</sup> Ar Shock tube experiments NO from 5.22 micron and O from NO-O (6500A) emissions. Rate constants from kinetic modeling.	5 × 10 <sup>-11</sup> exp(-27790/T)	3
Recommendation:			2.3 × 10 <sup>-11</sup> exp(-28450/T)	3

## Comments

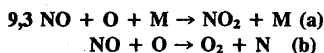
The results given by Ando and Asaba are about a factor of 7 higher than the rate expression derived from the recommendations of Baulch *et al.* for the reverse reaction and the thermodynamics of this process. However, our examination of the data for HNO + H (11,4) suggests that the measured value is lower than comparable exothermic hydrogen atom abstractions (H + HO<sub>2</sub> and H + HI). We

suggest a rate expression that is a factor of 3 smaller than that of Ando and Asaba with an uncertainty of a factor of 3. Note that the analysis of Ando and Asaba in the same system leads to rate constants for the H + NO → N + OH reaction that are a factor of 4 smaller than measurements of other workers. Since all the data were determined from computer simulations we are unsure how these differences are related.

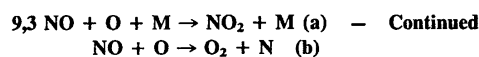
## References

Ando, H., and Asaba, T., "Rate Constants of Elementary Reactions in the High Temperature System of Nitric Oxide and Hydrogen" *Int. J. Chem. Kin.*, **8**, 259, 1976.

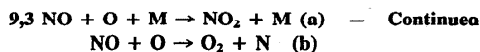
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Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Hanson and Salimian (1985) review	1500-5000		$k_b = 6.3 \times 10^{-15} T \exp(-20820/T)$	1.3
Atkinson <i>et al.</i> (1989) (review)	200-300		$k_a(\text{O}_2) = 8.6 \times 10^{-32} (T/300)^{-1.8}$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> ) $k_a(\text{N}_2) = 1.0 \times 10^{-31} (T/300)^{-1.6}$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> ) $k_{a\infty} = 3.0 \times 10^{-11} (T/300)^{0.3}$ (s <sup>-1</sup> )	1.5 1.25 1.5
Yarwood <i>et al.</i> (1988)	300-1300	Flash Photolysis-Resonance Fluorescence detection of O with 0.9-5.8 × 10 <sup>15</sup> NO in 1.6-3.5 × 10 <sup>18</sup> Ar. at 300-1000K Flash Photolysis-Shock tube with Resonance Absorption detection of O with 1.6-4.2 × 10 <sup>16</sup> NO in 4-5.2 × 10 <sup>18</sup> Ar	$k_a(\text{Ar}) = 6.7 \times 10^{-32} (T/300)^{-1.4}$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.5
Schieferstein <i>et al.</i> (1983)	200-370	2-9 × 10 <sup>16</sup> NO in 2.4-25 × 10 <sup>16</sup> He N <sub>2</sub> and CH <sub>4</sub> H <sub>2</sub> -laser photolysis of NO; O-atom by NO <sub>2</sub> chemiluminescence	$k_a(\text{He}) = 3.3 \times 10^{-29} T^{-1.1}$ $k_a(\text{NO}) = 3.3 \times 10^{-28} T^{-1.38}$ $k_a(\text{N}_2) = 3.2 \times 10^{-28} T^{-1.44}$ $k_a(\text{CH}_4) = 7.9 \times 10^{-28} T^{-1.55}$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.3 1.3 1.3 1.3
Sugawara <i>et al.</i> (1980)	298	6.5-33 × 10 <sup>18</sup> N <sub>2</sub> or He Pulse radiolysis. O atoms detected thru absorption	$k_a(\text{N}_2) = 7.7 \times 10^{-32}$ $k_a(\text{He}) = 4.2 \times 10^{-32}$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.1 1.1
Anderson and Stephens (1979)	237-397	VUV photolysis NO. O from NO <sub>2</sub> chemiluminescence	$k_a(\text{Ar}) = 1.3 \times 10^{-32} \exp(508/T)$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.2
Atkinson and Pitts (1978)	298	6-30 × 10 <sup>14</sup> NO, 0-7.5 × 10 <sup>16</sup> SO <sub>2</sub> , 7.5-16 × 10 <sup>17</sup> Ar. O from NO <sub>2</sub> VUV photolysis of NO. O from NO <sub>2</sub> chemiluminescence	$k_a(\text{N}_2) = 1.1 \times 10^{-31}$ $k_a(\text{SO}_2) = 2.6 \times 10^{-31}$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.2
Atkinson <i>et al.</i> (1977)	298-439	Trace NO in 1 × 10 <sup>18</sup> Ar VUV photolysis of NO Detection of O via NO <sub>2</sub> chemiluminescence	$k_a(\text{Ar}) = 1.46 \times 10^{-32} \exp(473/T)$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.1
Whytock <i>et al.</i> (1976)	217-500	3-230 × 10 <sup>14</sup> NO in 4-23 × 10 <sup>17</sup> N <sub>2</sub> . Flash photolysis of NO and resonance fluorescence detection of O	$k_a(\text{N}_2) = 15.5 \times 10^{-33} \exp(584/T)$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.1



Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Michael <i>et al.</i> (1976)	217–500	1–20 × 10 <sup>14</sup> NO in 2–40 × 10 <sup>18</sup> rare gas Flash photolysis of NO and resonance fluorescence detection of O	$k_a(\text{He}) = 10.8 \times 10^{-33} \exp(524/T)$ $k_a(\text{Ne}) = 9.3 \times 10^{-33} \exp(519/T)$ $k_a(\text{Ar}) = 9.1 \times 10^{-33} \exp(594/T)$ $k_a(\text{Kr}) = 9.5 \times 10^{-33} \exp(574/T)$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.1
Singleton <i>et al.</i> (1975)	298–473	5–25 × 10 <sup>16</sup> NO in 1–2 × 10 <sup>18</sup> N <sub>2</sub> O. Hg sensitized decomposition of N <sub>2</sub> O O detection via O + NO chemiluminescence rate constant by phase shift between photolysis and chemiluminescence	$k_a(\text{N}_2\text{O}) = 1.69 \times 10^{-32} \exp(619/T)$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.1
Gaetke and Troe (1975)	296–428	1.6 × 10 <sup>17</sup> NO <sub>2</sub> in 0–2.4 × 10 <sup>22</sup> N <sub>2</sub> Quantum yield for NO <sub>2</sub> disappearance under continuous photolysis	$k_{a\infty} = 3 \times 10^{-11} \text{ (s}^{-1}\text{)}$	1.2
Hippler <i>et al.</i> (1975)	295	1.5 × 10 <sup>17</sup> NO <sub>2</sub> 2.5–73 × 10 <sup>18</sup> inert gas NO; NO/NO <sub>2</sub> = 0 to 2 photolysis of NO <sub>2</sub>	$k_a(\text{He}) = 5.8 \times 10^{-32}$ $k_a(\text{Ne}) = 4.7 \times 10^{-32}$ $k_a(\text{Ar}) = 8.3 \times 10^{-32}$ $k_a(\text{CO}) = 9.1 \times 10^{-32}$ $k_a(\text{N}_2) = 7.5 \times 10^{-32}$ $k_a(\text{CO}_2) = 13.7 \times 10^{-32}$ $k_a(\text{CH}_4) = 14.5 \times 10^{-32}$ $k_a(\text{C}_2\text{H}_6) = 12.3 \times 10^{-32}$ $k_a(\text{larger hydrocarbons and fluorinated cmpds})$ 17 × 10 <sup>-32</sup> (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.2 1.2 1.2 1.2 1.2 1.2 1.2 1.2
Atkinson and Pitts (1974)	300–392	presumably same conditions as earlier work (1978)	$k_a(\text{N}_2\text{O}) = 2.65 \times 10^{-32} \exp(453/T)$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.1
Atkinson and Pitts (1974)	300	2–6 × 10 <sup>17</sup> NO in 1.6–3.0 × 10 <sup>18</sup> N <sub>2</sub> O Hg sensitized decomposition of N <sub>2</sub> O O detection via O + NO chemiluminescence rate constant by phase shift between photolysis and chemiluminescence	$k_a(\text{N}_2\text{O}) = 11.9 \times 10^{-32}$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.1
Furuyama <i>et al.</i> (1974)	298	5–15 × 10 <sup>16</sup> NO in 8–12 × 10 <sup>17</sup> N <sub>2</sub> O. Hg sensitized decomposition of N <sub>2</sub> O O detection via O + NO chemiluminescence rate constant by phase shift between photolysis and chemiluminescence	$k_a(\text{N}_2\text{O}) = 15.9 \times 10^{-32}$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.1
Gaetke <i>et al.</i> (1973)	300	0–2.4 × 10 <sup>22</sup> N <sub>2</sub> photolysis of NO <sub>2</sub>	$k_{a\infty} = 1.3 \times 10^{-11} \text{ (s}^{-1}\text{)}$	2
Baulch <i>et al.</i> (1973) (review)	200–500		$k_a = 3.0 \times 10^{-33} \exp(940/T) [\text{O}_2, \text{Ar}]$ (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.2



Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Recommendations:			$k_{a\infty} = 2.16 \times 10^{-9}(1/T)^{0.75}$	3
			$k_a(0, N_2) = 1.3 \times 10^{-23}(1/T)^{2.87}$	1.3 at 300 K
			$\exp(-781/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$	3 at 2500 K
			$F_c(N_2) = 0.95 - 10^{-4}T$	
			$k_a(0, CO_2) = 1.13 \times 10^{-25}(1/T)^{2.16}$	1.5 at 300 K
			$\exp(-529/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$	3 at 2500 K
			$F_c(CO_2) = 0.95 - 10^{-4}T$	
			$k_b = 3 \times 10^{-15}T \exp(-19500/T)$	1.5

### Comments

The extensive experimental results for channel *b* are in remarkably good agreement and we accept the recommendation of Hanson and Salimian,

$$k_b = 3 \times 10^{-15}T \exp(-19500/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor of 1.5 through the temperature range of 1000–4000 K. However, note that the A-factor is extraordinarily low for an abstraction process. It is suspected that the reaction involves a more complicated process involving addition and isomerization of the hot adduct.

There have been a large number of measurements for  $k_a$  in the third order region. Summaries of the work in argon and nitrogen are given in Figs. 1 and 2. Also included in these figures are the high temperature work for NO<sub>2</sub> decomposition as summarized by Baulch and the more recent study of Endo *et al.* (J. Phys. Chem., 1979, 83, 2083) after conversion into the reverse combination rate constants through the well established thermodynamics. The data on NO<sub>2</sub> decomposition are summarized in (10,0). The work of Endo *et al.* is especially notable for the wide variety of collisional partners. We will use their value for combination in the presence of CO<sub>2</sub> as a fixed point for our recommendations.

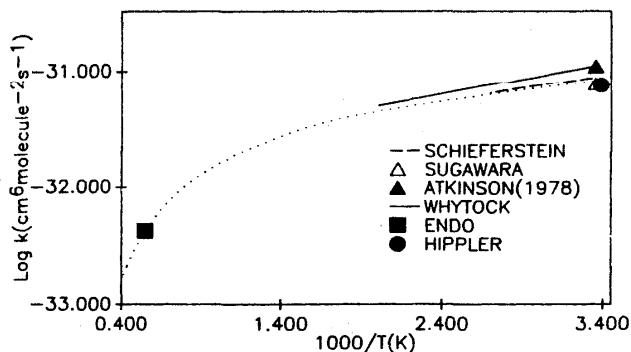


FIG. 1. Summary of experimental work on O+NO combination in N<sub>2</sub>. Dotted line represent our recommendation.

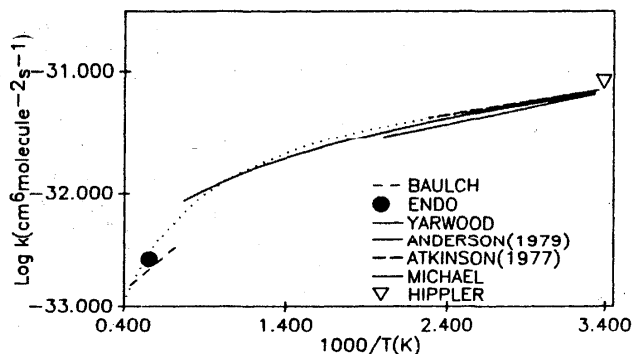


FIG. 2. Summary of experimental data on O+NO+Ar → NO<sub>2</sub>+Ar. The dotted line represent our fit to the data using the room temperature rate constants and the same temperature dependence of the step size down as for N<sub>2</sub>.

The most interesting feature of the kinetic data for the combination reaction is the high efficiencies of the collision partners. Smith (Int. J. Chem. Kin., 16, 423, 1984) has suggested that this is due to contributions from excited electronic states of NO<sub>2</sub>. Fortunately, for the present purposes there exist sufficient experimental data so that we have fitted the results purely on the basis of large step sizes. Of course if the excited electronic states have different reactivities their reactions will have to be added into the data base. The assumption implicit in this work is that electronic relaxation is fast. On this basis we recommend the following rate expressions for the combination of O and NO at limiting low pressures in the presence of N<sub>2</sub> and CO<sub>2</sub>.

$$k_a(0, N_2) = 1.3 \times 10^{-23}(1/T)^{2.87} \exp(-781/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

$$k_a(0, CO_2) = 1.13 \times 10^{-25}(1/T)^{2.16} \exp(-529/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

with an uncertainty of a factor of 1.3 near room temperature and increasing to a factor of 3 near 2500 K.

Pressure effects are not important until pressures close to 100 atm are attained. The results of Gaetke and Troe gives us a high pressure rate expression at the lower temperatures. When this is combined with the high pressure

results of Troe (Troe, J. Ber. Bunsenges. Physik. Chem., 72, 1016, 1968) on the reverse decomposition process, we arrive at the rate expression,

$$k_{a\infty} = 2.16 \times 10^{-9} (1/T)^{0.75} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an estimated uncertainty of a factor of 3. With this

as a base we have carried out RRKM calculations. The results of these calculations on a strong collision basis can be found in Tables 3 and 4.

For rate constants in the pressure dependent region we recommend the broadening factor  $F_c = 0.95 - 10^{-4}T$  for both the reactions with  $\text{CO}_2$  or  $\text{N}_2$  as the collision partner.

TABLE 3: Log ( $k/k(0)$ ) for the reaction  $\text{NO} + \text{O} + \text{NO}_2 \rightarrow \text{NO}_2 + \text{NO}_2$  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											
17.5											
18											
18.5	0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
19	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.03	-0.03	-0.03	-0.03
19.5	-0.09	-0.09	-0.09	-0.09	-0.09	-0.09	-0.08	-0.08	-0.08	-0.08	-0.08
20	-0.20	-0.20	-0.20	-0.20	-0.19	-0.19	-0.18	-0.18	-0.18	-0.18	-0.17
20.5	-0.40	-0.39	-0.39	-0.38	-0.38	0.37	0.36	-0.36	-0.35	-0.34	-0.34
21	-0.70	-0.69	-0.68	-0.67	-0.66	-0.65	-0.64	-0.63	-0.62	-0.61	-0.60
21.5	-1.10	-1.09	-1.08	-1.06	-1.04	-1.03	-1.01	-0.99	-0.98	-0.96	-0.95
22	-1.56	-1.55	-1.53	-1.51	-1.49	-1.47	-1.45	-1.43	-1.41	-1.39	-1.37

TABLE 4. Collision efficiency as a function of temperature and step size down for  $\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$  combination

Step Size ( $\text{cm}^{-1}$ )	Temp (K)				
	200	400	800	1600	3200
500	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$	$4.7 \times 10^{-1}$	$6.6 \times 10^{-1}$	$8.0 \times 10^{-1}$
700	$7.7 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.7 \times 10^{-1}$	$5.7 \times 10^{-1}$	$7.4 \times 10^{-1}$
900	$5.2 \times 10^{-2}$	$1.4 \times 10^{-1}$	$2.9 \times 10^{-1}$	$4.9 \times 10^{-1}$	$6.8 \times 10^{-1}$
1100	$3.7 \times 10^{-2}$	$1.1 \times 10^{-1}$	$2.4 \times 10^{-1}$	$4.3 \times 10^{-1}$	$6.3 \times 10^{-1}$
1300	$2.8 \times 10^{-2}$	$8.2 \times 10^{-2}$	$2.0 \times 10^{-1}$	$3.8 \times 10^{-1}$	$5.8 \times 10^{-1}$
1500	$2.2 \times 10^{-2}$	$6.6 \times 10^{-2}$	$1.7 \times 10^{-1}$	$3.4 \times 10^{-1}$	$5.4 \times 10^{-1}$
1700	$1.7 \times 10^{-2}$	$5.3 \times 10^{-2}$	$1.4 \times 10^{-1}$	$3.0 \times 10^{-1}$	$5.0 \times 10^{-1}$
1900	$1.4 \times 10^{-2}$	$4.4 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$	$4.6 \times 10^{-1}$
2100	$1.1 \times 10^{-2}$	$3.7 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.4 \times 10^{-1}$	$4.3 \times 10^{-1}$
2300	$9.3 \times 10^{-3}$	$3.1 \times 10^{-2}$	$9.0 \times 10^{-2}$	$2.1 \times 10^{-1}$	$4.0 \times 10^{-1}$
2500	$7.8 \times 10^{-3}$	$2.7 \times 10^{-2}$	$7.8 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.7 \times 10^{-1}$

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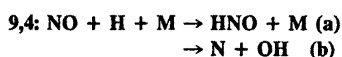
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July, 1989



Reference	Conditions		Reaction rate constant <i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty
	<i>T</i> range/K	[ <i>M</i> ] range/cm <sup>3</sup>		
Hanson and Salimian (1985) (review)	1750-4200		$k_b = 2.8 \times 10^{-10} \exp(-24560/T)$	1.5
Forte, (1981)	300-313	1.2 × 10 <sup>19</sup> - 2.9 × 10 <sup>22</sup> N <sub>2</sub> and Ar	$k_{a\infty} = 8.3 \times 10^{-10}$	4
Oka <i>et al.</i> (1977)	298-477	0.8 - 10 × 10 <sup>18</sup> total pressure of H <sub>2</sub> and N <sub>2</sub> with traces of Hg 0-0.9 mole fraction of NO, Mercury photo- sensitized decomposition of H <sub>2</sub> . Chemiluminescent detection of HNO.	$k_a(\text{H}_2) = 1.27 \times 10^{-32} \exp(364/T)$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> $k_a(\text{NO}, 298) = 5.27 \times 10^{-32}$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	1.1
Oka <i>et al.</i> (1977)	298	1.6 - 10 × 10 <sup>18</sup> H <sub>2</sub> , 3-4% NO, Hg Mercury photosensitized H <sub>2</sub> decomposition. Chemiluminescent det. of HNO	$k_a(\text{H}_2) = 4.3 \times 10^{-32}$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	1.1
Ahumada, <i>et al.</i> (1977)	298	1.8 - 20 × 10 <sup>18</sup> H <sub>2</sub> , He, Ne, Ar, Kr with H <sub>2</sub> (in rare gas) and NO. Hg photo- sensitized H <sub>2</sub> decomp. Lyman-alpha H-atom detection	$k_a(\text{H}_2) = 6.3 \times 10^{-32}$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> $k_a(\text{He}) = 4.3 \times 10^{-32}$ " $k_a(\text{Ne}) = 2.1 \times 10^{-32}$ " $k_a(\text{Ar}) = 3.9 \times 10^{-32}$ " $k_a(\text{Kr}) = 5.4 \times 10^{-32}$ "	1.1
Baulch <i>et al.</i> (1973) review	300-700		$k_a(\text{H}_2) = 1.5 \times 10^{-32} \exp(300/T)$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	1.5
Hikida, <i>et al.</i> (1971)	298	Pulse radiolysis in 4 - 60 × 10 <sup>18</sup> H <sub>2</sub> with 9 × 10 <sup>17</sup> NO. Lyman-alpha absorption for H-atom concentration	$k_a(\text{H}_2) = 3.9 \times 10^{-32}$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	

9,4: NO + H + M → HNO + M (a) — Continued  
 → N + OH (b)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Hartley and Thrush (1967)	293	Discharge flow in H <sub>2</sub> , CO <sub>2</sub> , N <sub>2</sub> O, SF <sub>6</sub> , H <sub>2</sub> O, Ar at 1.3–10 × 10 <sup>16</sup> total pressure, 10 <sup>11</sup> NO	$k_a(\text{H}_2) = 5.7 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k_a(\text{CO}_2) = 6.3 \times 10^{-32}$ “ $k_a(\text{N}_2\text{O}) = 6.8 \times 10^{-32}$ “ $k_a(\text{SF}_6) = 10.9 \times 10^{-32}$ “ $k_a(\text{H}_2\text{O}) = 18.8 \times 10^{-32}$ “ $k_a(\text{Ar}) = 3.1 \times 10^{-32}$ “ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	1.2
Clyne and Thrush (1962)	230–704	Discharge flow in H <sub>2</sub> , Ar, Ne, He at 1–10 × 10 <sup>16</sup> total pressure, trace NO	$k_a(\text{H}_2, 231) = 5.6 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k_a(\text{H}_2, 265) = 4 \times 10^{-32}$ “ $k_a(\text{H}_2, 294) = 3.9 \times 10^{-32}$ “ $k_a(\text{H}_2, 340) = 3.9 \times 10^{-32}$ “ $k_a(\text{H}_2, 433) = 3.1 \times 10^{-32}$ “ $k_a(\text{H}_2, 704) = 2.0 \times 10^{-32}$ “ $k_a(\text{Ar}, 293) = 2.3 \times 10^{-32}$ “ $k_a(\text{Ne}, 293) = 1.9 \times 10^{-32}$ “ $k_a(\text{He}, 293) = 1.7 \times 10^{-32}$ “	1.2
Recommendations:			$k_{a\infty} = 2.53 \times 10^{-9} (1/T)^{0.41}$ $k_a(0, \text{N}_2) = 2.47 \times 10^{-28} T^{-1.32}$ $\exp(-370/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c(0, \text{N}_2) = 0.82$ $k_a(0, \text{CO}_2) = 9.56 \times 10^{-29} T^{-1.17}$ $\exp(-212/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c(0, \text{CO}_2) = 0.82$ $k_b = 2.8 \times 10^{-10} \exp(-24560/T)$	4 1.5 up to 700 K 3 at 2500 K     1.5

### Comments

There are two main pathways for the reaction between H and NO. The direct association reaction (a) is reversed as the temperature is increased. The third pathway to form NH and O is about 90 kJ/mol more endothermic than channel (b) and can probably be ignored. All the results on rate constants for channel b are from shock tube work and derived on the basis of kinetic modeling. The results are in surprisingly good agreement and is probably due to the fact that partial equilibrium involving the hydrogen atoms are reached and therefore the experimental measurements are most sensitive to this reaction channel. More recently, Howard and Smith (J. Chem. Soc. 2, 77, 997, 1981) have made direct measurements on the rate constants for the reverse of (b) over the temperature range 250–515 K. The rate expression for (b) calculated through the equilibrium constant is  $k_b = 7.0 \times 10^{-11} \exp(-23300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  or roughly a factor of 3 smaller than the results of Hanson and Salimian. Considering the long temperature extrapolation, the agreement is impressive. We therefore accept the recommendation of Hanson and Salimian with an uncertainty of a factor of 2.

For the association reaction channel (a) except for hydrogen there is are no higher temperature data on collision efficiencies. There is however considerable

information on room temperature collision efficiencies. Unfortunately, there have been no studies with N<sub>2</sub> as the collisional partner and only one study using CO<sub>2</sub>. Our procedure is to accept Baulch's recommendation for H<sub>2</sub> and infer that the rate constants for N<sub>2</sub> and CO<sub>2</sub> as the collision partner are  $4.6 \times 10^{-32}$  and  $6.2 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  respectively at room temperature. For the higher temperature results we assume the temperature dependence of the step size down is that with H<sub>2</sub> as the collision partner. A plot of our fit and the data with H<sub>2</sub> as the collision partner can be found in Fig. 1. This leads to the following rate expressions.

$$k_a(0, \text{N}_2) = 2.47 \times 10^{-28} T^{-1.32} \exp(-370/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k_a(0, \text{CO}_2) = 9.56 \times 10^{-29} T^{-1.17} \exp(-212/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

with an uncertainty of a factor of 1.5 up to 700 K and increasing to a factor of 3 at 2500 K.

Under most conditions the reaction is at the termolecular limit. We therefore recommend use of the relevant expressions given above. However at the highest pressures in the range covered we begin to approach second order behavior. We have carried out RRKM calculations on the basis of the measurements of Forte at the highest



pressures. The recommended the high pressure rate expression is

$$k_{\infty} = 2.5 \times 10^{-9} (1/T)^{0.41} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 4.

The results of RRKM calculations assuming strong collisions and with HNO as the collision partner can be found in Table 1. Table 2 contains data on collision efficiencies as a function of temperature and step size down. For N<sub>2</sub> and CO<sub>2</sub> as the collision partner the rate constants in the intermediate pressure region, we suggest using F<sub>c</sub> = 0.82 with no temperature dependence.

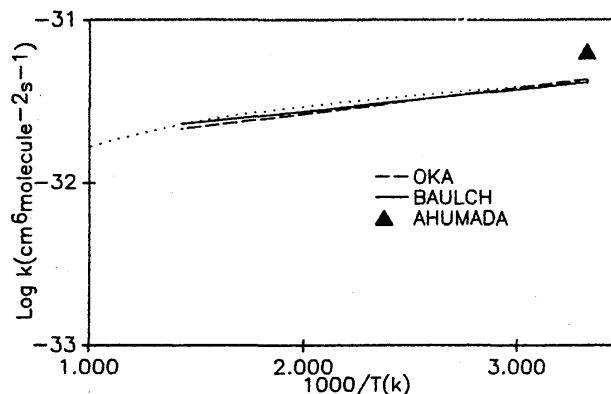


FIG 1. Experimental and fitted results (dotted line) for H<sub>2</sub> as collision-partner near 300 K.

Table 1. Log ( $k/k(0)$ ) for the reaction  $\text{NO} + \text{H} + \text{HNO} \rightarrow \text{HNO} + \text{HNO}$  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)											
18											
18.5											
19	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.00
19.5	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.01	-0.01	-0.01
20	-0.05	-0.05	-0.05	-0.05	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04
20.5	-0.13	-0.12	-0.11	-0.11	-0.10	-0.10	-0.10	-0.09	-0.09	-0.09	-0.09
21	-0.27	-0.25	-0.24	-0.23	-0.22	-0.22	-0.22	-0.21	-0.20	-0.20	-0.18
21.5	-0.51	-0.48	-0.47	-0.45	-0.43	-0.42	-0.41	-0.39	-0.38	-0.37	-0.36
22	-0.86	-0.82	-0.79	-0.77	-0.74	-0.72	-0.70	-0.68	-0.67	-0.65	-0.63

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 <sup>-1</sup> )	200	400	800	1600	3200
Temp(K)					
500	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$	$4.7 \times 10^{-1}$	$6.6 \times 10^{-1}$	$8.0 \times 10^{-1}$
700	$7.6 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.6 \times 10^{-1}$	$5.7 \times 10^{-1}$	$7.4 \times 10^{-1}$
900	$5.1 \times 10^{-2}$	$1.4 \times 10^{-1}$	$2.9 \times 10^{-1}$	$4.9 \times 10^{-1}$	$6.8 \times 10^{-1}$
1100	$3.6 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.3 \times 10^{-1}$	$4.3 \times 10^{-1}$	$6.2 \times 10^{-1}$
1300	$2.7 \times 10^{-2}$	$7.9 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.7 \times 10^{-1}$	$5.7 \times 10^{-1}$
1500	$2.0 \times 10^{-2}$	$6.2 \times 10^{-2}$	$1.6 \times 10^{-1}$	$3.3 \times 10^{-1}$	$5.3 \times 10^{-1}$
1700	$1.6 \times 10^{-2}$	$5.0 \times 10^{-2}$	$1.3 \times 10^{-1}$	$2.9 \times 10^{-1}$	$4.9 \times 10^{-1}$
1900	$1.3 \times 10^{-2}$	$4.1 \times 10^{-2}$	$1.1 \times 10^{-1}$	$2.5 \times 10^{-1}$	$4.5 \times 10^{-1}$
2100	$1.0 \times 10^{-2}$	$3.4 \times 10^{-2}$	$9.7 \times 10^{-2}$	$2.3 \times 10^{-1}$	$4.1 \times 10^{-1}$
2300	$8.5 \times 10^{-3}$	$2.8 \times 10^{-2}$	$8.3 \times 10^{-2}$	$2.0 \times 10^{-1}$	$3.8 \times 10^{-1}$
2500	$7.0 \times 10^{-3}$	$2.4 \times 10^{-2}$	$7.2 \times 10^{-2}$	$1.8 \times 10^{-1}$	$3.5 \times 10^{-1}$

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9,5:  $NO + OH + M \rightarrow HNO_2 + M$

Reference	Conditions		Reaction rate constant	Uncertainty
	$T$ range/K	[M] range/cm <sup>3</sup>	$k/cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$	
Atkinson <i>et al.</i> review(1989)	200-400		$k_0 = 7.4 \times 10^{-31} (T/300)^{-2.4} [O_2, N_2]$ $cm^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k_\infty = 1 \times 10^{-11}$	1.5 1.5
Burrows <i>et al.</i> (1983)	298	$3 - 16 \times 10^{16}$ M (He, N <sub>2</sub> , Ar. Resonance fluorescence detection of OH in discharge flow reactor	$k(\text{He}) = 6 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k(\text{N}_2) = 11 \times 10^{-31}$ " $k(\text{Ar}) = 7.4 \times 10^{-31}$ "	1.1 1.1 1.3
Anastasi and Smith (1978)	233-505	Traces of NO and HNO <sub>3</sub> or H <sub>2</sub> O in $0.35 - 17 \times 10^{18}$ N <sub>2</sub> ; also He and Kr at $0.8 \times 10^{18}$ . OH via photolysis of HNO <sub>3</sub> or H <sub>2</sub> O. Detection via resonance absorption	$k_\infty = 1.3 \times 10^{-11}$ , 233 $0.85 \times 10^{-11}$ , 298 $= 1.1 \times 10^{-11}$ , 405 $= 0.7 \times 10^{-11}$ , 505 $k(\text{He}) = 0.27 \times 10^{-12}$ , 296, 85 $\times 10^{18}$ $k(\text{Ar}) = 0.37 \times 10^{-12}$ , 296, 89 $\times 10^{18}$ $k_0(\text{N}_2) = 11.5 \times 10^{-31}$ , 233 $= 7.3 \times 10^{-31}$ , 296 $= 2.9 \times 10^{-31}$ , 405 $= 2.4 \times 10^{-31}$ , 505 $cm^6 \text{ molecule}^{-2} \text{ s}^{-1}$	1.2
Overend <i>et al.</i> (1976)	295	$8.3 - 250 \times 10^{17}$ M(He, SF <sub>6</sub> , CF <sub>4</sub> , H <sub>2</sub> O, N <sub>2</sub> ). Resonance fluorescence detection of OH. Flash photolysis generation of OH from H <sub>2</sub> O	$k_\infty = 1.83 \times 10^{-11}$ $k(\text{H}_2\text{O})/k(\text{Ar}) = 20$ $k(\text{H}_2\text{O})/k(\text{N}_2) = 8.33$ $k(\text{H}_2\text{O})/k(\text{SF}_6) = 2.7$ $k(\text{H}_2\text{O})/k(\text{CF}_4) = 2.44$ $k(\text{H}_2\text{O})/k(\text{He}) = 50$	1.1
Sie <i>et al.</i> (1976)	298	N <sub>2</sub> O, CO, NO in $3.1 - 24.7 \times 10^{18}$ H <sub>2</sub> . Photolysis at 2139nm. Final product analysis by gc	$k_\infty = 1.2 \times 10^{-11}$	1.2
Gordon and Mulac (1975)	435	$8 - 80 \times 10^{15}$ NO in $2.2? - 169 \times 10^{17}$ H <sub>2</sub> O	$7.5 \times 10^{-12}$	1.1
Harris and Wayne (1975)	300	Trace NO in $3 - 6 \times 10^{16}$ Ar Resonance fluorescence detection of OH, from $H + NO_2 \rightarrow OH + NO$	$k(\text{Ar}) = 7 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k(\text{N}_2) = 15 \times 10^{-31}$	1.4
Howard and Evenson (1975)	298	Trace NO in $2 - 14 \times 10^{16}$ M (Ar, He, N <sub>2</sub> ). Laser magnetic resonance detection of OH under discharge flow conditions	$k(\text{Ar}) = 4.4 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $k(\text{N}_2) = 7.8 \times 10^{-31}$ " $k(\text{He}) = 4.0 \times 10^{-31}$ "	1.2
Cox (1975)	300	$2.5 \times 10^{18}$ with 2 to 1 N <sub>2</sub> /O <sub>2</sub> and traces of HONO and NO <sub>x</sub> . Photolysis with stable product analysis	$k(\text{N}_2/\text{O}_2, 2) = 6.1 \times 10^{-12}$ , $2.5 \times 10^{18}$	1.3

9,5: NO + OH + M → HNO<sub>2</sub> + M - Continued

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Atkinson <i>et al.</i> (1975)	298	1–100 × 10 <sup>13</sup> NO in 8–200 × 10 <sup>17</sup> M (Ar, N <sub>2</sub> ). photolysis, resonance fluorescence detection of OH	k(Ar) = 3.3 × 10 <sup>-13</sup> , 8.1 × 10 <sup>17</sup> Flash = 7.2 × 10 <sup>-13</sup> ; 1.6 × 10 <sup>18</sup> = 1.04 × 10 <sup>-12</sup> ; 3.2 × 10 <sup>18</sup> = 2.07 × 10 <sup>-12</sup> ; 6.4 × 10 <sup>18</sup> = 3.2 × 10 <sup>-12</sup> ; 12.9 × 10 <sup>18</sup> = 4.8 × 10 <sup>-12</sup> ; 4.6 × 10 <sup>18</sup> k(N <sub>2</sub> ) = 4.94 × 10 <sup>-13</sup> ; 8.1 × 10 <sup>17</sup>	1.2
Anderson <i>et al.</i> (1974)	298	3.3–33 × 10 <sup>16</sup> in He, Ar, N <sub>2</sub> Discharge flow with resonance fluorescence detection of OH	k <sub>a</sub> (He) = 3.3 × 10 <sup>-31</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> k <sub>a</sub> (Ar) = 3.4 × 10 <sup>-31</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> k <sub>a</sub> (N <sub>2</sub> ) = 5.8 × 10 <sup>-31</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	
Morley and Smith (1972)	300	NO, NO <sub>2</sub> , H <sub>2</sub> and He 1 × 10 <sup>18</sup> . Photolysis of NO <sub>2</sub> to make O( <sup>1</sup> D) and reaction with H <sub>2</sub> for OH. OH concentration by resonance absorption	k(He) = 4.1 × 10 <sup>-31</sup> , 1 × 10 <sup>18</sup> k(H <sub>2</sub> ) = 2.3 × k(He), 1 × 10 <sup>18</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	1.2
Stuhl and Niki (1972)	298	3 × 10 <sup>14</sup> NO in 1.6–27 × 10 <sup>17</sup> He. Resonance fluorescence detection of OH	k <sub>a</sub> = 2 × 10 <sup>-13</sup> k(He) = 1 × 10 <sup>-13</sup> ; 1.6 × 10 <sup>17</sup> = 1.6 × 10 <sup>-13</sup> ; 3.2 × 10 <sup>17</sup>	1.5
Westenberg and deHaas (1972)	273–395	1.2–17.7 × 10 <sup>16</sup> He. ESR detection of OH from H + NO <sub>2</sub> OH + NO	k(He) = 1.3 × 10 <sup>-30</sup> , 273 = 0.8 × 10 <sup>-30</sup> , 298 = 3.1 × 10 <sup>-31</sup> , 395 cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	1.3
Recommendations			k <sub>a</sub> = 3.3 × 10 <sup>-12</sup> (1/T) <sup>0.05</sup> exp(363/T) k(0,sc) = 2 × 10 <sup>-25</sup> (1/T) <sup>2.13</sup> exp(185/T) cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> k(0,N <sub>2</sub> ) = 1.4 × 10 <sup>-24</sup> (1/T) <sup>2.51</sup> exp(34/T) cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> F <sub>c</sub> (N <sub>2</sub> ) = 0.62 k(0,CO <sub>2</sub> ) = 4.7 × 10 <sup>-25</sup> (1/T) <sup>2.3</sup> exp(124/T) cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> F <sub>c</sub> (CO <sub>2</sub> ) = 0.62	1.4 at 300 K 3 at 2500 K 1.5 at 300 K 4 at 2500 K 2 at 300 K 10 at 2500 K

## Comments

Atkinson and coworkers have summarized previous work near room temperature. We have used this as a base and from transition state and RRKM calculations extended the temperature and pressure ranges. The high pressure rate expression over all temperatures is

$$k_{\infty} = 3.3 \times 10^{-12} (1/T)^{0.05} \exp(363/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 1.4 near room temperature and increasing to a factor of 3 at 2500 K. There are no data on the collision efficiencies at high temperatures. The collision efficiencies and the corresponding step sizes down have been determined on the basis of the results for N<sub>2</sub> and Ar, (see Fig. 1) and extended to that for CO<sub>2</sub> using the temperature dependence from the NO<sub>2</sub>

system (9,4). They lead to the following limiting low pressure rate expressions.

$$k(0, \text{N}_2) = 1.4 \times 10^{-24} (1/T)^{2.51} \exp(34/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k(0, \text{CO}_2) = 4.7 \times 10^{-25} (1/T)^{2.3} \exp(124/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

with an estimated uncertainty of a factor of 1.5 at 300 K and extending to a factor of 4 at 2500 K for N<sub>2</sub> and a factor of 2 at 300 K and an order of magnitude for CO<sub>2</sub> at 2500 K. Note that in all these cases the collision efficiencies are large and in the case of CO<sub>2</sub> are very close to the strong collider limit. The results of RRKM calculations on the basis of the strong collider assumption can be found in Table 1. Collision efficiencies as a function of temperature and step sizes down are summarized in Table 2.

In the case of  $N_2$  and  $CO_2$ , the  $F_c$  values which can be used to determine fall-off value analytically are for both

cases 0.62. Figure 1 is a plot of the experimental result with  $N_2$  as the collision partner.

TABLE I. Log ( $k/k_\infty$ ) for the reaction  $NO + OH + HONO \rightarrow HONO + HONO$  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	-2.32	-2.58	-2.78	-2.94	-3.08	-3.21	-3.32	-3.43	-3.52	-3.60	-3.68
17.5	-1.86	-2.10	-2.30	-2.46	-2.60	-2.72	-2.83	-2.93	-3.03	-3.11	-3.19
18	-1.42	-1.65	-1.83	-1.99	-2.12	-2.24	-2.35	-2.45	-2.54	-2.62	-2.70
18.5	-1.02	-1.23	-1.40	-1.54	-1.67	-1.78	-1.88	-1.98	-2.07	-2.15	-2.22
19	-0.67	-0.85	-0.99	-1.12	-1.24	-1.34	-1.44	-1.53	-1.61	-1.69	-1.76
19.5	-0.39	-0.53	-0.65	-0.75	-0.85	-0.94	-1.03	-1.11	-1.18	-1.25	-1.32
20	-0.20	-0.29	-0.37	-0.45	-0.53	-0.60	-0.67	-0.74	-0.80	-0.86	-0.92
20.5	-0.09	-0.13	-0.18	-0.24	-0.29	-0.34	-0.39	-0.44	-0.49	-0.54	-0.58
21	-0.03	-0.05	-0.08	-0.11	-0.14	-0.17	-0.20	-0.23	-0.26	-0.29	-0.32
21.5	-0.01	-0.02	-0.03	-0.04	-0.05	-0.07	-0.08	-0.10	-0.12	-0.13	-0.15
22	-0.01	-0.01	-0.01	-0.02	-0.02	-0.03	-0.04	-0.04	-0.05	-0.06	

TABLE 2. Collision efficiency as a function of temperature and step size down for  $OH + NO + M \rightarrow HNO_2 + M$

Step Size ( $cm^{-1}$ )	200	400	800	1600	3200
Temp(K)					
500	$1.1 \times 10^{-1}$	$2.5 \times 10^{-1}$	$4.5 \times 10^{-1}$	$6.4 \times 10^{-1}$	$7.9 \times 10^{-1}$
700	$6.7 \times 10^{-2}$	$1.7 \times 10^{-1}$	$3.4 \times 10^{-1}$	$5.4 \times 10^{-1}$	$7.2 \times 10^{-1}$
900	$4.3 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.6 \times 10^{-1}$	$4.6 \times 10^{-1}$	$6.5 \times 10^{-1}$
1100	$3.0 \times 10^{-2}$	$8.6 \times 10^{-2}$	$2.1 \times 10^{-1}$	$3.9 \times 10^{-1}$	$5.9 \times 10^{-1}$
1300	$2.1 \times 10^{-2}$	$6.4 \times 10^{-2}$	$1.6 \times 10^{-1}$	$3.3 \times 10^{-1}$	$5.3 \times 10^{-1}$
1500	$1.5 \times 10^{-2}$	$4.8 \times 10^{-2}$	$1.3 \times 10^{-1}$	$2.8 \times 10^{-1}$	$4.8 \times 10^{-1}$
1700	$1.1 \times 10^{-2}$	$3.7 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.4 \times 10^{-1}$	$4.3 \times 10^{-1}$
1900	$8.5 \times 10^{-3}$	$2.8 \times 10^{-2}$	$8.3 \times 10^{-2}$	$2.0 \times 10^{-1}$	$3.8 \times 10^{-1}$
2100	$6.5 \times 10^{-3}$	$2.2 \times 10^{-2}$	$6.7 \times 10^{-2}$	$1.7 \times 10^{-1}$	$3.4 \times 10^{-1}$
2300	$5.0 \times 10^{-3}$	$1.8 \times 10^{-2}$	$5.5 \times 10^{-2}$	$1.4 \times 10^{-1}$	$3.0 \times 10^{-1}$
2500	$4.0 \times 10^{-3}$	$1.4 \times 10^{-2}$	$4.5 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$

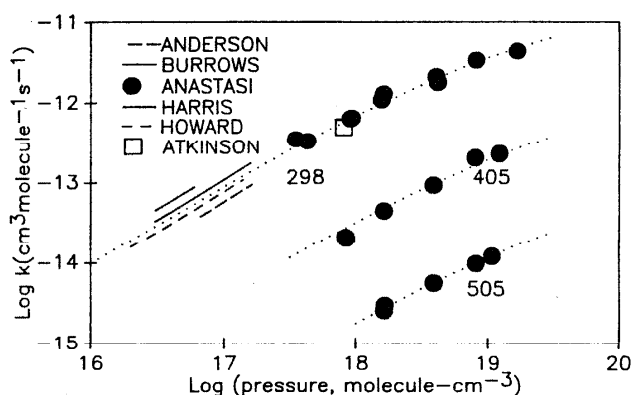


FIG. 1. Experimental data on the reaction of  $OH + NO + N_2 \rightarrow HNO_2 + N_2$ . This data was used to obtain the temperature dependences used in this evaluation. The dotted lines represent our best fit to the data. The 405 K and 505 K have been displaced by 1 and 2 log rate constants units to increase legibility.

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### 9,6: NO + HCHO → HNO + HCO

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Log K <sub>p</sub> = 0.8952 - 8.392 × 10 <sup>3</sup> /T - 9.033 × 10 <sup>4</sup> /T <sup>2</sup> + 1.710 × 10 <sup>7</sup> /T <sup>3</sup>				
Recommendations	1.7 × 10 <sup>-11</sup> exp(-20540/T)		10	

#### Comments

There are no experimental results on the rate constant for this reaction. Our recommendation is based on the estimated rate expression for the very exothermic reverse process or k(HNO + HCO → NO + H<sub>2</sub>CO) = 1 × 10<sup>-12</sup>exp(-1000/T) cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup>. Then through the equilibrium constant we find,

$$k(\text{NO} + \text{HCHO} \rightarrow \text{HNO} + \text{HCO}) = 1.7 \times 10^{-11} \exp(-20540/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 10.

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May, 1989

### 9,7: NO + HCO → HNO + CO

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Langford and Moore (1984)	295	0.17 - 1 × 10 <sup>16</sup> NO, 1 - 1.3 × 10 <sup>17</sup> H <sub>2</sub> CO or (HCO) <sub>2</sub> in 0 - 3 × 10 <sup>19</sup> N <sub>2</sub> . Laser photolysis of H <sub>2</sub> CO or (HCO) <sub>2</sub> and resonance absorption detection of HCO	1.26 × 10 <sup>-11</sup>	1.15
Veyret and Lesclaux (1981)	298-503	1 - 1.3 × 10 <sup>15</sup> NO, 1.2 × 10 <sup>18</sup> H <sub>2</sub> CO or CH <sub>3</sub> CHO in 0.13 - 1.3 × 10 <sup>19</sup> N <sub>2</sub> . Flash photolysis absorption detection of HCO	1.2 × 10 <sup>-10</sup> T <sup>-0.4</sup>	1.2
Reilly <i>et al.</i> (1978)	298?	3 - 10 × 10 <sup>15</sup> NO in 3 × 10 <sup>17</sup> H <sub>2</sub> CO. Flash photolysis of formaldehyde; HCO detection by intracavity dye laser spectroscopy.	1.4 × 10 <sup>-11</sup>	1.15
Shibuya <i>et al.</i> (1977)	298	1.2 × 10 <sup>15</sup> NO, 6.5 × 10 <sup>17</sup> CH <sub>3</sub> CHO in 1.6 × 10 <sup>19</sup> He; HCO detected via absorption at 613.8 nm from flash photolysis of acetaldehyde	8.7 × 10 <sup>-12</sup>	1.12
Recommendations			1.2 × 10 <sup>-11</sup>	1.4

## Comments

The recent measurements at room temperature are in good agreement. The mechanism as shown by Langford and Moore involves addition followed by the decomposition of the adduct. It is possible that at lower temperatures and high pressures the adduct may have lifetimes sufficient to undergo further reaction. One such reaction is from the process  $\text{NO} + \text{HCO} \rightarrow \text{HCONO} \rightarrow \text{NCO} + \text{OH}$ . It is thermodynamically less favorable and is probably a minor channel.

## References

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9,9 NO+NO → N<sub>2</sub>O + O

Reference	Conditions		Reaction rate constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty
	$T$ range/K	[M] range/cm <sup>3</sup>		
Koshi and Asaba (1979)	2700–3500	2–20% NO in 2.4–4.2 $4.2 \times 10^{18}$ Ar. Shock tube experiments with detection of NO by uv absorption and ir emission and O atom via chemiluminescence of O + NO reaction.	$8.1 \times 10^{-12} \exp(-33800/T)$	2
McCullough <i>et al.</i> (1977)	1750–2100	0.01–5% NO and 1%NO–1%H <sub>2</sub> in $4 \times 10^{18}$ Ar. Ceramic flow reactor. NO detection as end product via chemiluminescence.	$3 \times 10^{-12} \exp(-32110/T)$	2
Baulch <i>et al.</i> (1971)	1200–2000		$2.2 \times 10^{-12} \exp(-32100/T)$	2
Recommendations			$6.0 \times 10^{-12} \exp(-32900/T)$	2

## Comments

The work of McCullough *et al.* and Koshi and Asaba confirms the recommendations of Baulch *et al.* It is particularly notable that the new measurements bring into line older shock tube and flow tube determinations which were a factor of 10 too high. For the former, the deviations have been identified as due to neglect of boundary layer effects. Our recommendation is essentially the best line through the three sets of results.

## References

- Baulch D. L., Drysdale, D. D. and Horne, D. G. "Evaluated Kinetic Data for High Temperature Reactions Vol. 2, Homogeneous Gas Phase Reactions of the H<sub>2</sub>–N<sub>2</sub>–O<sub>2</sub> System", Butterworths, London, 1973.  
 Koshi, M. and Asaba, T. "Shock-Tube Study of Thermal Decomposition of Nitric Oxide between 2700–3500 K", *Int. J. Chem. Kin.*, **11**, 305, 1979.  
 McCullough, R. W., Kruger, C. H., and Hanson, R. K., "A Flow Reactor Study of Thermal Decomposition Rates of Nitric Oxide", *Combustion Science and Technology*, **15**, 213, 1977.

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 June, 1989

10,0: NO<sub>2</sub>+M→NO+O+M

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Endo <i>et al.</i> (1979)	1600–2200	4–30 × 10 <sup>18</sup> CO <sub>2</sub>	8.3 × 10 <sup>-16</sup> (1800)	2 (abs)
		Ne	3.3 × 10 <sup>-16</sup> "	1.2 (relativ
		Ar	2.5 × 10 <sup>-16</sup> "	to each
		Kr	2.5 × 10 <sup>-16</sup> "	other)
		Xe	2.8 × 10 <sup>-16</sup> "	
		N <sub>2</sub>	4.1 × 10 <sup>-16</sup> "	
		He	8.7 × 10 <sup>-16</sup> "	
		CF <sub>4</sub>	8.3 × 10 <sup>-16</sup> "	
		Reaction followed by UV absorption of NO <sub>2</sub>		
Baulch <i>et al.</i> (1974) (review)	1400–2400		1.8 × 10 <sup>-8</sup> exp(-33000/T)	1.25
Troe (1968)	1450–2000	1.8 × 180 × 10 <sup>19</sup> Ar 0.05–0.20% NO <sub>2</sub> Shock tube Reaction followed by UV absorption of NO <sub>2</sub>	2 × 10 <sup>14</sup> exp(-36180/T)s <sup>-1</sup>	3
Recommendations:			$k_{\infty} = 7.6 \times 10^{18} T^{-1.27} \exp(-36883/T) s^{-1}$	3
			$k(0, CO_2) = 359 T^{-2.66} \exp(-37392/T)$	2
			$F_c(CO_2) = 0.95 - 10^{-4} T$	
			$k(0, N_2) = 4.1 \times 10^4 T^{-3.37} \exp(-37644/T)$	2
			$F_c(N_2) = 0.95 - 10^{-4} T$	

## Comments

The existing experimental results in argon are in good agreement. The work of Endo *et al.* is no table in that it covers a wide range of third bodies. Except for the work of Troe, all the data pertain to reaction at the second order limit. Our recommendations,

$$k(0, CO_2) = 359 T^{-2.66} \exp(-37392/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(0, N_2) = 4.1 \times 10^4 T^{-3.37} \exp(-37644/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 2 are based on the rate expressions for the reverse combination reaction (9,3) and is within a factor of two of the direct measurements. Note that in order to fit the experimental data we have used very large and unrealistic step sizes (3000–4000 cm<sup>-1</sup>). Smith (Int. J. Chem. Kin., 16, 423, 1984) has suggested that this is due to contributions from excited electronic states of NO<sub>2</sub>.

The recommended rate expression at the high pressure limit is based on the work of Troe for the decomposition

process at high temperatures and the recommended numbers for the reverse reaction at low temperatures. This leads to the expression;

$$k_{\infty} = 7.6 \times 10^{18} T^{-1.27} \exp(-36883/T) s^{-1}$$

with an uncertainty of a factor of 2. With this as a basis we have carried out RRKM calculations to determine pressure effects. These are summarized in Tables 1 and 2.

For N<sub>2</sub> and CO<sub>2</sub> as third bodies we recommend the use of the following quantities in conjunction with the limiting high and low pressure values to obtain rate expressions over all temperature and pressures:

$$F_c(N_2) = 0.95 - 10^{-4} T$$

$$F_c(CO_2) = 0.95 - 10^{-4} T$$

Note that the high collision efficiencies means that to a good approximation one can use the strong collision assumption for many third bodies.

TABLE 1. Log ( $k/k(0)$ ) for the reaction  $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{O} + \text{NO}_2$  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											
17.5											
18											
18.5	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
19	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.03	-0.03	-0.03	-0.03
19.5	-0.09	-0.09	-0.09	-0.09	-0.09	-0.09	-0.08	-0.08	-0.08	-0.08	-0.08
20	-0.20	-0.20	-0.20	-0.20	-0.19	-0.19	-0.18	-0.18	-0.18	-0.18	-0.17
20.5	-0.40	-0.39	-0.39	-0.38	-0.38	-0.37	-0.36	-0.36	-0.35	-0.34	-0.34
21	-0.70	-0.69	-0.68	-0.67	-0.66	-0.65	-0.64	-0.63	-0.62	-0.61	-0.60
21.5	-1.10	-1.09	-1.08	-1.06	-1.04	-1.03	-1.01	-0.99	-0.98	-0.96	-0.95
22	-1.56	-1.55	-1.53	-1.51	-1.49	-1.47	-1.45	-1.43	-1.41	-1.39	-1.37

TABLE 2. Collision efficiency as a function of temperature and step size down for  $\text{NO}_2$  decomposition

Step Size ( $\text{cm}^{-1}$ )	200	400	800	1600	3200
Temp(K)					
500	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$	$4.7 \times 10^{-1}$	$6.6 \times 10^{-1}$	$8.0 \times 10^{-1}$
700	$7.7 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.7 \times 10^{-1}$	$5.7 \times 10^{-1}$	$7.4 \times 10^{-1}$
900	$5.2 \times 10^{-2}$	$1.4 \times 10^{-1}$	$2.9 \times 10^{-1}$	$4.9 \times 10^{-1}$	$6.8 \times 10^{-1}$
1100	$3.7 \times 10^{-2}$	$1.1 \times 10^{-1}$	$2.4 \times 10^{-1}$	$4.3 \times 10^{-1}$	$6.3 \times 10^{-1}$
1300	$2.8 \times 10^{-2}$	$8.2 \times 10^{-2}$	$2.0 \times 10^{-1}$	$3.8 \times 10^{-1}$	$5.8 \times 10^{-1}$
1500	$2.2 \times 10^{-2}$	$6.6 \times 10^{-2}$	$1.7 \times 10^{-1}$	$3.4 \times 10^{-1}$	$5.4 \times 10^{-1}$
1700	$1.7 \times 10^{-2}$	$5.3 \times 10^{-2}$	$1.4 \times 10^{-1}$	$3.0 \times 10^{-1}$	$5.0 \times 10^{-1}$
1900	$1.4 \times 10^{-2}$	$4.4 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$	$4.6 \times 10^{-1}$
2100	$1.1 \times 10^{-2}$	$3.7 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.4 \times 10^{-1}$	$4.3 \times 10^{-1}$
2300	$9.3 \times 10^{-3}$	$3.1 \times 10^{-2}$	$9.0 \times 10^{-2}$	$2.1 \times 10^{-1}$	$4.0 \times 10^{-1}$
2500	$7.8 \times 10^{-3}$	$2.7 \times 10^{-2}$	$7.8 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.7 \times 10^{-1}$

## References

Baulch D. L., Drysdale, D. D. and Horne, D. G. "Evaluated Kinetic Data for High Temperature Reactions Vol. 2, Homogeneous Gas Phase Reactions of the  $\text{H}_2\text{--N}_2\text{--O}_2$  System", Butterworths, London, 1973.

Endo, H., Glanzer, K., and Troe, J. "Shock Wave Study of Collisional Energy Transfer in the Dissociation of  $\text{NO}_2$ ,  $\text{ClNO}_2$ ,  $\text{O}_3$  and  $\text{N}_2\text{O}$ " J. Phys. Chem., **83**, 2083, 1979.

Troe, J. "Untersuchung der Dissoziation von  $\text{NO}_2$  bei hohen Drucken" Ber. Bunsenges. physik. Chem., **73**, 144, 1969.

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April, 1989

10,1:  $\text{NO}_2 + \text{H}_2 \rightarrow \text{HONO} + \text{H}$ 

Reference	Conditions		Reaction rate constant $k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Uncertainty
	T range/K	[M] range/ $\text{cm}^3$		
Log $K_p = 0.27429 - 6.3669 \times 10^3/T + 3.639 \times 10^5/T^2 - 5.1823/T^3$				
Slack and Grillo(1978)	760-1000	3.56% $\text{NO}_2$ , 29.6% $\text{H}_2$ in 1 to 4 atm air induction time measurements in shock tube from $\text{NO}_2$ disappearance	$4 \times 10^{-11} \exp(-14500/T)$	2.5
Recommendation:			$4 \times 10^{-11} \exp(-14500/T)$	5



## Comments

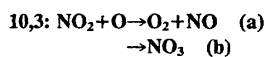
The results of Slack and Grillo are derived from an analysis of the complex kinetics of  $\text{H}_2\text{—O}_2\text{—NO}_2$  ignition. We have calculated the rate constant for this process using one-half the rate expression for  $\text{H} + \text{H}_2\text{O}_2$  (Tsang, J. Phys. Chem. Ref. Data, 15, 1087, 1986) and the thermodynamics of the process. This leads to the rate expression  $4 \times 10^{-11} \exp(-17200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The greater endothermicity of the  $\text{H} + \text{H}_2\text{O}_2$  reaction makes this a

lower limit. We therefore accept the recommendation Slack and Grillo with an uncertainty of a factor of 5.

## References

Slack, M. W. and Grillo, A. R. "Rate Coefficients of  $\text{H}_2 + \text{NO}_2 \rightarrow \text{HNO}_2 + \text{H}$  Derived from Shock Tube Investigations  $\text{H}_2\text{—O}_2\text{—NO}_2$  Ignition" Combustion and Flame 31, 275, 1978.

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Reference	Conditions		Reaction rate constant	Uncertainty
	<i>T</i> range/K	[M] range/cm <sup>3</sup>	<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Atkinson <i>et al.</i> (1989) review	230–350 200–400		$k_a = 6.5 \times 10^{-12} \exp(120/T)$ $k_b(0, \text{O}_2, \text{N}_2) = 9 \times 10^{-32} (T/300)^{-2}$ $k_{b\infty} = 2.2 \times 10^{-11}$	1.2
Hippler <i>et al.</i> (1975)	300	$1.5 \times 10^{17} \text{ NO}_2$ $2.5 - 73 \times 10^{18} \text{ inert gas}$ $\text{NO}; \text{NO}/\text{NO}_2 = 0 \text{ to } 2$ photolysis of $\text{NO}_2$	He, $9.6 \times 10^{-32}$ Ne, $8 \times 10^{-32}$ Ar, $9.6 \times 10^{-32}$ CO, $16.3 \times 10^{-32}$ N <sub>2</sub> , $8 \times 10^{-32}$ CO <sub>2</sub> , $23.4 \times 10^{-32}$ CH <sub>4</sub> , $29.2 \times 10^{-32}$ C <sub>2</sub> H <sub>6</sub> , $30.4 \times 10^{-32}$ larger hydrocarbons and fluorinated cmpds $30 - 70 \times 10^{-32}$ $k_{b\infty} = 2.2 \times 10^{-11}$	1.2
Gaedtke and Troe (1973)	300	$0 - 2.4 \times 10^{22} \text{ N}_2$ photolysis of $\text{NO}_2$	$k_{b\infty} = 2.2 \times 10^{-11}$	1.2
Baulch <i>et al.</i> (1973)			$k_a = 1.7 \times 10^{-11} \exp(-300/T)$ $k_{b\infty} = 1.8 \times 10^{-11}$ $k_b(0) = 6.3 \times 10^{-32} (\text{N}_2)$	1.25
Recommendations:			$k_a = 6.5 \times 10^{-12} \exp(120/T)$ $k_{b\infty} = 2.2 \times 10^{-11}$ $k_b(0, \text{N}_2) = 4.1 \times 10^{-20} T^{-4.08}$ $\exp(-1242/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c(\text{N}_2) = 0.79 - 1.8 \times 10^{-4} T$ $k_b(0, \text{CO}_2) = 3.7 \times 10^{-20} T^{-3.94}$ $\exp(-1146/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $F_c(\text{CO}_2) = 0.775 - 1.5 \times 10^{-4} T$	1.2 2 1.3 at 300 K 5 at 2500 K

## Comments

All the data are in the lower temperature range. The rate constants for channel (a) are so large that the temperature dependence must be very low. We therefore endorse the recommendation of the latest CODATA panel (Atkinson *et al.*, 1989) or

$$k_a = 6.5 \times 10^{-12} \exp(120/T).$$

For the addition channel (b) we use the high pressure rate expression recommended by Atkinson *et al.* or

$$k_{b\infty} = 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 2. The third order rate expression is calculated using the recommended room temperature number and assuming a linear dependence on temperature for the step size down or  $80(T/300) \text{ cm}^{-1}$ . This leads to the rate expression

$$k_b(0, \text{N}_2) = 4.1 \times 10^{-20} T^{-4.08} \exp(-1242/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

For  $\text{CO}_2$  as the third body we use the data of Hippler *et al.* giving  $k(0, \text{CO}_2)/k(0, \text{N}_2) = 3$ . This leads to a step size

down at room temperature of about  $250 \text{ cm}^{-1}$ . Assuming a temperature dependence similar to that for  $\text{N}_2$  we obtain the following rate expression

$$k_b(0, \text{CO}_2) = 3.7 \times 10^{-20} T^{-3.94} \exp(-1146/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$$

The uncertainties are a factor 1.3 near room temperature and increasing to a factor of 5 at 2500 K. The large latter value is due to our uncertainty in defining energy exchange effects at high temperatures. The step size down commensurate with the room temperature results are similar to that which we have found for hydrocarbons and we have assumed a similar correspondence at the

higher temperatures.

Pressure effects begin to become important in the 5 to 50 atmospheres region. The results of RRKM calculations on a strong collision basis can be found in Table 1. The collision efficiency for various assumed step sizes down can be found in Table 2.

In the context on Troe's formalism, we suggest the use of the following values to define the pressure dependence of channel b for  $\text{N}_2$  and  $\text{CO}_2$

$$F_c(\text{N}_2) = 0.79 - 1.8 \times 10^{-4} T$$

$$F_c(\text{CO}_2) = 0.775 - 1.5 \times 10^{-4} T.$$

TABLE 1: Log ( $k/k_\infty$ ) for the reaction  $\text{NO}_3 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{O} + \text{NO}_3$  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	-2.58	-2.87	-3.12	-3.34	-3.53	-3.70	-3.86	-4.00	-4.12	-4.24	-4.35
17.5	-2.10	-2.38	-2.63	-2.85	-3.04	-3.21	-3.36	-3.50	-3.63	-3.74	-3.85
18	-1.63	-1.91	-2.15	-2.37	-2.55	-2.72	-2.87	-3.01	-3.14	-3.25	-3.36
18.5	-1.20	-1.47	-1.70	-1.90	-2.08	-2.25	-2.40	-2.53	-2.66	-2.77	-2.87
19	-0.83	-1.06	-1.28	-1.47	-1.64	-1.80	-1.94	-2.07	-2.19	-2.30	-2.40
19.5	-0.52	-0.72	-0.91	-1.08	-1.24	-1.38	-1.51	-1.64	-1.75	-1.85	-1.95
20	-0.29	-0.44	-0.60	-0.74	-0.88	-1.01	-1.13	-1.24	-1.34	-1.43	-1.52
20.5	-0.14	-0.25	-0.36	-0.47	-0.58	-0.69	-0.79	-0.88	-0.97	-1.05	-1.13
21	-0.06	-0.12	-0.19	-0.27	-0.35	-0.43	-0.50	-0.58	-0.65	-0.71	-0.78
21.5	-0.02	-0.05	-0.09	-0.13	-0.18	-0.24	-0.29	-0.34	-0.39	-0.44	-0.49
22	-0.01	-0.02	-0.04	-0.06	-0.08	-0.11	-0.14	-0.17	-0.20	-0.24	-0.27

TABLE 2. Collision efficiency as a function of temperature and step size down for the reaction  $\text{NO}_2 + \text{O} + \text{M} \rightarrow \text{M} + \text{NO}_3$

Step Size ( $\text{cm}^{-1}$ )	200	400	800	1600	3200
Temp(K)					
500	$1.1 \times 10^{-1}$	$2.5 \times 10^{-1}$	$4.5 \times 10^{-1}$	$6.4 \times 10^{-1}$	$7.9 \times 10^{-1}$
700	$6.7 \times 10^{-2}$	$1.7 \times 10^{-1}$	$3.4 \times 10^{-1}$	$5.4 \times 10^{-1}$	$7.2 \times 10^{-1}$
900	$4.3 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.6 \times 10^{-1}$	$4.6 \times 10^{-1}$	$6.5 \times 10^{-1}$
1100	$2.9 \times 10^{-2}$	$8.5 \times 10^{-2}$	$2.0 \times 10^{-1}$	$3.9 \times 10^{-1}$	$5.9 \times 10^{-1}$
1300	$2.1 \times 10^{-2}$	$6.3 \times 10^{-2}$	$1.6 \times 10^{-1}$	$3.3 \times 10^{-1}$	$5.3 \times 10^{-1}$
1500	$1.5 \times 10^{-2}$	$4.7 \times 10^{-2}$	$1.3 \times 10^{-1}$	$2.8 \times 10^{-1}$	$4.8 \times 10^{-1}$
1700	$1.1 \times 10^{-2}$	$3.6 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.3 \times 10^{-1}$	$4.3 \times 10^{-1}$
1900	$8.3 \times 10^{-3}$	$2.8 \times 10^{-2}$	$8.2 \times 10^{-2}$	$2.0 \times 10^{-1}$	$3.8 \times 10^{-1}$
2100	$6.3 \times 10^{-3}$	$2.2 \times 10^{-2}$	$6.6 \times 10^{-2}$	$1.7 \times 10^{-1}$	$3.4 \times 10^{-1}$
2300	$4.9 \times 10^{-3}$	$1.7 \times 10^{-2}$	$5.4 \times 10^{-2}$	$1.4 \times 10^{-1}$	$3.0 \times 10^{-1}$
2500	$3.8 \times 10^{-3}$	$1.4 \times 10^{-2}$	$4.4 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.6 \times 10^{-1}$

## References

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- Wing Tsang  
June, 1989

10,4: NO<sub>2</sub>+H→NO+OH

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Agrawalla <i>et al.</i> (1981)	298	1–10×10 <sup>15</sup> NO <sub>2</sub> in 2×10 <sup>16</sup> Ar. OH detection infrared emission in flowing afterglow	7.2–12.5×10 <sup>-11</sup>	2
Michael <i>et al.</i> (1979)	230–400	3–12×10 <sup>12</sup> NO and 4–15×10 <sup>15</sup> CH <sub>4</sub> in 1–3.6×10 <sup>17</sup> Ar H-atom detection via resonance fluorescence of Lyman-alpha following flash photolysis	1.32×10 <sup>-10</sup>	1.1
	195–368	0.6–3.2×10 <sup>12</sup> NO <sub>2</sub> in 5–12×10 <sup>16</sup> He. H-atom detection via resonance fluorescence in discharge flow system	1.50×10 <sup>-10</sup>	1.2
Clyne and Monkhouse (1977)	298–653	5–50×10 <sup>-11</sup> NO <sub>2</sub> in 6×10 <sup>16</sup> He. H-atom detection via resonance fluorescence in discharge flow	4.8×10 <sup>-10</sup> exp(-400/T)	1.2
Bemand and Clyne	298	0.6–5.5×10 <sup>12</sup> NO <sub>2</sub> in 2× 10 <sup>16</sup> argon. H-atom detection via Lyman-alpha fluorescence in discharge flow	1.1×10 <sup>-10</sup>	1.2
Wagner <i>et al.</i> (1976)	240–460	4–13×10 <sup>12</sup> NO <sub>2</sub> in 6×10 <sup>16</sup> He. H-atom detection via Lyman-alpha fluorescence in discharge flow	7.1×10 <sup>-10</sup> exp(-505/T)	1.2
Baulch <i>et al.</i> (1973) review	298–630		5.8×10 <sup>-10</sup> exp(-740/T)	1.5 at 300 K 2 at 630 K
Recommendations			1.4×10 <sup>-10</sup>	1.3

## Comments

The earlier studies have been reviewed by Baulch. The subsequent measurements although of higher quality have not changed the situation to any great extent. The earlier recommendation at room temperature appears to be too small. The work of Michael and coworkers does not support the small temperature dependence suggested by the earlier workers. Fig. 1 summarizes the available experimental work. Our recommendation is based on the measurement of Michael and coworkers and lead to  $k(\text{H}+\text{NO}_2 \rightarrow \text{OH} + \text{NO}) = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , with an uncertainty of a factor of 1.3 near room temperature and increasing to a factor of 2 at 2500 K.

It is suspected that the reaction proceeds by way of a hot HONO. We have carried out RRKM calculations and find that only at the highest densities ( $10^{22} \text{ molecule/cm}^3$ ) and assuming deactivation on every collision are significant quantities of the HONO deactivated.

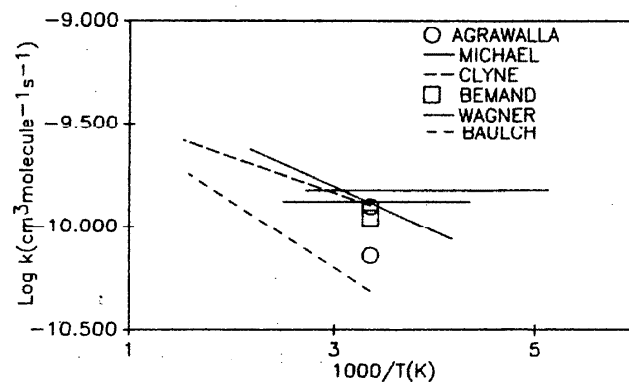


FIG. 1. Summary of experimental results on the H+NO<sub>2</sub>→OH+NO reaction.

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10.5: NO<sub>2</sub> + OH → HNO  
→ HO<sub>2</sub> + NO (b)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Atkinson <i>et al.</i> (1989)	200-300		cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> $k_a(\text{O}_2, 0) = 2.2 \times 10^{-30} (T/300)^{-2.9}$ $k_a(\text{N}_2, 0) = 2.6 \times 10^{-30} (T/300)^{-2.9}$ $k_{a\infty} = 5.2 \times 10^{-11} \text{ s}^{-1}$ $F_c = \exp(-T/353)$	1.2
Audley <i>et al.</i> (1984)	298	flow system at 2.5 × 10 <sup>19</sup> C <sub>2</sub> H <sub>6</sub> with small amount of NO <sub>2</sub> and traces of H <sub>2</sub> O <sub>2</sub> . Gas chromatographic detection of nitrogenated organics. Ratio of rate constants for OH + NO <sub>2</sub> and OH + C <sub>2</sub> H <sub>6</sub> determined.	$k_a = 2.2 \times 10^{-11} \text{ s}^{-1}$	1.4
Burrows <i>et al.</i> (1983)	295	3 - 16 × 10 <sup>16</sup> He Ar N <sub>2</sub> O <sub>2</sub> CO <sub>2</sub> in discharge flow. OH from H + NO <sub>2</sub> detected via resonance fluorescence	$k_a = 16 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $16 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $27 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $26 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ $45 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	1.2
Robertshaw and Smith (1982)	295	0 - 2.8 × 10 <sup>15</sup> NO <sub>2</sub> 3.1 × 10 <sup>15</sup> HNO <sub>3</sub> 1.5 × 10 <sup>17</sup> - 1 × 10 <sup>20</sup> Ar 0 - 2 × 10 <sup>20</sup> CF <sub>4</sub> ; OH from HNO <sub>3</sub> pulse photolysis and detected vis LIF	$k_{a\infty} > 3 \times 10^{-11}$ $k_a(\text{Ar}, 66 \times 10^{18}) = 0.75 \times 10^{-12}$ $k_a(\text{Ar}, 1.64 \times 10^{18}) = 1.68 \times 10^{-12}$ $k_a(\text{Ar}, 3.27 \times 10^{18}) = 2.68 \times 10^{-12}$ $k_a(\text{Ar}, 6.55 \times 10^{18}) = 3.33 \times 10^{-12}$ $k_a(\text{Ar}, 16.4 \times 10^{18}) = 6.30 \times 10^{-12}$ $k_a(\text{Ar}, 41.5 \times 10^{18}) = 10.5 \times 10^{-12}$ $k_a(\text{Ar}, 99.1 \times 10^{18}) = 14.3 \times 10^{-12}$ $k_a(\text{CF}_4, 1.5 \times 10^{18}) = 2.8 \times 10^{-12}$ $k_a(\text{CF}_4, 3.13 \times 10^{18}) = 5.1 \times 10^{-12}$ $k_a(\text{CF}_4, 6.39 \times 10^{18}) = 7.7 \times 10^{-12}$ $k_a(\text{CF}_4, 16.2 \times 10^{18}) = 14.3 \times 10^{-12}$ $k_a(\text{CF}_4, 41.1 \times 10^{18}) = 19.3 \times 10^{-12}$ $k_a(\text{CF}_4, 98.7 \times 10^{18}) = 15.3 \times 10^{-12}$ $k_a(\text{CF}_4, 71 \times 10^{18}) = 23.7 \times 10^{-12}$ $k_a(\text{CF}_4, 119 \times 10^{18}) = 25.6 \times 10^{-12}$ $k_a(\text{CF}_4, 151 \times 10^{18}) = 29.1 \times 10^{-12}$ $k_a(\text{CF}_4, 215 \times 10^{18}) = 36.5 \times 10^{-12}$	1.1

10,5: NO<sub>2</sub>+OH→HNO<sub>3</sub> (a) — Continued  
 →HO<sub>2</sub>+NO (b)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Anderson (1980)	225–398	3–6 × 10 <sup>16</sup> N <sub>2</sub> or He discharge flow OH from H+NO <sub>2</sub> detection via resonance fluorescence	k <sub>a</sub> = 1.6 × 10 <sup>-31</sup> exp(785/T)[N <sub>2</sub> ] cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> 1.7 × 10 <sup>-31</sup> [He, 300 K] cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup>	1.25
O'Brien <i>et al.</i> (1979)	301	ppm levels of NO <sub>2</sub> and Toluene in 2.5 × 10 <sup>19</sup> Air at 38% humidity. Photolysis of NO <sub>2</sub> in static system. Complex mechanism.	k <sub>a</sub> = 1.3 × 10 <sup>-11</sup>	1.3
Wine <i>et al.</i> (1979)	247–352	5.4 × 10 <sup>17</sup> , He 5.4 × 10 <sup>17</sup> , Ar 5.4 × 10 <sup>17</sup> , N <sub>2</sub> 5.4 × 10 <sup>17</sup> , SF <sub>6</sub> 9.5 × 10 <sup>17</sup> , Ar 9.5 × 10 <sup>17</sup> , N <sub>2</sub> 16 × 10 <sup>17</sup> , Ar 16 × 10 <sup>17</sup> , Ar 29 × 10 <sup>17</sup> , He 29 × 10 <sup>17</sup> , Ar 29 × 10 <sup>17</sup> , N <sub>2</sub> 29 × 10 <sup>17</sup> , SF <sub>6</sub> 62 × 10 <sup>17</sup> , Ar 62 × 10 <sup>17</sup> , N <sub>2</sub> 95 × 10 <sup>17</sup> , SF <sub>6</sub> 140 × 10 <sup>17</sup> , Ar 190 × 10 <sup>17</sup> , He 190 × 10 <sup>17</sup> , Ar 190 × 10 <sup>17</sup> , SF <sub>6</sub> 230 × 10 <sup>17</sup> , Ar with 10 <sup>15</sup> –10 <sup>16</sup> water and 10 <sup>13</sup> –10 <sup>14</sup> NO <sub>2</sub> . Flash photolysis of water and resonance fluorescence detection of OH	k <sub>a</sub> (M) × 10 <sup>13</sup> at 247 K 297 K 352 K 8.52 4.61 3.41 11.0 7.17 4.65 18.2 9.96 6.81 26.4 18.3 12.2 18.3 11.3 6.55 27.5 16.2 10.0 26.5 15.8 11.5 34.9 24.1 15.3 29.8 21.3 15.4 38.8 24.4 16.5 60.9 34.5 23.3 73.0 62.0 54.3 64.1 42.2 26.6 82.8 47.6 29.4 128 114 100 95.2 58.7 41.9 81.5 55.5 46.5 52.6 203 151 135 105 79.4	1.1
Campbell and Parkinson (1979)	292	3.4 × 10 <sup>18</sup> CO with traces of H <sub>2</sub> O <sub>2</sub> and NO <sub>2</sub> 1.9 × 10 <sup>18</sup> N <sub>2</sub> H <sub>2</sub> O <sub>2</sub> —NO <sub>2</sub> —CO—N <sub>2</sub> (major component) rate constants from CO <sub>2</sub> yields	k <sub>a</sub> = 4 × 10 <sup>-12</sup>  k <sub>a</sub> = 2 × 10 <sup>-12</sup>	1.3  1.3
Erler <i>et al.</i> (1977)	213–300	1–2.5 × 10 <sup>17</sup> He 10–30%CO <sub>2</sub> Discharge flow OH from H+NO <sub>2</sub> Detection via resonance fluorescence	k <sub>a</sub> = 1.5 × 10 <sup>-23</sup> T <sup>-2.9</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> k <sub>a</sub> = 4 × 10 <sup>-30</sup> cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> (CO <sub>2</sub> ,300)	1.25 1.12

10,5:  $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$  (a) — Continued  
 $\rightarrow \text{HO}_2 + \text{NO}$  (b)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Atkinson <i>et al.</i> (1976)	298	8.3 × 10 <sup>17</sup> , Ar 16.3 × 10 <sup>17</sup> , Ar 32 × 10 <sup>17</sup> , Ar 64 × 10 <sup>17</sup> , Ar 128 × 10 <sup>17</sup> , Ar 210 × 10 <sup>17</sup> , Ar 8.3 × 10 <sup>17</sup> , N <sub>2</sub> OH from vuv photolysis of H <sub>2</sub> O. Detection by resonance fluorescence	$k_a = 8.4 \times 10^{-13}$ 13.9 × 10 <sup>-13</sup> 22.5 × 10 <sup>-13</sup> 35.1 × 10 <sup>-13</sup> 51 × 10 <sup>-13</sup> 57 × 10 <sup>-13</sup> 1.25 × 10 <sup>-13</sup>	1.1
Anastasi and Smith (1976)	220–550	3.2 × 10 <sup>17</sup> , N <sub>2</sub> 5.5 × 10 <sup>17</sup> , N <sub>2</sub> 8.0 × 10 <sup>17</sup> , N <sub>2</sub> 16 × 10 <sup>17</sup> , N <sub>2</sub> 40 × 10 <sup>17</sup> , N <sub>2</sub> 80 × 10 <sup>17</sup> , N <sub>2</sub> 160 × 10 <sup>17</sup> , N <sub>2</sub> 8 × 10 <sup>17</sup> , SF <sub>6</sub> 16 × 10 <sup>17</sup> , SF <sub>6</sub> 160 × 10 <sup>17</sup> , SF <sub>6</sub> 8 × 10 <sup>17</sup> , He 40 × 10 <sup>17</sup> , He 8 × 10 <sup>17</sup> , Ar 8 × 10 <sup>17</sup> , O <sub>2</sub> Flash photolysis of HNO <sub>3</sub> . OH detection via resonance absorption. 0–10 <sup>16</sup> NO <sub>2</sub> ; 10 <sup>16</sup> HNO <sub>3</sub>	$k_a(\text{M}) \times 10^{13}$ at 220 238 265 296 358 450 550 16 11 7.5 7.4 4.5 24 36 26 17 14 8.3 4.1 64 37 26 26 14 6.1 3.2 100 61 47 43 21 10 7.4 130 140 140 96 62 (19) <sup>a</sup> (12) <sup>b</sup> 52 30 16 (3.6) <sup>c</sup> 180 150 110 (27) <sup>b</sup> 17 6.1 7.3 11 (a) 1.43 × 10 <sup>18</sup> (b) 11.7 × 10 <sup>18</sup> (c) 0.6 × 10 <sup>18</sup>	1.2
Harris and Wayne (1974)	298	2–8 × 10 <sup>16</sup> Ar " ? N <sub>2</sub> Discharge flow with resonance fluorescence detection of OH	$k_a = 1.5 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ 2.6 × 10 <sup>-30</sup> (cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> )	1.3
Gordon and Mulac (1975)	440	Pulse radiolysis in 17 × 10 <sup>19</sup> H <sub>2</sub> O with 1.1 × 10 <sup>17</sup> NO <sub>2</sub> Detection of OH by resonance absorption	$k_a = 5.3 \times 10^{-12}$ (435, H <sub>2</sub> O)	1.1
Anderson <i>et al.</i> (1974)	298	3.3–33 × 10 <sup>16</sup> in He, Ar, N <sub>2</sub> . Discharge flow with resonance fluorescence detection of OH	$k_a = 1 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ , He 1 × 10 <sup>-30</sup> , cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> , Ar 2.3 × 10 <sup>-30</sup> , cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> , N <sub>2</sub>	1.3
Howard and Evenson (1974)	296	1.3–10 × 10 <sup>17</sup> N <sub>2</sub> laser magnetic detection of OH in flow discharge	$k_a = 2.9 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$	1.2
Baulch (1973) review	298		$k_a(\text{He}) = 1.4 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1}$	1.5

10,5:  $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$  (a) — Continued  
 $\rightarrow \text{HIO}_2 + \text{NO}$  (b)

Reference	Conditions		Reaction rate constant	Uncertain
	<i>T</i> range/K	[ <i>M</i> ] range/cm <sup>3</sup>	<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Howard (1980)	452–1271	High temperature discharge flow reactor. Laser magnetic detection of OH. He + O <sub>2</sub> at 1–5.3 × 10 <sup>16</sup>	$k_0 = 3 \times 10^{-11} \exp(-3360/T)$	1.2
Recommendations			$k_{\infty} = 4 \times 10^{-11}$ $k_a(\text{N}_2, 0) = 1.77 \times 10^{-15} T^{-5.49} \exp(-1183/T)$ cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> $k_a(\text{CO}_2, 0) = 1.6 \times 10^{-15} T^{-5.4} \exp(-1100/T)$ 1200 K cm <sup>6</sup> molecule <sup>-2</sup> s <sup>-1</sup> $F_c(\text{N}_2) = 0.725 - 2.5 \times 10^{-4} T$ $F_c(\text{CO}_2) = 0.725 - 2.5 \times 10^{-4} T$ $k_0 = 3 \times 10^{-11} \exp(-3360/T)$	1.2, 300 K 2.5 at 1.2

### Comments

There are two reacting channels from the interaction of OH + NO<sub>2</sub>. For channel (b) we accept the recommendations of Howard. He has not only carried out very careful measurements over extended ranges but also reviewed the pertinent literature. For our purposes however, there is the possibility that the reaction proceed through the hot adduct HO—O—NO. This means that at high pressures we should consider the reactions of this species. In addition, the rate constants for the OH + NO<sub>2</sub> at higher pressures may have contributions from this source. This has been suggested by Robertshaw and Smith in the context of their high pressure measurements. In the following we have assumed that the nitric acid formation process is the only channel.

There have been a large number of studies involving the decay of OH in the presence of NO<sub>2</sub>. The data are replicated very well. This can be seen in Figs. 1 and 2. We have not included data involving more complex systems. They are in excellent agreement with these results. These studies are at the lower temperatures and except for Robertshaw and Smith at sufficiently low pressures so that nitric acid formation is undoubtedly the predominant reaction pathway. There are no direct studies of this type at temperatures in excess of 550 K. We have therefore used the shock tube results of Glanzer and Troe (Ber. Bunsenges Physik. Chem. 78, 71, 1974) and Harrison and coworkers (J. Amer. Chem. Soc., 84, 2478, 1962) to derive rate constants for the reverse reactions through the well established thermodynamics. A plot of the results can be found in Fig. 3. We believe that these high temperature results have an uncertainty of at least a factor of 2. In order to obtain rate constants for the temperature and pressure ranges covered in this evaluation, we select a high pressure rate expression of  $4 \times 10^{-11}$

cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> over all temperature ranges with an uncertainty of a factor of 2 and then carried out RRKM calculations on the basis of the strong collision assumption with nitric acid as the collision partner. The results can be found in Table 1. Table 2 contains collision efficiencies as a function of temperature and step size down.

In order to obtain information on collision efficiencies we first fitted the results of the studies of argon. These are the dotted lines in Figs. 1 and 3. We then first found a step size down that will fit the low temperature data on N<sub>2</sub> and CO<sub>2</sub> and assumed that the temperature dependence for argon will also hold for these two collision partners. The collisional efficiency values we calculate appear to be fairly constant. The step sizes down for Ar increased from 50 cm<sup>-1</sup> to 300 cm<sup>-1</sup> in the temperature range 300 to 1200 K. The general situation is very similar to that for the hydrocarbons.

$$k(\text{OH} + \text{NO}_2 + \text{N}_2 \rightarrow \text{HNO}_3 + \text{N}_2) = 1.77 \times 10^{-15} T^{-5.49} \exp(-1183/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$k(\text{OH} + \text{NO}_2 + \text{CO}_2 \rightarrow \text{HNO}_3 + \text{CO}_2) = 1.6 \times 10^{-15} T^{-5.4} \exp(-1100/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

In the intermediate pressure region we fit the results of RRKM calculation on the basis of Troe's formalism and arrive at

$$F_c(\text{N}_2) = 0.725 - 2.5 \times 10^{-4} T$$

$$F_c(\text{CO}_2) = 0.725 - 2.5 \times 10^{-4} T$$

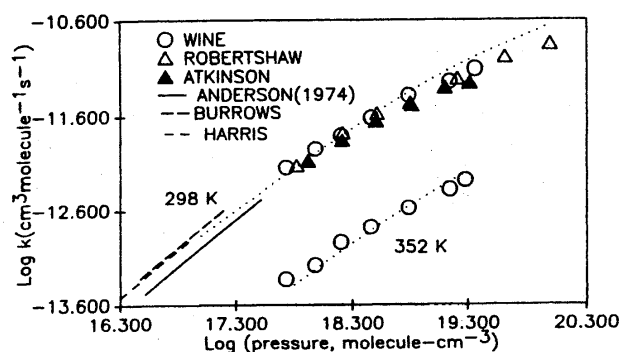


FIG. 1. Experimental results for the reaction of OH+NO<sub>2</sub> in argon at various temperatures. Results for 352 K have been reduced by one log unit to increase legibility. Dotted lines represent the results of our calculations.

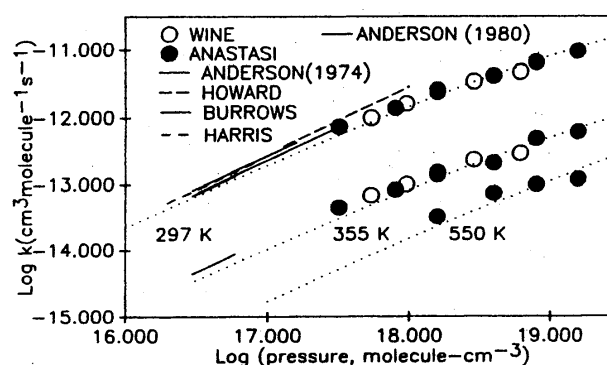


FIG. 2. Experimental results for the reaction of OH+NO<sub>2</sub> in nitrogen at various temperatures. Results for 355 K and 550 K have been reduced by one log unit to increase legibility. Dotted lines represent the results of our calculations.

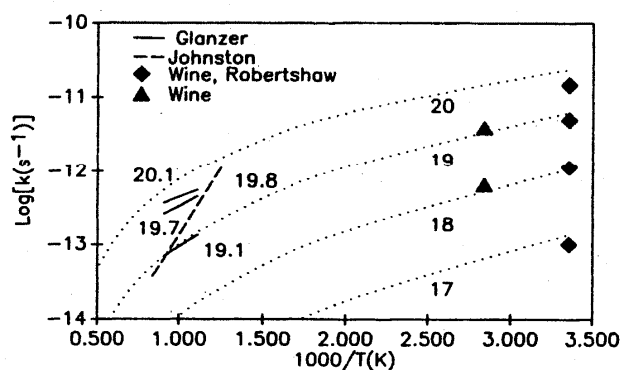


FIG. 3. Experimental results on the reaction OH+NO<sub>2</sub> in argon. High temperature results are from the reverse decomposition process. Points are interpolated from Fig. 1. Numbers are density in molecules/cm<sup>3</sup>. Dotted lines are our calculations.

TABLE 1. Log ( $k/k_{\infty}$ ) for the reaction  $\text{NO}_2 + \text{OH} + \text{HNO}_3 \rightarrow \text{HNO}_3 + \text{HNO}_3$  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	-1.83	-2.34	-2.77	-3.13	-3.45	-3.73	-3.98	-4.21	-4.41	-4.60	-4.77
17.5	-1.41	-1.89	-2.39	-2.66	-2.97	-3.24	-3.49	-3.71	-3.92	-4.10	-4.27
18	-1.03	-1.47	-1.86	-2.20	-2.50	-2.77	-3.01	-3.23	-3.43	-3.61	-3.78
18.5	-0.70	-1.09	-1.44	-1.76	-2.04	-2.30	-2.54	-2.75	-2.95	-3.13	-3.29
19	-0.43	-0.75	-1.06	-1.35	-1.62	-1.86	-2.08	-2.29	-2.48	-2.65	-2.81
19.5	-0.24	-0.48	-0.73	-0.98	-1.22	-1.45	-1.65	-1.85	-2.03	-2.19	-2.35
20	-0.12	-0.27	-0.47	-0.67	-0.87	-1.07	-1.26	-1.43	-1.60	-1.75	-1.89
20.5	-0.05	-0.14	-0.27	-0.42	-0.58	-0.74	-0.90	-1.05	-1.20	-1.34	-1.47
21	-0.02	-0.06	-0.13	-0.23	-0.35	-0.47	-0.59	-0.72	-0.84	-0.96	-1.08
21.5	-0.01	-0.02	-0.06	-0.11	-0.18	-0.26	-0.35	-0.45	-0.54	-0.63	-0.73
22		-0.01	-0.02	-0.05	-0.08	-0.13	-0.18	-0.24	-0.31	-0.37	-0.44



TABLE 2. Collision efficiency as a function of temperature and step size down for the reaction  $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ 

Step Size ( $\text{cm}^{-1}$ )	200	400	800	1600	3200
Temp (K)					
500	$1.1 \times 10^{-1}$	$2.4 \times 10^{-1}$	$4.3 \times 10^{-1}$	$6.3 \times 10^{-1}$	$7.8 \times 10^{-1}$
700	$6.0 \times 10^{-2}$	$1.6 \times 10^{-1}$	$3.2 \times 10^{-1}$	$5.2 \times 10^{-1}$	$7.0 \times 10^{-1}$
900	$3.7 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.4 \times 10^{-1}$	$4.3 \times 10^{-1}$	$6.3 \times 10^{-1}$
1100	$2.4 \times 10^{-2}$	$7.2 \times 10^{-2}$	$1.8 \times 10^{-1}$	$3.5 \times 10^{-1}$	$5.6 \times 10^{-1}$
1300	$1.6 \times 10^{-2}$	$5.0 \times 10^{-2}$	$1.3 \times 10^{-1}$	$2.9 \times 10^{-1}$	$4.9 \times 10^{-1}$
1500	$1.1 \times 10^{-2}$	$3.6 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.3 \times 10^{-1}$	$4.2 \times 10^{-1}$
1700	$7.5 \times 10^{-3}$	$2.5 \times 10^{-2}$	$7.6 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.6 \times 10^{-1}$
1900	$5.3 \times 10^{-3}$	$1.8 \times 10^{-2}$	$5.7 \times 10^{-2}$	$1.5 \times 10^{-1}$	$3.1 \times 10^{-1}$
2100	$3.7 \times 10^{-3}$	$1.3 \times 10^{-2}$	$4.2 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.6 \times 10^{-1}$
2300	$2.7 \times 10^{-3}$	$9.7 \times 10^{-3}$	$3.2 \times 10^{-2}$	$9.2 \times 10^{-2}$	$2.2 \times 10^{-1}$
2500	$1.9 \times 10^{-3}$	$7.0 \times 10^{-3}$	$2.4 \times 10^{-2}$	$7.2 \times 10^{-2}$	$1.8 \times 10^{-1}$

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Wing Tsang  
August, 1989

10,6:  $\text{NO}_2 + \text{HCHO} \rightarrow \text{HNO}_2 + \text{CHO}$ 

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	$k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	
Lin <i>et al.</i> (1990)	1140–1650	0.1–0.2% Trioxane 0.3–0.65% NO <sub>2</sub> and $2-4 \times 10^{18}$ Ar in Shock Tube. Reaction followed by detection of NO, CO and H <sub>2</sub> O. Computer simulation for rate constants.	$1.3 \times 10^{-21} T^{2.77} \exp(-6910/T)$	2
He <i>et al.</i> (1989)	393–476	2.7%–5.08% HCHO 3.44%–7.4% NO <sub>2</sub> in Ar at $5 \times 10^{19}$ FTIR detection of all products. Computer simulation for rate constants	$3.33 \times 10^{-13} \exp(-8080/T)$	2
Recommendations:			$1.3 \times 10^{-21} T^{2.77} \exp(-6910/T)$	2

## Comments

The recent work of Lin *et al.* is consistent with the lower temperature study of He *et al.* Although the rate expressions are derived on the basis of a computer simulation of the results, the rate expression is based on fits of many species profiles and therefore should be regarded with a high degree of confidence. The estimated uncertainty is a factor of 2.

## References

- He, Y., Kolby, E., Shumaker, P. and Lin, M. C. "Thermal Reaction of CH<sub>2</sub>O with NO<sub>2</sub> in the Temperature Range of 393–476K FTIR Product Measurement and Kinetic Modeling," in press.  
Lin, C. Y., Wang, H. T., Lin, M. C. and Melius, C. F., "A Shock Tube Study of the CH<sub>2</sub>O + NO<sub>2</sub> Reaction at High Temperatures" Int. J. Chem. Kin, in press.

W. Tsang  
June, 1989

 10,7:  $\text{NO}_2 + \text{CHO} \rightarrow \text{CO} + \text{HNO}_2$  (a)  
 $\rightarrow \text{H} + \text{CO}_2 + \text{NO}$  (b)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	$k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	
Lin <i>et al.</i> (1990)	1140–1650	0.1–0.2% Trioxane 0.3–0.65% NO <sub>2</sub> and $2-4 \times 10^{18}$ Ar in Shock Tube. Reaction followed by detection of NO, CO and H <sub>2</sub> O. Computer simulation for rate constants.	$k_a = 0.21 \times (1/T)^{-3.70} \exp(-1185/T)$ $k_b = 1.4 \times 10^{-8} (1/T)^{0.75} \exp(-970/T)$	2
He <i>et al.</i> (1989)	393–476	2.7%–5.08% HCHO 3.44%–7.4% NO <sub>2</sub> in Ar at $5 \times 10^{19}$ FTIR detection of all products. Computer simulation for rate constants	$k_a = 2.8 \times 10^{-11}$ $k_b = 1.5 \times 10^{-11}$	1.5
Timonen <i>et al.</i> (1988)	294–713	HCO from laser photolysis (308nm) of CH <sub>3</sub> CHO (0.05%) in 0–0.35% NO <sub>2</sub> in $2 \times 10^{16}$ He. MS- detection of HCO	$k_{a+b} = 2.5 \times 10^{-11} \exp(217/T)$	1.2
Recommendations			$k_a = 2.1 \times (1/T)^{-3.29} \exp(-1185/T)$ $k_b = 1.4 \times 10^{-8} (1/T)^{0.75} \exp(-970/T)$	2

## Comments

The lower temperature results of He *et al.* and Timonen *et al.* are in excellent agreement. Lin *et al.* have fitted their higher temperature results on the basis of RRKM calculations assuming that the reactions proceed through hot adducts. We recommend their results which cover the temperature range from 300–1800 K with an uncertainty of a factor of 1.3 near room temperature and increasing to a factor of 3 at 1800 K. Note that at high pressures and sufficiently low temperatures there is a chance that the adduct may be stabilized. This will mean that two new species must be considered. Under most conditions, however, the adduct will rapidly decompose.

## References

- He, Y., Kolby, E., Shumaker, P. and Lin, M. C. "Thermal Reaction of CH<sub>2</sub>O with NO<sub>2</sub> in the Temperature Range of 393–476K FTIR Product Measurement and Kinetic Modeling," *Int. J. Chem. Kin.*, in press.
- Lin, C. Y., Wang, H. T., Lin, M. C. and Melius, C. F., "A Shock Tube Study of the CH<sub>2</sub>O + NO<sub>2</sub> Reaction at High Temperatures" *Int. J. Chem. Kin.*, in press.
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Wing Tsang  
August, 1989

10,8: NO<sub>2</sub>+CO → CO<sub>2</sub>+NO

Reference	Conditions		Reaction rate constant <i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty
	<i>T</i> range/K	[ <i>M</i> ] range/cm <sup>3</sup>		
Milks <i>et al.</i> (1979)	950–1550	1.4–4% NO <sub>2</sub> and 3–5% CO in argon. Single pulse shock tube study with analysis of CO, CO <sub>2</sub> , NO, NO <sub>2</sub>	$5.4 \times 10^{-11} \exp(-16110/T)$	3
Freund and Palmer (1977) (also review)	1300–2000 500–2000	2–8% NO <sub>2</sub> and 25–50% CO in $2.4-4.2 \times 10^{18}$ argon in shock tube experiments. Reaction followed via NO <sub>2</sub> absorption and CO <sub>2</sub> emission.	$1.5 \times 10^{-10} \exp(-17000/T)$	2.5
Recommendation			$1.5 \times 10^{-10} \exp(-17000/T)$	2.5

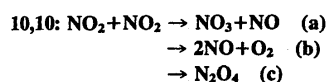
## Comments

The earlier data (previous to 1977) are in surprisingly good agreement and has been reviewed by Freund and Palmer and combined with their higher temperature results. The subsequent work of Milks *et al.* confirm the earlier recommendations (see Freund and Palmer, *Comb. Sci. Tech.*, **21**, 179, 1980). Our recommendation is therefore that of Freund and Palmer with an uncertainty of a factor of 2.5.

## References

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Wing Tsang  
September, 1989



Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	$k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	
Freund and Palmer(1977)	1419-1857	5.7-12% $\text{NO}_2$ in 1.7-7.3 $\times 10^{18}$ Ar. Shock tube experiments with detection of $\text{NO}_2$ from absorption.	$k_{a+b} = 6.6 \times 10^{-15}$ , 1660 K	3
Baulch <i>et al.</i> (1973)	600-1000 review		$k_b = 3.3 \times 10^{-12} \exp(-13500/T)$	1.3
Recommendation			$k_a = 1.6 \times 10^{-14} T^{.73} \exp(-10530/T)$ $k_b = 2.7 \times 10^{-12} \exp(-13147/T)$	2 at 300-600 K 5 at 2500 K 1.5 at 300- 1000 K 2 at 2500 K

### Comments

Channel (c) is reversed under all combustion related situations. For channel (a) we use the very reliable rate expression near room temperature recommended by Atkinson *et al.* (J. Phys. Chem. Ref. Data, 18, 881, 1989), and in conjunction with the thermodynamics derive the rate expression;

$$k_a = 1.6 \times 10^{-14} T^{.73} \exp(-10530/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

with an uncertainty of a factor 2 from 300 to 600 K and increasing to a factor of 5 at 2500 K.

For channel (b) we accept the recommendation of Baulch except that we change the rate expression slightly so that the rate expression given here will be exactly compatible with the thermodynamics and the rate expression recommended by Baulch *et al.* for the reverse reaction. This leads to the rate expression

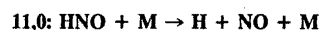
$$k_b = 2.7 \times 10^{-12} \exp(-13147/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} .$$

with an uncertainty of a factor of 1.5 from 300 K to 1000 K and increasing to a factor of 2 at 2500 K. All the existing work summarized by Baulch *et al.* rely on the decay of  $\text{NO}_2$ . As a result they are unable to truly differentiate between the two channels. At the lower temperatures channel (b) predominates. Note that the sum of the rate constants for the two processes is very close to the measurement of Freund and Palmer. Their data show considerable scatter and we have chosen a representative point.

### References

- Baulch D. L., Drysdale, D. D. and Horne, D. G. "Evaluated Kinetic Data for High Temperature Reactions Vol. 2, Homogeneous Gas Phase Reactions of the  $\text{H}_2\text{-N}_2\text{-O}_2$  System", Butterworths, London, 1973.  
 Freund, H. and Palmer, H. B., "Shock-Tube Studies of the Reactions of  $\text{NO}_2$  with  $\text{NO}_2$ ,  $\text{SO}_2$  and  $\text{CO}$ , Int. J. Chem. Kin., 9, 887, 1977.

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 October, 1989



Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	$k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	
Log $K_p = 6.403 - 1.172 \times 10^4/T + 2.542 \times 10^5/T^2 - 2.750 \times 10^7/T^3$				
Recommendations			$k_\infty = 1.2 \times 10^{16} T^{-0.43} \exp(-24929/T) \text{ s}^{-1}$ $k(0, \text{N}_2) = 0.01 T^{-1.61} \exp(-25585/T)$ $F_c = 0.83$ $k(0, \text{CO}_2) = 6.4 \times 10^{-4} T^{-1.24} \exp(-25172/T)$ $F_c = 0.83$	4 1.5 up to 700 K 3 at 2500 K

## Comments

There are no experimental data on the rate constants for this reaction. Our recommendations are based on the analysis of the data on the reverse reaction at low temperature, assumptions on the collision efficiencies for N<sub>2</sub> and CO<sub>2</sub> and the well established thermodynamics for this system. Fall off behavior on the basis of strong collisions

and HNO as the collision partner can be found in Table 1. Collision efficiencies as a function of step size down and temperature can be found in Table 2. For a more complete discussion, see 9,4.

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June, 1989

TABLE I: Log ( $k/k(0)$ ) for the reaction  $\text{HNO} + \text{HNO} \rightarrow \text{H} + \text{NO} + \text{HNO}$  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											
17.5											
18											
18.5											
19	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.00
19.5	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.02	-0.01	-0.01	-0.01
20	-0.05	-0.05	-0.05	-0.05	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04
20.5	-0.13	-0.12	-0.11	-0.11	-0.10	-0.10	-0.10	-0.09	-0.09	-0.09	-0.09
21	-0.27	-0.25	-0.24	-0.23	-0.22	-0.22	-0.22	-0.21	-0.20	-0.20	-0.18
21.5	-0.51	-0.48	-0.47	-0.45	-0.43	-0.42	-0.41	-0.39	-0.38	-0.37	-0.36
22	-0.86	-0.82	-0.79	-0.77	-0.74	-0.72	-0.70	-0.68	-0.67	-0.65	-0.63

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

Step Size (cm <sup>-1</sup> )	200	400	800	1600	3200
Temp (K)					
500	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$	$4.7 \times 10^{-1}$	$6.6 \times 10^{-1}$	$8.0 \times 10^{-1}$
700	$7.6 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.6 \times 10^{-1}$	$5.7 \times 10^{-1}$	$7.4 \times 10^{-1}$
900	$5.1 \times 10^{-2}$	$1.4 \times 10^{-1}$	$2.9 \times 10^{-1}$	$4.9 \times 10^{-1}$	$6.8 \times 10^{-1}$
1100	$3.6 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.3 \times 10^{-1}$	$4.3 \times 10^{-1}$	$6.2 \times 10^{-1}$
1300	$2.7 \times 10^{-2}$	$7.9 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.7 \times 10^{-1}$	$5.7 \times 10^{-1}$
1500	$2.0 \times 10^{-2}$	$6.2 \times 10^{-2}$	$1.6 \times 10^{-1}$	$3.3 \times 10^{-1}$	$5.3 \times 10^{-1}$
1700	$1.6 \times 10^{-2}$	$5.0 \times 10^{-2}$	$1.3 \times 10^{-1}$	$2.9 \times 10^{-1}$	$4.9 \times 10^{-1}$
1900	$1.3 \times 10^{-2}$	$4.1 \times 10^{-2}$	$1.1 \times 10^{-1}$	$2.5 \times 10^{-1}$	$4.5 \times 10^{-1}$
2100	$1.0 \times 10^{-2}$	$3.4 \times 10^{-2}$	$9.7 \times 10^{-2}$	$2.3 \times 10^{-1}$	$4.1 \times 10^{-1}$
2300	$8.5 \times 10^{-3}$	$2.8 \times 10^{-2}$	$8.3 \times 10^{-2}$	$2.0 \times 10^{-1}$	$3.8 \times 10^{-1}$
2500	$7.0 \times 10^{-3}$	$2.4 \times 10^{-2}$	$7.2 \times 10^{-2}$	$1.8 \times 10^{-1}$	$3.5 \times 10^{-1}$

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June, 1989

11,3  $\text{HNO} + \text{O} \rightarrow \text{OH} + \text{NO}$ 

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	
Recommendation			$6 \times 10^{-11}$	3

## Comments

There have been no measurements on the rate constants for this reaction. This is a very exothermic process. We base our recommendation on the rate expression for

$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$ . It is also consistent with our recommendation for  $\text{OH} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{NO}$ .

Wing Tsang  
June, 1989

11.4:  $\text{H} + \text{HNO} \rightarrow \text{H}_2 + \text{NO}$ 

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Dodonov <i>et al.</i> (1980)	298	HNO from excited H <sub>2</sub> mixed with NO at 2 × 10 <sup>17</sup> . Mass spec detection.	1.2 × 10 <sup>-10</sup>	large
Washida <i>et al.</i> (1978)	298	1–6 × 10 <sup>14</sup> NO, 0.3–20 × 10 <sup>14</sup> H in 1.5 × 10 <sup>17</sup> He in discharge flow Mass spec. detection of HNO via photoionization	> 1.6 × 10 <sup>-12</sup>	
Baulch <i>et al.</i> (1973) (review)	2000		8 × 10 <sup>-12</sup>	
Recommendation			3 × 10 <sup>-11</sup> exp(-500/T)	4

## Comments

The recommendation of Baulch *et al.* is based on studies in the post flame region with an assumed mechanism.

The rate constant at 2000 K appear to be small in comparison to analogous exothermic reactions (H + HO<sub>2</sub>, H + HI). The work of Dodonov and coworkers involves a poorly defined system, while that of Wahida *et al.* establishes a lower limit.

We therefore recommend at 2000 K a rate constant that is a factor of 3 larger than the recommendation of Baulch *et al.* with an uncertainty of a factor of 3. Combining this with an assumed activation energy of 4 kJ/mol gives us the rate expression

$$k(\text{H} + \text{HNO} \rightarrow \text{H}_2 + \text{NO}) = 3 \times 10^{-11} \exp(-500/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

with an uncertainty of a factor of 4 over the entire temperature range.

## References

- Baulch D. L., Drysdale, D. D. and Horne, D. G. "Evaluated Kinetic Data for High Temperature Reactions Vol 2, Homogeneous Gas Phase Reactions of the H<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> System, Butterworths, London, 1973.
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- Washida, N., Akimoto, H. and Okuda, M., "HNO Formed in the H + NO + M Reaction System", J. Phys. Chem., 82, 2293, 1978.

Wing Tsang  
June, 1989

11.5:  $\text{OH} + \text{HNO} \rightarrow \text{H}_2\text{O} + \text{NO}$ 

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Baulch <i>et al.</i> (1973)	2000K		6 × 10 <sup>-11</sup>	2
Recommendation			8 × 10 <sup>-11</sup> exp(-500/T)	3 at 2000 K > 10 at 300 K

## Comments

The experimental data have been reviewed by Baulch *et al.* Three similar types of measurements in the post flames region have been carried out and led to results that differ by an order of magnitude. Our recommendations are essentially that of Baulch except that we have added a small activation energy.

## References

- Baulch D. L., Drysdale, D. D. and Horne, D. G. "Evaluated Kinetic Data for High Temperature Reactions Vol 2, Homogeneous Gas Phase Reactions of the H<sub>2</sub>-N<sub>2</sub>-O<sub>2</sub> System", Butterworths, London, 1973.

Wing Tsang  
June, 1989

## 11,7:HNO+CHO→HCHO+NO

Reference	Conditions		Reaction rate constant	Uncertainty
	<i>T</i> range/K	[M] range/cm <sup>3</sup>	<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Recommendation			$1 \times 10^{-12} \exp(-1000/T)$	5

## Comments

There are no measurements on the rate constants for this reaction. This is a very exothermic reaction and therefore will have a low activation energy. The A-factor will be in the  $1 \times 10^{-12}$  cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> range. We recommend

$$k(\text{HNO} + \text{CHO} \rightarrow \text{HCHO} + \text{NO}) = 1 \times 10^{-12} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 5.

Wing Tsang  
April, 1989

11,10:HNO+NO<sub>2</sub>→HNO<sub>2</sub>+NO

Reference	Conditions		Reaction rate constant	Uncertainty
	<i>T</i> range/K	[M] range/cm <sup>3</sup>	<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Recommendation			$1 \times 10^{-12} \exp(-1000/T)$	5

## Comments

There are no data on the rate constants for this reaction. The recommended rate expression is based on the assumption that the reverse reaction will have an A-fac-

tor close to collisional. We have also assumed an activation barrier of 8 kJ/mol.

Wing Tsang  
August, 1989

11,11: HNO+HNO→H<sub>2</sub>O+N<sub>2</sub>O

Reference	Conditions		Reaction rate constant	Uncertainty
	<i>T</i> range/K	[M] range/cm <sup>3</sup>	<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
He <i>et al.</i> (1988)	450–520	0.5–4.0% CH <sub>3</sub> ONO in 2–180 × 10 <sup>17</sup> He. FTIR and GLC detection of final products from static reactor and kinetic modeling.	$1.4 \times 10^{-15} \exp(-1561/T)$	2
Cheskis <i>et al.</i> (1981)	298	2.3 × 10 <sup>17</sup> HCHO, 4 × 10 <sup>17</sup> CH <sub>3</sub> CHO in 2–125 × 10 <sup>17</sup> NO under flash photolysis. HNO detection via intracavity laser absorption	$1.5 \times 10^{-15}$	1.6
Callear and Carr (1975)	280–420	0.2–1% NO in 3–20 × 10 <sup>18</sup> H <sub>2</sub> under flash photolysis. HNO detection via uv absorption	5.35 × 10 <sup>-15</sup> (298) 1.4 × 10 <sup>-14</sup> (400)	1.3
Kohut and Lampe (1967)	300	< 1% NO in 1–2.4 × 10 <sup>18</sup> H <sub>2</sub> or D <sub>2</sub> . H/D from Hg photosensitized decomp. of H <sub>2</sub> /D <sub>2</sub>	$6.6 \times 10^{-16}$	large
Recommendation:			$1.4 \times 10^{-15} \exp(-1561/T)$	2 at 500 K 10 at 1000 K (see text)

## Comments

The existing experimental results are widely divergent. The more direct studies on HNO disappearance of Callear and Carr and Cheskis *et al.* leads to rate constants that are much larger than the measurements of He and coworkers which is based on N<sub>2</sub>O appearance. The work of Kohut and Lampe involves the steady state concentration of HNO as well as N<sub>2</sub>O appearance. HNO is not a stable species so that for all except the measurements of He and coworkers errors can arise from calibration problems. Nevertheless the differences are so large that we can only conclude that the HNO self-reaction involves a hot adduct which is stabilized under certain conditions and that N<sub>2</sub>O formation is probably a relatively minor channel. We therefore recommend the rate expression of He and coworkers for the reaction as written. It is however applicable over a very narrow range of conditions.

HNO self combination probably involves compounds which are as yet unspecified.

## References

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 Kohut, F. C. and Lampe, F. W. "Mass-Spectrometric Study of the Reactions of Deuterium and Hydrogen Atoms with Nitric Oxide", *J. Chem. Phys.*, **46**, 4075, 1967.

Wing Tsang  
 August, 1989

12,0 HNO<sub>2</sub>+M →OH+NO+M

Reference	Conditions		Reaction rate constant <i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Uncertainty
	<i>T</i> range/K	[M] range/cm <sup>3</sup>		
Log <i>K<sub>p</sub></i> = 7.547 - 1.051 × 10 <sup>4</sup> / <i>T</i> - 2.558 × 10 <sup>5</sup> / <i>T</i> <sup>2</sup> + 4.296 × 10 <sup>7</sup> / <i>T</i> <sup>3</sup>				
Recommendations			$k_{\infty} = 1.2 \times 10^{19} (1/T)^{1.23}$ $\exp(-25010/T) \text{s}^{-1}$ $k(0, \text{sc}) = 7.3 \times 10^5 (1/T)^{3.42}$ $\exp(-25200/T)$ $k(0, \text{N}_2) = 5 \times 10^6 (1/T)^{3.8}$ $\exp(-25340/T)$ $F_c(\text{N}_2) = 0.62$ $k(0, \text{CO}_2) = 1.7 \times 10^6 (1/T)^{3.59}$ $\exp(-25250/T)$ $F_c(\text{CO}_2) = 0.62$	1.4 at 300 K 5 at 2500 K

## Comments

There are no measurements on the rate constants for this process. Our recommendations are based on the results for the reverse combination rate constant (9,5) and the well established thermodynamics. This leads to the following rate expressions,

$$k_{\infty} = 1.2 \times 10^{19} (1/T)^{1.23} \exp(-25010/T) \text{s}^{-1}$$

$$k(0, \text{sc}) = 7.3 \times 10^5 (1/T)^{3.42} \exp(-25200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(0, \text{N}_2) = 5 \times 10^6 (1/T)^{3.8} \exp(-25340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(0, \text{CO}_2) = 1.7 \times 10^6 (1/T)^{3.59} \exp(-25250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The uncertainties are a factor of 1.4 at room temperature and increasing to a factor of 5 at 2500 K.

The results of RRKM calculations for strong colliders are summarized in Table 1. Collision efficiencies as a function of temperature and step sizes down can be found in Table 2. Note that in order to fit the low pressure results we used very high collision efficiencies and step sizes down. See additional comments in 9,5.

In the case of N<sub>2</sub> and CO<sub>2</sub>, the *F<sub>c</sub>* values which can be used to determine fall-off value analytically are for both cases 0.62.

Wing Tsang  
 June, 1989



TABLE 1. Log ( $k/k_\infty$ ) for the reaction HONO+HONO→HO+NO+HONO as a function of temperature and pressure assuming strong collision

T(K)	500	700	900	1100	1300	1500	1700	1900	2100	2300	2500
Log (density)											
17	-2.32	-2.58	-2.78	-2.94	-3.08	-3.21	-3.32	-3.43	-3.52	-3.60	-3.68
17.5	-1.86	-2.10	-2.30	-2.46	-2.60	-2.72	-2.83	-2.93	-3.03	-3.11	-3.19
18	-1.42	-1.65	-1.83	-1.99	-2.12	-2.24	-2.35	-2.45	-2.54	-2.62	-2.70
18.5	-1.02	-1.23	-1.40	-1.54	-1.67	-1.78	-1.88	-1.98	-2.07	-2.15	-2.22
19	-0.67	-0.85	-0.99	-1.12	-1.24	-1.34	-1.44	-1.53	-1.61	-1.69	-1.76
19.5	-0.39	-0.53	-0.65	-0.75	-0.85	-0.94	-1.03	-1.11	-1.18	-1.25	-1.32
20	-0.20	-0.29	-0.37	-0.45	-0.53	-0.60	-0.67	-0.74	-0.80	-0.86	-0.92
20.5	-0.09	-0.13	-0.18	-0.24	-0.29	-0.34	-0.39	-0.44	-0.49	-0.54	-0.58
21	-0.03	-0.05	-0.08	-0.11	-0.14	-0.17	-0.20	-0.23	-0.26	-0.29	-0.32
21.5	-0.01	-0.02	-0.03	-0.04	-0.05	-0.07	-0.08	-0.10	-0.12	-0.13	-0.15
22		-0.01	-0.01	-0.01	-0.02	-0.02	-0.03	-0.04	-0.04	-0.05	-0.06

TABLE 2. Collision efficiency as a function of temperature and step size down for HNO<sub>2</sub>+M=HO+NO+M

Step Size (cm <sup>-1</sup> )	200	400	800	1600	3200
Temp(K)					
500	$1.1 \times 10^{-1}$	$2.5 \times 10^{-1}$	$4.5 \times 10^{-1}$	$6.4 \times 10^{-1}$	$7.9 \times 10^{-1}$
700	$6.7 \times 10^{-2}$	$1.7 \times 10^{-1}$	$3.4 \times 10^{-1}$	$5.4 \times 10^{-1}$	$7.2 \times 10^{-1}$
900	$4.3 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.6 \times 10^{-1}$	$4.6 \times 10^{-1}$	$6.5 \times 10^{-1}$
1100	$3.0 \times 10^{-2}$	$8.6 \times 10^{-2}$	$2.1 \times 10^{-1}$	$3.9 \times 10^{-1}$	$5.9 \times 10^{-1}$
1300	$2.1 \times 10^{-2}$	$6.4 \times 10^{-2}$	$1.6 \times 10^{-1}$	$3.3 \times 10^{-1}$	$5.3 \times 10^{-1}$
1500	$1.5 \times 10^{-2}$	$4.8 \times 10^{-2}$	$1.3 \times 10^{-1}$	$2.8 \times 10^{-1}$	$4.8 \times 10^{-1}$
1700	$1.1 \times 10^{-2}$	$3.7 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.4 \times 10^{-1}$	$4.3 \times 10^{-1}$
1900	$8.5 \times 10^{-3}$	$2.8 \times 10^{-2}$	$8.3 \times 10^{-2}$	$2.0 \times 10^{-1}$	$3.8 \times 10^{-1}$
2100	$6.5 \times 10^{-3}$	$2.2 \times 10^{-2}$	$6.7 \times 10^{-2}$	$1.7 \times 10^{-1}$	$3.4 \times 10^{-1}$
2300	$5.0 \times 10^{-3}$	$1.8 \times 10^{-2}$	$5.5 \times 10^{-2}$	$1.4 \times 10^{-1}$	$3.0 \times 10^{-1}$
2500	$4.0 \times 10^{-3}$	$1.4 \times 10^{-2}$	$4.5 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$

12.3: HNO<sub>2</sub>+O→OH+NO<sub>2</sub>

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm	$k/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	
Kaiser and Japar (1978)	300-355	Low pressure discharge-flow with mass spect detection	$1-5 \times 10^{-15}$	
Recommendations:	300-2500		$2 \times 10^{-11} \exp(-3000/T)$	10

## Comments

Kaiser and Japar reported that at 300 K, the rate constant was  $1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and at 355 K, varied between  $1-5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which they interpreted in terms of a wall reaction. They suggest that the measured rate constant should be taken as an upper limit. The recommended value is based on the measured rate constant at 300 K and an assumed A factor of  $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

## References

Kaiser, E. W. and Japar, S. M., "Upper Limits to the Gas Phase Reaction Rates of HONO with NH<sub>3</sub> and O(3P) Atoms", J. Phys. Chem. **82**, 2753, 1978.

J. T. Herron  
September, 1989

12,4:  $\text{HNO}_2 + \text{H} \rightarrow \text{H}_2 + \text{NO}_2$ 

Reference	Conditions		Reaction rate constant	Uncertainty
	<i>T</i> range/K	[M] range/cm	$k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	
Recommendations:	300–2500		$2 \times 10^{-11} \exp(-3700/T)$	20

## Comments

There are no data. Although there are data for the reactions of OH, O, and H with  $\text{H}_2\text{O}_2$  which could serve as a model for comparison, there are problems with regard to mechanism (the low temperature data for the H +  $\text{H}_2\text{O}_2$  reaction have been interpreted in terms of a displacement reaction (for a discussion see Tsang and Hampson)). In the absence of such information, we have chosen the A factor to be the same as for O +  $\text{HNO}_2$ ,

and set the activation energy to give a rate constant at 300 K a factor of 10 smaller than the corresponding O +  $\text{HNO}_2$  reaction.

## References

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J. T. Herron  
September, 1989

12,5:  $\text{HNO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2$ 

Reference	Conditions		Reaction rate constant	Uncertainty
	<i>T</i> range/K	[M] range/cm <sup>3</sup>	$k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	
Atkinson <i>et al.</i> (1989) review	280–340		$1.8 \times 10^{-11} \exp(-390/T)$	2
Jenkin and Cox (1987)	278–342.5	Photolysis. $2 \times 10^{13}$ O <sub>3</sub> , $5 \times 10^{15}$ HO, $8 \times 10^{12}$ HNO <sub>2</sub> in $3.5 \times 10^{17}$ molec cm <sup>-3</sup> Ar	$1.8 \times 10^{-11} \exp(-390/T)$	1.6
Cox, Derwent, and Holt (1976) 296		Photolysis. $10^{14}$ – $10^{15}$ HNO <sub>2</sub> , $10^{12}$ – $10^{14}$ NO, $10^{12}$ – $10^{14}$ NO <sub>2</sub> , $10^{14}$ – $10^{17}$ CO, in $2.5 \times 10^{19}$ molec cm <sup>-3</sup> N <sub>2</sub> /O <sub>2</sub> mixture Relative to CO + OH	$5.9 \times 10^{-12}$	1.4
Cox, Derwent, and Holt (1976) 296		Photolysis. $2 \times 10^{14}$ HNO <sub>2</sub> , $10^{13}$ NO, $7 \times 10^{12}$ NO <sub>2</sub> , $10^{17}$ – $10^{18}$ H <sub>2</sub> in $2.5 \times 10^{19}$ molec cm <sup>-3</sup> N <sub>2</sub> /O <sub>2</sub> mixture Relative to H <sub>2</sub> + OH	$6.6 \times 10^{-12}$	1.3
Cox, Derwent, Holt, and Kerr (1976)	296	Photolysis. $1$ – $2 \times 10^{14}$ HNO <sub>2</sub> , $7.2 \times 10^{-12}$ $2$ – $10 \times 10^{13}$ NO, $5 \times 10^{12}$ – $10^{14}$ NO <sub>2</sub> , $5$ – $10 \times 10^{18}$ CH <sub>4</sub> in $2.5 \times 10^{19}$ molec cm <sup>-3</sup> N <sub>2</sub> /O <sub>2</sub> mixture Relative to CH <sub>4</sub> + OH		1.5
Fifer (1976)	1000–1400	Shock-tube. 12–33% NO, 2% H <sub>2</sub> O, 0.1–0.4% NO <sub>2</sub> in $2$ – $8 \times 10^{19}$ Ar	$2.6 \times 10^{-12}$	1.4
Recommendations:	300–2500		$2.1 \times 10^{-14} T \exp(-68/T)$	2 (300–1000 K) 5 (1000–2500 K)

### Comments

The earlier data of Cox and coworkers have been discounted (Cox, Derwent, and Holt (1976)), and we restrict our discussion to data published after 1975. The three papers published by Cox and coworkers since then give data on relative rate constants for the title reaction relative to the rate constants for the reaction of OH with CO, H<sub>2</sub>, and CH<sub>4</sub>. We have put these on an absolute basis using recommended values for the reference rate constants from Atkinson *et al.* The average of the three values is  $6.6 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The IUPAC recommendation (Atkinson *et al.* (1989)) is based on the data of Jenkin and Cox (1987). The latter measured directly the decay of OH. The reaction system is complex, and the derived rate constant requires a knowledge of several other rate constants. However, the dependence of the derived rate constant is not directly proportional to these other rate constants, and it is difficult to see how uncertainties in those quantities could contribute more than a 50% uncertainty to the final number. The relative rate data taken at atmospheric pressure are slightly higher than the absolute rate constants measured at 1.5 kPa. However, the difference is probably within the overall experimental uncertainty, and there is no reason to expect a significant pressure dependence.

The shock-tube results of Fifer (1976) are not in agreement with the lower temperature measurements. The interpretation of the shock-tube experiments is based on the assumption that the reaction  $\text{HNO}_2 \leftrightarrow \text{OH} + \text{NO}$  was in equilibrium and that the rate limiting step was  $\text{OH} + \text{HNO}_2$ . The assumption appears to be valid based on the great excess of NO used in these studies and the analysis of the system based on a steady state assumption for

OH (we have carried out a computer modeling calculation for the system to verify that OH was in a steady state under the conditions of the experiment).

In our judgement the lower temperature data must be given the greatest weight, but the disagreement between the two absolute data sets increases the degree of uncertainty in the recommendation. The recommended value is based on the data of Jenkin and Cox fitted to the expression  $k = A T \exp(-B/T)$ . At 1200 K, the recommended rate constant is about a factor of 10 greater than the shock-tube value.

### References

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### 12.7 $\text{HNO}_2 + \text{CHO} \rightarrow \text{H}_2\text{CO} + \text{NO}_2$

Reference	Conditions		Reaction rate constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty
	$T$ range/K	$[M]$ range/ $\text{cm}^3$		
$\text{Log}_{10}k_p = -1.2537 + 2.4644 \times 10^3/T - 5.5108 \times 10^4/T^2 + 9.7338 \times 10^5/T^3$				
Recommendation			$2 \times 10^{-21} T^{2.37} \exp(-1940/T)$	2, 400-500 K 5, 300, 1000 K

### Comments

There are no data on the rate constants for this reaction. However, from the rate expression for the reverse process (10,6) and the equilibrium constant we obtain the following rate expression,

$$k(\text{HNO}_2 + \text{CHO} \rightarrow \text{H}_2\text{CO} + \text{NO}_2) = 2 \times 10^{-21} T^{2.37} \exp(-1940/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 2 in the temperature range of 400-500 K and increasing to a factor of 5 at 300 K and 1000 K. Above 1000 K the instability of the reactants will make this process unimportant.

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April, 1989

## 13.0 HCN+M→H+CN+M

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Szekely <i>et al.</i> (1984)[a]	2700–3600	12–200 ppm HCN in 6–20 × 10 <sup>17</sup> Ar CN concentration via 388.0–388.4nm absorption	1.7 × 10 <sup>-8</sup> exp(-54650/ <i>T</i> )	2
Szekely <i>et al.</i> (1982)[b]	3570–5036	3–142 ppm HCN in 2.5–6 × 10 <sup>17</sup> Ar. CN concentration via emission at 388.3nm.	6.7 × 10 <sup>-10</sup> exp(-44740/ <i>T</i> )	2
Tabayashi <i>et al.</i> (1977)	2600–3600	0.2–1% HCN in 7–33 × 10 <sup>18</sup> Ar CN concentration via absorption at 388.3nm	2.1 × 10 <sup>-8</sup> exp(-50196/ <i>T</i> )	2
Roth and Just (1976)	2200–2700	125–500 ppm HCN in 6 × 10 <sup>18</sup> Ar. H-atom concentration by resonance absorption	9.5 × 10 <sup>-8</sup> exp(-59060/ <i>T</i> )	1.5
Recommendation			$k_{\infty} = 8.3 \times 10^{17} (1/T)^{0.93} \exp(-62294/T) / s$ $k(0, N_2) = 5.93 \times 10^2 (1/T)^2 \exp(-62845/T) / s$ $F_c(N_2) = 0.95 - 10^{-4} T$ $k(0, CO_2) = 2.1 \times 10^2 (1/T)^{2.44} \exp(-62800/T)$ $F_c(CO_2) = 0.875 - 0.5 \times 10^{-4} T$	1.5

## Comments

The results of all the investigations except for that of Tabayashi and coworkers are in substantial agreement. The rate expression for HCN decomposition in Argon at high temperatures can be expressed as;

$$k(\text{HCN} + \text{Ar} \rightarrow \text{H} + \text{CN} + \text{Ar}) = 5.6 \times 10^{11} (1/T)^{5.13} \exp(-66966/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with an uncertainty of a factor of 1.5 over the temperature range of 2200–5000 K. The expression given here has been determined on the basis of RRKM calculations at the low pressure limit using a step size down of 1000 cm<sup>-1</sup>. The fit can be found in Fig. 1. Unfortunately there are no data with other colliders. We assume that for N<sub>2</sub> and CO<sub>2</sub> the step size down is 1500 and 2000 cm<sup>-1</sup> respectively. This leads to the following low pressure rate expressions

$$k(\text{HCN} + \text{N}_2 \rightarrow \text{H} + \text{CN} + \text{N}_2) = 5.93 \times 10^2 (1/T)^2 \exp(-62845/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k(\text{HCN} + \text{CO}_2 \rightarrow \text{H} + \text{CN} + \text{CO}_2) = 2.1 \times 10^2 (1/T)^{2.44} \exp(-62800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Above 10–100 atmosphere pressure effects begin to be important. Assuming that the reverse combination rate expression for the reverse reaction is  $k(\text{CN} + \text{H} \rightarrow \text{HCN})$

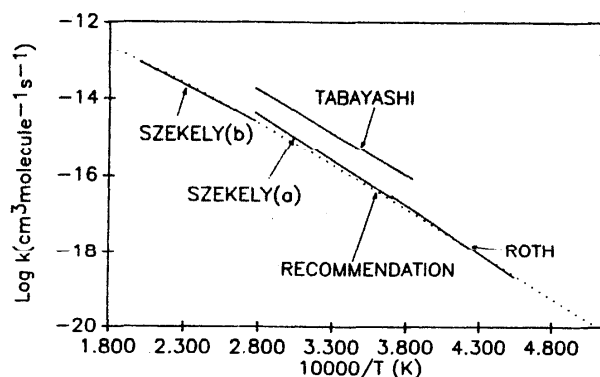


FIG. 1. Summary of experimental data on the reaction  $\text{HCN} + \text{Ar} \rightarrow \text{H} + \text{CN} + \text{Ar}$ . The dotted line represents our recommendation.

$= 2.99 \times 10^{-9} (1/T)^{0.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with an uncertainty of a factor of 3, leads to

$$k(\text{HCN} \rightarrow \text{H} + \text{CN}) = 8.3 \times 10^{17} (1/T)^{0.93} \exp(-62294/T)/s$$

for the reverse reaction. From RRKM calculations we arrive at the values of a  $k/k(0)$  as given in Table 1 for strong colliders. Collision efficiencies for various step sizes down are give in Table 2.

For  $\text{CO}_2$  and  $\text{N}_2$  the  $F_c$  values for converting  $k(0)$  and  $k_\infty$  to rate constants in the intermediate pressure region are

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

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

TABLE 1. Log ( $k/k(0)$ ) for the reaction  $\text{HCN} + \text{HCN} \rightarrow \text{HCN} + \text{HCN}$  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											
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

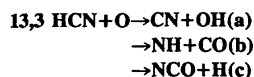
TABLE 2. Collision Efficiency as a Function of Temperature and Step Size Down for  $\text{HCN} + \text{M} \rightarrow \text{H} + \text{CN} + \text{M}$

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

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Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Szekely <i>et al.</i> (1984)	1800–2600	0.44%N <sub>2</sub> O;9.5%HCN in 2.5×10 <sup>18</sup> Ar. Shock tube experiments with absorption detection of NH at 336.1 nm.	$k_b = 3.7 \times 10^{-11} \exp(-7740/T)$	1.4
	2000–2500	116–660 ppm N <sub>2</sub> O and 182–770 ppm HCN. Shock tube experiments with absorption detection of CN at 388.0–388.4 nm	$k_a < 8.3 \times 10^{-11} \exp(-11000/T)$	
Perry and Melius (1984)	575–840	0.5–4.7×10 <sup>15</sup> NO 1.9–1.7×10 <sup>15</sup> O <sub>2</sub> 8.7–65×10 <sup>15</sup> N <sub>2</sub> O in 2–3×10 <sup>18</sup> Ar. Slow flow reactor. O generated by flash photolysis and detected by chemiluminescence. NCO detected by LP-LIF (separate experiments)	$k_{a+b+c} = 9.8 \times 10^{-12} \exp(-4030/T)$ $k_c = 3.3 \times 10^{-16} T^{1.47} \exp(-3800/T)$ $k_b = 9.0 \times 10^{-16} T^{1.21} \exp(-3850/T)$ $k_a = 4.5 \times 10^{-15} T^{1.58} \exp(-13400/T)$	1.1
Louge and Hanson (1984)	1440	0.8%N <sub>2</sub> O;HCN; 0.1%O <sub>2</sub> in Ar. Shock Tube experiments with NCO detection by absorption	$k_c = 8.3 \times 10^{-13}$	2
Roth <i>et al.</i> (1980)	1800–2500	5–40 ppm N <sub>2</sub> O and ppm HCN in 6×10 <sup>18</sup> Ar. Atomic resonance detection of H and O	$k_{c+b} = 1.2 \times 10^{-10} \exp(-7460/T)$ $k_{c+b+a}/k_{c+b} = 1.6$	1.425–200
Davis and Thrush (1968)	450–650	3.3×10 <sup>16</sup> N <sub>2</sub> with traces of O <sub>2</sub> , NO and HCN in discharge flow. O generated by N+NO→N <sub>2</sub> +O reaction and detected by chemiluminescence from O+NO reaction	$k_{a+b+c} = 8.7 \times 10^{-12} \exp(-4080/T)$	1.3
Recommendations:			$k_a = 3.3 \times 10^{-16} T^{1.47} \exp(-3800/T)$ $k_b = 9.0 \times 10^{-16} T^{1.21} \exp(-3850/T)$ $k_c = 4.5 \times 10^{-15} T^{1.58} \exp(-13400/T)$	2

### Comments

Considering the complexity of the process there is remarkably good agreement between all of the experiments. We summarize the results in Fig. 1. Our recommendations are based on the analysis given by

Perry and Melius. It appears to account in a satisfactory manner for all the data to within a factor of 2. The mechanism for channels (a) and (b) undoubtedly involves a hot adduct. It is possible that at lower temperatures and high pressures the adduct will be stabilized. It will then be necessary to consider the reactions of the adduct.

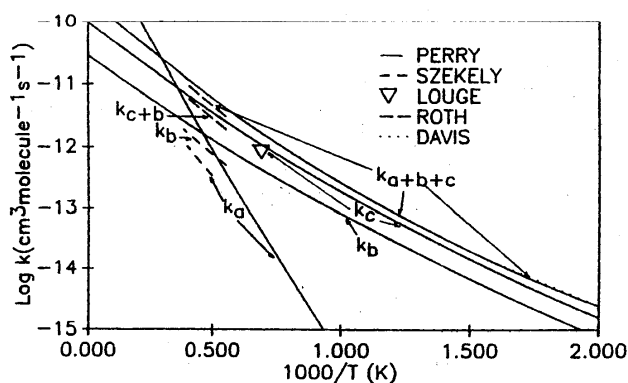
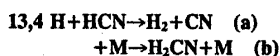


FIG. 1. Summary of data for the reaction O + HCN.

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September, 1989



Reference	Conditions		Reaction rate constant $k/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>		
$\text{Log}_{10}K_p(\text{a}) = 0.35091 - 3.5302 \times 10^3/T - 3.4662 \times 10^5/T^2 + 5.0453 \times 10^7/T^3$				
Baulch <i>et al.</i> (1981)	300–1000		$k_a = 6.3 \times 10^{-10} \exp(-12400/T)$	3
Recommendation:	300–2500		$k_a = 6.2 \times 10^{-10} \exp(-12507/T)$ $k_{b,\infty} = 5.5 \times 10^{-11} \exp(-2438/T)$ $k_b(\text{O}, \text{N}_2) = 4.4 \times 10^{-24} (1/T)^{2.73} \exp(-3855/T)$ $k_b(\text{O}, \text{CO}_2) = 4.3 \times 10^{-24} (1/T)^{2.63} \exp(-3791/T)$ $F_c = 0.95 - 10^{-4}T \quad (\text{CO}_2, \text{N}_2)$	100, 500 K 3 at 2500 K 100, 500 K 10 at 1200 K and above

## Comments

There have been no measurements on the rate constants for these reactions. The rate expression given by Baulch *et al.* for channel (a) is based on their recommendations for the rate expression of the reverse process and the thermodynamics. Our recommendation is based on a similar analysis using the rate expression given below for the  $\text{CN} + \text{H}_2 \rightarrow \text{HCN} + \text{H}(15,1)$  reaction and the thermodynamics. This leads to the rate expression

$$k(\text{HCN} + \text{H} \rightarrow \text{H}_2 + \text{CN}) = 6.2 \times 10^{-10} \exp(-12507/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

It is in excellent agreement with the estimate of Baulch *et al.* There is however an estimated uncertainty of 9 kJ/mol in the heat of formation of the CN radical. Together with the estimated uncertainty in the rate expression for the reverse reaction this can lead to an uncertainty of a factor of 100 at room temperature and de-

creasing to a factor 3 at 2500 K. Fortunately, this reaction can only be important at high temperatures.

At lower temperatures the addition of hydrogen may make contributions. Unfortunately the absence of any data on the kinetics of the process or on the thermodynamic properties of the radical makes it difficult to give reliable estimates at the lower temperatures. Nevertheless we have attempted to make an estimate. This is based on an assumed rate expression for the addition of hydrogen to HCN of

$$k(\text{H} + \text{HCN} \rightarrow \text{H}_2\text{CN}) = 5.5 \times 10^{-11} \exp(-2438/T) \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$$

This is over an order of magnitude smaller than the comparable reaction of hydrogen with ethylene and is not that much different than our estimate for  $\text{H} + \text{HCHO}$ . Combining this with the estimated thermodynamic properties of the  $\text{H}_2\text{CN}$  radical (M. Page, personal communication) the pressure dependent behavior of this reaction

is given on Table I. Collision efficiency as a function of step-size down and the temperature can be found in Table 2.

For reactions in  $N_2$  and  $CO_2$  we suggest the use of the following expressions;

$$k_b(O, N_2) = 4.4 \times 10^{-24} (1/T)^{2.73} \exp(-3855/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$$

$$k_b(O, CO_2) = 4.3 \times 10^{-24} (1/T)^{2.63} \exp(-3791/T) \text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$$

where we have assumed that the step size down

parameter can be represented in the form of  $80(T/300)^1$  for  $N_2$  and  $120(T/300)^1$  for  $CO_2$ . For most purposes these expressions can be used directly. For truly high pressures however use the following  $F_c$  expression

$$F_c = 0.95 - 10^{-4}T$$

It is appropriate for both collisional partners. The users of these expressions are cautioned on the provisional nature of these estimate. At the lower temperatures where this process will be most important we estimate an uncertainty of a factor of 100. This will decrease to a factor of 10 at temperatures in excess of 1200 K.

TABLE 1. Log ( $k/k_\infty$ ) for the reaction  $H + HCN \rightarrow H_2CN$  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	-3.35	-3.37	-3.42	-3.49	-3.56	-3.63	-3.71	-3.78	-3.85	-3.92	-3.98
17.5	-2.85	-2.87	-2.92	-2.99	-3.06	-3.13	-3.21	-3.28	-3.35	-3.42	-3.48
18	-2.35	-2.37	-2.42	-2.49	-2.56	-2.64	-2.71	-2.78	-2.85	-2.92	-2.99
18.5	-1.86	-1.88	-1.93	-1.99	-2.06	-2.14	-2.21	-2.29	-2.36	-2.42	-2.49
19	-1.37	-1.39	-1.44	-1.51	-1.58	-1.65	-1.73	-1.80	-1.87	-1.93	-2.00
19.5	-0.91	-0.93	-0.98	-1.05	-1.11	-1.19	-1.26	-1.33	-1.40	-1.46	-1.52
20	-0.52	-0.54	-0.59	-0.65	-0.71	-0.78	-0.84	-0.91	-0.97	-1.03	-1.09
20.5	-0.24	-0.26	-0.30	-0.35	-0.40	-0.45	-0.51	-0.56	-0.62	-0.67	-0.71
21	-0.09	-0.11	-0.13	-0.16	-0.20	-0.23	-0.27	-0.31	-0.35	-0.38	-0.42
21.5	-0.03	-0.04	-0.05	-0.07	-0.08	-0.10	-0.12	-0.15	-0.17	-0.19	-0.21
22	-0.01	-0.01	-0.02	-0.02	-0.03	-0.04	-0.05	-0.06	-0.07	-0.08	-0.09

TABLE 2. Collision efficiency as a function of temperature and step size down for the reaction  $OH + NO_2 + M \rightarrow HNO_3 + M$

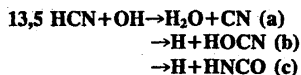
Step Size ( $\text{cm}^{-1}$ )	200	400	800	1600	3200
Temp (K)					
500	$1.1 \times 10^{-1}$	$2.5 \times 10^{-1}$	$4.4 \times 10^{-1}$	$6.4 \times 10^{-1}$	$7.9 \times 10^{-1}$
700	$6.4 \times 10^{-2}$	$1.6 \times 10^{-1}$	$3.3 \times 10^{-1}$	$5.3 \times 10^{-1}$	$7.1 \times 10^{-1}$
900	$4.0 \times 10^{-2}$	$1.1 \times 10^{-1}$	$2.5 \times 10^{-1}$	$4.5 \times 10^{-1}$	$6.4 \times 10^{-1}$
1100	$2.7 \times 10^{-2}$	$7.9 \times 10^{-2}$	$1.9 \times 10^{-1}$	$3.7 \times 10^{-1}$	$5.7 \times 10^{-1}$
1300	$1.8 \times 10^{-2}$	$5.7 \times 10^{-2}$	$1.5 \times 10^{-1}$	$3.1 \times 10^{-1}$	$5.1 \times 10^{-1}$
1500	$1.3 \times 10^{-2}$	$4.2 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.6 \times 10^{-1}$	$4.5 \times 10^{-1}$
1700	$9.3 \times 10^{-3}$	$3.1 \times 10^{-2}$	$8.9 \times 10^{-2}$	$2.1 \times 10^{-1}$	$4.0 \times 10^{-1}$
1900	$6.9 \times 10^{-3}$	$2.3 \times 10^{-2}$	$7.0 \times 10^{-2}$	$1.8 \times 10^{-1}$	$3.5 \times 10^{-1}$
2100	$5.1 \times 10^{-3}$	$1.8 \times 10^{-2}$	$5.5 \times 10^{-2}$	$1.5 \times 10^{-1}$	$3.0 \times 10^{-1}$
2300	$3.9 \times 10^{-3}$	$1.4 \times 10^{-2}$	$4.4 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.6 \times 10^{-1}$
2500	$2.9 \times 10^{-3}$	$1.1 \times 10^{-2}$	$3.5 \times 10^{-2}$	$9.9 \times 10^{-2}$	$2.3 \times 10^{-1}$

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August, 1989





Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Log <sub>10</sub> K <sub>p</sub> (a) = -0.27893 - 3.0125 × 10 <sup>2</sup> /T - 2.6722 × 10 <sup>5</sup> /T <sup>2</sup> + 3.5241 × 10 <sup>7</sup> /T <sup>3</sup>				
Miller and Melius (1986) theory	500-2500		k <sub>b</sub> = 5.3 × 10 <sup>-20</sup> T <sup>2.45</sup> exp(-6100/T) k <sub>c</sub> = 9.3 × 10 <sup>-30</sup> T <sup>4.71</sup> exp(248/T)	?
Fritz <i>et al.</i> (1984)	298-500	0.2-2 × 10 <sup>19</sup> HCN in 0.3-12 × 10 <sup>19</sup> N <sub>2</sub> OH from flash photolysis of HNO <sub>3</sub> in static system. Detected via resonance absorption	k <sub>a+b+c</sub> = 1.2 × 10 <sup>-13</sup> exp(-400/T)	1.4
Phillips, 1979	298-563	2-8 × 10 <sup>15</sup> HCN in 4 × 10 <sup>17</sup> He or Ar in discharge flow with OH from H + NO <sub>2</sub> . Resonance fluorescence detection of OH	k <sub>a+b+c</sub> = 1.6 × 10 <sup>-11</sup> (1/T)exp(-1863/T)	1.4
Szekely <i>et al.</i>	2460-2840	83-450 ppm C <sub>2</sub> N <sub>2</sub> 603-2320 ppm H <sub>2</sub> O in 1.7 × 10 <sup>18</sup> Ar. Shock tube study CN detected via absorption at 388.3nm OH detected via absorption at 306.67nm	k <sub>a</sub> = 2.9 × 10 <sup>-12</sup> (2100 K?) from reverse and equilibrium constant	1.5
Recommendations:			k <sub>a</sub> = 3.6 × 10 <sup>-17</sup> T <sup>1.5</sup> exp(-3887/T) k <sub>b</sub> = 5.3 × 10 <sup>-20</sup> T <sup>2.45</sup> exp(-6100/T) k <sub>c</sub> = 9.3 × 10 <sup>-30</sup> T <sup>4.71</sup> exp(248/T)	1.5 at 2500 K 3 at 1000 K 5 at 2000 K

### Comments

The only direct studies are those of Fritz and coworkers and Phillips for the total rate constant. The disagreement between the two set of data is, as suggested by Fritz *et al.*, due to the measurements being carried out at different pressures. The mechanism is clearly a direct abstraction (a) and an addition process followed by hydrogen ejection either before or after isomerization (b,c). At low temperatures and high pressures it will be necessary to consider the reactions of the HCOHN\* radical. Unfortunately, the properties of this radical are very uncertain and it is thus not possible to make an estimate of its lifetime. Our recommendation for the abstraction rate constant is based on the rate expression determined by Szekely and coworkers for the reverse reaction and the thermodynamics and the assumption of a T<sup>1.5</sup> dependence of the preexponential factor. It runs smoothly into the higher temperature results of Fritz and coworkers. The recommendations for channels (b) and (c) are the results of the theoretical calculations of Miller and Melius. It is in reasonable agreement with the results of flame studies by Haynes (Combustion and Flame,

1977, 28, 113), but is divergent from the results of Fenimore (17th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1979, pp. 669). It is probably not applicable to lower temperatures (below 1000K and higher pressures since the calculations does not take into account contributions from the hot adduct. We are also uncertain of the absolute reliability of this sort of calculations. However the flame results, which involves an assumed mechanism, does provide a check of the data.

### References

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 Fritz, B., Lorenz, K., Steinert, W. and Zellner, R., "Rate of Oxidation of HCN by OH Radicals at Lower Temperatures", *Oxidation Communications* **6**, 363, 1984.  
 Szekely, A., Hanson, R. K. and Bowman, C. T., "High Temperature Determination of the Rate Coefficient for the Reaction H<sub>2</sub>O + CN → HCN + OH" *Int. J. Chem. Kin.*, **16**, 1609, 1984.

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 October, 1989

13,7 HCN+CHO→HCHO+CN

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Log K <sub>p</sub> = -0.62848 - 7.4327 × 10 <sup>3</sup> /T - 3.782 × 10 <sup>4</sup> /T <sup>2</sup> - 3.9677 × 10 <sup>5</sup> /T <sup>3</sup>				
Recommendation:			1 × 10 <sup>-11</sup> exp(-17200/T)	20 at 300 K 4 at 1000 K

Comment

$$k(\text{HCN} + \text{CHO} \rightarrow \text{HCHO} + \text{CN}) = 1 \times 10^{-11} \exp(-17200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

There are no data on the rate constants for this reaction. However, the rate constants for the reverse reaction should be very fast. We combine the data on OH+HCHO and CN+ the secondary hydrogen in propane and estimate the rate expression for the CN+HCHO reaction as 4 × 10<sup>-11</sup> cm<sup>3</sup>molecule<sup>-1</sup>s<sup>-1</sup> and through the thermodynamics obtain

with an uncertainty of a factor of 20 at room temperature and decreasing to a factor of 4 at 1000 K.

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14,0: N<sub>2</sub>O → N<sub>2</sub> + O

Reference	Conditions		Reaction rate constant	Uncertainty																																																								
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>																																																									
Hanson and Salimian(1985) review	1500-3600		1.15xT <sup>-2.5</sup> exp(-32710/T)(Ar,Kr)	1.2																																																								
Loirat <i>et al.</i> (1985)	1080-1227	Static experiments with gas chromatographic analysis of reactant and products 9-60 × 10 <sup>17</sup> total pressure. N <sub>2</sub> O; 33N <sub>2</sub> O + 0.67CO <sub>2</sub> ; 05N <sub>2</sub> O 0.95N <sub>2</sub>	<table border="0"> <tr> <td></td> <td colspan="3" style="text-align: center;">molecule/cm<sup>3</sup></td> </tr> <tr> <td>T(K)</td> <td>9 × 10<sup>17</sup></td> <td>1.8 × 10<sup>17</sup></td> <td>6 × 10<sup>16</sup></td> </tr> <tr> <td>1080(N<sub>2</sub>O)</td> <td>6.8 × 10<sup>-3</sup></td> <td>4.4 × 10<sup>-3</sup></td> <td>3.4 × 10<sup>-3</sup></td> </tr> <tr> <td>(s<sup>-1</sup>)(N<sub>2</sub>)</td> <td>6.1 × 10<sup>-3</sup></td> <td>3.9 × 10<sup>-3</sup></td> <td>2.5 × 10<sup>-3</sup></td> </tr> <tr> <td>(CO<sub>2</sub>)</td> <td></td> <td>4.4 × 10<sup>-3</sup></td> <td></td> </tr> <tr> <td>1128(N<sub>2</sub>O)</td> <td>2.0 × 10<sup>-2</sup></td> <td>1.3 × 10<sup>-2</sup></td> <td>3.4 × 10<sup>-3</sup></td> </tr> <tr> <td>(s<sup>-1</sup>)(N<sub>2</sub>)</td> <td>1.8 × 10<sup>-2</sup></td> <td>1.2 × 10<sup>-2</sup></td> <td>6.6 × 10<sup>-3</sup></td> </tr> <tr> <td>(CO<sub>2</sub>)</td> <td></td> <td>1.1 × 10<sup>-2</sup></td> <td></td> </tr> <tr> <td>1178(N<sub>2</sub>O)</td> <td>5.7 × 10<sup>-2</sup></td> <td>3.4 × 10<sup>-2</sup></td> <td>1.9 × 10<sup>-2</sup></td> </tr> <tr> <td>(s<sup>-1</sup>)(N<sub>2</sub>)</td> <td>5.1 × 10<sup>-2</sup></td> <td>3.3 × 10<sup>-2</sup></td> <td>1.7 × 10<sup>-3</sup></td> </tr> <tr> <td>(CO<sub>2</sub>)</td> <td></td> <td>2.8 × 10<sup>-2</sup></td> <td></td> </tr> <tr> <td>1227(N<sub>2</sub>O)</td> <td>1.5 × 10<sup>-1</sup></td> <td>8.4 × 10<sup>-2</sup></td> <td>4.1 × 10<sup>-2</sup></td> </tr> <tr> <td>(s<sup>-1</sup>)(N<sub>2</sub>)</td> <td>1.3 × 10<sup>-2</sup></td> <td>8.4 × 10<sup>-2</sup></td> <td>4.0 × 10<sup>-3</sup></td> </tr> <tr> <td>(CO<sub>2</sub>)</td> <td></td> <td>7.2 × 10<sup>-2</sup></td> <td></td> </tr> </table>		molecule/cm <sup>3</sup>			T(K)	9 × 10 <sup>17</sup>	1.8 × 10 <sup>17</sup>	6 × 10 <sup>16</sup>	1080(N <sub>2</sub> O)	6.8 × 10 <sup>-3</sup>	4.4 × 10 <sup>-3</sup>	3.4 × 10 <sup>-3</sup>	(s <sup>-1</sup> )(N <sub>2</sub> )	6.1 × 10 <sup>-3</sup>	3.9 × 10 <sup>-3</sup>	2.5 × 10 <sup>-3</sup>	(CO <sub>2</sub> )		4.4 × 10 <sup>-3</sup>		1128(N <sub>2</sub> O)	2.0 × 10 <sup>-2</sup>	1.3 × 10 <sup>-2</sup>	3.4 × 10 <sup>-3</sup>	(s <sup>-1</sup> )(N <sub>2</sub> )	1.8 × 10 <sup>-2</sup>	1.2 × 10 <sup>-2</sup>	6.6 × 10 <sup>-3</sup>	(CO <sub>2</sub> )		1.1 × 10 <sup>-2</sup>		1178(N <sub>2</sub> O)	5.7 × 10 <sup>-2</sup>	3.4 × 10 <sup>-2</sup>	1.9 × 10 <sup>-2</sup>	(s <sup>-1</sup> )(N <sub>2</sub> )	5.1 × 10 <sup>-2</sup>	3.3 × 10 <sup>-2</sup>	1.7 × 10 <sup>-3</sup>	(CO <sub>2</sub> )		2.8 × 10 <sup>-2</sup>		1227(N <sub>2</sub> O)	1.5 × 10 <sup>-1</sup>	8.4 × 10 <sup>-2</sup>	4.1 × 10 <sup>-2</sup>	(s <sup>-1</sup> )(N <sub>2</sub> )	1.3 × 10 <sup>-2</sup>	8.4 × 10 <sup>-2</sup>	4.0 × 10 <sup>-3</sup>	(CO <sub>2</sub> )		7.2 × 10 <sup>-2</sup>		?
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Endo <i>et al.</i> (1979)	2000	Shock tube studies with reaction followed by UV absorption 4-30 × 10 <sup>18</sup> Ne Ar Kr Xe N <sub>2</sub> CF <sub>4</sub>	<table border="0"> <tr><td>6.6 × 10<sup>-16</sup></td></tr> <tr><td>3.5 × 10<sup>-16</sup></td></tr> <tr><td>3.0 × 10<sup>-16</sup></td></tr> <tr><td>2.3 × 10<sup>-16</sup></td></tr> <tr><td>4.5 × 10<sup>-16</sup></td></tr> <tr><td>2.2 × 10<sup>-15</sup></td></tr> </table>	6.6 × 10 <sup>-16</sup>	3.5 × 10 <sup>-16</sup>	3.0 × 10 <sup>-16</sup>	2.3 × 10 <sup>-16</sup>	4.5 × 10 <sup>-16</sup>	2.2 × 10 <sup>-15</sup>	2.0																																																		
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Baulch <i>et al.</i> (1973) review	1300-2500 1300-2500 888		$k_{\infty} = 1.3 \times 10^{11} \exp(-30000/T) \text{ s}^{-1}$ $k(0, \text{Ar}) = 8.3 \times 10^{-10} \exp(-29000/T)$ $k(0, \text{N}_2\text{O}) = 4.5 \times 10^{-9} \exp(-29800/T)$	1.5																																																								
Recommendations	700-2500		$k_{\infty} = 1.3 \times 10^{11} \exp(-30000/T)$ $k(0, \text{N}_2) = 1.2 \times 10^{-6} T^{-0.73} \exp(-31600/T)$ $F_c(\text{N}_2) = 1.167 - 1.25 \times 10^{-4} T$ $k(0, \text{CO}_2) = 2 \times 10^{-6} T^{-0.67} \exp(-31300/T)$ $F_c(\text{CO}_2) = 1.167 - 1.25 \times 10^{-4} T$	2																																																								

## Comments

Except for the most recent results of Loirat *et al.*, the existing data on this reaction are in excellent agreement. The recommendations of Baulch *et al.* and Hanson and Salamanian for the low pressure reaction rate constants in argon are in essential agreement. However, if one extrapolates the values to 900 K there appear to be a factor of 2 to 3 discrepancy with the older work of Johnston (J. Chem. Phys., 1953, 19, 663) using the collision efficiencies as summarized in the review of Baulch and coworkers. We have therefore made a slight adjustment of the rate expression for argon so as to fit the low temperature data. The general situation is summarized in Fig. 1. We have also included in Fig. 1 some of the results of Lorient *et al.* If their results are correct we will have to revise completely our thinking about this reaction. We believe that their measurements are seriously distorted by surface effects. With our recommendations for argon as a basis we have chosen step sizes down for N<sub>2</sub> that will lead to rate constants approximately a factor of 1.5 higher than our recommendations for argon. For CO<sub>2</sub> we have used the results of Endo and coworker with CF<sub>4</sub> as the collision partner. The data suggest that the rate constants will be a factor of 5 or 6 time larger than that in Ar. The high pressure recommendations of Baulch cover data ranging from 888–2100 K appear to be satisfactory. The results of RRKM calculations are summarized in Tables 1 and 2. Note that in order to fit the results very small step-sizes down are necessary. This is presumably a reflection of the spin forbidden nature of the reaction.

These considerations lead to the following closed expressions for N<sub>2</sub>O decomposition in N<sub>2</sub> and CO<sub>2</sub>;

$$\begin{aligned}k_{\infty} &= 1.3 \times 10^{11} \exp(-30000/T) \\k(0, \text{N}_2) &= 1.2 \times 10^{-6} T^{-0.73} \exp(-31600/T) \\F_c(\text{N}_2) &= 1.167 - 1.25 \times 10^{-4} T \\k(0, \text{CO}_2) &= 2 \times 10^{-6} T^{-0.67} \exp(-31300/T) \\F_c(\text{CO}_2) &= 1.167 - 1.25 \times 10^{-4} T.\end{aligned}$$

We estimate the uncertainties to be a factor of 2.

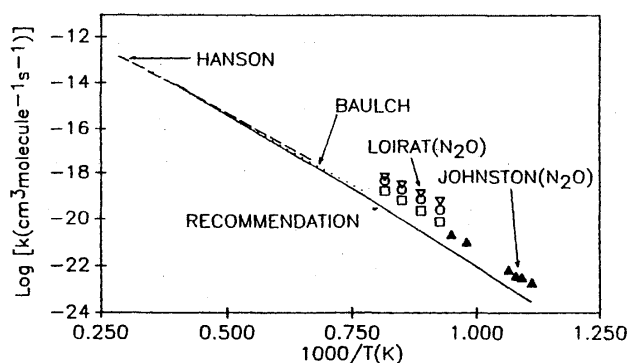


FIG. 1. Second order rate constants for N<sub>2</sub>O decomposition in the presence of argon. Triangles are results of Johnston in N<sub>2</sub>O. Open squares ( $9 \times 10^{17}$ ), circles ( $1.8 \times 10^{17}$ ) and triangles ( $6 \times 10^{16}$ ) are results of Lorient *et al.* in N<sub>2</sub>O and converted to second order rate constants. Note that due to the lack of pressure dependence in the work of Lorient *et al.*, their other points will fall close to the points in the plot.

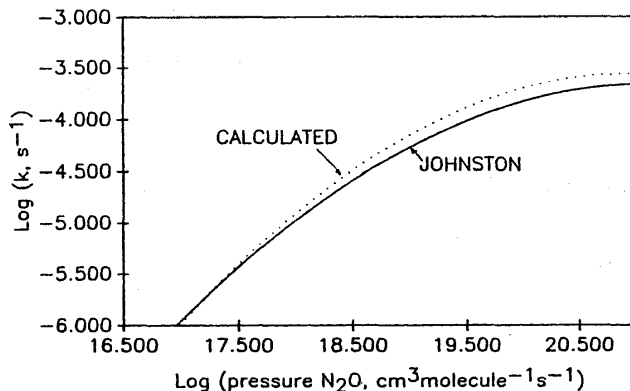


FIG. 2. Comparison of calculated and experimental pressure dependence for N<sub>2</sub>O decomposition in N<sub>2</sub>O.

TABLE I. Log ( $k/k_{\infty}$ ) for the reaction N<sub>2</sub>O + N<sub>2</sub>O → N<sub>2</sub> + O + N<sub>2</sub>O 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)											
16.0	-1.61	-1.65	-1.70	-1.76	-1.82	-1.88	-1.94	-2.00	-2.05	-2.10	-2.15
16.5	-1.14	-1.17	-1.22	-1.28	-1.34	-1.40	-1.45	-1.52	-1.57	-1.62	-1.67
17	-0.71	-0.74	-0.79	-0.85	-0.90	-0.96	-1.02	-1.07	-1.12	-1.17	-1.22
17.5	-0.37	-0.40	-0.44	-0.49	-0.55	-0.60	-0.65	-0.69	-0.74	-0.79	-0.83
18	-0.16	-0.18	-0.22	-0.25	-0.29	-0.33	-0.37	-0.41	-0.44	-0.48	-0.51
18.5	-0.06	-0.07	-0.09	-0.11	-0.13	-0.16	-0.18	-0.21	-0.23	-0.26	-0.28
19	-0.02	-0.03	-0.03	-0.04	-0.05	-0.07	-0.08	-0.09	-0.10	-0.12	-0.13
19.5	-0.01	-0.01	-0.01	-0.01	-0.02	-0.02	-0.03	-0.03	-0.04	-0.05	-0.05
20					-0.01	-0.01	-0.01	-0.01	-0.01	-0.02	-0.02
20.5										-0.01	-0.01

TABLE 2. Collision efficiency as a function of temperature and step size down for  $N_2O + M = N_2 + O + M$ 

Step Size ( $cm^{-1}$ )	50	100	200	400	800
Temp (K)					
500	$1.4 \times 10^{-2}$	$4.4 \times 10^{-2}$	$1.2 \times 10^{-1}$	$2.7 \times 10^{-1}$	$4.6 \times 10^{-1}$
700	$7.4 \times 10^{-3}$	$2.5 \times 10^{-2}$	$7.5 \times 10^{-2}$	$1.8 \times 10^{-1}$	$3.6 \times 10^{-1}$
900	$4.5 \times 10^{-3}$	$1.6 \times 10^{-2}$	$5.0 \times 10^{-2}$	$1.3 \times 10^{-1}$	$2.9 \times 10^{-1}$
1100	$3.0 \times 10^{-3}$	$1.1 \times 10^{-2}$	$3.6 \times 10^{-2}$	$1.0 \times 10^{-1}$	$2.3 \times 10^{-1}$
1300	$2.1 \times 10^{-3}$	$7.8 \times 10^{-3}$	$2.6 \times 10^{-2}$	$7.8 \times 10^{-2}$	$1.9 \times 10^{-1}$
1500	$1.6 \times 10^{-3}$	$5.8 \times 10^{-3}$	$2.0 \times 10^{-2}$	$6.2 \times 10^{-2}$	$1.6 \times 10^{-1}$
1700	$1.2 \times 10^{-3}$	$4.5 \times 10^{-3}$	$1.6 \times 10^{-2}$	$5.0 \times 10^{-2}$	$1.3 \times 10^{-1}$
1900	$9.3 \times 10^{-4}$	$3.5 \times 10^{-3}$	$1.3 \times 10^{-2}$	$4.0 \times 10^{-2}$	$1.1 \times 10^{-1}$
2100	$7.4 \times 10^{-4}$	$2.8 \times 10^{-3}$	$1.0 \times 10^{-2}$	$3.3 \times 10^{-2}$	$9.5 \times 10^{-2}$
2300	$6.0 \times 10^{-4}$	$2.3 \times 10^{-3}$	$8.3 \times 10^{-3}$	$2.8 \times 10^{-2}$	$8.2 \times 10^{-2}$
2500	$4.9 \times 10^{-4}$	$1.9 \times 10^{-3}$	$6.9 \times 10^{-3}$	$2.4 \times 10^{-2}$	$7.1 \times 10^{-2}$

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- Hanson, R. K. and Salimian, S. "Survey of Rate Constants in the N/H/O System" in "Combustion Chemistry" (Gardiner, W. C., ed) Springer-Verlag, New York, p361, 1985.

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14,3  $N_2O + O \rightarrow O_2 + N_2$  (a)  
 $\rightarrow NO + NO$  (b)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/ $cm^3$	$k/cm^3 molecule^{-1} s^{-1}$	
Hidaka <i>et al.</i> (1985)	1450-2200	2% $N_2O$ 2% $N_2O$ , 1% $H_2$ 1% $N_2O$ , 0.5% $H_2$ 0.5% $N_2O$ , 1% $H_2$ in argon at $2-17 \times 10^{18}$ total pressure. Shock tube experiments in incident and reflected shock Detection of $N_2O$ by infra-red emission. $N_2O$ , $O_2$ , $NO$ analysis by mass spectrometry from abstracted sample behind reflected shocks.	$k_a = 1.7 \times 10^{-9} \exp(-14100/T)$ $k_b = 9.3 \times 10^{-10} \exp(-14100/T)$	3
Hanson and Salimian (1985) review	1200-4100		$k_a = 1.7 \times 10^{-10} \exp(-14100/T)$ $k_b = 1.1 \times 10^{-10} \exp(-13400/T)$	2
Recommendation:			$k_a = 1.7 \times 10^{-10} \exp(-14100/T)$ $k_b = 1.1 \times 10^{-10} \exp(-13400/T)$	2

## Comments

The recent work of Hidaka and coworkers leads to rate constants that are close to an order of magnitude larger than the recommendations of Hanson and Salimian. The latter is very close to the earlier recommendations of Baulch and coworkers ("Evaluated Kinetic Data for High Temperature Reactions Vol. 2, Homogeneous Gas Phase Reactions of the  $H_2-N_2-O_2$  System", Butterworths, London, 1973) and contains a great deal of new data. It also includes data derived from the rate constant for the reverse process and the thermodynamics (see 9,9). The results of Hidaka and coworkers replicate the data from very similar experiments by Henrici and Bauer (J. Chem. Phys., 1969, 50, 1333). We suspect that there are problems in the interpretation of the  $N_2O-H_2$  system. One

possibility is the contributions from the reaction of  $OH+N_2O$ . The recommended rate expressions are those of Hanson and Salimian with an uncertainty of a factor of 2.

## References

- Hanson, R. K. and Salimian, S. "Survey of Rate Constants in the N/H/O System" in "Combustion Chemistry" (Gardiner, W. C., ed) Springer-Verlag, New York, p361, 1985.  
 Hidaka, Y., Takuma, H. and Suga, M. "Shock-tube Studies on  $N_2O$  Decomposition and  $N_2O-H_2$  Reaction", Bull. Chem. soc., Jpn, 58, 2911, 1985.

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14,4  $N_2O+H \rightarrow N_2+OH$ 

Reference	Conditions		Reaction rate constant $k/cm^3molecule^{-1}s^{-1}$	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>		
Hidaka <i>et al.</i> (1985)	1450-2200	2% $N_2O$ 2% $N_2O$ , 1% $H_2$ 1% $N_2O$ , 0.5% $H_2$ 0.5% $N_2O$ , 1% $H_2$ in argon at $2-17 \times 10^{18}$ total pressure. Shock tube experiments in incident and reflected shock Detection of $N_2O$ by infra-red emission. $N_2O$ , $O_2$ , $NO$ analysis by mass spectrometry from extracted sample behind reflected shocks	$2.5 \times 10^{-10} \exp(-7550/T)$	1.5
Hanson and Salimian (1985) (review)	700-2500		$1.3 \times 10^{-10} \exp(-7600/T)$	1.7
Recommendation			$1.6 \times 10^{-10} \exp(-7600/T)$	1.7

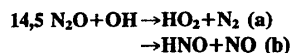
## Comment

The review of Hanson and Salimian endorses the recommendations of Baulch and coworkers ("Evaluated Kinetic Data for High Temperature Reactions Vol. 2, Homogeneous Gas Phase Reactions of the  $H_2-N_2-O_2$  System", Butterworths, London, 1973). The recent work of Hidaka and coworkers lead to rate constants that are slightly less than a factor of 2 larger. All of these values are within the spread of expected uncertainties. Our recommendations takes into account the work of Hidaka and coworkers through a slight increase in the rate expression of Hanson and Salimian.

## References

- Hanson, R. K. and Salimian, S. "Survey of Rate Constants in the N/H/O System" in "Combustion Chemistry" (Gardiner, W. C., ed) Springer-Verlag, New York, p361, 1985.  
 Hidaka, Y., Takuma, H. and Suga, M. "Shock-tube Studies on  $N_2O$  Decomposition and  $N_2O-H_2$  Reaction", Bull. Chem. soc., Jpn, 58, 2911, 1985.

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Reference	Conditions		Reaction rate constant	Uncertainty
	<i>T</i> range/K	[M] range/cm <sup>3</sup>	<i>k</i> /cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Chang and Kaufman (1977)	298–480	1–3 × 10 <sup>11</sup> OH from H + NO <sub>2</sub> with 0.6–21 × 10 <sup>14</sup> N <sub>2</sub> O in 2–14 × 10 <sup>15</sup> He. Resonance absorption detection of OH	<4 × 10 <sup>-16</sup>	
Biermann <i>et al.</i> (1976)	298	10 <sup>17</sup> H <sub>2</sub> O in 0–3 × 10 <sup>18</sup> N <sub>2</sub> O and 0–1.5 × 10 <sup>18</sup> Ar OH via flash photolysis and detected via resonance absorption	3.8 × 10 <sup>-17</sup>	1.3
Atkinson <i>et al.</i> (1976)	298–443	2–6 × 10 <sup>14</sup> H <sub>2</sub> O, 1–5 × 10 <sup>16</sup> N <sub>2</sub> O in 1–2 × 10 <sup>18</sup> Ar. OH from flash vacuum photolysis of OH. Detection via resonance absorption.	<2 × 10 <sup>-16</sup>	
Gordon and Mulac (1975)	440	2–20 × 10 <sup>17</sup> N <sub>2</sub> O in 1.7 × 10 <sup>19</sup> H <sub>2</sub> O. OH via pulse radiolysis. Detected through resonance absorption	<2 × 10 <sup>-14</sup>	
Recommendation			$k_{a+b} < 1.4 \times 10^{-11} \exp(-5000/T)$	

### Comments

The rate constants at lower temperatures for these reactions must be very small. Our recommendation is based on an assumed A-factor and an activation energy that leads to rate constants that match the upper limit of the results of Chang and Kaufman. Note that there are two possible channels. We suspect that at higher temperatures there will be some contribution from these reactions. In the decomposition of N<sub>2</sub>O in the presence of H<sub>2</sub> there appear to be a systematic and reproducible difference from decomposition in N<sub>2</sub>O alone (see 14,3). This may be due to the neglect of contributions from these reactions.

### References

- Atkinson, R., Perry, R. A., and Pitts, J. N., "Kinetics of the Reactions of OH Radicals with CO and N<sub>2</sub>O" *Chem. Phys. Lett.*, **44**, 204, 1976.
- Biermann, H. W., Zetzsch, C. and Stuhl, F., "Rate Constants for the Reaction of OH with N<sub>2</sub>O at 298 K" *Ber. Bunseng. physik. Chem.* **80**, 909, 1976.
- Chang, J. S. and Kaufman, F., "Upper Limits of the Rate Constants for the Reactions of CFCl<sub>3</sub>(F—11), CF<sub>2</sub>Cl<sub>2</sub>(F—12), and N<sub>2</sub>O with OH. Estimates of Corresponding Lower limits to their Tropospheric Lifetimes", *Geophysical Research Letters* **4**, 192, 1977.
- Gordon, S., and Mulac, W. A., "Reaction of the OH Radical Produced by the Pulse Radiolysis of Water Vapor", *Int. J. Chem. Kin., Symp.* No. 1, 289, 1975.

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Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm <sup>3</sup>	k/cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
Fujii <i>et al.</i> (1985)	1350–2100	2–6% CO; 1–6% N <sub>2</sub> O 46–38% Ar and 50% He at 1 × 10 <sup>19</sup> total pressure Shock tube experiments. Detection of CO and CO <sub>2</sub> via infra-red emission	5.3 × 10 <sup>-13</sup> exp(-10230/T)	2
Milks and Matula (1973)	1169–1655	2.74–5.02% CO, 0.74–1.4% N <sub>2</sub> O in 1.2–1.6 × 10 <sup>19</sup> Kr. Single pulse shock tube study with analysis of all products	3.5 × 10 <sup>-13</sup> exp(-8711/T)	3
Lin and Bauer (1969)	1317–1908	1–2.7%N <sub>2</sub> O, 2.9–5.1%CO in 1.2–4 × 10 <sup>19</sup> Ar. Single pulse shock tube study with analysis of CO <sub>2</sub> and N <sub>2</sub> O	1.8 × 10 <sup>-13</sup> exp(-11581/T)	3
Recommendations			5.3 × 10 <sup>-13</sup> exp(-10230/T)	2

### Comments

The reported data on the rate constants for this reaction vary by an order of magnitude. We recommend the rate expression determined by Fujii and coworkers. This represents a more recent and direct measurement. It is also in satisfactory accord with the results of Milks and Matula. The work of Lin and Bauer are about a factor of 7 smaller. A summary of the experimental data can be found in Fig. 1.

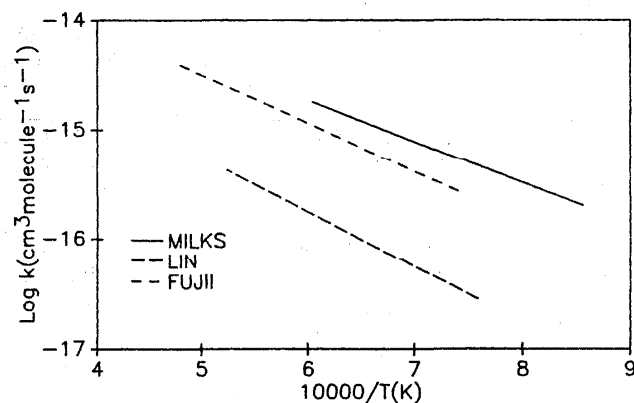


FIG. 1. Summary of experimental results for the reaction  $\text{N}_2\text{O} + \text{CO} = \text{N}_2 + \text{CO}_2$

Milks and Matula have recalculated Lin and Bauer's results on the basis of their mechanism and increased the rate constants by a factor of 3. On this basis, the agreement in the rate constant data is satisfactory.

Loriat, H., Caralp, F. and Destrain, M., (*J. Phys. Chem.*, **87**, 2455, 1983) and Zaslono, Losev, Mozzhukhin and Mukoseev (*Kinetics and Catalysis, English trans.*, **80**, 1141, 1979) have also published rate expressions. These are based on results from much more complex situations. It is not surprising that the results are quite divergent from the more direct results summarized here and are therefore not considered in this evaluation.

### References

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- Lin, M. C., and Bauer, S. H., "Bimolecular Reactions of  $\text{N}_2\text{O}$  with CO and the Recombination of O and CO as Studied in a Single Pulse Shock Tube" *J. Chem. Phys.*, **50**, 3377, 1969.
- Milks, D., and Matula, R. A. "A Single-Pulse Shock Tube Study of the Reaction Between Nitrous Oxide and Carbon Monoxide" 14th Symp. (Int'l) on Combustions, The Combustion Institute, Pittsburgh, Pa., p83, 1973.

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4. Equilibrium Constants of Formation<sup>a</sup>

$$\begin{aligned} \log_{10} K_p(\text{NO}) &= 0.66597 - 4.7332 \times 10^3/T + 5.7106 \times 10^3/T^2 - 6.8375 \times 10^5/T^3 \\ \log_{10} K_p(\text{NO}_2) &= -3.2867 - 1.7557 \times 10^3/T + 5.36775 \times 10^4/T^2 - 1.0784 \times 10^7/T^3 \\ \log_{10} K_p(\text{HNO}) &= -2.5774 - 5.0182 \times 10^3/T - 1.2174 \times 10^4/T^2 - 3.8111 \times 10^6/T^3 \\ \log_{10} K_p(\text{HNO}_2) &= -6.1717 - 3.8867 \times 10^3/T + 1.8123 \times 10^5/T^2 - 3.1981 \times 10^7/T^3 \\ \log_{10} K_p(\text{HCN}) &= 1.5772 - 6.76 \times 10^3/T - 1.2295 \times 10^5/T^2 + 1.6784 \times 10^7/T^3 \\ \log_{10} K_p(\text{N}_2\text{O}) &= -3.6213 - 4.7508 \times 10^3/T + 2.3675 \times 10^5/T^2 - 3.6071 \times 10^7/T^3 \\ \log_{10} K_p(\text{NO}_3) &= -7.5036 - 4.2093 \times 10^3/T + 3.7832 \times 10^5/T^2 - 5.7619 \times 10^7/T^3 \\ \log_{10} K_p(\text{NO}_3) &= -10.5161 + 6.4355 \times 10^3/T + 3.8676 \times 10^5/T^2 - 6.5309 \times 10^7/T^3 \end{aligned}$$

<sup>a</sup>Data are derived from Chase, 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.

## 5. Transport Properties

Parameters for the Lenard-Jones Potential used to calculate transport properties pertinent to unimolecular reactions

Compound	$\sigma$ (Angstroms)	$\epsilon/k$ (K)
Carbon Dioxide <sup>a</sup>	3.941	195.2
Argon <sup>a</sup>	3.542	93.3
Nitrogen <sup>a</sup>	3.798	71.4
Nitric Oxide <sup>a</sup>	3.492	116.7
Nitrogen Dioxide <sup>b</sup>	4.68	146.3
HNO <sup>b</sup>	3.492	116.7
Nitrous Acid <sup>c</sup>	4.68	146
Hydrogen Cyanide <sup>a</sup>	3.63	569.8
Nitrous Oxide <sup>a</sup>	3.828	232.4
Nitrogen Trioxide <sup>b</sup>	4.112	395
Nitric Acid <sup>b</sup>	4.24	390

<sup>a</sup>Reid, R. C., Prausnitz, J. M., and Poling, B. E., "The Properties of Gases and Liquids", McGraw Hill Book Company, New York, 1987.

<sup>b</sup>Troe, J., J. Chem. Phys., 66, 4758, 1977.

<sup>c</sup>Assumed to be similar to NO<sub>2</sub>.