Chemical Kinetic Data Base for Propellant Combustion
I. Reactions Involving NO, NO_2, HNO, HNO_2, HCN and N_2O

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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^{17}–10^{22} particles/cm^3. The results of the first years effort lead to coverage of all pertinent reactions of the following species; H, H_2, H_2O, O, OH, HCHO, CHO, CO, NO, NO_2, HNO, HNO_2, HCN, and N_2O.

Key words: 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[1] 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.

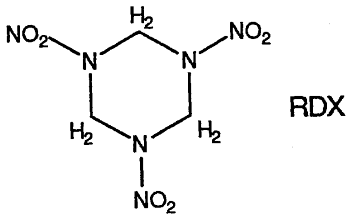

FIG. 1. Structural formula for RDX.

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^3 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[2]. 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[3], 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[4]. 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[4]. 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_2 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[5].

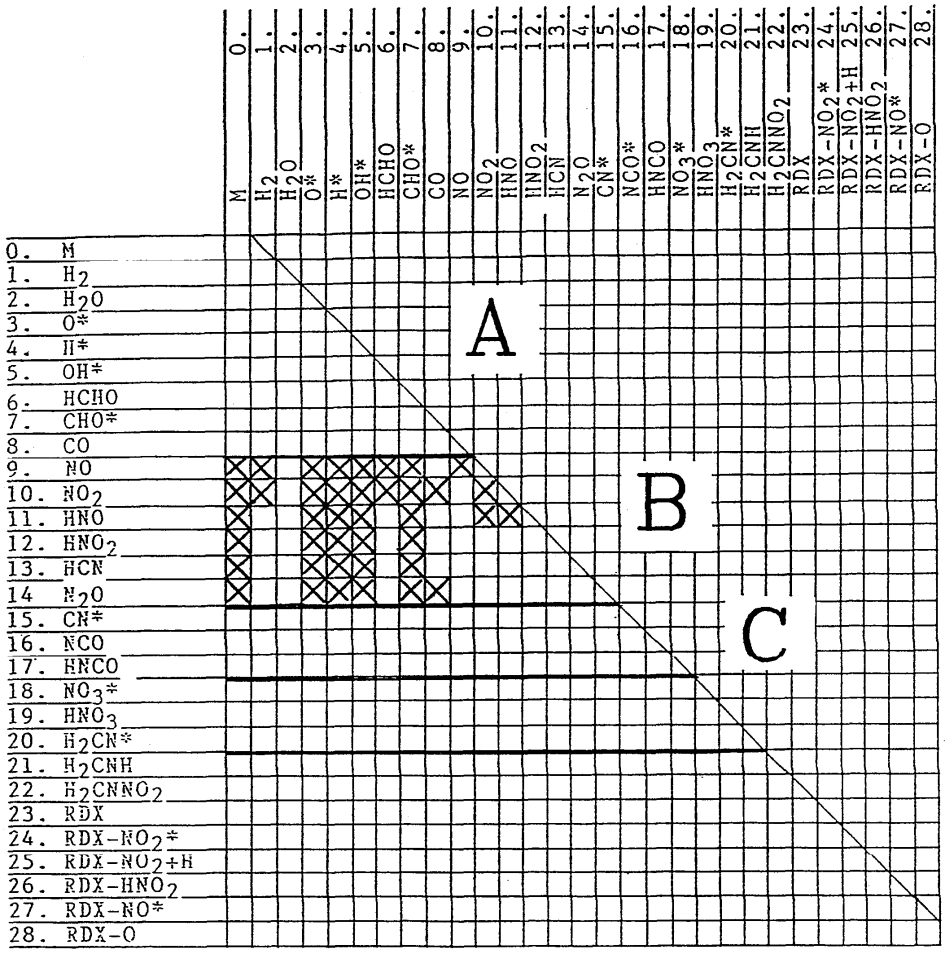

FIG. 2. Reaction grid of possible processes X reactions considered in present text; A, B, C subsets of reactions.

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 $cm^3molecule^{-1}s^{-1}$. In certain cases they may be unimolecular or ter-molecular. For these cases the units, s^{-1} and $cm^6molecule^{-1}s^{-1}$, 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[6]. 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[6] 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 $OH + NO_2$ at 1100 K in 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), ϵ/k for HNO_3 and 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 HNO_3—HNO_3 and HNO_3—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 $OH + NO_2$ and N_2. If we now take a step size down of 275 cm^{-1} we find from Table 2, $\beta(e) = 0.04$. The total collision efficiency is thus 0.038. The number density at 1 atms and 1100 K is 6.7×10^{18} molecules/cm^3. When multiplied by the collision efficiency of 0.031 we arrive at an equivalent density of 2.5×10^{17} molecules/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_∞ for N_2 and CO_2. The procedure is due to Troe[7]. The general relations are;

$$k = [k_0k_\infty/(k_0 + k_\infty/M)]^*F$$

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_∞ 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_∞ derived from the RRKM calculations with the Lindemann expression $[k_0k_\infty/(k_0 + k_\infty/M)]$ 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 HNO_3—N_2 given above we find for example $\log_{10}(k/k_\infty) = -2.73$.

We present estimated results with CO_2 as a collision partner because unlike hydrocarbon combustion systems, where reactions are carried out in a background of N_2, propellants carry their own oxidizers. Therefore, the reactive background is a more complex mixture of polyatomic gases. We have, perhaps arbitrarily, chosen CO_2 (triatomic and likely to be a more efficient collision partner then 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 NO_x formation and destruction at high temperatures and stratospheric ozone depletion in the low temperature regime. The careful reviews of Hanson and Salimian[8], Baulch *et al.*[9] and Atkinson *et al.*[5] 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[10]. 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

This work was carried out with the support of the Ballistics Research Laboratory, the Airforce Astronautics Laboratory, the Air Force Office of Scientic Research and the Office of Naval Research.

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2. Index of Reactions and Summary of Rate Expressions

No.	Reactions	Rate expressions ($cm^3 molecule^{-1} s^{-1}$ unless otherwise stated)	Uncertainties	Page
9,0	$NO+M \rightarrow N+O+M$	$1.6\times10^{-9}\exp(-74700/T)$	2	616
		$2.4\times10^{-9}\exp(-74700/T)[N_2]$		
		$4.0\times10^{-9}\exp(-74700/T)[CO_2]$		
9,1	$NO+H_2 \rightarrow HNO+H$	$2.3\times10^{-11}\exp(-28450/T)$	3	617
9,3	$NO+O+M \rightarrow NO_2+M$ (a)	$k_{a\infty}=2.16\times10^{-9}(1/T)^{0.75}$	3	618
	$NO+O \rightarrow O_2+N$(b)	$k_a(0,N_2)=1.3\times10^{-23}(1/T)^{2.87}$	1.3 at 300 K	
		$\exp(-781/T) cm^6 molecule^{-2} s^{-1}$	3 at 2500 K	
		$F_c(N_2)=0.95-10^{-4}T$		
		$k_a(0,CO_2)=1.13\times10^{-25}(1/T)^{2.16}$	1.5 at 300 K	
		$\exp(-529/T) cm^6 molecule^{-2} s^{-1}$	3 at 2500 K	
		$F_c(CO_2)=0.95-10^{-4}T$		
		$k_b=3\times10^{-15}T\exp(-19500/T)$	1.5	
9,4	$NO+H+M \rightarrow HNO+M$ (a)	$k_{a\infty}=2.53\times10^{-9}(1/T)^{0.41}$	4	622
	$\rightarrow N+OH$ (b)	$k_a(0,N_2)=2.47\times10^{-28}T^{-1.32}$	1.5 up to 700 K	
		$\exp(-370/T) cm^6 molecule^{-2} s^{-1}$		
		$F_c(0,N_2)=0.82$	3 at 2500 K	
		$k_a(0,CO_2)=9.56\times10^{-29}T^{-1.17}$		
		$\exp(-212/T) cm^6 molecule^{-2} s^{-1}$		
		$F_c(0,CO_2)=0.82$		

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

No.	Reactions	Rate expressions ($cm^3molecule^{-1}s^{-1}$ unless otherwise stated)	Uncertainties	Page
9,5	$NO+OH+M \rightarrow HNO_2+M$	$k_\infty=3{,}3\times10^{-12}(1/T)^{0.05}\exp(363/T)$ $k(0,sc)=2\times10^{-25}(1/T)^{2.13}$ $\exp(185/T)$ $cm^6molecule^{-2}s^{-1}$ $k(0,N_2)=1.4\times10^{-24}(1/T)^{2.51}$ $\exp(34/T)$ $cm^6molecule^{-2}s^{-1}$ $F_c(N_2)=0.62$ $k(0,CO_2)=4.7\times10^{-25}(1/T)^{2.3}$ $\exp(124/T)$ $cm^6molecule^{-2}s^{-1}$ $F_c(CO_2)=0.62$	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	$NO+HCHO \rightarrow HNO+HCO$	$1.7\times10^{-11}\exp(-20540/T)$	10	628
9,7	$NO+HCO \rightarrow HNO+CO$	1.2×10^{-11}	1.4	628
9,9	$NO+NO \rightarrow N_2O+O$	$6.0\times10^{-12}\exp(-32900/T)$	2	629
10,0	$NO_2+M \rightarrow NO+O+M$	$k_\infty=7.6\times10^{18}T^{-1.27}$ $\exp(-36883/T)s^{-1}$ $k(0,CO_2)-359T^{-2.66}$ $\exp(-37392/T)$ $F_c(CO_2)=0.95-10^{-4}*T$ $k(0,N_2)=4.1\times10^4T^{-3.37}$ $\exp(-37644/T)$ $F_c(N_2)=0.95-10^{-4}*T$	3 2 2	630
10,1	$NO_2+H_2 \rightarrow HONO+H$	$4\times10^{-11}\exp(-14500/T)$	5	631
10,3	$NO_2+O \rightarrow O_2+NO$ (a) $\rightarrow NO_3$ (b)	$k_a=6.5\times10^{-12}\exp(120/T)$ $k_{b\infty}=2.2\times10^{-11}$ $k_b(0,N_2)=4.1\times10^{-20}T^{-4.08}$ $\exp(-1242/T)$ $cm^6molecule^{-2}s^{-1}$ $F_c(N_2)=0.79-1.8\times10^{-4}T$ $k_b(0,CO_2)=3.7\times10^{-20}T^{-3.94}$ $\exp(-1146/T)$ $cm^6molecule^{-2}s^{-1}$ $F_c(CO_2)=0.775-1.5\times10^{-4}T$	1.2 2 1.3 at 300 K 5 at 2500 K	632
10,4	$NO_2+H \rightarrow NO+OH$	1.4×10^{-10}	1.3	634
10,5	$NO_2+OH \rightarrow HNO_3$ (a) $\rightarrow HO_2+NO$ (b)	$k_{a\infty}=4\times10^{-11}$ $k_a(N_2,0)=1.77\times10^{-15}(1/T)^{5.49}$ $\exp(-1183/T)$ $cm^6molecule^{-2}s^{-1}$ $k_a(CO_2,0)=1.6\times10^{-15}(1/T)^{5.4}$ $\exp(-1100/T)$ $cm^6molecule^{-2}s^{-1}$ $F_c(N_2)=0.725-2.5\times10^{-4}T$ $F_c(CO_2)=0.725-2.5\times10^{-4}T$ $k_b=3\times10^{-11}\exp(-3360/T)$	1.2 at 300 K 2.5 at 1200 K 1.2	635
10,6	$NO_2+HCHO \rightarrow HNO_2+CHO$	$1.3\times10^{-21}T^{2.77}\exp(-6910/T)$	2	641
10,7	$NO_2+CHO \rightarrow CO+HNO_2$ (a) $\rightarrow H+CO_2+NO$ (b)	$k_a=2.1\times(1/T)^{-3.29}\exp(-1185/T)$ $k_b=1.4\times10^{-8}(1/T)^{0.75}\exp(-970/T)$	2	641
10,8	$NO_2+CO \rightarrow CO_2+NO$	$1.5\times10^{-10}\exp(-17000/T)$	2.5	642
10,10	$NO_2+NO_2 \rightarrow NO_3+NO$ (a) $\rightarrow 2NO+N_2$ (b)	$k_a=1.6\times10^{-14}T^{-0.73}\exp(-10530/T)$ $k_b=2.7\times10^{-12}\exp(-13147/T)$	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 ($cm^3 molecule^{-1} s^{-1}$ unless otherwise stated)	Uncertainties	Page
11,0	$HNO + M \rightarrow H + NO + M$	$k_\infty = 1.2 \times 10^{16} T^{-0.43}$ $\exp(-24922/T) s^{-1}$ $k(0,N_2) = 0.01 T^{-1.61}$ $\exp(-25585/T)$ $F_c = 0.83$ $k(0,CO_2) = 6.4 \times 10^{-4} T^{-1.24}$ $\exp(-25172/T)$ $F_c = 0.83$	4 1.5 up to 700 K 3 at 2500 K	643
11,3	$HNO + O \rightarrow OH + NO$	3×10^{-11}	3	644
11,4	$H + HNO \rightarrow H_2 + NO$	$3 \times 10^{-11} \exp(-500/T)$	4	645
11,5	$OH + HNO \rightarrow H_2O + NO$ >10 at 300 K	$8 \times 10^{-11} \exp(-500/T)$	3 at 2000 K	645
11,7	$HNO + CHO \rightarrow HCHO + NO$	$1 \times 10^{-12} \exp(-1000/T)$	5	646
11,10	$HNO + NO_2 \rightarrow HNO_2 + NO$	$1 \times 10^{-12} \exp(-1000/T)$	5	646
11,11	$HNO + HNO \rightarrow H_2O + N_2O$	$1.4 \times 10^{-15} \exp(-1561/T)$	2 at 500 K 10 at 1000 K (see text)	646
12,0	$HNO_2 + M \rightarrow OH + NO + M$	$k_\infty = 1.2 \times 10^{19} (1/T)^{1.23}$ $\exp(-25010/T) s^{-1}$ $k(0,sc) = 7.3 \times 10^5 (1/T)^{3.42}$ $\exp(-25200/T)$ $k(0,N_2) = 5 \times 10^6 (1/T)^{3.8}$ $\exp(-25340/T)$ $F_c(N_2) = 0.62$ $k(0,CO_2) = 1.7 \times 10^6 (1/T)^{3.59}$ $\exp(-25250/T)$ $F_c(CO_2) = 0.62$	1.4 at 300 K 5 at 2500 K	647
12,3	$HNO_2 + O \rightarrow OH + NO_2$	$2 \times 10^{-11} \exp(-3000/T)$	10	648
12,4	$HNO_2 + H \rightarrow H_2 + NO_2$	$2 \times 10^{-11} \exp(-3700/T)$	20	649
12,5	$HNO_2 + OH \rightarrow H_2O + NO_2$	$2.1 \times 10^{-14}\ T \exp(-68/T)$ 5 (1000–2500 K)	2 at 300 K, 1000 K	649
12,7	$HNO_2 + CHO \rightarrow H_2CO + NO_2$	$2 \times 10^{-21} T^{2.37} \exp(-1940/T)$	2 at 400–500 K 5 at 300, 1000 K	650
13,0	$HCN + M \rightarrow H + CN + M$	$k_\infty = 8.3 \times 10^{17} (1/T)^{0.93}$ $\exp(-62294/T) s^{-1}$ $k(0,N_2) = 5.93 \times 10^2 (1/T)_2^{0.6}$ $\exp(-62845/T)$ $F_c(N_2) = 0.95 - 10^{-4} T$ $k(0,CO_2) = 2.1 \times 10^2 (1/T)^{2.4}$ $\exp(-62800/T)$ $F_c(CO_2) = 0.875 - 0.5 \times 10^{-4} T$	1.5	651
13,3	$HCN + O \rightarrow CN + OH$(a) $\rightarrow NH + CO$(b) $\rightarrow NCO + H$(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	$H + HCN \rightarrow H_2 + CN$ (a)	$k_a = 6.2 \times 10^{-10} \exp(-12507/T)$	100 at 500 K 3 at 2500 K	654
	$+ M \rightarrow H_2CN + M$ (b)	$k_{b\infty} = 5.5 \times 10^{-11} \exp(-2438/T)$ $k_b(0,N_2) = 4.4 \times 10^{-24} (1/T)_2^{0.73}$ $\exp(-3855/T) cm^6 molecule^{-2} s^{-1}$ $k_b(O,CO_2) = 4.3 \times 10^{-24} (1/T)^{2.63}$ $\exp(-3791/T) cm^6 molecule^{-2} s^{-1}$ $F_c = 0.95 - 10^{-4} T \quad (CO_2, N_2)$	100 at 500 K 10 at 1200 K and above	

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

No.	Reactions	Rate expressions ($cm^3molecule^{-1}s^{-1}$ unless otherwise stated)	Uncertainties	Page
13,5	$HCN+OH \rightarrow H_2O+CN$ (a) $\rightarrow H+HOCN$ (b) $\rightarrow H+HNCO$ (c)	$k_a=3.6\times10^{-17}T^{1.5}\exp(-3887/T)$ $k_b=5.3\times10^{-20}T^{2.45}\exp(-6100$ $k_c=9.3\times10^{-30}T^{4.71}\exp(248/T)$	1.5 at 2500 K 3 at 1000 K 5 at 2000 K	656
13,7	$HCN+CHO \rightarrow HCHO+CN$	$4\times10^{-12}\exp(-17200/T)$	3	657
14,0	$N_2O \rightarrow N_2 + O$	$k_\infty=1.3\times10^{11}\exp(-30000/T)$ $k(0,N_2)=1.2\times10^{-6}T^{-0.73}\exp(-31600/T)$ $F_c(N_2)=1.167-1.25\times10^{-4}T$ $k(0,CO_2)=2\times10^{-6}T^{-0.67}\exp(-31300/T)$ $F_c(CO_2)=1.167-1.25\times10^{-4}T$	2	657
14,3	$N_2O+O \rightarrow O_2+N_2$ (a) $\rightarrow NO+NO$ (b)	$k_a=1.7\times10^{-10}\exp(-14100/T)$ $k_b=1.1\times10^{-10}\exp(-13400/T)$	2	659
14,4	$N_2O+H \rightarrow N_2+OH$	$1.6\times10^{-10}\exp(-7600/T)$	1.7	660
14,5	$N_2O+OH \rightarrow HO_2+N_2$	$<1.4\times10^{-11}\exp(-5000/T)$		661
14,8	$N_2O+CO \rightarrow N_2+CO_2$	$5.3\times10^{-13}\exp(-10230/T)$	2	662

3. Chemical Kinetic Data Tables

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

	Conditions		Reaction rate constants	Uncertainties
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Thielen and Roth (1984)	2400–6200	Shock tube study in $1-5\times10^{18}$ Ar $10-10000$ppm NO with atomic resonance absorption detection of N and O-atoms	$1.6\times10^{-9}\exp(-74700/T)$	1.4
Koshi *et al.* (1979)	4000–7500	Shock tube study with $1.0-5.0\%$ NO in $3-15\times10^{17}$ Ar. NO concentration via i-r emission	$8.6\times10^{-9}\exp(-76030/T)$	3
Myerson(1973)	2600–6300	Shock tube study with $0.1-1.0\%$ NO in $2-20\times10^{17}$ Ar. atomic resonance absorption detection of O	$2.3\times10^{-10}\exp(-74700/T)$	2
Baulch *et al.* (1973) review	3000–5000		$3.8\times10^{-7}T^{-0.5}\exp(-74900/T)$	
Wray and Teare (1962)	4180–6580	0.5% NO in 1.5×10^{18} Ar. NO concentration followed by UV absorption at 1270 A	$6.6\times10^{-4}T^{-1.5}\exp(-75500/T)$	3
Recommendation			$1.6\times10^{-9}\exp(-74700/T)$ $2.4\times10^{-9}\exp(-74700/T)[N_2]$ $4.0\times10^{-9}\exp(-74700/T)[CO_2]$	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_2 and CO_2 respectively. This reaction is not expected to be important except at the highest temperatures.

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Thielen, K. and Roth, P., Resonance Absorption Measurements of N and O Atoms in High Temperature NO Dissociation and Formation Kinetics, 20th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA., **685**, 1984.

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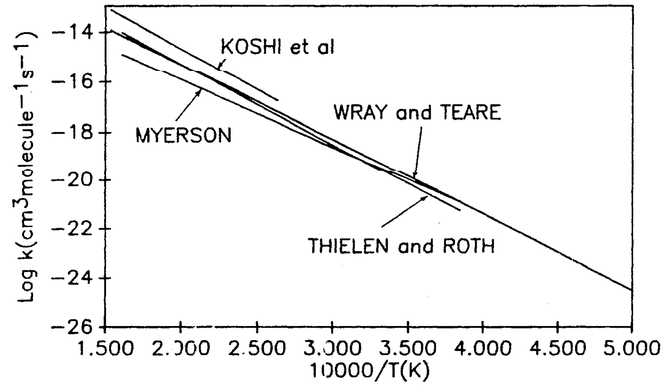

FIG. 1. Summary of experimental work on the reaction NO + Ar →N + O + Ar.

9,1 NO + H_2 → HNO + H

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Ando and Asaba (1976) (also review of much previous work)	2020–3250	$7-230\times10^{15}$ NO $6-180\times10^{15}$ H_2 in $8-54\times10^{17}$ Ar Shock tube experiments NO from 5.22 micron and O from NO—O (6500A) emissions. Rate constants from kinetic modeling.	$5\times10^{-11}\exp(-27790/T)$	3
Recommendation:			$2.3\times10^{-11}\exp(-28450/T)$	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_2 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.

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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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9,3 $NO + O + M \rightarrow NO_2 + M$ (a)
$NO + O \rightarrow O_2 + N$ (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Hanson and Salimian (1985) review	1500–5000		$k_b = 6.3 \times 10^{-15} T \exp(-20820/T)$	1.3
Atkinson *et al.* (1989)	200–300		$k_a(O_2) = 8.6 \times 10^{-32}(T/300)^{-1.8}$ (cm^{6}molecule^{-2}s^{-1})	1.5
(review)			$k_a(N_2) = 1.0 \times 10^{-31}(T/300)^{-1.6}$ (cm^{6}molecule^{-2}s^{-1})	1.25
			$k_{a\infty} = 3.0 \times 10^{-11}(T/300)^{0.3}$ (s^{-1})	1.5
Yarwood *et al.* (1988)	300–1300	Flash Photolysis-Resonance Fluorescence detection of O with $0.9-5.8 \times 10^{15}$ NO in $1.6-3.5 \times 10^{18}$ Ar. at 300−1000K Flash Photolysis-Shock tube with Resonance Absorption detection of O with $1.6-4.2 \times 10^{16}$ NO in $4-5.2 \times 10^{18}$ Ar	$k_a(Ar) = 6.7 \times 10^{-32}(T/300)^{-1.4}$ (cm^{6}molecule^{-2}s^{-1})	1.5
Schieferstein *et al.* (1983)	200–370	$2-9 \times 10^{16}$ NO in $2.4–25 \times 10^{16}$ He N_2 and CH_4 H_2-laser photolysis of NO; O-atom by NO_2 chemiluminescence	$k_a(He) = 3.3 \times 10^{-29} T^{-1.1}$ $k_a(NO) = 3.3 \times 10^{-28} T^{-1.38}$ $k_a(N_2) = 3.2 \times 10^{-28} T^{-1.44}$ $k_a(CH_4) = 7.9 \times 10^{-28} T^{-1.55}$ (cm^{6}molecule^{-2}s^{-1})	1.3 1.3 1.3 1.3
Sugawara *et al.* (1980)	298	$6.5-33 \times 10^{18}$ N2 or He Pulse radiolysis. O atoms detected thru absorption	$k_a(N_2) = 7.7 \times 10^{-32}$ $k_a(He) = 4.2 \times 10^{-32}$ (cm^{6}molecule^{-2}s^{-1})	1.1 1.1
Anderson and Stephens (1979)	237–397	VUV photolysis NO. O from NO_2 chemiluminescence	$k_a(Ar) = 1.3 \times 10^{-32} \exp(508/T)$ (cm^{6}molecule^{-2}s^{-1})	1.2
Atkinson and Pitts (1978)	298	$6-30 \times 10^{14}$ NO, $0-7.5 \times 10^{16}$ SO_2, $7.5-16 \times 10^{17}$ Ar. O from NO_2 VUV photolysis of NO. O from NO_2 chemiluminescence	$k_a(N_2) = 1.1 \times 10^{-31}$ $k_a(SO_2) = 2.6 \times 10^{-31}$ (cm^{6}molecule^{-2}s^{-1})	1.2
Atkinson *et al.* (1977)	298–439	Trace NO in 1×10^{18} Ar VUV photolysis of NO Detection of O via NO_2 chemiluminescence	$k_a(Ar) = 1.46 \times 10^{-32} \exp(473/T)$ (cm^{6}molecule^{-2}s^{-1})	1.1
Whytock *et al.* (1976)	217–500	$3-230 \times 10^{14}$ NO in $4-23 \times 10^{17}$ N_2. Flash photolysis of NO and resonance fluorescence detection of O	$k_a(N_2) = 15.5 \times 10^{-33} \exp(584/T)$ (cm^{6}molecule^{-2}s^{-1})	1.1

9,3 $NO + O + M \rightarrow NO_2 + M$ (a) – Continued
$NO + O \rightarrow O_2 + N$ (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Michael *et al.* (1976)	217–500	$1-20\times10^{14}$ NO in $2-40\times10^{18}$ rare gas Flash photolysis of NO and resonance fluorescence detection of O	$k_a(He)=10.8\times10^{-33}\exp(524/T)$ $k_a(Ne)=9.3\times10^{-33}\exp(519/T)$ $k_a(Ar)=9.1\times10^{-33}\exp(594/T)$ $k_a(Kr)=9.5\times10^{-33}\exp(574/T)$ (cm^{6}molecule^{-2}s^{-1})	1.1
Singleton *et al.* (1975)	298–473	$5-25\times10^{16}$NO in $1-2\times10^{18}$ N_2O. Hg sensitized decomposition of N_2O O detection via O + NO chemiluminescence rate constant by phase shift between photolysis and chemiluminenscence	$k_a(N_2O)=1.69\times10^{-32}\exp(619/T)$ (cm^{6}molecule^{-2}s^{-1})	1.1
Gaedtke and Troe (1975)	296–428	1.6×10^{17} NO_2 in $0-2.4\times10^{22}N_2$ Quantum yield for NO_2 disappearance under continuous photolysis	$k_{a\infty}=3\times10^{-11}$ (s−1)	1.2
Hippler *et al.* (1975)	295	1.5×10^{17} NO_2 $2.5-73\times10^{18}$ inert gas NO; $NO/NO_2=0$ to 2 photolysis of NO_2	$k_a(He)=5.8\times10^{-32}$	1.2
			$k_a(Ne)=4.7\times10^{-32}$	1.2
			$k_a(Ar)=8.3\times10^{-32}$	1.2
			$k_a(CO)=9.1\times10^{-32}$	1.2
			$k_a(N_2)=7.5\times10^{-32}$	1.2
			$k_a(CO_2)=13.7\times10^{-32}$	1.2
			$k_a(CH_4)=14.5\times10^{-32}$	1.2
			$k_a(C_2H_6)=12.3\times10^{-32}$	1.2
			k_a(larger hydrocarbons and fluorinated cmpds) 17×10^{-32} (cm^{6}molecule^{-2}s^{-1})	1.2
Atkinson and Pitts (1974)	300–392	presumably same conditions as earlier work (1978)	$k_a(N_2O)=2.65\times10^{-32}\exp(453/T)$ (cm^{6}molecule^{-2}s^{-1})	1.1
Atkinson and Pitts (1974)	300	$2-6\times10^{17}$NO in $1.6-3.0\times10^{18}N_2O$ Hg sensitized decomposition of N_2O O detection via O + NO chemiluminescence rate constant by phase shift between photolysis and chemiluminenscence	$k_a(N_2O)=11.9\times10^{-32}$ (cm^{6}molecule^{-2}s^{-1})	1.1
Furuyama *et al.* (1974)	298	$5-15\times10^{16}$ NO in $8-12\times10^{17}$ N_2O. Hg sensitized decomposition of N_2O O detection via O + NO chemiluminescence rate constant by phase shift between photolysis and chemiluminenscence	$k_a(N_2O)=15.9\times10^{-32}$ (cm^{6}molecule^{-2}s^{-1})	1.1
Gaedtke *et al.* (1973)	300	$0-2.4\times10^{22}$ N_2 photolysis of NO_2	$k_{a\infty}=1.3\times10^{-11}$ (s^{-1})	2
Baulch *et al.* (1973) (review)	200–500		$k_a=3.0\times10^{-33}\exp(940/T)$ [O_2, Ar] (cm^{6}molecule^{-2}s^{-1})	1.2

9,3 $NO + O + M \rightarrow NO_2 + M$ (a) — **Continued**
$NO + O \rightarrow O_2 + N$ (b)

Reference	Conditions T range/K	 [M] range/cm³	Reaction rate constant k/cm³molecule⁻¹s⁻¹	Uncertainty
Recommendations:			$k_{a\infty} = 2.16\times10^{-9}(1/T)^{0.75}$	3
			$k_a(0,N_2) = 1.3\times10^{-23}(1/T)^{2.87}$	1.3 at 300 K
			$\exp(-781/T)$cm^{6}molecule^{-2}s^{-1}	3 at 2500 K
			$F_c(N_2) = 0.95 - 10^{-4}T$	
			$k_a(0,CO_2) = 1.13\times10^{-25}(1/T)^{2.16}$	1.5 at 300 K
			$\exp(-529/T)$cm^{6}molecule^{-2}s^{-1}	3 at 2500 K
			$F_c(CO_2) = 0.95 - 10^{-4}T$	
			$k_b = 3\times10^{-15}T\exp(-19500/T)$	1.5

Comments

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

$$k_b = 3\times10^{-15}T\ \exp(-19500/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

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_2 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_2 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_2 as a fixed point for our recommendations.

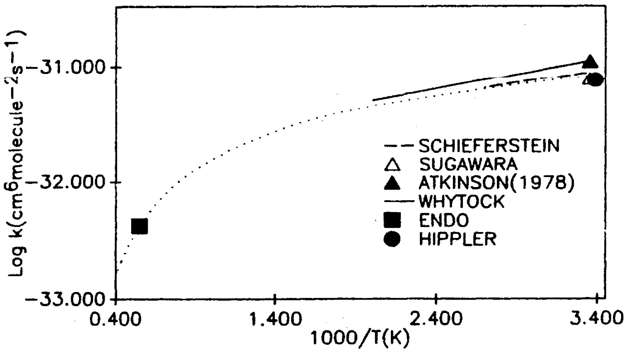

FIG. 1. Summary of experimental work on O+NO combination in N_2. Dotted line represent our recommendation.

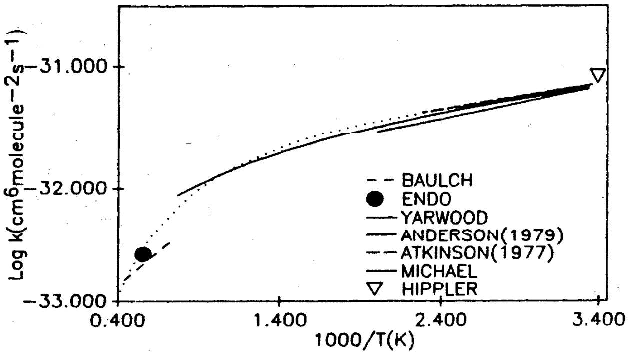

FIG. 2. Summary of experimental data on $O+NO+Ar \rightarrow NO_2+Ar$. The dotted line represent our fit to the data using the room temperature rate constants andthe same temperature dependence of the step size down as for N_2.

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_2. 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_2 and CO_2.

$$k_a(0,N_2) = 1.3\times10^{-23}(1/T)^{2.87}\ \exp(-781/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

$$k_a(0,CO_2) = 1.13\times10^{-25}(1/T)^{2.16}\ \exp(-529/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

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,

$$k_{a\infty} = 2.16\times10^{-9}(1/T)^{0.75}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

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 CO_2 or N_2 as the collision partner.

TABLE 3: Log (k/k(0)) for the reaction $NO+O+NO_2 \rightarrow NO_2+NO_2$ 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 $NO+O+M \rightarrow NO_2+M$ combination

Step Size (cm^{-1}) Temp (K)	200	400	800	1600	3200
500	1.2×10^{-1}	2.7×10^{-1}	4.7×10^{-1}	6.6×10^{-1}	8.0×10^{-1}
700	7.7×10^{-2}	1.9×10^{-1}	3.7×10^{-1}	5.7×10^{-1}	7.4×10^{-1}
900	5.2×10^{-2}	1.4×10^{-1}	2.9×10^{-1}	4.9×10^{-1}	6.8×10^{-1}
1100	3.7×10^{-2}	1.1×10^{-2}	2.4×10^{-1}	4.3×10^{-1}	6.3×10^{-1}
1300	2.8×10^{-2}	8.2×10^{-2}	2.0×10^{-1}	3.8×10^{-1}	5.8×10^{-1}
1500	2.2×10^{-2}	6.6×10^{-2}	1.7×10^{-1}	3.4×10^{-1}	5.4×10^{-1}
1700	1.7×10^{-2}	5.3×10^{-2}	1.4×10^{-1}	3.0×10^{-1}	5.0×10^{-1}
1900	1.4×10^{-2}	4.4×10^{-2}	$1.2\times10^{-}1$	2.7×10^{-2}	4.6×10^{-1}
2100	1.1×10^{-2}	3.7×10^{-2}	1.0×10^{-1}	2.4×10^{-2}	4.3×10^{-1}
2300	9.3×10^{-3}	3.1×10^{-2}	9.0×10^{-2}	2.1×10^{-2}	4.0×10^{-1}
2500	7.8×10^{-3}	2.7×10^{-2}	7.8×10^{-2}	1.9×10^{-2}	3.7×10^{-1}

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9,4: $NO + H + M \rightarrow HNO + M$ (a)
$\rightarrow N + OH$ (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Hanson and Salimian (1985) (review)	1750–4200		$k_b=2.8\times10^{-10}\exp(-24560/T)$	1.5
Forte, (1981)	300–313	$1.2\times10^{19}-2.9\times10^{22}$ N_2 and Ar	$k_{a\infty}=8.3\times10^{-10}$	4
Oka *et al*. (1977)	298–477	$0.8-10\times10^{18}$ total pressure of H_2 and N_2 with traces of Hg $0-0.9$ mole fraction of NO, Mercury photosensitized decomposition of H_2. Chemiluminescent detection of HNO.	$k_a(H_2)=1.27\times10^{-32}\exp(364/T)$ cm^{6}molecule^{-2}s^{-1} $k_a(NO,298)=5.27\times10^{-32}$ cm^{6}molecule^{-2}s^{-1}	1.1
Oka *et al*. (1977)	298	$1.6-10\times10^{18}$ H_2, 3–4%NO,Hg Mercury photosensitized H_2 decomposition. Chemiluminescent det. of HNO	$k_a(H_2)=4.3\times10^{-32}$ cm^{6}molecule^{-2}s^{-1}	1.1
Ahumada, *et al*. (1977)	298	$1.8-20\times10^{18}$ H_2,He,Ne Ar, Kr with H_2(in rare gas) and NO. Hg photosensitized H_2 decomp. Lyman-alpha H-atom detection	$k_a(H_2)=6.3\times10^{-32}$ cm^{6}molecule^{-2}s^{-1} $k_a(He)=4.3\times10^{-32}$ " $k_a(Ne)=2.1\times10^{-32}$ " $k_a(Ar)=3.9\times10^{-32}$ " $k_a(Kr)=5.4\times10^{-32}$ "	1.1
Baulch *et al*. (1973) review	300–700		$k_a(H_2)=1.5\times10^{-32}\exp(300/T)$ cm^{6}molecule^{-2}s^{-1}	1.5
Hikida, *et al*. (1971)	298	Pulse radiolysis in $4-60\times10^{18}$ H_2 with 9×10^{17} NO. Lyman-alpha absorption for H-atom concentration	$k_a(H_2)=3.9\times10^{-32}$ cm^{6}molecule^{-2}s^{-1}	

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

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Hartley and Thrush (1967)	293	Discharge flow in H_2,CO_2 N_2O, SF_6, H_2O, Ar at $1.3-10\times10^{16}$ total pressure, 10^{11} NO	$k_a(H_2)=5.7\times10^{-32}$ cm^{6}molecule^{-2}s^{-1} $k_a(CO_2)=6.3\times10^{-32}$ “ $k_a(N_2O)=6.8\times10^{-32}$ “ $k_a(SF_6)=10.9\times10^{-32}$ “ $k_a(H_2O)=18.8\times10^{-32}$ “ $k_a(Ar)=3.1\times10^{-32}$ “ cm^{6}molecule^{-2}s^{-1}	1.2
Clyne and Thrush (1962)	230–704	Discharge flow in H_2, Ar, Ne, He at $1-10\ \times10^{16}$ total pressure, trace NO	$k_a(H_2,231)=5.6\times10^{-32}$cm^{6}molecule^{-2}s^{-1} $k_a(H_2,265)=4\times10^{-32}$ “ $k_a(H_2,294)=3.9\times10^{-32}$ “ $k_a(H_2,340)=3.9\times10^{-32}$ “ $k_a(H_2,433)=3.1\times10^{-32}$ “ $k_a(H_2,704)=2.0\times10^{-32}$ “ $k_a(Ar,293)=2.3\times10^{-32}$ “ $k_a(Ne,293)=1.9\times10^{-32}$ “ $k_a(He,293)=1.7\times10^{-32}$ “	1.2
Recommendations:			$k_{a\infty}=2.53\times10^{-9}(1/T)^{0.41}$ $k_a(0,N_2)=2.47\times10^{-28}T^{-1.32}$ exp$(-370/T)$cm^{6}molecule^{-2}s^{-1} $F_c(0,N_2)=0.82$ $k_a(0,CO_2)=9.56\times10^{-29}T^{-1.17}$ exp$(-212/T)$cm^{6}molecule^{-2}s^{-1} $F_c(0,CO_2)=0.82$	4 1.5 up to 700 K 3 at 2500 K
			$k_b=2.8\times10^{-10}\exp(-24560/T)$	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 $k_b=7.0\times10^{-11}\exp(-23300/T)$ cm^{3}molecule^{-1}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_2 as the collisional partner and only one study using CO_2. Our procedure is to accept Baulch's recommendation for H_2 and infer that the rate constants for N_2 and CO_2 as the collision partner are 4.6×10^{-32} and 6.2×10^{-32} cm^{6}molecule^{-2}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_2 as the collision partner. A plot of our fit and the data with H_2 as the collision partner can be found in Fig. 1. This leads to the following rate expressions.

$$k_a(0,N_2)=2.47\times10^{-28}T^{-1.32}\exp(-370/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

$$k_a(0,CO_2)=9.56\times10^{-29}T^{-1.17}\exp(-212/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

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

$$k_{a\infty} = 2.5\times10^{-9}(1/T)^{0.41}\ \mathrm{cm^3 molecule^{-1} s^{-1}}$$

with an uncertainty of a factor of 4.

The results of RRKM calculations assumming 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_2 and CO_2 as the collision partner the rate constants in the intermediate pressure region, we suggest using $F_c = 0.82$ with no temperature dependence.

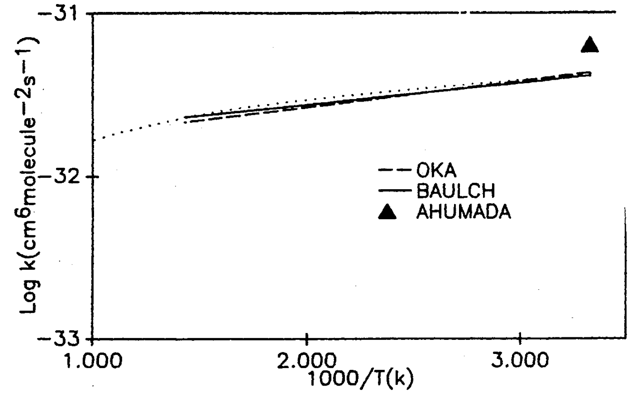

FIG 1. Experimental and fitted results (dotted line) for H_2 as collision-partner near 300 K.

Table 1. Log $(k/k(0))$ for the reaction $NO + H + HNO \rightarrow HNO + HNO$ 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 $H + NO + M = HNO + M$

Step Size (cm^{-1})	200	400	800	1600	3200
Temp(K)					
500	1.2×10^{-1}	2.7×10^{-1}	4.7×10^{-1}	6.6×10^{-1}	8.0×10^{-1}
700	7.6×10^{-2}	1.9×10^{-1}	3.6×10^{-1}	5.7×10^{-1}	7.4×10^{-1}
900	5.1×10^{-2}	1.4×10^{-1}	2.9×10^{-1}	4.9×10^{-1}	6.8×10^{-1}
1100	3.6×10^{-2}	1.0×10^{-2}	2.3×10^{-1}	4.3×10^{-1}	6.2×10^{-1}
1300	2.7×10^{-2}	7.9×10^{-2}	1.9×10^{-1}	3.7×10^{-1}	5.7×10^{-1}
1500	2.0×10^{-2}	6.2×10^{-2}	1.6×10^{-1}	3.3×10^{-1}	5.3×10^{-1}
1700	1.6×10^{-2}	5.0×10^{-2}	1.3×10^{-1}	2.9×10^{-1}	4.9×10^{-1}
1900	1.3×10^{-2}	4.1×10^{-2}	$1.1\times10-1$	2.5×10^{-1}	4.5×10^{-1}
2100	1.0×10^{-2}	3.4×10^{-2}	9.7×10^{-2}	2.3×10^{-1}	4.1×10^{-1}
2300	8.5×10^{-3}	2.8×10^{-2}	8.3×10^{-2}	2.0×10^{-1}	3.8×10^{-1}
2500	7.0×10^{-3}	2.4×10^{-2}	7.2×10^{-2}	1.8×10^{-1}	3.5×10^{-1}

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

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Atkinson *et al.* review(1989)	200–400		$k_0 = 7.4\times10^{-31}(T/300)^{-2.4}[O_2,N_2]$ cm^{6}molecule^{-2}s^{-1} $k_\infty = 1\times10^{-11}$	1.5 1.5
Burrows *et al.* (1983)	298	$3-16\times10^{16}$ M (He, N_2, Ar. Resonance fluorescence detection of OH in discharge flow reactor	$k(He)=6\times10^{-31}$ cm^{6}molecule^{-2}s^{-1} $k(N_2)=11\times10^{-31}$ " $k(Ar)=7.4\times10^{-31}$ "	1.1 1.1 1.3
Anastasi and Smith (1978)	233–505	Traces of NO and HNO_3 or H_2O in $0.35-17\times10^{18}$ N_2; also He and Kr at 0.8×10^{18}. OH via photolysis of HNO_3 or H_2O. Detection via resonance absorption	$k_\infty= 1.3\times10^{-11}$, 233 0.85×10^{-11}, 298 $= 1.1\times10^{-11}$, 405 $=0.7\times10^{-11}$, 505 $k(He) = 0.27\times10^{-12}$,296,.85$\times10^{18}$ $k(Ar) =0.37\times10^{-12}$,296,.89$\times10^{18}$ $k_0(N_2) =11.5\times10^{-31}$, 233 $= 7.3\times10^{-31}$, 296 $= 2.9\times10^{-31}$, 405 $= 2.4\times10^{-31}$, 505 cm^{6}molecule^{-2}s^{-1}	1.2
Overend *et al.* (1976)	295	$8.3-250\times10^{17}$ M(He,SF_6, CF_4,H_2O,N_2). Resonance fluorescence detection of OH. Flash photolysis generation of OH from H_2O	$k_\infty=1.83\times10^{-11}$ $k(H_2O)/k(Ar)=20$ $k(H_2O)/k(N_2)=8.33$ $k(H_2O)/k(SF_6)=2.7$ $k(H_2O)/k(CF_4)=2.44$ $k(H_2O)/k(He)=50$	1.1
Sie *et al.* (1976)	298	N_2O, CO, NO in $3.1-24.7\times10^{18}$ H_2. Photolysis at 2139nm. Final product analysis by gc	$k_\infty=1.2\times10^{-11}$	1.2
Gordon and Mulac (1975)	435	$8-80\times10^{15}$ NO in $2.2?-169\times10^{17}$ H_2O	7.5×10^{-12}	1.1
Harris and Wayne (1975)	300	Trace NO in$3-6\times10^{16}$ Ar Resonance fluorescence detection of OH, from $H+NO_2 \rightarrow OH+NO$	$k(Ar)=7\times10^{-31}$ cm^{6}molecule^{-2}s^{-1} $k(N_2)=15\times10^{-31}$	1.4
Howard and Evenson (1975)	298	Trace NO in $2-14\times10^{16}$ M (Ar, He, N_2).Laser magnetic resonance detection of OH under discharge flow conditions	$k(Ar)=4.4\times10^{-31}$ cm^{6}molecule^{-2}s^{-1} $k(N_2)=7.8\times10^{-31}$ " $k(He)=4.0\times10^{-31}$ "	1.2
Cox (1975)	300	2.5×10^{18} with 2 to 1 N_2/O_2 and traces of HONO and NO_x. Photolysis with stable product analysis	$k(N_2/O_2,2)=6.1\times10^{-12}$, 2.5×10^{18}	1.3

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

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Atkinson *et al.* (1975)	298	$1-100 \times 10^{13}$ NO in $8-200 \times 10^{17}$ M (Ar,N_2). photolysis, resonance fluorescence detection of OH	$k(Ar) = 3.3 \times 10^{-13}$; 8.1×10^{17} Flash $= 7.2 \times 10^{-13}$; 1.6×10^{18} $= 1.04 \times 10^{-12}$; 3.2×10^{18} $= 2.07 \times 10^{-12}$; 6.4×10^{18} $= 3.2 \times 10^{-12}$; 12.9×10^{18} $= 4.8 \times 10^{-12}$; 4.6×10^{18} $k(N_2) = 4.94 \times 10^{-13}$; 8.1×10^{17}	1.2
Anderson *et al.* (1974)	298	$3.3-33 \times 10^{16}$ in He, Ar, N_2 Discharge flow with resonance fluorescence detection of OH	$k_a(He) = 3.3 \times 10^{-31}$ cm^{6}molecule^{-2}s^{-1} $k_a(Ar) = 3.4 \times 10^{-31}$ cm^{6}molecule^{-2}s^{-1} $k_a(N_2) = 5.8 \times 10^{-31}$ cm^{6}molecule^{-2}s^{-1}	1.2
Morley and Smith(1972)	300	NO, NO_2, H_2 and He 1×10^{18}. Photolysis of NO_2 to make $O(^1D)$ and reaction with H_2 for OH. OH concentration by resonance absorption	$k(He) = 4.1 \times 10^{-31}$, 1×10^{18} $k(H_2) = 2.3 \times k(He)$, 1×10^{18} cm^{6}molecule^{-2}s^{-1}	1.2
Stuhl and Niki(1972)	298	3×10^{14} NO in $1.6-27 \times 10^{17}$ He. Resonance fluorescence detection of OH	$k_\infty = 2 \times 10^{-12}$ $k(He) = 1 \times 10^{-13}$; 1.6×10^{17} $= 1.6 \times 10^{-13}$; 3.2×10^{17}	1.5
Westenberg and deHaas (1972)	273–395	$1.2-17.7 \times 10^{16}$ He. ESR detection of OH from $H + NO_2$ $OH + NO$	$k(He) = 1.3 \times 10^{-30}$, 273 $= 0.8 \times 10^{-30}$, 298 $= 3.1 \times 10^{-31}$, 395 cm^{6}molecule^{-2}s^{-1}	1.3
Recommendations			$k_\infty = 3.3 \times 10^{-12}(1/T)^{0.05}\exp(363/T)$ $k(0,sc) = 2 \times 10^{-25}(1/T)^{2.13}$ $\exp(185/T)$ cm^{6}molecule^{-2}s^{-1} $k(0,N_2) = 1.4 \times 10^{-24}(1/T)^{2.51}$ $\exp(34/T)$ cm^{6}molecule^{-2}s^{-1} $F_c(N_2) = 0.62$ $k(0,CO_2) = 4.7 \times 10^{-25}(1/T)^{2.3}$ $\exp(124/T)$ cm^{6}molecule^{-2}s^{-1} $F_c(CO_2) = 0.62$	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

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_2 and Ar, (see Fig. 1) and extended to that for CO_2 using the temperature dependence from the NO_2 system (9,4). They lead to the following limiting low pressure rate expressions.

$$k(0,N_2) = 1.4 \times 10^{-24}(1/T)^{2.51} \exp(34/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

$$k(0,CO_2) = 4.7 \times 10^{-25}(1/T)^{2.3} \exp(124/T) \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

with an estimated uncertainty of a factor of 1.5 at 300 K and extending to a factor of 4 at 2500K for N_2 and a factor of 2 at 300K and an order of magnitude for CO_2 at 2500K. Note that in all these cases the collision efficiencies are large and in the case of CO_2 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_∞) 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 $OH+NO+M=HNO_2+M$

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

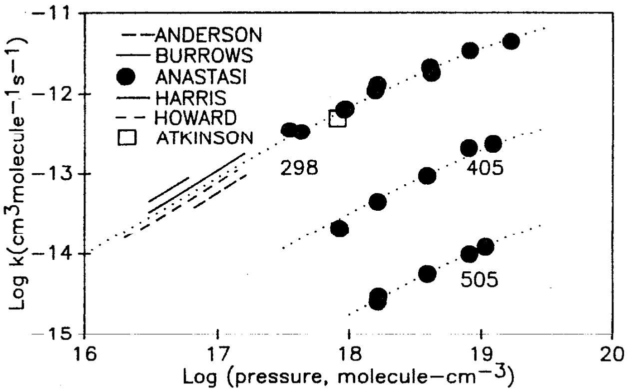

FIG. 1. Expermental data on the reaction of $OH+NO+N_2 \rightarrow HNO_2+N_2$. This data was used to obtain the temperature dependences used in this evaluation. The dotted lines represent our best fit to the data. The 405 K and 505 K have been displace by 1 and 2 log rate constants units to increase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

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Wing Tsang
June, 1989

9,6: NO + HCHO → HNO + HCO

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
$\log K_p = 0.8952 - 8.392\times10^3/T - 9.033\times10^4/T^2 + 1.710\times10^7/T^3$				
Recommendations		$1.7\times10^{-11}\exp(-20540/T)$	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 $k(HNO + HCO \rightarrow NO + H_2CO) = 1\times10^{-12}\exp(-1000/T)$ $cm^3molecule^{-1}s^{-1}$. Then through the equilibrium constant we find,

$$k(NO + HCHO \rightarrow HNO + HCO) = 1.7\times10^{-11}\exp(-20540/T)\ cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 10.

Wing Tsang
May, 1989

9,7: NO + HCO → HNO + CO

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	$k/cm^3molecule^{-1}s^{-1}$	
Langford and Moore (1984)	295	$0.17-1\times10^{16}$ NO, $1-1.3\times10^{17}$ H_2CO or $(HCO)_2$ in $0-3\times10^{19}$ N_2. Laser photolysis of H_2CO or $(HCO)_2$ and resonance absorption detection of HCO	1.26×10^{-11}	1.15
Veyret and Lesclaux (1981)	298–503	$1-1.3\times10^{15}$ NO, 1.2×10^{18} H_2CO or CH_3CHO in $0.13-1.3\times10^{19}$ N_2. Flash photolysis absorption detection of HCO	$1.2\times10^{-10}T^{-0.4}$	1.2
Reilly *et al.* (1978)	298?	$3-10\times10^{15}$ NO in 3×10^{17} H_2CO. Flash photolysis of formaldehyde; HCO detection by intracavity dye laser spectroscopy.	1.4×10^{-11}	1.15
Shibuya *et al.* (1977)	298	1.2×10^{15} NO, 6.5×10^{17} CH_3CHO in 1.6×10^{19} He; HCO detected via absorption at 613.8 nm from flash photolysis of acetaldehyde	8.7×10^{-12}	1.12
Recommendations			1.2×10^{-11}	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 NO + HCO→HCONO→NCO + OH. It is thermodynamically less favorable and is probably a minor channel.

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Wing Tsang
June, 1989

9,9 NO+NO → N_2O + O

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Koshi and Asaba (1979)	2700–3500	2−20% NO in 2.4−4.2 4.2×10^{18} Ar. Shock tube experiments with detection of NO by uv absorption and ir emission and O atom via chemiluminescence of O + NO reaction.	$8.1\times10^{-12}\exp(-33800/T)$	2
McCullough *et al.* (1977)	1750–2100	0.01−5% NO and 1%NO−1%H_2 in 4×10^{18} Ar. Ceramic flow reactor. NO detection as end product via chemiluminescence.	$3\times10^{-12}\exp(-32110/T)$	2
Baulch *et al.* (1971)	1200–2000		$2.2\times10^{-12}\exp(-32100/T)$	2
Recommendations			$6.0\times10^{-12}\exp(-32900/T)$	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

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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.

Wing Tsang
June, 1989

10,0: $NO_2+M \rightarrow NO+O+M$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm	k/cm^{3}molecule^{-1}s^{-1}	
Endo *et al.* (1979)	1600–2200	$4-30\times10^{18}$ CO_2	8.3×10^{-16} (1800)	2 (abs)
		Ne	3.3×10^{-16} "	1.2 (relativ to each other)
		Ar	2.5×10^{-16} "	
		Kr	2.5×10^{-16} "	
		Xe	2.8×10^{-16} "	
		N_2	4.1×10^{-16} "	
		He	8.7×10^{-16} "	
		CF_4	8.3×10^{-16} "	
		Reaction followed by UV absorption of NO_2		
Baulch *et al.* (1974) (review)	1400–2400		$1.8\times10^{-8}\exp(-33000/T)$	1.25
Troe (1968)	1450–2000	$1.8\times180\times10^{19}$ Ar $0.05-0.20\%$ NO_2 Shock tube Reaction followed by UV absorption of NO_2	$2\times10^{14}\exp(-36180/T)$s^{-1}	3
Recommendations:			$k_\infty=7.6\times10^{18}T^{-1.27}$ $\exp(-36883/T)$s^{-1}	3
			$k(0,CO_2)=359T^{-2.66}$ $\exp(-37392/T)$	2
			$F_c(CO_2)=0.95-10^{-4}*T$	
			$k(0,N_2)=4.1\times10^4T^{-3.37}$ $\exp(-37644/T)$	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,

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

$$k(0,N_2)=4.1\times10^4T^{-3.37}\exp(-37644/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

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^{-1}). Smith (Int. J. Chem. Kin., **16**, 423, 1984) has suggested that this is due to contributions from excited electronic states of NO_2.

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;

$$k_\infty=7.6\times10^{18}T^{-1.27}\exp(-36883/T)\text{s}^{-1}$$

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_2 and CO_2 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 $NO_2+NO_2 \rightarrow NO+O+NO_2$ 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 NO_2 decomposition

Step Size (cm^{-1})	200	400	800	1600	3200
Temp(K)					
500	1.2×10^{-1}	2.7×10^{-1}	4.7×10^{-1}	6.6×10^{-1}	8.0×10^{-1}
700	7.7×10^{-2}	1.9×10^{-1}	3.7×10^{-1}	5.7×10^{-1}	7.4×10^{-1}
900	5.2×10^{-2}	1.4×10^{-1}	2.9×10^{-1}	4.9×10^{-1}	6.8×10^{-1}
1100	3.7×10^{-2}	1.1×10^{-2}	2.4×10^{-1}	4.3×10^{-1}	6.3×10^{-1}
1300	2.8×10^{-2}	8.2×10^{-2}	2.0×10^{-1}	3.8×10^{-1}	5.8×10^{-1}
1500	2.2×10^{-2}	6.6×10^{-2}	1.7×10^{-1}	3.4×10^{-1}	5.4×10^{-1}
1700	1.7×10^{-2}	5.3×10^{-2}	1.4×10^{-1}	3.0×10^{-1}	5.0×10^{-1}
1900	1.4×10^{-2}	4.4×10^{-2}	$1.2\times10^{-}1$	2.7×10^{-2}	4.6×10^{-1}
2100	1.1×10^{-2}	3.7×10^{-2}	1.0×10^{-1}	2.4×10^{-2}	4.3×10^{-1}
2300	9.3×10^{-3}	3.1×10^{-2}	9.0×10^{-2}	2.1×10^{-2}	4.0×10^{-1}
2500	7.8×10^{-3}	2.7×10^{-2}	7.8×10^{-2}	1.9×10^{-2}	3.7×10^{-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 H_2—N_2—O_2 System", Butterworths, London, 1973.

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Wing Tsang
April, 1989

10,1: $NO_2+H_2 \rightarrow HONO+H$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^3molecule^{-1}s^{-1}	
Log K_p = $0.27429-6.3669\times10^3/T+3.639\times10^5/T^2-5.1823/T^3$				
Slack and Grillo(1978)	760–1000	3.56% NO_2, 29.6% H_2 in 1 to 4 atm air induction time measurements in shock tube from NO_2 disappearance	$4\times10^{-11}\exp(-14500/T)$	2.5
Recommendation:			$4\times10^{-11}\exp(-14500/T)$	5

Comments

The results of Slack and Grillo are derived from an analysis of the complex kinetics of H_2—O_2—NO_2 ignition. We have calculated the rate constant for this process using one-half the rate expression for $H+H_2O_2$ (Tsang, J. Phys. Chem. Ref. Data, **15**, 1087, 1986)and the thermodynamics of the process. This leads to the rate expression $4\times10^{-11}\exp(-17200/T)$ cm^{3}molecule^{-1}s^{-1}. The greater endothermicity of the $H+H_2O_2$ 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 f $H_2+NO_2\rightarrow HNO_2+H$ Derived from Shock Tube Investigations H_2—O_2—NO_2 Ignititon" Combustion and Flame **31**, 275, 1978.

Wing Tsang
June, 1989

10,3: $NO_2+O\rightarrow O_2+NO$ (a)
$\rightarrow NO_3$ (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Atkinson *et al.* (1989) review	230–350 200–400		$k_a=6.5\times10^{-12}\exp(120/T)$ $k_b(0,O_2,N_2)=9\times10^{-32}(T/300)^{-2}$ $k_{b\infty}=2.2\times10^{-11}$	1.2
Hippler *et al.* (1975)	300	1.5×10^{17} NO_2 $2.5-73\times10^{18}$ inert gas NO; $NO/NO_2=0$ to 2 photolysis of NO_2	He, 9.6×10^{-32} Ne, 8×10^{-32} Ar, 9.6×10^{-32} CO, 16.3×10^{-32} N_2, 8×10^{-32} CO_2,23.4×10^{-32} CH_4,29.2×10^{-32} C_2H_6,30.4×10^{-32} larger hydrocarbons and fluorinated cmpds $30-70\times10^{-32}$ $k_{b\infty}=2.2\times10^{-11}$	1.2
Gaedtke and Troe (1973)	300	$0-2.4\times10^{22}$ N_2 photolysis of NO_2	$k_{b\infty}=2.2\times10^{-11}$	1.2
Baulch *et al.* (1973)			$k_a=1.7\times10^{-11}\exp(-300/T)$ $k_{b\infty}=1.8\times10^{-11}$ $k_b(0)=6.3\times10^{-32}$ (N_2)	1.25
Recommendations:			$k_a=6.5\times10^{-12}\exp(120/T)$ $k_{b\infty}=2.2\times10^{-11}$ $k_b(0,N_2)=4.1\times10^{-20}T^{-4.08}$ $\exp(-1242/T)$ cm^{6}molecule^{-2}s^{-1} $F_c(N_2)=0.79-1.8\times10^{-4}T$ $k_b(0,CO_2)=3.7\times10^{-20}T^{-3.94}$ $\exp(-1146/T)$ cm^{6}molecule^{-2}s^{-1} $F_c(CO_2)=0.775-1.5\times10^{-4}T$	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

$$k_a = 6.5\times10^{-12}\exp(120/T).$$

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

$$k_{b\infty}=2.2\times10^{-11}\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

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

$$k_b(0,N_2)=4.1\times10^{-20}T^{-4.08}\exp(-1242/T)\text{cm}^6\text{molecule}^{-2}\text{s}^{-1}$$

For CO_2 as the third body we use the data of Hippler *et al.* giving $k(0,CO_2)/k(0,N_2)=3$. This leads to a step size down at room temperature of about 250 cm^{-1}. Assuming a temperature dependence similar to that for N_2 we obtain the following rate expression

$$k_b(0,CO_2) = 3.7\times10^{-20}T^{-3.94}\exp(-1146/T)\ \mathrm{cm^6molecule^{-2}s^{-1}}.$$

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 assummed 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 assummed 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 N_2 and CO_2

$$F_c(N_2) = 0.79-1.8\times10^{-4}T$$

$$F_c(CO_2) = 0.775-1.5\times10^{-4}T\,.$$

TABLE 1: Log (k/k_∞) for the reaction $NO_3+NO_3\rightarrow NO_2+O+NO_3$ 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 $NO_2+O+M\rightarrow M+NO_3$

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

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10,4: $NO_2+H \rightarrow NO+OH$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Agrawalla *et al.* (1981)	298	$1-10\times10^{15}$ NO_2 in 2×10^{16} Ar. OH detection infrared emission in flowing afterglow	$7.2-12.5\times10^{-11}$	2
Michael *et al.* (1979)	230–400	$3-12\times10^{12}$ NO and $4-15\times10^{15}$ CH_4 in $1-3.6\times10^{17}$ Ar H-atom detection via resonance fluorescence of Lyman-alpha following flash photolysis	1.32×10^{-10}	1.1
	195–368	$0.6-3.2\times10^{12}$ NO_2 in $5-12\times10^{16}$ He. H-atom detection via resonance fluoresence in discharge flow system	1.50×10^{-10}	1.2
Clyne and Monkhouse (1977)	298–653	$5-50\times10^{-11}$ NO_2 in 6×10^{16} He. H-atom detection via resonance fluorescence in discharge flow	$4.8\times10^{-10}\exp(-400/T)$	1.2
Bemand and Clyne	298	$0.6-5.5\times10^{12}$ NO_2 in 2×10^{16}argon. H-atom detection via Lyman-alpha fluorescence in disharge flow	1.1×10^{-10}	1.2
Wagner *et al.* (1976)	240–460	$4-13\times10^{12}$ NO_2 in 6×10^{16} He. H-atom detection via Lyman-alpha fluorescence in discharge flow	$7.1\times10^{-10}\exp(-505/T)$	1.2
Baulch *et al.* (1973) review	298–630		$5.8\times10^{-10}\exp(-740/T)$	1.5 at 300 K 2 at 630 K
Recommendations			1.4×10^{-10}	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 $k(H+NO_2 \rightarrow OH+NO) = 1.4\times10^{-10}$ cm^{3}molecule^{-1}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}molecule/cm^3) and assumming deactivation on every collision are significant quantities of the HONO deactivated.

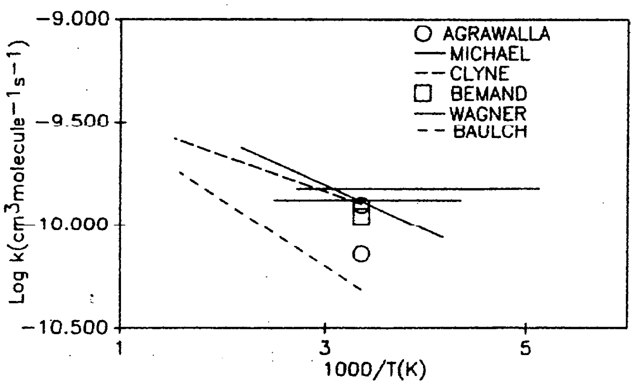

FIG. 1. Summary of experimental results on the $H+NO_2 \rightarrow OH+NO$ reaction.

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10,5: NO_2+OH→HNO
→HO_2+NO (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	*T* range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Atkinson *et al.* (1989)	200–300		cm^{6}molecule^{-2}s^{-1} $k_a(O_2,0)=2.2\times10^{-30}(T/300)^{-2.9}$ $k_a(N_2,0)=2.6\times10^{-30}(T/300)^{-2.9}$ $k_{a\infty}=5.2\times10^{-11}$ s^{-1} $F_c=\exp(-T/353)$	1.2
Audley *et al.* (1984)	298	flow system at 2.5×10^{19} C_2H_6 with small amount of NO_2 and traces of H_2O_2. Gas chromatographic detection of nitrogenated organics. Ratio of rate constants for OH+NO_2 and OH+C_2H_6 determined.	$k_a=2.2\times10^{-11}$ s^{-1}	1.4
Burrows *et al.* (1983)	295	$3-16\times10^{16}$ He	$k_a=16\times10^{-31}$ cm^{6}molecule^{-2}s^{-1}	1.2
		Ar	16×10^{-31} cm^{6}molecule^{-2}s^{-1}	
		N_2	27×10^{-31} cm^{6}molecule^{-2}s^{-1}	
		O_2	26×10^{-31} cm^{6}molecule^{-2}s^{-1}	
		CO_2	45×10^{-31} cm^{6}molecule^{-2}s^{-1}	
		in discharge flow. OH from H+NO_2, detected via resonance fluorescence		
Robertshaw and Smith (1982)	295	$0-2.8\times10^{15}$ NO_2 3.1×10^{15} HNO_3 $1.5\times10^{17}-1\times10^{20}$ Ar $0-2\times10^{20}CF_4$; OH from HNO_3 pulse photolysis and detected vis LIF	$k_{a\infty}>3\times10^{-11}$ $k_a(Ar,.66\times10^{18})=0.75\times10^{-12}$ $k_a(Ar,\ 1.64\times10^{18})=1.68\times10^{-12}$ $k_a(Ar,\ 3.27\times10^{18})=2.68\times10^{-12}$ $k_a(Ar,\ 6.55\times10^{18})=3.33\times10^{-12}$ $k_a(Ar,\ 16.4\times10^{18})=6.30\times10^{-12}$ $k_a(Ar,\ 41.5\times10^{18})=10.5\times10^{-12}$ $k_a(Ar,\ 99.1\times10^{18})=14.3\times10^{-12}$ $k_a(CF_4,1.5\times10^{18})=2.8\times10^{-12}$ $k_a(CF_4,3.13\times10^{18})=5.1\times10^{-12}$ $k_a(CF_4,6.39\times10^{18})=7.7\times10^{-12}$ $k_a(CF_4,16.2\times10^{18})=14.3\times10^{-12}$ $k_a(CF_4,41.1\times10^{18})=19.3\times10^{-12}$ $k_a(CF_4,98.7\times10^{18})=15.3\times10^{-12}$ $k_a(CF_4,71\times10^{18})=23.7\times10^{-12}$ $k_a(CF_4,119\times10^{18})=25.6\times10^{-12}$ $k_a(CF_4,151\times10^{18})=29.1\times10^{-12}$ $k_a(CF_4,215\times10^{18})=36.5\times10^{-12}$	1.1

10,5: $NO_2+OH \rightarrow HNO_3$ (a) — Continued
$\rightarrow HO_2+NO$ (b)

	Conditions		Reaction rate constant			Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}			
Anderson (1980)	225–398	$3-6\times10^{16}$ N_2 or He discharge flow OH from $H+NO_2$ detection via resonance fluorescence	$k_a=1.6\times10^{-31}$ exp(785/T)[N_2] cm^{6}molecule^{-2}s^{-1} 1.7×10^{-31} [He, 300 K] cm^{6}molecule^{-2}s^{-1}			1.25
O'Brien *et al.* (1979)	301	ppm levels of NO_2 and Toluene in 2.5×10^{19} Air at 38% humidity. Photolysis of NO_2 in static system. Complex mechanism.	$k_a=1.3\times10^{-11}$			1.3
Wine *et al.* (1979)	247–352		k_a(M)$\times10^{13}$ at			
			247 K	297 K	352 K	1.1
		5.4×10^{17},He	8.52	4.61	3.41	
		5.4×10^{17},Ar	11.0	7.17	4.65	
		5.4×10^{17},N_2	18.2	9.96	6.81	
		5.4×10^{17},SF_6	26.4	18.3	12.2	
		9.5×10^{17},Ar	18.3	11.3	6.55	
		9.5×10^{17},N_2	27.5	16.2	10.0	
		16×10^{17},Ar	26.5	15.8	11.5	
		16×10^{17},Ar	34.9	24.1	15.3	
		29×10^{17},He	29.8	21.3	15.4	
		29×10^{17},Ar	38.8	24.4	16.5	
		29×10^{17},N_2	60.9	34.5	23.3	
		29×10^{17},SF_6	73.0	62.0	54.3	
		62×10^{17},Ar	64.1	42.2	26.6	
		62×10^{17},N_2	82.8	47.6	29.4	
		95×10^{17},SF_6	128	114	100	
		140×10^{17},Ar	95.2	58.7	41.9	
		190×10^{17},He	81.5	55.5	46.5	
		190×10^{17},Ar	52.6			
		190×10^{17},SF_6	203	151	135	
		230×10^{17},Ar	105	79.4		
		with $10^{15}-10^{16}$ water and $10^{13}-10^{14}$ NO_2. Flash photolysis of water and resonance fluorescence detection of OH				
Campbell and Parkinson (1979)	292	3.4×10^{18} CO with traces of H_2O_2 and NO_2	$k_a=4\times10^{-12}$			1.3
		1.9×10^{18} N_2 H_2O_2—NO_2—CO—N_2(major component) rate constants from CO_2 yields	$k_a=2\times10^{-12}$			1.3
Erler *et al.* (1977)	213–300	$1-2.5\times10^{17}$ He $10-30\%CO_2$ Discharge flow OH from $H+NO_2$ Detection via resonance fluorescence	$k_a=1.5\times10^{-23}T^{-2.9}$cm^{6}molecule^{-2}s^{-1} $k_a=4\times10^{-30}$cm^{6}molecule^{-2}s^{-1} (CO_2,300)			1.25 1.12

10,5: $NO_2+OH \rightarrow HNO_3$ (a) — Continued
$\rightarrow HO_2+NO$ (b)

	Conditions		Reaction rate constant							Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}							
Atkinson *et al.* (1976)	298	8.3×10^{17},Ar	$k_a = 8.4\times10^{-13}$							1.1
		16.3×10^{17},Ar	13.9×10^{-13}							
		32×10^{17},Ar	22.5×10^{-13}							
		64×10^{17},Ar	35.1×10^{-13}							
		128×10^{17},Ar	51×10^{-13}							
		210×10^{17},Ar	57×10^{-13}							
		8.3×10^{17},N_2	1.25×10^{-13}							
		OH from vuv photolysis of H_2O. Detection by resonance fluorescence								
Anastasi and Smith (1976)	220–550		$k_a(M)\times10^{13}$ at							
			220	238	265	296	358	450	550	1.2
		3.2×10^{17},N_2	16	11	7.5	7.4	4.5			
		5.5×10^{17},N_2	24							
		8.0×10^{17},N_2	36	26	17	14	8.3	4.1		
		16×10^{17},N_2	64	37	26	26	14	6.1	3.2	
		40×10^{17},N_2	100	61	47	43	21	10	7.4	
		80×10^{17},N_2	130			66	49	15	10	
		160×10^{17},N_2	140			96	62	(19)[a]	(12)[b]	
		8×10^{17},SF_6	52			30	16		(3.6)[c]	
		16×10^{17},SF_6							6.6	
		160×10^{17},SF_6	180			150	110		(27)[b]	
		8×10^{17},He	17			6.1				
		40×10^{17},He							3.8	
		8×10^{17},Ar				7.3				
		8×10^{17},O_2				11				
		Flash photolysis of HNO_3. OH detection via resonance absorption. $0-10^{16}$ NO_2; 10^{16} HNO_3	(a) 1.43×10^{18} (b) 11.7×10^{18} (c) 0.6×10^{18}							
Harris and Wayne (1974)	298	$2-8\times10^{16}$ Ar	$k_a=1.5\times10^{-30}$ cm^{6}molecule^{-2}s^{-1}							1.3
		" ? N_2	2.6×10^{-30} (cm^{6}molecule^{-2}s^{-1})							
		Discharge flow with resonance fluorescence detection of OH								
Gordon and Mulac (1975)	440	Pulse radiolysis in 17×10^{19} H_2O with 1.1×10^{17} NO_2 Detection of OH by resonance absorption	$k_a=5.3\times10^{-12}$ (435,H_2O)							1.1
Anderson *et al.* (1974)	298	$3.3-33\times10^{16}$ in He, Ar, N_2.	$k_a=1\times10^{-30}$ cm^{6}molecule^{-2}s^{-1}, He							1.3
		Discharge flow with resonance fluorescence detection of OH	1×10^{-30},cm^{6}molecule^{-2}s^{-1}, Ar							
			2.3×10^{-30},cm^{6}molecule^{-2}s^{-1}, N_2							
Howard and Evenson (1974)	296	$1.3-10\times10^{17}$ N_2 laser magnetic detection of OH in flow discharge	$k_a=2.9\times10^{-30}$cm^{6}molecule^{-1}s^{-1}							1.2
Baulch (1973) review	298		k_a(He)$=1.4\times10^{-30}$cm^{6}molecule^{-1}s^{-1}							1.5

10,5: $NO_2+OH \rightarrow HNO_3$ (a) – Continued
$\rightarrow HO_2+NO$ (b)

	Conditions		Reaction rate constant	Uncertaint
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Howard (1980)	452–1271	High temperature discharge flow reactor. Laser magnetic detection of OH. He + O_2 at $1-5.3\times10^{16}$	$k_b=3\times10^{-11}\exp(-3360/T)$	1.2
Recommendations			$k_{a\infty}=4\times10^{-11}$ $k_a(N_2,0)=1.77\times10^{-15}T^{-5.49}\exp(-1183/T)$ cm^{6}molecule^{-2}s^{-1} $k_a(CO_2,0)=1.6\times10^{-15}T^{-5.4}\exp(-1100/T)$ cm^{6}molecule-^{2}s^{-1} $F_c(N_2)= 0.725-2.5\times10^{-4}T$ $F_c(CO_2)= 0.725-2.5\times10^{-4}T$ $k_b=3\times10^{-11}\exp(-3360/T)$	1.2,300 K 2.5 at 1200 K 1.2

Comments

There are two reacting channels from the interaction of OH + NO_2. 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_2 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 assummed 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_2. 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 4×10^{-11} cm^{3}molecule^{-1}s^{-1} 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_2 and CO_2 and assummed 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^{-1} to 300 cm^{-1} in the temperature range 300 to 1200 K. The general situation is very similar to that for the hydrocarbons.

$$k(OH+NO_2+N_2 \rightarrow HNO_3+N_2)=$$
$$1.77\times10^{-15}T^{-5.49}\exp(-1183/T)\ \mathrm{cm^6molecule^{-2}s^{-1}}$$

$$k(OH+NO_2+CO_2 \rightarrow HNO_3+CO_2)=$$
$$1.6\times10^{-15}T^{-5.4}\exp(-1100/T)\ \mathrm{cm^6molecule^{-2}s^{-1}}$$

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

$$F_c(N_2)= 0.725-2.5\times10^{-4}T$$

$$F_c(CO_2)= 0.725-2.5\times10^{-4}T$$

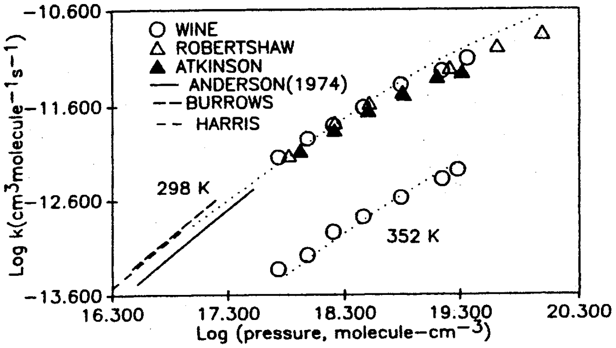

FIG. 1. Experimental results for the reaction of $OH+NO_2$ in argon at various temperatures. Results for 352 K have been reduced by one log unit to increase legibility. Dotted lines represent the results of our calculations.

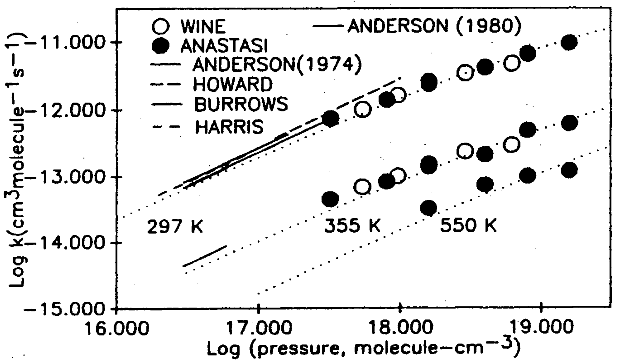

FIG. 2. Experimental results for the reaction of $OH+NO_2$ in nitrogen at various temperatures. Results for 355 K and 550 K have been reduced by one log unit to increase legibility. Dotted lines represent the results of our calculations.

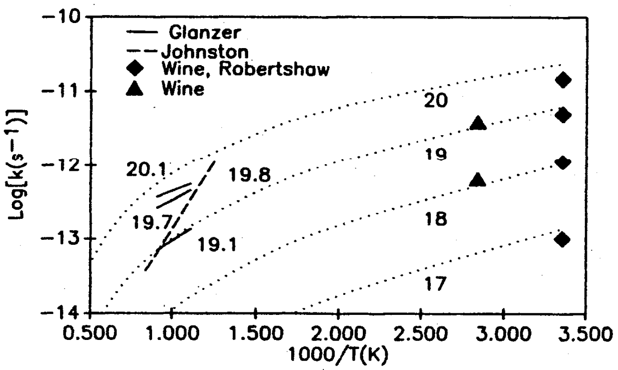

FIG. 3. Experimental results on the reaction $OH+NO_2$ in argon. High temperature results are from the reverse decomposition process. Points are interpolated from Fig. 1. Numbers are density in molecules/cm³. Dotted lines are our calculations.

TABLE 1. Log (k/k_∞) for the reaction $NO_2+OH+HNO_3 \rightarrow HNO_3+HNO_3$ 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 $OH+NO_2+M \rightarrow HNO_3+M$

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

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Wing Tsang
August, 1989

10,6: $NO_2+HCHO \rightarrow HNO_2+CHO$

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Lin *et al.* (1990)	1140–1650	0.1 – 0.2% Trioxane 0.3 – 0.65% NO_2 and $2-4\times10^{18}$ Ar in Shock Tube. Reaction followed by detection of NO, CO and H_2O. Computer simulation for rate constants.	$1.3\times10^{-21}T^{2.77}\exp(-6910/T)$	2
He *et al.* (1989)	393–476	2.7% – 5.08% HCHO 3.44% – 7.4% NO_2 in Ar at 5×10^{19} FTIR detection of all products. Computer simulation for rate constants	$3.33\times10^{-13}\exp(-8080/T)$	2
Recommendations:			$1.3\times10^{-21}T^{2.77}\exp(-6910/T)$	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

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Lin, C. Y., Wang, H. T., Lin, M. C. and Melius, C. F., "A Shock Tube Study of the CH_2O+NO_2 Reaction at High Temperatures" Int. J. Chem. Kin, in press.

W. Tsang
June, 1989

10,7: $NO_2+CHO \rightarrow CO+HNO_2$ (a)
$\rightarrow H+CO_2+NO$ (b)

Reference	Conditions		Reaction rate constant	Uncertainty
	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Lin *et al.* (1990)	1140–1650	0.1 – 0.2% Trioxane 0.3 – 0.65% NO_2 and $2-4\times10^{18}$ Ar in Shock Tube. Reaction followed by detection of NO, CO and H_2O. Computer simulation for rate constants.	$k_a=0.21\times(1/T)^{-3.29}\exp(-1185/T)$ $k_b=1.4\times10^{-8}(1/T)^{0.75}\exp(-970/T)$	2
He *et al.* (1989)	393–476	2.7% – 5.08% HCHO 3.44% – 7.4% NO_2 in Ar at 5×10^{19} FTIR detection of all products. Computer simulation for rate constants	$k_a=2.8\times10^{-11}$ $k_b=1.5\times10^{-11}$	1.5
Timonen *et al.* (1988)	294–713	HCO from laser photolysis (308nm) of CH_3CHO (0.05%) in 0 – 0.35% NO_2 in 2×10^{16} He. MS- detection of HCO	$k_{a+b}=2.5\times10^{-11}\exp(217/T)$	1.2
Recommendations			$k_a=2.1\times(1/T)^{-3.29}\exp(-1185/T)$ $k_b=1.4\times10^{-8}(1/T)^{0.75}\exp(-970/T)$	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 assumming 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_2O with NO_2 in the Temperature Range of 393–476K FTIR Product Measurment 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_2O+NO_2 Reaction at High Temperatures" Int. J. Chem. Kin, in press.

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Wing Tsang
August, 1989

10,8: $NO_2+CO \rightarrow CO_2+NO$

	Conditions		Reaction rate constant	Uncertainty
Reference	*T* range/K	[M] range/cm^3	*k*/cm^{3}molecule^{-1}s^{-1}	
Milks *et al.* (1979)	950–1550	1.4–4% NO_2 and 3–5% CO in argon. Single pulse shock tube study with analysis of CO, CO_2, NO, NO_2	$5.4\times10^{-11}\exp(-16110/T)$	3
Freund and Palmer (1977) (also review)	1300–2000 500–2000	2–8% NO_2 and 25–50% CO in $2.4-4.2\times10^{18}$ argon in shock tube experiments. Reaction followed via NO_2 absorption and CO_2 emission.	$1.5\times10^{-10}\exp(-17000/T)$	2.5
Recommendation			$1.5\times10^{-10}\exp(-17000/T)$	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

Milks, D., Adams, T. N. and Matula, R. A., "Single Pulse Shock Tube Study on the Reaction Between Nitrogen Dioxide (NO_2) and Carbon Monoxide (CO)", Comb. Sci. Tech., **19**, 151, 1979.

Freund, H. and Palmer, H. B., "Shock-Tube Studies of the Reactions of NO_2 with NO_2, SO_2 and CO", Int. J. Chem. Kin., **9**, 887, 1977.

Wing Tsang
September, 1989

10,10: $NO_2+NO_2 \rightarrow NO_3+NO$ (a)
$\rightarrow 2NO+O_2$ (b)
$\rightarrow N_2O_4$ (c)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Freund and Palmer(1977)	1419–1857	5.7 – 12% NO_2 in 1.7 – 7.3 × 10^{18} Ar. Shock tube experiments with detection of NO_2 from absorption.	$k_{a+b}=6.6\times10^{-15}$, 1660 K	3
Baulch *et al.* (1973)	600–1000 review		$k_b= 3.3\times10^{-12}\exp(-13500/T)$	1.3
Recommendation			$k_a = 1.6\times10^{-14}T^{.73}\exp(-10530/T)$ $k_b = 2.7\times10^{-12}\exp(-13147/T)$	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;

$$k_a = 1.6\times10^{-14}T^{.73}\exp(-10530/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

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

$$k_b = 2.7\times10^{-12}\exp(-13147/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\ .$$

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 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 H_2—N_2—O_2 System", Butterworths, London, 1973.

Freund, H. and Palmer, H. B., "Shock-Tube Studies of the Reactions of NO_2 with NO_2, SO_2 and CO, Int. J. Chem. Kin., **9**, 887, 1977.

Wing Tsang
October, 1989

11,0: HNO + M → H + NO + M

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Log K_p = $6.403-1.172\times10^4/T+2.542\times10^5/T^2-2.750\times10^7/T^3$				
Recommendations			$k_\infty=1.2\times10^{16}T^{-0.43}$ $\exp(-24929/T)\text{s}^{-1}$ $k(0,N_2)=0.01T^{-1.61}$ $\exp(-25585/T)$ $F_c=0.83$ $k(0,CO_2)=6.4\times10^{-4}T^{-1.24}$ $\exp(-25172/T)$ $F_c=0.83$	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_2 and CO_2 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 i Table 1. Collision efficiencies as a function of step siz down and temperature can be found in Table 2. For more complete discussion, see 9,4.

Wing Tsang
June, 1989

TABLE I: Log ($k/k(0)$) for the reaction $HNO+HNO \rightarrow H+NO+HNO$ 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 $HNO+M=H+NO+M$

Step Size (cm^{-1})	200	400	800	1600	3200
Temp (K)					
500	1.2×10^{-1}	2.7×10^{-1}	4.7×10^{-1}	6.6×10^{-1}	8.0×10^{-1}
700	7.6×10^{-2}	1.9×10^{-1}	3.6×10^{-1}	5.7×10^{-1}	7.4×10^{-1}
900	5.1×10^{-2}	1.4×10^{-1}	2.9×10^{-1}	4.9×10^{-1}	6.8×10^{-1}
1100	3.6×10^{-2}	1.0×10^{-2}	2.3×10^{-1}	4.3×10^{-1}	6.2×10^{-1}
1300	2.7×10^{-2}	7.9×10^{-2}	1.9×10^{-1}	3.7×10^{-1}	5.7×10^{-1}
1500	2.0×10^{-2}	6.2×10^{-2}	1.6×10^{-1}	3.3×10^{-1}	5.3×10^{-1}
1700	1.6×10^{-2}	5.0×10^{-2}	1.3×10^{-1}	2.9×10^{-1}	4.9×10^{-1}
1900	1.3×10^{-2}	4.1×10^{-2}	$1.1\times10^{-}1$	2.5×10^{-2}	4.5×10^{-1}
2100	1.0×10^{-2}	3.4×10^{-2}	9.7×10^{-2}	2.3×10^{-2}	4.1×10^{-1}
2300	8.5×10^{-3}	2.8×10^{-3}	8.3×10^{-2}	2.0×10^{-2}	3.8×10^{-1}
2500	7.0×10^{-3}	2.4×10^{-3}	7.2×10^{-2}	1.8×10^{-2}	3.5×10^{-1}

Wing Tsang
June, 1989

11,3 $HNO + O \rightarrow OH + NO$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Recommendation			6×10^{-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 $O+HO_2 \rightarrow OH+O_2$. It is also consistent with our recommendation for $OH+HNO \rightarrow H_2O+NO$.

Wing Tsang
June, 1989

11,4: $H+HNO \rightarrow H_2+NO$

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant $k/cm^3molecule^{-1}s^{-1}$	Uncertainty
Dodonov *et al.* (1980)	298	HNO from excited H_2 mixed with NO at 2×10^{17}. Mass spec detection.	1.2×10^{-10}	large
Washida *et al.* (1978)	298	$1-6\times10^{14}$ NO, $0.3-20\times10^{14}$ H in 1.5×10^{17} He in discharge flow Mass spec. detection of HNO via photoionization	$>1.6\times10^{-12}$	
Baulch *et al.* (1973) (review)	2000		8×10^{-12}	
Recommendation			$3\times10^{-11}\exp(-500/T)$	4

Comments

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

The rate constant at 2000 K appear to be small in comparison to analogous exothermic reactions ($H+HO_2$, $H+HI$). 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 assummed activation energy of 4 kJ/mol gives us the rate expression

$$k(H+HNO \rightarrow H_2+NO) = 3\times10^{-11}\exp(-500/T)cm^3molecule^{-1}s^{-1}$$

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_2—N_2—O_2 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: $OH+HNO \rightarrow H_2O + NO$

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant $k/cm^3molecule^{-1}s^{-1}$	Uncertainty
Baulch *et al.* (1973)	2000K		6×10^{-11}	2
Recommendation			$8\times10^{-11}\exp(-500/T)$	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 tht 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_2—N_2—O_2 System", Butterworths, London, 1973.

Wing Tsang
June, 1989

11,7:HNO+CHO→HCHO+NO

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant $k/cm^3molecule^{-1}s^{-1}$	Uncertainty
Recommendation			$1\times10^{-12}\exp(-1000/T)$	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 1×10^{-12} $cm^3molecule^{-1}s^{-1}$ range. We recommend

$$k(HNO+CHO\to HCHO+NO)=1\times10^{-12}\exp(-1000/T)\ cm^3molecule^{-1}s^{-1}$$

with an uncertainty of a factor of 5.

Wing Tsang
April, 1989

11,10:HNO+NO$_2$→HNO$_2$+NO

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant $k/cm^3molecule^{-1}s^{-1}$	Uncertainty
Recommendation			$1\times10^{-12}\exp(-1000/T)$	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-factor close to collisional. We have also assummed an activation barrier of 8 kJ/mol.

Wing Tsang
August, 1989

11,11: HNO+HNO→H$_2$O+N$_2$O

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant $k/cm^3molecule^{-1}s^{-1}$	Uncertainty
He *et al.* (1988)	450–520	0.5–4.0% CH_3ONO in $2-180\times10^{17}$ He. FTIR and GLC detection of final products from static reactor and kinetic modeling.	$1.4\times10^{-15}\exp(-1561/T)$	2
Cheskis *et al.* (1981)	298	2.3×10^{17} HCHO, 4×10^{17} CH_3CHO in $2-125\times10^{17}$ NO under flash photolysis. HNO detection via intracavity laser absorption	1.5×10^{-15}	1.6
Callear and Carr (1975)	280–420	0.2–1%NO in $3-20\times10^{18}$ H_2 under flash photolysis HNO detection via uv absorption	5.35×10^{-15} (298) 1.4×10^{-14} (400)	1.3
Kohut and Lampe (1967)	300	< 1% NO in $1-2.4\times10^{18}$ H_2 or D_2. H/D from Hg photosensitized decomp. of H_2/D_2	6.6×10^{-16}	large
Recommendation:			$1.4\times10^{-15}\exp(-1561/T)$	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_2O appearance. The work of Kohut and Lampe involves the steady state concentration of HNO as well as N_2O 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_2O 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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Wing Tsang
August, 1989

12,0 $HNO_2+M \rightarrow OH+NO+M$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Log K_p = $7.547-1.051\times10^4/T-2.558\times10^5/T^2+4.296\times10^7/T^3$				
Recommendations			$k_\infty=1.2\times10^{19}(1/T)^{1.23}$ $\exp(-25010/T)\mathrm{s}^{-1}$ $k(0,\mathrm{sc})=7.3\times10^5(1/T)^{3.42}$ $\exp(-25200/T)$ $k(0,N_2)=5\times10^6(1/T)^{3.8}$ $\exp(-25340/T)$ $F_c(N_2)=$ 0.62 $k(0,CO_2)=1.7\times10^6(1/T)^{3.59}$ $\exp(-25250/T)$ $F_c(CO_2)=0.62$	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,

$$k_\infty=1.2\times10^{19}(1/T)^{1.23}\exp(-25010/T)\mathrm{s}^{-1}$$

$$k(0,\mathrm{sc})=7.3\times10^5(1/T)^{3.42}\exp(-25200/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

$$k(0,N_2)=5\times10^6(1/T)^{3.8}\exp(-25340/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

$$k(0,CO_2)=1.7\times10^6(1/T)^{3.59}\exp(-25250/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

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_2 and CO_2, the F_c values which can be used to determine fall-off value analytically are for both cases 0.62.

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

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 $HNO^2 + M = HO + NO + M$

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

12,3: $HNO_2 + O \rightarrow OH + NO_2$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm	k/cm^{3}molecule^{-1}s^{-1}	
Kaiser and Japar (1978)	300–355	Low pressure discharge-flow with mass spect detection	$1-5\times10^{-15}$	
Recommendations:	300–2500		$2\times10^{-11}\exp(-3000/T)$	10

Comments

Kaiser and Japar reported that at 300 K, the rate constant was 1×10^{-15} cm^3 molecule^{-1} s^{-1} and at 355 K, varied between $1-5\times10^{-15}$ cm^3 molecule^{-1} 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 2×10^{-11} cm^3 molecule^{-1} s^{-1}.

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J. T. Herron
September, 1989

12,4: $HNO_2+H \rightarrow H_2+NO_2$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm	k/cm^{3}molecule^{-1}s^{-1}	
Recommendations:	300–2500		$2\times10^{-11}\exp(-3700/T)$	20

Comments

There are no data. Although there are data for the reactions of OH, O, and H with H_2O_2 which could serve as a model for comparison, there are problems with regard to mechanism (the low temperature data for the H + H_2O_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 + HNO_2, and set the activation energy to give a rate constant at 300 K a factor of 10 smaller than the corresponding O + HNO_2 reaction.

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J. T. Herron
September, 1989

12,5: $HNO_2+OH \rightarrow H_2O+NO_2$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Atkinson *et al.* (1989) review	280–340		$1.8\times10^{-11}\exp(-390/T)$	2
Jenkin and Cox (1987)	278–342.5	Photolysis. 2×10^{13} O_3, 5×10^{15} HO, 8×10^{12} HNO_2 in 3.5×10^{17} molec cm^{-3} Ar	$1.8\times10^{-11}\exp(-390/T)$	1.6
Cox, Derwent, and Holt (1976)	296	Photolysis. 10^{14}–10^{15} HNO_2, 10^{12}–10^{14}NO, 10^{12}–$10^{14}$$NO_2$, 10^{14}–10^{17}CO, in 2.5×10^{19} molec cm^{-3} N_2/O_2 mixture Relative to CO + OH	5.9×10^{-12}	1.4
Cox, Derwent, and Holt (1976)	296	Photolysis. $2\times10^{14}$$HNO_2$, 10^{13}NO, $7\times10^{12}$$NO_2$, 10^{17}–$10^{18}$$H_2$ in 2.5×10^{19} molec cm^{-3} N_2/O_2 mixture Relative to H_2 + OH	6.6×10^{-12}	1.3
Cox, Derwent, Holt, and Kerr (1976)	296	Photolysis. $1-2\times10^{14}$$HNO_2$, $2-10\times10^{13}$NO, $5\times10^{12}-10^{14}$ NO_2, $5-10\times10^{18}$ CH_4 in 2.5×10^{19} molec cm^{-3} N_2/O_2 mixture Relative to CH_4 + OH	7.2×10^{-12}	1.5
Fifer (1976)	1000–1400	Shock-tube. 12–33%NO, 2% H_2O, 0.1–0.4% NO_2 in $2-8\times10^{19}$ Ar	2.6×10^{-12}	1.4
Recommendations:	300–2500		2.1×10^{-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_2, and CH_4. 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 6.6×10^{-12} cm^3 molec^{-1} 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 $HNO_2 \leftrightarrow OH + NO$ was in equilibrium and that the rate limiting step was $OH + HNO_2$. 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 calcul tion for the system to verify that OH was in a steady stat under the conditions of the experiment).

In our judgement the lower temperature data must b given the greatest weight, but the disagreement betwee the two absolute data sets increases the degree of uncertainty in the recommendation. The recommended valu 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.

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12,7 $HNO_2+CHO\rightarrow H_2CO+NO_2$

Reference	Conditions T range/K	 [M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
$\mathrm{Log}_{10}K_p = -1.2537+2.4644\times10^3/T-5.5108\times10^4/T^2+9.7338\times10^5/T^3$				
Recommendation			$2\times10^{-21}T^{2.37}\exp(-1940/T)$	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,

$$k(HNO_2+CHO\rightarrow H_2CO+NO_2) = 2\times10^{-21}T^{2.37}\exp(-1940/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

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 $HCN+M\rightarrow H+CN+M$

Reference	Conditions T range/K	 [M] range/cm³	Reaction rate constant k/cm³molecule⁻¹s⁻¹	Uncertainty
Szekely *et al.* (1984)[a]	2700–3600	12–200 ppm HCN in $6-20\times10^{17}$ Ar CN concentration via 388.0–388.4nm absorption	$1.7\times10^{-8}\exp(-54650/T)$	2
Szekely *et al.* (1982)[b]	3570–5036	3–142 ppm HCN in $2.5-6\times10^{17}$ Ar. CN concentration via emission at 388.3nm.	$6.7\times10^{-10}\exp(-44740/T)$	2
Tabayashi *et al.* (1977)	2600–3600	0.2–1% HCN in $7-33\times10^{18}$ Ar CN concentration via absorption at 388.3nm	$2.1\times10^{-8}\exp(-50196/T)$	2
Roth and Just (1976)	2200–2700	125–500 ppm HCN in 6×10^{18} Ar. H-atom concentration by resonance absorption	$9.5\times10^{-8}\exp(-59060/T)$	1.5
Recommendation			$k_\infty=8.3\times10^{17}(1/T)^{0.93}$ $\exp(-62294/T)$/s $k(0,N_2)=5.93\times10^{2}(1/T)_2^{.6}$ $\exp(-62845/T)$/s $F_c(N_2)=0.95-10^{-4}T$ $k(0,CO_2)=2.1\times10^{2}(1/T)^{2.44}$ $\exp(-62800/T)$ $F_c(CO_2)=0.875-0.5\times10^{-4}T$	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;

$$k(HCN+Ar\rightarrow H+CN+Ar)=$$
$$5.6\times10^{11}(1/T)^{5.13}\exp(-66966/T)\text{cm}^3\text{molecule}^{-}1\text{s}^{-1}$$

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⁻¹. The fit can be found in Fig. 1. Unfortunately there are no data with other colliders. We assume that for N_2 and CO_2 the step size down is 1500 and 2000 cm⁻¹ respectively. This leads to the following low pressure rate expresssions

$$k(HCN+N_2\rightarrow H+CN+N_2)=$$
$$5.93\times10^{2}(1/T)_2{}^{.6}\exp(-62845/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

$$k(HCN+CO_2\rightarrow H+CN+CO_2)=$$
$$2.1\times10^{2}(1/T)^{2.44}\exp(-62800/T)\ \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}.$$

Above 10–100 atmosphere pressure effects begin to be important. Assumming that the reverse combination rate expression for the reverse reaction is $k(CN+H\rightarrow HCN)$ $=2.99\times10^{-9}(1/T)^{0.5}$ cm³molecule⁻¹s⁻¹ with an uncertainty of a factor of 3, leads to

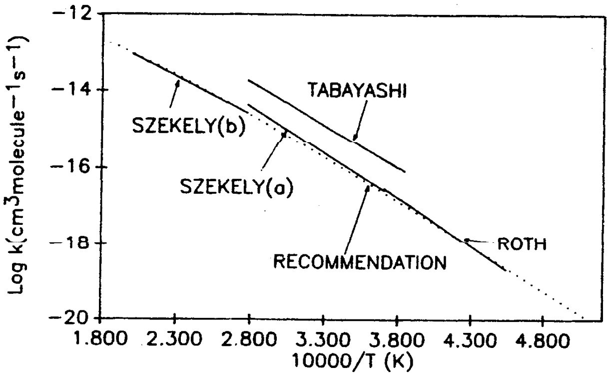

FIG. 1. Summary of experimental data on the reaction $HCN+Ar\rightarrow H+CN+Ar$. The dotted line represents our recommendation.

$$k(\mathrm{HCN}\rightarrow\mathrm{H}+\mathrm{CN})=8.3\times10^{17}(1/T)^{0.93}\exp(-62294/T)/\mathrm{s}$$

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 CO_2 and N_2 the F_c values for converting $k(0)$ an k_∞ to rate constants in the intermediate pressure regio are

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

$$F_c(CO_2)=0.875-0.5\times10^{-4}T\,.$$

TABLE 1. Log $(k/k(0))$ for the reaction HCN + HCN→HCN + 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 HCN + M = H + CN + M

Step Size (cm^{-1})	200	400	800	1600	3200
Temp (K)					
500	1.2×10^{-1}	2.7×10^{-1}	4.7×10^{-1}	6.6×10^{-1}	8.0×10^{-1}
700	7.8×10^{-2}	1.9×10^{-1}	3.7×10^{-1}	5.7×10^{-1}	7.4×10^{-1}
900	5.4×10^{-2}	1.4×10^{-1}	3.0×10^{-1}	5.0×10^{-1}	6.9×10^{-1}
1100	3.9×10^{-2}	1.1×10^{-1}	2.5×10^{-1}	4.4×10^{-1}	6.4×10^{-1}
1300	2.9×10^{-2}	8.5×10^{-2}	2.0×10^{-1}	3.9×10^{-1}	5.9×10^{-1}
1500	2.3×10^{-2}	6.8×10^{-2}	1.7×10^{-1}	3.4×10^{-1}	5.5×10^{-1}
1700	1.8×10^{-2}	5.6×10^{-2}	1.5×10^{-1}	3.1×10^{-1}	5.1×10^{-1}
1900	1.5×10^{-2}	4.7×10^{-2}	$1.3\times10-1$	2.7×10^{-2}	4.7×10^{-1}
2100	1.2×10^{-2}	3.9×10^{-2}	1.1×10^{-1}	2.5×10^{-2}	4.4×10^{-1}
2300	1.0×10^{-2}	3.3×10^{-2}	9.5×10^{-2}	2.2×10^{-2}	4.1×10^{-1}
2500	8.7×10^{-3}	2.9×10^{-3}	8.4×10^{-2}	2.0×10^{-2}	3.8×10^{-1}

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13,3 $HCN+O \rightarrow CN+OH(a)$
$\rightarrow NH+CO(b)$
$\rightarrow NCO+H(c)$

Reference	Conditions T range/K	[M] range/cm^3	Reaction rate constant k/cm^{3}molecule^{-1}s^{-1}	Uncertainty
Szekely *et al.* (1984)	1800–2600	0.44%N_2O;9.5%HCN in 2.5×10^{18} Ar. Shock tube experiments with absorption detection of NH at 336.1 nm.	$k_b=3.7\times10^{-11}\exp(-7740/T)$	1.4
	2000–2500	116−660 ppm N_2O and 182−770 ppm HCN. Shock tube experiments with absorption detection of CN at 388.0−388.4 nm	$k_a<8.3\times10^{-11}\exp(-11000/T)$	
Perry and Melius (1984)	575–840	$0.5-4.7\times10^{15}$ NO $1.9-1.7\times10^{15}$ O_2 $8.7-65\times10^{15}$ N_2O in $2-3\times10^{18}$ Ar. Slow flow reactor. O generated by flash photolysis and detected by chemiluminescence. NCO detected by LP-LIF (separate experiments)	$k_{a+b+c}=9.8\times10^{-12}\exp(-4030/T)$ $k_c=3.3\times10^{-16}T^{1.47}\exp(-3800/T)$ $k_b=9.0\times10^{-16}T^{1.21}\exp(-3850/T)$ $k_a=4.5\times10^{-15}T^{1.58}\exp(-13400/T)$	1.1
Louge and Hanson (1984)	1440	0.8%N_2O;HCN; 0.1%O_2 in Ar. Shock Tube experiments with NCO detection by absorption	$k_c=8.3\times10^{-13}$	2
Roth *et al.* (1980)	1800–2500	5–40 ppm N_2O and ppm HCN in 6×10^{18} Ar. Atomic resonance detection of H and O	$k_{c+b}=1.2\times10^{-10}\exp(-7460/T)$ $k_{c+b+a}/k_{c+b}=1.6$	1.425-200
Davis and Thrush (1968)	450–650	3.3×10^{16} N_2 with traces of O_2, NO and HCN in discharge flow. O generated by $N+NO \rightarrow N_2+O$ reaction and detected by chemiluminescence from O+NO reaction	$k_{a+b+c}=8.7\times10^{-12}\exp(-4080/T)$	1.3
Recommendations:			$k_a=3.3\times10^{-16}T^{1.47}\exp(-3800/T)$ $k_b=9.0\times10^{-16}T^{1.21}\exp(-3850/T)$ $k_c=4.5\times10^{-15}T^{1.58}\exp(-13400/T)$	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.

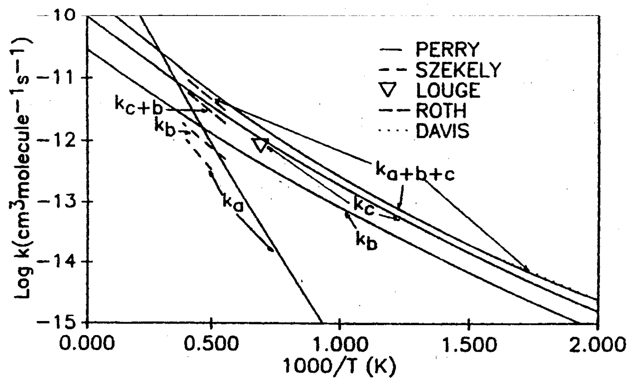

FIG. 1. Summary of data for the reaction O + HCN.

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Wing Tsang
September, 1989

13,4 $H+HCN \rightarrow H_2+CN$ (a)
$+M \rightarrow H_2CN+M$ (b)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
$\mathrm{Log}_{10}K_p(a) = 0.35091 - 3.5302 \times 10^3/T - 3.4662 \times 10^5/T^2 + 5.0453 \times 10^7/T^3$				
Baulch *et al*. (1981)	300–1000		$k_a = 6.3 \times 10^{-10}\exp(-12400/T)$	3
Recommendation:	300–2500		$k_a = 6.2 \times 10^{-10}\exp(-12507/T)$	100, 500 K 3 at 2500 K
			$k_{b\infty} = 5.5 \times 10^{-11}\exp(-2438/T)$ $k_b(0,N_2) = 4.4 \times 10^{-24}(1/T)^{2.73}$ $\exp(-3855/T)$ $k_b(O,CO_2) = 4.3 \times 10^{-24}(1/T)^{2.63}$ $\exp(-3791/T)$ $F_c = 0.95 - 10^{-4}T$ (CO_2, N_2)	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 $CN + H_2 \rightarrow HCN + H$(15,1) reaction and the thermodynamics. This leads to the rate expression

$$k(HCN + H \rightarrow H_2 + CN) = 6.2 \times 10^{-10}\exp(-12507/T)\mathrm{cm^3molecule^{-1}s^{-1}}$$

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 uncertainy of a factor of 100 at room temperature and decreasing 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 assummed rate expression for the addition of hydrogen to HCN of

$$k(H + HCN \rightarrow H_2CN) = 5.5 \times 10^{-11}\exp(-2438/T)\ \mathrm{cm^3molecule^{-1}s^{-1}}$$

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 H + HCHO. Combining this with the estimated thermodynamic properties of the H_2CN 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;

$$k_b(0,N_2) = 4.4\times10^{-24}(1/T)^{2.73}\exp(-3855/T)\mathrm{cm^6 molecule^{-2} s^{-1}}$$

$$k_b(O,CO_2) = 4.3\times10^{-24}(1/T)^{2.63}\exp(-3791/T)\mathrm{cm^6 molecule^{-2} s^{-1}}$$

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

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Wing Tsang
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13,5 $HCN+OH \rightarrow H_2O+CN$ (a)
$\rightarrow H+HOCN$ (b)
$\rightarrow H+HNCO$ (c)

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
$\mathrm{Log}_{10}K_p(\mathrm{a}) = -0.27893 - 3.0125\times10^2/T - 2.6722\times10^5/T^2 + 3.5241\times10^7/T^3$				
Miller and Melius (1986) theory	500–2500		$k_b = 5.3\times10^{-20}T^{2.45}\exp(-6100/T)$ $k_c = 9.3\times10^{-30}T^{4.71}\exp(248/T)$	?
Fritz *et al.* (1984)	298–500	$0.2-2\times10^{19}$ HCN in $0.3-12\times10^{19}$ N_2 OH from flash photolysis of HNO_3 in static system. Detected via resonance absorption	$k_{a+b+c} = 1.2\times10^{-13}\exp(-400/T)$	1.4
Phillips, 1979	298–563	$2-8\times10^{15}$ HCN in 4×10^{17} He or Ar in discharge flow with OH from $H+NO_2$. Resonance fluorescence detection of OH	$k_{a+b+c} = 1.6\times10^{-11}(1/T)\exp(-1863/T)$	1.4
Szekely *et al.*	2460–2840	$83-450$ ppm C_2N_2 $603-2320$ ppm H_2O in 1.7×10^{18} Ar. Shock tube study CN detected via absorption at 388.3nm OH detected via absorption at 306.67nm	$k_a = 2.9\times10^{-12}$(2100 K?) from reverse and equilibrium constant	1.5
Recommendations:			$k_a = 3.6\times10^{-17}T^{1.5}\exp(-3887/T)$ $k_b = 5.3\times10^{-20}T^{2.45}\exp(-6100/T)$ $k_c = 9.3\times10^{-30}T^{4.71}\exp(248/T)$	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 $T^{1.5}$ dependence of the preexpoential 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 asssummed mechanism, does provide a check of the data.

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Wing Tsang
October, 1989

13,7 $HCN+CHO \rightarrow HCHO+CN$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Log K_p = $-0.62848-7.4327\times10^3/T-3.782\times10^4/T^2-3.9677\times10^5/T^3$				
Recommendation:			$1\times10^{-11}\exp(-17200/T)$	20 at 300 K 4 at 1000 K

Comment

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^{-11} cm^{3}molecule^{-1}s^{-1} and through the thermodynamics obtain

$$k(HCN+CHO \rightarrow HCHO+CN) = 1\times10^{-11}\exp(-17200/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

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

Wing Tsang
October, 1989

14,0: $N_2O \rightarrow N_2 + O$

	Conditions		Reaction rate constant	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Hanson and Salimian(1985) review	1500–3600		$1.15\text{x}T^{-2.5}\exp(-32710/T)$(Ar,Kr)	1.2
Loirat *et al.* (1985)	1080–1227	Static experiments with gas chromatographic analysis of reactant and products $9-60\times10^{17}$ total pressure. N_2O;.33N_2O+0.67CO_2;.05N_2O 0.95N_2	molecule/cm^3 T(K) 9×10^{17} 1.8×10^{17} 6×10^{16} 1080(N_2O) 6.8×10^{-3} 4.4×10^{-3} 3.4×10^{-3} (s^{-1})(N_2) 6.1×10^{-3} 3.9×10^{-3} 2.5×10^{-3} (CO_2) 4.4×10^{-3} 1128(N_2O) 2.0×10^{-2} 1.3×10^{-2} 3.4×10^{-3} (s^{-1})(N^2) 1.8×10^{-2} 1.2×10^{-2} 6.6×10^{-3} (CO_2) 1.1×10^{-2} 1178(N_2O) 5.7×10^{-2} 3.4×10^{-2} 1.9×10^{-2} (s^{-1})(N^2) 5.1×10^{-2} 3.3×10^{-2} 1.7×10^{-3} (CO_2) 2.8×10^{-2} 1227(N_2O) 1.5×10^{-1} 8.4×10^{-2} 4.1×10^{-2} (s^{-1})(N^2) 1.3×10^{-2} 8.4×10^{-2} 4.0×10^{-3} (CO_2) 7.2×10^{-2}	? (see text)
Endo *et al.* (1979)	2000	Shock tube studies with reaction followed by UV absorption		2.0
		$4-30\times10^{18}$ Ne	6.6×10^{-16}	
		Ar	3.5×10^{-16}	
		Kr	3.0×10^{-16}	
		Xe	2.3×10^{-16}	
		N_2	4.5×10^{-16}	
		CF_4	2.2×10^{-15}	
Baulch *et al.* (1973) review	1300–2500		$k_\infty=1.3\times10^{11}\exp(-30000/T)$s^{-1}	1.5
	1300–2500		$k(0,Ar)=8.3\times10^{-10}\exp(-29000/T)$	
	888		$k(0,N_2O)=4.5\times10^{-9}\exp(-29800/T)$	
Recommendations	700–2500		$k_\infty=1.3\times10^{11}\exp(-30000/T)$ $k(0,N_2)=1.2\times10^{-6}T^{-0.73}\exp(-31600/T)$ $F_c(N_2)=1.167-1.25\times10^{-4}T$ $k(0,CO_2)=2\times10^{-6}T^{-0.67}\exp(-31300/T)$ $F_c(CO_2)=1.167-1.25\times10^{-4}T$	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 agreeement. However, if one extrapolates the values to 900 K there appear to be a factor of 2 to 3 discrepency 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 Loriat *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_2 that will lead to rate constants approximately a factor of 1.5 higher than our recommendations for argon. For CO_2 we have used the results of Endo and coworker with CF_4 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_2O decomposition in N_2 and CO_2;

$$k_\infty = 1.3\times10^{11}\exp(-30000/T)$$
$$k(0,N_2) = 1.2\times10^{-6}T^{-0.73}\exp(-31600/T)$$
$$F_c(N_2) = 1.167 - 1.25\times10^{-4}T$$
$$k(0,CO_2) = 2\times10^{-6}T^{-0.67}\exp(-31300/T)$$
$$F_c(CO_2) = 1.167 - 1.25\times10^{-4}T\,.$$

We estimate the uncertainties to be a factor of 2.

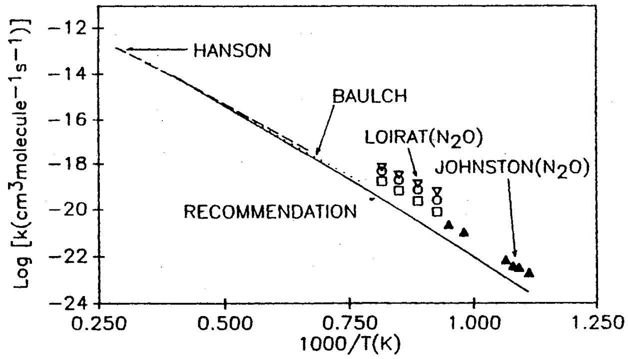

FIG. 1. Second order rate constants for N_2O decomposition in the presence of argon. Triangles are results of Johnston in N_2O. Open squares (9×10^{17}), circles (1.8×10^{17}) and triangles (6×10^{16}) are results of Loriat *et al*. in N_2O and converted to second order rate constants. Note that due to the lack of pressure dependence in the work of Loriat *et al*, their other points will fall close to the points in the plot.

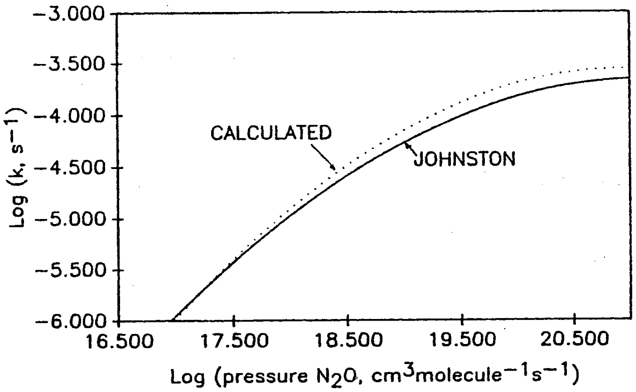

FIG. 2. Comparison of calculated and experimental pressure dependence for N_2O decomposition in N_2O.

TABLE I. Log (k/k_∞) for the reaction $N_2O+N_2O\rightarrow N_2+O+N_2O$ 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	1.4×10^{-2}	4.4×10^{-2}	1.2×10^{-1}	2.7×10^{-1}	4.6×10^{-1}
700	7.4×10^{-3}	2.5×10^{-2}	7.5×10^{-2}	1.8×10^{-1}	3.6×10^{-1}
900	4.5×10^{-3}	1.6×10^{-2}	5.0×10^{-2}	1.3×10^{-1}	2.9×10^{-1}
1100	3.0×10^{-3}	1.1×10^{-2}	3.6×10^{-2}	1.0×10^{-1}	2.3×10^{-1}
1300	2.1×10^{-3}	7.8×10^{-3}	2.6×10^{-2}	7.8×10^{-2}	1.9×10^{-1}
1500	1.6×10^{-3}	5.8×10^{-3}	2.0×10^{-2}	6.2×10^{-2}	1.6×10^{-1}
1700	1.2×10^{-3}	4.5×10^{-3}	1.6×10^{-2}	5.0×10^{-2}	1.3×10^{-1}
1900	9.3×10^{-4}	3.5×10^{-3}	1.3×10^{-2}	4.0×10^{-2}	1.1×10^{-1}
2100	7.4×10^{-4}	2.8×10^{-3}	1.0×10^{-2}	3.3×10^{-2}	9.5×10^{-2}
2300	6.0×10^{-4}	2.3×10^{-3}	8.3×10^{-3}	2.8×10^{-2}	8.2×10^{-2}
2500	4.9×10^{-4}	1.9×10^{-3}	6.9×10^{-3}	2.4×10^{-2}	7.1×10^{-2}

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Wing Tsang
September, 1989

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

	Conditions		Reaction rate constant	Uncertainty
Reference	*T* range/K	[M] range/cm^3	$k/cm^3 molecule^{-1}s^{-1}$	
Hidaka *et al*. (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 $2-17\times10^{18}$ 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.	$k_a=1.7\times10^{-9}\exp(-14100/T)$ $k_b=9.3\times10^{-10}\exp(-14100/T)$	3
Hanson and Salimian (1985) review	1200–4100		$k_a=1.7\times10^{-10}\exp(-14100/T)$ $k_b=1.1\times10^{-10}\exp(-13400/T)$	2
Recommendation:			$k_a=1.7\times10^{-10}\exp(-14100/T)$ $k_b=1.1\times10^{-10}\exp(-13400/T)$	2

Comments

The recent work of Hidaka and coworkers leads to rate constants that are close to an order of magnitude larger than the recomendations 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 T range/K	 [M] range/cm³	Reaction rate constant k/cm³molecule⁻¹s⁻¹	Uncertainty
Hidaka *et al.* (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 $2-17\times10^{18}$ 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	$2.5\times10^{-10}\exp(-7550/T)$	1.5
Hanson and Salimian (1985) (review)	700–2500		$1.3\times10^{-10}\exp(-7600/T)$	1.7
Recommendation			$1.6\times10^{-10}\exp(-7600/T)$	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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14,5 $N_2O+OH \rightarrow HO_2+N_2$ (a)
$\rightarrow HNO+NO$ (b)

	Conditions		Reaction rate constan	Uncertainty
Reference	T range/K	[M] range/cm^3	k/cm^{3}molecule^{-1}s^{-1}	
Chang and Kaufman (1977)	298–480	$1-3\times10^{11}$ OH from $H+NO_2$ with $0.6-21\times10^{14}$ N_2O in $2-14\times10^{15}$ He. Resonance absorption detection of OH	$<4\times10^{-16}$	
Biermann *et al.* (1976)	298	10^{17} H_2O in $0-3\times10^{18}$ N_2O and $0-1.5\times10^{18}$ Ar OH via flash photolysis and detected via resonance absorption	3.8×10^{-17}	1.3
Atkinson *et al.* (1976)	298–443	$2-6\times10^{14}$ H_2O, $1-5\times10^{16}$ N_2O in $1-2\times10^{18}$ Ar. OH from flash vacuum photolysis of OH. Detection via resonance absorption.	$<2\times10^{-16}$	
Gordon and Mulac (1975)	440	$2-20\times10^{17}$ N_2O in 1.7×10^{19} H_2O. OH via pulse radiolysis. Detected through resonance absorption	$<2\times10^{-14}$	
Recommendation			$k_{a+b}<1.4\times10^{-11}\exp(-5000/T)$	

Comments

The rate constants at lower temperatures for these reactions must be very small. Our recommendation is based on an assummed 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_2O in the presence of H_2 there appear to be a systematic and reproducible difference from decomposition in N_2O 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_2O" Chem. Phys. Lett., **44**, 204, 1976.

Biermann, H. W., Zetzsch, C. and Stuhl, F., "Rate Constants for the Reaction of OH with N_2O 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 $CFCl_3$(F—11),CF_2Cl_2(F—12), and N_2O 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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14,8 $N_2O + CO \rightarrow N_2 + CO_2$

	Conditions		Reaction rate constant	Uncertainty
Reference	*T* range/K	[M] range/cm^3	*k*/cm^{3}molecule^{-1}s^{-1}	
Fujii *et al.* (1985)	1350–2100	2–6% CO; 1–6% N_2O 46–38% Ar and 50% He at 1×10^{19} total pressure Shock tube experiments. Detection of CO and CO_2 via infra-red emission	$5.3\times10^{-13}\exp(-10230/T)$	2
Milks and Matula (1973)	1169–1655	2.74–5.02% CO, 0.74–1.4% N_2O in $1.2-1.6\times10^{19}$ Kr. Single pulse shock tube study with analysis of all products	$3.5\times10^{-13}\exp(-8711/T)$	3
Lin and Bauer (1969)	1317–1908	1–2.7%N_2O,2.9–5.1%CO in $1.2-4\times10^{19}$ Ar. Single pulse shock tube study with analysis of CO_2 and N_2O	$1.8\times10^{-13}\exp(-11581/T)$	3
Recommendations			$5.3\times10^{-13}\exp(-10230/T)$	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.

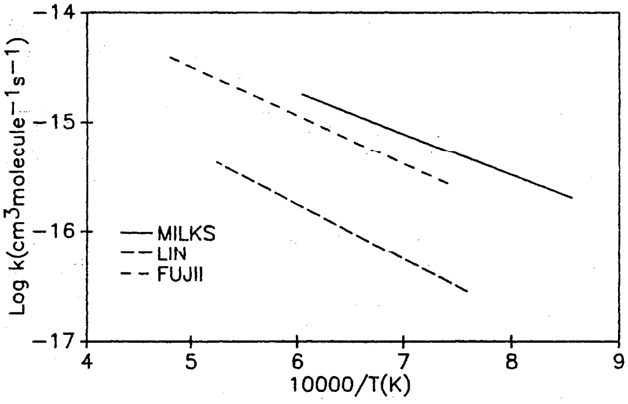

FIG. 1. Summary of experimental results for the reaction $N_2O + CO = N_2 + CO_2$

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 Zaslonko, 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

Fujii, N., Kakuda, T., Sugiyama, T. and Miyama, H., "Direct Determination of the Rate Constant for the Reaction $CO + N_2O \rightarrow CO_2 + N_2$", Chem. Phys. Lett., **122**, 489, 1985.

Lin, M. C., and Bauer, S. H., "Bimolecular Reactions of N_2O 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[a]

$\log_{10}K_p(\mathrm{NO}) = 0.66597–4.7332\times10^3/T+5.7106\times10^3/T^2–6.8375\times10^5/T^3$
$\log_{10}K_p(\mathrm{NO_2}) = -3.2867–1.7557\times10^3/T+5.36775\times10^4/T^2–1.0784\times10^7/T^3$
$\log_{10}K_p(\mathrm{HNO}) = -2.5774–5.0182\times10^3/T-1.2174\times10^4/T^2–3.8111\times10^6/T^3$
$\log_{10}K_p(\mathrm{HNO_2}) = -6.1717–3.8867\mathrm{X}10^3/T+1.8123\mathrm{X}10^5/T^2–3.1981\mathrm{X}10^7/T^3$
$\log_{10}K_p(\mathrm{HCN}) = 1.5772–6.76\mathrm{X}10^3/T-1.2295\mathrm{X}10^5/T^2+1.6784\mathrm{X}10^7/T_3$
$\log_{10}K_p(\mathrm{N_2O}) = -3.6213–4.7508\mathrm{X}10^3/T+2.3675\mathrm{X}10^5/T^2–3.6071\mathrm{X}10^7/T^3$
$\log_{10}K_p(\mathrm{NO_3}) = -7.5036–4.2093\mathrm{X}10^3/T+3.7832\mathrm{X}10^5/T^2–5.7619\mathrm{X}10^7/T^3$
$\log_{10}K_p(\mathrm{NO_3}) = -10.5161+6.4355\times10^3/T+3.8676\times10^5/T^2–6.5309\times10^7/T^3$

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[a] 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	σ(Angstroms)	ϵ/k(K)
Carbon Dioxide[a]	3.941	195.2
Argon[a]	3.542	93.3
Nitrogen[a]	3.798	71.4
Nitric Oxide[a]	3.492	116.7
Nitrogen Dioxide[b]	4.68	146.3
HNO[b]	3.492	116.7
Nitrous Acid[c]	4.68	146
Hydrogen Cyanide[a]	3.63	569.8
Nitrous Oxide[a]	3.828	232.4
Nitrogen Trioxide[b]	4.112	395
Nitric Acid[b]	4.24	390

[a] Reid, R. C., Prausnitz, J. M., and Poling, B. E., "The Properties of Gases and Liquids", McGraw Hill Book Company, New York, 1987.
[b] Troe, J., J. Chem. Phys., **66**, 4758, 1977.
[c] Assumed to be similar to NO_2.