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THE HOMOGENEOUS CHEMISTRY OF NO_x PRODUCTION AND REMOVAL FROM FOSSIL FUEL COMBUSTION GASES

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FINAL TECHNICAL REPORT

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ABSTRACT

The reduction of NO_x emissions from stationary combustion sources by non-catalytic homogeneous chemical addition is a promising technique. Demonstrations in laboratory experiments and on a number of field scale combustors have shown that the addition of ammonia to the exhaust flow significantly reduces the NO concentrations in a narrow temperature range. This report summarizes the work performed to understand the detailed chemical mechanism which makes this reduction occur. A model describing the NH_3/NO_x chemical system is developed, and rates of the key reactions identified are measured in a high temperature fast flow reactor. Product channels for certain important reactions are also identified. The experimental results are incorporated into the computer code, and the model predictions are compared with laboratory and field test results. Possible additives other than ammonia are evaluated and discussed.

TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
ABSTRACT	ii
1 INTRODUCTION	1-1
2 SELECTIVE CHEMICAL REDUCTION OF NO _x	2-1
3 EXPERIMENTAL	3-1
3.1 High Temperature Fast Flow Reactor (HFTTR)	3-1
3.2 Radical Sources and Detection	3-3
3.2.1 NH ₂	3-3
3.2.2 OH	3-3
3.2.3 H Atoms	3-4
3.2.4 NH	3-4
3.3 Rate Data Analysis	3-5
3.4 Mass Spectrometer Analysis	3-5
4 EXPERIMENTAL RESULTS AND ANALYSIS	4-1
4.1 Introduction	4-1
4.2 Rate Constant for the Reaction NH ₃ +NO → NH ₂ +HNO	4-1
4.3 Rate Constant for the OH+NH ₃ Reaction	4-1
4.4 Rate Constant for the NH ₂ +NO Reaction	4-2
4.5 Product Determination for the NH ₂ +NO Reaction	4-9
4.5.1 Hydroxyl Radical Products	4-10
4.5.2 Mass Spectrometer Results	4-11
4.5.3 Hydrogen Atom Products	4-13
5 COMPUTER MODEL FOR NH ₄ /NO _x Chemistry	5-1
5.1 Introduction	5-1
5.2 Chemical Reaction Set	5-1
5.3 Initial Conditions	5-5
5.4 A Description of the Model	5-5

TABLE OF CONTENTS Continued

<u>SECTION</u>	<u>PAGE</u>
5.5 Modeling Results	5-10
5.5.1 Reduction of NO by NH ₃ Addition	5-10
5.5.2 Time for Reduction	5-13
5.5.3 Pressure Dependence	5-16
5.5.4 NH ₃ Addition to Products of Combusted Coal . . .	5-16
5.5.5 Alternate Reducing Agents	5-19
6 DISCUSSION	
6.1 Summary of Results	6-1
6.2 Application to Pilot Scale Coal-Fired Combustion Facilities	6-2
6.3 Further Studies	6-3
7 ACKNOWLEDGEMENT	7-1
8 REFERENCES	8-1
9 PAPERS AND PRESENTATIONS	9-1
APPENDIX I.	I-1
APPENDIX II.	II-1

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
1	NO _x New Source Performance Standards for Electric Utility Steam Generating Units	1-2
2	NO _x Reduction Requirements	1-2
3	Rate Coefficients for NH ₂ +NO	4-4
4	Reaction Set	5-2
5	CO, CO ₂ Rates	5-3
6	NO ₂ Rates	5-4
7	H ₂ O ₂ Rates	5-4

LIST OF ILLUSTRATIONS

<u>FIGURE</u>	<u>PAGE</u>
3.1 High Temperature Fast Flow Reactor	3-3
4.1 Temperature Dependence of the Reaction Rate of $\text{OH}+\text{NH}_3$	4-3
4.2 Decay of NH_2 Fluorescence as a Function of Reaction Distance for Fixed Concentrations of Nitric Oxide at 775 K	4-5
4.3 Dependence of Pseudo-First Order Rate Constant on NO concentra- tion at 775 K	4-6
4.4 Temperature Dependence of Measured Rate Constants for NH_2+NO . .	4-7
4.5 Temperature Dependence of Measured Rate Constants for NH_2+NO . .	4-8
4.6 Mass Spectrometer Spectra for NH_2+NO Products	4-12
5.1 Fraction of Remaining NO as a Function of Initial Temperature for Varying Values of NH_2+NO Branching Ratio, f	5-9
5.2 Fraction of Remaining NO as a Function of Initial Temperature ($f=0.40$) for Varying Initial Concentrations of $[\text{NO}]$ and $[\text{NH}_3]$.	5-11
5.3 Effect of Varying Initial $[\text{NO}]_0$ Concentration and Change Upon Addition of $[\text{H}_2]$	5-12
5.4 Simplified Schematic of NH_3/NO Chemistry	5-14
5.5 Profile of $[\text{NO}]$ vs. Reaction Time for Various Initial Tempera- tures	5-15
5.6 NO Removal by Ammonia as a Function of System Pressure	5-17
5.7 Comparison of CH_4/O_2 Flame and Montana Rosebud Coal Calcula- tions With Combustion Tunnel Experimental Results of Muzio ⁽¹⁰⁾ .	5-18
5.8 NO Removal With Addition of $\text{H}_2\text{O}_2/\text{NH}_3$ Mixture	5-20
5.9 NO Reduction With Additions of N_2H_4 and $(\text{NH}_2)_2\text{CO}$	5-21

1. INTRODUCTION

The release of nitrogen oxides into the atmosphere during combustion of conventional fuels is a major potential health hazard. Significant sources of NO_x are stationary combustors used for electric power generation. As the price of clean fuels such as natural gas and oil increases and their availability decreases, a greater reliance is placed on the use of domestic coal and oil shales. In contrast to clean fuels, which contain little fuel nitrogen, coal and oil shale may consist of up to two percent by weight of bound nitrogeneous species, which could potentially be converted to nitric oxide upon combustion. This produces NO concentrations in the 10^3 ppm range, which is an order of magnitude more severe than released by clean fuels.

In recent years, the Environmental Protection Agency has place increasingly severe restrictions for NO_x emission upon stationary combustion sources.⁽¹⁾ The most recent regulations are summarized in Tables 1 and 2. Various methods have been proposed to meet these requirements, including pre-combustion treatment of the fuel to remove fuel-nitrogen, and staged combustion, in which a fuel-rich mixture first converts fuel nitrogen to N_2 , followed by an oxygen rich stage which completes combustion with little conversion of N_2 to NO. Exhaust gases can also be treated to remove NO, either catalytically, or by homogeneous selective chemical reduction, in which selected gases added to the exhaust flow chemically convert NO to N_2 . This promising approach was developed at Exxon Research,^(2,3) using ammonia as the reducing agent.

TABLE 1 - NO_x NEW SOURCE PERFORMANCE STANDARDS FOR ELECTRIC UTILITY STEAM GENERATING UNITS

FUEL TYPE	NO _x EMISSION LIMIT NG/J (LB/MILLION BTU) HEAT INPUT	
GASEOUS FUELS:		
COAL-DERIVED FUELS	210	(0.50)
ALL OTHER FUELS	86	(0.20)
LIQUID FUELS:		
COAL-DERIVED FUELS	210	(0.50)
SHALE OIL	210	(0.50)
ALL OTHER FUELS	130	(0.30)
SOLID FUELS:		
COAL-DERIVED FUELS	210	(0.50)
ANY FUEL CONTAINING MORE THAN 25%, BY WEIGHT, COAL REFUSE	EXEMPT FROM NO _x STANDARDS AND NO _x MONITORING RE- QUIREMENTS	
ANY FUEL CONTAINING MORE THAN 25%, BY WEIGHT, LIGNITE IF THE LIGNITE IS MINED IN NORTH DAKOTA, SOUTH DAKOTA, OR MONTANA, AND IS COMBUSTED IN A SLAG TAP FURNACE	340	(0.80)
LIGNITE NOT SUBJECT TO THE 340 NG/J HEAT INPUT EMISSION LIMIT	260	(0.60)
SUBBITUMINOUS COAL	210	(0.50)
BITUMINOUS COAL	260	(0.60)
ANTHRACITE CIAL	260	(0.60)
ALL OTHER FUELS	260	(0.60)

TABLE 2 - NO_x REDUCTION REQUIREMENTS

FUEL TYPE	PERCENT REDUCTION OF POTENTIAL COMBUSTION CONCENTRATION
GASEOUS FUELS	25%
LIQUID FUELS	30%
SOLID FUELS	65%

During the past five years a number of laboratory flame and flow experiments,⁽⁴⁻⁷⁾ simulation scale burner studies,^(6,8,9,10) and field scale trials^(3,11) have demonstrated that substantial exhaust NO_x reduction can be achieved by NH₃ and/or NH₃/H₂ addition to high temperature exhaust flows for gaseous fuel, fuel oil, and coal combustion (Thermal deNO_x process).

It seems clear that the reduction of NO in these experimental tests is due to reactions of NH_i (i=1,2) with NO to form molecular nitrogen.⁽²⁾ However, oxidation of NH_i radicals by O, OH, and O₂ can also lead to formation of NO. Thus, the detailed mechanism of the NH₃/NO homogeneous reaction process in exhaust flows is quite similar to the NO production/removal mechanism proposed to explain NO_x production from fuel bound nitrogen as developed by Fenimore^(12,13) and Haynes.^(14,15)

The effectiveness of NO_x removal is very temperature dependent, and this dependence can be shifted to higher or lower temperatures by varying the amounts and identities of the added gases. In order to intelligently design a system for optimum removal of NO_x under the variety of fuel loading and exhaust gas temperatures that occur in a full scale combustor system, one must understand the detailed chemical reaction mechanisms which govern the reduction of NO_x. Rather than tailor every reduction system individually, a standardized system could be designed that would vary the amounts of injected gases in a predetermined manner to most effectively reduce NO_x. This can only be accomplished if the chemistry governing that removal is understood as a function of flue gas composition, temperature and pressure.

The work described in this report was performed to gain a detailed understanding of the behavior of the NH₃/NO_x chemical system under combustor exhaust flow conditions. A chemical model is developed which predicts the concentration of all species of interest as a function of temperature and time. The reaction set is validated by comparison with a number of laboratory and small scale combustor studies. Many of the key reaction rates in the model are theoretical estimates, or have been measured only near room temperature, or were measured indirectly above 1500 K. Since reaction rates are often

very temperature sensitive, we felt it necessary to measure the key rates directly, and in some cases determine the relative branching into different product channels, over the range of temperatures which match those found in combustor exhaust flows.

An overview of the key reactions involved and the results of previous investigations is presented in Section Two of this report. Section Three and Appendix One describe the High Temperature Fast Flow Reactor (HTFFR), in which the rate measurements and product determinations were made, as well as the methods used to analyze the data. The results of these measurements are described in Section Four and Appendix Two. Section Five contains the results of the computer modeling and Section Six discusses the implications of these results and points out areas in which further study is needed.

1.1 Technical Progress Summary

During this eighth and final quarter of the contract, the remaining technical tasks were successfully completed. The status of each task is summarized below.

a. $\text{NH}_3 + \text{NO}$ Rate Constants (Task I)

The rates of reaction for NH_3 and NH_2 with NO were determined over the temperature range of 294 - 1200 K. The rate of $\text{NH} + \text{NO}$ was determined to be unimportant to the chemistry and was not measured. The products of the $\text{NH}_2 + \text{NO}$ reaction, which control the effectiveness of NO reduction, were determined. The results are described in Sections 3 and 4.

b. Oxidation Rates of NH_3 (Task II)

The key oxidation reaction is that of $\text{OH} + \text{NH}_3$, whose rate was determined over the temperature range of 294 - 1075 K. The reactions of O and H with NH_3 species are relatively unimportant. The results are presented in Section 4 and Appendix II.

c. Evaluation of Alternate Scavenger Precursors (Task III)

The use of chemicals other than ammonia was evaluated and tested using the chemical model developed in Task IV. These included H_2 , CO , H_2O_2 , N_2H_4 , various amines, and $(NH_2)_2CO$. The results are discussed and compared in Section 5.

d. Chemical Model for NH_3/NO_x Chemistry (Task IV)

A detailed chemical model which fully describes the NH_3/NO_x chemistry at combustor exhaust temperatures is developed and described in Section 5. This model utilizes 54 reactions to describe the interaction of NH_3 with NO in the exhaust stream. Using a few additional reactions, the behavior of alternate additives is predicted and compared with available experimental results. In addition, a condensed reaction set which suitably describes the reduction of NO by NH_3 is presented.

e. Conceptual Design of Pilot-Scale Experiments (Task V)

Utilizing the experimental and modeling results, a conceptual design for implementing a selective chemical reduction process is outlined in Section 6. Also included are recommendations for future work in this field which would aid in the development of a successful NO reduction system.

2. SELECTIVE CHEMICAL REDUCTION OF NO_x

The reduction of NO_x by NH₃ at combustion exhaust flow temperatures was first reported by Lyon.⁽²⁾ Based on a number of experiments,⁽²⁻¹¹⁾ subsequent modeling^(4,16-19) studies have sought to explain this "Thermal DeNO_x" process in terms of a detailed chemical mechanism. Much of the initial work was unsuccessful, generally because the reaction rate data available was insufficient. In the past three years, the overall behavior of the deNO_x system has been fairly well characterized. The salient features of it are:

- a) Reduction of NO in oxygen rich combustor exhausts by the addition of NH₃ is effective over a narrow temperature range centered about 1225 K. Below ~1100 K, no reduction occurs and above ~1400 K, the NH₃ is increasingly oxidized to form additional NO.
- b) The addition of H₂ lowers this temperature window by approximately 100 K.
- c) The amount of NH₃ required for substantial reduction is equal to the amount of NO originally present ($[NH_3]/[NO]_0 \equiv \beta = 1$).
- d) Greater amounts of NH₃ ($\beta > 1$) are more effective, but substantial NH₃ carryover into the exhaust occurs. The optimal value of β is between 1 and 2.⁽¹⁰⁾
- e) The time required for reduction has varied in the combustor experiments, with ~0.2s an average result.
- f) The final products appear to be N₂ and H₂O, with <50 ppm of N₂O, and <1 ppm of CN and alkyl and aryl amines. Also, CO₂ was not reduced to CO.⁽¹⁰⁾
- g) The addition of mono-, di-, and trimethylamines were moderately effective as reducing agents, while simple alkanes, CO, and H₂ alone were not.⁽¹⁰⁾

- h) Recent experimental results⁽²⁰⁾ on the $\text{NH}_3\text{-O}_2\text{-NO}$ system indicate that the addition of H_2O shifts the removal window to slightly higher temperatures and decreases the rate of NO removal.
- i) Additional O_2 has little effect on the reduction efficiency but does widen the window toward lower temperatures.⁽¹⁰⁾

From early attempts at modeling this process it was quickly concluded that the direct reaction of $\text{NH}_3 + \text{NO}$ to form $\text{N}_2 + \text{H}_2\text{O}$ could not explain the results. A more plausible reaction scheme involves the production of NH_2 radicals which reacted with NO to form $\text{N}_2 + \text{H}_2\text{O}$ through a series of intermediate reaction steps. In oxygen rich flows, amidogen (NH_2) is mainly formed by the H atom abstraction of NH_3 by OH.

For the mechanism to work, the products of reaction (1.2) must include radicals (OH, H, etc.) which attack additional NH_3 , since the amount of H, O, and OH initially present is insufficient to react substantially with NH_3 in the amount of time available. It is clear that these two reactions are the key to describing the thermal deNO_x process, and identification of the products of reaction (1.2) is crucial. It is for this reason that the experimental results reported in this paper have focussed on these reactions.

3. EXPERIMENTAL

3.1 High Temperature Fast Flow Reactor (HTFFR)

The experiments are carried out in a high temperature fast flow reactor, which is fully described in Appendix I. In brief, the flow tube is 7.26 cm in diameter, 120 cm long and constructed of alumina (Fig. 3.1). Kanthal heater elements radiatively control the temperature from 294 - 1500 K. Four perpendicular alumina side arms at the tube end permit laser or resonance lamp fluorescence detection. Provisions also exist for IR White cell absorption of IR active species. Flow gases can be monitored by a molecular beam sampling mass spectrometer to facilitate in the identification of reaction products. Gas temperatures are obtained with shielded W-5%Re/W-26%RE thermocouples using a technique^(21,22) which removes the contribution of wall radiation to the measurements.

Radicals are made with discharge flow techniques, utilizing a 2450 MHz microwave discharge source, and introduced through the inner of two coaxial alumina inlet tubes. By adding a second gas through the outer tube, new reactant species can be produced. For example, fluorine atoms made in the microwave source react with excess NH_3 , resulting in a clean source of NH_2 .⁽²³⁾ The concentration of radical reactants is always low enough to prevent secondary reactions.

The second reactant is added through a moveable quartz injector. Helium buffer gas is added at the entrance of the flow tube through mullite multi-channel arrays which preheat and laminarize the flow. Flow rates are determined using calibrated rotameters and flow speeds can be varied from 6 - 150 m s^{-1} .

Figure 3.1. High Temperature Fast Flow Reactor

3.2 Radical Sources and Detection

3.2.1 NH₂

As described above, NH₂ is made by reacting atomic fluorine with a slight excess of NH₃. It is detected using laser induced fluorescence. A nitrogen-pumped dye laser (Molelectron DL-14) is used to excite a selected transition in the X²B₁ - A²A₁ band of NH₂. Fluorescence is collected by a baffled, gated photomultiplier (Hamamatsu R763P). An interference filter ($\lambda_0 = 600$ nm, FWHM = 10 nm) is used to reduce the intense thermal emission background at higher temperatures. The signal is integrated and held in a peak detector. The laser pulse energy is measured by a fast vacuum photodiode in a similar manner. A master timing console⁽²⁴⁾ controls the firing of the laser, collection of signal and background data, and transmission of that data, via an IBM Model 7406 interface, to a Prime 400 computer for on-line averaging and analysis.

3.2.2 OH

Hydroxyl radicals are formed by the fast reaction of H+NO₂.⁽²⁵⁾ Hydrogen atoms formed by microwave dissociation of H₂ in He are mixed with excess NO₂ in the coaxial inlet tubes. These radicals are detected using the dye laser or a resonance lamp. The former method involves doubling the dye laser output frequency into the ultraviolet at 309.0 nm. This is the Q₂ (2,3) absorption line of the X²Π(v''=0 to A²Σ(v'=0) electronic transition. Fluorescence is monitored as with NH₂. With the use of the resonance lamp (made by flowing He saturated with water vapor through a microwave discharge), a Hamamatsu R763P photomultiplier is used in the photon counting mode. An interference filter ($\lambda_0 = 310$ nm, FWHM = 10 nm) rejects unwanted light. Details are provided in Appendix II.

3.2.3 H Atoms

Hydrogen atoms are made by microwave dissociation of an H_2/He mixture or by thermal dissociation of H_2 by a heated tungsten coil placed near the outlet of the outer coaxial tube. This latter technique decreases the loss of H atoms on the walls of the inlet tubes. Detection is accomplished using a resonance lamp in which 99.95% pure He is passed through a microwave discharge. Enough hydrogen impurity exists in this gas to provide Lyman- α radiation for absorption by H (121.6 nm). The fluorescence is monitored by an EMI G26E315 solar blind photomultiplier, wired with a positive anode for photon counting. The counts are processed by a Pacific Precision Instruments Model AD6 Amplifier/Discriminator and tabulated by a Monsanto Model 1505A Counter-Timer. All windows are also constructed from MgF_2 , are the imaging lenses. To reject all light except that from H atoms, a slow stream of O_2 passed in front of the PMT absorbs all UV radiation except in a window centered about the Lyman- α emission line.

3.2.4 NH

The production of NH radicals proved to be a difficult problem. Previous measurements involved the use of photolysis of NH_3 ⁽²⁶⁾ or HNCO ⁽²⁷⁾ as an NH source. In the present flow tube configuration, this method is not feasible. Instead, it was attempted to use the $\text{F}+\text{NH}_3$ reaction to generate NH radicals. For $\text{F} \gg \text{NH}_3$, one might expect sequential stripping the ammonia, since the reactions to form $\text{HF}+\text{NH}_i$ are very exothermic. The results of such experiments show that NH is indeed generated, as evidenced by a large chemiluminescence signal at 336.1 nm. Some NH_2 and N are also formed, though in lesser amounts. However, through a series of reactions not entirely understood, NH_4F , a solid white crystalline compound, rapidly forms and clogs the inlet lines. Since the NH reactions were judged to be of only secondary importance, other methods to produce a clean NH source were not pursued.

3.3 Rate Data Analysis

The analysis of rate data is essentially the same for all kinetic measurements and is described here for the $\text{NH}_2 + \text{NO}$ reaction. The details for the $\text{OH} + \text{NH}_3$ reaction are given in Appendix II. Rate measurements are made using pseudo-first order kinetic conditions with NO in excess. The total pressure is typically one Torr and flow velocities vary from 30 ms^{-1} at room temperature to 70 ms^{-1} at 1200 K. Removal rates of NH_2 by the uncoated alumina tube wall are measured by varying the NH_2 residence time at fixed pressure. This is done by varying the flow velocity. A constant pressure maintains the same radial diffusion characteristics. This was done during each run and the observed wall removal rates (k_w) ranged from 100 s^{-1} at 294 K to 300 s^{-1} at 1200 K. Great care was taken in characterization of the flow parameters, and corrections for both axial and radial diffusion and wall removal were made using the procedure outlined by Brown.⁽²⁸⁾ The corrections are small, with most values being about 30%. Although the value of k_w is only accurate to $\sim 50\%$, this uncertainty is reflected in the first order rate coefficient as an error of $<10\%$. Data were reproduceable, with little scatter, and the greatest source of error is believed due to the diffusion correction. The overall accuracy of the rate constants is estimated (± 10) at 25%.

3.4 Mass Spectrometer Analysis

Gases in the high temperature flow reactor may be sampled by a molecular beam mass spectrometer. The sampled gas is formed into a molecular beam via a sampling nozzle-skimmer arrangement illustrated in Fig. 6 of Appendix I. The beam is detected by a differentially-pumped quadrupole mass spectrometer with an electron bombardment ionizer (Extranuclear Laboratories). The beam is modulated at 100 Hz and synchronously detected on a lock-in amplifier. For the present product analysis experiments, mass ranges are scanned at a constant rate and relative product intensities obtained by integration of area under individual mass peaks.

There are certain corrections which are needed to properly analyze the mass spectra. A supersonic molecular beam which travels many nozzle diameters before detection along its axis will exhibit a phenomenon called "mass focusing", in which lighter gases radially expand faster than the heavier species. This leads to an enrichment in number density of the more massive molecules along the beam axis. This enhancement has been experimentally determined to be on the order of the ratio of the heavy/light molecular weights.⁽²⁹⁾ For example, helium gas containing 5% Ar at the sampling nozzle source (19:1 ratio), would appear as a $19 \times \frac{40}{4} = 1.9$ ratio at the detector.

The second correction accounts for different ionization cross sections of the various molecules. In the previous example, the real ratio of He/Ar detected at the quadrupole would be about eight times smaller (~0.24) because Argon has a higher ionization cross section than He. In general, diatomic and triatomic molecules have similar total ionization cross sections. However, they do dissociatively ionize (crack) in different proportions, depending on both the identity of the parent species, as well as the design and voltages in the particular ionizer. To avoid any problems here, individual in situ cracking patterns were measured for N₂, N₂O, NH₃, F₂, NO, H₂O, HF, and Ar (to form Ar⁺²). Using these corrections, the relative product yields for the NH₂+NO reaction were obtained. The results are presented in Section 4.5.2.

4. EXPERIMENTAL RESULTS AND ANALYSIS

4.1 Introduction

This section contains the results of the rate measurements for the key reactions of the NH_3/NO_x system. In particular, the greatest emphasis is placed on determining the products of the NH_2+NO reaction. This work represents the first high temperature measurement of the NH_2+NO reaction, as well as the first direct evidence for N_2 , H_2O , and OH as products.

4.2 Rate Constant for the Reaction $\text{NH}_3+\text{NO} \rightarrow \text{NH}_2+\text{HNO}$

As a consistency check, the rate for the reaction of ammonia with nitric oxide was measured. Over the temperature range of 294 - 1200 K, no NH_2 is detected at the sensitivity limit of the apparatus. Assuming that during normal NH_2 production all of the discharged F_2 dissociates and forms NH_2 , a lower limit to the detector sensitivity for NH_2 of $\sim 10^8$ molecules cm^{-3} ($\text{S/N}=1$) can be obtained. From these values, an upper limit for the rate coefficient of 5×10^{-17} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the range $T = 294 - 1200 \text{ K}$ is found. This is hardly surprising since the reaction is 56 kcal mol^{-1} (234 kJ mol^{-1}) endothermic, and the largest reasonable forward rate constant expected would be 10^{-19} at 1200 K, assuming a gas kinetic reverse rate. This exercise confirms the belief that this reaction is not important to the NO_x combustor exhaust stream chemistry.

4.3 Rate Constant for the $\text{OH}+\text{NH}_3$ Reaction

The reaction

is considered to be the prime initiation step in the NH_3/NO chemical system. The rate for this reaction was measured over the temperature range of 294 - 1075 K. Details of this work are presented in Appendix II. The rate is well described in the Arrhenius form by k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) = $(5.41 \pm 0.86) \times 10^{-12} \exp(-2120 \pm 143 \text{ cal mol}^{-1}/RT)$. This is illustrated in Fig. 4.1. The present results are in excellent agreement with previous results near room temperature;^(30,31) recent shock tube data⁽³²⁾ at higher temperatures is also in agreement with our results. Thus, it is our determination that the rate of this key initiation step is well characterized in the temperature range of interest.

4.4 Rate Constant for the $\text{NH}_2 + \text{NO}$ Reaction

The rate of disappearance of NH_2 in reaction with NO was measured at seven temperatures and results are displayed in Table 3. Typical data are shown in Figs. 4.2 and 4.3 for 775 K. A slight curvature at longer reaction times and larger concentrations of NO is seen, which is attributed to secondary reactions of hydroxyl radical products with the excess NH_3 to form NH_2 . These effects are seen only after the NH_2 signal has significantly decayed and do not affect the stated rate coefficient values. The measured rates are plotted versus $1/T$ and $\log T$ in Figs. 4.4 and 4.5, respectively. These clearly indicate that the temperature dependence cannot be represented by the simple Arrhenius form $k = Ae^{-E/RT}$. A least-square fit of the data to an empirical equation of the form:

$$k(T) = aT^n e^{-b/T} \quad (4.2)$$

gives:

$$a = 1.95 \times 10^{-4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, n = -2.46, \text{ and } b = 938 \text{ K}$$

Figure 4.1. Temperature Dependence of the Reaction Rate of OH+NH₃.

Although the fit is good in the 294 - 1200 K range, it should be emphasized that the values of these parameters are strongly coupled and have little significance in comparison to any theory. They are only useful as input to modeling codes which use this functional form.⁽³³⁾ In fact, the values of $k(T)$ used in our chemical model above 1200 K are obtained by graphical extrapolation, which appear to be more reasonable than those obtained from the computed fit.

TABLE 3 - RATE COEFFICIENTS FOR $\text{NH}_2 + \text{NO}$

T(K)	$(k \times 10^{+12} \text{ cm}^3 \text{ MOLECULE}^{-1} \text{ S}^{-1})$
294	7.1
475	6.2
625	5.9
775	4.7
900	4.5
1050	2.7
1200	2.3

The negative temperature dependence of the rate coefficient should be noted. The fall-off in reaction rate with temperature suggests that the reaction proceeds via a collision complex. As the relative collision energy is raised, the lifetime of the collision intermediate ($\text{NH}_2\cdot\text{NO}$) decreases, lessening the chance of reaching the product channel. Gehring⁽³⁴⁾ claims to have observed this complex in a beam sampling mass spectrometer. However, it should be noted that Lesclaux et al.,⁽³⁵⁾ failed to measure any difference in the $\text{NH}_2 + \text{NO}$ room temperature reaction rate over a pressure range of 4 to

Figure 4.2. Decay of NH_2 Fluorescence as a Function of Reaction Distance for Fixed Concentrations of Nitric Oxide at 775 K.
 $[\text{NO}] = 3.42 \times 10^{13}$ (o), 7.23×10^{13} (Δ), 1.28×10^{14} (+), 2.08×10^{14} (∇),
 and 3.12×10^{14} (X); Units of molecules cm^{-3} .

Figure 4.3. Dependence of Pseudo-First Order Rate Constant on NO concentration at 775 K.

Figure 4.4. Temperature Dependence of Measured Rate Constants for $\text{NH}_2 + \text{NO}$
Reaction: $-\text{Log } k \text{ vs. } 1/T$

Figure 4.5. Temperature Dependence of Measured Rate Constants for $\text{NH}_2 + \text{NO}$

Reaction: $\text{Log } k$ vs. $\text{Log } T$

A. Hack, et al. (Ref. 23)

B. Lesclaux, et al. (Ref. 35)

C. Present Work

700 Torr, suggesting that the reaction may be more direct than the results of Ref. (35) suggest. We failed to detect NH_2NO in our mass spectrometer. In general, a long-lived collision complex has a lifetime on the order of 10^{-11} s, so that our result is not surprising.

Figure 4.5 also shows the results of Hack⁽²³⁾ and Lesclaux,⁽³⁵⁾ who measured the rate coefficient over a limited range of temperatures. Previous room temperature^(34,36-38) and flame⁽³⁹⁾ (2020 K) results vary from 2×10^{-12} to $2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Although our results tend toward the lower end of this range, agreement with the previous efforts is well within combined experimental error.

4.5 Product Determination for the $\text{NH}_2 + \text{NO}$ Reaction

From the work of Miller et al.,^(16,18) and as discussed in the modeling section of this paper, the key reaction in describing the NO_x/NH_i chemistry at elevated temperatures is that of $\text{NH}_2 + \text{NO} \rightarrow \text{Products}$. In this section, we present the results in determining the identity and relative abundance of possible products. The possible reaction paths are as follows:

Using the various methods described below, we have distinguished the more important channels from among these many possibilities.

4.5.1 Hydroxyl Radical Products

Using an OH resonance lamp, induced fluorescence from product OH is seen. The following technique was used in an attempt to quantify the OH concentration. The reaction of $\text{H} + \text{NO}_2$ is used to prepare a quantity of OH in the flow tube, and the resonance fluorescence OH signal measured. Excess NH_3 is added to quantitatively convert the OH to NH_2 , and the laser induced fluorescence intensity of NH_2 is measured. The ratio of these signals gives the relative sensitivity of our detection methods to OH and NH_2 . Then NH_2 is produced, its intensity recorded, and excess NO added to drive the $\text{NH}_2 + \text{NO}$ reaction to completion. Measurement of the OH product intensity, coupled with the calibration results produces the relative yield of OH products. There are three major problems associated with this technique:

1. Since NH_2 and OH may have different rates of removal by the reactor walls, the assumption of quantitative conversion and detection is violated. However, it can be shown that wall removal effects cancel when all of the ratios are calculated.
2. The laser frequency may drift, giving erroneously low values for NH_2 . The calibration step is performed before and after the $\text{NH}_2 + \text{NO}$ reaction measurement to assure that the laser is stable.
3. Quenching of vibrationally excited products is assumed to be complete. The methods of detection assume all species are in $v=0$. However, this is probably not true since there are only ~4 ms between the time of product (either NH_2 or OH) formation and detection. Because this method necessitates using the resonance lamp and laser simultaneously, the laser beam scatters off the lamp, introducing a large amount of background. If the product quenching times are increased beyond 4 ms, the NH_2 signal/noise deteriorates. In all cases, the reactant NH_2 or OH were shown to be completely quenched.

The net effect of this uncertainty is to underestimate the yield of OH. Thus, we conclude that [OH] product branching from the reaction $\text{NH}_2 + \text{NO}$ is >0.20 .

A separate measurement of [OH] intensity using the pulsed, frequency-doubled dye laser, and estimating the detection sensitivity of the laser to [OH] gives a larger value, 0.5 ± 0.3 . In any case, this is the first reported experimental evidence that N_2 and H_2O are not the sole direct products.

4.5.2 Mass Spectrometer Results

Using the sampling molecular beam mass spectrometer, other direct products of the $\text{NH}_2 + \text{NO}$ reaction were sought at 300 K. In the initial configuration of the flow tube, reaction times were adjusted so that no secondary chemistry would occur. In addition, it is likely that any radical products formed are removed by the reactor walls before reaching the mass spectrometer. However, all stable products which had a fractional yield of >0.02 could be detected. Although ionization efficiencies vary slightly among molecules, a qualitative measurement of relative yields can be made. Sensitivity and molecular cracking pattern calibrations aided in the analysis as previously described.

The uncorrected mass spectra for the addition of NO to NH_2 (formed from $\text{F} + \text{NH}_3$) are shown in Fig. 4.6. The increase at masses 14 and 15 originate solely from cracking of the nitric oxide. Both masses 18 and 28 show a substantial increase, implying the N_2 and H_2O are direct products of the reaction of $\text{NH}_2 + \text{NO}$. Since the initial HF concentration equals that of NH_2 , an absolute branching ratio for N_2 and H_2O can be estimated. Assuming that wall removal of N_2 , H_2O , and HF are negligible, and using the known removal rate of NH_2 , we estimate that the fraction of products appearing as H_2O is 0.6 ± 0.2 . In addition, the $[\text{N}_2]/[\text{H}_2\text{O}]$ ratio is 1.5 ± 0.3 . The additional N_2 could originate from either the $\text{N}_2 + \text{H} + \text{OH}$ product channel or from $\text{N}_2\text{H} + \text{OH}$, where the N_2H is dissociated upon collisions with the flow reaction wall. Since the total N_2 concentration is

Figure 4.6. Mass Spectrometer Spectra for NH_2+NO Products

----- NH_2+NO
 ————— NH_2 Only (From $\text{F}+\text{NH}_3$)

equal to the total nitrogen product concentration (within the stated error bounds) and because the behavior of possible N_2H is not known, the mass spectrometer study cannot distinguish between the different possible radical product channels. These calculations have been corrected for differences in chart speed, ionization efficiency, scale sensitivity, and mass focussing.

If radicals such as N_2H , HNO , $HNNO$, and NH_2NO had reached the ionizer, signals at mass peaks 29, 31, 45, and 46, respectively should have been seen; no such signals were observed. Nitrous oxide (N_2O) was not seen, in agreement with other results.^(3,10)

4.5.3 Hydrogen Atom Products

The possibility of hydrogen atoms as products of the NH_2+NO reaction has been raised.^(2,16) Using the H atom resonance lamp, an attempt to detect H atoms was made at room temperature. This technique is extremely sensitive and can detect concentrations as low as 10^9 cm^{-3} . There is some problem due to a minute H_2 impurity in the F_2 , which is used to produce NH_2 . Despite this, upon addition of excess NO to NH_2 , no change in the count rate is seen, confirming preliminary reports by Wolfrum⁽⁴⁰⁾ that H atoms are not a significant product at 300 K.

5. COMPUTER MODEL FOR NH_1/NO_x CHEMISTRY

5.1 Introduction

A chemical model which describes the features of the NH_1/NO_x system was developed and tested using the Aerodyne Research, Inc. PACKAGE code.⁽⁵⁶⁾ This code was developed to model the chemistry of MHD generators and is much more sophisticated than the portion used in the present efforts. The flow conditions assumed in our modeling runs are that chemistry occurs along a constant diameter adiabatic channel with one dimensional flow. Species concentration are calculated as a function of time. Reverse rates for all reactions are calculated from equilibrium constants obtained from the current JANAF Thermochemical Tables. We have used a value of $84.2 \text{ kcal mol}^{-1}$ for the heat of formation of NH . Piper⁽⁴¹⁾ has reevaluated the data used to determine the current JANAF value of 90 kcal mol^{-1} and shows that there were a series of errors in the analysis. Our adoption of this value does not affect the main features of our results.

Rates are obtained from a variety of sources, but generally come from critical reviews of rate data by Jensen and Jones,⁽⁴²⁾ Westley,⁽²⁵⁾ Levy,⁽⁴³⁾ and NASA.⁽⁴⁴⁾ Experimental values are always preferred over theoretical estimates. Our experimental values and product analyses are incorporated into the model. A major problem in obtaining the best model is selecting rate constants when no experimental data exists. Theoretical calculations may differ over orders of magnitude. When this occurs we have chosen the most reasonable value which is physically realistic and works well within the framework of the model.

5.2 Chemical Reaction Set

The list of reactions used is given in Table 4. There are three groups of reactions in this set.

TABLE 4 - REACTION SET $k = AT^n e^{-E/RT}$ ($\text{cm}^3 - \text{molecule}^{-1} \text{ s}^{-1}$)

	A	n	E/R	Ref.		A	n	E/R	Ref.
$\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$	1.90-15	1.3	1825	42*	$\text{HNO} + \text{OH} \rightarrow \text{NO} + \text{H}_2\text{O}$	6.0-11	0	0	42*
$\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$	1.19-07	-0.861	8316	18*	$\text{NH} + \text{O}_2 \rightarrow \text{HNO} + \text{O}$	5.0-11	0	1710	18*
$\text{O} + \text{H}_2 \rightarrow \text{H} + \text{OH}$	3.0-14	1.0	4479	42*	$\text{OH} + \text{O} \xrightarrow{\text{M}} \text{HO}_2$	1.4-31	0	0	43
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	5.0-11	0	0	42*	$\text{H} + \text{O} \xrightarrow{\text{M}} \text{OH}$	1.0-29	-1.0	0	42
$\text{H} + \text{HO}_2 \rightarrow 2\text{OH}$	4.2-10	0	950	42*	$2\text{H} \xrightarrow{\text{M}} \text{H}_2$	3.0-30	-1.0	0	42
$\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	4.2-11	0	352	42*	$2\text{O} \xrightarrow{\text{M}} \text{O}_2$	3.0-34	0	-900	42
$\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}$	1.7-11	0	503	25*	$\text{H} + \text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}$	1.0-25	-2.0	0	42*
$\text{O} + \text{HO}_2 \rightarrow \text{O}_2 + \text{OH}$	8.0-11	0	500	42*	$\text{H}_2 + \text{O}_2 \rightarrow 2\text{OH}$	2.82-11	0	24043	18
$2\text{OH} \rightarrow \text{O} + \text{H}_2\text{O}$	1.0-11	0	550	42*	$\text{NH}_3 \xrightarrow{\text{M}} \text{NH}_2 + \text{H}$	4.2-08	0	47200	51
$\text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HO}_2$	2.0-32	0	-500	42*	$2\text{NH}_2 \rightarrow \text{NH}_3 + \text{NH}$	2.8-13	0.63	1812	43*
$2\text{N} \xrightarrow{\text{M}} \text{N}_2$	8.3-34	0	-498	43	$\text{NH}_3 + \text{N} \rightarrow \text{NH}_2 + \text{NH}$	3.5-13	0.5	11656	43
$\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$	1.3-10	0	38000	42*	$2\text{NH} \rightarrow \text{NH}_2 + \text{N}$	6.0-13	0.55	956	43
$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	1.1-14	1.0	3150	42*	$\text{NH}_2 + \text{O} \rightarrow \text{HNO} + \text{H}$	3.5-12	0	0	43
$\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}$	5.0-11	0	0	45*	$\text{NH} + \text{O}_2 \rightarrow \text{NO} + \text{OH}$	8.5-15	0	0	26
$\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}$	2.5-12	0	3040	25	$\text{HNO} + \text{H} \rightarrow \text{NH} + \text{OH}$	3.3-13	0.5	6540	49
$\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$	5.40-12	0	1067	46*	$\text{HNO} + \text{N} \rightarrow \text{NH} + \text{NO}$	1.7-13	0.5	1006	25
$\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$	4.57-11	0	8824	47	$\text{NH}_2 + \text{HO}_2 \rightarrow \text{HNO} + \text{H}_2\text{O}$	2.5-11	0	0	52*
$\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H} + \text{OH}$	7.80-05	-2.46	938 [†]	present work*	$\text{NH} + \text{N} \rightarrow \text{N}_2 + \text{H}$	1.0-12	0.5	0	25
$\text{NH}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{N}_2$	1.17-04	-2.46	938 [†]	present work*	$\text{NH} + \text{H} \xrightarrow{\text{M}} \text{NH}_2$	5.5-32	-0.5	0	49
$\text{NH}_2 + \text{O} \rightarrow \text{NH} + \text{OH}$	1.7-11	0	503	18	$\text{N} + \text{H} \xrightarrow{\text{M}} \text{NH}$	6.9-31	-0.5	0	25
$\text{NH}_2 + \text{OH} \rightarrow \text{NH} + \text{H}_2\text{O}$	5.0-14	0.68	650	48*	$\text{NH}_2 + \text{O}_2 \rightarrow \text{NH} + \text{HO}_2$	3.3-11	0	22647	18
$\text{NH}_2 + \text{H} \rightarrow \text{NH} + \text{H}_2$	8.3-13	0.5	1006	49	$\text{N} + \text{O} \xrightarrow{\text{M}} \text{NO}$	1.8-31	-0.5	0	25
$\text{NH} + \text{O} \rightarrow \text{NO} + \text{H}$	1.0-12	0.5	0	25	$\text{O} + \text{NH} \xrightarrow{\text{M}} \text{HNO}$	2.8-32	-0.5	0	25
$\text{NH} + \text{O} \rightarrow \text{N} + \text{OH}$	5.2-13	0.5	4000	25	$\text{O} + \text{HNO} \rightarrow \text{OH} + \text{NO}$	8.3-13	0.5	0	25
$\text{NH} + \text{OH} \rightarrow \text{N} + \text{H}_2\text{O}$	8.3-12	0.5	1006	25	$\text{N}_2\text{H}_4 \xrightarrow{\text{M}} 2\text{NH}_2$	6.6-09	0	20600	25
$\text{NH} + \text{H} \rightarrow \text{N} + \text{H}_2$	1.0-12	0.5	4000	25					
$\text{NH} + \text{NO} \rightarrow \text{N}_2 + \text{OH}$	4.7-11	0	0	50					
$\text{NO} + \text{H} \xrightarrow{\text{M}} \text{HNO}$	5.0-32	0	-300	42*					
$\text{HNO} + \text{H} \rightarrow \text{NO} + \text{H}_2$	8.0-12	0	0	42					

[†] These values good for $T \leq 1200$ K. Above 1200 K values extrapolated from Fig. 4.5, resulting in $k(1500) = 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for total $\text{NH}_2 + \text{NO}$ reaction rate.

* Rates used in shortened version of model.

1. $H_x - O_y$ Reactions: These include the interactions among H, OH, H_2O , and HO_2 , including three body recombinations (water shuffle reactions).
2. NH_x Oxidation Reactions: Included in this group are the reactions of N, NH, NH_2 , and NH_3 with H, OH, O, and O_2 . As there are multiple product channels for some of these reactions, we have used all except those which are very endothermic, and thus, unlikely to contribute to the chemistry.
3. Reactions of NO and HNO: These reactions provide for the removal of NO and HNO, as well as the conversion of HNO to NO. Included are the reactions of HNO and NO with NH_x , O, OH, and H where appropriate.

In obtaining this reaction set it is assumed that certain species are not present at high temperatures. These species include H_2O_2 , O_3 , NO_2 , HCN, and N_2O ; the last two having been observed at levels below 1 and 50 ppm, respectively. (3,10)

In certain situations, it is desirable to include reactions of CO, CO_2 , NO_2 , and H_2O_2 , the latter two being important below 1000 K. Tables 5, 6, and 7 list the additional sets of rates used. The CO- CO_2 rates are deleted from the main body of reactions because they have no effect on the chemistry between 750-1500 K with NH_3 addition.

TABLE 5 - CO, CO_2 RATES

$$k = AT^n e^{-E/RT} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{)}$$

REACTION	A	n	E/R	REF.
$CO + OH \rightarrow CO_2 + H$	2.5-17	1.3	-385	25
$CO_2 + H_2 \rightarrow CO + H_2O$	1.7-12	0.5	7550	25
$CO + HO_2 \rightarrow CO_2 + OH$	2.5-10	0.0	11900	25
$CO + O_2 \rightarrow CO_2 + O$	4.15-12	0.0	24000	25
$CO + HNO \rightarrow CO_2 + NH$	1.7-13	0.5	3520	25

TABLE 6 - NO₂ RATES

$$k = AT^n e^{-E/RT} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{)}$$

REACTION	A	n	E/R	REF.
$\text{H} + \text{NO}_2 \rightarrow \text{NO} + \text{OH}$	5.25-10	0	755	25
$\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}$	2.8-12	0	23400	25
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	3.3-12	0	-254	45

TABLE 7 - H₂O₂ RATES

$$k = AT^n e^{-E/RT} \text{ (cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\text{)}$$

REACTION	A	n	E/R	REF.
$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2.5-12	0.0	0	44
$\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$	2.7-12	0.0	2100	44
$2\text{OH} \xrightarrow{\text{M}} \text{H}_2\text{O}_2$	9.9-24	-2.9	0	44
$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	7.6-12	0.0	670	49
$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2 + \text{HO}_2$	2.8-12	0.0	1900	25

5.3 Initial Conditions

For most runs, the products of a CH_4/O_2 flame having an equivalence ratio of 0.93 and burnt in excess Argon (mole fraction 0.83) are used for initial concentrations in the computer calculations. This is similar to the burner studies of Branch,⁽⁵⁾ and are representative of the C/O/H gaseous products of a coal-fired combustor. Various amounts of NO, NH_3 , and H_2 are added to simulate the Thermal de NO_x process, and the concentration profiles as a function of time and initial temperatures are calculated. Alternate additives are tested, including $\text{H}_2\text{O}_2 + \text{NH}_3$, H_2H_4 , CO, and a mixture of $2\text{NH}_2 + \text{CO}$, which could be considered the analog of urea.

One additional case is presented in which we attempt to simulate a more realistic coal combustion scenario. Montana Rosebud coal is burnt with an equivalence ratio of 0.95 at 1800 K. If one estimates that a typical combustor exhaust flow cools at a rate of 450 degrees s^{-1} ,⁽⁵³⁾ then the time required before injecting NH_3 at a given exhaust temperature is determined. The model takes the equilibrium products of this coal combustion, and using a channel heat loss equivalent to 450 degrees s^{-1} , cools the gas while maintaining the finite rates for the NO chemistry (modified Zeldovich mechanism). The result is that the gas cools to equilibrium concentrations corresponding to the temperature desired, but the Zeldovich mechanism holds NO concentrations to those found at 1800 K (~900 ppm). These products are input to the rate package at temperatures between 1000 and 1500 K and the effect of NH_3 on NO reduction is determined.

5.4 A Description of the Model

The chemical mechanism by which NO is converted to H_2 and H_2O occurs in three phases. Under typical exhaust flow conditions, the first reaction is the initiation step, where hydroxyl radicals initially present react with NH_3 to produce NH_2 and H_2O .

The temperature dependence of this rate determines the low temperature behavior of the Thermal deNO_x process. H and O atoms also attack NH₃, hastening its conversion to NH₂.

The second phase involves the reaction of NH₂ with NO. This is the chain propagation step. The key to understanding the mechanisms lies in identifying the branching into the many possible product channels as mentioned in Subsection 4.5.

Reactions (5.4f) and (5.4h) are too endothermic to play an important role, which is in agreement with results mentioned in the previous section of this paper. If one assumes that reaction (5.4) is chain propagating, then it must, on the average, generate greater than one radical per reaction. Miller, et al.,⁽¹⁸⁾ have a detailed discussion about choosing which channels may be important, and in their modeling work, have chosen to assume that (5.4c) and (5.4d) predominate. Subsequent reactions of N_2H and N_2OH form N_2 and H_2O and in their model, enough H and OH radicals are produced to propagate the chain. We have used a simpler picture in our model, which is that reactions (5.4a) and (5.4b) represent the opposite ends of possible reaction sequences which combine to form between zero (5.4a) and two (5.4b) radicals/ reaction of NH_2 and NO. This choice is bolstered by the mass spectrometer measurements which infer that N_2 and H_2O are major direct products. The absence of N_2O in the mass spectrometer studies rules out reaction (5.4g). No H atoms were detected as products at 300 K, which implies that (5.4c) is the other major product channel. However, the bond strength of N_2H cannot be very large,⁽¹⁸⁾ and at the temperatures of interest, would most likely dissociate with a gas kinetic rate to form N_2+H , so that the choice of using (5.4b) is justifiable.

Our model has included both (5.4a) and (5.4b) in various ratios in order to estimate the optimum degree of branching in absence of any further experimental data. The sequence below, where f is the fraction of reaction (5.4) leading to radical products, simply describes the main NO removal steps.

The effect of varying f is seen in Fig. 5.1 with $[\text{NO}] = [\text{NH}_3] = 1700$ ppm. The large concentration dramatizes the effect. Below $f \approx 0.35$, the chemistry ceases. With increasing f , the removal of NO shifts to lower temperatures because more H and OH radicals are present to react with NH_3 and maintain the catalytic reaction sequence. Only when the $\text{NH}_3 + \text{OH}$ reaction rate is slowed (due to lower temperatures and concomittant lower initial OH concentrations as well as lower k_1) is the chemistry unable to proceed. If reaction (5.4a) were the only source of radicals for reactions (5.1) through (5.3), then f must be larger than 0.5 for chain propagation. However, separate calculations show that another constant source of radicals comes from the water shuffle reactions which rapidly replenish the OH and H radical pool, such as

Thus, it is possible to have a value of $f < .5$ and still maintain a chain reaction.

Using our experimental results for OH formation as a guide, we have chosen to use $f = 0.40$. It produces a temperature dependence with an optimal removal of NO at ~ 1225 K. If $f = 0.50$, this position decreases by about 50 K, which is incompatible with Thermal de NO_x flow simulation studies.

At higher temperatures (>1300 K), two events occur. First, the $\text{NH}_2 + \text{NO}$ reaction rate dramatically falls, slowing the destruction of NO and secondly, reactions which convert $\text{NH}_2 \rightarrow \text{NH} \rightarrow \text{HNO} \rightarrow \text{NO}$ become important.

Figure 5.1. Fraction of Remaining NO as a Function of Initial Temperature for Varying Values of NH_2+NO Branching Ratio, f .

$$[NO]_0 = [NH_3]_0 = 1700\text{ppm}, [CH_4]/[O_2]_{\text{mixture}} (\phi=0.93) \text{ in } 83\% \text{ Argon.}$$

Thus, at higher temperatures, radicals successfully compete with NO for reaction with NH_2 to form NH. The NH then reacts rapidly with the large amount of O_2 present to produce HNO, which is converted to NO.

5.5 Modeling Results

5.5.1 Reduction of NO by NH_3 Addition

For typical concentrations of NO (300 ppm), the model predicts the most efficient removal at 1175 - 1250 K (Fig. 5.2). As the ratio (β) of NH_3/NO increases, so does the efficiency for reduction near 1200 K. But increasing β narrows the width of the "window" on the high temperature side so that at temperatures greater than 1400 K, the excess ammonia is increasingly oxidized to NO.

The variation of removal effectiveness with initial NO concentration is shown in Fig. 5.3. Although slightly more efficient for 1700 ppm, the absolute concentration emitted out the stack is still higher. The most noticeable difference is the substantial betterment of removal above 1250 K. Also illustrated in Fig. 5.3 is the effect of adding a slight excess (over NO) of H_2 . As in agreement with laboratory studies, the window shifts to lower temperatures and retains approximately the same width.

The addition of hydrogen rapidly shifts the $\text{H}_x\text{-O}_y$ balance at all temperatures toward hydrogen-containing species (HO_2 , H_2O , OH, H). This results in the reaction of H atoms successfully complementing the reaction of additional

Figure 5.2. Fraction of Remaining NO as a Function of Initial Temperature ($f=0.40$) for Varying Initial Concentrations of $[NO]$ and $[NH_3]$

— $[NO]_0 = 300\text{ppm}, [NH_3]_0 = 450\text{ppm}$
 — • — $[NO]_0 = 300\text{ppm}, [NH_3]_0 = 300\text{ppm}$
 - - - $[NO]_0 = 300\text{ppm}, [NH_3]_0 = 150\text{ppm}$

Figure 5.3. Effect of Varying Initial $[\text{NO}]_0$ Concentration and Change Upon Addition of $[\text{H}_2]$.

- $[\text{NO}]_0 = [\text{NH}_3]_0 = 1700\text{ppm}$
- $[\text{NO}]_0 = [\text{NH}_3]_0 = 1700\text{ppm}, [\text{H}_2]_0 = 2000\text{ppm}$
- $[\text{NO}]_0 = [\text{NH}_3]_0 = 300\text{ppm}$
- $[\text{NO}]_0 = [\text{NH}_3]_0 = 300\text{ppm}, [\text{H}_2]_0 = 400\text{ppm}$

OH with NH_3 in the initiation steps, thereby shifting the reaction window to lower temperatures. At the same time, the upper window also shifts because the increased total radical concentration results in greater NO formation. (reactions 5.6 - 5.11).

To further validate our ideas about the key reaction steps, a reduced reaction set was run. It contained 24 reactions, half of which was the required water shuffle mechanism. These are denoted by asterisks in Table 4. The curve for NO reduction (300 ppm levels) with NH_3 was reproduced to within 1%. These reactions are felt to be the driving force in the reduction of NO and a simple schematic of this is illustrated in Fig. 5.4. Ammonia reacts with OH present to form NH_2 . Depending on the temperature, NH_2 reacts with NO to produce more radicals, or reacts with OH to create NH, with subsequent conversion to NO. The overall effect is that below 1100 K no reactions occur, between 1100 and 1300 K, NH_3 and NO are converted to N_2 , and above 1300 K, NH_3 is oxidized to NO.

5.5.2 Time for Reduction

At temperatures of maximum removal efficiency, the chemistry is essentially complete (95%) in 0.09s, decreasing with initial NO concentration. The reaction time also decreases sharply with increasing temperature, mainly due to the temperature dependence of the rate for conversion of NH_3 to NH_2 by OH (Fig. 5.5). These time scales compare favorably with experimental results. The concentrations of NH_3 and NO initially decrease at the same rate until most of the NO is removed or until NH_2 starts converting to NO at higher temperatures. In a real system, this would tend to raise the low temperature effectiveness, since reaction times are not necessarily restricted as in the experiments.

Figure 5.4. Simplified Schematic of NH₃/NO Chemistry

Figure 5.5. Profile of $[\text{NO}]$ vs. Reaction Time for Various Initial Temperatures.

$$[\text{NO}]_0 = [\text{NH}_3]_0 = 300\text{ppm}$$

5.5.3 Pressure Dependence

Because the exhaust flow in a full-scale facility may operate at local pressures above one atmosphere, we investigated the effect of pressure on nitric oxide reduction. The results for exhaust from a CH_4/O_2 flame ($\phi = 0.93$) with 300 ppm of NO at pressures of one, two, and three atmospheres is shown in Fig. 5.6, for 0.24s reaction time. The window shifts slightly to higher temperatures as the pressure is increased. Increasing the pressure favors three-body recombination reactions (decreasing collisional dissociations). It appears that this slows the reaction

widening the window above 1250 K since the net amount of NO formed is less. Below 1200 K, the same effect decreases the OH concentration, showing the low temperature behavior. The fractional removal at the optimum temperature is only slightly improved. The conclusion reached is that variations in pressure will not be deleterious to the selective chemical reduction process.

5.5.4 NH_3 Addition to Products of Combusted Coal

As described earlier, an attempt to see how effective ammonia addition would be with a more realistic system was made. The results are shown in Fig. 5.7. For comparison, the results of Muzio and Arand,⁽¹⁰⁾ in which a 200,000 Btu/hr combustion tunnel was fired with natural gas and 4% excess O_2 (300 ppm NO), are presented. Also included is the simpler CH_4/O_2 calculation discussed earlier. The good agreement among these results increases confidence in the ability of the model to make valid predictions.

Figure 5.6. NO Removal by Ammonia as a Function of System Pressure.

$t = 0.24s$

$$\frac{[NO]}{[NO]_0}$$

Figure 5.7. Comparison of CH_4/O_2 Flame and Montana Rosebud Coal Calculations With Combustion Tunnel Experimental Results of Muzio.⁽¹⁰⁾

5.5.5 Alternate Reducing Agents

A number of other possible reducing agents were evaluated using the computer. The results are described below. The equilibrium products of a CH_4/O_2 flame ($\phi=0.93$) with 300 ppm NO are used for starting concentrations.

a) Hydrogen Peroxide and Ammonia

Recent experimental evidence⁽⁵⁴⁾ suggests that peroxides could be used to lower the temperature window significantly. Using the NO_2 and H_2O_2 reaction sets (Tables 6 and 7), 300 ppm each of H_2O_2 and NH_3 were added. The results are shown in Fig. 5.8 for $t = 0.48\text{s}$. As expected, H_2O_2 provides the needed source of OH radicals independent of the NH_3+OH reaction, which had limited the low temperature reduction of NO. Although NO is almost entirely removed near 900 K, it is converted to NO_2 by the reaction

resulting in less net NO_x loss. The optimum temperature for total NO_x reduction rises to 1100 K. At higher temperatures, reduction is less effective than with NH_3 alone. The large excess of OH radicals formed from the decomposition of H_2O_2 react with NH_2 as well as NH_3 , and result in the formation of NO (reactions 5.6 - 5.11)

b) Hydrazine

The addition of hydrazine (N_2H_4) again attempts to overcome the low temperature limitation posed by the NH_3+OH reaction in that it provides, by thermal dissociation, an immediate source of NH_2 radicals. As with H_2O_2 , the temperature range for effective reduction of NO is lowered significantly, but with much less NO_2 formation, resulting in a broader curve (Fig. 5.9). The low temperature portion of the curve is controlled by the rate of N_2H_4 dissociation, which is too slow below 800 K. With no NH_3 present, the OH radical primarily attacks NH_2 , with this reaction becoming significant above 1200 K.

Figure 5.8. NO Removal With Addition of $\text{H}_2\text{O}_2/\text{NH}_3$ Mixture

Figure 5.9. NO Reduction With Additions of N₂H₄ and (NH₂)₂CO.

In these calculations, the only reaction involving hydrazine was the relatively slow three-body dissociation step

Since the overall chemistry of this process is not completely understood, the effect of radical attack and subsequent reactions could possibly change the results. Although H atoms simply abstract a hydrogen atom, O atoms do not.⁽⁵⁵⁾

The products of hydroxyl attack are unknown, although one might suggest H_2O and N_2H_3 as a reasonable choice. In any case, hydrazine appears to be a good reducing agent at first glance, but more data is needed to be certain.

c) Carbon Monoxide

Addition of 300 ppm of CO had no effect on nitric oxide reduction; CO was oxidized to CO_2 with little other effect. This agrees with the experimental results of Muzio and Arand.⁽¹⁰⁾

d) Urea

Another promising method of introducing NH_2 directly is the injection of urea $[(\text{NH}_2)_2\text{CO}]$, because of its abundance and low cost. We simulated urea using 300 ppm of NH_2 and 150 ppm of CO; making the assumption that its dissociation rapidly compared to reactions which would degrade its efficiency. The result is similar to that of N_2H_4 (Fig. 5.9) and the same caveats concerning radical reactions apply.

e) Mono, Di, and Trimethylamine

These amines have been shown to be moderately effective reducing agents, with a low and moderate temperature window.⁽¹⁰⁾ At higher temperatures, the methyl groups probably act like H atoms and the chemistry behaves like the NH_3/NO system. At lower temperatures (800 K), the usefulness of reduction is partially offset by the production of HCN at concentrations of 150 ppm.⁽¹⁰⁾ Hydrocarbon radicals will react with NO and form HCN, as in the reaction

The usefulness of these amines is limited by their cost and toxicity and are not particularly advantageous with respect to NH_3 , NH_2/H_2 or $\text{NH}_3/\text{H}_2\text{O}_2$.

6. DISCUSSION

6.1 Summary of Results

The abatement of nitric oxide emissions in combustion exhaust flows is a required objective of recent EPA regulations. A method in which this is accomplished with minimal expense and maximal versatility is desired. The selective chemical reduction process has the promise to meet these needs.

The efforts described in this report are an attempt to gain an understanding of the detailed chemical mechanism which governs the reduction of nitric oxide upon addition of ammonia, to identify what other chemical agents might be effective, and to investigate the circumstances under which the process would work on a full-sized combustor.

Using laboratory and pilot-scale combustor results as a guide, a model which describes the important features of the ammonia addition process is developed. Key reaction rates are measured, as is branching into various product channels. Incorporation of these results into the model provides a consistent description of the NH_i/NO_x chemical system, which is validated by comparison to the aforementioned laboratory results. The most important features of the NH_i/NO_x system under typical exhaust conditions are as follows:

1. The chemical reduction of nitric oxide is controlled by the reaction of $\text{NH}_2 + \text{NO}$.
2. The radical products of this reaction promote the formation of additional NH_2 by reaction with NH_3 , inducing a chain mechanism which converts NO to N_2 .
3. Low temperature (< 1100 K) formation of NH_2 is limited by the temperature dependence of NH_3 + radical reaction rates.

4. At high temperatures (>1300 K), OH concentrations are larger, and with a decreasing $\text{NH}_2 + \text{NO}$ rate, the reaction of hydroxyl with NH_2 to form NH becomes increasingly competitive. Once formed, NH rapidly reacts with the large excess of O_2 present to eventually form NO. In effect, the added NH_3 is converted to NO.
5. The reaction time is very temperature dependent, increasing dramatically as the temperature decreases.
6. The addition of H_2O_2 or H_2 with NH_3 is effective in lowering the temperature at which maximum efficiency is observed.
7. Below 1000 K, NO_2 formation becomes important, often offsetting the amount of NO reduction for these alternate additives.
8. NH_2 -compounds are effective and exhibit a broader temperature response. However, toxicity and expense may limit their usefulness.
9. CO and H_2 as sole additives are not effective in reducing NO.

6.2 Application to Pilot Scale Coal-Fired Combustion Facilities

There are several considerations outside the scope of this work which may have a bearing on the design and implementation of a flue gas selective chemical reduction system. These include designing an injection system which rapidly and evenly mixes the reduction gas throughout the flue exhaust in a time shorter than the reaction time (<20 ms). If the mixing is not uniform, then the reduction will quickly become diffusion limited, severely hampering the reduction efficiency. In addition, the injected gas should

not significantly cool the exhaust flow. This should not be a problem since only a few hundred ppm of gas will be injected, having little heat load on the system.

An understanding of the homogeneous reduction chemistry does become important when choosing the position of gas injection. Since flue gas temperatures at any given site in the exhaust flow may vary depending on the loading of the combustor, the type of fuel, and the amount of excess air used, it is desirable to place the injection ports where the exhaust temperature would always be equal to or less than 1250 K. Through the use of additives such as H_2O_2 or H_2 , efficient removal could be accomplished if the exhaust were up to 200 K cooler. It is advantageous to try and maintain the exhaust temperatures downstream of injection in order to prevent slowing of the reduction as the gas cools.

A minimum isothermal length should be equivalent to about half a second of flow time, which for a 10 ms^{-1} flow velocity would be five meters. To achieve optimum removal, an [NO] monitor upstream of the injector would be connected to a microprocessor, which would evaluate the amount of additives required, given [NO] and the temperature at the injection location.

6.3 Further Studies

Using the calculations obtained from the chemical model, it appears that 85% of the nitric oxide present in the exhaust flow could be converted to N_2 , which would satisfy existing EPA regulations. With the increased use of coal and oil shale, there may be problems associated with other chemical species present. Clearly, the large percentage of sulfur-containing species in these fuels may have a serious impact on the NH_3/NO_x system. Sulfur is a highly reactive chemical and could compete with NO for NH_3 . We are presently investigating the effect of these reagents on the selective chemical reduction of NO. Alkali metals are very reactive and their presence could also affect the reduction efficiency. With certain SO_2 reactions and with

alkali metals, the possibility of condensation could be important. The condensation process itself, and the heterogeneous chemistry associated with it are poorly understood and merit further study. Although the non-catalytic reduction of nitric oxides by chemical addition in exhaust flows was developed for use with coal or oil fired combustors, it would be advantageous to investigate the possibility of its use in other forms of combustors, such as pulverized beds, MHD exhausts, and gas turbines.

7. ACKNOWLEDGEMENT

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APPENDIX I.

A VERSATILE HIGH TEMPERATURE FLOW REACTOR FOR
KINETIC AND SPECTROSCOPIC STUDIES*

by

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ABSTRACT

A high temperature flow reactor has been constructed to perform kinetic and spectroscopic studies on species at temperatures between 300 and 1500 K. The species in the flow reactor may be detected or studied using: laser induced fluorescence, resonance fluorescence, infrared absorption, ultraviolet absorption, chemiluminescence, or molecular beam mass spectrometry. The features of the apparatus are described in detail, and the initial spectroscopic and kinetic studies are discussed.

*Prepared for publication in Review of Scientific Instruments.

INTRODUCTION

Flow tubes have been used routinely to perform kinetic measurements at temperatures between 200 and 600 K, and flame and shock tube techniques are commonly employed for temperatures above 1000 K. However, relatively few data are available in the 500 to 1500 K regime, which bridges the gap between low and high temperature measurements.¹⁻⁴

On the other hand, flow tubes have not generally been employed in the performance of quantitative infrared measurements. These have most often been performed in static cells, shock tubes, and burners.^{5,6} Static cells are not convenient for the study of transient species and are limited to approximately 1200 K. Shock tubes and burners are not generally useful below 1000 K, and they usually require equilibrium calculations of species number densities.

This paper describes a high temperature flow reactor which was developed to address both of these problems. It is designed to perform kinetic and spectroscopic studies over the temperature range of 300 to 1500 K. The kinetic measurements are facilitated by the capability to measure reactant and/or product number densities using a wide range of diagnostic techniques: laser induced fluorescence, discharge lamp resonance fluorescence, infrared absorption, ultraviolet absorption, chemiluminescence, and molecular beam mass spectrometry. In addition, the apparatus was designed to perform quantitative infrared absorption measurements, with the application of one or more of the other diagnostic capabilities to independently measure the number density of the absorb-

ing species. As a corollary, the multiplicity of diagnostic capabilities also permits the performance of visible/ultraviolet spectroscopic measurements of transient species.

I. DESCRIPTION OF THE APPARATUS

A. General

The high temperature flow reactor has been designed with the capability to perform both kinetic and spectroscopic studies of species at temperatures between 300 K and 1500 K. As a result the apparatus design is considerably more complicated than would be required if only kinetic studies were to be performed.^{4,7,8} This is due to the fact that only relative species concentrations need be measured to determine (pseudo-first order) rate constants,¹ but absolute species concentrations and well-defined path lengths are required for the performance of quantitative spectroscopic measurements. In addition, the apparatus has been designed to accomodate a great variety of measurement techniques, thereby providing the flexibility to study a wide range of species.

A block diagram of the major apparatus components is shown in Fig. 1. A gas handling system external to the flow reactor is used to prepare the several gas flows that are introduced into the reactor. One (or more) of these flows may be passed through microwave discharges to produce radical species. In the flow reactor, gases may be mixed to produce the reactions whose rates are to be measured, or reactions may be carried out in order to produce transient species for spectroscopic studies. The flowing gases then pass into an analysis region where a variety of diagnostic techniques may be employed to characterize the species present. The following measurements may be performed: infrared absorption using either resonance or arc lamps, ultraviolet/visible discharge lamp induced resonance fluorescence, ultraviolet/visible laser induced fluorescence, and molecular beam mass spectroscopy. This versatility permits the study of almost any species.

B. Vacuum Jacket and Flow Reactor

B.1. Overall description

The detailed design of the variable temperature flow reactor is shown in Fig. 2. The outer vacuum jacket is constructed of steel and is water cooled, as are the aluminum end plate assemblies. The water cooling protects temperature-sensitive components and insures dimensional stability for optical components (such as the White cell mirrors) mounted on the vacuum jacket flanges. The upstream end plate holds the alumina flow tube, as well as power, gas, and thermocouple feedthroughs. The downstream flange is used for experiments for which mass spectrometer sampling is not required. When the mass spectrometer is employed, the flow reactor is mated directly to the outer vacuum wall of the mass spectrometer. In the analysis region, eight 10 cm inside diameter flanges are spaced equally around the circumference of the vacuum jacket. Four of these ports are connected by alumina tubes to the main flow tube and provide for optical analysis of the hot flowing gas. One of the remaining four ports is presently connected to a Kinney KMBD 1602 mechanical pump and Roots blower with an effective pumping speed of approximately 1000 cfm (450 l/sec).

The main elements of the thermal design include the heating elements and the surrounding layer of refractory insulation. The insulation is composed of a self-supporting "spool" of rigid alumina fiber insulation (Zircar Products, Inc.), upon which is wound several layers of Zircar alumina fiber blanket insulation, followed by additional layers of alumina-silica blanket insulation (Carborundum Corp.). The insulation assembly has an inside diameter of 15 cm and is designed to withstand continuous operating temperatures of 1800 K. The

commercially available Kanthal A-1 heating elements (Thermcraft, Inc., type RH) have a design temperature rating of 1500 K and are operated at 120 VAC. The heating elements are arranged in a three zone configuration to minimize temperature gradients due to end effects. The heated length is 78 cm, with a total power capability of approximately 8 kW. The heaters are supplied with power by solid-state proportional temperature controllers and power supply units (Love Controls, Corp.). The fully assembled flow reactor achieves a temperature of 1500 K with a power consumption of approximately 3 kW. The thermal stresses developed in the alumina flow tube components are small enough that the apparatus is routinely heated from room temperature to 1500 K in approximately 4-6 hrs, and no damage to the alumina components has occurred during the 1½ years that the heated flow reactor has been in use.

The design of the gas flow system within the variable temperature flow reactor is relatively complicated due to the constraints required to provide the capability of performing quantitative spectroscopic measurements in the analysis region. The main flow in the 7.3 cm inside diameter 99.8% alumina flow tube is usually composed of He or Ar carrier gas. This gas is heated as it passes through two heat exchangers which are 2.5 cm thick mullite "honeycomb" hole arrays with 1.6 mm round holes and a 67% frontal open area (General Refractories Co.). These heat exchangers are required to heat the carrier gas at high flow rates (large Reynolds numbers), and they also serve to laminarize the carrier gas flow. Downstream of the heat exchangers, two concentric 99.8% alumina injectors permit the introduction of reactive species into the flow.

The gas in the inner injector (9.5 mm i.d., 12.7 mm o.d.) may be passed through a commercial 2450 MHz microwave discharge cavity (Ophthos Instrument Co.) before being introduced approximately 1-2 cm upstream of the end of the outer injector (14.3 mm i.d., 19.1 mm o.d.). The microwave discharge is used to generate atoms and free radicals which can be injected directly into the main carrier gas flow or can be mixed with a reactant gas in the outer coaxial tube before being injected into the main flow. This arrangement permits a great deal of flexibility in the preparation of reactant species for study. The heated gas then passes through an isothermal region of the flow tube with constant cross section. In this region a second reactant species may be introduced into the flow via a movable injector for the measurement of rate constants.¹ The present movable injector is constructed of 6.3 mm o.d. quartz tubing (with a temperature limit of approximately 1250 K). The gas is injected into the main flow from a 5 cm o.d. loop of tubing having 16 0.4-0.5 mm diameter holes to promote rapid and uniform mixing.

The main flow with its mixture of reactive species then passes through a subsonic nozzle (area ratio 3.3:1, 4.0 cm i.d.) to enter the analysis region, as shown in Fig. 3. A second, external flow (shield flow) of pure carrier gas is heated to the temperature of the main flow as it passes between the heating elements and the outside of the flow tube. Then, after the shield flow passes through a subsonic nozzle which is concentric with the main flow nozzle, the flows merge. The area ratio of the main flow nozzle to the shield flow nozzle is 1:1, and the corresponding flow rates should ideally also be equal so that the velocities of the two flows will be the same when they meet downstream of the nozzles (in order to minimize mixing due to shear forces). This results

in a fluid dynamic confinement of the reactive species in the main flow as they pass through the analysis region. In addition, small flows of carrier gas are added to each of four optics tubes as a purge gas in order to keep the optics clean. The flow of purge gas into the optics tubes is generally set at approximately 10 percent of the main flow (equally divided between the four optics tubes), although this ratio is not critical. The six flows of gas meet in the analysis region volume which is defined by a six-arm cross piece that is made from machinable alumina ceramic (Cotronics Corp. type 960). The cross piece supports the four optics tubes and the flow tube. (The front of the flow tube rests on two sapphire balls, thereby permitting the flow tube to expand without generating any stress on the cross piece.) However, the main purpose of the cross piece is to provide an environment in which the main flow from the flow tube will be well behaved as it traverses the optical analysis region, impinges on the mass spectrometer sampling orifice, and is exhausted by the mechanical pump. Thus, the design of this element of the flow system is particularly important to the success of the experimental program, and separate experimental studies, described below, were undertaken in order to insure that the design would adequately control the gas flow in the analysis region.

B.2. Flow simulation experiment

A crucial element of the apparatus design is the configuration of the flow system in the spectroscopic analysis region. In order for one to be able to perform quantitative spectroscopic measurements on the species

in the main flow, three criteria must be satisfied: (1) geometry of the gas flow must be well defined as it traverses the analysis region, (2) the flow in this region must be stable, and (3) the temperature of the gas flow must be well defined (preferably isothermal). These criteria may be satisfied by maintaining a stable cylindrical flow, without recirculation of absorbing species in the optics tubes. For high temperature gas flows and/or multi-pass absorption cells, this necessitates the use of a wall-less confinement of the absorbing gas species as they pass through the analysis region. This can only be accomplished by fluid mechanical confinement of the flowing gas.

Since this portion of the apparatus represented a novel design, it was felt that its design should be tested in a flow simulation experiment before the fabrication of the six-arm cross piece out of machinable alumina ceramic. This obviated the need for a major system redesign if the initial design proved to be inadequate and would establish the approximate range of operating flow conditions over which the fluid mechanical confinement of the absorbing species would be effective.

The flow simulation experiment was set up in the following manner: a half scale model of the flow system was fabricated out of plastic (polymethyl methacrylate) with flowmeters monitoring the main flow, the shield flow, and the four purge flows. The gas flow was simulated by using a water flow with the same Reynold's number, which is a standard technique in fluid mechanics and is valid for subsonic, incompressible flows.⁹ The flow pattern is determined by injecting Fluorescein dye into any one of the water flows and observing the bright fluorescence induced by illumination with a tungsten/halogen lamp.

The water flow velocity required for the simulation is obtained from the flow velocity of (for example) Ar that is to be simulated by equating the Reynolds numbers of the flows:

$$Re = \frac{\rho u d}{\eta} = \frac{\rho' u' d'}{\eta'} \quad (1)$$

where ρ is the density, u is the flow velocity, d is the tube diameter, η is the viscosity, and the prime refers to the conditions for water. Then, we let $d' = d/2$ and $\rho = \rho_0 P$, where $\rho_0 = 2.35 \times 10^{-6} \text{ g/cm}^3/\text{Torr}$ and P is the Ar pressure in Torr. Also, $\eta' = 1.0 \text{ g/cm}^3$, $\eta = 2.2 \times 10^{-4} \text{ poise}$, and $\eta' = 1.0 \times 10^{-2} \text{ poise}$ (at 293 K). This leads to the expression for the water flow velocity u' required for the simulation:

$$u' = 2.1 \times 10^{-4} P u \quad (2)$$

To simulate Ar flows at other temperatures, one would have to substitute the appropriate values of ρ_0 and η .

The flow simulation experiment was actually performed for a slightly different apparatus configuration from that shown in Fig. 3. In particular, the nozzle for the main flow had an area ratio of 2.1 (ratio of main flow to shield flow = 2:1),¹⁰ as opposed to the area ratio of 3.3 currently used in the high temperature flow reactor. The flow reactor was initially constructed with the smaller area ratio nozzle, but this design proved to be marginal for

reasons to be discussed below. The current configuration is more "conservative" with regard to the confinement of the main flow gas, and the general conclusions of the flow simulation experiment would therefore still be valid for the present design.

When the flow simulation experiments were performed, a number of interesting results were observed. The major result is that with a main flow Reynolds number greater than approximately 100 (for main:shield:purge flow rate ratios of 10:5:1) the main flow appears to be stable and cylindrical in form as it passes through the analysis region. Under these stable flow conditions, no recirculation pattern of the main flow water was observed in the "optics tubes". At lower Reynolds numbers the flow became unstable and main flow water entered the optics tubes. In addition, when dye was added to the water of the shield flow, a strong recirculation pattern of shield flow water was observed in the optics tubes, and this phenomenon persisted even at the highest main flow Reynolds number (560) used in the experiments. Thus, it may be concluded that a simpler flow configuration without a shield flow would not satisfy the analysis region design criteria since there would be recirculation of absorbing gas in the optics tubes. The more sophisticated design is successful because only the non-absorbing shield gas recirculates in the optics tubes, while the main flow of absorbing gas is confined by the shield flow to a cylindrical region in the center of the analysis region. In addition, since the shield gas will nominally be at the same temperature as the main flow, the column of absorbing gas should be essentially isothermal.

Although a flow simulation experiment of this type can successfully predict the bulk fluid dynamic properties of an apparatus, it has a shortcoming in that it can not simulate the effect of diffusion in the gas phase. This is important because species in the main flow which diffuse into the shield flow could recirculate in the optics tubes. This was observed to occur during a series of experiments to measure the temperature dependence of the spectral absorption coefficients of the ν_3 band of BF_3 ,¹¹ at which time the apparatus was operated in its original configuration with a main flow nozzle area ratio of 2.1. Subsequently, this area ratio was increased to 3.3 (the present design). In this configuration the main flow was determined to be well confined during measurements of the infrared band strength of BF_3 .¹² In addition, it was possible to verify visually the confinement of the main flow by observing in the analysis region the afterglow of an air discharge under the flow conditions used in the BF_3 experiments. This flow visualization experiment confirms that the apparatus is capable of successfully confining the species in the main flow as they pass through the analysis region. However, when different flow conditions are employed, it would be advisable to repeat the flow visualization experiment for those conditions in order to verify the confinement of the species in the main flow.

B.3. Flow tube diagnostics

In the course of performing kinetic and spectroscopic studies, a number of key parameters which characterize the gases must be accurately known. Calibration measurements to determine the temperature, pressure, flow rates, and flow development of the gases in the flow reactor are described in this section.

Radial Velocity Distribution of the Flow

Laminar flow exists in the main flow as long as the Reynolds number is below 2000. This is true for all present applications of the apparatus. When the carrier gas is introduced through the mullite arrays, the flow has a uniform radial velocity distribution (plug flow). As the gas flows down the tube, its velocity profile eventually becomes parabolic (Poiseuille flow). In analyzing kinetic data, the corrections for diffusion depend on the extent to which the flow has developed. Since the most accurate solutions to the flow equations which account for both radial and axial diffusion, as well as wall removal¹³⁻¹⁵ assume completely developed Poiseuille flow, it is desirable to operate in this regime. The inlet length required to fully develop parabolic flow is¹⁶⁻¹⁸

$$Z \simeq R_e d / 16 \quad (3)$$

where R_e is the Reynolds number and d the tube diameter. In the present apparatus the distance from the laminar discs to the position where reactants are injected for kinetic measurements is ~25 cm. Thus, fully developed flow will present if $R_e \leq 55$. Typically, $R_e \leq 10$ in our kinetics experiments so that the requirements should be satisfied.

To verify this, we constructed a Pitot tube,¹⁷ which measures the dynamic pressure of the gas as a function of radial position. For a compressible fluid, this pressure can be related to the flow velocity by¹⁹

$$v = 2.22 \times 10^5 \left\{ \left(\frac{\gamma}{\gamma-1} \right) \frac{1}{M} \left[\left(\frac{P}{P_o} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \right\}^{1/2} \text{ cm/s} \quad (4)$$

where P_o is the static pressure, P is the dynamic pressure, γ the heat capacity ratio, and M the gram molecular weight. For He at 294 K, a Reynolds number of 30, and at a distance of ~25-30 cm from the mullite arrays, the data shown in Fig. 4 were obtained. The circles are the measured velocities and the solid line is a parabola normalized to the center velocity. Poiseuille flow has been clearly established.

Gas Temperature Measurements

In any spectral or kinetic measurement, the gas temperature must be known. The problems encountered in measuring the gas temperature in a variable temperature flow reactor are twofold. First, the gas must be heated to the desired operating temperature before it reaches the reaction and measurement region of the tube and second, an ordinary thermocouple receives more energy via radiation from the walls than from the gas, leading to an erroneously high reading. The latter problem has been overcome by using a dual shielded thermocouple arrangement^{3,20} which was used to calibrate the temperature controller readings as a function of gas Reynolds number. As mentioned earlier, gas heating is accomplished with two mullite multihole arrays.

Moffat²⁰ has shown that under laminar flow conditions and with a properly designed thermocouple, the major source of error in the reading arises from radiative heat transfer between the TC junction and the reactor walls. This error is reduced by heat shields at least as much as a factor of $(n+1)$, where n is the number of concentric shields around the thermocouple. By comparing the readings from a doubly shielded and unshielded thermocouple, this error term can be calculated and the true gas temperature measured.

Such a device was constructed, using W-5%Re/W-26%Re thermocouples (.010"dia.), referenced to 0°C, and alumina tubular shields. The inner shield is 12 mm OD and the outer one 57 mm OD. Both are 0.5 mm thick and 7.5 cm long. Support is provided by very thin alumina tubes used as struts to minimize any conductive heat transfer. The unshielded thermocouple is ~5 cm upstream of the shielded TC.

The probe was inserted into the flow tube at a position midway through the kinetic measurements region. The corrected gas temperature was compared with the reading obtained from the thermocouple on the heater controller as well as with the "nominal" value obtained by reading the scale on its temperature meter. This was done as a function of gas Reynolds number (using Ar and He at various flow settings) for five elevated temperatures. The precision of the TC readings was ± 0.1 K with an accuracy estimated at ± 2 K. The controller could be read to ± 5 K. The difference between the nominal readings and the measured gas temperatures are shown in Fig. 5. For $Re < 200$, the true gas temperature is ca. 6 K lower than the nominal values. This varies by ± 10 K for various temperatures, but shows no particular trend. Thus for $Re < 200$, the gas temperature is known to ± 10 K. The difference between the heater TC and measured gas temperatures exhibits the same behavior.

As R_e approached 500, the difference between the nominal and true values precipitously increased. This most likely occurs because the smaller diffusion and faster flow speeds at these Reynolds numbers allowed insufficient time for the gas to be heated. The addition of a third mullite array would probably extend the range of R_e where the temperature is well characterized. By providing additional surface area over which the gas must pass, more heat can be transferred.

Flow Rates and Gas Pressures

Pressures are measured using an MKS Baratron Model 222AHS100 (1.5% accuracy) or MKS Baratron Models 310-BHS10, 301-BHS100 (.08% accuracy). The injector loop is used to measure the static pressure inside the flow tube. This was compared to other probes in the arms and entrance to the tube and all readings agreed to within 1%. Gas volumetric flow rates are obtained using Matheson rotameters which are periodically calibrated for each gas used.

C. Measurement Capabilities

C.1. Mass spectrometer

A molecular beam mass spectrometer may be interfaced to the high temperature flow reactor in order to measure the number density of species in the main gas flow. A cross sectional view of the mass spectrometer in a horizontal plane is shown in Fig. 6. A novel feature of the design is the capability to measure the mass spectra of gases sampled from two independent apparatus located at right angles to each other. Currently, the apparatus which is located in the axial beam position (at the left of the figure) is an atmospheric pressure, pulverized coal burner, for which the mass spectrometer measures the neutral and ionic species in the burner flame.²¹ This burner will not be discussed further in the present paper. However, it should be noted that the axial beam skimmer and the two inner chambers may be electrically biased individually in order to facilitate the measurement of ionic species. (For simplicity, the additional ion optics are not shown in the figure.)

The high temperature flow reactor is located in the crossed beam position (at the top of the figure). From either of the two apparatus positions, the instrument operates as a conventional molecular beam mass spectrometer.²² There are three stages of differential pumping. The first (nozzle-skimmer) chamber is pumped by a 16 in. diffusion pump (Varian type HS16), the middle chamber is pumped by a 4 in. diffusion pump (Varian type VHS-4), and the mass spectrometer chamber is pumped by a 6 in. diffusion pump (Varian type VHS-6). A three position gate valve mounted on the innermost

chamber permits operation of the mass spectrometer in one of three modes: cross beam entrance and exit apertures open and axial beam entrance aperture closed (so that the mass spectrometer can be kept evacuated with the outer two chambers at atmospheric pressure). Choppers (Bulova Corp.) located on the gate valve assembly permit the beams to be modulated before they enter the mass spectrometer chamber, thereby permitting the use of synchronous detection techniques for discrimination against background gases. The mass spectrometer proper is a standard commercial unit (Extranuclear Laboratories, Inc.) except for the ionizer (model 041-2) which has been modified to accept a cross beam, as well as an axial beam.

The present molecular beam mass spectrometer is a recent addition to the apparatus, and, therefore, its ultimate capabilities have yet to be realized. At the present time, when it is operated with completely resolved mass peaks ($\Delta m \approx \frac{1}{2}$ amu), it is capable of detecting (signal-to-noise ratio = 1, 1 sec time constant on lock-in amplifier) species at approximately 4 ppm for the cross beam at a source pressure of 2 Torr and approximately 1 ppm for the axial beam at a source pressure of one atmosphere.

C.2. Infrared absorption

The high temperature flow reactor has been designed with the capability to perform quantitative measurements of infrared spectral absorption coefficients. These measurements may be performed either at low spectral resolution using a

broadband radiation source and monochromator or at very high spectral resolution using a tunable diode laser as the radiation source. The infrared optical system is divided into two major subassemblies: one inside the flow reactor vacuum jacket and one external to the vacuum jacket.

The internal infrared optical system is shown in Fig. 7, which is a cross sectional view of the flow reactor in the analysis region. The internal optics are composed of three spherical mirrors (43.0 cm radius of curvature) which form a multi-pass absorption cell (White cell).²³ The White cell is capable of producing approximately 100 passes through the absorbing gas in the main flow, but it is typically operated in the range of 28-52 passes, which is a compromise between increased path length (optical depth) and increased reflectance losses as the number of passes is increased. The height of the "envelope" of infrared beams passing through the main flow is typically on the order of 2 cm, as compared with the main flow diameter of approximately 4 cm.

The design of the low spectral resolution, double beam external optical system is shown in Fig. 8. The infrared radiation source is a Perkin-Elmer Corp. "Opberman Source" which is used in their current infrared spectrometers. The radiation impinges on a mirror-bladed, 50 percent duty cycle chopping wheel (Valtec Corp.) which alternately allows it to pass into the White cell or reflects it, thereby bypassing the White cell. In Fig. 8, M2, M3, M4, M7 and M8 are flat mirrors; M1 and M9 are spherical mirrors; and M5 and M6 are off-axis paraboloid mirrors. The beam splitter is made of

uncoated zinc selenide, the monochromator is a Spex Minimate, and the detector is a Santa Barbara Research Corp. HgCdTe photoconductive detector. In front of this is placed an order-sorting (long-wavelength pass) filter to avoid interference from higher order diffraction in the monochromator. Since the optical system consists of reflective optics (except for the zinc selenide beam splitter), it is achromatic, and it can be aligned with the use of a helium-neon laser.

The design of the high spectral resolution external optical system is shown in Fig. 9. This system shares many of the components of the low spectral resolution system. The tunable diode laser is mounted in a closed cycle refrigerator (both from Laser Analytics, Inc.). The laser radiation is focused by a KRS5 lens on the monochromator slit, and the monochromator is used to isolate a single laser mode. Before entering the White cell, the laser radiation is chopped so that lock-in detection techniques can discriminate against blackbody radiation from the heated flow reactor which impinges on the HgCdTe detector. With the diode laser, either direct absorption or derivative absorption²⁴ techniques may be used to measure the absorption cross sections of individual spectral lines. This capability of detecting individual lines, as well as the relatively high laser power, permits an increase in measurement sensitivity compared to low spectral resolution detection techniques. At low spectral resolution, a BF_3 number density of $\sim 3 \times 10^{13} \text{ cm}^{-3}$ may be detected using the ν_3 band (signal-to-noise = 1, time constant = 0.4 sec).¹¹ On the other hand, at high spectral resolution

a BF number density of $\sim 10^{11} \text{ cm}^{-3}$ may be detected by direct absorption measurements, and a BF number density of $\sim 2 \times 10^{10} \text{ cm}^{-3}$ may be detected using derivative absorption techniques (signal-to-noise = 1, time constant = 0.4 sec).¹²

C.3. Laser-induced fluorescence

The use of laser-induced fluorescence extends the capability and sensitivity of detection to species such as NH_2 . A nitrogen-pumped dye laser (Molelectron DL14P) is introduced through the bottom arm of the flow tube (Fig. 10). In this configuration, the resonance lamp is removed and Brewster windows added to the arms along the laser path to prevent beam scattering. The visible laser beam is expanded to 12 mm diameter to avoid any possible saturation effects. (In the UV, this is unnecessary because that laser power is lower.) After passing through the flow tube, a portion of the beam is split off into an ITT FW-114A fast vacuum photodiode which is used as a power monitor. The fluorescence is imaged into a photomultiplier which is perpendicular to the path of the laser beam.

For each laser pulse, there are $10^{13} - 10^{15}$ photons. Even with good baffling, scattered light may create severe background problems. To avoid this, a gated detection system is used, and is controlled by a master electronics console, designed and built at Aerodyne.²⁵ This unit initiates the laser pulse, and after the desired delay time, gates the PMT on (20 ns risetime).^{26,27} The fluorescence is amplified, integrated, and fed to a peak detector, where the signal is held until read into a Prime 400 computer

via an IBM 7406 interface. The unit controls all delay and data integration times in increments of 10 ns. A parallel channel repeats this process for the laser power monitor. The laser is fired on alternate clock periods and the signal (difference between laser-on and laser-off values, normalized to the laser power for each pulse) is computed and displayed in real time on a video terminal. For a typical species such as OH, a concentration of $\sim 10^9$ molecules cm^{-3} can be detected in 10 seconds of counting with signal/background = 1.

C.4. Resonance fluorescence

A variety of atomic and molecular species can be detected using resonance fluorescence techniques. A general schematic of this configuration is illustrated in Figs. 2 and 10. The quartz resonance lamp is made by flowing the desired species, entrained in an inert carrier, through a 2450 MHz microwave discharge and focussing the resulting emission into the flow tube.

Fluorescence is imaged from the central 12 mm diameter region of the analysis region of the flow tube onto a photomultiplier configured for photon counting. The PMT is mounted on an arm perpendicular to the resonance lamp. The counts are amplified and discriminated by a Pacific Precision Instruments Model 3262/AD6 amplifier-discriminator and fed to a Monsato 1505A Counter-Timer. Appropriate interference filters are used to isolate the emission lines from unwanted scattered light, which can be very intense at elevated temperatures.

When detecting oxygen or hydrogen atoms, a solar blind EMI G-26E315 photomultiplier is used, with optics constructed from MgF_2 . For all other species (BF, NO, OH, NO_2 etc.), quartz optics and a Hamamatsu R763P phototube (160-850 nm response) are used.

As shown in Figs. 2 and 10, the optical paths are protected from stray light by black anodized aluminum baffles. Opposite the PMT is a blackened light trap, which suppresses scattering light so that the PMT views no direct source of emission other than the fluorescing gases. It is estimated that scattered light is attenuated by $\sim 10^{12}$. For a typical species such as NO, a concentration of $\sim 1.3 \times 10^{10}$ molecules cm^{-3} can be detected in 10 seconds of counting with a signal/background = 1.

C.5. Ultraviolet absorption

Species which have moderate absorption coefficients in the UV may be detected by direct absorption of continuum radiation from a xenon arc lamp (Varian Model VIX-500 UV). The lamp has a total output of 12 W integrated from 200 to 400 nm. Although the intensity decreases rapidly below 220 nm, there is still a useful continuum from 190 to 200 nm of 1 mW/nm. As shown in Fig. 7, the light is collimated by an internal parabolic reflector, passes through the center of the detection region, and is focused by a quartz lens onto the slit of a 1 m monochromator (McPherson Model 2051). The 1200 line/mm grating is blazed at $3000 \text{ \AA}$ and gives a resolution in first order of $0.1 \text{ \AA}$ with 10 μm slits. A beam splitter deflects a portion of the lamp output onto a reference photomultiplier tube so that intensity fluctuations may be compensated by ratioing the two beams. The optical axis for the UV absorption is perpendicular to the infrared axis permitting simultaneous measurements by the two techniques. For a typical species such as BF, a number density of $\sim 2 \times 10^{11} \text{ cm}^{-3}$ can be detected with a signal-to-noise = 1 with a time constant of 10 sec. This sensitivity is largely limited by fluctuations in the arc lamp.

C.6. Chemiluminescence

Visible and ultraviolet chemiluminescence spectra are taken by imaging emission from the central region of the flow axis onto the entrance slit of the monochromator using the same optical arrangement as in Fig. 7. Spectra are recorded with the IBM 7406 Interface and Prime 400 Computer using either analog or digital data from the phototube while wavelength is scanned by a stepping motor drive.

II. OPERATION

The high temperature flow reactor has been used for several spectroscopic and kinetic studies. These studies will be summarized briefly in order to illustrate the versatility of the apparatus.

The temperature dependence of the infrared spectral absorption coefficients of the ν_3 band of BF_3 was measured over the temperature range of 298 to 1440 K.¹¹ The BF_3 was simply mixed with the carrier gas in the main flow, and the infrared absorption coefficients were measured at low spectral resolution. The BF_3 number density in the flow tube was obtained from the gas flow rates and the pressure in the analysis region.

The infrared band strength of BF was determined to be $630 \pm 200 \text{ cm}^{-2} \text{ amagat}^{-1}$ by measuring the integrated line strength of a single vibration-rotation line at high spectral resolution.¹² The BF was produced by passing a mixture of BF_3 and He carrier gas through a microwave discharge. The BF number density in the analysis region was obtained by measuring its absorption of ultraviolet radiation along a path perpendicular to the path of the reaction of the infrared radiation.

The rate constant for the reaction of $\text{OH} + \text{NH}_3$ was measured over the temperature range of 294 to 1075 K²⁶ and found to be $(5.41 \pm 0.86) \times 10^{-12} \exp(-2120 \pm 143 \text{ cal mole}^{-1}/\text{RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The OH was produced by reaction of H (generated in a microwave discharge) with NO_2 , and the NH_3 was introduced into flow downstream through the ring injector. The progress of the reaction was monitored in the analysis region by measuring the OH number

density by resonance fluorescence or by measuring the NH_2 product number density by laser induced fluorescence.

Finally, the rate constant for the reaction of $\text{NH}_2 + \text{NO}$ was measured over the temperature range of 294 to 1200 K.²⁹ A least squares fit of the experimental data yielded the expression $k(T) = (1.95 \times 10^{-4})T^{-2.46} \exp(-938/T)$ $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The NH_2 was produced by reaction of F (generated in a microwave discharge) with NH_3 , and the NO was introduced through the ring injector. In the analysis region the NH_2 reactant number density was measured by laser induced fluorescence, the OH product number density was measured by laser induced fluorescence and resonance fluorescence, and the number densities of all the species in the main flow were measured using the molecular beam mass spectrometer.

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FIGURE CAPTIONS

Figure

1. Block diagram of major apparatus components.
2. Cross sectional view of high temperature flow reactor.
A - alumina flow tube, B - water cooled vacuum jacket, C - refractory insulation, D - ring injector, E - six arm cross piece to support flow tubes, F - discharge lamp, G - microwave discharge cavity, H - quartz lens, I - flow of gas to pumps, J - optical tube perpendicular to drawing, K - mass spectrometer sampling orifice, L - optics tube purge gas (1 of 4), M - kanthal heating elements, N - multihole mullite array (heat exchanger), O - shield gas, P - carrier gas, Q - reactant gases.
3. Cross sectional view of analysis region.
4. Measured velocity profile in flow tube. Solid line is parabola normalized to data point on centerline.
5. Difference between nominal readings and measured gas temperatures.
6. Cross sectional view of molecular beam mass spectrometer.
A - nozzle-skimmer chamber, B - middle chamber, C - mass spectrometer chamber, D - sampling nozzles, E - skimmers, F - choppers, G - gate valve assembly, H - mass spectrometer, I - nylon flanges permit electrical biasing for detection of ions from coal burner.
7. Cross sectional view of analysis region with infrared absorption and ultraviolet absorption diagnostics. Elements external to vacuum jacket not shown to scale. A - vacuum jacket, B - six arm cross piece, C - white cell mirrors, D - windows, E - arc lamp, F - beam splitter, G - interference filters, H - photomultipliers, I - mirror, J - quartz lens, K - chopper, L - monochromator.
8. View of low spectral resolution infrared optics. A - source, B - chopper, C - beam splitter, D - monochromator, E - detector, M1-M9 - mirrors.
9. View of high spectral resolution infrared optics. A - tunable diode laser, B - lens, C - monochromator, D - chopper, E - detector, M1-M8 - mirrors.
10. Cross section view of analysis region with laser induced fluorescence diagnostics. A - vacuum jacket, B - six arm cross piece, C - pulsed dye laser, D - beam expander, E - mirrors, F - Brewster angle windows, G - baffle assemblies, H - photodiode, I - light trap, J - quartz lens, K - interference filter, L - photomultiplier.

Figure 1

Figure 2

I-32

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

RATE CONSTANT FOR THE REACTION $\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$ OVER A WIDE TEMPERATURE RANGE

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The rate constant for the reaction of $\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$ has been measured in a high temperature fast flow reactor over the range 294–1075 K: $k = (5.41 \pm 0.86) \times 10^{-12} \exp[-(2120 \pm 143) \text{ cal mole}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This result is compared with literature values and discussed.

1. Introduction

The role of the reaction

$$\Delta H_{298}^0 = -10.7 \pm 1.5 \text{ kcal mol}^{-1} \quad (1)$$

is of importance in understanding atmospheric [1,2] and combustion [3,4] chemistry. Although well studied near room temperature [5–10], this reaction is also important at the elevated temperatures of combustors and combustor exhaust flows. It has been proposed as the key initiation step in the removal of NO_x by ammonia addition to combustor exhaust flows [3,11].

This work represents the first direct high temperature measurement of the $\text{NH}_3 + \text{OH}$ reaction rate constant, and shows that over a large range of temperatures, it can be well represented by an Arrhenius expression.

2. Experimental

The experiments are carried out in a high temperature fast flow reactor, illustrated in fig. 1. The apparatus is described in detail elsewhere [12,13], but in brief, a 7.26 cm diameter, 120 cm long alumina tube is used. Kanthal heater elements radiatively control

the temperature from 294–1500 K. Four perpendicular alumina side arms at the tube end permit resonance lamp fluorescence detection. Provisions also exist for IR White cell absorption of IR active species, and for laser induced fluorescence detection techniques. Flow gases can be monitored by a molecular beam sampling mass spectrometer to facilitate in the identification of reaction products. Gas temperatures are obtained with shielded W–5%Re/W–26%Re thermocouples using a technique [14,15] which removes the contribution of wall radiation to the measurement.

Radicals are made with discharge flow techniques, utilizing a 2450 MHz microwave discharge source, and introduced through the inner of two coaxial alumina inlet tubes. By adding a second gas through the outer tube, new reactant species can be produced. Hydrogen atoms made in the microwave source react with NO_2 , resulting in a clean source of OH. The concentration of OH is always kept low enough to prevent secondary reactions. An alternate source of H atoms is the use of heated tungsten coil to dissociate H_2 at the inserted end of the inner tube. Both production methods gave comparable results.

A second reactant, in this case ammonia, is added through a moveable quartz injector. Helium buffer gas is added at the entrance of the flow tube through mullite multichannel arrays which preheat and laminarize the flow. The purities of gases used are: He(99.995%), H_2 (99.999%), NH_3 (99.99%), and

Fig. 1. Cross-sectional view of high temperature flow reactor: (A) 7.3 cm i.d. alumina flow tube, (B) water-cooled vacuum jacket, (C) refractory insulation, (D) moveable loop injector, (E) six-arm cross to support flow tube, (F) OH resonance lamp, (G) microwave cavity, (H) focusing lens, (I) outlet to pumps, (J) PMT perpendicular to resonance lamp, (K) mass spectrometer sampling orifice, (L) optics tube purge gas (1 of 4), (M) Kanthal heating elements, (N) multihole mullite array, (O) external gas flow, (P) main flow inlet, (Q) reactant gas inlets.

NO_2 (99.5%). The NO_2 was further purified by reaction with O_2 to remove any residual NO . Flow rates are determined using calibrated rotameters and flow speeds can be varied from $6\text{--}150\text{ m s}^{-1}$.

The OH is detected using a resonance lamp, made by flowing a stream of helium saturated in water vapor through a microwave discharge, and focusing the emission into the flow tube. Fluorescence is captured by a Hamamatsu R763P photomultiplier. A 320 nm bandpass interference filter rejects unwanted light. The photon counts are amplified and shaped by a Pacific Precision Instruments model 3262/AD4 amplifier/discriminator and fed to a Monsanto model 1505A counter-timer. Data are corrected for scattered light from the lamp and any other sources of background.

Fig. 2. Decay of OH fluorescence as a function of reaction time for fixed concentrations of ammonia at 875 K. $\text{NH}_3 = 1.50$ ($\circ$); 3.51 ($\times$), 6.27 ($\triangle$), 9.53 ($\square$) and 13.4 (∇); units of $10^{13}\text{ molecules cm}^{-3}$.

3. Results

Hydroxyl decay is measured as a function of the injector position for a fixed NH_3 concentration with $[\text{NH}_3] \gg [\text{OH}]$ to ensure pseudo-first order kinetics. Some representative data are shown in fig. 2 for 875 K. Rate constants (k^I) for each measurement are obtained by a least squares fit to the slope of $-\ln(\text{signal})$ versus reaction time.

Removal rates of OH by the uncoated alumina tube wall are measured by varying the OH residence time at fixed pressure. This is done during each run and the observed k_w are shown in fig. 3. These values, along with estimated diffusion coefficients [16][‡] for OH in He, are used to correct for the effects of wall removal and axial and radial diffusion on the observed rates. This is most accurately accomplished using the procedure outlined by Brown [17]. The corrections are small, ranging from 15–36%. The corrected first order rate coefficients, k_{corr}^I , are listed along with the measured k_w in table 1. A least squares fit to k_{corr}^I versus $[\text{NH}_3]$ results in $k_{\text{NH}_3+\text{OH}}(T)$. A few of these curves are illustrated in fig. 4. The overall accuracy of the rate constants is estimated ($\pm 1\sigma$) at 20%.

[‡] The diffusion coefficient of OH in He is assumed to be equivalent to that of O in He.

Fig. 3. Temperature dependence of the measured OH wall removal rate.

4. Discussion

The temperature dependence of the measured rate constants can be represented by the Arrhenius expression, $k(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = A \exp(-E/RT)$, as shown in fig. 5. Also included are the data of Perry et al. [5] and Smith and Zellner [7,8], which are the most recent measurements over a range of temperatures.

A non-linear least squares fit to our present data results in values ($\pm 1\sigma$) for the pre-exponential factor $A = (5.41 \pm 0.86) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an activation energy of $E = 2120 \pm 143 \text{ cal mol}^{-1}$. This is indicated by the solid line in fig. 5.

A comparison of the present results with selected literature values is shown in table 2. Our room temperature value is in excellent agreement with recent work. In general, they tend to exhibit a slightly lower A factor than our high temperature results. The implication is that the temperature dependence has a slight upward curvature, as would be expected from transition state theory for this simple hydrogen atom extraction, and as recently observed for a series of reactions of OH with substituted alkanes [19]. Due to the nature of our apparatus it is difficult to accurately maintain a temperature below $\approx 500 \text{ K}$ (other than room temperature), thus in the present work measurements to determine the curvature directly

Fig. 4. Dependence of pseudo-first order rate constant on NH_3 concentration at various temperatures.

Table 1
Experimental rate data

T (K)	P (Torr)	v (cm/s)	k_w (s ⁻¹)	[NH ₃] (cm ⁻³)	k_{corr}^I (s ⁻¹)	$k_{\text{NH}_3+\text{OH}}$ (cm ³ molecule ⁻¹ s ⁻¹)
294	1.20	895	54.8	1.42(14)	40.4	$(1.42 \pm 0.28) \times 10^{-13}$
294	1.20	895	54.8	2.32(14)	61.9	
294	1.20	895	54.8	3.94(14)	78.9	
294	1.38	916	54.8	1.45(14)	58.6	
294	1.38	916	54.8	2.73(14)	94.2	
294	1.42	873	54.8	3.50(13)	26.6	$(1.45 \pm 0.29) \times 10^{-13}$
294	1.42	873	54.8	1.09(14)	41.2	
294	1.42	873	54.8	1.86(14)	48.5	
294	1.42	873	54.8	2.90(14)	72.8	
294	1.42	873	54.8	4.20(14)	80.5	
575	1.38	1790	45.9	5.08(13)	64.7	$(8.67 \pm 1.73) \times 10^{-13}$
575	1.38	1790	45.9	9.25(13)	99.7	
575	1.38	1790	45.9	1.65(14)	169.4	
575	1.38	1790	45.9	2.48(14)	233.9	
575	1.38	1790	45.9	1.26(14)	130.0	
775	1.43	2390	63.4	2.18(13)	53.5	$(1.43 \pm 0.28) \times 10^{-12}$
775	1.43	2390	63.4	4.62(13)	85.4	
775	1.43	2390	63.4	9.52(13)	157.2	
775	1.43	2390	63.4	1.52(14)	239.7	
775	1.43	2390	63.4	6.94(13)	120.6	
875	1.45	2590	75.7	1.50(13)	33.9	$(1.37 \pm 0.27) \times 10^{-12}$
875	1.45	2590	75.7	3.51(13)	60.4	
875	1.45	2590	75.7	6.27(13)	119.0	
875	1.45	2590	75.7	9.53(13)	154.7	
875	1.45	2590	75.7	1.34(14)	193.7	
975	1.39	3340	80.5	1.36(13)	43.2	$(2.39 \pm 0.47) \times 10^{-12}$
975	1.39	3340	80.5	2.73(13)	66.2	
975	1.39	3340	80.5	4.28(13)	99.6	
975	1.39	3340	80.5	7.05(13)	158.9	
975	1.39	3340	80.5	1.10(14)	273.0	
1075	1.62	3450	121.5	2.41(13)	59.3	$(1.93 \pm 0.36) \times 10^{-12}$
1075	1.62	3450	121.5	4.30(13)	104.5	
1075	1.62	3450	121.5	6.60(13)	162.3	
1075	1.62	3450	121.5	9.05(13)	192.0	
1075	1.62	3450	121.5	1.16(14)	240.2	

Table 2
Comparison of experimental rate determinations for NH₃ + OH with selected literature values

Room temperature rate constant (cm ³ molecule ⁻¹ s ⁻¹)	A (cm ³ molecule ⁻¹ s ⁻¹)	E (cal/mole)	Temperature range (K)	Method	Ref.
2.42×10^{-13}	$(5.3 \pm 0.8) \times 10^{-12}$	1830	298–669	flow reactor	[9]
$(2.7 \pm 0.3) \times 10^{-13}$	1.1×10^{-12}	870 ± 80	298–365	pulsed radiolysis	[10]
$(1.5 \pm 0.4) \times 10^{-13}$	—	—	298	flash photolysis	[6]
1.58×10^{-13}	2.3×10^{-12}	1600	228–472	flash photolysis	[7,8]
$(1.64 \pm 0.16) \times 10^{-13}$	2.93×10^{-12}	1710 ± 300	297–427	flash photolysis	[5]
$(1.44 \pm 0.29) \times 10^{-13}$	$(5.41 \pm 0.86) \times 10^{-12}$	2120 ± 143	294–1075	flow reactor	present work

Fig. 5. Temperature dependence of measured rate constants for $\text{NH}_3 + \text{OH}$ reaction.

could not be performed. Fitting all the points in fig. 5 to $k = AT^n \exp(-E/RT)$ was statistically unwarranted; thus any deviation from Arrhenius behavior is small. The conclusion can be drawn that the Arrhenius parameters extracted from the experiments below 500 K are indeed valid to temperatures above 1000 K, in the region of interest to many combustion and exhaust cleanup studies.

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