ARI-RP-49

FIFTH QUARTERLY TECHNICAL SUMMARY REPORT ON THE HOMOGENEOUS PRODUCTION AND REMOVAL OF NO_x FROM COMBUSTION EXHAUST GASES

By

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ABSTRACT

The rate constant for the reaction of NH_2+NO has been measured over the temperature range of 294-1200°K. It exhibits a decrease in value with increasing temperatures. An upper limit to the rate of reaction of NH_3+NO$\rightarrow$$NH_2$+HNO is also reported. The hydroxyl radical has been identified as one of the products of the NH_2+NO reaction, and the implications of this upon the modeling is discussed.

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1. INTRODUCTION

The production and removal of NO_x and other combustion products during fossil fuel combustion is a serious environmental problem for both stationary and mobile combustion driven energy systems. Since stationary systems are faced with increased utilization of coal, synthetic fuel oils derived from coal, or oil shale, and since all of these fuels have significant levels of fuel-bound nitrogen, NO_x formation may become acute.

Recent studies of the production of NO_x due to oxidation of fuel nitrogen strongly indicate that a critical role is played by the interaction of NH_x (x = 1,2,3) species with NO, O, OH and H. Studies have also shown that these reactions play a vital role in the efficient homogeneous removal of NO_x from combustion exhaust streams upon the addition of NH_3.

The work in progress has three basic objectives. The first objective is to determine rate constants for several of the basic chemical reactions which govern the formation of NO_x in the combustion of fuel-bound nitrogen and which also play a key role in the thermal deNO_x process. The specific reactions to be studied include the reaction of NH_3, NH_2 and NH with NO (Task 1), and the reactions of NH_3, NH_2, and NH with the combustion radicals O, OH, and H (Task 2). This report focuses on the measurement of reaction rates for NH_2 + NO and NH_3 + NO over the temperature range of 294-1200°K.

The second objective is to utilize the kinetic data obtained in Task 1 and Task 2 to identify the key NO_x radical scavenging species. Once the key NH_x radical(s) has been identified, gas additives other than NH_3 which can efficiently produce this NO_x scavenger will be evaluated under combustor exhaust flow conditions. This work may allow a major improvement in the efficiency of the homogeneous NO_x scavenger concept (Task 3).

The third objective is to evaluate the impact of the kinetic and mechanistic data gathered in Tasks 1,2, and 3 on the design of coal and synthoil combustors and on the implementation of homogeneous NO_x exhaust scavenging schemes. This will be accomplished by modeling the processes in the combustion stream (Task 4). This modeling will utilize existing computer codes, including Aerodyne's PACKAGE code. This modeling will allow assessment of the impact of the measured chemical parameters on exhaust NO_x content. The results of this computer modeling will be translated into conceptual designs for pilot scale experiments which demonstrate achievable impacts on exhaust NO_x content (Task 5).

2. TECHNICAL SUMMARY PROGRESS REPORT

A summary of progress achived during the last quarter is presented below. A time-phasing schedule for each key subtask is shown in Fig. 2.1.

Task 1: Measurement of NH_x + NO Rate Constants

The rate measurements for the reactions of NH_2 + NO$\longrightarrow$products and of NH_3 + NO$\longrightarrow$$NH_2$ + HNO have beem completed over the temperature range of 294-1200°K. The NH_2 reaction rate decreases substantially as the temperature is raised. Reaction of NO with NH_3 is extremely slow and probably plays no role in the NO_x system kinetics. The identification of OH as a reaction product of NH_2 + NO is of great importance in determining the correct kinetic scheme and is discussed in Section 3.

Task 2: Rate Data for NH_x Oxidation

Work on this task has begun. A resonance lamp and fluorescence detector capable of monitoring H and O atoms has been built. As demonstrated in Task 1, we can detect OH using laser-induced fluorescence. After a short period of testing, we will begin rate measurements of O, H, and OH with NH_x.

Task 3: Assessment of Rate Data To Determine Key NO Scavenger Species

We have begun an assessment of the published experimental reaction rates and kinetic models relevant to the homogeneous chemistry of NO_x in combustor exhaust streams. The impact of our experimental results on proposed models is detailed in the techncial discussion.

Subtasks

1.1 DEMONSTRATION OF APPARATUS CALIBRATION AND DETECTION EFFICIENCY

1.2 MEASUREMENT OF NH_x + NO RATES

3.1 ASSESSMENT OF RATE DATA TO DETERMINE KEY NO SCAVENGER SPECIES

2.1 RATE DATA FOR NH_x OXIDATION

4.1 CHEMICAL MODEL FOR NO CHEMISTRY

4.2 ASSESSMENT OF MEASURED RATE DATA FOR NO_x PRODUCTION AND SCAVENGING

3.2 TEST OF NO_x SCAVENGER CANDIDATES

5.1 CONCEPTUAL DESIGN FOR PILOT SCALE NO_x SCAVENGING TESTS

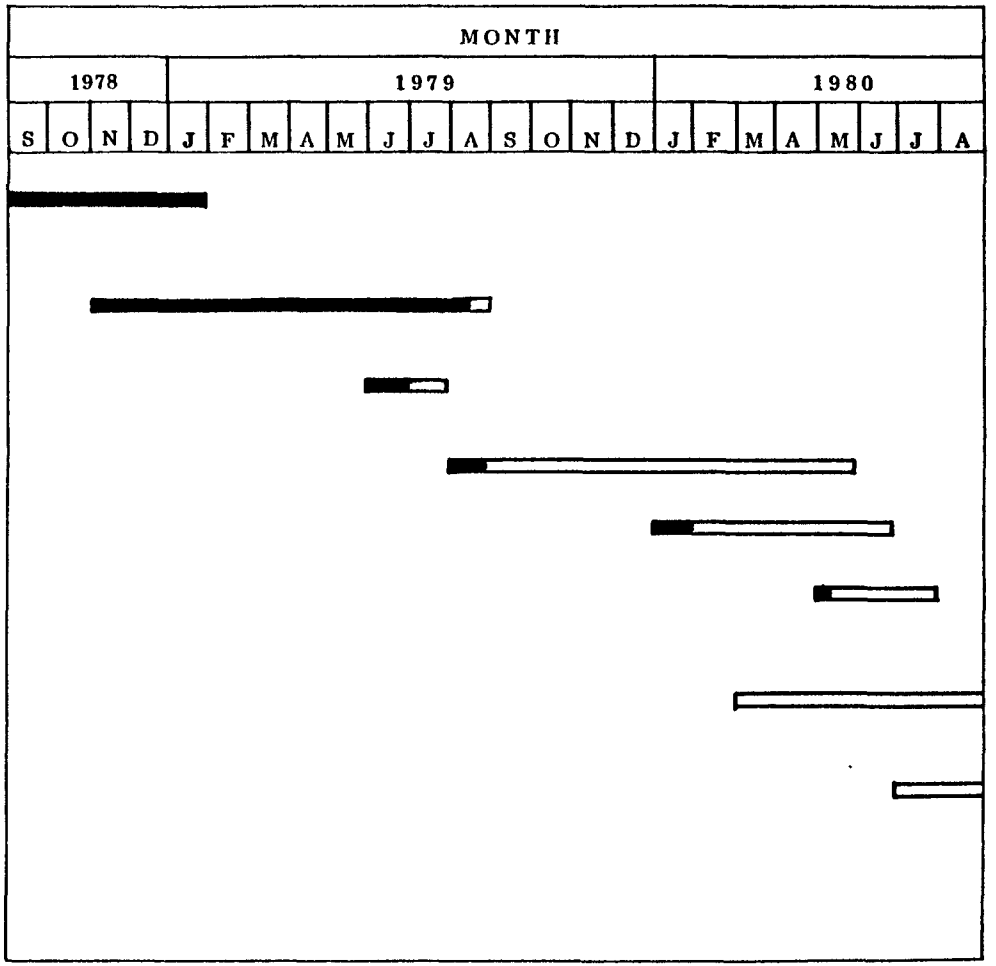

Figure 2.1 - Contract Subtask Schedule

3. NH_x/NO RATE MEASUREMENTS

3.1 Task Goals and Milestones

The goals of this task are to: (1) demonstrate the efficient production of NH and NH_2 in the flow reactor using discharge flow techniques; (2) demonstrate the efficient detection of NH and NH_2 in the flow reactor using laser-induced resonance fluorescence; (3) equip the flow reactor with calibrated gas handling equipment to introduce NO, NH_x and carrier gases; (4) demonstrate the use of the molecular beam mass spectrometer coupled to the flow reactor to detect NO, NH_3 and other flow gases; and (5) utilize each of the subsystems to measure the rate of reaction of NO with NH, NH_2, and NH_3 from room temperature to combustion temperatures.

The first three goals previously had been completed. In this last quarter, substantial progress has been made on the fifth and most important item, the rate measurements. The use of the mass spectrometer to identify reaction products will be done next month when the installation of an upgraded system will be completed.

3.2 Technical Discussion

3.2.1 Rate Measurements for the NH_2 + NO Reaction

Using the high temperature flow reactor which was described in previous reports,[1-4] the rate constant for the reaction,

$$NH_2 + NO \longrightarrow \text{Products} \quad , \qquad (1)$$

has been measured over the temperature range of 294-1200°K.

These measurements were made in two ways:

1) By fixing the concentration of NO and varying the distance from the detector to the reactant mixing region, and
2) By varying the NO concentration at a fixed place of injection into the gas stream.

In all cases, NH_2 was produced by the reaction,

$$NH_3 + F \longrightarrow NH_2 + HF \quad . \qquad (2)$$

The fluorine atoms are produced from F_2 entrained in a stream of excess helium, which flows through a microwave discharge (2450 MHZ, 90 Watts). At the highest temperatures, the microwave was not used because thermal dissociation of F_2 in the inlet tube produced sufficient atom concentrations. The experiments were run under pseudo-first order conditions, with NO always in excess. The carrier gas was helium, which insured that radial diffusion would be rapid. Typical operating parameters are shown in Table I.

TABLE 1 - TYPICAL OPERATING PARAMETERS

Temperature (^oK)	294-1200
Total Flow He (scc/s)	80-200
Mean Velocity (m/s)	29-70
Pressure (Torr)	1-3
Reynolds Number	27-5
Distance from Loop Injector to Detection Region (cm)	10-50
Diameter of Flowtube (cm)	7.26
Distance from NH_2 Source to Detection Region (cm)	75

To obtain the true rate constant, the effects of diffusion (radial and axial) and wall removal on the measured rate must be determined. Brown [5] has described a procedure which corrects for these effects within the ranges of diffusion and wall removal normally encountered in flow reactors. We have employed his program using NH_2 wall removal rates which were measured at each temperature during the course of the experiments. Although the high temperature values are only accurate to ~50%, this uncertainty is reflected in the corrected rate constant as a 10% error. The values for wall removal ranged from 120 s^{-1} at room temperature to 300 s^{-1} at 1200°K. This is equivalent to a γ (fraction of collisons with walls that lead to removal) of 0.008 - 0.010, which is reasonable for an untreated alumina surface.

Samples of the decay curves are illustrated in Figures 3.1 and 3.2. At very large concentrations of NO and longer reaction times, the curves exhibit a tendency to level off. This is due to a secondary reaction which forms NH_2, most probably

$$NH_3 + OH \longrightarrow NH_2 + H_2O \quad . \qquad (3)$$

Conditions were maintained to minimize this reaction by keeping the NH_3 concentration as low as possible, yet still in excess over fluorine.

The averaged reaction rates for NH_2 + NO are listed in Table II and plotted in Figure 3.3, which also displays the results of Hack [6] and Lesclaux [7]. It is clear that the reaction rate decreases with increasing temperature. Our results extend the measurements into the temperature range of interest for gas stream cleanup, and indicate that the rate above 1000°K may decrease even faster than low temperature extrapolations had indicated. This decrease has been postulated as the key reaction in determining the sharp temperature dependence of the thermal deNOX process.

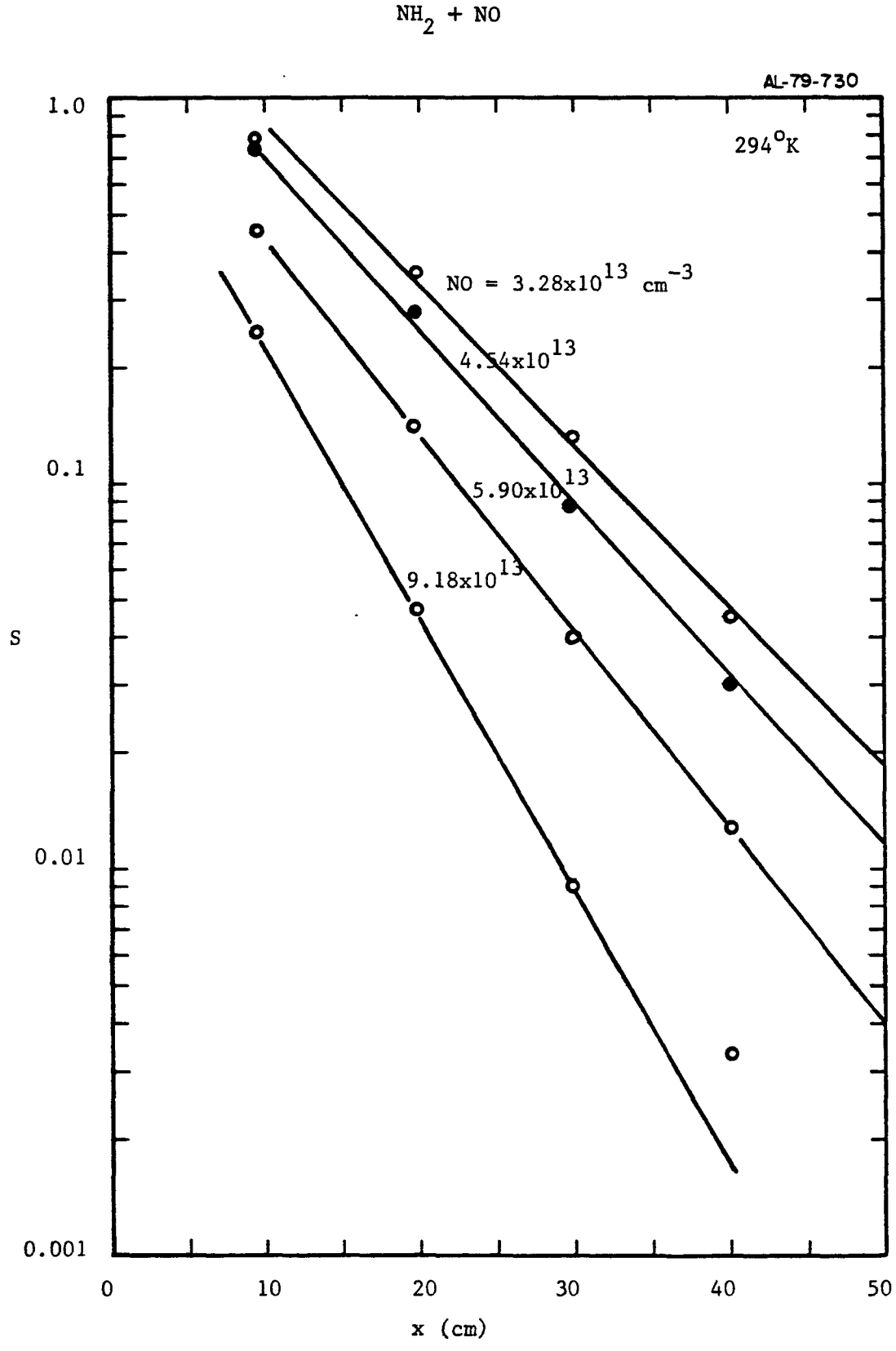

Figure 3.1 Typical Decay Rates for Fixed NO Concentrations.

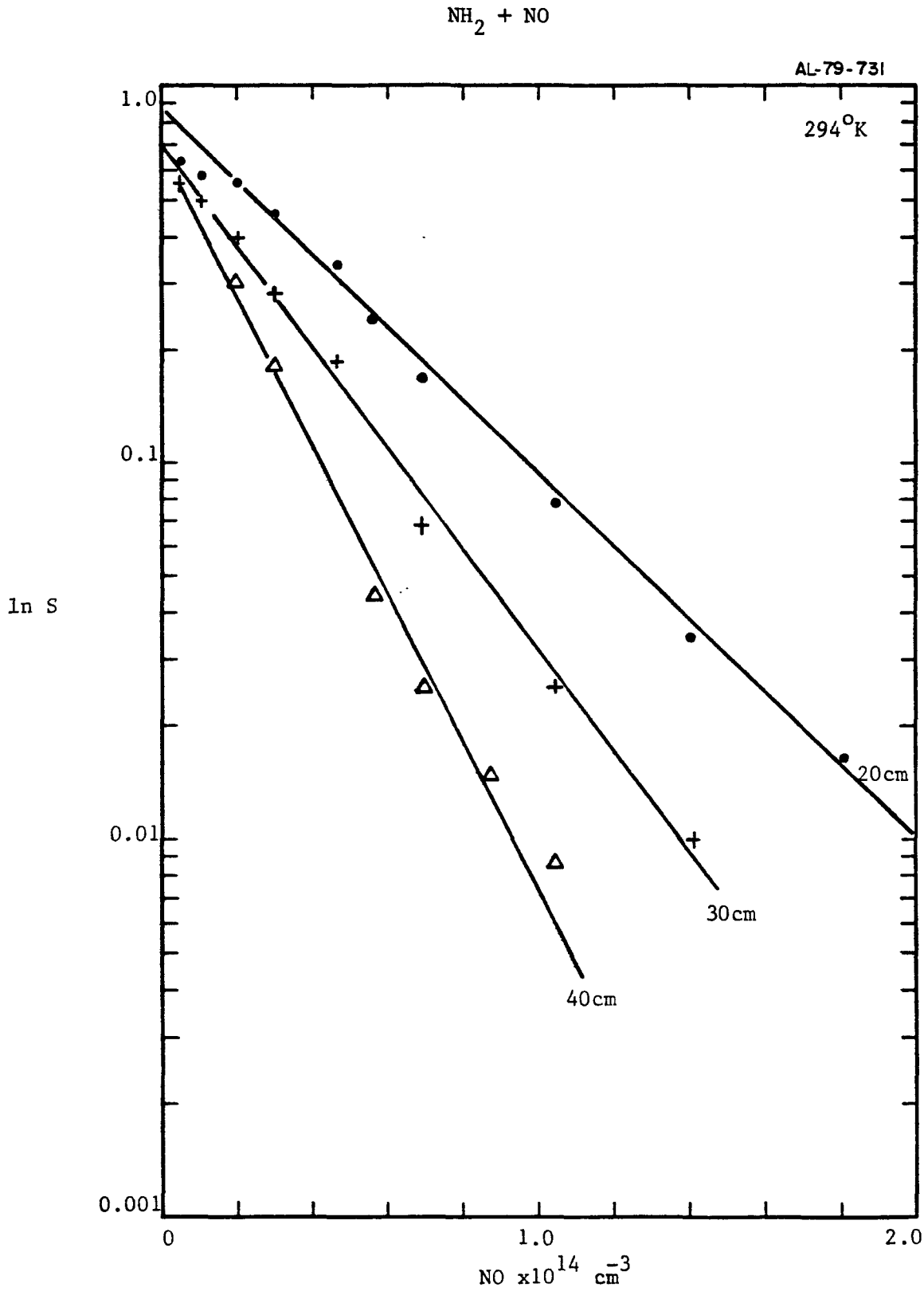

Figure 3.2 Typical Decay Rates for Fixed Injector Position.

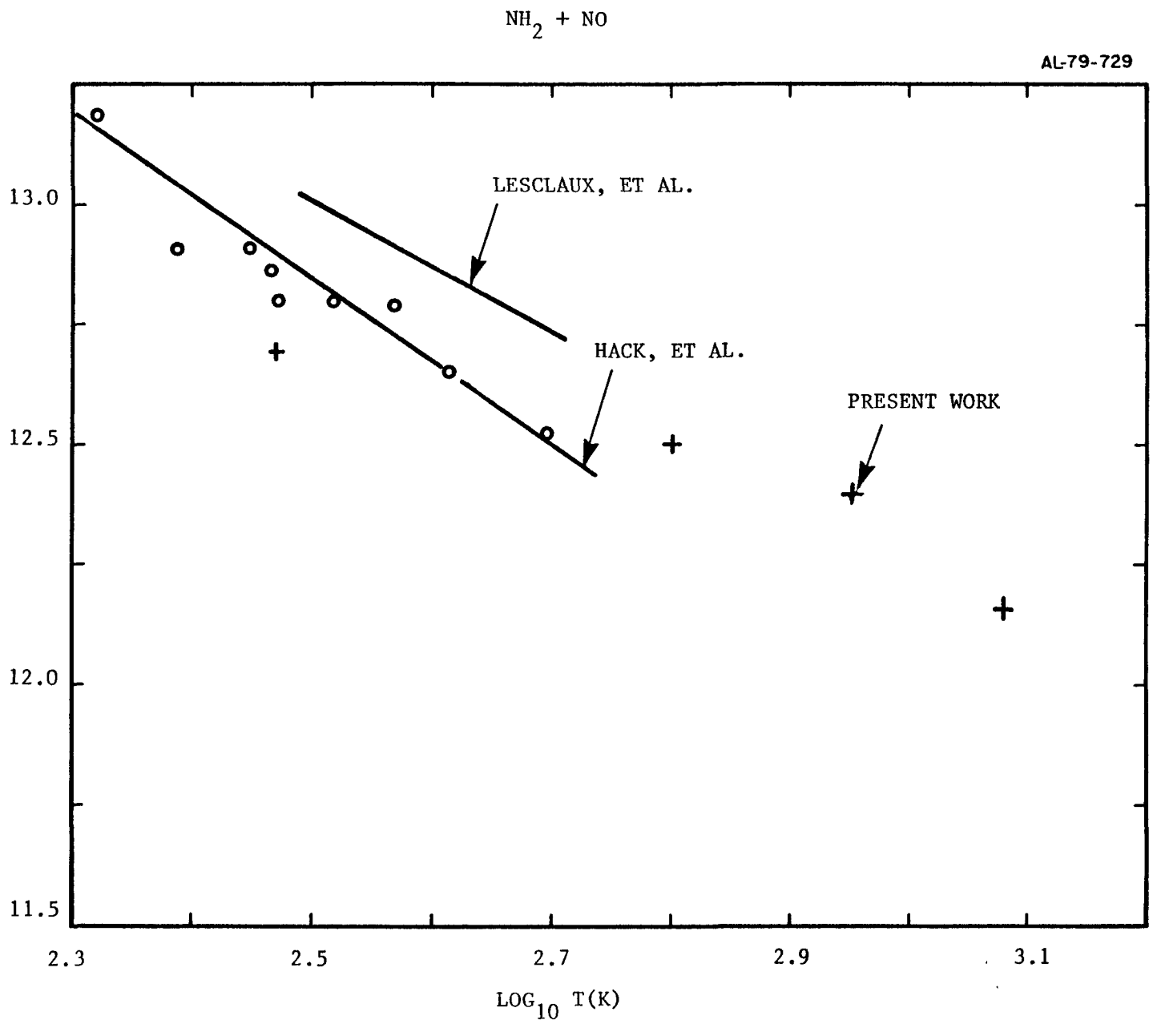

Figure 3.3 Temperature Dependence of Measured Rates.

TABLE 2 - REACTION RATE CONSTANT FOR NH_2 + NO	
T (K)	k (cm^3/molecule s)
294	$8.2 \pm 1.6 \times 10^{-12}$
625	$5.3 \pm 1.6 \times 10^{-12}$
900	$4.1 \pm 0.8 \times 10^{-12}$
1200	$2.4 \pm 0.5 \times 10^{-12}$

3.2.2 Reaction Products of the NH_2 + NO Reaction

In order to fully comprehend the detailed NO_x chemistry, key reaction products must be identified. This allows the determination of possible chain propagating and termination steps. Branch, et al[8] have reviewed the possible set of products from NH_2 + NO and suggest the most likely ones as N_2H + OH. Their NO_x removal mechanism would be :

$$NH_3 + OH \longrightarrow NH_2 + H_2O \quad ; \qquad (3)$$

$$NH_2 + NO \longrightarrow N_2H + OH \quad ; \qquad (4)$$

$$N_2H + NO \longrightarrow N_2 + HNO \quad ; \qquad (5)$$

$$HNO + M \longrightarrow H + NO + M \quad . \qquad (6)$$

Hydroxyl initially present would react with ammonia to form NH_2, which reacts with NO. In Branch's scheme, the N_2H subsequently forms N_2 + HNO. Collisional dissociation of the HNO results in an overall reaction mechanism which removes an NO molecule, and produces OH and H radicals. These both attack NH_3 and propagate the chain. Reaction (4) requires that OH be a product. Previously, no products of this reaction have been identified.

Using laser induced fluorescence, we measured a large signal of OH produced in the room temperature reaction of NH_2 + NO. The signal was dependent on NH_2 (F and NH_3 flow rates) as well as NO. As NH_3 was increased,

the OH began to decrease (reaction 3). This is the step which caused the curvature in some of our rate measurements. Although the indentification of OH as a reaction product is significant, the relative amount of branching to N_2H + OH products is not yet known. However, a crude estimation of the OH concentration, coupled with the measured rate constant, indicates that these products are a major channel. We are in the process of setting up an experiment to better quantify the importance of this channel.

3.2.3 Reaction of NH_3 + NO

The rate constant for the reaction,

$$NH_3 + NO \longrightarrow NH_2 + HNO \quad , \qquad (7)$$

was measured over the temperature range of 294-1200°K. At all temperatures, a very small signal was observed at the sensitivity limit of the apparatus. From reactant flow rates and a crudely measured sensitivity to NH_2 number density, it is concluded that $k_7 \leq 1 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. Therefore, it is improbable that this reaction has any importance on the homogeneous production on removal of NO_x in exhaust gas streams.

3.3 Work Forecast

During the next quarter we will measure the NH + NO reaction rate and continue the oxidation reaction studies. Efforts to model the NO_x chemistry will begin.

4. REFERENCES

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