ARI-RP-64

SECOND QUARTERLY TECHNICAL SUMMARY REPORT ON THE HOMOGENEOUS PRODUCTION AND REMOVAL OF NO_x FROM COMBUSTION EXHAUST FLOWS

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Prepared Under DOE Contract No. DE-AC21-80MC14737

Period Covered: November 1, 1980 to January 31, 1981

Submitted to:

The Office of Coal Utilization
U.S. Department of Energy

February 1981

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ABSTRACT

The addition of ammonia to the exhaust stream of stationary combustors is a promising approach toward reducing NO_x emissions. The use of high sulfur-content fuels will produce moderate quantities of SO_2 and other sulfur-bearing compounds which may affect the effectiveness of this thermal deNO_x process. Initial modeling efforts indicate that the presence of SO_2 is slightly beneficial in removing NO near 1250K. In addition, experiments show that the ammonia species (NH_i, $i=1,2,3$) do not directly form NO upon reaction with SO_2. Other products of these reactions are currently being measured.

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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 driven energy systems. Since stationary systems are faced with increased utilization of coal, oil shale, or synthetic fuel oils, all of which 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 indicate that a critical role is played by the interaction of NH_i (i=1,2,3) species with NO, O_2, OH, and H. Furthermore, these reactions play a vital role in the homogeneous removal of NO_x from combustion exhaust streams upon addition of NH_3 or NH_3-like compounds. Over the past two years, there has been an increased understanding of the chemistry of the NH_i/NO_x system at combustor exhaust temperatures. For an ammonia addition system to be effective in reducing NO_x emissions, it must work successfully in the presence of a variety of sulfur-bearing compounds present in the products of combusted coal and oil shale.

The work in progress has three major objectives. The first objective is to determine whether the reactions of SO_2 (the predominant sulfur-bearing compound present) + NH_i (i=1,2,3) directly produce NO_x in the temperature range of 300 - 1500 K (Task 1). As these reactions are of key importance, all other products of these reactions will also be identified (Task 2). Depending on the products and value of these rate constants, the effectiveness of NO removal by NH_3 could be dramatically affected.

The second objective is to screen and evaluate various sulfur-containing scavenger precursors such as SO, SO_2, HS, and H_2S to assess their impact on the NH_i/NO_x chemical system (Task 3). This will involve an evaluation of published experimental and theoretical rates for all pertinent reactions. For those key reactions where the data is either insufficient or nonexistant, the detailed rate constants will be measured using the High Temperature Fast Flow Reactor (HTFFR) facility at ARI (Task 4).

The third objective involves the evaluation and impact of the kinetic data on the effectiveness of NO removal by ammonia addition in the presence of sulfur-bearing compounds at combustor exhaust gas temperatures. This will be accomplished by modeling the process using Aerodyne's PACKAGE code (Task 5). This will allow a complete evaluation of the combined $NH_i/SO_x/NO_x$ chemical system on the abatement of NO emissions.

2. TECHNICAL SUMMARY PROGRESS REPORT

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

Task 1: Measurement of Global NO Formation Rate Constants

The purpose of this task is to measure the global rate constant for the formation of NO from the reactions of NH_i (i=1,2,3) with SO_2 over the temperature range 300 - 1500 K. Utilizing laser-induced fluorescence for the detection of NO, upper limits to global nitric oxide formation rate constants for these reactions were determined at 300 and 1200 K. In both cases, the rate coefficients are extremely small and indicate that these reactions are an insignificant source of NO.

Task 2: Identification of Other Products From the Reactions of $NH_i + SO_2$

Since virtually no nitric oxide was observed from the reactions of NH_i(i=1,2,3) + SO_2, the molecular beam sampling mass spectrometer was used to determine if reactions do occur and what their products might be. The mass spectrometer has been calibrated, species cracking patterns determined, and the product analysis studies are currently underway.

Task 3: Screen and Evaluate Key Sulfur-Containing Species and Reactions

The initial review of existing experimental and theoretical compilations for pertinent sulfur reactions was completed during the first quarter.(1) As new information becomes available, the reaction set is revised. This set of reactions forms the basis for modeling of the $NH_i/NO_x/SO_x$ system in Task 5.

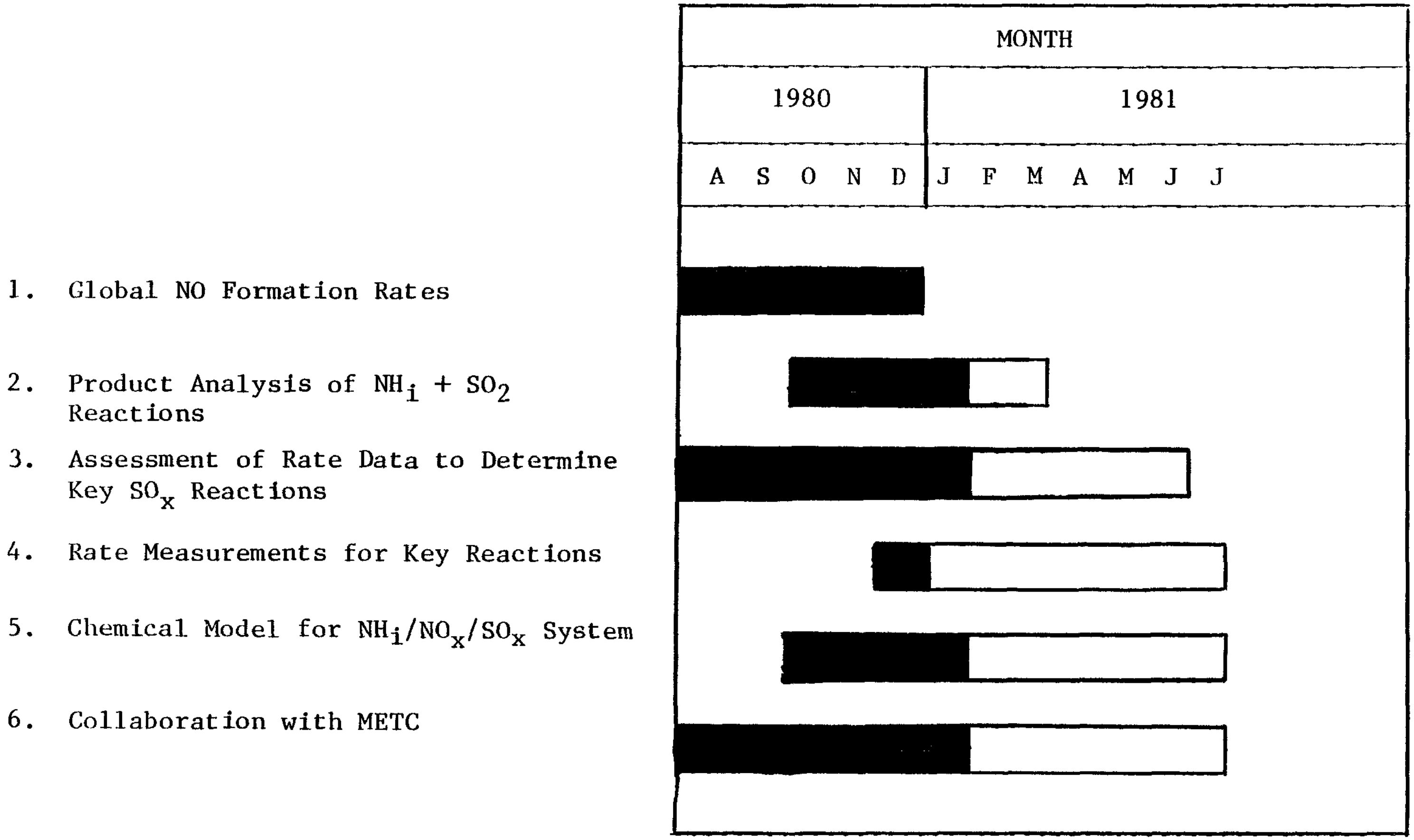

Figure 2.1 Contract Task Schedule

Task 4: Rate Constants for Key Reactions

From the evaluation of the reaction set in Task 3, it is clear that reactions of SO_x with a variety of other species may be of importance. Sources for SO have been designed and the required apparatus for detecting SO and SO_2 by laser induced fluorescence have been assembled.

Task 5: Computer Model for $NH_i/NO_x/SO_x$ Chemistry

Using the existing rate set for NH_i/NO_x and the information gathered on sulfur-compound reactions, some initial runs were made to test the sensitivity of the NH_i/NO_x chemistry to the presence of sulfur oxides. The results provide insight as to how the presence of SO_2 might affect the production or removal of NO by NH_3, and are presented in the technical discussion.

3. GLOBAL FORMATION RATES OF NO

3.1 Task Goals and Milestones

The goals of this task are to provide global rate constants for the formation of NO from the following reactions over the temperature range of 300 - 1500 K.

$$NH_3 + SO_2 \tag{3.1}$$

$$NH_2 + SO_2 \tag{3.2}$$

$$NH + SO_2 \tag{3.3}$$

The NO is detected using laser-induced fluorescence. At the sensitivity limit of the experiment, the NO signal is barely above the noise. Using calibrations described below, the rate coefficients of reactions 3.1 - 3.3 have been determined.

3.2 Technical Discussion

Using the Aerodyne High Temperature Fast Flow Reactor,(2) the global formation rate for NO has been determined for reactions 3.1 - 3.3, using laser induced fluorescence detection. The output of a N_2-pumped, tuneable dye laser (Molectron DL14P) is frequency doubled to produce 5 μJ pulses at 227.1 nm, which excites the $X^2\pi(v''=0) \rightarrow A^2\Sigma_1(v'=0)$ electronic transition of NO. Fluorescence is captured by a Hammamatsu R763P photomultiplier which integrates the signal and transmits it through a peak detector to the computer.

The detection electronics and details concerning the flow tube have been described elsewhere(2,3) and will not be discussed here. An interference filter (λ_o = 239.0 nm, FWHM = 23.5 nm) is used to discriminate against unwanted background light from the microwave source and radiating flow tube.

Commercial gases are used without further purification (NO = 99.0%, Matheson; NH_3 = 99.99%, Matheson; F_2 = 98.0%, Northeast Cryogenics; SO_2 = 99.98%, Linde; He = 99.995%, Matheson). All flows are measured using calibrated Matheson rotameters and the flow tube temperature has been previously calibrated.(2) During each experiment, the system is calibrated using a known amount of NO, diluted in helium. Under typical conditions, an NO concentration of 6.5×10^9 molecules cm^{-3} can be detected in 100 pulses with a S/N = 1.

NH_2 and NH are produced by reacting ammonia with fluorine atoms, which are made in a microwave discharge of F_2 in He. With NH_3 in excess, NH_2 + HF are the sole products. With fluorine in excess, NH is expected to be the major product, although we are not able to quantify this. Detection of NH using laser-induced fluorescence proved to be unsuccessful. However, the observed levels of chemiluminescence from NH implies its formation in moderate ($> 10^{11}$ cm^{-3}) concentrations.

From previous mass spectra, it was determined that the F_2 is completely dissociated, so that the initial concentration of NH_2 can be obtained. The concentrations of stable NH_3 and SO_2 are easily determined. By keeping $[SO_2]$ in excess, the reaction rate can be written in pseudo-first order form and integrated

$$NH_i + SO_2 \xrightarrow{k_i} NO + \text{other products} \tag{3.1}$$

$$\frac{\partial[NO]}{\partial t} = -\frac{\partial[NH_i]}{\partial t} = k_i[NH_i][SO_2] \qquad [SO_2] \sim \text{constant} \tag{3.2}$$

$$[NO] = [NH_i]_o \left(1 - e^{-[SO_2]_o k_i t}\right) \tag{3.3}$$

At 300 and 1200 K, the NO concentrations are measured under pseudo-first order conditions with reaction times of 49 and 17 ms, respectively. At 300 K, $[NO] < 2.3 \times 10^{10}$ cm^{-3} and $< 1.1 \times 10^{11}$ at 1200 K. Although the detection sensitivity to $[NO]$ is much better than these values, they are limited by the size of the statistical error caused by a moderate background fluorescence caused by the predissociation of SO_2,(21) which could not entirely be eliminated. Using the calculated NH_i initial concentrations, we find that the global formation rates of NO from the reaction of NH, NH_2, and NH_3 with SO_2 and the associated rate constants to be small (Table 1).

Included in these calculations are the effect on NO from secondary reactions ($NO + NH_i \rightarrow$ products). Using rate constants from Reference 10, the inclusion of secondary reactions affects only the $NH_2 + SO_2$ reaction, raising the maximum value of k by a factor of 4 at 1200 K, and by 35 at 300 K. However, these rate constants are still extremely small. Since it was not possible to quantify the initial $[NH]$ concentrations, the rate constants presented are conservative estimates. However, the real values are probably much smaller than presented. It is clear from these results that these reactions do not directly produce any significant amounts of NO in the range of temperatures important to combustor exhaust flows. Whether or not these reactions from other products is discussed in Section 4 of this report.

Table 1 - Global Rate Constants for $NH_i + SO_2 \rightarrow NO +$ Products

k in units of cm^3 $molecule^{-1}s^{-1}$

REACTANTS	TEMPERATURE	
	294 K	1200 K
$NH_3 + SO_2$	$< 3.9 \times 10^{-18}$	$< 4.8 \times 10^{-16}$
$NH_2 + SO_2$	$< 3.5 \times 10^{-16}$	$< 5.0 \times 10^{-15}$
$NH + SO_2$	$< 1 \times 10^{-16}$ (est.)	$< 1 \times 10^{-14}$ (est.)

4. IDENTIFICATION OF NH_I + SO_2 REACTION PRODUCTS

4.1 Task Goals and Milestones

Because the reactions of sulfur dioxide with NH_i(i=1,2,3) would directly affect the efficiency of NO reduction, it is important to identify the products of any such reactions. The direct NO formation rates are handled in Task I (Section 3 of this report). This task involves the identification and branching ratios to other products. Using a molecular beam sampling mass spectrometer, all major products of these reactions will be identified.

4.2 Mass Spectrometer Description

The mass spectrometer has been described elsewhere,(2,4) but in brief, gases from the flow tube are sampled through a 0.076 cm diameter nozzle into the first of three differentially pumped chambers. This molecular beam is skimmed and enters the ionizer of an Extranuclear quadrupole mass spectrometer. The sensitivity of this configuration permits detection of species concentration on the order of 1 ppm.

The gas compositions and flow rates are similar to those described in Section 3, with long reaction times used to allow slow reactions to reach completion. Other spectra are taken using shorter reaction times, in case the rates for production of a species happens to be faster. Thus, any major product channels in the temperature range 300 - 1200 K can be identified.

4.3 Present Status and Work Forecast

At this time, the preliminary calibrations of the mass spectrometer have been completed. Cracking patterns for all stable species involved have been measured and the product identification experiments have begun. Within a short time, the product channels will be identified and their ratios measured if these channels prove important.

5. SULFUR-BEARING SPECIES RATE COMPILATION

5.1 Task Goals and Milestones

The goals of this task are to evaluate the reactions and species which may be important in the reduction of NO emissions in combustor exhaust gases containing sulfur-bearing compounds such as COS and SO_2. In the first quarter, the comprehensive search and compilation of measured and theoretical reaction rates of sulfur species was completed. During this quarter, the rates were evaluated and a subset chosen for use in the initial computer model calculations.

5.2 Rate Compilation

Using computer searches as well as recent reviews, a list of reaction rates was compiled. These reactions involve the species S, S_2, HS, H_2S, CS, CS_2, COS, NS, HSO, HSO_2, H_2SO_4, SO, SO_2, S_2O, and SO_3. This list was presented in the First Quarterly Report.(1) In this quarter, the rates were critically evaluated and the most appropriate values for each reaction were selected. The rate coefficients, for the most part, are those listed in the First Quarterly. From this set of 88 reactions, 15 were chosen as having the greatest potential to affect the NH_i/NO_x chemistry. The criteria used in selecting these particular reactions are that they involve SO_2 (the chief sulfur bearing species in combustor exhaust streams) or have fast reaction rates with the important NH_i/NO_x species. These are presented in Table 2.

5.3 Work Forecast

As new rate information becomes available, it will be added to the list of reactions, which is periodically reviewed as the experimental and modeling efforts in this program and elucidate the importance of various species and reactions in abating NO emissions.

Table 2 - Sulfur Reactions Used in Initial Modeling Effort for $NH_i/NO_x/SO_x$ Chemical System

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

REACTION	A	n	E/R	REF.
$S + HS \rightarrow H + S_2$	1.0 - 10	0	0	5
$H + HS \rightarrow S + H_2$	2.5 - 11	0	0	6
$H + H_2S \rightarrow HS + H_2$	1.29 - 11	0	860	6
$2\ HS \rightarrow H_2S + S$	1.3 - 11	0	860	6
$OH + H_2S \rightarrow HS + H_2O$	1.4 - 11	0	225	7
$SO + OH \rightarrow H + SO_2$	9.67 - 11	0	0	7
$HS + O_2 \rightarrow SO + OH$	1.0 - 13	0	0	7
$S + OH \rightarrow SO + H$	6.7 - 11	0	0	8
$S + O_2 \rightarrow SO + O$	1.7 - 11	0	2820	7
$SO + SO_3 \rightarrow 2\ SO_2$	7.0 - 12	0	0	5
$H + SO_3 \rightarrow OH + SO_2$	2.0 - 15	0	0	9
$SO + O_2 \rightarrow SO_2 + O$	6.0 - 13	0	3300	7
$HO_2 + SO_2 \rightarrow SO_3 + OH$	1.0 - 18	0	0	7
$O + HS \rightarrow SO + H$	2.0 - 10	0	0	6
$O + SO_2 \xrightarrow{M} SO_3$	1.48 - 19	-3.75	0	7

6. COMPUTER MODEL FOR $NH_I/NO_X/SO_X$ CHEMISTRY

6.1 Task Goals and Milestones

Using data generated from experimental measurements, and rate coefficients obtained from the literature, a reaction set which can describe the detailed chemistry of the $NH_i/NO_x/SO_x$ system is to be developed. The basis for the NH_i/NO_x chemistry is a reaction set developed in previous work.(10) These calculations are performed using the Aerodyne PACKAGE Code. This model will assess the effect of the presence of SO_2 and/or other sulfur-containing species on the thermal $deNO_x$ process. During this quarter, a preliminary model involving SO_2 was conceived and tested. The results indicate how the presence of sulfur-bearing species may affect the $deNO_x$ process.

6.2 Technical Discussion

6.2.1 Improvements on PACKAGE Code

In addition to the existing capabilities of the PACKAGE code, a new feature was added. For each species in the reaction set, the program can calculate the contribution of each reaction containing that species towards its overall rate of change at any specified reaction time. For example, the species SO_2 appears in six reactions in the present set, and its concentration calculated every 25 ms, as are all of the other species. Under a set of circumstances, the total SO_2 concentration decreases with time, with $d\left[SO_2\right]/dt = \sum_{i=1}^{6} d\left[SO_2\right]_i/dt$. By printing the individual contributions of each reaction to the total rate of change of $\left[SO_2\right]$, we can determine which reactions are important and which ones have little effect on the rate set. As will be discussed below, for SO_2, only the reaction $SO_2 + O \xrightarrow{M} SO_3$ is important. Of course, other reactions containing SO_2 may still be critical to other species and should still be retained in the reaction set. By evaluating all of the major components, the unimportant reactions can be identified and rejected from the set.

In our Final Report on the NH_i/NO_x system,(10) a reduced reaction set containing 24 reactions (out of 54 in the larger set) was used which well represented the $deNO_x$ process (Table 3). Using this new feature in the PACKAGE code, the choice of these reactions has been verified.

6.2.2 Effect of SO_2 on the Thermal $deNO_x$ Process

A limited number of runs were performed using the short $deNO_x$ set (Table 3) and the short sulfur set (Table 2) under conditions similar to those tested previously. A mixture of CH_4/O_2 ($\phi = 0.93$) in 83% Ar is reacted to equilibrium at each desired temperature, providing initial concentrations for all species. Ammonia and nitric oxide are added (300 ppm) and the finite rate chemistry run for 475 ms, with concentrations printed every 25 ms. Different initial SO_2 concentrations and starting temperatures are chosen and the results compared with the regular $deNO_x$ calculations.

At 1250^oK, nitric oxide will be reduced to ~ 0.27 of its original values after 475 ms. In the presence of 300 ppm SO_2, reduction is improved to 0.20. This somewhat surprising result can be explained by examining the rate importance calculations, illustrated in Figs. 6.1 and 6.2. The hydroxyl radical is the key to following the $deNO_x$ chemistry. We see here that the channel for removing OH by reaction with NH_2 to form NH (and subsequently NO) strongly decreases upon addition of SO_2. Also, the OH production channels are smaller, indicating that less OH is formed. Examination of similar diagrams for O and NH_2 show that the reason for this lies in the reaction

$$SO_2 + O \overset{M}{\rightarrow} SO_3 \quad . \qquad (6\text{-}1)$$

Table 3 - NH_i/NO_x Short Reaction Set

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

REACTION	A	n	E/R	REF.
$H_2 + OH \rightarrow H + H_2O$	1.8 - 11	0	2330	11
$H + O_2 \rightarrow O + OH$	1.19 - 07	-0.861	8316	13
$O + H_2 \rightarrow H + OH$	3.0 - 14	1.0	4479	11
$OH + HO_2 \rightarrow H_2O + O_2$	4.0 - 11	0	0	7
$H + HO_2 \rightarrow 2OH$	3.2 - 10	0	0	7
$\rightarrow H_2 + O_2$	1.4 - 11	0	0	7
$\rightarrow H_2O + O$	9.4 - 13	0	0	7
$O + HO_2 \rightarrow O_2 + OH$	8.0 - 11	0	500	12
$2OH \rightarrow O + H_2O$	1.0 - 11	0	550	12
$H + O_2 \xrightarrow{M} HO_2$	2.0 - 32	0	-500	12
$H + OH \xrightarrow{M} H_2O$	1.0 - 25	-2.0	0	12
$NO + N \rightarrow N_2 + O$	3.4 - 11	0	0	7
$N + O_2 \rightarrow NO + O$	1.1 - 14	1.0	3150	14
$N + OH \rightarrow NO + H$	5.0 - 11	0	0	15
$NH_3 + OH \rightarrow NH_2 + H_2O$	5.4 - 12	0	1067	16
$NH_2 + NO \rightarrow N_2 + H + OH$	7.8 - 05	-2.46	938	10*
$\rightarrow N_2 + H_2O$	1.17 - 04	-2.46	938	10*
$NH_2 + OH \rightarrow NH + H_2O$	5.0 - 14	0.68	650	17
$NH + NO \rightarrow N_2 + OH$	4.7 - 11	0	0	18
$NO + H \xrightarrow{M} HNO$	5.0 - 32	0	-300	12
$HNO + OH \rightarrow NO + H_2O$	6.0 - 11	0	0	7
$NH + O_2 \rightarrow HNO + O$	5.0 - 11	0	1710	13
$2NH_2 \rightarrow NH_3 + NH$	2.8 - 13	0.63	1812	19
$NH_2 + HO_2 \rightarrow HNO + H_2O$	2.5 - 11	0	0	20

*Valid for $T \leq 1250$ K. Above 1200 K, rate drops to 1.0×10^{-12} at 1500 K. See Fig. 4.5 in Ref. 10.

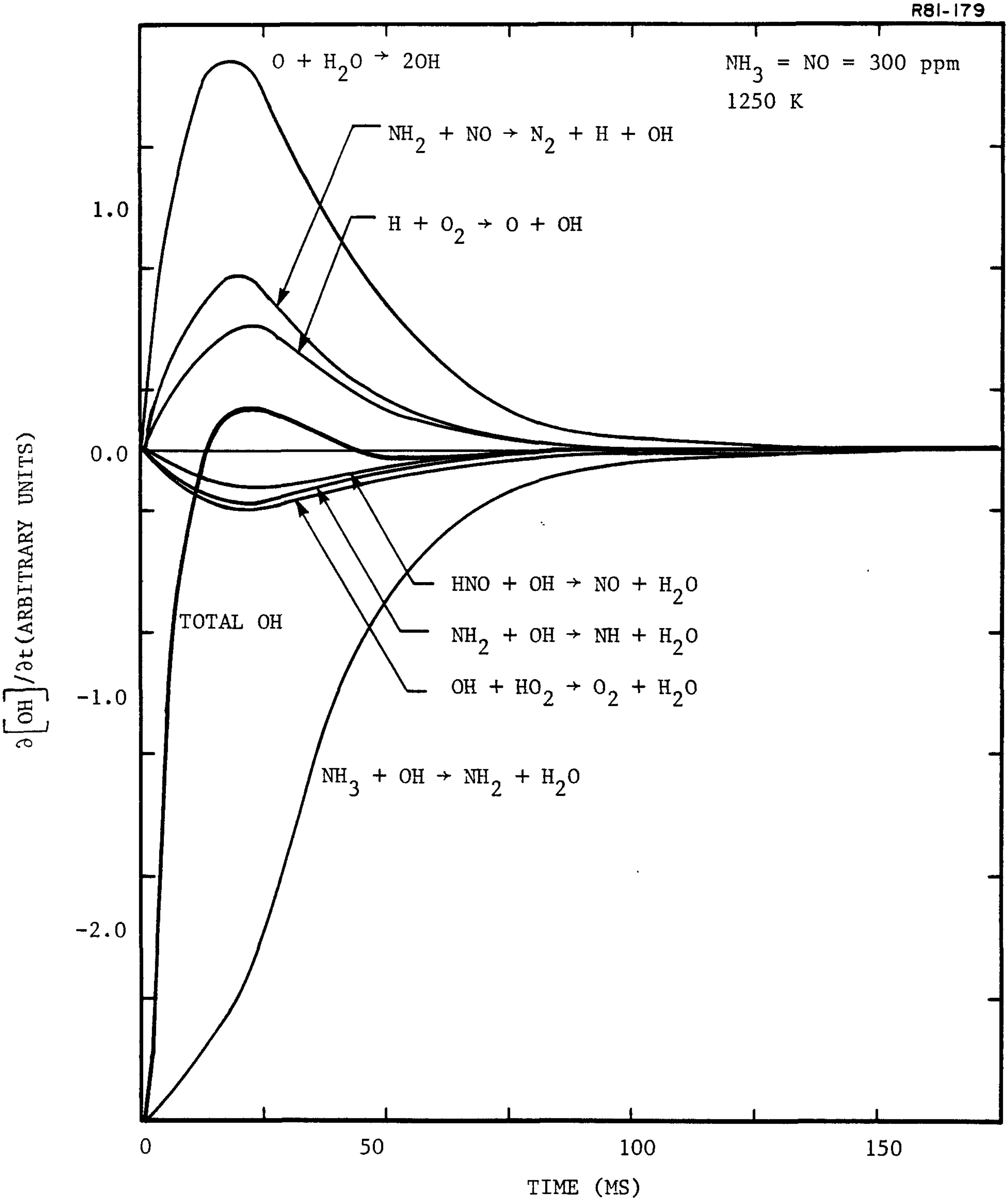

Figure 6.1. Individual Reaction Contribution to Formation and Destruction of OH: NH_i/NO_x Without SO_2.

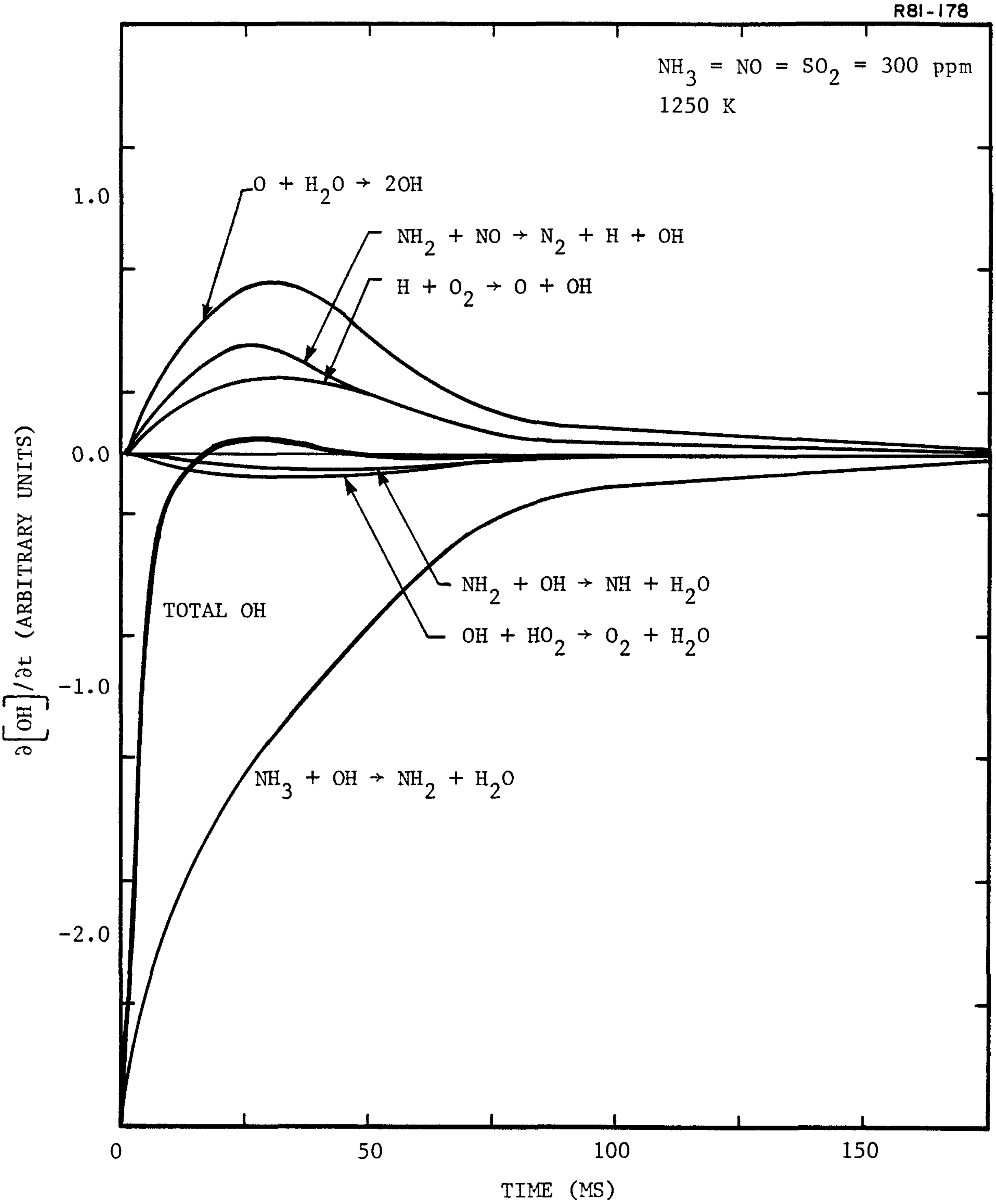

Figure 6.2. Individual Reaction Contribution to Formation and Destruction of OH: NH_i/NO_x with SO_2.

By tying up O atoms, the major OH formation reaction is slowed; thus, less OH are available to compete with NO for the NH_2 radical

$$O + H_2O \rightarrow 2\,OH \qquad (6\text{-}2)$$

$$NH_2 + OH \rightarrow NH + H_2O \qquad \text{(NO formation steps)} \qquad (6\text{-}3)$$

$$NH_2 + NO \left\{ \begin{array}{l} \rightarrow N_2 + OH + H \\ \\ \rightarrow N_2 + H_2O \end{array} \right\} \text{(NO removal steps)} \;. \qquad \begin{array}{r} (6\text{-}4a) \\ \\ (6\text{-}4b) \end{array}$$

Since the water shuffle reactions are rapid, it is clear that any species which can affect this balance will have an impact on the thermal $deNO_x$ process. In this example, SO_2 ties up oxygen atoms and provides a better pathway for NO reduction. When SO_2 is raised to 1000 ppm, the NO reduction increases an additional 4%, with slower formation and destruction times since $[OH]$ is smaller.

At 1100 K, little NO is removed with or without SO_2. In fact, the presence of SO_2 slows the removal here because it drains the available $[OH]$ needed to initiate the chemistry via the reaction

$$OH + NH_3 \rightarrow NH_2 + H_2O \quad . \qquad (6\text{-}5)$$

At 1500, one might expect a significant improvement in NO reduction, since the SO_2 reaction slows the NO formation reactions. However, the rate for the $SO_2 + O + M$ reaction decreases with increasing temperature, making O atom removal less important. Also, its effect is doubled since each O atom can produce 2 OH (rxn 6-2). The overall effect of SO_2 at 1500 K is that NO increases by a factor of 1.10, still less than 1.16 without SO_2, but not significantly. Thus, SO_2 has the effect of slightly improving NO reduction, and doesn't appear to inhibit it.

These results must be viewed with caution at this time. First of all, only a limited SO_x reaction set is used, and the inclusion of sulfur-NO reactions and of the radical HSO_2 may change the outcome. Because the thermodynamics of HSO_2 are poorly understood, it has not been included in the JANNAF thermochemical tables, from which reverse rate constants are calculated.

6.3 Work Forecast

During the next quarter, a more comprehensive set of reactions will be included in the model, including HSO_2, for which a reasonable set of thermodynamic parameters will be generated. Also to be included in the set are reactions of minor species present in combustion streams, such as CS, COS and CS_2, which may behave similarly to the CO-CO_2 subsystem. The effect of hydrogen addition in the presence of SO_2 will also be examined. Key reactions for which the experimental rate data is poor will be identified and the rates measured, if at all possible.

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