

LBL--32950

DE93 002574

THE REDUCTION OF NO_x BY HNCO

Nancy J. Brown

Jeronimo Garay

**LBL ENERGY AND ENVIRONMENT DIVISION
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720**

OCTOBER 1992

**WESTERN STATES SECTION/THE COMBUSTION INSTITUTE PAPER 92-95 FOR
THE 1992 FALL MEETING AT LAWRENCE BERKELEY LABORATORY**

**This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences,
Chemical Sciences Division of the U.S. Department of Energy, under contract No. DE-AC03-76SF00098.**

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

A chemical mechanism for the reduction of NO_x by HNCO has been constructed to model NO_x reduction in exhausts typical of natural gas combustion with the addition of radical boosters (fuel). Variables considered were the initial concentrations of NO, NO₂, CO, O₂, CH₄, H₂, and HNCO as well as initial temperatures. The chemical model was validated by comparing results with earlier model calculations of Miller and Bowman and with the experiments of Caton and Siebers and Lyon and Cole. Agreement with experiments was satisfactory.

The reduction chemistry must be preceded by thermal ignition chemistry which generates radicals. The lowest temperature for which ignition occurs is the optimum temperature for reduction and defines the beginning of the temperature window. Reduction was not achieved for the "natural gas exhaust" for a reasonable residence time. Additional H₂ added to the exhaust mixture enhanced reduction, but the addition of CO and CH₄ did not.

Under some conditions the computed sensitivity coefficient for nitrogen species and temperature exhibited self-similarity. Four reaction paths were identified which controlled the fate of the NO: the conversion of NO to NO₂ via HO₂, the conversion of NO₂ to NO via reaction with H or O, the reduction of NO via NCO, and the reduction of NO from reactions with NH_i species. The relative importance of the four was determined by the initial conditions.

I. INTRODUCTION

Standards for NO_x (NO and NO₂) are established to reduce air pollution emissions and to protect human health. NO_x affects (1) human health, (2) ozone concentrations, (3) the formation of PM₁₀ (fine particulate), (4) acid deposition, and (5) visibility degradation. Stringent emission standards, essential to preserve air quality, frequently push the limits of existing technology and require new abatement schemes. A relatively new technology for reducing NO_x to acceptable levels is the RAPRENO_x selective reduction process. The RAPRENO_x process has been patented by Perry (1988 and 1989) as a system for NO reduction using the sublimation of cyanuric acid (HNCO). In accord with the patent literature, any source and/or means of generating HNCO and admixing it with the effluent stream can be used. In this paper, we treat the HNCO as a gaseous substance that is added to the mixture containing NO_x.

The first objective of the present study was to perform a modeling and sensitivity analysis study to investigate the suitability of HNCO as a selective reducing agent for NO_x in post-combustion exhaust characteristic of natural gas combustion. A second objective was to determine how the identity and concentration of radical booster compounds affects the reduction chemistry. A third objective was to use sensitivity analysis and rate of production analysis to determine mechanistic details of the reduction chemistry.

Systems fueled with natural gas are used for power generation, cogeneration, and for natural gas and hybrid gas vehicles.

A particularly attractive use of natural gas-fired vehicles or hybrid natural gas vehicles is bus and truck fleets. Combustion using natural gas as a fuel and conducted under fuel-lean conditions is clean with very low CO and particulate emissions as well as relatively low NO_x. There are, however, hydrocarbon (mostly CH₄) emissions. The CO emissions are so low in natural gas-fired engines that three-way catalysts, which depend on critical levels of CO to achieve NO_x reductions, are ineffective (Kenney, 1991). This was the major motive for examining the possibility of using the selective reduction of NO_x by HNCO for natural gas-fired engines.

Improved NO_x reduction must be achieved without producing other undesirable species. Nitrous oxide (N₂O) is a product of the selective reduction of NO_x by HNCO. For the reduction to work well, the NO_x reduction must occur under conditions where the N₂O is destroyed.

II. PREVIOUS STUDIES OF THE REDUCTION OF NO_x BY HNCO

The RAPRENO_x process was patented by Perry (1988 and 1989). In the second patent the process is thus described: "An arrangement for reducing the NO content of a gas stream comprises contacting the gas stream with HNCO at a temperature effective for heat induced decomposition of HNCO and for resulting lowering of the NO content of the gas stream. Preferably, the HNCO is generated by the sublimation of cyanuric acid."

Isocyanic acid (HNCO) is formed from the decomposition of the cyanuric acid (HOCN)₃ at temperatures in excess of 600 K. The

cyanuric acid sublimates and decomposes on the surface or in the gas phase to form HNCO. When the isocyanic acid is mixed in with exhaust stream gases containing products of combustion and NO_x, several elementary reactions may occur, which result in the reduction of NO_x.

RAPRENO_x has been used to reduce NO_x in exhaust from diesel engines used for vehicles and power generation (Perry 1988). Reductions of NO_x in an oil-fired industrial-sized boiler with RAPRENO_x have been achieved by Sarv and Rodgers (1989) of Babcock and Wilcox.

There has been a number of studies on the reduction of NO_x by HNCO. Perry and Siebers (1986) demonstrated that a high degree of NO_x reduction was achieved if HNCO was added to an exhaust stream mixture at temperatures above 865 K for a flow tube (packed with iron spheres) containing simulated combustion exhaust and an exhaust mixture from a single-cylinder diesel engine.

Lyon and Cole (1990) investigated the reduction of NO by HNCO in a combined experimental and modeling study. They found three modes of NO reduction. The first is catalytic, and NO reductions at temperatures as low as 725 K were found to occur only in the presence of catalytic surfaces. They found non-catalytic reductions to occur at 975 K provided that the reaction is promoted by wet CO oxidation or other oxidizable gas (mode two). They also found that the HNCO could reduce NO by itself in a range of temperatures centered at 1425 K (mode three). This third mode of reduction involved NO + NCO and had the

disadvantage of converting the NO to N_2O . Their modeling calculations indicate that for the second mode, in the presence of wet CO or any other oxidizable fuel, the H₂CO reduces NO via a complex reaction mechanism very similar to that involved in the Thermal DeNO_x (the selective reduction of NO by NH₃) process patented by Lyon in 1975. For mode two, Lyon and Cole postulate that the NO reduction is a result of the NH₂ + NO reaction. Lyon and Cole indicate that the mode two reduction temperature range is largely dictated by the oxidation kinetics of the CO or other oxidizable gas, and is thus independent of whether the reducing agent is NH₃ or H₂CO.

Heap et al. (1988) also indicated that low temperature reductions of NO by H₂CO appear to be due to catalytic activity involving a stainless steel reactor. A later study by Chen et al. (1988) was concerned with NO reduction in a tunnel furnace simulating a pulverized coal boiler. They found that application of a number of selective NO reducing agents to an overall fuel-lean environment produced NO reduction behavior similar to Thermal DeNO_x. Siebers and Caton (1988) also confirmed the importance of surface decomposition of the H₂CO for initiating NO reduction for temperatures less than 900 K.

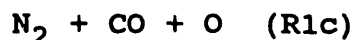
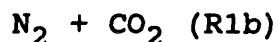
A model for the selective reduction of NO by H₂CO, when wet CO is present, was put forth by Miller and Bowman (1988, 1989 and 1991). They combined the Thermal DeNO_x and the moist CO mechanisms with the Perry and Siebers chemistry and modeled the experimental data of Siebers and Caton (1988) and Caton and Siebers (1988).

Results of the experimental studies of Caton and Siebers (1988, 1989 a and b, and 1990) in concert with the modeling studies of Miller and Bowman revealed that NO reduction occurs as a result of gas phase chemistry in the temperature regime 900 to 1350 K. Reductions of NO by as much as 100% have been achieved. The reduction depends upon temperature, O_2 , H_2O , and a "sufficient concentration" of a molecule which can react to generate radicals, e.g., CO, H_2 , H_2O_2 , C_2H_4 , or CH_4 . It also depends upon the initial NO concentration and the ratio of the initial HNCO/NO concentrations.

Caton and Siebers (1988, 1989 a and b) investigated the use of HNCO to reduce NO in a quartz flow reactor with diesel engine and simulated exhaust gases. They found that exhaust gases (O_2 , CO, and H_2O) played an important role in the overall NO reduction process, and that the absence of any one of these species caused the NO reduction process to shift to higher temperatures. Nitrous oxide was a significant reduction product in treated diesel exhausts, and it achieved a maximum concentration at approximately 1200 K. In their most recent study, Caton and Siebers (1990) investigated NO removal and N_2O formation for HNCO addition to surrogate exhaust gas containing H_2 , O_2 , CO, NO, CO_2 , and H_2O . They were interested in examining NO reduction and N_2O production as a function of H_2 /HNCO molar ratios. As the concentration of H_2 increased from 0 to 2950 ppm, the temperature for maximum NO reduction decreased. The ratio of N_2O produced to NO reduced is a maximum at 1100 K and equals approximately 1, while, at temperatures near 800 K, the ratio is 0.12.

If N_2O is produced at temperatures in excess of 1200 K, it is effectively destroyed by the reactions $\text{N}_2\text{O} + \text{H}$ and $\text{N}_2\text{O} + \text{OH}$. This has been confirmed by experimental and modeling studies of the combustion chemistry of nitrous oxide by Martin and Brown, (1989, 1990, 1990, 1990), and by measurements in utility exhaust by Muzio and colleagues (1990). The N_2O destruction reactions are thermally quenched at temperatures less than 1200 K. Typical exhaust temperature for natural gas-fired gas turbine, reciprocating, and lean-burn engines is between 775 and 975 K (Muzio, et al. 1990).

Predicting N_2O emissions as a product of the selective reduction of NO by HNCO requires accurate rate coefficients for the $\text{NCO} + \text{NO}$ reactions. There has only been one measurement of the reaction products and branching ratio at room temperature (Cooper and Hershberger, 1992).



Branching ratios as a function of temperature are critical for determining N_2O production.

Perry (1985) investigated the $\text{NO} + \text{NCO}$ reaction in the temperature range 294-538 K by measuring the disappearance of NCO by laser-induced fluorescence (LIF). No reaction products were

measured and the net rate coefficient for reaction was determined to be

$$k = 1.69 \times 10^{-11} \exp(+390 \pm 320/RT) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

for the temperatures 294-538 K, where R is the gas constant in 33cal K⁻¹, and T the temperature in Kelvins. The temperature dependence was negative and no pressure dependence was found for pressures of 3.3 to 13.3 kilopascals of argon.

Cookson et al. (1985) measured the rate coefficient for net reaction of NCO + NO at room temperature, and their results are in excellent agreement with Perry.

Cooper and Hershberger measured rate coefficients for R1a, R1b, and R1c at room temperature using pulsed laser photolysis with time-resolved infrared diode detection. The rate coefficients for R1a, R1b, and R1c are 1.09×10^{-11} , 1.45×10^{-11} , and $0.76 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.

Atakan and Wolfrum measured the net rate in the temperature range between 294 and 1260 K using laser photolysis/laser-induced fluorescence. The results were fitted to an expression for the net rate coefficient

$$k = (3.0 \pm 0.4) \times 10^{17} T^{-1.53 \pm 0.1} \exp[(-260 \pm 30)K/T]$$

with the units cm³ mol⁻¹s⁻¹. The curvature of the Arrhenius plot noted in these experiments is likely to be due to a change in reaction mechanism. The effects of these newer measurements on the prediction of NO reduction and N₂O production will be discussed subsequently.

III. THE MODEL

A. Construction of a Chemical Mechanism for RAPRENOx

The modeling studies conducted in this study used the following software: CHEMKIN-II (1991), DASSL (1982), a differential equation solver, and SENKIN (1991). These were used in conjunction with a chemical mechanism and The Chemkin Thermodynamic Data Base (1991). Driver routines and data reductions software were written by us. Calculations were run on a Cray X-MP computer. Sensitivity calculations were especially compute-intensive, requiring an hour or more of Cray time.

We constructed a mechanism for describing the reduction of NO by HNCO based upon the Miller-Bowman (1989) methane oxidation mechanism with nitrogen chemistry and the Miller-Bowman (M-B) (1991) mechanism for RAPRENOx. Their RAPRENOx mechanism consists of the following: 1) reactions of N/H/O species that are important in Thermal DeNOx; 2) reactions important in the oxidation of moist CO; and 3) reactions involving HNCO and NCO. We added CN and CH_n chemistry to the 1991 Miller-Bowman mechanism to model NO reduction by HNCO in exhaust mixtures containing CH_4 . Our mechanism contained Appendix A of the 1989 Miller-Bowman mechanism. The subset of reactions that is common to Appendix A and the 1991 Miller-Bowman mechanism has rate coefficients equal to the 1991 values. Reactions in the 1991 paper that are not included in Appendix A are included in the new mechanism. Reactions of C_3H_3 and C_4H_3 are not included because they are not important in lean mixtures. We used the $\text{NCO} + \text{O}_2$ rate coefficient reported by Perry (1985) rather than the Miller-Bowman 1991

value. The mechanism is shown in Table I and is subsequently referred to as the Brown-Garay (B-G) mechanism. It consists of 50 species and 256 reactions. This mechanism is used to compute all cases considered in this paper.

In Table I, the elements considered are given first, followed by the individual species. Parameters for the unimolecular reactions $\text{CH}_3 + \text{CH}_3 (+ \text{M})$ and $\text{CH}_3 + \text{H} (+ \text{M})$ are given in the standard CHEMKIN-II format. Rate coefficients for the forward reaction (k_f) are given in the form

$$k_f = AT^b \exp(-E/RT).$$

Units are moles, cubic centimeters, seconds, Kelvins and calories/mole. Phase is the gas phase and charge on the species considered is zero. The low and high temperatures define the range where the equilibrium constants can be calculated.

B. Sensitivity Analysis

Sensitivity coefficients, $S_{ji}(t)$, are the partial derivatives of the system solution, $X_j(t)$, with respect to the input parameters, k_i (rate coefficients). The S_{ji} are normalized with respect to the rate coefficient and the maximum value of the variable X_j^m as

$$S_{ji}[t] = (k_i \backslash (X_j^m)) (\delta X_j(t) / \delta k_i(t)). \quad (1)$$

The $X_j(t)$ are concentrations of the species or the temperatures as a function of time. When the sensitivity coefficients are normalized in this manner, the sensitivity coefficients give the relative change that occurs in the dependent variable per

relative change in the independent variable weighted by the fraction of the maximum that the independent variable is at a given time. The sign of the sensitivity provides the directional response, and the magnitude indicates the relative importance of the input parameter. Since reverse rate coefficients are calculated from the equilibrium constant and forward values, the sensitivities to the forward and reverse rate coefficients are equal. General mechanistic information can be derived by carefully analyzing the sensitivity coefficients as a function of time for the dependent variables.

IV. RESULTS AND DISCUSSION

A. Comparison with Experiment

We repeated the Miller-Bowman calculations for the concentration profiles and sensitivities using their 1991 mechanism and the initial concentrations indicated as Case A of Table II. We obtained identical results indicating that the input, problem solution, and post-processing were consistent.

Caton and Siebers (1988 and 1989 a and b) reported studies of RAPRENOx that can be modeled. It is important to discuss these experiments in more detail to understand their limitations in establishing model validity. Caton and Siebers added HNCO as a vapor mixed with air to pseudo-exhaust mixtures containing fixed amounts of O_2 , CO, CO_2 , NO, and H_2O . They preheated the reactants to $T=720$ K prior to the addition of the HNCO. They assumed that two things happened after 20% of the reactor residence time had lapsed: 1) reactants were heated to the reactor temperature, T_r

with T_r in the range 800 to 1350 K, and 2) H₂CO was mixed. In fact, reaction between the exhaust gas and H₂CO occurs in the reactor at an unspecified temperature (between the 720 K and T_r) while the H₂CO is mixing and the mixture is heating. This affects the early temporal behavior of the reacting system so that the values of concentrations of reactants after the mixing of the H₂CO has occurred are different from the starting values which are assumed in the model.

The B-G mechanism was used to model the Caton and Siebers experiments for Case A compositions (as given in Table II) for the temperature range 800 to 1350 K. The two models (B-G and M-B) differ most between 950 and 1075 K as illustrated by comparing Figures 1 and 2, respectively. The B-G model actually gives better agreement with experiments especially with respect to the H₂CO, CO, and CO₂ profiles, and for NO at 1125 K than the M-B model. Both models and experiments reveal that the maximum in N₂O concentration coincides with the maximum NO reduction. Although the models produce the trends noted experimentally, they do not reproduce the temperature dependence of the experimental concentration profiles.

Sensitivity and coefficients for Case A at 1050 are shown for NO in Figure 3 and N₂O in Figure 4. The sensitivities are normalized according to Eq.(1). Positive sensitivities are associated with reactions that inhibit NO removal. Even though our mechanism (Table I) is different from the M-B mechanism, we found the same trends in the sensitivity coefficients, although magnitudes differ.

The fate of the NO is most sensitive to behavior at 125 milliseconds, which corresponds to the mixing/heating period of the Caton and Siebers experiments. The crucial factor in NO removal is generation of the radical pool. This is confirmed by the very high sensitivity to the four reactions concerned with CO + H₂ oxidation: reaction 128 with a positive sensitivity, and reactions 63, 126, and 132 with negative sensitivity which generate radicals. The NO sensitivities exhibit self-similarity. As discussed by Rabitz and Smooke (1988), by appropriate scaling, the sensitivity functions of NO will fit on a single curve. This implies that the elementary reactions are not independent; a change in one can be offset by a change in another. Self-similarity occurs in dynamical systems where one or at most a few dependent variables dominate the physical behavior of the system. The existence of scaling suggests that the model can be simplified. For isothermal conditions, it is likely that one of the radical species is the dominant variable. This great sensitivity of NO removal processes to radical generation has been found for Thermal DeNOx and RAPRENOx by Miller and Bowman (1989 and 1991). The surprising result is that reactions that are associated with the primary NO removal process, that is, reactions 190, 196, and 192 exhibit positive sensitivities. These reactions compete for H and OH radicals and inhibit the radical generation. Reaction 182 is responsible for the NO₂ to NO conversion that occurs.

For the most important reactions, the N₂O sensitivities are of opposite sign to the NO sensitivities, which implies that reac-

tions that result in NO removal produce N_2O . The N_2O sensitivities also exhibit self-similarity. It is especially surprising that the $NCO + NO$ reaction has a negative sensitivity for N_2O .

The great sensitivity to the $H + O_2 + M \rightarrow HO_2 + M$ reaction (M is the total mixture concentration) should be examined. It is very difficult to measure individual third body efficiencies, and the efficiency with respect to $M = H_2O$ is of crucial importance to the NO reduction. We performed calculations with a factor of two increase in the H_2O efficiency and found only a factor of 5 difference in the percentage NO removal at 1050 K for the initial concentration of Case A. Predictive capability of the model is very dependent on the accuracy of this rate coefficient.

Rate of production analysis was performed for NO. The dominant path for NO removal was the $NO + NCO$ reaction. This was in competition with NO to NO_2 interconversion at early times. Another channel that was very important involved NO reactions with NH_i species that are important in Thermal De-NOx. The NCO reaction was approximately twice as effective in removing the NO as the NH_i reactions.

We also modeled the more recent experiments of Caton and Siebers (1990), in which NO reduction in pseudo-exhaust gas mixtures of O_2 , NO, and H_2 was investigated. HNCO was added to the exhaust after it had been heated from room temperature to 720 K. Agreement between our calculations and their 1990 experiments was poor.

We attempted to reconcile differences between our results and those of Caton and Siebers (1990). The concentration of the

"reactants" after preheat and immediately before the addition of the HNCO was not measured. This was probably not a serious error in the earlier experiments, but H_2 reacts in the gas phase and on surfaces in the presence of O_2 when it is heated to temperatures of 720 K (Brown et al. 1983).

To clarify whether H_2 reaction was possible under the conditions of the Caton and Siebers experiments, we investigated H_2 reactivity in the inlet/preheat system with a set of modeling experiments. We assumed that the heating occurs with a linear temperature profile, and modeled behavior in the preheater as a function of initial hydrogen concentration using the well-known H_2 /air kinetics. For the largest H_2 concentrations considered in the experiments, our results indicated as much as 50% of the H_2 reacted in the preheater. Caton and Siebers assumed no reaction occurred prior to the addition of HNCO, and this is difficult to reconcile with our modeling experiments. We are unable to predict the actual gas phase concentrations at the end of the preheat section because we do not know the actual temperature profile or the extent of surface reaction on the heated quartz walls. Nevertheless, we used our calculated concentrations as initial values for our modeling calculations, and agreement with experiment improved.

Lyon and Cole also published data that can be modeled. They performed a set of experiments in a plug flow reactor to determine the influence of wet CO on the ability of both HNCO and NH_3 to reduce NO. The mixture composition and temperature are Case L of Table II. The CO concentration was varied between 0 and

3%, and N_2 made up the balance. The reduction of NO was investigated isothermally for a residence time of 0.76 seconds.

Lyon and Cole modeled their experiments using the Dean, De Gregoria, Hardy, Lyon (DGHL) model (Lyon et al., 1987). We modeled their experiments using the B-G model. The results of the experimental study and the two sets of modeling results are shown in Figure 5. Our results tend to agree better with experimental values than the DGHL model, but they indicate that smaller CO concentrations result in a higher percentage of NOx reduction than found experimentally. We performed calculations under both isothermal and adiabatic conditions, and did not find significant differences between the two.

We substituted the rate coefficient of Atakan and Wolfrum for the Perry value of the $NCO + NO$ rate coefficient. The two rate coefficients yielded about the same amount of NO reduction for CO less than 0.5%, and for larger values of CO, the reduction of NO was about 10% greater with the Perry value. The N_2O production, which was a maximum for 0.5% CO, was approximately 125 ppm with the Perry rate coefficient and 110 ppm with the Atakan and Wolfrum value. We also used the Atakan and Wolfrum rate coefficient with the branching ratio of Cooper and Hershberger and found that the maximum N_2O decreased to approximately 50 ppm. The final NH_3 concentration (calculated for each initial value of CO) was a maximum at the CO concentration corresponding to the maximum NO reduction and then declined with increasing CO.

We calculated sensitivity coefficients for the addition of 0.5% CO, and these provided information about the importance of

De-NOx chemistry in the reduction. The plot of the 10 largest sensitivity coefficients for NO are shown in Figure 6. Sensitivities for other nitrogenous species were computed as well. The sensitivity structure is complex because there are three reaction paths that affect NO consumption. The sensitivities are not self-similar. The interconversion of NO and NO₂ is quite important throughout the reduction of NO. The reduction of NO occurs through the NCO + NO reaction as well as the NH_i + NO reactions. The sensitivities with respect to reactions 63, 126, 128, and 180 change sign. Negative sensitivities are found for the NCO + NO reaction and for reactions of NO + NH₂ going to N₂ + H₂O and NNH + OH. The N₂O sensitivities (which are not shown) did not undergo a sign change. Rate of production analysis revealed that the NCO and NH_i paths for reducing NO were nearly equal with the NH_i path being slightly larger.

B. Methane as a Radical Booster

A representative exhaust composition was obtained for a lean burning engine using natural gas as a fuel (Des Jardin, 1991). The exhaust more than likely includes radical concentrations, but they were not measured. Radicals, if present, would affect the reduction of NOx. The exhaust composition provided with the added HNCO and used in the modeling calculations is given in Table II as Case B2.

The reduction of NOx by HNCO was modeled for the Case B2 composition as a function of initial exhaust temperature for constant pressure adiabatic plug flow conditions for a residence time of one second. The one second residence time was chosen

because it is a reasonable upper limit for gas in an exhaust system (Lyon, 1990). Under these conditions, no NO_x reduction occurred for $T \leq 1135$ K, but there was conversion of the NO to NO₂. At 1140 and 1145 K, NO_x removal on the order of 10% of the original amount was determined. At 1150 K, NO₂ was converted to NO, the exhaust gas mixture underwent combustion and achieved a final temperature in excess of 1200 K, and additional NO was produced.

To understand whether or not reduction is dependent on thermal ignition and subsequent combustion of the exhaust mixture with the added HNCO, calculations were performed on mixtures at 1050 and 1100 K for residence times of 30 and 10 seconds, respectively. Assuming the mixture is flammable, ignition time depends upon the initial gas composition and temperature. Combustion of the exhaust depends upon there being sufficient time for ignition, and is associated with a temperature rise characteristic of the mixture. For Case B2, the temperature rise for combustion is approximately 66 K. Combustion occurred for the 1050 K mixture in less than 30 seconds and for the 1100 K mixture in less than 10 seconds. NO_x reduction at 1100 was 45%. Species profiles as a function of time were determined. The fate of NO was determined by three competitive processes: interconversion of NO and NO₂ by reactions 180, 181, and 182; reduction of NO by NCO via reaction 190; and reduction of NO by NH₃ via reactions 234, 235, and 240.

Sensitivities were also computed for NO, N₂O, NO₂, NH₃, HNCO, and temperature for the Case B2 mixture for an initial temperature of 1100 K. The ten most important reactions are the

same for the nitrogen species and temperature, and they are the following: (9), (1), (126), (181), (5), (128), (57), (61), (8), and (182). The ten most important reactions are those associated with thermal ignition chemistry and are not (except for reactions associated with NO and NO₂ interconversion) reactions involving nitrogen species. The sensitivities for the nitrogen species and temperature exhibit self-similarity. The NO sensitivities oscillate and change sign at three different times. The sensitivities indicate the strong coupling in the chemistry leading to NOx reduction, and the critical dependence on radical generation. The sensitivity structure is very similar to a case that will be discussed subsequently.

C. The Effect of Radical Boosters on NOx Reduction

1. The Effect of CH₄

The effect of adding "extra" CH₄ to the mixture B2 was investigated as Case C for initial CH₄ concentrations of 5.0, 7.5, 10, and 20 x 10⁻³ mole fraction. At an initial temperature of 1050 K, for a one second residence time, no significant chemistry occurred and NOx was not reduced. Initial CH₄ concentrations of 1 and 2% were investigated for initial temperatures in the range 1100 to 1200 K. No appreciable reaction occurred for temperatures below 1200 K because of insufficient time for ignition. At 1200 K, the mixtures burned and produced NO.

Adding CH₄ as a radical booster is ineffective for causing the reduction of NO. Reductions of NOx are negligible. When temperatures are sufficient for rapid ignition to occur (T ≥ 1200 K), the mixture burns and produces NOx.

2. The Effect of H₂

It was not possible for H₂CO to reduce NO_x in the prototypical natural gas exhausts because the "primary fuel" present in the exhaust was CH₄, due to difficulty in achieving ignition. In order to facilitate ignition, and thus, the reduction of NO_x by H₂CO, the effect of adding H₂ in variable amounts for a range of initial temperatures was investigated. All concentrations were renormalized so that total mole fraction was equal to 1.0 after the addition of H₂ to the mixture whose composition is given in Table II.

Tables III and IV are a summary of the effect of adding H₂ in concentrations of 2.5 and 7.5 x 10⁻³ mole fraction, respectively, to the Case B1 exhaust composition for initial temperatures in the range 800 to 1200 K. For the Case B1 exhaust composition, the effect of adding H₂ in the concentrations 500, 1000, and 1500 ppm at 1050 K was also investigated. The effect of adding variable H₂CO to a Case D mixture at an initial temperature of 1025 K is summarized in Table V. Finally, the effect of adding H₂ to a Case E mixture for a range of initial temperatures is summarized in Tables VI through IX. The letter "I" in the Tables indicates that ignition and combustion in the exhaust was incomplete, and "C" indicates that ignition and combustion are complete. "Completeness" in this sense implies that the mixture obtains a final temperature commensurate with the amount of "booster fuel" added to the mixture.

Examination of the Tables reveals that the optimum temperature for reduction is the lowest initial temperature for which

"completeness" is achieved for a given initial composition. As the H_2 concentration is increased, the optimum temperature for reduction decreases because the mixture becomes easier to ignite. As the initial H_2 concentration increases, the temperature window width shows a slight increase, then levels off, and is usually 50 K. The final mixture temperature determines where NOx reduction ceases and NOx production occurs, and the specific temperature for this decreases with increasing H_2 . The percentage of NOx reduced increases with increasing HNCO, but the breakthrough of N_2O , NH_3 and HNCO increases as well. It would appear that an HNCO/NOx ratio of 3 or 4 would be appropriate.

In Case E, the initial NOx is 4/3 that of Case B. Increasing the initial NOx had very little effect on the reduction at optimum conditions; however, as the initial temperature was increased beyond the optimum value, the NOx reduction was greater for the larger initial NOx. We also examined the reduction for the Case B1 conditions for an initial concentration of 7500 ppm H_2 with all the initial NOx present as NO to determine if the initial distribution of NOx between NO and NO_2 had any effect on the reduction. It did not.

As the initial H_2 concentration increases, the optimum temperature shifts to a lower value, and the final N_2O decreases. Nitrous oxide emissions at the optimum temperature can be as high as 70 ppm. Unfortunately, N_2O concentrations tend to be highest near the optimum reduction conditions. The breakthrough of NH_3 and HNCO tend to be quite high near the optimum temperature, and unlike N_2O , increase with initial H_2 concentration.

In order to determine a mechanistic understanding of the reduction process with added H_2 , concentration profiles, sensitivities, and rate of production analysis were analyzed in concert for Case B1 at 1050 K for the addition of 1500 ppm H_2 . Sensitivity coefficients of the various nitrogen species NO , NO_2 , N_2O , NH_3 , and $HNCO$, and temperature were computed. The concentrations of NO_x , N_2O , NH_3 , and $HNCO$ as a function of time are plotted in Figure 7. The NO_x profile declines gently in the first 0.5 seconds, changes slope and declines more until 0.57 seconds, then increases slightly until 0.62 seconds. The N_2O profile increases slightly until 0.55 seconds, rises steeply until 0.6 seconds, and then declines gently. The NH_3 increases gently, undergoes an abrupt increase and attains a maximum value at 0.57 seconds, and declines rapidly. The $HNCO$ profile declines gently until 0.53 seconds, decreases steeply until 0.57 seconds, and then declines less rapidly. Individual profiles of NO and NO_2 (not shown) show an immediate increase of NO and decrease in NO_2 at times less than 0.1 second. The NO then declines until 0.47 seconds while the NO_2 remains nearly constant. Approximately 1/3 of the NO is reduced during the first 0.5 seconds. At approximately 0.5 seconds there is rapid conversion of the NO_2 to NO evidenced by an increase in NO . There are four major processes which determine the fate of the NO during the time period between 0.5 and 0.65 seconds: the conversion of NO to NO_2 via HO_2 , the conversion of NO_2 to NO through reactions with H and O , the reduction of NO by NCO , and the reduction of NO by NH_i species.

The sensitivity coefficients as a function of time for the period of maximum sensitivity are shown for NO, N₂O, NO₂, NH₃, HNCO, and temperature in Figures 8-13, respectively. The ten most important reactions are the same for the nitrogen species and temperature. With the exception of the NO and NO₂ interconversion reactions 180 and 182, the important reactions are those concerned with thermal ignition, and do not involve nitrogen species directly. The oscillations in the NO sensitivity are due to the balance between the rates of production and destruction. When the two are balanced, the net NO rate is zero with resultant zero sensitivities. The radicals generated as a result of thermal ignition are used to affect the NO₂ conversion to NO, the reduction of NO via NCO and NH₁, and the conversion of NO to NO₂. The NO₂ chemistry ceases to be important after 0.57 seconds because the HO₂ has decreased enough that conversion of NO to NO₂ via HO₂ is no longer important. The competition between the formation of HO₂ and chain branching via H + O₂ dominates the region of highest NO sensitivity. Rate of production analysis confirmed that the major path for NO reduction was reactions with NH₁ species. The NH₁ reactions dominated the NCO path by at least a factor of 2, and it increased in importance with time. The HNCO and N₂O sensitivities had opposite signs, indicating the destruction of HNCO was crucial to the production of N₂O. The NH₃ sensitivities underwent a sign change at the time corresponding to the maximum in the NH₃ concentration. After the sign change in the NH₃ sensitivities and the third sign change in the NO sensitivities, reactions leading to the destruction of NH₃ also led to the

destruction of NO. We also saw evidence of the effect of HNCO chemistry on NO. The complex behavior in NO sensitivity is evidence of the complex chemistry occurring during the NO reduction. An oscillation in the NO sensitivity is also seen in Figure 8 of the Miller-Bowman 1991 paper.

The sensitivity coefficients for the nitrogen species and temperature were self-similar. Self-similarity obtains in a dynamical system where one or at most a few dependent variables dominate the physical behavior of the system. In an effort to learn if temperature was the dominant variable, the temperature profile computed for conditions being discussed was used as input for a second calculation using identical initial concentrations, the only difference in the second set being that temperature was no longer a dependent variable. Although some of the self-similar structure was lost, much of it was retained with the amount varying with the species. The magnitude of the sensitivities decreased markedly when the temperature profile was used as input. Two of the reactions of the most important ten were different. The self-similar structure of NO was only maintained in the region of largest sensitivity between the second and third sign changes. Self-similarity was lost for the sensitivities of NO₂ associated with reactions 128 and 129. For N₂O and HNCO, the sensitivity associated with reaction 5 lost its self-similar structure. The NH₃ sensitivity structure remained self-similar. Most likely there is another dependent variable (for example, OH) which plays a crucial role in dominating the system behavior.

Sensitivity coefficients were also computed for case B1 for the addition of 2.5×10^{-3} mole fraction of H_2 at 1050 K. The sensitivities were no longer self-similar. The reactions associated with the NO and NO_2 interconversions were not among the ten most important reactions, and were replaced with reactions 57 and 63. The magnitudes of the sensitivities also decreased markedly. The previous case of the addition of 1.5×10^{-3} mole fraction of H_2 was closer to a threshold set of conditions where the dynamical behavior of the system was more strongly coupled. Ignition and subsequent reduction were achieved more easily for the addition of the larger amount of H_2 . As shown in Table III, the threshold for "completeness" was achieved at a lower temperature of 1025 K where the reduction was optimum. The optimum conditions for reduction is always at the lowest value of initial temperature where "completeness" is achieved. It is likely that the optimum conditions yield the extreme coupling that gives rise to self-similarity.

3. The Effect of CO

The effect of CO as a radical booster was investigated by replacing H_2 in the case E compositions with additional CO by the amounts indicated in Tables VI through IX. The range of initial temperatures considered were 800 through 1175 K. NO_x was reduced by 19% for 2500 ppm additional CO at 1125 K, but NO_x was produced at 1130 K. Similar behavior was noted for the addition of 5000, 7500, and 10,000 ppm CO. As CO was increased, the temperature at which the optimum reduction occurred decreased, the percentage of NO_x reduced decreased, and NO_x was always produced for a 25

degree increment to the optimum temperature. The reduction of NO_x for an exhaust mixture characteristic of Case E with the H₂ replaced with additional CO was less than 20% and frequently less than 10%.

V. SUMMARY AND CONCLUSIONS

A chemical mechanism for the reduction of NO_x by HNCO has been constructed to model NO_x reduction in exhausts typical of natural gas combustion with the addition of radical boosters (fuel). The reduction was modeled assuming plug flow, and either isothermal combustion or constant pressure adiabatic combustion, using the SENKIN software with CHEMKIN-II, DASSL, and the Chemkin Thermodynamic Data Base of 1991. Variables considered were the initial concentrations of NO, NO₂, CO, O₂, CH₄, H₂, and HNCO as well as initial temperatures.

The chemical model was validated by comparing results with earlier model calculations of Miller and Bowman and with the experiments of Caton and Siebers and Lyon and Cole. The experiments were performed with mixtures of CO, O₂, H₂O, NO, and HNCO and not with CH₄ and H₂. Agreement with experiments was satisfactory.

The reduction chemistry must be preceded by thermal ignition chemistry which generates radicals. The lowest temperature for which ignition occurs is the optimum temperature for reduction and defines the beginning of the temperature window.

Reduction was not achieved for the prototypical "natural gas exhaust" for a reasonable residence time. Additional CH₄ was

added as a radical booster, and significant NOx reduction did not occur. Sensitivity analysis showed that radical generation is crucial for reduction to be achieved. Mixtures containing CH₄ as the only "exhaust fuel" could not be ignited at temperatures sufficiently low for reduction to occur. When final temperatures exceeded 1200 K, NO production, rather than NO reduction, occurred.

Hydrogen added to the exhaust mixtures enhanced ignition, and thus, reduction. As initial H₂ concentration increased, the optimum temperature for reduction decreased. The width of the temperature window increased slightly, leveled off, and achieved a value of approximately 50 K. The final combustion temperature determined where NOx reduction ceased and NOx production began, and the specific temperature where this occurred decreased with initial H₂ concentration. The emissions of N₂O, NH₃ and HNCO tended to be high near the optimum temperature. Emissions of N₂O were as high as 70 ppm under optimum conditions. The branching ratio of the NCO + NO reaction needed to be established before the N₂O could be predicted accurately.

Reduction increased with HNCO, and the breakthrough of N₂O, NH₃ and HNCO increased as well. It would appear that an HNCO/NOx ratio of 3 or 4 would be appropriate.

Increasing NOx had very little effect on the reduction in the "temperature window" for reduction, but did increase reduction for temperatures greater than the optimum value. The initial distribution of NOx between NO and NO₂ had no effect on the

reduction. Interconversion of NO and NO₂ preceded and occurred along with part of the reduction.

The sensitivity structure was rich and changed according to the exhaust composition and temperature. Sensitivity coefficients were calculated for NO, NO₂, N₂O, HNCO, NH₃, and temperature. The sensitivities used in concert with rate of production analysis and temporal species profiles revealed mechanistic information. Sensitivities calculated at the optimum temperature exhibited self-similarity. Four competitive reaction paths affected the fate of the NO: the conversion of NO to NO₂ via HO₂, the conversion of NO₂ to NO via reaction with H or O, the reduction of NO via NCO, and the reduction of NO from reactions with NH₁ species. The relative importance of the four was determined by the initial conditions. Important reactions were those that influenced ignition chemistry and radical generation. Two reactions that were always among the most important were $H + O_2 + M \rightarrow HO_2$, and the most important chain branching reaction, $H+O_2 \rightarrow OH+O$. The former was in competition with the latter.

There are caveats that need to be made before interpreting the results reported here. A real combustion exhaust would contain radicals that would facilitate the reduction of NO_x by HNCO. A real combustion exhaust would be neither isothermal nor adiabatic. Heat release would accompany the reduction process, but heat loss to the system would occur as well. Temperature is very important to the reduction because it determines whether ignition will occur and whether NO is reduced or produced.

Additional experiments are required to validate and refine the chemical model. The modeling results would be especially useful for guiding the selection of experimental conditions. Uncertainties in the model also could be diminished by reducing uncertainties in the most sensitive reactions. Three-body recombination reactions are important in the modeling, and different third-body efficiencies need to be measured more reliably. It is also important to measure branching ratios of reactions involving nitrogen species as a function of temperature.

ACKNOWLEDGMENT

This research has been supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098 and the California Institute of Energy Efficiency.

REFERENCES

- Atakan, B., and Wolfrum, J., (1991), Chem. Phys. Lett. 178, 157.
- Brown, N.J., Schefer, R.W., and Robben, F., (1983), Combust. and Flame 51, 263.
- Caton, J.A. and Siebers, D.L., (1990), 23rd Symp. (Int.) on Combust., The Combust. Inst., 225.
- Caton, J.A. and Siebers, D.L., (1989a), J. of Eng. for Gas Turbines and Power 111, 387.
- Caton, J.A. and Siebers, D.L., (1989b), Combust. Sci. Tech. 65, 277.
- Caton, J.A. and Siebers, D.L., (1988), "Comparison of Nitric Oxide Removal by Cyanuric Acid and by Ammonia," WSS/CI88-67. Presented at the 1988 Fall Meeting of the Western States Section/The Combustion Institute, October, 1988.
- Cookson, J.L., Hancock, G., and McKendrick, K.G., (1985), Ber. Bunsenges. Phys. Chem. 89, 335.
- Cooper, W.F., and Hershberger, J.F., (1992), J. Phys. Chem. 96, 771.
- Des Jardin, S., (1991), Private communication.
- Heap, M.P., Chen, S.L., McCarthy, J.M., Kramlich, J.C., and Pershing, D.W., (1988), Nature 335, 620.
- Kee, R.J., Rupley, F.M., and Miller, J.A., (1991), "Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical Kinetics," Sandia Report SAND89-8009 UC-401.
- Kee, R.J., Rupley, F.M., and Miller, J.A., (1991), "The Chemkin Thermodynamic Data Base," Sandia Report SAND87-8215B UC-4.
- Kenney, T.E., (1991), "A Whole New Ball Game: New Rules, New Tools." Presentation to Engineering Foundation Conference on Present and Future Engines for Automobiles II, Santa Barbara, CA.
- Lutz, A.E., Kee, R.J., and Miller, J.A., (1991), SENKIN, Sandia Report SAND8248 UC-401.
- Lyon, R.K. and Cole, J.A., (1990), Combust. and Flame 82, 435.
- Martin, R.J., and Brown, N.J., (1990), Combustion and Flame 82, 312.
- Martin, R.J., and Brown, N.J., (1990), Combustion and Flame 80, 238.

Martin, R.J. and Brown, Nancy J., (1989), Combustion and Flame 78, 365.

Martin, R.J., Lucas, D., and Brown, N.J., (1990), "Nitrogen Species Measurement in a Flash Ignited Combustion System", Poster Session 23rd Symp. (Int) on Combust., 78.

Miller, J.A., and Bowman, C.T., (1988), "Mechanism and Modeling of Nitrogen Chemistry in Combustion." WSS/CI88- . Presented at the 1988 Fall Meeting of the Western States Section/The Combustion Institute. October, 1988.

Miller, J.A., and Bowman, C.T., (1989), Prog. Energy Comb. Sci. 15, 287.

Miller, J.A. and Bowman, C.T., (1991), Int. J. Chem. Kinetics 23, 289.

Muzio, L.J., Martz, T.D., Montgomery, T.A., Quartucy, G.C., Cole, J.A., and Kramlich, 1990, "N₂O Formation in Selective Non-Catalytic NO_x Reduction Process," Presented at the American Flame Research Committee 1990 Fall International Symposium, November 1990.

Muzio, L.J., Montgomery, T.A., Samuelson, G.S., Kramlich, J.C., Lyon, R.K., and Kokkinos, A., (1990), 23rd Symp. (Int.) on Combust., The Combust. Inst., 245.

Perry, R.A., (1990), "Use of Isocyanic Acid to Reduce NO_x in a Commercial Diesel-Generator Set," Poster Session 23rd Symp. (Int) on Combust. 95.

Perry, R.A., (1989), "System for NO Reduction Using Sublimation of Cyanuric Acid," U.S. Patent 4,800,068.

Perry, R.A., (1988), "NO Reduction Using Sublimation of Cyanuric Acid," U.S. Patent 4,731,231.

Perry, R.A., (1988), "NO Reduction Using Cyanuric Acid: Pilot Scale Testing," WSS/CI88-68. Presented at the 1988 Fall Meeting of the Western States Section/The Combustion Institute, October, 1988.

Perry, R.A., (1985), J. Chem. Phys. 82, 5485.

Perry, R.A. and Siebers, D.L., (1986), Nature 324 18/25, 657.

Petzold, L.R., (1982) "A Description of DASSL: A Differential/algebraic System Solver," Sandia Report SAND82-8637.

Rabitz, H. and Smooke, M. D., (1988), J. Phys. Chem. 92, 1110.

Sarv, H. and Rodgers, L.W., (1989), "NO_x Reduction in an Industrial-scale Boiler by Injecting Cyanuric Acid Powder, "WSS/CI89-87. Presented at the 1989 Fall Meeting of the Western States Section/The Combustion Institute, October, 1989.

Siebers, D.L. and Caton, J.A., (1988), "Removal of Nitric Oxide from Exhaust Gas with Cyanuric Acid," WSS/CI88-66. Presented at the 1988 Fall Meeting of the Western States Section/The Combustion Institute, October, 1988.

LIST OF TABLES

TABLE I Chemical Mechanism used in study. Activation energies are given in cal/mol, and rate coefficients are given in $(\text{cm}^3/\text{mol s})^{n-1}$ where n is the order of reaction. Temperature is given in Kelvins.

TABLE II Initial composition for the various mixtures investigated in this study.

TABLE III Summary of NO_x reduction characteristics for Case B1 modeled as an adiabatic, constant pressure exhaust for a residence time of 1 sec. The superscripts i and f represent initial and final values, respectively. The initial H₂ concentration is 2500 ppm.

TABLE IV Summary of NO_x reduction characteristics for Case B1 modeled as an adiabatic, constant pressure exhaust for a residence time of 1 sec. The superscripts i and f represent initial and final values, respectively. The initial H₂ concentration is 7500 ppm.

TABLE V Summary of NO_x reduction characteristics for Case D modeled as an adiabatic, constant pressure exhaust for a residence time of 1 sec. The superscripts i and f represent initial and final values, respectively.

TABLE VI Summary of NO_x reduction characteristics for Case E modeled as an adiabatic, constant pressure exhaust for a residence time of 1 sec. The superscripts i and f represent initial and final values, respectively. The initial H₂ concentration is 2500 ppm.

TABLE VII Summary of NO_x reduction characteristics for Case E modeled as an adiabatic, constant pressure exhaust for a residence time of 1 sec. The superscripts i and f represent initial and final values, respectively. The initial H₂ concentration is 5000 ppm.

TABLE VIII Summary of NO_x reduction characteristics for Case E modeled as an adiabatic, constant pressure exhaust for a residence time of 1 sec. The superscripts i and f represent initial and final values, respectively. The initial H₂ concentration is 7500 ppm.

TABLE IX Summary of NO_x reduction characteristics for Case E modeled as an adiabatic, constant pressure exhaust for a residence time of 1 sec. The superscripts i and f represent initial and final values, respectively. The initial H₂ concentration is 10000 ppm.

LIST OF FIGURES

FIGURE 1 Concentration of indicated species in ppm as a function of reactor temperature in Kelvins for calculations run for Case A under isothermal plug flow conditions using the chemical mechanism given by Miller and Bowman.

FIGURE 2 Concentration of indicated species in ppm as a function of reactor temperature in Kelvins for calculations run for Case A under isothermal plug flow conditions using the chemical mechanism given by Brown and Garay in TABLE I.

FIGURE 3 Sensitivity of NO as a function of residence time in the reactor for the nine most important reactions of the mechanism given in TABLE I calculated at 1050 K under conditions given for Figure 2.

FIGURE 4 Sensitivity of N_2O as a function of residence time in the reactor for the nine most important reactions of the mechanism given in TABLE I calculated at 1050 K under conditions given for Figure 2.

FIGURE 5 Concentration of NO (ppm) as a function of initial CO mole percent for the mixture composition Case L. Calculations were performed assuming isothermal plug flow for a residence time of .76 seconds.

FIGURE 6 Sensitivity coefficients for NO as a function of residence time for the ten most important reactions for the B-G mechanism. Conditions are for Case L with 0.5% CO assuming isothermal conditions.

FIGURE 7 Concentration of $NO_x(NO+NO_2)$, N_2O , HNCO, and NH_3 (ppm) as a function of residence time (s) for mixture composition Case B1 at an initial temperature of 1050 K assuming adiabatic, constant pressure conditions.

FIGURE 8 Sensitivity coefficients of NO as a function of residence time for the ten most important reactions of B-G mechanism. Conditions are those of Figure 7.

FIGURE 9 Sensitivity coefficients of N_2O as a function of residence time for the ten most important reactions of B-G mechanism. Conditions are those of Figure 7.

FIGURE 10 Sensitivity coefficients of NO_2 as a function of residence time for the ten most important reactions of B-G mechanism. Conditions are those of Figure 7.

FIGURE 11 Sensitivity coefficients of NH_3 as a function of residence time for the ten most important reactions of B-G mechanism. Conditions are those of Figure 7.

FIGURE 12 Sensitivity coefficients of HNCO as a function of residence time for the ten most important reactions of B-G mechanism. Conditions are those of Figure 7.

FIGURE 13 Sensitivity coefficients of Temperature as a function of residence time for the ten most important reactions of B-G mechanism. Conditions are those of Figure 7.

TABLE I
(page 1)

CHEMKIN INTERPRETER OUTPUT: CHEMKIN-II Version 2.7 Feb. 1991
SINGLE PRECISION

ELEMENTS CONSIDERED	ATOMIC WEIGHT
1. H	1.00797
2. O	15.9994
3. C	12.0111
4. N	14.0067

SPECIES CONSIDERED	P H A S E	C H A R G E	MOLECULAR WEIGHT	TEMPERATURE		ELEMENT COUNT			
				LOW	HIGH	H	O	C	N
1. CH4	G	0	16.04303	300.0	5000.0	4	0	1	0
2. CH3	G	0	15.03506	300.0	5000.0	3	0	1	0
3. CH2	G	0	14.02709	250.0	4000.0	2	0	1	0
4. CH	G	0	13.01912	300.0	5000.0	1	0	1	0
5. CH2O	G	0	30.02849	300.0	5000.0	2	1	1	0
6. HCO	G	0	29.01852	300.0	5000.0	1	1	1	0
7. CO2	G	0	44.00995	300.0	5000.0	0	2	1	0
8. CO	G	0	28.01055	300.0	5000.0	0	1	1	0
9. H2	G	0	2.01594	300.0	5000.0	2	0	0	0
10. H	G	0	1.00797	300.0	5000.0	1	0	0	0
11. O2	G	0	31.99880	300.0	5000.0	0	2	0	0
12. O	G	0	15.99940	300.0	5000.0	0	1	0	0
13. OH	G	0	17.00737	300.0	5000.0	1	1	0	0
14. HO2	G	0	33.00677	300.0	5000.0	1	2	0	0
15. H2O2	G	0	34.01474	300.0	5000.0	2	2	0	0
16. H2O	G	0	18.01534	300.0	5000.0	2	1	0	0
17. C2H	G	0	26.03027	300.0	5000.0	1	0	2	0
18. C2H2	G	0	26.03024	300.0	5000.0	2	0	2	0
19. HCCO	G	0	41.02967	300.0	4000.0	1	1	2	0
20. C2H3	G	0	27.04621	300.0	5000.0	3	0	2	0
21. C2H4	G	0	28.05418	300.0	5000.0	4	0	2	0
22. C2H5	G	0	29.06215	300.0	5000.0	5	0	2	0
23. C2H6	G	0	30.07012	300.0	4000.0	6	0	2	0
24. CH2OH	G	0	31.03446	250.0	4000.0	3	1	1	0
25. CH3O	G	0	31.03446	300.0	3000.0	3	1	1	0
26. C3H2	G	0	38.04939	300.0	5000.0	2	0	3	0
27. CH2(S)	G	0	14.02709	300.0	4000.0	2	0	1	0
28. CH2CO	G	0	42.03764	300.0	5000.0	2	1	2	0
29. C	G	0	12.01115	300.0	5000.0	0	0	1	0
30. C4H2	G	0	50.06854	300.0	5000.0	2	0	4	0
31. HCCOH	G	0	42.03764	300.0	4000.0	2	1	2	0
32. N2	G	0	28.01340	300.0	5000.0	0	0	0	2
33. NO	G	0	30.00610	300.0	5000.0	0	1	0	1
34. N	G	0	14.00670	300.0	5000.0	0	0	0	1
35. NH	G	0	15.01467	300.0	5000.0	1	0	0	1
36. NH2	G	0	16.02264	300.0	5000.0	2	0	0	1
37. HNO	G	0	31.01407	300.0	5000.0	1	1	0	1
38. HCN	G	0	27.02582	300.0	5000.0	1	0	1	1
39. NCO	G	0	42.01725	300.0	5000.0	0	1	1	1
40. CN	G	0	26.01785	300.0	5000.0	0	0	1	1
41. N2O	G	0	44.01280	300.0	5000.0	0	1	0	2
42. NNH	G	0	29.02137	250.0	4000.0	1	0	0	2
43. HNCO	G	0	43.02522	300.0	4000.0	1	1	1	1
44. C2N2	G	0	52.03570	300.0	5000.0	0	0	2	2
45. NO2	G	0	46.00550	300.0	5000.0	0	2	0	1
46. HOCN	G	0	43.02522	250.0	4000.0	1	1	1	1
47. HCNO	G	0	43.02522	250.0	4000.0	1	1	1	1
48. H2CN	G	0	28.03379	300.0	4000.0	2	0	1	1
49. NH3	G	0	17.03061	300.0	5000.0	3	0	0	1
50. N2H2	G	0	30.02934	300.0	5000.0	2	0	0	2

TABLE I
(page 2)

REACTIONS CONSIDERED		(k = A T ^a exp(-E/RT))		
		A	b	E
1. CH ₃ +CH ₃ (+M)=C ₂ H ₆ (+M)		9.03e+16	-1.2	654.0
Low pressure limit:	0.31800e+42 -0.70300e+01	0.27620e+04		
TROE centering:	0.60410e+00 0.69270e+04	0.13200e+03		
H ₂	Enhanced by 2.000e+00			
CO	Enhanced by 2.000e+00			
CO ₂	Enhanced by 3.000e+00			
H ₂ O	Enhanced by 5.000e+00			
2. CH ₃ +H(+M)=CH ₄ (+M)		6.00e+16	-1.0	0.0
Low pressure limit:	0.80000e+27 -0.30000e+01	0.		
SRI centering:	0.45000e+00 0.79700e+03	0.97900e+03		
H ₂	Enhanced by 2.000e+00			
CO	Enhanced by 2.000e+00			
CO ₂	Enhanced by 3.000e+00			
H ₂ O	Enhanced by 5.000e+00			
3. CH ₄ +O ₂ =CH ₃ +HO ₂		7.90e+13	0.0	56000.0
4. CH ₄ +H=CH ₃ +H ₂		2.20e+04	3.0	8750.0
5. CH ₄ +OH=CH ₃ +H ₂ O		1.60e+06	2.1	2400.0
6. CH ₄ +O=CH ₃ +OH		1.02e+08	1.5	8604.0
7. CH ₄ +HO ₂ =CH ₃ +H ₂ O ₂		1.80e+11	0.0	18700.0
8. CH ₃ +HO ₂ =CH ₃ O+OH		2.00e+13	0.0	0.0
9. CH ₃ +O ₂ =CH ₃ O+O		2.05e+10	-1.6	29229.0
10. CH ₃ +O=CH ₂ O+H		0.00e+13	0.0	0.0
11. CH ₂ OH+H=CH ₃ +OH		1.00e+14	0.0	0.0
12. CH ₃ O+H=CH ₃ +OH		1.00e+14	0.0	0.0
13. CH ₃ +OH=CH ₂ +H ₂ O		7.50e+06	2.0	5000.0
14. CH ₃ +H=CH ₂ +H ₂		9.00e+13	0.0	15100.0
15. CH ₃ O+M=CH ₂ O+H+M		1.00e+14	0.0	25000.0
16. CH ₂ OH+M=CH ₂ O+H+M		1.00e+14	0.0	25000.0
17. CH ₃ O+H=CH ₂ O+H ₂		2.00e+13	0.0	0.0
18. CH ₂ OH+H=CH ₂ O+H ₂		2.00e+13	0.0	0.0
19. CH ₃ O+OH=CH ₂ O+H ₂ O		1.00e+13	0.0	0.0
20. CH ₂ OH+OH=CH ₂ O+H ₂ O		1.00e+13	0.0	0.0
21. CH ₃ O+O=CH ₂ O+OH		1.00e+13	0.0	0.0
22. CH ₂ OH+O=CH ₂ O+OH		1.00e+13	0.0	0.0
23. CH ₃ O+O ₂ =CH ₂ O+HO ₂		6.30e+10	0.0	2800.0
24. CH ₂ OH+O ₂ =CH ₂ O+HO ₂		1.40e+13	0.0	1500.0
25. CH ₂ +H=CH+H ₂		1.00e+10	-1.6	0.0
26. CH ₂ +OH=CH+H ₂ O		1.13e+07	2.0	3000.0
27. CH ₂ +OH=CH ₂ O+H		2.50e+13	0.0	0.0
28. CH+O ₂ =HCO+O		3.30e+13	0.0	0.0
29. CH+O=CO+H		5.70e+13	0.0	0.0
30. CH+OH=HCO+H		3.00e+13	0.0	0.0
31. CH+CO ₂ =HCO+CO		3.40e+12	0.0	690.0
32. CH+H=C+H ₂		1.50e+14	0.0	0.0
33. CH+H ₂ O=CH ₂ O+H		4.57e+14	-0.0	0.0
34. CH+CH ₂ O=CH ₂ CO+H		9.46e+13	0.0	-515.0
35. CH+C ₂ H ₂ =C ₃ H ₂ +H		1.00e+14	0.0	0.0
36. CH+CH ₂ =C ₂ H ₂ +H		4.00e+13	0.0	0.0
37. CH+CH ₃ =C ₂ H ₃ +H		3.00e+13	0.0	0.0
38. CH+CH ₄ =C ₂ H ₄ +H		6.00e+13	0.0	0.0
39. C+O ₂ =CO+O		2.00e+13	0.0	0.0
40. C+OH=CO+H		5.00e+13	0.0	0.0
41. C+CH ₃ =C ₂ H ₂ +H		5.00e+13	0.0	0.0
42. C+CH ₂ =C ₂ H+H		5.00e+13	0.0	0.0
43. CH ₂ +CO ₂ =CH ₂ O+CO		1.10e+11	0.0	1000.0
44. CH ₂ +O=CO+H+H		5.00e+13	0.0	0.0
45. CH ₂ +O=CO+H ₂		3.00e+13	0.0	0.0
46. CH ₂ +O ₂ =CO ₂ +H+H		1.60e+12	0.0	1000.0
47. CH ₂ +O ₂ =CH ₂ O+O		5.00e+13	0.0	9000.0
48. CH ₂ +O ₂ =CO ₂ +H ₂		6.90e+11	0.0	500.0
49. CH ₂ +O ₂ =CO+H ₂ O		1.90e+10	0.0	-1000.0
50. CH ₂ +O ₂ =CO+OH+H		8.00e+10	0.0	-500.0
51. CH ₂ +O ₂ =HCO+OH		4.30e+10	0.0	-500.0
52. CH ₂ O+OH=HCO+H ₂ O		3.43e+09	1.2	-447.0
53. CH ₂ O+H=HCO+H ₂		2.19e+08	1.8	3000.0
54. CH ₂ O+M=HCO+H+M		3.31e+16	0.0	81000.0
55. CH ₂ O+O=HCO+OH		1.80e+13	0.0	3000.0
56. HCO+OH=H ₂ O+CO		1.00e+14	0.0	0.0
57. HCO+M=H+CO+M		2.50e+14	0.0	16802.0
CO	Enhanced by 1.870e+00			
H ₂	Enhanced by 1.870e+00			
CH ₄	Enhanced by 2.010e+00			
CO ₂	Enhanced by 3.000e+00			
H ₂ O	Enhanced by 5.000e+00			

TABLE I
(page 3)

58.	HCO+H=CO+H2	1.19E+13	0.3	0.0
59.	HCO+O=CO+OH	3.00E+13	0.0	0.0
60.	HCO+O=CO2+H	3.00E+13	0.0	0.0
61.	HCO+O2=H2O2+CO	3.30E+13	-0.4	0.0
62.	CO+O+M=CO2+M	0.17E+14	0.0	3000.0
63.	CO+OH=CO2+H	1.51E+07	1.3	-758.0
64.	CO+O2=CO2+O	2.53E+12	0.0	47888.0
65.	H2O2+CO=CO2+OH	5.80E+13	0.0	22934.0
66.	C2H6+CH3=C2H5+CH4	5.50E-01	4.0	8300.0
67.	C2H6+H=C2H5+H2	5.40E+02	3.5	5210.0
68.	C2H6+O=C2H5+OH	3.00E+07	2.0	5115.0
69.	C2H6+OH=C2H5+H2O	8.70E+09	1.0	1810.0
70.	C2H4+H=C2H3+H2	1.10E+14	0.0	8500.0
71.	C2H4+O=CH3+HCO	1.00E+09	1.2	748.0
72.	C2H4+OH=C2H3+H2O	2.02E+13	0.0	5955.0
73.	CH2+CH3=C2H4+H	3.00E+13	0.0	0.0
74.	H+C2H4(+M)=C2H5(+M)	2.21E+13	0.0	2066.0
Low pressure limit: 0.63690E+28 -0.27600E+01 -0.54000E+02				
	H2	Enhanced by	2.000E+00	
	CO	Enhanced by	2.000E+00	
	CO2	Enhanced by	3.000E+00	
	H2O	Enhanced by	5.000E+00	
75.	C2H5+H=CH3+CH3	1.00E+14	0.0	0.0
76.	C2H5+O2=C2H4+H2O	8.43E+11	0.0	3875.0
77.	C2H2+O=CH2+CO	1.02E+07	2.0	1900.0
78.	C2H2+O=HCCO+H	1.02E+07	2.0	1900.0
79.	H2+C2H=C2H2+H	4.09E+05	2.4	864.3
80.	H+C2H2(+M)=C2H3(+M)	5.54E+12	0.0	2410.0
Low pressure limit: 0.26700E+28 -0.35000E+01 0.24100E+04				
	H2	Enhanced by	2.000E+00	
	CO	Enhanced by	2.000E+00	
	CO2	Enhanced by	3.000E+00	
	H2O	Enhanced by	5.000E+00	
81.	C2H3+H=C2H2+H2	4.00E+13	0.0	0.0
82.	C2H3+O=CH2CO+H	3.00E+13	0.0	0.0
83.	C2H3+O2=CH2O+HCO	4.00E+12	0.0	-250.0
84.	C2H3+OH=C2H2+H2O	5.00E+12	0.0	0.0
85.	C2H3+CH2=C2H2+CH3	3.00E+13	0.0	0.0
86.	C2H3+C2H=C2H2+C2H2	3.00E+13	0.0	0.0
87.	C2H3+CH=CH2+C2H2	5.00E+13	0.0	0.0
88.	OH+C2H2=C2H+H2O	3.37E+07	2.0	14000.0
89.	OH+C2H2=HCCOH+H	5.04E+05	2.3	13500.0
90.	OH+C2H2=CH2CO+H	2.18E-04	4.5	-1000.0
91.	OH+C2H2=CH3+CO	4.83E-04	4.0	-2000.0
92.	HCCOH+H=CH2CO+H	1.00E+13	0.0	0.0
93.	C2H2+O=C2H+OH	3.16E+15	-0.6	15000.0
94.	CH2CO+O=CO2+CH2	1.75E+12	0.0	1350.0
95.	CH2CO+H=CH3+CO	1.13E+13	0.0	3420.0
96.	CH2CO+H=HCCO+H2	5.00E+13	0.0	8000.0
97.	CH2CO+O=HCCO+OH	1.00E+13	0.0	8000.0
98.	CH2CO+OH=HCCO+H2O	7.50E+12	0.0	2000.0
99.	CH2CO(+M)=CH2+CO(+M)	3.00E+14	0.0	70980.0
Low pressure limit: 0.36000E+16 0.00000E+00 0.59270E+05				
100.	C2H+O2=CO+CO+H	5.00E+13	0.0	1500.0
101.	C2H+C2H2=C4H2+H	3.00E+13	0.0	0.0
102.	H+HCCO=CH2(S)+CO	1.00E+14	0.0	0.0
103.	O+HCCO=H+CO+CO	1.00E+14	0.0	0.0
104.	HCCO+O2=CO+CO+OH	1.60E+12	0.0	854.0
105.	CH+HCCO=C2H2+CO	5.00E+13	0.0	0.0
106.	HCCO+HCCO=C2H2+CO+CO	1.00E+13	0.0	0.0
107.	CH2(S)+M=CH2+M	1.00E+13	0.0	0.0
	H	Enhanced by	0.000E+00	
108.	CH2(S)+CH4=CH3+CH3	4.00E+13	0.0	0.0
109.	CH2(S)+C2H6=CH3+C2H5	1.20E+14	0.0	0.0
110.	CH2(S)+O2=CO+OH+H	3.00E+13	0.0	0.0
111.	CH2(S)+H2=CH3+H	7.00E+13	0.0	0.0
112.	CH2(S)+H=CH2+H	2.00E+14	0.0	0.0
113.	C2H+O=CH+CO	5.00E+13	0.0	0.0
114.	C2H+OH=HCCO+H	2.00E+13	0.0	0.0
115.	CH2+CH2=C2H2+H2	4.00E+13	0.0	0.0
116.	CH2+HCCO=C2H3+CO	3.00E+13	0.0	0.0
117.	C4H2+OH=C3H2+HCO	0.68E+12	0.0	-410.0
118.	C3H2+O2=HCO+HCCO	1.00E+13	0.0	0.0
119.	C4H2+O=C3H2+CO	1.20E+12	0.0	0.0
120.	C2H2+O2=HCCO+OH	2.00E+08	1.5	30100.0
121.	C2H2+M=C2H+H+M	4.20E+16	0.0	107000.0
122.	C2H4+M=C2H2+H2+M	1.50E+15	0.0	55800.0
123.	C2H4+M=C2H3+H+M	1.40E+15	0.0	82360.0
124.	H2+O2=2OH	1.70E+13	0.0	47780.0
125.	OH+H2=H2O+H	1.17E+09	1.3	3628.0
126.	O+OH=O2+H	4.00E+14	-0.5	0.0
127.	O+H2=OH+H	5.06E+04	2.7	6290.0

TABLE I
(page 4)

128.	H+O2+M=H2O+M			3.61E+17	-0.7	0.0
	H2O	Enhanced by	1.000E+01			
	H2	Enhanced by	2.000E+00			
	N2	Enhanced by	1.300E+00			
129.	OH+H2=H2O+O2			2.12E+15	-0.6	340.0
130.	H+H2=2OH			1.40E+14	0.0	1073.0
131.	O+H2=O2+OH			1.40E+13	0.0	1073.0
132.	2OH=O+H2O			6.00E+08	1.3	0.0
133.	H+H+M=H2+M			1.00E+18	-1.0	0.0
	H2	Enhanced by	0.000E+00			
	H2O	Enhanced by	0.000E+00			
134.	H+H+H2=H2+H2			9.20E+16	-0.6	0.0
135.	H+H+H2O=H2+H2O			6.00E+19	-1.2	0.0
136.	H+OH+M=H2O+M			1.60E+22	-2.0	0.0
	H2O	Enhanced by	5.000E+00			
137.	H+O+M=OH+M			6.20E+16	-0.6	0.0
	H2O	Enhanced by	5.000E+00			
138.	O+O+M=O2+M			1.89E+13	0.0	-1788.0
139.	H+H2=H2+O2			1.25E+13	0.0	0.0
140.	H2O2+H2=H2O2+O2			2.00E+12	0.0	0.0
141.	H2O2+M=OH+OH+M			1.30E+17	0.0	45500.0
142.	H2O2+H=H2O+H2			1.60E+12	0.0	3800.0
143.	H2O2+OH=H2O+H2O2			1.00E+13	0.0	1800.0
144.	CH+N2=HCN+N			3.00E+11	0.0	13600.0
145.	CN+N=C+N2			1.04E+15	-0.5	0.0
146.	CH2+N2=HCN+NH			1.60E+13	0.0	74000.0
147.	H2CN+N=N2+CH2			2.00E+13	0.0	0.0
148.	H2CN+M=HCN+H+M			3.00E+14	0.0	22000.0
149.	C+N2=CN+O			8.00E+13	0.0	0.0
150.	CH+N2=HCN+O			1.10E+14	0.0	0.0
151.	CH2+N2=HCN+O+H			1.39E+12	0.0	-1100.0
152.	CH3+N2=HCN+H2O			1.00E+11	0.0	15000.0
153.	CH3+N2=H2CN+OH			1.00E+11	0.0	15000.0
154.	HCCO+N2=HCN+CO			2.00E+13	0.0	0.0
155.	CH2(S)+N2=HCN+OH			2.00E+13	0.0	0.0
156.	HCNO+H=HCN+OH			1.00E+14	0.0	-12000.0
157.	CH2+N=HCN+H			5.00E+13	0.0	0.0
158.	CH+N=CN+H			1.30E+13	0.0	0.0
159.	CO2+N=N2+CO			1.90E+11	0.0	3400.0
160.	HCCO+N=HCN+CO			5.00E+13	0.0	0.0
161.	CH3+N=H2CN+H			3.00E+13	0.0	0.0
162.	C2H3+N=HCN+CH2			2.00E+13	0.0	0.0
163.	HCN+OH=CN+H2O			1.45E+13	0.0	10929.0
164.	OH+HCN=HOCN+H			5.85E+04	2.4	12500.0
165.	OH+HCN=HNCO+H			1.98E-03	4.0	1000.0
166.	OH+HCN=NH2+CO			7.83E-04	4.0	4000.0
167.	HOCN+H=HNCO+H			1.00E+13	0.0	0.0
168.	HCN+O=NC+O+H			1.38E+04	2.6	4980.0
169.	HCN+O=NH+CO			3.45E+03	2.6	4980.0
170.	HCN+O=CN+OH			2.70E+09	1.6	26600.0
171.	CN+H2=HCN+H			2.95E+05	2.5	2237.0
172.	CN+O=CO+N			1.80E+13	0.0	0.0
173.	CN+O2=NC+O			5.60E+12	0.0	0.0
174.	CN+OH=NC+O+H			8.00E+13	0.0	0.0
175.	CN+HCN=C2N2+H			2.00E+13	0.0	0.0
176.	CN+N2=NC+N2			3.00E+13	0.0	0.0
177.	CN+N2O=NC+N2			1.00E+13	0.0	0.0
178.	C2N2+O=NC+CN			4.57E+12	0.0	8880.0
179.	C2N2+OH=HOCN+CN			1.86E+11	0.0	2900.0
180.	H2O+N2=NO2+OH			2.11E+12	0.0	-479.0
181.	NO2+H=NO+OH			3.50E+14	0.0	1500.0
182.	NO2+O=NO+O2			1.00E+13	0.0	600.0
183.	NO2+M=NO+O+M			1.10E+18	0.0	66000.0
184.	NC+O=NH+CO			5.00E+13	0.0	0.0
185.	NC+O=NO+CO			2.00E+13	0.0	0.0
186.	NC+O=N2+CO			2.00E+13	0.0	0.0
187.	NC+OH=NO+HCO			5.00E+12	0.0	15000.0
188.	NC+O2=NO+CO2			3.01E+06	0.0	0.0
189.	NC+M=N+CO+M			3.10E+16	-0.5	48000.0
190.	NC+N2=N2+CO2			1.00E+13	0.0	-390.0
191.	NC+H2=HNCO+H			8.58E+12	0.0	9000.0
192.	HNCO+H=NH2+CO			2.90E+08	1.5	5300.0
193.	HNCO+M=NH+CO+M			1.14E+16	0.0	86800.0
194.	NH+HNCO=NH2+NC			3.00E+13	0.0	23700.0
195.	NH2+HNCO=NH3+NC			5.00E+12	0.0	6200.0
196.	HNCO+OH=NC+H2O			1.99E+12	0.0	5540.0
197.	HNCO+OH=NH2+CO2			6.62E+11	0.0	5540.0
198.	O+HNCO=NH+CO2			1.35E+12	0.0	10300.0
199.	O+HNCO=HNO+CO			1.90E+12	0.0	10300.0
200.	H2O+HNCO=NC+H2O2			3.00E+11	0.0	29000.0
201.	H2O+NH3=NH2+H2O2			3.00E+11	0.0	22000.0
202.	NH2+N2=N2+H2O			2.84E+18	-2.2	0.0

TABLE I
(page 5)

203.	NH+NO2=N2O+OH			1.00E+13	0.0	0.0
204.	NH+O=NO+H			2.00E+13	0.0	0.0
205.	NH+O2=HNO+O			1.00E+13	0.0	12000.0
206.	NH+O2=NO+OH			7.00E+10	0.0	1530.0
207.	NH+NO=N2O+H			2.40E+15	-0.8	0.0
208.	N2O+OH=N2+H2O			2.00E+12	0.0	10000.0
209.	N2O+H=N2+OH			7.00E+13	0.0	15200.0
210.	N2O+M=N2+O+M			6.95E+14	0.0	56530.0
	N2	Enhanced by	1.500E+00			
	O2	Enhanced by	1.500E+00			
	H2O	Enhanced by	5.000E+00			
211.	N2O+O=N2+O2			1.00E+14	0.0	28200.0
212.	N2O+O=NO+NO			1.00E+14	0.0	28200.0
213.	NH+OH=HNO+H			2.00E+13	0.0	0.0
214.	NH+OH=N+H2O			5.00E+11	0.5	2000.0
215.	NH+N=N2+H			3.00E+13	0.0	0.0
216.	NH+H=N+H2			1.00E+14	0.0	0.0
217.	NH2+NH=N2H2+H			5.00E+13	0.0	0.0
218.	2NH=N2+2H			2.54E+13	0.0	0.0
219.	NH2+N=N2+2H			7.20E+13	0.0	0.0
220.	N2H2+M=NNH+H+M			5.00E+16	0.0	50000.0
	H2O	Enhanced by	1.500E+01			
	O2	Enhanced by	2.000E+00			
	N2	Enhanced by	2.000E+00			
	H2	Enhanced by	2.000E+00			
221.	N2H2+H=NNH+H2			5.00E+13	0.0	1000.0
222.	N2H2+O=NH2+NO			1.00E+13	0.0	0.0
223.	N2H2+O=NNH+OH			2.00E+13	0.0	1000.0
224.	N2H2+OH=NNH+H2O			1.00E+13	0.0	1000.0
225.	N2H2+NO=N2O+NH2			3.00E+12	0.0	0.0
226.	N2H2+NH=NNH+NH?			1.00E+13	0.0	1000.0
227.	N2H2+NH2=NH3+NNH			1.00E+13	0.0	1000.0
228.	2NH2=N2H2+H2			5.00E+11	0.0	0.0
229.	NH2+O2=HNO+OH			4.50E+12	0.0	25000.0
230.	NH2+O=HNO+H			0.63E+14	-0.5	0.0
231.	NH2+O=NH+OH			0.75E+12	0.0	0.0
232.	NH2+OH=NH+H2O			4.00E+06	2.0	1000.0
233.	NH2+H=NH+H2			0.92E+13	0.0	3650.0
234.	NH2+NO=NNH+OH			0.40E+15	-1.2	0.0
235.	NH2+NO=N2+H2O			0.20E+15	-1.2	0.0
236.	NH3+OH=NH2+H2O			2.04E+06	2.0	586.0
237.	NH3+H=NH2+H2			0.30E+05	2.4	10171.0
238.	NH3+O=NH2+OH			2.10E+13	0.0	9000.0
239.	NNH=N2+H			1.00E+04	0.0	0.0
240.	NNH+NO=N2+HNO			5.00E+13	0.0	0.0
241.	NNH+H=N2+H2			1.00E+14	0.0	0.0
242.	NNH+OH=N2+H2O			5.00E+13	0.0	0.0
243.	NNH+NH2=N2+NH3			5.00E+13	0.0	0.0
244.	NNH+NH=N2+NH2			5.00E+13	0.0	0.0
245.	NNH+O=N2O+H			1.00E+14	0.0	0.0
246.	HNO+M=H+NO+M			1.50E+16	0.0	48600.0
	H2O	Enhanced by	1.000E+01			
	O2	Enhanced by	2.000E+00			
	N2	Enhanced by	2.000E+00			
	H2	Enhanced by	2.000E+00			
247.	HNO+O=OH+NO			1.00E+13	0.0	0.0
248.	HNO+O2=HO2+NO			1.00E+13	0.0	25000.0
249.	HNO+OH=NO+H2O			7.00E+13	0.0	0.0
250.	HNO+H=H2+NO			6.00E+12	0.0	0.0
251.	HNO+NH2=NH3+NO			2.00E+13	0.0	1000.0
252.	2HNO=N2O+H2O			3.95E+12	0.0	5000.0
253.	HNO+NO=N2O+OH			2.00E+12	0.0	20000.0
254.	N+NO=N2+O			3.27E+12	0.3	0.0
255.	N+O2=NO+O			0.40E+09	1.0	6200.0
256.	N+OH=NO+H			3.80E+13	0.0	0.0

NOTE: A units mole-cm-sec-K, E units cal/mole

TABLE II
Initial Mixture Composition

CASE	CH ₄	H ₂	O ₂	H ₂ O	CO	CO ₂	HNCO	NO	NO ₂	N ₂	T
A	0	0	12.3x10 ⁻²	4.5x10 ⁻²	1.26x10 ⁻³	0	1.41x10 ⁻³	3.3x10 ⁻⁴	0	8.29x10 ⁻¹	800-1350
B2	2.5x10 ⁻³	0	8.25x10 ⁻²	1.15x10 ⁻¹	5.5x10 ⁻⁴	5.77x10 ⁻²	6.62x10 ⁻⁴	1.1x10 ⁻⁴	4.5x10 ⁻⁵	7.4x10 ⁻¹	1050-1150
B1	2.49x10 ⁻³	variable	8.23x10 ⁻²	1.15x10 ⁻¹	5.48x10 ⁻⁴	5.76x10 ⁻²	6.60x10 ⁻⁴	1.1x10 ⁻⁴	4.5x10 ⁻⁵	7.39x10 ⁻¹	800-1200
C	variable	0	8.19x10 ⁻²	1.14x10 ⁻¹	5.46x10 ⁻⁴	5.72x10 ⁻²	6.57x10 ⁻⁴	1.1x10 ⁻⁴	4.47x10 ⁻⁵	7.35x10 ⁻¹	1050-1200
D	2.5x10 ⁻³	2.5x10 ⁻³	8.25x10 ⁻²	1.15x10 ⁻¹	5.5x10 ⁻⁴	5.77x10 ⁻²	variable	1.55x10 ⁻⁴	0	7.41x10 ⁻¹	1025
E	2.48x10 ⁻³	variable	8.18x10 ⁻²	1.15x10 ⁻¹	5.5x10 ⁻⁴	5.73x10 ⁻²	6.57x10 ⁻⁴	1.54x10 ⁻⁴	4.46x10 ⁻⁵	7.35x10 ⁻¹	800-1125
L	0	0	4.3x10 ⁻²	2.65x10 ⁻²	variable	0	4.9x10 ⁻⁴	1.45x10 ⁻⁴	0	9.3x10 ⁻¹	978

Concentrations in mole fractions.
Temperatures in Kelvins.

TABLE III

NO_x Reduction for Case B1 H2=2500 (ppm)

Ti	Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[H ₂ CO]i	[H ₂ CO]f	[NH3]f	% NO _x Reduced
800. I	800.	0.110E-03	0.109E-03	0.449E-04	0.452E-04	0.331E-07	0.000E-03	0.000E-03	0.131E-07	0
850. I	850.	0.110E-03	0.108E-03	0.449E-04	0.461E-04	0.373E-06	0.000E-03	0.000E-03	0.260E-06	0
900. I	902.	0.110E-03	0.106E-03	0.449E-04	0.441E-04	0.250E-05	0.000E-03	0.000E-03	0.278E-05	3
925. I	929.	0.110E-03	0.079E-04	0.449E-04	0.463E-04	0.500E-05	0.000E-03	0.042E-03	0.740E-05	6
950. I	959.	0.110E-03	0.017E-04	0.449E-04	0.542E-04	0.101E-04	0.000E-03	0.025E-03	0.150E-04	12
975. I	990.	0.110E-03	0.500E-04	0.449E-04	0.509E-04	0.157E-04	0.000E-03	0.002E-03	0.273E-04	18
1000. I	1030.	0.110E-03	0.242E-04	0.449E-04	0.016E-04	0.270E-04	0.000E-03	0.554E-03	0.510E-04	31
1025. C	1110.	0.110E-03	0.157E-04	0.449E-04	0.469E-05	0.000E-04	0.000E-03	0.282E-04	0.144E-04	86
1050. C	1135.	0.110E-03	0.357E-04	0.449E-04	0.704E-05	0.572E-04	0.000E-03	0.118E-04	0.475E-05	72
1100. C	1184.	0.110E-03	0.130E-03	0.449E-04	0.002E-05	0.287E-04	0.000E-03	0.787E-06	0.150E-06	10
1150. C	1233.	0.110E-03	0.271E-03	0.449E-04	0.398E-05	0.489E-05	0.000E-03	0.000E-03	0.114E-08	-77
1200. C	1282.	0.110E-03	0.398E-03	0.449E-04	0.272E-05	0.142E-06	0.000E-03	0.551E-10	0.524E-11	-158

TABLE IV

NO _x Reduction for Case B1 H2=7500 (ppm)										
Ti	Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[HNC0]i	[HNC0]f	[NH3]f	% NO _x Reduced
800. I	802.	0.109E-03	0.931E-04	0.447E-04	0.575E-04	0.154E-05	0.657E-03	0.653E-03	0.121E-05	2
850. I	871.	0.109E-03	0.605E-04	0.447E-04	0.563E-04	0.147E-04	0.657E-03	0.608E-03	0.187E-04	20
900. I	1005.	0.109E-03	0.615E-05	0.447E-04	0.724E-05	0.614E-04	0.657E-03	0.339E-03	0.120E-03	91
925. C	1044.	0.109E-03	0.417E-05	0.447E-04	0.280E-05	0.303E-04	0.657E-03	0.114E-03	0.803E-04	95
950. C	1070.	0.109E-03	0.610E-05	0.447E-04	0.259E-05	0.390E-04	0.657E-03	0.532E-04	0.344E-04	94
975. C	1095.	0.109E-03	0.144E-04	0.447E-04	0.473E-05	0.539E-04	0.657E-03	0.263E-04	0.135E-04	87
1000. C	1120.	0.109E-03	0.409E-04	0.447E-04	0.839E-05	0.585E-04	0.657E-03	0.102E-04	0.349E-05	87
1025. C	1144.	0.109E-03	0.107E-03	0.447E-04	0.122E-04	0.500E-04	0.657E-03	0.230E-05	0.427E-06	22
1050. C	1168.	0.109E-03	0.209E-03	0.447E-04	0.129E-04	0.323E-04	0.657E-03	0.340E-06	0.381E-07	-44
1075. C	1193.	0.109E-03	0.309E-03	0.447E-04	0.101E-04	0.162E-04	0.657E-03	0.439E-07	0.388E-08	-107
1100. C	1217.	0.109E-03	0.393E-03	0.447E-04	0.675E-05	0.620E-05	0.657E-03	0.433E-08	0.355E-09	-160

TABLE V

		NO _x Reduction Variable HNC0							
Ti	Tf	[NO]i	[NO]f	[NO ₂]i	[NO ₂]f	[N ₂ O]f	[HNC0]i	[HNC0]f	[NH ₃]f % NO _x Reduced
1025.	1105.	0.110E-03	0.730E-04	0.449E-04	0.520E-05	0.235E-04	0.105E-03	0.205E-05	0.493E-06 48
1025.	1107.	0.110E-03	0.303E-04	0.449E-04	0.579E-05	0.407E-04	0.330E-03	0.900E-05	0.320E-05 72
1025.	1108.	0.110E-03	0.210E-04	0.449E-04	0.537E-05	0.524E-04	0.495E-03	0.100E-04	0.037E-05 82
1025.	1110.	0.110E-03	0.157E-04	0.449E-04	0.409E-05	0.000E-04	0.000E-03	0.202E-04	0.144E-04 88
1025.	1112.	0.110E-03	0.130E-04	0.449E-04	0.401E-05	0.030E-04	0.025E-03	0.371E-04	0.200E-04 89

TABLE VI

NO_x Reduction for Case E H₂=2500 (ppm)

Ti	Tf	[NO]i	[NO]f	[NO ₂]i	[NO ₂]f	[N ₂ O]f	[H ₂ CO]i	[H ₂ CO]f	[NH ₃]f	% NO _x Reduced
800. I	800.	0.155E-03	0.154E-03	0.448E-04	0.452E-04	0.335E-07	0.660E-03	0.660E-03	0.101E-07	0
850. I	850.	0.155E-03	0.153E-03	0.448E-04	0.461E-04	0.402E-06	0.660E-03	0.659E-03	0.215E-06	0
900. I	902.	0.155E-03	0.150E-03	0.448E-04	0.442E-04	0.277E-05	0.660E-03	0.652E-03	0.237E-05	2
925. I	929.	0.155E-03	0.141E-03	0.448E-04	0.461E-04	0.629E-05	0.660E-03	0.641E-03	0.640E-05	6
950. I	958.	0.155E-03	0.124E-03	0.448E-04	0.535E-04	0.110E-04	0.660E-03	0.623E-03	0.134E-04	11
975. I	989.	0.155E-03	0.998E-04	0.448E-04	0.654E-04	0.179E-04	0.660E-03	0.601E-03	0.230E-04	17
1000. I	1024.	0.155E-03	0.664E-04	0.448E-04	0.812E-04	0.269E-04	0.660E-03	0.567E-03	0.375E-04	26
1025. C	1110.	0.155E-03	0.108E-04	0.448E-04	0.527E-06	0.670E-04	0.660E-03	0.280E-04	0.138E-04	88
1050. C	1135.	0.155E-03	0.380E-04	0.448E-04	0.774E-05	0.611E-04	0.660E-03	0.113E-04	0.437E-05	77
1075. C	1160.	0.155E-03	0.790E-04	0.448E-04	0.921E-05	0.473E-04	0.660E-03	0.342E-05	0.912E-06	55
1100. C	1184.	0.155E-03	0.139E-03	0.448E-04	0.872E-05	0.298E-04	0.660E-03	0.707E-06	0.132E-06	26
1125. C	1209.	0.155E-03	0.211E-03	0.448E-04	0.661E-05	0.146E-04	0.660E-03	0.947E-07	0.137E-07	-8

TABLE VII

NO_x Reduction for Case E H₂=5000 (ppm)

Ti	Tf	[NO] i	[NO] f	[NO ₂] i	[NO ₂] f	[N ₂ O] f	[H ₂ CO] i	[H ₂ CO] f	[NH ₃] f	% NO _x Reduced
800. I	800.	0.154E-03	0.148E-03	0.447E-04	0.437E-04	0.394E-06	0.059E-03	0.058E-03	0.182E-06	0
850. I	853.	0.154E-03	0.141E-03	0.447E-04	0.507E-04	0.301E-05	0.059E-03	0.049E-03	0.281E-05	3
900. I	920.	0.154E-03	0.090E-04	0.447E-04	0.585E-04	0.192E-04	0.059E-03	0.590E-03	0.208E-04	20
925. I	900.	0.154E-03	0.021E-04	0.447E-04	0.702E-04	0.310E-04	0.059E-03	0.552E-03	0.306E-04	33
950. I	1050.	0.154E-03	0.104E-04	0.447E-04	0.302E-05	0.010E-04	0.059E-03	0.100E-03	0.589E-04	92
975. C	1078.	0.154E-03	0.700E-05	0.447E-04	0.326E-05	0.527E-04	0.059E-03	0.510E-04	0.299E-04	94
1000. C	1103.	0.154E-03	0.104E-04	0.447E-04	0.539E-05	0.017E-04	0.059E-03	0.255E-04	0.125E-04	89
1025. C	1128.	0.154E-03	0.419E-04	0.447E-04	0.858E-05	0.011E-04	0.059E-03	0.101E-04	0.353E-05	74
1050. C	1152.	0.154E-03	0.902E-04	0.447E-04	0.112E-04	0.490E-04	0.059E-03	0.200E-05	0.500E-06	45
1075. C	1177.	0.154E-03	0.101E-03	0.447E-04	0.110E-04	0.320E-04	0.059E-03	0.440E-06	0.592E-07	3
1100. C	1201.	0.154E-03	0.277E-03	0.447E-04	0.917E-05	0.158E-04	0.059E-03	0.522E-07	0.542E-08	-44

TABLE VIII

NO_x Reduction for Case E H2=7500 (ppm)

Ti	Tf	[NO] i	[NO] f	[NO2] i	[NO2] f	[N2O] f	[H ₂ CO] i	[H ₂ CO] f	[NH ₃] f	% NO _x Reduced
800. I	802.	0.154E-03	0.138E-03	0.446E-04	0.573E-04	0.157E-05	0.657E-03	0.653E-03	0.938E-06	1
850. I	868.	0.154E-03	0.110E-03	0.446E-04	0.552E-04	0.147E-04	0.657E-03	0.611E-03	0.142E-04	16
900. I	983.	0.154E-03	0.125E-04	0.446E-04	0.517E-04	0.619E-04	0.657E-03	0.445E-03	0.680E-04	67
925. C	1044.	0.154E-03	0.467E-05	0.446E-04	0.322E-05	0.399E-04	0.657E-03	0.112E-03	0.702E-04	96
950. C	1070.	0.154E-03	0.664E-05	0.446E-04	0.302E-05	0.466E-04	0.657E-03	0.520E-04	0.322E-04	95
975. C	1095.	0.154E-03	0.153E-04	0.446E-04	0.529E-05	0.592E-04	0.657E-03	0.258E-04	0.127E-04	89
1000. C	1120.	0.154E-03	0.444E-04	0.446E-04	0.925E-05	0.623E-04	0.657E-03	0.972E-05	0.310E-05	72
1025. C	1144.	0.154E-03	0.115E-03	0.446E-04	0.132E-04	0.522E-04	0.657E-03	0.214E-05	0.356E-06	35
1050. C	1169.	0.154E-03	0.223E-03	0.446E-04	0.139E-04	0.334E-04	0.657E-03	0.305E-06	0.314E-07	-19
1075. C	1193.	0.154E-03	0.320E-03	0.446E-04	0.109E-04	0.167E-04	0.657E-03	0.384E-07	0.319E-08	-70
1100. C	1217.	0.154E-03	0.415E-03	0.446E-04	0.726E-05	0.645E-05	0.657E-03	0.375E-08	0.292E-09	-112

TABLE IX

NOx Reduction for Case E H2=10000 (ppm)

Ti	Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[HNCO]i	[HNCO]f	[NH3]f	% NOx Reduced
800. I	807.	0.154E-03	0.129E-03	0.445E-04	0.591E-04	0.461E-05	0.655E-03	0.643E-03	0.347E-05	5
850. I	920.	0.154E-03	0.321E-04	0.445E-04	0.638E-04	0.445E-04	0.655E-03	0.504E-03	0.471E-04	51
900. C	1037.	0.154E-03	0.419E-05	0.445E-04	0.344E-05	0.369E-04	0.655E-03	0.119E-03	0.804E-04	96
925. C	1063.	0.154E-03	0.503E-05	0.445E-04	0.285E-05	0.416E-04	0.655E-03	0.548E-04	0.354E-04	95
950. C	1088.	0.154E-03	0.142E-04	0.445E-04	0.513E-05	0.565E-04	0.655E-03	0.262E-04	0.130E-04	90
975. C	1113.	0.154E-03	0.470E-04	0.445E-04	0.978E-05	0.627E-04	0.655E-03	0.928E-05	0.273E-05	71
1000. C	1137.	0.154E-03	0.135E-03	0.445E-04	0.140E-04	0.532E-04	0.655E-03	0.174E-05	0.238E-06	24
1025. C	1161.	0.154E-03	0.257E-03	0.445E-04	0.150E-04	0.338E-04	0.655E-03	0.239E-06	0.204E-07	-37
1050. C	1185.	0.154E-03	0.365E-03	0.445E-04	0.117E-04	0.172E-04	0.655E-03	0.328E-07	0.235E-08	-89
1075. C	1210.	0.154E-03	0.450E-03	0.445E-04	0.799E-05	0.692E-05	0.655E-03	0.308E-08	0.253E-09	-130
1100. C	1234.	0.154E-03	0.518E-03	0.445E-04	0.544E-05	0.203E-05	0.655E-03	0.277E-09	0.192E-10	-163

FIGURE 1

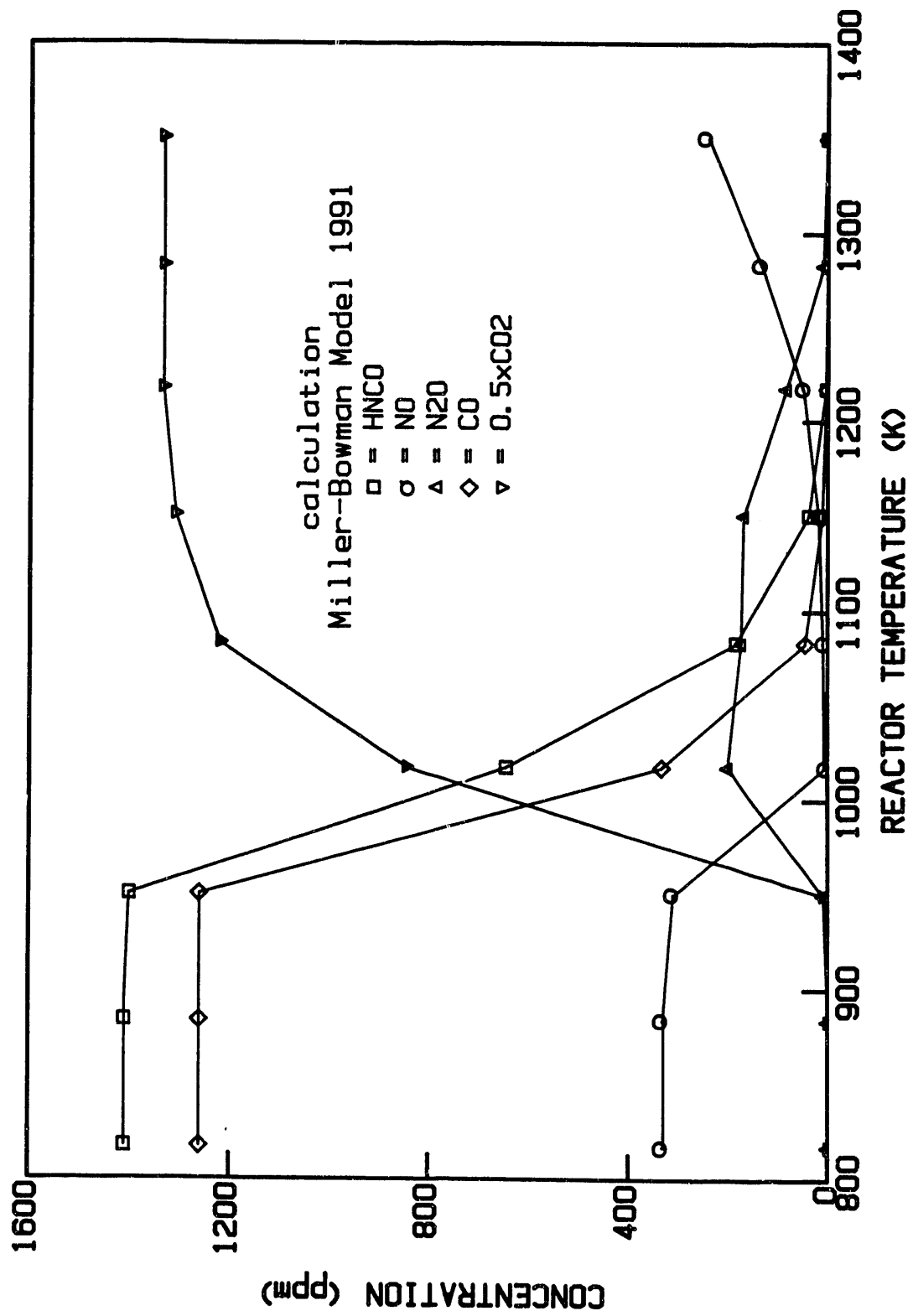


FIGURE 2

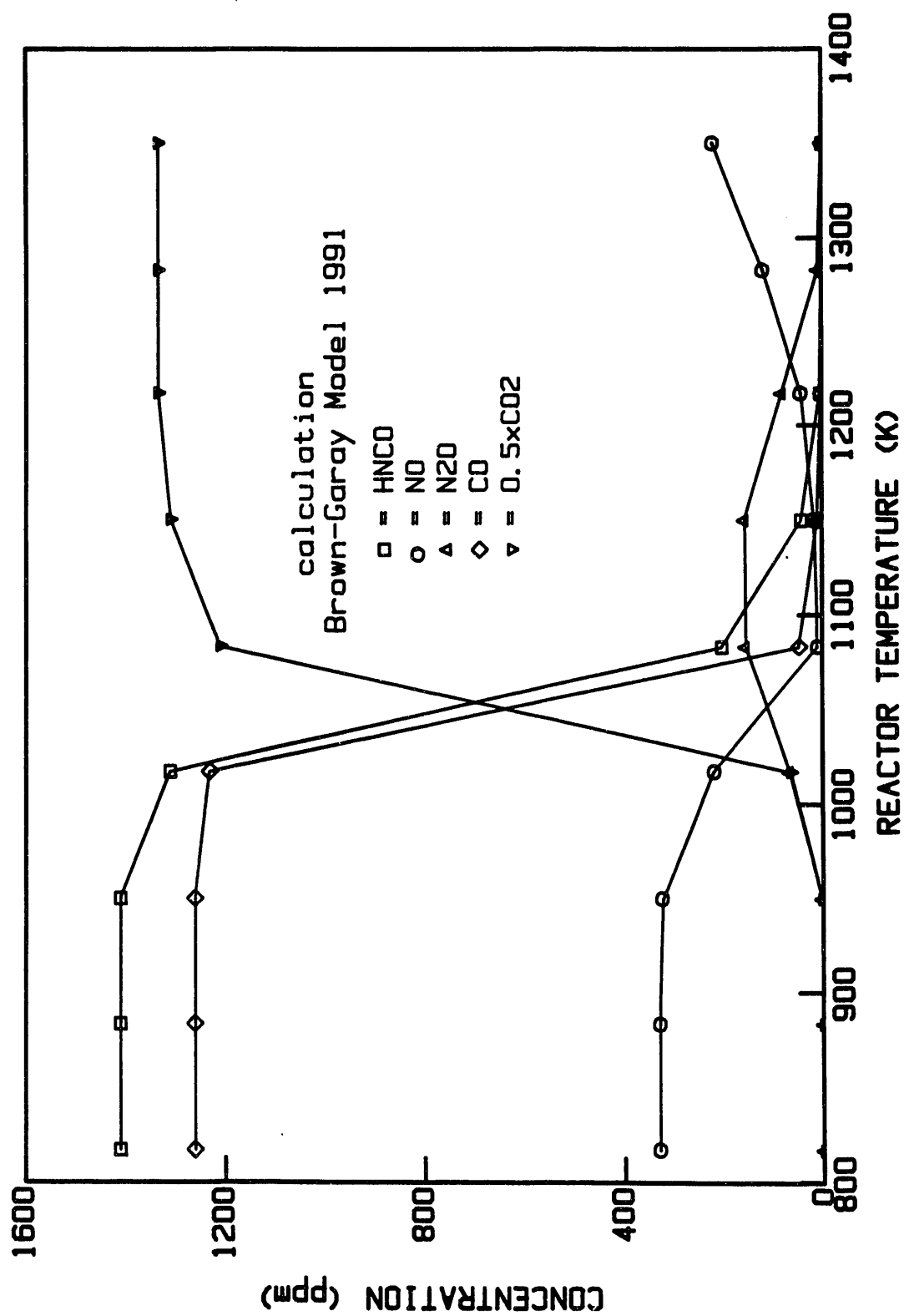


FIGURE 3

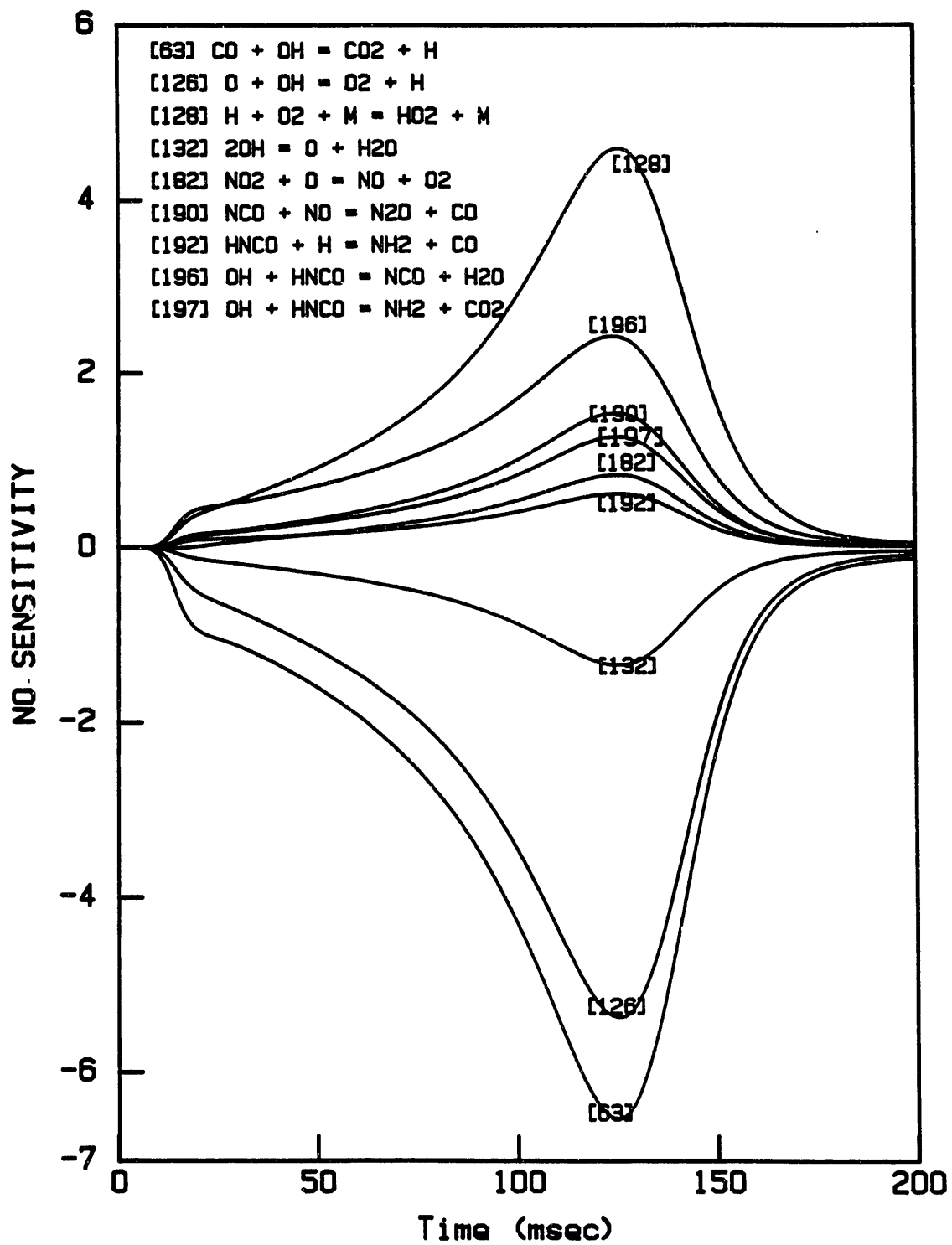


FIGURE 4

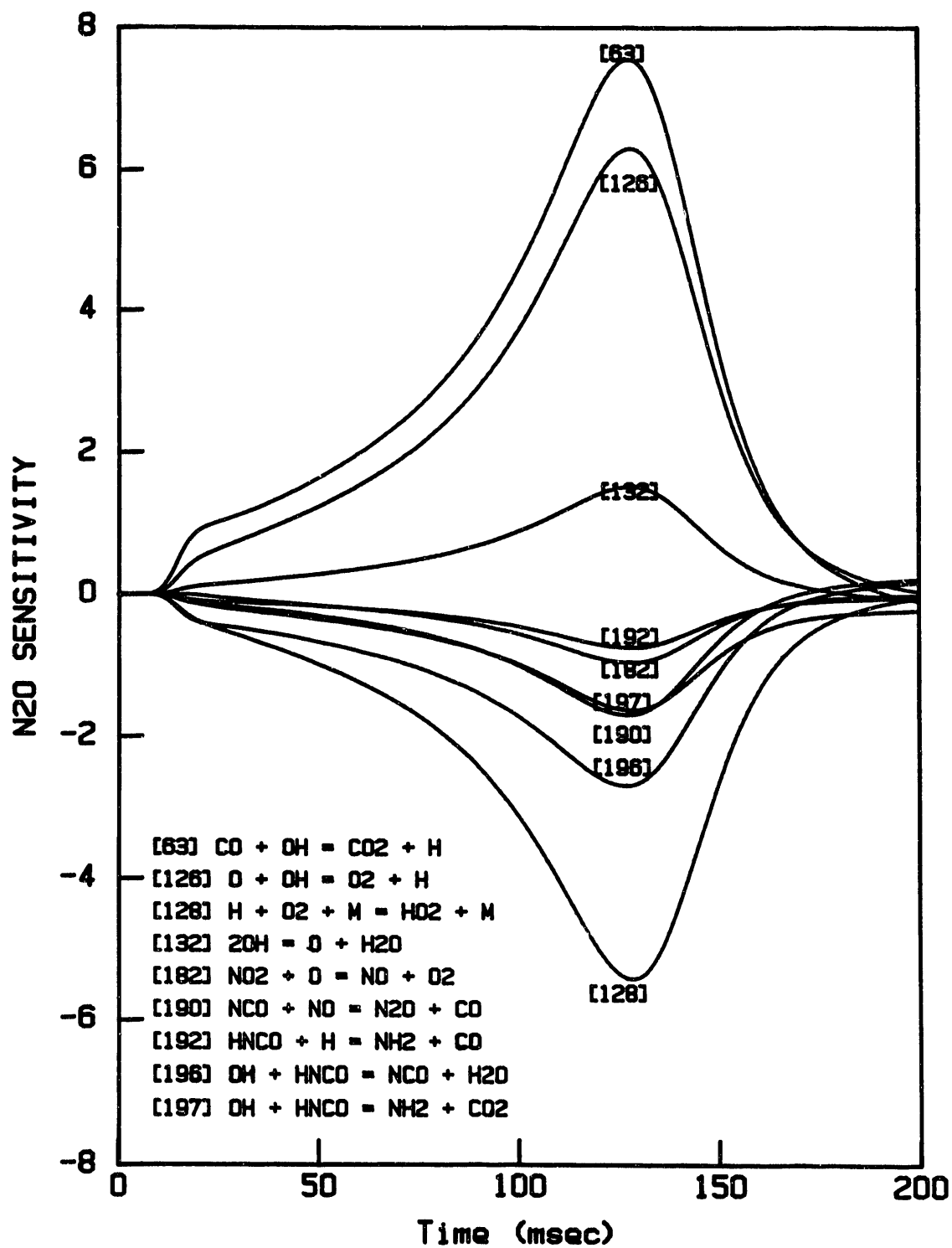


FIGURE 5

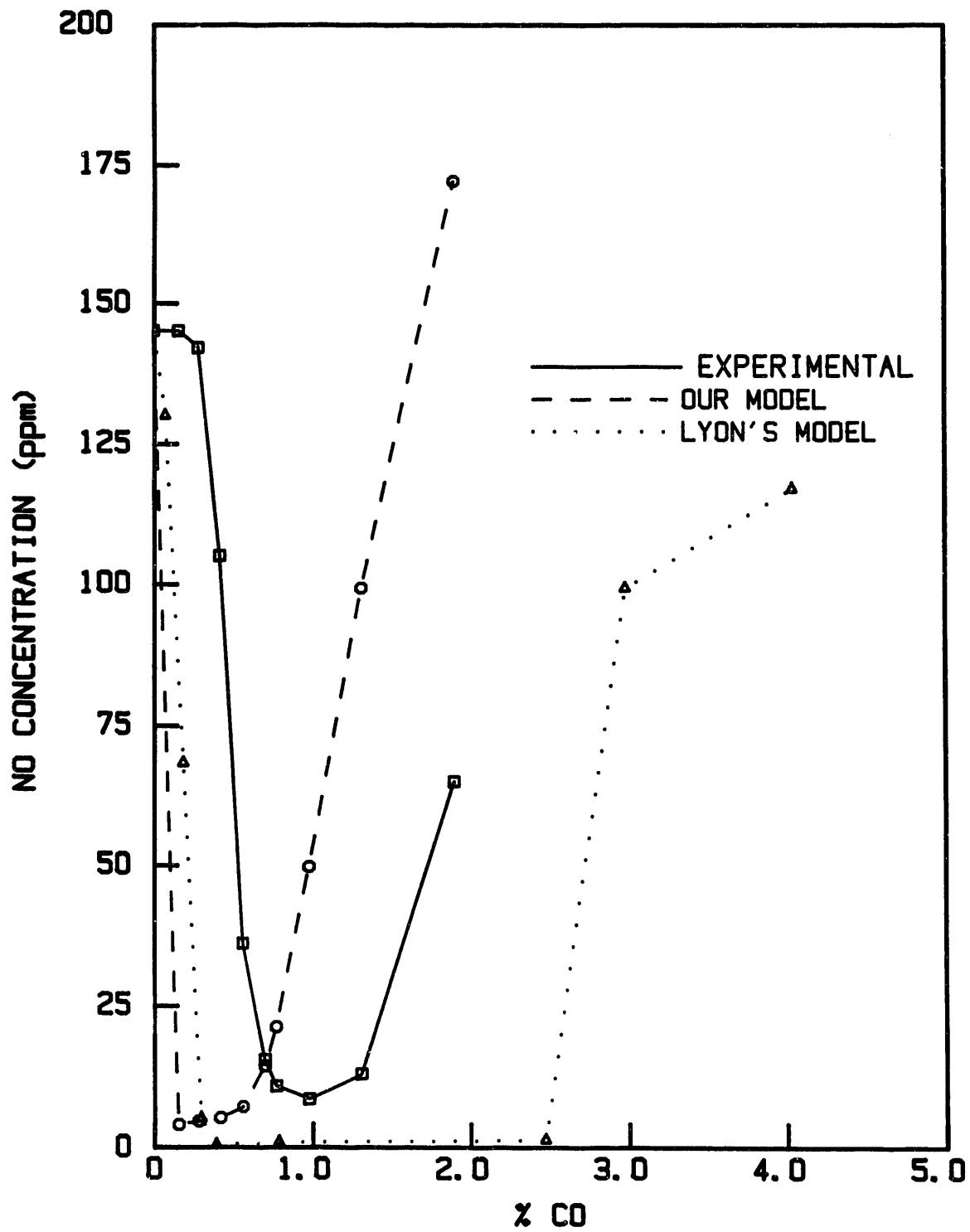


FIGURE 5

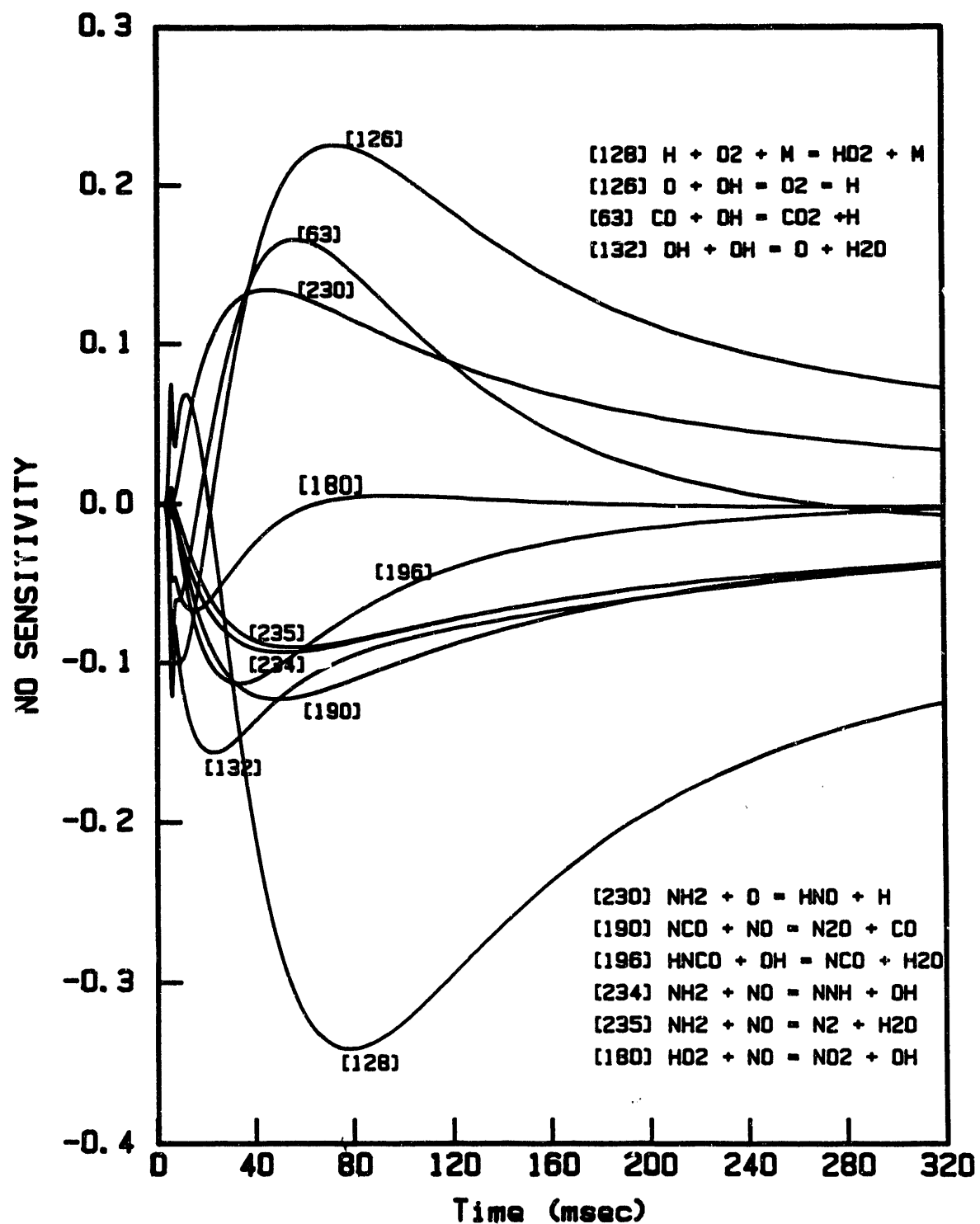


FIGURE 7

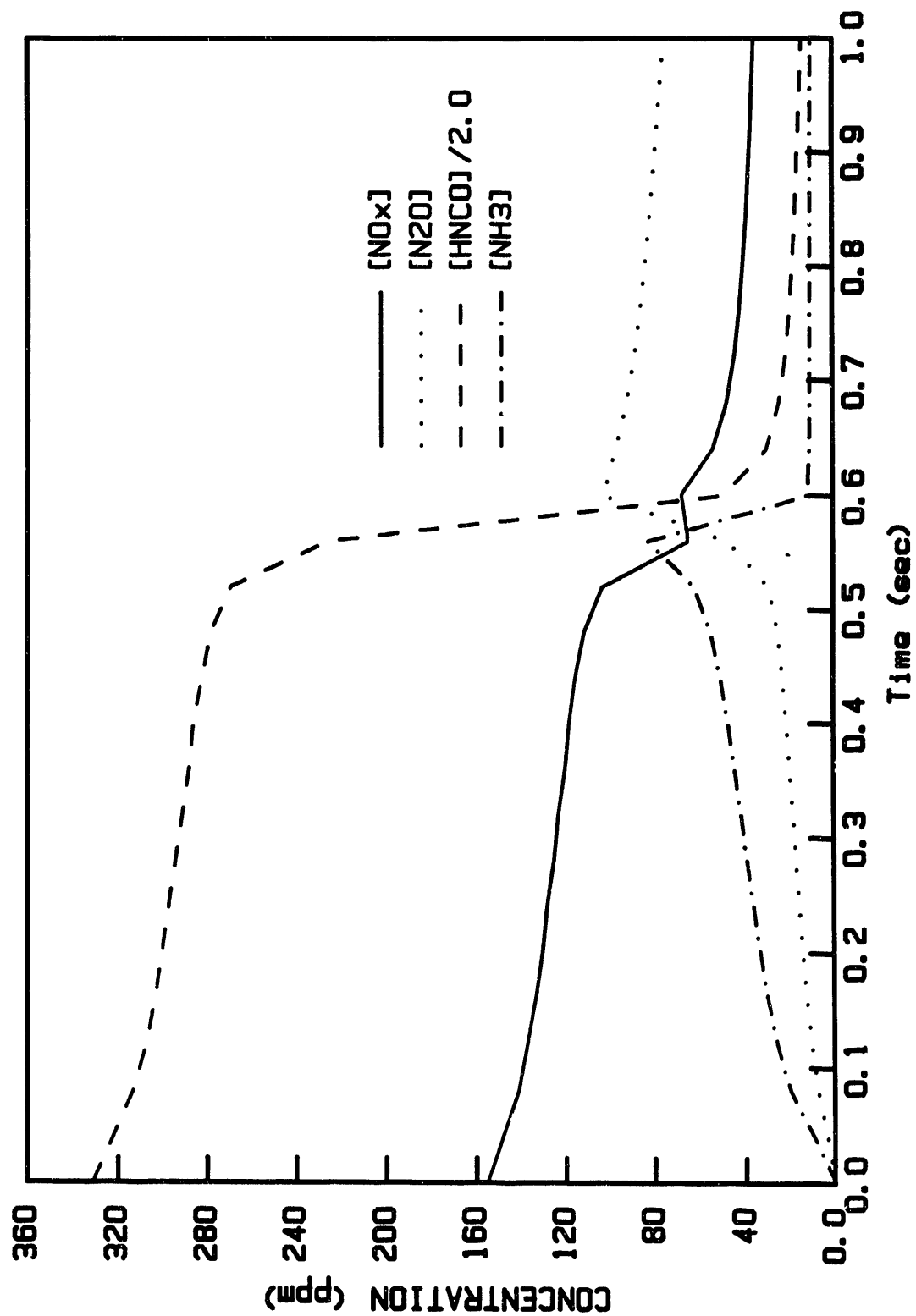


FIGURE 8

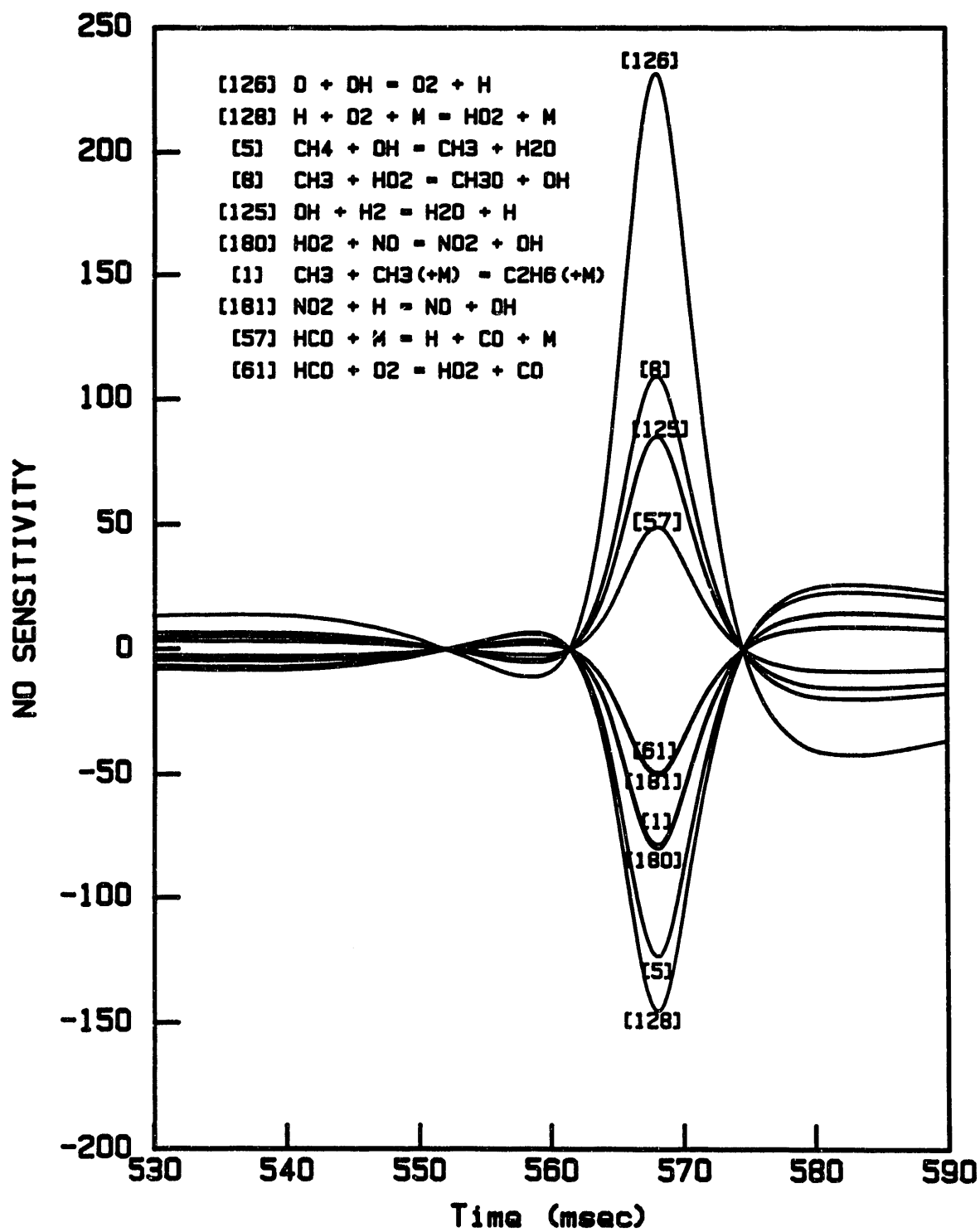


FIGURE 9

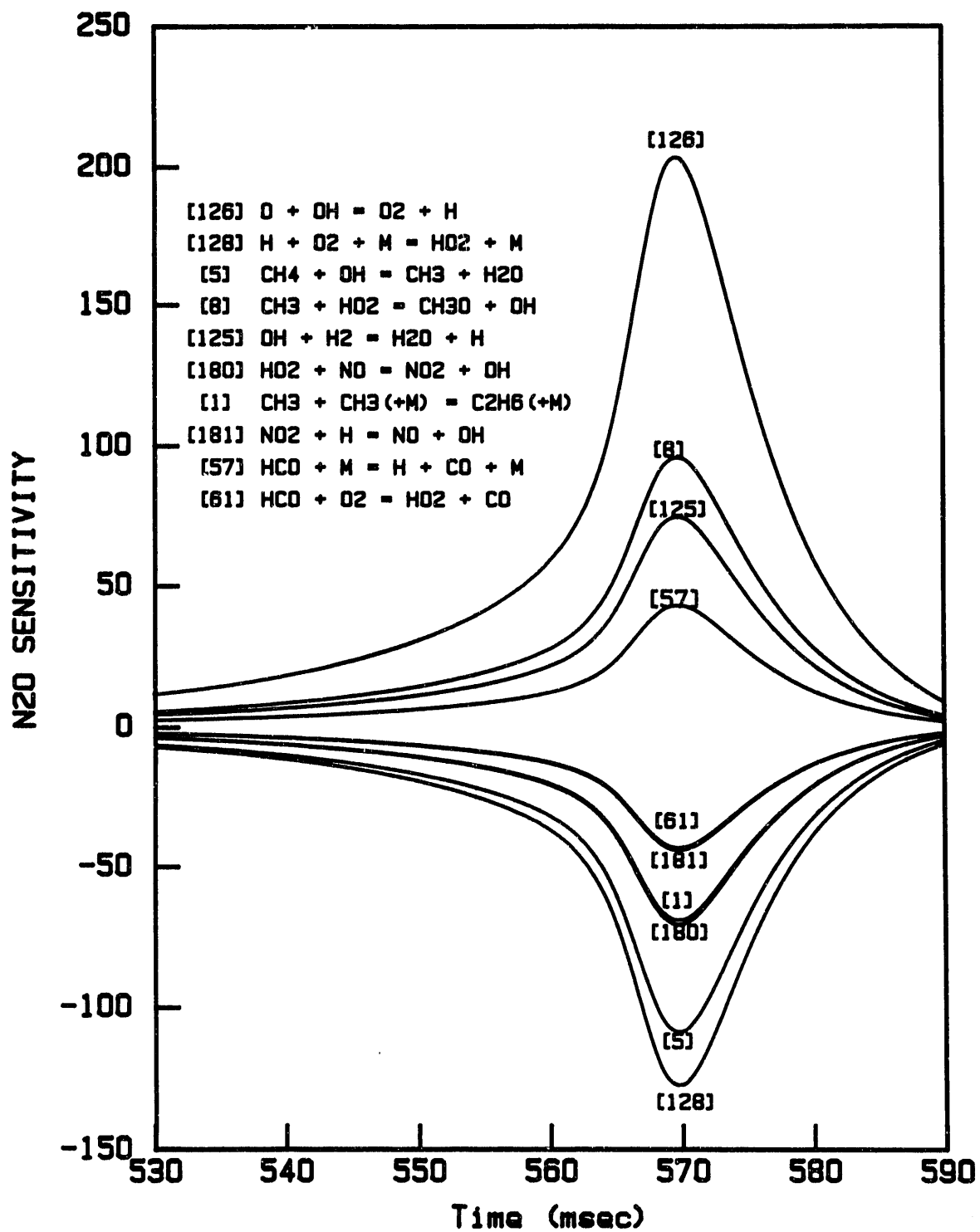


FIGURE 10

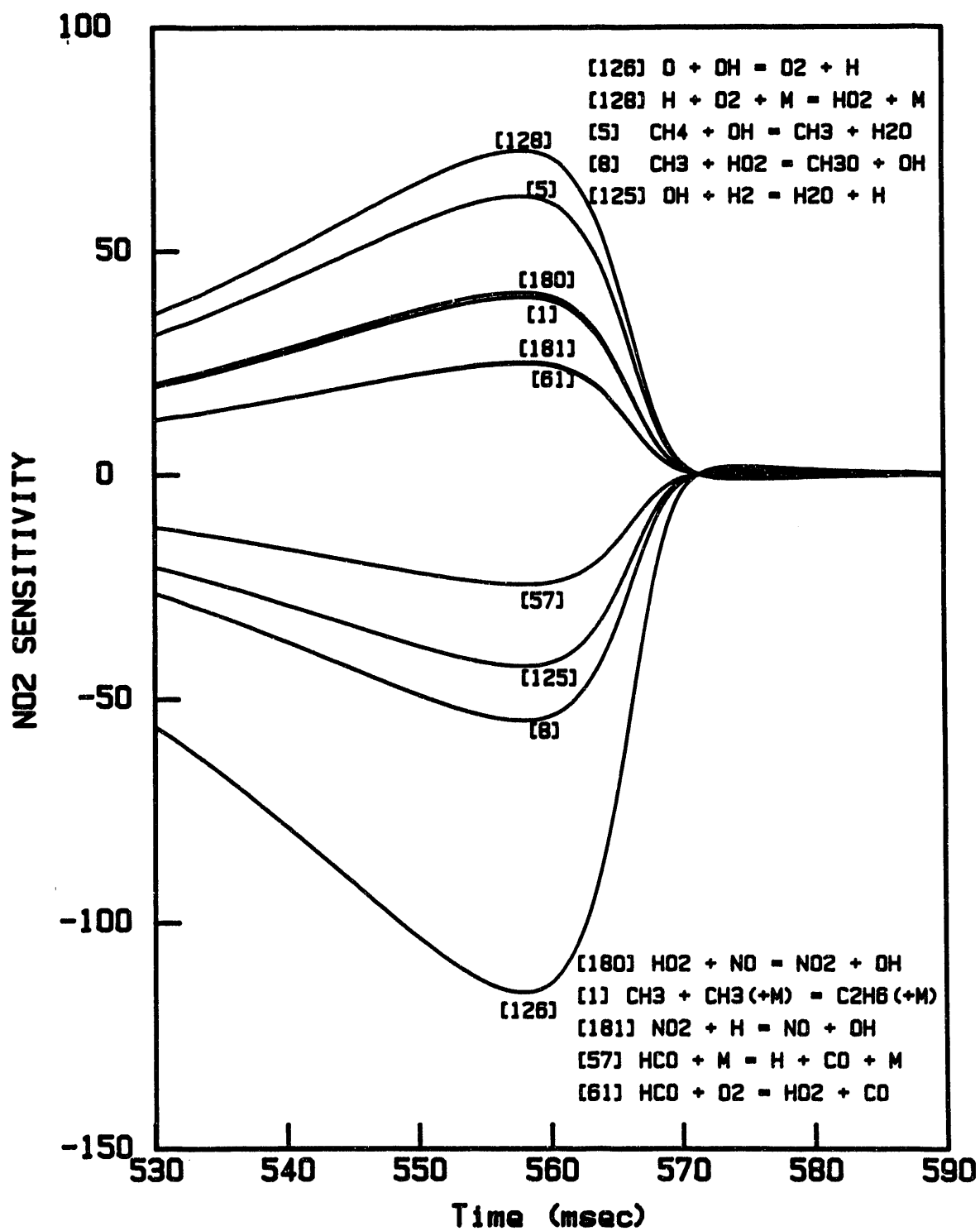


FIGURE 11

NH₃ Sensitivity

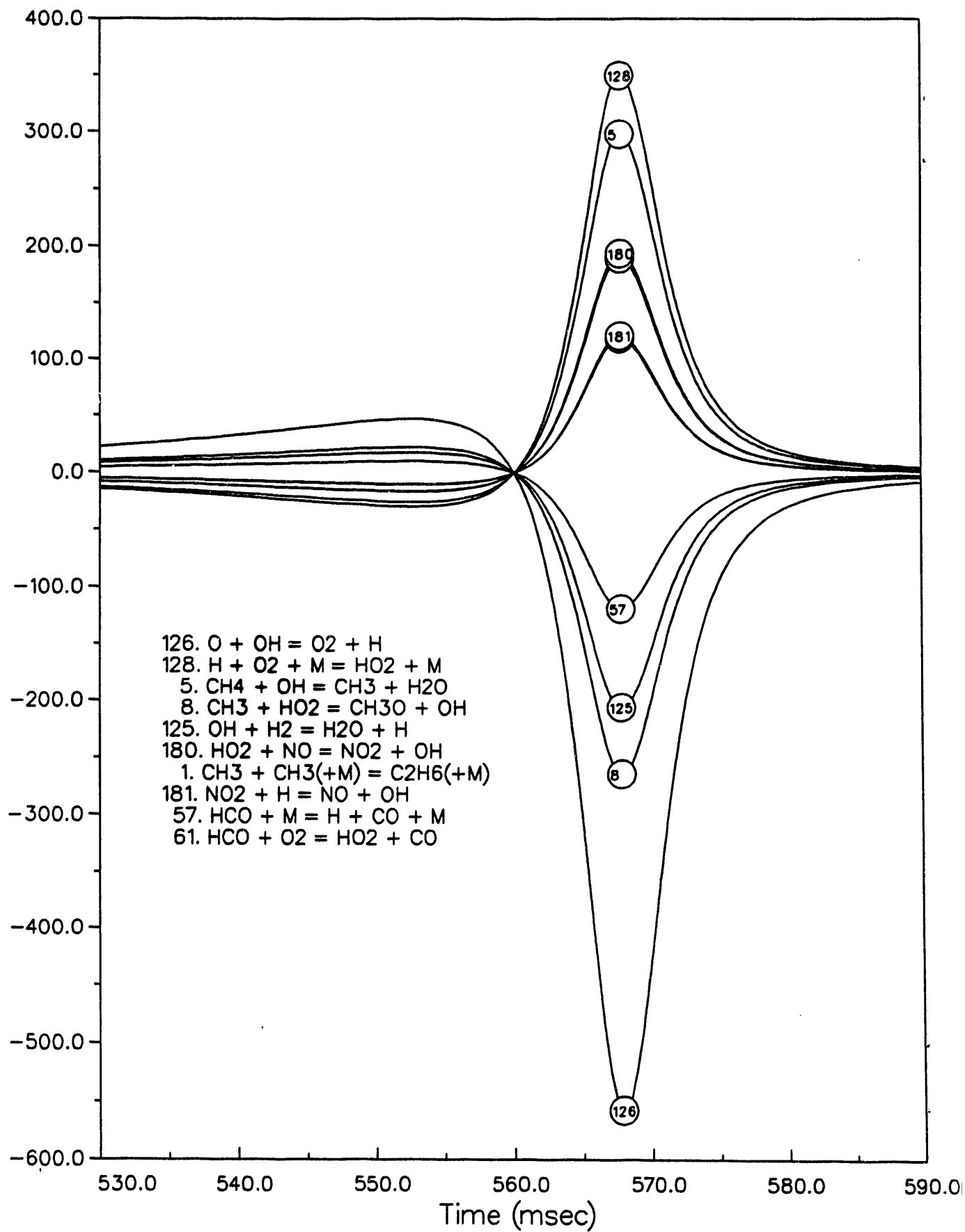


FIGURE 12

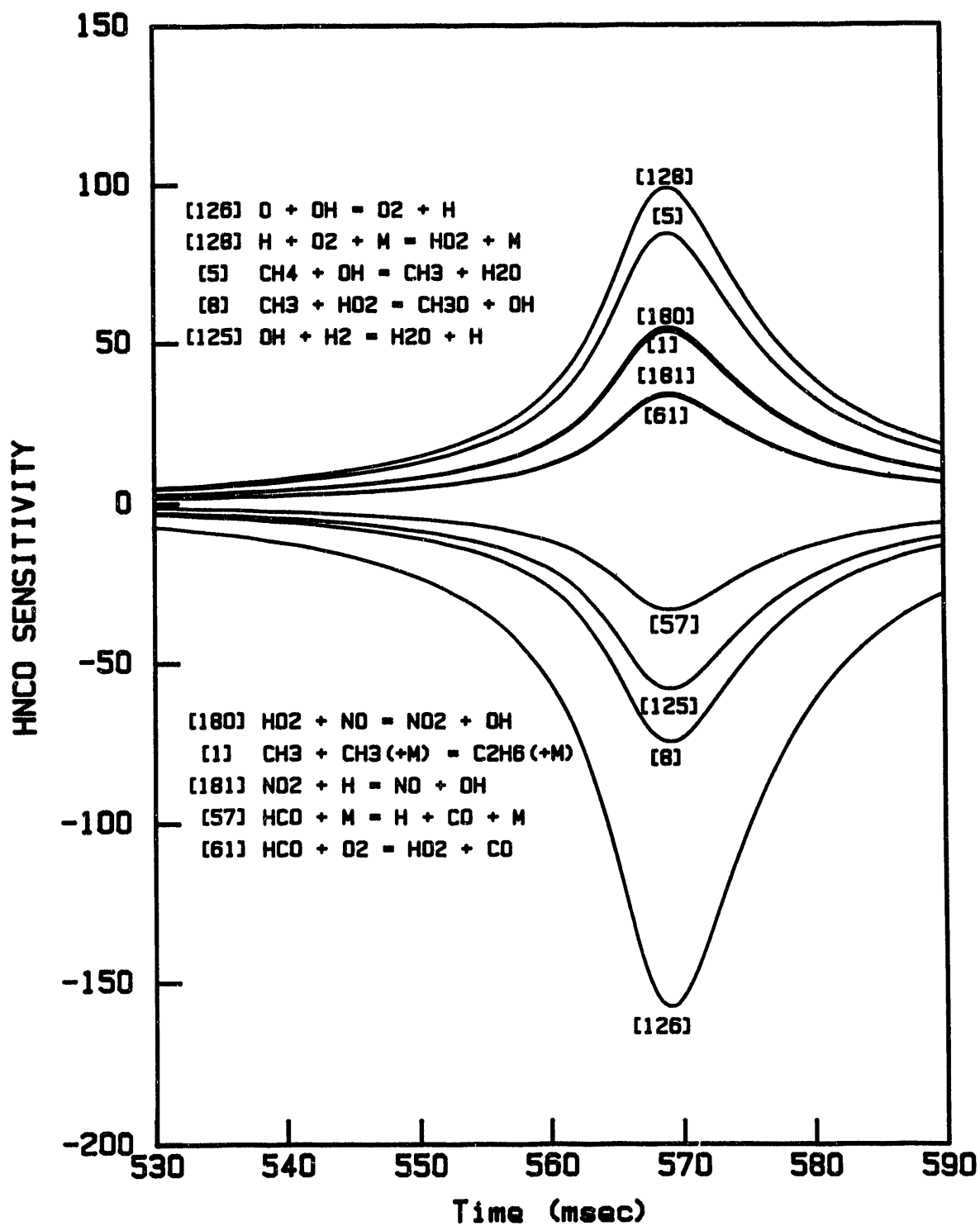
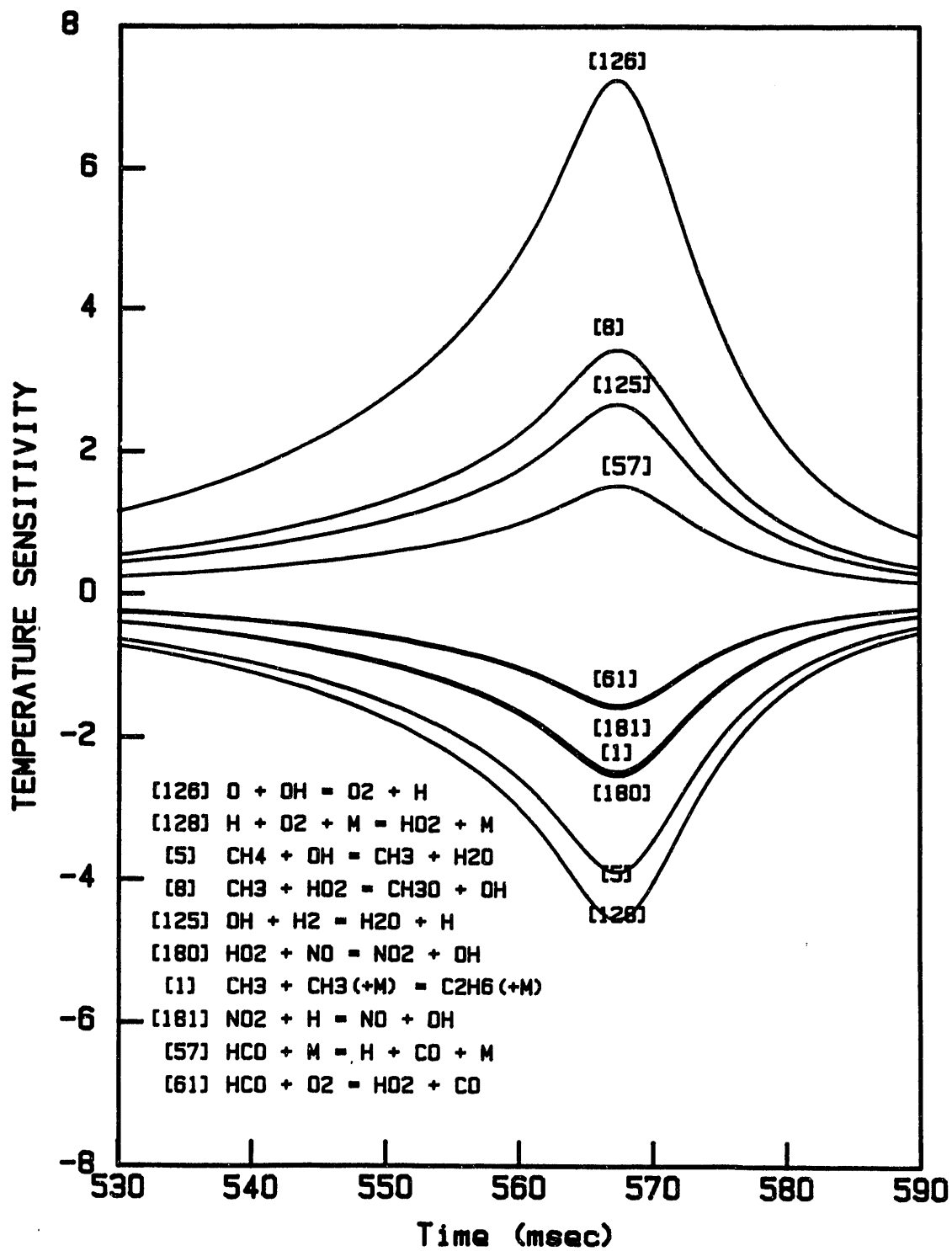


FIGURE 13



**DATE
FILMED
01/22/93**

