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MODELING AND SENSITIVITY ANALYSIS STUDY OF THE REDUCTION OF NOx BY HNCO

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EXECUTIVE SUMMARY

A chemical mechanism for the reduction of NOx by HNCO has been constructed to allow for the modeling of NOx reduction in exhausts typical of natural gas combustion. 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, NO_2, CO, CH_4 , H_2, and HNCO as well as initial temperatures. Exhaust residence time was nominally 1 second.

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, O_2, H_2O concentration and not with CH_4 and H_2. Agreement with experiments was satisfactory.

Reduction was not achieved for the prototypical "natural gas exhaust" for a reasonable residence time. Additional CH_4 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 CH_4 as the only "exhaust fuel" were not possible to ignite at temperatures sufficiently low for reduction to occur. When final temperatures exceeded 1200 K, NO production, rather than reduction, occurred.

Hydrogen added to the exhaust mixtures enhanced ignition, and thus, reduction. As initial H_2 concentration increases, the optimum temperature for reduction decreases. The width of the temperature window increases slightly, levels off, and achieves a value of approximately 50 K as initial H_2 increases. The final combustion temperature determines where NOx reduction ceases and NOx production increases, and the specified temperature where this occurs decreases with initial H_2 concentration.

Reduction increases with HNCO, and the breakthrough of NH_3 and HNCO increases 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. Emissions of N_2O are approximately 50 ppm under optimum conditions. The branching ratio in the NCO + NO reaction needs to be established before the N_2O can be predicted accurately. Interconversion of NO and NO_2 precedes reduction.

The sensitivity structure was rich and changed according to the exhaust composition and combustion conditions. The important reactions were those that influenced ignition chemistry and radical generation. Two reactions that were always among the most important were $H + O_2 + M \rightarrow HO_2$, which was in competition with the most important chain branching reaction of combustion, $H + O_2 \rightarrow OH + O$.

Sensitivity analysis revealed that N_2O production is due to NCO + NO, but that the reduction of NO also, and sometimes dominantly, occurs through reactions associated with the Thermal

De-NOx chemistry. The production of NH_3 and its subsequent reactions are very important to the reduction of NO. Comparing the sensitivities for various nitrogen species provided information about the characteristics of the chemical coupling in the system. Sensitivity analysis under conditions that made ignition easy to achieve, i.e., under the conditions of Lyon and Cole's experiments, indicated that the same reactions involving nitrogen species, NH_2 and NNH, important in De-NOx, are important when HNCO is used to reduce NOx.

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 NOx 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. More experiments are required to validate the chemical model. The modeling results would be especially useful for guiding the selection of experimental conditions. Uncertainties in the model also could be reduced by reducing uncertainties in the most sensitive reactions. Three-body recombination reactions are important in the modeling. Different third-body efficiencies need to be measured more reliably. Branching ratios of reactions involving nitrogen species need to be measured as a function of temperature.

I. BACKGROUND

A. Importance to California

Standards for NOx (NO and NO_2) are established to reduce air pollution emissions and to protect human health. NOx affects (1) human health, (2) ozone concentrations, (3) the formation of PM_{10} (fine particulate), (4) acid deposition, and (5) visibility degradation. In the South Coast Air Basin of California, emission limits for NO_x are relatively stringent. Although essential to preserve air quality, reductions of this magnitude frequently push the limits of existing technology and require new abatement schemes. A new technology for reducing NOx to acceptable levels is the RAPRENOx selective reduction process. The RAPRENOx 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. We treat the HNCO as a gaseous substance that is added to the mixture containing NOx. Methods of producing the HNCO as a gas will not be treated in this report.

In California, 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 NOx. There are, however, hydrocarbon (mostly CH_4) 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 NOx reductions, are ineffective (Kenney, 1991). This was the major motive for examining the possibility of using the selective reduction of NOx by HNCO for natural gas-fired engines.

Improved NOx reduction must be achieved without producing other undesirable species. Nitrous oxide (N_2O) is a product of the selective reduction of NOx by HNCO. For the reduction to work well, the NOx reduction must occur under conditions where the N_2O is destroyed. As discussed by Elkins (1989), N_2O is a greenhouse gas that absorbs infrared radiation 200 times more effectively than CO_2. Nitrous oxide has an atmospheric lifetime of approximately 150 years, and it reacts in the stratosphere to produce NO which plays one of the dominate roles in determining stratospheric ozone concentrations. Nitrous oxide is the principal source of NO in the stratosphere.

B. The Reduction of NOx by HNCO

The RAPRENOx process was patented by Dr. Robert A. Perry (1988 and 1989). In the second patent the process is described as "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 sublimes 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 NOx, several elementary reactions may occur, which result in the reduction of NOx.

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

There has been a number of studies of the reduction of NOx by HNCO. Perry and Siebers (1986) demonstrated that a high degree of NOx 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. They postulated that the important chemistry was

$$\begin{aligned}
&\mathrm{HNCO} && \text{-->}\ \mathrm{NH + CO}\\
&\mathrm{NH + NO} && \text{-->}\ \mathrm{H + N_2O}\\
&\mathrm{H + HNCO} && \text{-->}\ \mathrm{NH_2 + CO}\\
&\mathrm{OH + CO} && \text{-->}\ \mathrm{H + CO_2}\\
&\mathrm{NH_2 + NO} && \text{-->}\ \mathrm{N_2H + OH}\\
& && \text{-->}\ \mathrm{N_2 + H_2O}\\
&\mathrm{N_2H} && \text{-->}\ \mathrm{N_2 + H.}
\end{aligned}$$

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 HNCO reduces NO via a 0complex reaction mechanism very similar to that involved in the Thermal DeNOx (the selective reduction of NO by NH_3) process patented by Lyon in 1975. For mode two, Lyon and Cole postulate that the NO reduction is a result of the NH_2 + 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 NH_3 or HNCO.

Heap et al. (1988) also indicated that low temperature reductions of NO by HNCO 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 DeNOx. Siebers and Caton (1988) revealed that surface decomposition of the HNCO initiates NO reduction for temperatures less than 900 K.

The first model for the selective reduction of NO by HNCO when wet CO is present was put forth by Miller and Bowman (1988, 1989 and 1991). They combined the Thermal DeNOx 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). Miller and Bowman also computed sensitivity coefficients for the rate coefficients of their mechanism for NO and N_2O concentrations. Lyon and Cole also modeled their experiments concerned with the reduction of NO by HNCO in wet CO.

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 have 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) play 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 N_2O + H and N_2O + 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. As indicated by Muzio and colleagues (1990), the typical exhaust temperature for natural gas-fired gas turbine, reciprocating, and lean-burn engines is between 775 and 975 K.

C. Role of NCO Chemistry in RAPRENOx

The NCO radical is an important intermediate in fuel-bound nitrogen (Haynes et al., 1975) and in the reduction of NO by HNCO (Miller and Bowman, 1989). The NO + NCO reaction is one of the two most important reactions leading to N_2O formation during the combustion of hydrocarbon fuels containing fuel-bound nitrogen (Miller and Bowman, 1989). Although the rate for the net reaction has been measured, due to the difficulty of measuring the product species, both the products and the branching ratio remain undefined.

$N_2O + CO$ (R1a)

$NCO + NO \longrightarrow$

$N_2 + CO_2$ (R1b)

Branching ratios are critical for determining N_2O production.

Perry (1985) investigated the NO + NCO reaction in the temperature range 294-538 K. Reaction progress was determined 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

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

for the temperatures 294-538 K, where R is the gas constant in cal 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 (the sum of R1a and R1b) at room temperature, and their results are in excellent agreement with Perry.

D. Sensitivity Analysis

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

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

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. This can be seen by multiplying (1) by $(X_j(t)/X_j(t)$. The sign of the sensitivity provides the directional response, and the magnitude indicates the relative importance of the input parameter. In chemically reacting systems, sensitivity analysis involves studying how the system solutions (concentrations of reactant, intermediate, product species, and temperature) are affected by changes in input parameters (e.g., rate coefficients and thermodynamics parameters). Sensitivity analysis is used here to unravel the complex relationship between the input parameters and output variables associated with the reduction of NO by HNCO.

Models for reacting flow systems are complex and, by the addition of detailed chemical mechanisms, non-linear and difficult to understand within an intuitive framework (Rabitz 1986 and 1989). Full knowledge of the components entering a reactive flow model does not imply an understanding of their roles because it is the strong coupling among the parameters which leads to the actual system variables. General mechanistic information can be derived by carefully analyzing the sensitivity coefficients as a function of time for the dependent variables. The most important reactions are identified with sensitivity analysis, and by identifying these reactions, future research can be devoted to reducing uncertainties in their kinetics or thermochemistry so that model predictivity is improved. Another important feature of first order sensitivity analysis is that it may be used to identify unimportant reactions in complex models so that the models may be simplified.

For complex chemical systems, such as the one being considered, the sensitivity coefficients must be calculated numerically. There have been three approaches to the calculation of sensitivity coefficients for studies of reacting flows: (1) the Fourier amplitude sensitivity test approach of Cukier et al. (1973); (2) the direct method of Atherton et al. (1975), Dickinson and Galinas (1976), and Lutz et al. (1991); and (3) the Green's function method of Hwang et al. (1978) which has been further developed by Dougherty et al. (1979), Rabitz et al. (1983), Dacol and Rabitz (1984), and Yetter et al. (1985).

II. RESULTS AND DISCUSSION

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 which will be described subsequently and The Chemkin Thermodynamic Data Base (1991). Earlier versions of software were used, but results were shown to be invariant when the most recent versions were introduced. The AIM software developed by Kramer et al. (1982) for sensitivity analysis was also used, but because of its incompatibility with CHEMKIN-II, it was abandoned when the change from CHEMKIN I to CHEMKIN-II was made. 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.

Caton and Siebers (1988 and 1989 a and b) reported studies of RAPRENOx that can be modeled because they specified the initial exhaust gas composition. It is important to discuss these experiments in more detail to understand the 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, Tr with Tr in the range 800 to 1350 K, and 2) HNCO was mixed after a time period equal to 20% of the residence time in the reactor. In fact, reaction between the exhaust gas and HNCO occurs in the reactor at an unspecified temperature (between the 720 K and Tr) while the HNCO is mixing, and this affects the early temporal behavior of the reacting system.

The Miller and Bowman (1991) mechanism for RAPRENOx for modeling the Caton and Siebers (1989 a and b) and the Siebers and Caton (1988) experiments 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. The model produces all trends in the experimental data. Sensitivity and rate of production analysis show that reactions of HNCO with OH, O, and H play a major role in NO removal. The overall reduction mechanism is critically dependent on the production of radicals. The NCO + NO reaction exhibits a positive sensitivity.

We constructed a mechanism for describing the RAPRENOx process based on the Miller and Bowman 1991 study. We made some minor changes to the Miller-Bowman mechanism, which reflected more recent values of kinetic parameters. We were able to repeat their calculations and obtain the same level of agreement with the Caton and Siebers experiments. We also repeated their sensitivity calculations and obtained identical results. These duplicate calculations indicated that we were using the software correctly, and that our chemical mechanism produced results in agreement with theirs.

We then proceeded to model the more recent experiments of Caton and Siebers (1990). In these experiments, 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 experiments was poor.

We attempted to reconcile differences between our results and those of Caton and Siebers (1990). Dennis Siebers was contacted and he indicated that the concentration of the "reactants" in the reactor immediately before the addition of the HNCO was not measured. This was probably not a serious error in the earlier experiments, but H_2 can react 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 of reactants 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 encountered in the experiment, results of our modeling experiments indicated as much as 50% of the H_2 reacted in the preheater to form H_2O. 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 and 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.

There are other problems with modeling the Caton and Siebers experiments. After the preheat section, they assumed that the reactants took 20% of the residence time in the reactor section to achieve the reactor temperature. The reactor temperatures were in the range 800-1400 K. Heating the reactants from 720 K to a temperature in the range 800 to 1400 K requires time, and reactions occur during the heating period. The mixing of HNCO also requires time, and the reactants undergo reaction while they are being heated and mixed with the reducing agent. Since these processes are not characterized in the experiments, it was not possible to model them.

Results of our modeling calculations indicated that the pseudo exhausts used in the 1988 and 1989 a and b experiments, which did not contain H_2, did not react in the preheater. The Caton and Siebers (1988 and 1989 a and b) experiments were, however, subject to the errors discussed earlier regarding heating and mixing in the reactor section.

We added CN and CH_n chemistry to the Miller-Bowman mechanism to model NO reduction by HNCO in exhaust mixtures containing CH_4. The new mechanism contained the Appendix A of the 1989 Miller-Bowman mechanism. The subset of reactions that is common to Appendix A and the 1991 Miller-Bowman paper 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 NCO + 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 report.

Table I gives the kinetic mechanism used in the study. The elements considered are given first, followed by the individual species. True parameters for the unimolecular reactions CH_3 + CH_3 (+ M) and CH_3 + H (+ 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. Modeling Calculations

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 (Brown-Garay and Miller-Bowman) differ most between 950 and 1050 K as illustrated by comparing Figures 1 and 2, respectively. The Brown-Garay model actually gives better agreement with experiments especially with respect to the HNCO and CO profiles. Both models and experiments reveal that the maximum in N_2O

concentration coincides with the maximum NO reduction. Although the models produce the trends noted experimentally, they do not reproduce the temporal behavior of the experimental concentration profiles.

The sensitivity results for Case A calculations are shown for calculations performed at 1050 K for NO in Figure 3 and for N_2O in Figure 4. The sensitivities are normalized with respect to the value of the rate coefficient and the maximum value of the concentration as given in Eq. (1). Positive sensitivities in Figure 3 indicate that increasing the reaction rate will result in an increase in NO concentration. Positive sensitivities are associated with reactions that inhibit NO removal. Conversely, reactions with negative sensitivities are those which decrease the NO concentration and thus increase the reduction. Since reverse rate coefficients are calculated from the equilibrium constant and forward values, the sensitivities to the forward and reverse rate coefficients are equal. Even though our mechanism (given in Table I) is different from the Miller-Bowman mechanism, we found the same trends in the sensitivity coefficients although the magnitudes of our sensitivities differ from theirs.

The removal of NO is most sensitive to behavior at 125 milliseconds, which is quite "early" in the overall reaction, and occurs during the mixing 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 + H_2 oxidation: reaction 128 with a positive sensitivity in competition with reactions 63, 126, and 132 which generate radicals. 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. The NO_2 to NO conversion that occurs is due to reaction 182.

The N_2O sensitivities for the most important reactions are of opposite sign to the NO sensitivities, which implies that reactions that result in NO removal produce N_2O. 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 10% reduction of NOx 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.

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 for a residence time of 0.76 seconds.

Lyon and Cole modeled their experiments using the Dean, DeGregoria, Hardy, Lyon (DGHL) model (Lyon et al., 1987). We modeled the 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 also performed calculations in which we varied the rate coefficients of the most sensitive reactions. The rate coefficient that had the largest effect on the results was the $H + O_2 + M \rightarrow HO_2 + M$. Increasing the third body efficiency of this reaction with respect to H_2O to a value of 21 rather than the nominal value of 10 brought our modeling calculations into better agreement with experiment for CO concentrations in excess of 1.0%. 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.

We then contacted a California (Des Jarden, 1991) utility and obtained a sample exhaust gas composition characteristic of burning natural gas. This is given in Table II as Case B2. Radical species in the exhaust were not measured. Radicals, however, are present in exhaust mixtures of this type, and they do affect the reduction of NO since it is so strongly dependent on radical production.

The reduction of NOx by HNCO was modeled for the utility gas composition (Case B2) 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 NOx reduction occurred for T ≤1135 K. There was conversion of the NO to NO_2. At 1140 and 1145 K, NOx removal on the order of 10% of the original amount was determined. At 1150 K, NO_2 was converted to NO, the exhaust gas mixture underwent complete 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 complete combustion of the exhaust mixture, 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. Complete combustion depends upon there being sufficient time for ignition, and is associated with a temperature rise characteristic of the mixture in question. For Case B2, the temperature rise for complete combustion is approximately 66 K. Combustion was complete for the 1050 mixture in less than 30 seconds and for the 1100 K mixture in less than 10 seconds.

The concentrations of important nitrogenous species as a function of time are shown in Figures 6 and 7 for Case B2 at an initial temperature of 1100 K. Ignition occurs at approximately 5 seconds, and this is where the interesting chemistry occurs. The chemistry is extremely complex, and is even further complicated by distributing the NOx between NO and NO_2. In Figure 6, NOx is plotted and NO and NO_2 are separately plotted in Figure 7. Prior to ignition, the NOx and HNCO profiles decrease slowly while NH_3, N_2O, and temperature increase slowly. The NOx profile then declines more rapidly, assumes a constant value with zero slope, and then declines more rapidly. The NH_3 profile assumes a maximum value when the NOx profile begins to have zero slope at approximately 5.05 seconds, and the maximum precedes the abrupt drop in the HNCO profile. The end of the NOx profile zero slope region coincides with the maximum in the N_2O profile. In Figure 7, the scale of the region of interesting chemistry has been expanded. Conversion of NO_2 to NO is evident, followed by a decline in the NO after 5.08 seconds.

Sensitivities were also computed for the Case B2 mixture having an initial temperature of 1100 K. Considerable mechanistic information can be obtained by considering the sensitivities to a number of nitrogen-containing species in concert. The sensitivity coefficients for the nine most important reactions are shown for the following: NO in Figure 8; N_2O in Figure 9; NO_2 in Figure 10; NH_3 in Figure 11; HNCO in Figure 12; and temperature in Figure 13. All species and temperatures exhibit high sensitivity to the same set of reactions. The regime of high sensitivity corresponds to the plateau region of the NOx profile. The NO sensitivities oscillate and there are two sign changes in the sensitivities.

The NO and NH_3 sensitivities undergo the first sign change at the same time. The NH_3 and NO sensitivities are opposite in sign, which indicates that reactions responsible for increasing NH_3 result in a decrease in NO. The very distinctive coupling between the NO and NH_3 chemistry ceases when the NO sensitivities undergo the second sign change. Although of different magnitudes, the HNCO and temperature sensitivities have opposite signs. This indicates that reactions important for increasing the temperature result from radical production, which in turn, results in HNCO destruction through radical attack. At early times the NO_2 and HNCO sensitivities show similar trends because radical production is crucial to their reactivity. Reactions leading to temperature increases and radical production are also important for producing N_2O. The destruction of HNCO is strongly linked to N_2O production. Reactions important for increasing the temperature are those that result in radical production: reaction 9, the CH_3 + O_2 reaction which is the principal reaction in CH_4 ignition; reaction 126, the H + O_2 reaction which is a major chain branching reaction; reaction 57, the HCO + M reaction which produces CO; reaction 8, the CH_3 + HO_2 reaction which produces CH_3O, a precursor to CO. Reactions that inhibit a temperature increase by decreasing radical concentration are reaction 5, which produces CH_3, which can recombine via reaction 1, and reaction 128, which forms HO_2 in competition with chain branching. Reactions 61 and 182, which have negative sensitivities nearly equal to reaction 5, reduce the radical pool.

C. The Effect of Radical Boosters on NOx Reduction

The effect of adding "extra" CH_4 to the mixture B2 was investigated at a temperature of 1050 K. Initial CH_4 concentrations considered were 2.5, 5.0, and 10 x 10^{-3} mole fraction. For one second residence time, no significant chemistry occurred and NOx was not reduced. Initial CH_4 concentrations of 1% were considered for initial temperatures in the range 1100 to 1200 K, for Case C mixture composition. For the 1% CH_4 and an initial temperature of 1200 K, the mixture burned, achieved a final temperature of 1423 K, and NO was produced. At initial temperatures below 1200 K, one second was insufficient residence time for combustion to be complete.

Adding CH_4 as a radical booster does not work. Reductions of NOx are negligible. When temperatures are sufficient for rapid ignition to occur ($T \geq 1200$ K), the mixture burns and produces NOx. Production of NO always occurs for conditions under which combustion is complete and final temperatures exceed 1200 K. Radical generation is the most important process in the reduction of NOx by HNCO. Ignition must precede NOx reduction to generate sufficient radicals for the reduction to occur.

D. H_2 as a Radical Booster

It was not possible for HNCO to reduce NOx in the prototypical natural gas exhausts because the "primary fuel" present in the exhaust was CH_4, which is difficult to ignite. In order to facilitate ignition, and thus, the reduction of NOx by HNCO, the effect of adding H_2 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 H_2 addition to a mixture whose composition is given in Table II.

Tables III and IV are a summary of the effect of adding H_2 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 H_2 in the concentrations 500, 1000, and 1500 ppm at 1050 K was also investigated. The effect of adding variable HNCO to a Case D mixture at an initial temperature of 1025 K is summarized in Table V. Finally, the effect of adding H_2 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 combustion in the exhaust was incomplete, and C indicates complete combustion.

Examination of the Tables reveals that the optimum temperature for reduction is the lowest temperature at which complete combustion occurs 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 combustion temperature determines where NOx reduction ceases and NOx production occurs, and the specific temperature where this occurs decreases with increasing H_2. The percentage of NOx reduced increases with increasing HNCO, and the breakthrough of NH_3 and HNCO increases as well. It would appear that an HNCO/NOx ratio of 3 or 4 would be appropriate. Nitrous oxide emissions are approximately 50 ppm in the temperature window where 90% reduction occurs. The major difference in Cases B1 and E is that the Case E 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 is increased beyond the optimum value, the NOx reduction is greater for the larger initial NOx.

Sensitivities were calculated for two modeling calculations of the Case B1 type. The results of these calculations indicated the importance of radical generation chemistry as well as the role that NH_3 played in the reduction.

III. SUMMARY AND CONCLUSIONS

A chemical mechanism for the reduction of NOx by HNCO has been constructed to allow for the modeling of NOx reduction in exhausts typical of natural gas combustion. 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, NO_2, CO, CH_4 , H_2, and HNCO as well as initial temperatures. Exhaust residence time was nominally 1 second.

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, O_2, H_2O concentration and not with CH_4 and H_2. Agreement with experiments was satisfactory.

Reduction was not achieved for the prototypical "natural gas exhaust" for a reasonable residence time. Additional CH_4 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 CH_4 as the only "exhaust fuel" were not possible to ignite at temperatures sufficiently low for reduction to occur. When final temperatures exceeded 1200 K, NO production, rather than reduction, occurred.

Hydrogen added to the exhaust mixtures enhanced ignition, and thus, reduction. As initial H_2 concentration increases, the optimum temperature for reduction decreases. The width of the temperature window increases slightly, levels off, and achieves a value of approximately 50 K as initial H_2 increases. The final combustion temperature determines where NOx reduction ceases and NOx production increases, and the specified temperature where this occurs decreases with initial H_2 concentration.

Reduction increases with HNCO, and the breakthrough of NH_3 and HNCO increases 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. Emissions of N_2O are approximately 50 ppm under optimum conditions. The branching ratio in the NCO + NO reaction needs to be established before the N_2O can be predicted accurately. Interconversion of NO and NO_2 precedes reduction.

The sensitivity structure was rich and changed according to the exhaust composition and combustion conditions. The important reactions were those that influenced ignition chemistry and radical generation. Two reactions that were always among the most important were $H + O_2 + M \rightarrow HO_2$, which was in competition with the most important chain branching reaction of combustion, $H + O_2 \rightarrow OH + O$.

Sensitivity analysis revealed that N_2O production is due to NCO + NO, but that the reduction of NO also, and sometimes dominantly, occurs through reactions associated with the Thermal De-NOx chemistry. The production of NH_3 and its subsequent reactions are very important to the reduction of NO. Comparing the sensitivities for various nitrogen species provided information about the characteristics of the chemical coupling in the system. Sensitivity analysis under conditions that made ignition easy to achieve, i.e., under the conditions of Lyon and Cole's experiments, indicated that the same reactions involving nitrogen species, NH_2 and NNH, important in De-NOx, are important when HNCO is used to reduce NOx.

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 NOx 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. More experiments are required to validate the chemical model. The modeling results would be especially useful for guiding the selection of experimental conditions. Uncertainties in the model also could be reduced by reducing uncertainties in the most sensitive reactions. Three-body recombination reactions are important in the modeling. Different third-body efficiencies need to be measured more reliably. Branching ratios of reactions involving nitrogen species need to be measured as a function of temperature.

Acknowledgment

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FIGURE 12 Sensitivity of HNCO as a function of residence time for the ten most important reactions of B-G mechanism. Conditions are those of Figure 6.

FIGURE 13 Sensitivity of Temperature as a function of residence time for the ten most important reactions of B-G mechanism. Conditions are those of Figure 6.

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

                         --------------------
                         ELEMENTS     ATOMIC
                         CONSIDERED   WEIGHT
                         --------------------
                          1. H        1.00797
                          2. O        15.9994
                          3. C        12.0111
                          4. N        14.0067
                         --------------------
-------------------------------------------------------------------------------
                      C
                    P H
                    H A
                    A R
SPECIES             S G  MOLECULAR  TEMPERATURE      ELEMENT COUNT
CONSIDERED          E E  WEIGHT     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   30.02649  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   25.03027  300.0   5000.0   1  0  2  0
 18. C2H2           G 0   26.03824  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   50.06054  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
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```
                                                          (k = A T**b exp(-E/RT))
      REACTIONS CONSIDERED                                     A           b          E

  1. CH3+CH3(+M)=C2H6(+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
        H2           Enhanced by    2.000e+00
        CO           Enhanced by    2.000e+00
        CO2          Enhanced by    3.000e+00
        H2O          Enhanced by    5.000e+00
  2. CH3+H(+M)=CH4(+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
        H2           Enhanced by    2.000e+00
        CO           Enhanced by    2.000e+00
        CO2          Enhanced by    3.000e+00
        H2O          Enhanced by    5.000e+00
  3. CH4+O2=CH3+HO2                                        7.90e+13     0.0     56000.0
  4. CH4+H=CH3+H2                                          2.20e+04     3.0      8750.0
  5. CH4+OH=CH3+H2O                                        1.60e+06     2.1      2460.0
  6. CH4+O=CH3+OH                                          1.02e+08     1.5      8604.0
  7. CH4+HO2=CH3+H2O2                                      1.80e+11     0.0     18700.0
  8. CH3+HO2=CH3O+OH                                       2.00e+13     0.0         0.0
  9. CH3+O2=CH3O+O                                         2.05e+18    -1.6     29229.0
 10. CH3+O=CH2O+H                                          8.00e+13     0.0         0.0
 11. CH2OH+H=CH3+OH                                        1.00e+14     0.0         0.0
 12. CH3O+H=CH3+OH                                         1.00e+14     0.0         0.0
 13. CH3+OH=CH2+H2O                                        7.50e+06     2.0      5000.0
 14. CH3+H=CH2+H2                                          9.00e+13     0.0     15100.0
 15. CH3O+M=CH2O+H+M                                       1.00e+14     0.0     25000.0
 16. CH2OH+M=CH2O+H+M                                      1.00e+14     0.0     25000.0
 17. CH3O+H=CH2O+H2                                        2.00e+13     0.0         0.0
 18. CH2OH+H=CH2O+H2                                       2.00e+13     0.0         0.0
 19. CH3O+OH=CH2O+H2O                                      1.00e+13     0.0         0.0
 20. CH2OH+OH=CH2O+H2O                                     1.00e+13     0.0         0.0
 21. CH3O+O=CH2O+OH                                        1.00e+13     0.0         0.0
 22. CH2OH+O=CH2O+OH                                       1.00e+13     0.0         0.0
 23. CH3O+O2=CH2O+HO2                                      6.30e+10     0.0      2600.0
 24. CH2OH+O2=CH2O+HO2                                     1.48e+13     0.0      1500.0
 25. CH2+H=CH+H2                                           1.00e+18    -1.6         0.0
 26. CH2+OH=CH+H2O                                         1.13e+07     2.0      3000.0
 27. CH2+OH=CH2O+H                                         2.50e+13     0.0         0.0
 28. CH+O2=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+CO2=HCO+CO                                         3.40e+12     0.0       690.0
 32. CH+H=C+H2                                             1.50e+14     0.0         0.0
 33. CH+H2O=CH2O+H                                         4.57e+14    -0.8         0.0
 34. CH+CH2O=CH2CO+H                                       9.46e+13     0.0      -515.0
 35. CH+C2H2=C3H2+H                                        1.00e+14     0.0         0.0
 36. CH+CH2=C2H2+H                                         4.00e+13     0.0         0.0
 37. CH+CH3=C2H3+H                                         3.00e+13     0.0         0.0
 38. CH+CH4=C2H4+H                                         6.00e+13     0.0         0.0
 39. C+O2=CO+O                                             2.00e+13     0.0         0.0
 40. C+OH=CO+H                                             5.00e+13     0.0         0.0
 41. C+CH3=C2H2+H                                          5.00e+13     0.0         0.0
 42. C+CH2=C2H+H                                           5.00e+13     0.0         0.0
 43. CH2+CO2=CH2O+CO                                       1.10e+11     0.0      1000.0
 44. CH2+O=CO+H+H                                          5.00e+13     0.0         0.0
 45. CH2+O=CO+H2                                           3.00e+13     0.0         0.0
 46. CH2+O2=CO2+H+H                                        1.60e+12     0.0      1000.0
 47. CH2+O2=CH2O+O                                         5.00e+13     0.0      9000.0
 48. CH2+O2=CO2+H2                                         6.90e+11     0.0       500.0
 49. CH2+O2=CO+H2O                                         1.90e+10     0.0     -1000.0
 50. CH2+O2=CO+OH+H                                        8.60e+10     0.0      -500.0
 51. CH2+O2=HCO+OH                                         4.30e+10     0.0      -500.0
 52. CH2O+OH=HCO+H2O                                       3.43e+09     1.2      -447.0
 53. CH2O+H=HCO+H2                                         2.19e+08     1.8      3000.0
 54. CH2O+M=HCO+H+M                                        3.31e+16     0.0     81000.0
 55. CH2O+O=HCO+OH                                         1.80e+13     0.0      3080.0
 56. HCO+OH=H2O+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
        H2           Enhanced by    1.870e+00
        CH4          Enhanced by    2.810e+00
        CO2          Enhanced by    3.000e+00
        H2O          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=HO2+CO                                      3.30e+13   -0.4        0.0
 62. CO+O+M=CO2+M                                       6.17e+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    47688.0
 65. HO2+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                                     1.60e+09    1.2      746.0
 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+HO2                                   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     3428.0
 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.               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.
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                                   6.66e+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     3626.0
126. O+OH=O2+H                                          4.00e+14   -0.5        0.0
127. O+H2=OH+H                                          5.06e+04    2.7     6290.0
128. H+O2+M=HO2+M                                       3.61e+17   -0.7        0.0
        H2O           Enhanced by     1.000e+01
        H2            Enhanced by     2.900e+00
        N2            Enhanced by     1.300e+00
129. OH+HO2=H2O+O2                                      2.12e+15   -0.6      340.0
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131. O+HO2=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.			
H2O Enhanced by 0.			
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+HO2=H2+O2	1.25e+13	0.0	0.0
140. HO2+HO2=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=HO2+H2	1.60e+12	0.0	3800.0
143. H2O2+OH=H2O+HO2	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	1.00e+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+NO=CN+O	6.60e+13	0.0	0.0
150. CH+NO=HCN+O	1.10e+14	0.0	0.0
151. CH2+NO=HCNO+H	1.39e+12	0.0	-1100.0
152. CH3+NO=HCN+H2O	1.00e+11	0.0	15000.0
153. CH3+NO=H2CN+OH	1.00e+11	0.0	15000.0
154. HCCO+NO=HCNO+CO	2.00e+13	0.0	0.0
155. CH2(S)+NO=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=NO+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=NCO+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=NCO+O	5.60e+12	0.0	0.0
174. CN+OH=NCO+H	6.00e+13	0.0	0.0
175. CN+HCN=C2N2+H	2.00e+13	0.0	0.0
176. CN+NO2=NCO+NO	3.00e+13	0.0	0.0
177. CN+N2O=NCO+N2	1.00e+13	0.0	0.0
178. C2N2+O=NCO+CN	4.57e+12	0.0	8880.0
179. C2N2+OH=HOCN+CN	1.86e+11	0.0	2900.0
180. HO2+NO=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+16	0.0	66000.0
184. NCO+H=NH+CO	5.00e+13	0.0	0.0
185. NCO+O=NO+CO	2.00e+13	0.0	0.0
186. NCO+N=N2+CO	2.00e+13	0.0	0.0
187. NCO+OH=NO+HCO	5.00e+12	0.0	15000.0
188. NCO+O2=NO+CO2	3.01e+06	0.0	0.0
189. NCO+M=N+CO+M	3.10e+16	-0.5	48000.0
190. NCO+NO=N2O+CO	1.00e+13	0.0	-390.0
191. NCO+H2=HNCO+H	8.58e+12	0.0	9000.0
192. HNCO+H=NH2+CO	2.90e+08	1.5	6300.0
193. HNCO+M=NH+CO+M	1.14e+16	0.0	86000.0
194. NH+HNCO=NH2+NCO	3.00e+13	0.0	23700.0
195. NH2+HNCO=NH3+NCO	5.00e+12	0.0	6200.0
196. HNCO+OH=NCO+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. HO2+HNCO=NCO+H2O2	3.00e+11	0.0	29000.0
201. HO2+NH3=NH2+H2O2	3.00e+11	0.0	22000.0
202. NH2+NO2=N2O+H2O	2.84e+18	-2.2	0.0
203. NH+NO2=N2O+OH	1.00e+13	0.0	0.0
204. NH+O=NO+H	2.00e+13	0.0	0.0

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205. NH+O2=HNO+O                                    1.00e+13     0.0    12000.0
206. NH+O2=NO+OH                                    7.60e+10     0.0     1530.0
207. NH+NO=N2O+H                                    2.40e+15    -0.8        0.0
208. N2O+OH=N2+HO2                                  2.00e+12     0.0    10000.0
209. N2O+H=N2+OH                                    7.60e+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+NH2                                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                                    6.63e+14    -0.5        0.0
231. NH2+O=NH+OH                                    6.75e+12     0.0        0.0
232. NH2+OH=NH+H2O                                  4.00e+06     2.0     1000.0
233. NH2+H=NH+H2                                    6.92e+13     0.0     3650.0
234. NH2+NO=NNH+OH                                  6.40e+15    -1.2        0.0
235. NH2+NO=N2+H2O                                  6.20e+15    -1.2        0.0
236. NH3+OH=NH2+H2O                                 2.04e+06     2.0      566.0
237. NH3+H=NH2+H2                                   6.36e+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
```

TABLE II

Initial Mixture Composition

CASE	CH_4	H_2	O_2	H_2O	CO	CO_2	HNCO	NO	NO_2	N_2	T
A	0	0	12.3×10^{-2}	4.5×10^{-2}	1.26×10^{-3}	0	1.41×10^{-3}	3.3×10^{-4}	0	8.29×10^{-1}	800-1350
B2	2.5×10^{-3}	0	8.25×10^{-2}	1.15×10^{-1}	5.5×10^{-4}	5.77×10^{-2}	6.62×10^{-4}	1.1×10^{-4}	4.5×10^{-5}	7.4×10^{-1}	1050-1150
B1	2.49×10^{-3}	variable	8.23×10^{-2}	1.15×10^{-1}	5.48×10^{-4}	5.76×10^{-2}	6.60×10^{-4}	1.1×10^{-4}	4.5×10^{-5}	7.39×10^{-1}	800-1200
C	variable	0	8.19×10^{-2}	1.14×10^{-1}	5.46×10^{-4}	5.72×10^{-2}	6.57×10^{-4}	1.1×10^{-4}	4.47×10^{-5}	7.35×10^{-1}	1050-1200
D	2.5×10^{-3}	2.5×10^{-3}	8.25×10^{-2}	1.15×10^{-1}	5.5×10^{-4}	5.77×10^{-2}	variable	1.55×10^{-4}	0	7.41×10^{-1}	1025
E	2.48×10^{-3}	variable	8.18×10^{-2}	1.15×10^{-1}	5.5×10^{-4}	5.73×10^{-2}	6.57×10^{-4}	1.54×10^{-4}	4.46×10^{-5}	7.35×10^{-1}	800-1125
L	0	0	4.3×10^{-2}	2.65×10^{-2}	variable	0	4.9×10^{-4}	1.45×10^{-4}	0	9.3×10^{-1}	978

Concentrations in mole fractions.
Temperatures in Kelvins.

TABLE III

NOx Reduction for Case B1 H2=2500 (ppm)

Ti		Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[HNCO]i	[HNCO]f	[NH3]f	% NOx Reduced
800.	I	800.	0.110E-03	0.109E-03	0.449E-04	0.452E-04	0.331E-07	0.660E-03	0.660E-03	0.131E-07	0
850.	I	850.	0.110E-03	0.108E-03	0.449E-04	0.461E-04	0.373E-06	0.660E-03	0.659E-03	0.260E-06	0
900.	I	902.	0.110E-03	0.106E-03	0.449E-04	0.441E-04	0.250E-05	0.660E-03	0.653E-03	0.278E-05	3
925.	I	929.	0.110E-03	0.979E-04	0.449E-04	0.463E-04	0.560E-05	0.660E-03	0.642E-03	0.746E-05	6
950.	I	959.	0.110E-03	0.817E-04	0.449E-04	0.542E-04	0.101E-04	0.660E-03	0.625E-03	0.156E-04	12
975.	I	990.	0.110E-03	0.590E-04	0.449E-04	0.669E-04	0.157E-04	0.660E-03	0.602E-03	0.273E-04	18
1000.	I	1030.	0.110E-03	0.242E-04	0.449E-04	0.815E-04	0.270E-04	0.660E-03	0.564E-03	0.516E-04	31
1025.	C	1110.	0.110E-03	0.157E-04	0.449E-04	0.489E-05	0.600E-04	0.660E-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	0.660E-03	0.118E-04	0.475E-05	72
1100.	C	1184.	0.110E-03	0.130E-03	0.449E-04	0.802E-05	0.287E-04	0.660E-03	0.787E-06	0.156E-06	10
1150.	C	1233.	0.110E-03	0.271E-03	0.449E-04	0.398E-05	0.489E-05	0.660E-03	0.868E-08	0.114E-08	-77
1200.	C	1282.	0.110E-03	0.398E-03	0.449E-04	0.272E-05	0.142E-06	0.660E-03	0.551E-10	0.524E-11	-158

TABLE IV

NOx Reduction for Case B1 H2=7500 (ppm)

Ti		Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[HNCO]i	[HNCO]f	[NH3]f	% NOx Reduced
800.	I	802.	0.109E-03	0.931E-04	0.447E-04	0.575E-04	0.164E-05	0.657E-03	0.653E-03	0.121E-05	2
850.	I	871.	0.109E-03	0.665E-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	0.618E-05	0.447E-04	0.259E-05	0.396E-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	67
1025.	C	1144.	0.109E-03	0.107E-03	0.447E-04	0.122E-04	0.500E-04	0.657E-03	0.236E-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	0.346E-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	0.820E-05	0.657E-03	0.433E-08	0.365E-09	-160

TABLE V

NOx Reduction Variable HNCO

Ti	Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[HNCO]i	[HNCO]f	[NH3]f	% NOx Reduced
1025.	1105.	0.110E-03	0.738E-04	0.449E-04	0.520E-05	0.235E-04	0.165E-03	0.265E-05	0.493E-06	48
1025.	1107.	0.110E-03	0.363E-04	0.449E-04	0.579E-05	0.407E-04	0.330E-03	0.968E-05	0.326E-05	72
1025.	1108.	0.110E-03	0.218E-04	0.449E-04	0.537E-05	0.524E-04	0.495E-03	0.188E-04	0.837E-05	82
1025.	1110.	0.110E-03	0.157E-04	0.449E-04	0.469E-05	0.600E-04	0.660E-03	0.282E-04	0.144E-04	86
1025.	1112.	0.110E-03	0.130E-04	0.449E-04	0.401E-05	0.638E-04	0.825E-03	0.371E-04	0.206E-04	89

TABLE VI

NOx Reduction for Case E H2=2500 (ppm)

Ti	Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[HNCO]i	[HNCO]f	[NH3]f	% NOx 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	0.536E-04	0.116E-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	0.168E-04	0.448E-04	0.527E-05	0.670E-04	0.660E-03	0.286E-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

NOx Reduction for Case E H2=5000 (ppm)

Ti		Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[HNCO]i	[HNCO]f	[NH3]f	% NOx Reduced
800.	I	800.	0.154E-03	0.148E-03	0.447E-04	0.497E-04	0.394E-06	0.659E-03	0.658E-03	0.182E-06	0
850.	I	853.	0.154E-03	0.141E-03	0.447E-04	0.507E-04	0.361E-05	0.659E-03	0.649E-03	0.281E-05	3
900.	I	920.	0.154E-03	0.990E-04	0.447E-04	0.585E-04	0.192E-04	0.659E-03	0.596E-03	0.208E-04	20
925.	I	960.	0.154E-03	0.621E-04	0.447E-04	0.702E-04	0.310E-04	0.659E-03	0.552E-03	0.366E-04	33
950.	I	1050.	0.154E-03	0.104E-04	0.447E-04	0.362E-05	0.610E-04	0.659E-03	0.166E-03	0.589E-04	92
975.	C	1078.	0.154E-03	0.766E-05	0.447E-04	0.325E-05	0.527E-04	0.659E-03	0.518E-04	0.299E-04	94
1000.	C	1103.	0.154E-03	0.164E-04	0.447E-04	0.539E-05	0.617E-04	0.659E-03	0.255E-04	0.125E-04	89
1025.	C	1128.	0.154E-03	0.419E-04	0.447E-04	0.858E-05	0.611E-04	0.659E-03	0.101E-04	0.353E-05	74
1050.	C	1152.	0.154E-03	0.962E-04	0.447E-04	0.112E-04	0.496E-04	0.659E-03	0.286E-05	0.560E-06	45
1075.	C	1177.	0.154E-03	0.181E-03	0.447E-04	0.116E-04	0.320E-04	0.659E-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	0.659E-03	0.522E-07	0.542E-08	-44

TABLE VIII

NOx Reduction for Case E H2=7500 (ppm)

Ti		Tf	[NO]i	[NO]f	[NO2]i	[NO2]f	[N2O]f	[HNCO]i	[HNCO]f	[NH3]f	% NOx 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	0.528E-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	0.328E-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	0.636E-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	0.583E-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	0.282E-04	0.130E-04	90
975. C	1113.	0.154E-03	0.470E-04	0.445E-04	0.976E-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	0.146E-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	0.368E-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

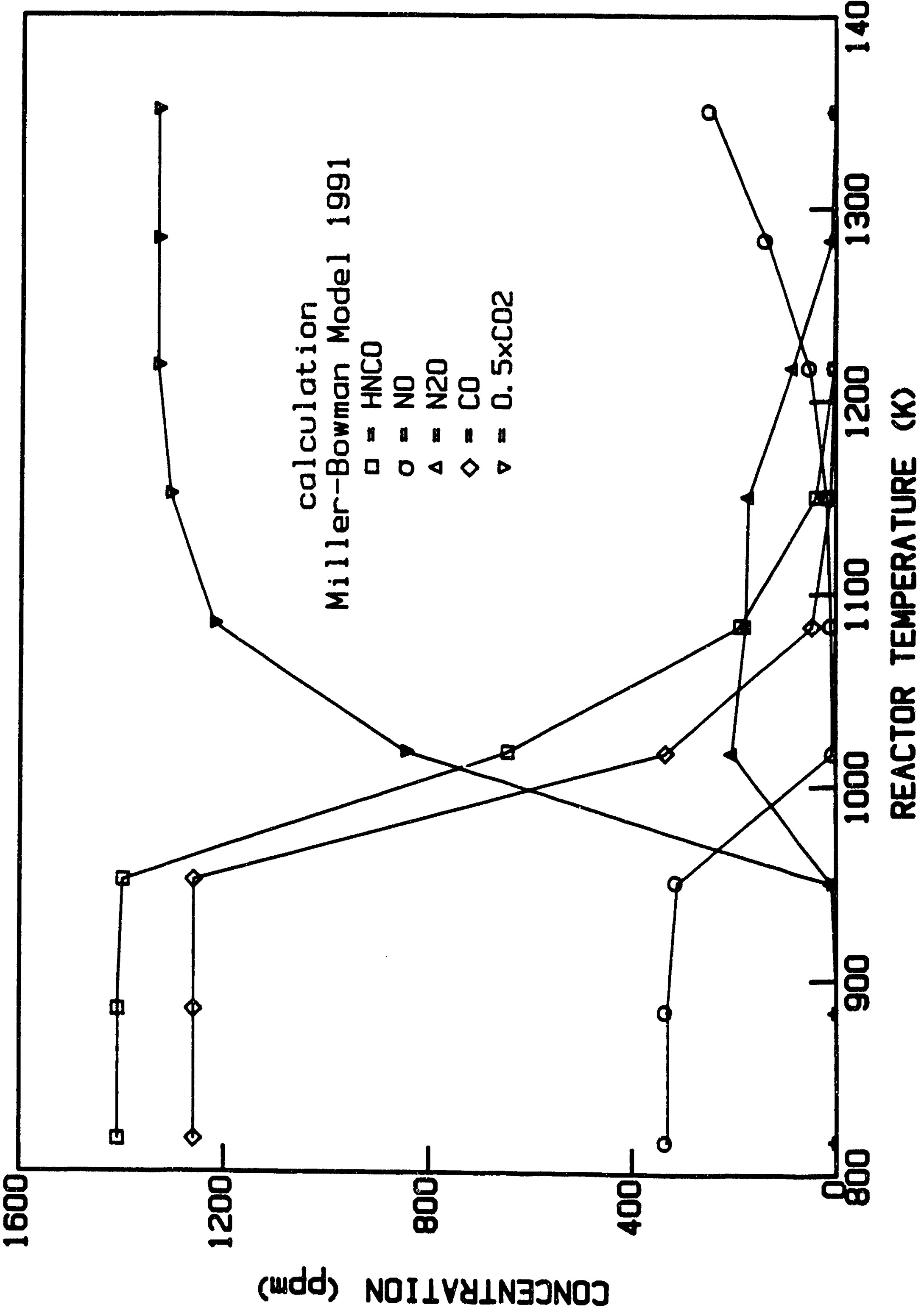

calculation
Miller-Bowman Model 1991
□ = HNCO
○ = NO
△ = N2O
◇ = CO
▽ = 0.5xCO2
CONCENTRATION (ppm)
0
400
800
1200
1600
REACTOR TEMPERATURE (K)
800
900
1000
1100
1200
1300
1400

Figure 1

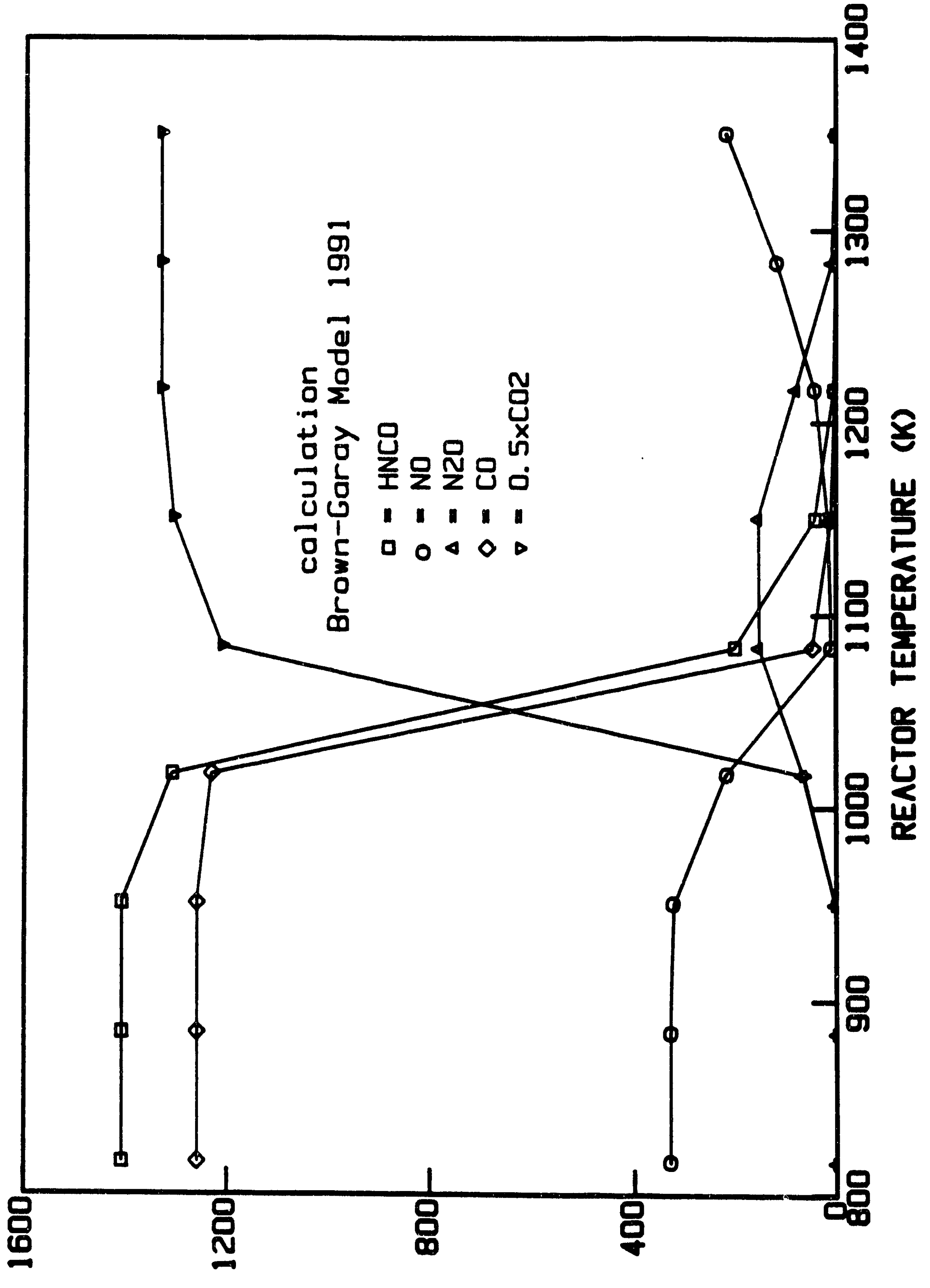

calculation
Brown-Garay Model 1991
□ = HNCO
○ = NO
△ = N2O
◇ = CO
▽ = 0.5xCO2
CONCENTRATION (ppm)
0
400
800
1200
1600
800
900
1000
1100
1200
1300
1400
REACTOR TEMPERATURE (K)

Figure 2

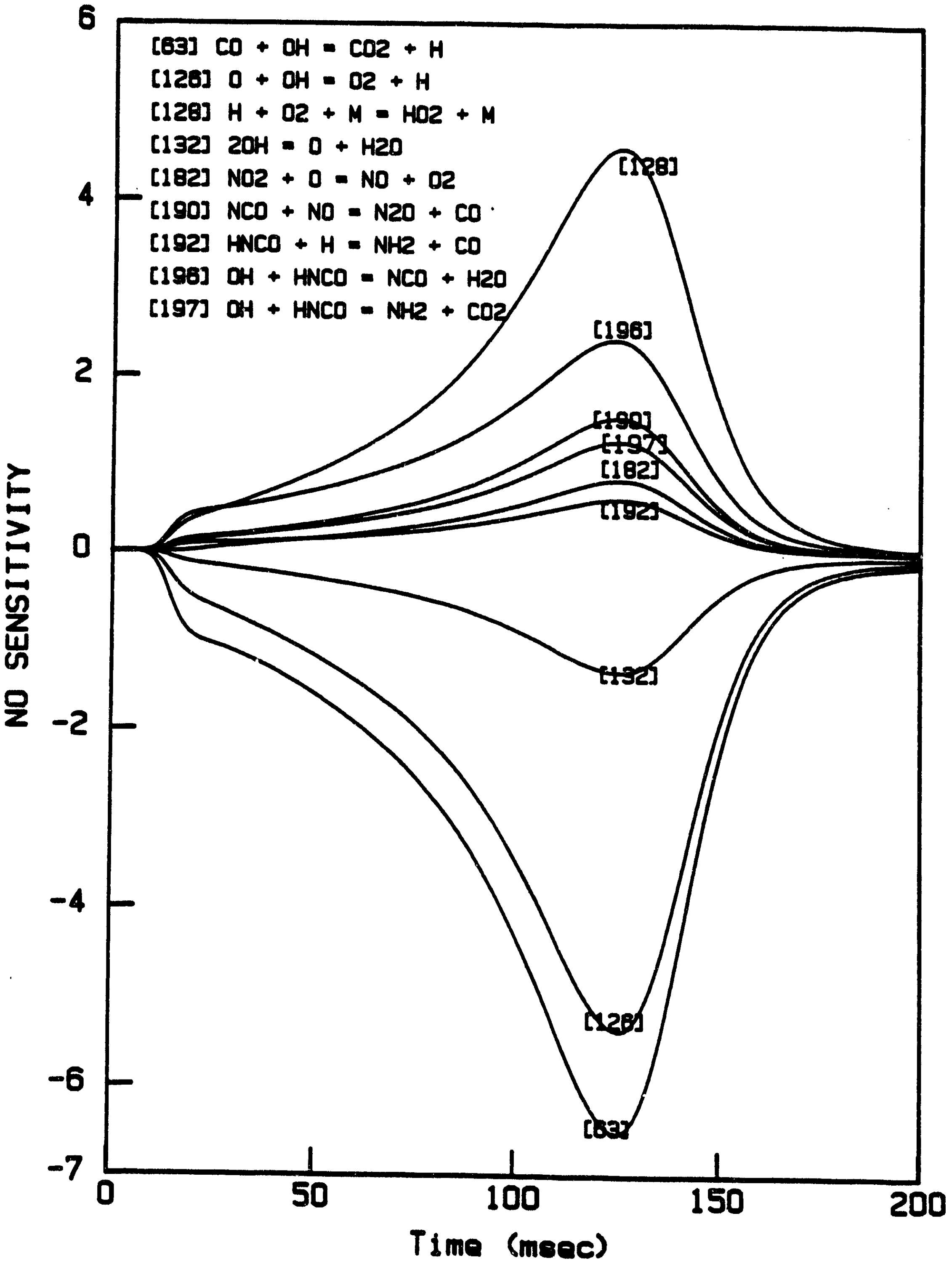
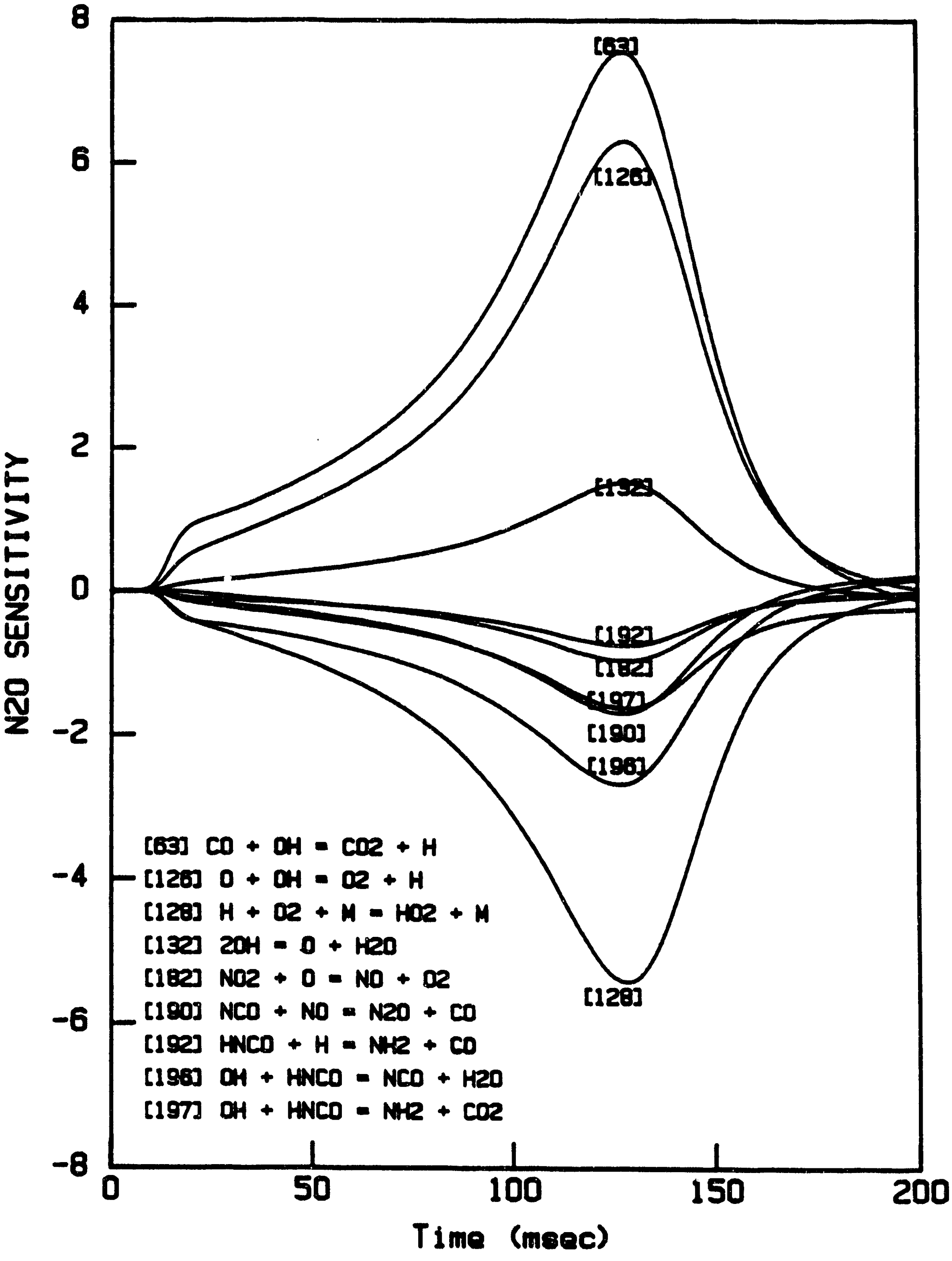
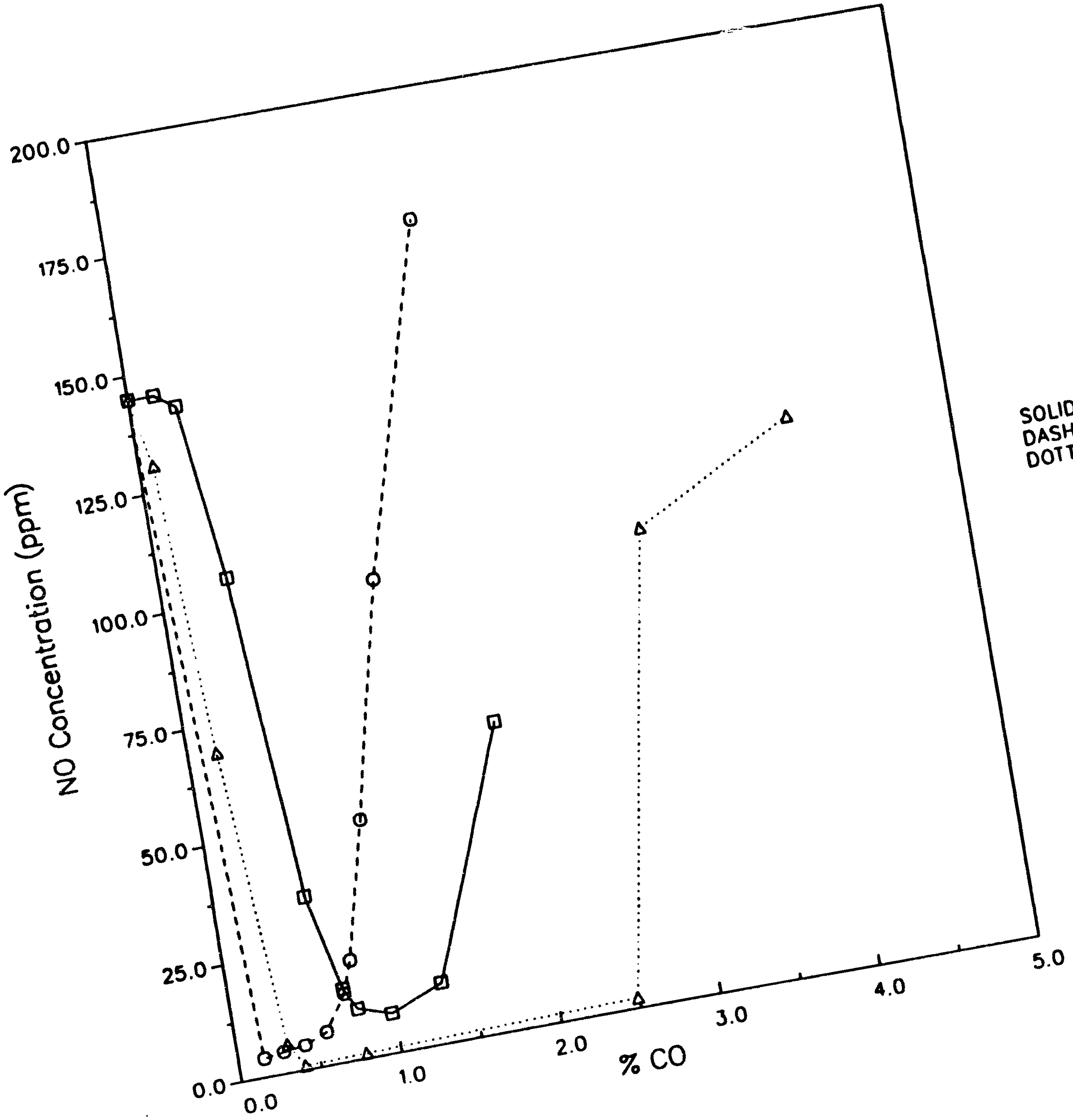

[63] CO + OH = CO2 + H
[126] O + OH = O2 + H
[128] H + O2 + M = HO2 + M
[132] 2OH = O + H2O
[182] NO2 + O = NO + O2
[190] NCO + NO = N2O + CO
[192] HNCO + H = NH2 + CO
[196] OH + HNCO = NCO + H2O
[197] OH + HNCO = NH2 + CO2
[128]
[196]
[190]
[197]
[182]
[192]
[132]
[126]
[63]
NO SENSITIVITY
6
4
2
0
-2
-4
-6
-7
0
50
100
150
200
Time (msec)

Figure 3



N2O SENSITIVITY
Time (msec)
8
6
4
2
0
-2
-4
-6
-8
0
50
100
150
200
[63]
[126]
[132]
[192]
[182]
[197]
[190]
[196]
[128]
[63] CO + OH = CO2 + H
[126] O + OH = O2 + H
[128] H + O2 + M = HO2 + M
[132] 2OH = O + H2O
[182] NO2 + O = NO + O2
[190] NCO + NO = N2O + CO
[192] HNCO + H = NH2 + CO
[196] OH + HNCO = NCO + H2O
[197] OH + HNCO = NH2 + CO2

Figure 4



SOLID LINE IS EXPERIMENTAL
DASHED LINE IS OUR MECHANISM
DOTTED LINE IS LYON MODEL

Figure 5

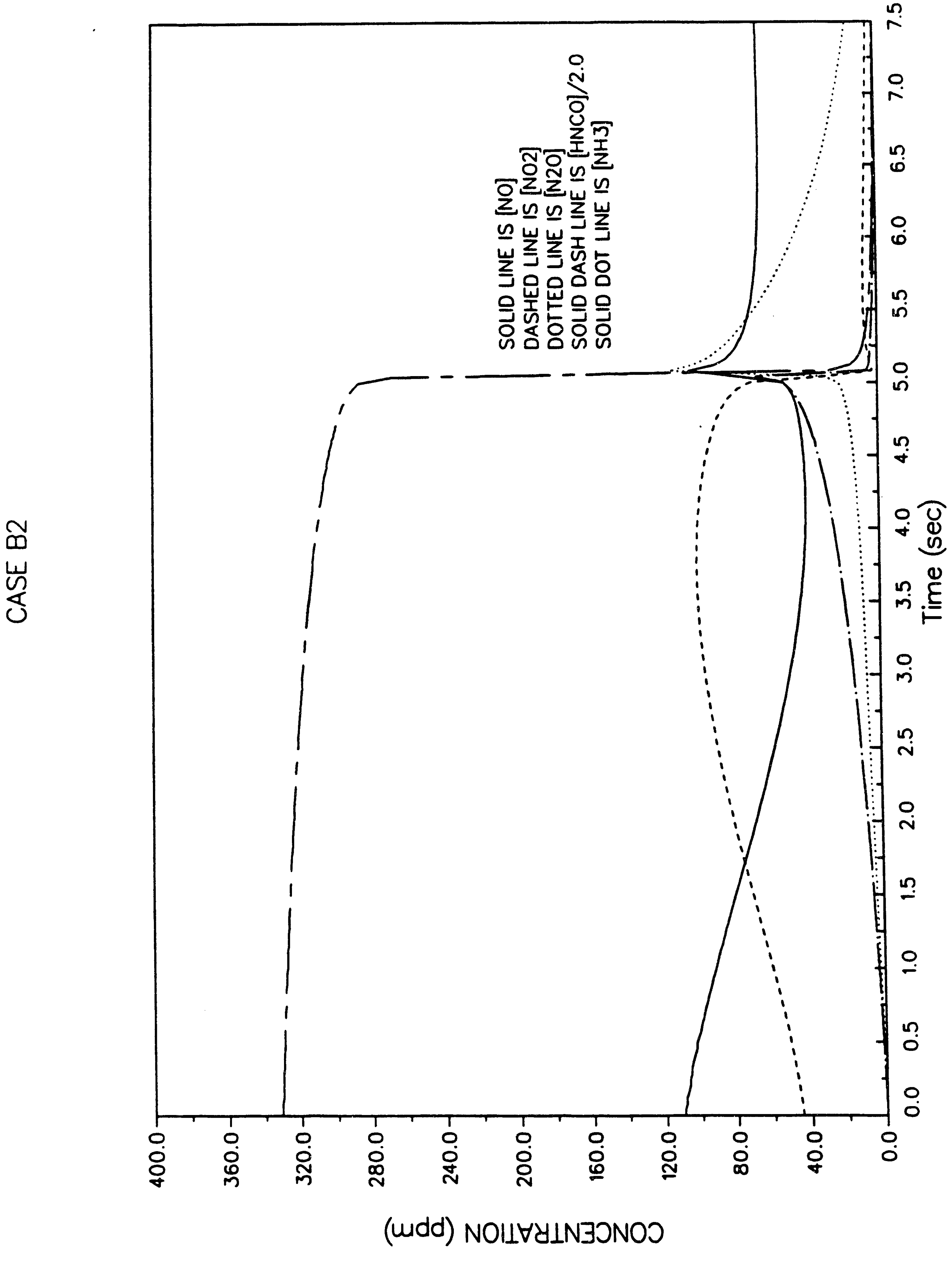
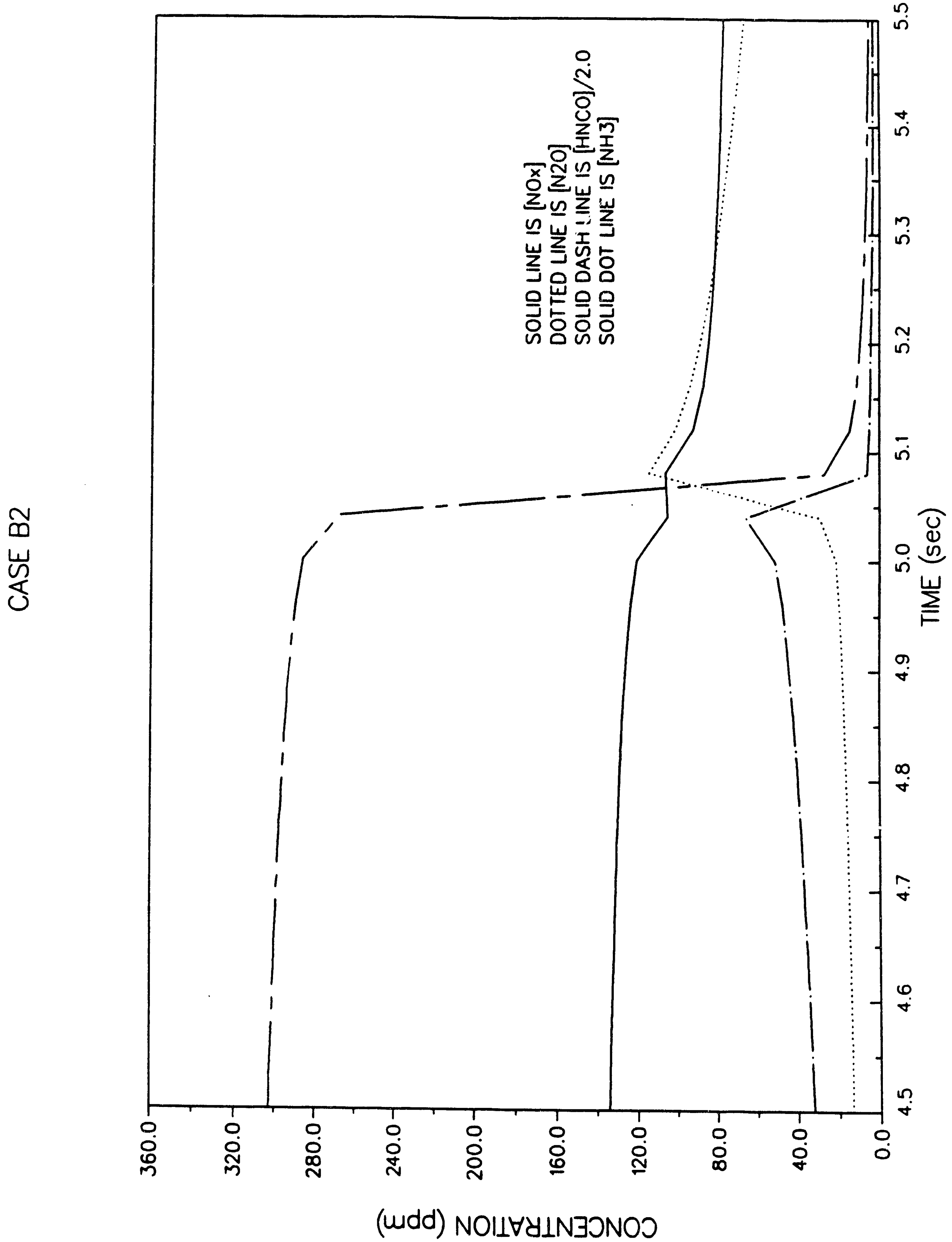

CASE B2
SOLID LINE IS [NO]
DASHED LINE IS [NO2]
DOTTED LINE IS [N2O]
SOLID DASH LINE IS [HNCO]/2.0
SOLID DOT LINE IS [NH3]
CONCENTRATION (ppm)
400.0
360.0
320.0
280.0
240.0
200.0
160.0
120.0
80.0
40.0
0.0
Time (sec)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

Figure 6



CASE B2

Figure 7

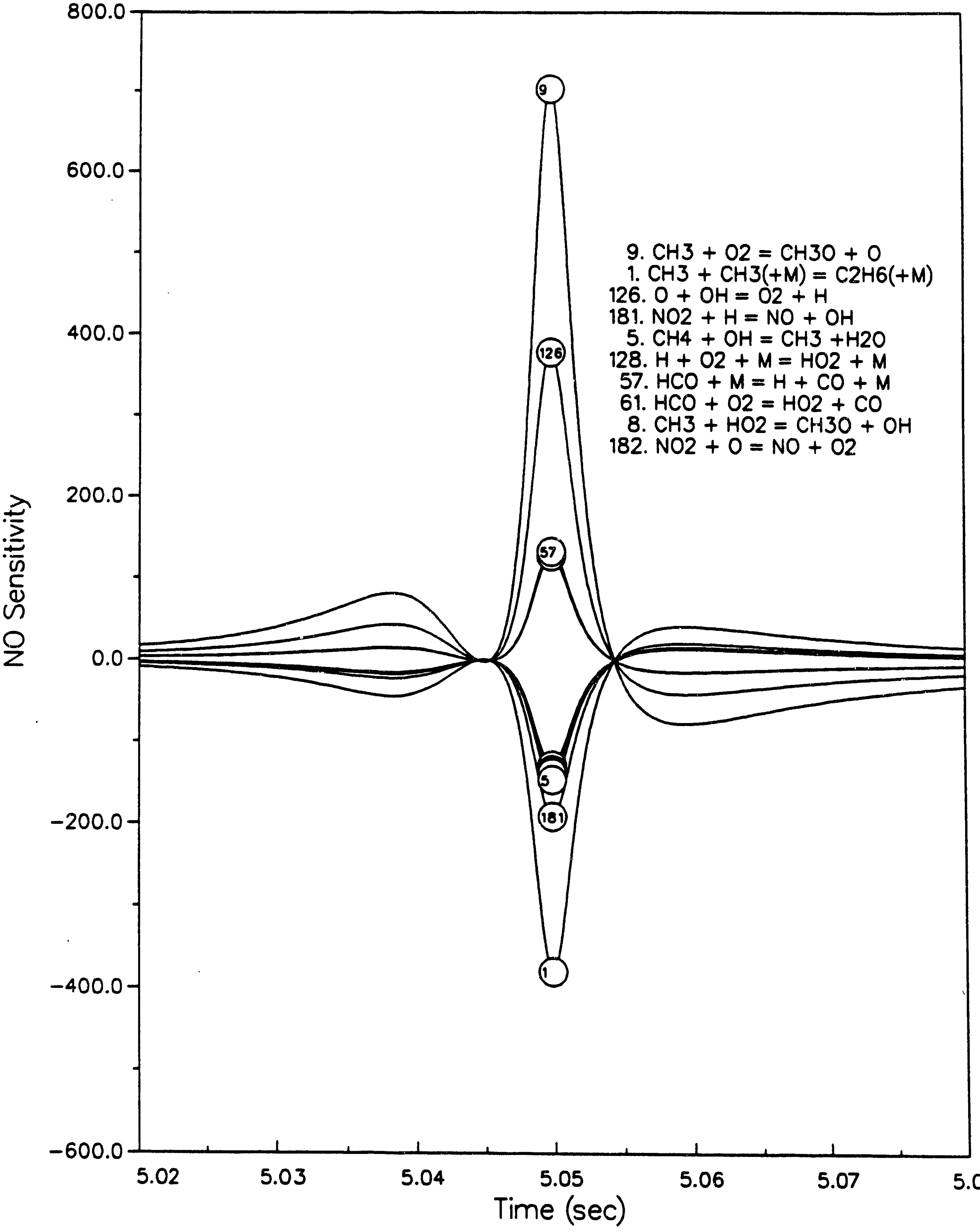

800.0
600.0
400.0
200.0
0.0
−200.0
−400.0
−600.0
NO Sensitivity
5.02
5.03
5.04
5.05
5.06
5.07
5.08
Time (sec)
9
126
57
5
181
1
9. CH3 + O2 = CH3O + O
1. CH3 + CH3(+M) = C2H6(+M)
126. O + OH = O2 + H
181. NO2 + H = NO + OH
5. CH4 + OH = CH3 +H2O
128. H + O2 + M = HO2 + M
57. HCO + M = H + CO + M
61. HCO + O2 = HO2 + CO
8. CH3 + HO2 = CH3O + OH
182. NO2 + O = NO + O2

Figure 8

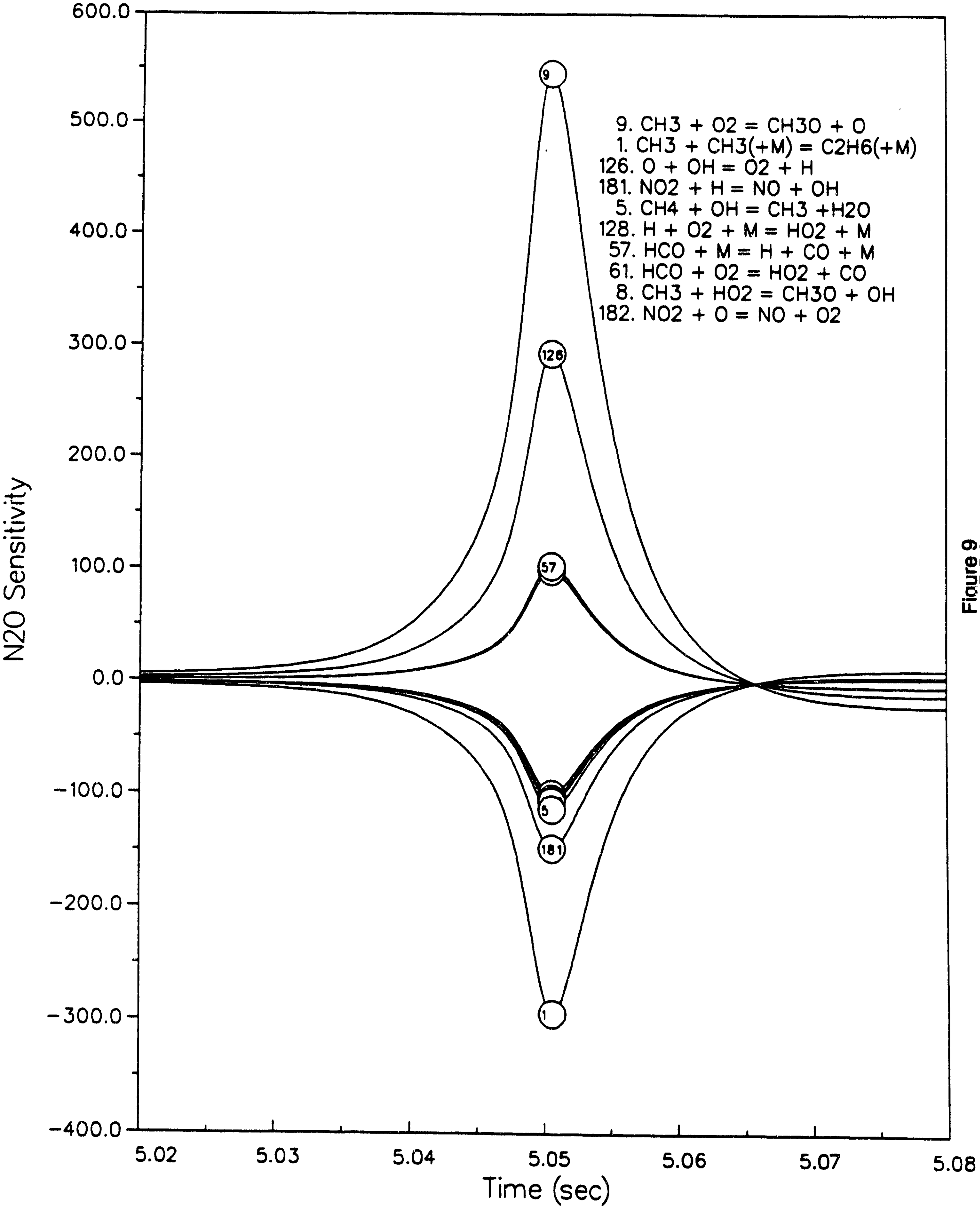

600.0
500.0
400.0
300.0
200.0
100.0
0.0
−100.0
−200.0
−300.0
−400.0
N2O Sensitivity
5.02
5.03
5.04
5.05
5.06
5.07
5.08
Time (sec)
9
126
57
5
181
1
9. CH3 + O2 = CH3O + O
1. CH3 + CH3(+M) = C2H6(+M)
126. O + OH = O2 + H
181. NO2 + H = NO + OH
5. CH4 + OH = CH3 +H2O
128. H + O2 + M = HO2 + M
57. HCO + M = H + CO + M
61. HCO + O2 = HO2 + CO
8. CH3 + HO2 = CH3O + OH
182. NO2 + O = NO + O2

Figure 9

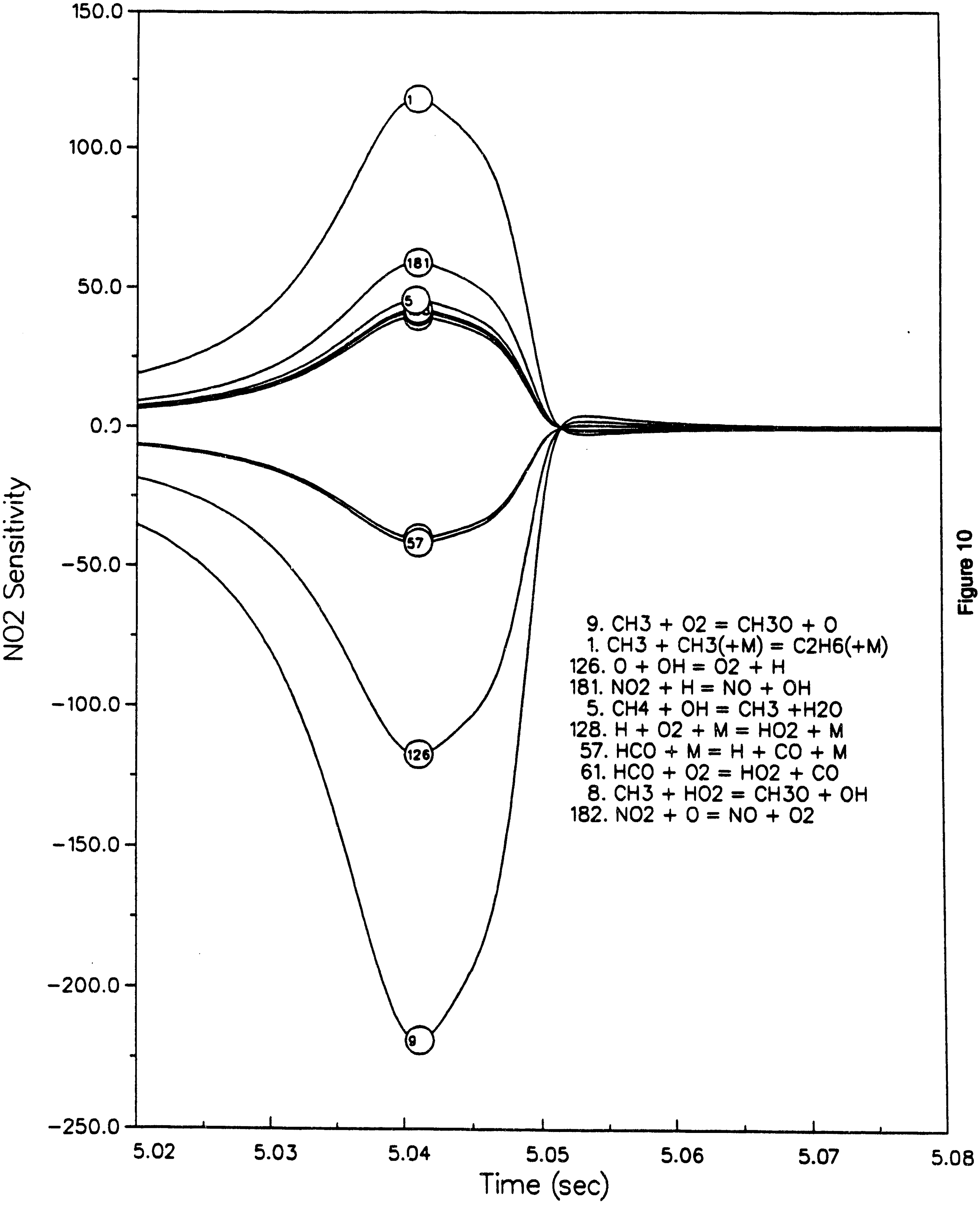

150.0
100.0
50.0
0.0
−50.0
−100.0
−150.0
−200.0
−250.0
NO2 Sensitivity
5.02
5.03
5.04
5.05
5.06
5.07
5.08
Time (sec)
1
181
5
57
126
9
9. CH3 + O2 = CH3O + O
1. CH3 + CH3(+M) = C2H6(+M)
126. O + OH = O2 + H
181. NO2 + H = NO + OH
5. CH4 + OH = CH3 +H2O
128. H + O2 + M = HO2 + M
57. HCO + M = H + CO + M
61. HCO + O2 = HO2 + CO
8. CH3 + HO2 = CH3O + OH
182. NO2 + O = NO + O2

Figure 10

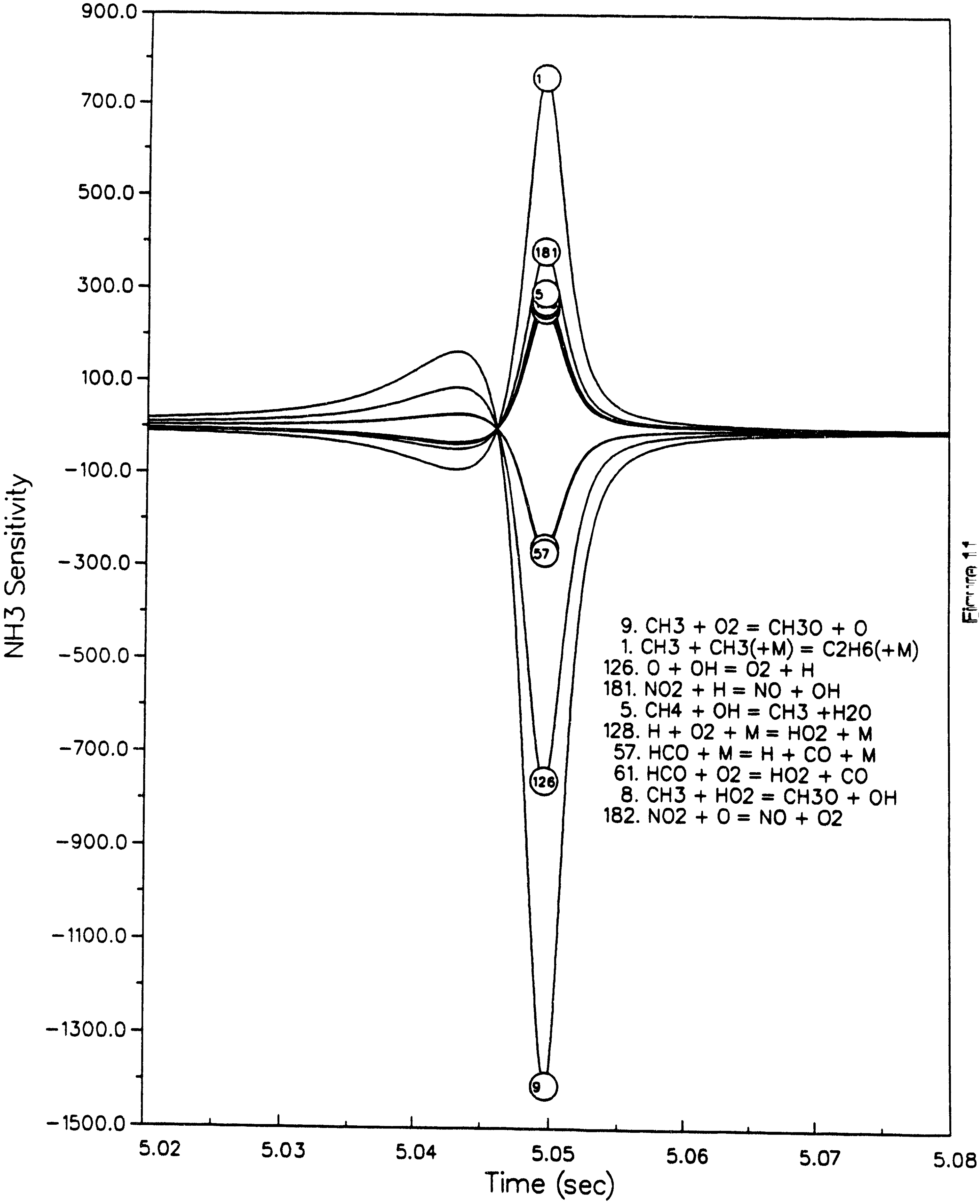

900.0
700.0
500.0
300.0
100.0
−100.0
−300.0
−500.0
−700.0
−900.0
−1100.0
−1300.0
−1500.0
NH3 Sensitivity
5.02
5.03
5.04
5.05
5.06
5.07
5.08
Time (sec)
1
181
5
57
126
9
9. CH3 + O2 = CH3O + O
1. CH3 + CH3(+M) = C2H6(+M)
126. O + OH = O2 + H
181. NO2 + H = NO + OH
5. CH4 + OH = CH3 +H2O
128. H + O2 + M = HO2 + M
57. HCO + M = H + CO + M
61. HCO + O2 = HO2 + CO
8. CH3 + HO2 = CH3O + OH
182. NO2 + O = NO + O2

Figure 11

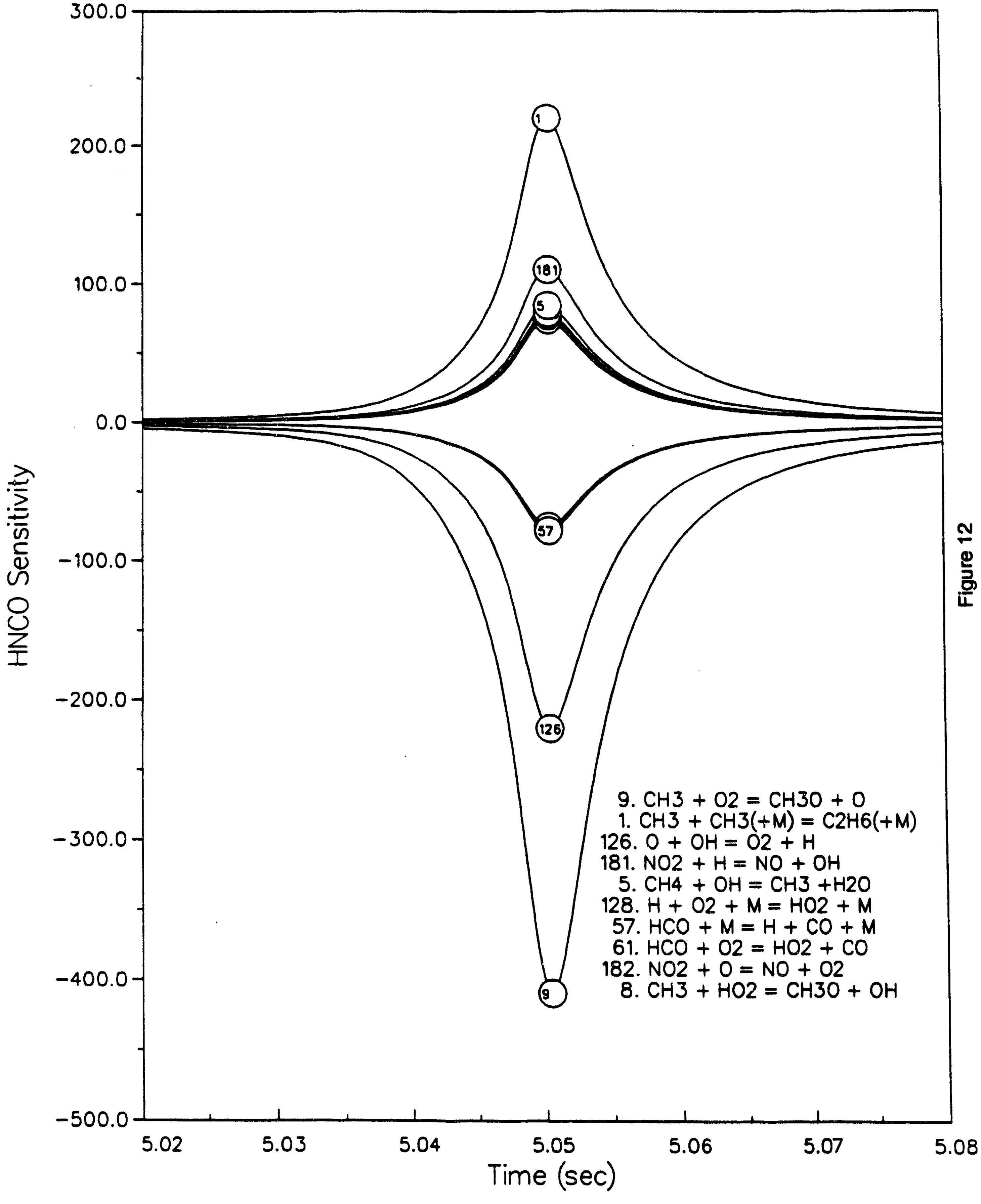

300.0
200.0
100.0
0.0
−100.0
−200.0
−300.0
−400.0
−500.0
HNCO Sensitivity
5.02
5.03
5.04
5.05
5.06
5.07
5.08
Time (sec)
1
181
5
57
126
9
9. CH3 + O2 = CH3O + O
1. CH3 + CH3(+M) = C2H6(+M)
126. O + OH = O2 + H
181. NO2 + H = NO + OH
5. CH4 + OH = CH3 +H2O
128. H + O2 + M = HO2 + M
57. HCO + M = H + CO + M
61. HCO + O2 = HO2 + CO
182. NO2 + O = NO + O2
8. CH3 + HO2 = CH3O + OH

Figure 12

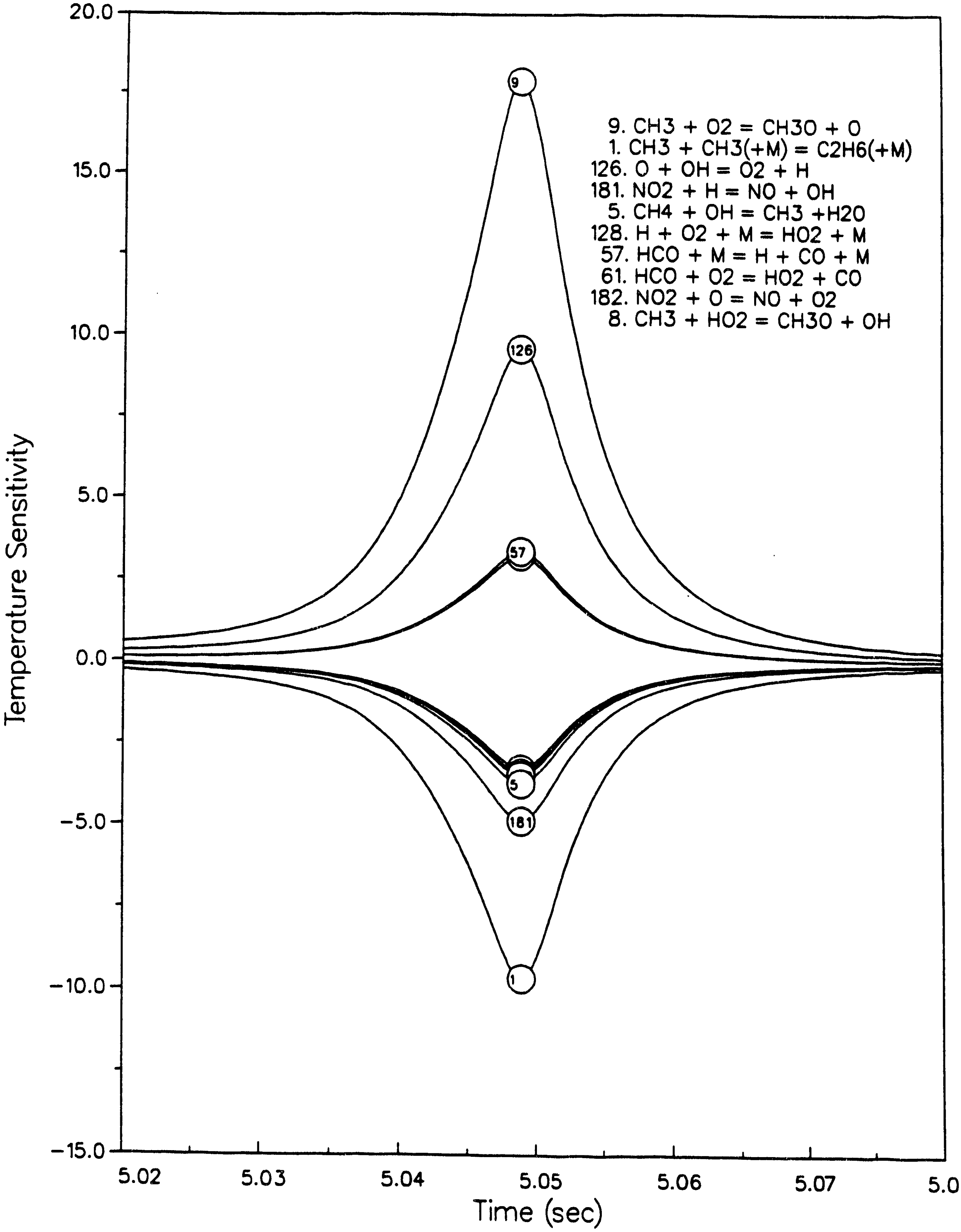

20.0
15.0
10.0
5.0
0.0
−5.0
−10.0
−15.0
Temperature Sensitivity
5.02
5.03
5.04
5.05
5.06
5.07
5.08
Time (sec)
9
126
57
5
181
1
9. CH3 + O2 = CH3O + O
1. CH3 + CH3(+M) = C2H6(+M)
126. O + OH = O2 + H
181. NO2 + H = NO + OH
5. CH4 + OH = CH3 +H2O
128. H + O2 + M = HO2 + M
57. HCO + M = H + CO + M
61. HCO + O2 = HO2 + CO
182. NO2 + O = NO + O2
8. CH3 + HO2 = CH3O + OH

Figure 13

END

DATE
FILMED

11/9/92