

11689

11689

p.24

NASA Technical Memorandum 103765  
AIAA - 91 - 0479

# Mechanisms and Modeling of the Effects of Additives on the Nitrogen Oxides Emission

(NASA-TM-103765) MECHANISMS AND MODELING OF  
THE EFFECTS OF ADDITIVES ON THE NITROGEN  
OXIDES EMISSION (NASA) 24 p C5CL 201

N91-22464

Unclass

G3/28 0011689

Krishna P. Kundu, H. Lee Nguyen, and M. Paul Kang  
*Lewis Research Center*  
*Cleveland, Ohio*

Prepared for the  
29th Aerospace Sciences Meeting  
sponsored by the American Institute of Aeronautics and Astronautics  
Reno, Nevada, January 7-10, 1991





# MECHANISMS AND MODELING OF THE EFFECTS OF ADDITIVES ON THE NITROGEN OXIDES EMISSION

Krishna P. Kundu,\* H. Lee Nguyen, and M. Paul Kang  
National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135

## SUMMARY

A theoretical study on the formation of the oxides of nitrogen in the combustion of hydrocarbons is presented in this communication. Our current understanding of the mechanisms and the rate parameters for gas phase reactions have been used to calculate the NO<sub>x</sub> emission. The possible effects of different chemical species on thermal NO<sub>x</sub>, on a long time scale have been discussed. The mixing of these additives at various stages of combustion has been considered and NO<sub>x</sub> concentrations have been calculated; effects of temperatures have also been considered. The chemicals such as hydrocarbons, H<sub>2</sub>, CH<sub>3</sub>OH, NH<sub>3</sub> and other nitrogenous species have been chosen as additives in this discussion. Results of these calculations can be used to evaluate the effects of these additives on the NO<sub>x</sub> emission in the industrial combustion systems.

## INTRODUCTION

The oxides of nitrogen play an important role in the photochemical processes that are responsible for the acid rain and smog formation (ref. 1). NO<sub>x</sub> is generated from nitrogen in air (ref. 2) and in the fuel (ref. 3) used in the combustion processes including the industrial boilers. Nitrogen and oxygen react at high temperature (ref. 4) to form NO<sub>x</sub> which has been described as thermal NO<sub>x</sub> while the fragments of hydrocarbons form the nitrogenous compounds which oxidize to prompt NO<sub>x</sub> (ref. 5). The three major types of nitrogen oxides are NO, NO<sub>2</sub> and N<sub>2</sub>O, and it is well known that their distribution in the emission is dependent on temperature.

It is well known that very little NO<sub>x</sub> is produced if the combustion takes place in fuel-rich condition when oxygen mostly reacts with the fuel. but in oxygen rich condition, particularly near the stoichiometric condition of burning (ref. 6), temperature of combustion is very high and the thermal NO<sub>x</sub> formation is very rapid. In this study, all the NO<sub>x</sub> have been assumed to be thermal NO<sub>x</sub> and these are formed during combustion.

The thermal NO<sub>x</sub> formation can be partially controlled by the modification of the design of the combustor (ref. 7). These modifications reduce the flame temperature and thus retards the formation of NO<sub>x</sub>. Although this technique reduces the NO<sub>x</sub> formation, in some cases it is not enough and it is necessary to reduce NO<sub>x</sub> still further. Post-combustion treatment (refs. 1, 8 to 12) of the exhaust gas is one way to reduce NO<sub>x</sub>. Various exhaust treatment processes are in use for specific types of combustion devices. For example, in the exhaust of spark-ignited automotive engines, noble metal catalyst is used along with combustion stoichiometry to reduce NO<sub>x</sub>; other alternative concepts of NO<sub>x</sub> reductions have also been considered (refs. 8 and 12). The concept of using additives to the exhaust stream for reduction of NO<sub>x</sub>

---

\*National Research Council - NASA Research Associate at Lewis Research Center.

has become popular; the concept of converting NO<sub>x</sub> chemically to some form which can be comparatively easily removed by washing with water, has also been used (ref. 13).

The various technologies that have been developed so far for the post-combustion treatment can be carried out in either dry or wet systems. The dry method includes homogeneous (noncatalytic reduction), catalytic reduction, sorption by solids (physical adsorption or chemical absorption) and catalytic decomposition. Most process development efforts have concentrated on the selective reduction of NO<sub>x</sub> by adding ammonia (ref. 8) and other nitrogenous compounds (ref. 10) to the exhaust stream either with or without catalyst (ref. 11). NH<sub>3</sub> in presence of other additives have also been considered to reduce NO<sub>x</sub> (ref. 14).

Wet methods for the removal of NO<sub>x</sub> are limited by the relatively inert nature of NO. This difficulty can be overcome by oxidation of NO to the more reactive NO<sub>2</sub> in the gaseous phase. In this study we have considered the effects of H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and CH<sub>3</sub>OH as possible additives to oxidize NO. Calculation results indicate that these methods are superior to the conventional oxidation methods (ref. 1).

This study has involved only modeling to estimate the potential of using additives to control NO<sub>x</sub>. Modeling can be considered as a reliable predictive tool within certain limit due in large part to the recent advances in the computer calculations and to the availability of detailed chemical kinetics models of hydrocarbons and nitrogen containing molecules.

#### Physical/Computation Models and Kinetic Mechanisms

In the present study, we are focussing on the use of additives to the control of NO<sub>x</sub>. The formation of NO<sub>x</sub> is dependent on temperature. At high temperature, particularly when the fuel-air ratio is close to 1, thermal NO<sub>x</sub> formation is very fast. Unless temperature is reduced, no additive is expected to reduce NO<sub>x</sub> so long both nitrogen and oxygen are present. So if the NO<sub>x</sub> has to be reduced in such condition, the exhaust emission has to be cooled before any additive is added. Since the objective of this study is to evaluate the effect of additives on the oxides of nitrogen, the exhaust emission was cooled to arbitrary temperature before the additives were added. It is however, necessary to know the concentrations of different species present in the emission in order to do the calculations. It may be assumed that the combustion is complete within a fraction of the second and therefore the composition of the emission in most cases have been assumed to be equivalent to the equilibrium composition. Figures 1(a) and (b) show that equilibrium compositions in the combustion of methane depend on various factors including the initial fuel and air temperatures. Since the objective of this report is to evaluate the effects of additives on the NO<sub>x</sub> emission, we have arbitrarily chosen a concentration of NO in combination with 4.2 percent oxygen and 10 percent water. We have also assumed that practically all the NO<sub>x</sub> in the equilibrium mixture is in the form of NO and no NO<sub>2</sub> is present. This assumption is justified because at higher temperature NO<sub>2</sub> is converted into NO.

We have also considered the effects of various additives in presence of hydrocarbon fragments. In order to do that, calculations were made using composition of the exhaust stream before the combustion was complete. In this case, the composition of the various species are different from the equilibrium composition. Application of modeling requires the knowledge of the concentrations of all these species including the radical species. We have therefore used a well stirred reactor model

of the combustion of methane at 0.5 to 0.8 equivalent ratio and chosen the concentration of different species at about 2 msec residence time. Lsens computer code developed by Bittker and Radhakrishnan (ref. 15) was used in these calculations. Plug flow reaction model of Lsens code was used to calculate the NO<sub>x</sub> concentrations after the additives were added. The thermodynamic data required in these calculations were obtained from the data set supplied with the Lsens code and also from Sandia report (ref. 16).

The chemical kinetic mechanism is essentially identical to that developed by Miller and Bowman (ref. 14); a few reaction species were however eliminated to make it fit to the Lsens code. This model was tested by actual comparison of the experimental data using WSR model of thermal NO<sub>x</sub> (ref. 17) formation in the combustion of methane at various fuel-air ratio. Few reactions of methanol and species derived from it as described by Westbrook and Dreyer (ref. 18), were included in this mechanisms; reactions (220,221,222,223) involving hydrazine and its decomposition products were also included. Table I shows the reactions used in this mechanism. This mechanism includes chemical processes of methane combustion, formation of NO by Zeldovitch and prompt NO<sub>x</sub> mechanism (refs. 2 and 5) as well as the removal of nitric oxide.

### Combustor Exhaust Gas Modeling

The primary objective of this study is to evaluate the effect of additives on NO<sub>x</sub> in presence or in absence of unburnt hydrocarbon fragments at various temperatures. In order to do that, emission products at arbitrary locations were chosen; these species were then cooled to different temperatures and the additives were added. Changes in NO<sub>x</sub> with time were calculated; calculations for a prolonged period were made in order to determine the usefulness of the particular additive. The calculation shows that the fragments of hydrocarbons have definite effects on the reactions involving NO<sub>x</sub>. Since the present study uses only methane as fuel, the amount of NO<sub>x</sub> produced may be much less than what is normally generated during burning of conventional fuels containing fuel-bound nitrogen. In our calculations we assumed that about 500 to 1000 ppm NO were present in the emission; the similar level of NO<sub>x</sub> was assumed in the emission containing hydrocarbon fragments also.

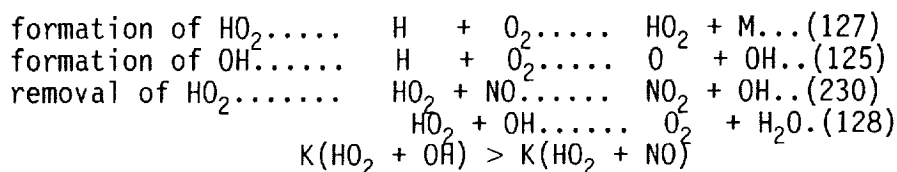
Figures 1 and 2 shows the equilibrium concentrations of NO and NO<sub>2</sub> at different fuel-air ratio. It appears that in the equilibrium condition NO<sub>x</sub> remains mostly in the form of NO. Table II shows the result of cooling the emission containing hydrocarbon fragments to different temperatures and following the reactions under constant temperature condition. It appears that at lower temperature there is a gradual growth of NO<sub>2</sub>, although total NO<sub>x</sub> is not affected. It also appears that NO<sub>2</sub> concentration gradually falls with increase in temperature. This suggests that probably hydrocarbon fragments help in the oxidation of NO to NO<sub>2</sub> and this oxidation seems to be more effective at lower temperature. Ito and Yano (ref. 22) showed in their studies on the combustion of methanol that the oxidation of methanol is catalyzed by NO. Later Lyon et al. (ref. 23) showed that methanol helps in the oxidation of NO, and the oxidation takes place mostly by HO<sub>2</sub>. It appears that similar oxidation of NO takes place in presence of hydrocarbon fragments as well.

In the present study the oxidation of NO in presence of hydrocarbons and methanol will be discussed. The reduction of NO to nitrogen in presence of nitrogenous compounds will also be discussed.

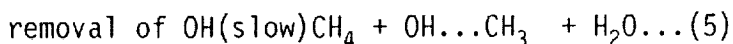
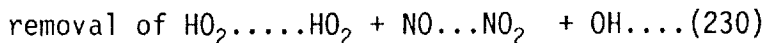
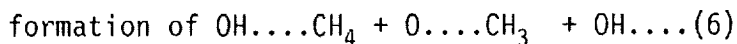
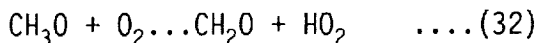
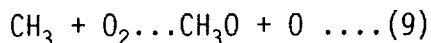
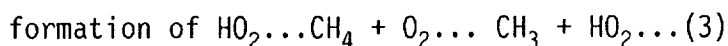
## Oxidation of NO to NO<sub>2</sub> Effect of Hydrogen, Hydrocarbons and Alcohols

It was mentioned before that probably HO<sub>2</sub> is the major oxidizing agent in the oxidation of NO. Since hydrogen can generate HO<sub>2</sub>, it may be assumed that hydrogen can oxidize NO. Figure 3(a) shows the effect of hydrogen on NO at various temperatures and figure 3(b) shows similar effect when additional oxygen was added. It appears that oxidation of NO requires large amount of hydrogen and even then the oxidation to NO<sub>2</sub> decreases with increase in temperature; moreover, additional oxygen does not help very much in the oxidation. At lower temperature a part of NO is oxidized to NO<sub>2</sub>, but as the temperature is increased NO<sub>2</sub> changes back to NO. It is true that at high temperature H and O<sub>2</sub> react to form both HO<sub>2</sub> and OH, and the rate of formation of OH is faster than the rate of formation of HO<sub>2</sub>; moreover, HO<sub>2</sub> reacts with OH. It therefore appears that HO<sub>2</sub> does not get much chance to oxidize NO. These results suggest that hydrogen is not a good additive towards oxidation of NO.

The major reactions in the oxidation of NO in presence of H<sub>2</sub> can be written as



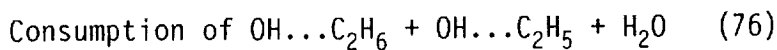
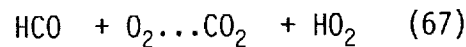
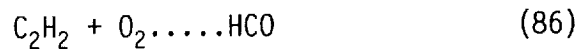
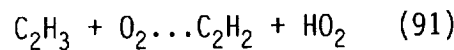
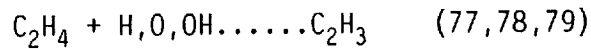
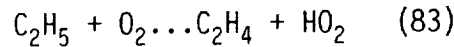
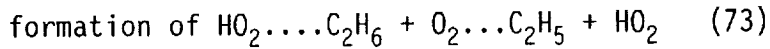
The study with hydrogen suggests that if we could use an additive that can generate HO<sub>2</sub> and also can scavenge OH, oxidation of NO would be more effective. Among the hydrocarbons methane is the simplest and it also generates HO<sub>2</sub>. Figures 4(b) and (a) show the effect of methane on NO with and without the presence of additional oxygen. It appears that the effect of methane is not different from what was observed with hydrogen. At lower temperature NO oxidizes partly to NO<sub>2</sub> and at higher temperature NO<sub>2</sub> changes back to NO. Although methane generates HO<sub>2</sub>, it is not a good scavenger of OH.



Addition of additional oxygen increases the formation of HO<sub>2</sub> but at the same time increases the rate of formation of OH; the net result is that the NO oxidation does not improve.

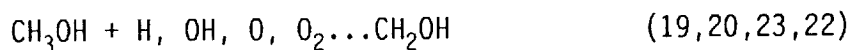
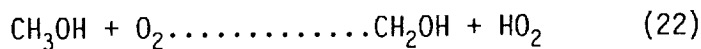
Addition of large amount of methane makes the emission fuel rich; in such case at higher temperature total NO<sub>x</sub> is reduced as shown in figure 5. In this case as oxygen is not available, hydrocarbon fragments generate species like CN, HCN or C<sub>2</sub>N<sub>2</sub> and these species react with NO. Figure 5 shows that at equivalent ratio 2.0 NO<sub>x</sub> is actually reduced by methane at higher temperature.

Figure 6(a) shows the effect on NO<sub>x</sub> at various temperature when ethane is added to the emission. In this case however, NO<sub>2</sub> is found to increase as the temperature increases. At about 1075 °K, NO is almost completely changed to NO<sub>2</sub>. It should be mentioned here that as soon as all of ethane is consumed, NO<sub>2</sub> changes back to NO and there is no more ethane present to regenerate NO<sub>2</sub>. According to the reactions assumed in the mechanism used in this study, ethane is a good scavenger for OH and the OH scavenging rate increases with increase in temperature. The major reactions taking place in this case can be written as



Therefore it appears that ethane is a good additive towards oxidation of NO. In fact as the length of the hydrocarbon chain increases, the oxidation of NO becomes more effective.

Calculations were also performed using methanol as additives. Figure 6(b) shows the effect of methanol on NO at various temperatures. The effect appears to be very similar to what was observed in case of ethane. The oxidation seems to be maximum around 1100 °K. It should be mentioned here that Lyon et al. actually observed this effect (ref. 23). As soon as methanol is consumed, the NO<sub>2</sub> changes back to NO. The reactions taking place with ethane or methanol are similar. Methanol generates HO<sub>2</sub> and also scavenges OH.

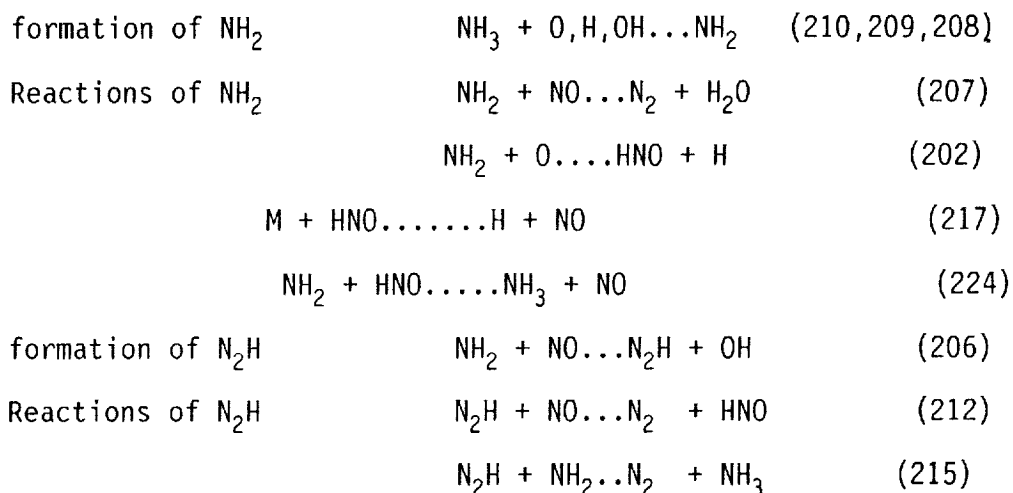


It appears therefore that both ethane and methanol are good additives towards oxidation of NO. Table III shows a comparison of behaviors of different additives towards oxidation of NO to NO<sub>2</sub>.

#### Reduction of NO to N<sub>2</sub> Effect of Nitrogenous Compounds

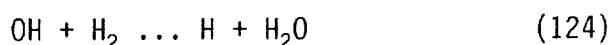
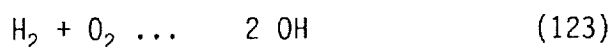
Calculations were performed for the cases of added NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> to the exhaust emission with and without another additive. Effect of NH<sub>3</sub> on NO<sub>x</sub> has been well studied. It is well known that NH<sub>3</sub> reduces NO within a narrow temperature range. Figure 7(a) shows the effect of ammonia addition to the exhaust stream at various temperatures. It was first pointed out by Fennimore (refs. 20 and 21) and later supported by many workers (ref. 6) that NH<sub>2</sub> is the most important species in the reduction of NO by ammonia. The reactions that take place can be described by the

schematic diagram (fig. 8(a)) as was presented by Miller and Bowman (ref. 14).  $\text{NH}_2$  either reacts with NO or is oxidized by oxygen atom; the species  $\text{N}_2\text{H}$  produced in the reaction of  $\text{NH}_2$  with NO reacts with  $\text{NH}_2$  or NO depending on their concentrations.



At lower temperatures  $\text{NH}_2$  concentrations are low as the concentrations of the oxidizing radicals which can oxidize ammonia are low. As the temperature increases,  $\text{NH}_2$  concentrations increase and the NO disappears faster. Increase in temperature also leads to the formation of NO and therefore reduction of NO decreases with further increase in temperature. This mechanism nicely explains the temperature window effect in the reduction of NO in presence of ammonia. The maximum reduction of NO appears to take place around 1150 °K, and this agrees very well with the experimental results. Since the formation of  $\text{NH}_2$  is dependent on the concentration of O atom which is generated from oxygen, it is expected that NO reduction efficiency should depend on the oxygen concentration. The above reaction scheme also suggests that increase in ammonia concentration will favor the NO reduction. Figures 8(b) and (c) show the effects of oxygen and ammonia concentrations on the reduction of NO. It should be mentioned here that this kind of dependence was actually observed by Lyon (ref. 19).

The present mechanism indicates that  $\text{NH}_2$  is the most important species in the reduction of NO. That ammonia does not reduce NO at lower temperature, is probably due to the fact that  $\text{NH}_2$  is not generated sufficiently at lower temperature. So if the  $\text{NH}_2$  formation could be expedited, probably NO reduction would be possible at lower temperature. Figure 7(b) shows that in presence of hydrocarbon fragments, NO reduction by ammonia takes place at lower temperature. Hydrocarbon fragments react with nitrogen and generate carbon-nitrogen compounds which react with NOx; at the same time hydrocarbon fragments burn to produce heat which help in the production of O atom, and O atoms react with ammonia to produce  $\text{NH}_2$ . Lyon (ref. 24) observed that addition of hydrogen shifts the temperature window to the lower temperature side in the NO reduction by ammonia. Figures 9(a) and (b) show the effect of addition of hydrogen on the reduction of NO in presence for ammonia. Obviously, the higher the concentration of hydrogen, the greater is the shift of the window. The addition of hydrogen generates heat to promote the generation of  $\text{NH}_2$ ; moreover reduction of NO takes place by hydrogen atoms





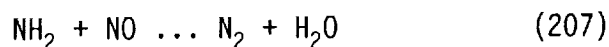
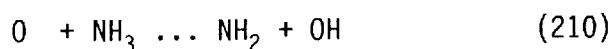
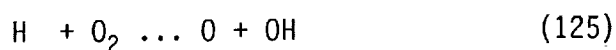
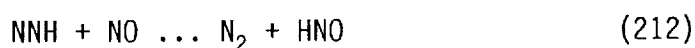
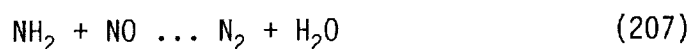
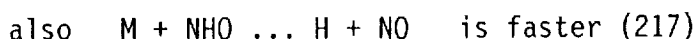


Figure 9(a) shows that in presence of 500 ppm hydrogen, maximum reduction of NO by ammonia takes place at temperature below 1100 °K, and at 1000 °K about 50 percent reduction of NO is possible. Figure 9(b) shows that with 5000 ppm of H<sub>2</sub>, NO reduction is practically complete at 950 °K. It appears that addition of H<sub>2</sub> only shifts the temperature window without changing much of its width. With increase in temperature, NO reduction efficiency gradually decreases.

Calculations were made to study the effects of methanol on the NO reduction by ammonia. Figure 10(a) shows the effect of temperature on the NO reduction by ammonia in presence of methanol. Here also as in the case of hydrogen, methanol generates heat and thus helps to produce NH<sub>2</sub>. Figure 10(b) shows the reaction temperatures at around 5 sec after the addition of alcohol-ammonia mixture. Addition of methanol at 975 °K, increases the reaction temperature to over 1100 °K. At lower temperature and at a shorter time however, methanol burning is incomplete and the temperature is lower; as a result, there is less amount of O atoms produced and therefore less amount of NH<sub>2</sub> is generated. As time passes, more O atoms are produced and more NH<sub>2</sub> is generated.



as temperature rises rate of formation of NH<sub>2</sub> increases



Again, methanol like hydrogen only shifts the temperature window without changing the width. This is because at higher initial temperature, the reaction temperature is higher and oxidation of NH<sub>2</sub> by O atoms becomes faster. Figure 10(b) shows a plot of the reaction temperature versus various initial temperature; it appears that addition of methanol actually raises the reaction temperature helping in the formation of NH<sub>2</sub>.

Table III shows a comparison of the effects of temperature on the addition of various fuels to the reduction of NO by ammonia. It thus appears that fuels help in the generation of NH<sub>2</sub> at lower initial temperature. Besides fuels, addition of H<sub>2</sub>O<sub>2</sub> also may help to generate NH<sub>2</sub> at lower initial temperature. Figure 11 shows the NO

reduction efficiency by  $\text{NH}_3$  at various initial temperatures when  $\text{H}_2\text{O}_2$  is added. It appears that although reduction of NO takes place at lower temperature, reduction efficiency is not very high. This is due to the fact that in this case  $\text{NH}_2$  is formed mostly by OH and oxidation of ammonia by OH is not very fast. As the temperature is raised, OH is formed in greater quantities, and more  $\text{NH}_2$  is produced. At still higher temperature, reduction of NO takes place like in normal case without  $\text{H}_2\text{O}_2$ .

#### Reduction of NO by Hydrazine

Hydrazine is another nitrogenous compound which is known (fig. 8(a)) to reduce NO. Hydrazine dissociates to form  $\text{NH}_2$  and the rate of formation of  $\text{NH}_2$  increases with increase in temperature. Since  $\text{NH}_2$  formation here is possible at lower temperature than with  $\text{NH}_3$ , NO reduction takes place at lower temperature with hydrazine than with ammonia. But  $\text{N}_2\text{H}_4$  also generates  $\text{NH}_3$  at lower temperature, and the reduction of NO is not complete until reaction temperature is reached to the level when ammonia starts forming  $\text{NH}_2$ .

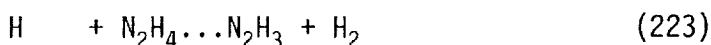
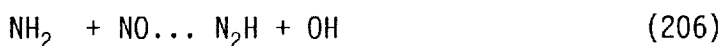
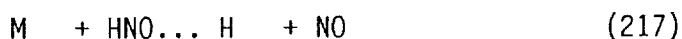
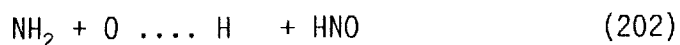
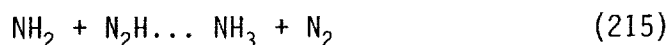
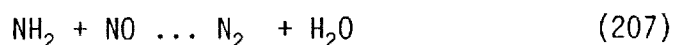
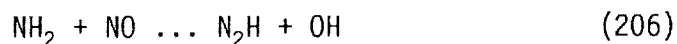


Table IV shows the effect of hydrazine on NO at various temperatures.

All the above discussions point out to the fact that reduction of NO in presence of ammonia takes place due to the formation of  $\text{NH}_2$  as an intermediate species. We therefore studied the NO reduction in presence of hypothetical  $\text{NH}_2$ . Figure 12 shows the temperature effect on NO reduction in presence of  $\text{NH}_2$ . It appears that NO reduction is much less with  $\text{NH}_2$  itself than when  $\text{NH}_3$  is used; in fact, at the condition of our study, no more than 50 percent of NO is reduced at any temperature. This is due to the fact that in case of ammonia the rate determining step in NO reduction is the formation of  $\text{NH}_2$ . In this case  $\text{NH}_2$  not only reacts with NO, it also reacts with  $\text{N}_2\text{H}$  forming  $\text{NH}_3$ , and  $\text{NH}_3$  does not dissociate at lower temperature. As the temperature is raised,  $\text{NH}_2$  reacts with O atoms as well as with NO. The major reactions may be written as



## SUMMARY OF RESULTS

Detailed chemical modeling has been performed to evaluate the effects of different chemical additives on the NO<sub>x</sub> emission in the industrial combustion systems. The exhaust stream was cooled and the additives were added to it. The chemical kinetic model used in this study was tested by other workers and was further verified by comparing the calculation results with actual experimental data. The Lsens code was used to calculate the NO<sub>x</sub> concentrations.

This study has two directions of approach. In one, conversion of NO<sub>x</sub> to NO<sub>2</sub> has been considered and in the other, reduction of NO<sub>x</sub> to unreactive nitrogen has been discussed. The additives considered for NO<sub>x</sub> oxidation to NO<sub>2</sub> were hydrocarbons like CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, hydrogen and methanol. Unless used in large quantities when the mixture becomes fuel-rich, these additives do not reduce NO<sub>x</sub> to nitrogen, rather oxidize NO to NO<sub>2</sub> at temperatures below 1100 K. It is however known that NO<sub>2</sub> can be removed from the exhaust stream by washing it with water.

NH<sub>3</sub> reduces NO<sub>x</sub> to nitrogen within a short temperature range between 1000 to 1400 K. Use of some fuels as co-additive can make the reaction take place at lower temperature. Addition of H<sub>2</sub>O<sub>2</sub> also shifts the reaction temperature in the same way. The effect of fuels like H<sub>2</sub> and methanol has been discussed. The function of these fuels is to generate heat and radicals to expedite the NH<sub>2</sub> formation; although H<sub>2</sub>O<sub>2</sub> does not generate heat, it helps to generate NH<sub>2</sub> radicals from ammonia through radical reactions. In presence of ammonia, the NO reduction takes place at lower temperature. Hydrazine behaves very similar to ammonia, but NO reduction takes place at a lower temperature when hydrazine is used. Effect of hypothetical NH<sub>2</sub> was tested; although NO reduction takes place at a low temperature, efficiency of NO reduction in presence of NH<sub>2</sub> is much less than what is expected in case of ammonia.

All these reactions used in this mechanism are dependent on the concentrations of oxygen, nitrogen oxides and also the additives. The reaction rates assumed in this study also have uncertainties. The results reported here should therefore be considered as qualitative and should not be assumed exact.

## REFERENCES

1. Rosenberg, H.S.; Curan, L.M., Slack, A.V., and Oxley, J.H., "Post Combustion Methods for Control of NO<sub>x</sub>/Emissions," Progress in Energy and Combustion Science, Vol. 6, 1988, pp. 287-302.
2. Zeldovich, Y.B., "The Oxidation of Nitrogen in Combustion Explosions," Acta Physicochemica USSR, Vol. 21, 1946, pp. 577-584.
- 3a. Fenimore, C.P., "Reactions of Fuel-Nitrogen in Rich Flame Gases," Combustion and Flame, Vol. 26, 1976, pp. 249-256.
- 3b. De Soete, G.G., "Overall Reaction Rates of NO and N<sub>2</sub> Formation from Fuel Nitrogen," Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1975, pp. 1093-1102.
- 3c. Morley, C., "The Formation and Destruction of Hydrogen Cyanide from Atmospheric and Fuel Nitrogen in Rich Atmospheric-Pressure Flames," Combustion and Flame, Vol. 27, 1976, pp. 189-204.

4. Baulch, D.L., Drysdale, D.D., Thorne, D.G., and Lloyd, A.C., Evaluated Kinetic Data for High Temperature Reactions, Vol. 1, CRC Press, Cleveland, OH, 1973.
5. Fenimore, C.P., "Formation of Nitric Oxide in Premixed Hydrocarbon Flames," Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1971, pp. 373-380.
6. Nguyen, H.L., Bittker, D.A., and Niedzwiecki, R.W., "Investigation of Low NO<sub>x</sub> Staged Combustor Concept in High-Speed Civil Transport Engines," NASA TM-101977, 1989.
7. Sarofim, A.F., and Flagan, R.C., "NO<sub>x</sub> Control for Stationary Combustion Sources," Progress in Energy and Combustion Science, Vol. 2, 1976, pp. 1-25.
8. Lyon, R.K., "Method for the Reduction of the Concentration of NO in Combustion Effluents Using Ammonia," US. Patent No. 3900554, 1975.
- 8b. Turchan, O.C., "Method of Reducing the Oxide of Nitrogen in Fossil Fuel Combustion and Combustion Gases Using Hydrazine and/or Hydrazine Compounds," US. Patent No. 4761270, 1988.
9. Arand, J.K., Muzio, L.J., and Scotter, J.G., "Urea Reduction of NO<sub>x</sub> in Combustion Effluents," US. Patent No. 4208386, 1980.
10. Perry, R.A., "NO Reduction by Using Sublimation of Cyanuric Acid," US. Patent No. 4731231, 1988.
11. Siebers, D.L., and Caton, J., "Reduction of Nitrogen Oxides by the Raprenox Process," Paper No. 53, Central States Station/The Combustion Institute Meeting, Indianapolis, IN, May 1988.
12. Wada, Y., and Yamatsuta, K., "Waste Gas Treatment Method," Japanese Early Patent Disclosure No. 54028771, 1979.
13. Murakami, N., Kojima, N., and Hasiguchi, M., "Oxidation of Nitric Oxide to Monometric Nitrogen Dioxide in Fuel Gas. I. Oxidation by Addition of Methanol," Nenryo Kyo Kaishi, Vol. 61, 1982, pp. 276-284.
14. Miller, J.A., and Bowman, C.T., "Mechanism and Modeling of Nitrogen Chemistry in Combustion," Progress in Energy and Combustion Science, Vol. 15, 1989, pp. 287-338.
15. Bittker, D.A., Scullin, V.J., "GCKP84-General Chemical Kinetics Code for Gas-Phase Flow and Batch Processes Including Heat Transfer Effects," NASA TP-2320, 1984.
16. Kee, R.J., Rupley, F.M., and Miller, J.A., "The Chemkin Thermodynamic Data Base," Sandia Report, SAND87-8215, 1987.
17. Bartok, W., Engleman, V.S., Goldstein, R., and Delvalle, E.G., "Basic Kinetic Studies and Modeling at Nitrogen Oxide Formation in Combustion Process," AICHE Symposium Series, Vol. 68, No. 126, 1972, pp. 30-32.
18. Westbrook, C.K., and Dreyer, F.L., "Chemical Kinetic Modeling of Hydrocarbon Combustion," Progress in Energy and Combustion Science, Vol. 10, 1984, pp. 1-57.

19. Lyon, R.K., and Benn, D., "Kinetics of The NO-NH<sub>3</sub>-O<sub>2</sub> Reaction," Seventeenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1979, pp. 601-610.
20. Fenimore, C.P., "Destruction of NO by NH<sub>3</sub> in Lean Burnt Gas," Combustion and Flame, Vol. 37, 1980, pp. 245-250.
21. Kimball-Linne, M.A., and Hanson, R.K., "Combustion-Driven Flow Reactor Studies of Thermal DeNO<sub>x</sub> Reactions Kinetics," Combustion and Flame, Vol. 64, 1986, pp. 337-351.
22. Yano, T., "Behavior of Methanol and Formaldehyde in Burnt Gas from Methanol Combustion; Effects of Nitric Oxide on Oxidation Reaction," JSME Bulletin, Vol. 26, No. 213, 1983, pp. 406-413.
23. Lyon, R.K., Cole, J.A., Kramlich, J.C., and Chen, S.L., "The Selective Reduction of SO<sub>3</sub> to SO<sub>2</sub> and the Oxidation of NO to NO<sub>2</sub> by Methanol," Combustion and Flame, Vol. 81, 1990, pp. 30-39.
24. Muzio, L.J., and Arand, J.K., "Gas Phase Decomposition of Nitric Oxide in Combustion Products," Sixteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1977, pp. 199-208.

TABLE I

M	+2.0CH3	=	C2H6	+	M	9.03E+16	-1.2	654.	(1)
THIRDBODY									
CO	2.0	H2	2.0	CO2	3.0	H2O		5.0	
END									
CH3	+	H	=	CH4	+	M	6.00E+16	-1.	0. (2)
THIRDBODY									
CO	2.0	H2	2.0	CO2	3.0	H2O		5.0	
END									
CH4	+	O2	=	CH3	+	H02	7.90E+13	0.	56000. (3)
CH4	+	H	=	CH3	+	H2	2.20E+04	3.	8750. (4)
CH4	+	OH	=	CH3	+	H2O	1.60E+06	2.1	2460. (5)
CH4	+	O	=	CH3	+	OH	1.02E+09	1.5	8604. (6)
CH4	+	H02	=	CH3	+	H2O2	1.80E+11	0.	18700. (7)
CH3	+	H02	=	CH3O	+	OH	2.00E+13	0.	0. (8)
CH3	+	O2	=	CH3O	+	O	2.05E+19	-1.6	29229 (9)
CH3	+	O	=	CH2O	+	H	8.00E+13	0.	0. (10)
CH2OH	+	H	=	CH3	+	OH	1.00E+14	0.	0. (11)
M	+	CH2OH	=	CH2O	+	H	1.00E+14	0.	25000. (12)
CH2OH	+	H	=	CH2O	+	H2	2.00E+13	0.	0. (13)
CH2OH	+	OH	=	CH2O	+	H2O	1.00E+13	0.	0. (14)
CH2OH	+	O	=	CH2O	+	OH	1.00E+13	0.	0. (15)
CH2OH	+	O2	=	CH2O	+	H02	1.48E+13	0.	1500. (16)
M	+	CH3OH	=	CH3	+	OH	3.02E+18	0.	80000. (17)
H	+	CH3OH	=	CH3	+	H2O	2.00E+12	0.	5300. (18)
H	+	CH3OH	=	CH2OH	+	H2	3.02E+13	0.	7000. (19)
OH	+	CH3OH	=	CH2OH	+	H2O	3.98E+12	0.	2000. (20)
CH3O	+	H	=	CH3	+	OH	1.00E+14	0.	0. (21)
CH3OH	+	O2	=	CH2OH	+	H02	3.98E+10	0.	50910. (22)
CH3OH	+	O	=	CH2OH	+	OH	1.70E+12	0.	2290. (23)
CH3OH	+	CH3	=	CH2OH	+	CH4	1.82E+11	0.	9800. (24)
CH3OH	+	H02	=	CH2OH	+	H2O2	6.31E+12	0.	19360. (25)
CH3	+	OH	=	CH2	+	H2O	7.50E+06	2.	5000. (26)
CH3	+	H	=	CH2	+	H2	9.00E+13	0.	15100. (27)
M	+	CH3O	=	CH2O	+	H	1.00E+14	0.	25000. (28)
CH3O	+	H	=	CH2O	+	H2	2.00E+13	0.	0. (29)
CH3O	+	OH	=	CH2O	+	H2O	1.00E+13	0.	0. (30)
CH3O	+	O	=	CH2O	+	OH	1.00E+13	0.	0. (31)
CH3O	+	O2	=	CH2O	+	H02	6.30E+10	0.	2600. (32)
CH2	+	H	=	CH	+	H2	1.00E+18	-1.56	0. (33)
CH2	+	OH	=	CH	+	H2O	1.13E+07	2.	3000. (34)
CH2	+	OH	=	CH2O	+	H	2.50E+13	0.	0. (35)
CH	+	O2	=	HCO	+	O	3.30E+13	0.	0. (36)
CH	+	O	=	CO	+	H	5.70E+13	0.	0. (37)
CH	+	OH	=	HCO	+	H	3.00E+13	0.	0. (38)
CH	+	CO2	=	HCO	+	CO	3.40E+12	0.	690. (39)
CH	+	H	=	C	+	H2	1.50E+14	0.	0. (40)
CH	+	H2O	=	CH2O	+	H	1.17E+15	-.75	0. (41)
CH	+	CH2O	=	CH2CO	+	H	9.46E+13	0.	-515. (42)
CH	+	CH2	=	C2H2	+	H	4.00E+13	0.	0. (43)
CH	+	CH3	=	C2H3	+	H	3.00E+13	0.	0. (44)
CH	+	CH4	=	C2H4	+	H	6.00E+13	0.	0. (45)
C	+	O2	=	CO	+	O	2.00E+13	0.	0. (46)
C	+	OH	=	CO	+	H	5.00E+13	0.	0. (47)
C	+	CH3	=	C2H2	+	H	5.00E+13	0.	0. (48)
C	+	CH2	=	C2H	+	H	5.00E+13	0.	0. (49)
CH2	+	CO2	=	CH2O	+	CO	1.10E+11	0.	1000. (50)
CH2	+	O	=	2.OH	+	CO	5.00E+13	0.	0. (51)
CH2	+	O	=	CO	+	H2	3.00E+13	0.	0. (52)

CH2	+	O2	=2.0H	+	CO2	1.60E+12	0.	1000.	(53)
CH2	+	O2	= CH2O	+	O	5.00E+13	0.	9000.	(54)
CH2	+	O2	= CO	+	H2O	1.90E+10	0.	-1000.	(55)
CH2	+	O2	= CO2	+	H2	6.90E+11	0.	500.	(56)
CH2	+	O2	= HCO	+	OH	4.30E+10	0.	-500.	(57)
CH2O	+	OH	= HCO	+	H2O	3.43E+09	1.18	-447.	(58)
CH2O	+	H	= HCO	+	H2	2.19E+08	1.77	3000.	(59)
M	+	CH2O	= HCO	+	H	3.31E+16	0.	81000.	(60)
CH2O	+	O	= HCO	+	OH	1.80E+13	0.	3080.	(61)
HCO	+	OH	= H2O	+	CO	1.00E+14	0.	0.	(62)
M	+	HCO	= H	+	CO	2.50E+14	0.	16802.	(63)

THIRDBODY

CO		1.9		H2		1.9		CH4		2.8		CO2		3.0
H2O		5.0		END										
HCO	+	H	=	CO	+	H2	1.19E+13	.25		0.		0.		(645)
HCO	+	O	=	CO	+	OH	3.00E+13	0.		0.		0.		(65)
HCO	+	O	=	CO2	+	H	3.00E+13	0.		0.		0.		(66)
HCO	+	O2	=	HO2	+	CO	3.00E+13	0.		0.		0.		(67)
CO	+	O	=	CO2	+	M	6.17E+14	0.		3000.		0.		(68)
CO	+	OH	=	CO2	+	H	1.51E+07	1.3		-758.		0.		(69)
CO	+	O2	=	CO2	+	O	1.60E+13	0.		41000.		0.		(70)
HO2	+	CO	=	CO2	+	OH	5.80E+13	0.		22934.		0.		(71)
C2H6	+	CH3	=	C2H5	+	CH4	5.50E-01	4.		8300.		0.		(72)
C2H6	+	O2	=	C2H5	+	HO2	1.00E+13	0.		51000.		0.		(73)
C2H6	+	H	=	C2H5	+	H2	5.40E+02	3.5		5210.		0.		(74)
C2H6	+	O	=	C2H5	+	OH	2.51E+13	0.		6360.		0.		(75)
C2H6	+	OH	=	C2H5	+	H2O	8.70E+09	1.05		1810.		0.		(76)
C2H4	+	H	=	C2H3	+	H2	1.10E+14	0.		8500.		0.		(77)
C2H4	+	O	=	CH3	+	HCO	3.32E+12	0.		1130.		0.		(78)
C2H4	+	OH	=	C2H3	+	H2O	2.02E+13	0.		5955.		0.		(79)
CH2	+	CH3	=	C2H4	+	H	3.00E+13	0.		0.		0.		(80)
M	+	C2H5	=	C2H4	+	H	2.00E+15	0.		30000.		0.		(81)
C2H5	+	H	=2.0CH3				1.00E+14	0.		0.		0.		(82)
C2H5	+	O2	=	C2H4	+	HO2	8.43E+11	0.		3875.		0.		(83)
C2H2	+	O	=	CH2	+	CO	1.02E+07	2.		1900.		0.		(84)
C2H2	+	O	=	HCCO	+	H	1.02E+07	2.		1900.		0.		(85)
C2H2	+	O2	=2.0HCO				3.98E+12	0.		28000.		0.		(86)
H2	+	C2H	=	C2H2	+	H	1.02E+07	2.		1900.		0.		(87)
H	+	C2H2	=	C2H3	+	M	5.54E+12	0.		2410.		0.		(88)

THIRDBODY

H2		2.0		CO		2.0		CO2		3.0		H2O		5.0
END														
C2H3	+	H	=	C2H2	+	H2	4.00E+13	0.		0.		0.		(89)
C2H3	+	O	=	CH2CO	+	H	3.00E+13	0.		0.		0.		(90)
C2H3	+	O2	=	C2H2	+	HO2	1.00E+12	0.		10000.		0.		(91)
C2H3	+	O2	=	CH2O	+	HCO	4.00E+12	0.		-250.		0.		(92)
C2H3	+	OH	=	C2H2	+	H2O	5.00E+12	0.		0.		0.		(93)
C2H3	+	CH2	=	C2H2	+	CH3	3.00E+13	0.		0.		0.		(94)
C2H3	+	C2H	=2.0C2H2				3.00E+13	0.		0.		0.		(95)
C2H3	+	CH	=	CH2	+	C2H2	5.00E+13	0.		0.		0.		(96)
OH	+	C2H2	=	C2H	+	H2O	3.37E+07	2.		14000.		0.		(97)
OH	+	C2H2	=	CH2CO	+	H	2.18E-04	4.5		-1000.		0.		(98)
OH	+	C2H2	=	CH3	+	CO	4.83E-04	4.		-2000.		0.		(99)
C2H2	+	O	=	C2H	+	OH	3.16E+15	-.6		15000.		0.		(100)
CH2CO	+	O	=	CO2	+	CH2	1.75E+12	0.		1350.		0.		(101)
CH2CO	+	H	=	CH3	+	CO	1.13E+13	0.		3428.		0.		(102)
CH2CO	+	H	=	HCCO	+	H2	5.00E+13	0.		8000.		0.		(103)
CH2CO	+	O	=	HCCO	+	OH	1.00E+13	0.		8000.		0.		(104)
CH2CO	+	OH	=	HCCO	+	H2O	7.50E+12	0.		2000.		0.		(105)
M	+	CH2CO	=	CH2	+	CO	3.00E+14	0.		70980.		0.		(106)

C2H	+	O2	=2.0CO	+	H	5.00E+13	0.	1500.	(107)
H	+	HCCO	= CH2	+	CO	1.00E+14	0.	0.	(108)
O	+	HCCO	=2.0CO	+	H	1.00E+14	0.	0.	(109)
HCCO	+	O2	=2.0CO	+	OH	1.60E+12	0.	854.	(110)
CH	+	HCCO	= C2H2	+	CO	5.00E+13	0.	0.	(111)
		2.0HCCO	=2.0CO	+	C2H2	1.00E+13	0.	0.	(112)
C2H	+	O	= CH	+	CO	5.00E+13	0.	0.	(113)
C2H	+	OH	= HCCO	+	H	2.00E+13	0.	0.	(114)
		2.0CH2	= C2H2	+	H2	4.00E+13	0.	0.	(115)
CH2	+	HCCO	= C2H3	+	CO	3.00E+13	0.	0.	(116)
C3H3	+	O2	= CH2CO	+	HCO	3.00E+10	0.	2868.	(117)
C3H3	+	O	= CH2O	+	C2H	2.00E+13	0.	0.	(118)
C2H2	+	O2	= HCCO	+	OH	2.00E+08	1.5	30100.	(119)
M	+	C2H2	= C2H	+	H	4.20E+16	0.	107000.	(120)
M	+	C2H4	= C2H2	+	H2	1.50E+15	0.	55800.	(121)
M	+	C2H4	= C2H3	+	H	1.40E+16	0.	82360.	(122)
H2	+	O2	=2.0OH			1.70E+13	0.	47780.	(123)
OH	+	H2	= H2O	+	H	1.17E+09	1.3	3626.	(124)
O	+	OH	= O2	+	H	4.00E+14	-0.5	0.	(125)
O	+	H2	= OH	+	H	5.06E+04	2.7	6290.	(126)
H	+	O2	= H02	+	M	3.61E+17	-0.7	0.	(127)
THIRDBODY									
H2O	18.6	H2	2.9	N2	1.3	END			
OH	+	H02	= H2O	+	O2	7.50E+12	0.	0.	(128)
H	+	H02	=2.0OH			1.40E+14	0.	1073.	(129)
O	+	H02	= O2	+	OH	1.40E+13	0.	1073.	(130)
		2.0OH	= O	+	H2O	6.00E+08	1.3	0.	(131)
M	+2.0H		= H2	+	M	1.00E+18	-1.	0.	(132)
H2	+2.0H		=2.0H2			9.20E+16	-0.6	0.	(133)
H2O	+2.0H		= H2	+	H2O	6.00E+19	-1.2	0.	(134)
H	+	OH	= H2O	+	M	1.60E+22	-2.	0.	(135)
THIRDBODY									
H2O	5.0	END							
H	+	O	= OH	+	M	6.20E+16	-0.6	0.	(136)
THIRDBODY									
H2O	5.0	END							
M	+2.0O	= O2	+	M	1.89E+13	0.	-1788.	(137)	
H	+	H02	= H2	+	O2	1.25E+13	0.	0.	(138)
		2.0H02	= H2O2	+	O2	2.00E+12	0.	0.	(139)
M	+	H2O2	=2.0OH	+	M	1.30E+17	0.	45500.	(140)
H2O2	+	H	= H02	+	H2	1.60E+12	0.	3800.	(141)
H2O2	+	OH	= H2O	+	H02	1.00E+13	0.	1800.	(142)
CH	+	N2	= HCN	+	N	3.00E+11	0.	13600.	(143)
CN	+	N	= C	+	N2	1.04E+15	-0.5	0.	(144)
CH2	+	N2	= HCN	+	NH	1.00E+13	0.	74000.	(145)
H2CN	+	N	= N2	+	CH2	2.00E+13	0.	0.	(146)
M	+	H2CN	= HCN	+	H	3.00E+14	0.	22000.	(147)
C	+	NO	= CN	+	O	6.60E+13	0.	0.	(148)
CH	+	NO	= HCN	+	O	1.10E+14	0.	0.	(149)
CH2	+	NO	= HCNO	+	H	1.39E+12	0.	-1100.	(150)
CH3	+	NO	= HCN	+	H2O	1.00E+11	0.	15000.	(151)
CH3	+	NO	= H2CN	+	OH	1.00E+11	0.	15000.	(152)
HCCO	+	NO	= HCNO	+	CO	2.00E+13	0.	0.	(153)
HCNO	+	H	= HCN	+	OH	1.00E+14	0.	12000.	(154)
CH2	+	N	= HCN	+	H	5.00E+13	0.	0.	(155)
CH	+	N	= CN	+	H	1.30E+13	0.	0.	(156)
CO2	+	N	= NO	+	CO	1.90E+11	0.	3400.	(157)
HCCO	+	N	= HCN	+	CO	5.00E+13	0.	0.	(158)
CH3	+	N	= H2CN	+	H	3.00E+13	0.	0.	(159)
C2H3	+	N	= HCN	+	CH2	2.00E+13	0.	0.	(160)



C3H3	+	N	=	HCN	+	C2H2	1.00E+13	0.	0.	(161)
HCN	+	OH	=	CN	+	H2O	1.45E+13	0.	10929.	(162)
OH	+	HCN	=	HOCN	+	H	5.85E+04	2.4	12500.	(163)
OH	+	HCN	=	HNCO	+	H	1.98E-03	4.	1000.	(164)
OH	+	HCN	=	NH2	+	CO	7.83E-04	4.	4000.	(165)
HOCN	+	H	=	HNCO	+	H	1.00E+13	0.	0.	(166)
HCN	+	O	=	NCO	+	H	1.38E+04	2.64	4980.	(167)
HCN	+	O	=	NH	+	CO	3.45E+03	2.64	4980.	(168)
HCN	+	O	=	CN	+	OH	2.70E+09	1.58	26600.	(169)
CN	+	H2	=	HCN	+	H	2.95E+05	2.45	2237.	(170)
CN	+	O	=	CO	+	N	1.80E+13	0.	0.	(171)
CN	+	O2	=	NCO	+	O	5.60E+12	0.	0.	(172)
CN	+	OH	=	NCO	+	H	6.00E+13	0.	0.	(173)
CN	+	HCN	=	C2N2	+	H	2.00E+13	0.	0.	(174)
CN	+	NO2	=	NCO	+	NO	3.00E+13	0.	0.	(175)
CN	+	N2O	=	NCO	+	N2	1.00E+13	0.	0.	(176)
C2N2	+	O	=	NCO	+	CN	4.57E+12	0.	8880.	(177)
C2N2	+	OH	=	HOCN	+	CN	1.86E+11	0.	2900.	(178)
NO2	+	O	=	NO	+	O2	1.00E+13	0.	600.	(179)
M	+	NO2	=	NO	+	O	1.10E+16	0.	66000.	(180)
NCO	+	H	=	NH	+	CO	5.00E+13	0.	0.	(181)
NCO	+	O	=	NO	+	CO	2.00E+13	0.	0.	(182)
NCO	+	N	=	N2	+	CO	2.00E+13	0.	0.	(183)
NCO	+	OH	=	NO	+	HCO	1.00E+13	0.	0.	(184)
M	+	NCO	=	N	+	CO	3.10E+16	-.5	48000.	(185)
NCO	+	NO	=	N2O	+	CO	1.00E+13	0.	-390.	(186)
NCO	+	H2	=	HNCO	+	H	8.58E+12	0.	9000.	(187)
HNCO	+	H	=	NH2	+	CO	2.00E+13	0.	3000.	(188)
NH	+	O2	=	HNO	+	O	1.00E+13	0.	12000.	(189)
NH	+	O2	=	NO	+	OH	7.60E+10	0.	1530.	(190)
NH	+	NO	=	N2O	+	H	2.40E+15	-.8	0.	(191)
N2O	+	H	=	N2	+	OH	7.60E+13	0.	15200.	(192)
M	+	N2O	=	N2	+	O	1.62E+14	0.	51600.	(193)
N2O	+	O	=	N2	+	O2	1.00E+14	0.	28200.	(194)
N2O	+	O	=	2.0NO			1.00E+14	0.	28200.	(195)
N2O	+	OH	=	N2	+	H02	2.00E+12	0.	10000.	(196)
NH	+	OH	=	HNO	+	H	2.00E+13	0.	0.	(197)
NH	+	OH	=	N	+	H2O	5.00E+11	.5	2000.	(198)
NH	+	N	=	N2	+	H	3.00E+13	0.	0.	(199)
NH	+	H	=	N	+	H2	1.00E+14	0.	0.	(200)
NH	+	O	=	NO	+	H	2.00E+13	0.	0.	(201)
NH2	+	O	=	HNO	+	H	6.63E+14	-.5	0.	(202)
NH2	+	O	=	NH	+	OH	6.75E+12	0.	0.	(203)
NH2	+	OH	=	NH	+	H2O	4.00E+06	2.	1000.	(204)
NH2	+	H	=	NH	+	H2	6.92E+13	0.	3650.	(205)
NH2	+	NO	=	NNH	+	OH	6.40E+15	-1.2	0.	(206)
NH2	+	NO	=	N2	+	H2O	6.20E+15	-1.2	0.	(207)
NH3	+	OH	=	NH2	+	H2O	2.04E+06	2.	566.	(208)
NH3	+	H	=	NH2	+	H2	6.36E+05	2.4	10171.	(209)
NH3	+	O	=	NH2	+	OH	2.10E+13	0.	9000.	(210)
		NNH	=	N2	+	H	1.00E+04	0.	0.	(211)
NNH	+	NO	=	N2	+	HNO	5.00E+13	0.	0.	(212)
NNH	+	H	=	N2	+	H2	1.00E+14	0.	0.	(213)
NNH	+	OH	=	N2	+	H2O	5.00E+13	0.	0.	(214)
NNH	+	NH2	=	N2	+	NH3	5.00E+13	0.	0.	(215)
NNH	+	O	=	N2O	+	H	1.00E+14	0.	0.	(216)
M	+	HNO	=	H	+	NO	1.50E+16	0.	48680.	(217)

THIRDBODY

H2O 10.0 02 2.0 N2 2.0 H2 2.0  
 END

HNO	+	OH	=	NO	+	H2O	3.60E+13	0.	0.	(218)
HNO	+	H	=	H2	+	NO	5.00E+12	0.	0.	(219)
M	+	N2H4	=	2.0NH2	+	M	3.98E+13	0.	26673.	(220)
H	+	N2H4	=	N2H3	+	H2	3.50E+11	0.	0.	(221)
N2H3	+	N2H3	=	2.0NH3	+	N2	1.30E+14	0.	0.	(222)
H	+	N2H4	=	NH2	+	NH3	3.50E+11	0.	0.	(223)
HNO	+	NH2	=	NH3	+	NO	2.00E+13	0.	1000.	(224)
		2.0HNO	=	N2O	+	H2O	3.95E+12	0.	5000.	(225)
HNO	+	NO	=	N2O	+	OH	2.00E+12	0.	26000.	(226)
N	+	NO	=	N2	+	O	3.27E+12	.3	0.	(227)
N	+	O2	=	NO	+	O	6.40E+09	1.	6280.	(228)
N	+	OH	=	NO	+	H	3.80E+13	0.	0.	(229)
H02	+	NO	=	N02	+	OH	2.11E+11	0.	-479.	(230)
N02	+	H	=	NO	+	OH	3.50E+14	0.	1500.	(231)
NH2	+	NH	=	N2H2	+	H	5.00E+13	0.	0.	(232)
		2.0NH	=	2.0H	+	N2	7.20E+13	0.	0.	(233)
NH2	+	N	=	2.0H	+	N2	7.20E+13	0.	0.	(234)
M	+	N2H2	=	NNH	+	H	5.00E+16	0.	50000.	(235)
THIRDBODY										
H2O		15.0	O2		2.0	N2		2.0	H2	2.0
END										
N2H2	+	H	=	NNH	+	H2	5.00E+13	0.	0.	(236)
N2H2	+	O	=	NH2	+	NO	1.00E+13	0.	0.	(237)
N2H2	+	O	=	NNH	+	OH	2.00E+13	0.	1000.	(238)
N2H2	+	OH	=	NNH	+	H2O	1.00E+13	0.	1000.	(239)
N2H2	+	NO	=	N2O	+	NH2	3.00E+12	0.	0.	(240)
N2H2	+	NH	=	NNH	+	NH2	1.00E+13	0.	1000.	(241)
N2H2	+	NH2	=	NH3	+	NNH	1.00E+13	0.	1000.	(242)
		2.0NH2	=	N2H2	+	H2	5.00E+11	0.	0.	(243)
NH2	+	O2	=	HNO	+	OH	4.50E+12	0.	25000.	(244)

TABLE II. - EFFECT OF TEMPERATURE ON THE CONVERSION  
OF NO TO NO<sub>2</sub>

[Emission from (WSR) combustion of methane at residence time around 1.5 msec (containing about 10 percent oxygen and hydrocarbon fractions) was used in this calculation.]

Temperature, K	NO, ppm		NO <sub>2</sub> , ppm		NO <sub>x</sub> , ppm	
	300 ms	1 sec	300 ms	1 sec	300 ms	1 sec
700	918	914	81.5	85	1000	1000
800	940	938	59.0	62	1000	1000
900	956	953	43.0	46	1000	1000
1000	972	971	27.0	28	1000	1000
1100	986	987	13.0	13	1000	1000
1200	993	991	6.0	9	1000	1000

TABLE III. - COMPARISON OF EFFICIENCIES OF  
DIFFERENT ADDITIVES TO OXIDIZE NO TO NO<sub>2</sub>

[NO = 500 ppm and time of reaction = 1 sec.  
H<sub>2</sub> = 3091 ppm, CH<sub>4</sub> = 1000 ppm, C<sub>2</sub>H<sub>6</sub> =  
500 ppm and CH<sub>3</sub>OH = 500 ppm; Oxygen =  
4.2 percent.]

Temperature, K	NO/(NO <sub>x</sub> ) <sub>i</sub>			
	CH <sub>4</sub>	H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> OH
700	----	0.71	0.99	0.99
800	----	.80	.99	.99
900	0.58	.86	.79	.98
950	.65	----	.36	.87
1000	.96	.93	.06	.45
1050	.98	----	.05	.12
1100	----	.01	.62	.07
1200	----	----	----	.88

TABLE IV. - EFFECT OF HYDRAZINE ON THE  
REDUCTION OF NO AT DIFFERENT  
TEMPERATURES

[400 ppm  $N_2H_4$  and 500 ppm NO; 4.2 per-  
cent oxygen.]

Temperature, K	NO/(NO <sub>x</sub> ) <sub>i</sub>		
	25 msec	300 msec	1 sec
1050	0.37	0.31	0.17
1100	.41	.21	.06
1150	.42	.11	.02
1200	.36	.06	.038

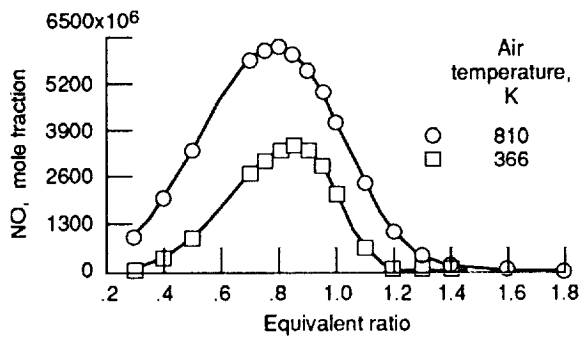


Figure 1.—Equilibrium concentrations of NO at different fuel-air ratios. Fuel, CH<sub>4</sub>; temperature, 366 K.

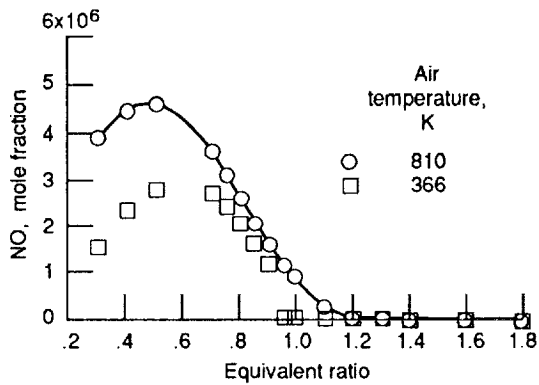
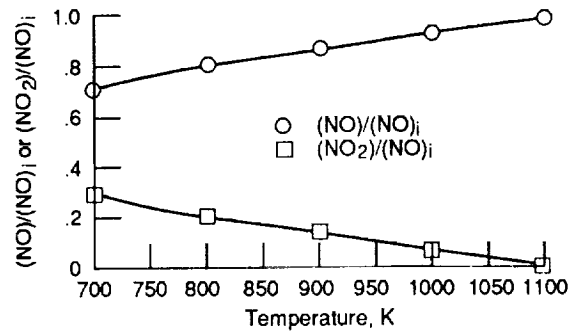
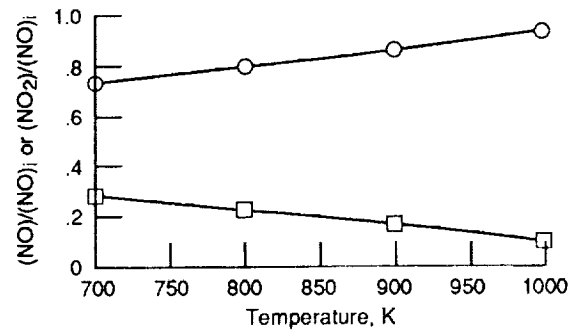


Figure 2.—Equilibrium concentrations of NO<sub>2</sub> at different fuel-air ratios. Fuel, CH<sub>4</sub>; temperature, 366 K.

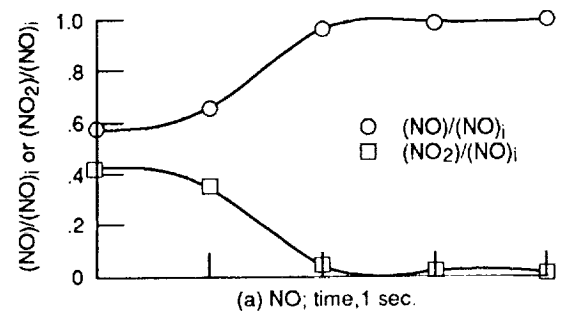


(a) 500 ppm NO and 3090 ppm H<sub>2</sub>.

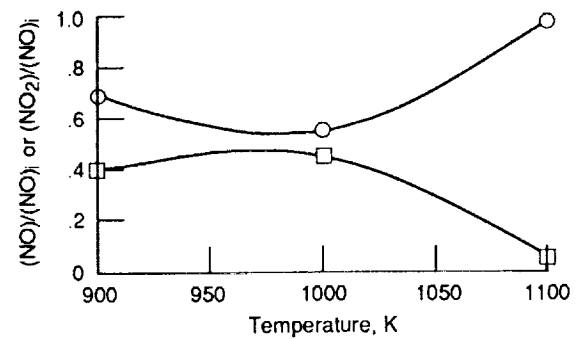


(b) 815 ppm NO and 4300 ppm H<sub>2</sub>. Oxygen, 17%.

Figure 3.—Effect of hydrogen on NO at various temperatures. Time, 1 sec.



(a) NO; time, 1 sec.



(b) NO<sub>x</sub>; time, 300 msec; oxygen, 10%.

Figure 4.—Effect of methane. 500 ppm NO and 1000 ppm CH<sub>4</sub>.

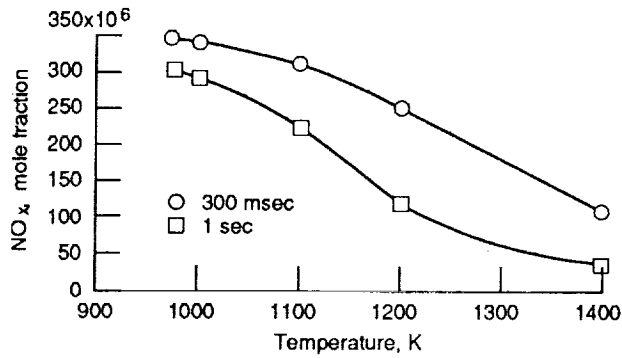
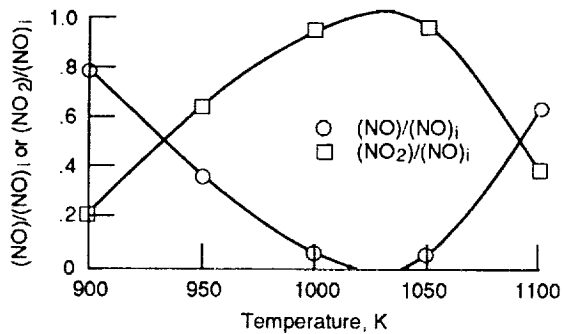
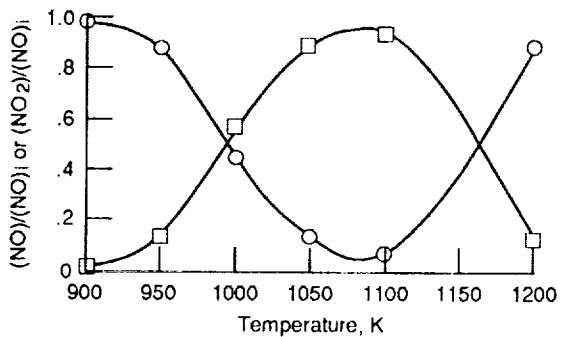


Figure 5.—Effect of methane ( $\phi = 2.0$ ) on NO.

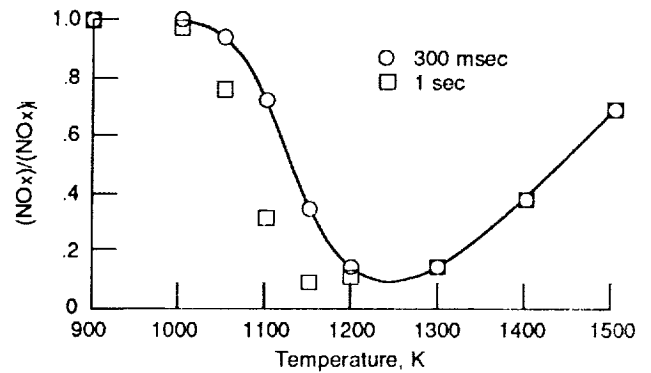


(a) NO<sub>x</sub>; 500 ppm NO and 500 ppm C<sub>2</sub>H<sub>6</sub>.

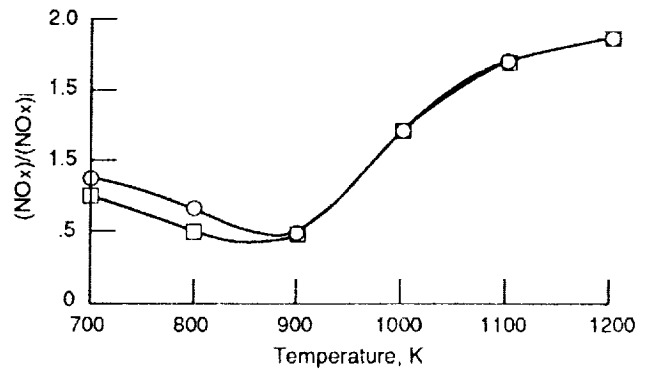


(b) NO; 500 ppm NO and 500 ppm CH<sub>3</sub>OH.

Figure 6.—Oxidation of NO to NO<sub>2</sub>; time, 1 sec.

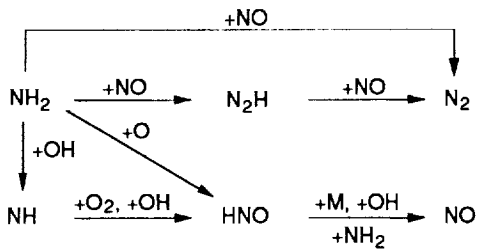


(a) The effect of ammonia addition to the exhaust system at various temperatures; 500 ppm NO and 500 ppm NH<sub>3</sub>.

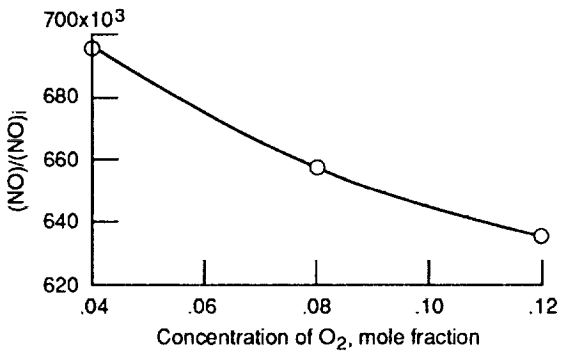


(b) The effect of ammonia on NO<sub>x</sub> in the presence of hydrocarbon fragment at various temperatures; 436 ppm NO and 463 ppm NH<sub>3</sub>.

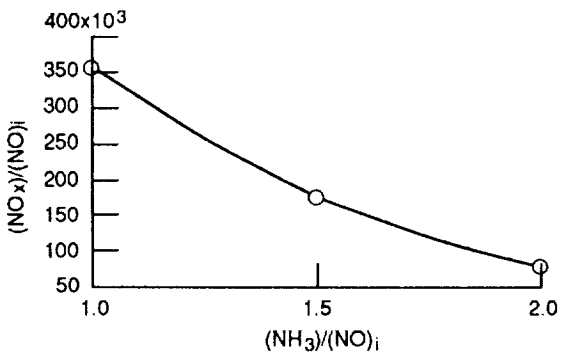
Figure 7.—Effect of temperature on NO reduction in presence of NH<sub>3</sub>.



(a) Reduction path diagram.

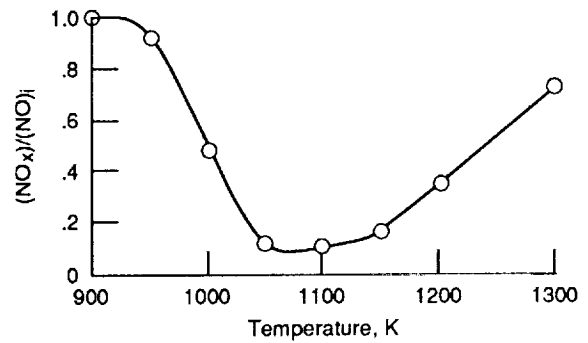


(b) Effect of oxygen concentration on reduction of NO by ammonia. Temperature, 1100 K; 500 ppm NO; 300 msec.

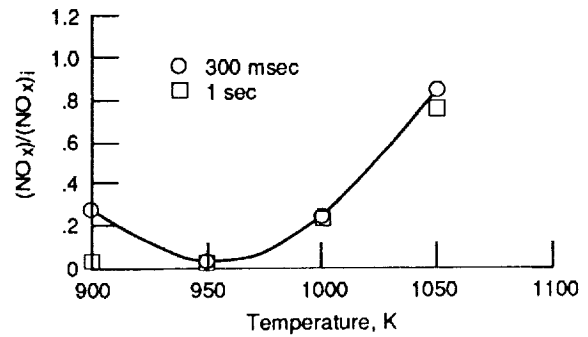


(c) Effect of ammonia and NO concentrations on NO<sub>x</sub>. Temperature, 1150 K; 500 ppm NO; 300 msec.

Figure 8.—Reduction of NO in presence of NH<sub>3</sub>.

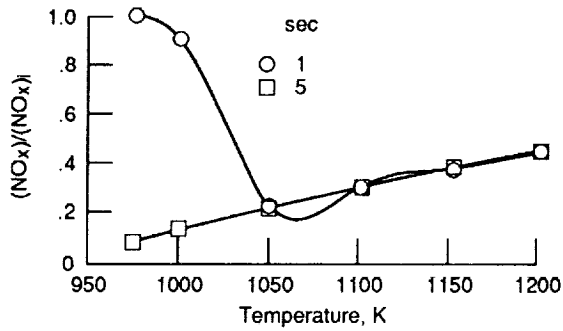


(a) 500 ppm NO, 500 ppm NH<sub>3</sub>, and 500 ppm H<sub>2</sub>.

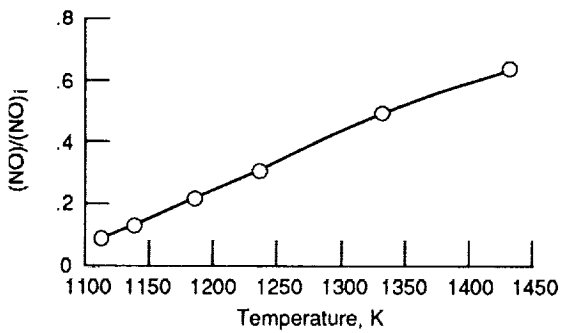


(b) 500 ppm NO, 500 ppm NH<sub>3</sub>, and 500 ppm H<sub>2</sub>.

Figure 9.—Effect of hydrogen on the reduction of NO by NH<sub>3</sub>.



(a) Effect of ammonia on  $\text{NO}_x$  in presence of methanol; 500 ppm NO, 800 ppm  $\text{NH}_3$ , and 500 ppm methanol.



(b) Effect of reaction temperature on reduction of NO by the addition of ammonia; 500 ppm NO, 750 ppm  $\text{NH}_3$ , and 500 ppm methanol. Time, 5 sec.

Figure 10.—Effect of methanol on the reduction of NO in presence of  $\text{NH}_3$ .

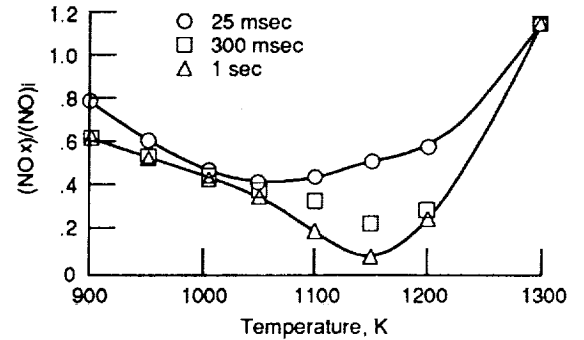


Figure 11.—Effect of  $\text{H}_2\text{O}_2$  on  $\text{NO}_x$  reduction by ammonia; 500 ppm  $\text{NH}_3$ , 500 ppm NO, and 500 ppm  $\text{H}_2\text{O}_2$ .

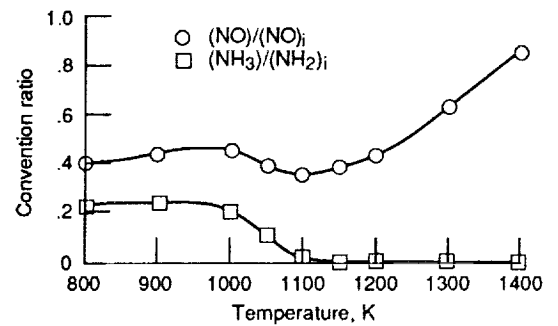


Figure 12.—Effect of temperature on NO reduction in the presence of  $\text{NH}_3$ .





1. Report No. <b>NASA TM-103765</b> <b>AIAA-91-0479</b>		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle <b>Mechanisms and Modeling of the Effects of Additives on the Nitrogen Oxides Emission</b>				5. Report Date	
				6. Performing Organization Code <b>E - 5969</b>	
7. Author(s) <b>Krishna P. Kundu, H. Lee Nguyen, and M. Paul Kang</b>				8. Performing Organization Report No. <b>537-02-20</b>	
				10. Work Unit No.	
9. Performing Organization Name and Address <b>National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135 - 3191</b>				11. Contract or Grant No.	
				13. Type of Report and Period Covered <b>Technical Memorandum</b>	
12. Sponsoring Agency Name and Address <b>National Aeronautics and Space Administration Washington, D.C. 20546 - 0001</b>				14. Sponsoring Agency Code	
15. Supplementary Notes <b>Prepared for the 29th Aerospace Sciences Meeting sponsored by the American Institute of Aeronautics and Astronautics, Reno, Nevada, January 7-10, 1991. Krishna P. Kundu, National Research Council - NASA Research Associate at Lewis Research Center. Responsible person, Krishna P. Kundu, (216) 433 - 3939.</b>					
16. Abstract <b>A theoretical study on the emission of the oxides of nitrogen in the combustion of hydrocarbons is presented in this communication. Our current understanding of the mechanisms and the rate parameters for gas phase reactions have been used to calculate the NOx emission. The possible effects of different chemical species on thermal NOx, on a long time scale have been discussed. The mixing of these additives at various stages of combustion has been considered and NOx concentrations have been calculated; effects of temperatures have also been considered. The chemicals such as Hydrocarbons, H2, CH3OH, NH3 and other nitrogenous species have been chosen as additives in this discussion. Results of these calculations can be used to evaluate the effects of these additives on the NOx emission in the industrial combustion systems.</b>					
17. Key Words (Suggested by Author(s)) <b>Modeling Additive Nitrogen oxide</b>			18. Distribution Statement <b>Unclassified - Unlimited Subject Category 28</b>		
19. Security Classif. (of the report) <b>Unclassified</b>		20. Security Classif. (of this page) <b>Unclassified</b>		21. No. of pages <b>24</b>	22. Price* <b>A03</b>