

# A Kinetic Model for the Reduction of Nitric Oxide by Hydrazine

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A chemical kinetic model is developed for the non-catalytic reduction of nitric oxide (NO) by hydrazine (N<sub>2</sub>H<sub>4</sub>). Since the reduction of NO was observed in an experimental reaction with N<sub>2</sub>H<sub>4</sub>, the hydrazine has been suggested as a new reductant of NO in addition to the conventional ammonia, urea and isocyanic acid. In the proposed kinetic model, a set of fifty one chemical reactions that includes the various branching reactions of N<sub>2</sub>H<sub>4</sub> to NH<sub>2</sub> and the well-known reaction  $\text{NO} + \text{NH}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$  is simultaneously considered with the usual partial equilibrium assumptions. The NO reduction is estimated to occur at a temperature range between 700 K and 1400 K, which is wider and lower than in the conventional Thermal DeNOx process. The maximum amount of the reduced NO is slightly less than that in the Thermal DeNOx. The effects of the other input parameters on the NO reduction rate are also discussed.

**Key Words:** Combustion Products, Chemical Reaction, Pollutant, Nitric Oxide, Reduction, Kinetic Model

## 1. Introduction

Among the combustion products, nitric oxides (NO<sub>x</sub>) are important air pollutants that play a critical role in forming the photo-chemical smog and the acid rain. Both nitric oxide, NO, and nitrogen dioxide, NO<sub>2</sub>, are produced in combustion, but the majority of nitrogen oxides are emitted as NO. Several methods have been suggested to control the emission of NO. They include the post-combustion treatments as well as the combustion modifications such as staged combustion and reburning. In many cases, the combustion modification methods are not enough by themselves to satisfy the allowed emission level.

One of the most effective post-combustion treatment methods is the chemical reduction of NO by adding a reductant. The main subject of the present investigation is the chemical reduction without the catalyst. A non-catalytic reduction process is especially appropriate in large combustion systems where the catalysts can not be

used or are not economical, such as in utility boilers or waste incinerators.

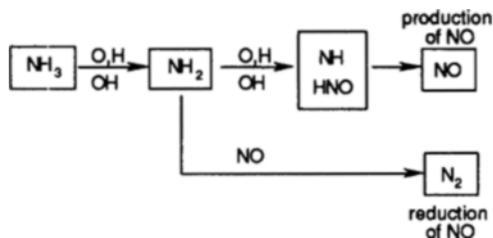
The best-known non-catalytic process for the reduction of NO is the Thermal DeNO<sub>x</sub>, invented by Lyon and patented by Exxon Research & Engineering. The Thermal DeNO<sub>x</sub> process has been widely studied by Muzio et al. (1979), Miller et al. (1981), Lucas and Brown (1982), Dean et al. (1982) and Branch et al. (1982). In this process, ammonia serving as a reductant is injected into exhaust gas, initiating a series of reactions that reduce the nitric oxides to molecular nitrogens. The process mechanism is summarized in Fig. 1. At high temperatures, NH<sub>3</sub> is oxidized to NH<sub>2</sub> through reactions with O, H, or OH radicals, and NO is reduced to N<sub>2</sub> via an apparent reaction



At still higher temperatures, however, NH<sub>2</sub> is oxidized to NH or HNO, which is highly reactive and causes the production of more NO. In practice, the reduction of NO by NH<sub>3</sub> is possible only at the temperature range between 1000 K and 1300 K. At temperatures lower than 900K, NO

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**Fig. 1** Overview of NO production or NO reduction in Thermal DeNOx(ammonia) process

can not be reduced due to the slow oxidation of  $\text{NH}_3$  to  $\text{NH}_2$ . At temperatures higher than 1400K, the production of NO due to NH exceeds the reduction. The temperature sensitivity of the  $\text{NH}_3$ -NO reaction makes the location of ammonia injection extremely important.

Other important processes for NO reduction are the NOxOUT (patented by Nalco-Fuel Tech. Inc.) and the RAPRENOx (invented by Perry). The NOxOUT is well described by Dhargalkar (1992) and the RAPRENOx has been recently studied by Perry and Siebers(1986), Miller and Fisk (1987), Miller and Bowman(1991), Cooper and Hershberger(1992), and Chen et al. (1991). They use urea( $\text{NH}_2\text{CONH}_2$ ) and isocyanic acid (HNCO) as reductants, respectively. Since urea is non-toxic and cheap, the NOxOUT has been more widely utilized. It was reported that in this process, the temperature range should be between 1000 and 1300 K. Although Perry observed the reduction of NO at the temperature as low as 700 K in 1987, it was reported later that the RAPRENOx is also effective at 1000 K. It is noted that the main reduction reaction for both processes is also given by Eq. (1).

More recently, Kim(1993) and Lee et al. (1994) have proposed hydrazine( $\text{N}_2\text{H}_4$ ) as a new reductant for the non-catalytic reduction of NO. A laboratory-scale experiment and its application to a waste incinerator have shown that a clear reduction of NO is possible with hydrazine. It is known that the N-N bond in hydrazine is weaker than the usual N-H bond. Therefore, at high enough temperatures,  $\text{N}_2\text{H}_4$  could generate  $\text{NH}_2$ ,



and NO could be effectively reduced via Eq. (1).

A patent for the non-catalytic reduction method by hydrazine is pending.

The thermodynamic properties of hydrazine are similar to those of water as described by Schirrmann(1989). Pure hydrazine is toxic and explosive, but the aqueous solution containing less than 38% hydrazine by volume is known to be safe and easy to handle. The price of hydrazine is also as low as other reductants for NO.

The present study proposes an analysis model which is capable of clarifying the NO reduction mechanism by hydrazine. The model should be able to predict quantitatively the reduction amount for various process conditions.

## 2. Kinetic Model

The important reactions associated with the chemical reaction involving  $\text{N}_2\text{H}_4$  and NO are listed in Table 1 together with the rate constants. These reactions have been selected from all the reactions listed in Hanson and Salimian(1984) by comparing the orders of magnitude in the reaction rate constants. The proposed kinetic model is based upon the partial equilibrium assumption which also serves as a basis for the kinetic model of the Thermal DeNOx. The concept of the partial equilibrium is described by Flagan and Seinfeld (1988). The assumption is valid because the endothermic reverse reactions are too slow to maintain the equilibrium among the one- or two-nitrogen containing species. In addition, it is assumed that the O, H, and OH radicals can reach an equilibrium very rapidly with  $\text{H}_2\text{O}$  and  $\text{O}_2$  and that the concentrations of the major species such as  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and  $\text{N}_2$  are constant.

Utilizing these simplifying assumptions, the number of concentrations of species to be determined is reduced to eight;  $\text{N}_2\text{H}_4$ ,  $\text{N}_2\text{H}_3$ ,  $\text{N}_2\text{H}_2$ ,  $\text{N}_2$ , H,  $\text{NH}_3$ ,  $\text{NH}_2$ , NH and NO. Therefore, the rate equations for the eight unknown concentrations may be written in terms of the concentrations of species and the rate constants of the 51 reactions listed in Table 1. The rate constants for the N-H-O reactions are provided by Hanson and Salimian(1984) as functions of temperature. When the initial values for the eight concentra-

**Table 1** List of reactions and the rate constants included in the calculation model

$$k = AT^B \exp(-\theta/T)$$

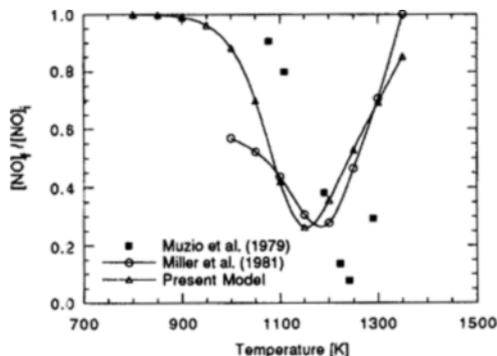
Reaction	Log(A/cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> T <sup>-B</sup> )	B	θ/K
1. N <sub>2</sub> H <sub>4</sub> +M → 2NH <sub>2</sub> +M	15.6	0	20,600
2. N <sub>2</sub> H <sub>4</sub> +H → N <sub>2</sub> H <sub>3</sub> +H <sub>2</sub>	13.1	0	1,260
3. N <sub>2</sub> H <sub>4</sub> +O → N <sub>2</sub> H <sub>2</sub> +H <sub>2</sub> O	13.8	0	600
4. N <sub>2</sub> H <sub>4</sub> +OH → N <sub>2</sub> H <sub>3</sub> +H <sub>2</sub> O	13.6	0	0
5. N <sub>2</sub> H <sub>4</sub> +NH <sub>2</sub> → N <sub>2</sub> H <sub>3</sub> +NH <sub>3</sub>	11.6	0.5	1,000
6. N <sub>2</sub> H <sub>3</sub> +M → N <sub>2</sub> H <sub>2</sub> +N <sub>2</sub> H <sub>2</sub> +H+M	16.0	0	25,000
7. N <sub>2</sub> H <sub>3</sub> +M → N <sub>2</sub> H <sub>2</sub> +NH <sub>2</sub> +NH+M	16.0	0	21,000
8. N <sub>2</sub> H <sub>3</sub> +H → NH <sub>2</sub> +NH <sub>2</sub>	12.2	0	0
9. N <sub>2</sub> H <sub>3</sub> +O → N <sub>2</sub> H <sub>2</sub> +OH	11.5	0.5	0
10. N <sub>2</sub> H <sub>3</sub> +O → N <sub>2</sub> H+H <sub>2</sub> O	11.5	0.5	0
11. N <sub>2</sub> H <sub>3</sub> +OH → N <sub>2</sub> H <sub>2</sub> +H <sub>2</sub> O	13.0	0	1,000
12. N <sub>2</sub> H <sub>3</sub> +NH <sub>2</sub> → N <sub>2</sub> H <sub>2</sub> +NH <sub>3</sub>	11.0	0.5	0
13. N <sub>2</sub> H <sub>3</sub> +N <sub>2</sub> H <sub>2</sub> → N <sub>2</sub> H <sub>4</sub> +N <sub>2</sub> H	13.0	0	5,000
14. N <sub>2</sub> H <sub>2</sub> +M → N <sub>2</sub> H+H+M	16.0	0	25,000
15. N <sub>2</sub> H <sub>2</sub> +H → N <sub>2</sub> H+H <sub>2</sub>	13.0	0	500
16. N <sub>2</sub> H <sub>2</sub> +O → N <sub>2</sub> H+OH	11.0	0.5	0
17. N <sub>2</sub> H <sub>2</sub> +OH → N <sub>2</sub> H+H <sub>2</sub> O	13.0	0	1,000
18. N <sub>2</sub> H <sub>2</sub> +NH <sub>2</sub> → N <sub>2</sub> H+NH <sub>3</sub>	13.0	0	2,000
19. N <sub>2</sub> H <sub>2</sub> +N <sub>2</sub> H <sub>2</sub> → N <sub>2</sub> H+N <sub>2</sub> H <sub>3</sub>	13.0	0	5,000
20. N <sub>2</sub> H+M → N <sub>2</sub> +H+M	14.3	0	10,000
21. N <sub>2</sub> H+H → N <sub>2</sub> +H <sub>2</sub>	13.6	0	1,500
22. N <sub>2</sub> H+O → N <sub>2</sub> +OH	13.0	0	2,500
23. N <sub>2</sub> H+O → N <sub>2</sub> O+H	13.0	0	1,500
24. N <sub>2</sub> H+OH → N <sub>2</sub> +H <sub>2</sub> O	13.5	0	0
25. N <sub>2</sub> H+NH <sub>2</sub> → N <sub>2</sub> +NH <sub>3</sub>	13.0	0	0
26. N <sub>2</sub> H+N <sub>2</sub> H → N <sub>2</sub> H <sub>2</sub> +N <sub>2</sub>	13.0	0	5,000
27. N <sub>2</sub> H+O <sub>2</sub> → N <sub>2</sub> +HO <sub>2</sub>	12.3	0	4,500
28. NH <sub>3</sub> +M → NH <sub>2</sub> +H+M	16.4	0	47,200
29. NH <sub>3</sub> +M → NH+H <sub>2</sub> +M	14.8	0	47,000
30. NH <sub>3</sub> +O → NH <sub>2</sub> +OH	13.3	0	4,470
31. NH <sub>3</sub> +OH → NH <sub>2</sub> +H <sub>2</sub> O	13.8	0	4,055
32. NH <sub>3</sub> +H → NH <sub>2</sub> +H <sub>2</sub>	14.1	0	10,820
33. NH <sub>2</sub> +M → NH+H+M	23.5	-2	46,000
34. NH <sub>2</sub> +H → NH+H <sub>2</sub>	13.3	0	0
35. NH <sub>2</sub> +O → NH+OH	14.1	-0.5	0
36. NH <sub>2</sub> +O → HNO+H	14.8	-0.5	0
37. NH <sub>2</sub> +OH → NH+H <sub>2</sub> O	11.7	0.5	1,000
38. NH <sub>2</sub> +NH <sub>2</sub> → N <sub>2</sub> H <sub>2</sub> +H <sub>2</sub>	13.6	0	6,000
39. NH <sub>2</sub> +O <sub>2</sub> → HNO+OH	12.3	0	7,500
40. NH <sub>2</sub> +O <sub>2</sub> → NH+HO <sub>2</sub>	13.7	0	1,000
41. NH+H → N+H <sub>2</sub>	11.8	0.5	0
42. NH+N → N <sub>2</sub> +H	11.8	0.5	4,000
43. NH+O → N+OH	11.8	0.5	0
44. NH+O → NO+H	11.7	0.5	1,000
45. NH+OH → N+H <sub>2</sub> O	12.0	0.5	1,000
46. NH+OH → HNO+H	11.3	0.5	1,000
47. NH+NH → N <sub>2</sub> H+N	12.0	0.5	1,000
48. NH+N <sub>2</sub> H <sub>4</sub> → NH <sub>2</sub> +N <sub>2</sub> H <sub>3</sub>	13.0	0	500
49. NH+N <sub>2</sub> H <sub>2</sub> → N <sub>2</sub> H+NH <sub>2</sub>	13.0	0	6,000
50. NH+O → HNO+O	19.8	-2.5	9,500
51. NH <sub>2</sub> +NO → N <sub>2</sub> +H <sub>2</sub> O	14.3	0	38,370

tions are given, the eight ordinary differential equations can be solved simultaneously by integration. The integration is done numerically using the 4th order Runge-Kutta method.

The input parameters for the analysis model are the initial values for the concentrations of the species, the temperature and the reaction time. Of course, the amount of the reduction of NO is determined by the difference between the NO concentration at the start and at the end of the reaction. The temperature might be held constant or decrease for the duration of the reaction process, depending on the cooling conditions.

### 3. Results and Discussion

Before further discussion, the results of the present analysis should be verified by comparing with the previously reported results. Unfortunately, the authors' experiment did not provide a quantitative result and the proposed analysis model is believed to be the first to deal with the reaction of NO and  $N_2H_4$ . An indirect way to verify the present model is to calculate the NO reduction for the initial conditions of zero  $N_2H_4$  concentration and a certain level of  $NH_3$  concentration and to compare the calculation results with those of Thermal DeNOx. While this comparison does not wholly justify the present method, at least some part of the model could be



**Fig. 2** Comparison of computed NO survival as a function of temperature for Thermal DeNOx with previous results (reaction time=0.7 sec, combustion product for natural gas with excess oxygen=4%,  $[NO]_i=300$ ppm,  $[NH_3]_i=480$ ppm)

confirmed.

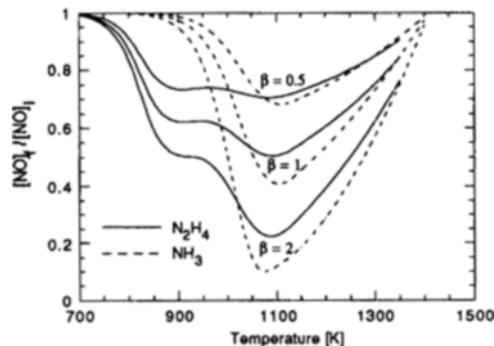
Figure 2 shows the ratio of the final to the initial NO concentration (the so-called NO survival) as a function of temperature, for the present model and for the previous investigations. The input parameters are the same for both the present model and the calculations by Miller et al. A close agreement is observed between the two results. The initial concentration of  $H_2O$  is not known in the calculation of Miller et al., which might cause the slight difference. As Miller et al. indicated, some discrepancy between the calculation results and the experimental findings of Muzio et al. is due to the ambiguity in the initial conditions and the cooling rates in each experiment.

#### 3.1 Reduction mechanism

To understand the NO reduction mechanism by hydrazine, the NO survival is plotted as a function of temperature for both ammonia and hydrazine in Fig. 3.  $\beta$  is defined as a ratio of the initial concentration of the reductant to the initial concentration of NO.

$$\beta = \frac{[NH_3]_i}{[NO]_i} \text{ or } \frac{[N_2H_4]_i}{[NO]_i} \quad (3)$$

In the calculation, the initial concentrations of the species other than NO,  $N_2H_4$ ,  $N_2$ ,  $H_2O$  and  $O_2$  were zero. The results presented in this paper are obtained under the following conditions unless specified otherwise:  $[NO]_i=500$ ppm,  $\beta=1$ , reac-

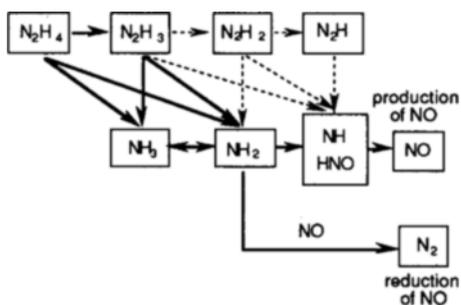


**Fig. 3** Comparison of computed NO survival as a functions of temperature by  $N_2H_4$  and by  $NH_3$  for different values of initial reductant concentration

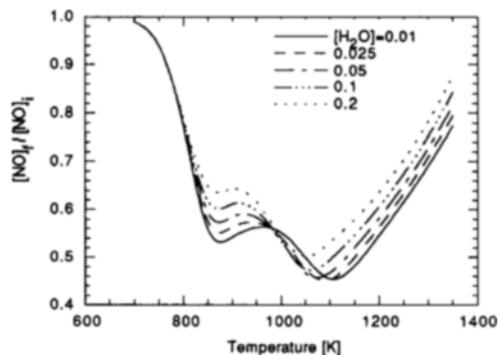
tion time = 1 sec,  $[H_2O]_i = 0.1$ ,  $[O_2]_i = 0.01$ , and total pressure = 1 atm.

Figure 3 demonstrates that the NO reduction by hydrazine occurs over a lower and wider temperature range than by ammonia. In other words, the NO reduction by hydrazine is possible at the temperature as low as 800 K. The primary reason is that hydrazine is more active in forming  $NH_2$  by the reaction 1 in Table 1. The high temperature limit of the reduction for hydrazine is about 1400 K, which is almost same as that for ammonia in this specific condition.

On the other hand, the maximum removal rate of NO by hydrazine is slightly less than that by ammonia. This seems to be associated with the "double-dented" shape of the NO survival curve for hydrazine. After a number of calculations and careful monitoring of the concentrations of other species during the reaction, it was found that the shape of the curve arises from the existence of two dominant paths from  $N_2H_4$  to  $NH_2$  as represented



**Fig. 4** Hydrazine branching paths for NO production and NO reduction (solid arrows: dominant paths)



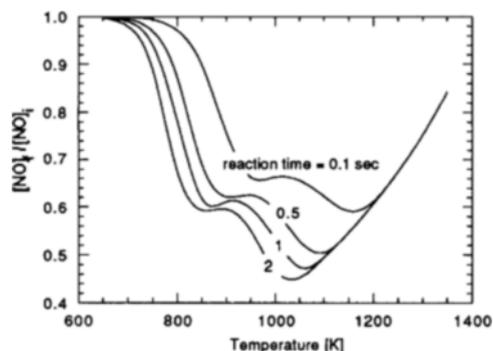
**Fig. 5** NO survival as a function of temperature for different values of reaction time

by solid arrows in Fig. 4. Clearly, the NO reduction at around 1000 K is mostly due to the direct branching of  $N_2H_4$  to  $NH_2$  as described above. The reduction at around 1200 K is due to the path through  $NH_3$  mainly via reaction 5 in Table 1. The issue of predominance between the two passages is determined by the input parameters as described below.

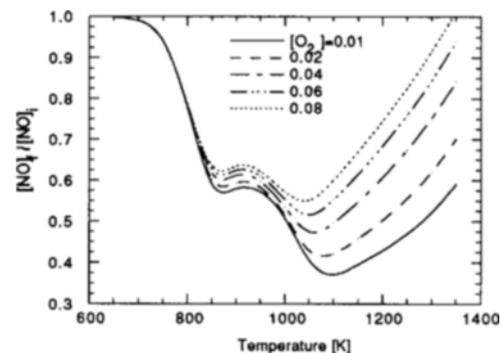
It is obvious that at the temperature lower than 800 K, NO is reduced because of the slow oxidation of  $N_2H_4$ . At temperatures higher than about 1500 K, the production of NO due to NH or HNO exceeds the reduction. Therefore, the  $N_2H_4$ -NO reaction is still temperature sensitive, albeit less severely than the  $NH_3$ -NO reaction.

### 3.2 Reaction time

Figure 5 shows the calculation results for different values of the reaction time. As the reaction time increases, the amount of NO removed increases and eventually reaches saturation. In the



**Fig. 6** NO survival as a function of temperature for different values of  $H_2O$  concentration



**Fig. 7** NO survival as a function of temperature for different values of  $O_2$  concentration

calculation conditions, most of the reduction occurs during the initial 0.5 second. At temperatures above 1200 K, all curves coincide, which means that the all reactions have reached their steady-state conditions within 0.1 sec.

### 3.3 H<sub>2</sub>O and O<sub>2</sub> concentrations

Figures 6 and 7 plot the calculated NO reduction for different values of the initial concentrations of H<sub>2</sub>O and O<sub>2</sub>, respectively. The H<sub>2</sub>O concentration is typically determined by the fuel, while the O<sub>2</sub> concentration depends on both the amount of excess air and the combustion conditions. These concentrations do not appreciably affect the NO reduction at temperatures around 800 K since the direct decomposition of N<sub>2</sub>H<sub>4</sub> to NH<sub>2</sub>, which serves as the main path, is independent of the concentrations of O, H and OH radicals. At higher temperatures, however, the NO reduction decreases as H<sub>2</sub>O or O<sub>2</sub> concentration is increased, because more O, H and OH radicals augment the formation of NH or HNO that produces NO. It can be observed that the effect of O<sub>2</sub> concentration on the NO reduction is greater than that of H<sub>2</sub>O concentration.

### 3.4 Initial NO concentration

Lastly, the effect of the initial concentration of NO needs to be discussed. As shown in Fig. 8, the proportion of the removed NO increases with the initial concentration. But at relatively low temperature range, it is independent of the initial concentration. This suggests that the temperature at the injection point of N<sub>2</sub>H<sub>4</sub> could be as low as

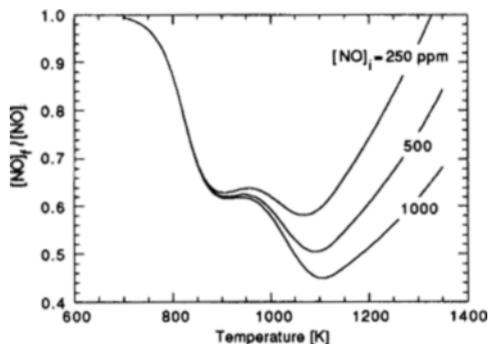


Fig. 8 NO survival as a function of temperature for different values of initial NO concentration

900 K when the NO contamination level is low, and should be around 1100 K when the NO contamination level is high for the optimal performance.

## 4. Conclusions

A chemical kinetic model has been developed to accurately depict the important features of the non-catalytic reduction of nitric oxides by hydrazine. It was found that the two distinct major branching paths from N<sub>2</sub>H<sub>4</sub> to NH<sub>2</sub> can exist and that the reduction of NO by hydrazine can occur over much wider temperature range than by ammonia. However, the maximum reduction efficiency may be slightly lower. Further investigations to experimentally confirm the feasibility of the proposed non-catalytic NO reduction process are needed.

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