Effect of H_2O_2 on Homogeneous Gas Phase NO Reduction Reaction with NH_3

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To study the effect of H_2O_2 on NO reduction with NH_3, the homogeneous gas phase reaction of NH_3—NO—H_2O_2—O_2 was investigated in a Pyrex flow reactor over the temperature range from 500°C to 600°C under one atmospheric pressure. H_2O_2 accelerated the NO reduction by NH_3 and caused it to be induced at a temperature of 500°C. In the absence of O_2, NOx reduction ratio of more than 90% was obtained for $NH_3/NO=5$ and $H_2O_2/NO=1$ at 550°C. In the presence of O_2 or an excess of H_2O_2, two side reactions, which cause the NOx reduction ratio to decrease, occur.

One of the side reactions is NO oxidation with H_2O_2. It was found experimentally that NO_2 inhibited NO reduction and that H_2O_2 was an NO oxidizing agent, as well as an NH_3 decomposing agent. The other side reaction was the formation of NO and NO_2, which resulted from the oxidation of NH_3 with O_2. Under the conditions of our experiments, the amount of O_2 in our reaction system was extremely high compared to the amounts of NO, NH_3 and H_2O_2 in the system. Thus NO_x was assumed to be produced by the oxidation of the NO reducing radicals, which were produced by the reaction of NH_3 with H_2O_2.

SCOPE

Owing to the peculiar properties of NH_3, which selectively reduces NO in the presence of a large amount of O_2, the reaction of NH_3 with NO has received much attention as a means of controlling NOx emission from combustion devices. Though this reaction has been studied extensively, much of the work has been concerned with the catalytic reaction because of the relatively low reactivity of NH_3. In contrast, it was proved by Lyon (1975) that the presence of an amount of O_2 sufficient to decompose NH_3 would induce an NO reduction reaction without a catalyst over the temperature range from 870 to 1100°C and, furthermore, that the addition of H_2 to the NH_3—NO—O_2 system would lower the reaction temperature to 700°C. However, from a practical viewpoint, a still lower temperature is desirable, but little is known about reaction promoting additives, apart from some atomic or intermediate addition reactions which are produced by a flash photolysis technique. Therefore, efforts have ben made to find other agents which give a large impetus to the reaction of NH_3 with NO.

As investigated by Wolfhard et al. (1949), Bradley et al. (1968), and Baldwin et al. (1960), it is well known that the oxidation of NH_3 is initiated by a reaction with OH radicals, and that H_2O_2 is decomposed into OH radicals. These reactions offer the possibiliity that H_2O_2 will accelerate the decomposition of NH_3 so that an NO reduction reaction will be promoted. The purpose of this paper is to report the effect of an H_2O_2 additive on the NH_3—NO—O_2 system and to reveal some characteristic features of this reaction.

CONCLUSIONS AND SIGNIFICANCE

The results which we obtained in our experiments show that H_2O_2 is very effective in accelerating the reaction of NH_3 with NO. The addition of H_2O_2 induced an NO reduction reaction at a temperature of 500°C. In this reaction system, the presence of O_2 and an excess of H_2O_2 caused two side reactions to occur, and these side reactions caused a decrease in the NOx reduction rate. One side reaction is the oxidation of NO with H_2O_2. NO_2 was experimentally proved to inhibit the reduction of NO with NH_3. The other side reaction is the formation of NOx from NH_3. When the amount of O_2 in a system is several hundred times that of NH_3, NH_3 is not only an NO reducing agent, but also a source of NOx.

EXPERIMENTAL APPARATUS AND PROCEDURES

Experiments and homogeneous gas phase reactions were carried out in a flow reactor. A schematic diagram of the experimental apparatus is given in Figure 1. Reactants passed through the electrically heated reaction vessel which was 1.3 m in length and 40 mm i.d. A mixture consisting of NO, O_2 and N_2 was preheated in the reactor preheating zone. At the inlet of the reaction zone, a second stream containing H_2O_2 and NH_3 was injected and mixed with the preheated reactants.

At the beginning of this present study, the surface of the reaction vessel was found to have a large influence on the reaction. Pyrex and quartz tubes were used and the experimental results obtained with the different vessels were compared. The data in Figure 2 show the influence of the surfaces. The percentage NOx reduction obtained with the quartz tube was lower than that obtained with the Pyrex tube. When they studied the homogeneous gas phase decomposition of H_2O_2, Baldwin and Brattan (1960) employed aged boric acid-coated vessels because the aged surface was inert with respect to both the HO_2 radical and H_2O_2. The Pyrex tube used in the present study obtained 14% boron oxide, which favorably effected the reaction of NH_3 with H_2O_2. Furthermore, Cullis and Newitt (1958) pointed out that the yields of H_2O_2 ob-

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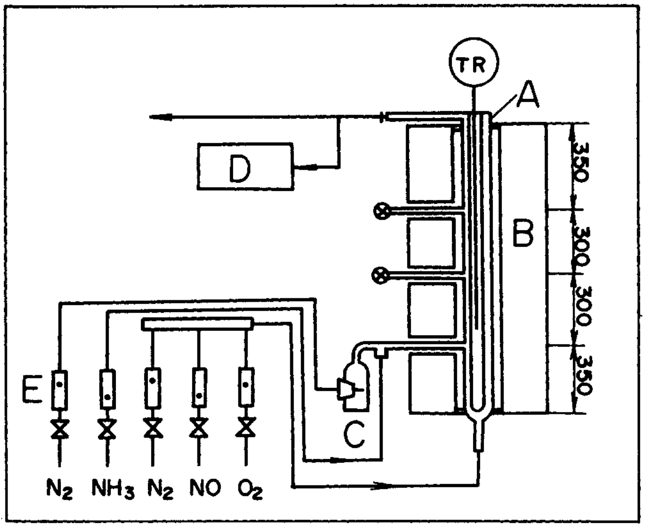

Figure 1. Experimental apparatus: A = reaction vessel; B = electrical furnace; C = spray vesel; D = NO/NOx analyser; E = rotameters.

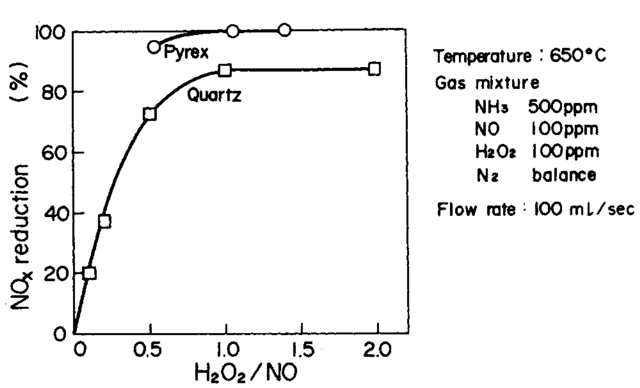

Figure 2. Influence of surface of reaction vessel on NOx reduction rate. Gas mixture, 100 ppm NO, 500 ppm NH_3, 0 ~ 200 ppm H_2O_2; Temperature, 650°C.

tained in the gas phase oxidation of alcohol was affected by the surface area-volume ratio (S/V) of the Pyrex reactor and that increases in the surface area led to marked reductions in the yields of H_2O_2. Our pre-examination of the Pyrex reactors with various S/V also showed that increases in the surface area led to decreases in the NOx reduction rate. In view of these facts, we used a pyrex reactor with an S/V of 1 cm^{-1}, which is approximately the same as the minimum S/V (0.88 cm^{-1}) of Cullis and Newitt's reactor.

Calibrated rotameters were used to control the flow rate of each reactant and to set the total flow rate at 100 mL/s (at 0°C and atmospheric pressure). H_2O_2 was sprayed into the N_2 stream and then injected into the reaction vessel. The H_2O_2 content of N_2 was determined from the change in aqueous concentration and then checked by chemical analysis. A chemiluminescence NO/NOx analyzer was attached at the reactor exit and NO and NO_2 were monitored. NH_3 was measured by chemical analysis.

The reaction temperature was measured with a traversing Pt/Pt-Rh thermocouple in the inner tube of the reaction vessel (6 mm o.d.). An example of the temperature profile in a reaction vessel is shown in Figure 3. The temperature distribution in the reaction zone was kept approximately uniform.

RESULTS AND DISCUSSION

Reaction of NH_3—NO—H_2O_2—O_2

Effect of H_2O_2 Addition on the Reaction of NH_3 with NO. The effect of H_2O_2 on the NH_3—NO—O_2 system is shown in Figure 4, where the percentage NOx reduction with and without H_2O_2 are expressed as a function of the reaction temperature and O_2 concentration. H_2O_2 was shown to promote the reaction of NH_3 with NO. In the absence of H_2O_2, the NO reduction reaction occurred at temperatures above 800°C, when excess O_2 existed, but without O_2 it did not occur even at 900°C.

In contrast, in the presence of H_2O_2, the NO reduction reaction occurred at 500°C. In the absence of O_2, the effect of H_2O_2 addition on the percentage NOx reduction was remarkable, with 90% at 550°C.

In Figure 4, the broken line represents the percentage H_2O_2 decomposition calculated from Baulch et al.'s kinetic data with reference to the gas phase H_2O_2 decomposition reaction

$$H_2O_2 + M \rightarrow OH + OH + M \qquad (1)$$

The coincidence of the H_2O_2 decomposition and NOx reduction temperatures indicates that H_2O_2 decomposition induces the reaction of NO with NH_3 and suggests that the radicals produced by H_2O_2 decomposition promote the reaction of NH_3 with NO.

A characteristic that is common to the NH_3—H_2O_2—NO—O_2 and NH_3—NO—O_2 reactions is that the higher the O_2 content is, the greater the decreases in the percentage NOx reduction.

Influence of the Amount of H_2O_2 on the NOx Reduction Rate. Figure 5 shows the influence of NH_3 and H_2O_2 concentrations on the NOx reduction at 550°C. The composition of the reactants was 15% O_2, 100 ppm NO and 200 ~ 500 ppm NH_3; the amount of H_2O_2 was varied from O to 150 ppm. A distinct maximum was observed near H_2O_2/NO of about unity in the relation between the percentage NOx reduction and the moler ratio of H_2O_2/NO. That is, the addition of excess H_2O_2 decreased the percentage NOx reduction. In this reaction system, in addition to the reduction of NO to N_2, NO_2 was produced in a side reaction. The amount of NO_2 increased with increases in H_2O_2 and with decreases in NH_3. These results can be explained by the assumptions that: (a) H_2O_2

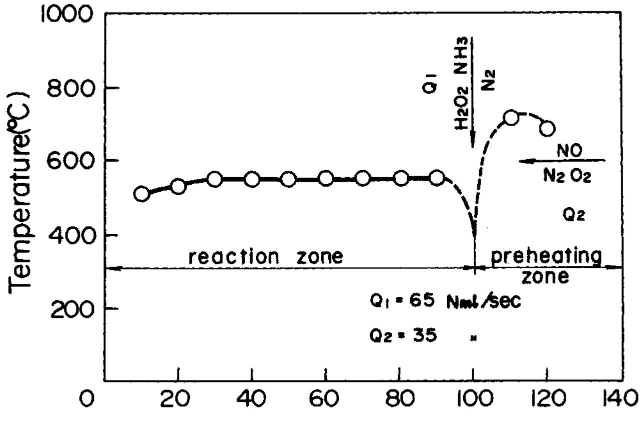

Figure 3. Example of temperature profile of reaction vessel.

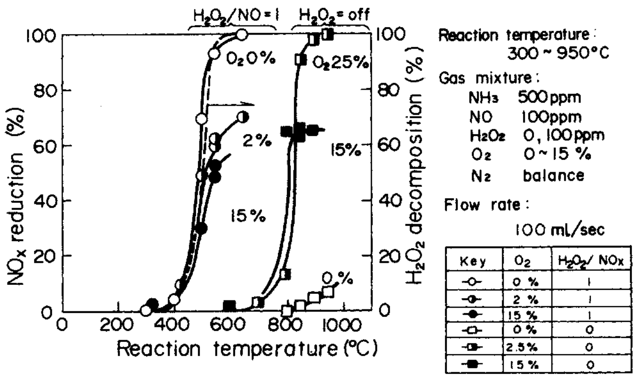

**Figure 4. Relationship of NOx reduction rate and temperature on NO—NH_3—O_2 and NO—NH_3—H_2O_2—O_2
Gas mixture: 100 ppm NO, 500 ppm NH_3,
0 or 100 ppm H_2O_2, 0 ~ 15% O_2.**

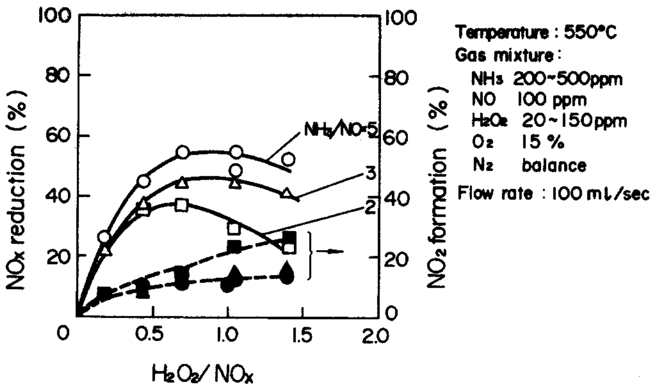

Figure 5. Effect of H_2O_2 and NH_3 concentrations on NO—NH_3—H_2O_2—O_2 reaction
-○-, -●-: $NH_3/NO=5$
-△-, -▲-: $NH_3/NO=3$
-□-, -■-: $NH_3/N=2$

oxidizes NO to NO_2 and that (b) NO_2 inhibits the NO reduction reaction.

In order to sustantiate the second assumption, an experiment on the NH_3—H_2O_2—NO—NO_2 system was conducted and the influence of NO_2 was confirmed. In Figure 6, the percentage NOx reduction is plotted against the initial molar ratio of NO_2/NOx. As can be seen from this figure, NO_2 inhibited the reduction of NO so much that a negative percentage NOx reduction was induced at NO_2/NOx ratios above 0.5. This means that NO formation occurred in a reaction system which included NO_2. Since, with the exception of NH_3, there is no other probable source of NO, NO_2 is assumed to oxidize NH_3 to NO, which finally causes a decrease in the percentage NOx reduction.

Influence of O_2 Concentration. As stated in the explanation of Figure 4, the NOx reduction was largely affected by the O_2 concentration. To obtain more information on the action of O_2, the dependence of the NOx reduction on the concentration of O_2 was investigated experimentally. O_2 was varied from 0 to 15% at a constant ratio of $NH_3/NO=5$ and at 550°C and 650°C. Without O_2 the percentage NOx reduction decreased and NO_2 increased, as shown in Figure 7.

These experimental results can be explained by assuming that the N contained in NH_3 is oxidized by O_2 to yield NO and NO_2.

NH_3 Decomposition. Measurement of the NH_3 decomposition was made at 550 and 650°C for 0 and 15% O. A log-log plot of the NH_3 decomposition against the molar ratio of H_2O_2/NH_3 is given in Figure 8. NH_3 decomposition exhibited a large dependence on the amount of H_2O_2 but little on the amount of O_2. This result is instructive because it furnishes us with a clue that can be used to clarify the reaction mechanism. It is obvious that H_2O_2, more correctly a radical produced from H_2O_2, decomposes NH_3. Furthermore, the fact that the NH_3 decomposition is unrelated to O_2 concentration, despite a decrease in the percentage NOx reduction with increases in O_2, lends support to the assumption that O_2 reacts with the intermediate radical produced from NH_3.

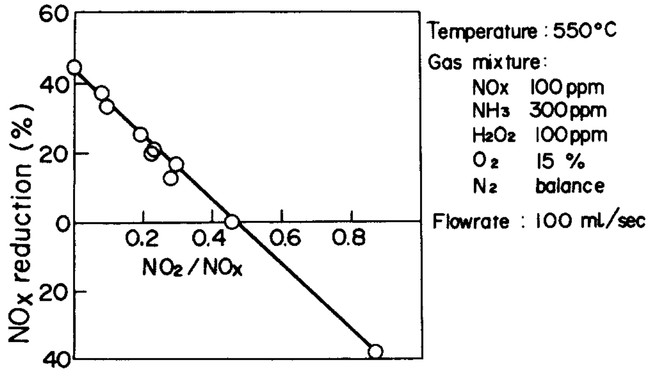

Figure 6. Influence of NO_2 on NOx reduction rate
Gas mixture: 100 ppm NOx, 300 ppm NH_3, 100 ppm H_2O_2, 15% O_2
Temperature: 550°C

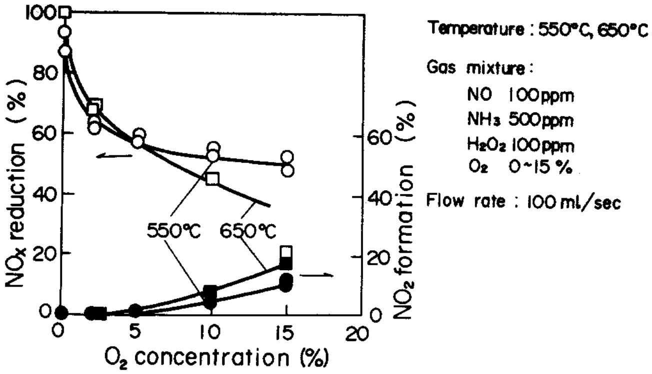

Figure 7. Effect of O_2 concentration on NO—NH_3—H_2O_2—O_2 reaction
Gas mixture: 100 ppm NO, 500 ppm NH_3, 100 ppm H_2O_2, 0 ~ 15% O_2
Temperature: 550°C and 650°C

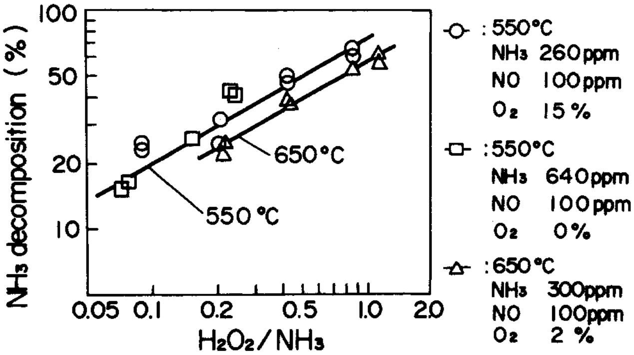

Figure 8. NH_3 decomposition:
550°C, 260 ppm NH_3, 100 ppm NO, 15% O_2
550°C, 640 ppm NH_3, 100 ppm NO, 0% O_2
650°C, 300 ppm NH_3, 100 ppm NO, 2% O_2

NO Oxidation Reaction with H_2O_2

One side reaction, proposed in the preceding section to account for NO_2 formation, is NO oxidation with H_2O_2. To obtain evidence for the occurrence of the reaction, the amount of NO_2 produced in the H_2O_2—NO system was measured. Since O_2, as well as H_2O_2, is a possible NO oxidizing agent, the experiments on the reaction of NO with H_2O_2 were done in the presence and absence of O_2 to see if O_2 might contribute to NO oxidation. The experimental results for the H_2O_2—NO—O_2 system are given in Figure 9. From

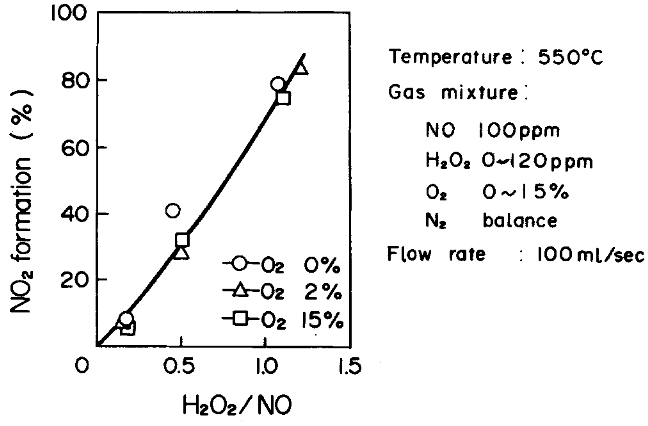

Figure 9. NO oxidation by H_2O_2 at 550°C
Gas mixture: 100 ppm NO, 0 ~ 120 ppm H_2O_2, 0 ~ 15% O_2

this figure it is apparent that H_2O_2 oxidizes NO to NO_2 and that NO_2 increases proportionally to the added H_2O_2. In spite of the large variations in O_2 concentration, there is little difference in the amount of NO_2 in the system. These results show that the amount of NO_2 in the system does not depend on the concentration of O_2 and that the simple reaction

$$2NO + O_2 \rightarrow 2NO_2$$

does not occur at 550°C.

NO and NO_2 Formation in HN_3—H_2O_2—O_2 System

Another side reaction is assumed to be the oxidation of the N contained in NH_3 with O_2. That is, NH_3 is not only an NO reducing agent, but also a source of NOx. To verify this reaction, it is necessary to detect NOx in the NH_3—H_2O_2—O_2 system. The results of experiments, which were done with various concentrations of O_2, are given in Figure 10. Both NO and NO_2 were produced in the presence of O_2 and the amounts of both increased as that of O_2 increased. Although attempts were also made to measure NO and NO_2 in the absence of O_2, neither of the two species could be detected under the conditions of the experiment. This result leads us to conclude that H_2O_2 does not oxidize NH_3 to NOx and that the existance of O_2 is indispensable to the NOx formation from NH_3.

Pathway of NH_3—NO—H_2O_2—O_2 System

Numerous early and recent studies have clarified some features of the reaction mechanism of NH_3 with NO. In these studies, for instance, as studied by Bamford (1939) and Gehring et al. (1974), the amino radical (NH_2) is an important reactive species and the decomposition of NH_3 to give NH_2 and the reaction of NH_2 with NO are the key elementary reactions. Furthermore, the hydroxyl radical (OH) plays an important role in the combustion process and Bradley et al. (1968) and Maclean and Wagner (1966) showed OH is efficient at abstraction hydrogen from NH_3. If the results described in this paper are combined with those obtained in other studies, then the following reaction scheme can be obtained for the reduction of NO.

$$H_2O_2 + M \rightarrow OH + OH\ L + M \tag{1}$$

$$NH_3 + OH \rightarrow NH_2 + H_2O \tag{2}$$

$$NH_2 + NO \rightarrow N_2 + H_2O \tag{3}$$

$$NH_2 + OH \rightarrow NH + H_2O \tag{4}$$

$$NH + NO \rightarrow N_2 + OH \tag{5}$$

In the NH_3—NO—H_2O_2—O_2 system, the decomposition of H_2O_2 into OH in Eq. 1 initiates the subsequent series of reactions. OH abstracts hydrogen from NH_3 to yield NH_2 and NO is reduced to N_2 and H_2O in Eqs. 3 and 5.

Two kinds of side reactions, which interrupt the NO reduction reaction can also be explained. One is the oxidation of NH_2 with O_2. Although it is well known that NH_2 is more reactive with NO than with O_2, the oxidation of NH_2 with O_2 occurs because the concentration of O_2 is higher than that of NO in our experiments. Some descriptions of this oxidation reaction have been reported, but there have been only a few studies which have predicted not only the appearance of NO but also that of NO_2. The following reaction scheme, proposed by Hussain and Norrish (1963) for the photolytic oxidation of NH_3 and supported by Bull's shock tube study (1968), accounts very well for our experimental results.

$$NH_2 + O_2 \rightarrow NHO + OH \tag{6}$$

$$NHO + O_2 \rightarrow NO_2 + OH \tag{7}$$

$$HNO + OH \rightarrow NO + H_2O \tag{8}$$

The other side reaction is the oxidation of NO with H_2O_2. As pointed out by Baldwin and Brattan (1960) and it is generally accepted that the H_2O_2 decomposition Eq. 1 is followed by the rapid reactions Eqs. 9 and 10).

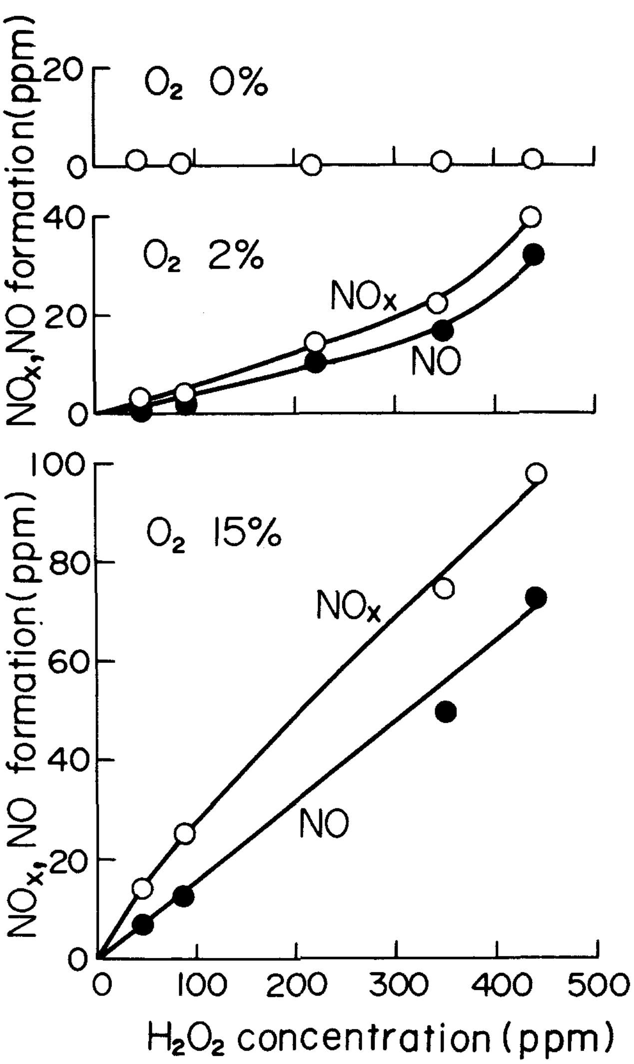

Figure 10. NO and NO_2 formation by NH_3 oxidation at 550°C
Gas mixture: 500 pm NH_3, 0 ~ 400 ppm H_2O_2,
0 ~ 15 % O_2

$$OH + H_2O_2 \rightarrow HO_2 + HO$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

During H_2O_2 decomposition, the active oxidizing intermediate radical HO_2 is formed with Eq. 9. A plausible elementary reaction for the NO_2 formation by the oxidation of NO with H_2O_2 is thought to be Eq. 11.

This reaction is well known in atmospheric photochemistry (Cox and Derwent, 1975).

$$NO + HO_2 \rightarrow NO_2 + OH \tag{11}$$

The NO_2 produced in the two side reactions reacts with NH_2 and yields NO.

$$NH_2 + NO_2 \rightarrow NO + NO + \tag{12}$$

Because we have no direct evidence about radicals and because the reaction of the NH_3—NO_2 system has been discussed in very few studies, we cannot discuss the details of the mechanism of Eq. 12 here. The investigation and clarification of the NO_2—NH_3 system will be left for future studies.

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Solution of Stiff Ordinary Differential Equations by Decomposition and Orthogonal Collocation

A fast and accurate method was developed for the integration of large sparse systems of stiff initial value ordinary differential equations. The system is ordered, decoupled and, if necessary, torn into subsystems (also called blocks) which are then solved by orthogonal collocation on finite elements. The size of these elements, or steps, is different for each subsystem and is a function of the stiffness of the set of equations constituting the subsystem. The steps are overlapped for maximum computational efficiency.

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SCOPE

Mathematical modeling of physical systems encountered in kinetics, process design, control, etc., often involve analysis of large sets of stiff initial value ordinary differential equations (ODE's). Such problems may occur, for example, in the kinetics of large multicomponent reactions (Farrow and Edelson, 1974) where some of the reaction rate constants are substantially larger than others, in the analysis of transient phase change distributions in the separations processes, or in circuit theory (Gear, 1971; Hachtel, 1971).

Over the past few years, many special solution techniques have been developed to handle stiff systems (Cash, 1976; Michelsen, 1976; Bui and Bui, 1979; Bui, 1979) but most of these are effective only for small problems, those consisting of approximately ten equations or less. The methods published for large systems (Gear, 1971; Hachtel, 1971; Hofer, 1976) have invariably involved some form of decomposition.

The decomposition procedure used in this method consists of selection of an output variable for each equation in the system, ordering the whole set of equations (putting them in the sequence in which they have to be solved), partitioning the equations into single equations plus the smallest cycles obtainable without tearing, and finally tearing some of these cycles by removing a variable (or variables) in a systematic manner to yield even smaller blocks and/or single equations.

The decomposed system is solved by orthogonal collocation on finite elements. Orthogonal collocation solutions are approximations in the form of the sums of orthogonal polynomials. The calculations involve substituting the sums for the unknown variables and evaluating the individual polynomials' coefficients by setting the residuals equal to zero at the collocation points. A series of ODE's is thus reduced to a series of algebraic equations.

The results obtained in this manner are valid only over a limited range of the independent variable, requiring the full region of interest to be divided into sections (also called finite elements, steps, or subintervals), and separate solutions are then calculated for all dependent variables for each section. A modified full step/half step method is used to determine the optimal size of the subintervals used for each block.

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