

## THERMAL REDUCTION OF NO BY NH<sub>3</sub>: KINETIC MODELING OF THE NH<sub>2</sub> + NO PRODUCT BRANCHING RATIO

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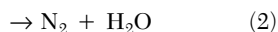
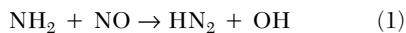
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The product-branching ratio for the reaction NH<sub>2</sub> + NO → HN<sub>2</sub> + OH (1) and N<sub>2</sub> + H<sub>2</sub>O (2) has been determined in the temperature range of 950–1200 K by pyrolysis of Ar-diluted NH<sub>3</sub> + NO mixtures and at 1173 and 1200 K by pyrolysis of Ar-diluted NH<sub>3</sub>-NO-CO mixtures. Analysis of the pyrolyzed and unpyrolyzed mixtures was carried out by the FTIR spectrometric method. Kinetic modeling of the decay rates of NH<sub>3</sub> and NO and the production rate of CO<sub>2</sub> by varying the branching ratio,  $\alpha_1 = k_1/(k_1 + k_2)$ , and keeping the known total rate constant ( $k_t = k_1 + k_2 = 9.6 \times 10^{14} T^{-0.85} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) unchanged at each temperature allows determination of the value of  $\alpha_1$  with good reproducibility. Kinetic modeling of  $\alpha_1$ , using previously measured H<sub>2</sub>O formation data [28] from the NH<sub>3</sub> + NO reaction in the temperature range of 1123–1273 K was also carried out. The branching ratio was found to increase rapidly from 0.27 at 950 K to 0.58 at 1273 K, which is fully consistent with the sharply rising trend recently reported from NH<sub>3</sub>-NO flame studies, in which  $\alpha_1 \approx 0.5$  at 1500 K and rose to 0.9 at 2000 K. These new findings cast doubt on the much lower values,  $\alpha_1 \leq 0.17$  at  $T \leq 1173$  K, obtained by laser kinetic measurements.

### Introduction

The reaction of NH<sub>2</sub> with NO has been shown to greatly affect the overall NO<sub>x</sub>-reduction efficiency of NH<sub>3</sub> and the burning velocity of the NH<sub>3</sub>-NO flame [1–6]. The reaction takes place primarily by the following two product channels [1–15]:



The relative importance of these reaction paths, as measured by the branching ratio  $\alpha_1 = k_1/(k_1 + k_2)$ , strongly influences the overall kinetics of the NH<sub>3</sub>-NO system. The thermal-neutral reaction, Eq. (1), generates two key chain carriers, H and OH, because HN<sub>2</sub> is unstable under combustion conditions. However, reaction (2), producing N<sub>2</sub> and H<sub>2</sub>O, is an exothermic chain-termination step that releases as much as 120 kcal mol<sup>-1</sup> energy. Therefore, these two reactions are highly competitive. Reaction (1) enhances the efficiency of NH<sub>3</sub> for NO<sub>x</sub> reduction and the overall NH<sub>3</sub> + NO reaction rate, whereas reaction (2) reduces the efficiency and reaction rate.

On the basis of the results of recent kinetic modeling on the structure of a quasi-equimolar NH<sub>3</sub>-NO

flat flame by Vandooren et al. [5] and on the burning velocity data of Andrew and Gray [16] by Brown and Smith, [6] the branching ratio for reaction (1),  $\alpha_1$ , has been determined to be  $\geq 0.5$  above 1500 K. This value is significantly higher than that deduced from laser kinetic measurements, most notably by Wolfrum and co-workers [11] and by Stephens et al. [12], who found  $\alpha_1$  to be  $\leq 0.2$  at  $T \leq 1200$  K. In a recent kinetic modeling of the NH<sub>3</sub> de-NO<sub>x</sub> process by Glarborg et al. [15], the temperature-dependent expression,  $\alpha_1 = 2.2 \times 10^{-3} T^{0.70}$ , was employed by fitting  $\alpha_1 = 0.11$  at 300 K and 0.3 at 1150 K. A large gap exists between the low-temperature (300–1000 K) kinetic data and the results of high-temperature (1500–2000 K) flame studies. The objective of the present work is to bridge the gap by presenting kinetic data in the temperature range of 950–1200 K using the pyrolysis-FTIR spectrometric method [17–19].

### Experimental

The pyrolysis of two mixtures, one of NH<sub>3</sub> and NO, the other of NH<sub>3</sub>, NO, and CO, both diluted with Ar, was carried out in a quartz reactor of volume

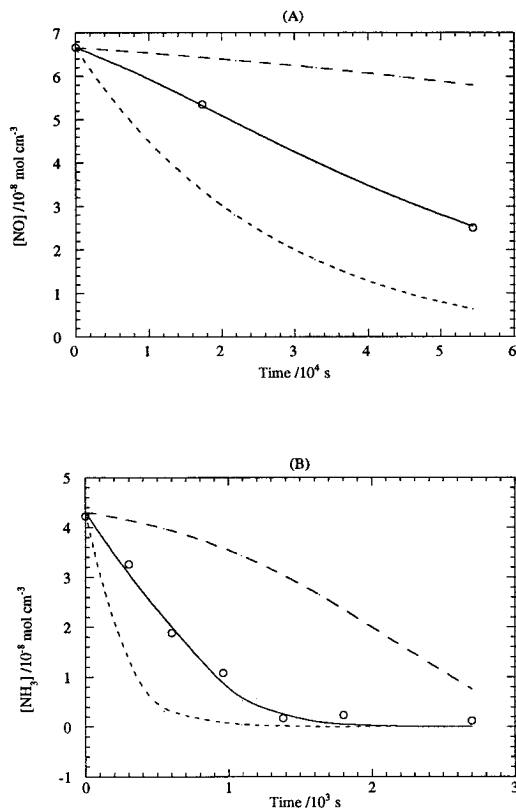


FIG. 1. Typical concentration versus time profile of NO (A) and NH<sub>3</sub> (B) for the reaction conditions and the  $\alpha_1$  values shown in Table 2 (Nos. 4 and 9, respectively), with kinetically modeled results shown by a solid curve, a short dash curve, and a long dash curve representing  $\alpha_1$ ,  $\alpha_1 + 0.1$ , and  $\alpha_1 - 0.1$ , respectively.

270 cm<sup>3</sup> with a surface-to-volume ratio of 0.748 cm<sup>-1</sup>. The reactor was heated by a double-walled cylindrical oven. Concentrations of the NH<sub>3</sub> and NO mixtures ranged from 0.6 to 3.7% NO and 0.3 to 0.9% NH<sub>3</sub>. The concentrations of the NH<sub>3</sub>, NO, and CO mixtures ranged from 2.0 to 2.7% NO, 0.8 to 1.0% NH<sub>3</sub>, and 4.9 to 6.3% CO. The reactor was heated to temperatures ranging from 950 to 1200 ± 1 K for the NH<sub>3</sub> and NO mixtures and at 1173 and 1200 ± 1 K for the NH<sub>3</sub>, NO, and CO mixtures.

Unpyrolyzed and pyrolyzed samples were analyzed by a Mattson Instrument Polaris Fourier Transform Infrared (FTIR) spectrometer with a resolution of 2 cm<sup>-1</sup>. Concentrations of NO, NH<sub>3</sub>, and CO<sub>2</sub> were determined by calibration curves of concentration versus absorbance at 1900 cm<sup>-1</sup>, 993 cm<sup>-1</sup>, and 668 cm<sup>-1</sup>, respectively. The calibration curves were plotted using data from samples of various appropriate concentration combinations of NO, NH<sub>3</sub>, CO, and CO<sub>2</sub> that were expanded into the

FTIR absorption cell at pressures ranging from 150 to 200 torr, corresponding to the pressures at which the pyrolyzed samples were analyzed. The curves were of good quality with little scatter of the data points, and the estimated error in our concentration measurements is smaller than 2–3%.

NH<sub>3</sub> was purified by degassing at 77 K and distillation at 228 K, attained by ethanol cooled with liquid N<sub>2</sub>. NO, which often contains NO<sub>2</sub> impurities, was purified by passing the gas through a silica gel trap, held at 195 K by an ethanol–dry ice slush, and then condensing it at 77 K by means of a liquid N<sub>2</sub> trap. Occasional pumping was also carried out to remove noncondensables. CO was purified by passing it through Cu/CuO filings at about 423 K and two liquid N<sub>2</sub> traps. FTIR spectra were taken to ascertain the purity of the gases. Ar of 99.999% purity, obtained from Specialty Gases, was used without further purification. Care was always taken to adequately purge and evacuate the vacuum lines while making the mixtures and expanding the gases into the reactor and the FTIR analysis cell.

## Results

Typical time-resolved concentration profiles of NO and NH<sub>3</sub> are shown in Fig. 1. The data were kinetically modeled via CHEMKIN [20] and SENKIN [21], using a mechanism composed primarily of reactions recently used in our simulation of the kinetics of the NH<sub>3</sub>-NO system initiated by a pulsed ArF (193 nm) laser near 1000 K [10] and reactions studied by others [22–24,26,27]. The total rate constant,  $k_t = k_1 + k_2 = 9.6 \times 10^{14} T^{-0.85} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , previously measured [10] for the NH<sub>2</sub> + NO reactions (1) and (2), was used and held constant at each temperature, and  $k_1$  was varied until the best fit with  $\alpha_1 = k_1/k_t$  was found.

In this system, NO reduction is initiated by NH<sub>3</sub> + NO → NH<sub>2</sub> + HNO, reaction (3), but because of the unavailability of an experimentally determined rate constant for this reaction, the value of  $k_3$  was obtained by variational transition state theory (VTST) calculation based on a high level ab initio MO result [25]:  $k_3 = 1.04 \times 10^7 T^{1.73} e^{-28,454/T} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Because of the high temperatures involved, the decay of NO and NH<sub>3</sub> was found to be controlled to a much greater extent by the mutually competitive reactions (1) and (2) than by reaction (3), as can be seen by the result of representative sensitivity analyses in Fig. 2. The reliability of the modeled  $\alpha_1$  values can also be seen in Fig. 1, where predicted profiles of NO and NH<sub>3</sub> with the branching ratio values of ±0.1 from best fit values of  $\alpha_1$  are plotted. Our branching ratio results for seven other temperatures and NH<sub>3</sub> and NO concentrations are summarized in Table 1. These results will be compared with other branching ratio data later.

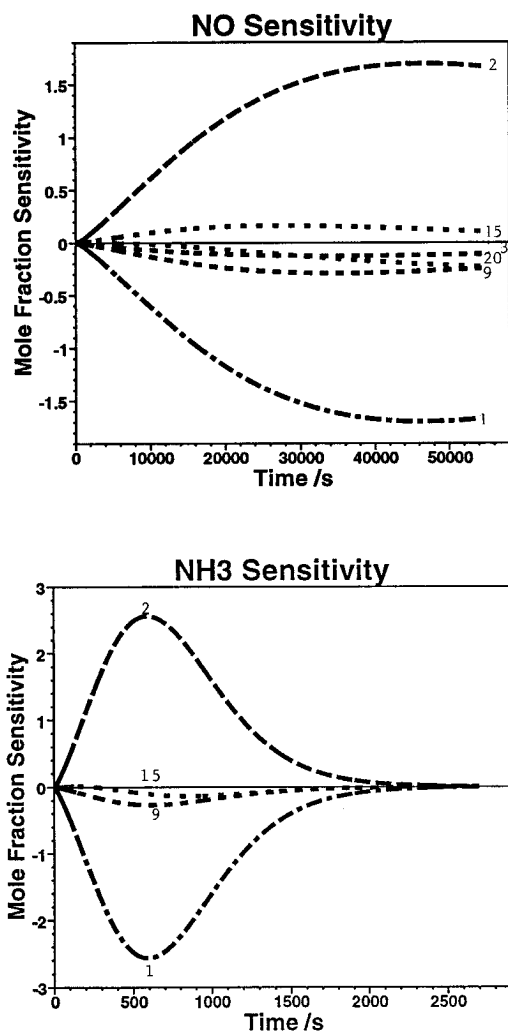
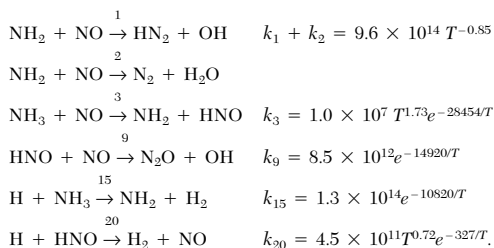


FIG. 2. Plot of normalized sensitivity coefficients for NO (A) and NH<sub>3</sub> (B) with the initial conditions and  $\alpha_1$  values presented in Table 2 (Nos. 4 and 9, respectively). The rate constants of the reactions identified in the figure are given as follows in units of  $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ :



Reactions were also carried out in the temperature range of 900–1200 K using CO as the OH-radical scavenger. As in the NH<sub>3</sub>-NO system, modeling of the NH<sub>3</sub>-NO-CO system was also carried out with CHEMKIN [20] and SENKIN [21]. Under our reaction conditions, however, CO<sub>2</sub> formation was found to be sensitive to the NH<sub>2</sub> + NO branching reactions only at 1173 K and higher temperatures. Reaction conditions and modeled branching ratio values are presented in Table 1.

As discussed later, in addition to modeling our own kinetic data, we carried out computer simulation of data published earlier by Poole and Graven [28] for H<sub>2</sub>O formation and briefly studied the work of Wise and Frech [29] for the rate of total pressure change.

#### Poole and Graven's H<sub>2</sub>O-Formation Data

Poole and Graven [28] used a flow technique for gravimetric measurement of H<sub>2</sub>O production from mixtures with varying amounts of NO and NH<sub>3</sub> diluted in N<sub>2</sub> or He to a total pressure of 800 torr. Two flow vessels were used: vessel I and vessel II of volumes 42.6 cm<sup>3</sup> and 324 cm<sup>3</sup> and surface-to-volume ratios of 5.6 cm<sup>-1</sup> and 2.3 cm<sup>-1</sup>, respectively. The temperature range was 1123–1273 K. The measured H<sub>2</sub>O-formation rate was found to follow the relationship

$$\frac{\Delta \text{H}_2\text{O}}{\Delta t} = \frac{k_a(\text{NH}_3)^{1/2}(\text{NO})}{1 - k_b(\text{NH}_3)^{1/2}(\text{NO})}$$

Poole and Graven noted that at 1223 K, vessel I, which had an S/V ratio twice as large, yielded a 20% larger value of  $k_a$  and concomitantly a smaller value of  $k_b$  than vessel II, resulting in an effective rate difference between the two vessels by less than 10%. This compensating effect resulted in an even smaller (3%) difference between the NH<sub>2</sub> + NO product branching ratios (see Table 2) that we modeled for the two vessels. In Fig. 3, the quantity  $\text{NO}/(\Delta \text{H}_2\text{O}/\Delta t)$  is plotted against  $\text{NH}_3^{-1/2}$ , as presented originally by Poole and Graven. Each of these data points was employed to model the NH<sub>2</sub> + NO product branching ratio, and the average value for each temperature was used to calculate the rate of H<sub>2</sub>O production; the result is shown as the solid curve in the figure. Table 2 summarizes the resulting average modeled branching ratio for the temperatures and conditions noted. The result of a sensitivity analysis for H<sub>2</sub>O production shows that reaction (1) is the dominant reaction and that the initiation process has little effect on H<sub>2</sub>O formation.

#### Wise and Frech's Total Pressure Measurement

Wise and Frech [29] pyrolyzed mixtures of 29.6–64.6% NH<sub>3</sub> and 31.6–70.4% NO in a quartz reaction vessel of 1560 cm<sup>3</sup> with a surface-to-volume ratio of 1.12 cm<sup>-1</sup> in the temperature range of 990–1150 K.

TABLE 1  
Summary of the present experimental conditions and modeled values of  $\alpha_1$   
for the NH<sub>3</sub>/NO pyrolysis system

No.	<i>T</i> /K	<i>P</i> /torr	No of exp.	[NO] <sub>0</sub> %	[NH <sub>3</sub> ] <sub>0</sub> <sup>b</sup>	[CO] <sub>0</sub> %	<i>t</i> /10 <sup>2</sup> s <sup>c</sup>	$\alpha_1 \pm \sigma^d$
1	950	706	3	4.39	9.85	—	844.2	0.272 ± 0.011
2	1000	705	3	1.07	4.53	—	684.9	0.297 ± 0.011
3	1000	704	3	3.70	9.48	—	287.4	0.267 ± 0.005
4	1050	706	2	0.666	8.73	—	543.6	0.398 ± 0.001
5	1100	708	5	0.904	3.93	—	110.4	0.291 ± 0.004
6	1100	703	5	3.38	7.84	—	48.0	0.398 ± 0.004
7	1150	704	3	0.848	8.92	—	43.8	0.449 ± 0.013
8	1173	708	8	2.18	2.43	—	7.20	0.345 ± 0.005
9	1200	709	6	0.869	4.22	—	2.70	0.458 ± 0.012
10	1100	708	6	2.89	9.41	6.64	36.0	0.69 <sup>e</sup>
11	1173	705	7	1.96	7.81	4.52	3.00	0.505 ± 0.011
12	1200	707	5	2.59	9.28	5.95	8.40	0.511 ± 0.009

<sup>a</sup>Concentrations of NO and CO are given in units of 10<sup>-7</sup> mol cm<sup>-3</sup>.

<sup>b</sup>Concentration of NH<sub>3</sub> is given in units of 10<sup>-8</sup> mol cm<sup>-3</sup>.

<sup>c</sup>The time given is the longest pyrolysis time for each set of conditions.

<sup>d</sup>For each set of conditions,  $\alpha_1 = k_1/(k_1 + k_2)$  is the average of the branching ratios from NH<sub>3</sub> or NO (whichever was most sensitive for each set of conditions) decay modeled for each data point.  $\sigma$  is the mean of the deviations of the branching values modeled using each of the individual data points from  $\alpha_1$ .

<sup>e</sup>This point is not reliable because of the relatively low sensitivity indicated by the result of a sensitivity analysis.

TABLE 2  
Summary of the our kinetic modeling values of  $\alpha_1$  by using Poole and Graven's [28] experimental conditions and  
H<sub>2</sub>O-formation data

No./ vessel	<i>T</i> /K	<i>P</i> /torr	No of exp.	[NO] <sub>0</sub> %	[NH <sub>3</sub> ] <sub>0</sub> <sup>b</sup>	<i>t</i> /s	$\alpha_1 \pm \sigma^d$
1/II	1123	800 <sup>c</sup>	10	1.07–5.32	5.35	7.995–11.26	0.494 ± 0.017
2/II	1223	800	9	1.30–5.30	5.24	0.895–1.205	0.517 ± 0.011
3/II	1223	800	10	5.24	1.08–5.40	0.840–1.177	0.521 ± 0.007
4/I	1223	800	7	4.91	1.13–4.94	0.806–1.056	0.538 ± 0.003
5/I	1273	800	12	4.88	0.49–4.89	0.187–0.308	0.581 ± 0.009
6/I	1273	800	8	1.22–4.88	4.88	0.282–0.381	0.528 ± 0.031

<sup>a</sup>Concentration is given in units of 10<sup>-6</sup> mol cm<sup>-3</sup>.

<sup>b</sup> $\alpha_1 = k_1/(k_1 + k_2)$  is the average of the branching ratios modeled for each point.

<sup>c</sup>All mixtures were diluted in Ar to 800 torr except for the last one, in which the mixture, consisting solely of NO and NH<sub>3</sub>, was slightly more than 800 torr.

<sup>d</sup> $\sigma$  is the average deviation of each data point from  $\alpha_1$ .

They monitored the progress of the reaction by observing the change in the total pressure of the system via a differential manometer filled with Fluorolube S. Wise and Frech found the following relationship between the total pressure change  $\Delta P$  of the system and the initial partial pressures of NH<sub>3</sub> and NO:  $\Delta P/\Delta t = A \exp(-54,700/RT)(\text{NH}_3)(\text{NO})^{1/2}$ , which, interestingly, is totally different from that of Poole and

Graven's H<sub>2</sub>O-formation measurements as presented in the preceding section.

Since the rate of total pressure change is a global quantity, we only briefly modeled Wise and Frech's  $\Delta P/\Delta t$  data, which were presented in their Figs. 1 and 2. The result of this modeling gave  $\alpha_1 = 0.41$  at both 994 and 1056 K, which is in reasonable agreement with the values given in Tables 1 and 2.

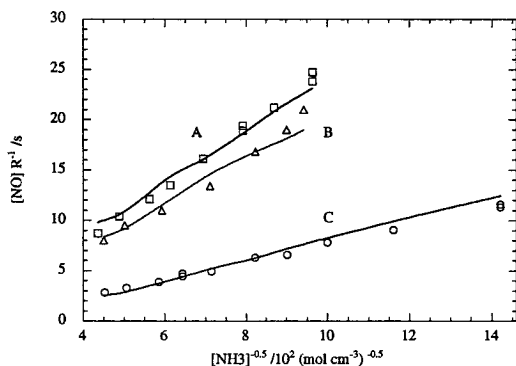


FIG. 3. Comparison of experimental and modeling results. The points are  $[\text{NO}]/(\Delta\text{H}_2\text{O}/\Delta t)$  versus  $[\text{NH}_3]^{-0.5}$  experimental results of Poole and Graven [28] with conditions as outlined in Table 2 (Nos. 3, 4, and 5, corresponding to A, B, and C, respectively); the solid curves are our modeled results.

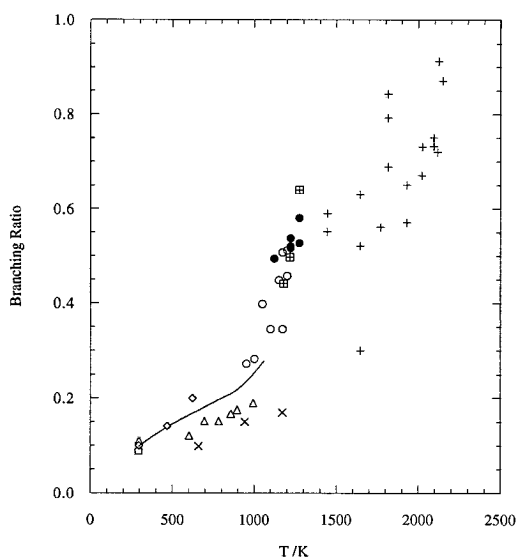


FIG. 4. Summary of the branching ratio  $\alpha_1$  as a function of temperature. O: This work; modeling of NH<sub>3</sub>, NO, and CO<sub>2</sub> concentration profiles. ●: Our modeling of Poole and Graven's [28] data. ■: Ref. 3. +: Ref. 5. Δ: Ref. 11. X: Ref. 12. ◇: Ref. 14. □: Ref. 9. solid curve: Ref. 30.

### Discussion

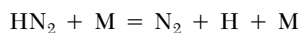
Our result, evaluated in the temperature range of 950–1200 K, although effectively bridging the gap between the low- ( $T \leq 1000$  K) and high- ( $T \geq 1500$  K) temperature data, strongly favors the higher values of the branching ratio reported by Bulatov [14], Hanson [3], Vandooren et al. [5], and that employed by Glarborg et al. in their recent modeling of the

(NH<sub>3</sub> – NO – O<sub>2</sub>) NH<sub>3</sub> de-NO<sub>x</sub> process [15]. It casts severe doubt on the lower values,  $\alpha_1 \leq 0.2$  at  $T \leq 1200$  K, obtained by Atakan et al. [11], as well as by Stephens and co-workers [12]. The greater OH-production efficiency in the low-temperature (300–1000 K) range has also been confirmed recently by measuring the yields of H<sub>2</sub>O and CO<sub>2</sub> in a laser-initiated reaction of NH<sub>3</sub>, NO, and CO by mass spectrometry [30], as shown in Fig. 4, which summarizes all experimentally determined  $\alpha_1$  values.

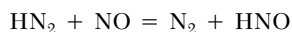
The low OH-production efficiencies at  $T \leq 1173$  K reported by Wolfrum et al. [11] and by Stephens co-workers [12], using laser-induced fluorescence and IR laser resonance absorption, respectively, although somewhat puzzling, could be attributed to the common difficulty in providing exact concentrations of a radical species for quantitative calibration over a wide range of temperatures. At high temperatures, the lack of accurate absorption cross-section data and the thermal instability of the OH-calibration source molecules such as H<sub>2</sub>O<sub>2</sub> may also become severe problems. Our direct determination of the rates of reactant (NH<sub>3</sub> and NO) decay and product (CO<sub>2</sub> and H<sub>2</sub>O) formation by FTIR spectrometry and/or mass spectrometry [30], aided by accurate calibrations, allowed us to circumvent the difficulty and minimize the uncertainty.

As can be seen in Fig. 4, our average values of  $\alpha_1$ ,  $0.278 \pm 0.011$  and  $0.289 \pm 0.009$ , at 950 and 1000 K, respectively, agree closely with the branching ratio values measured mass spectrometrically by Park and Lin [30], as well as with those employed by Glarborg et al. [15],  $\alpha_1 = 2.2 \times 10^{-3} T^{0.70}$ , in their modeling of experimental de-NO<sub>x</sub> data [31–33]. These authors [15] also concluded that the effect of the quartz reactor surface on the overall NO<sub>x</sub>-reduction kinetics is negligible under low surface-to-volume ( $S/V$ ) conditions used in typical pyrolytic experiments. In fact, our branching ratio modeling of Poole and Graven's [28] H<sub>2</sub>O-formation rates in the NH<sub>3</sub> + NO reaction indicates that an increase of  $S/V$  from 2.3 to 5.6 cm<sup>-1</sup> has only a negligible (3%) effect on  $\alpha_1$  for the NH<sub>2</sub> + NO reactions, which strongly affect the rates of H<sub>2</sub>O production. Under our temperature and pressure conditions with  $S/V = 0.5$  cm<sup>-1</sup>, which is much smaller than either of the  $S/V$  ratios of the vessels used by Poole and Graven [28], the effect of the quartz reactor surface on the modeled values of  $\alpha_1$  is believed therefore to be negligible.

The values of  $\alpha_1$  determined in the present study appear to be insensitive to the lifetime or the magnitudes of the rate constants of the HN<sub>2</sub> radical assumed in the mechanism. Under the conditions employed ( $T \geq 940$  K,  $P = 700$  torr Ar), an increase or decrease in the rate constants assumed for the following reactions involving HN<sub>2</sub>:



$$k = 1.0 \times 10^{14} e^{-1510/T} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$



$$k = 7.2 \times 10^{13} T^{-0.4} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

by two orders of magnitude separately resulted in no noticeable effect on the calculated concentration profiles of the reactants or products. In fact, the assumption of the direct production of the H atom in reaction (1), by using  $\text{NH}_2 + \text{NO} = \text{H} + \text{N}_2 + \text{OH}$ , resulted in no change in the modeled  $\alpha_1$  values. The same conclusion was reached in our recent mass spectrometric study of the  $\text{NH}_2 + \text{NO}$  reaction [30].

The sharp increase in the value of  $\alpha_1$  with temperature is challenging theoretically. The prediction of the branching ratio and the effect of temperature on its value quantitatively requires not only the full knowledge of the intermediates and transition states for the isomerization reactions involving these intermediates (as has been acquired by Melius [7], Walch [8], and Durant [9]), but also a full understanding of the interaction potential for the reactants ( $\text{NH}_2$  and  $\text{NO}$ ) and the radical products ( $\text{HN}_2$  and  $\text{OH}$ ) for a reliable calculation of the capturing and fragmenting processes, respectively. To more reliably calculate the rate constants for reactions (1) and (2) at different temperatures, an elaborate statistical approach such as variational RRKM theory should be used in conjunction with the multiple-reaction intermediates involved.

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**COMMENTS**

*W. Gardiner, Jr., University of Texas—Austin, USA.* under deNO<sub>x</sub> conditions (1200 K ≤ T ≤ 1400 K, P ≤ 1 atm).  
Could you please comment on the pressure dependence of the branching ratio of the NH<sub>2</sub> + NO reaction?

*Author's Reply.* On the basis of the results of our previous RRKM calculations [1], the overall rate constant for NH<sub>2</sub> + NO and those for the two product channels, N<sub>2</sub>H + OH and N<sub>2</sub> + H<sub>2</sub>O, are pressure-independent

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