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A Shock Tube Study of the Product Branching Ratio of the $NH_2 + NO$ Reaction at High Temperatures

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The product branching ratio of $NH_2 + NO \rightarrow NNH + OH$ and $NH_2 + NO \rightarrow N_2 + H_2O$ has been determined in the temperature range 1826−2159 K in a shock tube study. The pressure range behind reflected shock waves was 1.10 to 1.21 bar. The time history of the NH_2 radical was measured using a frequency modulation absorption technique. The initial gas mixture compositions were 8−28 ppm monomethylamine (CH_3NH_2), 0.4−1.2% ammonia (NH_3), and 0.4% NO, and the balance Ar. According to sensitivity analysis using a detailed 125-reaction mechanism, the NH_2 profiles are mainly sensitive to the branching ratio $\alpha = k_{1a}/(k_{1a} + k_{1b})$ under the experimental conditions of this study, and they exhibit only a small sensitivity to secondary reactions and the overall rate coefficient, $k_1 = k_{1a} + k_{1b}$. The branching ratio increases from 0.59 ± 0.02 at 1826 K to 0.66 ± 0.04 at 2159 K. These results are consistent with our earlier measurements of the branching ratio at lower temperature and agree with the theoretical result of Miller and Klippenstein.

Introduction

The $NH_2 + NO$ reaction is one of the key reactions in the Thermal De-NO_x process. This reaction has two major product channels.[1−4] One is a chain branching channel

$$NH_2 + NO \rightarrow NNH + OH \qquad (R1a)$$

and the other is a chain terminating channel

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad (R1b)$$

Two important kinetic parameters in modeling the Thermal De-NO_x process are the overall rate coefficient, $k_1 = k_{1a} + k_{1b}$, and the branching ratio of the $NH_2 + NO$ reaction, $\alpha = k_{1a}/(k_{1a} + k_{1b})$. From the results of many studies, including our two studies of this reaction,[5,6] the overall rate is well-known in the temperature range 200−2500 K. In addition, the branching ratio of this reaction has been investigated experimentally in many studies. A number of low-temperature direct flash photolysis studies yielded a relatively small increase of α with temperature.[7−10] An early combustion-driven flow reactor study by Kimball-Linne and Hanson yielded a sharp increase of the branching ratio at temperatures above 1000 K, leading to a value of $\alpha = 0.6$ at 1300 K.[11] The sharp increase of α at temperatures above 1000 K was reproduced by Park and Lin[12] and Halbgewachs et al.[13] Glarborg et al. determined the branching ratio in the temperature range 1211 K to 1370 K from flow reactor experiments and reported that α increases from 0.35 at 1211 K to 0.45 at 1370 K.[14] A recent reinterpretation[15] of the higher temperature experimental data of Park and Lin[12] and Halbgewachs et al.[13] yielded values of α that are in agreement with the results of Glarborg et al.[14] In addition to these studies, the results of our previous shock tube study of the branching ratio[6,16] are consistent with those of Glarborg et al.[14] and agree with Miller and Klippenstein's theoretical work.[4] Above 1800 K, only two experimental studies have been reported.[17,18] These data show a large scatter, and the resulting branching ratios are much larger than the α-values suggested by Miller and Klippenstein[4] and Glarborg et al.[3]

The objective of the present study is to measure the branching ratio of the $NH_2 + NO$ reaction at high temperatures more accurately using a shock tube facility and frequency modulation absorption spectroscopy of NH_2.

Method of Approach

In this study, gas mixtures containing small amounts of monomethylamine (CH_3NH_2, MMA) and an excess of NO and NH_3 together with argon as a diluent were used. Behind reflected shock waves, CH_3NH_2 rapidly decomposes via R2 to produce an NH_2 radical.[19,20]

$$CH_3NH_2 + M \rightarrow NH_2 + CH_3 + M \qquad (R2)$$

Once NH_2 is produced, it reacts rapidly with NO due to a high concentration of NO in the initial gas mixture. The branching channel of the $NH_2 + NO$ reaction gives OH and NNH radicals. The NNH radical rapidly decomposes into N_2 and an H atom through the unimolecular decomposition reaction (R3).

$$NNH \rightarrow N_2 + H \qquad (R3)$$

The OH radical and H atom react with excess NH_3 to produce NH_2 radicals.

$$NH_3 + OH \rightarrow NH_2 + H_2O \qquad (R4)$$

$$NH_3 + H \rightarrow NH_2 + H_2 \qquad (R5)$$

These reactions rapidly convert NH_3 into NH_2 because of the high concentration of NH_3. Consequently, each NH_2 radical produced by the branching channel (R1a) leads to the formation of two new NH_2 radicals, while the other channel (R1b) is chain

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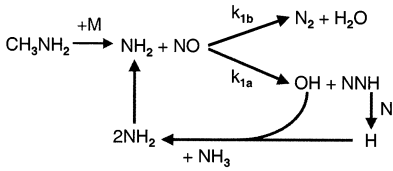

Figure 1. A diagram of the kinetic scheme for the branching ratio determination.

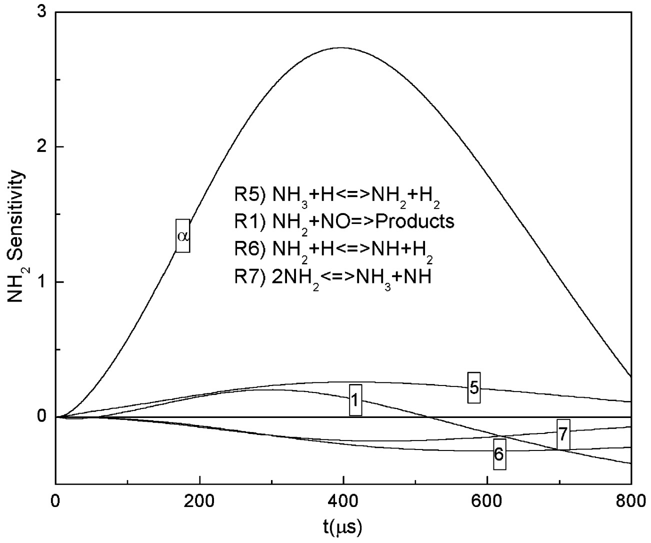

Figure 2. Results from NH_2 sensitivity analysis for the conditions of Figure 3: 28 ppm CH_3NH_2/3960 ppm NH_3/3800 ppm NO/Ar balance, $T = 1938$ K, $P = 1.19$ bar.

terminating and results in the loss of one NH_2 radical. Therefore, the trace of NH_2 radical is mainly controlled by the product branching ratio of the NH_2 + NO reaction. This kinetic approach is illustrated schematically in Figure 1.

According to the NH_2 sensitivity analysis shown in Figure 2, the influence of the secondary reactions, as well as that of the overall rate coefficient, is relatively small compared to the branching ratio. In addition, the uncertainty of the overall rate coefficient for the temperature range of the present study is very small, so that the overall rate coefficient has no significant impact on the branching ratio determination.

In our previous low-temperature study of the branching ratio of the NH_2 + NO reaction,[16] the NH_3 was photolyzed to produce a small amount of NH_2. However, using pyrolysis of CH_3NH_2 as the NH_2 source has advantages over photolysis of NH_3 at high temperatures. First, it is easy to control the initial mole fraction of NH_2 radicals since a known amount of CH_3NH_2 is supplied to the shock tube and the decomposition rate of CH_3NH_2 is well-known.[19,20] Second, CH_3NH_2 decomposes rapidly above 1800 K and more than 90% of the CH_3NH_2 is converted into NH_2, so that the NH_2 mole fraction measured using the FM system is self-calibrating. In addition, the experimental setup is much simpler than that of photolysis experiments.

As shown in Figure 3, the NH_2 mole fraction increases rapidly in the early stages of reaction due to the thermal decomposition of CH_3NH_2. The NH_2 starts to react with NO and produces H and OH atoms. The H and OH atoms react with excess NH_3, and the slope and peak of the NH_2 profile are sensitive to the branching ratio. In the present study, a detailed 125-reaction reaction mechanism used in our previous study of overall rate coefficient[5] was applied to obtain the branching ratio. The rate coefficients of the selected reactions used in the reaction mechanism are tabulated in Table 1.

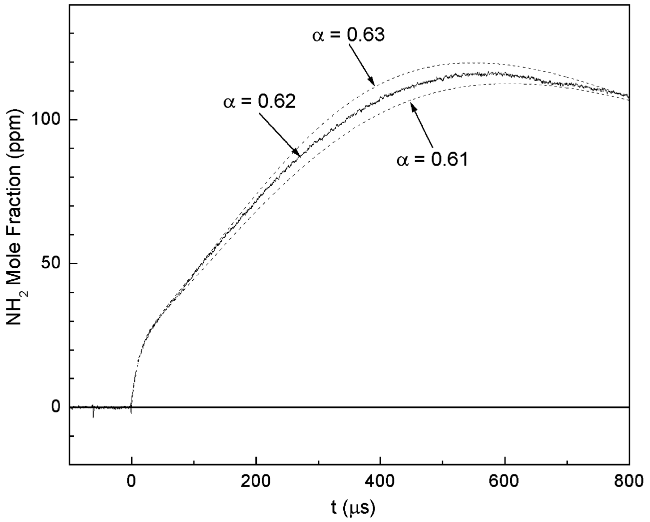

Figure 3. Example of NH_2 mole fraction profile: 28 ppm CH_3NH_2/3960 ppm NH_3/3800 ppm NO/Ar balance, $T = 1938$ K, $P = 1.19$ bar. Solid line is a fit to the data using a detailed kinetic model. Broken lines are ±0.01 variation in α (α = 0.62).

TABLE 1: Selected Reactions Used in the Reaction Mechanism

	Arrhenius parameters $k(T) = AT^n\exp(-E_a/RT)$			
reaction	A ($cm^3\,mol^{-1}\,s^{-1}$)	n	E_a ($J\,mol^{-1}$)	ref
R2 $CH_3NH_2 + M \rightarrow CH_3 + NH_2 + M$	8.17E16	0.0	255337	20
R3 $NNH \rightarrow N_2 + H$	6.70E07	0.0	0	3
R4 $NH_3 + OH \rightarrow NH_2 + H_2O$	2.00E13	2.04	2368	21
R5 $NH_3 + H \rightarrow NH_2 + H_2$	6.40E05	2.39	42555	21
R6 $NH_2 + H \rightarrow NH + H_2$	1.58E14	0.0	29267	5
R7 $NH_2 + NH_2 \rightarrow NH_3 + NH$	1.70E13	0.0	27899	5

Experiments

The shock tube facility and diagnostics used in the present study are similar to those used in our previous determination of the overall rate coefficient.[5] Temperature and pressure behind the reflected shock wave were calculated from the initial temperature and pressure and the shock speed measured over four intervals using five piezo-electric pressure gauges. The estimated uncertainty in reflected shock temperature is less than ±20 K at 1400 K over the time intervals of interest.

The NH_2 concentration was measured using a frequency modulation (FM) absorption technique.[22−25] With FM absorption, at least a factor of 30 reduction in the NH_2 detection limit can be achieved in comparison with direct laser absorption. A resonant type electrooptic modulator (New Focus 4421) was used. The modulation frequency and the modulation index were 1.2 GHz and 2.4, respectively. We routinely achieved a detection limit of 0.003% of equivalent absorption and an NH_2 detection limit of 0.2 ppm at 1400 K and 1 bar with 1 MHz bandwidth. Additional experimental details may be found in refs 16 and 20.

To reduce uncertainty in the initial CH_3NH_2 and NH_3 concentration due to wall adsorption, reactant mixtures were continuously supplied to the shock tube from a flow control system consisting of independent mass flow controllers. Test gas mixtures were prepared from commercial gas mixtures of 1028 ppm CH_3NH_2 (Ar balance, Specialty Gases of America), 5% NH_3 (Ar balance, Praxair), 1.98% NO (Ar balance, Praxair), and pure Ar (>99.9999%, Praxair). The NO_2 and N_2O impurities in the NO−Ar mixture were measured using FTIR spectroscopy, and the mole fractions of NO_2 and N_2O were 42 and 51 ppm, respectively. These impurities were included in the kinetics

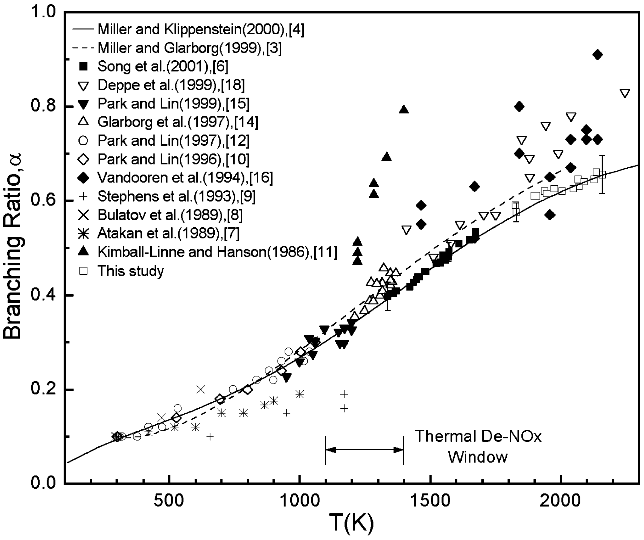

Figure 4. Summary of branching ratio data.

TABLE 2: Summary of α with Experimental Conditions

T (K)	P (bar)	x_{MMA} (ppm)	x_{NH_3} (ppm)	x_{NO} (ppm)	α
1826	1.21	8	4040	3880	0.590
1829	1.21	8	12160	4000	0.575
1897	1.18	9	4040	3880	0.610
1907	1.20	10	12170	4000	0.610
1938	1.19	28	3960	3800	0.620
1945	1.17	26	8070	3980	0.615
1975	1.16	26	8060	3970	0.625
2005	1.14	8	3880	4050	0.620
2048	1.18	28	8100	3990	0.625
2066	1.14	26	8050	3970	0.645
2069	1.18	25	3800	3960	0.630
2089	1.12	26	8060	3970	0.640
2127	1.10	8	4050	3890	0.645
2136	1.12	26	8030	3960	0.660
2159	1.13	24	3960	3800	0.655

simulations. The uncertainty in the initial concentration of reactants due to uncertainties in the base mixtures and the mixing process is less than 1%.

The temperature range of the experiments was 1826−2159 K, and the pressure range was 1.10−1.21 bar. The initial mole fraction of CH_3NH_2 was varied from 8 to 28 ppm, and the initial mole fraction of NO was 4000 ppm. Three different mole fractions of NH_3 (0.4%, 0.8%, and 1.2%) were used.

Results and Discussion

The measured branching ratio and experimental conditions are given in Table 2. The branching ratio increases from 0.59 at 1826 K to 0.66 at 2159 K. The uncertainty resulting from fitting errors, shown in Figure 3, is negligible due to the high sensitivity of the NH_2 detection system. The major source of uncertainty in the branching ratio determination at high temperatures is the uncertainty of the rates of R1 and the secondary reactions R5, R6, and R7, all of which are relatively well-known. The combined uncertainty in α is ± 3.5% at 1826 K and ± 7.5% at 2159 K.

$$NH_3 + H \rightarrow NH_2 + H_2 \tag{R5}$$

$$NH_2 + H \rightarrow NH + H_2 \tag{R6}$$

$$NH_2 + NH_2 \rightarrow NH_3 + NH \tag{R7}$$

Figure 4 shows a summary of the reported data for the branching ratio of the NH_2 + NO reaction. The high-temperature data in the present study are consistent with our previous low-temperature data using NH_3 photolysis. The results of this study also show good agreement with the theoretical work of Miller and Klippenstein.[4] In addition, the present values of α are consistent with the results of the recent De-NO_x modeling study by Glarborg et al.[14] and the lower temperature data given by Park and Lin[15] and Bulatov et al.[8] The results obtained in a NH_3/NO flame velocity modeling study by Vandooren at el.[17] and the results of a recent shock tube study by Deppe et al.,[18] who determined the branching ratio in the temperature range from 1500 to 2000 K directly from product measurements, seem to have overestimated α-values.

Conclusions

The branching ratio of the NH_2 + NO reaction has been determined using a simple kinetic scheme and a shock tube facility. To obtain the branching ratio, α, NH_2 traces were measured using frequency modulation spectroscopy. The branching ratio data of the present study are consistent with the results of our previous study, and show good agreement with the theoretical study of Miller and Klippenstein.[4]

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