Direct Determination of Product Branching for the NH_2 + NO Reaction at Temperatures between 302 and 1060 K

Joonbum Park and M. C. Lin*

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received: November 16, 1995; In Final Form: January 12, 1996⊗

The branching ratio of the two product channels of the NH_2 + NO reaction, α and β for the formation of N_2H + OH and N_2 + H_2O, respectively, have been determined independently at temperatures between 302 and 1060 K by mass spectrometry. For β determination, the concentration of H_2O was measured directly, whereas for α, the yield of OH was monitored by the CO_2 formed by its reaction with added CO. Both [H_2O] and [CO_2] were carefully calibrated with different standard mixtures before each measurement. α was found to increase gradually from 0.11 ± 0.02 at 302 K to 0.30 ± 0.02 at 1060 K, with the concomitant decrease of β from 0.89 ± 0.04 to 0.70 ± 0.03. The two independent measurements indicate for the first time that the relationship $\alpha + \beta = 1$ holds quantitatively throughout the temperature range studied.

Introduction

The branching ratio of the products formed in the NH_2 + NO reaction, a process of great influence in the efficiency of NH_3 as a de-NO_x agent, has been the subject of much controversy and discussion recently.[1−7] The reaction is believed to take place primarily by the following two product channels:

$$NH_2 + NO \rightarrow N_2H + OH \quad (1)$$

$$\rightarrow N_2 + H_2O \quad (2)$$

The recent suggestion of a possible third channel at high temperatures by Stephens et al.[6] could be accounted for by secondary radical reactions which do not produce either OH or H_2O.[8]

The branching ratio for OH production by reaction 1, $\alpha = k_1/(k_1 + k_2)$, reported by Atakan et al.[5] as well as by Stephens and co-workers[6] in the temperature range 298 ≤ T ≤ 1,200 K, α ≤ 0.2, has been shown to be significantly lower than the value determined by modeling the burning velocity data of NH_3−NO flames, α ≥ 0.5 above 1500 K.[9,10] In fact, Vandooren and co-workers[9] concluded that a value as high as 0.9 is required to account for their burning velocity measured near 2000 K.

More recently, Glarborg and co-workers[7] arrived at a temperature-dependent expression, $\alpha = 2.2 \times 10^{-3}T^{0.70}$ for the range of 300 < T < 1,400 K, which is sufficient for the modeling of thermal de-NO_x data provided that the lifetime of N_2H is long compared to the theoretically predicted value.

The branching ratio for OH production suggested by Glarborg et al.[7] in the temperature range 300−1400 K deviates significantly from the upper limits set by both Atakan et al.[5] and Stephens and co-workers.[6] There is an urgent need to resolve this discrepancy. In addition, the extrapolated value with Glarborg's expression, α = 0.36 at 1500 K, is noticeably lower than that required (α ≥ 0.5) to model the burning velocity of the NH_3−NO flame studied by Vandooren and co-workers.[9] The gap, however, could be accounted for by a sharp increase in α from 0.28 ± 0.02 at 1,000 K to 0.51 ± 0.02 at 1200 K as concluded in our recent kinetic modeling[11] of the experimentally measured NH_3 and NO removal rates by FTIR spectrometry and of the H_2O formation rate reported by Poole and Graven[12] using a gravimetric method. The theoretical basis of the drastic increase in the branching ratio for the NH_2 + NO reaction between 1000 and 2000 K is yet to be elucidated.

In the present study, we employ a mass spectrometric method to determine directly the production of H_2O and CO_2 from the laser-initiated reaction NH_3 with NO in the presence of added CO, which is utilized as a monitor for the OH radical by means of the well-known OH + CO → CO_2 + H reaction.[13] In this preliminary study, the experiment was carried out for the temperature range 302−1,060 K, in which the majority of experimental data has been reported.[3−6]

Experimental Section

Branching ratio measurements for the NH_2 + NO reaction were performed in the temperature range 302−1060 K using the high-pressure mass spectrometric sampling technique developed by Saalfeld and co-workers.[14,15] The sampling technique had been extensively applied by Gutman, Slagle, and collaborators[16−18] in conjunction with the excimer-laser generation of radical reactants. NH_2 radical was produced by photolysis of NH_3 at 193 mm. The concentration of the NH_2 radical generated from the photodissociation reaction was typically 1.5−5.0% depending on reaction temperature and photolysis laser energy, which varied from 30 to 40 mJ.

The reaction was studied with a quartz tubular Saalfeld reactor with an inner diameter of 10 mm and a heated length of 150 mm; the reactor has a conical sampling hole of 120 μm diameter, properly aligned with the detecting axis of a quadrupole mass spectrometer (Extrel Model C50). For the elevated temperature experiment, the reaction tube was heated with a nichrome ribbon which was insulated with ceramic wool. The reactor temperature could be varied from 300 to 1100 K. The reaction temperature was measured with a movable type K thermocouple, located near the center of the reaction tube with accuracy and uniformity of 2 K across the reaction zone.

The detection chamber was separated from the reaction chamber by a metal plate with a 1.0 mm orifice skimmer (Beam Dynamics Model 1) mounted at the center. The skimmer was located 3.0 mm from the sampling hole. The supersonic expansion chamber was pumped with an Edwards Diffstak Model 1160 diffusion pump with a pumping speed of 1300 L/s, providing a base pressure of 10^{-7} Torr. The detection chamber was evacuated with a Leybold turbomolecular pump having a pumping speed of 1000 L/s, giving a base pressure of 10^{-8} Torr.

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1996.

TABLE 1: Typical Reaction Conditions and Product Yield at Selected Temperatures Studied[a]

						$[CO_2]_t$[b]			$[H_2O]_t$[b]		
temp (K)	P_{tot}	$[NH_3]_0$	$[NH_2]_0$	$[CO]_0$	$[NO]_0$	exp.	α	calc.	exp.	β	calc.
302	6200	59.74	3.01	78.51	264.2	0.119	0.10	0.116	3.000	0.90	3.007
527	6720	69.38	2.52	89.94	263.9	0.106	0.14	0.104	2.623	0.86	2.628
695	6950	57.29	1.11	73.05	293.9	0.048	0.18	0.048	1.089	0.82	1.070
800	3900	82.01	2.30	205.7	169.1	0.201	0.20	0.202	2.349	0.80	2.352
930	4010	86.32	1.89	215.2	172.4	0.195	0.24	0.194	1.988	0.76	1.993
1004	4500	99.08	2.20	247.1	188.8	0.279	0.28	0.286	2.323	0.72	2.322
1060	4120	88.96	1.82	221.5	179.4	0.225	0.30	0.256	1.915	0.70	1.916

[a] The units of total pressure and all concentrations are in mTorr. [b] The signal amplitude was taken at $t = 15$ ms for CO_2 and $t = 10$ ms for H_2O in their concentration plateau regions.

The reaction tube housed in the expansion chamber was pumped with an Edwards rotary vacuum pump equipped with an oil trap to prevent the back diffusion of oil vapor. During experiment, the pressures in the expansion chamber and the detection chamber were kept at $(5-10) \times 10^{-5}$ and $(5-10) \times 10^{-6}$ Torr, respectively.

The positive ion signals of NH_3, CO_2, and H_2O were obtained by electron impact ionization at 70 eV followed by QMS mass selection. The time-resolved transient signal was averaged over 500 laser shots and recorded with a Nicolet 450 digital waveform acquisition system. The repetition rate was kept at 5 Hz, allowing enough time between pulses for the NH_3 signal level to return to its initial value.

All experiments were carried out under slow-flow conditions and with an excess amount of NO ($[NO] \gg [NH_2]$) so as to minimize NH_2 radical recombination and other secondary reactions in the mixture of NH_3, CO, NO, and He with total pressure of 5−10 Torr (mainly He diluent) in the reactor. The mixing of the reactants and additional helium buffer gas was achieved in a coiled stainless steel bellow tube prior to their introduction into the reactor. The concentration of each individual molecule was obtained by the following formula:

$$[R] = 9.66 \times 10^{16}(\%)\frac{P}{T}\frac{F_R}{F_T}\ \text{molecules/cm}^3$$

where (%) denotes the percentage of each molecule in its gas mixture, P is the total reaction pressure, T is the reaction temperature, F_R is the flow rate of each gas mixture, and F_T is the total flow rate of all gases. The flow rates were measured by using mass flowmeters (Brooks, Model 5850C) and the gas pressure was measured with an MKS Baratron manometer.

NH_3 (Aldrich), CO (Matheson), CO_2 (Aldrich), and H_2O (deionized water) were purified by standard trap-to-trap distillation. NO (Matheson) was purified by vacuum distillation through a silica gel trap maintained at 195 K to remove impurities such as NO_2. Silica gel was preheated and diffusion pumped for 12 h at 420 K to remove any condensed water. He (99.9995%) was used without further purification.

Results and Discussion

The product channel branching ratios of the NH_2 + NO reaction were measured by mass selected detection of H_2O and CO_2, which was produced by the reaction of the OH product with added CO molecules. The branching ratios for the production of N_2H + OH and N_2 + H_2O are defined by $\alpha = k_1/(k_1 + k_2)$ and $\beta = k_2/(k_1 + k_2)$, respectively.

To determine the α and β values, we kept the total rate constant ($k_t = k_1 + k_2$) for the NH_2 + NO reaction fixed for each temperature and only the relative values of k_1 and k_2 were varied. The total rate constant has been measured by many groups;[3−6,8] the value recommended by Baulch et al.[13] agrees closely with our recent determination.[8] The actual number densities of each product molecule were calculated by using carefully prepared calibration mixtures of H_2O, CO_2, and He.[19] In view of the fact that even under pseudo-first-order conditions, one cannot exclude radical−radical recombination and other secondary reactions,[8] kinetic modeling was carried out with the SENKIN program[20] using a set of reactions[8,11] to simulate the kinetics of the NH_2 + NO reaction at each experimental temperature. A randomly selected set of data for all temperatures studied is summarized in Table 1 together with kinetically modeled concentrations and branching ratios.

The results of our kinetic modeling for CO_2 and H_2O yields aided by sensitivity analysis indicate that the products derive predominantly from reactions 1 and 2, respectively. The modeled results are *not* affected by the lifetime of the N_2H radical with or without including the reaction

$$N_2H + NO \rightarrow N_2 + HNO$$

which is assumed to occur with the same rate constant as its isoelectronic analogue, HCO + NO → CO + HNO.[21] To test the possible N_2H lifetime effect, as suggested by Glarborg and co-workers[7] in their recent modeling of a more complex system containing NH_3, NO, O_2, and H_2O, we increased as well as decreased the adopted literature value for the rate constant of the $N_2H + M = N_2 + H + M$ reaction[22] by 2 orders of magnitude. No effect on the calculated yields of CO_2 and H_2O was observed. In fact, a similar test performed in the simulation of NH_3 and NO removal rates in the thermal reaction of the two compounds[11] near 1000 K resulted in undetectable changes in the calculated rates. In practice, one can effectively write reaction 1 as $NH_2 + NO = H + N_2 + OH$ with no detrimental consequences, particularly in the temperature regime of interest to the NH_3 de-NO_x process above 1000 K.

The kinetically modeled values of α and β based on the absolute yields of CO_2 and H_2O, respectively, are summarized in Figure 1 for the 302−1060 K temperature range. Each data point given in the figure represents the average value of five to seven separate runs. The value of α increases gradually from 0.11 ± 0.02 at 302 K to 0.30 ± 0.02 at 1060 K, whereas that of β decreases from 0.89 ± 0.04 at 302 K to 0.70 ± 0.03. These two independent sets of experimental data indicate that the relationship $\alpha + \beta = 1$ holds accurately from room temperature to 1000 K without significant deviation, supporting our earlier conclusion[8] that the mysterious "third channel" of the NH_2 + NO reaction at high temperatures[6] does not exist.

In Figure 2, we summarize the values of α determined by various groups,[2−7,11] including the results of our kinetic modeling[11] of experimentally measured NH_3 and NO removal rates as well as of the H_2O formation rates reported by Poole and Graven[12] covering the temperature range 940−1200 K, as alluded to above.

As is evident from the figure, the present value of α = 0.30

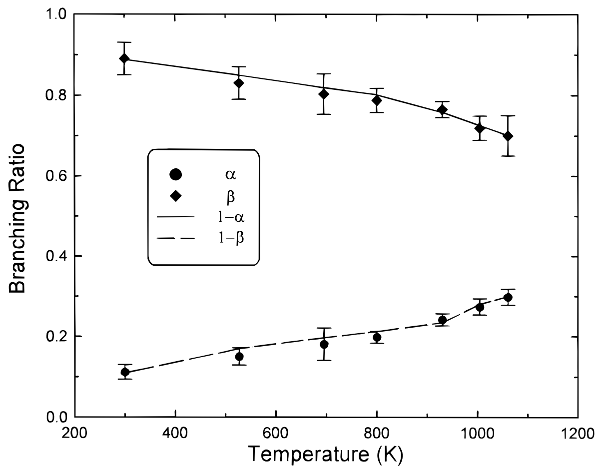

Figure 1. Branching ratios for $NH_2 + NO \rightarrow N_2H + OH$ (α) and $N_2 + H_2O$ (β) determined by the yields of CO_2 and H_2O, respectively, in the temperature range 302−1060 K.

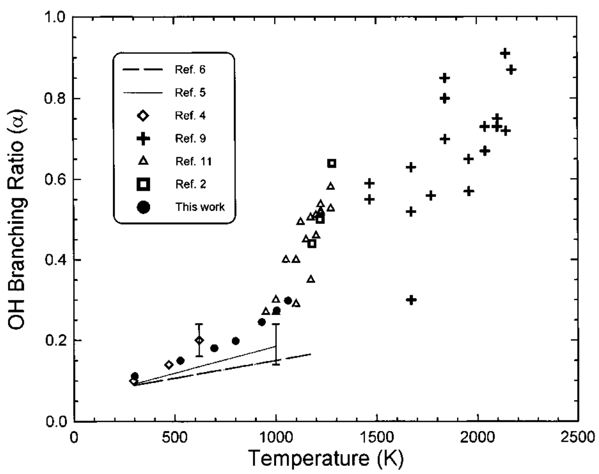

Figure 2. Summary of α as a function of temperature reported by various groups. For the result of ref 5, typical error limits are indicated for reference.

at 1060 K agrees closely with our kinetically modeled result, α = 0.3 ± 0.05 in the vicinity of 1050 (±50) K. The modeled result increases drastically from 0.27 at 950 K to 0.51 at 1200 K,[11] approaching the value recently arrived at by the burning rate modeling of NH_3−NO flames by Vandooren et al.[9] and by Brown and Smith.[10]

The sharp increase in the branching ratio of α above 1000 K and the merging of our kinetic result at 1200 K with that deduced from flame studies is significant. The high value of α above 1000 K implies that NH_3 can indeed be an efficient NO_x reducing agent[23] operating in the temperature range 1100−1400 K.

In summary, we have determined the NH_2 + NO reaction product branching by mass spectrometrically measuring the yields of H_2O and CO_2, using CO as the OH radical scavenger. Our result shows for the first time that the NH_2 + NO reaction produces only N_2H + OH (α) and $N_2 + H_2O$ (β) in the temperature range 302−1016 K with no evidence of a third product channel. Both branching ratios α and β were shown to be insensitive to the lifetime of the N_2H radical assumed in the modeling of H_2O and CO_2 yields. These results and those deduced from our recent kinetic modeling of the NH_3 + NO thermal reaction data suggest that the value increases sharply from 0.27 at 1060 K to 0.51 at 1200 K, merging closely with the value recently reported from NH_3−NO flame studies, α ≥ 0.5 at T ≥ 1500 K. The mechanistic basis of such a dramatic increase in product branching with temperature deserves a comprehensive theoretical investigation.

Acknowledgment. The authors gratefully acknowledge the support of this work by the Office of Naval Research (Contract N00014-89-J-1949) under the direction of Dr. R. S. Miller.

References and Notes

(1) Miller, J. A.; Branch, M. C.; Kee, R. J. *Combust. Flame* **1981**, *43*, 81.
(2) Kimball-Linne, M. A. ; Hanson, R. K. *Combust. Flame* **1986**, *64*, 377.
(3) Silver, J. A.; Kolb, C. E. *J. Phys. Chem.* **1982**, *86*, 3240.
(4) Bulatov, V. P.; Ioffe, A. A.; Lozovsky, V. A.; Sarkisov, O. M. *Chem. Phys. Lett.* **1989**, *161*, 141.
(5) Atakan, B.; Jacobs, A.; Wahl, M; Weller, R.; Wolfrum, J. *Chem. Phys. Lett.* **1989**, *155*, 609.
(6) Stephens, J. W.; Morter, C. L.; Farhat, S. K.; Glass, G. P.; Curl, R. F. *J. Phys. Chem.* **1993**, *97*, 8944.
(7) Glarborg, P.; Dam-Johansen, K.; Miller, J. A.; Kee, R. J.; Coltrin, M. E. *Int. J. Chem. Kinet.* **1994**, *26*, 421.
(8) Diau, E. W. G.; Yu, T.; Wagner, M. A. G.; Lin, M. C. *J. Phys. Chem.* **1994**, *98*, 4034.
(9) Vandooren, J.; Bian, J.; van Tiggelen, P. J. *Combust. Flame* **1994**, *402*.
(10) Brown, M. J.; Smith, D. B. *25th Symp. (Int.) on Combustion*; The Combustion Institute: Pittsburgh, 1994; p 1011.
(11) Halbgewachs, M. J.; Diau, E. W. G.; Mebel, A. M.; Lin, M. C.; Melius, C. F., to be published.
(12) Poole, D. R.; Graven, W. M. *J. Am. Chem. Soc.* **1961**, *83*, 283.
(13) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Esser, C.; Frank, P.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. J. *Phys. Chem. Ref. Data* **1992**, *21*, 411.
(14) Wyatt, J. R.; DeCorpo, J. J.; McDowell, M. V.; Saalfeld, F. E. *Rev. Sci. Instrum.* **1974**, *45*, 916.
(15) Wyatt, J. R.; DeCorpo, J. J.; McDowell, M. V.; Saalfeld, F. E. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *16*, 33.
(16) Slagle, I. R.; Gutman, D. *J. Am. Chem. Soc.* **1985**, *107*, 5342.
(17) Russell, J. J.; Seetula, J. A.; Gutrman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092.
(18) Slagle, I. R.; Gutman, D.; Davies, J. W.; Pilling, M. J. *J. Phys. Chem.* **1988**, *92*, 2455.
(19) Four different H_2O, CO_2 and He mixtures were used to calibrate the m/z 18 and 44 signals for individual runs. The Pyrex bulbs employed for these calibration mixtures were first saturated with several Torr of H_2O and then evacuated for preparation of samples. The H_2O concentrations obtained from the m/z 18 signals using various calibration mixtures agreed closely.
(20) Lutz, A. E.; Kee, R. J.; Miller, J. A. SENKIN: A FORTRAN Program for Predicting Homogeneous Gas-Phase Chemical Kinetics with Sensitivity Analysis; Sandia National Laboratories, Report No. SAND87-8248, 1988.
(21) Veyret, B.; Lesclaux, R. *J. Phys. Chem.* **1981**, *85*, 1918.
(22) Mertens, D. J.; Chang, A. Y.; Hanson, R. K.; Bowman, C. T. *Int. J. Chem. Kinet.*, **1989**, *21*, 1049.
(23) Lyon, R. K. *Int. J. Chem. Kinet.* **1976**, *8*, 318; U.S. Patent 3,900,554.

JP9533741