

COMMENTS

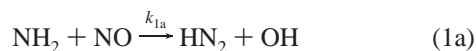
Product Branching Ratios in the $\text{NH}_2 + \text{NO}$ Reaction: A Re-Evaluation

J. Park and M. C. Lin*

Department of Chemistry, Emory University,
Atlanta, Georgia 30322

Received: March 18, 1999; In Final Form:
September 7, 1999

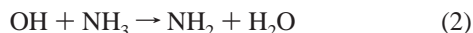
$\text{NH}_2 + \text{NO}$ is a critical reaction in the thermal reduction of NO_x by the Exxon process¹ in which NH_3 is employed as the reducing agent. The key reaction responsible for the reduction is $\text{NH}_2 + \text{NO}$ which can occur by the following two major channels:



The reaction has been studied by many investigators^{2–24} whose contributions to the kinetic and mechanistic aspects of the reaction have been cited and reviewed in our earlier publications.^{23–26} The key controversy remains in the effect of temperature on the branching ratio for the radical formation channel (1a), α_{1a} , above 1000 K. This product channel plays the most important role in the NH_3 de NO_x reaction because it generates almost simultaneously the two key chain carriers, OH and H; the latter can be readily formed by the decomposition of the transient species HN_2 at temperatures above 1000 K.

In our latest paper published in this journal on the $\text{NH}_2 + \text{NO}$ reaction,²⁴ we concluded that α_{1a} increased rapidly above 1000 K and merged effectively with the large branching ratio reported by Vandooren et al.²¹ from their modeling of the ammonia flame speed, $\alpha_{1a} > 0.5$, above 1500 K. Our conclusion was based on the kinetically modeled NO decay rates measured by the pulsed laser photolysis/mass spectrometry²⁴ and the NH_3 and NO decay rates determined in the pyrolysis/FTIR spectrometry.²⁰

In both modeling studies,^{20,24} we employed the rate constant for another influential process which regenerates the NH_2 radical,



reported by Diau et al.,²⁷ $k_2 = 1.98 \times 10^{12} \exp(-921/T) \text{ cm}^3/(\text{mol s})$, for the temperature range 273–433 K. The absolute value of the rate constant, although agreeing closely with others for the same temperature range, deviates from those determined at higher temperatures on account of the presence of a strong upward curvature above 1000 K as illustrated in the inset of Figure 1. The existence of the curvature is consistent with our theoretically predicted result for the reverse process, $\text{NH}_2 + \text{H}_2\text{O} \rightarrow \text{OH} + \text{NH}_3$, $k_{-2} = 2.33 \times 10^3 T^{2.94} \exp(-5566/T) \text{ cm}^3/(\text{mol s})$, computed with the transition state theory (TST) with tunneling corrections using the TST parameters obtained by a G2M/B3LYP/6-311G(d,p) calculation.²⁸ Figure 1 shows the

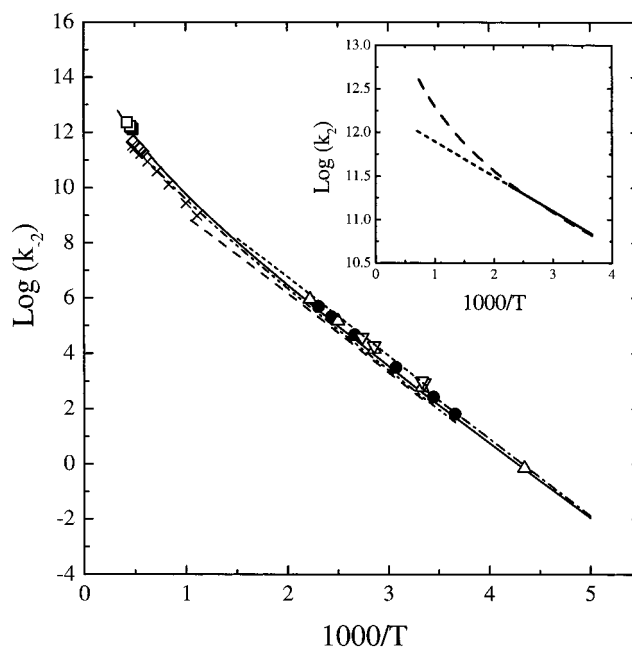


Figure 1. Arrhenius plot of the rate constant for the $\text{NH}_2 + \text{H}_2\text{O}$ reaction: solid curve (ref 28); dashed line (ref 32); dotted line (ref 33); dash-dotted curve (ref 34); dash-dot-dotted curve (ref 40); ref 27 (●); ref 35 (Δ); ref 36 (▽); ref 37 (□); ref 38 (×); ref 39 (◆). (Inset) Arrhenius plot of the $\text{OH} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{H}_2\text{O}$ reaction: solid line (ref 27); dashed curve (ref 30); dotted line (extrapolation of ref 27).

good correlation between the predicted k_{-2} and experimental values, including those for $\text{OH} + \text{NH}_3$ converted to k_{-2} with the equilibrium constant, $K_{-2} = 2.68 \times 10^{-2} T^{0.53} \exp(5846/T)$.²⁸ The employment of k_{-2} , instead of Diau's k_2 given above, reduces the values of α_{1a} by about 20% near 1200 K.

Figure 2 summarizes our newly modeled results and the existing data on α_{1a} , including the most recent result of Votsmeier et al.²⁹ As shown in the figure, the new values obtained by using the theoretically calculated k_{-2} agree closely with those reported by Votsmeier et al.²⁹ and the kinetically modeled results of Glarborg and co-workers.³⁰ To test the generality of the mechanism employed and the sensitivity of α_{1a} to k_2 or k_{-2} , we have also used the forward rate constant adopted by Glarborg et al. in their modeling,^{4,30} $k_2 = 2.00 \times 10^6 T^{2.04} \exp(-285/T) \text{ cm}^3/(\text{mol s})$; the values of α_{1a} thus obtained agree exactly with those evaluated with our k_{-2} . A least-squares analysis of α_{1a} based on our data (300–1200 K) and those of Glarborg and co-workers (1200–1370 K) and Votsmeier et al. (1330–1670 K) gives rise to the expression, $\alpha_{1a} = 9.69 \times 10^{-3} - 1.31 \times 10^{-4} T + 3.96 \times 10^{-7} T^2 - 9.72 \times 10^{-11} T^3$.

On the basis of our total rate constant for the $\text{NH}_2 + \text{NO}$ reaction²⁴ and the values of α_{1a} given above, the absolute rate constants for the branching channels 1a and 1b can be represented by

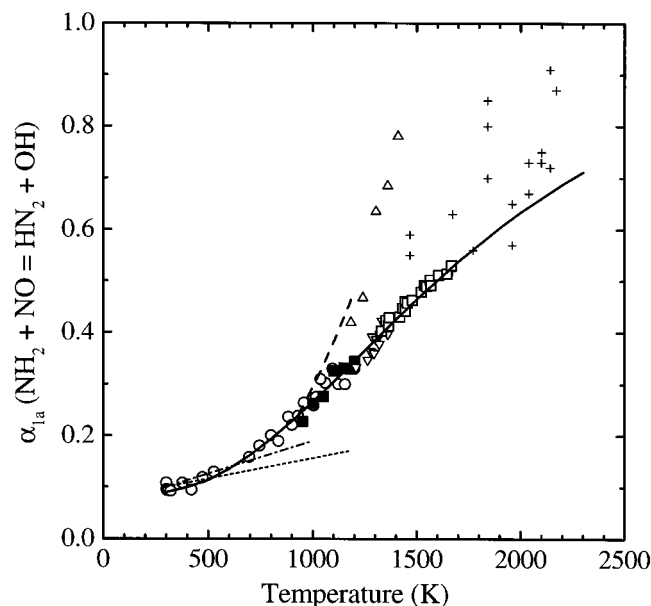


Figure 2. Branching ratio for $\text{NH}_2 + \text{NO} \rightarrow \text{HN}_2 + \text{OH}$ (α_{1a}) as a function of temperature: this work's remodeled result of ref 24 (○); remodeled result of ref 20 (■); ref 30 (▽); ref 29 (□); ref 21 (+); ref 3 (Δ); dash-dotted line (ref 17); dotted line (ref 19); dashed line (ref 24); solid line, the result of a least-squares analysis for α_{1a} based on this work and those of refs 28 and 30.

$$k_{1a} = 1.43 \times 10^7 T^{1.40} \exp(894/T) \text{ cm}^3/(\text{mol s})$$

$$k_{1b} = 1.20 \times 10^{17} T^{-1.61} \exp(-150/T) \text{ cm}^3/(\text{mol s}).$$

It should be noted that our low temperature ($T < 1000$ K) data were not affected significantly by the upward curvature of k_2 or k_{-2} and that the H_2O formation data reported by Poole and Graven³¹ from their pyrolytic study of $\text{NH}_3 + \text{NO}$ could no longer be sensitively modeled for α_{1a} .

Acknowledgment. The authors are grateful to the Office of Naval Research for support of this work, under the direction of Dr. J. Goldwasser through ONR Grant N00014-89-J-1949.

References and Notes

- (1) Lyon, R. K. *Int. J. Chem. Kinet.* **1976**, *8*, 318. U. S. patent 3,900,554.
- (2) Miller, J. A.; Branch, M. C.; Kee, R. J. *Combust. Flame* **1981**, *43*, 81.
- (3) Kimball-Linne, M. A.; Hanson, R. K. *Combust. Flame* **1986**, *64*, 377.
- (4) Glarborg, P.; Dam-Johansen, K.; Miller, J. A.; Kee, R. J.; Coltrin, M. E. *Int. J. Chem. Kinet.* **1994**, *26*, 421.
- (5) Perry, R. A.; Siebers, D. L. *Nature* **1986**, *324*, 657.
- (6) Wicke, B. G.; Grady, K. A.; Ratcliffe, J. W. *Combust. Flame* **1989**, *78*, 249.
- (7) Caton, J. A.; Siebers, D. L. *Combust. Sci. Technol.* **1989**, *65*, 277.
- (8) Lyon, R. K.; Cole, J. A. *Combust. Flame* **1990**, *82*, 435.
- (9) Miller, J. A.; C. T. Bowman, *Int. J. Chem. Kinet.* **1991**, *23*, 289.
- (10) Mertens, J. D.; Chang, A. Y.; Hanson, R. K.; Bowman, C. T. *Int. J. Chem. Kinet.* **1991**, *23*, 173.
- (11) Silver, J. A.; Kolb, C. E. *J. Phys. Chem.* **1982**, *86*, 3240.
- (12) Stief, L. J.; Brobst, W. D.; Nava, D. F.; Borkowski, R. P.; Michael, J. V. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1391.
- (13) Hack, W.; Schake, H.; Schröter, H.; Wagner, H. Gg. *17th Symposium (Int.) on Combustion*; The Combustion Institute: Pittsburgh, 1979; p 505.
- (14) Diau, E. W. G.; Yu, T.; Wagner, M. A. G.; Lin, M. C. *J. Phys. Chem.* **1994**, *98*, 4034.
- (15) Lesclaux, R.; Khê, Pham Van; Dezaudier, P.; Soullignac, J. C. *Chem. Phys. Lett.* **1975**, *35*, 493.
- (16) Bulatov, V. P.; Ioffe, A. A.; Lozovsky, V. A.; Sarkisov, O. M. *Chem. Phys. Lett.* **1989**, *161*, 141.
- (17) Atakan, B.; Jacobs, A.; Wahl, M.; Weller, R.; Wolfrum, J. *Chem. Phys. Lett.* **1989**, *155*, 609.
- (18) 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.
- (19) Stephens, J. W.; Morter, C. L.; Farhat, S. K.; Glass, G. P.; Curl, R. F. *J. Phys. Chem.* **1993**, *97*, 8944.
- (20) Halbgewachs, M. J.; Diau, E. W. G.; Mebel, A. M.; Lin, M. C.; Melius, C. F. *26th Symposium (Int.) on Combustion*; The Combustion Institute: Pittsburgh, 1996; p 2109.
- (21) Vandooren, J.; Bian, J.; van Tiggelen, P. *J. Combust. Flame* **1994**, *402*.
- (22) Brown, M. J.; Smith, D. B. *25th Symposium (Int.) on Combustion*; The Combustion Institute: Pittsburgh, 1994; p 1011.
- (23) Park, J.; Lin, M. C. *J. Phys. Chem.* **1996**, *100*, 3317.
- (24) Park, J.; Lin, M. C. *J. Phys. Chem. A* **1997**, *101*, 5.
- (25) Park, J.; Lin, M. C. *Recent Research Development in Physical Chemistry*; Transworld Research Network: India, 1998; Vol. 2, p 965.
- (26) Mebel, A. M.; Lin, M. C. *Int. Rev. Phys. Chem.* **1997**, *16*, 249.
- (27) Diau, E. W. G.; Tso, T. L.; Lee, Y. P. *J. Phys. Chem.* **1990**, *94*, 5261.
- (28) Mebel, A. M.; Moskaleva, L. V.; Lin, M. C. *THEOCHEM* **1999**, *461-462*, 223.
- (29) Votsmeier, M.; Song, S.; Hanson, R. K.; Bowman, C. T. *J. Phys. Chem. A* **1999**, *103* (11), 1566.
- (30) Glarborg, P.; Kristensen, P. G.; Dam-Johansen, K.; Miller, J. A. *J. Phys. Chem. A* **1997**, *101*, 3741.
- (31) Poole, D. R.; Graven, W. M. *J. Am. Chem. Soc.* **1961**, *83*, 283.
- (32) Espinosa-Garcia, J.; Corchado, J. C.; Sana, M. *J. Chem. Phys.* **1993**, *90*, 1181.
- (33) Hack, W.; Hoyeremann, K.; Wagner, H. Gg. *Ber. Bunsen-Ges. Phys. Chem.* **1974**, *78*, 386.
- (34) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. *Chemical kinetics and photochemical data for use in stratospheric modeling. Evaluation number 12*; JPL Publication 97-4, 1997.
- (35) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1329-1499.
- (36) Pagsberg, P. B.; Eriksen, J.; Christensen, H. C. *J. Phys. Chem.* **1979**, *83*, 582.
- (37) Zabielski, M. F.; Seery, D. J. *Int. J. Chem. Kinet.* **1985**, *17*, 1191.
- (38) Hanson, R. K.; Salimian, S. In *Combustion Chemistry*; Gardiner, W. C., Jr., Ed.; Springer-Verlag: New York, 1984.
- (39) Salimian, S.; Hanson, R. K.; Kruger, C. H. *Int. J. Chem. Kinet.* **1984**, *16*, 725.
- (40) Corchado, J. C.; Espinosa-Garcia, J.; Hu, W.-P.; Rossi, I.; Truhlar, D. G. *J. Phys. Chem.* **1995**, *99*, 687.