IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx22

$$NH_2 + NO_2 \rightarrow N_2O + H_2O \qquad (1)$$
$$\rightarrow N_2 + H_2O_2 \qquad (2)$$
$$\rightarrow H_2NO + NO \qquad (3)$$
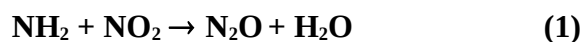
$\Delta H°(1) = -381.7$ kJ mol^{-1}

$\Delta H°(2) = -358.2$ kJ mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k / cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$3.8 \times 10^{-8}\, T^{-1.30}$	298-505	Kurasawa and Lesclaux, 1979	FP-LIF (a)
$(2.3 \pm 0.2) \times 10^{-11}$	298		
$(2.11 \pm 0.18) \times 10^{-11}$	297	Whyte and Phillips, 1983	PLP-LIF (a)
$(2.26 \pm 0.08) \times 10^{-11}$	298	Xiang et al., 1985	PLP-LIF (b)
$(2.1 \pm 0.4) \times 10^{-11}\, (T/298)^{-1.7}$	295-620	Bulatov et al., 1989	FP (c)
$1.35 \times 10^{-7}\, T^{-1.44} \exp(-135/T)$	300-910	Park and Lin, 1996, 1997	PLP-MS (d)
$(1.39 \pm 0.07) \times 10^{-11}$	300		
Branching Ratios			
$k_1/k = 0.14 \pm 0.02$	298	Quandt and Hershberger, 1996	PLP-TDLS (e)
$k_1/k = 0.59 \pm 0.03$	298	Meunier et al., 1996	PR-TDLS (f)
$k_3/k = 0.40 \pm 0.05$			
$k_1/k = 0.19 \pm 0.02$	300-990	Park and Lin, 1996, 1997	PLP-MS (g)
$k_1/k = 0.24 \pm 0.04$	298	Lindholm and Hershberger, 1997	PLP-TDLS (h)
$k_3/k = 0.76 \pm 0.1$			

Comments

(a) [NH$_2$] monitored by time resolved LIF at 598 nm.

(b) Pulsed infrared multiphoton dissociation NH$_3$, CH$_3$NH$_2$, or N$_2$H$_4$ used for NH$_2$ production. State selected NH$_2$ concentration monitored by time resolved LIF at 533 nm. The rate constant for NH$_2$(v"=1) was also measured and found to be less than that for ground state NH$_2$.

(c) [NH$_2$] was monitored by intracavity absorption. k was found to be independent of pressure over the range 13-870 mbar (10-650 Torr).

(d) NH$_2$ produced by pulsed laser photolysis at 193 nm of NH$_3$. NH$_3$, H$_2$O, N$_2$O, NO$_2$, and O$_2$ were detected by quadrapole mass spectrometry. Values of k were obtained from the concentration profiles of the [NO$_2$] decay and from the formation of H$_2$O and N$_2$O. Substantial modelling was used to correct for effects of secondary chemistry.

(e) Pulsed laser photolysis at 193 nm of NH_3-NO_2-SF_6 mixtures. $[N_2O]$, $[NO]$, and $[H_2O]$ were monitored by time resolved infrared diode laser absorption spectroscopy. Large yields of NO are produced by unidentified secondary chemistry precluding determination of k_3/k.

(f) Pulse radiolysis, of Ar-SF_6-NH_3-NO_2 mixtures at a total pressure of 40 mbar. $[NH_2]$, $[N_2O]$, and $[NO]$ were monitored by time resolved infrared diode laser spectroscopy.

(g) Technique as in (d). Branching ratios based on the N_2O yields. The value of k_1/k derived depends on the expression for k used in the detailed modelling of the system. In one of the studies[8] the expression for k of Glarborg et al.[10] was used and in the other study[5] values of k measured in the same study[5] were used. The same values of k_1/k was obtained in the two studies.

(h) Technique basically as in (e) but NH_2 generated by photolysis of ICN at 248 nm in the presence of NH_3, leading to the fast reaction $CN + NH_3 \rightarrow HCN + NH_2$. Use of this source eliminates excessive NO production by secondary chemistry and allows derivation of k_3/k from the measured NO yield $[NH_2]$, $[N_2O]$, and $[NO]$ were monitored.

Preferred Values

$k = 2.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.0 \times 10^{-11}$ $(T/298)^{-1.3}$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-500 K.
$k_1/k = 0.25$ over the temperature range 298-500 K.
$k_3/k = 0.75$ over the temperature range 298-500 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K
$\Delta n = \pm 0.7$
$\Delta k_1/k = \Delta k_3/k = \pm 0.15$ over the temperature range 298-500 K.

Comments on Preferred Values

At 298 K the results of Kurasawa and Lesclaux (1979), Whyte and Phillips (1983), Xiang et al. (1985), Bulatov et al. (1989) and Park and Lin (1997) are in reasonable agreement and our preferred value for k(298 K) is taken as an average of the values from these studies. Other studies are those of Hack et al. (1979) and Pagsberg et al. (1991). Hack et al. (1979), using a discharge flow technique over the range 250–500 K, obtained a significantly lower value at 298 K than those from the other studies, and this discrepancy increases at higher temperatures, approaching a factor of 4 at 500 K. The pulse radiolysis study of Pagsberg et al. (1991) also gives a low value at 298 K.

There are also significant differences in the values found for the temperature dependence of k. The results of Kurasawa and Lesclaux (1979) and of Park and Lin (1997) are in excellent agreement and are the basis for the temperature dependence of k in our preferred expression. Bulatov et al. (1989) observe a slightly greater temperature dependence but their results fall within the error limits assigned. Only the larger temperature dependence observed by Hack et al. (1979) ($k \propto T^{-3.0}$) appears to be incompatible with the other studies.

Theoretical treatments (Mebel et al., 1995) of the reaction mechanism suggest that channels (1) and (3) are the most probable and the experimental studies confirm this qualitatively but the quantitative agreement on the branching ratios is poor. The early study by Hack et al. (1979) suggested that channel (1) should predominate to the extent of 95% of the total reaction and Glarborg et al. (1995), who studied the NH_3/NO_2 reaction in a flow reactor over the range 850–1350 K, from their modeling of the changes in reactant and product concentrations concluded also that channel (1) predominates at low temperatures, but channel (3) is the more important at high temperatures. However the direct measurements favour channel (3) at all temperatures up to 900K (Park and Lin, 1996; 1997). The studies of Lindholm and Hershberger (1997) and of Park and Lin (1996; 1997) appear to be the most direct and are in reasonable agreement. Provisionally, the recommended

branching ratios are based on these studies (Park and Lin, 1996; 1997, Lindholm and Hershberger, 1997) but with substantial error limits.

No evidence has been found for the occurrence of channel (2) or for the other exothermic channels leading to $N_2 + 2HO$ and/or $2HNO$ (Lindholm and Hershberger, 1997).

References

Bulatov, V. P., Ioffe, A. A., Lozovsky, V. A. and Sarkisov, O. M.: Chem. Phys. Lett., 159, 171, 1989.

Glarborg, P., Dam-Johansen, K. and Miller, J. A.: Int. J. Chem. Kinet., 27, 1207, 1995.

Hack, W., Schacke, H., Schröter, M. and Wagner, H. Gg.: 17th Symp. (Int.) Combust., 505, 1979.

Kurasawa, H. and Lesclaux, R.: Chem. Phys. Lett., 66, 602, 1979.

Lindholm, N. and Hershberger, J. F.: J. Phys. Chem. A, 101, 4991, 1997.

Mebel, A. M., Hsu, C. C-., Lin, M. C. and Morokuma, K.: J. Chem. Phys., 103, 5640, 1995.

Meunier, H., Pagsberg P. and Sillesen, A.: Chem. Phys. Lett., 261, 277, 1996.

Pagsberg, P., Sztuba, B., Ratajczak, E. and Sillesen, A.: Acta Chem. Scand., 45, 329, 1991.

Park, J. and Lin, M. C.: J. Phys. Chem. A, 101, 2643, 1997.

Park, J. and Lin, M. C.: Int. J. Chem.Kinet., 28, 879, 1996.

Quandt, R. W. and Hershberger, J. F.: J. Phys. Chem., 100, 9407, 1996.

Whyte, A. R. and Phillips, L. F.: Chem. Phys. Lett., 102, 451, 1983.

Xiang, T.-X., Torres, L.M. and Guillory, W.A.: J. Chem. Phys., 83, 1623, 1985.