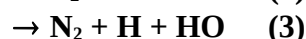
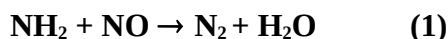


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NOx21

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This data sheet updated: 16th July 2001.



$$\Delta H^\circ(1) = -520.8 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(3) = -23.8 \text{ kJ mol}^{-1}$$

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

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
2.7×10^{-11}	300	Gordon et al., 1971	(a)
$(8.3 \pm 1.7) \times 10^{-12}$	298	Gehring et al., 1973	DF-MS (b)
$2.1 \times 10^{-8} T^{-1.25}$	300-500	Lesclaux et al., 1975	FP (c)
$(1.8 \pm 0.3) \times 10^{-11}$	300		
$(2.1 \pm 0.2) \times 10^{-11}$	298	Hancock et al., 1979	FP-LIF
$(1.7 \pm 0.4) \times 10^{-11}$	298	Sarkisov et al., 1978	FP (d)
$4.5 \times 10^{-7} T^{-1.85}$	210-500	Hack et al., 1979	DF-LIF
9.7×10^{-12}	298		
$2.77 \times 10^{-7} T^{-1.67}$	216-480	Stief et al., 1982	FP-LIF (e)
$(2.10 \pm 0.31) \times 10^{-11}$	298		
$4.4 \times 10^{-5} T^{-2.3} \exp(-684/T)$	294-1215	Silver and Kolb, 1982	DF-LIF (f)
$(9.59 \pm 2.4) \times 10^{-11}$	298		
$(1.7 \pm 0.5) \times 10^{-11}$	295	Andresen et al., 1982	PLP (g)
$(1.81 \pm 0.12) \times 10^{-11}$	297	Whyte and Phillips, 1983	PLP-LIF
1.7×10^{-11}	298	Dreier and Wolfrum, 1985	PLP (h)
$(1.3 \pm 0.4) \times 10^{-11}$	298		
$1.3 \cdot 10^{-8} T^{-(1.17 \pm 0.25)}$	294-1027	Atakan et al., 1989, 1990	PLP-LIF (i)
$(1.67 \pm 0.25) \times 10^{-11}$	298		
$5.6 \times 10^{-6} T^{-2.2}$	295-620	Bulatov et al., 1989	FP (d)
2.2×10^{-11}	298	Pagsberg et al., 1991	(j)
$5.43 T^{-4.02} \exp(-1034/T)$	293-612	Wolf et al., 1994	PLP-LIF
$(1.9 \pm 0.1) \times 10^{-11}$	295		
$2.2 \times 10^{-12} \exp[(525 \pm 80)/T]$	297-673	Diau et al., 1994	PLP (k)
$(1.45 \pm 0.08) \times 10^{-11}$	297		
1.4×10^{-11}	298	Yu and Lin, 1994	PLP (d)
$(1.9 \pm 0.3) \times 10^{-11}$	299	Imamura and Washida, 1995	PLP (l)
$1.38 \times 10^{-10} T^{-0.57} \exp(300/T)$	305-1037	Park and Lin, 1997	PLP-MS (m)
$(8.59 \pm 0.40) \times 10^{-12}$	305		
$(k_2 + k_3) = 1.4 \times 10^{-14} T^{0.53} \exp(502/T)$	300-1000		
$k_1 = 1.37 \times 10^{-9} T^{-0.93} \exp(192/T)$	300-1000		
$1.65 \times 10^{-7} T^{-1.54} \exp(-93/T)$	203-813	Wolf et al., 1997	PLP-LIF (n)
$(1.87 \pm 0.02) \times 10^{-11}$	295		
<i>Branching Ratios</i>			
$(k_2 + k_3)/k = 0.10 \pm 0.02$	295	Bulatov et al., 1989	FP-AS (d)

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
$(k_2 + k_3)/k = 0.10 \pm 0.025$	300	Atakan et al., 1989, 1990	PLP-LIF (i)
$k_1/k = 0.85$	295	Stephens et al., 1993	PLP-AS (o)
$(k_2 + k_3)/k = 0.10$	295		
$k_1/k = 0.7 \pm 0.2$	298	Quandt and Hershberger, 1996	PLP (p)
$k_1/k = 0.90$	300	Park and Lin, 1996, 1997	PLP-MS (q)
$(k_3 + k_4)/k = 0.10$	300		
$(k_2 + k_3)/k = 0.090 \pm 0.002$	298	Wolf, Yang, and Durant, 1997	DF-MS (r)

Comments

- (a) Pulse radiolysis of $\text{NH}_3\text{-NO}$ mixtures at 670 mbar (500 Torr) total pressure. $[\text{NH}_2]$ monitored by time-resolved absorption spectroscopy.
- (b) NO_2 was added to an excess of H atoms followed by addition of NH_3 . Analysis by time-of-flight mass-spectrometry. Vibrationally excited H_2O was observed as a product. The addition product NH_2NO was also observed to the extent of 5% of the N_2 formed.
- (c) $[\text{NH}_2]$ was monitored by absorption spectroscopy. No pressure dependence of k was observed over the range 2.7-930 mbar (2-700 Torr) of N_2 .
- (d) $[\text{NH}_2]$ was monitored by intracavity laser absorption.
- (e) $[\text{NH}_2]$ was monitored by LIF. Production of HO was looked for by resonance fluorescence and found under static conditions but not under flowing conditions. An upper limit of $(k_2 + k_3)/k \leq 0.22$ was obtained.
- (f) $[\text{NH}_2]$ was monitored by LIF. HO production was detected by RF or by LIF. A rate coefficient ratio $(k_2 + k_3)/k = 0.4 \pm 0.1$ was obtained but the data were later reanalysed by the authors to give a value of 0.12. H-atom production was looked for using RF; an upper limit of 0.05 was found for the branching ratio of channels leading to H atoms.
- (g) The rate coefficient was obtained by monitoring the production of vibrationally excited H_2O by observation of infrared and visible emissions. RA and LIF were used to monitor $[\text{HO}]$. $k_2/k \geq 0.65$ was obtained with the H-atom yield being ≤ 0.05 .
- (h) $[\text{NH}_2]$ and $[\text{N}_2]$ were monitored by coherent anti-Stokes Raman spectroscopy (CARS). Another independent value of the rate constant was obtained by monitoring the IR fluorescence of vibrationally excited H_2O .
- (i) $[\text{HO}]$ was monitored by LIF. The HO yield was determined by using HO production from H_2O_2 photolysis to calibrate for $[\text{HO}]$.
- (j) Pulse radiolysis, of $\text{Ar-SF}_6\text{-NH}_3\text{-NO}$ mixtures at a total pressure of ~ 50 mbar. $[\text{NH}_2]$ and $[\text{HO}]$ were monitored by time-resolved UV absorption spectroscopy. The observed yield of HO was small suggesting a value of $(k_2+k_3)/k \approx 0.07$.
- (k) $[\text{NH}_2]$ was monitored by cavity ring down absorption spectroscopy at 537.6 nm.
- (l) $[\text{NH}_2]$ was monitored by photoionization mass spectrometry.
- (m) Pulsed laser photolysis of $\text{NH}_3\text{-NO}$ mixtures. $[\text{H}_2\text{O}]$ and $[\text{NO}]$ were monitored by time-resolved mass-spectrometry and values of k were derived from detailed modelling of the $[\text{H}_2\text{O}]$ and $[\text{NO}]$ profiles. In a subsequent publication²⁴ the data are reanalysed and expressions derived giving k_1 and (k_2+k_3) up to temperatures above 2000 K but these expressions agree very closely with those cited here for $T \leq 1000$ K.
- (n) The expression $k = 2.66 \times 10^{-8} T^{-1.27} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ also provides a good fit to the data.
- (o) Pulsed laser photolysis of $\text{NH}_3\text{-NO}$ mixtures. $[\text{H}_2\text{O}]$, $[\text{HO}]$, $[\text{NH}_3]$, and $[\text{NH}_2]$ were monitored by infrared absorption spectroscopy.

- (p) Pulsed laser photolysis of NH₃-NO mixtures. [H₂O] and [NH₂] were monitored by infrared absorption spectroscopy. This was a preliminary study to an investigation of the branching in the NH₂+NO₂ reaction.
- (q) Pulsed laser photolysis of NH₃-NO-CO mixtures. Time-resolved mass-spectrometric measurements of [H₂O], [NO] and of [CO₂] produced by scavenging of HO by the CO.
- (r) NH₂ radicals were generated by the F+NH₃ reaction in a flow He carrier gas to which an NO-CO-He mixture was added downstream of the NH₂ generation point. [N₂] and [CO₂] were determined by mass-spectrometry. The ND₂+NO reaction was also studied.

Preferred Values

$k = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.6 \times 10^{-11} (T/298)^{-1.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 210-500 K.

$k_1/k = 0.9$ at 298 K.

$(k_2 + k_3)/k = 0.1$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K

$\Delta n = \pm 0.5$.

$\Delta k_1/k = \pm 0.05$ at 298 K.

$\Delta(k_2 + k_3)/k = \pm 0.03$ at 298 K.

Comments on Preferred Value

The values of the rate coefficients obtained in the pulsed photolysis studies are significantly higher than those obtained using the discharge flow technique. The reason for this discrepancy is not known. The preferred value at 298 K is therefore taken as the mean of the values reported in the below references. The temperature dependence is based on the data below 500 K in the temperature dependence studies of Lesclaux et al. (1975), Hack et al. (1979), Stief et al. (1982), Silver and Kolb (1982), Atakan et al. (1989; 1990), Bulatov et al. (1989), Wolf et al. (1994; 1997), Diau et al. (1994) and Park and Lin (1997).

The preferred values of the branching ratios are based on the direct measurements of Atakan et al. (1989; 1990), Stephens et al. (1993), Park and Lin (1996; 1997) and Wolf et al. (1997). The less direct study of Bulatov et al. (1989) and the preliminary study of Quandt and Hershberger (1996) are in satisfactory agreement with the preferred values.

There are now reasonably consistent measurements of the branching ratios up to ~1700 K. The value of $(k_2+k_3)/k$ remains virtually independent of temperature over the range covered by our recommendations but begins to rise steadily at temperatures in excess of 600K reaching a value of ~0.53 at 1700 K (Park and Lin, 1999).

References

- Andresen, P., Jacobs, A., Kleinermanns, C. and Wolfrum, J.: 19th Symp. (Int.) Combust., 11, 1982.
- Atakan, B., Jacobs, A., Wahl, W., Weller, R. and Wolfrum, J.: Chem. Phys. Lett. 155, 609, 1989.
- Atakan, B., Wolfrum, J. and Weller, R.: Ber. Bunsenges. Phys. Chem., 94, 1372, 1990.
- Bulatov, V. P., Ioffe, A. A., Lozovsky, V. A. and Sarkisov, O. M.: Chem. Phys. Lett., 162, 141, 1989.
- Diau, E. W., Yu, T., Wagner, M. A. G. and Lin, M. C.: J. Phys. Chem., 98, 4034, 1994.
- Dreier, T. and Wolfrum, J.: 20th Symp. (Int.) Combust., 695, 1985.
- Gehring, M., Hoyermann, K., Schacke, H. and Wolfrum, J.: 14th Symp. (Int.) Combust., 99, 1973.
- Gordon, S., Mulac, W. and Nangia, P.: J. Phys. Chem., 75, 2087, 1971.
- Hack, W., Schacke, H., Schroter, M. and Wagner, H. Gg.: 17th Symp. (Int.) Combust., 505, 1979.

Hancock, G., Lange, W., Lenzi, M. and Welge, K. H.: Chem. Phys. Lett., 33, 168, 1975.
Imamura, T. and Washida, N.: Laser Chem., 16, 43, 1995.
Lesclaux, R., Khe, P. V., Dezaudier, P. and Soullignac, J. C.: Chem. Phys. Lett., 35, 493, 1975.
Pagsberg, P., Sztuba, B., Ratajczak, E. and Sillesen, A.: Acta Chem. Scand., 45, 329, 1991.
Park, J. and Lin, M. C.: J. Phys. Chem., 100, 3317, 1996.
Park, J. and Lin, M. C.: J. Phys. Chem., 101, 5, 1997.
Park, J. and Lin, M. C.: J. Phys. Chem. A, 103, 8906, 1999.
Quandt, R. W. and Hershberger, J. F.: J. Phys. Chem., 100, 9407, 1996.
Sarkisov, O. M., Cheskis, S. G. and Sviridenkov, E. A.: Bull. Acad. Sci. USSR, Chem. Ser., 27, 2336, Eng. trans., 1978.
Silver, J. A. and Kolb, C. E.: J. Phys. Chem., 86, 3240, 1982.
Stephens, J. W., Morter, C. L., Farhat, S. K., Glass, G. P. and Curl, R. F.: J. Phys. Chem., 97, 8944, 1993.
Stief, L. J., Brobst, W. D., Nava, D. F., Barkowski, R. P. and Michael, J. V.: J. Chem. Soc. Faraday Trans., 2, 78, 1391, 1982.
Whyte, A. R. and Phillips, L. F.: Chem. Phys. Lett., 102, 451, 1983.
Wolf, M., Yang, D. L. and Durant, J. L.: J. Photochem. Photobiol., 80, 85, 1994.
Wolf, M., Yang, D. L. and Durant, J. L.: J. Phys. Chem. A, 101, 6243, 1997.
Yu, T. and Lin, M. C.: J. Phys. Chem., 98, 2105, 1994.