

**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.45  
NO<sub>x</sub>15**

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$$\Delta H^\circ(1) = -34.5 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(2) = -59.4 \text{ kJ mol}^{-1}$$

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

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(8.1 \pm 1.5) \times 10^{-12}$	296	Howard and Evenson, 1977	DF-LMR (a)
$3.3 \times 10^{-12} \exp[(254 \pm 50)/T]$	230-400	Howard, 1979	DF-LMR
$8.01 \times 10^{-12}$	299		
$5.7 \times 10^{-12} \exp[(130 \pm 270)/T]$	270-425	Leu, 1979	DF-RF (b)
$(9.8 \pm 1.6) \times 10^{-12}$	298		
$(1.1 \pm 0.3) \times 10^{-11}$	297	Glaschick-Schimpf et al., 1979	DF (c)
$(7.6 \pm 1.7) \times 10^{-12}$	293	Hack et al., 1980	DF-LMR/EPR (d)
$3.57 \times 10^{-12} \exp[(226 \pm 41)/T]$	423-1271	Howard, 1980	DF-LMR (e)
$7.6 \times 10^{-12}$	298*		
$(8.5 \pm 1.3) \times 10^{-12}$	297	Jemi-Alade and Thrush, 1990	DF-LMR (f)
$3.0 \times 10^{-12} \exp[(290 \pm 30)/T]$	206-295	Seeley et al., 1996	DF-CIMS (g)
$(8.0 \pm 0.5) \times 10^{-12}$	294		
$(9.6 \pm 1.5) \times 10^{-12}$	298	Bohn and Zetzsch, 1997	PLP-A (h)
$3.98 \times 10^{-12} \exp [(223 \pm 16.5)/T]$	183-300	Bardwell et al., 2003	DF-CIMS (i)
$(8.43 \pm 0.20) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(7.3 \pm 0.7) \times 10^{-12}$	298	Thrush and Wilkinson, 1981	DF-LMR (j)
<i>Branching ratios</i>			
$k_1/k > 0.95$	298	Bohn and Zetzsch, 1997	PLP-A (h)
$k_1/k = (1 \pm 0.05)$	183-300	Bardwell et al., 2003	DF-CIMS (i)
$k_2/k = 0.18\% \begin{smallmatrix} +0.04\% \\ -0.06\% \end{smallmatrix}$ (at 267 mbar N <sub>2</sub> )	298	Butkovskaya et al., 2005	DF-CIMS (k)
$k_2/k = 1.78 \times 10^{-5} \exp[(1374 \pm 63)/T]$ (at 267 mbar N <sub>2</sub> )	223-298 K		
$k_2/k = \{[(530 \pm 10)/T] + 8.53 \times 10^{-4} * P - (1.73 \pm 0.07)\}/100$ ( $P$ in mbar)	223-298	Butkovskaya et al., 2007	DF-CIMS (l)

**Comments**

- (a) [HO<sub>2</sub>] was monitored by LMR. An upper limit of  $4.5 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$  was established for the rate coefficient of the potentially pressure dependent third-order channel.

- (b) [HO] was monitored.
- (c) [HO<sub>2</sub>] was monitored in excess NO by the light emitted at 1.43 μm after energy transfer from O<sub>2</sub>(<sup>1</sup>Δ) produced by a microwave discharge in NO.
- (d) [HO<sub>2</sub>] was monitored by both LMR and EPR. The rate coefficient was observed to be pressure independent over the range 2.1-16.7 mbar (1.6-12.5 Torr).
- (e) The same technique was used as in similar earlier studies (Howard and Evenson, 1977; Howard 1979) from the same laboratory. The author combined the data from the present study with that at lower temperatures from the earlier studies to derive the expression  $k = 3.51 \times 10^{-12} \exp[(240 \pm 30)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the temperature range 232-1271 K. The rate coefficient for the reverse reaction was also measured over the range 425-1115 K and from the two studies a value of  $\Delta H^\circ(\text{HO}_2) = (10 \pm 2.5) \text{ kJ mol}^{-1}$  at 298 K was derived. The value of  $k$  at 298 K tabulated is obtained by extrapolation of the high temperature expression.
- (f) [HO<sub>2</sub>] was monitored by LMR and HO radicals were scavenged by C<sub>2</sub>F<sub>3</sub>Cl.  $k$  was observed to be independent of pressure over the range 1.1-17 mbar (0.8-13 Torr).
- (g) Turbulent flow technique was used. [HO<sub>2</sub>], [HO], and [NO<sub>2</sub>] were monitored by high pressure chemical ionisation mass-spectrometry.  $k$  was found to independent of pressure over the range 93-253 mbar N<sub>2</sub> (70-190 Torr) at 294 K.
- (h) Pulsed laser photolysis at 248 nm of H<sub>2</sub>O<sub>2</sub>/NO/O<sub>2</sub> mixtures at total pressures of 0.1, 0.5, and 1 bar. [OH] was monitored by time resolved CW UV laser absorption in the 308 nm region. The value of  $k$  was found to be independent of pressure. The rate of HO formation and HO<sub>2</sub> removal were found to be identical within experimental error indicating an HO yield > 95%.
- (i) Detection of HO, HO<sub>2</sub> and NO<sub>2</sub> using chemical ionisation with SF<sub>6</sub><sup>-</sup>. No pressure dependence of  $k$  between 75 and 220 Torr within the range of temperatures covered. Measurement of HO and NO<sub>2</sub> allowed derivation of the ≈ unity branching ratio for channel (1).
- (j) [HO] and [HO<sub>2</sub>] were monitored by LMR. The steady-state values of [HO] and [HO<sub>2</sub>] were measured in a system where their relative concentrations are related by  $[\text{HO}]/[\text{HO}_2] = k/k(\text{HO}+\text{H}_2\text{O}_2)$ .  $k$  was calculated using a rate coefficient of  $k(\text{HO}+\text{H}_2\text{O}_2) = 1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, 2008).
- (k) High pressure, turbulent flow tube study of HNO<sub>3</sub> formation. HNO<sub>3</sub> was detected by chemical ionisation using SF<sub>6</sub><sup>-</sup> ions and calibrated relative to its formation in the HO + NO<sub>2</sub> reaction. Unwanted formation of HNO<sub>3</sub> via the Reaction of HO with NO<sub>2</sub> (both from 1) was avoided by using excess NO or C<sub>6</sub>H<sub>12</sub> as HO scavenger. The yield of HNO<sub>3</sub> was found to increase in the presence of water vapour and with pressure between 133 and 533 Torr N<sub>2</sub>.
- (l)  $P$  in mbar. Same set-up as described in comment k, but with chemical amplification of the NO<sub>2</sub> and HNO<sub>3</sub> products via addition of CO and an extended study of the pressure dependence of the branching to HNO<sub>3</sub>. Also, HNO<sub>3</sub> and NO<sub>2</sub> signals were calibrated using reference standards rather than in-situ production.

### Preferred Values

$k = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 3.45 \times 10^{-12} \exp(270/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the range 200-400 K.

$k_2/k = \{[(530 \pm 10)/T] + 4.8 \times 10^{-4} * P - (1.73 \pm 0.07)\}/100$  ( $P$  in mbar)

### Reliability

$\Delta \log k = \pm 0.1$  at 298 K.

$\Delta(E/R) = \pm 100$  K.

$\Delta \log(k_2/k) = 0.3$

### *Comments on Preferred Values*

The preferred value of  $k$  at 298 K is the mean of the values of Howard and Evenson (1977), Howard (1979), Leu (1979), Hack et al. (1980), Jemi-Alade and Thrush (1990), Seeley et al. (1996), Bohn and Zetzsch (1997) and Bardwell et al. (2003). The temperature dependence was obtained by unweighted, least-squares fitting to the data reported by Howard (1979), Seeley et al. (1996) and Bardwell et al., (2003). The pre-exponential factor has been adjusted to fit the preferred value of  $k$  at 298 K.

Measurements of the branching ratios for HO formation (Bohn and Zetzsch, 1997), NO<sub>2</sub> formation (Bardwell et al. 2003) and HNO<sub>3</sub> formation (Butkovskaya *et al.*, 2005, 2007) show that the reaction proceeds almost entirely via channel (1) with less than 1% via a termolecular process to form HNO<sub>3</sub> under all atmospheric conditions. Although the possibility for HNO<sub>3</sub> formation via rearrangement of an initially formed HOONO adduct has been confirmed in the theoretical study of Zhang and Donahue (2006), further studies of the formation of HNO<sub>3</sub> in the title reaction are urgently required to reduce uncertainties.

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