IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet I.A3.45 NOx15

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$$HO_2 + NO \rightarrow NO_2 + HO \qquad (1)$$
$$HO_2 + NO + M \rightarrow HNO_3 + M \qquad (2)$$

$\Delta H°(1) = -34.5 \text{ kJ mol}^{-1}$
$\Delta H°(2) = -59.4 \text{ kJ mol}^{-1}$

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

k / cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(8.1 \pm 1.5) \times 10^{-12}$	296	Howard and Evenson, 1977	DF-LMR (a)
$3.3 \times 10^{-12} \exp[(254 \pm 50)/T]$	230-400	Howard, 1979	DF-LMR
8.01×10^{-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)
7.6×10^{-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		
Relative Rate Coefficients			
$(7.3 \pm 0.7) \times 10^{-12}$	298	Thrush and Wilkinson, 1981	DF-LMR (j)
Branching ratios			
$k_1/k > 0.95$	298	Bohn and Zetzsch, 1997	PLP-A (h)
$k_1/k = (1 \pm 0.05)$	183-300	Bardwell et al., 2003	DF-CIMS (i)
$k_2/k = 0.18\% \, ^{+0.04\%}_{-0.06\%}$ (at 267 mbar N$_2$)	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$_2$)	223-298 K		
$k_2/k = \{[(530 \pm 10)/T] + 8.53 \times 10^{-4} \times P - (1.73 \pm 0.07)\}/100$ (P in mbar)	223-298	Butkovskaya et al., 2007	DF-CIMS (l)

Comments

(a) [HO$_2$] was monitored by LMR. An upper limit of 4.5 x 10^{-30} cm^6 molecule^{-2} s^{-1} was established for the rate coefficient of the potentially pressure dependent third-order channel.

(b) [HO] was monitored.

(c) [HO$_2$] was monitored in excess NO by the light emitted at 1.43 μm after energy transfer from O$_2$($^1\Delta$) produced by a microwave discharge in NO.

(d) [HO$_2$] 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 x 10^{-12} exp[(240±30)/T] cm^3 molecule^{-1} 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 $\Delta H°$(HO$_2$) = (10±2.5) 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$_2$] was monitored by LMR and HO radicals were scavenged by C$_2$F$_3$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$_2$], [HO], and [NO$_2$] were monitored by high pressure chemical ionisation mass-spectrometry. k was found to independent of pressure over the range 93-253 mbar N$_2$ (70-190 Torr) at 294 K.

(h) Pulsed laser photolysis at 248 nm of H$_2$O$_2$/NO/O$_2$ 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$_2$ removal were found to be identical within experimental error indicating an HO yield > 95%.

(i) Detection of HO, HO$_2$ and NO$_2$ using chemical ionisation with SF$_6^-$. No pressure dependence of k between 75 and 220 Torr within the range of temperatures covered. Measurement of HO and NO$_2$ allowed derivation of the ≈ unity branching ratio for channel (1).

(j) [HO] and [HO$_2$] were monitored by LMR. The steady-state values of [HO] and [HO$_2$] were measured in a system where their relative concentrations are related by [HO]/[HO$_2$] = k/k(HO+H$_2$O$_2$). k was calculated using a rate coefficient of k(HO+H$_2$O$_2$) = 1.7 x 10^{-12} cm^3 molecule^{-1}s^{-1} (IUPAC, 2008).

(k) High pressure, turbulent flow tube study of HNO$_3$ formation. HNO$_3$ was detected by chemical ionisation using SF$_6^-$ ions and calibrated relative to its formation in the HO + NO$_2$ reaction. Unwanted formation of HNO$_3$ via the Reaction of HO with NO$_2$ (both from 1) was avoided by using excess NO or C$_6$H$_{12}$ as HO scavenger. The yield of HNO$_3$ was found to increase in the presence of water vapour and with pressure between 133 and 533 Torr N$_2$.

(l) *P* in mbar. Same set-up as described in comment k, but with chemical amplification of the NO$_2$ and HNO$_3$ products via addition of CO and an extended study of the pressure dependence of the branching to HNO$_3$. Also, HNO$_3$ and NO$_2$ signals were calibrated using reference standards rather than in-situ production.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.5×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	$3.45 \times 10^{-12} \exp(270/T)$	200-400
k_2/k	$\{[(530 \pm 10)/T] + 4.8 \times 10^{-4} \times P - (1.73 \pm 0.07)\}/100$ (P in mbar)	
Reliability		
$\Delta \log k$	± 0.1	298
$\Delta (E/\mathrm{R})$ /K	± 100	200-400
$\Delta\log(k_2/k)$	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_2 formation (Bardwell et al. 2003) and HNO_3 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_3 under all atmospheric conditions. Although the possibility for HNO_3 formation via rearrangement of an initially formed HOONO adduct has been confirmed in the theoretical study of Zhang and Donanhue (2006), further studies of the formation of HNO_3 in the title reaction are urgently required to reduce uncertainties. The yield of HNO_3 increases by added water, according to a factor $\{1 + 2 \times 10^{-17} [H_2O]\}$ at 298 K where $[H_2O]$ is in molecule cm^{-3} (Butkovskaya et al., 2009). This effect could be attributed to a chaperone mechanism involving HO_2-H_2O complexes or to large energy transfer efficiency of water as a collision partner of vibrationally excited HNO_3 (see Guide to the Gas Phase Data Sheets).

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