IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx2 I.A2.14

This datasheet last evaluated: 1st June 2012; last change in preferred values: 1st June 2012

$$H + O_2 + M \rightarrow HO_2 + M$$

$\Delta H° = -203.4$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$5.33 \times 10^{-32} (T/298)^{-1.77}$ [N_2]	226-298	Kurylo, 1972	FP-RF
$(5.46\pm0.7) \times 10^{-32} (T/298)^{-1.50}$ [N_2]	220-298	Wong and Davis, 1974	FP-RF
6.5×10^{-32} [N_2]	298	Cobos et al., 1985	PLP-UVA (a)
$6.2 \times 10^{-32} (T/300)^{-1.66}$ [N_2]	298-639	Hsu et al., 1989	DF-RF
$2.9 \times 10^{-33} \exp[(825\pm130)/T]$ [N_2]	298-580	Carleton et al., 1993	PLP-LIF/RA
4.6×10^{-32} [N_2]	298		
$3.9 \times 10^{-32} \exp[(600\pm1050)/T]$ [H_2O]	575-750		
$4.3 \times 10^{-32} (T/298)^{-1.232}$ [N_2]	296-700	Michael et al., 2002	LP-RA (b)
$3.1 \times 10^{-32} (T/298)^{-1.094}$ [O_2]			
$4.3 \times 10^{-32} (T/298)^{-1.23}$ [N_2]	300-900	Fernandes et al., 2008	LP-UVA (c)

Comments

(a) Measurements of the falloff curve between 1 and 200 bar, with determination of k_0, k_∞, and F_c.

(b) Laser photolysis-shock tube study with atomic resonance absorption detection of H-atoms. Measurements with M = N_2, Ar, Kr, Ne, and He at 30-260 mbar and room temperature; measurements with M = Ar, N_2, O_2 over the range 296-700 K.

(c) Measurements between 300 and 900 K, 1.5 and 950 bar, and with M = He, Ar, N_2 providing the major part of the falloff curve. Low pressure data extrapolate to the results from Michael et al. (2002). Previous falloff data by Cobos et al. (1985) and Hahn et al. (2004) are confirmed.

Preferred Values

$k = 1.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in 1 bar of N_2 at 300 K.

$k_0 = 4.3 \times 10^{-32} (T/300)^{-1.2}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 300-900 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 0.5$.

Comments on Preferred Values

The preferred values are from Michael et al. (2002) in close agreement with the data from Carleton et al. (1993). The high-pressure experiments from Fernandes et al. (2008) cover the major part of the falloff curves which is represented with $k_\infty = 9.5 \times 10^{-11}$ cm^3 molecule^{-1}s^{-1} and $F_c = 0.5$ independent of temperature. The detailed analysis reveals slight asymmetries of the falloff expression compared to that shown in the Introduction. It also suggests that k is smaller than the true k_0 by about 30 percent at 1 bar and 300 K. However, the falloff expression shown in the Introduction within experimental scatter can also be used. The most recent theoretical modellings (Harding et al., 2000; Troe, 2000; Michael et al., 2002; Fernandes et al., 2008; Sellevåg et al., 2008; Troe and Ushakov, 2008) well reproduce the experimental falloff curves.

High-pressure rate coefficients

Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	***Reference***	Technique/ Comments
Absolute Rate Coefficients			
$9.5 \times 10^{-11} (T/300)^{0.44}$	300-900	Fernandes et al., 2008	LP-UVA (a)

Comments

(a) See comment (c) for k_0.

Preferred Values

$k_\infty = 9.5 \times 10^{-11} (T/300)^{0.44}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 300-900 K.

$\Delta n = \pm 0.2$.

Comments on Preferred Values

The measurements of the major part of the falloff curves from Fernandes et al. (2008) are combined with the detailed modelling by Troe and Ushakov (2008) in close agreement with that by Sellevåg et al. (2008) which led to a theoretical k_∞ being 25 % lower than obtained by Troe and Ushakov (2008). Falloff curves are represented with $F_c = 0.5$ independent of the temperature over the range 300-900 K.

References

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