IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx10 I.A2.21

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$HO + HO + M \rightarrow H_2O_2 + M$

$\Delta H° = -210.7$ 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			
$(2.5 \pm 0.3) \times 10^{-31}$ [N_2]	300	Trainor and von Rosenberg, 1974	FP-RA
6.9×10^{-31} $(T/300)^{-0.8}$ [N_2]	253-353	Zellner et al., 1988	FP-RA
3.7×10^{-31} [He]	298	Forster et al., 1995	PLP-LIF (a)
9.0×10^{-31} $(T/300)^{-3.2}$ [N_2]	200-700	Fulle et al., 1996	PLP-LIF (b)

Comments

(a) Measurements were carried out with saturated LIF at total gas densities in the range 3.9×10^{19} to 3.4×10^{21} molecule cm^{-3}, covering the major part of the falloff curve. The apparent discrepancy between the results of Trainor and van Rosenberg (1974) and Zellner et al. (1988) disappears when the contribution of the reaction $HO + HO \rightarrow H_2O + O$ is taken into account.

(b) As comment (a). Only few points on the falloff curve were taken at temperatures different from 298 K such that a modelling of complete falloff curves was required to position the measurements. This modelling was done by Troe (2011) with theoretical $k_\infty = 3.8 \times 10^{-10}(T/300)^{-0.5}$ cm^{3}molecule^{-1}s^{-1} and $F_c = 0.43$ from Troe and Ushakov (2008). Both, the theoretical analyses from Sellevåg et al. (2009) and Troe (2011) suggest that the 200 K-data from Fulle et al. (1996) must be in error.

Preferred Values

$k = 6.2 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1} in 1 bar of N_2 at 300 K.
$k_0 = 9.0 \times 10^{-31}$ $(T/300)^{-3.2}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-700 K.

Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.
$\Delta n = \pm 0.5$.

Comments on Preferred Values

The analysis of the complete falloff curve by Forster et al. (1995) shows that the measurements from Trainor and van Rosenberg (1974), Zellner et al. (1988) and Forster et al. (1995) are all consistent. It is essential that falloff effects are taken into account, as noted in comment (b) and the comments on k_∞. Measurements of the rate of the reaction HO + HO $\rightarrow$ O + H_2O at 300 K and at pressure up to 10 mbar by Bahug and Macdonald (2007) gave a value of 2.7 x 10^{-12} cm^3 molecule-1 s^{-1}. This allows one to establish k_0 with better certainty.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.5 x 10^{-11}	253-353	Zellner et al., 1988	FP-RA
2.2 x 10^{-11}	298	Forster et al., 1995	PLP-LIF (a)
(2.6 ± 0.8) x 10^{-11}	200-400	Fulle et al., 1996	PLP-LIF (b)

Comments

(a) See comment (a) for k_0.

(b) See comment (a) for k_0. Measurements were carried out over the temperature range 200-700 K, indicating a negative temperature coefficient of k_∞, depending on uncertainties concerning the contribution from the reaction HO + HO $\rightarrow$ H_2O + O (see Bedjanian et al., 1999; Bahug and Macdonald, 2007).

Preferred Values

k_∞ = 3.9 x 10^{-11} $(T/300)^{-0.47}$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-1000 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200-400 K.

$\Delta n = \pm 0.2$.

Comments on Preferred Values

The measurements of limited parts of the falloff curves from Forster et al. (1995) and Fulle et al. (1996) are combined with the detailed theoretical modelling by Troe and Ushakov (2008) and Troe (2011). The theoretical analysis led to a value of F_c = 0.43 (± 0.02) nearly independent of the temperature between 300 and 1200 K. Minor asymmetries of the falloff expression were also suggested by the calculations, but can be neglected here (Troe, 2011).

References

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