IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx4

This data sheet updated: 2nd October 2001.

$O + HO_2 \rightarrow HO + O_2$

$\Delta H^\circ = -225.6$ kJ·mol^{-1}

Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$3.1 \times 10^{-11} \exp(200 \pm 28/T)$	229-372	Keyser, 1982[1]	DF-RF
$(6.1 \pm 0.4) \times 10^{-11}$	299		
$(5.4 \pm 0.9) \times 10^{-11}$	296	Sridharan, Qiu and Kaufman, 1982[2]	DF-RF
$(6.2 \pm 1.1) \times 10^{-11}$	298	Ravishankara, Wine and Nicovich, 1983[3]	PLP-RF
$(5.2 \pm 0.8) \times 10^{-11}$	300	Brune, Schwab and Anderson, 1983[4]	DF-RF
$2.91 \times 10^{-11} \exp[(228 \pm 75)/T]$	266-391	Nicovich and Wine, 1987[5]	PLP-RF
$(6.30 \pm 0.91) \times 10^{-11}$	298		

Preferred Values

$k = 5.8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 2.7 \times 10^{-11} \exp(224/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-400 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The recommended rate coefficient at 298 K is the mean of those obtained in the studies of Keyser,[1] Sridharan *et al*.,[2] Ravishankara *et al*.,[3] Brune *et al*.,[4] and Nicovich and Wine,[5] all of which are in excellent agreement. The temperature coefficient is the mean of the values obtained by Keyser[1] and Nicovich and Wine,[5] with the pre-exponential factor being based on this value of E/R and the recommended value of k at 298 K.

In the two most recent studies of the reaction mechanism, Keyser *et al*.[6] have shown that the yield of $O_2(^1\Sigma)$ from the reaction is $< 1 \times 10^{-2}$ per HO_2 radical removed and Sridharan *et al*.[7] have shown, in an ^{18}O labelling experiment, that the reaction proceeds via formation of an HO_2-^{18}O intermediate which

dissociates to HO and ^{18}OO by rupture of an O-O bond rather than via a four center intermediate yielding H^{18}O + OO.

References

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