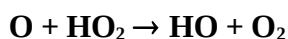


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx4

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet updated: 2nd October 2001.



$$\Delta H^\circ = -225.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$3.1 \times 10^{-11} \exp(200 \pm 28/T)$	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

$$k = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

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

Reliability

$$\Delta \log k = \pm 0.08 \text{ at } 298 \text{ K.}$$

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

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 Keyser¹ 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 $\text{O}_2(^1\Sigma)$ 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 $\text{HO}_2\text{-}^{18}\text{O}$ intermediate which

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

References

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