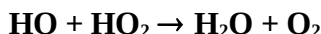


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx11

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This data sheet updated: 2nd October 2001.



$$\Delta H^\circ = -294.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.1^{+0.28}_{-0.39}) \times 10^{-10}$ (1 bar N ₂)	298	Braun, Hofzumahuas, and Stuhl, 1982 ¹	FP-UVA
$(1.1 \pm 0.28) \times 10^{-10}$	298	Dransfeld and Wagner, 1986 ²	DF-LMR
$4.8 \times 10^{-11} \exp[(250 \pm 50)/T]$	254-383	Keyser, 1988 ³	DF-RF
$(1.1 \pm 0.3) \times 10^{-10}$	299		
$(8.0^{+3.0}_{-2.0}) \times 10^{-11}$	298	Schwab, Brune, and Anderson, 1989 ⁴	DF-LMR
3.3×10^{-11}	1100	Hippler, Neunaber and	(a)
1.8×10^{-11}	1250	Troe, 1995 ⁵	
7.5×10^{-11}	1600		

Comments

- (a) Thermal decomposition of H₂O₂ in a shock tube. HO radicals were monitored by resonance absorption.

Preferred Values

$$k = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 4.8 \times 10^{-11} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{-}400 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.1 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

There has been some controversy over the effects of pressure on the rate coefficient for this reaction. Early discharge-flow measurements at low pressures of 1.3-13 mbar (1-10 Torr) consistently gave values of k approximately a factor of 2 lower than those obtained by other techniques at pressures close to atmospheric. The discharge-flow study of Keyser¹ appears to have resolved the problem. These results¹

suggest that the presence of small quantities of H and O atoms present in previous discharge-flow studies led to erroneously low values of k , and that there is no evidence for any variation in k with pressure. These findings¹ are accepted and we take the expression of Keyser¹ for k as our recommendation. There are a number of other studies in excellent agreement with the value recommended for k at 298 K, including relative rate studies of De More⁶ and Cox, Burrows and Wallington⁷ which demonstrate that $k(298\text{ K})$ is unaffected by H_2O pressure up to 21 mbar. The high temperature data suggest non-Arrhenius temperature dependence at temperatures above the range of our recommendation.

In another discharge-flow study, Keyser *et al.*,⁸ by monitoring the $\text{O}_2(\text{b}^1\Sigma) \rightarrow \text{X}(\text{b}^3\Sigma)$ transition at 762 nm, have shown that the yield of $\text{O}_2(\text{b}^1\Sigma)$ from the reaction is small ($<1 \times 10^{-3}$). The anomalous temperature dependence observed in the recent high temperature study² suggests a mechanism involving intermediate complex formation.

References

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