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

This data sheet updated: 2nd October 2001.

$HO + HO_2 \rightarrow H_2O + O_2$

$\Delta H^\circ = -294.6$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.1^{+0.28}_{-0.39}) \times 10^{-10}$ (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 Troe, 1995[5]	(a)
1.8×10^{-11}	1250		
7.5×10^{-11}	1600		

Comments

(a) Thermal decomposition of H_2O_2 in a shock tube. HO radicals were monitored by resonance absorption.

Preferred Values

$k = 1.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 4.8 \times 10^{-11} \exp(250/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 250-400 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.
$\Delta(E/R) = \pm 200$ 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 Keyser[1] appears to have resolved the problem. These results[1] 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 findings[1] are accepted and we take the expression of Keyser[1] 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 More[6] and Cox, Burrows and Wallington[7] which demonstrate that k(298 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 $O_2(b^1\Sigma) \rightarrow X(^3\Sigma)$ transition at 762 nm, have shown that the yield of $O_2(b^1\Sigma)$ from the reaction is small ($<1 \times 10^{-3}$). The anomalous temperature dependence observed in the recent high temperature study[2] suggests a mechanism involving intermediate complex formation.

References

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