IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx1

This data sheet updated: 2nd October 2001.

$$\mathbf{H + HO_2 \rightarrow H_2 + O_2} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow 2HO} \quad \mathbf{(2)}$$
$$\mathbf{\rightarrow H_2O + O} \quad \mathbf{(3)}$$

$\Delta H^\circ(1) = -232.6$ kJ·mol^{-1}
$\Delta H^\circ(2) = -156.2$ kJ·mol^{-1}
$\Delta H^\circ(3) = -225.2$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(7.4 \pm 1.2) \times 10^{-11}$	245-300	Sridharan, Qiu and Kaufman, 1982[1]	DF-RF
$(8.7 \pm 1.5) \times 10^{-11}$	245-300	Keyser, 1986[2]	DF-RF
Branching Ratios			
$k_1/k = 0.08 \pm 0.04$ $k_2/k = 0.90 \pm 0.04$ $k_3/k = 0.02 \pm 0.04$	245-300	Keyser, 1986[2]	

Preferred Values

$k = 8.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245-300 K.
$k_1 = 5.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245-300 K.
$k_2 = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245-300 K.
$k_3 = 2.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, independent of temperature over the range 245-300 K.

Reliability

$\Delta \log k = \pm 0.1$ over the temperature range 245-300 K.
$\Delta(E/R) = \pm 200$ K.
$\Delta \log k_1 = \pm 0.5$ over the temperature range 245-300 K.
$\Delta \log k_2 = \pm 0.1$ over the temperature range 245-300 K.
$\Delta \log k_3 = \pm 0.5$ over the temperature range 245-300 K.

Comments on Preferred Values

The study of Keyser[2] is the most detailed to date. Several species were monitored and the possible effects of side reactions were carefully analyzed. Values obtained for the overall rate coefficient and the branching ratios agree with the values obtained by Sridharan *et al*.[1] who used a similar technique. The recommended values for k and the branching ratios are the means of the values from these two studies.[1,2] In both cases,[1,2] k_1/k was not measured directly but obtained by difference. A direct measurement of this branching ratio is desirable.

The yield of $O_2(^1\Sigma)$ has been measured by Hislop and Wayne,[4] Keyser *et al*.,[5] and Michelangeli *et al*.[2] who report values of $(2.8 \pm 1.3) \times 10^{-4}$, $<8 \times 10^{-3}$ and $<2.1 \times 10^{-2}$, respectively.

Keyser[2] observed no effect of temperature on the rate coefficient k over the small range studied. This suggests that the value of $k_2 = 3.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 349 K obtained by Pagsberg *et al*.[7] is too low or there is a substantial negative temperature coefficient. We provisionally recommend $E/R = 0$ but only over the temperature range 245-300 K.

References

1 U. C. Sridharan, L. X. Qiu, and F. Kaufman, J. Phys. Chem. **86**, 4569 (1982).
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5 L. F. Keyser, K. Y. Choo, and M. T. Leu, Int. J. Chem. Kinet. **17**, 1169 (1985).
6 D. V. Michelangeli, K.-Y. Choo, and M.-T. Leu, Int. J. Chem. Kinet. **20**, 915 (1988).
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