

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx7

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 last evaluated: 12 July 2007; revision of preferred value.



$$\Delta H^\circ(1) = -120.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -197.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -189.7 \text{ kJ}\cdot\text{mol}^{-1}$$

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.3 \pm 0.4) \times 10^{-10}$	253-353	Streit et al., 1976	PLP (a)
$(1.95 \pm 0.3) \times 10^{-10}$	295	Amimoto et al., 1979	PLP-RA (b)
$(2.6 \pm 0.5) \times 10^{-10}$	300	Lee and Slanger, 1979	PLP (c)
$k_1 = (2.02 \pm 0.41) \times 10^{-10}$	298	Gericke and Comes, 1981	PLP-RA
$(1.95 \pm 0.2) \times 10^{-10}$	298	Wine and Ravishankara, 1981	PLP-RF (d)
$(2.07 \pm 0.18) \times 10^{-10}$	295	Takahashi et al., 2005	PLP-VUV/LIF (e)
$(2.1 \pm 0.3) \times 10^{-10}$	295	Carl	PLP-CL (f)
<i>Branching Ratios</i>			
$k_2/k = 0.01^{(+0.005}_{-0.01)}$	298	Zellner et al., 1980	FP-RA (g)
$k_3/k = 0.049 \pm 0.032$	298 ± 2	Wine and Ravishankara, 1982	PLP-RF (d)
$k_2/k = 0.006^{(+0.007}_{-0.006)}$	298	Gliniski and Birks, 1985	(h)
$k_3/k = 0.02 \pm 0.01$	295	Takahashi et al., 1996	PLP-VUV/LIF (i)
$k_3/k < 0.003$	295	Carl	PLP-CL (f)

Comments

- O(¹D) atoms were monitored by time-resolved emission from the O(¹D) → O(³P) transition at 630 nm.
- O(³P) atoms were measured by resonance absorption.
- O(¹D) atoms were measured by emission at 630 nm and, indirectly by O₂(¹Σ_g⁺ → ³Σ_g⁻) emission at 720 nm.
- O(³P) atom formation was monitored by RF.
- O(¹D) atoms were produced by 193 nm photolysis of N₂O, and monitored by on-resonant VUV LIF at λ = 115.2 nm.
- O(¹D) atoms were produced by photolysis of N₂O at 193 nm and monitored by time-resolved emission at 431 nm from CH(A²Δ), produced in the reaction of O(¹D) with C₂H, formed concurrently by photolysis of C₂H₂. *k* determined directly from first order decay of O(¹D) in excess H₂O. Residual emission from reaction of O(³P) with C₂H allows any quenching to be determined with high sensitivity.

- (g) The H₂ yield was measured by GC, together with the OH radical concentration by resonance absorption.
- (h) Photolysis of O₃-H₂O mixtures at 253.7 nm. The H₂ yield was measured by GC.
- (i) O(¹D) atoms were produced by photolysis of N₂O at 193 nm. O(¹D) and O(³P) monitored by VUV – LIF.

Preferred Values

$k = 2.14 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200-350 K.

$k_1 = 2.14 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 < 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_3 < 6.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

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

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

$\Delta \log k_1 = \pm 0.1$ at 298 K.

Comments on Preferred Values

The new studies of Takahashi et al. (2005) and Carl (2005) provide confirmation of the earlier experimental studies and are incorporated into the analysis. The preferred value for k is a mean of the values of Streit et al. (1976), Amimoto et al. (1979), Lee and Slanger (1979), Gericke and Comes (1981), Wine and Ravishankara (1981), Takahashi et al. (2005), and Carl (2005), all of which are in good agreement. Our recommendation for k_2/k is based on the data of Zellner et al. (1980) and Glinski and Birks (1985). For k_3/k we recommend the upper limit from Carl (2005), which was determined by a more sensitive method than used by Zellner et al. (1980), Wine and Ravishankara (1982), and Takahashi et al. (1996).

References

- Amimoto, S. T., Force, A. P., Gulotty, Jr., R. G., and Wiesenfeld, J. R.: J. Chem. Phys. 71, 3640, 1979.
- Carl, S. A.: Phys. Chem. Chem. Phys., 7, 4051, 2005.
- Gericke, K. H. and Comes, F. J.: Chem. Phys. Lett. 81, 218, 1981.
- Glinski, R. J. and Birks, J. W.: J. Phys. Chem. 89, 3449, 1985.
- Lee, L. C. and Slanger, T. G.: Geophys. Res. Lett. 6, 165, 1979.
- Streit, G. E., Howard, C. J., Schmeltekopf, A. L., Davidson, J. A., and Schiff, H. I.: J. Chem. Phys. 65, 4761, 1976.
- Takahashi, K., Takeuchi, Y., and Matsumi, Y.: Chem Phys. Lett. 410, 196, 2005.
- Takahashi, K., Wada, R., Matsumi, Y., and Kawasaki, M.: J. Phys. Chem., 100, 10145, 1996.
- Wine, P. H. and Ravishankara, A. R.: Chem. Phys. 69, 365, 1982.
- Wine, P. H. and Ravishankara, A. R.: Chem. Phys. Lett. 77, 103, 1981.
- Zellner, R., Wagner, G., and Himme, B.: J. Phys. Chem. 84, 3196, 1980.