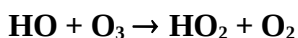


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx13

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.



$$\Delta H^\circ = -167.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

| $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Temp./K | Reference | Technique/ Comments |
|--|---------|---|------------------------|
| <i>Absolute Rate Coefficients</i> | | | |
| $1.3 \times 10^{-12} \exp(-956/T)$ | 220-450 | Anderson and Kaufman, 1973 ¹ | DF-RF |
| 5.3×10^{-14} | 298 | | |
| $(6.5 \pm 1.0) \times 10^{-14}$ | 298 | Kurylo, 1973 ² | FP-RF |
| $1.82 \times 10^{-12} \exp[-(930 \pm 50)/T]$ | 238-357 | Ravishankara, Wine and Langford, 1979 ³ | PLP-RF |
| $(7.96 \pm 0.39) \times 10^{-14}$ | 298 | | |
| $(6.5 \pm 1.0) \times 10^{-14}$ | 300 | Zahniser and Howard, 1980 ⁴ | DF-LMR (a) |
| $1.52 \times 10^{-12} \exp[-(890 \pm 60)/T]$ | 240-295 | Smith <i>et al.</i> , 1984 ⁵ | FP-RF (b) |
| $(7.46 \pm 0.16) \times 10^{-14}$ | 295 | | |
| $2.26 \times 10^{-12} \exp[-(976 \pm 50)/T]$ | 190-315 | Nizkorodov <i>et al.</i> , 2000 ⁶ | PLP-AS (c) |
| <i>Relative Rate Coefficients</i> | | | |
| $(7.0 \pm 0.8) \times 10^{-14}$ | 300 | Zahniser and Howard, 1980 ⁴ | DF-LMR (a) |

Comments

- Discharge flow system used. HO radicals were generated from the H + NO₂ reaction and monitored by LMR.
- Flash photolysis of O₃-H₂O mixtures in 1 atm He. HO radicals were monitored by resonance fluorescence.
- Pulsed laser photolysis of O₃-H₂O mixtures with OH detection by infrared laser spectroscopy. The sum of rate coefficients for OH + O₃ and HO₂ + O₃ reaction ($k + k(\text{HO}_2 + \text{O}_3)$) was measured density and was described accurately by the Arrhenius expression over the entire temperature range. If the recommended expression for $k(\text{HO}_2 + \text{O}_3)$ from this evaluation is and the resultant values of k are in excellent agreement with those from Ravishankara *et al.*³ and Smith *et al.*⁵
- Discharge flow system used. HO radicals were generated from the H + NO₂ and H + O₃ reactions, and HO₂ radicals were generated from the reaction H + O₂ + M. HO₂ and HO radicals were monitored by LMR. A rate coefficient ratio of $k/k(\text{HO}_2 + \text{O}_3) = 35 \pm 4$ (average of three systems

studied) was obtained and placed on an absolute basis by use of $k(\text{HO}_2 + \text{O}_3) = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (this evaluation).

Preferred Values

$k = 7.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.70 \times 10^{-12} \exp(-940/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-450 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

There is good agreement among the various studies¹⁻⁵ for the rate coefficient k . The recommended value for E/R is the mean of the values of Ravishankara *et al.*³, Smith *et al.*⁵ and Nizkorodov *et al.*⁶ except that the Anderson and Kaufman¹ study gave a somewhat slower rate, probably due to OH regeneration from the $\text{HO}_2 + \text{NO}$ reaction which has been revised upwards since this early study. The recommended 298 K rate coefficient is the mean of the values from these studies^{1,3,5} plus those of Kurylo² and Zahniser and Howard⁴. The pre-exponential factor is derived from the recommended values of E/R and the 298 K rate coefficient.

References

- ¹ J. G. Anderson and F. Kaufman, *Chem. Phys. Lett.* **19**, 483 (1973).
- ² M. J. Kurylo, *Chem. Phys. Lett.* **23**, 467 (1973).
- ³ A. R. Ravishankara, P. H. Wine, and A. O. Langford, *J. Chem. Phys.* **70**, 984 (1979).
- ⁴ M. S. Zahniser and C. J. Howard, *J. Chem. Phys.* **73**, 1620 (1980).
- ⁵ C. A. Smith, L. T. Molina, J. J. Lamb, and M. J. Molina, *Int. J. Chem. Kinet.* **16**, 41 (1984).
- ⁶ S. A. Nizkorodov, W. W. Harper, B. W. Blackman, D. J. Nesbitt, *J. Phys. Chem. A* **104**, 3964 (2000).