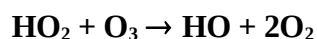


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx15

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This data sheet updated: 2nd October 2001.



$$\Delta H^\circ = -118 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-14} \exp[(-580 \pm 100)/T]$	245-365	Zahniser and Howard, 1980 ¹	DF-LMR
2.0×10^{-15}	298		
$1.8 \times 10^{-14} \exp[(-680 \pm 148)/T]$	253-400	Wang, Suto and Lee, 1988 ²	DF (a)
$(1.3 \pm 0.3) \times 10^{-15}$	233-253		
$(1.9 \pm 0.3) \times 10^{-15}$	298		
$(103 \pm 51) \exp[-(1323 \pm 160)/T + 0.88] \times 10^{-15}$	197-297	Herndon <i>et al.</i> , 2001 ³	DF-TOLAS (b)
$(2.0 \pm 0.2) \times 10^{-15}$	295		

Comments

- HO₂ radicals were monitored by photodissociation at 147 nm and HO radicals were detected by HO(A-X) fluorescence at 310 nm.
- Used turbulent flow reactor with pressure range 80-175 Torr. H¹⁸O₂ monitored in excess ¹⁶O₃ to avoid reformation of reactant.

Preferred Values

$$k = 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.03 \times 10^{-16} (T/300)^{4.57} \exp(693/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 250\text{-}340 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = {}^{+500 \text{ K}}_{-100 \text{ K}}$$

Comments on Preferred Values

A number of studies¹⁻⁵ are in close agreement on the value of k at 298 K, but there is some divergence concerning the temperature coefficient of k . The studies of Sinha *et al.*⁵, Wang *et al.*² and Herndon *et al.*³ agree that k exhibits non-Arrhenius behavior which is particularly noticeable at $T < 250$ K. There are experimental difficulties in working at these temperatures. At higher temperature the results

from these two studies^{2,5} also diverge, giving values of k differing by nearly a factor of 2 at 400 K. We therefore limit the temperature range of our recommendation to $T < 340$ K until this discrepancy is resolved.

The preferred value at 298 K is a mean of the results of Zahniser and Howard¹, Wang *et al.*², Herndon *et al.*³ and Sinha *et al.*⁵ The comparative dependent expression is obtained by putting an expression form $AT^n \exp(E/RT)$ to the data of Herndon *et al.*³ at $T \leq 297$ K and the averaged data of Zahniser¹, Wang² and Sinha⁵ at $298 < T < 340$ K.

Isotopic exchange studies⁷ of the reaction between $H^{18}O_2$ and O_3 show that at room temperatures the reaction proceeds almost exclusively by H atom transfer rather than by transfer of an oxygen atom. Moreover there is little change in this finding with temperature over the range 226-355 K,⁷ indicating that any curvature on the Arrhenius plot cannot be due to competition between these two reaction paths.

References

- ¹ M. S. Zahniser and C. J. Howard, *J. Chem. Phys.* **73**, 1620 (1980).
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- ⁶ D. D. Nelson, Jr. and M. S. Zahniser, *J. Phys. Chem.* **98**, 2101 (1994).