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

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$HO_2 + O_3 \rightarrow HO + 2O_2$

$\Delta H^\circ = -118$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.4 \times 10^{-14} \exp[(-580 \pm 100)/T]$	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 *et al*., 2001[3]	DF-TOLAS (b)
$(2.0 \pm 0.2) \times 10^{-15}$	295		

Comments

(a) HO_2 radicals were monitored by photodissociation at 147 nm and HO radicals were detected by HO(A-X) fluorescence at 310 nm.

(b) Used turbulent flow reactor with pressure range 80-175 Torr. $H^{18}O_2$ monitored in excess $^{16}O_3$ to avoid reformation of reactant.

Preferred Values

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

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

Reliability

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

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

Comments on Preferred Values

A number of studies[1-5] 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 Howard[1], 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 ≤ 297 K and the averaged data of Zahniser[1], Wang[2] and Sinha[5] at 298 < T < 340 K.

Isotopic exchange studies[7] 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

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