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

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$HO + O_3 \rightarrow HO_2 + O_2$

$\Delta H^\circ = -167.4$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.3 \times 10^{-12} \exp(-956/T)$	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	PLP-RF
$(7.96 \pm 0.39) \times 10^{-14}$	298	Langford, 1979[3]	
$(6.5 \pm 1.0) \times 10^{-14}$	300	Zahniser and Howard, 1980[4]	DF-LMR (a)
$1.52 \times 10^{-12} \exp[-(890 \pm 60)/T]$	240-295	Smith *et al*., 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 *et al.*, 2000[6]	PLP-AS (c)
Relative Rate Coefficients			
$(7.0 \pm 0.8) \times 10^{-14}$	300	Zahniser and Howard, 1980[4]	DF-LMR (a)

Comments

(a) Discharge flow system used. HO radicals were generated from the H + NO_2 reaction and monitored by LMR.

(b) Flash photolysis of O_3-H_2O mixtures in 1 atm He. HO radicals were monitored by resonance fluorescence.

(c) Pulsed laser photolysis of O_3-H_2O mixtures with OH detection by infrared laser spectroscopy. The sum of rate coefficients for OH + O_3 and HO_2 + O_3 reaction (k + $k(HO_2 + O_3)$ was measured density and was described accurately by the Arrhenius expression over the entire temperature range. If the recommended expression for $k(HO_2 + O_3)$ 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]

(d) Discharge flow system used. HO radicals were generated from the H + NO_2 and H + O_3 reactions, and HO_2 radicals were generated from the reaction H + O_2 + M. HO_2 and HO radicals were monitored by LMR. A rate coefficient ratio of $k/k(HO_2 + O_3) = 35 \pm 4$ (average of three systems

studied) was obtained and placed on an absolute basis by use of $k(HO_2 + O_3) = 2.0 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 300 K (this evaluation).

Preferred Values

$k = 7.3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.70 \times 10^{-12} \exp(-940/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-450 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

There is good agreement among the various studies[1-5] 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 Kaufman[1] study gave a somewhat slower rate, probably due to OH regeneration from the HO_2 + 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 Kurylo[2] and Zahniser and Howard[4]. The pre-exponential factor is derived from the recommended values of E/R and the 298 K rate coefficient.

References

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5 C. A. Smith, L. T. Molina, J. J. Lamb, and M. J. Molina, Int. J. Chem. Kinet. **16**, 41 (1984).
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