

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oClOx89; VII.A2.4

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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.65) \times 10^{-12} \exp(-483/T)$	277-461	Jeong et al. (1984)	DF-RF (a)
$(3.18 \pm 0.20) \times 10^{-13}$	295		
$(1.63 \pm 0.22) \times 10^{-13} (T/300)^{2.64} \times \exp((70 \pm 55)/T)$	295-850	Taylor et al. (1992)	PLP-LIF (b)
$(1.84 \pm 0.07) \times 10^{-13}$	295		

Comments

- (a) HO radicals generated by the reaction of H atoms with NO₂ in typically 3 Torr (4 mbar) of diluent gas (probably helium, but not specified).
- (b) HO radicals were produced by the 193 nm photolysis of N₂O to give O(¹D) atoms in the presence of H₂O vapor in 740 ± 10 Torr (986 ± 13 mbar) of helium diluent.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.9×10^{-13}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.55 \times 10^{-12} \exp(-868/T)$	290-360
<i>Reliability</i>		
$\Delta \log k$	0.15	298
$\Delta E/R$	± 300	

Comments on Preferred Values

The rate coefficients reported by Jeong et al. (1984) and Taylor et al. (1992) at temperatures of 400-460 K are in agreement. However for temperature below 400 K there is a significant discrepancy between the results from the two studies. The rate coefficients reported by Jeong et al. (1984) are greater than those from Taylor et al. (1992) with the discrepancy increasing with decreasing temperature. Such a trend suggests that reactive impurities may have influenced the rate coefficients reported by Jeong et al. (1984). Interestingly, as noted by Taylor et al. (1992), the reactant purification procedures and the resulting quoted purities (99.9%) were nominally the same in both studies. Possible olefinic impurities such as CH₂=CCl₂ and CHCl=CHCl are approximately two orders of magnitude more reactive than CH₂ClCHCl₂ towards HO radicals (Yamada et al., 2001). The presence of such impurities in the samples used by Jeong et al. (1984) is a likely explanation of the discrepancy between the results from Jeong et al. (1984) and Taylor et al. (1992) near room temperature. Fitting the three

parameter equation $k = CT^2 \exp(-D/T)$ to the data from Taylor et al. (1992) gives $k(\text{OH} + \text{CH}_2\text{ClCHCl}_2) = 4.41 \times 10^{-18} T^2 \exp(-208/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Centering this expression at 330 K with $A = C e^2 T^2$ and $B = D + 2T$ gives $k(\text{OH} + \text{CH}_2\text{ClCHCl}_2) = 3.55 \times 10^{-12} \exp(-868/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. At 298 K this expression gives $k(\text{OH} + \text{CH}_2\text{ClCHCl}_2) = 1.93 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

References

- Jeong, K.-M., Hsu, K.-J., Jeffries, J.B., and Kaufman, F.: J. Phys. Chem., 88, 1222, 1984.
Taylor, P.H., Jiang, Z., and Dellinger, B.: J. Phys. Chem., 96, 1293, 1992.
Yamada, T., El-Sinawi, A., Siraj, M., Taylor, P.H., Peng, J., Hu, X., Marshall, P.: J. Phys. Chem. A, 105, 7588, 2001.

