

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx53

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This data sheet last evaluated: June 2015; last change in preferred values: November 2003.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.24 \pm 0.19) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$6.13 \times 10^{-13} \exp[-(1244 \pm 90)/T]$	250-375	Watson et al., 1979	FP-RF
$(9.4 \pm 0.3) \times 10^{-15}$	301		
$4.45 \times 10^{-13} \exp[-(1150 \pm 60)/T]$	210-349	Gierczak et al., 1991	DF-LMR/FP-RF
$(9.44 \pm 0.75) \times 10^{-15}$	298		(a)
$7.72 \times 10^{-20} T^{2.35} \exp[-(458 \pm 30)/T]$	297-867	Yamada et al., 2000	PLP-LIF
$(1.08 \pm 0.16) \times 10^{-14}$	297		
<i>Relative Rate Coefficients</i>			
$6.48 \times 10^{-21} T^{2.82} \exp[-(620 \pm 40)/T]$	298-366	Hsu and DeMore, 1995	RR (b,c)
7.68×10^{-15}	298		
$8.28 \times 10^{-19} T^2 \exp[-(674 \pm 52)/T]$	298-356	Hsu and DeMore, 1995	RR (b,d)
7.66×10^{-15}	298		

Comments

- (a) Rate coefficients were measured over the temperature range 210-425 K. Those at the highest temperatures (400 K and 425 K) are higher than extrapolation of the linear Arrhenius plot obtained from the 210-349 K data.
- (b) HO radicals were generated by the photolysis of H₂O at 185 nm or from O₃-H₂O mixtures in the UV, in H₂O (or H₂O-O₃)-CHFClCF₃-CH₄ (or CHF₂CHF₂)-O₂-N₂ mixtures. The concentrations of CHFClCF₃ and CH₄ (or CHF₂CHF₂) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CHFClCF}_3)/k(\text{HO} + \text{CH}_4) = (0.35 \pm 0.04) \exp[(367 \pm 40)/T]$ and $k(\text{HO} + \text{CHFClCF}_3)/k(\text{HO} + \text{CHF}_2\text{CHF}_2) = (0.46 \pm 0.07) \exp[(300 \pm 52)/T]$ are placed on an absolute basis using $k(\text{HO} + \text{CH}_4) = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006) and $k(\text{HO} + \text{CHF}_2\text{CHF}_2) = 1.80 \times 10^{-18} T^2 \exp(-974/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008).
- (c) Relative to $k(\text{HO} + \text{CH}_4)$.
- (d) Relative to $k(\text{HO} + \text{CHF}_2\text{CHF}_2)$.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	8.7×10^{-15}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.5 \times 10^{-13} \exp(-1105/T)$	210-300

Reliability

$\Delta \log k$	± 0.20	298
$\Delta(E/R)$	± 300	210-300

Comments on Preferred Values

At room temperature, the absolute and relative rate coefficients of Howard and Evenson (1976), Watson et al. (1979), Gierczak et al. (1991), Hsu and DeMore (1995) and Yamada et al. (2000) range over a factor of ~ 1.6 , with the absolute rate coefficient of Howard and Evenson (1976) being the highest, possibly due to the presence of reactive impurities. The absolute rate coefficients of Yamada et al. (2000) are slightly higher than those of Watson et al. (1979) and Gierczak et al. (1991) over the temperature ranges common to these studies (295-375 K and 295-425 K, respectively), with the differences decreasing as the temperature increases [and with the 425 K rate coefficient of Gierczak et al. (1991) being very consistent with the 415 K and 438 K rate coefficients of Yamada et al. (2000)]. The relative rate coefficients of Hsu and DeMore (1995), using both CH_4 and CHF_2CHF_2 as reference compounds, are consistently lower than the absolute rate coefficients of Watson et al. (1979) and Gierczak et al. (1991), by ~ 15 -20% at 298 K. The rate coefficients of Watson et al. (1979), Gierczak et al. (1991) and Hsu and DeMore (1995) have been fitted to the three parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 7.48 \times 10^{-19} T^2 \exp(-606/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 210-425 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K and is derived from the three parameter equation with $A = C e^2 T^2$ and $B = D + 2T$. The temperature dependence obtained by Yamada et al. (2000) is in good agreement with the recommendation, corresponding to a value of B in an Arrhenius expression centered at 250 K of $B = 1046 \text{ K}$.

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: *Atmos. Chem. Phys.*, 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Wallington, T. J.: *Atmos. Chem. Phys.*, 8, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>
- Gierczak, T., Talukdar, R., Vaghjiani, G. L., Lovejoy, E. R. and Ravishankara, A. R.: *J. Geophys. Res.*, 96, 5001, 1991.
- Howard, C. J. and Evenson, K. M.: *J. Chem. Phys.*, 64, 4303, 1976.
- Hsu, K.-J. and DeMore, W. B.: *J. Phys. Chem.*, 99, 1235, 1995.
- Watson, R. T., Ravishankara, A. R., Machado, G., Wagner, S. and Davis, D. D.: *Int. J. Chem. Kinet.*, 11, 187, 1979.
- Yamada, T., Fang, T. D., Taylor, P. H. and Berry, R. J.: *J. Phys. Chem. A*, 104, 5013, 2000.

