

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx54

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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>			
$(2.84 \pm 0.43) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$1.24 \times 10^{-12} \exp[-(1056 \pm 70)/T]$	245-375	Watson et al., 1979	FP-RF (a)
$(3.6 \pm 0.4) \times 10^{-14}$	298		
$1.12 \times 10^{-12} \exp[-(1000 \pm 100)/T]$	293-429	Clyne and Holt, 1979	DF-RF
$(3.86 \pm 0.19) \times 10^{-14}$	293		
$1.1 \times 10^{-12} \exp[-(1040 \pm 140)/T]$	270-400	Liu et al., 1990	FP-RF
$(3.52 \pm 0.28) \times 10^{-14}$	298		
$1.18 \times 10^{-12} \exp[-(900 \pm 150)/T]$	232-426	Brown et al., 1990	DF-RF
$(5.9 \pm 0.6) \times 10^{-14}$	303		
$6.5 \times 10^{-13} \exp[-(840 \pm 40)/T]$	213-322	Gierczak et al., 1991	DF-LMR/ FP-RF (b)
$(3.69 \pm 0.37) \times 10^{-14}$	298		
$1.1 \times 10^{-12} \exp[-(940 \pm 200)/T]$	295-385	Nielsen, 1991	PR-RA
$(4.3 \pm 1.0) \times 10^{-14}$	295		
$2.20 \times 10^{-19} T^{2.88} \exp[-(226 \pm 51)/T]$	296-866	Yamada et al., 2000	PLP-LIF
$(3.67 \pm 0.24) \times 10^{-14}$	296.3		
<i>Relative Rate Coefficients</i>			
$7.84 \times 10^{-19} T^2 \exp[-(215 \pm 36)/T]$	298-359	Hsu and DeMore, 1995	RR (c)
$3.38 \times 10^{-14}$	298		

### Comments

- (a) The sample of  $\text{CHCl}_2\text{CF}_3$  used was shown by GC to contain 0.0227% of  $\text{C}_4\text{F}_5\text{HCl}_2$  and 0.0021% of  $\text{C}_4\text{F}_6\text{HCl}$ . After correction for possible contributions to the observed OH radical decays from these measured impurities, assuming a rate coefficient for reaction of the halogenated alkene impurities with HO radicals of  $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  independent of temperature, then the rate coefficient was estimated to be  $1.4 \times 10^{-12} \exp(-1102/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range of 245-375 K, with a rate coefficient at 298 K of  $3.49 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- (b) Rate coefficients were measured over the temperature range 213-380 K.
- (c) HO radicals were generated by the photolysis of  $\text{H}_2\text{O}$  at 185 nm, or  $\text{O}_3$  at 254 nm in the presence of  $\text{H}_2\text{O}$ , in  $\text{H}_2\text{O}$  (or  $\text{H}_2\text{O}-\text{O}_3$ )- $\text{CHCl}_2\text{CF}_3$ - $\text{CH}_3\text{CHF}_2$ - $\text{O}_2$ - $\text{N}_2$  mixtures. The concentrations of  $\text{CHCl}_2\text{CF}_3$  and  $\text{CH}_3\text{CHF}_2$  were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHCl}_2\text{CF}_3)/k(\text{HO} + \text{CH}_3\text{CHF}_2) = (0.28 \pm 0.03) \exp[(365 \pm 36)/T]$  is placed on an absolute basis using  $k(\text{HO} + \text{CH}_3\text{CHF}_2) = 2.80 \times 10^{-18} T^2 \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson et al., 2008).

## Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.6 \times 10^{-14}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$6.6 \times 10^{-13} \exp(-870/T)$	210-300
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.10$	298
$\Delta(E/R)$	$\pm 200$	210-300

### *Comments on Preferred Values*

The absolute rate coefficients of Howard and Evenson (1976), Watson et al. (1979) [corrected for impurities; see Comment (a)], Clyne and Holt (1979), Liu et al. (1990), Gierczak et al. (1991) and Yamada et al. (2000) and the relative rate coefficients of Hsu and DeMore (1995) are in reasonable agreement, but are significantly lower than the absolute rate coefficients of Brown et al. (1990) and Nielsen (1991). The absolute rate coefficients of Yamada et al. (2000) tend to be slightly higher than those of Watson et al. (1979) [corrected for impurities], Liu et al. (1990) and Gierczak et al. (1991), while the relative rate coefficients of Hsu and DeMore (1995) tend to be slightly lower. Although in this case the data of Clyne and Holt (1979) are in good agreement with the studies of Howard and Evenson (1976), Watson et al. (1979), Liu et al. (1990), Gierczak et al. (1991) and Yamada et al. (2000), because of discrepancies between their data and those of other investigators for most other haloalkanes studied, the data of Clyne and Holt (1979) have not been used in the evaluation. The rate coefficients of Howard and Evenson (1976), Watson et al. (1979) [corrected for impurities; see Comment (a)], Liu et al. (1990), Gierczak et al. (1991), Yamada et al. (2000) and Hsu and DeMore (1995) have been fitted to the three parameter equation  $k = CT^2 \exp(-D/T)$ , resulting in  $k = 1.42 \times 10^{-18} T^2 \exp(-370/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 213-866 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 250 K and is obtained from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ .

## References

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