

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx50

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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>			
$(1.5 \pm 0.3) \times 10^{-14}$	296	Howard and Evenson, 1976	DF-LMR
$3.72 \times 10^{-12} \exp[-(1627 \pm 50)/T]$	260-375	Watson et al., 1977	FP-RF
$(1.59 \pm 0.16) \times 10^{-14}$	298		
$1.95 \times 10^{-12} \exp[-(1331 \pm 37)/T]$	275-406	Chang and Kaufman, 1977	DF-RF
$(2.19 \pm 0.26) \times 10^{-14}$	298		
$2.4 \times 10^{-12} \exp[-(1394 \pm 113)/T]$	293-430	Clyne and Holt, 1979	DF-RF
$(1.81 \pm 0.16) \times 10^{-14}$	293		
$5.04 \times 10^{-12} \exp[-(1797 \pm 65)/T]$	278-457	Jeong and Kaufman, 1979;	DF-RF (a)
$(1.06 \pm 0.11) \times 10^{-14}$	293	Jeong et al., 1984	
$5.4 \times 10^{-12} \exp[-(1810 \pm 100)/T]$	253-363	Kurylo et al., 1979	FP-RF
$(1.08 \pm 0.20) \times 10^{-14}$	296		
$5.4 \times 10^{-12} \exp[-(1801 \pm 448)/T]$	359-402	Nelson et al., 1990	PR-RA
$1.3 \times 10^{-14}$	298*		
$9.1 \times 10^{-13} \exp[-(1337 \pm 150)/T]$	278-378	Finlayson-Pitts et al., 1992	DF-RF
$(1.0 \pm 0.1) \times 10^{-14}$	298		
$1.75 \times 10^{-12} \exp[-(1550 \pm 100)/T]$	233-379	Talukdar et al., 1992	PLP-LIF/ FP-LIF
$(9.5 \pm 0.8) \times 10^{-15}$	298		
$2.78 \times 10^{-18} T^{2.08} \exp[-(1068 \pm 108)/T]$	298-761	Jiang et al., 1992	PLP-LIF
$(1.1 \pm 0.1) \times 10^{-14}$	298		
$(1.2 \pm 0.2) \times 10^{-14}$	298	Lancar et al., 1993	DF-EPR
<i>Relative Rate Coefficients</i>			
$2.57 \times 10^{-14}$	298	Cox et al., 1976	RR (b)
$(9.0 \pm 2.9) \times 10^{-15}$	298 ± 3	Nelson et al., 1990	RR (c)
$1.15 \times 10^{-20} T^{2.82} \exp(-696/T)$	277-356	DeMore, 1992	RR (d)
$(1.06 \pm 0.05) \times 10^{-14}$	298		

## Comments

- The data were also fitted to a three parameter expression, resulting in  $k = 5.95 \times 10^{-20} T^{2.65} \exp[-(858 \pm 866)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .
- HO radicals were generated by the photolysis of  $\text{CH}_3\text{ONO-NO}$ -air mixtures at 1013 mbar pressure. Relative rate coefficients were obtained from measurements of the rates of NO formation as a function of the HONO and organic concentrations. Based on the effect of  $\text{CH}_3\text{CCl}_3$  on NO formation and a rate coefficient for the reaction of HO radicals with  $\text{CH}_4$  of  $6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson et al., 2006), the rate coefficient cited in the table is obtained.
- HO radicals were generated by the photolysis of HONO-air mixtures at 987 mbar pressure.

CH<sub>3</sub>CCl<sub>3</sub> and CH<sub>3</sub>Cl (the reference compound) were monitored during the experiments by GC. The measured rate coefficient ratio  $k(\text{HO} + \text{CH}_3\text{CCl}_3)/k(\text{HO} + \text{CH}_3\text{Cl}) = 0.25 \pm 0.08$  is placed on an absolute using  $k(\text{HO} + \text{CH}_3\text{Cl}) = 3.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K (Atkinson et al., 2008).

- (d) HO radicals were generated by the photolysis of H<sub>2</sub>O-O<sub>3</sub> mixtures at 254 nm in H<sub>2</sub>O-O<sub>3</sub>-CH<sub>3</sub>CCl<sub>3</sub>-CH<sub>4</sub>-Ar-O<sub>2</sub> mixtures. The concentrations of CH<sub>3</sub>CCl<sub>3</sub> and CH<sub>4</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CH}_3\text{CCl}_3)/k(\text{HO} + \text{CH}_4) = 0.62 \exp(291/T)$  is 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).

### Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$9.5 \times 10^{-15}$	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.2 \times 10^{-12} \exp(-1440/T)$	240-300
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.10$	298
$\Delta(E/R)$	$\pm 200$	

### Comments on Preferred Values

The absolute rate coefficients of Finlayson-Pitts et al. (1992) and Talukdar et al. (1992) are lower than the data from the studies of Howard and Evenson (1976), Watson et al. (1977), Chang and Kaufman (1977), Clyne and Holt (1979), Jeong and Kaufman (1979), and Jiang et al. (1992) in part due to the presence of reactive CH<sub>2</sub>=CCl<sub>2</sub> impurities in the CH<sub>3</sub>CCl<sub>3</sub> samples used (Jeong and Kaufman, 1979; Kurylo et al., 1979) and/or the formation of CH<sub>2</sub>=CCl<sub>2</sub> from thermal decomposition of CH<sub>3</sub>CCl<sub>3</sub> on surfaces (Finlayson-Pitts et al., 1992; Talukdar et al., 1992). A unit-weighted least-squares analysis of the absolute rate coefficients of Finlayson-Pitts et al. (1992) and Talukdar et al. (1992), using the expression  $k = CT^2 \exp(-D/T)$ , leads to  $k = 2.25 \times 10^{-18} T^2 \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 243-379 K. The preferred Arrhenius expression,  $k = A \exp(-B/T)$ , is centered at 265 K and is obtained from the three parameter equation with  $A = C e^2 T^2$  and  $B = D + 2T$ .

The relative rate coefficients of DeMore (1992) are slightly higher than the recommendation over the temperature range studied (277-356 K), by 11-15%. The relative rate coefficients of Nelson et al. (1990) and Cavalli et al. (1998) are in agreement with the preferred value at 298 K. The absolute rate coefficients of Kurylo et al. (1979) and Lancar et al. (1993) are slightly higher than, but consistent within the experimental uncertainties with, the preferred expression. The lowest temperature data point of Kurylo et al. (1979) appears to be anomalously high. Given the importance of this rate coefficient as a scaling factor to estimate global HO radical concentrations, further studies at sub-ambient temperatures would be useful.

### References

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