

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx40

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$$\Delta H^\circ = -74.4 \text{ kJ mol}^{-1}$$

## Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.21 \times 10^{-12} \exp[-(1636 \pm 151)/T]$	297-434	Atkinson et al., 1976	FP-RF
$(4.75 \pm 0.48) \times 10^{-15}$	296.9		
$(3.4 \pm 0.7) \times 10^{-15}$	$296 \pm 2$	Howard and Evenson, 1976	DF-LMR
$9.25 \times 10^{-13} \exp[-(1575 \pm 71)/T]$	250-350	Watson et al., 1977	FP-RF
$(4.8 \pm 0.46) \times 10^{-15}$	298		
$1.20 \times 10^{-12} \exp[-(1657 \pm 39)/T]$	253-427	Chang and Kaufman, 1977	DF-RF
$(4.25 \pm 0.28) \times 10^{-15}$	296		
$2.1 \times 10^{-12} \exp[-(1780 \pm 150)/T]$	263-373	Handwerk and Zellner, 1978	FP-RA
$(4.6 \pm 0.8) \times 10^{-15}$	293		
$9.5 \times 10^{-12} \exp[-(2300 \pm 200)/T]$	294-426	Clyne and Holt, 1979	DF-RF
$(3.3 \pm 0.7) \times 10^{-15}$	294		
$(4.58 \pm 0.59) \times 10^{-15}$	297	Paraskevopoulos et al., 1981	FP-RA
$5.03 \times 10^{-28} T^{5.11} \exp[(252 \pm 780)/T]$	293-492	Jeong and Kaufman, 1982;	DF-RF
$(4.83 \pm 0.32) \times 10^{-15}$	293	Jeong et al., 1984	
$8.1 \times 10^{-13} \exp[-(1516 \pm 53)/T]$	298-460	Orkin and Khamaganov, 1993	DF-EPR
$(4.9 \pm 0.45) \times 10^{-15}$	298		
$1.74 \times 10^{-12} \exp[-(1701 \pm 39)/T]$	302-382	Yujing et al., 1993	DF-RF
$5.99 \times 10^{-15}$	302		
$1.31 \times 10^{-22} T^{3.28} \exp[-(361 \pm 564)/T]$	294-807	Fang et al., 1996	PLP-LIF
$(4.65 \pm 0.66) \times 10^{-15}$	294		
<i>Relative Rate Coefficients</i>			
$4.44 \times 10^{-21} T^{2.82} \exp[-(645 \pm 45)/T]$	298-366	Hsu and DeMore, 1995	RR (a)
$4.83 \times 10^{-15}$	298		
$(2.9 \pm 0.7) \times 10^{-15}$	298	Cavalli et al. (1998)	RR (b)

## Comments

(a) HO radicals were generated by the UV photolysis of O<sub>3</sub> in the presence of water vapor. The

concentrations of CHF<sub>2</sub>Cl and CH<sub>4</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHF}_2\text{Cl})/k(\text{HO} + \text{CH}_4) = (0.24 \pm 0.03) \exp[(342 \pm 45)/T]$  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).

- (b) HO radicals were generated by the UV photolysis of O<sub>3</sub> at 254 nm in the presence of water vapor. The concentrations of CHF<sub>2</sub>Cl and CH<sub>4</sub> were measured by FTIR spectroscopy. The measured rate coefficient ratio of  $k(\text{HO} + \text{CHF}_2\text{Cl})/k(\text{HO} + \text{CH}_4) 0.482 \pm 0.112$  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
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$4.7 \times 10^{-15}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.9 \times 10^{-13} \exp(-1530/T)$	240-300
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.08$	298
$\Delta(E/R)$	$\pm 150$	240-300

### Preferred Values

$k = 4.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

$k = 7.9 \times 10^{-13} \exp(-1530/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 240-300 K.

#### *Reliability*

$\Delta \log k = \pm 0.08$  at 298 K.

$\Delta(E/R) = \pm 150$  K.

#### *Comments on Preferred Values*

The absolute rate coefficients of Atkinson et al. (1975), Howard and Evenson (1976), Watson et al. (1977), Chang and Kaufman (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982), Orkin and Khamaganov (1993) and Fang et al. (1996) are in good agreement, and the relative rate coefficients of Hsu and DeMore (1995) agree well with these absolute rate coefficients. The absolute rate coefficients of Clyne and Holt (1979) exhibit a significantly higher temperature dependence than those determined in the other absolute rate studies. The absolute rate coefficients of Yujing et al. (1993) are significantly higher than those of Atkinson et al. (1975), Howard and Evenson (1976), Watson et al. (1977), Chang and Kaufman (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982), Orkin and Khamaganov (1993) and Fang et al. (1996). The relative rate coefficient of Cavalli et al. (1998) lies substantially below those of the other studies. Accordingly, the studies of Clyne and Holt (1979), Yujing et al. (1993), and Cavalli et al. (1998) are not used in the evaluation of the rate coefficient for this reaction. The three parameter equation  $k = CT^2 \exp(-D/T)$  has been fitted to the absolute rate coefficients of Atkinson et al. (1975), Howard and Evenson (1976), Watson et al. (1977), Chang and Kaufman (1977), Handwerk and Zellner (1978), Paraskevopoulos et al. (1981), Jeong and Kaufman (1982), Orkin and Khamaganov (1993) and Fang et al. (1996) resulting in  $k = 1.52 \times 10^{-18} T^2 \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 250-807 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  $B = D$

+ 2*T*. The relative rate data of Hsu and DeMore (1995) agree to within 3% with the preferred values.

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