

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx23

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$$\Delta H^\circ = -39.2 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$1.45 \times 10^{-11} \exp[-(1379 \pm 44)/T]$	297-652	Clyne and Walker, 1973	DF-MS
$(1.47 \pm 0.35) \times 10^{-13}$	297		
$(9.9 \pm 0.9) \times 10^{-14}$	298	Watson et al. (1976)	FP-RF
$(3.7 \pm 1.0) \times 10^{-14}$	298	Jeoung et al., 1991	(a)
$(1.1 \pm 0.1) \times 10^{-13}$	298	Beichert et al., 1995	DF-RF
$8.0 \times 10^{-12} \exp[-(1390 \pm 80)/T]$	298-430	Talhaoui et al., 1996	DF-MS
$(7.6 \pm 1.3) \times 10^{-14}$	298		
$1.19 \times 10^{-16} T^{1.51} \exp(-571/T)$	297-854	Bryukov et al., 2002	DF-RF
$(8.9 \pm 0.9) \times 10^{-14}$	297		
<i>Relative Rate Coefficients</i>			
$1.9 \times 10^{-12} \exp(-980/T)$	286-593	Knox, 1962	RR (b,c)
6.9×10^{-14}	298		
$6.0 \times 10^{-12} \exp(-1280/T)$	240-593	Knox, 1962	RR (b,d)
8.4×10^{-14}	298		
$(1.13 \pm 0.07) \times 10^{-13}$	298	Beichert et al., 1995	RR (e)
$(1.19 \pm 0.13) \times 10^{-13}$	298	Brahan et al., 1996	RR (f)
$(1.1 \pm 0.1) \times 10^{-13}$	298	Catoire et al., 1996	RR (g)
$2.9 \times 10^{-12} \exp(-950/T)$	222-298	Orlando, 1999	RR (h)
1.18×10^{-13}	298		
$4.8 \times 10^{-12} \exp(-1160/T)$	297.3-526.9	Gola et al., 2009	RR (i)
1.04×10^{-13}	297.3		
$(3.77 \pm 0.32) \times 10^{-12} \exp[-(1011 \pm 24)/T]$	253-313	Nilsson et al., 2010	RR (j)
$(1.21 \pm 0.05) \times 10^{-13}$	298		

Comments

- (a) Very low pressure reactor with chemiluminescence and mass spectrometric detection. The reaction of Cl with CHCl₃ was studied as part of a complex chemical system.
- (b) Cl atoms were generated by photolysis of Cl₂ in Cl₂-CHCl₃-CH₄ or Cl₂-CHCl₃-CH₃Cl mixtures. Organic reactants and products monitored by GC.
- (c) Rate coefficient ratio of $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_4) = 0.286 \exp(259/T)$ was obtained and placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).
- (d) Rate coefficient ratio of $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_3\text{Cl}) = 0.26 \exp(-133/T)$ obtained, and placed on an absolute basis using $k(\text{Cl} + \text{CH}_3\text{Cl}) = 2.3 \times 10^{-11} \exp(-1150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2008).

- (e) Cl atoms were generated from the photolysis of Cl₂ in Cl₂-CHCl₃-CH₄ mixtures at atmospheric pressure of N₂, air or Ar. The concentrations of CHCl₃ and CH₄ were monitored by GC and a rate coefficient ratio $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_4) = 1.13 \pm 0.07$ was determined. This was placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).
- (f) Cl atoms were generated by photolysis of Cl₂ in Cl₂-CHCl₃-CH₄ or Cl₂-CHCl₃-CH₃Cl mixtures in an air or N₂ bath gas at 1023 mbar total pressure and 298 K. Rate coefficient ratios $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_4) = 1.26 \pm 0.07$ and $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_3\text{Cl}) = 0.243 \pm 0.028$ were placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{Cl} + \text{CH}_3\text{Cl}) = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006; Atkinson et al., 2008). The value presented in the table is the average of experiments using both CH₄ and CH₃Cl as reference reactants. The uncertainty quoted in the table encompasses the uncertainties associated with the two individual determinations (neglecting uncertainties in the reference rate coefficients).
- (g) Cl atoms were generated from the photolysis of Cl₂ in Cl₂-CHCl₃-CH₄ mixtures at 930 mbar total pressure of air. The relative removal rates of CH₂Cl₂ and CH₄ were measured by FTIR. A rate coefficient ratio $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_4) = 1.1 \pm 0.1$ was obtained and placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).
- (h) Cl atoms were generated from the photolysis of Cl₂ in Cl₂-CHCl₃-CH₄ mixtures at 930 mbar total pressure of O₂-N₂. The concentrations of CHCl₃ and CH₄ were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_4) = 0.436 \exp(290/T)$ was determined. This was placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).
- (i) Cl atoms were generated from the photolysis of Cl₂ in Cl₂-CHCl₃-CH₃Br mixtures at 133 mbar total pressure of N₂. The concentrations of CHCl₃ and CH₃Br were monitored by thermal conductivity GC. Rate coefficient ratios $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_3\text{Br})$ were placed on an absolute basis using $k(\text{Cl} + \text{CH}_3\text{Br}) = 3.32 \times 10^{-12} (T/298)^{1.42} \exp(-605/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Piety et al., 1998).
- (j) Cl atoms were generated from the photolysis of Cl₂ in Cl₂-CHCl₃-CH₄ and Cl₂-CHCl₃-CH₂F₂ mixtures at 930 mbar total pressure of N₂. The concentrations of CHCl₃, CH₄, and CH₂F₂ were monitored by FTIR spectroscopy. Rate coefficient ratios $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_4)$ and $k(\text{Cl} + \text{CHCl}_3)/k(\text{Cl} + \text{CH}_2\text{F}_2)$ were placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ and $k(\text{Cl} + \text{CH}_2\text{F}_2) = 6.93 \times 10^{-12} \exp(-1591/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006; Atkinson et al., 2008).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.1×10^{-13}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.14 \times 10^{-12} \exp(-884/T)$	220-400
<i>Reliability</i>		
$\Delta \log k$	± 0.06	298
$\Delta E/R$	± 200	

Comments on Preferred Values

The absolute rate constants of Watson et al. (1976), Beichert et al. (1995), and Bryukov et al. (2002), and the relative rate constants of Beichert et al. (1995), Brahan et al. (1996), Catoire et al. (1996), Orlando (1999), Gola et al. (2009), and Nilsson et al. (2010) are in good agreement. The value at 298 K reported by Knox et al. (1962) is for reasons which are unclear lower than the other studies. The 298 K recommendation is an average result from these studies. Fitting the Arrhenius expression to the data reported in these studies at

temperatures below 400 K and adjusting the A factor for consistency with the recommended rate coefficient at 298 K gives the recommended expression given above. Fitting the three-parameter equation $k = CT^2 \exp(-D/T)$ to the data from Beichert et al. (1995) and Bryukov et al. (2002), Beichert et al. (1995), Brahan et al. (1996), Catoire et al. (1996) and Orlando (1999), Gola et al. (2009), and Nilsson et al. (2010) gives $k = 3.27 \times 10^{-18} T^2 \exp(-287/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which can be used for temperatures up to 855 K.

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