IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oClOx20; IV.A2.94

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This data sheet last evaluated: June 2015; last change in preferred values: December 2007.

$$Cl + CH_2Cl_2 \rightarrow HCl + CHCl_2$$

$\Delta H° = -19.9$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(5.5 \pm 0.5) \times 10^{-13}$	298	Davis et al., 1970	FP-RF
$8.36 \times 10^{-11} \exp[-(1450 \pm 60)/T]$	298-621	Clyne and Walker, 1973	DF-MS
6.4×10^{-13}	298		
$(3.2 \pm 0.2) \times 10^{-13}$	298	Beichert et al., 1995	DF-RF
$1.48 \times 10^{-16} T^{1.58} \exp(-360/T)$	296-790	Bryukov et al., 2002	DF-RF
$(3.5 \pm 0.2) \times 10^{-13}$	297		
Relative Rate Coefficients			
3.7×10^{-13}	298	Niki et al., 1980	RR (a)
$1.9 \times 10^{-11} \exp(-1190/T)$	273-368	Tschuikow-Roux et al., 1988	RR (b)
3.5×10^{-13}	298		
$(3.45 \pm 0.18) \times 10^{-13}$	298	Beichert et al., 1995	RR (c)
$(3.51 \pm 0.14) \times 10^{-13}$	298	Catoire et al., 1996	RR (d)
$4.4 \times 10^{-12} \exp(-770/T)$	222-298	Orlando, 1999	RR (e)
3.2×10^{-13}	298		
$1.24 \times 10^{-12} \exp(-1070/T)$	298-527	Sarzyński et al., 2011	RR (f)
3.5×10^{-13}	298		

Comments

(a) Relative to $Cl + CH_3Cl$. Cl atoms were generated by the photolysis of Cl_2-CH_2Cl_2-CH_3Cl in air at 930 mbar and the concentrations of CH_2Cl_2 and CH_4 measured by FTIR. The measured rate coefficient ratio of $k(Cl + CH_2Cl_2)/k(Cl + CH_3Cl) = (0.76 \pm 0.08)$ was placed on an absolute basis using $k(Cl + CH_3Cl) = 4.8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(b) Cl atoms were generated by the photolysis of Cl_2 at 424 nm, and the concentrations of CH_2Cl_2 and CH_3Cl measured by GC. The measured rate coefficient ratio of $k(Cl + CH_2Cl_2)/k(Cl + CH_4) = (2.81 \pm 0.02) \exp[-(49 \pm 2)/T]$ is placed on an absolute basis by using the rate coefficient of $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(c) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_2Cl_2-CH_4 mixtures at atmospheric pressure of N_2, air or Ar. The concentrations of CH_3Cl and CH_4 were monitored by GC and a rate coefficient ratio $k(Cl + CH_2Cl_2)/k(Cl+CH_4) = 3.45 \pm 0.18$ was determined. This was placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(d) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_2Cl_2-CH_4 in air at 930 mbar total pressure. The relative removal rates of CH_2Cl_2 and CH_4 were measured by FTIR. A rate

coefficient ratio $k(Cl + CH_2Cl_2)/k(Cl+CH_4)$ = 3.51 ± 0.14 was obtained and placed on an absolute basis using $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(e) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_2Cl_2-CH_4 mixtures at 930 mbar total pressure of O_2-N_2. The concentrations of CH_2Cl_2 and CH_4 were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio $k(Cl + CH_2Cl_2)/k(Cl+CH_4)$ determined. This was placed on an absolute basis using $k(Cl + CH_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(f) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_2Cl_2-CH_3Br mixtures in 100 Torr (133 mbar) of N_2 diluent. The loss of CH_2Cl_2 and CH_3Br were monitored by GC. The individual rate coefficient ratios $k(Cl + CH_2Cl_2)/k(Cl+ CH_3Br)$ were placed on an absolute basis using $k(Cl + CH_3Br) = 1.78 \times 10^{-17} T^2 \exp(-396/T)$ cm^3 molecule^{-1} s^{-1} (http://iupac.pole-ether.fr).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	3.4×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$5.9 \times 10^{-12} \exp(-850/T)$	220-300
Reliability		
$\Delta \log k$	0.06	298
$\Delta E/R$	± 100	

Comments on Preferred Values

The results reported by all but the earliest two studies and in excellent agreement. Taking an average from the studies by Beichert et al. (1995), Bryukov et al. (2002), Niki et al. (1980), Tschuikow-Roux et al. (1988), Catoire et al. (1996), Orlando (1999), and Sarzyński et al. (2011) gives a room temperature rate coefficient of 3.4×10^{-13} cm^3 molecule^{-1} s^{-1}. The results from Davis et al. (1970) and Clyne and Walker (1973) lie significantly above those from all other studies suggesting possible systematic errors in these early studies. The temperature dependent rate coefficients of Orlando (1999), Bryukov et al. (2002), and Sarzyński et al. (2011) are in good agreement where they overlap at temperatures of 300- 400 K. The preferred temperature dependence is taken from a least squares fit to the data below 300 K, and has been adjusted to reproduce the recommended value of k at 298 K. A fit of the modified Arrhenius expression to the data from all studies except Davis et al. (1970) and Clyne and Walker (1973) gives $k = 8.51 \times 10^{-18} T^2 \exp(-234/T)$ cm^3 molecule^{-1} s^{-1} and is recommended for temperatures of 300 - 800 K.

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