IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.91 oClOx17

This data sheet last evaluated: June 2015; last change in preferred values: June 2011.

$Cl + CH_3Cl \rightarrow HCl + CH_2Cl$

$\Delta H° = -14.3$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.1 \times 10^{-10} \exp\{(-1790 \pm 70)/T\}$	300-604	Clyne and Walker, 1973	DF-MS
5.4×10^{-13}	300		
$3.4 \times 10^{-11} \exp\{(-1250 \pm 60)/T\}$	233-322	Manning and Kurylo, 1977	FP-RF
$(5.10 \pm 0.14) \times 10^{-13}$	296		
$(4.4 \pm 0.6) \times 10^{-13}$	298	Beichert et al., 1995	DF-RF
$4.0 \times 10^{-14} T^{0.92} \exp(-795/T)$	300-843	Bryukov et al., 2002	DF-MS
$(5.2 \pm 0.3) \times 10^{-13}$	300		
Relative Rate Coefficients			
$(4.8 \pm 0.4) \times 10^{-13}$	295 ± 2	Wallington et al., 1990	RR (a)
$(4.7 \pm 0.6) \times 10^{-13}$	298	Beichert et al., 1995	RR (b)
$1.0 \times 10^{-11} \exp\{(-915 \pm 120)/T\}$	222-298	Orlando, 1999	RR (c)
4.7×10^{-13}	298		
$(1.3 \pm 0.2) \times 10^{-11} \exp\{(-1470 \pm 10)/T\}$	298-527	Sarzyński et al., 2009	RR (d)
$(5.2 \pm 0.4) \times 10^{-13}$	298		

Comments

(a) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_3Cl-CH_4 air mixtures at 930 mbar total pressure. The concentrations of CH_3Cl and CH_4 were monitored by FTIR absorption spectroscopy and a rate coefficient ratio $k(Cl + CH_3Cl)/k(Cl+CH_4) = 4.79 \pm 0.39$ determined. This was 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).

(b) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_3Cl-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 $k(Cl + CH_3Cl)/k(Cl+CH_4) = 4.65 \pm 0.57$ was determined. This was 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).

(c) Cl atoms were generated from the photolysis of Cl_2 in Cl_2-CH_3Cl-CH_4 mixtures at 930 mbar total pressure of O_2-N_2. The concentrations of CH_3Cl and CH_4 were monitored by FTIR absorption spectroscopy and a temperature dependent rate coefficient ratio $k(Cl + CH_3Cl)/k(Cl+CH_4)$ determined. This was placed on an absolute basis by use of $k(Cl + CH_4) =$

6.6×10^{-12} exp (-1240/*T*) cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006).

(d) Cl atoms were generated by photolysis of Cl_2 in Cl_2-CH_3Cl-CH_3Br mixtures in 133 mbar of N_2 diluent. The concentrations of CH_3Cl and CH_4 were monitored by thermal conductivity GC. Rate coefficient ratios $k(Cl + CH_3Cl)/k(Cl+CH_3Br)$ were placed on an absolute basis using $k(Cl+CH_3Br) = 3.32 \times 10^{-12}$ $(T/298)^{1.42}$ exp(-605/*T*) cm^3 $molecule^{-1}$ s^{-1} (Piety et al., 1998).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 $molecule^{-1}$ s^{-1}	4.8×10^{-13}	298
k /cm^3 $molecule^{-1}$ s^{-1}	1.8×10^{-11} exp(-1081/*T*)	220-300
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 200	

Comments on Preferred Values

The results of all studies are in reasonable agreement at room temperature and below. The temperature dependence reported by Clyne and Walker (1973) is significantly greater than those reported by Manning and Kurylo (1977), Orlando (1999), Bryukov et al. (2002), and Sarzyński et al. (2009). The preferred 298 K rate coefficient is the average of the determinations by Manning and Kurylo (1977), Wallington et al. (1990), Beichert et al. (1995), Orlando (1999), and Bryukov et al. (2002) at room temperature. The temperature dependence was derived by least squares fitting to the data of Manning and Kurylo (1977), Wallington et al. (1990), Beichert et al. (1995), Orlando (1999), Bryukov et al. (2002), and Sarzyński et al. (2009) at temperatures below 300 K. The A factor was adjusted to reproduce the recommended value at 298 K.

Fitting the three-parameter equation $k = CT^2$ exp(-*D*/*T*) to the data from Manning and Kurylo (1977), Wallington et al. (1990), Beichert et al. (1995), Orlando (1999), Bryukov et al. (2002), and Sarzyński et al. (2009) gives $k = 2.00 \times 10^{-17}$ T^2 exp(-397/*T*) cm^3 $molecule^{-1}$ s^{-1} which can be used to estimate rate coefficients over the temperature range 300-900 K.

References

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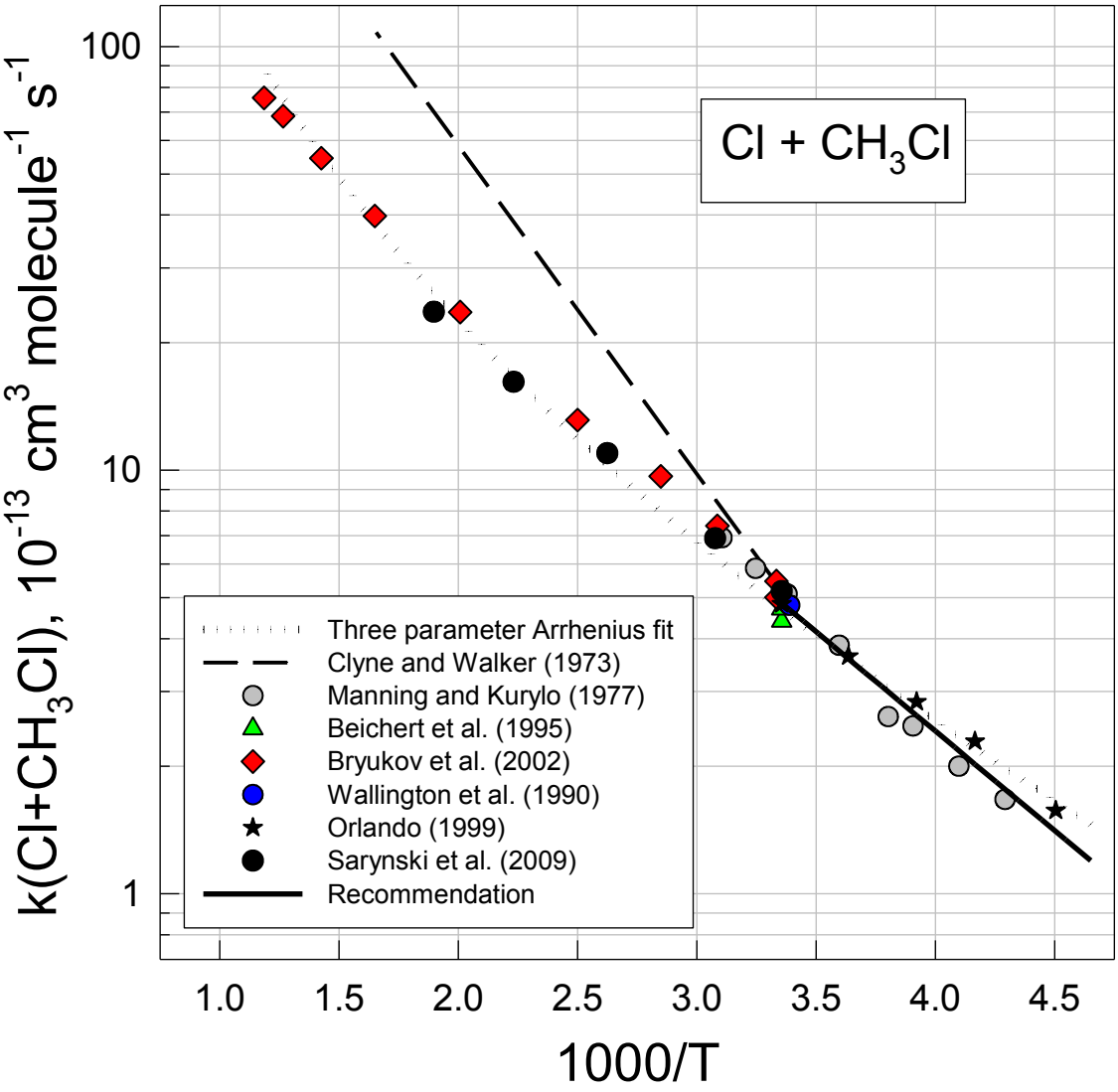
Cl + CH3Cl
k(Cl+CH3Cl), 10-13 cm3 molecule-1 s-1
100
10
1
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
1000/T
Three parameter Arrhenius fit
Clyne and Walker (1973)
Manning and Kurylo (1977)
Beichert et al. (1995)
Bryukov et al. (2002)
Wallington et al. (1990)
Orlando (1999)
Sarynski et al. (2009)
Recommendation