IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet oClOx22; IV.A2.94

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This data sheet last evaluated: June 2015; last change in preferred values: June 2014.

$Cl + CHFCl_2$ (HCFC-21) $\rightarrow HCl + CFCl_2$

$\Delta H° = -17.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$5.2 \times 10^{-12} \exp[-(1675 \pm 60)/T]$	298-430	Talhaoui et al., 1996	DF-MS
$(1.9 \pm 0.3) \times 10^{-14}$	296		
Relative Rate Coefficients			
$(1.0 \pm 0.2) \times 10^{-14}$	294	Glavas and Heicklen, 1985	RR (a)
$(2.1 \pm 0.4) \times 10^{-14}$	298	Tuazon et al., 1992	RR (b)
$4.04 \times 10^{-12} \exp(-1561/T)$	298-670	Kaiser and Jawad (2014)	RR (c)
2.0×10^{-14}	298		

Comments

(a) Steady-state photolysis of Cl_2-$CHFCl_2$-O_2-NO-NO_2-N_2 mixtures. The measured rate coefficient ratio is placed on absolute basis using a rate coefficient of $k(Cl + NO + M) = 1.0 \times 10^{-31}$ cm^6 molecule^{-2} s^{-1}.

(b) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FTIR spectroscopy. The measured rate coefficient was placed on absolute basis using a rate coefficient of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(c) Cl atoms were generated by either photolysis (for temperatures up to approximately 550 K) or thermal decomposition (for temperature above approximately 550 K) of Cl_2 in 760 Torr (1013 mbar) of N_2 diluent. The loss of $CHFCl_2$ was measured relative to that of CH_4 using GC/FID. The rate coefficient ratios were placed on an absolute basis using $k(Cl+CH_4) = 1.5 \times 10^{-17} T^2 \exp(-766/T)$ cm^3 molecule^{-1} s^{-1} (Calvert et al. 2007).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.0×10^{-14}	298
k /cm^3 molecule^{-1} s^{-1}	$4.84 \times 10^{-12} \exp(-1636/T)$	290-680
Reliability		
$\Delta \log k$	0.1	298
Δ E/R	$\pm$ 100	

Comments on Preferred Values

The preferred value at 298 K is based on the absolute study of Talhaoui et al. (1996) and the relative rate studies of Tuazon et al. (1992) and Kaiser and Jawad (2014). These results are preferred over the earlier, less direct results of Glavas and Heicklen (1985). There is excellent agreement in the temperature dependence reported by Talhaoui et al. (1996) and Kaiser and Jawad (2014). The recommended Arrhenius temperature dependence is based on a fit to the combined results from Talhaoui et al. (1996) and Kaiser and Jawad (2014). The A-factor has been adjusted to reproduce the recommended value of k at 298 K.

References

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