IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.90 oClOx16

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

$Cl + CH_3F$ (HFC-41) $\rightarrow HCl + CH_2F$

$\Delta H° = -12.8$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$5.1 \times 10^{-12} \exp[-(790 \pm 45)/T]$	216-296	Manning and Kurylo, 1977	FP-RF (a)
3.6×10^{-13}	298		
$(2.7 \pm 0.2) \times 10^{-13}$	298	Hitsuda et al., 2001	PLP-LIF (b)
$1.14 \times 10^{-12} \times (T/298)^{2.26} \exp\{-313/T\}$	200-700	Marinkovic et al., 2008	PFP-RF (c)
3.72×10^{-13}	298		
Relative Rate Coefficients			
$1.3 \times 10^{-11} \exp(-1050/T)$	273-368	Tschuikow-Roux et al., 1988	RR (d)
3.8×10^{-13}	298		
$(3.4 \pm 0.7) \times 10^{-13}$	298	Tuazon et al., 1992	RR (e)
$(3.24 \pm 0.51) \times 10^{-13}$	298	Wallington et al., 1992	RR (f)
$1.65 \times 10^{-11} \exp[(-1150 \pm 30)/T]$	298-527	Sarzyński et al., 2012	RR (g)
$(3.5 \pm 0.4) \times 10^{-13}$	298		

Comments

(a) Cl atoms were formed in the photolysis of CCl_4. The Arrhenius expression was derived by least squares fitting to tabulated data (excluding data obtained in experiments in which some fraction of the CH_3F was excited using a CO_2 laser to check for the effect of vibrational excitation of CH_3F on the rate of reaction with Cl atoms).

(b) Laser photolysis of HCl at 193 nm as Cl atom source. Both Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$) were detected by VUV-LIF.

(c) Cl atoms were generated by the 266 nm laser photolysis of $COCl_2$ in 33-133 mbar of nitrogen diluent in the presence of CH_3F. Chlorine atoms were monitored by resonance fluorescence in the 135-140 nm wavelength range.

(d) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC. Derived values of $A/A_{CH4} = (2.02 \pm 0.01)$ and $(E-E_{CH4})/R = (-190 \pm 6)$ K are 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).

(e) Cl atoms were generated by the photolysis of Cl_2 in CH_3F-CH_4-Cl_2 mixtures in 986 mbar of air diluent. The decays of the CH_3F and CH_4 were measured by FT-IR spectroscopy. The measured rate coefficient ratio $k(Cl + CH_3F)/k(Cl + CH_4) = 3.42 \pm 0.09$ was placed on absolute basis using $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006).

(f) Cl atoms were generated by the photolysis of Cl_2. The decays of the reactant and reference organic were measured by FT-IR spectroscopy. The measured rate coefficient ratio $k(Cl + CH_3F)/k(Cl + CH_4) = 3.24 \pm 0.19$ 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).

(g) Cl atoms were generated by the photolysis of Cl_2 in 70-1000 mbar (50-750 Torr) of N_2 diluent at 298-527 K. The decays of the reactant and reference organic were measured by gas chromatography. The measured rate coefficient ratios $k(Cl + CH_3F)/k(Cl + CH_4)$ were placed on an absolute basis using $k(Cl + CH_4) = 3.7 \times 10^{-13} \times (T/298)^{2.6} \exp(-385/T)$ cm^3 $molecule^{-1}$ s^{-1} (Pilgrim et al., 1997).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	3.6×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$4.9 \times 10^{-12} \exp(-781/T)$	200-300
Reliability		
$\Delta \log k$	± 0.04	298
$\Delta E/R$	± 100	

Comments on Preferred Values

The rate coefficients at 298 K reported by Manning and Kurylo (1977), Tschuikow-Roux et al. (1988), Tuazon et al. (1992), Wallington et al. (1992), Marinkovic et al. (2008), and Sarzyński et al. (2012) are in excellent agreement. The recommended value at 298 K is based on an average of all the determinations at this temperature excepting that of Hitsuda et al. (2001) which is approximately 25% lower than the others and is not considered further. The recommended expression for k covers the atmospherically relevant temperature range 200 – 300 K and was derived by fitting the Arrhenius expression least squares fitting to the data reported at 298 K and below with the A factor adjusted to give the recommended value at 298 K. Tschuikow-Roux et al. (1988) reported an Arrhenius expression which described their results but did not report individual data points. The Arrhenius expression reported by Tschuikow-Roux et al. (1988) is in excellent agreement with the values preferred here in the common temperature range but has a slightly greater temperature dependence. A steeper temperature dependence at high temperatures is observed in the work by Marinkovic et al. (2008) and Sarzyński et al. (2012).

Fitting the three-parameter equation $k = CT^2 \exp(-D/T)$ to the data from Manning and Kurylo (1977), Tschuikow-Roux et al. (1988), Tuazon et al. (1992), Wallington et al. (1992), Marinkovic et al. (2008), and Sarzyński et al. (2012) gives $k = 1.52 \times 10^{-17} T^2 \exp(-374/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 200-700 K. This three-parameter equation can be used to estimate rate constants at temperatures up to 700K.

References

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