IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet IV.A2.92 oClOx18

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$Cl + CH_2F_2$ (HFC-32) $\rightarrow HCl + CHF_2$

$\Delta H° = 0.5$ kJ mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$1.0 \times 10^{-11} \exp(-1470/T)$	281-368	Tschuikow-Roux et al., 1985	RR (a)
7.3×10^{-14}	298		
$(3.2 \pm 0.2) \times 10^{-14}$	295	Nielsen et al., 1992	RR (b)
$1.19 \times 10^{-17} T^2 \exp(-1023/T)$	253-553	Nilsson et al., 2009	RR (c)
$(3.34 \pm 0.16) \times 10^{-14}$	298		

Comments

(a) Cl atoms were generated by the photolysis of Cl_2. Product yield ratios were measured by GC. Kinetic data were derived by measuring the formation of CHF_2Cl and CH_3Cl following irradiation at 424 nm of CH_4-CH_2F_2-Cl_2 mixtures at a total pressure of about 27 mbar. Derived values of $A/A_{CH4} = (1.51 \pm 0.06)$ and $(E-E_{CH4})/R = (228 \pm 12)$ K were 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).

(b) Photolysis of Cl_2 in presence of CH_2F_2 and CH_4 in 920 mbar air or N_2 bath gas. The value obtained, $k(CH_2F_2)/k(CH_4) = 0.32 \pm 0.02$ was placed on an absolute value using $k(CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

(c) Photolysis of Cl_2 in presence of CH_2F_2 and CH_4 in 930-1200 mbar of N_2 diluent at 253 – 553 K. The values of $k(CH_2F_2)/k(CH_4)$ obtained at 200-300 K were 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). The values of $k(CH_2F_2)/k(CH_4)$ obtained at > 300 K were placed on an absolute basis using $k(Cl+CH_4) = 5.69 \times 10^{-19} T^{2.49} \exp(-609/T)$ cm^3 molecule^{-1} s^{-1} from Bryukov et al. (2002).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	3.3 x 10^{-14}	298
k /cm^3 molecule^{-1} s^{-1}	6.93 x 10^{-12} exp(-1591/T)	250-300
Reliability		
Δ log k	± 0.06	298
Δ E/R	± 200	

Comments on Preferred Values

In the relative rate studies by Nielsen et al. (1992) and Nilsson et al. (2009) the rate coefficient ratio $k(Cl+CH_2F_2)/k(Cl+CH_4)$ was measured by monitoring the loss of CH_2F_2 and CH_4 following UV irradiation of CH_2F_2–CH_4–Cl_2–N_2 mixtures. The loss of CH_2F_2 and CH_4 were monitored directly using in-situ FTIR spectroscopy or GC-FID. In the relative rate study by Tschuikow-Roux et al. (1985) the rate constant ratio $k(Cl+CH_2F_2)/k(Cl+CH_4)$ was measured by monitoring the formation of CHF_2Cl and CH_3Cl following UV irradiation of CH_2F_2–CH_4–Cl_2 mixtures. The formation of CHF_2Cl and CH_3Cl were measured by GC-FID and used to infer the loss of CH_2F_2 and CH_4. Tschuikow-Roux et al. (1985) found it necessary to to apply an "unexpectly large" correction factor of 5.838 to account for the response of the GC-FID to CHF_2Cl. The results from Nielsen et al. (1992) and Nilsson et al. (2009) are in excellent agreement and are preferred.

Fitting the three-parameter equation $k = CT^2 \exp(-D/T)$ to the data from Nielsen et al. (1992) and Nilsson et al. (2009) gives k = 1.24 x 10^{-17} T^2 exp(-1041/T) cm^3 molecule^{-1} s^{-1} over the temperature range 253-553 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 275 K and is derived from the three parameter equation with $A = C\,e^2\,T^2$ and $B = D + 2T$

References

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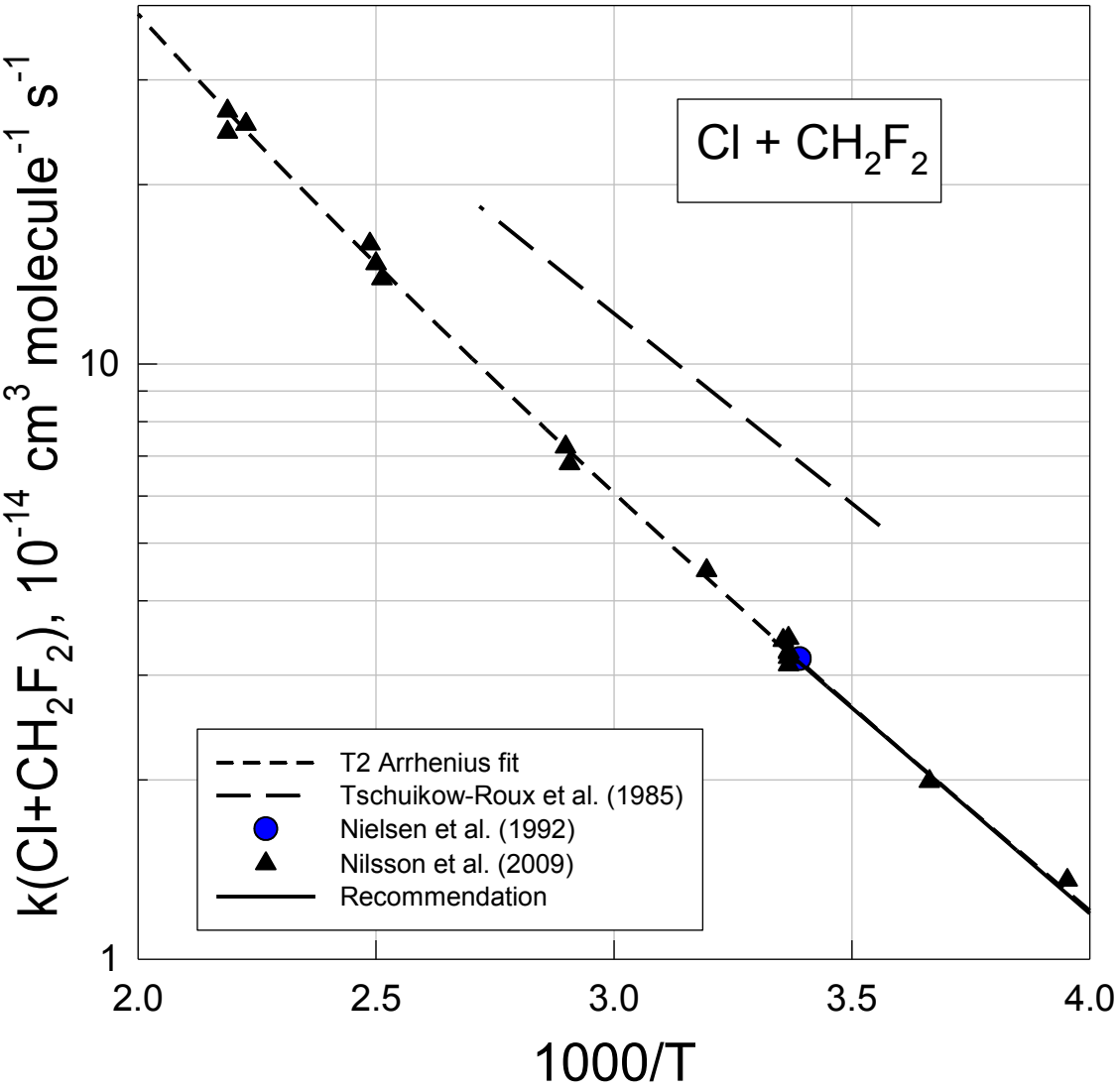
Cl + CH2F2
k(Cl+CH2F2), 10-14 cm3 molecule-1 s-1
10
1
2.0
2.5
3.0
3.5
4.0
1000/T
T2 Arrhenius fit
Tschuikow-Roux et al. (1985)
Nielsen et al. (1992)
Nilsson et al. (2009)
Recommendation