IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC9

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$Cl + HCHO \rightarrow HCl + HCO$

$\Delta H° = -61.9$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(7.48 \pm 0.50) \times 10^{-11}$	200-500	Michael et al., 1979	FP-RF
$1.09 \times 10^{-10} \exp[-(131 \pm 98)/T]$	223-323	Anderson and Kurylo, 1979	FP-RF
$(7.18 \pm 0.61) \times 10^{-11}$	293		
$(7.4 \pm 0.7) \times 10^{-11}$	298	Fasano and Nogar, 1981	PLP-CL
$(6.98 \pm 0.69) \times 10^{-11}$	298	Seakins et al., 2004	LP-IR (a)
Relative Rate Coefficients			
$(7.6 \pm 0.6) \times 10^{-11}$	298	Niki et al., 1978	RR (b)
$(6.8 \pm 1.4) \times 10^{-11}$	295	Poulet et al., 1981	RR (c)

Comments

(a) $Cl(^2P_{3/2})$ generated in 351 nm laser photolysis of Cl_2. Kinetic data obtained by monitoring the HCl product by IR emission spectroscopy.

(b) Competitive photo-chlorination between HCHO and C_2H_6 using FTIR. The measured rate coefficient ratio $k / k(Cl + C_2H_6) = 1.3 \pm 0.1$ is placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

(c) DF-MS study. Value of k derived from measured ratio of $k / k(Cl + C_2H_6) = 1.16 \pm 0.12$ and $k(Cl + C_2H_6) = 5.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

Preferred Values

$k = 7.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K.

$k = 8.1 \times 10^{-11} \exp(-34/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200 K to 500 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is an unweighted average of all studies listed above, which are in good agreement. The preferred temperature dependence is based on a least-squares fit to the 200-500 K data of Michael et al. (1979) and the 223-323 K data of Anderson and Kurylo (1979), with the pre-exponential factor adjusted to reproduce the recommended rate coefficient at 298 K. The reaction generates vibrationally excited products, HCl and HCO (Dong et al., 2003), with ≈ (91 ± 14) % of HCl formed as v=1 (Seakins et al., 2004). Kinetic isotope effects have been determined in relative rate studies as $k(Cl + HCHO) / k(Cl + DCDO) = 1.30$, $k(Cl + HCHO) / k(Cl + HCDO) = 1.201$, $k(Cl +$

HCHO) / k(Cl + HCH^{18}O) = 1.08 and k(Cl + H^{13}CHO) / k(Cl + DCDO) = 1.22 (Beukes et al., 2000; Feilberg et al., 2004).

References

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