IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC18

This datasheet last evaluated: June 2018; last change in preferred values: 2018

Cl + *n*-C_4H_9OH → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.96 \pm 0.19) \times 10^{-10}$	298	Garzón et al., 2006	LP-RF (a)
$3.12 \times 10^{-11} \exp[(548 \pm 65)/T]$	266-382		
Relative Rate Coefficients			
$(2.14 \pm 0.11) \times 10^{-10}$	298 ± 2	Nelson et al., 1990	RR (b)
$(2.25 \pm 0.11) \times 10^{-10}$	295	Wu et al., 2003	RR (c)
$(2.37 \pm 0.11) \times 10^{-10}$	295	Wu et al., 2003	RR (d)
$(2.09 \pm 0.21) \times 10^{-10}$	296	Hurley et al., 2009	RR (e)
$(2.43 \pm 0.35) \times 10^{-10}$			RR (f)
$(2.39 \pm 0.35) \times 10^{-10}$			RR (g)

Comments

(a) Cl atoms generated by Cl_2 photolysis at 308 nm and detected by RF at ≈ 135 nm. All experiments in He bath gas (26.7-266.7 mbar) with traces of O_2 to scavenge organic radicals. k was independent of pressure.

(b) Cl atoms were generated by photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)-N_2 (or O_2)-*n*C_4H_9OH-cyclohexane mixtures at 1 bar pressure. Concentrations of *n*C_4H_9OH and cyclohexane were measured by GC, and the rate coefficient ratio k(Cl + *n*C_4H_9OH) / k(Cl + cyclohexane) = (0.656 ± 0.045) was placed on an absolute basis by use of k(Cl + cyclohexane) / k(Cl + *n*-butane) = 1.59 (Aschmann and Atkinson, 1995) and k(Cl + *n*-butane) = 2.05 x 10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2018).

(c) Photolysis of Cl_2 in presence of *n*C_4H_9OH using propane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio k(Cl + *n*C_4H_9OH) / k(Cl + C_3H_8) = (1.61 ± 0.08) was put on an absolute basis using k(Cl + C_3H_8) = 1.4×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2018).

(d) Photolysis of Cl_2 in presence of *n*C_4H_9OH using cyclohexane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio k(Cl + *n*C_4H_9OH) / k(Cl + cyclohexane) = (0.726 ± 0.033) was put on an absolute basis using k(Cl + cyclohexane) = 3.26×10^{-10} cm^3 molecule^{-1} s^{-1} which was derived using k(Cl + cyclohexane) / k(Cl + *n*-butane) = 1.59 (Aschmann and Atkinson, 1995) and k(Cl + *n*-butane) = 2.05 x 10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2018).

(e) Cl was generated by the photolysis of Cl_2. Experiments were conducted in 700 Torr air with reactant concentrations monitored by FTIR. Using C_2H_2 as reference reactant, the rate coefficient ratio k(Cl + *n*C_4H_9OH) / k(Cl + C_2H_2) = (4.11 ± 0.41), was obtained. This was placed on an

absolute basis using $k(Cl + C_2H_2) = 5.09 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 700 Torr and 296 K (IUPAC, 2018).

(f) See note (e). Using C_2H_4 as reference reactant, the rate coefficient ratio $k(Cl + nC_4H_9OH) / k(Cl + C_2H_4) = (2.36 \pm 0.34)$, was obtained. This was placed on an absolute basis using $k(Cl + C_2H_4) = 1.03 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2018).

(g) See note (e). Using C_2H_6 as reference reactant, the rate coefficient ratio $k(Cl + nC_4H_9OH) / k(Cl + C_3H_6) = (0.89 \pm 0.09)$ was obtained. This was placed on an absolute basis using $k(Cl + C_2H_4) = 2.68 \times 10^{-10}$ (Kaiser and Wallington, 1996).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.2 x 10^{-10}	298
k /cm^3 molecule^{-1} s^{-1}	3.45 x 10^{-11} exp(550/T)	260-390
Reliability		
$\Delta \log k$	$\pm$ 0.05	298
$\Delta E/R$	$\pm$ 200	

Comments on Preferred Values

The preferred room temperature rate coefficient is an average value from the seven studies of this reaction, which are in good agreement. The temperature dependence is taken from Garzón et al. (2006) with the pre-exponential factor adjusted to return the preferred value of k at 298 K.

In the presence of NO, the products formed in air are butyraldehyde (molar yield of 0.38 ± 0.02), propionaldehyde (0.23 ± 0.03), acetaldehyde (0.12 ± 0.04) and formaldehyde (0.33 ± 0.03). In the absence of NOx, only butryaldehyde (0.38 ± 0.02) was observed (Hurley et al., 2009).

References

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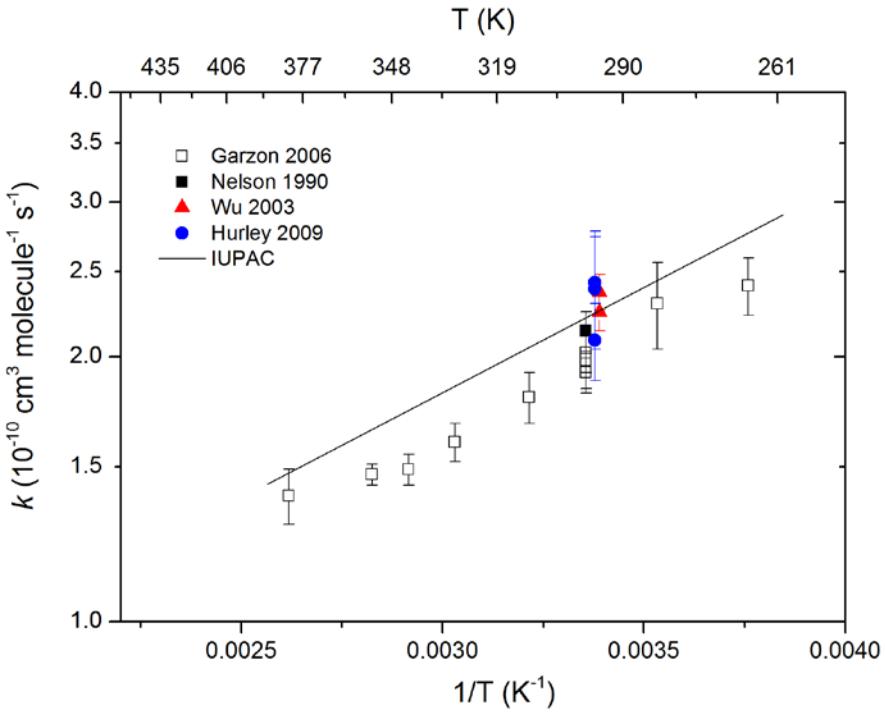

Rate coefficients for Cl + n-C_4H_9OH. The solid line (IUPAC) represents the preferred values.