

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC15

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This data sheet last evaluated: January 2008 (with changes in the preferred values)



Rate coefficient data: $k = k_1 + k_2$

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(9.4 \pm 1.4) \times 10^{-11} \exp[(45 \pm 32)/T]$	295-600	Taatjes et al., 1999	LP-IR (a)
$(1.09 \pm 0.9) \times 10^{-10}$	298		
$(1.02 \pm 0.19) \times 10^{-10}$	298	Seakins et al., 2004	LP-IR (b)
$(9.50 \pm 0.85) \times 10^{-11}$	295	Taketani et al., 2005	LP-LIF (c)
$(9.93 \pm 0.98) \times 10^{-11}$	298	Garzón et al., 2006	LP-RF (d)
$(5.25 \pm 1.4) \times 10^{-11} \exp[(190 \pm 68)/T]$	266-382		
<i>Relative Rate Coefficients</i>			
$(8.75 \pm 0.95) \times 10^{-11}$	295 ± 2	Wallington et al., 1988	RR (e)
$(1.06 \pm 0.06) \times 10^{-10}$	298 ± 2	Nelson et al., 1990	RR (f)
$(8.3 \pm 1.8) \times 10^{-11}$	295	Edelbuttel-Einhaus et al., 1992	RR (g)
$(9.4 \pm 0.8) \times 10^{-11}$	298	Taatjes et al., 1999	RR (h)
$(1.10 \pm 0.04) \times 10^{-10}$	295	Wu et al., 2003	RR (i)
$(1.02 \pm 0.04) \times 10^{-10}$	295	Wu et al., 2003	RR (j)
$(1.10 \pm 0.04) \times 10^{-10}$		Crawford et al., 2004	RR (k)
<i>Branching Ratios</i>			
$k_2/k_1 = 0.28 \exp(-350/T)$	295-600	Taatjes et al., 1999	(h)
$k_1/k = 0.92$	298		
$k_2/k = 0.08$	298		

Comments

- Cl atoms were generated by the 193 nm pulsed photolysis of CF_2Cl_2 or CFCl_3 , and kinetic parameters were obtained by analysis of HCl product formation profiles using transient IR absorption spectroscopy. Bath gas was 13.3 Torr CO_2 to quench vibrationally excited HCl. Use of deuterated ethanol enabled site specific rate coefficients to be determined via measurement of HCl yields. Complementary FTIR product analysis confirmed the result.
- $\text{Cl}(^2\text{P}_{3/2})$ generated in 351 nm laser photolysis of Cl_2 . Kinetic data obtained by monitoring the HCl product by IR emission spectroscopy.
- 193 nm photolysis of HCl to generate both excited $\text{Cl}(^2\text{P}_{1/2})$ and ground state $\text{Cl}(^2\text{P}_{3/2})$, which were detected using VUV LIF at 135.2 and 134.7 nm, respectively. $\text{Cl}(^2\text{P}_{3/2})$ decays were monitored in presence of CF_4 to ensure removal of $\text{Cl}(^2\text{P}_{1/2})$. The rate coefficient for excited Cl atoms was determined as $(6.4 \pm 1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 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
- Cl atoms were generated by photolysis of Cl_2 in Cl_2 - $\text{C}_2\text{H}_5\text{OH}$ - C_2H_6 -air (or N_2) mixtures at 1 bar total pressure. $\text{C}_2\text{H}_5\text{OH}$ and C_2H_6 were monitored by GC and a rate coefficient ratio $k(\text{Cl} +$

$C_2H_5OH) / k(Cl + C_2H_6) = 1.483 \pm 0.160$ determined. Placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).

- (f) Cl atoms were generated by photolysis of Cl_2 or $COCl_2$ in Cl_2 (or $COCl_2$)- N_2 (or O_2)-ethanol-cyclohexane mixtures at 1 bar pressure. Concentrations of ethanol and cyclohexane were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of $k(Cl + \text{cyclohexane}) / k(Cl + n\text{-butane}) = 1.59$ (Aschmann and Atkinson, 1995) and $k(Cl + n\text{-butane}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- (g) Isothermal discharge flow reactor at 1 mbar pressure, with molecular beam sampling and analysis by mass spectrometry. $k / k(Cl + C_2H_6)$ measured to be 1.4 ± 0.3 . Placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008). Supersedes earlier value reported from same laboratory (Khatoon et al., 1999).
- (h) Cl atoms were generated by the photolysis of Cl_2 in O_2 or N_2 bath gas. Loss of C_2H_5OH was measured relative to C_2H_6 using in-situ FTIR absorption spectroscopy. $k(Cl + C_2H_5OH) / k(Cl + C_2H_6)$ was measured to be 1.6 ± 0.13 , and is placed on an absolute basis by use of $k(Cl + C_2H_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008). The branching ratios were derived by product analysis.
- (i) Photolysis of Cl_2 in presence of ethanol using propane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio $k(Cl + C_2H_5OH) / k(Cl + C_3H_8) = (0.786 \pm 0.03)$ was put on an absolute basis using $k(Cl + C_3H_8) = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- (j) Photolysis of Cl_2 in presence of ethanol using cyclohexane as reference reactant and 1 atmosphere pressure of air as bath gas. Reactants analysed by GC. Rate coefficient ratio $k(Cl + C_2H_5OH) / k(Cl + \text{cyclohexane}) = (0.313 \pm 0.023)$ was put on an absolute basis using $k(Cl + \text{cyclohexane}) = 3.26 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which was derived using $k(Cl + \text{cyclohexane}) / k(Cl + n\text{-butane}) = 1.59$ (Aschmann and Atkinson, 1995) and $k(Cl + n\text{-butane}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008).
- (k) Relative rate study using DF-MS and cyclohexane as reference reactant. Rate coefficient ratio $k(Cl + C_2H_5OH) / k(Cl + \text{cyclohexane}) = (0.338 \pm 0.023)$ was put on an absolute basis using $k(Cl + \text{cyclohexane}) = 3.26 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which was derived using $k(Cl + \text{cyclohexane}) / k(Cl + n\text{-butane}) = 1.59$ (Aschmann and Atkinson, 1995) and $k(Cl + n\text{-butane}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008). A rate coefficient for reaction of Cl atoms with C_2H_5OD of $(1.18 \pm 0.22) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived using the same reference reactant.

Preferred Values

$k = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_1 = 9.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 = 0.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.0 \times 10^{-11} \exp(155/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260 - 400 K.

$k_2/k_1 = 0.28 \exp(-350/T)$ over the temperature range 290 - 600 K

Reliability

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

$\Delta(E/R) = \pm 150$ K.

Comments on Preferred Values

The four absolute studies and the relative studies of Nelson et al. (1990), Taatjes et al. (1999), Wu et al. (2003) and Crawford et al. (2004) indicate that the rate coefficient is within 10 % of $1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and provide the basis of our recommendation. The temperature dependence is taken

from the two studies that varied this parameter. The branching ratios for k_1 and k_2 are from Taatjes et al. (1999).

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