

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC7

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This data sheet updated: 3rd July 2005.



$$\Delta H^\circ(1) = -8.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -22.5 \text{ kJ}\cdot\text{mol}^{-1}$$

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 (k)</i>			
$1.36 \times 10^{-10} \exp[(44 \pm 25)/T]$	220-607	Lewis et al., 1980	DF-RF (a)
$(1.51 \pm 0.06) \times 10^{-10}$	298		
$(1.23 \pm 0.10) \times 10^{-10}$	298	Beichert et al., 1995	DF-RF (b)
$(1.38 \pm 0.03) \times 10^{-10}$	292-700	Pilgrim et al., 1997	PLP (c)
$(1.31 \pm 0.03) \times 10^{-10}$	297	Mellouki, 1998	PLP-RF (d)
$(1.33 \pm 0.03) \times 10^{-10}$	298	Hitsuda et al., 2001	PLP-LIF (e)
<i>Relative Rate Coefficients (k)</i>			
$(1.40 \pm 0.28) \times 10^{-10}$	296	Atkinson and Aschmann, 1985	RR (f)
$(1.45 \pm 0.28) \times 10^{-10}$	295	Wallington et al., 1988	RR (g)
$(1.34 \pm 0.28) \times 10^{-10}$	296	Hooshiyar and Niki, 1995	RR (h)
$(1.44 \pm 0.26) \times 10^{-10}$	298	Beichert et al., 1995	RR (i)
$(1.43 \pm 0.25) \times 10^{-10}$	297	Tyndall et al., 1997	RR (j)
<i>Relative Rate Coefficients (k_1 and k_2)</i>			
$k_1 = 7.0 \times 10^{-11} \exp[(-31 \pm 33)/T]$	299-468	Sarzynski and Sztuba, 2002	RR (k)
$(6.25 \pm 0.17) \times 10^{-11}$	299		
$k_2 = 5.2 \times 10^{-11} \exp[(118 \pm 25)/T]$	299-468		
$(7.73 \pm 0.14) \times 10^{-11}$	299		
<i>Branching ratios</i>			
$k_1/k = (0.43 \pm 0.03)$	297	Tyndall et al., 1997	RR (j)
$k_2/k = (0.57 \pm 0.03)$			
$k_1/k = 0.59 \exp[-(87 \pm 58)/T]$	295-469	Sarzynski and Sztuba, 2002	RR (k)
$k_1/k = (0.45 \pm 0.02)$	299		
$k_2/k = 0.43 \exp[(76 \pm 55)/T]$	295-469		
$k_2/k = (0.55 \pm 0.02)$	298		

Comments

- (a) Rate constant was measured at three temperatures: 220 K, 298 K and 607 K. Within experimental uncertainty, the three values of k obtained were the same. Authors gave as an alternative rate expression the simple mean of the three values: $k = (1.58 \pm 0.13) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (b) Both relative and absolute rate studies of reactions of Cl atoms with C₁-C₄ alkanes. Direct measurement of ratio $k / k(\text{Cl} + \text{C}_2\text{H}_6)$ is in good agreement with the ratio of the absolute values.

- (c) Cl atoms were generated from pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption.
- (d) Experiments carried out in 80 mbar He bath gas. O_2 added to prevent reformation of Cl atoms via $\text{R} + \text{Cl}_2$ which was used as Cl precursor (355 nm photolysis).
- (e) 193 nm photolysis of HCl as Cl source. Detection of both $\text{Cl}(^2\text{P}_{1/2})$ and $\text{Cl}(^2\text{P}_{3/2})$ using VUV-LIF. The rate constants for $\text{Cl}(^2\text{P}_{1/2})$ were found to be $\approx 30\%$ those of the $\text{Cl}(^2\text{P}_{3/2})$ ground state. The rate constant for $\text{Cl}(^2\text{P}_{3/2})$ with fully deuterated propane was found to be $0.86 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (f) Cl atoms were generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k / k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 0.681 \pm 0.025$ is placed on absolute basis by use of $k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (g) Cl atoms were generated by photolysis of Cl_2 in air at 990 mbar (740 Torr, 986 mbar) pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k / k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 0.711 \pm 0.019$ is placed on absolute basis by use of $k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (h) Cl atoms were generated by photolysis of Cl_2 in N_2 at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k / k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 0.656 \pm 0.009$ is placed on absolute basis by use of $k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (i) Cl atoms were generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k / k(\text{Cl} + \text{C}_2\text{H}_6) = 2.44 \pm 0.26$ is placed on absolute basis by use of $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (j) Cl atoms were generated by photolysis of Cl_2 in air or N_2 at a total pressure of 156 mbar to 666 mbar. Relative disappearance rates of organics studied were measured by GC or FTIR. Rate coefficient ratio $k / k(\text{Cl} + \text{C}_2\text{H}_6) = 2.42 \pm 0.10$ is placed on absolute basis by use of $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (k) Competitive photochlorination experiments with Cl atoms initially generated by the 420 nm photolysis of Cl_2 in N_2 at a total pressure of ≈ 133 mbar. Formation rates of $\text{CH}_3\text{CH}_2\text{CHCl}$ (abstraction of primary H) and $\text{CH}_3\text{CHClCH}_3$ (abstraction of secondary H) were measured relative to $\text{C}_2\text{H}_5\text{Cl}$ (from reference compound ethane) by GC. The absolute rate coefficients reported in the table were derived by use of $k(\text{Cl} + \text{C}_2\text{H}_6) = 8.3 \times 10^{-11} \exp(-100 / T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).

Preferred Values

$k = 1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200 K to 700 K.

$k_1/k = 0.59 \exp(-90 / T)$

$k_2/k = 0.43 \exp(75 / T)$

Reliability

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

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

Comments on Preferred Values

The preferred value of the overall rate coefficient, k , at room temperature is the mean of the absolute values reported by Lewis et al. (1980), Beichert et al. (1995), Pilgrim et al. (1997), Mellouki (1998) and Hitsuda et al. (2001), and the relative values reported by Atkinson and Aschmann (1985), Wallington et al. (1988), Hooshiyar and Niki (1995), Beichert et al. (1995), Tyndall et al. (1997), and Sarzynski and Sztuba (2002). Lewis et al. (1980) and Pilgrim et al. (1997) have shown that the overall

rate coefficient is independent of temperature between 220 and 700 K. This is confirmed by the results of Sarzynski and Sztuba (2002) who showed that although k_1 and k_2 have weak temperature dependences, the sum of $k_1 + k_2$ is independent of temperature between 299 and 468 K. The branching ratios derived by Tyndall et al. (1997) and Sarzynski and Sztuba (2002) are in good agreement at 298 K. Temperature dependent branching ratios have only been determined by Sarzynski and Sztuba (2002), and their values are adopted.

References

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