

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC10

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$$\Delta H^\circ(1) = -57.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -37.3 \text{ kJ}\cdot\text{mol}^{-1}$$

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</i>			
$(6.6 \pm 1.4) \times 10^{-11}$	210-343	Payne et al., 1990	FP-RF
$(7.3 \pm 0.7) \times 10^{-11}$	295	Tyndall et al., 1999	LP-RF (a)
$(7.5 \pm 0.8) \times 10^{-11}$	298	Kegley-Owen et al., 1999	LP-TDLAS (b)
$(8.3 \pm 0.1) \times 10^{-11}$	295	Smith et al., 2002	LP-IR (c)
$(8.8 \pm 1.5) \times 10^{-11}$	298	Seakins et al., 2004	LP-IR (d)
$(7.7 \pm 1.1) \times 10^{-11}$	298	Seakins et al., 2004	LP-IR (e)
<i>Relative Rate Coefficients</i>			
$(7.9 \pm 1.2) \times 10^{-11}$	298	Niki et al., 1985	RR (f)
$(8.1 \pm 0.8) \times 10^{-11}$	295 ± 2	Wallington et al., 1988	RR (g)
$(6.1 \pm 0.5) \times 10^{-11}$	298	Bartels et al., 1989	RR (h)
$(8.8 \pm 1.0) \times 10^{-11}$	298	Tyndall et al., 1999	RR (a)
<i>Branching Ratios</i>			
$k_2/k < 0.01$	298	Niki et al., 1985	(f)
$k_2/k < 0.07$	298	Bartels et al., 1989	(h)

Comments

- (a) In the absolute study, Cl atoms were generated from the 308 nm photolysis of Cl₂. 1.3 mbar of O₂ added to total pressure of 27-120mbar N₂ or He to scavenge CH₃CO and reduce regeneration of Cl, some correction was however still necessary. In the relative rate study, broad band irradiation of Cl₂ was the source of Cl atoms. Experiments were carried out in 933 mbar N₂, with analysis of CH₃CHO and reference compound (C₂H₆ and C₂H₄) with FTIR. $k(\text{Cl} + \text{CH}_3\text{CHO}) / k(\text{Cl} + \text{C}_2\text{H}_6) = 1.49 \pm 0.1$, $k(\text{Cl} + \text{CH}_3\text{CHO}) / k(\text{Cl} + \text{C}_2\text{H}_4) = 0.90 \pm 0.05$. The data have been placed on an absolute basis using $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2005).
- (b) Cl atoms were generated from the 308 nm photolysis of Cl₂ at total pressures of 13 – 67 mbar N₂. Kinetic parameters were derived by monitoring HCl formation ($v = 0$) by infra-red tuneable diode laser absorption spectroscopy. N₂O was added to quench vibrationally excited HCl, O₂ was added to reduce secondary regeneration of Cl via reaction of CH₃CO with Cl₂. 54 % (± 15 %) of the HCl was formed vibrationally excited in the $v = 1$ state.
- (c) Cl(²P_{3/2}) generated in 193 nm laser photolysis of CF₂Cl₂. Kinetic data obtained by monitoring the HCl product by tuneable infrared diode laser absorption spectroscopy. 54 % (± 4 %) of the HCl was formed vibrationally excited in the $v = 1$ state.

- (d) Cl(²P_{3/2}) generated in 351 nm laser photolysis of Cl₂. Kinetic data obtained by monitoring the HCl product by IR emission spectroscopy.
- (e) Cl(²P_{3/2}) generated in 351 nm laser photolysis of Cl₂. Kinetic data obtained by monitoring the HCl product by tuneable infrared diode laser absorption spectroscopy.
- (f) Cl atoms were generated by photolysis of Cl₂ at 930 mbar (700 Torr) total pressure of N₂. Relative decay rates of CH₃CHO and C₂H₆ measured, and the measured rate coefficient ratio is placed on an 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). The branching ratio was determined from FTIR spectroscopic product analysis.
- (g) Cl atoms were generated from the photolysis of Cl₂ in Cl₂-N₂-CH₃CH₃CHO-C₂H₆ mixtures and the relative decay rates of CH₃CH₃CHO and C₂H₆ measured. The measured rate coefficient ratio is placed on an 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).
- (h) DF-MS study. Relative decay rates of CH₃CHO and C₂H₆ were monitored, and the measured rate coefficient ratio is placed on an 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). The branching ratio was derived from the products observed by MS.

Preferred Values

$k = 8.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 210-340 K.
 $k_2/k < 0.01$ at 298 K.

Reliability

$\Delta \log k = \pm 0.07$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficients of Tyndall et al. (1999), Kegley Owen et al. (1999), Smith et al. (2002) and Seakins et al. (2004), combined with the relative rate coefficients of Niki et al. (1985), Wallington et al. (1988) and Tyndall et al. (1999). The lack of a temperature dependence of the rate coefficient is consistent with the data of Payne et al. (1990). The branching ratio is derived from the data of Niki et al. (1985). The measurement of Scollard et al. (1993) was carried out relative to CH₃C(O)CH₃ which is not considered sufficiently well defined to derive an accurate relative rate coefficient. Deuterium kinetic isotope effects were determined to be: $k(\text{Cl} + \text{CH}_3\text{CHO}) / k(\text{Cl} + \text{CH}_3\text{CDO}) = 1.34 \pm 0.02$, $k(\text{Cl} + \text{CH}_3\text{CHO}) / k(\text{Cl} + \text{CD}_3\text{CDO}) = 1.32 \pm 0.02$, $k(\text{Cl} + \text{CD}_3\text{CHO}) / k(\text{Cl} + \text{CH}_3\text{CDO}) = 1.35 \pm 0.02$, $k(\text{Cl} + \text{CD}_3\text{CHO}) / k(\text{Cl} + \text{CD}_3\text{CDO}) = 1.39 \pm 0.02$ (Beukes et al., 2000).

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