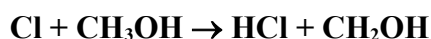


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X\_VOC14

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This data sheet last evaluated: June 2013; last change in preferred values: June 2011.



$$\Delta H^\circ = -29.8 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(6.33 \pm 0.70) \times 10^{-11}$	200-500	Michael et al., 1979	FP-RF
$(6.21 \pm 0.49) \times 10^{-11}$	298		
$(5.1 \pm 1.0) \times 10^{-11}$	298	Payne et al., 1988	DF-MS (a)
$(6.14 \pm 0.67) \times 10^{-11}$	$298 \pm 2$	Dóbe et al., 1993	DF-EPR
$(5.1 \pm 0.4) \times 10^{-11}$	$295 \pm 2$	Tyndall et al., 1999	LP-RF
$(5.6 \pm 0.2) \times 10^{-11}$	295	Smith et al., 2002	LP-IR (b)
$(5.38 \pm 0.25) \times 10^{-11}$	298	Seakins et al., 2004	LP-IR (c)
$(5.83 \pm 0.77) \times 10^{-11}$	298	Seakins et al., 2004	LP-IR (d)
$(5.35 \pm 0.24) \times 10^{-11}$	295	Taketani et al., 2005	LP-LIF (e)
$3.55 \times 10^{-10} \exp[-(559 \pm 40)/T]$	266-380	Garzón et al., 2006	LP-RF (f)
$(5.44 \pm 0.34) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(4.65 \pm 0.41) \times 10^{-11}$	$295 \pm 2$	Wallington et al., 1988	RR (g)
$(5.0 \pm 0.34) \times 10^{-11}$	$298 \pm 2$	Nelson et al., 1990	RR (h)
$(5.5 \pm 0.6) \times 10^{-11}$	295	Tyndall et al., 1999	RR (i)
$7.99 \times 10^{-11} \exp(-153/T)$	291-475	Kaiser and Wallington, 2010	RR (j)

### Comments

- Reaction between Cl and CH<sub>3</sub>OD was studied.
- Cl(<sup>2</sup>P<sub>3/2</sub>) generated in 193 nm laser photolysis of CF<sub>2</sub>Cl<sub>2</sub>. Kinetic data obtained by monitoring the HCl product by tuneable infrared diode laser absorption spectroscopy. 12 % (± 2 %) of the HCl was formed vibrationally excited in the  $\nu = 1$  state.
- Cl(<sup>2</sup>P<sub>3/2</sub>) generated in 351 nm laser photolysis of Cl<sub>2</sub>. Kinetic data obtained by monitoring the HCl product by IR emission spectroscopy.
- Cl(<sup>2</sup>P<sub>3/2</sub>) generated in 351 nm laser photolysis of Cl<sub>2</sub>. Kinetic data obtained by monitoring the HCl product by tuneable infrared diode laser absorption spectroscopy. 25 % (± 4%) of the HCl was formed vibrationally excited in the  $\nu = 1$  state.
- 193 nm photolysis of HCl to generate both excited Cl(<sup>2</sup>P<sub>1/2</sub>) and ground state Cl(<sup>2</sup>P<sub>3/2</sub>), which were detected using VUV LIF at 135.2 and 134.7 nm, respectively. Cl(<sup>2</sup>P<sub>3/2</sub>) decays were monitored in presence of CF<sub>4</sub> to ensure removal of Cl(<sup>2</sup>P<sub>1/2</sub>). The rate coefficient for excited Cl atoms was determined as  $(3.5 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

- (f) Cl atoms generated by Cl<sub>2</sub> photolysis at 308 nm and detected by RF at  $\approx$  135 nm. All experiments in He bath gas (26.7-266.7 mbar) with traces of O<sub>2</sub> to scavenge organic radicals.  $k$  was independent of pressure.
- (g) Cl atoms were generated by the photolysis of Cl<sub>2</sub> in Cl<sub>2</sub>-CH<sub>3</sub>OH-C<sub>2</sub>H<sub>6</sub>-air (N<sub>2</sub>) mixtures at 1 bar total pressure. Concentrations of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>6</sub> were monitored by GC and a rate coefficient ratio  $k(\text{Cl} + \text{CH}_3\text{OH}) / k(\text{Cl} + \text{C}_2\text{H}_6) = 0.802 \pm 0.071$  determined. This rate coefficient ratio is placed on an absolute basis by use of  $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, 2011).
- (h) Cl atoms were generated from the photolysis of Cl<sub>2</sub> or COCl<sub>2</sub> in Cl<sub>2</sub> (or COCl<sub>2</sub>)-N<sub>2</sub> (or O<sub>2</sub>)-CH<sub>3</sub>OH-cyclohexane mixtures at 1 bar pressure. Concentrations of CH<sub>3</sub>OH and cyclohexane were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of  $k(\text{Cl} + \text{cyclohexane}) / k(\text{Cl} + n\text{-butane}) = 1.59$  (Aschmann and Atkinson, 1995) and  $k(\text{Cl} + n\text{-butane}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, 2011).
- (i) Broad band irradiation of Cl<sub>2</sub> as source of Cl atoms. Experiments were carried out in 700 Torr N<sub>2</sub>, with analysis of CH<sub>3</sub>OH and reference compound (C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>) with FTIR.  $k(\text{Cl} + \text{CH}_3\text{OH}) / k(\text{Cl} + \text{C}_2\text{H}_6) = 0.94 \pm 0.04$ ,  $k(\text{Cl} + \text{CH}_3\text{OH}) / k(\text{Cl} + \text{C}_2\text{H}_4) = 0.63 \pm 0.03$ . The data have been placed on an absolute basis using  $k(\text{Cl} + \text{C}_2\text{H}_6) = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, 2011).
- (j) Cl atoms were generated by the photolysis of Cl<sub>2</sub> in Cl<sub>2</sub>-CH<sub>3</sub>OH-C<sub>2</sub>H<sub>6</sub> mixtures at 500 to 950 Torr (667-1120 mbar) N<sub>2</sub>. Relative removal rates of CH<sub>3</sub>OH and C<sub>2</sub>H<sub>6</sub> were monitored by GC-FID to determine temperature dependent ratios,  $k(\text{Cl} + \text{CH}_3\text{OH}) / k(\text{Cl} + \text{C}_2\text{H}_6)$ . These were placed on an absolute basis using a temperature dependent rate constant for Cl + C<sub>2</sub>H<sub>6</sub> which takes into account parameterisations for the rate constant at high temperatures presented by Bryukov et al. (2003) and Hickson et al. (2010).

### Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$5.5 \times 10^{-11}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.1 \times 10^{-11} \exp(-75/T)$	200-500
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.07$	298
$\Delta(E/R)$	$\pm 200$	200-500

### Comments on Preferred Values

All studies of this rate coefficient are in good agreement at room temperature. The preferred 298 K value is the unweighted average of all the studies listed above, with the exception of Wallington et al. (1988), which has been superseded by a more recent study from the same group (Tyndall et al., 1999). The inclusion of the data of Payne et al. (1988) on Cl + CH<sub>3</sub>OD is justified considering the strong body of evidence showing that the H-abstraction proceeds solely at the CH<sub>3</sub>-group at room temperature (see Payne et al., 1988; Radford et al., 1981; Meier et al., 1984; Dóbé et al., 1994 and Jodkowski et al., 1998).

The temperature dependence of  $k$  is less well defined. The data of Michael et al. (1979), which cover the largest temperature range, suggest that any temperature dependence is weak. A weighted fit to their data with an Arrhenius expression gives  $k = 6.67 \times 10^{-11} \exp[-(17 \pm 52)/T]$ . This is supported (indirectly) by time resolved measurement of relative HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> concentrations formed in the photolysis of Cl<sub>2</sub> in the presence of CH<sub>4</sub> and CH<sub>3</sub>OH and

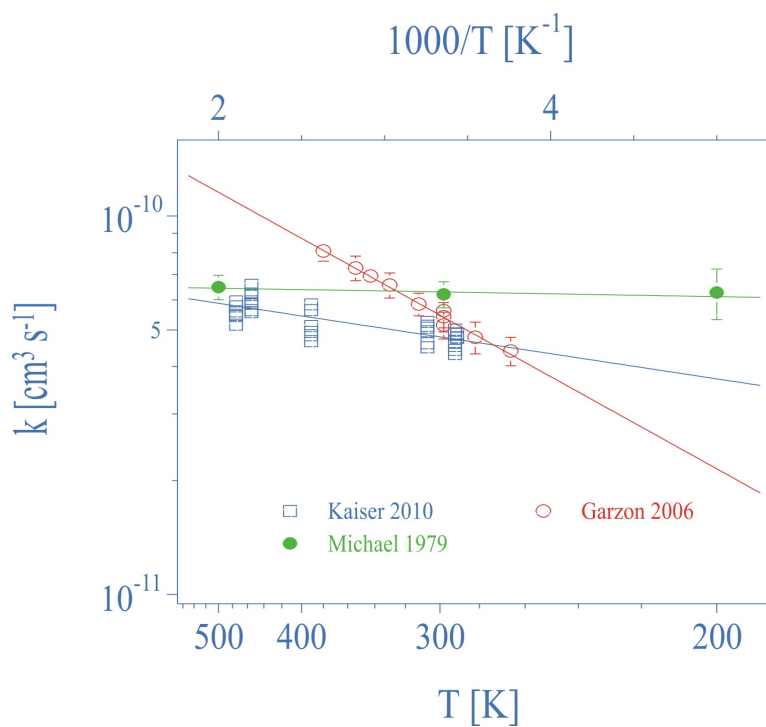
O<sub>2</sub> by Lightfoot et al. (1990). In contrast, the absolute studies of Garzón et al. (2006) indicate a significant activation barrier. The relative rate measurements by Kaiser et al., (2010) indicate a weak but significant temperature dependence although their data is dependent on the temperature dependence of the reference reaction, Cl + C<sub>2</sub>H<sub>6</sub>, at high temperatures which is not well defined (see IUPAC Cl + C<sub>2</sub>H<sub>6</sub> datasheet, II.A7.169).

The balance of evidence thus suggests that the experiments of Garzon et al (2006) have overestimated the activation barrier and we take an average of the E/R values of Michael et al (1979) and Kaiser et al. (2010), with the pre-exponential factor adjusted to reproduce the preferred value of *k* at 298 K. The uncertainty in E/R has been increased to reflect the discrepancies in the available data.

Feilberg et al. (2008) report kinetic isotope effects of:  $k(\text{Cl} + \text{CH}_3\text{OH})/k(\text{Cl} + (13)\text{CH}_3\text{OH}) = 1.055 \pm 0.016$ ,  $k(\text{Cl} + \text{CH}_3\text{OH})/k(\text{Cl} + \text{CH}_3(18)\text{OH}) = 1.025 \pm 0.022$ ,  $k(\text{Cl} + \text{CH}_3\text{OH})/k(\text{Cl} + \text{CH}_2\text{DOH}) = 1.162 \pm 0.022$ ,  $k(\text{Cl} + \text{CH}_3\text{OH})/k(\text{Cl} + \text{CHD}_2\text{OH}) = 1.536 \pm 0.060$ , and  $k(\text{Cl} + \text{CH}_3\text{OH})/k(\text{Cl} + \text{CD}_3\text{OH}) = 3.011 \pm 0.059$ .

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Temperature dependent studies of  $k(\text{Cl} + \text{CH}_3\text{OH})$ . The solid lines are Arrhenius fits to the individual datasets.