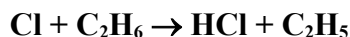


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC5

Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. The citation for this data sheet is: Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr/>. This datasheet last evaluated: June 2011; last change in preferred values: June 2011.



$$\Delta H^\circ = -8.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(6.7 \pm 0.7) \times 10^{-11}$	298	Davis et al., 1970	FP-RF (a)
$7.29 \times 10^{-11} \exp[-(61 \pm 44)/T]$	222-322	Manning and Kurylo, 1977	FP-RF
$(5.93 \pm 0.44) \times 10^{-11}$	296		
$(4.0 \pm 1.2) \times 10^{-11}$	*	Schlyer et al., 1978	DF-RF
$(5.95 \pm 0.28) \times 10^{-11}$	298	Ray et al., 1980	DF-MS
$9.01 \times 10^{-11} \exp[-(133 \pm 15)/T]$	220-604	Lewis et al., 1980	DF-RF
$(5.48 \pm 0.30) \times 10^{-11}$	298		
$8.20 \times 10^{-11} \exp[-(86 \pm 10)/T]$	203-343	Dobis and Benson, 1991	(b)
$(6.10 \pm 0.11) \times 10^{-11}$	298		
$(7.05 \pm 1.4) \times 10^{-11}$	298	Kaiser et al., 1992	PLP-IRA
$(5.9 \pm 0.6) \times 10^{-11}$	297	Stickel et al., 1992	PLP-TDLS
$(5.53 \pm 0.21) \times 10^{-11}$	298	Beichert et al., 1995	DF-RF
$(5.75 \pm 0.45) \times 10^{-11}$	298	Tyndall et al., 1997	FP-RF
$8.6 \times 10^{-11} \exp[-(135 \pm 26)]$	292-600	Pilgrim et al., 1997	PLP (c)
$(5.5 \pm 0.2) \times 10^{-11}$	292		
$(6.5 \pm 0.3) \times 10^{-11}$	297	Mellouki, 1998	PLP-RF
$(5.85 \pm 0.55) \times 10^{-11}$	298	Hitsuda et al., 2001	PLP-LIF
$4.91 \times 10^{-12} T^{0.47} \exp[-82/T]$	299-1002	Bryukov et al., 2003	DF-RF
$(5.34 \pm 0.4) \times 10^{-11}$	299	Bryukov et al., 2003	
$7.32 \times 10^{-11} \exp[-(74 \pm 13)/T]$	177-353	Hickson et al., 2004	DF-RF
5.72×10^{-11}	296		
$(5.04 \pm 0.08) \times 10^{-11}$	195	Choi et al., 2006	FP-IRA
4.34 ± 0.61	167	Hickson et al., 2010	RF (d)
4.16 ± 0.43	124		
3.39 ± 0.44	72		
2.86 ± 0.30	48		
<i>Relative Rate Coefficients</i>			
$(6.6 \pm 1.8) \times 10^{-11}$	296	Atkinson and Aschmann, 1985	RR (e)
$(6.4 \pm 0.8) \times 10^{-11}$	298	Atkinson and Aschmann, 1987	RR (e)
$(7.05 \pm 0.5) \times 10^{-11}$	295	Wallington et al., 1988	RR (e)
$(6.0 \pm 1.3) \times 10^{-11}$	296	Hooshiyar and Niki, 1995	RR (f)
$(5.4 \pm 1.2) \times 10^{-11}$	298	Beichert et al., 1995	RR (g)
$(5.5 \pm 1.2) \times 10^{-11}$	297	Tyndall et al., 1997	RR (h)
$(5.7 \pm 0.5) \times 10^{-11}$	298	Finlayson-Pitts et al., 1999	RR (i)

* Room temperature

Comments

- (a) The authors corrected for non-linearity between Cl atom concentration and fluorescence signal, which resulted in a larger value of k . It is not clear if this correction was appropriate.
- (b) Very low pressure reactor study. Cl atoms were generated by microwave discharge of Cl₂-He mixtures, with MS analysis of reactants and products.
- (c) Cl atoms generated from pulsed laser photolysis of CF₂Cl₂ at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption at the R(3) line of the fundamental vibrational transition.
- (d) Continuous supersonic flow (Laval nozzle).
- (e) Cl atoms generated by photolysis of Cl₂ in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. The rate coefficient ratios $k/k(\text{Cl} + n\text{-C}_4\text{H}_{10})$ obtained were: 0.324 ± 0.009 (Atkinson and Aschmann, 1985), 0.313 ± 0.004 (Atkinson and Aschmann, 1987) and 0.344 ± 0.026 (Wallington et al., 1988). These were placed on an 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 2011).
- (f) Cl atoms generated by photolysis of Cl₂ in N₂ at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 0.294 \pm 0.023$ is placed on an 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 2011).
- (g) Cl atoms generated by photolysis of Cl₂ in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 0.261 \pm 0.013$ 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 2011).
- (h) Cl atoms generated by photolysis of Cl₂ in air or N₂ at a total pressure of 156 mbar to 666 mbar (117-500 Torr). Relative disappearance rates of organics studied were measured by GC or FTIR. Rate coefficient ratio $k/k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 0.267 \pm 0.037$ 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 2011).
- (i) Cl atoms generated by photolysis of Cl₂, SOCl₂, or CCl₃COCl in air or N₂ at 1 bar pressure. Rate coefficient ratio $k/k(\text{Cl} + n\text{-C}_4\text{H}_{10}) = 0.277 \pm 0.025$ 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 2011).

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	5.8×10^{-11}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.05 \times 10^{-11} \exp(-60/T)$	180-330
<i>Reliability</i>		
$\Delta \log k$	± 0.05	298
$\Delta(E/R)$	50	180-330

Comments on Preferred Values

There are many absolute studies of this reaction, which are in generally very good agreement at room temperature. The preferred 298 K rate coefficient is the unweighted average of the absolute rate coefficients from Manning et al. (1977), Ray et al. (1980), Lewis et al. (1980), Dobis and Benson (1991), Stickel et al. (1992), Beichert et al. (1995), Tyndall et al. (1997), Hitsuda et al. (2001), Bryukov et al. (2003) and Hickson et al. (2004).

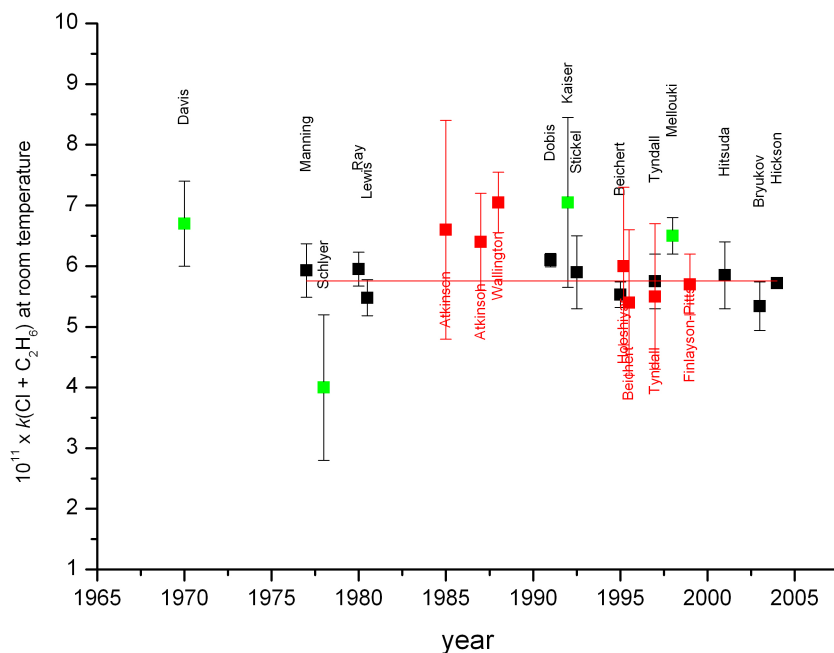
Some variation in the values of k obtained may relate to secondary chemistry involving reaction of Cl with C₂H₅ (increasing k) or re-generation of Cl via C₂H₅ + Cl₂ (reducing k). Via numerical modelling, Hickson et al. (2004) assessed the potential role of secondary chemistry in several previous datasets and found that the conditions employed could have led to significant errors in the values of k obtained. The effect may however have been ameliorated by wall loss of C₂H₅ in the low pressure flow tube studies and thus cannot be assessed retrospectively. The more recent relative rate studies (Hooshiyar and Niki, 1995; Beichert et al., 1995; Tyndall et al., 1997; Finlayson-Pitts et al., 1999) yield values of k which are entirely consistent with the preferred value from the absolute studies. There have also been some competitive chlorination studies with CH₄ as reference reactant (Kelly et al., 1970; Lee et al., 1977; Lin et al., 1978; Pritchard et al., 1955; Knox and Nelson 1959 and Tschuikov-Roux et al., 1985), though these were conducted with derivation of $k(\text{Cl} + \text{CH}_4)$ as the goal.

There are five absolute studies of the temperature dependence of k , covering the range 48 to 1002 K. Bryukov et al. (2003) derived the expression $k(\text{Cl} + \text{C}_2\text{H}_6) = 7.23 \times 10^{-13} \text{ T}^{0.7} \exp(117/\text{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to fit their high temperature data and those of all prior datasets (down to about 200 K). This expression results in an increase in k at temperatures below ~ 180 K. This is however the opposite of the trend observed subsequently by Hickson et al. (2010), who suggest $k(\text{Cl} + \text{C}_2\text{H}_6) = 1.27 \times 10^{-11} \text{ T}^{0.27} \exp(-14/\text{T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This expression reproduces all datasets (including that of Pilgrim et al. out to ~ 700 K) apart from that of Bryukov et al., which has a much steeper dependence on temperature above room temperature. There is no simple expression which can reasonably reproduce all data sets over the range of temperatures studies and until this is resolved, we confine our recommendations to a temperature range adequate to cover all conditions in the atmosphere.

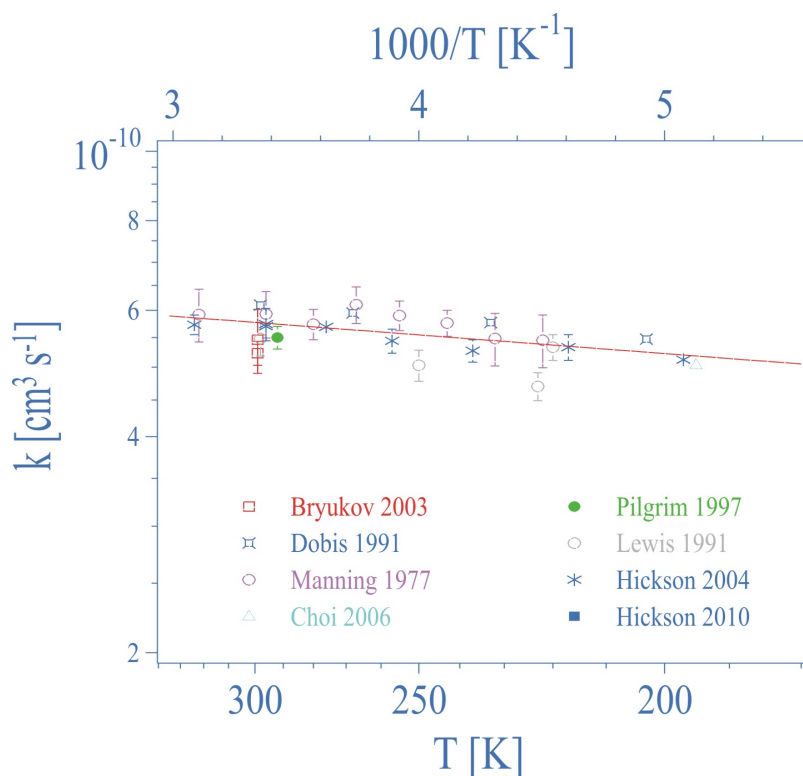
The temperature dependent parameterisation of k for atmospheric conditions (180 – 330 K) was obtained by analysing the data in this temperature range only. This included data from Manning and Kurylo (1977), Dobis and Benson (1991), Pilgrim et al. (1997) and Hickson et al. (2004) and also reproduces the preferred 298 K value.

References

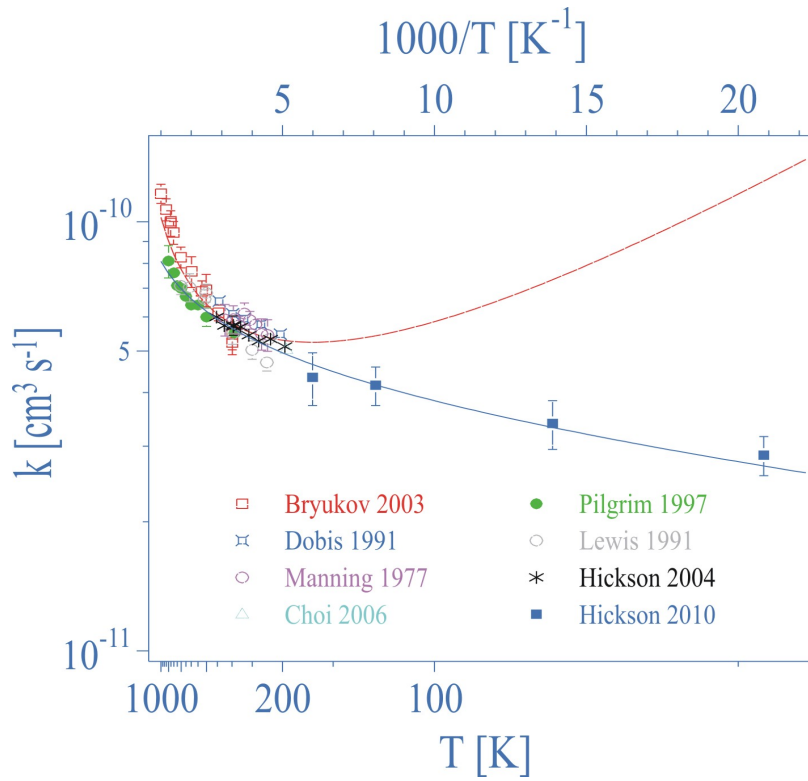
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Room temperature measurements of $k(\text{Cl} + \text{C}_2\text{H}_6)$. The solid line is the unweighted average of all absolute measurements excluding those marked in green symbols. Red symbols and text are relative rate studies.



Temperature dependent datasets between 180 and 340 K. The red line represents preferred values for atmospheric modelling.



Temperature dependent datasets between 48 and 1002 K. The red line is the parameterisation of Bryukov et al. (2003), the blue line the parameterisation of Hickson et al. (2010).