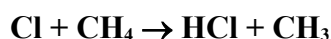


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC2

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This data sheet updated: 9th August 2002.



$$\Delta H^\circ = 7.6 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$7.94 \times 10^{-12} \exp[-(1260 \pm 35)/T]$	218-401	Watson <i>et al.</i> , 1976 ¹	FP-RF (a)
$(1.13 \pm 0.1) \times 10^{-13}$	298		
$7.93 \times 10^{-12} \exp[-(1272 \pm 51)/T]$	218-322	Manning and Kurylo, 1977 ²	FP-RF
$(1.04 \pm 0.1) \times 10^{-13}$	296		
$6.51 \times 10^{-12} \exp[-(1229 \pm 27)/T]$	200-299	Whytock <i>et al.</i> , 1977 ³	FP-RF (b)
$(1.13 \pm 0.07) \times 10^{-13}$	299		
$(1.08 \pm 0.07) \times 10^{-13}$	298	Michael and Lee, 1977 ⁴	DF-RF
$1.06 \times 10^{-11} \exp[-(1415 \pm 100)/T]$	268-423	Lin, Leu and DeMore, 1978 ⁵	DF-MS
$(9.6 \pm 0.9) \times 10^{-14}$	296		
$8.2 \times 10^{-12} \exp[-(1320 \pm 20)/T]$	200-300	Zahniser, Berquist and	DF-RF (c)
$(9.9 \pm 1.5) \times 10^{-14}$	298	Kaufman, 1978 ⁶	
$7.4 \times 10^{-12} \exp[-(1291 \pm 68)/T]$	220-298	Keyser, 1978 ⁷	DF-RF (d)
$(1.01 \pm 0.02) \times 10^{-13}$	298		
$3.2 \times 10^{-12} \exp[-(1063 \pm 34)/T]$	221-298	Ravishankara and Wine, 1980 ⁸	PLP-RF (e)
$(9.65 \pm 0.55) \times 10^{-14}$	298		
$8.06 \times 10^{-12} \exp[-(1300 \pm 113)/T]$	233-338	Heneghan, Knoot and	(f)
$(9.60 \pm 0.50) \times 10^{-14}$	298	Benson, 1981 ⁹	
$(9.93 \pm 0.13) \times 10^{-14}$	298	Dobis and Benson, 1987 ¹⁰	(f)
$(9.17 \pm 0.75) \times 10^{-14}$	294	Sawerysyn <i>et al.</i> , 1987 ¹¹	DF-MS
$(9.40 \pm 0.40) \times 10^{-14}$	298	Beichert <i>et al.</i> , 1995 ¹²	DF-RF
$7.0 \times 10^{-12} \exp[-(1270 \pm 60)/T]$	181-291	Seeley, Jayne and	(g)
$(9.9 \pm 0.3) \times 10^{-14}$	298*	Molina, 1996 ¹³	
$(1.00 \pm 0.10) \times 10^{-13}$	298	Matsumi <i>et al.</i> , 1997 ¹⁴	PLP-LIF
$3.7 \times 10^{-13} (T/298)^{2.6} \exp(-385/T)$	292-800	Pilgrim, McIlroy and	PLP (h)
$(9.3 \pm 0.9) \times 10^{-14}$	292	Taatjes, 1997 ¹⁵	
$(1.07 \pm 0.03) \times 10^{-13}$	297	Mellouki, 1998 ¹⁶	PLP-RF
$6.5 \times 10^{-12} \exp[-(1235 \pm 34)/T]$	218-298	Wang and Keyser, 1999 ¹⁷	DF-RF
$(1.01 \pm 0.06) \times 10^{-13}$	298		

Comments

- (a) These values were derived using the original data, but correcting for the presence of C₂H₆ (see Addenda to Watson, 1977¹⁸).
- (b) Non-linear Arrhenius behaviour was observed over the entire temperature range (200 K to 500 K) of measurements. Data for the temperature range 200 K to 299 K are well represented by the Arrhenius expression given in the table.³

- (c) Non-linear Arrhenius behaviour was observed over the entire temperature range (200 K to 504 K) of measurements. Data for the temperature range 200 K to 300 K are well represented by the Arrhenius expression given in the table.⁶
- (d) Non-linear Arrhenius behaviour was observed over the entire temperature range (220 K to 423 K) of measurements. Data for the temperature range 220 K to 298 K are well represented by the Arrhenius expression given in the table.⁷
- (e) Non-linear Arrhenius behaviour was observed. At temperatures at and below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture. Ravishankara and Wine⁸ suggested that this was due to a non-equilibration of the $^2P_{1/2}$ and $^2P_{3/2}$ spin states of atomic chlorine at high values of the pseudo-first order rate constant, k' , i.e., if the mixture did not contain an efficient spin equilibrator, e.g, Ar or CCl₄, the bimolecular rate constant decreased at high CH₄ concentrations, i.e., high values of k' . The Arrhenius expression for k between 221 K and 298 K was derived from the data shown in their table II (excluding the high CH₄ concentration data in the He-Cl₂-CH₄ system).
- (f) Very low pressure reactor system with MS detection of reactants and products.
- (g) Turbulent flow tube technique at pressures near 80 mbar (60 Torr). The Cl atom decay was monitored by RF.
- (h) 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. Non-linear Arrhenius behaviour was observed between 292 K and 800 K and was described by the modified Arrhenius expression given in the table.

Preferred Values

$k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200 K to 300 K.

Reliability

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

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred Arrhenius expression is derived from a least-squares fit to the experimental data between 200 K and 300 K reported in the studies of Watson *et al.*,¹ Manning and Kurylo,² Whytock *et al.*,³ Michael and Lee,⁴ Lin *et al.*,⁵ Zahniser *et al.*,⁶ Keyser,⁷ Ravishankara and Wine,⁸ Heneghan *et al.*,⁹ Dobis and Benson,¹⁰ Sawerysyn *et al.*,¹¹ Beichert *et al.*,¹² Seeley *et al.*,¹³ Matsumi *et al.*¹⁴ and Pilgrim *et al.*¹⁵ The data used were restricted to the 200 K to 300 K temperature range because of the curvature in the Arrhenius plot at higher temperatures reported in the studies of Whytock *et al.*,³ Zahniser *et al.*,⁶ Keyser,⁷ Ravishankara and Wine⁸ and Pilgrim *et al.*¹⁵ Therefore, for some studies only a subset of the data reported in the study was used. Results of the most recent studies (Mellouki¹⁶ and Wang and Keyser¹⁷) are in excellent agreement with the preferred values. Results of relative rate studies were not used in this evaluation in the derivation of the preferred values. In general, the relative rate data (refs. 5 and 18 to 21) used in previous evaluations are in good agreement with the preferred values at room temperature, but are significantly lower than the preferred values at low temperatures.

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