IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC28

This data sheet updated: 12th November 2002.

$Cl + CH_3CN \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$\leq 2.0 \times 10^{-15}$	298	Kurylo and Knable, 1984[1]	FP-RF
$3.46 \times 10^{-11} \exp[-(2785 \pm 115)/T]$	478-723	Poulet *et al.*, 1984[2]	DF-MS (a)
$(8.89 \pm 1.24) \times 10^{-15}$	295		
$(1.24 \pm 0.20) \times 10^{-14}$	296	Tyndall *et al.*, 1996[3]	PLP-RF
Relative Rate Coefficients			
$7.2 \times 10^{-12} \exp(-2200/T)$	370-413	Olbregts, Brasseur and Arijs, 1984[4]	RR (b)
$1.7 \times 10^{-11} \exp[-(2140 \pm 200)/T]$	274-345	Tyndall *et al.*, 1996[3]	RR (c)
$(1.22 \pm 0.15) \times 10^{-14}$	296		

Comments

(a) Data were obtained over the range 295 K to 723 K, and a curved Arrhenius plot was observed.

(b) Relative formation rates of products were monitored in a competitive chlorination system between CH_3CN and $CHCl_3$. Placed on an absolute basis by use of $k(Cl + CHCl_3) = 4.9 \times 10^{-12} \exp(-1240/T)$ cm^3 molecule^{-1} s^{-1}.[5]

(c) Relative decay rates of CH_3CN and the reference gas were monitored by FTIR. For the temperature dependent study the reference compound was CH_4. In a completely independent system, relative values at 296 K were also derived using as the reference compound CD_4, CF_3CCl_2H or CH_4. Based on three independent determinations by both absolute and relative rate methods the authors derived the value $k = (1.15 \pm 0.20) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K and the Arrhenius expression $k = 1.6 \times 10^{-11} \exp[-(2140 \pm 200)/T]$ cm^3 molecule^{-1} s^{-1} over the temperature range 274 K to 345 K.

Preferred Values

$k = 1.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 1.6 \times 10^{-11} \exp(-2140/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 270 K to 350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
$\Delta(E/R) = \pm 300$ K.

Comments on Preferred Values

The preferred values are based on the results reported by Tyndall *et al*.[3] The results of this study over a wide range of experimental conditions, using both relative and absolute rate methods, are preferred over results of earlier studies by Kurylo and Knable,[1] Poulet *et al*.[2] and Olbregts *et al*.[4] In the study of Tyndall *et al*.,[3] the room temperature rate coefficient was found to be independent of pressure over the range 7 mbar to 930 mbar (5 Torr to 700 Torr). Analysis of end products in smog-chamber experiments indicate that the reaction proceeds predominantly if not exclusively by H-abstraction.[3,6] The atmospheric fate of the resultant CH_2CN radical is discussed by Tyndall *et al*. [6]

References

1 M. J. Kurylo and G. L. Knable, J. Phys. Chem. **88**, 3305 (1984).

2 G. Poulet, G. Laverdet, J. L. Jourdain, and G. Le Bras, J. Phys. Chem. **88**, 6259 (1984).

3 G. S. Tyndall, J. J. Orlando, T. J. Wallington, J. Sehested, and O. J. Nielsen, J. Phys. Chem. **100**, 660 (1996).

4 J. Olbregts, G. Brasseur, and E. Arijs, J. Photochem. **24**, 315 (1984).

5 IUPAC (2013), http://iupac.pole-ether.fr

6 G. S. Tyndall, J. J. Orlando, T. J. Wallington, and M. D. Hurley, J. Phys. Chem. A. **105**, 5380 (2001).