IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC20

This data sheet updated: 12th November 2002.

Cl + HC(O)OH → HCl + HCO_2 (1)

→ HCl + HOCO (2)

$\Delta H°(2) = -52$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
(1.83 ± 0.12) x 10^{-13}	295 ± 2	Li, Osbourne and Smith, 2000[1]	FP-IR (a)
Relative Rate Coefficients			
(2.15 ± 0.12) x 10^{-13}	295 ± 2	Wallington *et al*., 1990[2]	RR (b,c)
(1.83 ± 0.10) x 10^{-13}	295 ± 2	Wallington *et al*., 1990[2]	RR (b,d)

Comments

(a) Cl-atoms made in the flash photolysis of Cl_2 in He at 10 Torr. O_2 was added to convert HOCO to CO_2, which was monitored by transient IR absorption spectroscopy to obtain kinetic data. A small correction (< 10%) was applied to take HC(O)OH dimerisation into account.

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-air-HC(O)OH-CH_3Cl (or CH_4) mixtures at 930 mbar (700 Torr) total pressure. HC(O)OH and CH_3Cl (or CH_4) were monitored by FTIR absorption spectroscopy during the experiments.

(c) Relative to k(Cl + CH_3Cl). Placed on an absolute basis by use of k(Cl + CH_3Cl) = 4.9 x 10^{-13} cm^3 molecule^{-1} s^{-1}.[3]

(d) Relative to k(Cl + CH_4). Placed on an absolute basis by use of k(Cl + CH_4) = 9.9 x 10^{-14} cm^3 molecule^{-1} s^{-1}.[3]

Preferred Values

k = 1.9 x 10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficient of Li, Osbourne and Smith[1] and the relative rate coefficients obtained by Wallington *et al*.[2]

Tyndall *et al*.[4] have observed that CO_2 is the sole carbon-containing product formed from this reaction in air or N_2 diluent, and conclude from comparison of the rate coefficients for the

reactions of the Cl atom with HC(O)OH, $CH_3C(O)OH$[5] and $CD_3C(O)OH$[5] that reaction channel (2) dominates.

References

1 Q. Li, M.C. Osbourne and I.W.M. Smith, Int. J. Chem. Kin. **32**, 85 (2000).
2 T. J. Wallington, J. M. Andino, J. C. Ball, and S. M. Japar, J. Atmos. Chem. **10**, 301 (1990).
3 IUPAC (2013), http://iupac.pole-ether.fr
4 G. S. Tyndall, T. J. Wallington, and A. R. Potts, Chem. Phys. Lett. **186**, 149 (1991).
5 S. Koch and G. K. Moortgat, Chem. Phys. Lett. **173**, 531 (1990).