IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet X_VOC21

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$$\mathbf{Cl + CH_3C(O)OH \rightarrow HCl + CH_2C(O)OH} \quad \mathbf{(1)}$$
$$\mathbf{\rightarrow HCl + CH_3C(O)O} \quad \mathbf{(2)}$$

$\Delta H°(2) = 11$ kJ·mol^{-1}

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.8 \pm 0.4) \times 10^{-14}$	298 ± 1	Koch and Moortgat, 1990	RR (a)
$(2.5 \pm 0.3) \times 10^{-14}$	295	Crawford et al., 1999	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-$CH_3C(O)OH$-CH_4-N_2 mixtures at 1 bar total pressure. The concentrations of $CH_3C(O)OH$ and CH_4 were measured by IR absorption spectroscopy. The rate coefficient ratio $k(Cl + CH_3C(O)OH) / k(Cl + CH_4) = 0.28 \pm 0.04$ is placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005). An analogous experiment using $CD_3C(O)OH$ yielded a rate coefficient of $k(Cl + CD_3C(O)OH) = (7.5 \pm 0.2) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, indicating that the reaction proceeds mainly by channel (1).

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2-$CH_3C(O)OH$-CH_4 mixtures in N_2 or air at 933 mbar total pressure. The concentrations of $CH_3C(O)OH$ and CH_4 were measured by IR absorption spectroscopy. The rate coefficient ratio $k(Cl + CH_3C(O)OH) / k(Cl + CH_4) = 0.25 \pm 0.03$ is placed on an absolute basis by use of $k(Cl + CH_4) = 1.0 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2005).

Preferred Values

$k = 2.65 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient an average of the similar studies of Koch and Moortgat (1990) and Crawford et al. (1999) The measured rate coefficient ratio of $k(Cl + CH_3C(O)OH)/k(Cl + CD_3C(O)OH) = 3.7$ at (298 ± 1) K indicates that channel (1) dominates at 298 K (Koch and Moortgat, 1990).

References

Crawford, M. A., Wallington, T. J., Szente, J. J., Maricq, M. M., and Francisco, J. S.: J. Phys. Chem. A 103, 365, 1999.
IUPAC, 2013, http://iupac.pole-ether.fr
Koch, S. and Moortgat, G. K.: Chem. Phys. Lett. 173, 531, 1990.