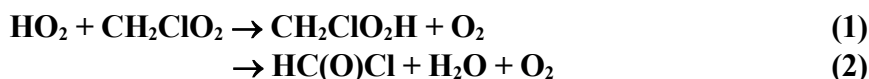


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oClOx73

Website: <http://iupac.pole-ether.fr>. See website for latest evaluated data. 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., Troe, J. and Wallington, T.J.: Atmos. Chem. Phys., 9, 4141, 2008.

This data sheet last evaluated: June 2015; last change in preferred values: December 2004.



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$3.26 \times 10^{-13} \exp[(822 \pm 63)/T]$ $(4.9 \pm 0.6) \times 10^{-12}$	251-600 298	Catoire et al., 1994	FP-UVA (a)
<i>Branching Ratios</i>			
$k_1/k = 0.27 \pm 0.05$ $k_2/k = 0.73 \pm 0.12$	295	Wallington et al., 1996	UVP-FTIR (b)

Comments

- (a) Flash photolysis-UV absorption study of $\text{Cl}_2\text{-CH}_3\text{Cl-CH}_3\text{OH-O}_2\text{-N}_2$ mixtures at a total pressure of 1013 mbar. Kinetic data were obtained by analyzing pairs of decay curves recorded at two monitoring wavelengths, with differing contributions to the total absorption made by CH_2ClO_2 and HO_2 radicals.
- (b) Steady-state photolysis of $\text{Cl}_2\text{-CH}_3\text{Cl-H}_2\text{-O}_2\text{-N}_2$ mixtures at total pressures of 933 mbar with FTIR spectroscopic monitoring of the removal of CH_3Cl and formation of $\text{CH}_2\text{ClO}_2\text{H}$ and HCOCl as a function of the initial concentration ratio $[\text{H}_2]/[\text{CH}_3\text{Cl}]$.

Preferred Values

$k = 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.2 \times 10^{-13} \exp(820/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250-600 K.

$k_1/k = 0.3$

$k_2/k = 0.7$

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 300$ K.

$\Delta(k_1/k) = \pm 0.1$ at 298 K.

$\Delta(k_2/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred branching ratios are based on the results of the product study of Wallington et al. (1996), which demonstrate the participation of both reaction channels, with channel (2) dominating at 298 K. This is fully consistent with previous studies of the oxidation of CH_3Cl

(Sanhueza and Heicklen, 1975; Niki et al., 1980), in which near-quantitative formation of HCOCl was observed, even though CH_2ClO_2 was believed to be partially removed by reaction with HO_2 . Tentative observation of $\text{CH}_2\text{ClO}_2\text{H}$ at yields up to ca. 10% in these earlier studies is also consistent with the branching ratios reported by Wallington et al. (1996).

The preferred rate coefficient values are based on the sole kinetics study of Catoire et al. (1994). These results indicate that the rate coefficients of the reactions of CH_2ClO_2 and CH_3O_2 radicals with the HO_2 radical at 298 K are similar, as are their temperature dependences. This is in marked contrast to the self-reactions of CH_2ClO_2 and CH_3O_2 radicals where chlorine substitution greatly enhances the rate coefficient. Confirmation of the above data is required.

References

- Catoire, V., Lesclaux, R., Lightfoot, P. D. and Rayez, M.-T.: *J. Phys. Chem.* 98, 2889, 1994.
Niki, H., Maker, P. D., Savage, C. M. and Breitenbach, L. P.: *Int. J. Chem. Kinet.* 12, 1001, 1980.
Sanhueza, E. and Heicklen, J.: *J. Phys. Chem.* 79, 7, 1975.
Wallington, T. J., Hurley, M.D. and Schneider, W.F.: *Chem. Phys. Lett.* 251, 164, 1996.