

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet IV.A2.93 oClOx19

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$1.2 \times 10^{-11} \exp(-1230/T)$	273-368	Tschuikow-Roux et al., 1988	RR (a)
1.9×10^{-13}	298		
$(1.10 \pm 0.25) \times 10^{-13}$	298	Tuazon et al., 1992	RR (b)

Comments

- (a) Cl atoms were generated by the photolysis of Cl_2 . Product yield ratios were measured by GC. Kinetic data were derived by measuring the formation of CHFCl_2 and CH_3Cl following UV irradiation at 424 nm of CH_4 - CH_2FCl - Cl_2 mixtures at a total pressure of about 28 mbar. Derived values of $A/A_{\text{CH}_4} = (1.92 \pm 0.01)$ and $(E-E_{\text{CH}_4})/R = (-8 \pm 2)$ K were placed on an absolute basis using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).
- (b) Photolysis of Cl_2 in presence of CH_2FCl and CH_4 in 986 mbar (740 Torr) air bath gas. The loss of CH_2FCl and CH_4 were measured by FTIR spectroscopy. The rate constant ratio obtained, $k(\text{Cl} + \text{CH}_2\text{FCl})/k(\text{Cl} + \text{CH}_4) = 1.10 \pm 0.02$ was placed on an absolute value using $k(\text{CH}_4) = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 2006).

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.1×10^{-13}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$6.8 \times 10^{-12} \exp(-1230/T)$	270-370
<i>Reliability</i>		
$\Delta \log k$	± 0.3	298
$\Delta E/R$	± 500	

Comments on Preferred Values

In the relative rate study by Tuazon et al. (1992) the rate constant ratio $k(\text{Cl} + \text{CH}_2\text{FCl})/k(\text{Cl} + \text{CH}_4)$ was measured by monitoring the loss of CH_2FCl and CH_4 following UV irradiation of CH_2FCl - CH_4 - Cl_2 -air mixtures. The loss of CH_2FCl and CH_4 were monitored directly using in-situ FTIR spectroscopy. In the relative rate study by Tschuikow-Roux et al. (1988) the rate coefficient ratio $k(\text{Cl} + \text{CH}_2\text{FCl})/k(\text{Cl} + \text{CH}_4)$ was measured by monitoring the formation of CHFCl_2 and CH_3Cl following UV irradiation of CH_2FCl - CH_4 - Cl_2

mixtures. The formation of CHFCl_2 and CH_3Cl were measured by GC-FID and used to infer the loss of CH_2FCl and CH_4 . Tschuikow-Roux et al. (1988) applied a large (5.089) correction factor to account for the response of the GC-FID to CHFCl_2 . In light of the less direct approach and large correction made in the work of Tschuikow-Roux et al. (1988) the room temperature result of Tuazon et al. (1992) is preferred. The recommended value is based on the room temperature results of Tuazon et al. (1992) and the temperature dependence reported by Tschuikow-Roux et al. (1988).

References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Atmos. Chem. Phys., 6, 3625, 2006; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>
- Tschuikow-Roux, E., Faraji, F., Paddison, S., Niedzielski, J. and Miyokawa, K.: J. Phys. Chem., 92, 1488, 1988.
- Tuazon, E. C., Atkinson, R. and Corchnoy, S. B.: Int. J. Chem. Kinet., 24, 639, 1992.

