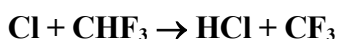


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet of FOx111

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: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This data sheet last evaluated: September 2011; last change in preferred values: September 2011.



$$\Delta H^\circ = 17.9 \text{ kJ mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(4.3 \pm 1.5) \times 10^{-16}$	298	Jourdain et al., 1976	FT-MS (a)
<i>Relative Rate Coefficients</i>			
$4.6 \times 10^{-13} \exp[-(3520)/T]$	303-399	Coomber and Whittle, 1966	RR (b)
3.4×10^{-18}	298		

Comments

- (a) The reaction rate coefficient was measured using a flow reactor, employing a microwave discharge in Cl_2 for the generation of Cl atoms with mass spectrometric detection of reactants and products. Experiments were performed in 0.3-3 Torr of helium diluent.
- (b) The reaction rate coefficients were measured using a competitive method with Cl atoms generated via photolysis of Cl_2 at 366 nm (mercury lamp). The expression in the table above was derived from the measured ratios $k_{\text{CH}_4}/k_{\text{C}_2\text{F}_5\text{H}} = 12.4 \exp[(1450 \pm 40)/RT]$ and $k_{\text{C}_2\text{F}_5\text{H}}/k_{\text{CHF}_3} = 1.16 \exp[(3080 \pm 70)/RT]$ which leads to $k_{\text{CH}_4}/k_{\text{CHF}_3} = 14.4 \exp[(4530 \pm 80)/RT] = 14.4 \exp[(2280 \pm 40)/T]$. Using $k(\text{Cl} + \text{CH}_4) = 6.6 \times 10^{-12} \exp(-1240/T)$ (Atkinson et al., 2006) gives $k(\text{Cl} + \text{CHF}_3) = 4.6 \times 10^{-13} \exp(-3520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. At 298 K this expression gives $k(\text{Cl} + \text{CHF}_3) = 3.4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 6 \times 10^{-16}$	298

Comments on Preferred Values

The rate coefficient reported by Jourdain et al. at 298 K is two orders of magnitude greater than that obtained from extrapolation of the data from Coomber and Whittle. The reaction endothermicity of 17.9 kJ mol^{-1} provides a lower limit for the activation energy ($E_a/R = 2150$) which combined with

an estimate of 1×10^{-12} for the A factor gives an upper limit of $k(\text{Cl} + \text{CHF}_3) < 7 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. In the absolute rate study by Jourdain et al. a contribution from reaction with reactive impurities is difficult to exclude. The study by Coomber and Whittle gives a rate coefficient ratio of $k(\text{Cl} + \text{CH}_4)/k(\text{Cl} + \text{C}_2\text{HF}_5) = 144$ which is approximately a factor of two lower than the ratio of the recommended rate coefficients $k(\text{Cl} + \text{CH}_4)/k(\text{Cl} + \text{C}_2\text{HF}_5) = 385$ (Atkinson et al., 2006; 2008). The recommended upper limit of $k(\text{Cl} + \text{CHF}_3) < 6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is based on the result from Jourdain et al.

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>
- 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.*, 8, 4141, 2008; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>
- Coomber, J.B. and Whittle, E.: *Trans. Faraday Soc.*, 62, 2183, 1966.
- Jourdain, J. L., Poulet, G., Barassin, J., Le Bras, G. and Combourieu J.: *Pollut. Atmos.*, 75, 256, 1977.