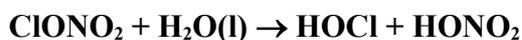


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.16 HET_H2OL_16

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 hard copy without explicit written permission.

This data sheet evaluated: 15th January 2009; last change in preferred values: 15th January 2009.



Experimental data

Parameter	[X]/ M	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>				
$\gamma = 0.027 \pm 0.0025$	pure water	275-285	Dieber et al, 2004	DFT-MS (a)

Comments

- (a) Uptake rates measured onto 200 μ m pure water droplets following loss of reactant in conventional droplet train apparatus. Droplet temperature controlled by evaporative cooling with adjustment of p(H₂O). Uptake coefficient determined with a simple correction for diffusion effects. No gas phase products were detected.

Preferred Values

Parameter	Value	T/K
α	0.108 \pm 0.033	273-290
$H(k')^{1/2}$ (M atm ⁻¹ s ^{-1/2})	1.2 x 10 ⁵	273-290
<i>Reliability</i> $\Delta \log(\alpha)$	± 0.15	273-290

Comments on Preferred Values

The cited work is the only study of reactive uptake of ClONO₂ on liquid water substrates, all of the other reported studies used solid substrates (ice) or sulphuric acid solutions. These studies showed that uptake led to HOCl and HNO₃ formation by hydrolysis. No gas phase products were observed from uptake on water droplets due to the high solubility of the products. The measured uptake coefficient was independent of temperature over the small range investigated, but increased significantly when Br⁻ was present in solution (see data sheet for ClONO₂ + Cl⁻/Br⁻). This was interpreted in terms of decreasing chemical lifetime of ClONO₂(aq) due to reaction with Br⁻. This allowed evaluation of the accommodation coefficient by extrapolation of the uptake coefficients corrected for gas phase diffusion effects, to high [Br⁻] using the resistance model:

$$\frac{1}{Y} - \frac{1}{Y_{diff}} = \left\{ \frac{1}{\alpha} + \frac{c}{4HRT (D_l k^1)^{0.5}} \right\}^{-1} \quad \text{where } k^l = k^l[\text{Br-}] \text{ s}^{-1}$$

This gave $\alpha = (0.108 \pm 0.011)$ at 274.5 K. The recommended accommodation coefficient is based on this analysis. The value of $H\sqrt{k^1}$ can also be derived using the resistance model, assuming that the reduction in uptake coefficient into water compared to the accommodation limited rate, is due to slow rate of hydrolysis in solution. A value of $D_l = 5.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was used for this analysis. There are no reported values of H or D_l .

References

Deiber, G.; George, Ch.; le Calve, S.; Schweitzer, F.; Mirabel, Ph., *Atm. Chem. Phys.*, 4(5), 1291-1299, (2004).