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

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

$ClONO_2 + H_2O(l) \rightarrow HOCl + HONO_2$

Experimental data

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

Comments

(a) Uptake rates measured onto 200mm pure water droplets following loss of reactant in conventional droplet train apparatus. Droplet temperature controlled by evaporative cooling with adjustment of $p(H_2O)$. 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 ± 0.033	273-290
$H(k^l)^{1/2}$ (M atm^{-1}s$^{-1/2}$)	1.2×10^5	273-290
Reliability		
$\Delta \log(\alpha)$	± 0.15	273-290

Comments on Preferred Values

The cited work is the only study of reactive uptake of $ClONO_2$ on liquid water substrates, all ot the other reported studies used solid substrates (ice) or sulphuric acid solutions. These studies showed that uptake led to HOCl and HNO_3 formation by hydrolysis. No gas phase products were observed from uptake on water droplets due to the high solubilty 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 $ClONO_2$ + Cl-/Br-). This was interpreted in terms of decreasing chemical lifetime of $ClONO_2$(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:

$$\frac{1}{\gamma} - \frac{1}{\gamma_{diff}} = \left\{ \frac{1}{\alpha} + \frac{c}{4HRT\,(D_l k^1)^{0.5}} \right\}^{-1}$$ where $k^I = k^{II}$[Br-] s^{-1}

This gave α = (0.108 ± 0.011) at 274.5 K. The recommended accommodation coefficient is based on this analysis. The value of $H\sqrt{k^I}$ 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 x 10^{-6} cm^{-2} 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).