IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.10 HET_SALTS_10

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

$ClONO_2 + Cl^-/Br^- \rightarrow Cl_2/ClBr + HNO_3$

Experimental data

Parameter	[X]/ M	Temp./K	Reference	Technique/ Comments
Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$				
$\gamma = 0.0244 \pm 0.0023$	0.1M NaCl	274.6	Dieber et al, 2004	DFT-MS (a)
$\gamma = 0.041 \pm 0.0067$	0.01M NaBr	274.1		
$\gamma = 0.046 \pm 0.0019$		277		
$\gamma = 0.047 \pm 0.0011$		280.8		
$\gamma = 0.044 \pm 0.0027$	0.025M	274.3		
$\gamma = 0.041 \pm 0.0043$	NaBr	276.2		
$\gamma = 0.055 \pm 0.0060$	0.05M NaBr	274		
$\gamma = 0.054 \pm 0.0039$		277		
$\gamma = 0.053 \pm 0.0028$		281		
$\gamma = 0.057 \pm 0.0048$	0.10M NaBr	274.9		
$\gamma = 0.049 \pm 0.0024$		276.2		
$\gamma = 0.056 \pm 0.0008$		279.9		
$\gamma = 0.0655 \pm 0.0015$	0.5M NaBr	274.4		
$\gamma = 0.0663 \pm 0.0011$		276.5		
$\gamma = 0.073 \pm 0.0106$	1.0M NaBr			

Comments

(a) Uptake rates measured onto 200mm 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. γ measured as function of [NaCl] and [NaBr]. On NaCl γ was not significantly larger than on pure water, but Cl_2 was observed as a unique gas-phase product. On NaBr droplets γ increased with increasing $[Br^-]$ and was essentially independent of temperature over the small range investigated for all $[Br^-]$. Both BrCl and Br_2 were detected as gas phase products.

Preferred Values

Parameter	Value	T/K
α_b	0.108	273-290
$H\sqrt{k^{II}}$ ($M^{1/2}$ $atm^{-1}s^{-1/2}$) (Br^-)	1.0×10^6	273-290

Reliability

$\Delta \log (\alpha)$	± 0.2	273-290
$\Delta \log (H\sqrt{k^{II}})$	± 0.15	273-290

Comments on Preferred Values

The cited work is the only study of reactive uptake of $ClONO_2$ on aqueous halide substrates NaCl and NaBr; all the other reported studies used either solid substrates (ice) or sulphuric acid solutions. These studies showed that uptake led to XCl (X= Cl or Br) and HNO_3 formation. The dihalogens can partition to the gas phase, depending on their solubilty. No gas phase products were observed from uptake on water droplets due to the high solubilty of the products.

The measured uptake coefficient on NaCl was not significantly greater than on pure water droplets (see data sheet for $ClONO_2 + H_2O$, VI.A2.16). However it is expected that Cl_2 rather than HOCl will be formed as products. When Br^- was present in solution, γ increased with increasing [Br-] and was independent of temperature over the small range investigated for all [Br-]. This was interpreted in terms of the resistance model with increasing liquid phase reaction rate of $ClONO_2$(aq) due to reaction with Br- allowing accommodatopn controlled uptake at high [Br-];

$$\gamma = \left\{ \frac{1}{\alpha} + \frac{c}{4HRT\,(D_l k^1)^{0.5}} \right\}^{-1} \quad \text{where } k^I (s^{-1}) = k^{II} \times [Br^-]_{aq}\,(M)$$

This allowed evaluation of the reactive uptake parameters for uptake on Br- containing solutions at 274.5 K: $\alpha_b = (0.108 \pm 0.011)$ and the product $H\sqrt{k^{II}} = 1.0 \times 10^6$ $M^{1/2}$ $atm^{-1}s^{-1/2}$ from a plot of uptake coefficients corrected for gas phase diffusion effects $(1/\gamma - (1/\gamma_{diff})$, vs $1/[NaBr]^{1/2}$, according to the resistance model with D_l assumed to be 5×10^{-6} cm^2s^{-1}. The recommended uptake parameters are based on this analysis. There are no reported values of H or D_l for $ClONO_2$.

References

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

ψ = μ1 + μ2*M0		
	ςαλυε	Ερρορ
μ1	9.823	0.69476
μ2	1.1816	0.12939
Χηισθ	3.822	NA
P	0.97685	NA