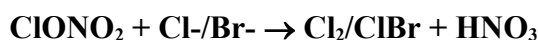


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.10 HET_SALTS_10

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>				
$\gamma = 0.0244 \pm 0.0023$	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		
$\gamma = 0.053 \pm 0.0028$	0.10M NaBr	281		
$\gamma = 0.057 \pm 0.0048$		274.9		
$\gamma = 0.049 \pm 0.0024$		276.2		
$\gamma = 0.056 \pm 0.0008$	0.5M NaBr	279.9		
$\gamma = 0.0655 \pm 0.0015$		274.4		
$\gamma = 0.0663 \pm 0.0011$	1.0M NaBr	276.5		
$\gamma = 0.073 \pm 0.0106$				

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 $p(\text{H}_2\text{O})$. 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 $[\text{Br}^-]$ and was essentially independent of temperature over the small range investigated for all $[\text{Br}^-]$. Both BrCl and Br_2 were detected as gas phase products.

Preferred Values

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

Reliability

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

Comments on Preferred Values

The cited work is the only study of reactive uptake of ClONO₂ 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 HNO₃ formation. The dihalogens can partition to the gas phase, depending on their solubility. No gas phase products were observed from uptake on water droplets due to the high solubility of the products.

The measured uptake coefficient on NaCl was not significantly greater than on pure water droplets (see data sheet for ClONO₂ + H₂O, VI.A2.16). However it is expected that Cl₂ 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 ClONO₂(aq) due to reaction with Br⁻ allowing accommodation controlled uptake at high [Br⁻];

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

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 $H\sqrt{k^l} = 1.0 \times 10^6 \text{ M}^{1/2} \text{ atm}^{-1} \text{ s}^{-1/2}$ from a plot of uptake coefficients corrected for gas phase diffusion effects ($1/\gamma - (1/\gamma_{\text{diff}})$), vs $1/[\text{NaBr}]^{1/2}$, according to the resistance model with D_l assumed to be $5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. The recommended uptake parameters are based on this analysis. There are no reported values of H or D_l for ClONO₂.

References

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

$\psi = \mu_1 + \mu_2 * M_0$		
	ζάλυε	Ερρορ
μ_1	9.823	0.69476
μ_2	1.1816	0.12939
Χητισθ	3.822	NA
P	0.97685	NA

