

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.9 HET_SALTS_9

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

ClNO₂ + Cl-/Br- → products

Experimental data

Parameter	[X]/M	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>				
4.8 x 10 ⁻⁶	4.6M NaCl	300	Behnke et al., 1997	WWFT-FTIR (a)
(1.4±0.2)x10 ⁻⁵	0.5 and 1 mM NaBr, HBr	275,291	Frenzel et al, 1997	WWFT-FTIR (b)
$\gamma_0 = 9.0 \times 10^{-6}$		282		
$\gamma_{ss} = (6.7 \pm 1.3) \times 10^{-6}$	10 ⁻⁴ M NaBr	275 - 288		WWFT- FTIR/MS (c)
$\gamma_{ss} = (8.2 \pm 1.0) \times 10^{-4}$	10 ⁻² M NaBr			
$\gamma_{ss} = (8.8 \pm 2.6) \times 10^{-4}$	1M NaBr			
$\gamma_{ss} = (1-10) \times 10^{-4}$	10 ⁻⁴ to 1M NaBr aqueous film	274	Fickert et al., 1998	WWFT-MS (d)
(6±2) x 10 ⁻³	0.05 to 6M NaCl aqueous film; pH < 2	298	Roberts et al., 2008	WWFT- CRDS/CIMS (e)

Comments

- (a) Variable length (10-80 cm) wetted-wall flow tube at 1 bar of synthetic air. The liquid film thickness was between 0.8 and 1.2 mm at a surface speed of 2-10 cm s⁻¹. The gas flow rate was in the range 200-400 mL min⁻¹ at 291K resulting in an average linear flow velocity of 15-30 cm s⁻¹. The initial [ClNO₂] was measured upstream, the unreacted ClNO₂ was measured downstream of the WWFT using FTIR. Between pure H₂O and 1M NaCl γ decreases by more than a factor of ten.
- (b) Uptake study in a variable length wetted-wall flow tube at P=1 atm of synthetic air. Experimental details may be found in the data sheet for ClNO₂ + H₂O under (b). The uptake coefficients were obtained by fitting the measured initial time/position-dependent concentration profiles in the range 0 to 7s using a complex reaction mechanism including gas phase and liquid diffusion. Observed reaction products included BrNO₂, Br₂, NO₂ in the gas phase and Cl⁻, NO₂⁻ and NO₃⁻ in the condensed phase
- (c) Uptake experiment in a wetted-wall flow tube equipped with FTIR/long-path absorption and ion-trap mass spectrometry for gas phase detection of ClNO₂ and products. The uptake coefficients were independent of temperature in the stated range and scaled linearly when plotted as 1/ γ vs. [NaX]⁻¹ with X = I-. The main gas phase product was Br₂.

- (d) Uptake study in a wetted-wall tubular flow reactor on a falling film of pure water and aqueous alkali halide salt solutions at 14 to 18 Torr of He as a carrier gas. The reactant was monitored using a differentially-pumped MS. The value of γ_{SS} remains unchanged upon addition of 1M NaCl whereas it increased upon addition of 0.1M OH⁻. Analysis of uptake rates measured under gas –phase diffusion controlled conditions (0.5 M KOH film) gave the cited value for the accommodation coefficient on aqueous surfaces, $\alpha = (9 \pm 4) \times 10^{-3}$. Estimates of the diffusion coefficients D^{ClNO_2} in He, N₂ and H₂O are reported as 275±26, 75±6 and 100±20 Torr cm s⁻¹ respectively. Parameters determining reactive uptake rates into Br⁻ solutions were determined interdependently as $H^2D_1k^{II} = (0.101 \pm 0.015) \text{ M cm}^2 \text{ s}^{-2}$. The gas phase products were found to be Br₂, BrNO₂ and minor amounts of BrCl. Br₂ was a secondary reaction product resulting from the condensed phase reaction of BrNO₂ with Br⁻.
- (e) Uptake study in a tubular flow reactor where N₂O₅ was converted to ClNO₂ by reaction on aqueous slurry of NaCl and the resultant ClNO₂ reacted with NaCl/oxalic acid solution at pH =18. Relatively fast uptake of ClNO₂ attributed to acid catalysed reaction producing Cl₂ as the main product. The reactant N₂O₅ was monitored by CRDS after thermal-decomposition to NO₃. Products were monitored by I-CIMS. Analysis of uptake rates gave an estimate of $> 10^7 \text{ M}^{-1}\text{s}^{-1}$ for the rate constant for the reaction of ClNO₂ with Cl⁻.

Preferred Values

Parameter	Value	T/K
α	0.01	274
$k^{II} (\text{M}^{-1}\text{s}^{-1}) (\text{Cl}; \text{pH} < 2)$	$> 10^7$	
$H^2D_1k^{II} (\text{M cm}^2 \text{ s}^{-2}) (\text{Br})$	0.101 ± 0.015	274
<i>Reliability</i>		
$\Delta \log (\alpha)$	± 0.3	

Comments on Preferred Values

The results of the earlier studies are in broad agreement, and the recent work revealed an important change in mechanism at conditions low pH leading to Cl₂ production. The uptake of ClNO₂ into the aqueous phase is slow into neutral solutions containing Cl⁻ but is significantly enhanced in acid solutions (pH<2). Cl₂ is not formed from neutral solutions but is produced with high yield at pH = 1.8 even at [Cl⁻] = 0.05 M (Roberts et al. 2008), probably due to an acid catalysed reaction. Uptake is also significantly enhanced on introduction of Br⁻ in the condensed phase, with formation of products BrNO₂/Br₂ which will partition rapidly to the gas phase. Reactive uptake is controlled by chemical reaction in the bulk, i.e. in terms of the resistance model:

$$\mathcal{V} = \left\{ \frac{1}{\alpha} + \frac{c}{4HRT (D_1k^1)^{0.5}} \right\}^{-1} \quad \text{where } k^I = k^{II} \times [X^-]_{\text{aq}} (\text{M}, X = \text{Cl}^- \text{ or } \text{Br}^-)$$

The preferred value of α_b is taken from the work of Fickert et al.(1998). The preferred values for uptake on Cl⁻ are based on the work of Roberts et al.(2008), who used a value of $H = 4 \times 10^{-2} \text{ M.atm}^{-1}$ in their analysis. The preferred values for uptake on Br⁻ are based on the thorough

analysis reported in the work of Fickert et al. (1998). The liquid phase diffusion coefficient has not been determined but a value of $\sim 1 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ is normally used.

References

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