IUPAC Task Group on Atmospheric Chemical kinetic Data Evaluation – Data Sheet V.A1.51 HI51

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$BrONO_2 + HCl\ (ice) \rightarrow BrCl + HNO_3$

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Experimental uptake coefficients: γ			
0.32 ± 0.1	190	Allanic et al., 1997	Knudsen-MS (a)
0.25 ± 0.1	200		

Comments

(a) ≈20 μm thick ice film made by vapour deposition and located in a Knudsen reactor operated in either continuous flow or pulsed mode. Ice surface was pre-treated with HCl before exposure to $BrONO_2$ (the flows of HCl and $BrONO_2$ were not concurrent). Values of the uptake coefficient listed in the Table are taken from pulsed valve experiments (which are in good agreement with continuous flow results). The amount of HCl on the surface was stated to be sufficient to result in phase change (surface melting).

Preferred Values

Parameter	Value	T/K
γ	0.3	190 - 200
Reliability		
$\Delta \log \gamma$	0.3	190 - 200

Comments on Preferred Values

The preferred value of γ is taken from the single quantitative study of this parameter. At the experimental temperatures covered, the uptake coefficient for $BrONO_2$ on an ice surface containing HCl is essentially the same as that on pure ice (see $BrONO_2$ + ice datasheet). When HCl is present, the uptake of $BrONO_2$ can form BrCl either directly (R1) or via reaction of the HOBr product of R2 with HCl (R3) (Hanson and Ravishankara, 1993;Allanic et al., 1997).

$BrONO_2 + HCl$	$\rightarrow BrCl + HNO_3$	(R1)
$BrONO_2 + H_2O$	$\rightarrow HOBr + HNO_3$	(R2)
$HOBr + HCl$	$\rightarrow BrCl + H_2O$	(R3)

In their study of $BrONO_2$ uptake to ice / HCl surfaces, Allanic et al. (1997) observed that at short exposure time, prompt release of BrCl was observed and HOBr appeared as gas-phase product only when surface HCl had been depleted. The ratio of HOBr to BrCl released to the gas-phase thus depends on the surface concentration of HCl (and therefore on the gas-phase HCl concentration) and the surface residence time of HOBr. The experimental studies do not define the relative importance of release of HOBr versus BrCl under atmospheric conditions

(e.g. HCl concentrations resulting in submonolayer coverages). As the formation of HOBr via hydrolysis is very efficient, it is possible that the direct formation for BrCl via (R1) will generally not take place in the atmosphere.

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References

Allanic, A., Oppliger, R. and Rossi, M. J.: J. Geophys. Res. 102, 23529-23541, 1997.
Hanson, D. R. and Raivshankara, A. R. Reactions of halogen species on ice surfaces. In *The tropospheric chemistry of ozone in the polar regions*; Niki, H., Becker, K. H., Eds.; Springer-Verlag, Berlin-Heidelberg:, 1993.