IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet V.A5.14 HNDT14

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$ClONO_2$ + HBr (NAT) → BrCl + products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
γ			
> 0.3	200	Hanson and Ravishankara, 1992	CWFT-CIMS (a)

Comments

(a) Ice surfaces (2-10 μm thick) were made by vapour deposition and doped with HNO_3 (the amount of HNO_3 was not given). The geometric surface area was used to calculate the uptake coefficient. Experiments were conducted with either HBr (5×10^9 – 10^{11} molecule cm^{-3}) or $ClONO_2$ (10^{10} – 10^{11} molecule cm^{-3}) in excess to give the same value of γ. BrCl was observed as primary gas-phase product, but not quantified. When HBr was in excess, some BrCl was converted to Br_2. Note that the same value of γ (and the same product) was also obtained for pure ice.

Preferred Values

Parameter	Value	T/K
γ_{gs} ($ClONO_2$)	0.56	180 – 200 K
θ_{HBr}	$4.14 \times 10^{-10}[HBr]^{0.88}$	188 K
Reliability		
Δ log γ	0.3	200 K

Comments on Preferred Values

The single study (Hanson and Ravishankara, 1992) of the reaction of $ClONO_2$ and HBr on a NAT-like (or HNO_3 doped) surface shows that the reaction proceeds very efficiently and that BrCl escapes to the gas-phase at low HBr concentrations. There is no difference in the uptake coefficient if pure ice or NAT-like surfaces are used and we adopt the same parameterisation for γ_{net} as for pure ice, which relies on a parameterisation for the HBr surface coverage (see datasheet on HBr + ice).

$\gamma_{net} = \gamma_{ER}$ ($ClONO_2$) θ_{HBr} with [HBr] in molecule cm^{-3}.

Note that the parameterisation, which is only valid for $\theta_{HBr} \leq 1$ and assumes that the maximum coverage is 1×10^{15} molecule cm^{-2}, generates uptake coefficients that are in close to or greater than 0.3 for [HBr] $\geq 10^{10}$ molecule cm^{-3}, as observed by Hanson and Ravishankara, 1992.

References

Hanson, D. R. and Ravishankara, A. R.: J. Phys. Chem. 96, 9441-9446, 1992.