IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.45 HI45

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$ClONO_2$ + HBr (ice) → $HONO_2$ + BrCl

Uptake coefficient data

Parameter	Temp/K	Reference	Comment
Uptake coefficients for $ClONO_2$			
$\gamma_{ss} \geq 0.3$	201	Hanson and Ravishankara, 1992	CWFT-CIMS(a)
$\gamma_{ss} = 0.56 \pm .0.11$	180-200	Allanic et al, 2000	Knud-MS(b)

Comments

(a) Ice layers 2-10 μm thick were condensed from the vapor phase. An efficient reaction with $\gamma_{SS} \geq 0.3$ was observed on pure ice, HNO_3-treated ice and on cold Pyrex at 50% r.h., where γ scales with the amount of adsorbed HBr.. No difference in reactivity was found between pure ice and HNO_3-treated ice. Significant diffusion corrections had to be made using calculated diffusion coefficients for $ClONO_2$ in He.

(b) The ice samples were generated from vapor phase deposition. Fast secondary interfacial reactions prevent the observation of the expected primary product BrCl.

Preferred values

Parameter	Value	T/K
$\gamma_{ER}(ClONO_2)$	0.56	180 – 200
$\gamma_s(ClONO_2)$	γ_{ER} (($ClONO_2$) x θ_{HBr}	180 – 200
θ_{HBr}	4.14 x $10^{-10}[HBr]^{0.88}$ at 188 K	180 - 200

[HBr] in molecule cm^{-3}.

Reliability

$\Delta(\gamma_{ER})$	±0.2	185 – 210 K.

Comments on Preferred Values

Heterogeneous reaction of $ClONO_2$ with HBr occurs rapidly on ice surfaces at temperatures relevant for the UTLS. BrCl is a likely product of this reaction, but has not been observed in the gas phase due to secondary reactions (Allanic et al, 1997). Both cited studies were at temperatures and HBr concentrations corresponding to stability regions of the phase diagram for HBr hydrate (Chu and Chu, 1998). Under these conditions with $p_{HBr} > p_{ClNO3}$, the reactive uptake coefficient was practically independent of temperature and p_{HBr}, except on pyrex when γ increased with [HBr]. The Knudsen cell results (Oppliger et al, 1997) which do not require correction for gas phase diffusion form the basis of our recommendation for γ_0.

Carslaw and Peter (1997) described the reaction rate for $ClONO_2$ + HX and related stratospheric reactions on ice particles in terms of surface coverage of HX, using a modified Langmuir-Hinshelwood model. As for the $ClONO_2$ + HCl reaction the reactive uptake coefficient of $ClONO_2$ as a function of $[HBr]_g$ is given by the product of γ_0 and the dimensionless surface coverage of HBr. i.e assuming an Ely-Rideal type mechanism. HBr adsorption doesn't follow a Langmuir model under the laboratory experimental conditions used (see data sheet for HBr + ice). The recommended expression for the reactive uptake coefficient at 188 K uses the current IUPAC recommended parameterisation for $\theta_{HBr} = 4.14 \times 10^{-10}\ [HBr]^{0.88}$ at this temperature. This is only valid for surface coverages up to $\theta_{HBr} = 1$, calculated with this isotherm.

Values given by this parameterisation for $p_{HBr} < 10^{-7}$ Torr at 188 K are shown on Fig 1.

References

Allanic, A., Oppliger, R., van den Bergh, H. and Rossi, M.J.: Zeitschr. f. Phys. Chem. 214, 1479 (2000).

Chu, L.T. and Chu, L.: J. Phys. Chem. A 103, 384 (1999).

Carslaw, K. S., and Peter, Th., Geophys.Res.Lett., 24, 1743, (1997).

Hanson, D.R. and Ravishankara, A.R.: J. Phys. Chem. 96, 9441 (1992).

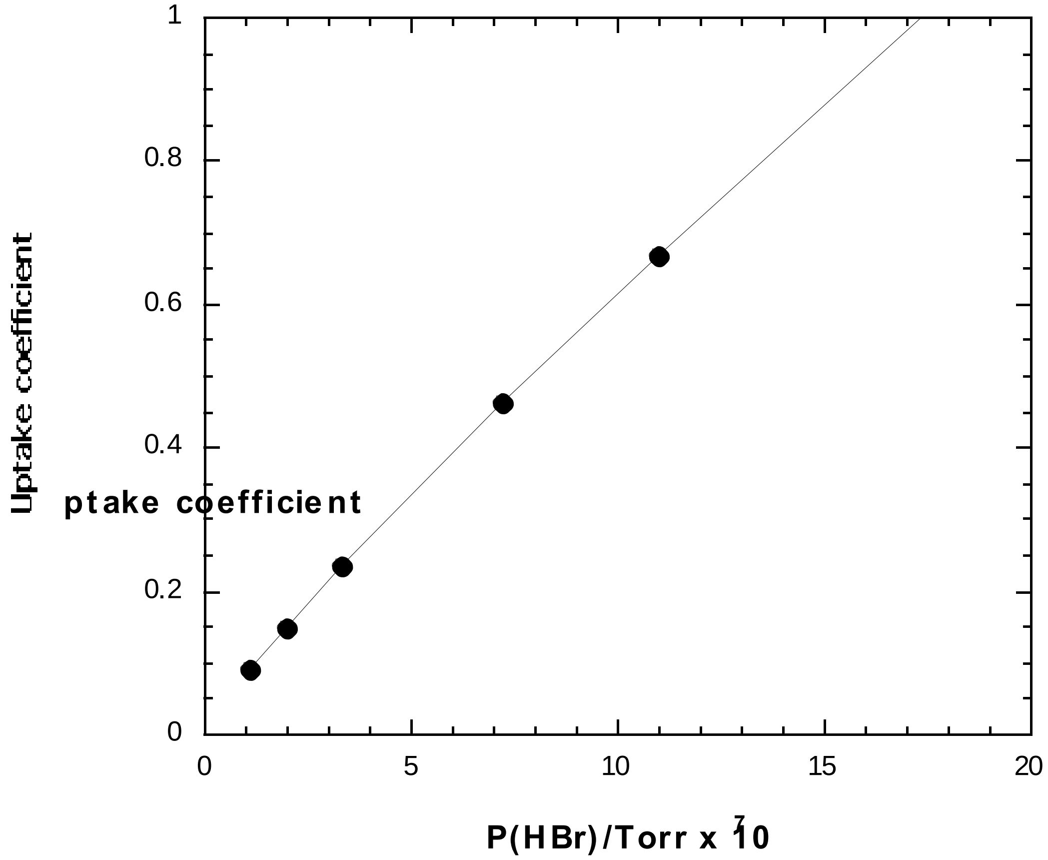

Figure 1. The recommended parameterization for P(HBr) dependence of the uptake coefficient of $ClONO_2$ on ice in the presence of HBr.

Fig 1