IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet V.A1.31 HI31

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HOBr + ice

Experimental data

Parameter	Temp./K	Reference	Technique/Comments
Experimental uptake coefficients: γ, γ₀			
$\gamma_{ss} = (2.0 \pm 1.0) \times 10^{-3}$	228	Abbatt, 1994	CWFT-MS (a)
$\gamma_0 = 0.27 \pm 0.04$ $\gamma_0 = 0.15 \pm 0.03$	190 200	Allanic, Oppliger and Rossi, 1997	Knud(b)
$\gamma_{ss} = 0.11 \pm 0.03$ $(2 \pm 1) \times 10^{-2}$ $(2.1 \pm 0.5) \times 10^{-3}$ $(5.8 \pm 3.4) \times 10^{-4}$	190.5 210.1 222.9 238.6	Chu and Chu, 1999	CWFT-MS (c)
$\gamma_{ss} = 0.37$ 0.30 ± 0.03 0.20 ± 0.04 $(4.7 \pm 2) \times 10^{-2}$ $(2 \pm 0.1) \times 10^{-2}$	175 185 190 200 210	Chaix, Allanic and Rossi, 2000	Knud(d)
$\gamma_{ss} = (4.0 \pm 0.7) \times 10^{-2}$ $\gamma_{ss} = (3.0 \pm 0.1) \times 10^{-3}$	205 227	Mössinger, Hynes and Cox, 2002	CWFT-MS(e)
Partition coefficients			
$K = 5.9 \times 10^5$ (cm^{-1}) $K = 4.2 \times 10^5$ (cm^{-1}) $K = 0.34 \times 10^5$ (cm^{-1})	198 204 209	Chu, and Chu, 1999	CWFT-MS (f)

Comments

(a) HOBr (5×10^{11} molecule cm^{-3}) was generated *in situ* by reaction of Br_2 with OH in the flow tube injector. Frozen film ice surface. No evidence for reversible adsorption of HOBr on ice, and no gas-phase products observed. For concentrations exceeding 10^{12} molecule cm^{-3} second-order kinetics for HOBr disappearance was observed.

(b) ice films (20 µm thick) were generated from vapor phase deposition. Both steady-state and real-time pulsed admission of HOBr gave indentical γ values.

(c) Vapour deposited ice films. [HOBr] in range 2–22 x 10^{11} molecule cm^{-3}. The uptake coefficient has a strong negative temperature dependence. Correction applied using a pore diffusion model, but the uncorrected values of γ are given in the table.
(d) Continuous flow and pulsed exposure. The uptake coefficient has a strong negative temperature dependence with an activation energy E_a=-9.7±1.0 kcal/Mol over the range 185 to 228K.
(e) Frozen film ice surface; γ independent of [HOBr] in range (2 – 22) x 10^{11} molecule cm^{-3}.
(f) Experimental conditions as in(c). HOBr uptake measured as function of P_{HOBr}r. Uptake saturated after about 250 min exposure and integrated uptake amounts at 198, 204 and 209 K (in molecules cm^{-2}) were fitted to the isotherm $\theta = K_p P_{HOBr}$.

Preferred Values

Parameter	Value	T/K
α_s	0.35	180 – 210
γ	3.8 x 10^{-13} exp(5130/T)	200 – 240
Reliability		
Δ log (α/γ)	± 0.3	180 – 210
Δ log (α/γ)	± 0.3	200 – 240
Δ (*E/R*) /K	± 1000	200 – 240

Comments on Preferred Values

The results of experimental studies of the uptake kinetics of HOBr onto ice films show very good agreement. All studies show that initial uptake is irreversible and at low concentration (<10^{12} molecule cm^{-3}) is first order in [HOBr]. At higher concentrations second order uptake kinetics are observed. After initial exposure γ is essentially time-independent showing little saturation at modest exposure times, although at very long exposure times Chu and Chu(1999) achieved saturation of the residual ice film under conditions of an evaporating film. No gas phase products have been observed following HOBr uptake. The results are interpreted in terms of formation of stable hydrates of HOBr after adsorption on ice films, although the thermodynamic equilibrium properties of the HOBr-ice system are unknown.

γ is weakly temperature dependent at T<190K, which is attributed to surface accommodation and is the basis of the preferred value for α_s. Above 200 K γ is strongly temperature dependent, decreasing from 0.3 at 190 K to < 0.0005 at 240 K. Chu and Chu (1999) and Mossinger et al (2002) were unable to fit the temperature dependence of γ over the whole range using a simple precursor-adsorption kinetic model with a single set of parameters, noting a discontinuity in the temperature trend between 210 and 230 K. This was attributed to a change to a more mobile ice surface in this region, but other mechanistic factors could be responsible. The recommended values for the steady-state uptake coefficient over the range 200 – 240K are given by an Arrhenius fit to the data in this range.

The adsorption studies of Chu and Chu show that continued exposure of ice films to HOBr eventually lead to saturation. However the adsorbed amounts far exceeded 1 ML and could not therefore be described using a Langmuir model. The parameters reported by Chu and Chu did not describe the adsorption process well and no recommendation is given for HOBr partitioning.

References

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Allanic, A., Oppliger, R., and Rossi, M.J.: J. Geophys. Res. 102, 23529 (1997).
Chaix, L., Allanic, A. and Rossi, M.J.: J. Phys. Chem. A 104, 7268 (2000).
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Mössinger, J.C., Hynes; R.G. and Cox, R.A., J. Geophys. Res. 107, 4740 (2002), doi:10.1029/2002JD002151.

Figure 1 Temperature dependence of uptake coefficient of HOBr on ice