IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.32 HI32

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HI + ice

Experimental data

Parameter	Temp./ K	Reference	Technique/Comments
Experimental uptake coefficients: γ, γ_0			
$\gamma_0,\gamma_{SS} > 0.27$ $\gamma_0,\gamma_{SS} = 0.26 \pm 0.02$ $\gamma_0,\gamma_{SS} = 0.20 \pm 0.03$	190 200 210	Flückiger *et al*., 1998	Knud-MS (a)
$\gamma_0,\gamma_{SS} = 0.02 \pm 0.004$ $\gamma_0 = > 0.1$	212-233 <212	Percival, Mössinger and Cox, 1999	CWFT-MS (b)
Partition coefficients			(isotherm of the form $\theta = K[HI]^f$ (molecule cm^{-2})
$K = 2.29 \times 10^5$ (cm) $K = 0.54 \times 10^5$ (cm)	188 195	Chu, and Chu, 1997	CWFT-MS (c)

Comments

(a) Both transient (pulsed valve) as well as steady-state experiments have been performed in the HI dose range of 10^{14} molecule per pulse to 10^{16} molecules per pulse, leading to peak molecular densities of (5.6-560) x 10^{10} molecule cm^{-3}.

(b) Frozen film ice. The HI concentrations were in the range (1-30) x 10^{12} molecule cm^{-3} and the γ values were independent of concentration. No evidence for saturation.

(c) Uptake of HI into vapour deposited ice films, thickness 1.8±0.4 μm, measured as a function of P_{HBr} over range (0.24 – 25) x 10^{-7} Torr in 0.4 Torr of He. No added water vapour, allowing film to evapourate after ~1 hr. Continuous uptake was observed until film evaporated and total desorption of HI was observed at this point. Integrated uptake was approximately a linear function of HI pressure at $P_{HI} < \sim 10^{-7}$ Torr, but uptake amount increased more rapidly at higher [HI], suggesting surface melting. Uptake amount also increased with film thickness at higher P_{HI}. The results are interpreted in terms of formation of HI.2H_2O hydrates, within the ice film. The data were fitted to the equation: $\log P_{HI} = \log K + f \log\theta$, giving $f = 0.80 \pm 0.05$ (average value for 188 and 195 K), but a value of K was not reported. The uptake is strongly temperature dependent and an adsorption enthalpy of -72.3 kJ mol^{-1} is reported from their

analysis. The quoted K values were obtained in this evaluation from a linear fit to the data below [HI] ~ 1 x 10^{10} molecule cm^{-3} .

Preferred Values

Parameter	Value	T/K
γ_o	0.2	190 - 210
K_{LinC} / cm	2.29 x 10^5	188
K_{LinC} / cm	0.54 x 10^5	195
Reliability		
Δ log (γ)	± 0.3	200
Δ (K_{LinC}) / cm	± 0.3	190

Comments on preferred values

Only two groups have reported the uptake coefficient for HI on ice films over a range of temperature. All studies report continuous uptake with no saturation of the ice surface and this is attributed to formation of HI hydrates which are incorporated into the surface layers of the ice film. The values of the uptake coefficient and the temperature dependence are in poor agreement, the differences probably resulting partly from the differences in the morphology the ice films. Flückiger, et al (1998), Percival, et al (1999), and Chu et al. (2000).

Chu and Chu (1997) report comprehensive measurements of HI uptake at 188 and 195 K. The uptake amounts increased with P_{HBr} and greatly exceeded ML coverage for geometric surface area, even at low [HI]. This is attributed to hydrate formation. Thus uptake amounts cannot be described by the Langmuir model, and are best described by an isotherm of the form $\theta = K[HI]^f$ (molecule cm^{-2}). However at low [HI] coverage is approximately linear and the recommended partition coefficient for HBr on ice is obtained from a linear fit to the data below [HI] ~ 1 x 10^{10} molecule cm^{-3}.

References

Chu, L.T. and Chu, L.: J. Phys. Chem. B 103, 6271 (1997).

Flückiger, B., Thielmann, A., Gutzwiller, L. and Rossi, M.J.: Ber. Bunsenges. Phys. Chem. 102, 915 (1998).

Percival, C.J., Mössinger, J.C. and Cox, R.A.: Phys. Chem. Chem. Phys. 1, 4565 (1999).

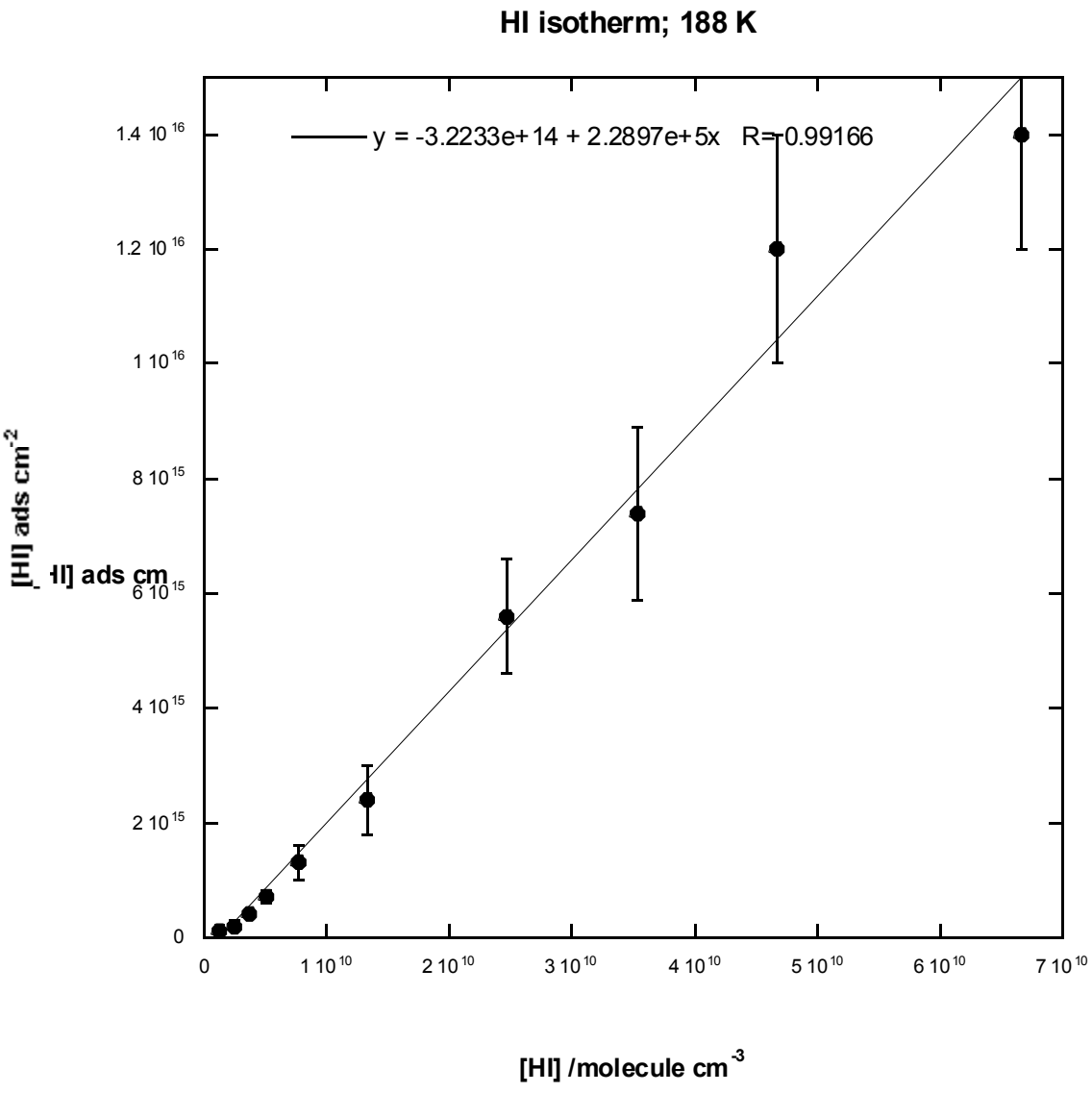

Figure1. Absorption isotherm for HI uptake on ice film at 188 K