IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.28 HI28

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HOCl + ice

Experimental data

Parameter	Temp./K	Reference	Technique/Comment
Experimental uptake coefficients: γ, γ_0			
$\gamma_0 = 8.5 \times 10^{-2}$	180 200	Oppliger, Allanic and Rossi, 1997	Knud(a)
Partition coefficients K_{linC} (cm^{-1})			
79	191	Hanson and Ravishankara, 1992	CWFT-CIMS(b)
3270 513 215 161	189 198 208 221	Chu and Chu, 1999	CWFT(c)

Comments

(a) Knudsen cell reactor using pulsed admission of HOCl and MS detection. The ice samples were generated from vapour phase deposition and resulted typically in a 20 μm thick film. A balancing H_2O flow was set in order to keep the composition of the interface constant. Uptake rate constants for HOCl have been measured for doses <2.5 x 10^{14} molecule corresponding to <2.5% of a monolayer. At higher doses and in steady-state uptake experiments, strong saturation effects were found

(b) HOCl was generated from the reaction HCl + $Ca(ClO)_2$ and *in-situ* by the reaction of $ClONO_2$ with ice surface; Uptake of gaseous HOCl (concentration ~ 2 x 10^9 molecule cm^{-3}) on pure ice was reversible at 191 K, the surface saturating within a few seconds, followed by rapid desorption when exposure ceased. The fractional surface coverage in all the reported experiments did not exceed 0.01. A value of ~10^7 atm^{-1} was estimated for the Langmuir constant at 191K from the *in-situ* experiments; values of ΔH_{ads} and ΔS_{ads} of -58 ± 8 kJ mol^{-1} and -167 ± 41.8 J mol^{-1} K^{-1} respectively were estimated from data in the in the range 191 – 211K. HOCl did not adsorb on HNO_3 doped ice.

(c) Uptake of [HOCl] ~ 3 x 10^{10} molecule cm^{-3} on vapour deposited ice was reversible at 189 K, the surface saturating with a coverage of ~ 1 x 10^{14} molecule cm^{-2} within a few seconds. The uptake was followed by complete desorption when exposure ceased. Cited data for

temperature dependence of partition coefficient at constant P_{HOCl} = 8 x 10^{-7} mbar are taken from fig 4 of Chu and Chu (1999). A value of ΔH_{ads} of -34 ± 8 kJ mol^{-1} was estimated from the data.

Preferred Values

Parameter	Value	T/K
γ_0	0.085	180 – 200
N_{max} / molecule cm^{-2}	3 x 10^{14}	
K_{LinC} / cm	3.06 x 10^{-6} exp(3840/T)	190 -220
Reliability		
Δ log (γ_0)	± 0.3	180 – 200
Δ (K_{LinC}) / cm	± 0.5	205
Δ (E/R) /K	± 1200	

Comments on preferred values

The available data show that the uptake rate of HOCl on ice is time dependent and absorption is reversible and rather weak. Under these conditions uptake coefficients are difficult to measure and only one study, that of Oppliger et al (1997) using a Knudsen cell at very low doses, reports a value for γ.

The only study reporting surface coverages measured from loss of HOCl from the gas phase is that of Chu and Chu (1999) and these are used here to derive partition coefficients, assuming N_{max} = 3 x 10^{14} molecule cm^{-3}. Hanson and Ravishankara derive Langmuir constants indirectly from release of HOCl following its production in the $ClONO_2$ + H_2O reaction, but the values expressed as partition coefficients are considerably lower, probably due to the presence of the co-product HNO_3 which is likely to compete strongly with HOCl for adsorption sites. The temperature dependence observed by Chu and Chu (1999) gives a curved Van't Hoff plot (see Fig 1) and the derived adsorption enthalpy cannot be considered reliable. Nevertheless the values of K from a fit to a *log K vs I/T* plot of their data is recommended for use to estimate HOCl coverage for UTLS conditions.

References

Chu L. and Chu, L.T.: J. Chem. Phys.A., 103 691-699,(1999).

Hanson, D.R. and Ravishankara, A.R.: J. Phys. Chem. 96, 2682 (1992).

Oppliger, R., Allanic, A. and Rossi, M.J.: J. Phys. Chem. A 101, 1903 (1997).

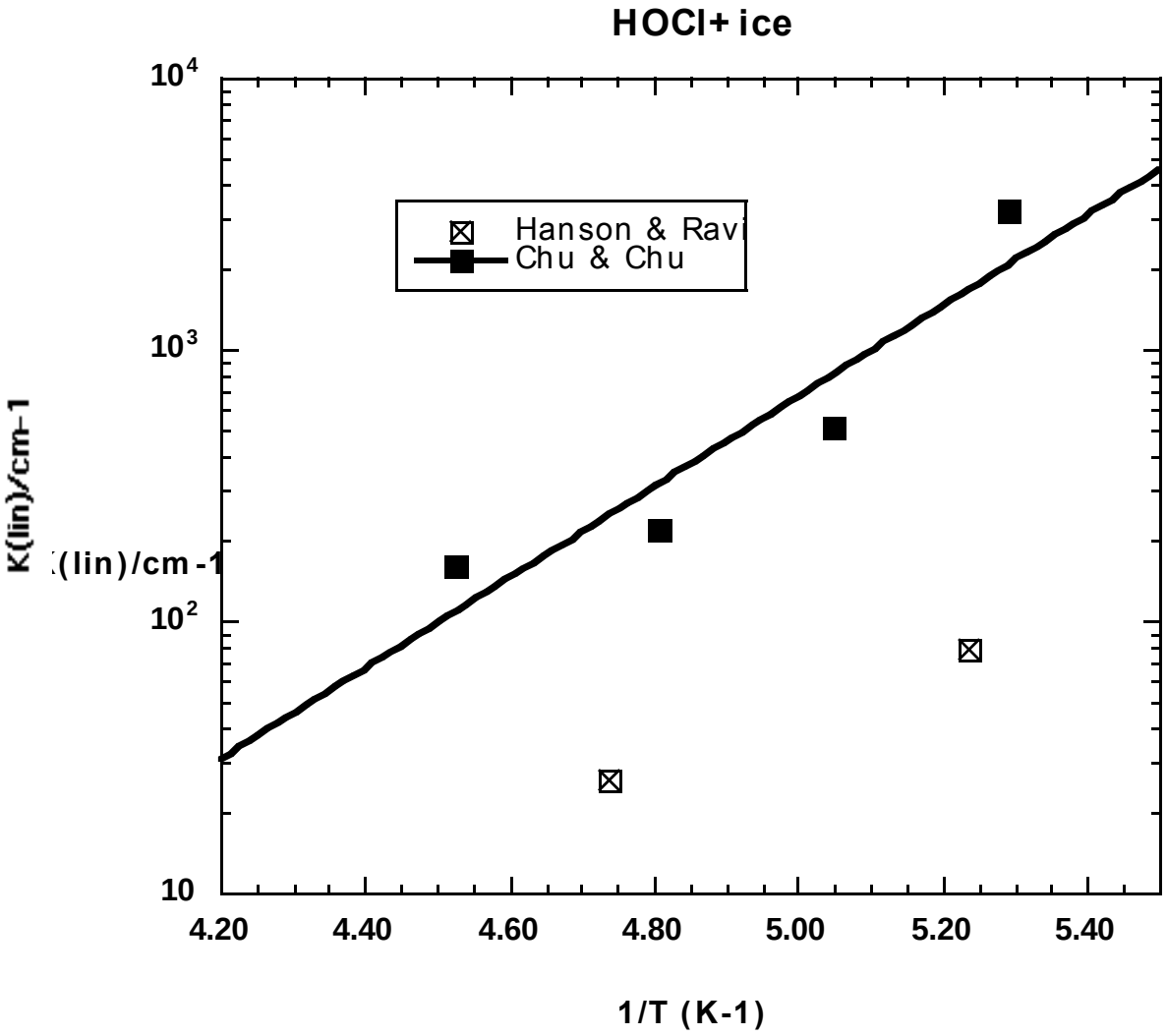

Figure 1. Van't Hoff plot of adsorption equilibrium constants for uptake of HOCl on ice