IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.41 HI41

$HOCl + HCl(ice) \rightarrow Cl_2 + H_2O$

Uptake coefficient data

Parameter	Temp/K	Reference	Comments
Uptake coefficients: γ_{ss} (HOCl)			
≥ 0.3 (+0.7, -0.1)	191	Hanson and Ravishankara, 1992	CWFT-CIMS (a)
0.16±0.1	202	Abbatt and Molina, 1992	CWFT-MS(b)
0.24 (+0.5, -0.15)	195		
0.34±0.20	188	Chu, Leu and Keyser, 1993	CWFT-MS(c)
0.15	160	Oppliger, Allanic and Rossi, 1997	Knud(d)
	200		
0.15	188	Chu and Chu, 1999	CWFT-MS(e)
	200		

Comments

(a) Kinetics study on vapour deposited ice film. The initial [HOCl] was 2×10^9 molecule cm^{-3}. The decay rate of HOCl was identical for [HCl] = 2×10^9 or 2×10^{10} molecule cm^3, indicating surface saturation of HCl. Cl_2 product was rapidly released from ice surface.

(b) The uptake of HOCl in the presence of excess HCl is time-independent. Uptake rate shows a negative temperature dependence: γ increases from 0.16 to 0.24 when the temperature drops from 202 to 195K.

(c) The ice film was deposited from water vapor saturated He and consisted of μm-sized granules. The thickness ranged from 3.7 to 34.7 μm which were calculated and calibrated gravimetrically. The internal surface was measured using BET gas adsorption measurments. P_{HOCl} ranged from (1.7 to 24) x 10^{-7} mbar and P_{HCl} from (1.2 to 10.6) x 10^{-6} mbar. Taking into account a structural model for the ice substrate a lower limit value of γ_{SS} =0.13±0.08 was obtained.

(d) Uptake experiment performed in a Knudsen flow reactor with MS detection using both steady-state and real-time pulsed valve admission of HOCl and HCl with a balancing H_2O flow. The ice samples were generated from vapor phase deposition of approximately 2×10^5 monolayers of H_2O (20 μm thick). Mass balance studies indicate that HOCl reacts with all HCl taken up by the ice sample even though the rate of formation of Cl_2 decreases towards the end of the reaction. The rate of Cl_2 formation upon HOCl exposure to HCl-doped ice slows down in the presence of HNO_3 hydrates.

(l) The ice was condensed from the vapor phase at 188.5 K and flow tube pressure was 0.37 mbar. Cited values for γ are not corrected for pore diffusion. Uptake of HOCl mbar (P_{HOCl} = 9.7 x 10^{-7} mbar) was continuous and γ_{HOClss} was independent of [HCl] over range (1.9 – 11.0) x 10^{-6} mbar; at lower [HCl] ($P_{HOCl} \approx P_{HCl}$) γ decreased, presumably due to depletion of the surface HCl. An Ely-Rideal mechanism was proposed for the surface reaction, but no supporting evidence was presented.

Preferred values

Parameter	Value	T/K
γ_{ER} (HOCl)	0.1	180 - 220
γ (HOCl)	γ_{ER} (HOCl) x [HCl]$_s$	180 - 220
[HCl]$_s$ / molecule cm^{-2}	K_{linC}(HCl) x [HCl]$_g$	

Reliability

Δ log (γ_{ER})	± 0.1	298

Comments on preferred values

All studies report rapid uptake of HOCl onto ice films doped with HCl. Cl$_2$ is the sole product with a yield of 100%. The conditions of these experiments all corresponded to near maximum coverage of HCl in the ice or HCl hydrate stability region. Surface melting was also a likely occurance under these conditions (McNeill et al, 2006). The reported γ values are in reasonably good agreement and there is a suggestion of a negative temperature dependence (see Fig.2). However, considering the small temperature range and the cited experimental errors, which arise substantially from the large corrections necessary to account for the effect of gas phase diffusion on the measured rate constants in the CWFT studies, we recommend a temperature independent value of γ_{max}. The preferred value is a mean of the values obtained from all studies cited and the T range is extended to 220 K.

Only the study of Chu and Chu (1999) observed an [HCl] dependence of the uptake coefficient on pure ice surfaces, although Abbatt and Molina (1992) noted that uptake of HOCl on HNO$_3$-doped ice was much slower and exhibited [HCl] dependence. Fig 1 shows a plot of the uptake coefficient calculated as a function of p(HCl) at 188 K, assuming both Ely-Rideal and Langmuir Hinshelwood mechanisms, together with the results of Chu & Chu. Neither model captures the observed fall-off in γ at low p(HCl), which almost certainly results from reagent depletion as (p(HCl) ≤ p(HOCl)). The recommend a reactive uptake coefficient for HOCl as a function of [HCl]$_g$ is given by γ_0 x θ(HCl) calculated using the recommended value of K_{linC} for HCl on ice (see data sheet V.A1.27) with N_{max} = 3 x 10^{14} molecule cm^{-3}. In the presence of HNO$_3$ a competitive Langmuir isotherm can be used to obtain θ_{HCl}.

References

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Chu, L.T., Leu, M.-T. and Keyser, L.F.: J. Phys. Chem. 97, 12798 (1993).
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HOCl+ HCl; 188K

uptake coefficient

p(HOCl)

p(HCl)/Torr x 10^7

0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02

0   20   40   60   80   100

■ Chu&ChuChu(expt)
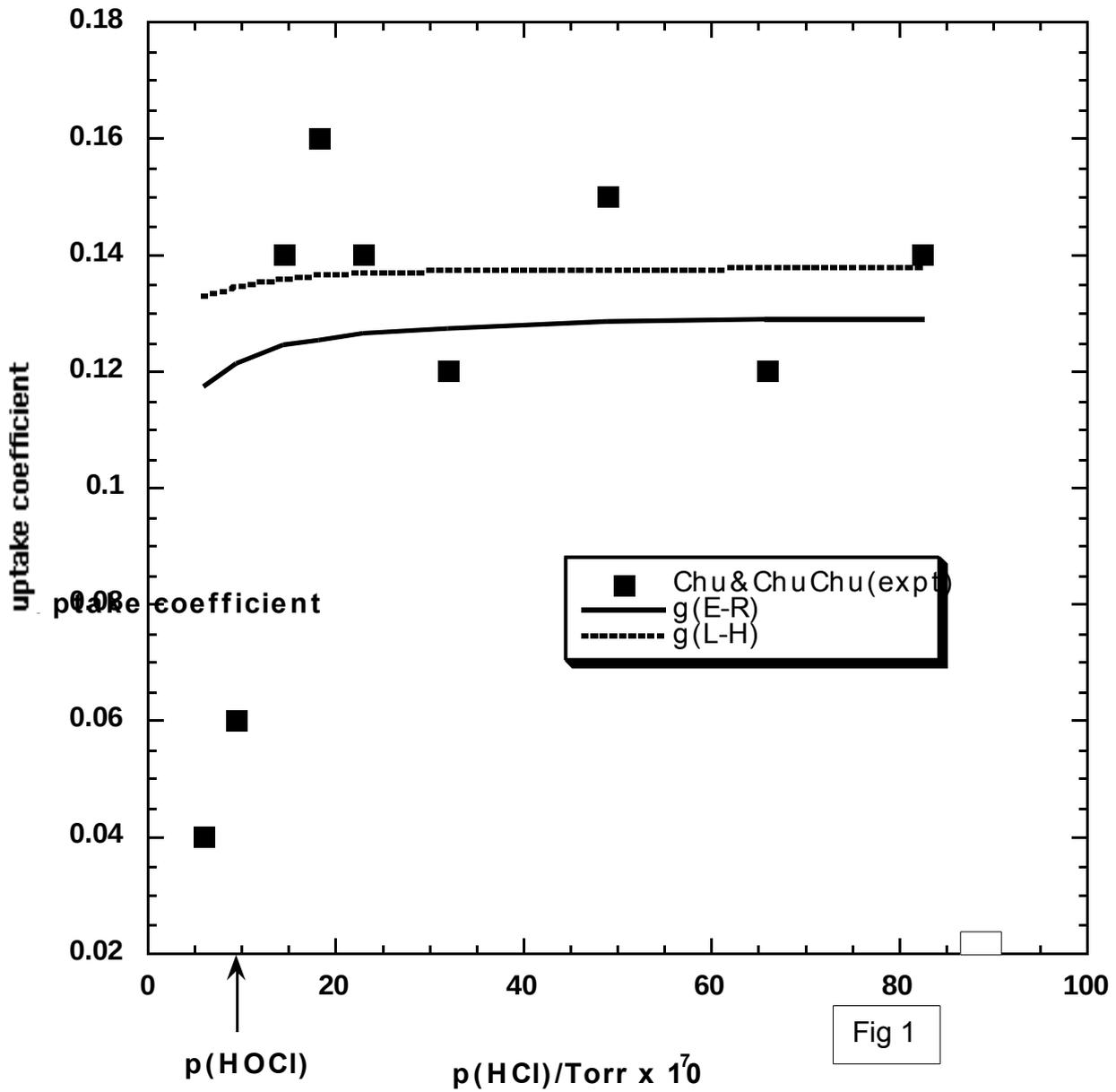— g(E-R)
---- g(L-H)

uptake coefficient

Fig 1

Figure 1. The recommended parameterization for P(HCl) dependence of the uptake coefficient of HOCl on ice in the presence of HCl at 188 K.

Figure 2. The temperature dependence of the observed uptake coefficients of HOCl on ice in the presence of excess HCl.