# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.42 HI42


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**HOCl + HBr(ice) → BrCl + H2O**

**Uptake coefficient data**

| *Parameter* | Temp./K | Reference | Technique/Comments |
|---|---|---|---|
| *Experimental uptake coefficients: γ, $\gamma_0$* | | | |
| $\gamma_{ss}$ (HOCl) = 0.06 – 0.38<br>$\gamma_{ss}$ (HOCl) = 0.01 – 0.07 | 189<br>220 | Chu and Chu, 1999 | CWFT-MS(a) |

**Comments**

(a) The ice was condensed from the vapor phase at the experimental temperature. Ice film thickness was 2.4 ± 0.2 μm at 189 K and 42 ± 4 μm at 220 K; flow tube pressure was 0.37 mbar. Cited values for $\gamma$ are not corrected for pore diffusion which reduced the value of $\gamma$ by a factor of 2 to10. Uptake of HOCl ($P_{HOCl}$ = 9.7 x $10^{-7}$ mbar) was continuous, and $\gamma_{SS}$ (HOCl) increased with $[HBr]_g$; The range of values given in the table at 188 K were obtained with $P_{HBr}$ over range (1.5 – 88.0) x $10^{-7}$ mbar, and at 220 K the values given in the table were obtained with $P_{HBr}$ over range (1.1 – 15.9) x $10^{-6}$ mbar. These trends were deduced to be consistent with an Ely-Rideal mechanism for the surface reaction, but the parameterisation of surface [HBr] in terms of $P_{HBr}$ was not given.

**Preferred values**

| **Parameter** | **Value** | **T/K** |
|---|---|---|
| $\alpha_s$ (HOCl) | 0.3 | 180 - 220 |
| $\gamma$ (HOCl) | $1/(\alpha_s + 2.7/\theta_{HBr})_s$ | 180 - 220 |
| $\theta_{HBr}$ / molecule $cm^{-2}$ | 4.14 x$10^{-10}$ x $[HBr]^{0.88}$ | |
| *Reliability* | | |
| $\Delta(\alpha_s)$ | ± 0.15 | 188 |

***Comments on preferred values***

The single study by Chu and Chu (1999) reports rapid irreversible uptake of HOCl onto ice films doped with HBr, in contrast to the uptake of HOCl on pure ice films, which is reversible. Products BrCl and $Br_2$ were observed but their yield was <<100%. The uptake coefficient increased with $P_{HBr}$ at both 188 K and 220 K but was much lower for equivalent $P_{HBr}$ at 220 K ( see Fig 1). However this may refect an effect of ice film thickness (2.4 ± 0.2 μm at 189 K and 42 ± 4 μm at 220 K); the conditions of these experiments corresponded to the HBr hydrate stability region (Chu and Chu, 1997), where *surface* [HBr] may be lower on a thicker film due to transfer into the bulk. The preferred value of $\alpha_s$ for the range 188-220 K is the value obtained at high $P_{HBr}$ on the thinner film at 188K.

The evidence for Ely-Rideal kinetics suggested by Chu and Chu (1999) is not convincing and HBr adsorption doesn't follow a Langmuir model under the laboratory experimental conditions used (see data sheet for HBr + ice). Nevertheless, a reasonable fit to the data from Chu and Chu (1997) is obtained using the IUPAC recommended expression for $\theta_{HBr}$ at 188 K (= $4.14 \times 10^{-10}$ $[HBr]^{0.88}$), in a Langmuir-Hinshelwood model for the uptake with $N_{max} = 3 \times 10^{14}$ molecule $cm^{-2}$, $\alpha_s$ = 0.3 and ks = $3.3 \times 10^{-15}$ $cm^2$ $molecule^{-1}$ (see Fig 1). These parameters give the recommend expression for $\gamma$ at 188 K, but this model cannot be used at other temperatures in the absence of an HBr adsorption isotherm.

## References

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

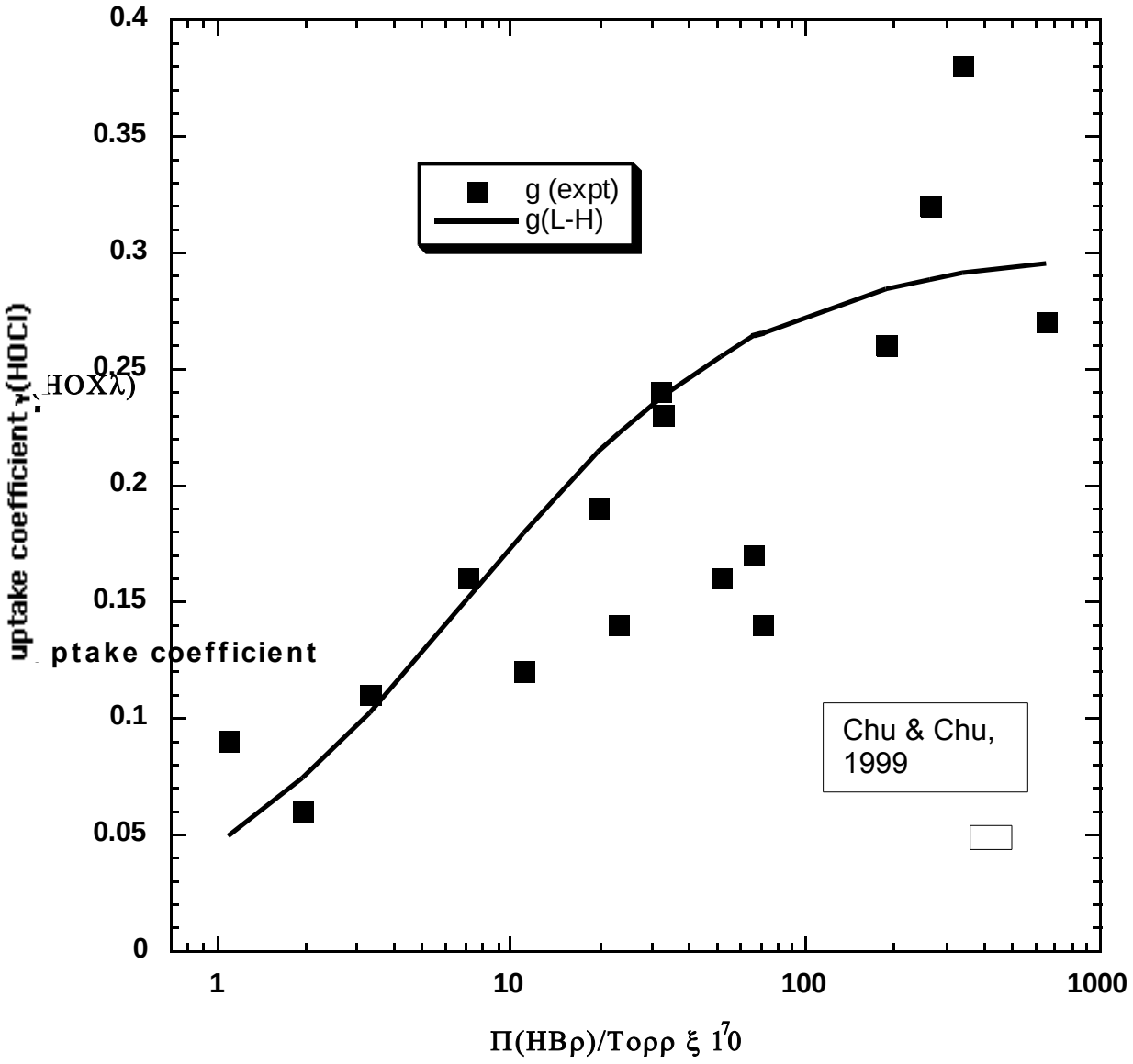


Fig 1

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