

## IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet V.A1.11

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This datasheet last evaluated: June 2008; last change in preferred values: April 2010

### HONO + Ice → Products

#### Experimental Data

<i>Parameter</i>	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: <math>\gamma</math></i>			
$\gamma_0 = 1.0 \times 10^{-3}$	180-200	Fenter and Rossi, 1996	Kn-MS (a)
$\gamma_{ss} = 1.0 \times 10^{-3}$	190	Seisel and Rossi, 1997	Kn-MS (a)
$\gamma_0 = 3.7 \times 10^{-3}$	178	Chu et al, 2000	CWFT-MS (b)
$\gamma_0 = 1.6 \times 10^{-3}$	192		
$\gamma_0 = 6.4 \times 10^{-4}$	200		
<i>Surface partition coefficients: <math>K_{linC}</math> (cm)</i>			
$1.0 \times 10^{-05} \exp(3843/T)$	170-205	Chu et al, 2000	CWFT-MS (b)
$2.1 \times 10^{-09} \exp(3849/T)$	170-200	Bartels-Rausch et al., 2002	PBFT-RC (c)
$7.4 \times 10^{-09} \exp(5400/T)$	213-253	Kerbrat et al., 2010	PBFT-RC (d)

#### Comments

- (a) Ice prepared both by vapour-phase deposition and by cooling of a sample of distilled water. HONO prepared from acidified NaNO<sub>2</sub> solution, with NO and NO<sub>2</sub> as major contaminants. Saturation of the uptake takes place after deposition of 3% of a monolayer ( $3 \times 10^{14}$  cm<sup>-2</sup>) at a HONO concentration of about  $10^{12}$  cm<sup>-3</sup> in the reactor. The uptake appeared to be reversible.
- (b) Uptake experiment using a laminar flow tube equipped with mass spectrometric detection at 0.5 Torr of He. The ice film (about 30 μm thick) was prepared by vapour deposition. The HONO concentration was measured using IR absorption spectroscopy upstream of the flow tube and was roughly 10% of the total associated NO<sub>x</sub> inflow. The tabulated  $\gamma_0$  values refer to the geometric surface area of the ice film. The correction using pore diffusion theory would reduce them by a factor of 20 to 50. The initial uptake coefficient shows a pronounced negative temperature dependence with a  $\Delta E/R$  value of 27.2 kJ/mol, which was ascribed to a precursor mediated uptake process. The surface coverages reported at equilibrium range from  $10^{13}$  to  $3 \times 10^{14}$  molecule cm<sup>-2</sup> (geometric surface area) in the range from 205 to 174 K at a HONO pressure of  $2.5 \times 10^{-7}$  mbar. No pressure dependence given. An adsorption enthalpy of  $-33.9 \pm 8.8$  kJ/mol was derived. The tabulated  $K_{linC}$  was derived from the reported surface coverages divided by the gas phase pressure and fitted versus  $1/T$ . The intercept leads to a standard adsorption entropy of  $80.7$  Jmol<sup>-1</sup>K<sup>-1</sup>.
- (c) HONO-ice partitioning coefficients derived from packed ice bed (PB) experiments at atmospheric pressure using radioactively labelled HONO at concentrations of 3 ppbv and

below. Ice prepared from freezing water drops 0.5mm in diameter in liquid N<sub>2</sub> and then annealing at 258K for at least 12 hours. HONO was prepared by converting NO<sub>2</sub> quantitatively to HONO on a solid organic reductant. NO was the main contaminant (in similar amounts). The adsorption enthalpy of  $-32 \pm 2$  kJ/mol was derived by solving a migration model of linear gas chromatography and assuming a value of the adsorption entropy of  $42 \text{ Jmol}^{-1}\text{K}^{-1}$  (based on  $A_0 = 6.7 \times 10^6 \text{ m}^2$ ) based on theoretical arguments. The tabulated  $K_{\text{linC}}$  was derived from these values.

(d) Experiments were performed in an atmospheric pressure flow tube filled with 0.5mm diameter ice spheres. The ice was prepared by freezing water in liquid N<sub>2</sub> and then annealing at 258 K. Ice spheres were sieved. No effect of changing ice particle diameter to 0.8mm was observed. HONO was produced from NO<sub>2</sub> partially labelled with the radioactive isotope <sup>13</sup>N by reaction with a solid organic reductant. Migration profiles of labelled HONO molecules along the flow tube were measured using gamma detectors, non-labelled HONO was detected downstream of the flow tube. The HONO breakthrough curves showed strong tailing, i.e., the HONO signal never reached the initial concentration again, interpreted as a slow diffusive uptake into the interior of the polycrystalline ice spheres. Breakthrough curves were used to extract a value for  $H\sqrt{D}=1.6 \times 10^{-2} \text{ m s}^{-1/2}$  that allows parameterization of this diffusive uptake. This was then used to correct the steady state partition coefficient derived from the migration profiles of the labelled molecules to obtain the values for  $K_{\text{linC}}$  presented in the table in parameterized form.

#### Preferred Values

Parameter	Value	T/K
$\alpha_S$	0.02	180 - 220
$K_{\text{linC}} / \text{cm}$	$1.5 \times 10^{-8} \exp(5200/T)$	180 - 250
$N_{\text{max}} / \text{cm}^{-2}$	$3 \times 10^{14}$	180 - 250

<i>Reliability</i>		
$\Delta \log \alpha_S$	$\pm 0.3$	180 - 220
$\Delta(E/R) / \text{K}$	$\pm 100$	180 - 250
$\Delta \log N_{\text{max}} / \text{cm}^{-2}$	$\pm 0.1$	180 - 250

#### Comments on Preferred Values

At low temperature, the rate of uptake of HONO is strongly time dependent and rapidly drops to zero, indicating saturation of the surface. The study by Fenter and Rossi (1996) was performed on frozen aqueous solutions, while that by Chu et al. (2000) was performed on vapour deposited ice. When referred to the geometric ice surface area, the initial uptake coefficients derived in both studies agree, while in case of correction for pore diffusion the values by Chu et al. (2000) are an order of magnitude lower. The times needed to saturate the surface observed in both studies are consistent with a value of  $\alpha_S = 0.02$ . Then, the initial uptake kinetics may be described by

$$\gamma = \alpha_S e^{-Bt} \quad \text{with} \quad B = \frac{\alpha_S \bar{c}}{4} \left( \frac{[\text{HONO}]_g}{N_{\text{max}}} + \frac{1}{K_{\text{linC}}^{\text{HONO}}} \right)$$

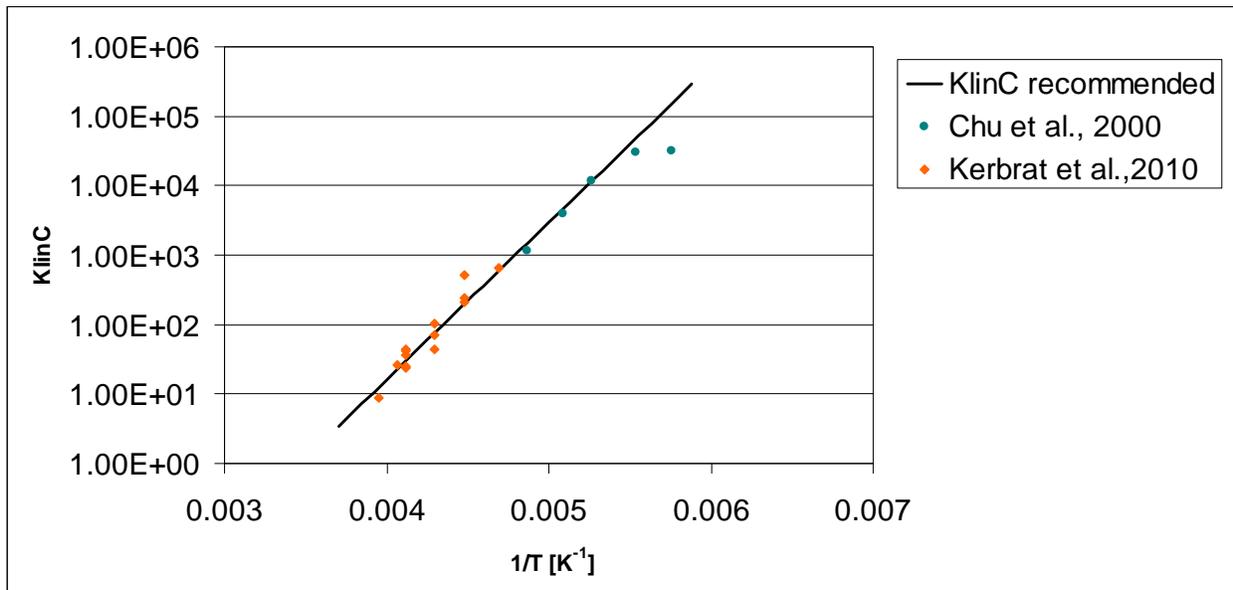
It is likely that the effective time resolution was not sufficient to resolve  $\alpha_s$  by the initial uptake coefficient due to adsorption equilibrium as has been shown for other flow tube studies, which may also have an effect on the temperature dependence.

At higher temperature, Kerbrat et al. (2010) report a significant longterm contribution to uptake suggested to be driven by slow diffusion into the interior of the polycrystalline ice matrix used in their experiment. They corrected the data obtain a surface partition coefficient and an effective solubility in the bulk condensed phase. However, the relevance of bulk uptake remains uncertain as long as the reservoirs into which diffusion occurs are neither identified nor quantified for ice of direct atmospheric relevance. We therefore only recommend parameters for partitioning of HONO to the ice surface.

Chu et al. (2000) report surface coverage as a function of temperature that is consistent with the higher temperature data by Kerbrat et al. (2010). The data indicate saturation at about  $3 \times 10^{14}$  molecules  $\text{cm}^{-2}$ . We therefore neglect the two lowest temperature data points of Chu et al. and combine the others with those by Kerbrat et al. (2010) to obtain the temperature dependence of  $K_{\text{linC}}$ . The partitioning coefficients reported by Bartels-Rausch et al. (2002) heavily rely on an estimate for the adsorption entropy, which is highly uncertain as it strongly depends on an assumed adsorption mechanism. We therefore do not include these data in the recommendation for  $K_{\text{linC}}$ . The adsorption enthalpy related to the recommended parameterization is 43 kJ/mol, which is close to the enthalpy of solvation of HONO in water of 41 kJ/mol, as reported by Park and Lee (1988), indicating hydration of the HONO molecule at the ice surface.

### References

- Bartels-Rausch, T., Eichler, B., Zimmermann, P., Gäggeler, H. W., Ammann, M.: *Atmos. Chem. Phys.* 2, 235-247, 2002.
- Chu, L., Diao, G. and Chu, L.T.: *J. Phys. Chem. A* 104, 3150, 2000.
- Fenter, F.F. and Rossi, M.J.: *J. Phys. Chem.* 100, 13765, 1996.
- Kerbrat, M., Huthwelker, T., Gäggeler, H. W., and Ammann, M.: *J. Phys. Chem. C*, 114, 2208-2219, 2010.
- Park, J. Y.; Lee, Y. N.: *J. Phys. Chem.* 92, 6294–6302, 1988.



Partitioning of HONO to ice: Data by Chu et al. (2000) and Kerbrat et al. (2010) (symbols) and recommended temperature dependence (solid line).

## IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet V.A1.38

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### Experimental Data

Parameter	Temp. /K	Reference	Technique/Comments
<i>Experimental uptake coefficients: <math>\gamma</math></i>			
$\gamma_{\text{SS}} = (6 \pm 2) \times 10^{-2}$	180	Fenter and Rossi, 1996	Kn-MS(a)
$\gamma_{\text{SS}} = (4.5 \pm 1.5) \times 10^{-2}$	190		
$\gamma_{\text{SS}} = (3.0 \pm 0.5) \times 10^{-2}$	200		
$\gamma_{\text{SS}} = (1.7 \pm 0.6) \times 10^{-4}$ ( $P_{\text{HCl}} = 2.3 \times 10^{-6}$ mbar)	191	Diao and Chu, 2005	CWFT-MS (b)
$\gamma_{\text{SS}} = (1.4 \pm 0.4) \times 10^{-2}$ ( $P_{\text{HCl}} = 2.3 \times 10^{-5}$ mbar)			

### Comments

- (a) Ice prepared both by vapour-phase deposition and by cooling of a sample of distilled water. HONO prepared from use of acidified  $\text{NaNO}_2$  solution, with NO and  $\text{NO}_2$  as major contaminants. HONO concentration was about  $10^{12} \text{ cm}^{-3}$  in the reactor. Under conditions of excess HONO ranging from 1.5 up to tenfold, the rate of uptake of HONO is controlled by the rate of HCl uptake on ice, and vice versa. Both the uptake of HONO and HCl converge to steady state after several tens of seconds, after which there is quantitative conversion of HCl and HONO to ClNO.
- (b) 30  $\mu\text{m}$  thick vapor-deposited ice film doped with HCl in the range  $6.5 \times 10^{-7}$  to  $1.7 \times 10^{-4}$  mbar prior to exposure to HONO. Cited values for  $\gamma$  are corrected for gas phase diffusion but not for pore diffusion, which reduced the value of  $\gamma$  by a factor of 8 to 50. At HCl pressures below  $5 \times 10^{-6}$  mbar, to which the ice was exposed,  $\gamma_{\text{SS}}(\text{HONO})$  slightly decreased with pressure. At higher HCl pressures,  $\gamma_{\text{SS}}(\text{HONO})$  scales with  $P_{\text{HCl}}$  and coverage. An Eley Rideal type mechanism is suggested for the high pressure range, where the uptake coefficient scales with the surface coverage to the power of 1.67. NOCl has been observed as a product and using this product as observable leads to identical  $\gamma_{\text{SSHONO}}$  within experimental uncertainty. Correlation of relative rates with the reactions of HONO with HBr and HI confirm the nucleophilic character of the reaction.

### Preferred Values

Parameter	Value	T/K
$\alpha_s$	0.02	180 - 220
$k_s$ / $\text{cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.0 \times 10^{-19}$	180 - 220

$\Delta \log \alpha_s$	$\pm 0.3$	180 - 220
$\frac{\Delta \log k_s}{/ \text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}}$	$\pm 0.3$	180 - 220

### Comments on preferred values

Both studies report rapid uptake of HONO to ice doped with HCl. 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 occurrence under these conditions (McNeill et al, 2006). The kinetic data by Fenter and Rossi (1996) agree well with those of Diao and Chu (2000) at the highest pressures used, given that different ice surfaces and different HCl exposures were used.

The Eley Rideal type mechanism suggested by Diao and Chu (2000) is not supported as no HONO pressure dependence is reported. Fenter and Rossi note that the rate of loss of one of the reactants is limited by the amount of the other reactant adsorbed on the surface. We therefore rather suggest using a Langmuir-Hinshelwood type mechanism with the following expression for the uptake coefficient:

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s} \quad \text{with} \quad \Gamma_s = \frac{4k_s [\text{HCl}]_s K_{\text{LangC}}(\text{HONO}) N_{\text{max}}}{\bar{c} (1 + K_{\text{LangC}}(\text{HONO}) [\text{HONO}]_g)}$$

The surface coverage of HCl should be taken as  $[\text{HCl}]_s = N_{\text{max}} \frac{K_{\text{LangC}}(\text{HCl}) [\text{HCl}]_g}{1 + K_{\text{LangC}}(\text{HCl}) [\text{HCl}]_g}$

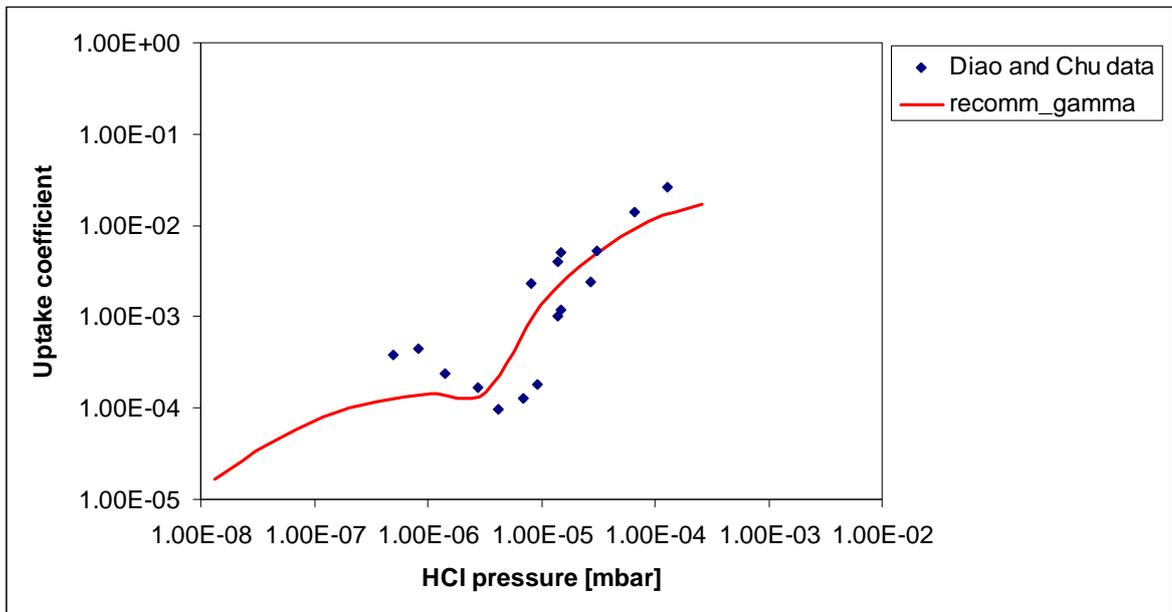
with  $K_{\text{LangC}}(\text{HCl}) = 7.3 \times 10^{-17} \times \exp(2858/T) \text{ cm}^3 \text{ molecule}^{-1}$  (see data sheet V.A1.27).

Similarly,  $K_{\text{LangC}}(\text{HONO}) = 3.3 \times 10^{-20} \exp(3840/T) \text{ cm}^3$  and  $N_{\text{max}}(\text{HONO}) = 3.0 \times 10^{14} \text{ molecule cm}^{-2}$  (see data sheet V.A1.11).

This parameterisation gives a reasonable agreement with the Diao and Chu (2000) data.. The same parameterization also fits well the high pressure data, when surface coverages as reported by Diao and Chu (2000) are used at pressures  $10^{-5}$  mbar and above. The recommended parameterization also reproduces the temperature dependence of the uptake coefficient, which was observed to decrease by a factor of two between 180 and 200 K (Fenter and Rossi, 1996).

### References

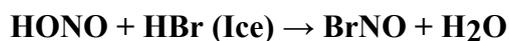
- Diao, G. and Chu, L.T.: J. Phys. Chem. A 109, 1364 (2005)  
 Fenter, F.F., and Rossi, M.J.: J. Phys. Chem. 100, 13765 (1996).  
 McNeill, V. F., Loerting, Th., Geiger, F.M., Trout, B.L., and Molina, M. J., Proc. Nat. Acad. Sci., 103, 9422 (2006).



The recommended parameterization for P(HCl) dependence of the uptake coefficient of HONO on ice in the presence of HCl.

## IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet V.A1.39

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### Experimental Data

Parameter	Temp. /K	Reference	Technique/Comments
<i>Uptake coefficients: <math>\gamma</math></i>			
$\gamma_{\text{SS}} = 2.0 \times 10^{-2}$ (HBr doped ice)	180-	Seisel and Rossi, 1997	Kn-MS(a)
$\gamma_{\text{SS}} = 2.5 \times 10^{-2}$ (concurrent HONO and HBr excess)	200		
$\gamma_{\text{SS}} = (2.3 \pm 0.3) \times 10^{-2}$ (frozen HBr solution)	190		
$\gamma_{\text{SS}} = (1.6 \pm 0.2) \times 10^{-3}$ ( $P_{\text{HBr}} = 3.9 \times 10^{-8}$ mbar)	191	Chu et al., 2000	CWFT-MS (b)
$\gamma_{\text{SS}} = (1.7 \pm 0.8) \times 10^{-2}$ ( $P_{\text{HBr}} = 8.7 \times 10^{-5}$ mbar)	191		
$\gamma_{\text{SS}} = (5.7 \pm 4.0) \times 10^{-4}$ ( $P_{\text{HBr}} = 3.3 \times 10^{-8}$ mbar)	200		
$\gamma_{\text{SS}} = (1.6 \pm 0.7) \times 10^{-2}$ ( $P_{\text{HBr}} = 8.7 \times 10^{-5}$ mbar)	200		
$\gamma_{\text{SS}} = (8.7 \pm 1.6) \times 10^{-4}$ ( $P_{\text{HBr}} = 6.8 \times 10^{-7}$ mbar)	230		
$\gamma_{\text{SS}} = (4.5 \pm 1.1) \times 10^{-3}$ ( $P_{\text{HBr}} = 4.5 \times 10^{-5}$ mbar)	230		
$\gamma_{\text{SS}} = (3.1 \pm 1.0) \times 10^{-4}$ ( $P_{\text{HBr}} = 6.5 \times 10^{-7}$ mbar)	191	Diao and Chu, 2005	CWFT-MS (c)
$\gamma_{\text{SS}} = (2.1 \pm 0.3) \times 10^{-2}$ ( $P_{\text{HBr}} = 6.8 \times 10^{-5}$ mbar)	191		

### Comments

- (a) Uptake of HBr ( $2 \times 10^{11}$  to  $8 \times 10^{12}$  molecule  $\text{cm}^{-3}$ ) and HONO ( $1 \times 10^{11}$  to  $1 \times 10^{13}$  molecule  $\text{cm}^{-3}$ ) on vapor-deposited ice films and on frozen aqueous solutions. HONO was prepared from acidified  $\text{NaNO}_2$  solution, with NO and  $\text{NO}_2$  as major contaminants. The rate law for HONO uptake is first order. Pulsed valve admission of HONO resulted in  $\gamma$  values consistent with the steady-state experiments. The uptake of HONO on HBr-doped ice is first order in HONO. No temperature dependence of  $\gamma_0$  is observed in the range 180 to 210K. Less than 20% of the HBr taken up on the ice reacts with HONO. Continuous uptake of HONO was observed for concurrent exposure of HONO and HBr to ice. HONO is quantitatively converted to BrNO.
- (b) 30  $\mu\text{m}$  thick vapor-condensed  $\text{H}_2\text{O}$  ice film doped with HBr in the range  $10^{-8}$  mbar to  $10^{-4}$  mbar prior to exposure to HONO. The tabulated  $\gamma$  values are based on the geometric surface area of the film. Correction for pore diffusion into the ice substrate decreased the  $\gamma$  value by a factor of 8 to 50. Pseudo-first order conditions apply as the amount of

(pre)adsorbed HBr was always larger than HONO. Starting at an HBr uptake of  $10^{15}$  molecules  $\text{cm}^{-2}$   $\gamma_{\text{ss}}$  scales with  $P_{\text{HBr}}$ , while the uptake coefficients remains more or less constant at pressures below  $10^{-6}$  mbar.  $\gamma$  decreases with temperature. An Eley Rideal type mechanism was suggested for the high pressure range. BrNO has been observed as a product, and using this product as observable leads to identical  $\gamma_{\text{ss}}$  within experimental uncertainty.

- (c) 30  $\mu\text{m}$  thick vapor-condensed  $\text{H}_2\text{O}$  ice film doped with HBr in the range  $10^{-6}$  mbar to  $10^{-4}$  mbar prior to exposure to HONO. The tabulated  $\gamma$  values are based on the geometric surface area of the film. Correction for pore diffusion into the ice substrate decreased the  $\gamma$  value by a factor of 8 to 50. The lower  $\gamma$  values compared to those reported by Chu et al. (2000) are attributed to a lower exposure of the films to HBr prior to reaction with HONO. Correlation of relative rates with the reactions of HONO with HBr and HI confirm the nucleophilic character of the reaction.

### Preferred Values

Parameter	Value	T/K
$\alpha_s$	0.02	180 - 220
$k_s$ / $\text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$	$7.0 \times 10^{-18}$	180 - 220
<i>Reliability</i>		
$\Delta \log \alpha_s$	$\pm 0.3$	180 - 220
$\Delta \log k_s$ / $\text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$	$\pm 0.3$	180 - 220

### Comments on preferred values

All three studies report rapid uptake of HONO to ice doped with HBr. The conditions of these experiments were such that the HBr-ice phase was not well defined for HBr pressures above  $10^{-6}$  mbar. The kinetic data by Seisel and Rossi (1996) seem to converge with those of Chu et al. (2000) and Diao and Chu (2005) at the highest pressures used. The uptake coefficient for a frozen HBr solution was also similar to that at the maximum pressures. The absence of a temperature dependence reported by Seisel and Rossi (1997) contrasts the temperature dependence reported by Chu et al. (2000). This may be due to the significantly higher HONO pressures used by Seisel and Rossi (1997), which could have led to saturating HONO coverages based on the recommended partitioning coefficient for HONO. This may have been the reason why the time to reach steady state uptake was indeed temperature dependent. The Eley Rideal type mechanism suggested by Diao and Chu (2000) is not supported as no HONO pressure dependence was reported. Seisel and Rossi (1997) also did not observe a further increase of the BrNO formation with HONO pressure at the highest pressures. We therefore suggest using the following expression describing a Langmuir-Hinshelwood type mechanism with adsorbed HBr reacting with adsorbed HONO:

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s} \quad \text{with} \quad \Gamma_s = \frac{4k_s [\text{HBr}]_s K_{\text{LangC}}(\text{HONO}) N_{\text{max}}(\text{HONO})}{\bar{c} (1 + K_{\text{LangC}}(\text{HONO}) [\text{HONO}]_g)}$$

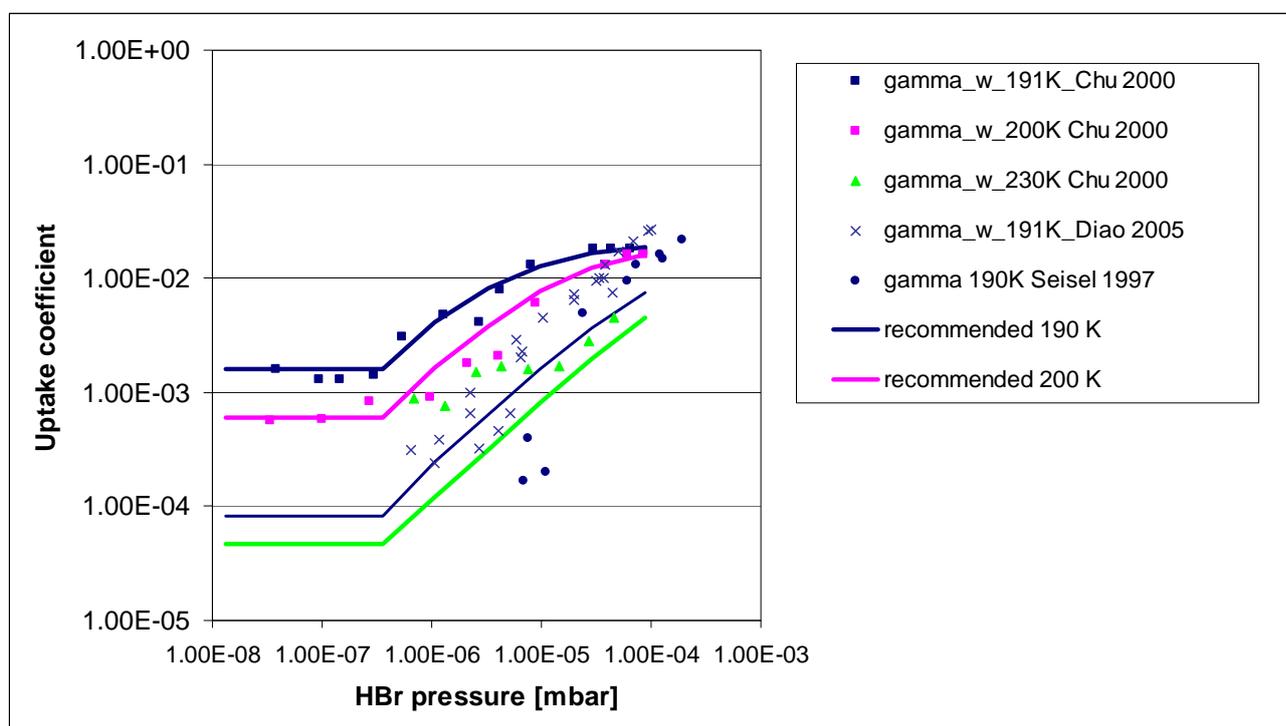
We recommend using  $[\text{HBr}]_s = 3 \times 10^{14} \text{ cm}^{-2}$  at HBr pressures between  $10^{-8}$  and  $10^{-7}$  mbar and the expression  $[\text{HBr}]_s = 414000 [\text{HBr}]^{0.88} \text{ cm}^{-2}$  at pressures above  $10^{-7}$  mbar (see data sheet V.A1.30)

From the recommendations presented for HONO on ice on V.A1.11, we use  $K_{LangC}(HONO) = 3.3 \times 10^{-20} \exp(3840/T) \text{ cm}^3 \text{ molecule}^{-1}$  and  $N_{\max}(HONO) = 3.0 \times 10^{14} \text{ molecule cm}^{-2}$ .

Taking the recommended pressure dependence of HBr surface coverage and the recommended surface reaction rate constant gives a nice agreement with the Chu et al. (2000) data at pressures above  $10^{-6}$  mbar, and notably also reproduces the temperature dependence. However, at atmospherically relevant low pressures, where the conditions presumably fall into the ice stability regime, the same parameterization only fits, when a saturating surface coverage of  $3 \times 10^{14} \text{ cm}^{-2}$  is assumed similar to the HCl case. This indicates that the interfacial concentration accessible to HONO is similar to HCl at similar pressures in the ice stability regime. The data by Diao and Chu (2005) are somewhat lower than those of Chu et al. (2000). This may be due to the different internal surface areas or depths into bulk ice HBr has diffused, which then leads to different effective reactant concentrations exposed to HONO. We therefore recommend a large uncertainty associated with the surface reaction rate constant. The recommended equation also nicely explains the difference between the Seisel and Rossi (1997) and the Chu et al. (2000) data, the difference being driven by the HONO pressure dependence.

### References

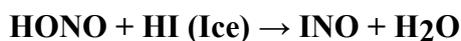
- Diao, G. and Chu, L.T.: J. Phys. Chem. A 109, 1364 (2005)  
 Chu, L., Diao, G. and Chu, L.T.: J. Phys. Chem. A 104, 3150 (2000).  
 Seisel, S. and Rossi, M.: Ber. Bunsenges. Phys. Chem. 101, 943-955 (1997).



The recommended parameterization for the p(HBr) dependence of the uptake coefficient of HONO on ice in the presence of HBr.

## IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet V.A1.40

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### Experimental Data

Parameter	Temp. /K	Reference	Technique/Comments
<i>Experimental uptake coefficients: <math>\gamma</math></i>			
$\gamma_{\text{SS}} = (2.9 \pm 0.9) \times 10^{-4}$ ( $P_{\text{HI}} = 1.1 \times 10^{-7}$ mbar)	191	Diao and Chu, 2005	CWFT-MS (a)
$\gamma_{\text{SS}} = (3.0 \pm 0.8) \times 10^{-2}$ ( $P_{\text{HI}} = 8.9 \times 10^{-5}$ mbar)	191		

### Comments

- (a) 30  $\mu\text{m}$  thick vapor-condensed  $\text{H}_2\text{O}$  ice film doped with HI in the range  $10^{-7}$  mbar to  $10^{-5}$  mbar prior to exposure to HONO. The tabulated  $\gamma$  values are based on the geometric surface area of the film. Correction for pore diffusion into the ice substrate decreased the  $\gamma$  value by a factor of 6 to 50. INO could not be directly observed. It was suspected that INO formed on the ice film would react with I(ad) on the stainless steel surfaces between the ice film and the MS to form  $\text{I}_2$  that was detected. I(ad) would form from dissociative adsorption of HI. Correlation of relative rates with the reactions of HONO with HBr and HCl indicate the nucleophilic character of the reaction.

### Preferred Values

Parameter	Value	T/K
$\alpha_s$	0.02	180 - 220
$k_s$ / $\text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$	$1.6 \times 10^{-18}$	180 - 220
<i>Reliability</i>		
$\Delta \log \alpha_s$	$\pm 0.3$	180 - 220
$\Delta \log k_s$ / $\text{cm}^2 \text{molecule}^{-1} \text{s}^{-1}$	$\pm 0.3$	180 - 220

### Comments on preferred values

The single study by Diao and Chu (2005) reports rapid uptake of HONO to ice doped with HI. The conditions of these experiments were such that the HI-ice phase was not well defined above HI pressures above  $10^{-6}$  mbar. The Eley Rideal type mechanism suggested by Diao and Chu (2000) is not supported as no HONO pressure dependence was reported. We therefore rather suggest the following expression for the uptake coefficient, describing a Langmuir-Hinshelwood type mechanism:

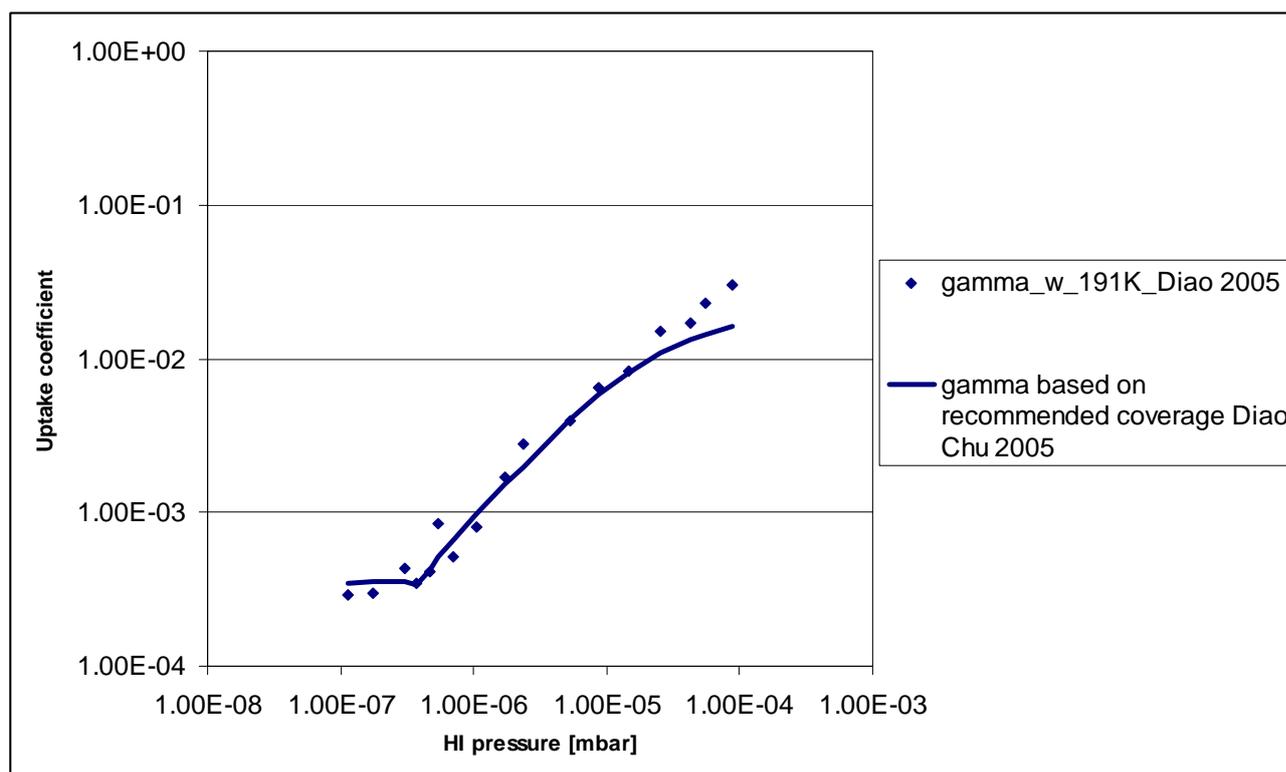
$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s} \quad \text{with} \quad \Gamma_s = \frac{4k_s[HI]_s K_{LangC}(HONO)N_{max}(HONO)}{\bar{c}(1 + K_{LangC}(HONO)[HONO]_g)}$$

The surface coverage of HI should be taken as  $[HI]_s = 3.0 \times 10^{14} \text{ cm}^{-2}$  at HI pressures between  $10^{-8}$  and  $10^{-7}$  mbar and as  $[HI]_s = 8.0 \times 10^{20} [HI] \text{ cm}^{-2}$  at HI pressures above  $10^{-7}$  mbar (see data sheet V.A1.32)

With  $k_s$  and  $\alpha_s$  as recommended above, and  $K_{LangC}(HONO) = 3.3 \times 10^{-20} \exp(3840/T) \text{ cm}^3 \text{ molecule}^{-1}$  based on the value for  $K_{linC}$  and  $N_{max}(HONO) = 3.0 \times 10^{14} \text{ molecule cm}^{-2}$  reported in the data sheet V.A1.11, a nice agreement with the data at pressures above  $10^{-6}$  mbar. As is evident, at atmospherically relevant low pressures, where the conditions presumably fall into the ice stability regime, only the saturating surface coverage of  $3 \times 10^{14} \text{ cm}^{-2}$  leads to agreement with experimental data, similar to the HCl case. This indicates that the interfacial concentration accessible to HONO is similar to the case of HCl and HBr at similar pressures. Given that the surface area may not be well characterized in the experiments, we recommend a large uncertainty associated with the surface reaction rate constant.

### References

Diao, G. and Chu, L.T.: J. Phys. Chem. A 109, 1364 (2005)



The recommended parameterization for P(HI) dependence of the uptake coefficient of HONO on ice in the presence of HI.