

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation Data Sheet HI11; V.A1.11

Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hard copy without explicit written permission. The citation for this data sheet is: Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J., *Atmos. Chem. Phys.*, 10, 9059-9223, 2010; IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This data sheet last evaluated: June 2014; last change in preferred values: April 2010.

### HONO + Ice → Products

#### Experimental Data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: <math>\gamma_0</math>, <math>\gamma_{ss}</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><math>K_{inc}</math> (cm)</i>			
$1.0 \times 10^{-5} \exp(3843/T)$	170-205	Chu et al, 2000	CWFT-MS (b)
$2.1 \times 10^{-9} \exp(3849/T)$	170-200	Bartels-Rausch et al., 2002	PBFT-RC (c)
$7.4 \times 10^{-9} \exp(5400/T)$	213-253	Kerbrat et al., 2010a	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  $K_{inc}$  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 J mol<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. (2010a) report a significant long term 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 to obtain a surface partition coefficient and an effective solubility in the bulk condensed phase. Pinzer et al. (2010) measured the effective diffusivity of HONO through a snow sample, which had less grain boundaries than the packed bed sample of Kerbrat et al. (2010a). The effective diffusivity was consistent with the partition coefficient measured by Kerbrat et al. (2010a) and did not show evidence for partitioning into the bulk. 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.

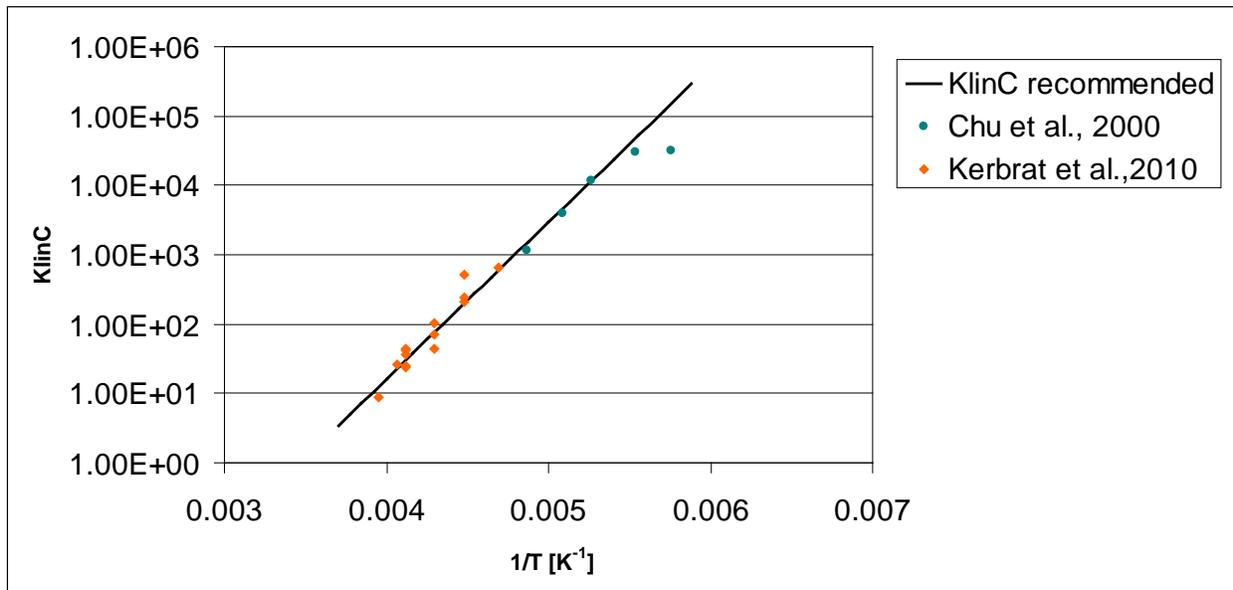
Chu et al. (2000) report surface coverage as a function of temperature that is consistent with the higher temperature data by Kerbrat et al. (2010a). The data indicate saturation at about  $3 \times 10^{14}$  molecules  $\text{cm}^{-2}$ . We therefore neglect the two lowest temperature data points of Chu et al. and combine the others with those by Kerbrat et al. (2010a) to obtain the temperature dependence of KlinC. 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 KlinC.

In coadsorption experiments with acetic acid, Kerbrat et al. (2010b) found that the uptake of HONO could be consistently explained by a competitive Langmuir adsorption model with the corresponding partitioning coefficients.

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, 3150-3158, 2000.
- Fenter, F.F. and Rossi, M.J.: *J. Phys. Chem.* 100, 13765-13775, 1996.
- Kerbrat, M., Huthwelker, T., Gäggeler, H. W., and Ammann, M.: *J. Phys. Chem. C*, 114, 2208-2219, 2010a.
- Kerbrat, M., Huthwelker, T., Bartels-Rausch, T., Gäggeler, H. W., and Ammann, M.: *Phys. Chem. Chem. Phys.*, 12, 7194-7202, 2010b.
- Park, J. Y.; Lee, Y. N.: *J. Phys. Chem.* 92, 6294-6302, 1988.
- Pinzer, B. R., Kerbrat, M., Huthwelker, T., Gäggeler, H. W., Schneebeli, M., and Ammann, M.: *J. Geophys. Res.*, 115, D03304, 2010.



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