IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.30 HET_SL_30

The citation for this data sheet is: IUPAC Task group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.
This data sheet last evaluated: June 2011; last change in preferred values: June 2011.

HONO + HBr (aqueous sulphuric acid aerosol) → BrNO + H_2O

Experimental data

Parameter	p_{HBr} /mbar	p_{HONO} /mbar	[H_2SO_4] /wt %	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ						
$\gamma_{HBr} = 4.0 \times 10^{-2}$	10^{-5} - 10^{-4}	10^{-5} - 10^{-4}	40	210	Seisel and Rossi, 1997	Kn-MS (a)
$\gamma_{HBr} = 4 \times 10^{-4}$	10^{-5} - 10^{-4}	10^{-5} - 10^{-4}	95	270		
$\gamma_{HONO} = 5.5 \times 10^{-3}$	10^{-5} - 10^{-4}	10^{-5} - 10^{-4}	40	210		
$\gamma_{HONO} = 2 \times 10^{-3}$	10^{-5} - 10^{-4}	10^{-5} - 10^{-4}	52-69	210-230		
$\gamma_{HONO} = 2.2 \times 10^{-2}$	10^{-5} - 10^{-4}	10^{-5} - 10^{-4}	95	270		

Comments

(b) H_2SO_4 solutions were prepared by dilution of a 95 wt% solution. HONO was prepared by adding H_2SO_4 to $NaNO_2$. Formation of BrNO was observed for all solution compositions. Uptake coefficients as listed in the table were due to the total uptake of HBr and not corrected for solubility limited uptake of HBr alone.

Preferred Values

Parameter	Value	T/K
α_b	1	200 – 300
k_b (M^{-1} s^{-1})	0.1	200 – 300
Reliability		
Δ log (α_b)	0.7	200 – 300
Δ log (k_b)	1	200 – 300

Comments on Preferred Values

Seisel and Rossi (1997) observed conversion of HONO to BrNO. The interpretation of the kinetic data is somewhat complicated by the fact that solubility limited uptake of HBr or HONO was not always clearly separated from reaction limited uptake. E.g., at low wt%, the uptake of HBr was not sensitive to the presence of HONO; similarly, at high wt%, the uptake of HONO was not sensitive to the presence of HBr. At intermediate compositions, the uptake coefficients seem to represent reaction limited conditions. Taking into account the composition dependent solubilities of HBr and HONO and assuming a simple bulk reaction to drive uptake leads to reasonable agreement with data especially for the HONO uptake coefficient, and reproduces the decreasing trend of the uptake coefficient of HBr with increasing wt% and the slightly increasing uptake coefficient of HONO over the same composition range. In absence of a more extensive data set over a larger range of pressures, we refrain from invoking a surface reaction to explain the relatively high uptake coefficients at high wt%, which are clearly underestimated by the model.

The uptake coefficient of HONO is given by:

$$\frac{1}{\gamma_{HONO}} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{b,HONO}}$$

$$\Gamma_{b,HONO} = 4H^*_{HONO} RT \sqrt{D_{l,HONO} \cdot k_b^{II} p_{HBr} H^*_{HBr}} \left[\coth\left(\frac{r_p}{l_{HONO}}\right) - \left(\frac{l_{HONO}}{r_p}\right) \right] / \bar{c}_{HONO}$$

For the effective solubility of HONO, we suggest using the expression recommended on datasheet VI.A4.7: $H^* = A \exp(B\ (wt\%)) + C \exp(D\ (wt\%))$, with $A = 4.2 \times 10^{-6} \exp(4873/T)$; $B = 13.16/T - 0.0856$; $C = 2.0 \times 10^{8} \exp(-14000/T)$; $D = 297.3/T - 0.474$

The diffusion coefficient for HONO is parameterized by $D_{l,HONO} = C_{HONO}\ T\ /\eta$; with $C_{HONO} = 6.90 \times 10^{-8}$ cm^2 cP K^{-1} s^{-1} , estimated as suggested by Klassen et al. (1998), but using a molar volume of 36 cm^3/mol (da Silva et al., 2006).
For the viscosity, we suggest using the parameterization presented by Shi et al. (2001), which fits well to data by Williams and Long (1995) but extends into tropospherically more relevant dilute solutions at high T:

$\eta = A T^{-1.43} \exp(448K / (T - T_0))$,

with $A = 169.5 + 5.18\ (wt\%) - 0.0825\ (wt\%)^2 + 3.27 \times 10^{-3}\ (wt\%)^3$,

and $T_0 = 144.11 + 0.166\ (wt\%) - 0.015\ (wt\%)^2 + 2.18 \times 10^{-4}\ (wt\%)^3$

According to data sheet VI.A4.17, the solubility of HBr can be parameterised by:
$\log_{10} H_{HBr}^* = 1000\ m\ /\ T + b$,
where $m = m_1[H_2SO_4]^2 + m_2[H_2SO_4] + m_3$ and $b = b_1[H_2SO_4]^2 + b_2[H_2SO_4] + b_3$ and the H_2SO_4 concentration $[H_2SO_4]$ is in wt.%.
m_1 (wt.% $^{-2}$ K)= -1.977×10^{-4}; m_2 (wt.% $^{-1}$ K)= -2.096×10^{-2}; m_3 (K)= 4.445;
b_1 (wt.% $^{-2}$)= -8.979×10^{-5}; b_2 (wt.% $^{-1}$)= 2.141×10^{-2}.

The reactivo-diffusive length needed to account for finite particle sizes is given by $l_{HONO} = (D_{l,HONO}/(k_b p_{HBr}\ H^*_{HBr}))^{0.5}$.

Similarly, the uptake coefficient of HBr is given by:

$$\frac{1}{\gamma_{HBr}} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{b,HBr}}$$

$$\Gamma_{b,HBr} = 4H^*_{HBr} RT \sqrt{D_{l,HBr} \cdot k_b^{II} p_{HONO} H^*_{HONO}} \left[\coth\left(\frac{r_p}{l_{HBr}}\right) - \left(\frac{l_{HBr}}{r_p}\right) \right] / \bar{c}_{HBr}$$

The diffusion coefficient of HBr can be expressed as $D_{l,HBr} = 7.9 \times 10^{-8}\ T\ /\ \eta$ as explained on datasheet VI.A4.17. The reactivo-diffusive length needed to account for finite particle sizes is given by $l_{HBr} = (D_{l,HBr}/(k_b p_{HONO}\ H^*_{HONO}))^{0.5}$.

References

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Klassen, J. K., Hu, Z., and Williams, L. R.: J. Geophys. Res., 103, 16197-16202, 1998.

Seisel, S., and Rossi, M. J.: Ber. Bunsen Ges. Phys. Chem. Chem. Phys., 101, 943-955, 1997.

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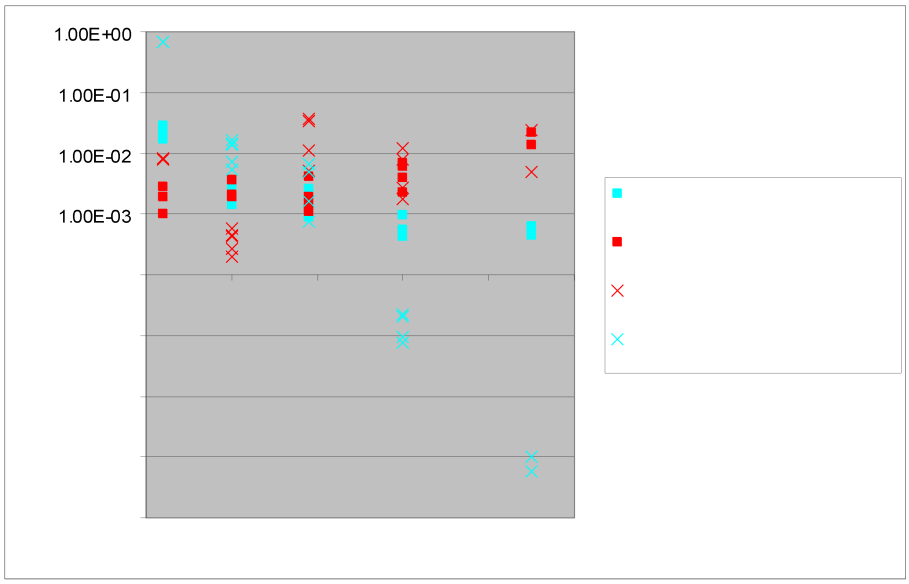

Figure 1: Uptake coefficient of HBr (plain light blue squares) and of HONO (plain red squares) due to reaction with HONO and HBr, respectively, as a function of solution composition, as reported by Seisel and Rossi (1997). Note that the data encompass temperatures between 210 and 270 K, see experimental data table. The crosses are values obtained using the bulk reaction uptake model, each for the specific conditions (pressure, temperature, composition) of each data point reported by Seisel and Rossi.