

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation
Data Sheet HI39; V.A1.39

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This datasheet last evaluated: June 2014; last change in preferred values: April 2010



Experimental Data

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

Comments

- (a) Uptake of HBr (2×10^{11} to 8×10^{12} molecule cm $^{-3}$) and HONO (1×10^{11} to 1×10^{13} molecule cm $^{-3}$) on vapor-deposited ice films and on frozen aqueous solutions. HONO was prepared from acidified NaNO₂ solution, with NO and NO₂ as major contaminants. The rate law for HONO uptake is first order. Pulsed valve admission of HONO resulted in γ values consistent with the steady-state experiments. The uptake of HONO on HBr-doped ice is first order in HONO. No temperature dependence of γ_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 μm thick vapor-condensed H₂O ice film doped with HBr in the range 10^{-8} mbar to 10^{-4} mbar prior to exposure to HONO. The tabulated γ values are based on the geometric surface area of the film. Correction for pore diffusion into the ice substrate decreased the γ 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 cm $^{-2}$ γ_{ss} scales with P_{HBr} , while the uptake coefficients remains more or less constant at pressures below 10^{-6} mbar. γ 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 γ_{ss} within experimental uncertainty.

- (c) 30 μm thick vapor-condensed H_2O ice film doped with HBr in the range 10^{-6} mbar to 10^{-4} mbar prior to exposure to HONO. The tabulated γ values are based on the geometric surface area of the film. Correction for pore diffusion into the ice substrate decreased the γ value by a factor of 8 to 50. The lower γ 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
α_s	0.02	180 - 220
$k_s / \text{cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$	5.0×10^{-18}	180 - 220
<i>Reliability</i>		
$\Delta \log \alpha_s$	± 0.3	180 - 220
$\Delta \log k_s / \text{cm}^2 \text{ molecule}^{-1} \text{ s}^{-1}$	± 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:

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

With

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s}$$

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 in datasheet V.A1.11, we use $K_{\text{LangC}}(\text{HONO}) = 5.0 \times 10^{-23} \exp(5200/T) \text{ cm}^3 \text{ molecule}^{-1}$ and $N_{\max}(\text{HONO}) = 3.0 \times 10^{14} \text{ molecule cm}^{-2}$.

Taking the recommended pressure dependence of HBr surface coverage and the recommended surface reaction rate constant results in good 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, 1364-1373, 2005.
 Chu, L., Diao, G. and Chu, L.T.: J. Phys. Chem. A 104, 3150-3158, 2000.
 Seisel, S. and Rossi, M.: Ber. Bunsenges. Phys. Chem. 101, 943-955, 1997.

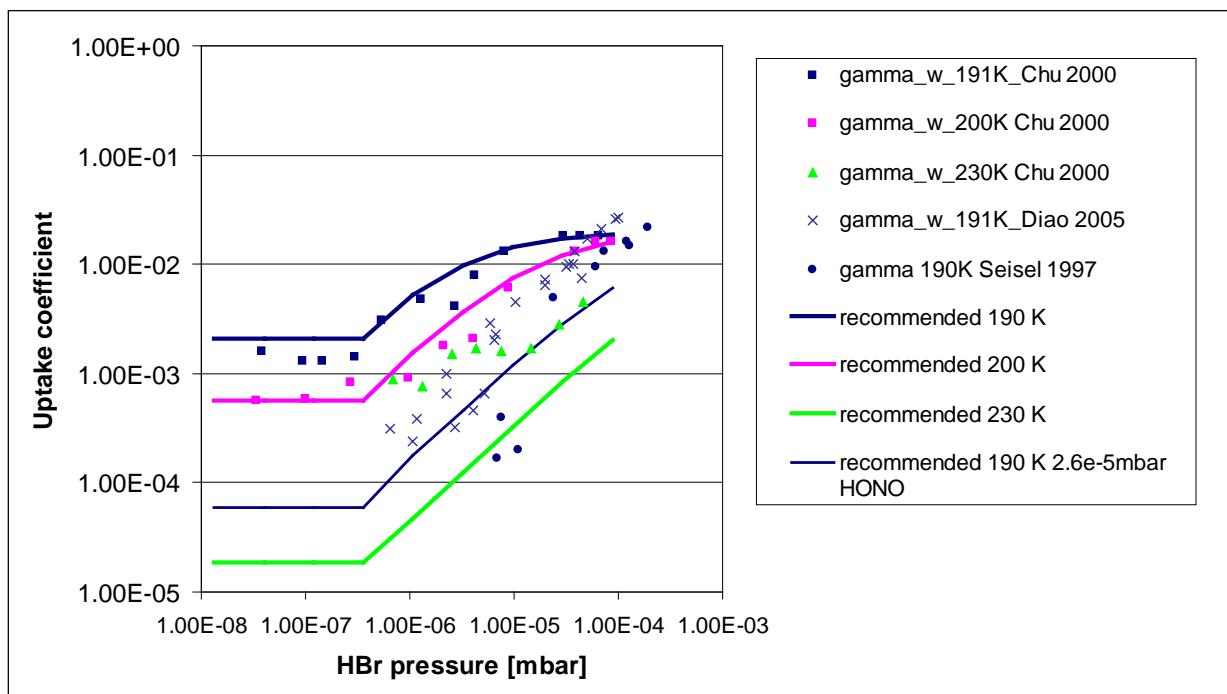


Figure 1: The recommended parameterization for the $p(\text{HBr})$ dependence of the uptake coefficient of HONO on ice in the presence of HBr (lines), along with available experimental data (symbols).