IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation
Data Sheet HI40; V.A1.40

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

HONO + HI (Ice) → INO + H_2O

Experimental Data

Parameter	*p*HI /mbar	Temp./K	Reference	Technique/Comments
Uptake coefficients: γ_{ss}				
$(2.9\pm0.9)\times10^{-4}$	1.1×10^{-7}	191	Diao and Chu, 2005	CWFT-MS (a)
$(3.0\pm0.8)\times10^{-2}$	8.9×10^{-5}	191		

Comments

(a) 30 μm thick vapor-condensed H_2O ice film doped with HI in the range 10^{-7} mbar to 10^{-5} 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 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 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**
α_s	0.02	180 - 220
k_s / $cm^2 molecule^{-1} s^{-1}$	8.0×10^{-19}	180 – 220
Reliability		
$\Delta \log \alpha_s$	± 0.3	180 - 220
$\Delta \log k_s$ / $cm^2 molecule^{-1} s^{-1}$	± 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:

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

The surface coverage of HI should be taken as $[HI]_S = 3.0\times10^{14}$ cm^{-2} at HI pressures between 10^{-8} and 10^{-7} mbar and as $[HI]_S = 8.0\times10^{20}$ [HI] cm^{-2} at HI pressures above 10^{-7} mbar (see datasheet V.A1.32)

With k_s and α_S as recommended above, and K_{LangC}(HONO) = 5.0×10^{-23} exp(5200/T) cm^3 molecule^{-1} based on the value for K_{linC} and N_{max}(HONO) = 3.0×10^{14} molecule cm^{-2} reported in the datasheet V.A1.11, good agreement with the data at pressures above 10^{-6} mbar is obtained. 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 x 10^{14} 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, 1364-1373, 2005.

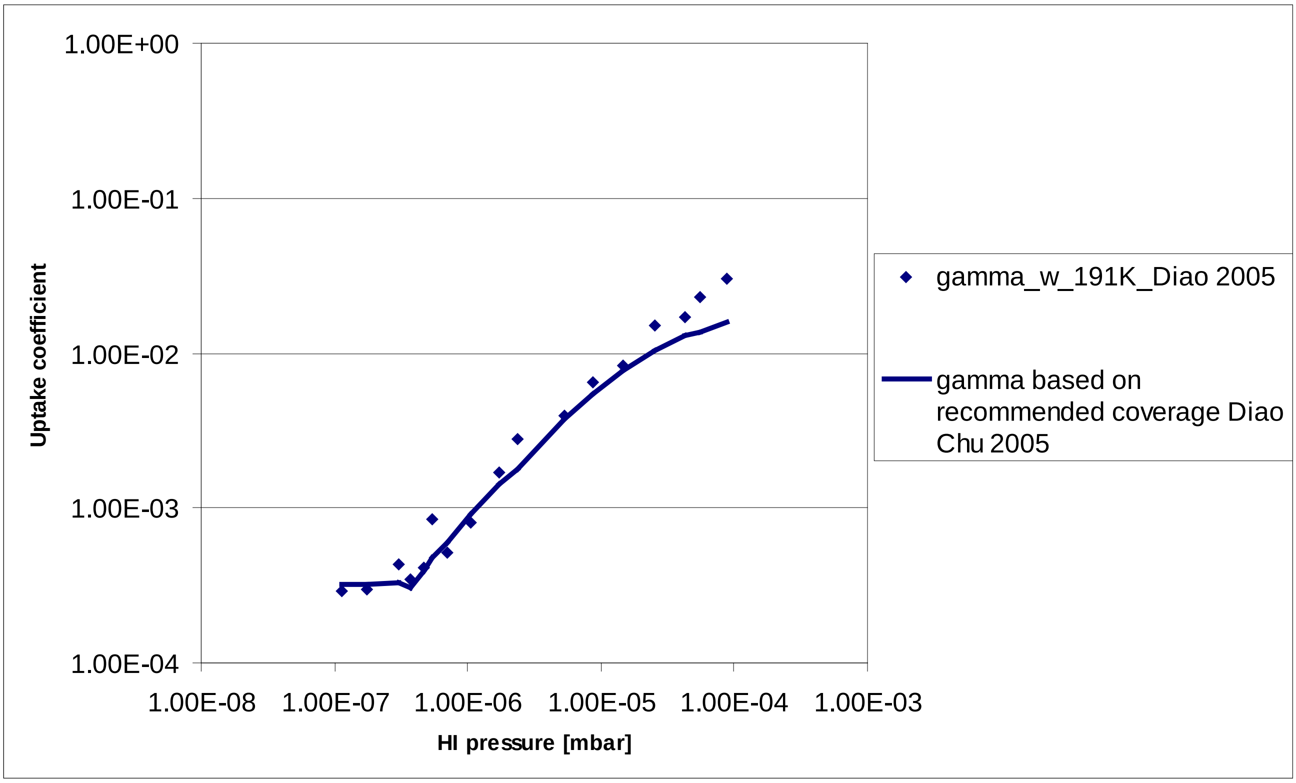

Figure 1: The recommended parameterization for p(HI) dependence of the uptake coefficient of HONO on ice in the presence of HI.