IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation
Data Sheet HI38; V.A1.38

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HONO + HCl (Ice) → ClNO + H_2O

Experimental Data

Parameter	p_{HCl} /mbar	Temp./K	Reference	Technique/Comments
γ_{ss}(HONO)				
$(6\pm2)\times10^{-2}$		180	Fenter and Rossi, 1996	Kn-MS(a)
$(4.5\pm1.5)\times10^{-2}$		190		
$(3.0\pm0.5)\times10^{-2}$		200		
$(1.7\pm0.6)\times10^{-4}$	2.3×10^{-6}	191	Diao and Chu, 2005	CWFT-MS (b)
$(1.4\pm0.4)\times10^{-2}$	2.3×10^{-5}			

Comments

(a) Ice prepared both by vapour-phase deposition and by cooling of a sample of distilled water. HONO prepared from use of acidified $NaNO_2$ solution, with NO and NO_2 as major contaminants. HONO concentration was about 10^{12} molecule 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) 30μm thick vapor-deposited ice film doped with HCl in the range 6.5×10^{-7} to 1.7×10^{-4} mbar prior to exposure to HONO. Cited values for γ are corrected for gas phase diffusion but not for pore diffusion, which reduced the value of γ by a factor of 8 to 50. At HCl pressures below 5×10^{-6} mbar, to which the ice was exposed, γ_{ss}(HONO) slightly decreased with pressure. At higher HCl pressures, γ_{ss}(HONO) scales with p_{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 γ_{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
α_s	0.02	180 – 220
k_s / cm^{2}molecule^{-1}s^{-1}	4.0×10^{-19}	180 – 220
Reliability		
Δ log α_s	± 0.3	180 - 220
Δ log k_s / cm^{2}molecule^{-1}s^{-1}	± 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 occurance 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:

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

with

$$\Gamma_s = \frac{4k_s[\mathrm{HCl}]_s K_{LangC}(HONO) N_{\max}}{\bar{c}\left(1 + K_{LangC}(HONO)[HONO]_g\right)} .$$

The surface coverage of HCl should be taken as

$$[HCl]_S = N_{\max} \frac{K_{LangC}(HCl)[HCl]_g}{1 + K_{LangC}(HCl)[HCl]_g}$$

with $K_{\mathrm{LangC}}(\mathrm{HCl}) = 7.3\times10^{-17}$ exp(2858/T) cm^3 molecule^{-1} (see data sheet V.A1.27).

Similarly, $K_{\mathrm{LangC}}(\mathrm{HONO}) = 5.0\times10^{-23}$ exp(5200/T) cm^3 and $N_{\max}(\mathrm{HONO}) = 3.0\times10^{14}$ 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, 1364-1373, 2005.

Fenter, F.F., and Rossi, M.J.: J. Phys. Chem. 100, 13765-13775, 1996.

McNeill, V. F., Loerting, Th., Geiger, F.M., Trout, B.L., and Molina, M. J., Proc. Nat. Acad. Sci., 103, 9422-9427, 2006.

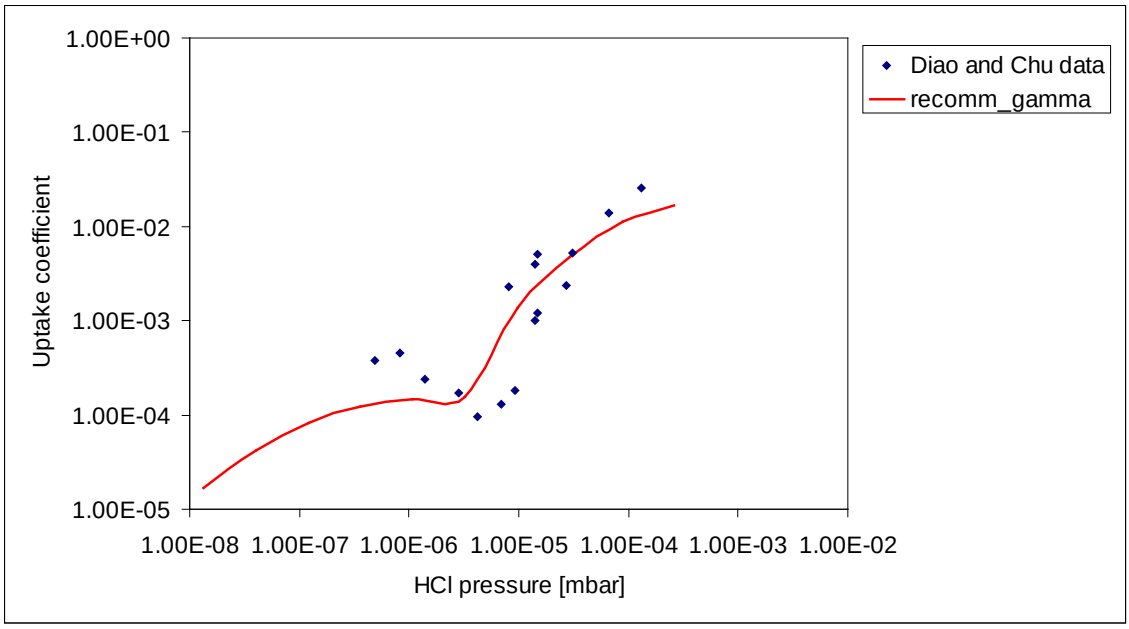

Figure 1: The recommended parameterization for the p(HCl) dependence of the uptake coefficient of HONO on ice in the presence of HCl (red line), along with the data by Diao and Chu (2005).