IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.29 HET_SL_29

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HONO + HCl (aqueous sulphuric acid aerosol) $\rightarrow$ ClNO + H$_2$O

Experimental data

Parameter	p_{HCl} /mbar	p_{HONO} /mbar	[H$_2$SO$_4$] /wt %	Temp ./K	Reference	Technique/ Comments
Uptake coefficients: γ						
$\gamma_{HCl} = (2.0 \pm 0.5) \times 10^{-2}$	4.0×10^{-7}	6.7×10^{-7}	60.8	208	Zhang et al., 1996	CWFT-CIMS (a)
$\gamma_{HCl} = (1.1 \pm 0.4) \times 10^{-2}$			65.1	213		
$\gamma_{HCl} = (1.6 \pm 0.1) \times 10^{-2}$			68.0	217		
$\gamma_{HCl} = (2.0 \pm 0.2) \times 10^{-2}$			71.3	223		
$\gamma_{HCl} = (0.5 - 1.0) \times 10^{-4}$	1.5×10^{-5}	1.3×10^{-5}	62.5-65	225-230	Fenter and Rossi, 1996	Kn-MS (b)
$\gamma_{HCl} = (2.0 \pm 0.7) \times 10^{-3}$			60	225-230		
$\gamma_{HONO} = 1.1 \times 10^{-3}$	4.8×10^{-6}		50	250	Longfellow et al., 1998	RWFT-CIMS (c)
$\gamma_{HONO} = 1.5 \times 10^{-2}$	1.6×10^{-4}		50	250		
$\gamma_{HONO} = 3.7 \times 10^{-2}$	8.5×10^{-7}		50	205		
$\gamma_{HONO} = 1.5 \times 10^{-1}$	1.2×10^{-5}		50	205		
$\gamma_{HONO} = 3.8 \times 10^{-2}$	4.4×10^{-6}		60	219		
$\gamma_{HONO} = 9.2 \times 10^{-2}$	2.8×10^{-5}		60	219		
$\gamma_{HONO} = 9.4 \times 10^{-3}$	2.8×10^{-6}		60	230		
$\gamma_{HONO} = 5.9 \times 10^{-2}$	5.4×10^{-5}		60	230		
$\gamma_{HONO} = 2.9 \times 10^{-3}$	5.6×10^{-6}		60	250		
$\gamma_{HONO} = 2.4 \times 10^{-2}$	9.6×10^{-5}		60	250		
$\gamma_{HONO} = 6.8 \times 10^{-2}$ ($r_p = 64$ nm)	4.8×10^{-4}		60	250		
$\gamma_{HONO} = 5.5 \times 10^{-2}$ ($r_p = 232$ nm)	4.8×10^{-4}		60	250		
$\gamma_{HONO} = 1.5 \times 10^{-2}$ ($r_p = 83$ nm)	1.2×10^{-4}		60	250		
$\gamma_{HONO} = 1.5 \times 10^{-2}$ ($r_p = 306$ nm)	1.2×10^{-4}		60	250		
$\gamma_{HCl} = 5.1 \times 10^{-3}$		1.1×10^{-7}	70	215		
$\gamma_{HCl} = 1.1 \times 10^{-2}$		1.6×10^{-6}	70	215		
$\gamma_{HCl} = 1.0 \times 10^{-3}$		1.6×10^{-6}	67	250		
$\gamma_{HCl} = 5.2 \times 10^{-3}$		1.1×10^{-5}	67	250		
$\gamma_{HCl} = 3.3 \times 10^{-4}$		3.1×10^{-6}	70	269		
$\gamma_{HCl} = 1.3 \times 10^{-3}$		1.6×10^{-5}	70	269		

Comments

(a) Coated wall flow tube with CIMS detection of HONO after reaction with SF_6^-. 0.1 mm thick liquid H_2SO_4. The total pressure was 0.5 mbar He; the partial pressure of HONO and HCl was around 6×10^{-7} mbar and 6×10^{-7} mbar, respectively. The sulphuric acid composition was controlled by maintaining fixed temperature and H_2O partial pressure of 6×10^{-4} mbar in the gas flows. ClNO was observed as product with approximately unity yield. Separation of solubility driven HCl uptake from reaction driven uptake was achieved by allowing enough time for establishing steady state at each injector position.

(b) Knudsen cell reactor with MS detection. H_2SO_4 solutions were prepared by dilution of a 95 wt% solution. HONO and HCl were prepared by adding H_2SO_4 to $NaNO_2$ and NaCl, respectively. MS traces were consistent with full conversion of HCl into ClNO in presence of HONO. Reaction probabilities (as listed in the table) were obtained from the difference of the HCl loss in presence and absence of HONO to account for HCl uptake due to solubility of HCl alone.

(c) Most uptake experiments were performed in a 2.2cm i.d. coated wall flow tube and a 1.84 cm i.d. rotating wetted wall flow tube with CIMS detection of HONO. The reaction of HONO with SF_6- was revisited to come up with an improved estimate of the rate constant and the branching ratio for the formation of SF_5- vs $HFNO_2$-. The observed loss of HONO in the flow tube was corrected for the hydrolysis reaction of the product ClNO yielding back HONO by taking into account the reaction probability of ClNO of 2.5×10^{-3} on 60 wt% and 3.0×10^{-3} on 50 wt% solutions at 250 K determined in separate experiments. HONO uptake to deliquesced NaCl at 268 K did not lead to detectable amounts of HONO. A few experiments were performed with aerosol particles also listed in the table.

Preferred Values

Parameter	Value	T/K
α_s	1	200 – 300
$\Gamma_{s,HONO}$	$9 \times 10^4 \exp(-3000/T)$ [HCl] H_{NO+}*	200 – 300
H_{NO+}* (M atm^{-1})	$C \exp(D$ (wt%))	200 – 300
C (M atm^{-1})	$2.0 \times 10^8 \exp(-14000/T)$	200 – 300
D ((wt%)$^{-1}$)	297.3/T-0.474	200 – 300
k_b (M^{-1} s^{-1})	$25[H^+]$ T/η	200 – 300
$\Gamma_{s,HCl}$	4×10^{-3} [NO$^+$] H_{HCl}*	200 – 300
Reliability		
$\Delta \log (\alpha_s)$	0.3	200 – 300
$\Delta \log (H^*)$	0.3	200 – 300
$\Delta \log (k_b)$	0.3	200 – 300

Comments on Preferred Values

The available studies agree that efficient reaction of HONO with HCl occurs in sulphuric acid solutions to yield ClNO. Most likely, the reaction proceeds through one of the protonated forms of HONO, e.g., $NO^+HSO_4^-$. The data by Longfellow et al. (1998) cover a sufficiently wide parameter range to allow constraining the kinetics. The pressure dependence observed for the uptake of HONO in presence of HCl deviates from the expectation based on bulk reaction alone and thus is indicative of a surface process. While Longfellow et al. reported individual contributions for the surface vs bulk terms to overall uptake for each individual solution composition and temperature, we adopt here a more general parameterisation. Following a similar procedure as for HOCl and HCl, the bulk reaction is parameterised with the acid concentration and the viscosity to represent diffusion limited kinetics of an acid catalysed reaction that largely controls temperature and composition dependence.

In absence of limitations by surface accommodation or surface to bulk transfer, for the uptake of HONO, the uptake coefficient simplifies to:

$$\frac{1}{\gamma_{HONO}} = \frac{1}{\alpha_s} + \cfrac{1}{\Gamma_{s,HONO} + \cfrac{1}{\cfrac{1}{\Gamma_{sb,HONO}} + \cfrac{1}{\Gamma_{b,HONO}}}} \approx \frac{1}{\Gamma_{s,HONO} + \Gamma_{b,HONO}}$$

The surface reaction is assumed to be a direct reaction between NO+ and HCl. In absence of data constraining their surface concentrations, we simply assume that the latter is proportional to the bulk concentration, which is tied to the gas phase pressures through the Henry's Law constant. The equilibrium constant describing the concentration of NO+ is given by the second term of the expression for the solubility of HONO given in datasheet VI.A4.7, as given in the preferred value table. The concentration of HCl is calculated using the expression for the solubility recommended in datasheet VI.A4.14:

$H^*_{HCl} = (0.094 - 0.61X + 1.2X^2) \exp(-8.68 + (8515 - 10718X^{0.7})/T)$

The mole fraction, X, of sulfuric acid is given by $X = wt\%/(wt\% + (100 - wt\%)98/18$.

The bulk reaction rate constant requires knowing the proton concentration. We suggest using the parameterisation of Shi et al.:

$[H^+] = \exp[60.51 - 0.095wt\% + 0.0077wt\%^2 - 1.61 \times 10^{-5}wt\%^3 - (1.76 + 2.52 \times 10^{-4} wt\%^2)T^{0.5} + (-805.89 + 253.05wt\%^{0.076})/T^{0.5}]$

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:

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

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

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

This allows calculating the contribution of the bulk reaction according to:

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

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) using a molar volume of 36 cm^3/mol (da Silva et al., 2006). The reactivo-diffusive length needed to account for finite particle sizes is given by $l_{HONO} = (D_{l,HONO}/(k_b p_{HCl} H^*_{HCl}))^{0.5}$

Similarly, for the uptake coefficient of HCl, the expression for the combined contribution of surface and bulk processes, is given by:

$$\frac{1}{\gamma_{HCl}} = \frac{1}{\alpha_s} + \cfrac{1}{\Gamma_{s,HCl} + \cfrac{1}{\cfrac{1}{\Gamma_{sb,HCl}} + \cfrac{1}{\Gamma_{b,HCl}}}}$$

The surface accommodation coefficient is assumed to be one. For calculating $\Gamma_{s,HCl}$, the tendency of HCl to adsorb to the surface is again expressed as proportional to the Henry's Law constant, while the concentration of NO$^+$ is given by $p_{HONO} H_{NO+}^*$. $\Gamma_{sb,HCl} = k_{sol}/k_{des}$ is obtained using $k_{sol} =$

7.84 × 10¹⁰ /η(cP) and k_{des} = 8.0 × 10¹⁷ exp(-5000/T) from datasheet VI.A4.14. The expression for the resistance due to the bulk reaction is given by:

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

The diffusion coefficient of HCl can be expressed as $D_{l,HCl}$ = 7.8 × 10⁻⁸ T / η as explained on datasheet VI.A4.14. The reactivo-diffusive length needed to account for finite particle sizes is given by $l_{HCl} = (D_{l,HCl}/(k_b p_{HONO} H^*_{HONO}))^{0.5}$.

This surface and bulk reaction model relatively well describes the available data. The strongly non-linear dependencies of the solubility of HONO and HCl impose strong constraints on adjusting the model to the data, only three parameters in the two surface reaction terms and one for the bulk rate coefficient expression are adjusted. Assuming the bulk reaction only does not allow bringing the HONO uptake coefficients into consistency with the HCl uptake coefficients, and it would lead to quite strong disagreement with the pressure dependence for both, 50 and 60 wt% solutions. The only temperature dependence in the formalism required to fit the data was for the surface reaction of HONO, likely to represent the temperature dependence of the surface coverage. The case for the surface process for HCl is relatively poor. Longfellow et al. did not include it given the scatter in the data, even though the slope of the pressure dependence appears to be steeper than expected for bulk only reaction. We include this surface reaction to also improve agreement with the Zhang et al. data, even though it leads to some overestimate of the Longfellow data at 219 K, but we refrain from including a temperature dependence there in absence of more data to constrain it. The HCl uptake coefficients reported by Fenter and Rossi (1996) appear to be at least an order of magnitude lower than expected based on the relatively large HONO pressures used.

References

Zhang, R., Leu, M.-T. and Keyser, L.F.: J. Phys. Chem. 100, 339 (1996).

Shi, Q., Jayne, J. T., Kolb, C. E., Worsnop, D. R., and Davidovits, P.: J. Geophys. Res., 106, 24259-24274, 2001.

Longfellow, C. A., Imamura, T., Ravishankara, A. R., and Hanson, D. R.: J. Phys. Chem. A, 102, 3323-3332, 1998.

da Silva, G., Dlugogorski, B. Z., and Kennedy, E. M.: AIChE Journal, 52, 1558-1565, 2006.

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

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

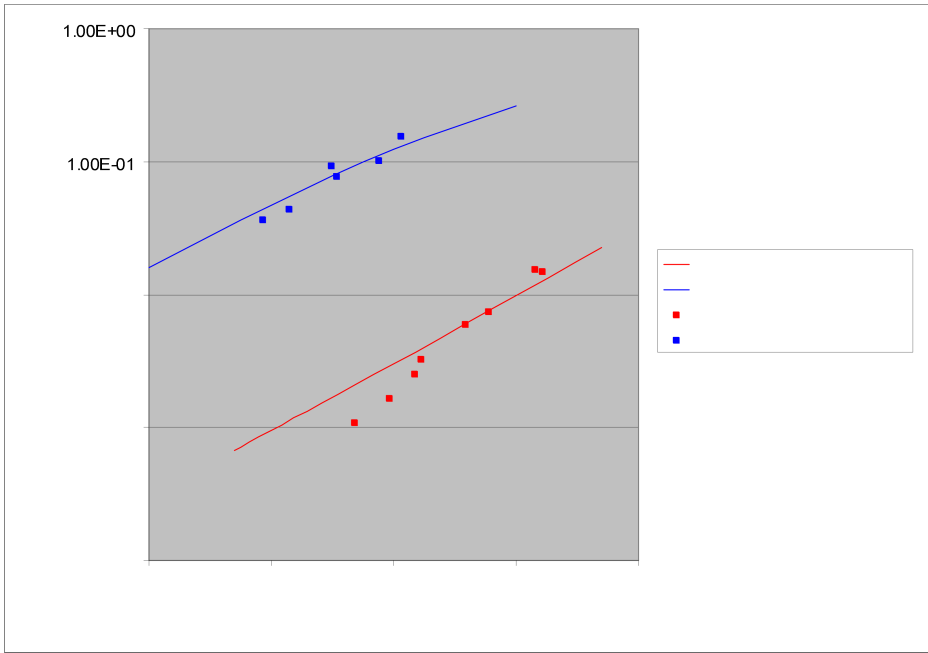Williams, L. R., and Long, F. S.: J. Phys. Chem., 99, 3748-3751, 1995.

Figure 1: Uptake coefficient of HONO due to reaction with HCl in 50 wt% sulphuric acid as a function of HCl pressure.
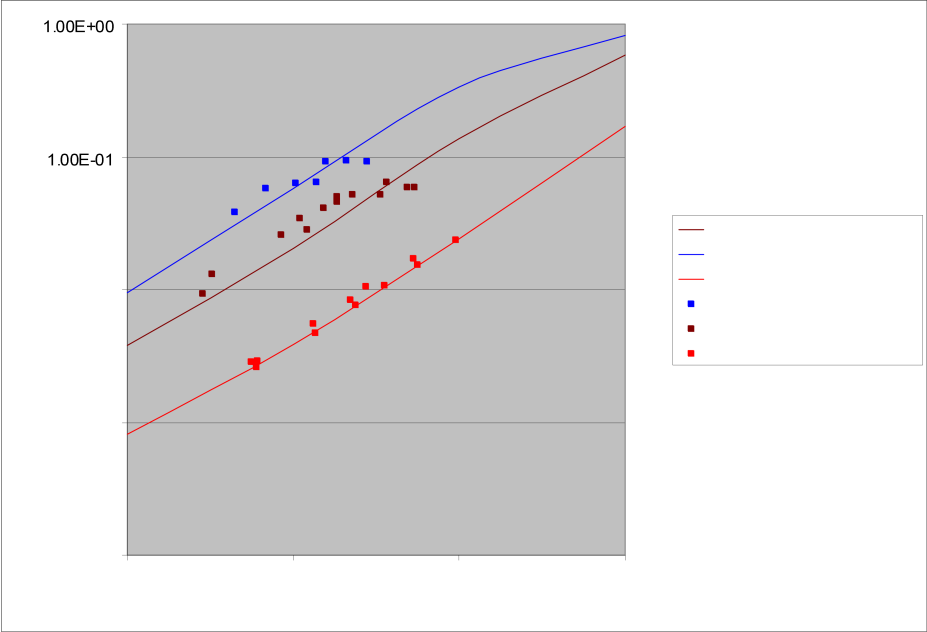

Figure 2: Uptake coefficient of HONO due to reaction with HCl in 60 wt% sulphuric acid as a function of HCl pressure.
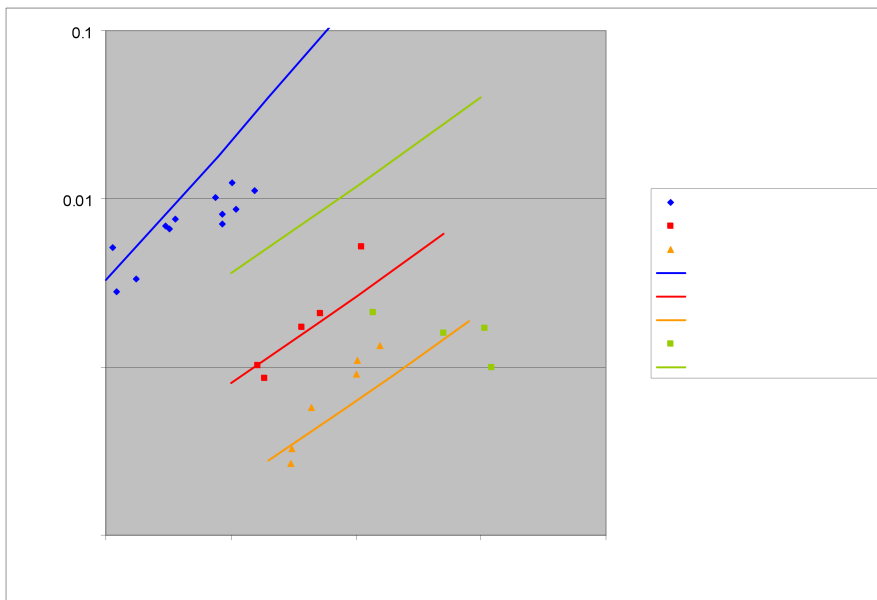
Figure 3: Uptake coefficient of HCl due to reaction with HONO in 60 and 70 wt% sulphuric acid as a function of HONO pressure.
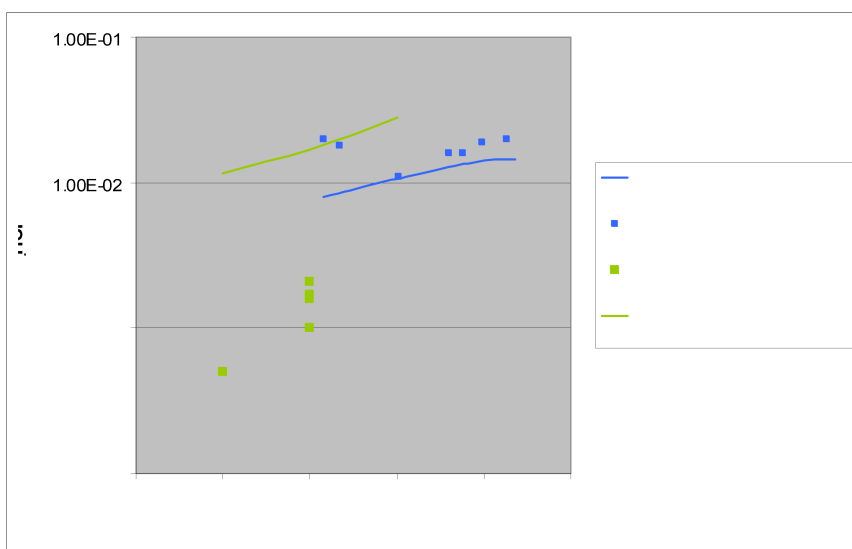

Figure 4: Uptake coefficient of HCl due to reaction with HONO as a function of solution composition for the data of Zhang et al., for which solutions were equilibrated with $p(H_2O)$= 6.7×10^{-4} mbar. The Fenter and Rossi data were not purposely performed at constant water pressure, but were mostly around 7×10^{-4} mbar. HONO pressures were 6.7×10^{-7} mbar in the experiments by Zhang et al. and about 10^{-5} mbar in those by Fenter and Rossi.