

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.7 HET_SL_7

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HONO + H₂SO₄ (aqueous) → products

Experimental data

<i>Parameter</i>	[H ₂ SO ₄] /wt %	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>				
$\gamma_{ss} = (1.60 \pm 0.09) \times 10^{-2}$	65.3	213.5	Zhang, Leu and Keyser, 1996	CWFT-CIMS (a)
$\gamma_{ss} = (3.2 \pm 0.5) \times 10^{-2}$	68.8	218.6		
$\gamma_{ss} = (6.6 \pm 0.6) \times 10^{-2}$	71.3	222.6		
$\gamma_{ss} = (9.1 \pm 1.6) \times 10^{-2}$	73.0	226.1		
$\gamma_{ss} = (2.0 \pm 0.5) \times 10^{-4}$	55	220	Fenter and Rossi, 1996	Kn-MS (b)
$\gamma_{ss} = (2.0 \pm 0.5) \times 10^{-3}$	60	215-235		
$\gamma_{ss} = (5.5 \pm 1.0) \times 10^{-2}$	80	250-265		
$\gamma_{ss} = 0.31 \pm 0.02$	95	220-273		
$\gamma = (2.8 \pm 1.4) \times 10^{-6}$	60	298	Baker, Ashbourn and Cox, 1999	AFT-CLD (c)
$\gamma = (8.1 \pm 2.7) \times 10^{-6}$	60			
<i>Solubility: H^* ($M \text{ atm}^{-1}$)</i>				
$(4.2 \pm 0.5) \times 10^2$	31.5	250	Becker et al., 1996	Static-TDLAS/IC (d)
$(1.1 \pm 0.2) \times 10^2$	31.5	267		
$(3.1 \pm 0.5) \times 10^1$	31.5	283		
$(2.0 \pm 0.2) \times 10^1$	31.5	298		
$(3.1 \pm 0.5) \times 10^2$	51.2	249		
$(6.4 \pm 0.7) \times 10^1$	51.2	267		
$(1.7 \pm 0.3) \times 10^1$	51.2	283		
7.3 ± 0.1	51.2	298		
$(4.3 \pm 0.2) \times 10^4$	67.3	251		
$(1.2 \pm 0.5) \times 10^4$	67.3	268		
$(4.1 \pm 1.0) \times 10^3$	67.3	283		
$(1.6 \pm 0.2) \times 10^3$	67.3	298		
1.3×10^7	83	295	Longfellow et al., 1998	RWFT-CIMS (e)
9.8×10^3	71	295		
1.2×10^3	66	296		
1.5×10^6	79	295		
2.8×10^8	79	250		
4.6×10^9	79	230		
2.6×10^3	65	270		
9.0×10^3	65	249		
1.6×10^5	65	220		
6.1 ± 1.1	50.5	300.5	Baker, Ashbourn and Cox, 1999	Bubbler-CLD (c)
10.2 ± 1.1	57.2	302		
14 ± 2	58.2	303		

15 ± 3	59.1	299	
25 ± 4	59.3	300	
38 ± 6	61.0	300	
<i>rate constants k_{II} ($M^{-1} s^{-1}$)</i>			
300 ± 40	50.5	300.5	Baker, Ashbourn and Cox, Bubbler-CLD (c) 1999
185 ± 40	56.5	301.5	
122 ± 15	57.2	302	
81 ± 10	58.2	303	
39 ± 5	59.1	299	
32 ± 4	59.3	300	
7.8 ± 0.8	61.0	300	
4.5 ± 0.5	61.4	298.5	
0.13 ± 0.01	65.4	300	

Comments

- (a) CIMS detection of HONO after reaction with SF₆. 0.1 mm thick liquid H₂SO₄. The partial pressure of HONO was around 6×10^{-7} mbar. The sulphuric acid composition was controlled by maintaining a fixed temperature and H₂O partial pressure of 6×10^{-4} mbar in the gas flows. Persistent uptake over more than 1 hour was interpreted as formation of NO⁺HSO₄⁻ in the film. Its precipitation as a solid was not observed.
- (b) H₂SO₄ solutions prepared by dilution of 95 wt%. Saturation of the HONO uptake takes place after deposition of 3% of a monolayer. The uptake appears to be reversible.
- (c) Typically 10⁷ particles cm⁻³ of 120 nm diameter were entrained in an aerosol laminar flow tube and interacted with HONO in the concentration range 305 to 610 ppb. Aerosol diagnostics included a counter and an optical extinction measurement in the 200 to 390 nm range whereas the gas phase was monitored using a NO_x chemiluminescence analyzer. The observed uptake coefficient was found to be roughly proportional to the partial pressure of HONO in these experiments. Separate bubbler experiments were performed to measure the bimolecular rate constant for the reaction 2HONO => NO + NO₂ + H₂O. The rate constant was found to fall off sharply beyond 56 wt% sulphuric acid. The rate constant was not sufficient to explain the observed uptake of HONO to aerosol particles by reaction in the bulk, so that a surface reaction mechanism was invoked.
- (d) Solubility of HONO in a 11-L Pyrex glass reactor was measured directly by monitoring both gas phase composition by tunable diode laser spectrometry and liquid phase by ion chromatography. Formation of NO₂ due to 2 HONO = NO + NO₂ + H₂O was observed. Since the NO₂ concentration equilibrated with time, this reaction was included into calculating the effective solubility. A further, very slow overall loss of HONO and concomitant formation of N₂O with time was also observed.
- (e) Determination of solubility was 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. Depending on the sulphuric acid concentration range, solubility could be determined in relative or absolute modes. No kinetics of uptake of HONO alone was reported.

Preferred Values

Parameter	Value	T/K
α_b	> 0.05	220 – 300
A ($M \text{ atm}^{-1}$)	$4.2 \times 10^{-6} \exp(4873/T)$	
B ($(\text{wt}\%)^{-1}$)	$13.16/T - 0.0856$	
C ($M \text{ atm}^{-1}$)	$2.0 \times 10^8 \exp(-14000/T)$	
D ($(\text{wt}\%)^{-1}$)	$297.3/T - 0.474$	
k_b ($M^{-1} s^{-1}$)	320	298

γ_{gs}	$< 10^{-5}$	298
<i>Reliability</i>		
$\Delta \log (\alpha_{\text{b}})$	undetermined	
$\Delta \log (H^*)$	0.3	220 – 300
$\Delta \log (k_{\text{b}})$	0.1	298
$\Delta \log (\gamma_{\text{gs}})$	undetermined	

Comments on Preferred Values

Solubility of HONO in H₂SO₄ solutions depends strongly on composition. The exponential decrease with sulphuric acid content up to about 50wt% is due to a salting out effect at decreased water activity (Becker et al., 1996). Dissociation of HONO into H⁺ and NO₂⁻ is only important below 1 wt% (see datasheet V.A1.7; Park and Lee, 1988). Above about 55 wt%, solubility of HONO increases strongly due to the formation of either of NO⁺, H₂ONO⁺, NO⁺HSO₄⁻, or a combination thereof (Burley and Johnston, 1992, and references therein; Riordan et al., 2005). The available studies determining the effective solubility of HONO directly by Becker et al. (1996), Longfellow et al. (1998) and Baker et al. (1999) agree very well as far as they overlap in composition and temperature. We recommend using an expression based on a parameterisation proposed by Becker et al. (1996):

$$H^* (\text{M atm}^{-1}) = A \exp(B (\text{wt}\%)) + C \exp(D (\text{wt}\%))$$

The preferred constants A, B, C and D listed in the table were determined by further taking into account the data at lower temperature and higher wt% by Longfellow et al. (1998). While the low wt% part represented by the first term in the expression for H* can be traced back to the salting coefficient based on the Setschenow equation (see Becker et al. (1996) for details), the other parameters were adjusted to broadly fit the available data without explicitly sorting out equilibria with NO⁺, H₂ONO⁺ and NO⁺HSO₄⁻.

Uptake of HONO into sulphuric acid solutions can be driven by the effective solubility encompassing dissociation, protonation and the disproportionation into NO₂ and NO, assuming that the time scale for equilibration is given by diffusion in the liquid phase:

$$\frac{1}{\gamma} = \frac{1}{\alpha_{\text{b}}} + \frac{1}{\Gamma_{\text{sol}}} \quad \text{with} \quad \Gamma_{\text{sol}} = \frac{4 \cdot H_{\text{HONO}}^* RT}{\bar{c}_{\text{HONO}} \cdot \sqrt{\pi}} \cdot \sqrt{\frac{D_{\text{L,HONO}}}{t}} \quad (1)$$

The diffusion coefficient for HONO is parameterized by $D_{\text{L,HONO}} = C_{\text{HONO}} T / \eta$; with $C_{\text{HONO}} = 6.90 \times 10^{-8} \text{ cm}^2 \text{ cP K}^{-1} \text{ s}^{-1}$, estimated as suggested by Klassen et al. (1998) using a molar volume of 36 cm³/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:

$$\eta = AT^{-1.43} \exp(448\text{K} / (T-T_0)), \quad (2)$$

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

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

The kinetic experiments by Zhang et al. (1996) and Fenter and Rossi (1996) were likely limited by solubility and bulk accommodation. With $\alpha_{\text{b}} > 0.05$ and the recommended values for the effective solubility, the above equation yields uptake coefficients consistent with those reported for times between 10 and 100 seconds.

The bulk reaction rate constant k_{b} for the disproportionation reaction was adopted from Baker et al. (1996) by assuming that the reduction of the effective bimolecular rate constant was due to the decreasing concentration of unprotonated HONO in solution. For the calculation of the concentration of unprotonated HONO, the first term of the recommended expression for the effective solubility can be used:

$$[\text{HONO}] = p_{\text{HONO}} A \exp(B (\text{wt}\%)) \quad (3)$$

This leads to effective rates consistent with those measured by Baker et al. This rate constant is far too small to affect uptake of HONO to sulfuric acid appreciably over the short time scales of the kinetic experiments. The reaction of HONO with $\text{NO}^+\text{HSO}_4^-$ to yield N_2O was not quantified in the study by Wiesen et al. (1995) in a way that would allow extracting a rate constant.

For the conditions of the aerosol flow tube experiments by Baker et al. (1999), gas phase HONO rapidly equilibrates with the solution of the submicron particles, so that the uptake coefficient was due to an irreversible loss process in the particle phase. Since the bulk reaction rate constant k_b was several orders of magnitude too low to explain the measured uptake coefficients, uptake was attributed to a surface process. Baker et al. suggest an Eley-Rideal type reaction, which was adopted here for a recommendation of an upper limit for γ_{gs} in the atmospherically relevant HONO concentration range.

References

- Baker, J., Ashbourn, S.F.M. and Cox, R.A.: *Phys. Chem. Chem. Phys.* 1, 683 (1999).
- Becker, K. H., Kleffmann, J., Kurtenbach, R., and Wiesen, P.: *J. Phys. Chem.*, 100, 14984-14990, 1996.
- da Silva, G., Dlugogorski, B. Z., and Kennedy, E. M.: *AIChE Journal*, 52, 1558-1565, 2006.
- Fenter, F. F., and Rossi, M. J.: *J. Phys. Chem.*, 100, 13765-13775, 1996.
- Klassen, J. K., Hu, Z., and Williams, L. R.: *J. Geophys. Res.*, 103, 16197-16202, 1998.
- Longfellow, C. A., Imamura, T., Ravishankara, A. R., and Hanson, D. R.: *J. Phys. Chem. A*, 102, 3323-3332, 1998.
- Shi, Q., Jayne, J. T., Kolb, C. E., Worsnop, D. R., and Davidovits, P.: *J. Geophys. Res.*, 106, 24259-24274, 2001.
- Wiesen, P., Kleffmann, J., Kurtenbach, R., and Becker, K. H.: *Faraday Discuss.*, 121-127, 1995.
- Williams, L. R., and Long, F. S.: *J. Phys. Chem.*, 99, 3748-3751, 1995.
- Zhang, R., Leu, M.-T. and Keyser, L.F.: *J. Phys. Chem.* 100, 339 (1996).

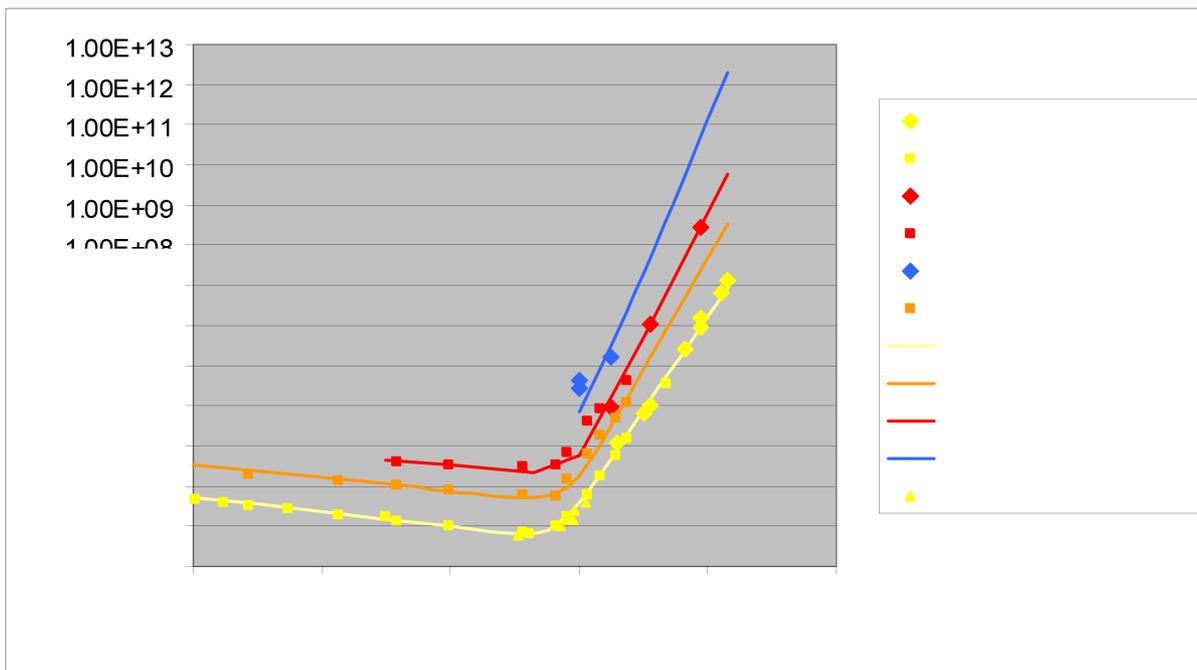


Figure 1: Effective Henry's Law constant as a function of sulphuric acid concentration. Symbols denote data, lines denote calculated values based on the recommended expression.

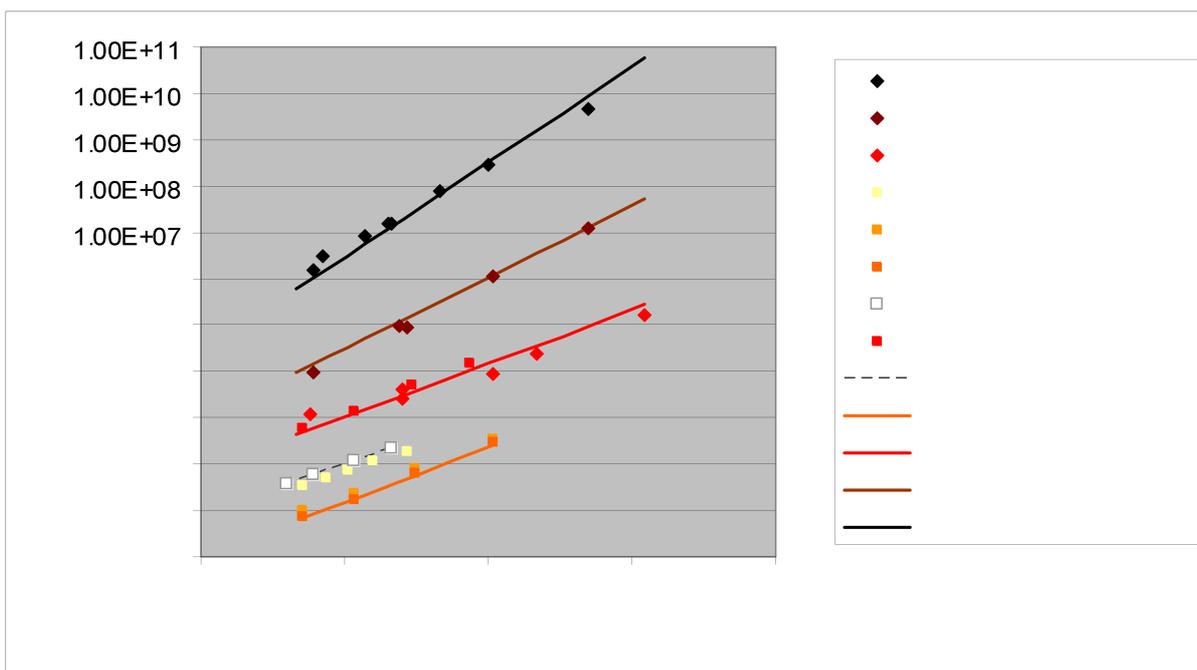


Figure 2: Effective Henry's Law constant as a function of temperature. Symbols denote data, lines denote calculated values based on the recommended expression.

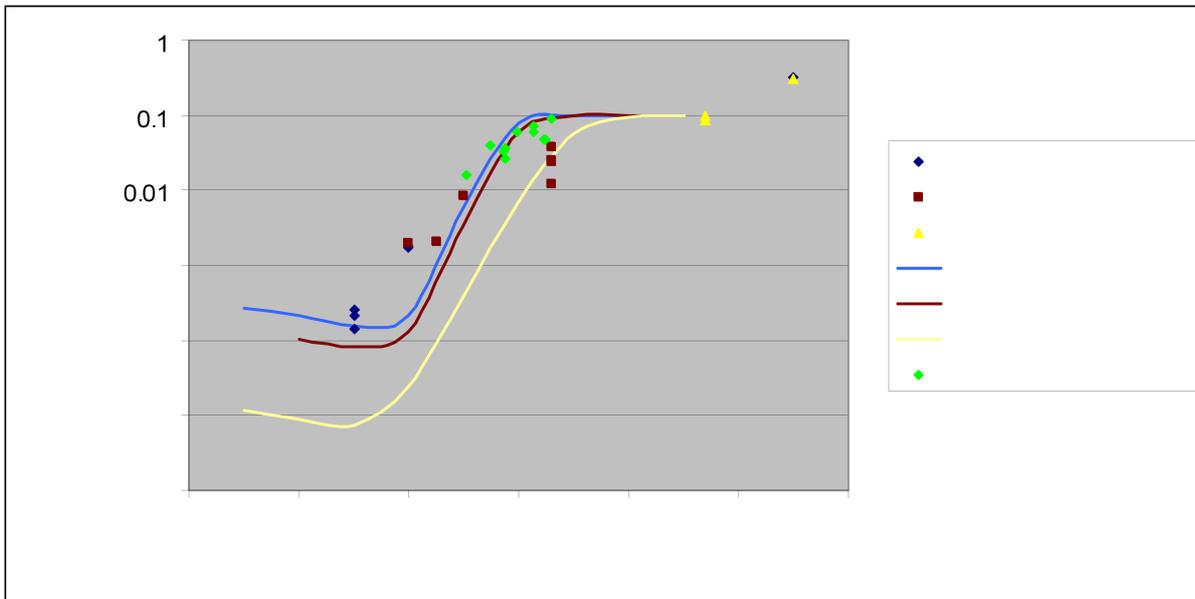


Figure 3: Measured uptake coefficients (symbols) of HONO into sulphuric acid as a function of sulphuric acid wt%. The lines are calculated using equation (1) evaluated at 100s and a bulk accommodation coefficient of 0.1.

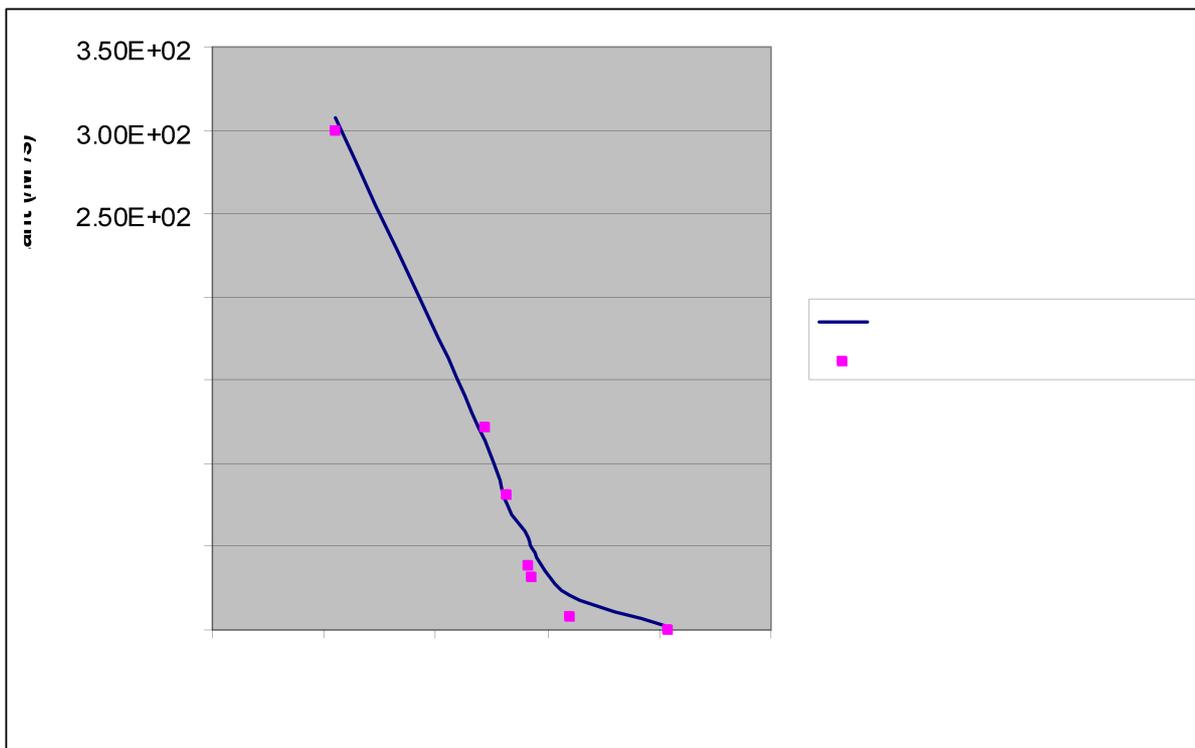


Figure 4: Effective bimolecular rate constant for the reaction $\text{HONO} \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$. Symbols represent data, the solid line is based on the preferred value of the rate coefficient using expression (3) to calculate the concentration of non-protonated HONO in the solution.