# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.9 HET_SL_9



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**$HO_2NO_2 + H_2SO_4 \rightarrow$ products**

## Experimental data

| *Parameter* | $[H_2SO_4]$ /wt % | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|---|
| *Uptake coefficient: $\gamma_0$* | | | | |
| 0.23 | 58.3 | 207.9 | Zhang, Leu and Keyser, 1997 | CWFT-CIMS (a) |
| 0.20 | 58.3 | 213.5 | | |
| 0.13 | 58.3 | 218.9 | | |
| 0.07 | 58.3 | 226.8 | | |
| $H^*(D_l)^{0.5}$ | | | | |
| $2.95\times10^{-10}\exp(5940/T)$ | 52.9 | 209-229 | Zhang, Leu and Keyser, 1997 | CWFT-CIMS (a) |
| $1.37\times10^{-8}\exp(4980/T)$ | 58.3 | 208-227 | | |
| $1.31\times10^{-5}\exp(3320/T)$ | 66.4 | 201-215 | | |
| $1.75\times10^{-3}\exp(2030/T)$ | 73.8 | 204-224 | | |

## Comments

(a) Coated-wall laminar flow reactor using CIMS detection of PNA using both $SF_6^-$ and $I^-$ as source ions. PNA is either detected as $HO_2NO_2\bullet F^-$ or $HO_2NO_2^-$. The first-order rate coefficient measured at a typical PNA concentration of 5 x $10^7$ molecule $cm^{-3}$ was corrected for gas phase diffusion (10% for the smallest and a factor of four for the largest $\gamma$ values) using a gas phase diffusion constant of PNA in He of P $D_g$ = 319 mbar $cm^2$ $s^{-1}$. Liquid sulphuric acid films were approximately 0.1 mm thick. The uptake of PNA was reversible when the flow was halted. The time dependence of $\gamma$ was interpreted as solubility limited uptake and used to extract $H^*(D_l)^{0.5}$ values. Representative expressions for these are listed in the table.

## Preferred Values

| Parameter | Value | T/K |
|---|---|---|
| $\alpha_b$ | >0.2 | 205-225 |
| $H^*$(M atm$^{-1}$) | $5.5\times10^{-23}$ exp ($wt$ (0.52-1.05× $10^{-4}$($wt$-53)$^2$) exp ((20683-346.29 $wt$ + 2.044 $wt^2$)/T) | 205-225 |
| $c$ (cm$^2$ cP K$^{-1}$ s$^{-1}$) | $6.02\times10^{-8}$ | 205-225 |
| $\Delta H^0_{soln}$ | -58.6 kJ Mol$^{-1}$ | |

| | | |
|---|---|---|
| $S^0_{soln}$ | -159.0 J Mol$^{-1}$ K$^{-1}$ | |

*Reliability*

| | | |
|---|---|---|
| $\Delta\log(\alpha_b)$<br>$\Delta\log(H)$<br>$\Delta\Delta H^0_{soln}$<br>$\Delta S^0_{soln}$ | undetermined<br>± 0.15<br>± 4.5 kJ Mol$^{-1}$<br>± 15 J Mol$^{-1}$ K$^{-1}$ | 205-225 |

*Comments on Preferred Values*

The only study available presents a careful analysis of time dependent uptake of PNA into liquid sulphuric acid films. The largest initial uptake coefficient reported forms the basis for a lower limit to $\alpha_b$. To obtain the recommended values for H* from the $H^*(D_l)^{0.5}$ values reported by Zhang et al. (1997), we estimate the diffusion coefficient based on the Wilke and Chang (1955) method, as suggested by Klassen et al. (1998) for a range of other species:

$$c = \frac{7.4\times10^{-8}\sqrt{\kappa_{solvent}}}{V_A^{0.6}} \qquad (1)$$

Klassen et al. (1998) found $\kappa_{solvent} = 64$ to well represent $H_2SO_4$ solutions in this concentration range. With the partial molar volume $V_A$ of 45.183 cm$^3$mol$^{-1}$, we obtain the value for $c$ listed above that can be used to calculate the diffusion coefficient via $D_{l,HO2NO2} = c\ T/\eta$. For the viscosity, we suggest to use 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:

$$\eta = a T^{-1.43} \exp(448K/(T-T_0)), \qquad (2)$$

with $a = 169.5 + 5.18\ wt - 0.0825\ wt^2 + 3.27 \times 10^{-3}\ wt^3$,

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

The $c$ values (and thus also the diffusion coefficients) are about a factor of 2 higher than those estimated by Zhang et al. based on another approach.

The effective solubilities of PNA in $H_2SO_4$ are strongly T-dependent but only slightly dependent upon $H_2SO_4$ concentration owing to the fact that PNA is a weak acid whose degree of dissociation is vanishingly small at relevant [$H_2SO_4$].

The resulting T-dependence of H* allowed the evaluation of the dissolution parameters of PNA according to the following reaction: (1) $HO_2NO_2(g) \rightleftarrows HO_2NO_2(aq)$; (2) $HO_2NO_2(aq) \rightleftarrows O_2NO_2^- + H^+$. The values of $\Delta H^0_{soln}$ and $S^0_{soln}$ varied from -62.8 to -54.4 kJ Mol$^{-1}$ and -174 to -143.9 J Mol$^{-1}$ K$^{-1}$ in the given $H_2SO_4$ concentration range.

No reaction products were detected in agreement with the identical shape of the uptake and desorption trace of PNA.

## References

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

Wilke, C. R., and Chang, P.: Aiche Journal, 1, 264-270, 10.1002/aic.690010222, 1955.

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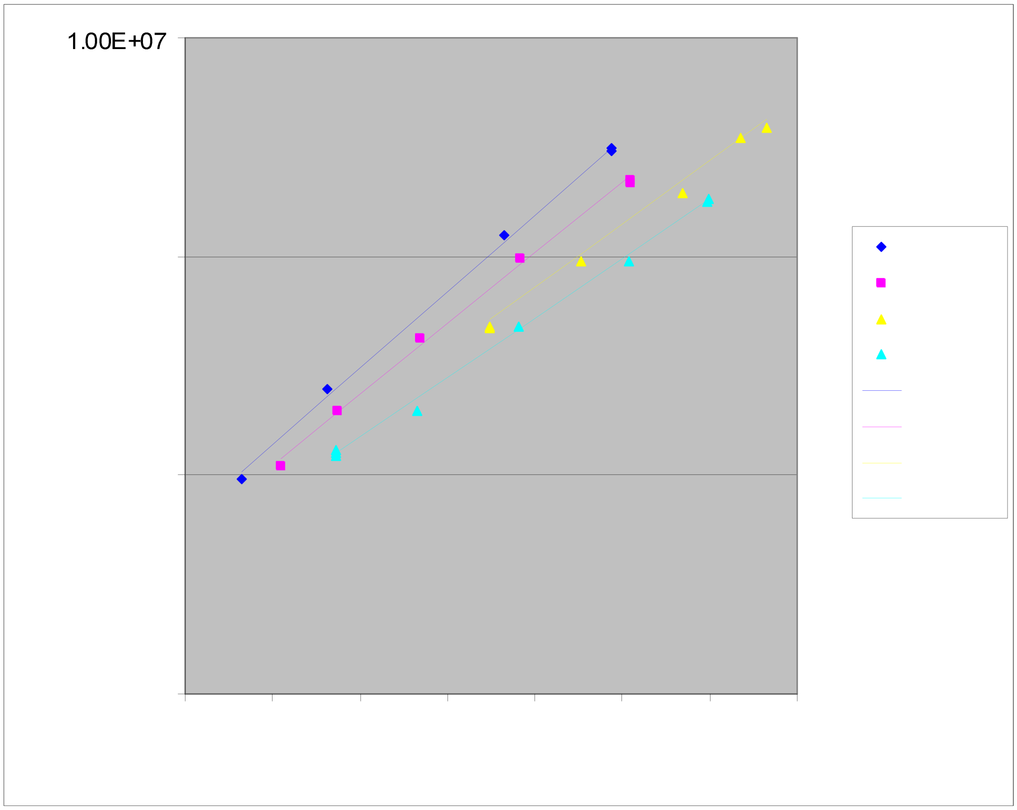


Figure 1: effective solubility of PNA in liquid sulphuric acid solution. Symbols are data by Zhang et al. (1997); the lines represent the preferred values based on the expression given in the table.