

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A3.6 HET_O_6

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This data sheet evaluated: 15th January 2009; last change in preferred values: 15th January 2009.

N₂O₅ + H₂O (ammonium bisulphate aerosols)

Experimental data

<i>Parameter</i>	RH/ %	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>				
0.020 ± 0.0036	13	293	Mozurkewitch and Calvert, 1988	AFT-CL (a)
0.0218 ± 0.0055	35			
0.050 ± 0.0055	45			
0.0482 ± 0.0055	62.5			
0.0382 ± 0.0055	77.5			
0.0015 ± 0.00042	13	295±1	Kane et al., 2001	AFT- CIMS/SMPS (b)
0.0031 ± 0.0023	32			
0.012 ± 0.0032	38			
0.018 ± 0.0027	48			
0.022 ± 0.0019	63			
0.035 ± 0.011	74			
0.046 ± 0.012	89			
0.069 ± 0.0095	99			
0.020 ± 0.0020	60	295±2	Folkers et al, 2003	FTIR/SMPS/ APC (c)
0.0190 ± 0.0040	67			
0.0187 ± 0.0043	79.7			
0.0025 - 0.0063 (+natural organic)	55 - 83			
0.0031 ± 0.0017	20	298	Hallquist et al., 2003	AFT- CL/SMPS (d)
0.0041 ± 0.0020	35			
0.018 ± 0.008	50			
0.023 ± 0.0013	70			
0.015 ± 0.006	80			
0.030 ± 0.0022	50	263		
0.0140 ± 0.0062	50	268		
0.0129 ± 0.0045	50	273		
0.036 ± 0.0018	50	283		
0.0037 ± 0.008	50	308		
0.0133 ± 0.0009	30	298	Badger, 2006	AFT- CL/SMPS (e)
0.015 ± 0.002	50			
0.0196 ± 0.0009	60			
0.024 ± 0.001	70			

0.036±0.009	50	263	Griffiths and Cox, 2009	AFT- CL/SMPS (f)
0.005±0.002	50	268		
0.014±0.006	50	278		
0.012±0.001	50	283		
0.011±0.001	50	288		
0.016±0.003	50	293		
0.003±0.001	50	303		

Comments

- (a) Atmospheric pressure aerosol flow tube with N_2O_5 ($\approx 10^{13}$ molecule cm^{-3}) measured by a modified chemiluminescence method, via thermal dissociation to NO_3 and titration with NO , which was detected. Aerosols generated in a constant output atomiser, dried, and size selected with a differential mobility analyser (DMA) coupled to a condensation particle counter (CPC), to count the particles. The monodisperse aerosol was then equilibrated at controlled humidity before entry into the flow tube. The size and surface area of the aerosol in the flow tube was calculated from the deliquescence properties of the aerosol, determined in separate tandem DMA experiments. The typical diameter, d_{mean} was 0.08-0.2 μm , with surface area density of $1 - 5 \times 10^{-5}$ cm^2/cm^3 . Uptake coefficients were determined from the first order rate constants for N_2O_5 decay, corrected for wall loss, which were linearly dependent on surface area. Diffusion limitation was negligible for the size range used.
- (b) Atmospheric pressure aerosol flow tube with detection of N_2O_5 [(5 to 200) $\times 10^{12}$ molecule cm^{-3}] by CIMS using I^- reagent ion. Aerosols generated in a constant output atomiser and were dried and equilibrated at controlled humidity before entry into the flow tube. The size distribution was measured with a scanning mobility particle sizer (SMPS) coupled to a condensation particle counter (CPC). The surface area of the aerosol in the flow tube was calculated from the observed size distribution assuming the particles are spherical. The mean diameter, d_{mean} was 0.12 μm , with surface area density of 0.0016 cm^2/cm^3 . Uptake coefficients were determined from the first order rate constants for N_2O_5 decay, corrected for wall loss, and for diffusion limitation to the particle surface using the size resolved Knudsen number for the non-monodisperse aerosol. Although the values of γ showed some scatter (only selected values from the 17 data points reported are cited), a large increase with RH throughout the range 13-99% was observed, which was fitted by the expression: $\gamma = 2.79 \times 10^{-4} + 1.3 \times 10^{-4} \times (\text{RH}) - 3.43 \times 10^{-6} \times (\text{RH})^2 + 7.52 \times 10^{-8} \times (\text{RH})^3$. No dependence on the uptake coefficient on $[\text{N}_2\text{O}_5]$ was observed.
- (c) Static aerosol chamber with inert teflon walls at ambient pressure and temperature. N_2O_5 ($\approx 10^{13}$ molecule cm^{-3}) produced in situ by reaction of NO_2 with ozone. Gas phase species measured by FTIR and UV spectroscopy. Polydisperse aerosol (dia.=20nm – 5 μm) generated by spraying dilute ammonium bisulphate solutions, with size distribution measured by SMPS for particle diameters <700nm and for larger diameters by aerodynamic particle sizer. Uptake coefficients determined by fitting experimental time dependence of species with a numerical model of chemistry and integrated aerosol surface area. To investigate effect of organic film on uptake, NH_4HSO_4 coated by organic oxidation products of ambient VOC with added ozone. A noticeable reduction in γ was observed in this case.
- (d) Atmospheric pressure aerosol flow tube with N_2O_5 (7.5 - 125 $\times 10^{13}$ molecule cm^{-3}) measured by via thermal dissociation to NO_3 and titration with NO , which was detected by O_3 -chemiluminescence. Deliquesced aerosols were generated in a constant output atomiser, and conditioned by equilibration with an additional excess flow of controlled RH. Size distribution determined with a differential mobility analyser (DMA) coupled to Faraday cup electrometer to count the particles. The typical peak diameter, d_{max} was 200 nm, with surface area density of (7-37) $\times 10^{-5}$ cm^2/cm^3 . Uptake coefficients were determined from the first order rate constants for N_2O_5 decay, after correction for wall loss and diffusion effects. The measured uptake

coefficients were independent of $[N_2O_5]$ or on RH above 50%, but γ declined with decreasing RH below 50%. This falloff was attributed to decreased liquid water amounts in the deliquesced aerosol at low RH.

- (e) Same experimental details as (d); the aerosol surface area in range $0.06 - 0.27 \text{ m}^2\text{m}^{-3}$ with an area weighted particle diameter of 260 nm.
- (f) Same experimental method as in (d), except that the halocarbon-wax-coated flow tube and the DMA were contained in a modified low temperature chamber so that aerosol S_a could be measured at the same temperature as the gas uptake region, leading to improved accuracy of uptake measurements. N_2O_5 mixing ratios were around 300 ppbv and aerosol surface area density varied in the range 0.02 to $0.5 \text{ cm}^2 \text{ cm}^{-3}$. The aerosol volume to surface ratio varied between 3 and $4 \times 10^{-9} \text{ m}$.

Preferred Values

Parameter	Value	T/K
α	0.035	298
γ (50% RH)	$94.9 - T + 3.53 \times 10^{-3}T^2 - 4.14 \times 10^{-6}T^3$	260 - 305
k' (s^{-1})	$k'' \times [H_2O]_{\text{aq}}$ (M)	
k'' ($\text{M}^{-1} \text{ s}^{-1}$)	1.0×10^5	298
<i>Reliability</i>		
$\Delta \log(\alpha)$	± 0.3	298
$\Delta \log(\gamma)$ at 50% RH	± 0.5	260 - 305

Comments on Preferred Values

All studies used deliquesced or supersaturated aqueous NH_4HSO_4 aerosols, with uptake coefficients measured as a function of RH. γ was generally seen to increase with RH over the range 20 – 90% but there is poor agreement between the different studies. The early study of Mozurkewitch and Calvert reported much larger uptake coefficients than from more recent work even after the 15% downward revision of their reported γ values suggested by Freid et al. (1995). The results of Kane et al are very scattered at $RH < 50\%$ and show a large increase in γ above 70% RH which has not been reproduced in any of the other studies, which γ show little dependence on RH above $\sim 50\%$ RH, with a value of ~ 0.02 , similar to that for uptake on ammonium sulphate. We suggest some source of systematic error in measurement of the surface area of the particles is responsible for the high uptakes reported by Mozurkewitch and Calvert and Kane et al. (at high RH). The former authors suggest that evaporation of NH_3 could lead to acidification of the particles, forming H_2SO_4 which is more reactive. Kane et al. give insufficient experimental detail of the sizing method using SMPS to evaluate the reliability of SA measurements at high RH. We therefore recommend an expression giving an approximately constant value of γ above 70% RH at 298 K.

The γ value is similar to that on pure water drops (~ 0.015 at 298 K), and only slightly lower than that on H_2SO_4 droplets ($\gamma = 0.036 \pm 0.008$, Hallquist et al, 2000). The uptake leads to hydrolysis of N_2O_5 and formation of HNO_3 which mostly transfers to the gas phase. The lack of a dependence on the water content of deliquesced droplets at $RH > 50\%$, suggests that uptake is controlled by a surface process, either mass accommodation or surface reaction. At lower RH, γ declines. Since NH_4HSO_4 aerosols do not effloresce easily this result suggests that uptake at lower RH is limited by the rate of hydrolysis of N_2O_5 in the bulk liquid phase, and hence on $[H_2O]_{\text{aq}}$. For very small particles at low RH uptake rate can become dependent on particle volume.

The recommended expression for RH dependence uses a size dependent resistance-model formulation:

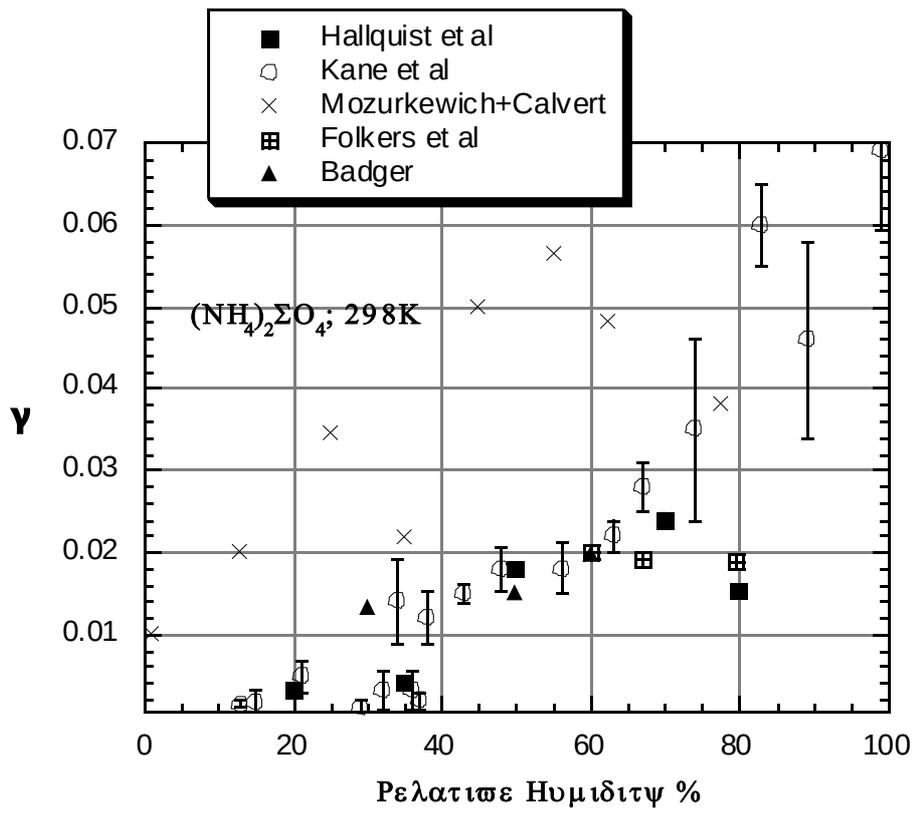
$$\gamma = \left\{ \frac{1}{\alpha_b} + \frac{c}{4HRT (D_l k^l)^{0.5}} \left[\coth\left(\frac{r}{l}\right) - \left(\frac{l}{r}\right) \right] \right\}^{-1}$$

The recommended value of $\alpha_b = 0.035$ is based on γ observed for uptake on malonic acid (Thornton *et al* (2004)) and H₂SO₄ droplets (Hallquist *et al*, 2003). k^l is calculated using the recommended liquid phase rate constant for N₂O₅ + [H₂O]_{aq} : $k^l = 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, which is intermediate between the values derived by Thornton *et al.* (2003) from hydrolysis of on malonic acid aerosol ($2.5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$) and by Mentel *et al.* (1999) from uptake on NaNO₃ aerosols ($1.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$). Figure 1 shows the RH dependence of γ using water mass fractions taken from the AIM database and using $D_l = 1 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ and 2 M atm^{-1} . The expression fits the >50% RH data well but overestimates uptake rates at low RH. The reacto-diffusive parameter ($\{D_l/k^l[\text{H}_2\text{O}]\}^{0.5}$) predicts a significant size dependence of γ for $r < 100 \text{ nm}$.

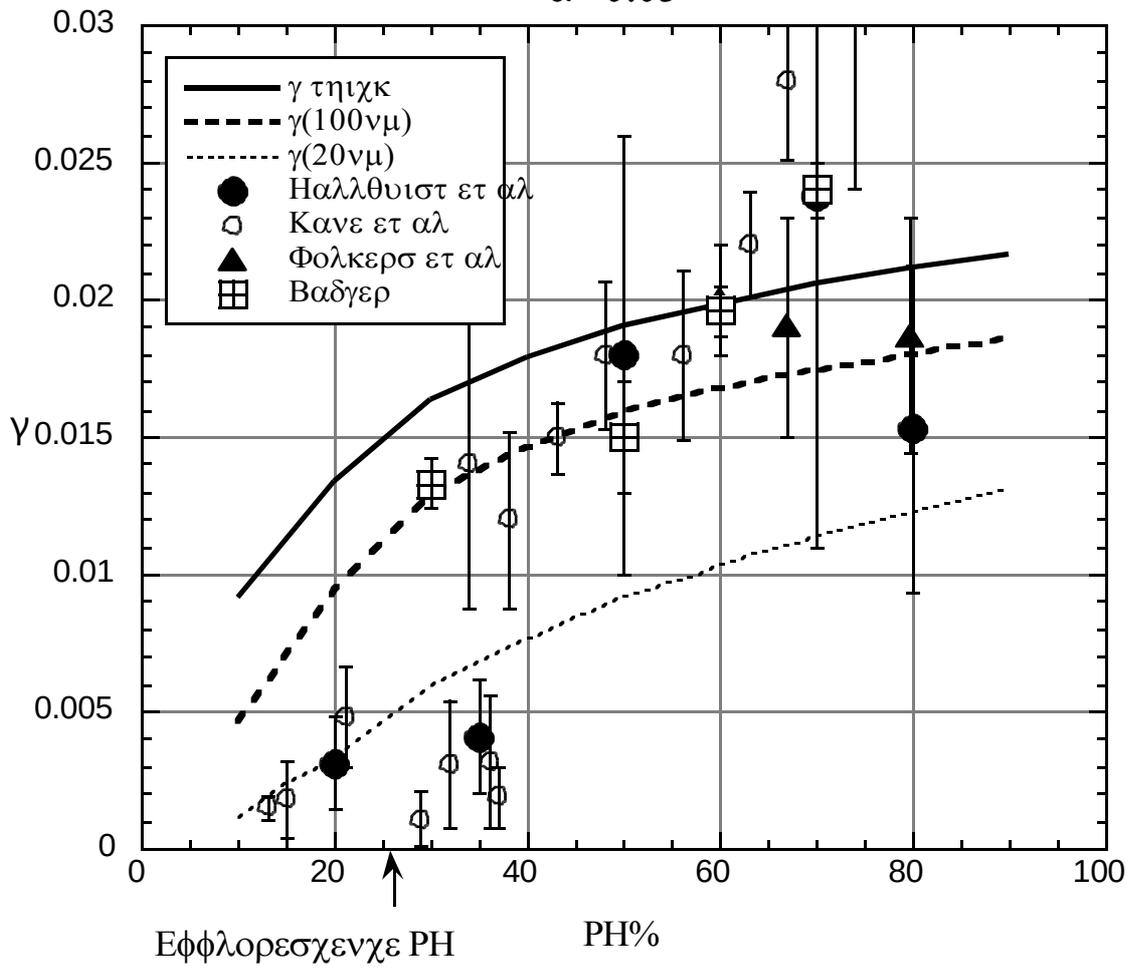
Hallquist *et al* (2003) reported a temperature dependence of N₂O₅ uptake on NH₄HSO₄ aerosols at constant RH of 50%. Their data showed considerable scatter but generally γ increased as T decreased in the range 263 -308 K, but with a region of apparently zero temperature dependence between 270 - 290 K. The recent results of Griffiths and Cox (2009), which had reduced uncertainties in determination of the actual S_a of the aerosol, confirm this complex trend. In view of this agreement, we tentatively recommend an empirical cubic fit to the data, to provide a temperature dependence of γ in the range 260 -305 K, with large error limits.

References

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Ammonium Bisulphate; $k'' = 1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$
 $\alpha = 0.03$



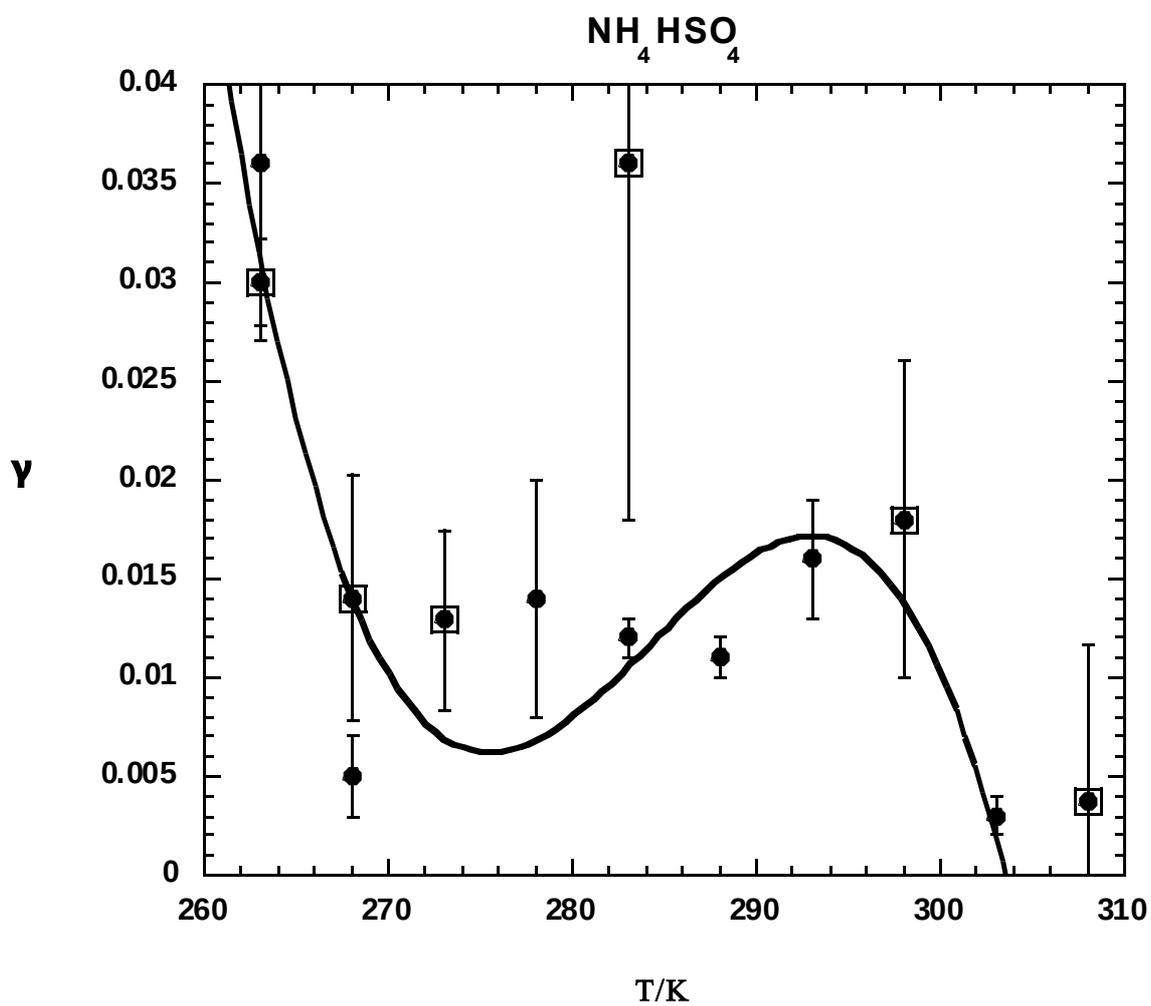


Figure 3: Uptake coefficients for heterogeneous uptake of N_2O_5 by ammonium bisulfate aerosol at 50% RH. Filled circles: Griffiths et al., 2008; open squares: Hallquist et al., 2003; Line shows cubic fit to data of Griffiths et al.