

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A3.5 HET_O_5

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

N₂O₅ + H₂O (ammonium sulphate aerosols)

Experimental data

<i>Parameter</i>	RH/ %	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>				
0.043 ± 0.005	60	293	Mozurkewitch and Calvert, 1988	AFT-CL (a)
0.017 ± 0.002	93.5	297	Hu and Abbatt, 1997	AFT-CIMS/OPC (b)
0.023 ± 0.004	83.0			
0.053 ± 0.006	68.5			
0.044 ± 0.008	50,0			
0.00094 ± 0.00059	8	295±1	Kane et al., 2001	AFT-CIMS/SMPS (c)
0.0038 ± 0.0008	37			
0.012 ± 0.0009	55			
0.020 ± 0.0023	72			
0.033 ± 0.0013	86			
0.042 ± 0.0022	92			
0.0182 ± 0.0034	62.1	295±2	Folkers et al, 2003	FTIR/SMPS/APC (d)
0.0025 - 0.0063 (+natural organic)	55 - 83			
0.0024 ± 0.0006	20	298	Hallquist et al., 2003	AFT-CL/SMPS (e)
0.0047 ± 0.0013	35			
0.0141 ± 0.0040	50			
0.0149 ± 0.0052	70			
0.0164 ± 0.0048	80			
0.025 ± 0.0013	50	288		
0.0141 ± 0.0040	50	298		
0.0040 ± 0.008	50	308		
0.0057 ± 0.0013	25		Badger et al, 2006	AFT-CL/SMPS (f)
0.0150 ± 0.0040	50			
0.0160 ± 0.0052	60			
0.0190 ± 0.0048	70			
0.00063 ± 0.00004 (6% humic acid)	25			
0.0040 ± 0.0010 (6% humic acid)	50			
0.0083 ± 0.0006 (6% humic acid)	70			

0.035±0.002	50	263	Griffiths and Cox, 2009	AFT-CL/SMPS (g)
0.028±0.002	50	275		
0.020±0.005	50	283		
0.010±0.002	50	293		
0.005±0.002	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 (7×10^{12} molecule cm^{-3}) by CIMS using I^- reagent ion. The aerosols were generated in an ultrasonic nebuliser and were equilibrated with the ambient humidity before entry into the flow tube. The size distribution, measured with an optical particle counter (OPC), was used to calculate the surface area of the aerosol in the flow tube. The peak in the surface area distribution, d_{max} was between 2 and 4 μm . The counter was calibrated by collection of aerosol of known composition in a aqueous trap (assumed 100% efficient) and measurement of the electrical conductivity of the trapped electrolyte. Uptake coefficients were determined from the first order rate constants for N_2O_5 decay, corrected for wall loss (Brown correction), and for diffusion limitation to the particle surface assuming an average diameter, d_{max} , of the non-monodisperse aerosol. Cited errors on γ is $\pm 1\sigma$ precision; the estimated potential systematic error arising mainly from measurement of the SA was $\pm 25\%$.
- (c) 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 8-92% 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.
- (d) 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 sulphate solutions, with size distribution measured by SMPS and aerodynamic particle size for particle diameters < 700nm. Uptake coefficients determined by fitting experimental time dependence of species with a numerical model of chemistry and

integrated aerosol surface area. $(\text{NH}_4)_2\text{SO}_4$ coated by organic oxidation products of ambient VOC with added ozone.

- (e) 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 $(7 \text{ to } 37) \times 10^{-5}$ 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 $[\text{N}_2\text{O}_5]$ or on RH above 50%, but γ declined with decreasing RH below 50%. This falloff was attributed to decreased liquid water amounts in the aerosol at low RH, supported by even lower γ values for ‘dry’ aerosols below the efflorescence RH.
- (f) Same experimental details as (e); study focussed on effect of mixed AS-humic acid aerosols on γ . the aerosol surface area in range $0.12 - 0.50$ m^2m^{-3} with an area weighted particle diameter of ~ 300 nm.
- (g) Same experimental method as in (e), 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 4×10^{-9} m.

Preferred Values

Parameter	Value	T/K
α	0.03	298
γ	$0.244 - 7.9 \times 10^{-4} \cdot T(\text{K})$	260 -305
k^I (s^{-1})	$k^{II} \times [\text{H}_2\text{O}]_{\text{aq}} (\text{M})$	
k^{II} ($\text{M}^{-1} \text{s}^{-1}$)	1.0×10^5	298
<i>Reliability</i>		
$\Delta \log(\alpha)$	± 0.3	298
$\Delta \log(\gamma)$	± 0.3 at 50% RH	260 -305

Comments on Preferred Values

Uptake studies conducted on aqueous $(\text{NH}_4)_2\text{SO}_4$ aerosols as a function of relative humidity show broad agreement in uptake coefficient values, but there are differences in detail. Only data for deliquesced aerosols are presented; at RH below the efflorescence RH for $(\text{NH}_4)_2\text{SO}_4$ aerosol ($\sim 37\%$) the particles may crystallise and under these conditions the uptake coefficient reduces dramatically to $\gamma < 0.001$ due to reduced liquid volume. In most studies γ shows little dependence on humidity above $\sim 50\%$ RH with $\gamma = 0.015 - 0.02$ at 298 K, but below 50% RH γ declines significantly as RH reduces. Exceptions are the study of Hu and Abbatt (1997) in which γ increased as RH reduces below 95% and Kane et al. (2001) in which γ continued to increase monotonically above 50% RH. These opposite trends have not been reproduced in any of the other studies and suggest some source of systematic error. Hu and Abbatt used larger particles and a size calibration a trapping method was used, which could have underestimated the aerosol surface area of smaller particles at lower RH. 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 50% RH at 298 K.

The γ value above 50% RH is close to that on pure water drops (~ 0.015 at 298K), 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 partially transfers to the gas phase. The lack of a dependence on the water content of deliquesced droplets at relative humidity $>50\%$, suggests that uptake is controlled by a surface process, either mass accommodation or surface reaction. At lower RH, γ declines, but the data show large scatter, which may be due to the presence of a mixed size population of solid and liquid particles, as a result of efflorescence. These data suggest that uptake at lower RH is limited by the rate of hydrolysis of N_2O_5 in bulk liquid phase, hence depends on $[\text{H}_2\text{O}]_{\text{aq}}$ and, for small particles, on particle volume.

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

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

The recommended value of $\alpha = 0.03$ is based on γ observed for uptake on water, malonic acid (Thornton *et al* (2004)) and H_2SO_4 droplets. The recommended liquid phase rate constant k^{I} ($= k^{\text{II}} \times [\text{H}_2\text{O}]_{\text{aq}}$), calculated using $k^{\text{II}} = 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, which is intermediate between the values derived by Thornton *et al.*(2003) from uptake of N_2O_5 on malonic acid aerosol ($2.5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$) and by Mentel et al (1999) from uptake on NaNO_3 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} , values used in the analyses for k^{II} . The expression fits the $>50\%$ rh data well but overestimates uptake rates at low RH. The reacto-diffusive parameter ($l = \{D_l/k^{\text{II}}[\text{H}_2\text{O}]\}^{0.5}$) predicts a significant size dependence of γ for $r < 100 \text{ nm}$.

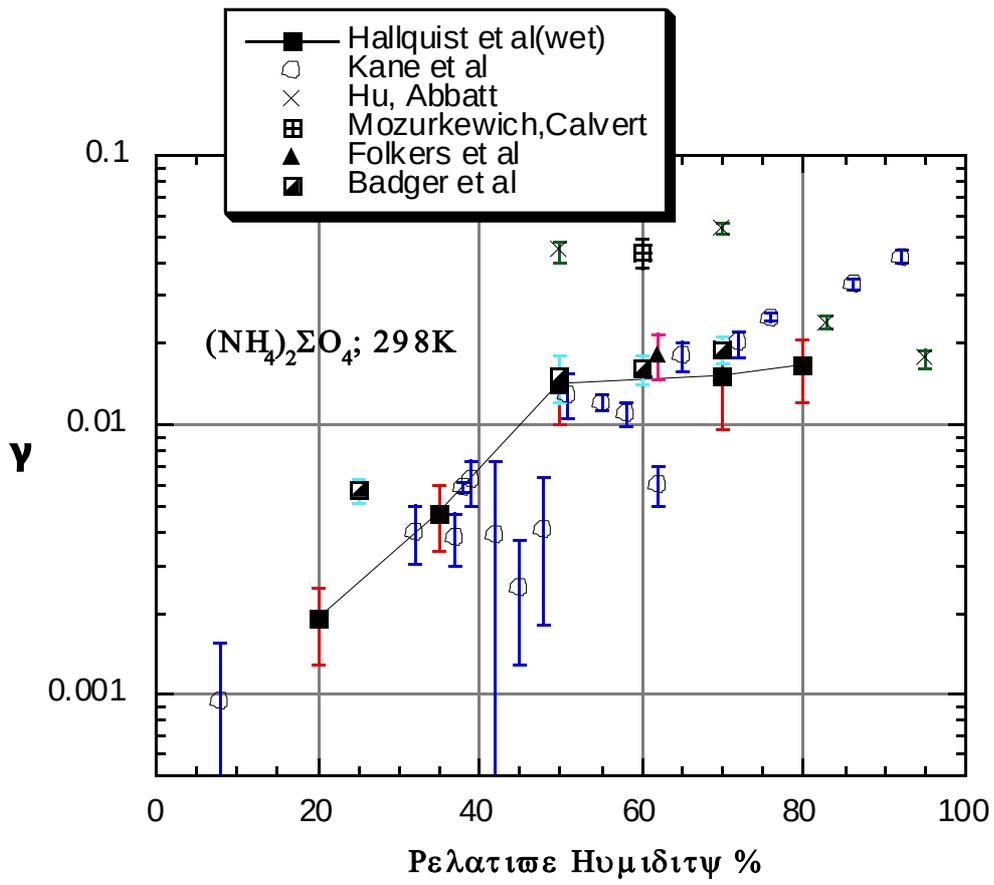
The temperature dependence of N_2O_5 uptake reported earlier by Hallquist et al (2003) has recently been confirmed by Griffiths and Cox (2009), using improved determination of aerosol size and S_a . There is a substantial negative temperature dependence of γ at constant RH of 50%. This is consistent with accommodation controlled uptake but the effect is much larger than the T dependence of α deduced from the results obtained for H_2SO_4 droplets at 50% RH. The recommended expression is an empirical linear fit to the data over the stated temperature range and should be used with caution outside this range.

References

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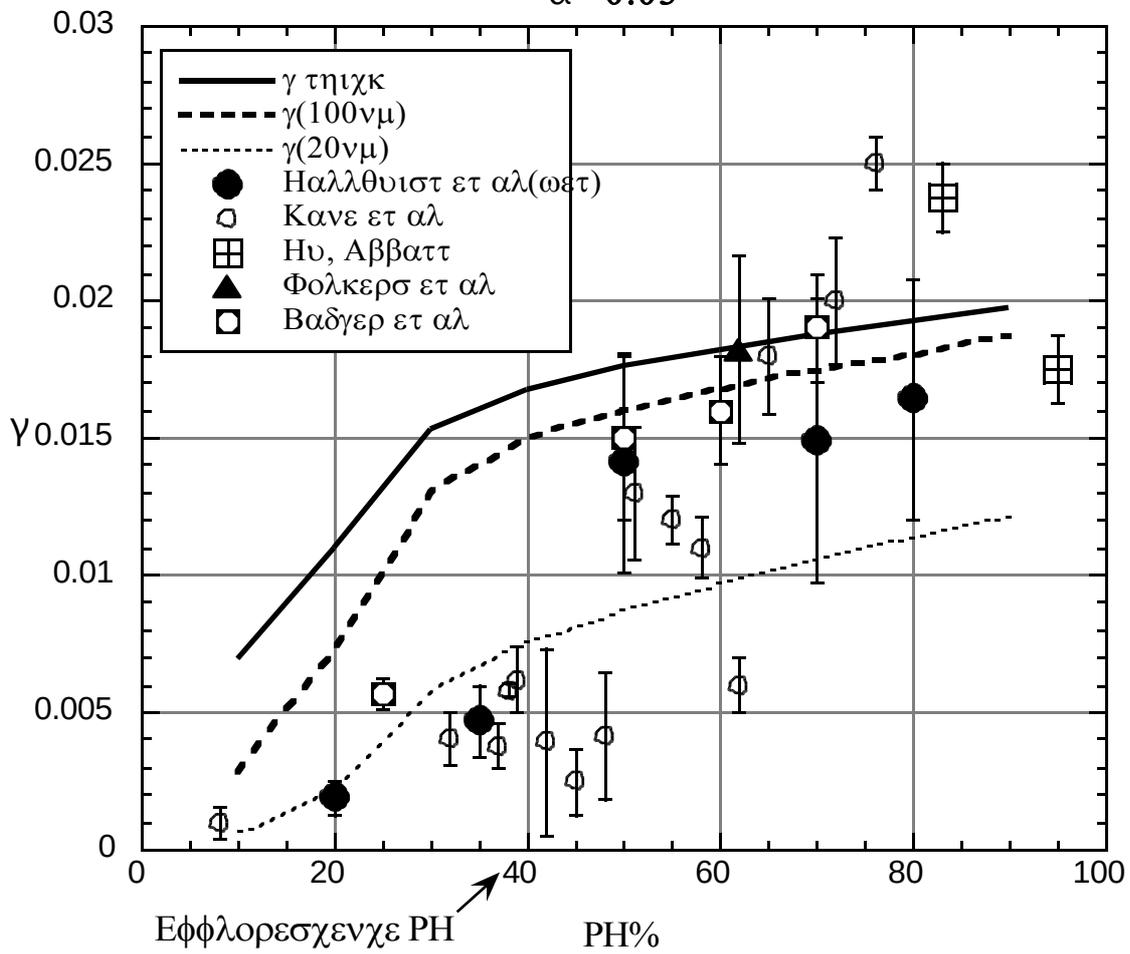
Mozurkewich, M. and Calvert, J.G.: J. Geophys. Res. 93, 15889 (1988).

Thornton, J.A., Braban, C.F. and Abbatt, J.P.D.: Phys. Chem. Chem. Phys 5, 4593-4603 (2003).



Ammonium Sulphate; $k'' = 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$

$\alpha = 0.03$



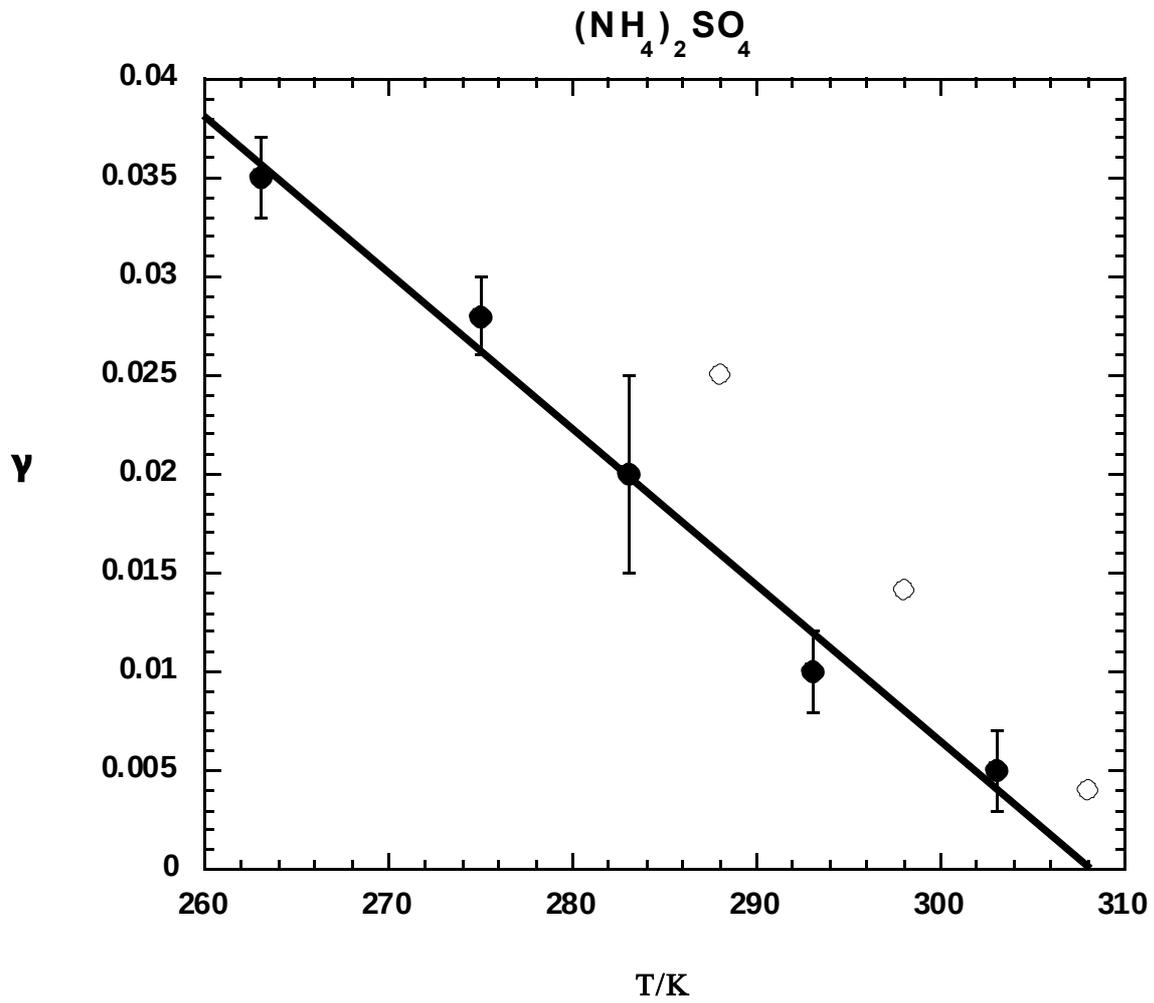


Figure 2: Uptake coefficients for heterogeneous uptake of N_2O_5 by ammonium sulfate aerosol. Filled circles: Griffiths et al., 2008.; Open circles: Hallquist et al., 2003. Line shows linear fit to data of Griffiths and Cox, 2009..