

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A3.7 HET_O_7

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

N₂O₅ + H₂O (Na/NH₄ nitrate aerosols)

Experimental data

Parameter	RH/ %	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>				
0.0018 ± 0.0020	48	295±2	Wahner et al, 1999	FTIR/SMPS/APC (c)
0.0032 ± 0.0006	62			
0.023 ± 0.012	88			
0.0040 (NH ₄ NO ₃)	54			
0.0065 (NH ₄ NO ₃)	60			
0.0090 (NH ₄ NO ₃)	70			
0.016 (NH ₄ NO ₃)	79			
0.00048 ± 0.00011	20	298	Hallquist et al., 2003	AFT-CL/SMPS (d)
0.00049 ± 0.00023	30			
0.00065 ± 0.00025	50			
0.0010 ± 0.00022	70			
0.00063 ± 0.00064	50	263		
0.00151 ± 0.00096	50	278		
0.00031 ± 0.00096	50	288		

Comments

- (a) Static aerosol chamber with inert teflon walls at ambient pressure and temperature. N₂O₅ ($\approx 10^{13}$ molecule cm⁻³) produced in situ by reaction of NO₂ with ozone. Gas phase species measured by FTIR and UV spectroscopy. Polydisperse aerosol (dia.= 20nm – 5 μ m) generated by spraying dilute ammonium bisulphate solutions, with size distribution measured by SMPS for particle diameters <700nm and aerodynamic particle sizer for larger diameters by. The mean volume/surface ratio of the aerosol ($= r_{av}/3$) was typically 1.1×10^{-5} cm³/cm². Uptake coefficients determined by fitting experimental time dependence of species with a numerical model of chemistry and integrated aerosol surface area.. At high RH γ for uptake on NaNO₃ aerosols was similar to that observed for sulphates and NaCl, but as RH declined γ declined to values a factor of 10 lower at ~50% RH. A similar trend was observed for uptake on deliquesced NH₄NO₃ aerosols.
- (b) Atmospheric pressure aerosol flow tube with N₂O₅ ($7.5 - 125 \times 10^{13}$ molecule cm⁻³) measured by via thermal dissociation to NO₃ and titration with NO, which was detected by O₃-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 $(1.9 - 7.01) \times 10^{-3} \text{ cm}^2/\text{cm}^3$. 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 approximately a factor of 10 – 20 lower than on sulphate aerosols at comparable RH and showed a weak increase with RH over the range 20 – 80%. No significant temperature dependence of γ was observed over the range 263 – 298 K.

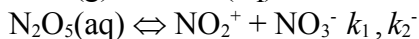
Preferred Values

Parameter	Value	T/K
α_b	0.03	298
$k^I (\text{s}^{-1})$ $k^{II} (\text{M}^{-1} \text{s}^{-1})$	$k^{II} \times [\text{H}_2\text{O}]_{\text{aq}} (\text{M})$ $1 \times 10^5 \left\{ 1 - \frac{k_2[\text{NO}_3^-]}{k_2[\text{NO}_3^-] + k_3[\text{H}_2\text{O}]} \right\}$	298
k_2/k_3	0.020	298
<i>Reliability</i>		
$\Delta \log (\alpha_b)$	± 0.3	298
$\Delta \log (\gamma)$	± 0.3 at 50% RH	

$[\text{NO}_3^-]$ and $[\text{H}_2\text{O}]$ are molar concentrations of nitrate ion and water in aqueous aerosol

Comments on Preferred Values

Both studies show that the uptake of N_2O_5 on aerosols containing nitrate is much reduced except at RH near 100%. The so called ‘nitrate effect’ was first described by Wahner et al (1996) and was accounted for by a liquid phase hydrolysis mechanism involving reversible dissociation of solvated N_2O_5 , according to the reaction mechanism:



Thus the hydrolysis rate in solution was inhibited by the presence of nitrate ions which reduced uptake rate, making it chemically controlled as opposed to accommodation controlled. The γ values observed by Hallquist et al. were substantially smaller than observed by Mentel et al, who used aerosols with particles of larger mean size. This difference can be qualitatively accounted for by the effect of increased reacto-diffusive length as a result of the slower liquid phase hydrolysis, leading to volume-controlled uptake in small particles.

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

$$\gamma = \left\{ \frac{1}{\alpha_b} + \frac{c}{4HRT (D_1 k^I)^{0.5}} \left[\coth\left(\frac{r}{l}\right) - \left(\frac{l}{r}\right) \right] \right\}^{-1}$$

The recommended value of $\alpha_b = 0.03$ is based on γ observed for uptake on malonic acid (Thornton *et al* (2004)) and H_2SO_4 droplets. and $k^I (= k^{II} \times [\text{H}_2\text{O}]_{\text{aq}})$ calculated using an expression for k^{II} modified for the presence of NO_3^- based on a hydrolysis mechanism steady-state treatment of the NO_2^+ reactive intermediate:

$$k^{II} = k_0^{II} \left\{ 1 - \frac{k_2[\text{NO}_3^-]}{k_2[\text{NO}_3^-] + k_3[\text{H}_2\text{O}]} \right\}$$

k_0^{II} , the value in the absence of NO_3^- , was set at $1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, which is intermediate between the values derived by Thornton *et al.* from hydrolysis of on malonic acid aerosol ($2.5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$)

s^{-1}) and by Mentel et al from uptake on NaNO_3 aerosols ($1.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$), and $k_2/k_3 = 0.020$ (adjusted to fit). Figure 1 shows the RH dependence of γ using water and nitrate concentrations taken from the AIM database, and with $H(D_i)^{0.5} (\text{M}\cdot\text{atm}^{-1}\text{cm s}^{-0.5}) = 2.0 \times 10^{-5}$.

The reacto-diffusive parameter ($D_i/k^{0.5}$) predicts a significant size dependence of γ for $r < 100$ nm. The expression for 100nm particles fits the Mentel data quite well but overestimates uptake rates observed by Hallquist et al.(2003) at higher RH.

Hallquist et al (2003) offer the only reported temperature dependence of N_2O_5 uptake. They observed no significant temperature dependence of γ at constant RH of 50%. This is consistent with aqueous chemistry control of uptake rate.

References

- Hallquist, M., Stewart, D.J., Stephenson, S.K. and Cox, R.A.: Phys. Chem. Chem. Phys. 5, 3453 (2003).
- Mentel, T.F, Sohn,M. and Wahner, A.: Phys. Chem. Chem. Phys. 1, 5451 (1999).
- Thornton, J.A., Braban, C.F. and Abbatt, J.P.D.: Phys. Chem. Chem. Phys 5, 4593-4603 (2003).
- Wahner, A., Mentel, T.F, Sohn,M. and Steir, J., J Geophys. Res., 103 (D23) 31103 (1998).

NaNO3_gamma_1e5_0.02

