

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A3.8 HET_O_8

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

N₂O₅ + H₂O (aqueous organic aerosols)

Experimental data

Parameter	RH/ %	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>				
<i>Malonic Acid</i>				
0.0020 ± 0.0005	10	298	Thornton et al., 2003	AFT-CIMS
0.009 ± 0.001	20			(a)
0.0165 ± 0.002	30			
0.022 ± 0.0035	40			
0.025 ± 0.003	50			
0.031 ± 0.004	70			
<i>Humic acid</i>				
0.0001 ± 0.0001	25	298	Badger, 2006	AFT-
0.0003 ± 0.0001	50			CL/SMPS (e)
0.0010 ± 0.0004	75			
<i>Oxalic Acid (solid)</i>				
0.0031 ± 0.001	74	295±2	Griffiths et al., 2008	FTIR/SMPS/ AFT/CL (c)
<i>Malonic Acid</i>				
0.008 ± 0.003	30			
0.012 ± 0.002	50			
0.0169 ± 0.0042	64			
0.016 ± 0.003	65			
<i>Succinic Acid</i>				
< 0.0006	30			
< 0.0003	50			
0.0052 ± 0.0003	55			
0.0051 ± 0.0008	64			
0.006 ± 0.001	65			
0.009 ± 0.003	70			
<i>Glutaric acid</i>				
0.0006 ± 0.0003	30			
0.0040 ± 0.0009	50			
0.0081 ± 0.0004	65			
0.0113 ± 0.0029	67			
0.008 ± 0.002	75			

Comments

- (a) Measurements of the reactive uptake coefficient for N₂O₅ hydrolysis, γ , on sub-micron organic aerosols in an aerosol flow tube at 1 bar and at room temperature, as a function of relative humidity (RH), aerosol phase, N₂O₅ partial pressure, and mean aerosol size. Aerosol phase and

relative humidity were determined simultaneously, and chemical ionization mass spectrometry was used to detect the decay rate of N_2O_5 in the presence of malonic acid or azelaic acid aerosol. The γ on solid malonic acid was determined to be less than 0.001 (RH=10–50%), and on solid azelaic acid, γ was 0.0005 ± 0.0003 . The values cited are for aqueous malonic acid aerosol. Evidence presented for an inverse dependence of γ on the initial concentration of N_2O_5 between $(1.5 - 7) \times 10^{11}$ molecule cm^{-3} , and a dependence on particle size for aerosol with surface area-weighted radii less than 100 nm at 50% RH. Super-saturated malonic acid aerosol results are consistent with N_2O_5 hydrolysis being both aerosol volume-limited where, for $RH < 50\%$, water is the limiting reagent, and also with a surface-specific process. The rate coefficient for reaction of N_2O_5 with H_2O in solution retrieved for from the volume-limited regime was $2.4 \times 10^4 M^{-1}s^{-1}$.

- (b) Atmospheric pressure aerosol flow tube with N_2O_5 ($\sim 5 \times 10^{12}$ molecule cm^{-3}) measured via thermal dissociation to NO_3 and titration with NO , which was detected by O_3 -chemiluminescence. Aqueous humic acid aerosols were generated from filtered solutions of its Na salt 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). The typical peak diameter, d_{max} was 170 nm, with surface area density of 1.2 to 5.0×10^{-2} 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 γ on humic acid aerosol increased linearly with RH in the range 25 – 75% RH and was typically a factor of 50 lower than on sulphate. Uptake on aerosols of a range of internally mixed composition of humic acid and $(NH_4)_2SO_4$ were also measured. Even 6 wt % of humic acid caused a factor of >2 reduction in uptake coefficient on $(NH_4)_2SO_4$ at 70% RH. This falloff was attributed to a decrease in bulk accommodation coefficient of N_2O_5 at the surface due to surfactant properties of humic acid.
- (c) Uptake measurements on aqueous dicarboxylic acids (malonic, succinic, glutaric, oxalic) made using two different systems at 1 bar pressure: an aerosol flow tube system as described in comment (b); and a large static aerosol chamber, with N_2O_5 ($\approx 10^{13}$ molecule cm^{-3}) produced in situ by reaction of NO_2 with ozone, and gas phase species measured by FTIR and UV spectroscopy. Poly-dispersed aerosol (diam.range = 20 nm – 5 μm) generated by spraying dilute solutions of carboxylic acids, with size distribution measured by SMPS for particle diameters < 700 nm 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. The results for uptake on dicarboxylic acid aerosols at different humidities and phase were in good agreement using the two methods. The γ values all increased linearly with RH up to 70% and for succinic and glutaric acid were distinctly lower than for malonic acid. For the latter, γ values were lower than observed by Thornton et al, 2003, and were not observed to level off above 50% RH. This was attributed to a nitrate effect caused by accumulation of HNO_3 product in the aqueous particles. Rate constants for liquid phase reaction of $N_2O_5 + H_2O$ were obtained in this study for malonic acid: $1.8 \times 10^4 M^{-1}s^{-1}$; for succinic acid: $0.79 \times 10^4 M^{-1}s^{-1}$; for glutaric acid: $1.2 \times 10^4 M^{-1}s^{-1}$ from analysis of the volume limited uptake data.

Preferred Values

Parameter	Value	T/K
α (dicarboxylic acids)	0.035	298
α (humic acid)	$3.1 \times 10^{-5} \exp(0.046 \times RH(\%))$	298
k^l (s^{-1})	$k^{ll} \times [H_2O]_{aq}$ (M)	
k^{ll} ($M^{-1} s^{-1}$) malonic acid	1.0×10^5	298
k^{ll} ($M^{-1} s^{-1}$) succinic acid	3.0×10^4	298
k^{ll} ($M^{-1} s^{-1}$) glutaric acid	5.0×10^4	298

Comments on Preferred Values

All studies used deliquesced or supersaturated aqueous aerosols, with uptake coefficients measured as a function of RH. γ was generally seen to increase with RH over the range 20 – 90%, although for malonic acid the γ value at RH > 50% Thornton *et al* (2004) is constant and close to that on H₂SO₄ droplets ($\gamma = 0.036 \pm 0.008$). The lack of a dependence on the water content of deliquesced droplets at RH > 50%, suggests that uptake is controlled by surface accommodation. At lower RH for malonic and for the C4 and C5 acids, γ declines, which suggests that uptake is limited by the rate of hydrolysis of N₂O₅ in the bulk liquid phase, and hence on [H₂O]_{aq}. For very small particles at low RH uptake rate can become dependent on particle volume. The uptake rates observed by Griffiths *et al* (2009) are lower than observed by Thornton *et al*, 2003. This was attributed to a nitrate effect caused by accumulation of HNO₃ product in the aqueous particles, also indicated in the decline of γ with [N₂O₅] observed by Thornton *et al.*(2003) A numerical model was developed by Griffiths *et al.* involving explicit treatment of the coupled processes involved in uptake, including the nitrate effect. The rate coefficient for reaction of N₂O₅ with H₂O in solution obtained using this model to analyse malonic acid data for 70% RH ([H₂O] = 23M) was $k^{II} = 2.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ This is larger than that deduced by Thornton *et al*, 2003, $k^{II} = 2.5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, leading to the conclusion that rate constants derived assuming volume limited uptake are too low. Thus the rate constants derived in their study from analysis of the linear region; for succinic acid: $0.79 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; for malonic acid : $1.8 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$; and for glutaric acid: $1.2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ are also likely to be underestimated

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

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

The recommended value of $\alpha_b = 0.035$ is based on γ observed for uptake on malonic acid. k^I is calculated using the recommended liquid phase rate constant for N₂O₅ + [H₂O]_{aq} : $k^{II} = 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$, which is intermediate between the values derived by Thornton *et al.* (2003) from hydrolysis of N₂O₅ 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 for malonic acid, calculated using [H₂O]_{aq} from water mass fractions taken from the AIM database, and using $H(D_l)^{0.5} (\text{M.atm}^{-1}\text{cm s}^{-0.5}) = 6.3 \times 10^{-3}$. The expression fits the average values reported for malonic acid in the range 30 – 60% RH reasonably well, but the RH dependence is weaker than observed over the range. The reacto-diffusive parameter ($\{D_l/k^{II}[\text{H}_2\text{O}]\}^{0.5}$) predicts a significant size dependence of γ for $r < 100 \text{ nm}$.

The lower uptake rates observed on succinic and glutaric acid particles cannot be entirely rationalised by reduced water mass fractions or acidity/nitrate effects (C.Badger, PhD thesis, U.of Cambridge, 2006), suggesting that the effective liquid phase rate constants (k^{II}) is lower for these acids by ~70% and 50% compared to the recommended value for malonic acid.

The recommended uptake coefficient for N_2O_5 on humic acid as a function of RH is based on the results of Badger et al, 2006.

References

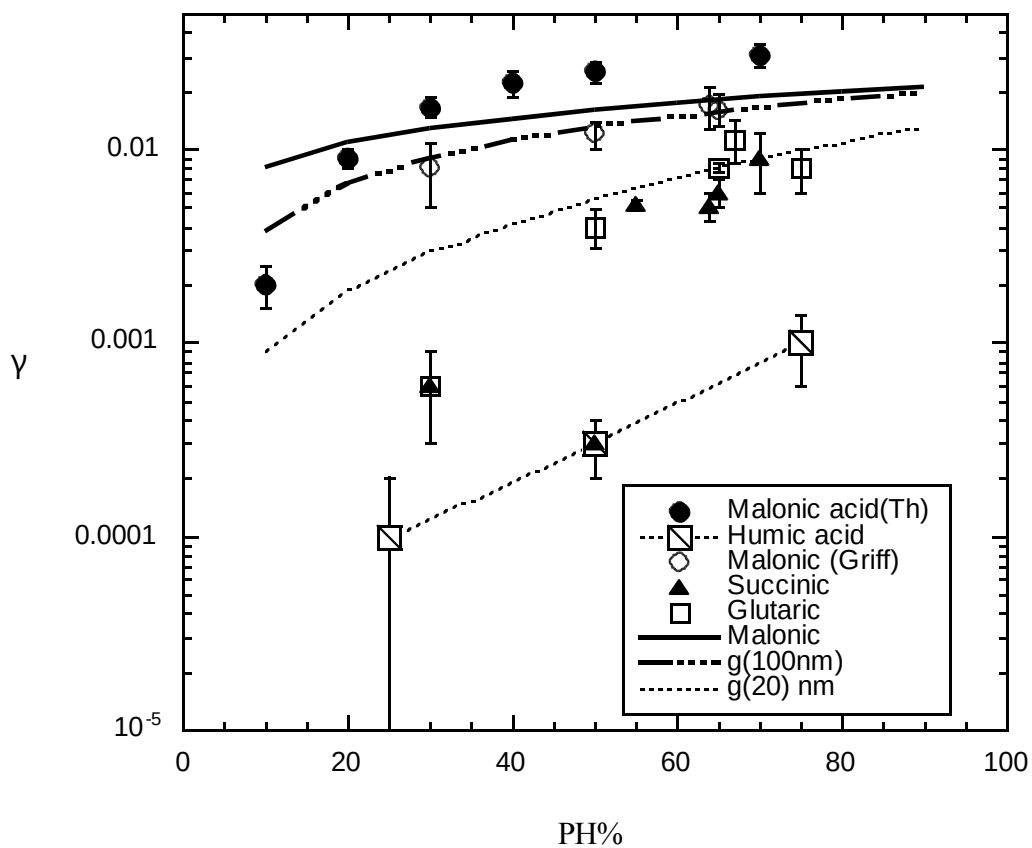
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N2O5 + organic acids



N2O5 + Humic acid(aqueous Na salt)

