

## 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: 15<sup>th</sup> January 2009; last change in preferred values: 15<sup>th</sup> January 2009.

### N<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O (aqueous organic aerosols)

#### Experimental data

| Parameter  | RH/ % | Temp./K | Reference              | Technique/ Comments      |
|--|-------|---------|------------------------|--------------------------|
| <i>Uptake coefficients: <math>\gamma, \gamma_{ss}, \gamma_0</math></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/<br>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 N<sub>2</sub>O<sub>5</sub> hydrolysis,  $\gamma$ , 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, N<sub>2</sub>O<sub>5</sub> 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  $\gamma$  on solid malonic acid was determined to be less than 0.001 (RH=10–50%), and on solid azelaic acid,  $\gamma$  was  $0.0005 \pm 0.0003$ . The values cited are for aqueous malonic acid aerosol. Evidence presented for an inverse dependence of  $\gamma$  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  $5.0 \times 10^{-2}$   $cm^2/cm^3$ . 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  $\gamma$  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  $\mu m$ ) 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  $\gamma$  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,  $\gamma$  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 |
|--|--|-----|
| $\alpha$ (dicarboxylic acids)              | 0.035  | 298 |
| $\alpha$ (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  | $1.0 \times 10^5$                              | 298 |
| $k^{ll}$ ( $M^{-1} s^{-1}$ ) succinic acid | $3.0 \times 10^4$                              | 298 |
| $k^{ll}$ ( $M^{-1} s^{-1}$ ) glutaric acid | $5.0 \times 10^4$                              | 298 |

*Comments on Preferred Values*

All studies used deliquesced or supersaturated aqueous aerosols, with uptake coefficients measured as a function of RH.  $\gamma$  was generally seen to increase with RH over the range 20 – 90%, although for malonic acid the  $\gamma$  value at RH > 50% Thornton *et al* (2004) is constant and close to that on H<sub>2</sub>SO<sub>4</sub> 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,  $\gamma$  declines, which suggests that uptake is limited by the rate of hydrolysis of N<sub>2</sub>O<sub>5</sub> in the bulk liquid phase, and hence on [H<sub>2</sub>O]<sub>aq</sub>. 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 HNO<sub>3</sub> product in the aqueous particles, also indicated in the decline of  $\gamma$  with [N<sub>2</sub>O<sub>5</sub>] 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 N<sub>2</sub>O<sub>5</sub> with H<sub>2</sub>O in solution obtained using this model to analyse malonic acid data for 70% RH ([H<sub>2</sub>O] = 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  $\gamma$  observed for uptake on malonic acid.  $k^I$  is calculated using the recommended liquid phase rate constant for N<sub>2</sub>O<sub>5</sub> + [H<sub>2</sub>O]<sub>aq</sub> :  $k^{II} = 1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ , which is intermediate between the values derived by Thornton *et al.* (2003) from hydrolysis of N<sub>2</sub>O<sub>5</sub> 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<sub>3</sub> aerosols ( $1.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ ). Figure 1 shows the RH dependence of  $\gamma$  for malonic acid, calculated using [H<sub>2</sub>O]<sub>aq</sub> 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  $\gamma$  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<sub>2</sub>O<sub>5</sub> on humic acid as a function of RH is based on the results of Badger et al, 2006.

### References

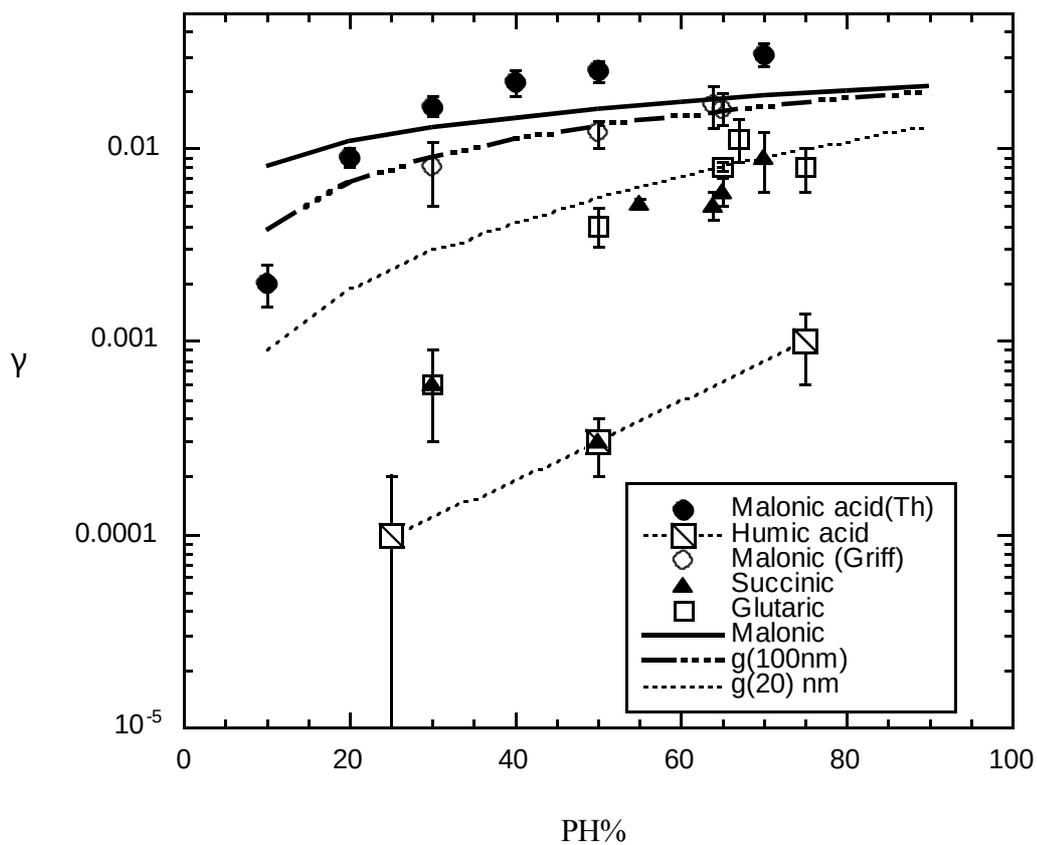
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### N2O5 + organic acids



### N2O5 + Humic acid(aqueous Na salt)

