### UPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HET\_Org\_ID

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HO2 + secondary organic aerosol  products

Experimental data

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | precursor VOC | [VOC] \ppb | O3 \ppb | NOX \ppb | oxidation conditions | aerosol surface /cm2 cm-3 | RH / % | Temp. /K | Reference | Technique/ Comments |
|  |  |  |  |  |  |  |  |  |  |  |
| *Uptake coefficients*: *γ* |  |  |  |  |  |  |  |  |  |  |
| < 0.004 | α-pinene | 600 | 280 |  | ozonolysis smog ch. | 1.3×10-4 | 50 | 293±2 | Lakey et al., 2016 | AFT-LIF (a) |
| < 0.006 | α-pinene | 200 | 310 |  | ozonolysis smog ch. | 7.1×10-5 | 80 |  |  |  |
| < 0.018 | α-pinene | 500 |  | 350 | photochem. smog ch. | 6.3×10-5 | 50 |  |  |  |
| < 0.001 | α-pinene | 500 |  |  | photochem. PAM ch. | 2.9×10-4 | 50 |  |  |  |
| 0.004± 0.002 | TMB | 2000 |  |  | photoch. PAM ch. | 2.9×10-4 | 50 |  |  |  |
| 0.004± 0.003 | TMB | 2000 |  |  | photochem. PAM ch. | 2.3×10-4 | 50 |  |  |  |
| < 0.005 | α-pinene | 500 |  |  | photochem. PAM ch. | 1.9×10-4 | 50 |  |  |  |
| < 0.001 | α-pinene | 1000 |  |  | photoch. PAM ch. | 3.9×10-4 | 80 |  |  |  |

Comments

(a) Uptake of HO2 (~ 109 molecule cm-3) to secondary organic aerosol generated from α-pinene or trimethylbenzene (TMB) either in a 27 m3 smog chamber (dark or irradiated by Xe-arc (> 280 nm) and black lamps (320 – 400 nm) ) or in a potential aerosol mass (PAM) chamber (0.46 m long and 0.22 m inner diameter, irradiated by low pressure Hg lamps). The secondary organic aerosol was passed through charcoal and cobalt oxide denuders for removal of oxidants, VOC and NOx. HO2 was generated by the photolysis of H2O in N2 or air and detected as OH (by LIF) following conversion in reaction with NO.

Preferred Values

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
| *γ* | < 0.001 | 290 – 300 |

Comments on Preferred Values

Uptake coefficients of HO2 to secondary organic aerosol particles derived from α-pinene under dark ozonolysis and photochemical oxidation conditions were below the detection limit for all experiments reported in the single study by Lakey et al. (2016). we prefer the lowest value (obtained using the highest surface area) as an upper limit for HO2 uptake to secondary organic aerosol. Lakey et al. (2016) suggest that RO2 radicals surviving in the particle phase may explain the uptake observed for SOA derived from oxidation of TMB in the PAM chamber.

Assuming that SOA resembles an aqueous phase chemical system, the rate of loss of aqueous-phase HO2 is quadratically dependent on [HO2]p and [O2-]p:

HO2 (g)  O2- (p) + H+ (p) R1

HO2 (p) + HO2 (p)  H2O2 (p) + O2 (p) R2

O2- (p) + HO2 (p) (+H2O(*p*))  H2O2 (p) + O2 (p) + OH- (p) R3

The uptake coefficient is thus strongly dependent on the gas-phase concentration of HO2 and becomes small at low, atmospherically relevant HO2 concentrations. Thornton and Abbatt (2005) suggest that the rate of loss of HO2 from the gas-phase (in molecule cm-3 s-1) is best described by a system in thermodynamic (Henry’s law) equilibrium so that (Thornton et al., 2008):

 (2)

*c* denotes the mean thermal velocity of HO2, *N*av Avogadro’s number and *r*p the particle radius. For an aqueous solution, the effective solubility, *H*eff = *H*HO2 (1+*K*eq/[H+], *K*eq = 2.1  10-5 M at 298 K (Jacob, 2000), *H*HO2 = 9.5  10-6 exp(5910/T) (Hanson et al., 1992). *k*aq can be calculated from the rate coefficients for R2 (*k*2) and R3 (*k*3) (Bielski et al., 1985) and the pH:



The uptake coefficient calculated based on equation (2) for a particle radius of 100 nm and pH = 4 becomes 4  10-4, consistent with the preferred upper limit of 0.001. Lakey et al. (2016) caution that diffusive resistance in the potentially highly viscous SOA may lead to a further reduction of the uptake coefficient, which is not represented by equation (2).

# References

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Lakey, P. S. J., Berkemeier, T., Krapf, M., Dommen, J., Steimer, S. S., Whalley, L. K., Ingham, T., Baeza-Romero, M. T., Pöschl, U., Shiraiwa, M., Ammann, M., and Heard, D. E.: Atmos. Chem. Phys., 16, 13035-13047, 2016.

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