UPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HET_Org_ID

The citation for this datasheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.
This datasheet last evaluated: June 2017; last change in preferred values: June 2017

HO_2 + secondary organic aerosol → products

Experimental data

	precursor VOC	[VOC] \ppb	O_3 \ppb	NO_X \ppb	oxidation conditions	aerosol surface /cm^2 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 HO_2 (~ 10^9 molecule cm^{-3}) to secondary organic aerosol generated from α-pinene or trimethylbenzene (TMB) either in a 27 m^3 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. HO_2 was generated by the photolysis of H_2O in N_2 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 HO_2 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 HO_2 uptake to secondary organic aerosol. Lakey et al. (2016) suggest that RO_2 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 HO_2 is quadratically dependent on $[HO_2]_p$ and $[O_2^-]_p$:

HO_2 (g)	$\rightarrow O_2^-$ (p) + H^+ (p)	R1
HO_2 (p) + HO_2 (p)	$\rightarrow H_2O_2$ (p) + O_2 (p)	R2
O_2^- (p) + HO_2 (p) (+$H_2O(p)$)	$\rightarrow H_2O_2$ (p) + O_2 (p) + OH^- (p)	R3

The uptake coefficient is thus strongly dependent on the gas-phase concentration of HO_2 and becomes small at low, atmospherically relevant HO_2 concentrations. Thornton and Abbatt (2005) suggest that the rate of loss of HO_2 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):

$$\frac{1}{\gamma} = \frac{3cN_{Av}}{8000\left(H^{\text{eff}}RT\right)k_{aq}[\text{HO}_2]r_p} \qquad (2)$$

c denotes the mean thermal velocity of HO_2, N_{av} Avogadro's number and r_p the particle radius. For an aqueous solution, the effective solubility, $H^{\text{eff}} = H^{\text{HO2}}$ $(1+K_{eq}/[H^+]$, $K_{eq} = 2.1 \times 10^{-5}$ M at 298 K (Jacob, 2000), $H^{\text{HO2}} = 9.5 \times 10^{-6}$ 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:

$$k_{aq} = \frac{k_2 + \left(\frac{K_{eq}}{[H^+]aq}\right)k_3}{\left(1+\frac{K_{eq}}{[H^+]aq}\right)^2}$$

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

Bielski, B. H. J., Cabelli, D. E., Arudi, R. L., and Ross, A. B., J. Phys. Chem. Ref. Data, 14, 1041-1100, 1985.

Hanson, D. R., Burkholder, J. B., Howard, C. J. and Ravishankara, A. R.: J. Phys. Chem. 96, 4979-4985, 1992.

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.

Thornton, J., and Abbatt, J. P. D., J. Geophys. Res.-Atmos., 110, D08309, doi:10.1029/2004JD005402, 2005.