

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A3.10 HET\_O\_10

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### HO<sub>2</sub> + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (aq) → products

#### Experimental data

	RH / %	Temp./K	[Cu(II)] \ M	p(HO <sub>2</sub> ) / mbar	Reference	Technique/ Comments
<i>Accommodation coefficients: α<sub>b</sub></i>						
> 0.5	42	295	0.01-0.1	2×10 <sup>-6</sup>	Thornton and Abbatt, 2005	AFT-CIMS (a)
> 0.5	45	296 ± 2	0.5	4×10 <sup>-9</sup>	Taketani et al., 2008	AFT-LIF (b)
0.4± 0.3	53-65	292	0.5	6×10 <sup>-9</sup>	George et al., 2013	AFT-LIF (c)
0.23± 0.07	60	293±2	0.5	4×10 <sup>-8</sup>	Lakey et al., 2015	AFT-LIF (d)
<i>Uptake coefficients: γ</i>						
0.1	42	295		2×10 <sup>-6</sup>	Thornton and Abbatt, 2005	AFT-CIMS (a)
0.11± 0.03	45	296 ± 2		4×10 <sup>-9</sup>	Taketani et al., 2008	AFT-LIF (b)
0.15± 0.03	55					
0.17± 0.04	65					
0.19± 0.04	75					
0.003± 0.005	55	292	<10 <sup>-4</sup>	(0.6-6)×10 <sup>-8</sup>	George et al., 2013	AFT-LIF (c)
0.01± 0.01	65-75					
0.008± 0.003	60±3	293±2	1.2×10 <sup>-6</sup>	4×10 <sup>-8</sup>	Lakey et al., 2015	AFT-LIF (d)
0.008± 0.002			1.2×10 <sup>-5</sup>			
0.008± 0.002			5.9×10 <sup>-5</sup>			
0.042± 0.006			1.2×10 <sup>-4</sup>			
0.089± 0.016			1.2×10 <sup>-3</sup>			
0.26± 0.027			1.1×10 <sup>-2</sup>			
0.26± 0.023			0.56			
0.004± 0.002	60	293±2		4×10 <sup>-8</sup>	Lakey et al., 2016	AFT-LIF (e)

#### Comments

(a) Uptake of HO<sub>2</sub> (2.5-5.0 × 10<sup>10</sup> molecule cm<sup>-3</sup>) to deliquescent particles (mean, surface area weighted radius of 125 nm) at RH = 40-45 % containing 0.01 – 0.1 M CuSO<sub>4</sub>, and buffered to

a pH of 5.1. HO<sub>2</sub> was formed in the reaction of H atoms with O<sub>2</sub> (the former made in a microwave discharge of H<sub>2</sub>). Detection of HO<sub>2</sub> was by CIMS as O<sub>2</sub><sup>-</sup> using F<sup>-</sup> reagent ions, or conversion of HO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> and detection of the product (as HSO<sub>4</sub><sup>-</sup>) using I<sup>-</sup> ions.

- (b) Uptake of HO<sub>2</sub> ( $\sim 10^8$  molecule cm<sup>-3</sup>) to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles (mean surface area weighted diameter of 80-110 nm) at RH between 45 and 75 %. HO<sub>2</sub> was generated by the photolysis of H<sub>2</sub>O in air and detected as OH (by LIF) following conversion in reaction with NO. The particles contained CuSO<sub>4</sub> ( $\sim 0.5$  M) to scavenge HO<sub>2</sub> in order to determine  $\alpha_b$ .
- (c) Uptake of HO<sub>2</sub> ( $6 \times 10^8 - 2 \times 10^9$  molecule cm<sup>-3</sup>) to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles (mean surface area weighted diameter of 100-200 nm, aerosol surface area varied between 0 and  $10^{-3}$  cm<sup>2</sup> cm<sup>-3</sup>) at RH between 45 and 75 %. HO<sub>2</sub> was generated by the photolysis of H<sub>2</sub>O in N<sub>2</sub> or air and detected as OH (by LIF) following conversion in reaction with NO. The particles contained CuSO<sub>4</sub> ( $\sim 0.5$  M) to scavenge HO<sub>2</sub> in order to determine  $\alpha_b$ . For the experiments in the absence of Cu(II), aerosol precursor solutions contained Fe and Cu at less than 1.8  $\mu$ M. Separate experiments (not reported in the table) indicate about an order of magnitude higher uptake coefficients at short reaction times ( $< 10$  s, in the mixing region) in comparison to the standard experiments (10 – 20 s). The uptake coefficient decreased by about a factor of 4 with increasing HO<sub>2</sub> pressure over the range studied; average values are given in the table.
- (d) Setup as in (c), with initial HO<sub>2</sub> concentration at about  $10^9$  molecule cm<sup>-3</sup>. The Cu(II) molarity was estimated by assuming that the Cu(II) to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> molarity ratio is the same in the equilibrated aerosol as in the precursor solution in the solution atomizer. Water content was estimated using the E-AIM model and assuming that Cu(II)SO<sub>4</sub> behaves like (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in solution.
- (e) Setup as in (c), with slightly different configuration for gas flows (AFT operated below ambient pressure, at 915 mbar).

### Preferred Values

Parameter	Value	T/K
$\alpha_b$	$> 0.2$	290 - 300
$k_{\text{TMI}}$ (M <sup>-1</sup> s <sup>-1</sup> )	$5 \times 10^5$	290 - 300
$k_2$ (M <sup>-1</sup> s <sup>-1</sup> )	$2.4 \times 10^9 \exp(-2360/T)$	290 - 300
$k_3$ (M <sup>-1</sup> s <sup>-1</sup> )	$1.6 \times 10^{10} \exp(-1510/T)$	290 - 300
<i>uncertainty</i>		
$\Delta \log(k_{\text{TMI}})$	1	290 - 300
$\Delta \log(k_{2,3})$	0.3	290 - 300

### Comments on Preferred Values

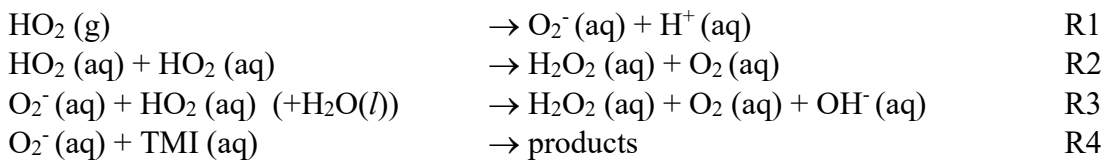
The most recent dataset by Lakey et al. (2015) explicitly confirms the role of Cu(II) as an efficient scavenger of HO<sub>2</sub> and that the uptake of HO<sub>2</sub> to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is accommodation limited at Cu(II) molarity above 0.01 M (Figure 1); similar to the conclusion by Mozurkewich et al. (1987) with (NH<sub>4</sub>)HSO<sub>4</sub>. All measured uptake coefficients are above 0.2, independent of the HO<sub>2</sub> concentration between  $10^7$  and  $10^{10}$  molecule cm<sup>-3</sup>, and independent of composition of the aqueous substrate other than Cu(II). The reason for the rather small discrepancies between the estimates of  $\alpha_b$  among the available studies may be related to the interaction time period used for the evaluation of the first order loss rates in the aerosol flow tube, as discussed by Lakey et al. (2015), who observed some negative time dependence at short interaction times, but also some non-first order behavior. The preferred lower limit for  $\alpha_b$  considers all available data for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, but also those for the other aqueous substrate in order to provide an internally consistent recommendation.

In the absence of CuSO<sub>4</sub>, non-exponential loss of HO<sub>2</sub> was observed by Thornton and Abbatt (2005), which the authors attributed to the aqueous phase self-reaction of HO<sub>2</sub>. Consistent with the

idea of self-reaction, George et al. (2013) and Lakey et al. (2016) observed much smaller uptake coefficients at lower HO<sub>2</sub> concentration. The reason for the discrepancy to the Taketani et al. (2008) data remains unknown. Possible reasons include different flow tube residence times and surface to volume ratios, and possible contamination by transition metals. George et al. (2013) and Lakey et al. (2016) observed substantial variability in HO<sub>2</sub> uptake which correlated with Cu and Fe content in precursor solutions used in the aerosol nebulizer and discarded all experiments with Fe and Cu contents above 10<sup>-6</sup> M.

Lower uptake coefficients have been reported for HO<sub>2</sub> interacting with dry (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles with Taketani et al. (2008) reporting values of 0.04 - 0.05, Gershenzon reporting 0.011, and George et al. reporting <0.004.

The uptake of HO<sub>2</sub> in aqueous solution is presently believed to be driven by self-reaction and acid-base dissociation of HO<sub>2</sub> (pKa ~ 4.7) with formation of H<sub>2</sub>O<sub>2</sub> (R2, R3). In the presence of transition metal ions (TMI) the reaction of HO<sub>2</sub> and especially O<sub>2</sub><sup>-</sup> (R4) can be important:



If a first-order loss process for HO<sub>2</sub> or O<sub>2</sub><sup>-</sup> in the aqueous phase dominates (e.g. reaction with TMI such as Cu(II)), the uptake coefficient can be calculated from the expression below:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{TMI}}}$$

$$\frac{1}{\Gamma_{\text{TMI}}} = \frac{c}{4H^{\text{eff}} RT \sqrt{D_1 k_{\text{TMI}} [\text{TMI}] [\coth(r_p / l_{\text{rd}}) - (l_{\text{rd}} / r_p)]}} \quad l_{\text{rd}} = \sqrt{\frac{D_1}{k_{\text{TMI}} [\text{TMI}]}} \quad (1)$$

$$H^{\text{eff}} = H^{\text{HO}_2} (1 + K_{\text{eq}} / [\text{H}^+])$$

$$K_{\text{eq}} = 2.1 \times 10^{-5} \text{ M at 298 K (Jacob, 2000)}$$

$$H^{\text{HO}_2} = 9.5 \times 10^{-6} \exp(5910/T) \text{ M atm}^{-1} \text{ (Hanson et al., 1992)}$$

$$D_1 = \{1 \times 10^{-5} (T/298)\} / (1.09 \times 10^8 \exp(-0.068T) + 0.873) \text{ cm}^2 \text{ s}^{-1}$$

$k_{\text{TMI}}$  is the second order rate coefficient for the reaction of HO<sub>2</sub> and O<sub>2</sub><sup>-</sup> with transition metal ions. The parameterization for the diffusion coefficient is from (Schwartz, 1984; Thornton et al., 2008), where the denominator was derived from a fit to the water viscosity data of Hallett (1963). This parameterization for  $D_1$  remains a reasonable approximation for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solutions, but needs to be revised in presence of organic solutes that lead to strong changes to viscosity. The size dependent correction factor, with  $r_p$  denoting the particle radius and  $l_{\text{rd}}$  the reacto-diffusive length, assures proper representation when the kinetic regime changes from reaction-diffusion towards volume limited kinetics at low TMI concentrations. Eq. (1) explains the increase of  $\gamma$  between 10<sup>-4</sup> and 10<sup>-2</sup> M as shown in Figure 1, consistent with the data by Lakey et al. (2015), where the Cu(II) to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> ratio was varied. As discussed by Lakey et al. (2015), Thornton et al. (2008) and Mozurkewich et al. (1987), the apparent first order loss rate coefficient of HO<sub>2</sub> / O<sub>2</sub><sup>-</sup> is around three orders of magnitude lower than based on the second order rate coefficient for dilute aqueous solutions (Bielski et al., 1985) possibly due to high ionic strength effects. A value  $k_{\text{TMI}} = 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  is consistent with the Lakey et al. (2015) data (without specifying the difference in reactivity for HO<sub>2</sub> / O<sub>2</sub><sup>-</sup>). We provide large error bounds on this value, and further experiments are needed with pH and Cu(II) and other TMI varied to constrain it further.

According to the reaction scheme (R1-R4) above, in the absence of TMI, the rates of loss of aqueous-phase HO<sub>2</sub> are quadratically dependent on [HO<sub>2</sub>]<sub>aq</sub> and [O<sub>2</sub><sup>-</sup>]<sub>aq</sub> and are thus strongly dependent on the gas-phase concentration of HO<sub>2</sub>. At low, relevant HO<sub>2</sub> concentrations the liquid phase reactions become rate limiting and  $\gamma$  is expected to be much smaller, as observed in dilute solutions by Mozurkewich et al. (1987) and also in the George et al. and Lakey et al. data for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Thornton and Abbatt (2005) suggest that the rate of loss of HO<sub>2</sub> from the gas-phase (in molecule cm<sup>-3</sup> s<sup>-1</sup>) is best described by a system in thermodynamic (Henry's law) equilibrium:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{self}}} \quad \frac{1}{\Gamma_{\text{self}}} = \frac{3cN_{Av}}{8000(H^{\text{eff}} RT)k_{aq}[\text{HO}_2]_p} \quad (2)$$

$k_{aq}$  can be calculated from the rate coefficients for R2 ( $k_2$ ) and R3 ( $k_3$ ) (Bielski et al., 1985) and the pH:

$$k_{aq} = \frac{k_2 + \left( \frac{K_{eq}}{[H^+]_{aq}} \right) k_3}{\left( 1 + \frac{K_{eq}}{[H^+]_{aq}} \right)^2} \quad (3)$$

Equation (2) consistently links the George et al. (2013) data at low HO<sub>2</sub> concentration with those of Thornton and Abbatt (2005) at higher HO<sub>2</sub> concentration (Figure 2). We therefore prefer equations (1) and (2) to consistently describe uptake of HO<sub>2</sub> in presence and absence of transmission metal ions. At low HO<sub>2</sub> concentrations, the overall  $\gamma$  can be obtained by adding the corresponding resistors:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{TMI}} + \Gamma_{\text{self}}} \quad (4)$$

Equation (4) explains the measured dependence of  $\gamma$  over the full range of Cu(II) contents, as shown in Figure 2. Equations (1) and (2) also help to rationalize the dependence of  $\gamma$  on relative humidity, observed both by George et al. (2013) and Taketani et al. (2008), as with increasing humidity the pH tends to increase and the radius as well. As discussed by Hanson et al. (1992) and Thornton and Abbatt (2005), the parameterization suggested here is very sensitive to the solubility of HO<sub>2</sub> ( $H^{\text{HO}_2}$ ), its temperature dependence and on the aerosol pH.

Further experiments with systematic variation of different transition metals, aerosol pH and HO<sub>2</sub> concentration would help to better constrain the parameterization.

We refer to recent publications for a more detailed description of the effect of different parameterisation schemes (Thornton et al., 2008; Macintyre and Evans, 2011).

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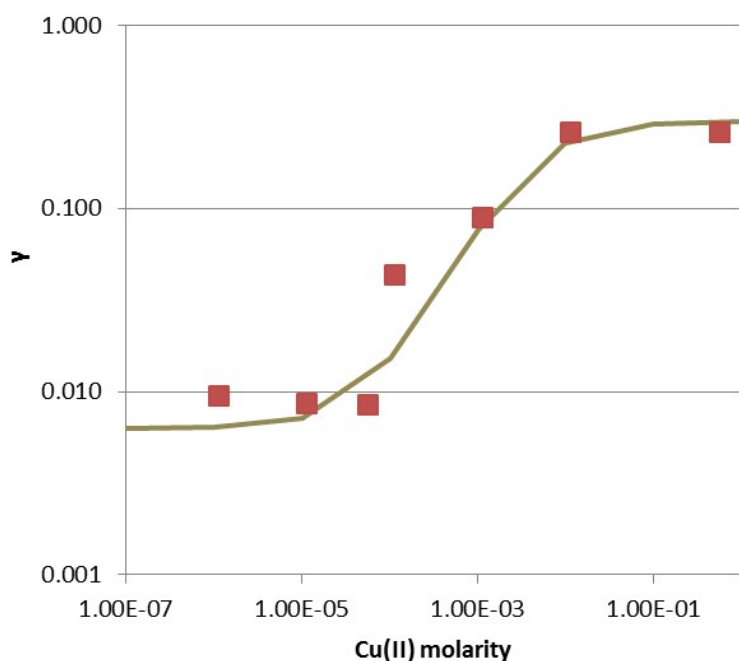


Figure 1: Uptake coefficient of HO<sub>2</sub> on mixed CuSO<sub>4</sub> / (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosol as a function of Cu(II) molarity. Symbols: data by Lakey et al. (2015); solid line: calculated based on equations (1) – (4), at pH 5.2, 100nm particle radius,  $\alpha_b = 0.3$  and with  $k_{TMI} = 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

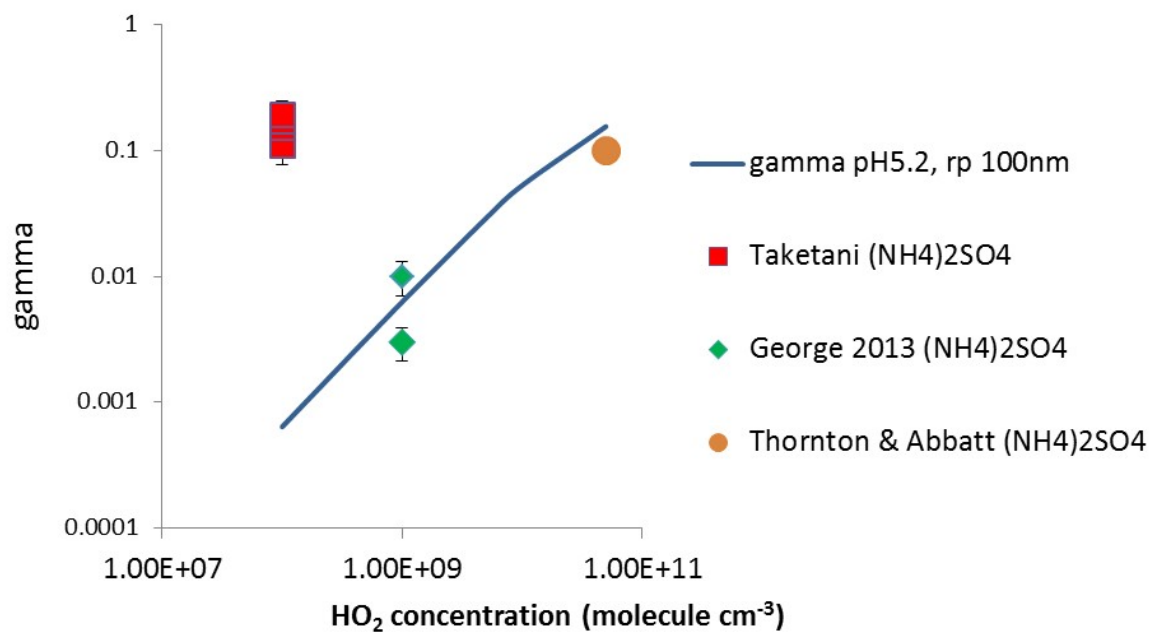


Figure 2: Uptake coefficient of  $\text{HO}_2$  on  $(\text{NH}_4)_2\text{SO}_4$  aerosol in absence of  $\text{Cu(II)}$ . Symbols: data; solid line: calculated based on the parameterization given in equation (2) for self-reaction only,  $\text{pH} = 5.2$ ,  $100\text{nm}$  particle radius, and  $\alpha_b = 0.3$ .