

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HET_O_11

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This datasheet last evaluated: June 2017; last change in preferred values: June 2017

HO₂ + NH₄NO₃ (aq) → products

Experimental data

	RH / %	Temp./K	[Cu(II)] \ M	p(HO ₂) / mbar	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>						
0.005± 0.002	29-70	292	<10 ⁻⁴	(0.6-6)×10 ⁻⁸	George et al., 2013	AFT-LIF (a)

Comments

(c) Uptake of HO₂ (6×10⁸ – 2×10⁹ molecule cm⁻³) to NH₄NO₃ particles (mean surface area weighted diameter of 100-200 nm, aerosol surface area varied between 0 and 10⁻³ cm² cm⁻³) at RH between 29 and 70 %. HO₂ was generated by the photolysis of H₂O in N₂ or air and detected as OH (by LIF) following conversion in reaction with NO. Aerosol precursor solutions contained Fe and Cu at less than 1.8 μM. Separate experiments (not reported in the table) indicate a ≈ 70% higher uptake coefficient 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 2 with the HO₂ concentration increasing from 1.1×10⁹ – 2.7×10⁹ molecule cm⁻³; average values are given in the table.

Preferred Values

Parameter	Value	T/K
α_b	> 0.2	290 - 300
γ	0.005	290 - 300
k_{TMI} (M ⁻¹ s ⁻¹)	5 × 10 ⁵	290 - 300
k_2 (M ⁻¹ s ⁻¹)	2.4×10 ⁹ exp(-2360/T)	290 - 300
k_3 (M ⁻¹ s ⁻¹)	1.6×10 ¹⁰ exp(-1510/T)	290 - 300
<i>uncertainty</i>		
$\Delta\log(\gamma)$	0.3	290 - 300
$\Delta\log(k_{\text{TMI}})$	1	290 - 300
$\Delta\log(k_{2,3})$	0.3	290 - 300

Comments on Preferred Values

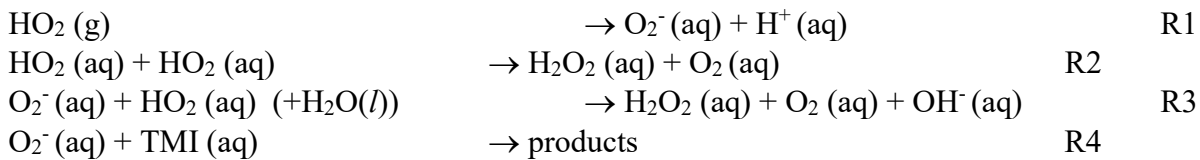
While no study is available, in which bulk mass accommodation was rate limiting, we still prefer a value of α_b of > 0.2 in order to have an internally consistent recommendation among all aqueous substrates.

Our preferred value for γ is based on the uptake coefficient reported in the single study by George et al. (2013), which is in line with measurements on other aqueous substrates from the same group

(George et al., 2013; Lakey et al., 2015, 2016), but in contrast with much higher values found by Taketani et al. (2008, 2009), as discussed on the datasheets for ammonium sulfate, ammonium bisulfate and halide solutions. Possible reasons include different flow tube residence times and surface to volume ratios, and possible contamination by transition metals.

Gershenzon et al. (1995) reported a value of 1.4×10^{-2} for the uptake coefficient on dry NH_4NO_3 .

The uptake of HO_2 in aqueous solution with $\text{pH} > 5$ is presently believed to be driven by self-reaction and acid-base dissociation of HO_2 ($\text{pK}_a \sim 4.7$) with formation of H_2O_2 (R2, R3). In the presence of transition metal ions (TMI) the reaction of HO_2 and especially O_2^- (R4) can be important:



If a first-order loss process for HO_2 or O_2^- in the aqueous phase dominates (e.g. reaction with TMI such as Cu(II)), the uptake coefficient can be calculated from the expression below:

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

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

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

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

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

k_{TMI} is the second order rate coefficient for the reaction of HO_2 and O_2^- with transition metal ions; the preferred value is justified in the datasheet VI.A3.10. For low viscosity aqueous solutions, the diffusivity of HO_2 can be approximated by that in pure water (Schwartz, 1984; Thornton et al., 2008):

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

where the denominator was derived from a fit to the water viscosity data of Hallett (1963). D_1 needs to be assessed individually 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_{rd} the reacto-diffusive length, assures proper representation when the kinetic regime changes from reaction-diffusion towards volume limited kinetics at low TMI concentrations.

In the absence of TMI, the rates of loss of aqueous-phase HO_2 are quadratically dependent on $[\text{HO}_2]_{\text{aq}}$ and $[\text{O}_2^-]_{\text{aq}}$. The uptake coefficient is thus strongly dependent on the gas-phase concentration of HO_2 and becomes small at low, relevant HO_2 concentrations. Thornton and Abbatt (2005) suggest that the rate of loss of HO_2 from the gas-phase (in molecule $\text{cm}^{-3} \text{ s}^{-1}$) is best described by a system in thermodynamic (Henry's law) equilibrium so that (Thornton et al., 2008):

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

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

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

We suggest using equations (1) and (2) to consistently describe uptake of HO₂ in presence and absence of transition metal ions. As Figure 1 shows, equation (2) is consistent with the data point reported by George et al. (2013). The absence of dependence on relative humidity may result from a slightly decreasing pH with increasing humidity and at the same time an increasing radius due to the hygroscopic growth, with both effects possibly nullifying each other.

As discussed by Hanson et al. (1992) and Thornton and Abbatt (2005), the parameterization suggested here is very sensitive to the solubility of HO₂ (H^{HO_2}), its temperature dependence and on the aerosol pH. Further experiments with systematic variation of different transition metals, aerosol pH and HO₂ concentration would help to better assess the uncertainty of 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).

References

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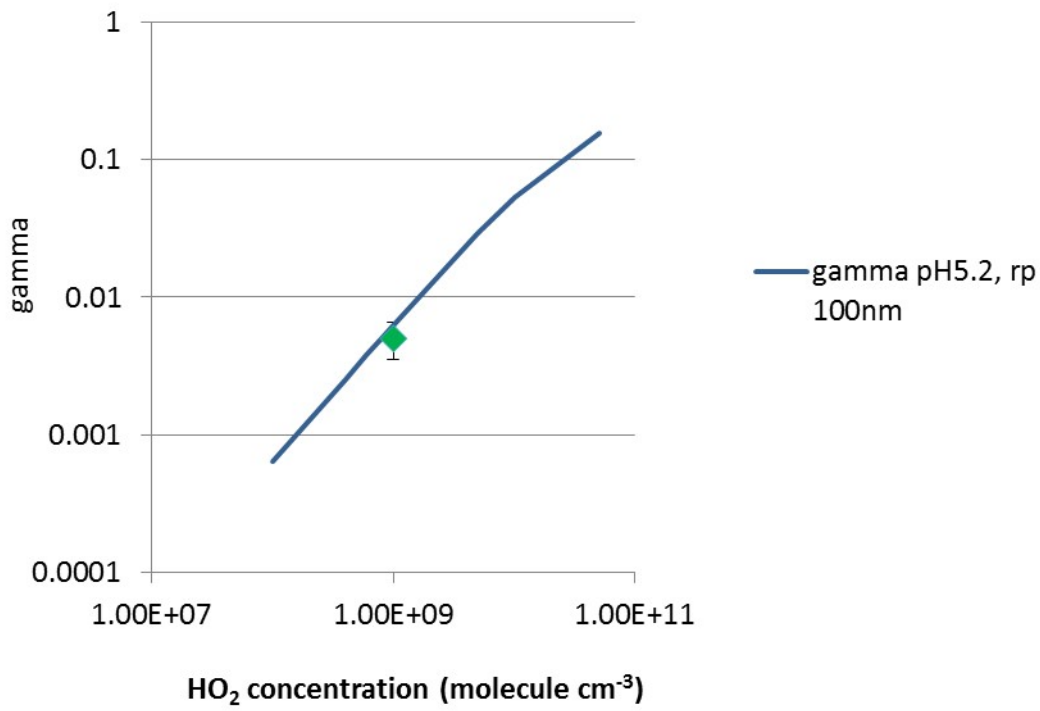


Figure 1: Uptake coefficient of HO_2 on NH_4NO_3 aerosol in absence of Cu(II) . Symbols: data; solid line: calculated based on parameterization given by equation (2) for self-reaction only, for $\text{pH} = 5.2$, 100nm particle radius, and $\alpha_b = 0.3$.