

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation Data Sheet VI.A2.02 HET_SALTS_2

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HO₂ + Cl⁻/Br⁻/I⁻ (aq) → products

Experimental data

	RH / %	Temp./K	p(HO ₂) / mbar	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>					
0.1 ± 0.03 (NaCl)	53-75	296 ± 2	4 × 10 ⁻⁹	Taketani et al., 2008	AFT-LIF (a)
0.1 ± 0.04 (SSS)	53-75	296 ± 2	4 × 10 ⁻⁹	Taketani et al., 2009	AFT-LIF (b)
0.1 ± 0.03 (NS)	53-75				
0.07 ± 0.03 (KCl)	75				
0.016 ± 0.008 (NaCl)	54	292	(0.6-6) × 10 ⁻⁸	George et al., 2013	AFT-LIF (c)
0.01 ± 0.02 (NaCl)	67-76				
<i>Accommodation coefficients: α_b</i>					
0.65 ± 0.17		296 ± 2	4 × 10 ⁻⁹	Taketani et al., 2008	AFT (a)
0.55 ± 0.19		296 ± 2	4 × 10 ⁻⁹	Taketani et al., 2009	AFT (b)

Comments

- (a) Uptake of HO₂ (~10⁸ molecule cm⁻³) to aqueous NaCl particles (mean surface area weighted diameter of 80-110 nm) at RH between 45 and 75 %. HO₂ was generated by the photolysis of H₂O in air and detected as OH (by LIF) following conversion in reaction with NO. In experiments to determine α_b the particles contained CuSO₄ (~0.5 M) to scavenge HO₂. The authors originally reported: $\gamma(\text{NaCl}) = 0.11 \pm 0.03$, 0.09 ± 0.02 and 0.10 ± 0.02 at RH = 53, 63 and 75 %, respectively.
- (b) Same experimental set up as (a). SSS = synthetic sea-salt, NS = natural seawater. The authors originally reported: $\gamma(\text{SSS}) = 0.07 \pm 0.03$, 0.12 ± 0.04 and 0.13 ± 0.04 at RH = 35, 50 and 75 %, respectively. $\gamma(\text{NS}) = 0.10 \pm 0.03$, 0.11 ± 0.02 and 0.10 ± 0.03 at RH = 35, 50 and 75 %, respectively. In experiments to determine α_b aqueous KCl particles contained CuSO₄ (~0.5 M) to scavenge HO₂.

- (c) Uptake of HO₂ ($6 \times 10^8 - 2 \times 10^9$ molecule cm⁻³) to NaCl 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 45 and 75 %. HO₂ was generated by the photolysis of H₂O in 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 about a factor of 4 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 up to 80% with increasing HO₂ pressure over the range studied; average values are given in the table.

Preferred Values

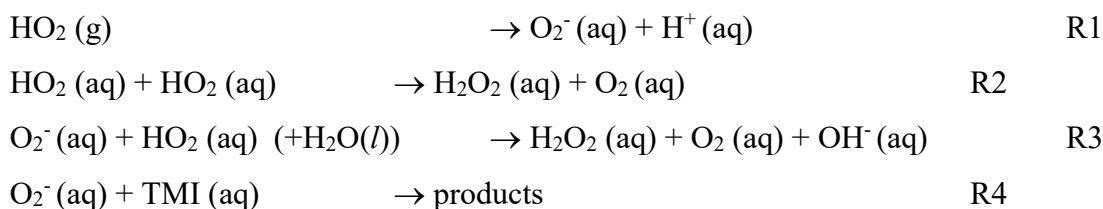
Parameter	Value	T/K
α_b	> 0.2	290 - 300
γ	0.02	290 - 300
k_{TMI} (M ⁻¹ s ⁻¹)	5×10^5	290 - 300
k_2 (M ⁻¹ s ⁻¹)	$2.4 \times 10^9 \exp(-2360/T)$	290 - 300
k_3 (M ⁻¹ s ⁻¹)	$1.6 \times 10^{10} \exp(-1510/T)$	290 - 300
<i>uncertainty</i>		
$\Delta \log(\gamma)$	0.7	290 - 300
$\Delta \log(k_{\text{TMI}})$	1	290 - 300
$\Delta \log(k_{2,3})$	0.3	290 - 300

Comments on Preferred Values

The lower limit for α_b is the same as that preferred for other organic and inorganic aqueous substrates in order to provide an internally consistent recommendation for all aqueous aerosol types. It is consistent with the values reported by Taketani et al. (2008, 2009) for NaCl, synthetic and authentic sea salt.

Our preferred value for γ is based on the uptake coefficient reported in the study by George et al. (2013) for NaCl, 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 aqueous organic aerosols. Possible reasons include different flow tube residence times and surface to volume ratios, and possible contamination by transition metals.

The uptake of HO₂ in aqueous solution is presently believed to be driven by self-reaction and acid-base dissociation of HO₂ (pK_a ~ 4.7) with formation of H₂O₂ (R2, R3). In the presence of transition metal ions (TMI) the reaction of HO₂ and especially O₂⁻ (R4) can be important:



If a first-order loss process for HO₂ or O₂⁻ in the aqueous phase dominates (e.g. reaction with TMI such as Cu(II)), the uptake coefficient can be calculated from the expression below:

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

$$\frac{1}{\Gamma_{\text{TMI}}} = \frac{c}{4H^{\text{eff}}RT\sqrt{D_1k_{\text{TMI}}[\text{TMI}][\coth(r_p/l_{\text{rd}}) - (l_{\text{rd}}/r_p)]}} \quad l_{\text{rd}} = \sqrt{\frac{D_1}{k_{\text{TMI}}[\text{TMI}]}} \quad (1)$$

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

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

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

k_{TMI} is the second order rate coefficient for the reaction of HO_2 and O_2^- with transition metal ions. The preferred value for k_{TMI} and its reliability is justified in detail in datasheet HET_O_10 / 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). This parameterization for D_1 remains a reasonable approximation for sea salt 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_{rd} the reacto-diffusive length, assures proper representation when the kinetic regime changes from reaction-diffusion towards volume limited kinetics at low TMI concentrations.

According to the reaction scheme above, in the absence of TMI, the rates of loss of aqueous-phase HO_2 are quadratically dependent on $[\text{HO}_2]_{\text{aq}}$ and $[\text{O}_2^-]_{\text{aq}}$ and are thus strongly dependent on the gas-phase concentration of HO_2 . At low, relevant HO_2 concentrations the liquid phase reactions become rate limiting and γ is expected to be much smaller as observed by George et al. (2013). 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:

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

Equation (2) predicts uptake coefficients in the range of that measured by George et al. (2013) on deliquesced NaCl for pH between 5 and 6. While natural sea water may have a higher pH, it is unlikely that such a high pH value persisted in the aerosol generated from re-dissolved authentic sea salt, and is unlikely to be the cause of the high uptake coefficients measured by Taketani et al. (2009). In addition, as discussed by Hanson et al. (1992) and Thornton and Abbatt (2005), there is considerable uncertainty (factor of 2.5) associated with the solubility of HO_2 (H^{HO_2}) and its temperature dependence. The difference in pH is also likely the reason why the HO_2 uptake measured by George et al. (2013) is a factor of two to five higher than for other aqueous substrates.

At low HO_2 concentrations, the overall γ can be obtained by adding the corresponding resistors:

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

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

Experiments conducted using dry salt surfaces at room temperature reveal a much lower uptake coefficient than those reported for aqueous particles (George et al., 2013; Taketani et al., 2008, 2009) with values ranging from <0.004 (George et al. (2013) on NaCl), $1.8\text{-}2.3 \times 10^{-3}$ (Loukhovitskaya et al. 2009 on NaCl, NaBr and SSS bulk surfaces), 7.5×10^{-3} (Antsupov 1988), $12\text{-}13 \times 10^{-3}$ (Remorov 2002; Gershenson, 1995 on NaCl) and 18×10^{-3} (Gershenson, 1995 on KCl). Although disagreeing considerably on absolute values of the uptake coefficient (perhaps reflecting different modes of sample presentation) they all return strong, negative dependencies of γ on the temperature and show that at most temperatures γ is independent of the HO₂ concentration, the exception being at the highest temperatures studied by Remorov, where they saw that γ decreased at lower [HO₂]. Remorov et al. (2002) (bulk NaCl) and Loukhovitskaya et al. (2009) (bulk MgCl₂.6H₂O) both observed a decrease in HO₂ uptake when the RH was increased. This starkly contrasts the observation of Taketani et al. that γ increased when the RH was increased. In combination with the observation of H₂O₂ as sole product (at 0.5 yield, Loukhovitskaya et al., 2009), these observations indicate that, on solid particles, the uptake is driven by reversible surface accommodation of HO₂ and subsequent self-reaction with no role played by halide ions.

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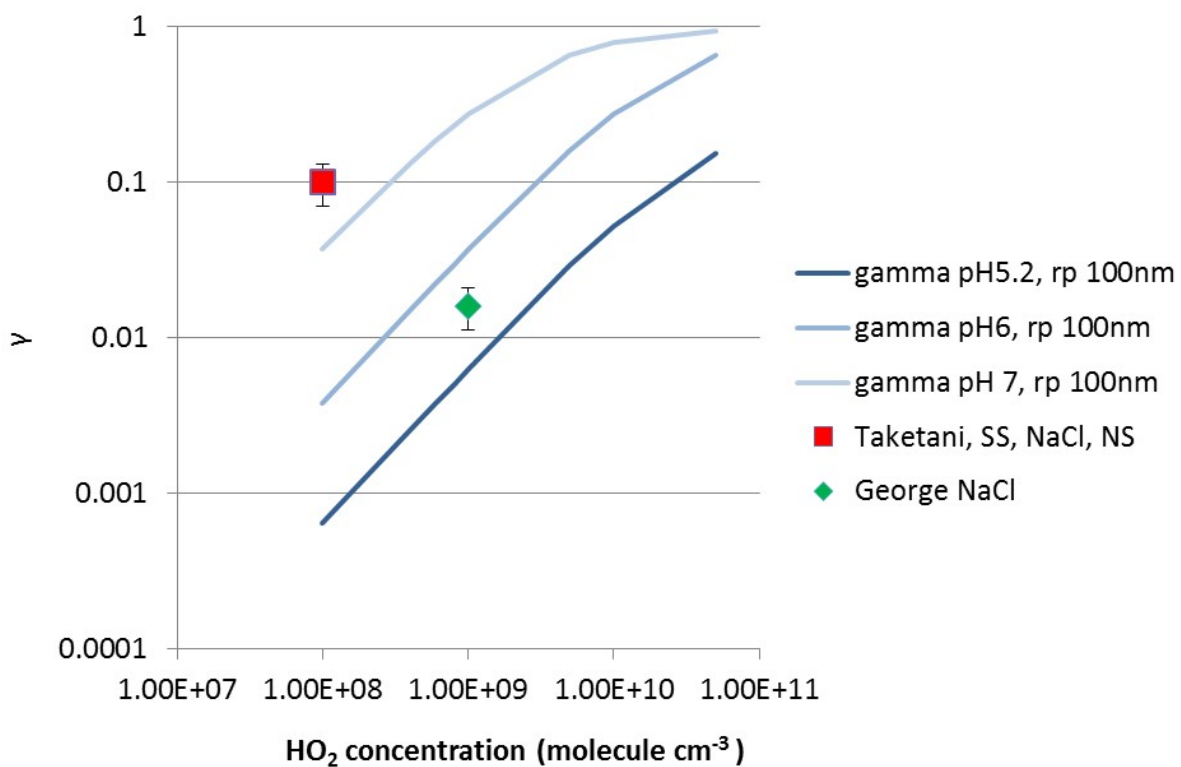


Figure 2: Uptake coefficient of HO_2 on seasalt aerosol in absence of Cu(II) . Symbols: data; solid line: calculated based on the parameterization given in equation (2) for self-reaction only, with pH 5, 6 and 7, 100 nm particle radius, and $\alpha_b = 0.3$.