

IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet VI.A2.02

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This datasheet evaluated: May 2012; last change in preferred values: May 2012.

HO₂ + Cl⁻/Br⁻/I⁻ (aq) → products

Experimental data

	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>			
0.1 ± 0.03 (NaCl, RH 53-75 %)	296 ± 2	Taketani et al., 2008	AFT (a)
0.1 ± 0.04 (SSS, RH 53-75 %)	296 ± 2	Taketani et al., 2009	AFT (b)
0.1 ± 0.03 (NS, RH 53-75 %)			
0.07 ± 0.03 (KCl, RH 75 %)			
<i>Accommodation coefficients: α_b</i>			
0.65 ± 0.17	296 ± 2	Taketani et al., 2008	AFT (a)
0.55 ± 0.19	296 ± 2	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.

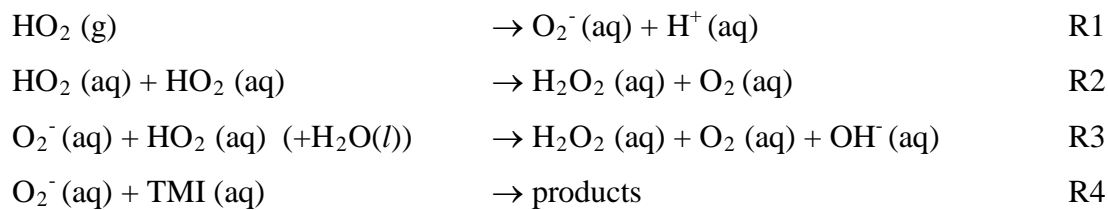
Preferred Values

Parameter	Value	T/K
α	> 0.5	290 - 300
γ	0.1	290 - 300
<i>Reliability</i>		
$\Delta \log \gamma$	1	290 - 300

Comments on Preferred Values

Taketani et al. (2008) observed exponential HO₂ decay to aqueous NaCl particles with γ equal to 0.65 ± 0.17 when CuSO₄ was present, defining the lower limit to α_b . In the absence of CuSO₄ γ was independent of RH and close to 0.1. Taketani et al. (2009) used synthetic sea salt and natural sea salt to derive similar results. Our preferred values for uptake of HO₂ to aqueous sea-salt particles are based on this data-set. As the mechanism for HO₂ loss in the particle remains unknown (see below) we add substantial uncertainty to the preferred value of γ .

The uptake of HO₂ in aqueous solution with pH > 5, is presently believed to be driven by self-reaction and acid-base dissociation of HO₂ (pKa ~ 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)), and assuming equal rates of reaction throughout the particle, the uptake coefficient can be calculated from the expression below:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{\bar{c}}{4H^e \dot{R}^f \sqrt{k_r T} \left[\frac{T}{M} \right] D_1}$$

$H^{\text{eff}} = H^{\text{HO}_2} (1 + K_{\text{eq}}/[\text{H}^+])$, $K_{\text{eq}} = 2.1 \times 10^{-5}$ M at 298 K (Jacob, 2000), $H^{\text{HO}_2} = 9.5 \times 10^{-6} \exp(5910/T)$ (Hanson et al., 1992) and $D_1 = [1 \times 10^{-5} (T/298)] / (1.09 \times 10^8 \exp(-0.068T) + 0.873)$ cm² s⁻¹ (Schwartz, 1984; Thornton et al., 2008) where the denominator in the D_1 term was derived from a fit to the water viscosity data of Hallett (1963).

According to the reaction scheme above, in the absence of TMI, the rates of loss of aqueous-phase HO₂ are quadratically dependent on [HO₂]_{aq} and [O₂⁻]_{aq} and are thus strongly dependent on the gas-phase concentration of HO₂. At low HO₂ concentrations (e.g. as found in the atmosphere) the liquid phase reactions become rate limiting and γ is expected to be much smaller as observed in dilute solutions by Mozurkewich et al. (1987) and the simple formalism above breaks down. 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):

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{3\bar{c}N_A}{8 \left(H^e \dot{R}^f \right)^2 k_d \left[H_2 \right] r}$$

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

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

This formalism predicts that the loss of HO₂ to particles is favoured by high HO₂ mixing ratios, low temperatures (higher solubility) and low pH. At low concentrations of HO₂ (where the self reaction and reaction with O₂⁻ are inefficient), values of γ of < 0.005 are calculated, which are however much less than the uptake coefficients of Taketani et al. (2008, 2009) who investigated the uptake of low concentrations of HO₂ to aqueous salt particles. 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 HO₂ (H^{HO_2}) and its temperature dependence. Until these apparent discrepancies and uncertainties have been resolved by further experiments, we make no recommendation for parameterising HO₂ uptake to halide containing aqueous aerosol, but suggest that a value close to 0.1 is appropriate for marine environments where sea salt aerosols will be deliquescent. 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).

Experiments conducted using dry salt surfaces at room temperature reveal a much lower uptake coefficient than those reported for aqueous particles (Taketani et al., 2008, 2009) with values ranging from $1.8\text{-}2.3 \times 10^{-3}$ (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. (2008, 2009) 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 independent of the presence of halide ions.

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