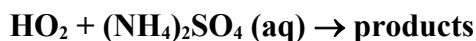


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A3.10 HET_O_10

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



Experimental data

	Temp./K	Reference	Technique/ Comments
<i>Accommodation coefficients: α</i>			
> 0.5	298	Thornton and Abbatt, 2005	AFT (a)
> 0.5	296 ± 2	Taketani et al., 2008	AFT (b)

Comments

- (a) Uptake of HO₂ ($2.5\text{-}5.0 \times 10^{10}$ molecule cm⁻³) to deliquescent particles (mean, surface area weighted radius of 125 nm) at RH = 40-45 % containing 0.01 – 0.1 M CuSO₄, and buffered to a pH of 5.1. HO₂ was formed in the reaction of H atoms with O₂ (the former made in a microwave discharge of H₂). Detection of HO₂ was by CIMS as O₂⁻ using F⁻ reagent ions, or conversion of HO₂ to H₂SO₄ and detection of the product (as HSO₄⁻) using I⁻ ions.
- (b) Uptake of HO₂ ($\sim 10^8$ molecule cm⁻³) to (NH₄)₂SO₄ 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. The particles contained CuSO₄ (~ 0.5 M) to scavenge HO₂ in order to determine α_b .

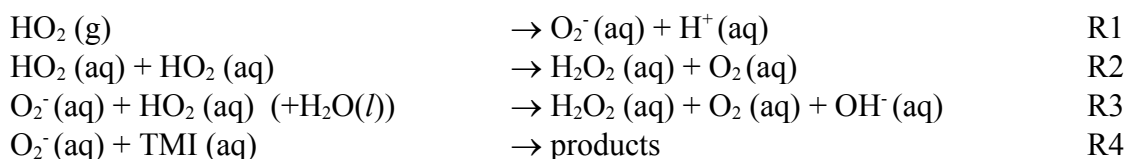
Preferred Values

Parameter	Value	T/K
α	> 0.5	290 - 300

Comments on Preferred Values

Thornton and Abbatt derived an average experimental uptake coefficient of $\gamma = 0.5 \pm 0.1$ on particles containing CuSO₄ and suggest that this is a lower limit to the accommodation coefficient. In the absence of CuSO₄ non-exponential loss of HO₂ was observed, which the authors attributed to the aqueous phase self reaction of HO₂ and derived an aqueous-phase rate coefficient of $1 \pm 0.25 \times 10^7$ M⁻¹ s⁻¹ for this process, consistent with kinetic data on the reaction of HO₂ with itself and with O₂⁻. Using significantly lower HO₂ concentrations, Taketani et al (2008) observed exponential HO₂ decays with γ equal to ~ 0.5 when CuSO₄ was present, defining the lower limit to α_b . In the absence of CuSO₄ γ increased with RH with values of 0.11 (45 %), 0.15 (55%), 0.17 (65%) and 0.19 (75%). Taketani et al speculate that the RH dependence stems from the effect of particle size changes with RH and the reaction occurring in the transition regime between surface and volume limited uptake. Lower uptake coefficients have been reported for HO₂ interaction with dry (NH₄)₂SO₄ particles with Taketani et al. (2008) reporting values of 0.04 - 0.05 and Gershenzon reporting 0.011.

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:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{\bar{c}}{4H^{eff} RT \sqrt{k_{TMI} [TMI] D_1}}$$

$H^{eff} = H^{HO_2} (1 + K_{eq}/[H^+])$, $K_{eq} = 2.1 \times 10^{-5}$ M at 298 K (Jacob, 2000), $H^{HO_2} = 9.5 \times 10^{-6} \exp(5910/T)$ (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):

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{3\bar{c}N_A}{8000(H^{eff} RT)^2 k_{aq} [HO_2]_r}$$

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

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

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 (whereby 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 who investigated the uptake of low concentrations of HO₂ to (NH₄)₂SO₄ 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. The above schemes also do not account for the RH dependence of uptake observed by Taketani et al (2008)..

Until these apparent discrepancies have been resolved by further experiments, we make no recommendation for parameterising HO₂ uptake to aqueous aerosol. 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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