

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.20 HET_H2OL_20

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HO₂ + H₂O (aq) → products

Experimental data

	Temp./K	Reference	Technique/ Comments
<i>Accommodation coefficients: α</i>			
> 0.01	275	Hanson et al, 1992	WWFT-LIF (a)

Comments

- (a) Uptake of HO₂ ($5\text{--}30 \times 10^{10}$ molecule cm⁻³) to a film (0.2 mm thick) of de-ionised water, or water containing 10⁻³ M CuSO₄. HO₂ was formed in the reaction of F with H₂O₂ and detected as OH after reaction with NO. HO₂ uptake was limited by diffusion through the 1 Torr of He bath gas. Levels of HO₂ were sufficiently low to neglect loss due to gas-phase self reaction. Addition of CuSO₄ had no effect on HO₂ loss rates.

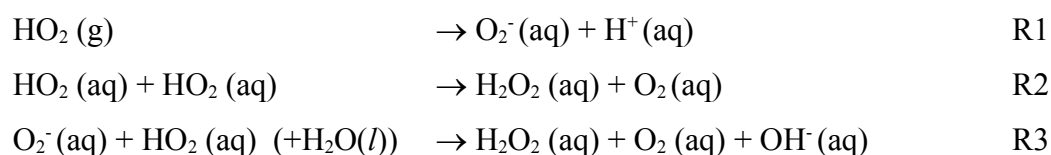
Preferred Values

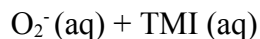
Parameter	Value	T/K
α_b	> 0.5	270-300
<i>Reliability</i> $\Delta(\log \alpha_b)$	undetermined	

Comments on Preferred Values

The sole experimental study of the uptake of HO₂ to pure water returned a lower limit to the accommodation coefficient of $\alpha_b > 0.01$. This is consistent with molecular dynamics calculations of the HO₂-water interaction (Morita et al., 2004) which suggest that the accommodation coefficient could be unity and also with more sensitive experiments on other aqueous surfaces such as (NH₄)₂SO₄ and NH₄HSO₄ (see datasheets VI.A3.09 and VI.A3.10). We thus prefer a value of α_b of > 0.5.

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 (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:





→ products

R4

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:

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

$H^{\text{eff}} = H^{\text{HO}_2} (1 + K_{\text{eq}}/[\text{H}^+])$, $K_{\text{eq}} = 2.1 \times 10^{-5}$ 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):

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{3\bar{c}N_A}{8000(H^{\text{eff}} RT)^2 k_{\text{aq}} [\text{HO}_2] r}$$

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

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

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 for (NH₄)₂SO₄ particles (see datasheet VI.A3.10).

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).

References

- Bielski, B. H. J., Cabelli, D. E., Arudi, R. L., and Ross, A. B., *J. Phys. Chem. Ref. Data*, 14, 1041-1100, 1985.
- Hanson, D. R., Burkholder, J. B., Howard, C. J. and Ravishankara, A. R.: *J. Phys. Chem.* 96, 4979-4985, 1992.
- Jacob, D. J., *Atmos. Env.*, 34, 2131-2159, 2000.
- Macintyre, H. L., and Evans, M. J., *Atmos. Chem. Phys.*, 10, 7409-7414, 2010.
- Morita, A., Kanaya, Y., and Francisco, J. S., *J. Geophys. Res.-Atmos.* 109, 2004.
- Mozurkewich, M., McMurry, P. H., Gupta, A., and Calvert, J. G., *J. Geophys. Res.-Atmos.*, 92, 4163-4170, 1987.
- Schwartz, S. E., *J. Geophys. Res.-Atmos.*, 89, 1589-1598, 1984.
- Thornton, J., and Abbatt, J. P. D., *J. Geophys. Res.-Atmos.*, 110, D08309, doi:10.1029/2004JD005402, 2005.