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

$HO_2 + H_2O$ (aq) $\rightarrow$ products

Experimental data

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

Comments

(a) Uptake of HO_2 ($5\text{-}30 \times 10^{10}$ molecule cm^{-3}) to a film (0.2 mm thick) of de-ionised water, or water containing 10^{-3} M $CuSO_4$. HO_2 was formed in the reaction of F with H_2O_2 and detected as OH after reaction with NO. HO_2 uptake was limited by diffusion through the 1 Torr of He bath gas. Levels of HO_2 were sufficiently low to neglect loss due to gas-phase self-reaction. Addition of $CuSO_4$ had no effect on HO_2 loss rates.
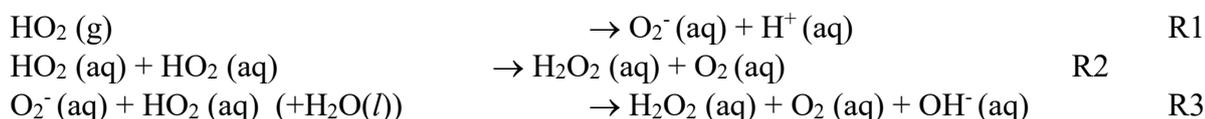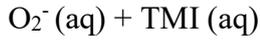
Preferred Values

Parameter	Value	T/K
α_b	> 0.2	270-300
Reliability		
$\Delta (\log \alpha_b)$	undetermined	

Comments on Preferred Values

The sole experimental study of the uptake of HO_2 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 HO_2-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 $(NH_4)_2SO_4$ and NH_4HSO_4 (see datasheets VI.A3.09 and VI.A3.10). We thus prefer a value of α_b of > 0.2 in order to have an internally consistent recommendation for all aqueous substrates.

The uptake of HO_2 in aqueous solution is presently believed to be driven by self-reaction and acid-base dissociation of HO_2 (pKa ~ 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:

HO_2 (g)	$\rightarrow O_2^-$ (aq) + H^+ (aq)	R1
HO_2 (aq) + HO_2 (aq)	$\rightarrow H_2O_2$ (aq) + O_2 (aq)	R2
O_2^- (aq) + HO_2 (aq) (+$H_2O(l)$)	$\rightarrow H_2O_2$ (aq) + O_2 (aq) + OH^- (aq)	R3

$$O_2^- \text{ (aq) + TMI (aq)} \qquad\qquad \rightarrow \text{ products} \qquad\qquad\qquad \text{R4}$$

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:

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

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

$H^{\text{eff}} = H^{HO2} (1+K_{\text{eq}}/[H^+]$, $K_{\text{eq}} = 2.1 \times 10^{-5}$ M at 298 K (Jacob, 2000) and $H^{HO2} = 9.5 \times 10^{-6}$ exp(5910/T) M atm^{-1} (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. $D_l = \{1 \times 10^{-5}(T/298)\}/(1.09 \times 10^8 \exp(-0.068T) + 0.873)$ cm^2 s^{-1} (Schwartz, 1984; Thornton et al., 2008) where the denominator in the D_l term was derived from a fit to the water viscosity data of Hallett (1963). 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. As discussed by Thornton et al. (2008) and Mozurkewich et al. (1987), the apparent first order loss rate coefficient of HO_2 / O_2^- in the presence of TMI is around three orders of magnitude lower than based on the second order rate coefficient for dilute aqueous solutions (Bielski et al., 1985) possibly due to high ionic strength effects. Therefore, the value recommended for deliquesced organic and inorganic aqueous aerosols is most likely too low for dilute aqueous solutions. We therefore do not provide a recommendation for k_{TMI} for this case. Further heterogeneous kinetics experiments with variation of pH, [Cu(II)] and use of other TMI are needed to constrain γ for dilute aqueous solutions.

According to the reaction scheme (R1-R4) above, in the absence of TMI, the rates of loss of aqueous-phase HO_2 are quadratically dependent on $[HO_2]_{\text{aq}}$ and $[O_2^-]_{\text{aq}}$ and are thus strongly dependent on the gas-phase concentration of HO_2. At low, atmospherically relevant, HO_2 concentrations 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 also in the George et al. (2013) and Lakey et al. (2016) data for $(NH_4)_2SO_4$ and for aqueous organic aerosols. Thornton and Abbatt (2005) suggest that the rate of loss of HO_2 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):

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_{\text{self}}} \qquad \frac{1}{\Gamma_{\text{self}}} = \frac{3cN_{Av}}{8000(H^{\text{eff}}RT)k_{aq}[HO_2]r_p} \qquad (2)$$

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

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

Equations (1) and (2) consistently describe the uptake of HO_2 in the presence and absence of transmission metal ions. At low HO_2 concentrations, the overall γ can be obtained by adding the corresponding resistors:

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

Equation (4) explains the measured dependence of γ over the full range of Cu(II) concentrations, with the caveats for the rate coefficients for dilute aqueous solutions mentioned above. As discussed by Hanson et al. (1992) and Thornton and Abbatt (2005), the parameterization suggested here is very sensitive to the solubility of HO_2 (H^{HO2}), its temperature dependence and on the aerosol pH. 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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