IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A3.09 HET_O_9

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$HO_2 + NH_4HSO_4$ (aq) → products

Experimental data

	Temp./K	Reference	Technique/ Comments
Accommodation coefficients: α			
> 0.2	293	Mozurkewich et al, 1987	AFT (a)

Comments

(a) Uptake of HO_2 (10^8-10^9 molecule cm^{-3}) to deliquesced particles (0.05 to 0.1 μm) containing $CuSO_4$. HO_2 was formed by passing a mixture of H_2 and H_2O over a hot Nichrome wire and detected by chemically amplified conversion to NO_2. Levels of HO_2 were sufficiently low to neglect loss due to gas-phase self-reaction. The average experimental uptake coefficient was $\gamma = 0.4 \pm 0.08$ with no measurable dependence on the $CuSO_4$ molality between 0.006-0.07 M. The uptake coefficient dropped sharply when the $CuSO_4$ solution was less than ~10^{-3} M and was zero when less than 10^{-4} M. The authors make a conservative estimate of 0.2 for the lower limit to the accommodation coefficient, α_b.
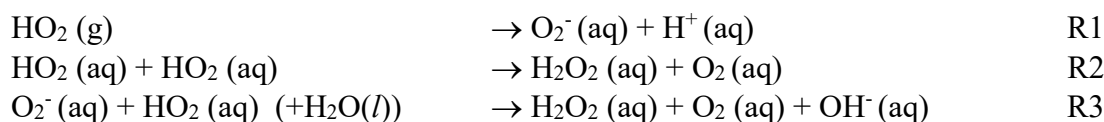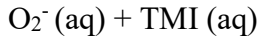
Preferred Values

Parameter	Value	T/K
α_b	> 0.2	293 K
k_{TMI} (M^{-1} s^{-1})	5×10^5	290 – 300
k_2 (M^{-1} s^{-1})	2.4×10^9 exp(-2360/T)	
k_3 (M^{-1} s^{-1})	1.6×10^{10} exp(-1510/T)	

Comments on Preferred Values

The single experimental investigation of HO_2 uptake to NH_4HSO_4 derived a lower limit to the accommodation coefficient of 0.2, which is consistent with results on other aqueous surfaces where uptake coefficient as large as 0.5 have been measured (e.g. VI.A3.10).

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

O$_2^-$ (aq) + TMI (aq)   → products   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:

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

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

$$H^{eff} = H^{HO2}(1 + K_{eq}/[H^+])$$

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

$H^{HO2} = 9.5 \times 10^{-6} \exp(5910/T)$ 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. For low viscosity aqueous (NH$_4$)HSO$_4$ solutions, the diffusivity of HO$_2$ can be approximated by that in pure water (Schwartz, 1984; Thornton et al., 2008):

$$D_l = \{1\times10^{-5}(T/298)\}/(1.09\times10^8 \exp(-0.068T) + 0.873)\ \text{cm}^2\ \text{s}^{-1}$$

where the denominator was derived from a fit to the water viscosity data of Hallett (1963). This parameterization 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. As discussed by Lakey et al. (2015), Thornton et al. (2008) and Mozurkewich et al. (1987), the apparent first order loss rate coefficient of HO$_2$ / O$_2^-$ is much lower than expected and must be around three orders of magnitude lower than the value for dilute aqueous solutions (Bielski et al., 1985). Taking the value $k_{TMI} = 5 \times 10^5$ M^{-1} s^{-1} (without specifying the difference in reactivity for HO$_2$ / O$_2^-$), Eq. (1) explains the rapid drop of uptake below 10^{-2} M Cu(II) and below detection limit for Cu(II) contents below 10^{-3} M in the study of Mozurkewich et al. (1987). We provide large error bounds on gamma, and further experiments are needed with variation of pH and Cu(II) and other TMI to constrain it further.

According to the reaction scheme (R1-R4) above, in the absence of TMI, the rate of loss of aqueous-phase HO$_2$ is quadratically dependent on [HO$_2$]$_{aq}$ and [O$_2^-$]$_{aq}$ and is thus strongly dependent on the gas-phase concentration of HO$_2$. At low HO$_2$ 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). 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):

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

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

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

We suggest using equations (1) and (2) to consistently describe uptake of HO$_2$ in presence and absence of transmission metal ions.

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.

Further experiments with systematic variation of different transition metals, aerosol pH and HO_2 concentration would help to better constrain the parameterization.

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.

Lakey, P. S. J., George, I. J., Whalley, L. K., Baeza-Romero, M. T., and Heard, D. E.: Environ. Sci. Technol., 49, 4878-4885, 2015.

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.

Thornton, J. A., Jaegle, L., and McNeill, V. F.: J. Geophys. Res. 113, doi:D05303 10.1029/2007jd009236, 2008.