IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.2 HET_SL_2

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$HO_2 + H_2SO_4$ (aq) $\rightarrow$ products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ			
> 0.05	249.5	Hanson et al, 1992	WWFT-LIF (a)
> 0.1	243	Gershenzon et al., 1995	CRFT-EPR (b)
0.055 ± 0.02	223	Cooper and Abbatt, 1996	CWFT-RF (c)
< 0.01	295	Thornton and Abbatt, 2005	AFT-CIMS (d)
Accommodation coefficients: α_b			
> 0.2	223	Cooper and Abbatt, 1996	CWFT-RF (c)
0.8 ± 0.3	295	Thornton et al, 2005	AFT-CIMS (d)

Comments

(a) Uptake of HO_2 (5-30 $\times$ 10^{10} molecule cm^{-3}) to 28 wt. % H_2SO_4 films $\approx$ 0.3 mm thick. 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.

(b) HO_2 was detected either directly ($[HO_2]$ = 3-5 $\times$ 10^9 molecule cm^{-3}) or as OH following reaction with NO ($[HO_2]$ = 1-3 $\times$ 10^{11} molecule cm^{-3}). H_2SO_4 films were either 80 or 96 wt. %.

(c) Uptake of HO_2 to 55 wt % H_2SO_4 to determine γ. α was determined by doping the H_2SO_4 with with 0.1 M $CuSO_4$. HO_2 was formed in the reaction of F with H_2O_2 and detected as OH after reaction with NO.

(d) H_2SO_4 aerosol (diameter $\approx$ 100 nm) at 35 – 40 % RH. α was determined by doping the H_2SO_4 aerosol (made from 0.0005 – 0.005 M aqueous solutions) with 0.1 M $CuSO_4$. No dependence on RH was observed over the small range covered. HO_2 (at concentrations of $\approx$ 4 $\times$ 10^{10} molecule cm^{-3}) was formed in the reaction of H with O_2 and detected as O_2^- using F^- as chemi-ion or as HSO_4^- following conversion to H_2SO_4 (addition of NO and SO_2) and ionisation with I^-. Loss of HO_2 to 55 wt. % H_2SO_4 was indistinguishable from loss due to the reactor walls, hence the upper limit to γ.
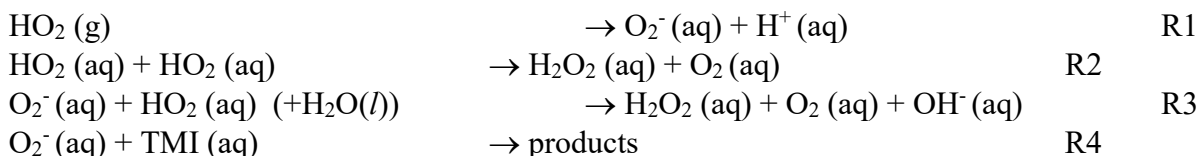
Preferred Values

Parameter	Value	T/K
α_b	> 0.2	220 - 300
γ	0.005	220 - 300
k_{TMI} (M^{-1} s^{-1})	5×10^5	220 - 300
k_2 (M^{-1} s^{-1})	$2.4 \times 10^9 \exp(-2360/T)$	220 - 300
k_3 (M^{-1} s^{-1})	$1.6 \times 10^{10} \exp(-1510/T)$	220 - 300
uncertainty		
$\Delta\log(k_{TMI})$	1	220 - 300
$\Delta\log(k_{2,3})$	0.3	220 - 300

Comments on Preferred Value

Two studies (Cooper and Abbatt, 1996; Thornton and Abbatt, 2005) show that bulk mass accommodation of HO_2 to sulphate aerosol is very efficient with values of α_b close to unity. We prefer the lower limit of 0.2 in order to provide an internally consistent recommendation for all aqueous substrates (see, 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)	$\rightarrow O_2^-$ (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^- (aq) + TMI (aq)	$\rightarrow$ 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; the preferred value is justified in the datasheet VI.A3.10.

The parameterisation of Shi et al. (2001) can be used to estimate the proton activity:

$[H^+] = \exp[60.51 - 0.095wt + 0.0077wt^2 - 1.61 \times 10^{-5}wt^3 - (1.76 + 2.52 \times 10^{-4} wt^2)T^{0.5} + (-805.89 + 253.05wt^{0.076})/T^{0.5}]$

The diffusion coefficient for HO_2 is parameterized by $D_{l,HONO} = C_{HO2} T/\eta$; with $C_{HO2} = 1.04 \times 10^{-7}$ cm^2 cP K^{-1} s^{-1}, estimated as suggested by Klassen et al. (1998) using a molar volume of 18 cm^3 mol^{-1} (da Silva et al., 2006). For the viscosity, η, the parameterization presented by Shi et al. (2001) fits well to data by Williams and Long (1995) but extends into tropospherically more relevant dilute solutions at high temperature:

$\eta = A T^{-1.43} \exp(448K /(T-T_0))$,

with $A = 169.5 + 5.18\,(wt) - 0.0825\,(wt)^2 + 3.27 \times 10^{-3}\,(wt)^3$,

and $T_0 = 144.11 + 0.166\,(wt) - 0.015\,(wt)^2 + 2.18 \times 10^{-4}\,(wt)^3$

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.

In the absence of TMI, the rates of loss of aqueous-phase HO_2 are quadratically dependent on $[HO_2]_{aq}$ and $[O_2^-]_{aq}$. The uptake coefficient is thus strongly dependent on the gas-phase concentration of HO_2 and becomes small at low, relevant HO_2 concentrations. 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):

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

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 the uptake of HO_2 in the presence and absence of transmission metal ions. As Figure 1 shows, equation (2) is in particular consistent with the lower limits reported by Hanson et al. (1992) and the upper limit estimated by Thornton and Abbatt (2005) at 295 K, a result of the interplay of the temperature dependence of solubility and the rate coefficients (eq. 3). 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 pH. The extrapolation to low temperatures, the effect of high viscosity and high proton activity introduce substantial uncertainty represented by expanded error limits.

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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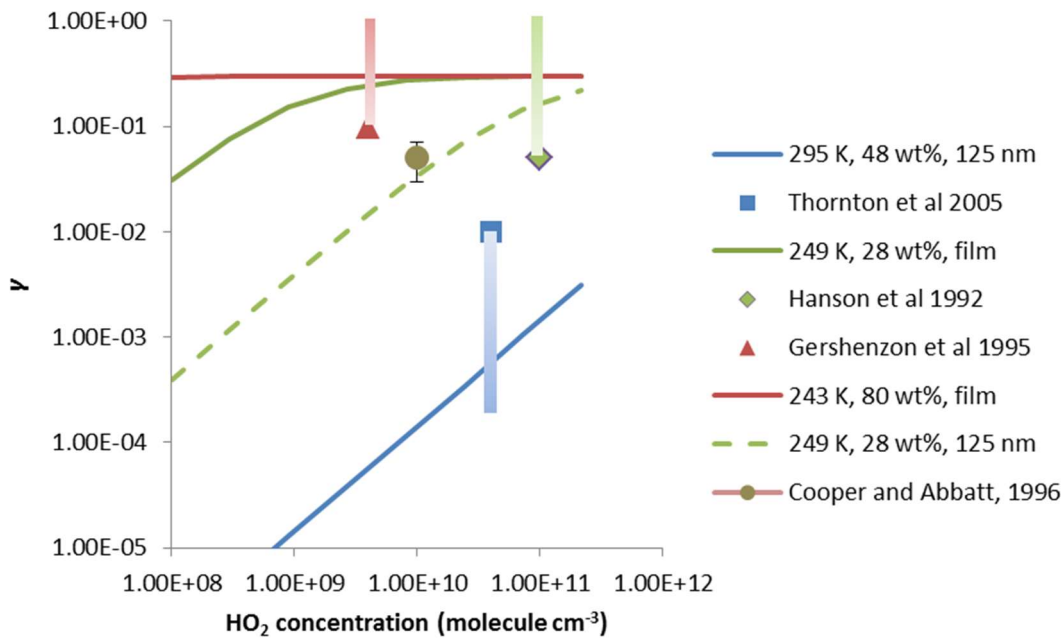
Figure 1: Uptake coefficient of HO$_2$ on sulfuric acid as a function of HO$_2$ concentration. Symbols: data, with the lighter end of the vertical bars indicating the upper or lower limit for part of the data points; lines: γ based on Equation (2).