IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A4.28 HET_SL_28

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$BrONO_2 + H_2SO_4$ (aq) → products

Experimental data

Parameter	H_2SO_4 / wt%	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ				
0.5(+0.5, -0.25)	45	210	Hanson and	CWFT-CIMS (a)
0.4(+0.6, -0.2)	60	210	Ravishankara, 1995	
0.3(+0.7, -0.1)	70	220		
1.0 (0.1 μm radius)	48	229	Hanson et al., 1996	AFT-CIMS (b)
0.81 (0.1 μm radius)	47	249		
0.75 (0.1 μm radius)	66	272		
0.26 (0.1 μm radius)	76.5	294		
0.8	66	250	Hanson, 2003	RWFT and AFT-CIMS (c)
0.95	72	250		
0.5	75	250-293		
0.2	79	250-293		
0.15	82	250-293		

Comments

(a) Uptake measurement on a wetted wall flow tube coupled to CIMS detection. The source ion was SF_6^- and $BrONO_2$ and HOBr were monitored as $BrONO_2 \bullet F^-$ and SF_5O^-, respectively. Large corrections (factor 5) to the observed loss rates of $BrONO_2$ were made to take diffusive effects into account. HOBr was detected as the primary hydrolysis product of the title reaction at a typical partial pressure of $BrONO_2$ of (1-3) x 10^7 molecule cm^{-3}.

(b) Aerosol flow reactor operated at total pressures (N_2) ranging from 239 ± 40 (majority of experiments) to 825 ± 13 mbar between 249 and 298K. $BrONO_2$ (10^{12} molecule cm^{-3}), HOBr and HNO_3 were detected as $BrONO_2 \bullet F^-$, SF_5O^- and NO_3^-, respectively, using SF_6^- as reagent ion. The sulfuric acid aerosol particle size distribution was log-normal with a typical surface area-weighted peak radius of 0.1μm. Uptake coefficients γ were independent of the particle radius over a range of 0.05 to 0.17 μm for 78% wt H_2SO_4 particles at 298K. In some experiments, HCl was added to the H_2SO_4 in order to trap HOBr (as BrCl) in order to prevent potential regeneration of $BrONO_2$ from reaction of HNO_3 with HOBr.

(c) Rotating CWFT with stirring of the H_2SO_4 film (58 – 85 wt. %, 240 - 293 K) at 0.5 – 2.6 mbar total pressure. The aerosol flow tube was operated at room temperature and 160 Torr total pressure. Initial $BrONO_2$ concentration was 10^{11}-10^{12} cm^{-3} in the RWFT and 10^{12}-10^{13}

cm^{-3} in the AFT. Uptake coefficients showed a strong fall off towards high H_2SO_4 wt%, a few representative values are listed in the table.

Preferred Values

Parameter	Value	T/K
α_b	0.8	210 - 300
Γ_b	0.11 + exp(29.2 -0.40 wt)	210 – 230
Reliability		
$\Delta\log(\alpha_b)$	± 0.10	210 - 300
$\Delta\log(\gamma)$	± 0.15	210 - 300

Comments on Preferred Values

The three studies yield consistent results, with values of γ close to unity in diluted (45 wt. %) H_2SO_4, and decreasing to 0.15 at ~80 wt. %. Owing to the large rate constant for $BrONO_2$ hydrolysis in the condensed phase (the authors estimate a diffusion-limited rate constant k^{II} on the order of 10^9 M^{-1} s^{-1}) no size-dependence of γ is expected, because the reacto-diffusive length, $(D_l/k^{II})^{0.5}$ is short. HOBr (and HNO_3) is seen as the major product of $BrONO_2$ uptake to H_2SO_4. Some Br_2 was also observed, which likely stems from reactions of HOBr and not from an additional $BrONO_2$ loss process.

Since the $BrONO_2$ solubility is not known, a detailed parameterisation of the uptake coefficient is not possible. We therefore adopt the expression suggested by Hanson (2003) that reproduces the uptake coefficients measured on both bulk and aerosol from all three studies:

$$\frac{1}{\gamma} = \frac{1}{\alpha_b} + \frac{1}{\Gamma_b}$$

References

Hanson, D.R., Ravishankara, A.R.: Geophys. Res. Lett. 22, 385-388, 1995.

Hanson, D.R., Ravishankara, A.R., Lovejoy, E.R.: J. Geophys. Res. 101, 9063-9069, 1996.

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