IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.16 HET_SL_16

$HOBr + H_2SO_4 \rightarrow$ products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ			
> 0.06 (60 wt. % H_2SO_4)	228	Abbatt, 1994	CWFT-MS (a)
Solubility: H (M atm^{-1})			
3.8×10^5 (69.8 wt. %)	212	Abbatt, 1995	CWFT-MS (b)
9.0×10^4 (69.8 wt. %)	228		
$\approx 1 \times 10^6$ (60 wt. % H_2SO_4)	210	Hanson and Ravishankara, 1995	CWFT-CIMS (c)
4.6×10^{-4} exp {(4500 ± 480)/T}	213 - 238	Waschewsky and Abbatt, 1999	CWFT-MS (d)
1.4×10^5 (58 – 69 wt. %)	250	Hanson, 2003	CWFT-CIMS (e)
$\approx 4 \times 10^4$	260		
$\approx 2.5 \times 10^4$	270		

Comments

(a) HOBr ($0.5 – 5 \times 10^{12}$ molecule cm^{-3}) was generated by the reaction sequence: $H + NO_2 \rightarrow OH + NO$ and $OH + Br_2 \rightarrow HOBr$, ionised by electron impact and detected as HOBr$^+$. The carrier gas flow was humidified to maintain the H_2SO_4 concentration.

(b) HOBr ($<1 \times 10^{12}$ molecule cm^{-3}) was generated by the reaction sequence: $H + NO_2 \rightarrow OH + NO$ and $OH + Br_2 \rightarrow HOBr$, ionised by electron impact and detected as HOBr$^+$. The carrier gas flow was humidified to maintain the H_2SO_4 concentration (69.8 wt %). Some evidence was found for a second-order component of HOBr loss due to self reaction. Values of $HD_l^{1/2} = (30 ± 15)$ and $(20 ± 10)$ M atm^{-1} cm s$^{-1/2}$ were obtained at 212 and 228, respectively and converted to the values listed in the table using diffusion coefficients calculated as described by Klassen et al. (1998).

(c) HOBr detected using SF_6^- chemi-ions. The evolution of the HOBr signal following uptake of BrONO$_2$ ($1-3 \times 10^{-7}$ Torr) to the H_2SO_4 surface was analysed to derive time dependent uptake coefficients and solubility. A value of $HD_l^{1/2}$ of 110 (± 40) M atm^{-1} cm s$^{-1/2}$ was converted to the solubility listed in the table using $D_l \approx 10^{-8}$ cm^2 s^{-1}.

(d) HOBr ($\approx 5 \times 10^{-10}$ atm, measured by UV absorption at 254 nm) was generated ex-situ by passing a humidified flow of Br$_2$ in He over HgO, ionised by electron impact and detected as HOBr$^+$. The carrier gas flow was humidified to maintain the H_2SO_4 concentration. The time dependent HOBr signal was used to derive values of $HD_l^{1/2}$ at different temperatures and H_2SO_4 concentrations (59.7 – 70.1 wt. %). The uptake to fresh H_2SO_4 surfaces was found to be as much as a factor of two larger than to surfaces previously exposed to HOBr. Only data from fresh surfaces is reported. Values of $HD_l^{1/2}$ were converted to H_{HOBr} using diffusion coefficients calculated as described by

Klassen et al. (1998). The temperature dependence of the solubility yields a heat of dissolution of -38 (± 4) kJ mol^{-1}.

(e) Rotating CWFT with stirring of the H_2SO_4 film (58 – 70 wt. %). HOBr (typically 10^{-10} atm) was generated by reacting $BrONO_2$ with water and detected using SF_6^- chemi-ions. H_{HOBr} was determined by measuring the equibrium amount of HOBr taken up to a known volume of H_2SO_4. Correction was applied to take into account the uptake of e.g. Br_2O with the total error assigned as 50 %. The temperature dependence of the solubility yields a heat of dissolution of -52 (± 15) kJ mol^{-1}. Values of H_{HOBr} at tempertaures other than 250 K were not listed and no parameterisation was given, hence the values in the table at 260 and 270 K were taken from a plot and are approximate.

Preferred Values

Parameter	Value	T/K
H_{HOBr}	5.22×10^{-5} exp (5427 /T)	210 – 270

Reliability

$\Delta \log H_{HOBr}$	0.5	210 - 270

Comments on Preferred Value

At low HOBr concentrations its uptake is time dependent and reversible (Waschewsky and Abbatt, 1999; Hanson 2003) so that a net uptake coefficient is insufficient to describe the interaction, which is driven by solubility and liquid phase diffusion. Waschewsky and Abbatt (1999) suggest that the previous observation (Abbatt, 1995) of irreversible loss of HOBr to a H2SO4 surface was due to self-reaction caused by high [HOBr]. Waschewsky and Abbatt (1999) and Hanson (2003) found no significant variation of H_{HOBr} with H_2SO_4 concentration at any given temperature, potentially a result of protonation which may increase the effective solubility at high H_2SO_4 wt % and compensate the expected decrease in physical solubility.

The data of Waschewsky and Abbatt (1999) and Hanson (2003) were obtained in different temperature regimes and extrapolated data are in poor agreement with much larger values (at some temperatures by a factor of > 10) obtained by Hanson (2003). Hanson (2003) presents arguments that larger values of H_{HOBr} are more compatible with measurements of the rate coefficient for reaction of HOBr with HCl in H_2SO_4, which otherwise would exceed the diffusion limit. In addition, he argues that the use of time dependent uptake coefficients to derive H_{HOBr} is more prone to systematic error that measurements in an equilibrated solution that also do not require estimates of D_l. Following Hanson (2003), our preferred value for H_{HOBr} uses an average heat of solvation from Waschewsky and Abbatt (1999) and Hanson (2003), and the value of H_{HOBr} at 250 K derived by Hanson (2003).

References

Abbatt, J. P. D.: Geophys. Res. Lett. 21, 665-668, 1994.
Abbatt, J. P. D.: J. Geophys. Res. 100, 14009-14017, 1995.
Hanson, D. R.: J. Geophys. Res. 108, 2003.
Hanson, D. R. and Ravishankara, A. R.: Geophys. Res. Lett. 22, 385-388, 1995.
Klassen, J. K., Hu, Z. and Williams, L. R.: J. Geophys. Res. 103, 16197-16202, 1998.
Waschewsky, G. C. G. and Abbatt, J. P. D.: J. Phys. Chem. A 103, 5312-5320, 1999.