IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A4.26 HET_SL_26

The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, http://iupac.pole-ether.fr.
This data sheet evaluated: May 2010; last change in preferred values: May 2010.

HOBr + HCl (aqueous sulphuric acid aerosol)$\rightarrow$ BrCl + H$_2$O

Experimental data

Parameter	wt% H$_2$SO$_4$	Temp./K	Reference	Technique/ Comments
γ(HOBr)				
0.023	69.8% (HCl = 0.22x10^{12}cm^{-3})	228	Abbatt, 1995	CWFT-MS (a)
0.060	(HCl = 0.96x10^{12} cm^{-3})			
0.12	(HCl = 2.5x10^{12} cm^{-3})			
0.20	(HCl = 6.0x10^{12} cm^{-3})			
0.2	60% (p(HCl) =2.7x10^{-7} mbar)	210	Hanson & Ravishankara, 1995	CWFT-MS (b)
γ(HCl)				
0.11±0.04	59.7% (p(HOBr) = 8x10^{-7} mbar)	228	Waschewsky and Abbatt, 1999	CWFT-MS (c)
0.032±0.008	65.6% (p(HOBr) = 1x10^{-6} mbar)	228		
0.060±0.015	70.1% (p(HOBr) = 3.4x10^{-5}) mbar)	228		
0.19	58%; (p(HOBr) = 1x10^{-5} mbar)	250	Hanson, 2003	CWFT-CIMS (d)
0.07				
0.011	62%; (p(HOBr) = 1x10^{-5} mbar)			
0.002	65%; (p(HOBr) = 1x10^{-5} mbar)			
	69.5%; (p(HOBr) = 1x10^{-5} mbar)			

Comments

(a) 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$_2$SO$_4$ concentration (69.8 wt %). Excess HCl (gas phase concentration (0.2-7.0) x 10^{12} molecule cm^3) added simultaneously with HOBr (>1 x 10^{12} molecule cm^3). HOBr loss was first order, and no sytematic dependence of γ on [HOBr] was observed. Using measured values of $HD_1^{1/2}$ for HOBr ((20 $\pm$ 10) M atm^{-1} cm s$^{-1/2}$) and for H* for HCl the cited γ value constrains the bimolecular rate constant for the HOBr + HCl reaction to be 1.4 x 10^5 M^{-1} s^{-1}.

(b) HOBr was generated from the hydrolysis reaction of BrONO2 on 60% H$_2$SO$_4$ and detected using SF$_6^-$ chemi-ions. BrCl was observed as a gas phase product indicating a fast effective bimolecular reaction on H$_2$SO$_4$. A bimolecular rate constant for the HOBr + HCl reaction of (0.3-1) x 10^5 M^{-1} s^{-1} was derived from the uptake data.

(c) HOBr ($\approx 5 \times 10^{-10}$ bar, 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 $HOBr^+$. Decay of HCl and formation of BrCl was measured in presence of excess HOBr. Uptake coefficients determined from both kinetic curves were within 10%. γ increased with $p(HOBr)^{1/2}$ at 65-70%. Bimolecular rate constants for the HOBr + HCl reaction derived from the uptake data using $H^*(HOBr)$ determined in the same study were in the range of $(1.6 - 270) \times 10^5$ M^{-1} s^{-1}, increasing strongly with wt% H_2SO_4 and less so with temperature (213 -228 K). The [H_2SO_4] dependence is attributed to an acid catalysed mechanism and the temperature dependence to diffusion limitation. The following expression is given for calculations of γ for stratospheric conditions: $k^{II} = \exp(0.542 \times (wt\% H_2SO_4) - 6.44\times10^3/T + 10.3)$

(d) 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. First order loss of HCl was measured in the presence of excess HOBr $(0.2-2.0) \times 10^{-10}$ bar. Γ_b was extracted assuming $\alpha = 1.0$, and was $\propto p(HOBr)^{1/2}$. Using H_{HCl} from Carslaw et.al. (1995) and H_{HOBr} determined in the same study (see reaction VI.A4.16) values of k^{II} were derived. The values ($k^{II} = (2.5-6.0) \times 10^7$ M^{-1} s^{-1} over the range 58 -69.5% H_2SO_4 at 250 K) showed a lower dependence on acid strength compared to results of Waschewsky, G. C. G. and Abbatt, J. P. D., (1999), obtained at lower temperatures.

Preferred Values

Parameter	Value	T/K
α_s	1.0	190 - 250
H^*_{HOBr}/M.bar^{-1}	$5.22 \times 10^{-5} \exp(5427/T)$	210 - 270
H^*_{HCl}/M.bar^{-1}	$(0.094-0.61X+1.2X^2) \exp(-8.68+(8515-10718X^{0.7})/T)$	203
k^{II}(M^{-1}s^{-1})	$\exp(154-1.63.W) \exp(-(38500-478.W)/T)$	200-230
$D_{l\ HCl}$/cm^{2}s^{-1}	7.8×10^{-8} T/η	190-240

W = wt% H_2SO_4 , X = mole fraction H_2SO_4

Reliability

$\Delta \log(\alpha)$	0.3	298

Comments on Preferred Values

The experimental studies show that the uptake coefficient of HOBr or HCl on H_2SO_4/H_2O containing HCl or HOBr increases with the concentration of the co-reactant in solution. The γ_{HOBr} values from the earlier study of Abbatt (1995) are uncertain because the assumed relative solubilities of HOCl and HCl were incorrect. The measured γ_{HCl} in the studies of Waschewsky and Abbatt (1999) and Hanson (2003) agree well and the γ values show a strong increase with the water content of the H_2SO_4 and a rather weak temperature dependence. The kinetics are consistent with the resistance model with a large surface accommodation coefficient ($\alpha_s = 1$), and rate of uptake controlled by bulk phase chemical reaction HOBr+HCl:

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_b} \qquad\qquad (1)$$

$$\Gamma_b = \frac{4RTH_{HOBr}}{c}\sqrt{D_l k^{II} H^*_{HCl} p_{HCl}} \qquad \text{for } \gamma_{HOBr} \qquad (2)$$

$$\text{or } \Gamma_b = \frac{4RTH^*_{HCl}}{c}\sqrt{D_l k^{II} H^*_{HOBr} p_{HOBr}} \qquad \text{for } \gamma_{HCl} \qquad (3)$$

where H^* are the Henry's solubility constants and D_l are the liquid diffusion coefficients for HOBr and HCl which are a function of mole fraction of H_2SO_4, X.

There are significant differences in the heterogeneous reaction rate constants derived from the experimental uptake coefficients in the two studies. Thus the values of k^{II} derived by Waschewsky and Abbatt, (1999) from their data at 213 - 238 K was a factor of ~ 8 lower than the values expected from extrapolation from the 250 K value of k^{II} derived by Hanson (2003), based on an estimated activation energy of 15 kJ mol^{-1}. This discrepancy can be largely attributed to the use of different values for H(HOBr) in the derivation of k^{II}. The preferred value for H(HOBr) = 5.22×10^{-5} exp (5427 /T) is based on Hanson (2003) (see IUPAC evaluation VI.4.16), which showed only a weak dependence on acid strength in the range 60 - 70% H_2SO_4. Using this choice of H(HOBr) Hanson gave coherent set of k^{II} as a function of T and wt% H_2SO_4, from the results of all studies. k^{II} showed a very strong T-dependence at 60 wt% acid and a much weaker one at 70%. Hanson gives an expression for k^{II} for stratospheric conditions (W = wt% H_2SO_4):

$$k^{II}(\text{M}^{-1}\text{s}^{-1}) = \exp(154-1.63 \cdot W) \exp(-(38500-478 \cdot W)/T)$$

This equation reproduces the experimentally derived k^{II} values at 210 – 228 K but the predicted values at 238 and 250 K are over estimated by a factor of 3 and 6 respectively. Nevertheless this is the recommended expression to calculate the values of the uptake coefficients for stratospheric conditions, using eqs.(1)–(3). The X-dependent expressions used for H^*_{HCl}(based on Shi et al, 2001; see this evaluation: VI.A4.14) and for H^*_{HOBr} (based on Hanson, 2003; see this evaluation: VI.A4.16), are given in the Table of preferred values. The expression for D_l(HCl) from Klassen et al.,1998, based on viscosity data given by Shi et al., 2001 (see this evaluation: VI.A4.25).

Figure 1 shows a comparison of calculated γ_{HCl} with selected experimental values grouped for acid strengths of ~59, 65 and 70%. The prediction is only good for lower acid strengths and temperatures.

References

Abbatt, J. P. D.: J. Geophys. Res. 100, 14009-14017, 1995.

Hanson, D.R. and Ravishankara, A.R.: Geophys. Res. Lett. 22, 385 (1995).

Hanson, D.R.: J. Phys. Chem. A102, 4794 (1998)

Hanson, D. R.: J. Geophys. Res. 108, doi:10.1029/2002JD002519, 2003.

Klassen, J. K., Hu, Z. and Williams, L. R.: J. Geophys. Res. 103, 16197, 1998.

Shi, Q., Jayne, J. T., Kolb, C. E., Worsnop, D. R., and Davidovits, P.: J. Geophys. Res., 106, 24259, 2001.

Waschewsky, G. C. G. and Abbatt, J. P. D.: J. Phys. Chem. A 103, 5312 1999.

Figure 1: Plot of p(HOBr) dependence of uptake coefficient γ(HCl) at different H_2SO_4wt%. symbols show experimental data: open symbols = 70%; half filled symbols = 65%; closed symbols = 59%. Lines show predicted uptake coefficients using recommended parameters. Temperature = 213 - 250 K.

γ(HBr+ HOBr) 213 - 250 K