IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.11 HET_SALTS_11

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HOBr + Cl^-/Br^- (aq) → products

Experimental data

Parameter	aqueous solution	Temp./ K	Reference	Technique/ Comments
Uptake coefficients, γ				
> 0.2	NaCl (pH 0.3, 75 % RH)	295	Abbatt and Waschewsky, 1998	AFT-CIMS (a)
> 0.2	NaCl (pH 7.2, 75 % RH)			
< 1.5 × 10^{-3}	NaCl (unbuffered, 75 % RH)			
8 × 10^{-3}	NaCl and Natural salt (pH ≈ -1 to –0.7, RH > 75%)	296	Pratte and Rossi, 2006	AFT-MS (b)
Accommodation coefficient, α				
> 0.01	NaCl / NaBr (pH 2-5)	274	Fickert et al., 1999	WWFT-MS (c)
0.6 ± 0.2	NaBr	296 ± 2	Wachsmuth et al., 2002	AFT (d)

Comments

(a) Flow tube at 933-1013 mBar N_2. Number density (1-4 × 10^4 cm^{-3}) and diameter (2-4 μm) of the NaCl particles were measured using an optical particle counter. HOBr (2-10 × 10^{12} molecule cm^{-3}), was made by passing damp N_2 with traces of Br_2 over HgO and was detected as SF_5O^- using SF_6^- chemi-ions. No uptake observed to unbuffered and non-acidified chloride solutions. Uptake coefficient to acidified and buffered solutions is a lower limit, owing to diffusion limitations.

(b) Atmospheric pressure flow tube. Aerosols (≈ 200-300 nm diameter, 1.7 - 11 × 10^{-4} cm^2 cm^{-3} total surface area density) were made from acidified salt solutions (0.034 M Cl^-) at pH of 1. The salts used were pure NaCl, re-crystallised sea-salt (RSS) and natural sea-salt (NSS). The composition of the aerosol (1.7 – 4.4 M Cl^-, 2.5 – 6.4 M H_2SO_4) was varied by varying the relative humidity. Measured uptake coefficients were found to suddenly increase from ≈ 2 × 10^{-3} to 8 × 10^{-3} at RH ≈ 75–80 % for NaCl and RSS and remain high. For NSS a different behaviour was observed with a peak in γ (also ≈ 8 × 10^{-3}) at RH = 75 % and lower values (factor of 4 or more) at both higher and lower RH.

(c) Slow flowing aqueous film (50 – 100 μm thick) on the internal surface of a flow tube operated at ≈ 13-35 mbar He or N_2. HOBr, Br_2 and BrCl were detected as positive ions using electron impact ionisation. HOBr (≈ 10^{12} molecule cm^{-3}) was eluted into the flow tube from an aqueous solution. The lower limit to α was obtained from the pressure dependence of the uptake coefficient to an acidified film and assuming a value for the diffusion coefficient of HOBr in H_2O.

(d) Very low concentrations (≈ 300 molecule cm^{-3}) of HOBr detected using radioactive labelling. Uptake to 0.2 M NaBr aerosol particles (diameter 50-60 nm) at RH = 37 % and pH < 6. A small correction (4 %) for diffusion was applied.

Preferred Values

Parameter	Value	T/K
α_b	0.6	296
k_{ter} (M^{-2} s^{-1})	> 5.6×10^9	296
H (M atm^{-1})	6.1×10^3	296
D_l (cm^2 s^{-1})	1.4×10^{-5}	296

Reliability

$\Delta \log (\alpha_b)$	±0.3

Comments on Preferred Values

The large uptake coefficients reported for HOBr reacting with acidified aqueous bromide and chloride indicate that the accommodation coefficient is large (Abbatt and Waschewsky, 1998; Wachsmuth et al, 2002) and possibly unity. In terms of the resistance model, the uptake coefficient for HOBr reacting with sea-salt is given by:

$$\gamma = \left\{ \frac{1}{\alpha} + \frac{c}{4HRT(D_l k')^{0.5}} \right\}^{-1}$$

where $k' = k_{ter}\,[H^+][Cl^-]$ and the ionic concentrations are in M. R is 8.206×10^{-2} L atm K^{-1} mol^{-1}. The termolecular rate constant, k_{ter}, was taken from Vogt et al. (1996), the solubility and diffusion coefficient for HOBr were taken from Frenzel et al. (1998).

This expression predicts uptake coefficients that are close to the accommodation coefficient for pH < 7 when applied to fresh sea-salt with $[Cl^-]$ ≈ 5.3 M. This is in accord with the large lower limit to the uptake coefficient measured by Abbatt and Waschewski, but is higher than the uptake coefficients (factor 20) determined by Rossi and Pratte, 2006. The observation of much lower uptake coefficients when the droplets are not acidified and / or buffered (Abbatt and Waschewsky, 1998) is related to rapid depletion of available $[H^+]$ when using large concentrations of HOBr.

The important aqueous phase reactions in sea-salt aerosol containing chloride and bromide ions may be briefly summarised as follows:

$HOBr + Cl^- + H^+$	$\rightarrow BrCl + H_2O$	R1
$BrCl + Br^-$	$\Leftrightarrow Br_2Cl^-$	R2
Br_2Cl^-	$\Leftrightarrow Br_2 + Cl^-$	R3

The relative efficiency of Br_2 and BrCl release from acidified halide solutions (pH < 3 or buffered to < 5.6) with varying bromide / chloride ratios was found (Fickert et al., 1999) to be consistent with aqueous phase equilibrium constants for R2 and R3 (Wang et al., 1994).

Following bulk accommodation to salt solutions with the approximate composition of sea-water ([Cl^-] / [Br^-] ≈ 700), HOBr reacts almost exclusively with H^+ / Cl^- to release mainly Br_2. Only at reduced [Br^-] are significant amounts of BrCl released (Fickert et al., 1999). Fickert et al (1999) found that yields of Br_2 (or BrCl at low Br^-) were close to 100 % of the HOBr taken into solution as long as the pH was lower than ≈ 7.

Several experimental investigations of the uptake of HOBr to dry and frozen halide surfaces (both pure chloride or bromide or mixed) have revealed a similar chemistry to that outlined above (Kirchner et al., 1997; Mochida et al., 1998; Chu et al., 2002; Huff and Abbatt, 2002, Adams et al, 2002). On pure chloride samples, BrCl is released at high yield and on pure bromide samples, Br_2 is the sole product. On mixed chloride / bromide samples both Br_2 and BrCl are observed, with a dependence on initial composition and temperature of the surface.

References

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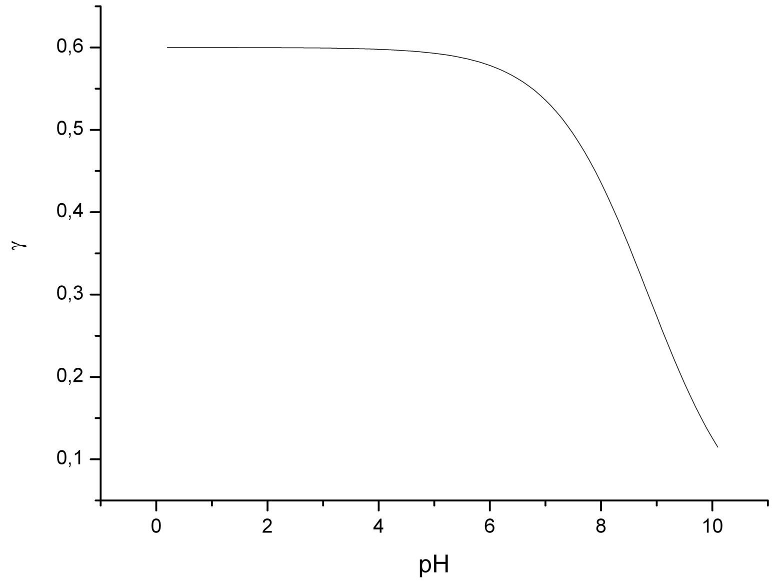

Uptake coefficients for HOBr on aqueous salt aerosol with $[Cl^-]$ = 5.3 M calculated with the parameterisation given above.