IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.13 HET_SALTS_13

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BrCl + Br^-(aq) → Products

Experimental data

Parameter	aqueous solution	Temp./K	Reference	Technique/ Comments
Accomodation coefficient, α				
0.33 ± 0.18		270 - 285	Katrib et al., 2001	DT-MS (a)

Comments

(a) BrCl was eluted into the gas phase from an aqueous solution and detected by mass spectrometer at *m/z* = 116. Br_2 and Cl_2 were present as impurities. Droplet size was ≈ 150 μm. The uptake of BrCl to bromide solutions did not follow first-order kinetics and no values of γ were reported. The accommodation coefficient was ontianed from experiments using a different aqueous phase scavenger of BrCl. No uptake was observed for pure H_2O aat pH = 5.6 ($\gamma < 10^{-3}$).

Preferred Values

Parameter	Value	*T*/K
α_b	0.33	270 - 280
Reliability		
Δ log (α)	± 0.5	270 - 280

Comments on Preferred Values

The only experimental study of the uptake of BrCl to bromide containing aqueous solutions (5×10^{-2} M) (Katrib et al., 2001) did not return values of γ. This was reported as being due to complications involving reaction of Cl_2 impurity with the surface resulting in non first-order kinetics. BrCl is known to react in aqueous solutions with Br^- to form Br_2Cl, which is in equilibrium with Br_2 and Cl^-. The net reaction can be written as:

$$BrCl + Br^- \rightarrow Br_2 + Cl^-$$

Using the expression below and literature values for the aqueous-phase solubility of BrCl at 275 K (H = 4.6 M atm^{-1}, Bartlett and Margerum, 1999), the rate constant for reaction of BrCl with Br^- ($k_{Br} > 10^8$ M s^{-1}, Wang et al., 1994) an aqueous-phase diffusion coefficient of 10^{-5} cm^2 s^{-1} and the value of α reported above results in uptake coefficients between 0.02 and 0.2 when $[Br^-]$ is varied between 10^{-3} and 1 M. The rate of uptake is thus accommodation controlled at high $[Br^-]$ ($\gamma \rightarrow \alpha_b$) and chemically controlled at low $[Br^-]$. The calculated value for γ obtained at 5×10^{-2} M bromide ($\gamma \approx 9 \times 10^{-2}$) appears to be consistent with the raw data presented in Figure 2 of Katrib et al., from which (by comparison with uptake to NaI) γ is less than 0.1.

$\gamma_b = \left\{ \frac{1}{\alpha_b} + \frac{c}{4HRT(D_l k')^{0.5}} \right\}^{-1}$ and $k' = k_{Br}[Br^-]$ where $[Br^-]$ is the bromide activity.

This is however a simplification of the chemical interactions of molecular halogens in halide solutions, which are characterised by rapid equilibria involving several di- and tri-halogen species (Wang et al., 1999) and it is not obvious that a first-order analysis to obtain γ is appropriate. This may in part explain the observations of unusual kinetics of Katrib et al. (2001). Accurate modelling of the uptake and release of halogens from sea-water requires a more detailed treatment of the aqueous phase processes than possible here.
Studies of the uptake of BrCl to dry and frozen bromide containing surfaces indicate conversion to Br_2, as written above (Huff and Abbatt, 2000).

References

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