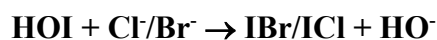


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.12 HET_SALTS_12

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This data sheet evaluated: 15th January 2009; last change in preferred values: 15th January 2009.



Experimental data

Parameter	[X]/M	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$</i>				
$\gamma = 2.2 \times 10^{-3}$	2 (Cl-) pure water	274	Braban et al, 2007	WWFT-EIMS (a)
$\gamma = 2.0 \times 10^{-3}$				

Comments

- (a) The uptake of HOI ($5\text{--}50 \times 10^{10}$ molecules cm^{-3}) to aqueous surfaces was studied in the wetted-wall flow tube with MS detection at $m/z = 144$. Several combinations of dissolved concentrations of Cl^- and Br^- in solutions of different pH were used. Uptake on pure water films was also measured. Experiments were all conducted at 274 K and at flow tube total pressures of 13 and 20 Torr. HOI was prepared *in situ* via the reaction of O atoms (generated in a microwave discharge) with $\text{C}_2\text{H}_5\text{I}$ or $\text{C}_3\text{H}_7\text{I}$ in a flow of He at reduced pressure. The uptake coefficient values were independent of composition or pH of the solution, except for pure water or very low electrolyte concentration. Calculations using HOI diffusion coefficients of $D_{\text{H}_2\text{O}}^{\text{HOI}} = 36.8 \text{ cm}^2 \text{ s}^{-1} \text{ Torr}^{-1}$, and $D_{\text{He}}^{\text{HOI}} = 318.2 \text{ cm}^2 \text{ s}^{-1} \text{ Torr}^{-1}$ at 274 K, obtained by extrapolation from the data of Holmes *et al.* (2000), showed that uptake is gas phase diffusion limited in all cases. Uptake of HOI produced dihalogens ICl and IBr which were partially released to the gas phase; IBr was preferentially released whenever Br^- was present with Cl^- .

Preferred Values

Parameter	Value	T/K
α	>0.1	298

<i>Reliability</i>		
$\Delta \log(\alpha)$	Not determined	298

Comments on Preferred Values

Uptake and reaction of HOI in aqueous films evidently occurs rapidly. However the results do not allow determination of the accommodation coefficient for HOI on aqueous surfaces as the uptake was diffusion limited, based on the diffusion coefficients reported by Holmes *et al.*,

(2001); only a lower limit of $\alpha_{\text{HOI}} > 2.2 \times 10^{-3}$ can be deduced. Other studies using different surfaces suggest that α is substantially higher. A lower limit of $\alpha_{\text{HOI}} = 0.3$ was given by Holmes *et al.* for HOI aqueous sulfuric acid surfaces, and $\alpha_{\text{HOI}} > 0.12$ on dry salt particles at 253 K. Mossinger and Cox observed a reactive uptake coefficient of $\gamma = 0.06$ on solid sea salt aerosol at 23%RH, which leads to formation of IBr and ICl products. Thus it is highly likely that the accommodation coefficient of HOI on aqueous surfaces is at least 0.1 at ambient temperatures.

Rate coefficients for $\text{HOI} + \text{X}^-$ in solution have not been reported. For HOBr the reaction is fast and is accommodation limited under atmospheric conditions, and the same is likely for reactive uptake of HOI into salt droplets. The dihalogen products ICl and IBr formed by reaction with Cl^- or Br^- will partition rapidly to the gas phase. In mixed halide solutions IBr is preferentially released whenever Br^- is present with Cl^- , and ICl is only released when Br^- has been chemically depleted.

References

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- Holmes, N. S., Adams, J. W. and Crowley, J. N., Phys. Chem. Chem. Phys., **3**, 1679, 2001.
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