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

Website: http://iupac.pole-ether.fr. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hard copy without explicit written permission.
This data sheet evaluated: 15th January 2009; last change in preferred values: 15th January 2009.

$HOI + Cl^-/Br^- \rightarrow IBr/ICl + HO^-$

Experimental data

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

Comments

(a) The uptake of HOI (5–50 × 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 C_2H_5I or C_3H_7I 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_{H2O}^{HOI} = 36.8 cm^2 s^{-1} $Torr^{-1}$, and D^{HOI}_{He} = 318.2 cm^2 s^{-1} $Torr^{-1}$ 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
Reliability		
$\Delta \log(\alpha)$	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 $\alpha_{HOI} > 2.2 \times 10^{-3}$ can be deduced. Other studies using different surfaces suggest that α is substantailly higher. A lower limit of $\alpha_{HOI} = 0.3$ was given by Holmes *et al*. for HOI aqueous sulfuric acid surfaces, and $\alpha_{HOI} > 0.12$ 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 HOI + 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

Braban, C. F.; Adams, J.W.; Rodriguez, D.; Cox, R.A., Crowley, J.N. and Schuser, G.: Phys. Chem. Chem. Phys., **9**, 3136, 2007.

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

Mossinger, J.A. and Cox, R.A., J.Phys.Chem.A, 105, 5165, 2001

Wachsmuth, M., Gaeggeler, H.W., Von Glasow, R., and Ammann, M., Atm.Chem.Phys., 2, 121, 2002.