IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.8 HET_SALTS_8

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HOCl + Cl⁻/Br⁻ (aq) → products

Experimental data

Parameter	Aqueous solution	Temp./K	Reference	Technique/ Comments
Uptake coefficients, γ				
$(0.39 - 1.79) \times 10^{-3}$	Natural salt (pH ≈ -0.7 to −1, RH 75% - 85 %)	296	Pratte and Rossi, 2006	AFT-MS (a)
$< 2 \times 10^{-4}$	Cl⁻ and RSS (pH ≈ -0.7 to −1, RH 75% - 85 %)			

Comments

(a) Atmospheric pressure flow tube. Aerosols (≈ 200-300 nm diameter, $1.7 - 11 \times 10^{-4}$ cm² 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 ($3 - 3.8$ M Cl⁻, $2.5 - 6.4$ M H_2SO_4) was varied by adjusting the relative humidity. No uptake of HOCl was observed for NaCl and RSS.

Preferred Values

Parameter	Value	T/K
γ	$< 2 \times 10^{-4}$	296

Comments on Preferred Values

Pratte and Rossi (2006) observed a low uptake coefficient for HOCl to natural sea-salt solutions, with a negative dependence of γ on relative humidity (i.e. with a positive dependence on ion concentrations). Uptake to pure chloride solution with the same composition was not observed.

The observation of Pratte and Rossi (2006), of measurable uptake onto aqueous NSS, but not to aqueous RSS (presumably with similar chloride / bromide composition) is difficult to understand. No products were observed in that study, so it is not possible to determine which reaction was driving the uptake. Pratte and Rossi also speculate that the high H_2SO_4 concentration may inhibit the uptake.

Inserting values for the termolecular rate constant for reaction of HOCl with H⁺ / Cl⁻ ($k_{ter} = 1.5 \times 10^4$ M⁻² s⁻¹, Wang and Margerum, 1994) the solubility of HOCl ($H_{HOCl} = 6.6 \times 10^2$ M atm⁻¹, Huthwelker et al., 1995) a value for the liquid phase diffusion coefficient of 2×10^{-5} cm² s⁻¹ and an accommodation coefficient (α_b) of between 1 and 0.01 into the expression below gives rise to values of γ between ≈ 0.1 and 0.01 at 290 K for 2 M Cl⁻ and a pH of 2.

$$\gamma = \left\{ \frac{1}{\alpha} + \frac{c}{4HRT(D_l k_{ter}[\text{H}^+][\text{Cl}^-])^{0.5}} \right\}^{-1}$$

Uptake coefficients of this magnitude should have been observable. Note that the forward reaction forms Cl_2 ($HOCl + H^+ + Cl^- \rightarrow Cl_2 + H_2O$) which may hydrolyse back to HOCl. The equilibrium constant $K = [HOCl][H^+][Cl^-] / [Cl_2]$ is circa 1×10^{-3} M^2 at 25 °C, so that, a pH of 2 and 2 M Cl^- result in an equilibrium ratio of HOCl / $Cl_2 \approx 0.05$.

Experiments on solid salt surfaces (Huff and Abbatt, 2000; Santschi and Rossi, 2005) revealed no reactivity for HOCl on chloride surfaces, but high reactivity for pure bromide and mixed bromide / chloride surfaces. The uptake of HOCl to a frozen, mixed chloride / bromide surface at 248 K has been shown to result in formation of mainly Br2 (and little BrCl) as gas-phase product. This presumably arises via conversion of BrCl (initially formed) with surface bromide.

$$HOCl + Br^- + H^+ \qquad \rightarrow BrCl + H_2O$$

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

Until further data is available, we prefer to recommend an upper limit to γ for reaction of HOCl with chloride / bromide containing aqueous particles.

References

Huff, A. K. and Abbatt, J. P. D.: J. Phys. Chem. 104, 7284-7293, 2000.

Huthwelker, T., Clegg, S. L., Peter, T., Carslaw, K. and Luo, B. P.: J. Atmos. Chem. 21, 81-95, 1995.

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Santschi, C. and Rossi, M. J.: Phys. Chem. Chem. Phys. 7, 2599-2609, 2005.

Wang, T. X. and Margerum, D. W.: Inorg. Chem. 33, 1050-1055, 1994.