

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.1 HET\_SALTS\_1

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The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This data sheet last evaluated: June 2009; last change in preferred values: June 2009.

### OH + aqueous sea salt aerosol → products

#### Experimental data

<i>Parameter</i>	RH/ %	<i>Temp./K</i>	Reference	Technique/ Comments
<i>Uptake coefficients: <math>\gamma</math></i>				
$\approx 0.2$ (82 % r.h.)	82	297	Knipping et al., 2000	(a)
$> 0.1$ (70 – 80 % r.h.)	70-80	298	Laskin et al., 2006	(b)

#### Comments

- (a) NaCl aerosol was produced using a nebulizer and dispersed in a chamber. Formation of  $\text{Cl}_2$  was observed with atmospheric pressure chemical ionization MS in presence of  $0.63$  to  $3.4 \times 10^{14} \text{ cm}^{-3}$  of  $\text{O}_3$  and 254 nm light in the chamber.  $\text{Cl}_2$  formation was simulated with a kinetic model that was extended in the follow up study by Knipping and Dabdub (2002). The uptake coefficient given in the table is the result of fitting the simulation to experimental data based on a parameterization of a surface reaction between OH and  $\text{Cl}^-$ . Parallel uptake of OH into the bulk of the particles (with  $\alpha_b = 0.1$ ) and aqueous phase chemistry therein was considered as well.
- (b) NaCl aerosol was produced using a nebulizer followed by drying, resulting in  $0.9 \mu\text{m}$  mean diameter particles that were deposited on 300 mesh gold grids. The grids were exposed to OH from  $\text{O}_3$  photolysis in an ambient temperature, atmospheric pressure flow cell. The humidity was first raised to 85% RH to safely induce deliquescence and then kept between 70 and 80 % for the experiments. OH concentrations were around a few  $10^9 \text{ cm}^{-3}$ . Offline particle analysis using SEM/EDX was used to determine Cl loss as a function of time using Na as reference. Wet particle sizes were inferred from dry particle sizes. The uptake coefficient is considered a lower limit as gas phase diffusion limitations existed.

#### Preferred Values

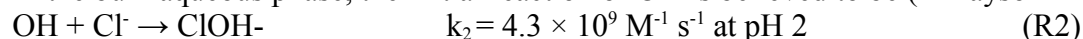
<b>Parameter</b>	<b>Value</b>	<b>T/K</b>
$\alpha_b$	$> 0.1$	298
$\gamma_{\text{gs}}$	$0.04 \times ([\text{Cl}^-]/M)$	298
<i>Reliability</i>		
$\Delta \log (\alpha_b)$	undetermined	
$\Delta \log (\gamma_{\text{ER}})$	1	298

## Comments on Preferred Values

The only direct experimental investigation of the reaction of OH with deliquesced NaCl provides a lower limit to the uptake coefficient (Laskin et al., 2006). The chamber experiment by Knipping et al. (2000) provided evidence for formation of Cl<sub>2</sub> from the reaction of OH with deliquesced NaCl due to an overall reaction (R1).



In the bulk aqueous phase, the initial reaction of OH is believed to be (Finlayson-Pitts, 2003)



Known bulk aqueous phase kinetics was unable to explain Cl<sub>2</sub> formation in the study by Knipping et al. (2000) and later by Knipping and Dabdub (2002). Therefore, an Eley-Rideal type surface reaction was proposed to bring experiment and simulation into agreement, which is recommended in parameterized form as a function of the chloride concentration. Note that in this case the surface process acts parallel to bulk accommodation and bulk reaction:

$$\gamma = \gamma_{gs} + \left( \frac{1}{\alpha_b} + \frac{1}{\Gamma_b} \right)^{-1} \text{ with } \Gamma_b = \frac{4HRT}{\bar{c}} \sqrt{D_1 k_b}$$

where  $k_b^1$  is the first order rate coefficient in the bulk aqueous phase, e.g., due to reaction (R2). However, in many cases multiple reactions may occur in parallel in the bulk. For the Henry's Law constant it is suggested to use the value recommended for pure water (see data sheet VI.A1.17, this evaluation).

Evidence for the formation of OH<sup>-</sup> was provided by Laskin et al. (2003) and by Shaka et al. (2007), who demonstrated formation of OH<sup>-</sup> in deliquesced MgCl<sub>2</sub>. For  $\alpha_b$ , we recommend the same lower limit as for dilute aqueous solutions.

On dry sea salt, measured uptake coefficients are on the order of 10<sup>-2</sup> as reviewed by Rossi (2003) and Finlayson-Pitts (2003). Recently, the humidity dependence of the uptake coefficient of OH with sea salt was observed to be consistent with the humidity dependent uptake of OH on MgCl<sub>2</sub> and CaCl<sub>2</sub>, the low deliquescing components of sea salt (Park et al., 2008, 2009), consistent with a much higher OH loss at the surface of hydrated halides.

## References

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