

## IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet VI.A1.17 HET\_H2OL\_17

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### OH (g) + H<sub>2</sub>O (l) → products

#### Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: <math>\gamma</math></i>			
$\gamma_{ss} > 3.5 \times 10^{-3}$	275	Hanson et al., 1992	WWFT-LIF(a)
(4.2±2.8)×10 <sup>-3</sup> pH 5.6	293	Takami et al., 1998	(b)
(8.2±2.6)×10 <sup>-3</sup> pH 1			
(1.2±0.3)×10 <sup>-2</sup> pH 11			
<i>Accommodation coefficients: <math>\alpha_b</math></i>			
1	281-312	Takami et al., 1998	(b)

#### Comments

- (a) OH [(0.5-3) × 10<sup>11</sup> molecule cm<sup>-3</sup>] was generated through the reaction H + NO<sub>2</sub> and was monitored using LIF. Deionized water was flowed down the vertical flow tube at 274.5 K and 12 mbar total pressure. The value listed in the table was corrected for gas phase diffusion. The diffusion coefficient for OH in H<sub>2</sub>O has been taken to be the value of the self-diffusion coefficient for H<sub>2</sub>O.
- (b) A carrier gas flow impinging on a flowing water surface at about 100mbar total pressure. The uptake coefficient was derived from the OH gradient above the liquid measured using laser-induced fluorescence and after correction for gas phase diffusion. The uptake coefficient was found to decrease during the first 300 ms. The observed pH dependence was in agreement with bulk reaction limited uptake due to reaction with HSO<sub>4</sub><sup>-</sup>, OH<sup>-</sup>, O<sup>-</sup> and self reaction, simulated with a kinetic model of diffusion and reaction in the bulk liquid. For the highest uptake coefficients, best agreement between model simulation and data was obtained for  $\alpha_b = 1$ . A slight negative temperature dependence of the uptake coefficient was observed.

#### Preferred Values

Parameter	Value	T/K
$\alpha_b$	>0.1	275 - 310
$H^*$	$\exp(1010/T) (1 + 1.2 \times 10^{-12} \times 10^{pH})$	275 - 310
<i>Reliability</i>		
$\Delta \log (\alpha_b)$	undetermined	
$\Delta \log (H^*)$	0.7	275 - 310

### Comments on Preferred Values

The available studies of the interaction of OH with liquid water agree that the bulk accommodation coefficient is large, likely close to 1. In both experiments, gas phase diffusion affected the observed kinetics. Hanson et al. (1992) likely observed uptake driven by the self reaction of OH in the bulk, if the Henry's Law coefficient is on the order of 100 M atm<sup>-1</sup>. Takami et al. (1998) come to a similar conclusion and explain their pH dependent data by applying a kinetic model for the bulk liquid using the following reactions (Buxton et al., 1988):



The expression for the effective Henry's Law constant given above is adopted from Takami et al., with the temperature dependence as suggested by Hanson et al. (1992). The temperature dependence of the rate constant of the OH self reaction in water above tropospheric temperatures has been investigated in detail by Elliot et al. (1990) and Janik et al. (2007).

At low pH (due to the fast reaction with HSO<sub>4</sub><sup>-</sup>) and high pH (self reaction and increase of effective Henry's Law constant), the uptake coefficients were high enough to constrain the value of α<sub>b</sub> close to 1. Given the degrees of freedom to adjust the simulations, a lower limit to α<sub>b</sub> of 0.1 is recommended. The negative temperature dependence of the observed uptake coefficient was likely due to the interplay of temperature dependencies of the effective Henry's Law constant and the diffusion coefficient, rather than α<sub>b</sub>. High values for α<sub>b</sub> were predicted by molecular dynamics simulations (Roeselova et al., 2003).

### References

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