

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.17 H117

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This data sheet last evaluated: April 2010; last change in preferred values: April 2010.

### HC(O)OH + ice

#### Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Partitioning coefficients: <math>K_{linC}</math></i>			
$5.8 \times 10^{-11} \exp(6500/T)$	187-221	von Hessberg et al., 2008	CWFT-CIMS (a)
$1.5 \times 10^{-8} \exp(5143/T)$	208-228	Symington et al, 2010	CWFT-MS (b)

#### Comments

- (a) Ice film made by freezing distilled water. Uptake was found to be reversible and equilibrium surface coverages were calculated using the geometric ice surface area. Values of  $N_{max} = 2.2 \times 10^{14}$  molecule  $cm^{-2}$  (independent of temperature) and  $\Delta H_{ads} = -51 \pm 6$  kJ  $mol^{-1}$  were reported. The HC(O)OH concentration was varied between  $2 \times 10^9$  and  $2 \times 10^{11}$  molecule  $cm^{-3}$ . The fraction of dimers present was calculated to be less than 10 % for all temperatures and concentrations except for 187 K and  $[HC(O)OH] > 2 \times 10^{10}$  molecule  $cm^{-3}$ .
- (b) Ice film made by freezing distilled water. Uptake of HC(O)OH ( $\approx 3 \times 10^9$  and  $2 \times 10^{12}$  molecule  $cm^{-3}$ ) was found to be reversible and equilibrium surface coverages were calculated using the geometric ice surface area. Equilibrium uptake of HC(O)OH to ice at various temperatures was analysed using the Langmuir isotherm to derive a value of  $N_{max}$  of  $2.1 \times 10^{14}$  molecule  $cm^{-2}$ . The temperature dependent expression of  $K_{linC}$  was derived by fitting to the three data points. A value of  $\Delta H_{ads} = -44 \pm 3$  kJ  $mol^{-1}$ , was reported.

#### Preferred Values

Parameter	Value	T/K
$K_{linC} / cm$	$4.0 \times 10^{-12} \exp(7000/T)$	187 - 221 K
$N_{max} / molecules cm^{-2}$	$2.2 \times 10^{14}$	
<i>Reliability</i>		
$\Delta (E/R) / K$	$\pm 500$	
$\Delta \log N_{max}$	0.1	

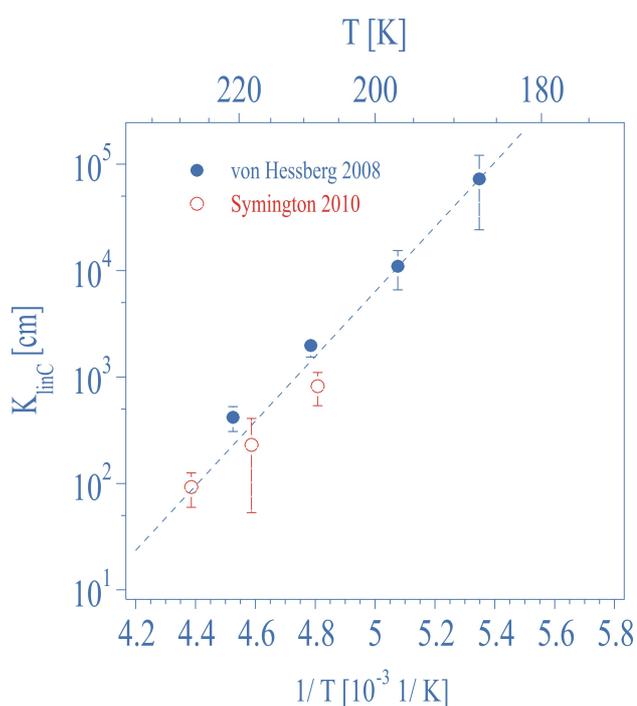
#### Comments on Preferred Values

There are two experimental studies of the reversible uptake of HC(O)OH to pure ice surfaces. Both studies used the same experimental approach and the values of the equilibrium

partitioning coefficients and  $N_{\max}$  are in reasonable agreement. The preferred value therefore takes both datasets into account. Reported values of  $N_{\max}$  are consistent with other oxidized organics (Abbatt, 2003). Other experimental studies have provided evidence for a strong (hydrogen bonding) interaction between HC(O)OH and H<sub>2</sub>O molecules at the surface of ice films, which does not lead to spontaneous ionization (Souda 2003; Bahr et al., 2005). These observations are supported by theoretical studies (Compoin et al., 2002), which show that HC(O)OH is hydrogen bound to two neighbouring H<sub>2</sub>O molecules.

## References

- Abbatt, J. P. D.: Chem. Rev. 103, 4783-4800, 2003.  
 Bahr, S., Borodin, A., Hofft, O., Kempter, V. and Allouche, A.: J. Chem. Phys. 122, 2005.  
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 Symington, A., Cox, R. A. and Fernandez, M. A.: Z. Phys. Chem., in press 2010.  
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Temperature dependent partition coefficients for formic acid uptake to ice. The dashed line is the recommended value.