

## Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet V.A1.56 HI56

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### CF<sub>3</sub>C(O)OH + ice

#### Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Partition coefficients: <math>K_{\text{linC}}</math> /cm</i>			
1300±900 (reversible)	200	Symington et al, 2010	CWFT-MS (a)
2100±600	208		
1900±800	218		
1000±300 (reversible)	218		
2100±900	228		
1100±900 (reversible)	228		

#### Comments

- (a) Ice film made by freezing distilled water. CF<sub>3</sub>C(O)OH concentration varied between  $\approx 1.5 \times 10^{10}$  and  $9 \times 10^{12}$  molecule cm<sup>-3</sup>. Uptake was found to be only partially reversible with amounts desorbed only 60% of amount adsorbed, following establishment of equilibrium surface coverage. The data was analysed using the Langmuir isotherm model applied to both integrated surface coverage based on uptake (total adsorption) and desorption (reversible adsorption) amounts. For data selected for CF<sub>3</sub>C(O)OH concentrations  $< 2.5 \times 10^{12}$  molecule cm<sup>-3</sup>,  $N_{\text{max}}$  (molecule cm<sup>-2</sup>) was found to be  $2.2 \times 10^{14}$  for total component, and  $1.1 \times 10^{14}$  for the reversible component. Linear least squares fit of was used to determine the optimum values of  $K_{\text{linC}}$  in the experimental temperature range; the average values for total adsorption (irreversible + reversible) were 2100±800 cm and for reversible adsorption: 1150±500 cm. There was no significant dependence of  $N_{\text{max}}$  or  $K_{\text{LinC}}$  on temperature in the range 200–228 K and thus a value of  $\Delta H_{\text{ads}}$  could not be obtained. The partition constants obtained from the experimental data were validated using a simple one-dimensional numerical model to simulate individual uptake profiles and retrieve partition constants for specific conditions of temperature and concentration, over the temperature range 200–228 K. The analysis confirmed that the temperature dependence was small and showed that the Langmuir constants decreased at high surface coverages. The irreversible component of uptake of CF<sub>3</sub>C(O)OH was attributed to hydrate formation on the surface.

#### Preferred Values

Parameter	Value	T/K
$K_{\text{linC}}$ / cm (total uptake)	2100	208 -238
$K_{\text{linC}}$ / cm (reversible uptake)	1150	200 -238
$N_{\text{max}}$ / molecule cm <sup>-2</sup> (total)	$2.2 \times 10^{14}$	200 - 240
$N_{\text{max}}$ / molecule cm <sup>-2</sup> (reversible)	$1.0 \times 10^{14}$	200 - 240

<i>Reliability</i>		
$\Delta K_{linC} / \text{cm}$	$\pm 800$	200 - 240
$\Delta \log N_{max}$	0.1	

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### *Comments on Preferred Values*

The study by Symington et al. (2010) appears to be only experimental study of the uptake of  $\text{CF}_3\text{C}(\text{O})\text{OH}$  (TFA) to pure ice surfaces. As with the aliphatic carboxylic acids, reversible uptake is observed, following Langmuir kinetics at low surface coverage (Sokolov and Abbatt, 2002; Von Hessberg et al, 2008). However there is an irreversible component of adsorption which also follows Langmuir kinetics, and which accounts for  $\sim 40\%$  of the uptake on fresh ice surfaces. The partition constants for total and reversible uptake were obtained from analysis using Langmuir plots, and these were confirmed using a simple 1-dimensional model with two distinct surface sites to simulate individual uptake profiles and retrieve partition coefficients for reversible and total uptake. The model reproduced observed uptake over the experimental concentration and temperature range (200-228K). Two sets of  $K_{linC}$  and  $N_{max}$  values are recommended based on this study. In view of the absence of significant temperature dependence from the data analysis, temperature independent values of  $K_{linC}$  are recommended for both reversible and total uptake. Both processes should be included in modelling in modelling the uptake of TFA in ice clouds.

The irreversible component of uptake of TFA uptake is attributed to formation of a stable TFA hydrate. Co-adsorption experiments of TFA with acetone on ice demonstrated that the presence of strongly adsorbing TFA enhanced acetone uptake, in a manner similar to inorganic acids such as HCl (McNeill et al, 2006). This is attributed to modification of the ice surface layers by TFA in the region of the thermodynamic stability boundaries for TFA hydrates in the bulk phase diagram, allowing uptake into the bulk.

### **References**

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 von Hessberg, P., Pouvesle, N., Winkler, A. K., Schuster, G. and Crowley, J. N.: Phys. Chem. Chem. Phys. 10, 2345, 2008.