IUPAC Task Group on Atmospheric chemical Kinetic Data Evaluation – Data Sheet V.A1.58 HI58

This data sheet last evaluated : June 2015; last change in preferred values: June 2015.

CF_3CH_2OH + ice

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Partitioning coefficients: K_{linC}/cm			
108 ± 6	208	Symington et al, 2012	CWFT-MS (a)
30 ± 5	218		
8 ± 2	228		
156 ± 35	203	Moreno et al., 2012	CWFT-MS (b)
62.0 ± 17	206		
27.0 ± 6	216		
11.6 ± 3.7	223		

Comments

(a) Ice film made by freezing distilled water. Equilibrium surface coverages were calculated using the geometric ice surface area. Uptake of CF_3CH_2OH to ice in the temperature range given was found to be completely reversible, with adsorbed amounts at equilibrium equal to the desorbed amounts following exposure. Adsorption and desorption was analysed using the Langmuir isotherm. The following expression for the temperature dependence of partitioning is based on the experimental values for K_{LinC} over the range 208 – 228 K: $3.74 \times 10^{-12} \exp(6427/T)$. The value of $N_{max} = (4.8 \pm 0.4) \times 10^{14}$ molecule cm^{-2} was retrieved from a linearised Langmuir plot at 208 K; retrieval at higher temperatures was inaccurate because coverage was too far from saturation. The Van't Hoff plot yielded values of $\Delta H_{ads} = (-61.8 \pm 0.9)$ $kJmol^{-1}$, $\Delta S_{ads} = (-132 \pm 4)$ $Jmol^{-1}K^{-1}$.

(b) Uptake of CF_3CH_2OH $(0.1–34.0) \times 10^{12}$ molecule cm^{-2} on a surface film formed by freezing liquid water or aqueous HNO_3 solution on inner wall of flow tube. For experiments on pure ice, the adsorption was fully reversible and the data could be described in terms of the Langmuir isotherm over the temperature range 203–223 K. Analysis of the isotherm for gave $(N_{max} = 2.8 \pm 0.6) \times 10^{14}$ molecule cm^{-2}, independent of temperature. The cited K_{linC} values were obtained from the product $K_{LangC}(T) \times N_{Max}$ $(= K_{linC})$ at each temperature which was within 5% of the slope of the linearised Langmuir plots at the lower concentrations. On HNO_3 doped ice the number of adsorbed molecules was slightly lower than over pure ice, but at 233 K, there was a significant increase in adsorbed CF_3CH_2OH molecules. which was attributed to the presence of liquid HNO_3 solution at the surface. The temperature dependence of the dimensionless adsorption enthalpy gave $\Delta H_{ads} = (-46 \pm 16)$ $kJmol^{-1}$ (error is $2\sigma + 5\%$).

Preferred Values

Parameter	Value	T/K
K_{linC} / cm	$4.2 \times 10^{-10} \exp(5390/T)$	203 -228
N_{max} / molecule cm^{-2}	2.8×10^{14}	203 -228

Reliability		
$\Delta(E/R)$ / K	± 1000	200 - 230
ΔN_{max}	± 0.5 x 10^{14}	203 - 231

Comments on Preferred Values

The studies of Symington et al. and Moreno et al. both reported that the uptake of trifluoroethanol on ice surfaces was fully reversible and could be described in terms of the Langmuir isotherm for the range of concentrations and temperatures studied. The reported partition coefficients were in good agreement, but the N_{max} value reported by Symington et al, determined only at 208K was significantly higher than reported by Moreno, which showed no temperature dependence over the experimental range: 203 – 223K. The latter result is preferred as the data showed higher precision overall. The preferred expression for the temperature dependence of is a least squares fit to all the K_{linC} values from the two studies covering the range 203 – 228 K.

The uptakes were independent of whether the ice was deposited at the experimental temperature or at a higher temperature, followed by cooling to the experimental temperature, confirming that the results can be applied to ice formed in different ways. Moreno et al also reported uptakes on HNO_3-doped ice at 203 – 235 K. At 203- 223 K the number of adsorbed molecules was ~5% lower than on pure ice. At temperaures above 231 K the amount of reversible uptake was enhanced in the presence of nitric acid due to the coexistance of a liquid solution phase. Partitioning of CF_3CH_2OH to ice was comparable to its non-halogenated analogue, ethanol (Sokolov and Abbatt, 2002). Thus CF_3 substitution does not appear to influence significantly the interaction of alcohols with the ice surface (Moreno et al. 2012b).

References

Moreno, E., Aranda, A., Dıaz-de-Mera, Y., Martınez, E., Bravo, I. and Rodrıguez, D., Phys. Chem. Chem. Phys., 14, 4425, 2012.

Moreno, E., Aranda, A., Dıaz-de-Mera, Y., Notario.A, Rodrıguez, and A. Bravo, I., Atmos.Environment, 60, 76, 2012b.

Symington, A., Leow, Lay May, Griffiths, P.T., and Cox, R.A., J.Phys.Chem. A, 116, 5990, 2012

Sokolov, O. and Abbatt, J. P. D.: J. Phys. Chem. 106, 775-782, 2002.

Fig 1 Temperature dependence of K_{linC} for uptake of CF_3CH_2OH on ice