

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.5 H15

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H₂O₂ + ice

Experimental data

Parameter	Temp./K	Reference	Technique/Comments
<i>Experimental uptake coefficients: γ</i>			
0.02	228-270	Conklin et al., 2002	PC (a)
<i>Partition coefficients: K</i>			
$K_{linC} = 1.56$	228	Clegg and Abbatt, 2001	CWFT-MS (b)
$K_V = 8.3 \times 10^4$	270	Conklin et al., 2002	PC (a)
$K_V = 1.24 \times 10^5$	262		
$K_V = 5.78 \times 10^5$	243		
$K_V = 1.07 \times 10^7$	228		
$K_{linC} = 2.1 \times 10^{-5} \exp(3800 / T)$	203-233	Marécal et al., 2010	(c)

Comments

- (a) Column packed with $\approx 200 \mu\text{m}$ ice spheres. H₂O₂ ($\approx 10^{10}$ - 10^{12} molecule cm⁻³) detected using liquid phase enzymatic fluorometry. Due to the long duration of the experiments (up to 20 hours), some of the uptake observed (exceeding 1 monolayer at the lowest temperatures) is due to bulk dissolution of H₂O₂. Equilibrium gas-to-ice volume partitioning coefficients were extracted from experimental data when the net uptake was zero, or by using an advection-dispersion model of H₂O₂ transport in the column (at 228 K). The coefficient K_V includes both surface and bulk H₂O₂.
- (b) Ice films were made by freezing water. The uptake of H₂O₂ was observed to be totally reversible. The geometric surface area was used to calculate the coverage. The value of K_{linC} presented in the Table was determined from data presented in a plot and uses the observed linear relationship between N (surface coverage in molecule cm⁻² of ice) and [H₂O₂]. No significant dependence of K_{linC} on temperature was observed.
- (c) The parameters for K_{linC} were reported in an modelling study of the effect of H₂O₂ uptake to cirrus clouds. Though no experimental details are given by Marécal et al., the method used was CWFT with CIMS and MS detection of H₂O₂ (MPI-Mainz group, Pouvesle et al.).

Preferred Values

Parameter	Value	T/K
K_{linC} / cm	$2.1 \times 10^{-5} \exp(3800 / T)$	200 - 240
N_{max} / molecule cm^{-2}	4.5×10^{14}	200 - 240
<i>Reliability</i>		
$\Delta \log K_{linC}$	0.5	200 - 240
$\Delta \log N_{max}$	0.3	200 - 240

Comments on Preferred Values

The experimental data show that the interaction of H_2O_2 ice is reversible, and that, at long exposure times, both surface and volume uptake are observed. The solubility in ice appears to be a factor of ≈ 200 smaller than in liquid water, extrapolated to the same temperature (Conklin and Bales, 1993).

Partitioning to the ice surface is surprisingly weak, and no temperature dependence was detected in the one published study of this parameter (Clegg and Abbatt, 2001). A further value of $K_{linC} = 2.1 \times 10^{-5} \exp(3800 / T)$ has been reported by Marécal et al. (2010) in a modelling study. This value is based on unpublished experimental work (Pouvesle et al., from the MPI-Mainz group) using a coated wall flow tube, though no experimental details are given. This parameterisation results in values of K_{linC} which are orders of magnitude larger than reported by Clegg and Abbatt (2001).

The larger partition coefficient measured by Pouvesle et al. is more consistent with the emerging picture of the interaction of hydrogen bonding trace gases with ice surfaces in which a distinct inverse relationship between the vapour pressure of the trace gas and the partition coefficient is observed (Sokolov and Abbatt, 2002). For this reason we prefer the value reported by Marécal et al. (2010) but with expanded error limits to reflect the divergence in the available studies and the fact that it has not yet been published. We also adopt the value of N_{max} reported by Pouvesle et al.)

References

- Clegg, S. M., and Abbatt, J. P. D.: J. Phys. Chem. A 105, 6630-6636, 2001.
Conklin, M. H., Sigg, A., Neftel, A., and Bales, R. C.: J. Geophys. Res. 98, 18367-18376, 1993.
Marécal, V., Pirre, M., Riviere, E. D., Pouvesle, N., Crowley, J. N., Freitas, S. R. and Longo, K. M.: Atmos. Chem. Phys. 10, 4977-5000, 2010.
Sokolov, O and Abbatt, J. P. D.: J. Phys. Chem. A, 106, 775-782, 2002.