IUPAC Task Group on Atmospheric Chemical Kinetic data Evaluation – Data Sheet VI.A4.13 HET_SL_13

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$CH_3C(O)OONO_2 + H_2SO_4 \rightarrow$ products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ			
$\gamma_0 = 0.008$ (85 wt. % H_2SO_4)	200	Zhang and Leu, 1997	WWFT-CIMS (a)
Solubility: H^* (M atm^{-1})			
6.47×10^4 (46 wt. % H_2SO_4)	199	Zhang and Leu, 1997	WWFT-CIMS (a)
5.54×10^3 (46 wt. % H_2SO_4)	216		
2.0×10^4 (54 wt. % H_2SO_4)	208		
8.75×10^2 (54 wt. % H_2SO_4)	226		
2.42×10^4 (59 wt. % H_2SO_4)	208		
4.01×10^3 (59 wt. % H_2SO_4)	216		
5.58×10^4 (72 wt. % H_2SO_4)	208		
3.31×10^3 (72 wt. % H_2SO_4)	222		

Comments

(a) PAN was observed to be reversibly adsorbed on sulfuric acid. The quantity $H^*(D_l)^{0.5}$ was determined from the time-dependent uptake of PAN on sulfuric acid. The solubility constant H^* was extracted using calculated diffusion coefficients based on the model developed by Luo et al. (1994) using the measured viscosities of H_2SO_4/H_2O solution from Williams and Long. The H^* values were found to depend strongly on temperature and less strongly on acid composition (46-72 wt %). For example, the effective H^* at 208 – 222 K on 72 wt % H_2SO_4 was approximately a factor of 2 – 3 higher than extrapolated from measurements at higher temperatures for more dilute solutions.

Preferred Values

Parameter	**Value**	**T/K**
α	>0.008	190 – 230
$\ln H^*$	$-\Delta H/RT + \Delta S/R$	
ΔH /kJ mol^{-1}	50.2 (46 wt H_2SO_4 %)	195 – 220
ΔH /kJ mol^{-1}	78.2 (72 wt % H_2SO_4)	208 - 220
ΔS /J $mol^{-1}K^{-1}$	160 (46 wt % H_2SO_4)	195 – 220
ΔS /J $mol^{-1}K^{-1}$	284 (72 wt % H_2SO_4)	195 – 220

Reliability

$\Delta \log \alpha$	± 0.7

$\Delta \log H$	± 0.3

Comments on Preferred Values

At concentrations lower than 72 wt. % PAN uptake is reversible and solubility controls the amount taken up to the solution. The preferred values for the effective Henry's law solubility, H^*, are taken from the study by Zhang and Leu,(1997), which are consistent with studies on water surfaces at higher temperatures (Kames and Schurath, 1995). The temperature dependence of H^* for a given acid composition can be expressed as: $\ln H^* = -\Delta H/RT + \Delta S/R$. The values of the PAN solvation enthalpy and entropy ΔH and ΔS vary with acid composition in the range 46-72 wt %. The values given in the Table are for the lower and upper end of composition range and cover the range 200 – 222 K.

Measurement of accommodation coefficients in the time dependent regime leading to saturation is difficult as adsorption and desorption are not separated in time. The recommendation is based on the initial uptake coefficient reported by Zhang and Leu,(1997), and is given a large uncertainty.

References

Zhang, R, and Leu, M. T.: J. Geophys. Res., 102, 8837 1997.
Kames, J., and Schurath, U., J. Atmos. Chem., 12, 169 1995.