IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.15 HI15

SO$_2$ + ice

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
Experimental uptake coefficients: γ_0, γ_t			
$\gamma_0 = (0.8\text{-}3.0) \times 10^{-5}$	191	Chu et al. 2000 (a)	CWFT-MS (a)
$\gamma_t = (0.4\text{-}1.4) \times 10^{-6}$	213-238	Clegg and Abbatt, 2001 (b)	CWFT-MS (b)
Partition coefficient: KlinC(cm)			
36.5 ([SO$_2$] = 6.6 x 10^{10} cm^{-3})	191	Chu et al. 2000 (a)	CWFT-MS (a)
5.5 (pH=6; [SO$_2$] = 1.3 x 10^{10} cm^{-3})	228	Clegg and Abbatt, 2001 (b)	CWFT-MS (b)
7.1 (pH=6; [SO$_2$] = 4.2 x 10^{10} cm^{-3})			
1.2 (pH=6; [SO$_2$] = 4.2 x 10^{12} cm^{-3})			
0.47 (pH=4.1; [SO$_2$] = 4.2 x 10^{10} cm^{-3})			
333 (pH=10.4; [SO$_2$] =2.1 x 10^{10} cm^{-3})			

Comments

(a) Ice films were formed by vapour-deposition at 190-211 K with a thickness of ~2.5-3.0 μm. The SO$_2$ partial pressure ranged from 1.0 x10^{-6} to 2.3 x10^{-5} mbar. The initial uptake coefficients, γ_0, were corrected for axial and laminar diffusion. Corrections for surface roughness were performed using a layered pore diffusion model; giving the "true" value for the uptake coefficient, γ_t. The variability in the reported γ_0 values is due to a three-fold change in the SO$_2$ partial pressure and variability in the surface area and roughness of the vapour-deposited water-ice films. On exposure the surfaces were rapidly saturated, and a single measurement reported a surface coverage of $\theta = 2.4$ x 10^{12} molecules/cm^2 for $P_{SO_2} = 1.0$ x10^{-6} mbar at 191 K. These data were used to evaluate the cited value of K_{LinC}.

(b) Ice films made by freezing a water-coated pyrex sleeve within the flow tube. The SO$_2$ partial pressure ranged from 3 x10^{-7} to 1.7 x10^{-4} mbar. The uptake saturated rapidly at a given SO$_2$ partial pressure and surface coverage on pure ice over the whole range varies approximately with $P_{SO_2}^{0.5}$. The coverage, θ, was much less than a monolayer (N_{max} was estimated to be 5 x 10^{14} molecules/cm^2 for the ice surfaces prepared in this way) and shows a strong decrease with decreasing pH. The number of molecules desorbed from the ice surface was about equal to the number of molecules adsorbed, indicating that the adsorption process is fully reversible. The partition constants cited in the table were evaluated from surface coverages at selected P_{SO_2} given in Figure 4 of Clegg and Abbatt's paper, with emphasis on at the lower concentrations (<1.3 x 10^{-6} mbar) where θ was approximately proportional to P_{SO_2}.

Preferred values

Parameter	Value	T/K
K_{linC} / cm	6.3	228
K_{linC} / cm	$7.3 \times 10^{-4} \exp(2065/T)$	190-250

Reliability

$\Delta (\ln KlinC)$	± 0.3	228
$\Delta (E/R) /K$	± 1000	190-250

N_{ads} / molecule cm^{-2} = $K_{linC}[SO_2]$

Comments on Preferred values

Chu et al. (2000) determined the initial SO_2 uptake coefficient to be ~1 x 10^{-5} on water-ice films at 191 K but they did not observe the reversible uptake reported by Clegg and Abbatt (2001). The weak reversible adsorption does not allow accurate determination of uptake coefficients and no recommendation is made for γ.

Clegg and Abbatt (2001) suggest that their observed dependence of the uptake on the $[SO_2]^{0.5}$ is due to dissociation of the hydrated form of SO_2 to HSO_3^- on the ice surface. This was tested by raising and lowering the pH of their ice surfaces. It was found that SO_2 uptake was enhanced at higher pH and was inhibited at lower pH (due to surface protons inhibiting the dissociation of adsorbed SO_2). A simple precursor model was developed by Clegg and Abbatt (2001) to explain the observed SO_2 uptake behaviour. The total adsorbed $S(IV)^{tot}$ (= $[SO_2]_{ads}$ + $[HSO_3^-]_{ads}$) at equilibrium is given as a function of $[SO_2]_g$ by the expression: $[S(IV)^{tot}]_{ads} = K_I[SO_2]$ + $(K_I K_2[SO_2])^{0.5}$. For ice at natural pH (~ 6) the experimental data at 228 K for $[SO_2]$ in the range 10^{11} - 10^{13} molecule cm^{-3} were approximated by the expression: $[S(IV)_{tot}]_{ads} = K[SO_2]^{0.5}$, where $K = 1.2 \times 10^6$ molecule$^{1/2}$ cm$^{-1/2}$, indicating $[HSO_3^-]$ is the predominant adsorbed species. This model is also consistent with up linear dependence on $[SO_2]$ at low P_{SO_2} and K_{linC} can be identified with $K_I[SO_2]$. The recommended partition coefficient at 228K was evaluated from data of Clegg and Abbatt for SO_2 on ice at partial pressures ≤1.3 x 10^{-6} mbar ($[SO_2] \le 1 \times 10^{13}$ molecule cm^{-3}).

Chu et al. reported a single measurement of partitioning to pure ice at 191 K, from which a value of K_{LinC} = 36.5 cm can be derived, assuming this reflects linear dependence on $[SO_2]$. This is substantially higher than the value at 228 K, which suggests a negative T dependence as expected for reversible adsorption. An Arrhenius fit to the data points at 191 and 228 K yields the recommended expression for the temperature dependence of K_{linC}.

Some support for the negative temperature dependence comes from the thesis work of Langenberg (1997) who derived ΔH_{ads} = -21±3 kJmol^{-1} and ΔS_{ads} = 39±10 Jmol^{-1}K^{-1} from uptake of SO_2 on a packed column over the temperature range 207 - 267 K. These results yield an expression for KlinC = 6.4 x 10^{-6} exp(2527/T) cm, and a value of 0.42 cm at 228, somewhat lower than the preferred value obtained by Clegg and Abbatt on ice at pH=6.
Clegg and Abbatt (2001) observed an *increase* in the surface coverage as the temperature was increased from 213 K to 228 K at a constant P_{SO_2} of 4 x 10^{-5} mbar (corresponding to a surface coverage of 1.5 x 10^{12} cm^{-2} at 228 K). An Arrhenius fit to these data is consistent with earlier partitioning data for SO_2 to ice (Clapsaddle and Lamb,1989) and gives the expression: $[S(IV)_{tot}]_{ads}$ = {5.6 x 10^{12} exp(-4425/T)}x$[SO_2]^{0.5}$ molecule$^{1/2}$ cm$^{-1/2}$. It was suggested that the increase in surface coverage with temperature is due to the existence of a quasi-liquid layer on the ice surface, which increases in thickness and facilitates the dissociation of SO_2 or can

accommodate more S(IV) species, as temperature increases. However Huthwelker et al., (2001) showed, on the basis of a detailed analysis of uptake rates, amounts, and temperature dependence reported from earlier experimental data (Clapsaddle and Lamb, 1989; Conklin et al. 1989), that SO_2 dissociates and diffuses into an internal reservoir for example comprised of veins and nodes, but not into a quasi-liquid layer on the ice surface.

References

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