

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.24 HI24

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CH₃C(O)CH₃ + ice

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Experimental uptake coefficients: γ, γ_0</i>			
$\gamma_0 > 0.02$	198	Winkler et al., 2002	CWFT-MS (a)
$\gamma_0 > 0.1$	< 165	Hudson et al., 2002	Knudsen (b)
$\gamma_0 > 0.2$	< 150		
$\gamma_0 = 0.009$	200	Behr et al., 2004	CWFT-MS (c)
$\gamma_0 = 0.006$	193-218	Behr et al., 2006	CWFT-MS (d)
<i>Surface accommodation coefficients: α_s</i>			
0.004 - 0.043		Bartels-Rausch et al., 2005	CWFT-CIMS (e)
<i>Surface partition coefficients: K_{inc}</i>			
$1.25 \times 10^{-10} \exp(5375/T)$	198-223	Winkler et al., 2002	CWFT-MS (f)
$3.8 \times 10^{-10} \exp(4727/T)$	140-170	Hudson et al., 2002	Knudsen (g)
$1.25 \times 10^{-15} * T * \exp(6610/T)$	193-213	Dominé and Rey-Hanot, 2002	MS (h)
$1.32 \times 10^{-11} \exp(5795/T)$	193-223	Peybernès et al. 2004	CWFT-MS (i)
$3.21 \times 10^{-13} \exp(6255/T)$	198-228	Bartels-Rausch et al., 2004	CC-CIMS (j)
$1.73 \times 10^{-12} \exp(6134/T)$	203-223	Bartels-Rausch et al., 2005	CWFT-CIMS (e)
$3.0 \times 10^{-7} \exp(3849/T)$	193-218	Behr et al., 2006	CWFT-MS (k)

Comments

- 50-100 μm thick ice film (geometric area $\approx 100 \text{ cm}^2$) made by freezing water. γ_0 (calculated from the geometric ice surface area) is a lower limit as adsorption and desorption were not separated in time.
- Vapour deposited ice film of geometric area $\approx 5 \text{ cm}^2$. γ_0 values taken from a Figure. γ_0 is a lower limit as adsorption and desorption were not separated in time.
- Vapour deposited ice film. Uptake coefficient extracted from experimental data by numerical analysis of the flow tube, taking adsorption and desorption processes into account.
- Vapour deposited ice film. Uptake coefficient extracted from experimental data by numerical analysis of the flow tube, taking adsorption and desorption processes into account. Evidence for two types of adsorption sites was found, the uptake coefficient refers to “aged” ice which the authors suggest is hexagonal (I_h) ice. A value of 0.008 was obtained for fresh cubic (I_c) ice.
- Atmospheric pressure flow tube. Gas-transport modelling enabled S_0 and partitioning coefficients to be extracted from experimental data based on the assumption that $\Delta S_{\text{ads}} = (-101 \pm 16) \text{ J mol}^{-1} \text{ K}^{-1}$ taken from Bartels-Rausch et al. (2004). The Enthalpy of adsorption was derived as $\Delta H_{\text{ads}} = (-46 \pm 2) \text{ kJ mol}^{-1}$. The surface partitioning coefficient, K_{inc} , reported here is

determined from a Van't Hoff analysis of the raw coverage data, which corresponded to $\Delta S_{\text{ads}} = -87 \text{ Jmol}^{-1} \text{ K}^{-1}$ and $\Delta H_{\text{ads}} = -51 \text{ kJ mol}^{-1}$ as reported in Bartels-Rausch et al. (2005) on p. 4537.

- (f) K_{linC} ($\text{cm}^{-2}/\text{cm}^{-3}$) determined from linear relationship between N (surface coverage in molecule cm^{-2} of ice) and $[\text{acetone}]$ (units of molecule cm^{-3}) at low coverage where $N < 1 \times 10^{13}$ molecule cm^{-2} ($K_{\text{linC}} = N / [\text{acetone}]$). The geometric surface area was used to calculate the coverage. Analysis of datasets including measurements at higher coverage using a Langmuir isotherm resulted in somewhat lower values of the partitioning coefficient, potentially a result of adsorbate-adsorbate interactions. $N_{\text{max}} = (2.7 \pm 0.7) \times 10^{14} \text{ cm}^{-2}$. Heat of adsorption derived as $\Delta H_{\text{ads}} = (-46 \pm 7) \text{ kJ mol}^{-1}$.
- (g) The geometric surface area of the vapour deposited ice film was used to calculate the coverage. Equilibrium uptake of $\approx 4 \times 10^{-7}$ mbar acetone ($\approx 10^{10}$ molecule cm^{-3}) to ice at various temperatures was analysed using the Langmuir isotherm. The expression for K_{linC} uses the reported value of ΔS_{ads} (via Trouton's rule) = $-87.9 \text{ Jmol}^{-1} \text{ K}^{-1}$ and $\Delta H_{\text{ads}} = -39.3 \text{ kJmol}^{-1}$ and is derived from $K_{\text{LangP}} (\text{atm}^{-1}) = \exp\{-(T^* 87.9 - 39300) / 8.314 * T\}$ using $N_{\text{max}} = 4 \times 10^{14}$ molecules cm^{-2} .
- (h) The geometric surface area of the $\approx 1\text{mm}$ thick ice film (made by freezing water) was used to calculate the coverage. The partitioning coefficient, $K_{\text{linP}} = 90.53 \exp(6610/T) \text{ cm}^{-2} \text{ Pa}^{-1}$, was determined from linear relationship between N (surface coverage in molecule cm^{-2} of ice) and acetone pressure in Pa. Enthalpy of adsorption derived as $\Delta H_{\text{ads}} = (-46 \pm 7) \text{ kJ mol}^{-1}$.
- (i) Partitioning coefficient, K_{langC} reported as $9.61 \times 10^{-26} \exp(5795/T) \text{ molecule}^{-1} \text{ cm}^3$. The geometric surface area of the ice film (made by freezing water) was used to calculate the coverage. $N_{\text{max}} = (1.37 \pm 0.13) \times 10^{14} \text{ molecule cm}^{-2}$. Enthalpy of adsorption derived as $\Delta H_{\text{ads}} = (-48.1 \pm 3.1) \text{ kJ mol}^{-1}$. Analysis using a BET isotherm resulted in a value of $\Delta H_{\text{ads}} = (-50.3 \pm 2.5) \text{ kJ mol}^{-1}$. The corresponding value of N_{max} was $(1.30 \pm 0.18) \times 10^{14} \text{ molecule cm}^{-2}$.
- (j) Measurement of retention times of acetone in a chromatographic column packed with ice crystals or spheres. Ice surface area derived by BET analysis of methane adsorption isotherms. Crystallinity of ice surfaces had no influence on the coverage. Enthalpy and entropy of adsorption derived as $\Delta H_{\text{ads}} = (-52 \pm 2) \text{ kJ mol}^{-1}$ and $\Delta S_{\text{ads}} = (-101 \pm 16) \text{ Jmol}^{-1} \text{ K}^{-1}$, respectively, so that $K_{\text{p}}^0 = \exp\{-(T^* 101 - 52000) / 8.314 * T\}$. The expression for K_{linC} was calculated using $V/A = 6.05 \times 10^{-8} \text{ cm}$. This work is considered to supersede the previous determination from this group using the same method (Guimbaud et al., 2003).
- (k) Vapour deposited ice film. The partitioning coefficient, K_{langC} , determined from experimental data by numerical analysis of the flow tube, was reported as $5.0 \times 10^{-22} \exp(3849/T) \text{ molecule}^{-1} \text{ cm}^3$. K_{linC} was calculated using the reported value of $N_{\text{max}} = 6.0 \times 10^{14} \text{ molecule cm}^{-2}$. Enthalpy of adsorption (for aged or hexagonal I_{h} ice) derived as $\Delta H_{\text{ads}} = (-32 \pm 6) \text{ kJ mol}^{-1}$. A higher value of $\Delta H_{\text{ads}} = (-49 \pm 3) \text{ kJ mol}^{-1}$ was obtained for freshly deposited ice, which the authors suggest may correspond to a cubic ice phase (I_{c}).

Preferred Values

Parameter	Value	T/K
K_{linC} / cm	$1.0 \times 10^{-11} \exp(5850/T)$	195 - 230
N_{max} / molecule cm ⁻²	2.7×10^{14}	
<i>Reliability</i>		
$\Delta(E/R)$	± 100	210 - 250
$\Delta \log N_{max}$	0.1	

Comments on Preferred Values

The experimental studies of the acetone – ice interaction are in reasonable agreement and show that the adsorption of acetone to ice is completely reversible. Consistent values of the adsorption enthalpy, ΔH_{ads} and equilibrium partitioning have been obtained. In order to explain ice-age dependent surface coverages, Behr et al. (2006) suggest that their vapour deposited ice initially was a mixture of cubic (I_c) and hexagonal ice (I_h), with $I_c \rightarrow I_h$ interconversion taking place over a period of hours after deposition.

Values of the maximum surface coverage on ice films made from freezing liquid water, N_{max} , vary between 1.3×10^{14} molecules cm⁻² (Peybernès et al., 2002) and 2.7×10^{14} molecule cm⁻² (Winkler et al., 2002). The latter value is consistent with values for other traces gases on similar ice surfaces, and with molecular dynamics calculations (Picaud et al., 2000).

The preferred partitioning coefficient, K_{linC} , is based on the CWFT data of Winkler et al. (2002), Dominé and Rey-Hanot (2002), Peybernès et al. (2004) and Bartels-Rausch et al. (2005) and provides a simple parameterisation appropriate for low acetone concentrations, whereby $N = K_{linC}[\text{acetone}]$ with the acetone concentration in units of molecule cm⁻³ and N in units of molecule cm⁻². Equilibrium surface coverages at higher concentrations can be calculated using the full form of the Langmuir isotherm (Winkler et al., 2002; Peybernes 2004).

The data of Hudson et al., 2002 and Behr et al. 2006 were obtained using vapour deposited ice and represent the lowest and highest partitioning coefficients, respectively at e.g. 210 K. The data of Bartels et al., 2004 were obtained using packed ice / snow and the differences in coverage may reflect a different surface type. Journet et al. (2005) showed that vapour deposited ice could, for a given geometric surface area, accommodate 3-4 times as much acetone as ice formed from freezing liquid water.

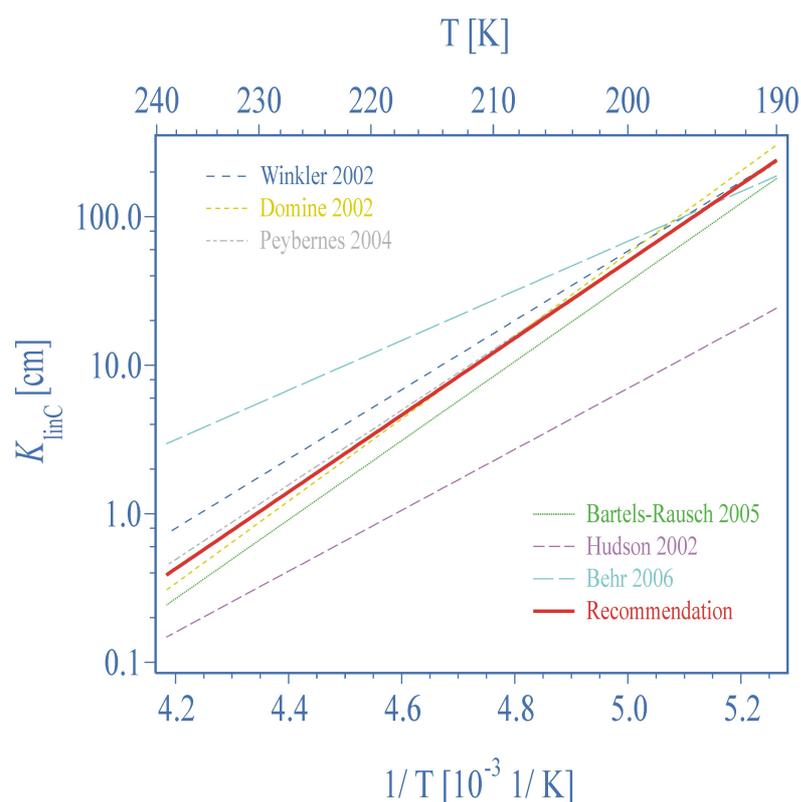
No evidence was found for enhanced uptake on ice films containing 1 monolayer of HNO₃ (Hudson et al., 2002) Whereas frozen HNO₃ / H₂O solutions (0.2-3 N) resulted in greatly enhanced, reversible uptake of acetone and a change in shape of the adsorption isotherm, with values of N_{max} approaching > 100 monolayers (Journet et al., 2005). In contrast, frozen H₂SO₄ solutions (0.2 N) yielded results similar to pure ice.

Theoretical and surface spectroscopic investigations suggest that the carbonyl oxygen atom of acetone is hydrogen bonded to the ice surface via dangling OH groups (Schaff and Roberts, 1996; Schaff and Roberts, 1998; Mitlin and Leung, 2002; Marinelli and Allouche, 2001).

Measurements of the experimental uptake coefficient are problematic due to the simultaneous desorption of acetone from the surface, which, apart from at the lowest temperatures, will result in determination of a lower limit. As the experimental uptake coefficient should be smaller than the surface accommodation coefficient, the value of α_s derived by Bartels-Rausch et al. (2005) appears to be rather low. Similarly, the uptake coefficients extracted using a flow tube model by Behr et al. are much lower than the lower limits presented by Hudson et al. (2002) and Winkler et al. (2002). No recommendation is given for γ or α_s .

References

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Partitioning coefficients, K_{linC} in cm^2/cm^3 for acetone on ice.