

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A1.12 HI12

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HNO₃ + ice

Experimental data

<i>Parameter</i>	Temp./K	Reference	Technique/ Comments
<i>Experimental uptake coefficients: γ</i>			
<i>γ_0</i>			
$\gamma_0 > 0.2$	197	Leu, 1988	CWFT-MS (a)
$\gamma_0 > 0.3$	191-200	Hanson, 1992	CWFT-MS (b)
$\gamma_0 > 0.2$	208-248	Abbatt, 1997	CWFT-MS (c)
$\gamma_0 > 5 \times 10^{-3}$	220-223	Zondlo, Barone and Tolbert, 1997	Knud (d)
$\gamma_{ss} = (2 \pm 1) \times 10^{-4}$			
$\gamma = 0.3$	200	Seisel, Flückiger and Rossi, 1998	Knud (e)
$\gamma = 0.27 \pm 0.08$	180	Aguzzi and Rossi, 2001	Knud (f)
0.25 ± 0.10	190		
0.17 ± 0.05	200		
0.09 ± 0.03	210		
$\gamma = (3.3 \pm 0.6) \times 10^{-2}$	214	Hynes, Fernandez and Cox, 2002	CWFT-MS (g)
1.2×10^{-2}	218		
6.0×10^{-3}	235		
$\gamma_0 = 7 \times 10^{-3}$	209	Hudson et al., 2002	Knud (h)
$\gamma_0 = 3 \times 10^{-3}$	220		
<i>Partition coefficients: $K(cm)$</i>		* calculated in this evaluation (see comments)	
4.64×10^4 *	218	Abbatt, 1997	CWFT-MS (c)
2.00×10^4 *	228		
0.83×10^4 *	238		
0.32×10^4 *	248		
$(1.06 \pm 0.16) \times 10^3$ (2 site model)	218	Hynes, Fernandez and Cox, 2002	CWFT-MS (g)
$(0.48 \pm 0.072) \times 10^3$ (2 site model)	228		
$(10.05 \pm 3.22) \times 10^4$	214	Ullerstam et al, 2005	CWFT_MS (i)
$(5.53 \pm 1.93) \times 10^4$	229		
$(1.74 \pm 0.51) \times 10^4$	239		
10.26×10^4	214	Cox et. al. 2005	CWFT-MS (j)
3.91×10^4	229		
1.75×10^4	239		

Comments

- (a) Fast flow tube reactor with MS detection. Ice condensed from the vapor phase onto the cold flow tube. γ corrected for gas diffusion using estimated diffusion coefficients.
- (b) Fast flow tube reactor with CIMS detection of HNO_3 at $p_{\text{HNO}_3} = (1 - 4) \times 10^{-7}$ mbar. Ice condensed from the vapor phase onto the cold flow tube. γ corrected for gas diffusion using estimated diffusion coefficients. Evidence for time-dependent uptake due to surface saturation.
- (c) Coated-wall flow tube with MS detection. Pressure = 1.3 mbar of He. The ice surfaces were prepared by wetting the inner wall of a tube which was inserted into the cooled flow tube resulting in a smooth ice film. Initially, HNO_3 is taken up rapidly independent of the HNO_3 partial pressure with γ as cited. Uptake then saturates at a surface coverage of $N_{\text{max}} \sim 0.2$ to 0.3 monolayers. Subsequently, small rates of uptake following a $T^{-0.5}$ rate law were observed corresponding to diffusional loss processes on the ice. The heterogeneous interaction is nearly irreversible as only about 25% of the quantity of HNO_3 was recovered after the HNO_3 flow was halted. The formation of an amorphous albeit stable surface layer of $\text{HNO}_3\text{-H}_2\text{O}$ is postulated as the HNO_3 partial pressures are well below those for formation of stable hydrates. The integrated amount of HNO_3 adsorbed was weakly dependent on p_{HNO_3} in the range $(1.7 - 41) \times 10^{-7}$ mbar at 218 K, and increased with decreasing temperature at approximately constant p_{HNO_3} (6.5 to 9.0×10^{-7} mbar). The cited Langmuir equilibrium constants were calculated from the reported equilibrium surface coverages using a single site model with N_{max} assumed = 2.7×10^{14} molecule cm^{-2} .
- (d) Two-chamber flow reactor equipped with FTIR reflection-absorption as well as MS detection. The flow reactor configuration only allowed uptake coefficients lower than 5×10^{-3} to be measured. At low p_{HNO_3} , uptake partially saturates after deposition of approximately one monolayer and reaches steady state. Above $\sim 2.7 \times 10^{-5}$ mbar of HNO_3 uptake occurs continually at γ_0 without signs of saturation. The former uptake regime is interpreted as leading to an amorphous mixture of $\text{HNO}_3\text{-H}_2\text{O}$, whereas the continuous uptake leads to a supercooled liquid mixture of a typical composition of 3:1 to 4:1 $\text{H}_2\text{O-HNO}_3$.
- (e) Uptake experiment in a Knudsen flow reactor equipped with a residual gas MS and simultaneous grazing-incidence FTIR reflection-absorption spectrometry.
- (f) Uptake experiment in a Knudsen flow reactor on ice films condensed from the vapor phase and on frozen bulk H_2O . Pulsed valve and steady state uptake experiments resulted in identical values for γ after correction for the interaction of HNO_3 with the Teflon coating. γ shows a strong negative temperature dependence for $T \geq 195\text{K}$ with $E_a = -28 \pm 4$ kJ mol^{-1} and a constant value of 0.3 below that temperature.
- (g) Coated wall flow tube study at 2.3 mbar He using MS detection of HNO_3 . p_{HNO_3} was in the range $(0.4\text{-}2.7) \times 10^{-6}$ mbar and led to time-dependent uptake converging to steady-state conditions after typically 200s of uptake. γ for HNO_3 uptake was unaffected by the presence of HCl in comparable quantities at 218K. Surface coverages were determined from integrated uptake prior to saturation. They showed little variation with p_{HNO_3} in the range and maximum surface coverage was 3×10^{14} molecule cm^{-2} at 218 K and 228 K. Partition coefficient was determined using 2-site Langmuir isotherm fit to experimental data at 218 and 228 K, with $N_{\text{max}} = 10^{15}$ molecule cm^{-2} . The enthalpy of HNO_3 adsorption onto ice was $-(54.0 \pm 2.6)$ kJ/mol , evaluated using the Van't Hoff equation and the values of K_{eq} cited.
- (h) Uptake experiment in a Knudsen flow reactor equipped with simultaneous reflection-I.R. absorption spectroscopy and MS. Surface area of vapour deposited ice, measured by BET method using butane adsorbent gas, was a factor of 2.27 larger than the geometric area of the

base surface. γ values were time dependent in the ice stability region at low $P(\text{HNO}_3)$. Initial values cited for $p_{\text{HNO}_3} \sim 1 \times 10^{-6}$ mbar. Surface coverages were determined from integrated uptake prior to saturation, and showed a strong T dependence below 214 K.

- (i) Coated wall flow tube with p_{HNO_3} in range 10^{-8} hPa - 10^{-6} hPa detected using CIMS. Ice films formed by freezing liquid water. At $T > 214$ K surface coverages measured in both unsaturated regime at low partial pressure and close to saturation. Maximum surface coverage was $(2.1 - 2.7) \times 10^{14}$ molecule cm^{-2} independent of temperature. The uptake is nearly irreversible as only 10- 40% of the quantity of HNO_3 desorbed after the HNO_3 exposure was halted. At 200 K continuous uptakes were observed without saturation and little desorption. Partition coefficients were determined using single-site Langmuir isotherm fit to experimental data at 214, 229 and 239 K, giving the expression: $K_{\text{LangP}}(\text{hPa}^{-1}) = -(5.1 \pm 0.4) \times 10^5 T + (12.3 \pm 0.9) \times 10^7$. The enthalpy of HNO_3 adsorption onto ice was $-(30.3 \pm 6)$ kJ/mol, evaluated using the Van't Hoff equation, and similar values were obtained from T-dependence of integrated desorption.
- (j) Model of gas flow and surface exchange in CWFT with a single site Langmuir mechanism. The model was used to reanalyse experimental results from Ullerstam et al (see note (i)). The experimental time-dependent uptake profiles were best fitted with an additional process involving diffusion of the adsorbed molecules into the ice film. The model allowed true surface coverages to be distinguished from total uptake including transfer to the bulk, leading to more accurate estimates of the Langmuir constant, K_{eq} , for surface adsorption. At $T \geq 229$ K, K_{eq} decreased by up to 30% as p_{HNO_3} decreased from the saturated region; the cited values are midrange.

Preferred Values

Parameter	Value	T/K
α_s	0.1	190 - 240
$N_{\text{max}} / \text{molecule cm}^{-2}$	2.7×10^{14}	214 - 240
$K_{\text{linC}} / \text{cm}$	$7.5 \times 10^{-5} \exp(4585/T)$	214 - 240
<i>Reliability</i>		
$\Delta \log(\alpha_s)$	± 0.3	190 - 240
$\Delta(K_{\text{linC}}) / \text{cm}$	± 0.1	228
$\Delta(E/R) / \text{K}$	± 700	

Comments on Preferred Values

There have been many experimental studies of nitric acid – ice interaction but mostly at temperatures and concentrations corresponding to stability regions for either hydrate or supercooled $\text{HNO}_3/\text{H}_2\text{O}$ solutions. Under these conditions at $T < 210$ K uptake is continuous and irreversible. At higher temperatures in the ‘ice stability’ region, uptake rate is time dependent, declining from an initial rapid uptake ($\gamma > 0.2$) to very slow uptake when the surface is saturated at $\theta \sim 3.0 \times 10^{14}$ molecules cm^{-2} . Surface coverages at low p_{HNO_3} on ice films in the temperature range 210-240 K have been quoted in a number of studies (Abbatt, 1997, Hudson et al., 2002, Hynes et al., 2002, Ullerstam et al., 2005 and Cox et al., 2005, and also Arora et al., 1999 (who measured HNO_3 uptake on ice particles). There is good agreement in the measured uptakes near saturation in the CWFT studies. For example, for a temperature of 228 K, a gas-phase concentration of 3×10^{10} molecule cm^{-3} of HNO_3 results in equilibrium surface coverages (N_{max}) of 1.9×10^{14} molecules cm^{-2} (Abbatt, 1997), 1.6×10^{14} molecules cm^{-2} (Hynes et al., 2002), 2.4

$\times 10^{14}$ molecules cm^{-2} (Ullerstam et al. 2005). The Knudsen cell study of Hudson et al (2002) shows much lower saturated coverages at 220 K and a huge increase with decreasing temperature.

Values of the maximum surface coverage, N_{max} , vary between $1.2 \pm 0.2 \times 10^{14}$ molecules cm^{-2} (230 K, Arora et al, 1999), $(2.1 - 2.7) \times 10^{14}$ molecule cm^{-2} (214 -239 K, Ullerstam et al., 2005), and 3×10^{14} molecule cm^{-2} (Hynes et al, 2002). These values are consistent with values for other traces gases on similar ice surfaces, and with molecular dynamics calculations (Abbatt, 2003).

Partitioning coefficients in the table were derived using a single site Langmuir model for the data reported by the Abbatt group and a 2-site model for the Hynes data, who also used a high value of $N_{\text{max}} = 10^{15} \text{ cm}^{-2}$ in their fit. Ullerstam et al showed that the 2-site model failed when tested against data at low p_{HNO_3} . Variable values of the derived equilibrium partition coefficients and adsorption enthalpy, ΔH_{ads} , result from different models used to interpret the results. Bartels-Rausch et al reported $\Delta H_{\text{ads}} = -44 \text{ kJ mol}^{-1}$ from chromatographic measurements of HNO_3 retention in a packed ice column, which lies midway between the other reported values. The preferred partitioning coefficient is based on the data of Ullerstam et al., 2005, using the refined analysis given in the study of Cox et al., 2005. This may be used in the full form of the single site Langmuir isotherm :

$$\theta = \frac{N_{\text{max}} K_{\text{eq}} [\text{HNO}_3]}{1 + K_{\text{eq}} [\text{HNO}_3]}$$

together with the recommended N_{max} value, based on the values given by Ullerstam, 2005, to provide a simple parameterisation appropriate for equilibrium surface coverages at concentrations up to $\sim 5 \times 10^{-7}$ mbar in the given temperature range. At lower temperatures and higher p_{HNO_3} , near the phase boundary for thermodynamic stability of hydrates or supercooled $\text{HNO}_3/\text{H}_2\text{O}$ solutions, uptake is continuous with no saturation and the Langmuir model cannot be used. Note however that all flow tube studies report that the adsorption of HNO_3 to ice is not completely reversible, even in the HNO_3/ice stability regime. Surface spectroscopic investigations (Zondlo et al., 1997; Hudson et al, 2002) suggest that adsorbed HNO_3 is solvated to form nitrate ions, suggesting that adsorbed molecules enter the surface layer of the ice film. Measurements of the uptake coefficient are problematic in CWFT experiments, due to the difficulty in separating adsorption and desorption kinetics and to diffusion limitations, which will result in determination of a lower limit. Knudsen cell measurements of γ_0 indicate a surface accommodation coefficient of ~ 0.3 at $T < 200 \text{ K}$. The uptake coefficient decreases with time as increasing amounts of HNO_3 are adsorbed in the ice film, and most measurements are affected by this. The recommended value for γ_0 is based on the measurements of Abbatt (1997) Hanson (1992) and Aguzzi and Rossi (2001).

Ullerstam and Abbatt (2005) showed that on growing ice the long term uptake of nitric acid is significantly enhanced compared to an experiment performed at equilibrium, i.e. at 100% relative humidity (RH) with respect to ice. The fraction of HNO_3 that is deposited onto the growing ice surface is independent of the growth rate and may be driven by the solubility of the nitric acid in the growing ice film rather than by condensation kinetics alone.

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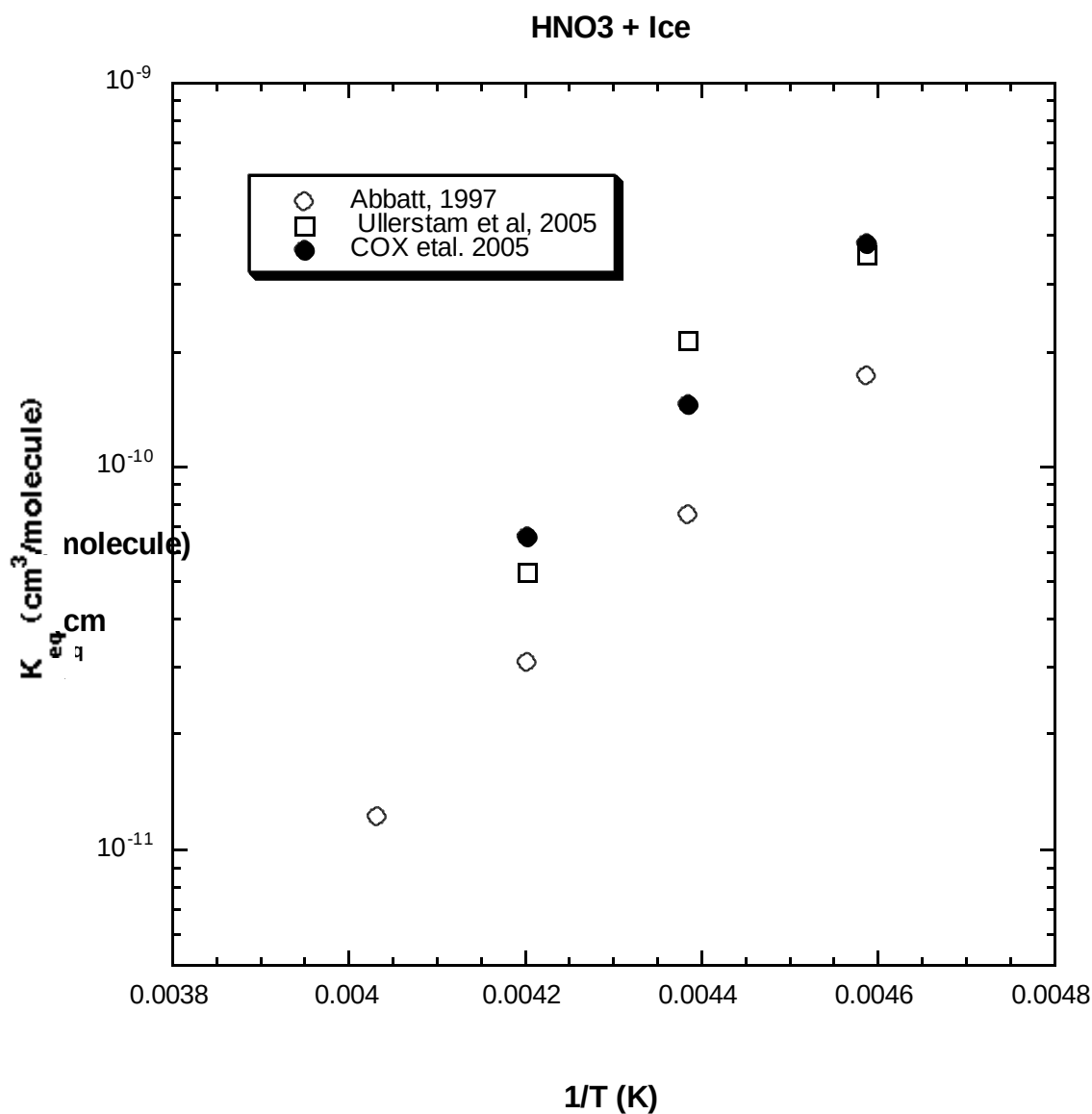
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HNO3+ice_data

