

IUPAC Taskgroup on Atmospheric Chemical Kinetic Data Evaluation Data Sheet HI8; V.A1.8

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This datasheet last evaluated: June 2014; last change in preferred values: December 2007.

NO₂ + ice → products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients: γ</i>			
$\gamma_{ss} < 1.0 \times 10^{-4}$	195	Leu, 1988	CWFT-MS (a)
$\gamma_{ss} < 5.0 \times 10^{-6}$	193-243	Saastad, et al., 1993	Static -MS (b)
<i>K_{inc} (cm)</i>			
$3.07 \times 10^{-09} \exp(2646/T)$	140- 150K	Bartels-Rausch et al., 2002	PBFT-RC (c)

Comments

- Uptake experiment in an ice-coated flow tube coupled to electron-impact MS. The ice film was deposited from water vapor.
- Measurement of the total pressure drop in a static system over bulk ice and frozen 70% H₂SO₄-H₂O monitored by MS.
- NO₂-ice partitioning coefficients derived from packed ice bed (PB) experiments using radioactively labelled NO₂ at concentrations of 3 ppbv and below. Ice prepared from freezing water drops in liquid N₂ and then annealing at 258 K during at 12 h. The technique involves observing the migration of radioactively labelled NO₂ molecules along the temperature gradient established along the flow tube. The adsorption enthalpy of -22 ± 1 kJ mol⁻¹ was derived by solving a migration model of linear gas chromatography and assuming a value of the adsorption entropy of -39 Jmol⁻¹K⁻¹ (based on $A_0 = 6.7 \times 10^6$ m²) based on theoretical arguments. The tabulated K_{inc} was derived from these values. Due to the very low partitioning coefficient of NO₂, adsorption could only be observed at very low temperature, i.e. between 140 and 150 K. From the absence of a concentration dependence, the authors conclude that N₂O₄ was not involved in the adsorption process that governed partitioning.

Preferred Values

Parameter	Value	T/K
$K_{\text{inc}} / \text{cm}$	$3.07 \times 10^{-09} \exp(2646/T)$	190 – 250
<i>Reliability</i>		
$\Delta(E/R) / \text{K}$	± 100	190 - 250

Comments on Preferred Values

Due to the low interaction energy, the adsorption kinetics or equilibrium of NO_2 can not be observed at relevant temperatures. The partitioning derived from Bartels-Rausch et al. (2002) is tied to the observation at 144 K. Therefore the extrapolation to higher temperature is somewhat problematic and should be treated with caution as the properties of the ice surface may change towards higher temperatures.

The low interaction energy has been confirmed using surface spectroscopy techniques (Ozensoy et al., 2006, Wang and Koel, 1999, Rieley et al., 1996, Kim and Kang, 2010). Kim and Kang (2010), using reactive ion scattering, reported evidence for the desorption of HONO following deposition of submonolayer amounts of NO_2 and increasing the temperature to 140 K. They suggested that conversion of NO_2 to HONO occurred. At higher NO_2 coverages, they also found the formation of nitrate at the surface that could be ascribed to disproportionation of NO_2 . Since the highly endothermic reaction $\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{OH}$ is unlikely to occur, the true reductant for NO_2 at low coverages remains uncertain, and the relevance for NO_2 chemistry on ice under atmospheric conditions remains unclear.

References

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