

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet V.A5.2 HNDT2

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H₂O + NAT

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
<i>Uptake coefficients, γ</i> $2.0 \times 10^{-3} \leq \gamma_{ss} \leq 1.0 \times 10^{-2}$	197	Middlebrook <i>et al.</i> , 1992	Static reactor/ FTIR (a)
<i>Accommodation coefficients, α</i> (2.2 – 6.0) $\times 10^{-2}$ (α) (β -NAT)	192-202	Biermann <i>et al.</i> , 1998	Slow-Flow reactor/FTIR (b)
0.32 \pm 0.14 (α) (α -NAT)	179-185	Delval and Rossi, 2005	SFR – FTIR (c)
0.15 \pm 0.12 (β -NAT)			
0.38 \pm 0.12 (α -NAT)	189-195		
0.069 \pm 0.047 (β -NAT)			
0.56 \pm 0.31 (α -NAT)	205-208		
0.0166 \pm 0.001 (β -NAT)			

Comments

- (a) Isothermal film growth experiment in a static chamber with time-dependent FTIR monitoring of optical density at 3371 cm⁻¹ during deposition of NAT film on Si support. $p_{\text{H}_2\text{O}} = (2.0 - 4.0) \times 10^{-4}$ mbar and $p_{\text{HNO}_3} = (5.3 - 40) \times 10^{-7}$ mbar. The spread of the γ values given in the table corresponds to the range in the HNO₃ pressure. A doubling of H₂O at the upper limit of the HNO₃ pressure left the uptake coefficient unchanged.
- (b) Evaporation experiment performed in a 100 cm³ slow-flow cell fed by a thermostatted bubbler containing a binary H₂O/HNO₃ solution ($[\text{H}_2\text{O}]/[\text{HNO}_3] = 68$) and using N₂ as a carrier gas at 0.85 mb. Polished Au-coated support was used as a mirror for near-normal incidence FTIR absorption. The α values have been calculated from the thickness vs. time curves obtained from FTIR absorption and optical constants of ice and NAT and do not include mass transport corrections. They must therefore be regarded as lower limiting values. No apparent temperature dependence was found. The vapor pressure of an ice film is altered neither by condensed NAT nor an ice-free NAT layer located on top of pure ice.
- (c) Measurement of H₂O evaporation rate using a multidagnostic stirred flow reactor using a quartz crystal microbalance (QCMB), FTIR absorption in transmission and residual gas MS. The ice sample was vapor-deposited on either a Au-coated SiO₂ crystal (QCMB) or a Si-window (FTIR) at 190 K upon which typically between a few and 200 monolayers of HNO₃ were deposited, respectively. The evaporation rate of H₂O was recorded as a function of time and ranged from the rate of pure ice evaporation at the start of the experiment to decomposition of β -NAT at the end. FTIR absorption of thin ice films doped with HNO₃ pointed to the existence of pure ice, α - and β -NAT, in this sequence, upon evaporation.

Preferred Values

$$\begin{array}{lll} \alpha (\alpha\text{-NAT}) = 0.32 & \alpha (\beta\text{-NAT}) = 0.15 & T = 182 \text{ K} \\ \alpha (\alpha\text{-NAT}) = 0.38 & \alpha (\beta\text{-NAT}) = 7.0 \times 10^{-2} & T = 192 \text{ K} \end{array}$$

$$\alpha(\alpha\text{-NAT}) = 0.56 \quad \alpha(\beta\text{-NAT}) = 1.7 \times 10^{-2}$$

$$T = 207 \text{ K}$$

Reliability

$$\Delta \log \alpha = 0.3$$

Comments on Preferred Values

The kinetic uptake data of Middlebrook *et al.* (1992) have been obtained from a pressure measurement inside a static reactor and observation of the changes in optical density of the growing film using FTIR absorption, whereas Biermann *et al.* (1998) have measured the evaporation rates at small undersaturation of H₂O close to equilibrium. Delval and Rossi (2005) have measured $\alpha(\text{H}_2\text{O})$ from time-dependent evaporation rates under conditions that precluded adsorption processes (low partial pressure of H₂O, hence strong H₂O undersaturation owing to fast pumping conditions). The Middlebrook *et al.* (1992) and Biermann *et al.* (1998) values (γ_{ss}) are lower limits to H₂O accommodation on β -NAT, the stable crystalline modification of NAT. The results of Delval and Rossi (2005) approach those corresponding to the upper limit of Middlebrook *et al.* (1992) at the high temperature end, in agreement with the known trend of α to decrease with increasing temperature (negative temperature dependence) in analogy to the interaction of H₂O with pure ice in the same temperature range. The general agreement of $\alpha(\text{H}_2\text{O})$ for β -NAT in the narrow overlapping temperature range of Biermann *et al.* (1998) and Delval and Rossi (2005) is satisfactory although the former do not report a specific temperature dependence. However, the positive temperature dependence of α of Delval and Rossi (2005) on α -NAT, a metastable form of crystalline NAT and a precursor during formation of β -NAT, is unexpected and not yet understood. The larger α value for amorphous compared to crystalline ice in the given temperature range is in agreement with the results of Speedy *et al.* (1996) if we identify the α -NAT phase with an amorphous state of the condensate. Although β -NAT was the stable species in the H₂O/HNO₃ system in the kinetic experiments of Delval and Rossi (2005) in agreement with the phase diagram, the IR-spectroscopic identification of both α - and β -NAT have been made using HNO₃ doses that were a factor of 30 to 50 larger to enable the spectroscopic detection of thin films of NAT in the mid-IR spectral region. The significant scatter in the α -values for α and β -NAT of Delval and Rossi (2005) is perhaps due to the time scale of α - to β -NAT conversion that is competitive with H₂O evaporation.

References

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