

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A1.04 HET_H2OL_4

Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hard copy without explicit written permission.

The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This data sheet evaluated: June 2011; last change in preferred values: June 2011.

NO₃ + H₂O (aq) → Products

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
α_b			
$> 4 \times 10^{-2}$	273 ± 1	Rudich et al., 1996	WWFT-AS (a)
$> 2 \times 10^{-3}$	293	Thomas et al., 1998	(b)
$4.2^{+2.2}_{-1.7} \times 10^{-3}$	293 ± 1	Schütze et al., 2005	(c)
H (M atm ⁻¹)			
0.6 ± 0.3	273 ± 1	Rudich et al., 1996	WWFT-AS (a)
1.8	293	Thomas et al., 1998	(b)
0.2 ± 0.1	293 ± 1	Schütze et al., 2005	(c)

Comments

- (a) Flow tube operated at 12-23 mbar. NO₃ (2-10 × 10¹¹ molecule cm⁻³) was formed by the thermal dissociation of N₂O₅ and detected by diode laser absorption at 662 nm over a 12.6 m pathlength. A lower limit for α_b was estimated from reactive uptake measurements (see datasheet VI.A2.05). The dependence of uptake coefficient, γ , on Cl⁻ concentrations was combined with a literature value (Exner et al., 1992) for the rate coefficient for Cl⁻ with NO₃ (2.76 × 10⁶ M⁻¹s⁻¹ at 273 K) to determine a value of $HD_l^{0.5}$ of (1.9 ± 0.4) × 10⁻³ M atm⁻¹ cm s^{-0.5}. Assuming a value of D_l of (1.0 ± 0.5) × 10⁻⁵ cm² s⁻¹ enabled a solubility of NO₃ in H₂O to be derived.
- (b) Uptake of NO₃ (generated by mixing NO with O₃ at ≈ 400 °C) to 0.1 M chloride solution was monitored using three serial coiled glass denuders (2 mm id). Nitrate in solution was determined following reduction to NO₂⁻ and the Saltzman reaction. Large diffusion limitations result in only a lower limit to γ .
- (c) Single droplet (≈ 7 mm³) suspended from a pipette in a flow tube (10 mbar He) with UV-Vis absorption spectroscopy for concentration measurement in both gas and aqueous phases (NO₃⁻ at 235 nm, NO₃ using the 662 nm feature. NO₃ was generated by reacting NO₂ with O₃ at 393 K to keep the N₂O₅ level low (≈ 5 %). HNO₃ was formed at ≈ the same concentration as NO₃. Uptake of NO₃ to the droplet was monitored by nitrate anion absorption. A value of $HD_l^{0.5}k^{0.5} = (1.9 \pm 0.2) \text{ M atm}^{-1} \text{ cm s}^{-0.5}$ was derived.

Preferred Values

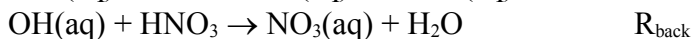
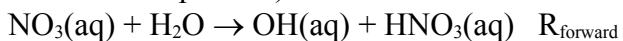
Parameter	Value	T/K
α_b	1.3×10^{-2}	273
$k_{H_2O} (M^{-1} s^{-1})$	23	273
$H (M atm^{-1})$	0.6	273
<i>Reliability</i>		
$\Delta \log (\alpha_b)$	0.5	273
$\Delta \log (k_{H_2O})$	0.5	273
$\Delta \log (H)$	0.5	273

Comments on Preferred Values

The accommodation coefficient, α_b , was derived from uptake of NO_3 to salt solutions as described in datasheet VI.A2.05.

The solubility, H , of NO_3 has been determined on several occasions, the more recent results suggest that it is low, with numbers of (0.6 ± 0.3) and $(1.8 \pm 1.5) M^{-1} atm^{-1}$ derived by Rudich et al (1996b) and Thomas et al (2005) compared to e.g. $12 M^{-1} atm^{-1}$ reported by Chameides (1986). We prefer the results of Rudich et al., in order to maintain an internally consistent set of parameters for modelling NO_3 uptake to both pure water and halide solutions (see VI.A2.05).

Rudich et al. (1996) observed reactive uptake of NO_3 in the absence of halide ions (or other detectable impurities) and attributed this to the hydrolysis of NO_3 :



with a rate constant of $k_{H_2O} = 23_{-13}^{+30} M^{-1} s^{-1}$ for the forward reaction. Similarly, Schütze et al. (2005) observed reactive uptake and formation of nitrate ions in the interaction of NO_3 with a pure H_2O droplet with an uptake coefficient of $\sim 10^{-4}$ implying a hydrolysis rate coefficient of $670_{-580}^{+2300} M^{-1} s^{-1}$ if nitrate (i.e. aqueous phase HNO_3) was formed only as shown above. Even the lower limits of these rate constants are incompatible (by orders of magnitude) with the observations of Thomas et al (1998), who derive an upper limit of $0.5 M^{-1} s^{-1}$ for k_{H_2O} .

Whilst Rudich et al., made efforts to eliminate reaction with impurities in their water film and ruled out gas-phase reactions as being responsible for NO_3 loss, Thomas et al. hypothesise that impurities, a surface (rather than bulk) reaction of NO_3 or non-laminar flow in the liquid film of Rudich et al could contribute to observation of an apparent, large hydrolysis rate constant. On the other hand, calculations of the equilibrium constant for reaction of NO_3 with water Rudich et al (1996b) combined with the measured rate constant for the back reaction (Katsamura et al., 1991) result in $k_{H_2O} = 6 M^{-1} s^{-1}$ at 298 K, roughly consistent with the observations.

Whilst recognising that there is very large uncertainty associated with values of each of α_b , H and k_{H_2O} , we adopt the results of Rudich et al. (1996) so that the following expression, when used to calculate an uptake coefficient for NO_3 on pure water, returns a value of $\gamma \sim 2 \times 10^{-4}$, which is consistent with their experimental observations.

$$\gamma = \left\{ \frac{1}{\alpha_b} + \frac{c}{4HRT(D_l k_{H_2O}')^{0.5}} \right\}^{-1}$$

with $D_l \sim 1 \times 10^{-5} cm^2 s^{-1}$.

The aqueous phase products of NO_3 hydrolysis are suggested to be OH and HNO_3 . Clearly, further work on the uptake and reaction of NO_3 on water is required to reduce uncertainties associated with this process.

References

- Chameides, W. L., J. Geophys. Res. 91, 14571-14572, 1986.
- Exner, M., Herrmann, H. and Zellner, R.: Ber. Bunsen. Ges. Phys. Chem. Chem. Phys 96, 470-477, 1992.
- Rudich, Y., Talukdar, R. K., Ravishankara, A. R. and Fox, R. W.: J. Geophys. Res. 101, 21023-21031, 1996.
- Schütze, M. and Herrmann, H.: J. Atmos. Chem. 52, 1-18, 2005.
- Thomas, K., Volz-Thomas, A., Mihelcic, D., Smit, H. G. J. and Kley, D.: J. Atmos. Chem. 29, 17-43, 1998.