IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.6 HET_SALTS_6

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$N_2O_5 + Cl^-/Br^-$ (aq) $\rightarrow$ products
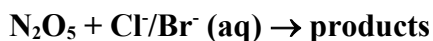
Experimental data

Parameter	Aqueous solution	Temp./K	Reference	Technique/ Comments
Uptake coefficients, γ				
$(3.9 \pm 0.13) \times 10^{-2}$	NaCl (1 M)	263	George et al., 1994	DT-HPLC (a)
$(3.7 \pm 1.2) \times 10^{-2}$		268		
$(1.4 \pm 0.3) \times 10^{-2}$		273		
$(1.4 \pm 0.08) \times 10^{-2}$		278		
$(3.2 \pm 0.2) \times 10^{-2}$	NaCl (1.7 – 5.1 M)	291	Behnke et al., 1997	Aerosol chamber (b)
$(1.8 \pm 0.3) \times 10^{-2}$	NaCl (1M) NaBr (0.1 – 1 M) NaI (0.1 – 1 M)	262-278	Schweitzer et al., 1998	DT-MS (c)
0.64×10^{-2}	NaCl (RH = 30 %)	295 ± 2	Stewart et al., 2004	AFT-CIMS (d)
0.9×10^{-2}	NaCl (RH = 50 %)			
1.04×10^{-2}	NaCl (RH = 70 %)			
0.78×10^{-3}	NaCl (RH = 80 %)			
1.6×10^{-2}	natural sea-salt (RH = 30 %)			
2.8×10^{-2}	natural sea-salt (RH = 50 %)			
1.3×10^{-2}	natural sea-salt (RH = 70 %)			
3.1×10^{-2}	natural sea-salt (RH = 80 %)			
$(2.2 \pm 0.4) \times 10^{-2}$	synthetic sea-salt (RH = 50 %)	295	Thornton and Abbatt, 2005	AFT-CIMS (e)
$(3.0 \pm 0.8) \times 10^{-2}$	synthetic sea-salt (RH = 65 %)			
$(2.4 \pm 0.5) \times 10^{-2}$	synthetic sea-salt (RH = 70 %)			

Comments

(a) N_2O_5 made in-situ by reacting NO with O_3. Droplet train flow tube operated at 27-80 mbar He with $80 - 150$ μm droplets. Trace gas concentration measured by FTIR at entrance to flow tube, nitrate content of droplets analysed by HPLC to derive uptake coefficients. This required knowledge of the relative efficiency of nitrate and nitryl-chloride products.

(b) Teflon aerosol smog chamber at 1 atm. pressure. Initial concentration of N_2O_5 determined by FTIR. Subsequent to reaction of N_2O_5 with aerosol, NO_3 (in equilibrium with gas-phase N_2O_5) was photolysed and NO_x was analysed to indirectly derive total un-reacted N_2O_5. N_2O_5 taken up to the aerosol was calculated from the difference in initial and final concentrations. The amount of $ClNO_2$ was determined by its photolytic conversion to Cl atoms (determined by

hydrocarbon consumption). Aerosol number and size distribution (average diameter ≈ 150 nm) were obtained using a DMA-CPC. Values for the uptake coefficient supersede those reported in short communications by Behnke et al. (1991, 1992, 1993).

(c) N_2O_5 made in-situ by reacting NO with O_3. $80 - 150$ μm droplets. Gas analysed by ion-trap MS and FTIR (for $ClNO_2$ formation).

(d) Uptake of N_2O_5 (100-700 ppbv at atmospheric pressure) to particles of aqueous aerosol of pure NaCl or natural sea-salt with diameters of ~ 60-250 nm at RH between 30 and 80 %. N_2O_5 was detected as the change in NO signal (monitored with ta CLD) following thermal dissociation to NO_3 and titration with NO. The measured uptake coeficients were strongly influenced by droplet size, indicating volume limited uptake. Once corrected for diffuso-reactive effects, the uptake coefficients (listed in the table) were independent of RH.

(e) Uptake of N_2O_5 (8-30 ppbv at atmospheric pressure) to particles of aqueous aerosol of synthetic sea-salt (containing Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and Br^-) with surface area weighted particle radii of 90 to 150 nm. N_2O_5 was detected as NO_3^- using I^- prmary ions. No significant influence of particle size (varied e.g. for RH = 50 % from 85 to 134 nm) on γ was observed. The presence of (an estimated) monolayer of hexanoic acid reduced the uptake coefficient (at RH = 70 %) to $(8 \pm 4) \times 10^{-3}$ but had no effect at RH = 50 %.
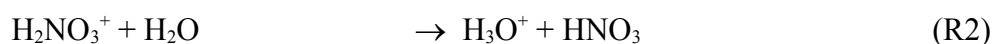
Preferred Values

Parameter	Value	T/K
γ	0.02	260 - 300
K_3 / k_2	450	298

Reliability

Δ log (γ)	±0.3	260 - 300
Δ log (k_3 / k_2)	±0.3	298

Comments on Preferred Values

The preferred values of γ are independent of RH and temperature and refer to the uptake of N_2O_5 to pure water-halide solutions. The presence of nitrate and / or organic components can reduce γ (datasheets VI.A3.7 and VI.A3.8). Indeed, Thornton and Abbatt (2005) argue that the particle size dependence of γ observed by Stewart et al. (2004) was not entirely due to reacto-diffusive length considerations but also to use of high gas-phase N_2O_5 resulting in high particle nitrate content, which suppresses the uptake of N_2O_5. Both Stewart et al. (2004) and Thornton and Abbatt (2005) showed that the uptake cofficient on sea-salt dried to below the crystallisation RH was much lower. For aqueous particles with RH > 50 %, γ is independent of chloride or bromide concentration or relative humidity. Within experimental scatter and the range covered there is also no dependence of γ on the temperature, with datasets on synthetic salt surfaces at 295 K giving the same uptake coefficient as NaCl and NaCl/NaBr containing aqueous solutions at ~ 270 K.

The observation that the uptake coefficient is insensitive to the aqueous composition (content of chloride, bromide or iodide) and that the yield of $ClNO_2$ following uptake of N_2O_5 to chloride solutions of concentration ≥ 1 M approaches unity (Behnke et al., 1997; Schweitzer et al. 1998; Roberts et al., 2009) has led to the following mechanism being proposed, with dissociation of N_2O_5 (R1) the rate limiting step.

$$N_2O_5 + H_2O \qquad \Leftrightarrow H_2NO_3^+ + NO_3^- \qquad (R1)$$

$$H_2NO_3^+ + H_2O \qquad \rightarrow H_3O^+ + HNO_3 \qquad (R2)$$

$$H_2NO_3^+ + Cl^- \qquad \rightarrow ClNO_2 + H_2O \qquad (R3)$$

From the reaction scheme above, the yield of $ClNO_2$ is defined by competition between hydrolysis (with rate coefficient k_2) and reaction with chloride anions (rate coefficient k_3) so that:

$$\frac{[ClNO_2]}{\Delta[N_2O_5]} = \left(\frac{k_2[H_2O]}{k_3[Cl^-]} + 1 \right)^{-1}$$

Schweitzer et al. (1999) reported unity (1.00 ± 0.14) yield of $ClNO_2$ per N_2O_5 taken up to 1 M Cl^- solution. Within the error bounds this is consistent with the results of Behnke et al. (1999) who used the WWFT method to derive yields of $ClNO_2$ from 0.4 (at their lowest, non-zero chloride concentration) to > 0.9 at 2 M chloride and above. From their data they calculated k_3 / k_2 (at 291 K) = 836 ± 32. On synthetic sea-salt (50 % RH) Thornton and Abbatt (2005) derived a lower limit to the $ClNO_2$ yield of 50 %. Roberts et al. (2009), measured chloride molarity dependent yields of $ClNO_2$ over the range 0.02 to 0.5 M Cl^-. A number of chloride containing substrates were examined including $(NH_4)HSO_4$, $(NH_4)_2SO_4$, water, oxalic acid, sea-salt. The yield of $ClNO_2$ depended only on the chloride concentration, though there may have been evidence for a slightly enhanced yield at low pH. They calculated k_3 / k_2 (at 297 K) = 450 ± 100. Bertram and Thornton examined the effect of chloride and nitrate concentrations on the $ClNO_2$ yield from the uptake of N_2O_5 to mixed nitrate /chloride particles and derived k_3 / k_2 (at 298 K) = 483 ± 175.

Our preferred value for the value of k_3 / k_2 (at 298 K) is based on the most detailed study (Roberts et al., 2009). Roberts et al. suggest that k_2 (but not the ion recombination reaction, k_3) is likely to have a large barrier and thus be slower at lower temperatures, which would result in a larger k_3 / k_2 and thus larger $ClNO_2$ yield for a given Cl^- concentration. The experimental datasets are however not precise enough to clarify if the larger k_3 / k_2 value of Behnke et al. is due to use of slightly lower temperatures in their experiments or if it is related to use of various ionic strength solutions and thus Cl^- activities. We note also that, at low pH the yield of $ClNO_2$ can be depleted due to conversion to Cl_2 (Roberts et al., 2008). This is covered in datasheet VI.A2.9 dealing with $ClNO_2$ uptake.

Schweitzer et al. (1999) report $BrNO_2$ and Br_2 formation when using NaBr solutions and I_2 when using NaI solution.

There have been a number of studies on the uptake of N_2O_5 to dry salt surfaces (Finlayson-Pitts, 1989; Leu et al., 1995; Fenter et al., 1996; Msibi et al., 1998; Koch et al., 1999; Hoffmann et al., 2003). These studies also report high yields of $ClNO_2$ when N_2O_5 reacts with a chloride surface (Finlayson-Pitts et al., 1996; Fenter et al. 1996, Koch et al., 1999; Hoffmann et al., 2003). The reaction with bromide leads to Br_2 formation, presumably via formation of $BrNO_2$, which can further react with surface bromide (Fenter et al., 1996):

$$N_2O_5 + Br^- \rightarrow BrNO_2 + NO_3^-$$

$$BrNO_2 + Br^- \rightarrow Br_2 + NO_2^-$$

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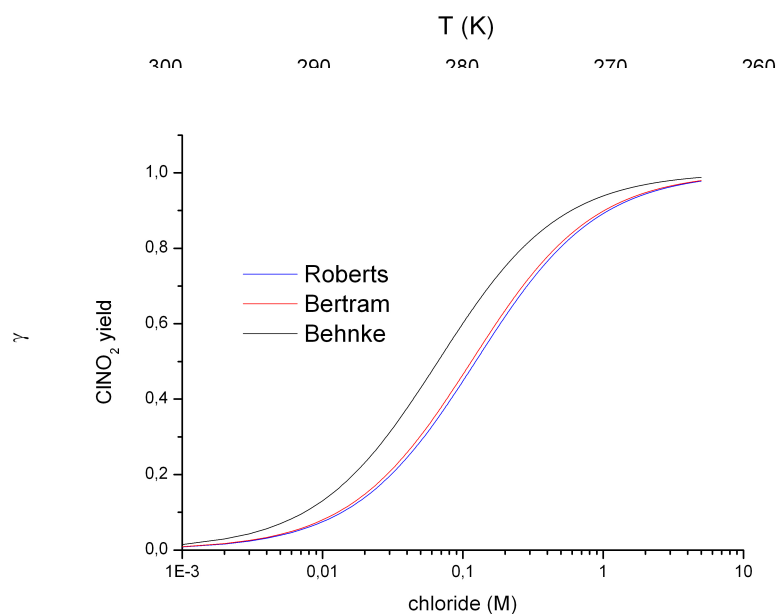
Yield of $ClNO_2$ per N_2O_5 reacted on chloride surfaces at 298 K. The Uptake IUPAC preferred value is that of Roberts (2009).   IUPAC preferre