IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.4 HET_SALTS_4

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NO_2 (g) + aqueous sea salt aerosol → products

Experimental data

Parameter	RH / %	Temp./K	Reference	Technique/ Comments
Uptake coefficients: γ				
$\gamma < 10^{-4}$	50-80	292	Behnke et al., 1996	(a)
$\gamma < 10^{-4}$	75	298	Abbatt and Waschewsky, 1998	AFT-CIMS (b)
$(3.7\pm0.5) \times 10^{-4}$	90	279	Harrison and Collins, 1998	AFT-CLD (c)
$(2.8\pm0.5) \times 10^{-4}$	85	279		
$\approx 10^{-4}$ (1 mM NaCl)		298	Yabushita et al., 2009	(d)
Solublity, H (M atm^{-1})				
$(5.5\pm0.6) \times 10^{-2}$		284	Cape et al., 1993	(e)
Liquid phase rate constants				
$k^{II}_{R1} = (1.8\pm0.7) \times 10^{6}$ M^{-1} s^{-1} (30 g l^{-1} NaCl)		284	Cape et al., 1993	(e)
$k^{I}_{R2} = 1.4 \times 10^{-6}$ M s^{-1}	80	293	Karlsson and Ljungström, 1995	AFT-IC (f)
$k^{I}_{R2} = 1.7 \times 10^{-6}$ M s^{-1}		283		
$k^{I}_{R2} = 4.4 \times 10^{-6}$ M s^{-1}		273		

Comments

(a) Deliquesced NaCl aerosol (70μg m^{-3}) was exposed to 58 ppb of NO_2 in a chamber, leading to about 10% of NO_2 loss after about three hours in the dark, which was used to estimate the uptake coefficient listed in the table, based on the size distribution measured by SMPS. Switching on simulated sunlight did not result in Cl atoms expected from photolysis NOCl, but rather in OH radicals presumably from photolysis of HONO formed via hydrolysis of NOCl.

(b) Uptake experiment on liquid NaCl in atmospheric pressure aerosol flow tube using CIMS detection. The NaCl aerosol produced with a nebulizer had a bimodal distribution (large average diameter: 2-4 μm, small: <1μm) with typical surface areas and particle number densities in the range of 1-6×10^{-3} cm^2/cm^3 and 1 to 4×10^4 particles/cm^3, respectively. The

solution nebulized was either unbuffered NaCl solution, or solution adjusted to pH=0.3 with HCl, or to pH=7.2 with NaH_2PO_4/Na_2HPO_4. No NO_2 loss could be detected between 3×10^{12} and 2×10^{14} molecules/cm^3. The value of γ is an upper limit based on the detection limit.

(c) Uptake experiment on dry and deliquesced NaCl aerosol in atmospheric pressure flow tube at 2 ppm of NO_2. NO_2 loss was monitored using a chemiluminescence detector. A nylon filter and a filter impregnated with sodium carbonate was used to prevent HNO_3 and HONO, respectively, from being detected by the CLD. NO_2 decay rates were determined as a function of the aerosol surface to volume ratio determined by SMPS, from which the uptake coefficient was derived. The values for the conditions of deliquesced NaCl aerosol are listed in the table. Surprisingly, the uptake coefficient for dry NaCl particles at 50% relative humidity was even higher, 10^{-3}.

(d) Microdroplets were generated by nebulization of aqueous halogenide solutions into ppmv $NO_2(g)/N_2$ ($1\text{-}5\times10^{14}$ cm^{-3}) mixtures at atmospheric pressure, leading to interaction times of about 1 ms. Droplets were then expanded into a mass spectrometer. The rate of appearance of nitrate, from which the uptake coefficient was estimated, had a maximum in the 10^{-3} M range for chloride, bromide and iodide, which is listed in the table. The uptake coefficient for these solutions was 4 orders of magnitude larger than that on neat water.

(e) NO_2 at partial pressures of 10 to 100 ppb was passed through 1.0 l of aqueous solution in a fritted bubbler in a thermostatted vessel. The loss of NO_2 was measured with a chemiluminescence detector. Apart from pure water, the aqueous solutions used were 30 g l^{-1} NaCl, two synthetic sea salt mixtures at comparable concentration, and authentic coastal sea-water. The solubility derived from the kinetic experiments was independent of the type of solution. However, the rate constants for the solutions were higher, up to a factor of 10 for sea-water. The authors caution that the distribution of NO_2 in the reactor may have not been uniform, leading to an overestimate of the rate constants.

(f) The flow reactor consisted of six 10 l halocarbon wax coated glass tubes connected in series. Sea salt aerosol was produced by nebulizing synthetic sea water and bringing to charge equilibrium with a ^{85}Kr source. The particle size distribution was measured with an electrostatic classifier coupled to an aerosol electrometer. The geometric mean number diameter was between 100 and 120 nm. Nitrogen dioxide concentrations ranged from 50 to 500 ppbv and were monitored with a chemiluminescence detector. Particles were collected on a filter after the flow reactor and after a $KMnO_4$ coated denuder removing gas phase NO_2. Experiments at humidities below the deliquescence of the particles indicated a lower limit for the uptake coefficient of 3×10^{-4} with negative humidity dependence. The first order loss rate constants for chloride at 80% relative humidity listed in the table were derived from experiments at 190 ppb NO_2. The authors ascribed this loss entirely to the reaction $2\,NO_2 + Cl^- \rightarrow NO_3^- + NOCl$.

Preferred Values

| Parameter	Value	T/K
k_{R2}^{II} / M^{-1} s^{-1}	200	298
Reliability		
$\Delta \log (k)$	0.7	

Comments on Preferred Values

While a significant number of studies have investigated the reaction of NO_2 with solid NaCl and other sea salt proxies (Rossi (2003) and references therein) and also the significant impact of humidity on these reactions, only a few studies have addressed the uptake to deliquesced sea salt particles representative of marine boundary layer conditions. The only aerosol flow tube study that covers relevant low NO_2 concentrations is that by Abbatt and Waschewsky (1998), which reports an upper limit for γ consistent with the results from the chamber experiment by Behnke et al. (1996). The high uptake coefficients obtained by Harrison and Collins (1998) are likely the result of an experimental artifact, e.g., due to the fact that particles were deposited on a filter before analysis of the gas phase, leading to additional residence time during which they were effectively exposed to NO_2. These high uptake coefficients are not used to recommend a value for the bulk accommodation coefficient, α_b.

Apart from the hydrolysis reaction (R1), a possible fate of NO_2 at low concentration is reaction (R2):

$$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{R1}$$
$$2\ NO_2 + NaCl \rightarrow NOCl + NaNO_3 \tag{R2}$$
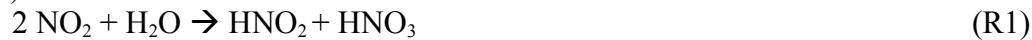
Karlsson and Ljungström (1995) determined removal rates of chloride in an aerosol flow tube experiment of 1.7×10^{-6} M s^{-1} at 190ppb NO_2 at 293 K, which increased with decreasing temperature. Taking the Henry's Law constant for pure water of 1.4×10^{-2} M atm^{-1} (Cheung et al., 2000) and a chloride concentration of 4.4 M, this would lead to a liquid phase rate constant for (R2) of 200 M^{-1} s^{-1}, which is the basis for the recommendation. Karlsson and Ljungström observed NOCl in a separate bubbler experiment with higher NO_2 concentration. Behnke et al. hypothesised that NOCl hydrolysed to form HONO in their chamber experiment.

The NO_2 loss rates measured by Cape et al. (1993) in a 0.5 M NaCl solution at 283 K between 10 and 100 ppb of NO_2 were not different from those in pure water and ascribed entirely to the hydrolysis reaction. Cape et al. observed NO_2 removal rates enhanced by up to a factor of 10 in authentic sea water, which they ascribed either to catalysis of the hydrolysis reaction or to an unknown reaction with another species. The magnitude of the hydrolysis rate constant reported by Cape et al. was likely affected by non-uniform distribution of reactants in the reactor. We therefore do not provide a recommendation for R1 here, but suggest using the rate constant recommended for pure water on data sheet VI.A1.3, 3.0×10^7 M^{-1} s^{-1}, also for deliquesced sea salt aerosol.

Bambauer et al. (1994) determined the rate of nitrate formation in cloud chamber experiments, in which the cloud droplets contained mM amounts of NaCl. The reaction order was about 1, in disagreement with Cape et al. (1993). An uptake coefficient was not extracted, nor was the possibility explored that reaction (R2) could have interfered with the hydrolysis of NO_2. For droplets of similar composition, Yabushita et al. (2009) observed a very large uptake coefficient and suggest that NO_2 hydrolysis is enhanced in presence of millimolar concentrations of halogenide ions through formation of a charge transfer complex NO_2-X$^-$ at the solution – air interface, which could account for the discrepancy between the Bambauer et al. and Cape et al. studies that were otherwise discussed in terms of different mixing regimes. Given that the NO_2 concentrations in the experiment by Yabushita et al. were three orders of magnitude above atmospheric, the extent of such a surface process for deliquesced sea salt particles remains uncertain, and no recommendation is given.

The value reported for the solubility by Cape et al. (1993) is affected by the same issues as the rate constants mentioned above, as they are interconnected through $Hk_2^{1/2}$, which is the

parameter directly retrieved from their experiments. As Cape et al. did not see a difference in solubility between pure water and chloride solution, we recommend using the solubility for pure water reported by Cheung et al. (2000).

References

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