IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet VI.A2.7 HET_SALTS_7

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$$HNO_3 (g) + Cl^- (aq) \rightarrow HCl (g) + NO_3^- (aq)$$
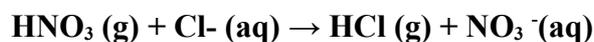
Experimental data

Parameter	RH/%	Temp./K	Reference	Technique/ Comments
Uptake coefficients: $\gamma, \gamma_{ss}, \gamma_0$				
$\gamma > 0.2$ (deliquesced NaCl)	75	298	Abbatt and Waschewsky, 1998	AFT-CIMS (a)
$\gamma = 0.5\pm0.2$ (deliquesced sea salt)	55	300	Guimbaud et al., 2002	AFT-RC (b)
$\gamma_0=(4.9\pm2.7) \times 10^{-3}$ (deliquesced NaCl)	80	298	Tolocka et al., 2004	AFT-AMS (c)
$\gamma_0=0.15\pm0.05$ (deliquesced NaCl)	60	298	Saul et al., 2006	AFT-AMS (d)
$\gamma_0=0.15\pm0.05$ (deliquesced NaCl/MgCl$_2$)	60	298		
$\gamma = 0.21-0.11$ (deliquesced NaCl), $\gamma = 0.25-0.12$ (NaCl/MgCl$_2$) $\gamma = 0.27-0.12$ (sea salt)	55-80 55-80 55-80	298	Liu et al., 2007	(e)
$\gamma = 0.5^{+0.5}_{-0.2}$ (deliquesced NaCl)	60	296	Stemmler et al., 2008	AFT-RC/IC (f)

Comments

(a) NaCl aerosol was produced using a nebulizer. The particle sizes were measured using an optical particle counter and were in the range of 2 to 4 μm. The HNO_3 concentration (about 10^{13} cm^{-3}) was measured downstream of the flowtube using chemical ionization mass spectrometry.. The uptake coefficient was calculated from the measured apparent first order loss rate constant including correction for diffusion in the gas phase, leading to the lower limit given in the table.

(b) Sea salt aerosol was produced by nebulizing a sea salt solution. The particle size distribution (with a mode around 70nm) was monitored by SMPS.. Experiments were performed at 55% RH. HNO_3 (in the concentration range of 10^{11} to 10^{13} cm^{-3}) was labeled with the short-lived radioactive tracer ^{13}N. Both, the loss of HNO_3(g) and appearance of aerosol phase product was monitored. The uptake coefficient (with only minor correction by diffusion) was independent of gas phase concentration up to 10^{12} cm^{-3} and decreased at higher concentration due to depletion of chloride in the particulate phase. The Aerosol Inorganic Model (AIM) was used to confirm that the low concentration data were obtained under conditions far from equilibrium of the HNO_3 (g,aq)-HCl (g,aq) system.

(c) NaCl aerosol produced using a nebulizer, from which a monodisperse aerosol (100-220nm diameter) was selected using a differential mobility analyzer. The size distribution was measured using SMPS. The product aerosol was sampled into a real-time laser ablation (193nm) single particle time-of-flight mass spectrometer operating in negative-ion mode, from which the mole fraction of chloride and nitrate was obtained. Removal of chloride from the particulate phase was used to derive an uptake coefficient for HNO_3. The reported uptake

coefficient was independent of HNO$_3$ concentration between 10^{12} and 10^{13} cm^{-3}. The small uptake coefficients were explained by slow formation of HCl in the aqueous phase that appeared to limit uptake of HNO$_3$, the main argument being the observed size dependence that could not be due to gas phase diffusion or liquid phase diffusion.

(d) Same experimental approach as in (c). Additionally, mixtures of NaCl with 0.114 mole fraction of MgCl$_2$ were used. The differences in the setup included changes to the flow reactor design that led to systematic errors in the quantification of the actual HNO$_3$ concentration in the reactor of the previous study. With this revised setup, the observed chloride mole fractions as a function of exposure time at 2×10^{12} cm^{-3} of HNO$_3$ was consistent with those in the previous study. However, the uptake coefficient derived using the correct HNO$_3$ concentration led to uptake coefficients between 0.1 and 0.2, still depending on size. Therefore, it is still suggested that formation of HCl in the aqueous phase is limiting uptake of HNO$_3$.

(e) NaCl aerosol produced using a nebulizer and then deposited onto TEM grids (formvar on nickel grids) using an impactor. Experiments were performed by impinging a laminar jet of humidified HNO$_3$ (10^{11} cm^{-3}) in N$_2$ onto the sample. The loss of HNO$_3$ over the sample was measured by a chemiluminescence detector. Chemical processing of individual particles was monitored using offline scanning electron microscopy connected with energy dispersive X-ray analysis. The dry particle diameter was 0.9μm, the wet particle size was estimated from the dry diameter measured in the SEM and hygroscopic growth curves in the literature. The dynamics of the trace gas – particle on the substrate interaction was accompanied by CFD to support the relationship between the measured loss rate, the particle density and the uptake coefficient on individual particles. It showed that the net uptake coefficient was largely controlled by gas phase diffusion and was therefore dependent on the (wet) particle diameter. The decrease of the uptake coefficient with increasing RH above the efflorescence point is explained by the decreasing chloride concentration in the particle, assuming that the formation of HCl is the rate limiting factor. A correction is not applied to account for gas phase diffusion and to report a true uptake coefficient at the particle surface.

(f) Same experimental approach as in (b) with only slight modifications. The main aim was to investigate the effects of surfactants on the HNO$_3$ uptake. In the absence of surfactants, the uptake coefficients were consistent with those reported by Guimbaud et al., 2002. Offline, ion chromatographic analysis of filter samples confirmed the complete displacement of reacted chloride. The revised error analysis included a discussion of the mixing time in the flow tube and re-equilibration in the denuder system.

Preferred Values

Parameter	Value	T/K
α_b	>0.5	298
Reliability		
$\Delta \log (\alpha_b)$	± 0.3	298

Comments on Preferred Values

The available studies agree that the acid displacement
NaCl (aq) + HNO$_3$ (g) $\rightarrow$ NaNO$_3$ (aq) + HCl (g)
drives the uptake of HNO$_3$ to sea salt solutions and their proxies, deliquesced NaCl or mixtures of NaCl with MgCl$_2$, and that the uptake is fast. This is in line with many studies on solid halogenide salts, where the uptake coefficient of HNO$_3$ showed a strong dependence on the amount of surface adsorbed water, providing evidence that chloride ion (partially or fully hydrated) is required to drive acid displacement (see Rossi (2005) and references therein). The Abbatt and Waschewsky (1998) and the Liu et al. (2007) data were affected to a varying degree by gas phase diffusion, so that those reported uptake coefficients should be considered as lower limits. Regarding the absolute values of the uptake coefficient, the Saul et al. (2006) data based on an improved calibration of the HNO$_3$ concentration are considered to supersede the Tolocka et al. (2004) data. Therefore, the available studies agree fairly well. From the very
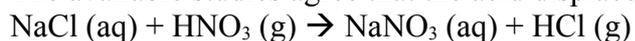
high solubility of HNO_3, the very fast rates for its dissociation in the aqueous phase, and the very fast protonation of chloride, we conclude that solubility, reaction or diffusion cannot limit the rate of uptake of HNO_3, which was suspected to be responsible for the size and humidity dependence by Saul et al., Liu et al. and also earlier by ten Brink (1998). We therefore recommend the bulk accommodation coefficient observed by Guimbaud et al. (2002) and Stemmler et al. (2008) as a lower limit. With NaCl solution in excess, HNO_3 – protons are nearly completely displaced into the gas phase as HCl at equilibrium due to the divergent behaviour of the activity coefficients of chloride and nitrate at high ionic strength (Brimblecombe and Clegg, 1988).

References

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