

# Reactive uptake coefficients for heterogeneous reaction of $\text{N}_2\text{O}_5$ with submicron aerosols of NaCl and natural sea salt

D. J. Stewart, P. T. Griffiths, and R. A. Cox

Centre for Atmospheric Science, Dept. of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

Received: 1 December 2003 – Published in Atmos. Chem. Phys. Discuss.: 26 January 2004

Revised: 5 July 2004 – Accepted: 5 July 2004 – Published: 25 August 2004

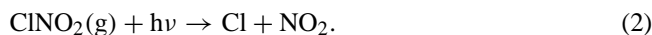
**Abstract.** The kinetics of uptake of gaseous  $\text{N}_2\text{O}_5$  on submicron aerosols containing NaCl and natural sea salt have been investigated in a flow reactor as a function of relative humidity ( $RH$ ) in the range 30–80% at  $295 \pm 2$  K and a total pressure of 1 bar. The measured uptake coefficients,  $\gamma$ , were larger on the aerosols containing sea salt compared to those of pure NaCl, and in both cases increased with increasing  $RH$ . These observations are explained in terms of the variation in the size of the salt droplets, which leads to a limitation in the uptake rate into small particles. After correction for this effect the uptake coefficients are independent of relative humidity, and agree with those measured previously on larger droplets. A value of  $\gamma=0.025$  is recommended for the reactive uptake coefficient for  $\text{N}_2\text{O}_5$  on deliquesced sea salt droplets at 298 K and  $RH > 40\%$ .

## 1 Introduction

The quantity of halogen salts injected into the atmosphere in the form of aerosol from sea spray evaporation is very large. Observations made over many years have shown a deficit in the halide ions,  $\text{Cl}^-$  and  $\text{Br}^-$  in the marine aerosol relative to bulk sea water ratio of  $\text{X}^-/\text{Na}^+$ . The deficit in  $\text{Cl}^-$  is more noticeable in the smaller size fraction of the marine aerosol and in coastal regions (Keene et al., 1990; Pszenny et al., 1993; Ayers et al., 1999). It is believed to arise from the release of halogen from the salt particles or droplets in the form of volatile chlorine-containing gases such as HCl, dihalogens (Vogt et al., 1996) and the nitryl halides ( $\text{XNO}_2$ ) (Finlayson-Pitts et al., 1989).

One mechanism which has been proposed for release of Cl from the marine aerosol is reaction of  $\text{N}_2\text{O}_5$  with aqueous NaCl giving aqueous  $\text{NaNO}_3$  and gaseous nitryl chlo-

ride,  $\text{ClNO}_2$ , which can subsequently be photo-dissociated by sunlight to give chlorine atoms and  $\text{NO}_2$  (Ayers et al., 1999; Vogt et al., 1996):

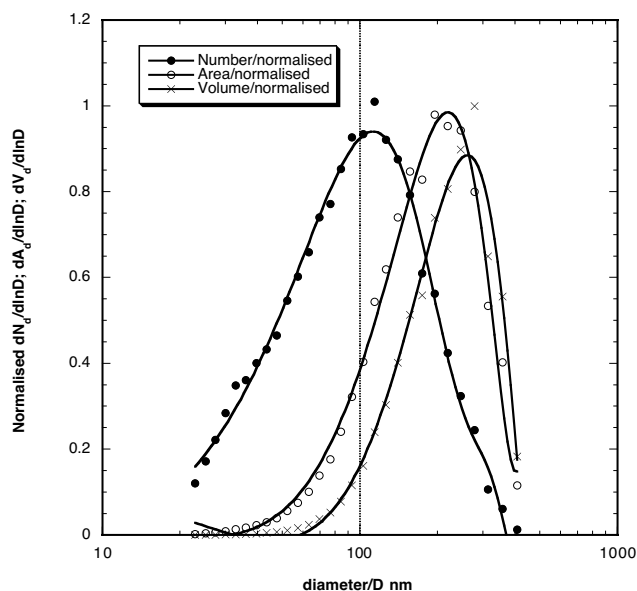


This mechanism serves to release reactive chlorine atoms which can add to the oxidising capacity of the atmosphere. Also, since 50% of the  $\text{NO}_x$  is returned to the gas phase, the loss of  $\text{NO}_x$  species by heterogeneous conversion of  $\text{N}_2\text{O}_5$  to nitrate is reduced, compared to hydrolysis when 2 molecules of  $\text{HNO}_3$  are formed.

There have been a number of investigations (Livingstone and Finlayson-Pitts 1991; Leu et al., 1995; Fenter et al., 1996) of the kinetics of  $\text{N}_2\text{O}_5$  reaction with solid NaCl crystals at low humidity, to represent the marine aerosol. These studies show small uptake coefficients of  $< 1 \times 10^{-3}$ , when corrected for sample porosity and crystal presentation. However marine aerosol produced from sea spray over the oceans consists mainly of deliquesced liquid droplets, even when the relative humidity falls below the deliquescence point at 75%  $RH$ . Thus the various studies of uptake of  $\text{N}_2\text{O}_5$  into aqueous NaCl are more relevant for the marine aerosols.

Behnke and co-workers (Behnke et al., 1997) studied  $\text{N}_2\text{O}_5$  uptake on liquid NaCl aerosols with a known size distribution in a static chamber, and on bulk NaCl solutions in a wetted wall flow reactor. The uptake coefficient of  $\text{N}_2\text{O}_5$  on the aerosols was determined by modelling the time dependence of the concentration of  $\text{N}_2\text{O}_5$  which was produced in situ by the reaction of  $\text{O}_3$  with  $\text{NO}_2$ . The initial  $\text{N}_2\text{O}_5$  concentrations were in the range 15–22 ppb. The uptake coefficients were measured at relative humidities between 77–94%, corresponding to NaCl molarity of 1.7–5.1 M at 292 K. A value of  $\gamma=0.032 \pm 0.002$  was determined and found to be independent of relative humidity in the above range. The flow reactor experiments showed that  $\text{ClNO}_2$  was the sole

Correspondence to: R. A. Cox  
(rac26@cam.ac.uk)



**Fig. 1.** Size distribution of aqueous sea salt aerosol generated from nebulisation of a 0.3 M solution without drying the particle stream, at a temperature of 298 K and an *RH* of 50%. The distributions plotted are based on the total number, surface area and volume of particles in each size bin, from an average of 8 DMA scans.

gaseous product of reactive uptake at NaCl concentrations > 1.0 M (n.b. [Cl<sup>-</sup>] ~ 6 M in deliquesced sea salt aerosol), although the yield declined below 0.5 M NaCl, presumably due to competition with the hydrolysis of N<sub>2</sub>O<sub>5</sub> to form HNO<sub>3</sub>:



The uptake of ClNO<sub>2</sub> into water was much slower,  $\gamma = (4.84 \pm 0.13) \times 10^{-6}$ , and so under the experimental conditions and also in the marine atmosphere, ClNO<sub>2</sub> is expected to partition to the gas phase.

George et al. (1994) and Schweitzer et al. (1998) have investigated N<sub>2</sub>O<sub>5</sub> uptake on a fast droplet train (80–150 μm diameter particles) equipped with FTIR/long-path absorption and ion-trap mass spectrometry for gas phase detection of N<sub>2</sub>O<sub>5</sub> (concentration = 20–2000 ppm) and products. The recommended mean uptake coefficient was  $\gamma = 0.018 \pm 0.003$ , which was independent of temperature in the range 263–278 K, as well as of the NaCl concentration up to 1 M. The earlier droplet train experiments (George et al., 1994), in which the extent of reaction was followed by measuring the NO<sub>3</sub><sup>-</sup> concentration in the collected droplets, gave similar values of  $\gamma$ .

In this paper we report the first direct measurements of the reactive uptake coefficient of N<sub>2</sub>O<sub>5</sub> onto submicron aerosols of NaCl and natural sea salt, using an aerosol flow reactor operating at atmospheric pressure with direct measurement of N<sub>2</sub>O<sub>5</sub> uptake. The reactive uptake coefficients were measured on aerosols dried below the efflorescence point (41%)

and for liquid deliquesced particles in the *RH* range 30–80%. The results are compared with previous measurements of uptake on solutions containing NaCl.

## 2 Experimental

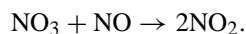
Uptake coefficients of N<sub>2</sub>O<sub>5</sub> on aerosol particles were determined using the novel aerosol generator and flow tube reactor described by Hallquist et al. (2000, 2003). Submicron aerosols of chloride salts were generated using a nebuliser in which a bulk solution of the desired salt is pumped through a fine needle at a flow rate of 5–10 sccm. At the end of this needle the droplets come into contact with a fast (~500 sccm) flow of nitrogen gas from a 1 mm jet creating a liquid spray of the salt solution. Behind the needle is a metal plate onto which the larger particles (diameter > ~1 μm) impact and drop back into the solution reservoir, but the smaller particles remain entrained in the gas stream and exit the nebuliser. The aerosol flow passed through a diffusion dryer (optional) and a dilution section to prepare aerosols consisting either of solid crystalline particles or deliquesced/supersaturated liquid droplets, depending on the drying procedure, the *RH*, and the properties of the salt aerosol. After adjustment of the *RH* to the required value between 30% and 80%, the salt aerosols were conditioned by passing them along a jacketed temperature controlled cylindrical tube (5 cm dia. × 90 cm length) at constant humidity and temperature (298 K). In this work aerosols produced using the dryers are termed “dry” and those prepared by by-passing the dryers are termed “wet”. After the conditioner the aerosol was divided into two flows. A flow of ca. 2.8 sLpm was used for aerosol characterisation and the remainder (~1.2 sLpm) passed into the halocarbon wax coated flow reactor.

The aerosol was characterised using a differential mobility analyser (DMA) (Hauke model EMS VIE-08), with a Faraday cup electrometer serving as the detector. Since most of the experiments were carried out at high *RH*, the sheath air-flow in the DMA was humidified to match the *RH* of the aerosol flow, thereby preventing any change in aerosol particle size during measurement. Figure 1 shows a typical size distribution obtained from the nebuliser containing solution of sea salt (0.3 M as sodium chloride; Community Food Ltd., 99+ %), which was dried and conditioned at 50% *RH*. The size distribution in terms of particle number is approximately log normal, i.e. the plot of dN/dlnD shows a symmetrical distribution with a maximum at D<sub>max</sub>; the standard deviation on the geometric mean size was ln σ = 0.62.

Figure 1 also shows the distribution in terms of surface area (cm<sup>2</sup>/cm<sup>3</sup>) and particle volume (cm<sup>3</sup>/cm<sup>3</sup>) expressed as the functions  $d(4\pi(D/2)^2N)/d\ln D$  and  $d(4\pi(D/2)^3N/3)/d\ln D$ , respectively, obtained for each of the 36 size fractions measured in the DMA. The diameter at the maxima in aerosol surface area and volume distributions are 195 nm and 280 nm, and both distributions appear

monomodal. The total number, surface area ( $S_a$ ) and volume ( $V_a$ ) of the aerosol were obtained by summing the values for each size bin over the whole distribution. The aerosol generator took approximately one hour to stabilise after setting the flows. After this time the particle number density remained constant to within  $\pm 7\%$  over the time of a kinetic run (ca. 1 h); the aerosol surface area typically varied by less than 10% over the same period. The size distributions of the aerosols, prepared from a 0.3 M solution of pure NaCl, were similar to those prepared from natural sea salt.

The methods of synthesis, handling and measurement of N<sub>2</sub>O<sub>5</sub> have been described in detail in a recent publication (Hallquist et al., 2003). N<sub>2</sub>O<sub>5</sub> was prepared by oxidising NO with excess O<sub>3</sub>, and stored at 195 K. The N<sub>2</sub>O<sub>5</sub> was introduced into the aerosol flow tube from a sliding injector in a slow flow (50 sscm) of dried nitrogen gas which entrained N<sub>2</sub>O<sub>5</sub> from a cold trap at 240 K. The concentration of N<sub>2</sub>O<sub>5</sub> at the exit of the flow tube was determined by titration with nitric oxide as described before (Hallquist et al., 2003). After exiting the flow tube the sample gas stream was mixed with NO and was then heated to 385 K, where the N<sub>2</sub>O<sub>5</sub> decomposes thermally. The NO<sub>3</sub> produced reacts quantitatively with the excess NO present to produce NO<sub>2</sub>:



NO was measured by means of a calibrated commercial nitrogen oxides monitor (Thermo Environmental Instruments Model 42C). The change in NO ( $\Delta\text{NO}=[\text{N}_2\text{O}_5]$ ) was shown to be a linear function of the flow rate through the N<sub>2</sub>O<sub>5</sub> trap. The detection limit of N<sub>2</sub>O<sub>5</sub> was 0.4 ppb with S/N=2. Calculations based on the known formation kinetics and equilibrium constant of ClNO<sub>2</sub>, which is a known product of the reaction of N<sub>2</sub>O<sub>5</sub> with aqueous NaCl, showed that its decomposition temperature was in excess 450 K and therefore interference with the detection of N<sub>2</sub>O<sub>5</sub> by NO titration was unlikely.

The kinetics of N<sub>2</sub>O<sub>5</sub> loss in the flow tube was measured by changing the position of the sliding injector to vary the contact time between the N<sub>2</sub>O<sub>5</sub> and the aerosol, monitoring the change in N<sub>2</sub>O<sub>5</sub> concentration at the same time. The linear flow velocity was 2.2 cm s<sup>-1</sup> and the time for mixing the two flows was estimated to be  $\sim 5$  s (Hallquist et al., 2000). Kinetic data were collected for contact times of 15–45 s. The aerosol flow was switched out of the flow tube before and after each kinetic run and the N<sub>2</sub>O<sub>5</sub> wall loss was measured, again by varying the injector position.

The N<sub>2</sub>O<sub>5</sub> reactant concentration was measured at the end of the flow tube for a range of reaction zone lengths corresponding to reaction time,  $t$ , and the first order rate coefficient,  $k$ , was determined from plots of  $\ln[\text{N}_2\text{O}_5]$  vs.  $t$ . The first order loss rate coefficients were corrected for diffusion and wall losses under non-plug flow conditions, using the method of Brown (1978). In the corrections the gas-phase diffusion coefficient,  $D_g$ , for N<sub>2</sub>O<sub>5</sub> was assumed to be 0.1 cm<sup>2</sup> s<sup>-1</sup> as calculated by Hu and Abbatt (1997). The

corrected first order rate coefficient,  $k^I$ , was then used to determine the uptake coefficient,  $\gamma$ .

The rate equation for a heterogeneous reaction in a cylindrical flow tube is:

$$\frac{d[X]}{dt} = k^I[X] \quad \text{where} \quad k^I = \frac{\gamma \cdot \omega \cdot S_a}{4}, \quad (\text{E1})$$

where  $\gamma$  is the uptake coefficient,  $\omega$  is the average molecular speed,  $S_a$  is the surface area of the aerosol per unit gas volume. This equation assumes a monodisperse aerosol of particles small enough so that gas phase diffusion does not limit the rate of uptake. The size-averaged values of  $\gamma$  obtained from Eq. (E1) are representative of the effective radius, i.e.  $\gamma = \gamma(r_s)$ . The effective radius is given by  $r_s = 3V_a/S_a$  where  $V_a$  is the volume of the aerosol per unit volume.

However, for polydisperse aerosols such as used in this study, the uptake rate coefficient is an average value over the whole distribution of particles radius  $r_i$ , i.e.

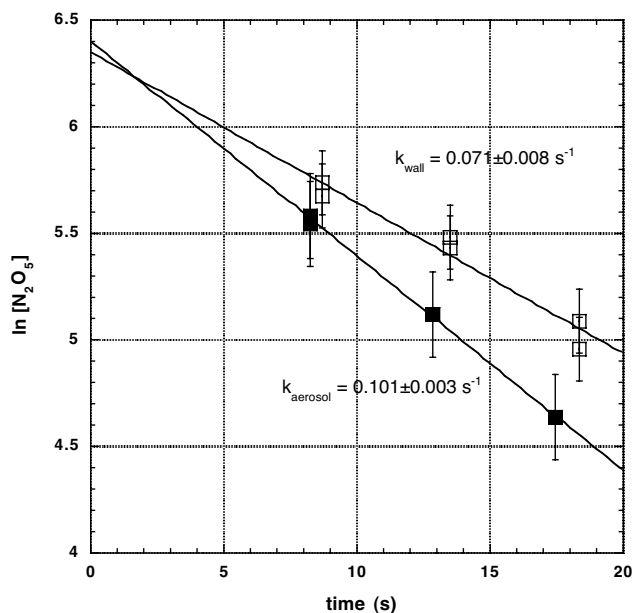
$$k^I = \sum_i k(r_i) = \sum_i \frac{\gamma(r_i) \omega N_i \pi r_i^2}{1 + \gamma(r_i) \left( \frac{0.75 + 0.283 Kn_i}{Kn_i(Kn_i + 1)} \right)} \quad (\text{E2})$$

This equation takes into account the gas phase diffusion limitation for large particles in the term containing the Knudsen number ( $Kn_i = 3D_g/\omega r_i$ ), as discussed by Fuchs and Sutugin (1970) and Fried et al. (1994). It also specifies a size dependence uptake coefficient  $\gamma(r_i)$ , arising for example from slow chemical processing in small particles, as discussed by Hanson et al. (1994).

For the case of a size-independent uptake coefficient, we found that the value of  $\gamma(r_s)$  derived by iterative solution of Eq. (E2), using the data from the DMA to calculate  $N_i$ , is not significantly different from the value obtained using Eq. (E1) and the total surface area,  $S_a$ . We conclude that the particle radii and uptake coefficients are too small for diffusion limitations to be significant. The possible size dependence of the values of  $\gamma(r_s)$  calculated using Eq. (E1) is discussed further below.

### 3 Results

Uptake experiments were conducted for aerosols of pure NaCl and natural sea salt at  $RH$  of 30, 50, 70 and 80%. Aerosol surface areas were in the range  $(0.7\text{--}3.0) \times 10^{-3}$  cm<sup>2</sup> cm<sup>-3</sup>. Aerosols at 50%  $RH$  were prepared either dry or wet as described above. Figure 2 shows logarithmic decay plots for N<sub>2</sub>O<sub>5</sub> with and without NaCl aerosol present in the flow tube at 50%  $RH$ . The initial N<sub>2</sub>O<sub>5</sub> mixing ratio was 156 ppbv and the surface area  $(9.8 \pm 0.33) \times 10^{-4}$  cm<sup>2</sup> cm<sup>-3</sup>. Wall loss of N<sub>2</sub>O<sub>5</sub> was relatively rapid in these experiments and the difference in slope of the decay plots with and without aerosol, particularly in the case of NaCl, was rather small, leading to large statistical errors in the determination of the uptake coefficients. Nevertheless the decay rate in the presence of aerosol was always



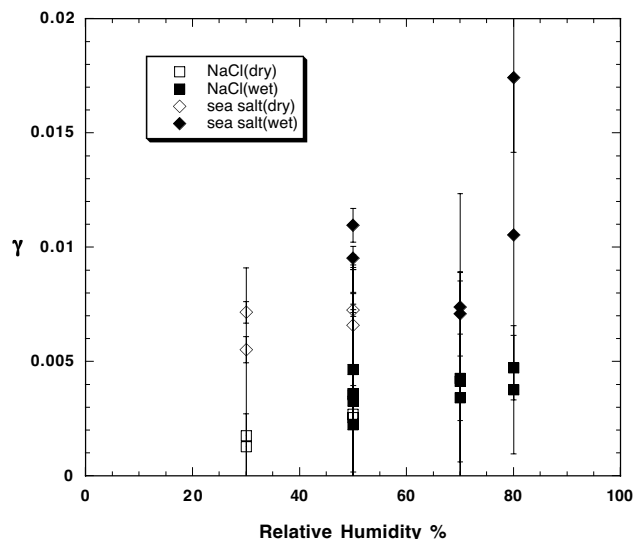
**Fig. 2.** First order loss plot for  $N_2O_5$  decay in presence and absence of sea salt aerosol.  $RH=50\%$ , “wet” aerosol. Aerosol surface area= $0.00098\text{ cm}^2\text{ cm}^{-3}$ .

observed to be larger than the wall loss and the retrieved values of  $\gamma$  ( $r_s$ ) for a given set of conditions were generally well within a factor of 2. All the individual measurements are plotted as a function of  $RH$  in Fig. 3.

Pure NaCl exhibits a region of supersaturation between the deliquescence point at  $75\%$   $RH$  and the efflorescence point at  $\sim 41\%$   $RH$  (Tang et al., 1977; Czizco et al., 2000). Thus in our experimental system, solid NaCl aerosols will only be formed after drying the initially produced aerosol below the efflorescence humidity and rehumidifying to  $<75\%$   $RH$ . This was confirmed in our laboratory by infrared spectroscopic observations of NaCl aerosols produced from the nebuliser at higher concentrations. Thus the “dry” aerosols made from pure sodium chloride are likely to contain solid NaCl.

The characterisation of aerosols prepared from artificial sea salt in a nebuliser has been reported by Czizco et al. (1997) who used infra-red spectroscopy to investigate the water content as a function of  $RH$  and mode of preparation. They found that the aerosols contained significant quantities of water even at relative humidities below the efflorescence point. They later showed that the spectral features were due to liquid water, rather than hydrates of  $Mg^{2+}$ , and they concluded that sea salt aerosols would be liquid droplets under most tropospheric conditions (Czizco and Abbatt, 2000). It is likely that the sea salt aerosols used in this study consisted of liquid droplets.

The uptake measurements shown in Fig. 3 indicate that reactive uptake of  $N_2O_5$  onto the aerosols containing chloride increases with  $RH$ . Uptake on the “dry” particles of NaCl at  $RH=50\%$  is lower ( $\gamma\sim 0.0019\pm 0.0015$ ) than on deliquesced



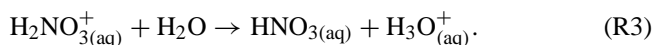
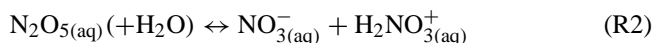
**Fig. 3.** Relative humidity dependence of the uptake coefficient for  $N_2O_5$  on NaCl (diamonds) and sea salt (squares) aerosols. The filled points show data obtained by drying a liquid aerosol; open points show data obtained by humidifying dried particles. Error limits from propagation of error in individual rate plots.

aerosols of NaCl ( $\gamma\sim 0.0035\pm 0.0007$ ), although the difference may not be significant. On sea salt aerosol there is also a significant difference between the aerosols which had been dried and those prepared from deliquesced particles ( $\gamma=0.0069\pm 0.0003$  versus  $\gamma=0.0102\pm 0.0007$ ). The uptake on the sea salt aerosols was greater than on pure NaCl aerosol at all relative humidities, and increased only moderately from  $\gamma=0.0065$  at  $30\%$   $RH$  to  $\gamma=0.014$  at  $80\%$   $RH$ . The results are summarised in Table 1 which shows the mean values of  $\gamma$  ( $r_s$ ) for each set of conditions, together with the surface area mean radius, mean specific surface area and volume of the particles. Only the uptake coefficient on sea salt at  $80\%$   $RH$ ,  $\gamma=0.014$ , approaches that for uptake of  $N_2O_5$  on water or NaCl droplets or on sulphate aerosols at high humidity, which lie in the range 0.02 to 0.04.

## 4 Discussion

### 4.1 Mechanism of $N_2O_5$ reaction on aerosols

The following mechanism involving the formation of a protonated nitric acid intermediate has been proposed recently (Thornton et al., 2003) for reactive uptake of  $N_2O_5$  onto neutral or weakly acid aqueous solutions leading to hydrolysis with formation of two molecules of  $HNO_3$ :



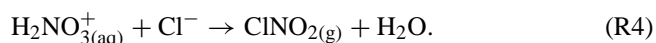
**Table 1.** Average values of N<sub>2</sub>O<sub>5</sub> uptake coefficients.

<i>RH</i> (%)	Effective radius, <i>r<sub>s</sub></i> /nm	Mean Area <i>S<sub>a</sub></i> /cm <sup>-2</sup> cm <sup>-3</sup> × 10 <sup>4</sup>	Volume <i>V<sub>a</sub></i> /cm <sup>3</sup> cm <sup>-3</sup> × 10 <sup>9</sup>	<i>γ</i> <sup>+</sup> × 10 <sup>-3</sup>	No. of expts.
<b>Sea salt</b>					
30	84	8.9	2.46	6.3 ± 0.8	3
50 (dry)*	68	9.7	2.22	6.9 ± 0.5	2
50	105	10.0	3.50	10.2 ± 0.7	2
70	248	30	24.8	6.4 ± 1.5	3
80	148	9.32	4.57	14.0 ± 3.0	2
<b>NaCl</b>					
30 (dry)*	77	7	1.77	1.5 ± 0.3	2
50 (dry)*	63	10	2.11	1.9 ± 1.5	3
50	92	24.2	7.41	3.5 ± 0.8	5
70	181	25	15.1	3.9 ± 0.5	3
80	180	15	9.0	4.3 ± 0.5	2

\* “dry” aerosols passed through dryers before adjustment of humidity;

<sup>+</sup> error represents spread of individual values.

Hydrolysis of N<sub>2</sub>O<sub>5</sub> to form HNO<sub>3</sub> occurs in aqueous droplets but the experiments on bulk NaCl solutions (Behnke et al., 1997) indicated that ClNO<sub>2</sub> formation was the dominant reaction path up to at least 93% *RH*. On this basis, the formation of ClNO<sub>2</sub> following uptake into >1 M NaCl solutions can be attributed to the following reaction involving Cl<sup>-</sup>:



The protonated nitric acid intermediate, formed in a pseudo first order dissociative reaction involving water molecules, replaces the NO<sub>2</sub><sup>+</sup> ion in earlier proposed mechanisms (George et al., 1994; Behnke et al., 1997; Schweitzer et al., 1998; Hallquist et al., 2003; Sohn et al., 1999).

The body of experimental information suggests that reactive uptake of N<sub>2</sub>O<sub>5</sub> on aqueous aerosols at *RH* > 50% and on bulk liquid films occurs at a similar rate for both hydrolysis and reaction with halide ions. This would be expected if the uptake is controlled by accommodation or solvation of gaseous N<sub>2</sub>O<sub>5</sub> at the surface (reaction R1), followed by fast reaction of the solvated N<sub>2</sub>O<sub>5</sub> molecules in the bulk phase close to the surface to form either nitric acid or nitryl chloride + sodium nitrate. In this case the rate of reaction in the liquid phase is not the rate-determining step, and consequently the uptake rate should be independent of the activities of H<sub>2</sub>O or Cl<sup>-</sup> in the droplets. In NaCl-containing aerosols these activities will respectively decrease and increase as *RH* decreases. The fall off in uptake coefficient at low humidity, and the larger uptake coefficient of aerosols made from sea salt observed in the present work, is therefore not consistent with this mechanism, unless the accommodation process itself (reaction R1) is affected by changes in *RH* and the resulting activities of the ions in solution.

#### 4.2 Effect of particle size

The mean size of the salt aerosols used in this work tended to increase with increasing *RH* due to increasing water content. A possible explanation of the apparent *RH* dependence lies in the potential effect of droplet size on the measured uptake coefficients on small droplets, when the liquid phase reaction takes place throughout the particle volume (Hanson and Lovejoy, 1997). According to the theory of gas uptake into liquid aerosol droplets, the measured uptake coefficients are given by the equation:

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4HRT\sqrt{D_l k_r}} \left( \coth q - \frac{1}{q} \right)^{-1}, \quad (\text{E3})$$

where  $\alpha$  is the mass accommodation coefficient,  $\omega$  is the mean velocity of N<sub>2</sub>O<sub>5</sub> molecules in the gas phase,  $H$  is the Henry's law constant for N<sub>2</sub>O<sub>5</sub> in water,  $D_l$  is the liquid phase diffusion coefficient,  $R$  is the gas constant and  $T$  is the absolute temperature.  $k_r$  is the pseudo first order rate constant for reaction of N<sub>2</sub>O<sub>5</sub> in the liquid phase.

The term involving the parameter  $q$ , i.e. the ratio of particle radius,  $r$ , to the reacto-diffusive length,  $l$ , accounts for the size dependence of  $\gamma$  in small particles when liquid phase reactions are rate determining. The reacto-diffusive length,  $l (= \sqrt{D_l/k_r})$  is a measure of the mean distance from the gas/liquid interface that a molecule diffuses in the droplets before reaction takes place.

When reaction in the condensed phase is rapid, the uptake rate is controlled by surface accommodation and the measured value of  $\gamma$  corresponds to  $\alpha$  under these conditions. If reaction in solution is slow it becomes rate determining, and the uptake rate is controlled by reaction in solution. If the reaction volume in the aerosol is confined by liquid phase

**Table 2.** Calculation of reacto-diffusive length for N<sub>2</sub>O<sub>5</sub> in sea-salt and NaCl droplets.

RH (%)	k <sub>r</sub> /s <sup>-1</sup> × 10 <sup>-4</sup>		q		γ <sub>thick</sub>	
	E4	E3	E4	E3	E4	E3
<b>Sea salt</b>						
30	3.79	57.5	0.51	2.02	0.050	0.016
50 (dry)*	9.32	52.5	0.67	1.56	0.080	0.022
50	3.39	46.0	0.61	2.25	0.048	0.028
70	1.30	40.3	0.89	4.98	0.030	0.013
80	8.08	65.0	1.32	1.48	0.080	0.031
<b>NaCl</b>						
30	0.79	10	0.21	0.77	0.023	0.0064
50 (dry)*	1.21	11.5	0.22	0.75	0.029	0.0132
50	1.65	20.5	0.37	1.31	0.033	0.0090
70	0.95	7.1	0.56	1.53	0.025	0.0104
80	1.08	17.0	0.59	2.35	0.027	0.0078

\* “dry” aerosols passed through driers before adjustment of humidity.

diffusion to a thin volume shell,  $l \ll r$  and  $q \gg 1$ . In this case the factor  $(\coth q - 1/q) = 1$ , resulting in a size-independent uptake coefficient. If reaction is slow enough,  $q \ll 1$ , and the reactant will diffuse throughout the droplet. In this case the overall reaction rate depends on the droplet volume,  $V/S$ ;  $\gamma$  becomes size-dependent and is given by the following expression:

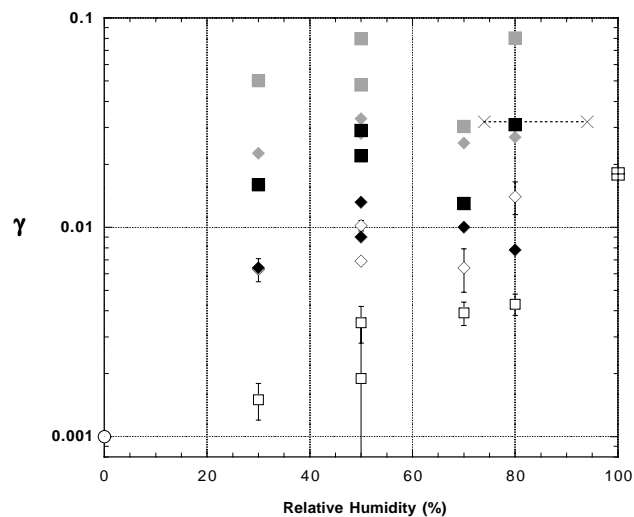
$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\omega}{4HRT \frac{V}{S} k_r} \quad (\text{E4})$$

The uptake coefficient in the region of transition between these two regimes is corrected by the correction factor  $(\coth q - 1/q)^{-1}$  in Eq. (E3). This equation allows evaluation of the equivalent “thick film” uptake coefficient,  $\gamma_{\text{thick}}$ , from the size-average uptake coefficient  $\gamma(r_s)$  measured under size limited conditions, by evaluating:

$$\left(\frac{1}{\gamma} - \frac{1}{\alpha}\right)^{-1} = \left(\coth q - \frac{1}{q}\right) \gamma_{\text{thick}} \quad (\text{E5})$$

for  $r=r_s$ . The “thick film” uptake coefficient can be compared with uptake coefficients measured on larger droplets and bulk liquid films (George, 1994; Behnke, 1997; Schweitzer, 1998).

Calculation of  $\gamma_{\text{thick}}$ , requires determination of  $k_r$  in order to calculate the reacto-diffusive length,  $l$ , and hence  $q$ . Since we do not know a priori whether the measured size-averaged uptake coefficients relate to the conditions for surface area or volume dependent uptake, we have used both Eqs. (E3) and (E4) to calculate  $k_r$ . In these calculations we assumed that all particles have a liquid phase, and we used  $\alpha=0.025$ , based on the values for reactive uptake of N<sub>2</sub>O<sub>5</sub> on aqueous salt films and aerosols at high RH from earlier studies,  $H=2 \text{ M atm}^{-1}$



**Fig. 4.** Comparison of the uptake coefficients, corrected for size effects.  $\gamma_{\text{thick}}$  values for N<sub>2</sub>O<sub>5</sub> uptake on NaCl (black diamond) and sea salt (black square) using Eq. (3), sea salt (grey diamond) using Eq. (4) obtained in this study; results from large droplets (oplus) Schweitzer et al. (1998), deliquesced NaCl aerosols (x) Zetsch et al. (1992), and dry NaCl powders (O) Livingston and Finlayson-Pitts (1991). The open points show experimental uptake coefficients obtained in this work. Error limits show spread of experimental values.

and  $D_l(\text{N}_2\text{O}_5)=1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (Jacob, 2000). The calculation of  $k_r$  from Eq. (E4) is straightforward. The values of  $\gamma(r_s)$  for the effective particle radius  $r_s$  and of  $V_a$  and  $S_a$  given in Table 1, were used to evaluate  $k_r$ . The values are given in Table 2 together with the corresponding values of  $q$  ( $=r_s/l$ ). Calculation of  $k_r$  from Eq. (E3), which contains the size dependent factor  $(\coth q - 1/q)$  was done using an iterative technique with the size distributions obtained from the DMA measurements during each experiment. Initially the reacto-diffusive length ( $=\sqrt{D_l/k_r}$ ) was calculated using the  $k_r$  values from Eq. (E4). These were then used to evaluate  $q$  and compute the size dependent  $\gamma(r_i)$  values for each size bin in the distribution. These values were then entered into the summation in Eq. (E2) to give a corresponding value for the overall uptake rate coefficient which can be compared with the observed rate coefficient,  $k^l$ . In general, we found that the pseudo first-order liquid phase rate coefficient,  $k_r$  calculated using Eq. (E4) underestimates the overall uptake rate coefficient, and that best fits are obtained with values of  $k_r$  about a factor of 10 higher than those obtained from Eq. (E4). These values are also given in Table 2 together with the corresponding values of  $q$ . In both cases the values of  $k_r$  show no significant trend with RH but the values for sea salt aerosol tend to be higher than for NaCl. A possible cause of this is the occurrence of efflorescence in the smaller NaCl particles at  $\text{RH} < 75\%$ , which would decrease the effective volume for reaction.

The values of  $q$  around unity indicate that the experimental conditions mostly correspond to the transition region between surface area and volume dependence of the rate of heterogeneous reaction. The rate constant  $k_r$  obtained in this study can be assigned to the rate determining step for liquid phase reaction of N<sub>2</sub>O<sub>5</sub> and is of the same magnitude as the value of  $k_r=2.5\text{--}4.0\times 10^5\text{ s}^{-1}$ , deduced from uptake studies using aqueous sulphate (Sohn, 1999) and organic acid aerosols (Thornton, 2003; Volkert, 2003). This is expected if a common mechanism for hydrolysis and ClNO<sub>2</sub> formation is operating.

In this work we have used relatively high initial [N<sub>2</sub>O<sub>5</sub>] (100–700 ppb) and a possible cause of the inhibition of the liquid phase reaction could be the accumulation of significant amounts of NO<sub>3</sub><sup>−</sup> in the aqueous phase, which has been shown to reduce the effective uptake rate of N<sub>2</sub>O<sub>5</sub> into sodium nitrate aerosols (Sohn et al., 1999). We have estimated the amount of NO<sub>3</sub><sup>−</sup> present in the droplets resulting from N<sub>2</sub>O<sub>5</sub> hydrolysis, using the measured uptake coefficients, assuming them to be time independent. Typically the average molarity of NO<sub>3</sub><sup>−</sup> calculated for 20 s reaction time was in the range 0.3–3 M for NaCl experiments and 0.1–0.8 M for sea salt. An unknown additional contribution to aerosol nitrate could result from evaporation of HNO<sub>3</sub> formed by N<sub>2</sub>O<sub>5</sub> hydrolysis at the flow tube walls. Concentrations of NO<sub>3</sub><sup>−</sup> > 1 M distributed homogeneously in the droplets would begin to cause inhibition of N<sub>2</sub>O<sub>5</sub> reactions, according to the proposal of Sohn et al. (1999). Finally, we note that the amount of NO<sub>3</sub><sup>−</sup> formed was in most cases a factor of 10 less than the NaCl initially present in the aerosol and therefore depletion of Cl<sup>−</sup> is not a likely cause of the lower rates in NaCl.

The final columns in Table 2 shows values of the equivalent “thick film” uptake coefficients,  $\gamma_{\text{thick}}$ , calculated using Eq. (E5), and the values of  $q$  derived using Eqs. (E3) and (E4). The thick film uptake coefficients are plotted in Fig. 4, together with literature values from Behnke et al. (1997) and Schweitzer et al. (1998). The values of  $\gamma_{\text{thick}}$  for sea salt aerosols show no trend with  $RH$  and have mean values of  $\gamma_{\text{thick}}=0.022\pm 0.008$  (Eq. E3) and  $0.034\pm 0.015$  (E4). The values of  $\gamma_{\text{thick}}$  for NaCl aerosol have a mean value of  $0.0093\pm 0.003$  (Eq. E3) and  $0.021\pm 0.006$  (Eq. E4). Considering the uncertainties we consider these values to be in good agreement with the temperature independent value of  $\gamma=0.018\pm 0.003$  reported by Schweitzer (1998) for uptake onto  $\sim 100\text{ }\mu\text{m}$  NaCl droplets. Overall, the  $\gamma_{\text{thick}}$  values are essentially independent of humidity and of the activity of H<sub>2</sub>O and of Cl<sup>−</sup> in the liquid phase, which is in accord with conclusions from the earlier studies and with the mechanism proposed for N<sub>2</sub>O<sub>5</sub> reaction in aqueous electrolyte aerosols.

The experimental observations in this study, which provide the first direct measurements of the reactive uptake kinetics of N<sub>2</sub>O<sub>5</sub> on submicron aerosols containing NaCl, have confirmed previous conclusions regarding the rate and mechanism of this heterogeneous process. We have demonstrated

that the low uptake coefficients observed at  $RH < 80\%$  ( $\gamma=10^{-2}$  to  $10^{-3}$ ) are due to the limiting effect of volume of the small particles on the uptake rate. The uptake coefficient of  $\gamma=0.02\text{--}0.03$ , obtained in the laboratory experiments on NaCl-containing solutions is fast enough for the reaction of N<sub>2</sub>O<sub>5</sub> to form ClNO<sub>2</sub> to occur readily in sea salt aerosol droplets in the marine boundary layer. The sea salt aerosol mostly resides in the large particle mode (mean diameter  $\sim 3.5\text{ }\mu\text{m}$ ) where diffusion in the gas phase can become rate limiting. However, for a reactive uptake coefficient of  $\gamma=0.025$ , reaction will become controlled by gas diffusion only for particles with diameter  $> 10\text{ }\mu\text{m}$ . Thus the heterogeneous reaction rate causing Cl<sup>−</sup> deficit by release of ClNO<sub>2</sub> into the gaseous phase will be principally determined by the  $\gamma$  values. The uptake coefficients will be reduced for particles with diameter  $< 100\text{ }\mu\text{m}$ .

*Acknowledgements.* D. J. Stewart thanks NERC for a studentship. P. T. Griffiths thanks NERC for support under DIAC. We thank J. Thornton, C. Braban and J. Abbatt (University of Toronto) for a preprint of their work on N<sub>2</sub>O<sub>5</sub> uptake on organic acids.

Edited by: J. Crowley

## References

- Ayers, G. P., Gillett, R. W., Caaney, J. M., and Dick, A. L.: Chloride and bromide loss from sea salt particles in Southern Ocean air, *J. Atmos. Chem.*, 33, 299–319, 1999.
- Behnke, W., Krüger, H.-U., Scheer, V., and Zetzsch, C. J.: Formation of atomic Cl from sea spray via photolysis of nitryl chloride: Determination of the sticking coefficient of N<sub>2</sub>O<sub>5</sub> on NaCl aerosol, *J. Aerosol Sci.*, S23, S933–4, 1992.
- Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO<sub>2</sub>, from the reaction of gaseous N<sub>2</sub>O<sub>5</sub> with NaCl solution: Bulk and aerosol experiments, *J. Geophys. Res.*, 102, 3795–3804, 1997.
- Brown, R. L.: Tubular Flow Reactors with first-order kinetics, *J. Res. Nat. Bur. Stand.*, 83, 1–8, 1978.
- Czizco, D. J. and Abbatt, J. P. D.: Infrared observations of the response of NaCl, MgCl<sub>2</sub>, NH<sub>4</sub>HSO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> aerosols to changes in relative humidity from 289 to 238 K, *J. Phys. Chem. A*, 104, 2038–2047, 2000.
- Czizco, D. J., Nowak, J. B., Hu, J. H., and Abbatt, J. P. D.: Infrared spectroscopy of model tropospheric aerosols as a function of relative humidity: observation of deliquescence and crystallisation, *J. Geophys. Res.*, 102, 18 843–18 850, 1997.
- Fenter, F. F., Caloz, E., and Rossi, M. J.: Heterogeneous kinetics of N<sub>2</sub>O<sub>5</sub> uptake on salt with a systematic study of the role of surface presentation, *J. Phys. Chem.*, 100, 1008–1013, 1996.
- Finlayson-Pitts, B. J., Ezell, M. J., and Pitts, J. N.: Formation of chemically active chlorine compounds by reaction of atmospheric NaCl particles with gaseous N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub>, *Nature*, 337, 241–244, 1989.
- Fried, A., Henry, B. E., Calvert, J. G., and Mozurkewich, M.: The reaction probability of N<sub>2</sub>O<sub>5</sub> with sulfuric acid aerosols at stratospheric temperatures, *J. Geophys. Res.*, 99, 3517–3532, 1994.

- Fuchs, N. A. and Sutugin, A. G.: Highly dispersed aerosols, Ann Arbor Science, Ann Arbor MI, 1970.
- George, C., Ponche, J. L., Mirabel, P., Behnke, W., Scheer, V., and Zetzsch, C.: Study of the uptake of N<sub>2</sub>O<sub>5</sub> by water and NaCl solutions, *J. Phys. Chem.*, 98, 8780–8784, 1994.
- Hallquist, M., Stewart, D. J., Baker, J., and Cox, R. A.: Hydrolysis of N<sub>2</sub>O<sub>5</sub> on sulphuric acid aerosols, *J. Phys. Chem. A*, 104, 3984–3990, 2000.
- Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N<sub>2</sub>O<sub>5</sub> on submicron sulphate aerosols, *Phys. Chem. Chem. Phys.*, 5, 3453–3463, 2003.
- Hanson, D. R. and Lovejoy, E. R.: The reaction of ClONO<sub>2</sub> with submicrometer sulfuric acid aerosol, *Science*, 267, 1326–1328, 1995.
- Hanson, D. R., Ravishankara, A. R., and Solomon, S.: Heterogeneous reactions on sulfuric acid aerosols: a framework for model calculations, *J. Geophys. Res.*, 99, 3615–3629, 1994.
- Hu, J. H. and Abbatt, J. P. D.: Reaction probabilities for N<sub>2</sub>O<sub>5</sub> hydrolysis on sulfuric acid and ammonium sulphate aerosols at room temperature, *J. Phys. Chem.*, 101, 871–878, 1997.
- Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, 34, 2131–2138, 2000.
- Keene, W. C., Pszenny, A. A. P., Jacob, D. J., Duce, R. A., Galloway, J. N., Schultz-Tokos, J. J., Sievering, H., and Boatman, J. F.: The geochemical cycle of reactive chlorine through the marine troposphere, *Global Biog.*, 4, 407–430, 1990.
- Leu, M.-T., Timonen, R., Keyser, L. F., and Yung, Y. L.: Heterogeneous reactions of HNO<sub>3</sub>(g)+NaCl(s)→HCl(g)+NaNO<sub>3</sub>(s) and N<sub>2</sub>O<sub>5</sub>(g)+NaCl(s)→ClONO<sub>2</sub>(g)+NaNO<sub>3</sub>(s), *J. Phys. Chem.*, 99, 13 203–13 212, 1995.
- Livingston, F. E. and Finlayson-Pitts, B. J.: The reaction of gaseous N<sub>2</sub>O<sub>5</sub> with solid NaCl at 298 K: Estimated lower limit to the reaction probability and its potential role in tropospheric and stratospheric chemistry, *Geophys. Res. Lett.*, 18, 17–20, 1991.
- Mentel, T. F., Sohn, M., and Wahner, A.: Influence of organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub>, *Phys. Chem. Chem. Phys.*, 1, 5451–5457, 1999.
- Pszenny, A. A. P., Keene, W. C., Jacob, D. J., Fan, S., Maben, J. R., Zetwo, M. P., Springer-Young, M., and Galloway, J. N.: Evidence of inorganic chlorine gases other than hydrogen chloride in marine surface air, *Geophys. Res. Lett.*, 20, 699–702, 1993.
- Schweitzer, F., Mirabel, P., and George, C.: Multiphase Chemistry of N<sub>2</sub>O<sub>5</sub>, ClONO<sub>2</sub> and BrNO<sub>2</sub>, *J. Phys. Chem. A*, 102, 3942–3952, 1998.
- Sohn, F., Mentel, T. F., and Wahner, A.: Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Phys. Chem. Chem. Phys.*, 1, 5451–5457, 1999.
- Tang, I. N., Munkelwitz, H. R., and Davis, J. G.: Aerosol Growth Studies II: preparation and growth measurements of monodisperse salt aerosols, *J. Aerosol Sci.*, 8, 149–159, 1977.
- Thornton, J. A., Braban, C. F., and Abbatt, J. P. D.: Hydrolysis of N<sub>2</sub>O<sub>5</sub> on sub-micron organic aerosols: the effect of relative humidity, particle phase and particle size, *Phys. Chem. Chem. Phys.*, 5, 4593–4603, 2003.
- Vogt, R., Crutzen, P. J., and Sander, R. A.: Mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, *Nature*, 383, 327–330, 1996.
- Volkers, M., Mentel, T. F., and Wahner, A.: Influence of an organic coating on the reactivity of aqueous aerosols probed by the heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub>, *Geophys. Res. Lett.*, 30 (12), 1644, doi:10.1029/2003GL017168, 2003.
- Zetzsch, C. and Behnke, W.: Heterogeneous photochemical sources of atomic Cl in the troposphere, *Ber. Bunsenges. Phys. Chem.*, 96, 488–493, 1992.