1.5 KNUDSEN CELL STUDIES OF THE UPTAKE AND REACTION OF HNO_3 AND N_2O_5 ON SUB-LAYERS OF NaCl.

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1. INTRODUCTION

Heterogeneous reactions involving oxides of nitrogen and sea salt aerosols, rich in NaCl, have the potential to contribute to the tropospheric halogen budget. For example, reactions of sodium chloride (NaCl) with dinitrogen pentoxide (N_2O_5) and with nitric acid (HNO_3) generate photochemically active nitryl chloride ($ClNO_2$), and photochemically inert hydrochloric acid (HCl), respectively. [*Allen, et al.,* 1996; *Behnke, et al.,* 1997; *Behnke, et al.,* 1991; *Behnke and Zetzsch,* 1990; *Beichert and Finlayson-Pitts,* 1996; *Davies and Cox,* 1998; *DeHaan and Finlayson-Pitts,* 1997; *Fenter, et al.,* 1994; *Fenter, et al.,* 1996; *Finlayson-Pitts,* 1983; *George, et al.,* 1994; *Ghosal and Hemminger,* 1999; *Ghosal and Hemminger,* 2002; *Koch, et al.,* 1999; *Laux, et al.,* 1996; *Laux, et al.,* 1994; *Leu, et al.,* 1995; *Livingston and Finlayson-Pitts,* 1991; *Msibi, et al.,* 1994; *Schweitzer, et al.,* 1998; *Zangmeister and Pemberton,* 1998; *Zangmeister and Pemberton,* 2001; *Zetzsch and Behnke,* 1992] Reactions (1) and (2) may contribute to the observed chloride deficits in sea salt particles observed in the marine boundary layer (MBL). [*Junge,* 1956; *Keene, et al.,* 1990; *McInnes, et al.,* 1994; *Mouri and Okada,* 1993; *Moyers and Duce,* 1972]

$$N_2O_{5\,(g)} + NaCl_{(s)} \rightarrow NaNO_{3\,(s)} + ClNO_{2\,(g)} \qquad (1)$$
$$HNO_{3\,(g)} + NaCl_{(s)} \rightarrow NaNO_{3\,(s)} + HCl_{(g)} \qquad (2)$$

The reaction of HNO_3 with solid NaCl and the reaction of N_2O_5 with solid NaCl, NaCl aerosol, and aqueous NaCl solutions have been studied previously using a number of different analytical techniques. These studies are summarized in Tables 1 and 2, respectively.

The reported reaction probabilities for the uptake of HNO_3 with NaCl (Table 1) range over two orders of magnitude, possibly due to differences in NaCl particle sizes, sample preparation, diffusion into openings between multiple salt layers, surface saturation effects, and the amount of SAW on the salt surface. These parameters affect the treatment of the reactive surface area, in essence, how much of the particle surface area is actually available for uptake and reaction. It is clearly important to understand whether the available reaction area is equal to the geometric surface area.

The reported values for the uptake and reaction of N_2O_5 (Table 2) are relatively slow, 10^{-3} or less, for reaction with solid NaCl compared to reaction with deliquesced aerosol particles or aqueous solutions of NaCl, $\sim 10^{-2}$. The large uptake associated with aerosol particles and aqueous solutions approaches that for the hydrolysis uptake of N_2O_5, which is thought to occur via autoionization followed by reaction of NO_2^+ with water to produce HNO_3. [*Behnke, et al.,* 1997; *DeMore, et al.,* 1997; *George, et al.,* 1994; *Mentel, et al.,* 1999; *Mozurkewich and Calvert,* 1988; *Robinson, et al.,* 1997; *Wahner, et al.,* 1998]

$$N_2O_5 + H_2O \rightarrow 2\,HNO_3 \qquad (3)$$

However, in the presence of NaCl, NO_2^+ could also react with Cl^- to produce $ClNO_2$. [*Behnke, et al.,* 1997; *Schweitzer, et al.,* 1998] Thus, there is a competition between water and chloride for reaction with N_2O_5.

Table 1. Summary of Previous Studies on the Reaction of HNO_3 with Solid NaCl at 298 K.

NaCl Type	Uptake Coefficient (γ)	Technique
S.C. [*Laux, et al.,* 1994]	$(4 \pm 2) \times 10^{-4}$	XPS/UHV
G. P. [*Fenter, et al.,* 1994]	$(2.8 \pm 0.3) \times 10^{-2}$	Knudsen cell/MS
S. C. [*Leu, et al.,* 1995]	$(1.3 \pm 0.4) \times 10^{-2}$	Flow system/MS
G. P., S. C., and Sp. C. Films [*Fenter, et al.,* 1996]	$(2.0 \pm 1.0) \times 10^{-2}$	Knudsen cell/MS
G. P. and S. C. [*Beichert and Finlayson-Pitts,* 1996]	$(1.4 \pm 0.6) \times 10^{-2}$	Knudsen cell/MS
G. P. (Pressed) [*Davies and Cox,* 1998]	$(0.8 - 9) \times 10^{-4}$	Flow system/MS
Sp.C. Films [*Koch, et al.,* 1999]	$(3.0 \pm 1.0) \times 10^{-2}$	Molecular diffusion tube
G. P. and S. C. [*Ghosal and Hemminger,* 1999]	$(1.3 \pm 0.6) \times 10^{-3}$	XPS/UHV
Recrystallized NaCl [*Zangmeister and Pemberton,* 2001]	$(5.9 \pm 0.8) \times 10^{-2}$	Raman spectroscopy
S. C. [*Ghosal and Hemminger,* 2002]	$\leq (5 \pm 3) \times 10^{-3}$	XPS/UHV

S.C. = single crystal; G. P. = ground powders; Sp.C.= spray-coated

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Table 2. Summary of Previous Work on the Uptake and Reaction of N_2O_5 on Solid and Aqueous NaCl.[a]

NaCl Phase	Technique	Uptake Coefficient (γ)	Yield of $ClNO_2$ (%)
Solid	FTIR [*Livingston and Finlayson-Pitts,* 1991]	$> 2.5 \times 10^{-3}$	60 – 100
	Annular Reactor [*Msibi, et al.,* 1994]	1×10^{-3}	n.d.[b]
	Flow Tube/EI MS [*Leu, et al.,* 1995][c]	$< 10^{-4}$	n.d.[b]
	Knudsen Cell/MS [*Fenter, et al.,* 1996]	$(0.5 – 2.0) \times 10^{-3}$ [d]	60
	Diffusion Tube/MS [*Koch, et al.,* 1999]	$(3 \pm 1) \times 10^{-4}$	100
Aerosol particles	Chamber/IC [*Behnke, et al.,* 1991; *Zetzsch and Behnke,* 1992]	$(2.4 – 5.0) \times 10^{-2}$ [e]	61 – 31 [f]
	Droplet train tech/FTIR [*George, et al.,* 1994][f]	$(1.4 – 3.9) \times 10^{-2}$ [g]	n.d.[b]
	Chamber/FTIR [*Behnke, et al.,* 1997]	$(3.2 \pm 0.2) \times 10^{-2}$ [h]	65
	Droplet train tech/FTIR & MS [*Schweitzer, et al.,* 1998]	1.5×10^{-2} [g]	100 ± 14
Solution	Annular Reactor [*Msibi, et al.,* 1994]	$\sim 1.5 \times 10^{-2}$	n.d.[b]
	Wetted Wall Flow Tube/FTIR [*Behnke, et al.,* 1997][h]	n.d.[b]	95 [i]

[a] At room temperature, unless otherwise noted; [b] n.d. = not determined; [c] Conducted at 223 and 296 K; [d] For spray-coated NaCl, finely ground NaCl powders, and coarse NaCl grains; [e] Over a relative humidity (RH) range of 71 to 92%; [f] Highest yield for lowest % RH where droplets are more concentrated; [g] Over a temperature range of 262 – 278 K; [h] For concentrations of NaCl in solution $\geq$ 1 M and RH between 77.3 and 93.9%; [i] For a 5M NaCl concentration in which the $ClNO_2$ yield plateaued

Additionally, a number of studies have reported surface adsorbed water (SAW) on NaCl powders which is not readily removed after extensive pumping at temperatures up to 200 °C, [*Aguzzi and Rossi,* 1999; *Beichert and Finlayson-Pitts,* 1996; *Davies and Cox,* 1998; *Gebel and Finlayson-Pitts,* 2001; *Ghosal and Hemminger,* 1999; *Ghosal and Hemminger,* 2002] and that can play an important role in the uptake of N_2O_5 on NaCl. This suggests that even on relatively dry solids, the hydrolysis reaction may be important. The HNO_3 formed in reaction (3) also produce HCl from reaction with Cl^-, reaction (2). The overall uptake and reaction of N_2O_5 with NaCl in the presence of water could ultimately yield two HCl molecules or one $ClNO_2$ molecule for every one N_2O_5 molecule that reacts.

We report here experiments on both reactions (1) and (2), designed to clarify the issue of the available reaction surface and to elucidate which reaction path, hydrolysis or reaction with chloride, dominates the uptake of N_2O_5 on NaCl. Atmospheric implications of these results are discussed.

2. EXPERIMENTAL METHODS

Uptake experiments of both HNO_3 and N_2O_5 were performed at room temperature using a glass Knudsen cell equipped with a moveable lid (to cover or expose the salt sample), discussed in detail elsewhere. [*Beichert and Finlayson-Pitts,* 1996; *DeHaan and Finlayson-Pitts,* 1997; *Gebel and Finlayson-Pitts,* 2001] Salt samples, using less than one layer of salt particles (fractional layers), were placed in either a halocarbon-coated (Halocarbon Products, Series 1500) stainless-steel or a Teflon sample holder. Factional salt layer samples were used to minimize diffusion of the reactant gas between salt particles. Salt particles were prepared either by grinding and sieving single crystal NaCl cuttings (164 ± 102 , 291 ± 184, and 428 ± 328 μm) or simply sieving NaCl powders (312 ± 160 μm). Salt sizes were confirmed using scanning electron microscopy. Experiments were conducted at concentrations of $(0.2 – 9.0) \times 10^{12}$ molecules cm^{-3} HNO_3 and N_2O_5 to maintain molecular flow conditions within the cell. 'Wet' salt samples were prepared by pumping on the salt for only several minutes, enough time to evacuate the cell, whereas, 'dry' salt samples were pumped on for several hours until the *m/z* =18 signal decreased to baseline.

The reactant and/or product gases existed the Knudsen cell through a glass aperture (3.8, 5.9, or 8.5 mm diameter, chosen to optimize the signal) into a vacuum chamber quadrupole mass spectrometer (ABB Extrel EMBA II 150-QC) with electron impact ionization. The reactants and products were monitored using the m/z signals of the highest intensities: HNO_3 (*m/z* = 46), HCl (*m/z* = 36), $ClNO_2$ (*m/z* = 35 and 46), and N_2O_5 (*m/z* = 46).

The observed uptake coefficient, γ_{obs}, is determined by the ratio of the loss of reactant gas molecules through the exit aperture to the loss on the salt surface. [*Caloz, et al.,* 1997; *Fenter, et al.,* 1994; *Fenter, et al.,* 1997; *Finlayson- Pitts and Pitts,* 2000; *Golden, et al.,* 1973; *Hoffman, et al.,* 2002a; *Hoffman, et al., 2002b*; *Quinlan, et al.*, 1990]

$$\gamma_{obs} = \left(\frac{I_o}{I_r} - 1\right)\left(\frac{A_{aperture}}{A_{surface}}\right) \qquad \textbf{(I)}$$

where I_o and I_r are steady-state reactant signals in the absence and presence of a reactive surface, respectively, $A_{aperture}$ is the area of the exit aperture from the Knudsen cell to the mass spectrometer, and $A_{surface}$ is the reactive surface area. Commonly, the reactant gas concentration, which is proportional to the signal, is used to calculate γ_{obs}. As an alternative approach, the reaction probabilities were calculated using the products from reactions (1), (2) and (3). [*Hoffman, et al.,* 2002a; *Hoffman, et al.,* 2002b]

$$\gamma_{HNO_3} = \left(\frac{[HNO_3]_o}{[HNO_3]_o - [HCl]} - 1 \right) \left(\frac{A_{aperture}}{A_{surface}} \right) \qquad \textbf{(II)}$$

$$\gamma_{N_2O_5} = \left(\frac{[N_2O_5]_o}{[N_2O_5]_o - [ClNO_2] - \frac{1}{2}[HCl]^{Hydrolysis}} - 1 \right) \left(\frac{A_{aperture}}{A_{surface}} \right) \qquad \textbf{(III)}$$

The geometric surface area, $A_{geometric}$, (19.0 cm^2) was corrected [*Hoffman, et al.,* 2002a; *Hoffman, et al.,* 2002b] to reflect the true reactive surface area, $A_{sufrace}$, when the entire geometric surface area is not covered by salt using fractional salt layer samples. The portion of the salt sample available for reaction includes the tops of the particles and a fraction of the particle sides. The top area (A_{top}) can be readily calculated using the number of particles and the average area per particle side, determined using SEM. If a reactant molecule strikes a "hole" between two particles, it can either be scatter away from the surface never coming into contact with a salt particle, or if at an appropriate angle, it may strike the side of an adjacent NaCl particle. The fraction (F) of the salt sides that a reactant molecule hits will be determined by the proximity of the particles to each other and the scattering angle, calculated using the cosine law of molecular scattering [*Boeckmann,* 1986] adjusted for openings between particles. The true reactive surface area can than be estimated according to equation (**IV**):

$$\text{True reactive area} = A_{top} + (A_{geometric} - A_{top}) \times F \qquad \textbf{(IV)}$$

N_2O_5 was synthesized by reaction of NO_2 with excess O_3. [*Hoffman, et al.,* 2002a] Hydrolysis of N_2O_5 occurs on surfaces of the synthesis traps, generating HNO_3 as an impurity ranging from 8 to 39 %. The amount of HNO_3 impurity was determined by FTIR using a 10 cm glass cell and the published cross sections from Wangberg *et al.* (1997) of 9.29×10^{-19} and 8.56×10^{-19} cm^2 molecule^{-1} for HNO_3 and N_2O_5, respectively. This HNO_3 impurity, in addition to that produced from N_2O_5 hydrolysis, could also contribute to any observed production of HCl (reaction 2). The amount of HCl formed was corrected for the amount produced from this impurity. [*Hoffman, et al.,* 2002a]

3. RESULTS AND DISCUSSION

3.1 HNO_3 on NaCl

Figure 1 shows a typical loss of HNO_3 and generation of HCl for uptake on fractional layers of NaCl.

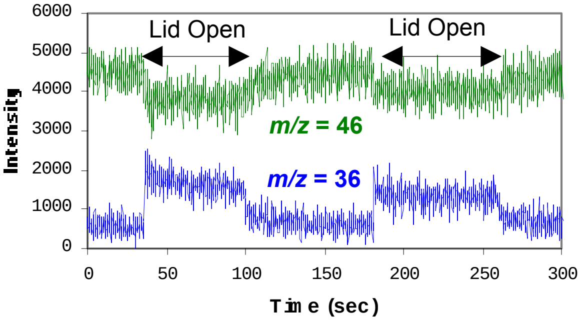

Figure 1. Uptake of HNO_3 and production of HCl for 0.9 particle layers of 164 μm 'wet' NaCl particles that had been pumped on for several minutes at room temperature. Exit aperture diameter was 3.9 mm, and $[HNO_3]_o = 3.2 \times 10^{12}$ molecules cm^{-3}.

Figure 2 shows the average data points for multiple experiments using both 'wet' and 'dry' NaCl. As expected, after correcting for the true available reactive surface area, the reaction probabilities show no trend in γ_{HNO3} with fractional particle layers. Additionally, the uptake of HNO_3 on 'dry' salts is indistinguishable from that on 'wet' salts. The average reaction probability for ground, sieved single crystal salt (164, 291, and 428 n particles) is $(6.5 \pm 4.2) \times 10^{-4}$ (2s). The average for the sieved powders (312 μm) is slightly smaller $(4.0 \pm 1.5) \times 10^{-4}$ (2s), but still within the combined experimental uncertainties. The overall steady-state reaction probability for all salt particles sizes is $(6.2 \pm 4.2) \times 10^{-4}$ (2s), a factor of 20 smaller than previously reported studies using multiple salt layers (Table 1) and multiple layer experiments conducted in this laboratory (results not shown). [*Hoffman, et al.,* 2002b]

Previously proposed models for HNO_3 uptake involve water adsorbed onto salt surface steps, edges and defects. [*Allen, et al.,* 1996; *Davies and Cox,* 1998; *Fenter, et al.,* 1994; *Fenter, et al.,* 1996; *Ghosal and Hemminger,* 1999; *Laux, et al.,* 1996; *Sporleder and Ewing,* 2001; *Zangmeister and Pemberton,* 2001] This SAW is thought to increase the mobility of the nitrate species, resulting in clusters of 3-dimensional $NaNO_3$ microcrystallites, [*Allen, et al.,* 1996; *Laux, et al.,* 1996] regenerating a fresh reaction site. The uptake and reaction observed in the present study indicate the occurrence of this clustering due to the reaction continuing well beyond the time to saturate the NaCl surface with $NaNO_3$ (~40 s for conditions shown in Figure 1). These microcrystallites are likely in the form of asymmetrical crystals [*Allen, et al.,* 1996; *Laux, et al.,*

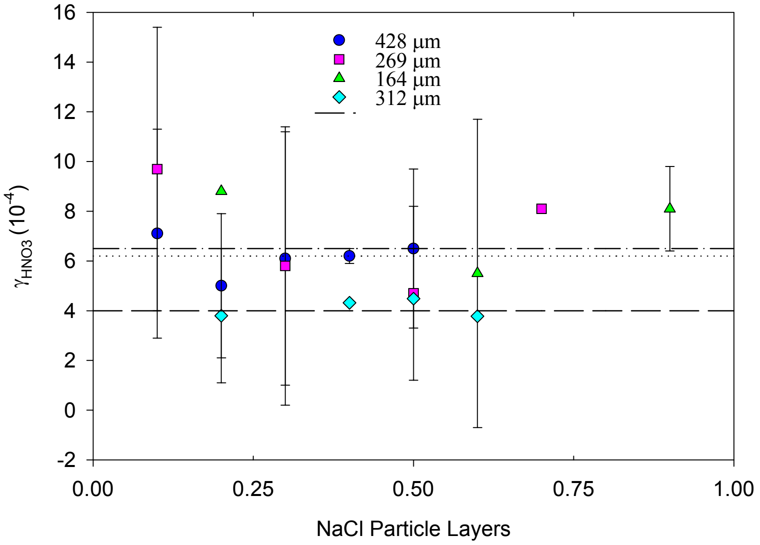

Figure 2. γ_{HCl} versus NaCl particle layers calculated using a true reactive area. Error bars represent two standard deviations of the mean for multiple experiments conducted for some fractional particle layers experiments. (—·—·) $\gamma_{ground} = (6.5 \pm 4.2) \times 10^{-4}$; (- - - -) $\gamma_{sieved} = (4.0 \pm 1.5) \times 10^{-4}$; and (······) $\gamma_{overall} = (6.2 \pm 4.2) \times 10^{-4}$.

1996; *Sporleder and Ewing,* 2001; *Zangmeister and Pemberton,* 2001] and/or “strings” [*Zangmeister and Pemberton,* 1998] decorating the NaCl surface. However, the fraction of the salt surface unavailable for reaction after these microcrystals form is not known.

To estimate an initial reaction probability representative of a fresh, unreacted NaCl surface, the decrease in γ_{HNO3} as a function of reaction time was measured. Results are summarized in Figure 3.

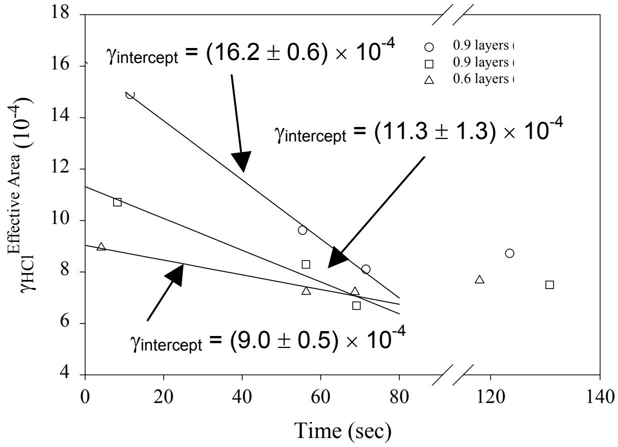

Figure 3. Extrapolation of the steady-state reaction probability to obtain the initial reaction probability calculated using an effective surface area for multiple exposures of 0.9 and 0.6 layers of 164 µm NaCl.

The high initial uptake at ~10 s may be due to reaction with OH^- on surface defects [*Beichert and Finlayson-Pitts,* 1996] and/or more rapid uptake into a fresh unreacted NaCl surface, absent of $NaNO_3$. Extrapolation back to t = 0 gives an initial reaction probability for an unreacted NaCl surface of $\gamma_0 = (1.2 \pm 0.7) \times 10^{-3}$, which is in excellent agreement with previous reported initial, zero coverage value on NaCl(100) [*Ghosal and Hemminger,* 1999], and the maximum value calculated using a single site Langmuir model for Davies and Cox (1998) data for the limit of high water. [*Ghosal and Hemminger,* 2002]

The apparent discrepancies between the results of Leu *et al*. (1995) and Davies and Cox (1998) appear to be reconcilable. If the entire salt surface area were available in the Leu *et al*. [*Leu, et al.,* 1995] studies, the corrected value of the average reaction probability would be about 1 × 10^{-3}, similar to that for a fresh, unreacted NaCl surface in this work, and the results of Ghosal and Hemminger, (2002) and Davies and Cox (1998).

3.2 N_2O_5 on NaCl

Figure 4 shows a typical N_2O_5 uptake experiment on NaCl in which there is a sharp decrease in the signal at *m/z* =46 and an increase in the product signal (*m/z* = 35 and 36). The ratio of the *m/z* = 36 to 35 signal is less than that for a pure sample of HCl under these conditions, 4.8 versus 6.4, indicating that $ClNO_2$ is a product of the N_2O_5 reaction.

Table 3 summarizes the reaction probabilities for N_2O_5 uptake on NaCl calculated using the true reactive

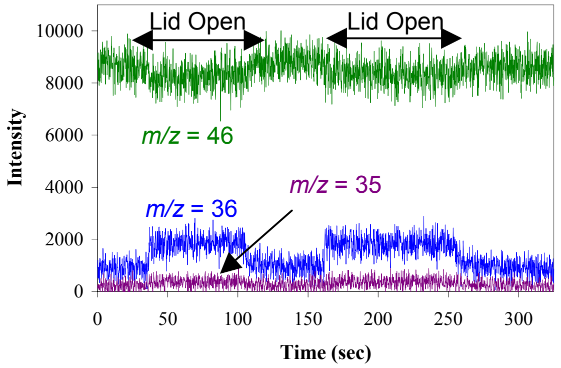

Figure 4. Uptake of N_2O_5 on 0.5 layers of 312 μm NaCl particles that had been pumped on for several minutes at room temperature (experiment #1, Table 3). True reactive surface area = 14.5 cm^2, and $[N_2O_5]_o = 4.0 \times 10^{12}$ molecules cm^{-3} (corrected for a maximum 39% HNO_3 impurity).

surface area and the $ClNO_2$ branching ratios (BR). There is no trend in the reaction probability with the number of salt layers, as expected if the true reactive surface area is properly treated. Although the average reaction probability for uptake on 'dry' salts is larger than uptake on 'wet' salts, the values agree within experimental errors; the same is true for the branching ratio for $ClNO_2$ production. Additionally, the fraction of HCl due to hydrolysis is 0.70 ± 0.24 (2s). The overall average reaction probability for N_2O_5 on solid NaCl is $(2.9 \pm 1.7) \times 10^{-3}$ (2s). The average $ClNO_2$ branching ratio is 0.76 ± 0.26 (2s), indicating that the reaction of NO_2^+ with Cl^- dominates over hydrolysis.

Uptake experiments were also conducted on synthetic sea salt (SSS), however, due to the presence of highly hygroscopic components of SSS which causes particles to clump together, only multiple salt layer experiments were studied. The results are summarized in Table 4. This clumping tends to minimize the available openings between particles and hence, diffusion of the gas beyond the top salt layers. This is a reasonable assumption given that the reaction probability using the geometric surface area does not increase with the number of salt layers (Table 4). Hence, the reaction probability for SSS is reported only using the geometric surface area of the sample holder (19.0 cm^2).

The reaction probability for N_2O_5 on SSS is a factor of 5 larger for 'wet' SSS than for 'dry' SSS. Additionally, γ_{N2O5} for 'wet' SSS is ~ one order of magnitude larger than for 'wet' NaCl. The average $ClNO_2$ yield is 0.98 ± 0.12 (2s) indicating hydrolysis of N_2O_5 on SSS powders does not contribute significantly to the reaction.

Overall, the results for the uptake and reaction of N_2O_5 on NaCl and SSS indicate that N_2O_5 hydrolysis is occurring on SAW in competition with reaction to yield $ClNO_2$. Surprisingly, the yield of $ClNO_2$ is higher for reaction on SSS than on NaCl, although SSS holds comparatively more SAW. The formation of $ClNO_2$ dominates for both NaCl and SSS reactions, with yields that are in the range reported in previous studies (Table 2) of the N_2O_5 reaction with NaCl solids, particles and aqueous solutions. We propose a mechanism (Figure 5) for the uptake and reaction of N_2O_5 with SAW on solid NaCl which is similar to a model proposed by Beichert and Finlayson-Pitts (1996). The present model differs, however, from the Beichert and Finlayson-Pitts (1996) model in that the proposed chemistry can take place either at the air-water interface or in the "bulk" of the liquid. Secondary reactions of $ClNO_2$ for the reaction in the bulk phase may result in the removal of some $ClNO_2$ and hence, yields less than 100%.

4. ATMOSPHERIC IMPLICATIONS

In the marine boundary layer, the reaction of N_2O_5 with sea salt aerosols (1) to yield photolyzable $ClNO_2$ occurs in competition with reaction of HNO_3 with sea salt aerosols (2) to generate photochemically inert HCl.

Table 3. Summary of Uptake and Reaction of N_2O_5 on Fractional Layers of NaCl

Exp	Particle Size (μm)	No. of Particle Layers	Corrected[c] $[N_2O_5]_o$ (10^{12} molecules cm^{-3})	Fraction of HCl from Hydrolysis[d]	γ_{N2O5}[e] (10^{-3})	BR^{ClNO2} [f]
'Wet' Particles[a]						
1	312	0.5	4.0	0.74	3.6	0.75
2		0.4	2.7	0.75	2.4	0.78
3		0.3	3.2	0.72	1.7	0.50
4		0.1	3.2	0.50	2.5	0.60
			Average (± 2s):	0.68 ± 0.24	2.6 ± 1.6	0.66 ± 0.26
'Dry' Particles[b]						
5	428	0.6	5.4	0.60	3.4	0.95
6		0.5	5.6	0.79	2.7	0.75
7		0.4	5.4	0.83	4.2	0.76
			Average (± 2s):	0.72 ± 0.22	3.4 ± 1.5	0.82 ± 0.22

[a] Samples pumped on for several minutes; [b] Samples pumped on for more than two hours; [c] $[N_2O_5]_o$ after correction for HNO_3 impurity; [d] Fraction of HCl from hydrolysis versus from uptake and reaction of HNO_3 impurity; [e] Calculated using an effective surface area based on the tops of the particles and a fraction of the

Table 4. Summary of Uptake and Reaction of N_2O_5 on Multiple Layer SSS.

Exp.	Particle Size (μm)	No. of Particle Layers	Corrected[c] $[N_2O_5]_0$ (10^{13} molecules cm^{-3})	Fraction of HCl from Hydrolysis[d]	γ_{N2O5}[e] (10^{-3})	BR^{ClNO2} [f]
'Dry' Particles[b]						
8	10	149	2.3	0.0	2.4	1.0
9		22	2.5	0.0	5.0	1.0
10	400	4.2	6.6	0.0	5.4	1.0
11		2.2	4.0	0.59	10.3	0.85
				Average (± 2s):	5.8 ± 6.6	0.96 ± 0.15
'Wet' Particles[a]						
12	400	1.0	3.0	0.0	36.7	1.0
13		1.0	6.9	0.0	30.9	1.0
				Average (± 2s):	33.8 ± 8.2	1.0

[a] Samples pumped on for several minutes; [b] Samples pumped on for more than two hours; [c] $[N_2O_5]_0$ after correction for HNO_3 impurity; [d] Fraction of HCl from hydrolysis versus from uptake and reaction of HNO_3 impurity; [e] Calculated using an effective surface area based on the tops of the particles and a fraction of the particle sides; [f] Branching ratio of $ClNO_2$.

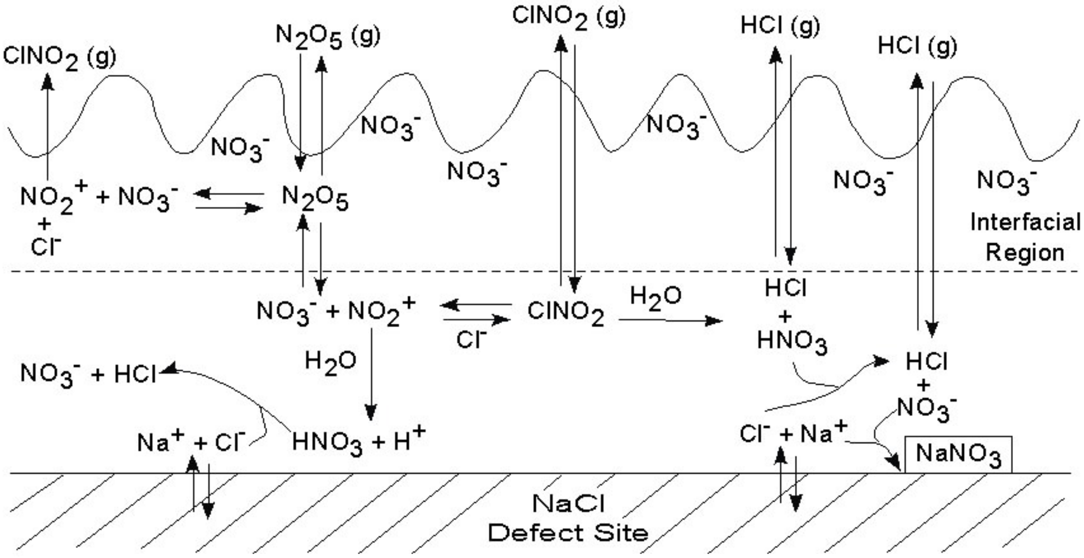

Figure 5. Schematic diagram of uptake of N_2O_5 onto NaCl holding surface adsorbed water.

The relative importance of N_2O_5 and HNO_3 reactions depends on their reaction probabilities as well as their atmospheric concentrations. Using typical concentrations of HNO_3 (~25 ppt) [*Finlayson-Pitts and Hemminger,* 2000] and N_2O_5 (100 ppt) [*Brown, et al.,* 2001] in populated coastal areas, the relative rate of reaction of NaCl with N_2O_5 will be about a factor of 5 greater than with HNO_3; i.e. $\gamma_{N2O5}[N_2O_5] \cong \gamma_{HCl}[HNO_3]$. Using γ_{N2O5} and the number of collisions per second of N_2O_5 with the salt surface, the amount of $ClNO_2$ formed in 12 hours overnight by reaction (1) could be ~ 1.0 ppb. The rate of chlorine atom generation from $ClNO_2$ relative to Cl_2 can be estimated using peak $[ClNO_2]$ = 1.0 ppb and $[Cl_2]$ ~ 150 ppt, [*Spicer, et al.,* 1998] and photolysis rate constants of 4.1×10^{-5} and 3.3×10^{-4} s^{-1}, respectively. Rates of Cl production are comparable, 0.7×10^{6} and 1.2×10^{6} atoms cm^{-3} s^{-1}, respectively.

5. ACKNOWLEDGEMENTS

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