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LETTERS

Effect of Water on the HNO_3 Pressure Dependence of the Reaction between Gas-Phase HNO_3 and NaCl Surfaces

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We show here that the dissociative adsorption of HNO_3(g) on NaCl to form $NaNO_3$(s) and HCl(g) follows single-site Langmuir adsorption behavior. X-ray photoelectron spectroscopy is also used to show that the amount of "strongly adsorbed water" on the surfaces of NaCl particles strongly depends on the particle size. Particles of 1−10 μm diameter show large quantities of adsorbed water that remain on the sample up to temperatures of 200 °C. Particles in the size range of 500 μm diameter have less, but still easily measurable, amounts of strongly adsorbed water. Water desorbs completely from low defect density NaCl(100) surfaces under vacuum at temperatures well below room temperature. We present a model for the recently reported HNO_3 pressure dependence of the reactive sticking coefficient of HNO_3 on NaCl under steady-state reaction conditions. The origin of the pressure dependence in the model is the competition between site blocking on the surface by the build-up of the $NaNO_3$ reaction product and the water-induced 3-D recrystallization of the $NaNO_3$ that frees up reactive sites for further reaction.

Introduction

Recent studies indicate that reactions of atmospheric pollutants N_2O_5 and $ClNO_2$ on the surfaces of sea salt particles may be a significant source of reactive chlorine-containing species (e.g., $ClNO_2$ and Cl_2) in the marine troposphere. These reactions compete with the reaction of nitric acid with NaCl which forms the relatively unreactive HCl.

$$HNO_3\,(g) + NaCl\,(s) \rightarrow NaNO_3\,(s) + HCl\,(g) \qquad (1)$$

In polluted regions of the marine troposphere, collected sea salt particles have been observed to show a Cl/Na ratio that is less than that expected from the ocean water composition which has often been attributed to reaction 1.[1−5] Several laboratories have carried out quantitative studies of the reaction probability for reaction 1 in an effort to assess the importance of such chemistry to the marine troposphere. Values of the reactive sticking coefficient (γ) for HNO_3 (g) on NaCl powders have been measured by Beichert and Finlayson-Pitts[6] [$\gamma = (1.4 \pm 0.6) \times 10^{-2}$] and by Fenter et al.[7] [$\gamma = (1.3 \text{ to } 5.5) \times 10^{-2}$ depending on surface studied] using Knudsen cell methods. Leu et al.[8] have reported a value of $\gamma = (1.3 \pm 0.4) \times 10^{-2}$ obtained using a flow reactor technique. They report that the value of γ shows a dependence on the HNO_3 pressure that they attribute to "saturation effects". Laux et al.[9,10] have used X-ray photoelectron spectroscopy (XPS) to follow the reaction of HNO_3(g) with a low defect density NaCl(100) surface. They report an average value of $\gamma = (4 \pm 2) \times 10^{-4}$ for dry HNO_3 reacting with this low defect density surface. An average value was reported since their measurements were not under steady-state conditions and saturation of the reaction was observed.

Recently, Davies and Cox[11] have reported on flow reactor measurements of γ over a range of HNO_3 pressures. They report values of γ from $\gamma = 8 \times 10^{-5}$ at $[HNO_3] = 7 \times 10^{13}$

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molecules/cm^3 to $\gamma = 8.5 \times 10^{-4}$ at $[HNO_3] = 4.7 \times 10^{11}$ molecules/cm^3. Thus their measurements show a decrease in γ with increasing HNO_3 pressure similar to that observed by Leu et al.,[8] although the pressure ranges examined in the two studies do not overlap substantially. Experiments by Beichert and Finlayson-Pitts[6] show that the water content of the NaCl particles plays a critical role in the detailed mechanism of reaction 1. Allen et al.[12] and Laux et al.[9,10] have used TEM and XPS to demonstrate that the initial product of the reaction of dry HNO_3 with NaCl is a uniform, ultrathin, passivating $NaNO_3$ film. The result of the passivating nature of the $NaNO_3$ film formed by reaction 1 is that the reaction stops after only 1−2 layers of NaCl have reacted with HNO_3 from the gas phase. They also demonstrate conclusively that one of the roles water plays in this chemistry is to enhance ionic mobility in the $NaNO_3$ film resulting in recrystallization of the $NaNO_3$ into 3-d crystallites which are phase separated from the NaCl. The importance of water to the reorganization of the nitrate product was also suggested by diffuse reflection infrared spectroscopy experiments of Vogt and Finlayson-Pitts.[22−24] The water-induced recrystallization of the $NaNO_3$ product opens up fresh NaCl surface for further reaction, thus allowing the reaction to proceed to the extent that ultimately a substantial amount of the Cl can be extracted from a NaCl particle. All of the Knudsen cell and flow reactor measurements of γ mentioned above were carried out under steady-state reaction conditions. Since in the absence of adsorbed water the reaction saturates, water must play a critical role in all of those experimental measurements.

Davies and Cox[11] have presented a model to explain the HNO_3 pressure dependence of γ. Their model is based on an assumption that the initial dissociative adsorption of HNO_3 on NaCl follows a two-site Langmuir adsorption model: one surface site being required for the NO_3^- and one surface site for the H^+. Blocking of two surface sites for each dissociatively adsorbed HNO_3 leads to a prediction that γ will exhibit a $[HNO_3]^{-0.5}$ dependence. The $[HNO_3]^{-0.5}$ dependence provides a good fit to the HNO_3 pressure dependence that they measured for γ.[11] This important new work by Davies and Cox has stimulated us to investigate the site requirement for the dissociative adsorption of HNO_3 on NaCl.

In this letter we show that the dissociative adsorption of HNO_3 on NaCl is well described by a *single-site* Langmuir model. This observation, combined with our understanding of the impact of water on the chemistry of HNO_3 on NaCl suggests an alternate model for the HNO_3 pressure dependence of γ that is based on the fact that HNO_3 dissociative adsorption on NaCl must be accompanied by water-induced mobilization of the $NaNO_3$ to obtain steady-state reaction conditions. We also show that the surface water content of NaCl particles depend strongly on the particle size.

Experimental Section

X-ray photoelectron spectroscopy experiments have been carried out using a multitechnique ultrahigh vacuum surface analysis instrument (VG Instuments ESCALAB MkII). The details of the instruments and the method of independently dosing nitric acid and/or water on the NaCl samples have been described in detail previously.[13,14] NaCl(100) samples were prepared as thin wafers by cleavage from a rectangular single-crystal block. Powdered samples were produced by grinding pieces of single-crystal NaCl. The powdered samples were mounted for introduction into the vacuum chamber by pressing into a tungsten mesh. This provided a secure way to hold the samples in a vacuum and to heat the samples and monitor their temperature.

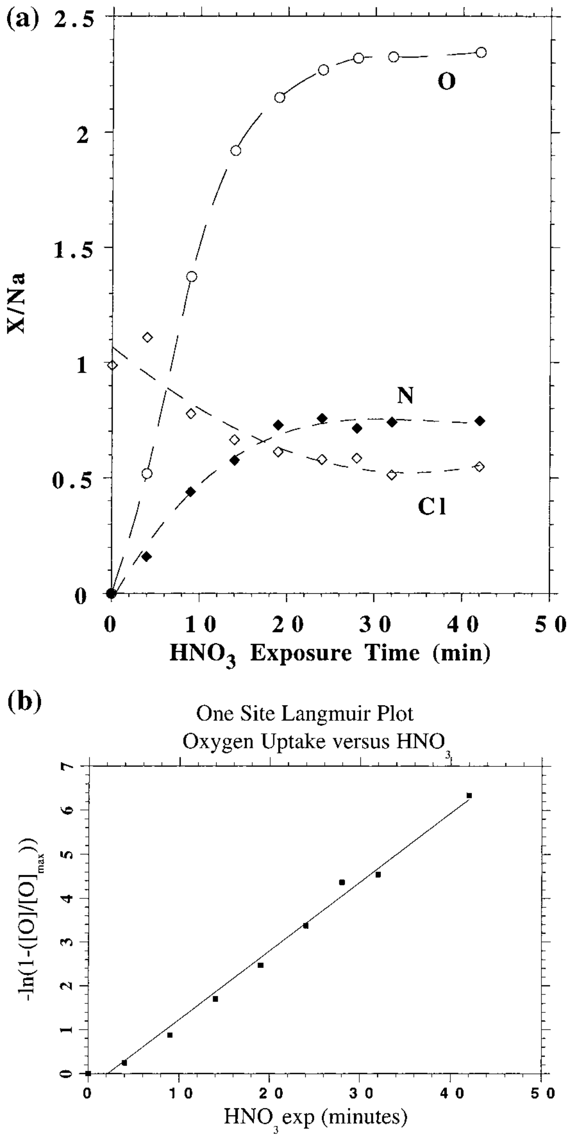

Figure 1. (a) O, N, and Cl surface concentrations (relative to Na) as a function of dry HNO_3 exposure time for the NaCl(100) surface; the HNO_3 flux at the surface was equivalent to a gas-phase concentration of HNO_3 of 1×10^{11} molecules/cm^3. (b) Plot of $-\ln(1 - [O]/[O]_{max})$ versus the dry HNO_3 exposure time, where [O] is the oxygen surface concentration shown in Figure 1a, and $[O]_{max}$ is the high exposure saturation value of the oxygen surface concentration shown in Figure 1a. The solid line is a linear least-squares fit to the data, indicating a good fit to a simple one-site Langmuir adsorption model.

XPS peak areas for N, Cl, O, and Na were measured after standard Shirley-type background subtraction. Standard XPS sensitivity factors for N, O, and Cl (0.489, 0.721, 0.925, respectively, relative to the F sensitivity factor of 1.00) were used to quantify the surface concentrations of these elements.[15,16] The XPS sensitivity factor for Na is not well established in the literature,[15,16] so we used a relative sensitivity factor of 3.8, developed for our instrument and experimental conditions, that gives a Na:Cl ratio of 1:1 for freshly cleaved, clean NaCl.

Results and Discussion

Figure 1a shows the results of X-ray photoelectron spectroscopy measurements as a function of HNO_3 exposure to a NaCl(100) surface. In this figure we plot the O, N, and Cl surface composition (relative to Na) of the NaCl(100) surface as a function of HNO_3 exposure. As we have pointed out earlier in

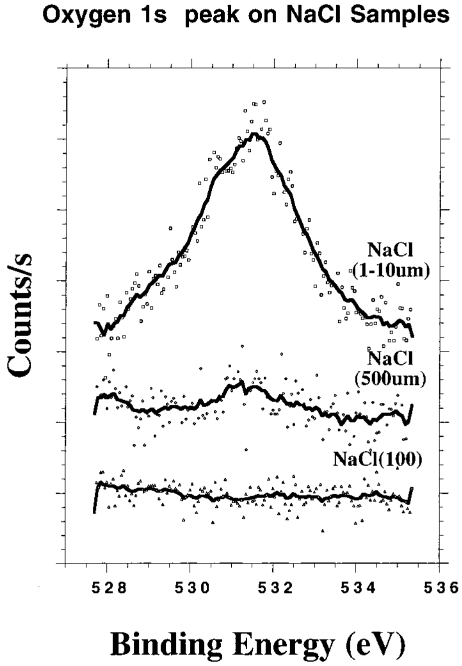

Figure 2. O 1s X-ray photoelectron spectra from freshly prepared NaCl samples shortly after introduction to the vacuum chamber and pump down to ultrahigh vacuum at room temperature. Spectra from a NaCl(100) single crystal, and NaCl powders with particle diameters of 500 μm and 1−10 μm are shown as labeled.

this article, the reaction is seen to saturate after an ultrathin film of $NaNO_3$ is formed on the surface. If the dissociative adsorption of HNO_3 on NaCl follows a *single-site* Langmuir model we would expect the surface oxygen content to show the following behavior:[17]

$$\ln\left(1 - \frac{[O]}{[O]_{max}}\right) = -kt$$

where [O] and $[O]_{max}$ are the oxygen surface concentration at time t and at saturation respectively, and k can be combined with the known HNO_3 flux to calculate the reactive sticking coefficient at zero coverage.

Figure 1b shows a plot of $-\ln(1 - [O]/[O]_{max})$ versus t as would be indicated by a single-site Langmuir model. The high quality of the straight-line fit shown in Figure 1b indicates that the single-site Langmuir model provides an excellent description of the dissociative adsorption of HNO_3 on NaCl. This is not especially surprising since it is expected that H^+ should be a highly mobile species on the surface at room temperature and should not act as an effective site blocker. The slope of the line in Figure 1b also provides us with the zero coverage value for the reactive sticking coefficient of HNO_3 on NaCl(100).

$\gamma_{\text{zero coverage}} = (1.3 \pm 0.6) \times 10^{-3}$

Figure 2 shows the O 1s photoelectron spectra for three different kinds of NaCl samples immediately after introduction to the vacuum chamber and pump down to ultrahigh vacuum conditions. The O 1s binding energy that we observe (531.5 eV) is consistent with either a surface hydroxide species or possibly intact water that is strongly coordinated with a surface Na^+ site. With this caveat in mind we will refer to this as strongly adsorbed water throughout the remainder of this paper. The large (~1 cm^2) NaCl(100) surface shows no surface oxygen indicative of the well-known fact that water does not dissociate on such low defect surfaces and H_2O desorbs from these surfaces at temperatures well below room temperature under vacuum conditions.[18−20] The other curves in Figure 2 correspond to large NaCl particles (~500 μm diameter), and small NaCl particles (~10 μm diameter). The surface water content is clearly significantly larger for the smallest particles. The major point to be made here is that NaCl powdered samples with particle diameters ≤ 500 μm contain substantial amounts of strongly adsorbed "water". On the basis of XPS experiments we have done as a function of sample annealing temperature, this "strongly adsorbed water" is stable on the surface at temperatures up to 200 °C.[21]

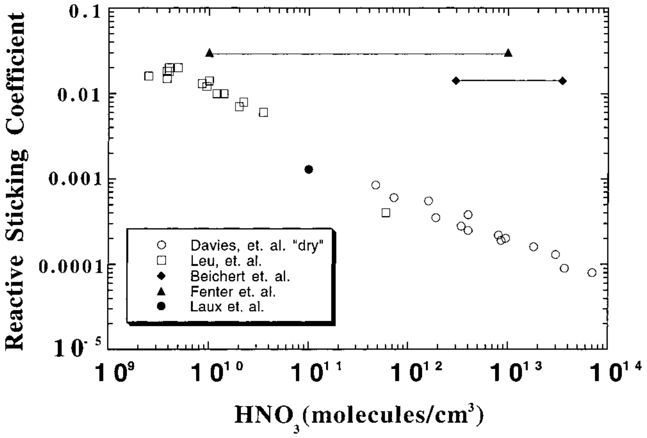

Figure 3. Measured values of the reactive sticking coefficient for HNO_3 on NaCl from a number of different laboratories as a function of HNO_3 gas-phase concentration. ▲ = Fenter et al.,[7] ◆ = Beichert and Finlayson-Pitts,[6] □ = Leu et al.,[8] ○ = Davies and Cox,[11] ● = Laux et al.,[9] Beichert and Finlayson-Pitts,[6] and Fenter et al.[7] report values which were observed to be independent of HNO_3 gas-phase concentration over the ranges indicated by the horizontal lines.

Figure 3 shows the values which have been reported for the reactive sticking coefficient (γ) of HNO_3 on NaCl as a function of the HNO_3 gas-phase concentration. We have put the zero coverage reactive sticking coefficient obtained from Figure 1b on this plot at the corresponding value of $[HNO_3] = 1 \times 10^{11}$ molecules/cm^3, which was the effective dosing pressure of our experiments. All of the other measurements shown in Figure 3 correspond to values obtained under steady-state conditions where water must play a significant role in the restructuring of the surface as the reaction proceeds. The Knudsen cell measurements of Fenter et al.[7] and Beichert and Finlayson-Pitts[6] were carried out on small particles and do not show a dependence on HNO_3 gas-phase concentration. The data of Davies and Cox[11] exhibit the HNO_3 pressure dependence which they have described as a $[HNO_3]^{-0.5}$ dependence.

Our observation, shown in Figure 1b, that the dissociative adsorption of HNO_3 on NaCl is well described by a one-site Langmuir adsorption model (a two-site model fit is very poor) suggests that an alternate explanation for the HNO_3 pressure dependence of γ is necessary. It is likely that the underlying cause of the HNO_3 pressure dependence lies in the fact that the surface nitrate product of the reaction acts to passivate the surface in the absence of sufficient water to enhance the ionic mobility and allow recrystallization and phase separation of the $NaNO_3$. Thus, we propose that the following two reactions provide a description of the origin of the pressure dependence of γ which has been reported by Leu et al.[8] and Davies and Cox.[11]

$$HNO_3(g) + \text{NaCl Site} = NO_3^-(ads) + HCl(g) \qquad (2)$$

$$NO_3^-(ads) + H_2O(ads) = NaCl\ Site + NaNO_3(s) \tag{3}$$

where NaCl Site represents a surface site which is open for reaction, and NO_3^-(ads) represents a surface nitrate species which is immobile and has blocked the original reactive site. The second reaction indicates that the original reactive site can be regenerated in the presence of adsorbed water that acts to increase the nitrate mobility. It should be recognized that we do not quantitatively understand at this time how much water is required on the surface to mobilize the NO_3^-(ads) species. Thus, the stoichiometry of the second reaction relative to H_2O(ads) could be something other than unity. Indeed, it is likely that the actual process is relatively complex and as we learn more about the surface mobility of the species involved we will be able to elaborate on this simple model. This simple model does, however, provide a description of the HNO_3 pressure dependence of the reaction that is also consistent with the three major things that we have learned about this system:

(1) that the dissociative adsorption of HNO_3 on solid NaCl follows a one-site Langmuir adsorption model, (2) that the initial nitrate formed on the surface blocks subsequent reactions, and (3) that water enhances the mobility of the nitrate thereby opening up blocked sites for further reaction.

The rate of dissociative adsorption of HNO_3 on NaCl can be written simply as

$$-\frac{d[HNO_3]}{dt} = \frac{\gamma \bar{c}}{4}[HNO_3]\frac{S}{V} \tag{4}$$

where $\bar{c}$ is the molecular speed of gas-phase HNO_3, S is the NaCl surface area, and V is the reaction cell volume. Similarly, standard expressions can be written for the rate of reactions 2 and 3 as

$$-\frac{d[HNO_3]}{dt} = k_2[HNO_3][NaCl\ Site] \tag{5}$$

and

$$\frac{d[NO_3^-(ads)]}{dt} = k_2[HNO_3][NaCl\ Site] - k_3[NO_3^-(ads)][H_2O(ads)] \tag{6}$$

where k_2 and k_3 are the rate constants of reactions 2 and 3, respectively. Using eqs 4−6, one can obtain the following expression for γ under steady-state conditions:

$$\gamma = k_2 A\left\{\frac{B[H_2O]}{[HNO_3] + B[H_2O]}\right\} \tag{7}$$

where A is the total number of surface sites (open + blocked), k_2 is the rate constant of reaction 2, $B = 4k_3/k_2\bar{c}$, and k_3 is the rate constant of reaction 3.

Equation 7 indicates that for reactions run under steady-state conditions of constant water content a plot of γ versus $C/([HNO_3] + C)$ (with C constant at a given water content) should be linear, with a slope equal to k_2A. Figure 4 shows such a plot for the data of Davies and Cox[11] that were obtained under conditions that they describe as "dry". The fact that they obtained steady-state conditions does indicate at least some minimal amount of water that is required to avoid the passivation of the reaction by $NaNO_3$(ads) was present on their samples. The fit between the model of reactions 2 and 3 and the pressure-dependent data of Davies and Cox is quite good. The best fit of the model to the Davies and Cox[11] "dry" data was obtained as shown in Figure 4 with a value of $C = 8.0 \times 10^{11}$. The fact that the data and the fitted line do not show a zero intercept is likely due to the fact that the model assumes steady-state reaction conditions which would likely not pertain at very high HNO_3 concentrations. We have also fit the more limited data set published by Davies and Cox for conditions of 1.00 mbar water vapor pressure with a value of $C = 1.0 \times 10^{13}$. Since C is directly related to the amount of adsorbed water, this indicates that the amount of water on the surface in the "dry" experiments of Davies and Cox is over an order of magnitude less than that in their experiments utilizing 1.00 mbar water vapor. The conditions reported by Davies and Cox for their "dry" experiments utilized water vapor pressures that they estimated to be $\sim 2 \times 10^{-4}$ mbar.[11] The very small amount of adsorbed water suggested by our model is not unreasonable and could be associated predominantly with "strongly adsorbed water" remaining from the sample preparation procedures.

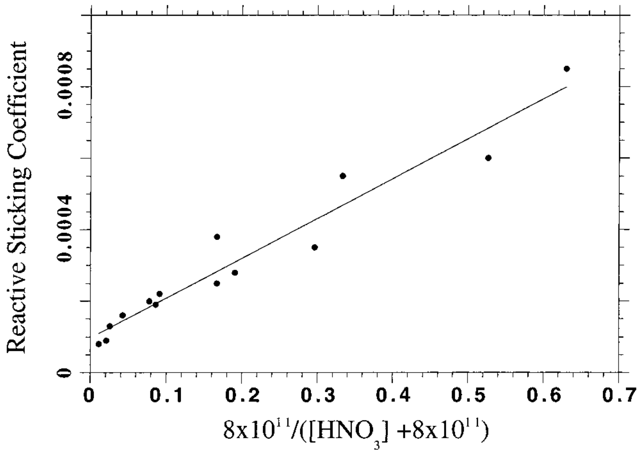

Figure 4. Plot of the reactive sticking coefficient for HNO_3 on NaCl particles (~0.5 mm diameter) measured by Davies and Cox[11] as a function of $C/([HNO_3] + C)$. The constant $C = 8.0 \times 10^{11}$ was chosen to obtain the best linear least-squares fit to the data. This functional form for the behavior of the reactive sticking coefficient on the HNO_3 gas-phase concentration is suggested by the model described in the text.

The maximum value of the reactive sticking coefficient which can be obtained from the model of eqs 2 and 3 occurs in the limit of high H_2O(ads) concentrations, when the overall steady-state reaction is not limited by the site blocking of NO_3^-(ads). Under such conditions, the maximum value of γ can be obtained from the slope of the plot in Figure 4.

$$\gamma_{max} = 1.1 \times 10^{-3}$$

This value is in excellent agreement with our measured value, using NaCl(100) single crystals, for the *zero coverage* value of γ of $(1.3 \pm 0.6) \times 10^{-3}$. This is reasonable since the zero coverage value of γ should be unaffected by the passivation/saturation shown in the data of Figure 1 and should therefore be comparable to the values of γ measured under steady-state conditions when the water-assisted nitrate reorganization is fast and not limiting.

It is interesting to note that the model presented here of reactions 2 and 3 would predict that under conditions of high adsorbed water concentration the value of the reactive sticking coefficient would be independent of HNO_3 pressure. This is consistent with the pressure-independent Knudsen cell observations of Fenter et al.[7] and Beichert and Finlayson-Pitts.[6]

However, the maximum value of γ of 1.1×10^{-3} is still significantly lower than the values reported by Fenter et al.[7] and Beichert and Finlayson-Pitts.[6] Both of those experiments utilized substantially smaller crystallites which might have more defects and as a result more adsorbed water. It is highly likely that there is a change in reaction mechanism between conditions that utilize large crystallites with little adsorbed water and those that use small crystallites with large amounts of adsorbed water. For example, Beichert and Finlayson-Pitts[6] have suggested that under conditions of their experiments it is possible that the reaction should be viewed as HNO_3 uptake into a liquidlike aqueous phase, rather than reactive adsorption onto a solid surface. This is consistent with the data we show here in Figure 2 that demonstrates that the amount of "strongly adsorbed water" on 1−10 μm diameter NaCl particles is much greater than that observed on larger particles or single-crystal surfaces. A fundamental description of the origin of these differences is still needed.

Conclusions and Implications for Sea Salt Chemistry in the Marine Troposphere. Analysis of our XPS data for the dissociative adsorption of HNO_3 on NaCl(100) shows that this reactions follows single-site Langmuir adsorption behavior. Our experiments also show that in the absence of adsorbed water, the nitrate product of reaction 1 forms an ultrathin passivation layer on the NaCl surface and the reaction stops. We have previously published TEM results that show that adsorbed water leads to an enhanced ionic mobility and the 3-D recrystallization of the nitrate layer to open up fresh NaCl reactive sites.[12] We have presented here a model that shows that the passivation of the surface by the nitrate product, combined with water-induced regeneration of the active sites, results in a HNO_3 pressure dependence of the values of the reactive sticking coefficient measured under steady-state conditions. Our model provides a good description of the experimental pressure-dependent data of Davies and Cox.[11] It also predicts that at high surface water content the reactive sticking coefficient will be independent of pressure. However, our model combined with the data of Davies and Cox and our measurements on NaCl(100) surfaces suggests a maximum value for the reactive sticking coefficient of 1.1×10^{-3}, well below the values reported by Fenter et al.[7] and Beichert and Finlayson-Pitts.[6] It is likely that the origin of this difference lies in the water content of the samples. Thus, an assessment of the appropriate value to use for γ in models of sea salt chemistry in the marine troposphere requires the development of an understanding of the water content of sea salt particles in the atmosphere as well as a more detailed mechanistic understanding of the role that strongly adsorbed water plays in the chemistry on small particles of NaCl. Studies on the chemistry of HNO_3 with NaCl powders of different particle sizes as a function of adsorbed water content are underway in our laboratory at this time in an effort to provide insight into these questions. In the absence of a complete mechanistic understanding of the effects of water on the rates of reactions such as those discussed here, it should none-the-less be recognized that the water content in true sea salt particles[25] in the marine troposphere is more like that of the small particles studied by Beichert and Finlayson-Pitts[6] that exhibit values of γ in the range of $(1.4 \pm 0.6) \times 10^{-2}$.

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