# Surface-Catalyzed Chlorine and Nitrogen Activation: Mechanisms for the Heterogeneous Formation of CINO, NO, NO<sub>2</sub>, HONO, and N<sub>2</sub>O from HNO<sub>3</sub> and HCl on Aluminum Oxide Particle Surfaces

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**Supporting Information** 



ABSTRACT: It is well-known that chlorine active species (e.g., Cl<sub>2</sub>, ClONO<sub>2</sub>, ClONO) can form from heterogeneous reactions between nitrogen oxides and hydrogen chloride on aerosol particle surfaces in the stratosphere. However, less is known about these reactions in the troposphere. In this study, a potential new heterogeneous pathway involving reaction of gaseous HCl and HNO<sub>3</sub> on aluminum oxide particle surfaces, a proxy for mineral dust in the troposphere, is proposed. We combine transmission Fourier transform infrared spectroscopy with X-ray photoelectron spectroscopy to investigate changes in the composition of both gas-phase and surface-bound species during the reaction under different environmental conditions of relative humidity and simulated solar radiation. Exposure of surface nitrate-coated aluminum oxide particles, from prereaction with nitric acid, to gaseous HCl yields several gas-phase products, including ClNO, NO2, and HNO3, under dry (RH < 1%) conditions. Under humid more conditions (RH > 20%), NO and N<sub>2</sub>O are the only gas products observed. The experimental data suggest that, in the presence of adsorbed water, CINO is hydrolyzed on the particle surface to yield NO and NO<sub>2</sub>, potentially via a HONO intermediate. NO2 undergoes further hydrolysis via a surface-mediated process, resulting in N2O as an additional nitrogencontaining product. In the presence of broad-band irradiation ( $\lambda > 300$  nm) gas-phase products can undergo photochemistry, e.g., CINO photodissociates to NO and chlorine atoms. The gas-phase product distribution also depends on particle mineralogy (Al<sub>2</sub>O<sub>3</sub> vs CaCO<sub>3</sub>) and the presence of other coadsorbed gases (e.g., NH<sub>3</sub>). These newly identified reaction pathways discussed here involve continuous production of active ozone-depleting chlorine and nitrogen species from stable sinks such as gas-phase HCl and HNO3 as a result of heterogeneous surface reactions. Given that aluminosilicates represent a major fraction of mineral dust aerosol, aluminum oxide can be used as a model system to begin to understand various aspects of possible reactions on mineral dust aerosol surfaces.

# ■ INTRODUCTION

The importance of heterogeneous chemistry of halogen species and nitrogen oxide on polar stratospheric cloud (PSC) particles has been well established and accounts for the observed large-scale ozone depletion during the Antarctic springtime.<sup>1,2</sup> During the polar sunrise, "low ozone events", i.e., levels of 40 ppb ozone depleted over a period of 5 days to <5 ppb, have been observed.<sup>3-7</sup> Reasons for this decrease have been attributed to elevated levels of chlorine (Cl<sub>2</sub>) and bromine (Br<sub>2</sub>) that directly or indirectly destroy ozone in the stratosphere.<sup>7,8</sup> Although bromine was thought to be mostly responsible for the ozone loss, the presence of chlorine atoms has been inferred from the distribution of hydrocarbons<sup>9,10</sup> and <sup>13</sup>C/<sup>12</sup>C ratio of CO.<sup>11</sup>

The known mechanism begins with increased concentrations of atmospheric HCl and  $ClONO_2$ , by the breakdown of chlorine

sources, i.e., chlorofluorocarbon, in the presence of sunlight.<sup>12</sup> Numerous studies have shown that heterogeneous reactions occurring on PSCs play an important role in the conversion of these inactive chlorine compounds into more labile and reactive forms.<sup>13</sup> It has been shown that, in PSCs, both solid and liquid particles can promote heterogeneous reactions such as<sup>14</sup>

$$CIONO_2 + H_2O \rightarrow HOCI + HNO_3$$
(1)

$$HOCl + HCl \rightarrow Cl_2 + H_2O$$
(2)

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$$
(3)

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Figure 1. Cartoon representation of nitrogen and chlorine activation from heterogeneous reactions of nitrogen oxides and hydrogen chloride on tropospheric particles. Dust particles emitted from the Earth's crust react with atmospheric  $HNO_3$  (or  $NO_2$ ) to form an adsorbed nitrate layer on the particle surface. These "aged" particles can then react with HCl from open oceans leading to active nitrogen and chlorine species. It should be noted the sun can further initiate reactions for photoactive species on the surface and the gas phase.

Although heterogeneous chlorine activation on PSCs have been well established, less is known about heterogeneous chlorine activation on the surface of aerosol particles more relevant to the troposphere such as mineral dust aerosol. In a recent field study, Hobe et al. suggest that elevated levels of reactive chlorine, including ClO, in the upper troposphere and lower stratosphere near the tropics can be due to heterogeneous chlorine activation on cirrus ice clouds/or liquid aerosols at lower temperatures.<sup>15</sup> Therefore, exploring new reaction pathways involved in the production of active chlorine and nitrogen species from sources such as gas-phase HCl and HNO3 may provide additional information on tropospheric aerosol chemistry and potentially tropospheric ozone concentrations. Atmospheric HCl is reported at higher concentrations, few parts per billion (ppbv), in polluted areas and in some indoor settings.<sup>16-20</sup> The major anthropogenic sources of gasphase HCl includes coal burning, waste incineration, chlorinated hydrocarbons, automobile exhaust, burning of garbage, biomass and agricultural products.<sup>21–23</sup> Industrial activities, i.e., petroleum and semiconductor manufacturing, also contribute to a significant fraction of atmospheric HCl.<sup>24</sup> The existence of gasphase HCl in the marine atmosphere is well established as sea salt arising from wave action, contains a large amount of chlorine ions, a source of gaseous HCl.<sup>20</sup>

In addition to reactive chlorine species, nitrogen oxides, in particular NO, NO<sub>2</sub>, and N<sub>2</sub>O, are important in determining atmospheric ozone concentrations in the lower and upper atmosphere. These nitrogen oxides participate in a complex series of chemical and photochemical reactions to produce tropospheric ozone in a nonlinear relationship with respect to ozone concentrations. Therefore, peak ozone levels are affected by the amount of nitrogen oxides present in the gas phase, which depends on the ground base emissions and subsequent reactions in the lower atmosphere.<sup>25–27</sup> N<sub>2</sub>O serves as a major source of stratospheric NO<sub>x</sub> and thus contributes to catalytic ozone destruction. Ravishankara et al. indicate that N<sub>2</sub>O is currently the single most important ozone depleting substance, and is anticipated to remain the largest throughout the 21st century.<sup>28</sup>

In the atmosphere, nitrogen oxides readily react with particulate matter (e.g., mineral dust and sea salt aerosol) to yield adsorbed nitrate.<sup>29</sup> Valuable information regarding chemical speciation on the surface has been obtained using FTIR spectroscopy.<sup>30–35</sup> Several surface species have been proposed following the adsorption of nitrogen oxides on mineral oxide surfaces, which include nitrate (NO<sub>3</sub><sup>-</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), and nitrosyl (NO<sup>+</sup>). Under humid conditions, it has been shown that coadsorbed water molecules readily solvate adsorbed nitrate ions on the aluminum oxide surface forming inner and outer sphere complexes.<sup>36</sup>

During the past decade, several field and model studies have reported conversion of inorganic chloride into gaseous chloride atom precursors, nitryl chloride (ClNO), in marine or costal atmosphere as well as in midcontinental regions.<sup>37,38</sup> On the basis of field measurements, Tobo et al. shows conversion of Ca-rich mineral dust particles to more soluble  $Ca(NO_3)_2$  and CaCl<sub>2</sub> salts in the presence of atmospheric HNO<sub>3</sub> and HCl.<sup>39</sup> These studies further highlight a possible source of tropospheric nitryl chloride might be the reactions between adsorbed nitrogen (e.g.,  $N_2O_5$ ) and chloride species on aerosol dust particles.<sup>40,41</sup> However, the exact role of halogen compounds in the lower troposphere and the reaction mechanisms involve is poorly understood. In a recent study by Raff et al., a surfacemediated coupling of nitrogen oxides and halogen activation cycles has been shown in which uptake of gaseous NO2 and  $N_2O_5$  on solid silica substrate generates adsorbed intermediates,  $NO^+NO_3^-$  and  $NO_2^+NO_3^-$ , that reacts with HCl to yield ClNO and ClNO<sub>2</sub>, respectively.<sup>42</sup> Both of these compounds can readily yield chlorine atoms in the troposphere.<sup>43</sup> Given the importance to this emerging chlorine chemistry in the lower part of the atmosphere as discussed in a recent article by von Glasow,<sup>44</sup> these types of studies can provide important insights into the chemistry of these processes.

In the current study, we explore new heterogeneous chemistry of dust particles in which gaseous HCl is activated in the presence of adsorbed nitrate, from reaction of nitric acid, on aerosol particles yielding gas-phase chlorine and nitrogen species. Figure 1 shows a cartoon representation that illustrates possible continued chemistry of aged dust particles. The figure

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shows that aged dust, as a result of heterogeneous reaction with atmospheric HNO<sub>3</sub> to yield adsorbed nitrate, can interact with gas-phase HCl in the marine environment to yield several reactive nitrogen and chlorine species, including ClNO and NO<sub>x</sub>. Here we combine transmission Fourier transform infrared (FTIR) spectroscopy with X-ray photoelectron spectroscopy (XPS) to investigate changes in both gas-phase and surface adsorbed species during the reaction between adsorbed nitrate and gaseous HCl under different relative humidity conditions. Given that aluminum oxides and aluminosilicates contribute  $\sim$ 8% by mass to the total dust burden in the atmosphere, 36,45,46 aluminum oxides are used as model systems to begin to understand various aspects of nitrogen oxide and hydrogen chloride reactions on mineral dust aerosol, with a few experiments done on calcium carbonate, another reactive component of mineral dust for comparison. For the first time we show that exposure of surface nitrate-coated alumina surfaces to gaseous HCl yields several gas-phase products, including ClNO, NO<sub>2</sub>, and HNO<sub>3</sub> under dry (<1 %RH) conditions. At higher relative humidity, we observe significant production of NO and N<sub>2</sub>O only. The results from the current study further highlight that photodissociation ( $\lambda$  > 300 nm) of the secondary gas-phase species, ClNO, yields NO and chlorine radicals. The gas-phase product distribution depends on a number of factors including particle mineralogy, simulated solar radiation, relative humidity and the presence of other coadsorbed gases such as NH<sub>3</sub>. This work also suggests a possible reaction mechanism for the formation of chlorine atom precursor nitryl chloride and several other active nitrogen species under different atmospherically relevant conditions.

## **EXPERIMENTAL METHODS**

**Source Materials.** Commercially available  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Degussa, aluminum oxide C) and CaCO<sub>3</sub> (OMYA) with surface areas of 101 (±4) and 10 (±0.4) m<sup>2</sup> g<sup>-1</sup>, respectively, were used in these experiments. Dry gaseous nitric acid was taken from the vapor of a 1:3 mixture of concentrated HNO<sub>3</sub> (70.6% HNO<sub>3</sub>, Mallinckrodt) and 95.9% H<sub>2</sub>SO<sub>4</sub> (Mallinckrodt). Dry gas-phase hydrogen chloride was generated from the vapor of concentrated HCl (37% HCl, Fisher). Distilled H<sub>2</sub>O (Fisher, Optima grade) was degassed prior to use.

Transmission FTIR Spectroscopy of Adsorbed and Gas-Phase Species. The experimental setup and the preparation of saturated surfaces of adsorbed nitrate have been previously described in detail in earlier work.36,47 In brief, approximately 5.5 mg of alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Degussa) powder, a model for mineral dust surfaces, was pressed onto half of a tungsten grid and evacuated for 12 h in the FTIR cell to remove adsorbed water from the surface. The alumina surface was then exposed to nitric acid vapor for 30 min at a pressure of approximately 1.70 Torr at 298 K followed by a 4 h evacuation of the FTIR cell to remove all weakly adsorbed products. From previous studies, this process is known to produce a saturated surface coverage of adsorbed nitrate on alumina.<sup>25,47</sup> The calculated nitrate coverage, when normalized to the BET surface area, is determined to be 5  $\pm$  1  $\times$  10<sup>14</sup> molecules cm<sup>-2.25</sup>. Following introduction of gas-phase HCl and water vapor (adjusted to different relative humidity values), the valve connecting the FTIR cell to the mixing chamber was closed, letting gasphase products accumulate inside the cell as the nitrate-coated surface was reacting with HCl. During the experiment, infrared spectra were recorded with a single beam Mattson RS-10000 spectrometer equipped with a narrow band MCT detector.

Typically, 250 scans were collected with an instrument resolution of 4 cm<sup>-1</sup> in the spectral range extending from 900 to 4000 cm<sup>-1</sup>. Absorbance spectra for gas and adsorbed species were obtained by referencing single beam spectra of the blank grid and the oxide-coated grid to single beam spectra collected prior to the nitric acid exposure.

After 2 h of the reaction, the secondary gas-phase products were exposed to light ( $300 < \lambda < 700$  nm) using a broad-band Hg light source and a broad-band filter, as described previously.<sup>47,48</sup> The experimental setup for these experiments is described in detail in our previous work.<sup>47</sup> Selected experiments were done with CaCO<sub>3</sub> (OMYA, 98% CaCO<sub>3</sub>).

Ex-situ X-ray Photoelectron Spectroscopy. Reacted alumina was removed from the tungsten grid and analyzed using a custom-designed Kratos Axis Ultra X-ray photoelectron spectrometer with a monochromatic Al K $\alpha$  X-ray source. The powder alumna sample was pressed onto an indium foil, on a copper stub, and introduced into the XPS analysis chamber, which had a pressure that was maintained in the  $10^{-9}$  Torr range during analysis. Wide energy range survey scans were acquired using the following parameters: energy range from +1200 to -5 eV, pass energy of 160 eV, step size of 1 eV, dwell time 200 ms, X-ray spot size  $700 \times 300$  mm<sup>2</sup>. High resolution spectra were acquired using the following parameters: energy range 50-20 eV depending on the peak examined, pass energy of 20 eV, step size of 0.1 eV, dwell time of 1000 ms. The data collected were analyzed using CasaXPS data processing software.

# RESULTS AND DISCUSSION

As discussed here, laboratory measurements show that surface reactions of  $HNO_3$  and HCl produce active nitrogen and chlorine species, including ClNO, NO, NO<sub>2</sub>, and N<sub>2</sub>O.

Analysis of Gas-Phase Products from the Reaction between Adsorbed Nitrate and Gas-Phase HCl. Heterogeneous uptake of nitric acid on aluminum oxide yields a chemisorbed nitrate layer on the particle surface as discussed in our previous work and by several others.<sup>25,36,49-51</sup> Vibrational frequencies of adsorbed nitrate have been assigned and interpreted using quantum chemical calculations of binuclear aluminum oxyhydroxy cluster models.<sup>36</sup> Under conditions of lowest relative humidity (<1 %RH ), adsorbed nitrate binds to the oxide surface in different modes of coordination as monodentate, bidentate, and bridging, based on the assignment of the peaks in the nitrate ion  $\nu_3$  spectral region between 1200 and 1650 cm<sup>-1,25,36</sup> In the presence of water vapor, coadsorbed water solvates the nitrate ion forming inner and outer sphere complexes which are represented by peaks in the region between 1300 and 1450 cm<sup>-1</sup> in the FTIR spectrum.<sup>36</sup>

Gas-phase product formation upon exposure of the nitrated particle surface to 100 mTorr of gaseous HCl is shown in Figure 2. FTIR spectra of gas-phase products were recorded as a function of reaction time under dry conditions (<1 %RH ) and wet conditions (45  $\pm$  1 %RH) at 298 K. Under dry conditions (Figure 2a,b), the data show that several gas-phase products appear and grow in intensity as the reaction proceeds. On the basis of the vibrational frequency, the major gas-phase products as ClNO, HNO<sub>3</sub>, and NO<sub>2</sub> (Table 1) can be identified.<sup>52–55</sup> It should be noted that some fraction of gas-phase HNO<sub>3</sub> at t = 0 is formed by the displacement of surface adsorbed nitrate during the uptake of gas-phase HCl. Quantitative analysis of instantaneous HCl loss from the gas phase indicates this HNO<sub>3</sub> from the displacement can account for ~8% of the total HNO<sub>3</sub>



Figure 2. Gas-phase product formation from the reaction between gas-phase HCl (100 mTorr) and adsorbed nitrate on aluminum oxide under dry conditions of <1 %RH (a and b) and wet conditions of 45  $\pm$  1 %RH (c and d) at 298 K. Gas-phase absorption bands are identified based on the assignments given in Table 1. Gas-phase concentrations are calculated based on the conversion factors given in Table 1.

Table 1. Assignment of Major Infrared Absorption Bandsand Conversion Factors Used To Calculate Gas-PhaseProduct Concentrations

gas- phase products	vibrational mode	frequency <sup>a</sup> a (cm <sup>-1</sup> )	integrated bsorbance spect range (cm <sup>-1</sup> )	tral conversion (mol L <sup>-1</sup> )				
$HNO_3$	$\nu_2$	1709	1654-1754	$0.87 \times 10^{-4 b}$				
HCl	$ u_1 $	2886	2614-3090	$5.58 \times 10^{-4}$ b				
ClNO	$ u_1 $	1800	1760-1854	$0.92 \times 10^{-4}$				
$NO_2$	$\nu_3$	1616	1540-1670	$0.31 \times 10^{-4 d}$				
NO	$\nu_1$	1874	1750-1980	$3.08 \times 10^{-4 d}$				
$N_2O$	$ u_1 $	2224	2124-2271	$0.69 \times 10^{-4 d}$				
<sup><i>a</i></sup> Reference	es 52–55.	<sup>b</sup> Experimentally	y determined	values. <sup>c</sup> Reference				
52. Keterences 53–55.								

at time,  $t \sim \text{zero}$ . Time-course spectra shown in Figure 2a reveal a significant change in the gas-phase product distribution during the course of the reaction. Gas-phase concentrations obtained from FTIR analysis followed by the reaction between gaseous HCl and adsorbed nitrate under dry conditions is shown in Figure 2b. The results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Gas-phase concentrations of individual species were determined by converting integrated absorbances to concentrations using calibration factors, given in Table 1.

Interestingly, under humid conditions, i.e.  $45 \pm 1$  %RH. (Figure 2c,d), the gas-phase product distribution is quite different with no ClNO or HNO<sub>3</sub> formed. Instead, there is the growth of NO, NO<sub>2</sub>, and N<sub>2</sub>O as a function of reaction time.<sup>53–55</sup> FTIR spectra of gas-phase product formation upon exposure of nitrated alumina surface to gas-phase HCl under wet condition ( $45 \pm 1$  %RH) at 298 K is shown in Figure 2c. The variation of gas-phase concentration under these conditions can be seen in Figure 2d. A comparison of the gas-phase product distribution and total gas-phase production between dry (<1 %RH ) and wet ( $45 \pm 1$  %RH) conditions. This large difference leads to several additional experiments focused on gas product formation under a wider range of



Figure 3. Gas-phase product formation from the reaction between gas-phase HCl (2 Torr) and adsorbed nitrate on aluminum oxide under dry conditions of (<1 %RH) (a and b) and wet conditions of ( $45 \pm 1$  %RH) (c and d) at 298 K. Gas-phase absorption bands are identified based on the assignments given in Table 1. Gas-phase concentrations are calculated based on the conversion factors given in Table 1.

relative humidities ranging from % RH  $\sim$ 3 to 80 and with higher pressures of HCl to explore possible reaction pathways in the reaction between adsorbed nitrate and gas-phase HCl. Although higher HCl pressures are used to observe possible reaction products with FTIR spectroscopy, these experiments are correlated to the results of lower HCl pressure experiments.

Gas-phase product formation upon exposure of surface nitrate to 2 Torr of gaseous HCl under dry and wet conditions is shown in Figure 3. Parts a and c of Figure 3 are enlarged regions of the respective FTIR spectra between 1200 and 2500 cm<sup>-1</sup> to illustrate the gas-phase product formation. Clearly, we observe similar products, under both dry (<1 %RH) and wet ( $45 \pm 1$  %RH) conditions, but with higher ClNO production compared with lower HCl pressures, and lower NO<sub>2</sub> concentrations as shown in Figure 3b,c. These preliminary data suggest that NO<sub>2</sub> might be participating in one or more secondary reactions, especially in the presence of higher HCl pressures.

Effect of Relative Humidity on Gas-Phase Product Distribution. Water is relatively abundant in the atmosphere and plays an important role in many processes. The three-component system,  $HCl-HNO_3-H_2O$ , has been the subject in numerous

atmospheric investigations, theoretical<sup>56–58</sup> and experimental,<sup>59–61</sup> and has clearly proven that in the presence of water along with HNO<sub>3</sub> result in the formation of stable complexes. It is well established that in PSCs hydrogen chloride binds to the particle surface, in the presence of HNO<sub>3</sub> and H<sub>2</sub>O (nitric acid hydrates), leading to the transformation of HCl into more photolabile  $Cl_2$ .<sup>62–64</sup> A study by Weiser et al. on the Arctic stratosphere under synoptic conditions showed that HCl dissolved in liquid particles along with HNO<sub>3</sub>–H<sub>2</sub>O, following an unexpected ratio.<sup>65</sup> Here the experiments were carried out under different humid conditions, including % RH 3, 8, 12, 20, 45, and 80.

The relative gas-phase product distributions under different relative humidity conditions are shown in Figure 4. The plot, showing the relative gas-phase concentrations of ClNO, NO<sub>2</sub>, HNO<sub>3</sub>, HCl, N<sub>2</sub>O, and NO under <1 %RH, 3, 8, 12, 20, 45, and 80 %RH after 120 min of the reaction time, were obtained by normalizing the gas-phase concentrations to the largest gas-phase product under all conditions studied, which is ClNO at % RH < 1. On the basis of the results observed under different relative humidities, RH greater than 8% appears to yield a different gas-phase product distribution. Thus, these data will be used in the following discussion to



Figure 4. Relative gas-phase concentrations obtained from FTIR spectra following the reaction between gas-phase HCl and adsorbed nitrate on aluminum oxide 298 K under different relative humidities, ranging from <1 %RH to 80 %RH. The gas-phase concentrations have been normalized to the largest gas-phase product species under all the conditions, ClNO at <1 %RH.

understand the variation of gas-phase product formation as a function of relative humidity. The FTIR spectra of the gasphase product formation at % RH 12 clearly indicates early formation of ClNO and NO<sub>2</sub> in higher concentrations followed by decay as the reaction progress (not shown). Loss of ClNO and NO<sub>2</sub> at longer time scale suggests initiation of secondary reactions yielding more gas-phase or surface products. In addition to ClNO and NO<sub>2</sub>, here we observe formation of NO and N<sub>2</sub>O, the major gas-phase products at higher relative humidities, % RH < 20.

The rate of secondary gas-phase production is greatest initially (t < 20 min), followed by a slower rate of change over time. Initial rates of gas-phase product formation under different relative humidies at 298 K, determined from linear regression analysis, are given in Table 2. The rates are

Table 2. Surface Area Normalized Initial Rate of Gas-PhaseProduct Formation during the Reaction between Gas-PhaseHCl and Adsorbed Nitrate on Aluminum Oxide ParticleSurfaces under Different Relative Humidity Conditions<sup>a</sup>

	surface area normalized initial rates of gas production $\times 10^{-5}$ (molecules m <sup>-3</sup> s <sup>-1</sup> cm <sup>-2</sup> ) <sup>b</sup>						
% relative humidity	ClNO(g)	$NO_2(g)$	NO(g)	$N_2O(g)$			
<1 (at low HCl pressure)	0.48 (±0.05)	1.8 (±0.10)					
<1	41 (±3)	3.40(±0.14)					
12	38 (±2)	$2.60(\pm 0.12)$	8.0 (±0.4)	0.35 (±0.021)			
20	1.1 (±0.1)		18 (±1)	1.1 (±0.010)			
45 (at low HCl pressure)		2.30(±0.15)	1.12 (±0.06)	0.010(±0.0010)			
45			31 (±2)	4.8 (±0.2)			
80			56 (±1)	4.8 (±0.4)			

<sup>*a*</sup>Results presented here are the average value of triplicate measurements, determined from linear regression, and the reported error represents one standard deviation. Gas-phase product formation data from the first 20 min were used in the rate determination. <sup>*b*</sup>Rates are normalized to the corresponding BET surface area.

normalized to the BET surface area of  $\gamma$ -alumina. It can be clearly seen from these data that production of ClNO and

 $NO_2$  is highest in % RH < 12 and addition of more water vapor enhances formation of NO and  $N_2O$  at higher rates. The information from these experiments can begin to elucidate the mechanism involve with the reaction between adsorbed nitrate and gas-phase HCl on mineral dust particle surfaces.

Mechanism for the Production of Secondary Gas-Phase Products. Before further discussing the heterogeneous interactions of gaseous HCl with adsorbed nitrate and the gasphase products that form, it is first instructive to consider what is known about uptake of HNO<sub>3</sub> and HCl on metal oxide surfaces in general and, in particular, on alumina. It is wellknown that heterogeneous uptake of HNO<sub>3</sub> by the metal oxide surface yields adsorbed nitrate via<sup>25,31–36</sup>

$$HNO_3(g) + OH^-(a) \rightarrow NO_3^-(a) + H_2O$$
(4)

Upon exposure to gaseous HCl, the FTIR spectra of the nitrated surface at each relative humidity undergo changes. Most notably there is a decrease in the intensity of the spectral bands associated with molecularly adsorbed nitric acid and chemisorbed nitrate ion as indicated by the analysis of difference spectra shown in Figure 5. Under dry conditions, <1 %RH (Figure 5a), peaks at 1265, 1625, and 1558 cm<sup>-1</sup> associated with adsorbed bidentate and bridged nitrate species disappear whereas the peaks at 1517, 1319, and 944 cm<sup>-1</sup>, associated with monodentate nitrate species appear to shift and increase in intensity.<sup>36</sup> In addition, molecularly adsorbed nitric acid, characterized by the peak at 1679 cm<sup>-1</sup>, also disappears from the surface. A new absorption band at 1425 cm<sup>-1</sup>, attributed to partially solvated nitrate, is seen to grow as the surface is exposed to HCl(g). Under wet conditions,  $45 \pm 1$  %RH (Figure 5b), the peaks at 1408 and 1339 cm<sup>-1</sup> associated with solvated nitrate species are observed to disappear along with the peak at 1631 cm<sup>-1</sup> for coadsorbed water, indicating the participation of surface water in the reaction at higher relative humidity.

In addition to FTIR data, the presence of adsorbed nitrate and chloride on the alumina particle surface was further confirmed by ex-situ XPS analysis in the N 1s and Cl 2p binding regions, as seen in Figure 6a,b, respectively. In these experiments, alumina was first analyzed prior to exposure to any gas-phase reactants and this spectrum is labeled as "Before reaction" in both binding energy regions. The alumina surface, exposed to nitric acid, is shown as "After reaction with HNO<sub>3</sub>" and this "nitrated" alumina surface is further reacted with gasphase HCl and these XPS data are labeled "After reaction with HCl". High resolution XPS data, after exposure to HNO<sub>3</sub> acid, showed a peak in the N1s binding energy region at 407 eV, which is consistent with the presence of adsorbed nitrate as discussed in detail in Baltrusaitis et al.<sup>66</sup> Quantitative analysis of the nitrate peak area shows  $\sim$ 33% of the initial surface coverage of adsorbed nitrate is consumed during the formation of ClNO and other gas-phase products within 20 min of the reaction. In addition, a new peak in the Cl 2p binding energy region for surface adsorbed chlorine was observed, indicating a significant uptake of HCl during the reaction (Figure 6b).<sup>67</sup> Adsorption of HCl, on metal oxide surfaces such as alumina is thought to occur via two distinct reaction mechanisms. The first involves the dissociation of HCl onto aluminum oxygen pairs forming OH and Al–Cl species.<sup>68,69</sup> Several theoretical and laboratory studies have confirmed the formation of new OH groups and, thus, existence of this mechanism. In the second pathway, the reaction likely occurs via analogous mechanism, dissociative adsorption of HCl, whereupon chloride replaces a surface OH



Figure 5. FTIR difference spectra of surface adsorbed nitrate under (a) dry and (b) wet conditions at 298 K, illustrating the changes of the surfacebound species during the reaction between adsorbed nitrate and gaseous HCl. Each spectrum was referenced to the surface spectrum prior to exposure to HCl. Gas-phase absorptions were then subtracted from each spectrum.



Figure 6. Representative XPS of high resolution (a) N 1s region and (b) Cl 2p region before and after the reaction between gas-phase HCl and adsorbed nitrate under dry on aluminum oxide particle surfaces (<1 %RH) condition at 298 K.

group via an exchange mechanism.<sup>70</sup> In a recent study, McInroy et al.<sup>71</sup> highlighted the importance of replacing surface OH

groups by chlorine, followed by a loss of water molecule, to regenerate a more acidic Lewis acid site for further reaction. Thus, HCl is actively taken up by the alumina surface via the ionic dissociation mechanism,

$$HCl(g) \rightarrow H^+(a) + Cl^-(a)$$
 (5)

Moreover, the loss of adsorbed nitrate as quantified by XPS suggests that changes in the mode of coordination of adsorbed nitrate seen in FTIR (Figure 5a) may be due to a number of possibilities including rearrangement of adsorbed nitrate coordination upon uptake of gas-phase HCl, reaction to form ClNO and adsorption of products and adsorption site competition due to readsorption processes.

It is well established that nitrate ion is a strong oxidizing agent in highly acidic solutions that is capable of changing the oxidation state of halogen species.<sup>72–74</sup> Therefore, here we propose that interaction between adsorbed nitrate and chloride, on acidic alumina surface, yields NO<sup>+</sup>NO<sub>3</sub><sup>-</sup> via acid catalysis, as given in eq 6.

$$2NO_{3}^{-}(a) + 2H^{+}(a) + 2CI^{-}(a)$$
  

$$\rightarrow NO^{+}NO_{3}^{-}(a) + 2OH^{-}(a) + Cl_{2}(g)$$
(6)

This surface complex has been proposed to readily react with further HCl forming gas-phase ClNO and HNO<sub>3</sub>, as major products.<sup>42</sup> The overall reaction mechanism is given in eq 7.

$$NO^+NO_3^-(a) + HCl(g) \rightarrow ClNO(g) + HNO_3$$
 (7)

The secondary gas-phase product,  $HNO_3$ , is readsorbed on the alumina surface result in more adsorbed nitrate. This agrees with FTIR data shown in Figure 2 and 3 that indicated an early production of gas-phase  $HNO_3$  followed by a decay as a function of reaction time.

Gas-phase NO<sub>2</sub> is formed via desorption of  $NO^+NO_3^-$  in a self-reaction of adsorbed nitrogen species in analogues to the reaction mechanism between gas-phase NO and NO<sub>3</sub>, according to eq 8.<sup>75,76</sup>

$$NO^+NO_3^-(a) \to 2NO_2(g) \tag{8}$$

On the basis of the observations under dry conditions, it appears that gas-phase  $NO_2$  is in equilibrium with  $NO^+NO_3^-(a)$  due to the fact that it is not the major gas-phase product. It also

must be mentioned that this mechanism is solely based on the observed ClNO and  $NO_2$  products species and must therefore be viewed as one of the many possible reaction schemes, such as follows.

$$NO_{3}^{-}(a) + CI^{-}(a) + 2H^{+}(a) \rightarrow HOCl(g) + HONO(g)$$
(9)

$$HONO(g) + Cl^{-}(a) + H^{+}(a) \rightarrow ClNO(g) + H_2O(a)$$
(10)

$$HOCl(g) + Cl^{-}(a) + H^{+}(a) \rightarrow Cl_{2}(g) + H_{2}O(a)$$
(11)

The proposed reaction mechanism was further validated using mass balance calculations of nitrogen-containing species in the overall reaction for the dry conditions, net reaction of eqs 5–8. These calculations show that more than 85% of the surface-bound nitrate, initially present on the surface and reacted with HCl, can be found in the gas-phase as ClNO, NO<sub>2</sub> and HNO<sub>3</sub>, indicating that the proposed reaction pathway is the primary mechanism taking place under these conditions. The discrepancy can be due to other reaction pathways and uptake by the reaction chamber walls.

As seen in Figures 2 and 3, under humid conditions, NO and N2O are formed as major gas-phase products with a concomitant loss of ClNO and NO2. Previous studies have shown that hydrolysis on aqueous solutions may be a loss process for ClNO in the atmosphere.<sup>77,78</sup> In contrast to these observations, Raff et al.42 discuss an enhancement of CINO production on the SiO<sub>2</sub> surface in the presence of thin films of adsorbed water (9-13 %RH), competing with the hydrolysis reaction. This study further claims the observed enhancement occurs via a barrierless channel where water acts as a conduit to transfer a proton from HCl to nitrate, facilitating the formation of ClNO. In our studies with active alumina surface, we observed higher production of ClNO at lower relative humidities (<12 %RH), yet no significant enhancement. In alumina, atmospheric water vapor readily adsorbs on the particle surface and dissociates, resulting in a hydroxyl terminated surface.<sup>79</sup> Adsorbed water can hydrogen bond to these hydroxyl groups in equilibrium with water vapor. It has been shown that coadsorbed water molecules readily solvate adsorbed nitrate ions on the aluminum oxide surface forming inner and outer sphere complexes.<sup>36</sup> For alumina, it has been shown that the first layer of adsorbed water forms around 17 %RH and this takes place at slightly lower relative humidities in the presence of adsorbed nitrate.<sup>25,36</sup> Water uptake on alumina has been discussed in detail in our previous studies.<sup>25</sup> On the basis of all these information and observations, at higher relative humidities (% RH > 12), formation of 2-4layers of water on the particle surface may lead to heterogeneous hydrolysis of ClNO via eqs 12 and 13 to yield NO and NO<sub>2</sub><sup>77,78</sup>

$$CINO(g) + H_2O \rightarrow HONO(g) + HCl(g)$$
 (12)

$$2\text{HONO}(g) \rightarrow \text{NO}(g) + \text{NO}_2(g) + \text{H}_2\text{O}(a)$$
(13)

Furthermore, NO<sup>+</sup>NO<sub>3</sub><sup>-</sup>(a) reacts with water to produce more HONO via  $^{52,80}$ 

$$\mathrm{NO}^{+}\mathrm{NO}_{3}^{-}(a) + \mathrm{H}_{2}\mathrm{O}(g) \rightarrow \mathrm{HONO}(g) + \mathrm{HNO}_{3}(g) \tag{14}$$

It is well-known that  $N_2O$  is formed during the heterogeneous hydrolysis of gas-phase  $NO_2$  via HONO on acidic oxide surfaces.  $^{80-82}$  Reactions of HONO and its protonated forms

 $(H_2ONO^+ \text{ or possibly NO}^+)$  have shown to generate hyponitrous acid, HON=NOH. The self-reaction of  $(HON)_2$  is known to decompose to  $N_2O$  over a wide range of pH values, including highly acidic conditions. The net reaction yields  $N_2O$ and  $HNO_3$  according to

TT+

$$8NO_2 + 3H_2O \xrightarrow{\Pi} N_2O + 6HNO_3$$
 (15)

Thus, a surface-mediated secondary reaction of a primary gasphase product,  $NO_2$ , a product that can be easily seen in the infrared spectra at lower RHs, may be responsible for the higher  $N_2O$  concentrations observed, especially at longer reaction times.

Role of the Particle Surface in the Reaction Mechanism. The proposed mechanism above for the formation of secondary gas-phase products from the reaction between HNO<sub>3</sub> and HCl, given by eqs 4-7, occurs via surface adsorbed intermediates. To better understand and further confirm the involvement of particle surface, selected control experiments were carried out in the absence of alumina surface. The gas-phase product formation from homogeneous reaction of gaseous HCl and HNO<sub>3</sub> is shown in Figure 7. According to



**Figure 7.** Gas-phase product (ClNO and NO<sub>2</sub>) formation from the reaction between gas-phase HCl and HNO<sub>3</sub> under dry (<1 %RH) condition at 298 K. (a) FTIR spectra. (b) Variation of gas-phase products. In (b) the two dash lines represent corresponding gas-phase product variations in the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface.

Figure 7a showing FTIR spectra of the gas phase, significantly lower production of ClNO and  $NO_2$  can be seen compared to that of in the presence of alumina surface. This is further highlighted in Figure 7b that shows a comparison of ClNO and



**Figure 8.** Gas-phase product formation from the reaction between gas-phase HCl and adsorbed nitrate on CaCO<sub>3</sub> under dry conditions at 298 K. Surface of the CaCO<sub>3</sub> contains (a) micropuddles of Ca(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O (where x = 1, 2, 3, or 4) and (b) a coating of Ca(NO<sub>3</sub>)<sub>2</sub>(aq) obtained by following two different methods described in the text.

 $NO_2$  production in the presence (dash line) and absence (solid line) of the surface. Initial rates of gas-phase product formation under different relative humidities at 298 K, determined from linear regression analysis shows that ClNO and  $NO_2$  production under dry (<1 %RH) conditions is approximately 40-fold enhanced for ClNO production during the first 20 min and is 4-fold greater for  $NO_2$ . At longer time scales the enhancement for ClNO decreases to about 10-fold.

The homogeneous reaction between HNO<sub>3</sub> and HCl, in the presence and absence of water is well documented.<sup>14,83–85</sup> On the basis of reactants and identified gas-phase products in several studies, the proposed overall reaction is similar to the one observed with aqua regia.<sup>14,86</sup> In this reaction pathway, gas-phase nitric acid dissociates to yield NO<sub>2</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> which react with Cl<sup>-</sup> from gaseous HCl to form ClNO<sub>2</sub> that readily dissociates to Cl<sub>2</sub> and HONO. HONO reacts with more Cl<sup>-</sup> to yield ClNO. The overall reaction of the proposed mechanism has been described as

$$3HCl + HNO_3 \rightarrow Cl_2 + ClNO + 2H_2O$$

and the individual steps are given as

$$2HNO_3 \longrightarrow H_2O + NO_2^+ + NO_3^- \quad (16a)$$

$$3(\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-)$$
 (16b)

$$H^+ + NO_3^- \longrightarrow HNO_3$$
 (16c)

$$Cl^{-} + NO_{2}^{+} \longrightarrow ClNO_{2}$$
 (16d)

$$Cl^{-} + CINO_2 \longrightarrow Cl_2 + NO_2^{-}$$
 (16e)

$$NO_2^- + H^+ \longrightarrow HONO$$
 (16f)

$$Cl + HONO \longrightarrow CINO + OH^{-}$$
(16g)  
$$H^{+} + H_2O \longrightarrow H_2O$$
(16h)

 $3HCl + HNO_3 \longrightarrow Cl_2 + CINO + 2H_2O$  (Net 16)

Thus, ClNO is formed even in the absence of a surface, yet the product yields are much smaller compared to the heterogeneous process. Interestingly, the overall reaction for the heterogeneous process, the net reaction of eqs 4-7, is similar to the overall reaction obtained for the homogeneous ClNO formation (Net 16). Based on the mechanism propossed here, the production of ClNO from the surface-mediated process is similar to the homogeneous pathway, making it difficult to distinguish between the two. Furthermore, according to the proposed heterogeneous mechanism, three HCl molecules are needed for one nitric acid to form one ClNO. Thus, at lower HCl pressures, HCl becomes the limiting factor lowering the production of ClNO and yielding more NO<sub>2</sub> from the surface, as seen in the data shown in Figure 2.

Effect of Particle Mineralogy on the Proposed Reaction Mechanism. The new reaction pathway proposed in this study for the formation of ClNO and NO2 highly depends on surface acidity and coadsorbed water. Aerosol particles with different surface mineralogy are known to exhibit variations in their surface acidity and the extent of water uptake. Therefore, further investigation was done using CaCO32 that has shown lower surface acidity and higher water uptake. In our previous work, CaCO<sub>3</sub> has also been used as a model system to show that water plays a major role during the uptake of HNO<sub>3</sub> on calcium carbonate due to the fact that coadsorbed water increases the ionic mobility of adsorbed ions on the surface, leading to the formation of micropuddles of calcium nitrate.<sup>87</sup> These micropuddles are associated with additional water even after evacuation forming  $Ca(NO_3)_2 \cdot xH_2O$ . These micropuddles are formed during successive cycles of HNO3 exposures followed by H<sub>2</sub>O vapor exposures. Secondary gasphase product formation, under dry (<1 %RH) condition, from the reaction between gaseous HCl and adsorbed nitrate on CaCO<sub>3</sub>, in the presence of additional associated water, is shown in Figure 8a. As evidence by these data, the gas-phase production, in particular of ClNO, is less compared to that of alumina surface. This difference is further confirmed by the calculated initial rates of gas-phase product formation given in Table 3. Surprisingly, the initial rate of NO<sub>2</sub> formation with CaCO<sub>3</sub> is higher compared to alumina surface under the same conditions. There was no N<sub>2</sub>O formation even at higher relative humidities when CaCO3 was used as the reactive surface (not shown here). Therefore, it can be proposed that heterogeneous hydrolysis of NO2 to yield N2O does not occur on the CaCO3 surface due to lower acidity of the carbonate surface leading to a higher gas-phase concentration of NO<sub>2</sub>. Additional experiments were carried out using CaCO<sub>3</sub> in which adsorbed nitrate associated with even more water,  $Ca(NO_3)_2(aq)$ , was obtained by exposing the carbonate surface to a gaseous mixture of  $HNO_3$  and  $H_2O$  (at 80 %RH) followed by a 4 h evacuation.

Table 3. Surface Area Normalized Initial Rate of Gas-Phase Product Formation during the Reaction between Gas-Phase HCl and Adsorbed Nitrate on  $CaCO_3$  under Dry and Wet Conditions<sup>*a*</sup>

	surface area no 10	surface area normalized initial rates of gas production $10^{-9}$ (molecules. m <sup>-3</sup> s <sup>-1</sup> cm <sup>-2</sup> ) <sup>b</sup>				
% relative humidity	ClNO(g)	NO <sub>2</sub> (g)	NO(g)	$N_2O(g)$		
<1	6.2 (±0.25)	6.4 (±0.35)				
45			1.7 (±0.069)			

<sup>*a*</sup>Results presented here are the average value of triplicate measurements, determined from linear regression, and the reported error represents one standard deviation. Gas-phase product formation from the first 20 min were used in the rate determination. <sup>*b*</sup>Rates are normalized to the corresponding BET surface area.

The gas-phase products formation from this surface upon exposure to HCl, under dry (<1 %RH) condition, is shown in Figure 8b. There is even less gas-phase production and formation of NO. Production of NO can be attributed to heterogeneous hydrolysis of ClNO, in the presence of extra water on the surface even under dry conditions. Therefore, additional water associated with secondary structures on particle surface greatly influence gas-phase product distribution and the data from these experiments further confirm the propossed reaction mechanism for the heterogeneous of HCl and adsorbed nitrate.

Surface-mediated acid catalysis is the key step in the proposed reaction mechanism, especially during the formation of the adsorbed NO<sup>+</sup>NO<sub>3</sub><sup>-</sup> intermediate. Gas-phase NH<sub>3</sub> is also known to titrate surface acidity upon adsorption.<sup>88</sup> In the next set of experiments, the effect of coadsorbed ammonia was investigated by exposing adsorbed ammonium nitrate on alumina surface to gas-phase HCl. Exposure of adsorbed nitrate to gas-phase ammonia  $(NH_3)$  yields a thin layer of ammonium nitrate, one or two monolayers of adsorbed NH<sub>4</sub>NO<sub>3</sub>, over the particle surface.<sup>89</sup> Under these conditions, lower gas-phase production was observed. The presence of unreacted HCl, even after 120 min of reaction time, further verified less reactivity of the surface. The initial rates of ClNO and NO<sub>2</sub> production were determined to be 1.4  $(\pm 0.05) \times 10^9$  and 0.11  $(\pm 0.01) \times$  $10^9$  molecules m<sup>-3</sup> s<sup>-1</sup> cm<sup>-2</sup>, respectively. The lower reactivity, in the presence of coadsorbed NH<sub>3</sub>, can be partially attributed to less availability of surface protons for the acid catalysis. Less accessibility to reaction sites during HCl uptake can be another plausible explanation for the low production of ClNO.

**Photochemistry of Secondary Gas-Phase Products.** Given that photochemistry dominates the daytime gas-phase chemistry of the atmosphere, and new light induced pathways continue to be discovered,<sup>90</sup> there is quite a lot of information available in the literature to realize that the surface and near surface regions of particles catalyze photochemical reactions that perturb the composition of the atmosphere. The photochemistry of secondary gas-phase species, in particular ClNO, has long been a subject of active interest. ClNO absorbs radiation throughout the visible and near-ultraviolet region.<sup>91,92</sup> On the basis of numerous studies, it is well-known that ClNO photodissociates to yield gas-phase NO and chlorine atoms via,<sup>52,80</sup>

$$\operatorname{ClNO}(g) \xrightarrow{\mu\nu} \operatorname{Cl}^{\bullet} + \operatorname{NO}(g)$$
 (17)

1...

From the analysis of ClNO spectrum and theoretical calculations, the quantum yield of this photochemical reaction is determined to be roughly equal to 1 in the wavelength region from 365 to 635 nm.<sup>93,94</sup>

Strong overlap between the ClNO absorption cross section and the solar actinic flux point out greater NO and Cl yields from the photodissociation under atmospheric conditions, potentially leading to an accelerated ozone depletion. In this study, photolysis of secondary gas-phase species was monitored by irradiation of the FTIR cell with broad-band ( $\lambda > 300$ ) light, after completion of the reaction (120 min) between HCl and adsorbed nitrate on alumina. Gas-phase product formation upon irradiation at 298 K, under dry (<1 %RH) and wet (45 ± 2 %RH) conditions, are shown in Figure 9a,b, respectively. As



Figure 9. Gas-phase product formation upon irradiation of secondary gas-phase products yielded from the reaction between gas-phase HCl and adsorbed nitrate on aluminum oxide particle surfaces at 298 K under (a) dry (<1 %RH) and (b) wet (45  $\pm$  2 %RH) conditions.

seen in Figure 9a, we observed formation of NO with a simultaneous decay of the major gas-phase product, ClNO, upon photolysis under dry conditions. In addition, HNO<sub>3</sub> and NO<sub>2</sub> showed a similar loss from the gas phase with broad-band irradiation. On the basis of mass balance calculations for eq 17, more than 75% of the photoproduced NO is present in the gas phase and the rest is adsorbed on the particle surface, as evidenced by a weak peak in the surface spectrum at 1701 cm<sup>-1</sup> for the N–O stretching band associated with adsorbed NO (not shown here).<sup>47</sup> Under humid conditions (Figure 9b), no additional gas-phase species were observed, but a continuance production of NO and N<sub>2</sub>O.

In good agreement with previous studies, here active Cl and NO species are generated from photodissciation of ClNO under dry conditions. Chlorine atoms can then initiate chain reactions inside the FTIR cell, starting with the reaction with ClNO that results in even more NO and  $Cl_2$ .<sup>92</sup>

$$\operatorname{Cl}^{\bullet} + \operatorname{ClNO}(g) \to \operatorname{NO}(g) + \operatorname{Cl}_{2}(g)$$
 (18)

Similarly, active Cl can potentially react with gas-phase  $HNO_3$  and HCl, yielding more products to the reaction mixture. Moreover, the reaction mixture becomes even more complex due to photoreduced products of adsorbed nitrate, NO,  $NO_2^{-7}$ , and  $NO_2^{.47,53,95-99}$ 

Thus, the daytime chemistry of HCl and adsorbed nitrate is even more complicated to understand compared to the nighttime chemistry and influences the chemical balance of the atmosphere to a greater extent. These laboratory experiments further provide evidence for the formation of highly reactive chlorine atoms on aerosol dust particles that is currently not included in atmospheric chemistry models.

## CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

Conversion of atmospheric nitric acid and hydrogen chloride to ClNO, NO, NO<sub>2</sub>, Cl, and Cl<sub>2</sub>, through an adsorbed nitrate intermediate under different atmospherically relevant conditions, has been shown. Numerous field studies have shown, via heterogeneous interactions, HNO3 reacts with mineral dust and other atmospheric aerosols to yield adsorbed nitrate, nitrate coatings, and concentrated nitrate solutions.<sup>79</sup> Atmospheric mixing of dust particles, having nitrated surfaces, with sea salt in marine environments is one potential way of initiating the formation of ClNO and other active gas-phase species. Besides from sea salt, atmospheric HCl originating from various natural and anthropogenic sources can react with adsorbed nitrate on mineral dust particles to result in similar gas-phase products. The reaction pathway involves a surfacebound NO<sup>+</sup>NO<sub>3</sub><sup>-</sup> intermediate that is produced in an acid catalysis reaction between adsorbed nitrate and chlorine. Coadsorption of gas-phase NH<sub>3</sub> on nitric acid reacted alumina decreases the surface acidity result in a significant drop in ClNO production confirming the importance of acid catalysis in the reaction mechanism.

Additionally, there is a significant dependence of the gasphase product distribution on relative humidity and, therefore, adsorbed water on the surface. At higher relative humidities, ClNO undergoes hydrolysis on the surface, yielding HONO that dissociates to NO and NO2. NO2 is further hydrolyzed on acidic surfaces forming N2O in a complex mechanism. The involvement of additional water associated with the particle surface was confirmed in experiments done on CaCO<sub>3</sub> particle surfaces. The studies with CaCO<sub>3</sub> also underline the importance of particle mineralogy as well as acidity of the reactive surface on gas-phase product formation. On the basis of the mechanisms discussed here, we predict that heterogeneous formation of ClNO from gas-phase HNO<sub>3</sub> and HCl is similar to the overall reaction for the homogeneous process, making it difficult to distinguish between the two. However, the heterogeneous mechanism should correlate with mineral dust loading.

The chemistry involved with nitrogen and chorine activation on dust particle surface becomes even more complex in the presence of sunlight. During the daytime, ClNO photodissociates to NO and chlorine atoms, initiating a chain of secondary reactions with other gas-phase species in the atmosphere. These active nitrogen and chlorine species are capable of further participating in nitrogen and chlorine cycles. Thus, heterogeneous conversion of HNO<sub>3</sub> and HCl to labile nitrogen and chlorine species in the atmosphere could potentially alter the peak concentration and geographical distribution of ozone.

# ASSOCIATED CONTENT

#### Supporting Information

Complete listing for refs 15, 20, 24, 37, and 41. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

## Notes

The authors declare no competing financial interest.

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