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$ClNO_2$ Production from N_2O_5 Uptake on Saline Playa Dusts: New Insights into Potential Inland Sources of $ClNO_2$

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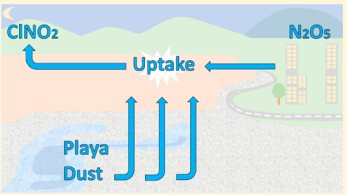
Supporting Information

ABSTRACT: Nitryl chloride ($ClNO_2$), formed when dinitrogen pentoxide (N_2O_5) reacts with chloride-containing aerosol, photolyzes to produce chlorine radicals that facilitate the formation of tropospheric ozone. $ClNO_2$ has been measured in continental areas; however, the sources of particulate chloride required to form $ClNO_2$ in inland regions remain unclear. Dust emitted from saline playas (e.g., dried lakebeds) contains salts that can potentially form $ClNO_2$ in inland regions. Here, we present the first laboratory measurements demonstrating the production of $ClNO_2$ from playa dusts. N_2O_5 reactive uptake coefficients (γ_{N2O5}) ranged from ~10^{-3} to 10^{-1} and $ClNO_2$ yields (φ_{ClNO2}) were >50% for all playas tested except one. In general, as the soluble ion fraction of playa dusts increases, γ_{N2O5} decreases and φ_{ClNO2} increases. We attribute this finding to a transition from aerosol surfaces dominated by silicates that react efficiently with N_2O_5 and produce little $ClNO_2$ to aerosols that behave like deliquesced chloride-containing salts that generate high yields of $ClNO_2$. Molecular bromine (Br_2) and nitryl bromide ($BrNO_2$) were also detected, highlighting that playas facilitate the heterogeneous production of brominated compounds. Our results suggest that parameterizations and models should be updated to include playas as an inland source of aerosol chloride capable of efficiently generating $ClNO_2$.



1. INTRODUCTION

Reactive halogens are potent oxidizers that influence the earth's climate and air quality by reducing the lifetime of methane (CH_4) and affecting budgets of tropospheric ozone (O_3), a greenhouse gas and criteria air pollutant.[1,2] The chlorine radical ($Cl^{\cdot}$) is a reactive halogen that is efficient at oxidizing volatile organic compounds (VOCs), augmenting tropospheric O_3 production,[3−9] and facilitating the formation of secondary organic aerosol (SOA).[10] In urban environments, the most common precursor to $Cl^{\cdot}$ is nitryl chloride ($ClNO_2$).[11−13]

$ClNO_2$ is produced following the heterogeneous reaction of dinitrogen pentoxide (N_2O_5), a nighttime reservoir for nitrogen oxides (NO_X) in polluted environments, on chloride-containing aerosols.[11] N_2O_5 is taken up onto aerosols with an efficiency referred to by the reactive uptake coefficient (e.g., γ_{N2O5}), which is the probability that colliding N_2O_5 molecules undergo irreversible reaction on or in a particle. N_2O_5 has been shown to react with deliquesced inorganic salts with values of γ_{N2O5} ranging from 0.015 to 0.2 from laboratory studies[14−23] as well as field work (e.g., McDuffie et al. 2018a and references therein).[13,24−32] Upon solvation, N_2O_5 is proposed to form a nitrate ion (NO_3^-) and a hydrated intermediate ($H_2ONO_{2(aq)}^+$), which can further react with water to form nitric acid (HNO_3).[33] However, in the presence of aqueous chloride ($Cl^-_{(aq)}$), the $H_2ONO_2^+{}_{(aq)}$ intermediate can react to produce $ClNO_{2(aq)}$.[11,13,14,34] The rate constant for the reaction of the N_2O_5 intermediate with $Cl^-_{(aq)}$ has been estimated to be a factor of 500−800 larger than the reaction with H_2O, causing even small concentrations of $Cl^-_{(aq)}$ in aerosols to influence the product yield.[14,22,34] $ClNO_{2(aq)}$ volatilizes and photolyzes to produce atomic chlorine ($Cl^{\cdot}$) while recycling a nitrogen dioxide (NO_2) molecule.[35] The photolysis of $ClNO_2$ is estimated to contribute significantly to the total tropospheric $Cl^{\cdot}$ budget, and therefore it is critical to constrain sources of aerosol chloride.[2,36]

$ClNO_2$ production in coastal regions has been widely reported both from field observations[2,12,32,36−42] and laboratory measurements using salt solution mimics.[14,22,23,42,43] This process has now been accepted as a major pathway for the production of $ClNO_2$;[2,44] however, recent field measurements show elevated $ClNO_2$ mixing ratios in continental regions,[13,25−27,29−31] suggesting that sources of chloride-containing aerosol other than sea spray aerosol can also produce $ClNO_2$. Potential sources of particulate chloride that can facilitate the inland production of $ClNO_2$ include biomass burning aerosol,[45] road salts,[46] and industrial emissions from coal-fired power plants.[27,31,47] However, other under-explored yet potentially important sources of particulate chloride found

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inland are drying saline lake beds (playas). Evaporite minerals (e.g., salts) associated with playas, including halite (NaCl), are derived from saline groundwater or dissolved minerals in surface waters that evaporate, leaving behind a salt-rich, erodible crust that can be mobilized as dust by aeolian processes and may be a significant source of chloride-containing aerosol.[48−56] Playas, in North America and globally, are disproportionately potent emitters of dust aerosols.[57,58] Gaseous halogen oxides (e.g., ClO and BrO) have been observed over playas including the Great Salt Lake,[59] Salar de Uyuni,[60] and the Dead Sea;[61] suggesting that playa surfaces can participate in halogen chemistry. Additionally, crustal aerosol originating from playas in the southwestern United States was suggested to indirectly contribute to the formation of $ClNO_2$ during the Nitrogen, Aerosol Composition, and Halogens on a Tall Tower (NACHTT) campaign through the acid displacement of supermicron particulate chloride leading to the formation of hydrochloric acid (HCl) that partitions to submicron particles and facilitates the production of $ClNO_2$.[62−64] However, the direct production of $ClNO_2$ from saline playas has never been measured.

Here, we present the first laboratory measurements of the reactive uptake of N_2O_5 and yield of $ClNO_2$ at different relative humidities (RHs) from saline playa dusts collected from southwestern North America. We show that all playa dusts tested, except one, generated $ClNO_2$ at significant yields and that some generated brominated products. We end with a discussion of the implications of our work for updating current parameterizations of the formation of $ClNO_2$ in inland regions.

2. MATERIALS AND METHODS

2.1. Generation of Playa Dust Particles. Surface samples were obtained from seven saline playas in southwestern North America that are known dust emitters: Black Rock Desert (Nevada),[65−68] Great Salt Lake (Utah),[69] Lordsburg Playa (New Mexico),[70,71] Owens (dry) Lake (California),[72−74] Salt Flat Basin (Texas),[75] Salton Sea (California),[76] and Sulphur Springs Draw (Texas).[77,78] Two samples from Owens Lake collected on the same day were used in this study: the first sample was a white, hard salt "crust",[48] and the second sample was a soft, sand-silt-clay "sediment".[48] Photos of these two samples are available in Figure S1 of the Supporting Information (SI). Coordinates for all samples and additional information on the playas and their characteristics are available in Figure S2 and Table S1. All of the playa sediment samples were used "as is" except for the sample obtained from the Great Salt Lake, which was dried at 45 °C for 48 h.

Our custom dry aerosol generation set up, described in the SI, includes a mechanical agitation method using a wrist action shaker similar to other dry aerosol generation systems.[79] The output was conditioned in a ∼19 L dilution drum,[80] and supermicron particles were removed using a cyclone (Mesalabs) with a PM_1 (particles with aerodynamic diameter >1 μm) cutoff. We chose to restrict our study to submicron aerosols that are most susceptible to long-range transport[81] and would have a larger spatial impact on halogen activation. Following the cyclone, excess charge was eliminated using a ^{210}Po neutralizer.[82] A humidified dilution flow of ultrahigh purity N_2 (∼5 L min^{-1}) was introduced to condition the RH of the dust-laden flow, which was measured using a humidity probe (model HMP60; Vaisala) just prior to the entrance of the aerosol flow tube (AFT) to ensure that the aerosol was fully conditioned to the expected RH. The humidity in the AFT for our experiments ranged from 10−60% RH. The aerosol concentration was stable for up to ∼15 min using this set up, longer than a typical uptake duration of ∼10 min.

2.2. Aerosol Kinetics Flow Tube Set Up. Our experimental setup is depicted in Figure S3. Generated aerosols orthogonally entered a 90 cm long, 6 cm inner diameter Pyrex AFT coated with halocarbon wax (Halocarbon Corp.) to minimize wall losses. N_2O_5 was generated continuously in a Teflon vessel by first forming NO_3 by reaction of NO_2 (10 ppm standard; Airgas) and O_3 generated with a UV-pen lamp (Jelight Model 610). NO_3 was then allowed to react further with excess NO_2 to produce N_2O_5 in equilibrium with NO_2 and NO_3 at room temperature.[15,22,42,83,84] The final flow was ∼0.1 L min^{-1}, which was introduced via a Teflon lined stainless steel movable injector along the centerline of the AFT. We utilized the central 50 cm as the reaction zone to ensure fully developed laminar flow. N_2O_5, $ClNO_2$, Br_2, $BrNO_2$, and other halogenated species were detected using an iodide-adduct chemical ionization mass spectrometer (CIMS) as $[I\cdot(N_2O_5)]^-$ (234.9 amu), $[I\cdot(ClNO_2)]^-$ (207.9 and 209.9 amu), $[I\cdot(Br_2)]^-$ (284.9, 286.9, and 288.9 amu), and $[I\cdot BrNO_2]^-$ (251.9 and 253.9 amu) with isotope ratios confirming assignment of our ion peaks.[42,85] Additional details of this instrument are available in the SI. The humidified total particle surface area was measured at the exit of the AFT after the aerosol had been humidified using a scanning mobility particle sizer (SMPS; model 3082, TSI, Inc.) and an aerosol particle sizer (APS; model 3321, TSI, Inc.). To ensure that the measured particle surface area was representative of humidified conditions during experiments in the AFT, both instruments sampled humidified flow for ∼1 h prior to the start of the experiment in order to equilibrate the RH of the DMA sheath flow. To preserve the laminar regime in the AFT, the APS sample flow was diluted by a factor of ∼10. Figure S4 shows a typical size distribution observed during our work.

2.3. Determination of γ_{N2O5} and Yields of $ClNO_2$. We determined the reaction probability of N_2O_5, γ_{N2O5}, via particle modulation.[83] At a fixed injector position, we modulated the dust output through the AFT in ∼15 min intervals; this allowed ∼5 min for steady-state conditions to develop in the reaction zone where aerosols and N_2O_5 interacted followed by ∼10 min of averaging signal. The N_2O_5 signal was determined in the presence of both reactor walls and aerosols and then reactor walls alone; thus the pseudo-first-order rate constant for N_2O_5 loss, k_{het}, was calculated using eq 1[83]

$$k_{het} = -\frac{1}{\Delta t}\ln\frac{[N_2O_5]_{w/aerosol}}{[N_2O_5]_{w/o\ aerosol}} \quad (1)$$

where Δt is the reaction time, $[N_2O_5]_{w/aerosol}$ is the N_2O_5 signal in the presence of aerosol, and $[N_2O_5]_{w/o\ aerosol}$ is the N_2O_5 signal in the absence of aerosol. The reactive uptake coefficient, γ_{N2O5}, was then calculated using eq 2

$$\gamma = \frac{4k_{het}}{\omega S} \quad (2)$$

where ω is the mean molecular speed of N_2O_5 and S is the aerosol total surface area concentration. For each experiment, we repeated this procedure five times at every humidity using different particle surface areas, which produced linear correlations (<10% error by weighted least-squared fits) between k_{het} and S (see Figure S5). Values of γ_{N2O5} were

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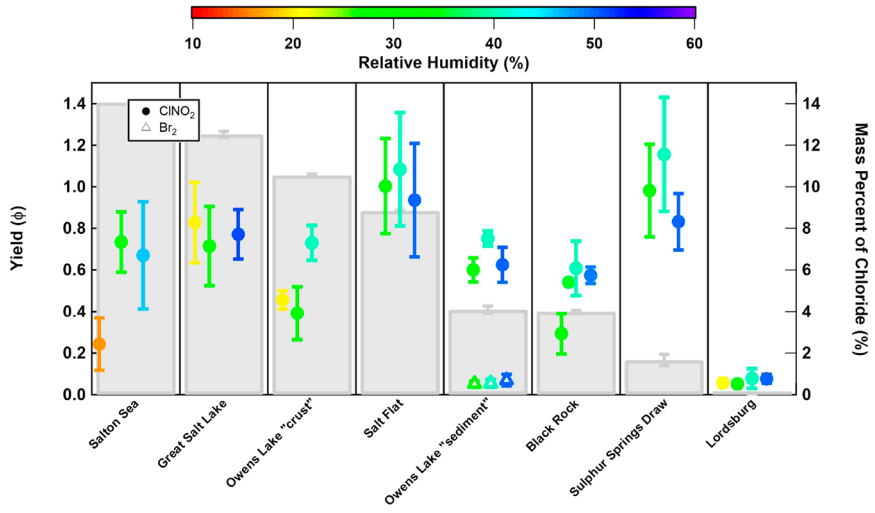

Figure 1. Yields of $ClNO_2$ and Br_2 for playa samples determined at different humidities (left axis) displayed in order from highest chloride content (left) to lowest chloride content (right). Error bars represent one standard deviation between repetitions. Markers are colored based on the RH for which the yield values were determined. Gray bars (right axis) correspond to the sample chloride content, measured via IC.

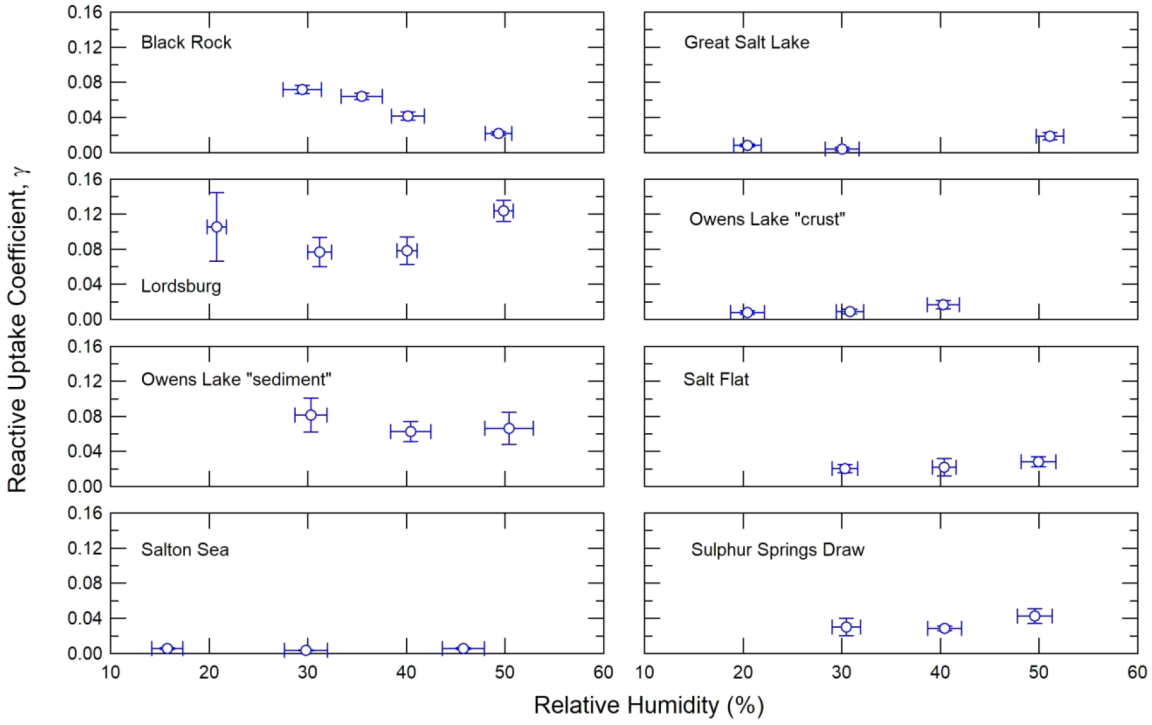

Figure 2. Reactive uptake coefficients, γ, of N_2O_5 on different playa samples are shown as a function of RH. Vertical error bars represent $\pm 1\sigma$ of 5 repetitions at each RH.

then corrected for gas-phase diffusion limitations[86] (<5% error) and non plug flow conditions[87] using a wall loss measurement that was made at the end of each run (~10% error).

The largest correction to our measurements was the determination of *S*. Corrections based on aerosol density and shape were applied,[88] details for which can be found in the SI. The playa samples used in our experiments are not composed solely of silicate minerals typical of most mineral dust; rather, they are a combination of silicate minerals and significant amounts of evaporites. To account for the density contributions of silicate minerals and evaporite salts, we measured the soluble ion content of the playa samples using ion chromatography (IC) (see Table S2 and information in the SI). We attribute the soluble ions to evaporite mass (density ~1.3 g cm^{-3})[89] and the remainder of our sample mass to silicates (density ~2.7 g cm^{-3}),[90] an assumption based on previous dust measurements.[55] Taking these corrections into account, we estimate that the APS overpredicts *S* by ~20−40% on average (see Table S2). Uncorrected values of γ_{N2O5} and corrected values of γ_{N2O5}, referred to as γ_{true}, are shown in Table S3.

The yield of $ClNO_2$ (φ_{ClNO2}) is defined as the amount of $ClNO_2$ produced per amount of N_2O_5 reacted. Yields of $ClNO_2$ were determined by performing routine calibrations for the sensitivity of $ClNO_2$ relative to N_2O_5 by flowing N_2O_5 over

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a wetted NaCl slurry, which theoretically produces $ClNO_2$ with a yield of unity for fully deliquesced aerosol.[11,36,42] The generated $ClNO_2$ is then introduced to a stream of humidified air to calibrate the response of the CIMS to N_2O_5 and $ClNO_2$ at different RHs. We also calibrated the CIMS to Cl_2 and Br_2 using permeation tubes with known emissions rates (74 and 65 ng min^{-1} certified emission rate at 40 °C by KIN-TEK, respectively) and varied the flow rate into the carrier gas stream to test the instrument response to different additions of Cl_2 and Br_2. To report yields of Br_2 observed in this work, we estimated that ∼1.8 ppb N_2O_5 was introduced to the AFT during our experiments using a collision limit calculation.[91] This gave us an upper limit for the instrument sensitivity to N_2O_5 (∼18 Hz ppt^{-1} for every MHz of total reagent ion signal) and thus a lower limit for the mixing ratio of N_2O_5. As a result, φ_{Br2} values reported in this work are upper limits.

2.4. Estimating the Salt and Liquid Content of Playa Dusts. To compare the observed yields of $ClNO_2$ from our samples to those predicted with the current laboratory-based parameterizations, we used IC data and experiment RH conditions as inputs into ISORROPIA-II[92] to predict the liquid water and aqueous chloride content of the aerosols as a function of RH. We chose ISORROPIA-II for its ability to handle complex mixtures, including K^+, Mg^{2+}, and Ca^{2+}, which are present in non-negligible concentrations in our samples and impact the aerosol liquid water content and amount of aqueous chloride due to their highly hygroscopic nature.[93] Table S4 in the SI contains a complete list of measured cations and anions for each playa sample. We then used the model output to predict theoretical values for φ_{ClNO2} using eq 3[22]

$$\phi_{ClNO_2} = \left(1 + \frac{k_{H_2O}[H_2O_{(l)}]}{k_{Cl^-}[Cl^-_{(aq)}]}\right)^{-1} \quad (3)$$

where we use a value of k_{H_2O}/k_{Cl^-} of 1/483,[22] but note that there is spread in this value.[14,34]

3. RESULTS AND DISCUSSION

3.1. $ClNO_2$ Yields and N_2O_5 Reactive Uptake Coefficients from Saline Playa Dusts. As shown in Figure 1 and Table S3, all of the playa dust samples used in this study produced $ClNO_2$, with several playa dusts generating $ClNO_2$ at high yields (φ_{ClNO2} > 0.5). Figure 1 is organized by decreasing chloride mass fraction, and the playas with chloride mass concentrations above 1% generate appreciable $ClNO_2$. Aerosols generated from each playa sample showed differing trends between RH and γ_{N2O5} (Figure 2), which is consistent with previous laboratory studies that also showed that an increase in RH can increase, decrease, or have no effect on γ_{N2O5} depending on the mineralogy of the aerosol.[90,94−96] Similar values of φ_{ClNO2} and γ_{N2O5} were observed for the Sulphur Springs Draw and Salt Flat playa samples with φ_{ClNO2} ∼ 1 and γ_{N2O5} ranging from 0.020 to 0.043 (Figure 2). These values are consistent with deliquesced chloride salts and match our results for a NaCl standard used as a check on our results (Table S3). Dust generated from the Great Salt Lake also produced $ClNO_2$ in high yields (φ_{ClNO2} ∼ 0.7−0.8); however, γ_{N2O5} values were lower, in the range of 0.004−0.019, and increased with RH (Figure 2). Little variation in the values of both φ_{ClNO2} and γ_{N2O5} were observed for dust generated from the Sulphur Springs Draw, Salt Flat, and Great Salt Lake at the three RHs tested, which is surprising given that we performed dry generation on our samples and were well below the deliquescence RH of pure NaCl (∼75%).[89,97] One possible explanation for reactive uptake below the NaCl deliquescence RH is the presence of chloride-containing evaporites other than halite (NaCl) such as magnesium chloride and/or calcium chloride that are more hygroscopic than NaCl.[93,98] Another possible explanation for our results is the presence of hydrated salts in our samples, which are typically observed in playa and salt crust evaporites[74,99,100] and were previously suggested to explain the observed water uptake properties for dusts generated from the Great Salt Lake and Salt Flat.[55] These hydrates and other hygroscopic minerals are the best candidates for providing aqueous chloride needed to facilitate the production of $ClNO_2$ at low RH from these samples.

The Owens Lake "crust" and Salton Sea samples showed increasing values of both φ_{ClNO2} and γ_{N2O5} with increasing RH. The yield of $ClNO_2$ increased from 0.39 to 0.73 for the Owens Lake "crust" and from 0.24 to 0.74 for the Salton Sea; γ_{N2O5} increased from 0.008 to 0.017 for the Owens Lake "crust" and from 0.004 to 0.006 for the Salton Sea. The best explanation for our observations is the presence of crystalline salts at low RH that become increasingly deliquesced with increasing RH and provide aqueous chloride that is available to react with N_2O_5. Previous laboratory studies have demonstrated that γ_{N2O5} and φ_{ClNO2} are strongly dependent on particle phase,[101−103] supporting this explanation. The Owens Lake "sediment" sample, however, was highly reactive with N_2O_5 (γ_{N2O5} ∼ 0.063 to 0.081) and generated $ClNO_2$ in appreciable yields (φ_{ClNO2} ∼ 0.6 to 0.75) at all RHs tested. The different γ_{N2O5} and φ_{ClNO2} for the Owens Lake "crust" and the "sediment" reflects the different types of material that were collected and analyzed. The "sediment" sample represents a mixture of materials derived from both the evaporite surface and the salt-silt-clay crust directly underneath, including highly hygroscopic sodium carbonates and sodium sulfates[55] that best explain our high values of γ_{N2O5} and φ_{ClNO2}. In contrast, the "crust" sample was a hard, white material composed of pure salts that do not fully deliquesce at the humidities used in this work.[50−52,74,104,105] These results underscore the heterogeneity of mineral content not only across playas but also within the same playa.[106]

In contrast to the Salton Sea and the Owens Lake "crust" samples that show increasing values of both γ_{N2O5} and φ_{ClNO2} with RH, dust generated from the Black Rock Desert showed increasing yields of $ClNO_2$ (0.3−0.6) but a decrease in N_2O_5 reactivity (0.07−0.02) with increasing RH. Our values of γ_{N2O5} for this sample are strikingly similar to previous work that probed the reactive uptake of N_2O_5 on illite.[95] The reaction between N_2O_5 and the hydroxyl groups (−OH) on the surface of silicates, such as illite, is thought to be more efficient than the hydrolysis mechanism resulting in high values of γ_{N2O5}.[107,108] Our results for the Black Rock Desert playa are best explained by a blend of reactive aluminosilicates and evaporites where the silicates are highly reactive with N_2O_5 at low RH. As the RH increases, the evaporites provide an increasing amount of deliquesced chloride, which reduces γ_{N2O5} and increases φ_{ClNO2} with RH. High values of γ_{N2O5} (∼0.08 to 0.12) were also observed for the Lordsburg playa, which has been shown to contain a dominant fraction of silicates and low concentrations of hygroscopic evaporite minerals.[55,109] In contrast to all of the other samples, the Lordsburg playa dust generated little $ClNO_2$ (φ_{ClNO2} ∼ 0.05 to 0.08) likely due to the lack of Cl^- in the sample (0.06 ± 0.02

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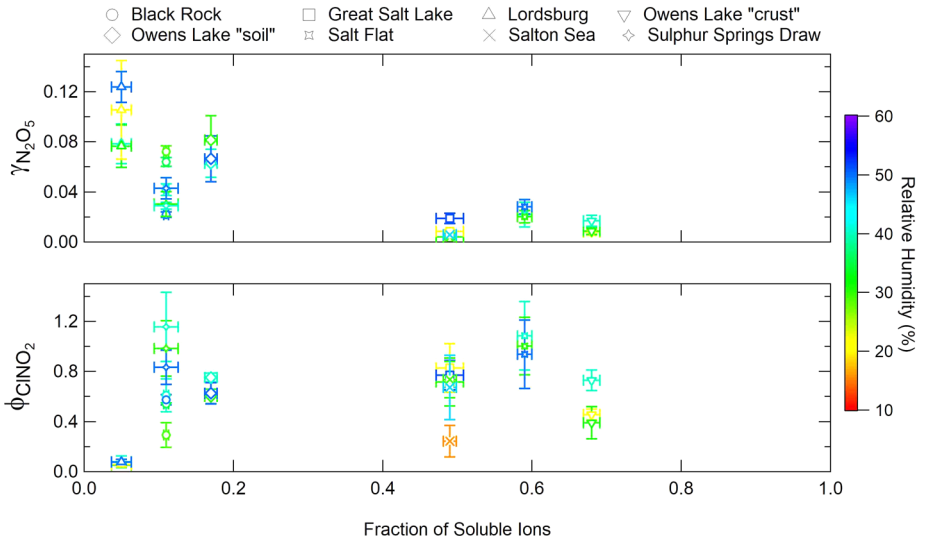

Figure 3. γ_{N2O5} and φ_{ClNO2} are shown as a function of the soluble ion content measured by IC. Values are colored by RH. Vertical error bars represent $\pm 1\sigma$ of 5 repetitions at each RH.

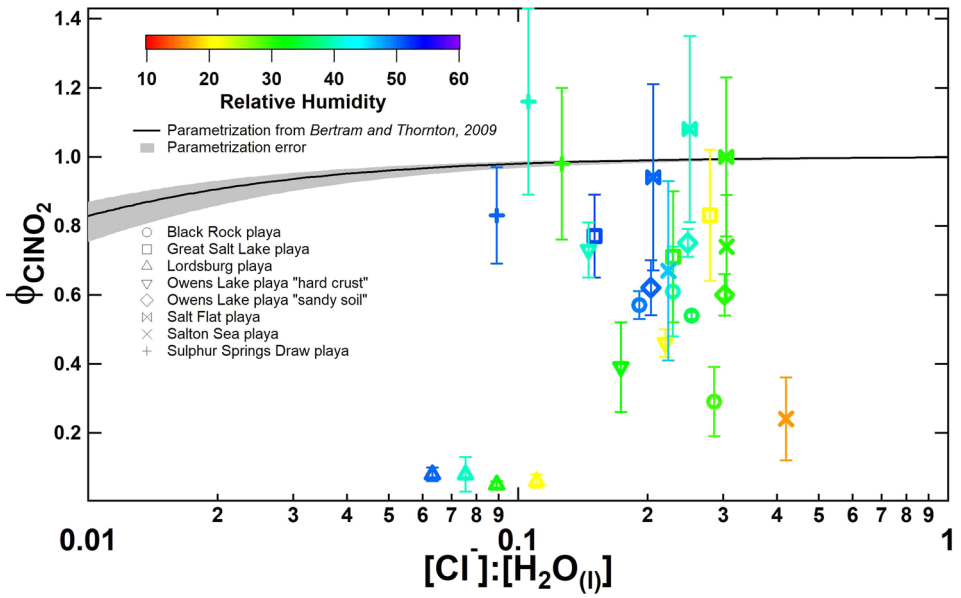

Figure 4. Measured values of φ_{ClNO2} plotted against the aerosol chloride-to-water ratio derived from the aqueous-phase chloride content and predicted liquid water content obtained from ISORROPIA-II, which was run in two modes: (i) solid precipitates are allowed to form (not shown) and (ii) only metastable liquid solutions are allowed to form (filled markers). Values are colored by RH. Solid line represents the parameterization by Bertram and Thornton, (2009)[22] for yields of $ClNO_2$ as a function of the aerosol chloride-to-water ratio, with shading representing the associated error.

wt %; see Figure 1 and Table S4). Altogether, these results highlight the impact of the mixed mineralogy of playas on their reactivity toward N_2O_5 and the production of $ClNO_2$.

3.2. Evaporite Content and Predicted Yields of $ClNO_2$.

In order to probe the relationship between playa dust composition, φ_{ClNO2}, and γ_{N2O5}, the measured soluble inorganic ion content (Table S4) was used to estimate the amount of evaporites associated with each playa sample. In general, playa dusts with lower mass fractions of soluble ions (e.g., evaporites) have high values of γ_{N2O5}, and as the soluble ion content increases, values of γ_{N2O5} converge to ~0.02−0.03, consistent with N_2O_5 uptake on deliquesced inorganic salts observed in laboratory studies (see Figure 3).[14,15,21−23,42,110,111] Conversely, φ_{ClNO2} generally increased with increasing fractions of soluble ions until plateauing at ~50% soluble fraction (corresponding to approximately >5% chloride by mass in Figure 1).

The decreasing trend in γ_{N2O5} and increasing trend in φ_{ClNO2} with increasing evaporite content, shown in Figure 3, reflects the competition between silicates and evaporites for N_2O_5 and the impact of this competition on the reaction products formed. Samples with low evaporite content (<20%) have a large mass fraction of silicates that react efficiently with N_2O_5 resulting in high values of γ_{N2O5}.[95,107,108] For these samples, the scarcity of soluble ions, including chloride (Figure 1), coupled with previous observations of the formation of absorbed nitrates when N_2O_5 reacts with silicates[108] best explain the low yields of $ClNO_2$ from samples with very low soluble ion (evaporite) content. Conversely, samples with high evaporite content (≥50%) behave similarly to deliquesced, chloride-

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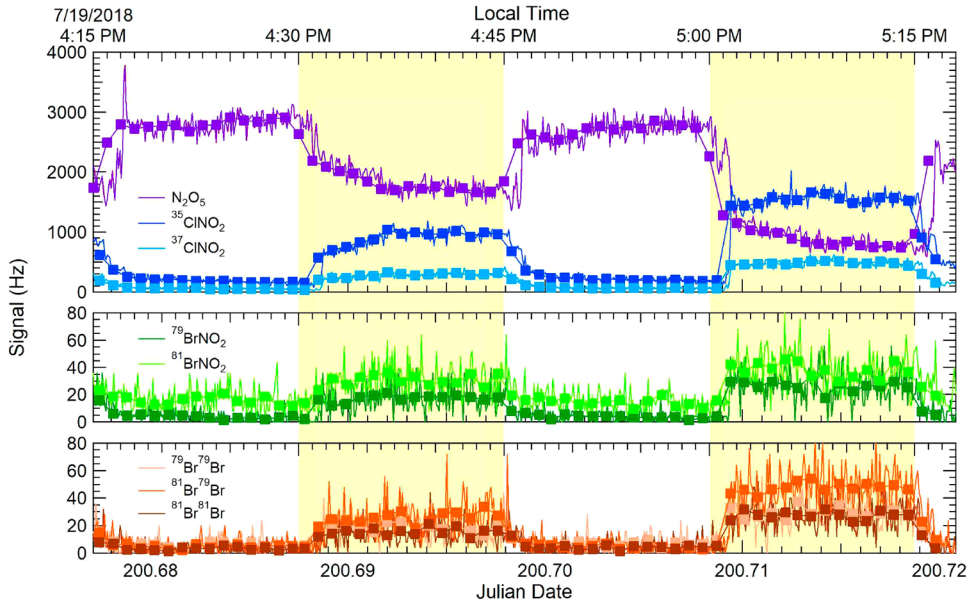

Figure 5. Example timeseries for N_2O_5 loss by particle modulation (top panel), $ClNO_2$ production (second panel), $BrNO_2$ production (third panel), and Br_2 production (bottom panel) for the Owens Lake "sediment" sample. Markers are minute-averaged data to enhance visual clarity. Tinted background indicates periods of N_2O_5 uptake onto aerosol.

containing salts with values of $\gamma_{N2O5} \sim 0.03$ and high values of φ_{ClNO2} (>0.5). One notable exception to this trend is the Salton Sea, which had the lowest values of γ_{N2O5} (0.004–0.006) out of all the playas and somewhat low φ_{ClNO2} (0.2–0.7) despite having a mass fraction of evaporites (49%) on par with other samples that have much higher values of γ_{N2O5} and φ_{ClNO2}. The Salton Sea is uniquely influenced by persistent anthropogenic activities, including agricultural runoff,[112] that influence the composition of the dust emitted from this sample.[49,113] While particulate nitrate (NO_3^-), which has been shown to suppress N_2O_5 uptake via the "nitrate effect",[19,22] was not measured in significant concentrations (<0.4 wt %, see Table S4), organic compounds from pesticides, herbicides, fertilizers, and other anthropogenic sources are commonly found at the Salton Sea.[114] Organic coatings have been shown to suppress γ_{N2O5}[15,23,115−117] and φ_{ClNO2}[43] consistent with our low values of γ_{N2O5} and φ_{ClNO2} for the Salton Sea.

We also used the soluble inorganic ion content data as model input for ISORROPIA-II to estimate aerosol liquid water content and aqueous chloride concentration as a function of RH. These results were used to predict φ_{ClNO2} from eq 3. The experimentally measured φ_{ClNO2} values plotted against the chloride-to-water ratio evaluated by ISORROPIA-II are shown in Figure 4. This model is run in two ways: either insoluble compounds are allowed to precipitate, or aerosols are assumed to form only metastable solutions. Both modes gave similar results, and we show results using metastable solutions. φ_{ClNO2} was overpredicted in all cases except two: Salt Flat and Sulphur Springs Draw. These two dust samples have the highest measured φ_{ClNO2} values, are well-predicted by ISOROPIA-II and eq 3), and have values of γ_{N2O5} consistent with deliquesced NaCl (see Figures 1 and 2 and Table S3). For other samples, the disagreement between our measurements and predictions shown in Figure 4 depends on several factors. The most obvious source of uncertainty is the aerosol phase. When predicting the aerosol liquid water content, carbonates and hydrates are not factored into current thermodynamic predictions; yet, these compounds have been suggested to be important for explaining the water uptake and chemical properties of playa aerosols in previous studies.[55,56] Neglecting these compounds would lead to underpredictions of liquid water content and overpredictions of $ClNO_2$ yields. Further, playa dust aerosol generation involves saltation and sandblasting processes that can result in nonuniform distributions of evaporites within the aerosol population in terms of particle size. In this work, the inorganic ion content was not measured as a function of aerosol size, and thus the PM_1 used in our experiments has a different evaporite concentration and composition than the bulk inorganic ion data used to predict the liquid water content and yields of $ClNO_2$.

The Lordsburg playa is the only sample for which $ClNO_2$ production was inefficient (~0.05–0.08); yet, ISORROPIA-II estimates a $Cl^-_{(aq)}/H_2O_{(l)}$ ratio high enough to efficiently generate $ClNO_2$ from eq 3. These results are best explained by the presence of silicates on the aerosol surface[55,109] that dominate N_2O_5 uptake and limit the production of $ClNO_2$. These competing reactions with silicates and other competitive nucleophiles, the suppressing effect of organic coatings, and the uptake and direct reaction of $ClNO_2$ in aqueous phase particles are not factored into eq 3 when predicting yields of $ClNO_2$, which would lead to an overprediction of $ClNO_2$ by eq 3.[118] The surface composition of the aerosol is also important when predicting yields of $ClNO_2$.[111] Therefore, a critical look at how mineralogy and surface chemistry (for instance, organic coatings, clay coatings, or isolated evaporite structures on aerosol surfaces) affect both the reactivity of N_2O_5 and the production of competing products is warranted and will be the subject of a companion paper.

3.3. Production of Br_2 and $BrNO_2$. In addition to $ClNO_2$, appreciable amounts of molecular bromine (Br_2) were also detected when dust generated from the Owens Lake "sediment" and Sulphur Springs Draw samples was reacted with N_2O_5 (see Figures 1 and 5 and Table S3). φ_{Br2} values from the Sulphur Springs Draw were too small to accurately quantify (<0.02) and were 0.054–0.07 from the Owens Lake "sediment" sample. Our Br_2 yields are surprisingly low

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considering that measured chloride-to-bromide ratios (Cl^-/Br^-), by mass, were ~26 for Sulphur Springs Draw and ~46 for the Owens Lake "sediment" sample. We would expect similar yields of $ClNO_2$ and Br_2 of ~0.5 for both samples based on previous work.[84] Additionally, for Black Rock (Cl^-/Br^- ~ 102), Great Salt Lake (Cl^-/Br^- ~ 77), Owens Lake "crust" ($Cl^-:Br^-$ ~ 53), and Lordsburg (Cl^-/Br^- ~ 0.7), some Br_2 production was expected. $BrNO_2$ was also observed in trace quantities when dust generated from the Owens Lake "sediment" sample was reacted with N_2O_5 (Figure 5). Although we could not quantify the yield of $BrNO_2$ (φ_{BrNO2}) from this sample, this observation is still novel and represents, to our knowledge, the first observations of $BrNO_2$ production from playa dusts and the first observation of $BrNO_2$ produced during an AFT study from real aerosol sources as opposed to commercially available salt standards. The production of Br_2 and $BrNO_2$ from the Owens Lake "sediment" sample and our observation that φ_{ClNO2} is less than unity further demonstrate the important role of competing nucleophiles, such as Br^-, when predicting yields of $ClNO_2$.[118]

Br_2 is thought to be formed either by $BrNO_2$ reacting with excess bromide or via $ClNO_2$ reacting with bromide either to form $BrNO_2$ (the latter then reacting with bromide to form Br_2) or to form BrCl (that reacts further with bromide to from Br_2). We did not observe BrCl in any experiment, consistent with previous observations.[84,119] Fickert et al.,1998[119] demonstrated that when $ClNO_{2(g)}$ is taken up by dilute bromide solutions ($<10^{-4}$ M), $BrNO_2$ is the dominant product, and for more concentrated solutions ($>10^{-3}$ M), Br_2 production is favored. However, in the absence of $ClNO_2$, Schweitzer et al.,1998[120] proposed that $BrNO_2$ efficiently reacts with Br^- to form Br_2 as a final product. We similarly observed Br_2 as the only detected gas-phase product in our AFT when using pure NaBr solutions (~0.002 M) likely because the aerosol bromide concentration was high enough to facilitate the conversion to Br_2. Using the aerosol liquid water content predicted by ISOROPPIA-II, we predict a molar concentration of $[Br^-] \sim 10^{-6}$ M for all of our playa samples resulting in dilute Br^- solutions that should produce low yields of both $BrNO_2$ and Br_2. It is still not entirely clear why the Owens Lake "sediment" produced appreciable Br_2 and $BrNO_2$, whereas Sulphur Springs Draw produced only detectable Br_2 considering the Cl^-/Br^- and $[Br^-]$ were similar for both playa samples. Our best explanation is that a more concentrated solution of Br^- forms for the Sulphur Springs Draw sample than the Owens Lake "sediment" sample and that the higher φ_{ClNO2} from the Sulphur Springs Draw would produce enough $ClNO_2$ to promote Br_2 formation via pathways described by Schweitzer et al., 1998 and Frenzel et al., 1998. Thus, prediction of the pathways for $ClNO_2$ production vs Br_2 production following reaction with N_2O_5 may not be as straightforward on playa surfaces compared to that of surfaces of simple brines and requires more in depth chemical knowledge beyond the Cl^-/Br^- value.

3.4. Atmospheric Implications. Our results demonstrate that saline dusts react efficiently with N_2O_5 to produce trace halogen gases in high yields, which are both important parameters for high production rates of $ClNO_2$. During the NACHTT campaign, a recent study in Colorado where $ClNO_2$ was measured in an inland environment, playa dusts were speculated to contribute some of the observed inland budgets of $ClNO_2$ via an indirect production mechanism caused by the acid displacement of particulate chloride from supermicron playa dust particles leading to the formation and partitioning of HCl to submicron particles that can then form $ClNO_2$.[62] Our results demonstrate that in addition to this indirect production mechanism, playa dusts are a potentially important source of particulate chloride that can also facilitate the direct production of $ClNO_2$ from reactions between N_2O_5 and submicron particles. The long-range transport of submicron playa dust particles to mountain and urban receptor sites has been observed,[52,56,121] highlighting the atmospheric relevance of our laboratory studies. Future laboratory and field studies are warranted to determine the relative importance of direct and indirect production mechanisms of $ClNO_2$ from playa dusts in different inland environments.

Yields of $ClNO_2$ from N_2O_5 uptake are typically estimated to be a function of aerosol liquid water and chloride content;[14,22,34] however, yields of $ClNO_2$ generated from playa dusts were typically overpredicted when only aerosol liquid water content and aqueous chloride were considered. We find that while some of the playa samples used in this work do behave like deliquesced NaCl, which is well-captured by this parameterization, most of our observed yields of $ClNO_2$ vary as a function of mineralogy and RH. It is likely that the mineral content, surface mineralogy, chemical composition, and the presence of hydrates play an important yet underappreciated role in determining the liquid water content and phase of particulate chloride present in playa dust aerosols (e.g., whether the chloride is aqueous or not) that is not captured in predictions of the $ClNO_2$ yield made using eq 3). Size-resolved differences in playa dust composition and reactions between minerals and N_2O_5 that compete with water and chloride resulting in a yield of $ClNO_2$ less than unity are also important considerations to accurately predict yields of $ClNO_2$ from saline dusts. Future work is needed to explore these mechanisms in detail on saline dust particles.

In addition to $ClNO_2$, some of the samples also generated Br_2 and $BrNO_2$ when reacted with N_2O_5. While halogen oxides (e.g., ClO and BrO) have been observed above playas,[59−61,122,123] our measurements demonstrate the potential for playa dusts to generate halogenated trace gases at high yields following nighttime heterogeneous chemistry. Because $Cl^\cdot$ atoms are more reactive with VOCs (and facilitate O_3 production) while $Br^\cdot$ atoms are more reactive with O_3 (and destroy O_3), an understanding of the distribution of brominated and chlorinated products generated from playa dusts is important for modeling tropospheric O_3 concentrations.[2] The CMAQ model has recently been updated to consider the heterogeneous production of $ClNO_2$ from biomass burning aerosol, sea salts, and industrial sources of aerosols.[44] On the basis of our findings, saline dusts should also be incorporated in CMAQ and analogous models as an important source of particulate chloride, and the direct formation of $ClNO_2$ from submicron playa dust particles demonstrated herein should also be included in order to accurately quantify the impact of this chemistry on inland budgets of $ClNO_2$ and the subsequent impacts on tropospheric O_3. Further, the spatial extent of playas and their emissions are expected to increase in the future as both salinization and aridification increase globally as a result of anthropogenic land use and water use practices.[124−126] Our findings suggest that increased emissions from playas will significantly impact budgets of inland $ClNO_2$ and other reactive halogens with subsequent impacts on budgets of ground-level O_3 and regional air quality.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b01112.

Description of the playa samples, dust generation setup, gas-phase compound detection, and soluble ion detection; five figures (playa photos, playa locations, laboratory setup, representative aerosol size distributions, and example of linearity between S and k_{het}) and four tables (sample coordinates, corrections to S measurements, γ_{N2O5} and φ values for all samples, and IC data) are also included (PDF)

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Notes

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