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High level ab initio calculations of clusters comprised of water, HCl, and ON-ONO2 are used to study nitrosyl chloride (ClNO) formation in gas phase water clusters, which are also mimics for thin water films present at environmental interfaces. Two pathways are considered, direct formation from the reaction of gaseous HCl with ON-ONO2 and an indirect pathway involving the hydrolysis of ON-ONO2 to form HONO, followed by the reaction of HONO with HCl to form ClNO. Surprisingly, direct formation of ClNO is found to be the dominant channel in the presence of water despite the possibility of a competing hydrolysis of ON-ONO2 to form HONO. A single water molecule effectively catalyzes the ON-ONO2 + HCl reaction, and in the presence of two or more water molecules the reaction to form ClNO becomes spontaneous. Direct formation of ClNO is fast at room and ice temperatures, indicating the possible significance of this pathway for chlorine activation chemistry in both the polar and midlatitude troposphere, in volcanic plumes and indoors. The reaction enthalpies, activation energies, and rate constants for all studied reactions are reported. The results are discussed in light of recent experiments.

1. Introduction

Heterogeneous reactions are known to play an important role in the atmosphere.1 In the stratosphere (upper atmosphere), the dramatic springtime loss of ozone in the Antarctic to generate an “ozone hole” is due to reactions of HCl with ClONO2 and N2O5 on the surfaces of polar stratospheric clouds, reactions that are otherwise too slow in the gas phase to be of importance.2–7 Heterogeneous chemistry is also believed to be important in the troposphere (lower atmosphere), but much less is known about the kinetics and mechanisms because of the difficulty of studying reactions on complex substrates at one atmosphere pressure in air and at high water vapor concentrations.

Only recently has the possibility of interactions of surface-bound oxides of nitrogen with other species been recognized. Raff and co-workers8 showed experimentally that gaseous HCl reacts with surfaces exposed to NO2 and H2O to generate ClNO, which could be a source of highly reactive chlorine atoms both outdoors and indoors. This was shown to have the potential to impact ozone levels in coastal urban areas. The proposed mechanism involves the asymmetric NO2 dimer and NO+NO2− as key surface-bound intermediates.9 Figure 1, for example, shows that a band due to ClNO (centered at 1805 cm−1) appears when HCl and water vapor are added to a reaction cell containing NO2 (seen initially at ~1600 cm−1) and high surface area silica. The reaction is essentially immediate under these conditions and results in the formation of ClNO in a yield of 47 ± 1% (2 s) relative to the amount of NO2 consumed. The silica used in these experiments mimics the oxide surfaces present on urban surfaces and in mineral dust9–11 that are important substrates for heterogeneous tropospheric chemistry.

Figure 1. Transmission FTIR spectroscopy is used to monitor the reaction during the addition of HCl (165 ppm) and water vapor (~2% relative humidity) at t = 200 s to a reaction cell containing NO2 (35 ppm) and SiO2 pellets. Red and green lines follow the concentration of NO2 and ClNO, respectively, as a function of time. Two spectra taken at t = 0 s (red spectrum) and t = 400 s (green spectrum) are overlapped and shown in the inset. These spectra show that the NO2 band, which is positioned at ~1600 cm−1 at time zero, is replaced upon addition of HCl/water mixture by the ClNO band at 1805 cm−1 and water vapor lines.

Little is known about the detailed kinetics and mechanisms of the heterogeneous formation of ClNO. Such reactions on surfaces are typically close to thermoneutral and can be driven in either direction depending on the concentrations of reactants and products. As a result, it is critical to have quantitative estimates of all possible reaction paths in both directions, and in particular, to elucidate the role of water that is typically present on tropospheric surfaces.

To complicate matters further, it has been recognized for decades that NO2 in the presence of water vapor and surfaces generates gas phase HONO.9,12–14 This hydrolysis reaction merits computational studies for several reasons. First, nitrous acid...
absorbs light in the 300–400 nm region and photolyzes to form OH + NO with a quantum yield of one.\textsuperscript{15} This is a major OH source at sunrise, and even when averaged over 24 h, accounts for as much as half of the total OH generated during the day.\textsuperscript{16,17} The hydroxyl radical reacts rapidly with organic compounds in air, initiating a complex set of reactions involving oxides of nitrogen (NO\textsubscript{x}) and forming a variety of secondary air pollutants such as O\textsubscript{3} and particles,\textsuperscript{2} which have well-known deleterious effects on health, visibility, and climate.\textsuperscript{18–21} As a result, understanding NO\textsubscript{2} hydrolysis is important in its own right.

Not only is the NO\textsubscript{2} hydrolysis reaction important due to its potential to form nitrous acid, but the hydrolysis may occur in parallel with the HCl reaction, potentially suppressing the formation of ClNO. In addition, if nitrous acid is formed it may react with HCl, providing an alternative pathway for ClNO formation.

In previous work, it was surprising that water vapor enhanced the ClNO production from surface-deposited NO\textsubscript{2} and gaseous HCl.\textsuperscript{3} Although the catalytic role of water has been recognized in other systems of atmospheric relevance,\textsuperscript{22–26} this particular case is unusual in that water can also hydrolyze NO\textsubscript{2} to form HONO in a competing channel. As a result, it is important to examine computationally the kinetics and mechanisms of both the NO\textsubscript{2} hydrolysis and the reaction with HCl in the presence of water. The computations also address the usefulness and effectiveness of small water clusters for modeling air/water interface reactions and the chemistry occurring in water clusters in the gas phase\textsuperscript{26} in the environment. Furthermore, the calculations elucidate the temperature dependence of the reactions, which is critical because this chemistry may occur in polar regions as well, where very active chemistry and photochemistry involving oxides of nitrogen has been observed.\textsuperscript{30–33} This chemistry potentially contributes to chemistry indoors as well\textsuperscript{8} and thus may be of general environmental importance.

2. The Computational Model

The anticipated surface-enhanced reactions that may lead to the formation of ClNO in the atmosphere were computationally modeled. The potential source of ClNO was taken to be asymmetric N\textsubscript{2}O\textsubscript{4}, namely ON-ONO\textsubscript{2}, which has been proposed to be a key intermediate form of surface deposited NO\textsubscript{2}.\textsuperscript{9} Pimentel et al. conducted a series of DFT/B3LYP calculations on two possible pathways for the formation of the asymmetric NO\textsubscript{2} dimer, ON-ONO\textsubscript{2}.\textsuperscript{34,35} They predicted that one channel takes place via NO\textsubscript{2} dimerization to form the most stable symmetric NO\textsubscript{2} dimer, which then isomerizes into ON-ONO\textsubscript{2}.\textsuperscript{34} A fairly high energy barrier of 31 kcal/mol was found for the isomerization in the gas phase. Water significantly lowers the isomerization energy requirements to 21 kcal/mol, which however is still quite substantial for a thermal reaction. Direct dimerization of NO\textsubscript{2} to form ON-ONO\textsubscript{2}, investigated in the gas phase, was found to be barrierless and exothermic and is thus thermodynamically and kinetically favorable.\textsuperscript{35}

The asymmetric NO\textsubscript{2} dimer, ON-ONO\textsubscript{2} is a highly reactive species that may react directly with HCl to form ClNO

\[
\text{ON-ONO}_2 + \text{HCl} \rightleftharpoons \text{CINO} + \text{HNO}_3 \quad (1)
\]

On the other hand, ON-ONO\textsubscript{2} may also undergo hydrolysis to yield HONO

\[
\text{ON-ONO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HONO} + \text{HNO}_3 \quad (2)
\]

Formation of ClNO from HONO and HCl (reaction 3) in the gas phase is slow.\textsuperscript{36–42}

In short, there are two plausible channels for ClNO formation: A direct reaction between ON-ONO\textsubscript{2} (reaction 1) and an indirect 2-step channel involving formation of HONO and its further reaction with HCl (reaction 2 followed by reaction 3). The relative importance of these and the role of water is unknown. The present study is designed to address these significant gaps in our understanding.

The following assumptions were made. First, NO\textsubscript{2} on the surface is assumed to be in the form of the highly reactive asymmetric NO\textsubscript{2} dimer, namely ON-ONO\textsubscript{2}. It is further assumed that an HCl molecule from the gas phase collides directly with ON-ONO\textsubscript{2} on the surface, or it gets trapped on the water surface long enough to form a complex with ON-ONO\textsubscript{2}. A similar picture is considered for the reaction between HONO and HCl.

In all cases, only a few water molecules are considered to be essential active participants and hence are included in the model cluster. The rest of the water molecules constituting the water surface play a secondary role and are considered to be spectator molecules. In other words, the surface reaction is modeled as taking place in a small cluster that involves the bare minimum number of reactive species, ON-ONO\textsubscript{2} or HONO, HCl, and/or the critical number of water molecules, which is determined by following the trend in the effect that water exhibits on the particular reaction. This approach was taken to make calculations viable at higher ab initio levels of theory such as second order perturbation theory (MP2) and coupled cluster theory, while at the same time evaluating whether such microscopic models are able to provide useful insights into the macroscopic systems studied in laboratory experiments and found in the atmosphere where ClNO formation is taking place.

Structures and stabilities of the model clusters were investigated at ab initio levels of theory. The transition states and minima that were located enabled calculations of rate constants under thermal conditions. Dynamic reaction path (DRP) calculations were performed providing snapshots of the reaction along the trajectory, thus allowing us to probe important questions regarding lifetimes of the complexes with respect to the time scale of the reaction. It should be noted that the reaction rate constants derived from our models are not meant to represent absolute rate constants. They are strictly meant to probe the relative importance of the reaction pathways leading to the formation and loss of ClNO. Unique insights into the reaction mechanisms and the role of water are provided by these calculations. Finally, some parallels between the experimental and model systems are drawn, and the applicability of these to actual atmospheric systems is addressed.

3. Methodology

Computational Details. The reaction mechanisms were explored by locating stationary points on the potential energy surfaces by employing second-order Møller–Plesset\textsuperscript{43–45} (MP2) perturbation theory with the cc-pVDZ basis set\textsuperscript{46,47} (denoted MP2/cc-pVDZ). The MP2 level of theory was chosen due to its effectiveness in modeling water clusters and complexes of water with N\textsubscript{2}O\textsubscript{4}.\textsuperscript{48–51} Minima and saddle point optimizations\textsuperscript{52–54} were carried out with the largest component of the analytic
A successful DRP trajectory to yield ClNO formation was enough to permit such calculations at a picosecond time scale. A least linear motion path method was used to obtain an initial guess of the transition state structure.

A recent study found that MP2 paired with a variety of basis sets, including cc-pVDZ that was used in the current work, does not give very accurate interaction energies when applied to systems incorporating cyclic hydrogen bonding interactions, which are present in many of the stationary points located in this study. Thus, to attain high accuracy for reported activation energies, rate constants, reaction enthalpies, and binding energies, single point energy coupled cluster calculations, CCSD(T)\(^{63,64}\) with the cc-pVTZ basis set\(^{56,47}\) [denoted as CCSD(T)/cc-pVTZ] were performed on the stationary structures already located on the MP2/cc-pVDZ potential energy surface. Zero point energy (ZPE) contributions to the activation energy at CCSD(T)/cc-pVTZ were calculated by scaling the MP2/cc-pVDZ harmonic ZPE by 0.95.\(^{65}\) Rate constants were calculated at four temperatures, 250.15, 273.15, 298.15, and 323.15 K using transition state theory. Binding energies, \(E_{\text{bind}}\) were calculated using CCSD(T)/cc-pVTZ single point energies corrected for ZPE contributions.

Dynamic reaction path calculations\(^{56-73}\) that utilize classical trajectories and ab initio potential energy surfaces were performed when the computed lifetime of the reaction was short enough to permit such calculations at a picosecond time scale. A successful DRP trajectory to yield CINO formation was obtained at the MP2/cc-pVDZ level of theory by providing an initial kinetic energy \(E_k = \frac{3}{2}RT\) = 9.8 kcal/mol at \(T = 300\) K to the already located (ON-ONO\(_2\))·(HCl)·(H\(_2\)O) minimum structure.

All of the calculations were carried out using the GAMESS\(^{74,75}\) package, and MacMolPlot\(^{76}\) was used for molecular visualization.

**Experimental Methods.** The reaction of HCl with NO\(_2\) in the presence of fumed SiO\(_2\) pellets was studied using Fourier transform infrared (FTIR) spectroscopy. Both the apparatus and experimental techniques are described in detail elsewhere.\(^8\) In short, nitrogen dioxide was admitted from a 4 L bulb on the attached vacuum line resulting in a concentration of 35 parts per million by volume (ppm) in a reaction cell (\(V = 43\) cm\(^3\)) containing 1.0 g of SiO\(_2\) powder (BET surface area 329 m\(^2\)/g) that was pressed into pellets. The reaction was initiated by opening the reaction cell for 10 s to an attached 490 cm\(^3\) bulb containing HCl (99.995%, Matheson) and water vapor. The final concentrations of HCl and water vapor in the reaction cell were 165 ppm and 1.4 \(\times\) 10\(^{16}\) molecules cm\(^{-3}\) (~2% relative humidity), respectively. Concentrations of NO\(_2\), CINO, HCl, and H\(_2\)O were determined from calibrations measured in our laboratory. Nitrogen dioxide was synthesized from the reaction of NO with oxygen and CINO was prepared from the reaction of NO with Cl\(_2\), as described previously.\(^4,48\)

### 4. Results and Discussion

The present study addresses significant gaps in our understanding regarding the relative importance of the two plausible CINO-forming channels. They are the direct reaction between ON-ONO\(_2\) and HCl (reaction 1) and the indirect two-step channel involving formation of HONO and its subsequent reaction with HCl (reaction 2 followed by reaction 3). Of particular interest is the role of water in these reactions.

**Binding Energies.** The binding energies for selected binary complexes are calculated as differences in CCSD(T) single point energies of the binary complexes and separate species minima found on the MP2 surface. The values are corrected for scaled ZPE contributions and plotted in Figure 2. The highest binding energy of 9.1 kcal/mol was found in the case of the HNO\(_3\)·water complex. Binding energies of around 6 kcal/mol were calculated for HONO·water and (HONO)·(HNO\(_3\)) complexes. The complex of CINO·water was found to be one of the most weakly bound, with a binding energy of only 2.4 kcal/mol.

A somewhat surprising finding is that the HCl·water binding energy is higher than that of water·water. However, similar results have been published by Geiger et al. who reported a higher binding energy for (HCl)·(H\(_2\)O)\(_3\) than for the water·water tetramer complexation\(^7\) where the formation of a shorter hydrogen bond in the former complex was associated with the stronger binding. The calculations presented here also exhibit a shorter hydrogen bond of 1.83 Å for the (HCl)·(H\(_2\)O) complex as compared to 1.94 Å in water dimer.

**ON-ONO\(_2\) + HCl.** The reaction of ON-ONO\(_2\) with HCl was investigated in the absence and presence of one and two water molecules that were, upon optimization, bound in the reactants. Structures of the reactants, transition states, and products are
shown in Figure 3, while activation energies and reaction enthalpies are given in Figure 4.

A weakly bound (ON-ONO₂)·(HCl) complex with a binding energy of only 2.4 kcal/mol (Figure 2) was formed without a barrier upon optimization of initially located minima at a 4 Å distance. This complex (Figure 3, R₀) is reactive toward the formation of ClNO and HNO₃ with an activation energy of 11.5 kcal/mol. The reaction proceeds through a four-membered transition state structure that is strained, as evidenced by a H–Cl–N angle of only 33° (Figure 3, TS₀). The reaction is exothermic by 10 kcal/mol. The products CINO and HNO₃ are weakly bound (2.3 kcal/mol), suggesting that CINO may be easily desorbed into the gas phase from thin films containing nitric acid.

Upon addition of one water molecule to the above-mentioned (ON-ONO₂)·(HCl) minimum energy structure, a (ON-ONO₂)·(HCl)·(H₂O) complex was formed without a barrier (Figure 3, R₀→R₁). This species is even more reactive toward CINO formation with an activation energy of only 5.3 kcal/mol. In this eight-membered transition state (TS₁), the water molecule is incorporated into the previously mentioned four-membered ring, thus opening the H–Cl–N angle from 33° in the absence of water to 94° in the presence of water and relieving the ring strain. Thus, water stabilizes the transition state by facilitating proton transfer from HCl to NO₃⁻ via H₃O⁺, where δ = +0.528. Formation of CINO in the presence of one water molecule is also exothermic with ΔH_r = −12.9 kcal/mol.

A barrierless channel for CINO formation was found through an optimization carried out in the presence of a second water molecule placed at a 4 Å distance from the (ON-ONO₂)·(HCl)·(H₂O) minimum structure (Figure 3, R₁→P₂).

The rate constants calculated in the absence and presence of one water molecule (Figure 5 and 6) and the absence of a barrier in the presence of two water molecules indicate that all of these reactions are irreversible with respect to the formation of CINO. At room temperature, the forward reaction rate constant in the absence of water is 6 orders of magnitude larger than that for the reverse reaction, with the gap increasing in the presence of water.

Clearly, water has a profound effect on the kinetics of this reaction. The forward reaction is very slow in the absence of water, k_f(298 K) = 2 × 10^2 s⁻¹, whereas the addition of one water molecule accelerates the reaction by 5 orders of magnitude, k_f(298 K) = 2 × 10^7 s⁻¹. Temperature has a small positive effect on the rate constants (e.g., for one water, k_f(250 K) = 4 × 10^6 s⁻¹). The rate constants are derived from transition states of the clusters undergoing a reaction and do not include steps leading to the formation of prereaction complexes. Negative temperature dependence is often observed for reactions involving water clusters. This effect is due to the decreasing formation probability of clusters in the gas phase with increasing

Figure 3. Reaction mechanism for direct CINO formation from the reaction of ON-ONO₂ and HCl studied in the absence and presence of 1 and 2 water molecules. Stationary structures are obtained at the MP2/cc-pVDZ level of theory, labeled as R (reactant), TS (transition state), and P (product), accompanied by a number of water molecules involved in the reaction. Bond lengths are given in Ångströms.

Figure 4. Activation energies for forward, ΔE_a→ (kcal/mol), and reverse reactions, ΔE_a← (kcal/mol), and reaction enthalpies for forward reactions, ΔH_r (kcal/mol), calculated at the CCSD(T)/cc-pVTZ level of theory. The numerical values are shown in the table below.
temperature. The calculations here do not include such an effect, since the model deals with clusters formed on a water surface. For this case, we carry out rate calculations for the clusters as thermally equilibrated reagents.

The high rate of the water catalyzed forward reaction (Figure 3, \( R_1 \rightarrow P_1 \)) is computationally convenient for ab initio DRP calculations, as the reaction is complete within \( \sim 250 \) fs. The energy and relevant bond lengths are plotted as a function of the reaction coordinate in Figure 7. In particular, proton transfers between HCl and \( H_2O \) and \( H_3O^+ \) and \( NO_3^- \) were followed. The oscillation frequency of the proton changes at the time of its transfer and returns to a regular pattern as soon as the transfer is complete. These irregular patterns in proton oscillations are observed for each proton transfer event (circled in Figure 7).

The first proton transfer takes place between HCl and \( H_2O \) to form \( H_3O^+ \), as the system reaches the transition state. The second proton is then transferred from \( H_3O^+ \) to \( NO_3^- \) as the products ClNO and HNO3 are formed and water is regenerated at \( \sim 200 \) fs into the reaction time. At the same time the energy decreases by nearly 10 kcal/mol.

These rapid proton transfers occur on a time scale similar to one reported for the proton transfer from \( H_3O^+ \) to \( NO_3^- \) in large water clusters.\(^5^0\) Interestingly, \( H_5O_2^+ \) does not seem to transfer \( H^+ \) as effectively (see the rate constants in Figures 5 and 6). Therefore, our study suggests that the above reaction is fundamentally a single water molecule catalysis.

The ionization of ON-ONO2 was followed as a function of partial charges on the NO\( ^{\delta^+} \) and NO\( ^{\delta^-} \) moieties as it complexes to HCl and water (Figure 3, ON-ONO2, \( R_0 \) and \( R_1 \)). The partial charge on NO\( ^{\delta^+} \) increases from \( +0.335 \) in the free molecule to \( +0.390 \) upon complexation with HCl. Subsequent addition of a water molecule leads to yet another increase in the partial charge of \( \delta^+ \) to \( \delta = +0.450 \). The distance between the NO\( ^{\delta^+} \) and NO\( ^{\delta^-} \) moieties increases from 1.74 Å in the free molecule to 1.83 Å in the complex with water and HCl. These trends indicate that ON-ONO2 tends to ionize upon binding to HCl/H\(_2O\), similar to the previous findings\(^9\) where ON-ONO2 ionizes within femtoseconds on small water clusters.

ON-ONO2 + H\(_2O\). Hydrolysis of NO\(_2\) to form HONO, reaction 2, is well documented\(^9\) and is expected to provide a competing reaction pathway to the direct formation of CINO.

Figure 5. The unimolecular rate constants, \( k \) (s\(^{-1}\)), for the reactions studied plotted as a function of temperature. The values of rate constants are calculated using transition state theory at four different temperatures, 250, 273, 298, and 323 K. Lines connecting the data points are guides for the eye.

Figure 6. The reaction mechanism for CINO formation. The unimolecular rate constants, \( k \) in s\(^{-1}\), calculated at 250 K and room temperature. The values are tabulated for both forward and reverse reactions as a function of the number of bound water molecules in reactants of forward reactions.
via reaction 1. Furthermore, it is possible that it may be the dominant channel and that HONO rather than ON-ONO_2 is the key precursor to ClNO formation via reaction 2.

The hydrolysis of ON-ONO_2 was investigated computationally, and the stationary structures are presented in Figure 8. Water binds without barrier to ON-ONO_2 to form a (ON-ONO_2)·(H_2O) complex, R1, having a binding energy of 3.5 kcal/mol (Figure 2). The hydrolysis reaction proceeds through the six-membered ring transition structure TS1 that is characterized by increased ionization within the ON-ONO_2 and H—OH species. This is shown by comparing the TS1 partial charges on the water moiety, δ(H) = +0.251 and δ(OH) = −0.093, with those in the reactant R1, δ(H) = +0.150 and δ(OH) = −0.152. Likewise, the charges on the ON-ONO_2 fragment in TS1, δ(ON) = +0.433 and δ(NO_3) = −0.592, may be compared with those in R1, δ(ON) = +0.397 and δ(NO_3) = −0.395. An activation energy of 8.7 kcal/mol must be overcome for HONO to be formed (Figure 4). The binding energy of HONO to HNO_3 in P1 is somewhat high (−6.0 kcal/mol in Figure 2) indicating that HONO may remain adsorbed to the surfaces containing nitric acid.

In contrast to the N_2O_4 + HCl reaction where a single water molecule is responsible for catalysis, an additional water molecule has little effect on the activation energy for N_2O_4 hydrolysis. Instead, the (ON-ONO_2)·(2H_2O) complex is formed without a barrier upon initial placement of the additional water molecule at a 4 Å distance from (ON-ONO_2)·(H_2O), (Figure 8, R1→R2). Complex R2 reacts via transition state TS2 to form HONO with an activation energy of 9.2 kcal/mol in the presence of an additional water molecule, compared to the activation energy of 8.7 kcal/mol calculated in the presence of only one water molecule. The ON-ONO_2 + H_2O reaction is thermodynamically favorable with a reaction enthalpy of −9.7 kcal/mol in the absence and −13.8 in the presence of one bound water molecule (Figure 4).

The calculated rate constants favor the forward reaction that forms HONO (Figures 5 and 6) at all temperatures. Temperature has a small effect on the rate constant with only a roughly 10-fold increase from 250 to 298 K. Although hydrolysis of ON-ONO_2 is a relatively fast process, direct formation of ClNO is 2 orders of magnitude faster, even when catalyzed by only one water molecule, not to mention the barrierless channel that exists in the presence of two water molecules. Nevertheless, these two pathways of HONO and ClNO formation are...
The reaction of HONO with HCl is considered as a second step in an indirect ClNO formation process. All reactants, transition states and products are shown in Figure 9. The reaction mechanism was studied in the absence and then in the presence of one and two water molecules. In the absence of water, HCl binds weakly to HONO with a binding energy of 2.7 kcal/mol (Figure 2). Proton transfer from HCl to HONO takes place through a strained four-membered ring TS0, which is reflected in the relatively high activation energy of 19.1 kcal/mol. The reaction is exothermic by 2.7 kcal/mol. These findings are in qualitative agreement with a previously published theoretical study, which reported \( \Delta E_a = 12.5 \text{ kcal/mol} \) and \( \Delta H_f = -5.5 \text{ kcal/mol} \). The CINO and H\(_2\)O are weakly bound products, P0, with a binding energy of 2.4 kcal/mol (Figure 2), indicating that CINO may be easily desorbed from aqueous clusters or thin films.

The first and second water molecules bind to R0 without a barrier to form structures R1 and R2, respectively (Figure 9). An interesting feature of transition states TS1 and TS2 is that water forms a new ring, rather than being incorporated into the existing four-membered ring. This is somewhat unexpected when compared to the reactions of ON-ONO\(_2\) with HCl, where water relieves the ring strain. However, the activation energies are still lowered to 15.9 and 12.7 kcal/mol in the presence of one and two water molecules, respectively. In the case of the HONO reaction with HCl, water stabilizes the transition states through hydration of Cl\(^{+}\), thus allowing for an increase in partial charge from \(-0.536\) to \(-0.621\) and finally \(-0.667\), in the absence and presence of one and two water molecules, respectively. Thus, water facilitates the ionization of HCl.

To explore the reactivity of fully ionized HCl, the reaction of the smallest stable zwitterionic cluster, H\(_2\)O\(^+\)·(H\(_2\)O)\(_2\)·Cl\(^{-}\), with HONO was examined (Figure 10). Complexation of HONO and the zwitterionic cluster proceeds without a barrier to yield the structure labeled R in Figure 10. Within the complex R, the proton may be transferred from one complexed water molecule to another via transition state \( TS(R-I) \) that contains the H\(_2\)O\(^+\)·Cl\(^{-}\) species (circled in Figure 10). The activation energy for this proton transfer is calculated to be \(-0.7 \text{ kcal/mol} \). The small negative value of calculated activation energy indicates the absence of an energy barrier. Furthermore, structures R and I are in thermoneutral equilibrium.

In short, upon barrierless and thermoneutral reorganization within complex R, the complex I is formed, in which the protonated water molecule is adjacent to the complexed HONO molecule. Thus, in complex I, HONO protonation is enabled and CINO may be formed via transition state \( TS(I-P) \) with a calculated activation energy of 9.2 kcal/mol.

**CINO + H\(_2\)O.** It is of interest to examine the CINO hydrolysis reaction as a possible pathway for the decomposition of CINO. Loss of CINO observed in the atmosphere may be attributed to its hydrolysis to form HONO and HCl, which corresponds to the reverse of the HONO + HCl reactions discussed above and presented in the Figure 9. The most important finding is that as the number of water molecules increases from one to five, the CINO hydrolysis becomes very fast and irreversible. When CINO is complexed to five water molecules, the hydrolysis rate constant is calculated to be \( 5 \times 10^{10} \text{ s}^{-1} \), with a reaction enthalpy of \(-8.4 \text{ kcal/mol} \). Thus, hydrolysis of CINO is kinetically and thermodynamically favorable when CINO is complexed to such high number of water molecules.

**Comparison of Model Predictions and Experimental Results.** Experiments firmly establish that CINO is formed from the heterogeneous reaction of NO\(_2\) with HCl and that the reaction is enhanced by water.\(^8\) The yield of CINO was measured to increase from 25% under relatively dry conditions to \( \sim 50\% \), which is the maximum yield expected for the reaction represented by reaction 1. Attempts to generate CINO from the reaction of HCl on silica previously exposed to HONO were unsuccessful.\(^8\)

Model calculations provide unique insights into the mechanism of CINO formation. The investigated reactions and corresponding reaction rate constants at 250 K and room temperatures are summarized in Figure 6. Formation of CINO takes place predominantly via direct reaction of HCl with ON-ONO\(_2\). There is a pronounced catalytic effect due to incorporation of a single H\(_2\)O molecule into the ring of the transition state structure. This relieves the ring strain compared to the four-membered transition state formed in the absence of water. Furthermore, a barrierless channel was found in the presence of two water molecules. This reaction is very fast even at low temperatures, making this relevant for chemistry in the tropopause,\(^10\) the midlatitude and polar troposphere,\(^8,30,33\) in volcanic plumes,\(^101–103\) and indoors.\(^8\) Catalytic effects of incorporating water into the transition state have been identified in other systems of atmospheric interest,\(^26–29\) including the reaction of HCl with ClONO\(_2\) to form Cl\(_2\), which occurs on polar stratospheric clouds.\(^25\)
The calculations show that the competing hydrolysis of ON-ONO₂ is not fast enough to significantly suppress the direct channel leading to CINO formation. The indirect formation of CINO via the reaction of HONO with HCl can only make a secondary contribution, which is again in agreement with the experimental observations.8

The calculations also predict that the hydrolysis of ClNO strongly depends on the number of water molecules present and becomes very fast in the presence of five water molecules. This is consistent with measurements of the uptake and hydrolysis of ClNO in bulk liquid water.104,105 Conversely, the loss of ClNO during experiments done in the presence of high surface area silica at relative humidities between 9 and 13% is slow with a first order rate constant of $10^{-5}$ s$^{-1}$. Water on silica surfaces, including glass and quartz, is known to form a structured, “icelike” layer due to strong hydrogen-bonding interactions with surface SiOH groups.106 It is only at high relative humidity, approaching 80%, that sufficient water is adsorbed. At this point, water–water interactions become important and the spectroscopic signature starts to be indicative of that of bulk liquid water.107 The slow ClNO hydrolysis on silica in the presence of water vapor at 9–13% relative humidity indicates that the strongly adsorbed water is not freely available to react with CINO.

In the case of ClNO formed during the reaction of HCl with surface-adsorbed oxides of nitrogen, there is an additional factor to consider. Reaction 2 generates HNO₃ simultaneously with the formation of ClNO. It is known that nitric acid forms hydrates with one, two, and three water molecules on the surface.51,108,109 Furthermore, the highest calculated binding energy among investigated binary complexes is found for the (HNO₃)·(H₂O) complex (9.1 kcal/mol see Figure 2). Thus, HNO₃ may bind water that would otherwise be available to hydrolyze the formed CINO. This emphasizes the importance of water on surfaces and its impact on the chemistry of atmospherically relevant surfaces. At the lower relative humidity (<70%) typical of many atmospheric situations, water adsorbed on surfaces does not behave like bulk liquid water. In the case of NO₂ and its reaction with HCl, surface-adsorbed water participates in NO₂ hydrolysis and catalyzes the reaction with HCl, yet the generated CINO is not hydrolyzed. At higher relative humidity (>70%) and in systems where water films resemble bulk water, the hydrolysis of CINO will likely dominate and prevent appreciable exchange of ClNO from the surface to the gas-phase, as shown experimentally for the uptake of CINO on aqueous solutions.105 This highlights the unique chemistry associated with heterogeneous reactions in the atmosphere and the importance of understanding at a molecular level the nature of water and its interactions with surfaces and with atmospheric gases.

5. Concluding Remarks

This work shows that small clusters can successfully model reactions that take place at the water/air interface to provide insights into the mechanisms and kinetics of these reactions. While using only one or two water molecules is not representative of water on surfaces in the troposphere, it was chosen to explore the catalytic effect of water on the rates of the heterogeneous reactions of interest. The clusters provide a representation of water at the water/air interface where oxides of nitrogen are present and HCl approaches from the air above. It is, of course, possible that the HCl is also trapped for a brief duration of time at the water surface, before forming an (ON-ONO₂)·(H₂O)·(HCl) complex. Thus, model clusters comprised of (ONONO₂)·(H₂O)·(HCl) encompass the species that are actively involved in the chemistry, while omitting the
spectator water molecules that are less important. Our studies of N₂O₄ hydrolysis started with asymmetric ON-ONO₂. Theoretical treatment of the hydrolysis of symmetric N₂O₄ has been reported and the reaction was shown to proceed with a significant barrier (>30 kcal/mol). The following parallels can be drawn between the model cluster and the experimental system. The gas phase calculations show that once ON-ONO₂ encounters HCl, a complex will form without a barrier. The subsequent reaction will take place rapidly, as indicated by the femtoseconds time scale observed in the DRP simulations of the reaction in the presence of one water molecule, as well as by the lack of an energy barrier in the presence of two water molecules. The most important computational finding is that a single water molecule catalytic effect was observed, thus favoring direct CINO formation rather than ON-ONO₂ hydrolysis.

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References and Notes
