Chlorine activation indoors and outdoors via surface-mediated reactions of nitrogen oxides with hydrogen chloride

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Gaseous HCl generated from a variety of sources is ubiquitous in both outdoor and indoor air. Oxides of nitrogen (NOy) are also globally distributed, because NO formed in combustion processes is oxidized to NO2, HNO3, N2O5 and a variety of other nitrogen oxides during transport. Deposition of HCl and NOy onto surfaces is commonly regarded as providing permanent removal mechanisms. However, we show here a new surface-mediated coupling of nitrogen oxide and halogen activation cycles in which uptake of gaseous NO2 or N2O5 on solid substrates generates adsorbed intermediates that react with HCl to generate gaseous nitrosyl chloride (CINO) and nitryl chloride (CINO2), respectively. These are potentially harmful gases that photolyze to form highly reactive chlorine atoms. The reactions are shown both experimentally and theoretically to be enhanced by water, a surprising result given the availability of competing hydrolysis reaction pathways. Airshed modeling incorporating HCl generated from sea salt shows that in coastal urban regions, this heterogeneous chemistry increases surface-level ozone, a criteria air pollutant, greenhouse gas and source of atmospheric oxidants. In addition, it may contribute to surface-level ozone, a criteria air pollutant, greenhouse gas and source of atmospheric oxidants. In addition, it may contribute to

Formation of NO+NO3 is thought to be from autoionization of asymmetric N2O4 (ONONO2), possibly formed by sequential uptake and reaction of NO2 on the surface (15). Recent theoretical studies (16) show that once ONONO2 is formed, it is converted within femtoseconds to NO+NO3. Based on experimental studies of NO2 on ice films, conversion of NO+NO3 to HONO via reaction [3] is also fast (17, 18). To the best of our knowledge, there are no reports of other reactions of the ion pair that compete with the reaction with water.

Heterogeneous chemistry | lower atmosphere

Gaseous HCl levels reaching concentrations of a few parts-per-billion (ppb) (vol/vol) have been measured in polluted air and in some indoor settings (1–6). Direct emissions include garbage burning (7), incineration of municipal and medical wastes, burning of biomass, agricultural products and coal, and industrial processes, e.g., semiconductor and petroleum manufacturing (5). Natural sources in air include volcanic eruptions and reactions of sea salt and organochlorine compounds (5). Removal indoors and in the boundary layer is largely by deposition. Because many of these HCl sources involve combustion or occur in polluted urban areas, oxides of nitrogen are typically present simultaneously.

Although heterogeneous nitrogen oxide reactions on airborne particles and boundary layer surfaces are known to be important in the atmosphere, their kinetics and mechanisms remain elusive (8). For example, the hydrolysis of NO2 on surfaces,

\[ 2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \]  

[1]

generates gas phase nitrous acid (HONO), a major OH source in continental regions (8, 9), and HNO3. Nitric acid and other, as yet unidentified, oxides of nitrogen, NOy (NOy = NO + NO2 + HNO3 + N2O5 + ...), are strongly adsorbed on surfaces and when they are irradiated, generate HONO, NO and NO2 (10–13), even in supposedly “clean” systems (14). Based on a variety of experimental studies, the surface complex NO+NO3 has been proposed to be a key intermediate (8) in the hydrolysis of NO2 and the precursor of HONO in this system:

\[ \text{NO}^+\text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3. \]  

[3]

This article presents a combination of experiments and theory that demonstrate new chemistry in which surface-bound oxides of nitrogen from the uptake of NO2 or N2O5 react with gaseous HCl to form CINO and CINO2, respectively, potentially harmful gases (21) that photolyze to form chlorine atoms. We show that uptake of oxides of nitrogen and HCl on surfaces is not necessarily a permanent removal mechanism, but rather can be an intermediate step on the way to generating more reactive gases. Fundamental molecular insights gained from theoretical calculations confirm the experimental observations that water has a remarkable effect on this chemistry and imply that this chemistry is likely under atmospheric conditions, both outdoors and indoors. Indeed, our airshed model calculations demonstrate the potential importance of this


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novel chemistry in polluted marine regions where HCl from sea salt reactions and NO2 from urban emissions coexist. It is clear from this work that uptake of oxides of nitrogen and HCl on surfaces may contribute to chemistry and photochemistry in previously unrecognized ways both indoors and outdoors, including in coastal regions and downwind of waste, coal and biomass combustion, and industrial processes that generate HCl.

Results and Discussion

NO2 Surface Reaction. The experiments use a flow system designed to deliver controlled amounts of NO2, HCl and water vapor in a stream of nitrogen to one of a set of parallel borosilicate glass reaction chambers before passing through an optical cell in a Fourier transform infrared (FTIR) spectrometer. One chamber contains silica (SiO2) powder pressed into pellets, which provide large surface areas for the heterogeneous chemistry, whereas the second, empty chamber acts as a bypass. Silica powder is selected to mimic silicate-rich urban surfaces and some of the oxide surfaces present in mineral dust (8, 22, 23), which are important substrates for heterogeneous tropospheric chemistry. Fig. 1A shows that CINO is formed efficiently when a stream of reactants passes through the chamber containing SiO2, but not the bypass. The likely mechanism involves reaction of NO2+HCl:

$$\text{NO}_2 + \text{HCl} \rightarrow \text{CINO} + \text{HNO}_3. \quad [5]$$

The average ratio of CINO formed to NO2 reacted, $\Delta$[CINO]/$\Delta$[NO2], is $0.39 \pm 0.01$ (2 s) at a relative humidity of 0.5%. The reactor containing SiO2 has $\sim 10^4$ times more surface area than the bypass, and its effect on CINO formation confirms the heterogeneous nature of the reaction, which is extremely slow in the gas phase (24).

To study the relative humidity dependence, a cell used in static mode (i.e., where reactants are added to the cell and allowed to react in situ) is positioned in the FTIR such that the IR beam interrogates the gas over the top of a bed of SiO2 pellets. Nitrogen dioxide is introduced from a bulb on the attached vacuum line and dioxide is introduced from a bulb on the attached vacuum line and interface may be much slower than what is expected to occur in bulk water (28, 29).

As shown in Fig. 1B, $\Delta$[CINO]/$\Delta$[NO2] is 0.25 under anhydrous conditions, but doubles to the theoretical yield implied by reactions [2] and [5] when the relative humidity is $>5\%$ ($3 \times 10^{16}$ molecules cm$^{-3}$). Not only does the conversion of NO2 to CINO occur at relative humidities (RH) found in the atmosphere, but surprisingly, water actually enhances the reaction despite the possibility of competition from reaction [3]. A catalytic role of water in thermal and photochemical reactions has been reported for other systems (25–27). However, to the best of our knowledge it has not been reported for a case involving thin water films on a solid substrate where water can also participate in a competing reaction. It is also notable that separate experiments (see SI Text) show that water vapor does not enhance the heterogeneous hydrolysis of CINO in this system. This suggests that under some conditions, loss of CINO to aerosol particles and surfaces at the terrestrial-air interface may be much slower than what is expected to occur in bulk water (28, 29).

Fig. 1C shows the effect of adding water alone to a reaction chamber containing NO2 and SiO2 pellets. The gas-phase concentration of NO2 decreases with each addition of water vapor as it is taken upon the SiO2 surface, facilitating NO2 uptake, and forming gas phase HONO via reaction [3]. When HCl is added, CINO is formed rapidly, indicating that under these conditions reaction [5] competes with reaction [3]. Although these experiments are performed using higher mixing ratios than found in the atmosphere, the fact that similar CINO yields are obtained with NO2 concentrations varying over 2 orders of magnitude (Fig. 1A–C) is a good indication that this chemistry will occur at lower concentrations typically found in air both indoors and outdoors.

Because HONO is known to react with HCl heterogeneously to form CINO (30, 31), the possibility that HONO is initially formed in reaction [3] and then reacts further with HCl to form CINO must be considered. This can be ruled out because the amount of CINO that is possible from the direct reaction of HCl with gaseous HONO at 80 min (Fig. 1C) is <3% of the reacted NO2, much less than observed. This shows that the CINO precursor must be adsorbed to the SiO2 surface before the introduction of HCl. Theoretical studies
predict that HONO adsorbs to SiO2 surfaces (32), so that the gaseous HONO observed in Fig. 1C could be in equilibrium with far greater amounts of surface-adsorbed HONO or nitrate (although given that HONO is formed simultaneously, HONO will be the major species). However, control experiments in which SiO2 is exposed to gaseous HONO followed by HCl do not produce CINO (see SI Text and Fig. S1), ruling this pathway out as a major source.

The proposed mechanism and the effect of water in enhancing CINO formation are supported by theory. A series of high level ab initio calculations [using the General Atomic and Molecular Electronic Structure System (GAMESS) (33)] are performed to gain insight into the role of water in CINO formation. The starting reactive species in the calculations is the asymmetric dimer, ONONO2 in gas-phase clusters comprised of HCl and a varying number of water molecules. Previous studies have shown that gas-phase clusters are suitable models for surface reactions where the substrate is not involved in the chemical mechanism (34).

Molecular dynamics “on-the-fly” calculations [using second-order perturbation theory (MP2) with the cc-pVDZ basis set, denoted MP2/cc-pVDZ], are performed to elucidate the mechanism (Fig. 2). Water acts as a conduit to transfer a proton from HCl to NO2, facilitating the formation of the products CINO and HONO. Energetics are attained at the coupled cluster [CCSD(T)/cc-pVTZ] level of theory by conducting single point energy calculations on the stationary structures obtained on the MP2/cc-pVDZ surface. In the absence of water, the activation energy for CINO formation is 11.5 kcal mol\(^{-1}\). Addition of 1 water molecule lowers the activation energy to 5.3 kcal mol\(^{-1}\). The formation of CINO is exothermic by 10.0 kcal mol\(^{-1}\) in the absence of water and 12.9 kcal mol\(^{-1}\) in the presence of 1 water molecule. A barrierless channel is found for CINO formation in the presence of 2 water molecules at the MP2/cc-pVDZ level of theory. Thus, the theoretical results support the experiments described above and demonstrate the critical role of water in enhancing the formation of CINO.

**N2O5 Reaction.** Gaseous HCl may also react with other oxides of nitrogen such as N2O5 on surfaces to form CINO2 (35). The reaction likely occurs through an analogous mechanism to that for NO2, whereupon absorption to the surface, NO2 autoionizes to NO2\(^+\) NO3\(^-\) and then reacts with HCl,

\[
\text{NO2}^+ + \text{HCl} \rightarrow \text{CINO2} + \text{HNO3} \tag{6}
\]

In competition with water, reaction [4]. The gas-phase reaction is otherwise slow in the absence of sufficient surface area (24). Spectral evidence for the role of NO2\(^+\) as the key intermediate in reaction of HCl with N2O5 was obtained using attenuated total reflection FTIR (ATR-FTIR) spectroscopy. As shown in Fig. 3, sharp bands at 2,370 cm\(^{-1}\) and 1,667 cm\(^{-1}\), and a weak absorbance between 3,500 and 2,500 cm\(^{-1}\) appear in the spectrum measured immediately after the internal reflection element (IRE) is exposed to 10 Torr of N2O5 (solid line). The band at 2,370 cm\(^{-1}\) is assigned to the ν2(NO2-antisymmetric) stretching mode of linear NO2, consistent with previous observations of this ion in the gas phase and at low temperatures in frozen matrices and on metallic substrates (35–39). The band at 1,667 cm\(^{-1}\) is due to the ν3(NO2-antisymmetric) stretch of HNO3. Broad bands between 3,500 and 2,500 cm\(^{-1}\) are assigned to ν(O–H) stretches of nitric acid complexed to surface-adsorbed water (40). The weak signals typically observed for surface-adsorbed species using ATR-FTIR required the use of higher concentrations than found in the atmosphere. However, ionization of N2O5 on surfaces is expected to be operational at lower concentrations as well (19, 20).

Similar to the NO2 case where water promotes the formation of NO2\(^+\)NO3\(^-\) from ONONO2 (16), water is expected to play an essential role in autoionization of N2O5. Indeed, calculations at the MP2/cc-pVDZ level of theory show that ionization of N2O5 into a NO2\(^+\) NO3\(^-\) ion pair takes place in the presence of 1 or more water molecules (Fig. 4). The largest effect is observed upon addition of the first water molecule, which triggers an increase in the separation of the NO2\(^+\) and NO3\(^-\) moieties by 0.2 Å compared with free N2O5. Furthermore, the calculated partial charges on these 2 moieties increase dramatically from \(\delta(\text{NO2}^+) = +0.127\) and \(\delta(\text{NO3}^-) = -0.127\) in the free N2O5 molecule, to \(\delta(\text{NO2}^+) = +0.274\) and \(\delta(\text{NO3}^-) = -0.284\) in the (N2O5)\(\text{H}_2\)O complex. This trend of increasing separation and partial charges on NO2\(^+\) and NO3\(^-\) moieties continues upon addition of the second and third water molecules. Hence, water enhances the reactivity of N2O5 by promoting the formation of the (NO2\(^+\))(NO3\(^-\)) ion pair.

The IR absorption band stemming from NO2\(^+\) is completely removed and nitric acid bands increase when the IRE is exposed to excess HCl in the ATR-FTIR experiment shown in Fig. 3 (dashed line), supporting the mechanism where surface-adsorbed NO2\(^+\) is the key intermediate in the conversion of N2O5 to CINO2 (19, 20).
In separate experiments (Fig. 5A) using transmission FTIR spectroscopy, ClONO2 is clearly formed in the gas-phase when HCl is added to a cell containing N2O5. Again, the reaction is more efficient in the presence of water, as demonstrated in Fig. 5B.

Theory again supports the experimental observations and proposed mechanism, showing that water aids the reaction of NO2 with HCl. The reaction was investigated theoretically by conducting a series of optimizations of the (NO2)(HCl) complex in the absence and presence of water at the MP2/cc-pVDZ level of theory. As shown in Fig. 5C, a barrierless channel for the formation of NO2 from NO3 and HCl is found in the presence of 2 water molecules. Upon addition of the second water molecule the product NO2 is formed having a Cl–N bond length of 2.22 Å and a Cl–O–N–O of 144°, comparable to the 1.96 Å and 135° found for the calculated free molecule. Water clearly facilitates the formation of ClONO2, similar to the trend observed in the CINO case. There is some similarity to the reactions of ClONO2 or N2O5 with HCl on bulk ice at low temperatures (54); in those cases, Cl atoms from the dissociation of solvated HCl is the reactive species (35, 41, 42). However, Cl atoms at the top of the air-water interface are largely undissociated (34, 40, 43–45). Given this and the fact that water adsorbed on solid substrates at room temperature does not behave like water in the bulk (46–48), it is likely that the reactant in the surface-mediated reaction reported here is molecular HCl.

Atmospheric Implications. Extrapolation to atmospheric conditions both outdoors and indoors relies on similar surface-bound nitrogen oxides being present on real surfaces. Evidence for the universality of reaction [1] is that it has been shown to occur on many different surfaces, including Teflon, borosilicate glass and silica (8), boundary layer surfaces outdoors [e.g., vegetation, building materials etc. (49, 50)], on typical indoor surfaces (51, 52) and on airborne dust particles (50, 53). It is also well known that N2O5 is taken up on surfaces and hydrolyzed (54). Due to such uptake, there is a reservoir of strongly adsorbed reactive oxides of nitrogen on surfaces in both environmental chambers (14) and in the field (13).

Experiments were performed at RH up to 25%, typical of drier environments. However, the role of water suggests that this chemistry will continue to higher RH. When gaseous HCl is present as well as oxides of nitrogen, e.g., in coastal areas and downwind of certain industrial settings, incineration facilities (5), biomass burning (55), in buildings such as medieval churches and in volcanic plumes (2, 5), it will be converted to CINO and CINO2. CINO absorbs light well into the visible region (Fig. 6), forming Cl + NO with unit quantum yield (54). As seen in Fig. 6, its absorption cross section in the near UV overlaps strongly not only with solar radiation but also with that from typical fluorescent lights used indoors. Formation of CINO indoors is certainly possible. Indoor surfaces are frequently exposed to NO2 generated from indoor combustion sources or from an influx of polluted outside air (56). It has been proposed that corrosive chlorine containing gases such as HCl [e.g., from cigarette smoke, decomposition of chlorine-containing polymers, and cleaning agents] are responsible for observed elevated levels of Cl− found in indoor relative to outdoor air (57). Thus, if formed indoors, CINO could serve as a source of highly reactive chlorine atoms that would participate in the complex chemistry known to occur there (52, 58). In addition, the presence of CINO in the indoor environment could have important ramifications for the reliability and lifetime of electronics susceptible to corrosion (59). To the best of our knowledge, chlorine atom chemistry has not been considered in typical indoor air environments.

Outdoors, CINO and CINO2 are important chlorine atom precursors on short time scales because of their rapid photolysis, having calculated lifetimes of only 5 and 30 min, respectively, at a solar zenith angle of 0° (54). Hydrochloric acid also forms Cl atoms...
through its reaction with OH, but this is slow, with a lifetime for HCl with respect to this reaction of $\approx 14$ days at an OH concentration of $10^6$ radicals cm$^{-3}$. In the presence of sufficient NO, chlorine atoms enhance the formation of ozone through well-known organic-N$_2$O cycles (54) so heterogeneous HCl-to-CINO conversion could speed up the formation of ozone and other photochemically generated species in polluted coastal urban areas, changing their peak concentration and geographical distribution. Ozone is an important trace gas with documented health effects, a greenhouse gas, and a significant atmospheric oxidant and precursor to the OH radical (54).

The potential role of heterogeneous HCl-to-CINO conversion in a coastal airshed (see Fig. S2) is probed using a model (60) that employs state-of-the-art modules for both gas-phase and heterogeneous/multiphase reaction mechanisms, and dynamic aerosol predictions (60, 61). Although this model represents the Southern California air basin, it is typical of polluted coastal regions elsewhere. Two simulations are examined: A base case that provides benchmark predictions of the ambient concentrations of O$_3$, ClNO and HCl without the surface mediated conversion, and a test case that assumes that every HCl molecule deposited generates 1 gaseous CINO molecule. This in effect assumes that HCl is the limiting reagent. Although this might appear to be the extreme case, it is not necessarily the upper limit for conversion of HCl to CINO because the reaction probability in the model is expressed as a function not only of the deposition velocity of HCl but also of the total surface area of the domain. Surface areas in the model do not include the additional geometric area due to structures such as buildings, nor the molecular scale porosity of surfaces; these can contribute significantly to chemistry in the boundary layer (50). It also assumes that HCl will continue to compete with water vapor for the NO$^+$-N$_2$O$_5$ intermediate under typical atmospheric conditions. The ratio of HCl/H$_2$O that was experimentally accessible here was typically of the order of $10^{-3}$ whereas in air, it is $\approx 10^{-6}$ to $10^{-7}$. Whether this assumption is justified awaits measurement of the relative rate constants for reactions [3] and [5].

Fig. 7A shows the geographical distribution and concentrations of O$_3$, CINO and HCl at the times at which they each peak within the modeling domain. Fig. 7B shows the increase in concentrations, $\Delta$O$_3$, $\Delta$CINO, and $\Delta$HCl, above those predicted for the base case due to the inclusion of surface-mediated HCl-to-CINO conversion. The locations with the greatest impact from the new CINO source are mainly in the downwind regions of the domain and show up to 40 ppb more O$_3$ ($\approx 20\%$ increase) in a 1-h averaging time relative to the base case, and up to 2S ppb increase over an 8-h averaging time. For comparison, the current U.S. Environmental Protection Agency (EPA) 8-h average standard is 75 ppb. Additional test cases performed with varying conversion probabilities suggest that increases in ozone levels scale linearly with the HCl-to-CINO conversion probability so that a smaller CINO yield generates proportionally smaller amounts of O$_3$ above the base case.

It is noteworthy that this heterogeneous chemistry of oxides of nitrogen with gaseous HCl is the inverse of mechanisms of chlorine activation from sea salt particles in coastal areas involving chloride, which can generate a variety of photochemically active chlorine atom precursors (5, 62–64). For example, reactions of gaseous NO$_2$ and N$_2$O$_5$ with chloride ions in sea salt particles are known to generate CINO and ClINO$_2$ (20, 63–66). Although the former reaction is likely too slow to generate significant amounts of CINO in coastal environments, the latter is believed to be responsible for the formation of ClINO$_2$ measured recently in air (67), where measured mixing ratios of ClINO$_2$ were greater than expected based on the measured concentrations of N$_2$O$_5$ and chloride in sea salt particles. It is possible that the chemistry reported here may have contributed to the measured ClINO$_2$. This heterogeneous chemistry is also expected to be important around salt lakes such as the Dead Sea (68) and the Great Salt Lake (69), and during dust storms where enhanced HCl uptake has been observed (70). Plumes from biomass (55) and garbage burning (7) are other cases where this chemistry may be significant.

Unusual chlorine activation near the midlatitude tropopause has been reported that appears to be associated with high particle surface areas, relatively high water vapor concentrations and mixing of tropospheric and stratospheric air (71). Although reaction of HCl with ClINO$_2$ on polar stratospheric clouds (PSCs) in polar regions is known to generate Cl$_2$, this unusual midlatitude chemistry does not appear to require PSCs. The heterogeneous reaction of HCl with surface-bound oxides of nitrogen to form CINO would be consistent with the need for high surface areas and water vapor for midlatitude tropopause chlorine activation.

In short, the combination of experiments and theory reported here suggests a new and unique coupling of surface-mediated nitrogen oxide and halogen activation cycles that will generate CINO and ClINO$_2$ in a wide variety of outdoor air environments, and indoors where it has not been considered. Although a technique to measure ClINO$_2$ at ppt levels has been developed (67), this is not the case for CINO, but is clearly needed. Similar chemistry is expected for HBr, leading to photozolyzable bromine species such as BrNO and BrNO$_2$ that cause O$_3$ destruction through well-known cycles (54).

Materials and Methods

Experimental Details. Infrared spectra were collected using a Thermo Nicolet Avatar 370 Fourier transform infrared (FTIR) spectrometer equipped with a liquid nitrogen-cooled Hg-Cd-Te (MCT) detector. Background single beam spectra were obtained from the average of 200–2,000 interferograms whereas single beam spectra obtained during the reaction were obtained from the average of 6–2,000 interferograms; in all cases, spectra were recorded at 1-cm$^{-1}$ resolution. The IR transmission cells were made of borosilicate glass with an optical path length of either 12 or 10 cm and an inner diameter of 2.5 cm. The ends were closed with germanium windows and sealed with Viton “O”-rings. Concentrations of NO$_2$, CINO and H$_2$O were determined from calibrations measured in our laboratory. Absolute cross sections of nitrous acid from Barney et al. (72) were applied. Hydrogen chloride absorption cross sections were obtained from a reference spectrum available in the Pacific Northwest National Laboratory vapor phase infrared spectral library (73). All experiments were conducted at 22 ± 1°C under dark conditions.

Gases were handled with an all-glass vacuum line with Teflon stopcocks and Kalrez “O”-rings. Nitrogen dioxide was synthesized from the reaction of NO (Matheson, 99%) with excess oxygen (Oxygen Service, 99.993%), followed by trap-to-trap purification. Nitric oxide was purified by passing it through an aerodynamically ice bath trap at 195 K before use. Nitrosyl chloride (CINO) was synthesized from the reaction of 1 eq of Cl$_2$ (Matheson, 99.5%) and slightly more than 2 eq of nitric oxide, followed by repeated freeze-thaw cycles at liquid nitrogen temperatures to drive the reaction to completion in the liquid phase.
The vessel containing ClNO was held at 195 K and the excess nitric oxide and chlorine were removed under vacuum until a constant vapor pressure above the walls. For the reaction, N2O5 is added to the IR cell. After 10 min, anhydrous HCl (99.995%, Matheson) or a mixture of HCl and water vapor. The concentration range of NO2 used in these experiments was 35–200 ppm; the amount of HCl added to the IR cell was between 150–800 ppm. These experiments were limited to <20% RH because of the strong absorption of water vapor in the infrared, and condensation of water in the mixing bulb used to prepare the HCl/H2O mixture that would be needed to give higher RH once it was expanded into the reaction cell.

Measurements of the relative humidity dependence of the ClNO yield from the HCl + NO2 reaction were carried out in a static system using a 10-cm path length IR cell (V = 43 cm³) containing 1.0 g of fumed SiO2 pellets. The IR cell was evacuated overnight at ~10⁻⁴ Torr and heated at 125 °C to drive off most of the surface-adsorbed water before each experiment. After cooling to room temperature, NO2 was introduced from a bulb on the attached vacuum line. After ~10 min, the IR cell was opened for 10 s to an attached 493-cm³ bulb containing anhydrous HCl (99.995%, Matheson) or a mixture of HCl and water vapor. The concentration range of NO2 used in these experiments was 35–200 ppm; the amount of HCl added to the IR cell was between 150–800 ppm. These experiments were limited to <20% RH because of the strong absorption of water vapor in the infrared, and condensation of water in the mixing bulb used to prepare the HCl/H2O mixture that would be needed to give higher RH once it was expanded into the reaction cell.

Studies of the NO2 + HCl reaction. Before experiments, the surface inside an empty 10-cm path length IR cell is conditioned by repeated exposure to ~1 Torr of N2O5 from a preconditioned 4-L glass bulb, followed by evacuation for 1 h at ~10⁻⁴ Torr to eliminate adsorbed water and reduce the loss rate of N2O5 to the walls. For the reaction, N2O5 is added to the IR cell. After ~10 min, anhydrous HCl or a mixture of HCl and water vapor is added from a 493-cm³ glass bulb attached in the reactant mixture. Single beam spectra were continuously collected as the stream of NO2 (5 ppm), HCl (10 ppm) and water vapor (~0.5% relative humidity measured using the infrared absorbance of selected water lines) was alternated between flowing through the empty or SiO2-filled chamber. Uptake of NO2 on the SiO2 surface decreases somewhat over time, likely due to the dehydration of the surface with repeated exposures. In addition, water may be tied up in complexes of (HNO3)₂(H₂O)₃ as nitric acid (40) accumulates on the surface according to reaction (1).
to the IR cell. Addition of HCl occurs at t = 0 in Fig. 5 A and B. Spectra of surface-adsorbed NO$_2$ before and after the reaction with HCl (Fig. 3) are obtained with an ATR probe (Axicon Analytical) mounted in the sample compartment of the spectrometer and inserted into a vacuum-tight borosilicate glass reaction chamber (80 cm$^3$). The internal reflection element (IRE) installed at the end of the probe is a ZnSe rod, 0.6 cm dia. × 4 cm long with 45° conical ends. Interior surfaces of the reaction chamber are first conditioned by repeated exposure to ~10 Torr of N$_2$O$_3$, followed by evacuation for 15 min at ~10$^{-4}$ Torr. The IRE is then exposed to 10 Torr of anhydrous N$_2$O$_5$ for 30 min before introducing 20 Torr of anhydrous HCl from a bulb on the attached vacuum line.

**Computational Details.** Ab initio calculations (33, 75) are performed with second-order Moller-Plesset perturbation theory using the cc-pVDZ basis set (79, 80). Geometry and saddle point optimizations (81–83) are carried out with the largest component of the analytic gradient (76, 84) being smaller than 10$^{-5}$ Hartree/Bohr. Double differencing of analytic gradients is used in the Hessian calculations (85). Minima are confirmed by an all-positive Hessian, whereas transition states have only 1 negative Hessian eigenvalue. Intrinsic reactive coordinate calculations (86–90) are conducted to connect the transition state with the corresponding minima. Molecular dynamics calculations (91–95) “on the-fly” that have been successfully applied in related studies (34) are performed starting from the located minimum structure that is obtained upon the geometry optimization of ONONO$_2$H$_2$O and HCl.

To account for effects of reported activation energies and reaction enthalpies, single point energy coupled cluster calculations [CCSD(T)] (96, 97)] with the cc-pVTZ basis set (79, 80) are performed on the stationary structures already located on the MP2/cc-pVDZ potential energy surface. Zero point energy (ZPE) contributions to the activation energy are calculated by scaling the MP2/cc-pVDZ harmonic ZPE by 0.95 (98). All of the calculations are carried out using the GAMESS (33, 75) package and MacMolPlt (99) is used for molecular visualization.

**Aired Model Details.** The emission inventory selected for the University of California Irvine-California Institute of Technology airshed model simulations of this study is from August 6, 1997, which was used in the 2003 Air Quality Management Plan designed by the South Coast Air Quality Management District of California. A map of the aired and surrounding areas is shown in fig. 52.

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44. Finlayson-Pitts BJ (1983) Reaction of NO2 with NaCl and atmospheric implications of the chemistry of NaCl and NaBr.


48. Ishida K, Morokuma K, Komornicki A (1977) The intrinsic reaction coordinate. An ab initio study of SiH4 → SiH5-.


Corrections

STATISTICS


The authors note the following: It has been brought to our attention that the algorithm introduced in our paper (ABC-PRC) can produce a biased posterior sample, most noticeably through underestimation in distributional tails. This result occurs as the likelihood ratio in the sequential Monte Carlo incremental weights is approximated by using two unbiased Monte Carlo estimates. One way to avoid a biased posterior sample in the ABC-PRC algorithm is to directly evaluate the importance sampling distribution using a near-optimal backwards kernel. Hence the need for the Monte Carlo estimate in the denominator of the likelihood ratio is circumvented, and an unbiased sampler is obtained. As such, a corrected ABC-PRC algorithm would be:

**ABC-PRC Algorithm (corrected):**

PRC1 Initialize $\epsilon_1, \ldots, \epsilon_T$, and specify initial sampling distribution $\mu_1$.
Set population indicator $t = 1$.

PRC2 Set particle indicator $i = 1$.

PRC2.1 If $t = 1$ sample $\theta^* \sim \mu_1(\theta)$ independently from $\mu_1$.
If $t > 1$ sample $\theta^*$ from the previous population $\{\theta_{t-1}^{(i)}\}$ with weights $\{W_{t-1}^{(i)}\}$, and perturb the particle to $\theta^{**} = K_t(\theta^* | \theta^*)$ according to a transition kernel $K_t$.

Generate a data set $x^{**} \sim f(x | \theta^{**})$.
If $p(S(x^{**}), S(x_0)) \geq \epsilon_t$ then go to PRC2.1.

PRC2.2 Set $\theta_t^{(i)} = \theta^{**}$ and

$$W_t^{(i)} = \begin{cases} \pi(\theta_t^{(i)}) / \mu_1(\theta_t^{(i)}) & \text{if } t = 1 \\ \pi(\theta_t^{(i)}) / \sum_{j=1}^N W_{t-1}(\theta_{t-1}^{(j)}) K_t(\theta_t^{(j)} | \theta_{t-1}^{(j)}) & \text{if } t > 1 \end{cases}$$

where $\pi(\theta)$ denotes the prior distribution for $\theta$.
If $i < N$, increment $i = i + 1$ and go to PRC2.1.

PRC3 Normalize the weights so that $\sum_{i=1}^N W_t^{(i)} = 1$.

If $ESS = \left[\sum_{i=1}^N (W_t^{(i)})^2\right]^{1/2} < E$ then resample with replacement, the particles $\{\theta_t^{(i)}\}$ with weights $\{W_t^{(i)}\}$ to obtain a new population $\{\theta_t^{(i)}\}$, and set weights $\{W_t^{(i)} = 1/N\}$.

PRC4 If $t < T$, increment $t = t + 1$ and go to PRC2.

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COMMENTARY


The authors note that on page 10875, right column, the sentence beginning on line 22, “For example, ultrathin sheets of silicon are flexible, for the same reason that any material in thin film form is flexible: bending strains are inversely proportional to thickness” should instead appear as “For example, ultrathin sheets of silicon are flexible, for the same reason that any material in thin film form is flexible: bending strains are directly proportional to thickness.”

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The authors note that on page 13648, Equation 5 appeared incorrectly. Further, in Equation 6 on page 13649, the formula for nitryl chloride should have read: CINO₂. These errors do not affect the conclusions of the article. The corrected equations appear below.

$$\begin{align*}
\text{NO}^+ + \text{NO}_3^- + \text{HCl} \rightarrow \text{CINO} + \text{HNO}_3 & \quad [5] \\
\text{NO}_2^+ + \text{NO}_3^- + \text{HCl} \rightarrow \text{CINO}_2 + \text{HNO}_3 & \quad [6]
\end{align*}$$

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