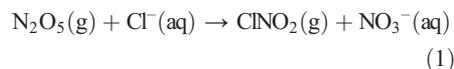


N₂O₅ Oxidizes Chloride to Cl₂ in Acidic Atmospheric Aerosol

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Molecular chlorine (Cl₂) has been observed in the mid-latitude marine boundary layer at mixing ratios ranging from a few tens to several hundred parts per trillion by volume (1–3). Cl₂ photolyzes readily to atomic chlorine, a highly reactive species that affects abundances of ozone (both production and destruction), aerosol formation, and important trace gases as varied as methane, mercury, and naturally occurring sulfur compounds. A number of possible mechanisms have been proposed for the conversion of chloride to Cl₂ (4, 5); however, the detailed processes involved remain uncertain. We show that reaction of dinitrogen pentoxide (N₂O₅) with aerosol phase chloride yields Cl₂ at low pH (<2) and should constitute an important halogen activation pathway.

It has been known for some time that heterogeneous uptake of N₂O₅ to NaCl or sea salt aerosol results in the efficient production of nitryl chloride (ClNO₂) (6).



Such surfaces are highly hygroscopic such that their chemistry resembles that of concentrated aqueous solutions (5). Recently, we showed that the reaction in Eq. 1 occurs in the atmosphere on particles of moderate to low chloride content (7).

This formation has also been observed in laboratory experiments (8, 9), but those studies lacked detail in the Cl⁻ concentrations and pH ranges of potential interest. We report a series of laboratory experiments on the reactivity of N₂O₅ on a variety of halide-containing substrates, for example, ammonium sulfate, ammonium bisulfate, and oxalate (table S1). We used iodide ion chemical ionization mass spectrometry to simultaneously measure ClNO₂, Cl₂, and Br₂ (10). These studies confirmed that the N₂O₅ converts to ClNO₂ at low Cl⁻ concentrations on a range of substrates pertinent to atmospheric aerosol, but they also revealed the presence of an additional channel, the direct formation of Cl₂.

To confirm that ClNO₂ was an intermediate in this Cl₂ formation, we used a salt slurry to nearly quantitatively convert (94%) a flow of N₂O₅ in air to ClNO₂ and passed the resulting stream over a deliquesced mixture of oxalic acid and NaCl (pH ≈ 1.8). Figure 1 shows that ClNO₂ was efficiently converted to Cl₂ under these conditions. ClNO₂ is normally insoluble and relatively unreactive, as indicated by the low uptake coefficients ($\gamma = 0.3 \times 10^{-6}$ to 5×10^{-6}) on water or NaCl solutions, at neutral pH (4). The uptake coefficient estimated from our low pH experiment was much higher, $\gamma = 6 \times 10^{-3} \pm 2 \times 10^{-3}$. Coupled with a Henry's Law constant of 4×10^{-2} M atm⁻¹, this value implies a first-order loss coefficient in

solution of 1.6×10^7 s⁻¹ and rate coefficients for reaction of ClNO₂ with Cl⁻ $\geq 10^7$ M⁻¹ s⁻¹ at low pH. Moreover, our measurements of the ClNO₂-to-Cl₂ conversion of 60 to 100% [see (10) for detailed measurement precision] indicate that the overall conversion of N₂O₅ to Cl₂ is an efficient process on acidic aerosol particles in the atmosphere.

Production of Cl₂ from either N₂O₅ or ClNO₂ was observed on aqueous solutions of NaCl, (NH₄)HSO₄, or oxalic acid, at pH less than or equal to 2 and at Cl⁻ concentrations as low as 0.05 M (10). The acid catalysis observed in our work implies that there are significant barriers to this chemistry at neutral pH and that a solution or quasi-liquid layer is needed for the reaction to proceed. A more detailed discussion of the proposed mechanism is included in (10).

This process of Cl₂ formation has not been previously considered in atmospheric chemistry. Low-pH aerosol particles have been observed in the lower troposphere (2), and thermodynamic models suggest that chloride concentrations above 0.05 M can exist on such particles (11). Moreover, low-temperature models predict that chloride-containing aerosol should exist in the upper troposphere and lower stratosphere (12). Therefore, implications for tropospheric and stratospheric chemistry should be further explored through future laboratory, field, and modeling studies.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/1158777/DC1

Materials and Methods

Fig. S1

Table S1

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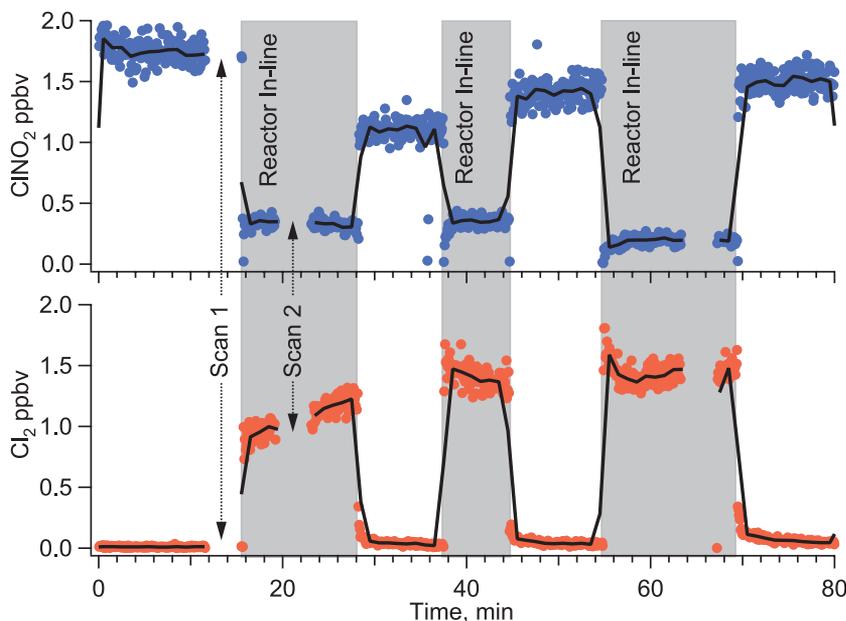


Fig. 1. Efficient reaction of ClNO₂ with Cl⁻ to form Cl₂ (60 to 100% conversion within measurement precision) on deliquesced oxalic acid and NaCl. Mixing ratios were in parts per billion by volume, ppbv. Mass scans 1 and 2 are shown in fig. S1.