GEOPHYSICAL RESEARCH LETTERS, VOL. 36, L20808, doi:10.1029/2009GL040448, 2009

Laboratory studies of products of N_2O_5 uptake on Cl^- containing substrates

James M. Roberts,[1] Hans D. Osthoff,[1,2,3] Steven S. Brown,[1] A. R. Ravishankara,[1,4]
Derek Coffman,[5] Patricia Quinn,[5] and Timothy Bates[5]

Received 6 August 2009; revised 23 September 2009; accepted 1 October 2009; published 30 October 2009.

[1] The reaction of dinitrogen pentoxide with chloride-containing substrates over a concentration range relevant to the atmosphere was examined using cavity ring-down spectroscopy (CaRDS) and chemical ionization mass spectrometry (CIMS). The main product, nitryl chloride ($ClNO_2$), was formed in efficiencies in the range 0.2 to 0.8 for chloride concentrations of 0.02 to 0.5M. These values are somewhat lower than those from previous, less detailed, measurements carried out mainly at much larger chloride concentrations in NaCl-water mixtures. Substrates having pH<2 also evolved molecular chlorine (Cl_2), with $ClNO_2$ as an intermediate. The $ClNO_2$ yields are compared to recent field measurements of N_2O_5 and $ClNO_2$ as a function of aerosol chloride concentration and shown to quantitatively explain the observations. **Citation:** Roberts, J. M., H. D. Osthoff, S. S. Brown, A. R. Ravishankara, D. Coffman, P. Quinn, and T. Bates (2009), Laboratory studies of products of N_2O_5 uptake on Cl^- containing substrates, *Geophys. Res. Lett.*, *36*, L20808, doi:10.1029/2009GL040448.

1. Introduction

[2] Efficient reaction of dinitrogen pentoxide (N_2O_5) with sodium chloride (NaCl) or sea salt to produce nitryl chloride ($ClNO_2$) has been observed by *Finlayson-Pitts et al.* [1989] and has been suggested in modeling studies as a mechanism for chlorine activation (i.e., conversion of un-reactive chlorine chemicals to reactive forms) in the troposphere [*Erickson et al.*, 1999; *McFiggans et al.*, 2002; *Pechtl and von Glasow*, 2007]. Generally, these modeling studies have inferred only modest $ClNO_2$ formation, limited either by the low N_2O_5 in the remote marine boundary layer where sea salt aerosol is abundant, or low sea salt surface areas in polluted coastal areas where N_2O_5 can be abundant. Recent observations of $ClNO_2$ in the polluted marine boundary layer (MBL) [*Osthoff et al.*, 2008; *Kercher et al.*, 2009] have shown $ClNO_2$ to be significantly more abundant than such model estimates, and strongly imply that chlorine activation by dinitrogen pentoxide also occurs on sub-micron aerosol of modest chloride content ($[Cl^-]$ = 0.01 to 0.1 M). Previous laboratory measurements have shown that conversion of N_2O_5 to $ClNO_2$ could also occur on solutions of low chloride content ($[Cl^-]$<1M) at neutral un-buffered pH [*Behnke et al.*, 1997], and on $NaCl/NaNO_3$ particles at lower [Cl-] [*Bertram and Thornton*, 2009]. Neither study emphasized the low $[Cl^-]$ concentration region nor examined the variety of aerosol substrates present in the troposphere, e.g., $(NH_4)HSO_4$, $(NH_4)_2SO_4$, and lower pH (2 to 3 pH units) solutions.

[3] Here we report $ClNO_2$ yields in the reactive uptake of N_2O_5 on substrates that mimic atmospheric aerosols. Bulk Cl^- containing substrates were exposed to N_2O_5 in a flow system in which uptake of N_2O_5, and production of $ClNO_2$ and Cl_2, were measured simultaneously. The results were compared to published results for pure NaCl solutions [*Behnke et al.*, 1997], and $NaNO_3$/NaCl particles [*Bertram and Thornton*, 2009], and are used to infer the importance of N_2O_5 uptake on sub-micron aerosol as a general source for tropospheric $ClNO_2$. In addition, the data are fit to a competitive reaction model that permits the production of $ClNO_2$ due to N_2O_5 uptake to be parameterized as a function of aerosol chloride concentration. A number of experiments in which Cl_2 evolution was also observed from low pH substrates (pH < 2) have been described previously by *Roberts et al.* [2008] and so are not described here.

2. Experimental Methods

[4] Figure 1 shows the schematic of the apparatus used to measure the $ClNO_2$ production from N_2O_5 uptake. The total gas flows through the apparatus ranged from 5 to 7 standard liters per minute (SLPM), the geometric surface areas of the test substrates were 10.1 cm^2. The reactor was at ambient pressure, (625 Torr), and ambient temperature (297±2K). The tubing and reactor were constructed of all PFA−Teflon. Mixing ratios of N_2O_5 flowing through the reactor ranged from 1 to 6 ppbv (parts per billion by volume). They were produced by adding a small flow of N_2O_5, from a sample at 195K, to the humidified air stream (25−40% RH) and measured by Cavity Ring-down Spectroscopy (CaRDS) [*Dubé et al.*, 2006]. $ClNO_2$ and Cl_2 were measured at the exit of the flow reactor via chemical ionization mass spectrometry with iodide as the reactant ion (I^- CIMS) at masses 162 $\{I{\bullet}Cl\}^-$ and 197 $\{I{\bullet}Cl_2\}^-$, respectively [*McNeill et al.*, 2006; *Osthoff et al.*, 2008; *Roberts et al.*, 2008]. Calibration of the CaRDs was based on the absorption cross section of NO_3 [*Dubé et al.*, 2006; *Osthoff et al.*, 2007], and the transmission of NO_3 and N_2O_5 through the optical system was validated by the nitric oxide (NO) titration method described by *Fuchs et al.* [2008].

---

[1] Chemical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, Colorado, USA.

[2] Cooperative Institute for Research in the Environmental Sciences, University of Colorado, NOAA, Boulder, Colorado, USA.

[3] Now at the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada.

[4] Also at Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, USA.

[5] Pacific Marine Environment Laboratory, NOAA, Seattle, Washington, USA.

0094-8276/09/2009GL040448$05.00

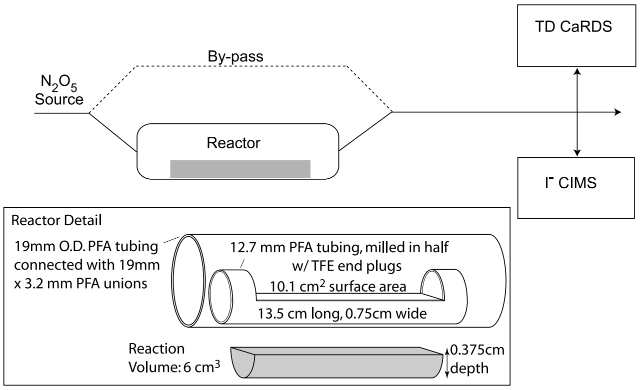

Figure 1. Schematic diagrams of the flow system used for the exposure of bulk solutions to N_2O_5, and the details of the reactor and sample holder.

[5] $ClNO_2$ was calibrated by three different methods [*Osthoff et al.*, 2008], quantitative conversion of N_2O_5 on deliquesced NaCl, and odd-nitrogen (NOy) measurement or UV absorption measurements of a synthetic $ClNO_2$ sample. The quantitative conversion of N_2O_5 on deliquesced NaCl, which was also observed by *Behnke et al.* [1997] and *Schweitzer et al.* [1998], was used routinely in this work. Detection limits were 0.5 pptv for N_2O_5 (1 second), 5 pptv for $ClNO_2$ (30 sec average), and 3pptv for Cl_2 (30 sec average). The overall uncertainties in the measurements were ±(25%+0.5pptv) for N_2O_5, ±(20%+5 pptv) for the $ClNO_2$ measurements, and ±(40%+3pptv) for the Cl_2 measurements. The N_2O_5 taken up in these experiments ranged from 400 to 1350 pptv and the $ClNO_2$ produced ranged from detection limit up to 1200 pptv. Thus the signal-to-noise ratios were extremely good for the larger yields.

[6] The loss of N_2O_5 to the walls of the reactor and tubing in the absence of any substrate or solution was measured repeatedly during the course of the experiment and was found to be 50 ±50 pptv. This "blank" value, assumed to be lost even in the presence of the sample, was subtracted from the measured concentration of N_2O_5 taken up and the uncertainty associated with this was accounted for in the value quoted for N_2O_5 above. The uncertainties in the ratio of $ClNO_2$ produced to N_2O_5 taken up were propagated in quadrature from uncertainties in the individual concentrations. It should be recognized, however, that these uncertainties are conservative since the method of calibrating $ClNO_2$ from the known unit yield of the N_2O_5 reaction at high [Cl^-] results in a relative uncertainty that is somewhat lower.

Table 1. Summary of Substrates and Results of N_2O_5 and $ClNO_2$ Uptake Experiments[a]

Gas Phase Species	Substrate	Result
N_2O_5 and HCl[b]	None, CIMS inlet only	No $ClNO_2$ or Cl_2
N_2O_5	0.3M $(NH_4)HSO_4$ + 0.053M Cl^-	$ClNO_2$, Cl_2 pulses[c]
N_2O_5	NaCl/0.3M $(NH_4)HSO_4$, pH∼2	$ClNO_2$, Cl_2
N_2O_5	0.15M $(NH_4)_2SO_4$ + [Cl^-][d]	$ClNO_2$
N_2O_5	D.I Water + [Cl^-][d]	$ClNO_2$
N_2O_5	NaCl + $HCl_{(conc)}$	Cl_2
N_2O_5	NaCl + Oxalic acid	$ClNO_2$, Cl_2
N_2O_5	Oxalic + [Cl^-][d]	$ClNO_2$, Cl_2
$ClNO_2$	NaCl + Oxalic acid	Cl_2
N_2O_5	Sea Salt + Oxalic acid	$ClNO_2$, Cl_2
N_2O_5	Oxalic acid + 0.5M Cl^- + 0.5M Br^-	$ClNO_2$, Cl_2

[a] cf. *Roberts et al.* [2008].

[b] HCl was added at final mixing ratio of 5ppbv.

[c] Thought to arise from short term surface acidification due to hydrolysis of N_2O_5 to HNO_3.

[d] [Cl^-] denotes a range of chloride ion concentrations of between 0.001 and 1M.

[7] Sample substrates were prepared either by preparation of solutions of known concentration in distilled water, or by creation of a slurry by addition of a small amount of water to a sample of the appropriate solid. In the case of ammonium bisulfate, $(NH_4)HSO_4$, a stoichiometric amount of H_2SO_4 was added to an $(NH_4)_2SO_4$ solution resulting in a 0.3M HSO_4^- solution. The solutions or solid/liquid mixtures, were placed in a shallow, open-faced Teflon reservoir of known surface area, which was then placed within the PFA reaction chamber. The substrates tested during this study are listed in Table 1. pH was measured either by pH test paper (uncertainty ± 0.5 pH units) or by a pH meter (not corrected for ionic strength, uncertainty ±0.2 pH units).

3. Results

[8] Results of a typical N_2O_5 uptake experiment are shown in Figure 2. N_2O_5 in humidified zero air was either sampled directly by the TD-CaRDS and I^-CIMS instruments or after passing through the flow reactor that contained samples of the substrate. The amount of $ClNO_2$ produced was determined from the difference between the amount of $ClNO_2$ measured with the reactor in-line, and the background $ClNO_2$ counts present in the CIMS when the reactor was out of line. The amount of N_2O_5 taken up was determined by the difference between the N_2O_5 remaining in the gas stream after reaction, and the N_2O_5 that would have been in the gas stream had no uptake occurred, as determined by interpolation of the N_2O_5 levels before and

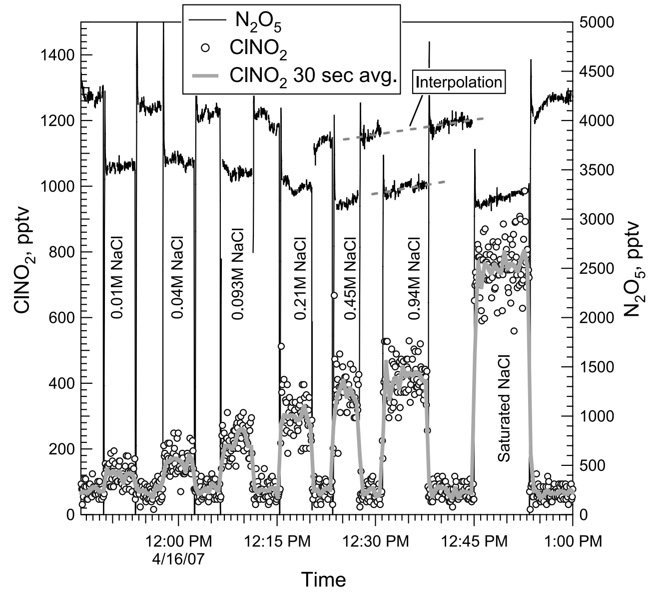

Figure 2. Measured N_2O_5, and $ClNO_2$ following the exposure of $(NH_4)HSO_4$ to N_2O_5 at a series of [Cl^-]. The solid line is 1 second N_2O_5, the dots are individual $ClNO_2$ measurements and the dashed line is the 30 second average $ClNO_2$.

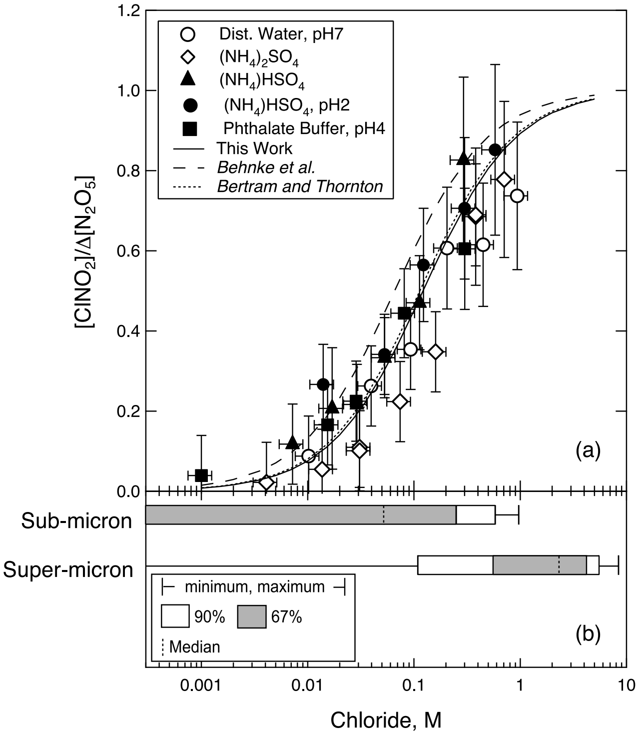

Figure 3. (a) The efficiency of conversion of N_2O_5 to $ClNO_2$ as a function of substrate chloride concentration, and (b) the range of sub- and super-micron chloride concentrations measured during the TexAQS-GoMACCS 2006 field study in the Gulf of Mexico. The curves in Figure 3a are fits to the competitive reaction model for the measurements in this work (solid line), *Behnke et al.* [1997] (dashed line), and *Bertram and Thornton* [2009] (dotted line).

after reaction (as in the example shown in Figure 2) and corrected for the "blank" uptake. In cases where the N_2O_5 signal was not stable for an entire cycle of these measurements, the N_2O_5 taken up was determined by the fall or rise in N_2O_5 when the reactor was placed in-line or taken out of line, respectively. The $ClNO_2$ production efficiency was taken as the ratio of the measured $ClNO_2$ production to the N_2O_5 loss. It is clear from simple mass balance considerations that changes in concentration due to loss of water to the humidified stream, or loss of Cl^- from the surface layer are small on the time scale of the experiments. Moreover, no systematic changes in $ClNO_2$ production were observed over the course of an individual exposure.

[9] The results of uptake experiments are shown in Figure 3a, and a fit to this data using the model described below is shown, along with similar fits from *Behnke et al.* [1997], and *Bertram and Thornton* [2009]. The conversion efficiencies measured in our work were in a range that agreed with, or was slightly lower (25–30%), than the previous results. There was no systematic dependence of the $ClNO_2$ production efficiency on the nature of the substrate, aside from chloride content.

4. Discussion

[10] The mechanism for the production of $ClNO_2$ from N_2O_5 uptake on chloride-containing solutions has been discussed previously [*Behnke et al.*, 1997; *Rossi*, 2003; *Bertram and Thornton*, 2009] and is thought to proceed through the reversible solvation of N_2O_5 in aqueous solution and ionization, which is the rate-limiting step in the uptake process;

$$N_2O_{5(g)} + \text{aerosol} \leftrightarrow N_2O_{5(aq)} \tag{1}$$

$$N_2O_{5(aq)} \leftrightarrow NO_2^+{}_{(aq)} + NO_3^-{}_{(aq)} \tag{2}$$

A number of experimental observations suggest that reaction (2) is rate limiting for the overall reactive uptake of N_2O_5, and that the branching between different reaction products arises from the competitive reaction of nitronium ion (NO_2^+) with either water or other anions in solution. First, the uptake coefficient of N_2O_5 is larger on aqueous surfaces compared to dry or surfactant-coated solutions [*Thornton and Abbatt*, 2005], so that the availability of water for the solvation and ionization process is critical. Second, the presence of nitrate in solution suppresses uptake of N_2O_5 [*Mentel et al.*, 1999; *Wahner et al.*, 1998; *Bertram and Thornton*, 2009], indicating that reaction (2) is reversible and that NO_3^- ions can compete for reaction of NO_2^+ in solution. Third, this work as well as preceding work [*Behnke et al.*, 1997; *Rossi*, 2003; *Bertram and Thornton*, 2009] has shown that the coefficient for uptake of N_2O_5 is independent of the chloride concentration.

[11] The dependence of $ClNO_2$ formation on chloride ion concentration is attributed to the competitive reaction of nitronium ion, NO_2^+ with either H_2O or Cl^-;

$$NO_2^+{}_{(aq)} + H_2O \rightarrow HNO_{3(aq)} + H^+ \tag{3}$$

$$NO_2^+{}_{(aq)} + Cl^-_{(aq)} \rightarrow ClNO_2{}_{(aq)} \tag{4}$$

In our experimental system the NO_3^- resulting from N_2O_5 uptake was much too small in concentration ($\ll 10^{-4}$M) to affect the NO_2^+ concentrations; therefore, we can assume that Reactions 3 and 4 are the only important reactions of NO_2^+, and the data can be fit to a competitive reaction expression;

$$\frac{[ClNO_2]}{\Delta[N_2O_5]} = \frac{1}{\frac{k_3[H_2O]}{k_4[Cl^-]} + 1} \tag{5}$$

The fit of this expression to data from this study resulted in a ratio k_4/k_3 of 450 ± 100 as shown in Figure 3a. The analysis from *Behnke et al.* [1997] resulted in a ratio k_4/k_3 of 836 ± 32, and the analysis given by *Bertram and Thornton* [2009] resulted in a ratio of 483±175, and these are also shown in Figure 3a. It should be noted that *Behnke et al.*'s [1997] measurements had far fewer data points in the low $[Cl^-]$ range, and were for pure NaCl/water solutions. Also, the uncertainty quoted by *Behnke et al.* [1997] was apparently for the fit only and did not include all the experimental uncertainties. The analysis of *Bertram and Thornton* [2009] was based on a smaller number of measurements on mixed $NaNO_3$/NaCl particles, and included only one data point in the lower chloride range (0.001 to 0.3 M) most relevant to the current study. The three k_4/k_3 ratio determinations are of similar magnitude and yield similar estimates for $ClNO_2$ production as a function of aerosol chloride. There is reasonable agreement among the three determinations considering that the present study had more detailed measurements at lower concentrations. In addition, none of the studies corrected their data for the ionic strengths, which would have the effect of lowering the activity of Cl^- solutions that contained other salts, i.e., most of our results, and all but one of the *Bertram and Thornton* [2009] data points. This would bring our results slightly closer ($\leq$30%) to *Behnke et al.*'s [1997] results.

[12] The extent of $ClNO_2$ production in the polluted MBL has been recently explored by *Osthoff et al.* [2008] who found that yields in the range of 10 to 65% were required to explain the ambient measurements of $ClNO_2$. The aerosol chloride concentrations measured in conjunction with the TexAQS-GoMACCS 2006 study [*Osthoff et al.*, 2008] are also shown in Figure 3 for both the sub- and super-micron size ranges. The super micron fraction was mostly dust and sea salt, while the sub micron chloride was thought to have originated from partitioning of gas phase HCl, derived for example from acid displacement from sea salt, to the submicron aerosol [*Osthoff et al.*, 2008]. It is clear that those atmospheric concentrations, and results of our laboratory measurements, are consistent with the chemistry proposed by *Osthoff et al.* [2008] to explain ambient $ClNO_2$ measurements. Aerosol chloride concentrations sufficient to make the yield of $ClNO_2$ large can be maintained by equilibration with gas-phase HCl on a time scale rapid compared to the uptake of N_2O_5.

[13] The measurements presented here were made at room temperature, however some idea of the temperature dependence of $ClNO_2$ formation can be estimated from the likely temperature dependencies of the individual processes. The reaction of NO_2^+ with Cl^-, because it is an ion-ion reaction, is likely to have little or no activation energy, and thus have a small temperature dependence. The reaction of NO_2^+ with H_2O is slower at room temperature (k_4/k_3 is in the range 450 to 836), which implies an activation energy sufficient to result in a much slower reaction at lower temperatures. Accordingly, the yield of $ClNO_2$ may increase at lower temperature, for a given Cl^- concentration.

5. Conclusions

[14] The production of $ClNO_2$ from the uptake of N_2O_5 on model substrates was measured as a function of chloride ion concentration and pH. The production efficiencies ($ClNO_2$ produced per N_2O_5 taken up) varied as a function of [Cl^-] in a manner consistent with a simple competitive reaction model [*Behnke et al.*, 1997; *Bertram and Thornton*, 2009], and were in the range necessary to explain the recent measurements of $ClNO_2$ in the polluted MBL [*Osthoff et al.*, 2008; *Kercher et al.*, 2009]. There are some indications of a dependence on the nature of the substrate in that the lower pH substrates had slightly higher production efficiencies; however these differences were not outside the uncertainties of the measurements. Observational evidence suggests that N_2O_5 uptake is rate-limited by solvation and ionization, and that product branching, including $ClNO_2$ formation, is determined by the subsequent reactions of NO_2^+ cation. Species other than H_2O or Cl^- could potentially compete for NO_2^+ and give rise to new and, as yet, unexplored chemicals, although these possibilities were not explored in this work.

[15] Mass balance considerations show that sustained production of $ClNO_2$ (and Cl_2) requires the continued partitioning of gas-phase HCl to particle surfaces. These results also imply that since only modest aerosol chloride concentrations are required to produce substantial $ClNO_2$, this chemistry is probably not limited to near coastal or MBL environments and may have widespread importance anywhere there is NO_x pollution, since NO_x pollution has been shown to be the main driver of N_2O_5 chemistry [*Aldener et al.*, 2006; *Brown et al.*, 2006]. However, production of Cl_2 will likely require higher [Cl^-] and hence will be limited to coastal or MBL areas. Future measurements of N_2O_5, $ClNO_2$, Cl_2, and HCl should be made along side aerosol chloride and acidity, to determine the importance of this chemistry to regional and global chemistry.

[16] **Acknowledgments.** We thank the crew of the NOAA R/V Ronald H. Brown for their help during the TexAQS-GoMACCS 2006 study. This work was supported in part by the NOAA's Health of the Atmosphere Program and NOAA's Climate Goal.

References

Aldener, M., et al. (2006), Reactivity and loss mechanisms of NO_3 and N_2O_5 in a polluted marine environment: Results from in situ measurements during New England Air Quality Study 2002, *J. Geophys. Res.*, *111*, D23S73, doi:10.1029/2006JD007252.

Behnke, W., et al. (1997), Production and decay of $ClNO_2$, from the reaction of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments, *J. Geophys. Res.*, *102*, 3795–3804, doi:10.1029/96JD03057.

Bertram, T. H., and J. A. Thornton (2009), Towards a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, *Atmos. Chem. Phys. Discuss.*, *9*, 15,181–15,214.

Brown, S. S., et al. (2006), Variability in nocturnal nitrogen oxide processing and its role in regional air quality, *Science*, *311*, 67–70, doi:10.1126/science.1120120.

Dubé, W. P., S. S. Brown, H. D. Osthoff, M. R. Nunley, S. J. Ciciora, M. W. Paris, R. J. McLaughlin, and A. R. Ravishankara (2006), Aircraft instrument for simultaneous in situ measurement of NO_3 and N_2O_5 via pulsed cavity ring-down spectroscopy, *Rev. Sci. Instrum.*, *77*, 034101, doi:10.1063/1.2176058.

Erickson, D. J., III, et al. (1999), A general circulation model based calculation of HCl and $ClNO_2$ production from sea salt dechlorination: Reactive chlorine emission inventory, *J. Geophys. Res.*, *104*, 8347–8372, doi:10.1029/98JD01384.

Finlayson-Pitts, B. J., et al. (1989), Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N_2O_5 and $ClONO_2$, *Nature*, *337*, 241–244, doi:10.1038/337241a0.

Fuchs, H., W. P. Dubé, S. Ciciora, and S. S. Brown (2008), Determination of inlet transmission and conversion efficiencies for in situ measurements of the nocturnal nitrogen oxides, NO_3, N_2O_5, and NO_2, via pulsed cavity ring-down spectroscopy, *Anal. Chem.*, *80*, 6010–6017, doi:10.1021/ac8007253.

Kercher, J. P., et al. (2009), Chlorine activation by N_2O_5: Simultaneous, in situ detection of $ClNO_2$ and N_2O_5 by chemical ionization mass spectrometry, *Atmos. Meas. Technol. Discuss.*, *2*, 119–151.

McFiggans, G., et al. (2002), Active chlorine release from marine aerosols: Roles for reactive iodine and nitrogen species, *J. Geophys. Res.*, *107*(D15), 4271, doi:10.1029/2001JD000383.

McNeill, V. F., J. Patterson, G. M. Wolfe, and J. A. Thornton (2006), The effect of varying levels of surfactant on the reactive uptake of N_2O_5 to aqueous aerosol, *Atmos. Chem. Phys.*, *6*, 1635–1644.

Mentel, T. F., et al. (1999), Nitrate effect in the heterogeneous hydrolysis of dinitrogen pentoxide on aqueous aerosols, *Phys. Chem. Chem. Phys.*, *1*, 5451–5457, doi:10.1039/a905338g.

Osthoff, H. D., et al. (2007), Temperature dependence of the NO_3 absorption cross-section above 298 K and determination of the equilibrium constant for $NO_3 + NO_2 \leftrightarrow N_2O_5$ at atmospherically relevant conditions, *Phys. Chem. Chem. Phys.*, *9*, 5785–5793, doi:10.1039/b709193a.

Osthoff, H. D., et al. (2008), High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nat Geosci.*, *1*, 324–328, doi:10.1038/ngeo177.

Pechtl, S., and R. von Glasow (2007), Reactive chlorine in the marine boundary layer in the outflow of polluted continental air: A model study, *Geophys. Res. Lett.*, *34*, L11813, doi:10.1029/2007GL029761.

Roberts, J. M., et al. (2008), N_2O_5 oxidizes chloride to Cl_2 in acidic atmospheric aerosol, *Science*, *321*, 1059, doi:10.1126/science.1158777.

Rossi, M. J. (2003), Heterogeneous reactions on salts, *Chem. Rev.*, *103*, 4823–4882, doi:10.1021/cr020507n.

Schweitzer, F., et al. (1998), Multiphase chemistry of N_2O_5, $ClNO_2$, and $BrNO_2$, *J. Phys. Chem. A*, *102*, 3942–3952, doi:10.1021/jp980748s.

Thornton, J. A., and J. P. D. Abbatt (2005), N_2O_5 reaction on submicron sea salt aerosol: Kinetics, products, and the effect of surface active organics, *J. Phys. Chem. A*, *109*, 10,004–10,012, doi:10.1021/jp054183t.

Wahner, A., et al. (1998), Heterogeneous reaction of N_2O_5 on sodium nitrate aerosol, *J. Geophys. Res.*, *103*, 31,103–31,112, doi:10.1029/1998JD100022.

T. Bates, D. Coffman, and P. Quinn, Pacific Marine Environment Laboratory, NOAA, 7600 Sand Point Way NE, Bldg. 3, Seattle, WA 98115, USA.

S. S. Brown, A. R. Ravishankara, and J. M. Roberts, Chemical Sciences Division, Earth System Research Laboratory, NOAA, 325 Broadway, Boulder, CO 80305-3337, USA. (james.m.roberts@noaa.gov)

H. D. Osthoff, Department of Chemistry, University of Calgary, 2500 University Dr. NW, Calgary, AB T2N 1N4, Canada.