



Halogen activation from the uptake of N_2O_5 on sea salt in the marine boundary layer during TexAQS-GoMACCS 2006



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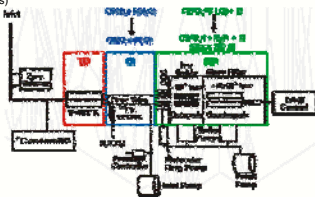
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Abstract

The nitrate radical, NO_3 , formed from reaction of NO_2 with O_3 and dinitrogen pentoxide, N_2O_5 , formed from subsequent reaction of NO_2 with NO_2 drive several important chemical processes, including oxidation of VOCs (by NO_3) and removal of NO_3 ($= NO + NO_2$) by the heterogeneous reaction of N_2O_5 to form either nitric acid, HNO_3 , and/or aerosol nitrates. Laboratory studies have shown that heterogeneous uptake of N_2O_5 on sea salt aerosol produces nitryl chloride, $CINO_2$. Photolysis of $CINO_2$ is believed to be a potential source of Cl atoms, an important oxidant of VOCs in the marine boundary layer. In spite of the potential importance of this halogen activation mechanism, field investigations have yet to directly confirm it. We have measured NO_3 and N_2O_5 by cavity ring-down spectroscopy, and observed $CINO_2$ by I chemical ionization mass spectrometry, on board the NOAA research vessel Ronald H. Brown during the Texas Air Quality Study - Gulf of Mexico Atmospheric Composition and Climate Study (TexAQS/GoMACCS) 2006. In this presentation, we highlight a few aspects of the interaction between nitrogen oxide and halogen cycles in the subtropical marine boundary layer, including $CINO_2$ production from N_2O_5 uptake on sea salt aerosol and $CINO_2$ removal via deposition and photolysis.

Chemical Ionization Mass Spectrometer¹

- used primarily for quantification of peroxyacyl nitrates (PANs)
- employs soft chemical ionization with iodide (I⁻) reagent ion
- used here to measure $CINO_2$ (as $CINO_2+I$)



Calibration

The PAN-CIMS was calibrated (post-campaign) using NO_3 instrument. With this method, $CINO_2$ was thermally ($>300^\circ C$) dissociated, reduced to NO , and quantified by O_3 chemiluminescence.

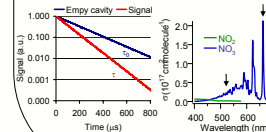
- UV absorption spectrometer. The mixing ratio of $CINO_2$ was quantified via its absorption at 215 nm.
- N_2O_5 depletion method. $CINO_2$ was synthesized in situ by flowing gaseous N_2O_5 over wetted sodium chloride crystals. The depletion of N_2O_5 was monitored by CaRDS. Unity yield of $CINO_2$ was assumed.

The three methods yielded consistent results.

To verify the absence of an inlet artifact (for example, $CINO_2$ generation from N_2O_5 on the inlet walls), synthetic N_2O_5 (up to 30 ppbv) was added to the inlet in the field without corresponding enhancement in the $CINO_2$ signal.

Cavity Ring-Down Spectrometer^{2,3}

- Used to measure NO_2 , NO_3 , and N_2O_5 . NO_2 and NO_3 are measured directly, and N_2O_5 is converted to NO_2 in a heated channel.
- Detection limits (1s): < 0.5 pptv (NO_2 , N_2O_5), 100 pptv (NO_3).



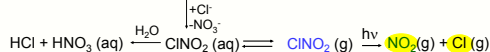
Concentration: $\alpha = N \sigma$ absorption (cm^{-1})
 $\alpha = N \sigma = \frac{R_L}{c} \left(\frac{1}{t} - \frac{1}{t_0} \right)$ molecular number density (cm^{-3})
 σ absorption cross section (cm^2)
 c speed of light ($cm \cdot s^{-1}$)
 t ring-down time constant in the presence of an absorber
 t_0 ring-down time constant in the absence of an absorber
 R_L minimum detectable absorption
 σ_{min} standard deviation in σ
 $\alpha_{min} \approx 5 \times 10^{-11} cm^{-1}$
 t_0 is determined by titration with NO or zero air.

TexAQS-GoMACCS 2006

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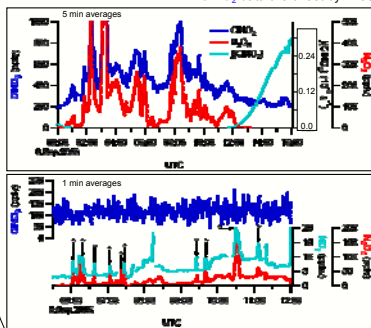
Formation of $CINO_2$



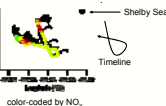
Uptake of N_2O_5 on sea salt ($\gamma \approx 2.5 \times 10^{-2}$) produces $CINO_2$ in up to unity yield. Subsequent photolysis is believed to generate Cl radicals.⁴⁻¹⁰

Measurements of $CINO_2$

$CINO_2$ data are offset by ~ 150 pptv.

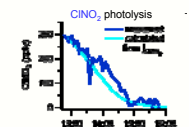
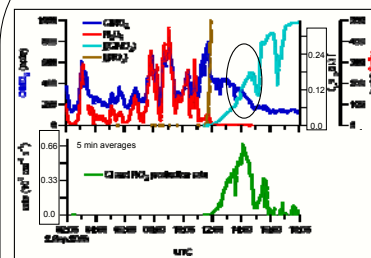


- At night, the mixing ratios of $CINO_2$ and N_2O_5 were tightly correlated.
- The slopes of correlation plots (not shown) were variable.
- The largest $CINO_2$ signals were observed in air of mixed marine (sea salt) and anthropogenic origin (largest formation rates of N_2O_5), for example on Sept 8, when R/V Brown was on station at 'Barbour's cut' near the entrance of the Houston ship channel.
- On Sept 5 (6-12 UTC), R/V Brown sampled emissions from an oil platform ('Shelby Sea') at close range (transport time < 10 min). N_2O_5 was, and $CINO_2$ was not, observed in fresh plumes (in contrast to other ship plumes, see time series at the bottom of the poster), corroborating the absence of an inlet artifact and $CINO_2$ formation mechanism.

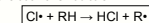


Halogen activation

$CINO_2$ data are offset by ~ 150 pptv.



- $d[Ci]/dt = d[NO_2]/dt + [CINO_2] \times ([CINO_2])$
- Assumed CIMS baseline offset ~ 150 pptv.
- Integrated Cl and NO_3 yield ~ 350 pptv ($= [CINO_2]$ before sunrise).
- Calculated Cl and NO_3 yields are upper limits.
- \Rightarrow Recycling of NO_3
- \Rightarrow Generation of Cl radicals.



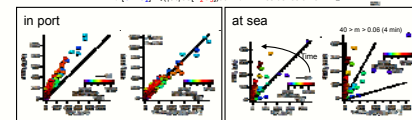
Production and loss of $CINO_2$

- Integration of production and loss terms yields $[CINO_2]$:

$$\frac{d[CINO_2]}{dt} = [CINO_2] \left(\frac{d[CINO_2]}{dt} + k_{loss}[CINO_2] - k_{prod}[CINO_2] \right)$$

k_{prod} mean molecular speed of N_2O_5 ($\sim 240 m \cdot s^{-1}$)
 γ uptake coefficient (~ 0.025)
 k_{loss} yield of $CINO_2$
 $S_{aerosol}$ aerosol surface density ($\mu m^2 \cdot cm^{-3}$)
 k_{loss} loss rate coefficient for $CINO_2$ (e.g., deposition, hydrolysis)

- Data most consistent with:
- $\gamma_{CINO_2} \rightarrow 1$ (for $[Cl] > 0.05 M$)
- $\gamma_{N_2O_5} \rightarrow 0.03$ (high)
- $\gamma_{loss} \rightarrow 0$ (limited by sunrise)



Conclusions

- $CINO_2$ has been observed in the marine boundary layer for the first time.
- Mixing ratios of $CINO_2$ were correlated with the product of N_2O_5 mixing ratio and aerosol surface.
- Early morning photolysis of $CINO_2$ was observed, with Cl production rates as high as $1 \times 10^6 cm^{-3} s^{-1}$.

References

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Acknowledgments

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