



# 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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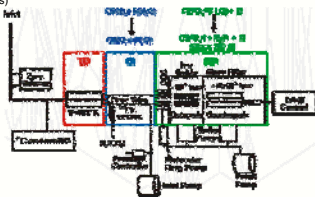
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## Abstract

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  $NO_2$ ) 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 Spectrometer<sup>1</sup>

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



### Calibration

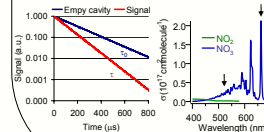
- The PAN-CIMS was calibrated (post-campaign) using  $NO_2$  instrument. With this method,  $CINO_2$  was thermally ( $>300^\circ C$ ) dissociated, reduced to  $NO$ , and quantified by  $O_3$  chemiluminescence.
- UV absorption spectrometer. The mixing ratio of  $CINO_2$  was quantified via its absorption 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<sup>2,3</sup>

- 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 ( $NO_3$ ).



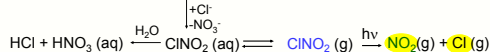
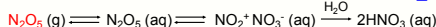
**Concentration:**  $\alpha = N \sigma c$   
 $\alpha = N \sigma \left( \frac{1}{t} - \frac{1}{t_0} \right) / c$   
 $\alpha$  absorption ( $cm^{-1}$ )  
 $N$  molecular number density ( $cm^{-3}$ )  
 $\sigma$  absorption cross section ( $cm^2$ )  
 $c$  speed of light ( $cm \cdot s^{-1}$ )  
 $t$  ring-down time constant in the presence of an absorber  
 $t_0$  ring-down time constant in the absence of an absorber  
**Sensitivity:**  $\alpha_{min} = \frac{R_d \sqrt{2} \pi \nu_0}{C L}$   
 $\alpha_{min} \approx 5 \times 10^{-11} cm^{-1}$   
 $R_d$  standard deviation in  $t_0$   
 $\nu_0$  ratio of the absorption path over which the absorber is present with respect to the total cavity length  
 $t_0$  is determined by titration with NO or zero air.

## TexAQS-GoMACCS 2006

Texas Air Quality Study - Gulf of Mexico Atmospheric Composition and Climate Study, July 27 - Sept. 11, 2006  
<http://www.esrl.noaa.gov/2006>



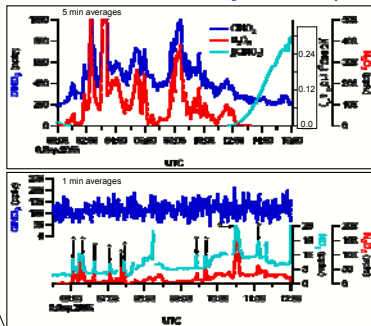
## Formation of $CINO_2$



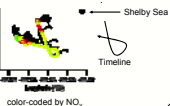
Uptake of  $N_2O_5$  on sea salt ( $\gamma \approx 2.5 \times 10^{-2}$ ) produces  $CINO_2$  in up to unity yield. Subsequent photolysis is believed to generate Cl radicals.<sup>4-10</sup>

## Measurements of $CINO_2$

$CINO_2$  data are offset by  $\sim 150$  pptv.

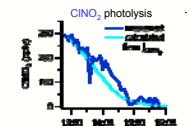
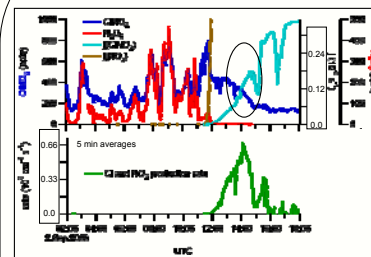


- At night, the mixing ratios of  $CINO_2$  and  $N_2O_5$  were tightly correlated.
- The slopes of correlation plots (not shown) were variable.
- The largest  $CINO_2$  signals were observed in air of mixed marine (sea salt) and anthropogenic origin (largest formation rates of  $N_2O_5$ ), for example 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.

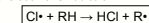


## Halogen activation

$CINO_2$  data are offset by  $\sim 150$  pptv.



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



## Production and loss of $CINO_2$

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

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

$$S_{CINO_2} = \gamma_{CINO_2} \frac{d[N_2O_5]}{dt} + k_{CINO_2} [N_2O_5]$$

$$k_{loss} = k_{deposition} + k_{hydrolysis}$$

$$k_{deposition} = v_w \frac{A}{V} \quad k_{hydrolysis} = k_{hydrolysis} [H_2O]$$

$$v_w = \text{mean molecular speed of } N_2O_5 \quad A = \text{uptake coefficient} \quad V = \text{volume}$$

$$k_{hydrolysis} = \text{loss rate coefficient for } CINO_2$$

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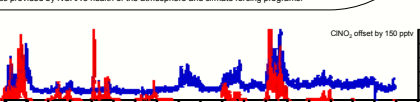
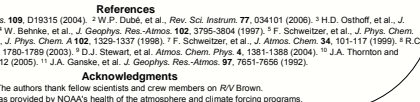
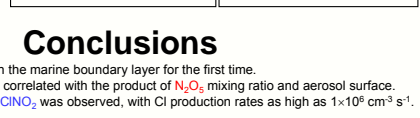
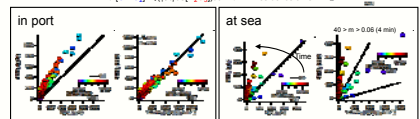
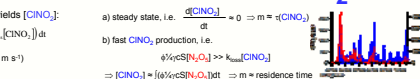
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## Conclusions

- $CINO_2$  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

- <sup>1</sup> D.L. Slusher, et al., *J. Geophys. Res.-Atmos.* 109, D19315 (2004). <sup>2</sup> W.P. Dubé, et al., *Rev. Sci. Instrum.* 77, 034101 (2006). <sup>3</sup> H.D. Osthoff, et al., *J. Geophys. Res.-Atmos.* 111, D12305 (2006). <sup>4</sup> W. Bahke, et al., *J. Geophys. Res.-Atmos.* 102, 3795-3804 (1997). <sup>5</sup> F. Schweizer, et al., *J. Phys. Chem. A* 102, 3942-3952 (1998). <sup>6</sup> A. Frenzel, et al., *J. Phys. Chem. A* 102, 1329-1337 (1998). <sup>7</sup> F. Schweizer, et al., *J. Atmos. Chem.* 34, 161-171 (1999). <sup>8</sup> R.C. Hoffman, et al., *Phys. Chem. Chem. Phys.* 5, 1780-1789 (2003). <sup>9</sup> D.J. Stewart, et al., *Atmos. Chem. Phys.* 4, 1381-1388 (2004). <sup>10</sup> J.A. Thornton and J.P.D. Abbatt, *J. Phys. Chem. A* 109, 10004-12 (2005). <sup>11</sup> J.A. Ganske, et al., *J. Geophys. Res.-Atmos.* 97, 7651-7656 (1992).

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