HNO_3 and VOCs Measurements Using ID-CIMS and PTR-MS during TexAQS II 2006

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ABSTRACT

Part I: An ID-CIMS developed at the Texas A&M University and a commercial PTR-MS were deployed at the UH Moody Tower from August 17 to October 15, 2006 to measure gaseous HNO_3 and VOCs. The ID-CIMS was set to collect data at 0.1 Hz corresponding to a detection limit of 30 pptv. Daytime HNO_3 followed the solar cycle and was consistent with its role in the photochemical processes. HNO_3 daily high ranged from 0.2 to 2 ppbv in the early afternoon and occasionally nighttime peaks were also observed, which could be originated from either NO_3 / N_2O_5 + $H_2O(g)$ reaction or transported aged plumes. The PTR-MS was continuously monitoring about 20 VOC species and the detection limits ranged from a few hundred pptv (e.g. benzene) to a few ppbv (e.g. propene). Observations at the UH site showed influences from the ship-channel petrochemical industries. Propene was the major alkene species detected and a record of 0.8 ppmv was observed in the morning of August 20. Aromatic VOCs were consistent with the local traffic conditions. Oxygenated VOCs (e.g. acetaldehyde and ketones) showed correlations with ozone productions. Biogenic VOCs (e.g. isoprene and monoterpenes) were not significant at the UH site.

Part II: A commercial compact PTR-MS (IONICON ANALYTIK) was deployed at the Aldine site from September 13 to 30, 2006 to participate in the Houston Triangle Campaign, which was designed to characterize the outflow from the ship-channel area in both gas phase and aerosol phase compositions. The PTR-MS was continuously monitoring about 20 VOC species and the detection limits ranged from a few hundred pptv (e.g. benzene) to a few ppbv (e.g. propene). Unlike the UH Moody Tower, the Aldine site was about 20 miles to the NW of the ship-channel area. Thus no tremendous propene peaks were observed at the Aldine site. However acetaldehyde, a major oxidation product from olefin, did show good correlations with propene. Isoprene and nighttime monoterpenes were recorded at this surface site. Aromatic VOCs also showed traffic influences. During late nights of September 19 and 20, good correlations were found between VOC (including isoprene, toluene, MVK, MACR, MEK, and methylglyoxal) and the organic aerosol mass loading, which indicated that VOC oxidation processes could contribute to the SOA formations.

Introduction

Tropospheric Ozone Production:

$CO + OH \rightarrow CO_2 + H$

$H + O_2 \rightarrow HO_2$

$HR + OH \rightarrow HO_2 + R$, (HR = VOCs)

$HO_2 + NO \rightarrow NO_2 + OH$

$NO_2 + h\nu \rightarrow NO + O(^3P)$

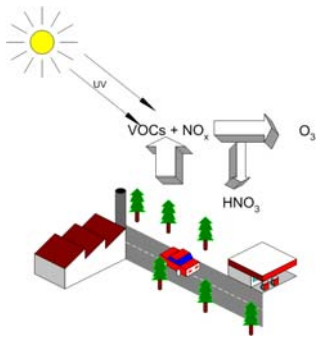
$O(^3P) + O_2 \rightarrow O_3$

$R + O_2 \rightarrow RO_2$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

$RO_2 + HO_2 \rightarrow ROOH + O_2$

$OH + NO_2 \rightarrow HNO_3$



Ion–Molecule Reaction:

$A^{(+ \text{ or } -)} + X \rightarrow X'^{(+ \text{ or } -)}$ + others, k_1

$[X'] = k_1 [A] [X] \Delta t$, therefore $[A] = [X'] / k_1[X] \Delta t$,

where $\Delta t = L/U_t$ and L is the length of the drift-tube and U_t is the total velocity of the reagent ion.

$U_t = U_i + U_f$,

where U_i is ion drift velocity and U_f is flow velocity in the drift tube.

$U_i = uE$,

where u is ionic mobility of the ion and E is the voltage gradient in the drift tube.

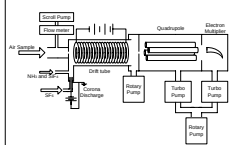
$u = u_0(760/P)(T/273)$

where u_0 is the reduced ionic mobility measured from experiments.

Instrumentations

Ion-Drift Chemical Ionization Mass Spectrometry (Fortner et al., 2004):

Setup for HNO_3 detection



Ion Chemistry

$SF_6 + e^- \rightarrow SF_6^-$

$SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$

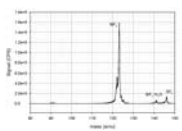
$SiF_5^- + HNO_3 \rightarrow SiF_5 \cdot HNO_3$ adduct, k

$k = 3.8 \times 10^{-10}$ cm^3 molecule^{-1}

(Huey et al., 1996)

$[HNO_3] = [SiF_5^- \cdot HNO_3] / (k[SiF_5^-]\Delta t)$

Spectrum of Reagent Ion



•A permeation tube (VICI Metronics) containing 68% HNO_3 solution was used to calibrate the ID-CIMS

•The HNO_3 background signals were checked by putting a 2-inch ID nylon filter before the inlet

Proton-Transfer-Reaction Mass Spectrometry:

PTR-MS at the T0 Site

$H_3O^+(H_2O)_n + R \rightarrow RH^+ + H_2O_{(n+1)}$, (R = VOCs)

where n = 0, 1 and corresponding rate constants are k'_0 and k'_1, respectively.

$[R] = [RH^+] / (k'_0[H_3O^+] + k'_1[H_3O^+ \cdot H_2O])[R]\Delta t$.

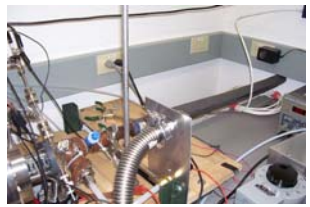
•Instrument was running 24 hours a day

•The majority of the time 24 masses were scanned sequentially in single ion mode at 2 seconds per mass

Moody Tower Experiments

Instrument Setup:

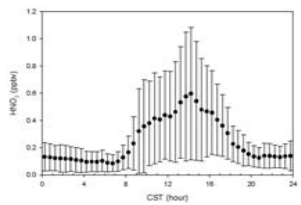
ID-CIMS and PTR-MS were set up inside trailer two



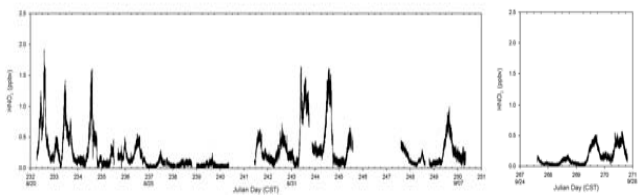
ID-CIMS inlet inside the trailer

Preliminary Results:

HNO_3:

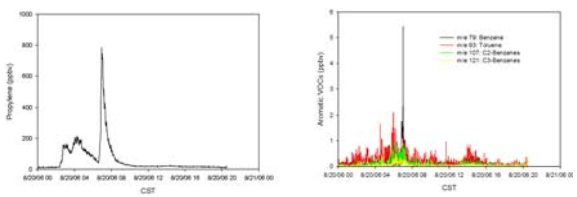


Hourly average HNO_3 diurnal profile



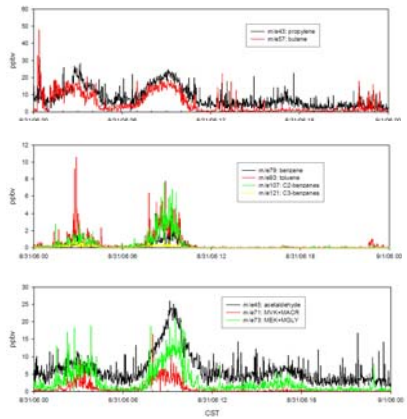
HNO_3 time series for the whole campaign

Propylene and aromatic VOCs on Aug 20, 2006:



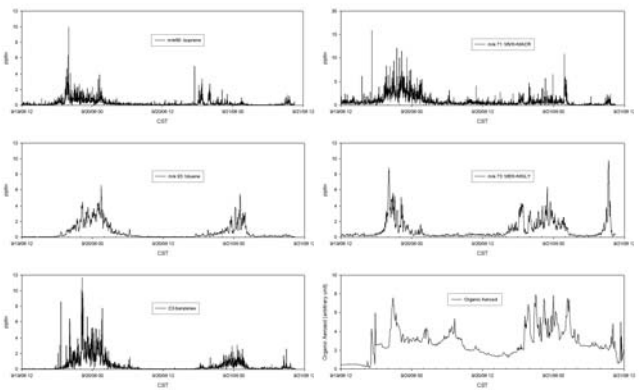
On 20 Aug 2006, a 800 ppbv propylene peak was recorded in the early morning. Meanwhile aromatic VOCs including benzene, toluene, C2-benzenes, and C3-benzenes were also observed.

Aug 31 VOCs at UH



Alkenes, aromatic VOCs, and OVOCs observed on Aug 31 at UH.

VOCs at Aldine



Isoprene, toluene, C2-benzenes, OVOCs, and organic aerosol mass loading observed from Sep 19 to 21 at Aldine.

References:

Fortner, C. E., J. Zhao, and R. Zhang, *Anal. Chem.*, 76 (2004) 5436-5440.

Huey, L.G., and E. R. Lovejoy, *Int. J. Mass Spectrom. Ion Processes.*, 155 (1996) 133-140.