1. INTRODUCTION

1.1 Background

During August and September 2006 the University of Houston (UH) contributed to the Texas Air Quality Study II (TexAQS-II) through a broad variety of activities. UH set up and coordinated the Moody Tower supersite on the UH campus which included about 50 scientists. At this site a comprehensive data set was collected covering meteorological parameters, gas-phase chemistry using in-situ and long path instrumentation, physical and chemical aerosol properties including analysis of inorganic and organic aerosol content, and highly resolved measurements of the atmospheric radiation field including a wide range of photolysis rates which are critical for photochemical processes.

The umbrella project performed at the Moody Tower site was the "TexAQS II Radical Measurement Project (TRAMP)" funded by the Houston Advanced Research Center (HARC Grant No. H-78 UofH). The main research goal of this project was to provide data sets to determine and quantify sources and sinks for radicals in the urban atmosphere of Houston during the TexAQS II field campaign in 2006. Elucidating the radical budget is critical to developing a better understanding of the formation processes of secondary species in the Houston area.

Figure 1-1 describes in principle the fast reaction cycles involved in the formation of secondary species as well as the removal mechanisms from those cycles for nitrogen and carbon containing species. The hydroxyl radical (OH) is the most important oxidant in the atmosphere and controls the atmospheric lifetimes of most trace gases. OH is produced in photolysis processes of ozone (O_3), formaldehyde (HCHO) and nitrous acid (HONO). OH initiates oxidation reactions with NO_x, CO, anthropogenic and biogenic VOCs. These reactions form peroxy radicals (RO_2) which in turn will cause the conversion of NO to NO_2 and subsequently the formation of O_3. Within the degradation of VOC also car-bonyls will be formed which either may be photolyzed (e.g. formaldehyde) or oxidized by OH and

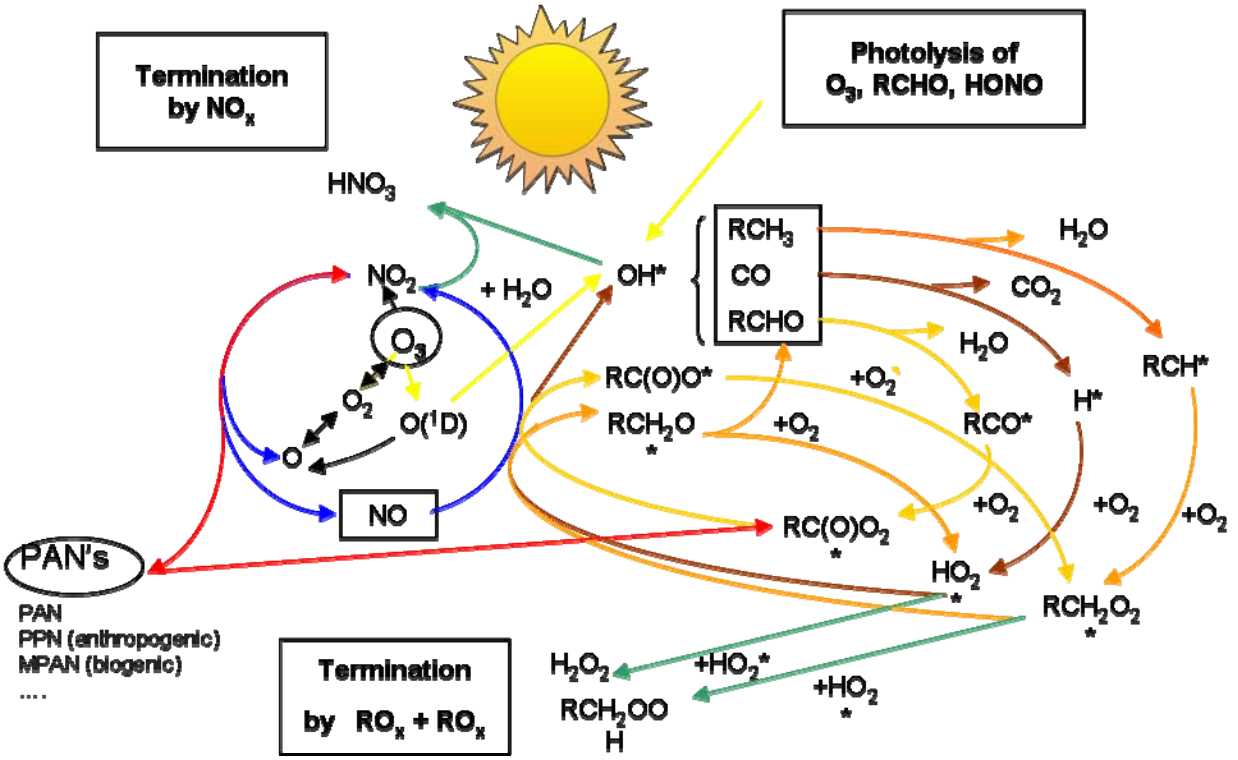

Figure 1-1. Daytime photochemical Processes.

finally contribute to the formation of peroxycarboxylic nitric anhydrides (PANs). Loss mechanisms for OH involve reactions between peroxy radicals leading to hydrogen peroxide (H_2O_2) and organic peroxides, e.g. methylhydroperoxide (MHP) and hydroxylmethylhydroperoxide (HMHP), and reactions with NO_2 leading to nitric acid (HNO_3) and PAN.

TERC projects H78 [*University of Houston*, 2007] and H86 [*University of Houston*, 2008] performed detailed studies to the radical budget in the Houston area. Critical uncertainties of the processes described in Figure 1-1 are associated with the direct emissions of the OH radical precursors HCHO and HONO from flares, smoke stacks, and other point sources, as well as from mobile sources. For HONO, surface-induced formation of HONO, possibly linked to the previous deposition of HNO_3, has not yet been sufficiently investigated. Closely related to this latter issue is the fact that daytime HONO levels and its sources are not well understood.

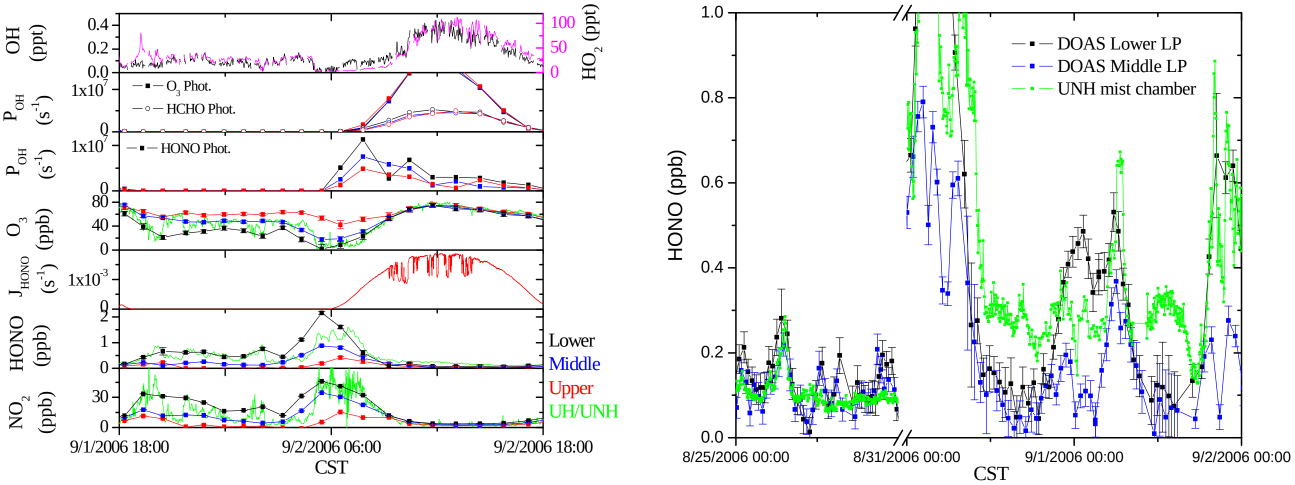

Figure 1-2. Left: Vertical profiles of various parameters, including HONO mixing ratios and P(OH) induced by HONO (data based on UCLA DOAS measurements). Right: Measurements of HONO by Mist Chamber/Ion Chromatography (MC/IC) by UNH and LP DOAS by UCLA.

Strong vertical gradients of HONO were observed during many nights and mornings during TRAMP, with HONO mixing ratios up to 2 ppb near the ground close to sunrise as shown in Figure 1-2. Also, this presentation shows time series of the OH production rate, P(OH), calculated for three primary sources, O_3, HCHO, and HONO photolysis. As it can be nicely seen, HONO is an important source in the morning and P_{HONO}(OH) is altitude dependent, because photolysis starts before the NBL breaks up. In accordance with higher mixing ratios close to the surface also strongest P_{HONO}(OH) occurs at the levels closer to the ground. These measurements were performed on the roof of the Moody Tower. It is yet not well understood what environment or type of surface, i.e. concrete, glass, road, organic surfaces, soil (in particular humics in soil) etc., may favor HONO formation and eventually have an impact on OH formation. Porosity, determining the area surface and the presence of water films may play a role.

Since even small differences in HONO mixing ratios can have a significant impact on the OH production rate P(OH), it is indispensable to determine ambient HONO levels as accurate as possible. Figure 1-2, right, compares the two instrumentations available for HONO measurements during TRAMP. During most day and nighttimes LP-DOAS and MC/IC measurements agreed well, both at low and at high ranges. Only on few occasions, under specific wind directions during daytimes, the MC/IC system showed higher values than the LP-DOAS. Such a difference during daytime can have significant implications on assumptions of HONO sources as well as on OH production rates. At this point it is unclear what causes these disagreements. Possible interferants may include nitrophenols, alkyl amines, aromatic amines, and organic nitrite.

Analysis of measurements of HONO and HNO_3 performed by the University of New Hampshire within H86 suggests potential heterogeneous production of HONO from HNO_3 associated with rush hour organic aerosol. Figure

1-3, left, shows HONO peaks during rush hour while HNO_3 is at a minimum. At the same time organic aerosol [i.e. (m/z) ratio = 44/57] is at a minimum. Presumably it is less-processed, hydrocarbon-like organic aerosol (likely emitted directly). This is also supported by ancillary CO and acetylene data which suggest vehicular impact. HONO concentrations are also well correlated with organic mass (Figure 1-3, right), and thus with surface area. potential heterogeneous production of HONO from HNO_3 associated with rush hour primary organic aerosol. First analysis shows that both temperature and relative humidity are not driving these processes. However, radiation may presumably favor these processes.

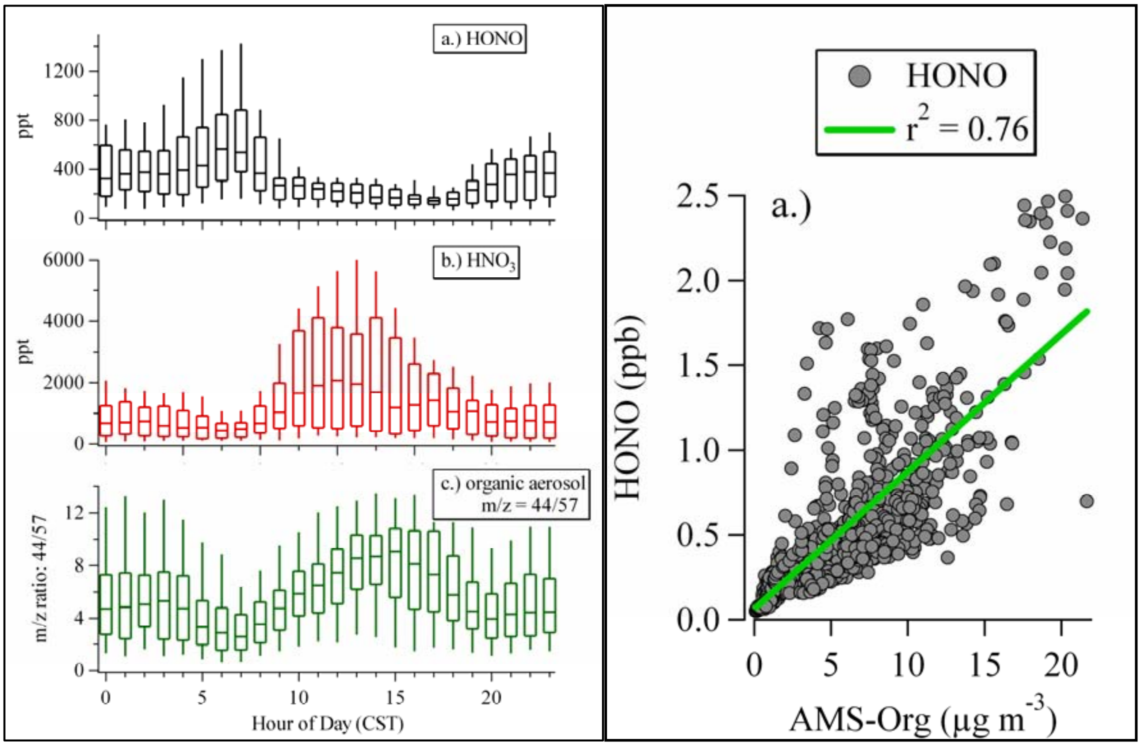

Figure 1-3. Left: Hourly diurnal plots for a.) HONO, b.) HNO_3, and c.) m/z 44/57 ratio for AMS organic aerosol. Mid-box lines represent median concentrations, box tops and bottoms represent 75th and 25th percentile concentrations, and whiskers represent 90th and 10th percentile concentrations. Right: Scatter plot of HONO vs. AMS-organics.

Apart from secondary production HCHO can also be formed emitted primarily. Figure 1-4 shows results of HCHO-CO relationships obtained at the Moody Tower based on in situ instrumentation and discriminated between wind sectors predominantly impacted by air masses originating from urban areas and those originating from the Ship Channel. The data set is also split into night and daytime measurements. Nighttime measurements include the rush hour times. Best correlation between HCHO and CO is found for "urban" air masses at night with a slope of about 7 pptv ppbv^{-1}. Though for nighttime "Ship Channel" air masses correlation is weaker indicating additional dependencies, the slope is quite similar. From these observations an upper limit for the primary emissions of formaldehyde from mobile sources can be estimated to be around 0.5-0.7 % of the CO emissions.

The measurements shown in Figure 1-4 represent an approach to determine traffic related HCHO emissions. Strictly speaking they cannot be considered unambiguously roadside measurements due to the distance of the Moody Tower to primary sources.

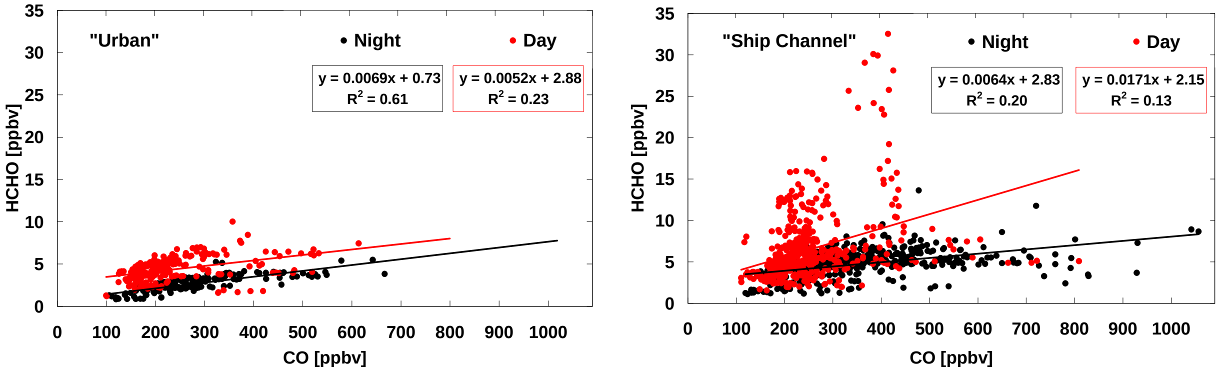

Figure 1-4. Relationships of HCHO to CO obtained at the Moody Tower during nighttimes (8 pm -8 am CST), including rush hours, and during daytime (8 am – 8 pm CST). “Urban” (panel A) is defined as wind direction between 270° – 360°, whereas “Ship Channel” (panel B) is defined as wind direction between 22.5° – 112.5°. In both cases only wind speeds > 0.5 m/s were considered (CO data courtesy NOAA-ARL).

In addition to traffic related sources it also appears that flares may emit primary HCHO. Determination of HCHO/CO ratios in flares as obtained by Baylor aircraft flights suggest that flare emission can have significantly higher HCHO/CO ratios than under traffic induced conditions, i.e. up to 2-5% of flare CO emissions, depending on the distance to the plume center. The amount of releases of possible primary HCHO from stacks is not yet fully addressed.

Based on the findings obtained in the H78 and H86 studies the objective of SHARP (Study of Houston Atmospheric Radical Precursors) is continue and finalize in-depth data analysis of TRAMP and to perform additional focused field studies in the Houston area on the emission sources of HONO and HCHO.

1.2 Project Goals

Projects H78 and H86 have identified major uncertainties in our understanding of the radical budget in Houston. These include primary emissions of nitrous acid (HONO) and formaldehyde (HCHO) from point sources as well as from area sources including surface related processes for the formation of HONO. Another important uncertainty was found in daytime HONO levels. A better quantification of these OH sources is needed to improve the description of ozone (O_3) chemistry in air quality models in Houston. The accurate description of ozone chemistry is required to develop efficient strategies to reduce pollution in Houston and to develop the Houston –SIP.

The SHARP project is designed to address the following issues identified as a result of projects H78 and H86:

- Direct emissions of the OH radical precursors HCHO and HONO from flares, smoke stacks, and other point sources, as well as from mobile sources, are currently not well quantified.
- Surface-induced formation of HONO has not yet been sufficiently investigated.
- Daytime HONO levels and its sources are not well understood

These uncertainties lead to limitations in our current ability to model radicals and ozone formation, and affect the simulated effectiveness of control strategies.