

1 Introduction

Urban atmospheric chemistry and ozone formation is driven by radical species, i.e. the hydroxyl radical, OH, during the day and the nitrate radical, NO₃, during the night. An accurate quantitative description of this radical chemistry, as well as the chemistry and sources of the various radical precursors, is essential to the understanding of air quality.

During the day OH dominates atmospheric chemistry. On global scales OH is predominantly formed through the photolysis of ozone, followed by reaction of O¹D with water. In urban areas, such as Houston, other formation processes become important (Figure 1.1). As we showed in the 2006 TRAMP experiment the photolysis of nitrous acid, HONO, dominates during the early morning and continues to contribute throughout the day. Later in the morning formaldehyde, HCHO, photolysis, forming HO₂ which is rapidly converted to OH in the presence of NO, is the most important HO_x source. Later during the day ozone photolysis dominates. However, HONO and HCHO photolysis still contribute ~10-25% to the OH formation during this time.

Because OH radical chemistry is the driver of urban air pollution chemistry it is crucial to understand the source of the various radical precursors.

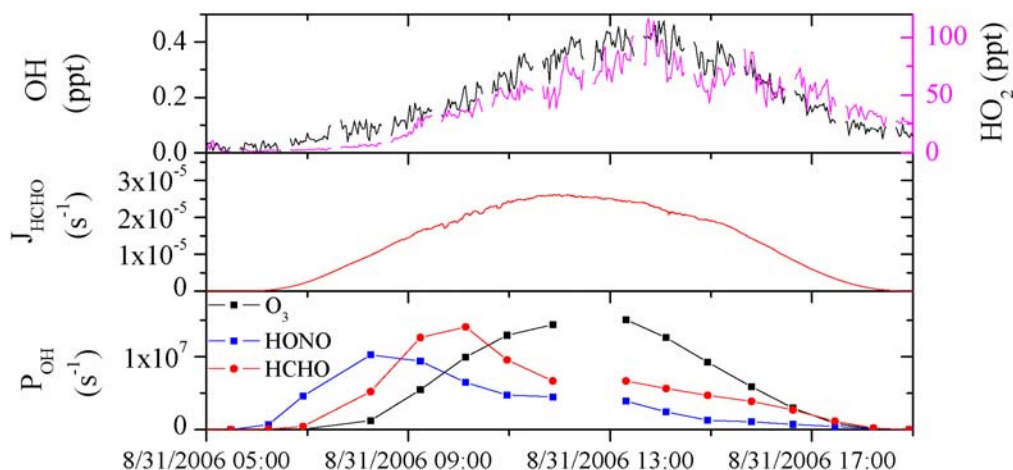


Figure 1.1: Comparison of the contributions of O₃, HCHO and HONO photolysis to the OH formation on 8/31/06 in Houston Texas.

Project H104C was thus aimed to study chemistry and sources of radicals and their precursors in Houston. The first two tasks of the project concentrated on providing new data on the direct emissions of formaldehyde, nitrous acid, and other trace species from point sources in Houston. While observations made at the University of Houston during the TRAMP campaign in 2006 clearly showed plumes of HCHO, which were often correlated with plumes of SO₂ (Figure 1.2), little was known about the direct emission of HCHO from industrial facilities, i.e. smoke stacks and flares. A modeling study by the Univ. of North Carolina suggested that additional direct emissions of HCHO were needed to balance the radical budget for the Houston area.

The first task of this project was thus to measure the average HCHO emission rate of the industrial complex in Texas City using a novel remote sensing approach based on two MAX-DOAS instruments (one from UCLA and one from WSU) operating in tandem upwind and

downwind of the facilities. The second task was the construction and deployment of a new portable Imaging-DOAS system to measure emissions from individual point sources in Houston. The details and results of both tasks will be discussed in Sections 2 and 3.

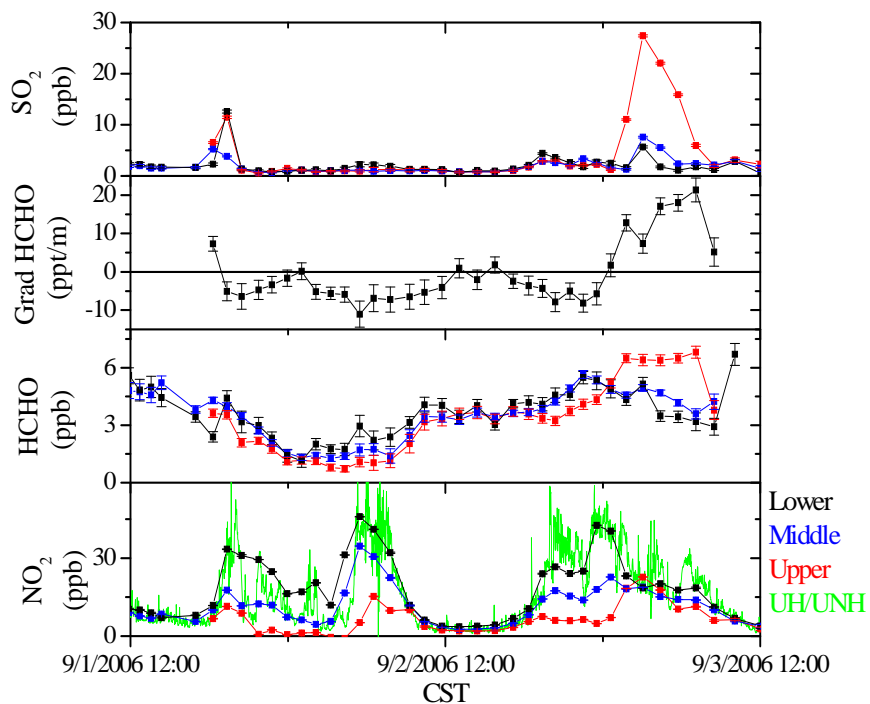


Figure 1.2: Observation of HCHO and SO₂ made by LP-DOAS between UH and downtown Houston during TRAMP in 2006. A plume of HCHO and SO₂ is observed after midnight of 9/3/06. Also shown are the strong vertical profiles of NO₂ found at night in Houston. The color coding in the figure shows the altitude intervals (black 20-70m, blue: 70-130m; red: 130-300m). Shown in green are the in-situ data measured by UH at Moody Tower.

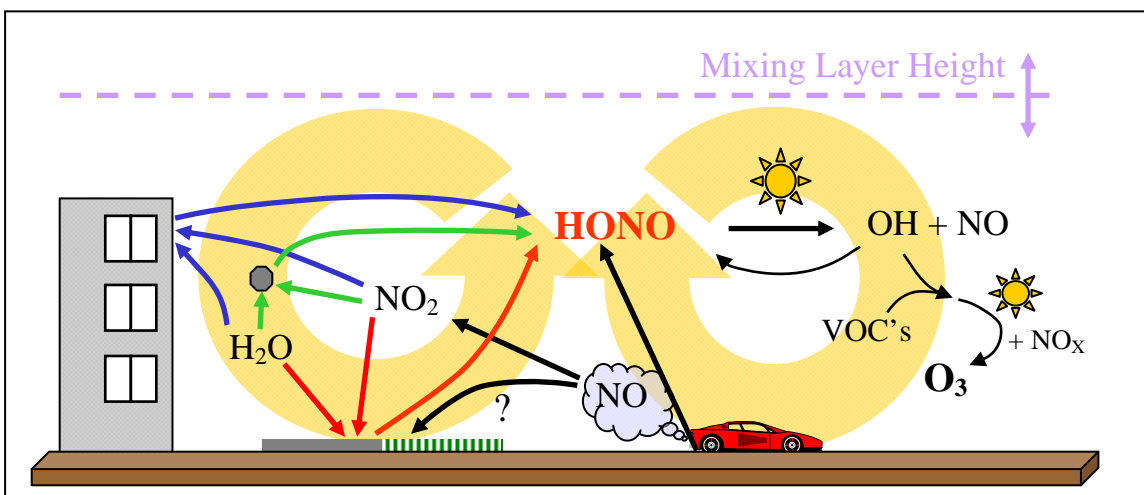


Figure 1.3: Schematics of HONO chemistry in the atmosphere.

Another focus of this project was the study of the nocturnal chemistry and transport processes in the nocturnal boundary layer of Houston, in particular with respect to the formation of the OH radical precursor nitrous acid, the NO₃ radical chemistry, and the NO_x budget. As described above, HONO is an important OH precursor in the urban atmosphere, which can considerably contribute to the HO_x budget (Figure 1.3). Despite this potentially important role, our understanding of HONO formation is poor. Urban air quality models are currently not able to correctly model HONO at night and during the day since in both cases the basic chemical formation processes are unclear. While we have a somewhat better understanding of the nighttime processes, several possible daytime processes have been suggested to efficiently form HONO.

In addition, nocturnal NO₃ radical chemistry can impact the NO_x budget in urban areas and thus indirectly impact ozone and particle formation during the next day. Both nocturnal HONO and NO₃ chemistry are strongly impacted by vertical transport and mixing at night.

The third task of this project (Section 4) thus provides a detailed analysis of the observations from the 2006 TRAMP experiment in Houston and simulations by using a 1D chemical transport model to study the influence of vertical mixing. The result of this provides guidance for the improvement of urban air quality models of the Houston area.

To further study HONO chemistry and to revisit the findings of an unidentified nitrite compound in the Houston atmosphere the last task (Section 5) of this research project was the participation in the HINT field experiment in Houston in April and May 2009. Two specific goals of this experiment were the intercomparison of ambient HONO measurement techniques and the investigation of daytime HONO formation.

2 Measurements of Formaldehyde Fluxes in Texas City by Dual Multi-Axis DOAS

Please see Joined Report H104A - Measurements of Formaldehyde Fluxes in Houston, Texas - for this part of the project.