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1. INTRODUCTION

In this paper, we evaluate the instantaneous O_3 chemical production rates, NO_x (= $NO + NO_2$), loss rates, and ozone production efficiency within ozone plumes sampled on the west side of Houston, Texas, during the Texas 2000 Air Quality Study. We emphasize days during which rapid increases associated with plume passage were observed in the 15-min average ozone mixing ratio, O_3.

The basis for this work will be observations of key nitrogen species and VOCs collected from the top of a skyscraper on the western edge of the city. These observations are used in a 0-dimensional model to quantify the chemical kinetics within parcels of air associated with ozone levels in excess of 100 ppb. We identify the key VOCs affecting ozone production and assess the relative role of anthropogenic versus biogenic VOCs to local ozone production. We also examine how the daily variations in ozone production and ozone production efficiencies are related to differences in VOC/NO_x ratios.

2. OBSERVATIONS AND MODELING SYSTEM

The photochemical mechanism used here is that of Zaveri and Peters, referred to as CBM-Z (see Zaveri and Peters, 1999; Zaveri et al., 2003 and references therein). CBM-Z employs the lumped-structure approach for condensing organic species and reactions, and is based on the widely used Carbon Bond Mechanism (CBM-IV) for use in urban air-shed models.

Observations made from the 65th floor of the Williams Tower in western Houston were used to initialize this model. This station was located at an altitude of 250 m above ground level (AGL) in western Houston and was operational between

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August 15 and September 15, 2000, sampling 24 hours a day, and 7 days a week. This site was run as part of the Texas 2000 Air Quality Study (TX2000AQS). Measurements of hydrocarbons, O_3, NO, NO_y, CO, SO_2, PAN, HNO_3, HONO, HCHO, temperature and relative humidity were made and recorded as 15-min average values. A complete description of the measurement techniques is given in Berkowitz et al. (2003).

3. OBSERVATIONS AND ANALYSIS

Constant-altitude back-trajectories for ozone events were derived from observations made by a profiler network deployed during the Texas 2000 Air Quality Study (described in Berkowitz et al., 2003), and show that prior to their arrival at the Williams Tower, air parcels associated with these high ozone levels decelerated and passed over the industrial region to the east of the Williams Tower. This path took the parcels over a part of Houston with many petrochemical stacks, potentially adding a rich mix of VOCs and NO_x.

There were only two high ozone events (defined here as $O_3 > 100$ ppb) during which hydrocarbon canister samples were taken; August 21 and September 12, both at 1300 LST. A comparison of the 1300 LST VOC mixing ratios at the start of the two intervals during which ozone mixing ratios >100 ppb and intervals on seven other days at 1300 LST, when mixing ratios <100 ppb, show that the dominant hydrocarbons at the start of these high ozone events, by mixing ratio, were the alkanes (ethane, 2-methylpropane, propane, 2-methylbutane), followed by acetylene, ethane, and other olefins. Mixing ratios on 1300 LST on seven "non-event" days (August 28, 29, 30, 31, September 1, 2, and 6) had higher values of ethane, propane, and isoprene than on "event" days. The alkene mixing ratios were generally greater during the two high ozone events than at the corresponding times of non-event days.

To assess the relative contribution of VOCs measured at the Williams Tower to the total reactivity, we examined the product of the

observed mixing ratio of the compounds with their individual OH reactivity, this being a measure the relative speed with which hydrocarbons produce free radicals (e.g., RO_2, HO_2) that in turn lead to the subsequent oxidation of NO to NO_2, and eventually, the production of O_3.

Surprisingly, the average reactivity of isoprene on the two event days (August 21 and September 12) was found to be less ($1 s^{-1}$) than on the non-event days ($1.6 s^{-1}$). The reduction in the contribution from isoprene was offset by an increase in the reactivity associated with a few alkanes (2-methylpropane, 2-methylbutane) but this reduction in the importance of isoprene was primarily offset by the added reactivity associated with ethene, propene, and cyclohexene, these being alkenes associated with stack emissions from the Ship Channel.

The most important non-biogenic contributors to the reactivity were cyclohexene (which had reactivity >0.1 s^{-1} on seven out of the nine samples), ethene (having a reactivity greater than $1 s^{-1}$ on six out of the nine samples) and propene, which had a reactivity $>1 s^{-1}$ in five out of the nine samples. The only alkane that made a significant contribution to the reactivity on these days was 2-methylpentane. While other individual VOCs made relatively minor contributions to the reactive mix, their cumulative mixing ratios did contribute up to half of the remaining reactivity on other days (e.g., September 12 when the reactivity inferred from the canister analysis was $3.42 s^{-1}$ and isoprene contributed roughly one-quarter of this reactivity.

4. PRODUCTION RATES AND OZONE PRODUCTION EFFICIENCY

The ozone production efficiency, OPE, quantifies the number of molecules of O_3 generated per molecule of NO_x oxidized; a high value refers to a greater number of O_3 molecules formed at the cost of other NO_x-oxidation products such as HNO_3, HONO or PAN. Figures 1a-c illustrate the dependence of OPE to NO_x, to total non-methane hydrocarbons (TNMHC) and to the ratio of TNMHC/NO_x. The values of OPE shown here were derived from the model estimate of $-(\partial O_3/\partial t)/(\partial NO_x/\partial t)$ at the end of one hour. OPE was found to be high at low NO_x (Figure 1a), consistent with Zaveri et al. (2003). A weak positive correlation was found with hydrocarbon levels (Figure 1b). And a surprisingly strong linear dependence of OPE was found as a function of the ratio of these quantities (Figure 1c; OPE = 2 + .3[TNMOC/ NO_x] with $r^2 = 0.83$), consistent with a similar feature noted by Daum et al. (2000) in their analysis of emissions from the Nashville urban plume.

The maximum OPE was associated with the canister sample taken on September 1 at 1300 LST, with OPE = 8.2, the minimum found on August 28 at 0900 LST and the average for these 18 canister samples was 4.4. Daum et al. (2003), using a slightly different definition of OPE in their analysis of similar quantities elsewhere in Houston, report OPE values from the Ship Channel of just under 5 to more than 12, and with the urban area samples ranged between
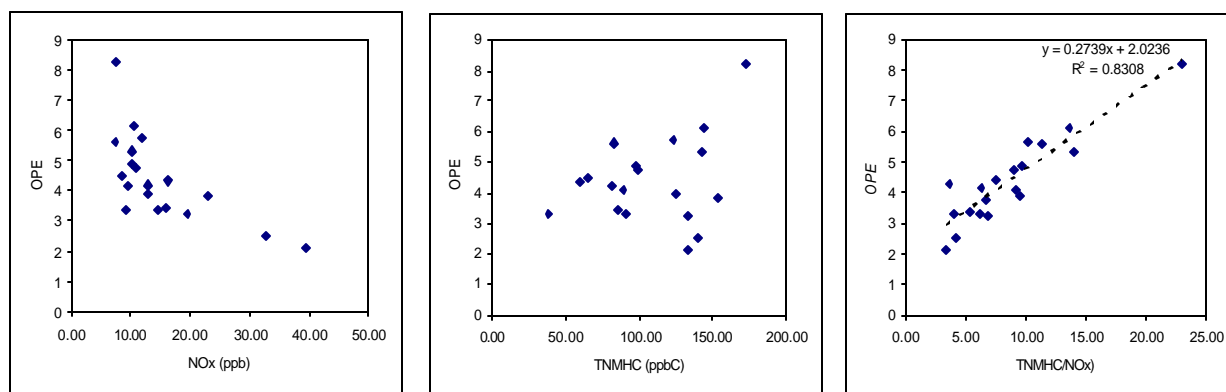

Figure 1: Simulated Ozone Production Efficiency as a Function of a) Observed NO_x, b) Observed Total Non-Methane Hydrocarbons (TNMHC), and c) the Ratio of NO_x/TNMHC

approximately 3.5 and 6. Ozone production rates for this set of measurements at the Williams Tower varied between 0.6 and 18 ppb hr^{-1} with an average value of 10 ppb hr^{-1}, comparable to values measured by Daum over the downtown Houston area, but much smaller than P(O$_3$) rates evaluated to the north of Galveston, where reported values exceeded 50 ppb hr^{-1}.

5. SUMMARY

Observations from a chemical monitoring station 250 m AGL on the west side of Houston Texas show that while isoprene dominates the reactivity of the chemical mix on a daily basis, it is the addition of reactive alkanes that are associated with very rapid increases in O$_3$. On these days with rapid increases in O$_3$, the dominant VOCs, by mixing ratio were ethane, propane, 2-methylpropane, ethene, n-butane, and 2-methylbutane. These compounds, in conjunction with a series of back-trajectories, suggest that stack emissions from eastern Houston are directly linked to high O$_3$ episodes in western Houston.

6. REFERENCES

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