10.3 EFFICIENCY OF OZONE PRODUCTION IN THE HOUSTON PLUME

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1. INTRODUCTION

Over the past 4 years the DOE Atmospheric Chemistry Program has conducted photochemical field programs in several large urban areas, including Phoenix (May-June 1998), Philadelphia (July-August, 1999), and Houston (August-September, 2000). Our strategy has been to study O_3 production in a diverse range of environments and to exploit differences between these environments to further our understanding of the overall O_3 formation process. In each city the DOE G-1 aircraft was used to measure O_3, CO, VOCs, NO, NO_2, NO_y, HCHO, SO_2, and peroxides. These observations are part of a larger data set that includes surface sites and other aircraft platforms. For a description of the scope of the field campaigns in Phoenix, Philadelphia, and Houston see Fast et al. (2000), Philbrick et al. (2000), and the Texas Air Quality Study web page (www.utexas.edu/research/ceer/texaqs/), respectively.

Ozone levels in Houston were much higher than Phoenix or Philadelphia . Eight flights spread over 7 days encountered peak O_3 concentrations between 150 and 211 ppb. Maximum O_3 in Phoenix and Philadelphia were 101 and 147 ppb, respectively. We ascribe the high O_3 levels in Houston to an efficient utilization of NO_x, ie a high ozone production efficiency (OPEx). This quantity is defined as the number of molecules of O_3 formed per NO_x molecule converted to oxidation products. Figure 1 illustrates one method of determining OPEx, as a slope of a graph of O_x (O_3+NO_2) vs. NO_z (Trainer et al., 1993). NO_z is the sum total of all NO_x oxidation products determined as the difference between NO_y (total odd nitrogen) and NO_x (NO+NO_2), i.e., NO_z = NO_y-NO_x. Figure 1 shows that photochemistry has produced comparable amounts of NO_z in Phoenix and Houston, but that O_x levels in Houston are more than double that in Phoenix because the photochemistry uses NO_x much more efficiently. There is day to day and place to place variability in OPEx according to the type of plume and its processing conditions. Representative values for Houston, Phoenix, and Philadelphia are OPEx = 7-12, 3, and 4, respectively.

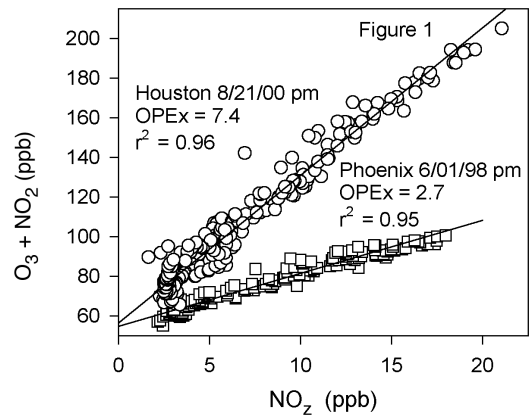

Figure 1. O_x vs NO_z for a high O_3 day in Houston and Phoenix. Lines are from a linear least squares regression.

2. CALCULATIONS

Aircraft based observations have been used as input to a constrained steady state (CSS) box model (Kleinman et al., 1997). The limiting factor in doing CSS calculations is, in general, the availability of VOC data which is collected in canisters and analyzed by J. Rudolph's research group at York University. CSS calculations have been done at over a 100 sampling points in Phoenix and Philadelphia and over 200 in Houston. The calculations yield the concentrations of free radicals; the O_3 production rate, P(O_3); and the rate of NO_x oxidation equal to the production rate of NO_z, P(NO_z). The ratio of P(O_3) to P(NO_z) is the number of molecules of O_3 produced per NO_x molecule at the time and place that the calculation is performed. This quantity is an instantaneous analog of OPEx.

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Presented at the American Meteorological Society 82nd Annual Meeting, Orlando, FL, Jan. 13-17, 2002.

Equation (1) is a steady state analytic formula for $P(O_3)/P(NO_z)$ similar to that derived by Derwent and Davies (1994), Daum et al. (2000) and Carpenter et al. (2000):

$$P(O_3)/P(NO_z) = \Sigma\, Y_i\, k_i\, [VOC_i]/k_N[NO_2] \qquad (1)$$

where the k_i's are rate constants for reaction of VOC_i with OH, k_N is the rate constant for OH $+NO_2$, and Y_i is the number of peroxy radicals produced from reaction of OH with a VOC as determined from the stoichiometry of the reaction. VOCs are broadly defined to include all substance which react with OH producing a peroxy radical. In Fig. 2 we test our analytic formula by comparing values of $P(O_3)/P(NO_z)$ obtained from CSS calculations with that obtained from Eq. (1). For this purpose we have used calculations based on the Phoenix data set. There is seen to be qualitative agreement as long as NO_x concentrations are greater than 1-2 ppb. Figure 2 also shows that $P(O_3)/P(NO_z)$ increase at low NO_x concentration in agreement with the work of Liu et al. (1987) and Lin et al. (1988).

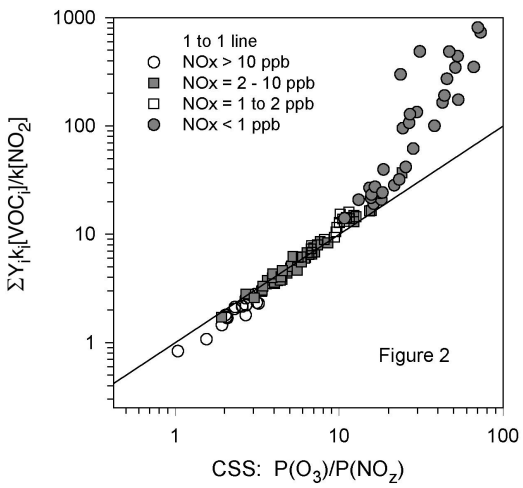

Figure 2. Test of approximate formula given by Equation (1) Each data point is from a CSS calculation based on aircraft observations during the Phoenix field campaign.

Figure 3 shows a comparison between $P(O_3)/P(NO_z)$ for Houston, Philadelphia, and Phoenix. Again we see the expected increase at low NO_x concentration. At NO_x levels greater than a few ppb, where most of the O_3 is formed the instantaneous $P(O_3)/P(NO_z)$ for Houston is greater than Philadelphia which is greater than Phoenix. This variation is in the right direction and of the right magnitude to qualitatively explain the observed city to city differences in OPEx.

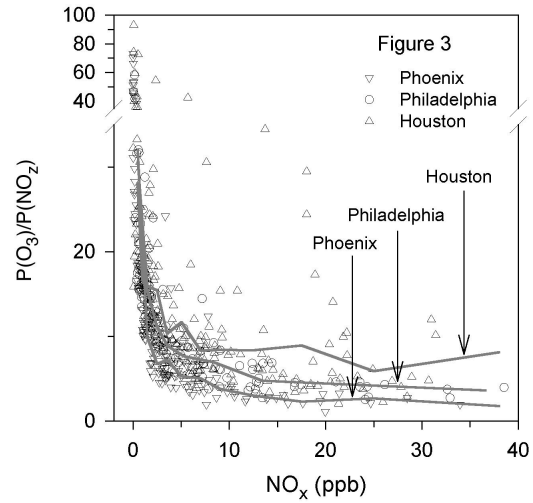

Figure 3. Value of $P(O_3)/P(NO_z)$ from CSS calculations vs NO_x concentration illustrating city to city differences. Data points are individual calculations. Symbol type identifies city. Broken lines are averaged over a range of NO_x concentration.

According to (1), $P(O_3)/P(NO_z)$ depends on a VOC to NO_2-OH reactivity ratio. This leads us to look at VOC reactivity as a possible cause for high OPEx. All three cities are large and have the attendant pollution problems due to mobile sources. In Phoenix, mobile sources are the predominant emission source (Heisler et al., 1997), less so in Philadelphia, and still less so in Houston. There is a very large concentration of petrochemical facilities in Houston near the ship channel just east of the city center. Most of the high $P(O_3)/P(NO_z)$ data points in Fig. 3 are due to samples collected in this region. There is a subset of ship channel samples containing 10's of ppb of ethene and propene. These concentrations are an order of magnitude more than expected for vehicular emissions, based on VOC measurements by W. Lonneman in the Houston Washburn Tunnel.

3. CONCLUSIONS

Ozone levels observed during a field campaign in Houston were significantly higher than that observed in Phoenix or Philadelphia. An examination of the slope of O_x versus NO_z in the urban plumes shows that NO_x is used 2 to 3 times more efficiently in Houston as compared with Phoenix and Philadelphia. Representative values of OPEx are 7-12, 3, and 4, in Houston, Phoenix, and Philadelphia. Aircraft observations have been used to calculate $P(O_3)/P(NO_z)$. Values in Houston are significantly higher than in Phoenix and Philadelphia. We show that $P(O_3)/P(NO_z)$ is proportional to a VOC/NO_2-OH reactivity ratio. High

values of $P(O_3)/P(NO_z)$ in Houston are due to emissions of reactive olefins from the ship channel region. It is significant that high values of $P(O_3)/P(NO_z)$ occur at NO_x levels up to several 10's of ppb. Not only is the chemistry efficient but it will be long lasting. The occurrence of high NO_x and high OPEx is fostered by the co-location of VOC and NO_x sources in the Houston industrial areas.

4. ACKNOWLEDGEMENTS

We thank pilot Bob Hannigan and the rest of the flight crew for a job well done. York University provided us with their usual high quality analysis of hydrocarbon canisters. Interactions with the Texas National Resources Conservation Commission, the Southern Oxidants Study, and other colleagues participating in TEXAQS 2000 are appreciated. We acknowledge the support of the Atmospheric Chemistry Program within the Office of Biological and Environmental Research of DOE for providing the G-1 aircraft. This research was performed under sponsorship of the U.S. DOE under contracts DE-AC02-98CH10886.

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