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1. INTRODUCTION

Nonmethane hydrocarbons (NMHCs) are precursors to oxidant formation. They are oxidized by hydroxyl radical (OH) to form a complex mixture of peroxy radicals that oxidize NO to NO₂ without consuming ozone (O₃) and thus allow O₃ to increase in the atmospheric boundary layer. The composition, concentrations, and reactivities of the NMHCs that compose biogenic and anthropogenic emissions vary greatly. Thus, for a particular urban area, the strength of the emissions from these various sources will have a substantial effect on the regional production of oxidants.

Diurnal variations in concentrations of NMHCs were measured during June 2001 near the top of the Bank One building (elevation 139 m) in Phoenix, Arizona. Samples were also taken from the fourth floor of the nearby Ramada Inn hotel during the morning rush hour to evaluate the vehicular emission signature. Distributions of NMHCs near the top of the Bank One building will be compared with those measured at the surface to examine photochemical processing of the NMHCs.

2. EXPERIMENTAL ASPECTS

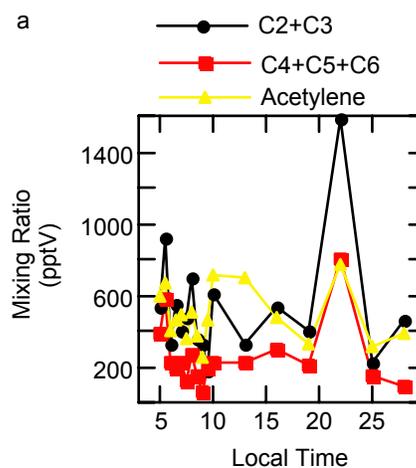
A 5-min sample was collected at the Bank One building every half-hour between 0500 and 0930 LT and every three hours between 1000 and 0400 LT. At the Ramada Inn, a 10-min sample was collected at 0600 LT. An automated sampler (Doskey and Bialk 2001) was used to collect samples in Summa[®] passivated stainless steel canisters. The sampler consisted of a Neuberger Viton[®] diaphragm pump; a 2-position, 3-port valve; a 10-port, multiposition valve (VICI, Houston, TX); and a digital valve sequence programmer (VICI, Houston, TX). All connecting tubing and fittings were coated with Silcosteel[®] (Restek, Bellefonte, PA).

The air samples were analyzed with two systems consisting of panel-mounted sample preconcentration units and Hewlett-Packard (HP 5890) high-resolution gas chromatographs with flame ionization detectors (FIDs). The analytic systems were described in detail by Doskey and Bialk (2001). Briefly, the whole-air samples were preconcentrated at -185°C in a 16-cm section of Silcosteel[®] tubing (0.216 cm ID) packed with 9 cm of

fused silica wool (Alltech Associates, Inc., Deerfield, IL). The analytes were thermally desorbed at approximately 100°C for 2 min and were transferred to either (1) a 60-m ∞ 0.32-mm-ID fused-silica capillary column coated with a 1-μm-thick film of polydimethylsiloxane (DB-1; J&W Scientific, Folsom, CA) or (2) a 30-m ∞ 0.53-mm-ID porous-layer open tubular column coated with alumina (GS-Alumina; J&W Scientific, Folsom, CA). The FIDs were calibrated daily with a mixture of C₂-C₆ *n*-alkanes, benzene, and toluene at a level of 10 ppb each (Scott Specialty Gases, Inc., Plumsteadville, PA). The C₂ and C₃-C₁₂ hydrocarbons were resolved on the GS-Alumina and DB-1 columns, respectively (Fukui and Doskey 1996). The comparability of the two analytic systems was verified by quantifying the C₃ and C₄ hydrocarbons in the same air sample on both analytic systems.

3. RESULTS AND DISCUSSION

The discussion will focus on samples collected on 19 June and 28-30 June. Diurnal variations of the mixing ratios of the olefins and acetylene for the two periods are shown in Figs. 1a and 1b, respectively. The C₂-C₆



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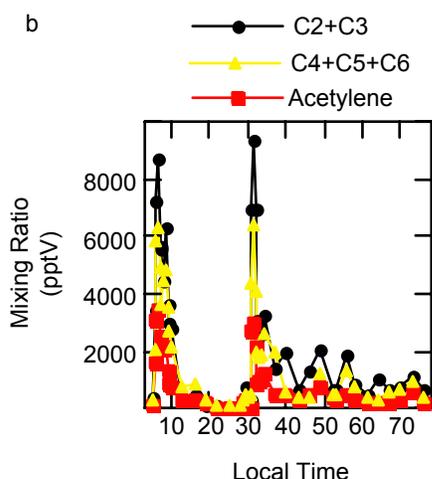


Fig. 1. Diurnal variations of acetylene and the C₂-C₆ olefins on (a) 19 June 2001 and (b) 28-30 June 2001 at the Bank One building in Phoenix.

olefins typically account for much of the reactivity with OH of the NMHCs in many urban areas (Doskey and Kotamarthi 2002). Isoprene, a C₅ olefin of biogenic origin was a very minor component of this group of NMHCs in Phoenix, indicating that anthropogenic emissions dominated the NMHC distribution. Mixing ratios of the three groups of unsaturated NMHCs were higher by nearly a factor of 10 on Thursday, 28 June, and Friday, 29 June, than on Tuesday, 19 June. Levels of NMHCs on Saturday, 30 June, were lower by a factor of 4 than on the previous two days, indicating a typical reduction in motor vehicle traffic on the weekend. Acetylene is commonly used as a marker of vehicle exhaust (Doskey et al. 1992). For both periods, the C₂ + C₃ and C₄ + C₅ + C₆ olefins and acetylene exhibited similar trends, indicating a common source.

The highest mixing ratios before 1000 LT at the Bank One building occurred at different times (Figs. 1a and 1b). If the sampling location at an elevation of 139 m is intercepting NMHC emissions from the surface, these data may indicate that variations in the strength of vertical mixing occur during the early morning hours. On 29 and 30 June, the sharpest decline in mixing ratios occurred before 1000 LT. The reactivities of the olefins and acetylene with OH follow the general trend C₄ + C₅ + C₆ > C₂ + C₃ > acetylene. Observed mixing ratios of these groups of NMHCs declined at similar rates during the morning periods, possibly indicating that little chemical processing occurred. Instead, vertical mixing might be responsible for much of the decrease in the NMHC mixing ratios.

Figure 2 shows the diurnal variation of the toluene/benzene ratio and the mixing ratio for acetylene for 28-30 June. The toluene/benzene ratio can be used

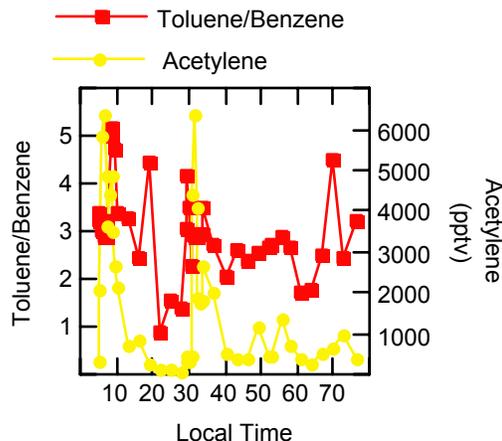


Fig. 2. Diurnal variations of acetylene and the toluene/benzene ratio on 28-30 June 2001 at the Bank One building in Phoenix.

to indicate the source of the NMHCs and the degree of photochemical processing. Ratios for urban areas with NMHC distributions dominated by vehicle emissions are typically about 2 (Doskey and Kotamarthi 2002). Because toluene reacts more rapidly than benzene, ratios in photochemically aged air masses will be less than 2. Ratios in the early morning hours in Phoenix were greater by at least a factor of 1.5 than the ratios observed in other major cities with similar vehicle numbers. Also, the highest levels of the ratio did not always coincide with peaks in the acetylene mixing ratios. These observations indicate an additional source of toluene in Phoenix or lower emissions of benzene.

Figure 3 compares the ratios of 14 NMHCs to acetylene for 0600 and 0630 LT on 28 June at the Ramada Inn and the Bank One building, respectively, with ratios for samples collected in the Washburn Tunnel in Houston during the Texas 2000 Air Quality Study (Lonneman 2001). The average NMHC distribution for the Washburn Tunnel samples was corrected for background air to obtain a vehicle emission signature. The sample collected on 28 June at 0630 LT from the Bank One building contained the highest level of acetylene observed on that day (Fig. 1b), indicating the strength of the vehicle exhaust emissions. The normalized distribution of the NMHCs at 0630 LT is similar to the distribution observed at the Ramada Inn and in the Washburn Tunnel. However, ratios for ethane, propane, 2-methyl propane, and *n*-butane in Phoenix were larger because the distribution at 0630 LT was not corrected for background air. At 0830 LT, the toluene/benzene ratio was about 5 at the Bank One building, and the acetylene levels were lower than those observed at 0630 LT (Figure 2).

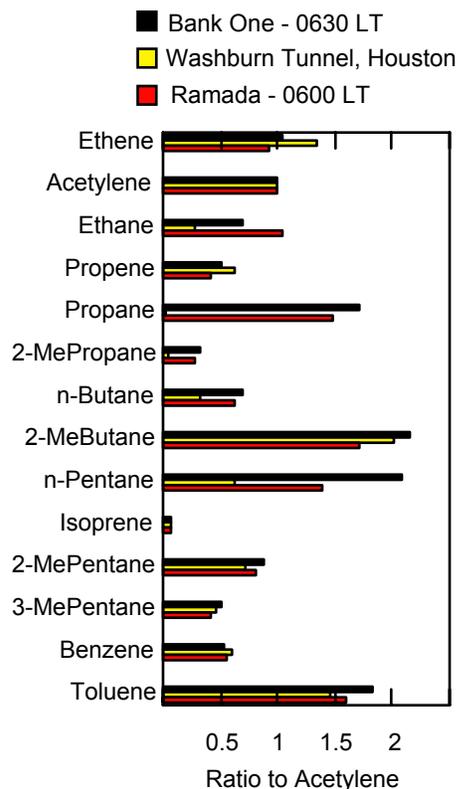


Fig. 3. Comparison of NMHC distributions, normalized to acetylene, for samples collected at the Bank One building and Ramada Inn hotel in Phoenix with the distribution in vehicle emissions in the Washburn Tunnel in Houston (Lonneman 2001).

Figure 4 compares the normalized distribution of NMHCs at 0630 and 0830 LT at the Bank One building with the average distribution in the Washburn Tunnel samples. The results show elevated levels of *n*-pentane and toluene at 0830 LT in Phoenix with respect to the Washburn Tunnel distribution, indicating that NMHC emissions are present in addition to vehicle exhaust in Phoenix. Figure 5 compares the ratios of 14 NMHCs to acetylene for 0630 and 0830 LT at the Bank One building with a whole-gasoline profile from Atlanta (Conner et al. 1995). The whole-gasoline profile represents a signature for unburned gasoline that could be emitted from saturated fuel vapor recovery systems of vehicles. The profile at 0830 LT in Phoenix is very similar to the whole-gasoline profile, indicating a source of NMHCs in addition to tailpipe emissions. The very hot conditions in Phoenix are most likely responsible for elevated emissions of unburned gasoline.

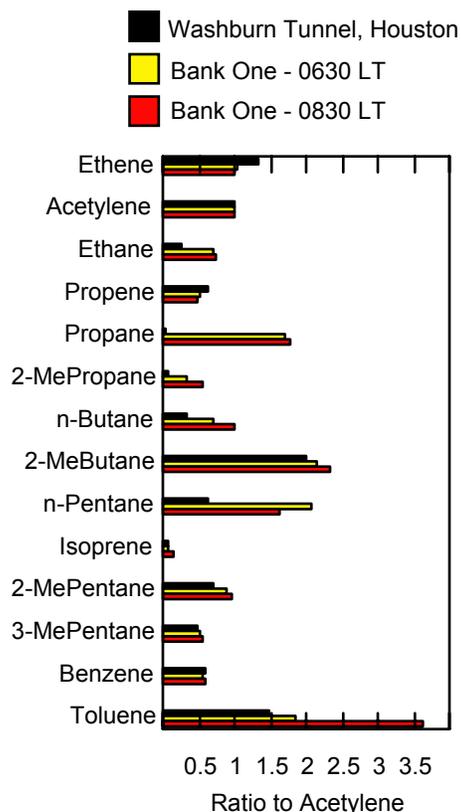


Fig. 4. Comparison of NMHC distributions, normalized to acetylene, for samples collected at 0630 and 0830 LT at the Bank One building in Phoenix with the distribution in vehicle emissions in the Washburn Tunnel in Houston (Lonneman 2001).

4. CONCLUSIONS

Samples were collected at an elevation of 139 m from the Bank One building in Phoenix to characterize the NMHC distribution of ambient air in the downtown area and to evaluate diurnal variations in chemical processing. The NMHC distributions were characteristic of vehicle emissions. The C₃-C₆ olefins represent the greatest source of reactivity with OH of the NMHCs. On some days, mixing ratios of olefinic hydrocarbons and acetylene at 1200 LT were lower by more than a factor of 10 than the levels observed in the early morning. Mixing ratios of the various groups of olefins and acetylene declined at similar rates during the morning hours, despite significant differences in their reactivities with OH. Thus, vertical mixing in a developing atmospheric boundary layer appears to be responsible for much of the change in mixing ratios during the morning. However, further analysis of the ratios of individual NMHCs to acetylene that is underway might indicate that some chemical processing does occur. Toluene/benzene ratios in Phoenix sporadically exhibit

values of 3-5, indicating sizable emissions of unburned gasoline in addition to tailpipe emissions.

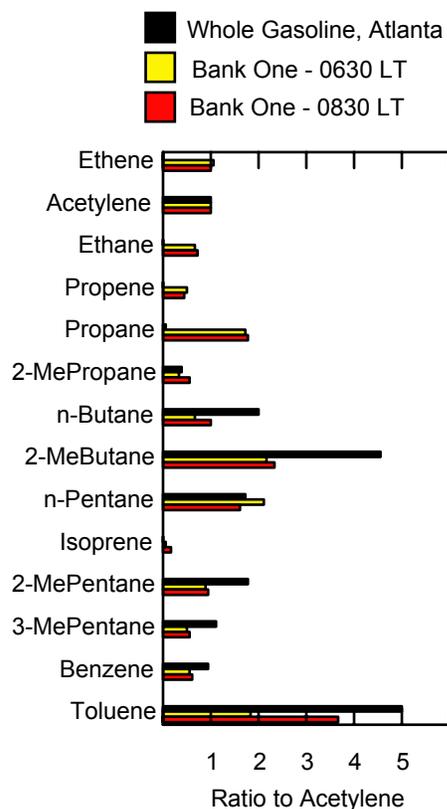


Fig. 5. Comparison of NMHC distributions, normalized to acetylene, for samples collected at 0630 and 0830 LT at the Bank One building in Phoenix with the profile for a whole-gasoline sample collected in Atlanta (Conner et al. 1995).

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