A STUDY OF SOURCE ATTRIBUTION OF UNSATURATED HYDROCARBONS FOR OZONE PRODUCTION IN THE HOUSTON-GALVESTON AREA WITH THE EXTENDED SAPRC99 CHEMICAL MECHANISM

Beata Czader* and Daewon W. Byun
Department of Chemistry & Institute for Multidimensional Air Quality Studies (IMAQS)
E-mail: bczader@uh.edu, Daewon.Byun@mail.uh.edu
Web address: www.imaqs.uh.edu

1. INTRODUCTION

Preliminary analyses of the TexAQS 2000 suggest that large emissions of unsaturated hydrocarbons may cause the transient high ozone events [Allen et al., 2001]. Current photochemical models do not explain many experimental results from the TexAQS 2000 campaign, such as the ozone "spikes" and associated formaldehyde "spikes". The source of high formaldehyde is expected to be the product of the photochemical reactions of the unsaturated hydrocarbons such as ethylene and propylene. Currently used chemical mechanisms such as CB4 [Gery et al., 1989] and SAPRC-99 [Carter, 2000a], represent ethylene as an explicit species but propylene is grouped with other hydrocarbons and its reactivity and molecular mass is averaged as lumped species. Another highly reactive organic compound, 1,3-butadiene, is emitted in significant amounts in Harris County and is not represented explicitly by chemical mechanism.

2. GOALS

- Study the relationship between measured formaldehyde spikes and alkenes emissions.
- Study the differences in the reactivity obtained with different chemical mechanisms.
- Study the differences coming from different emission inventories employed in simulations: National Emission Inventory 1999 (NEI) vs. Texas Emission Inventory 2000 (TEI).

* *Corresponding author address*: Beata Czader, Chemistry Department, University of Houston, 4800 Calhoun Rd., Fleming Bldg. Room 136, Houston, Texas, 77204

3. METHOD

The SAPRC-99 [Carter, 2000b] mechanism represents organic species in more detail and this mechanism was subject to modifications in the present study. Propylene was excluded from OLE1 species in the original SAPRC99 mechanism and considered explicitly as PROPENE. Also, 1,3-butadiene was excluded from OLE2 species and represented as BUTADIENE13. The extended SAPRC99 mechanism is called SAPRC99ext. In order to take advantage of the extended mechanism, the emission assignments were changed based on the profile number and SAROAD code. The new gspro file, necessary to process emissions with SMOKE [Houyoux et al, 2000], was created with new molar and mass fractions calculated [Gipson, 2001] for these and other VOC species. The most significant reactions of propylene and 1,3-butadiene with hydroxyl radical (HO), ozone (O3), nitrate radical (NO3) and ground state oxygen atom (O3P) were added to the SAPRC99 mechanism [Carter, 2000a]. Reaction products of OLE1 and OLE2 as well as their kinetic parameters were updated [Carter, 2000c, 2004] after the compositions of these lumped surrogates were changed.

4. RESULTS

The CMAQ air quality model [Byun and Ching,1999] was run with different emission inventories (NEI99, TEI2000) and different chemical mechanisms: CB4, SAPRC99 and SAPRC99ext.

Simulations with TEI (base4a.pto2n2) emissions show considerably higher alkene concentrations in the Ship Channel, near Texas City and Free Port, and their downwind areas than the simulation with NEI. There are temporal differences between TEI and NEI in Ethylene emissions due to the fact that TEI includes time-

dependent speciated emissions reported for the episode period (Aug. 23 –Aug. 31, 2000) while the NEI is based on the annual emissions inventory. The simulations with SAPRC99ext show that there is much more propylene in OLE1 surrogate then any other olefin.

The influence of different olefins on formaldehyde and ozone production was studied through both integrated reaction rate and integrated process rate analyses. The results with TEI and NEI, and both CB-4 and SAPRC99 mechanisms show that isoprene contributes to formaldehyde concentration at higher proportion than alkene reactions, except for the Ship Channel area. There is more formaldehyde being produced by ethylene reactions simulated with SAPRC99 than CB4 mechanism. On the other hand formaldehyde obtained from reactions with OLE (CB4 mechanism) is higher than combined contribution of OLE1 and OLE2 (SAPRC99). There is generally more formaldehyde produced when TEI inventory was used in the simulations. Figure 1 shows the formaldehyde produced from propylene with TEI and SAPRC99ext mechanisms at 1 pm CST, August 25, 2000, this is when the maximum formaldehyde production occurred. The OLE1 contribution to formaldehyde formation is not significant, which implies that the formaldehyde is produced mainly from propylene, not from other components of OLE1 group. The contribution of OLE2 and BUTADIENE13 to formaldehyde concentration is even less than OLE1.

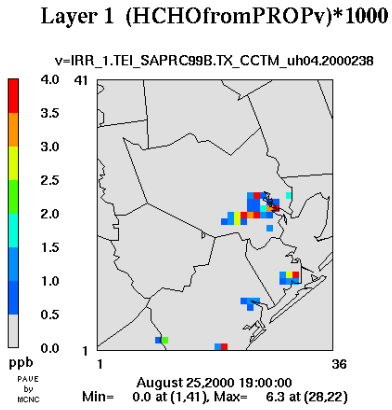

Figure 1 Formaldehyde produced from propylene reactions simulated with TEI, SAPRC99ext for Aug. 25, 2000 at 19 UTC (1 pm CST)

The simulation results were compared with surface and elevated measurement data. Figure 2 shows the comparison of simulated propylene concentration against elevated measurement data. At higher elevations simulated Propylene concentrations are much lower than measured values for both NEI and TEI, but for some days simulated surface concentrations of propylene are much higher than observed (Figure 3).

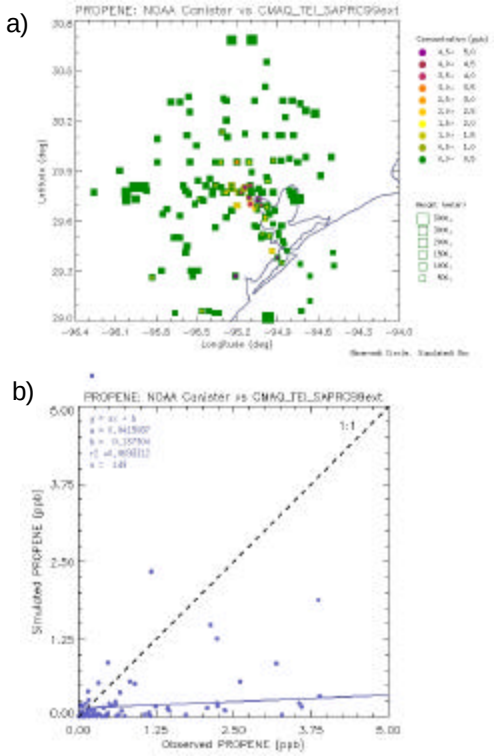

Figure 2 Comparison of modeled propylene concentrations against aircraft canister measured values. (a) Spatial distribution, which shows that when model and measurements are close, the color of the squares (simulated) and closed circles (observed) are similar; (b) scatter diagram, which shows that simulated propylene concentrations are much too low compared with aircraft measurements. Simulations were done with CMAQ model, Texas Emission Inventory (TEI) and SAPRC99ext mechanism.

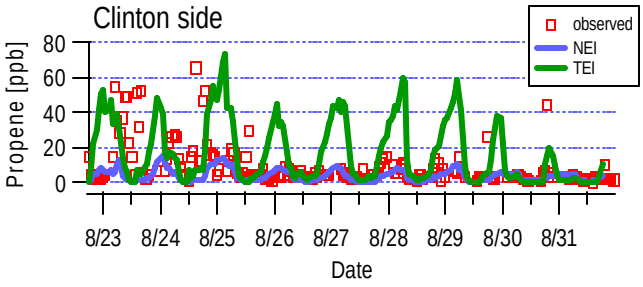

Figure 3 Comparison of modeled propylene concentrations against surface data at Clinton side. Simulations were done with SAPRC99ext mechanism.

5. CONCLUSIONS

- Simulated with the TEI, elevated concentration of ethylene, propylene and other olefins are lower in comparison with NOAA aircraft data. But the values at the surface matches with observed data for some days of the episode, and are higher than measured for other days. The results with the NEI show much lower elevated olefin concentrations and for some days of the episode (Aug. 23, 24, and 25, 2000) lower surface concentration. These results imply that vertical distribution of emission in the inventories may not reflect the reality.
- The concentration of 1,3-butadiene is similar for simulations with TEI and NEI and matches the surface measured values.
- The differences in ozone production between SAPRC99 and SAPRC99ext are not significant (around 1 ppb) however extension to SAPRC99 mechanism helps to identify the source-receptor relations better.

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