Comparison of the SAPRC and Carbon Bond photochemical mechanisms under conditions relevant to Southeast Texas

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Houston-Galveston versus other Urban Areas

• For NOx sensitive urban areas all versions of SAPRC and CB mechanisms yield similar O₃ predictions (Dodge, 2000)
• For modeling done of summer 2000 in southeast Texas, SAPRC99 predicts concentrations of O₃ that are 30-50 ppb higher than in all versions of CB-IV
Predictions of domain-wide max O₃ concentrations in CAMx on August 30, 2000

Differences can exceed 45 ppb
Percentage reductions to max O$_3$ concentrations in response to 75% NOx cuts

Domain-wide maxima in O$_3$ concentrations differ at high NOx emission conditions but largely disappear at low NOx conditions.
Policy implications of differences between SAPRC and CB-IV

• SAPRC predicts consistently larger relative reductions in O$_3$ than CB-IV under significant NOx reductions
• SAPRC is particularly more sensitive to NOx emissions than CB-IV on certain high-O$_3$ days
• Demonstrating attainment for the 8-hr O$_3$ standard considers relative reductions in O$_3$ predicted by the mechanisms
• Differences in mechanism NOx sensitivity important for attaining the 8-hr O$_3$ standard particularly on high-O$_3$ days
What are the unique features of atmospheric chemistry in Houston?

• Regions with very high hydrocarbon reactivity near high NOx emission density
• Significant differences in free radical sources between two mechanisms and between the mechanisms and observations
• Not strictly a Houston phenomenon; similar differences in mechanisms reported for LA (Yarwood, et al., 2003)
1. What are the reasons for the differences in $O_3$ predictions between SAPRC and CB-IV?

2. Which mechanism is a more accurate representation of Houston’s $O_3$ formation chemistry?
Reasons for Differences in $O_3$ predictions between SAPRC and CB-IV

- Aromatics Chemistry
- Free Radical Sources and Sinks
Sensitivity studies in Box Model

- Simplifies transport and diffusion but represents chemical transformations in detail
- Re-created differences in SAPRC and CB-IV in box model
- Representative of Houston conditions, particularly locations with high $O_3$ concentrations
Ozone Predictions in Box Model under high-O3 Houston conditions when VOC emissions are assumed to be single explicitly-modeled species.

- Ethylene

- Isoprene

- Formaldehyde
Ozone Predictions in Box Model under high-O$_3$ Houston conditions when VOC emissions are assumed to be single Mono-substituted Aromatics

Toluene

Ethylbenzene
Aromatics Chemistry in SAPRC vs. CB-IV

- OH-initiated reactions of aromatics yield ring-retaining and ring-opening products
  - Ring-retaining products include stable cresols
  - Ring-opening products include reactive dicarboxyl species (e.g., methyl glyoxal)
- Different branching ratios of ring-retaining vs. ring-opening products in SAPRC and CB-IV
- SAPRC predicts much higher ring-opening products which lead to more free radicals
- In isolation, does not explain the entire difference between SAPRC and CB-IV
Consistent Toluene inventories between SAPRC and CB-IV on August 25, 2000 at hour 11:00

**SAPRC**
Layer 1 ARO1a*1000

![SAPRC Map](image1)

**CB-IV**
TOLb*1000 8/25 CB4

![CB-IV Map](image2)

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August 25,2000 11:00:00
Min= 0.00 at (1,1), Max= 2.78 at (27.30)
Prediction of Cresols (lumped) in SAPRC versus CB-IV on August 25, 2000 at hour 11:00

SAPRC

Layer 1 CRESa\times1000

CB-IV

CRESb\times1000 8/25 CB4

Min= 0.0000 at (1,1), Max= 0.0964 at (26,30)
Differences in O$_3$ predictions on August 30th, 2000 eliminating Aromatic emissions versus basecase
Reasons for Differences in $O_3$ predictions between SAPRC and CB-IV

- Aromatics Chemistry
- Free Radical Sources and Sinks
Relative production of higher aldehydes by SAPRC and CB-IV at hour 13:00 on August 25th at location of max difference in $O_3$.
1. What are the reasons for the differences in O₃ predictions between SAPRC and CB-IV?

2. Which mechanism is a more accurate representation of Houston’s O₃ formation chemistry?
Designing Experiments as part of a large air quality field program, TexAQSII

- Potential observable for evaluating aromatics chemistry: \[ \frac{\sum \text{Cresols}}{\sum \text{Toluene}} \]

- Nitric acid, OH, and NO\textsubscript{2} concentrations can be measured in evaluating free radical termination

- Higher Aldehydes concentrations can be markers for radical sources
Designing Experiments as part of a large air quality field program, TexAQSII

- Potential observable for evaluating aromatics chemistry: cresol to benzaldehyde ratio or $\frac{\sum \text{Cresols}}{\sum \text{Toluene}}$
Designing Experiments as part of a large air quality field program, TexAQSII

- RCHO + OH
- RCO3 + NO
- PROD + OH
- RNO3 + OH

Higher aldehydes concentrations, organonitrate