

# The SAPRC Chemical Mechanisms

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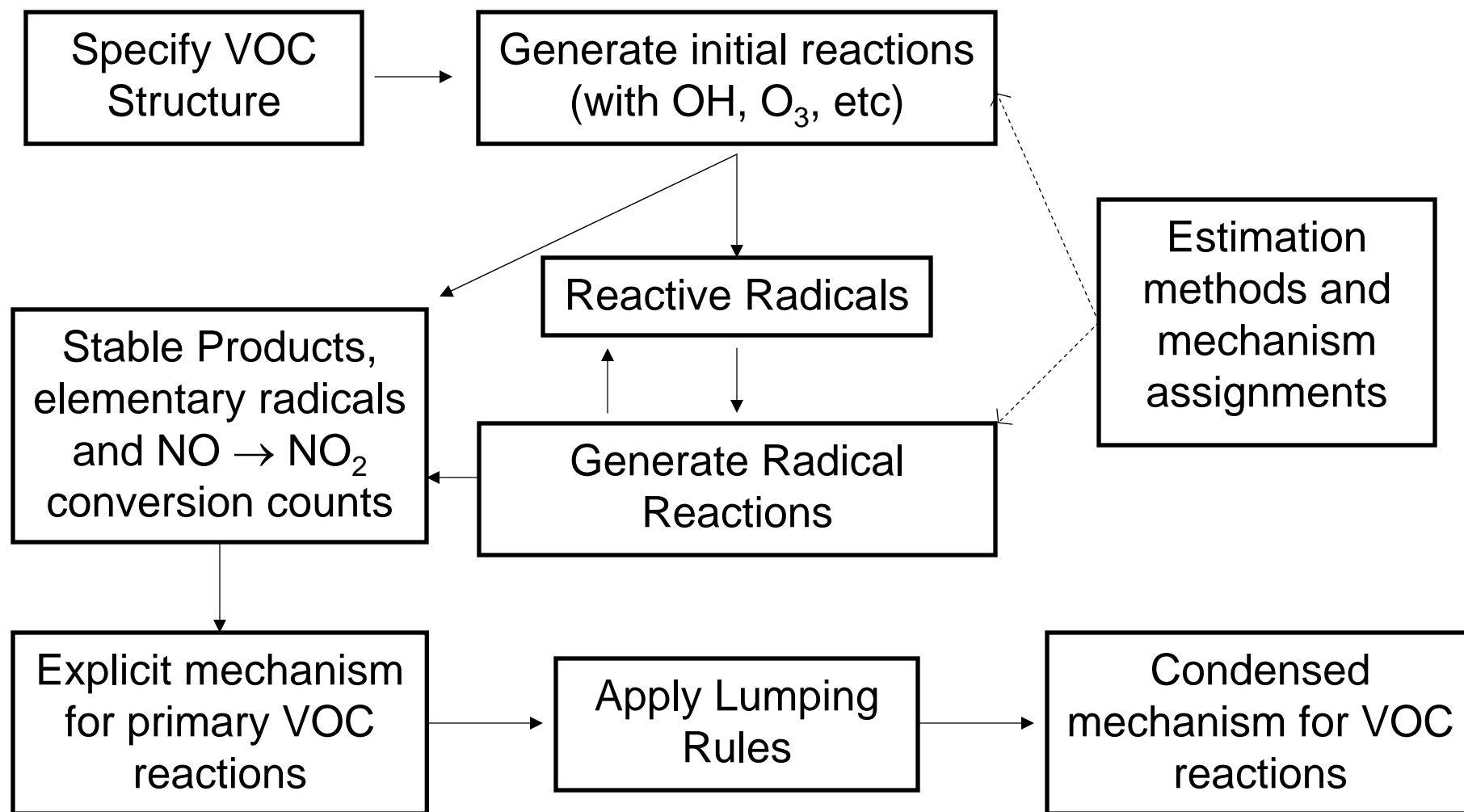
## Outline

- Major components of the SAPRC mechanisms
- Mechanism generation system
- Status of SAPRC mechanism updates
  - Preliminary updated aromatics mechanism
  - Preliminary evaluation against chamber data
- Remaining mechanism update work and issues

# Major Components of SAPRC Mechanisms

- Base Mechanism
  - Reactions of inorganics and common organic products
- Mechanisms for individual VOCs
  - Currently, mechanisms derived for over 550 types of VOCs
  - **Mechanism generation system** used to derive fully explicit mechanisms that are condensed using “lumping rules”
  - Simplified mechanisms used for compounds whose explicit mechanisms cannot be estimated (e.g. aromatics)
- Condensed mechanisms for airshed models
  - Mechanisms for limited number of “lumped model species” are derived from those of mixture of VOCs they represent
  - These depend on the composition of the mixture taken as representative of VOC emissions from all sources

# Mechanism Generation System



# Mechanism Generation System Capabilities

- Generates mechanisms for reactions of alkanes, alkenes, alkynes, aldehydes, ethers, esters, nitrates, acids and most of their oxidation products with OH, O<sub>3</sub>, NO<sub>3</sub>, O<sup>3</sup>P and photolysis
- Measured rate constants (or rate constant ratios) are used where available. Estimation methods are used otherwise.
- Estimation Methods
  - Structure-reactivity estimates for OH, O<sub>3</sub>, and NO<sub>3</sub> reactions
  - Nitrate yields from RO<sub>2</sub>+NO based on size of the RO<sub>2</sub> radical and limited data on effects of substituents
  - Alkoxy radical estimates based (primarily) on correlations between rate constants and heats of reaction.
  - Other estimates based on extrapolations from known reactions adjustments to fit chamber data

# Limitations of Mechanism Generation System

- Only generates mechanisms for systems with  $\text{NO}_x$ . (Peroxy radicals reacted only with NO. Peroxy + peroxy reactions are not generated.  $\text{RC(O)O}_2\cdot$  radicals are treated as products)
- Limitations in thermochemical group estimate data limits types of alkoxy radicals for which estimates can be made.
- Estimation methods are very uncertain for photolysis reactions.
- Unsaturated radicals might undergo a wide variety of reactions for which estimation methods are unknown or very uncertain. Thermochemical data insufficient to support estimation methods
- System does not take steric effects into account
- The system used for SAPRC-99 could not process compounds with more than one double bond or more than one ring. (This capability has since been added.)

## Examples of Sizes of Generated Mechanisms

| <u>Compound</u>                       | <u>Reactions</u> | <u>Products</u> |
|---------------------------------------|------------------|-----------------|
| n-Butane                              | 20               | 8               |
| Butoxy ethanol                        | 54               | 22              |
| Propylene glycol methyl ether acetate | 84               | 27              |
| n-Dodecane                            | 120              | 37              |
| 6-methyl tetradecane                  | 521              | 167             |
| 2-methyl-2-octyl cyclohexane          | 1618             | 520             |
| Toluene (preliminary new system)      | 172              | 22              |

Note: - This does not count the oxidation product reactions  
- Peroxy + peroxy reactions are not generated

# Status of SAPRC Mechanisms

- The current version in use is SAPRC-99
  - Represents the state of the science as of 1999
  - Used to calculate the MIR reactivity scale used in some CARB regulations. (Scales updated in 2002 with some VOCs' mechanisms updated)
  - Many airshed models use “Fixed Parameter” SAPRC-99 with condensed model species based on the “base ROG” mixture used in the reactivity scale calculations
- Updated SAPRC mechanism still under development. Anticipated completion is March, 2007. Current status:
  - Rate constants in base mechanism updated
  - Preliminary new explicit aromatics mechanisms developed
  - Limited evaluation against chamber data

# Major Objectives of SAPRC Mechanism Updates

- Update rate constants and reactions to current state of science
- Add chlorine chemistry
- Improve mechanisms for aromatics
  - Address problems with mechanism simulating chamber data
  - Base mechanism on explicit chemistry, not parameterization
- Update and enhance mechanism generation system
  - Update estimation methods and assignments as needed
  - Enhance capabilities, e.g., to support generating explicit mechanisms for aromatics and chlorine atom reactions
- Improve capability to be adapted to secondary PM models
- Develop new condensed mechanisms from detailed version (including highly condensed version as an alternative to CB4)



# Status of Mechanism Updates -- Base Mechanism

- Updates to inorganic, ClO<sub>x</sub>, and simple organic product mechanisms complete but not fully evaluated

| Potentially important rate constant changes                                | Change |
|--|--------|
| Glyoxal + hv → Radicals  | 149% * |
| Lumped higher aldehyde + hv → Radicals (Solar light)                       | 147% * |
| Generic peroxy + HO <sub>2</sub> → Generic hydroperoxides + O <sub>2</sub> | -48%   |
| Methacrolein and lumped C <sub>5</sub> isoprene product photolysis         | 45% *  |
| Methyl glyoxal photolysis  | 42% *  |
| OH + NO <sub>2</sub> + M → HNO <sub>3</sub> + M (1 atm, 298K)              | 18%    |
| NO <sub>2</sub> + hv → NO + O( <sup>3</sup> P) (Solar light)               | 8% *   |

\* Solar light

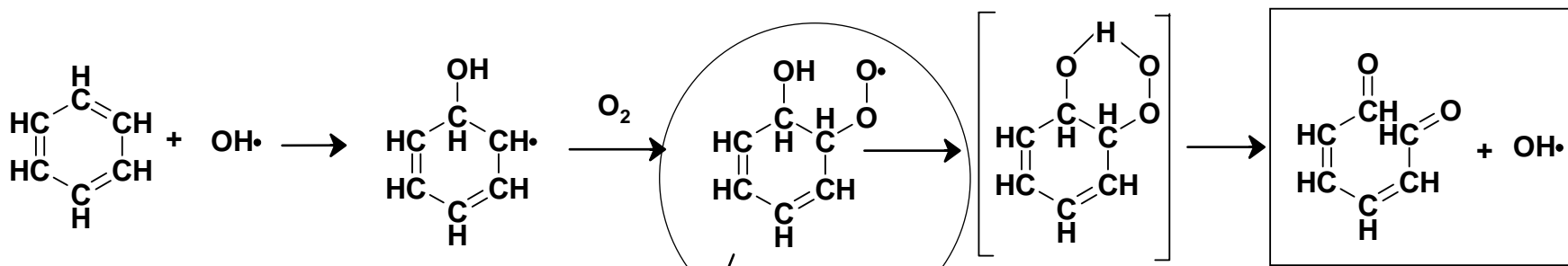
# Status of Mechanism Updates -- Mechanism Generation System

- Assigned VOC + OH, O<sub>3</sub>, NO<sub>3</sub>, and O<sup>3</sup>P rate constants updated
- Capability to generate chlorine atom + VOC reactions added
  - Structure-reactivity methods to estimate rate constants
  - Mechanisms can be generated for saturated compounds, but alkene mechanism generation limited by lack of thermochemical group data for Cl-containing radicals
- Capability to represent compounds and radicals with more than one ring and more than one double bond added
  - Necessary for generation of mechanisms for aromatics
- Methods developed to generate initial reactions of OH with alkylbenzenes and reactions of OH, O<sub>3</sub>, and NO<sub>3</sub> with the unsaturated dicarbonyl ring opening products
  - No methods exist to estimate unsaturated dicarbonyl photolyses, which need to be specified manually

# Status of Mechanism Updates -- Aromatic Mechanisms

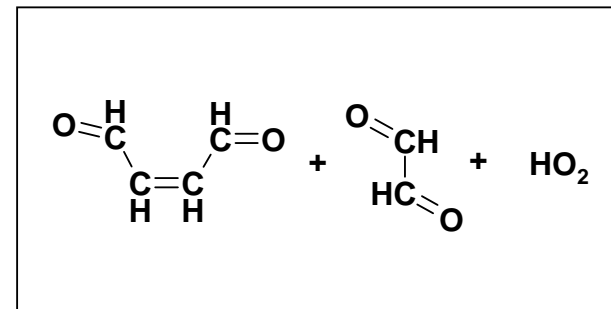
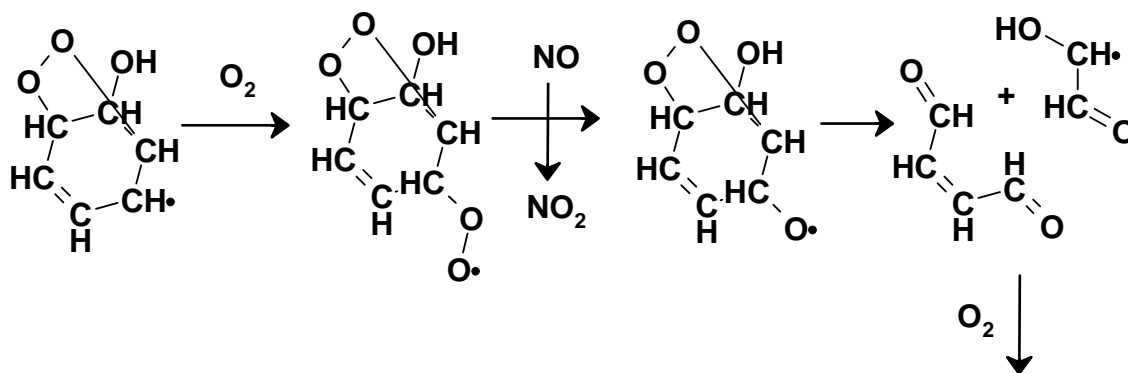
- SAPRC-99 uses parameterized species with adjusted yields and photolysis rates for uncharacterized ring opening products.
  - Adjusted to fit aromatic - NO<sub>x</sub> experiments.
  - Model gives poor fits to effects of adding CO to aromatic - NO<sub>x</sub> experiments and to measurements of direct reactivity
- Aromatic mechanism update approach:
  - Derive explicit mechanisms for ring-opening reactions and reactions of unsaturated dicarbonyl ring-opening products, based on data in Calvert et al. review to extent possible.
  - Adjust uncertain photolysis mechanisms based on simulations of chamber data with furans and aromatics
  - Determine if explicit mechanisms can correctly predict reactivity differences among alkylbenzene isomers
  - Derive condensed mechanisms for airshed models based on explicit mechanisms so developed.

# Ring Opening Mechanism Assumed

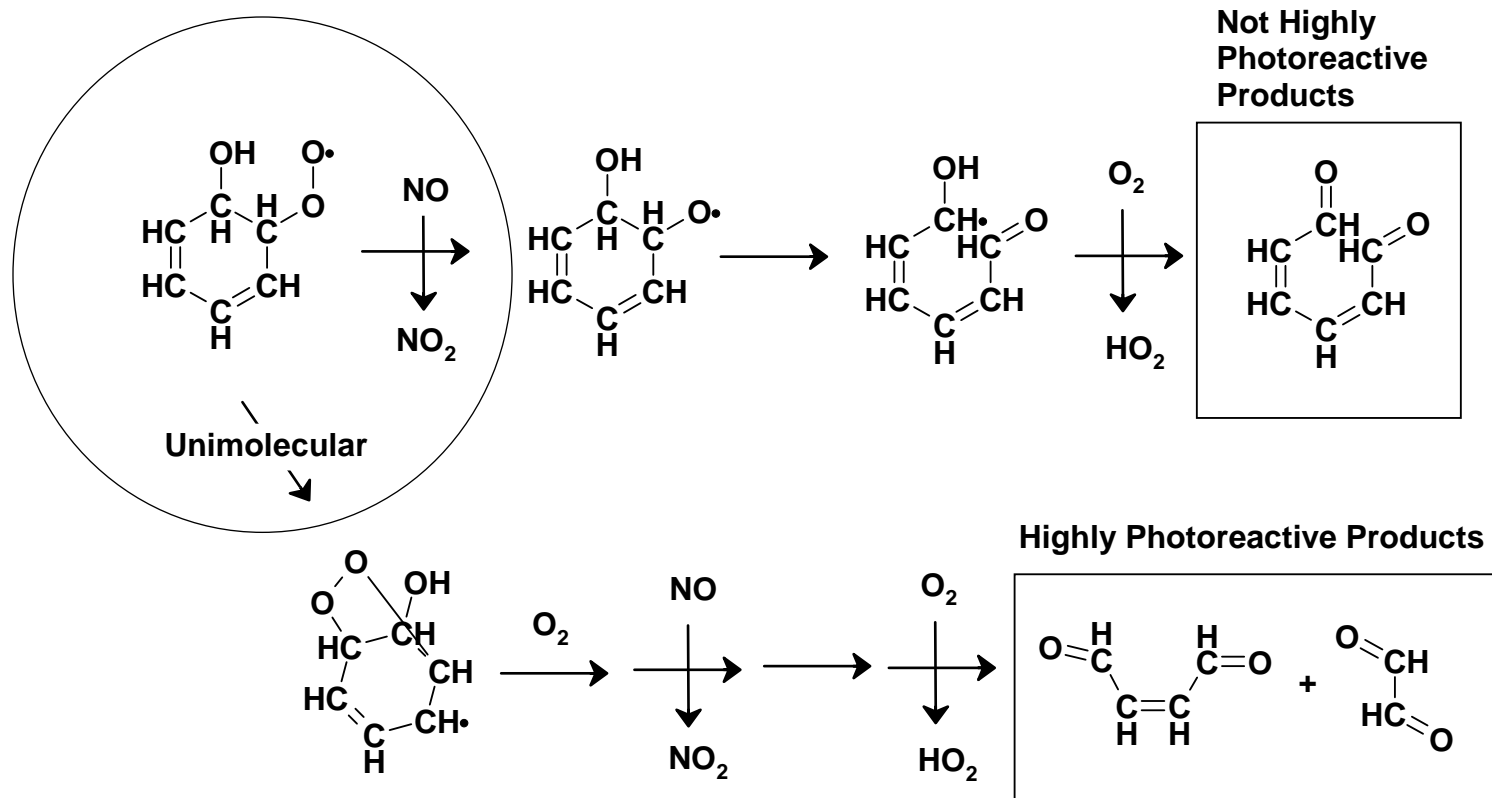


Note:

- Branching ratios do not depend on  $\text{NO}_x$  levels
- Yields of  $\alpha$ -dicarbonyls based on measurements
- Unsaturated 1,4-dicarbonyl yields based on  $\alpha$ -dicarbonyl co-product yields
- Rest of ring opening is OH + diunsaturated dicarbonyl, formed with no  $\text{NO}$  to  $\text{NO}_2$  conversions



# Alternative Ring Fragmentation Mechanism

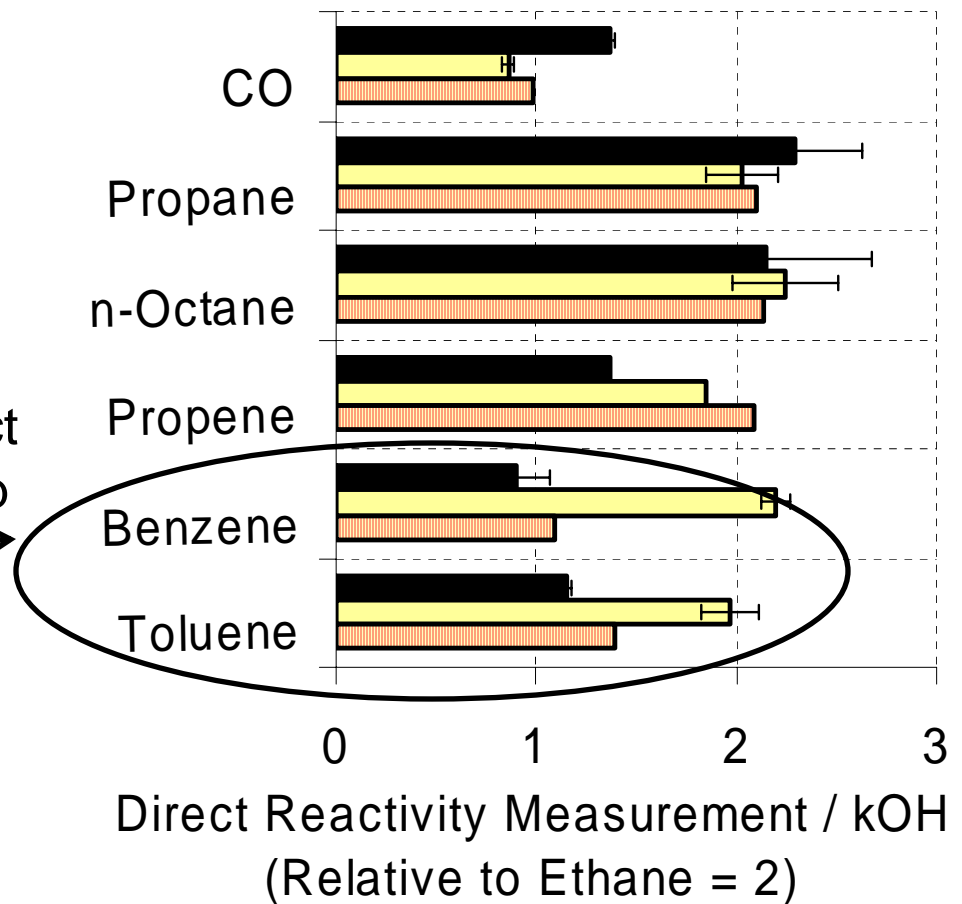


This mechanism predicts that the yields of  $\alpha$ -dicarbonyls and the highly photoreactive unsaturated dicarbonyl products will depend on NO<sub>x</sub> levels. This is not consistent with product yield or chamber data.

# Model Performance Simulating a Measurement of Direct Reactivity

- Direct reactivity is the number of NO to NO<sub>2</sub> conversions caused by a VOC's reactions
- A HONO + VOC photolysis flow system gives a measurement sensitive to direct reactivity
- SAPRC-99 overpredicts direct reactivities of aromatics by up to a factor of 2
- New aromatics mechanism more consistent with direct reactivity data

■ Experimental    □ SAPRC-99  
▨ New Mechanism



# Reactions of Aromatic Products

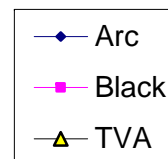
- Parameterized mechanisms for phenols and cresols unchanged
- Each unsaturated dicarbonyl product formed from benzene, toluene, and xylene isomers is represented explicitly.
  - OH, O<sub>3</sub>, and NO<sub>3</sub> reactions derived using the mechanism generation system
  - Unsaturated 1,4-dicarbonyls assumed to photolyze rapidly, based on data in Calvert et. al. review. Preliminary version assumes that radical formation pathways dominate, based on simulations of toluene and m-xylene - NO<sub>x</sub> experiments.
  - Unsaturated 1,6-dicarbonyls are assumed **not** to photolyze rapidly to radicals, based on limited data given in Calvert et. al. review.
- Assumptions concerning photolysis of unsaturated dicarbonyls may be revised based on evaluations against chamber data

## Status of Mechanism Updates -- Preliminary Evaluation Using Chamber Data

|                               |   |
|-------------------------------|---|
| Acetaldehyde,<br>Formaldehyde | Similar model performance as<br>SAPRC-99  |
| Ethene                        | Somewhat less O <sub>3</sub> than SAPRC-99  |
| Propene,<br>trans-2-Butene    | Radical yields in O <sub>3</sub> reactions now<br>can be increased to be consistent<br>with current evaluations   |
| Toluene, m-Xylene             | Must assume unsaturated dicarbonyl<br>photolysis forms mainly radicals to fit<br>O <sub>3</sub> formation rates. Different model<br>performance than SAPRC-99 |
| Benzene                       | O <sub>3</sub> formation rates overpredicted  |
| New Surrogate<br>Experiments  | Some differences from SAPRC-99<br>but similar overall quality of fits   |



# Model Performance Simulating Aldehyde and Alkene - NOx Experiments



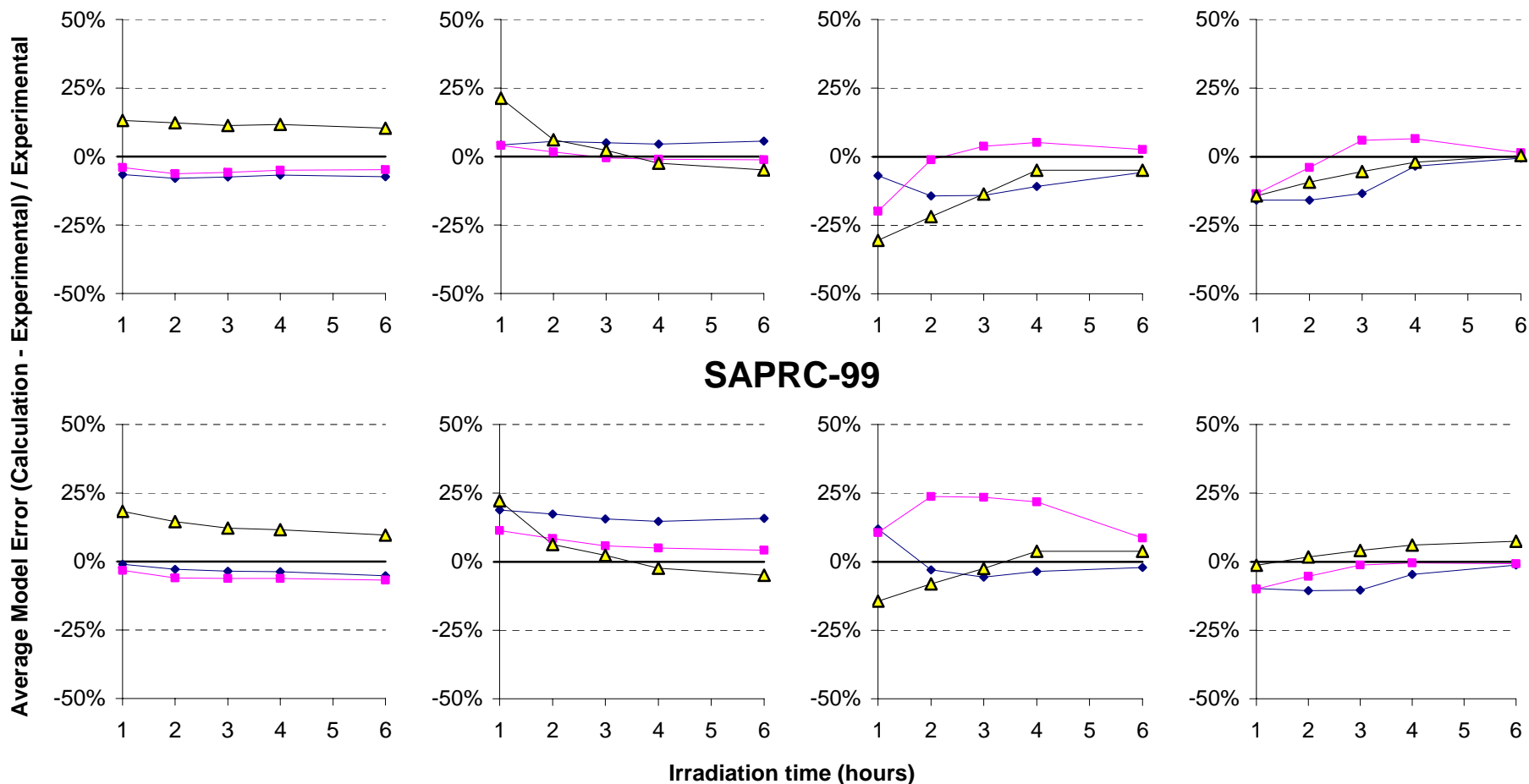
Formaldehyde

Acetaldehyde

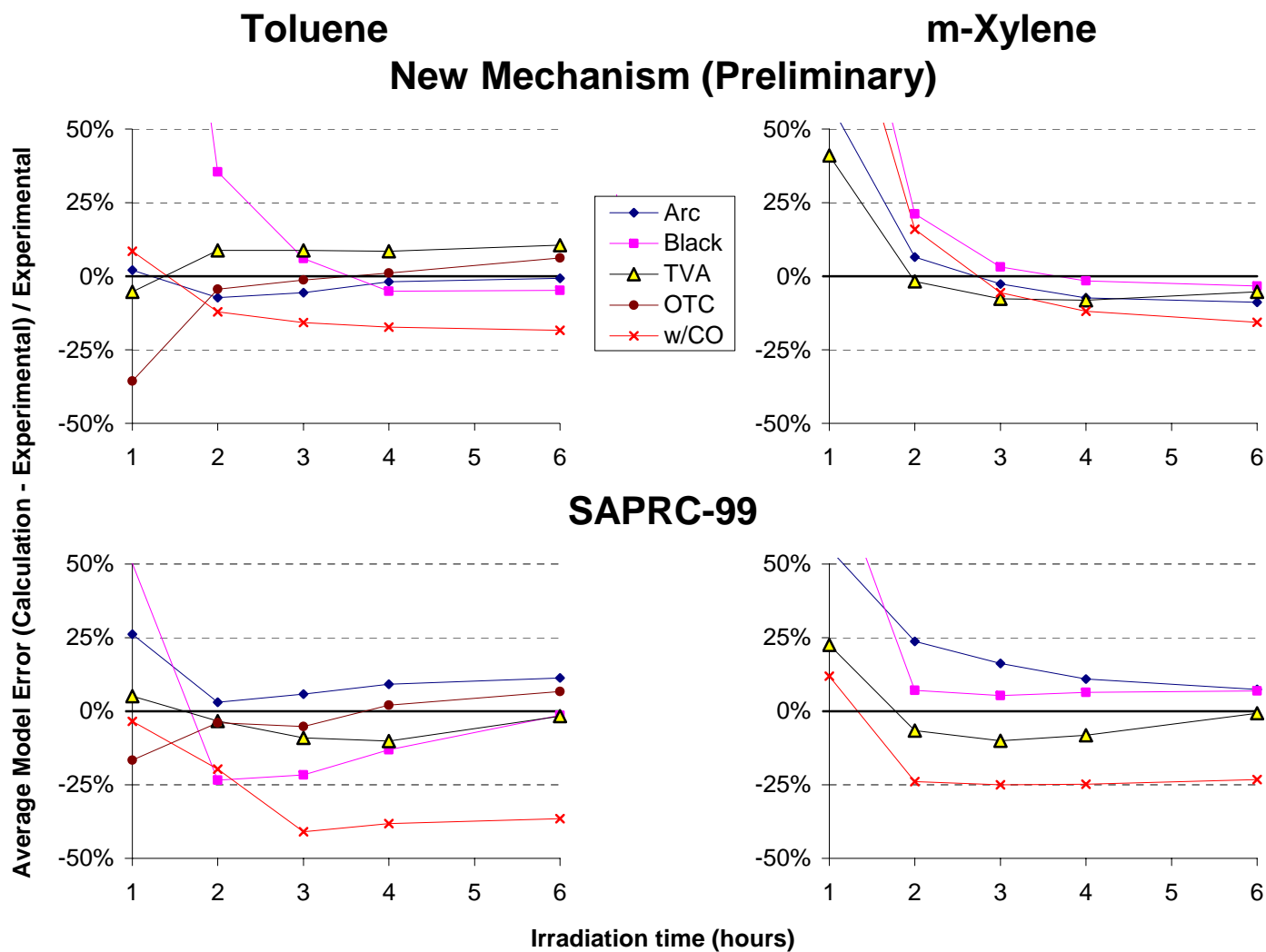
Ethene

Propene

New Mechanism

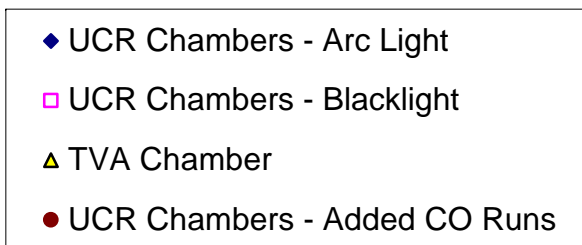
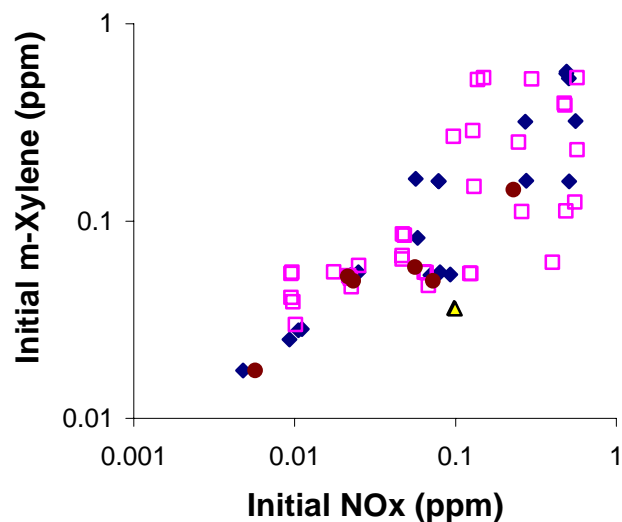


# Model Performance in Simulating Toluene and m-Xylene - NOx Experiments



# Matrix of m-Xylene - NO<sub>x</sub> Experiments

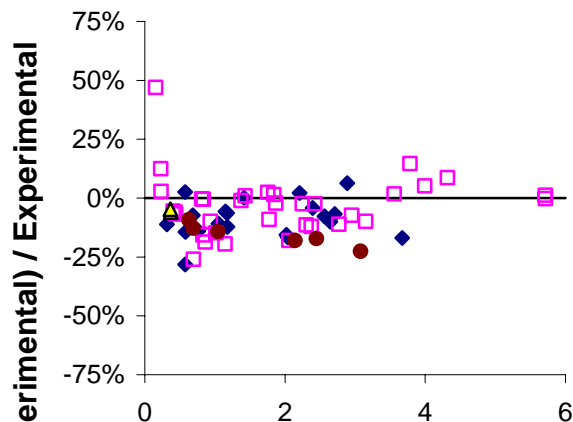
Run Matrix



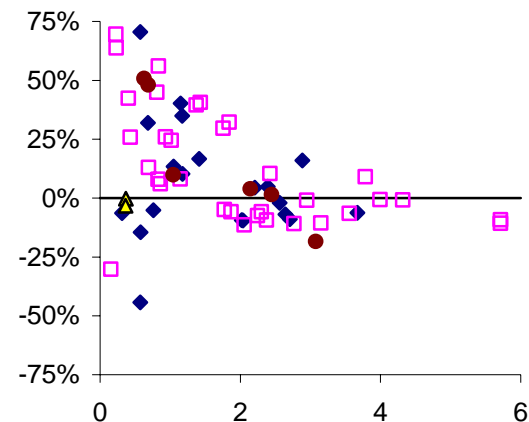
Note:  
No correlation of fits  
with initial NO<sub>x</sub> levels

New Mechanism

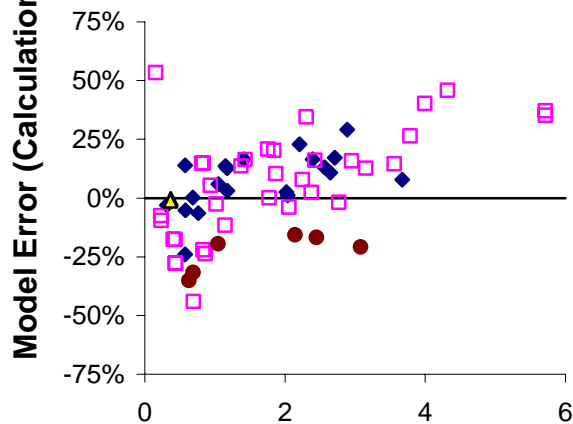
Final Δ([O<sub>3</sub>]-[NO])



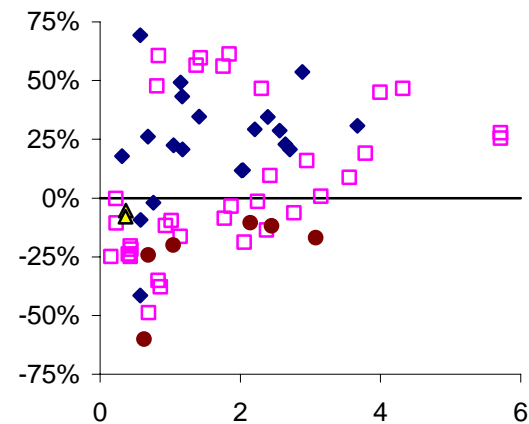
Hour 2 Δ([O<sub>3</sub>]-[NO])



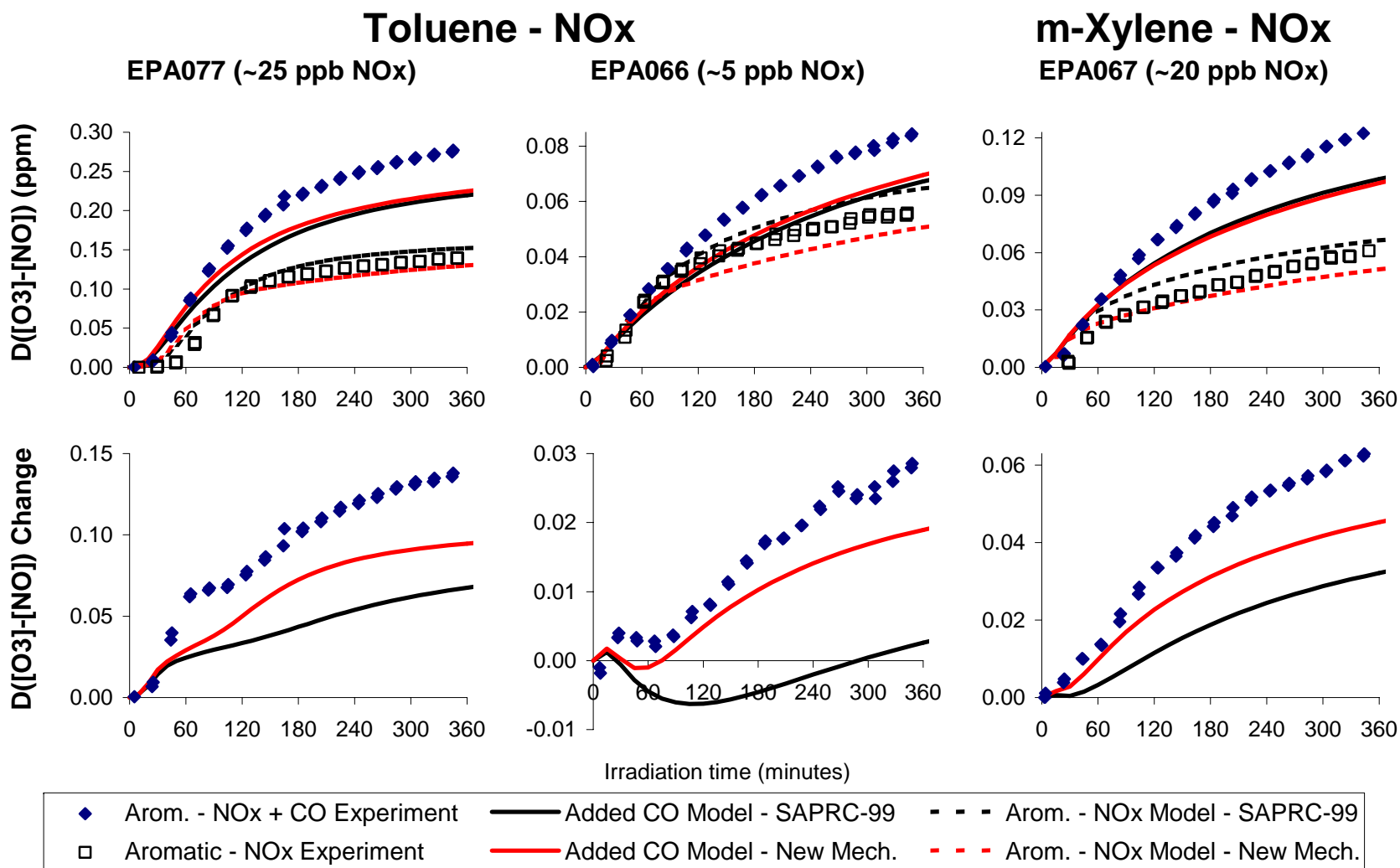
SAPRC-99



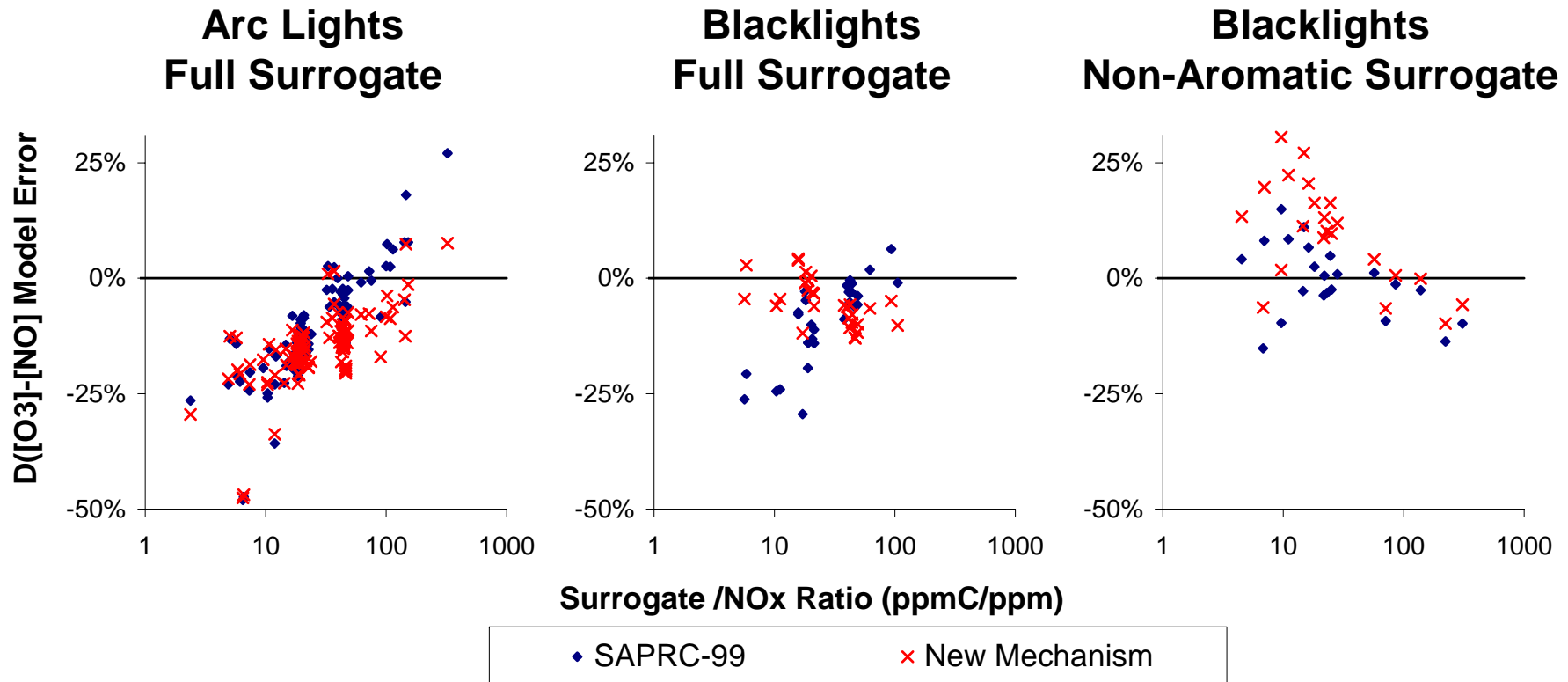
Initial m-Xylene / NO<sub>x</sub> Ratio



# Model Performance in Simulating Effect of Adding CO to Aromatic - NOx Experiments



# Model Performance Simulating UCR-EPA Chamber Surrogate - NOx Runs



# Remaining Mechanism Update Work

## Basic Chemistry Updates

- Complete evaluation, adjustments, and assessment of explicit aromatics mechanisms, using chamber data for benzene through trimethylbenzenes
- Re-assess parameterized mechanisms used for phenols and naphthalenes
- Re-assess  $O_3$  and  $O^3P$  + alkene mechanisms based on fits to chamber data for updated mechanism and current evaluations
- Incorporate new data of Atkinson et. al. on products formed in alkane photooxidations
- Review and update as needed estimation methods used in mechanism generation system
- Other updates?

# Remaining Mechanism Update Work (cont'd)

## Mechanism Adaptation

- Condense explicit aromatics mechanism to efficient size for airshed models and general aromatics representations
- Adaptations for PM modeling:
  - Add new model specie(s) to base mechanism to represent formation of condensable oxidation products.
  - Derive mechanism generation lumping rules for assignments to condensable products (use vapor pressure estimates?)
  - Consider new treatment of peroxy radical operators to permit separate representation of condensable hydroperoxides.
- Develop mechanism condensation approaches
  - Level 1: Minimum compromising of chemical accuracy
  - Level 2: Computational efficiency comparable to CB4/05

# Remaining Mechanism Update Work (cont'd)

## Mechanism Evaluation

- Evaluate mechanism against large body of chamber data
  - Experiments used in SAPRC-99 evaluation
  - New UCR EPA chamber experiments at lower NO<sub>x</sub> levels
  - Incremental reactivity experiments in UCR chambers with a wide variety of compounds
  - TVA chamber experiments
  - Available UNC chamber experiments
  - Available Euphore experiments?
- Compare performance with SAPRC-99 and make corrections or adjustments where appropriate
- Evaluate condensed versions against detailed version and appropriate chamber data.



# Remaining Issues

- New aromatics mechanism is not completely consistent with available laboratory and chamber data and theory
- Biases in model simulations of surrogate experiments still exist
- Uncertainties in alkene + O<sub>3</sub> and O<sup>3</sup>P mechanisms
- Improved thermochemical database needed to extend estimation methods. (Quantum calculations may be useful.)
- Representation of oxidation products is highly approximate and not well evaluated against chamber data
- Approaches for representing SOA formation highly uncertain
- Need improved computer algorithms for efficient and flexible mechanism implementation.
- others?