Development of the Updated SAPRC Chemical Mechanism

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August 28, 2007

Outline

- Overview of the SAPRC mechanisms

- Updates for SAPRC-07

- Anticipated changes in ambient ozone predictions

- Changes in ozone reactivity (MIR) values

- Recommendations

Mechanism Use and Requirements

Used in airshed models to:

- Represent the chemistry of formation of secondary pollutants (e.g., O_3) from emitted VOCs and NO_x

- Predict relative ozone reactivity scales for VOCs ($\Delta O_3 / \Delta VOC$) for regulatory applications (e.g, MIR scale used in California)

Requirements

- Represent current state of science of atmospheric chemistry

- Give predictions consistent with environmental chamber results

- Appropriately represent the hundreds of types of VOCs for reactivity scale calculations

- Represent complex ambient mixtures in airshed calculations in computationally efficient manner

Major Components of SAPRC Mechanisms

Base Mechanism

- Reactions of inorganics and common organic products

Mechanisms for individual VOCs (hundreds of VOCs represented)

- <u>Mechanism generation system</u> used to derive fully explicit mechanisms that are condensed using "lumping rules"

- Estimated mechanisms are 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" derived from those of the mixture of individual VOCs they represent

- These depend on the composition of the mixture taken as representative of VOC emissions from all sources

SAPRC-99 Mechanism Generation System

- Generates mechanisms for reactions of alkanes, alkenes, alkynes, aldehydes, ethers, esters, nitrates, acids and most of their oxidation products with OH, O_3, NO_3, O^3P 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_3, and NO_3 reactions
  - Nitrate yields from RO_2+NO based on size of the RO_2 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

Operation of Mechanism Generation System
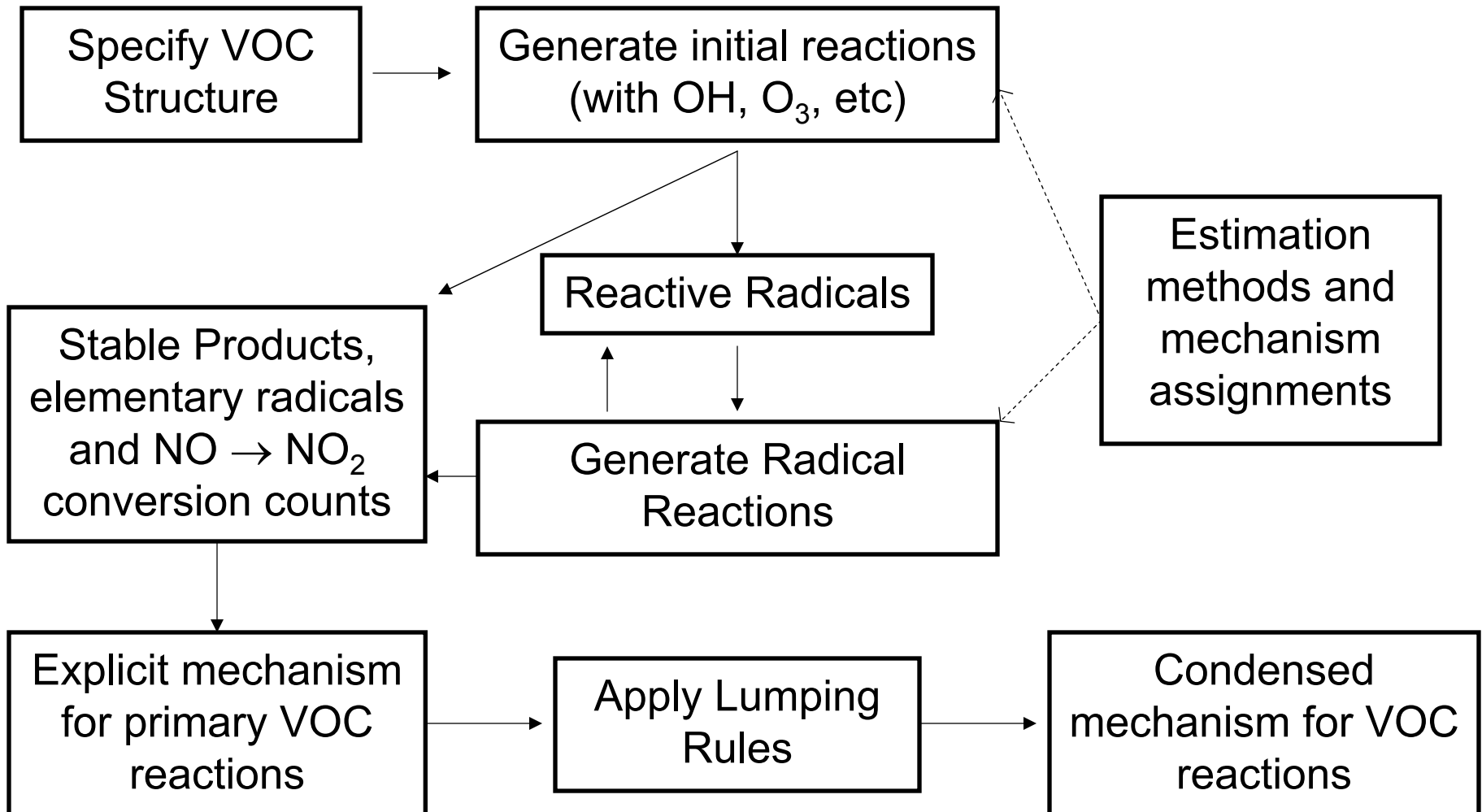
Examples of Sizes of Generated Mechanisms

Compound	Reactions	Products
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 (SAPRC07 system)	172	22

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

Limitations of
SAPRC-99 Mechanism Generation System

- Only generates mechanisms for systems with NO_x. (Peroxy radicals reacted only with NO. Peroxy + peroxy reactions are not generated. $RC(O)O_2\cdot$ 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.

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 version (SAPRC-07) is now complete

- Developed under CARB funding, draft report approved by RSC

- Development, evaluation, and documentation completed. Implementation work remains.

Major Objectives of Mechanism Update

- Update rate constants and reactions to current state of science

- Add chlorine chemistry

- Improve mechanisms for aromatics to incorporate new data and improve performance in simulating available chamber data.

- 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

- Represent additional types of VOCs of interest to the CARB

- Develop new condensed mechanisms from detailed version (including a highly condensed version as an alternative to CB4)

Mechanism Updates -- Base Mechanism

- Inorganic and organic product mechanisms updated based on recent evaluations and data

- Added Inorganic ClO_x reactions and new model species to represent reactive Cl-substituted carbonyl oxidation products

| Potentially important rate constant changes	Change
$OH + NO_2 + M \rightarrow HNO_3 + M$ (1 atm, 298K)	+19%
Generic peroxy + $HO_2 \rightarrow$ Generic hydroperoxides + O_2	-47%
$NO_2 + h\nu \rightarrow NO + O(^3P)$	+8% *
Lumped higher ketone (PROD2) photolysis	-75% *
Methyl glyoxal photolysis	42% *
Methacrolein and lumped C_5 isoprene product photolysis	45% *
	* Solar light

Mechanism Updates -- Mechanism Generation System

- Assigned VOC + OH, O_3, NO_3, and O^3P 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
  - Used as aid in development of mechanisms for aromatics

- Methods developed to generate initial reactions of OH, O_3, and NO_3 with the unsaturated dicarbonyl ring opening products
  - No methods exist to estimate unsaturated dicarbonyl photolyses, which need to be specified manually

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_x experiments.
  - Model gives poor fits to effects of adding CO to aromatic - NO_x experiments and to measurements of direct reactivity

- SAPRC-07 aromatic mechanism update approach:
  - Estimate 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.
  - Condensed mechanisms for airshed models derived based on explicit mechanisms so developed
  - Adjust relative yields of photoreactive and non-photoreactive products based on simulations of chamber data

Ring Opening Mechanism Assumed
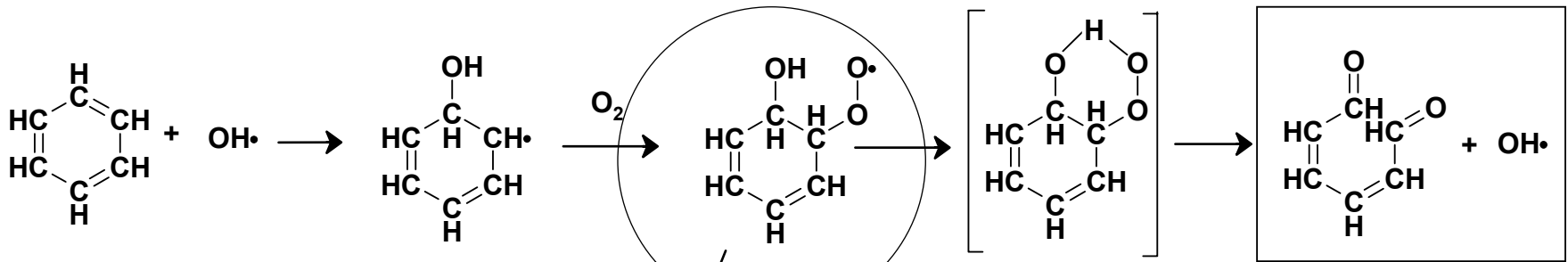
Note:

- Branching ratios <u>do not</u> depend on NO_x levels

- Yields of α-dicarbonyls based on measurements

- Unsaturated 1,4-dicarbonyl yields based on α-dicarbonyl co-product yields

- Rest of ring opening is OH + diunsaturated dicarbonyl, formed with <u>no</u> NO to NO_2 conversions
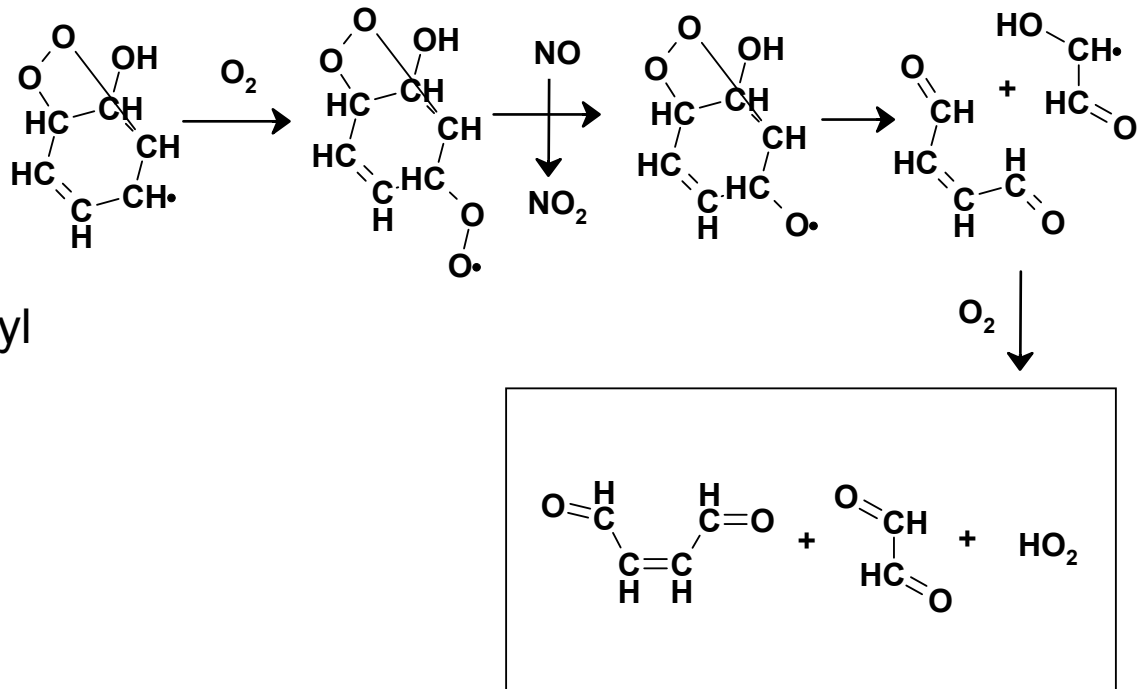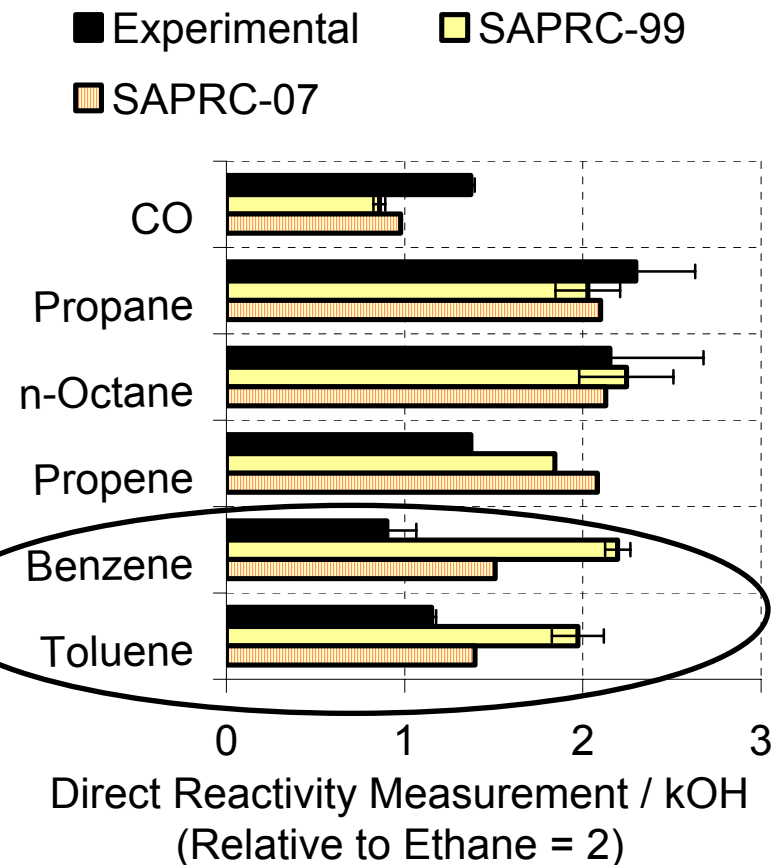
Alternative Ring Fragmentation Mechanism

Not Highly Photoreactive Products

Highly Photoreactive Products

Unimolecular
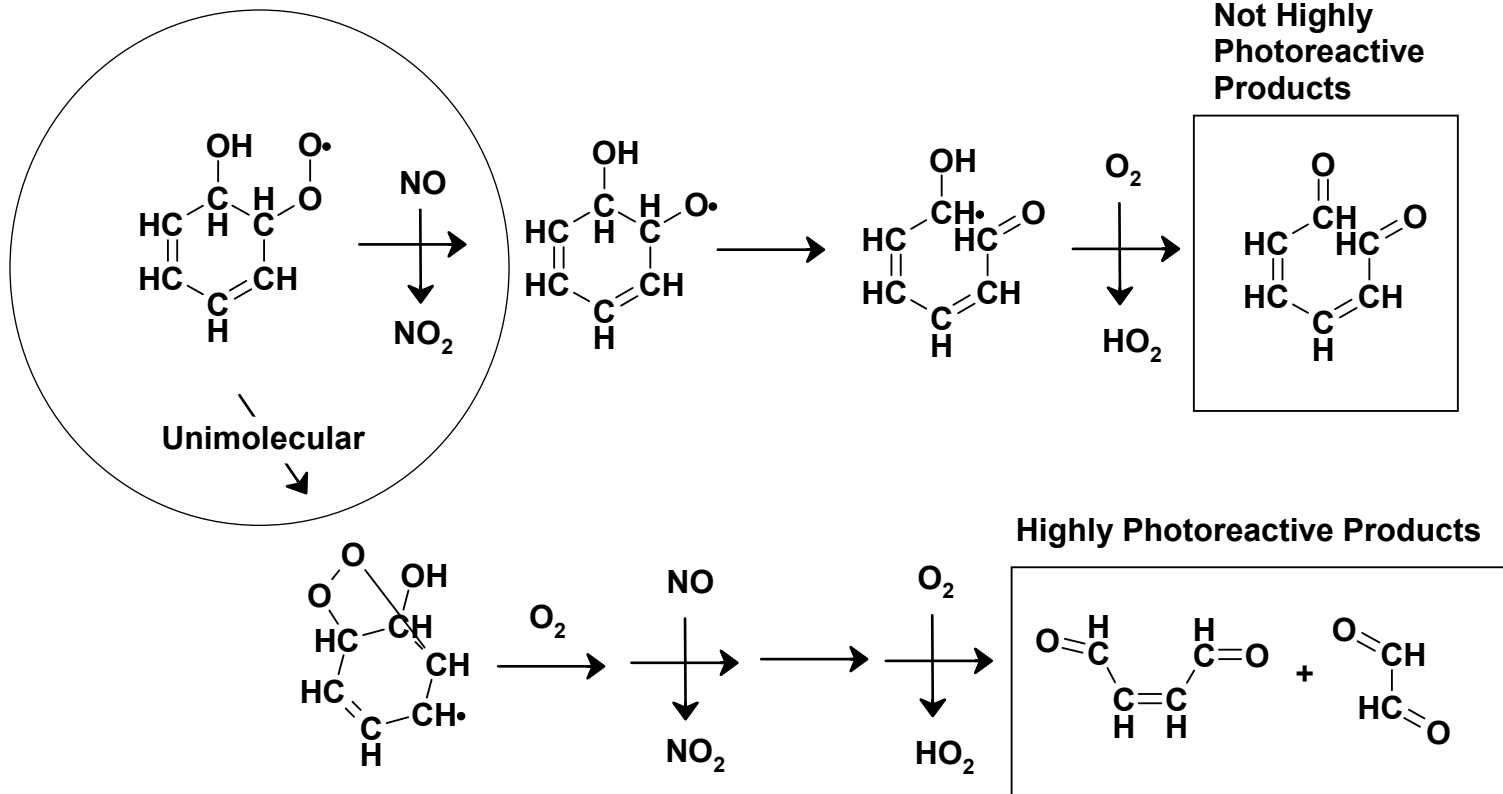
This mechanism predicts that the yields of α-dicarbolyls and the highly photoreactive unsaturated dicarbonyl products will depend on NO_x levels. <u>This is not consistent with product yield or chamber data.</u>
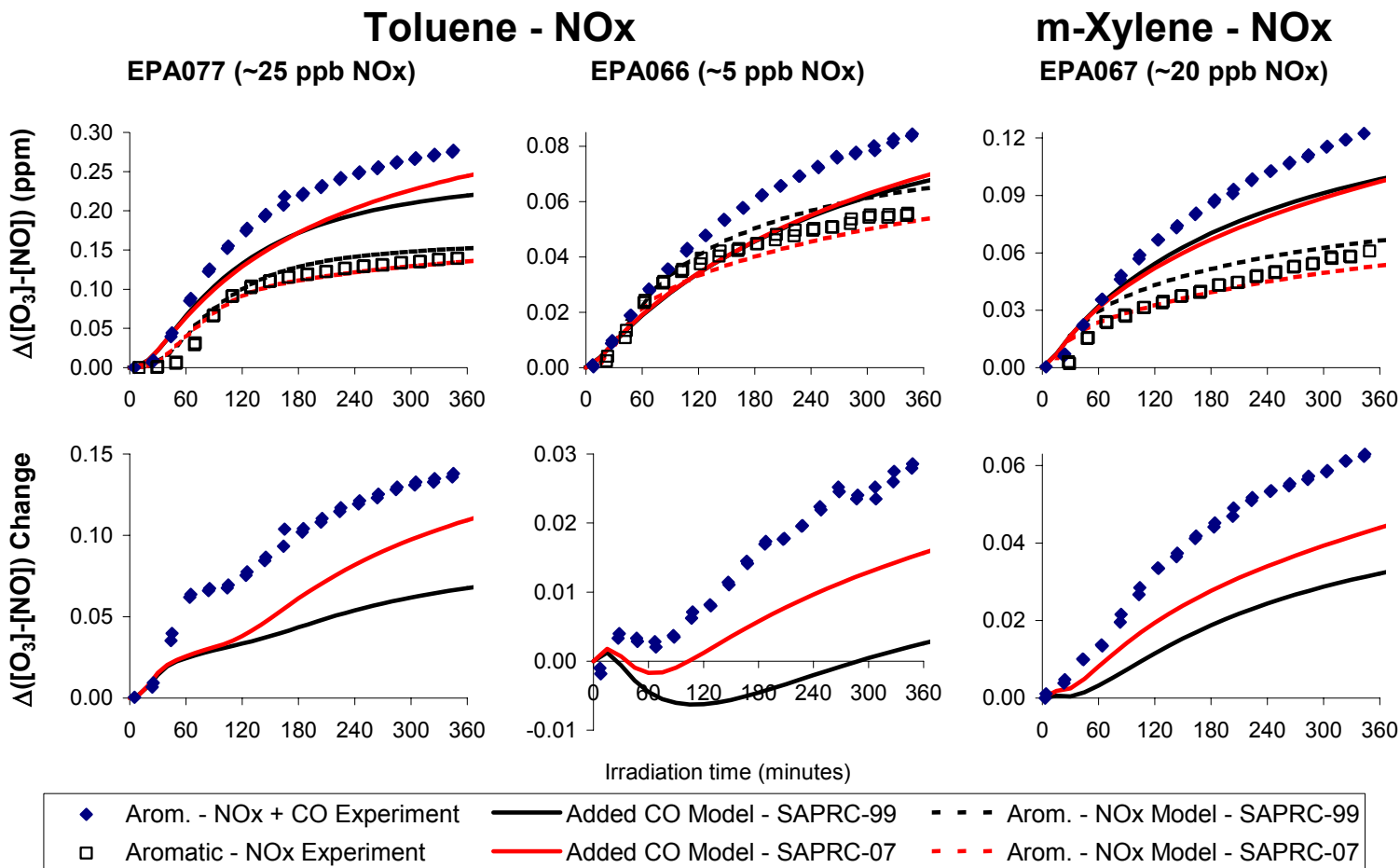
Reactions of Aromatic Products

- Parameterized mechanisms for phenols and cresols unchanged

- Mechanisms for α-dicarbonyls updated based on evaluations

- Mechanism for model species representing unsaturated dicarbonyls derived based on estimated mechanisms for such compounds formed from the alkylbenzenes

- For unsaturated 1,4-dialdehydes and aldehyde-ketones:
  - Assumed to photolyze rapidly based on data in Calvert et al.
  - Two model species used: one (AFG1) that photolyzes to form radicals and one (AFG2) that forms stable molecules
  - Relative yields of these adjusted based on simulations of chamber data for individual aromatics

- For di-unsaturated 1,6-dicarbonyls and also 1,4-diketones:
  - Lumped into separate model species (AFG3) that is assumed not to photolyze, based on data in Calvert et al.

Model Performance Simulating a Measurement of Direct Reactivity

- Direct reactivity is the number of NO to NO_2 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

- SAPRC-07 aromatics mechanism somewhat more consistent with direct reactivity data

Direct Reactivity Measurement / kOH
(Relative to Ethane = 2)

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

Toluene - NOx

EPA077 (~25 ppb NOx)   EPA066 (~5 ppb NOx)

m-Xylene - NOx

EPA067 (~20 ppb NOx)

Legend:
- ◆ Arom. - NOx + CO Experiment
- □ Aromatic - NOx Experiment
- — Added CO Model - SAPRC-99
- — Added CO Model - SAPRC-07 (red)
- - - - Arom. - NOx Model - SAPRC-99
- - - - Arom. - NOx Model - SAPRC-07 (red)

Mechanism Updates -- Improved Capability for Representing Low-NO$_x$ Products

- Approximate methods are required to represent the peroxy + peroxy reactions important under low NO$_x$ conditions for the mechanisms to have reasonable size.

- Because of the way this is represented in SAPRC-99 (like CB4/05), it is difficult to "un-lump" model species for organic hydroperoxides or organic nitrate products.

- But higher molecular weight organic hydroperoxides and organic nitrates may be important precursors to SOA

- SAPRC-07 uses a new representation of peroxy radical reactions that permits use of separate hydroperoxide and organic nitrate species, depending on volatility or other factors

- For example, the current mechanism uses a separate model species for aromatic hydroperoxides, which may be useful to model NO$_x$-dependence of SOA yields from aromatics
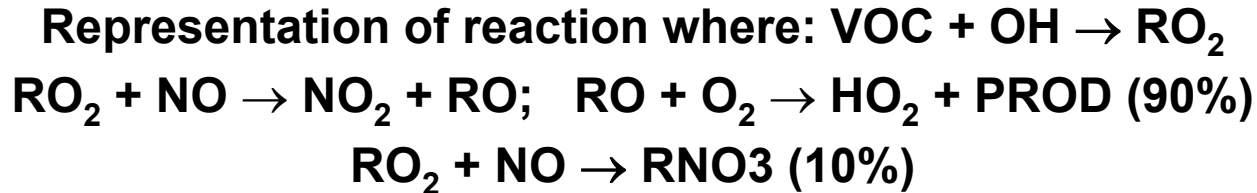
Representation of Peroxy Products

(Excluding nitrate formation)

Reaction	Explicit Products	SAPRC-99	SAPRC-07
$RO_2 + NO$	Alkoxy radical products	Alkoxy radical products	Alkoxy radical products
$RO_2 + HO_2$	Hydroperoxide product	Alkoxy radical products + single lumped ROOH	Hydroperoxide product depends on RO_2
$RO_2 + RCO_3$	Disproportionation products		Ketone product depends on RO_2
$RO_2 + RO_2$	½ disproportionation products	Alkoxy radical products	Ketone product depends on RO_2
	½ Alkoxy radical products		Alkoxy radical products

Major Reaction when NOx is low
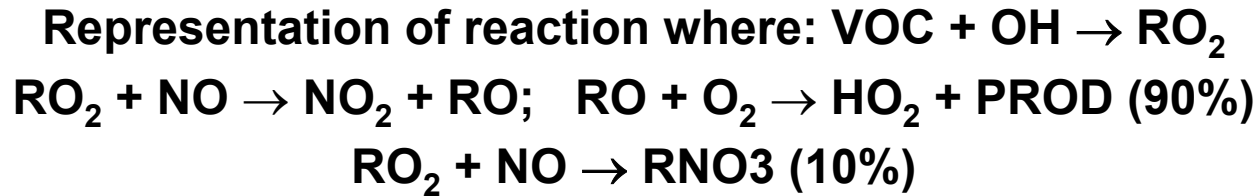
Example of Representation of Peroxy Products

Representation of reaction where: VOC + OH $\rightarrow$ RO$_2$

RO$_2$ + NO $\rightarrow$ NO$_2$ + RO;   RO + O$_2$ $\rightarrow$ HO$_2$ + PROD (90%)

RO$_2$ + NO $\rightarrow$ RNO3 (10%)

Represented in SAPRC-99 as:

VOC + OH $\rightarrow$ 0.9 {RO2-R. + PROD} + 0.1 RO2-N.

Reaction	RO2-R.	PROD	RO2-N.
NO	- NO + NO$_2$ + HO$_2$	PROD	- NO + RNO3
NO$_3$	- NO$_3$ + NO$_2$ + HO$_2$	PROD	- NO + MEK + HO$_2$
HO$_2$	- HO$_2$ + ROOH	PROD	- HO$_2$ + ROOH
RO$_2$· $\rightarrow$ RO·	- RO$_2$	PROD	- RO$_2$ + ½ MEK + ½ PROD2 + HO$_2$
RO$_2$· $\rightarrow$ oth	- RO$_2$	PROD	- RO$_2$ + ½ MEK + ½ PROD2 + HO$_2$
RC(O)O$_2$·	- RC(O)O$_2$·	PROD	- RC(O)O$_2$· + PROD2

Example of Representation of Peroxy Products

Representation of reaction where: VOC + OH $\rightarrow$ RO$_2$

RO$_2$ + NO $\rightarrow$ NO$_2$ + RO; RO + O$_2$ $\rightarrow$ HO$_2$ + PROD (90%)

RO$_2$ + NO $\rightarrow$ RNO3 (10%)

Represented in SAPRC-07 as:

VOC + OH $\rightarrow$ 0.9 {RO2C + xHO2 + xPROD} + 0.1 {RO2XC + zRNO3} + yROOH

Reaction	RO2C	xHO2	RO2XC	xPROD	yROOH	zRNO3
NO	- NO + NO$_2$	HO$_2$	- NO	PROD		RNO3
NO$_3$	- NO$_3$ + NO$_2$	HO$_2$	- NO$_3$	PROD		
HO$_2$	- HO$_2$		- HO$_2$		ROOH	
RO$_2$· $\rightarrow$ RO·	- RO$_2$	HO$_2$	- RO$_2$	PROD		PROD2 + HO$_2$
RO$_2$· $\rightarrow$ oth	- RO$_2$		- RO$_2$		PROD2	
RCO$_3$·	- RCO$_3$·		- RCO$_3$·		PROD2	

Mechanism Updates – Mechanisms for Many Types of VOCs Added or Improved

- Number of distinct VOC mechanisms increased from 585 to 710 (a 21% increase)

- Added or improved mechanisms include:

    - Added alkanes and alkenes in emissions inventories not previously represented

    - Separate estimated mechanisms for higher alkylbenzenes, depending on structure (SAPRC-99 used "lumped molecule" representation based on methylbenzenes)

    - Improved estimates for halogenated compounds, based on chlorine chemistry

Evaluation Against Chamber Experiments

- Mechanism evaluated against available UCR and TVA environmental chamber data base + some UNC experiments

Chambers	UCR	TVA	UNC
Indoor - Blacklight or mixed	4	1	
Indoor - Arc light	4		
Outdoor	1		1

Types of Experiments	Runs	VOCs	Types
Characterization	247		10
Single VOC	671	46	
Incremental Reactivity	571	111	
Mixtures	949		22

- Performance simulating chamber data comparable to SAPRC99 (somewhat better in some cases, not quite as good in others)

Evaluation Results:
Model Errors for All Single VOC Experiments
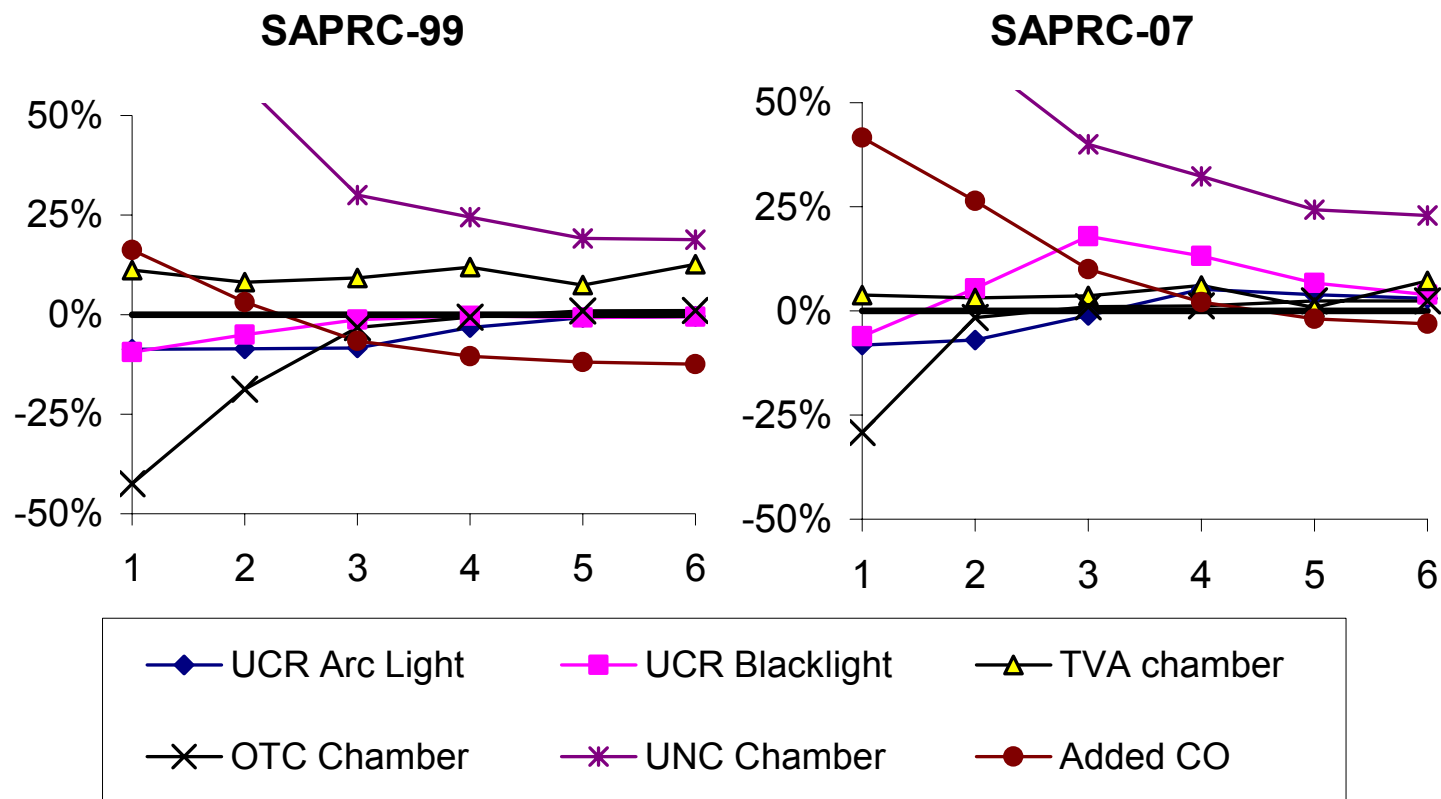

Average Model Error vs Hour of Run
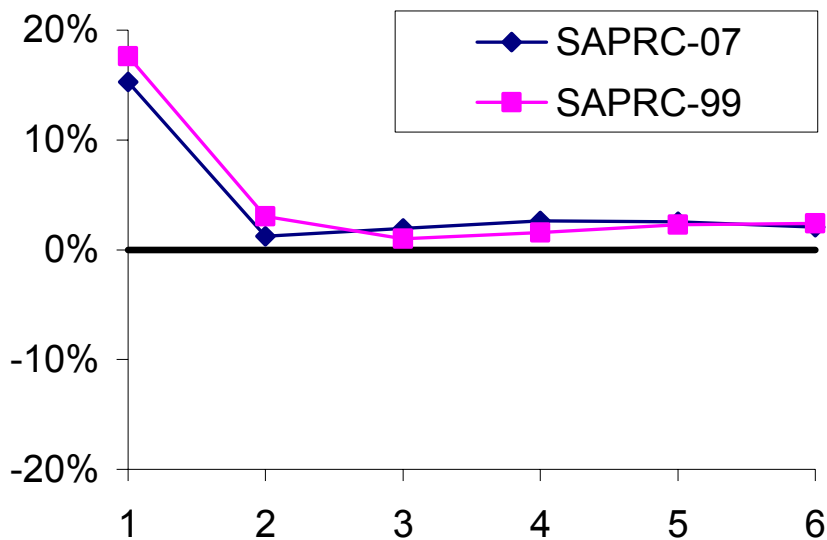
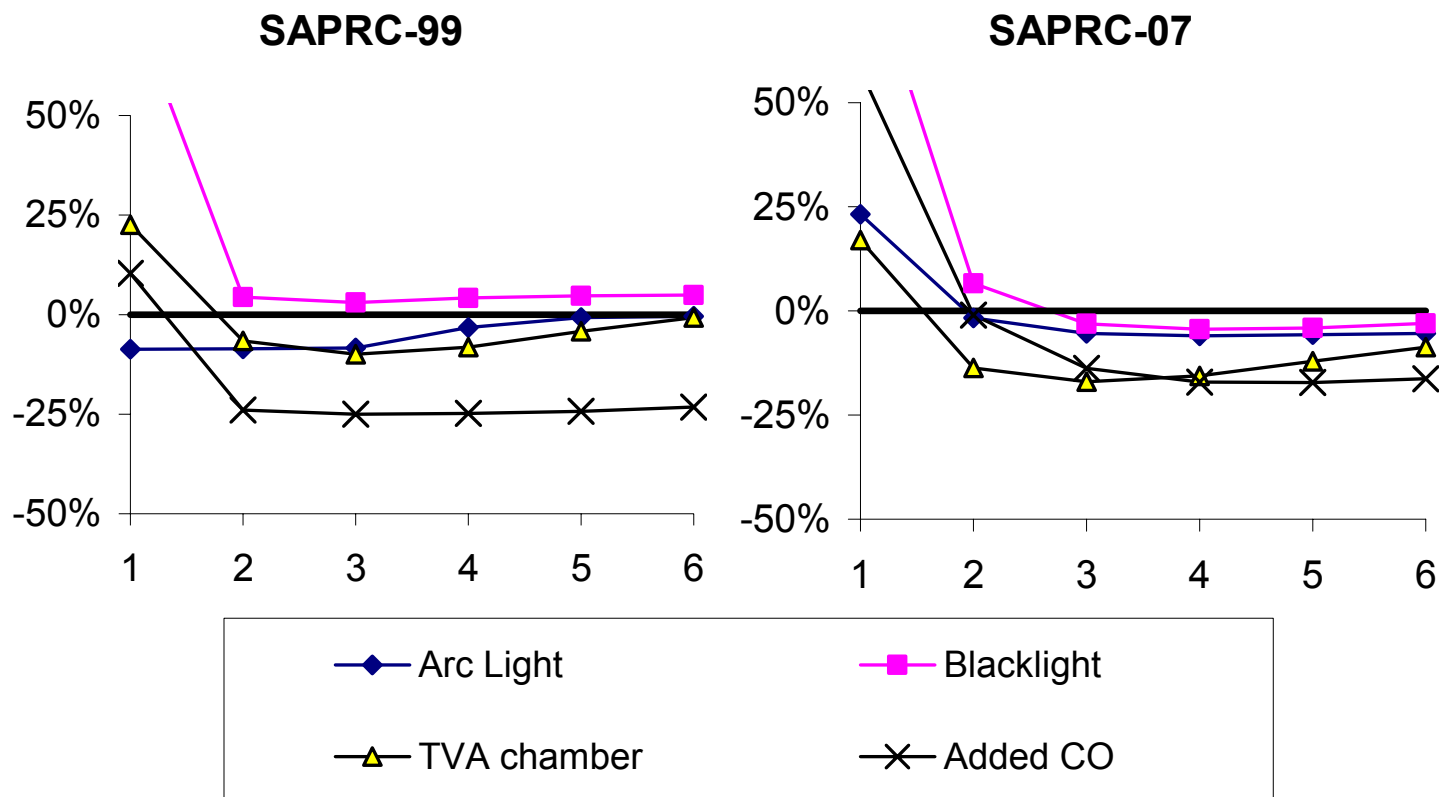**Final Model Error Distribution (fraction of runs vs error range)**
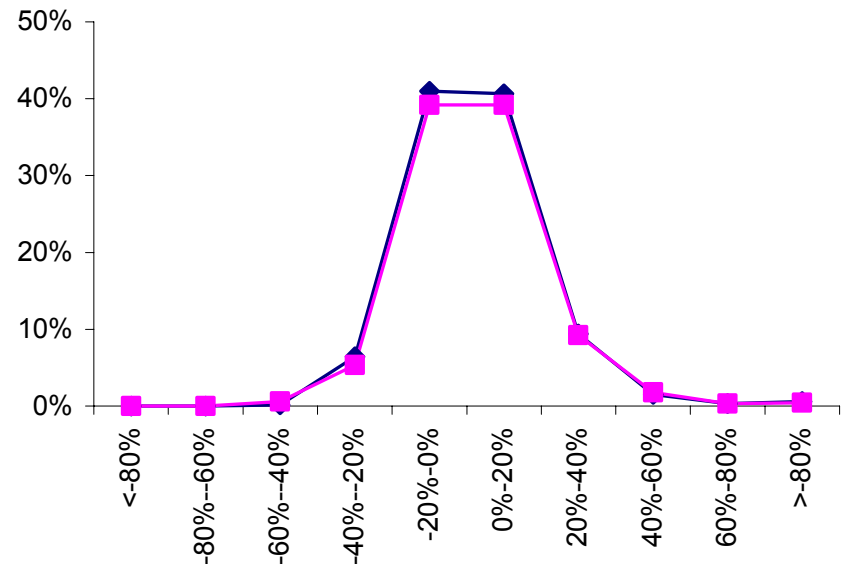
Evaluation Results:
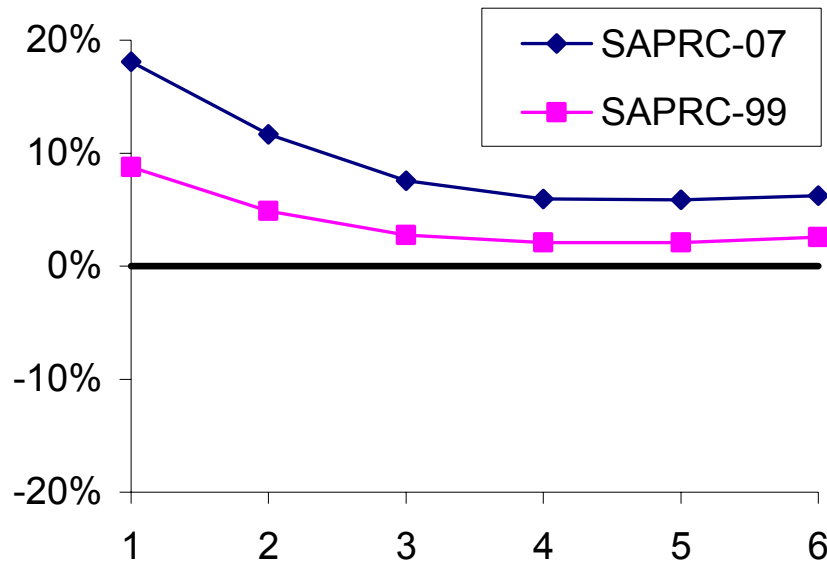# Model Errors for Propene Experiments

Average model error vs. hour of run

Evaluation Results:
Model Errors for m-Xylene Experiments

Average model error vs. hour of run

SAPRC-99   **SAPRC-07**

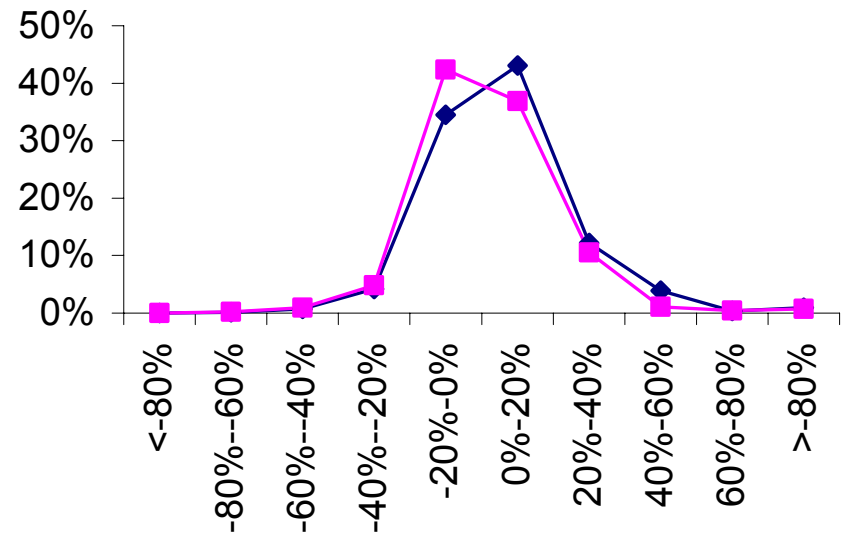Legend: Arc Light, Blacklight, TVA chamber, Added CO

Evaluation Results:
Model Errors for All Mixture Experiments
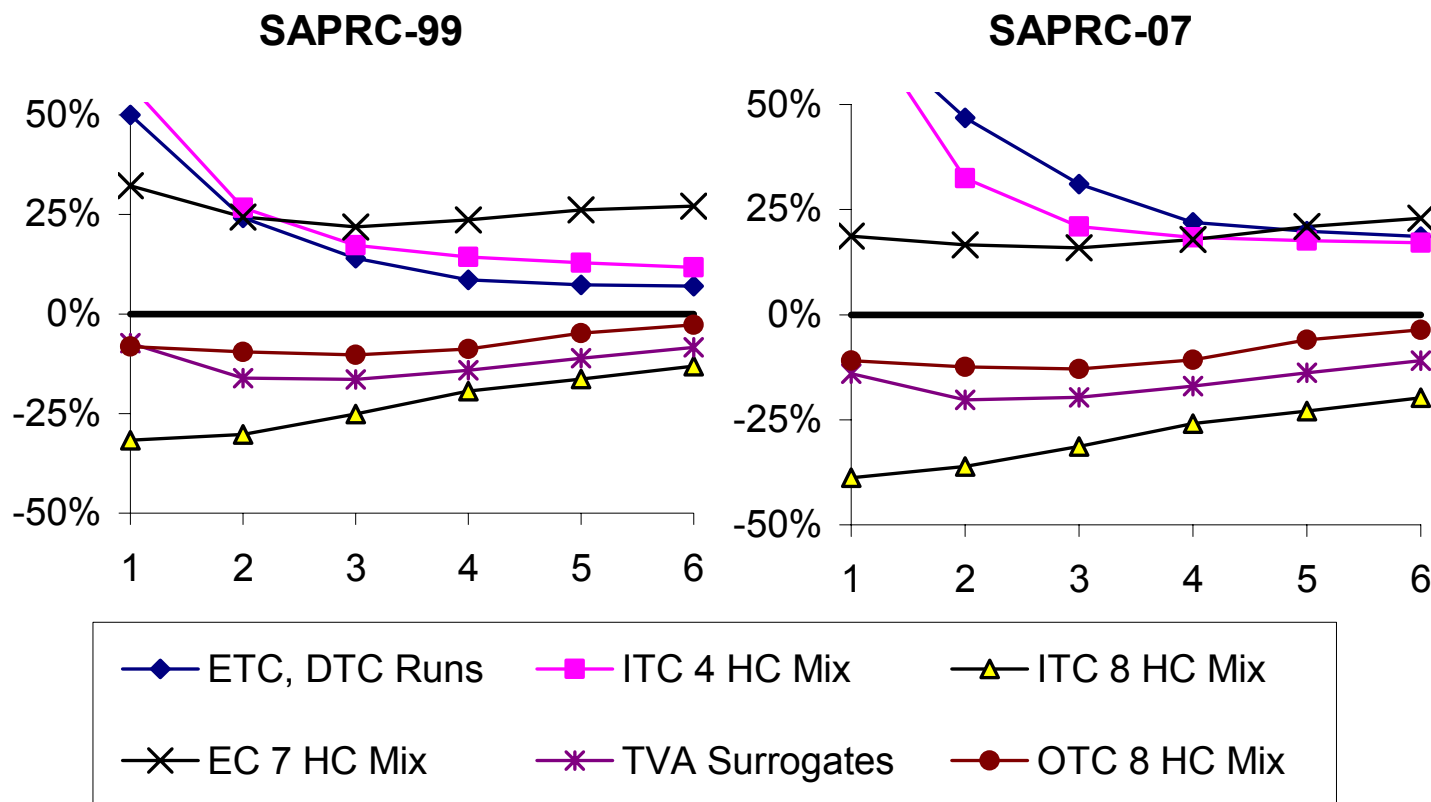
**Average Model Error
vs Hour of Run**

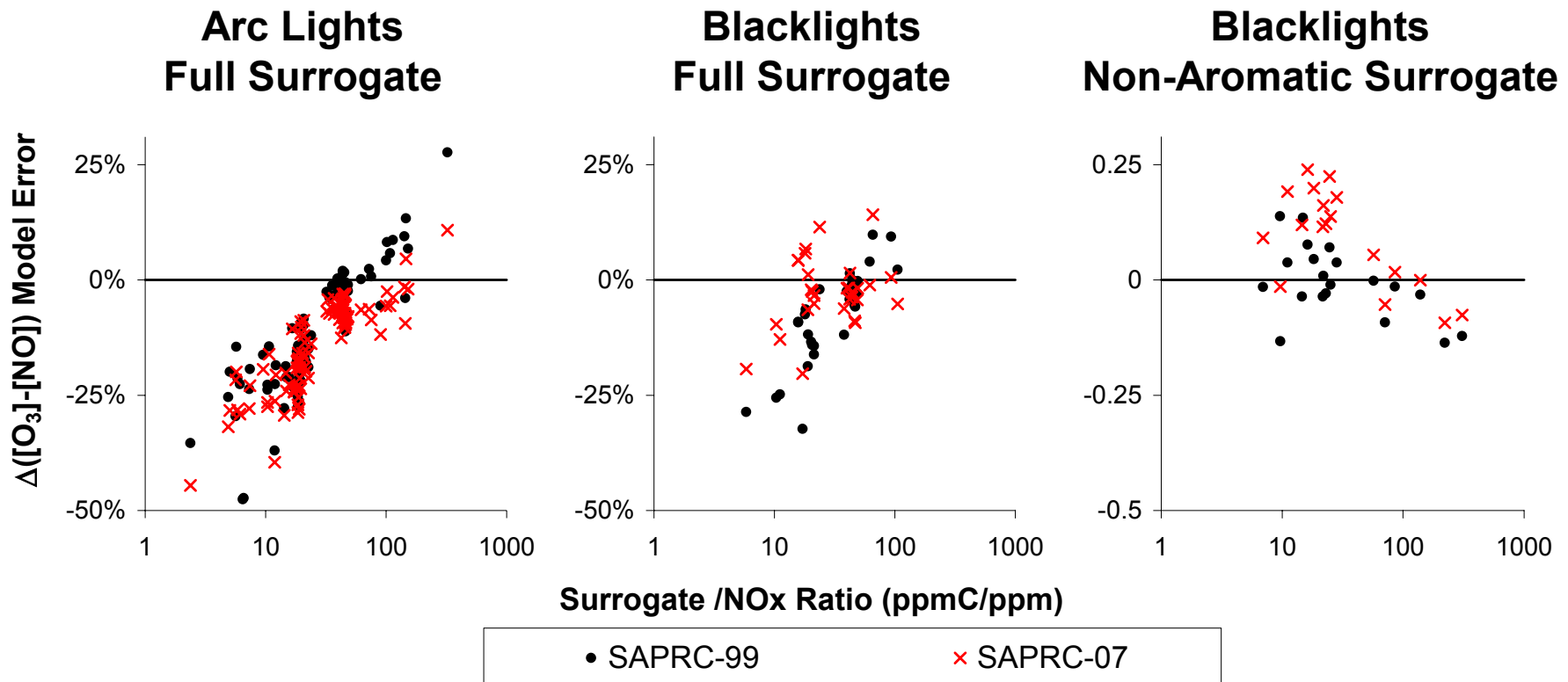**Final Model Error Distribution
(fraction of runs vs error range)**

Evaluation Results: Model Errors for Earlier UCR and TVA Mixture Experiments

Average model error vs. hour of run

SAPRC-99

SAPRC-07

Legend:
- ETC, DTC Runs
- ITC 4 HC Mix
- ITC 8 HC Mix
- EC 7 HC Mix
- TVA Surrogates
- OTC 8 HC Mix

Model Performance Simulating
UCR-EPA Chamber Surrogate - NOx Runs

**Arc Lights
Full Surrogate**

**Blacklights
Full Surrogate**

**Blacklights
Non-Aromatic Surrogate**

Δ([O₃]-[NO]) Model Error

Surrogate /NOx Ratio (ppmC/ppm)

• SAPRC-99   × SAPRC-07

- Problem of O_3 underprediction at low ROG/NO_x still exists

Lumped Mechanism for Airshed Models

- A "Fixed Parameter" mechanism for airshed models was derived using same lumping approach as "Fixed Parameter" SAPRC-99

- Parameters for lumped species based on the base ROG mixture used in the reactivity scenarios
  - Mixture based on ambient air measurements in mid-1980's (Probably needs to be updated)
  - Same mixture as used for "Fixed Parameter" SAPRC-99

- Emissions assignments have been updated and added to emissions speciation database

- Mechanism slightly larger than SAPRC-99. **Because of time constraints, more condensed versions of SAPRC-07 have not yet been developed**

- Used as base case in reactivity calculations

Calculation of Updated Reactivity Scales

- Updated mechanism used to calculate MIR, MOIR, EBIR, and "Base Case" reactivity scales.

- The scenarios and calculation methodology used is exactly the same as used for SAPRC-99 reactivity scales.

- Reactivities calculated for a total of 1064 Types of VOCs, including
  - 710 VOCs represented explicitly
  - 302 VOCs represented by the "Lumped molecule" method
  - 52 Complex mixtures (e.g., exhausts, petroleum distillates)

- This includes 293 types of VOCs not in 2002 SAPRC-99 scales.

- Note: Reactivities of amines have been deleted until an improved estimated amine mechanisms can be developed.

Effect of Mechanism Update on Calculated Maximum O_3 in the Box Model Scenarios Used for the Reactivity Scale Calculations
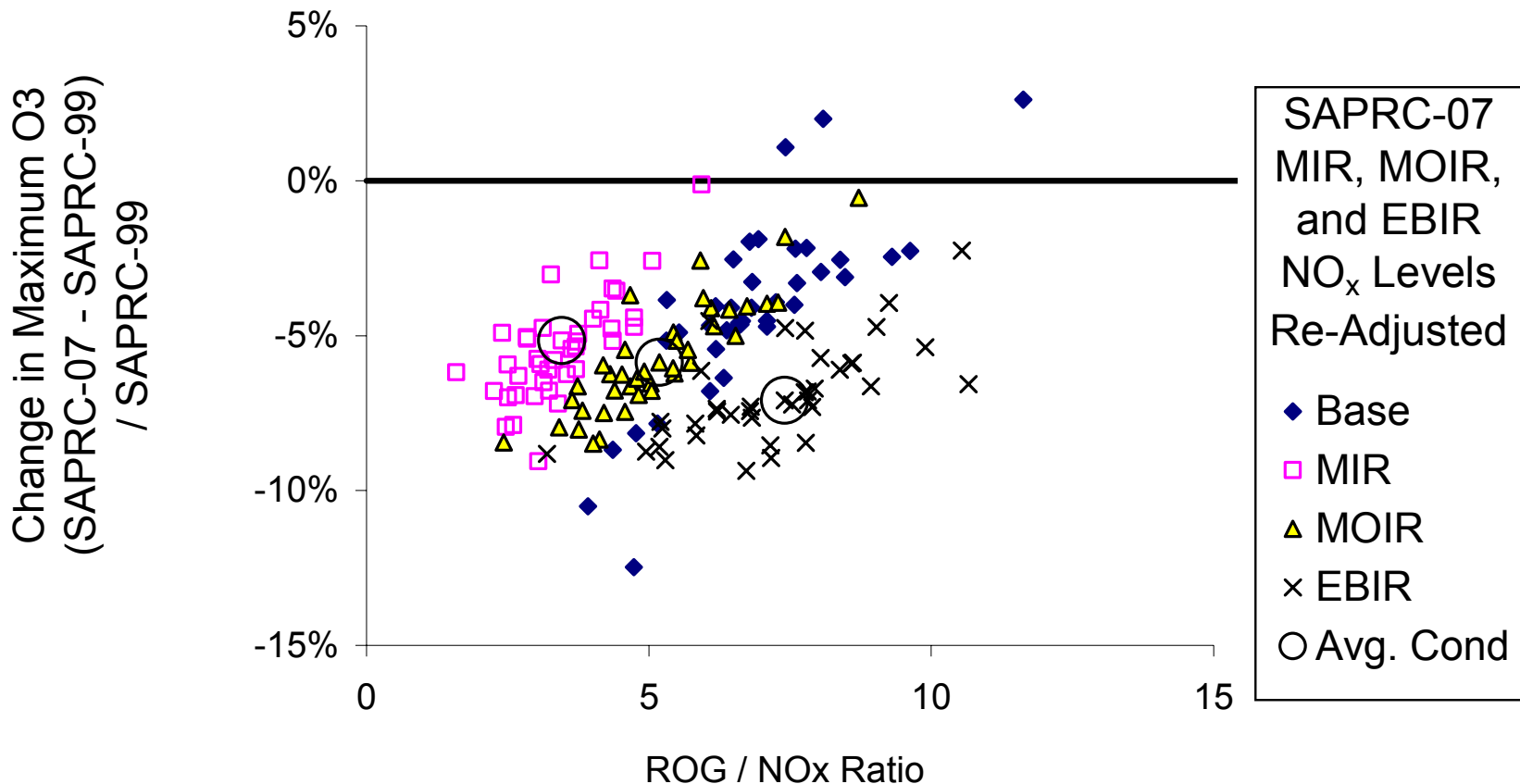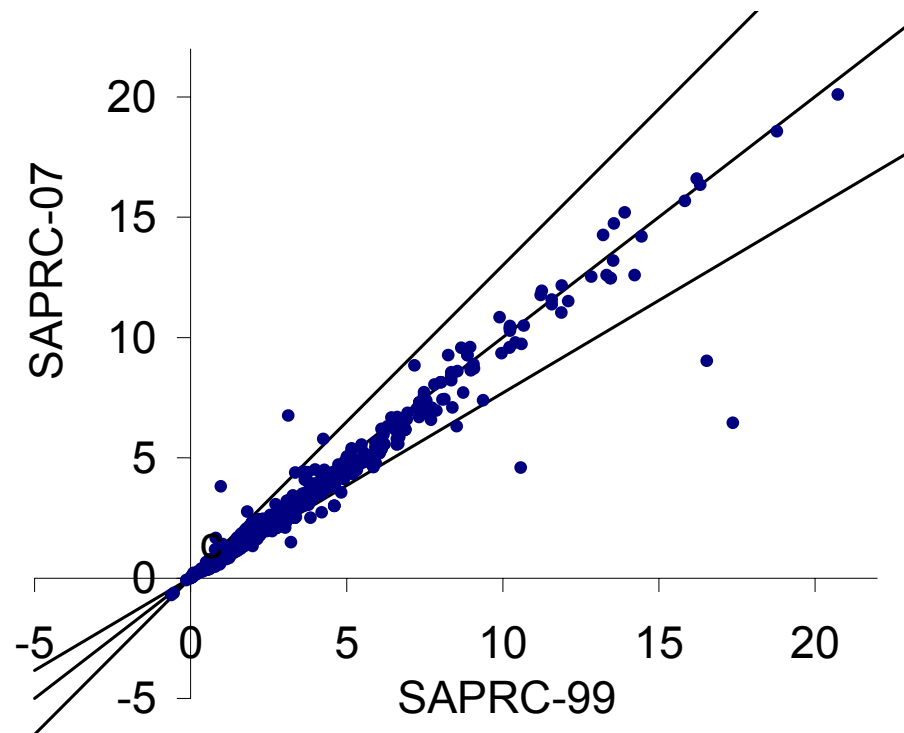
Effect of Mechanism Update on Calculated Maximum O_3 in the Box Model Scenarios With Same NO_x Levels
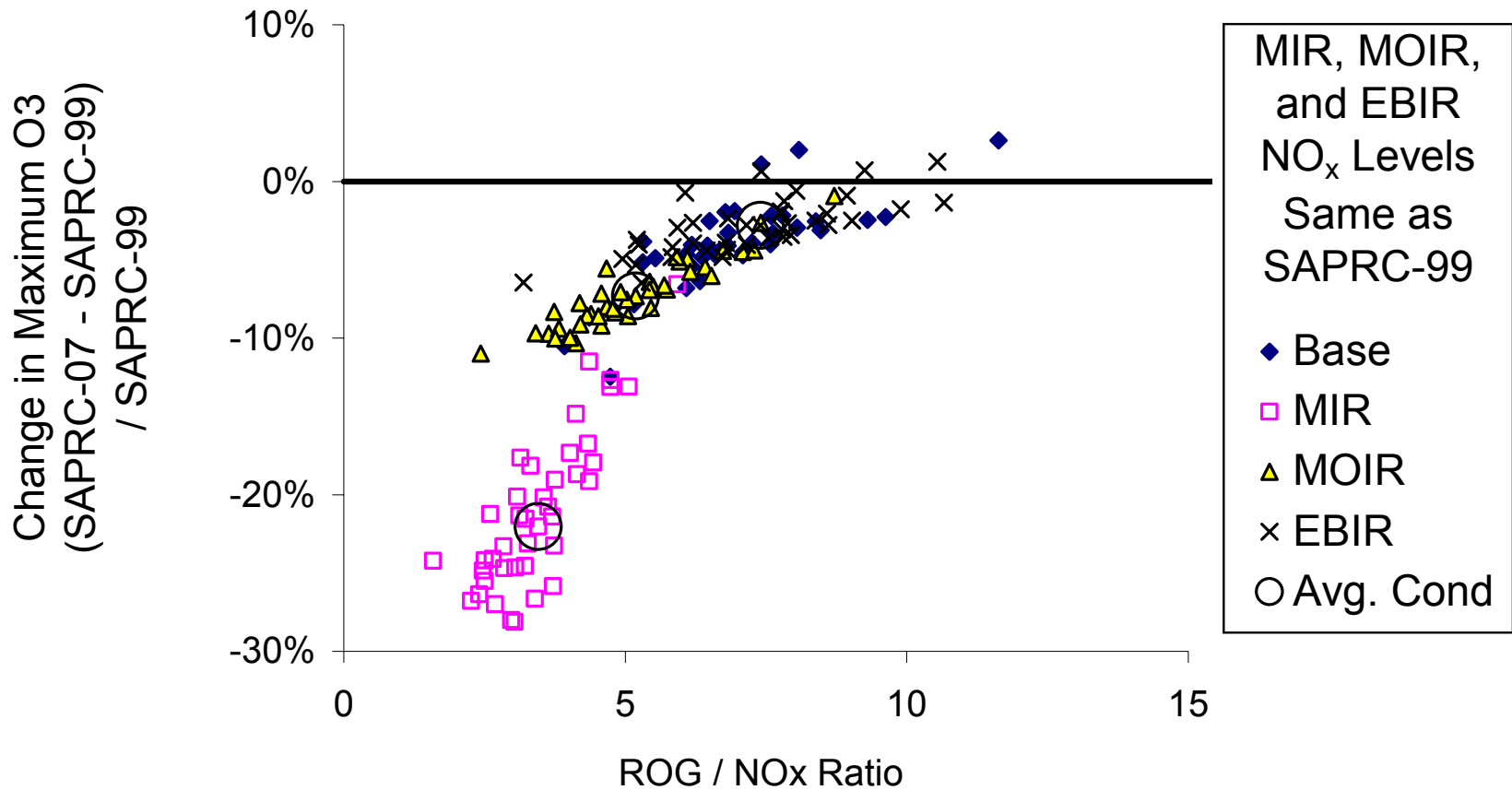
Changes in Ozone Reactivity Values in the MIR Scale

Incremental Reactivity
(gm O3 / gm VOC)
MIR Scale

- Compounds

—— 1:1 and +/- 30% lines

VOCs with Large MIR Changes

Compound	Approx. MIR (mass basis)		Reason for change
	Old	New	
3-Methoxy-1-butanol	1.0	3.8	Rate constant error corrected
2-(Cloromethyl)-3-chloropropene	3.1	6.8	Chloronated ketones assumed to be more photoreactive
Trans-1,2-dichloro-ethene	0.8	1.7	Chloroacetaldehyde believed to be more photoreactive
Indene	3.2	1.5	Represented by styrene (was represented by tetralin)
Furan	16.5	9.0	More explicit mechanism (was represented by m-xylene)

Remaining Work – Near Term

- Mechanism needs to be implemented into full airshed models
  - Files to implement mechanism in preparation
  - Software modifications may be needed to implement new peroxy radical "Operator" reactions

- New mechanisms for amines need to be developed
  - New chamber data indicate that amine mechanisms in the draft report are invalid and had to be deleted
  - Analysis of amine chamber data underway and estimated amine mechanisms be available by end of September

- Condensed version of mechanism needs to be developed (not currently funded)

- Mechanism needs to undergo peer review

Recommended Research – Base Mechanism

- **Reasons for model performance problems in simulating existing chamber data need to be elucidated**
  - Why do current mechanisms underpredict O_3 in surrogate experiments at low concentrations and ROG/NOx?
  - Why did mechanism updates cause fits to chamber data to be slightly worse for some types of mixture experiments?
  - What is the implications of these discrepancies in simulations of ambient conditions?
  - What uncertain rate constants affect these performance issues?
  - What is most needed research to address these issues?

- Uncertainty analysis and process analysis may be useful, but new mechanism performance analysis approaches are needed.

Recommended Research -- Aromatics

- Although updated and more chemically reasonable, the aromatics mechanisms is still highly simplified and not consistent with all current laboratory and chamber results

- Attempts to develop explicit mechanisms that can predict reactivity differences among aromatic isomers were not successful

- **Improved aromatics mechanisms will probably require breakthroughs in measurement methods and theory**
    - Need reliable methods to identify *and quantify all* products
    - Need better *theory* and *estimation methods* that can predict reactions of ring-opening intermediates and products

- In the meantime, systematic examination of effects of alternative aromatics representations may be useful to assess effects of aromatics uncertainties on model predictions

Recommended Research – Mechanism Generation System

- The mechanism generation system is critical for estimating mechanisms for many VOCs for which no data are available.

- There was not sufficient time in the project to update the many estimation methods used in the system. This is still needed.

- Lack of estimation assignments for reactions of halogenated radicals makes generation of chlorine + alkene reactions difficult

- Methods to estimate volatility of products (to serve as a basis for lumping for SOA models) needs to be implemented.

- The mechanism generation system and its estimation methods need to be documented in the peer-reviewed literature

- Estimation methods should be compared with those used in the European Master Chemical Mechanism

Recommended Research – Mechanism Adaptation to SOA Predictions

- Adapting SAPRC-07 for PM and SOA predictions represents an integrated approach for developing improved mechanisms for both ozone and PM. This requires:

  - Adding new organic product model species to represent low-volatility SOA precursors (including hydroperoxides and nitrates.)

  - Incorporating estimates of volatility in the mechanism generation system

  - Evaluating PM predictions against results of *well characterized* chamber experiments with PM measurements *at ambient concentration levels*.

- More funding for well-characterized chamber experiments for PM mechanism evaluation is needed

Recommended Research – Environmental Chamber Database

- Need to take advantage of unique capabilities of UCR EPA chamber for PM and SOA Mechanism evaluation

  - Allows well-characterized experiments at ambient levels

  - New advanced instrumentation obtained from a Keck grant

  - Current support level insufficient to maintain existing facility

- Methods needed to improve sensitivity of chamber experiments to effects of oxidation products on reactivity

- Chamber data are still not adequate to evaluate model predictions of temperature effects on pollutant formation

- Mechanisms still highly uncertain for some types of compounds

  - Examples include amines, most halogenated compounds

Recommended Research –
Updated Reactivity Scale

- The work of the RRWG towards developing improved reactivity assessment methods needs to be completed.

- **At a minimum, the scenarios used in the current reactivity calculations are way out of date and need to be updated**.
  - Derivation of existing scenarios is poorly documented
  - The scenarios represent pollutant levels much higher than current situation (the LA Scenario gives $O3^{max}>500$ ppb!)
  - Methods exist to derive box model scenarios from grid calculations

- The base ROG mixture needs to be updated based on current emissions and measurements. (Also needed for updated lumped mechanisms)

- Failure to use best scenarios and methods will eventually cause loss of credibility of reactivity-based regulatory programs