

Development of the Updated SAPRC Chemical Mechanism

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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 ($\Delta O_3 / \Delta \text{VOC}$) 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)

- Mechanism generation system 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 Mechanism Generation System

- Generates mechanisms for reactions of a wide variety of non-aromatic organics with OH, O₃, NO₃, O³P and by photolysis
- Measured rate constants (or rate constant ratios) are used where available. Estimation methods are used otherwise.
- Estimation Methods
 - Structure-reactivity estimates for OH, O₃, and NO₃ reactions
 - Nitrate yields from RO₂+NO based on available (limited) data
 - Alkoxy radical estimates based (primarily) on correlations between rate constants and heats of reaction.
 - Other estimates based on extrapolations from known reactions or adjustments to fit chamber data
- Limitations
 - Not applicable or reliable for all types of compounds
 - Currently only estimates reactions in presence of NO_x

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 where possible
- 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

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 → HNO ₃ + M (1 atm, 298K)	+19%
Generic peroxy + HO ₂ → Generic hydroperoxides + O ₂	-47%
NO ₂ + hv → NO + O(³ P)	+8% *
Lumped higher ketone (PROD2) photolysis	-75% *
Methyl glyoxal photolysis	42% *
Methacrolein and lumped C ₅ isoprene product photolysis	45% *

* Solar light

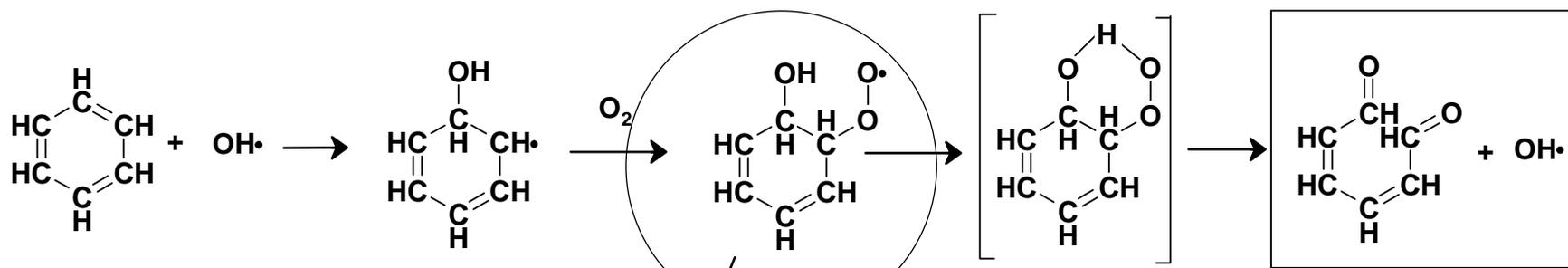
Mechanism Updates -- Mechanism Generation System

- Assigned VOC + OH, O₃, NO₃, and O³P 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, O₃, and NO₃ 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

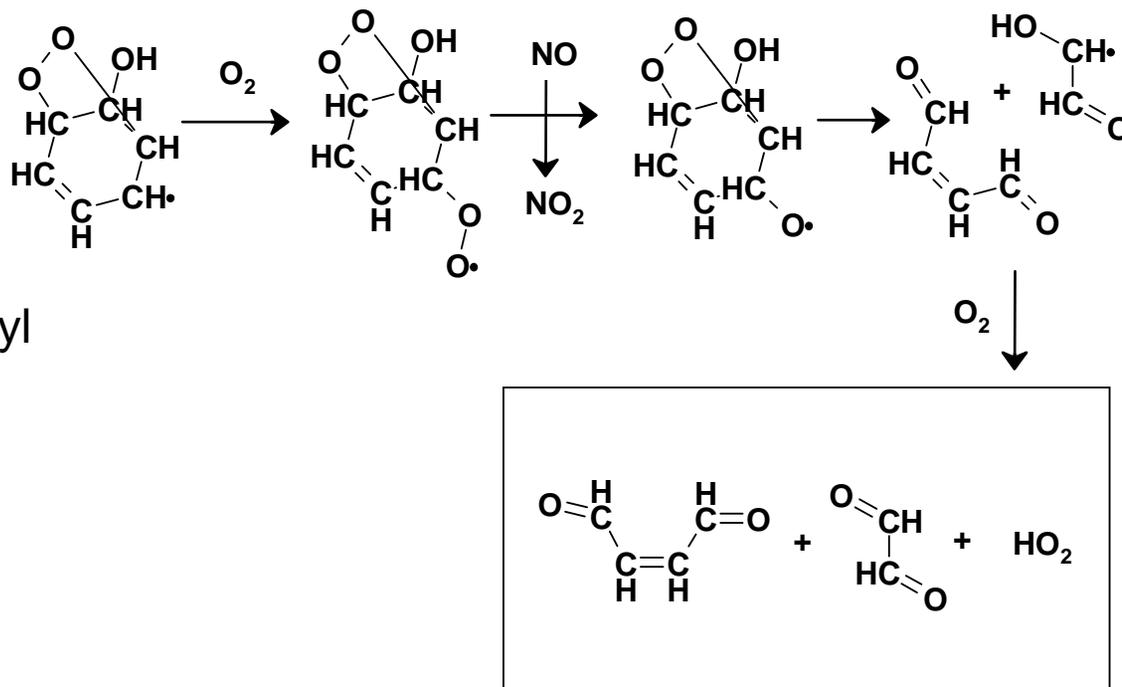
- SAPRC-99 uses parameterized species with adjusted yields and photolysis rates for uncharacterized ring opening products.
 - Adjusted to fit aromatic - NO_x experiments.
 - Model gives poor fits to effects of adding CO to aromatic - NO_x experiments and to measurements of direct reactivity
- SAPRC-07 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

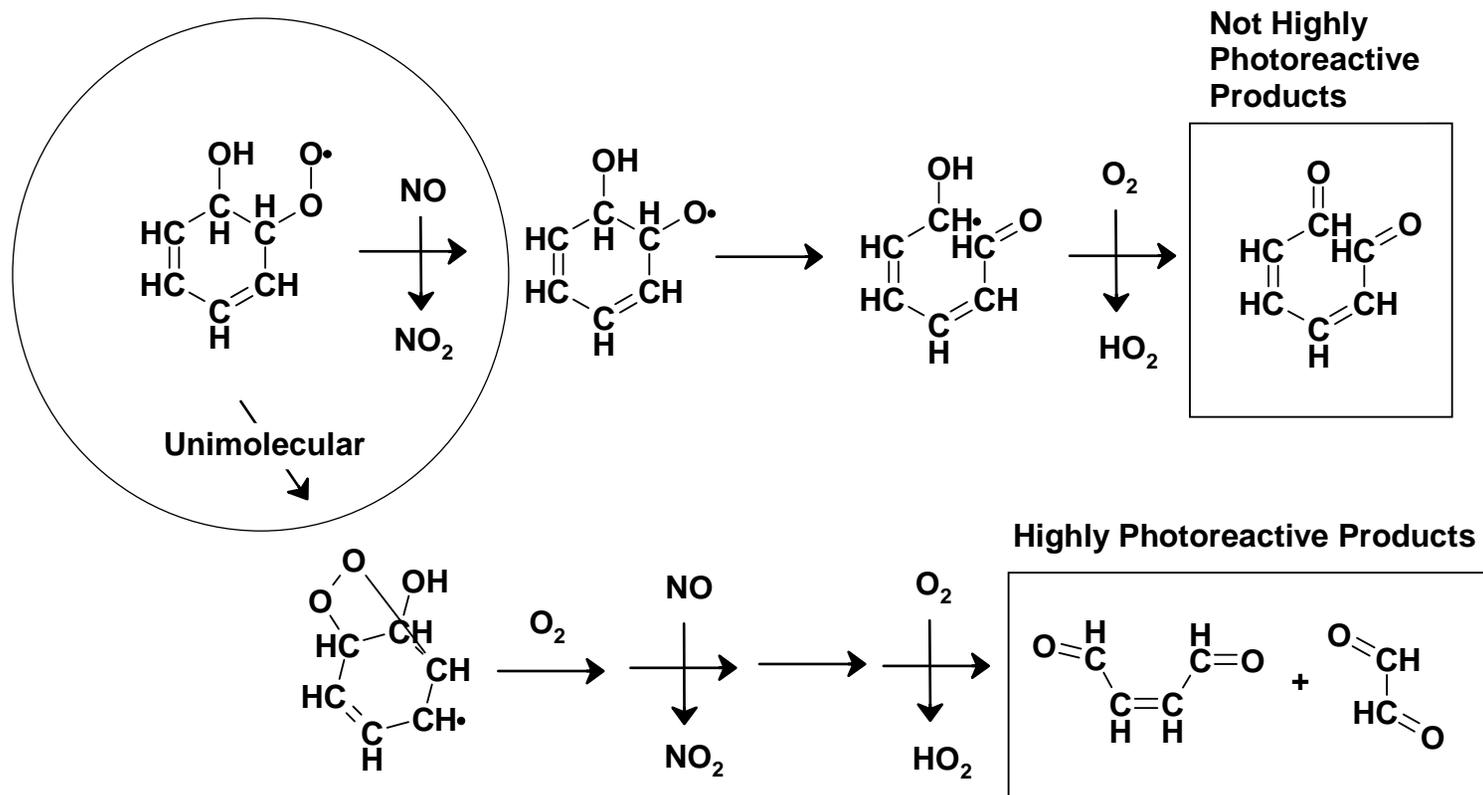


Note:

- Branching ratios do not 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 no NO to NO_2 conversions



Alternative Ring Fragmentation Mechanism



This mechanism predicts that the yields of α -dicarbonyls and the highly photoreactive unsaturated dicarbonyl products will depend on NO_x levels. This is not consistent with product yield or chamber data.

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.

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

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

- Number of distinct VOC mechanisms increased from 585 to 739 (a 27% 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 (also added CH₃I)

Evaluation Against Chamber Experiments

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

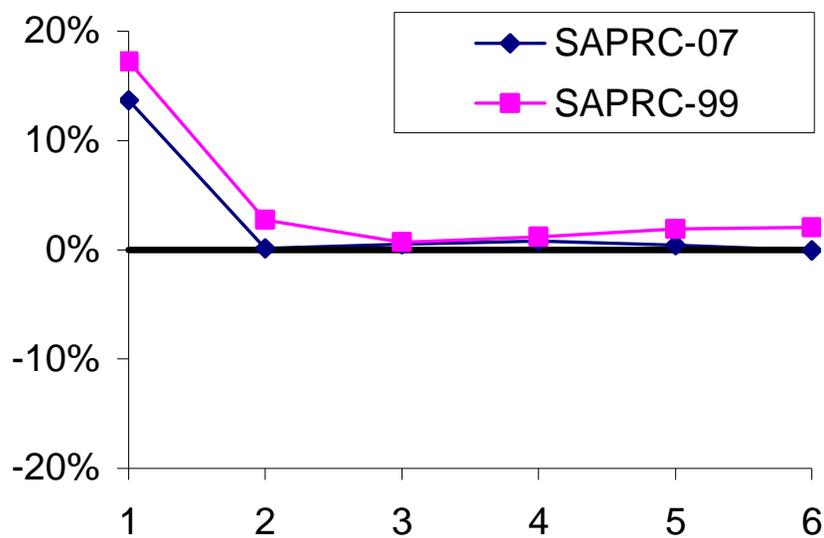
Number of Chambers	UCR	TVA	UNC
Indoor - Blacklight or mixed	4	1	
Indoor - Arc light	4		
Outdoor	1		1

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

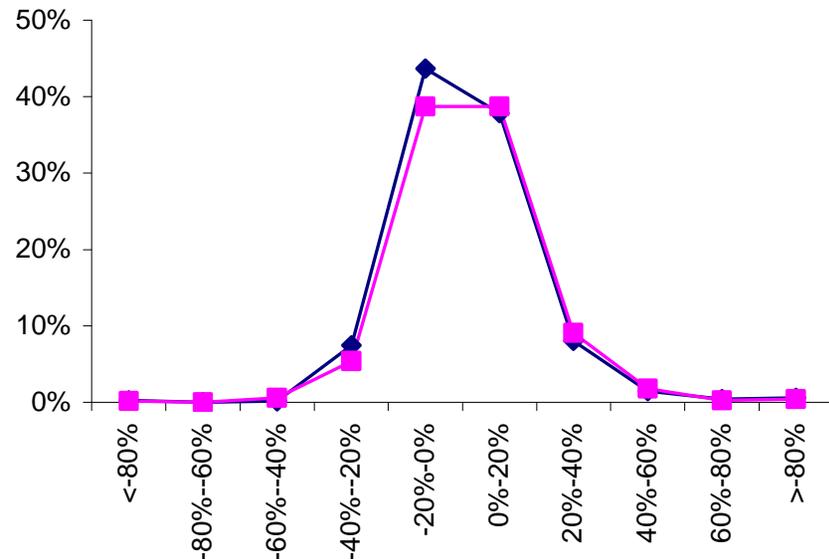
- Performance simulating chamber data comparable to SAPRC99 (somewhat better in some cases, not quite as good in others)

Evaluation Results: Model Errors for All Single VOC Experiments

Average Model Error
vs Hour of Run

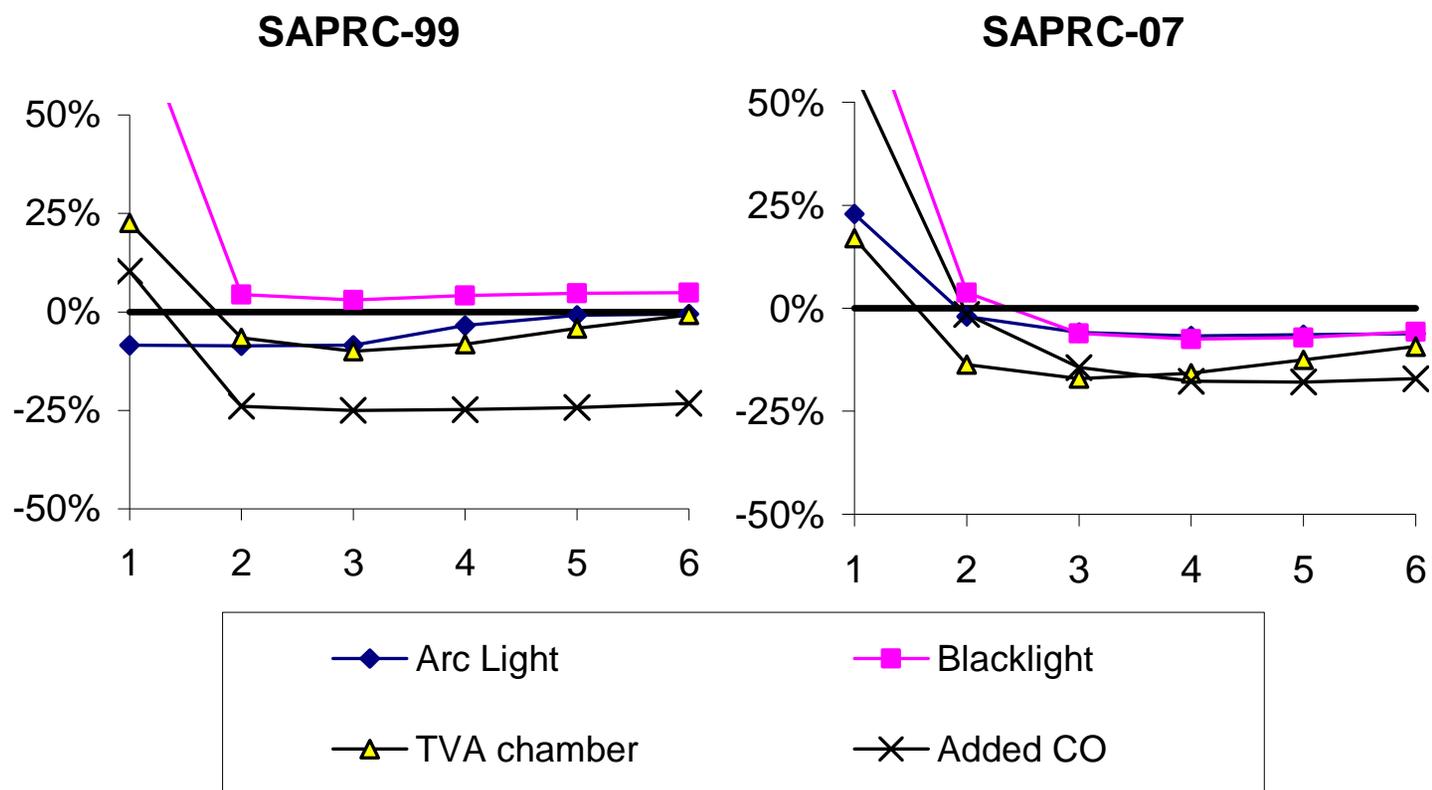


Final Model Error Distribution
(fraction of runs vs error range)



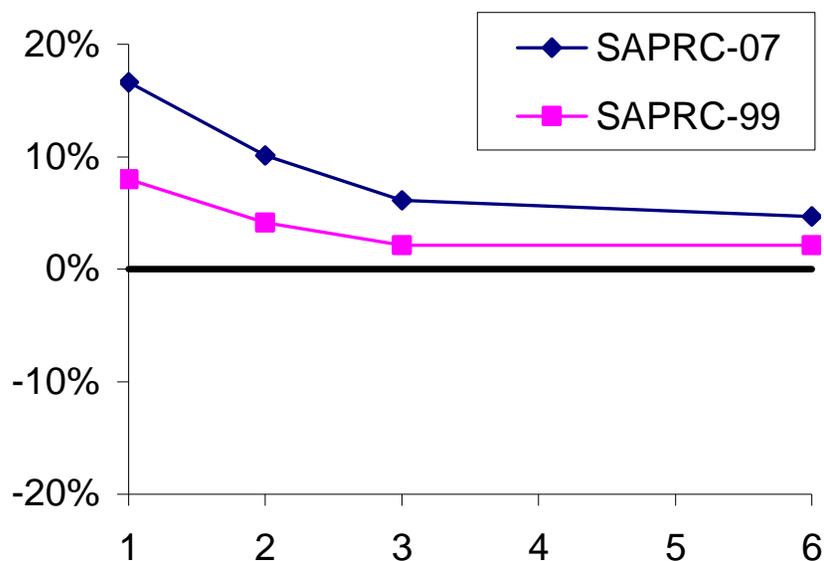
Evaluation Results: Model Errors for m-Xylene Experiments

Average model error vs. hour of run

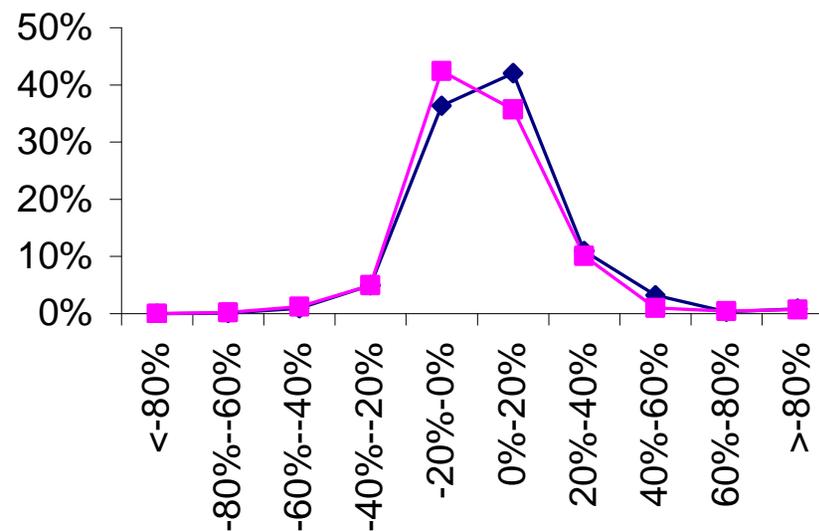


Evaluation Results: Model Errors for All Mixture Experiments

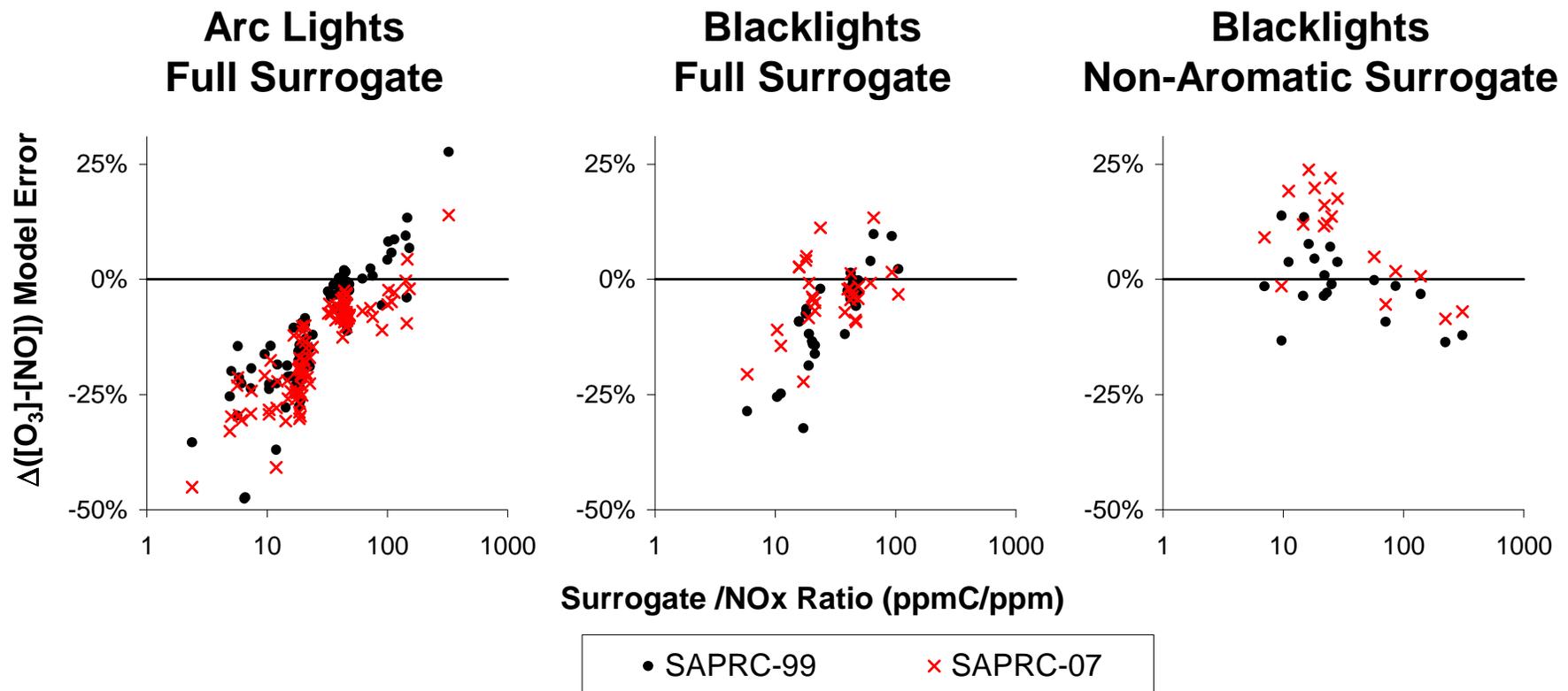
Average Model Error
vs Hour of Run



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



Model Performance Simulating UCR-EPA Chamber Surrogate - NOx Runs

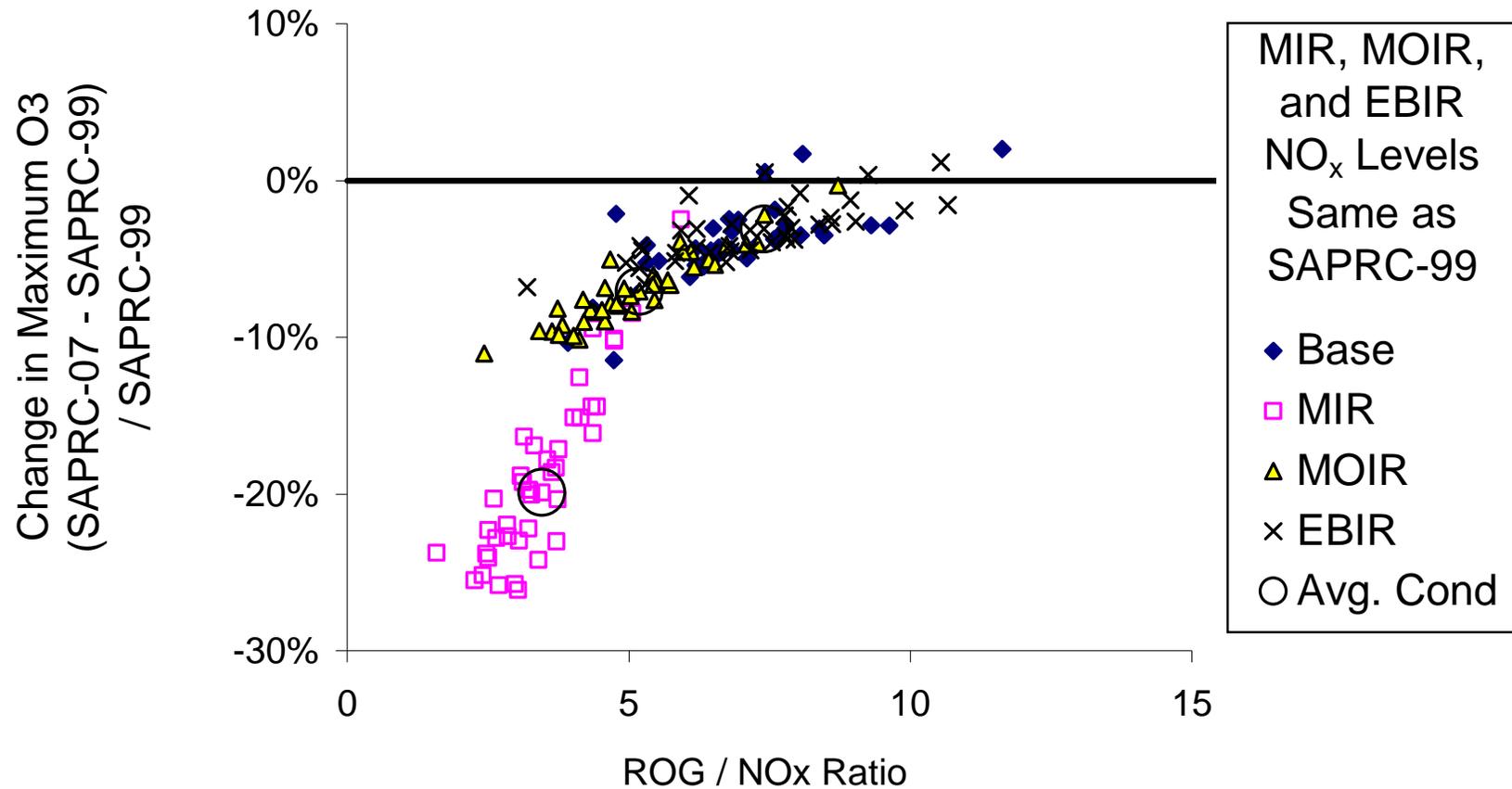


- Problem of O₃ underprediction at low ROG/NO_x still exists

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.
- Used as base case in reactivity calculations

Effect of Update on Calculated Ozone in the Box Model Reactivity Scenarios



Condensed SAPRC-07

- Condensed versions of SAPRC-07 have been developed
 - Up to about half the number of species and reactions as uncondensed SAPRC-07. Comparable in size to CB05.
 - Essentially same O₃ predictions for wide range of conditions.
 - Changes small for PANs, OH radicals, most other species.
 - Effects on H₂O₂ usually less than 10%, but depends on which peroxy radical lumping method is used.
- Chemical validity is directly traceable to detailed SAPRC-07
 - Based on detailed mechanisms for hundreds of VOCs
 - Can be readily modified if the base ROG mixture used to derive the lumped species parameters is changed
 - Can be readily updated if the underlying detailed mechanism is updated, by re-applying the condensation procedures.

Condensation Approaches Employed

Two alternative peroxy radical representations:

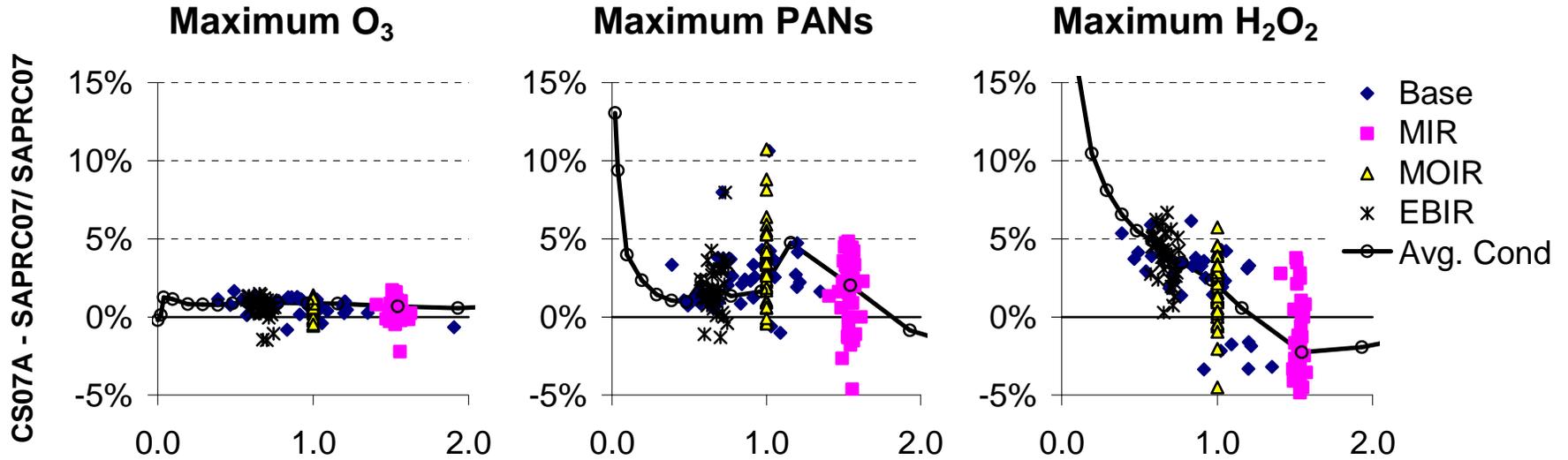
- A. Use representation in SAPRC-99 (and CB05) (CS07A)
- B. Retain SAPRC-07 peroxy representation (CS07B)

Other Condensations

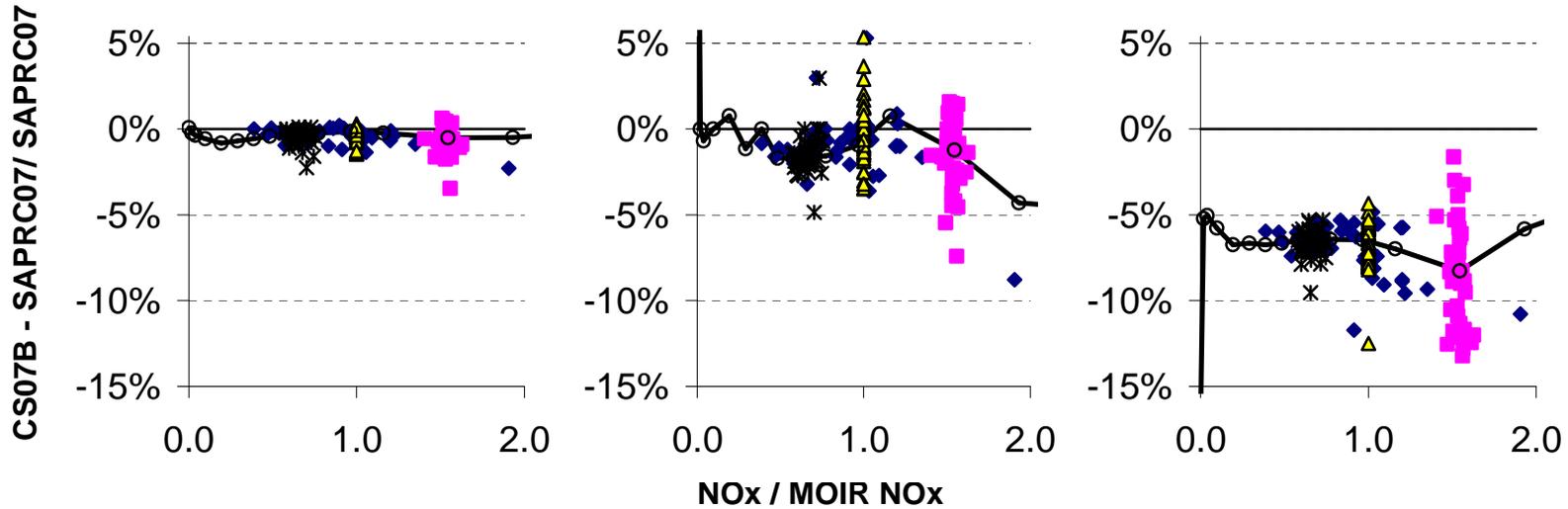
1. Lump low reactivity products and other minor condensations
2. Lump Higher PANs with PAN2 (but PAN still explicit)
3. Use 1-product isoprene mechanism
4. Simplify aromatics mechanisms
5. Simplify chlorine mechanism
6. Reduce number of lumped alkane species for ambient mixtures

Results for Reactivity Scenarios

Condensed CS07A vs SAPRC-07



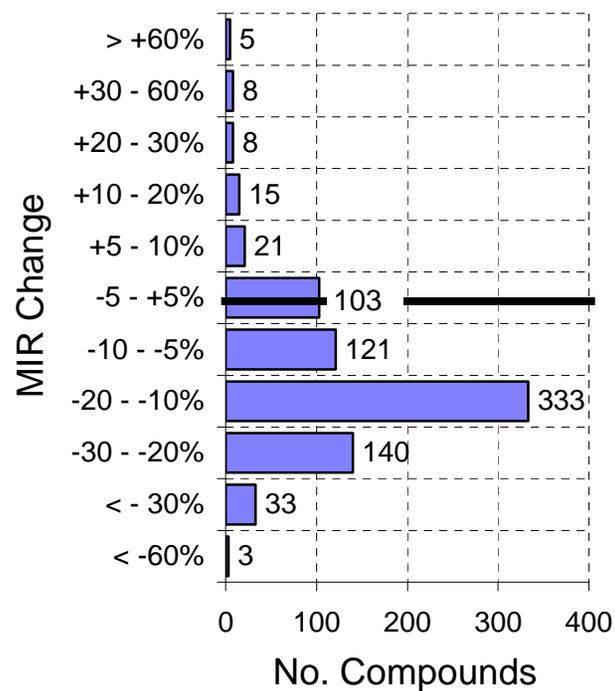
Condensed CS07B vs SAPRC-07



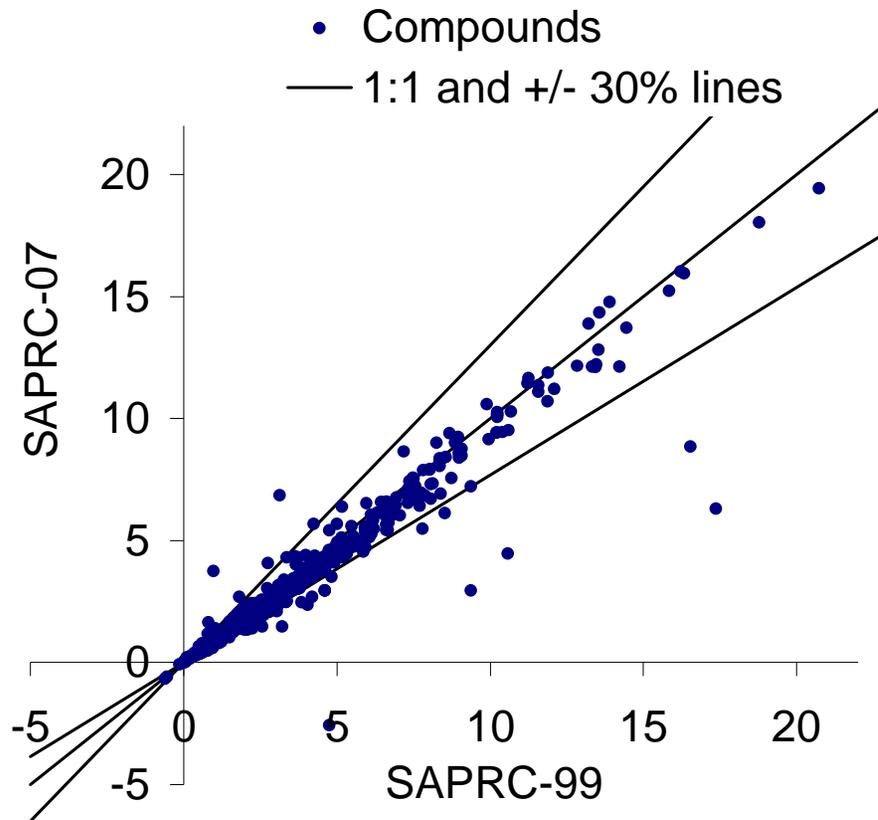
Calculation of Updated Reactivity Scales

- 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 1135 Types of VOCs, including
 - 739 VOCs represented explicitly
 - 320 VOCs represented by the “Lumped molecule” method
 - 76 Complex mixtures (e.g., exhausts, petroleum distillates)
- This includes 358 types of VOCs not in 2002 SAPRC-99 scales.
 - New compounds of interest or found in inventories
 - 24 Complex hydrocarbon mixtures derived to represent the 24 hydrocarbon “bins” used in CARB regulations

Changes in MIR Ozone Reactivity Values



Base ROG Mixture: -5% Change



MIR Incremental Reactivity
(gm O₃ / gm VOC)

VOCs with Large MIR Changes

Compound	Approx. MIR [*]		Reason for change
	Old	New	
3-Methoxy-1-butanol	1.0	3.8	Rate constant error corrected
2-Amino-2-methyl-1-propanol	4.8	-2.7	New data and mechanisms for amines
2-(Cloromethyl)-3-chloropropene	3.1	6.8	Chloronated ketones believed to be more photoreactive
1,2-Dibromoethane	0.05	0.1	Approximate representation of Br compounds changed

* grams O₃ / gram VOC

VOCs with Large MIR Changes (continued)

Compound	Approx. MIR [*]		Reason for change
	Old	New	
1,2-Dichloroethane	0.1	0.2	Chlorinated aldehydes believed to be more photoreactive
Trans-1,2-dichloroethene	0.8	1.6	Chlorinated aldehydes believed to be more photoreactive
Dimethyl amine	9.4	2.9	New data and mechanisms for amines
Mesityl oxide (2-methyl-2-penten-4-one)	17.4	6.3	Now represented by the lumped isoprene product. SAPRC-99 generated mechanism not reasonable.

* grams O₃ / gram VOC

Recommended research

- **Base Mechanism**
 - Reasons for model performance problems in simulating existing chamber data need to be elucidated
 - Uncertainty in OH + NO₂ rate constant needs to be reduced
 - Uncertainty analysis and process analysis may be useful, but new approaches are needed.
- **Aromatics Mechanisms**
 - Although improved, aromatics mechanisms are still highly simplified and not consistent with all current laboratory data
 - Improvements will probably require breakthroughs in both measurement methods and theory
 - Systematic examination of effects of alternative mechanisms may be useful to assess effects of uncertainties on models

Recommended research (continued)

- **Mechanism Generation System**
 - The many estimation methods need to be updated, expanded and documented in the peer-reviewed literature
 - Predictions should be compared with those in the MCM
 - Methods to estimate volatility needs to be implemented to serve as a basis for lumping for SOA models
- **Adaptation for PM Modeling**
 - Models for SOA formation need to be improved
 - Model species need to be added to represent low volatility SOA precursors
 - Well characterized chamber experiments with PM data *at ambient concentration levels* needed to evaluate mechanism

Recommended research (concluded)

- **Environmental Chamber Database**
 - Need to take advantage of unique capabilities of UCR EPA chamber for PM and SOA Mechanism evaluation
 - Methods needed to improve sensitivity of chamber experiments to effects of oxidation products on reactivity
 - Mechanisms still uncertain for some types of compounds
- **Reactivity Scale Calculation**
 - The work of the RRWG towards developing improved reactivity assessment methods needs to be completed.
 - **At a minimum, the scenarios used for MIR calculations are way out of date and need to be updated.**
 - The base ROG mixture is also out-of-date and needs to be updated

Related Anticipated CARB Research

- **Base Mechanism**
 - Ongoing CARB contract could cover development of version of SAPRC-07 with lower $k(\text{OH} + \text{NO}_2)$ for sensitivity studies
- **Aromatic Mechanisms**
 - Ongoing CARB Contract 07-730 calls for some work on developing improved aromatic mechanisms
- **Mechanism Generation System**
 - No work in this area is presently funded
- **Adaptation for PM Modeling**
 - CARB recently approved a project to adapt SAPRC-07 for PM modeling (David Cocker, co-investigator)

Related Anticipated CARB Research (continued)

- **Environmental Chamber Database**
 - Project to adapt SAPRC-07 for PM modeling includes extensive set of SOA experiments in UCR EPA chamber
 - Methods to improve chamber reactivity experiments are being developed for CARB Coatings reactivity project
 - CARB Coatings project will cover reactivity experiments for additional classes of compounds
- **Reactivity Scale Calculation**
 - The CARB is funding a project to update the base ROG
 - The EPA may be funding improving the box model scenarios used to calculate MIR
 - Work on improving the calculation methodology is presently unfunded