DEVELOPMENT AND EVALUATION OF THE
SAPRC-99 CHEMICAL MECHANISM

OUTLINE

DESCRIPTION OF MECHANISM
MECHANISM GENERATION SYSTEM
ESTIMATION METHODS
MECHANISM EVALUATION
LUMPED MECHANISM FOR AIRSHED MODELS
UPDATED VOC REACTIVITY SCALE
UNCERTAINTY ASSIGNMENTS
COMPONENTS OF MECHANISM

BASE MECHANISM REPRESENTS INORGANICS AND COMMON ORGANIC PRODUCTS

~400 TYPES OF VOCs CAN BE REPRESENTED EXPPLICITLY OR IN MIXTURES

“LUMPED MOLECULE” ASSIGNMENTS MADE FOR ~200 OTHER VOCs CLASSES IN EMISSIONS INVENTORIES.

A MECHANISM GENERATION SYSTEM IS USED TO DERIVE MECHANISMS FOR MOST VOCs

- EXPLICIT MECHANISMS GENERATED FOR REACTIONS IN NOx, GIVEN THE VOC STRUCTURE
- MEASURED RATE CONSTANTS OR YIELDS USED WHEN KNOWN, ESTIMATES WHEN NEEDED.
- “LUMPING RULES” USED TO DETERMINE THE REPRESENTATION WITH THE BASE MECHANISM

PARAMETERIZED MECHANISMS (ADJUSTED TO FIT CHAMBER DATA) ARE USED FOR AROMATICS, TERPENES, AND A FEW OTHER VOCs

A CONDENSED MECHANISM IS DEVELOPED FOR USE IN AIRSHED MODELS OR TO REPRESENT THE “BASE CASE” IN REACTIVITY SIMULATIONS.

MECHANISM USED TO UPDATE MIR AND OTHER REACTIVITY SCALES

UNCERTAINTY CLASSIFICATIONS MADE FOR ALL VOC CLASSES WHOSE REACTIVITIES CAN BE MODELED.
BASE MECHANISM

STATISTICS

- 187 REACTIONS, 54 REACTIVE SPECIES (AT LEAST 6 CAN BE IN STEADY STATE), 11 NON-REACTING PRODUCT OR COUNTER SPECIES

INORGANIC REACTIONS

- ALL RATE CONSTANTS UPDATED
- INCLUDES SO₂ BUT NOT HALOGEN SPECIES REACTIONS.

ORGANIC PRODUCTS

- ALL RATE CONSTANTS UPDATED
- ALL C₁ PRODUCTS ARE NOW REPRESENTED EXPLICITLY (HCHO, MEOH, COOH, HCOOH)
- ISOPRENE PRODUCTS (4-PRODUCT MECHANISM) ADDED.
- NEW SPECIES (PROD2) ADDED TO REPRESENT MORE REACTIVE OXYGENATE PRODUCTS PREVIOUSLY REPRESENTED BY MEK
- GPAN [HC(O)C(O)OONO₂] NOW LUMPED

RADICAL SPECIES

- METHYL PEROXY, ACETYL PEROXY RADICALS NOW REPRESENTED SEPARATELY
- HIGHER PEROXY AND OTHER RADICALS STILL REPRESENTED USING SAPRC-90 “OPERATORS”
- OTHER ORGANIC RADICALS REPRESENTED BY PRODUCTS THEY FORM IN PRESENCE OF NOₓ
# Reactive Organic Product Model Species

<table>
<thead>
<tr>
<th>Category</th>
<th>Species</th>
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</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>Lumped C3+ Aldehydes</td>
<td>Acetone</td>
</tr>
<tr>
<td>Ketones, etc with kOH &lt; $5 \times 10^{-12}$ cm$^3$ molec$^{-2}$ sec$^{-1}$</td>
<td>Ketones, etc with kOH &gt; $5 \times 10^{-12}$ cm$^3$ molec$^{-2}$ sec$^{-1}$</td>
</tr>
<tr>
<td>Methanol</td>
<td>Methyl Hydroperoxide</td>
</tr>
<tr>
<td>Higher Organic Hydroperoxides</td>
<td></td>
</tr>
<tr>
<td>Lumped Organic Nitrates</td>
<td>Peroxy Acetyl Nitrate</td>
</tr>
<tr>
<td>PPN And Other Higher Alkyl PAN Analogues</td>
<td>PAN Analogues Formed From Aromatic Aldehydes</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>Methyl Vinyl Ketone</td>
</tr>
<tr>
<td>Other Isoprene Products</td>
<td>Methacrolein PAN Analogue</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>Methyl Glyoxal</td>
</tr>
<tr>
<td>Biacetyl</td>
<td>Non-Photoreactive Aromatic Fragmentation Products</td>
</tr>
<tr>
<td>Photoreactive Aromatic Fragmentation Products ($\alpha$-Dicarbonyl Spectrum)</td>
<td>Photoreactive Aromatic Fragmentation Products (Acrolein Spectrum)</td>
</tr>
<tr>
<td>Phenol</td>
<td>Cresols</td>
</tr>
<tr>
<td>Nitrophenols</td>
<td>Aromatic Aldehydes</td>
</tr>
</tbody>
</table>
MECHANISM GENERATION AND ESTIMATION SYSTEM

GENERATES MECHANISMS FOR VOCs CONTAINING FOLLOWING GROUPS:

<table>
<thead>
<tr>
<th>CH₃⁻</th>
<th>-CH₂⁻</th>
<th>&gt;CH⁻</th>
<th>&gt;CH&lt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0H⁻</td>
<td>-OH</td>
<td>-CHO</td>
<td>-CO⁻</td>
</tr>
<tr>
<td>=CH₂⁻</td>
<td>=CH⁻</td>
<td>=C&lt;</td>
<td></td>
</tr>
</tbody>
</table>

SYSTEM CURRENTLY CANNOT PROCESS VOCs WITH MORE THAN ONE DOUBLE BOND OR RING OR THAT FORM RADICALS WHOSE ΔHᶠ CANNOT BE ESTIMATED

GENERATES REACTIONS AND ESTIMATES RATE CONSTANTS OR BRANCHING RATIOS FOR

- VOC + OH
- ALKENE + O₃
- ALKENE + NO₃
- ALKENE + O³P
- ALDEHYDE + NO₃
- ALDEHYDE + hν → R· + HCO·
- KETONE + hν → R· + R’CO·
- RONO₂ + hν → RO· + NO₂
- R· + O₂
- RO₂ + NO → yN RONO₂ + (1-yN) RO· + NO₂
- FULL VARIETY OF KNOWN ALKOXY RADICAL REACTIONS
- CRIGIEE BIRADICAL REACTIONS
EXAMPLES OF ESTIMATION METHODS EMPLOYED

VOC + OH RATE CONSTANTS, BRANCHING RATIOS

- GROUP-ADDITIVITY METHOD OF ATKINSON AS UPDATED BY KWOK AND ATKINSON
- PRESENT SYSTEM ASSUMES ALL OH + ALKENE REACTION IS ADDITION TO DOUBLE BOND

VOC + O_3 RATE CONSTANTS, BRANCHING RATIOS

- REACTIONS AT CH_2=CH-, CH_2=CH<, -CH=CH-, -CH=C<, AND >C=C< ASSUMED TO HAVE SAME RATE CONSTANTS AND BRANCHING RATIOS
- ESTIMATES FOR EACH GROUP TYPE DERIVED USING DATA FOR REPRESENTATIVE COMPOUNDS.
- RATE CONSTANTS NOT WELL ESTIMATED, BUT ARE KNOWN FOR MOST VOCs OF INTEREST

ALKENE + NO_3 RATE CONSTANTS, BRANCHING

- REACTIONS AT CH_2=CH-, CH_2=CH<, -CH=CH-, -CH=C<, AND >C=C< ASSUMED TO HAVE SAME RATE CONSTANTS AND BRANCHING RATIOS
- 100% ADDITION TO LEAST SUBSTITUTED END ASSUMED FOR UNSYMmetrical GROUPS

ALDEHYDE + NO_3 RATE CONSTANTS

- BASED ON NO_3 + ACETALDEHYDE WITH SUBSTITUENT CORRECTION FACTORS
EXAMPLES OF ESTIMATION METHODS EMPLOYED (CONTINUED)

ALDEHYDE PHOTOLYSIS RATES, BRANCHING
- Photolysis rates for all C3+ aldehydes assumed to be same as propionaldehyde
- R· + HCO· assumed to be only reaction
- Quantum yield based on propionaldehyde

ALKYL KETONE PHOTOLYSIS RATES, BRANCHING
- Absorption cross sections of MEK used
- Overall quantum yields derived from modeling ketone - NOx and ketone reactivity chamber data.
- Results indicate quantum yields decline with carbon number
- R· + R’CO· assumed to be only reaction
- Most energetically favored route assumed to dominate
ADJUSTED AND ESTIMATED OVERALL QUANTUM YIELDS FOR C₄₊ ALKYL KETONES

- Adjusted to Fit 2-Butanone Chamber Data
- Adjusted to Fit 2-Pentanone
- Adjusted to Fit 4-Methyl-2-Pentanone
- Adjusted to Fit 2-Heptanone

SAPRC-99 Estimate
SAPRC-90 Estimate
EXAMPLES OF ESTIMATION METHODS EMPLOYED (CONTINUED)

NITRATE YIELDS FROM RO$_2$+NO: SECONDARY ALKYL PEROXY RADICALS

INCREASES WITH SIZE OF MOLECULE AND REDUCES O$_3$ REACTIVITIES FOR LARGER MOLECULES

NEW DATA FROM ATKINSON’S LAB INDICATES PREVIOUS C$_8$+ NITRATE YIELDS ARE TOO HIGH

SECONDARY RO2 NITRATE YIELDS vs.CARBON NO.

- New or Corrected Data
- SAPRC-99 Est’d
- Old Data
- SAPRC-90 Est’d

NO LONGER NECESSARY TO ASSUME NO NITRATE FORMATION FROM OH-SUBSTITUTED RO$_2$’S TO FIT C$_8$+ N-ALKANE CHAMBER DATA
EFFECTS OF SUBSTITUENTS ON NITRATE YIELDS FROM RO$_2$+NO

ALMOST NO EXPERIMENTAL DATA ON NITRATE YIELDS FROM SUBSTITUTED RO$_2$ RADICALS

BUT NITRATE YIELDS CAN BE DERIVED BY ADJUSTING SO MODEL SIMULATIONS FIT VOC REACTIVITY CHAMBER DATA

SUBSTITUENTS TEND TO REDUCE NITRATE YIELDS RELATIVE TO SECONDARY ALKYL RO$_2$ RADICALS

![Graph showing the relationship between estimated secondary RO$_2$ nitrate yields and predicted nitrate yields.](image)

NO PREDICTABLE DEPENDENCE OF TYPE OF SUBSTITUENT ON AMOUNT OF YIELD REDUCTION
NITRATE YIELD ESTIMATES FOR MECHANISM

SECONDARY ALKYL PEROXY RADICALS
• USE FIT TO DATA AS FUNCTION OF CARBON NUMBER, TEMPERATURE AND PRESSURE

PRIMARY AND TERTIARY ALKYL PEROXY RADICALS AND SUBSTITUTED PEROXY RADICALS
• USE ESTIMATES FOR SECONDARY RO₂’S WITH CARBON NUMBER REDUCED BY 1.5

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![Graph showing nitrate yield estimates for various compounds.](image-url)
ESTIMATES FOR ALKOXY RADICAL REACTIONS

USE $K = A \cdot \exp(-E_A / RT)$, WITH SEPARATE ESTIMATES FOR $A$ AND $E_A$.

REACTION WITH $O_2$

- ETHOXY A FACTOR ASSUMED FOR PRIMARY RO·;
  ISOPROPYOXY FOR SECONDARY RO·.

- ACTIVATION ENERGY ($E_A$) ESTIMATED BY CORRELATION BETWEEN $E_A$ AND $\Delta H_R$.

- IF CORRELATION GIVES LOW OR NEGATIVE $E_A$, MINIMUM OF 0.6 KCAL/MOLE ASSUMED.

1,4-H SHIFT ISOMERIZATION

- BALDWIN ET AL (1977) ESTIMATED A FACTOR USED.

- $E_A$ ESTIMATED USING CORRELATION BETWEEN BREAKING C-H BOND DISSOCIATION ENERGY AND $E_A$ FOR $CH_3O\cdot + RH$ AND ALKOXY ISOMERIZATIONS.

- SUBSTITUENT CORRECTION FACTORS ESTIMATED TO BE (SUBST. FACTOR FOR OH ABSTRACTION)$^{1.5}$.
ESTIMATED FOR ALKOXY RADICAL REACTIONS
(CONTINUED)

β-SCISSION DECOMPOSITIONS

• A factor estimates of Atkinson used

• $E_A$ estimated using $E_A \approx E_A A + E_A B \Delta H_R$, where

  • $E_A B \approx 0.44$ is derived from data for reactions forming $CH_3^\cdot$ and is assumed to be the same for all reactions

  • $E_A A$ is assumed to depend only on the radical formed, and is derived for each based on available data

• Product branching ratios for large variety of VOCs used to derive $E_A A$ for various types of reactions

• Estimated $E_A$ for many reactions are negative. Minimum $E_A$ of 0.75 KCAL/MOLE used

• Estimates are highly uncertain for reactions forming substituted radicals

• Correlation between ionization potential and $E_A A$ does not work in all cases

ESTER REARRANGEMENT

• $RCH(O\cdot)-O-CO-R' \rightarrow RCO\cdot + R'C(O)OH$

• Rate constant estimated so it dominates for $CH_3CH(O\cdot)-O-CO-CH_3$ yet isomerization of $CH_3CH_2CH(O\cdot)-O-CO-CH_3$ occurs, for model to fit butyl acetate chamber data
EXAMPLES OF $E_A A$ PARAMETERS FOR ESTIMATING ACTIVATION ENERGIES FOR $\beta$-SCISSION REACTIONS, AS A FUNCTION OF RADICAL FORMED

- Filled symbol, + or X:
  - Derived from data

- Open symbol:
  - Derived assuming linear relation between IP and $E_A A$ for reactions forming radicals of the same type, using slope shown.
CRIGIEE BIRADICAL REACTIONS
(FORMED FROM O₃ + ALKENES AND ALKYNES)

REACTIONS OF EXCITED BIRADICALS ARE ASSUMED TO BE INDEPENDENT OF REACTION FORMING THEM

CH₂OO BIRADICALS
• BRANCHING RATIOS RECOMMENDED BY ATKINSON

RCHOO BIRADICALS
• APPARENT INCONSISTENCY BETWEEN LABORATORY OH YIELDS AND CHAMBER DATA
• PUBLISHED OH YIELDS FROM O₃ + 1-ALKENES IN ABSENCE OF NOₓ SUGGEST OH YIELD IS ~55% FOR ALL RCHOO’s
  • 1-BUTENE - NOₓ CHAMBER DATA CANNOT BE FIT BY MODEL UNLESS OH YIELD REDUCED TO ~5%
  • 1-HEXENE - NOₓ CHAMBER DATA CANNOT BE FIT BY MODEL UNLESS OH YIELD REDUCED TO ~0%
• MECHANISM ASSUMES OH YIELDS DECLINE WITH SIZE OF BIRADICAL, TO BE CONSISTENT WITH CHAMBER DATA

RR’COO BIRADICALS
• ASSUMED TO REACT PRIMARILY TO FORM OH, E.G.
  >CHC(OO)- → >C=C(OOH)- → >C=C(O·)- + OH
• THIS MECHANISM IS CONSISTENT WITH LABORATORY OH YIELDS AND CHAMBER DATA FOR INTERNAL ALKENES.
MECHANISMS DERIVED BY ADDING NON-GENERATED REACTIONS TO MECHANISM GENERATION SYSTEM

ISOPRENE AND ISOPRENE PRODUCTS
- Added reactions based on mechanism of Carter and Atkinson (1996)
- Isoprene products represented using “four product” model of Carter (1996)

ACROLEIN AND CROTONALDEHYDE
- Added reactions derived by analogy with those for isoprene products
- Acrolein photolysis quantum yield adjusted to fit chamber data

ALKYNES
- Initial OH, O₃ reactions added to system. Subsequent reactions could be generated
VOCs REPRESENTED USING
ASSIGNED OR PARAMETERIZED MECHANISMS

THE MECHANISM GENERATION SYSTEM WAS NOT
USED FOR THE FOLLOWING CLASSES OF VOCs

BENZENE AND ALKYL BENZENES

- REACTIONS FORMING PHENOLS, AROMATIC
  ALDEHYDES SAME AS PREVIOUS

- RING FRAGMENTATION PRODUCTS:
  - GLYOXAL, METHYL GLYOXAL, BIACETYL, IN
    OBSERVED OR ESTIMATED YIELDS
  - NON-PHOTOREACTIVE DICARBONYLS (E.G.,
    \( \text{CH}_3\text{C(O)CH=CH-CH=CH-C(O)-CH}_3 \))
  - TWO PHOTOREACTIVE DICARBONYL PRODUCTS
    WITH YIELDS ADJUSTED TO FIT AROMATIC - NO\textsubscript{x}
    CHAMBER RUNS WITH DIFFERING LIGHTS

- SEPARATE MECHANISMS DERIVED FOR BENZENE,
  TOLUENE, ETHYLBENZENE, ALL XYLENE AND
  TRIMETHYLBENZENE ISOMERS

- P-XYLENE AND 1,2,4-TRIMETHYL BENZENE DATA
  FIT BY LOWER PHOTOREACTIVE PRODUCT YIELDS.

- OTHER ALKYL BENZENES REPRESENTED BY
  CLOSEST ANALOGUE (“LUMPED MOLECULE”)

VOCs REPRESENTED USING ASSIGNED OR PARAMETERIZED MECHANISMS (CONTINUED)

NAPHTHALENES AND TETRALIN
- PARAMETERIZED MECHANISM ADJUSTED TO FIT BLACKLIGHT CHAMBER DATA
- NECESSARY TO ASSUME FORMATION OF PAN-PRECURSOR-LIKE PRODUCTS TO FIT DATA

TERPENES
- ESTIMATED SIMPLIFIED MECHANISMS WITH SOME ADJUSTMENTS TO FIT CHAMBER DATA
- ESSENTIALLY SAME MECHANISMS AS SAPRC-93

OTHER VOCs WITH REACTIVITY DATA (STYRENE, NMP, AROMATIC ISOCYANATES)
- ESTIMATED OR PARAMETERIZED MECHANISMS WITH SOME ADJUSTMENTS TO FIT CHAMBER DATA AS DESCRIBED IN VARIOUS REPORTS
- SOME PARAMETERS HAD TO BE REOPTIMIZED TO FIT CHAMBER DATA WITH NEW BASE MECHANISM

AMINES AND HALOGENATED COMPOUNDS
- CRUDE “PLACEHOLDER” MECHANISMS USED TO GIVE APPROXIMATE REPRESENTATIONS FOR VOCs WITH KNOWN kOH’s.
EVALUATION OF MECHANISM AGAINST CHAMBER DATA

MECHANISM TESTED USING CHAMBER RUNS IN UCR CHAMBER DATA BASE THROUGH MID-1999

<table>
<thead>
<tr>
<th>TYPE OF EXPERIMENT</th>
<th>RUNS</th>
<th>VOCs</th>
</tr>
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<tbody>
<tr>
<td>CHARACTERIZATION RUNS</td>
<td>76</td>
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<tr>
<td>VOC - NO(_x) RUNS</td>
<td>484</td>
<td>37</td>
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<tr>
<td>INCREMENTAL REACTIVITY RUNS</td>
<td>447</td>
<td>80</td>
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<tr>
<td>MISCELLANEOUS MIXTURE - NO(_x)</td>
<td>95</td>
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<tr>
<td>“BASE CASE” SURROGATE - NO(_x) MIXTURES WITH REACTIVITY RUNS</td>
<td>561</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>TYPES OF CHAMBERS</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>WALLS</td>
<td>LIGHTS</td>
<td>RH</td>
<td>VOL (L)</td>
<td>RUNs</td>
<td></td>
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<tr>
<td>TEFLOM FILM</td>
<td>BLACKLIGHT</td>
<td>50%</td>
<td>6000</td>
<td>139</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEFLOM FILM</td>
<td>BLACKLIGHT</td>
<td>DRY</td>
<td>3000-6000</td>
<td>1066</td>
<td></td>
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<tr>
<td>TEFLOM FILM</td>
<td>XENON ARC</td>
<td>DRY</td>
<td>2500-5000</td>
<td>323</td>
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<td>TEFLOM FILM</td>
<td>XENON ARC</td>
<td>50%</td>
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<td>TEFLOM FILM</td>
<td>SUNLIGHT</td>
<td>DRY</td>
<td>20,000</td>
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RESULTS OF EVALUATION

DISTRIBUTION PLOT OF MODEL PERFORMANCE SIMULATING $\Delta([O_3]-[NO])$ IN ALL RUNS MODELED

(Number of experiments vs. (calculated - experimental) / experimental)

HOUR IN RUN
- 1
- 2
- 3
- 4
- 5
- 6

(number of experiments)

50% -60%
SUMMARY OF RESULTS OF SIMULATION OF SINGLE VOC OR VOC REACTIVITY RUNS

GENERALLY SATISFACTORY PERFORMANCE OR FITS TO WITHIN UNCERTAINTY OF THE DATA

- MOST VOCs EXCEPT AS INDICATED BELOW
- NITRATE YIELDS AND OTHER ADJUSTMENTS MADE IN A NUMBER OF CASES

NOT TOTALLY SATISFACTORY SIMULATIONS SUGGEST SOME PROBLEMS WITH THE MECHANISMS

- C₄⁺, 1-ALKENES — LOW OH YIELDS IN O₃ REACTION HAD TO BE USED TO FIT DATA
- 3,4-DIETHYL HEXANE — NITRATE YIELDS AND OTHER NEEDED ADJUSTMENTS NOT MADE
- CYCLOHEXANONE — MODEL FITS SOME REACTIVITY EXPERIMENTS BUT NOT ALL
- T-BUTYL ALCOHOL — DATA WOULD BE BETTER FIT IF LOWER kOH USED
- DIMETHYL GLUTARATE (DBE-4) — MODEL FITS SOME REACTIVITY EXPERIMENTS BUT NOT ALL
- β-PINENE — O₃ IN PINENE - NOₓ RUNS OVER-PREDICTED. FAIR FITS TO REACTIVITY RUNS
- BENZENE — SOME RUNS AND EFFECTS ON OH RADICAL LEVELS NOT WELL SIMULATED

HALOGENATED ORGANICS REPRESENTED WITH HIGHLY SIMPLIFIED “PLACEHOLDER” MECHANISMS

- TRICHLOROETHYLENE — SURPRISINGLY GOOD FITS CONSIDERING CRUDITY OF MECHANISM
- N-PROPYL AND N-BUTYL BROMIDES - LOW NOₓ DATA POORLY SIMULATED
**LUMPED MECHANISM FOR AIRSHED MODELS**

INCLUDES **BASE MECHANISM** PLUS REACTIONS OF FOLLOWING VOC SPECIES:

<table>
<thead>
<tr>
<th>VOC</th>
<th>MOD SPEC</th>
<th>RATE CONSTANT RANGE (ppm$^{-1}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>METHANE</td>
<td>CH4</td>
<td>EXPLICIT</td>
</tr>
<tr>
<td>ALKANES AND OTHER NON-AROMATIC SPECIES THAT REACT ONLY WITH OH (LARGE NUMBER OF CLASSES USED TO AVOID REACTIVITY WEIGHTING)</td>
<td>ALK1, ALK2, ALK3, ALK4, ALK5, ALK6</td>
<td>$k_{OH}$</td>
</tr>
<tr>
<td>ETHENE</td>
<td>ETHE</td>
<td>EXPLICIT</td>
</tr>
<tr>
<td>ISOPRENE</td>
<td>ISOP</td>
<td>EXPLICIT</td>
</tr>
<tr>
<td>TERPENES</td>
<td>TRP1</td>
<td>TERPENES</td>
</tr>
<tr>
<td>OTHER ALKENES</td>
<td>OLE1, OLE2</td>
<td>$k_{OH}$</td>
</tr>
<tr>
<td>AROMATICS (REACTIVITY WEIGHTING ONLY FOR BENZENES)</td>
<td>ARO1, ARO2</td>
<td>$k_{OH}$</td>
</tr>
</tbody>
</table>
LUMPED MECHANISM FOR AIRSHED MODELS (CONTINUED)

RATE AND PRODUCT YIELD PARAMETERS FOR THE ALK\textsubscript{N}, TRP1, OLE\textsubscript{N}, AND ARO\textsubscript{N} SPECIES DERIVED FROM THE MIXTURE OF VOCs THEY REPRESENT

A “FIXED PARAMETER” VERSION DEVELOPED USING PARAMETERS DERIVED FROM THE AMBIENT ROG MIXTURE USED IN THE REACTIVITY SCENARIOS

FILES TO IMPLEMENT FIXED PARAMETER VERSION FOR MODELS-3 WERE DELIVERED TO THE EPA

WORK IS NEEDED ON EMISSIONS - TO - MODEL SPECIES ASSIGNMENTS

STATISTICS FOR LUMPED MECHANISM

- 215 REACTIONS, 66 REACTIVE SPECIES (AT LEAST 6 CAN BE IN STEADY STATE ), 11 NON-REACTING PRODUCT OR COUNTER SPECIES

MECHANISM USED FOR REACTIVITY SIMULATIONS CONSIST OF LUMPED MECHANISM + EXPLICIT REACTIONS OF THE VOC BEING ASSESSED
# EFFECTS OF MECHANISM UPDATES ON MAXIMUM INCREMENTAL REACTIVITIES (MIRs)

<table>
<thead>
<tr>
<th>VOC or Mixture</th>
<th>SAPRC-97</th>
<th>SAPRC-99</th>
<th>Δ%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Incremental Reactivities (gm O₃ / gm VOC)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ambient Mixture</td>
<td>4.06</td>
<td>3.98</td>
<td>-2%</td>
</tr>
<tr>
<td><strong>Relative Reactivities (mass basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>0.08</td>
<td>0.09</td>
<td>12%</td>
</tr>
<tr>
<td>n-Decane</td>
<td>0.13</td>
<td>0.24</td>
<td>91%</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>1.40</td>
<td>1.53</td>
<td>9%</td>
</tr>
<tr>
<td>Isoprene</td>
<td>2.30</td>
<td>2.89</td>
<td>25%</td>
</tr>
<tr>
<td>a-Pinene</td>
<td>0.96</td>
<td>1.13</td>
<td>19%</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.26</td>
<td>1.07</td>
<td>-15%</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>3.49</td>
<td>2.78</td>
<td>-20%</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.71</td>
<td>1.15</td>
<td>61%</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.09</td>
<td>0.33</td>
<td>276%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.42</td>
<td>0.47</td>
<td>13%</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>0.56</td>
<td>0.92</td>
<td>63%</td>
</tr>
<tr>
<td>Methyl t-Butyl Ether</td>
<td>0.18</td>
<td>0.22</td>
<td>25%</td>
</tr>
<tr>
<td>2-Butoxyethanol</td>
<td>0.57</td>
<td>0.84</td>
<td>47%</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>1.62</td>
<td>2.33</td>
<td>44%</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>0.35</td>
<td>0.40</td>
<td>14%</td>
</tr>
<tr>
<td>Mineral Spirits &quot;B&quot; (Type II-C)</td>
<td>0.35</td>
<td>0.24</td>
<td>-29%</td>
</tr>
</tbody>
</table>
Effects of Mechanism Updates on Exhaust Reactivity Adjustment Factors (RAFs) Calculated Using the MIR Scale

<table>
<thead>
<tr>
<th>Exhaust Type</th>
<th>SAPRC-99 RAF</th>
<th>Δ%</th>
<th>SAPRC-97 RAF</th>
<th>Δ%</th>
<th>SAPRC-90 RAF</th>
</tr>
</thead>
<tbody>
<tr>
<td>RFA</td>
<td>1.00</td>
<td>-</td>
<td>1.00</td>
<td>-</td>
<td>1.00</td>
</tr>
<tr>
<td>M85</td>
<td>0.38</td>
<td>14%</td>
<td>0.34</td>
<td>-10%</td>
<td>0.37</td>
</tr>
<tr>
<td>E85</td>
<td>0.67</td>
<td>11%</td>
<td>0.61</td>
<td>-4%</td>
<td>0.63</td>
</tr>
<tr>
<td>CNG</td>
<td>0.19</td>
<td>16%</td>
<td>0.16</td>
<td>-9%</td>
<td>0.18</td>
</tr>
<tr>
<td>LPG</td>
<td>0.52</td>
<td>12%</td>
<td>0.46</td>
<td>-8%</td>
<td>0.50</td>
</tr>
<tr>
<td>Phase 2</td>
<td>0.99</td>
<td>1%</td>
<td>0.98</td>
<td>0%</td>
<td>0.98</td>
</tr>
</tbody>
</table>
EXAMPLES OF REACTIVITY UNCERTAINTY CLASSIFICATIONS

CONSIDERED TO BE RELATIVELY UNCERTAIN

- n-Butane
- Propene
- 2-Butoxyethanol

MECHANISM MAY CHANGE, BUT MIR CHANGE IS EXPECTED TO BE LESS THAN A FACTOR OF TWO

- n-Octane
- 1-Pentene
- Toluene
- 2-Ethoxyethanol

REACTIVITY MAY CHANGE BY A FACTOR OF TWO IF COMPOUND STUDIED OR IF BASE MECHANISM CHANGED

- n-Dodecane *
- Branched C12 Alkanes
- Trans-2-Hexene
- s-Butyl Benzene
- Ethyl t-Butyl Ether

* Given higher uncertainty classification because of sensitivity to changes in the base mechanism
EXAMPLES OF REACTIVITY UNCERTAINTY CLASSIFICATIONS (CONTINUED).

CLASSIFICATIONS WHERE UNCERTAINTY ADJUSTMENTS ARE RECOMMENDED IF USED IN REACTIVITY-BASED REGULATIONS.

REACTIVITY IS EXPECTED TO CHANGE IF COMPOUND IS STUDIED

• 1-Octene
• C8 Internal Alkenes
• Methyl Acetylene
• Vinyl Acetate

SIGNIFICANT CHANCE OF MECHANISM BEING INCORRECT IN IMPORTANT RESPECTS

• Cyclopentadiene
• Indan

MECHANISM IS PROBABLY INCORRECT OR VOC IS REPRESENTED BY A “PLACEHOLDER” MECHANISM

• Ethyl Amine
• Vinyl Chloride
• Benzotrifluoride