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 EXPLICITLY 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 NO_x, 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 SO_2 BUT NOT HALOGEN SPECIES REACTIONS.

ORGANIC PRODUCTS

- ALL RATE CONSTANTS UPDATED
- ALL C_1 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 [$HC(O)C(O)OONO_2$] 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 NO_x

REACTIVE ORGANIC PRODUCT MODEL SPECIES

- Formaldehyde
- Lumped C3+ Aldehydes
- Ketones, etc with kOH < $5x10^{-12}$ cm^3 $molec^{-2}$ sec^{-1}
- Acetaldehyde
- Acetone
- Ketones, etc with kOH > $5x10^{-12}$ cm^3 $molec^{-2}$ sec^{-1}

- Methanol
- Methyl Hydroperoxide
- Higher Organic Hydroperoxides

- Lumped Organic Nitrates
- PPN And Other Higher Alkyl PAN Analogues
- Peroxy Acetyl Nitrate
- PAN Analogues Formed From Aromatic Aldehydes

- Methacrolein
- Other Isoprene Products
- Methyl Vinyl Ketone
- Methacrolein PAN Analogue

- Glyoxal
- Biacetyl
- Photoreactive Aromatic Fragmentation Products (α-Dicarbonyl Spectrum)
- Methyl Glyoxal
- Non-Photoreactive Aromatic Fragmentation Products
- Photoreactive Aromatic Fragmentation Products (Acrolein Spectrum)

- Phenol
- Nitrophenols
- Cresols
- Aromatic Aldehydes

MECHANISM GENERATION AND ESTIMATION SYSTEM

GENERATES MECHANISMS FOR VOCs CONTAINING FOLLOWING GROUPS:

CH_3-	-CH_2-	>CH-	>CH<
-O-	-OH	-CHO	-CO-
-ONO_2	=CH_2	=CH-	=C<

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

GENERATES REACTIONS AND ESTIMATES RATE CONSTANTS OR BRANCHING RATIOS FOR

- VOC + OH
- ALKENE + O_3
- ALKENE + NO_3
- ALKENE + O^3P
- ALDEHYDE + NO_3
- ALDEHYDE + $h\nu \rightarrow R\cdot + HCO\cdot$
- KETONE + $h\nu \rightarrow R\cdot + R'CO\cdot$
- RONO2 + $h\nu \rightarrow RO\cdot + NO2$
- $R\cdot + O_2$
- $RO2 + NO \rightarrow y_N\ RONO2 + (1-y_N)\ RO\cdot + NO2$
- 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)

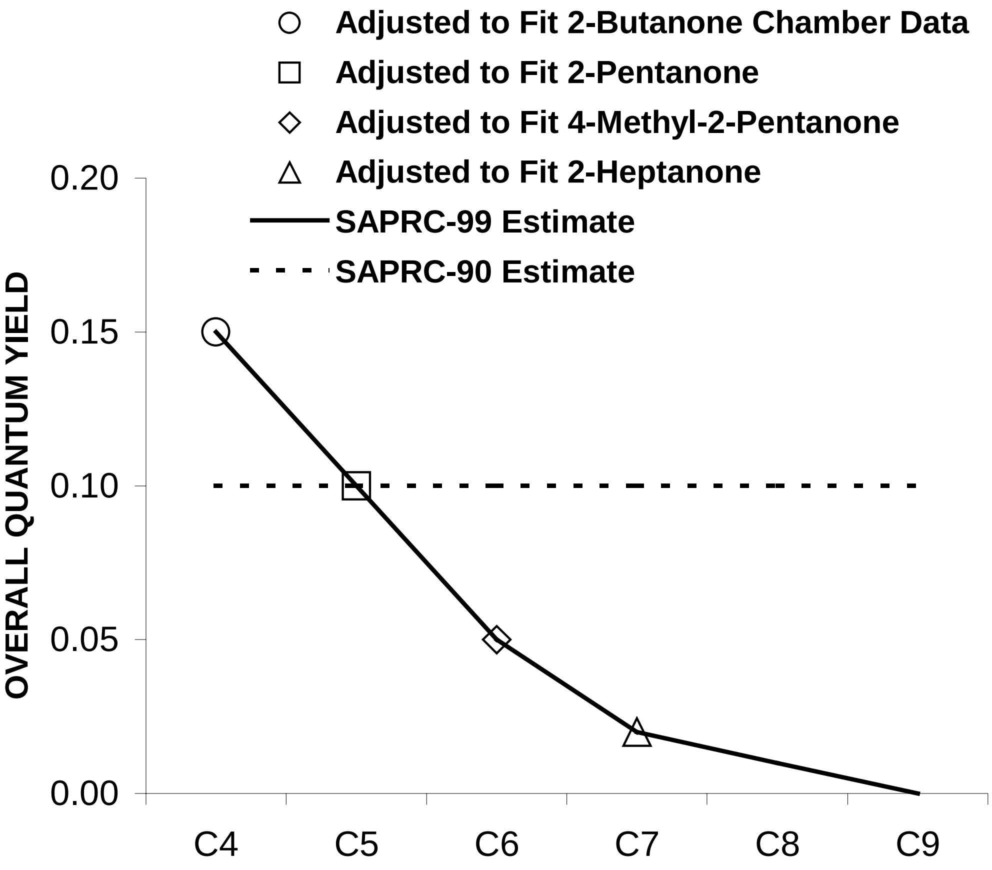
ALDEHYDE PHOTOLYSIS RATES, BRANCHING

- PHOTOLYSIS RATES FOR ALL C_{3+} 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 - NO_x 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 C_{4+} ALKYL KETONES

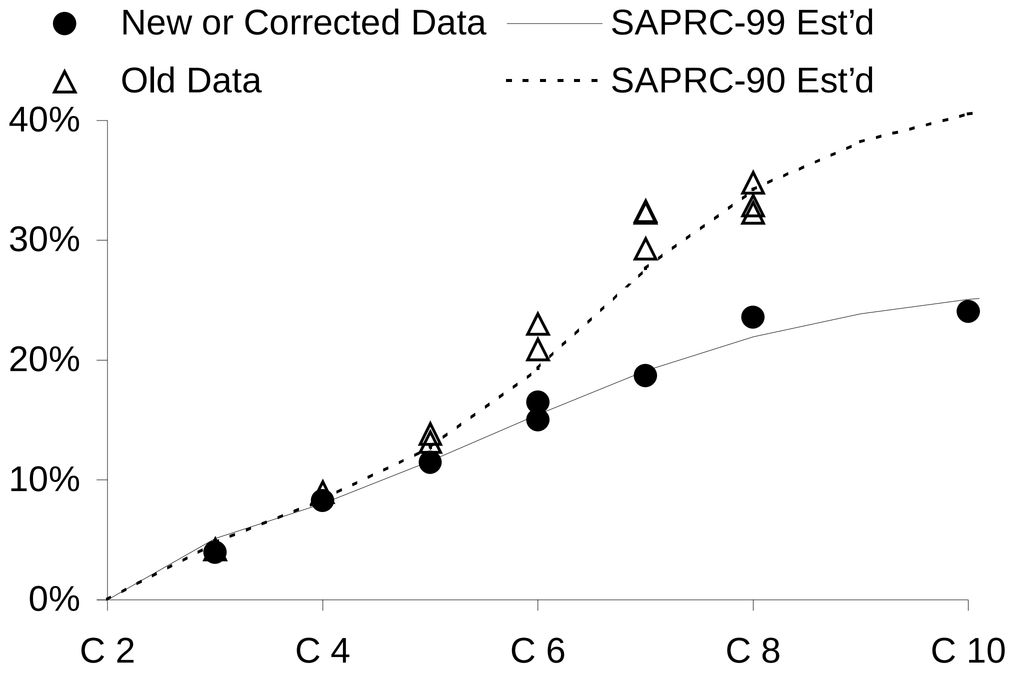


EXAMPLES OF ESTIMATION METHODS EMPLOYED (CONTINUED)

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.

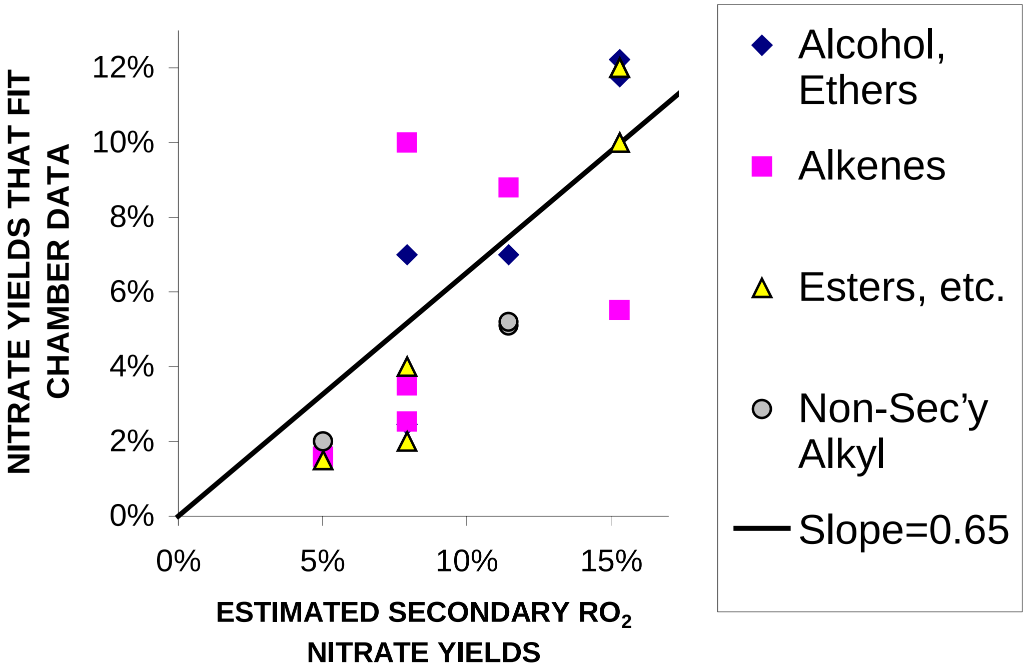
NO LONGER NECESSARY TO ASSUME NO NITRATE FORMATION FROM OH-SUBSTITUTED RO_2'S TO FIT C_{8+} N-ALKANE CHAMBER DATA

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



NO PREDICTABLE DEPENDENCE OF TYPE OF SUBSTITUENT ON AMOUNT OF YIELD REDUCTION

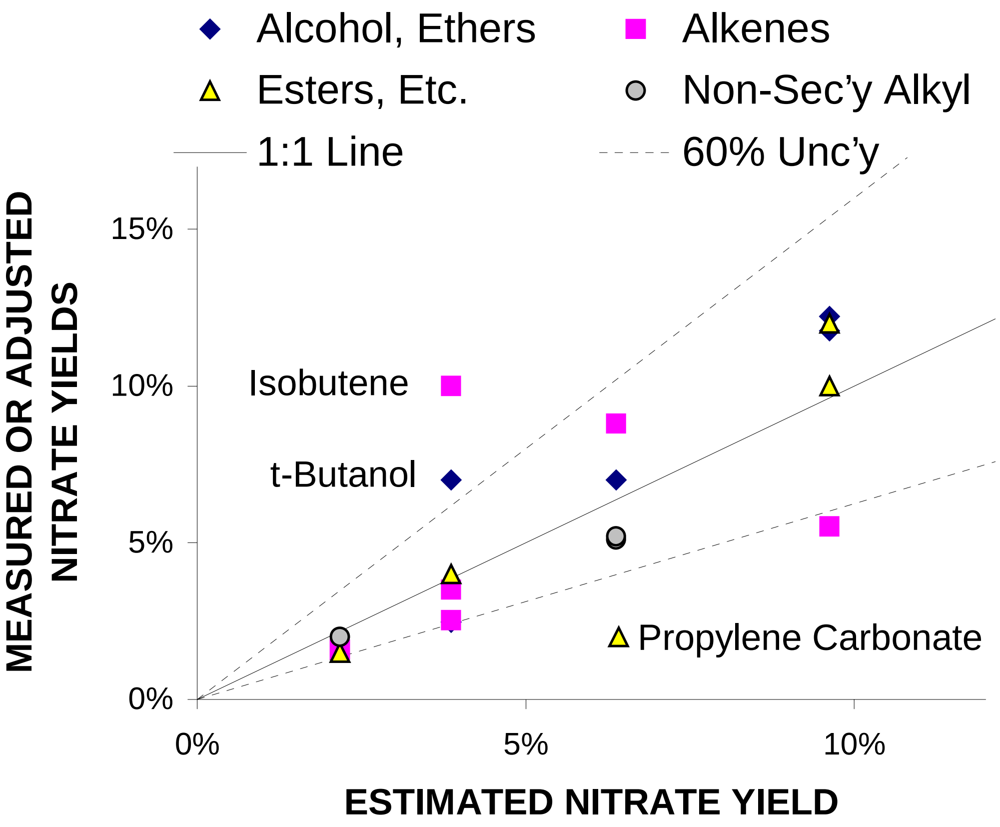
NITRATE YIELD ESTIMATES FOR MECHANISM

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 RO_2'S WITH CARBON NUMBER REDUCED BY 1.5



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·; ISOPROPOXY FOR SECONDARY RO·
- ACTIVATION ENERGY (E_A) ESTIMATED BY CORRELATION BETWEEN E_A AND ΔH_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 $(\text{SUBST. FACTOR FOR OH ABSTRACTION})^{1.5}$

ESTIMATED FOR ALKOXY RADICAL REACTIONS (CONTINUED)

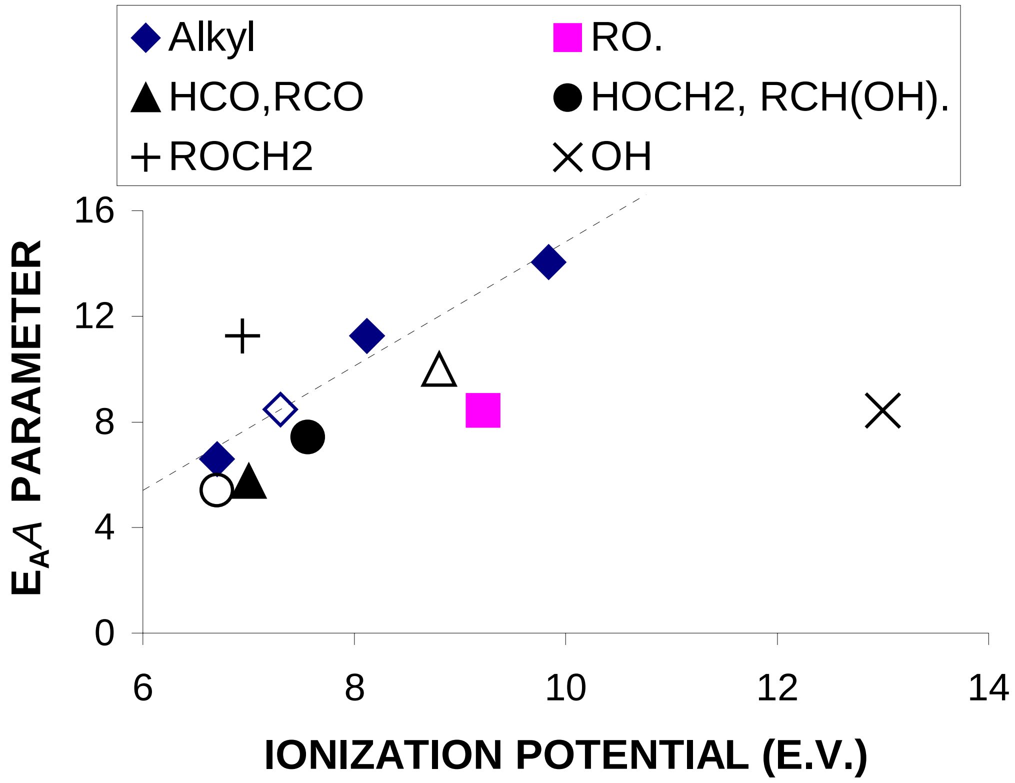
β-SCISSION DECOMPOSITIONS

- A FACTOR ESTIMATES OF ATKINSON USED
- E_A ESTIMATED USING $\boxed{E_A \approx E_A\mathit{A} + E_A\mathit{B}\cdot\Delta H_R}$, WHERE
  - $E_A\mathit{B} \approx 0.44$ IS DERIVED FROM DATA FOR REACTIONS FORMING $CH_3\cdot$ AND IS ASSUMED TO BE THE SAME FOR ALL REACTIONS
  - $E_A\mathit{A}$ 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 $E_A\mathit{A}$ 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 $E_A\mathit{A}$ DOES NOT WORK IN ALL CASES

ESTER REARRANGEMENT

- $RCH(O\cdot)\text{-}O\text{-}CO\text{-}R' \rightarrow RCO\cdot + R'C(O)OH$
- RATE CONSTANT ESTIMATED SO IT DOMINATES FOR $CH_3CH(O\cdot)O\text{-}CO\text{-}CH_3$ YET ISOMERIZATION OF $CH_3CH_3CH_2CH(O\cdot)\text{-}O\text{-}CO\text{-}CH_3$ OCCURS, FOR MODEL TO FIT BUTYL ACETATE CHAMBER DATA

EXAMPLES OF $E_A A$ PARAMETERS FOR ESTIMATING ACTIVATION ENERGIES FOR β-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 O_3 + ALKENES AND ALKYNES)

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

CH_2OO BIRADICALS

- BRANCHING RATIOS RECOMMENDED BY ATKINSON

RCHOO BIRADICALS

- **APPARENT INCONSISTENCY BETWEEN LABORATORY OH YIELDS AND CHAMBER DATA**
- PUBLISHED OH YIELDS FROM O_3 + 1-ALKENES IN ABSENCE OF NO_x SUGGEST OH YIELD IS ~55% FOR ALL RCHOO's
  - 1-BUTENE - NO_x CHAMBER DATA CANNOT BE FIT BY MODEL UNLESS OH YIELD REDUCED TO ~5%
  - 1-HEXENE - NO_x 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.

  $>CHC(OO)- \rightarrow >C=C(OOH)- \rightarrow >C=C(O\cdot)- + OH$

- 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, O_3 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 ALKYLBENZENES

- 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., $CH_3C(O)CH=CH-CH=CH-C(O)-CH_3$
  - TWO PHOTOREACTIVE DICARBONYL PRODUCTS WITH YIELDS ADJUSTED TO FIT AROMATIC - NO_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 ALKYLBENZENES 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

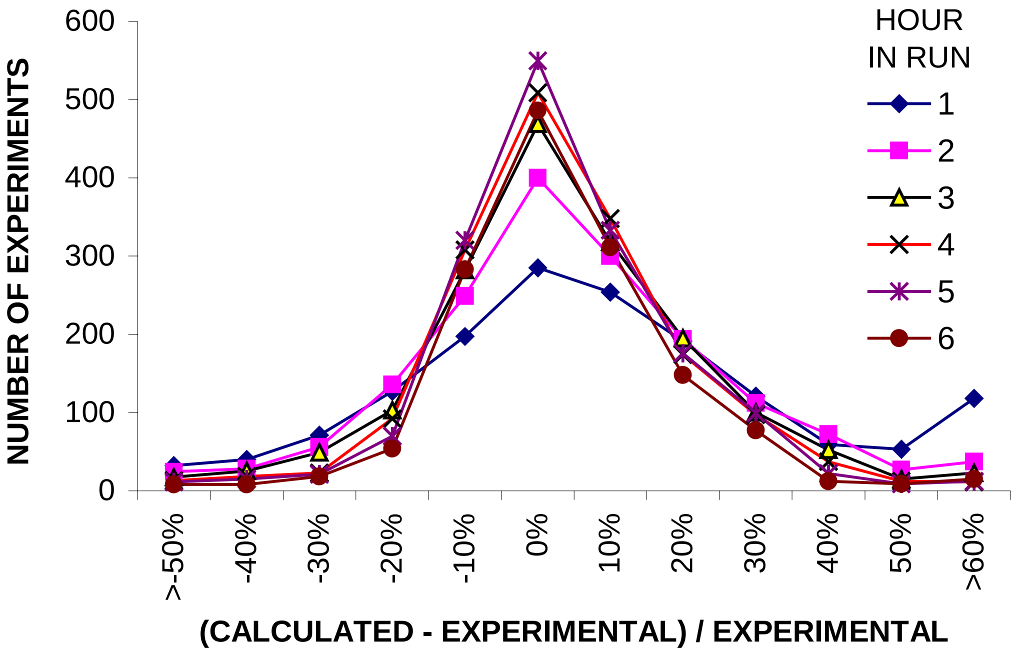
TYPE OF EXPERIMENT	RUNS	VOCs
CHARACTERIZATION RUNS	76	
VOC - NO_x RUNS	484	37
INCREMENTAL REACTIVITY RUNS	447	80
MISCELLANEOUS MIXTURE - NO_x	95	
"BASE CASE" SURROGATE - NO_x MIXTURES WITH REACTIVITY RUNS	561	

TYPES OF CHAMBERS

WALLS	LIGHTS	RH	VOL (L)	RUNs
TEFLON FILM	BLACKLIGHT	50%	6000	139
TEFLON FILM	BLACKLIGHT	DRY	3000-6000	1066
TEFLON FILM	XENON ARC	DRY	2500-5000	323
TEFLON COATED AL, QUARTZ	XENON ARC	50%	6400	107
TEFLON FILM	SUNLIGHT	DRY	20,000	42

RESULTS OF EVALUATION

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



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

- C_{4+} 1-ALKENES — LOW OH YIELDS IN O_3 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 — O_3 IN PINENE - NO_x 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 NO_x DATA POORLY SIMULATED

LUMPED MECHANISM FOR AIRSHED MODELS

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

VOC	**MOD SPEC**	**RATE CONSTANT RANGE (ppm^{-1} min^{-1})**
METHANE	CH4	EXPLICIT
ALKANES AND OTHER NON-AROMATICS THAT REACT ONLY WITH OH (LARGE NUMBER OF CLASSES USED TO AVOID REACTIVITY WEIGHTING)	ALK1	$kOH < 5x10^{2}$
	ALK2	$5x10^{2} < kOH < 2.5x10^{3}$
	ALK3	$2.5x10^{3} < kOH < 5x10^{3}$
	ALK4	$5x10^{3} < kOH < 1x10^{4}$
	ALK5	$1x10^{4} < kOH < 2x10^{4}$
	ALK6	$kOH > 2x10^{4}$
ETHENE	ETHE	EXPLICIT
ISOPRENE	ISOP	EXPLICIT
TERPENES	TRP1	TERPENES
OTHER ALKENES	OLE1	$kOH < 7x10^{4}$
	OLE2	$kOH > 7x10^{4}$
AROMATICS (REACTIVITY WEIGHTING ONLY FOR BENZENES)	ARO1	$KOH < 2x10^{4}$
	ARO2	$KOH > 2x10^{4}$

LUMPED MECHANISM FOR AIRSHED MODELS (CONTINUED)

RATE AND PRODUCT YIELD PARAMETERS FOR THE ALK_N, TRP1, OLE_N, AND ARO_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)

VOC or Mixture	SAPRC-97	SAPRC-99	Δ%
<u>Incremental Reactivities (gm O3 / gm VOC)</u>			
Ambient Mixture	4.06	3.98	-2%
<u>Relative Reactivities (mass basis)</u>			
Ethane	0.08	0.09	12%
n-Decane	0.13	0.24	91%
1-Hexene	1.40	1.53	9%
Isoprene	2.30	2.89	25%
a-Pinene	0.96	1.13	19%
Toluene	1.26	1.07	-15%
m-Xylene	3.49	2.78	-20%
p-Xylene	0.71	1.15	61%
Acetylene	0.09	0.33	276%
Ethanol	0.42	0.47	13%
Ethylene Glycol	0.56	0.92	63%
Methyl t-Butyl Ether	0.18	0.22	25%
2-Butoxyethanol	0.57	0.84	47%
Formaldehyde	1.62	2.33	44%
Methyl Ethyl Ketone	0.35	0.40	14%
Mineral Spirits "B" (Type II-C)	0.35	0.24	-29%

EFFECTS OF MECHANISM UPDATES ON EXHAUST REACTIVITY ADJUSTMENT FACTORS (RAFs) CALCULATED USING THE MIR SCALE

Exhaust	**SAPRC-99**		**SAPRC-97**		**SAPRC-90**
Type	**RAF**	**Δ%**	**RAF**	**Δ%**	**RAF**
RFA	1.00	-	1.00	-	1.00
M85	0.38	14%	0.34	-10%	0.37
E85	0.67	11%	0.61	-4%	0.63
CNG	0.19	16%	0.16	-9%	0.18
LPG	0.52	12%	0.46	-8%	0.50
Phase 2	0.99	1%	0.98	0%	0.98

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