DEVELOPMENT AND EVALUATION OF THE SAPRC-99 CHEMICAL MECHANISM

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DESIGN OBJECTIVES

ALL MECHANISMS

CAN BE USED IN URBAN AND REGIONAL MODELS FOR PREDICTING AIR QUALITY

REPRESENT THE STATE OF THE SCIENCE IN ATMOSPHERIC CHEMISTRY

GIVE PREDICTIONS CONSISTENT WITH LABORATORY AND CHAMBER DATA

SAPRC MECHANISMS

CAN CALCULATE IMPACTS AND REACTIVITY SCALES FOR THE MAJOR EMITTED VOCs

ALLOWS MODELS TO INCORPORATE ALL THE CHEMICAL DETAIL IN EMISSIONS DATA

COMPONENTS OF THE SAPRC-99 MECHANISM

BASE MECHANISM USED FOR INORGANICS AND COMMON ORGANIC PRODUCTS

MECHANISMS FOR ~400 TYPES OF VOCs

- FOR EXPLICIT REPRESENTATION, OR
- TO DERIVE PARAMETERS FOR LUMPED MODEL SPECIES

A MECHANISM GENERATION SYSTEM USED TO DERIVE MECHANISMS FOR MANY VOCs

PARAMETERIZED MECHANISMS USED FOR AROMATICS AND A FEW OTHER VOCs

ADAPTATIONS FOR AIRSHED MODELS:

- “ADJUSTABLE PARAMETER” VERSION TO INCORPORATE CHEMICAL DETAIL
- “FIXED PARAMETER” VERSION FOR MODELS WITH SOFTWARE LIMITATIONS

MECHANISM USED TO UPDATE MIR AND OTHER REACTIVITY SCALES

BASE MECHANISM

REPRESENTS INORGANICS AND COMMON ORGANIC PRODUCTS

187 REACTIONS, 54 REACTIVE SPECIES, 11 NON-REACTING PRODUCT SPECIES

ALL RATE CONSTANTS UPDATED. FIRST COMPREHENSIVE UPDATE SINCE SAPRC-90

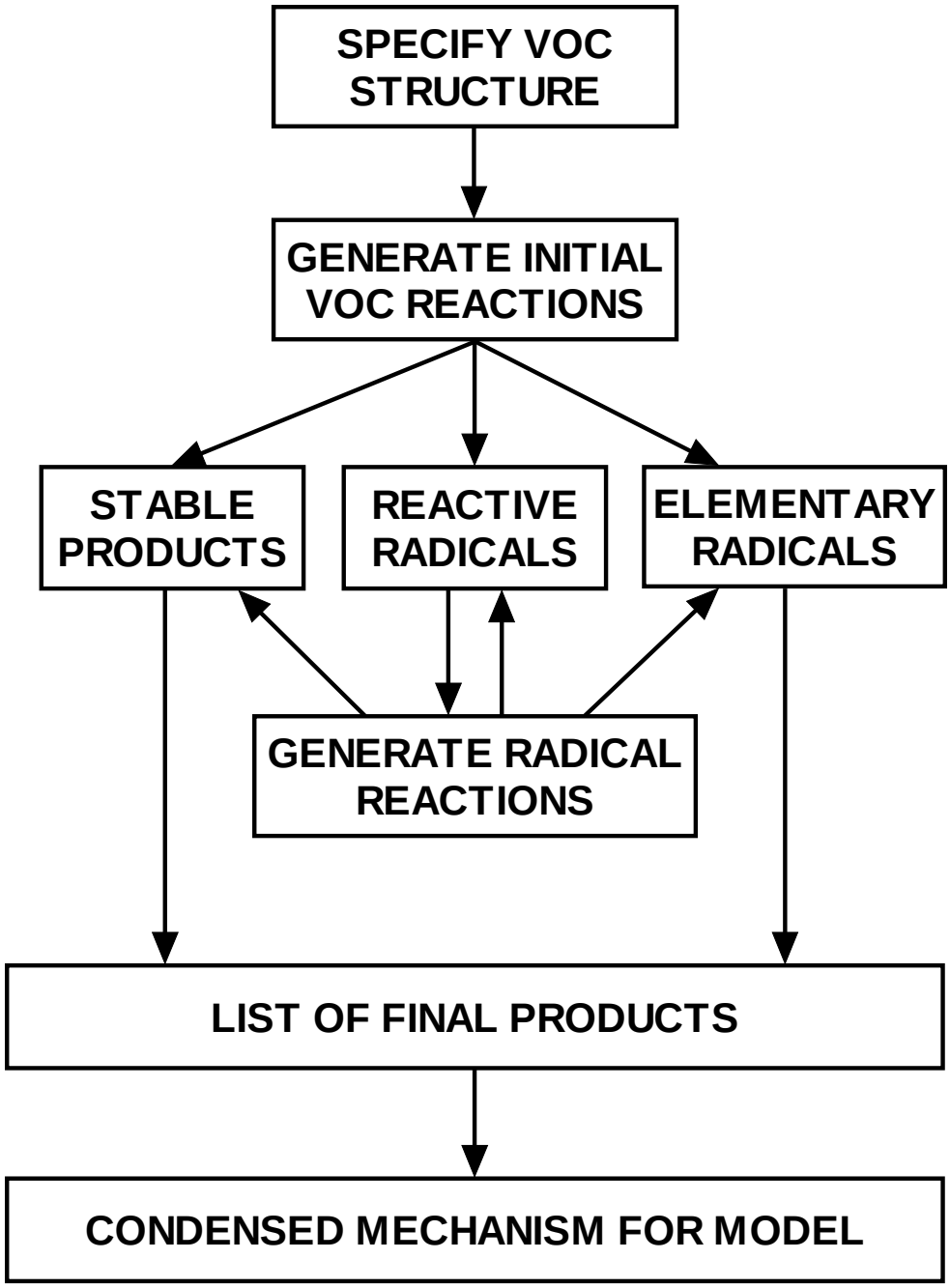
NUMBER OF COMMON ORGANIC PRODUCT SPECIES INCREASED

SLIGHTLY LESS APPROXIMATE TREATMENT OF LOW NO_x PEROXY RADICAL REACTIONS

REACTIVE ORGANIC PRODUCTS IN BASE MECHANISM

- Formaldehyde, Acetaldehyde, Acetone
- Lumped C3+ Aldehydes
- Lumped Ketones, etc with kOH < $5x10^{-12}$
- Lumped Ketones, etc with kOH > $5x10^{-12}$
- Methacrolein, Methyl Vinyl Ketone
- Lumped Other Isoprene Products
- Methanol, Methyl Hydroperoxide
- Lumped Higher Organic Hydroperoxides
- Organic Nitrates
- PAN, Higher PANs, PBzN, MPAN
- Glyoxal, Methyl Glyoxal, Biacetyl
- Lumped Non-Photoreactive Aromatic Ring Opening Products
- 2 Photoreactive Aromatic Products (α-Dicarbonyl and Acrolein Action Spectra)
- Phenol, Cresols, Nitrophenols
- Aromatic Aldehydes (Benzaldehyde)

MECHANISM GENERATION SYSTEM



CAPABILITIES OF MECHANISM GENERATION SYSTEM

GENERATES MECHANISMS FOR VOCs CONTAINING FOLLOWING GROUPS:

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

(CURRENTLY CANNOT PROCESS VOCs WITH MORE THAN ONE DOUBLE BOND OR RING)

GENERATES FULLY EXPLICIT MECHANISMS FOR FOLLOWING REACTIONS:

- VOC + OH, O_3, NO_3, O^3P, $h\nu$
- ALKYL + O_2
- PEROXY + NO
- VARIOUS ALKOXY REACTIONS
- CRIGIEE BIRADICAL REACTIONS

MEASURED RATE CONSTANTS (OR RATIOS) ARE USED WHEN INFORMATION AVAILABLE

VARIOUS ESTIMATION METHODS ARE USED WHEN NECESSARY.

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
1-Methyl-2-Octyl Cyclohexane	1618	520

“LUMPING RULES” ARE USED TO CONVERT THE EXPLICIT MECHANISMS TO LUMPED REPRESENTATIONS FOR THE MODEL.

EXAMPLES OF ESTIMATION METHODS EMPLOYED

VOC + OH RATE CONSTANTS, BRANCHING

- GROUP-ADDITIVITY METHOD OF ATKINSON, KWOK AND ATKINSON
- ASSUMES ALL OH + ALKENE REACTION IS ADDITION TO DOUBLE BOND

VOC + O_3 AND NO_3 RATE CONSTANTS, BRANCHING RATIOS

- RATE CONSTANTS ASSUMED TO DEPEND ONLY ON NUMBER OF SUBSTITUENTS ABOUT DOUBLE BOND.
- NO_3 ADDITION ASSUMED TO OCCUR AT LEAST SUBSTITUTED END

ALDEHYDE PHOTOLYSIS

- SAME PHOTOLYSIS RATES FOR ALL C_{3+} ALDEHYDES
- PRODUCTS ARE R· + HCO·

KETONE PHOTOLYSIS

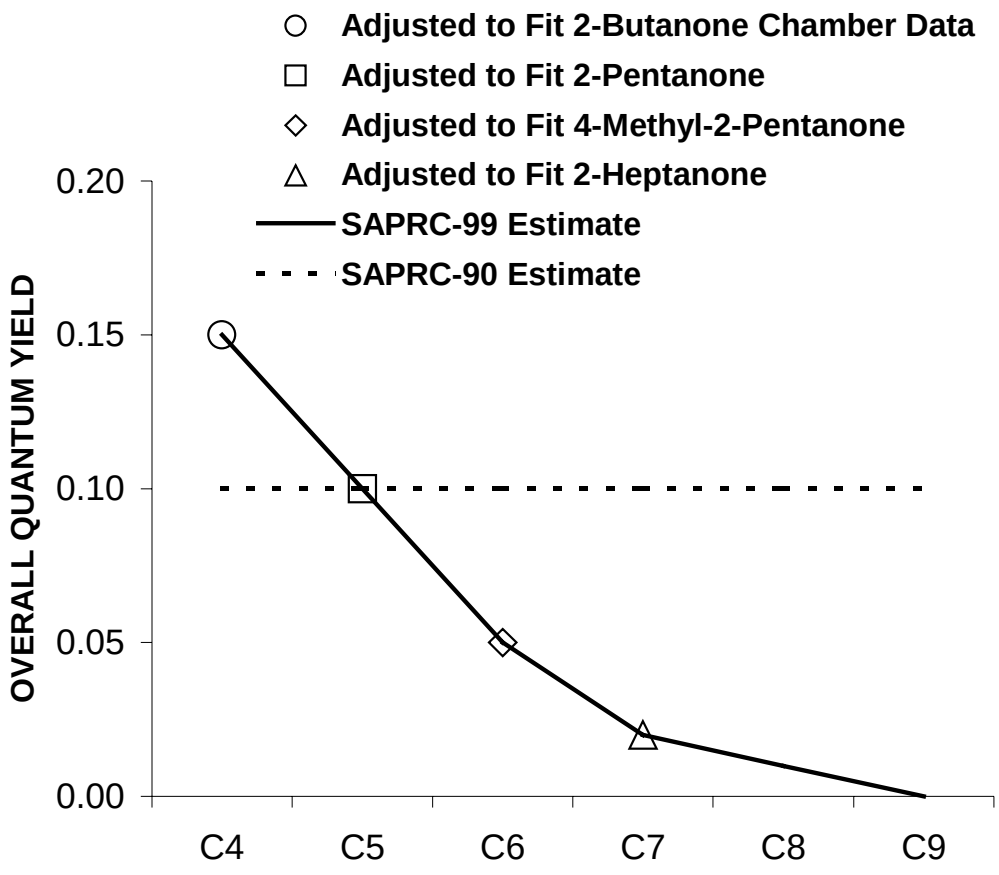
REACTION ASSUMED TO BE

$$KETONE + h\nu \rightarrow R\cdot + R'CO\cdot$$

WITH LOWEST ΔH_R ROUTE DOMINATING

MEK ABSORPTION CROSS SECTIONS USED

OVERALL QUANTUM YIELDS ADJUSTED TO FIT CHAMBER DATA

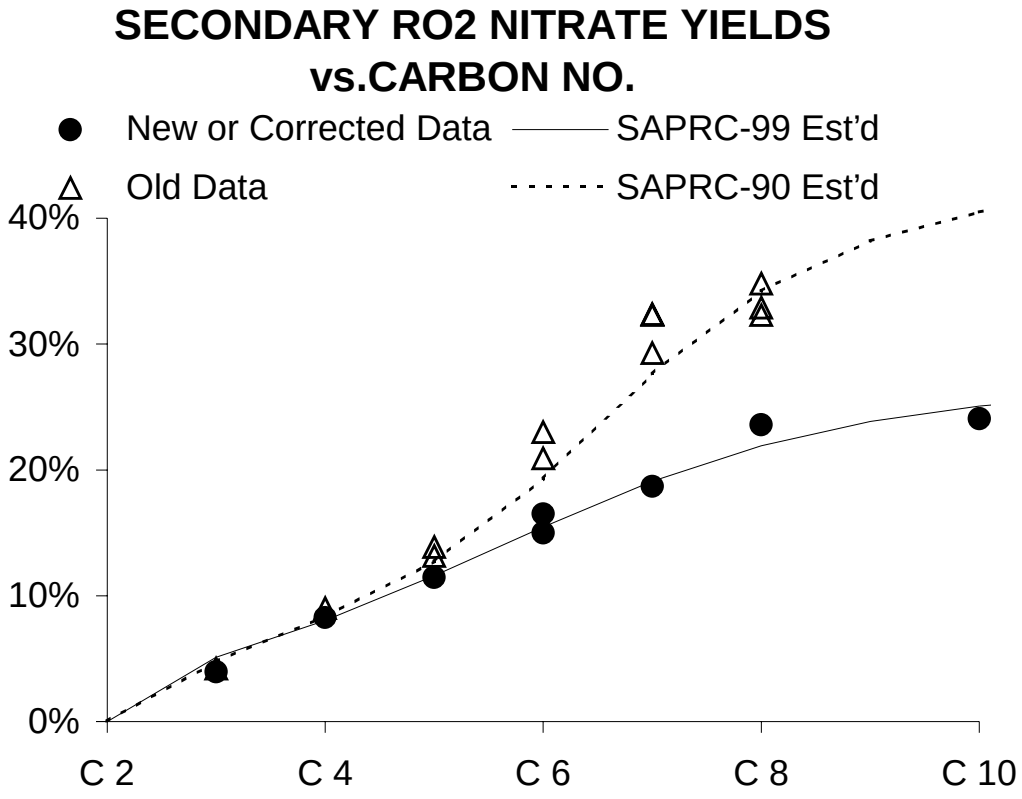


NITRATE YIELDS FROM RO_2+NO

$RO_2 + NO \rightarrow RO\cdot + NO_2$ (PROPAGATING)

$RO_2 + NO + M \rightarrow RONO_2 + M$ (TERMINATING)

NEW DATA FROM ATKINSON'S LAB GIVE LOWER NITRATE YIELDS FOR C_{8+} RADICALS



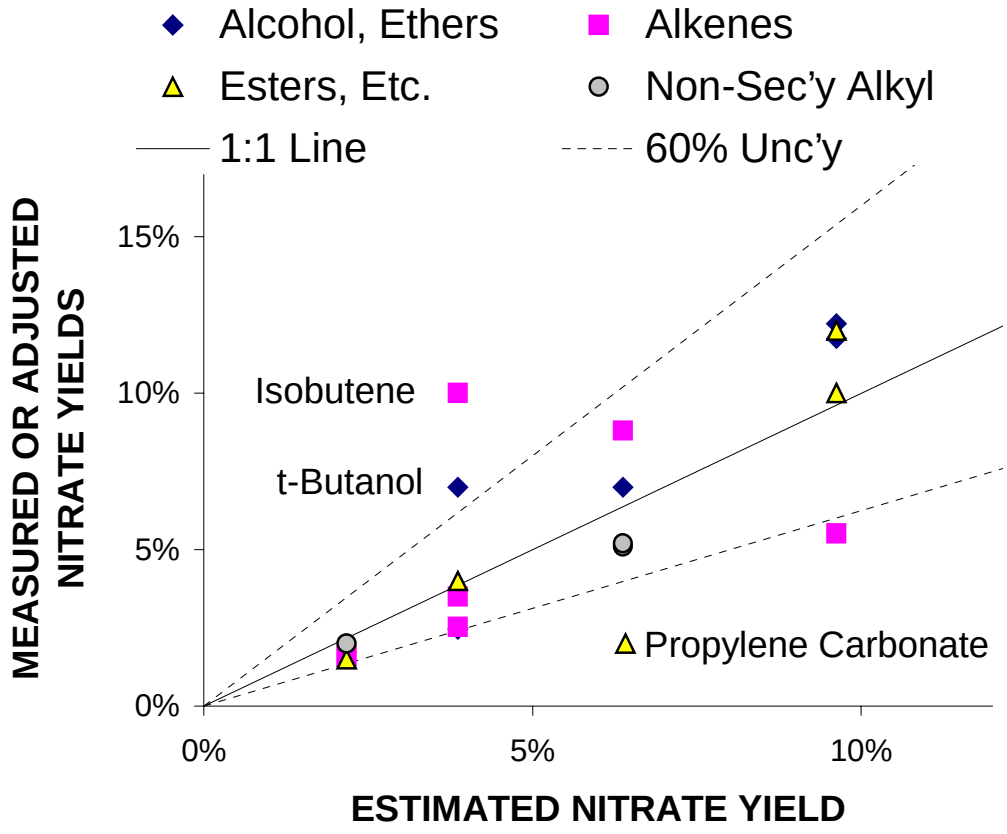
GIVES MUCH BETTER FITS OF MODEL TO CHAMBER DATA FOR MINERAL SPIRITS

EFFECTS OF STRUCTURE AND SUBSTITUENTS ON NITRATE YIELDS

AVAILABLE INFORMATION PRIMARILY FROM ADJUSTMENTS TO FIT CHAMBER DATA

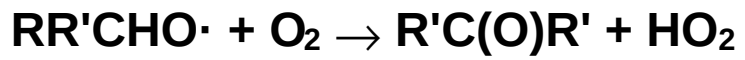
DEPENDENCE ON STRUCTURE IS UNCLEAR

BEST FITS OBTAINED BY USING ESTIMATES FOR SECONDARY RO_2 RADICALS WITH CARBON NUMBERS REDUCED BY 1.5



ESTIMATES FOR VARIOUS ALKOXY RADICAL REACTION

EXAMPLES OF TYPES OF REACTIONS:



RATE CONSTANTS ARE ESTIMATED USING SEPARATE ESTIMATES OF A FACTORS AND ACTIVATION ENERGIES.

A FACTOR ESTIMATES ARE BASED ON RECOMMENDATIONS IN LITERATURE

ACTIVATION ENERGIES ARE ESTIMATED USING VARIOUS CORRELATIONS E_A AND ΔH_R FOR THE DIFFERENT TYPES OF REACTIONS

CRIGIEE BIRADICAL REACTIONS FOR 1-ALKENES

O_3 + RCH=CH2 $\rightarrow$ RCHO + CH_2OO (50%)

O_3 + RCH=CH2 $\rightarrow$ RCHOO + HCHO (50%)

OH YIELD DATA ARE INCONSISTENT

COMPOUND	OH YIELDS MEASURED IN ABSENCE OF NO_x	OH YIELDS USED TO FIT CHAMBER DATA
PROPENE	33%	32%
1-BUTENE	41%	12%
1-PENTENE	37%	-
1-HEXENE	32%	8%

USED IN MODEL FOR CH_2OO BIRADICALS:

ATKINSON RECOMMENDATION: (12% OH)

USED IN MODEL FOR RCHOO BIRADICALS:

RADICAL YIELD DECREASES WITH SIZE OF MOLECULE TO FIT CHAMBER DATA

PARAMETERIZED MECHANISMS

MECHANISM GENERATION SYSTEM CAN'T BE USED FOR FOLLOWING TYPES OF VOCs:

AROMATICS

SIMILAR MECHANISMS AS PREVIOUSLY, EXCEPT MORE MODEL SPECIES USED TO REPRESENT RING-OPENING PRODUCTS

RING-OPENING PRODUCT YIELDS ADJUSTED TO FIT CHAMBER DATA

TERPENES, AROMATIC ISOCYANATES, NMP, STYRENE

ESTIMATED SIMPLIFIED MECHANISMS ADJUSTED TO FIT CHAMBER DATA

AMINES AND HALOGENATED COMPOUNDS

"PLACEHOLDER" MECHANISMS USED FOR VERY APPROXIMATE REPRESENTATIONS

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	

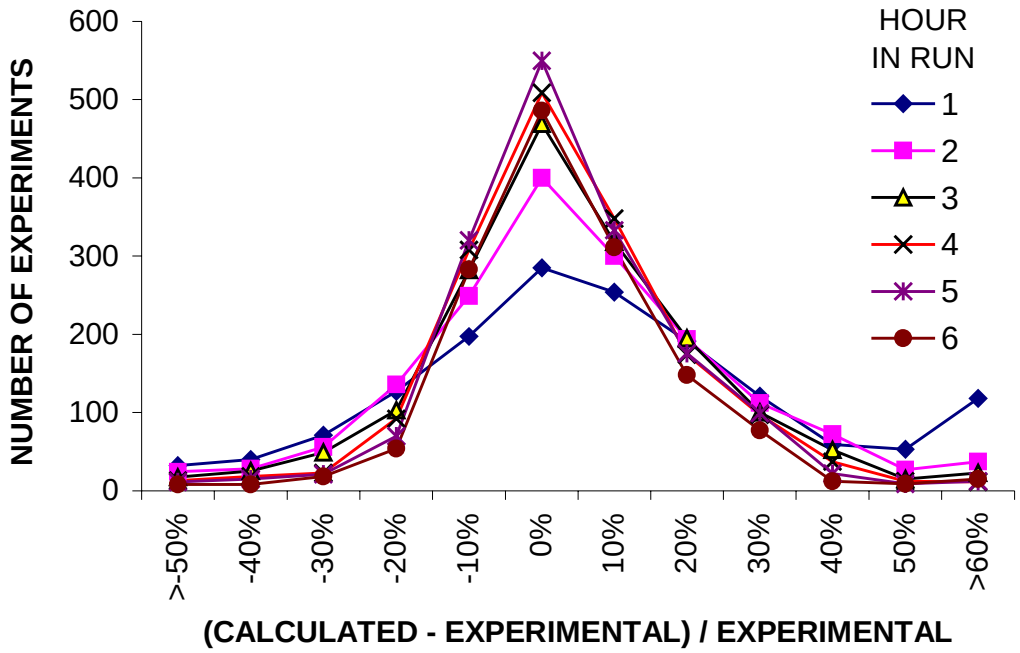
TYPES OF CHAMBERS USED IN EVALUATION

WALLS	LIGHTS	RH	VOL (L)	RUNS
TEFLON FILM	BLACK LIGHTS	50%	6000	139
TEFLON FILM	BLACK LIGHTS	DRY	3000-6000	1066
TEFLON FILM	XENON ARC	DRY	2500-5000	323
TEFLON COATED ALUM., QUARTZ	XENON ARC	50%	6400	107
TEFLON FILM	SUN	DRY	20,000	42

EVALUATION USING UNC AND TVA CHAMBER DATA STILL NEEDS TO BE CARRIED OUT

RESULTS OF EVALUATION

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



EVALUATION RESULTS FOR INDIVIDUAL VOCs

GENERALLY SATISFACTORY FITS (AFTER ADJUSTMENTS IN SOME CASES) FOR MOST VOCs EXCEPT AS INDICATED

C_{4+} 1-ALKENES	HAVE TO USE LOW OH YIELDS IN O_3 REACTION TO FIT DATA
3,4-DIETHYL HEXANE	SOME NEEDED ADJUST-MENTS NOT MADE
CYCLOHEX-ANONE	FITS SOME BUT NOT ALL RUNS
β-PINENE	O_3 OVERPREDICTED IN PINENE - NO_x RUNS. FITS REACTIVITY RUNS OK
T-BUTANOL	BETTER FIT IF kOH LOWER
DBE-4	FITS SOME BUT NOT ALL RUNS
TCE, ALKYL BROMIDES	“PLACEHOLDER” MECHANISM USED FOR HALOGENATED VOCs

EFFECTS OF MECHANISM UPDATES ON MAXIMUM INCREMENTAL REACTIVITIES

VOC or Mixture	SAPRC-97	SAPRC-99	Δ%
Incremental Reactivities (gm O_3 / gm VOC)			
Ambient Mixture	4.06	3.71	-9%
Relative Reactivities (mass basis)			
Ethane	0.08	0.08	6%
Formaldehyde	1.62	2.42	49%
m-Xylene	3.49	2.86	-18%
p-Xylene	0.71	1.15	61%
2-Butoxyethanol	0.57	0.78	37%
Acetylene *	0.09	0.34	285%
n-Decane	0.13	0.22	76%
Mineral Spirits II-C	0.35	0.21	-39%
M85 Exhaust RAF	0.34	0.38	13%
CNG Exhaust RAF	0.16	0.18	14%

* Large increase in glyoxal + $h\nu \rightarrow$ radicals

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

EXHAUST TYPE	MECHANISM VERSION 1999-2000		1997		1990
	RAF	Δ %	RAF	Δ %	RAF
RFA	1.00	-	1.00	-	1.00
M85	0.38	13%	0.34	-8%	0.37
E85	0.66	8%	0.61	-3%	0.63
CNG	0.18	14%	0.16	-11%	0.18
LPG	0.51	12%	0.46	-8%	0.50
Phase 2	0.99	1%	0.98	0%	0.98

Changes shown are relative to the previous version.

EXAMPLES OF REACTIVITY UNCERTAINTY CLASSIFICATIONS

CONSIDERED TO BE RELATIVELY UNCERTAIN

- n-Butane
- 2-Butoxyethanol

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

- 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

***** 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 MAJOR RESPECTS

- Cyclopentadiene
- Indan

MECHANISM IS PROBABLY INCORRECT OR “PLACEHOLDER” MECHANISM IS USED

- Ethyl Amine
- Vinyl Chloride
- Benzotrifluoride

INFORMATION AVAILABLE ON THE WEB

http://cert.ucr.edu/~carter/reactdat.htm

REPORT DOCUMENTING MECHANISM, ESTIMATION METHODS, AND EVALUATION

STOCKWELL'S REVIEW OF THE MECHANISM

UPDATED REACTIVITY SCALES

LINKS TO OTHER INFORMATION, E.G.:

http://cert.ucr.edu/~carter/SAPRC99.htm

FILES AND SOFTWARE IMPLEMENTING THE MECHANISM

http://cert.ucr.edu/~carter/mechgen.htm

WEB ACCESS TO THE MECHANISM GENERATION SYSTEM

http://cert.ucr.edu/~carter/bycarter.htm

OTHER DOWNLOADABLE REPORTS

ACKNOWLEDGEMENTS

CALIFORNIA AIR RESOURCES BOARD

- MAJOR FUNDING OF MECHANISM DEVELOPMENT
- CHAMBER EXPERIMENTS ON CONSUMER PRODUCTS VOCs

VARIOUS PRIVATE SECTOR GROUPS

- CHAMBER EXPERIMENTS FOR MANY INDIVIDUAL COMPOUNDS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

- IMPLEMENTATION OF MECHANISMS INTO MODELS-3

CHEMICAL MANUFACTURERS ASSOCIATION

- MECHANISM GENERATION SYSTEM ENHANCEMENTS TO IMPROVE REPRESENTATION OF PRODUCTS