

CURRENT STATUS OF THE DEVELOPMENT AND EVALUATION OF AN UPDATED DETAILED MECHANISM FOR VOC OXIDATION

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Extended Abstract

The development of chemical mechanisms for airshed models involves several steps. Basic kinetic and mechanistic data are used to construct the "known" portion of the mechanism, but there are significant portions of the mechanism, particularly concerning VOC reactions, where the detailed processes are unknown. These uncertain portions must be tested by model simulations of environmental chamber data, and in many cases (particularly for aromatics) need to be revised or adjusted for model predictions to be consistent with these data. However, environmental chamber experiments themselves have uncertainties, particularly with regard to heterogeneous reactions on the walls, background contaminants, etc. Therefore, a separate "chamber effects" model needs to be developed and evaluated (using "characterization" runs) for use when evaluating mechanisms. The mechanisms for representative VOCs are then used as a basis for estimating reactions of other VOCs for VOC reactivity assessment, or for serving as the basis of developing condensed mechanisms for airshed models.

The "SAPRC-90" mechanism, documented by Carter et al (1990), is the most detailed mechanism in the published literature which has been evaluated against chamber data. It uses explicit representations for 11 VOCs and simple oxidation products, generalized reactions with assigned rate constants and product yield parameters for 148 VOCs, and represents many others using a "surrogate species" approach. It was derived based on kinetic and mechanistic data as of the end of 1989. This mechanism was evaluated using simulations of >500 experiments from four different chambers at two laboratories. The mechanism fit O₃ yield and NO oxidation rates to within ±30% for 63% of the run, and within ±50% for 85% of the runs, with a few runs being poorly simulated (Carter and Lurmann, 1991). The mechanism had a ~15% bias towards overpredicting O₃ and NO oxidation in simulations of mixture runs.

This mechanism is currently being updated as part of work we are carrying out for the California Air Resources Board. The first updated version, which we designate "SAPRC-91", employed updated cross sections for formaldehyde photolysis and updates in the kinetics for PAN formation. Both changes (particularly the latter) change caused the mechanism to be more "reactive", and worsened the bias towards overprediction of O₃ formation and NO oxidation in the simulations of the mixture runs. Subsequent updates, which are documented by Carter et al. (1993a), made the mechanism even more reactive. The major change was increasing, by factors of 2-3, the radical yields in the O₃ + alkene reactions, based on recent laboratory data from Atkinson's group and elsewhere. Other refinements were made to mechanisms of individual VOCs to improve model simulations of more recent experiments, though no significant changes were made to the aromatics mechanisms. A preliminary detailed mechanism for isoprene and its major known oxidation products (methacrolein and MVK) was developed based on simulations of a variety of experiments with these compounds.

Among the major new inputs available for evaluating and updating mechanisms are incremental reactivity experiments. These consist of measuring adding the test compound on the results of a "base case" reactive organic gas (ROG) surrogate - NO_x - air experiment designed to simulate or approximate ambient conditions. These have the advantages of being useful for testing mechanisms for individual compounds under conditions more closely resembling urban atmospheres, and are also less sensitive to chamber effects. Incremental reactivity experiments also provide the only meaningful method to test mechanisms for alkanes and other compounds with no internal radical sources, since NO_x - air experiments with these compounds alone are so highly sensitive to chamber effects that they are useless for this purpose.

Three types of incremental reactivity experiments have been carried out at our laboratories. A large number of VOCs have been studied using a highly simplified ROG surrogate and relatively high NO_x conditions (Carter et al., 1993b). These experiments are useful for mechanism evaluation because they are highly sensitive to mechanism differences (Carter et al., 1995a). More recently a smaller number of representative VOCs have been studied using a more realistic ROG surrogate under both relatively high and relatively low NO_x conditions (Carter et al., 1995a). It was found that the updated mechanism performed significantly better in simulating alkene reactivity than SAPRC-90, and that the mechanisms for the branched alkanes had to be refined to be consistent with the new reactivity results, indicating that the estimation methods for this class of compounds needs to be improved. The reactivity experiments also indicated that there are significant reactivity differences among xylene and trimethylbenzene isomers which are not accounted for by either mechanism. This isomeric difference is also seen in single aromatic - NO_x experiments we are now carrying out for the purpose of developing mechanisms for each separate isomer.

Thus the updated mechanism performed at least as well and often much better than the SAPRC-90 mechanism in simulating the reactivity results. This is despite the fact that the major updates made the mechanism more "reactive", and made the bias in simulating mixture runs seen in the evaluation of SAPRC-90 (Carter and Lurmann, 1991) worse. To investigate the possibility that the positive bias may be due to a problem with the chamber effects model, we re-evaluated the radical source assignments used when evaluating the SAPRC-90 mechanism and in the preliminary evaluations of the updated versions. As discussed in detail by Carter et al. (1995b), we found that the previous radical source assignments, which are based on using decay rates of trace compounds to estimate OH radical levels, may be too high, especially for Teflon film chambers. Much better simulations of NO oxidation rates in n-butane - NO_x and CO - NO_x experiments (which are highly sensitive to this parameter) are obtained when the chamber radical input rates are reduced. Using the lower radical input rates derived from n-butane and CO experiments eliminated the positive bias in the simulations of the mixture experiments using the updated mechanism, and caused the SAPRC-90 mechanism to have a very slight bias towards underprediction. This is much more consistent with the expectation based on the basic laboratory data and the evaluations using the incremental reactivity experiments.

To summarize, most updates to the mechanism have tended to make it more "reactive", particularly for the alkenes. Underprediction biases of the earlier mechanism seem to have been masked by use of inappropriately high chamber radical sources when they were evaluated. Note that this includes the evaluation of the RADM-2 mechanism as well (Carter and Lurmann, 1990). However, although the current version of the updated mechanism performs better than previous versions in simulating available chamber data, it still does not account for observed reactivity differences among aromatic isomers. Also, we have recently found that the mechanism tends to underpredict O₃ in aromatic and mixture runs in new Teflon bag chamber experiments using a xenon arc light source, and in new outdoor chamber runs where special procedures were used to characterize the light spectrum and intensity (Carter et al., 1995b). Work in progress consists of documenting and updating the mechanisms for biogenics, conducting experiments to serve as a basis for optimizing mechanisms for individual aromatic isomers, and investigating problems in simulation of new xenon arc and outdoor chamber experiments.

References¹

Carter, W. P. L. (1990): "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds," *Atm. Environ.*, 24A, 481-518.

Carter, W. P. L., and F. W. Lurmann (1990): "Evaluation of the RADM Gas-Phase Chemical Mechanism," Final Report, EPA-600/3-90-001.

¹References dated 1993 or later are available in Portable Document Format (PDF) via anonymous FTP at cert.ucr.edu, subdirectory /pub/carter/pubs. The footnotes below give the file names used. Software for reading or printing PDF files are available by FTP from ftp.adobe.com, subdirectory pub/Adobe/Applications/Acrobat.

- Carter, W. P. L. and F. W. Lurmann (1991): "Evaluation of a Detailed Gas-Phase Atmospheric Reaction Mechanism using Environmental Chamber Data," *Atm. Environ.* 25A, 2771-2806.
- Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1993a)²: "An Experimental and Modeling Study of the Photochemical Ozone Reactivity of Acetone," Final Report to Chemical Manufacturers Association Contract No. KET-ACE-CRC-2.0. December 10.
- Carter, W. P. L., J. A. Pierce, I. L. Malkina, D. Luo and W. D. Long (1993b)³: "Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds," Report to Coordinating Research Council, Project No. ME-9, California Air Resources Board Contract No. A032-0692; South Coast Air Quality Management District Contract No. C91323, United States Environmental Protection Agency Cooperative Agreement No. CR-814396-01-0, University Corporation for Atmospheric Research Contract No. 59166, and Dow Corning Corporation. April 1.
- Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1995a)⁴: "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NO_x," Draft final report to Coordinating Research Council, Inc., Project ME-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323. March 24.
- Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1995b)⁵: "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying Chamber and Light Source," Final report to National Renewable Energy Laboratory Contract XZ-2-102075, Coordinating Research Council, Inc. Project ME-9, California Air Resources Board Contract A032-0692, and South Coast Air Quality Management District Contract C91323. March 26.

²FTP file ACETREPT.PDF.

³FTP file RCT1REPT.PDF.

⁴FTP file RCT2REPT.PDF.

⁵FTP file EXPLREPT.PDF.

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MECHANISM FOR VOC OXIDATION**

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OUTLINE

OVERVIEW OF DEVELOPMENT AND EVALUATION OF
CHEMICAL MECHANISM FOR AIRSHED MODELS

FEATURES OF THE SAPRC-90 DETAILED MECHANISM

EVALUATION OF THE SAPRC-90 MECHANISM

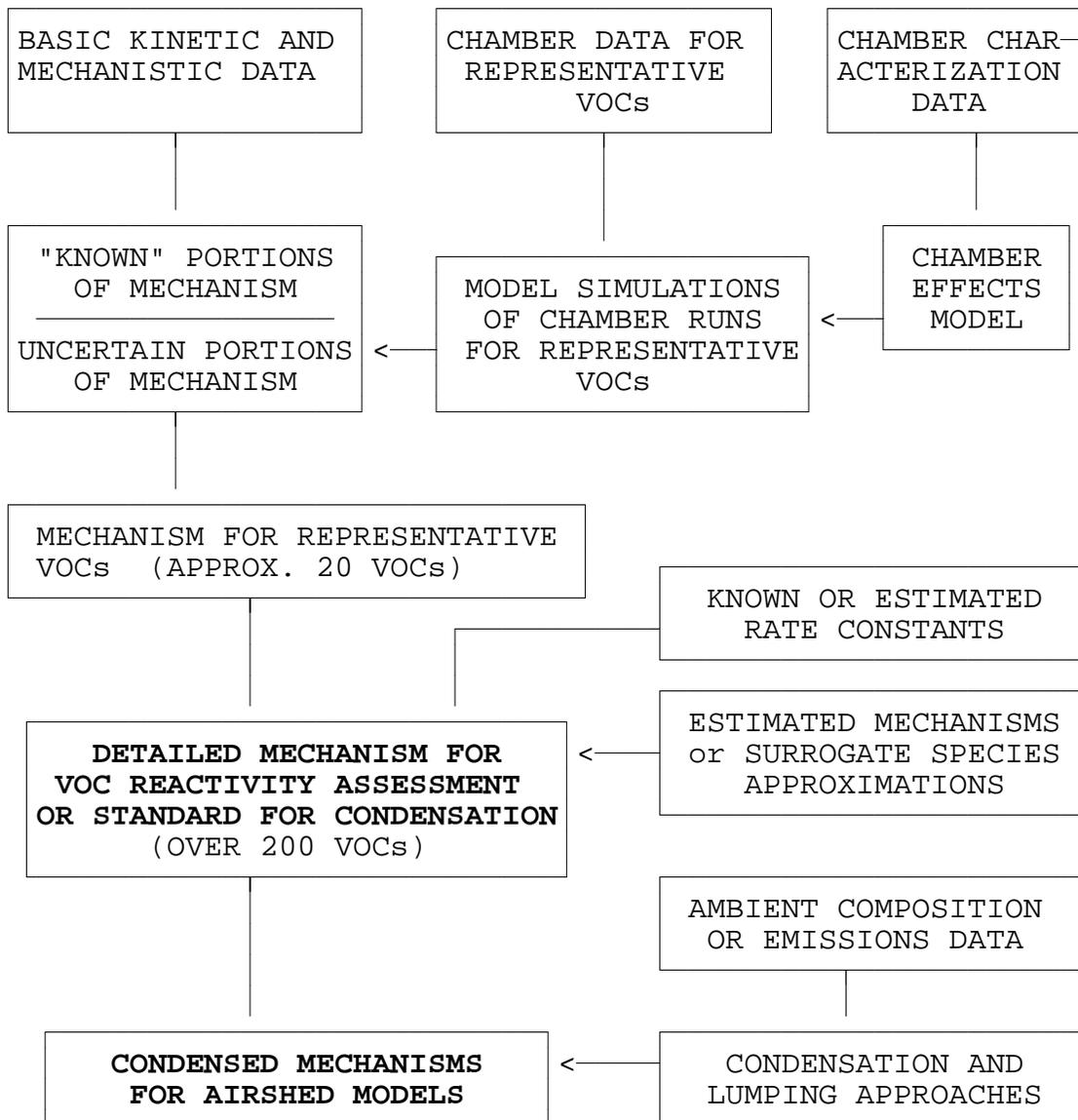
UPDATES TO THE MECHANISM TO DATE

UPDATES TO THE CHAMBER CHARACTERIZATION MODEL

CURRENT STATUS OF EVALUATION OF THE UPDATED
MECHANISM.

CURRENT PROBLEMS AND WORK IN PROGRESS

OVERVIEW OF THE DEVELOPMENT OF CHEMICAL MECHANISMS FOR AIRSHED MODELS



TYPES OF ENVIRONMENTAL CHAMBER EXPERIMENTS USED FOR MECHANISM TESTING

CHARACTERIZATION EXPERIMENTS

- USED TO DERIVE CHAMBER EFFECTS MODEL

SINGLE VOC-NO_x-AIR RUNS:

- MOST STRAIGHTFORWARD TEST OF A VOC'S MECHANISM
- USED FOR MECHANISM DEVELOPMENT
- *NOT A "REALISTIC" ENVIRONMENT*
- *NOT USEFUL FOR VOCs WITH NO RADICAL SOURCES.*

COMPLEX MIXTURE-NO_x-AIR RUNS:

- TESTS MECHANISMS' ABILITY TO SIMULATE PHOTOCHEMISTRY UNDER REALISTIC CONDITIONS.
- *NOT USEFUL FOR MECHANISM DEVELOPMENT.*

REACTIVITY EXPERIMENTS (MIXTURE-NO_x-AIR COMBINED WITH MIXTURE-NO_x-AIR RUNS WITH TEST VOC ADDED):

- CAN TEST MECHANISMS OF SINGLE VOCs UNDER REALISTIC CONDITIONS.
- LESS SENSITIVE TO CHAMBER EFFECTS.
- *NOT SAME AS ATMOSPHERIC REACTIVITY.*

FEATURES OF THE SAPRC-90 DETAILED MECHANISM

LEVEL OF DETAIL:

EXPLICIT REPRESENTATION OF REACTIONS OF:

INORGANICS, FORMALDEHYDE,
ACETALDEHYDE, PROPIONALDEHYDE,
ACETONE,
PAN, PHENOL
GLYOXAL, PAN ANALOGUE FROM GLYOXAL,
METHYL GLYOXAL ETHENE

REPRESENTED BY GENERALIZED REACTIONS WITH INDIVIDUAL KINETIC AND PRODUCT YIELD PARAMETERS:

- GENERALIZED ALKANE/AROMATICS (158)
62 ALKANES, 19 AROMATICS,
77 OTHER SPECIES WHICH REACT ONLY WITH OH
- GENERALIZED ALKENES (44)
37 NON-BIOGENIC 7 BIOGENIC

REPRESENTED USING "SURROGATE SPECIES" APPROACH

- 8 ALDEHYDES (PROPIONALDEHYDE)
- 13 KETONES (METHYL ETHYL KETONE)
- 2 AROMATIC ALDEHYDES (BENZALDEHYDE)
- HIGHER PAN ANALOGUES (PPN)
- GENERALIZED CRESOL (LUMPED "CRES")
- GENERALIZED ALKYL NITRATE (LUMPED "RNO₃")
- TWO GENERALIZED "UNKNOWN AROMATIC RING-FRAGMENTATION PRODUCT" SPECIES.

DERIVATION OF THE SAPRC-90 DETAILED MECHANISM

BASED ON EVALUATIONS OF KINETIC AND MECHANISTIC DATA AS OF THE END OF 1989

PARAMETERS FOR ALKANES DERIVED FROM DETAILED EXPLICIT MECHANISMS COMPUTER-GENERATED USING KINETIC ESTIMATES OF CARTER AND ATKINSON (1985).

PARAMETERS FOR ALKENES BASED ON DATA FOR ETHENE, PROPENE, 1-BUTENE AND 2-BUTENES.

BENZENE, TOLUENE, M-XYLENE,
1,3,5-TRIMETHYLBENZENE, NAPHTHALENE,
DIMETHYLNAPHTHALENE MECHANISMS ADJUSTED TO FIT CHAMBER DATA.

MECHANISMS FOR OTHER AROMATICS DERIVED BY ASSUMING SAME PRODUCT YIELDS AS ONE OF ABOVE.

RADICAL YIELDS FROM $O_3 + 1$ -ALKENE REACTIONS ADJUSTED DOWNWARD BASED ON SIMULATIONS OF CHAMBER DATA.

EVALUATION OF SAPRC-90 MECHANISM

561 EXPERIMENTS FROM FOLLOWING CHAMBERS USED:

SAPRC EC: 5800-LITER TEFLON COATED ALUMINUM, QUARTZ WINDOWS, XENON ARC, 50% RH

SAPRC ITC: ~6000-LITER FEP TEFLON BAG, BLACKLIGHTS, 50% RH

SAPRC OTC: DUAL ~25,000 LITER FEP TEFLON BAG, OUTDOOR, DRY

UNC CHAMBER: DUAL ~150,000 LITER FEP TEFLON ON RIGID FRAMEWORK, OUTDOOR, VARIABLE RH

SINGLE COMPOUND SAPRC EC, ITC RUNS USED FOR DEVELOPMENT AND EVALUATION. MIXTURE, OTC, AND UNC RUNS USED FOR EVALUATION ONLY.

DATA DO NOT GIVE GOOD TESTS FOR ALKANE MECHANISMS.

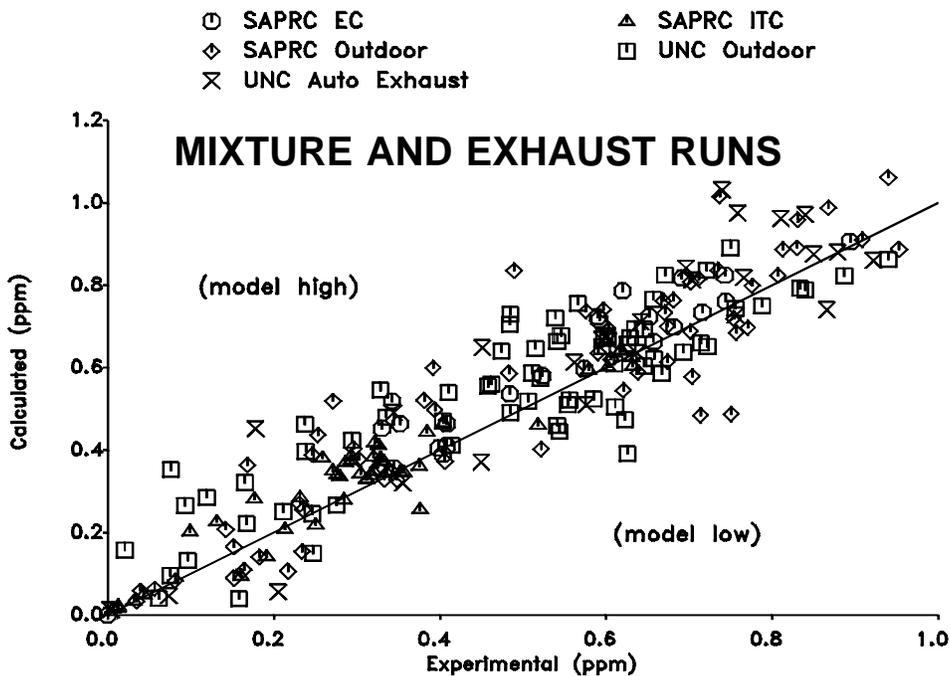
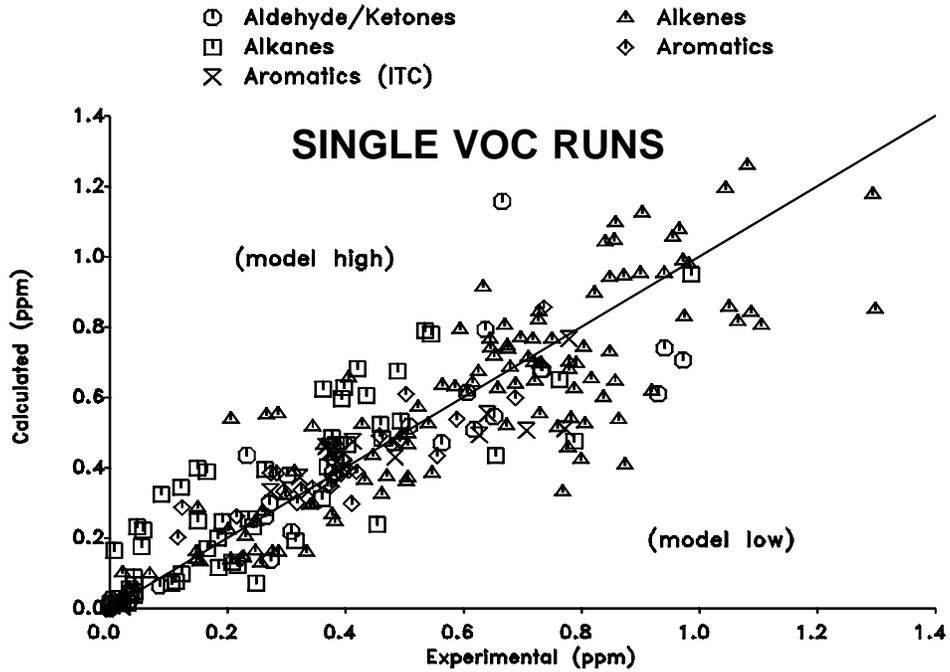
FIT O₃ YIELD, NO OXIDATION RATE WITHIN ±30% FOR 63% OF THE RUNS, WITHIN ±50% FOR 85% OF RUNS.

VARIABLE PERFORMANCE, SOME RUNS POORLY SIMULATED

~15% BIAS FOR OVERPREDICTION IN MIXTURE RUNS.

DATA NOT SUITABLE FOR TESTING ALKANE MECHANISMS

RESULTS OF MODEL SIMULATIONS OF MAXIMUM OZONE IN CHAMBER EXPERIMENTS USING THE SAPRC-90 MECHANISM



CURRENTLY IMPLEMENTED UPDATES TO THE DETAILED SAPRC MECHANISM

UPDATED FORMALDEHYDE CROSS SECTIONS. (SLIGHTLY HIGHER PHOTOLYSIS, SMALL EFFECT ON PREDICTIONS.)

UPDATED KINETICS FOR PAN FORMATION. (GREATER O₃ FORMATION RATES IN MOST EXPERIMENTS.)

SIGNIFICANT INCREASE IN RADICAL YIELDS FROM O₃ + ALKENE REACTIONS BASED ON NEW OH YIELD DATA.

<u>TOTAL RADICALS / REACTION</u>	<u>WAS</u>	<u>NOW</u>
ETHENE	0.12	0.24
MONOSUBSTITUTED ALKENES	0.36	0.8
DISUBSTITUTED INTERNAL ALKENES	0.6	1.2
TRISUBSTITUTED ALKENES	0.5	1.7

RONO₂ YIELDS IN OH REACTIONS INCREASED TO IMPROVE SIMULATIONS OF CHAMBER DATA FOR ISOBUTENE (10%) AND TERPENES (25%).

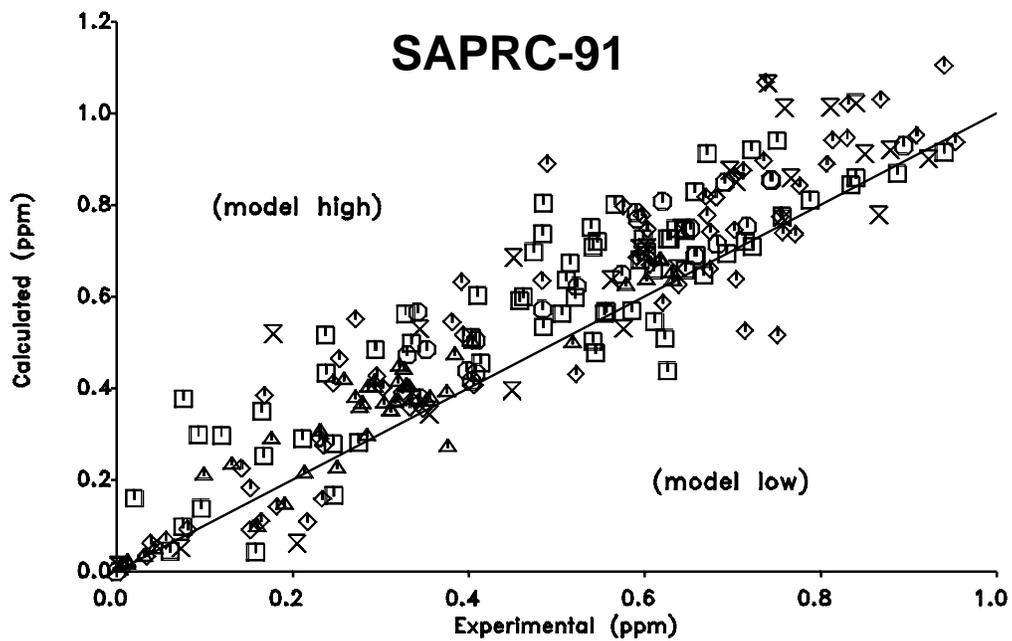
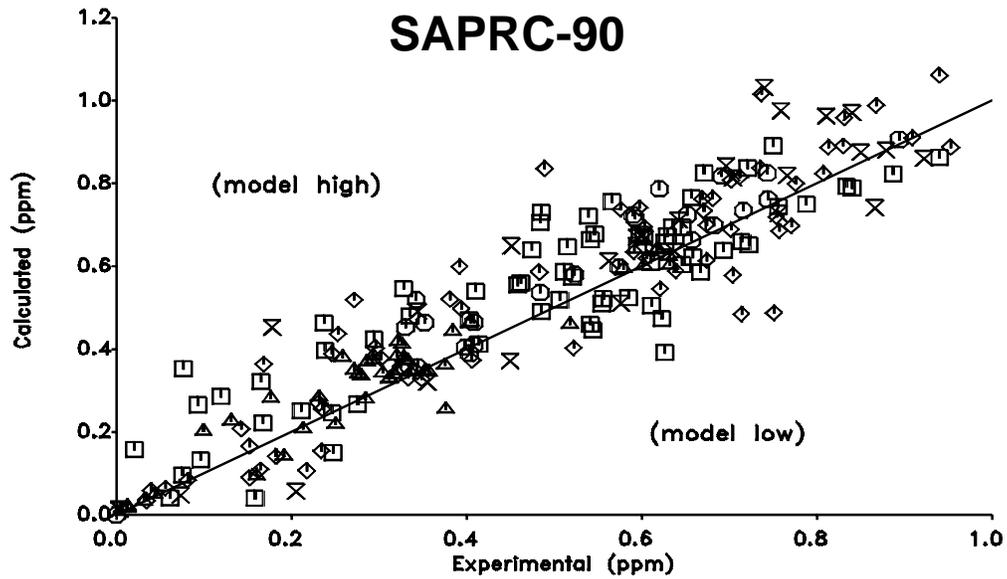
PRELIMINARY DETAILED MECHANISM FOR ISOPRENE ADJUSTED TO FIT SIMULATIONS OF ISOPRENE, METHACROLEIN, MVK EXPERIMENTS.

REFINED MECHANISMS FOR ISOBUTANE AND ISOCTANE TO IMPROVE SIMULATIONS OF REACTIVITY EXPERIMENTS.

NO SIGNIFICANT CHANGE FOR AROMATIC MECHANISMS EXCEPT FOR MORE REASONABLE ACTION SPECTRA FOR UNKNOWN PRODUCTS (ESSENTIALLY NO EFFECT.)

RESULTS OF MODEL SIMULATIONS OF MAXIMUM OZONE IN SURROGATE MIXTURE AND AUTO EXHAUST - NO_x CHAMBER EXPERIMENTS

- SAPRC EC
- ◇ SAPRC Outdoor
- × UNC Auto Exhaust
- △ SAPRC ITC
- UNC Outdoor



INCREMENTAL REACTIVITY EXPERIMENTS

MEASURES EFFECT OF A TEST COMPOUND ON RESULTS OF "BASE CASE" SURROGATE VOC - NO_x - AIR EXPERIMENT

TESTS MECHANISM FOR A VOC UNDER CONDITIONS MORE CLOSELY REPRESENTING URBAN ATMOSPHERES

LESS SENSITIVE TO MODELS FOR CHAMBER EFFECTS — ALLOWS TESTS OF ALKANE MECHANISMS.

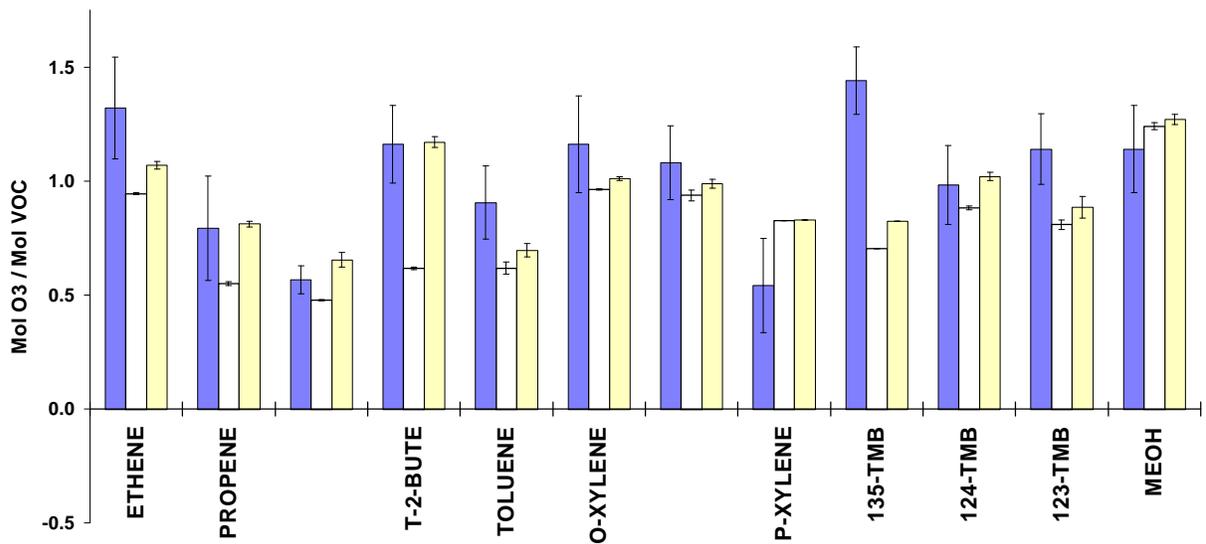
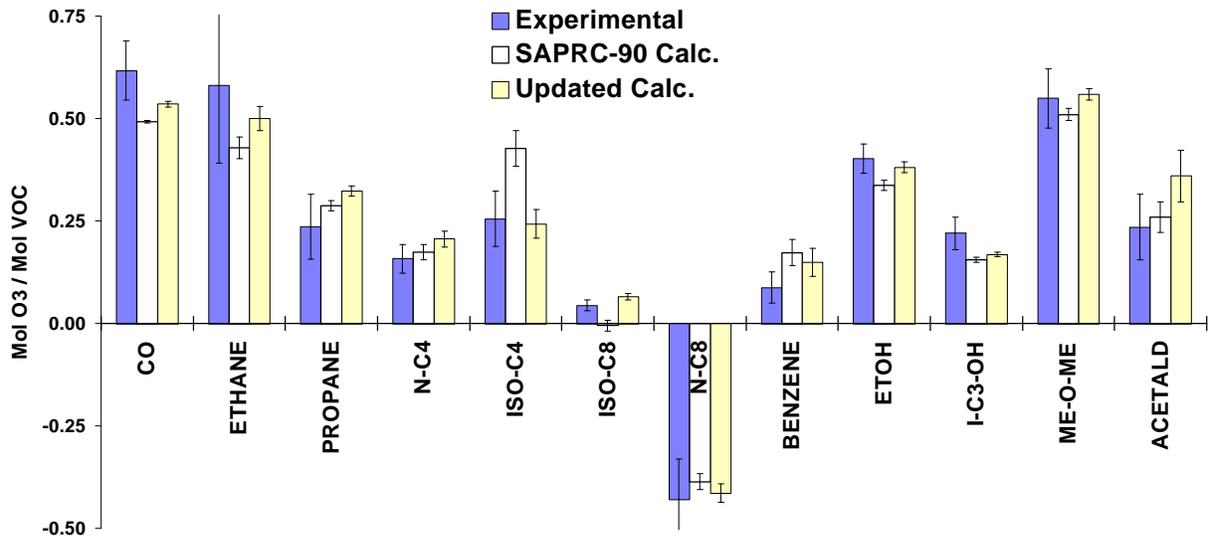
COMPARISON OF EXPERIMENTAL AND CALCULATED **MECHANISTIC REACTIVITY** USED TO ASSESS MECHANISM.

$$\text{MECHANISTIC REACTIVITY} = \frac{\text{CHANGE IN O}_3 \text{ FORMED + NO OXIDIZED CAUSED BY ADDING TEST COMPOUND TO EXPERIMENT}}{\text{AMOUNT OF TEST COMPOUND REACTED IN EXPERIMENT}}$$

REACTIVITY EXPERIMENTS CARRIED OUT:

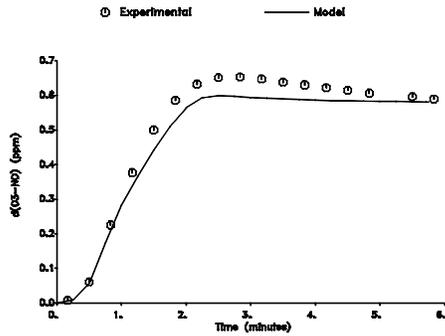
- SIMPLE ROG SURROGATE, HIGH NO_x: MOST SENSITIVE TO VOC DIFFERENCES.
- COMPLEX SURROGATE, HIGH NO_x: CORRELATES WELL WITH ATMOSPHERIC MAXIMUM REACTIVITY.
- COMPLEX SURROGATE, LOW NO_x: TESTS MODEL PREDICTIONS OF LOW NO_x REACTIVITY.

EXPERIMENTAL AND CALCULATED AVERAGE MECHANISTIC REACTIVITIES FOR THE MINI-SURROGATE EXPERIMENTS

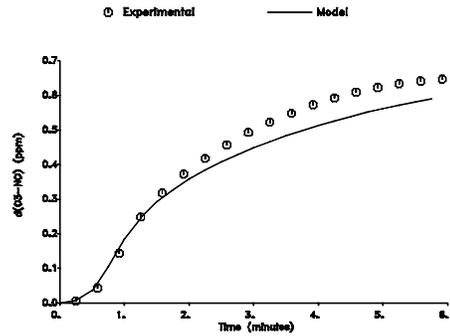


EXPERIMENTAL VS CALCULATED $d(O_3-NO)$ IN AROMATIC ISOMER - NO_x EXPERIMENTS

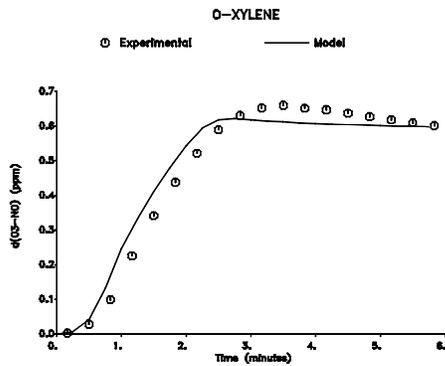
M-XYLENE



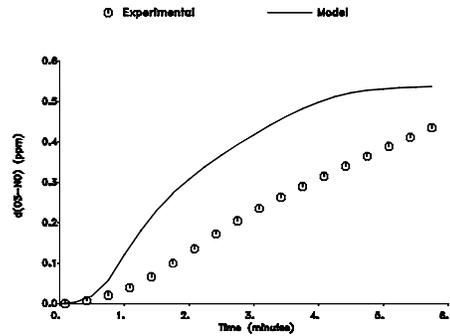
1,3,5-TRIMETHYLBENZENE



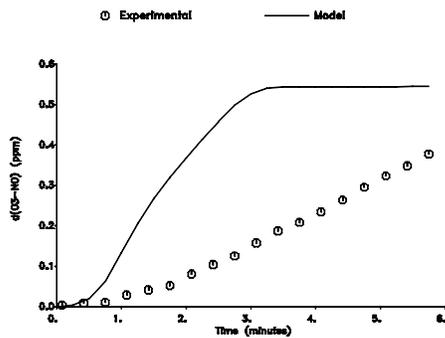
O-XYLENE



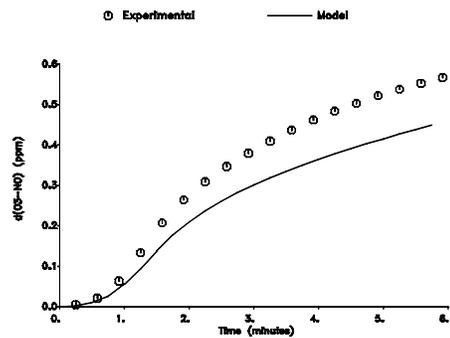
1,2,4-TRIMETHYLBENZENE



P-XYLENE



1,2,3-TRIMETHYLBENZENE



RE-EVALUATION OF CHAMBER RADICAL SOURCE

SIMULATIONS CANNOT FIT CHAMBER DATA UNLESS A SIGNIFICANT CHAMBER RADICAL SOURCE IS ASSUMED.

THE POSITIVE FOUND IN THE EVALUATION OF SAPRC-90 IS MADE WORSE BY MECHANISM UPDATE. BIAS MAY BE DUE TO IMPROPER RADICAL SOURCE ASSIGNMENTS.

FOR SAPRC CHAMBERS, SAPRC-90 EVALUATION USED RADICAL SOURCES DERIVED FROM DECAY RATES OF TRACE (~10 PPB) ALKENES IN NO_x - AIR EXPERIMENTS.

NO AND O₃ IN N-BUTANE - NO_x AND CO - NO_x ARE BETTER FIT WITH LOWER RADICAL SOURCE.

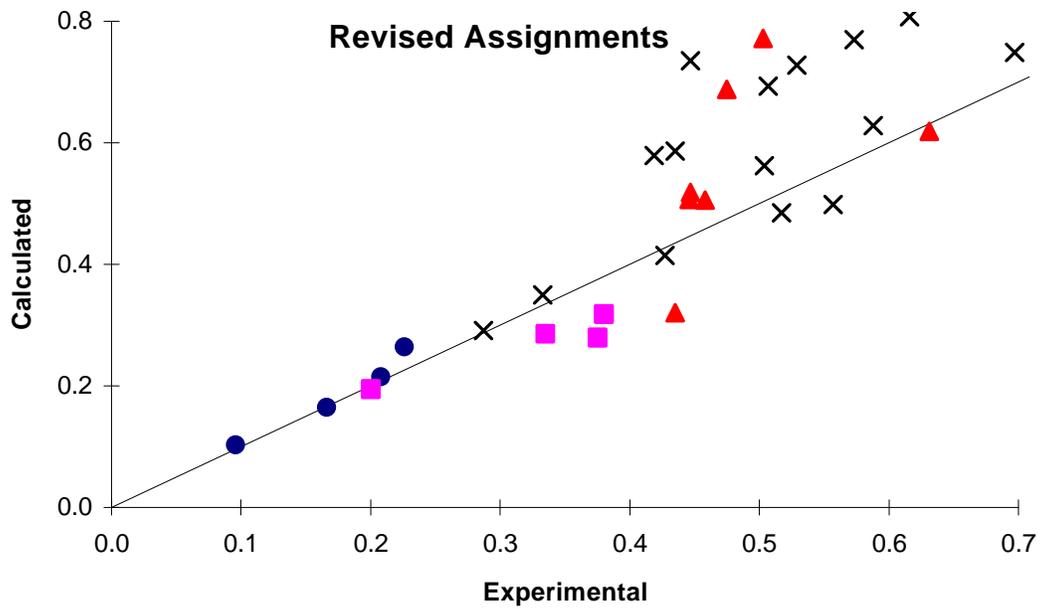
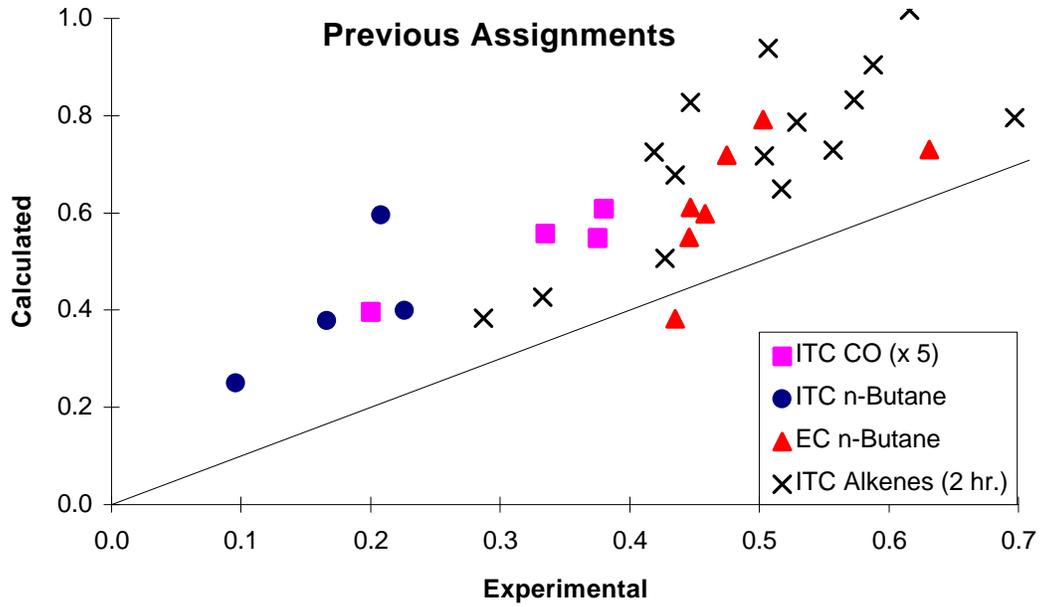
- SAPRC ITC: FACTOR OF 2 OR GREATER REDUCTION, DEPENDING ON REACTION BAG
- SAPRC EC: ~25% REDUCTION

MIGHT BE AN ARTIFACT AFFECTING DECAY RATES OF TRACE PPB) ALKENES IN FEP TEFLON REACTION BAGS.

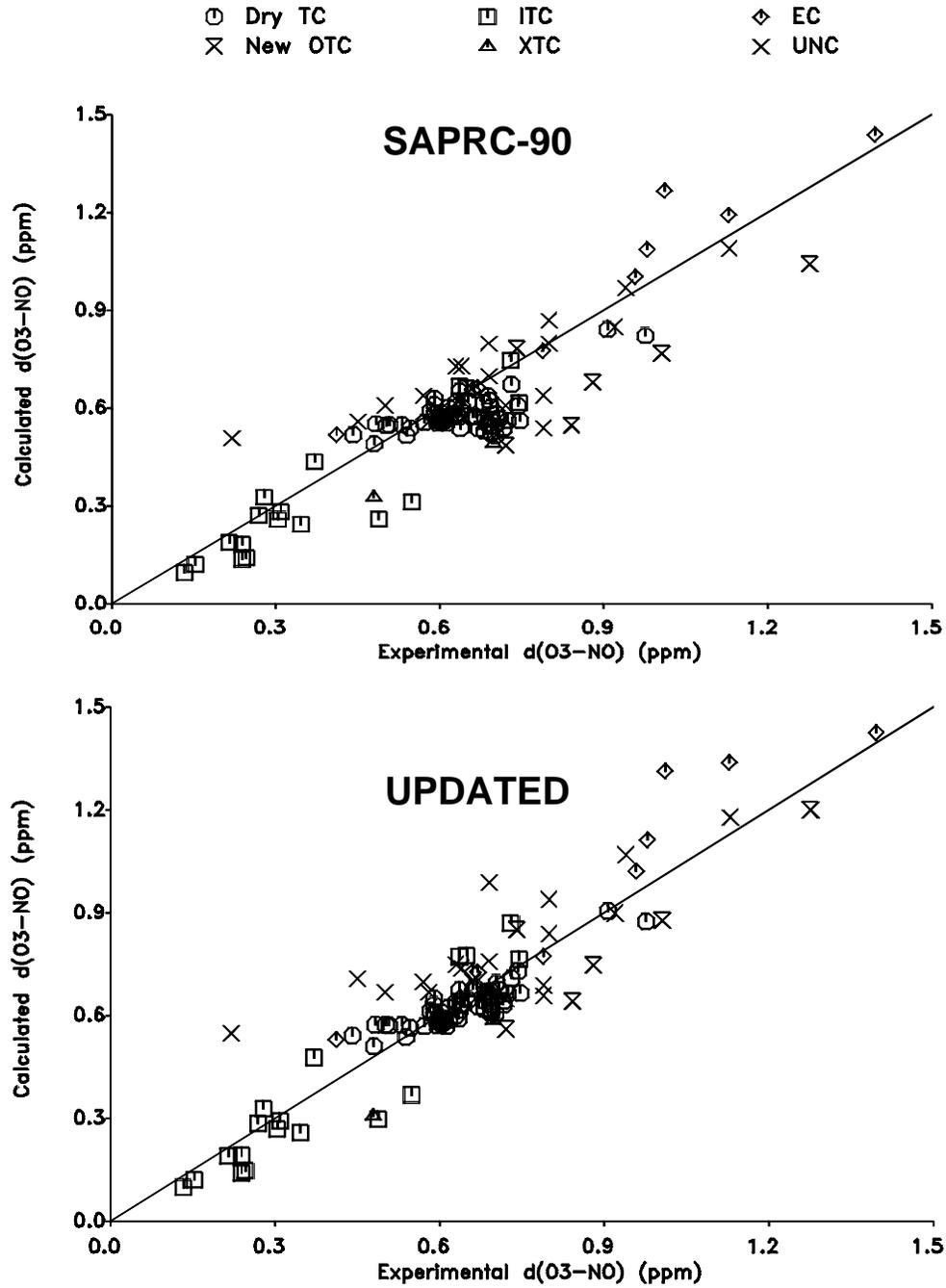
USE OF N-BUTANE-NO_x AND CO-NO_x EXPERIMENTS IS NOW THE PREFERRED METHOD TO DERIVE RADICAL SOURCE.

- REMOVES MODEL BIAS FOR UPDATED MECHANISM
- MORE CONSISTENT RESULTS AMONG DIFFERENT REACTION BAGS AND CHAMBERS.

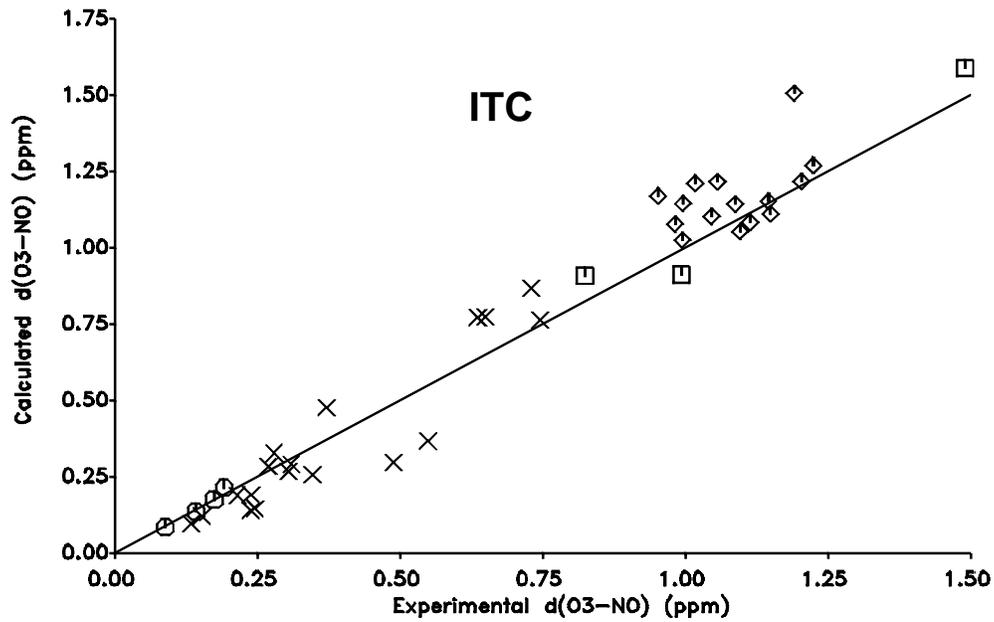
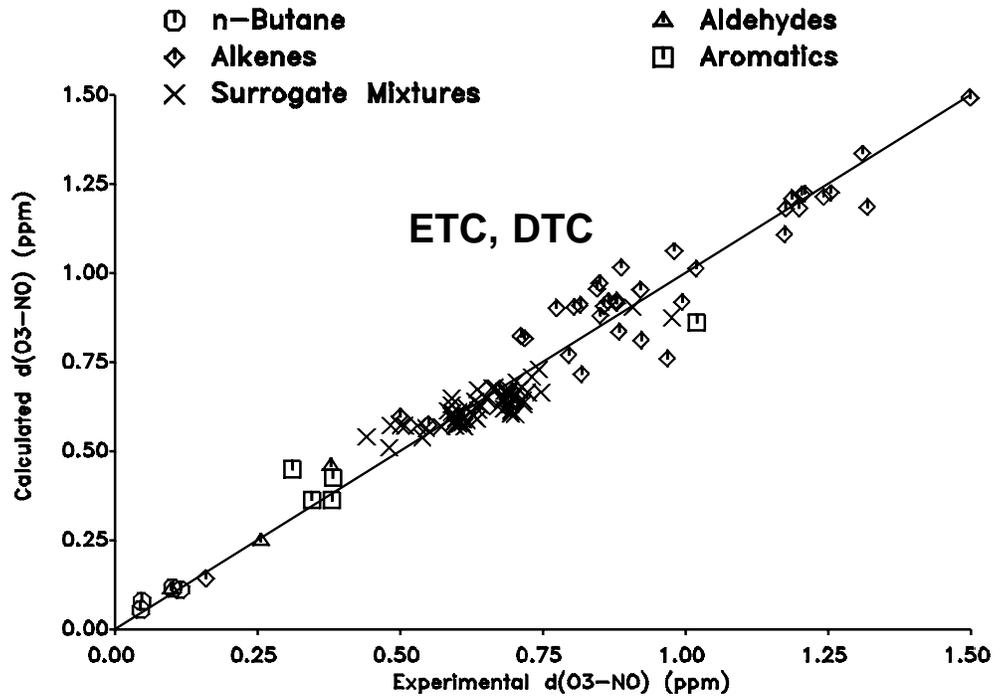
EFFECT OF RADICAL SOURCE RE-ASSIGNMENTS ON SIMULATIONS OF NO OXIDIZED + OZONE FORMED IN SELECTED ITC AND EC RUNS



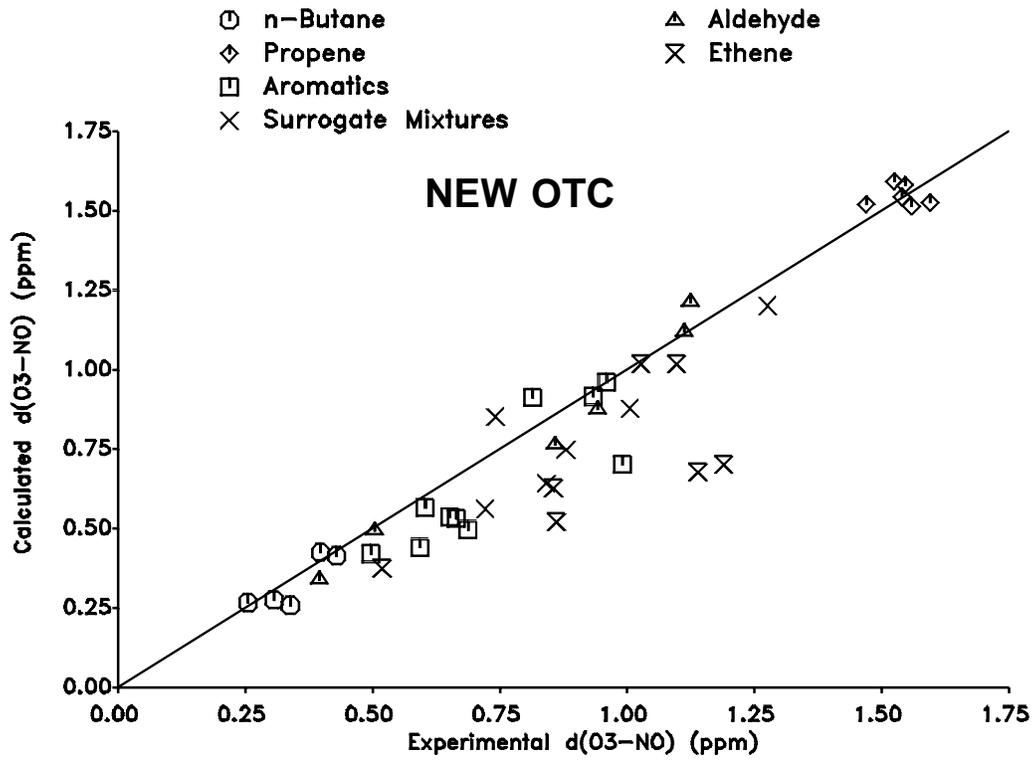
RESULTS OF MODEL SIMULATIONS OF MAXIMUM OZONE IN MIXTURE - NO_x CHAMBER EXPERIMENTS USING THE UPDATED CHAMBER EFFECTS ASSIGNMENTS



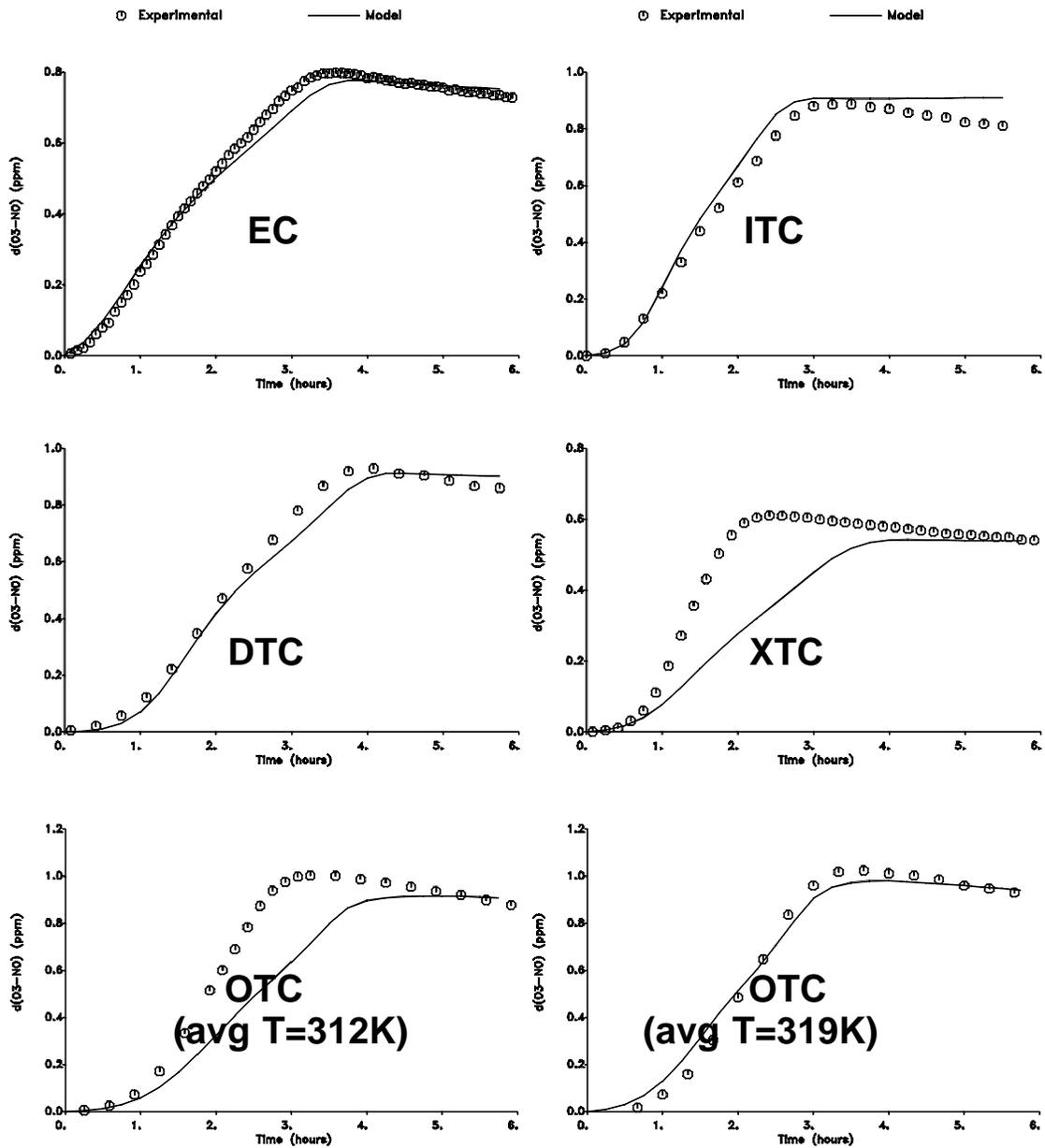
SIMULATIONS OF 5-HOUR $\Delta([O_3]-[NO])$ USING THE UPDATED SAPRC MECHANISM



SIMULATIONS OF 5-HOUR $\Delta([O_3]-[NO])$ USING THE UPDATED SAPRC MECHANISM



EFFECT OF CHAMBER ON SIMULATIONS OF TOLUENE - NO_x EXPERIMENTS USING THE UPDATED MECHANISM



SUMMARY

MOST UPDATES HAVE TENDED TO MAKE THE MECHANISM MORE "REACTIVE", PARTICULARLY FOR ALKENES.

HIGH RADICAL SOURCES MAY HAVE MASKED UNDERPREDICTION BIASES IN EARLIER EVALUATIONS.

WITH NEW RADICAL SOURCE ASSIGNMENTS, UPDATES REDUCE OVERALL BIASES IN CHAMBER SIMULATIONS.

THE CURRENT MECHANISM DOES NOT ACCOUNT FOR REACTIVITY DIFFERENCES IN AROMATIC ISOMERS

THE CURRENT MECHANISM TENDS TO UNDERPREDICT O₃ IN AROMATIC AND MIXTURE RUNS IN THE NEW SAPRC XENON ARC TEFLON CHAMBER AND IN NEW OTC RUNS.

ABILITY TO SIMULATE ISOPRENE AND TERPENE CHAMBER DATA HAS BEEN IMPROVED.

WORK IN PROGRESS:

- DOCUMENTING UPDATED ISOPRENE AND TERPENE MECHANISMS. CONDENSING ISOPRENE MECHANISM.
- EXPERIMENTS UNDERWAY SO AROMATIC ISOMER MECHANISMS CAN BE SEPARATELY OPTIMIZED.
- PROBLEMS IN SIMULATIONS OF NEW XTC AND OTC RUNS ARE BEING INVESTIGATED.