EVALUATION OF CHEMICAL MECHANISMS FOR ATMOSPHERIC OZONE FORMATION FROM BIOGENIC COMPOUNDS

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RIVERSIDE, CA

Presented at the
A&WMA International Conference on

REGIONAL PHOTOCHEMICAL MEASUREMENT AND MODELING STUDIES

November 8-12, 1993
San Diego, California

BACKGROUND

OZONE IS FORMED FROM THE INTERACTIONS OF VOLATILE ORGANIC COMPOUNDS (VOCs) WITH NO_x IN THE ATMOSPHERE.

BIOGENIC SOURCES ARE A NON NEGLIGIBLE CONTRIBUTOR TO THE VOC EMISSIONS IN MANY AREAS WHERE OZONE EXCEEDS AIR QUALITY STANDARDS.

MODELS MAY NOT CORRECTLY PREDICT EFFECTS OF OZONE CONTROL STRATEGIES IF THEY DO NOT REPRESENT REACTIONS OF BIOGENIC COMPOUNDS APPROPRIATELY.

A VARIETY BIOGENIC VOCs HAVE BEEN IDENTIFIED, BUT ISOPRENE AND THE MONOTERPENES ARE BELIEVED TO BE THE MOST IMPORTANT.

ISOPRENE AND THE MONOTERPENES ARE AMONG THE MOST RAPIDLY REACTING OF THE EMITTED VOC SPECIES.

ENVIRONMENTAL CHAMBER EXPERIMENTS PROVIDE THE ONLY MEANS TO TEST WHETHER THE MODELS CAN CORRECTLY PREDICT HOW BIOGENIC VOCs AFFECT OZONE.

BACKGROUND
(CONTINUED)

ISOPRENE HAVE BEEN EXTENSIVELY STUDIED, BUT ITS MECHANISM IS COMPLEX AND HAS UNCERTAINTIES.

- REACTION WITH OH, O_3, AND NO_3 CAN BE IMPORTANT IN THE ATMOSPHERE. REACTION WITH $O(^3P)$ IS NON-NEGLIGIBLE IN MOST CHAMBER EXPERIMENTS.
- KNOWN PRODUCTS ACCOUNT FOR ONLY ~60% OF THE OH REACTION ROUTES.
- MAJOR UNCERTAINTIES IN THE O_3, NO_3, AND $O(^3P)$ REACTIONS AFFECT PREDICTIONS OF O_3 FORMATION.

RATE CONSTANTS FOR TERPENE REACTIONS ARE KNOWN, BUT MECHANISMS ARE HIGHLY UNCERTAIN. PRODUCT STUDIES GIVE POOR CARBON BALANCES.

MOST AIRSHED MODELS INCLUDE SEPARATE REACTIONS FOR ISOPRENE, BUT TERPENES ARE USUALLY LUMPED WITH OTHER ALKENES.

ISOPRENE MECHANISMS HAVE BEEN TESTED TO VARYING DEGREES USING ENVIRONMENTAL CHAMBER DATA, BUT NOT USING THE FULL DATA BASE.

INSUFFICIENT CHAMBER DATA HAS BEEN AVAILABLE TO DEVELOP AND TEST MECHANISMS FOR TERPENES.

OBJECTIVES OF THIS STUDY

ISOPRENE

DEVELOP A DETAILED MECHANISM FOR ISOPRENE AND ITS PRODUCTS REFLECTING CURRENTLY AVAILABLE DATA.

CONDUCT CHAMBER EXPERIMENTS USEFUL FOR THE DEVELOPMENT AND EVALUATION OF THIS MECHANISM.

COMPARE THE PERFORMANCE OF THE VARIOUS PROPOSED ISOPRENE MECHANISMS IN SIMULATING CHAMBER DATA.

DETERMINE THE BEST METHOD TO REPRESENT ISOPRENE IN AIRSHED MODELS.

TERPENES

CONDUCT CHAMBER EXPERIMENTS TO DEVELOP AND TEST MECHANISMS FOR O_3 FORMATION FROM TERPENES.

USE THESE DATA TO EVALUATE ALTERNATIVE METHODS FOR REPRESENTING TERPENES IN AIRSHED MODELS.

DETERMINE THE BEST METHOD TO REPRESENT TERPENES IN AIRSHED MODELS.

SUMMARY OF ISOPRENE MECHANISMS

CARBON BOND IV (CB-4)

- EXPLICIT REPRESENTATION OF INITIAL REACTIONS.
- ISOPRENE PRODUCTS REPRESENTED BY MIX OF CB-4 MODEL SPECIES (ETHENE, ALD2, ETC.)
- PRODUCT MIX ADJUSTED USING MODEL SIMULATION OF UNC OUTDOOR CHAMBER RUNS.

SAPRC-90 (CARTER, 1990)

- EXPLICIT REPRESENTATION OF INITIAL REACTIONS.
- MECHANISM AND PRODUCTS OF THESE REACTIONS. REPRESENTED SAME WAY AS FOR OTHER 1-ALKENES
- NOT ADJUSTED TO FIT EXISTING CHAMBER RUNS.

RADM-2

- ESSENTIALLY THE SAME APPROACH AS SAPRC-90.

PAULSON AND SEINFELD

- EXPLICIT REPRESENTATION OF THE MAJOR REACTIONS AND PRODUCTS.
- PRODUCT YIELDS AND MECHANISM EVALUATION BASED ON CALTECH OUTDOOR CHAMBER RUNS.

NEW DETAILED MECHANISM (THIS WORK)

- EXPLICIT REPRESENTATION OF MAJOR REACTIONS AND PRODUCTS.
- SOME DIFFERENCES FROM PAULSON AND SEINFELD.
- UNCERTAIN PARAMETERS ADJUSTED TO FIT INDOOR CHAMBER RUNS.

CHAMBER DATA BASE FOR EVALUATING ISOPRENE MECHANISMS.

UNC OUTDOOR CHAMBER (UNC)

- ~150,000-LITER RIGID CHAMBER CONSTRUCTED OF 5-MIL FEP TEFLON FILM
- USED FOR **ISOPRENE - NO_x** RUNS.

SAPRC EVACUABLE CHAMBER (EC)

- ~6000-LITER CHAMBER WITH TEFLON-COATED WALLS AND QUARTZ WINDOWS
- XENON ARC LIGHT SOURCE
- USED FOR **ISOPRENE - NO_x, METHACROLEIN - NO_x,** AND **MVK - NO_x** RUNS.

SAPRC TEFLON / BLACKLIGHT CHAMBERS (ITC, ETC, DTC)

- 3000-6000 LITER 2-MIL FEP TEFLON REACTION BAGS
- BLACKLIGHT LIGHT SOURCE
- USED FOR **ISOPRENE - NO_x, METHACROLEIN - NO_x,** AND **MVK - NO_x** RUNS.
- ALSO USED FOR **ISOPRENE INCREMENTAL REACTIVITY** EXPERIMENTS.
- NOT USED PREVIOUSLY FOR MODEL EVALUATION.

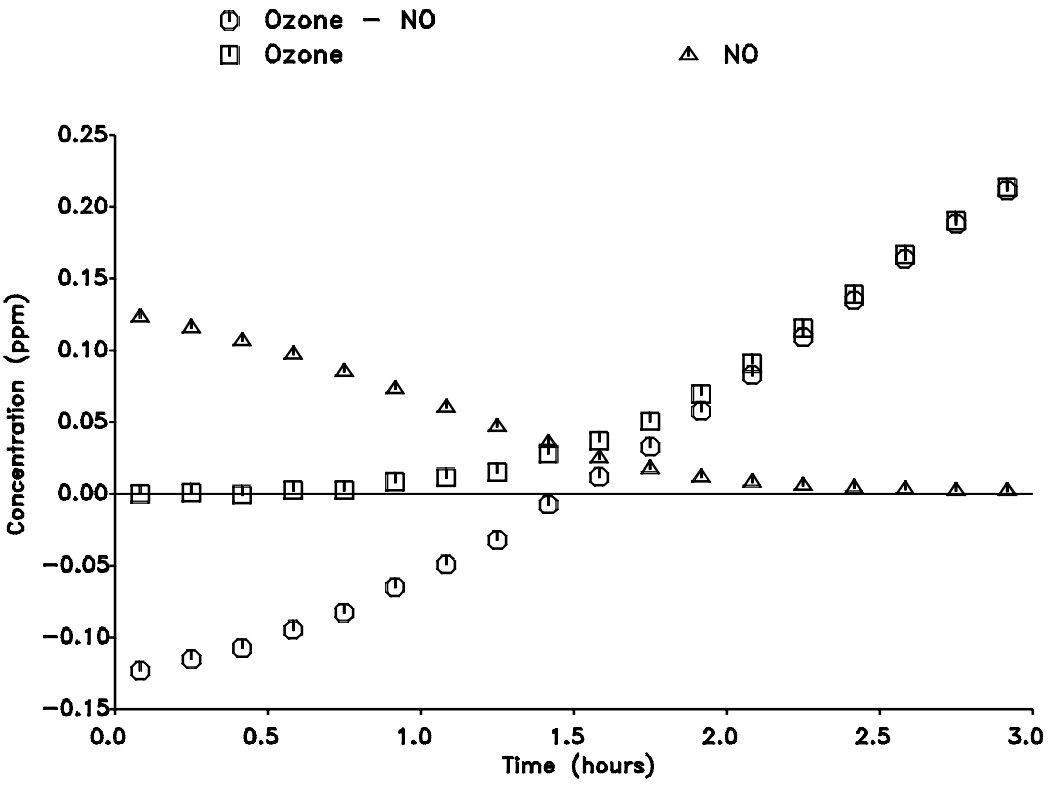
SAPRC XENON ARC TEFLON CHAMBER (XTC)

- 6000-LITER 2-MIL FEP TEFLON REACTION BAG
- XENON ARC LIGHT SOURCE
- USED FOR **ISOPRENE - NO_x** AND **METHACROLEIN - NO_x** RUNS.
- NOT USED PREVIOUSLY FOR MODEL EVALUATION.

CHANGE IN O_3 - NO IS A USEFUL MEASURE OF OZONE REACTIVITY IN AN EXPERIMENT

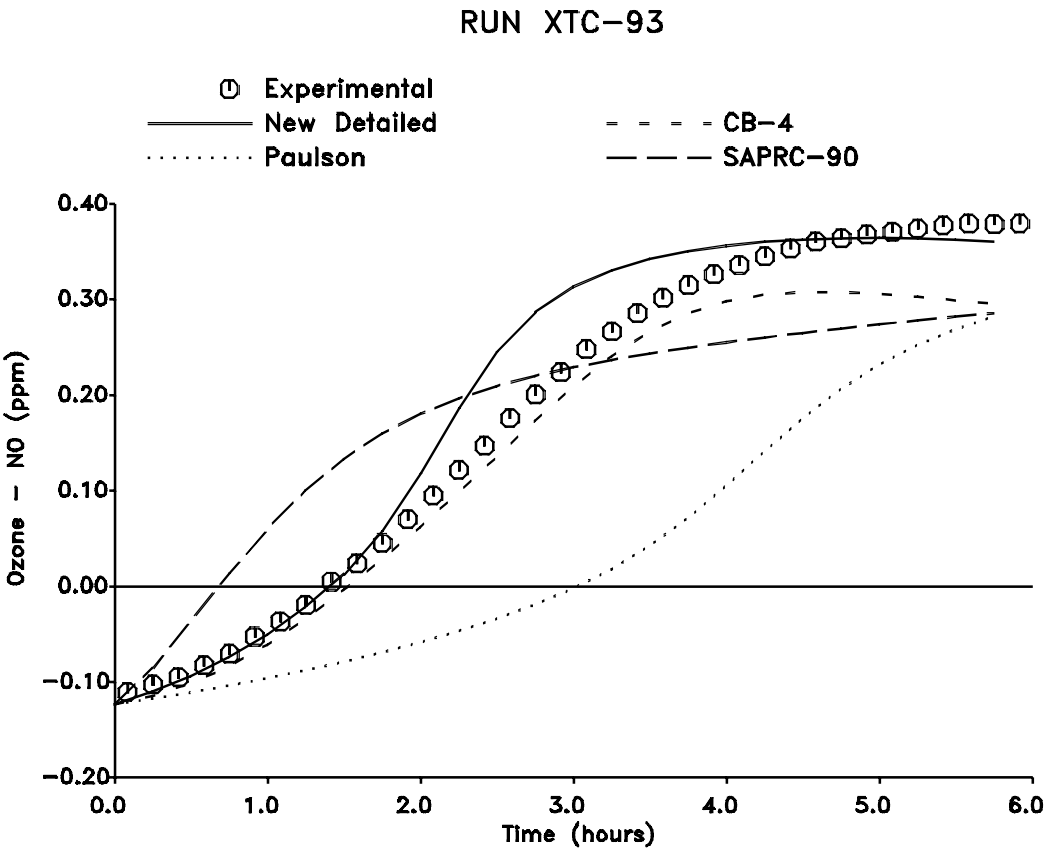
PROCESSES CAUSING O_3 FORMATION IS MANIFESTED BY NO CONSUMPTION IN THE INITIAL STAGES OF THE RUN.

FIT OF MODEL TO O_3 - NO SHOWS HOW WELL IT SIMULATES THESE PROCESSES DURING BOTH PERIODS.



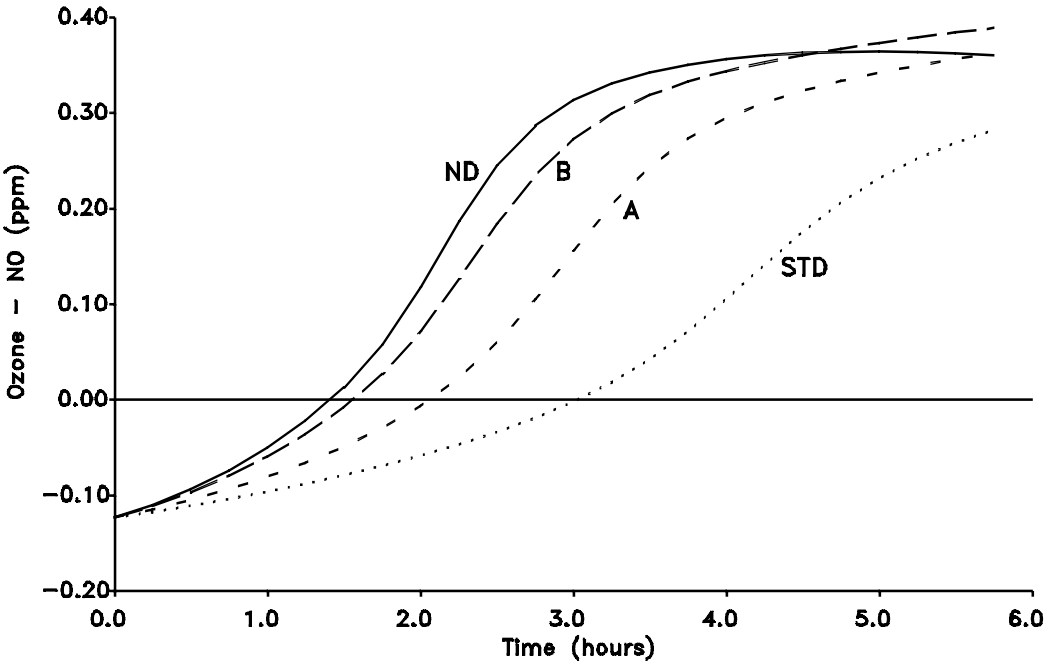
EXAMPLES OF MODEL PREDICTIONS OF NO CONSUMED + O_3 FORMED IN ISOPRENE - NO_x EXPERIMENTS

(RUN USING XENON ARC LIGHT SOURCE)



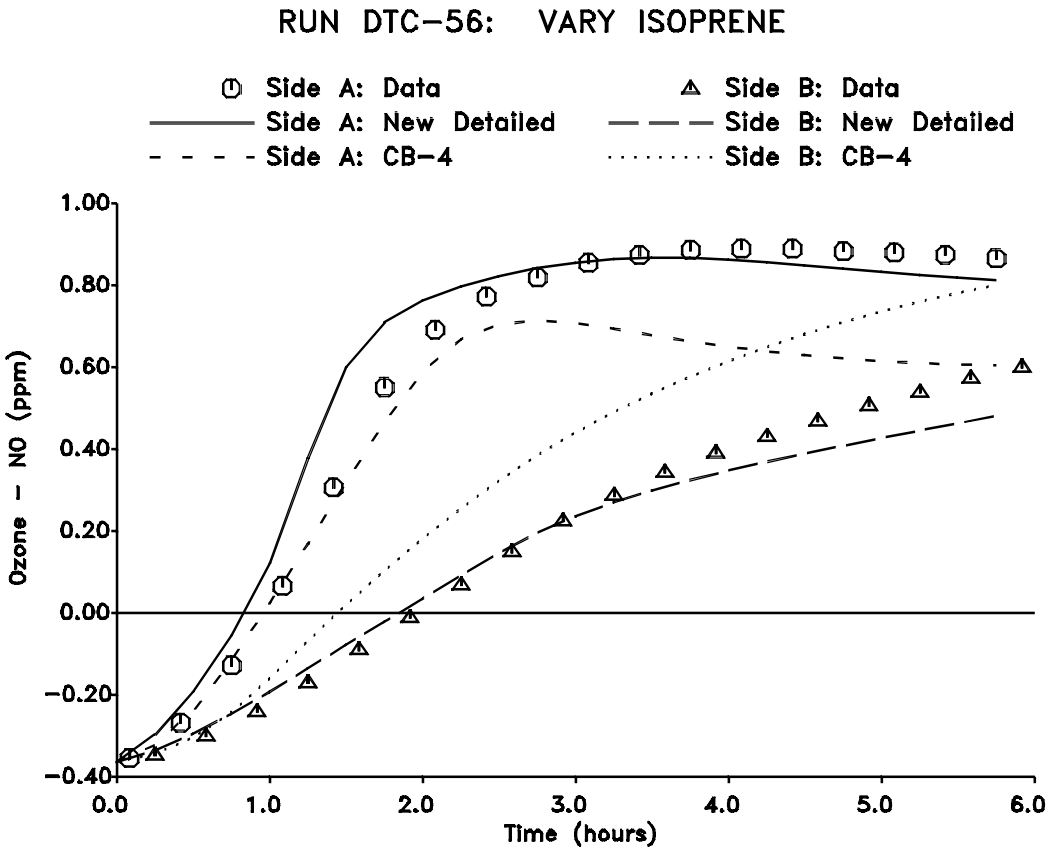
INVESTIGATION OF CAUSES OF THE UNDERPREDICTION OF REACTIVITY BY THE PAULSON AND SEINFELD MECHANISM

ND = NEW DETAILED MECHANISM
STD = UNADJUSTED PAULSON MECHANISM
A = ALKYL NITRATE IN OH REACTION REDUCED
B = SAME AS A, PLUS RADICAL YIELD IN $O(^3P)$ REACTION INCREASED.

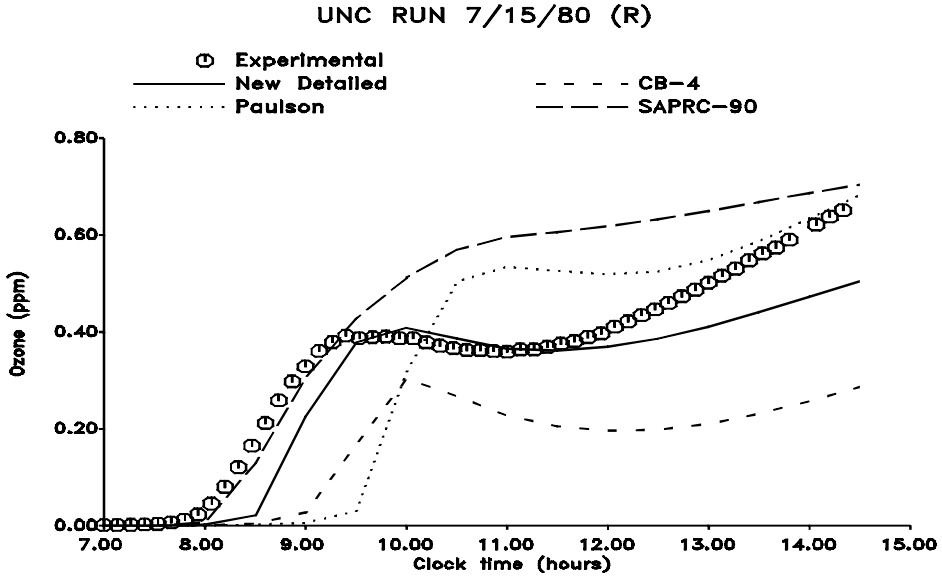


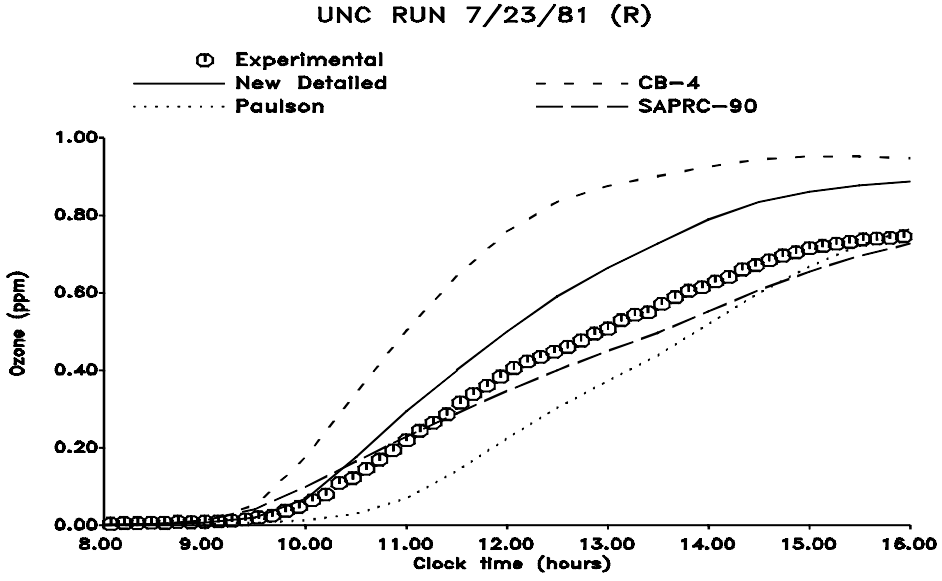
EXAMPLES OF MODEL PREDICTIONS OF NO CONSUMED + O_3 FORMED IN ISOPRENE - NO_x EXPERIMENTS

EFFECT OF VARYING ADDED ISOPRENE (RUN IN BLACKLIGHT / TEFLON CHAMBER)

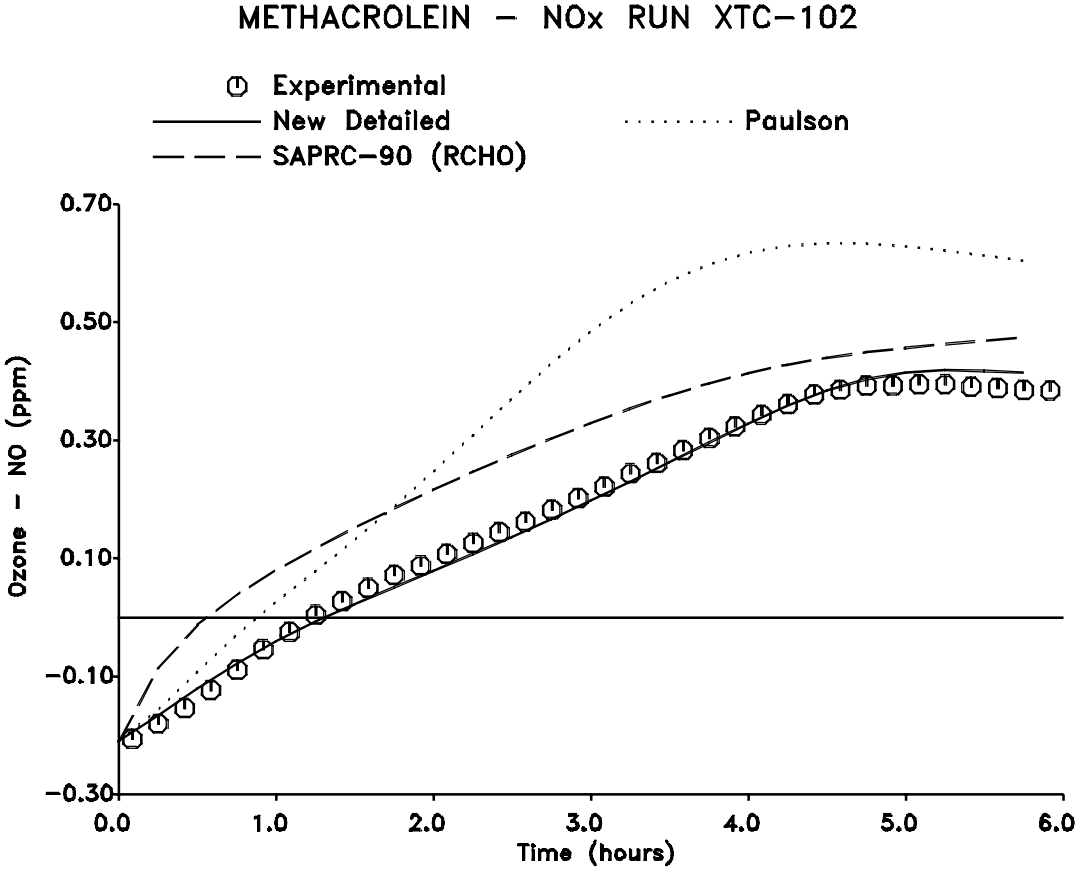


EXAMPLES OF MODEL PREDICTIONS OF O_3 FORMED IN ISOPRENE - NO_x EXPERIMENTS IN THE UNC OUTDOOR CHAMBER





EXAMPLES OF MODEL PREDICTIONS OF NO CONSUMED + O_3 FORMED IN A METHACROLEIN - NO_x EXPERIMENT



UNCERTAINTIES IN ISOPRENE - NO_x MECHANISM WHICH AFFECT MODEL SIMULATIONS OF CHAMBER EXPERIMENTS

NITRATE YIELD IN OH REACTION.

- PAULSON AND SEINFELD USE 14% BASED ON ESTIMATES FROM IR BANDS IN A PRODUCT STUDY. THIS CAUSES UNDERPREDICTION OF REACTIVITY.
- NEW DETAILED MECHANISM USES 8% TO FIT DATA

RADICAL YIELDS IN $O(^3P)$ REACTION. VALUE ASSUMED IN MODEL AFFECTS NITRATE YIELD WHICH BEST FITS DATA.

RADICAL YIELDS IN NO_3 REACTION [DECOMPOSITION VS O_2 REACTION OF $RCH(O\cdot)CH_2ONO_2$].

RATE CONSTANT FOR O_3 REACTION WITH PREDICTED C_5 PRODUCTS [$HOCH_2CH=C(CH_3)CHO$, $(HOCH_2)_2C=CHCHO$, $HOCH_2C(CH_3)=CHCHO$].

QUANTUM YIELDS IN PHOTOLYSES OF UNSATURATED OXYGENATED PRODUCTS[1].

RADICAL YIELDS IN O_3 REACTION WITH UNSATURATED OXYGENATED PRODUCTS[1].

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[1] ADJUSTED TO FIT RESULTS OF METHACROLEIN AND MVK - NO_x CHAMBER RUNS.

SUMMARY OF RESULTS OF EVALUATION OF ISOPRENE MECHANISMS

THERE ARE TOO MANY UNCERTAIN PARAMETERS TO BE DETERMINED BY MODEL SIMULATIONS OF CHAMBER RUNS.

NO MECHANISM CAN FIT ALL THE CHAMBER DATA NO MATTER HOW MANY PARAMETERS ARE ADJUSTED.

THE PAULSON MECHANISM UNDERPREDICTED RATES OF O_3 FORMATION IN ALL CHAMBER RUNS WE MODELED. (THE CALTECH CHAMBER DATA WAS NOT MODELED).

THE CARBON BOND MECHANISM GIVES GOOD FITS TO SOME EXPERIMENTS, BUT DOES NOT PREDICT HOW O_3 CHANGES WITH VARYING REACTANT CONCENTRATIONS.

THE APPROXIMATE REPRESENTATION USED IN THE SAPRC-90 AND RADM-2 MECHANISMS PERFORM POORLY IN SIMULATING MOST CHAMBER RUNS.

THE NEW DETAILED MECHANISM HAS BEST OVERALL PERFORMANCE, BUT OVERPREDICTS O_3 FORMATION RATES IN RUNS WITH XENON ARC LIGHT SOURCES.

METHODS TO CONDENSE THE DETAILED MECHANISM FOR USE IN AIRSHED MODELS ARE BEING INVESTIGATED.

ACKNOWLEDGEMENTS

THIS WORK WAS FUNDED PRIMARILY BY

U. S. ENVIRONMENTAL PROTECTION AGENCY
COOPERATIVE AGREEMENT CR817773-01-0

ADDITIONAL FUNDING FOR ISOPRENE EXPERIMENTS
WAS PROVIDED BY

SOUTHERN OXIDANT STUDY
UCAR CONTRACT NO. 59166