ENVIRONMENTAL CHAMBER STUDIES OF ATMOSPHERIC OZONE FORMATION FROM SELECTED BIOGENIC COMPOUNDS

by

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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.

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 HAVE BEEN AVAILABLE TO DEVELOP AND TEST MECHANISMS FOR TERPENES.

OBJECTIVES OF THIS STUDY

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.

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.

DETERMINE THE BEST METHOD TO REPRESENT ISOPRENE IN AIRSHED MODELS.

REPRESENTATIVE MONOTERPENES STUDIED

α-PINENE

Δ^3-CARENE

β-PINENE

SABINENE

RELEVANT KINETIC AND MECHANISTIC INFORMATION CONCERNING THE REPRESENTATIVE TERPENES

	α-PINENE	Δ^3-CARENE	SABINENE	β-PINENE
OH REACTION				
k(OH) x 10^{11}	5.4	8.0	11.7	7.9
IDENTIFIED PRODUCTS	~30%	~35%	~20%	~30%
O_3 REACTION				
k(O_3) x 10^{17}	8.7	3.7	8.6	1.5
OH YIELD	0.85	1.06	0.26	0.35
IDENTIFIED PRODUCTS	~20	<10%	~50%	~25%

Notes

- T=298°K rate constants in units of cm^3 $molec^{-1}$ sec^{-1}
- Observed products are those predicted from general alkene mechanisms.
- Data from review by Atkinson (J. Phys. Chem. Ref. Data, in press, 1994)

METHODS USED TO REPRESENT TERPENE REACTIONS IN AIRSHED MODELS

CARBON BOND 4

- REPRESENTED BY CARBON BOND SPECIES:
  - α-PINENE: 0.5 OLE + 1.5 ALD2 + 6 PAR
  - β-PINENE: OLE + 8 PAR
  - SABINENE: OLE + 8 PAR
- α-PINENE BASED ON MODEL SIMULATIONS OF UNC CHAMBER RUNS.

"LUMPED MOLECULE" MECHANISMS (RADM-2, LCC, ETC)

- LUMPED WITH HIGHER ALKENES WHOSE MECHANISM ARE BASED ON THAT FOR 2-BUTENES.

SAPRC-90 "DETAILED" MECHANISM (CARTER, 1990)

- INITIAL REACTIONS WITH OH, O_3, NO_3, AND $O(^3P)$ REPRESENTED EXPLICITLY.
- GENERAL ALKENE MECHANISMS USED FOR SUBSEQUENT REACTIONS AND PRODUCTS.

PRELIMINARY UPDATED SAPRC MECHANISM

- SAME AS ABOVE, BUT WITH RADICAL YIELDS IN O_3 REACTION INCREASED TO BE CONSISTENT WITH MEASURED OH YIELDS.

AVAILABLE TERPENE - NO_x ENVIRONMENTAL CHAMBER DATA

UNC OUTDOOR CHAMBER (PREVIOUS STUDIES)

α-PINENE

BLACKLIGHT TEFLON CHAMBERS (THIS WORK)

α-PINENE
β-PINENE
Δ^3-CARENE
SABINENE
D-LIMONENE

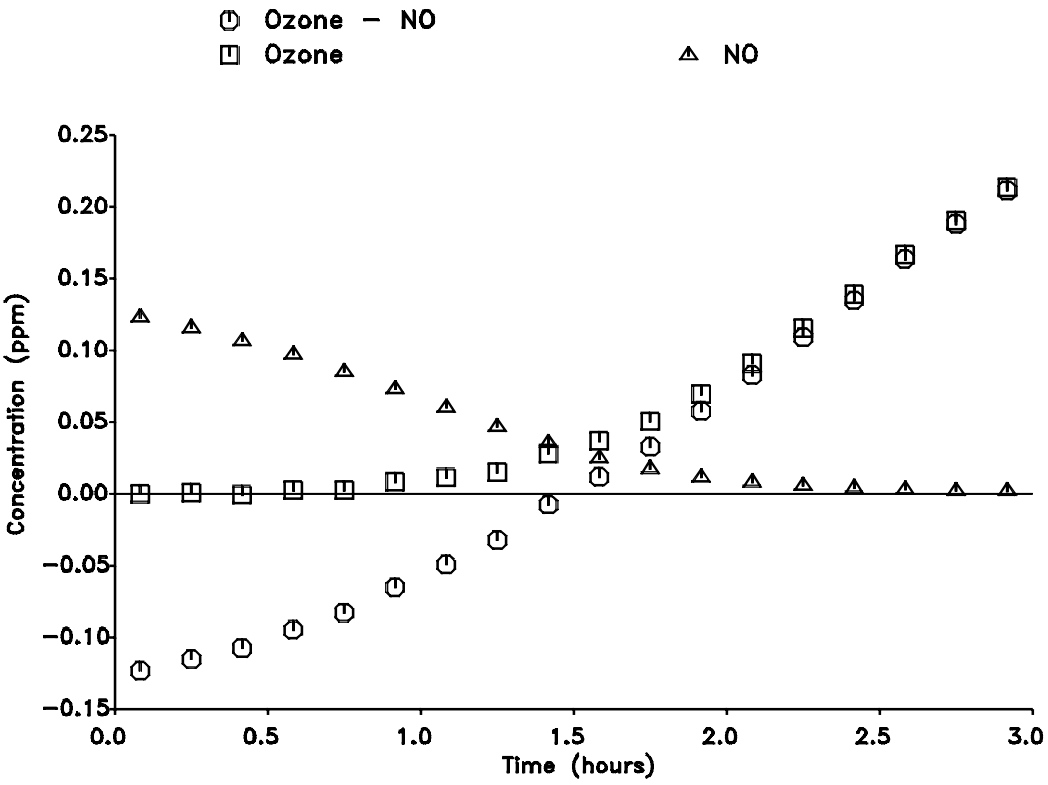
XENON ARC TEFLON CHAMBER (THIS WORK)

α-PINENE
β-PINENE

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

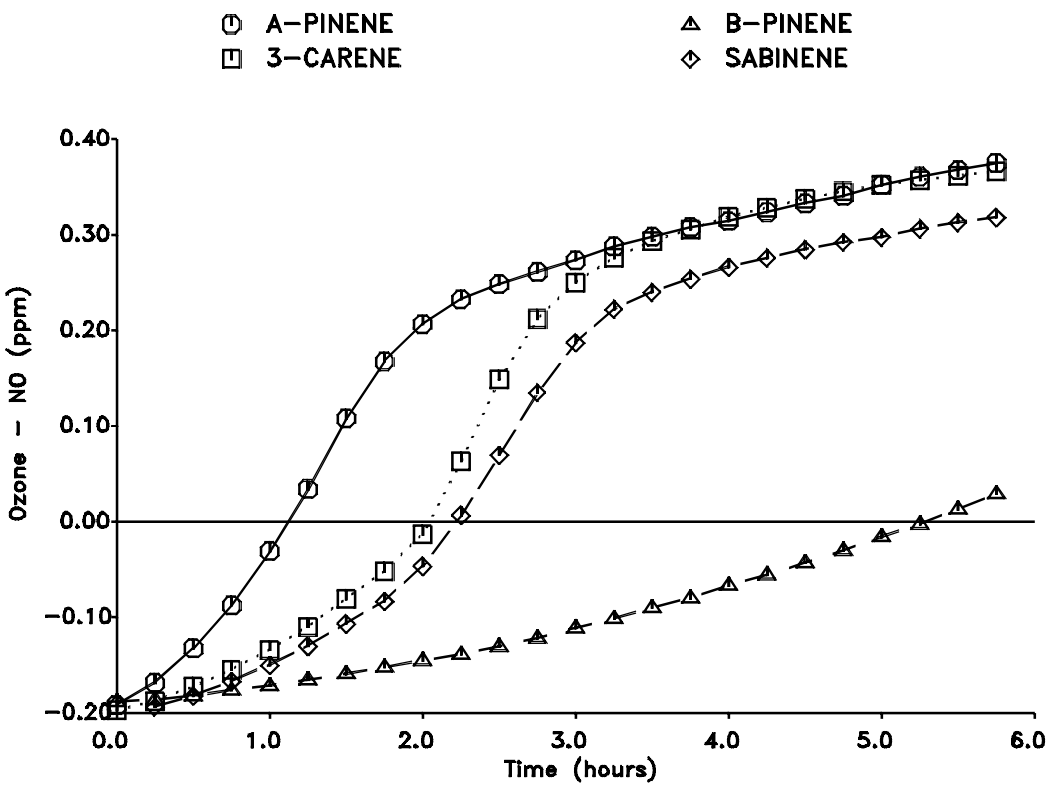
PROCESSES CAUSING O_3 FORMATION IS MANIFESTED BY NO CONSUMPTION IN THE INITIAL STAGES OF THE RUN.

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

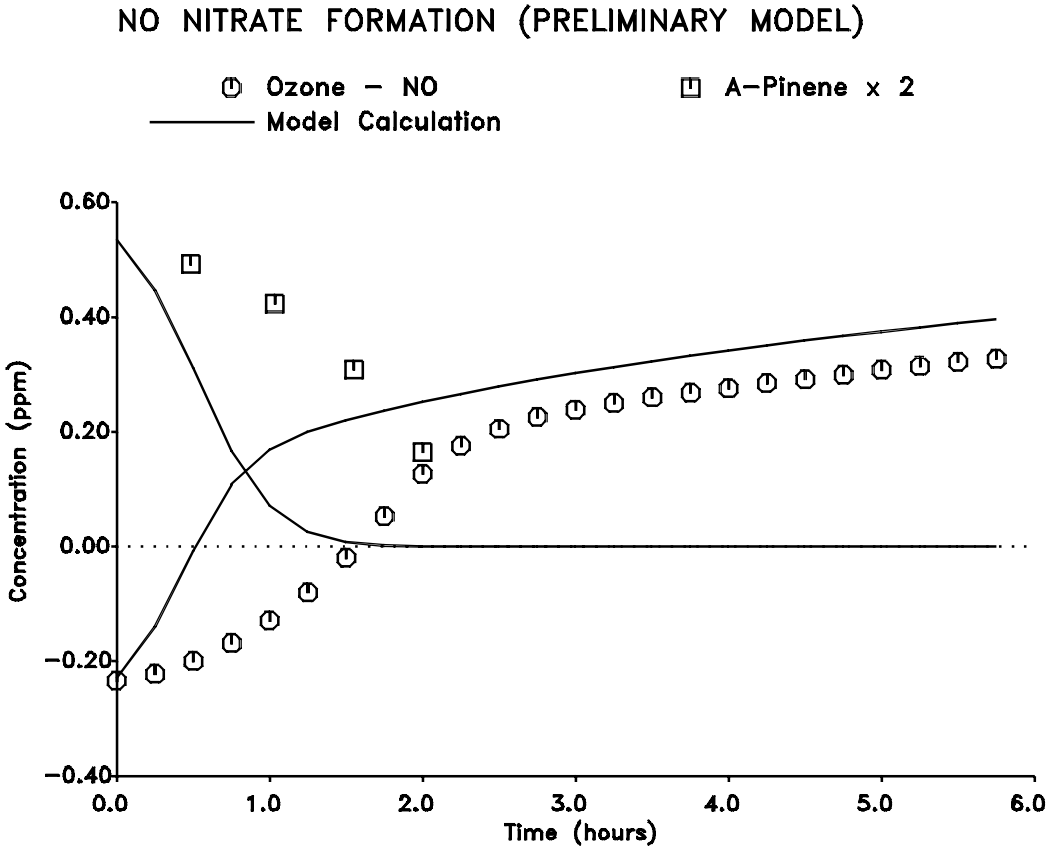


CONCENTRATION-TIME PROFILES FOR O_3 - NO IN REPRESENTATIVE TERPENE - NO_x EXPERIMENTS

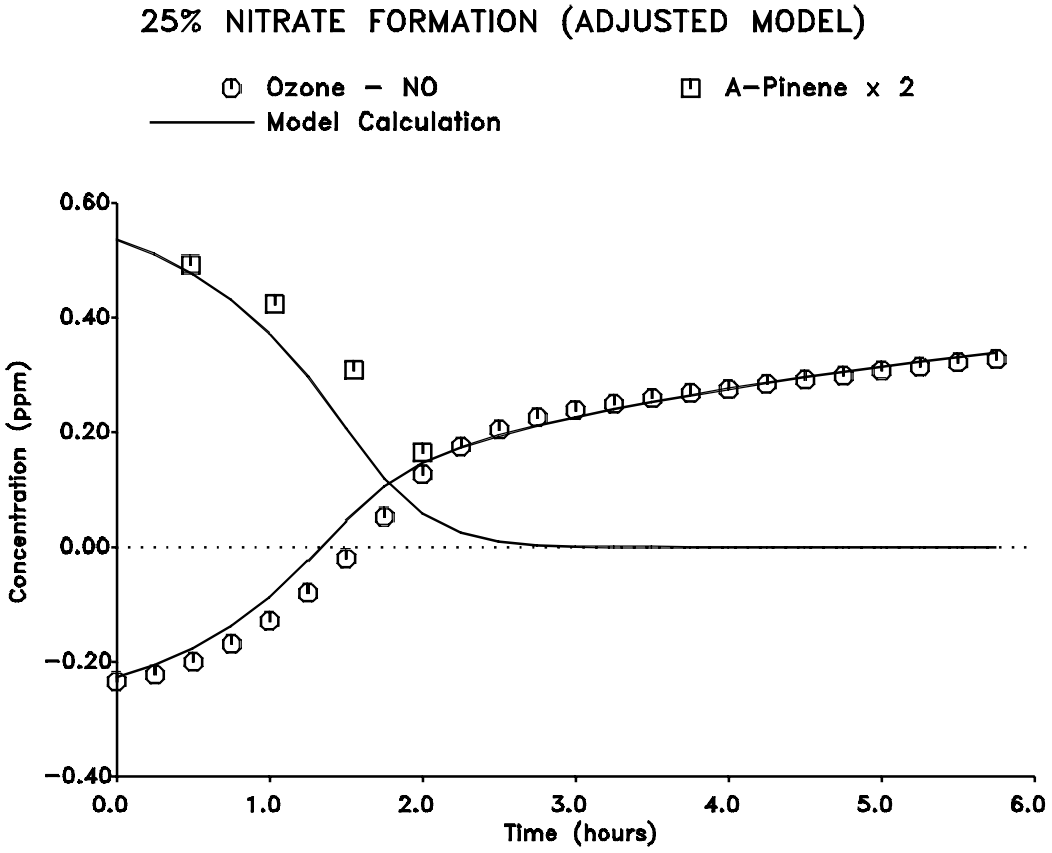
(INITIAL TERPENE = ~0.3 PPM; NO_x = ~0.25 PPM
~3000-LITER BLACKLIGHT CHAMBER)



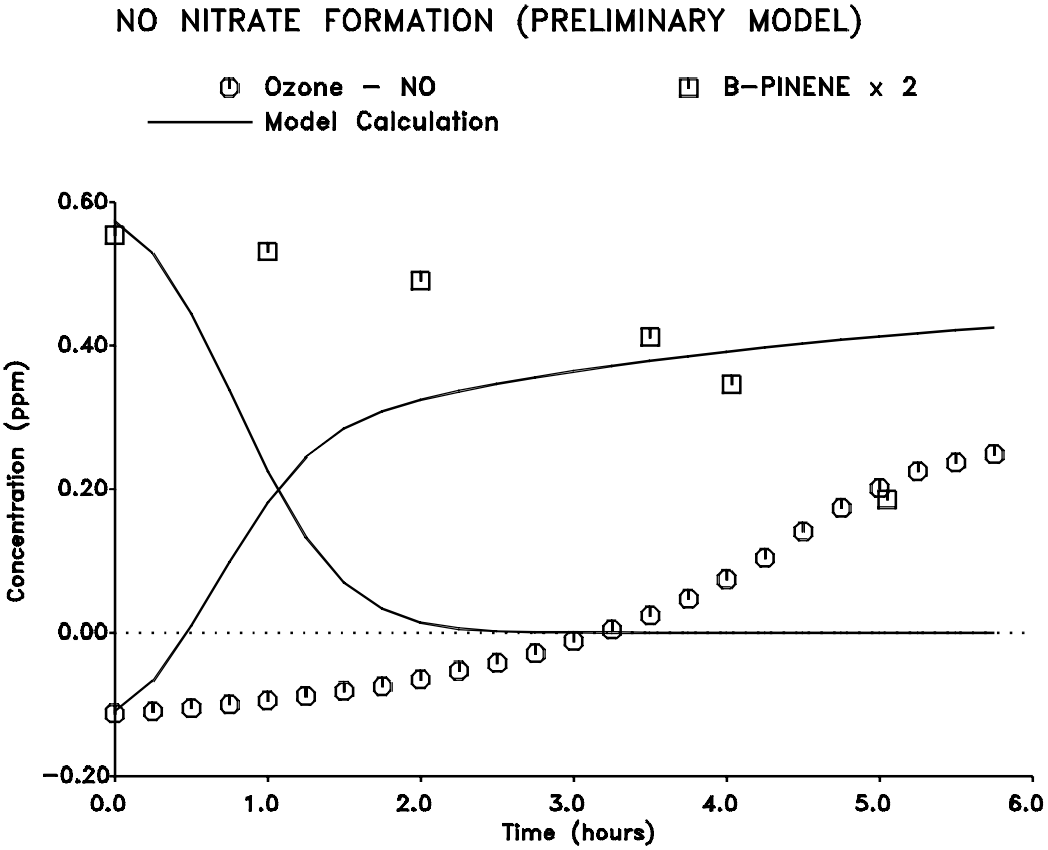
MODEL SIMULATIONS OF AN α-PINENE EXPERIMENT USING THE PRELIMINARY UPDATED SAPRC MECHANISM



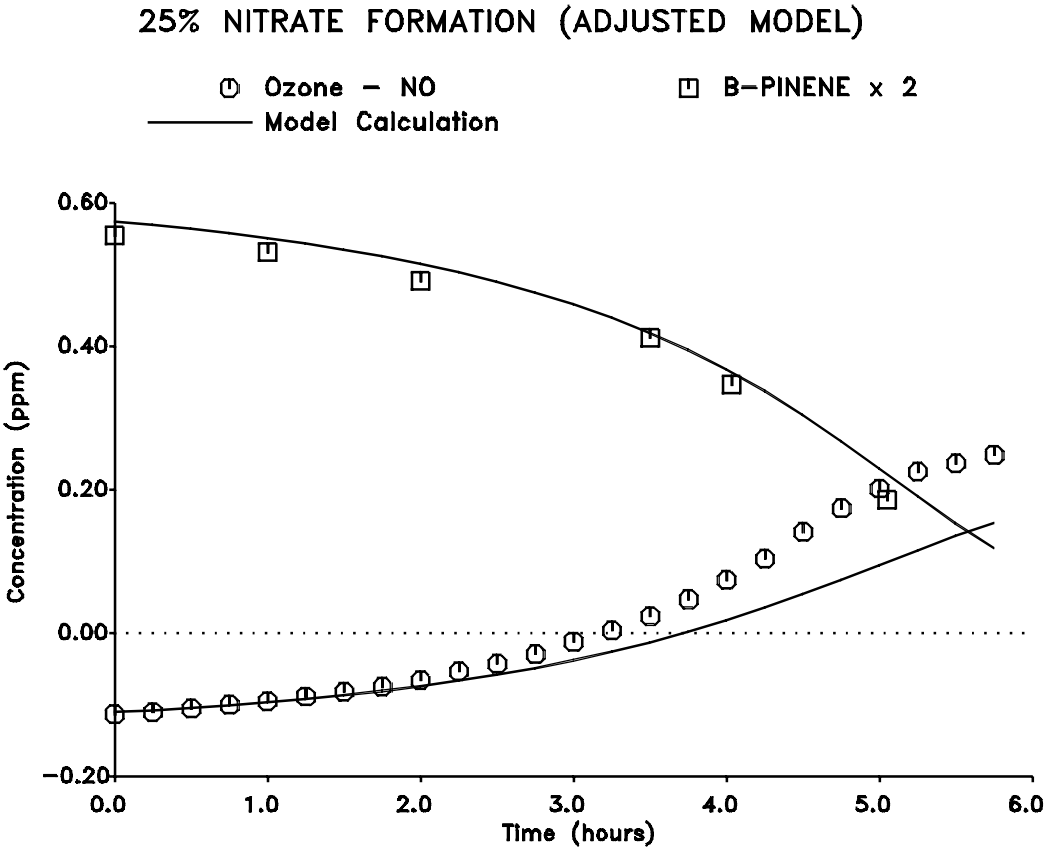
MODEL SIMULATIONS OF AN α-PINENE EXPERIMENT USING THE UPDATED SAPRC MECHANISM. ASSUMING 25% ALKYL NITRATE FORMATION IN THE OH REACTION



MODEL SIMULATIONS OF A β-PINENE EXPERIMENT USING THE PRELIMINARY UPDATED SAPRC MECHANISM

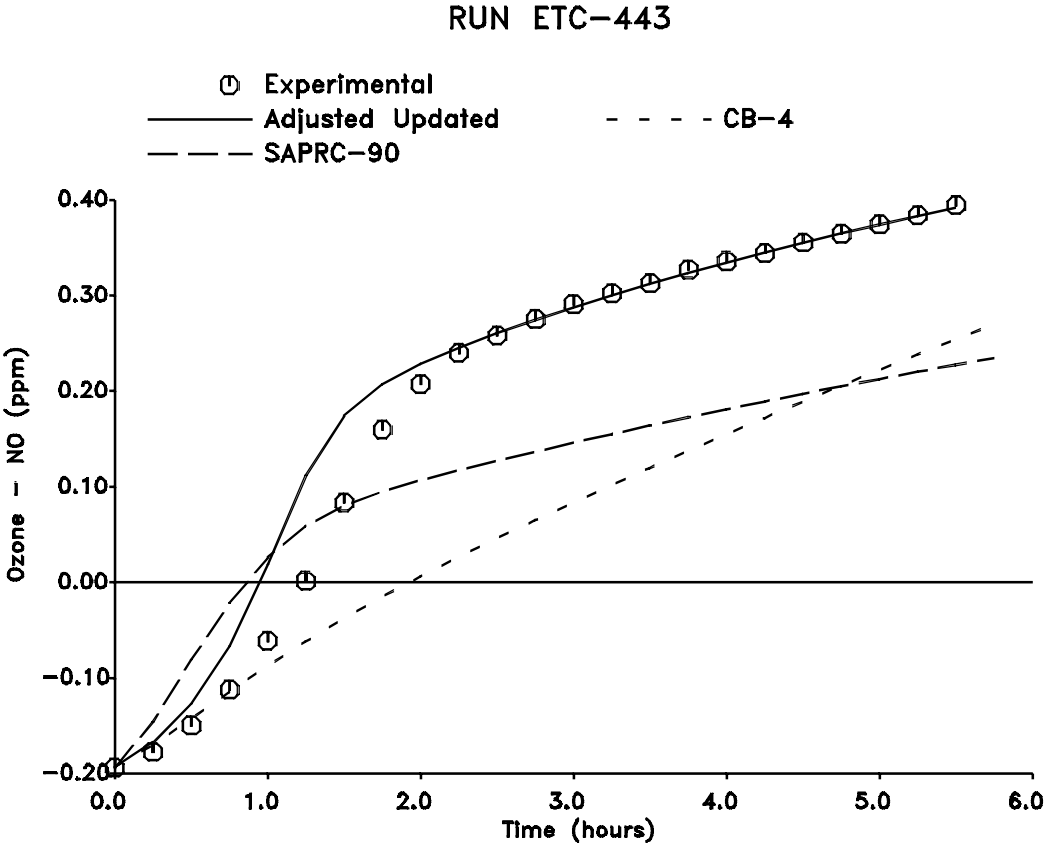


MODEL SIMULATIONS OF A β-PINENE EXPERIMENT USING THE UPDATED SAPRC MECHANISM. ASSUMING 25% ALKYL NITRATE FORMATION IN THE OH REACTION



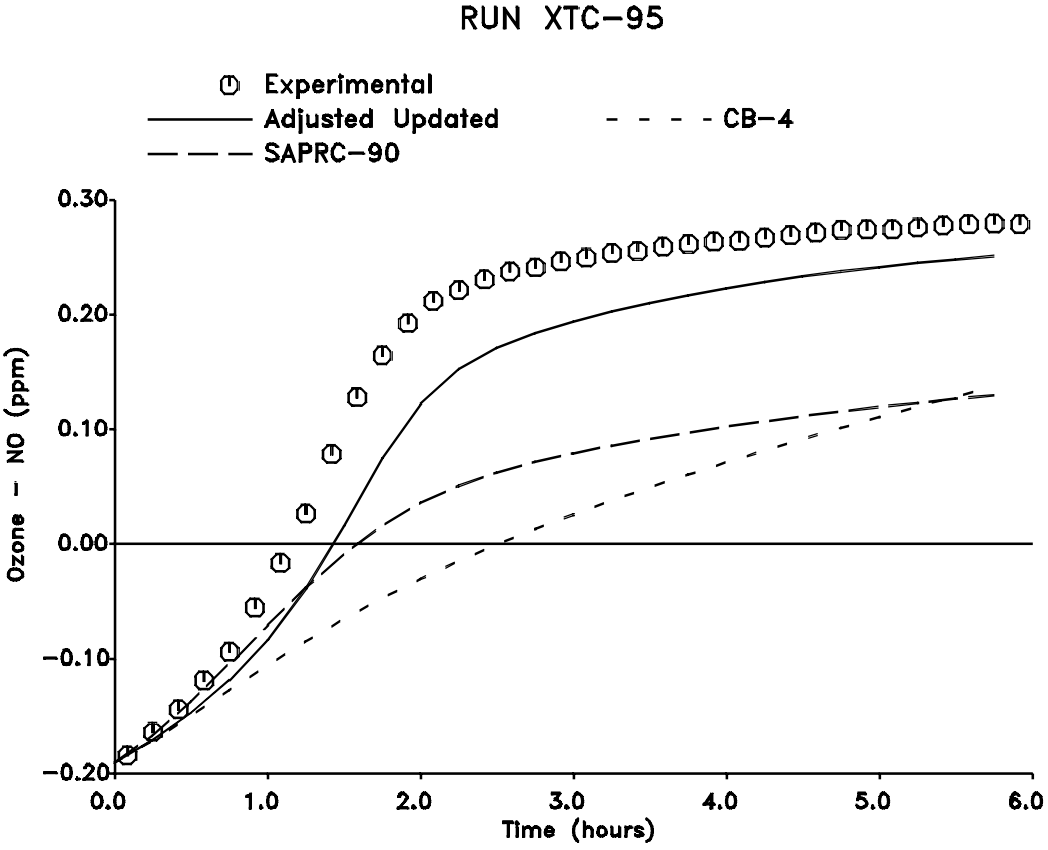
MODEL SIMULATIONS OF NO CONSUMED + O_3 FORMED IN AN α-PINENE - NO_x EXPERIMENT

CHAMBER RUN WITH BLACKLIGHT LIGHT SOURCE

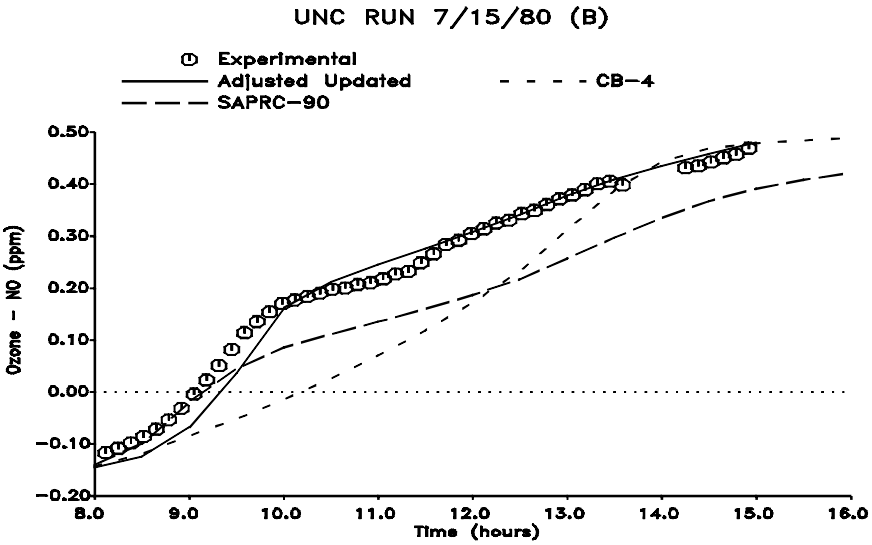


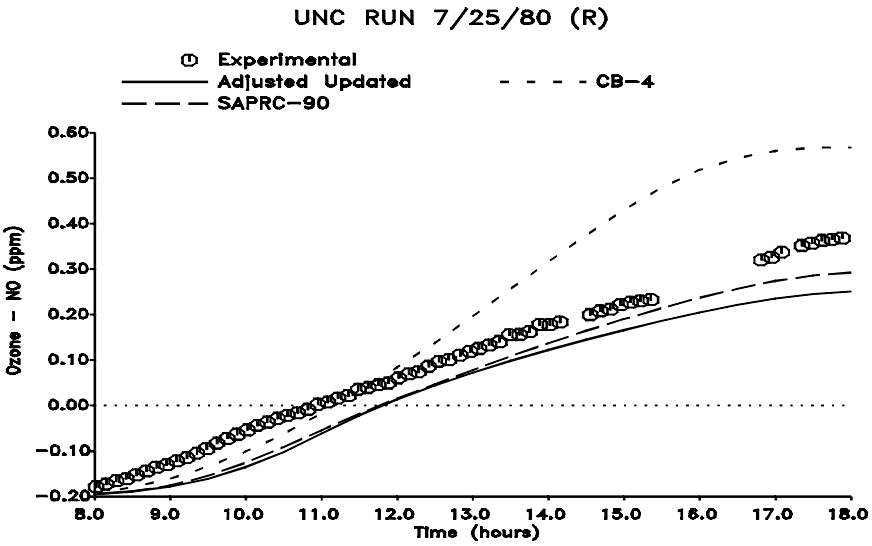
MODEL SIMULATIONS OF NO CONSUMED + O_3 FORMED IN AN α-PINENE - NO_x EXPERIMENT

CHAMBER RUN WITH XENON ARC LIGHT SOURCE



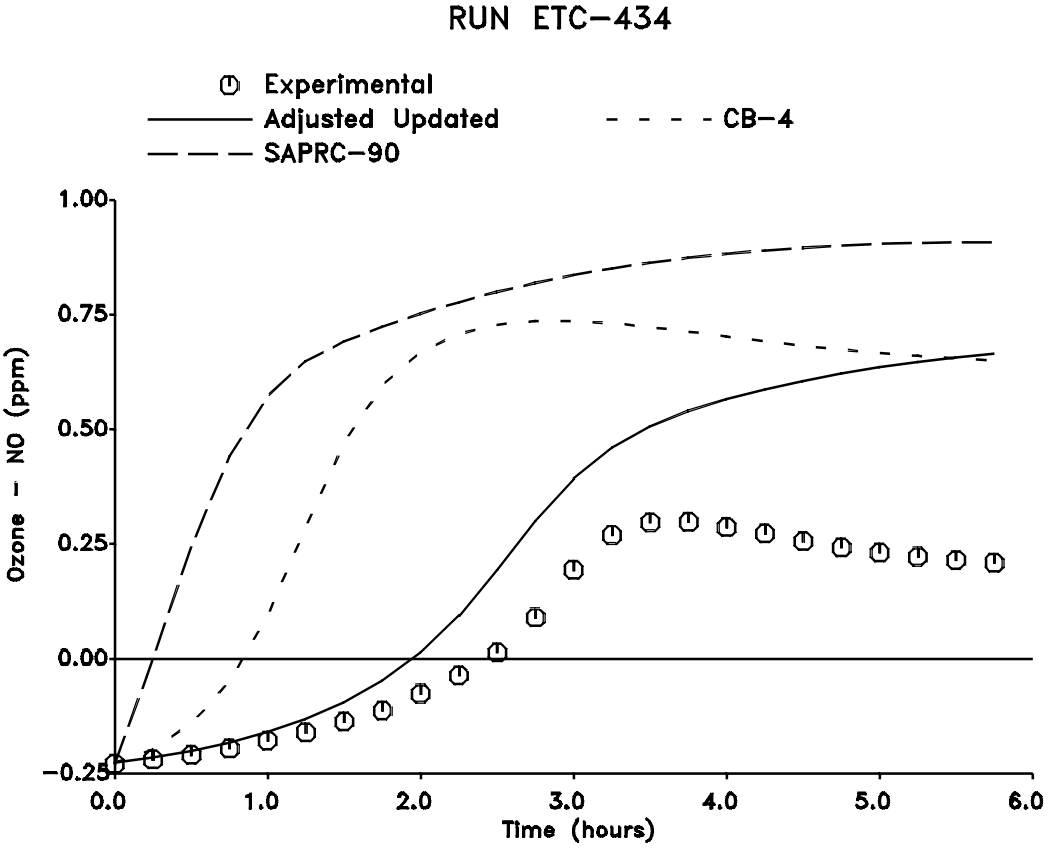
MODEL SIMULATIONS OF O_3 FORMED IN α-PINENE - NO_x EXPERIMENTS IN THE UNC OUTDOOR CHAMBER





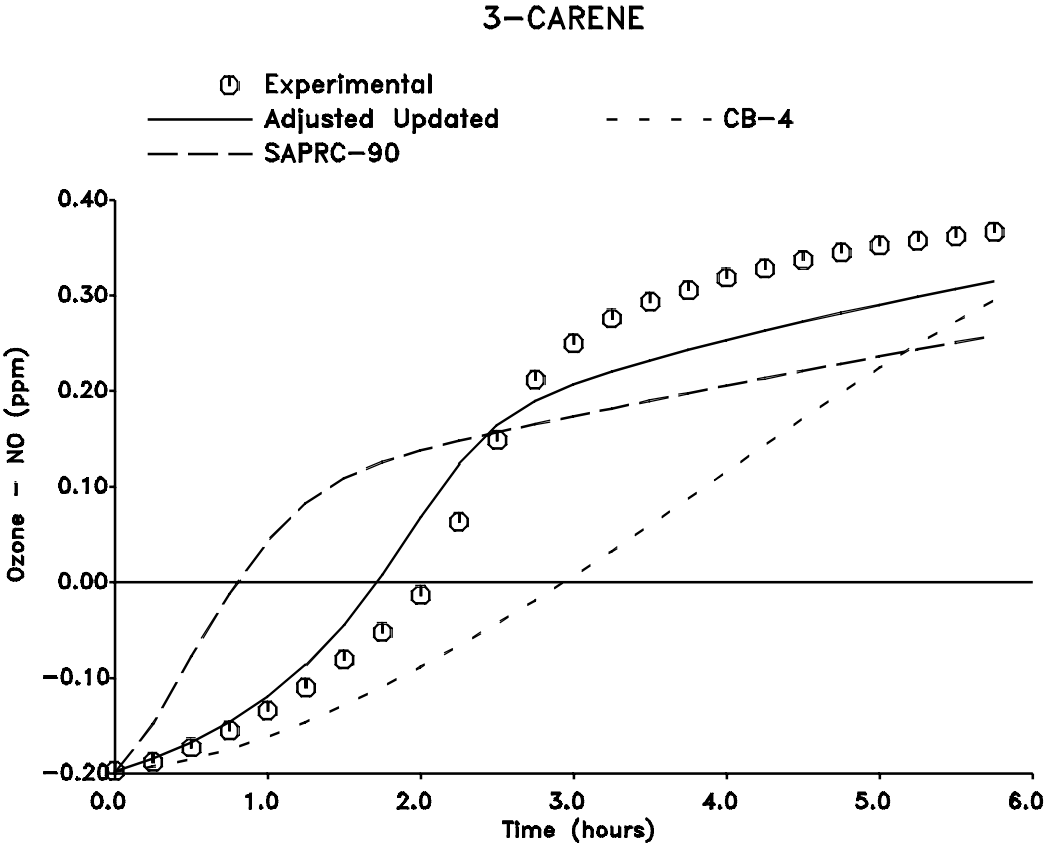
MODEL SIMULATIONS OF NO CONSUMED + O_3 FORMED IN A β-PINENE - NO_x EXPERIMENT

CHAMBER RUN WITH BLACKLIGHT LIGHT SOURCE



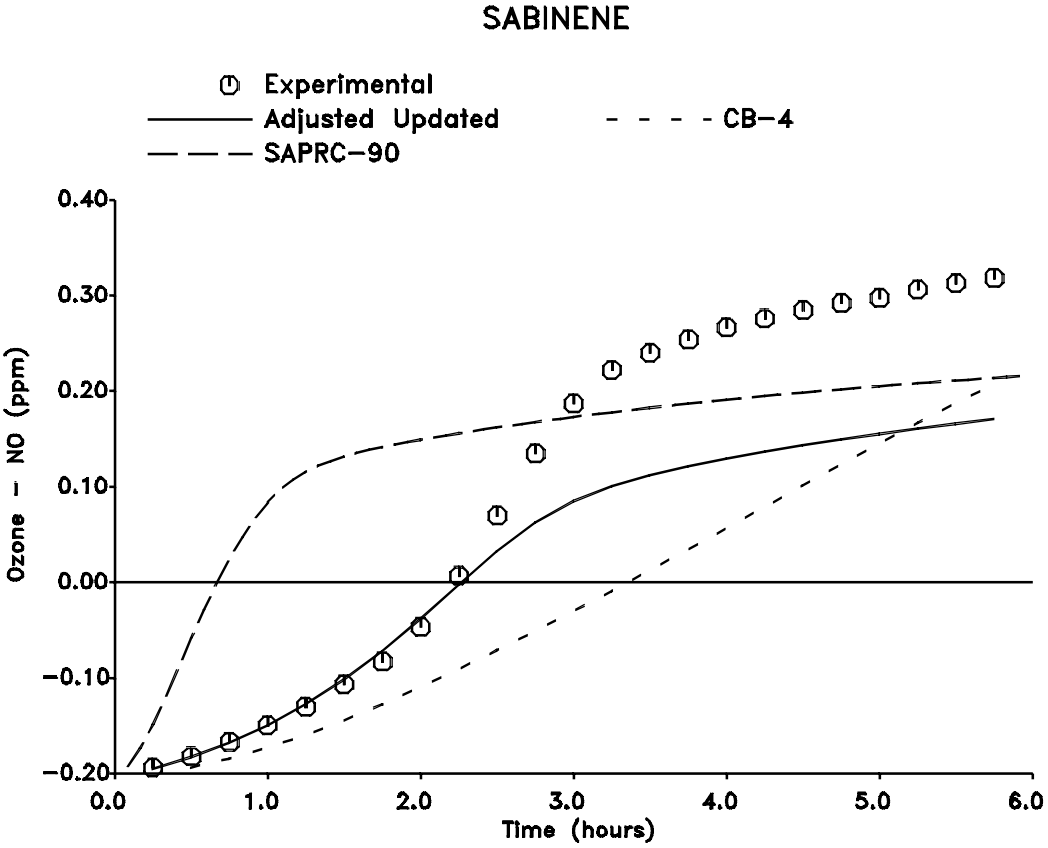
MODEL SIMULATIONS OF NO CONSUMED + O_3 FORMED IN A Δ^3-CARENE - NO_x EXPERIMENT

CHAMBER RUN WITH BLACKLIGHT LIGHT SOURCE

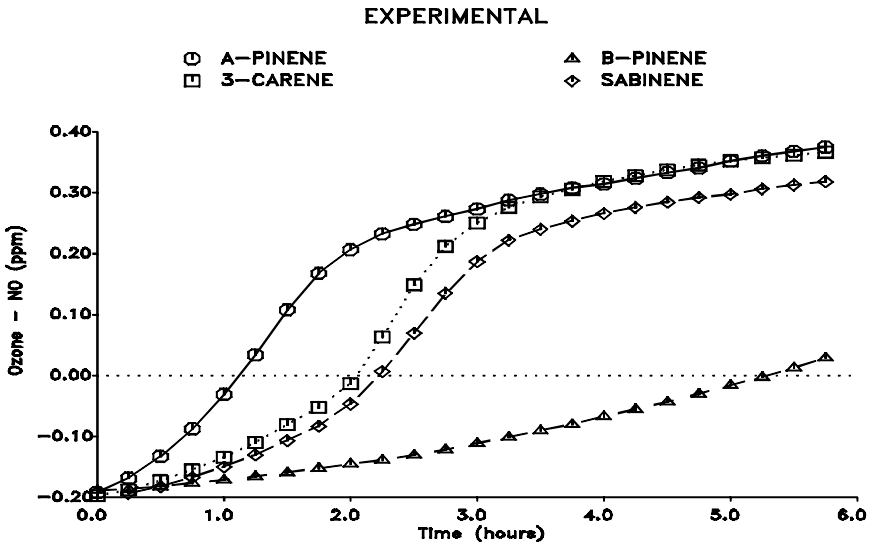


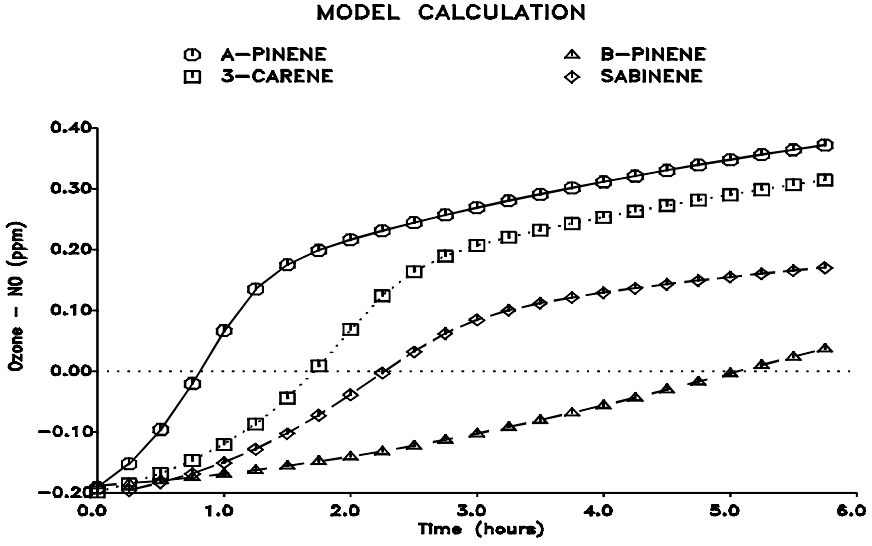
MODEL SIMULATIONS OF NO CONSUMED + O_3 FORMED IN A SABINENE - NO_x EXPERIMENT

CHAMBER RUN WITH BLACKLIGHT LIGHT SOURCE



EXPERIMENTAL AND CALCULATED EFFECT OF TERPENE ISOMER ON OZONE FORMATION





SUMMARY OF RESULTS OF MODEL SIMULATIONS OF TERPENE EXPERIMENTS

THE METHODS CURRENTLY USED TO REPRESENT TERPENES IN AIRSHED MODELS ARE UNSATISFACTORY.

TERPENES ARE SUFFICIENTLY DIFFERENT FROM OTHER ALKENES THAT AIRSHED MODELS SHOULD USE SEPARATE MODEL SPECIES TO REPRESENT THEM.

THE CHAMBER DATA INDICATE THAT TERPENES ARE STRONG RADICAL INHIBITORS UNTIL O_3 IS FORMED, THEN THEY ARE STRONG RADICAL INITIATORS.

TERPENE ISOMERS DIFFER SIGNIFICANTLY IN THEIR EFFECTS ON OZONE FORMATION. THE RATES AND OH YIELDS IN THE O_3 REACTION ARE THE CRITICAL FACTORS.

AN UPDATED MECHANISM CAN PREDICT O_3 FORMATION RATES IN TERPENE EXPERIMENTS IF IT ASSUMES ~25% FORMATION OF ORGANIC NITRATES IN THE OH REACTION.

BUT THE MECHANISM DOES NOT CORRECTLY SIMULATE EFFECT OF TERPENE ISOMERS ON FINAL O_3 YIELDS.

MORE DATA ARE NEEDED TO IMPROVE REPRESENTATION OF PRODUCT REACTIONS.

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