EVALUATION OF ATMOSPHERIC PROCESSES FOR OZONE FORMATION FROM VEHICLE EMISSIONS

by

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ATMOSPHERIC IMPACTS OF VEHICLE EMISSIONS

MOTOR VEHICLES EMIT OXIDES OF NITROGEN (NO_x), CARBON MONOXIDE (CO), AND VOLATILE ORGANIC COMPOUNDS (VOCs) INTO THE ATMOSPHERE.

THESE ADVERSELY AFFECT AIR QUALITY IN A NUMBER OF WAYS

- SOME COMPOUNDS (E.G., CO, BENZENE) ARE DIRECTLY TOXIC.
- NO_x FORMS HNO_3, WHICH CONTRIBUTES TO ACID DEPOSITION.
- NO_x FORMS NITRATE AEROSOL, CONTRIBUTES TO PARTICULATE. POLLUTION, VISIBILITY DEGRADATION.
- NO_x AND VOCs REACT IN SUNLIGHT TO FORM OZONE AND "PHOTOCHEMICAL SMOG"

THIS DISCUSSION WILL FOCUS ON THE OZONE IMPACTS.

- O_3 IS A MAJOR AIR QUALITY PROBLEM IN MANY AREAS OF THE U.S.
- DIFFICULTY IN ACHIEVING O_3 STANDARDS IS FORCING VEHICLE EMISSIONS REGULATIONS.

EVALUATION OF IMPACTS OF VEHICLE EMISSIONS ON OZONE

REQUIRES AN ABILITY TO PREDICT HOW VOC AND NO_x EMISSIONS CHANGES WILL AFFECT O_3 IN THE ATMOSPHERE.

NOT A SIMPLE PROBLEM.

- CHEMISTRY OF O_3 FORMATION FROM VOCs AND NO_x IS COMPLEX AND UNCERTAIN.
- VOCs DIFFER IN THEIR EFFECTS ON O_3 FORMATION ("REACTIVITIES").
- THIS MEANS THAT MASS OF VOC EMISSIONS IS NOT THE ONLY FACTOR AFFECTING O_3 IMPACTS, **ESPECIALLY FOR ALTERNATIVE FUELS**
- OZONE IMPACT OF EMISSIONS (BOTH ABSOLUTE AND RELATIVE) DEPEND ON ENVIRONMENTAL CONDITIONS.

ALL THESE FACTORS MUST BE TAKEN INTO ACCOUNT WHEN ASSESSING OZONE IMPACTS OF ALTERNATIVE FUEL USE.

FORMATION OF O_3 FROM NO_x

THE ONLY SIGNIFICANT CHEMICAL REACTION WHICH FORMS OZONE IN THE TROPOSPHERE IS THE PHOTOLYSIS OF NO_2

$$NO_2 + h\nu \xrightarrow{k_1} NO + O \qquad O + O_2 \xrightarrow{M} O_3$$

BUT THIS IS REVERSED BY THE RAPID REACTION OF O_3 WITH NO:

$$NO + O_3 \xrightarrow{k_2} NO_2 + O_2$$

THESE PROCESSES RESULT IN A "PHOTOSTATIONARY STATE" BEING ESTABLISHED, WHERE O_3 IS PROPORTIONAL TO THE NO_2 TO NO RATIO

$$[O_3] \cong \frac{k_1}{k_2} \cdot \frac{[NO_2]}{[NO]}$$

IF OTHER REACTANTS ARE NOT PRESENT TO CONVERT NO TO NO_2, ONLY VERY LOW LEVELS OF OZONE ARE FORMED.

ROLE OF VOCs IN OZONE FORMATION

WHEN VOCs REACT THEY FORM RADICALS WHICH CONVERT NO TO NO_2. FOR EXAMPLE:

$$CH_3CH_3 + OH \rightarrow H_2O + CH_3CH_2\cdot \xrightarrow{O_2} CH_3CH_2OO\cdot$$

$$CH_3CH_2OO\cdot + NO \rightarrow CH_3CH_2O\cdot + NO_2$$

$$CH_3CH_2O\cdot + O_2 \rightarrow CH_3CHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

OVERALL:

$$CH_3CH_3 + 2\ O_2 + 2\ NO \xrightarrow{OH} CH_3CHO + 2\ NO_2 + H_2O$$

COMBINED WITH:

$$NO_2 + O_2 \overset{h\nu}{\rightleftharpoons} NO + O_3$$

YIELDS:

$$CH_3CH_3 + 2\ O_2 + h\nu \xrightarrow{NO_X\ OH} CH_3CHO + H_2O + 2\ O_3$$

OZONE FORMATION CONTINUES UNTIL NO_x IS REMOVED

MAJOR NO_x SINKS:

- $OH + NO_2 \longrightarrow HNO_3$
- $NO_2 + O_3 \xrightarrow{NO_2} NO_3 \xrightleftharpoons{H_2O} N_2O_5 \longrightarrow 2\ HNO_3$ (NIGHTTIME SINK)
- ALDEHYDES $\xrightarrow{OH}\xrightarrow{O_2}$ RCO-OO. $\xrightarrow{NO_2}$ RCO-OONO$_2$ (PANs)
- AROMATICS $\xrightarrow{OH}\xrightarrow{O_2}$ PHENOLS $\xrightarrow{NO_3,\ NO_2}$ NITROPHENOLS
- ALKANES $\xrightarrow{OH}\xrightarrow{O_2}$ RO_2 $\xrightarrow{NO}$ $RONO_3$

NO_x IS REMOVED IN THE ATMOSPHERE MORE RAPIDLY THAN VOCs.

THEREFORE, NO_x AVAILABILITY ULTIMATELY LIMITS THE AMOUNT OF O_3 WHICH CAN BE FORMED.

IMPLICATIONS OF ATMOSPHERIC CHEMISTRY FOR OZONE CONTROL STRATEGIES

NO_x CONTROL:

- NO_x ULTIMATELY LIMITS O_3 FORMATION. THEREFORE, NO_x CONTROL REDUCES O_3 LEVELS DOWNWIND.
- NO_x INHIBITS THE RATE OF O_3 FORMATION. THEREFORE, NO_x CONTROL MAKES O_3 HIGHER NEAR THE SOURCE AREAS. THIS IS BECAUSE:
  - NO MUST BE CONSUMED BEFORE O_3 FORMED, AND
  - NO_2 IS A RADICAL INHIBITOR, AND SLOWS DOWN VOC REACTIONS FORMING O_3.

VOC CONTROL:

- VOC's ENHANCE THE RATE OF O_3 FORMATION. THEREFORE, VOC CONTROL MOST EFFECTIVE IN REDUCING O_3 NEAR THE SOURCE AREAS.
- VOC CONTROL IS LESS EFFECTIVE IN REDUCING O_3 IN DOWNWIND AREAS WHERE O_3 IS NO_x-LIMITED.

VOC REACTIVITY

VOCs DIFFER IN THEIR EFFECTS ON OZONE FORMATION. THE TERM **REACTIVITY** IS USED TO REFER TO THIS.

SEVERAL DIFFERENT ASPECTS OF A VOCs ATMOSPHERIC REACTIONS AFFECT A VOC'S REACTIVITY:

- HOW FAST IT REACTS.
- HOW MANY MOLECULES OF NO ARE OXIDIZED WHEN IT REACTS.
- EFFECTS OF ITS REACTIONS ON RADICAL LEVELS. THIS AFFECTS HOW MUCH O_3 IS FORMED FROM REACTIONS OF THE OTHER VOCs.
- ITS EFFECTS ON RATES OF NO_x REMOVAL. O_3 FORMATION ENDS ONCE NO_x IS REMOVED. (IMPORTANT ONLY WHEN O_3 IS NO_x-LIMITED.)
- REACTIVITIES OF ITS MAJOR OXIDATION PRODUCTS.

QUANTIFICATION OF REACTIVITY

A USEFUL MEASURE OF THE EFFECT OF A VOC ON OZONE FORMATION IS ITS **INCREMENTAL REACTIVITY**:

$$\left[\begin{array}{c}\text{INCREMENTAL}\\ \text{REACTIVITY}\\ \text{OF A VOC IN}\\ \text{A POLLUTION}\\ \text{EPISODE}\end{array}\right] = \lim_{[\text{VOC}] \to 0} \frac{\left[\begin{array}{c}\text{OZONE FORMED}\\ \text{IN THE}\\ \text{EPISODE WITH}\\ \text{THE VOC ADDED}\end{array}\right] - \left[\begin{array}{c}\text{OZONE FORMED}\\ \text{IN THE}\\ \text{EPISODE}\end{array}\right]}{[\text{VOC ADDED}]}$$

THIS CAN BE MEASURED EXPERIMENTALLY IN SMOG CHAMBERS OR CALCULATED FOR POLLUTION EPISODES USING AIRSHED MODELS.

THIS DEPENDS ON THE CONDITIONS OF THE EPISODE AS WELL AS ON THE VOC.

ENVIRONMENTAL FACTORS WHICH AFFECT REACTIVITY

AVAILABILITY OF NO_x

- MOST IMPORTANT SINGLE FACTOR. VOCs HAVE GREATEST EFFECT ON O_3 WHEN NO_x IS HIGH; VOCs FORM NO O_3 WHEN NO_x IS ABSENT.
- ROG/NO_x RATIO IS COMMONLY USED TO MEASURE NO_x AVAILABILITY.

NATURE OF OTHER VOCs PRESENT.

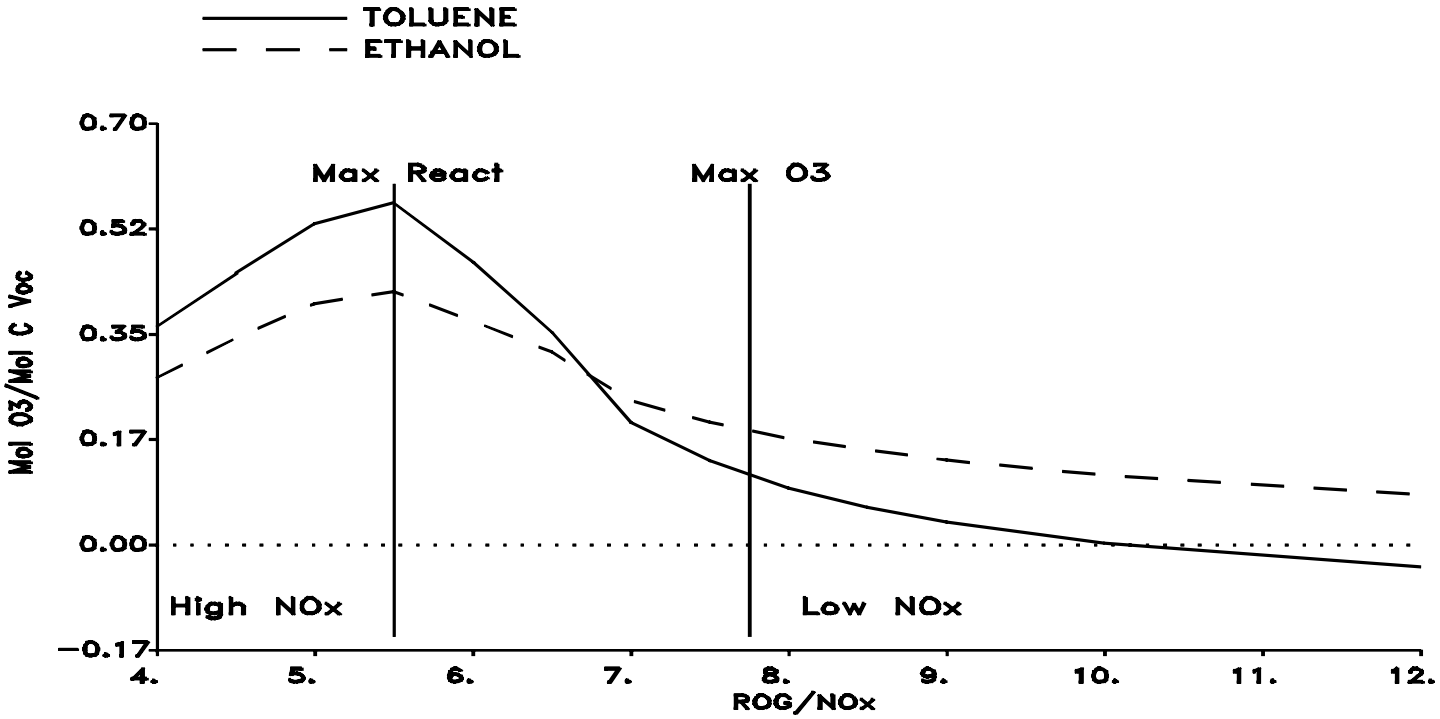
- VOCs WITH STRONG RADICAL SOURCES DECREASE THE IMPORTANCE OF RADICAL SOURCES OR SINKS IN AFFECTING A VOC's REACTIVITY.

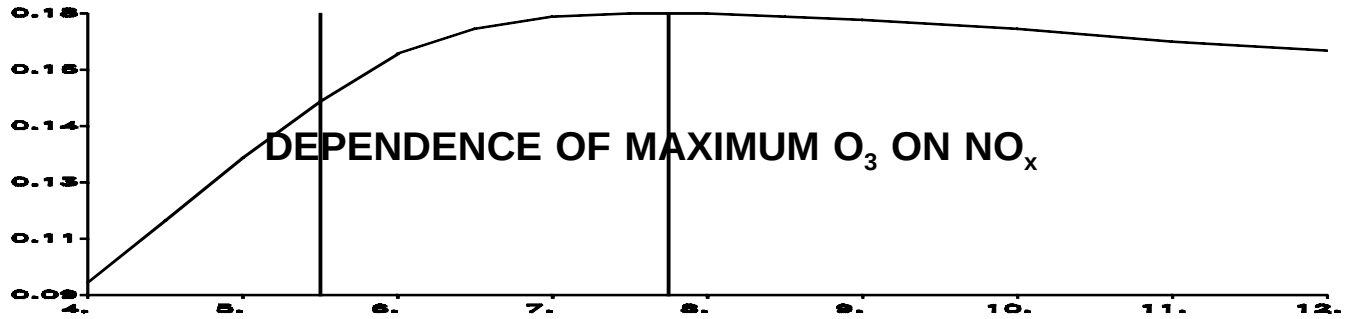
AMOUNTS OF SUNLIGHT AND TEMPERATURE:

- AFFECTS OVERALL RATES OF REACTION.
- AFFECTS DEPENDENCE OF REACTIVITY ON ROG/NO_x RATIO. (MORE SUNLIGHT LIKE INCREASING ROG/NO_x)

TRANSPORT, ALOFT AND BACKGROUND POLLUTANTS, EMISSION SCHEDULES, AMOUNTS OF DILUTION, ALSO AFFECT REACTIVITY AND VOC/NO_x DEPENDENCIES.

DEPENDENCE OF INCREMENTAL REACTIVITY ON NO_x





DEPENDENCE OF MAXIMUM O_3 ON NO_x

EXAMPLES OF INCREMENTAL REACTIVITY SCALES

MAXIMUM INCREMENTAL REACTIVITY (MIR) SCALE: AVERAGE OF INCREMENTAL REACTIVITIES IN REPRESENTATIVE SCENARIOS WHERE NO_x LEVELS ARE ADJUSTED TO YIELD MAXIMUM INCREMENTAL REACTIVITIES.

- BASED ON VOC IMPACTS IN ENVIRONMENTS MOST SENSITIVE TO VOCs.
- USED IN BY CARB TO CALCULATE "REACTIVITY ADJUSTMENT FACTORS" FOR SETTING ALTERNATIVE FUEL EMISSIONS STANDARDS.

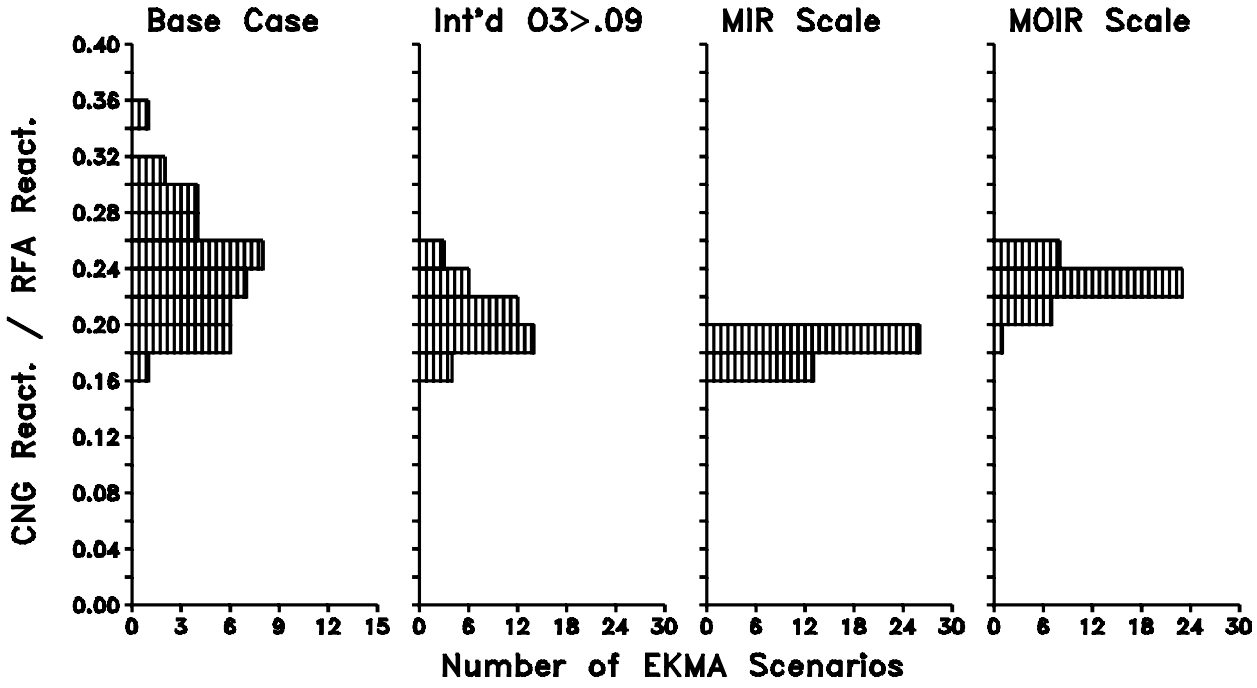
MAXIMUM OZONE INCREMENTAL REACTIVITY (MOIR) SCALE: AVERAGE OF INCREMENTAL REACTIVITIES IN REPRESENTATIVE SCENARIOS WHERE NO_x LEVELS ARE ADJUSTED TO YIELD HIGHEST OZONE CONCENTRATIONS.

- BASED ON VOC IMPACTS IN ENVIRONMENTS WITH HIGHEST O_3 LEVELS.

BASE CASE SCALES: INCREMENTAL REACTIVITIES IN SETS OF SCENARIOS REPRESENTING OZONE EXCEEDENCE EPISODES IN VARIOUS URBAN AREAS.

- USEFUL FOR ASSESSING HOW REACTIVITY VARIES WITH ENVIRONMENTAL CONDITIONS.

DISTRIBUTION OF REACTIVITY ADJUSTMENT FACTORS FOR CNG EXHAUST IN VARIOUS REACTIVITY SCALES



MEASUREMENT OR CALCULATION OF ATMOSPHERIC REACTIVITY

CHAMBER EXPERIMENTS ONLY **APPROXIMATE** ATMOSPHERIC REACTIVITY

- CAN'T DUPLICATE ALL CONDITIONS WHICH AFFECT REACTIVITY
- CHAMBER EXPERIMENTS HAVE WALL EFFECTS, HIGHER NO_x LEVELS, STATIC CONDITIONS, HIGHER AMOUNTS OF ADDED TEST VOC, ETC.

ATMOSPHERIC REACTIVITY CAN BE CALCULATED USING COMPUTER AIRSHED MODELS, GIVEN:

- MODELS FOR AIRSHED CONDITIONS
- CHEMICAL MECHANISMS FOR THE VOC's ATMOSPHERIC REACTIONS

MODEL CALCULATIONS OF ATMOSPHERIC REACTIVITY **CAN BE NO MORE RELIABLE THAN THE CHEMICAL MECHANISM** USED.

GREATEST UTILITY OF EXPERIMENTS IS TESTING THE RELIABILITY OF A MECHANISM TO PREDICT ATMOSPHERIC REACTIVITY.

TYPES OF ENVIRONMENTAL CHAMBER EXPERIMENTS USED TO TEST ATMOSPHERIC CHEMICAL MECHANISMS

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 ALL VOCs

COMPLEX MIXTURE-NO_x-AIR RUNS:

- TESTS MECHANISMS' ABILITY TO SIMULATE O_3 FORMATION UNDER REALISTIC CONDITIONS
- NOT USEFUL FOR MECHANISM DEVELOPMENT FOR INDIVIDUAL VOCs

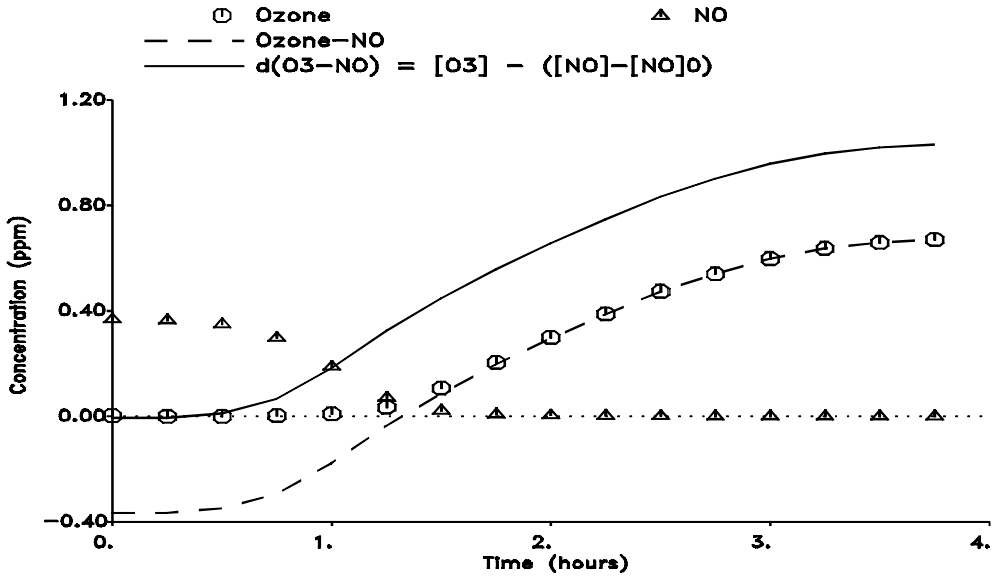
REACTIVITY EXPERIMENTS (EFFECT OF ADDING VOC TO MIXTURE)

- TESTS MECHANISMS OF SINGLE VOCs UNDER REALISTIC CONDITIONS
- TESTS MECHANISM'S ABILITY TO PREDICT INCREMENTAL REACTIVITY
- NOT SAME AS ATMOSPHERIC REACTIVITY.

CHANGE IN O_3 - NO IS A USEFUL MEASUREMENT OF PROCESSES AFFECTING O_3 FORMATION IN AN EXPERIMENT

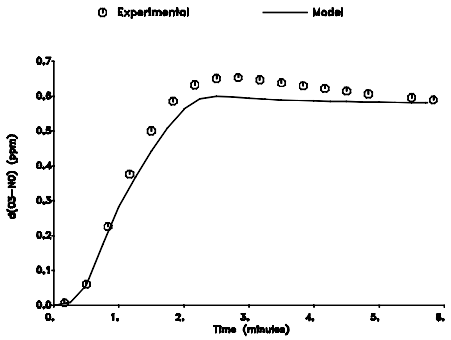
PROCESSES CAUSING O_3 FORMATION IS MANIFESTED BY NO CONSUMPTION IN THE INITIAL STAGES OF THE RUN.

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

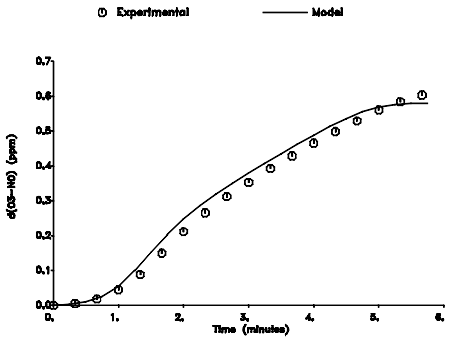


EXPERIMENTAL VS CALCULATED d(O_3-NO) IN AROMATIC ISOMER - NO_x EXPERIMENTS

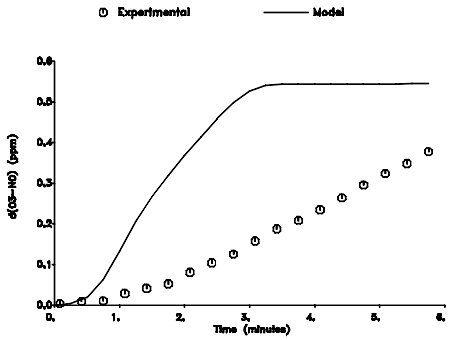
M-XYLENE



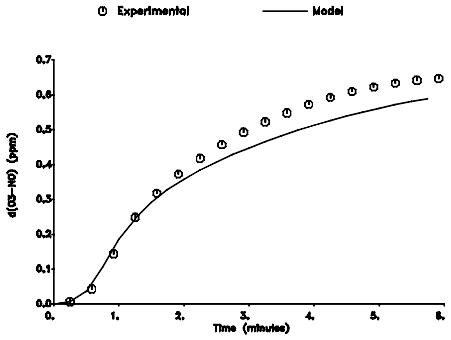
O-XYLENE



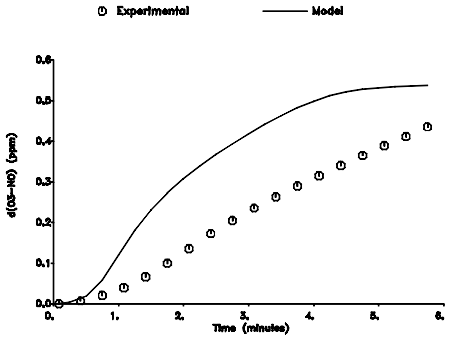
P-XYLENE



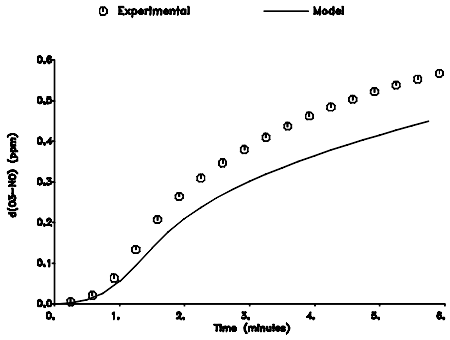
1,3,5-TRIMETHYLZENZENE



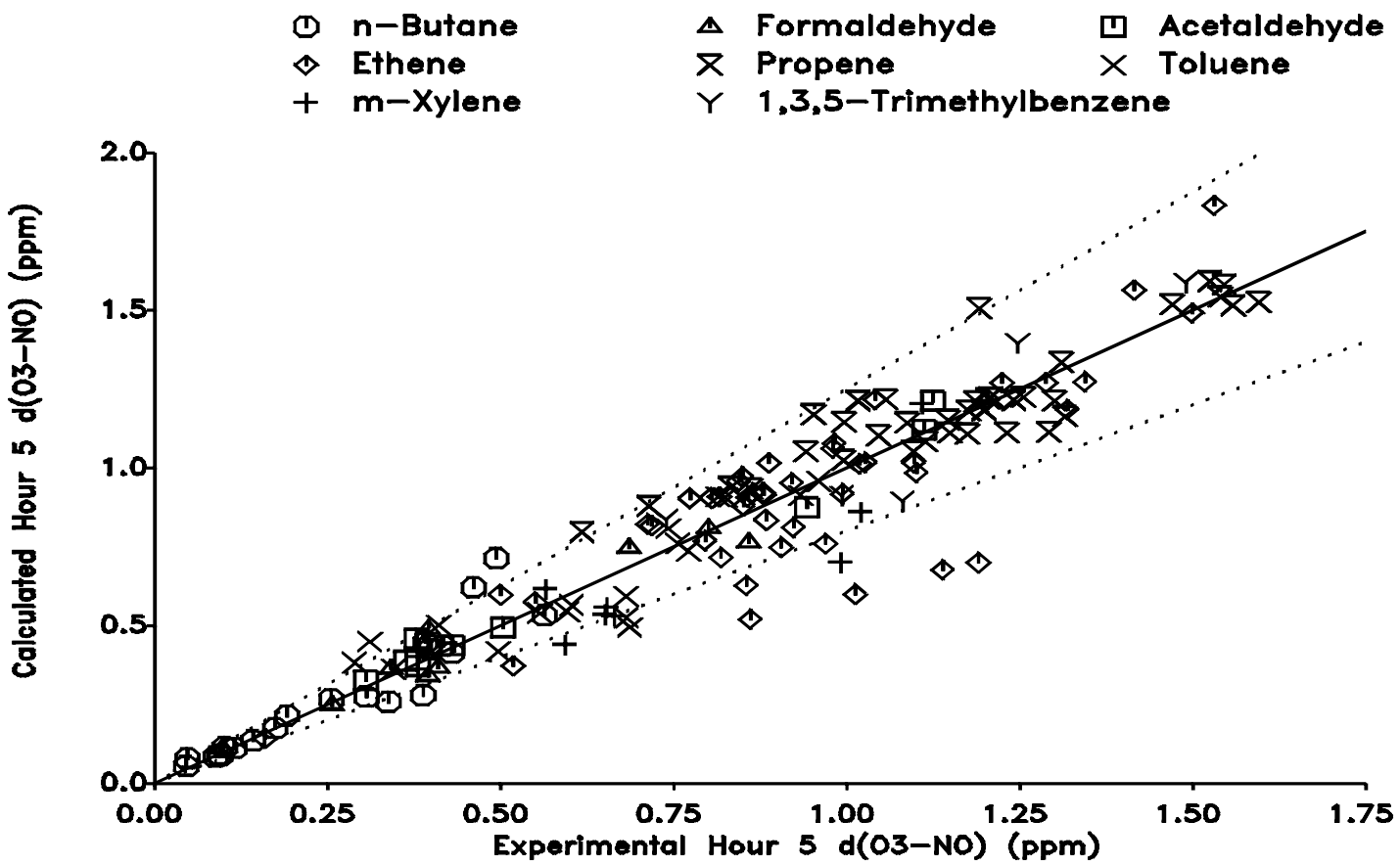
1,2,4-TMB



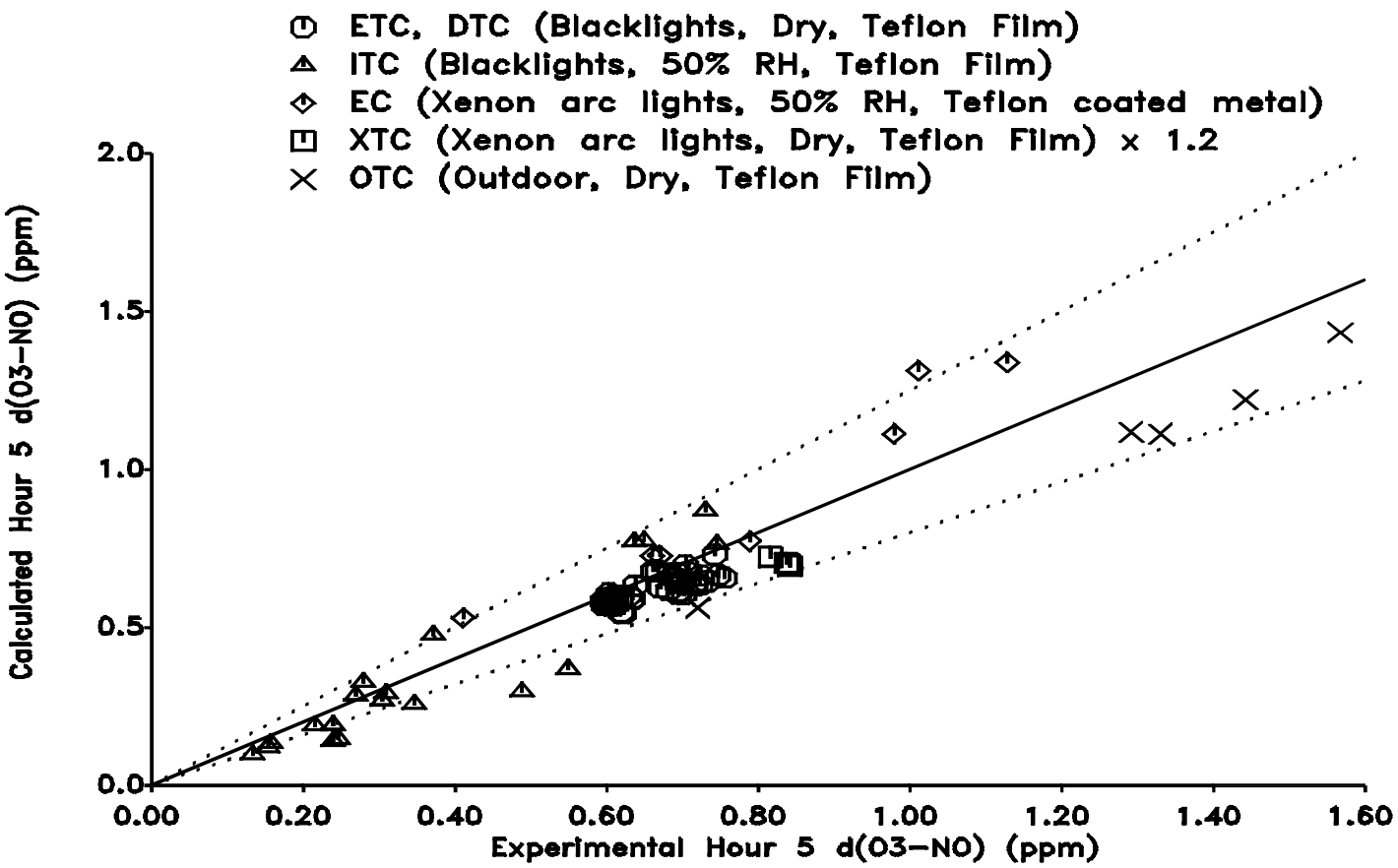
1,2,3-TRIMETHYLBENZENE



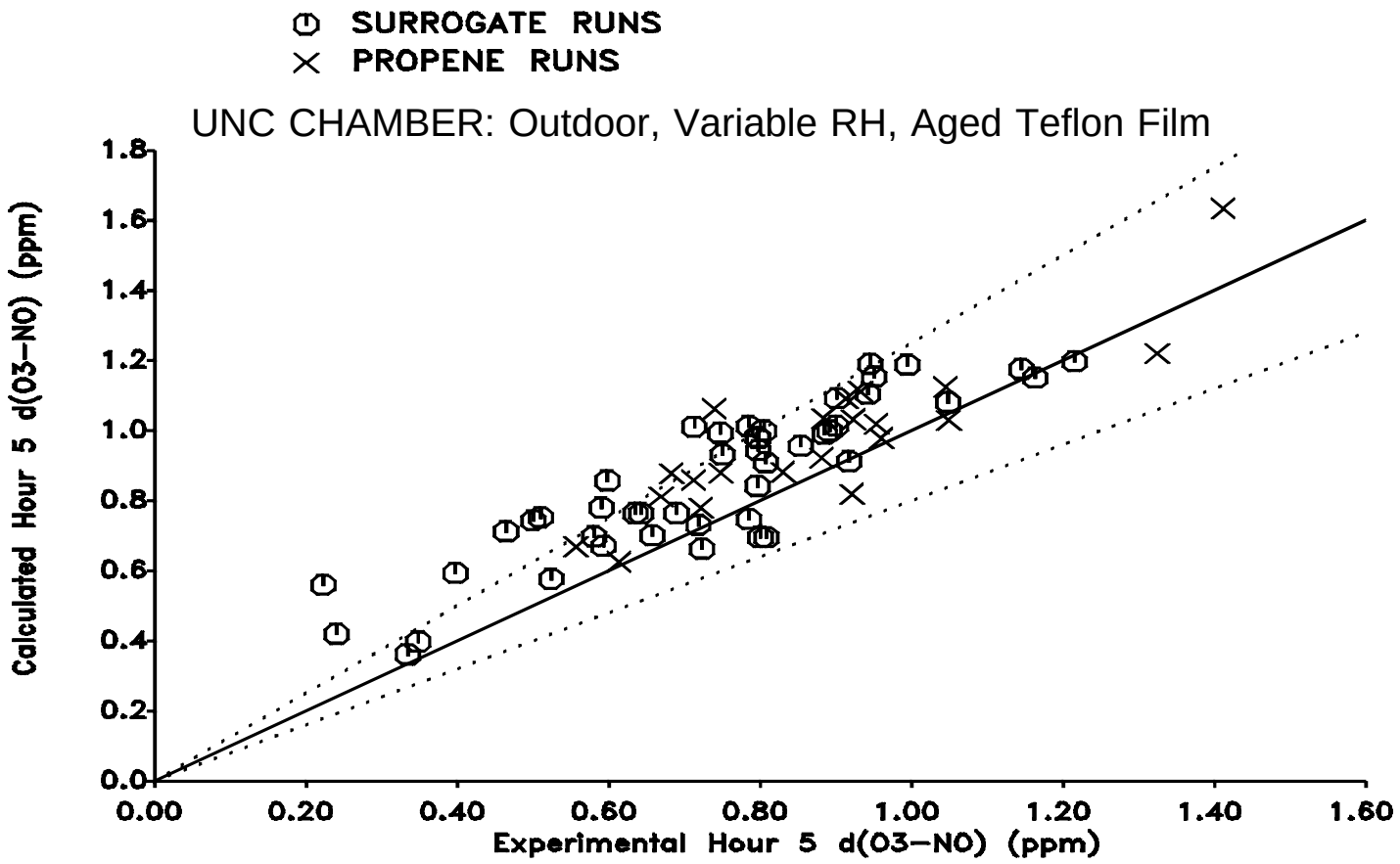
COMPARISON OF EXPERIMENTAL AND CALCULATED d(O_3-NO) IN UCR SINGLE COMPOUND - NO_x EXPERIMENTS



COMPARISON OF EXPERIMENTAL AND CALCULATED $d(O_3\text{-}NO)$ IN UCR SURROGATE MIXTURE - NO_x EXPERIMENTS

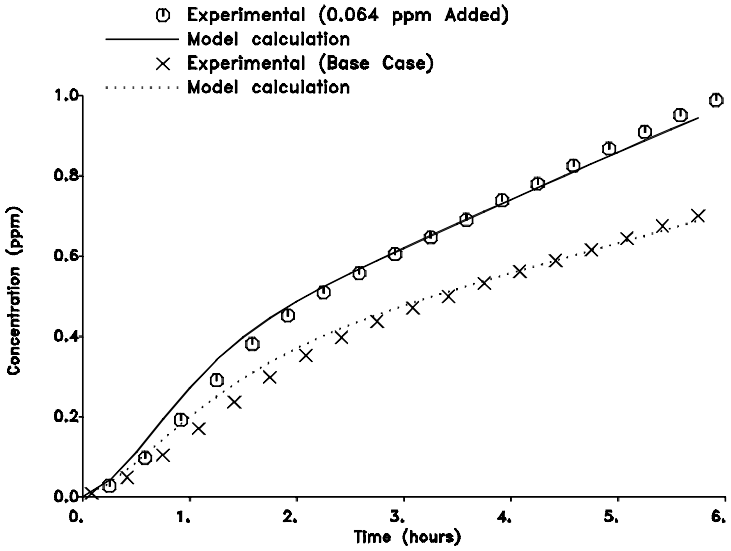


COMPARISON OF EXPERIMENTAL AND CALCULATED $d(O_3\text{-}NO)$ IN UNC PROPENE AND SURROGATE MIXTURE - NO_x EXPERIMENTS

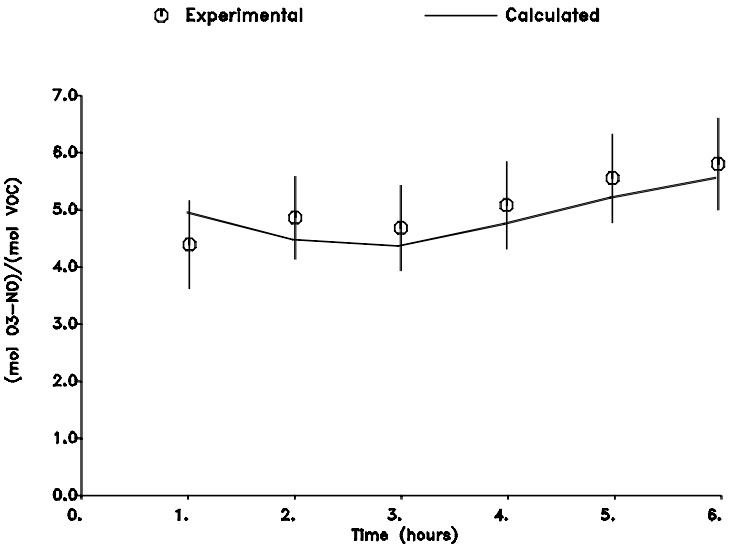


EXMPLE OF AN INCREMENTAL REACTIVITY EXPERIMENT: EFFECT OF M-XYLENE UNDER LOW ROG/NO_x CONDITIONS

$\Delta([O_3]-[NO])$ vs TIME

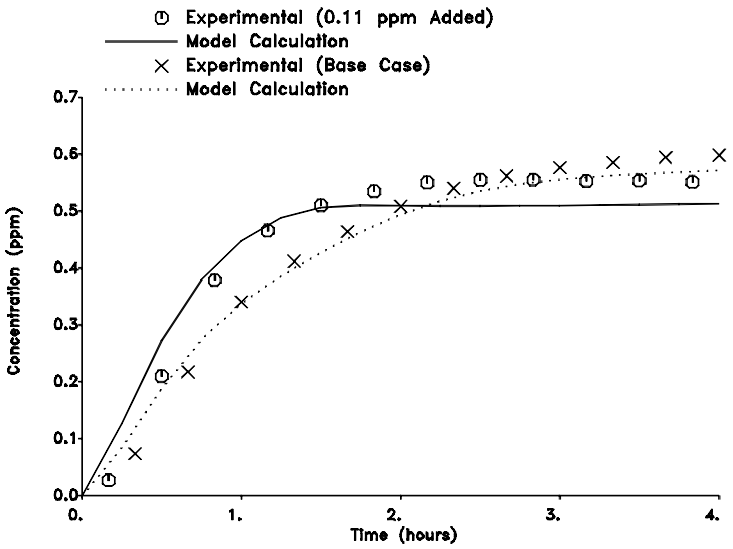


{CHANGE IN $\Delta([O_3]-[NO])$} / (M-XYLENE REACTED) VS TIME

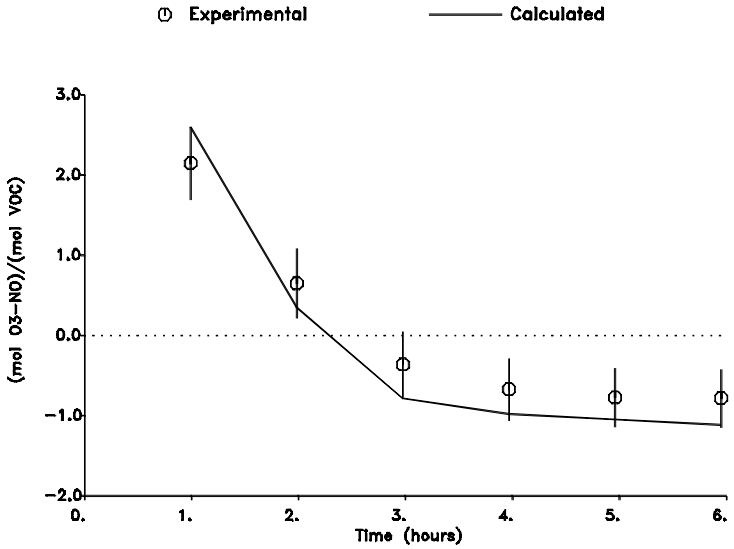


EXMPLE OF AN INCREMENTAL REACTIVITY EXPERIMENT: EFFECT OF M-XYLENE UNDER HIGH ROG/NO_x CONDITIONS

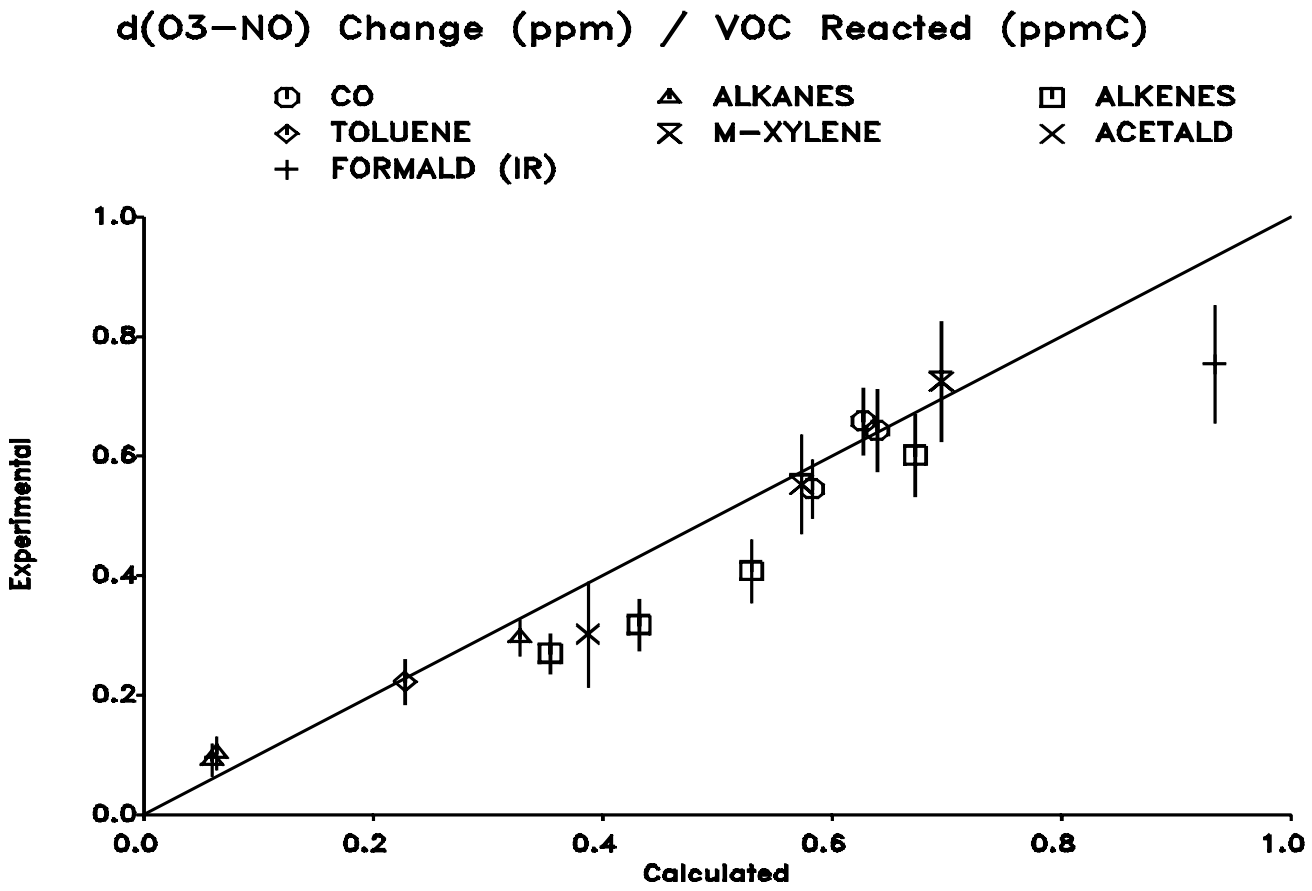
$\Delta([O_3]-[NO])$ vs TIME



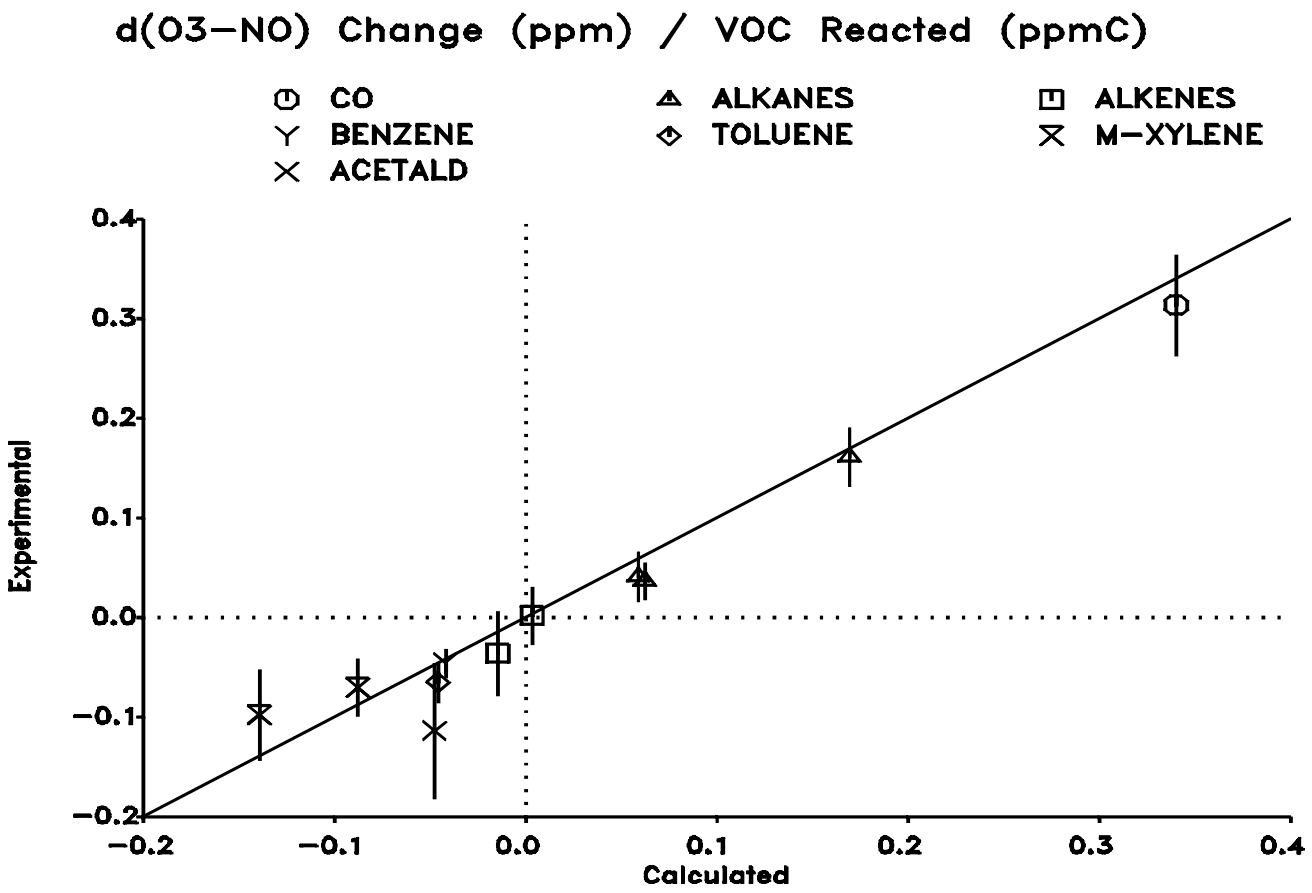
{CHANGE IN $\Delta([O_3]-[NO])$} / (M-XYLENE REACTED) VS TIME



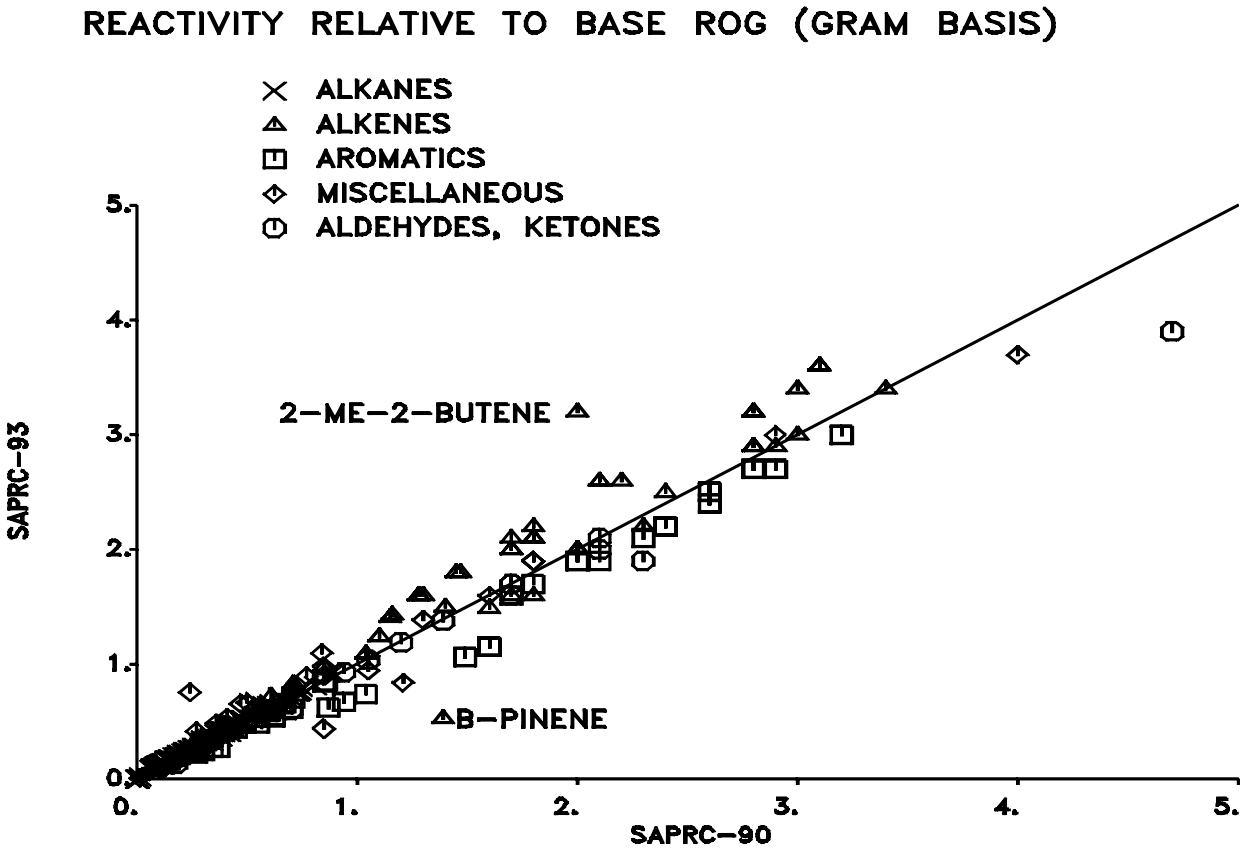
MODEL PERFORMANCE IN SIMULATING INCREMENTAL REACTIVITIES UNDER HIGH NO_x CONDITIONS



MODEL PERFORMANCE IN SIMULATING INCREMENTAL REACTIVITIES UNDER LOW NO_x CONDITIONS



EFFECT OF RECENT SAPRC MECHANISM UPDATES ON MAXIMUM INCREMENTAL REACTIVITY SCALE



CURRENT STATUS OF THE CHEMICAL MECHANISMS USED TO PREDICT O_3 IMPACTS OF VOCs AND NO_x

MANY UNCERTAINTIES IN VOC REACTION MECHANISMS, ESPECIALLY FOR AROMATICS. PARAMETERIZED MODELS ADJUSTED TO FIT CHAMBER DATA.

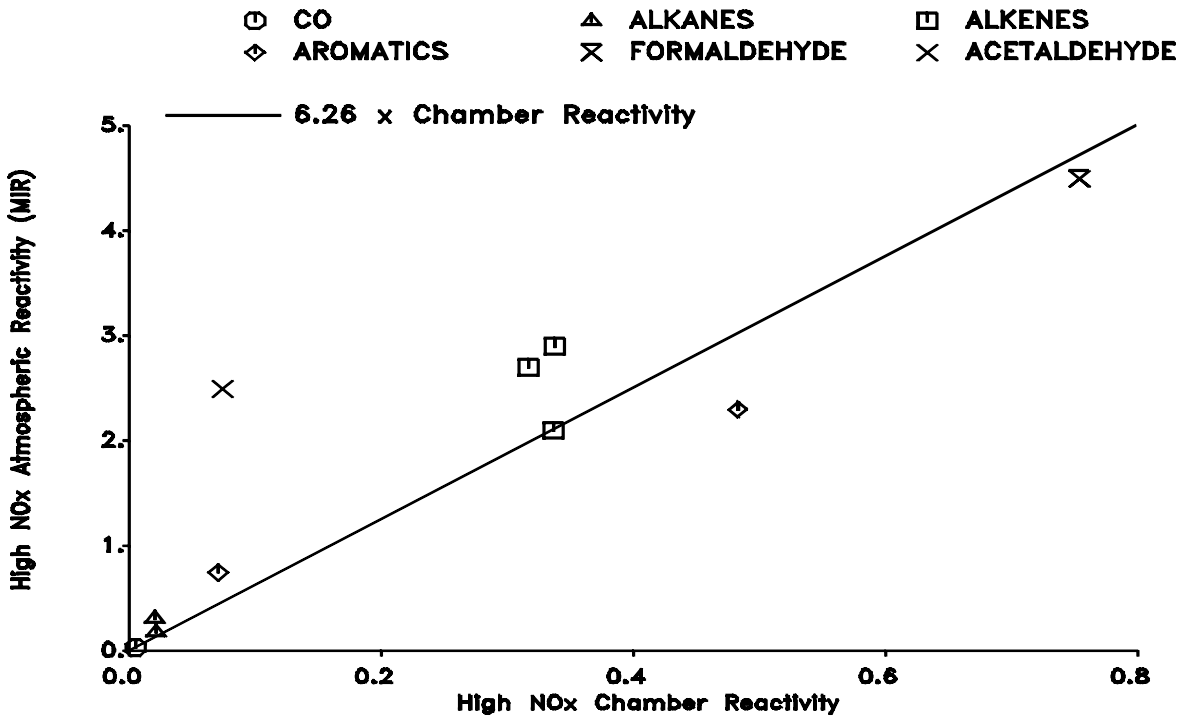
MECHANISMS CAN SIMULATE O_3 AND NO IN MOST WELL-CHARACTERIZED EXPERIMENTS WITHIN $\pm$ 30%. SOME EXCEPTIONS AND INCONSISTENCIES.

- POOR REPRESENTATION OF SOME AROMATIC ISOMERS.
- UNEXPLAINED VARIABILITIES IN SIMULATIONS OF ETHENE RUNS
- POSSIBLE UNDERPREDICTION BIAS IN NEW SAPRC OUTDOOR AND XENON ARC LIGHT EXPERIMENTS.
- APPARENT OVERPREDICTION BIAS IN UNC OUTDOOR EXPERIMENTS.

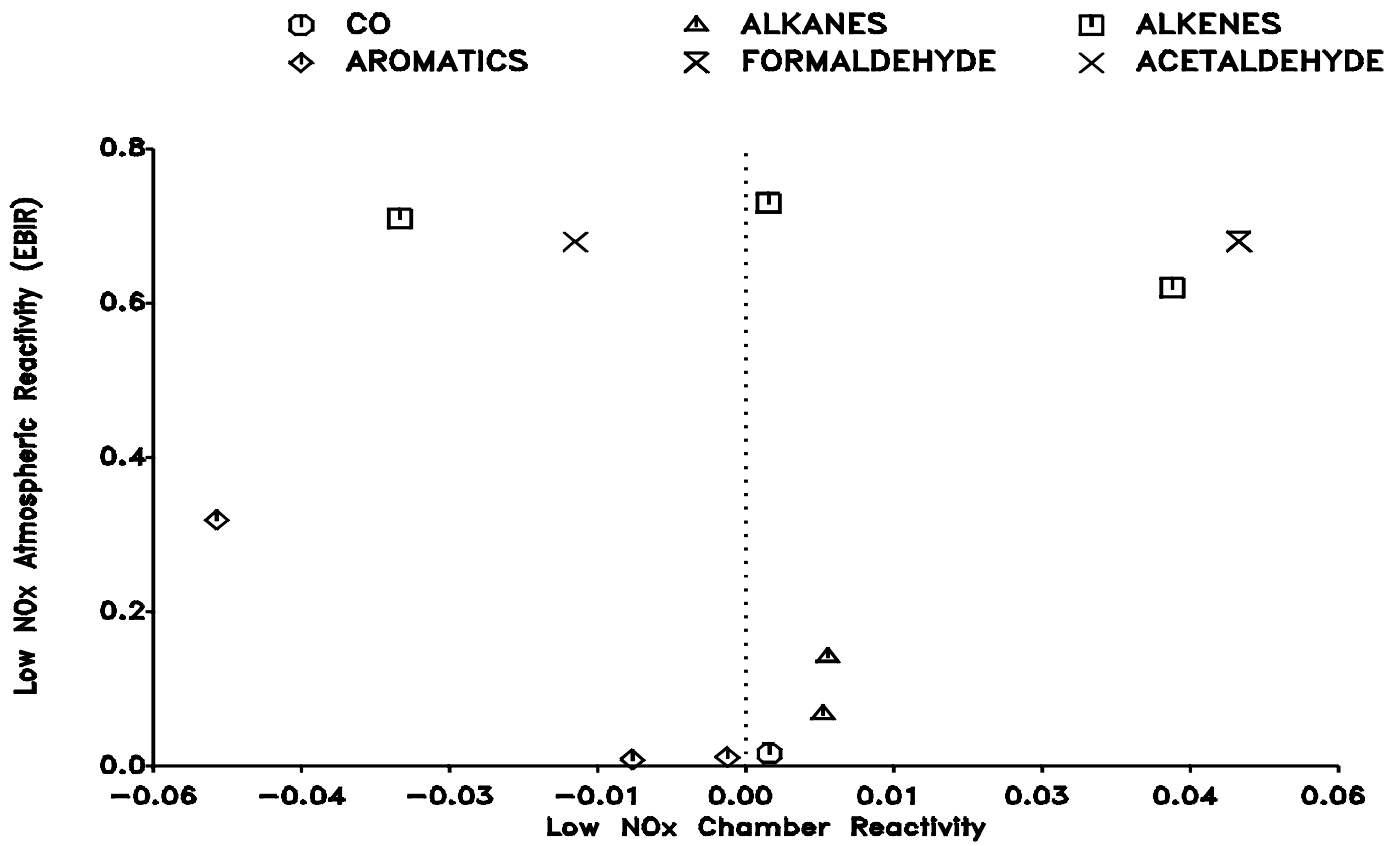
INCREMENTAL REACTIVITIES HAVE NOT BEEN SYSTEMATICALLY MEASURED USING REALISTIC LIGHT SOURCES SUCH AS SUNLIGHT OR XENON ARCS.

EFFECTS OF CHEMICAL MECHANISM UNCERTAINTY ON AIRSHED MODEL PREDICTIONS OF REACTIVITY HAVE NOT BEEN ADEQUATELY ASSESSED.

CORRESPONDENCE BETWEEN RESULTS OF UCR HIGH NO_x INCREMENTAL REACTIVITY EXPERIMENTS AND CALCULATED HIGH NO_x (MIR) ATMOSPHERIC REACTIVITY SCALE



CORRESPONDENCE BETWEEN RESULTS OF UCR LOW NO_x INCREMENTAL REACTIVITY EXPERIMENTS AND CALCULATED LOW NO_x (EBIR) ATMOSPHERIC REACTIVITY SCALE



RECOMMENDATIONS

CHEMICAL MECHANISM RESEARCH NEEDS:

- MECHANISTIC STUDIES OF UNCERTAIN VOC REACTIONS.
- IMPROVE ENVIRONMENTAL CHAMBER DATA BASE AND RESOLVE INCONSISTENCIES AMONG DIFFERENT CHAMBERS.

COMPREHENSIVE UNCERTAINTY ANALYSIS SHOULD ALWAYS BE A PART OF ANY ALTERNATIVE FUEL IMPACT ASSESSMENT. ASSESS EFFECTS OF:

- UNCERTAINTIES IN CHEMICAL MECHANISM.
- UNCERTAINTIES AND VARIABILITIES IN EMISSIONS DATA.
- VARIABILITY OF OZONE IMPACTS WITH AMBIENT CONDITIONS.

ANALYSES USING SIMPLIFIED (EKMA) MODELS MULTIPLE REACTIVITY SCALES ARE MUCH MORE USEFUL FOR UNCERTAINTY ANALYSIS THAN COMPLEX, COMPREHENSIVE MODEL SIMULATIONS.

NO SINGLE APPROACH SHOULD BE RELIED UPON FOR COMPARING ALTERNATIVE FUEL IMPACTS. DIFFERENCES (OR SIMILARITIES) IN RESULTS USING DIFFERENT METHODS INDICATE OVERALL UNCERTAINTY.

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