

DEVELOPMENT OF A DIRECT REACTIVITY MEASUREMENT METHOD FOR VOLATILE ORGANIC COMPOUNDS

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Outline

- Background: Factors affecting O₃ Reactivity of VOCs; Mechanism Evaluation Needs
- Direct Reactivity: What it is; How to Measure; Relationship to Other Reactivity Measures
- Experimental Approaches Examined
- Results
- Ongoing Work
- Conclusions

VOC REACTIVITY

The atmospheric oxidation reactions of Volatile Organic Compounds (VOCs) result in enhanced formation of ground-level ozone from NO_x .

VOCs differ in their effects on ozone formation. The term **reactivity** is used to refer to this.

Several aspects of a VOC's atmospheric reactions affect its O_3 reactivity:

- Direct Effects:
 - How fast it reacts;
 - How much O_3 is formed directly from its reactions and those of its products
- Indirect Effects
 - Whether it enhances or inhibits radicals. Affects how fast O_3 is formed from all VOCs
 - Whether it enhances rates of NO_x removal. This affects ultimate O_3 yields when NO_x is limited.

The VOCs effect on O_3 also depends on the nature of the environment where it reacts

QUANTIFICATION OF REACTIVITY

A useful measure of the effect of a VOC on ozone formation is **incremental reactivity**:

Incremental Reactivity of a VOC in an Episode	=	Lim [VOC]→0	O ₃ Formed when VOC added to Episode	-	O ₃ Formed in an Episode
			Amount of VOC Added to Emissions in Episode		

This depends on the conditions of the episode as well as on the VOC

Because of this, atmospheric reactivities must be calculated using computer airshed models, given:

- Models for airshed conditions
- Chemical Mechanisms for the VOC's atmospheric reactions

Such calculations can be no more reliable than the chemical mechanism used

Experiments are needed to test the reliability of mechanisms to predict atmospheric reactivity

ENVIRONMENTAL CHAMBER EXPERIMENTS

Environmental chamber reactivity experiments have been the primary means used to evaluate mechanisms for predicting effects of VOCs on O₃

These involve determining effect of adding the VOC to standard “ROG Surrogate - NO_x - air irradiation experiments.

Using different kinds of ROG surrogates and ROG/NO_x ratios give results that have different sensitivities to different mechanism aspects.

- High ROG/NO_x “Mini-Surrogate” experiments most sensitive to radical effects
- Standard “Full Surrogate” experiments give best correlation to atmospheric MIR
- Low NO_x “Full Surrogate” experiments more sensitive to NO_x removal effects

Such experiments have been used to derive and evaluate mechanisms of ~60 types of VOCs for the SAPRC-99 reactivity scales

LIMITATIONS OF ENVIRONMENTAL CHAMBER EXPERIMENTS FOR MECHANISM EVALUATION

- Very expensive to carry out (now \geq \$40K per VOC)
- Requires special expertise available at only a few laboratories
- Lower sensitivity to effects of oxidation products than predicted for the atmosphere
- Ambiguous mechanism evaluation data when more than one aspect of the mechanism is uncertain
- Not well suited for low volatility compounds

MEASUREMENT OF DIRECT REACTIVITY

Direct reactivity is the effect of the VOC on O₃ formation directly due to its reactions or reactions of its products

One of the important factors affecting O₃ reactivity in the atmosphere

Often ambiguous to evaluate in environmental chamber reactivity experiments

- Radical initiation/inhibition effects can dominate results of High NO_x experiments
- NO_x removal effects can dominate results of low NO_x experiments
- Errors in these indirect effects could mask (compensate for) errors in mechanism affecting direct reactivity in the atmosphere.

A direct reactivity measurement method could reduce the ambiguities in mechanism evaluation, especially for radical inhibiting VOCs

A direct reactivity measurement using a flow system may be more suitable to use with low volatility compounds than chamber experiments

EXPERIMENTAL APPROACHES TO MEASURE DIRECT REACTIVITY

Requirements

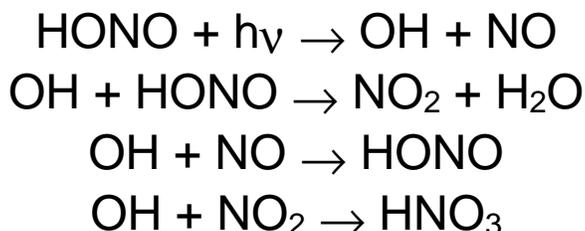
- Sensitive to $\text{NO} \rightarrow \text{NO}_2$ conversion processes that are responsible for O_3 formation
- Both radicals and NO_x in excess to reduce sensitivity to indirect effects

HONO Photolysis System

- Large internal radical source and sink processes
- NO_x present in excess
- Major reactions in absence of VOC result in consumption of HONO and formation of NO , NO_2 , and HNO_3
- Addition of reactive VOC causes NO to NO_2 conversions that reduce NO levels and (if enough VOC is added) O_3 formation
- Effect of added VOC on $\Delta([\text{O}_3]-[\text{NO}])$ reflects the NO to NO_2 conversions caused by the added VOC, which is its direct reactivity.

CHEMISTRY OF HONO PHOTOLYSIS SYSTEM

Reactions in the absence of added VOC

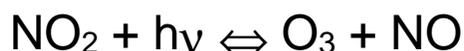


Net effect is formation of NO, NO₂ and HNO₃.

Additional reactions in presence of VOC



Net effect is lower NO formation and (if enough VOC is added) formation of O₃ through reactions



For low amount of added VOC:

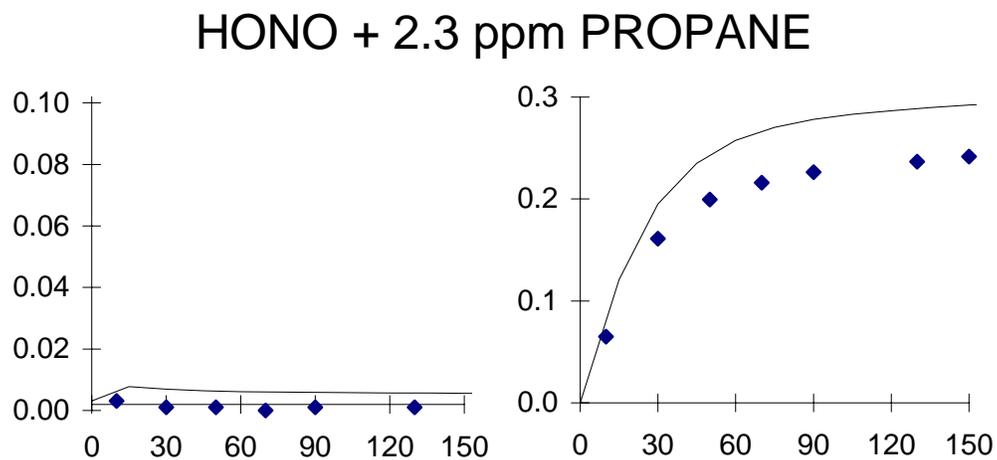
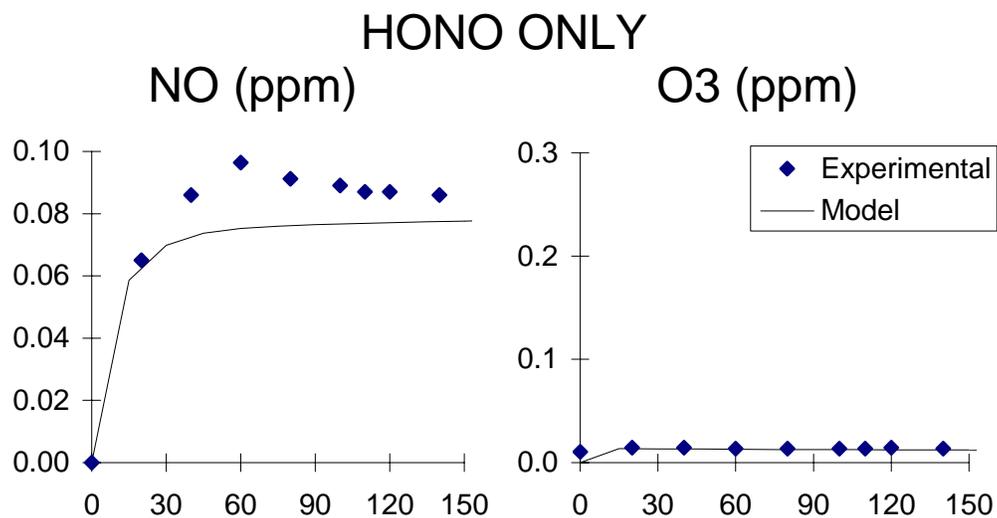
$$\frac{([\text{O}_3] - [\text{NO}])_{\text{VOC}} - ([\text{O}_3] - [\text{NO}]_{\text{no VOC}})}{[\text{VOC added}]}$$

is approximately proportional to

kOH(VOC) × NO conversions per VOC reacted

Therefore, $\Delta([\text{O}_3] - [\text{NO}]) / [\text{VOC}]$ provides a measure of the VOC's direct reactivity

EXAMPLE OF ENVIRONMENTAL CHAMBER IRRADIATIONS OF HONO – AIR AND HONO – VOC – AIR MIXTURES



Concentration (ppm) vs Irradiation Time (minutes)

Runs DTC686A and B

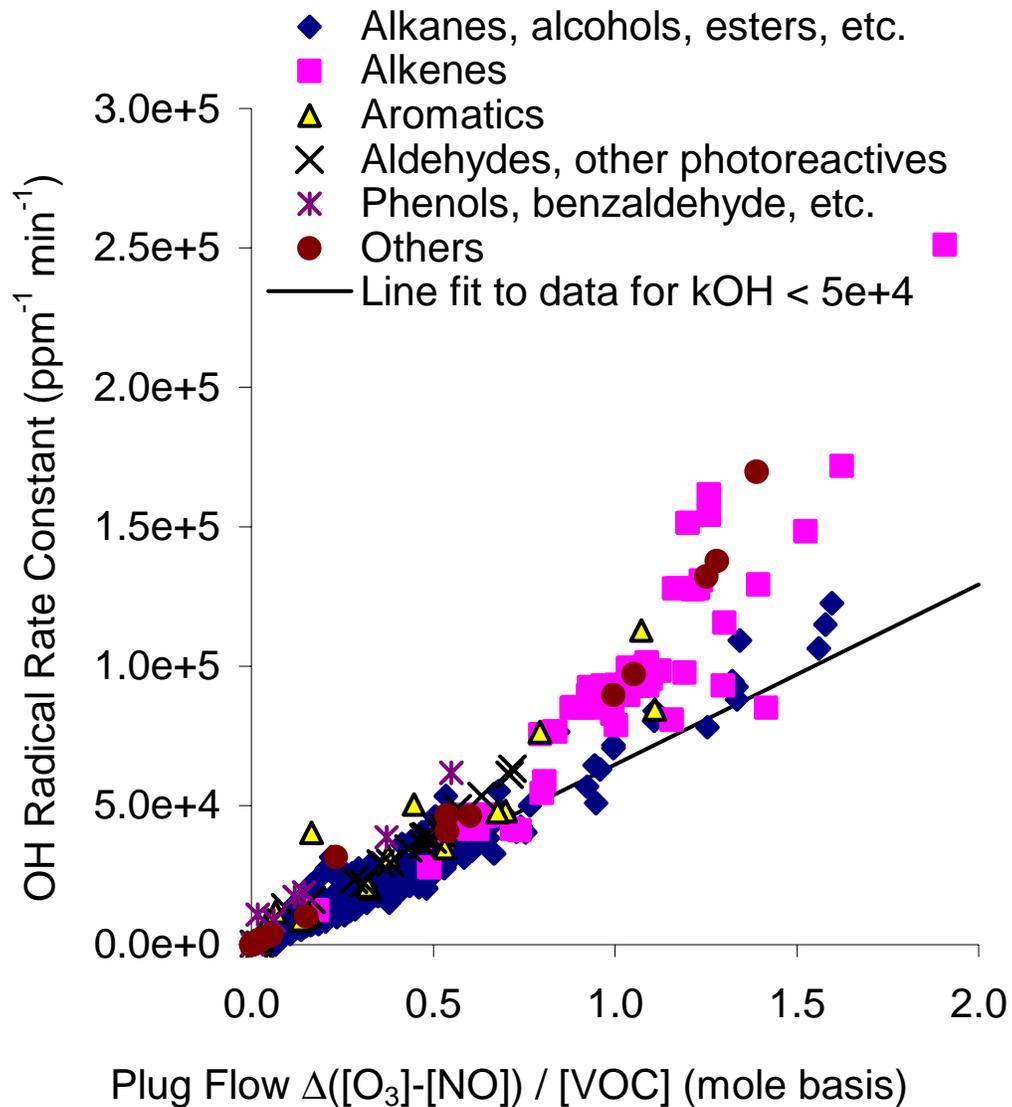
Initial HONO \approx 0.35 ppm

NO₂ photolysis rate \approx 0.17 min⁻¹, Blacklight irradiation

CALCULATED SENSITIVITIES OF EXPERIMENTS OR SIMULATIONS TO VARIOUS MECHANISM COMPONENTS

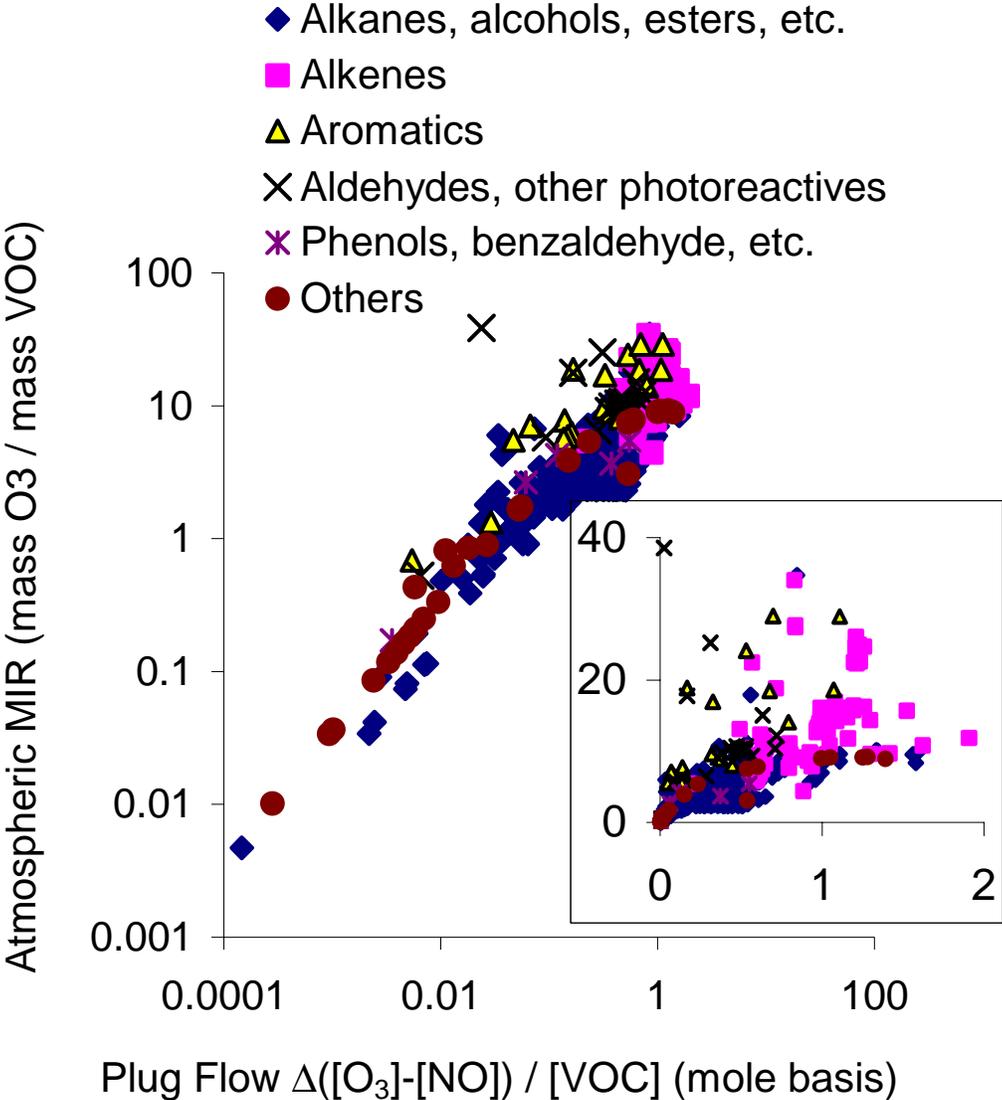
Type of Experiment or Simulation	Mechanistic Reactivity of Mechanism Component (mol O ₃ / mol VOC reacted)		
	NO to NO ₂ Convert.	Pure Radical Source	Ketone Product Form.
<u>HONO + VOC Experiment</u>			
Stirred Flow	0.7	0.32	1.7
Plug Flow	0.9	0.12	0.14
<u>Environmental Chamber Reactivity Experiment</u>			
Mini-Surrogate	0.6	6.0	0.16
High NO _x Surg.	0.6	3.0	0.33
Low NO _x Surg.	0.4	-0.3	0.09
<u>Atmospheric Reactivity Simulation</u>			
MIR	0.6	2.4	4.1
EBIR	0.4	1.1	1.4

CORRESPONDENCE BETWEEN K(OH) AND DIRECT REACTIVITY MEASURED BY A HONO PHOTOLYSIS SYSTEM



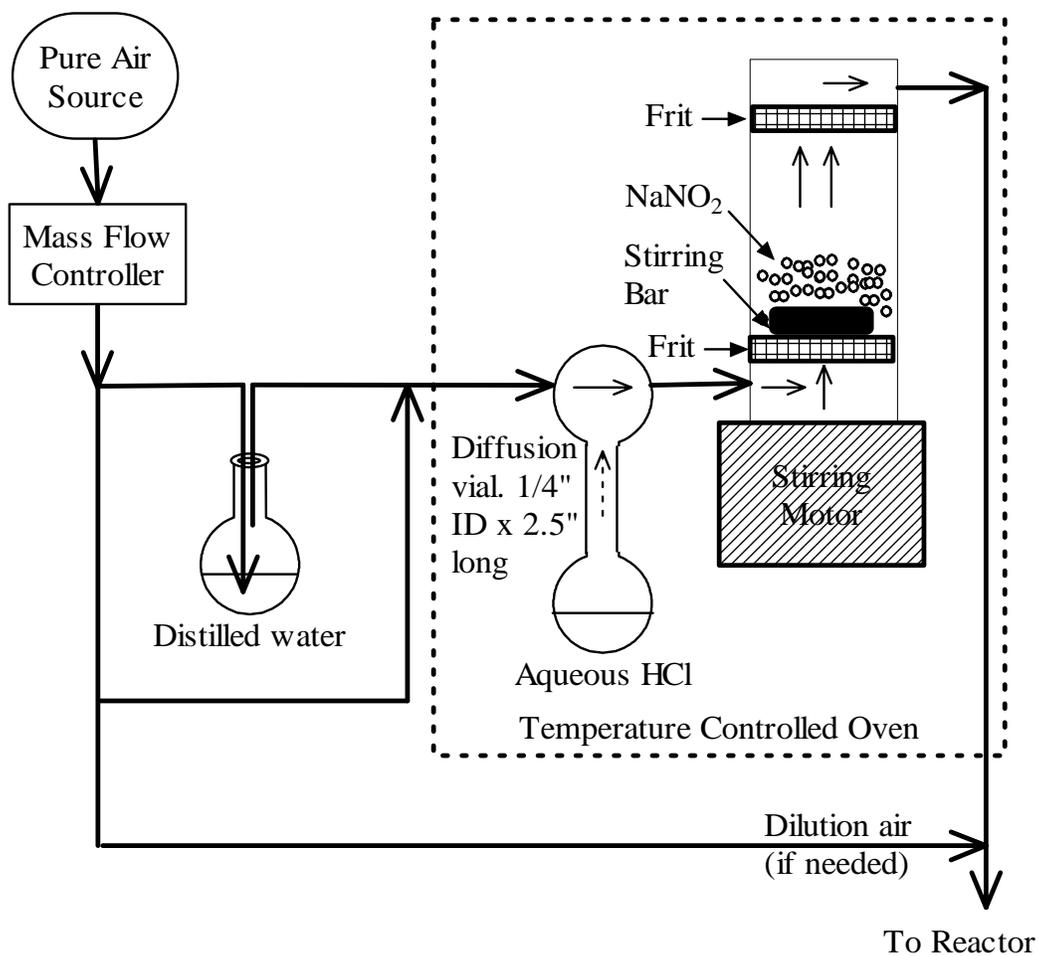
PLOT SHOWS SAPRC-99 PREDICTIONS OF PLUG FLOW HONO + VOC EXPERIMENTS

CORRESPONDENCE BETWEEN MIR AND DIRECT REACTIVITY MEASURED BY A HONO PHOTOLYSIS SYSTEM



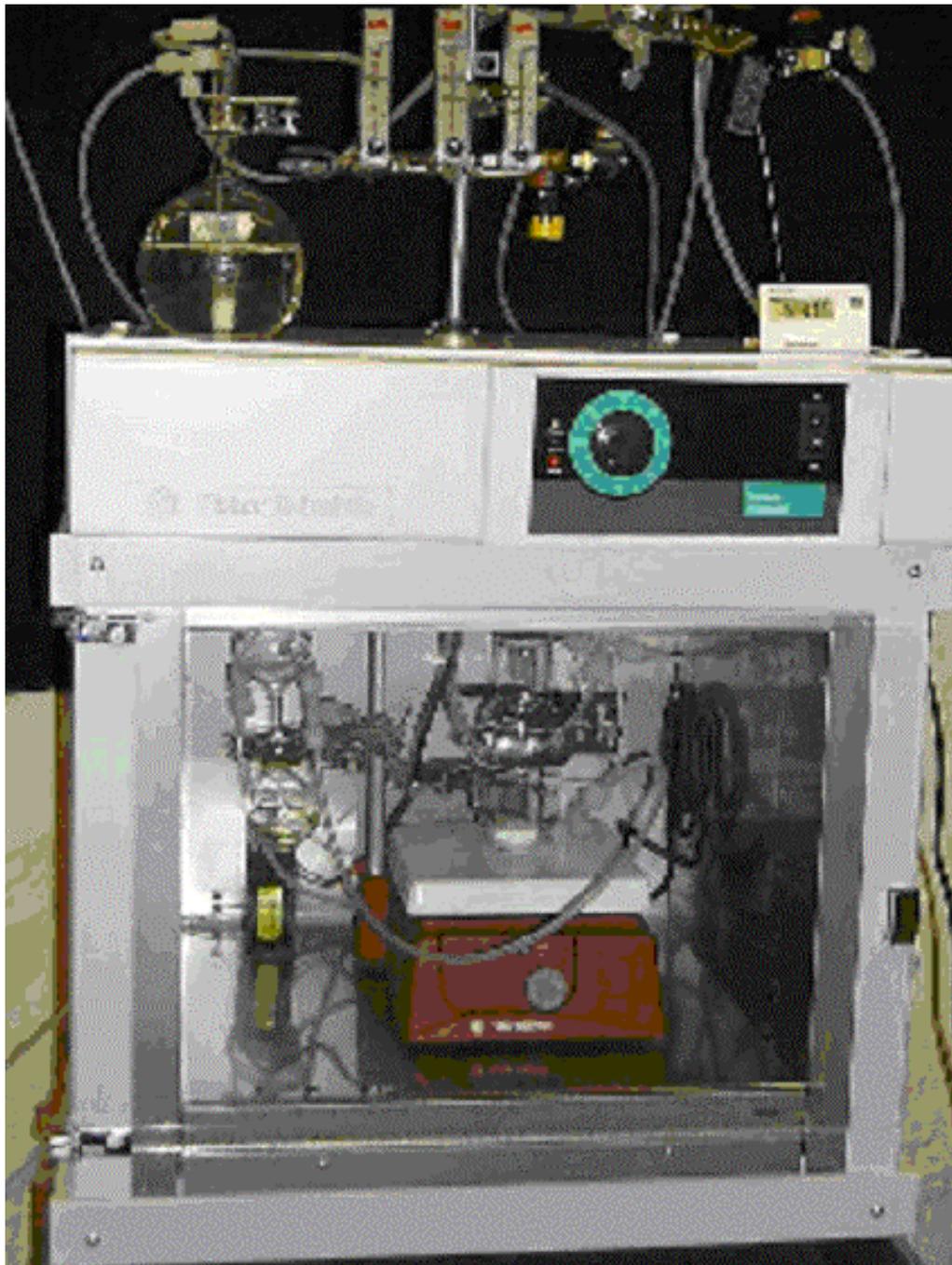
PLOT SHOWS SAPRC-99 PREDICTIONS OF
PLUG FLOW HONO + VOC EXPERIMENTS

HONO GENERATION SYSTEM USED



- Based on method of Febo et al (1995)
- Formed via $\text{HCl} + \text{NaNO}_2 \rightarrow \text{NaCl} + \text{HONO}$
- Produces HONO output of $\geq \sim 0.2$ millimole /min ($\geq \sim 5$ ppm in air at 1 liter/minute)
- No measurable HCl at this output level. HONO purity of $\sim 90\%$ ($\sim 5\%$ each NO, NO₂).

PHOTOGRAPH OF HONO GENERATION SYSTEM



ALTERNATIVE EXPERIMENTAL APPROACHES FOR HONO – VOC REACTION SYSTEM

Static System

Irradiation of HONO and HONO + VOC in a static reactor or environmental chamber

Advantages:

- Simplest to characterize for modeling

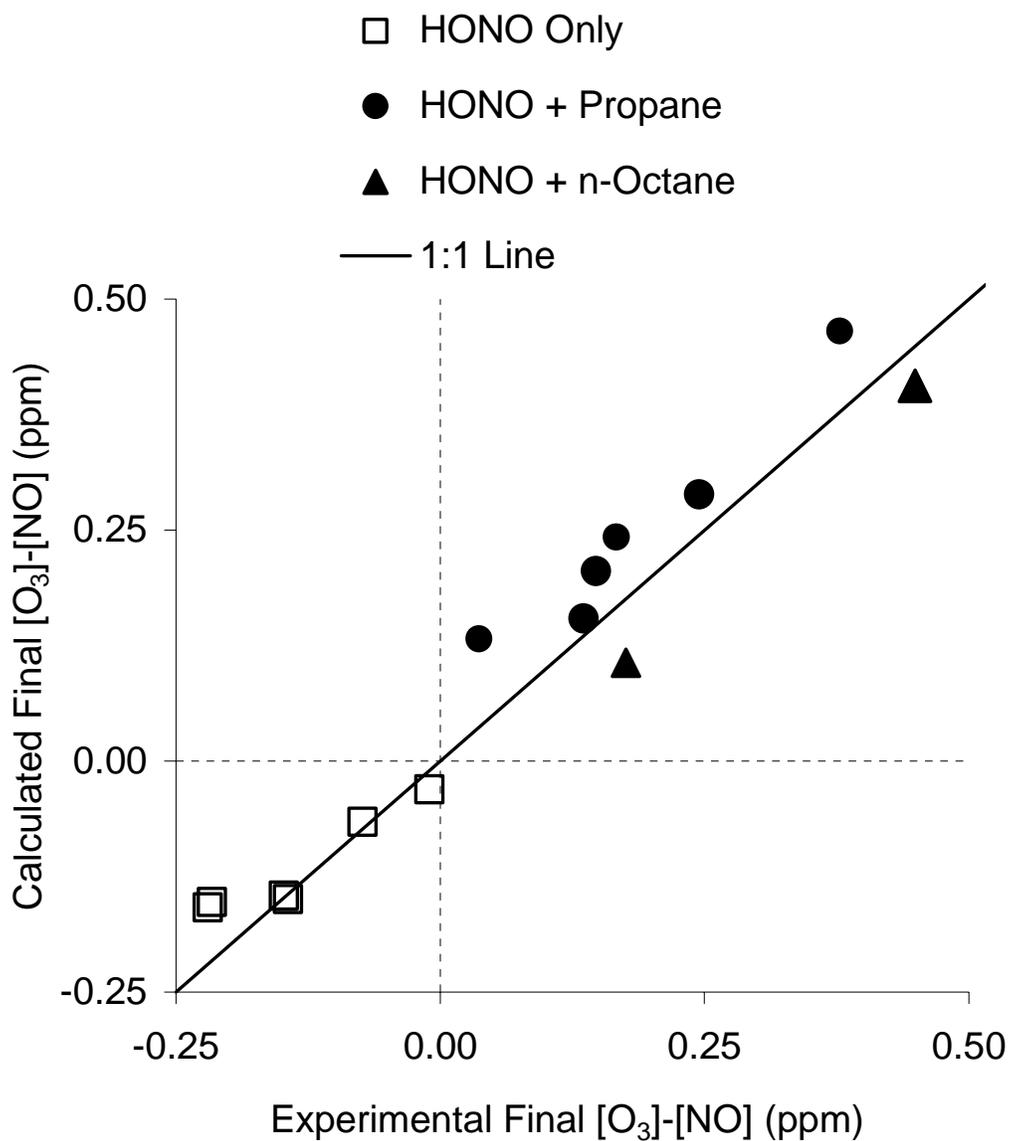
Disadvantages:

- Difficult to reproduce conditions from run to run
- Time consuming to carry out
- Not well suited for low volatility compounds

Because of its disadvantages, only a limited number of static experiments were conducted to evaluate ability to model HONO chemistry

Results of experiments were generally consistent with model predictions, but there was some run-to-run variability

EXPERIMENTAL VS CALCULATED [O₃]-[NO] FOR THE STATIC HONO + VOC IRRADIATIONS



ALTERNATIVE EXPERIMENTAL APPROACHES (CONT'D)

Continuous Flow Systems

HONO or HONO + VOC mixtures are continuously flowed through an irradiated reactor with the output sampled.

Can be carried out in stirred flow or plug flow modes

Advantages

- Easily interfaced to HONO generation system, which produces continuous output
- Continuous VOC injection potentially better suited to low volatility compounds
- Potentially able to obtain more data points per unit time than static methods
- Potential to develop self-contained system that can be used to conduct experiments at lower cost and effort

Disadvantages

- Dynamic systems more uncertain to model
- Uses lower volume reactors where surface absorption effects may be more important

ANALYTICAL METHODS EMPLOYED

Chemiluminescence NO - NO_x Analyzer

- Needed to determine $\Delta([O_3]-[NO])$ caused by added VOC and to determine level of NO impurity in HONO
- “NO₂” channel gives 100% response to HONO, so can be used to determine HONO input

O₃ Analyzer

- Needed to determine $\Delta([O_3]-[NO])$ with high added VOC

Specific NO₂ Analysis (by TDLAS)

- TDLAS or GC-Luminol used periodically to determine level of NO₂ impurity in HONO input
- NO and NO₂ impurity levels found to be similar.
- Not normally used or needed for experiments

GC Analysis of Test VOC

- Needed to determine amount of VOC added
- Most labor intensive aspect of most experiments
- Problems with data precision for low volatility VOCs

FIRST SERIES: STIRRED FLOW EXPERIMENTS

Stirred flow method involves use of a reactor that can be assumed to be well mixed

Modeled Assuming

$$d[C]_t/dt = ([C]_0 - [C]_t) (F / V) + \text{ChemTrans}(C,t)$$

Where

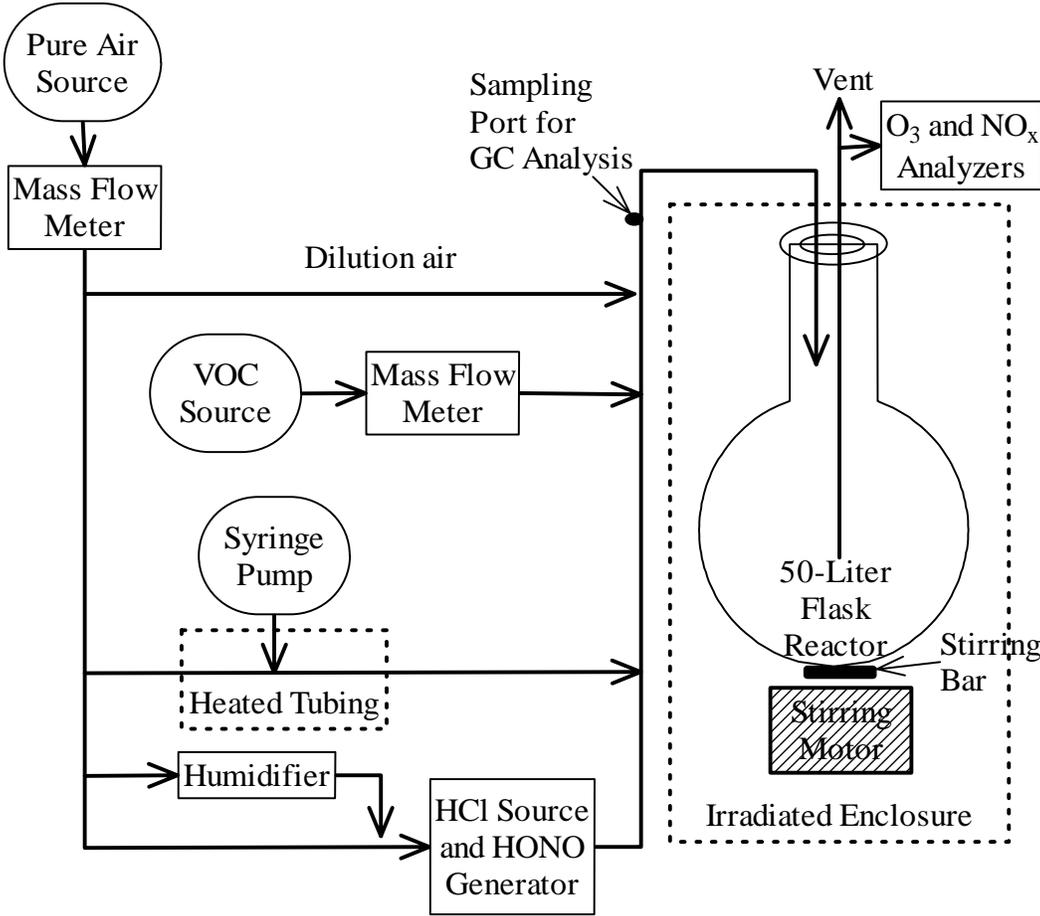
- $[C]_0$ = concentration entering the reactor
- $[C]_t$ = concentration in the mixed reactor
- F = flow
- V = reactor volume
- $\text{ChemTrans}(C,t)$ = chemical reaction rates

Employed in first series of experiments because design allows for longer reaction times, to give larger $\Delta([O_3]-[NO])$ changes with added VOCs.

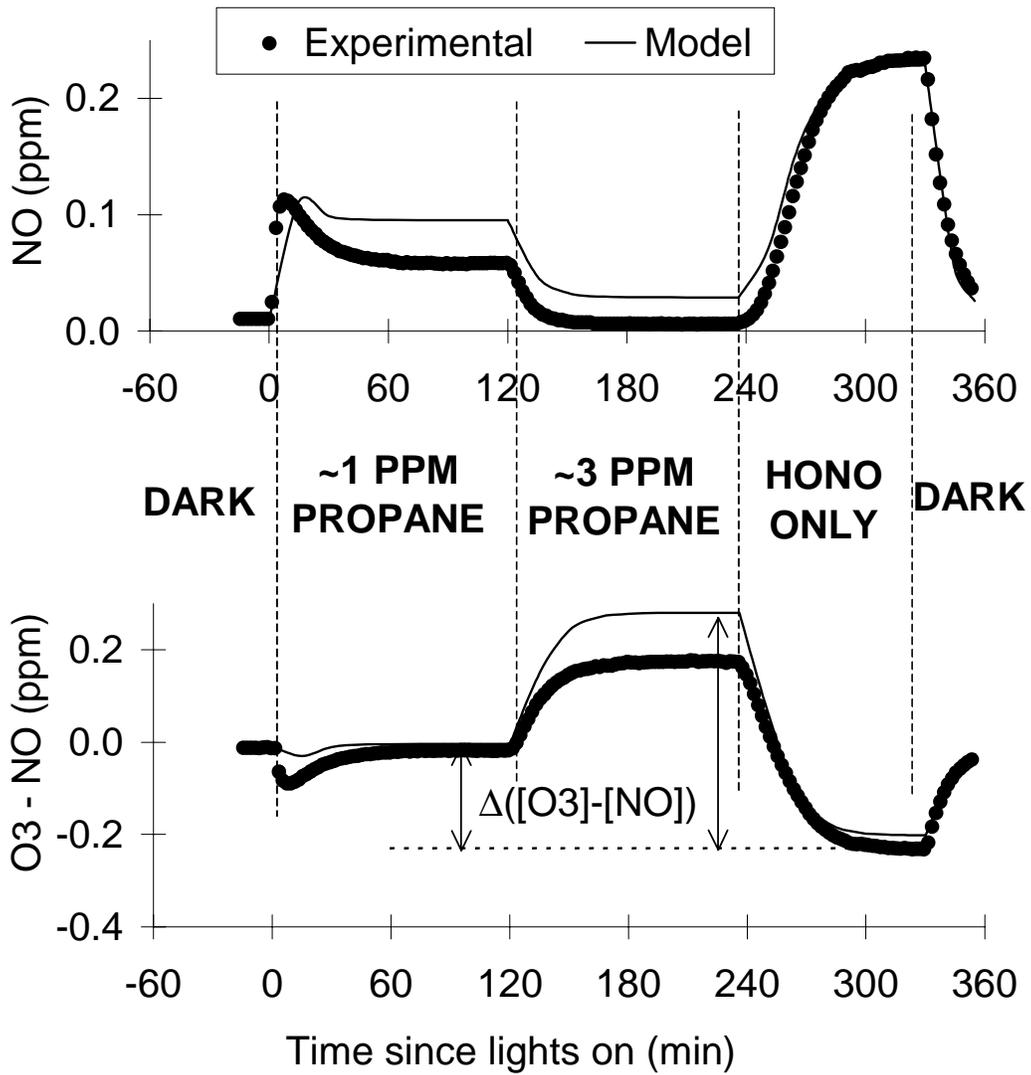
Conditions:

- 50-liter unstirred or stirred Pyrex carboy or 50-liter stirred Pyrex flask used as reactor
- Typical reactor flow: ~5 liter/minute.
- Typical initial HONO ~0.7 ppm
- Irradiated in blacklight chamber enclosure with NO_2 photolysis rate of $\sim 1.1 \text{ min}^{-1}$.

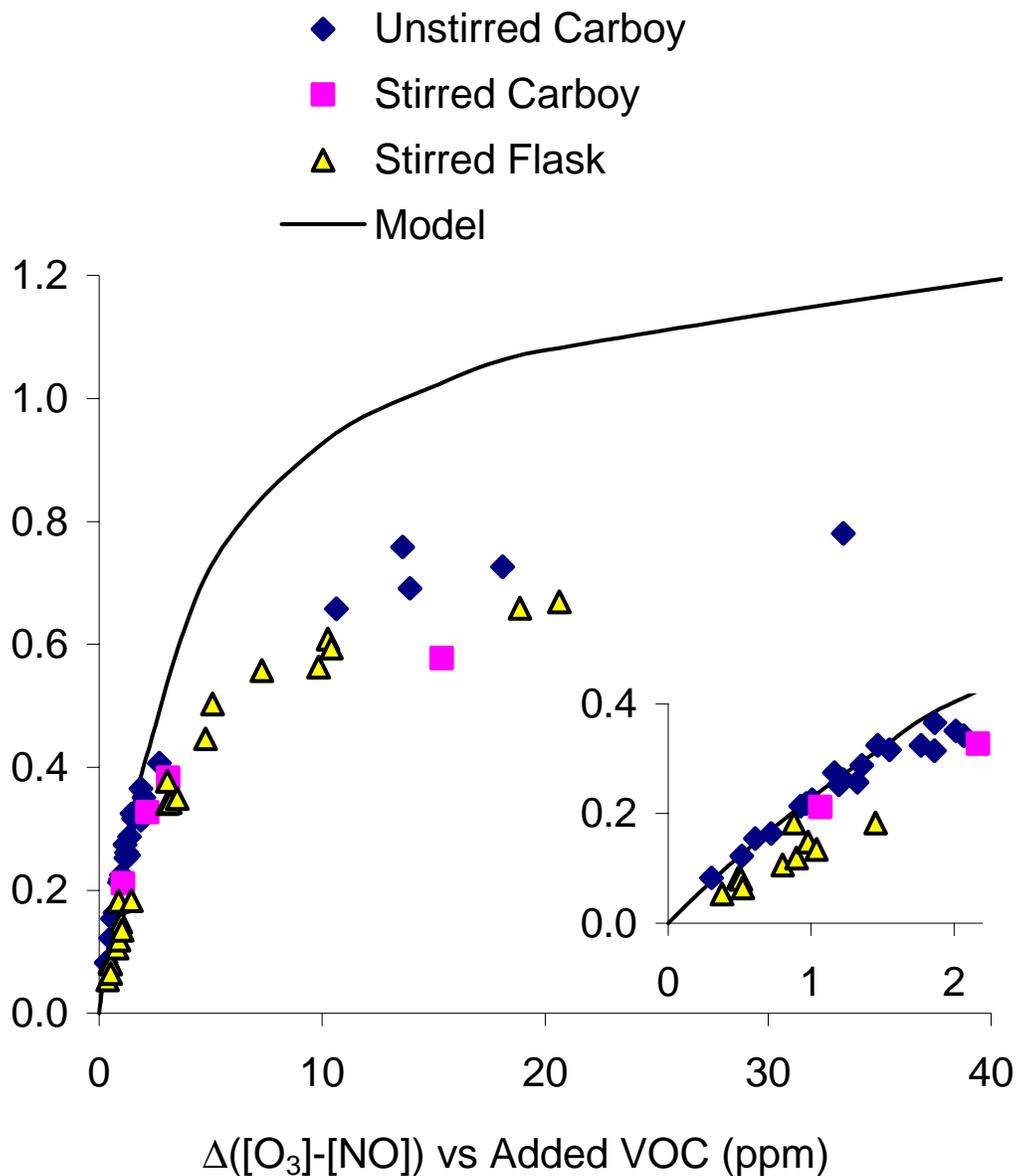
EXAMPLE LAYOUT OF STIRRED FLOW SYSTEM



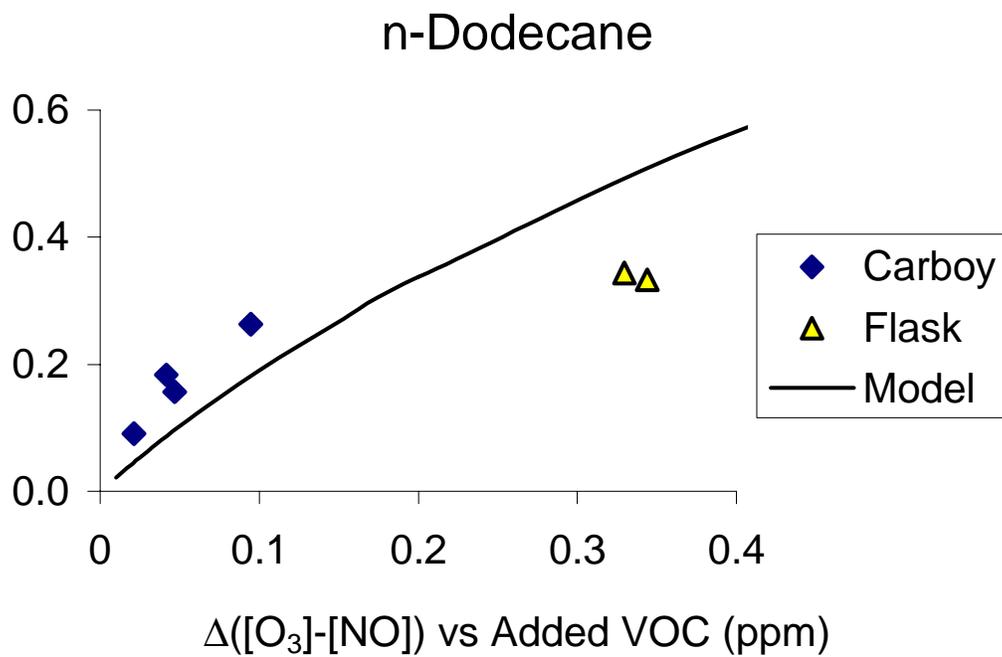
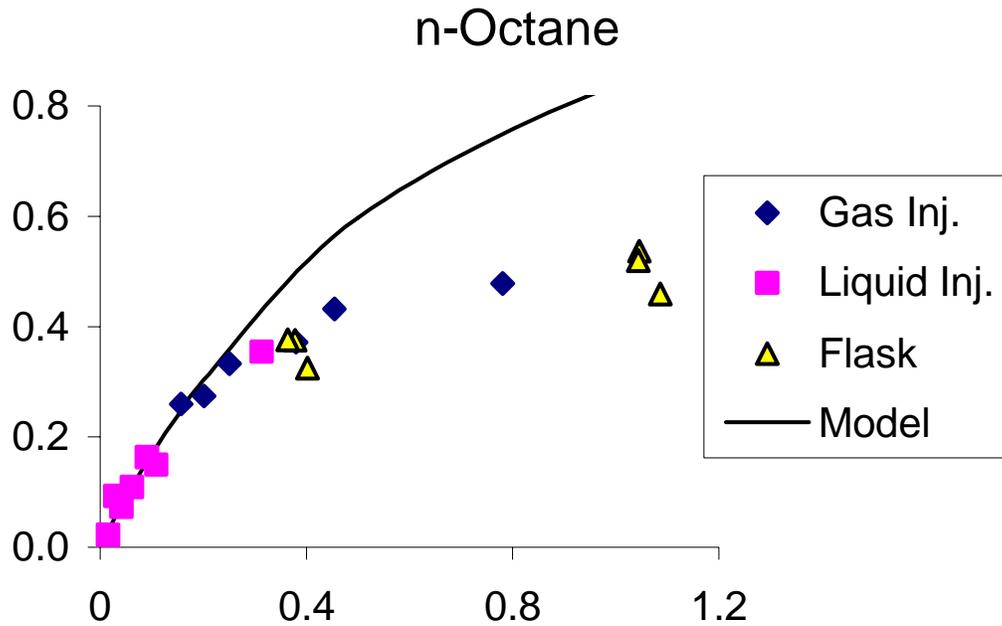
EXAMPLE OF STIRRED FLOW EXPERIMENT RESULTS



RESULTS OF PROPANE EXPERIMENTS IN STIRRED FLOW REACTORS



N-OCTANE AND N-DODECANE STIRRED-FLOW EXPERIMENTS



SUMMARY OF DIRECT REACTIVITY RESULTS USING STIRRED FLOW SYSTEM

Compound	Low Concentration Limit $\Delta([\text{O}_3]-[\text{NO}]) / [\text{VOC}]$ (molar basis)		
	Experimental	Calculated	Model Bias
Propane	0.30	0.26	-14%
n-Butane	0.73	0.70	-5%
n-Hexane	1.55	1.56	0%
n-Octane	2.15	1.83	-15%
n-Decane	3.16	2.05	-35%
n-Dodecane	5.24	2.17	-59%
CO	0.025	0.020	-20%
Acetone	0.109	0.080	-27%

Problems with Stirred Flow Results

- Consistent model underprediction of $\Delta([\text{O}_3]-[\text{NO}])$ at high added VOC
- Higher than expected effect of molecule size on direct reactivities of homologous n-alkanes cannot be explained.

SECOND AND THIRD SERIES: PLUG FLOW EXPERIMENTS

Plug flow method involves use of a tube-shaped reactor where it is assumed that mixing in the direction of the flow is negligible

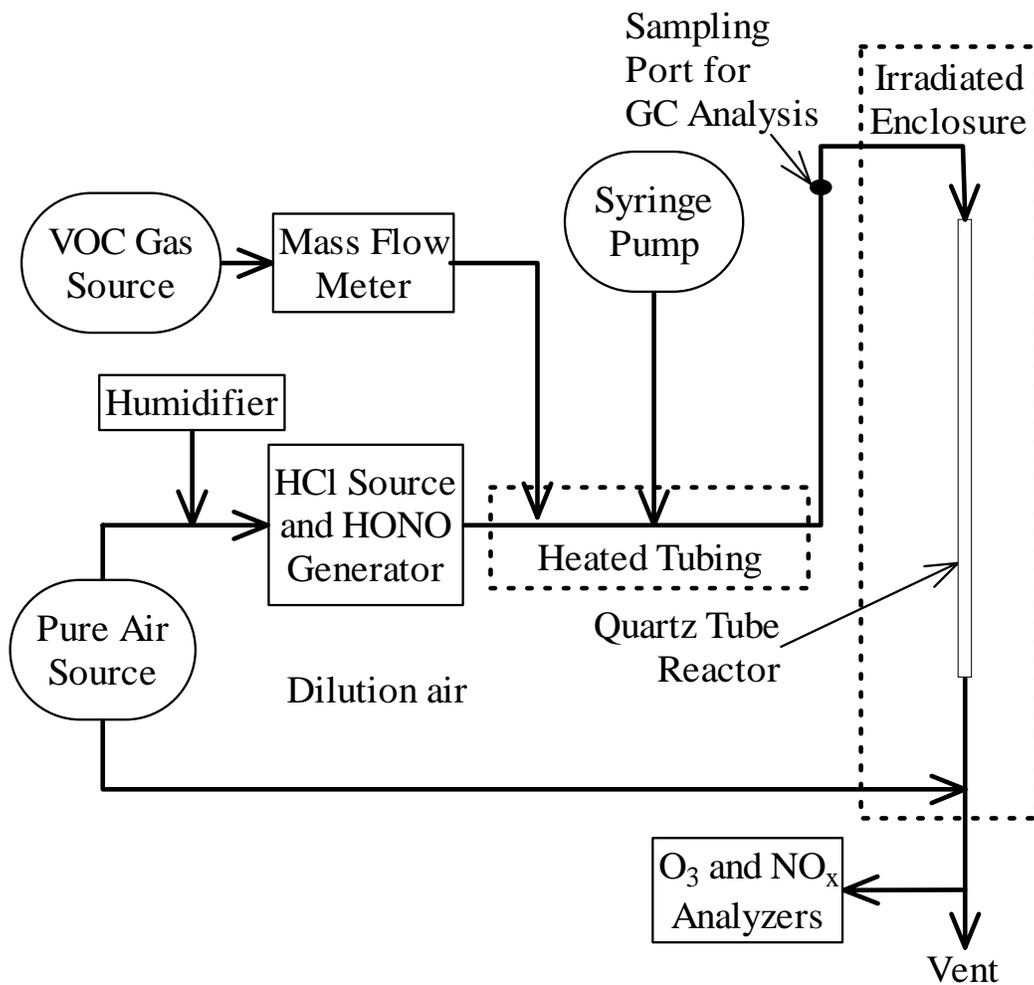
Modeled as a static system with reaction time given by the volume divided by the flow rate

Examined as an alternative approach because of inconsistency with results of stirred flow system with model predictions

Two series of experiments carried out:

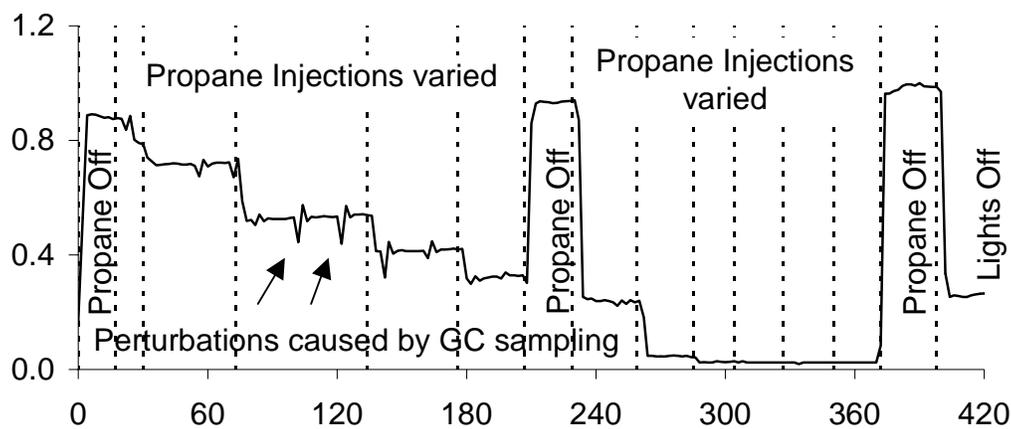
Condition	First Series	Second Series
Reactor	29 m x 0.75 cm ID PFA Teflon Tube (1.3 liters)	86 cm x 1.8 cm ID quartz tube (0.283 liters)
Flow	~1 liter/minute	0.5 liter/minute
Rxn Time	1.3 min.	0.6 min.
HONO	~3.3 ppm	~4 ppm
Lights	Blacklights	Blacklights
$k_{\text{PHOT}}(\text{NO}_2)$	~0.6 - 1 min ⁻¹	0.6 min ⁻¹

EXAMPLE LAYOUT OF PLUG FLOW SYSTEM (WITH QUARTZ TUBE)

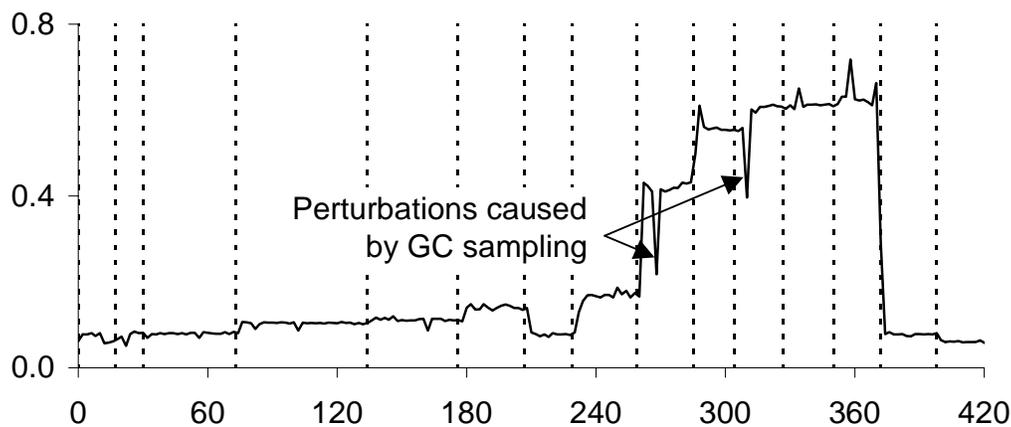


EXAMPLE DATA WITH PLUG FLOW SYSTEM (29 M PFA TUBE): PROPANE EXPERIMENT

NO (ppm)

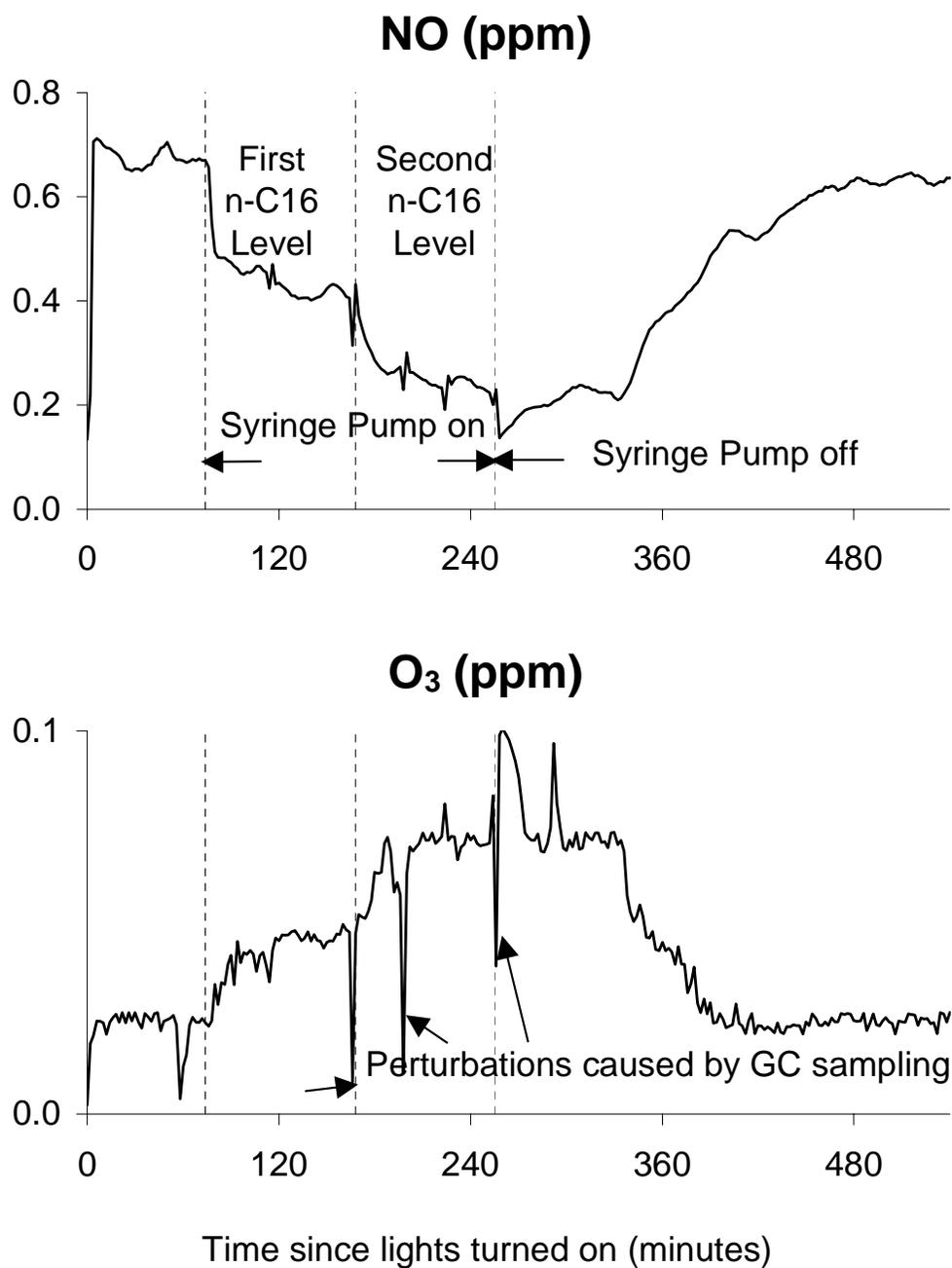


O₃ (ppm)

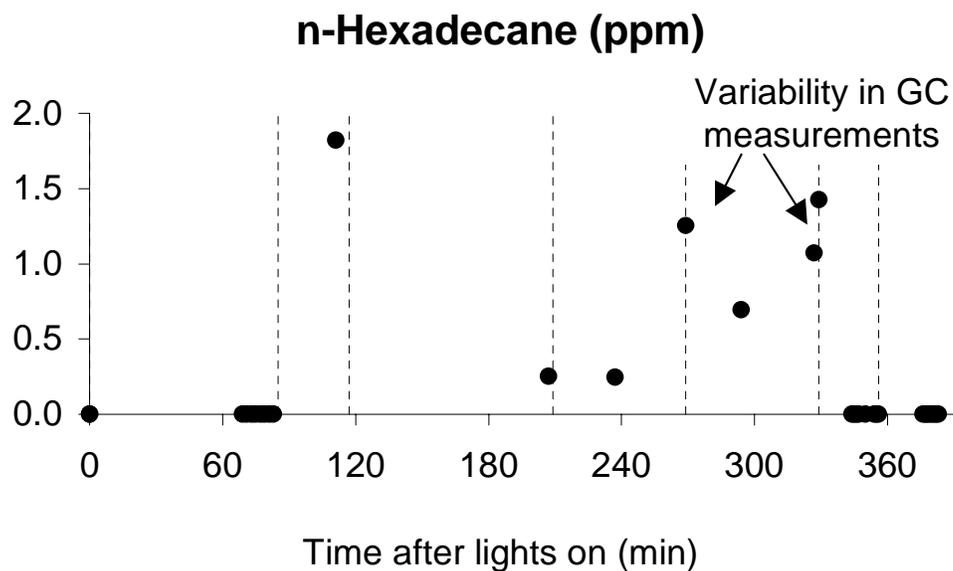
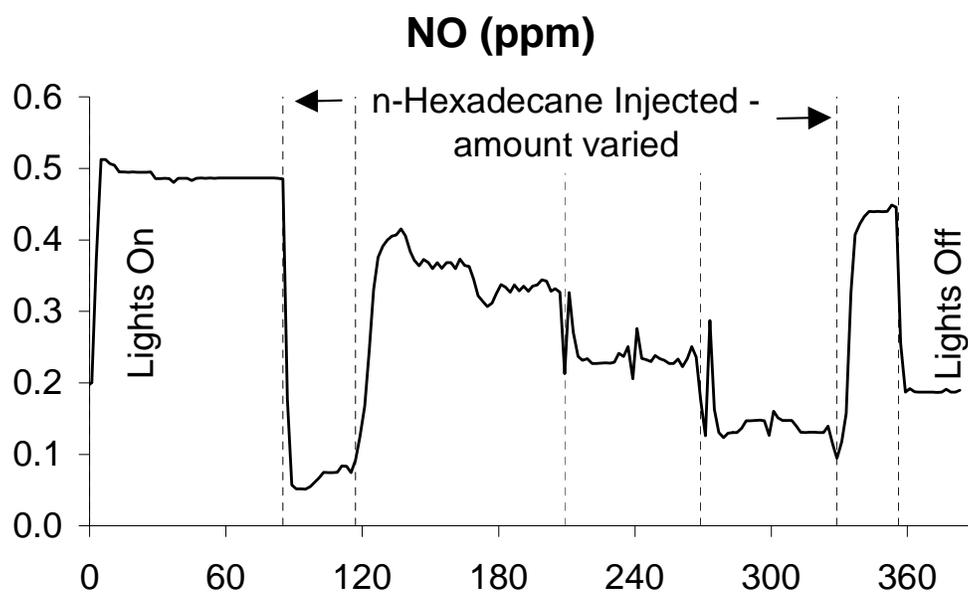


Time since lights turned on (minutes)

EXAMPLE DATA WITH PLUG FLOW SYSTEM (29 M PFA TUBE): N-HEXADECANE EXPERIMENT

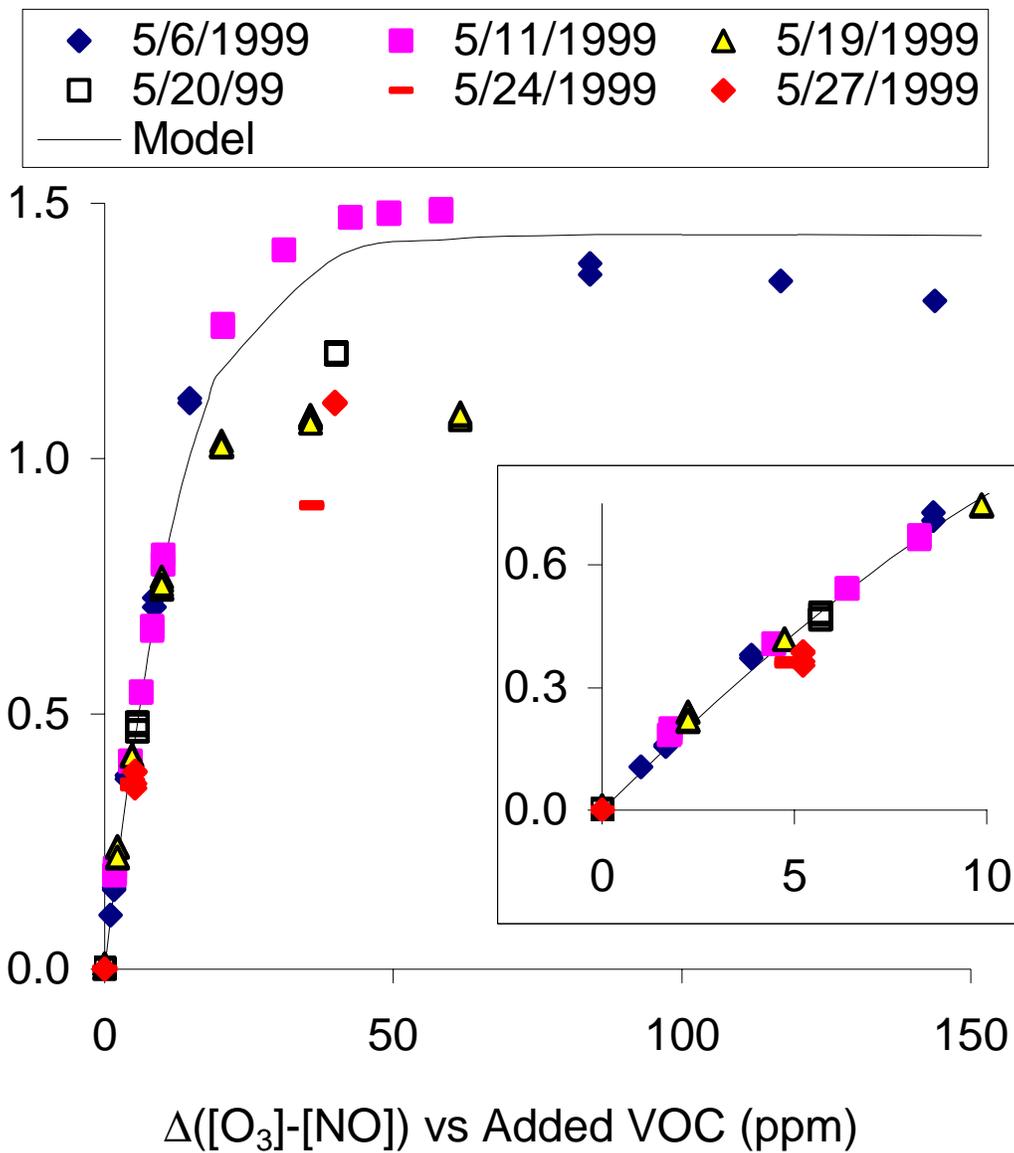


EXAMPLE DATA WITH PLUG FLOW SYSTEM (86 CM QUARTZ TUBE): N-HEXADECANE EXPERIMENT



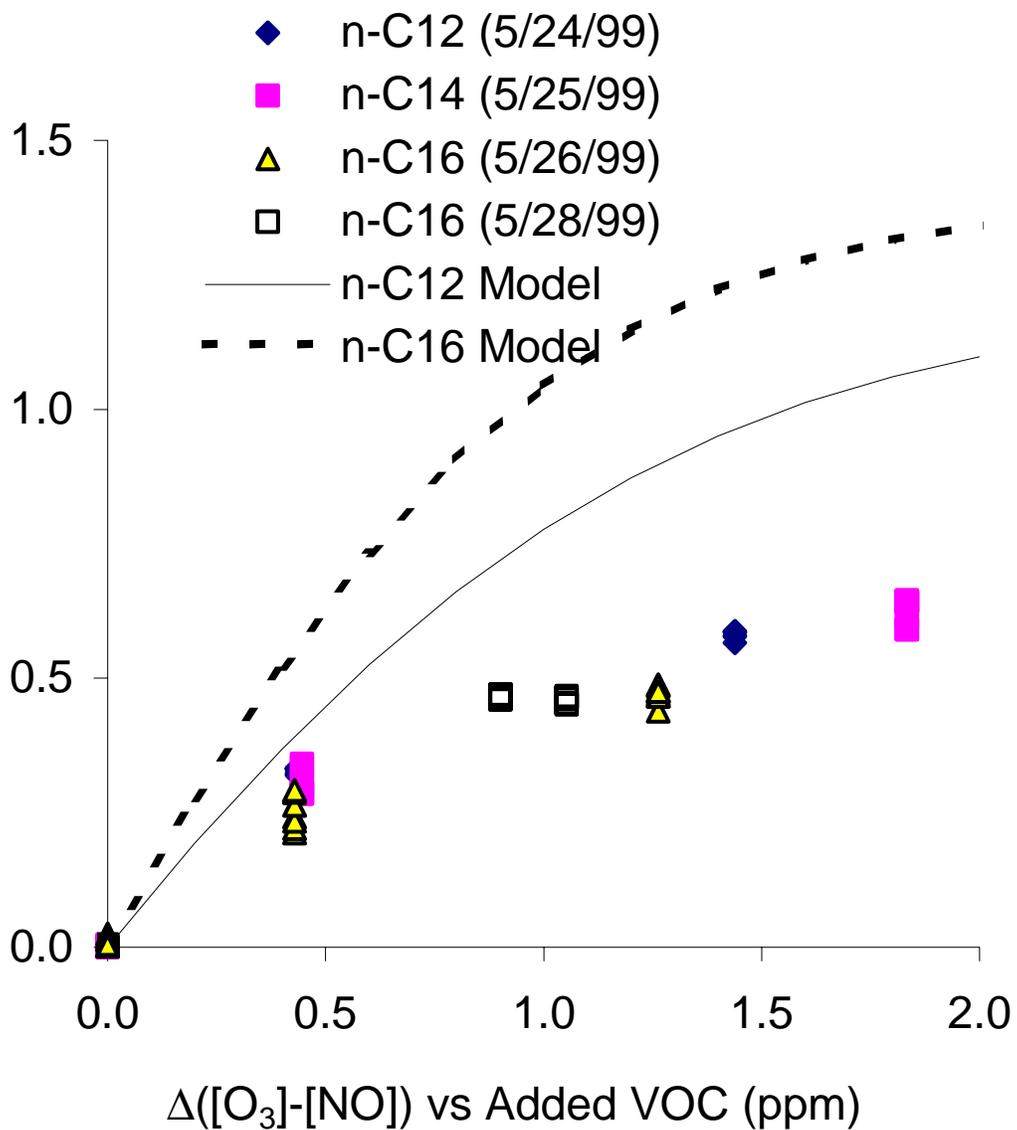
EXAMPLE RESULTS OF PLUG FLOW EXPERIMENTS WITH 29M PFA TUBE

PROPANE



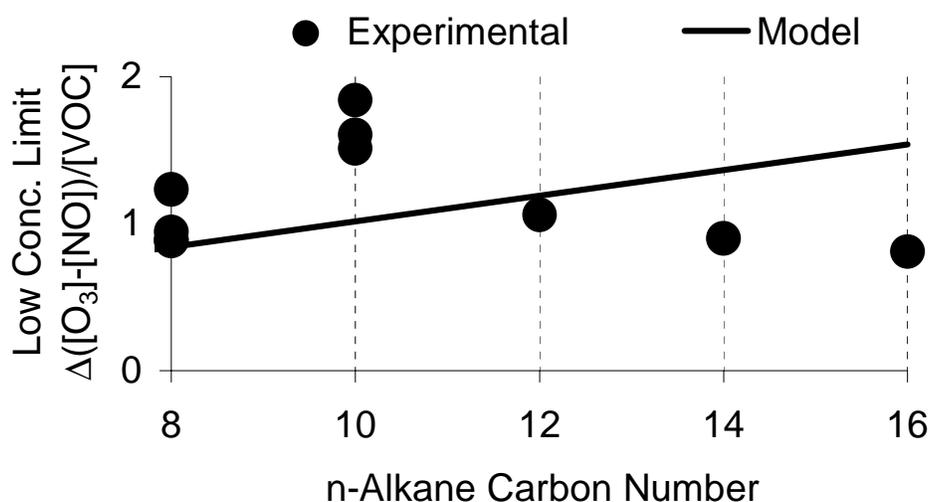
EXAMPLE RESULTS OF PLUG FLOW EXPERIMENTS WITH 29M PFA TUBE

n-Dodecane through n-Hexadecane



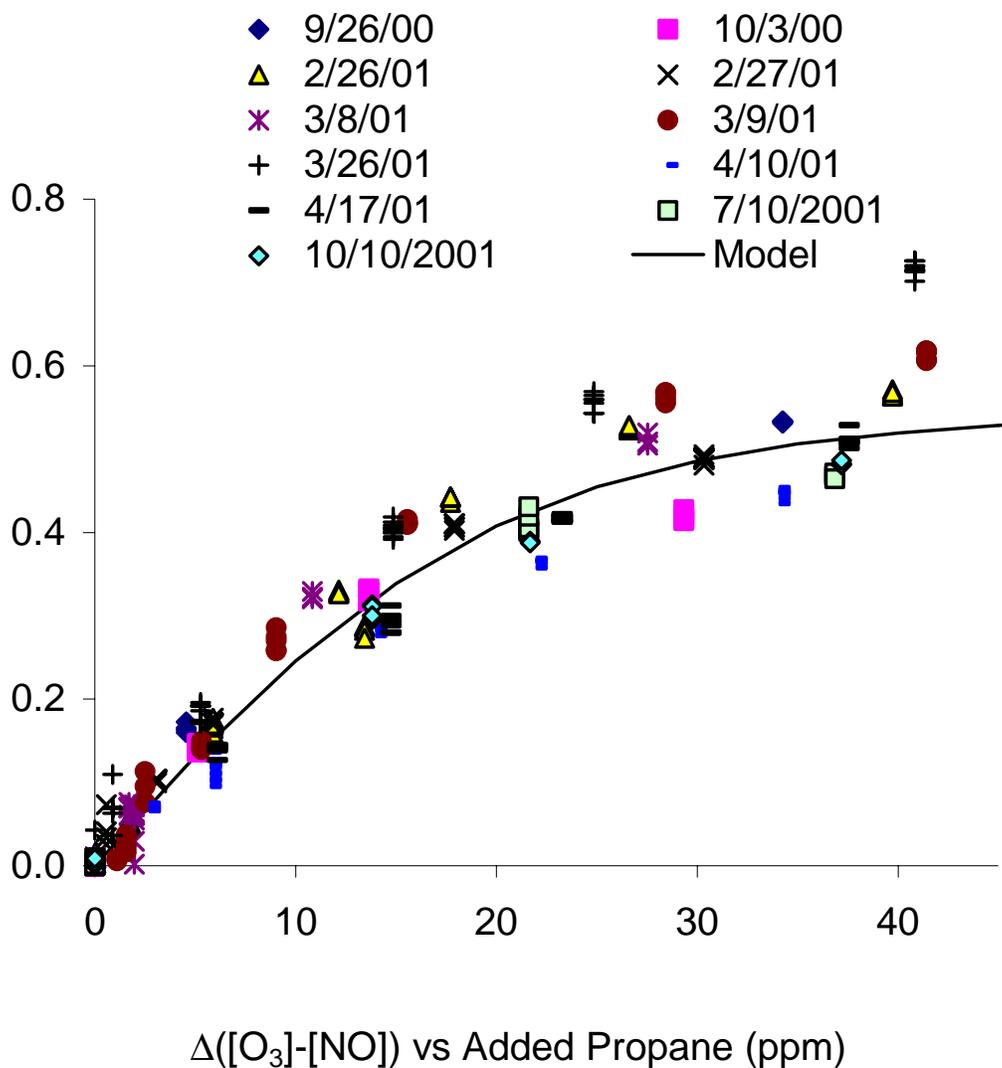
SUMMARY OF DIRECT REACTIVITY RESULTS USING THE 29 M PFA TUBE PLUG FLOW SYSTEM

Compound	Low Concentration Limit $\Delta([\text{O}_3]-[\text{NO}]) / [\text{VOC}]$		
	Measured	Calculated	Model Bias
Propane	0.10	0.11	9%
n-Octane	0.99	0.90	-9%
n-Decane	1.65	1.01	-39%
n-Dodecane	1.06	1.07	1%
n-Tetradecane	0.90	1.39	55%
n-Hexadecane	0.81	1.58	95%



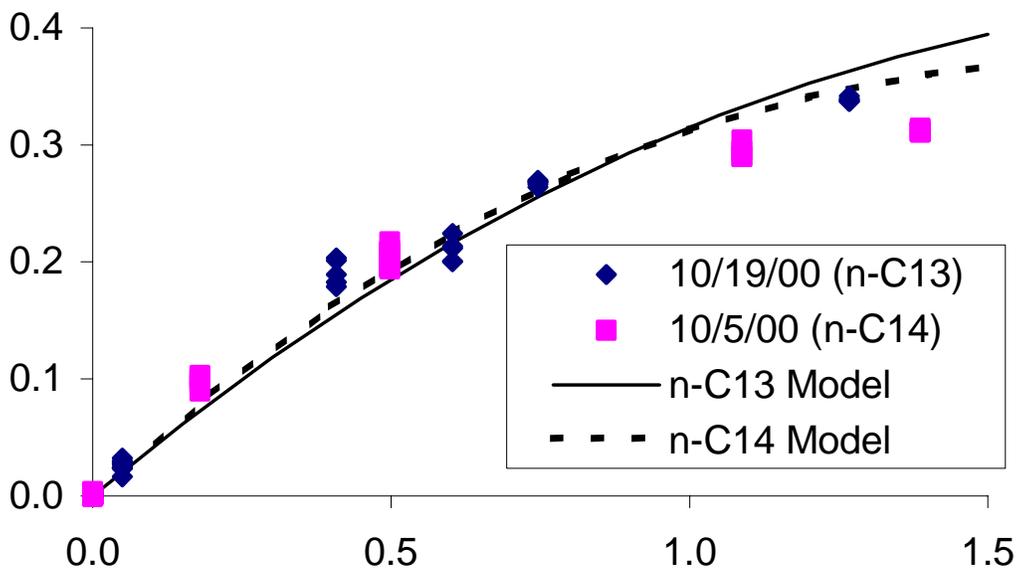
EXAMPLE RESULTS OF PLUG FLOW EXPERIMENTS WITH QUARTZ TUBE

PROPANE

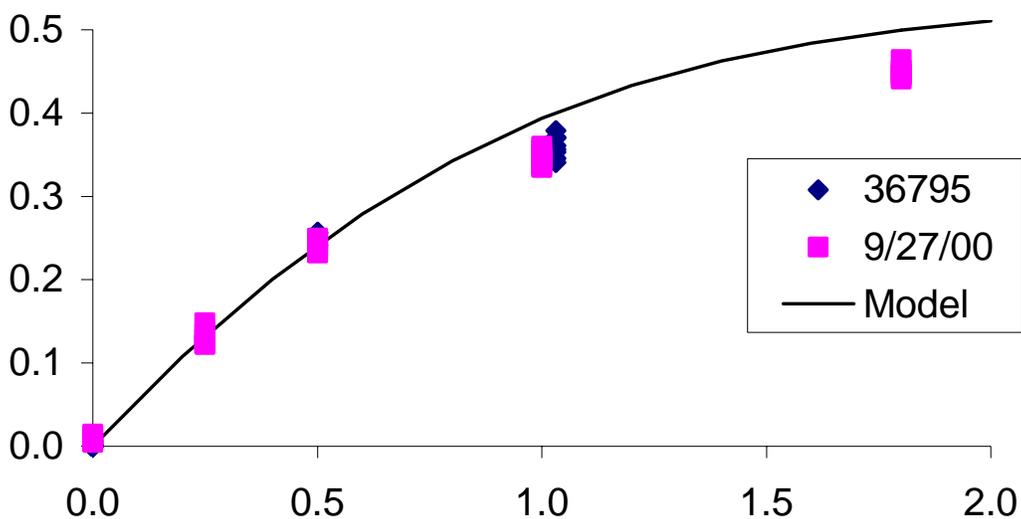


EXAMPLE RESULTS OF PLUG FLOW EXPERIMENTS WITH QUARTZ TUBE

n-C₁₃ and n-C₁₄

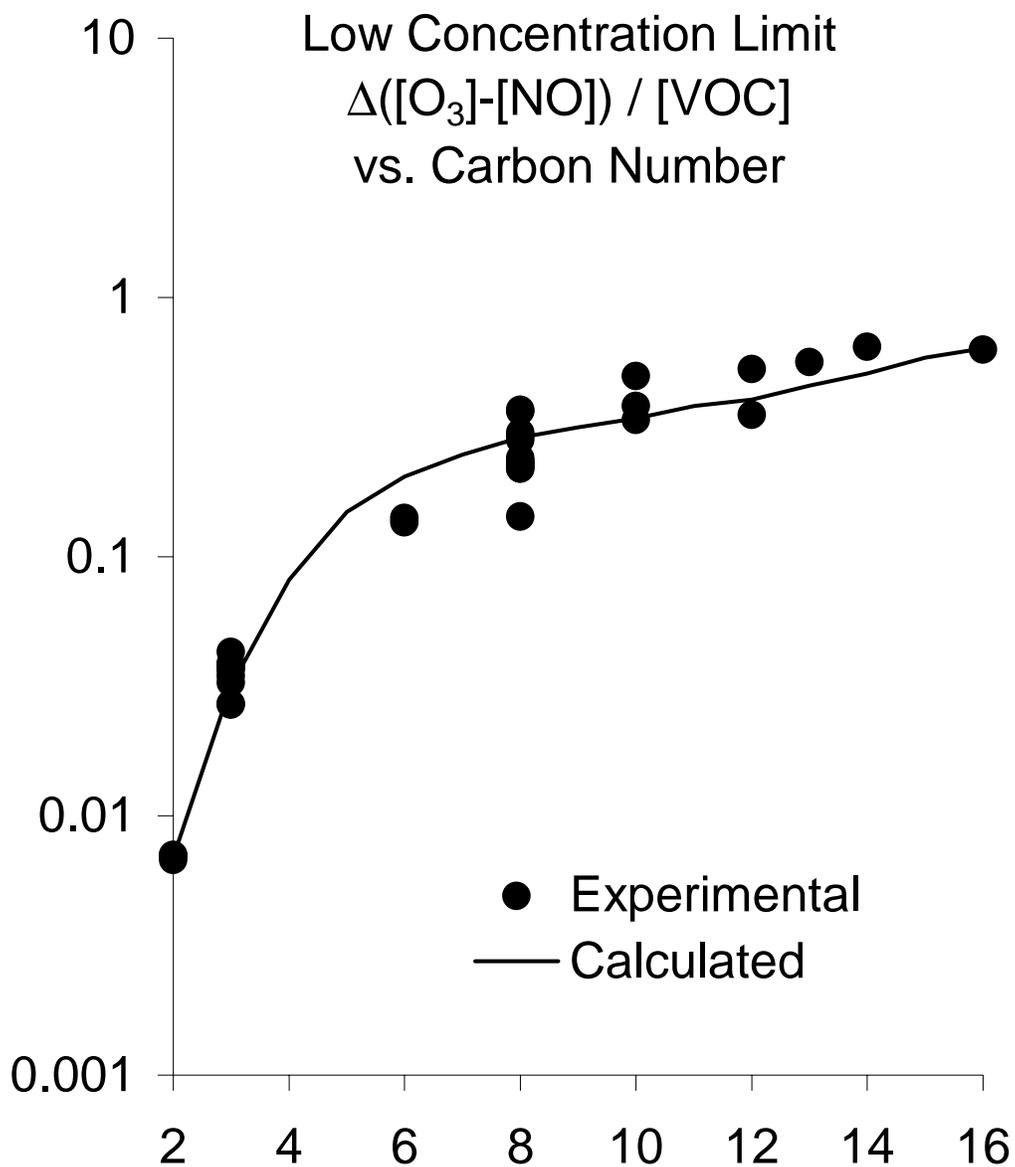


n-C₁₆

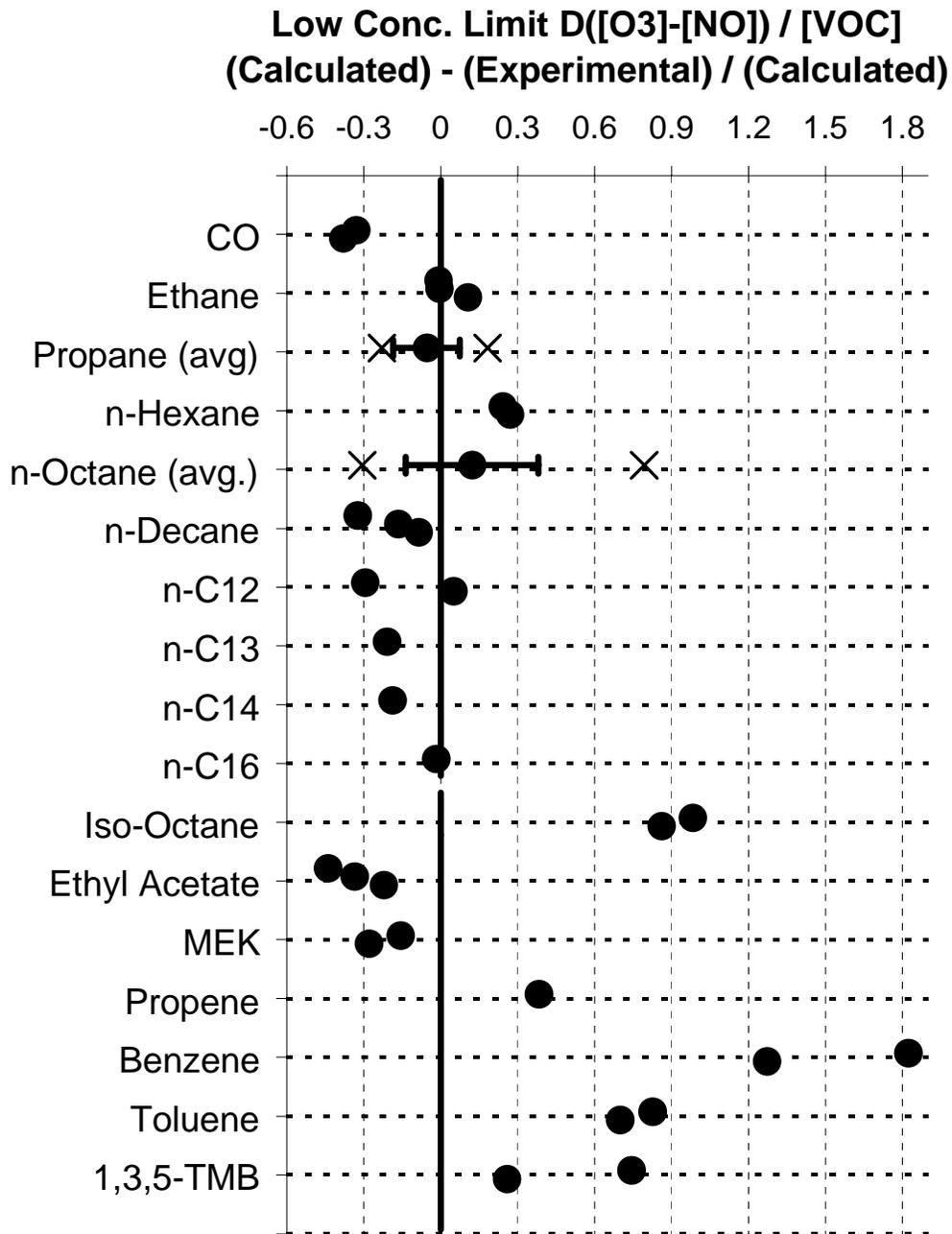


$\Delta([O_3]-[NO])$ vs Added VOC (ppm)

RESULTS OF QUARTZ TUBE PLUG FLOW EXPERIMENTS FOR THE HOMOLOGOUS N-ALKANES



MODEL PERFORMANCE IN SIMULATING PLUG FLOW QUARTZ TUBE DATA FOR ALL COMPOUNDS STUDIED



PROBLEMS AND ONGOING WORK

PROBLEMS

Reliability and reproducibility of the syringe pump injection system needs to be improved

GC Analysis of low volatility compounds is time-consuming and very imprecise

Apparently successful experiments with C₁₂₊ n-alkanes could not be reproduced because of injection and analysis problems

GC Methods not suitable for quantifying complex mixtures. Need either a reliable liquid injection system or a total carbon analysis system

Difficult to improve the injection system without a continuous total carbon analysis system

ONGOING WORK

A total carbon analysis system being developed based on catalytic conversion of VOCs to CO₂, and measuring CO₂ in CO₂-free air

Preliminary tests indicate that this gives good data for volatile compounds, but suggest hang-up of heavy VOCs on current converter system

CONCLUSIONS

Measuring effects of VOCs on $[O_3]$ - $[NO]$ in HONO irradiations provides a sensitive measure of the direct effects of VOCs on O_3 formation

The method of Febo et al (1995) can generate the clean and stable levels of HONO required

Stirred flow experiments gave data that are not entirely consistent with model predictions

Best results were obtained in plug flow experiments using a 86 cm x 1.6 cm ID quartz tube as the reactor with a 0.6 min. reaction time

Plug flow experiments were successfully applied to n-hexadecane, suggesting it may be suitable for other low volatility compounds

But problems with reproducibly injecting and analyzing low volatility compounds must be solved before it can be routinely used for them

The plug flow system needs to be integrated with a total carbon analysis system for this to be practical for low volatility compounds or mixtures

Work on integrating a total carbon analysis to this system is underway for another CARB contract.