

**EVALUATION OF THE SAPRC-99 CHEMICAL
MECHANISM USING NEW ENVIRONMENTAL
CHAMBER DATA**

By

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Summary

The accompanying poster (Carter et al, 2003) describes the new environmental chamber facility designed for chemical mechanism evaluation research.

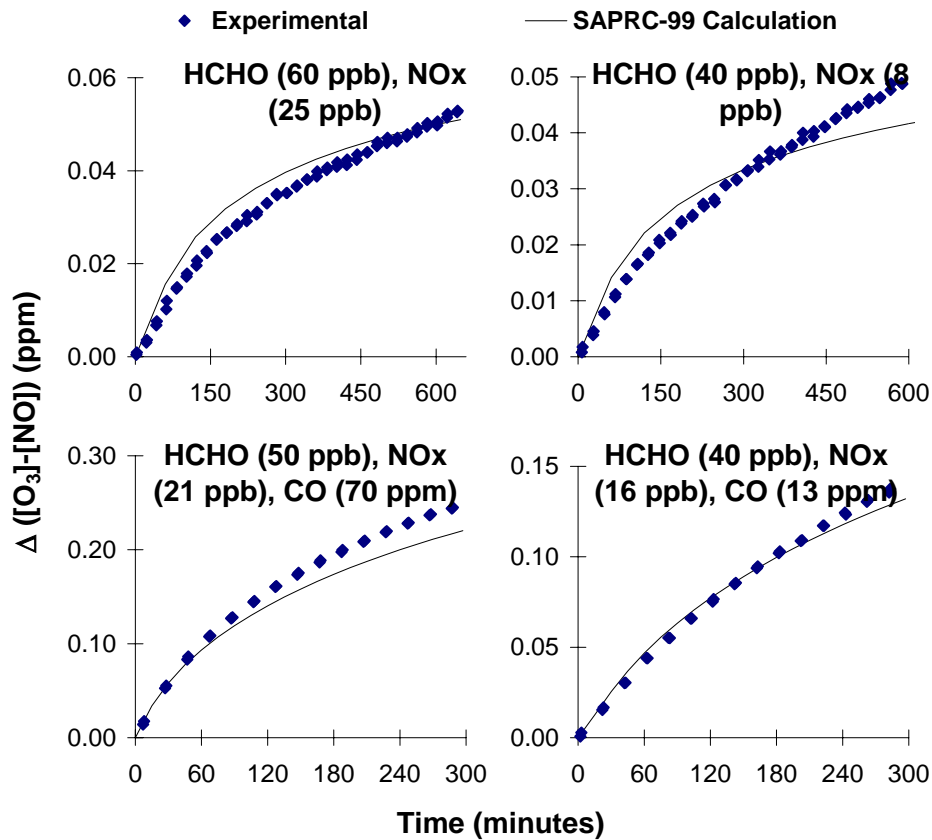
Experiments useful for mechanism evaluation have been conducted since early 2003. (Approximately 25 dual chamber runs.)

These include the following:

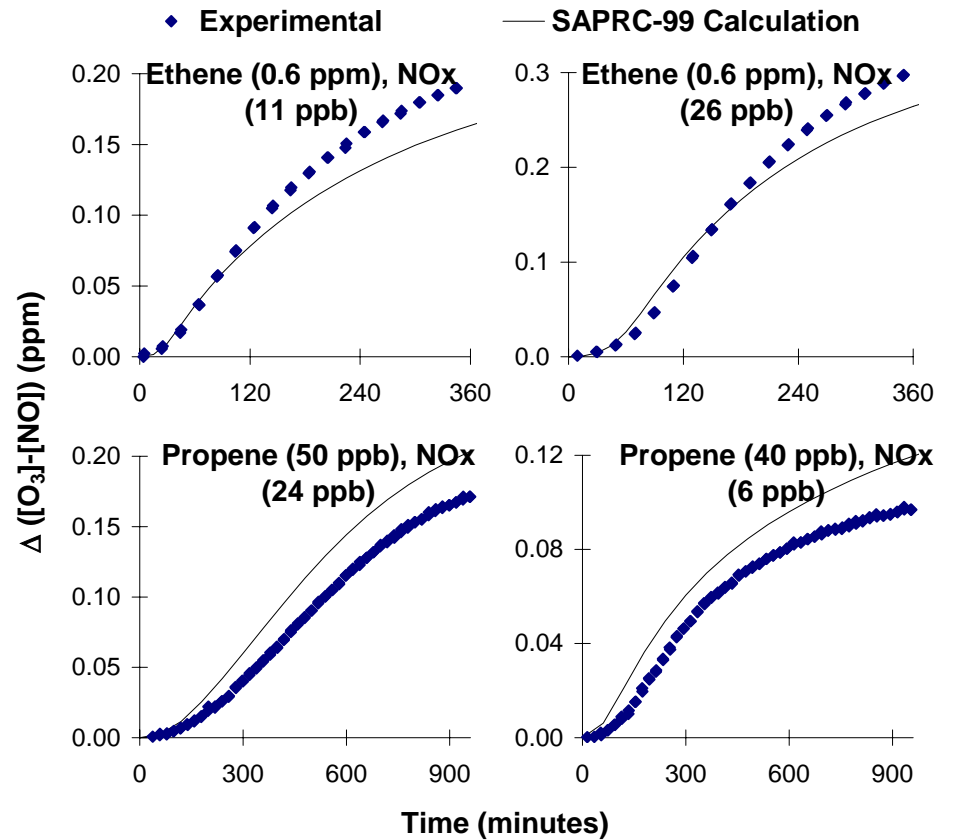
- VOC – NO_x – Air Irradiations with:
 - Formaldehyde
 - Ethene
 - Propene
 - Toluene
 - M-Xylene
 - Ambient ROG Surrogate
- Experiments with lower NO_x than employed previously (down to ~2 ppb)
- Aromatic experiments with varying sensitivity to mechanism radical sources
- Ambient Surrogate Experiments with varying VOC and NO_x levels

Results of these experiments were used to evaluate O₃ predictions of **the SAPRC-99 Chemical Mechanism** (Carter, 2000)

Formaldehyde - NO_x and Formaldehyde - CO - NO_x



Ethene - NO_x and Propene - NO_x

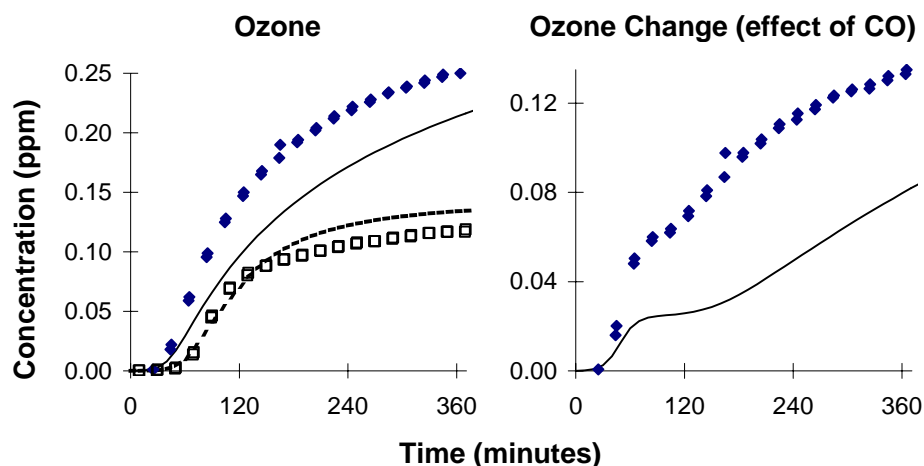


- $\Delta([O_3]-[NO])$ shows NO to NO₂ conversions that cause O₃ formation.
- Addition of CO shows effect of HCHO on radical levels (CO is a “Radical Amplifier”)
- Similar model performance in 8-25 ppb range.

- Model tends to underpredict O₃ in ethene and overpredict it in propene experiments.
- Similar model performance in 5-25 ppb range

Toluene - NO_x and Toluene - CO - NO_x

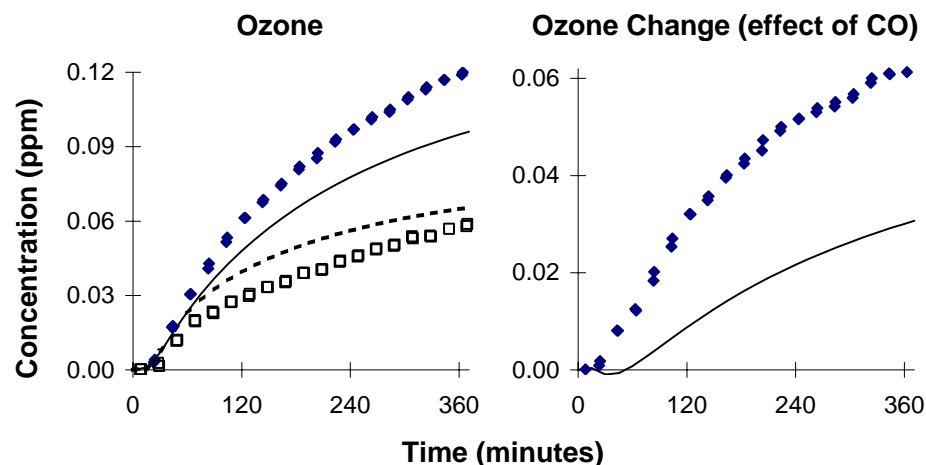
(150 ppb Toluene, 24 ppb NO_x. 115 ppm CO added)



- ◆ Experiment Aromatic - NO_x - CO or Effect of CO
- Model or Aromatic - NO_x - CO Effect of CO
- Aromatic - NO_x Experiment
- - - Aromatic - NO_x Model

m-Xylene - NO_x and m-Xylene - CO - NO_x

(17 ppb m-Xylene, 5 ppb NO_x. 50 ppm CO added)



- ◆ Experiment Aromatic - NO_x - CO or Effect of CO
- Model or Aromatic - NO_x - CO Effect of CO
- Aromatic - NO_x Experiment
- - - Aromatic - NO_x Model

- Model gives fair fits to toluene and m-xylene - NO_x experiments with NO_x ranging from 5-25 ppb.
- Model predicts adding CO will cause significant increase in O₃ because of “radical amplifier” effect of CO on aromatic’s internal radical sources.
- Significant (almost factor of 2) underprediction of CO effect suggests model has insufficient internal radical sources.
- This may be compensated for in aromatic - NO_x irradiations by model having too many NO to NO₂ conversions (“direct reactivity” overpredicted)
- This is consistent with result of other experiments, which indicate model overprediction of direct reactivities of aromatics.

Measurement and Model Prediction of Direct Reactivity

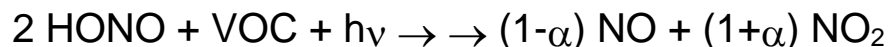
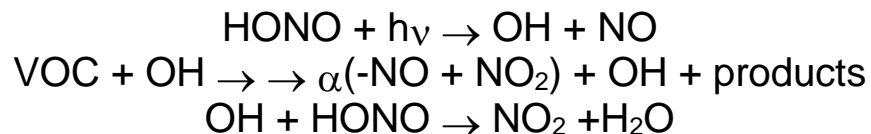
(NO to NO₂ Conversions caused directly by reaction of VOC and its reactive products)

Experimental Method

HONO Photolysis System

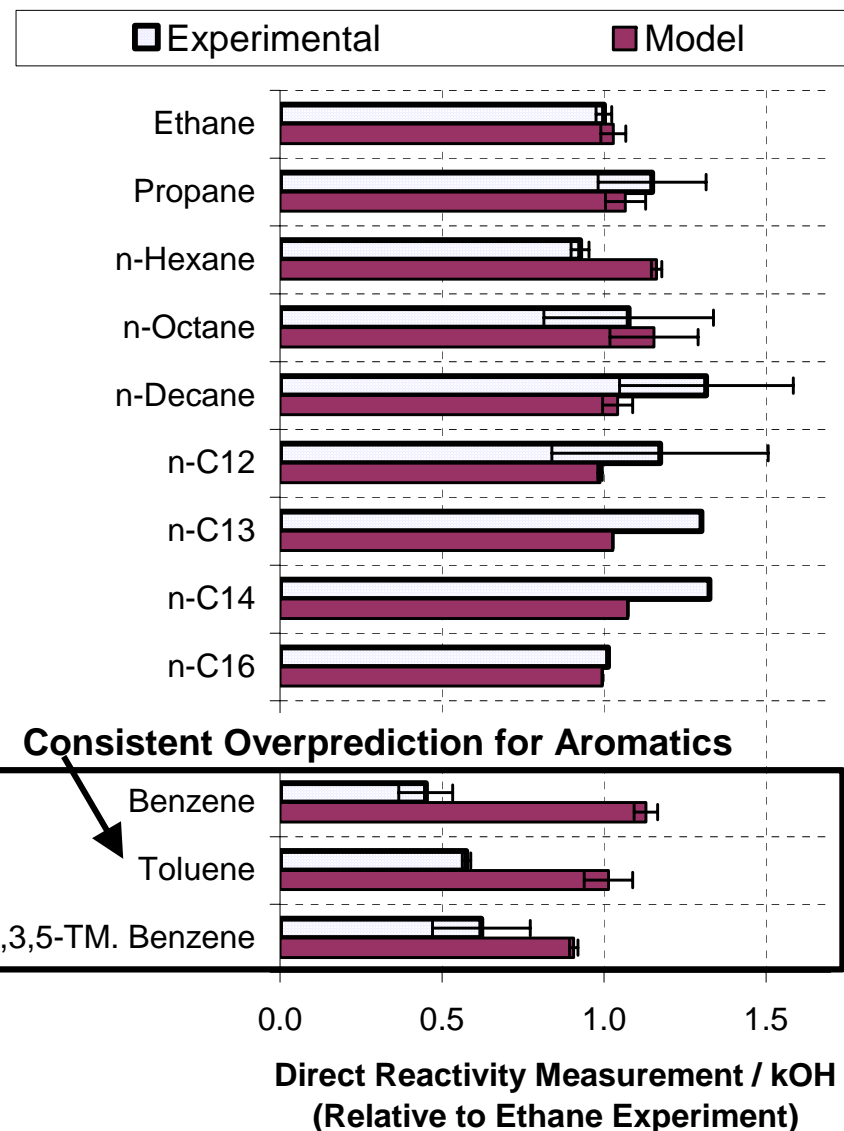
- Major net process in excess HONO without VOC:
 $2 \text{HONO} + h\nu \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$
- Large radical source from HONO photolysis makes system insensitive to VOC radical sources
- NO_x present in excess so system insensitive to VOC radical sinks

- NO to NO₂ conversions from added VOCs reduce NO and (if enough VOC is added) form O₃, e.g.,



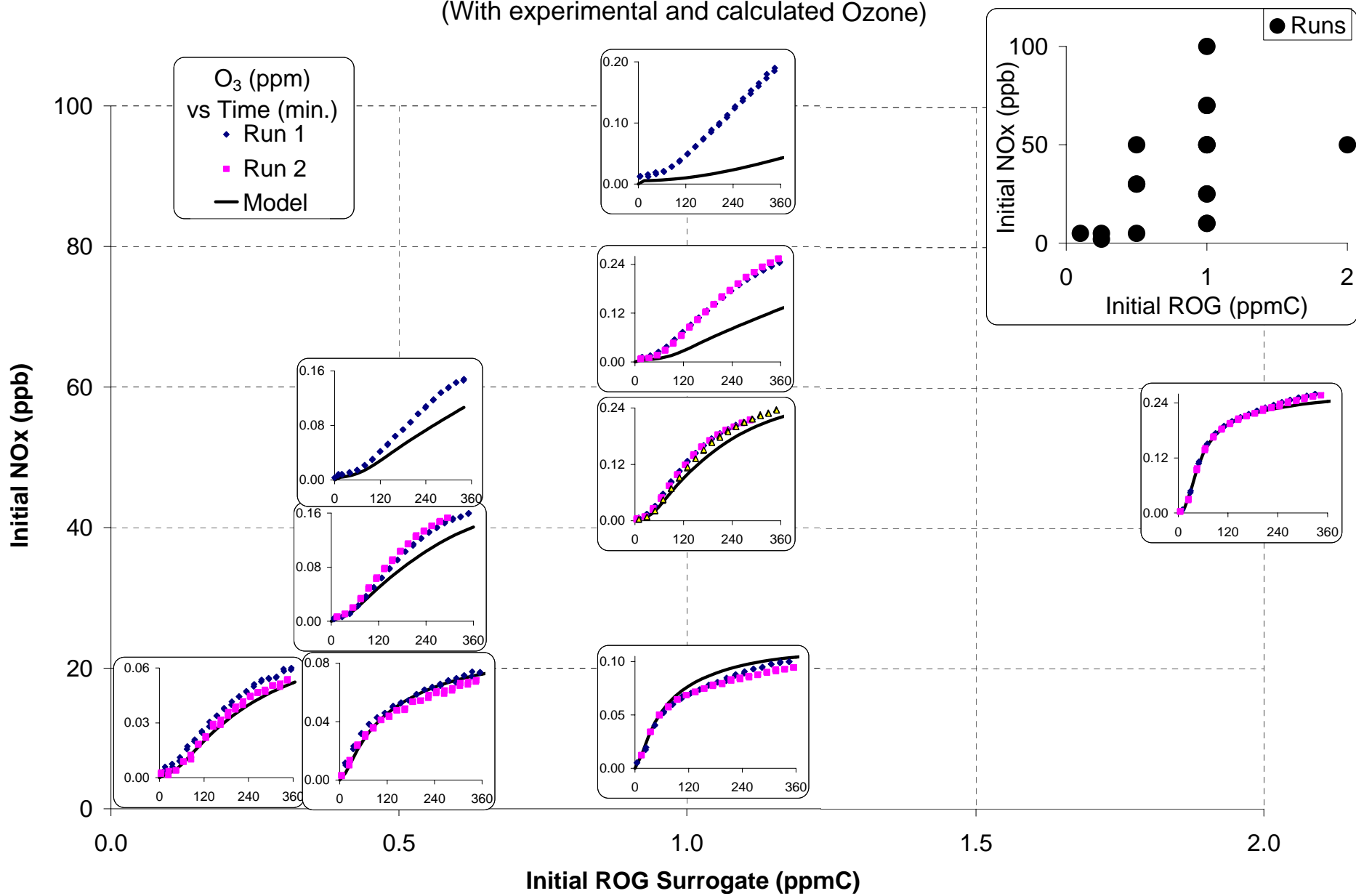
- Effect of added VOC on $\Delta([\text{O}_3]-[\text{NO}])$ reflects the NO to NO₂ conversions caused by the added VOC, **which is its direct reactivity.**
- Experiment consists a plug flow system with HONO or HONO + VOC flowing through an irradiated 86 cm x 1.8 cm quartz tube reactor

Results for n-Alkanes and Aromatics

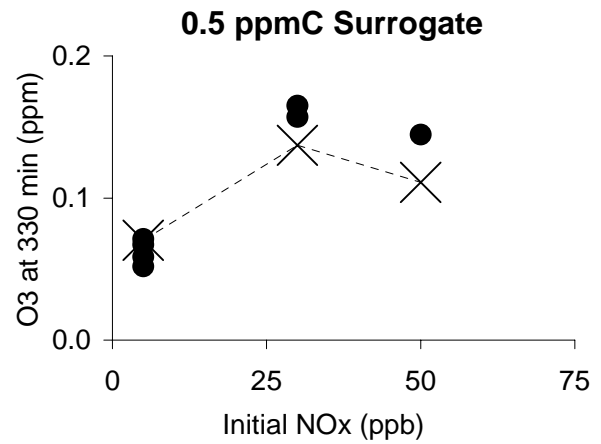
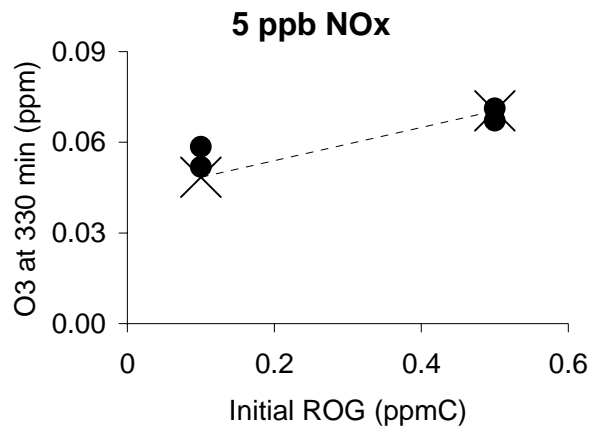
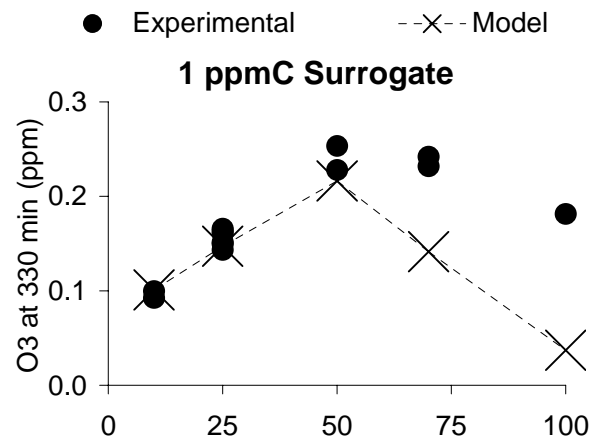
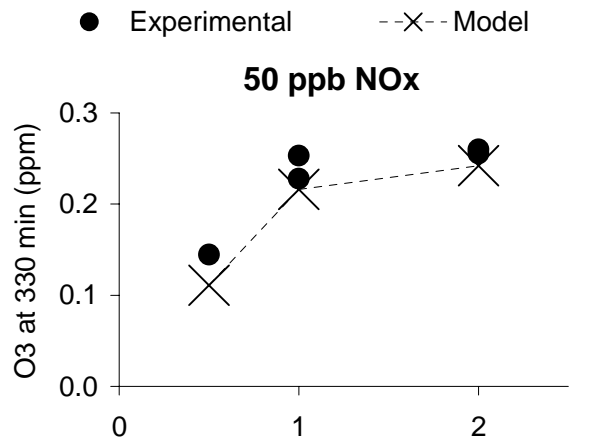


Matrix of Ambient Surrogate - NOx Evaluation Experiments

(With experimental and calculated Ozone)



Experimental and Calculated Final O₃ In Ambient Surrogate Evaluation Experiments



Preliminary Conclusions

Results to date are generally not inconsistent with previous mechanism evaluation results, but extend the range of evaluation conditions.

Results to date do not indicate unexpected problems with mechanism evaluation at NO_x levels as low as ~5 ppb. (Most previous data had $\text{NO}_x \geq \sim 50$ ppb)

But these and other data reveal problems with the SAPRC-99 mechanism:

- Mechanism apparently underpredicts radical levels and overpredicts direct NO to NO_2 conversions in aromatic photooxidations
- Mechanism underpredicts O_3 formation rates at low ROG/NO_x ratios (high NO_x). This *may* be a manifestation of the aromatic mechanism problem.

The RADM-2 and RACM mechanisms haven't been evaluated, but they have similar treatments of aromatic chemistry so probably have similar problems.

Preliminary evaluations by Tonnesen and co-workers (unpublished results) suggest that aromatic mechanism problems may be even worse for CB4.

References

- Carter, W. P. L., C. G. Sauer, D. R. Fitz, K. Bumiller, C. Bufalino, I. Malkina, J. T. Pisano, M. Smith, and D. R. Cocker III, "A New Environmental Chamber Facility for Atmospheric Chemical Mechanism Evaluation," Presented at the Gordon Conference on Atmospheric Chemistry, Big Sky Resort, Montana, September 7-12, 2003. See <http://www.cert.ucr.edu/~carter/epacham> for additional information.
- Carter, W. P. L. (2000): "Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment," Report to the California Air Resources Board, Contracts 92-329 and 95-308, May 8. Available at <http://www.cert.ucr.edu/~carter/absts.htm> #saprc99.