

**EVALUATION OF ATMOSPHERIC IMPACTS OF  
SELECTED COATINGS VOC EMISSIONS**

Progress Report to the  
California Air Resources Board  
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## **Summary of Progress**

During the period of this report the initial evaluation of the base case for the environmental chamber incremental reactivity experiments was completed, and at least two types of such experiments were carried out for each of the five selected petroleum distillates. Additional work was carried out on the direct reactivity method, and it may be suitable for evaluation of hydrocarbon mixtures in the C<sub>12</sub> or lower range, but resources available for that task have been expended. Funding was obtained from the California South Coast Air Quality Management District (SCAQMD) to supplement and extend some portions of this project. For that reason, we propose that future reports for this project be merged with reports for this SCAQMD project to provide a more comprehensive documentation of these related activities. Progress in these areas, and work for the upcoming period, are in the following sections.

## **Environmental Chamber Experiments**

Table A-1 in Appendix A gives a summary of the UCR EPA chamber experiments that were carried out during the period of this report that are relevant to this project. Note that some experiments, particularly the earlier surrogate evaluation runs, were funded by the EPA but are included here because of their relevance to this project. The table indicates the date of the experiments, summarizes the purpose and applicable conditions, and gives a very brief summary of the major results.

The summary of the results on Table A-1 includes an indication of the results of preliminary model simulations of these experiments. These calculations used the current SAPRC-99 mechanism and, unless indicated otherwise, the standard chamber effects model derived for this chamber. However, mechanism evaluation was not the major effort for this program during this period, and a more detailed discussion of this will be reserved for a subsequent report. The model simulations carried out during this period were primarily to determine if the data being obtained were reasonable and consistent with general expectations and past experience with similar experiments.

The data processing and data quality assurance for these experiments are not yet complete, and any discussion of the results of these experiments must be considered to be preliminary and subject to change. This is particularly true for the model calculations, since the input data probably will change at least to some extent when the data processing is completed. However, the general trends discussed here probably will not change.

## **Surrogate Evaluation Experiments**

The first set of experiments that were carried out relevant to this program were the base case surrogate evaluation experiments. Since the reactivity experiments for this project consist primarily of determining the effect of the test compound or mixture on O<sub>3</sub> formation in some “base case” experiment simulating the chemistry of ambient conditions, establishing an appropriate base case for this purpose is important. One of the advantages of using the UCR EPA chamber for this project is that it permits use of base case experiments with lower pollutant concentrations than employed in previous chamber reactivity studies, and that are more representative of current ambient conditions. However, since ambient simulation experiments have not been conducted previously at these lower pollutant concentrations, it is necessary to determine a new set of base case experiments for reactivity studies at these levels. As part of this, it is necessary to conduct ambient simulation and reactivity experiments for representative compounds for the range of relevant conditions that need to be considered.

Ambient simulation base case experiments require choice of an appropriate reactive organic gas (ROG) surrogate mixture to represent the reactive organics that are important in affecting ozone formation in the ambient simulation. It was decided to continue using the 8-component “full surrogate” that was employed in our previous reactivity studies for the initial reactivity studies for this project. This

is because as discussed previously (Carter et al, 1995) this gives a reasonably good representation of ambient anthropogenic VOC emissions as represented in current models, and use of more detailed mixtures would not give significantly different reactivity results. In addition, there was insufficient funding in this project to cover the experiments that would be necessary to develop a new base case ROG Surrogate. Fortunately, new data do not indicate a compelling need to make significant changes to the surrogate composition for reactivity studies, and the use of the same mixture as employed previously also provides a linkage to previous reactivity studies in our laboratories. The composition of this mixture, given as ppm of component per ppmC of nominal ROG surrogate, is given in Table 1.

The representative compounds chosen for the base case evaluation study were n-octane and m-xylene. These were chosen because these are reasonably well-studied compounds that have quite different reactivity characteristics, and representative of the major types of compounds in petroleum distillates. As is the case with the other higher alkanes present in petroleum distillates, n-octane is a relatively strong radical inhibitor that also has a relatively high direct reactivity for O<sub>3</sub> formation. As is the case with the other aromatics that are present in some types of petroleum distillates, m-xylene tends to form strong radical initiating products that increase the initial rates of O<sub>3</sub> formation, but tend to have relatively strong NO<sub>x</sub> sinks in their mechanisms that tend to suppress O<sub>3</sub> in under low NO<sub>x</sub> conditions. These different reactivity characteristics respond differently as ROG and NO<sub>x</sub> conditions in base case experiments change, and thus are useful for assessing how changing base case conditions affect reactivities. There is already a large database of different types of reactivity experiments with these compounds (e.g., see Carter, 2000) that can be used for comparison with the results obtained in this chamber.

Before beginning these experiments, we sought input from the CARB staff concerning the NO<sub>x</sub> levels they would consider to be appropriate to use for reactivity studies in the new chamber. The guidance we obtained in this regard was as follows:

“For the CMAQ runs in South Coast in 2000, the NO<sub>x</sub> levels of 1, 50, and 500 ppb are the low end, typical, and high end. The focus of future experiments should be in the range of 1-50 ppb since runs with higher NO<sub>x</sub> levels are available from other investigators (TVA and CSIRO).” (Luo, 2003)

Based on this, we decided that ~25 ppb NO<sub>x</sub> probably would be appropriate for the incremental reactivity experiments, with the surrogate evaluation experiments focusing on the ≤ 50 ppb NO<sub>x</sub> range. (Note that this represents a considerably lower range than employed previously, where NO<sub>x</sub> levels in the “low NO<sub>x</sub>” experiment was ~125 ppb.) The ROG concentrations would be determined so that the ROG/NO<sub>x</sub> ratio gives the desired reactivity characteristics for mechanism evaluation.

Table 1. Composition of base case reactive organic gas (ROG) surrogate employed in this project.

Component	Relative amount (ppb / ppmC ROG)
Ethene	16.3
Propene	13.6
trans-2-Butene	13.6
n-Butane	89.8
n-Octane	23.1
Toluene	20.7
m-Xylene	20.6
Formaldehyde	18.3

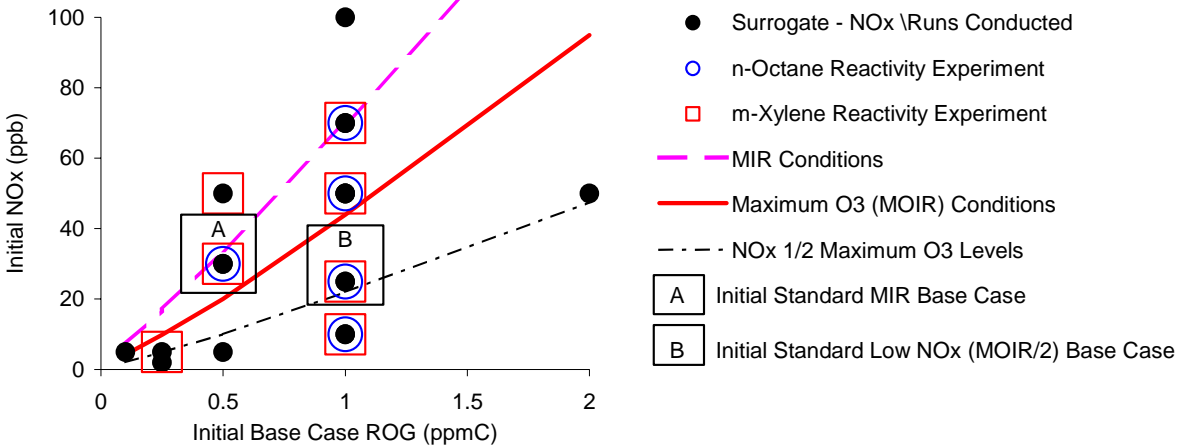


Figure 1. Matrix of initial NO<sub>x</sub> and base case ROG employed in the surrogate evaluation study.

Figure 1 shows the matrix of initial NO<sub>x</sub> and base case ROG levels employed for the surrogate reactivity experiments for this project. The ROG and NO<sub>x</sub> levels for used for the incremental reactivity experiments with n-octane and m-xylene and those for the two standard base case conditions used in the petroleum distillate reactivity experiments are also shown. The lines show the ROG and NO<sub>x</sub> levels that yield maximum incremental reactivities of the base ROG surrogate (MIR), that yield maximum calculated O<sub>3</sub> concentration (MOIR). The line at 1/2 MOIR NO<sub>x</sub> levels, which is considered to be an appropriate representative of low NO<sub>x</sub> conditions for VOC reactivity assessment<sup>1</sup>, is also shown.

The results of the preliminary model simulations of these experiments will be described in more detail in subsequent reports. Qualitative descriptions of the O<sub>3</sub> simulations for the individual experiments are given in Table A-1. Briefly, it was found that the model gave reasonably good simulations of the experiments at NO<sub>x</sub> levels at or lower than MOIR conditions, but at MIR and higher NO<sub>x</sub> levels there is a bias for the model to underpredict O<sub>3</sub> formation rates, with this bias increasing both with increasing NO<sub>x</sub> / ROG ratios and with absolute NO<sub>x</sub> levels. Examples of this can be seen in the simulations of the base case experiments used in the coatings reactivity study as shown on Figure 2, below. The reactivity simulations with n-octane and m-xylene were generally consistent with expectations based on previous experiments, though the quality of the simulations of the effects of added compound were not as good in the experiments where the base case conditions were not well simulated, as expected.

For the initial reactivity experiments, it was decided to use two base case experiments, one representing MIR conditions and one representing low NO<sub>x</sub> conditions. Since the MOIR NO<sub>x</sub> conditions that are optimum for O<sub>3</sub> formation represent the borderline between VOC-limited and NO<sub>x</sub> limited conditions, it was decided to employ NO<sub>x</sub> levels half those of MOIR (designated “MOIR/2” in the tabulations in Table A-1) for the low NO<sub>x</sub> experiments. This is sufficiently low that the experiment is NO<sub>x</sub> limited yet not so low that the experiments become insensitive to added VOCs.

Based on these considerations, the experiments designated “A” and “B” on Figure 1 were chosen to be used as the base cases for the incremental reactivity experiments for the coatings reactivity project. These experiments were chosen because they had the desired MIR or MOIR/2 relative NO<sub>x</sub> levels, and had the 25-30 ppb total NO<sub>x</sub> level that was in the middle of the range recommended by the CARB staff

<sup>1</sup> Although much lower relative NO<sub>x</sub> levels occur in the atmosphere, conditions of much lower NO<sub>x</sub> / ROG ratios tend to be relatively insensitive to added VOCs and thus not useful for reactivity assessment.

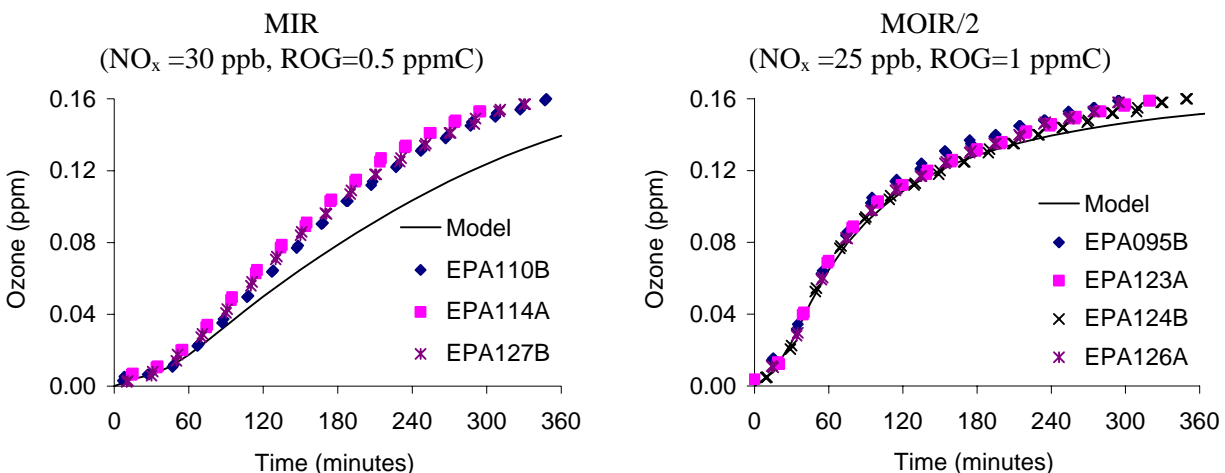


Figure 2. Experimental and calculated O<sub>3</sub> for the two base case experiments that were chosen for use in the coatings reactivity study. Results of selected replicate experiments are shown.

(Luo, 2003), as discussed above. Ozone data from replicate experiments and results of model simulations of these two types of base case experiments are shown on Figure 2.

### Incremental Reactivity Experiments

As indicated on Table A-1, incremental reactivity experiments using each of the two base case conditions were carried out for each of the six petroleum distillates selected for study. A summary of the major characteristics of the petroleum distillates, indicating the runs carried out, is given on Table 2. In most cases one experiment of each type were carried out, with the exception being the lower NO<sub>x</sub> experiment for ASTM-3C1, which was repeated because of an experimental problem with the first run.

The data from the more recent experiments have not been completely processed, and data for all the experiments are subject to change. Nevertheless, the available data are sufficient to obtain a qualitative indication of the effects of these petroleum distillates on O<sub>3</sub> formation and radical levels in these experiments. This is shown on Figure 3 and Figure 4, which show plots of the effects of the added distillates on  $\Delta([O_3]-[NO])$ , the sum of NO oxidized and O<sub>3</sub> formed in the experiments. It can be seen that in terms of qualitative effects on enhancing (or inhibiting) NO oxidation and O<sub>3</sub> formation in the MIR experiments, the order is Aromatic-100 >> ASTM-1A > VMP naphtha  $\approx$  ASTM-1B  $\approx$  ASTM-3C1 > ASTM-1C. The effects on O<sub>3</sub> formation and NO oxidation is considerably less in the low NO<sub>x</sub> experiments, though Aromatic-100 seems to inhibit final O<sub>3</sub> to a somewhat greater extent than alkane-dominated distillates.

Preliminary model calculations were carried out on most of the base case experiments and the experiments with added VMP naphtha. The results of the simulations of O<sub>3</sub> formed and NO oxidized in the VMP naphtha runs are shown on Figure 3. It can be seen that the simulation of the effect of the added naphtha is very good in the low NO<sub>x</sub> experiment and fair in the MIR run. However, the simulation of the effect of the added naphtha in the MIR run may have been better if the model performed better in simulating the base case experiment. This bias in the model in simulating MIR experiments will complicate the modeling analysis of all such runs, unless the problem can be resolved.

Table 2. Summary of petroleum distillates used in reactivity experiments carried out during this period.

Designation	Average Carbon Numbers and Type Distributions						Runs Numbers	
	Avg C	Arom.	n-Alk	Br-Alk	Cyc-Alk	Olefins	MIR	MOIR/2
VMP Naphtha	8.7	0.2%	13%	44%	42%	0.1%	137	126
ASTM Type 1A	10.7	19%	15%	32%	34%	-	167	153
ASTM Type 1B	10.8	-	14%	30%	56%	-	151	139
ASTM Type 1C	10.8	6%	14%	31%	49%	-	168	152
ASTM Type 3C1	11.0	-	-	96%	4%	-	163	138,150
Aromatic 100	9.1	100%	-	-	-	-	127	124

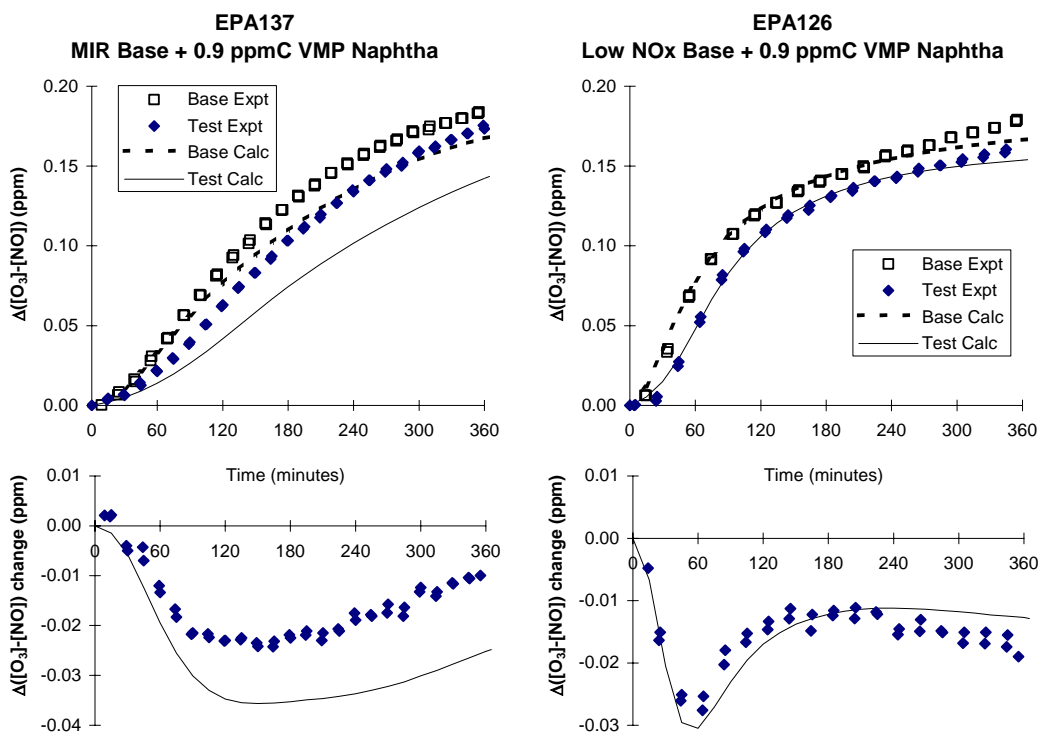


Figure 3. Experimental and calculated effects of VMP naphtha on  $O_3$  formation and NO oxidation in the MIR and low  $NO_x$  incremental reactivity experiments. The top plots show the experimental and calculated  $\Delta([O_3]-[NO])$  data, while the bottom plots show the experimental and calculated differences in these quantities between the experiments with and without the added naphtha.

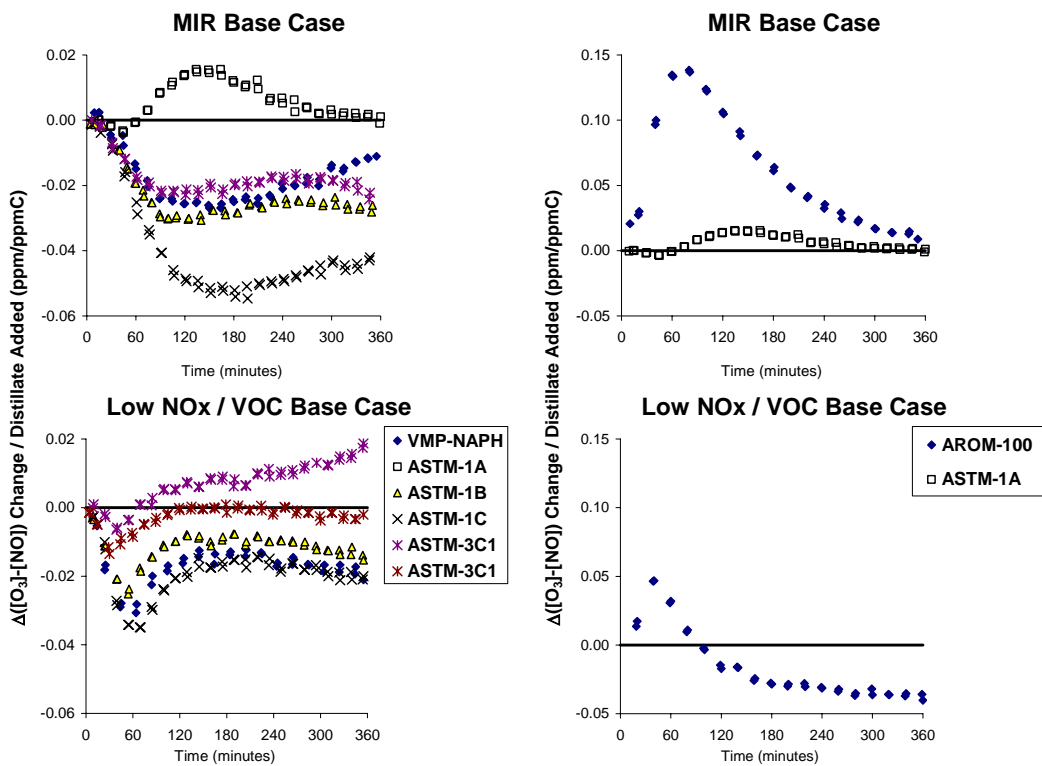


Figure 4. Experimental effects of the other petroleum distillates on  $O_3$  formation and NO oxidation in the incremental reactivity experiments. The plots show the differences in  $\Delta([O_3]-[NO])$  between the experiments with and without the added petroleum distillate, relative to the amount of distillate added.

### Development of Direct Reactivity Method

One component of this project was adapting the HONO flow direct reactivity developed in a previous CARB project (Carter and Malkina, 2002) so it can be used for petroleum distillates and other coatings constituents. In the previous report we discussed adapting this HONO flow system to a total carbon analyzer so its use would not be restricted to compounds analyzable by gas chromatography. The total carbon analyzer was based on quantitatively converting the VOC to  $CO_2$ , and then analyzing the  $CO_2$  so produced using a high sensitivity  $CO_2$  analyzer. At the time of the previous report it was found that this analytical method worked satisfactorily with higher volatility compounds, but exhibited unacceptable memory effects with the lower volatility petroleum distillates such as those of interest for this project.

During this period, it was found that the memory problem could be addressed by utilizing a smaller amount of combustion catalyst heated to a higher temperature than employed previously. Tests showed good conversion with no significant memory effects for mineral spirits samples, and good agreement between GC measurements and total carbon data for propane and n-octane. Direct reactivity measurement experiments were carried out using this system using propane, n-octane, n-dodecane, n-tetradecane, and mineral spirits sample "B" used in the Safety-Kleen study (Carter et al, 1997). The latter material has an ASTM classification of IIC and an average carbon number of around 12. The direct reactivity results, given as the low-added-VOC  $\Delta([O_3]-[NO])$  limit divided by the carbons injected, are shown on the left hand plots of Figure 5. The error bars on the plots show the standard deviations of

replicate experiments, and they indicate that good reproducibility was obtained, even for the lower volatility materials. The direct reactivities normalized to the average of those measured for propane are shown on the right hand plot in the figure.

The results of model calculations of the direct reactivity measurements are also shown on Figure 5. Although in our previous experiments we were able to get reasonably good agreement between experimental and model calculations for the n-alkanes through n-dodecane, it can be seen that with the current setup there is a consistent bias of the model to overpredicting the measured direct reactivity. Numerous measurements of light intensity and flows were made to determine whether the conditions were not correctly characterized, but the data do not indicate any known problems in this regard. We were unable to investigate this further because the resources in this project that were allocated to this task have been exhausted.

The right hand plots on Figure 5 show that the model bias can be removed by normalizing the direct reactivity data to that measured for propane, at least for compounds through n-dodecane and the C<sub>12</sub> mineral spirits sample. This suggests that this method may be useful for assessing relative direct reactivities, using compounds with known mechanisms, such as propane or n-octane, as the standard. Thus, it may be useful for evaluating model predictions of relative direct reactivities of the petroleum distillates studied for this project, since, as indicated on Table 2, these are primarily C<sub>~11</sub>. However, the experimental relative direct reactivities are lower than predicted for n-tetradecane, suggesting that there may be absorption problems with higher molecular weight compounds. Thus, this method as presently employed apparently will not be useful for materials much less volatile than n-dodecane.

Since the resources available to this task have been expended, further development work on this method cannot be carried out for this project. However, this method as currently implemented may provide useful mechanism evaluation data for the six petroleum distillates, though probably not for Texanol® and lower volatility materials. The decision on whether to utilize it for these compounds will depend on the results of the modeling analysis of the chamber experiments, which has not yet been completed.

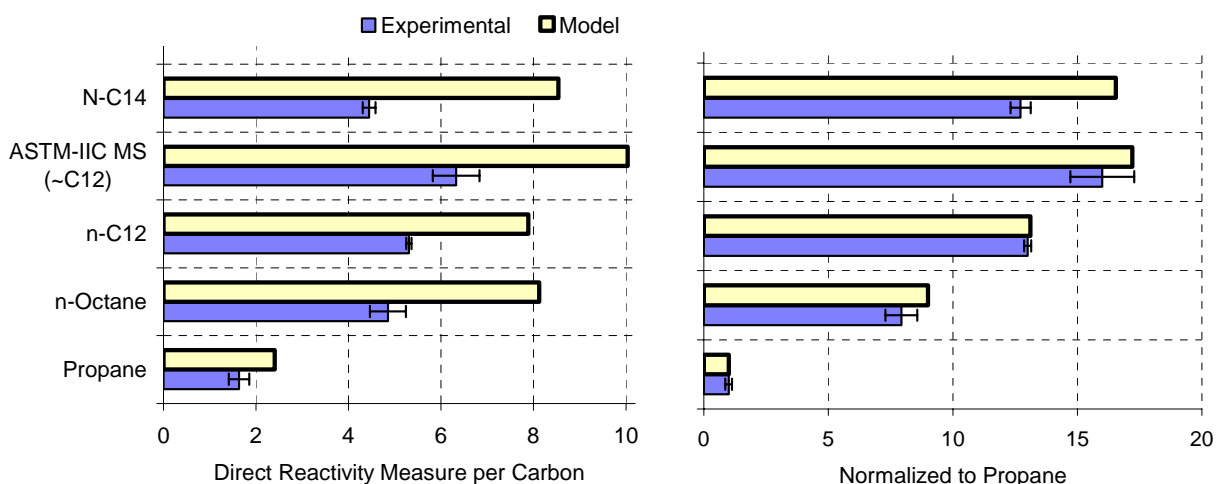


Figure 5. Comparison of experimental and calculated direct reactivity measurements made using the current configuration.



## Future Schedule

During the upcoming period, the priority for this project will be conducting the environmental chamber experiments for Texanol® and analyzing the results of the petroleum distillate experiments discussed above. Additional petroleum distillate experiments, including possibly direct reactivity measurements, may be conducted if appropriate.

As indicated above, we have obtained funding from the SCAQMD to supplement and extend this project. Specific tasks that are relevant to this project include (1) conducting environmental chamber experiments for at least three additional coatings VOCs, and (2) making measurements of PM formation in conjunction with the CARB and SCAQMD coatings reactivity experiments. Although this effort is funded by SCAQMD, since it is relevant to this project the results will be reported jointly to the CARB and SCAQMD as deliverables for both projects. In addition to providing these agencies more comprehensive reports covering all aspects of coatings-related reactivity research at our laboratories, this joint reporting makes most efficient use of the Principal Investigator's time, permitting either more analysis or more experiments to be conducted with the available resources.

The issue of which coatings materials to study for the SCAQMD project was discussed at RRAC meeting in Sacramento on December 3, in which SCAQMD staff participated by teleconference. It was decided to focus the initial efforts on experiments with ethylene and propylene glycol, with the additional compound(s) to study to be determined later. During the upcoming period we will develop the methods and probably begin conducting experiments with these compounds.

We have already had some progress in making PM measurements in conjunction with the experiments for this project, as indicated in some of the comments in Table A-1. The necessary characterization and other experiments needed to support this effort are being carried out under other funding, and will be continued during the upcoming period. Progress and ongoing work in this area will be described in more detail in a later report.

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## Appendix A. Tabulation of Chamber Experiments

Table A-1. Summary of UCR EPA chamber experiments carried out during the period of this report that are relevant to this project. Note that these include experiments for the CARB “Low NO<sub>x</sub>” evaluation project (contract 01-305) that will be discussed in more detail in a separate report for that project.

Run [a]	Date	Type [b]	Purpose and Applicable Conditions.	Results
082	3/18/03	ROG=1 ppmC, NO <sub>x</sub> =50 ppb Surrogate	Variable ROG and NO <sub>x</sub> surrogate evaluation. Same reactants on both sides for side equivalency test.	Good side equivalency. Fair fit to model simulation; predicted O <sub>3</sub> somewhat low.
083	3/20/03	ROG=1 ppmC, NO <sub>x</sub> =50 ppb Surrogate + n-Octane	Incremental reactivity test experiment with a previously studied VOC as part of the variable ROG and NO <sub>x</sub> surrogate evaluation. 250 ppb n-octane added to Side B.	Added n-octane causes significant reduction in m-xylene consumption rates and slight reduction in O <sub>3</sub> formation in initial states of experiment. Model somewhat underpredicts base case O <sub>3</sub> and somewhat overpredicts O <sub>3</sub> inhibition by n-octane.
084	3/21/03	ROG=1 ppmC, NO <sub>x</sub> =50 ppb Surrogate + m-Xylene	Incremental reactivity test experiment for variable ROG and NO <sub>x</sub> surrogate evaluation. 30 ppb m-xylene added to Side A.	Added m-xylene causes increased initial O <sub>3</sub> formation but slight reduction in final O <sub>3</sub> level. Model somewhat underpredicts O <sub>3</sub> in base case and somewhat overpredicts effect of m-xylene on initial O <sub>3</sub> formation rates.
085	3/25/03	ROG=1 ppmC, NO <sub>x</sub> =10 ppb Surrogate + n-Octane	Low NO <sub>x</sub> incremental reactivity test experiment for variable ROG and NO <sub>x</sub> surrogate evaluation. 200 ppb n-octane added to Side B.	Added n-octane causes significant reduction in m-xylene consumption rates and moderate reduction in O <sub>3</sub> formation during experiment. Model overpredicts base case O <sub>3</sub> and slightly overpredicts O <sub>3</sub> inhibition by n-octane.
086	3/27/03	ROG=1 ppmC, NO <sub>x</sub> =10 ppb Surrogate + m-Xylene	Low NO <sub>x</sub> incremental reactivity test experiment for variable ROG and NO <sub>x</sub> surrogate evaluation. 25 ppb m-xylene added to Side B.	Added m-xylene causes slightly increased O <sub>3</sub> formation rate during first hour of the experiment, but causes reduced O <sub>3</sub> during remainder of run. Model overpredicts O <sub>3</sub> during later stages of the run and underpredicts the effects of m-xylene on final O <sub>3</sub> .
095	4/15/03	ROG=1 ppmC, NO <sub>x</sub> =25 ppb ("MOIR/2") Surrogate + n-Octane	Incremental reactivity test experiment for variable ROG and NO <sub>x</sub> surrogate evaluation. 200 ppb n-octane added to Side A. Note that this base case will become the standard "MOIR/2" base case for the coatings reactivity study.	Added n-octane causes significant reduction in m-xylene consumption rates and moderate reduction in O <sub>3</sub> formation during the first two hours of the experiment. Model somewhat underpredicts the base case O <sub>3</sub> formation rate and overpredicts the inhibition effects of n-octane on O <sub>3</sub> .

Table A-1 (continued)

Run [a]	Date	Type [b]	Purpose and Applicable Conditions.	Results
096	4/16/03	ROG=1 ppmC, NO <sub>x</sub> =100 ppb Surrogate	Variable ROG and NO <sub>x</sub> surrogate evaluation. Same reactants on both sides for side equivalency test. (Desired initial NO <sub>x</sub> was 50 ppb, but 100 ppb injected because of injection calculation error.)	Good side equivalency. Very significant model underprediction of O <sub>3</sub> formation.
097	4/17/03	ROG=0.5 ppmC, NO <sub>x</sub> =5 ppb Surrogate	Low NO <sub>x</sub> variable ROG and NO <sub>x</sub> surrogate evaluation. Same reactants on both sides for side equivalency test.	Fair side equivalency; slightly more O <sub>3</sub> on Side A. Generally good fits of model simulation to O <sub>3</sub> .
098	4/18/03	ROG=0.1 ppmC, NO <sub>x</sub> =5 ppb Surrogate	Low NO <sub>x</sub> variable ROG and NO <sub>x</sub> surrogate evaluation. Same reactants on both sides for side equivalency test.	Fair side equivalency; slightly more O <sub>3</sub> on Side A. Generally good fits to model simulation to O <sub>3</sub> .
100	4/22/03	ROG=0.25 ppmC, NO <sub>x</sub> =5 ppb Surrogate + m-Xylene	Low NO <sub>x</sub> incremental reactivity test experiment for variable ROG and NO <sub>x</sub> surrogate evaluation. 15 ppb m-xylene added to Side B. Initial formaldehyde uncertain because of lack of formaldehyde data and possible problems with formaldehyde injection.	Added m-xylene had only a minor effect on the initial O <sub>3</sub> formation rate but caused reduced final O <sub>3</sub> yields. Model evaluation uncertain because of uncertainty in initial formaldehyde.
101	4/23/03	ROG=0.25 ppmC, NO <sub>x</sub> =2 ppb Surrogate	Low NO <sub>x</sub> variable ROG and NO <sub>x</sub> surrogate evaluation. Same reactants on both sides for side equivalency test.	Fair side equivalency; slightly more O <sub>3</sub> on Side A. Generally good fits of model simulation to O <sub>3</sub> .
103	4/25/03	CO - NO <sub>x</sub> Irradiation	Characterization run to evaluate chamber radical source. 50 ppm CO and 25 ppb NO <sub>x</sub> injected in both sides.	O <sub>3</sub> and apparent radical source higher on side A. Model simulations fit O <sub>3</sub> data with Apparent radical input relative to the NO <sub>2</sub> photolysis rates of 25 and 15 ppt for Sides A and B, respectively.
105	4/29/03	Actinometry	The NO <sub>2</sub> photolysis rate was measured at various locations, including inside each reactor.	The measured NO <sub>2</sub> photolysis rates were 0.264 and 0.259 min <sup>-1</sup> inside Sides A and B, respectively. These are the same to within the experimental uncertainty, and within the range observed in previous and subsequent in-reactor actinometry experiments. The data indicate no trend in light intensity during the period of these experiments.

Table A-1 (continued)

Run [a]	Date	Type [b]	Purpose and Applicable Conditions.	Results
108	5/7/03	ROG=1 ppmC, NO <sub>x</sub> =70 ppb Surrogate + m-Xylene	Incremental reactivity test experiment with a previously studied VOC as part of the variable ROG and NO <sub>x</sub> surrogate evaluation. 20 ppb m-xylene added to Side A.	Addition of m-xylene caused increase in O <sub>3</sub> formation rate and final O <sub>3</sub> . Model significantly underpredicted O <sub>3</sub> formation in the base case and because of this did not give particularly good fit to effect of m-xylene addition.
110	5/9/03	ROG=0.5 ppmC, NO <sub>x</sub> =30 ppb ("MIR") Surrogate + m-Xylene	Incremental reactivity test experiment for variable ROG and NO <sub>x</sub> surrogate evaluation. 10 ppb m-xylene added to Side A. Note that this base case will become the standard "MIR" base case for the coatings reactivity study. PM data taken for both reactors.	Added m-xylene caused increase in O <sub>3</sub> formation rate and final O <sub>3</sub> . Model somewhat underpredicted rate of O <sub>3</sub> formation but approximately simulated the effect of added m-xylene. Significantly more PM formed on the added m-xylene side (A).
112	5/12/03	CO - Air	Characterization run to evaluate apparent NO <sub>x</sub> offgasing rates. 100 ppm CO added to both sides. No NO <sub>x</sub> injected.	More O <sub>3</sub> formed in Side A than Side B. Model simulations fit using ratios of NO <sub>x</sub> offgasing to NO <sub>2</sub> photolysis rates of 20 and 8 ppt for Sides A and B, respectively.
113	5/13/03	ROG=1 ppmC, NO <sub>x</sub> =70 ppb Surrogate + n-Octane	Incremental reactivity test experiment with a previously studied VOC as part of the variable ROG and NO <sub>x</sub> surrogate evaluation. 200 ppb n-octane added to Side B.	Added n-octane caused a significant reduction in the m-xylene consumption rate and a moderate reduction in O <sub>3</sub> formation throughout the run. The model somewhat underpredicted the O <sub>3</sub> formation rate in the base case experiment but predicted the effect of the added n-octane reasonably well.
114	5/14/03	Standard MIR [c] Surrogate + n-Octane	Incremental reactivity test experiment with previously studied VOC using the standard MIR base case. 100 ppb n-octane added to Side B.	Added n-octane caused a significant reduction in the m-xylene consumption rate and a moderate reduction in O <sub>3</sub> formation throughout the run. The model somewhat underpredicted the O <sub>3</sub> formation rate in the base case experiment but predicted the effect of the added n-octane reasonably well.
115	5/15/03	CO - HCHO - Air	Characterization and control experiment that is sensitive to NO <sub>x</sub> offgasing rates and is useful for actinometry because HCHO consumption is expected to be due only to photolysis. 80 ppm CO and 100 ppb formaldehyde injected into both sides. No NO <sub>x</sub> injected.	The formaldehyde consumption rates were 9.2 and 7.1 x 10 <sup>-4</sup> min <sup>-1</sup> on Sides A and B, respectively. These correspond to calculated NO <sub>2</sub> photolysis rates of respectively 0.25 and 0.19 min <sup>-1</sup> , which are within the uncertainty range of the measurement. Somewhat more O <sub>3</sub> was formed in Side A. The data were fit with apparent NO <sub>x</sub> offgasing rates, relative to the NO <sub>2</sub> photolysis rate, of 10 and 5 ppt, respectively.

Table A-1 (continued)

Run [a]	Date	Type [b]	Purpose and Applicable Conditions.	Results
120	5/29/03	Actinometry	The NO <sub>2</sub> photolysis rate was measured at various locations, including inside each reactor.	The measured NO <sub>2</sub> photolysis rates were 0.262 and 0.251 min <sup>-1</sup> inside Sides A and B, respectively. These are within the range observed in previous and subsequent in-reactor actinometry experiments, and indicate no trend in light intensity during the period of these experiments.
123	6/5/03	Standard MOIR/2 [c] Surrogate + m-Xylene	Incremental reactivity test experiment with previously studied VOC using the standard MOIR/2 base case. 30 ppb m-xylene added to Side B.	Added m-xylene caused slight increase in O <sub>3</sub> formation rate and reduction in final O <sub>3</sub> . Model predicted initial increase effect but underpredicted suppression of final O <sub>3</sub> .
124	6/6/03	Standard MOIR/2 Surrogate + Aromatic-100	Standard MOIR/2 incremental reactivity experiment for Aromatic-100. 500 ppbC Aromatic 100 injected Side B.	Added aromatic-100 caused increase initial O <sub>3</sub> formation rate but reduction in final O <sub>3</sub> and reduction in m-xylene consumption rate. Aromatic-100 experiment not yet modeled.
126	6/10/03	Standard MOIR/2 Surrogate + VMP Naphtha	Standard MOIR/2 incremental reactivity experiment for VMP Naphtha. 900 ppb VMP Naphtha injected into Side B.	Added naphtha caused reduction in O <sub>3</sub> . Model gave good simulation of results.
127	6/11/03	Standard MIR Surrogate + Aromatic-100	Standard MIR incremental reactivity experiment for Aromatic-100. 500 ppbC Aromatic 100 injected Side B.	Added Aromatic-100 caused large increase in O <sub>3</sub> formation rate but only small change in final O <sub>3</sub> . Aromatic-100 experiment not yet modeled.
128	6/16/03	ROG=0.5 ppmC, NO <sub>x</sub> =50 ppb Surrogate + n-Octane	Low ROG/NO <sub>x</sub> Incremental reactivity test experiment with a previously studied VOC as part of the variable ROG and NO <sub>x</sub> surrogate evaluation. 20 ppb m-xylene added to Side B.	Addition of m-xylene caused increase in O <sub>3</sub> formation rate and final O <sub>3</sub> . Model somewhat underpredicted O <sub>3</sub> formation in the base case, but gave fair prediction of effect of added m-xylene.
133	7/2/03	CO - HCHO - Air	Characterization and control experiment that is sensitive to NO <sub>x</sub> offgasing rates and is useful for actinometry because HCHO consumption is expected to be due only to photolysis. 80 ppm CO and 100 ppb formaldehyde injected into both sides. No NO <sub>x</sub> injected.	The formaldehyde consumption rates were 1.2 x 10 <sup>-3</sup> on both sides, which was about 25% higher than in the previous such experiment and also higher than expected from the NO <sub>2</sub> actinometry data. Somewhat more O <sub>3</sub> was formed in Side A. The data were fit with apparent NO <sub>x</sub> offgasing rates, relative to the NO <sub>2</sub> photolysis rate, of 10 and 5 ppt, respectively.

Table A-1 (continued)

Run [a]	Date	Type [b]	Purpose and Applicable Conditions.	Results
136	7/10/03	Aromatic-100 - NO <sub>x</sub> + CO	Mechanism evaluation experiment for Aromatic-100 of the type found useful for other aromatics. 0.9 ppmC of Aromatic-100 and 50 ppb NO <sub>x</sub> injected in both sides, and 90 ppm CO injected into Side A. No PM data.	Considerably more O <sub>3</sub> formed on side with CO. Experiment not yet modeled.
137	7/11/03	Standard MIR Surrogate + VMP Naphtha.	Standard MIR incremental reactivity experiment for VMP Naphtha, 900 ppmC VMP Naphtha injected Side B.	Added naphtha caused reduction in O <sub>3</sub> . Model underpredicted base case O <sub>3</sub> but gave fair fit to effect of naphtha.
138	7/14/03	Standard MOIR/2 Surrogate + ASTM-3C1	Standard MOIR/2 incremental reactivity experiment for ASTM-3C1. 900 ppb ASTM-3C1 injected into Side B.	Added mixture caused only a slight increase in O <sub>3</sub> but a reduction in m-xylene consumption rate. ASTM-3C1 experiment not yet modeled.
139	7/15/03	Standard MOIR/2 Surrogate + ASTM-1B	Standard MOIR/2 incremental reactivity experiment for ASTM-1B. 900 ppb ASTM-1B injected into Side B.	Added mixture caused slight decrease in O <sub>3</sub> throughout the run. ASTM-1B experiment not modeled.
140	7/16/03	CO - NO <sub>x</sub> Irradiation	Characterization run to evaluate chamber radical source. 50 ppm CO and 25 ppb NO <sub>x</sub> injected in both sides.	O <sub>3</sub> and apparent radical source slightly higher on side A. Model simulations fit O <sub>3</sub> data with Apparent radical input relative to the NO <sub>2</sub> photolysis rates of 12 and 10 ppt, respectively.
143	7/22/03	Standard MIR Surrogate Side Equivalency Test	Assess side equivalence with standard MIR surrogate experiment. Standard MIR surrogate injected into both sides.	Good side equivalency observed for O <sub>3</sub> and other gas-phase measurements. However, about 50% more PM formed on Side A.
149		M-Xylene - NO <sub>x</sub>	X-xylene mechanism and PM evaluation experiment. 50 ppb NO on both sides, and 75 and 150 ppb m-xylene on Sides A and B, respectively. PM data from both sides, but data had problems and are not reliable.	O <sub>3</sub> formation started earlier on higher m-xylene side but final O <sub>3</sub> was lower. Model approximately simulated O <sub>3</sub> on low m-xylene side but overpredicted O <sub>3</sub> on the higher m-xylene side.
150	8/5/03	Standard MOIR/2 Surrogate + ASTM-3C1	Standard MOIR/2 incremental reactivity experiment for ASTM-3C1. 900 ppb ASTM-3C1 injected into Side B.	Data from this experiment are not completely processed. Added mixture had only small effect on O <sub>3</sub> .
151	8/6/03	Standard MIR Surrogate + ASTM-1B	Standard MIR incremental reactivity experiment for ASTM-1B, 900 ppmC ASTM-1B injected Side B.	Added mixture caused reduction in O <sub>3</sub> throughout the run and significant reduction in m-xylene consumption rate. ASTM-1B experiment not yet modeled.

Table A-1 (continued)

Run [a]	Date	Type [b]	Purpose and Applicable Conditions.	Results
152	8/7/03	Standard MOIR/2 Surrogate + ASTM-1C	Standard MOIR/2 incremental reactivity experiment for ASTM-1C. 900 ppb ASTM-1C injected into Side B.	Data from this experiment are not completely processed. Added mixture reduced O <sub>3</sub> throughout the experiment and significantly suppressed m-xylene consumption rate.
153	8/8/03	Standard MOIR/2 Surrogate + ASTM-1A	Standard MOIR/2 incremental reactivity experiment for ASTM-1A. 900 ppb ASTM-1A injected into Side B.	Data from this experiment are not completely processed. Added mixture reduced final O <sub>3</sub> and m-xylene consumption rate.
156	8/14/03	O <sub>3</sub> Decay	Ozone dark decay determination and control experiment for effect of dark O <sub>3</sub> on PM measurements. ~300 ppb O <sub>3</sub> injected in both sides and monitored for only 2 hours because of equipment problems.	O <sub>3</sub> dark decay rates were ~4 x 10 <sup>-4</sup> on both sides, which is higher than assumed in the chamber model, but the measurement is uncertain because of the short exposure time. Nucleation observed on Side A but not B. No measurable PM volume.
158	8/16/03	O <sub>3</sub> Decay	Repeat of previous O <sub>3</sub> decay experiment but with longer exposure time. ~300 ppb O <sub>3</sub> injected in both sides and monitored for 2 hours.	O <sub>3</sub> dark decay rates were 0.8-1.2 x 10 <sup>-4</sup> , which is slightly lower than assumed in the chamber model. Nucleation occurred on both sides, but PM number was higher on Side A and Side A had small but measurable PM volume.
159	8/18/03	Standard MIR Surrogate Side Equivalency Test	Assess side equivalence with standard MIR surrogate experiment. Standard MIR surrogate injected into both sides.	Good side equivalency observed for O <sub>3</sub> and other gas-phase measurements. However, about two times more PM formed on Side A.
160	8/19/03	CO - Air	Characterization run to evaluate apparent NO <sub>x</sub> offgasing rates. 100 ppm CO added to both sides. No NO <sub>x</sub> injected.	Slightly more O <sub>3</sub> formed in Side A than Side B. Model simulations fit using ratios of NO <sub>x</sub> offgasing to NO <sub>2</sub> photolysis rates of ~18 and 12 ppt for Sides A and B, respectively. No PM formation.
163	8/22/03	Standard MIR Surrogate + ASTM-3C1	Standard MIR incremental reactivity experiment for ASTM-3C1, 900 ppmC ASTM-3C1 injected Side A.	Data from this experiment are not completely processed. Added mixture suppressed O <sub>3</sub> and m-xylene consumption rate.
167	8/28/03	Standard MIR Surrogate + ASTM-1A	Standard MIR incremental reactivity experiment for ASTM-1A, 900 ppmC ASTM-1A injected Side B.	The added mixture caused only a small change in O <sub>3</sub> but reduced the m-xylene consumption rate. The ASTM-1A experiment was not yet modeled.
168	8/29/03	Standard MIR Surrogate + ASTM-1C	Standard MIR incremental reactivity experiment for ASTM-1C, 900 ppmC ASTM-1B injected Side A.	The data from this experiment are not completely processed. The added mixture reduced both O <sub>3</sub> and the m-xylene consumption rate.

[a] EPA Run number. Gaps in run numbers reflect experiments using the blacklight light source carried out PM

Table A-1 (continued)

evaluation for other projects, or experiments that were aborted because of equipment or instrumentation problems.

- [b] Unless indicated otherwise, "Surrogate" refers to the 8-component "Full Surrogate" as used in previous environmental chamber incremental reactivity studies in our laboratories.
- [c] The designation "Standard MIR Surrogate" refers to experiments with 0.5 ppmC base case surrogate and 30 ppb NO<sub>x</sub>, The designation "Standard MOIR/2 Surrogate" refers to experiments with 1 ppmC base case surrogate and 25 ppb NO<sub>x</sub>.