Near-Term Research Plan for UCR-EPA Chamber

Prepared for the RRWG UCR EPA Chamber Advisory Committee

William P. L. Carter
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The purpose and the initial research plan for the UCR EPA chamber was described in detail the report and draft research plan that was submitted to the EPA and the RRWG early in 2002. Updates to the progress on this project are given in a report submitted in August, 2002, immediately prior to the last RRWG meeting. Progress and current status of the project was also discussed with the RRWG Advisory Committee for the UCR EPA Chamber project. During this meeting, the Committee was advised that because the costs and time required to complete the chamber facility was much greater than initially anticipated, it will not be possible to carry out the full research plan that was described in the proposal and the draft plan submitted in early 2002, and that a revised research plan was needed. The Committee requested that we prepare a new plan that more appropriately reflects the current reality. This is discussed in this document.

The experiments proposed for the near term with the currently available and remaining funding are listed and discussed in Table 1. The major construction of the UCR-EPA chamber has just been completed, and we are now beginning to carry out the leak tests and initial characterization experiments. Because the funding on the current EPA project is expected to last no longer than 1-2 months, the priority for the remaining funding will be the minimum characterization and basic evaluation needed to begin using the facility for the architectural coatings reactivity project for the CARB. This is appropriate because at present the CARB architectural coatings project is the major remaining source of funding that is currently in place for experiments in this facility, and also because architectural coatings reactivity research was one of the priorities for the EPA project as well. In addition, the low NO_x aromatic experiments on Table 1 will address in part research to be included in the low NO_x mechanism evaluation project to be carried out for the CARB.

The other priorities in the EPA project, such as evaluation of temperature effects, more comprehensive low NO_x mechanism evaluation experiments, and evaluations of aerosol formation potentials, will be deferred until additional funding is available. There is an earmark in the 2003 Federal budget that passed the House for CE-CERT to get ~$750K next year for various projects, of which at least $250K will be made available for this facility. However, the 2003 budget has not yet passed, and the funds may not be immediately available. We are also submitting a proposal to the EPA for use of the chamber to evaluate observationally based methods, which would provide ~$170K for chamber experiments in the coming year. However, for this to be fully funded the EPA will need additional funds for OBM research in its 2003 budget, which is not a certainty. If and when these additional funds become available, we will submit a revised near-term research plan to the RRWG UCR EPA Chamber Advisory Committee for review and comments.

Table 1. Description of proposed experiments to be carried out with the remaining EPA funds and for the CARB architectural coatings reactivity experiments.

Type of Run	Description and Purpose
	Basic Characterization [a]
Leak Tests	The reactors are filled with pure air, CO and/or NO are injected into the enclosure, and the influx of these pollutants into the reactor is monitored over a 24 hour or longer period. The input rate of CO and NO should not exceed the permeation rate or the reactor will need to be repaired before proceeding.
Pure Air Irradiation 2 Runs (over time)	At least one-day irradiation of purified air with no reactant injections. Multi-day run preferable if background effects are low. The O_3 formation rate is useful for a relatively easy preliminary evaluation of background effects. However, the results affected by a number of factors (background NO_x, VOC, and radical sources [b]), so the results do not provide an unambiguous determination of background effects parameters. However, data are useful in conjunction with results of experiments sensitive to specific effects.
O_3 Dark Decay and dilution test 1-2 Runs	Inject 50-100 ppb of O_3 and an easily monitored amount of CO (~50 ppm) in the chamber and monitor in the dark for about 12 hours or more. The CO data indicate whether any dilution is occurring during the experiment, which should be negligible. The O_3 decay relative to the CO decay (if any) indicates the rate of loss of O_3 on the walls, which must be taken into account when modeling O_3 formation in experiments. However, the O_3 dark decay rate in these large Teflon® reactors is generally very small.
CO - Air Irradiation 1-2 Runs	At least one-day irradiation of 50-100 ppm of purified CO with no other reactant injections. Multi-day run preferable if background effects are low. The O_3 formation rate is sensitive to background NO_x effects and background radical sources (with the NO_x effects expected to be the more important [b]), but not sensitive to background VOCs.
CO - Formaldehyde - Air Irradiation 1-2 Runs	6-12 hour irradiation of 50-100 ppm of purified CO and ~100 ppb formaldehyde with no other reactant injections. The O_3 formation rate is sensitive to background NO_x effects but not radical sources or background VOCs, making it a specific experiment for determining NO_x effects. Also, the CO scavenges the OH radicals, so the formaldehyde is consumed primarily by photolysis, making this a useful formaldehyde actinometry experiment. Formaldehyde actinometry is a useful measurement of light intensity and also tests the model prediction of formaldehyde photolysis rates.
CO - NO_x Irradiation 6 Runs (over time)	6-12 hour irradiation of 50-100 ppm of CO with varied amounts of NO_x, injected as either NO or NO_2. Results are sensitive primarily to background radical source. Amount of NO_x injected varied to determine dependence of radical source on NO_x, and changing the initial NO/NO_2 ratio affects the average NO_2 concentration. Experiments in the pillowbag reactor indicate the radical source is dependent on the NO_2 concentration.
n-Butane - NO_x Irradiation 1-2 Runs	6-12 hour irradiation of ~1 ppm of n-butane with varied amounts of NO_x, injected as either NO or NO_2. This is an alternative to CO - NO_x experiment as a measure of the chamber radical source, and should give the same results. It will be carried out at at least one NO_x level for verification purposes.

Table 1 (continued)

Type of Run	Description and Purpose
Formaldehyde - NO_x 1-2 Runs	6-12 hour irradiation of ~25 ppb each of formaldehyde and NO. Model simulations indicate that O_3 formation in these experiments is very sensitive to background VOC effects. But should be conducted in conjunction with the formaldehyde - CO - air and formaldehyde - CO - NO_x experiments to evaluate the representation of the formaldehyde photolysis and gas-phase mechanism for the conditions of this chamber.
Formaldehyde - CO - NO_x 1-2 Runs	6-12 hour irradiation of ~25 ppb each of formaldehyde and NO and 50-100 ppm of CO. This is not strictly a chamber characterization run because model predictions indicate it should not be sensitive to background NO_x, VOC, or radical source effects. However, it is a useful control in conjunction with the characterization runs containing formaldehyde to evaluate the model representation of the homogeneous portion of the mechanism.
HNO_3 Dark and Light Decay [c] 0-2 Runs	About 25 ppb of HNO_3 and an easily monitored amount of CO is injected and monitored in the dark for at least 6-12 hours or until half is lost (whichever occurs first), and then it is irradiated for 6-12 hours. Useful to determine wall loss and photolysis rates for HNO_3, for use when HNO_3 data are used in mechanism evaluation experiments. See note [b].
Propene - NO_x Control ≥2 Runs (over time)	Propene and NO_x are irradiated for at least 6 hours, with the NO_x concentration set at the level to be used for most reactivity experiments, and the propene concentration set so that most of the NO_x is consumed before the end of the irradiation, and so that measurable amounts of H_2O_2 is expected to be formed. Should not be sensitive to major chamber effects. Useful for evaluating the ability of the mechanism and chamber model to simulate major aspects of reactivity in a well-characterized chemical system where the major manifestations of photochemical smog are occurring.
	<u>Basic Mechanism Evaluation - Simple Systems</u>
Acetaldehyde - NO_x 1 Run	About 50 ppb acetaldehyde and 10 ppb NO_x irradiated for 12 hours. Verifies applicability of light model to acetaldehyde photolysis and model predictions of processes involving PAN and HNO_3 formation under low NO_x conditions. One experiment (with different reactant levels in each of the dual reactors) should be sufficient if results are consistent with model predictions, as is expected.
Ethene - NO_x 1 Run	Approximately 25 ppb NO_x and 200 ppb ethene irradiated for ~12 hours, with different reactant concentrations used in the other reactor. This provides a necessary test of the ability of the model to predict the reactivity of this important surrogate component. Additional experiments may be conducted if results are not as expected. Note that significant formation of hydroxy PAN (GPAN) is expected, and this will be measured using the thermal converter system being developed to evaluate nitrate yields for the ACC.

Table 1 (continued)

Type of Run	Description and Purpose
Toluene - NO_x 3 Runs	NO_x varied from 10 to 50 ppb and toluene varied from 25 to 100 ppb, respectively with an additional experiment with a lower NO_x /toluene ratio. These experiments are needed to evaluate whether current aromatic mechanisms extrapolate to lower NO_x conditions than used previously in their evaluation. Additional experiments may be conducted if results are not consistent with model predictions.
Toluene - CO - NO_x 2 Runs	Approximately 20 ppm CO added to an above toluene - NO_x system. This will evaluate model predictions of effects of aromatics on NO to NO_2 conversions by other species. Model predicts that relatively small amounts of CO will significantly perturb the aromatic - NO_x systems. This type of experiment provides a simplified example of the role of aromatics in the surrogate - NO_x systems used in VOC reactivity determinations.
m-Xylene - NO_x 1-2 Runs	At least one experiment with 10 or 25 ppb NO_x and ~15 ppb m-xylene will be conducted to evaluate low NO_x aromatic mechanism for m-xylene. Additional experiments may be conducted as needed.
m-Xylene - CO - NO_x 1-2 Runs	Approximately 10 ppm CO added to the m-xylene experiment, probably in the other reactor at the time of the above m-xylene experiment. Purpose similar to the toluene - CO - NO_x experiment. Relatively small amounts of CO are predicted to perturb the m-xylene system significantly, and provide evaluation of aspects of the mechanism not given by experiments with m-xylene alone. This provides an additional test of the model predictions of how aromatics affect the surrogate - NO_x systems used in VOC reactivity determinations.
	Surrogate Evaluation
Surrogate - NO_x Tests 3-4 Runs	Exploratory experiments to determine the appropriate surrogate - NO_x system to use for reactivity evaluation for the CARB coatings reactivity program. NO_x levels will be determined in consultation with the CARB, RRAC, and RRWG. Base ROG composition will probably be the same as used for the "full surrogate" in previous reactivity studies, but will be finalized after discussions with the CARB, RRAC, and RRWG. Base ROG levels will be determined to provide the appropriate ROG/NO_x levels for MIR and low NO_x reactivity evaluation, as predicted by the model and evaluated by experiments. Dual chamber runs will employ different ROG and/or NO_x levels
CO Reactivity 1-2 Runs	Appropriate levels of CO added to surrogate - NO_x system at two NO_x levels to evaluate whether reactivity predictions for a simple mechanism are consistent with model predictions. This is primary to evaluate the surrogate mechanism and its suitability to represent the base case in reactivity experiments.
n-Octane Reactivity 1-2 Runs	Appropriate levels of n-octane added to surrogate - NO_x system at two NO_x levels to evaluate whether reactivity predictions for a compound that is a simple representative of major petroleum distillate components are consistent with model predictions. This is a necessary control for evaluation experiments for petroleum distillates and other compounds with higher alkane-like mechanisms, such as Texanol®[d].

Table 1 (continued)

Type of Run	Description and Purpose
Modified ROG Surrogate Tests 0-4 Runs	Previous reactivity studies included experiments with a "Mini-Surrogate" base ROG mixture which, though not a good representation of ambient VOCs, provided a means to test aspects of VOC's mechanisms with different sensitivities than runs with the more realistic surrogate. However, this type of experiment may of lower priority for overall mechanism evaluation if the "direct reactivity" measurement method being developed as part of the CARB project is shown to be successful for providing useful mechanism evaluation data to complement standard surrogate experiments. Since we have not yet completed our evaluation of the ultimate utility of direct reactivity data, the need for modified surrogate tests have not been determined. This type of experiment may be deferred until later in the project for this reason. CARB Coatings Research Project (To be conducted using CARB funding)
Petroleum Distillate Reactivity	Appropriate levels of petroleum distillate samples selected by the CARB and the RRAC will be added to surrogate – NO_x mixtures, with the base case surrogate – NO_x mixture in one of the dual reactors, and the same mixture with the petroleum distillate sample added to the other. Experiments with ROG and NO_x levels corresponding to MIR-like and low NO_x conditions will be conducted. The initial experiments will be with the highest volatility petroleum distillate that is selected for study. Experiments with modified ROG surrogates such as a "mini-surrogate" may be conduced later in the project, if needed.
Texanol®[d] Reactivity	Appropriate levels of hydroxy-2,2,4-trimethylpentyl isobutyrate isomers will be added to the standard low and high NO_x surrogate base case mixtures. Experiments with modified ROG surrogates such as a "mini-surrogate" may be conduced later in the project, if needed. Although studies of Texanol® is a priority for this project, they will be conducted later in the program because they are expected to be more difficult because of their low reactivity.

[a] The number of experiments in the "Basic Characterization" group refers only to the number of experiments required for initial characterization. Radical source and background effects characterization runs and control experiments also need to be carried out from time to time in conjunction with ongoing reactivity and other mechanism evaluation experiments to assess changes in chamber effects over time.

[b] Formaldehyde measurements during the preliminary pure air and CO - air experiments indicate that some background formation of formaldehyde is occurring, and modeling of these experiments indicate that this is sufficient to account for the background radical source in the absence of NO_x.

[c] This experiment is only useful if HNO_3 can be monitored with sufficient sensitivity and specificity for mechanism evaluation in low and moderate NO_x experiments. This requires that the TDLAS sensitivity for HNO_3 be improved above its present capability. These improvements are expected, but if they are not successful these experiments will be deferred until useful specific HNO_3 data can be obtained. Note that modified "NO_y" instruments are not considered to be sufficiently reliable for HNO_3 analysis to be useful for mechanism evaluation.

[d] Texanol® is a commercial trade name for hydroxy-2,2,4-trimethylpentyl isobutyrate isomers. This compound is a priority for study in the CARB program because of its importance in water-based coatings. It is referred to here by the trade name for simplicity.