

DEVELOPMENT OF A NEXT-GENERATION ENVIRONMENTAL CHAMBER FACILITY FOR CHEMICAL MECHANISM AND VOC REACTIVITY RESEARCH

Summary of Progress August 21, 2002 - February 20, 2003

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Introduction

The objective this EPA-funded project is to develop an environmental chamber facility that is needed for studies of photochemical air pollution formation under more realistic conditions and with more comprehensive measurements than previously has been possible. This facility can then be employed for evaluating gas-phase and gas-to-particle atmospheric reaction mechanisms, for determining how best to use ambient measurement data for predicting effects of control strategies, and for evaluating the reliability of ambient measurement instrumentation.

The project was initiated in late 1999, the design and construction of the facility was completed in early 2003, and initial characterization and mechanism evaluation experiments are now underway. A detailed report describing progress through October of 2001 was submitted to the EPA, and a summary report summarizing progress through August 20, 2002 was submitted to the EPA and the RRWG Advisory Committee for this project. The status of the project and funding situation was also summarized in the latter summary report. These reports are available at the project web site at <http://www.cert.ucr.edu/~carter/epacham>, and should be consulted for details concerning the background and status of the progress through the dates they were prepared. This report provides an update on the progress on this project through February 20, 2003, and also provides an update of the current funding situation and research plan.

Revised Work Plan

Because the costs and time required to complete the chamber facility was much greater than initially anticipated, it was determined that it will not be possible to carry out the full research plan that was described in the proposal and in the draft plan submitted in early 2002 without additional funding. The RRWG oversight group for this project requested that we prepare a revised work plan for near-term experiments that more appropriately reflects the current funding realities than the previous plan. A list of what we consider a minimum set of experiments to be carried out with the available funding was prepared and provided to the RRWG oversight group in January of 2003. This list of is reproduced on Table 1 of this report. This includes the minimum set of characterization experiments for basic mechanism

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 |
|---|--|
| | <u>Basic Characterization</u> [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 ₂ O 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. |
| 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. |

Table 1 (continued)

| Type of Run | Description and Purpose |
|---|--|
| 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. |
| <u>Surrogate Evaluation</u> | |
| 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 | <p>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.</p> <p><u>CARB Coatings Research Project</u> (To be conducted using CARB funding)</p> |
| Petroleum Distillate Reactivity | <p>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 conducted later in the project, if needed.</p> |
| Texanol®[d] Reactivity | <p>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 conducted 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.</p> |

- [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 HNO₃ 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 HNO₃ be improved above its present capability. These improvements are expected, but if they are not successful these experiments will be deferred until useful specific HNO₃ data can be obtained. Note that modified “NO_y” instruments are not considered to be sufficiently reliable for HNO₃ 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.

evaluation under dry conditions at a single temperature, a minimum set of low NO_x mechanism evaluation experiments necessary to carry out VOC reactivity assessments under lower pollutant conditions, and the experiments called for in the CARB coatings project. The RRWG oversight group did not communicate any significant problems with this revised work plan.

Progress Since August, 2002

The main objectives for the work carried out since August of 2002 were to complete preparation of the chamber in its final configuration and to make progress in the minimal set of characterization and basic mechanism evaluation experiments outlined in the revised work plan discussed above. Generally, good progress was made towards these objectives. The work carried out and problems encountered in this project since the period covered by the previous summary report is briefly summarized below.

- A number of experiments were carried out using the single reactor to characterize the performance of the chamber in this preliminary configuration. A number of leak and background contamination problems were encountered that had to be corrected, mostly by repairing leaks or improving the sealing of the temperature-controlled enclosure. The reactor design involving the moveable rigid framework was evaluated and methods to control it based on continuously maintaining positive pressure at a desired level were developed and evaluated. The system was tested by injecting high concentrations of CO in the enclosure and then monitoring CO levels in the reactor. Eventually satisfactory results were obtained, with CO increases in the reactor being the same as predicted from results of permeation experiments.
- The new spectral system for the Vortek arc light source was installed and evaluated, and other upgrades were made to the system to improve the ease and reliability of its operation. Although some problems were encountered with bad electrodes and cracking of the spectral filter windows, reasonably good operation was obtained once the electrodes were replaced and minor redesigns were made to the spectral window. Based on the satisfactory performance of the system, the final invoice from Vortek was approved for payment.
- The second reactor and associated mixing and sampling systems were installed. Once this was completed, we could conduct simultaneous irradiations of two reactors in a single experimental run, thus doubling the productivity and making the system more suitable for reactivity experiments. However, the reactor mixing and exchange system as initially installed had some design problems and cannot be used for equalizing reactants in the two reactors until modifications are made. It was decided to postpone these modifications until after the characterization experiments were completed. This is because the characterization experiments did not require exactly equal reactants in both reactors, and because the process of carrying out the characterization experiments may indicate needs for other modifications and improvements, which are most efficiently made at the same time the problems with the mixing system is corrected.
- The first of the series of apparently successful experiments with the reactor and lighting system in its current configuration was carried out in mid January of 2003. A chronological list of experiments carried out since then up to the date of this report, briefly indicating the purpose and summarizing in general terms the results, is given in Table 2. This is based roughly on the research plans and priorities communicated to the RRWG in January and indicated on Table 1 as “Basic Characterization” and “Basic Mechanism Evaluation – Simple Systems”, except that experiments involving HNO₃ have not been carried out because the HNO₃ analysis system is still offline. As indicated on Table 2, this series of experiments are nearly complete, and most appear to be reasonably successful. Some results of preliminary analysis are discussed below.

Table 2. Summary of EPA chamber experiments carried out with using the current dual-reactor configuration as of 2/21/03.

| Run ID | Date | Type | Purpose and Applicable Conditions. | Results |
|--------|---------|-----------------|---|--|
| EPA055 | 1/10/03 | CO - Air | Determine NOx and formaldehyde offgasing | Some problems with lamp and reactor, but results useable. |
| EPA056 | 1/14/03 | CO - Air | Repeat of previous experiment | Low but non-negligible apparent NOx offgasing rate, somewhat lower than previous run. Small amount of formaldehyde offgasing |
| EPA057 | 1/15/03 | CO - NOx | Determine radical source and formaldehyde offgasing at ~50 ppb initial NOx. NO injected on one side, NO2 the other to vary NO2 but not NOx. | Radical source rate comparable to NOx offgasing rates indicated by CO - air runs. Small amount of formaldehyde offgasing also consistent with previous runs. |
| EPA058 | 1/16/03 | CO - NOx | Similar to previous run but with higher (~90 ppb) initial NOx. | Radical source and formaldehyde offgasing parameters consistent with previous experiment. |
| EPA059 | 1/17/03 | O3 Dark decay | CO added to test for dilution and O3 added to test for O3 loss on walls in dark. | No measurable dilution. O3 decay rate in range observed for other Teflon film reactors. |
| EPA060 | 1/21/03 | CO - Air | Determine reproducibility and consistency of NOx and formaldehyde offgasing | Results very similar to EPA056, indicating consistent offgasing rates. |
| EPA061 | 1/22/03 | CO - NOx | Determine radical source with low (~10 ppb) initial NOx | Radical source in range observed with CO - NOx runs at higher NOx. |
| EPA062 | 1/24/03 | Actinometry | NO2 photolysis rate measured inside one of the reactors and some light uniformity measurements made in same reactor. | Results indicated NO2 photolysis rate in the reactor at the power setting used in these experiments was 0.26 min ⁻¹ , which was somewhat lower than previously thought. Light uniformity fair but additional measurements will be needed to completely characterize this. |
| EPA063 | 1/28/03 | CO - HCHO - Air | This amounts to formaldehyde actinometry because photolysis is calculated to be the major loss process. Also provides data on NOx offgasing rate independent of radical source parameter. | Formaldehyde consumption rate consistent with NO2 photolysis rate measured in previous run. Apparent NOx offgasing rate in range observed in CO - air runs. |
| EPA064 | 1/30/03 | n-Butane - NOx | Measure radical source rate using a somewhat different chemical system. 50 ppb NOx. | Apparent radical source comparable to those indicated by the CO - NOx runs. |

Table 2 (continued)

| Run ID | Date | Type | Purpose and Applicable Conditions. | Results |
|--------|---------|---------------------|---|--|
| EPA065 | 2/3/03 | Propene - NOx | Test performance of mechanism and characterization data with simple, reasonably well tested, chemical system, but at variable and low NOx. ~6 ppb NOx on one side, ~15 ppb NOx on the other. Also test mechanism for proposed base ROG surrogate component. | Results of both high and NOx sides fit reasonably well by mechanism, but only if no radical source is assumed. O3 formation somewhat predicted if radical source indicated by CO and n-butane - NOx runs used. |
| EPA066 | 2/4/03 | Toluene - NOx + CO | Obtain a preliminary test of the toluene mechanism under low NOx conditions. ~5 ppb NOx both sides. CO added to one side only to determine effect of "radical amplifier" species. Also test mechanism for proposed base ROG surrogate component. | O3 slightly overpredicted on side without CO but not by much. O3 underpredicted on added CO side. Therefore, model does not correctly predict effect of adding CO on O3 in the toluene - NOx system. |
| EPA067 | 2/7/03 | m-Xylene - NOx + CO | Similar purpose and procedure as for previous run, except with m-xylene. Also test mechanism for proposed base ROG surrogate component. | Qualitatively similar to toluene run. O3 somewhat overpredicted on side without CO but underpredicted in side with CO. |
| EPA068 | 2/10/03 | HCHO - CO - NOx | Evaluate basic mechanism for formaldehyde and CO under conditions that should be relatively insensitive to chamber effects. Initial CO varied. NOx ~ 20 ppb. | Model performed very well in simulating both experiments. |
| EPA069 | 2/11/03 | HCHO - NOx | Sensitive to background VOC contamination. Also basic mechanism and characterization evaluation. | Initial O ₃ formation rate somewhat slower and final O ₃ somewhat higher than predicted by model, but discrepancy not large. Assuming non-negligible background VOCs does not improve fit, indicating that this is probably not important. |
| EPA070 | 2/12/03 | CO - NOx | Evaluate consistency of radical source after experiments with various systems. | Apparent radical source consistent with previous experiments. Results very well fit using default chamber model. |
| EPA071 | 2/14/03 | CO - NOx (high NOx) | Evaluate radical source at much higher NOx levels than previous experiments, to determine NOx dependency. Also vary NO ₂ . ~260 ppb NO added to one side, ~200 ppb NO ₂ added to the other. | Results of added NO experiment reasonably well fit by default model, if some initial HONO is also assumed to be present. Results of high NO ₂ experiment were unexpected and indicated a LOWER radical source than the default model. This is still being analyzed. |
| EPA072 | 2/19/02 | Toluene - CO - NOx | This was intended to be like EPA066 except with larger amounts of NOx (~15 ppb), but CO was injected on both sides by mistake, so the same toluene - CO - ~15 ppb NOx mixture was irradiated on both sides. | The results were similar to the lower NOx toluene - CO - NOx experiment in that the O ₃ was somewhat higher than predicted by the model. |

Table 2 (continued)

| Run ID | Date | Type | Purpose and Applicable Conditions. | Results |
|-----------|---------|--------------------|--|--|
| EPA073 | 2/21/03 | Ethene - NOx | Test performance of mechanism and characterization data with simple chemical system, but at variable and low NOx. ~10 ppb NOx on one side, ~25 ppb NOx on the other. Also test mechanism for proposed base ROG surrogate component. | Final O ₃ on both sides somewhat higher than predicted by the model, but generally results consistent with model predictions. |
| Scheduled | | Toluene - NOx + CO | Toluene mechanism evaluation at NOx levels characteristic of TVA experiments. Repeat of EPA072 but with CO injected only on one side. Also, NOx increased to 25 ppb and added CO increased to 50 ppm so the data will span a larger NO _x concentration range. | |
| Scheduled | | CO - Air | Determine if change in NOx offgasing parameter after conducting a number of experiments with added NOx | |

- A preliminary series of light characterization measurements were carried out. The results indicated that the light intensity was somewhat less than initially estimated, though sufficiently high for the objectives of the experiments to be conducted. The actinometry experiment indicated that the NO₂ photolysis rate in the conditions of the experiments listed on Table 2 was ~0.26 min⁻¹, which is within the range observed by our previous chamber experiments and higher than that obtained in the CE-CERT Xenon Teflon Chamber (CTC). This is with a lamp power setting of 400 amps, which is somewhat lower than the Vortek-recommended maximum of 500 amps that was used in some preliminary experiments. It was determined that it is best for routine experiments to use a lower than maximum lamp power setting to maximize electrode lifetime and improve reliability. The light uniformity was found to be within ±10% in the preliminary measurements, though additional uniformity measurements will be needed to fully characterize this.
- Preliminary modeling and analysis of the completed experiments listed on Table 2 was carried out. Although there are some discrepancies and characterization uncertainties, the model performed reasonably well simulating these experiments for a preliminary analysis. The preliminary modeling and characterization results are discussed further in the following sections.
- Although the Vortek arc lighting system was performing satisfactory during most (though not all) of the experiments listed in Table 2, it is clear that the system cannot be counted on to function reliability 100% of the time, and that significant down times where major components need to be repaired or replaced should be anticipated. In order to have a backup lighting system to permit at least some experiments to continue during such periods, it was decided to construct a blacklight irradiation system in the enclosure that can be when the Vortek is not operational. Blacklights also have the advantages of being significantly more reliable than arc light systems because of their relative simplicity, and are significantly less expensive both in terms of labor and consumables to operate. Therefore, they can be used for experiments where cost and simplicity are higher priorities than closely matching the solar spectrum, and for experiments to assess light source effects without changing reactors. The blacklight system was designed, its components were ordered and received, and all the construction that can be carried out prior to installation in the enclosure was completed. The installation of the blacklight system will be carried out when

we complete the series of experiments listed on Table 2, at which time we will repair the mixing system and make other minor upgrades. When the blacklights are not in use they will be covered with reflective aluminum so their presence will not perturb the light from the arc system.

- Discussions were held with Dr. David Cocker of CE-CERT concerning conducting particle size and number distribution measurements during the course of various types of experiments in this chamber. Preliminary measurements were made during a few of the most recent experiments. This is discussed further below. The necessary equipment was acquired for Dr. Cocker for the EPA project, but until now they have not been used with this chamber.
- Discussions were held with Dr. William Brune of Penn State concerning use of his equipment to make radical measurements in a proposed program for the EPA. He visited the laboratory and we concluded there should be no significant problems interfacing his equipment, and we are all looking forward to an exciting and productive project. If funds can be made available in time, the experiments could be carried out as early as summer of 2003.

Preliminary Characterization Results

Qualitative discussions of the results of the preliminary analysis of the characterization experiments are given in Table 2. The light characterization data are being collected and analyzed in conjunction with ongoing experiments and will be discussed later. Once the major leaks were fixed and proper positive pressure control procedures were implemented dilution and contamination by enclosure air was reduced to insignificant levels. This was tested by injecting ~100 ppm of CO in the enclosure and monitoring CO increases in the reactor. The CO increase was in good agreement with results of permeation experiments discussed in the first EPA chamber report. Dilution obtained by monitoring CO in the reactor was found to be essentially zero within the precision of the measurements.

The major “wall effects” parameters that are of concern are background offgassing of NO_x, reactive VOC species such as formaldehyde, and the “chamber radical source”. Magnitudes of NO_x and formaldehyde offgassing and radical source input rates that correspond to the results of the characterization experiments in this chamber are summarized on Table 3, where they are compared with comparable results for previous UCR indoor Teflon chambers, the TVA chamber, and the clean “pillowbag” reactors evaluated in the first phase of the EPA chamber study. Magnitudes of chamber wall effects parameters for other chambers used for mechanism evaluation, such as the UNC outdoor chamber, the SAPRC EC, etc, are comparable to or greater than those for the previous UCR Indoor Teflon Chambers. The TVA chamber is of interest because it is the only previous indoor chamber where low NO_x experiments were conducted, and the pillow bag reactor experiments are of interest because they employed similar “clean” conditions but much smaller reactors.

The results of the experiments to date in the new chamber indicate that the NO_x offgassing rates are 1-2 ppb/day, which is an order of magnitude lower than in the previous chambers used for mechanism evaluation, about a factor of 2 lower than in the TVA chamber, and within the range observed with the pillowbag reactors. However, the pillowbag reactor experiments had about 50% higher light intensities, so on a light-intensity-adjusted basis the NO_x input rates in the new chamber were higher than the minimum observed in the pillowbag reactors. On the other hand, the NO_x input rates appear to be much less variable in the larger reactor, which is equally if not more important for chamber effects. The somewhat higher background NO_x levels in the UCR EPA enclosure compared to the flushed “outer bags” used in the pillowbag experiments may be contributing, but probably not to a major extent. We tentatively conclude that ~1 ppb/day is probably the lowest apparent NO_x offgassing rate that can be achieved in this and other Teflon film chambers. Increasing the volume apparently does not reduce the apparent NO_x offgassing below the minimum observed in the smaller reactors under the cleanest conditions.

Table 3. Summary of chamber wall effects parameters and relevant characteristics of representative Teflon chambers

| | Previous UCR Indoor Teflon Chambers | TVA Chamber | Clean “Pillow Bag” Reactors | Current UCR EPA Chamber |
|---|---|---|--|---|
| Volume | 3-6 m ³ | 28 m ³ | ~3 m ³ | 90 m ³ |
| Enclosure | None (2 mil walls) | None (5 mil walls) | Flushed Teflon Bag (NO _x and HCHO ≤ 1 ppb) | Flushed room (NO _x ≤5 ppb, HCHO ≤25 ppb) |
| k ₁ range | 0.15 – 0.24 min ⁻¹ | 0.39 min ⁻¹ | 0.43 min ⁻¹ | 0.26 min ⁻¹ |
| NO _x offgasing | ~20 ppb/day (limited data) | 2-5 ppb/day | 1 ppb/day or higher (variable) | 1-2 ppb/day |
| Radical source (as HONO) | 10-40 ppb/day @ NO ₂ ≤250 ppb | ≤~5 ppb/day (dominated by HCHO source) | 5-7 ppb/day @ ~50 ppb NO ₂ | 1-2 ppb/day |
| Radical Source NO ₂ dependence | May be a small NO ₂ dependence (~55 ppb/day @ ~400 ppb NO ₂) | Could not be determined | NO ₂ dependent above ~50 ppb (~40 ppb/day @ 150 ppb NO ₂) | Not apparent up to ~100 ppb NO ₂ |
| HCHO Offgasing | Insufficient high sensitivity HCHO data to assess | ≥30 ppb/day (not counting secondary source) | (Not yet assessed but probably lower than UCR EPA) | 7-8 ppb/day |
| O ₃ Dark Decay Rate | ~1%/hr | 4%/hr | ~0.9%/hr assumed | 0.8%/hr |

The magnitudes of the chamber radical source that fit the characterization data to date in the new chamber were also 1-2 ppb/day, or essentially the same as the apparent NO_x offgasing rates. The total NO_x levels, which ranged from ≤10 to ~250 ppb in these experiments, had no measurable effect on the magnitude of the chamber radical source. This is in contrast with the results of the radical source measurements in the pillowbag reactors, where the radical source was found to be highly dependent on the estimated average NO₂ concentrations in experiments with NO_x ranging from ~5 to ~150 ppb. However, the current wall model includes an NO₂ – dependent “dark HONO” source based on HONO measurements made in smaller Teflon bag reactors, and if this is removed from the wall model it may well be necessary to include an NO₂ – dependent radical source to simulate these data. This will need to be assessed further once more data become available.

In any case, the magnitudes of the apparent chamber radical source needed to simulate the characterization data in this new chamber are significantly lower than in any other chamber previously used for mechanism evaluation, with the possible (though unlikely) exception of the TVA chamber. (Only an upper limit for the radical source could be determined for the TVA chamber because the relatively large formaldehyde offgasing in that chamber overwhelms determinations of any other radical sources.) The apparent chamber radical source in the new chamber is approximately an order of magnitude lower than the range observed in the other chambers used in previous mechanism evaluations.

Nevertheless, it should be noted that even with its relatively low apparent magnitude, the modeling of at least some of the low NO_x mechanism evaluation experiments carried out during this period or planned for the future are not completely insensitive to the chamber radical source. Therefore, it is important that this be characterized properly, and its consistency over time assessed. This will be evaluated further when more data become available and are more completely analyzed.

Low but measurable amounts of formaldehyde were formed in irradiations in this chamber, even in pure air, CO - NO_x, or other experiments where no formaldehyde or formaldehyde precursors were injected. Some formaldehyde formation is expected from the reactions of methane in the matrix air, since the methane removal catalyst was not operational during the period of these experiments, but formaldehyde formation in this reaction in the CO experiments is predicted to be negligible. The data in essentially all such experiments could be modeled assuming a continuous light-dependent formaldehyde offgasing rate corresponding to 7.5 ppb/day at the light intensity of these experiments. (The concentrations of formaldehyde resulting from this are predicted to be much less because most of the formaldehyde input is predicted to react during the course of the experiments.) This is a relatively low offgasing rate that could not be detected with formaldehyde analyzers used in most previous UCR and other chamber experiments, and is insufficient to account for the apparent chamber radical source observed in the previous UCR Indoor and Outdoor Teflon chambers and in most previous other chambers. It is also significantly less than the relatively high formaldehyde offgasing rate necessary to model the formaldehyde data in the TVA chamber experiments, which dominates the apparent radical source in that chamber. Nevertheless, this apparent formaldehyde offgasing has a non-negligible effect on low VOC experiments and also on results of modeling radical source characterization experiments, and therefore must be included as an important component of the characterization model.

The source of the apparent formaldehyde offgasing in the Teflon reactors is unknown, but it is unlikely to be due to buildup of contaminants from previous exposures or contamination from the enclosure. The apparent formaldehyde offgasing rate is quite consistent in many experiments, with no significant differences between the two reactors. This is despite the fact that the East or "Side B" reactor was constructed several months after the West or "Side A" reactor, which was used in at least 17 experiments before the second reactor was built. In addition the background formaldehyde level in the enclosure was quite variable during this period, and no apparent correlation between this and the apparent formaldehyde offgasing rates in the reactor was observed. Unlike the case for the TVA chamber, the data are best modeled by assuming only direct formaldehyde offgasing, as opposed to some formaldehyde being formed from light-induced reactions of some undetected contaminant. A comprehensive assessment of formaldehyde data in the previous pillowbag reactor experiments has not yet been carried out.

Although the data are not entirely analyzed in this respect, there does not appear to be any indication of a need to assume the presence of other reactive background VOCs causing excess NO to NO₂ conversions other than those caused by the background formaldehyde. Formaldehyde - NO_x experiments are predicted to be highly sensitive to the presence of background reactive VOCs, and the results indicate no significant problem in this regard (see Table 2).

Preliminary Mechanism Evaluation Results

All the experiments through EPA-073 were modeled using the SAPRC-99 mechanism and the characterization model derived to fit the characterization data discussed in the previous section. Qualitative results of the ability of the model to simulate the major results are indicated in the "Results" column on Table 2. Since the characterization and other experiments are still underway, the results must be considered to be preliminary. There are some discrepancies and characterization uncertainties that need further investigation, such as the fact that the propene and some other experiments are better simulated using lower chamber radical source inputs than indicated by the characterization experiments. However,

an interesting preliminary result is that none of the experiments to date indicate significant degradation of model performance in O₃ simulations at low NO_x conditions compared to its well-established performance in simulating O₃ formation in the higher concentration experiments used in its development and previous evaluations. Whether this is generally applicable, applicable to predictions of species other than O₃ and to PM formation still needs to be determined, however.

The simulations of the aromatic experiments were interesting in that the model consistently underpredicted the effects of adding CO on NO oxidation and O₃ formation in the toluene - NO_x and m-xylene - NO_x experiments, at both relatively high and low NO_x levels. In particular, in all these experiments the O₃ formed and NO oxidized was underpredicted in the aromatic, NO_x, CO experiments, while it was slightly overpredicted in the reactors without the added CO. CO addition has been used as a “radical amplifier”, since its reactions with OH cause additional NO to NO₂ conversions without having other effects on the system. It may be that the SAPRC-99 mechanism does not predict sufficient radical formation in aromatic mechanisms, and compensate for this deficiency by overpredicting the NO to NO₂ conversions in aromatic photooxidations. This is consistent with the fact that preliminary “direct reactivity” measurements described in our previous report to the CARB (Carter and Malkina, 2002, see <http://www.cert.ucr.edu/~carter/absts.htm#rmethrpt>) indicated that the SAPRC-99 mechanism is overpredicting NO to NO₂ conversions in aromatic mechanisms. The present aromatic mechanisms were adjusted to fit results of single aromatic - NO_x experiments, and the balance of this compensation of errors will be different in the added CO experiments, where the CO “amplifies” the effects of the new radical formation in the mechanism. We are unaware of the aromatic mechanisms being tested in with this particular type of experiment previously, and obviously this needs to be investigated further with modeling as well as further experimental studies.

Plans for Upcoming Period

During the upcoming quarter, we plan to complete or make significant progress in the following areas:

- We should complete basic characterization and mechanism evaluation experiments listed in Table 2, and complete our initial analysis of the results. The analysis will almost certainly indicate that at least some additional characterization measurements are needed, particularly concerning light intensity and uniformity. Additional characterization experiments will be carried out as needed, but this will not be the dominant focus of the effort during the coming period.
- The remaining facility modifications and deferred maintenance will be carried out early in the upcoming period. The priority will be fixing the mixing and exchange system so that reactant levels can be equalized in the two reactors, as required for the incremental reactivity experiments to be carried out for the CARB coatings project. The backup backlight system will be installed as time permits or when the Vortek is down – whichever happens first. The scheduling has not been finalized, but will be done in such a way to minimize the “down time” when no experiments can be conducted yet make the improvements and repairs that are still needed.
- The standard surrogate to be used for the base case ROG surrogate for the CARB coatings and future VOC reactivity projects will be evaluated. The initial plan is to base it on the 8-component “full surrogate” used in previous reactivity studies, though perhaps replacing n-butane with another compound of similar reactivity for to simplify the GC analysis process. The possibility of adding 1,3,5-trimethylbenzene (135-TMB) to give a more sensitive tracer for radical levels will also be investigated. The latter will require aromatic - NO_x, aromatic - CO - NO_x, and possibly other aromatic mechanism evaluation experiments (see below).

- Although not strictly speaking within the scope of the chamber projects, it will be necessary to improve the performance of the mechanism in predicting the effects of CO or other “radical amplifiers” on aromatic - NO_x systems in order to adequately characterize the base case surrogate for reactivity experiments. The possibility of significant improvements resulting from increasing radical sources and reducing direct reactivity as indicated by the preliminary mechanism evaluation experiments discussed above will be investigated. This may permit the use of 135-TMB in the base ROG surrogate, which as discussed by Carter and Malkina (2002) was prevented by aromatic mechanism problems that may be related to this issue.
- Experiments for the CARB coatings project will begin as soon as the base case experiment is established and shown to be consistent with model predictions. The initial experiments will be with the highest volatility sample selected for study, or “Aromatic 100”, assuming that the samples to be used are provided in due course.
- The PM measurement instruments will be interfaced to the chamber and the evaluation of the facility for PM studies will begin. This will be done in such a way as not to interfere with the planned characterization and O₃ reactivity measurements, but to begin to provide a demonstration of the utility of this facility for well-characterized PM studies. If results look favorable, we may conduct studies on effects of added seed aerosol on gas-phase reactivity experiments and characterization results. Such a study would be essential to experiments to make PM measurements during the course of gas-phase mechanism evaluation and O₃ reactivity experiments.
- In the unlikely event that the proposed EPA study of indicator species and radical measurements in the chamber becomes funded in time, we will begin preparations for the experiments to be carried out in using the Penn State radical measurement instrumentation. As indicated above, Brune’s group would be able to begin the collaboration as early as summer of this year.

Current Funding Situation

We estimate that the annual cost of operating this facility at a minimal level to be approximately \$750K per year, with approximately \$1.5 - \$2 million per year being required to take full advantage of its capabilities. The EPA funding to construct and characterize the chamber was sufficient to cover the work carried out in this report, though it is close to being exhausted. Although we had previously estimated it would be exhausted in January, because of cutbacks in personnel time and the willingness of some to work on a less-than-full-time basis during the last two months, the remaining EPA funding may in fact carry us into March. Therefore, the CARB funds for the coatings project was not needed for the initial characterization work described here, though it, or some other funding source, will be needed to complete the evaluation of the base case experiments that is needed before useful reactivity experiments can begin.

We have approximately \$200K from the California Air Resources Board (CARB) to conduct experiments on architectural coatings VOCs. The CARB staff informed the PI that their approval is needed before we begin using these funds for this purpose because of a concern that the facility may not be sufficiently well characterized for this project. We believe that the facility is sufficiently well characterized in terms of chamber effects to begin working on this project at the present time, and we will be requesting approval for this project to proceed.

We also have approximately \$80K from the CARB to conduct experiments for low NO_x mechanism evaluation. As discussed above, some potentially important low NO_x mechanism evaluation experiments have already been carried out during the period of this report in conjunction with the initial characterization experiments. It may be appropriate to use some of these funds for experiments needed for aromatic mechanism improvement as indicated by the results of the experiments we have already

conducted. Although not strictly speaking a “low NO_x” issue, it is a serious mechanism problem that has implications on model reliability for all current mechanisms. This also needs to be resolved as part of the reactivity assessment studies, as part of the need to reliably model base case experiments in such studies.

The California South Coast Air Quality Management District (SCAQMD) has indicated an interest in providing approximately \$200K in the coming year to supplement and extend the CARB coatings project and/or related ozone reactivity research using the chamber. We hope to get an update on the status of this prior to or during the March 7 teleconference on this project.

After discussions with the EPA, we prepared a collaborative proposal with Dr. Bill Brune of Penn State University to conduct environmental chamber experiments with radical measurements for the purpose of obtaining data needed to evaluate observational based methods (OBMs) for predicting effects of emissions changes on O₃ and other secondary pollutants based on ambient measurements. The amount requested was approximately \$240K, of which approximately \$175K is for chamber experiments at UCR and approximately \$65K is for Penn State to bring their LIF and associated radical measurement instrumentation to our laboratory and operate it during the experiments. The study would involve ~35 experiments with these enhanced measurements and associated characterization and evaluation runs. The most efficient and cost-effective approach is to conduct the experiments for this project during the same period, which could be as early as summer of 2003.

The proposal for this OBM study is now being reviewed by the EPA. One problem is that the EPA contracts administration may require the proposal to go to competitive bids, even though it is obvious to everyone that there is no other facility in the United States where this type of work could be carried out without providing another ~\$3 million to construct a new one elsewhere. The net effect of using competitive bids would be to delay the project and perhaps increase the total cost as a result. In addition to potentially causing a funding shortfall around the end of the year, this could delay making needed improvements to the TDLAS systems that are included in the budget for this project but would also benefit the reactivity and mechanism evaluation programs.

The portions of the Federal FY03 budget that was finally passed in February 2003 included the language “\$675,000 to the University of California, Riverside for continued research of advanced vehicle design, advanced transportation systems, vehicle emissions, and atmospheric pollution at the CE-CERT facility”. Our understanding from Joe Norbeck, the director of CE-CERT, is that approximately \$225K of this would be used for the chamber, but the exact distribution will be determined by the EPA in discussions with CE-CERT. In any case, it is essential that there is no significant delay in making these funds available, especially if funding the OBM proposal is delayed.

Assuming that there are no excessive delays in obtaining the new EPA funding, it is expected that priorities for the new earmark funds would include supporting the infrastructure needed to reduce costs and improve capabilities for using the chamber for current and potential future projects, and support development, characterization, and demonstration of PM research capabilities in the new chamber. Although use of the facility for gas-phase VOC and ozone reactivity research provided the major incentive for the original earmark and is the priority of the current funded projects, in the long run the major unique strength will be capability to provide well-characterized data on PM as well as gas-phase chemistry, and how they interact. This is discussed further in the following section.

Future Research Initiatives

Now that this facility has been developed and we are beginning to demonstrate its capability, we are beginning the process of identifying the potential new sources of funding that will be needed for it to be supported on an ongoing basis. Although gas-phase mechanism evaluation and VOC ozone reactivity

research will continue to be important, this type of research alone may not be sufficient to completely support this facility on an ongoing basis. However, we believe that there are a number of other research areas where this facility has unique capabilities that are not available elsewhere, and thus may potentially provide sources of future support. These are briefly summarized below.

Research on Gas and Aerosol Phase Interactions. Three important areas include: heterogeneous chemistry on aerosol surfaces as a removal mechanism for reactive NO_x ; the effects of aerosols on destroying atmospheric free radicals; and the loss of gas phase VOC to the aerosol phase. Each of these processes have the potential to affect the gas phase chemistry and to alter the expected effectiveness of VOC versus NO_x controls for attaining O_3 standards. This has not been systematically assessed where the gas-phase processes are controlled and well characterized while the relevant aerosol measurements are being made.

Investigation of Temperature Effects on Gas and Aerosol Phase Pollutants. Although ambient temperatures vary widely and models predict significant temperature effects on secondary pollutant formation, model predictions of temperature effects have never been systematically evaluated under simulated ambient conditions. Secondary PM formation in particular is expected to be highly temperature sensitive, but the theories predicting this have not been tested. Aromatics are important O_3 and PM precursors but the parameterized mechanisms used for them in current models have no provision for potentially important temperature effects.

Investigation of Humidity Effects on Gas and Aerosol Phase Pollutants. Most previous experiments at the UCR chambers have been conducted at low relative humidities. It will be important to study the variability of formation of O_3 and nitric acid (HNO_3) as a function of humidity. It will be especially important to characterize the chamber at higher humidity levels as we begin the aerosol experiments will also be carried out at high humidity levels. Humidity is known to have significant effects on PM formation and properties, yet these have only begun to be studied, and not under conditions where the gas-phase processes are also well characterized.

Research on PM Formation Potentials of Organics. Organics are known to be a major source of secondary PM and it is also known that they can differ significantly in their PM formation potentials. As is becoming the case with O_3 reactivity, eventually regulatory policies for VOCs will have to take their "PM Reactivities" into account if they are to be efficient and effective. Although chamber data on PM formation potentials of organics exist, existing data have not been under controlled conditions for gas-phase processes, and data does not exist on how these PM formation potentials are affected by temperature, humidity, and the nature of any other aerosols that may be present. This information is needed before scientifically-based "PM reactivity factors" can be incorporated in regulatory policies.

Development and Evaluation of Models for Secondary PM Formation. Model predictions of secondary PM formation is essential to development of effective PM control strategies, but current models use highly parameterized representations based on limited or poorly characterized data, are appended to gas-phase mechanisms not developed with PM modeling in mind, and have not been tested under well-characterized and controlled simulated atmospheric conditions. The UCR EPA chamber is well suited for providing the types of experiments most needed for PM mechanism evaluation under the variety of relevant simulated atmospheric conditions. CE-CERT has an established track record in mechanism development and gas-phase and PM modeling needed to design the most useful experiments and take maximum advantage of the results. Much of the experiments carried out for the other purposes discussed above could be utilized for this purpose, and these would be carried out with the needs for model evaluation in mind.

Research on Characterization of Secondary Air Toxics. Although some Hazardous Air Pollutants (HAPs) are emitted directly, hazardous compounds can also be formed as oxidation products of less toxic emitted VOCs. Collaborations can be established with other groups at UCR and elsewhere with expertise in analysis of gas- and aerosol-phase HAPs to assess HAP-formation potentials of various sources. Toxicological studies, such as being carried out at the University of North Carolina and previously at APRC at UCR could also be conducted in conjunction with the gas-phase measurements. Although such studies are being carried out at other facilities, experiments in this chamber will be sufficiently well characterized for quantitative model evaluation. This will permit use of these data to develop and evaluate models for quantitative predictions of HAP formation in the atmosphere.

Availability Research. Current VOC reactivity models assume that all emitted VOCs remain in the gas phase sufficiently long to participate in the gas-phase reactions that promote ozone formation. However, this may not always be the case for low volatility of "sticky" VOCs. It may be possible to utilize the large chamber to evaluate this by placing various types of surfaces in the reactor and assessing how their presence affects the reactivities of the compounds of interest. Since CE-CERT does not have extensive experience in this area, such a project would need to be carried out in collaboration with others, perhaps with contractors funded as part of RRWG projects to develop joint atmospheric/availability models for reactivity assessment purposes.