

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

Progress Report to the
California Air Resources Board
Contract No. 00-333

For the Period
November 16, 2002 through March 15, 2003

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March 26, 2003

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Summary of Progress

During the period of this report the initial characterization of the UCR EPA chamber for use in this project was completed, and this will be discussed in more detail in the bulk of this report. Although this characterization effort was funded by the EPA, it is highly relevant to this project because most of the effort for this program will be experiments in that chamber, and it is necessary to demonstrate that the chamber is sufficiently well characterized before this project can proceed. It is concluded that although additional characterization information is desirable and will eventually be obtained under future EPA and other funding, this chamber is now at least as well characterized as any environmental chamber previously used for mechanism evaluation, and therefore suitable for use in this project.

Progress was also made in obtaining more consistent data in the direct reactivity measurement method, and this is briefly discussed in the following section. In addition, the types of petroleum distillates to be studied in the environmental chamber were discussed with the CARB staff and the Reactivity Research Advisory Committee. The initial experiments for this program will focus on VM&P Naphtha and Aromatic 100, and samples will be provided by the ACC around the end of March. This will be discussed further in a later report.

Development and Evaluation of a Direct Reactivity Measurement Method

In the previous report we discussed the adaptation of the total carbon analysis method to the HONO flow direct reactivity measurement system and modifications made to improve the analysis of low volatility compounds. Although the results were encouraging, the flows and some experimental conditions were not well characterized and the results were not well simulated by the model. During this reporting period improvements were made to the system to make the results more reproducible and consistent, and to reduce uncertainties in the flows, which are critical to obtaining well-characterized data. Tests were conducted using propane, n-octane, n-tetradecane, n-dodecane, and the Mineral Spirits Sample "B" used for the Safety-Kleen study.

The results of the experiments are still being analyzed and will be discussed in a subsequent report once the analysis is complete. Although the number of experiments using the current configuration was relatively limited because the need to focus our efforts on the EPA chamber characterization, it is probable that a sufficient number of experiments have been conducted to assess the utility of the method with this configuration. Further experiments with this method will probably not be conducted until this analysis is complete.

Characterization of the UCR EPA Chamber

The statement of work for this project calls for conducting reactivity experiments with selected coatings constituents using the new UCR EPA chamber that is being developed under EPA funding. This is because this chamber represents the current state of the art in environmental chamber technology, and is designed so that experiments can be carried out at lower, and more realistic, pollutant concentrations than was previously possible. However, because the chamber had not been completed or characterized when the program was proposed, the CARB Research Screening Committee and the CARB staff required assurance that the chamber was completed and sufficiently well characterized for the purpose of this project before it could be used for this project.

During the period of this report the UCR EPA chamber construction was essentially completed, and the initial characterization experiments were carried out with the chamber in its final configuration. This effort and the results of the experiments through February 20, 2003 are described in the EPA

Chamber progress reports available at the project web site at <http://www.cert.ucr.edu/~carter/epacham>. Results relevant to the characterization of this chamber for use in this project are described below.

Current Chamber Configuration

With the completion of the second reactor in late 2002, the major construction of the UCR EPA chamber was essentially completed. In its current configuration, the system consists of two ~90,000-liter collapsible reactors constructed of 2 mil FEP Teflon® film inside a 20' x 20' x 40' temperature controlled "clean room" continuously flushed with purified air. The Teflon® film reactors are held in place using a rigid bottom frame and moveable top frames. The floor is covered with Teflon® film and has openings for the mixing system to mix reactants within and between the reactors, as desired. The moveable top frame is controlled by motors that raise the top to allow the reactors to expand when filled or lower the top to allow the volume to contract when the reactors are being emptied. These motors are in turn controlled by pressure sensors that raise or lower the reactors as needed to maintain slight positive pressure. During experiments the top frames are slowly lowered to maintain continuous positive pressure as the reactor volumes decrease due to sampling or leaks. The experiment is terminated once the volume of one of the reactor reaches about 1/3 the maximum value, which turned out to take approximately 9 hours for the older "A" reactor, and longer for the newer "B" reactor. This permits experiments of up to 9 hours to be conducted without either reactor being diluted or exposed to trace contaminants from the enclosure during the experiments. Longer experiments can be conducted if the experiments are run in dynamic mode with continual dilution with purified air, but such experiments are not required for the current project.

The light source consists of a single 200 KW argon arc light affixed to the wall of the enclosure opposite to the reactors. The final spectral filter for the light source was installed and the resulting spectrum met our specifications. The walls, floor and ceiling of the enclosure are covered with reflective aluminum to maximize light intensity and uniformity. The reactors are located in the half of the 20' x 40' room at the opposite end of the wall with the light, with the half of the room closest to the light being empty, since this was calculated to achieve maximum light uniformity. Preliminary light uniformity measurements were carried out in one of the reactors, and although additional measurements will be needed the results indicate that the light uniformity is at least $\pm 20\%$ within the volume of the reactors, and is probably better than that.

Although various problems with the light source were encountered in the initial experiments, they eventually were resolved and the overall performance of the light is now considered to be satisfactory, and the final invoice to the vendor was approved. However, to preserve electrode life and enhance reliability, it was decided to run most of the experiments at somewhat less (~80%) than the vendor-recommended maximum power. The initial actinometry experiment with the reactors and light source in the final configuration indicated an NO₂ photolysis rate within the reactor of 0.26 min⁻¹. Although somewhat less than the maximum sunlight intensity of ~0.5-0.6 mW m⁻², this is comparable or higher than the light intensities used in our previous indoor chambers, and in the appropriate range for VOC reactivity assessment. Since this is not utilizing maximum power, experiments with higher light intensities can be carried out if needed for specialized experiments. All the initial characterization experiments discussed in the following section were conducted using this 80% maximum light intensity, with an NO₂ photolysis rate of 0.26 min⁻¹.

Characterization Measurements and Experiments

The initial characterization experiments that were carried out with the chamber in its current configuration are listed on Table 1, which also includes qualitative discussions of the results of the preliminary analyses of these experiments. Also included on the table are initial low NO_x mechanism evaluation and the first of the initial surrogate evaluation experiments that were carried out in

Table 1. 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 NO _x 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 NO _x offgasing rate, somewhat lower than previous run. Small amount of formaldehyde offgasing
EPA057	1/15/03	CO - NO _x	Determine radical source and formaldehyde offgasing at ~50 ppb initial NO _x . NO injected on one side, NO ₂ the other to vary NO ₂ but not NO _x .	Radical source rate comparable to NO _x offgasing rates indicated by CO - air runs. Small amount of formaldehyde offgasing also consistent with previous runs.
EPA058	1/16/03	CO - NO _x	Similar to previous run but with higher (~90 ppb) initial NO _x .	Radical source and formaldehyde offgasing parameters consistent with previous experiment.
EPA059	1/17/03	O ₃ Dark decay	CO added to test for dilution and O ₃ added to test for O ₃ loss on walls in dark.	No measurable dilution. O ₃ decay rate in range observed for other Teflon film reactors.
EPA060	1/21/03	CO - Air	Determine reproducibility and consistency of NO _x and formaldehyde offgasing	Results very similar to EPA056, indicating consistent offgasing rates.
EPA061	1/22/03	CO - NO _x	Determine radical source with low (~10 ppb) initial NO _x	Radical source in range observed with CO - NO _x runs at higher NO _x .
EPA062	1/24/03	Actinometry	NO ₂ photolysis rate measured inside one of the reactors and some light uniformity measurements made in same reactor.	Results indicated NO ₂ 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 was within ±~15% or better in most measurements, 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 NO _x offgasing rate independent of radical source parameter.	Formaldehyde consumption rate consistent with NO ₂ photolysis rate measured in previous run. Apparent NO _x offgasing rate in range observed in CO - air runs.
EPA064	1/30/03	n-Butane - NO _x	Measure radical source rate using a somewhat different chemical system. 50 ppb NO _x .	Apparent radical source comparable to those indicated by the CO - NO _x runs.

Table 1 (continued)

Run ID	Date	Type	Purpose and Applicable Conditions.	Results
EPA065	2/3/03	Propene - NO _x	Test performance of mechanism and characterization data with simple, reasonably well tested, chemical system, but at variable and low NO _x . ~6 ppb NO _x on one side, ~15 ppb NO _x on the other. Also test mechanism for proposed base ROG surrogate component.	Results of both high and NO _x sides fit reasonably well by mechanism, but only if no radical source is assumed. O ₃ formation somewhat predicted if radical source indicated by CO and n-butane - NO _x runs used.
EPA066	2/4/03	Toluene - NO _x + CO	Obtain a preliminary test of the toluene mechanism under low NO _x conditions. ~5 ppb NO _x both sides. CO added to one side only to determine effect of "radical amplifier" species. Also test mechanism for proposed base ROG surrogate component.	O ₃ slightly overpredicted on side without CO but not by much. O ₃ underpredicted on added CO side. Therefore, model does not correctly predict effect of adding CO on O ₃ in the toluene - NO _x system.
EPA067	2/7/03	m-Xylene - NO _x + 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. O ₃ somewhat overpredicted on side without CO but underpredicted in side with CO.
EPA068	2/10/03	HCHO - CO - NO _x	Evaluate basic mechanism for formaldehyde and CO under conditions that should be relatively insensitive to chamber effects. Initial CO varied. NO _x ~20 ppb.	Model performed very well in simulating both experiments.
EPA069	2/11/03	HCHO - NO _x	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 - NO _x	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 - NO _x (high NO _x)	Evaluate radical source at much higher NO _x levels than previous experiments, to determine NO _x 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 - NO _x	This was intended to be like EPA066 except with larger amounts of NO _x (~15 ppb), but CO was injected on both sides by mistake, so the same toluene - CO - ~15 ppb NO _x mixture was irradiated on both sides.	The results were similar to the lower NO _x toluene - CO - NO _x experiment in that the O ₃ was somewhat higher than predicted by the model.

Table 1 (continued)

Run ID	Date	Type	Purpose and Applicable Conditions.	Results
EPA073	2/21/03	Ethene - NO _x	Test performance of mechanism and characterization data with simple chemical system, but at variable and low NO _x . ~10 ppb NO _x on one side, ~25 ppb NO _x 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.
EPA073	2/21/03	Ethene - NO _x	Test performance of mechanism and characterization data with simple chemical system, but at variable and low NO _x . ~10 ppb NO _x on one side, ~25 ppb NO _x on the other. Also test mechanism for proposed base ROG surrogate component. 6 Hour irradiation.	Model gives good fit to initial NO oxidation rates but slightly underpredicts final O ₃ in both experiments. Model somewhat underpredicts final ethene consumption rate and final formaldehyde yield in higher NO _x experiment, but these data well fit in low NO _x run.
EPA074	2/25/03	Toluene - NO _x + CO	Repeat of previous toluene experiments with higher NO _x levels. Approximately 25 ppb NO _x and 150 ppb toluene injected to both reactors, with ~45 ppm CO added to one reactor.	The results were similar to the previous, lower NO _x toluene runs in that the model gave a slight overprediction of the O ₃ formed in the toluene - NO _x experiment, but significantly underpredicted O ₃ formed in the added CO experiment.
EPA075	2/26/03	Acetaldehyde - NO _x + CO	Basic low NO _x mechanism evaluation for acetaldehyde, a photoreactive species whose results were reasonably well monitored in previous experiments. Approximately 10 ppb NO _x and ~150 ppb acetaldehyde injected into both reactors, with ~100 ppm CO also added to one reactor.	Much more O ₃ formed on side with added CO (~110 vs. 17 ppb). Model gave very good fit to data on side with added CO, but significantly overpredicted rate of NO oxidation and O ₃ formation on the acetaldehyde - NO _x side. Uncertainties in acetaldehyde analysis could account for this discrepancy because simulations of the added CO side were found not to be highly sensitive to changes in acetaldehyde level.
EPA076	2/27/03	CO - Air	Determine if change in NO _x offgasing parameter after conducting a number of experiments with added NO _x . Approximately 75 ppm CO injected into both sides with no NO _x injections.	O ₃ formation in reactor A in good agreement with default model prediction, but somewhat less O ₃ was formed in B, with the data being fit using a ~40% lower NO _x offgasing rate. O ₃ formation in some of the earlier CO - air experiments was consistent with this lower rate, so the difference is within the run-to-run variability.

Table 1 (continued)

Run ID	Date	Type	Purpose and Applicable Conditions.	Results
EPA077	2/28/03	Toluene - NO _x + CO	Repeat of previous higher NO _x toluene experiment EPA074, except with particle measurement instrumentation on line. Irradiation carried out for longer period than EPA074 but data after the first 6 hours not suitable for modeling because of problems with the light source.	The gas-phase results were essentially the same as EPA074, indicating good reproducibility of the data. Measurable particle formation was observed, as expected for an aromatic-containing run, but the data have not been completely analyzed.
EPA078	3/2/03	CO - Air attempt	Repeat of EPA076 to check reproducibility of NO _x offgasing and investigate possible side inequivalency in this regard.	Run aborted because of failure of light system.
	3/3/03 – 3/7/03	Construction	The reactors were opened to fix the mixing and exchange system. Also, the framework for the backup blacklight system was installed in the enclosure.	
EPA079	3/11/03	CO - Air	See EPA078. Also, check for changes in NO _x offgasing after repairs to mixing system. ~75 ppm CO injected into both reactors with no NO _x injection. PM measurements taken to determine chamber background PM levels.	Results entirely consistent with model predictions and (unlike EPA076) good side equivalency observed. No PM formation observed, as expected.
EPA080	3/13/03	Old Standard "Low NO _x Full Surrogate"	Replicate reactants and approximate conditions of the standard "Low NO _x Full Surrogate" experiments used in previous reactivity studies. Injected ~100 ppb NO _x and ~4 ppmC "Full Surrogate" components, to duplicate approximate average for previous low NO _x full surrogate experiments. Irradiation for 6 hours.	Results are similar to results of low NO _x full surrogate experiments carried out previously in the CTC and reasonably consistent with model predictions. Good side equivalency observed. Model gives good fit to rates of NO oxidation and O ₃ formation and satisfactory fits to the maximum O ₃ concentration.

conjunction with these runs. The initial mechanism and surrogate evaluation experiments will not be discussed further here except to note the qualitative initial model performance results as indicated on the table.

Characterization of Contamination by Outside Air

Minimizing contamination of the reactor by outside air was an important design goal of the new chamber. The first step in this regard is to place the reactors in a "clean room" enclosure continuously flushed with pure air and maintained at a slight positive pressure with respect to the outside laboratory. This is important because even if the reactors do not leak experiments have shown that there is non-negligible permeation of NO_x, CO and other contaminants through the 2 mil Teflon® film used. The contents of the enclosure is continuously monitored during the course of experiments, and although the enclosure was cleaner than ambient or laboratory air, it did have measurable NO_x and formaldehyde backgrounds. The backgrounds were relatively high initially, but were reduced significantly before the experiments discussed in this report by finding and plugging leaks. Generally NO_x levels in the enclosure before or during irradiations are less than 10 ppb and formaldehyde less than 25 ppb, though NO_x and formaldehyde levels of less than 5 ppb is characteristic of the most recent experiments. Although not as

clean as the outer bag enclosures used in the pillowbag experiments for the EPA project, this is sufficiently low that permeation of contaminants should be negligible.

Introduction of contaminants into the reactor is also minimized by use of pressure control to assure that the reactors are always held at slight positive pressures with respect to the enclosure. Thus leaks are manifested by reduction of the reactor volume rather than dilution of the reactor by enclosure air. 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. Similar results were obtained in experiments where NO was injected in the enclosure and monitored in the reactor. Dilution obtained by monitoring CO in the reactor was found to be essentially zero with in the precision of the measurements.

Wall Effects Characterization

The major “wall effects” parameters that are of concern are background offgasing of NO_x, reactive VOC species such as formaldehyde, and the “chamber radical source”. Magnitudes of NO_x and formaldehyde offgasing and radical source input rates that correspond to the results of the characterization experiments in this chamber are summarized on Table 2, 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 offgasing 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. Although the NO_x input rates are lower in some of the pillowbag experiments, they appear to be much less variable in the larger reactor, which is equally if not more important for chamber effects. We tentatively conclude that ~1 ppb/day is probably the lowest apparent NO_x offgasing rate that can be achieved in this and other Teflon film chambers. Increasing the volume apparently does not reduce the apparent NO_x offgasing below the minimum observed in the smaller reactors under the cleanest conditions. This offgasing rate is lower than achieved in any other chamber used previously for mechanism evaluation, and allows well-characterized experiments at much lower NO_x conditions than was previously possible.

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 be assessed further once more data become available. In any case, the current characterization data are sufficient to characterize the chamber radical source in the new chamber for the purpose of mechanism evaluation and VOC reactivity assessment.

Table 2. 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

In any case, the apparent chamber radical source is as well or better characterized in this chamber than in any previously employed for mechanism evaluation, and its magnitude in most cases is significantly lower than in the other chambers. (The only possible exception in this regard is the TVA chamber, where the formaldehyde offgasing was so high that other chamber radical sources could not be assessed.) This may make uncertainties concerning the chamber radical source somewhat less of a factor in mechanism evaluation than was the case in the past.

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 monitored as the chamber is employed for ongoing experiments, so that its consistency over time can be assessed. As was the case with previous chamber programs, periodic radical source characterization experiments need to be included among the mechanism evaluation and reactivity assessment experiments for any projects in this chamber, and this will be the case for this coatings reactivity assessment project as well..

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. (Formaldehyde offgasing at comparable or higher magnitudes probably also occur in the other chambers, but the formaldehyde monitoring instruments employed were not sufficient to detect this. The TDLAS formaldehyde monitoring instrumentation employed in the new chamber represents a significant advance in this regard.) This apparent formaldehyde offgasing has a non-negligible effect on very low VOC and radical source characterization experiments, so it must be included in the characterization model. However, it has a relatively minor impact on modeling most experiments used for VOC mechanism evaluation or reactivity assessment.

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 1).

Light Characterization

Light characterization data are obtained during the course of most experiments in the new chamber, and also in periodic special actinometry runs. Information about relative changes in light intensity is obtained using a QSL PAR spherical radiometer located in front of the reactors near the center of the enclosure that takes continuous measurements during all irradiation experiments. NO₂ actinometry measurements were also made during many experiments with using the quartz tube method, with the tube located above the PAR radiometer in the center of the enclosure in front of the reactor. However, these data only indicate upper limit absolute light intensities, since the sensors are located in front of the reactors with respect to the light, and they do not take into account any effects of the reactor walls on light intensity. Therefore, the primary measurements of light intensity are obtained in special actinometry experiments where the PAR radiometer and the NO₂ actinometry quartz tube are placed inside the reactors. One such experiment (EPA062, see Table 1) was conducted thus far with the chamber

in the current configuration, and the results indicated the NO₂ photolysis rate of 0.26 min⁻¹ as indicated above. Additional actinometry experiments of this type will be conducted periodically to monitor changes in light intensity within the reactors.

The spectrum of the light is measured during each experiment using a LiCor LI1800 spectroradiometer. The spectrum of this light source was found to be within the specifications called for when the light was ordered, as discussed in the reports to the EPA on this project. The spectrum was not found to change significantly with time (at least during the period discussed by this report), so an average spectrum is used for modeling. However, this will continue to be monitored during the course of ongoing experiments in case changes occur due to changes in the lamp system or spectral filter.

The formaldehyde-CO-air experiment EPA063 can be considered to be a formaldehyde actinometry measurement because model calculations predict that photolysis should be the only significant reaction consuming formaldehyde in this experiment. The formaldehyde data were well fit by exponential decay curves and the decay rates were the same in both sides within the ±2% precision of the decay rate measurement, with the measured decay rate being 0.00102 min⁻¹. Based on SAPRC-99 absorption cross sections and quantum yields and the averaged measured spectral distribution, this corresponds to an NO₂ photolysis rate of 0.28 min⁻¹, which is in good agreement with the 0.26 min⁻¹ obtained in the NO₂ actinometry experiment. This suggests less than ~10% uncertainty in the light intensity determination, which is considered to be satisfactory for the purpose of mechanism evaluation.

As discussed in the reports to the EPA, based on theoretical considerations we expect light intensity in the reactors to be uniform to within ±10% or better. This was evaluated in an initial series of light uniformity measurement made inside one of the reactors during the course of the actinometry experiment EPA062, by rotating the PAR radiometer in a circle with a 3' radius approximately 6' from the reactor floor. The results indicated the light uniformity within this radius was within ±10%, though the measurement was not as precise as hoped for because of unexpected measurement variability. Additional uniformity measurements will be made during subsequent actinometry experiments. However, at present we consider the uniformity to be at least as good as in the SAPRC XTC or the CE-CERT CTC xenon arc chambers that were used in previous mechanism evaluations, because of the similarities in light placement and enclosure design.

Discussion

Although we believe that the UCR EPA chamber incorporates a number of improvements in the state of the art of environmental chamber technology, it is important to recognize that in many respects it is very similar to the indoor chambers we have previously employed for chemical mechanism evaluation. Although the characterization experiments discussed above showed some differences between the previous chambers in terms of reduced magnitudes of some background or wall effects, overall the types of chamber effects and the factors that must be considered when modeling them are essentially the same. This is expected because the same chamber wall material and type of air purification system is used in this chamber as has been employed previously, and the light source is quite comparable in spectral characteristics to the Xenon arcs used in the SAPRC EC and XTC and the CTC. Therefore, much of the large characterization database and our extensive experience with modeling runs from these previous chambers are also applicable to the characterization and modeling of runs in this chamber. This means that even though the number of characterization experiments in the new chamber is relatively limited compared to the older chambers, this limited number of experiments does not necessarily mean a limited amount of relevant characterization information. The data obtained thus far from this chamber indicate that the types of chamber effects that have caused greatest uncertainties in evaluations using other chambers tend to have lower magnitudes and may be less variable in the new chamber, which should result in relatively less uncertainty in modeling experiments in this chamber. In view of this, we consider this new chamber now to be at least as well characterized as those used previously for mechanism

evaluation, and if anything the characterization uncertainties may be of less importance in mechanism evaluations in this chamber compared to other chambers, assuming that the types of experiments are comparable. Of course, the characterization uncertainty will be greater in experiments employing conditions outside the range of those previously studied, such as very low NO_x conditions or variable temperatures or humidities. But this would be the case regardless of which chamber were employed.

Since most of the experiments for this project will consist of reactivity experiments where the test compound or mixture is added to a base case surrogate- NO_x experiment, the ability of the model to mechanism to simulate the base case result is of particular concern. Although we are just starting the series of surrogate evaluation experiments applicable to this project, the results thus far do not indicate there will be major problems in this chamber if we use the same surrogates as employed in previous studies. In particular, the last run listed on Table 1, run EPA080, is essentially a repeat of the standard “low NO_x full surrogate” employed essentially in previous studies. The results of the experiment is very similar to previous low NO_x full surrogate runs, and the model performed at least as well in simulating that run as it does in simulating comparable runs in the older chambers. Therefore, it is reasonable to expect that we should get comparable model performance in simulating other types of surrogate experiments as we would in other chambers.

Based on these considerations, we conclude that this chamber is now ready for use in this architectural coatings VOC reactivity study, and is the best available chamber for this purpose. No additional characterization experiments need to be conducted to obtain useful data for this project except for those that always have to be carried out as part of ongoing experiments for control and monitoring purposes. Assuming that the temperature, humidity, and other important run conditions are not varied, the ratio of characterization to mechanism or reactivity evaluation experiments should be approximately the same as was the case of our previous mechanism evaluation or reactivity studies.

Surrogate Evaluation

Because of limited time and funding and feedback we have obtained from the CARB staff, we have decided not to develop new base case surrogate mixtures at this time. Instead, at least initially, we will focus on the same 8-component “full surrogate” as employed in our previous reactivity studies. However, to take advantage of the low pollution capabilities of this chamber, we will investigate reducing the total base ROG and NO_x concentrations of the base case experiment. In the previous programs, the standard base case experiments consisted of ~150 or ~350 ppb NO_x and 4 ppmC base ROG surrogate. Based on preliminary input from the CARB staff, it appears that ~50 ppb is considered to be “typical” NO_x, the NO_x levels used in the previous experiments are clearly higher than representative. Therefore, we will investigate cutting down the ROG to ~1 ppmC, and varying the NO_x in the 20 – 50 ppb range to obtain reactivity data at differing NO_x levels. Experiments using surrogate and NO_x levels in this range will be carried out to determine if the results of the new base case experiments are as consistent with model predictions as they are at the higher concentration levels, and to determine which ROG/NO_x ratios are appropriate to use to assess reactivity as a function of NO_x levels. If the base case experiments and reactivity experiments with VOCs with known mechanisms can be as adequately modeled at the lower concentration levels as they are at the higher levels employed in the previous studies, the lower concentration experiments will be used for this project. This is because the lower concentrations provide a better representation of current atmospheric pollution levels, and also because lower concentrations make it more likely that experiments with low volatility compounds can be successfully carried out.

Reactivity experiments with the “mini-surrogate” were also included in previous reactivity assessment studies because experiments with this surrogate were found to have different sensitivities to direct vs. indirect reactivity effects, and thus were useful for more comprehensive mechanism evaluation.

However, if the direct reactivity measurement method turns out to be useful to assess direct reactivity effects, use of these experiments, in conjunction with the more atmospherically realistic full surrogate experiments at different NO_x levels, may be sufficient for this purpose. Therefore, the initial reactivity experiments will focus on use of the full surrogate experiments, and the decision of whether to use a “mini-surrogate” or other experiments to complement these data for the purpose of direct vs. indirect reactivity evaluation will be not be made until we decide whether direct reactivity measurements using the HONO flow system can provide useful data. This is discussed further below.

Future Schedule

During the upcoming period, we expect to complete the surrogate evaluation experiments and determine the base case experiments that will be used for the reactivity experiments with the coatings constituents. These will included dual chamber surrogate - NO_x experiments and incremental reactivity experiments for n-octane and m-xylene at the different concentration ranges. Incremental reactivity experiments provide both a base case experiment for surrogate evaluation as well as reactivity data to test model predictions of reactivity for that base case, while dual surrogate - NO_x experiments give information on side equivalency and reproducibility. The final decision as to the concentration ranges to use for the base case for the coatings reactivity experiments will not be made until we analyze the results of these initial experiments and consult with the CARB staff concerning model performance and the appropriateness of the concentration range employed.

We expect to receive the VM&P Naphtha and Aromatic 100 sometime during the upcoming quarter, along with the analytical data on these samples. We will then test injections of these samples into test chambers and perhaps conduct initial test irradiation experiments to test handling and analysis methods. The reactivity experiments with these samples will begin once the concentration levels for the base case experiments are determined. The information provided with these samples will be analyzed to determine how to appropriate represent these compounds in the current mechanism, and to assess effects of uncertainties resulting from any limitations in the data provided.

We also hope to complete our analysis of the available data concerning the direct reactivity measurement method, and make the final decision as to whether to continue to pursue this method. This decision will be made after discussions with the CARB staff concerning the analysis of the results to date and the implications concerning the budget for this project. This may involve conducting additional experiments to further evaluate the method if this is agreed to be appropriate. If it is decided to proceed with this approach, it will be employed to obtain mechanism evaluation data for representative compounds and samples, including those to be studied for this project.