

**ENVIRONMENTAL CHAMBER STUDIES OF
OZONE IMPACTS OF COATINGS VOCs**

**Research Proposal to the
California Air Resources Board**

by

University of California, Riverside
Center for Environmental Research and Technology
College of Engineering

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ABSTRACT

The College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside (UCR) proposes to carry out environmental chamber studies to reduce uncertainties in ozone impact estimates for volatile organic compounds (VOCs) in coatings, and to develop improved experimental methods to evaluate mechanisms for predicting ozone impacts for VOCs in general. This project has two major objectives. The first is to develop and test modifications to our incremental reactivity environmental chamber experiments that will give results that give better correlations with incremental reactivities in the atmosphere. The second is to reduce uncertainties in reactivity estimates for coatings VOCs of concern for which mechanisms and reactivity estimates are either highly uncertain or do not exist. Existing chamber experiments are not as sensitive to mechanisms for secondary reactions of VOC oxidation products as is calculated to be the case for the atmosphere, and therefore do not provide adequate evaluations of this aspect of their ozone impact mechanisms. Addressing this will require developing experiments where integrated OH radical levels are comparable to those calculated for atmospheric scenarios, and approaches will include increasing overall light intensity or duration of the experiments and/or conducting experiments with added radical initiators. The new procedures will be utilized to test mechanisms for selected important representative coatings VOCs. The specific compounds to be studied will be determined in consultation with the CARB staff and the Technical Advisory Committee of the ongoing "Paints and Architectural Coatings Environmental Study" being carried out by the Environmental Research Institute at UCR.

The amount requested is for this project is \$200,041. The period of performance is March 1, 2008 through February 28, 2010.

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BACKGROUND AND PROBLEM STATEMENT

Coatings use involves emissions of volatile organic compounds (VOCs) into the atmosphere, where they can react and contribute to the formation of ground-level ozone. Since ground-level ozone exceeds air quality standards in many areas of the United States, ozone reduction is a major reason that coatings VOCs are subject to regulatory action. However, the impact of VOC emissions on ozone formation is complex, depending significantly on the environment and the nature of the VOC. This needs to be taken into account when developing cost-effective control strategies for coatings VOCs. Otherwise, costly VOC regulations may have relatively little impact on meeting air quality standards, and opportunities for effective VOC control may be missed.

The only practical way to take all the complex environmental and chemical factors into account when assessing effects of VOC control on ozone is to use air quality models to predict the effects of emissions changes on air quality. Such models require appropriate representation of emissions, ambient conditions, and the physical and chemical transformations that occur in the atmosphere. A critical component of such models with regard to predictions of effects of VOCs on ozone formation is the chemical mechanism, which is the component in the model that represents the chemical transformations by which VOCs cause ozone formation. If significant portions of the chemical mechanism are incorrect or incomplete, then inappropriate VOC control strategies may result.

The atmospheric reactions by which VOCs cause ozone formation are complex and have many uncertainties, and consequently the chemical mechanisms used in airshed models cannot be relied upon to give correct predictions unless they have been adequately tested against experimental data. Data from Environmental Chambers, where the chemical reactions by which VOCs contribute to ozone formation are studied under controlled conditions, currently provide the best way to test chemical mechanisms independently of the many other uncertainties in airshed models regarding emissions, meteorology, and other ambient conditions. Because of this, evaluation against environmental chamber data has been extensively relied upon in the development of current chemical mechanisms (Jeffries et al, 1992; Dodge, 2000)

The SAPRC-99 chemical mechanism (Carter, 2000) has been the most widely used mechanism in the United States for calculating relative impacts (reactivities) of VOCs on ozone formation, and is the basis of the MIR ozone reactivity scale (Carter, 1994) used in California regulations for alternative vehicle fuels (CARB, 1993) and aerosol coatings (CARB, 2000). This scale is also being considered as a basis for reactivity-based regulations for architectural coatings VOCs (CARB, 2007). This mechanism, and its corresponding reactivity scales, has recently been updated to the SAPRC-07 mechanism (Carter, 2007a). The SAPRC-07 MIR scale is expected to be used in the next update of California's reactivity-based regulations, and the implementation of the SAPRC-07 mechanism in airshed models is expected in the near future.

The validity of the MIR values for the various types of coatings VOCs depends on the validity of the mechanisms for compounds involved. As indicated above, these mechanisms are highly complex and need to be evaluated against environmental chamber data. For most of the major types of coatings VOCs the SAPRC-99 and SAPRC-07 mechanisms have been shown to simulate the available environmental chamber data reasonably well, giving us some confidence in the validity of their current MIR values. These include various alkane and aromatic mixtures as occur in petroleum distillates, and various types of oxygenated compounds with glycol, ether, and ester groups for which major representative compounds have been estimated, or experimentally evaluated estimation methods have been derived (e.g., see Carter, 2000, Carter and Malkina, 2005, Carter, 2007a, and references therein). However, coatings also include compounds for which environmental chamber data are not available, and for which data for chemically

similar compounds are not sufficient to develop mechanisms. In these cases, MIR values are either highly uncertain or not available. Although many of these compounds are only minor constituents of most coatings, in some cases they are present in sufficient quantities that using high "upper limit" MIR values (e.g., see Appendix D of Carter, 2000) significantly affect the reactivity estimates of the materials. Recent studies have been carried out to reduce MIR estimates for amines and other compounds (Carter, 2007b), but uncertainties remain in the mechanisms for these compounds, and other compounds remain for which data are needed to reduce uncertainties in reactivity estimates.

However, uncertainties exist in reactivity estimates even for compounds that have been extensively studied. Although the SAPRC-99 and SAPRC-07 mechanisms for the major coatings constituents were extensively evaluated against available environmental chamber data, limitations in the data have resulted in limitations in the extent to which the mechanisms have been evaluated, and therefore in the reliability of their reactivity values. Until recently, most of the chamber experiments used for mechanism evaluation have been carried out under relatively high reaction concentrations, making extrapolations to lower concentrations that are more representative of ambient conditions uncertain. Because of this, the "next generation" UCR EPA environmental chamber was constructed to permit mechanism evaluation experiments to be carried out at under more controlled conditions and at lower concentrations than previously possible (Carter et al, 2002, 2005a,b). This chamber has subsequently been used for evaluating mechanisms at lower NO_x concentrations than employed previously, for determining effects of changing total VOC and NO_x levels on ozone formation (Carter, 2004; Carter et al, 2005a,b) and for evaluating atmospheric ozone impacts of selected architectural coatings (Carter and Malkina 2005; Carter et al, 2005c) and pesticide VOCs (Carter and Malkina, 2007; Carter, 2007c).

The results of experiments in the new chamber indicated that although the SAPRC-99 and SAPRC-07 mechanisms generally performed satisfactorily in simulating O₃ under low NO_x conditions, and in simulating the ozone impacts of most of the coatings VOCs that were studied, some potentially significant problems remain. With regard to the mechanisms in general, they were found to consistently underpredict O₃ formation under conditions of relatively low VOC/NO_x ratios that are characteristic of conditions used to derive the MIR scale, and new data, as well as this underprediction bias, indicate significant problems with current mechanisms for aromatic hydrocarbons. Although aromatic hydrocarbons are not important constituents in most coatings solvents (except as a minor component of some solvent-borne coatings), they are important constituents affecting atmospheric ozone formation, and mechanism errors for these highly reactive compounds could result in inappropriate control strategies being predicted for all VOCs, because they affect the chemical environment where the VOCs react. Although the aromatics mechanisms incorporated in SAPRC-07 represent an improvement over those in SAPRC-99 in many respects, most of these performance problems in simulating the available environmental chamber data still remain (Carter, 2007a).

With regard to most of the major coatings VOCs that were studied, the recent experiments indicated that in general the mechanism performed reasonably well in simulating their incremental reactivities¹ observed in these experiments, once provision was made for the tendency of the general mechanism to underpredict O₃ in the experiments representing MIR conditions (Carter and Malkina 2005; Carter et al, 2005c; Carter, 2007a). However, a concern exists concerning how well the experiments represent ambient conditions, and therefore how useful they are in evaluating the mechanism under those conditions. In particular, many important types of coatings VOCs are observed to have very low or even negative effects on ozone formation in environmental chamber experiments but are predicted, using the same mechanism that accurately simulates these chamber data, to have a positive effect on ozone formation in the atmosphere. This is shown on Figure 1, where model simulations of the effects on ozone

¹ The Incremental Reactivity of a compound is the change in ozone formed when a small amount is added to the chamber or atmospheric simulation, divided by the amount added

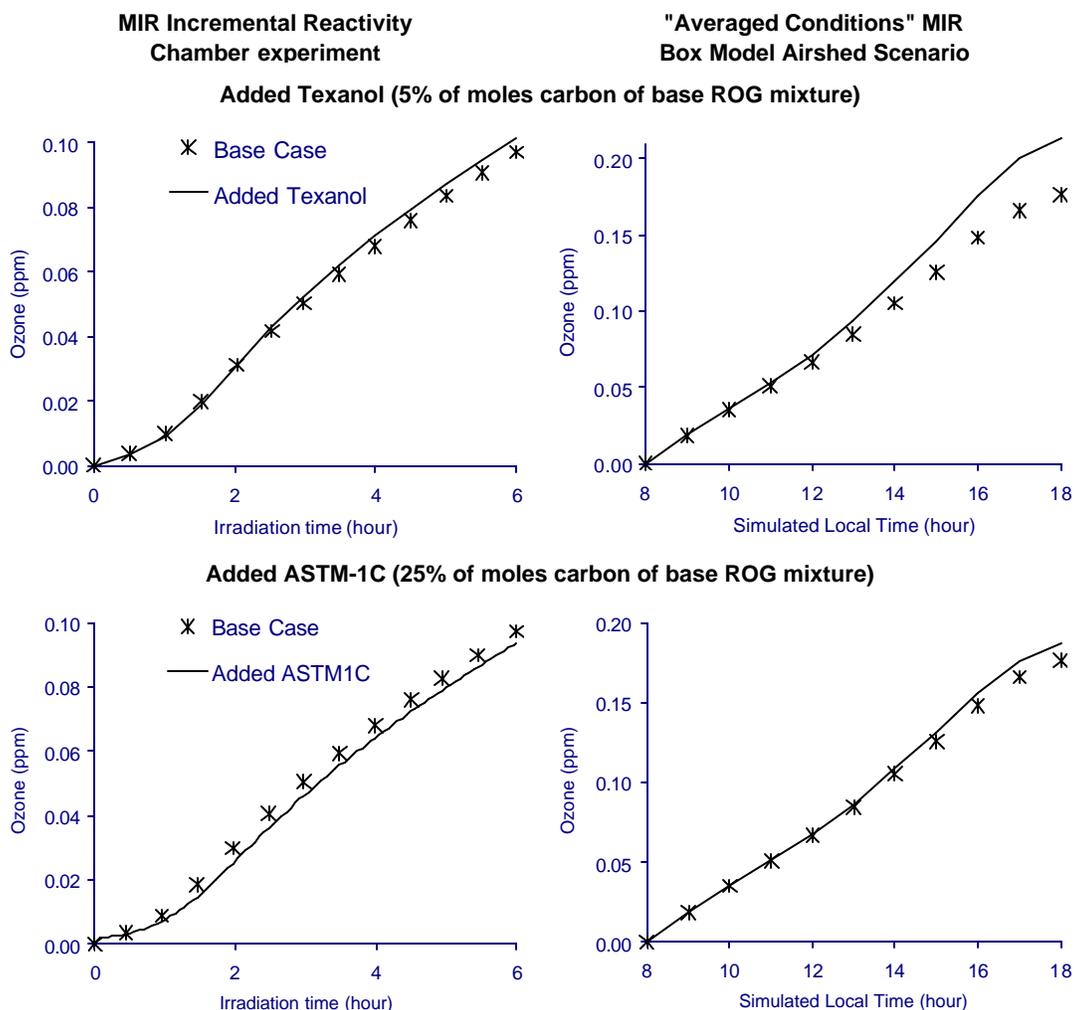


Figure 1. Comparisons of environmental chamber and atmospheric incremental reactivity simulations for equal relative additions of Texanol® or ASTM-1C solvent. (Based on calculations from Carter and Malkina, 2005, but updated for SAPRC-07 mechanism).

formation when adding Texanol®² or an ASTM-1C hydrocarbon solvent to simulations of an environmental chamber experiment are compared with the effects of adding the same relative amount in an airshed simulation representing conditions used to derive the MIR scale (Carter, 1994). (Texanol® is an important VOC constituent of water-based coatings, and the ASTM-1C solvent is representative of those used in solvent-based coatings.) It can be seen that the mechanism predicts Texanol® has very small effect on O₃ formation in the chamber experiment but a significantly larger effect on O₃ in the atmospheric simulation, and that the hydrocarbon solvent is predicted to have a negative effect on ozone in the experiment but a positive effect in the atmosphere.

The differences in the chamber and atmospheric results can be attributed to different sensitivities of atmospheric and chamber conditions to various aspects of the mechanisms of these compounds.

² Texanol is a registered trademark of Eastman Chemical Company. It is a mixture of the two isobutyrate monoesters of 2,2,4-trimethyl-1,3-pentanediol.

Compounds such as Texanol® and the constituents of hydrocarbon solvents used with coatings tend to have negative impacts on ozone formation because they inhibit radical levels (and thus reduce O₃ formation from all VOCs present) while they have positive impacts on ozone because of the NO to NO₂ conversions in the radicals formed in their direct reactions. These tend to have opposite effects, with the net reactivity tending to be driven by the balance between them. Carter and Malkina (2005) attributed results such as shown on Figure 1 to the negative radical inhibition effect being relatively more important in the chamber than the atmosphere, compared to the positive effect of the direct NO to NO₂ conversions.

However, a more detailed analysis of the factors affecting reactivity indicate that the relative importances of radical inhibition and direct ozone formation effects is not the only, or even the most important, factor causing differences between the environmental chamber and atmospheric simulations. For compounds that react in the atmosphere primarily with OH radicals, which is the case for compounds such as Texanol® and the constituents of hydrocarbon solvents, an assessment of these factors can be made by treating them as mixtures of "pure mechanism species" that separately represent different aspects of their mechanism³. For most of the coatings VOCs, the major relevant mechanism aspects can be classified as NO to NO₂ conversions⁴ resulting from the reactions of radicals formed in the reactions of the compounds themselves, radical inhibition and NO_x removal resulting from organic nitrate formation in the peroxy + NO reactions, and the effects of the reactions of the organic oxidation products that are formed.

The relative importances of these major mechanistic processes in affecting incremental reactivities in simulations of various atmospheric and environmental chamber conditions are shown on Table 1⁵. The example is shown for n-undecane, which is representative of the major constituents of hydrocarbon solvents used in coatings applications, but the results for Texanol® and most higher molecular weight glycol ether solvents used in water-based coatings are qualitatively similar. The reactivities for radical inhibition and product contributions are shown relative to those for the NO to NO₂ conversions in the primary reaction because the latter are generally important (and positive) under all conditions as long as NO_x is present, and tend to vary least with conditions (other than generally declining as NO_x decreases below those for MIR conditions). The relative importances of radical inhibition (or initiation) and product reactivity effects tend to be most variable with conditions, and Table 1 indicates how these differ with various types of conditions.

It is immediately apparent from Table 1 that the major difference between the atmospheric simulations and the simulations of the experiments used in the coatings study of Carter and Malkina (2005) concerns the relative importances of the reactions of the organic products in contributing to overall ozone impacts. In terms of overall magnitude, the model predicts that the contributions of the reactions of the n-undecane products are comparable to the radical inhibition effects in the atmospheric simulations, but are relatively unimportant in the simulations of the chamber experiments. Since in the case of alkanes (and also compounds such as Texanol®) the reactions of the products tend to have a positive contribution to reactivity, this would explain why these compounds are calculated to have positive effects of ozone in

³ See Carter and Atkinson, 1987, for a discussion of pure mechanism species. Note that for the purpose of this proposal it is sufficient to understand that their calculated relative reactivities provide a means to estimate the relative importances of different aspects of mechanisms in affecting ozone impacts under different conditions.

⁴ NO to NO₂ conversions is the process directly responsible for ozone formation in the atmosphere because ozone in the lower atmosphere is formed primarily from the photolysis of NO₂ and consumed by reaction with NO.

⁵ These calculations were carried out using the SAPRC-99 mechanism, but the results using SAPRC-07 are expected to be similar.

Table 1. Ratios of incremental reactivities of pure mechanism species calculated for atmospheric conditions and various types of environmental chamber experiments.

Chamber Experiment or Atmospheric Scenario	Integrated OH Levels (ppt-min)	Mechanism species incremental reactivity ratios, weighted for the mechanism of n-undecane [a]	
		Organic nitrate formation (radical inhibition) relative to NO to NO ₂ conversions in the primary reaction	Reactions of organic products, relative to NO to NO ₂ conversions in the primary reaction
<u>Atmospheric Simulations</u>			
Box model airshed scenario with averaged conditions of those used to calculate the MIR scale (left hand plots on Figure 1)	127	-0.66	0.84
Box model airshed scenario with averaged conditions of those used to calculate the EBIR (low NO _x) scale	184	-0.90	0.69
<u>Simulated Environmental Chamber Experiments used in Coatings Reactivity Study (Carter and Malkina 2005)</u>			
Model of standard UCR EPA environmental chamber experiment representing MIR conditions (right hand plots on Figure 1)	41	-0.61	0.07
Model of standard UCR EPA environmental chamber experiment representing low NO _x conditions	28	-0.83	0.04
<u>Simulated Hypothetical Environmental Chamber Experiments with Modified Conditions</u>			
Same as standard MIR experiment except for twice the light intensity and reaction time	83	-0.65	0.40
Same as above except UVA lights and 50% RH used to increase OH input from O ₃ photolysis	97	-0.11	0.61
Same as standard MIR experiment except for twice the light intensity and reaction time and also HONO input at a rate of 16 ppb/hour	209	-0.02	0.79

[a] Ratios of pure mechanism species incremental reactivities, weighted by their relative importances in the SAPRC-99 oxidation mechanism for n-undecane. N-undecane is a representative constituent of hydrocarbon solvents used in coatings applications.

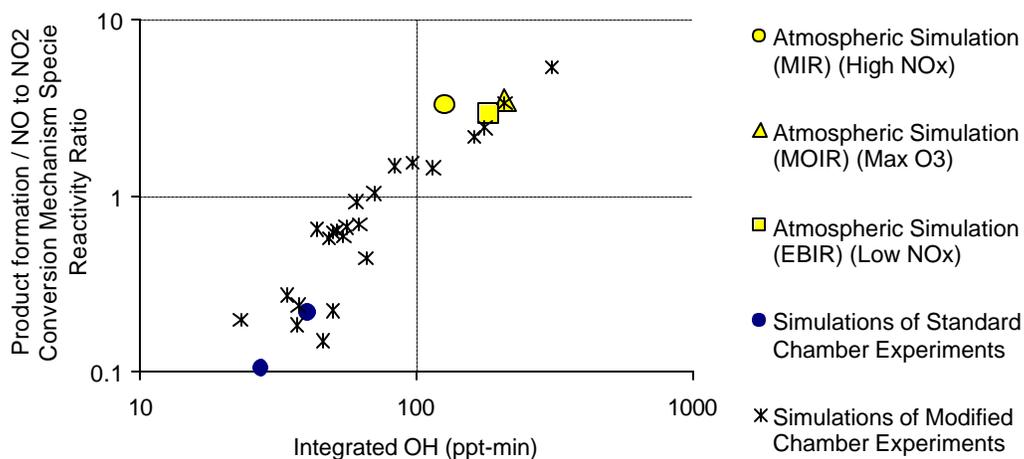


Figure 2. Plots of ratios of incremental reactivities of mechanism species representing secondary product reactions to those representing NO to NO₂ conversions in the primary reactions against integrated OH levels in various atmospheric and environmental chamber simulations. Calculated using the SAPRC-99 mechanism.

atmospheric simulations while they have smaller or negative effects on ozone in the chamber experiments.

The fact that the chamber experiments are predicted to be much less sensitive to the reactions of the organic products than is the case for the atmosphere has potentially significant implications for mechanism evaluation. In particular, it means that chamber experiments may not be good tests of the mechanisms for the reactions of the atmospheric products. Mechanisms that give incorrect predictions of atmospheric reactivities because of inappropriate representations of the reactions of the products may give satisfactory simulations of chamber data because the chamber results are relatively insensitive to product reactions. This is particularly a concern because the SAPRC-07 and SAPRC-99 mechanisms, like essentially all mechanisms used in airshed models in the United States, employ a relatively limited number of model species to represent the reactions of the many types of organic oxidation products that might be formed (Carter, 2000, 2007a). It may be that the actual errors in MIR estimates introduced by uncertainties in the representations of reactive products may not be large for many compounds, but without experimental data sensitive to this aspect of the mechanism this is difficult to assess.

The relatively low sensitivity of the current chamber experiments to product reactivity effects can be attributed to lower calculated overall integrated radical levels in the experiments compared to the atmospheric simulations. The integrated OH levels calculated for the various atmospheric and chamber simulations are shown on Table 1, and Figure 2 shows plots of calculated ratios of product formation to NO to NO₂ conversion reactivities for the atmospheric and chamber simulations, including a number of chamber simulations not shown on Table 1. It can be seen that there is a direct correlation between the integrated OH and the relative importance of product reactions in the reactivity results. The higher the overall radical levels in the experiment, the greater the extent of secondary reactions of the products prior to the end of the experiment, and the greater contribution of their mechanism to the overall reactivity.

Therefore, to improve the ability of the chamber experiments to represent atmospheric conditions, and, perhaps more importantly, to better test aspects of the mechanisms concerning the reactions of the

products, it is necessary to increase integrated OH levels in the experiments. One obvious way to do this is to increase the length of time of the experiment and also to increase the overall light intensity. This brings both the light intensity and reaction time close to (or greater than) that in the atmosphere. Table 1 shows that this gives integrated OH levels and sensitivities to product reactions that are closer to, but still not quite as high as, those calculated to the atmosphere. Therefore, time and light intensity are not the only factors differentiating the chamber experiments and the atmosphere.

An important source of radicals in the atmospheric simulation, which is relatively minor in these chamber experiments, is the photolysis of O_3 to form excited O^1D atoms, which can react with water to form OH. This is less important in the chamber experiment because (1) the O_3 photolysis to form O^1D is caused by the shortest UV wavelengths, which are somewhat less intense in the chamber light source than the atmosphere, and (2) the chamber experiments are unhumidified, so less of the O^1D that is formed reacts with H_2O to form OH. This can be rectified by using lights that are richer in UV, such as UVA lights, and by humidifying the experiments. A simulation where the UV is enriched to higher than atmospheric by using UVA lights and with humidified air (as well as with the light intensity and irradiation time doubled) is also shown on Table 1. This increases the integrated OH and the sensitivity to product reactions still closer to, though still not quite as high as, atmospheric levels. On the other hand, this modification also reduces the sensitivity of the experiment to radical termination effects, making the experiment somewhat less representative of the atmosphere in this respect.

Another way to increase radical levels in the experiments is to introduce radical initiators into the experiments. Of the initiators examined in the test calculations, the best results were obtained by adding HONO, which photolyzes rapidly to form OH and NO, which does not, by itself, promote ozone formation. Table 1 shows the results of a calculation with sufficient HONO added to the experiment to cause the integrated OH levels, and therefore the sensitivity of ozone to the product reactions, to be comparable to those in the atmospheric simulation. However, this simulation has even less sensitivity to radical inhibition effects than the experiment with the enhanced OH input from O_3 photolysis, and also this high level of HONO input does not represent atmospheric conditions.

Therefore, there must be other differences between the conditions of the atmosphere and the chamber experiments that are affecting the results besides just irradiation time, light intensity, UV intensity, humidity, and input of radical initiators. Other aspects were investigated in the process of preparing this proposal, but other changes did not give better results than those discussed above. For example, decreasing total reactant concentrations or increasing dilution rates did not significantly improve the results.

To conclude, although the new UCR EPA chamber represents a significant advance in environmental chamber technology in permitting well-characterized experiments at ambient or near-ambient reactant concentrations, the experiments as currently carried out are still not perfect representatives of ambient conditions. In terms of mechanism evaluation, the most serious problem is the relative insensitivity of the chamber experiments to mechanisms for the reactions of the reactive products, which are much more important in affecting ozone impacts in the atmosphere than in the current experiments. At a minimum, modifications to the experiments need to be investigated to increase sensitivity of the results to secondary product reactions, so this aspect of the mechanism can be more adequately evaluated. This could be done by increasing light intensity and irradiation time and/or by increasing radical input by O_3 photolysis or introduction of HONO. However, if methods could be developed that increase integrated radical levels without also reducing sensitivity to radical effects, then incremental reactivities measured in chamber experiments will give much better correspondences to reactivities in the atmosphere. The best methods to do this need to be investigated.

OBJECTIVES

This project has two major objectives. The first is to reduce uncertainties in reactivity estimates for coatings VOCs of concern to the CARB for which mechanisms and reactivity estimates are either highly uncertain or do not exist. The general approach will be to conduct chamber experiments with the compounds and use the data obtained, and other available information and mechanistic estimates and theoretical considerations, to derive the improved mechanisms and reactivity values for the compounds studied and related compounds. The compounds to be studied will be determined in consultation with the CARB staff and appropriate stakeholder groups.

The second major objective is to develop and test modifications to our incremental reactivity environmental chamber experiments that will give results that give better correlations with incremental reactivities in the atmosphere. Experiments will be developed whose results are as sensitive to reactions of the oxidized products as is predicted for atmospheric conditions. This will require developing experiments where integrated OH radical levels are comparable to those calculated for atmospheric scenarios. If feasible, it would also be desirable that the modifications to the experiments that give greater sensitivity to reactions of the product do so in such a way that the sensitivity of the results to radical initiation and inhibition effects are not significantly reduced. If this is not feasible, then separate experiments will be developed for evaluating the different aspects of the mechanisms. This may actually be preferable for comprehensive mechanism evaluation, since it reduces the chances for compensating errors. The new procedures will be utilized to test mechanisms for several representative coatings VOCs. At a minimum this will include Texanol® and selected alkane compounds that are representative of those in petroleum distillates that are most widely used in coatings. Additional compounds may be studied if possible within the resources available for this project. This will depend on the cost and complexity of the new experiments, which will not be known until the methods for the experiments are developed, and the number of compounds that need to be studied to satisfy the first objective of this project.

Note that because the improved incremental reactivity experiments will enhance our ability to address the first objective of this project, to reduce uncertainties in reactivity estimates of coatings VOCs, work on the second objective, developing improved experimental methods, will be carried out first.

The results of this project will be utilized to reduce uncertainties in reactivity estimates for all coatings VOCs, and may, if applicable, be useful for reducing the uncertainty of the mechanism in general.

APPROACH

Facility Description

The environmental chamber experiments will be carried out using the UCR EPA chamber, which is described in more detail elsewhere (Carter, 2002, 2004; Carter et al, 2005a,b). This chamber was constructed under EPA funding to address the needs for an improved environmental chamber database for mechanism evaluation (Carter et al., 1999). The objectives, design, construction, and initial evaluation of this chamber facility are described in more detail elsewhere (Carter et al, 1999, Carter, 2002, 2004). This chamber was successfully utilized in our “low NO_x” mechanism evaluation study for the CARB (Carter, 2004), for experiments to reduce uncertainties in reactivities of coatings VOCs (Carter and Malkina, 2005; Carter et al, 2005c), pesticides (Carter and Malkina, 2007; Carter, 2007c), and amines (Carter, 2007b), and is being continuously utilized for ongoing PM studies (Carter et al, 2005c; Song et al, 2005, 2007a-c). Descriptions of the chamber and procedures generally are given in the references cited above, but are briefly summarized below.

The UCR EPA chamber consists of two ~85,000-liter Teflon® reactors located inside a 16,000 cubic ft temperature-controlled “clean room” that is continuously flushed with purified air. The clean room design is employed in order to minimize background contaminants into the reactor due to permeation or leaks. The primary light source consists of a 200 KW argon arc lamp with specially designed UV filters that give a UV and visible spectrum similar to sunlight. Banks of blacklights are also present to serve as a backup light source for experiments where blacklight irradiation is sufficient, but these will probably not be used for the experiments discussed in this proposal that are designed to simulate ambient conditions. The interior of the enclosure is covered with reflective aluminum panels in order to maximize the available light intensity and to attain sufficient light uniformity, which is estimated to be ±10% or better in the portion of the enclosure where the reactors are located (Carter, 2002). The reactors are attached to a semi-flexible moveable framework that allows the reactors to be emptied between experiments and reduces the volume under positive pressure control to prevent dilution due to sampling or leaks during experiments. A high-volume mixing system with Teflon® pipes and Teflon®-coated flanges is used to mix the reactors and to exchange reactants between the reactors to achieve equal concentrations when desired. A diagram of the enclosure and reactors is shown on Figure 3

An AADCO air purification system that provides dry purified air at flow rates up to 1500 liters min⁻¹ is used to supply the air to flush the enclosure and to flush and fill the reactors between experiments. The air is further purified by passing it through cartridges filled with Purafil® and heated

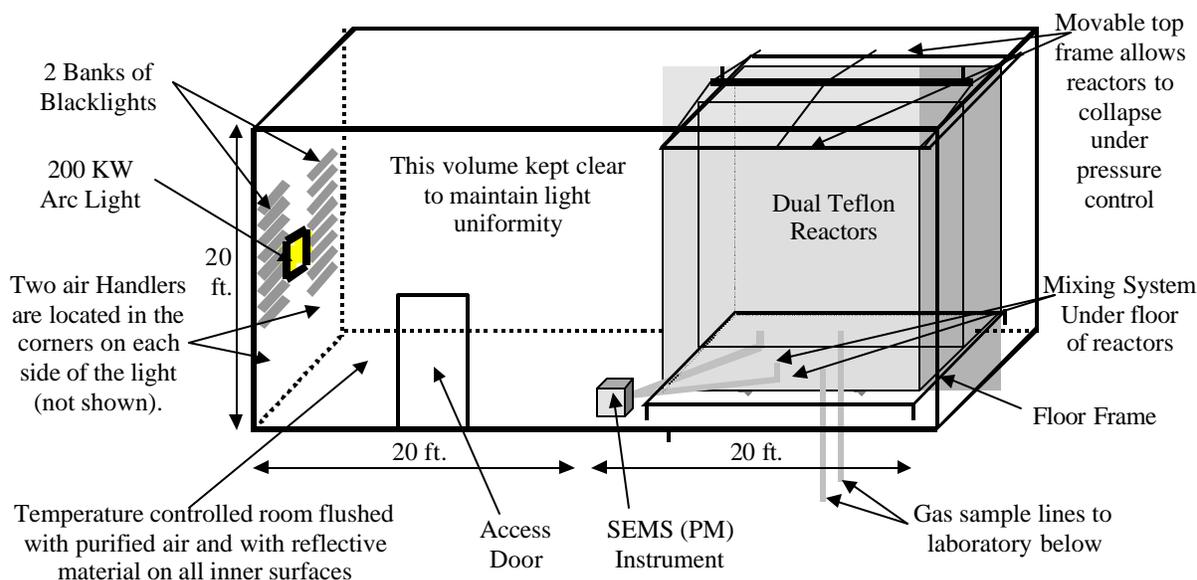


Figure 3. Schematic of the UCR EPA environmental chamber reactors and enclosure.

Carulite 300® which is a Hopcalite®-type catalyst and also through a filter to remove particulate matter. The measured NO_x , CO, and non-methane organic concentrations in the purified air were found to be less than the detection limits of the instrumentation employed.

The chamber enclosure is located on the second floor of a two-floor laboratory building that was designed and constructed specifically to house this facility (Carter, 2002). Most of the analytical instrumentation (except for the PM instrumentation) is located on the ground floor beneath the chamber, with sampling lines leading down as indicated on Figure 3.

The analytical instrumentation available for this project is listed by Carter et al (2005a,b) and in recent reports describing experiments using this chamber, cited above. (A significant amount of additional advanced PM instrumentation has since been acquired as a result of a recent Keck grant, but a discussion of this is beyond the scope of this proposal.) The procedures generally employed in experiments in this chamber are also described in those reports. These procedures will generally be employed in this project, except as discussed below.

As discussed elsewhere (Jeffries et al, 1992; Carter and Lurmann, 1991; Carter et al, 1995a) chamber effects can affect the results of model simulations of chamber data and it is important to have an appropriate chamber characterization model when using chamber data for mechanism evaluation. As discussed by Carter (2004), the UCR EPA chamber to be used in this study has already been characterized for this purpose, and this will be used as a starting point. Appropriate characterization experiments will be conducted periodically during the course of this program to determine if the existing characterization model is still applicable, and the chamber effects model will be modified as needed.

Investigation of Methods for Improving Chamber Experiments

Model simulations and process analyses will be carried out to comprehensively investigate sources of differences in sensitivities to various aspects of VOC's mechanisms in predictions of ozone formation in environmental chamber and ambient simulations. In addition to analyses of "pure mechanism species" reactivities such as discussed above, we will examine differences in integrated reaction rates of various types of reactions, and effects of parameters such as dilution, light intensity, light spectra, and types of reactants present on experimental results. Although simply increasing reaction time and light intensity will improve integrated radical levels and thus representativeness of ambient simulations, there are practical limits to how much these can be increased, and other methods need to be investigated. These and other experimental limitations will be considered when examining alternative methods to make chamber experiments more representative of ambient conditions. The SAPRC-07 mechanism (Carter, 2007a) and models for conditions of the UCR EPA chamber experiments (Carter and Malkina, 2005; Carter et al, 2005a-c), and the models for the airshed scenarios used to calculate the MIR and other reactivity scales (Carter, 1994) will be used as the starting point in the modeling analysis.

Once various experimental approaches are indicated based on the modeling analysis discussed above, appropriate modifications will be made to the UCR EPA chamber facility so that such experiments can be carried out. The UCR EPA chamber was employed in our previous studies of coatings reactivity (Carter and Malkina, 2005; Carter et al, 2005c) and this facility, and methods of procedure for carrying out the chamber experiments and analyzing the data, are described elsewhere (Carter et al, 2005a-c, Carter and Malkina, 2005). Although the specific modifications to be made will be determined as part of this project, they may include, but not necessarily be limited to, increasing the duration of the experiments, increasing the light intensity, enriching the UV in the experiments, humidifying the experiments (if the UV is increased), and introducing radical initiators such as HONO. Considerations involving each of these are discussed briefly below.

Increasing the duration of the experiments is feasible in that most of the instrumentation is automated so measurements of most species (except for VOCs monitored by gas chromatography) can be made even when personnel are not present. The main factor limiting the duration of experiments is reduction of the volume of the reactor due to sampling and leaks while the experiment is underway. To continue the experiments longer than about a day will require diluting the chamber with pure air during the irradiation so that the volume does not become excessively low. However, if the dilution is excessive, the ozone and pollutant levels will decrease, and effects of added VOCs may be more difficult to measure. Also, since losses due to leaks are unavoidable and may not be reproducible, methods for diluting the reactors in a reproducible and well-characterized manner will require some development effort. Therefore, without investigation it is difficult to predict what will be the practical limit for increasing the duration of the experiments without compromising quality of characterization and sensitivity to reactivity effects, but it is expected that at least a 50% to twofold increase in reaction time (i.e., 9-12 hours instead of the current 6-hour irradiation time) should be feasible.

Increasing the light intensity is also feasible up to a point, and depends on the light source(s) employed. The UCR EPA chamber as presently configured has both an argon arc light source and banks of blacklights, though for many studies the argon arc light source has been preferred because it gives a better representation of sunlight in the longer wavelength regime that affects photolyses of NO₃ radicals and aromatic photooxidation products (Carter, 2002; Carter et al, 1995b). The arc light is currently operated at approximately 50% of maximum power in order to reduce maintenance costs and because of limitations of the current cooling capacity of our chamber enclosure, which is presently in need of repair. This power level gives a light intensity that yields an NO₂ photolysis rate of ~0.26 min⁻¹, which is about 40% of the direct overhead sun NO₂ photolysis rate of 0.57 min⁻¹ predicted by the solar model used to calculate the Carter (1994) reactivity scales. If the enclosure cooling system is repaired and we accept

higher operating costs, it may be feasible to operate closer to the maximum power level, though a 50-75% increase may be the practical limit. Installing a second arc light is not considered to be a reasonable option because of cost.

The total light intensity can also be increased by utilizing the blacklights, either in conjunction with the arc lights or by themselves with additional banks installed. This will be at the expense of having a somewhat less representative spectrum in the visible range, but this is not as significant an issue in evaluating mechanisms for coatings VOCs as it is for aromatics or photoreactive compounds. In particular, blacklights give satisfactory spectra in the UV range that is important in affecting most photolysis reactions, including any photoreactive products that may be formed from the oxidations of the alkane, glycol, ether, or ester constituents of coatings. For coatings VOC reactivity research, if one had to choose between a more representative spectrum in the visible region or better sensitivity to product reactivity for mechanism evaluation, the latter choice would be the higher priority. However, the present bank of blacklights in the UCR EPA chamber only yields an NO_2 photolysis rate of 0.16 min^{-1} , which is even lower in intensity than the arc light run at the present power setting, and would yield only a ~60% increase in light intensity if used to supplement the arc light.

Adding additional banks of blacklights is probably the most cost-effective way to increase the light intensity above the present capability of the facility. This would also permit utilization of blacklights with higher UV output, should that option be desired. For that reason, this will be the primary approach that is expected to be employed for this proposed project.

Although the UV output of the present arc or blacklight systems is generally satisfactory for simulating sunlight for most photolysis reactions, both are somewhat lower than solar in the very short UV that is the most important in affecting the photolysis of O_3 to form O^1D . As discussed above this photolysis reaction is calculated to be a more important source of OH radicals in ambient simulations than in chamber experiments. Options for increasing the UV output include changing the spectral filter on the arc light so it cuts off less UV (at the expense of allowing some even shorter UV light in than occurs in ambient conditions) or utilizing UVA or UVB blacklights. The latter would require different types of connections than presently used for the blacklights in our facility, so would require installation of additional banks of lights. But as discussed above installing additional banks of blacklights is probably the most cost-effective way to significantly increase light intensity in our chamber.

If increasing OH radical input from O_3 photolysis to O^1D is desired, it is also necessary to run the experiments using humidified air. Fortunately, a humidification system has already been developed and successfully tested under separate funding, and is available for use for this project at no additional cost.

Model calculations carried out thus far indicate that the most effective way to increase integrated OH radical levels and sensitivities of ozone formation to product reactions is to inject HONO during the chamber experiments. Although HONO occurs in the atmosphere, the levels are generally much less than would be the case if it were injected at the levels required to significantly increase radical levels in our experiments. However, it may be the most practical surrogate compound for atmospheric radical sources that may be difficult to duplicate experimentally. If a better way is not found to increase radical levels in the experiments to satisfy the objectives of this project, we will investigate the use of HONO injections as a means of developing an experiment that is sensitive to secondary product reactions.

HONO is not a stable compound that can be purchased in pure form, and generating it without also forming significant amounts of NO and NO_2 impurities is not straightforward. We had previously developed a very clean HONO source as part of a project to develop a "direct reactivity" measurement using a HONO photolysis flow system (Carter and Malkina, 2002). Unfortunately, that system does not have sufficient capacity to produce the amounts of HONO required to have the desired effect in our large

chamber, and it would have to be scaled up by a factor of ~10. This is probably feasible, but some development work would be required. If appropriate, this would be investigated as part of this project.

Because of cost considerations, it will probably not be feasible to investigate all possible approaches for increasing integrated radical levels in our experiments. Cost effectiveness analyses will be conducted as part of the project, but it is expected that the most cost effective approaches will be to increase the light intensity by increasing the number of blacklights and utilizing the blacklights in conjunction with the arc light, and fabricating a controlled dilution system to permit experiments to be carried out with longer durations with the degree of characterization required for mechanism evaluation. Increasing the UV will also be investigated but it may not be cost effective given the relatively modest increase in integrated radical levels currently calculated to result. The feasibility of using HONO as a radical source will be investigated, but this will not be given the highest priority if it is calculated not to result in experiments that are representative of atmospheric conditions.

The modified experimental system will be tested by conducting experiments with single compounds with known mechanisms (such as propene and formaldehyde), and ambient reactive organic gas (ROG) - NO_x surrogates to be used as base cases in incremental reactivity experiments. The results will then be compared with the predictions of the SAPRC-99 mechanism (or an updated version if it is available) to assure that we are characterizing the conditions of the experiments adequately for mechanism evaluation. If problems are encountered, an investigation will be carried out to determine if it is due to problems with characterizing experimental conditions or problems with the mechanism for the compound. The former will be suspected if the problems are found with modeling the experiments with the simple chemical systems, in which case either the characterization will be improved or the experiment will be modified so it can be easier to characterize. The latter will be suspected if the experiments with the simpler chemical systems can be modeled but not the experiments with the ambient ROG surrogates. In this case, the results will be used as part of our ongoing mechanism development work. For evaluating incremental reactivity experiments, the mechanism for the base case system will then be adjusted so the base case experiments can be adequately simulated.

Once the simple chemical systems and base case experiments are adequately simulated in model calculations, we will conduct incremental reactivity experiments using VOCs whose mechanisms are considered to be reasonably well characterized and for which extensive chamber data are already available. The first compound to be used for testing purposes will be n-butane. Although not a coatings constituent, n-butane has similar reactivity characteristics in terms of predicted impacts of product reactions, and has the advantage that the atmospheric reaction mechanisms of the major reactive products (acetaldehyde and methyl ethyl ketone) are reasonably well characterized and are explicitly represented in the mechanism. In order for the incremental reactivity experiments to be useful for evaluating mechanisms for VOCs with uncertain mechanisms, it must be shown that such experiments with VOCs with known mechanisms can be adequately modeled.

Assuming that satisfactory results with n-butane can be obtained, testing will also be carried out with n-octane, which is also well studied, and is chemically more representative of coatings VOCs. There are uncertainties in its mechanism that are not present in the case for n-butane in that its major reactive products are not explicitly represented in the current mechanism, and Roger Atkinson (private communication, 2006) has data suggesting that they may in fact be more reactive than the lumped species used in current mechanism to represent reactions. This would not be evident when modeling previous chamber data because of the lower sensitivity to product reactions, but may be evident when modeling new experiments designed to be more sensitive to these reactions. This needs to be determined for a well-studied compound such as n-octane before investigating this effect in less well-studied coatings constituents such as Texanol® or C₁₀-C₁₂ alkanes.

Application of Improved Approaches to Representative Coatings VOCs

If the new type of reactivity experiment developed in the previous task is found to be satisfactory, it will be applied to representative VOCs that are important in coatings. The specific compounds to be studied will be determined in conjunction with discussions with the CARB staff and members of the coatings industry, but our suggestions in this regard is that these include Texanol® and n-decane. Additional compounds may be studied if resources permit. The number of compounds that can be studied using the new technique(s) is difficult to predict, since it depends on the number of experiments required to develop and adequately test and characterize the new method, and also the complexity and difficulty of the experiments themselves. If the experiments have longer than a day irradiation time, then the total number of experiments that can be carried out will be decreased accordingly, since the major cost of conducting the experiments (once the methods are developed) are salaries and other items that depend on elapsed time.

Studies of Selected Coatings VOCs with Unknown Mechanisms

As discussed above, there are a number of VOCs present in coatings for which no mechanism and reactivity factors have been derived or whose reactivities are sufficiently uncertain to cause problems in reactivity-based coatings regulations. To address this, part of this project will include experimental and mechanism development studies of at least three types of VOCs that have not been studied previously. The compounds to be studied will be determined by the CARB staff after discussions with us and with appropriate stakeholder groups.

The experimental procedures to be employed will be determined as part of this project. If the improved methods developed as discussed above are available on the time frame needed by the CARB staff to have improved reactivity values for these compounds, and if these are judged to be necessary and appropriate for these compounds, then these methods will be used. However, if the new methods require significantly more time and resources than those employed previously, and if the previous methods are judged to be sufficient for the compounds to be studied, then the methods utilized in previous coatings and pesticide reactivity studies may be employed. These are discussed in previous reports (Carter and Malkina, 2005; Carter et al, 2005c; Carter and Malkina, 2007). Utilization of the previous methods may allow more compounds to be studied within the available resources, with the more resource-intensive newer methods being reserved for the most important compounds with the highest emissions.

As with previous recent studies of coatings and pesticide VOC reactivity (Carter et al, 2005c, Carter and Malkina, 2007), measurements will be made of the impacts of the VOCs on PM formation during the course of the mechanism evaluation experiments. The results will provide at least qualitative indications of the relative impact of the compounds studied on secondary organic aerosol (SOA) formation. Although developing and evaluating predictive SOA models is beyond the scope of this project, the data obtained may be useful for these purposes for other projects.

Chemical Mechanism Development

Previously Unstudied Compounds

For each compound studied, we will survey the available literature concerning the kinetics, mechanisms, and theories for the relevant reactions of the compound or related compounds, and use this as a basis for deriving initial mechanisms or mechanism options. Estimation methods such as those incorporated in the SAPRC-07 mechanism estimation system (Carter, 2007a), or developed based on more recent literature, will be employed where appropriate. If the information about the compound is

extremely limited or the mechanism is expected to be so complex and uncertain that any attempt at explicit mechanisms would be mostly speculation (as has been the case for aromatic hydrocarbons until recently), then alternative parameterized mechanism that incorporate expected overall effects of the reactions will be developed. The preliminary mechanisms for the compounds will be incorporated into the SAPRC-07 mechanism.

The preliminary mechanisms for the compounds will be utilized to estimate the appropriate amount to add in the incremental reactivity experiments, and assess if additional experiments, such as single compound - NO_x irradiations, may be useful. The results of the experiments will then be used to test the mechanisms by conducting model simulations of the experiments to determine if the mechanisms can correctly predict the effects of the compounds on various measures of reactivity. These include O₃ formation, NO oxidation, OH radical levels (as determined by *m*-xylene consumption rates), consumption rate of the test compound (if reliable analytical methods are available), and formation of formaldehyde, PAN, HNO₃ and other monitored products. The mechanisms will be adjusted or modified as needed to give predictions that are consistent with the available data, while still being consistent with available literature data and chemical reasonableness.

If the available data and theories are not sufficient to narrow down the possibilities to a single mechanism, alternative mechanisms will be developed that are consistent with the data. These can then be used to assess the effects of the uncertainty as to which alternative is correct on ozone impact assessments, as discussed below.

The final report for this project will include recommendations as to additional research most needed to reduce uncertainties in mechanisms for the selected compounds of interest. Recommendations will be made on how to represent these compounds in airshed models.

Compounds Studied Using New Experimental Methods

As discussed above, experiments using the new methods to be developed for this project will be carried out on representative coatings VOC compounds that have been studied previously, whose mechanisms are already incorporated in SAPRC-07. The ability of the existing mechanism to simulate the available data will be assessed as part of the analysis of the data obtained. It is possible that the existing mechanism may not adequately simulate the new data that are more sensitive to the mechanisms used for the reactive products if there are deficiencies in the methods used in SAPRC-07 to represent these products. If this is found to be the case, then modified mechanisms with more explicit representations of the products will be employed to determine if this gives better simulations of the data. The SAPRC-99 and SAPRC-07 mechanisms employ “adjusted product mechanism” approaches that give more explicit representations of reactions of products for the purpose of calculating atmospheric reactivities (see Carter, 2000 for a discussion of this method and Carter, 2007a for updates for SAPRC-07). If this gives better simulations of the new data, then the adjusted product mechanisms will be used in the atmospheric reactivity simulations. If not, then sources of the discrepancies will be investigated and adjustments to the product mechanisms will be made as appropriate.

The final report for this project will include recommendations as to additional research most needed to reduce uncertainties in mechanisms for reactive product compounds of significance in affecting reactivities of the important coatings VOCs.

General Mechanism Updates

Since the SAPRC-07 mechanism has been recently developed, it is not expected that the next round of complete base mechanism updates will occur during the period of this project. However, the newly updated mechanism is expected to undergo peer review, implementation, and testing during the period of this project, so modifications and/or updates may occur during this period. In addition, the analysis of the results of the experiments using the new methodologies developed for this project may indicate that modifications are needed in the general methods used to represent reactions of reactive oxidation products in SAPRC-07. If so, appropriate modifications will be made to the general mechanism and the modified and/or updated mechanism will be utilized in the subsequent modeling and mechanism development and evaluations for this project.

Any modifications or updates to the SAPRC-07 mechanism made during the period of this project will be incorporated into the existing documentation for the mechanism (Carter, 2007a), with the updated or enhanced documentation being made available at the SAPRC mechanism web site at <http://www.cert.ucr.edu/~carter/SAPRC>.

Ozone Impact Assessments

The experimentally evaluated or updated or new estimated mechanisms developed for this project will be used to calculate the ozone reactivities of the studied compounds in the MIR, MOIR, EBIR, “base case” and other ozone reactivity scales using the scenarios and reactivity assessment methods we have developed previously (Carter, 1994, 2000, 2007a). If alternative mechanisms or mechanisms with significant uncertainties are developed for particular compounds, then reactivities will be calculated using the alternative mechanism or varied within the uncertainty range to determine the corresponding uncertainty in the MIR or other reactivity scale. Recommendations will be made as to the “best estimate” and upper and lower limit reactivities for the compounds, and the reactivity estimates will be assigned uncertainty classifications such as those given in the SAPRC-07 documentation (Carter, 2007a).

MANAGEMENT, REPORTING AND DELIVERABLES

Management

The Principal Investigator for this project will be Dr. William P. L. Carter, who is the developer of the SAPRC chemical mechanisms and has been the Principal Investigator for a number of projects employing environmental chambers, including the UCR EPA chamber, to obtain data for mechanism development and evaluation and VOC reactivity assessment. Information about Dr. Carter's research, qualifications, and publications is available at <http://www.cert.ucr.edu/~carter>. Mr. Dennis Fitz, the Manager of the Atmospheric Processes Group at CE-CERT will assist Dr. Carter in the administration of this project, and in particular with the infrastructure improvements and maintenance that is involved.

This project will be carried out at the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California at Riverside (UCR). The UCR Office of Research Affairs will be responsible for contractual matters and the CE-CERT business office will be responsible for administration of fiscal affairs.

This project will be carried out in conjunction with the "Paints and Architectural Coatings Environmental Study" (PACES) being carried out by the Environmental Research Institute (ERI) at UCR. Dr. Joseph M. Norbeck of ERI is the overall Principal Investigator of this project and Mr. Charles Bufalino of CE-CERT is the overall technical project manager. The PACES project has been funded primarily by the National Paint and Coatings Association, but co-funding from regulatory agencies, including the CARB through their funding of this proposal, is anticipated. This project has a Technical Advisory Committee, consisting of representatives of the coatings industry, EPA, SCAQMD, and CARB, that meet periodically to discuss progress and research priorities on this project. If this proposal is funded, it is expected that the priorities and progress for research on this proposal will be covered as part of the agenda for these meetings as well.

Schedule

The period of performance of this project is for two years starting March 1, 2008. We expect to be ready to begin the development work for the improved chamber experiments as soon as the funding is available. Relatively early in the project we expect to have meetings with the CARB staff and the PACES advisory committee to discuss priorities of compounds to be studied and progress on our development of improved methods for environmental chamber reactivity assessment. It is expected that the methods development will be completed sometime in the fall of 2008, and most of the chamber experiments will be completed during the first year of the project.

Reporting and Deliverables

Periodic reports will be submitted to the ARB giving brief summaries of the progress and status of the program, problems encountered, and anticipated future schedules. These reports will be approximately quarterly or as required by the ARB. Additional reports concerning specific elements of the project, such as documentation of methods for assessing reactivity and uncertainty, will also be produced where appropriate and if requested by the CARB. The CARB may distribute these reports to other agencies or their industry advisory groups, such as the PACES advisory committee, as they deem appropriate. At the end of the project, a draft final report will be prepared documenting the work carried out and discussing the conclusions and recommendations resulting from the program as a whole. The final report will be independent of the quarterly reports and will not contain citations to them, though it may

make reference to additional reports concerning specific elements of the project. Final versions of the draft annual reports or final report will be submitted within 30 days following receipt of comments from the CARB.

Environmental chamber data obtained for this program will be added to the UCR environmental chamber database for mechanism evaluation, and documented and made available to modelers through the Internet as described by Carter et al. (1995a). Software, spreadsheets and documentation developed for this program will also be made available on the Internet.

The reactivity estimates and uncertainty classifications for the coatings compounds for which reactivity estimates were derived in this work will be added to the reactivity tabulations for all compounds for which reactivities have been estimated, and made available to the ARB and the public on the SAPRC mechanism web site at <http://www.cert.ucr.edu/~carter/SAPRC>

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