EVALUATION OF ATMOSPHERIC IMPACTS OF SELECTED COATINGS VOC EMISSIONS

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

by

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

February 8, 2001

Principal Investigator:
Dr. William P. L. Carter
Center for Environmental Research and Technology
College of Engineering, University of California, Riverside, CA 92521
Phone: (909) 781-5791; FAX (909) 781-5790

Contact for Contractual Matters:
Hannah Petzenbaun, Director
David Serrano, Assistant Director
Office of Research Affairs, University of California, Riverside, CA 92521
Phone: (909) 787-5535; FAX (909) 787-4483

ABSTRACT

The College of Engineering Center for Environmental Research and Technology (CE-CERT) proposes a three-year experimental and methods and model development program aimed at reducing the uncertainties in estimating the impacts of architectural coatings emissions on photochemical ozone formation and other measures of air quality. This will include several components. Methods developed under a previous project for assessing ozone impacts of low volatility compounds will be further developed and evaluated for applicability to low volatility coatings components such as Texanol. The feasibility of conducting environmental chamber experiments for mechanism evaluation for such low volatility components will be investigated, and experiments will be carried out to investigate the ozone and other impacts of those or other selected coatings VOCs. Methods to reduce and quantify uncertainties in ozone and other impact estimates for petroleum distillate mixtures used in coatings will also be investigated. The specific coatings compounds and petroleum distillate mixtures chosen for study will be determined in consultation with the ARB staff and industry advisory groups. The total amount requested for this program is $59,984.

CONTENTS

BACKGROUND

Quantification of VOC Reactivity

Many different types of volatile organic compounds (VOCs) are emitted into the atmosphere, where they can affect photochemical ozone formation and other measures of air quality. Because VOCs can react in the atmospheres at different rates and with different mechanisms, the different types of VOCs can differ significantly in their effects on air quality. Therefore, VOC control strategies that take these "reactivity" differences into account can potentially achieve ozone reductions and other air quality benefits in a more cost-effective manner than strategies that treat all non-exempt VOCs equally. Reactivity-based control strategies have already been implemented in the California Clean Fuel/Low Emissions Vehicle (CF/LEV) regulations (CARB, 1993), are now being implemented in California's aerosol coatings regulations (CARB, 2000), and are being considered for other stationary source applications. If California is successful in implementing reactivity-based regulations as a cost-effective way to reduce ozone, it is reasonable to expect that this approach will be adopted in other jurisdictions as well.

Implementation of reactivity-based controls requires some means to measure and quantify relative ozone impacts of different VOCs. This is not a simple problem, because the ozone impact of a VOC depends on the environment where the VOC is emitted as well as the nature of the VOC (e.g., see Carter and Atkinson, 1989). The effect of a VOC on ozone formation in a particular environment can be measured by its "incremental reactivity", which is defined as the amount of additional ozone formed when a small amount of the VOC is added to the environment, divided by the amount added. Although this can be measured in environmental chamber experiments, such experiment cannot be assumed to be the same as incremental reactivities in the atmosphere (Carter and Atkinson, 1989; Carter et al., 1995a). This is because it is not currently practical to duplicate in an experiment all the environmental factors that affect relative reactivities; and, even if it were, the results would only be applicable to a single type of environment. The only practical means to assess atmospheric reactivity, and how it varies among different environments, is to estimate its atmospheric ozone impacts using airshed models. However, such model calculations are no more reliable than the chemical mechanisms upon which they are based. While the initial atmospheric reaction rates for most VOCs are reasonably well known or at least can be estimated, for most VOCs the subsequent reactions of the radicals formed are complex and have uncertainties that can significantly affect predictions of atmospheric impacts. Laboratory studies can reduce these uncertainties, but for most VOCs they will not provide the needed information in the time frame required for current regulatory applications. For this reason, environmental chamber experiments and other experimental measurements of reactivity are necessary to test and verify the predictive capabilities of the chemical mechanisms used to calculate atmospheric reactivities.

Therefore, experimental measurements of reactivity play an essential role in reactivity quantification. They provide the only means to assess as a whole all the many mechanistic factors that might affect reactivity, including the role of products or processes that cannot be studied directly using currently available techniques. Because of this, the ARB and others have funded programs of environmental chamber studies to provide data needed to reduce uncertainties in reactivity assessments of the major classes of VOCs present in emissions, and the data obtained were used in the development of the most recent mechanism for deriving ozone reactivity scales (see Carter, 2000 and references therein). Although there has been significant progress, the number of compounds that were adequately studied represent only a fraction of those presently in the emissions inventories, and do not include many new products that may be used in the future.

Much of the recent work on developing and evaluating mechanisms for predicting atmospheric VOC reactivity has been carried out in our laboratories. In the past several years, we have applied a standard methodology for this purpose, which was used in essentially all of the studies cited above. This involves measuring the effect of the VOC on O_3 formation, NO oxidation, and OH radical levels when the VOC is added to environmental chamber experiments employing reactive organic gas (base ROG) mixtures representing those present in polluted atmospheres and NO_x. Two different ROG mixtures and ROG/NO_x ratios are used to test mechanism performance under different conditions. Although such data are useful for mechanism evaluation, they have several potentially significant limitations. These include the following.

- Comprehensive environmental chamber studies for mechanism evaluation are expensive, now costing at least $40K per compound. This is assuming that there are particular difficulties involved in handling or analysis. This limits the number of compounds that can be studied.

- The methods that have been used to obtain data to evaluate reactivity mechanisms are not well suited to compounds with very low volatility or very high affinity for surfaces. Nevertheless, many compounds of this type have sufficiently high vapor pressure to participate in the gas-phase photochemical smog reactions, and therefore need to be regulated as VOCs.

- If more than one aspect of the VOCs mechanism is uncertain and has to be adjusted to fit the chamber data, then compensating errors in the mechanism may be possible that will affect the validity of atmospheric reactivity predictions. Although carrying out chamber experiments using different ROG mixtures and ROG/NO_x ratios that have differing sensitivities to different aspects of the VOCs mechanisms, these experiments do not completely isolate these factors.

- The current experiments evaluate the mechanisms at higher concentrations than occur in most current ambient polluted scenarios, particularly those that are closer to attainment of the current air quality standards. If the mechanism has compensating errors or does not correctly represent processes that are more important at lower concentrations, it may not correctly extrapolate from chamber to ambient conditions.

- Model calculations indicate that the type of environmental chamber experiments currently used for mechanism evaluation tend to have much lower sensitivity to atmospheric reactions of the VOC's major oxidation products than is predicted to be the case in the atmosphere. For example, a change in the method used to represent reactive products of higher molecular weight saturated VOCs caused an increase of up to 25% in predicted atmospheric Maximum Incremental Reactivities (MIRs) for such compounds, while having essentially no effect on model simulations of existing chamber experiments with these compounds. This means that the current data are not adequate to evaluate this important aspect of the VOC's mechanism.

Three programs are currently underway to develop improved methods to assess VOC reactivity that have the potential to address at least some of these deficiencies. The objectives and current progress on these programs are summarized in the "Related Programs" section of this proposal, and aspects relevant to this proposal are briefly summarized below.

Under funding from the CARB (Contract 97-314), we are investigating development of new experimental methods to assessing or screening reactivity characteristics of VOCs or complex VOC mixtures that may involve lower cost, be more suitable for low volatility compounds or complex mixtures, and provide data to evaluate components of reactivity with reduced compensating errors. The major focus has been developing a HONO flow system designed to measure "direct" reactivity, i.e., the rate that the VOC causes the NO to NO_2 conversions that are directly responsible for O_3 formation. This is an important aspect of VOC reactivity that is not unambiguously tested in chamber experiments because of sensitivity to other aspects of the mechanism. The flow system also has potential for use with

lower volatility compounds and complex mixtures that are not well suited for study using current environmental chamber methods. Results thus far are promising but additional evaluation is needed before its utility can be ultimately determined.

Under seed funding from the American Chemistry Council (ACC) we are evaluating a method designed to measure total PAN and organic nitrate yields in the atmospheric reactions of VOCs. This is an important aspect affecting reactivities of major classes of emitted compounds such as alkanes, glycols, ethers, esters, etc. If successful, this method would provide a valuable complement to the "direct reactivity" reactivity measurement method being developed under the CARB program, because this provides information on the effects of the VOC on radical levels, which is another important component or reactivity. However, the ACC funding is sufficient only to assess the feasibility of the method, not to apply it to specific compounds of interest.

Under major funding from the United States EPA (Agreement CR 827331), we are developing a "Next Generation" environmental chamber facility suitable for, among other things, evaluating mechanisms under much lower reactant concentrations than has been possible with existing environmental chamber technology. This will involve a very large volume (up to 225 m^3) indoor chamber with a 200 kw argon arc light source inside a "clean room" flushed with purified air, with advanced instrumentation to measure relevant gas-phase species and aerosol parameters needed for mechanism evaluation. The new chamber should be completed in late spring or summer of 2001. In the meantime, research is being carried out using smaller ($\leq$5 m^3) reactors to characterize background and wall effects under "clean" conditions. Current results of the background effects evaluation indicate that mechanism evaluation data can probably be attained with NO_x levels as low as 1 ppb in these small reactors, suggesting that even lower NO_x levels may be attainable when the new facility with the larger reactors is completed.

This new facility will provide a means to evaluate mechanisms under concentrations regimes much more representative of current and near-attainment atmospheric conditions, and also under low NO_x conditions characteristic of downwind or rural conditions. In addition, model calculations indicate that chamber experiments carried out at the lower reactant concentrations attainable with this facility will be much more sensitive to reactions of the organic oxidation products than is the case with the current chambers. Depending on the conditions and length of time of the experiments, the sensitivities of the results to the product mechanisms can be equal or greater than those calculated for the atmosphere. This will allow this aspect of the mechanisms to finally be evaluated. The enhanced analytical capabilities of the facility will also permit evaluations of the effects of the VOCs on other measures of air quality besides O_3, and also allow more detailed testing of the mechanisms.

Reactivity Research Needs for VOCs in Architectural Coatings

Emissions from architectural coatings are an important component of the stationary source VOC inventory. Because of this, the California Air Resources Board (CARB) is considering implementing additional controls for VOC emissions from architectural coatings. The possibility of taking reactivity into account in these new regulations is being considered because this can potentially make the new regulations more cost-effective and flexible. However, the uncertainties in quantification of ozone impacts of coatings VOCs are a concern. Because of the variety of types of coatings in use, a variety of types of VOCs can be emitted and need to have their reactivities quantified.

Reactivity estimates are currently available for a wide variety of VOCs (Carter, 2000), which includes many of those that are emitted from architectural coatings. These are based on the current version of the SAPRC-99 mechanism, which incorporates results of environmental chamber and laboratory studies of a variety of representative compounds (Carter, 2000, and references therein).

However, an examination of the results of a recent survey of coatings VOCs carried out by the CARB indicate that there are at least two important types of coatings VOCs where additional reactivity research is needed. These are briefly discussed below.

The first concerns Texanol (2,2,4-trimethyl-1,3-pentanediol isobutyrate, CAS number 25265-77-4), which is an additive in many coatings formulations. It is actually a mixture of two isomers that rapidly interconvert (Morgott, Eastman Kodak Co, private communication). Although methods exist to estimate the mechanism and reactivities of these glycol esters (Carter, 2000), they are based on data for much lower molecular weight and much lower volatility compounds. No environmental chamber or mechanistic data are available to evaluate the estimated mechanism for this compound, and its low volatility makes it difficult to study using existing chamber and laboratory methods.

The second type of coatings VOC where research is needed concerns various types of petroleum distillate fractions, variously referred to as "Mineral Spirits", "Naphtha", "Stoddart Solvent", "Lactol Spirits," etc. These generally are highly complex mixtures of alkanes and (in some cases) aromatics in various boiling point ranges. Experimental data and reactivity estimates are available concerning the reactivities of several mineral spirits or similar mixtures (Carter et al, 1997, 2000a,b), though their applicability to other types of petroleum distillates is uncertain. The reactivity estimates depend on the types of alkane and aromatics present, which in many cases are uncertain. The CARB staff developed a general method to estimate ozone impacts of petroleum distillates based on boiling point ranges and other known characteristics (CARB, 2000 – see Appendix C), but the performance of this method in deriving actual impacts has not been evaluated. In addition, model simulations of reactivities of high molecular weight alkanes are sensitive to mechanisms used for their photooxidation products, which are not well evaluated using current chamber data and which may not be appropriately represented using current mechanisms. The reactivity estimates for the aromatic components of the higher molecular weight fractions may be even more uncertain, since these are represented in the model by lower molecular weight aromatics that may have significantly different reactivities.

These are not the only types of coatings VOCs for which reactivity estimates are uncertain, though these are currently considered to be the most important in terms of contribution of uncertain VOCs to present emissions estimates. For example, alcohol amines are also present to some extent in coatings emissions, but because of lack of data only highly over-simplified "placeholder" mechanisms are used to represent them in current airshed models. Although their contributions may be small in terms of mass, because of the high estimated reactivities for amines compared to most other coatings VOCs they might make a disproportionate contribution to the uncertainty in reactivity estimates of some coatings formulations. An assessment needs to be made of concerning the various types of coatings VOCs currently or being considered for use, not only in terms of their mass emissions, but also in terms of the uncertainty ranges of their likely ozone impacts.

OBJECTIVES

The objectives of this three-year project is to carry out, at least in part, research most needed to reduce uncertainties in ozone reactivity estimates for selected major types of Coatings VOCs. The specific types of compounds to be studied will be determined after consultation with the CARB staff and an advisory group representing the coatings industry and other interested groups to be established by the CARB. It is expected that the focus of this project will be on developing and applying procedures to reduce the uncertainties in ozone reactivity estimates for Texanol and perhaps other types of low volatility coatings constituents, and for the various types of petroleum distillate materials. This could include, but not necessarily be limited to, the following tasks:

- Further develop and evaluate the direct reactivity method developed under the current ARB and ACC projects so they can be applied to low volatility materials.

- Investigate procedures for studying ozone and other impacts of low volatility materials in the new environmental chamber facility being developed for the EPA.

- Use the procedures developed as indicated above to obtain experimental data to evaluate the ozone and other impacts of Texanol and perhaps other selected low volatility coatings VOCs. Use the results to evaluate and if necessary refine the mechanism used to estimate their atmospheric reactivities.

- Develop improved procedures for estimating ozone impacts of various types of petroleum distillates and quantifying uncertainties of reactivity estimates for these materials in cases where limited data are available.

- Utilize methods developed under the ongoing programs to assess reactivity characteristics relevant to ozone impacts of various types of petroleum distillates and to evaluate and if necessary refine the estimation procedures developed under this project.

Other selected types of coatings VOCs may also be studied as part of this project, as determined based on results of discussion with the CARB and their industry advisory group(s), and considerations of the overall scope of funding for this project.

APPROACH

The specific tasks and priorities for this three-year project will depend significantly on the results of the current ongoing related programs discussed below, and on the results of discussion with the CARB staff and their industry advisory group(s). Given below is a proposed set of projects and tasks that currently appear to be the most useful, based on discussions with the CARB and the current status of our present projects. This can serve as the starting point in our discussions with the CARB and industry groups once this project is underway.

Note that because of the relatively limited level of funding available to this project, some of the tasks listed below would need to be cut back or removed if others are given increasing emphasis or new tasks are added. On the other hand, if other funding is obtained that can be applied to any of these tasks, then the level of effort on the other tasks can be correspondingly increased. In addition, the scope of the experiments carried out using the new chamber facility during the latter period of this project will depend on the availability of ongoing funding for this facility once the current EPA funding runs out.

Reactivity and Uncertainty Survey of Coatings VOCs

The overall objective in research in coatings VOC reactivity is to reduce uncertainties in quantification of ozone and other impacts of VOC emissions from the various coatings emissions. Prioritization of research to reduce these uncertainties therefore requires an ability to estimate, at least approximately, the contribution of reactivity uncertainties for individual types of VOCs to the overall uncertainty in the coatings emissions inventory. This requires knowledge or estimates not only of the relative contributions to mass emissions of the different types of VOCs, but also the magnitudes in the relative reactivities and also the magnitudes in the uncertainties in these reactivity. In particular, a relatively minor component on a mass basis may dominate the overall uncertainty in reactivity estimates if the magnitude of the reactivity and the reactivity uncertainty of this component is high, and the other

components have low reactivity and low reactivity uncertainty. Therefore, a mass emissions analysis alone, or even a reactivity-weighted emissions analysis may not give the full picture in terms of prioritizing research to reduce uncertainties. A quantification of the reactivity uncertainty for the individual compounds is also needed.

As part of this project, we will derive and document estimates and procedures that can be used to conduct an uncertainty prioritization analysis that can be applied to various types of VOC emissions sources, including, but not necessarily limited to, coatings. This will involve assigning, for each type of emitted VOC, a numerical estimate of the reactivity of the VOC and the magnitude of the uncertainty of the reactivity. The reactivity and reactivity uncertainty estimates will be given in terms of several VOC classification systems, including, but not necessarily limited to, that used for speciation in ARB emissions inventory, CAS numbers, and SAPRC-99 detailed model species. Spreadsheets will be set up and documented to allow reactivity and uncertainty analyses for VOC emissions specified in terms of these classification systems.

The reactivities will be quantified using an appropriate method agreed to by the CARB staff, probably the current version of the MIR scale as given by Carter (2000), updated as appropriate based on new information that may become available. Two types of uncertainty will be considered, and procedures will be developed and documented for making estimates of the magnitude of each.

The first major type of reactivity uncertainty is chemical mechanism uncertainty, which reflects the possible errors in the MIR (or other reactivity quantification) due to errors in the chemical mechanism. Quantifying these uncertainties in a systematic manner is a major ongoing area of research, and it is really only feasible for compounds that have been reasonably well studied. Work carried out by Milford and co-workers (e.g., see Wang et al, 2000a,b, and references therein) indicate that for well-studied compounds the uncertainty in absolute MIRs on the order of $\pm 30\%$, and for relative MIRs (i.e, reactivities of the VOC relative to the average of all VOC emissions) the uncertainty is on the order of $\pm 15\%$. Since the purpose of reactivity scales is to determine the relative benefit of controlling one type of VOC compared to another, the relative reactivities are the quantities of interest in this analysis, though it is expected that they will be given in absolute reactivity units because these are what are currently used in reactivity analyses using the MIR scale.

The uncertainty is obviously more difficult to estimate for compounds that are not as well studied, and the procedures for quantifying them must necessarily be based on subjective estimates. However, the uncertainty classification system included with the SAPRC-99 reactivity scales (Carter, 2000) can serve as a guideline in this regard. Table 1 shows an example of how numerical uncertainties may be assigned to relative MIR estimates individual compounds based on the Carter (2000) uncertainty classifications. Although these uncertainty assignments are largely arbitrary and subjective, and may be biased low in some cases, at least they provide a means of obtaining numerical uncertainty estimates that can serve as guidance of where research to reduce uncertainties may be most useful. They can also serve as a means to give industry an indication of the approximate chemical uncertainty of the formulations they are using or considering for use. Although the uncertainty assignments shown on Table 1 can serve as a starting point, they will be refined as appropriate as part of this project based on further evaluation of results of ongoing uncertainty studies, and discussions with the CARB staff and industry groups.

The other major source of uncertainty that must be considered is compositional uncertainty. This is not applicable for VOC classifications that identify individual chemicals (e.g., acetone, toluene, or 2-butoxyethanol), but is applicable to complex mixtures such as petroleum distillates, or ambiguous classifications that may include compounds of differing reactivity (e.g., "glycol ether" or "C_{12} aromatics"). Note that Texanol itself has some compositional uncertainty because it is actually a mixture of two isomers, though in this case the compositional uncertainty is probably small compared to the

Table 1.	Summary of uncertainty classes assigned to SAPRC-99 model species, and subjective estimates of numerical percentage of chemical mechanism uncertainties in relative MIR values associated with each.

Code	Description	MIR Unc'y
1	Considered to be relatively uncertain, or some uncertainties but reactivity is not expected to change significantly.	15%
2	Uncertain mechanism may change somewhat if refined, but change is expected to be less than a factor of two. If the compound is predicted to inhibit O_3, changes are not expected to affect predicted inhibition, but may affect magnitude of inhibition. This code is also used for well-studied compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.	15%
3	Uncertain and may change if compound is studied (or studied further) or estimation methods are updated. Change in MIR could be as much as a factor of two. This code is also used for (1) compounds whose reactivities are expected to be sensitive to the representation of the reactive products, whose accuracy is difficult to test experimentally and (2) compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.	30%
4	Uncertain and is expected to change if compound is studied or estimation methods are updated. It is recommended that uncertainty adjustments be employed in regulatory applications.	60%
5	Non-negligible chance of the estimate being incorrect in significant respects. It is recommended that uncertainty adjustments be employed in regulatory applications.	100%
6	Current mechanism is probably incorrect, but biases in atmospheric reactivity predictions are uncertain. It is recommended that uncertainty adjustments be employed in regulatory applications.	>100%

mechanism uncertainty. Compositional uncertainty can be estimated by considering the reasonable range of possible compositions the mixture may take, and the ranges of reactivity resulting from these different compositions. The problem of estimating compositional uncertainties of reactivities of petroleum distillates is discussed in a separate section of this proposal. Compositional uncertainties for other applicable VOC classes will be derived as needed, based on consultation with CARB and industry working groups who may be familiar with the types of VOCs in questions. The assumptions and ranges of representative compositions used when deriving these uncertainties will be documented.

The deliverable for this task will be a spreadsheet and associated documentation that can be used to conduct reactivity contribution and uncertainty analysis given any mixture of coatings or other VOCs. This can be applied to an entire emissions inventory to prioritize overall research needs or to a single coatings or solvent formulation to estimate the reactivity and uncertainty for that product or formulation. If CE-CERT is able to obtain the necessary updated coatings emissions inventory we use this spreadsheet to analyze research needs that can serve as guidance for this project. If the data cannot be supplied because of confidentiality considerations, then the available documentation and worksheets should be sufficient for others to carry out the analysis, and provide us with any overall results that may be of relevance to the conduct of this project.

The discussion in the subsequent sections is based on the assumption that the results of this analysis will support the current belief by the CARB staff that the most important uncertainties relative to coatings VOCs concern Texanol and petroleum distillate solvents. If the results indicate differently, then substitutions may be made if deemed appropriate after discussions with the CARB staff and the industry advisory group.

Environmental Chamber Studies of Selected Coatings VOCs

Although other reactivity measurement methods such as discussed below can potentially provide valuable information, environmental chamber experiments are needed to fully evaluate all aspects of the mechanism that may affect reactivity under atmospheric conditions. Therefore as part of this project we will evaluate the feasibility of obtaining useful environmental chamber data for Texanol or other selected coating VOC(s) of interest, and if the results are positive then mechanism evaluation environmental chamber experiments will be carried out. If the results indicate that useful data will not be obtained, then one or more replacement compounds will be studied, to be determined after discussions with the CARB and the industry advisory panel. Additional compounds may be studied if available funding permits, depending on the level of effort expended on the other tasks, and the priorities set after discussions with the CARB and the advisory panel.

The types of environmental chamber experiments useful for mechanism evaluation have been discussed previously (e.g., see Carter et al, 2000a-c, Carter, 2000). For compounds such as Texanol and most of the other types of compounds used with coatings, the most useful data is obtained using "incremental reactivity" experiments, where the effects of adding the test compound to "base case" surrogate - NO_x mixtures is determined. Experiments using differing base case reactive organic gas (ROG) /NO_x ratios and different base ROG mixtures are used to test mechanisms under different chemical conditions. However, because the chamber experiments will be carried out in conjunction with separate "direct reactivity" measurements, the availability of such data may reduce variety of different conditions that would need to be represented in the chamber experiments for adequate mechanism evaluation. This will be assessed as part of this project.

Under funding from the U.S. EPA, we are in the process of developing a "Next Generation" environmental chamber facility for mechanism evaluation and VOC reactivity assessment research. The objectives and current status of this project is briefly summarized in the "Related Programs" section of this proposal. As indicated there, we expect the new facility to be available for evaluation in the summer of 2001 and probably available for use for this and other programs in early 2002. However, our existing chambers as used in our previous studies (e.g., see Carter et al, 1995, 2000a-c) are available now and can be used where appropriate for tests and initial evaluation.

A diagram showing the current plans for the environmental chamber enclosure is shown on Figure 1. The reactors will be located in a temperature-controlled housing specifically designed by a contractor specializing in refrigerated rooms and environmental enclosures. The light source will be a 200 kw argon arc light to provide a good simulation of the spectrum and intensity of sunlight under controlled conditions. Calculations carried out by the light source vendor indicated that best uniformity in light intensity is obtained using the configuration shown on Figure 1. The enclosure will be flushed with purified air to minimize contamination by pollutants permeating through the reactor walls, as tests have shown that this permeation can be non-negligible when very low concentration experiments are carried out.

The new environmental chamber will have significant advantages for addressing the objectives of this project. Because of the more sensitive analytical instrumentation and the steps taken to minimize background effects, use of this facility will permit the incremental reactivity experiments to be carried out
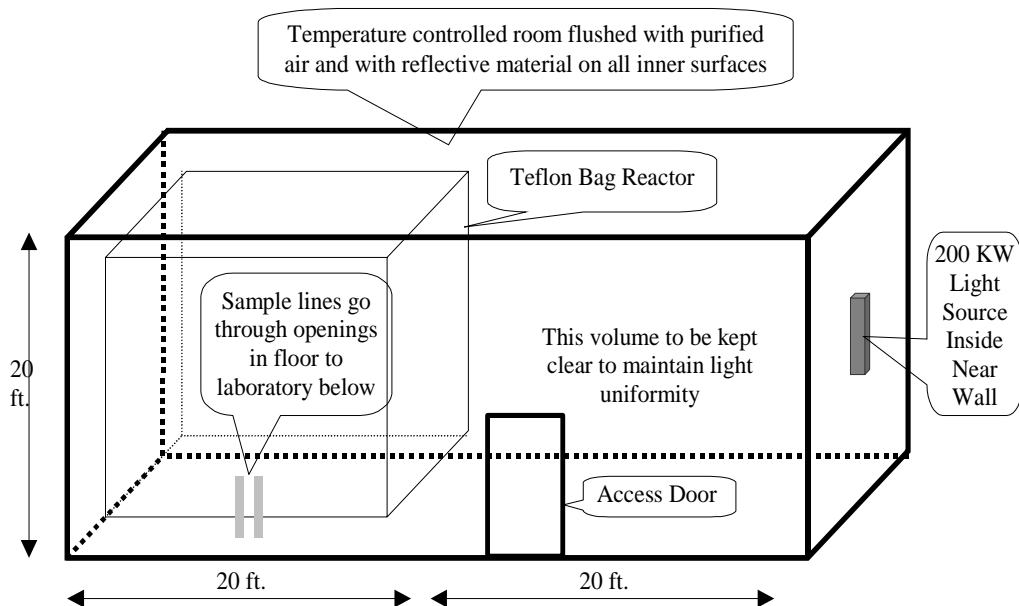
Figure 1.   Schematic of the environmental chamber being developed for the EPA project, with its associated temperature controlled enclosure and light source.

at reactant concentrations that are at least an order of magnitude lower than have been employed previously. Use of lower reactant concentrations has a number of advantages for mechanism evaluation, and therefore will be the approach employed in this project. The lower concentrations are more representative of the concentration range that occurs in most current ambient atmospheres, as well as future case scenarios that must be considered when developing implementation plans. Calculations indicate that at the lower concentrations the results will be more sensitive to reactions of the test VOC's oxidation products, allowing this potentially important aspect of the VOC's mechanism to be more adequately evaluated. In addition, use of lower concentrations should reduce some of the problems of working with low volatility compounds such as Texanol, especially when larger volume chambers are also employed.

Although we anticipate that use of the larger chamber and lower concentrations should increase the likelihood of useful data being obtained with Texanol, tests will be carried out to evaluate how best to carry out the experiments before utilizing the large chamber. Methods to inject and analyze it in the gas phase will be evaluated using smaller reactors constructed of similar material as the large chamber. If no quantitative gas-phase analysis method is found, injection methods and surface absorption behavior will be evaluated using experiments in purified air using the total carbon analyzer developed for the direct reactivity flow system, as discussed above. The results of these tests should serve as a basis to assess the feasibility of conducting chamber experiments with the compound that are sufficiently well characterized for mechanism evaluation, and also to determine the best approach to employ.

Application of Direct Reactivity Measurement Method to Coatings Constituents

Although environmental chamber experiments provide the best method for evaluating the overall performance of the mechanisms for predicting reactivity under atmospheric conditions, as discussed

above they are expensive and also they do not provide an unambiguous evaluation of all important components of the mechanism. As discussed above, the direct reactivity of a VOC, which is the rate at which the VOC reacts and converts NO to NO_2, is an important component of VOC reactivity that is difficult to test unambiguously using environmental chamber experiments because other mechanistic factors also affect the results. Direct reactivity reflects not only how rapidly the VOC reacts in the atmosphere, but also the amount of ozone formation that can be directly attributed to its reactions[1]. If it is uncertain whether the model has a correct representation of this important component of reactivity for a VOC, it cannot be relied upon to give accurate predictions of its effect on ozone formation in the atmosphere.

Measurements of this quantity not only provide useful data for more unambiguous evaluation of this component of the mechanism, if it can be carried out more easily and inexpensively than chamber studies, it can provide a potentially valuable reactivity screening tool. Direct reactivity measurements are particularly useful for VOCs whose atmospheric reaction rate constants are unknown and difficult to measure, or for complex mixtures of VOCs that may have varying rate constants or mechanisms. Thus, they would be particularly useful for the two main types of coatings VOCs of interest in this project. In the case of Texanol, which is expected to react in the atmosphere primarily with OH radicals, its low volatility probably prevents accurate measurements of the rate constant for this reaction using methods currently employed for this purpose. In the case of petroleum distillates, the large number of components means that at best the chemical compositions can only be determined approximately and generally in terms of representative or "generic" species, and in most cases the distribution of components is uncertain. This results in a corresponding uncertainty in the representation of the mechanism and the rate constant in the model.

For that reason, development of a low-cost direct reactivity measurement method has been a priority in ongoing CARB contract 97-314. The direct reactivity measurement method being developed for that project involves use of a test VOC is continuously injected into a HONO-air flow, and the mixture is irradiated in a plug flow system. The amount of NO consumed and O_3 formed compared to when the HONO is flow irradiated in the absence of the test VOC provides a measure of the rate at which the reactions of the VOC converts NO to NO_2, which is the process responsible for ozone formation.

A schematic of the version of the flow reactor system that we propose to use for this project is shown on Figure 2. The HONO generation system uses the method of Febo et al (1995) to produce relatively high purity HONO in air at concentrations of 5 ppm or higher. A syringe pump is used to inject the liquid VOC into the HONO – air gas stream. The amount of VOC injected can be calculated from the flow rates and injection rate of the syringe pump, and can be verified by measurements by GC-FID or other means. The use of the syringe pump to inject the VOC reactant has the advantages that low volatility compounds can be injected at a controlled rate and also that complex mixtures such as petroleum distillates can be injected without fractionation based on volatility. Moderately elevated temperature (e.g., around $60^{o}C$ or so) can be used in the VOC injection system to insure that the injected VOC is vaporized, and tests have shown that the HONO is reasonably stable during the injection process.

Currently the direct reactivity method has been evaluated for the homologous n-alkanes for propane through n-$C_{16.}$ A summary of recent results are shown on Figure 3, which slows a plot of a

---

[1] On the other hand, the indirect reactivity is the change in ozone formation caused by the effect of the VOC's reactions on the reactions of the other VOCs that are present. For example, if the VOC's reactions cause radical levels to increase because of radical initiation processes, it would have a high indirect reactivity because it causes more of the other VOCs present to react and form ozone than would otherwise be the case. Incremental reactivities of VOCs are affected by both these compositions of reactivity, but their relative importance tends to depend significantly on environmental conditions.
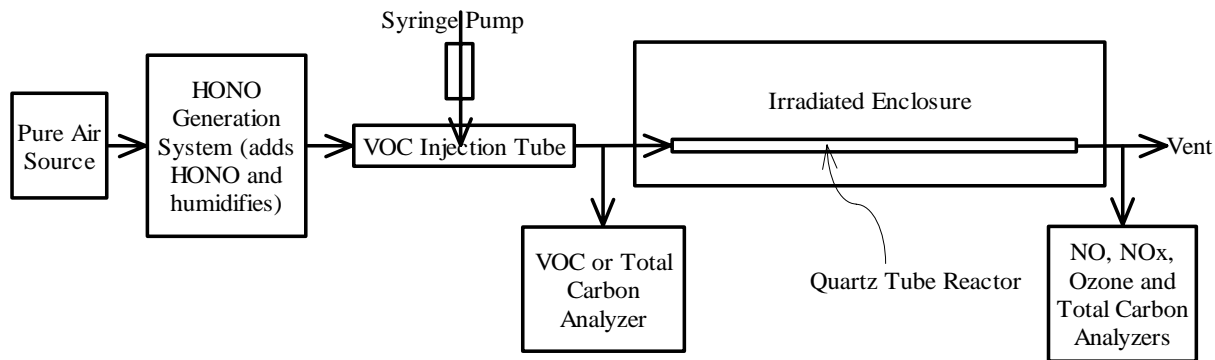
Figure 2.   Schematic of the flow reactor system used to measure direct reactivity.
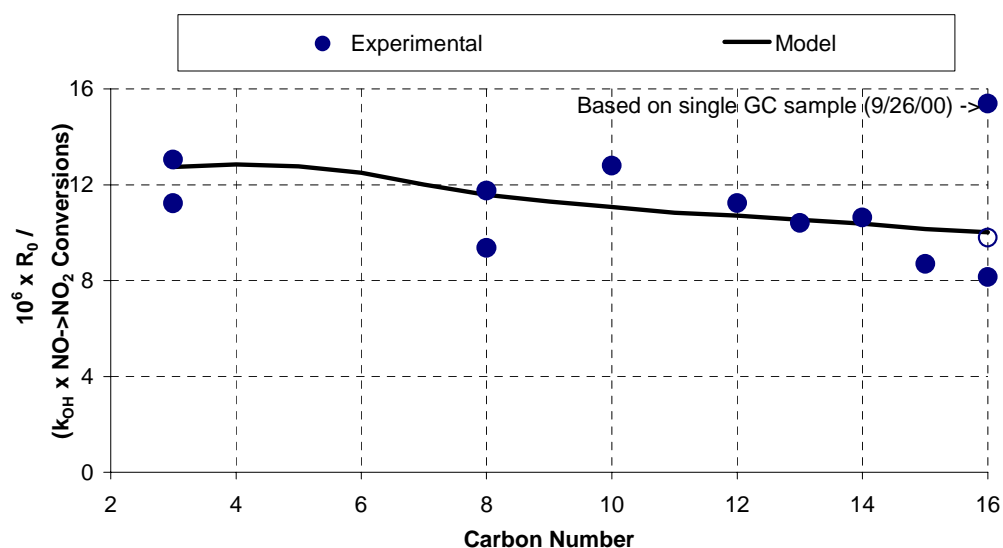
Figure 3.   Plots of the direct reactivity measured at the limit of low added VOC normalized by the OH rate constant times the number of NO to NO_2 conversions in the SAPRC-99 mechanism against carbon number for the homologous $C_3 – C_{16}$ n-alkanes that were studied using a plug flow method. The open circle shows the 9/26/00 n-C_{16} data obtained using the calculated amount of n-C_{16} injected rather than the amount measured by the single GC sample.

normalized direct reactivity measure (see figure caption for details) against carbon number. Results of model calculations are also shown. It can be seen that good agreements between experimental results and model calculations are obtained up to n-C_{15} and perhaps n-C_{16}. Note that n-C_{16} has a similar room temperature vapor pressure as Texanol (around 5-10 ppm), suggesting that it may be feasible to use this method to obtain useful data for this compound. However, the polar groups on Texanol may give it greater affinity to surfaces than is the case for an alkane with the same vapor pressure.

The main limitation to the method as currently applied to low volatility compounds and complex mixtures is measuring the amount of VOC injected to assure that it agrees with the amount calculated from the liquid and gas flows. This is particularly important for low volatility compounds because absorption on surfaces may mean that the gas-phase concentration is less than the concentration calculated from the flows. Unfortunately, low volatility compounds are also the most difficult to analyze reliably. In addition, the chromatographic measurements are also the most expensive and time-consuming aspect of carrying out experiments using the method as currently employed.

The approach we expect to employ to address this limitation is to use a total carbon analysis system to measure the amount of VOC compound or mixture injected into the gas phase flow reactor. However, it is important that the appropriate type of total carbon analysis be employed. Simple FID is not suitable in all cases because the per-carbon response depends on the compound. Methods that rely on GC or backflush approaches to separate methane from the VOCs of interest are not considered suitable for heavy or sticky compounds because of concern of hang-up in the complex valving or GC columns that are needed. To address these problems, the analysis will be conducted by converting all the carbon in the analysis stream to CO_2 using a high-temperature catalytic combustor, and analyzing the CO_2 (either directly using IR methods such as employed for ambient CO analysis, or by conversion to methane using a methanizer, and analyzing the methane by FID). Methane and CO_2 will be kept out of the system by using only purified, methane and CO_2-free air as the diluent in the flow reactor. The combustor converting the gas-phase VOC to CO_2 will be located as close to the flow reactor as possible to minimize losses of the low volatility reactant(s) to the walls, and heated sample lines will be used. Filters will be used so only gas-phase carbon is measured.

Possible losses or absorption of the low volatility reactants to the walls of the flow reactor during the course of the experiment is a concern. The flow reactor used in the current configuration is a quartz tube approximately 1 meter long with approximately 1 cm ID. To determine the extent to which the low volatility materials may be absorbed on the walls of the reactor, the total carbon analysis will be carried out both before the gas-stream enters the photolyzed flow reactor, and after it exits the reaction zone. If the lights are on there may be some loss of gas-phase carbon if the VOC forms condensable oxidation products, but this should be a minor effect since the extent of conversion of the VOC in the reactor as presently designed is relatively small. Loss by gas-phase reaction can also be eliminated by making measurements with the lights off or with the HONO omitted.

If the gas-phase concentration changes significantly due to exposure to VOC to the reactor, then it may be necessary to carry out the reaction at elevated temperature. However, since in general the rate constants and numbers of NO to NO_2 conversions will be temperature-dependent, the measurements at elevated temperatures may not be applicable to atmospheric conditions. In this case, the approach will be to measure the direct reactivity as a function of temperature, and extrapolate back to ambient temperature. Because this approach it will significantly increase the complexity of the experiment and the experimental system, it will not be used unless we conclude that it is the only feasible method to obtain useful reactivity information.

An alternative to the syringe pump injection method that may be applicable to coatings VOCs would be to replace the VOC injection tube and syringe pump with an enclosure with a surface with the material coated on it, from which it can evaporate. This may permit coatings VOC emissions to be assessed in a

manner more similar to their actual use. The possible utility of this approach will be discussed with the CARB staff and the industry working groups during the course of the project. It may also be investigated as an alternative injection method if problems are encountered with the syringe pump method with the coatings VOCs of interest.

This method will be used to measure the direct reactivity of Texanol and other selected VOCs of relevance to this project. The specific compounds or mixtures to be assessed will be determined in consultation with the CARB and the industry working groups.

Development and Evaluation of Procedures to Quantify Reactivities and Uncertainties for Petroleum Distillates

Petroleum distillates (e.g., "mineral spirits", "naphtha", etc.) are complex mixtures of primarily alkanes or in some cases aromatics that are widely used as solvents in coatings and other applications. We have previously shown that reactivity estimates of these materials can be made provided that information is available concerning the carbon number distribution, the distributions of normal, branched, and cyclic alkanes, and the amounts and types of aromatics that may be present (Carter et al, 1997, 2000a,b). Although problems were encountered using earlier versions of the SAPRC mechanism (Carter et al, 1997), the SAPRC-99 mechanism has been shown to give predictions that are reasonably consistent with environmental chamber data for several types of mineral spirits and other materials (Carter et al, 2000a,b). However, this analysis requires extensive data that are not available for many types of petroleum distillate products that are currently in use, and the few materials that have been studied may not be representative of the full distribution of such solvents that are in use.

Because of the need to derive reactivity estimates for such materials in its aerosol coatings regulations (CARB, 2000), the California Air Resources Board developed general procedures for estimating MIRs for hydrocarbon solvents based on their boiling points, aromatic fractions, and (if available) type of alkane primarily present (Kwok et al, 2000). This is an important contribution towards reducing uncertainties in reactivity estimates for these important types of VOCs. Unfortunately, the method is not adequately documented because most of the compositional data used in the analysis was proprietary, and the documentation did not provide information necessary to revise the estimates should the underlying reactivity scale be modified or updated. In addition, information and procedures necessary to estimate compositional uncertainties as a function of the amount of available information was not provided.

For this project we propose to evaluate the procedures derived by the CARB staff based on available information, and extend them so they can be used with other reactivity scales and for making estimates of compositional uncertainty. We will work with the CARB and relevant industry groups to explore the possibility of obtaining the necessary compositional information, and in determining the best method to report the results that adequately document the analysis while addressing proprietary concerns. The major extensions of the CARB work will be that estimates will be given in terms of representative distributions of compounds so that they can be used with any type of reactivity scale, and that compositional uncertainty analyses will be included. The latter will require a systematic examination of distributions of compositions as a function of available information, and the distribution of possible reactivity ranges for the various possible compositions that are consistent with the available information. The more the available information limits the possible types of compositions, the lower the magnitude of the compositional uncertainty.

The results will be incorporated into the spreadsheets and procedures for deriving reactivity and reactivity uncertainty estimates for all types of coatings and other VOCs as discussed above. The information can then be used for determining the extent to compositional uncertainty for petroleum

distillates contribute to the overall uncertainty in the ozone impact estimates for coatings and other types of sources. It will also provide a means to estimate the extent to which the uncertainty will be reduced if improved compositional information can be provided, and the types of information that is the most useful for reducing the overall uncertainty. This can serve as the basis for determining the most cost-effective approach to reducing this overall uncertainty.

The reliability of the hydrocarbon solvent reactivity estimation procedures also need to be evaluated experimentally. The ability to apply the procedures to other reactivity scales besides MIR will provide a means by which this can be done. In particular, the "direct reactivity", as discussed above, is simply another type of reactivity quantification that can be calculated for individual compounds and can be derived for the hydrocarbon solvent mixtures using the same reactivity estimation procedures as applied for MIR. The direct reactivity predictions can then be experimentally tested using the experimental procedures discussed above. The results can then be compared with the predicted direct reactivities to determine if they agree with the estimated value to within the estimated uncertainty level. Conclusions can then be drawn concerning the overall reliability of the method and its applicability to the wide variety of hydrocarbon solvents in use.

This experimental evaluation will be carried out using representative solvents to be determined after consultation with the CARB staff and relevant industry groups. The number of solvents tested will depend on the cost of the direct reactivity testing procedure, which has not yet been determined.

RELATED PROGRAMS

The objectives and current status of ongoing projects at our laboratories that are relevant to this proposal are summarized below. Note that the results of these programs, which are still underway, will in general affect the specific tasks to be carried out for this proposed program.

Development of a Next-Generation Environmental Chamber Facility for Chemical Mechanism and VOC Reactivity Research. United States Environmental Protection Agency Agreement CR 827331

Objectives

The objectives of this four-year, $2.9 million project are to develop the next-generation environmental chamber facility needed for evaluating gas-phase and gas-to-particle atmospheric reaction mechanisms, for determining secondary aerosol yields, and for measuring VOC reaction products and radical and NO_x indicator species under more realistic and varied environmental conditions than previously has been possible. The facility will then be employed to provide data that are most relevant to today's pollution problems and control strategy issues.

The first two years of the project is devoted primarily to research on chamber design, facility development, and chamber characterization and evaluation. The remainder of the program will involve conducting experiments needed for model evaluation and to address issues of relevance to regulatory assessment and control strategy development. These would include, but not necessarily be limited to, the following:

- Determining whether current predictions of effects of VOC and NO_x changes on ozone and secondary aerosol formation are applicable to lower pollutant concentrations.

- Assessing differences among VOCs in terms of effects on ozone, secondary aerosol formation, and other pollutants under low-NO_x conditions. Current ozone reactivity scales (e.g., Carter,

1994) for VOCs were developed for more polluted urban conditions and may not be appropriate for lower NOx environments.

- Providing information needed to evaluate whether control strategies aimed at replacing reactive VOCs with less reactive but more persistent compounds may adversely affect ozone or other pollutants when they are transported downwind.

- Determining major oxidation products formed by organics when they react under low-NO_x conditions. This is important to developing scientifically-based models for low-NO_x reactions of VOCs, as well as to understanding the ultimate environmental fates and impacts of these compounds, which in some cases may affect global climate change.

- Determining the effects of temperature on secondary pollutant formation and VOC reactivity. Current environmental chamber facilities are not adequate to evaluate these effects, but limited studies of temperature effects indicate that temperature effects are probably significant.

- Determining the effects of temperature and humidity on secondary organic aerosol formation from various VOCs. The results will be compared with data obtained using outdoor chamber systems to evaluate the range of applicability of those data.

- Evaluating the budgets of HO_x and NO_y, and evaluating the usefulness of indicators of O_3 and $P(O_x)$ sensitivity to precursors for conditions typical of ambient atmospheres.

- Evaluating impacts of various types of VOC sources, such as architectural coatings, on formation of ozone, secondary PM, and other pollutants in various environments.

- Utilizing the facility to test equipment to be used for monitoring trace pollutants in ambient air under controlled conditions where the actual pollutant concentrations, and the history and source of the air mass being monitored, are known.

The specific research plan and the priorities for the specific projects will be determined based on the results of the initial evaluation experiments and discussions with a technical advisory group consisting of representatives of the EPA and other regulatory agencies, industry groups, and atmospheric chemistry researchers.

Current Status

Progress was made towards this objective in several areas during the first year of this project. A successful international workshop was held in Riverside California concerning the atmospheric chemistry of ozone and particle formation and environmental chamber research. During this workshop the objectives and proposed work plan for this project were discussed, and useful feedback and input was obtained from environmental chamber and other researchers from the United States and Europe.

Plans were developed concerning the design and construction of the environmental chamber facility, which will be housed in a new laboratory building constructed in part for this purpose. A schematic of the environmental chamber and its associated temperature-controlled enclosure and light source is shown on Figure 1, above. The construction of the building for the chamber laboratory and the light source is just now underway, and it expected to be completed in late March of 2001. Near-term needs for analytical instrumentation are being assessed, and some equipment was purchased and ordered.

A series of experiments are being carried out to evaluate NO_x offgasing effects in Teflon bag reactors, since this is expecting to be the main factor limiting how low pollutant concentrations can be usefully employed in environmental chamber data. A minimum NO_x offgasing rate of ~1 ppb per day is observed in the ~5 m^3 test reactors, though lower background NO_x levels should be obtained in the full

size (~200 m^3) chamber. Research will continue on evaluating chamber effects and low NO$_x$ experiments using the existing chamber facility. The current research plan and schedule for the upcoming period are being developed based on the results obtained.

Development and Application of Improved Methods for Measurement of Ozone Formation Potentials 0f Volatile Organic Compounds. California Air Resources Board Contract No. 97-314

Objectives

The overall objective of this three-year program are to develop and evaluate improved methods for measuring and estimating ozone formation potentials of VOCs that are important in stationary source emissions. This involves experimental, modeling, and methods development work. The specific tasks as stated in the proposal include the following:

- Evaluate whether modified ROG surrogates for incremental reactivity experiments can provide more precise information on integrated OH radical levels, to improve the utility of the data for mechanism evaluation.

- Develop alternative and methods for assessing or screening reactivity characteristics of VOCs that can reduce uncertainties in reactivity estimates for VOCs or complex mixtures that have not been studied in environmental chamber experiments, or cannot that cannot be studied using current environmental chamber methods.

- Develop different types of experiments to be sensitive to different aspects of the mechanisms, or that may be appropriate for different types of samples, depending on their chemical characteristics.

- Develop procedures for analyzing or utilizing results of such experiments for making estimates of atmospheric reactivities, and their associated uncertainty ranges.

- Evaluate the experimental and data analysis procedures developed in this project using compounds whose reactivity characteristics are known.

- Conduct the experimental and mechanism development studies most useful for reducing the uncertainties in reactivity estimates for the major classes of consumer product VOCs, and for assessing the most appropriate reactivity measurement methodology for particular classes of compounds.

Current Status

Use of a modified mixture in the mini-surrogate reactivity chamber experiments based on using a more reactive OH radical tracer was investigated, but it was found that the improvement in precision in integrated OH radical levels was not sufficient to justify changing the standard procedures used to assess reactivity.

The major effort on this project to date has been development and testing of a direct reactivity measurement method based on reacting the test compounds in a HONO flow system (see discussion above). The initial experiments employed a stirred flow reactor and data were obtained using a wide variety of compounds. Some problems with data being inconsistent with model predictions and irreproducibility of results were obtained, and alternative approaches were investigated. The best success to date was obtained using a plug flow system with a relatively short reaction tube, as shown in Figure 2, above. The results with the homologous n-alkanes (see Figure 3, above) indicate that the method may be

suitable for low volatility compounds, and may also be suitable for complex mixtures such as petroleum distillates. Work is continuing on the best methods to quantitatively inject and monitor the reactant VOC.

As discussed below, under ACC funding we are conducting preliminary experiments to evaluate a separate method to measure total nitrate yields. If successful, this will provide complementary data to the direct reactivity data, since for most stationary source VOCs nitrate formation is the most important single factor affecting the indirect reactivity characteristics of the VOC. If the results indicate the method can provide useful data concerning this aspect of reactivity, appropriate procedures for analyzing the results and incorporating them with the direct reactivity measures will be developed as part of this project.

Development and Evaluation of an Experimental Method to Measure Total Organic Nitrate Yields in the Atmospheric Reactions of Volatile Organic Compounds. American Chemistry Council Contract SC-18.0-UCR-Carter.

Objectives

Dr. Ron Cohen and co-workers at the University of California at Berkley developed a system that exploits the thermochemistry and kinetics of nitrogen oxides in combinations with a NO_2-specific detector to provide a measure of total concentrations of different types of nitrogenous compounds. Their system involves a sampling system that heats the sample at a controlled but variable temperature for a brief amount of time before it enters an NO_2-specific detector. Depending on the temperature, the nitrate or peroxynitrate compounds decompose to NO_2 and are detected as NO_2. They have employed this system in a number of ambient monitoring projects to monitor total organic nitrate, PAN, and nitric acid levels (Cohen, personal communication, 2000).

The objective of this project is to adapt this method to measuring total yields organic nitrates and peroxynitrates from individual VOCs when these compounds react in the presence of NO_x in the atmosphere. It will be evaluated by comparing nitrate and peroxynitrate yields from selected organic compounds where these yields have been measured directly using other methods, and for compounds where they have been determined by adjustments to fit chamber data. If the evaluation indicates the method has utility, protocols will be developed for making these measurements for which reactivity data are not available, and for using these data when deriving mechanisms for predicting ozone and other impacts of the VOCs in the atmosphere.

A secondary objective of this project will be to adapt the thermal dissociation, NO_2 analysis method for measuring total nitrate and peroxynitrate levels in environmental chamber experiments carried out for mechanism evaluation. This would significantly enhance the analytical capabilities of the "Next Generation" environmental chamber facility we are developing for the EPA (see above).

Current Status

Preliminary experiments were carried out testing the thermal converter system with pure compounds (propyl nitrate, PAN, HONO, NO_2, and HNO_3), using a GC-luminol system developed at CE-CERT to monitor NO_2, and commercial NO-NO_x analyzer to monitor NO and total NO_x species. The results show good conversion for PAN but less than 75% conversion for propyl nitrate, and non-quantitative decomposition of HONO to NO + NO_2 throughout the entire temperature range. Although additional experiments are required, the preliminary results with propyl nitrate are not very encouraging for use of the thermal converter method with our GC-Luminol NO_2 analyzer for quantitative monitoring of high molecular weight organic nitrates. This is in spite of the fact that Cohen and co-workers obtained much better conversions of propyl nitrate to NO_2 in tests that they carried out. The reason for the difference appears to be due to the fact that they monitor NO_2 at low pressures, and thus they can "freeze"

the decomposition by sampling directly from the converter at low pressure to avoid the complex chemistry that appears to be occurring at atmospheric pressure between the heated converter and the analyzer in our experiments. However, the use of the laser-induced fluorescence method as employed by Cohen and co-workers (Thornton et al, 2000) or some other low-pressure method to monitor NO_2 such as tunable diode laser absorption spectroscopy (TDLAS) is not an optimal solution for this project because of the extremely high cost of the necessary instrumentation and their operation.

Fortunately, there is an alternative approach that can be employed to obtain the data needed at a more affordable cost. This is to use the standard "NO_x" analyzer with an appropriate scrubber to remove HNO_3 to monitor total nitrates + PANs + NO_2, in conjunction with the GC-luminol system with the thermal converter at a temperature around 150-200 C to monitor NO_2+PANs. The total organic nitrates can therefore be determined as the difference between these two measurements. The utility of this approach is currently being investigated.

SCHEDULE

The schedule for this three-year project is flexible because the specific tasks to be carried out and their priorities will depend on results of projects that are currently underway and results of consultations with the CARB and the relevant industry advisory group. It is expected that the project will be initiated with a meeting with the CARB and the advisory group do discuss the priorities for this project and how it relates to other related projects. It is probable that the first priority may be to work on the reactivity and uncertainty survey procedures, since the objective of that task is to determine priorities for reducing uncertainties. However, the timing of that task will depend on the availability of the emissions survey data needed for the analysis. It is expected that meetings will be held with the CARB staff and their advisory group on at least an annual basis to review the work carried out and to establish the schedule and priorities as the project proceeds.

REPORTING AND DELIVERABLES

Quarterly reports will be submitted to the CARB giving brief summaries of the progress and status of the program, problems encountered, and anticipated future schedules. 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 their industry advisory groups and consultants, as they deem appropriate. At the end of the project, a draft final report will be prepared documenting the work carried out during the second year 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. (1995). Software, spreadsheets and documentation developed for this program will also be made available on the Internet.

BUDGET

The total amount requested for this three-year project is $59,984. This covers the cost of the Principal Investigator's time to supervise the project, conduct the analyses and prepare the reports, the cost of the laboratory personnel to develop and evaluate the experimental methods and conduct the environmental chamber experiments, and the laboratory fees for operating the chamber conducting the experimental tests.

REFERENCES

CARB (1993): "Proposed Regulations for Low-Emission Vehicles and Clean Fuels -- Staff Report and Technical Support Document," California Air Resources Board, Sacramento, CA, August 13, 1990. See also Appendix VIII of "California Exhaust Emission Standards and Test Procedures for 1988 and Subsequent Model Passenger Cars, Light Duty Trucks and Medium Duty Vehicles," as last amended September 22, 1993. Incorporated by reference in Section 1960.

CARB (2000): "Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, 'Determination of Volatile Organic Compounds in Consumer Products'," California Air Resources Board, Sacramento, CA, May 5.

Carter, W. P. L. (2000): "Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment," Report to the California Air Resources Board, Contracts 92-329 and 95-308, May 8. Available at http://cert.ucr.edu/~carter/absts.htm#saprc99 and http://www.cert.ucr.edu/~carter/reactdat.htm.

Carter, W. P. L., D. Luo, I. L. Malkina, and D. Fitz (1995): "The University of California, Riverside Environmental Chamber Data Base for Evaluating Oxidant Mechanism. Indoor Chamber Experiments through 1993," Report submitted to the U. S. Environmental Protection Agency, EPA/AREAL, Research Triangle Park, NC., March 20. Available at http://cert.ucr.edu/~carter/absts.htm#databas.

Carter, W. P. L., D. Luo, and I. L. Malkina (1997): "Investigation of the Atmospheric Ozone Formation Potentials of Selected Mineral Spirits Mixtures," Report to Safety-Kleen Corporation, July 25. Available at http://cert.ucr.edu/~carter/absts.htm#msrept.

Carter, W. P. L., D. Luo, and I. L. Malkina (2000a): "Investigation of the Atmospheric Ozone Formation Potentials of Selected Branched Alkanes and Mineral Spirits Samples," Draft Report to Safety-Kleen Corporation, August 18.

Carter, W. P. L., D. Luo, and I. L. Malkina (2000b): "Investigation of the Ozone Formation Potentials of Exxsol® D95, Isopar-M®, and the Exxate® Fluids," Draft Report to ExxonMobil Chemical Company, August 25, 2000.

Carter. W. P. L., D. Luo and I. L. Malkina (2000c): "Investigation of Atmospheric Reactivities of Selected Consumer Product VOCs," Report to California Air Resources Board, May 30. Available at http://cert.ucr.edu/~carter/absts.htm#cpreport.

Febo, A., C. Perrino, M. Gerardi and R. Sparapini (1995): "Evaluation of a High-Purity and High Stability Continuous Generation System for Nitrous Acid," Environ. Sci. Technol. 29, 2390-2395.

Kwok, E. S. C., C. Takemoto and A. Chew (2000): "Methods for Estimating Maximum Incremental Reactivity (MIR) of Hydrocarbon Solvents and their Classification," Appendix C to "Initial Statement of Reasons for the Proposed Amendments to the Regulation for Reducing Volatile Organic Compound Emissions from Aerosol Coating Products and Proposed Tables of Maximum Incremental Reactivity (MIR) Values, and Proposed Amendments to Method 310, 'Determination of Volatile Organic Compounds in Consumer Products'," California Air Resources Board, Sacramento, CA, May 5.

Thornton, J. A., P. J. Wooldridge, and R. C. Cohen (2000): "Atmospheric NO_2: In Situ Laser-Induced Fluorescence Detection at Parts per Trillion Mixing Ratios," Anal. Chem, 72, 528-539.

Wang, L., Milford, J.B., Carter, W.P.L. (2000a): "Reactivity estimations for aromatic compounds, I uncertainty in chamber-derived parameters," Atmos. Environ., 34, 4337-4348.

Wang, L.; Milford, J.B.; Carter, W.P.L. (2000b): "Reactivity estimations for aromatic compounds, II uncertainties in incremental reactivities," Atmos. Environ., 34, 4349-4360.