

**IMPROVED REACTIVITY ESTIMATES
FOR VOLATILE ORGANIC COMPOUNDS USED
IN ARCHITECTURAL COATINGS**

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

by

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Center for Environmental Research and Technology
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ABSTRACT

The College of Engineering Center for Environmental Research and Technology (CE-CERT) proposes expand the scope of our existing three-year California Air Resources Board (CARB) agreement 00-333 to carry out the additional work needed to reduce the uncertainties in estimating the impacts of architectural coatings emissions on photochemical ozone formation and other measures of air quality. The scope of the existing project includes completing development and initial application of a direct reactivity screening method for coatings constituents, conducting environmental chamber experiments to assess ozone and other impacts of Texanol, and developing improved procedures for quantifying reactivities and uncertainties for petroleum distillates. The additional funding will provide for a more comprehensive set of chamber experiments on major water- and solvent-based coatings constituents, and application of the direct reactivity screening method to the full variety of coatings constituents. The environmental chamber experiments will employ the state-of-the art facility being developed under EPA funding for mechanism evaluation under a wider range of conditions than previously practical, including lower pollutant levels. The additional funding will permit chamber experiments chamber experiments and direct reactivity measurements for selected petroleum distillates, particularly the higher reactivity materials whose ozone impacts are most uncertain, and chamber experiments with selected water-based coatings constituents not being studied under the current project. 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 the additional work is \$240,129, and the period of performance is December 1, 2001 through November 30, 2004.

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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 (CARB, 1993) and aerosol coatings regulations (CARB, 2000), and are now being considered for other stationary source applications.

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 O₃ 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, costing at least \$40K per compound using the environmental chambers employed in our previous studies. 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 that have been 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. This is because of the relatively high reactant concentrations (which suppress radical levels) and relatively short reaction times employed in most current experiments. 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. The new facility being developed under EPA funding, discussed below, should permit use of the lower reactant concentrations and longer reaction times that are needed to address this.

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, and a fourth program aimed specifically in assessing uncertainties in architectural coating reactivity has just been funded. The objectives and current progress on the three ongoing programs are summarized in the "Related Programs" section of this proposal, and aspects relevant to this proposal are briefly summarized below. The objectives and scope of the new program to study architectural coatings reactivity are discussed in the following section.

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 NO₂ conversions that are directly responsible for O₃ 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 m³) 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 the fall of 2001. In the meantime, research is being carried out using smaller (≤5 m³) 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, including low NO_x conditions characteristic of downwind or rural conditions. It will also permit obtaining mechanism evaluation data under controlled conditions as a function of temperature, a factor that is known to affect ozone formation potentials for which well-characterized data have been extremely limited. 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 O₃, 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. This is briefly discussed below.

Table 1 shows the VOCs in the CARB draft coatings emissions inventory in terms of their estimated contribution to ozone formation from water-based and solvent-based coatings. Although the data shown are preliminary and subject to revision as the additional and improved data become available, they give an indication of where the research priorities may lie. The table shows both the approximate mass contributions of the various constituents to total emissions of water or solvent-based coatings and the approximate relative contributions of these constituents to ozone formation, based on the current SAPRC-99 Maximum Incremental Reactivity (MIR) scale. The table also indicates the mechanism uncertainty classification given for the compounds by Carter (2001), and also indicates whether environmental chamber data are available to verify the ozone impact predictions of the mechanisms. The compounds are ordered by relative contribution to ozone formation based on these MIR values, which gives a somewhat different ordering than that by mass contributions.

Table 1 shows that ethylene glycol, Texanol, and 2-(2-butoxyethoxy) ethanol are the top three compounds from the water-based coatings survey whose mechanisms have not been experimentally evaluated using environmental chamber data. Although ethylene glycol is on the top of the list in terms of estimated contribution to ozone, its reactivity estimates are not considered particularly uncertain because of its relatively simple mechanism that is considered to be reasonably well understood. However, experimental data confirming the model predictions of its ozone impacts would be very useful. The reason it has not been studied previously is that it is a very “sticky” compound to work with and analyze, making it difficult to obtain sufficiently high quality chamber data to be useful for mechanism evaluation. However, with improved environmental chamber technology (discussed below) it may now be possible to obtain useful mechanism evaluation data for this compound. However, direct reactivity measurements, discussed later in this proposal, may be sufficient to evaluate the major uncertainty in the ethylene glycol mechanism, which is the rate constant for its reaction with OH radicals.

Texanol (2,2,4-trimethyl-1,3-pentanediol isobutyrate isomers) is first on the list of water-based coatings constituents in terms of mass contributions of unstudied coatings VOCs, but is second to ethylene glycol in terms of estimated ozone contribution because of its relatively low estimated reactivity. Unlike ethylene glycol, this compound has a number of possible reaction routes and a number of potentially significant uncertainties in its estimated mechanism. Texanol 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. Because of its relatively high molecular weight, PM impacts of emissions of this compound may also be a concern. This has not been evaluated. Because of this, experimental studies of the ozone impacts of Texanol have been given the highest priority by the CARB.

Table 1. VOCs in the CARB draft coatings emissions inventory that contribute to more than 1% of the estimated total ozone formation potential of the coatings category, as estimated using the MIR scale. Mechanism uncertainty classification and availability of chamber data are also shown.

Compound or VOC type	Weight % of TOG [a]	Est'd MIR [b]	Unc'y. Code [c]	Chamber Data Avail.	Approx. O ₃ Cont'n % [d]
<u>Water-Based Coatings</u>					
Propylene Glycol	28%	2.8	1	Yes	35%
Ethylene Glycol	16%	3.4	2	No	24%
Texanol isomers	28%	0.9	3	No	11%
Aggregated VOCs (<1%) [e]	9%	~2	-	No	9%
2-(2-Butoxyethoxy)-Ethanol	4%	3.0	3	No	6%
Various Petroleum Distillates [f]	5%	2.0	4	Some [g]	5%
2-(2-Methoxyethoxy) Ethanol	1.0%	2.9	3	No	1.3%
2-Butoxyethanol	0.9%	2.9	1	Yes	1.2%
<u>Solvent-Based Coatings</u>					
Various Petroleum Distillates [f]	71%	2.0	4	Some [g]	64%
C8 Disubstituted Benzenes	5%	5.2	3	Yes [h]	11%
Toluene	3%	4.0	2	Yes	6%
1,2,4-Trimethyl Benzene	1%	7.2	2	Yes	2%
Methyl Ethyl Ketone	2%	1.5	1	Yes	2%
Aggregated VOCs (<1%) [e]	2%	~2	-	-	2%
Ethanol	2%	1.7	1	Yes	1.5%
4-Methyl-2-Pentanone	0.5%	4.3	2	Yes	1.1%

- [a] Based on data in the CARB's draft architectural coatings profiles #1901 and 1902. Vinyl acetate in the water-based coatings profile #1901 is not included in the analysis because it is believed to be a monomer that is consumed in the curing process and therefore is not emitted.
- [b] Incremental reactivities in the Maximum Incremental Reactivity (MIR) scale in units of grams ozone per gram of VOC. Based on data tabulated by Carter (2000b).
- [c] Uncertainty classification for ozone reactivity estimates as given by Carter (2000). See Table 3, below, for the definitions of the codes. Generally, a classification of "3" or larger means that experiments are needed to reduce the uncertainty in the reactivity estimate.
- [d] Relative contribution to ozone total ozone formation for the profile based on the weight fractions and the estimated MIR values. Calculated as the product of MIR times weight fraction for the component, divided by the sum of the product of MIR times weight fraction for all components in the profile.
- [e] MIR is estimated to be approximately 2, based on the weighted average of MIRs for all identified compounds in the water-based coatings profile.
- [f] MIR is estimated using CARB's profile #1930 "Thinning Solvent/Mineral Spirits (Calpoly Slo 1996)".
- [g] Chamber experiments have been carried out on some primarily alkane mineral spirits samples. As discussed in the text, these may not be good representatives of many of the types of petroleum distillates used in coatings.
- [h] Chamber data are available for all three xylene isomers. However, the different isomers have quite different reactivities, so the MIR is uncertain if the isomers are not identified.

The third compound on the water-based coatings list in terms of estimated ozone impact is 2-(2-Butoxyethoxy)-Ethanol, also known as butyl carbitol. Various other glycol ethers also contribute to ozone impact estimates for water-based coatings. Although their mass emissions are less than that of Texanol in the current survey, they are estimated to have approximately three times the ozone impact of Texanol, and because of this the estimated ozone impact of all the glycol ethers in the survey is almost as great as that estimated for Texanol. Experimental data have been obtained concerning aspects of the mechanisms of 2-(2-Butoxyethoxy)-Ethanol (Atkinson et al, 2001), but the ozone impact predictions of the mechanism derived for this compound, and of the estimated mechanisms for the other glycol ethers on Table 1 have not been tested experimentally.

Table 1 also shows that the various types of petroleum distillate fractions, variously referred to as “Mineral Spirits”, “Naphtha”, “Stoddard Solvent”, “Lactol Spirits,” etc, are extremely important in solvent-based coatings, and also contribute to some extent to water-based coatings reactivity. 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, and in some cases experimental complications limited the precision of the data. 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) that apparently performs reasonably well in giving reactivity predictions that are consistent with estimates based on more extensive compositional data¹. However, the performance of this (or any other) method in deriving actual ozone impacts has not been experimentally 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

A list of the various types of petroleum distillates identified in the CARB Architectural Coatings Survey is given in Table 2. As with Table 1, both the weight fractions and the estimated relative contributions to ozone formation, based on assigned MIR values, are shown, with the entries sorted in order of estimated ozone contribution. The MIR estimates are based on the protocol developed by the CARB for making MIR estimates for such compounds (CARB, 2000), discussed above. Note that there is a relatively wide range in reactivity estimates, ranging from approximately 8 grams O₃ per gram solvent for all-aromatic mixtures, to less than 1 gram O₃ per gram solvent for the all-alkane medium to high molecular weight materials. Thus there is a significant variability in the reactivity estimates for the petroleum distillates.

It is important to recognize that with one exception the only types of petroleum distillates whose ozone impacts have been studied in environmental chamber are all-alkane materials with relatively low reactivities, with MIRs of less than 0.8 grams O₃ per gram solvent. Thus they are estimated to have lower ozone impacts than any of the materials listed in Table 2, with the possible exception of “medium aliphatic solvent naphtha”. The only exception is the “Sample A” material studied in our Safety-Kleen project (Carter et al, 1997), and even in this case the MIR is still only ~1.3, lower than most materials listed on Table 2. This is a recycled material from Safety-Kleen’s cleaning operations containing

¹ The performance of the ARB method in giving predictions that are consistent with those using more extensive compositional data cannot be independently verified because the data employed are proprietary.

Table 2. Results of preliminary CARB survey of sales of various types of petroleum distillates, and estimated ozone impact contributions based on the MIR scale.

Common Name	CAS No.	Sales [a]		MIR Values [b]	Approx. MIR % [c]
		Tons	Wt. %		
Stoddard solvent	8052-41-3	3,272	18.9%	2.5	24.6%
Aromatic 100	64742-95-6	907	5.2%	7.5	20.0%
Protected data [d, e]	-	2,633	15.2%	~2	~15%
Medium aliphatic solvent naphtha	64742-88-7	5,678	32.7%	0.9	15.1%
VM & painters naphtha	64742-89-8	1,278	7.4%	2.0	7.6%
Petroleum naphtha, heavy alkylate	64741-65-7	1,155	6.7%	1.6	5.6%
Distillate(petroleum), hydrotreated light	64742-47-8	857	4.9%	1.4	3.5%
Kerosene	8008-20-6, 64742-81-0	317	1.8%	1.8	1.7%
Other VOC [e, f]	-	270	1.6%	~2	~1.6%
Petroleum ether	8032-32-4	299	1.7%	1.6	1.4%
Hydrotreated heavy naphtha	64742-48-9	396	2.3%	1.2	1.4%
Heavy aromatic naphtha solvent	64742-94-5	64	0.4%	5.0	0.9%
Solvent-refined heavy paraffinic distillate	64741-88-4	112	0.6%	1.4	0.5%
Naphtha	8030-30-6	67	0.4%	2.1	0.4%
Solvent naphtha, petroleum, heavy aliphatic	64742-96-7	19	0.1%	~2	~0.1%
Proprietary VOCs [e, g]	-	15	0.1%	~2	~0.1%
Heavy straight-run naphtha	64741-41-9	11	0.1%	~2	~0.1%

[a] Sales data obtained from 1998 ARB Architectural Coating Survey. These data do not include ingredients classified as: copolymers, pigments, resins, surfactants, or solids.

[b] Incremental reactivities in the MIR scale in units of grams ozone per gram of solvent. Unless noted otherwise, the MIR values were determined by ARB personnel during development of aerosol coating regulation.

[c] Relative contribution to ozone total ozone formation from the various types of petroleum distillates, based on sales amounts and the estimated MIR values.

[d] Protected data includes those ingredients that were used by fewer than three companies.

[e] The MIR is estimated to be near the approximate average of the non-aromatic solvents listed.

[f] "Other VOC" is a common name that was assigned to certain ingredients that had relatively ambiguous names (e.g., solvent blend, aromatic mixture, light distillate). Whenever possible, the CAS number was used to determine a more specific description for ambiguous names. However, for those ingredients where the CAS number was not provided or could not be verified, the term "Other VOC" was used.

[g] "Proprietary VOC" is a common name that was assigned to ingredients that were designated as proprietary or trade secret by the manufacturers.

relatively small amounts of aromatics and alkenes (~6% and ~2%, respectively), and is probably not representative of the types of mineral spirits used with coatings.

Although the composition information used to derive the MIR values shown on Table 2 are not available, the relatively high MIRs for many of the materials is probably due to significant aromatic content. This indicates the importance of the aromatics in affecting reactivity estimates for many types of petroleum distillates, including specifically the top two on the list in terms of estimated ozone impact (CARB, 2000). Note that the second most important solvent in terms of estimated ozone impact is the all-aromatic “aromatic-100” solvent, which, because of its high reactivity, contributes approximately 20% to the estimated ozone impact while contributing only ~5% to the mass. The first material on the list in terms of reactivity contribution is not the first material in terms of mass percent, but makes a relatively large contribution to ozone because it is estimated to have over three times the ozone impact as all-alkane materials.

The potential importance of aromatics in contributing to ozone impacts of petroleum distillates represents a significant source of uncertainty the ozone impact estimates for solvent-based coatings. This is not only because of the ozone impact estimates are highly sensitive to the aromatic contents, which in some cases may be uncertain, but also because of the significant variability and uncertainty in reactivity estimates for aromatics in general. The details of atmospheric reaction mechanisms for aromatics are still sufficiently poorly characterized that it is not possible to derive or estimate explicit mechanisms for aromatics *a-priori*. Therefore, the only way to estimate ozone impacts for aromatics is to derive parameterized mechanisms adjusted to fit environmental chamber data. Such data have been obtained for benzene, all the mono-, di-, and trimethylbenzene isomers, and for ethyl benzene, allowing reactivity estimates for these individual compounds to be derived. However, the data used to derive these mechanisms were obtained at relatively high pollutant concentration conditions, and because of the mechanism uncertainty the validity of extrapolating those mechanisms to the lower concentration regime in ambient atmospheres is uncertain. In addition, the results indicate a relatively wide variation in reactivity among isomers or compounds expected to have similar structure, with (for example) the MIR for m-xylene being 2.5 times higher than that for p-xylene and the MIR for ethylbenzene being only 70% that of toluene, despite its higher OH radical rate constant. Currently reactivity estimates for the higher molecular weight aromatics that may be present in petroleum distillates are based assuming similar per-molecule O₃ impacts as the lower molecular weight compounds, but considering the wide variation of aromatic reactivity with structure this assumption is clearly quite uncertain. Thus, data are clearly needed to evaluate our ability to estimate ozone impacts of the more reactive, aromatic-containing petroleum distillates.

These are not the only types of coatings VOCs for which reactivity estimates are uncertain, though the materials discussed are currently considered to be the most important in terms of contribution of uncertain VOCs to present emissions estimates. Note that any assessment of research needs related to coatings reactivity needs to take into account not only current mass emissions, but the likelihood of these emissions increasing in the future and the magnitude and uncertainty ranges of their likely ozone impacts

CURRENT ARCHITECTURAL COATINGS REACTIVITY RESEARCH PROJECT

Based on the considerations discussed above, the CARB has recently contracted with our laboratory (CARB contract No. 00-333) to conduct the initial research most needed to address the uncertainties in ozone reactivity estimates for architectural coatings. The funding made available for this three-year contract was \$59,984. This funding is not sufficient to cover the research needs that were identified in the proposal for the program, so the work plan for this project was determined after discussion with the CARB staff and the Reactivity Research Advisory Committee (RRAC) in a meeting held in Sacramento on March 1, 2001. Based on the discussions at that meeting and subsequent discussions with the CARB staff, it was decided to restrict the scope of the program to the following four major tasks.

- 1) Reactivity and uncertainty survey of coatings VOCs;
- 2) Environmental chamber studies of Texanol;
- 3) Application of a direct reactivity measurement method to selected coatings constituents; and
- 4) Development and evaluation of procedures to quantify reactivity and uncertainty of petroleum distillates.

The background, objectives, and methods for these tasks are summarized in this section.

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 3 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 3 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 “C₁₂ 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 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

Table 3. 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%

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.

Some preliminary work on this task has already been completed, and the results are summarized in the “Reactivity Research Needs” portion of the Background section to this proposal. The discussion in the subsequent sections of this proposal based on the assumption that the results of a more comprehensive and updated analysis will be consistent with the current preliminary results indicating the importance of Texanol, ethylene glycol, glycol ethers, and the more reactive types of petroleum distillate solvents. If the results of an updated analysis indicate differently, then substitutions may be made if deemed appropriate after discussions with the CARB staff and the RRAC.

Environmental Chamber Studies of Texanol

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 an important component of any project to reduce uncertainties in estimates of atmospheric impacts of coatings VOCs would be to conduct environmental chamber experiments to assess their effects on formation of ozone, PM, and other

measures of air quality. The results can then be used for evaluating mechanisms or reactivity estimation methods for these types of VOCs.

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 permit experiments where other important conditions are varied, such as temperature and overall reactant concentrations. 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 fall 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 schematic diagram of the environmental chamber enclosure is shown on Figure 1. The dual Teflon bag 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 chamber is located in a new laboratory building specifically constructed to house it and the associated laboratory and offices. At the present time (early August, 2001) the construction of the chamber building is complete and we are beginning to move laboratory equipment and offices into the building, the construction of the chamber enclosure is nearly complete, and the light source and associated equipment is has just been delivered. Selected photographs taken during the construction of the new building, chamber housing, laboratory, and argon lamp housing are shown in Figure 2.

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 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.

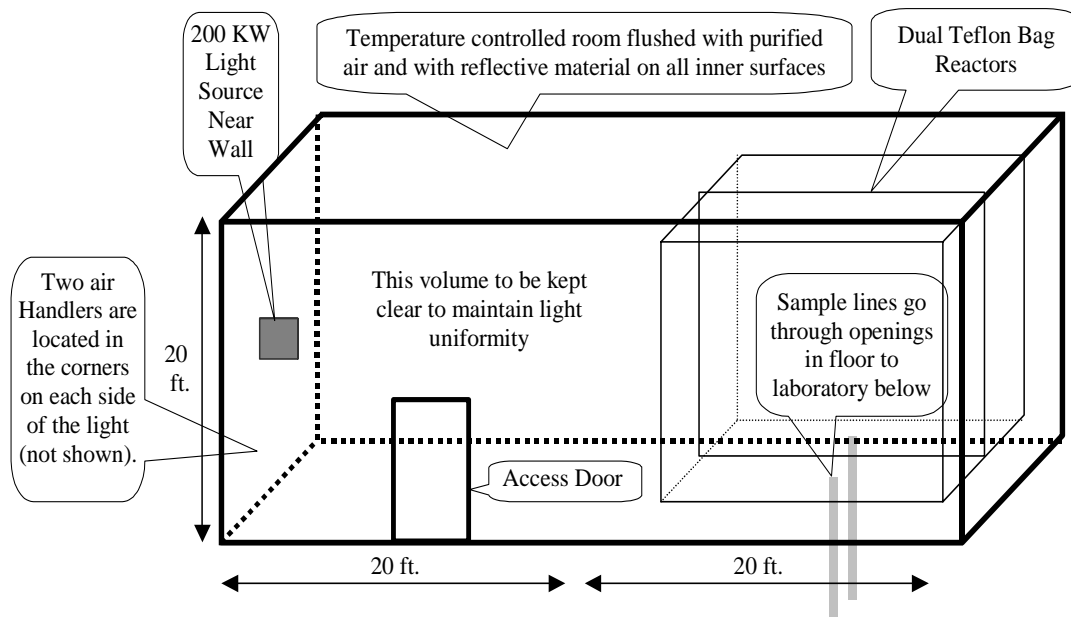


Figure 1. Schematic of the environmental chamber being developed for the EPA project, with its associated temperature controlled enclosure and light source.

Although we anticipate that use of the larger chamber and lower concentrations should increase the likelihood of useful data being obtained with low volatility materials such as 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 below. The results of these tests will serve as a basis for determining the best approach to employ to obtain useful mechanism evaluation data for such compounds.

The analytical and characterization instrumentation that we expect to use and the measurements that will be made in the environmental chamber experiments carried out during the first phase of this project are summarized on Table 4. It is expected that additional instrumentation will be acquired later utilizing the remaining EPA funds, and if appropriate this instrumentation may be used in the experiments carried out during the second or third year of this project.

We estimate that approximately 7 environmental chamber experiments should be sufficient for evaluating atmospheric impacts of a test compound or mixtures of interest, and how these impacts vary with reactant levels. This includes experiments with varying base case reactive organic gas (ROG) composition and levels, varying NO_x levels, varying amounts of added test compound or mixture added, and a minimum number of replicates and characterization and control experiments. Some of the characterization experiments during the initial period of this project can be covered by funding from the EPA project since it part of the overall characterization of the new facility. For subsequent years the cost



Figure 2. Selected photographs of the new environmental chamber building, enclosure and light source taken during its construction. (a) Outside view of laboratory building. (b) Construction of air purification and chamber refrigeration systems. (c) Laboratory room underneath new chamber. (d) Outside chamber enclosure in the upstairs laboratory. (e) Inside chamber enclosure looking towards the where the lights will be located, showing reflective materials on all surfaces, the access door, and the intakes for air handler. The light will be located about three feet directly above the person's head. (f) Argon arc lamp and enclosure (taken at the factory during its construction).

Table 4. Summary of analytical instrumentation to be employed and measurements to be made during the initial experiments to be carried out for this project.

Instrument	Used to Monitor
Commercial Ozone Analyzer	Ozone
Commercial Chemiluminescent NO-NO _x Analyzer	NO Sum of NO ₂ , PAN and other nitrogen-containing species converted to NO by a high temperature catalyst.
ECO-Physics High Sensitivity NO analyzer	NO
GC-Luminol NO ₂ /PAN Analyzer	NO ₂ PAN
Tunable Diode Laser Absorption Spectrometer (TDLAS) #1	NO ₂ HNO ₃
TDLAS #2	Formaldehyde H ₂ O ₂
Commercial CO Monitor	CO
GC Luminol or TDLAS NO ₂ analyzer interfaced to thermal reaction tube [a]	Total peroxy nitrates Total organic nitrates
Various GC-FID Instruments	VOCs and some organic oxidation products.
Dasgupta Formaldehyde analyzer [b]	Formaldehyde
HPLC system with DNPH sampler [c]	Formaldehyde and other aldehydes
Scanning electrical mobility spectrometers (SEMS) with condensation particle counter	Aerosol size and number distribution

[a] Under development. Probably will work satisfactorily for total peroxy nitrates but suitability for total organic nitrates is more uncertain.

[b] On order. If this performs satisfactorily, the TDLAS formaldehyde channel may be used for another species.

[c] Will probably not be used for most experiments.

of the necessary control and characterization runs will be shared as appropriate by all projects using the facility.

The statement of work for the current project calls for carrying out at least five environmental chamber experiments with Texanol. This may be sufficient for evaluating the impacts of this compound at a single temperature, since the costs of the control and characterization experiments are covered by the EPA project as part of the overall characterization of the new facility. Additional funding would be needed to obtain chamber data on other important coatings constituents with uncertain ozone impacts, such as the various types of petroleum distillates.

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, they are expensive and also they do not provide an unambiguous evaluation of all the 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 NO₂, 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 reactions². 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, and for complex mixtures of VOCs that may have varying rate constants or mechanisms. Thus, they would be particularly useful for the 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 ethylene glycol, such data would be useful to verify the OH rate constant for this compound, for which there is some disagreement in the literature (Aschmann and Atkinson, 1998). 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, and continues to be a priority in the existing coatings reactivity project. 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 O₃ 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 NO₂, 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 3. 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

² 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.

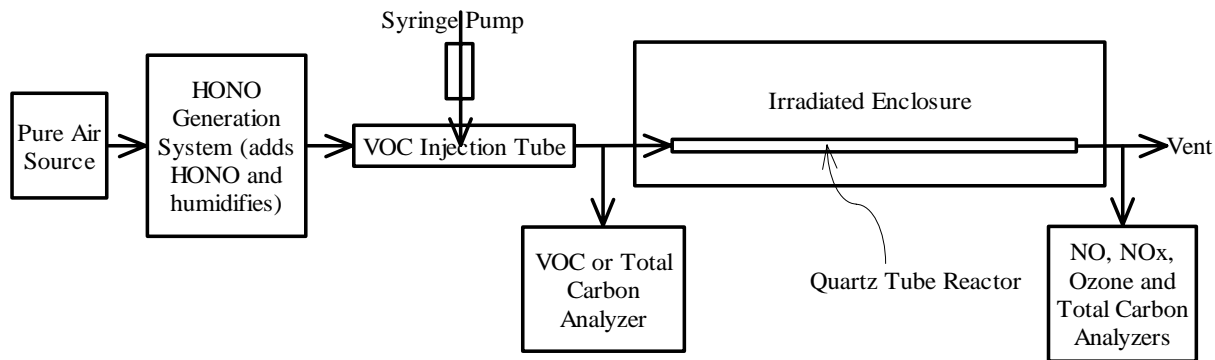


Figure 3. Schematic of the flow reactor system used to measure direct reactivity.

petroleum distillates can be injected without fractionation based on volatility. Moderately elevated temperature (e.g., around 60°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-C₁₆ and a few other representative VOCs. Figure 4 gives plots of discrepancies between experimentally measured and model simulated direct reactivities for most of the VOCs that have been studied using the current method, excluding runs with obvious experimental problems. It can be seen that good agreements between experimental results and model calculations are obtained up to n-C₁₆ (though one n-C₁₆ run was rejected because the measured n-C₁₆ levels did not agree with the calculated amounts injected). Note that n-C₁₆ 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 or ethylene glycol may give them greater affinities to surfaces than is the case for an alkane with the same vapor pressures.

Figure 4 shows that although generally the model fits the data to within $\pm 25\%$ for the normal alkanes, there seems to be a consistent problem with the model prediction of direct reactivities for the aromatics, especially benzene. This suggests a possible problem with the aromatics mechanisms that needs to be investigated further. The data for iso-octane (2,2,4-trimethylpentane) also suggest a problem with the direct reactivity mechanism for this compound. Additional experiments with other classes of compounds are currently underway as part of the ongoing work on CARB contract 97-314, and these results will be needed before more definitive conclusions can be made.

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

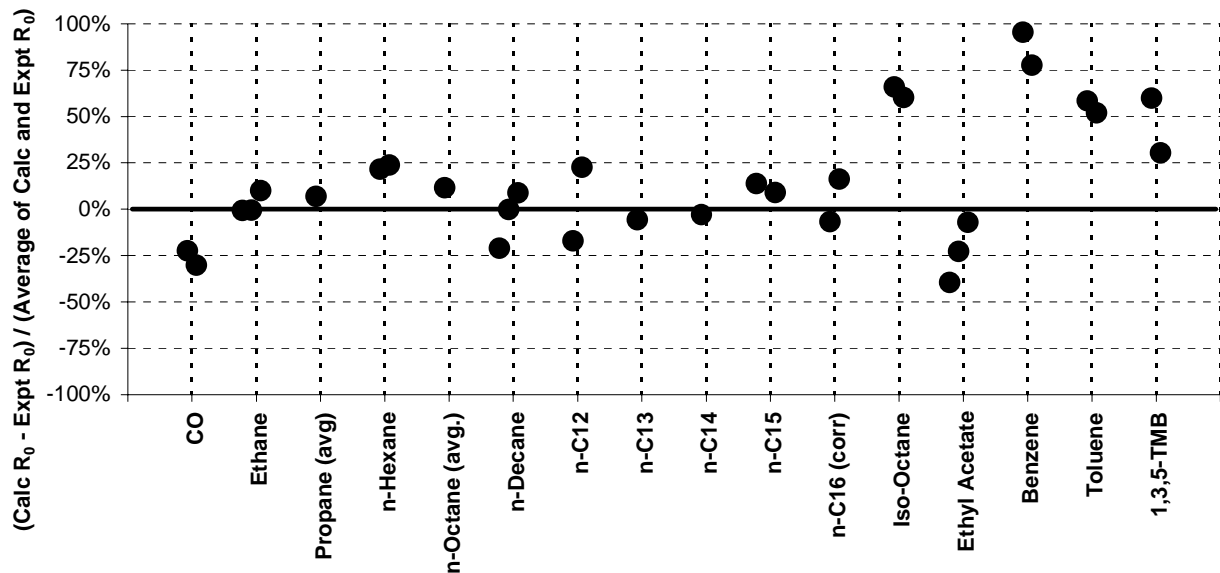


Figure 4. Plots of discrepancies between experimental and model calculated direct reactivities for compounds that have been studied to date using the direct reactivity measurement system as currently employed.

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 CO₂ using a high-temperature catalytic combustor, and analyzing the CO₂ (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 CO₂ will be kept out of the system by using only purified, methane and CO₂-free air as the diluent in the flow reactor. The combustor converting the gas-phase VOC to CO₂ 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.

We have already carried out a preliminary evaluation of the feasibility of proposed method to measure total gas-phase carbon concentrations using a CO₂ analyzer loaned to us for evaluation. The results indicated that the method works for high volatility compounds and will probably work for low volatility compounds if steps are taken to minimize surface absorption. A CO₂ analyzer has been ordered using the remaining funds from an ACC gift provided at the beginning of the project to aid in the initial development of this method.

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. For the data to be useful for reactivity evaluation, the temperature in the reactor must be sufficiently high that all of the injected VOC is available for gas-phase reaction. However, since in general the rate constants and numbers of NO to NO₂ 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.

The budget for the existing contract is probably sufficient to complete the development of the method for application to low volatility compounds and complex mixtures, and to apply it to Texanol and a few other selected VOCs or mixtures of relevance to this project. However, it is probably not sufficient for a complete assessment of all the types of VOCs of relevance, particularly if a number of different types of petroleum distillate samples need to be assessed, or if the results indicate problems with the current mechanism.

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 full documentation for the method is not publicly available because most of the compositional data used in the analysis was proprietary, and the publicly available 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 which 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 composition and reactivity estimation procedures also needs to be evaluated experimentally. One way to do this is to conduct environmental chamber experiments with the solvent and compare the experimental results with results of model predictions obtained using the composition derived using the procedure, and the chemical mechanism used to calculate the reactivities of the constituents. Such experiments are beyond the scope of the current project, but are included in this proposed extension, discussed below. A less costly approach is to conduct “direct reactivity” measurements of the solvents as discussed above, and compare the results with the model predictions obtained using the same composition and mechanism. 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 direct reactivity experiments with 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. The funding available for the existing project may not be sufficient to experimentally study all the types of petroleum distillates that may be of interest.

OBJECTIVES

The objectives and current scope of our existing three-year program to reduce uncertainties in reactivity estimates for coatings VOCs were summarized in the previous section. The objective of this proposed supplement is to conduct the additional environmental chamber and direct reactivity screening measurement research needed to more completely address the overall objectives of this project. These include the following tasks:

- Conduct environmental chamber experiments to determine the effects of at least five other selected types of coatings constituents on ozone and PM formation under a range of reactant concentrations. At least four of these would be selected types of petroleum distillates representing different reactivity ranges, but an additional water-based coatings constituent may also be studied. The results will then be used to evaluate the predictions of existing and updated atmospheric reaction mechanisms or reactivity estimation methods for this compound or mixture. The

existing program covers the cost of experiments on Texanol, but not for studies of petroleum distillates or other water-based coatings compounds.

- Apply the direct reactivity screening method to the full range of compounds and petroleum distillates being used or considered for use in architectural coatings in California. The existing program covers the completion of the development of the method for architectural coatings VOCs, but does not cover the cost for its application beyond a few representative compounds.

The priorities for specific compounds or mixtures to be studied will be determined as part of the overall project, in conjunction with discussions with the CARB staff and the CARB Reactivity Research Advisory Committee (RRAC). The procedures to be developed under the currently funded program to assess reactivities and uncertainties in petroleum distillates, along with results of market surveys and input from industry groups, will be used to guide the selection of specific types of petroleum distillates chosen for study.

APPROACH AND SCOPE

The scope of work and procedures to be employed in the two major components of this proposed extension of our coatings VOC reactivity project are discussed in this section. Except as noted below, the current plan is to employ the procedures and facility proposed to be employed in our current project, which were discussed above in the background section.

Environmental Chamber Studies of Selected Coatings VOCs

The preliminary reactivity and uncertainty survey of coatings VOCs as currently carried out indicate that environmental chamber experiments are needed to reduce uncertainties in estimated reactivities for the petroleum distillate constituents of solvent-based coatings (particularly those high in aromatics), and the water-based coating constituents Texanol, ethylene glycol, and perhaps others. The currently funded project is sufficient to cover the cost of conducting environmental chamber experiments on Texanol in the state-of-the-art chamber facility being constructed at our laboratory, but not for studying any additional compounds. Under this extension, we propose conducting at least 35 additional environmental chamber experiments in our new facility, which should be sufficient for reducing the uncertainties in mechanisms for at least five, and possibly more, types of VOCs besides Texanol.

The facility and procedures we propose to employ for the additional VOCs studied under this extension will be the same as will be employed for Texanol, as was discussed above. In particular, the new EPA-funded chamber facility will be employed so that the compounds can be studied at lower reactant concentrations and with more extensive analytical instrumentation than was used in our previous studies. This facility and its associated analytical instrumentation have been discussed in section describing our current coatings reactivity project, above.

We estimate that approximately 7 environmental chamber experiments should be sufficient to evaluate the reactivity characteristics of a particular type of VOC or petroleum distillate solvent at ambient temperature. These will consist of “incremental reactivity” experiments where the test compound or mixture is added to a “base case reactive organic gas (ROG) surrogate” - NO_x mixture representing the other pollutants present in ambient air, so the effects of adding these compounds or mixtures to the emissions can be determined. Two reaction bags will be employed, one with the base case ROG and NO_x mixture and the other with the same base case mixture with the test compound or mixture added. The minimum of 7 experiments consists of at least three separate experiments to determine the effects of

varying NO_x levels, ROG/NO_x ratios and base ROG surrogate composition, at least one additional experiment to assess the effects of varying the amount of test compound or mixture added, and at least three additional experiments for replicates or control or characterization purposes.

The proposed extension provides for conducting at least 42 environmental chamber experiments, which should be sufficient for studying at least six additional coatings constituents besides Texanol. The specific constituents to be studied will be determined after consultation with the CARB staff and the RRAC, but are expected to consist of at least four different petroleum distillate samples (at least three having significant aromatic content), and perhaps ethylene glycol or another previously unstudied water-based coatings constituent. Additional constituents may be studied if it is determined that it is not necessary to conduct the full set of experiments for all the constituents, based on the results of experiments with similar materials. Additional constituents may also be studied if the cost of conducting the direct reactivity experiments, discussed in the following section, is less than anticipated, or if it is determined that additional chamber experiments should be given higher priority.

Although the major objective behind this project is to obtain data needed to reduce uncertainties in predictions of ozone impacts of the selected coatings constituents, data concerning the secondary PM impacts of these constituents can also be obtained for relatively little additional funding. Since the instrumentation to measure PM number and size distributions will be available as part of the EPA-funded facility (see Table 4), the additional cost would involve only the staff time required to operate the instrument and analyze the data, which should be less than about \$400 per experiment. The CARB will probably eventually need secondary PM impact data as part of its overall research program, and obtaining this information in conjunction with these experiments would be much more cost-effective than conducting separate experiments for this purpose. The current budget assumes that aerosol data will be obtained and analyzed in about 10 of the proposed experiments, or two experiments per compound studied. Fewer experiments with PM analysis may be needed if some or most of the constituents studied are found not to have measurable PM impacts.

Application of Direct Reactivity Measurement Method to Coatings Constituents

The budget for the existing contract is probably sufficient to complete the development of the method for application to low volatility compounds and complex mixtures (or to determine if the method will not be useful for this application), and if appropriate to apply it to Texanol and a few other selected VOCs or mixtures of relevance to this project. However, unless the cost for applying the method once developed is much lower than is currently the case, the available funding will probably not be sufficient for a complete assessment of all the types of VOCs of relevance. In particular, as indicated in Table 2 there are a number of different types of petroleum distillates used in coatings, and evaluations of all the major types would be useful to evaluate the reactivity and uncertainty estimation methods developed under the current program, as discussed in the Background section. Additional experiments with individual compounds may also be needed if the results indicate problems with the current mechanism.

The budget for the existing project covers the cost for one person working in the lab on this project for one full month. This will be increased by 1.4 months under this proposed supplement. If it takes three working days to evaluate a compound or mixture once the method is developed, this means that at least 10 additional compounds or mixtures can be evaluated if the costs of conducting the experiments are approximately the same as the costs of the current evaluations we are carrying out with the more volatile compounds. If we are successful in developing a suitable total carbon analysis method to verify the amounts of reactant injected in the gas phase during these experiments, the cost per compound may be significantly reduced. However, this may be offset by additional efforts involved with obtaining useful data for lower volatility compounds such as Texanol or complex mixtures such as petroleum distillates.

At the present time we cannot rule out the possibility that the direct reactivity method being developed under current programs may eventually be determined not to be satisfactory for evaluating coatings constituents. On the other hand, if the method as developed is significantly less labor intensive to operate than currently is the case, we may be able to carry out an adequate evaluation of coatings VOCs with much less than the funding that is requested. In either case, we will make recommendations to the CARB and the RRAC as to how the funding budgeted for this project might be best employed to achieve the objectives of this project. The most likely option would be to increase the number of environmental chamber experiments so a larger variety of compounds can be studied, or so the compounds studied could be evaluated under a wider variety of conditions. If none of the funding in this proposed supplement that is allocated to the application of the direct reactivity measurement method is used for this purpose, then an estimated 10 additional chamber experiments can be carried out. This is almost enough to conduct a relatively complete set of chamber experiments on an additional compound, or a smaller number of experiments on several compounds.

RELATED PROGRAMS

The objectives and current status of the other ongoing or proposed projects at our laboratories that are relevant to this proposal are summarized below. Note that the results of some of these programs that 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 NO_x 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 O₃ 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 is now complete, and the construction of the major components of the new chamber and light source are nearing completion. Selected photographs of the facility during the latter stages of its construction are shown on Figure 2, above. Near-term needs for analytical instrumentation are being assessed, and most of the equipment to be used during the initial states of this project have been acquired. Funding is available for additional analytical equipment, but purchase of additional equipment will be deferred until analytical needs and priorities are fully assessed, and the amount of operational funding available from other sources have been determined.

A series of experiments are being carried out to evaluate NO_x offgasing effects in Teflon bag reactors, since this is expected 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 m³ test reactors, though lower background NO_x levels should be obtained in the full size (~200 m³) 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 Of 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 3, above. The results with the homologous n-alkanes (see Figure 4, 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.

Work is also underway in measuring direct reactivities for the more volatile compounds for which the method as currently employed appears to be working well. The results are compared with model predictions of direct reactivity to indicate whether there are systematic problems with the method itself or with model predictions of direct reactivity predictions of various types of compounds. The results to date, shown on Figure 4, above, indicate that there may be problems with direct reactivity predictions for aromatics and at least some branched alkanes.

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 Berkeley developed a system that exploits the thermochemistry and kinetics of nitrogen oxides in combinations with a NO₂-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 NO₂-specific detector. Depending on the temperature, the nitrate or peroxyxynitrate compounds decompose to NO₂ and are detected as NO₂. 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 peroxyxynitrates from individual VOCs when these compounds react in the presence of NO_x in the atmosphere. It will be evaluated by comparing nitrate and peroxyxynitrate 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, NO₂ analysis method for measuring total nitrate and peroxyxynitrate 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, NO₂, and HNO₃), using a GC-luminol system developed at

CE-CERT to monitor NO₂, 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 + NO₂ 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 NO₂ 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 NO₂ in tests that they carried out. The reason for the difference appears to be due to the fact that they monitor NO₂ 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 NO₂ 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 HNO₃ to monitor total nitrates + PANs + NO₂, in conjunction with the GC-luminol system with the thermal converter at a temperature around 150-200 C to monitor NO₂+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.

Development and Evaluation of A Gas-Phase Atmospheric Reaction Mechanism for Low NO_x Conditions. Proposal submitted to the California Air Resources Board. Recommended for funding by the CARB Research Screening Committee, July, 2001.

The overall objective of this project is to evaluate and improve the performance of current versions of the SAPRC chemical mechanism for simulating atmospheric transformations under low and very low NO_x conditions. The specific objectives will include the following:

- Complete the development of the “Low NO_x” version of the SAPRC-99 mechanism that is designed to more accurately predict organic product formation under very low NO_x conditions.
- Evaluate the performance of both the standard and the low NO_x versions of the SAPRC-99 mechanism in simulating available environmental chamber simulating low NO_x conditions, including TVA and CSIRO chamber experiments not used previously in SAPRC mechanism evaluation.
- Utilize the new UCR environmental chamber facility being developed under EPA funding to carry out selected low NO_x mechanism evaluation experiments deemed to be the most useful for mechanism evaluation in the near term.
- Update or modify the mechanisms as appropriate based on the results of the evaluation against chamber data and other data that may become available.

The results of this study will then be used to develop recommendations concerning mechanisms to use when modeling low NO_x conditions in regional model simulations, and priorities for future research aimed at reducing uncertainties in chemical mechanisms used in regulatory and research applications.

SCHEDULE

This proposed supplement will not affect the schedule of the initial tasks for the existing contract, nor will it affect the ending date of the existing three-year project. The schedule for the initial tests 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. The first priority is the work on the reactivity and uncertainty survey, and as discussed above this work has already begun. The next priority will be the work on the petroleum distillate reactivity and uncertainty estimation methods, since the results should be taken into account when selecting which types of distillates should be studied experimentally. The work on developing the direct reactivity measurement method is currently being covered by ongoing CARB "Methods" project (Agreement 97-314), which ends at the end of 2001. If the results indicate that the method will be useful for this project, the work on any further development and application of this method will begin in early 2002.

The major environmental chamber experiments will probably not begin until 2002 because of the need to characterize the new EPA chamber once it is constructed. However, work on developing injection and analysis methods for Texanol can be initiated prior to that using our existing chambers. It is expected that the first priority will be to carry out at least some of the chamber experiments using Texanol, though at least a few of the Texanol experiments will be deferred until the last year of the project to take advantage of any improved methods and new equipment that may be available by then. This approach will also be used for the other compounds or mixtures that will be studied using environmental chamber experiments.

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

The proposed supplement will not affect the reporting requirements of the existing CARB contract 00-333, and if this supplement is funded under a separate contract then all the reports for the two contracts will be combined. 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 already available for the existing contract 00-333 is \$59,984. This covers the cost of the Principal Investigator's time to supervise the project, conduct the reactivity and uncertainty analyses discussed in this proposal, and prepare the reports, the cost of conducting the approximately five environmental chamber experiments on Texanol, and the equivalent of approximately one full-time month in the laboratory developing and applying the direct reactivity measurement method.

The amount requested in this proposal is \$240,129, which brings the total cost of this and our existing architectural coatings reactivity to \$300,113. This consists of approximately \$13,000 for additional Principal Investigator's time to oversee the project, analyze and report on the results, and attend the additional RRAC meetings required, approximately \$38,000 for an additional 1.4 full-time months in the laboratory for applying the direct reactivity measurement method, approximately \$184,000 to conduct the 42 additional environmental chamber experiments at an estimated cost of approximately \$4800 per experiment, and approximately \$5000 to include aerosol measurements and analysis in 12 of the experiments. An itemized budget is attached to this proposal.

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