

ITEM NO.: 10
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STAFF EVALUATION OF A DRAFT RESEARCH FINAL REPORT

TITLE: Investigation of Atmospheric Reactivities of Selected Stationary Source VOCs

CONTRACTOR: University of California, Riverside

PRINCIPAL INVESTIGATOR: William P. L. Carter, Ph.D.

AMOUNT: \$211,396

DURATION: 24 Months

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I. SUMMARY

Volatile organic compounds (VOCs) react in the atmosphere to produce different amounts of ozone. This ozone-forming potential is called reactivity. Control strategies that take reactivity into account, rather than treat all VOCs equally, can potentially achieve ozone reductions in a more cost-effective manner. The ARB is currently developing amendments to the aerosol coatings regulations, which would establish reactivity-based limits for aerosol coatings. In support of the amendments, this project investigated the reactivities of several compounds important to the consumer products inventory.

Environmental chamber experiments were conducted to measure the effect of the selected compounds on ozone formation. The results were then used to derive the chemical mechanisms necessary to quantify reactivity. As part of this contract, Dr. Carter has written SAPRC99, the chemical mechanism used to calculate reactivity values for ARB regulations. Dr. Carter updated a previous version of the SAPRC chemical mechanism by improving the base mechanism, updating the kinetic

parameters to reflect the most recent literature, adding classes of VOCs, which are important for the consumer products inventory, and performing experiments and computer modeling to determine VOC reactivity and deduce their chemical mechanisms. Additionally, because it is necessary to consider the uncertainty associated with an estimate of reactivity when designing a regulation, the SAPRC documentation also provides a quantification of the uncertainty associated with each reactivity value.

II. TECHNICAL SUMMARY

Objective

The objective of this project was to reduce the uncertainties associated with reactivity values for the consumer products inventory. Environmental chamber experiments and computer model calculations were carried out to determine the best chemical mechanism for a compound or class of compounds. Results of the experiments were used as part of Dr. Carter's revision of the chemical mechanism. The revised mechanism, SAPRC99, was used to calculate a table of reactivities, which will be used in modifications to the aerosol coatings regulation.

Background

Different VOCs react in the atmosphere at different rates and with different mechanisms. As a result, a given amount of two compounds can produce very different amounts of ozone. For example, one gram of ethane will produce 0.31 grams of ozone while, under the same conditions, one gram of formaldehyde will produce 8.97 grams of ozone. A compound's ozone-forming potential is called its reactivity. Control strategies that take reactivity into account, rather than treat all VOCs equally, can potentially achieve ozone reductions in a more cost-effective manner. The U.S. Environmental Protection Agency (U.S. EPA) uses reactivity as the determining factor in deciding whether to exempt a VOC. In 1990, ARB adopted the Low Emission Vehicle/Clean Fuels regulation, the first regulation to use reactivity in a more complex manner than the simple 2-bin exemption type of regulation. Stationary Source Division staff are currently developing amendments to the aerosol coating regulations, which

would establish reactivity-based limits for aerosol coatings.

In support of the aerosol coatings amendments, this project investigated the reactivities of several compounds important to the consumer products inventory. The compounds which were studied were selected after consultation with members of the Reactivity Research Advisory Committee. The committee, which consists of representatives from various manufacturers, provided input as to which compounds would be most useful in reducing uncertainties in reactivity estimates for consumer product VOCs. Some compounds, such as isopropanol, were studied because of their importance in the inventory. Other compounds were selected as representative of important classes of compounds; for example, ethyl acetate, n-butyl acetate, and methyl isobutyrate were studied to provide mechanistic information about the atmospheric reactions of esters. Other compounds studied included cyclohexane, methyl ethyl ketone, cyclohexanone, methyl isobutyl ketone, three isomers of octanol, diethyl ether, propylene glycol methyl ether acetate, and 4-hydroxy-2-pentanone.

Reactivity experiments can measure a compound's reactivity under the conditions in the chamber. However, chamber experiments are not conducted under atmospheric conditions, so that a compound's atmospheric reactivity must be calculated using computer models. These calculations require a chemical mechanism to describe the reactions of the chemicals in the atmosphere. The data collected in this project was used to improve Dr. Carter's chemical mechanism.

Project Summary

Incremental reactivity experiments were conducted to measure the effect on ozone formation of the chosen compounds. For those compounds for which inadequate information was available, the rate constant for the reaction of the compound with OH was measured. Product studies were also conducted for a few compounds.

The results of the experiments were then compared with model simulations. When necessary, the chemical mechanism was adjusted to better fit the experimental data.

For example, to fit the methyl ethyl ketone data, the quantum yield for the photodecomposition of the ketone was increased from 0.1, the value used in SAPRC90, to 0.15. This change in quantum yield was then made part of the improved SAPRC99 mechanism. One very important result of this work was the discovery of a previously unsuspected reaction for esters. The reaction involves the transfer of an alpha hydrogen to the carbonyl oxygen, followed by decomposition to form an acid and alkoxy radical. This reaction has a significant effect on the reactivities and products of many esters.

An improved, updated version of Dr. Carter's chemical mechanism was also delivered as part of this project. While the experimental work performed in this contract was very important in improving reactivity estimates for some classes of compounds, it is actually a very small portion of the improvements to SAPRC99, since the mechanism was evaluated against the results of approximately 1700 experiments on over 80 types of VOCs.

SAPRC99 consists of several components: the base mechanism, the assignments and/or estimation procedures, and the lumping procedures. The base mechanism contains the reactions of the inorganic species, the common organic products, and the intermediate radicals leading to these products. A comprehensive review of the literature was used to update all of the kinetic parameters and reaction mechanisms used in the base mechanism. Only a very small number of compounds are included in the base mechanism. The reactions of the majority of compounds are derived using software, which generates the chemical mechanism for the atmospheric reactions of the VOC in the presence of NO_x . This mechanism generation software is an entirely new feature developed for SAPRC99. The derived mechanisms are used as the basis for the condensed mechanism, which is used in the air quality model. The last major component of the mechanism is the lumping procedures that are used to represent complex mixtures or VOCs for which assignments or estimates are not available.

The updated mechanism was used to calculate reactivity values used in the reactivity-based aerosol coatings regulation that will be presented to the Board later this year. Additionally, because it is necessary to consider the uncertainty associated with an estimate of reactivity when designing a regulation, the SAPRC documentation also provides a quantification of the uncertainty associated with each reactivity value. After discussion with ARB staff regarding the format of the uncertainty estimation, Dr. Carter assigned each compound a number between 1 and 6. Compounds with an uncertainty of 1 are considered to have reactivities that are not expected to change significantly if further research is done. The estimated uncertainty associated with the reactivity value increases with increasing uncertainty code. For compounds with an uncertainty of 6, the “current mechanism is probably incorrect, but biases in atmospheric reactivity predictions are uncertain.” The aerosol coatings regulation uses these uncertainty assignments. Lastly, a condensed version of the mechanism was developed for use in regional models.

III. STAFF COMMENTS

The final report has been reviewed by staff from the Research, Planning and Technical Support, and Stationary Source Divisions (SSD). SSD funded a peer review of SAPRC99 by Dr. William Stockwell. In addition, SAPRC99 and the peer review have been assessed by members of ARB’s Reactivity Scientific Advisory Committee (RSAC).

The final report summarizes the results of the experimental work in a clear and concise manner and provides lucid summaries of the effects of the experiments on the overall chemical mechanism. The project achieved its objective of reducing the uncertainties associated with reactivity predictions for classes of compounds that are important to the consumer product inventory. Only minor editorial changes and the addition of an Executive Summary to the report are needed.

The SAPRC99 mechanism is a monumental achievement. It has assignments for ~400

types of VOCs and can be used to estimate reactivities for ~550 VOC categories. In August of 1998, the RSAC and Dr. Carter requested that, due to the complexity of the mechanism, a peer review be conducted. SSD released an RFP and awarded the contract to Dr. William Stockwell of Dessert Research Institute. Dr. Stockwell reviewed the base mechanism, using standard databases and the most recent literature. He also reviewed the assigned mechanistic parameter method, use of the lumping procedures, and handling of uncertainty. He recommended some changes. The conclusion of the peer review was the mechanism is “within the realm of the best available science.” In October of 1999, the RSAC met to comment on SAPRC99 and the peer review. They commended both Drs. Carter and Stockwell and stated that they found SAPRC99 to be a state-of-the-science chemical mechanism. Dr. Carter has already made the editorial changes to the SAPRC documentation recommended by staff.

IV. STAFF RECOMMENDATIONS

Staff recommends the Research Screening Committee accept the draft final report and SAPRC99 documentation, subject to inclusion of appropriate revisions and additions in response to the staff comments and any changes and additions specified by the Committee.