



Project Summary

Evaluation of the RADM Gas-Phase Chemical Mechanism

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A program was conducted to evaluate the gas-phase mechanism developed for the Regional Acid Deposition Model (RADM). An initial review of the mechanism was carried out, resulting in several modifications being made prior to its further evaluation. New methods were developed for processing emissions input for the RADM model and for representing aggregated VOCs in the model. The mechanism was tested by comparing predictions against results of over 550 environmental chamber experiments carried out at two laboratories. A series of 90 test problems for assessing gas-phase mechanisms in regional models was developed and used to test several condensation approaches for the RADM mechanism. As a result of this study, two modified RADM mechanisms were developed and evaluated. The most important of the modifications concerned the representation of aromatic hydrocarbons. Based on the results of the evaluation, it was concluded that the modified RADM mechanism represents the current state of the art and is suitable for use in a regional acid deposition model. However, there are still major uncertainties in our understanding of atmospheric chemistry and available chamber data are not sufficient for evaluating many important aspects of regional oxidant mechanisms.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of

the same title (see Project Report ordering information at back).

Introduction

The Regional Acid Deposition Model (RADM) plays a central role in the National Acid Precipitation Assessment Program's (NAPAP) plan to develop an understanding of source-receptor relationships for acidifying pollutants. This model is needed to formulate appropriate and cost-effective emission control policies to mitigate the potentially damaging effects of acid deposition. While transport, deposition, and chemistry all play important roles in the acid deposition phenomenon, the chemistry plays a particularly important role in determining the response of the acid deposition system to major changes in NO_x and SO_x emissions. The chemistry submodel is the only component of the overall modeling system that is capable of predicting nonlinearity in the relationship between source emissions and acid deposition. Thus, it is critically important that any chemical mechanism incorporated into the RADM model be fully evaluated using the best available data and that it be recognized by the scientific community as representing the current state-of-the-art in our understanding of atmospheric chemistry.

Because of the importance of chemistry in the Regional Acid Deposition Model, the EPA contracted the Statewide Air Pollution Research Center (SAPRC) at the University of California and Lurmann Associates to conduct a comprehensive evaluation of the gas-phase chemical mechanism proposed for use in RADM-II. As part of this effort, an initial review of the mechanism for consistency with current

kinetic and mechanistic data was carried out; new methods were developed for processing VOC emissions input and for representing aggregated VOCs in the model; the mechanism was tested against the results of over 550 environmental chamber experiments; a series of test problems for assessing gas-phase mechanisms in regional models was developed and used to test several condensation approaches for the mechanism; and two modified versions of the mechanisms were developed and evaluated. SAPRC and Lurmann and Associates were assisted in this effort by Dr. William R. Stockwell of the State University of New York, the developer of the RADM-II chemical mechanism, Dr. Paulette Middleton of the National Center of Atmospheric Research, who is responsible for preparation of emissions data used by the RADM mechanism, Dr. Harvey E. Jeffries at the University of North Carolina (UNC), who is responsible for the UNC chamber experiments whose results were used as part of the evaluation effort, and by Dr. Roger Atkinson at SAPRC, who assisted in the initial review of the mechanism for consistency with current data.

The research findings from the various efforts in this program, and recommendations for future research, are summarized below.

Evaluation of Kinetic and Mechanistic Parameters

At the beginning of this study, an initial review of a preliminary version of the RADM-II chemical mechanism was carried out, and a number of changes were recommended. A procedure was developed for determining rate constants and products for the reactions of lumped organic species based on the detailed speciation of the national emissions inventory. Many of these initial recommendations were adopted and incorporated into the preliminary version of the RADM-II mechanism prior to its evaluation against the environmental chamber data.

Based on the results of testing the RADM mechanism against chamber data and sensitivity testing under a range of atmospheric conditions, two alternate versions of the RADM mechanism were developed and evaluated. The first alternate mechanism, referred to as the recommended modified RADM mechanism (RADM-M), had the following changes relative to the preliminary version of the mechanism: (1) the representation of the unknown aspects of the aromatic photooxidation mechanism

was changed to improve its performance in simulating chamber data; (2) a more condensed representation of the >C3 alkanes was incorporated; (3) several rate constant and product yields for lumped species were updated based on a new analysis of the emissions data; (4) an error in the methylglyoxal quantum yields that resulted in overestimation of its photolysis rate was corrected; (5) several reactions omitted from the NO₃+ alkene reaction system were added; and (6) the representation of the reactions of nitrophenols was revised to improve its chemical fidelity.

Because implementation of the RADM mechanism was almost completed by the time the RADM-M mechanism was developed and evaluated, a second alternate mechanism was proposed that involved primarily changes in parameter values. This version is referred to as the recommended modified parameter version (RADM-P). This incorporated an improved aromatic oxidation mechanism, which performs approximately as well as that in RADM-M, but uses the larger number of species employed in the RADM mechanism. It also incorporated the updated lumped species rate constant and product yields, the reduced methylglyoxal quantum yields, and the addition of the omitted NO₃+ alkene reactions that were incorporated in RADM-M. The RADM developers have adopted the RADM-P mechanism and this version is now being implemented in the full RADM-II model.

Processing of the VOC Emissions Inventory for the RADM Mechanism

At the start of this program, only a very preliminary emission inventory interface had been developed for the RADM mechanism; hence, a large effort was directed towards developing emissions aggregation procedures for use with the RADM model. A new two-step system was developed for this purpose. The first step involved aggregating the detailed VOC emissions data into a 32-class VOC grouping based on reactivity and relative contributions to total emissions. The second step involved further aggregating these emissions groups into the more limited number of VOC species used in the RADM mechanism. This effort was carried out jointly as part of this program and the RADM development effort.

The aggregation of the emissions groups into the RADM species involves use of a new reactivity weighting scheme that allows for VOCs reacting at different rates, but with similar mechanisms, to be

represented by the same model species. This is based on estimating how much of the VOCs and the model species undergoes chemical reaction in the model simulation and adjusting the amounts of the latter so they are approximately equal. Although approximate, the use of reactivity weighting is preferable to the alternatives of either ignoring compounds of low but non-negligible reactivity, or representing them by much more reactive model species.

Another feature of this aggregation system is the use of detailed emissions data to derive the rate constants and product yield coefficients of lumped species in the mechanism based on those for the aggregate of compounds they represent. A software system recently developed as part of another program and the 1985 NAPAP anthropogenic emissions inventory were used for this purpose. This is considered a significant advancement that optimizes the linkage between the chemical mechanism and the emissions inventory.

Mechanism Evaluation Against Chamber Data

The gas-phase chemistry is one of the few modules in the atmospheric modeling system that can be independently tested against experimental data. Although the present chamber data base is not suitable for testing all aspects of the mechanism, particularly those involving predictions of acidic or peroxy species or simulations of very low NO_x conditions that prevail in rural regions, it is suitable for testing predictions of ozone formation and rates of NO_x oxidation under urban conditions. To a lesser extent, the data can be used to test the mechanisms' ability to simulate formation of peroxyacetyl nitrate and formaldehyde under urban conditions. Simulation of urban-like conditions is important because urban areas represent the major sources of the pollutants that are transported to remote areas with sensitive receptors.

A comprehensive evaluation of the RADM, RADM-M, and RADM-P mechanisms against environmental chamber data was performed in this study. The approach involved simulating a large number (~550) of experiments from four different chambers and statistically evaluating the mechanisms' performance. Data from (1) the SAPRC evacuable indoor chamber (EC); (2) the SAPRC indoor Teflon chamber (ITC); (3) the SAPRC outdoor Teflon chamber (OTC), and (4) the UNC outdoor chamber

were utilized for this purpose. Prior to conducting the evaluation, procedures for characterizing chamber-dependent processes were reviewed and updated. Most of the updated procedures concerned the UNC outdoor chamber where a new light characterization model developed at UNC was utilized. Organic compounds in experiments employing complex mixtures of organics were aggregated using the procedures that will be employed when the mechanism is used in RADM. Thus no run-to-run adjustment of chamber-dependent or mechanistic parameters was used in the evaluation.

The major findings from the evaluation of the RADM, RADM-M, and RADM-P mechanisms against environmental chamber data are as follows:

- Testing against experiments with mixtures of organics designed to represent current VOC emissions showed that the RADM mechanisms perform as well as other chemically up-to-date mechanisms. The mechanisms are able to predict the maximum ozone and NO_x oxidation rate with a small bias and a mean error of 20% on the average.

- Testing of the RADM mechanism against single organic-NO_x-air experimental data produced mixed results. With a few exceptions, the RADM mechanism performed as well as can reasonably be expected for experiments containing species for which the mechanism was designed. The predictions for experiments with formaldehyde and propene were reasonably good. Predictions for acetaldehyde and methyl ethyl ketone systematically underpredicted ozone and NO_x oxidation rates, but there are too few experiments to draw definitive conclusions on the adequacy of this portion of the mechanism. The mechanism has a bias towards underpredicting reactivity in ethene runs due to the omission of the reaction of O(³P) atoms with ethene. This reaction, however, is unimportant under conditions where the model will be applied. The mean error in the ozone predictions for the 1-butene runs is greater than is the case for propene, but the bias is reasonably small. The predictions for the trans-2-butene simulations are poor, but there are too few of these experiments to test this portion of the mechanism adequately. The mechanisms had large errors in simulating the alkane runs due to the extreme sensitivity of these runs to chamber effects that tend to vary

unpredictably from run to run. Compared to the errors, the biases in the predictions of ozone and NO_x oxidation rates in the alkane runs were relatively low. In these regards, the performance of the RADM mechanisms is comparable to those of other recent mechanisms that have been tested against these data.

- The performance of the RADM mechanism in tests against single aromatic species was not as good as that reported for other chemically up-to-date mechanisms. The testing showed that the RADM aromatics mechanism has a bias towards overpredicting ozone and NO_x oxidation rates for the more slowly reacting compounds and underpredicting those same characteristics for the faster reacting compounds. This results in fairly large errors in ozone predictions on the average for toluene, xylenes, and mesitylene.
- The RADM-M and RADM-P mechanisms were designed to improve the performance of the mechanism in simulating the aromatic hydrocarbon runs. This design objective was achieved. The performance of these mechanisms in simulating the results of these runs was comparable to other current mechanisms.
- Because of the importance of biogenic emissions in regional model applications, the RADM mechanism has a separate species to represent isoprene. However, the performance of this mechanism in simulating isoprene experiments was not as good as those for most other alkenes. Improving the performance of the RADM mechanism in representing isoprene would probably require adding additional species to the mechanism.
- The RADM mechanisms performed surprisingly well in simulating the α -pinene runs, despite the fact that the mechanisms do not represent this compound explicitly. However, there are only a limited number of such runs, and the apparent good performance may be fortuitous.
- The RADM mechanisms' performance for species other than those for which it was designed, such as propionaldehyde, 1-hexene, benzene, naphthalenes, and tetralin, was generally poor. However, the level of performance of the RADM mechanism in this regard is certainly comparable to what one would expect for other condensed mechanisms designed for use in Eulerian atmospheric models. Satisfactory

performance in simulating these compounds would probably require adding new species to the mechanism. This is probably not worthwhile given the relatively small contributions of these compounds to overall VOC reactivity in most regional model applications.

- The RADM mechanisms do not predict maximum formaldehyde and PAN concentrations as accurately as they predict maximum ozone concentrations or NO oxidation rates. This is also the case with other current mechanisms that have been evaluated against these data. In the case of formaldehyde, some of the poor performance may be attributed to uncertainties in the quality of the experimental data. In the case of PAN a positive bias is expected since the PAN species in the mechanism is used to represent a number of related compounds in addition to PAN. However, in some cases the performance of the mechanism in simulating these species represents an area of concern.
- It is very unlikely that mechanisms could achieve the high level of performance on ozone and NO_x oxidation rates found in complex mixture runs without accurately simulating the production and destruction of OH radicals. These results indirectly suggest that the mechanisms are able to reasonably predict OH concentrations and, therefore, the probable yields of nitric acid and sulfuric acid in daylight hours.

Sensitivity Testing of Alternate Mechanistic Assumption

Given the nonlinear couplings in mechanisms, it is often difficult to predict *a priori* the conditions and species for which changes in mechanistic assumptions will have large effects. Therefore, it is important in evaluating alternative mechanistic assumptions to make sure the testing is performed over a wide range of conditions. To address this, a large number of test problems (90) were developed to represent a wide range of chemical conditions for purposes of evaluating selected mechanistic assumptions.

The predictions of the RADM mechanism were compared to those of a detailed version that included all possible peroxy-peroxy radical combination reactions. The results showed that even for hydrogen peroxide and organic peroxides, which are very sensitive to peroxy-peroxy radical reactions, the RADM mechanism gave predictions that

were almost identical to those of the detailed version in all cases. Tests were also carried out to determine if a more condensed representation of peroxy-peroxy radical reactions could be used in the RADM model. The more condensed representation did not yield predictions that agreed as closely with those of the detailed mechanism, though the differences were probably not significant. The results suggest that the treatment of peroxy radicals in the RADM mechanism is satisfactory.

Tests were carried out to determine if a more condensed representation of the reactions of alkanes could be employed in the RADM model. The results indicated there are no significant differences in model predictions if the two higher alkane classes in RADM are combined, provided the combined class has the appropriate mechanistic parameters. These results served as the basis for the representation of alkanes in the recommended RADM-M mechanism.

Test calculations indicated that the versions of the RADM mechanism incorporating our recommended modifications (RADM-M and RADM-P) can in some cases be quite different from the original mechanism in predicting species of interest in acid deposition

models. The differences between the mechanisms tend to be the greatest in the simulations of urban conditions. This is due primarily to the recommended changes in the mechanisms for the aromatics. The modified mechanisms tended to predict slightly lower levels of ozone and in some cases significantly lower levels of peroxide or acid species under some conditions. On the other hand, the modifications had smaller effects on predictions of nitric acid or sulfate. This indicates that implementing the recommended changes in the mechanism might in some cases have non-negligible effects on results of regional model simulations.

Conclusions and Recommendations

The RADM gas-phase chemical mechanism and its associated emissions aggregation system, revised as a result of this program, represents the current state-of-the-science. Therefore, it is suitable for use in the current version of the Regional Acid Deposition Model. However, there remain significant uncertainties in our understanding of atmospheric chemistry and further research is needed to reduce these uncertainties. The research needed to

address the major uncertainties in the representation of gas-phase chemistry in regional acid deposition models is as follows:

- Development of methods for more accurate representation of biogenic VOC emissions in condensed gas-phased mechanisms.
- Additional environmental chamber studies to acquire data for testing mechanisms for the terpenes.
- Improvement of VOC emissions inventories, especially for biogenic organics.
- Development of new environmental chamber technology capable of testing predictions of gas-phase mechanisms under low-NO_x conditions and for testing predictions of acidic and peroxide species. This includes research into surface effects that affect results of environmental chamber experiments.
- Additional mechanistic studies concerning the gas-phase atmospheric chemistry of aromatic hydrocarbons, higher alkanes, isoprene, and terpenes.
- Development of new instrumentation needed for making further advances in elucidating reaction mechanisms.

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The complete report, entitled "Evaluation of the RADM Gas-Phase Chemical Mechanism," (Order No. PB90-164526/AS; Cost: \$45.00, (subject to change) will be available only from:

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