



Project Summary

Validation Testing of New Mechanisms With Outdoor Chamber Data

H. E. Jeffries, K. G. Sexton, J. R. Arnold, and J. L. Li

The UNC smog chamber data base was used to compare the performance of two state-of-the-science photochemical mechanisms: the Carbon Bond Four Mechanism and the Carter, Atkinson, Lurmann Mechanism. A number of tasks had to be performed before the comparisons could be conducted. These included comparing and reconciling the thermal rate constants used in the two mechanisms, re-assessing the photolytic rates for the UNC chamber and producing a new radiation transfer model, performing new experiments with new instrumentation for formaldehyde and hydrogen peroxide to confirm older data, and analyzing three years of ambient hydrocarbon data to determine a default composition for use in EKMA comparisons. A series of chamber experiments was modeled with both mechanisms to assess their performance for specific chemistry. A series of State Implementation Plan EKMA calculations was also performed with both mechanisms for a range of conditions.

Although there were other differences between the two photochemical methods, both mechanisms showed good agreement for ozone and oxides of nitrogen chamber data. The agreement for other products such as formaldehyde and peroxyacetylnitrate was not as good. Neither mechanism was considered superior to the other either in fitting smog chamber data or in predicting VOC control requirements.

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 four separate reports of the same title (see Project Report ordering information at back).

Introduction

The U.S. Environmental Protection Agency (EPA) has a long-standing program to develop accurate photochemical mechanisms for incorporation into air-quality models. The EPA has sponsored the development of two basic types of mechanisms: the Carbon Bond approach with its emphasis on conservation of carbon mass, and the surrogate approach with its emphasis on quasi-explicit chemistry. Neither approach has a clear theoretical advantage; both require that choices be made between detail and accuracy, and each may have specific advantages in particular applications.

The work described in this summary compared two specific mechanisms: the Carbon Bond Four mechanism (CB4) developed by System Application Inc. and the Carter, Atkinson, Lurmann mechanism (CAL) developed by the University of California, Riverside (UCR) and Environmental Research and Technology (ERT). During their development, both mechanisms had been tested using selected data from the UNC and UCR chambers and were found to agree reasonably well with these data. Of concern was whether the two mechanisms would predict similar VOC control requirements when used in EPA's EKMA procedure, and, if not, to determine why the mechanisms disagreed.

This comparison task involved six activities: (1) comparison of rate constants for the portion of the mechanisms considered to be "well known", and a reconciliation of the differences, (2) a complete re-assessment of the photolytic rates used to simulate the UNC outdoor chamber, (3) conducting a two-month outdoor chamber experimental program comparing five methods for measuring formaldehyde and three methods for hydrogen peroxide - products that the mechanisms were not predicting well, (4) simulating a selected set of UNC chamber experiments using identical inputs for both mechanisms, (5) analysis of ambient NMOC data to determine default hydrocarbon compositions for use in EKMA, (6) comparison of the mechanisms' performance in a series of State Implementation Plan scenarios using the EKMA method. An overview of each of these tasks is described below.

Rate Constant Comparison

When the inorganic and carbonyl reaction sets of both mechanisms were compared in the early part of the program, significant differences were found. The differences were reconciled with the mechanisms' authors and the resulting versions of the mechanisms are now comparable in their inorganic and carbonyl sections.

Photolytic Rate Calculation

As part of the experimental portion of this program, a computerized, portable, spectroradiometer was used to collect a large body of spectral irradiance measurements outside and inside the UNC chamber. These data showed that neither mechanism developer had correctly calculated in-chamber photolytic rates, nor had the UNC researchers supplied sufficient information to estimate the rates properly. In addition, analysis of these spectral data showed that the method that had been used for more than 12 years, a look-up table based upon Peterson's calculation of actinic flux, provided a poor approximation of the radiation field at the UNC site because of the effect of aerosols on the radiant flux. In response to these findings, a new radiation transfer model was developed. This model uses the World Radiation Center extraterrestrial solar flux and a one-layer approximation of atmospheric transmission due to Rayleigh scattering, total column ozone, total column water vapor, and aerosol absorption and scattering to compute the surface spectral

irradiance and surface spherical spectral irradiance. It incorporates three aerosol models that are sensitive to relative humidity and composition. In addition, the model includes two broad-band models, one for the total solar radiation (TSR) sensor and one for the Eppler ultraviolet (UV) radiometer.

Studies were conducted to determine the solar spectrum optical properties of the TFE Teflon film used to enclose the UNC chamber. Additional studies were conducted to determine the spectral albedo of the reflective chamber floor. Chamber geometry relative to the sun's path was re-assessed and a full chamber transmission model was developed. By operating radiometers inside and outside the chamber, sufficient information was collected to develop an in-chamber actinic flux model.

The TSR and UV radiometer data for 286 days from 1976 to 1986, were re-assessed and modeled with the broad-band radiation models. Cloud effects were then introduced into the model and correction factors for the theoretical model were derived for each day. Finally, the actinic flux (spherical spectral irradiance) at 16-minute intervals for the 286 days was calculated.

New Formaldehyde and Hydrogen Peroxide Data

In past tests by the developers, the mechanisms have generally failed to predict the observed formaldehyde (HCHO) product profiles in the UNC chamber data. The model developers suggested that the UNC HCHO data could be too high by a factor of two. Further, in a previous study conducted at UNC, a laser system was used to monitor hydrogen peroxide (H_2O_2) and the results were difficult to understand given today's knowledge of H_2O_2 chemistry. Therefore, an intercomparison study of five HCHO methods and three H_2O_2 methods was undertaken. Research groups from EPA, NCAR, Texas Tech University, UniSearch, Inc., and UNC set up their HCHO methods at the UNC smog chamber laboratory to collect HCHO data during chamber experiments over a two-week period. The NCAR, Texas Tech, and UniSearch groups also made H_2O_2 measurements.

The results show that HCHO monitoring methods can perform nearly identically, if the calibration sources are reconciled. The standard UNC HCHO method was shown to be in very close agreement with the other methods and,

not as suggested by the modeler subject to a positive interference of up a factor of two.

The hydrogen peroxide data from three measurement methods were in good agreement in the range 0-800 ppb H_2O_2 . The half-life for H_2O_2 in the UNC chamber, however, was extremely short ranging from 1 hour in the dark to 10 minutes in the noon sun. Furthermore, the addition of 350 ppm CO , which should have increased the half-life by recycling hydroxyl radicals back to hydroperoxy radicals, actually accelerated the loss of H_2O_2 dramatically. Most confusing of all, during the accelerated decay of the 350 ppb H_2O_2 there was loss of 55 ppm CO .

Similarly, during experiments designed to produce large quantities of H_2O_2 from chemical reactions of VOC and NO_x , only 4-10 ppb was ever observed. The assumption is that the in-situ-produced H_2O_2 also decays rapidly, and therefore high levels are never reached in the chamber.

Speculation as to the mechanism of H_2O_2 loss in the UNC chamber includes direct absorption on the walls, absorption into a thin water film on the walls, or a catalytic process involving the absorbed nitrogen species, CO , and H_2O_2 that rapidly consumes H_2O_2 and, by a chain process, CO .

The basic conclusion reached from these results is that the chamber walls in the UNC chamber are sufficiently reactive towards H_2O_2 that it is not possible to produce data to test mechanism pathways for generating H_2O_2 . Based upon the nitric acid data reported by the UniSearch laser system, nitric acid also is probably lost almost as rapidly to the walls.

Demonstration Modeling with New Inputs

To demonstrate the effect of different mechanism rate constants and reaction products, 22 dual UNC chamber experiments were modeled with both mechanisms using the same simulation conditions. The 22 case days included 1 single hydrocarbon component experiments and 12 mixture experiments. The following points were noted:

1. Both mechanisms show excellent agreement with experimental data for HCHO- NO_x systems.
2. In ethylene experiments, the mechanisms show good fits to NO , NO_2 , O_3 , and ethylene decay profiles.

Both mechanisms, however, underpredict the formation of HCHO and CO.

3. Neither mechanism does well at simulating 1-butene experiments on cool days; both mechanisms are much too reactive in producing ozone. CAL, however, produces an excellent fit to t-2-butene. CB4's surrogate of two ALD2s for t-2-butene shows too little reactivity throughout the simulation, but does begin to converge towards the correct ozone concentration near the end of the experiment.
4. CB4 does better than CAL in simulating toluene experiments; CAL is better than CB4 in simulating xylene experiments. Both mechanisms, however, overpredict HCHO in these systems by nearly a factor of two or three. Both mechanisms predict PAN fairly well in the xylene experiments, but both overpredict PAN in the toluene experiments with CAL predicting nearly twice as much PAN as CB4. Both mechanisms overestimate the reactivity of o-xylene compared to m-xylene and both underpredict CO formation in these systems.
5. In a HC mixture with no aromatics, both mechanisms provide excellent fits to NO, NO₂ and O₃, and correctly simulate the decay of propylene, ethylene, n-pentane and n-butane. HCHO is underpredicted, however (by 50% in the case of UNCMIX).
6. In the SynAuto HC mixture experiments, both mechanisms provide excellent fits to NO, NO₂ and O₃, and to propylene, ethylene and toluene decays. HCHO predictions tend to be much closer, suggesting a compensation between an overproduction in the aromatics chemistry and an underproduction in the olefin chemistry.
7. Both mechanisms are uniformly too reactive in generating ozone for the SynUrban mixture experiments, even though the propylene, ethylene, and toluene decays are well fitted.

Urban Hydrocarbon Composition

The application of the two mechanisms in EKMA control strategy calculations requires the specification of an urban hydrocarbon composition. Previously, SAI had supplied the so-called "default" hydrocarbon composition, but new data from several EPA projects to monitor hydrocarbons in ambient air and to

speciate the hydrocarbons using gas chromatography provided a new data base. An analysis of this data base was done by OAQPS and another was done by ERT as part of the CAL mechanism development. The carbon fractions obtained in these two efforts were significantly different. A new analysis of the data was undertaken for both the CB4 and CAL mechanisms using a single set of assumptions and speciation guidance from the model developers. A total of 66 city-years of detailed HC data (comprising 773 individual analyses) was available. A total of 56 HC samples collected aloft by Washington State University was also added to the data base. These data were speciated into the carbon fractions for hydrocarbon species used in the two mechanisms. Fractions for each mechanism are reported for each city-year, for five clusters of city years with similar internal composition, and for the total. The five clusters were determined using two forms of cluster analysis. Multiple regression was also used to confirm the overall average carbon fractions. Four analyses of automobile exhaust from the UNC autoexhaust smog chamber study were also speciated to assist modelers in testing chamber data in the same manner as atmospheric data. Recommendations for default carbon fractions for both mechanisms were developed and the fractions have now been included in the computer code for OZIPM4. Selected simulations using both mechanisms were also conducted to demonstrate the effects of HC composition on ozone predictions.

EKMA Control Calculation Comparison

A number of EKMA calculations were carried out with both mechanisms using the OZIPM4 program. The conditions selected were derived from cases used for State Implementation Plan development. Fourteen cases were simulated for Nashville, Tulsa, Puget, Washington DC, Phoenix, Philadelphia, and New York. Baseline ozone values range from 0.13 to 0.234 ppm and calculated VOC reduction estimates ranged from 13% to 57%. Sometimes CB4 predicted the higher control requirement and sometimes CAL predicted the higher control requirement. The two mechanisms gave control requirements that differed at most by only 7%.

In a series of sensitivity tests, the CB4 mechanism showed more sensitivity to external radical sources (e.g. hydrocarbon aloft) than did CAL. CB4 calculated

controls also exhibited a much larger sensitivity to temperature than did CAL. CB4 showed a 10% change in control requirements for a 5°F change in simulation temperature while CAL showed only a 5% change for the same temperature variation. This sensitivity is directly related to the different temperature dependencies used in the two mechanisms to describe the formation of PAN. CB4 uses a much higher negative value for the activation energy than does CAL. The CB4 value is based upon fits needed to simulate winter experiments in the UNC chamber, whereas the CAL value is based upon the limited temperature range of the kinetic data for this reaction that are found in the literature. The large value used in the CB4 must be regarded as speculation until experimental tests confirm or refute the value. This may limit the application of these mechanisms to ambient temperatures above about 75 degrees F.

Conclusions

In this project, two state-of-the-science photochemical mechanisms were compared. Many differences occurring during the development of the mechanisms were examined and resolved where possible. Other activities needed to obtain common inputs, such as photolysis rates, were undertaken.

The mechanisms were compared against chamber experiments. Both mechanisms simulate HCHO/NO_x systems nearly perfectly. Both mechanisms simulate ethylene systems reasonably well, but require variable "wall radical" sources to fit ozone, NO_x, and ethylene data. Neither mechanism fits HCHO product data in these systems. For organics more complex than ethylene, the two mechanisms do diverge and the quality of the fits varies. For example, CAL is better for propylene, neither is very good for 1-butene, but CAL is much better for trans-2-butene. CB4 is better for toluene and CAL is better for xylene. Neither is very good at predicting PAN or HCHO formation from aromatics. Both are good for simple urban-like mixtures, and both are good for synthetic autoexhaust. Both, however, are too reactive for synthetic urban hydrocarbon mixtures. Both mechanisms give similar predictions of control requirements in EKMA applications, but CB4 is very temperature sensitive.

Finally, neither mechanism is superior to the other in either fitting smog chamber data or in predicting VOC control requirements. Thus the choice between them must be made on other grounds.

H. E. Jeffries, K. G. Sexton, J. R. Arnold, and J. L. Li are with the University of North Carolina, Chapel Hill, NC 27514.

Marcia C. Dodge is the EPA Project Officer (see below).

The complete report consists of four volumes, entitled "Validation Testing of New Mechanisms with Outdoor Chamber Data:" (4 volume set: Order No. PB 89-159 024/AS; Cost: \$81.00)

"Volume 1. Comparison of CB4 and CAL Mechanisms," (Order No. PB 89-159 032/AS; Cost: \$28.95)

"Volume 2. Analysis of VOC Data for the CB4 and CAL Photochemical Mechanisms," (Order No. PB 89-159 040/AS; Cost: \$21.95)

"Volume 3. Calculation of Photochemical Reaction Photolysis Rates in the UNC Outdoor Chamber," (Order No. PB 89-159 057/AS; Cost: \$21.95)

"Volume 4. Appendixes to Photochemical Reaction Photolysis Rates in the UNC Outdoor Chamber," (Order No. PB 89-159 065/AS; Cost: \$21.95)

The above documents will be available only from: (Costs subject to change)

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Atmospheric Research and Exposure Assessment Laboratory

U.S. Environmental Protection Agency

Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use \$300

EPA/600/S3-89/010

000085833 PS
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604