Conference Summary

International Conference on Atmospheric Chemical Mechanisms

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by

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The International Conference on Atmospheric Chemical Mechanisms was held on December 6-8, 2006, in Davis California, under funding from the California Air Resources Board, with additional support provided by the American Chemistry Council. The overall objectives of the conference were to foster continued research and development of atmospheric photochemical mechanisms for modeling formation of ozone, particulate matter (PM) and hazardous air pollutants. Specific objectives include: identifying strengths and weakness of existing mechanisms; discussing and encouraging improvements in mechanisms accuracy and efficiency; exploring the role of new scientific tools for developing improved mechanisms; discussing methods to condense detailed mechanisms for use with 3-D models; reviewing techniques for implementing mechanisms in models; and envisioning future mechanisms for regulatory models. Specific questions to be addressed included short term research needs and implementation issues and longer term needs for developing improved mechanisms and assuring continued progress in the future. The conference had approximately 100 participants from various universities, research institutions and regulatory agencies, and included participants from the U.S, Canada, Europe, and Australia.

The conference consisted of several sessions followed by a panel discussion and a summary presentation, and there was also a poster session. The conference program giving a listing of the presentations and presenters is given in Appendix A. Brief summaries of major points made in the oral presentations and the panel discussion and associated comments from the participants are given in the following sections. These are organized by general topic, and not necessarily by order of presentation. For details concerning the individual presentations, the reader is referred to the URL given at the bottom of the conference program table in Appendix A, from which all of the oral presentations that were given can be obtained.

Policy Summary

Presentations were given concerning the regulatory perspectives in California, the U.S. EPA, and in Europe. The regulatory approach as related to the use of atmospheric chemical mechanisms differs in the United States and Europe. In the U.S., the models are used primarily for the design and evaluation of potential emission control strategies that would lead to the attainment of health-based Ambient Air Quality Standards. Historically, in the United States there was a choice between controlling all possible sources to the best extent possible (e.g., by using the Best Available Control Technology or BACT) and setting and achieving health-based performance standards (e.g. National Ambient Air Quality Standards or NAAQS) that would allow a more tailored approach to emission control. The current program in the United States is a combination of both choices, with the latter choice being the driving force. Thus, air quality models have become an indispensable component of the regulatory program in the United States. Model accuracy is important because the models are used to evaluate candidate, expensive control strategy alternatives. Mechanisms are important components of such models because they are important to predictions of secondary pollutants, which is the basis of many of the standards. Mechanism verification (to the extent possible) is important because errors in the model predictions can lead to inappropriate policy choices.

In Europe, it appears that the focus is on pollutant reduction as the primary goal, rather than meeting specified standards. The specific pollutant reductions that are implemented in the regulations are determined primarily by political negotiation, with model predictions apparently not playing a central role in determining strategies. Emissions inventories are a large focus for policymakers in Europe, and much work is being carried out in this area. However, "integrated assessment" modeling is used for cost-benefit analyses, to aid the political process.

Regulatory Modeling Issues and Applications

Both California and the U.S. EPA are increasingly interested in models representing multiple types of pollutants at once (e.g., "one atmosphere" or "multi-pollutant framework"). (However, there is a concern that this may not be the optimum approach -- models focusing on specific pollutants may be more efficient.) There is also an interest and desire to model multiple spatial and temporal scales. The modeling domains have become much larger, and annual average PM standards are requiring models to be run for an entire simulated year or longer. These are placing a greater demand on the complexity and level of detail of the models and the chemical mechanism, and also on the need for computational efficiency. In addition, the new air quality standards are requiring reduced uncertainties, which is placing additional demands on the models and mechanism. Modeling toxic air pollutants will also require a significant increase in mechanism detail.

The EPA's research budget in recent years has focused to an increasing extent on PM research, with fundamental oxidant research being de-emphasized. The reduced funding of gas-phase mechanism development is a concern not only because of the role of gas-phase chemistry in PM formation (and the desire for a "multi-pollutant framework") but also because of new relationships being found between O_3 and mortality. Integrated strategies are needed for hazardous air pollutants and criteria pollutants. There is also a concern about exposure modeling now, with more focus on resolution and perhaps insufficient concern about chemistry.

One modeling application where the chemical mechanism is important that is used in both the United States (particularly California) and Europe is relative reactivities of VOCs. Reactivity scales have the advantage that they can "represent a lot of chemistry in a single number". However, that number can change depending on conditions, and also with time in multi-day scenarios. Calculation of these scales requires a detailed chemical mechanism because the focus is on individual compounds. They are used in some California regulations, and are being calculated for policy-relevant assessments in Europe. Reactivity scales calculated for Europe using MCM and a European multi-day trajectory correlate reasonably well with those calculated using SAPRC-99 in one-day box model scenarios (as used in California regulations), though there is some scatter, and in some cases significant differences in day 2+ effects. Reactivity scales can also be calculated for emissions sources for more directly policy-relevant applications.

Source apportionment is another modeling application of interest to policymakers. Chemical mechanisms necessarily play an important role if the interest is in secondary pollutants such as O_3 or secondary PM. One presentation discussed using chemical mechanisms in source apportionment modeling of secondary nitrate and organic aerosols (SOA). The method involved labeling species and products in the mechanism so secondary reactions and products can be traced back to their sources. (This involves adding duplicate species to the mechanism for particular sources -- which increases the number of reactions and species in the mechanism but not the "stiffness".) The results suggest we may be "missing the boat" on some sources of SOA, but it is not clear what. However, source apportionment using this method is only as accurate as the model or the mechanism -- adequate model evaluation is critical. An alternative method of conducting source apportionment is adjoint sensitivity analysis, which is discussed below.

General Modeling Issues and Analyses

Air quality modeling has a number of considerations in addition to chemical mechanisms, including input data (emissions, meteorology, etc.), computational aspects, performance evaluation, and sensitivity and uncertainty analysis. Although discussion of emissions was beyond the scope of this meeting, this is an important input, and directly related to chemical mechanism needs. For example, solvents are >50% of the anthropogenic VOC emissions inventory, and they encompass a wider variety of compounds than in the other sources that are generally used as the basis for current mechanisms. These compounds need to be represented and tracked better in models, and this may be an area where mechanism development work is needed.

There are thousands of types of emitted VOCs, and mechanisms differ in numbers of explicitly represented VOCs, lumping strategies, and level of detail of products. The issue of speciation of NO_x, though simpler in that only three compounds are usually involved (NO, NO_2, and HONO), is also an important model input. PM is also emitted directly and needs to be speciated appropriately, and models differ in how this is represented. It is generally believed that emissions uncertainties are as large as or larger than gas-phase mechanism uncertainties.

Care must be taken in model performance evaluation. Mechanisms should be evaluated separately from their use in 3-D models, such as using environmental chamber data as discussed further below. (However, sometimes evaluations against ambient data may provide insights beyond what can be obtained from chamber experiments -- a good example being the HONO issue that was discussed at the meeting.) The temptation to change model inputs based on mechanism performance is a concern, because it is a likely source of compensating error.

Sensitivity analysis is an important component to model evaluation, to understanding model performance, and to error analysis. Error analysis (sensitivity analysis combined with uncertainty analysis of the inputs) is important to assessing model outputs for policy applications and also for guiding research for chemical mechanisms and reducing uncertainties for inputs, and should be given more attention than it is. Several error analysis methods have been applied to chemical mechanism uncertainties. In general for ozone predictions the most important uncertainties depend on scenario conditions, particularly degree of VOC or NO_x-limitation, but the most important uncertainties were the OH + NO_2 rate constant, the absorption cross sections and quantum yields for NO_2, the photolysis of O_3 to O^1D, and PAN chemistry. A problem with such uncertainty analysis is analyzing uncertainty caused by what is potentially missing in the model. This can be addressed by evaluating the sensitivities to adding new processes to a model – the limitation is that the new process must first be hypothesized.

There appear to be two general approaches for conducting sensitivity analyses in 3-D models, beyond simple "brute force" approaches that are usually not practical for comprehensive analyses. The decoupled, direct method (DDM) solves extra model equations to calculate sensitivity along with concentrations, to produce source-based sensitivities. This produces sensitivities of many outputs to a limited number of inputs, which can be used, for example, to assess spatial distributions in changes of O_3 to overall changes in total NO_x or VOC emissions. The adjoint sensitivity analysis procedure (ASAP) solves extra model equation similar to DDM, but does so backwards in time to produce receptor-based sensitivities producing sensitivities of a limited number of outputs to a large number of inputs. This can be used, for example, to determine spatial distributions of emissions sensitivities to ozone at a particular receptor, or determining sensitivities of a receptor to multiple inputs such as mechanism parameters.

Another difference in sensitivity analysis approaches, whether DDM or ASAP, is whether sensitivities are assessed with respect to multiplicative scaling of existing parameters, producing "baseline" sensitivity", or to additive perturbations in inputs, referred to as "potential" sensitivities. Most sensitivity analyses are of the former type, which are useful for assessing sensitivities to existing inputs; the latter can be used to assess effects of new emissions sources, and also effects of adding processes to the mechanisms or models that were not there before.

Sensitivity assessment algorithms can also be used for 3-D variable optimization or chemical data assimilation in 3-D models. Assimilation of observations into chemical transport models can be useful for top-down estimates of the emissions inventory and potentially for tuning mechanisms (though this must be done carefully to avoid introducing compensating errors -- see above), and can potentially improve analysis of input fields and model forecasting skills. The tools are reasonably mature and are being used in scientific studies to assimilate field campaign data. Near term research directions include assimilation of aerosol observations, assimilation of satellite data, and developing methods to "correctly" invert emissions and boundary input. Longer term research directions include developing advanced algorithms, using models to design field campaigns, and using observations to improve chemical mechanisms. The latter application is discussed further in the "Process Optimization Methods" section, below.

Process analysis is an approach for probing model performance that goes beyond sensitivity analysis. This involves tracking the internal processes that occur in models (such as rates of individual reactions, fluxes from one cell to another, etc.) during the course of the model simulation, and then analyzing the results in post-processing steps. Process analysis is potentially useful for examining why different mechanisms perform differently. Processes that can be examined include the radical and NO_x cycles involved in O_3 formation, and tracking relative importances of chemistry vs. transport vs. initial conditions in explaining simulated concentration changes. Recent algorithm improvements permit using Lagrangian models within an Eulerian model to track chemical evolution in plumes. Process analysis can also be useful for quality assurance, and was successfully applied to locate errors in models regarding inappropriate representation of various processes. Other potential application is source apportionment and simulations of industrial upsets. Process analysis research and its applications that need to be investigated further include its use for mechanism reduction and for better communication of modeling results to decision makers.

Chemical Mechanisms - General Issues

Chemical mechanisms serve several functions besides serving as an operator within models, since they serve as an archive of contemporary knowledge, an explanatory vehicle for our knowledge or ignorance, and a device for communicating scientific notions. Ideally mechanisms can serve as a link between laboratory studies and models; and this is an objective for many detailed or explicit mechanisms. However, "models are always simpler than the real world", and this simplification is achieved by intentional generalization, distortion, or deletion, or unintentional omissions or misrepresentation of processes that are unknown. Evaluation -- testing to see if the mechanism is useful for answering questions -- is important, but it is *not validation*. Models can give the "right answer for the wrong reason" because of compensating errors. Compensating errors that remain undetected provide a significant risk for failure in modeling applications.

Fully explicit mechanisms do not have inherent validity, and can give incorrect predictions because of errors or omissions due to limitations in our knowledge. For this reason, "engineering mechanisms" that are designed to simulate available observations without necessarily representing the underlying chemical detail may have more predictive capabilities -- at least for the range of conditions for which they were evaluated. However, use of such mechanisms beyond the conditions where they were evaluated is problematic, and they are less useful as an archive of knowledge, a link between laboratory studies and models, or a basis for expansion to a multi-pollutant framework.

Current gas-phase mechanisms used or being implemented for use in the United States (specifically, CB4, CB05, and SAPRC-99, discussed below) have been found to give somewhat different predictions of O_3 in regional models. The differences seem to be the greatest in urban areas, where O_3 is the most sensitive to VOCs. Houston seems to be a particularly mechanism-sensitive area when it comes to O_3 predictions, and regional modeling results that were presented suggest that this may also be the case for Chicago. The mechanism differences give rise to differences in predictions of effects of VOC and NO_x control, at least in Houston and Chicago, and this may be the case for other urban areas as well. These differences persist even after aromatics are removed, and are attributed to differences in predictions of radicals and radical precursors, such as sources of aldehydes in SAPRC that are not in CB4. On the other hand, the current mechanisms used in the U.S. (at least SAPRC-99 and CB4) give very similar predictions of O_3 (and effects of VOC and NO_x controls) in NO_x-limited regions, which represent by far the largest geographical extent in the United States. However, the relatively small spatial extent of urban areas does not mean that O_3 predictions in such areas are unimportant.

In terms of predictions of absolute O_3 formation in urban areas, the concentration order is SAPRC-99 > CB05 > CB4. In terms of order of development, CB4 was developed first, followed by SAPRC-99 a few years later, with CB05 being developed relatively recently. This suggests that mechanisms may be tending to agree more as our knowledge improves. However, this does not rule out the possibility that the newer mechanisms are making the same mistakes, since they are based on the same body of knowledge.

There was relatively limited discussion of comparing ozone predictions of other mechanisms besides the three discussed above, though Derwent stated that the MCM (the semi-explicit mechanism widely used in Europe, discussed below) gives almost identical ozone predictions as CB4 in trajectory model simulations of long-range transport over Europe. However, SAPRC-99 and CB4 give very similar predictions over large areas of the U.S., and it is unknown whether the differences between MCM and CB4 would be greater if the comparison focused on O_3 formation in urban areas such as Chicago or Houston, which were found to be more mechanism-sensitive.

Emissions processing is of potential concern when comparing chemical mechanisms in model calculations. Emissions processing for different mechanisms is not straightforward, and current procedures may not necessarily result in consistent speciation assignments or even use of the same inventories. Care must be taken in this regard when conducting mechanism intercomparisons. However, the large differences in Houston were found using emissions processed using Carter's speciation database, which is designed to address these speciation consistency issues.

Description of Current Gas-Phase Mechanisms

The gas-phase mechanisms described in the conference are summarized below in approximate order of comprehensiveness and level of chemical detail. Combined gas-phase and condensed phase mechanisms and purely condensed phase mechanisms that were also described at the meeting are described in the following section.

Master Chemical Mechanism (MCM). The objective in the development of this mechanism is to represent the state of the art, serve as a "benchmark" organic mechanism, and provide a link between laboratory studies and models. This is a "near explicit" mechanism for a large number of emitted VOCs and also their major oxidation products. It is simplified somewhat by excluding the less important pathways and products. The MCM is manually generated using a standard protocol (that is published), which includes various semi-empirical estimation methods. The MCM is widely used in Europe for research and sometimes policy applications, and is becoming more widely used in the United States. (However, because of its large size it is not generally used in 3-D modeling applications in the U.S, though as discussed later it can be used in such applications.) This mechanism is presently not fully peer reviewed (though its protocols are published in peer-reviewed journal articles), but there is work on addressing this problem with an advisory panel. The aromatics mechanism in MCM performs poorly simulating chamber data and is an area where significant improvement is needed. This mechanism is available and is described at its website at http://mcm.leeds.ac.uk/MCM/, which has recently been enhanced.

SAPRC Mechanisms. The objective in the development of this mechanism is to represent the state of the art and to give accurate predictions of the atmospheric impacts of the many different types of emitted organic compounds that are of interest. Because the emphasis is on accurate predictions, the performance of the mechanism in its evaluation against chamber data is given equal or greater priority than consistency with the available laboratory data. The mechanism has a detailed version that represents the many emitted compounds explicitly, and a lumped version for airshed models that uses a more limited number of lumped species whose mechanisms are based on the detailed mechanisms for the distribution of compounds they represent. The formulation of the detailed version is similar to the MCM, except that the reactions of the secondary products are lumped. A *mechanism generation system* is an important feature of its development; the objective and general approach is similar to the MCM development protocol, except it is automated. The current mechanism in use is SAPRC-99, but an updated version is in development, and should be available in early 2007. The aromatics mechanism formulation and performance in SAPRC-99 is unsatisfactory, and improving this is an important priority in the mechanism update effort, as well as a complete update of the rate constants. As part of this process a more explicit aromatics mechanism has been developed that gives somewhat improved simulations of the available chamber data, but it is still not fully consistent with available laboratory data.

Other Self-Generated Mechanisms. The group at University of Paris is working on developing a completely self-generating approach to derive fully explicit mechanisms for the primary VOCs and all their oxidation products. It uses protocols and approximations similar to those used to derive the MCM and the SAPRC mechanism generation system, except that (unlike MCM) most of the reaction routes are represented and (unlike SAPRC) essentially all the product reactions are also represented. This requires assimilation of laboratory data with estimates. It can be used to evaluate the ultimate fate of carbon when VOCs are fully oxidize, and how organic reactivities evolve after the first reaction step. The eventual goal is to ultimately extend this to generate mechanisms for formation of SOA, which will require methods to estimate volatility. Methods to systematically reduce these generated mechanisms are also being developed. Presently mechanisms have been developed for representative individual compounds such as hydrocarbons and their oxidation products (not aromatics), but this mechanism is not as comprehensive as SAPRC or MCM in terms of the types of VOCs that can be represented.

RACM Mechanisms. The RACM mechanisms are updated and somewhat expanded versions of RADM2, which was developed to predict regional atmospheric chemistry and acid rain formation. These are moderately condensed mechanisms that are extensively used in Europe as an alternative to the much larger MCM. RACM2 is currently being developed as an update to RACM1, with new schemes for aromatics, biogenic VOCs, and acetone, and other updates. It gives differences in predictions of radical levels in simulations of forest canopies relative to RACM1, though predictions of indicator ratios are similar. Substantial nitrate and OH radical formation occurs in forest canopies, and it is important that mechanisms represent these processes properly. This is an important objective in the current RACM2 development and evaluation effort.

Updated Carbon Bond Mechanism (CB05). The Carbon Bond 4 (CB4) mechanism is relatively condensed mechanism that is widely used in regulatory and other applications. It is widely used in part because of its relatively high computational efficiency. An updated and slightly expanded version of this mechanism, designated CB05, has recently been developed, and is being evaluated as a replacement for CB4 for regulatory modeling. The rate constants have been completely updated based on current evaluations, the inorganic reaction set was expanded to better represent urban to remote conditions, and NO_x recycling reactions were added. The latter is considered to be an important feature of the new mechanism in better representing multi-day effects. This mechanism has been evaluated against the database of chamber experiments, though it was not modified as a result of this evaluation. The performance in simulating most experiments is similar to or better than that of CB4 or (except for aromatics) the condensed version of SAPRC-99. The aromatics mechanism was not significantly modified and neither CB4 nor CB05 perform satisfactorily in simulating most of the aromatics chamber data, and improvements are needed in this regard. However, experiments in different chambers can yield different evaluation results, and there is a need to study the sources of these differences before evaluating mechanisms with these data. There is also a need for experimental studies of NO_x recycling from organic nitrates.

Generic Reaction Set (GRS) Model. This is not really a mechanism, but a parameterized model based on observations that is used to predict the dependence of O_3 on reactive organic gases (ROG)s and NO_x. The objective is to use it for screening models, to efficiently do multi-episode (or all year) modeling to determine which episode is best to use for further study with full mechanisms. The GRS was developed based on simulating smog chamber data, and for that reason can perform better than some detailed or explicit mechanisms in simulating some of the data. Some complexity has been added to improve performance in simulating the data and extend treatment of key radical species. The current version (GRS2) now has 22 "reactions". However, the GRS model does not perform very well in simulating O_3 in rural areas, and tends to overestimate O_3 under low ROG/NO_x conditions. For ROG/NO_x ratios between 3.5 and 15.6, GRS2 predicts observed O_3 to within ± 10-20%.

Mechanisms and Models for PM Formation

Several combined gas-phase and condensed phase mechanisms, whose primary objective is prediction of PM formation, were described at the meeting. In general, these consist of a gas-phase mechanism joined with a partitioning model and a condensed phase reaction mechanism or model. These mechanisms have varying levels of detail. Gas phase mechanisms need to be expanded to support PM predictions. Specific mechanisms and models that were presented are briefly summarized below.

LM-ART is an example of a comprehensive chemical transport model for predicting formation of aerosols. RADM2 is used as the starting point for the gas-phase mechanism. The model can predict radiative characteristics of aerosols, which are affected by the chemical composition. The model represents various modes of aerosol formation, based on the chemical nature of the particles, such as sulfate, nitrates, soot, mineral dust, etc, and includes representations for heterogeneous reactions. There are a number of areas of improvement that are needed, which are applicable to all such models, and therefore are discussed separately below.

CACM/MCMPO. CACM is a gas-phase mechanism that was developed using SAPRC-99 as the starting point, but made more explicit to support secondary PM modeling. MCMPO is a gas-to-particle partitioning model that treats mass transfer to organic aerosol using an equilibrium approach, but considers partitioning to aqueous aerosol separately. Recent work has been carried out to adapt this mechanism to modeling PM formation from terpenes, and this has included some evaluations using environmental chamber experiments. This mechanism has a representation for the NO_x-dependence of SOA formation from aromatics, but this modeled dependence is not as strong as observed in some recent chamber experiments. This mechanism and model has been implemented in CMAQ and has been used to model SOA formation in the Eastern US domain and for other applications.

The Kamens Group is developing predictive kinetic models for aerosol formation, based on a gas-phase mechanism to predict formation of condensable products, and representing partitioning to the gas phase, using a kinetic approach. The specific examples of toluene and terpenes were discussed, and the mechanism gives reasonable simulations of PM formation and gas-phase species in several smog chamber experiments. Hydration reactions of glyoxal are important -- it gets hydrated in the aqueous phase and doesn't return to the gas phase -- and the PM product distribution changes as a function of the amount of aerosol present.

Donahue discussed an alternative approach for modeling secondary organic aerosol formation. Organic emissions are treated as semi-volatile, with a range of vapor pressures that are represented in the model with an "ensemble" of vapor pressure bins with wide ranges of magnitudes. The objective is to describe the full volatilities of emissions -- from generation to generation, and to represent chemical "processing" or organics. Multi-step processes occur over lifetimes of ~7 days. The distribution of volatilities change as processing goes on. This model tends to give lower urban/regional gradients in aerosol formation than other PM models. We need to consider what happens to individual compounds, and at what point vapor pressures start going *up* rather than *down* as chemical processing goes on.

Full aqueous phase mechanisms, such as the CAPRAM mechanisms, can be even more complex than the gas-phase mechanisms. Many of the same radical + organic processes occur, plus additional ones such as ion reactions that do not occur in the gas phase. Data are being obtained concerning relevant radical + organic reactions in the gas phase, and also data for developing estimation methods. Peroxy + peroxy reactions are important in solution, since the NO is not present in the aqueous phase to react with these radicals as occurs in the gas phase. The CAPRAM mechanism is described further and is available at http://projects.tropos.de/capram/. This mechanism can be incorporated into models, but condensation would probably be beneficial for efficient implementation. An automated generation approach may be useful, but work in this area is not currently underway.

Uncertainties and areas of needed improvements and research in mechanisms for PM formation were discussed in several presentations. The issues that were brought up include the following:

- Polymerization or oligomerization inside particles is a major area of uncertainty that is ignored or probably not adequately treated by current models. A related issue is partitioning of volatile compounds such as glyoxal, and reaction in the condensed phase to form non-volatile species.
- The heterogeneous formation of HONO and hydrolysis of N_2O_5 are important uncertainties that affect gas-phase chemistry as well as PM.
- It is uncertain whether mineral dust or other forms of PM has an effect on O_3 formation.
- 3-D models need improvements in treatments of nucleation of sulfuric acid, halogen species, and organics.
- An important uncertainty is how well PM mechanisms perform in the actual atmosphere, which is much more complex than chamber experiments. The mechanisms and models indicate that the

nature of the PM that is present can significantly affect PM formation and the heterogeneous reactions that are represented in the model.

Environmental Chamber Data and Mechanism Evaluation

As discussed above, our knowledge of atmospheric chemistry is insufficient to rely on the predictions of mechanisms a-priori, and mechanisms need to be evaluated. Modeling environmental chamber data provides the most straightforward means to evaluate mechanism, though modeling ambient measurements also plays an important role because the chambers do not completely represent atmospheric conditions. For instance, environmental chamber data have characterization uncertainties such as chamber effects that mechanism evaluators need to take appropriately into account to avoid compensating errors. Modelers also need to be aware of measurement uncertainties and biases in evaluations using either environmental chamber or ambient data.

There are several environmental chamber databases and environmental chambers currently in operation providing data relevant to mechanism evaluation, mainly in Europe and the United States, but also in Australia. There are differences in the use of chambers in these regions. In the United States, the emphasis has been on the use of chambers for evaluating the predictive capabilities of mechanisms for use in modeling for policy studies. In Europe, the emphasis has been more on the use of the chamber for mechanistic studies and to evaluate and support measurement methods for use in field campaigns, and there is greater emphasis on application of advanced analytical methods. The Australian chamber database has been used for primarily developing the GRS mechanism, which has already been discussed above. The remainder of this discussion will focus on the American and European chambers.

Europe has a number of chamber groups, each operating more or less independently, though there are collaborations. Eurochamp is a 3.9 million Euro program for 5 years, and distributed over 12 laboratories, to coordinate European chamber research. (Its web site is at http://www.eurochamp.org). This project includes work on a well-documented chamber database, which may be available next spring. Another important objective is initiating effective interdisciplinary collaborations between atmospheric scientists and other disciplines. Joint projects include development and refinement of analytical methods and development of chemical modeling techniques. European smog chambers are being used for studies of radical balance, and data have been obtain concerned the heterogeneous formation of HONO. Model predictions of radical levels are not satisfactory, and there is need to obtain data to elucidate this. The major European chambers used for gas phase studies are SAPHIR and EUPHORE, and both have been used for mechanistic studies of various systems. Several European smog chambers are also involved with aerosol research. Most mechanism evaluation studies in European chambers have focused on use of the MCM, though RACM has been used in some studies.

The U.S. Environmental chamber database includes a very extensive set of chamber experiments on a wide variety of compounds carried out at the University of California at Riverside (UCR), a fairly extensive set of outdoor chamber experiments at the University of North Carolina (UNC), and a limited number experiments in the now-dismantled TVA chamber. The UCR chamber experiments serve as the primary basis for the evaluation of the SAPRC chemical mechanisms, discussed above, including experiments for evaluating mechanisms for >80 types of compounds and various mixtures. The new UCR EPA chamber is producing mechanism evaluation data at lower NO_x levels than previously available, and is also providing data on PM impacts. Significant differences in model performance are seen in simulating this dataset with the SAPRC-99, preliminary updated SAPRC, CB4, and CB05 mechanisms. There have been some uses of UCR chamber data for evaluating MCM (not discussed at this meeting), but the primary use of this database to date has been evaluating SAPRC and other mechanisms for U.S. regulatory applications.

The new UCR EPA chamber has also been used to carry out experimental studies of indicator ratios for sensitivities of O_3 to VOC and NO_x controls, whose utility for this purpose has previously been deduced only by modeling. The model was found to underpredict O_3 at low ROG/NO_x, fit HNO_3, underpredict H_2O_2 and significantly underpredict OH (though the latter may be due to instrumentation problems); but the indicator ratios are reasonably consistent with the model predictions. However, the indicator ratios do not seem to be very "robust" because their indications of sensitivity appear to depend on the ROG levels. Also, there may be differences between a smog chamber and the atmosphere because of generally lower OH concentrations and possibly also due to wall effects. In addition, indicators do not predict the magnitude of emissions control needed to attain air quality goals and they are not able to determine if attainment of NAAQS is feasible with a VOC or NOx control strategy. Those may limit their direct usefulness in policy making. However, indicators could be used, within their stated limitations, to gain more confidence in air-quality model simulations that are used design and evaluate emissions control strategies.

The UNC and TVA chamber data have also been used for evaluating mechanisms for ozone formation, and some differences among chambers are seen in mechanism evaluations, such as the recent evaluation of CB05. UNC chamber data are also being obtained for evaluating kinetic mechanisms for PM formation, such as being carried out by the Kamens group, discussed above. UNC is also undertaking a major study involving use of an environmental chamber for determining effects of secondary pollutants on cultured cells, which is providing a new kind of chamber data that could highlight important health-based reaction pathways that may be missing in current chemical mechanisms.

Limitations to the existing chamber database were discussed. Care must be taken when using chamber data to evaluate condensed mechanisms, especially if the distributions of compounds in the experiments are not the same as the distribution assumed when deriving the mechanisms of the lumped model species used to represent them. A better approach may be to evaluate detailed mechanisms, which are then used as the basis for deriving condensed versions. The current chamber database is not adequate for evaluating mechanisms for secondary products, whose reactions become important over longer time frames than most experiments. Conducting experiments over long time frames is difficult using existing chambers and methodologies. Methods are needed to evaluate mechanisms for multi-day effects such as NO_x recycling and secondary and multi-step oxidation product reactivity.

The utility of chambers for instrument comparison needs to be exploited to a greater extent. This has value to evaluating instruments for field projects and also provides opportunities for advanced measurements for at lest some mechanism evaluation experiments. This is being done to a significant extent in Europe but much less so in the United States.

There was also a suggestion that there is a need to compare chambers with each other under similar conditions to test the chambers themselves and the instrumentation they employ. Some differences were noted in mechanism performance between different chambers in the evaluation of CB05 that need to be better understood. However, these differences may be due to differences in concentration ranges or types of experiments rather than characterization problems with the chambers themselves.

Regardless of the chamber or the objectives of the chamber studies, the environmental chamber data need to be made more readily available so mechanism developers can use what is available. Most mechanisms are not adequately evaluated against chamber data, and even the most evaluated mechanisms focus on use of only a subset of the available data. For example, MCM evaluation has focused on use of European chambers, while SAPRC evaluation has focused on UCR chambers. The Eurochamp program will make an important contribution if it is really successful in making the European database generally available, and there are discussions about expanding it to include the UCR and other U.S. databases. The UCR database is documented and available for runs prior to 1995, but data for more recent runs, including those in the new UCR EPA chamber, are not completely documented and generally available as of yet.

Process Optimization Methods

Two presentations were given regarding methods and tools for optimization of complex processes used in other area of mechanism research that may be applicable to the development and optimization of ground-level atmospheric chemistry mechanisms. The general problem involves fitting data from multiple sources, which may be conflicting, and which have varying levels of uncertainty associated with them. Data and models are "not additive" -- systems for synthesis are needed. One project that is just beginning is PrIMe (Process Informatics Model -- see http://PrIMekinetics.org), which is a collaborative effort to compile data, models, and tools for model development and optimization in the combustion field. Atmospheric mechanism developers were invited to participate with their data and models. Although the database for atmospheric mechanisms would be large (consisting not only of the large chamber database, but also relevant database of complex laboratory studies from which rate constants and mechanisms are derived by modeling) the general concepts and objectives behind PrIMe should be applicable.

A specific example of applying consistency and optimization tools was given in the context of upper atmospheric datasets and models. The objective was to "use all knowledge to get the best possible mechanism". The optimization was complicated by the fact that no model could be found to fit all "targets", indicating that some data must be inconsistent. It was necessary to determine which targets to eliminate to give best fits with "liberal error bars" and rate constant changes. In principle, multiple mechanisms can be optimized to see differences in predictions based on the same data set. In many respects this application had similar problems as fitting to chamber data, though the number of parameters and size of the dataset is much greater.

In principle, the algorithms used for chemical data assimilation in 3-D models could be used for the problem of optimizing uncertain chemical mechanism parameters to simulate environmental chamber experiments. Although there are thousands of experiments in the existing chamber data base, many of which having extensive measurement data, the computational problem is probably less compute-intensive than simulating the thousands of cells involved in 3-D models. This is an area of database development and software implementation of existing algorithms that need to be explored.

Basic Chemical Studies and Measurements

Although the focus of this conference was on mechanisms as a whole, there were several presentations on basic chemical studies or measurements that are relevant to important components of the mechanisms, and that indicate that changes to current mechanisms are probably needed.

Roger Atkinson presented results that the 4-hydroxycarbonyls formed in large yields in the reactions of the longer chain alkanes cyclize to form dihydrofurans. The reaction is reversed by H_2O, so its importance depends on humidity. These compounds are highly reactive, much more so than the products assumed in the current mechanisms. Unfortunately, current chamber data are not adequately sensitive to these secondary reactions to test this aspect of the mechanism, although they may have non-negligible impacts on reactivity, even in 1-day reactivity scales such as MIR. These reactions also form SOA, so need to be taken into account in models of SOA formation.

Ian Barnes discussed reactions of aromatic ring-retaining products, which are important in aromatic photooxidation mechanisms. Rate constants and product studies were reported that need to be incorporated into mechanisms. The main products of OH + Phenol are dihydroxy phenols (up to 80%)., but trihydroxy phenols are not formed from dihydroxyphenols. Instead they appear to form primarily carbonyl compounds. Maleic anhydride is also formed in 4-7% yields. But no glyoxal, etc and no indication of unsaturated 1,4-dicarbonyls in reactions of phenols. Ketene formation may also be occurring. The reactions of phenols with NO_3 form nitrophenols, and the reactions of these compounds were also studied. Evidence was obtained that nitrophenols may photolyze relatively rapidly to form HONO, which is a potentially significant process that is not represented in current mechanisms. High aerosol yields are also formed in the reactions of nitrophenols. Mechanisms need to be updated to take these potentially important results into account.

Heterogeneous formation of HONO is an important issue that was brought up in a number of presentations. HONO is a highly photoreactive source of radicals and NO_x, and its formation affects gas-phase chemistry as well as PM. Ambient observations suggest there is a heterogeneous HONO source as well as possibly direct HONO emissions. Also there is a need to include a light-induced heterogeneous HONO source for models to simulate HONO measurements in the daytime. This may be a similar process as the "chamber radical source", with the magnitude of this source derived from ambient data being within the range derived from modeling some older chamber experiments, but being greater than the HONO offgasing rate measured in the SAPHIR chamber or indicated by modeling chamber effects in the new large chamber at UCR.

Quantum Chemistry

In principle, quantum chemistry can be a valuable tool to elucidate uncertain aspects of chemical mechanisms where laboratory data are missing or insufficient. Computer power is advancing so it may eventually be practical for molecules of useful size. For example, it was shown to provide useful predictions for the isoprene system that are reasonably consistent with laboratory data. However, quantum chemistry as currently applied has had some failures, suggesting that its predictions need to be used with caution. In the peroxy + NO $\rightarrow$ organic nitrate system the quantum calculations have predicted activation energies that are much too high, apparently as a result of using inappropriate transition states. There are also problems with recent calculations of the mechanisms of simple peroxy + peroxy reactions. However, quantum chemistry may have utility in "pruning branches" and "testing new branches" in reaction routes, and possibly in obtaining semi-quantitative information on structure activity relationships. Attempts have been made to apply quantum chemistry analysis to the aromatics mechanism, but the results have problems. Quantum chemistry methods may not quite be ready to be useful for elucidating this problem.

A near term utility of quantum chemistry would be to fill out the thermochemical database that is needed to support estimation methods that use semi-empirical correlations between rate constants and heats of reactions. Heats of reaction are more straightforward to calculate than rate constants, which require finding appropriate transition states.

Mechanism Reduction

Much of the current basic mechanism development effort is focused on developing explicit or detailed mechanisms such as MCM. In principle, such mechanisms have the most direct link with basic laboratory data and theory, can be derived using various protocols or mechanism generation methods incorporating current knowledge and various estimation methods, and are generally more straightforward to evaluate. However, condensed mechanisms are needed for modeling applications where computer time and memory are issues. Therefore, several presentations were given on developing and applying systematic procedures for reducing chemical mechanisms. Several methods can be employed. One is to find redundant reactions and species based on either sensitivity analysis or determining what influences what, directly or indirectly, and remove those whose "importance" falls below a certain threshold. The quasi-steady state approximation can also be applied in some cases to reduce species that need to be transported and also reduce mathematical "stiffness". Lumping can also be employed to reduce the number of species. In one case, the SAPRC-99 mechanism was reduced from 72 species and 216 reactions to 19 species and 104 reactions, with a factor of ~10 improvement in computer time. The reduced mechanism gave good agreements with the full mechanism in predictions of O_3 but tended to underpredict NO_x by about 10%. In another application, the MCM α-pinene mechanism for SOA formation was reduced. Some biases were seen in the reduced mechanism, probably because of species removal.

The test calculations used for sensitivity analyses and determining what is or is not important are important. One study may have used too short reaction times, and the reduced mechanism will need to be evaluated using multi-day or 3-D models. Lumping may be a preferred approach over removal for "unimportant" since it may reduce biases resulting when processes are removed.

Mechanism Implementation

Since highly detailed or nearly explicit mechanisms have the greatest *potential* for chemical accuracy and also can simulate multiple types of species, use of these mechanisms may be preferred at least for some model applications. Future capabilities are moving to multi-pollutant modeling, which will place additional demands on the chemical mechanisms. It has been shown to be possible to conduct full model simulations using the very large MCM with a sparse matrix solver, so current computers and software are now capable of implementing such mechanisms. However, resource constraints are an important consideration in many model applications, particularly applications such as air quality forecasting, simulations of annual averages, or simulations of multiple iterations of control strategies. Even though today's models consume less time processing chemistry because of additional processes, more efficient solvers, and parallel processing, this doesn't eliminate the need for faster mechanisms.

Several solvers exist for implementing mechanisms, with the most accurate solvers tending to be the most time-consuming, and the fastest solvers having the greatest potential for introducing numerical error. Studies of effects of using faster solvers compared to the "gold standard" SMV-Gear have been carried out using the CB05 mechanism. Differences for O_3 are very small except at the lowest O_3 levels and the greatest differences (~-20 + 30%) are for N_2O_5.

One of the problems with mechanism implementation, which is inhibiting the use of new or more flexible mechanisms in many modeling applications is the lack of *flexible* mechanism implementation methods for the most efficient solvers. Implementation of mechanisms for emissions processing is another resource constraint that also makes implementation of new or more flexible mechanisms difficult. The need for flexibility is as important here as the need for flexibility in implementation in solvers. This is beyond the scope of this conference, but is an important part of practical mechanism implementation.

Panel Discussions

At the end of the meeting there was a panel discussion where panel members were asked to comment on short and long-term research needs, what should be done to make sure we have appropriate chemical mechanisms, and how we make sure we continue to make progress. This was followed by comments from the audience on these and related issues. The panel members and questions put to them are given with the conference program in Appendix A. Given below is a summary of the comments and recommendations made during these discussions, organized by topic.

Policy Issues

- We need to learn to communicate better with policy makers, and give them better explanations of what models can and can not do. Sensitivity and process analysis may be useful in this regard
- We need improvements in uncertainty and sensitivity analysis methods – and also how to communicate these results to regulators.
- Need to consider "what to do if it [modeling] doesn't work"
- There is a real concern about maintaining the mechanism development community. Most of the mechanism developers are nearing retirement and funding may not be adequate to attract young scientists into this field.
- Perhaps increasing linkages with health-related impacts would improve funding sources for mechanism development.
- We should increase collaboration between U.S. and European counterparts, and encourage collaborations among younger scientists around the world.

General Modeling Issues

- A short term but important research need is to resolve differences in predictions between CURRENT mechanisms, and understand the causes of these differences. This is needed to give us more confidence, and a better understanding of the uncertainties, in predictions of current models
- Sensitivity and uncertainty analysis should be encouraged
- Need to get away from using single models for assessment studies.
- Need to improve model representation of sub-grid effects -- especially exposure models
- Mercury is an important air quality issue, and we need to have mercury chemistry in models, and this chemistry needs to be better described.
- We need a "gold standard" for transport in 3-D models

General Mechanism Issues

- Use of detailed mechanism is necessary for three reasons: for multi-day simulations, for large releases of reactants, and for reactivity-based substitution simulations. But we need to be cautious of detailed mechanisms because they may not necessarily be the best representation of what’s going on.
- Because of gaps in our knowledge, explicit mechanisms may not necessarily fit data, and not have satisfactory predictive capabilities in some cases. Use of "engineering" mechanisms may be better for the time being if they give better predictions. This has been the approach needed for aromatics, at least for the time being.
- The generation of chemistry mechanisms that are sufficiently condensed to be used in models – including estimation of reaction rates, branching, etc, needs more work. Several promising methods are being used, but have not been fully tested.
- Systematic mechanism reduction and semi-empirical methods need to be developed and tested.
- Modeling problems with organic aerosol need to be addressed. Need better mechanisms for SOA.

- Need consistency between gas-phase, aqueous chemistry and SOA formation, i.e. need to better than just adding products for aerosol onto the end of a mechanism designed for gas-phase chemistry.
- Need to appropriately represent "free troposphere" chemistry as well as regional model chemistry in models
- There is concern about how well mechanisms handle temperature and pressure. Mechanisms need to have temperature- and pressure-dependent rate constants <u>and branching ratios</u> (generally they have the former in most but not all cases but usually not the latter). Temperature and pressure varies considerably in modeling domains. Temperature variation at ground level can be significant, especially from coastal to inland areas. Temperature and pressure effects rate constants and branching ratios of many processes.
- It is becoming apparent that NO_x recycling is important, and models need to appropriately represent it. Mechanisms need to be applied to Health impact predictions
- Experimental data *and theoretical calculations* need to be incorporated into mechanisms
- We should incorporate field data with theoretical data.
- Need improved estimation methods to support deriving detailed mechanisms
- Halogen chemistry may be important, especially in coastal environments.

Basic Chemistry Issues

- Data evaluations are important to mechanism development, and need to be better supported. Important to continue AND EXPAND evaluation efforts. Evaluations should cover larger molecules. Evaluations should be expanded to mechanisms for SOA formation, and we also need evaluations for aqueous reactions. But we need to be more critical of evaluations -- need opportunity for discussions of recommendations. Need to have a representative and large enough group that multiple reviewers/evaluators work on the same reaction(s).
- We need a better understanding of the chemistry of SOA formation.
- Aromatics chemistry continues to be highly uncertain – perhaps we need a fundamentally new approach. Product studies do not seem to be solving the problem. No present mechanism is consistent with all the available data. (One possible short-term fix to aromatics problem may be to develop a highly parameterized [and perhaps “unrealistic”] mechanism to mimic aromatic reactions until a more acceptable solution can be found.)
- We need more experimental data, and should encourage new, breakthrough analytical techniques. New analytical techniques are needed to make further progress.
- We do not really understand HONO -- especially photolytic sources. Also need to find the missing HONO sources, and the potential for HONO formation from nitrophenols and perhaps other organics, and from heterogeneous processes.
- Organic nitrate concentrations may be a large portion of the NO_z but we don’t have many measurements of the chemistry of these compounds. We need more information on their mechanisms.
- There are still uncertainties in how well the current chemical mechanisms represent chemistry under low-NO_x conditions, and the products.

- Need to look broadly and examine even the reactions that we thought we knew well (like alkanes), they still can have surprises. Ozone and PM formation can be sensitive to even relatively simple reactions.
- The heterogeneous hydrolysis of N_2O_5 is important and still has significant uncertainties.
- Need more kinetics of nitrate radical reactions, which are important at nighttime and in canopies.
- Need data and mechanisms on chemistry of solvents. The chemistry of solvents is uncertain, but they can be a large fraction of the total VOC emission inventory. We especially need more information on the chemistry of oxygenated products, products from reactions with nitrate radical, and peroxy reactions.

Mechanism Evaluation Issues

- We need to make it easier for mechanism developers to evaluate their mechanisms against the FULL chamber database.
- We all need more data from experimental chambers, and U.S. scientists should utilize the work being done in European chambers, and vice versa. We should put data from US chambers in EUROCHAMP databases.
- The database of experimental chamber data should also include data of model runs which analyze these data as well in order to make model data available to the public.
- The PrIMe system provides an opportunity for making data available for mechanism evaluators and this option needs to be explored as well.
- Database systems need long term funding. Libraries can potentially play a role in long term database support
- The experimenters need to access the models -- provides useful information about the experiments. Modeling provides a test bed for chamber data.
- We should perform more multi-day studies, both modeling and experimental. But multi-day experiments are hard to do in smog chambers – maybe use secondary NOx injection in current chambers. Current chamber experiments are not sensitive to effects of reactions of the products, so these aspects of the mechanisms are not being adequately evaluated.
- Incremental reactivities measured in environmental chamber experiments are not necessarily the same as in the atmosphere because it is not practical to duplicate all relevant atmospheric conditions in a chamber experiment. An important factor is the lower sensitivity of chamber experiments to reactions of secondary organic products because of generally shorter reaction times and integrated radical levels. This presents a problem in evaluating how well mechanisms represent reaction products as well as causing differences in chamber vs. ambient reactivities. Conducting experiments over longer time periods and at higher light intensity could address this problem at least to some extent.
- Studies of mechanisms at low NO_x (RO_2+RO_2) conditions are needed.
- Need instruments to measure oxygenated compounds in the field.
- Field data should be utilized for mechanism evaluation.

Mechanism Implementation Issues

- Need to develop systematic mechanism reduction methods. Condensed mechanisms should be derived from detailed mechanisms to the extent possible (but this is not always possible -- then "engineering" mechanism may be needed if that's the way to have predictive capability)
- Need FLEXIBLE as well as fast solvers for mechanism implementation.
- Also need flexible emissions processing to permit implement new or flexible mechanisms and lumping schemes.

Next Steps

The general consensus was that this meeting was a success and such meetings should be held periodically, perhaps every 2 years. The possibility of alternating between meetings in the U.S. and Europe was discussed. The possibility of having the next meeting focus on PM mechanisms was discussed. It was mentioned that a meeting was planned in Texas next spring or summer to focus on PM mechanisms, and perhaps this will address that objective.

There is an opportunity to have a special section or issue of the journal *Atmospheric Environment* for papers presented at this meeting. After the meeting the organizers will poll the presenters to see if there is sufficient interest, and if so what would be an appropriate deadline for submission. The Journal is flexible on the deadline, which could be as far out as we wish.

There is also a consensus that there needs to be collaborations on databases for evaluating mechanisms. Preliminary discussions are being held about incorporating some of the U.S. environmental chamber databases into the Eurochamp effort, and it is hoped that this collaboration will proceed. The possibility of using the PrIMe system will also be investigated.

The organizers of this conference have created a list server to foster further communications among the participants of this meeting. Approved users may post queries and respond to queries at: AtmosChemMech@ucdavis.edu. All conference attendees have been included on the initial list of approved users. Requests for addition, removal, or email address changes for the list should be directed to Donna Reid at dvreid@ucdavis.edu.The first order of business is to come to a consensus concerning the conference summary (this document). This document is a first draft, and to fully reflect the accomplishments of the meeting it needs the inputs of the participants concerning errors or omissions of what was presented, for editorial content, and to improve its utility as a conveying a sense of the information and recommendations that were presented at the meeting.

The slides or overheads used for the oral presentations given at the meeting are available through the conference web site accessible via http://airquality.ucdavis.edu, and are directly available http://www.cert.ucr.edu/~carter/Mechanism_Conference. These were edited or corrected in some cases. Authors or editors who did not previously review or edit their presentation slides should review their presentations as available at this web site, and if appropriate send corrected versions to Bill Carter at carter@cert.ucr.edu. PDF format is preferred because this is the format that will be used when posted, but Power Point format can be accepted because they can be used to create PDF files. Authors are also requested to replace any animations that do not display properly when converted to PDF with representative static figures or text.

Acknowledgements and Disclaimers

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However, this conference summary has not yet been reviewed by all the attendees or authors, and is subject to change.

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Appendix A. Conference Program *

Title	Presenter
	Regulatory Perspectives
Regulatory Perspectives - California	John DaMassa, California Air Resources Board, USA
Regulatory Perspectives - U.S. EPA	Rich Scheffe, US EPA, USA
Regulatory Perspectives - Europe	Dick Derwent, rdscientific, UK
	Objectives
Objectives of the Conference	Ajith Kaduwela, California Air Resources Board, USA
	Session A: Current Status and Significant Issues in the Development and Usage of Chemical Mechanisms
Current Status and Significant Issues in Chemical Mechanisms	Harvey Jeffries, University of North Carolina at Chapel Hill, USA
EUROCHAMP - A European Infrastructure Project for Atmospheric Simulation Chambers - Current Progress and Future Directions with Respect to Chemical Mechanisms	Peter Wiesen, Bergische Universitaet Wuppertal, Germany (Presented by Ian Barnes)
Chemical Mechanism Needs of Photochemical Modelers from a One-Atmosphere Perspective	Robert Harley, University of California at Berkeley, USA
Effects of Using the CB05 versus SAPRC99 versus CB4 Chemical Mechanism on Model Predictions	Deborah Luecken, EPA, USA
Modelling the Chemical Composition of Particles and Needs for Improvements in Chemical Mechanisms	Bernhard Vogel, Karlsruhe Research Centre (FZK), Germany
	Session B: Chemical Mechanisms for Regional and Urban Scale Air Quality Modeling
The Master Chemical Mechanism (MCM) - Updates and Improvements	Andrew Rickard, University of Leeds, UK
The SAPRC Chemical Mechanisms	William Carter, University of California at Riverside, USA
Regional Atmospheric Chemistry Mechanism, RACM	William Stockwell, Howard University, Washington, D.C., USA
Development and Applications of CACM/MPMPO	Robert Griffin, University of New Hampshire, USA

Title	Presenter
An Updated Carbon Bond Mechanism	Garry Z. Whitten, Smograys, California, USA
The GRS Model for Ozone Formation	Merched Azzi, Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia

Poster Presentations

Study of Volatile Organic Compound Emissions Uncertainty in the Houston-Galveston Area Utilizing an Extended SAPRC99 Chemical Mechanism for the TexAQS 2000 Episode	Daewon W. Byun, Beata Czader, Soontae Kim, Mark Estes, and William Carter
Photochemical Heterogeneous Atmospheric Oxidation	Hazem S. El-Zanan and William R. Stockwell
Oxygenated Hydrocarbons in the New RACM2	Wendy S. Goliff and William R. Stockwell
Formation of Organic Nitrates in an Urban Plume	Roberto Sommariva, Michael Trainer, Joost A. de Gouw, Paul D. Goldan, William Kuster, James M. Roberts, Carsten Warneke, S. Min, A. R. Ravishankara
On N2O5 Heterogeneous Reaction Probability	Qi Ying, Jin Lu, and Michael Kleeman
Modeling the Transition From Predominantly Gas-to Predominantly Aerosol-Phase Products From OH Reactions With the Homologous Series of C10 to C15 n-Alkanes	Carolyn E Jordan, Paul J Ziemann, Robert J. Griffin, Yong-Bin Lim, Roger Atkinson, and Janet Arey
Measurements of Rate Coefficients for the Gas Phase Reaction of OH Radicals with Several Oxygenated Biogenic Compounds	James B Burkholder
Modeling Secondary Organic Aerosol Formation	Jianjun Chen, Robert J. Griffin, and Robert W. Talbot
The Role of Key Reaction Pathways in Accounting for the Differences in Ozone Predictions by the Carbon Bond and SAPRC Photochemical Mechanisms under Conditions Relevant to Southeast Texas	Maedeh Faraji, Yosuke Kimura, Elena McDonald-Buller, and David T. Allen
In-Situ Measurement of Total Alkyl-and Multifuctional Nitrates During INTEX-B	Anne Perring, Timothy H. Bertram, Paul J. Wooldridge, Donald R. Blake, Nicola J. Blake, and Ronald C. Cohen
Determination of Evaporation Rates and Vapor Pressures of Very Low Volatility Compounds: A Study of the C-4-C10 Diacarbolyic Acids	Christopher Cappa, Edward Lovejoy and A.R. Ravishankara

Conference Proggram (continued)

Title	Presenter
Session C: Evaluation of Chemical Mechanisms	
Current Research in European Environmental Chambers: Measurements and Models	Theo Brauers, Jülich Research Centre, Germany
The University of California, Riverside, Environmental Chamber Database and Evaluation of SAPRC and Other Chemical Mechanisms	William Carter, University of California at Riverside, USA
Empirical Evaluation of Observation Based Methods for Assessing Ozone Sensitivity to VOC in NOx	Gail Tonnesen, University of California at Riverside, USA
Organic Oxidation Mechanisms and Organic Aerosol	Neil Donahue, Carnegie-Mellon University, Pittsburgh, USA
A Kinetic Mechanism for Predicting Secondary Organic Aerosol Formation from Toluene Oxidation in the Presence of NOx and Natural Sunlight	Richard Kamens - University of North Carolina, Chapel Hill, USA
Session D: Research Focus on The Next Improvements on Chemical Mechanism Development And Applications - I	
Atmospheric Chemistry of Alkanes - Recent Developments	Roger Atkinson, University of California at Riverside, USA
Mechanism of the Photooxidation of Aromatic Hydrocarbon Ring-Retaining Products	Ian Barnes, Bergische Universitaet Wuppertal, Germany
Interfaces Between Gas Phase Mechanisms and Aqueous Chemistry	Hartmut Herrmann, The Institute for Tropospheric Research (IfT) Leipzig, Germany
Session E: Research Focus on the Next Improvements in Chemical Mechanism Development And Applications - II	
Practical Aspects of Chemical Data Assimilation	Adrian Sandu, Virginia Tech at Blacksburg, USA
Photochemical Mechanism Reduction for the SAPRC Mechanism	Jung Lee, University of California at Davis, USA
Transforming Data into Knowledge - Process Informatics for Combustion Chemistry	Michael Frenklach, Department of Mechanical Engineering, University of California at Berkeley, and Environmental Energy Technologies Division, Lawrence Berkeley NationalLaboratory, USA
Applying Consistency and Optimization Tools to Atmospheric Datasets: An Upper Atmosphere Ozone/Hydroxyl Example	Gregory Smith, SRI International, California, USA

Conference Proggram (continued)

Title	Presenter
A Self-Generating Approach for Explicit Mechanism	Bernard Aumont, Universites Paris, Creteil, France
Mechanism Reduction for the Formation of Secondary Organic Aerosol for Integration into a 3-Dimensional Regional Air Quality Model	Adam Xia, York University, Ontario, Canada
Testing the Speed of a 13,500-Reaction Chemical Mechanism with SMVGEAR II and the Accuracy of the Mechanism Against Smog Chamber Data	Diana Ginnebaugh, Stanford University, USA
Source Apportionment of Secondary Air Pollutants	Michael Kleeman, University of California at Davis, USA

Session F: Use of Other Scientific Tools to Aid the Development of Chemical Mechanisms

Process Analysis for Photochemical Reaction Mechanisms	William Vizuete, University of North Carolina, Chapel Hill, USA
Development and Application of a Lagrangian Process Analysis Tool for Tracking the Chemistry of Plumes Within a 3-D Eulerian Photochemical Model	Yosuke Kimura, University of Texas at Austin, USA
Analysis of a Photochemical Reaction Mechanism Using the Adjoint Sensitivity Analysis Procedure	Philip Martien, Bay Area Air Quality Mgmt. District, San Francisco, USA
Role of Quantum Chemistry in Atmospheric Chemical Mechanism Development	Renyi Zhang, Texas A&M University, USA (Presented by Jun Zhao)
Failures and Limitations of Computational Chemistry for Two Key Problems in the Atmospheric Chemistry of Peroxy Radicals	Ted Dibble, State University of New York, Syracuse, USA

Session G: The Cost-Benefit Analysis of Regulatory Chemical Mechanisms

Accuracy and Cost Considerations in Choosing a Chemical Mechanism for Operational Use	Kenneth Schere, US EPA, USA
Application of a Master Chemical Mechanism (MCM) for Ozone Policy Assessment in Europe	Dick Derwent, rdscientific, UK
Evaluating the SAPRC and Carbon Bond Chemical Mechanisms for Use in Southeast Texas	Maedeh Faraji, University of Texas at Austin, USA
The Regulatory Role of Chemical Mechanisms and Future Needs	Ajith Kaduwela, California Air Resources Board, USA

Conference Proggram (continued)

Title	Presenter
Panel Discussion	
Panel Questions: From your viewpoint, what are the most pressing short-term needs (i.e. current applications) for improving chemical mechanisms? What are the most important areas for longer-term improvement? What should government and industry be doing to make sure we have appropriate chemical mechanisms? Are we on the right path? How do we make sure we continue to make progress and motivate new faculty and students?	Deborah Luecken, US EPA, USA (moderator) Roger Atkinson, University of California at Riverside, USA Ian Barnes, Bergische Universitaet Wuppertal, Germany Dick Derwent, Rdscientific, UK Harvey Jeffries, University of North Carolina at Chapel Hill, USA Eileen McCauly, California Air Resources Board, USA Kenneth Schere, US EPA, USA
Summary	
Summary of the Conference and Next Steps	William Carter, University of California at Riverside, USA

* The overheads used for the oral presentations, which were edited in some cases, are available at http://www.cert.ucr.edu/~carter/Mechanism_Conference