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Project Summary

Modeling of Auto Exhaust Smog Chamber Data for EKMA Development

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A new generalized mechanism for photochemical smog has been developed. The mechanism is suitable for use in the Empirical Kinetics Modeling Approach (EKMA) to estimate the amount of control of volatile organic compounds that is needed to achieve the National Ambient Air Quality Standard for ozone. The mechanism developed in this study is called the CBM-X, and it is the fourth lumped-parameter mechanism to be designed in accordance with the carbon-bond reaction concept. In the carbon bond mechanisms, organics are grouped according to the type of carbon bonding that is found in the various classes of organics. Carbon atoms with similar bonding are treated similarly, regardless of the molecules in which they occur. The principal features that distinguish the CBM-X from previous carbon bond mechanisms include separating formaldehyde from the other oxygenates, treating toluene separately from the other aromatics and including a more detailed, up-to-date representation of aromatic hydrocarbon chemistry.

The CBM-X was tested by comparing the predictions obtained with the mechanism against smog chamber data of dilute auto exhaust/oxides of nitrogen mixtures obtained in the outdoor smog chamber facility operated by the University of North Carolina.

This Project Summary was developed by EPA's Atmospheric Sciences Research 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

For several years, the U.S. Environmental Protection Agency has sponsored a coordinated research program consisting of chemical kinetics studies, smog chamber experiments, and kinetic model development, with the ultimate goal of developing models capable of simulating the photochemical reactions that take place in the lower troposphere. As a result of this program, considerable effort has been devoted to the development of reaction mechanisms for photochemical air pollution, either through the numerous direct contributions of the EPA program or through the stimulus the program has provided others. Part of this effort has involved developing chemical kinetics mechanisms for use in the Empirical Kinetics Modeling Approach (EKMA). EKMA is a technique for relating ozone concentrations downwind of an urban area to the early-morning concentrations of O_3 precursors in that urban area. In the EKMA approach, a very simple moving box model is used to generate a series of ozone isopleths that depict maximum afternoon ozone concentrations as a function of 6-9 AM ambient levels of VOC and NO_x. Ozone isopleths can be generated for any city by using emission and meteorological inputs that are appropriate for that city. The isopleths are used to calculate the amount of VOC control that is needed to reduce O_3 from some present-day value to the 0.12 ppm air quality standard.

The mechanism originally developed in 1976 for use in EKMA was a surrogate species mechanism in which the reactivity of urban organic emissions was represented in terms of a simple propylene/

n-butane mixture. Since that time our knowledge of the chemical processes responsible for photochemical oxidant formation has increased considerably. The objective of this present study was to make use of that knowledge to develop an improved, state-of-the-science mechanism for use in EKMA.

Formulation of the Mechanism

The CBM-X can be viewed as consisting of three different components. The first component, the central "core" of the mechanism, consists of a set of inorganic reactions and a set of reactions for those carbonyl species that are central to most photooxidation systems. These carbonyl species include formaldehyde, and acetaldehyde, glyoxal, and methyl glyoxal. The core mechanism serves as the basis for all mechanism development studies at Systems Applications. All species in the core mechanism are treated explicitly, that is, there is no lumping or condensation of any of the species or reactions.

The second component of the CBM-X consists of those hydrocarbons that, because of their importance to the smog-forming process, are also treated explicitly. The hydrocarbons for which detailed, explicit reaction mechanisms are included are ethene, toluene, and m-xylene.

The third component of the CBM-X consists of those reactions and species that are treated according to the carbon-bond, lumped structure approach. The paraffins and all olefins except for ethene are treated in this fashion. One lumped species, referred to as PAR, is used to represent the single-bonded carbon atoms in these species. The lumped species OLE is used to represent the carbon-carbon double bonds of olefins.

In addition to using explicit chemistry and the lumped structure approach to simplify the reaction scheme, a surrogate mechanism approach is also used to represent some of the organics in the atmospheric mix. The surrogate species approach consists of using chemical reactions for one species to represent the chemistry of another, similar species. The surrogate approximation is used when a compound is sufficiently similar in its photooxidation behavior to an already existing class that it can be included in that class without modifications to the chemical parameters of the mechanism. The surrogate approximation is also used for compounds whose behavior is not known in detail; the behavior of such compounds must be estimated by analogy with other known compounds. The CBM-X uses surrogate approximations to describe a number of compounds. The behavior of olefins with two or more alkyl groups (e.g., isobutene, internal olefins) is simulated as a mixture of the aldehyde and ketone products. In this case the surrogate approximation is justified by the fact that such very reactive olefins oxidize to their products so rapidly that product behavior dominates. A second surrogate approximation is used for monoalkylated aromatics (e.g., ethylbenzene). These species are assumed to be similar to toluene for which a condensed explicit mechanism is used. In keeping with the carbon balance considerations of the carbon bond approach, the excess alkyl carbon in these molecules is treated as the lumped species PAR. Another surrogate approximation is used for chlorinated ethenes, which are assumed to be similar to ethene itself. And lastly, aldehydes with three or more carbon atoms are treated as acetaldehyde.

The CBM-X contains 146 reactions and 65 species. A complete description of this mechanism, including a listing of the individual reactions and species that comprise the mechanism, is given in the Project Report.

Testing of the Mechanism

Individual aspects of the CBM-X mechanism were tested against smog chamber data obtained by the University of North Carolina (UNC) during the irradiation of one-component organic and NO_x systems. The components of the CBM-X mechanism that were tested in this fashion included formaldehyde, acetaldehyde, methylglyoxal, ethene, toluene, and m-xylene.

The complete CBM-X mechanism was tested against data obtained by UNC during their outdoor chamber study of auto exhaust/NO_x mixtures. In this study, both sides of the UNC chamber were charged with dilute auto exhaust and NO_x mixtures from catalyst-equipped automobiles operated under varying test cycles and with different fuels. The experiments covered a wide range of hydrocarbon-to-NO_x ratios. Twenty experiments from the UNC chamber were simulated in this phase of the study.

Results

The CBM-X mechanism was found to provide good agreement to the chamber data obtained for the one-component organic/NO_x systems. The CBM-X also was able to simulate reasonably well the auto exhaust runs that were performed in the UNC chamber. In some cases, however, there were discrepancies between the experimental and simulated results. There were two general areas in which the predictions differed from the experimental data. In runs where ozone reached a peak and then declined, (generally a high HC/NO_x), the simulations often overpredicted the peak ozone and underpredicted subsequent ozone decay. This overprediction of ozone often occurred coincidentally with an underprediction of PAN. It is quite possible, therefore, that some feature of the PAN formation and decay was responsible for the overprediction of peak ozone. There was also a tendency for the mechanism to underpredict formaldehyde in nearly all cases. In general, however, the predictions for most species agreed well with the experimental data.

Conclusions

The mechanism developed in this study is a hybrid of explicit chemistry, surrogate approximations and lumped/generalized chemistry. It was designed to handle the broad features of urban smog chemistry and to be applicable for use in EKMA. The experimental data base used to test the CBM-X was well suited for developing mechanisms to describe photochemical smog formation within urban areas. Although additional efforts are needed before all the details of smog photochemistry are elucidated, the mechanism formulated in this study has been sufficiently tested to render it useful for EKMA control strategy applications.

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The complete report, entitled "Modeling of Auto Exhaust Smog Chamber Data for EKMA Development," (Order No. PB 85-186 492/AS; Cost: $28.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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