



Project Summary

Development of a Chemical Kinetic Mechanism for the U.S. EPA Regional Oxidant Model

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The U.S. Environmental Protection Agency (EPA) is presently developing an air quality simulation model to simulate the transport, dispersion, and transformation of photochemical oxidants on a regional scale. Systems Applications, Inc., under contract with the U.S. EPA, provided a chemical kinetic mechanism for use in this Regional Oxidant Model. The development of this chemical kinetic mechanism and its evaluation with smog chamber data are described in this report.

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 directed its attention towards the development of an air quality simulation model to describe the formation of photochemical smog on a regional scale. The objective of the study described in this Project Report was to develop a chemical kinetics mechanism for use in EPA's Regional Oxidant Model (ROM). Before this study was undertaken, kinetics mechanisms had been developed for use in urban oxidant models only. These mechanisms do not treat a number of phenomena that are of importance on a regional scale. The urban oxidant models, for example, do not treat nighttime chem-

istry and, therefore, they cannot be used for simulations that extend beyond one day. In addition, the urban oxidant mechanisms do not consider the role of biogenic hydrocarbons in the smog-forming processes. In the rural environment, these natural hydrocarbons may contribute to ozone formation. The objective of this study was to develop a mechanism for use in the ROM that could treat the buildup of oxidants over a multi-day period and consider the role of biogenic as well as anthropogenic hydrocarbons on oxidant formation in the rural environment.

Description of the Mechanism

The ROM mechanism developed in this effort was 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. Breaking the organic molecule into groups of carbon bonds offers several advantages over mechanisms that use one organic species to represent an entire class of organic compounds. A carbon-bond mechanism allows the conservation of carbon mass. It also leads to a more accurate representation of kinetic data for an entire class of organic compounds. For example, the rates of the reactions of olefins with OH radicals cover a wide range of values that depends on the olefin. The use of a carbon-bond representation allows one to simulate this spread of reactivity to some extent, whereas a lumped repre-

sensation approximates all olefin-OH reaction rates with a single value. The principal disadvantage of the carbon-bond representation is that intramolecular processes such as decomposition and side-chain activation may require special treatment.

The expanded carbon-bond mechanism that was developed in this effort can be viewed as consisting of three different components. The first component, the central "core" of the mechanisms consists of a set of inorganic reactions and a set of reactions for those organic species that are central to most photooxidation systems. These organic species include formaldehyde and acetaldehyde. The "core" is termed the Standard Mechanism and it serves as the basis for all mechanism development studies at Systems Applications. All species in the Standard Mechanism are treated explicitly, that is, there is no lumping or condensation of any of the species or reactions.

The second component of the ROM mechanism 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, m-xylene, and isoprene.

The third component of the mechanism 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 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 ROM mechanism uses

surrogate approximations to describe several species. 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 mono-alkylated 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. In addition, aldehydes with three or more carbon atoms are treated as acetaldehyde. Surrogate approximations are also used for some of the products formed during the photooxidation of isoprene. In particular, such approximations are used to treat methyl vinyl ketone and methacrolein.

Testing of the Mechanisms

The ROM mechanism was tested against smog chamber data obtained by the University of California at Riverside (UCR) and the University of North Carolina (UNC) at Chapel Hill. The UCR study was designed to provide a data base for simulating multi-day effects. A 50,000-l dual-mode outdoor Teflon chamber was used in that study. Experiments consisted of irradiating NO_x and an eight-component surrogate mix for two to four days. In some experiments NO_x was injected on subsequent days to simulate NO_x emissions into an aged air mass.

The UNC study was designed to provide a data base for simulating the photooxidation of isoprene. In the UNC experiments, mixtures of isoprene and NO_x were irradiated in their outdoor smog chamber facility. A range of isoprene-to-NO_x ratios were used in these experiments.

In general, very good agreement was obtained between the two sets of chamber data and the ROM mechanism. Details of the results obtained during the testing of the mechanism are contained in the Project Report.

Condensation of the Mechanism

The ROM mechanism that was tested against the UCR and UNC chamber data

consisted of 170 reactions and 78 species. Subsequent to the testing of this mechanism, the mechanism was condensed, and the predictions obtained with this condensed mechanism were compared to those obtained with the original, more expanded mechanism. Excellent agreement was found between the two sets of simulations. The condensed ROM mechanism contains 115 reactions and 47 species. A complete description of these mechanisms is contained in the Project Report.

Summary

The ROM mechanism is based on the carbon-bond representation and provides an expanded treatment of hydrocarbon chemistry in comparison to previous carbon-bond mechanisms. It treats, for example, aromatics in two major classes (toluene and xylene), and carbonyl compounds in four classes (formaldehyde, two aldehyde compounds and ketones). The mechanism also includes a reaction scheme for biogenic hydrocarbons.

The condensed ROM mechanism that was developed in this effort is suitable for use in EPA's sophisticated Regional Oxidant Model. Included in the Project Report are instructions on how to exercise the ROM mechanism in this model. In particular, detailed guidance is given on how emissions data should be partitioned into the various organic groupings that are used in the mechanism.



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The complete report, entitled "Development of a Chemical Kinetic Mechanism for the U.S. EPA Regional Oxidant Model," (Order No. PB 85-185 858/AS; Cost: \$22.00, subject to change) will be available only from:

*National Technical Information Service
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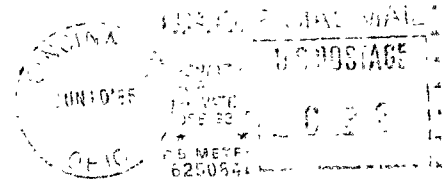
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