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Project Summary

Validation Data for Photochemical Mechanisms: Experimental Results

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The smog chamber facility of the University of North Carolina (Chapel Hill) was used to collect experimental data of various hydrocarbon and oxides of nitrogen (NO_X) systems. These data are intended to be used by atmospheric model developers for testing and validating kinetic mechanisms of photochemical smog formation. The previous set of experiments conducted in the UNC outdoor smog chamber for initial development and testing of chemical kinetics was organized and analyzed. New experiments were then performed to: (1) provide "missing" data; (2) resolve differences between model predictions and the existing experimental data; (3) extend the range of urban-like conditions in the data base; and (4) aid in model construction and testing as requested by model developers. In this study, 71 dual experiments were performed using NO_X and various individual hydrocarbons and hydrocarbon mixtures. In addition, a number of experiments were conducted to better understand and characterize: (1) the chamber when operated dynamically to simulate continuous emissions and meteorological dilution, and (2) the light inside the smog chamber.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The UNC smog chamber facility is used to measure the reactants and products that participate in the photochemical smog formation process. The smog chamber, located outdoors in rural North Carolina, is an A-frame structure covered with Teflon film. The chamber is partitioned into two sections, each with a volume of 156 m^3, so that two experiments can be conducted simultaneously. The dual chamber is operated under natural conditions of solar radiation, temperature and relative humidity. The smog chamber data collected are used to test photochemical mechanisms Earlier mechanism testing against chamber data had shortcomings in that the range of test data available was not great enough to encompass the range of conditions likely to occur in an urban situation. This is in part because previous testing had concentrated on the immediate need to study basic chemistry and reactivity issues. Modeling results and analysis of the existing smog chamber and support data indicated four areas where additional research was needed to test chemical mechanisms more completely. An overview of the chamber experiments conducted in each of these areas is described in the following four sections.

Provide Missing Data

Experiments were conducted to fill missing gaps in the existing database. The "missing data" fell into three broad categories: missing smog chamber experiments of individual hydrocarbons, missing information that would aid modelers in simulating the urban environment, and experiments to test new developments (new species and new chemistry) in the more recent chemical mechanisms. In addition, some previous experiments that were of limited usefulness due to weather problems, lack of product data, or poor supporting calibration data were repeated.

In this portion of the study, a number of toluene, m- and o-xylene and trimethylbenzene experiments were carried out. Experiments were also conducted in which these aromatic species were added to simple and complex hydrocarbon mixtures. Experiments were also conducted utilizing urban-like hydrocarbon mixtures to demonstrate the effect of reduced total hydrocarbon (hydrocarbon control) and hydrocarbon substitution. Model simulations using the Empirical Kinetics Modeling Approach (EKMA) indicated that small amounts of aldehydes could have significant effects on reactivity. Therefore, smog chamber experiments were carried out where varying amounts of formaldehyde were added to urban surrogate mixtures. The results showed that the effect of the added formaldehyde depended on the general reactivity of the system and the hydrocarbon-to-NO_x ratio. Less reactive systems could be made more reactive by addition of formaldehyde while reactive systems were less effected.

Model/Data Differences

Some previous experiments conducted with ethylene and aromatic hydrocarbons proved to be difficult to simulate. The observed changes in reactivity with changes in the HC-to-NO_x ratio could not be simulated. To resolve these differences, a number of ethylene experiments were conducted with the aid of special analytical techniques; these experiments were carried out over a wide range of ethylene-to-NO_x ratios. Several experiments were also carried out using a six-component aromatics mix to test the representation of aromatic hydrocarbons that are used in some of the newer mechanisms. Other experiments were conducted in which the same concentration of NO_x and total hydrocarbon was added to the two sides of the chamber, but the ratio of toluene to m-xylene in the two sides was varied. Experiments were also conducted to test the chemistry of new species and new reactions that are included in the latest state-of-the-science photochemical mechanisms.

Urban-Like Conditions

New synthetic hydrocarbon mixtures for auto exhaust and urban conditions were designed. Several experiments were conducted with these mixtures where the same level of NO_x but different amounts of hydrocarbon were added to the two sides of the chamber. These experiments were designed to test the models ability to simulate the effect on ozone production of varying the hydrocarbon-to-NO_x ratio.

Assistance for Modelers

Many experiments were conducted as requested by different modelers. The Unisearch tunable laser system for formaldehyde, hydrogen peroxide and nitric acid and their high sensitivity luminol NO_2 monitor were used in several experiments to obtain data eithe rarely obtained or that would valida measurements made earlier with othe methods. Some experiments wer conducted to investigate the reactivity several aromatic oxidation products. Th use of isobutene as a surrogate f formaldehyde was also tested. Ozon photolysis was studied with the aid nitrous oxide. Butane and biacet experiments were conducted to hel characterize the smog chamber.

A number of dynamic experimen were also carried out to test the rea world effects of continuous emissior and meteorological dilution. The dynam experiments that were carried out in previous UNC study had some problem in that modelers had difficulty dete mining the emission and dilution rate These problems were investigated ar resolved. Model simulations of a ke dynamic experiment carried out in th present study are presented in th Project Report. The sun position ar structure effects on the chamber we also studied to better understand ar estimate the photolytic rates inside th chamber.

Conclusions

A database of the 346 experimen conducted in past UNC chamber studi and the 71 new experiments carried o in the present study has been prepar to aid modelers in evaluating chemic mechanisms. This database has alrea been supplied to modelers for analys under EPA contracts and it is no available for use by others in th scientific community. Copies of th database on floppy diskettes and oth supporting information are available fro the authors.

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The complete report, entitled "Validation Data for Photochemical Mechanisms: Experimental Results," (Order No. PB 89-124 614/AS; Cost: $15.95, subject to change) will be available only from:
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