♨EPA Project Summary

Chemical Transformation Modules for Eulerian Acid Deposition Models Volume II. The Aqueous-Phase Chemistry

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This study was carried out as part of the research effort of the National Center for Atmospheric Research in the development of a Eulerian acid deposition model. It focuses upon the review and evaluation of mechanistic and kinetic data for aqueous-phase reactions that lead to the production of acidic substances in the environment. The intent of this research is to provide a framework that can be used to develop a state-of-the-art aqueous-phase mechanism for use in the Regional Acid Deposition Model under development at NCAR. In the research effort described in this report, 31 tables of kinetic data and 27 tables of thermodynamic data were compiled and evaluated. A set of recommended rate expressions and kinetic data was then prepared for the predominant aqueous-phase pathways leading to acid generation in the troposphere.

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

Early signs of ecological damage have been observed in certain sensitive areas of the world that are deficient in soils with a good acid buffering capacity and that are recipients of a large input of acids through "acid rain" and/or dry deposition. Scientists throughout the world are actively working to assess the extent of damage that has occurred and can be expected to occur in years ahead. Government leaders of many nations are attempting to evaluate alternative control strategies for acid deposition that can alleviate the existing and potential future problems.

The understanding of the nature and importance of the various chemical pathways to acid generation within the troposphere is one of the several prerequisites to the development of scientifically sound strategy for the control of acid deposition. The present study was initiated as part of the research effort at the National Center for Atmospheric Research to develop a regional, Eulerian acid deposition model.

In most existing acid deposition models that have been employed in control strategy development, no attempt has been made to incorporate the many complex chemical processes that control acid generation. Existing models often involve the use of only fixed rates of transformation of SO_2 and NO_x to sulfuric acid and to nitric acid, respectively. Uncertainties in the source-receptor relationships that these models provide arise from many factors; among others, they are very sensitive to the rates of chemical transformation of the precursors to the acids. This sensitivity arises largely

from the fact that the precursors of the acids and the acids themselves are not removed from the atmosphere with equal facility. Once sulfur dioxide is oxidized to sulfuric acid aerosol, it is dry deposited much less rapidly than is SO_2. If aerosols composed of sulfuric acid and its salts (ammonium bisulfate, ammonium sulfate, etc.) are incorporated into precipitating clouds, then the deposition of these species can be faster than that of gaseous SO_2. On the other hand, the nitric acid formed in the troposphere is much more rapidly deposited on the surface of the earth than are its precursors, NO and NO_2. Thus, the amount of acid and the chemical nature of the acids deposited at sites many kilometers from the source of the precursors are sensitive functions of the rates with which the acids are formed as well as the rates with which these acids are transported by the motion of the air mass in which they are contained. It follows that the development of chemical modules for use in acid deposition models should be based upon chemical mechanisms that describe acid generation in terms of known rate laws and chemical theory. The intent of the effort described in this Project Report was to review and evaluate available mechanistic and kinetic data for aqueous-phase reactions that lead to acid generation in the troposphere. The data compiled in this study will provide a framework for developing a chemical module for the NCAR regional acid deposition model.

Approach

An extensive review of the literature was undertaken to identify all possible chemical reactions that might be relevant to aqueous-phase cloud chemistry. Reactions were subdivided into reversible and irreversible categories. Reversible reactions were quantitatively described in terms of the appropriate mass action expressions, stoichiometric coefficients, equilibrium constants, and reaction enthalpies. Irreversible reactions were described likewise in terms of their stoichiometries, empirical rate laws or, in some special cases, fundamental rate expressions, rate constants, and activation parameters.

Based on this literature review, the data were compiled into two sets of tables. One set of tables contains kinetic data for the reactions of interest; the other set contains thermodynamic data for the aqueous-phase reactions of relevance to acid formation. After the tables were compiled, the major pathways for aqueous-phase acid formation were identified and the kinetic data for these reactions were critically evaluated. As a result of this evaluation, we prepared a set of recommended rate expressions and kinetic data for use in acid deposition modeling.

Results

Thirty-one tables of kinetic data were compiled in this study. Twenty-five of these tables contain data for aqueous-phase reactions involving free radicals. The majority of these tables focus on hydroxyl radicals as the principal oxidant. The other tables focus on the kinetics of S(IV) oxidation by O_3, H_2O_2, O_2 (catalyzed by Fe^{+3} and Mn^{+2}), organic species such as PAN and nitrogen-containing species. Kinetic data for the oxidation of N(III) are also presented.

Twenty-seven tables of thermodynamic data were compiled. Special attention was devoted to processes involving gas-liquid, metal-ligand, acid-base, precipitation-dissolution and aldehyde - S(IV) adduct equilibria.

A set of recommended rate expressions and kinetic data was prepared for the predominant pathways leading to S(IV) oxidation. These pathways include reaction of S(IV) with H_2O_2, O_3, O_2 (Fe^{+3} and Mn^{+2} catalyzed), OH, HONO, CH_3OOH, CH_3CO_3H, PAN, HO_2, HCHO, and soot.

Special attention was devoted to a critical evaluation of rate data for the S(IV)-O_3 reaction. Kinetic data obtained by five different investigators were analyzed. It was found that the data of most of the investigators could be fit by a multi-term rate law of the following form:

$$-d[S(IV)]/dt = (K_0a_0 + k_1a_1 + k_2a_2)[S(IV)][O_3]$$

Conclusions

In this study we formulated a reasonably complete set of aqueous-phase reactions in an attempt to identify all of the potentially significant acid-forming processes. The chemistry module that is to be used in our acid deposition model must be highly simplified in order to conserve computer time and allow efficient operation of the model. Because of this, considerable simplification of the reaction scheme presented in this study will be needed before it is suitable for use in our acid deposition model. In conducting this simplification, however, we do not want to sacrifice the ability of the model to predict the rates of acid generation with reasonable accuracy. We have concluded that the only way one can test adequately the scientific accuracy of any highly abbreviated chemical reaction scheme is scheme that includes all relevant acid-forming chemical processes. This is the approach that we have adopted in the study.

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