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THE DIRECT DETERMINATION OF ATOM AND RADICAL CONCENTRATIONS IN THERMAL REACTIONS OF HYDROCARBONS AND OTHER GASES

MASTER

Progress Report
for Period January 1, 1980 to December 31, 1980

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Abstract

This is the fifth annual progress report on this project. During the period covered by the first four reports (June 1976 through December 1979) a shock tube and an optical system to measure H and D atom concentrations were built and fully characterized. The performance of our microwave discharge lamps was defined by numerous high-resolution spectroscopic profiles, while empirical calibrations were made using mixtures of D_2-N_2O-Ar and hexamethylethane-Ar. H and D atom concentrations were measured in gas mixtures containing H_2, D_2, O_2, CD_4, C_2H_6, C_2D_6, C_3H_8 and C_3D_8 in various proportions, and rate constants of several elementary reactions were deduced from the data.

During 1979 the apparatus was modified by addition of an ultraviolet monochromator so that measurements of O, OH and other species besides H and D may be measured. During the past year empirical calibrations for O atom concentrations were made, and correlated with O-atom line shapes measured earlier. Measurements of O atom concentrations were made in several H_2-O_2-Ar and D_2-O_2-Ar mixtures, and rate constants of elementary reactions deduced from these measurements. A series of calculations of thermodynamic properties of CH_3, CD_3, C_2D_2, C_2D_4, C_2H_6 and C_2D_6, which were either unavailable or outdated, was made for use in our work. A microcomputer system was installed to speed data acquisition and processing.

Introduction

The general purpose of this project is to study hydrocarbon oxidation by making measurements of H, O, and OH and other free radicals involved. This information will be of practical value in engineering design to improve the efficiency and reduce the pollution of combustion devices such as automobile and aircraft engines.

In previous years we developed and characterize resonance absorption apparatus, and studied the formation of H and D atoms in a number of reacting gas mixtures. Many of these observations could be interpreted in terms of rate constants for specific chemical reactions. We also made modifications of the apparatus to make measurements of other species. During the past year we calibrated our apparatus for measuring O atom concentrations, and measured O atom concentrations in a series of gas mixtures containing H_2, D_2 and O_2.

Data and Discussion

Analysis for H and D Atoms. Three papers published in 1978 and 1979 (1,2,3) described our microwave discharge lamps, the shapes of the H and D Lyman-α spectral lines emitted by them, and the methods of calibration for H and D atom concentrations in our shock tube. Since calibration curves based on line shapes and empirical calibrations are in good agreement, we consider that our H and D measurements are based on a strong theoretical and experimental foundation.

Analysis for O Atoms. During the past year an extensive series of calibrations for O atoms has been made by dissociating mixtures of 1 to 20 ppm N_2O in argon at temperatures of 1900 to 2600K. Under these conditions the N_2O dissociates, with very small amounts of side reactions, within the shock tube residence time of 1 to 2 milliseconds, so that steady concentrations of O atoms, determined by stoichiometry, were obtained. In contrast to the calibration curves for H and D, the calibration curves for O atoms showed little dependence on temperature.

Calibration curves were also obtained from our measurements of O atom line shapes made earlier. These agreed well with the curve found empirically, so again we consider that our calibration curves are well known. A paper describing this work is nearly finished and the manuscript will be sent to DOE within the current contract year.

Pyrolysis of CD_4. The paper on this work, referred to in last year's report, has now been published (4). Six copies are attached to this report.

Shock tube measurements of D_2-O_2-Ar, H_2-O_2-Ar and CD_4-O_2-Ar mixtures. Measurements of D and H atoms in these reaction mixtures were reported earlier. The results have recently been published (5) and six copies are attached to this report. The reactions on which data were obtained most directly are

$$H\ (D) + O_2 \longrightarrow OH\ (OD) + O$$

$$H\ (D) + O_2 + Ar \longrightarrow HO_2\ (DO_2) + Ar$$

Our rate constants for the H reactions are in quite good agreement with data obtained by other methods, but the rate constants for the D reactions were found to be smaller than indicated by the one previous study. Moreover, this result is not easily explained in terms of theories of isotope effects, although application of the theory is not simple.

A study of O atom concentrations in similar gas mixtures has recently been completed. These lead to rate constants for the H reactions in excellent agreement with our earlier results, but the rate constants for the D reactions are higher than found before, although we still find an isotope effect. That is, from the H and D atom measurements we found (for both of the reactions given above) $k_H/k_D = 4.5$, while from the O atom measurements we found $k_H/k_D = 1.8$. A paper on this work is in preparation for presentation at the 13th Shock Tube Symposium this summer, and we will be sending approval copies to DOE in a few months.

<u>Absorption Coefficient of O_2</u>. We reported earlier our measurements of the absorption coefficient of O_2 for H and D Lyman-α over the temperature range 800 - 1700 K, and the evaluation of the absorption cross-sections for O_2 with v = 1 and v = 2. This information has now been published (6) and six copies of the paper are attached.

<u>Pyrolysis of Propane</u>. Dilute mixtures of C_3H_8 and C_3D_8 were pyrolyzed in the shock tube, and H and D atom concentrations measured. These measurements gave rate constants for the reaction $C_3H_8 \rightarrow CH_3 + C_2H_5$ and its deuterium analog. Details of these studies were presented at the 18th Combustion Symposium in the summer of 1980, and will appear in the symposium proceedings (7).

Pyrolysis of Ethane. Dilute mixtures of C_2H_6 and C_2D_6 were pyrolyzed in the shock tube, and H and D atom concentrations measured. Results of this work were discussed in last year's progress report. Interpretation of the data proved to be more complicated than we had realized, but we have now written a paper that is almost ready to be submitted for publication. Copies will be submitted to DOE for approval within the current contract year.

Oxidation of Ethane and Propane. These measurements were made last year. It seems that under our low concentration conditions the principal reaction involving O_2 is

$$\text{H (or D)} + O_2 \rightarrow \text{OH (or OD)} + \text{O}$$

As indicated before, we plan to measure O atom concentrations in these mixtures before attempting to deduce other rate constants from them.

Calculations of Thermodynamic Data. Thermodynamic properties of CH_3, CD_3, CD_4, C_2H_6, C_2D_6, C_2D_4 and C_2D_2, which are involved in our work, were calculated in the JANAF format from spectroscopic data since literature values were either unavailable or outdated. Since then we have also calculated properties of azomethane and azomethane-d_6, which decompose to produce CH_3 and CD_3 in shock tube experiments. A paper on this work has been submitted to Journal of Physical and Chemical Reference Data and is in the review and revision process. The computer program used to make these calculations can be used to make others as needed. One matter of concern to us is the evaluation of the contributions of vibrational anharmonicities to the thermal functions at temperatures above about 1500 K. This is a problem of general importance in combustion chemistry that has not been fully addressed by compilers of thermodynamic data so far. Since we often use thermodynamic data of gases at high temperatures to relate forward and reverse rate constants, we plan to devote a modest effort to develop at least approximate methods of accounting for these effects.

Automation of Data Acquisition. The microcomputer to collect and process data has now been set up. So far we have used it only to process our data in the conventional computer mode, but recently we obtained and tested an interface board which enables the computer to acquire data from the digital oscilloscope. After making some changes this board now works well, and we have successfully transferred data from the oscilloscope to the computer. It will now require only a moderate amount of programming to bring the system up to its full capability of data collection as well as calculations.

Plans for the Balance of the Year

We plan to study the reaction

$$O + H_2\ (D_2) \rightarrow OH\ (OD) + H\ (D)$$

by measuring O atom concentrations in mixtures of N_2O with H_2 or D_2 in argon. The N_2O will produce O atoms which will then react with the H_2 or D_2, so that the O atom concentration (which reached a steady value in our calibration measurements as all the N_2O became dissociated) will now go through a maximum and then decrease, the rate of decrease depending on the rate constant for the above reaction. Preliminary calculations indicate that no other reactions should affect the O atom concentrations under our conditions, so clean measurements of the rate constants of these reactions should be possible. Moreover, by measuring the O atom concentrations in both cases, the isotope effect in the reaction should be obtained accurately.

We then plan to study the O atom concentrations in oxidation of C_2H_6 and C_3H_8, and their deuterium analogs. These data can be combined with measurements we have already made of H and D concentrations in the same systems, to clarify the mechanisms and lead to elementary reaction rate constants. We plan to start with propane since it is of greatest interest as a model compound for larger hydrocarbons.

We also plan to complete the programming of our microcomputer so that it can completely acquire and process our data.

Personnel Involvement

The Principal Investigator, Dr. Gordon Skinner, spent approximately 45% of his time during the summer quarter (June 15 to August 31, 1980) and 20% of his time during the balance of 1980. He plans to devote about 20% of his time to the project between Jan. 1 and May 31, 1981.

Dr. Krishna M. Pamidimukkala (he now uses this name instead of P.M.M. Krishna, as given in last year's report) spent 100% of his time on the project in 1980. He plans to continue to spend 100% of his time on the project through May 31, 1981.

Dr. David R. Wood, Associate Professor of Physics, has continued his interest in the spectroscopic part of the project. He has been particularly interested in modelling the profiles of the spectral lines of N and O that were obtained earlier. He has spent about 15% of his time on this work, at no cost to the project, and will be an author of the paper on calibrations for O atoms.

Dr. Joseph Kohler, Associate Professor of Computer Science, has rendered valuable assistance in setting up the microcomputer for data acquisition. He not only designed the system but constructed two of the circuit boards, spending altogether about 10% of his time during 1980, at no cost to the project. He will continue to assist us during the next few months while the final touches are put on the system.

Mr. C. Steven Dick is a Wright State undergraduate who participated in several ways, such as making calculations and organizing our literature file, during the first half of 1980, spending 8-10 hours per week on the project. He has now graduated and is attending medical school. Mr. Laurance Webb, another Wright State undergraduate, spent about 12 hours per week on the project during the summer quarter of 1980, helping Dr. Kohler set up and test the microcomputer system.

Mr. Howard DuFour, instrument machinist, spent about 25 hours on the project during 1980.

All of these personnel involvements have been in compliance with the contract.

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