COO-2944-3 TLC

MASTER

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

Progress Report
for Period January 1, 1978 to December 31, 1978

G.B. Skinner, C.-C. Chiang, and D.R. Wood

Wright State University
Dayton, Ohio 45435

January 1979

Prepared for

United States Department of Energy
Under Contract No. EY-76-S-02.2944.A003

EB

NOTICE

Abstract

This is the third annual progress report on this project. During the period covered by the first two reports (June 1976 through December 1977) a shock tube and an optical system to measure H and D atom concentrations was built and fully characterized. The performance of our microwave discharge lamps was defined by numerous high-resolution spectroscopic profiles, while empirical calibrations were made by shock-heating mixtures of D_2-N_2O-Ar. Some measurements of H and D atom concentrations in H_2-O_2-Ar and D_2-O_2-Ar mixtures were made.

During 1978 the empirical calibrations were completed by shock-heating mixtures of hexamethyethane in argon at temperatures near 1000 K. These data, combined with the higher-temperature D_2-N_2O-Ar data and correlated using mathematical functions based on the line shapes, have led to dependable calibration curves for both H and D over a wide temperature range. H and D atom concentrations have been made for mixtures of H_2-O_2-Ar, D_2-O_2-Ar, CD_4-Ar, CD_4-O_2-Ar, and C_3H_8-Ar, and absorption measurements made for O_2-Ar mixtures. Numerous calculations have been made, based on the data, and several papers written.

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.

Our first research goal, which has now been accomplished, has been to develop dependable means of analysis for these substances, particularly H (and its isotopic variant D). The method we have used is resonance absorption spectroscopy, our light source being a microwave discharge lamp. Following this, we have been measuring H and D concentrations in a variety of gas mixtures, and interpreting these data in terms of rate constants for specific chemical reactions. In the near future we will extend our work to the analysis of O and OH.

Data and Discussion

Spectroscopic Measurements. We described in last year's progress report how we measured profiles of the H and D Lyman-α lines emitted by microwave discharge lamps. The experimental work and most of the calculations had been completed during 1977. This material has now been written up for publication (1). It has been submitted to Journal of Chemical Physics, and review copies have been submitted to DOE.

A short paper describing a microwave discharge lamp of somewhat novel design was submitted with last year's progress report, in draft form. This paper has been published in Review of Scientific Instruments (2), and 6 reprints are attached with this progress report.

We have additional spectroscopic data on O and N atomic lines that we plan to use for analysis for these species. We are still making calculations related to these lines, and plan to publish the results when these calculations are complete.

Shock-Tube Calibrations for H and D Atoms. We had described in the previous progress report our observations of D atoms in N_2O-D_2-Ar mixtures heated to 1900 - 3000 K in our shock tube. These provided an empirical calibration over this temperature range that was in quite good agreement with our calibrations based on line shapes.

During the past year we completed our empirical calibrations by observing H atoms produced by shock-heating 2,2,3,3-tetramethylbutane, or hexamethylethane. The rate at which this substance decomposes to form, among other products, H atoms, has been carefully measured by Tsang (3). These data, obtained mainly in the 1000 - 1200 K range, could be correlated very well with the N_2O-D_2-Ar data at higher temperatures and with our line shape measurements. These calibrations and the related calculations are described in a paper (4) that has been submitted to Journal of Chemical Physics, and also to DOE for review.

We now consider that we can measure H and D atom concentrations with absolute accuracy of ±25% over the temperature range 900 - 2600 K with a time resolution of less than 5 microseconds. This capability enables us to make our kinetic measurements with a great deal of confidence.

Shock Tube Measurements on D_2-O_2-Ar and H_2-O_2-Ar Mixtures. In 1977 we obtained some data on H and D atom concentrations in mixtures of 1% H_2 0.5% O_2 - 98.5% Ar, 0.1% H_2 - 0.05% O_2 - 99.85% Ar, 1% D_2 - 0.5% O_2 - 98.5% Ar, and 0.1% D_2 - 0.05% O_2 - 99.85% Ar over the temperature range 1000 - 2000 K. These systems are good ones to start with since they have been extensively studied by several methods, yet there have been few measurements of atom concentrations for them. We have made additional measurements on the above mixtures, and also on mixtures of 5% H_2 - 2.5% O_2 - 92.5% Ar and 5% D_2 - 2.5% O_2 - 92.5% Ar. From these data we have been able to deduce rate constants for the reactions:

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

and

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

The data for the H reactions are in quite good agreement with data obtained by other methods, but the rate constants for the D reactions are smaller than indicated by the one previous study. Calculation of the isotope effect in these reactions is complicated by the fact that the HO_2 (DO_2) activated complex of the first reaction is a relatively stable free radical, so the complex is probably unusually long-lived. We expect to prepare a paper on the experimental results before the end of this contract year.

Absorption Coefficient of O_2. In the course of the above work we found that, while O_2 does not absorb Lyman-α radiation much at room temperature, its absorption coefficient increases greatly at high temperatures. This requires us to limit the O_2 concentrations we may use in experiments. We have made measurements on this absorption coefficient and also on the time required for it to occur (which appears to be related to the vibrational relaxation time) and are preparing a paper on this. We have also found that a small amount of H_2 greatly increases the rate of vibrational relaxation.

Pyrolysis and Oxidation of CD_4. We have measured the concentrations of D atoms in the pyrolysis of several dilute mixtures of CD_4 in argon, obtaining rate constants for the reactions:

$$CD_4 + Ar \longrightarrow CD_3 + D + Ar$$

and

$$D + CD_4 \longrightarrow D_2 + CD_3$$

At the low CD_4 concentrations studied, no other reactions were significant, so the interpretation of the data was relatively simple. The data for CD_4 decomposition were compared to other values for CH_4 via the RRKM theory, while an activated complex theory calculation was used to analyze the results for the second reaction. A paper on this work has been written (5) and submitted for publication and presentation at the American Chemical Society national meeting in April, 1979. Copies have also been submitted to DOE.

Addition of up to 1% of O_2 to these mixtures actually reduced the D concentration somewhat, via the reaction:

$$D + O_2 \rightarrow OD + O$$

and subsequent reactions produced less D than were lost by this reaction. The rate constant for the above reaction that was determined from our $D_2 + O_2 + Ar$ studies fit well with that found from the $CD_4 - O_2 - Ar$ mixtures, indicating that our lower-than-expected value may be correct.

<u>Pyrolysis of Propane.</u> Dilute mixtures (5 and 20 ppm) of propane in argon have been studied at 1200 - 1500 K, at which temperatures measurable quantities of H have been found. At these temperatures the free radicals C_2H_5, $CH_2CH_2CH_3$ and CH_3CHCH_3 are quite unstable, so the production of H atoms is a direct measure of the rate of dissociation of propane, by the reaction:

$$C_3H_8 \rightarrow CH_3 + C_2H_5$$

followed by

$$C_2H_5 \rightarrow C_2H_4 + H$$

Subsequent reactions of CH_3 and H with C_3H_8 tend to be slow at these low concentrations, and we cannot use higher concentrations of C_3H_8 because it absorbs quite strongly at H Lyman-α. However, we do have the advantage of being able to measure the initial rate of dissociation directly, which is difficult or perhaps impossible to do by other high temperature techniques. We are still making calculations based on these experiments.

Plans for the Balance of the Year

We plan to make additional measurements of H and D atom concentrations in hydrocarbon-containing mixtures during the balance of the year. These will include propane-oxygen, ethane, and ethane-oxygen mixtures in argon. We will also study one or both of these compounds in deuterated form.

We also plan to set up the monochromator which was resently obtained, and prepare to measure O atom concentrations by resonance absorption. Knowledge of concentrations of both H and O atoms will assist greatly in deducing reaction mechanisms and kinetic data. In these experiments we again plan to make empirical calibrations which can be correlated with our line shape measurements to yield dependable calibration curves over a temperature range.

Personnel Involvement

The Principal Investigator, Dr. Gordon Skinner, spent approximately 40% of his time on the project during the summer quarter (June 15 to Aug. 31, 1978) and 20% of his time during the balance of 1978. He plans to devote about 20% of his time between Jan. 1 and May 31, 1979.

Dr. C.-C. Chiang, post-doctoral fellow, spent 100% of his time on it during 1978, and plans to spend 100% of his time through May 31, 1979.

Dr. David R. Wood, Associate Professor of Physics, has donated about 15% of his time to the project during 1978, because of his professional interest in the spectroscopic component of the project. He has been very helpful in this work, and hence has been made a co-author of this report and of journal articles to which he has contributed (1,2).

Mr. Howard Dufour, instrument machinist, has spent about 30 hours on the project during 1978.

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

References

1. A. Lifshitz, G.B. Skinner and D.R. Wood, "Resonance Absorption Measurements of Atom Concentrations in Reacting Gas Mixtures.1. Shapes of H and D Lyman-α Lines in a Microwave Source." Submitted to J. Chem. Phys.

2. A. Lifshitz, G.B. Skinner and D.R. Wood, Rev. Sci. Instrum., 49, 1322 (1978).

3. W. Tsang, J. Chem. Phys., 44, 4283 (1966).

4. C.-C. Chiang, A. Lifshitz, G.B. Skinner and D.R. Wood, "Resonance Absorption Measurements of Atom Concentrations in Reacting Gas Mixtures.2. Calibration of Microwave Sources Over a Wide Tempperature Range." Submitted to J. Chem. Phys.

5. C.-C. Chiang, J.A. Baker and G.B. Skinner, "Resonance Absorption Measurements of Atom Concentrations in Reacting Gas Mixtures.3. Pyrolysis of CD_4 Behind Shock Waves", Submitted to American Chemical Society Symposium Series.