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

Progress Report
for Period January 1, 1979 to December 31, 1979

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Abstract

This is the fourth annual progress report on this project. During the period covered by the first three reports (June 1976 through December 1978) 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 H_2-O_2-Ar, D_2-O_2-Ar, CD_4-Ar, CD_4-O_2-Ar and C_3H_8-Ar mixtures, and absorption measurements made for O_2-Ar mixtures. Several calculations of elementary rate constants were made, based on the above data.

During 1979 H and D atom measurements were extended to C_3H_8-O_2-Ar, C_3D_8-Ar, C_3D_8-O_2-Ar, C_2H_6-Ar, C_2H_6-O_2-Ar, C_2D_6-Ar and C_2D_6-O_2-Ar mixtures. Most of these data have been interpreted in terms of elementary reactions, and several calculations of elementary reaction rate constants have been made. Our apparatus has been modified so concentrations of O, OH and other species besides H and D can be determined by absorption spectroscopy and measurements with our new system are being made. Two papers based on this work were published in 1979, and three presentations made at scientific meetings.

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 characterized resonance absorption spectroscopic apparatus, and studied the formation of H and D atoms in a number of reacting gas mixtures. Many of these observations can be interpreted in terms of rate constants for specific chemical reactions. During the past year we continued our measurements of H and D atom concentrations, and have also modified our apparatus to make measurements of O atoms and free radicals.

Data and Discussion

Analysis for H and D Atoms. Our first long paper describing our measurements of the shapes of H and D Lyman-α lines emitted by microwave discharge lamps has been published in Journal of Chemical Physics (1). A second paper describing empirical calibrations for H and D concentrations in our shock tube, using the N_2O-D_2 method around 2000K and 2,2,3,3-tetramethyl butane pyrolysis around 1000K, was also published (2). Reprints of both of these papers have been submitted to DOE.

Since calibration curves calculated from the line shapes agreed well with the empirical calibrations, we consider that our H and D measurements are based on a strong theoretical and experimental foundation.

Pyrolysis of CD_4. Measurements of D atom concentrations in CD_4-Ar mixtures, referred to in last year's report, were presented at the American Chemical Society meeting in April, 1979. However, the ACS decided not to publish a symposium volume, so the paper was submitted to Journal of Physical Chemistry, and has recently been accepted for publication (3). The original paper was submitted to DOE, and reprints will be submitted when available.

Shock tube measurements on 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 reactive mixtures had been reported earlier. Several of the same reactions appear in both methane and hydrogen oxidation, so it was convenient to present these oxidation studies in one paper (4). The reactions on which data have been obtained most directly are

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

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

Our reactions 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. This conclusion is indicated by both the D_2-O_2-Ar and CD_4-O_2-Ar data. This result is somewhat unexpected from theories of isotope effects, but application of the theory is not simple. A number of theorists are taking this reaction under consideration, and results may come soon. A paper on these reactions was presented at the Twelfth International Symposium on Shock Tubes and Waves in the Summer of 1979, and will be published in the Proceedings. Copies were submitted to DOE shortly before the Symposium.

Absorption coefficient of O_2. In the course of our oxidation studies we found that O_2 absorbs H and D Lyman-α radiation much more strongly at high temperatures than at room temperature. We found that the increase in absorption coefficient can be interpreted in terms of the increase in vibrational excitation of O_2 at higher temperatures. Absorption cross-sections have been calculated for O_2 with $v = 1$ and $v = 2$. A paper on this work was submitted to DOE and has been accepted for publication in Journal of Quantitative Spectroscopy and Radiative Transfer (5).

Pyrolysis of Propane. Dilute mixtures of 5 and 20 ppm of C_3H_8, and also of 5, 20 and 100 ppm of C_3D_8 in argon were pyrolyzed in the shock tube, and H and D concentrations measured. These measurements give direct information on the rate of dissociation of propane by the reaction

$$C_3H_8 \rightarrow CH_3 + C_2H_5$$

and its deuterium analog, since at our low concentrations and relatively high temperatures the methyl radicals are relatively unreactive, while the ethyl radicals dissociate rapidly to produce C_2H_4 and H. It seems that rates of dissociation of C_3H_8 and C_3D_8 are nearly the same, which would be expected since the deuterium substitution produces only a secondary isotope effect.

A paper describing this work has been prepared and will be submitted soon to DOE. We plan to present this work at the Combustion Symposium this Summer.

Pyrolysis of Ethane. This reaction, which has been extensively studied by ourselves and others in the past, mainly by analysis for stable products, does not lead to the formation of H atoms directly, as does propane pyrolysis, but only later in the reaction scheme. It is generally considered that the first reaction is

$$C_2H_6 \rightarrow 2\ CH_3$$

and at moderate temperatures and concentrations the next reaction is

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$

following which H atoms are formed by dissociation of C_2H_5. At our low concentrations the reaction of CH_3 with C_2H_6 occurs slowly, so large concentrations of H are not produced unless we to to fairly high temperatures where the reaction rate constants are higher. In a recently published study (6), Roth and Just concluded, from work using the resonance absorption technique, that at very high temperatures (∿ 2000 K) ethane dissociates so rapidly to methyl radicals that no H would be formed by reaction of CH_3 with C_2H_6. They did observe H, and considered that it comes from the reaction

$$2\ CH_3 \rightarrow C_2H_5 + H,$$

the C_2H_5 dissociating also so the overall process is

$$2\ CH_3 \rightarrow C_2H_4 + 2\ H$$

At the same time, it seems likely that the process

$$2\ CH_3 \rightarrow C_2H_4 + H_2$$

is also occurring.

On the whole, our experimental results, which include pyrolysis of 10 and 50 ppm C_2H_6 and 10, 50 and 200 ppm C_2D_6 in argon, confirm these ideas of Roth and Just about the high temperature reactions. We also have enough data at lower temperatures (1200 - 1400 K) to draw conclusions about the rate constants for the dissociation of C_2H_6 and C_2D_6 in that range. These data (which are still at relatively high temperatures compared to other studies on the dissociation of C_2H_6) can be combined with other data from our laboratory and other places, and lead to a very good kinetic model for ethane dissociation (and also CH_3 combination) over a broad temperature range.

This work is now being prepared for publication and will be submitted to DOE in the near future, probably by the end of the contract year.

Oxidation of Ethane and Propane. We have carried out an extensive series of measurements of H and D atoms using the following mixtures in argon:

10 ppm C_2H_6 + 400 ppm O_2
50 ppm C_2H_6 + 2000 ppm O_2
10 ppm C_2D_6 + 400 ppm O_2
50 ppm C_2D_6 + 2000 ppm O_2
20 ppm C_3H_8 + 200 ppm O_2
20 ppm C_3H_8 + 2000 ppm O_2
20 ppm C_3D_8 + 200 ppm O_2
20 ppm C_3D_8 + 2000 ppm O_2

The presence of O_2 modified the H and D concentrations, mainly, we think, via the reaction

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

which we studied earlier as part of the H_2/O_2 or D_2/O_2 system. Initially the effect is to reduce the number of H atoms, but later in the reaction process the production of layer numbers of other free radicals (OH and O) that can react with the hydrocarbons can lead to an increase in the concentrations of H and D.

We have been able to develop reaction schemes based on our H and D measurements, but since several reactions are involved we have not been able to deduce rate constants for them all. Before publishing these data we would like to obtain O and possibly OH concentrations in these same mixtures, so that our calculated rate constants will be firmly based on a substantial body of experimental data.

Calculations of Thermodynamic Data. To use along with our kinetic data we have made calculations of thermodynamic functions for several substances for which literature data are unavailable or else not up to date. Our calculations cover the range from room temperature to 3000 K. Substances include CH_3, CD_3,

CD_4, C_2H_6, C_2D_6, C_2D_4, and C_2D_2. We have also made less accurate calculations for C_2H_5 and C_2D_5. We will submit these tables and consider publication in an appropriate journal.

Measurements of O Atom Concentrations. We have installed the McPherson Model 218 monochromator on the shock tube, and set up the necessary vacuum system. This instrument resolves the O triplet near 1300 A very easily in the fourth order using a 1200 groove/mm grating blazed at 5000 A. For high intensity we use wide slits (0.5-1 mm), under which conditions the lines are not resolved, but are well separated from other radiation emitted by our microwave discharge lamp. We have carried out a number of experiments to measure the absorption coefficient of O_2 at this wavelength, and are preparing to calibrate the system for O atoms using the dissociation of N_2O.

Automation of Data Acquisition. We have installed the digital storage oscilloscope, so we no longer have to make measurements from photographs, which was both very time consuming and somewhat limiting in accuracy. At present we simply record the data on a strip chart recorder, from which measurements can be made more easily and accurately. However, we have also ordered a number of components to set up a microcomputer which will be able to accept and process the data, thereby saving more time and also allowing use of statistical methods that have been cumbersome to apply (involving preparation of large numbers of punched cards) with our present manual data collection system.

Plans for the Balance of the Year

We plan to calibrate the O atom measurement system using N_2O dissociation, and to calculate calibration curves by combining these measurements with the line shape measurements made earlier on the high-resolution monochromator. This will be followed by O atom measurements in several of the reaction mixtures in which H and D atom concentrations have already been measured.

We also will assemble the microcomputer system as components come in, and program it to handle our data.

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, 1979) and 20% of his time during the balance of 1979. He plans to devote about 20% of his time to the project between Jan. 1 and May 31, 1980.

Dr. C.-C. Chiang, post-doctoral fellow, spent 100% of his time on it between Jan. 1 and May 31, 1979. Having spent two years on the project, he left at the end of May to pursue additional post-doctoral studies at Stanford University.

Dr. P.M.M. Krishna, post-doctoral fellow, had planned to join the project in June, but had difficulties obtaining a visa to come from India to the U.S.A., and actually joined us on October 15, 1979, since which time he has devoted full time to the project. He plans to spend 100% of his time through May 31, 1980 on it.

Dr. David R. Wood, Associate Professor of Physics, has continued his interest in the spectroscopic part of the project, and has spent about 15% of his time during 1979 carrying out an analysis of the N atom line shapes emitted by our microwave lamp. He will probably continue to help on the analysis of the O atom line shapes, and will be a co-author on papers resulting from this work.

Mr. Scot Pencil and Mr. C. Steven Dick are Wright State undergraduates who have participated in several ways (such as making calculations, assembling the vacuum system and organizing our literature file) on a part-time basis. Mr. Pencil graduated last August, while Mr. Dick will continue to work 8-10 hours per week through May, 1980.

Mr. Howard Du Four, instrument machinist, has spent about 30 hours on the project during 1979.

All of these personnel involvements have been in compliance with the contract. Because of the unavoidable delay in Dr. Krishna's joining the project, we have asked for and obtained permission to use the unused funds from the salary budget to purchase items needed to improve our vacuum system and purchase computer components for data acquisition and processing.

References

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