KINETICS OF THE THERMAL DECOMPOSITION OF DIMETHYLMERCURY

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Kenneth Brant Yerrick
1962

C. 2

ABSTRACT

KINETICS OF THE THERMAL DECOMPOSITION OF DIMETHYLMERCURY

by Kenneth Brant Yerrick

Previous studies concerned with the thermal decomposition of dimethylmercury have produced disagreement as to the kinetic order of the reaction and the mechanism by which it proceeds.

The method used to study the reaction for the present research was a static system. Since the reaction was studied in the gas phase, a conventional vacuum system was employed. The gaseous reaction products were analyzed qualitatively by gas chromatography. The kinetic studies have been made for the temperature range 275-330°C and for the concentration range 0.3×10^{-6} to 7.0×10^{-6} moles cc^{-1}. On the basis of the experimental data obtained, the following empirical rate expression has been postulated:

$$-\frac{d(D)}{dt} = k_a(D) + k_b(D)^2$$

In this expression (D) is the concentration of dimethylmercury; k_a and k_b are first and second order rate constants; respectively. These rate constants have been evaluated by a method of successive approximations. Least squares analyses have yielded the following Arrhenius rate equations:

$$k_a = 2.6 \times 10^9 \exp(-39{,}400/RT), \quad (\text{sec.}^{-1})$$

$$k_b = 9.5 \times 10^{26} \exp(-70{,}600/RT), \quad (\text{cc. mole}^{-1}\ \text{sec.}^{-1})$$

The gaseous reaction products analyzed by gas chromatography were found to be (excluding methane) ethane, ethylene, acetylene, propane, propene, n-butane, 1-butene and 2-methylpropene. Some preliminary studies of the carbonaceous deposit which is formed on the reactor walls are discussed.

The lack of experimental data has prevented the postulation of a plausible mechanism for the decomposition reaction. On the basis of the observations made in this study, further experimental studies have been proposed.

KINETICS OF THE THERMAL DECOMPOSITION OF DIMETHYLMERCURY

By

Kenneth Brant Yerrick

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1962

To My Wife Carole

To My Wife Carole

To My Wife Carole

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. Morley E. Russell for his guidance, assistance and encouragement which he so generously gave throughout the investigation and preparation of this thesis. Appreciation is gratefully extended to the author's parents whose understanding and patience guided him through his early years. Thanks is also given to Mr. F. E. Hood for his assistance in the development of the apparatus; and to Drs. C. H. Brubaker and R. B. Bernstein who kindly furnished the dimethylmercury.

****

TABLE OF CONTENTS

LIST OF TABLES

TABLE Page

LIST OF FIGURES

LIST OF FIGURES

LIST OF APPENDICES

APPENDIX Page

INTRODUCTION

I. Historical Background

The interest in the decomposition of dimethylmercury has stemmed from the extensive use of this compound as a source of methyl radicals which are formed by the photolytic or thermal scission of the mercury-carbon bond. A review (to 1953) of the photolytic decomposition appears in a monograph by Steacie (1). The most important steps of various proposed mechanisms are thought to be:

$$\mathrm{Hg(CH_3)_2} \xrightarrow{h\nu} \mathrm{HgCH_3\cdot + CH_3\cdot} \qquad \underline{1}$$

$$\mathrm{HgCH_3\cdot} \longrightarrow \mathrm{Hg + CH_3\cdot} \qquad \underline{2}$$

$$\mathrm{2CH_3\cdot} \longrightarrow \mathrm{C_2H_6} \qquad \underline{3}$$

$$\mathrm{CH_3\cdot + Hg(CH_3)_2} \longrightarrow \mathrm{CH_4 + CH_3HgCH_2\cdot} \qquad \underline{4}$$

At room temperature the gaseous product is primarily ethane with the production of methane increasing as the temperature increases. The methane presumably arises from a process such as reaction $\underline{4}$.

The photolytic decomposition of dimethylmercury is fairly well understood; especially with regard to the general mechanism presented above. On the other hand, there is a great deal of controversy regarding the thermal decomposition. In general, there is good agreement among those who have investigated the thermal decomposition with respect to steps $\underline{1}$, $\underline{2}$, and $\underline{3}$ presented above. The disagreement arises concerning the remainder of the mechanism; especially the methane producing step.

Cunningham and Taylor (2) made a cursory examination of the pyrolysis reaction in a static system at temperatures of 302 and 348°C. They found no measurable amount of decomposition up to 290°C. They reported methane and ethane as the gaseous products with increasing amounts of methane as the temperature was increased. In contrast to the photolytic decomposition, they reported that a carbonaceous deposit was formed on the walls of the reaction vessel which they postulated to be of a $(CH_2)_n$ nature. Their basis for this postulation stems from the experimental observations that less than 60% of the carbon from the decomposed dimethylmercury could be found in the product gases and also no free hydrogen was detected in the gaseous products. Cunningham and Taylor made no attempt to determine the rate of the pyrolysis or its kinetic order.

To verify the formation of methyl radicals, which are postulated in all mechanisms, Lossing and Tickner (3) decomposed dimethylmercury in a flow system at 850°C. They determined the presence of methyl radicals by use of a mass spectrometer. The product gases from the decomposition were allowed to leak from the reactor through an orifice into the ionization chamber of the spectrometer. They were able to detect a measurable amount of methyl radicals, thus supporting the postulate that methyl radicals are formed during the thermal decomposition. Lossing and Tickner reported an activation energy for the overall reaction of 42 kcal/mole in the temperature range 611-850°C and pressures of dimethylmercury of 2.8 and 8.1 microns.

Gowenlock, Polanyi and Warhurst (4) employed a flow system at temperatures of 500-600°C and reported first order kinetics. They found that there was no appreciable inhibition due to the addition of toluene to the system. They also reported appreciable amounts of ethylene in the gaseous products. In contrast to Cunningham and Taylor, who reported more methane than ethane at 300°C, Gowenlock *et al*.

reported ethane in a greater abundance than methane in the temperature range 500-600°C. When Gowenlock et al. interpreted their data, they related $k_{obs.}$ to k_1, which is the rate constant for the initial rupture of the carbon-mercury bond. They reported an activation energy of 51.5 kcal/mole for the temperature range 500-600°C and total pressures of approximately 10 mm Hg. On the basis of their observations, they proposed the following non-chain mechanism:

$$Hg(CH_3)_2 \longrightarrow CH_3\cdot + HgCH_3\cdot \qquad \underline{1}$$

$$HgCH_3\cdot \longrightarrow CH_3\cdot + Hg \qquad \underline{2}$$

$$2\ CH_3\cdot \longrightarrow C_2H_6 \qquad \underline{3}$$

$$CH_3\cdot + Hg(CH_3)_2 \longrightarrow CH_4 + CH_3HgCH_2\cdot \qquad \underline{4}$$

$$CH_3\cdot + CH_3HgCH_2\cdot \longrightarrow C_2H_5HgCH_3 \qquad \underline{5}$$

$$2\ CH_3HgCH_2\cdot \longrightarrow (CH_3HgCH_2)_2 \qquad \underline{6}$$

Gowenlock et al. reported no experimental evidence for reactions 5 and 6 and they concluded that reaction 6 plays only a minor role in the decomposition process.

Using a flow system, Price and Trotman-Dickenson (5) examined the pyrolysis reaction over approximately the same temperature range (465-608°C) as Gowenlock et al. The data of Price and Trotman-Dickenson agree very well with that reported by Gowenlock et al. The total pressure employed by Price and Trotman-Dickenson was approximately 20 mm Hg and they reported an activation energy of 50.1 kcal/mole. Since they employed the toluene-carrier technique, Price and Trotman-Dickenson assumed a somewhat different mechanism.

$$Hg(CH_3)_2 \longrightarrow HgCH_3\cdot + CH_3\cdot \qquad \underline{1}$$

$$HgCH_3\cdot \longrightarrow Hg + CH_3\cdot \qquad \underline{2}$$

$$2\ CH_3\cdot \longrightarrow C_2H_6 \qquad \underline{3}$$

$$CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2\cdot \qquad \underline{4}$$

$$2\ C_6H_5CH_2 \longrightarrow (C_6H_5CH_2)_2 \qquad \underline{5}$$

Yeddanapalli, Srinivasan and Paul (6) used a static system (305-342°C) to study the pyrolysis reaction. They reported that at the lower temperatures it was difficult to choose between first order and three-halves order kinetics but at the higher temperatures the data pointed decidedly to three-halves order kinetics. Therefore Yeddanapalli <u>et</u> <u>al</u>. selected three-halves order for the entire temperature range of 305-342°C. They also observed that methane and ethane were the main reaction products with methane being in greater abundance. They reported small amounts of hydrogen, ethylene and acetylene in the gaseous products. Yeddanapalli <u>et</u> <u>al</u>. also observed the carbonaceous deposit on the reactor walls. They obtained an overall activation energy of 44.7 kcal/mole in the temperature range 305-342°C and at total pressures of approximately 40 mm Hg. In order to account for the experimental data observed, they postulated the following mechanism.

$$Hg(CH_3)_2 \longrightarrow HgCH_3\cdot + CH_3\cdot \qquad \underline{1}$$

$$HgCH_3\cdot \longrightarrow Hg + CH_3\cdot \qquad \underline{2}$$

$$2\ CH_3\cdot \longrightarrow C_2H_6 \qquad \underline{3}$$

$$CH_3\cdot + Hg(CH_3)_2 \longrightarrow CH_4 + CH_3HgCH_2\cdot \qquad \underline{4}$$

$$CH_3HgCH_2\cdot \longrightarrow HgCH_2{:} + CH_3\cdot \qquad \underline{5}$$

They proposed that the small quantities of hydrogen, acetylene and ethylene might be due partly to the decomposition of the $HgCH_2\colon$ radical in reaction 5 to give $CH_2\colon$ radical which would undergo disproportionation and polymerization reactions to give $(CH_x)_n$ and hydrogen. Ganesan (7) recently recalculated the data of Yeddanapalli et al. using a novel method and obtained an activation energy of 48.2 kcal/mole which agrees better with the activation energy reported by other workers.

Laurie and Long (8) reinvestigated the pyrolysis over approximately the same temperature range (294-343°C) as that of Yeddanapalli et al. Laurie and Long also used a static system to study the decomposition; however, they used a "clean" reactor (reactor cleaned thoughly before each experiment) whereas other investigators have employed a "conditioned" reactor (several decompositions carried out before taking kinetic data). Laurie and Long reported first order kinetics near 300°C but they observed that the order increased to nearly three-halves order at 343°C. They reported an activation energy of 51.3 kcal/mole for the pyrolysis in the temperature range 294-333°C at total pressures of approximately 70 mm Hg. Long (9, 10) proposed that the principal hydrocarbon product, methane, is produced by methyl radicals abstracting a hydrogen atom from hydrocarbons such as ethane. Long proposed the following mechanism.

$$Hg(CH_3)_2 \longrightarrow HgCH_3\cdot + CH_3\cdot \qquad \underline{1}$$

$$HgCH_3\cdot \longrightarrow Hg + CH_3\cdot \qquad \underline{2}$$

$$2\,CH_3\cdot \longrightarrow C_2H_6 \qquad \underline{3}$$

$$CH_3\cdot + C_2H_6 \longrightarrow CH_4 + C_2H_5\cdot \qquad \underline{4}$$

$$CH_3\cdot + C_2H_5\cdot \longrightarrow CH_4 + C_2H_4 \qquad \underline{5}$$

$$CH_3\cdot + C_2H_5\cdot \longrightarrow C_3H_8 \qquad \underline{6}$$

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_2H_6 + C_2H_4 \qquad \underline{7}$$

$$C_2H_5\cdot + C_2H_5\cdot \longrightarrow C_4H_{10} \qquad \underline{8}$$

Cattanach and Long (11) reinvestigated the decomposition reaction over approximately the same temperature range (303-332°C) as Laurie and Long (294-343°C). Cattanach and Long studied the effect of added nitrogen, ethane and azomethane in order to confirm the mechanism proposed by Long.

Russell and Bernstein (12, 13) studied both the inhibited and uninhibited thermal decomposition of dimethylmercury in a static system from 265-350°C. Although they made no attempt to determine the order of the uninhibited reaction, their data agrees with the observations of the other investigators. In the cyclopentane-inhibited reaction they observed that the decomposition exhibited first order kinetics with methane being the major product. Due to the inhibition from cyclopentane and from the isotope effect data, they postulated that at least short chains are formed in the decomposition reaction. On the basis of their experimental observations, Russell and Bernstein proposed the following mechanism for the uninhibited reaction.

$$Hg(CH_3)_2 \longrightarrow CH_3\cdot + HgCH_3\cdot \qquad \underline{1}$$

$$HgCH_3\cdot \longrightarrow CH_3\cdot + Hg \qquad \underline{2}$$

$$2\ CH_3\cdot \longrightarrow C_2H_6 \qquad \underline{3}$$

$$CH_3\cdot + Hg(CH_3)_2 \longrightarrow CH_4 + CH_3HgCH_2\cdot \qquad \underline{4}$$

$$CH_3\cdot + Hg(CH_3)_2 \longrightarrow C_2H_6 + HgCH_3\cdot \qquad \underline{5}$$

of t
tha
stu
inv
org
Sin
vi
a v
th
(ca
m
pr
th
or
in
it
pl

$$CH_3\cdot + CH_3HgCH_2\cdot \longrightarrow C_2H_5HgCH_3 \qquad \underline{6}$$

$$CH_3HgCH_2\cdot \longrightarrow HgCH_3\cdot + CH_2\colon \qquad \underline{7}$$

$$CH_2\colon + Hg(CH_3)_2 \longrightarrow C_2H_5HgCH_3 \qquad \underline{8}$$

$$2\ CH_2\colon \longrightarrow C_2H_4 \qquad \underline{9}$$

II. Objectives of Present Study

Since there has been some disagreement as to the kinetic order of the thermal decomposition of dimethylmercury, it seemed possible that this inconsistency could be better evaluated if the reaction was studied under a wider range of experimental conditions. Previous investigators who employed a static system observed a variation in the order of the reaction as the temperature was increased (6, 8, 12). Since the previous work employing static systems was conducted in the vicinity of 300°C, it appeared advisable to investigate the reaction over a wider temperature range. Furthermore, earlier investigations of this pyrolysis have shown some tendency for the observed rate constant (calculated on the basis of first order) to be a function of the dimethylmercury pressure (6, 8, 12). This pressure dependence was studied previously for dimethylmercury pressures less than 80 mm Hg. With this in mind, it seemed advisable to study a wider pressure range in order to establish the order of the reaction. Since a detailed qualitative investigation of the gaseous products had not been conducted previously, it appeared this would perhaps be beneficial in proposing a more complete mechanism for the decomposition reaction.

EXPERIMENTAL

I. Apparatus

The experimental work was conducted in a conventional Pyrex high vacuum system. All stopcocks and joints which were exposed to dimethylmercury were lubricated with Dow Corning high vacuum silicone grease. The important details of the decomposition apparatus will be discussed in succeeding sections of this thesis.

A. Vacuum System

The vacuum system was maintained at a high vacuum by a 2-stage mercury diffusion pump in conjunction with a Welch Duo-Seal rotary vacuum pump. The pressure in the system was measured qualitatively by an RCA type 1946 thermocouple vacuum gage and associated circuit which had been calibrated with a McLeod type vacuum gage. The operating pressure within the system was always maintained at less than one micron.

Due to the toxicity of dimethylmercury; two manifold traps, one on each side of the diffusion pump, were cooled with liquid air to prevent dimethylmercury from escaping to the atmosphere. Upon the completion of an experiment, any dimethylmercury in the first trap was allowed to distill to the second trap which was situated between the diffusion pump and the rotary pump. The second trap was then removed to an efficient hood and the contents allowed to distill to the outside atmosphere. The dimethylmercury remaining after decomposition was stored in a storage bulb ("used" storage bulb) which was kept at -78°C.

One section of the vacuum system was designed for purification operations. This section contained a U-tube filled with P_2O_5 and was in series with several other U-traps which were employed in trap to trap distillations.

B. Reactor

A schematic diagram of the reactor is shown in Figure 1. The body of the reactor was constructed of 77 mm Vycor tubing and contained a 7 mm Vycor axial thermocouple well. The inlet was constructed of Pyrex capillary tubing connected to the reactor with a 13 mm graded seal. The surface area of the reactor was estimated to be 630 cm^2 and its volume was found to be 870 ± 1 cc.

The Vycor vessel was encased in two concentric aluminum tubes which extended approximately 3 cm above and below the body of the vessel (Figure 1). The reactor was heated by five independent windings of Nichrome resistance wire. Winding W_1 was wound the entire length of the aluminum shell and was connected to a Leeds and Northrup Electromax Controller Model 6251-7. This instrument controlled the temperature of the reactor to better than $\pm 0.2^{\circ}C$ at $275^{\circ}C$ for a period of four days. Windings W_2 and W_3 were wound around the upper one-half and lower one-half of the aluminum shell respectively, and were separated from W_1 by a thin layer of asbestos. Winding W_4 extended from the reactor inlet to the stopcock and was covered with approximately one inch of asbestos. Winding W_5 was coiled at the lower end of the reactor inside the heavy envelope of asbestos which encased the entire reactor. All windings were powered by Central Scientific Company "Powerstat" variable voltage transformers. Ten Chromel-Alumel thermocouples were used to measure the temperature of the reactor relative to an ice bath at $0^{\circ}C$. The average value of thermocouples one through eight was recorded as the reactor temperature. A typical temperature profile of the reactor may be found in Table I.

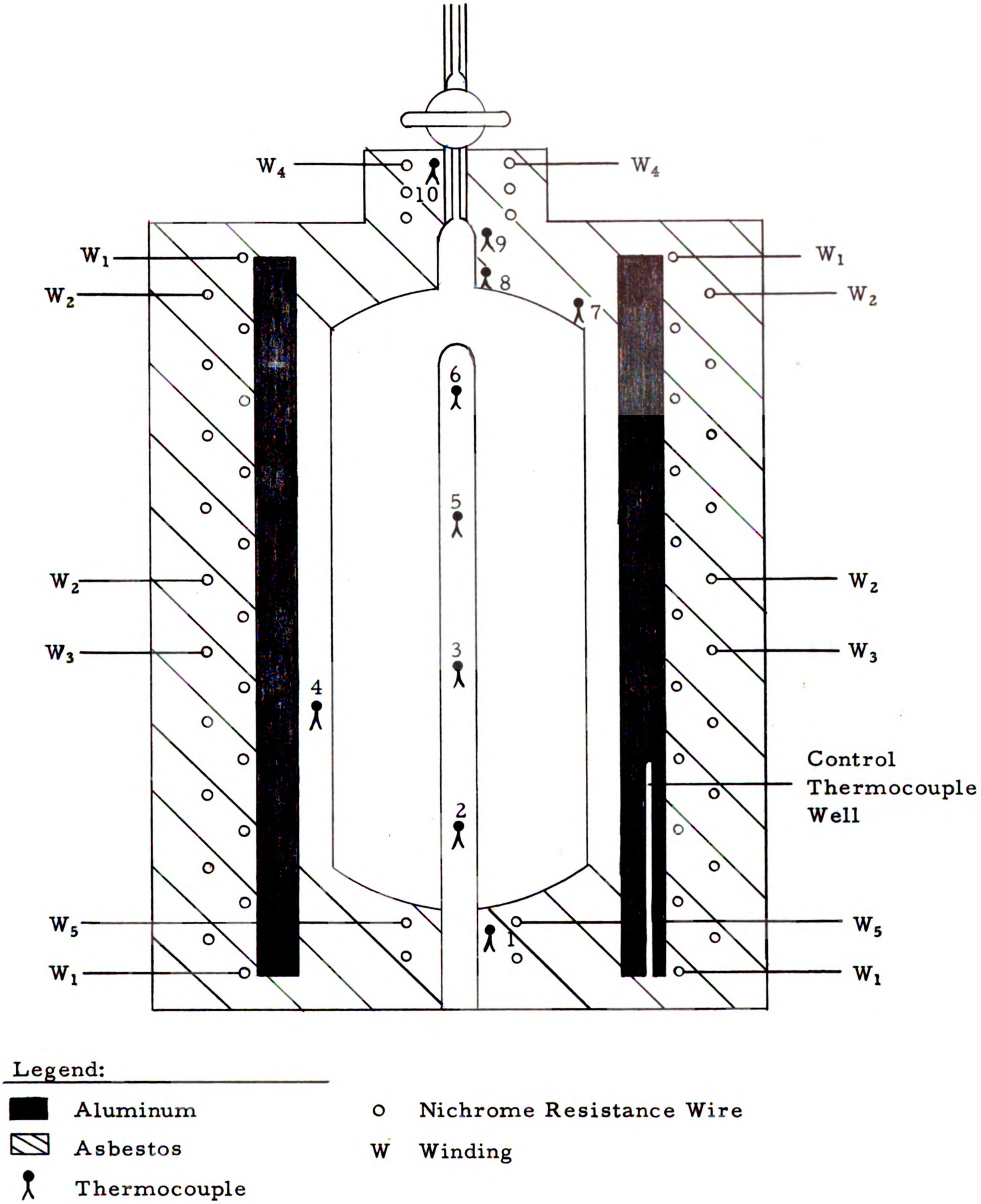

Figure 1. Details of Reactor.

Table 1. Temperature Profile of Reactor (Experiment II-6-33).

Number	Potentiometer[1] reading (mv)	Temperature[2] (°C)
Main thermocouples		
1	13.471	330.2
2	13.473	330.3
3	13.473	330.3
4	13.474	330.3
5	13.474	330.3
6	13.470	330.2
7	13.471	330.2
8	13.464	330.1
Average	13.471 ± 0.002*	330.3 ± 0.1*
Auxiliary thermocouples		
9	12.990	318.9
10	6.035	147.9

[1] Rubicon Type B Potentiometer.

[2] Values taken from Reference Tables for Thermocouples (14).

*Average Deviation.

Since the reactor deposits a polymer-like material on the reactor walls (2), several preliminary decompositions were performed to "condition" the reactor before recording any kinetic data.

C. Gas Chromatography

The gas chromatography apparatus used for the analysis of the gaseous reaction products was a Perkin-Elmer Model 154D Vapor Fractometer utilizing a thermo-conductivity detector. The fractometer was employed in conjunction with a Fischer Recordall electronic strip-chart recorder and associated circuit. Helium was used as the carrier gas in the fractometer.

The gas-liquid partition column was constructed of 7 mm. o.d. stainless steel tubing which measured 3.85 m in length. The packing material used in the column was "dimethylsulfolane" (2,4-dimethyl-tetrahydrothiophene-1,1-dioxide) on Chromosorb and was obtained from the Perkin-Elmer Corporation. The column was operated at room temperature ($\sim 23^{o}C$). Further details of the experimental procedure for handling the gas samples will be discussed in the portion of this thesis entitled Experimental, section IV.

II. Materials

A. Dimethylmercury

The dimethylmercury was prepared by allowing methylmagnesium iodide (prepared from iodomethane) to react with mercuric chloride according to the method of Gilman and Brown (15). The dimethylmercury was kindly furnished by R. B. Bernstein and C. H. Brubaker. The material received from C. H. Brubaker was fractionated through an 8 inch column packed with glass-helices. The fraction boiling from $89\text{-}92^{o}C$ (740 mm Hg) was collected and mixed with the material from

R. B. Bernstein. The two fractions were mixed and fractionated again through the same column and the 91.5-92.0°C (740 mm Hg) fraction collected which was used for the experiments. It was stored at room temperature in a Pyrex container kept in the dark. When the dimethylmercury was admitted to the vacuum system, it was further purified by passage through P_2O_5 and a trap to trap distillation from -38°C to -194°C. The middle fraction (about 80% of the total) was retained from this distillation and stored under vacuum at -78°C. The infrared spectrum of the dimethylmercury appears in Figure 2 (Spectrum A) and was obtained with a Perkin-Elmer Model 21 double beam spectrophotometer with sodium chloride optics and a 0.107 mm. pure liquid cell with sodium chloride windows. The spectrum agrees quite well with the data reported by Gutowsky (16). The peak at 4.3 μ, however, does not appear in the liquid spectrum of reference 16 but it does appear in the gas spectrum.

B. Carbon Dioxide

In certain experiments the total pressure of the system was increased by the addition of carbon dioxide. The carbon dioxide was Matheson "bone dry" with a stated purity > 99.9% and it was used with no further purification. An evacuated bulb was filled with carbon dioxide and connected to the vacuum system. The carbon dioxide was then transferred to a U-trap at -194°C and the volatile substances vented to the manifold. The carbon dioxide was degassed several times by allowing the trap to warm to -78°C and recooling to -194°C followed by venting to the manifold. A trap to trap distillation from -78°C to -194°C was performed and the carbon dioxide sent to a storage bulb kept at -78°C.

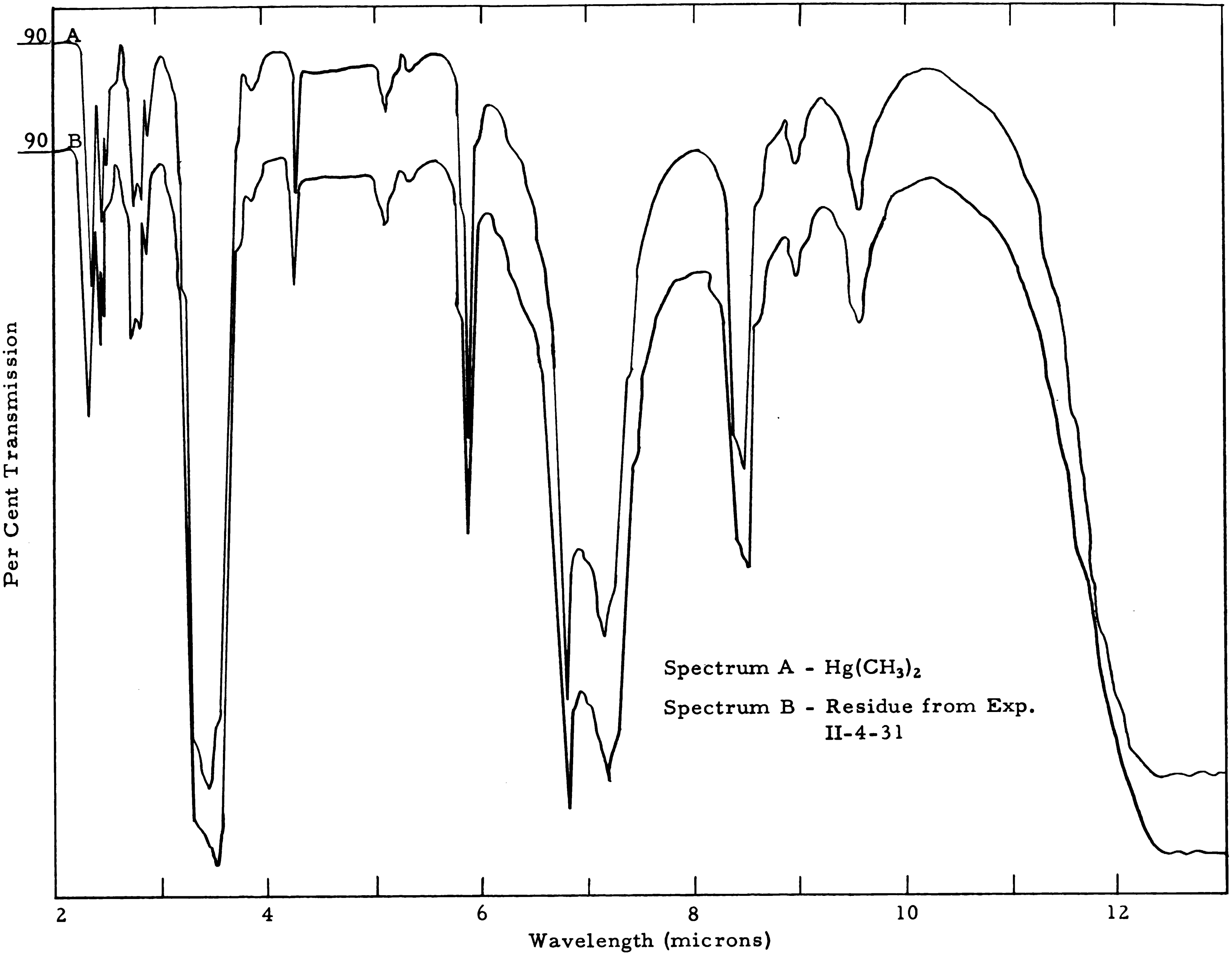

Figure 2. Spectral Comparisons.

III. Operating Procedure

A. Typical Dimethylmercury Experiment

An evacuated sample bulb was thoughly cleaned before weighing and the dimethylmercury, stored at -78°C, was warmed up and a quantity of it frozen at -194°C into the previously weighed sample bulb and the bulb weighed again. The sample bulb was then connected to the vacuum system and a quantity of dimethylmercury was vaporized into the reactor. The excess dimethylmercury in the inlet was frozen at -194°C into a small U-trap in the inlet system. The U-trap was warmed to 0°C and the excess dimethylmercury frozen into the sample bulb which was weighed again to determine the amount of sample in the reactor. The excess dimethylmercury from the introduction of the sample was then returned to the storage bulb at -78°C. The sample bulb was again evacuated and weighed as a check against the original weighing. The temperature of the reactor was recorded several times during the period of decomposition.

After a predetermined period of time, the reactor stopcock was opened and its contents frozen into a U-trap at -194°C. The product volatile at -194°C, assumed to be methane (4, 8, 10), was passed through a -194°C trap and vented to the manifold. The U-trap was warmed to 0°C and the volatile products frozen into another trap at -194°C. This trap was then warmed to -97°C and the volatile products were either vented to the manifold or removed by means of a Toepler pump to be retained for gas chromatographic analysis. The residual material from the -97°C trap was warmed up, transferred to the sample bulb, and weighed as dimethylmercury. The infrared spectrum of this material for an experiment carried out to 16.2% decomposition appears as spectrum B in Figure 2.

For certain experiments which required high pressures of dimethylmercury, heating tapes were used to heat the sample bulb and the inlet independently (sample bulb, ~90°C; inlet, ~120°C). The same procedure of introduction and removal of dimethylmercury was followed in these experiments except for the heating of the sample bulb and the inlet.

Experiments were conducted to determine the loss of dimethylmercury incurred during the course of an experiment due to the absorption of dimethylmercury by the stopcock grease. The reactor was cooled to 230°C at which temperature no measurable decomposition occurs and the procedure described previously for the introduction and removal of dimethylmercury was carried out for various concentrations of dimethylmercury. The loss of dimethylmercury was observed to be a function of the total amount of dimethylmercury used. For example, using a total dimethylmercury sample of 600 mg there was a 1.2 mg loss (0.2% loss). The loss was only slightly greater in the experiments in which the sample bulb and inlet were heated (less than 0.3% of the total sample). Each sample was therefore corrected for this deviation.

B. Experiments with Carbon Dioxide

The dimethylmercury was introduced using the same procedure described previously (see Experimental, sec. III-A). After the dimethylmercury had been introduced into the reactor, the carbon dioxide was admitted to the reactor at its own vapor pressure at -78°C. The total pressure (dimethylmercury plus carbon dioxide) was measured by means of a manometer in the inlet system. The same procedure was followed for the removal of the products as was described in a previous section of this thesis.

IV. Analysis of Products

A. Gaseous Products

As mentioned previously, the gaseous products were analyzed gas chromatographically using a gas-liquid partition column packed with "dimethylsulfolane" on Chromosorb. A gas syringe was used to inject the products into the fractometer. Figure 3 illustrates the gas sampling bulb.

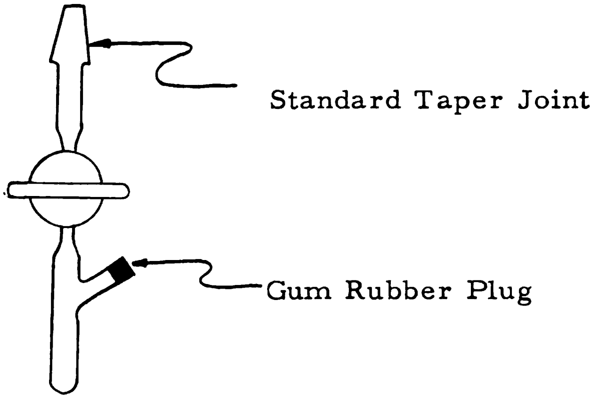

Figure 3. Gas Sampling Bulb

The gaseous products which were retained from the -97°C trap (see Experimental, sec. I-C) were frozen into the gas sampling bulb at -194°C. Since the products were all gases at room temperature, the sample was removed from the bulb by injecting the needle of the gas syringe through the gum rubber plug. After a quantity of the products had been admitted to the gas syringe, the needle was extracted until only the tip remained in the rubber plug. The plunger of the syringe was then depressed slightly to minimize the amount of air rushing into the syringe upon complete extraction of the needle from the rubber plug. This sample was then injected into the carrier gas stream of the fractometer.

RESULTS

I. Kinetic Data

The following rate expression was used to correlate the data obtained for the thermal decomposition of dimethylmercury.

$$-\frac{d(D)}{dt} = k_a (D) + k_b (D)^2$$

This empirical expression can be integrated to give (see Appendix 2):

$$\ln \left[\frac{(D_0)}{(D)} \cdot \frac{k_a + k_b (D)}{k_a + k_b (D_0)} \right] = k_a t$$

In this expression (D_0) and (D) are respectively, the initial concentration of dimethylmercury and the concentration at any time t. The data for the thermal decomposition of dimethylmercury is summarized in Tables II, III, IV, V, and VI. The following expression was used to evaluate k_a and k_b (see Appendix 2).

$$(D_0) = \frac{\alpha - 1}{k_b t \left[1 - \frac{k_a t}{2!} + \frac{(k_a t)^2}{3!} - \ldots \right]} - \alpha \frac{k_a}{k_b}$$

where

$$\alpha = \frac{(D_0)}{(D)}$$

A least squares analysis of the data at the temperatures studied gave the following Arrhenius rate equations for the decomposition reaction

$$k_a = 2.6 \times 10^9 \exp(-39{,}400/RT), \ (\text{sec.}^{-1})$$

$$k_b = 9.5 \times 10^{26} \exp(-70{,}600/RT), \ (\text{cc. mole}^{-1} \text{ sec.}^{-1})$$

The Arrhenius plots for k_a and k_b appear in Figures 4 and 5, respectively. Table VII summarizes the least squares data for k_a and k_b for the temperatures at which the decomposition was studied.

Table II. Thermal Decomposition of Dimethylmercury at 275°C.

Exp.	T(°C)	$[D_0] \times 10^6$ (moles cc^{-1})	t (sec.)	f *
II-66	275.5	0.526	313,680	0.170
II-61	275.8	1.636	217,620	0.122
II-62	275.3	3.848	220,680	0.163
II-63	275.3	5.454	187,200	0.149
II-64	275.3	6.786	185,760	0.160

*Extent of decomposition, $f = 1 - \frac{(D)}{(D_0)}$

Table III. Thermal Decomposition of Dimethylmercury at 289°C.

Exp.	T(°C)	$[D_0] \times 10^6$ (moles cc^{-1})	t (sec.)	f
II-83	289.3	0.728	125,220	0.146
II-76	289.2	1.206	97,080	0.127
II-82	289.2	1.736	106,200	0.158
II-77	289.2	2.746	76,200	0.133
II-80	289.2	3.601	93,900	0.154
II-81	289.2	4.825	80,520	0.151
II-78	289.3	5.865	70,260	0.152
II-79	289.2	7.052	63,900	0.153

Table IV. Thermal Decomposition of Dimethylmercury at 303°C.

Exp.	T(°C)	$[D_0] \times 10^6$ (moles cc^{-1})	t (sec.)	f
I-12	303.7	0.312	33,180	0.153
I-15	303.8	1.488	26,100	0.139
I-16	303.8	1.734	26,100	0.158
I-14	303.8	1.799	26,100	0.148
I-22	303.5	2.915	22,800	0.162
I-25	303.8	3.486	20,160	0.152
I-23	303.7	3.862	19,800	0.168
I-20	303.6	6.683	14,700	0.157
I-24	303.8	7.305	13,380	0.158

Table V. Thermal Decomposition of Dimethylmercury at 319°C.

Exp.	T(°C)	$[D_0] \times 10^6$ (moles cc^{-1})	t (sec.)	f
II-67	319.2	0.746	9,240	0.124
II-69	319.3	2.416	7,260	0.185
II-71	319.3	2.488	6,000	0.166
II-73	319.2	2.812	5,400	0.162
II-70	319.3	2.834	5,880	0.157
II-74	319.2	4.117	3,960	0.159
II-72	319.3	5.416	3,360	0.162

Table VI. Thermal Decomposition of Dimethylmercury at 330°C.

Exp.	T(°C)	$[D_0] \times 10^6$ (moles cc.$^{-1}$)	t (sec.)	f
II-39	330.3	0.220	11,160	0.149
II-37	330.3	0.255	10,800	0.170
II-36	330.4	0.270	8,440	0.122
II-35	330.3	0.380	7,440	0.134
II-34	330.3	0.434	7,440	0.163
II-53*	330.0	0.638	7,200	0.184
II-54*	330.0	0.699	6,600	0.189
II-32	330.3	0.727	6,960	0.167
II-33	330.3	0.845	5,820	0.153
II-30	330.2	1.631	3,660	0.135
II-31	330.2	1.792	4,200	0.162
II-41	330.3	2.742	2,460	0.137
II-40	330.3	2.821	2,940	0.165
II-38	330.2	3.108	2,820	0.166
II-42	330.1	3.401	2,220	0.146
II-45	330.3	3.822	2,100	0.154
II-43	330.3	3.917	2,040	0.147
II-44	330.3	4.626	1,800	0.152
II-46	330.3	4.942	1,740	0.149
II-47	330.3	5.459	1,680	0.162
II-48	330.2	5.907	1,440	0.150
II-49	330.3	6.378	1,380	0.147
II-50	330.3	6.436	1,440	0.162

*Approximately 6.7×10^{-5} moles cc.$^{-1}$ of CO_2 added (~580 mm. Hg)

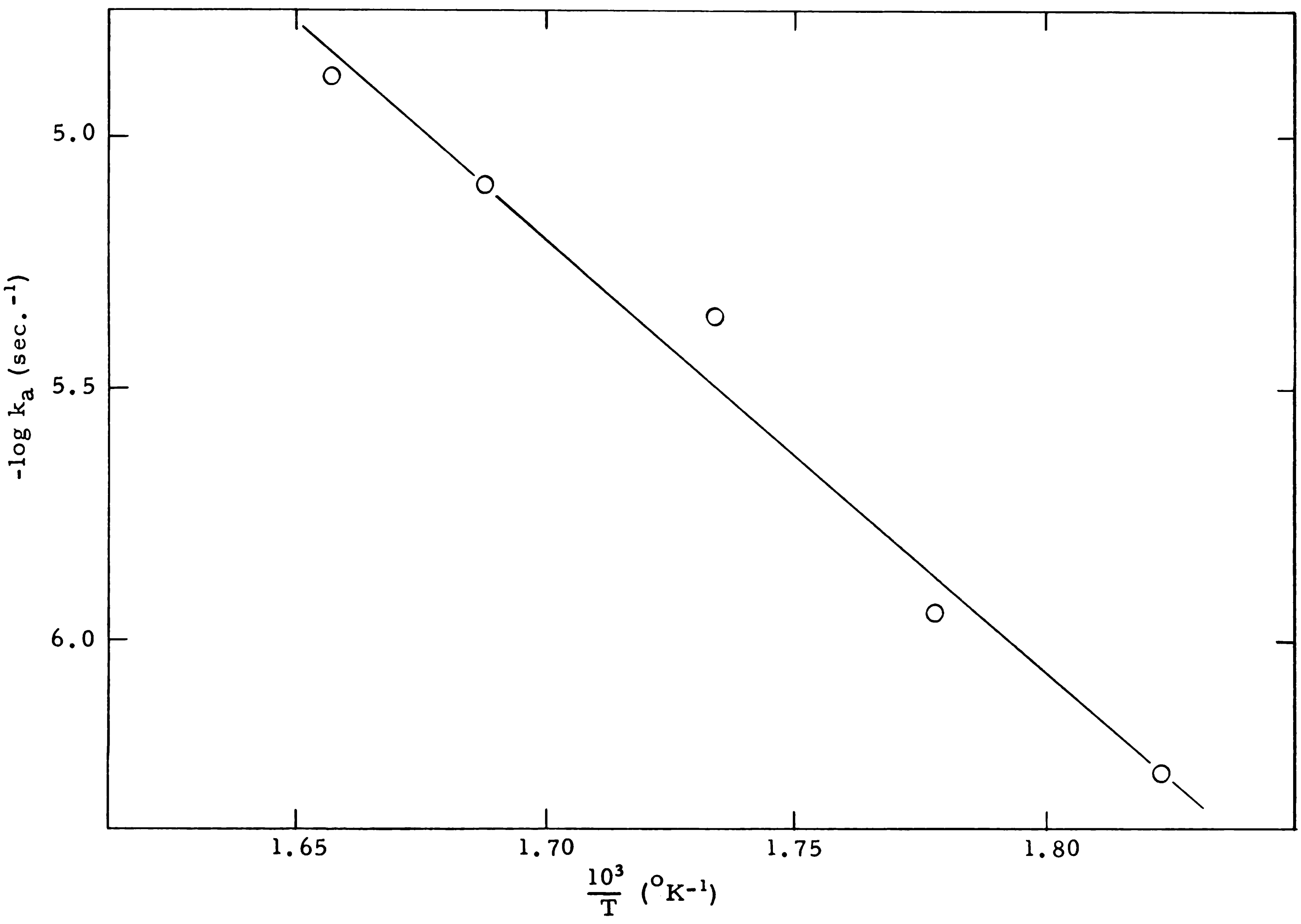

Figure 4. Arrhenius Plot for k_a.

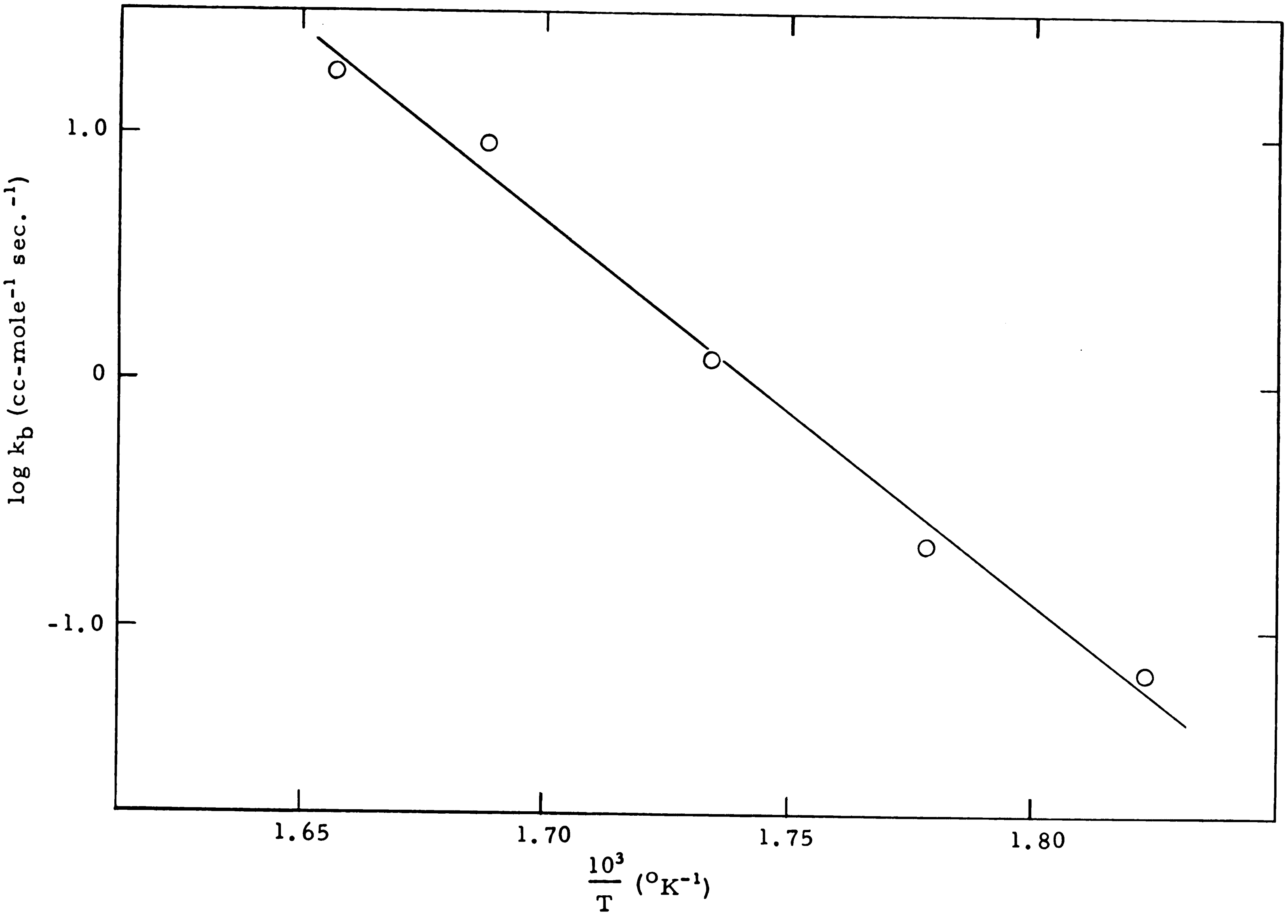

Figure 5. Arrhenius Plot for k_b.

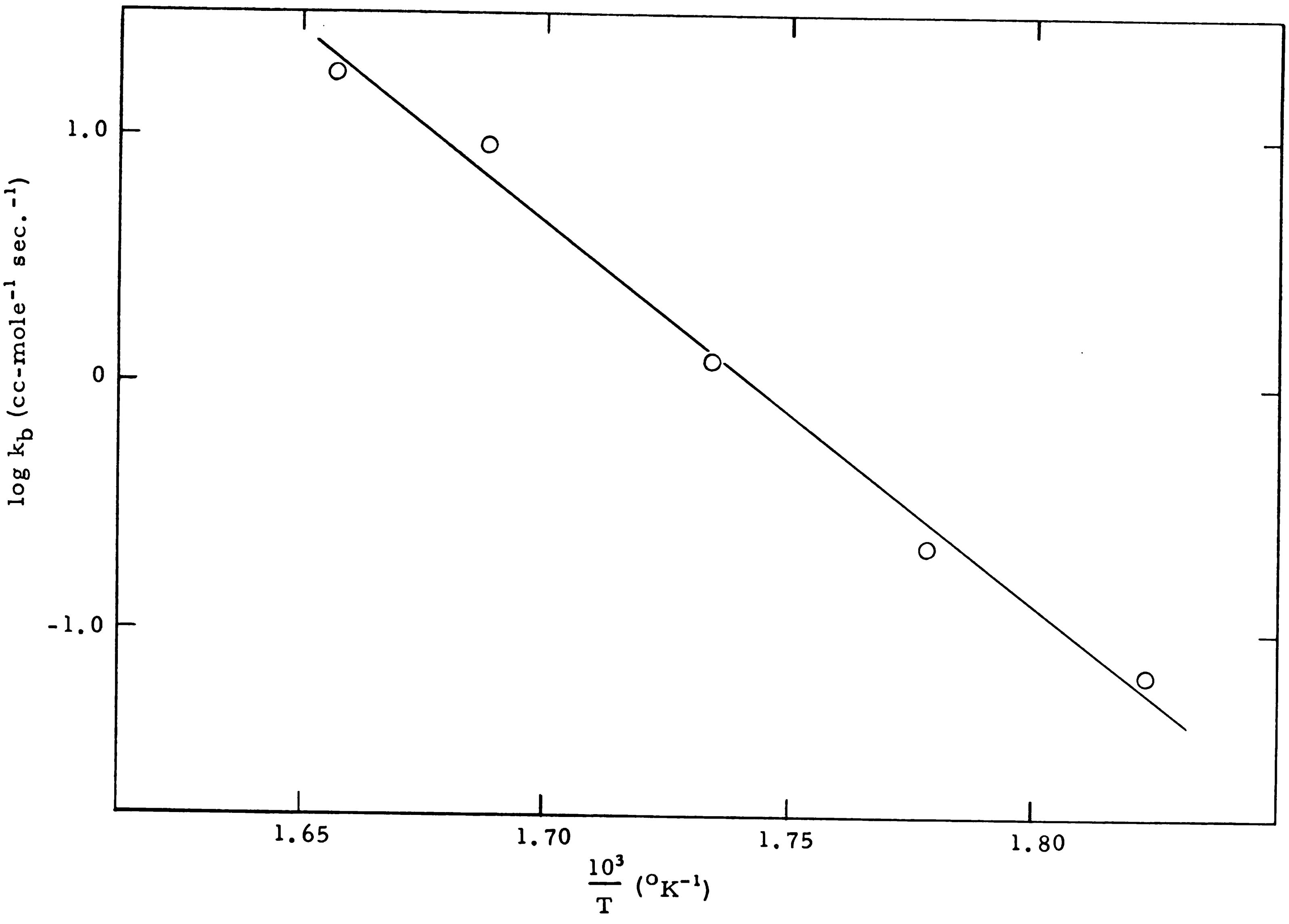

Figure 5. Arrhenius Plot for k_b.

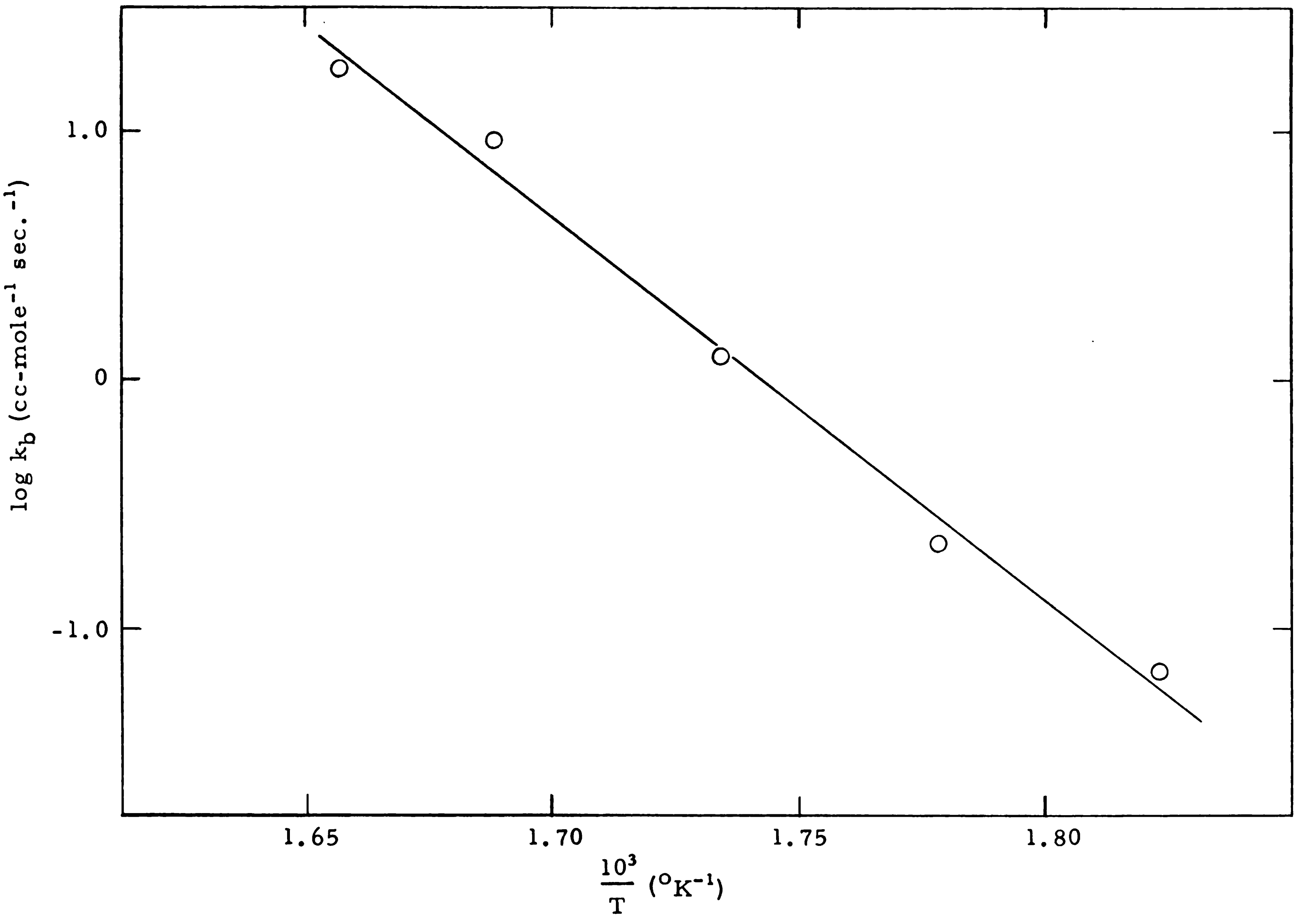

Figure 5. Arrhenius Plot for k_b.

Table VII. Temperature Dependence of the Rate Constants k_a and k_b.

T(°C)	$k_a \times 10^6$, (sec.$^{-1}$)	k_b, (cc.mole^{-1} sec.$^{-1}$)
275	0.547	0.0644
289	1.14	0.221
303	4.39	1.24
319	8.01	9.22
330	13.2	18.2

II. Analysis of Products

As mentioned previously (see Experimental, sec. IV), the gaseous products were analyzed by gas chromatography. Three gas chromatograms for experiments conducted at different temperatures are represented in Figure 6. The symbols X4 and X1 in Figure 6 refer to the attenuation of the signal from the detector to the recorder. In all three experiments represented in Figure 6, the methane was removed (see Experimental, sec. III) before the chromatographic analysis. Chromatogram A represents an experiment conducted at 319°C and 16.2% decomposition; whereas, chromatogram B represents an experiment at 303°C and approximately 50% decomposition. The substances represented in chromatogram C were obtained by combining the products of two experiments at 289°C with an average decomposition of 15.2%. The combined products from these two experiments at 289°C were submitted to a trap to trap distillation in an attempt to separate the less volatile substances which were present in small concentrations. The gaseous products were identified by matching their elution times with those of known hydrocarbons analyzed under the same conditions. The products were found to be ethane, ethylene, acetylene, propane, propene, n-butane, 1-butene and 2-methylpropene.

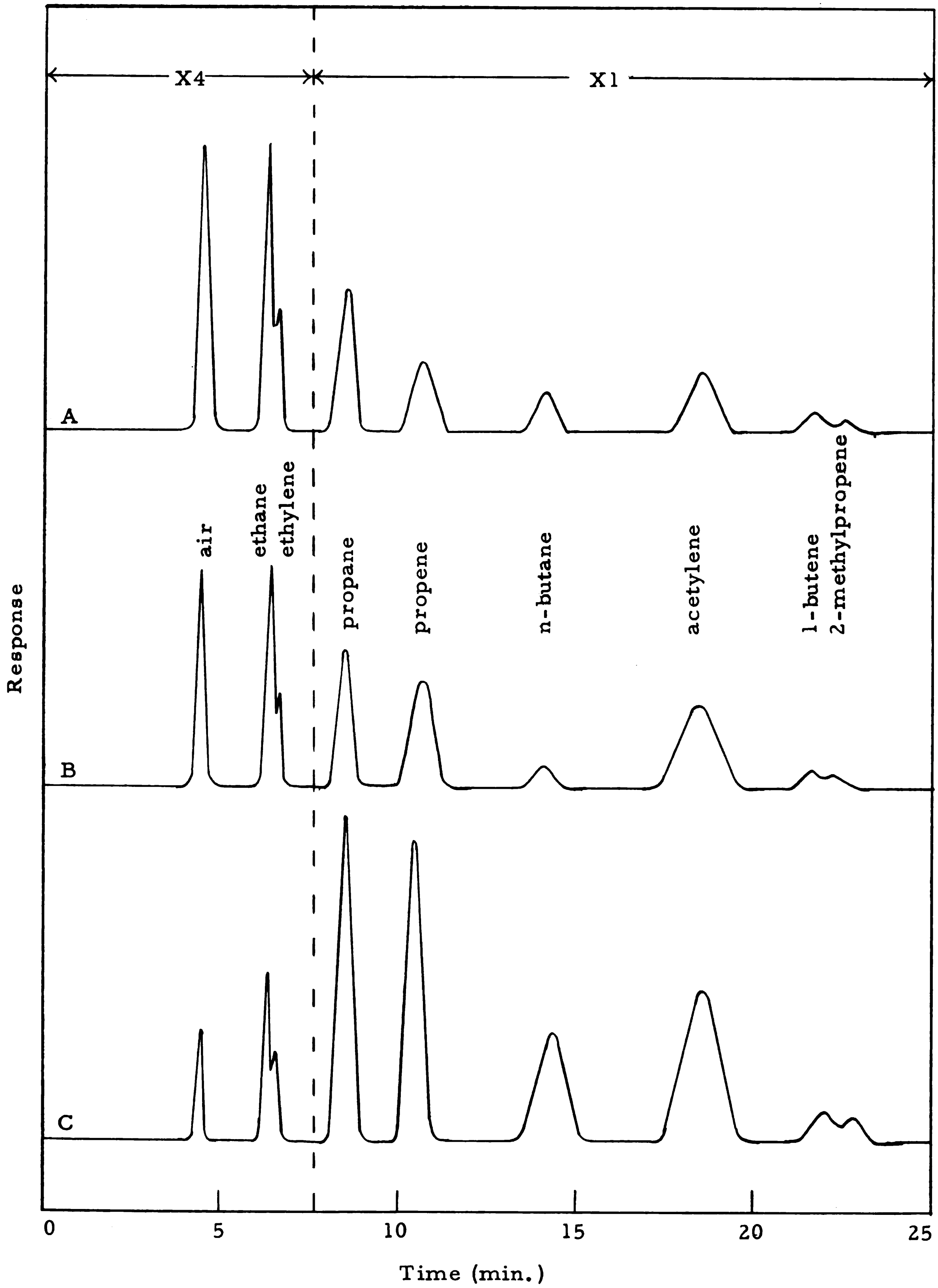

Figure 6. Gas Chromatograms of Gaseous Products.

DISCUSSION OF RESULTS

I. Kinetic Data

A. Rate Expression

As previously mentioned, the following empirical rate expression was employed to correlate the data obtained during the present study:

$$-\frac{d(D)}{dt} = k_a(D) + k_b(D)^2$$

This expression integrates to give:

$$k_a t = \ln\left[\frac{(D_0)}{(D)} \cdot \frac{k_a + k_b(D)}{k_a + k_b(D_0)}\right]$$

To facilitate the evaluation of k_a and k_b this equation can be written as (see Appendix 2):

$$(D_0) = \frac{\alpha - 1}{k_b t\left[1 - \frac{k_a t}{2!} + \frac{(k_a t)^2}{3!} - \ldots\right]} - \alpha\frac{k_a}{k_b}$$

The procedure for the evaluation of k_a and k_b can be found in Appendix 3. The parameter α in this expression is related to f, the extent of decomposition, by the relation:

$$\alpha = \frac{1}{1-f} = \frac{(D_0)}{(D)}$$

An arbitrary restriction was placed on α for the evaluation of k_a and k_b. The only experiments used in the calculations were those which satisfied the restriction that $\alpha = \bar{\alpha} \pm 0.04$ (where $\bar{\alpha}$ is an average value of α and was approximately 1.180 at all temperatures) which corresponds to $f = \bar{f} \pm 0.03$. This restriction was placed on the values of α because of the method of evaluating k_a and k_b. In order to test this restriction, values of α were calculated from the following expression:

$$\ln \alpha = k_a t - \ln \left[\frac{k_a + k_b(D)}{k_a + k_b(D_0)} \right]$$

where

$$\alpha = \frac{(D_0)}{(D)}$$

The calculated values of α, denoted as α_c, are compared in Table VIII with the experimental values of α for a series of experiments carried out to various extents of reaction at 330°C. Since the average value of α for all temperatures was approximately 1.180 and from the comparison of α and α_c in Table VIII, it appears that the restriction placed on α ($\alpha = \bar{\alpha} \pm 0.04$) is reasonable for the evaluation of k_a and k_b.

The validity of the empirical rate expression was investigated using the following form of the integrated rate equation:

$$t_c = \frac{1}{k_a} \quad \ln \left[\frac{(D_0)}{(D)} \cdot \frac{k_a + k_b(D)}{k_a + k_b\,(D_0)} \right]$$

From this equation, the calculated time of reaction, t_c, was evaluated for the experiments performed at 319°C. The calculated time of reaction, t_c, and the experimental time of reaction, t, are compared in Table IX.

For all of the temperatures investigated in the present study there appeared to be a linear dependence of the apparent first order rate constant as a function of dimethylmercury concentration. This is shown in Figure 7 for the temperature 303°C. For small extents of reaction, this linear dependence can be shown to be consistent with the empirical rate expression adopted in the present study. The presentation of these arguments appears in Appendix 4. As a test of

Table VIII. Comparison of α and α_c at 330°C.

Exp.	$(D_0) \times 10^6$ (mole·cc^{-1})	$(D) \times 10^6$ (moles·cc^{-1})	α_c	α	t (sec.)
II-55	3.303	3.064	1.080	1.078	1,140
II-60	3.247	2.904	1.119	1.118	1,680
II-57	3.218	2.738	1.174	1.175	2,340
II-59	3.151	2.447	1.277	1.288	3,360
II-56	3.200	2.396	1.329	1.336	4,200
II-58	3.135	2.195	1.420	1.428	5,400

Average deviation of α from α_c = 0.005.

Table IX. Comparison of t_c and t at 319°C (α = 1.182).

Exp.	$(D_0) \times 10^6$ (moles cc^{-1})	$(D) \times 10^6$ (moles cc^{-1})	t_c (sec.)	t (sec.)
II-67	0.746	0.653	9,220	9,240
II-69	2.416	1.968	7,300	7,260
II-71	2,488	2,075	6,270	6,000
II-73	2.812	2.358	5,540	5,400
II-70	2.834	2.388	5,650	5,880
II-74	4.117	3.461	4,050	3,960
II-72	5.416	4.540	3,290	3,360

Average deviation of t from t_c = 123 sec.

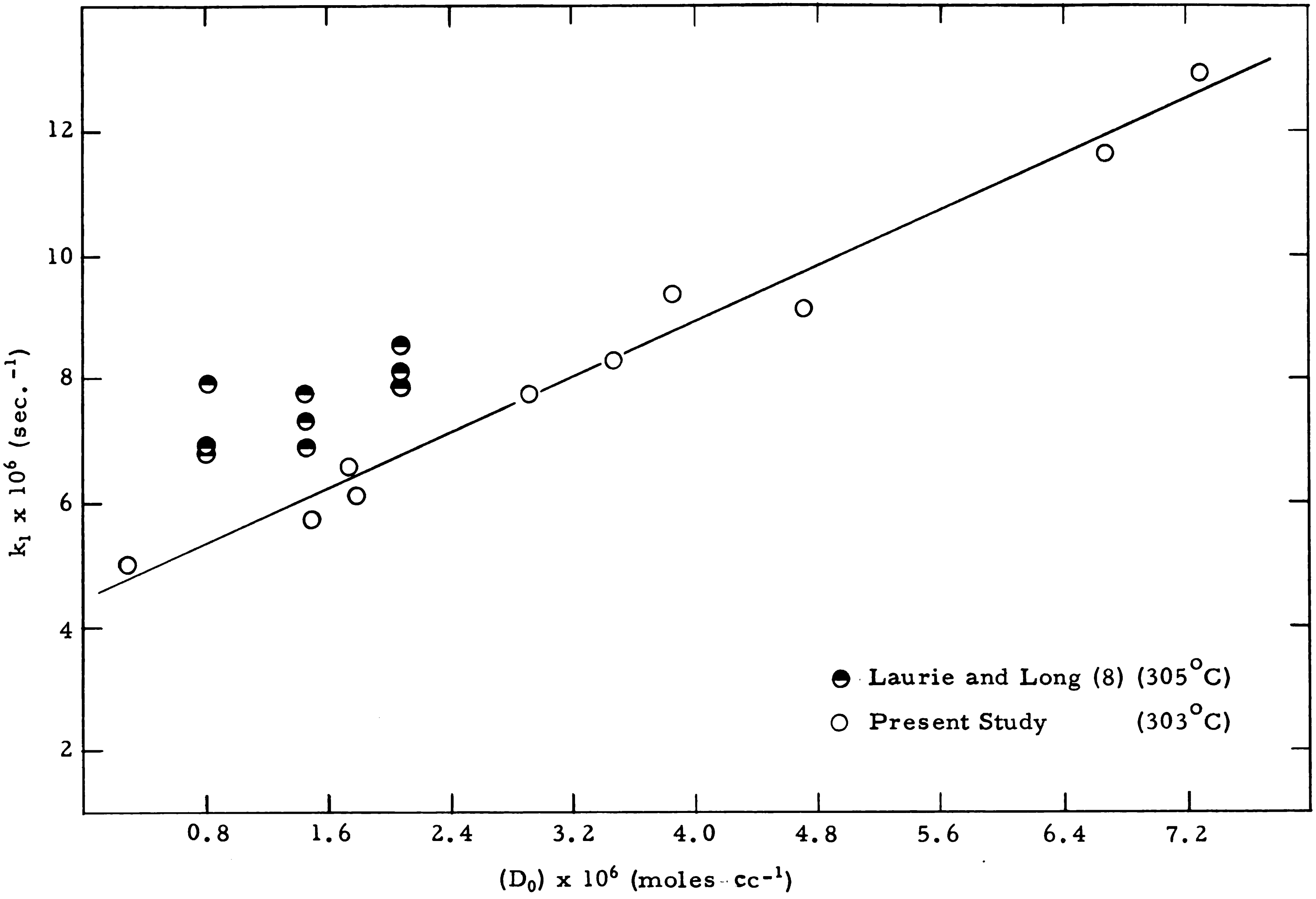

Figure 7. Dependence of First Order k on (D_0).

these arguments, a least squares analysis was performed on the apparent first order rate constant as a function of dimethylmercury concentration at each temperature. These values of the first order rate constant were compared with those calculated from experimental data. The results of these comparisons appear in Table X.

From the experiments with carbon dioxide, it appears that an inert gas has no appreciable effect on the rate of the reaction. This indicates that the reaction was not studied in the region where the apparent first order rate constant "falls off."

B. Comparison of the Data of Other Investigations

A comparison of the data reported by other investigators employing static systems shows that the data obtained in the present study are consistent. Laurie and Long (8), who reported first order kinetics for the pyrolysis, investigated a dimethylmercury concentration range of 0.8×10^{-6} to 2.2×10^{-6} moles cc^{-1} at 305°C. The data of the present study were calculated on the basis of first order kinetics in an attempt to illustrate the effect of dimethylmercury concentration on the apparent first order rate constant. These data are compared in Figure 7 with the data of Laurie and Long. The scattering of the data of the investigators does not seem to warrant the postulation of first order kinetics.

Furthermore, the concentration of dimethylmercury appears to influence the Arrhenius activation energy of the reaction. This can be illustrated if the activation energy of the assumed first order reaction is studied as a function of dimethylmercury concentration. Using the data of the present study, first order rate constants were calculated for three different dimethylmercury concentrations. These data are presented in the form of Arrhenius plots in Figure 8. The solid circles in Figure 8 represent the same concentration range used by Laurie and

Table X. Summary of First Order Rate Data.

$T(^{\circ}C)$	Per Cent d[1]
275	5.8
289	4.3
303	4.9
319	2.9
330	3.4

[1] Per Cent d = $\dfrac{\Sigma \left| \dfrac{k_L - k_1}{k_L} \right|}{n} \times 100$

k_L = first order k from least squares

k_1 = experimental first order k

n = number of experiments treated

Per Cent d = per cent average deviation

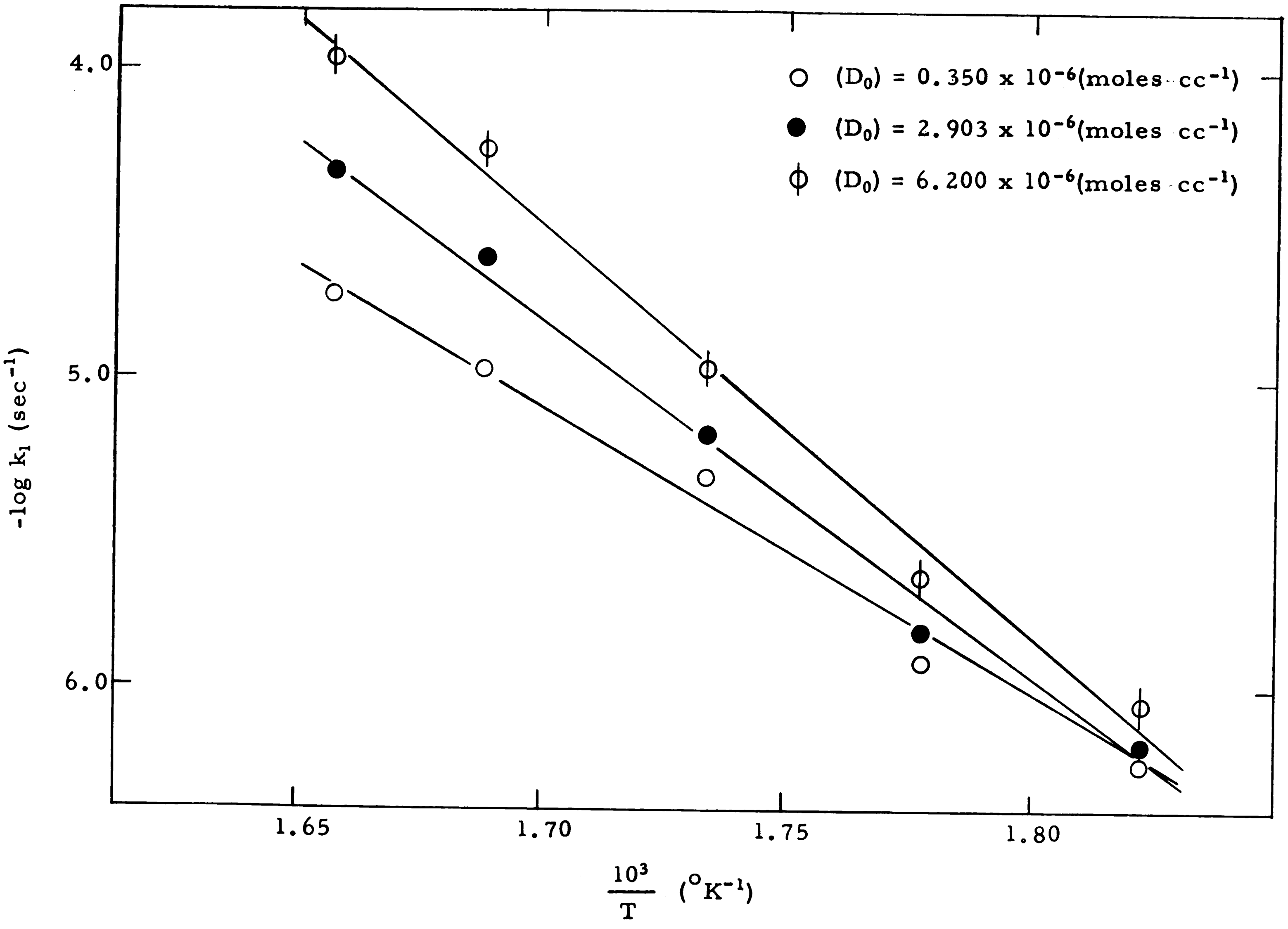

Figure 8. Effect of (D_0) on the Activation Energy of First Order.

Long to obtain the value of 51.3 kcal.mole^{-1} for the activation energy of the pyrolysis reaction. From Figure 8, for the same concentration range, a value of 53.0 kcal.mole^{-1} was obtained for the activation energy based on first order kinetics. At a concentration of 0.350 x 10^{-6} moles cc.$^{-1}$, the activation energy from Figure 8 is 43.3 kcal.mole^{-1}; at 6.200 x 10^{-6} moles cc.$^{-1}$, it becomes 60.5 kcal.mole^{-1}.

Yeddanapalli et al. (6) also investigated the influence of dimethylmercury on the reaction over a range of 0.307 x 10^{-6} to 1.678 x 10^{-6} moles cc^{-1} (11.79 - 64.37 mm. Hg). They correlated their data on the basis of three-halves order kinetics. Their experiments on the effect of dimethylmercury concentration were conducted at a higher temperature (342°C) than any of the data in the present study. For this reason an extrapolation of the data of the present study was necessary in order to compare the two investigations. The values of k_a and k_b obtained by extrapolation of the Arrhenius plots (Figures 4 and 5) to 342°C were used to calculate values of α_c for the individual experiments of Yeddanapalli et al. The comparison of α, the experimental value obtained by Yeddanapalli et al.; and α_c, the value calculated using k_a and k_b from the present study, is shown in Table XI. Based on this comparison it appears as though the data are consistent.

It is of some interest here to again note the observations of previous investigators with respect to the effect of temperature on the kinetic order of the reaction. Yeddanapalli et al. (6) reported that at 305°C and 323°C there was little to choose between first and three-halves order kinetics. On the other hand, at the highest temperature, 342°C, the three-halves order rate constants were decidedly more consistent than the first order constants. Hence, they reported three-halves order for the entire temperature range 305-342°C. Laurie and Long (8), who reported first order kinetics, observed that the reaction appeared to be first order in the range 294-332°C but at 343°C the order apparently increased to three-halves.

Table XI. Comparison of α and α_c at 342°C (Data from reference 6).

p_0[1] (mm Hg)	p[2] (mm Hg)	f	t (sec.)	α	α_c[3]
11.79	9.91	0.160	3,600	1.189	1.184
18.32	14.74	0.195	3,600	1.243	1.233
24.84	19.00	0.235	3,600	1.307	1.287
39.31	29.24	0.256	3,600	1.344	1.349
64.37	44.89	0.303	3,600	1.435	1.456

$k_a = 2.77 \times 10^{-5}$ (sec^{-1})

$k_b = 1.69 \times 10^{-6}$ (mm^{-1} sec^{-1})

[1] initial dimethylmercury pressure

[2] final dimethylmercury pressure

[3] $\ln \alpha_c = k_a t - \ln \left[\frac{k_a + k_b p}{k_a + k_b p_0} \right]$

average deviation of α from α_c = 0.012.

These observations can be shown to be qualitatively consistent with the empirical rate expression adopted in the present study. This expression was presented earlier as

$$-\frac{d(D)}{dt} = k_a (D) + k_b (D)^2$$

In this expression k_a is the rate constant for a first order process whose activation energy was found to be 39.4 kcal.mole^{-1}. The activation energy for k_b, the second order process, was found to be 70.6 kcal.mole^{-1}. Considering these activation energies for the empirical rate expression, the second order process would be expected to become more important as the temperature is increased. The apparent order of the reaction would then increase with increasing temperature.

II. Reaction Products

A. Gaseous Products

Previous investigators have not concerned themselves with a detailed study of the gaseous reaction products. Laurie and Long (8) reported methane, ethane and small amounts of ethylene with methane being in the greatest abundance. Yeddanapalli *et al.* (6) reported methane present in larger quantities than ethane as well as trace amounts (less than 1% of total) of ethylene, acetylene and hydrogen. Russell and Bernstein (12) analyzed the gaseous products by mass spectroscopy and reported methane, ethane, ethylene, propane, propylene, C_4H_8* and C_4H_{10}.* The gaseous reaction products observed in the present study were identified by gas chromatography and were found to be ethane, ethylene, acetylene, propane, propene, n-butane, 1-butene and 2-methylpropene. The methane was always discarded and therefore

---

*No attempt was made to distinguish the isomers.

was not detected by the gas chromatography analysis. Due to the method of analysis in the present study it was not possible to obtain the concentrations of the various product gases.

B. Solid Product

Some preliminary experiments were conducted in an attempt to characterize the carbonaceous deposit (2, 6, 8, 11) which is formed on the walls of the reactor. An attempt was made to dissolve the substance in several organic solvents but it appeared to be insoluble. However, the deposit was soluble in concentrated nitric acid and the resulting solution gave a positive test for mercury. Furthermore, several decompositions were conducted and the amount of mercury collected was considerably less than the amount that should have been produced based on the amount of dimethylmercury decomposed. These preliminary experiments suggest that perhaps the carbonaceous deposit contains mercury.

III. Mechanism

A reasonable mechanism could not be postulated for the pyrolysis of dimethylmercury in view of the data obtained in the present study. It is apparent that several more aspects of the reaction should be investigated before a plausible mechanism can be postulated.

IV. Further Experimental Studies

On the basis of the preceding discussion of the pyrolysis reaction, a number of experiments suggest themselves as useful in the postulation of a plausible mechanism:

(1) Careful studies of the heterogeneous nature of the reaction should be conducted by packing the reaction vessel to increase the surface/volume ratio.

(2) The reaction should be investigated using larger concentrations of dimethylmercury.

(3) The methane producing step should be clarified; perhaps by adding deuterated ethane to the reaction mixture to determine whether methane is produced by hydrogen abstraction from compounds such as ethane or by hydrogen abstraction from dimethylmercury.

(4) A carbon/hydrogen ratio and a quantitative mercury balance might be conducted on the carbonaceous deposit in an attempt to characterize it, if possible.

(5) The reaction might better be followed by intermittent sampling of the reaction mixture in conjunction with a quantitative analysis of the gaseous products.

BIBLIOGRAPHY

1. E. W. R. Steacie, Atomic and Free Radical Reactions, New York, Reinhold Publishing Corporation, 1954, p. 386.
2. J. P. Cunningham and H. S. Taylor, J. Chem. Phys. 6, 359 (1938).
3. F. P. Lossing and A. W. Tickner, J. Chem. Phys. 20, 907 (1952).
4. B. G. Gowenlock, J. C. Polanyi, and E. Warhurst, Proc. Roy. Soc. A218, 269 (1953).
5. S. J. W. Price and A. F. Trotman-Dickenson, Trans. Faraday Soc. 53, 939 (1957).
6. L. M. Yeddanapalli, R. Srinivasan and V. J. Paul, J. Sci. Ind. Research (India) 13B, 232 (1954).
7. R. Ganesan, J. Sci. Ind. Research (India) 20B, 228 (1961).
8. C. M. Laurie and L. H. Long, Trans. Faraday Soc. 51, 665 (1955).
9. L. H. Long, Trans. Faraday Soc. 51, 673 (1955).
10. L. H. Long, J. Chem. Soc., 3410 (1956).
11. J. Cattanach and L. H. Long, Trans. Faraday Soc. 56, 1286 (1960).
12. M. E. Russell and R. B. Bernstein, J. Chem. Phys. 30, 607 (1959).
13. M. E. Russell and R. B. Bernstein, J. Chem. Phys. 30, 613 (1959).
14. H. Shenker, J. I. Lauritzen Jr., R. J. Corrucini and S. T. Lonberger, Reference Tables for Thermocouples, Nat. Bur. Stnds. Circular 561, 1955, p. 26.
15. H. Gilman and R. E. Brown, J. Am. Chem. Soc. 52, 3314 (1930).
16. H. S. Gutowsky, J. Chem. Phys. 17, 128 (1949).
17. E. W. Washburn *et al.*, International Critical Tables, New York, McGraw-Hill, Inc., 1926, p. 53, Vol. I.

APPENDICES

APPENDIX 1

Thermocouple Calibrations

Zinc, c.p. grade, was covered by powdered carbon in a porcelain crucible and was melted with a Chromel-Alumel thermocouple in good thermal contact with the melted zinc. After cooling, the temperature became constant and the e.m.f. was read using a Rubicon Type B Potentiometer. The e.m.f. recorded was 17.21_2 mv. From Reference 14:

17.21_2 mv = 419.3°C

melting point of Zn = 419.4°C (17)

The same procedure was carried out using cadmium, c. p. grade, for the calibration

potentiometer reading = 13.07_0 mv = 320.8°C (14)

melting point of Cd = 320.9°C (17)

No corrections were applied to the temperature readings.

APPENDIX 2

Derivation of Rate Expression

$$[D_0] = \frac{a - 1}{k_b t \left[1 - \frac{k_a t}{2!} + \frac{(k_a t)^2}{3!} - \ldots\right]} - a\frac{k_a}{k_b}$$

Assuming the empirical expression:

$$-\frac{d(D)}{dt} = k_a(D) + k_b(D)^2 \qquad (1.1)$$

and rearranging this expression in an integrable form:

$$\int_{D_0}^{D} \frac{d(D)}{[k_a + k_b(D)](D)} = -\int_{o}^{t} dt \qquad (1.2)$$

integration gives:

$$\frac{1}{k_a} \ln \left[\frac{(D)}{(D_0)} \cdot \frac{k_a + k_b(D_0)}{k_a + k_b(D)}\right] = -t \qquad (1.3)$$

or

$$\frac{(D)}{(D_0)} \frac{k_a + k_b(D_0)}{k_a + k_b(D)} = e^{-k_a t} \qquad (1.4)$$

let $a = (D_0)/(D)$ (1.5)

expansion of $e^{-k_a t}$ gives:

$$e^{-k_a t} = 1 - k_a t + \frac{(k_a t)^2}{2!} - \frac{(k_a t)^3}{3!} + \ldots \qquad (1.6)$$

substituting (1.5) and (1.6) in equation (1.4) gives:

$$\frac{k_a + k_b(D_0)}{\alpha k_a + k_b(D_0)} = 1 - k_a t + \frac{(k_a t)^2}{2!} - \frac{(k_a t)^3}{3!} + \cdots \qquad (1.7)$$

Upon expansion and collection of terms the following expression is obtained:

$$\frac{(1 - \alpha)}{t} = [\alpha\, k_a + k_b(D_0)] \left[-1 + \frac{k_a t}{2!} - \frac{(k_a t)^2}{3!} + \cdots \right] \qquad (1.8)$$

and after rearranging equation (1.8) becomes:

$$[D_0] = \frac{\alpha - 1}{k_b t \left[1 - \frac{k_a t}{2!} + \frac{(k_a t)^2}{3!} - \cdots \right]} - \alpha \frac{k_a}{k_b} \qquad (1.9)$$

APPENDIX 3

Evaluation of k_a and k_b

The rate constants k_a and k_b were evaluated from the following expression by successive approximations using the method of least squares.

$$(D_0) = \frac{a - 1}{k_b t \left[1 - \frac{k_a t}{2!} + \frac{(k_a t)^2}{3!} - \cdots\right]} - a \frac{k_a}{k_b} \qquad (1.1)$$

A least squares analysis was carried out for a plot of (D_0) vs. $1/t$ which yielded approximate values of k_a and k_b. The values of t used in this expression were the times of reaction, calculated on the basis of first order, required to obtain the average extent of reaction. Using these values of k_a and k_b, a second approximation was performed by calculating values of H and performing a least squares analysis for (D_0) vs. H .

$$H = \frac{1}{k_b t \left[1 - \frac{k_a t}{2!} + \frac{(k_a t)^2}{3!} - \cdots\right]} \qquad (1.2)$$

After three such approximations ((D_0) vs. H), an extrapolation was made for t to the time required for the average extent of reaction, t_r, which involved the use of the following expression:

$$t_r = \frac{1}{k_a} \ln \left[\frac{k_a + k_b (D)}{k_a + k_b (D_0)} \cdot \frac{(D_0)}{(D)}\right] \qquad (1.3)$$

The values of k_a and k_b used in this expression were the values obtained from the previous approximations. These values of t_r were then used in equations (1.1) and (1.2) and the successive approximations performed in the same manner as previously discussed.

APPENDIX 4

Relationship of k_a and k_b to First Order Rate Expression

The apparent first order rate expression can be expressed as

$$k_1 t = \ln \frac{(D_0)}{(D)} = -\ln(1-f)$$

where $$\frac{(D_0)}{(D)} = \frac{1}{1-f}$$

For small values of f the term -ln(1-f) can be expanded to give

$$f + \frac{f^2}{2}$$

$$k_1 t = f\left(1 + \frac{f}{2}\right)$$

From the present study

$$-\frac{d(D)}{dt} = k_a(D) + k_b(D)^2$$

For small extents of reaction, i.e., small f, this can be expressed as

$$-\frac{\Delta(D)}{\Delta t} = \frac{(D_0) - (D)}{t} = k_a(\bar{D}) + k_b(\bar{D})^2$$

where $$(\bar{D}) = \frac{(D_0) + (D)}{2}$$

$$\frac{(D_0) - (D)}{(\bar{D})} = [\ k_a + k_b\ (\bar{D})\ ]\ t$$

$$\frac{(D_0) - (D)}{\frac{(D_0) + (D)}{2}} = [\ k_a + k_b\ (\bar{D})\ ]\ t$$

since $(D_0) = \frac{(D)}{1-f}$, the above expression reduces to

For s

For

orde

Fro

whi

$$\frac{f}{1-\frac{f}{2}} = [k_a + k_b(\bar{D})]\, t$$

For small values of f

$$\frac{f}{1-\frac{f}{2}} \simeq f\left(1 + \frac{f}{2}\right)$$

$$[k_a + k_b(\bar{D})]\, t = f\left(1 + \frac{f}{2}\right)$$

For small extents of reaction, this expression is similar to the first order rate expression

$$k_1 t = f\left(1 + \frac{f}{2}\right)$$

From this

$$k_1 = k_a + k_b(\bar{D})$$

$$k_1 = k_a + k_b \left[\frac{(D_0) + (D)}{2}\right]$$

since $(D) = (D_0)\,(1 - f)$

$$k_1 = k_a + k_b(D_0)\left(1 - \frac{f}{2}\right)$$

which shows the dependence of k_1 on (D_0).