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STUDIES OF ETHYL RADICAL REACTIONS AND THE  
PYROLYSIS OF DIETHYLMERCURY

BY

A. C. LALONDE

A THESIS

Submitted to the Faculty of Graduate Studies through the  
Department of Chemistry in Partial Fulfillment  
of the Requirements for the Degree of  
Master of Science at the  
University of Windsor

Windsor, Ontario

1970

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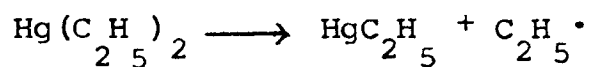
THIS THESIS HAS BEEN EXAMINED AND APPROVED BY:

A. J. Price  
D. M. Kenney  
Alex Gnyf

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ABSTRACT

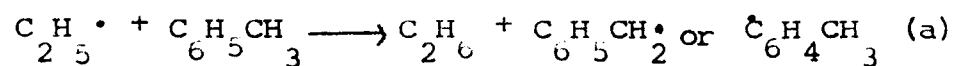
In the presence of excess toluene, and over the temperature range 328°C to 400°C, and per cent decompositions of 10% to 99%, the decomposition of diethylmercury occurs according to



where  $\log k(\text{sec.}^{-1}) = 15.4 - (45,700/2.303RT)$ .

The progress of the decomposition was measured by the amount of residual alkyl in the liquid products collected. Agreement on the basis of analysis of ethane, ethylene, butane, and n-propyl benzene was obtained in the latter portion of the work after devising an efficient method of collecting all these products.

Hydrogen abstraction from toluene by ethyl radicals, produced from the pyrolysis of diethylmercury was studied over a temperature range of 344°C to 385°C and per cent decompositions of 20% to 85%. From the limited data obtained, the process which occurs according to



was found to have an activation energy of  $E = 8.7 \text{ kcal./mole}$  and a  $\log A(\text{mole}^{-1} \text{ cc. sec.}^{-1}) = 11.00$ .

## ACKNOWLEDGEMENTS

I am greatly indebted to Dr. S. J. W. Price for his guidance, assistance and concern throughout this study.

I am also grateful to the Province of Ontario for fellowships awarded to me during the course of this work.

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TABLE OF NOMENCLATURE

|               |   |   |
|---------------|---|---|
| A             | - | Frequency factor of the Arrhenius Equation                |
| A, B, C       | - | Moments of Inertia for a molecule                         |
| D             | - | Bond Dissociation Energy                                  |
| E             | - | Arrhenius Activation Energy                               |
| h             | - | Planck's Constant   |
| K             | - | Transmission Coefficient                                  |
| $k_a$         | - | Rate constant for Rate of Abstraction of Hydrogen         |
| $k_r$         | - | Rate constant for Rate of Recombination of Ethyl Radicals |
| k             | - | Rate Constant for the Decomposition of Diethylmercury     |
| $k_d, k_{d2}$ | - | Specific literature values                                |
| n             | - | Number of Atoms in a molecule                             |
| R             | - | Gas Constant  |
| S             | - | Number of Degrees of Freedom                              |
| T             | - | Absolute Temperature                                      |
| v             | - | Vibrational Frequency                                     |
| $\sigma$      | - | Symmetry numbers  |
| $k^1$         | - | Boltzmann's Constant                                      |

## CHAPTER I

### INTRODUCTION

#### General Introductory Remarks

The thermal decomposition of diethylmercury has been studied in an  $N_2$  flow system both in the absence and presence of toluene (1). In the presence of toluene, the mechanism proposed did not include hydrogen abstraction from toluene by ethyl radicals to form ethane. The toluene to alkyl ratios were about 30 to 1 in these runs in which case the ethane to ethylene ratio was 1 to 1. This study was done in a toluene carrier system and a wide range of toluene to alkyl ratios were studied in order to determine if and when hydrogen abstraction from toluene would occur.

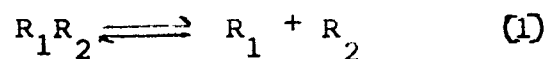
Also, previous workers had done a material balance on the basis of gas analysis and residual mercury analysis. (1,2) There was no liquid analysis done to determine the residual alkyl and n-propyl benzene. This study proposed to obtain a material balance on the basis of residual alkyl and product analysis.

There also seemed to be some doubt as to the validity of the rate constants determined in the  $N_2$  carrier system. When compared to the static system study done (3), agreement seemed good at lower temperatures but extrapolation of

the static system data to a higher temperature, comparable to the flow system temperatures, indicated an almost four-fold discrepancy. An attempt was made to resolve this discrepancy.

Determination of Bond Dissociation Energies  
by the Kinetic Method

The bond dissociation energy of a molecule  $R_1R_2$  is defined as the heat of reaction of (1) at absolute zero and in the ideal gas state.



This bond energy,  $D(R_1 - R_2)$ , can be equated to  $E$ , the activation energy, when the activation energy of the reverse of (1) is assumed to be zero. Then, it can be said that the activation energy of the forward reaction is equal to the bond dissociation energy.

Justification for this assumption is considerable (4 - 9). If the recombination reaction of  $R_1$  and  $R_2$  were to have an activation energy, this would imply that two atoms of appropriate spin would be repulsed on recombination. This repulsion would be seen as a hump on the potential energy curve, (Fig. 1). When no potential energy barrier for the recombination reaction exists, the unimolecular rate constant can be written as

$$k = \frac{KkT}{h} \frac{\phi^*(T)}{\phi(T)} e^{-D/RT}$$

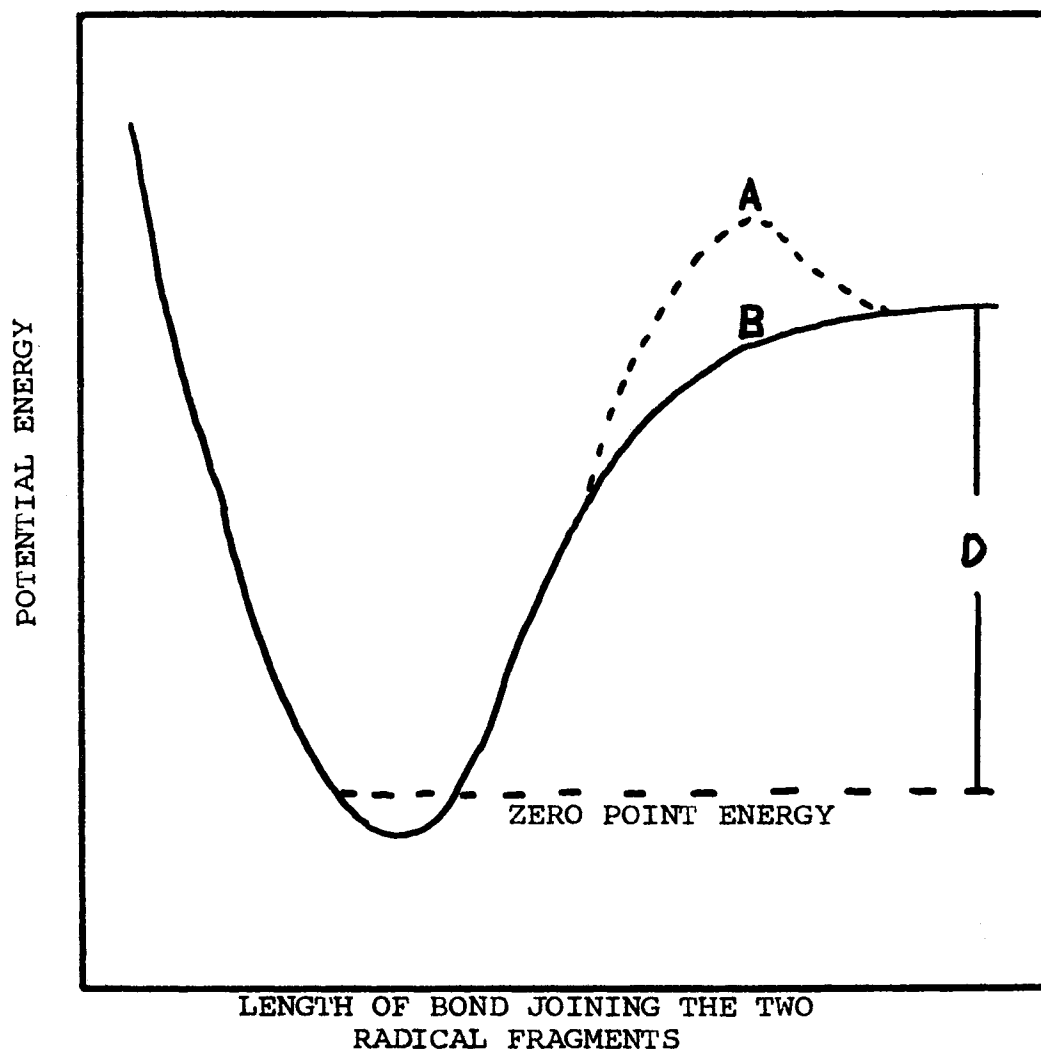


FIGURE 1: Potential energy curve for unimolecular decomposition into two radicals.

- (A) Energy of activation for recombination, finite
- (B) Energy of activation for recombination, zero

The total partition functions  $\phi(T)$ , for the normal molecule and  $\phi^*(T)$ , for the activated complex each include translational ( $\lambda(T)$ ), rotational ( $r(T)$ ) and vibrational ( $v(T)$ ) components.

The translational partition function for both the activated complex and normal molecule, may be written as

$$\lambda(T) = \frac{(2\pi mkT)^{3/2}}{h^3}$$

The rotational partition function for a linear molecule will be

$$r(T) = \frac{8\pi^2 I kT}{h^2 \sigma}$$

and that for a non-linear molecule will be

$$r(T) = \frac{8\pi^2 (2\pi kT)^{3/2} (ABC)^{1/2}}{h^3 \sigma}$$

both of which will be nearly the same for the normal molecule and the activated complex.

If we assume that the vibrational partition function for all modes other than the one leading to dissociation are nearly equal for the normal molecule and the activated complex, we can say

$$k = \frac{1}{h} \left( 1 - e^{-h\nu/kT} \right) e^{-D/RT}$$

This equation leads to two outer limits for  $k$ . If the temperatures are low where the vibrational frequency is high, as in the case of strong bonds

$$k = \frac{1}{h} K k_B T e^{-D/RT}$$

or

$$\frac{d(\ln k)}{dT} = \frac{1}{T} + \frac{D}{RT^2}$$

At the other extreme, that is, in the case of high temperatures,

$$k = K_0 e^{-D/RT}$$

Hence

$$\frac{d(\ln k)}{dT} = \frac{D}{RT^2}$$

Then, by comparison with the Arrhenius equation where

$$\frac{d(\ln k)}{dT} = \frac{E}{RT^2}$$

The dissociation energy can be expressed in terms of  $E$  within the following limits

$$(D) \leq E \leq (D + RT)$$

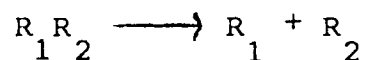
Therefore, it can be said that the bond dissociation energy is very nearly equal to the activation energy which, in this study, was determined both from product analysis and residual alkyl. This conclusion is based on the assumption that the activation energy referred to, is in the pressure independent



region.

### Toluene Carrier Technique

Measuring the activation energy of the reaction:



involves the determination of the rate of the primary dissociation. The rupture of the bond between  $R_1$  and  $R_2$  must be energetically favoured in order for it to take precedence over other possible ruptures.

In using the toluene carrier technique, the toluene is ordinarily 50 to 100 times in excess of the alkyl. This is done in order to overcome the problems that would occur if the free radicals formed were to react with the parent molecule or undergo recombination.

When hydrogen abstraction from toluene occurs, approximately 96% of the products will be benzyl radicals and 4% will be radicals formed by abstraction from the ring in either the ortho, meta, or para positions. The benzyl radicals will then react to form either  $C_6H_5CH_2R$  or dibenzyl, the former being predominant if the concentration of  $R$  is appreciable. The dimerization reaction only occurs outside the hot zone under the conditions used (10).

The possibility of toluene undergoing decomposition must also be accounted for. If the temperatures used are sufficiently high, the toluene will decompose. The products formed

by this decomposition would primarily be  $\text{CH}_4$ ,  $\text{H}_2$ , and dibenzyl (formed from the benzyl radicals). These will be either distinguishable or undistinguishable. In the prior case, there is obviously no problem. In the latter case, suitable corrections can be made (11). In either case, toluene decomposition, to any great extent, would cause problems in collecting the desired products while still removing the large quantities of  $\text{H}_2$  and  $\text{CH}_4$  that would be produced.

In using the toluene carrier flow system, assumptions are made that plug flow exists and that thermal equilibrium exists over the length of the reaction zone. These requirements were met in this study.'

In order to ensure that plug flow existed, the vessel used is constructed with a two step inlet system in the pre-heat zone (Fig. 2) so that the incoming gases might expand gradually. This gradual expansion of the gases would minimize any possibility of channelling of the gases by dispersing the flow as it enters the reaction zone. Turbulence and channelling would cause serious errors in contact time and reaction volume according to Batten's study (12). Consequently, the above means were taken to overcome this problem.

Thermal equilibrium must also be obtained. According to Mulcahy and Pethard (13), a rate constant with an accuracy of about 10% can be obtained under the following conditions: the ratio of contact time,  $t_c$  (sec.), to pressure,  $p$  (cm.), should be greater than 0.5. To avoid errors due to diffusion,  $t_c/p$

should be less than 3 to 50% conversion and less than 10 at 25% conversion. The experiments performed in this study had a ratio of  $t_c/p$  ranging from 0.78 to 3.82 and satisfy the conditions proposed by Mulcahy and Pethard.

CHAPTER II  
EXPERIMENTAL TECHNIQUE

Apparatus and Procedure

Figure 2 shows a schematic diagram of the toluene carrier flow system used for this work. The vacuum source was a two stage mercury diffusion pump backed by a two-stage oil-sealed rotary vane fore pump, Balzers Duo5.

Pyrex glass was used throughout the system with the exception of the reaction vessel which was quartz glass. The reaction vessel was joined into the pyrex glassware of the system by graded quartz-to-pyrex seals. All ground glass joints were lubricated with Dow Corning High Vacuum Silicone Grease. Heated taps were lubricated with Apiezon T Grease, and unheated taps were lubricated with Apiezon N Grease. Ace Glass greaseless viton "O" ring taps were used for both the carrier and the alkyl inlet sections of the system.

The electrically heated furnace was constructed from a quartz cylinder three inches in diameter and twenty-four inches long with a wall thickness of one-quarter inch. The quartz cylinder was wound with chromel-A resistance ribbon 2 mm. wide and 0.2 mm. thick, having a resistance of 0.603 ohms per foot. The windings were cemented into place with Sauereisen Cement Number 31. Figure 3 indicates the number

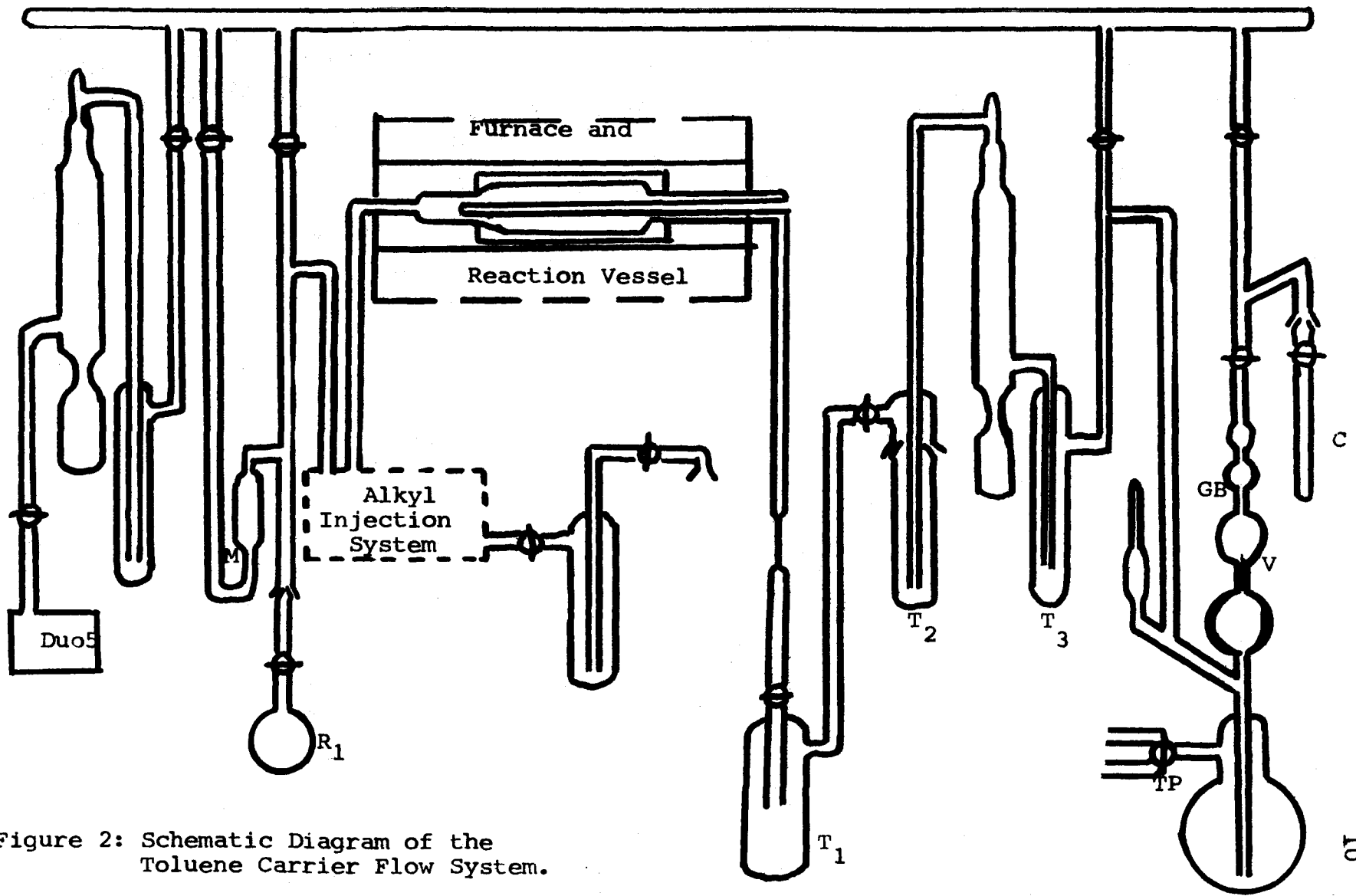


Figure 2: Schematic Diagram of the Toluene Carrier Flow System.

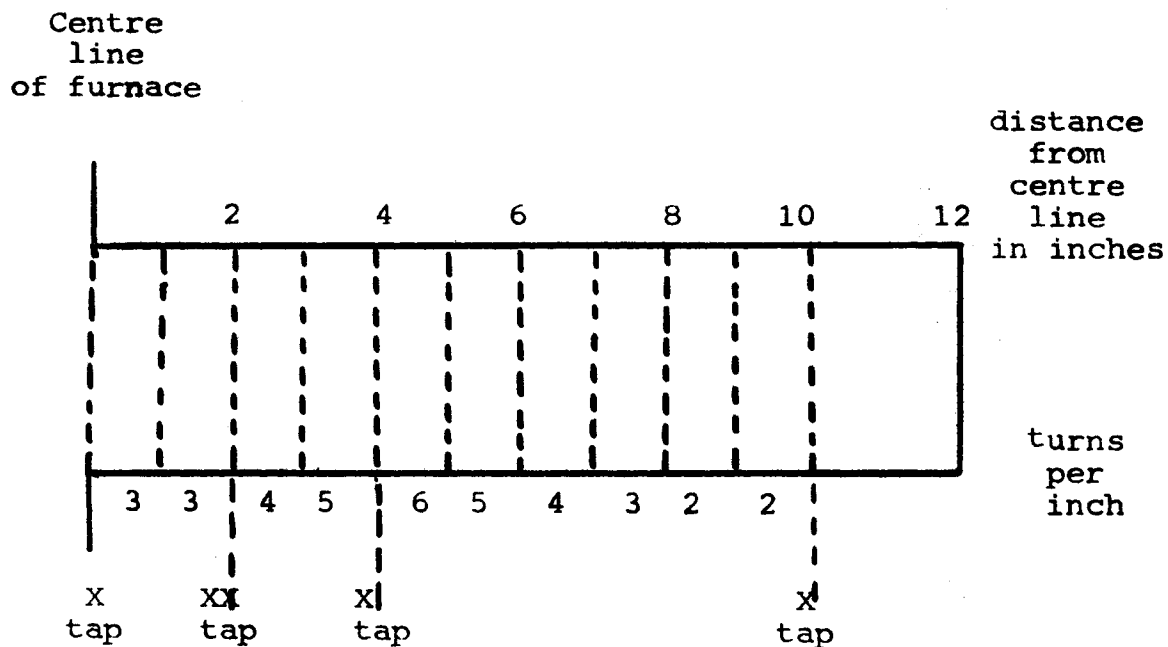


Figure 3: Placement of heating windings and taps in furnace construction.

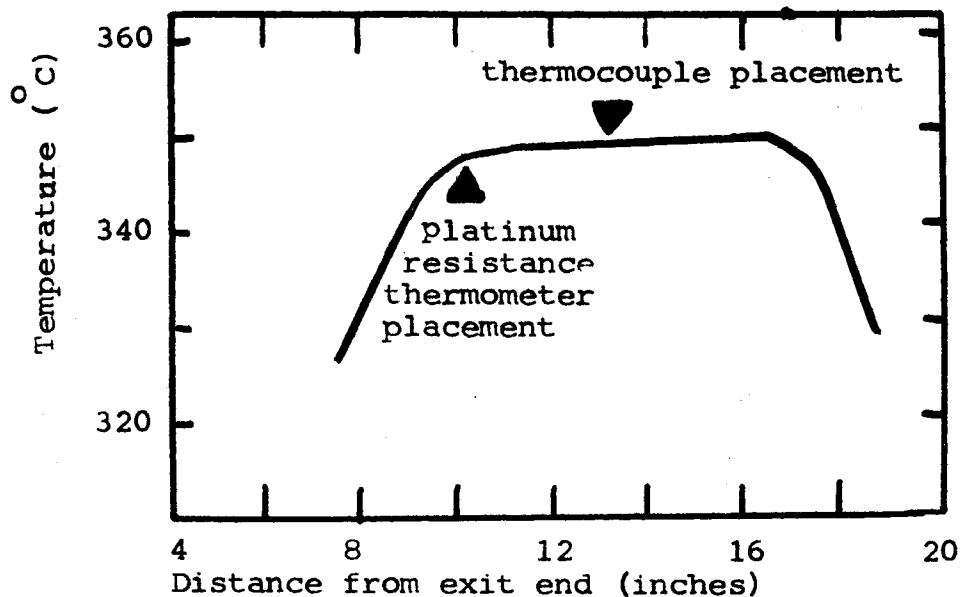


Figure 4: A typical temperature profile.

of windings per inch and the seven points at which the windings were tapped in order to adjust the temperature profile by shunt resistances. In addition, an inconel liner, 2.5 inches in diameter, 12 inches long, and 0.25 inches thick was placed in the centre of the furnace. This evened out the temperature profile and provided a sharp temperature fall-off at each end of the vessel.

The quartz tube was then centered in a box (12 x 12 x 24 inches) constructed of 0.25 inch asbestos with a 0.75 inch angle iron frame. The ends of the box had 3 inch diameter holes to accommodate the quartz tube. The box was filled with powdered alumina for insulation. The furnace was connected through a Variac to a 220 volt a. c. power supply. The maximum operating temperature of the furnace is 1100°C.

The temperature of the furnace was controlled by a Sunvic Resistance Thermometer Controller Type RT 2. The temperature was monitored using a chromel-P-alumel thermocouple which could be moved along the length of the vessel in an axial thermocouple well. This was used in conjunction with a Leeds and Northrup Millivolt Potentiometer, Type 8691. The temperature varied within  $\pm 2^\circ\text{C}$  along the reaction zone and fell off sharply at the ends (Figure 4).

The reaction vessels were made of fused quartz with graded quartz to pyrex seals a few inches beyond the ends of the furnace. The vessels were 40 mm. OD. and 6.5 to 8 inches long sealed to 20 mm. ends. The thermocouple well was in the axial position and measured 10 mm. OD. tubing running the length of

the reaction vessel.

The tubing at the inlet side of the reaction vessel was wound with Chromel "A" asbestos covered heating wire. Variacs were used in conjunction with the heating wires in order to control their temperature. Temperatures up to 90<sup>o</sup> C could be obtained. The use of heating wire prevented the condensation of the reactants before entering the vessel.

The toluene was stored in bulb R<sub>1</sub>. All references will be made to Figure 2 unless otherwise specified. The toluene bulb was removed before and after each run in order to weigh it and determine the amount of toluene used. Pressure was maintained during the runs by constant temperature baths of either water or acetone in a dewar surrounding the bulb. The toluene pressure was read periodically during a run using a differential manometer with dioctylphthalate and mercury with a magnification factor of 7.0 times that of mercury.

The alkyl was stored in a removable vessel R<sub>2</sub> (Figure 5). For each run, a small amount of alkyl was distilled from R<sub>2</sub> to a finger F<sub>1</sub>. The tap to R<sub>2</sub> was then shut. The pressure of the alkyl in F<sub>1</sub> was adjusted by a constant temperature bath of water. The alkyl pressure was at all times greater than the toluene pressure. After the run, any remaining alkyl in F<sub>1</sub> was distilled back to the vessel R<sub>2</sub>. The amount of alkyl used in each run was determined by weighing R<sub>2</sub> before and after each run.

After a steady temperature and a vacuum of 10<sup>-4</sup> mm. or better were obtained, the run was started. The flow of to-



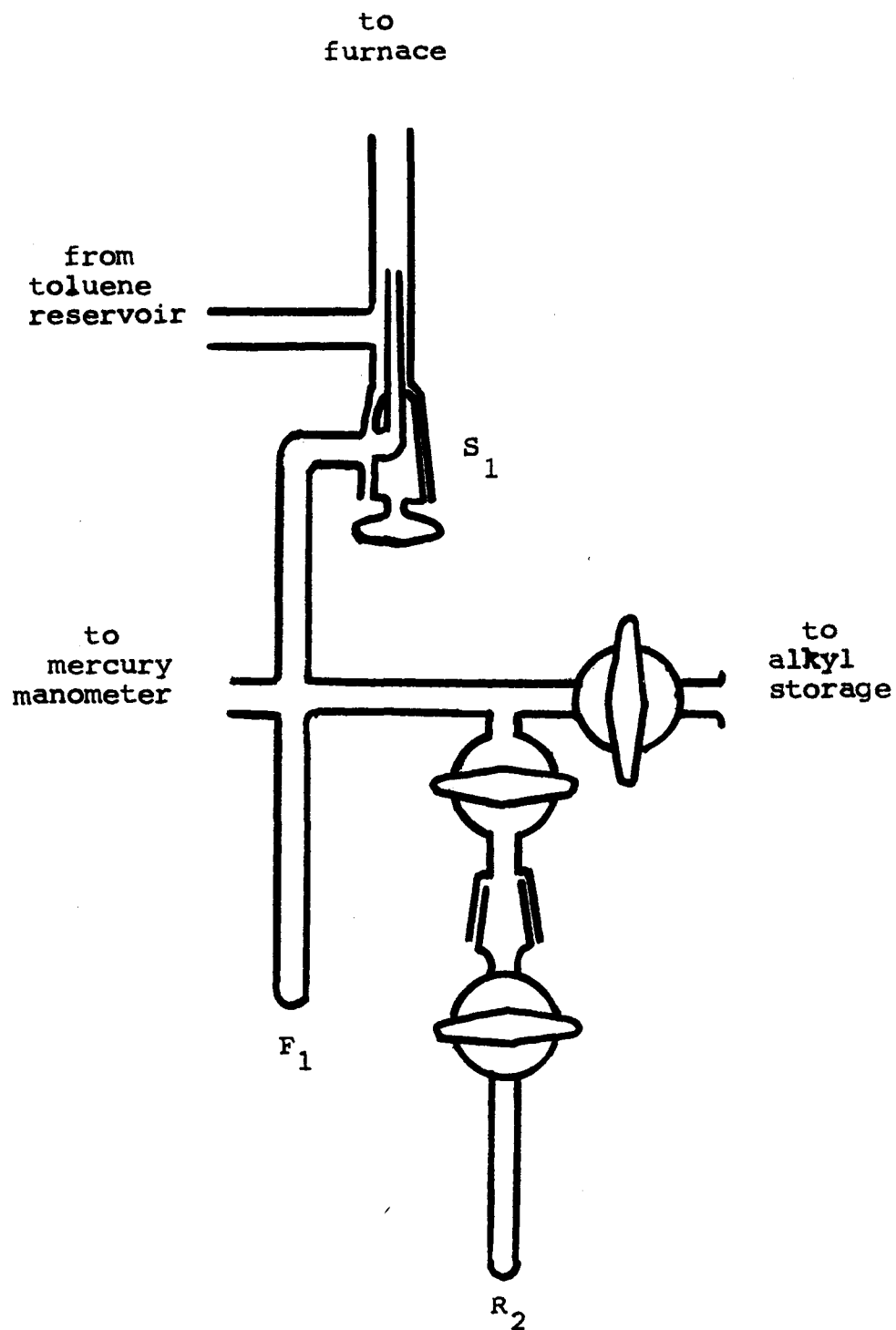


Figure 5: Alkyl Injection System

luene was started and the initial differential manometer reading taken. After a 2 to 8 minute flow of toluene, tap  $S_1$  was opened to start the alkyl flow. The alkyl flow was permitted to proceed from 25 to 70 minutes depending on the conditions used. This was then followed by another 2 to 8 minute flow of toluene. All variable reaction conditions were monitored throughout the run.

Gaseous products were continuously collected in the buret (GB) by means of a Toeppler (TP) pump.

Trap  $T_1$ , thermostated at  $-60^{\circ}\text{C}$  with an acetone-dry ice bath, collected most of the liquid products and undecomposed alkyl. Trap  $T_2$  and  $T_3$  thermostated at  $-80^{\circ}\text{C}$  with an acetone-dry ice bath collected any liquid products which were not trapped out by  $T_1$ .

After the run the remaining gas products were collected and the pressure, volume, and temperature of the gas mixture collected were taken. The gas sample was then analyzed on a gas chromatograph.

The gas chromatographic analysis was carried out using a Perkin Elmer 154 gas chromatograph equipped with a 1/4 in., 6 foot silica gel column. The column was used at  $80^{\circ}\text{C}$  and with a helium pressure of 15 pounds/sq. inch. The schematic diagram (Figure 6) demonstrates the injection system used for the gas product analysis.

The sample C was placed in position with a steel bar resting on the break seal and this region was evacuated. The break seal was broken by raising the steel bar with a magnet

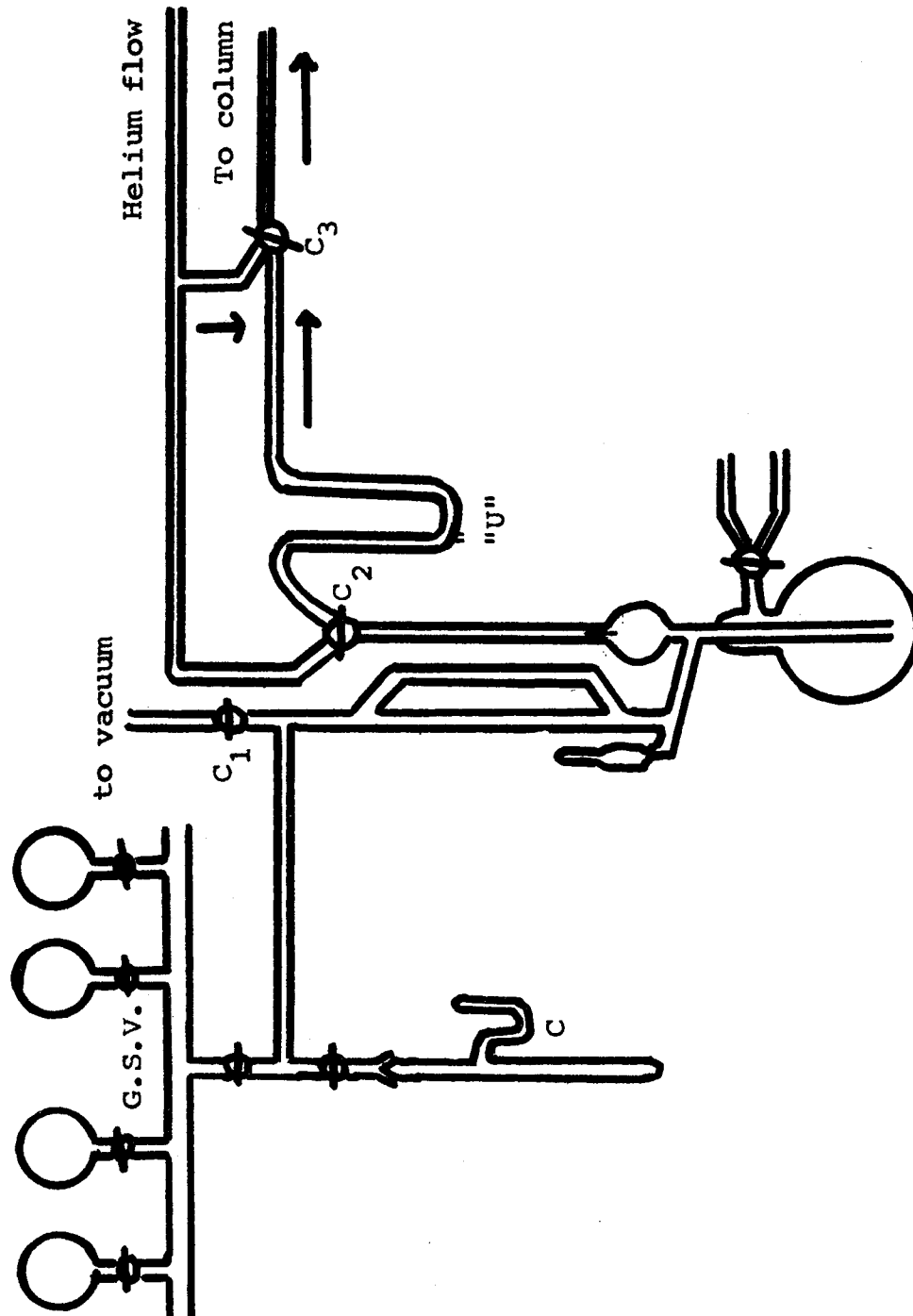


Figure 6: Schematic diagram of the injection system used for gas analysis.

and dropping it on the seal. A part of the sample was then transferred to the gas buret and the pressure was measured.  $C_2$  was opened and the mercury level raised to transfer the sample to the "U" tube.  $C_2$  was then turned to allow the helium flow to enter the "U" tube simultaneously as  $C_3$  was turned to connect the "U" tube to the column. Gas storage vessels (G.S.V.) supplied a source of pure gases on which calibration curves were done for each set of analyses using the same injection technique. Peak heights could then be compared between the pure gases and the gas mixtures collected from the runs.

The liquid samples collected in  $T_1$  were distilled to  $T_2$ . The liquid samples from the runs were not allowed to warm up beyond  $-5^{\circ}\text{C}$ . The samples in  $T_2$  were removed from the system when they were still below  $-5^{\circ}\text{C}$  and poured into a vessel, pre-cooled to  $-5^{\circ}\text{C}$ . The vessel containing the liquid was then placed in a salt water and ice bath at  $-5^{\circ}\text{C}$  and analyzed immediately on a Perkin Elmer 800 gas chromatograph equipped with a flame ionization detector. A 0,02 inch ID. 150 foot open tubular column coated with polypropylene glycol (Perkin Elmer R) was used. Nitrogen was used as the carrier gas. The column temperature was set at  $60^{\circ}\text{C}$  and the injector temperature was set at  $200^{\circ}\text{C}$ .

This gas and liquid products collection technique was the final technique used and is the recommended technique on the basis of the results obtained. This will be elaborated upon in the discussion.

Standards were made containing the components found in

the liquid samples. These standards were made such that the concentrations of the components were comparable to those of the liquid samples from the runs.

The standards for residual alkyl analysis and for n-propyl benzene analysis were done by weight.

The standards for the analysis of butane in solution were made in the following way. A known weight of toluene was allowed to flow through the system and collected in  $T_2$  using an acetone and dry ice bath in the same manner as an ordinary run. The acetone and dry ice bath was then replaced by a liquid  $N_2$  bath. A known volume and pressure of butane contained in a glass vessel was then distilled into  $T_2$  with the toluene by replacing the toluene bulb with the butane vessel and allowing the butane to flow through the system in the same way as the toluene. After the distillation was complete, the liquid  $N_2$  bath was replaced with the acetone and dry ice bath and the trap  $T_2$  was then allowed to warm up. Some of the butane would then go into solution with the toluene and some would flow through the system and be collected and measured in the gas buret as previously described. The gas collected was then analyzed on the Perkin Elmer 154 to determine the amount of butane recovered. This amount of butane could then be subtracted from the initial amount distilled into the toluene. Consequently, the concentration of butane in toluene was known. This liquid standard was then removed from the system under the same conditions as the liquid samples collected at the end of the run. This standard was then analyzed imme-

diately on the Perkin Elmer 800.

These standards were used for calibration and the determination of the composition of the liquid sample was done on the basis of peak heights. Calibrations were done for each set of analyses.

### Preparation of Materials

#### A Toluene

The toluene was toluene from sulfonic acid supplied by Eastman Organic Chemicals Number X325. It was dried by refluxing over sodium ribbon under vacuum and then degassed by bulb to bulb distillation.

#### B Diethylmercury

Two different sources of diethylmercury were used.

Diethylmercury was prepared in the laboratory in the following manner: magnesium turnings were placed into a three-necked flask fitted with an efficient stirrer, a dual condenser and closed to the atmosphere. All the air in the flask was flushed out with nitrogen. Five hundred mls. of dried ethyl ether (dried by standing with Na ribbon) were added to the flask. The ethyl iodide, diluted with ethyl ether by a volume of three to one, was added dropwise from a separatory funnel. Sufficient stirring was provided during the whole addition. Before being used, the ethyl iodide was refluxed over silver hydroxide and distilled into a clean flask as the ethyl iodide had been standing for a few months.

Once the addition of the ethyl iodide was complete, the Grignard was then refluxed for one to two hours. The Grignard was then decanted from the unused magnesium and put in a separatory funnel.

Using the same set up as for the making of the Grignard, mercuric chloride, previously dried in a dessicator, was added to the reaction flask with three hundred mls. of ethyl ether. The Grignard was then added dropwise from the separatory funnel and the mixture was refluxed for three hours.

The solution was then cooled in ice. The excess Grignard was hydrolyzed by adding 250 ml. of water or an equal amount of an ammonium chloride solution containing a small amount of ammonium hydroxide slowly. The ether layer was separated and washed with 25 ml. portions of water. The resulting ether solution was dried over 10 grams of anhydrous  $\text{CaCl}_2$ . Most of the ether was removed by evaporation under reduced pressure and the remaining solution was fractionally distilled through a glass bead column. The  $\text{HgEt}_2$  fraction was collected and stored under its own vapour pressure.

For the last portion of the study,  $\text{HgEt}_2$  was purchased from Alpha Inorganics. This stock was tested on the gas chromatograph and found to contain less than .5% impurities.

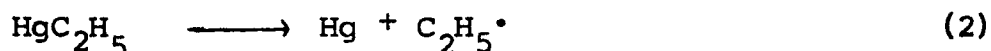
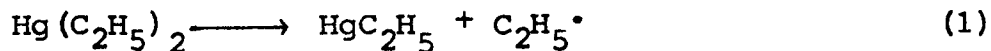
## CHAPTER III

### EXPERIMENTAL RESULTS AND DISCUSSION

The laboratory data obtained from experiments on diethylmercury, including both the experimental conditions and product analysis, are presented in Table I.

#### Proposed Mechanism

The decomposition of diethylmercury occurs in two steps, the second following rapidly after the first, according to the following :



In a toluene carrier system, the ethyl radicals produced by the thermal decomposition may abstract hydrogen atoms from either the toluene side chain or the toluene ring. Ethyl radicals may also recombine to produce butane or disproportionate to produce ethylene and ethane. These constitute the major ethyl radical reactions.

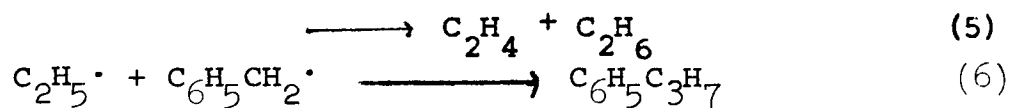
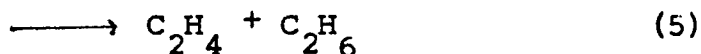
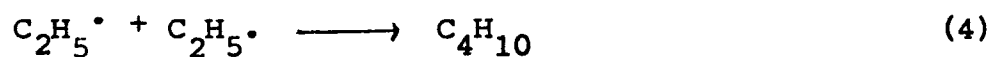
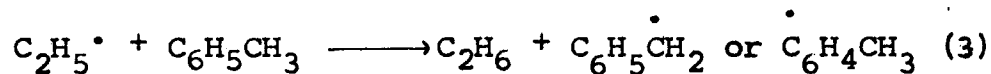




TABLE I  
THE PYROLYSIS OF DIETHYLMERCURY  
EXPERIMENTAL CONDITIONS AND PRODUCT ANALYSIS

| Run    | Temp.<br>°<br>( K ) | Pressure<br><sup>-3</sup><br>(Atm. x 10 ) | Time<br>*<br>(min.) | Toluene<br><sup>-2</sup><br>(moles x 10 ) | Alkyl<br><sup>-3</sup><br>(moles x 10 ) | Toluene/Alkyl<br>(molar ratio) |
|--------|---------------------|---|---------------------|---|---|--------------------------------|
| Hg 154 | 673.06              | 8.08                                      | 4,55,8              | 5.72                                      | 0.2740                                  | 208/1                          |
| Hg 155 | 672.06              | 8.18                                      | 4,55,4              | 6.07                                      | 0.3459                                  | 176/1                          |
| Hg 190 | 667.80              | 6.20                                      | 3,53,4              | 3.90                                      | 0.6190                                  | 63/1                           |
| Hg 187 | 667.76              | 6.12                                      | 3,43,4              | 2.76                                      | 0.2537                                  | 109/1                          |
| Hg 202 | 662.76              | 8.00                                      | 3,53,4              | 5.64                                      | 0.5985                                  | 94/1                           |
| Hg 71  | 661.41              | 8.29                                      | 3,29,3              | 2.56                                      | 0.9890                                  | 26/1                           |
| Hg 72  | 659.66              | 8.22                                      | 3,25,2              | 2.32                                      | 0.4840                                  | 48/1                           |
| Hg 181 | 659.66              | 6.17                                      | 3,23,4              | 1.68                                      | 0.2747                                  | 61/1                           |
| Hg 184 | 659.16              | 4.04                                      | 3,23,4              | 1.66                                      | 0.2634                                  | 63/1                           |
| Hg 185 | 659.16              | 4.13                                      | 3,23,4              | 1.44                                      | 0.1999                                  | 72/1                           |
| Hg 175 | 658.91              | 5.50                                      | 3,23,4              | 1.58                                      | 0.2640                                  | 62/1                           |

\* prerun, duration of alkyl flow, post-run.

TABLE I

(Continued)

| Run    | $C_2H_6$<br>(moles $\times 10^{-4}$ ) | $C_2H_4$<br>(moles $\times 10^{-4}$ ) | $C_4H_{10}$<br>(moles $\times 10^{-4}$ ) | n-propyl benzene<br>(moles $\times 10^{-4}$ ) | residual alkyl<br>(moles $\times 10^{-4}$ ) |
|--------|---------------------------------------|---------------------------------------|--|---|---|
| Hg 154 | 0.6999                                | 0.3560                                | 0.4620                                   | 0.3605  | 0.0258                                      |
| Hg 155 | 0.2300                                | 0.0776                                | 0.4368                                   | 0.3020  | 0.0460                                      |
| Hg 190 | 0.8019                                | 0.3840                                | 2.4390                                   | 0.4343  | 0.1191                                      |
| Hg 187 | 0.4963                                | 0.2913                                | 1.3642                                   | 0.3090  | 0.0360                                      |
| Hg 202 | 0.8906                                | 0.3817                                | 2.2950                                   | 0.2135  | 0.3428                                      |
| Hg 71  | 1.2520                                | 0.7788                                | 1.0300                                   | 0.6214  | 0.7535                                      |
| Hg 72  | 0.7080                                | 0.4097                                | 0.4710                                   | 0.3985  | 0.3748                                      |
| Hg 181 | 0.5377                                | 0.2854                                | 1.0899                                   | 0.2332  | 0.3360                                      |
| Hg 184 | 0.4100                                | 0.2149                                | 1.5340                                   | 0.2867  | 0.3959                                      |
| Hg 185 | 0.3417                                | 0.1682                                | 1.1860                                   | 0.1676  | 0.2881                                      |
| Hg 175 | 0.4236                                | 0.2259                                | 1.1650                                   | 0.1759  | 0.2393                                      |

TABLE I

(Continued)

| Run    | $t_c$<br>(sec.) | % Decomposed<br>Alkyl | % Undecomposed<br>Alkyl | $\frac{10^3}{o}$<br>T (K) | **                   |            | **                   |            |
|--------|-----------------|-----------------------|-------------------------|---------------------------|----------------------|------------|----------------------|------------|
|        |                 |                       |                         |                           | $k_{g-1}$<br>(sec. ) | $\log k_g$ | $k_{m-1}$<br>(sec. ) | $\log k_m$ |
| Hg 154 | 1.47            | 42.70                 | 0.95                    | 1.485                     | 0.38                 | -0.424     | 2.03                 | 0.600      |
| Hg 155 | 1.30            | 21.44                 | 1.33                    | 1.487                     | 0.19                 | -0.732     | 3.32                 | 0.520      |
| Hg 190 | 1.52            | 52.49                 | 1.92                    | 1.497                     | 0.49                 | -0.311     | 2.59                 | 0.414      |
| Hg 187 | 1.71            | 75.37                 | 1.42                    | 1.498                     | 0.82                 | -0.087     | 2.49                 | 0.395      |
| Hg 202 | 1.38            | 50.77                 | 5.73                    | 1.509                     | 0.51                 | -0.288     | 2.07                 | 0.317      |
| Hg 71  | 1.70            | 23.81                 | 7.61                    | 1.512                     | 0.16                 | -0.795     | 1.50                 | 0.176      |
| Hg 72  | 1.61            | 25.40                 | 7.75                    | 1.516                     | 0.18                 | -0.741     | 1.59                 | 0.199      |
| Hg 181 | 1.54            | 58.91                 | 12.25                   | 1.516                     | 0.57                 | -0.237     | 1.37                 | 0.135      |
| Hg 184 | 1.03            | 75.55                 | 15.03                   | 1.517                     | 1.36                 | 0.135      | 1.84                 | 0.264      |
| Hg 185 | 1.20            | 76.29                 | 14.41                   | 1.517                     | 1.19                 | 0.077      | 1.61                 | 0.206      |
| Hg 175 | 1.42            | 59.63                 | 9.05                    | 1.518                     | 0.64                 | -0.194     | 1.69                 | 0.229      |

\*\*  $k_g$ , rate constant based on product analysis,  $k_m$ , rate constant based on alkyl analysis

TABLE I

(Continued)

| Run    | Temp.<br>°<br>( K ) | Pressure<br><sup>-3</sup><br>(Atm. x 10 ) | Time<br>*<br>(min.) | Toluene<br><sup>-2</sup><br>(moles x 10 ) | Alkyl<br><sup>-3</sup><br>(moles x 10 ) | Toluene/Alkyl<br>(molar/ratio) |
|--------|---------------------|---|---------------------|---|---|--------------------------------|
| Hg 156 | 658.76              | 8.21                                      | 4,64,4              | 7.24                                      | 0.3959                                  | 183/1                          |
| Hg 192 | 657.91              | 4.93                                      | 3,43,4              | 1.86                                      | 0.3260                                  | 57/1                           |
| Hg 201 | 657.66              | 8.02                                      | 3,51,4              | 5.30                                      | 0.4050                                  | 131/1                          |
| Hg 191 | 656.81              | 9.20                                      | 3,43,4              | 4.92                                      | 0.3460                                  | 142/1                          |
| Hg 59  | 656.66              | 8.46                                      | 4,40,3              | 3.90                                      | 0.7490                                  | 52/1                           |
| Hg 58  | 656.16              | 10.20                                     | 4,50,3              | 6.23                                      | 1.0198                                  | 61/1                           |
| Hg 103 | 655.91              | 8.08                                      | 2,26,2              | 2.45                                      | 0.4300                                  | 57/1                           |
| Hg 222 | 654.29              | 5.88                                      | 3,52,4              | 3.37                                      | 0.4550                                  | 74/1                           |
| Hg 167 | 654.16              | 6.21                                      | 3,52,4              | 3.92                                      | 0.4840                                  | 81/1                           |
| Hg 169 | 654.16              | 4.62                                      | 3,23,4              | 1.40                                      | 0.1910                                  | 73/1                           |
| Hg 189 | 654.06              | 6.25                                      | 3,53,4              | 3.48                                      | 0.5447                                  | 64/1                           |
| Hg 170 | 653.96              | 5.78                                      | 5,30,5              | 1.85                                      | 0.3420                                  | 54/1                           |

TABLE I

(Continued)

| Run    | $C_2H_6$<br>(moles $\times 10^{-4}$ ) | $C_2H_4$<br>(moles $\times 10^{-4}$ ) | $C_4H_{10}$<br>(moles $\times 10^{-4}$ ) | n-propyl benzene<br>(moles $\times 10^{-4}$ ) | residual alkyl<br>(moles $\times 10^{-4}$ ) |
|--------|---------------------------------------|---------------------------------------|--|---|---|
| Hg 156 | 0.7907                                | 0.3396                                | 0.1512                                   | 0.5185  | 0.4430                                      |
| Hg 192 | 0.4887                                | 0.2805                                | 2.4160                                   | 0.2316  | 0.2569                                      |
| Hg 201 | 0.9115                                | 0.3820                                | 2.6413                                   | 0.3168  | 0.4989                                      |
| Hg 191 | 0.5507                                | 0.2203                                | 1.4320                                   | 0.3497  | 0.4170                                      |
| Hg 59  | 0.9100                                | 0.4720                                | 0.5040                                   | 0.4094  | 0.7490                                      |
| Hg 58  | 1.5610                                | 0.7804                                | 0.6967                                   | 0.7564  | 1.3870                                      |
| Hg 103 | 0.4205                                | 0.2403                                | 0.3816                                   | 0.3044  | 0.4540                                      |
| Hg 222 | 0.6048                                | 0.2981                                | 3.1524                                   | 0.2366  | 0.6188                                      |
| Hg 167 | 0.7702                                | 0.3526                                | 1.6983                                   | 0.4585  | 0.5009                                      |
| Hg 169 | 0.4420                                | 0.2398                                | 1.0826                                   | 0.2084  | 0.3253                                      |
| Hg 189 | 0.7224                                | 0.3510                                | 2.3340                                   | 0.7219  | 0.4730                                      |
| Hg 170 | 0.5224                                | 0.2703                                | 1.5160                                   | 0.2443  | 0.3920                                      |

TABLE I

(Continued)

| Run    | $t_c$<br>(sec.) | % Decomposed | Alkyl | % Undecomposed | Alkyl | $10^3$<br>$T(^{\circ}K)$ | $k_g^{-1}$<br>(sec.) | $\log k_g$ | $k_m^{-1}$<br>(sec.) | $\log k_m$ |
|--------|-----------------|--------------|-------|----------------|-------|--------------------------|----------------------|------------|----------------------|------------|
| Hg 156 | 1.33            | 24.64        | 11.19 | 11.19          | 1.518 | 0.21                     | -0.670               | 1.55       | 0.190                |            |
| Hg 192 | 2.10            | 89.40        | 7.87  | 7.87           | 1.520 | 1.07                     | 0.029                | 1.21       | 0.083                |            |
| Hg 201 | 1.42            | 85.05        | 12.31 | 12.31          | 1.521 | 1.34                     | 0.128                | 1.48       | 0.170                |            |
| Hg 191 | 1.48            | 57.58        | 12.09 | 12.09          | 1.523 | 0.58                     | -0.238               | 1.43       | 0.154                |            |
| Hg 59  | 1.58            | 18.68        | 10.46 | 10.46          | 1.522 | 0.13                     | -0.888               | 1.43       | 0.154                |            |
| Hg 58  | 1.51            | 22.02        | 13.60 | 13.60          | 1.524 | 0.17                     | -0.782               | 1.31       | 0.116                |            |
| Hg 103 | 1.56            | 20.07        | 10.57 | 10.57          | 1.525 | 0.14                     | -0.844               | 1.44       | 0.157                |            |
| Hg 222 | 1.68            | 81.77        | 13.60 | 13.60          | 1.528 | 1.02                     | 0.007                | 1.19       | 0.075                |            |
| Hg 167 | 1.51            | 51.40        | 10.34 | 10.34          | 1.529 | 0.48                     | -0.322               | 1.49       | 0.175                |            |
| Hg 169 | 1.40            | 79.82        | 17.00 | 17.00          | 1.529 | 1.14                     | 0.059                | 1.27       | 0.103                |            |
| Hg 189 | 1.74            | 59.33        | 8.68  | 8.68           | 1.529 | 0.52                     | -0.286               | 1.40       | 0.148                |            |
| Hg 170 | 1.72            | 59.40        | 11.45 | 11.45          | 1.529 | 0.52                     | -0.282               | 1.26       | 0.099                |            |

TABLE I

(Continued)

| Run    | Temp.<br>°<br>( K ) | Pressure<br><sup>-3</sup><br>(Atm. x 10 ) | Time<br>*<br>(min.) | Toluene<br><sup>-2</sup><br>(moles x 10 ) | Alkyl<br><sup>-3</sup><br>(moles x 10 ) | Toluene/Alkyl<br>(molar ratio) |
|--------|---------------------|---|---------------------|---|---|--------------------------------|
| Hg 161 | 653.60              | 7.90                                      | 7,52,5              | 5.15                                      | 0.3030                                  | 170/1                          |
| Hg 159 | 653.41              | 8.08                                      | 4,64,4              | 7.61                                      | 0.3270                                  | 223/1                          |
| Hg 162 | 653.25              | 8.28                                      | 3,56,4              | 5.67                                      | 0.3100                                  | 183/1                          |
| Hg 102 | 651.91              | 8.08                                      | 2,26,2              | 2.28                                      | 0.3920                                  | 58/1                           |
| Hg 200 | 650.41              | 7.33                                      | 3,73,4              | 5.70                                      | 0.6630                                  | 86/1                           |
| Hg 158 | 649.41              | 8.37                                      | 4,55,5              | 6.00                                      | 0.3260                                  | 184/1                          |
| Hg 64  | 646.91              | 7.99                                      | 3,34,3              | 3.00                                      | 0.6980                                  | 43/1                           |
| Hg 65  | 646.66              | 8.36                                      | 4,34,2              | 3.09                                      | 0.8580                                  | 36/1                           |
| Hg 221 | 645.41              | 5.82                                      | 3,60,4              | 3.88                                      | 0.4210                                  | 92/1                           |
| Hg 157 | 645.16              | 9.11                                      | 5,54,4              | 5.75                                      | 0.2750                                  | 209/1                          |
| Hg 122 | 643.56              | 8.08                                      | 5,17,5              | 1.75                                      | 0.5455                                  | 32/1                           |
| Hg 199 | 643.31              | 6.86                                      | 3,33,4              | 2.83                                      | 0.2670                                  | 106/1                          |

TABLE I

(Continued)

| Run    | $C_2H_6$<br>(moles $\times 10^{-4}$ ) | $C_2H_4$<br>(moles $\times 10^{-4}$ ) | $C_4H_{10}$<br>(moles $\times 10^{-4}$ ) | n-propyl benzene<br>(moles $\times 10^{-4}$ ) | residual alkyl<br>(moles $\times 10^{-4}$ ) |
|--------|---------------------------------------|---------------------------------------|--|---|---|
| Hg 161 | 0.5829                                | 0.2373                                | 1.0679                                   | 0.4859  | 0.4686                                      |
| Hg 159 | 0.7793                                | 0.2716                                | 0.4167                                   | 0.1178  | 0.6250                                      |
| Hg 162 | 0.6508                                | 0.2405                                | 1.7251                                   | 0.7089  | 0.6531                                      |
| Hg 102 | 0.5304                                | 0.3056                                | 0.4205                                   | 0.2553  | 0.6040                                      |
| Hg 200 | 1.2140                                | 0.5427                                | 3.4890                                   | 0.3363  | 0.8987                                      |
| Hg 158 | 0.7170                                | 0.2712                                | 0.9812                                   | 0.9643  | 0.8345                                      |
| Hg 64  | 0.9463                                | 0.5038                                | 0.7404                                   | 0.3347  | 1.8220                                      |
| Hg 65  | 0.8199                                | 0.4558                                | 0.6653                                   | 0.3860  | 2.3290                                      |
| Hg 221 | 0.5356                                | 0.2429                                | 2.3662                                   | 0.1853  | 1.2550                                      |
| Hg 157 | 0.4273                                | 0.0655                                | 0.7345                                   | 0.0860  | 0.9500                                      |
| Hg 122 | 0.2521                                | 0.3159                                | 0.1488                                   | 0.1352  | 2.2960                                      |
| Hg 199 | 0.4569                                | 0.2019                                | 1.1240                                   | 0.1757  | 0.9297                                      |



TABLE I

(Continued)

| Run    | $t_c$<br>(sec.) | % Decomposed<br>Alkyl | % Undecomposed<br>Alkyl | $\frac{10^3}{T(^{\circ}K)}$ | $k_g^{-1}$<br>(sec.) | $\log k_g$ | $k_m^{-1}$<br>(sec.) | $\log k_m$ |
|--------|-----------------|-----------------------|-------------------------|-----------------------------|----------------------|------------|----------------------|------------|
| Hg 161 | 1.47            | 56.81                 | 15.47                   | 1.530                       | 0.57                 | -0.242     | 1.27                 | 0.103      |
| Hg 159 | 1.31            | 30.60                 | 19.10                   | 1.530                       | 0.28                 | -0.558     | 1.22                 | 0.085      |
| Hg 162 | 1.42            | 81.38                 | 21.05                   | 1.531                       | 1.18                 | 0.073      | 1.10                 | 0.040      |
| Hg 102 | 1.70            | 24.65                 | 15.38                   | 1.534                       | 0.17                 | -0.779     | 1.10                 | 0.040      |
| Hg 200 | 1.74            | 83.45                 | 13.56                   | 1.537                       | 1.03                 | 0.013      | 1.15                 | 0.059      |
| Hg 158 | 1.42            | 59.94                 | 25.50                   | 1.540                       | 0.64                 | -0.192     | 1.54                 | 0.020      |
| Hg 64  | 1.68            | 23.39                 | 26.09                   | 1.546                       | 0.16                 | -0.799     | 0.80                 | -0.098     |
| Hg 65  | 1.71            | 17.44                 | 27.14                   | 1.546                       | 0.11                 | -0.950     | 0.76                 | -0.120     |
| Hg 221 | 1.67            | 67.57                 | 29.78                   | 1.549                       | 0.67                 | -0.172     | 0.72                 | -0.140     |
| Hg 157 | 1.60            | 37.23                 | 34.50                   | 1.550                       | 0.29                 | -0.535     | 0.67                 | -0.177     |
| Hg 122 | 1.04            | 9.17                  | 42.09                   | 1.554                       | 0.09                 | -1.033     | 0.83                 | -0.079     |
| Hg 199 | 1.49            | 65.55                 | 34.83                   | 1.554                       | 0.71                 | -0.147     | 0.71                 | -0.152     |

TABLE I

(Continued)

| Run    | Temp.<br>(°K) | Pressure<br>(Atm. x 10 <sup>-3</sup> ) | Time<br>(min.) | Toluene<br>(moles x 10 <sup>-2</sup> ) | Alkyl<br>(moles x 10 <sup>-3</sup> ) | Toluene/Alkyl<br>(molar ratio) |
|--------|---------------|--|----------------|--|--------------------------------------|--------------------------------|
| Hg 61  | 640.41        | 8.35                                   | 3,40,3         | 3.61                                   | 0.7517                               | 48/1                           |
| Hg 62  | 640.41        | 8.27                                   | 3,40,3         | 3.76                                   | 0.6846                               | 55/1                           |
| Hg 63  | 639.91        | 8.27                                   | 3,40,5         | 3.69                                   | 0.7535                               | 49/1                           |
| Hg 198 | 635.69        | 7.43                                   | 3,33,4         | 3.26                                   | 0.2280                               | 143/1                          |
| Hg 105 | 635.16        | 7.20                                   | 2,16,2         | 2.50                                   | 0.4300                               | 58/1                           |
| Hg 218 | 634.91        | 6.30                                   | 3,40,4         | 2.82                                   | 0.5630                               | 50/1                           |
| Hg 121 | 630.66        | 8.08                                   | 3,20,3         | 2.17                                   | 0.6783                               | 32/1                           |
| Hg 66  | 629.97        | 8.08                                   | 5,40,3         | 3.50                                   | 0.6148                               | 57/1                           |
| Hg 67  | 629.66        | 8.08                                   | 4,40,3         | 3.46                                   | 1.0160                               | 34/1                           |
| Hg 194 | 627.41        | 6.86                                   | 4,42,4         | 3.70                                   | 0.3939                               | 94/1                           |
| Hg 216 | 626.66        | 6.30                                   | 8,39,4         | 2.80                                   | 0.2500                               | 112/1                          |
| Hg 220 | 617.56        | 6.13                                   | 4,40,4         | 2.76                                   | 0.1890                               | 146/1                          |

TABLE I

(Continued)

| Run    | $C_2H_6$<br>(moles $\times 10^{-4}$ ) | $C_2H_4$<br>(moles $\times 10^{-4}$ ) | $C_4H_{10}$<br>(moles $\times 10^{-4}$ ) | n-propyl benzene<br>(moles $\times 10^{-4}$ ) | residual alkyl<br>(moles $\times 10^{-4}$ ) |
|--------|---------------------------------------|---------------------------------------|--|---|---|
| Hg 61  | 0.7612                                | 0.3824                                | 0.6670                                   | 0.2988  | 3.0250                                      |
| Hg 62  | 0.8110                                | 0.4064                                | 0.4593                                   | 0.3126  | 2.6760                                      |
| Hg 63  | 0.8611                                | 0.4410                                | 0.5545                                   | 0.3186  | 3.2180                                      |
| Hg 198 | 0.2865                                | 0.1139                                | 0.6308                                   | 0.0493  | 1.2200                                      |
| HG 105 | 0.1708                                | 0.1948                                | 0.1293                                   | 0.1160  | 2.9660                                      |
| Hg 218 | 0.3741                                | 0.1871                                | 2.3078                                   | 0.1624  | 2.3630                                      |
| Hg 121 | 0.2375                                | 0.3079                                | 0.2551                                   | 0.0864  | 3.3370                                      |
| Hg 66  | 0.5162                                | 0.2466                                | 0.2686                                   | 0.2241  | 3.7670                                      |
| Hg 67  | 0.3815                                | 0.2070                                | 0.2605                                   | 0.2550  | 5.5870                                      |
| Hg 194 | 0.3280                                | 0.1524                                | 1.0760                                   | 0.1126  | 2.1280                                      |
| Hg 216 | 0.2009                                | 0.0792                                | 0.6639                                   | 0.0792  | 1.6264                                      |
| Hg 220 | 0.1428                                | 0.0610                                | 0.2493                                   | 0.0451  | 1.4790                                      |

TABLE I

(Continued)

| Run    | $t_c$<br>(sec.) | % Decomposed<br>Alkyl | % Undecomposed<br>Alkyl | $10^3$<br>$T(^{\circ}K)$ | $k_g^{-1}$<br>(sec.) | $\log k_g$ | $k_m^{-1}$<br>(sec.) | $\log k_m$ |
|--------|-----------------|-----------------------|-------------------------|--------------------------|----------------------|------------|----------------------|------------|
| Hg 61  | 1.73            | 18.47                 | 40.20                   | 1.561                    | 0.12                 | -0.927     | 0.53                 | -0.280     |
| Hg 62  | 1.67            | 17.88                 | 39.09                   | 1.561                    | 0.12                 | -0.927     | 0.56                 | -0.252     |
| Hg 63  | 1.70            | 18.11                 | 42.72                   | 1.563                    | 0.12                 | -0.929     | 0.50                 | -0.302     |
| Hg 198 | 1.42            | 37.44                 | 53.50                   | 1.573                    | 0.33                 | -0.480     | 0.43                 | -0.369     |
| Hg 105 | 0.88            | 8.60                  | 68.88                   | 1.574                    | 0.10                 | -0.989     | 0.43                 | -0.370     |
| Hg 218 | 1.72            | 47.40                 | 41.95                   | 1.575                    | 0.37                 | -0.426     | 0.51                 | -0.300     |
| Hg 121 | 1.02            | 8.42                  | 62.50                   | 1.585                    | 0.09                 | -1.064     | 0.46                 | -0.338     |
| Hg 66  | 1.77            | 12.39                 | 58.27                   | 1.587                    | 0.07                 | -1.126     | 0.30                 | -0.519     |
| Hg 67  | 1.78            | 6.72                  | 55.00                   | 1.588                    | 0.04                 | -1.408     | 0.34                 | -0.480     |
| Hg 194 | 1.50            | 34.85                 | 54.02                   | 1.594                    | 0.29                 | -0.543     | 0.41                 | -0.385     |
| Hg 216 | 1.69            | 33.71                 | 65.79                   | 1.596                    | 0.24                 | -0.614     | 0.25                 | -0.606     |
| Hg 220 | 1.73            | 19.73                 | 78.10                   | 1.619                    | 0.13                 | -0.895     | 0.14                 | -0.844     |

TABLE I

(Continued)

| Run    | Temp.<br>° ( K ) | Pressure<br>(Atm. x 10 <sup>-3</sup> ) | Time<br>(min.) | Toluene<br>(moles x 10 <sup>-2</sup> ) | Alkyl<br>(moles x 10 <sup>-3</sup> ) | Toluene/Alkyl<br>(molar ratio) |
|--------|------------------|--|----------------|--|--------------------------------------|--------------------------------|
| Hg 54  | 617.48           | 9.44                                   | 4,51,3         | 5.54                                   | 0.7290                               | 76/1                           |
| Hg 196 | 616.16           | 5.74                                   | 3,33,4         | 2.16                                   | 0.3421                               | 63/1                           |
| Hg 117 | 612.56           | 1.37                                   | 4,84,2         | 2.70                                   | 0.7940                               | 34/1                           |
| Hg 106 | 612.16           | 6.07                                   | 4,20,2         | 1.97                                   | 0.5180                               | 38/1                           |
| Hg 114 | 610.56           | 6.25                                   | 2,30,2         | 10.08                                  | 1.4190                               | 71/1                           |
| Hg 118 | 609.96           | 9.64                                   | 3,51,3         | 6.59                                   | 1.4640                               | 45/1                           |
| Hg 119 | 609.28           | 8.42                                   | 3,45,3         | 4.82                                   | 0.6990                               | 69/1                           |
| Hg 219 | 608.91           | 5.64                                   | 8,40,4         | 4.14                                   | 0.2208                               | 187/1                          |
| Hg 109 | 608.66           | 8.51                                   | 2,30,2         | 2.11                                   | 0.8790                               | 24/1                           |
| Hg 95  | 607.56           | 7.89                                   | 2,60,4         | 5.03                                   | 0.3900                               | 129/1                          |
| Hg 93  | 606.91           | 8.42                                   | 3,47,2         | 4.22                                   | 0.9530                               | 44/1                           |
| Hg 90  | 601.76           | 8.08                                   | 2,61,2         | 5.29                                   | 0.7900                               | 67/1                           |
| Hg 91  | 601.36           | 8.04                                   | 2,60,2         | 5.03                                   | 0.9690                               | 52/1                           |

34

TABLE I

(Continued)

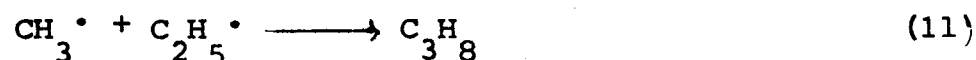
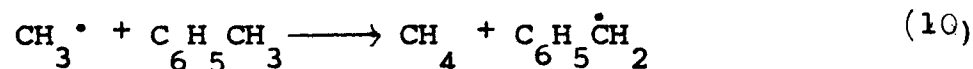
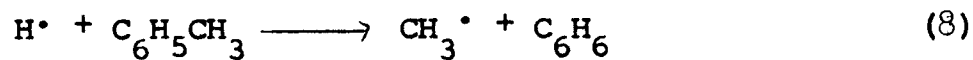
| Run    | $C_2H_6$<br>(moles $\times 10^{-4}$ ) | $C_2H_4$<br>(moles $\times 10^{-4}$ ) | $C_4H_{10}$<br>(moles $\times 10^{-4}$ ) | n-propyl benzene<br>(moles $\times 10^{-4}$ ) | residual alkyl<br>(moles $\times 10^{-4}$ ) |
|--------|---------------------------------------|---------------------------------------|--|---|---|
| Hg 54  | 0.4078                                | 0.1943                                | 0.1473                                   | 0.3605  | 5.6200                                      |
| Hg 196 | 0.1410                                | 0.0672                                | 0.4049                                   | 0.0509  | 2.6950                                      |
| Hg 117 | 0.0747                                | 0.0832                                | 0.0528                                   | 0.0216  | 7.2590                                      |
| Hg 106 | 0.0258                                | 0.0258                                | 0.0131                                   | 0.0360  | 1.2850                                      |
| Hg 114 | 0.0407                                | 0.0376                                | 0.0187                                   | 0.0396  | 9.7830                                      |
| Hg 118 | 0.1689                                | 0.1620                                | 0.0281                                   | 0.1173  | 12.5300                                     |
| Hg 119 | 0.0681                                | 0.0658                                | 0.0070                                   | 0.0765  | 6.1642                                      |
| Hg 219 | 0.1456                                | 0.0678                                | 0.1398                                   | 0.0644  | 1.5160                                      |
| Hg 109 | 0.2222                                | 0.2417                                | 0.1453                                   | 0.1496  | 5.7950                                      |
| Hg 95  | 0.3120                                | 0.1460                                | 0.1070                                   | 0.0567  | 3.3300                                      |
| Hg 93  | 0.1554                                | 0.0671                                | 0.0389                                   | 0.0208  | 8.0529                                      |
| Hg 90  | 0.0681                                | 0.0281                                | 0.0179                                   | 0.0369  | 7.0000                                      |
| Hg 91  | 0.1235                                | 0.0512                                | 0.0261                                   | 0.0203  | 8.5500                                      |

TABLE I

(Continued)

| Run    | $t_c$<br>(sec.) | % Decomposed<br>Alkyl | % Undecomposed<br>Alkyl | $\frac{10^3}{T(K)}$ | $k_g^{-1}$<br>(sec.) | $\log k_g$ | $k_m^{-1}$<br>(sec.) | $\log k_m$ |
|--------|-----------------|-----------------------|-------------------------|---------------------|----------------------|------------|----------------------|------------|
| Hg 54  | 1.69            | 8.62                  | 77.00                   | 1.619               | 0.53                 | -1.270     | 0.15                 | -0.820     |
| Hg 196 | 1.71            | 15.62                 | 78.75                   | 1.623               | 0.10                 | -1.000     | 0.15                 | -0.84      |
| Hg 117 | 0.84            | 1.79                  | 91.37                   | 1.632               | 0.02                 | -1.665     | 0.11                 | -0.967     |
| Hg 106 | 1.21            | 1.20                  | 24.80                   | 1.634               | 0.01                 | -2.037     | 0.10                 | -0.940     |
| Hg 114 | 0.36            | 0.54                  | 68.93                   | 1.638               | 0.02                 | -1.823     | 0.10                 | -0.988     |
| Hg 118 | 1.04            | 1.72                  | 85.61                   | 1.639               | 0.02                 | -1.777     | 0.15                 | -0.825     |
| Hg 119 | 1.10            | 1.60                  | 88.14                   | 1.641               | 0.15                 | -1.833     | 0.12                 | -0.940     |
| Hg 219 | 1.62            | 12.62                 | 68.65                   | 1.642               | 0.08                 | -1.080     | 0.23                 | -0.634     |
| Hg 109 | 2.43            | 5.14                  | 81.10                   | 1.643               | 0.02                 | -1.662     | 0.09                 | -1.070     |
| Hg 95  | 1.87            | 9.35                  | 86.00                   | 1.648               | 0.05                 | -1.286     | 0.08                 | -1.084     |
| Hg 93  | 1.86            | 1.69                  | 84.51                   | 1.648               | 0.007                | -2.147     | 0.09                 | -1.044     |
| Hg 90  | 1.87            | 1.56                  | 88.70                   | 1.661               | 0.007                | -2.147     | 0.06                 | -1.200     |
| Hg 91  | 1.92            | 0.87                  | 88.30                   | 1.663               | 0.002                | -2.622     | 0.06                 | -1.220     |

Also the following minor reactions occurred.



However, these reactions occurred to only a small extent as confirmed by the negligible amount of methane and propane detected even at the highest temperatures under which the reaction was studied. Also, the benzene produced (which would be equal to the methane plus propane) was analyzed on the gas chromatograph and found to be negligible.

The extent of ethyl radical decomposition can be roughly predicted from studies done previously (13A) where the rate constant for the decomposition was calculated to be

$$k_d = 1.8 \times 10^{18} e^{-(32400/RT)} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

on the basis of using the parameter  $s^{\ddagger} = 3$ .

On the basis of Kassel theory, with  $s \approx 6$ ,  $k$  was calculated to be

$$k_{d2} = 1.4 \times 10^{17} e^{-(32400/RT)} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

These two literature values can be compared to the experimen-



tally determined rate of disappearance of ethyl radicals when forming ethane by abstraction from the toluene. This rate can be written as

$$-\frac{d(\text{C}_2\text{H}_5\cdot)}{dt} = k_3 (\text{C}_2\text{H}_5\cdot)(\text{C}_6\text{H}_5\text{CH}_3)$$

which can be compared to the rate of disappearance of ethyl radicals due to ethyl radical decomposition given above by  $k_d$  (estimated  $k_{d2}$  also used but result given no weight.

At  $645^\circ\text{A}$ ,  $\log k_{d2}$  is 6.5 and  $\log k_3$  is 8.1 and therefore the amount of ethyl radicals undergoing decomposition can be said to be about 1/40 th of the ethyl radicals attacking the toluene to form ethane. Also, at  $645^\circ\text{A}$ ,  $\log k_d$  is 7.1 and  $\log k_3$  is 8.1. In this case, the amount of ethyl radicals undergoing decomposition would be about 1/7 th of the ethyl radicals attacking the toluene. Therefore, on the basis of the

literature value, the amount of ethylene produced during the decomposition of diethylmercury can not all be attributed to the disproportionation reaction of the ethyl radicals. Roughly, 1/10 th of the ethylene formed could be attributed to the decomposition of the ethyl radicals. In terms of calculations, this would only affect the  $k_a/k_r^{1/2}$  to a small extent and need not be accounted for. Therefore, the aforementioned major ethyl radical reactions will be the only ones considered for calculations.

The rate constants for this study were calculated from

the first order equation

$$k = \frac{2.303}{t_c} \log \frac{100}{100 - X}$$

The contact time was evaluated from the expression

$$t_c = \frac{V}{22416} \times \frac{P}{760} \times \frac{273}{T} \times \frac{1}{F}$$

where V is in cc. and corresponds to the volume of the reaction zone, P, in mm. corresponds to the total pressure and T in °K, corresponds to the temperature of the reaction zone. F is the molar flow rate through the reaction zone and is in units of moles/sec.. The per cent decomposition occurring is represented by X. The per cent decomposition on the basis of products analyzed was

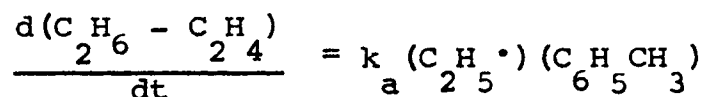
$$\frac{(1/2(\text{moles of ethane} + \text{moles of ethylene} + \text{moles of n-propyl benzene}) + (\text{moles of butane})) \times 100}{\text{moles of diethylmercury}}$$

The per cent undecomposed alkyl, represented by 100 - X, was calculated by

$$\frac{\text{moles of residual alkyl} \times 100}{\text{moles of diethylmercury used}}$$

#### Hydrogen Abstraction by Ethyl Radicals

The rate expressions for the abstraction and recombination reactions may be written as



and

$$\frac{d(C_4H_{10})}{dt} = k_r (C_2H_5)^2$$

Then,

$$\frac{k_a}{k_r^{1/2}} = \frac{d(C_2H_6 - C_2H_4)/dt}{(d(C_4H_{10})/dt)^{1/2} [C_6H_5CH_3]}$$

where

$$\frac{d(C_2H_6 - C_2H_4)}{dt} = \frac{\text{moles } C_2H_6 - \text{moles } C_2H_4}{V \times t}$$

and moles  $C_2H_6$  represents the total number of moles of ethane produced and moles  $C_2H_4$  represents the total number of moles of ethylene produced.  $V$  is the volume of the reaction vessel in cc., and  $t$  is the length of the alkyl run in seconds.

Also,

$$\frac{d(C_4H_{10})}{dt} = \frac{\text{moles of } C_4H_{10}}{V \times t}$$

where moles of  $C_4H_{10}$  represents the total number of moles of butane produced in the run.

Assuming ideal gas conditions, the toluene concentration can be expressed as

$$[C_6H_5CH_3] = \frac{n}{V} = \frac{P}{RT} = \frac{\text{Pmm.}/760}{82.06 \times T \text{ K}}$$

Then  $k_a/k_r^{1/2}$  can be expressed in terms of experimental parameters as follows

$$\frac{k_a}{k_r^{1/2}} = \frac{(\text{moles } C_2H_6 - \text{moles } C_2H_4) \times 760 \times 82.06 \times T}{(\text{moles } C_2H_4)^{1/2} (V \times t)^{1/2} \times P}$$

This derivation of  $k_a/k_r^{1/2}$  assumes that the ethyl radicals are produced at a constant and uniform rate. The former is achieved by maintaining the pressure of the alkyl constant throughout the run. The latter can not be achieved. This condition will only be approached at the low decompositions. However, at high decomposition the ethyl radicals will be at a high concentration at the beginning of the reaction zone favouring the recombination reaction and at a low concentration at the end favouring the abstraction reaction. These factors are believed to be somewhat self compensating. (14,15)

#### Variations in Technique

During the initial work done on diethylmercury in this study, a great discrepancy was found between the log k values obtained on the basis of residual alkyl and the log k values based on product analysis, (Table I). Those based on residual alkyl were considerably higher and these produced a straight line over an alkyl decomposition range of 10% to 99%. On the other hand, the log k values based on product analysis produced an Arrhenius plot with a great deal of scatter and a flattening out at high temperatures where the per cent decomposition seemed to be no higher than 35%. This large

discrepancy between the two sets of results as well as the poor and inconsistent results from product analysis led to the probability that not all the gases were being collected. This initial assumption was made on the basis of previous workers (1) who reported a 4:1:1 ratio of butane to ethane to ethylene in the gas products collected. Initial work in this study yielded gas samples which were approximately only 20% butane as compared to the expected 80%. Therefore, the initial system was altered and several variations in trap set ups and trap temperatures were tried in order to attempt to collect the remainder of the butane believed to be present.

Figure 7 represents the initial trapping system used with  $T_2$  and  $T_3$  being at  $-80^{\circ}\text{C}$  using acetone and dry ice baths. Replacing the bath around  $T_3$  with a liquid  $\text{N}_2$  bath resulted in an increase of butane in the gas products. (It should be noted that using a liquid  $\text{N}_2$  trap on  $T_3$  meant that the gas collection in the gas buret had to be done after the run instead of continuously during the run. This system of collection brought the log k values in closer agreement with those based on the residual alkyl analysis but there was still a considerable discrepancy as indicated in Table II.

Another method attempted consisted of replacing the  $-80^{\circ}\text{C}$  bath around  $T_2$  with a bath at  $-50^{\circ}\text{C}$  after the initial bulk of the gas was in the gas buret. Warming up  $T_2$  in this fashion, yielded more gas products. However, it was difficult to determine when  $T_2$  had warmed up to  $-50^{\circ}\text{C}$

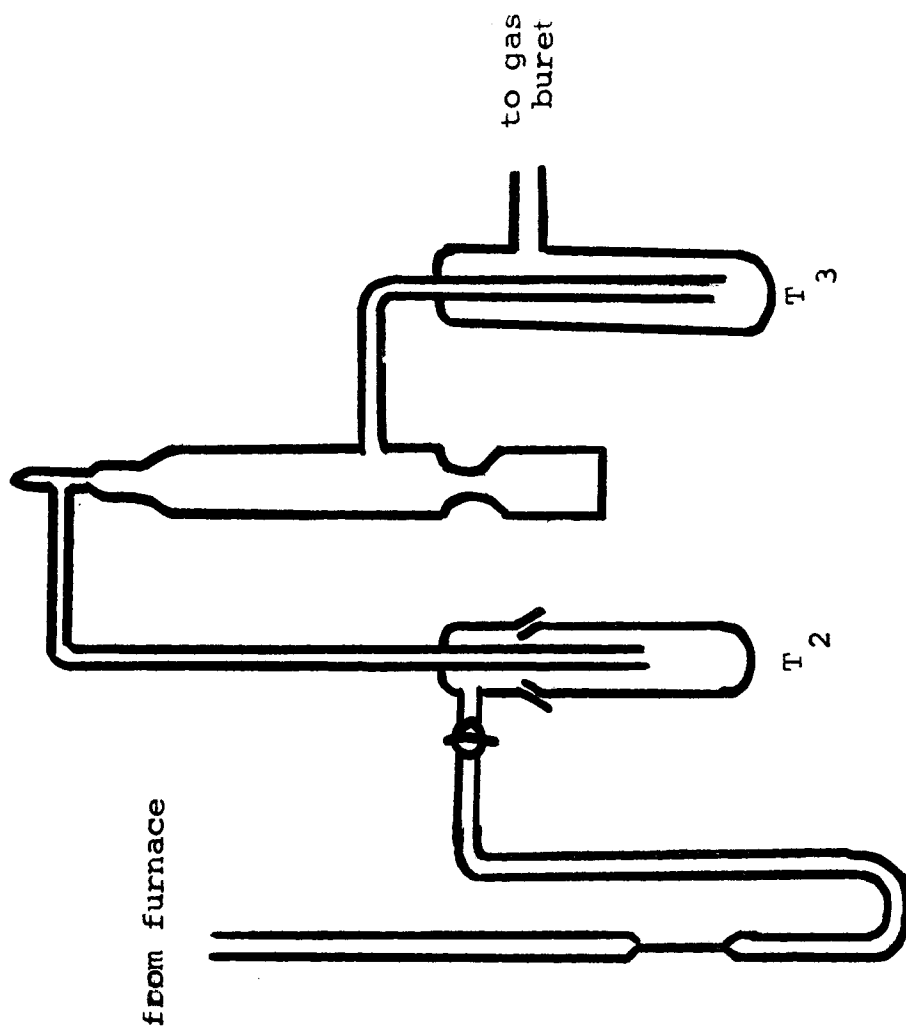


Figure 7: Initial trapping system

and this method proved unsatisfactory. Only run 162 yielded results that were satisfactory. An attempt was then made to find a more reliable method.

The system was then altered, Figure 8, to include another trap of a larger volume. This trap acted as an inefficient trap, collecting most of the liquid products but allowing the butane to pass through with more facility. This initial trap  $T_1$ , was cooled with acetone and dry ice baths. Several temperatures ranging from  $-22^{\circ}\text{C}$  to  $-80^{\circ}\text{C}$  were tried and yielded varying results in butane collected. The optimum temperature for this bath surrounding  $T_1$  was determined to be  $-60^{\circ}\text{C} \pm 5^{\circ}\text{C}$ , as indicated by runs 184 and 185 (Table II).

It should be noted that in some runs,  $T_3$  was at  $-196^{\circ}\text{C}$ . With three traps in the system, there was no difference observed in the results when  $T_3$  was at  $-196^{\circ}\text{C}$  as opposed to the usual  $-80^{\circ}\text{C}$ .

Even though the addition of  $T_1$  improved results even further, the effectiveness of this addition of  $T_1$  appeared to be influenced by other conditions such as the amount of toluene used and the amount of butane produced. If the amount of toluene used was large, more butane would be lost in the solution and if the temperatures were low, the percentage of the total butane produced that would be dissolved in the toluene would be greater. Also, the contact time seemed to influence the amount of butane lost from the gas sample. The shorter contact times seemed to provide better results. These

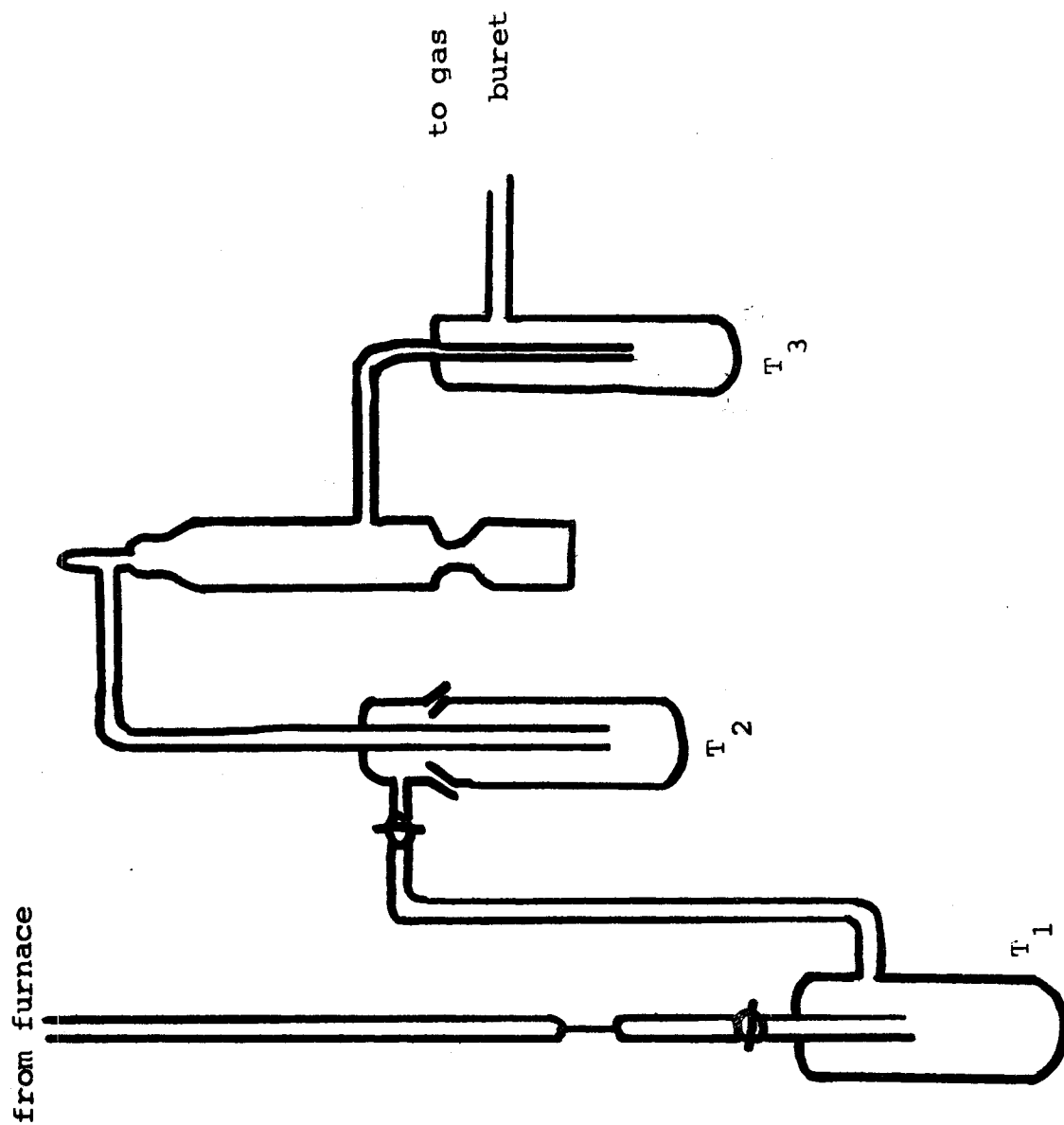


Figure 8: Final trapping system



TABLE II  
 SAMPLE RESULTS FROM VARIATIONS IN NUMBER OF TRAPS AND THEIR TEMPERATURES

| Run    | Trap Temperatures     |                       |                       | % of Butane<br>In Gas Sample | $k_{g-1}$<br>(sec. ) | $k_{m-1}$<br>(sec. ) |
|--------|-----------------------|-----------------------|-----------------------|------------------------------|----------------------|----------------------|
|        | $T_1$ ( $^{\circ}$ C) | $T_2$ ( $^{\circ}$ C) | $T_3$ ( $^{\circ}$ C) |                              |                      |                      |
| Hg 154 | *                     | -80                   | -80                   | 30.45                        | 0.38                 | 2.03                 |
| Hg 156 | *                     | -80                   | -80                   | 11.80                        | 0.21                 | 1.55                 |
| Hg 157 | *                     | -80                   | -196                  | 57.60                        | 0.29                 | 0.67                 |
| Hg 159 | *                     | -80                   | -196                  | 28.40                        | 0.28                 | 1.22                 |
| Hg 161 | *                     | -80                   | -196                  | 58.40                        | 0.57                 | 1.27                 |
| Hg 162 | *                     | -80                   | -196                  | 66.00                        | 1.18                 | 1.10                 |
| Hg 169 | -22                   | -80                   | -80                   | 61.40                        | 1.14                 | 1.27                 |
| Hg 175 | -22                   | -80                   | -80                   | 64.25                        | 0.64                 | 1.69                 |
| Hg 181 | -40                   | -80                   | -80                   | 57.00                        | 0.57                 | 1.37                 |
| Hg 184 | -60                   | -80                   | -80                   | 71.10                        | 1.36                 | 1.84                 |
| Hg 185 | -65                   | -80                   | -80                   | 69.80                        | 1.19                 | 1.61                 |
| Hg 187 | -70                   | -80                   | -80                   | 63.50                        | 0.82                 | 2.49                 |

\*  $T_1$  not yet incorporated into system

were general trends in the results which pointed to the probability that the butane was being trapped in the solution and being lost when removed from the system and warmed to room temperature.

During the initial work, the liquid sample was usually warmed up to at least room temperature before being stored and analyzed. Under these conditions, some of the butane trapped in the toluene would escape and not be seen on the gas chromatograph. Consequently, great care was taken in order to ensure that the liquid sample did not warm up beyond  $-5^{\circ}\text{C}$  (the boiling point of butane being  $-0.5^{\circ}\text{C}$ ). These samples were analyzed immediately to avoid any butane loss.

In maintaining the liquid sample at or below  $-5^{\circ}\text{C}$  during the collection, great care had to be taken in order to ensure that some of the residual alkyl was not lost. At  $-80^{\circ}\text{C}$  (the initial temperature of the liquid in  $T_2$ ), the alkyl is a white solid. This solid had a tendency to adhere to the walls and the stem of the trap. Therefore, after the entire liquid sample had been distilled into  $T_2$  from  $T_1$ , the bath on  $T_2$  was lowered just enough so that all the products in the trap would distill down to the bottom of the trap. Once the upper portion of the trap (above the liquid) appeared to be devoid of any coating, the acetone and dry ice bath was replaced with an ice and salt water bath at  $-10^{\circ}\text{C}$ . This was allowed to remain around the trap for at least 15 minutes in order to ensure that all the liquid in the trap had reached

the same temperature as the bath. If the liquid is at too low a temperature when removed from the system, some of the residual alkyl will not be in solution. The values obtained on the basis of product analysis for these latter runs agreed closely with those obtained from residual alkyl analysis (Table III). Table IV shows the trap conditions used for all runs.

#### Surface Effects

In order to check for any surface effects, a vessel packed with quartz rods was used. This vessel had a volume of 117 cc. as compared to the unpacked vessel used which had a volume of 165.cc.. This increased the surface to volume ratio from 1.25 to  $21.2 \frac{\text{cm.}^2}{\text{cc.}}$ , which corresponds to a 17 fold increase in the surface to volume ratio.

As shown in Table V, the rate constants in the packed vessel varied from about 20% to 45% above those in the unpacked vessel. This indicates that the reaction in the unpacked vessel is essentially homogeneous (probably better than 97%).

#### Effect of Contact Time

There was no contact time effect observed where contact times were varied from 0.37 to 2.47 sec. as indicated by Table VI. These contact times give limits on the contact time to pressure ratio of 0.78 to 3.82, where the contact

TABLE III

## RESULTS FROM RUNS USING FINAL TECHNIQUE

| Run    | Gaseous moles $\times 10^{-4}$ | Butane Collected<br>Liquid moles $\times 10^{-4}$ | $k_g^{-1}$<br>(sec.) | $k_m^{-1}$<br>(sec.) |
|--------|--------------------------------|---|----------------------|----------------------|
| Hg 199 | 1.1242                         | 0.2080  | 0.71                 | 0.71                 |
| Hg 200 | 3.4897                         | 0.9950  | 1.03                 | 1.14                 |
| Hg 201 | 2.1488                         | 0.4925  | 1.34                 | 1.47                 |
| Hg 216 | 0.3719                         | 0.2920  | 0.24                 | 0.25                 |
| Hg 220 | 0.1240                         | 0.2493  | 0.13                 | 0.14                 |
| Hg 221 | 1.6522                         | 0.7140  | 0.67                 | 0.72                 |

TABLE IV  
TRAP CONDITIONS USED FOR ALL RUNS

| Runs<br>(inclusive)  | Trap Temperatures            |                              |                              |
|----------------------|------------------------------|------------------------------|------------------------------|
|                      | $T_1$ ( $^{\circ}\text{C}$ ) | $T_2$ ( $^{\circ}\text{C}$ ) | $T_3$ ( $^{\circ}\text{C}$ ) |
| Hg 54 to Hg 154      | *                            | -80                          | -80                          |
| Hg 156               | *                            | -80                          | -80                          |
| Hg 155               | *                            | -80                          | -196                         |
| Hg 157 to Hg 159     | *                            | -80                          | -196                         |
| ** Hg 161 & Hg 162   | *                            | -80                          | -196                         |
| Hg 167 & Hg 170      | -22                          | -80                          | -196                         |
| Hg 169 & Hg 175      | -30                          | -80                          | -196                         |
| Hg 181               | -40                          | -80                          | -80                          |
| Hg 184               | -60                          | -80                          | -80                          |
| Hg 185               | -65                          | -80                          | -80                          |
| Hg 187               | -70                          | -80                          | -80                          |
| Hg 188 to Hg 191     | -60                          | -80                          | -80                          |
| *** Hg 192 to Hg 222 | -60                          | -80                          | -196                         |

\*  $T_1$  not yet incorporated into the system

\*\*  $T_2$  warmed to  $-50^{\circ}\text{C}$  after the run

\*\*\* Liquid analysis done for butane

TABLE V  
SURFACE EFFECTS

| Run      | Temp.<br>(°K) | k<br>m <sup>-1</sup><br>(sec. ) |
|----------|---------------|---------------------------------|
| * Hg 122 | 643.56        | 0.83                            |
| Hg 199   | 643.31        | 0.71                            |
| * Hg 121 | 630.66        | 0.46                            |
| Hg 66    | 629.97        | 0.30                            |
| Hg 67    | 629.66        | 0.34                            |
| Hg 114   | 610.56        | 0.10                            |
| * Hg 118 | 609.96        | 0.15                            |
| * Hg 119 | 609.28        | 0.12                            |
| Hg 109   | 608.66        | 0.09                            |

\* Runs done using the packed vessel

TABLE VI  
CONTACT TIME EFFECTS

| Run    | Temp.<br>(°K) | $t_c$<br>(sec.) | $k_m^{-1}$<br>(sec.) |
|--------|---------------|-----------------|----------------------|
| Hg 114 | 610.56        | 0.37            | 0.10                 |
| Hg 106 | 612.16        | 1.21            | 0.12                 |
| Hg 109 | 608.66        | 2.43            | 0.09                 |
| Hg 105 | 635.16        | 0.88            | 0.43*                |
| Hg 62  | 640.41        | 1.67            | 0.56                 |
| Hg 63  | 639.91        | 1.70            | 0.50                 |
| Hg 61  | 640.41        | 1.73            | 0.53                 |

\* Corrected to 640.0 K,  $k_m^{-1}$  is 0.52 sec.

time is in sec. and the pressure is in cm.. The lack of any observed effect on  $k$  is in accordance with the predictions of Mulcahy and Pethard (13).

#### Pressure Effects

Pressures used varied from 1 mm. to 7.8 mm. and were found to have no effect on the rate constants obtained (Table VII). Higher pressures were not used because of the low vapour pressure of diethylmercury. Heating the alkyl above  $55^{\circ}\text{C}$  caused slight decomposition in the finger during the run. In order to avoid this, the alkyl was not heated higher than  $55^{\circ}\text{C}$  which corresponds to a vapour pressure of about 15.0 mm.. Even though higher pressures were not checked, there is no reason to expect any pressure effect.

#### Ratio and Concentration Effects

In order to ensure that the decomposition was first order, the initial concentration of the alkyl was varied at a given temperature while the toluene pressure was kept more or less constant. Table VIII lists various runs where the initial concentration of the alkyl varies from  $0.811 \times 10^{-9}$  to  $6.96 \times 10^{-9}$  moles/cc.. This data indicates that the initial alkyl concentration has no appreciable effect on  $k$ , the rate constant. It can then be said that the decomposition is a first order reaction within the limits of experimental error.

In the majority of runs, the ethane to ethylene ratio



TABLE VII  
PRESSURE EFFECTS

| Run    | Temp.<br>(°K) | Pressure<br>(Atm. x 10 <sup>-2</sup> ) | k <sub>m</sub> <sup>-1</sup><br>(sec. ) |
|--------|---------------|--|---|
| Hg 106 | 612.16        | 4.62                                   | 0.12                                    |
| Hg 117 | 612.56        | 1.04                                   | 0.11                                    |
| Hg 54  | 617.48        | 7.18                                   | 0.15                                    |
| Hg 220 | 617.56        | 4.67                                   | 0.14                                    |
| Hg 196 | 616.16        | 4.28                                   | 0.15                                    |
| Hg 157 | 645.16        | 9.11                                   | 0.67                                    |
| Hg 199 | 643.31        | 6.86                                   | 0.71                                    |
| Hg 221 | 645.41        | 5.82                                   | 0.72                                    |

TABLE VIII

EFFECT OF INITIAL ALKYL CONCENTRATION ON RATE CONSTANTS

| Run    | Temp.<br>(°K) | Initial alkyl<br>Concentration<br>(moles/cc. x 10 <sup>-9</sup> ) | k <sub>m -1</sub><br>(sec. <sup>-1</sup> ) |
|--------|---------------|---|--|
| Hg 191 | 656.81        | 1.59  | 1.43                                       |
| Hg 103 | 655.91        | 2.75  | 1.44                                       |
| Hg 59  | 656.66        | 2.98  | 1.43                                       |
| Hg 71  | 661.41        | 6.96  | 1.50                                       |
| Hg 72  | 659.66        | 5.45  | 1.58                                       |
| Hg 156 | 658.76        | 0.86  | 1.55                                       |

was between 1.61 to 2.97. As discussed in a previous section, approximately 10% of the ethylene produced could come from ethyl radical decomposition. Therefore, if no ethane is formed by abstraction from toluene by ethyl radicals, the ethane to ethylene ratio should be 0.9 to 1.0. At low ratios of toluene to alkyl (toluene pressure being approximately constant), this ethane to ethylene ratio should be approached, and at high toluene to alkyl ratios, the ethane to ethylene ratio should increase. These trends are generally confirmed by the results listed in Table IX. However, runs 118 to 122 inclusive were the packed vessel runs where the added surface probably accelerated the ethylene decomposition to an extent where more than 10% of the ethylene produced could be attributed to ethyl radical decomposition. Run 118 shows even a greater effect because it was the first run done after the packed vessel had been placed into the the system and the surface of the packed vessel was probably not yet conditioned. The other few runs, 105, 117, 106, 114, and 109, where the ratio was unexpectedly low, were runs where different capillaries had been placed into the system. The furnace had therefore been exposed and its surface was probably not yet reconditioned. These were the only two conditions under which these unexpected deviations occurred.

Arrhenius Parameters for  $k_a/k_r^{1/2}$

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An Arrhenius plot was made of  $k_a/k_r^{1/2}$  (Figure 9) and

TABLE IX  
 VARIATIONS IN THE ETHANE TO ETHYLENE RATIO

| Approximate<br>Temp.<br>Range | Runs   | <u>Toluene</u><br><u>Alkyl</u><br>(molar ratio) | <u>Ethane</u><br><u>Ethylene</u><br>(molar ratio) |
|-------------------------------|--------|---|---|
| 673                           | Hg 154 | 208/1   | 1.96/1  |
| to                            | Hg 155 | 176/1   | 2.42/1  |
| 667                           | Hg 187 | 109/1   | 2.09/1  |
|                               | Hg 190 | 63/1  | 2.13/1  |
| 663                           | Hg 202 | 94/1  | 2.34/1  |
| to                            | Hg 185 | 72/1  | 2.03/1  |
| 659                           | Hg 184 | 63/1  | 1.91/1  |
|                               | Hg 175 | 62/1  | 1.87/1  |
|                               | Hg 181 | 61/1  | 1.89/1  |
|                               | Hg 72  | 48/1  | 1.73/1  |
|                               | Hg 71  | 26/1  | 1.61/1  |
| 659                           | Hg 156 | 183/1   | 2.33/1  |
| to                            | Hg 191 | 142/1   | 2.50/1  |
| 656                           | Hg 201 | 131/1   | 2.39/1  |
|                               | Hg 58  | 61/1  | 2.00/1  |
|                               | Hg 103 | 57/1  | 1.75/1  |
|                               | Hg 192 | 57/1  | 1.74/1  |
|                               | Hg 59  | 52/1  | 1.93/1  |

TABLE IX  
(Continued)

| Approximate<br>Temp.<br>Range | Runs   | <u>Toluene</u><br><u>Alkyl</u><br>(molar ratio) | <u>Ethane</u><br><u>Ethylene</u><br>(molar ratio) |
|-------------------------------|--------|---|---|
| 654                           | Hg 159 | 223/1   | 2.87/1  |
| to                            | Hg 162 | 183/1   | 2.71/1  |
| 652                           | Hg 161 | 170/1   | 2.46/1  |
|                               | Hg 167 | 81/1  | 2.19/1  |
|                               | Hg 222 | 74/1  | 2.02/1  |
|                               | Hg 169 | 73/1  | 1.84/1  |
|                               | Hg 189 | 64/1  | 2.05/1  |
|                               | Hg 102 | 58/1  | 1.74/1  |
|                               | Hg 170 | 54/1  | 1.93/1  |
| 650                           | Hg 158 | 184/1   | 2.65/1  |
| to                            | Hg 221 | 92/1  | 2.21/1  |
| 645                           | Hg 200 | 86/1  | 2.24/1  |
|                               | Hg 64  | 43/1  | 1.88/1  |
|                               | Hg 65  | 36/1  | 1.80/1  |
| 645                           | Hg 199 | 106/1   | 2.27/1  |
| to                            | Hg 62  | 55/1  | 1.99/1  |
| 640                           | Hg 63  | 49/1  | 1.95/1  |
|                               | Hg 61  | 48/1  | 1.99/1  |
|                               | Hg 122 | 32/1  | 0.80/1  |

TABLE IX  
(Continued)

| Approximate<br>Temp.<br>Range | Runs   | <u>Toluene</u><br><u>Alkyl</u><br>(molar ratio) | <u>Ethane</u><br><u>Ethylene</u><br>(molar ratio) |
|-------------------------------|--------|---|---|
| 635                           | Hg 198 | 143/1   | 2.52/1  |
| to                            | Hg 105 | 58/1  | 0.88/1  |
| 630                           | Hg 66  | 57/1  | 2.09/1  |
|                               | Hg 218 | 50/1  | 2.00/1  |
|                               | Hg 67  | 34/1  | 1.84/1  |
|                               | Hg 121 | 32/1  | 0.77/1  |
| 627                           | Hg 216 | 112/1   | 2.54/1  |
| to                            | Hg 194 | 94/1  | 2.15/1  |
| 623                           |        |   |   |
| 617                           | Hg 220 | 146/1   | 2.34/1  |
| to                            | Hg 54  | 76/1  | 2.10/1  |
| 612                           | Hg 196 | 63/1  | 2.10/1  |
|                               | Hg 106 | 38/1  | 1.00/1  |
|                               | Hg 117 | 34/1  | 0.90/1  |
| 610                           | Hg 114 | 71/1  | 1.08/1  |
| to                            | Hg 119 | 69/1  | 1.03/1  |
| 609                           | Hg 118 | 45/1  | 1.04/1  |

TABLE IX  
(Continued)

| Approximate<br>Temp.<br>Range | Runs   | <u>Toluene</u><br><u>Alkyl</u><br>(molar ratio) | <u>Ethane</u><br><u>Ethylene</u><br>(molar ratio) |
|-------------------------------|--------|---|---|
| 609                           | Hg 219 | 187/1   | 2.15/1  |
| to                            | Hg 95  | 129/1   | 2.14/1  |
| 602                           | Hg 90  | 67/1  | 2.43/1  |
|                               | Hg 91  | 52/1  | 2.35/1  |
|                               | Hg 93  | 44/1  | 2.32/1  |
|                               | Hg 109 | 24/1  | 0.92/1  |

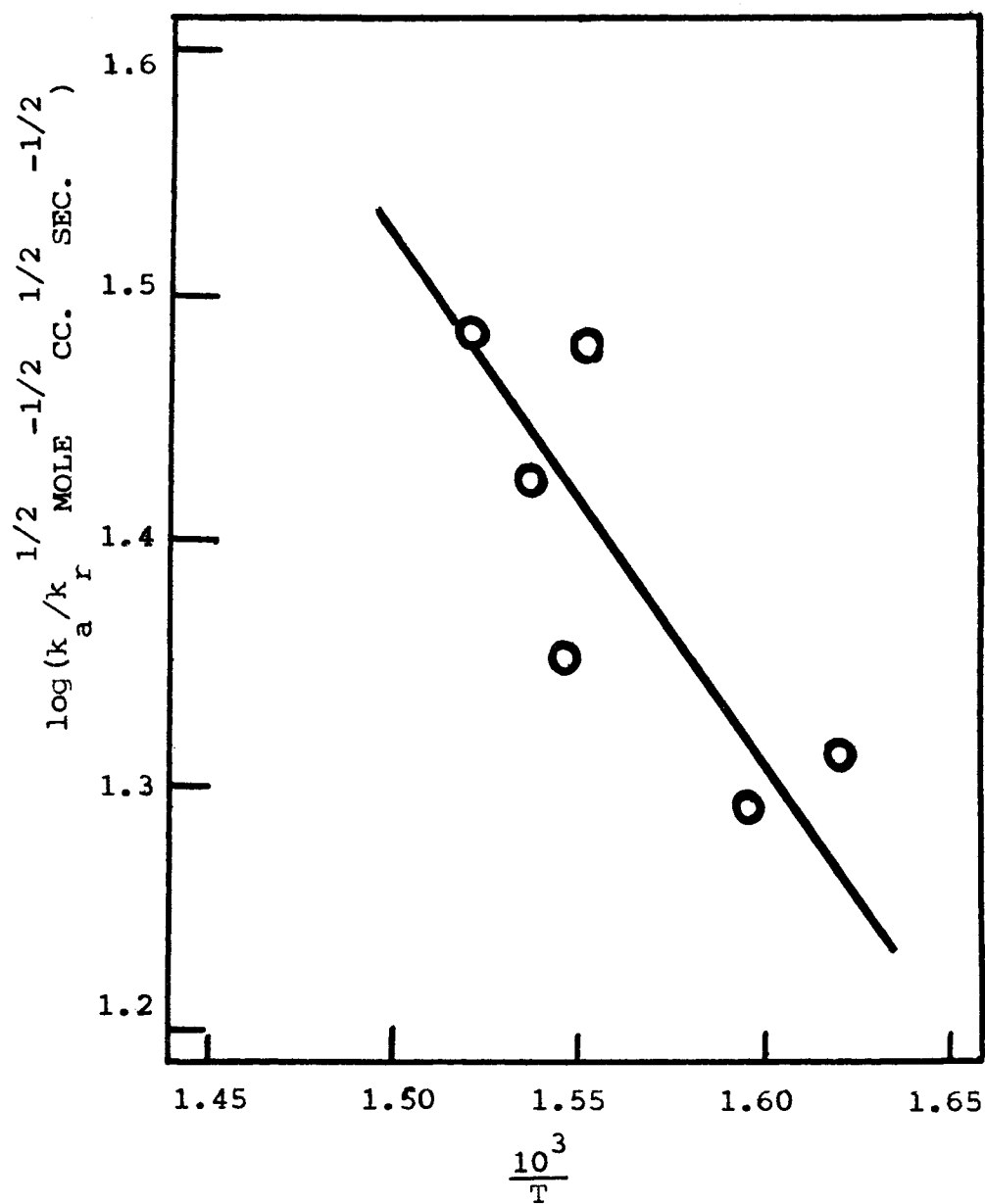


Figure 9: Arrhenius plot for the rate of abstraction of hydrogen from toluene by ethyl radicals.



Table X lists the values obtained. Only six points were available for this plot because of the difficulty encountered (for the major part of the study) in recovering all the butane produced. These last few runs were the runs to which the final technique discussed in the previous section was used. With only six runs, it is difficult to get an accurate line on the Arrhenius plot. These ratios are very easily affected and consequently the log of the ratios are scattered. However, using the line of best fit, the expression for the rate constant for the abstraction reaction can be written as

$$k_a \cdot 10^{11.0} e^{(-8,700/RT)} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

The log A value is based on the A value of  $2.0 \times 10^{13}$  for the recombination of ethyl radicals obtained by Shepp and Kutschke. (7).

The activation energy of 8.7 kcal/mole and the log A value of 11.0 are credible when compared to previous studies on abstraction by methyl radicals. The log A ( $\text{mole}^{-1} \text{ cc. sec.}^{-1}$ ) value obtained by Dunlop was 10.77 (16) and that obtained by Kominar was 11.04 (14). The activation energies obtained were slightly lower than those obtained in this study. Dunlop determined an activation energy of 7.4 kcal./mole and Kominar determined the value to be 7.89 kcal./mole. A slight increase in activation energy for ethyl radical abstraction of hydrogen from toluene can be expected. Considering, the limited number of  $k_a/k_r^{1/2}$  values available and the limited temperature range,

TABLE X

RESULTS ON THE RELATIVE RATES OF ABSTRACTION AND RECOMBINATION

| Run    | Temp. (°K) | $\frac{10^3}{T(^{\circ}\text{K})}$ | $k_a/k_r^{1/2}$ | $\log (k_a/k_r^{1/2})$ |
|--------|------------|------------------------------------|-----------------|------------------------|
| Hg 201 | 657.66     | 1.521                              | 30.85           | 1.49                   |
| Hg 200 | 650.41     | 1.537                              | 27.14           | 1.43                   |
| Hg 221 | 645.41     | 1.549                              | 22.47           | 1.35                   |
| Hg 199 | 643.31     | 1.554                              | 29.75           | 1.47                   |
| Hg 216 | 626.66     | 1.596                              | 19.61           | 1.29                   |
| Hg 220 | 617.56     | 1.619                              | 21.53           | 1.33                   |

the values obtained seem very reasonable.

#### Arrhenius Parameters for the Decomposition of Diethylmercury

The decomposition of diethylmercury was studied over a temperature range of 328 °C to 400 °C and a per cent decomposition of 10% to 99%. The Arrhenius plot, based on residual alkyl analysis is shown in Fig. 10. The line drawn through these points may be represented by

$$\log k = 15.4 - (45,700/2.303RT).$$

A comparison of the results of this study with a static system study (3) and work done in an N<sub>2</sub> flow system (1) is shown in Figure 11. The static system study was done over a temperature range of 223 °C to 293 °C. The Arrhenius line for this study is given by

$$\log k = 14.43 - (41,900/2.303RT).$$

The N<sub>2</sub> carrier flow system was done over a temperature range of 320 °C to 420 °C. The Arrhenius line can be represented by

$$\log k = 14.1 - (42,500/2.303RT).$$

Extrapolation of the line obtained from the static system study provides a basis for direct comparison of the k values from these two previous studies and from this study.

Not much reliance can be placed on the Arrhenius para-

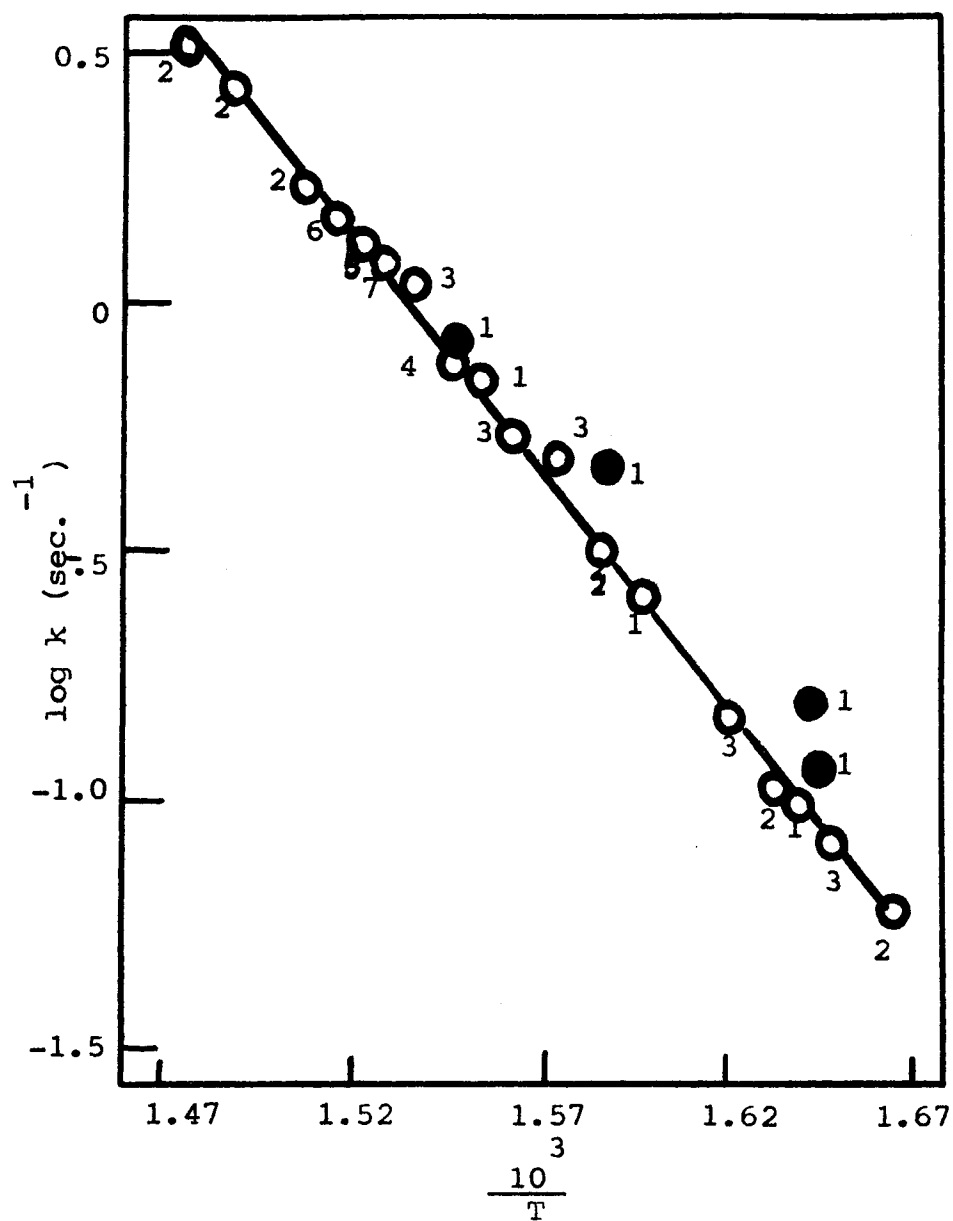


Figure 10: Arrhenius plot for the decomposition of diethylmercury based on liquid analysis. Numbers indicate number of runs averaged.

● packed vessel runs  
○ unpacked vessel runs

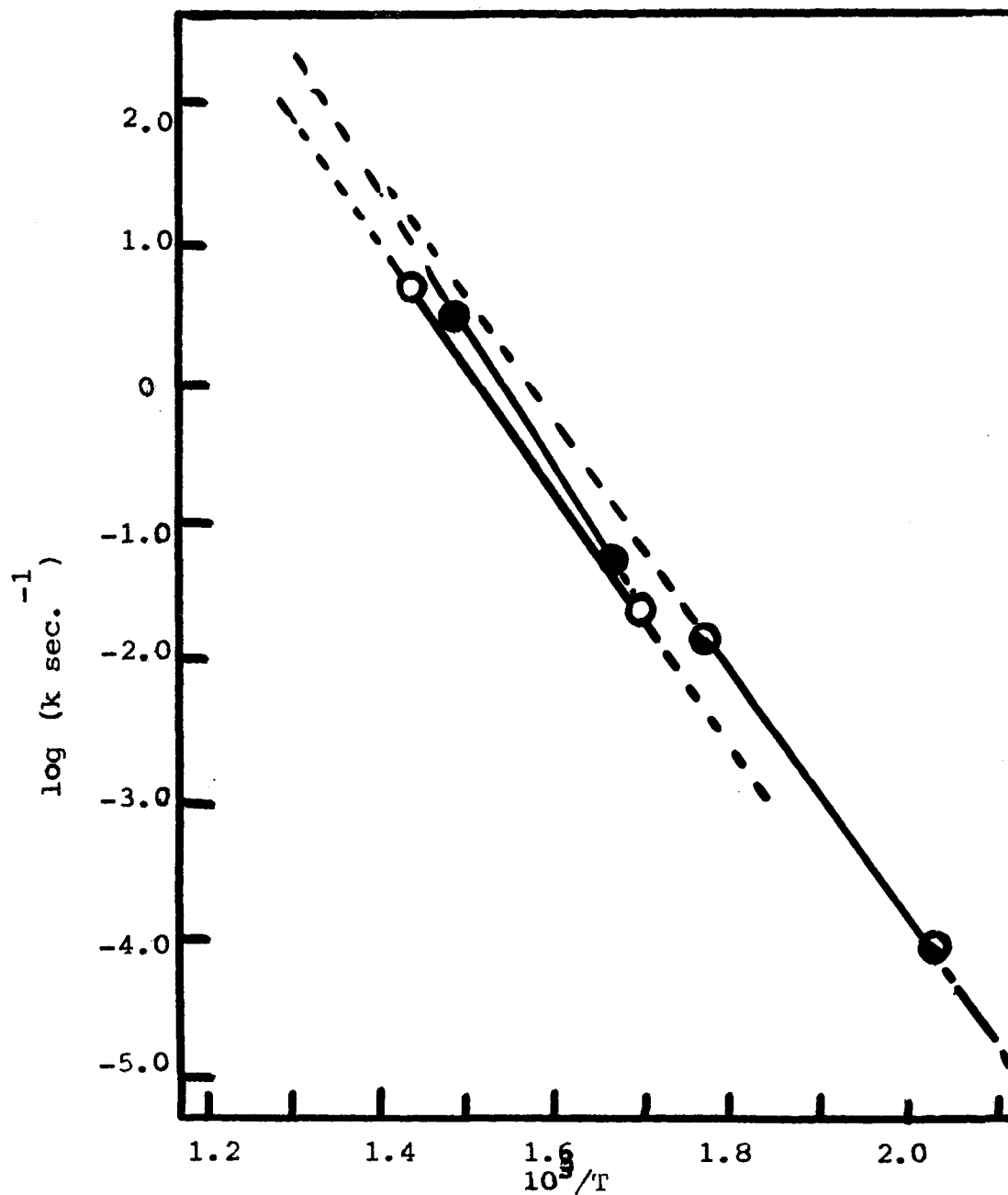


Figure 11: Arrhenius plot for the decomposition of diethylmercury. Solid lines indicate the temperature range studied.

- $N_2$  flow system study
- ◐ static system study
- this study

meters determined in the static study. Very little information is available on this study as its results appear only in Dissertation Abstracts. These investigators report a surface catalyzed decomposition with an activation energy of 22.1 kcal./mole. There was only a slight surface effect observed in this study. This led to the possibility that their reaction vessel was probably not treated properly before use. However, there is no definite information given with regard to this.

There is also some doubt as to the reliability of the parameters obtained from the study done in the  $N_2$  carrier system because of the extremely low contact times used (.1 to .3 sec.) with total pressures of  $10 \pm 1$  mm.. As discussed previously, the ratio of the contact time (sec.) to pressure (cm.) must be greater than 0.5 in order to achieve an extent of thermal equilibrium that will give an accuracy of about 10%. Also, in order to avoid problems due to diffusion, this ratio should also be less than 3 up to 50% conversion and less than 10 up to 25% conversion.

The ratios used by these investigators varied from .1 to .3 which do not lie within the desired ranges.

Benson and O'Neal have predicted an Arrhenius equation of

$$\log k = 15.5 - (46.5/2.303RT)$$

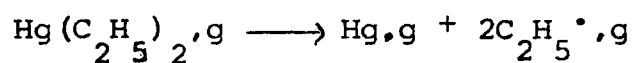
They have arrived at these values on the basis of transition state theory and statistical thermodynamics and claim that earlier studies report Arrhenius parameters that are too low.

The Arrhenius parameters obtained in this study compare favourably with those predicted by Benson and O'Neal (17).

#### Bond Dissociation Energies

Taking  $\Delta H_{f298}^{\circ}(\text{C}_2\text{H}_5\cdot, \text{g}) = 25.7$  kcal./mole, (17), and  $\Delta H_{f298}^{\circ}(\text{Hg}, \text{g}) = 14.7$  kcal./mole, (17), and  $\Delta H_{f298}^{\circ}(\text{Hg}(\text{C}_2\text{H}_5)_2, \text{g}) = 15.9$  kcal./mole, (17), gives  $D_1(\text{C}_2\text{H}_5\text{Hg} - \text{C}_2\text{H}_5) + D_2(\text{C}_2\text{H}_5) = 50.2$  kcal./mole. Equating the value for the activation energy obtained in this study, 45.7 kcal./mole, to  $D_1$  gives  $D_2 = (D_1 + D_2) - D_1 = 50.2 - 45.7 = 4.5$  kcal./mole.

It should be noted however, that actually  $D_1 + D_2$  for the process



is only approximately equal to  $\Delta H_{f298}^{\circ}$  for the above. By definition,  $D_1 + D_2$  should equal  $\Delta H_{00}^{\circ}$  for the process. The  $C_p$  values required to calculate  $\Delta H_{00}^{\circ}$  from  $\Delta H_{298}^{\circ}$  are not available. However,  $\Delta H_{00}^{\circ}$  would be greater than  $\Delta H_{298}^{\circ}$  probably by only 2 kcal./mole.

## BIBLIOGRAPHY

1. H. V. CARTER, E. I. CHAPPELL, and E. WARHURST. J. Chem. Soc., 106 (1956).
2. K. J. IVIN, and E. W. R. STEACIE, Proc. Roy. Soc. A, 208, 25 (1951).
3. W. PASTFIELD. Dissertation Abstracts, 15, 1325 (1958).
4. R. J. KOMINAR, M. G. JACKO, and S. J. PRICE. Can. J. Chem. 45, 575 (1967).
5. A. SHEPP. J. Chem. Phys. 24, 939 (1956).
6. G. B. KISTIAKOWSKY and E. K. ROBERTS. J. Chem. Phys. 21, 1637 (1953).
7. A. SHEPP and K. O. KUTSCHKE. J. Chem. Phys. 26, 1020 (1957).
8. S. G. WHITEWAY and C. R. MASSON. J. Chem. Phys. 25, 233 (1956).
9. P. B. AYSCOUGH. J. Chem. Phys. 24, 944 (1956).
10. M. SZWARC. Proc. Roy. Soc. A 207, 5 (1951).
11. S. J. PRICE. Can. J. Chem. 40, 1310 (1962).
12. J. J. BATTEN. Aust. J. Appl. Sci. 12, 11 (1961).
13. M. F. R. MULCAHY and MARY R. PETHARD. Aust. J. Chem. 16, 527 (1963).
- 13A. M. C. LIN and M. H. BACK. Can. J. Chem. 44, 2357 (1966).
14. R. J. KOMINAR. Ph.D. Dissertation, University of Windsor (1968).
15. S. J. W. PRICE. Ph.D. Dissertation, University of Edinburgh, (1958).
16. A. N. DUNLOP. M.Sc. Thesis, University of Windsor (1968).
17. S. W. BENSON and H. E. O'NEAL. In "Kinetic Data on Gas Phase Unimolecular Reactions" NSRDS - NBS 21, Washington (1970).



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