

THE PHOTOCHEMICAL REACTIONS OF 2,7-DIMETHYLOCTANE

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THE PHOTOCHEMICAL REACTION OF 2,7-DIMETHYLOCTANE

THESIS

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TABLE OF CONTENTS

	Page
LIST OF TABLES	iv
LIST OF ILLUSTRATIONS	v
Chapter	
I. INTRODUCTION	1
II. THE APPARATUS AND PROCEDURE	8
III. EXPERIMENTAL DATA AND RESULTS	12
IV. CONCLUSIONS	18
BIBLIOGRAPHY	20

LIST OF TABLES

Table	Page
1. Physical Constants of the Fractions from the First Run.	14
2. Physical Constants of the Fractions from the Second Run	15

LIST OF ILLUSTRATIONS

Figure	Page
1. Apparatus	9
2. Graph of Pressure Versus Time for Run One. . .	16
3. Graph of Pressure Versus Time for Run Two. . .	17

CHAPTER I

INTRODUCTION

There are three principal ways in which a system receiving radiant energy of a suitable frequency from an outside source may utilize this energy. It may simply convert the absorbed energy into heat; it may itself radiate energy as resonance radiation, fluorescence, or phosphorescence; or the energy may give rise to chemical changes in the system.¹ This latter dissipation of the absorbed energy leads to a photochemical reaction.

As early as the time of Aristotle the importance of light in such processes as the photosynthesis of plants in the presence of chlorophyll and the bleaching of naturally occurring dyes was observed.² It was not until the beginning of the nineteenth century, however, that any qualitative statement of the role which light plays in these reactions was formulated. At this time T. von Grothuss (1817) and later J. W. Draper (1841) proposed what is generally known as the first law of photochemistry, i.e., only radiations which are absorbed by the reacting system are effective in producing

(1) R. O. Griffith and A. McKeown, Photo-processes in Gaseous and Liquid Systems, p. 355.

(2) Ibid., p. 357.

chemical change.³ It does not follow that all absorbed radiation is effective chemically.

A quantitative law governing the interpretation of photo-processes is the law of photochemical equivalence advanced by Albert Einstein in 1912. It states that any molecule or atom activated by light absorbs only one quantum of the light which causes the activation.⁴ The energy acquired by an atom or molecule in absorbing a quantum depends on the frequency of the incident light and is given by Planck's equation

$$E = h\nu$$

where h is Planck's constant equal to 6.624×10^{-27} erg.sec. and ν is the frequency of the light. The energy per mole is

$$E = N h \nu = \frac{N h c}{\lambda}$$

where $N = 6.023 \times 10^{23}$ molecules per mole = Avogadro's number, $c = 2.9977 \times 10^{10}$ cm. per sec. = the velocity of light, and λ is the wavelength of the incident light. Dividing by 4.184×10^{10} to obtain the energy in kcal. per mole,

$$E = \frac{2.859 \times 10^{-3}}{\lambda} \frac{\text{kcal.}}{\text{mole}} .$$

Thus for ultraviolet radiation of $2537 \overset{\circ}{\text{A}}$, $E = 112.8$ kcal. per mole.

The value calculated from thermochemical data and thermal decompositions of hydrocarbons of the energy necessary to

- (3) Samuel Glasstone, Textbook of Physical Chemistry, p. 1155.
 (4) Carl F. Prutton and Samuel H. Maron, Fundamental Principles of Physical Chemistry, p. 764.

produce rupture of the first C-H bond in methane (a primary C-H bond) is 103 kcal. per mole and that for C-C bond cleavage in ethane is 89.5 kcal. per mole.⁵ Further calculations indicate that a primary C-H bond has 2.5 kcal. more energy than a secondary C-H bond, which in turn has 4 kcal. more energy than a tertiary C-H bond.⁶ These results are in agreement with those obtained by Rice who placed the two figures at 1.2 kcal. and 4.0 kcal. respectively.⁷ Therefore, the energy of radiation of 2537 Å is more than sufficient to produce rupture of C-C and C-H bonds in hydrocarbons.

Since hydrocarbons do not themselves absorb radiation of this frequency, it becomes necessary to use a "photosensitizer," that is, a substance which absorbs radiation of the required frequency and is able to transmit the energy received to another molecule through collision with this molecule. In the case of hydrocarbons mercury vapor serves as a suitable photosensitizer.

In previous studies at North Texas State College several relatively low molecular weight hydrocarbons have been subjected to ultraviolet radiation. Gary⁸ and Oliver⁹ irradiated

(5) Norrish, Transactions of the Faraday Society, 30, 103 (1934).

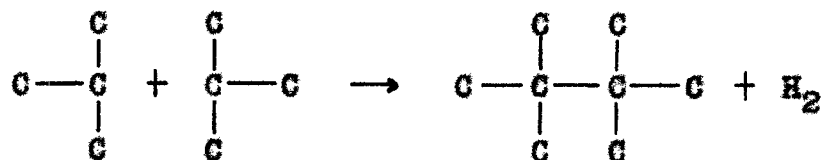
(6) Smith and Taylor, J. Chem. Phys., 7, 390 (1939).

(7) F. O. Rice, J. Am. Chem. Soc., 55, 3035 (1933).

(8) Felice Gary, Mercury Sensitized Photo-Chemical Action on a Mixture of Isobutane and Isobutene, Unpublished M. S. thesis, Dept. of Chem., North Texas State College, August, 1937.

(9) Bob Oliver, The Photo-Alkylation of C Hydrocarbons, Unpublished M. S. thesis, Dept. of Chem., North Texas State College, August, 1942.

mixtures of isobutane and isobutene and found that higher molecular weight hydrocarbons were produced. Stallings¹⁰ found that under similar treatment pure isobutane produced principally 2,2,3,3-tetramethylbutane according to the reaction



with an approximate yield of 7% of the theoretical. Sutton¹¹ irradiated 2,3-dimethylbutane and found that the principal products were C₁₂H₂₆ hydrocarbons. He further determined that C-H rather than C-C bond scission predominated.

Further investigations were made by Walker¹² who treated isopentane with 2537 Å radiation. He isolated 3,3,4,4-tetramethylhexane as the primary product. This result indicates that the reaction involves the loss of a tertiary hydrogen atom from the isopentane with the subsequent recombination of two isopentyl free radicals to form the tetramethylhexane - a reaction analogous to that obtained using isobutane.

- (10) James Stallings, Mercury-Sensitized Photo-Reactions of Isobutane, Unpublished M. S. thesis, Dept. of Chem., North Texas State College, May, 1943.
- (11) Cecil C. Sutton, The Mercury-Sensitized Photo-Reactions of 2,3-Dimethylbutane, Unpublished M. S. thesis, Dept. of Chem., North Texas State College, August, 1947.
- (12) Russell Walker, Photo-Chemical Reactions of Isopentane, Unpublished M. S. thesis, Dept. of Chem., North Texas State College, August, 1945.

Layne¹³ irradiated cyclohexane in the presence of mercury vapor and found that bicyclohexyl was formed. In addition, small amounts of tri- and tetracyclohexyl were tentatively identified and an orange residue, which was presumed to be a cyclohexyl polymer, was observed to remain on the reaction tubes. Substantially the same results were obtained by Farmer and Moore¹⁴ through the thermal decomposition of cyclohexane in the presence of tertiary butyl peroxide, with the exception that in this case a much greater percentage of the orange polymer was formed due to the presence of tertiary butoxy free radicals.

Holland¹⁵ exposed both cumene and methylcyclohexane to 2537 Å radiation and found that no detectable reaction occurred during the cumene runs. A definite reaction was observed with methylcyclohexane which produced unidentified high molecular weight hydrocarbons. Sworski, Hentz, and Burton¹⁶ exposed both cumene and tertiary butylbenzene to ultraviolet radiation and interpreted the results in terms of

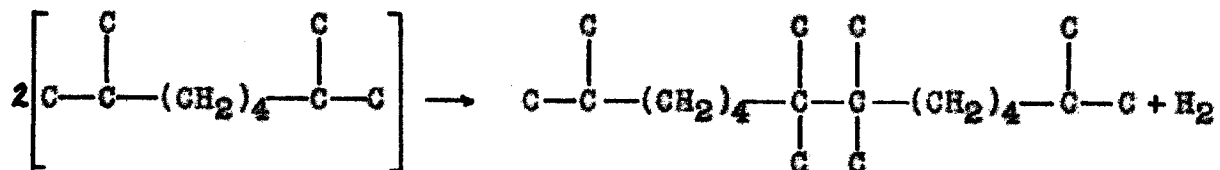
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- (13) Kenneth Layne, The Mercury-Sensitized Photochemical Reactions of Cyclohexane, Unpublished M. S. thesis, Dept. of Chemistry, North Texas State College, August, 1950.
- (14) E. H. Farmer and C. G. Moore, (Brit. Rubber Producers' Research Ass'n, Welwyn Garden City, Engl.), J. Chem. Soc., 131-41 (1951).
- (15) Walter Holland, Cumene and Methylcyclohexane Photochemistry, Unpublished M. S. thesis, Dept. of Chem., North Texas State College, August, 1951.
- (16) Thomas J. Sworski, Robert R. Hentz, and Milton Burton, (Univ. of Notre Dame, Indiana), J. Am. Chem. Soc., 73, 1998-2001 (1951).

hydrogen production by C-H bond cleavage β and γ to the benzene ring and methyl radical production by C-C bond cleavage β to the benzene ring. Extremely low quantum yields of non-condensable gases were reported, 1.3×10^{-4} and 2.4×10^{-4} respectively.

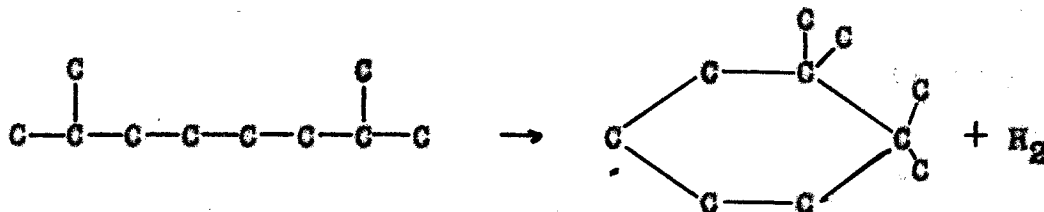
Ivanov, Savinova, and Zhakhovskaya¹⁷ irradiated 2,7-dimethyloctane with ultraviolet light while bubbling oxygen through the liquid at the rate of 5 ml. per minute for 180-200 hours at either 70-5 °C or 85-8 °C. They obtained both the diperoxide $\text{Me}_2\text{CH}(\text{CH}_2)_3\text{CH}(\text{OOH})\text{C}(\text{OOH})\text{Me}_2$, and the monoperoxide, $\text{Me}_2\text{CH}(\text{CH}_2)_4\text{C}(\text{OOH})\text{Me}_2$, after separation and purification of the products.

On the basis of these findings, i.e., the predominance of C-H bond rupture over that of the C-C bond, the relative strengths of primary, secondary, and tertiary C-H bonds as given above, and the observed reactivity of similar hydrocarbons under the influence of mercury sensitized ultraviolet radiation, it is to be expected that 2,7-dimethyloctane would also react to produce higher molecular weight hydrocarbons through the cleavage of a tertiary C-H bond and recombination of the dimethyloctyl free radicals thus formed. The principal products of this reaction is expected to be 2,7,7,8,8,13-hexamethyltetradecane according to the reaction

(17) K. I. Ivanov, V. K. Savinova, and V. P. Zhakhovskaya, Doklady Akad. Nauk S.S.S.R., 59, 703-6 (1948).



Other possible products are tetramethylcyclohexane formed by cyclization of the octyl free radical as shown below.



Mono-, di-, or trimethylcyclohexane could possibly be formed by this cyclization with the subsequent splitting out of methyl radicals. Other cosanes and possibly some contanes can be expected due to the recombination of two or more of the octyl radicals. In addition, if any C-C bond scission occurs, a variety of hexanes and heptanes are possible products.

CHAPTER II

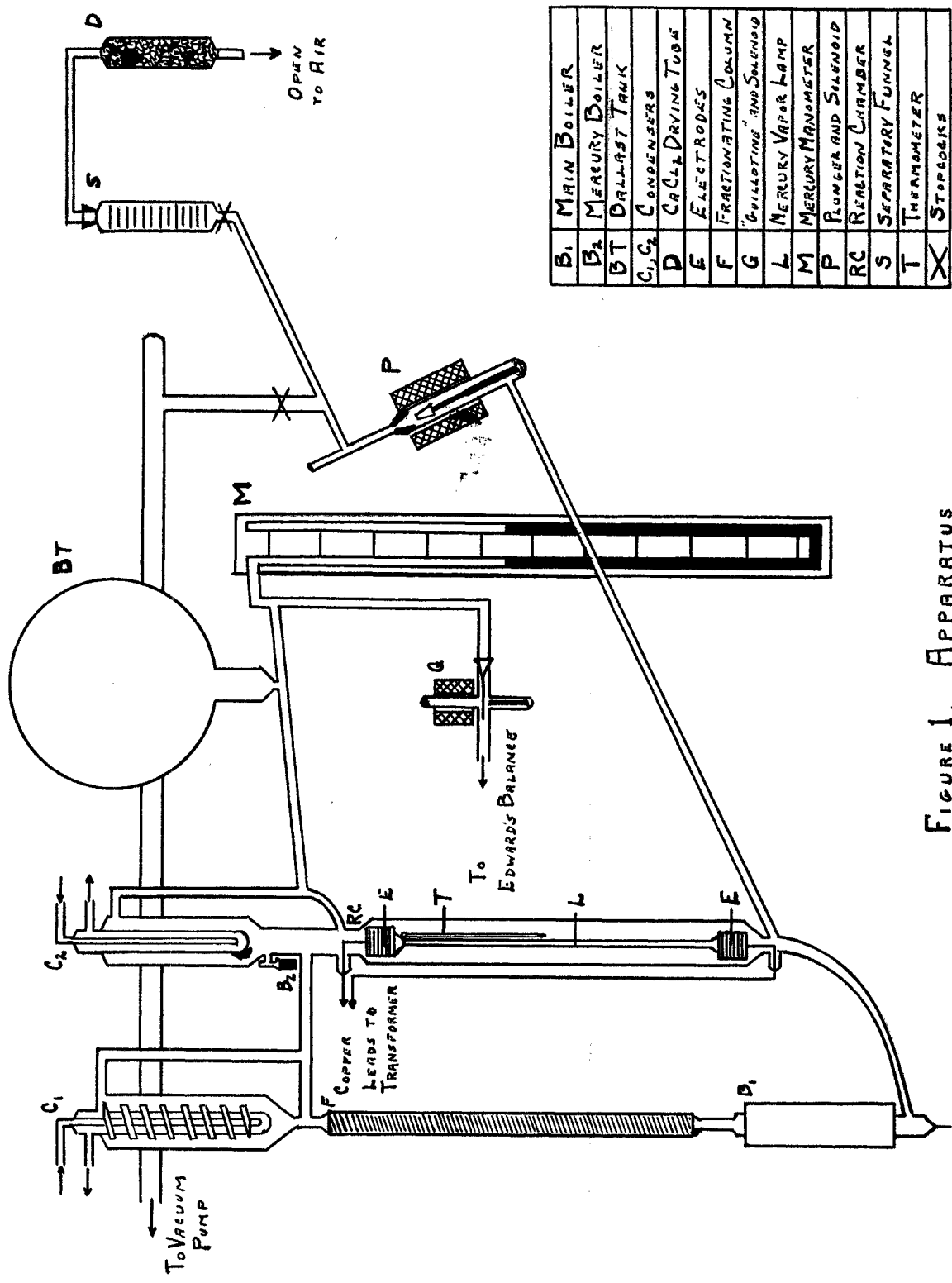
THE APPARATUS AND PROCEDURE

It was decided that in these experiments a smaller, more compact system was needed than that used earlier by Layne¹ and Holland² in their investigations of the mercury sensitized photoreactions of cyclohexane and methylcyclohexane. In addition, it was necessary to devise a method to completely isolate the system from the atmosphere during the runs. This was accomplished by eliminating all ground glass joints and stopcocks from the portion of the apparatus to be isolated.

The apparatus used is shown diagrammatically in Figure 1. It consisted principally of a charge container, S; two plunger and solenoid systems, P which separates the charge container from the rest of the apparatus, and G which leads to an Edwards gas density balance; a mercury manometer, M; a three liter ballast tank, BF; two condensers, C₁, C₂; a mercury boiler, B₂; a fractionating column, F; a main boiler, B₁; one thermometer, T; one reaction chamber, RC; one Westinghouse Sterilamp WL 782-10, L, powered by 1000 volt (open

(1) R. O. Griffith and A. McKeown, Photo-processes in Gaseous and Liquid Systems, p. 355.

(2) Ibid., p. 357.



B1	MAIN BOILER
B2	MERCURY BOILER
BT	DALLAST TANK
C1, C2	CONDENSERS
D	CaCl2 DRYING TUBES
E	ELECTRODES
F	FRACTIONATING COLUMN
G	"GILLIOT'S" AND SOLENOID
L	MERCURY VAPOR LAMP
M	MERCURY MANOMETER
P	PLUNGER AND SOLENOID
RC	REACTION CHAMBER
S	SEPARATOR FUNNEL
T	THERMOMETER
X	STOPCOCKS

FIGURE 1. APPARATUS

secondary coltage) Westinghouse Sterilamp transformer, Style ST-70; and two stopcocks.

The fractionating column and the mercury boiler were each wrapped with No. 22 B & S nichrome resistance wire to heat them during the runs. Both were powered with a 135 volt (maximum)-7.5 ampere powerstat as was heater on the main boiler. Both condensers C_1 and C_2 were water cooled.

The apparatus was checked for leaks in advance of each run by evacuating to 2 mm. pressure and noting the pressure increase over a period of approximately 5 hours. It was required that no pressure increase be observed. At the beginning of each run the system was evacuated to 2 mm. pressure and a known volume of 2,7-dimethyloctane introduced into the system from the separatory funnel, S. The ground glass joint at P was then closed by the action of a solenoid on an iron core imbedded in the plunger. The portion of the system between S and P was re-evacuated and the line between them sealed with a portable oxygen-natural gas torch. The water supply to the condensers C_1 and C_2 was turned on, and the heaters on the main boiler, the mercury boiler, and the fractionating column were brought up to operating temperature. These temperatures were adjusted in such a way as to produce a unidirectional flow of the octane vapor up through the fractionating column, past the condensers, and down through the reaction chamber and back into the main boiler. The ultra-violet lamp was then turned on. As the runs proceeded, the

temperatures of the boilers and the fractionating column were raised to maintain this unidirectional flow.

The progress of the reaction was followed by recording the manometer pressure and the temperature of the Sterilamp at intervals during the run. The runs were stopped when thermal decomposition could be observed. The indications of thermal decomposition are a marked darkening of the material in the main boiler and a sharp rise in the rate of manometer pressure increase.

When reaction was stopped the permanent gases in the system were removed and their molecular weight measured by breaking the capillary contained in the guillotine with a solenoid acting on an iron plunger and allowing these gases to pass through an acetone-dry ice freeze-out trap and into the Edwards balance. The liquid product was removed by breaking the tip on the main boiler and catching it in a flask. The products were separated by fractionation in a Podbielniak Series 3300 Semi-Automatic Micro High Temperature Distillation Analyzer and their physical constants determined.

CHAPTER III

EXPERIMENTAL DATA AND RESULTS

Two runs were made in the apparatus as described in the previous chapter. At the start of the first run, the system was charged with 107 ml. of 2,7-dimethyloctane. It was estimated that during the charging process approximately 1.5 cm. of mercury of air leaked into the system. This run was allowed to continue for seven hours and an absolute pressure of 1400 mm. of mercury developed during this time. For the second run, 40 ml. of the charge stock was introduced into the system and irradiated for 94 hours. An absolute pressure of 113.8 mm. was developed during this run. At the conclusion of the second run it was noted that both the sterilamp and the reaction tube were lightly coated with a deep red solid material which was presumed to be polymeric.

The 2,7-dimethyloctane used in the first run was obtained from the Eastman Kodak Company, Rochester, New York, and was used with no further purification. The material charged into the system for the second run was recovered by fractionation of the product from the first run. The physical constants of this fraction were boiling range, 156.5-156.9°C at 743.5 mm.; d_4^{20} , 0.7242; n_D^{21} , 1.4074. These data check the constants recorded in the literature.¹

(1) G. Egloff, Physical Constants of the Hydro-Carbons, I, 71.

The molecular weight of the permanent gases produced during the first and second runs were determined to be 17.64 and 2.499 respectively. This indicates that perhaps a mixture of hydrocarbon gases and hydrogen was formed in the first run while hydrogen was almost exclusively the product of the second run.

At the conclusion of each of the runs the liquid products were removed, fractionated, and their physical constants determined; the boiling ranges of the fractions refractive indices with a Bausch and Lomb Abbe refractometer, and densities with a pycnometer. The refractivity intercepts were calculated according to the formula derived by Kurtz and Ward.²

$$\text{Refractivity intercept} = n - d/2$$

where d is the density and n the refractive index. The refractivity intercept of a hydrocarbon is characteristic of the homologous series to which it belongs. The average value for the paraffins is 1.0462, for the saturated monocyclics, 1.0396, the saturated polycyclics, 1.0285, and the aromatics, 1.0629.

The physical constants of the fractions from Run One are given in Table 1.

(2) S. S. Kurtz and A. L. Ward, "The Refractivity Intercept and the Specific Refraction Equation of Newton," J. Franklin Institute (1936), pp. 222, 565.

TABLE 1
 PHYSICAL CONSTANTS OF THE FRACTIONS FROM THE FIRST RUN

Fractions	Boiling Range @ 760 mm.	25 d_4	20 n_4	Refractivity Intercept
1	71.3- 73.3	.7472	1.3984	1.0248
2	128.1-128.6	.7236	1.4072	1.0454
3*	155.6-178.8	.7615	1.4189	1.03815
4	152.5-154.3	.7258	1.4071	1.0442
5	154.3-154.7	.7242	1.4072	1.0451
6	154.7-155.0	.7225	1.4078	1.0465
7	155.6-155.5	.7187	1.4075	1.0481
8	156.5-156.9	.7179	1.4074	1.0484
9	156.2-156.7	.7183	1.4077	1.4085
	@ 21 mm.			
10	56.0- 56.5	.7164	1.4080	1.4098
11	94.8- 98.4	1.4307
12	106.7-.....	1.4330
13**	148.7-150.3	.8835	1.4343	0.9926
14**	170.69497	1.4528	0.9785
15**	205.2-205.7	1.0183	1.4862	0.9771

* Contains "chaser," decalin.

** Contains "chaser," dibutyl phthalate.

Table 2 lists the physical constants of the fractions from the second run.

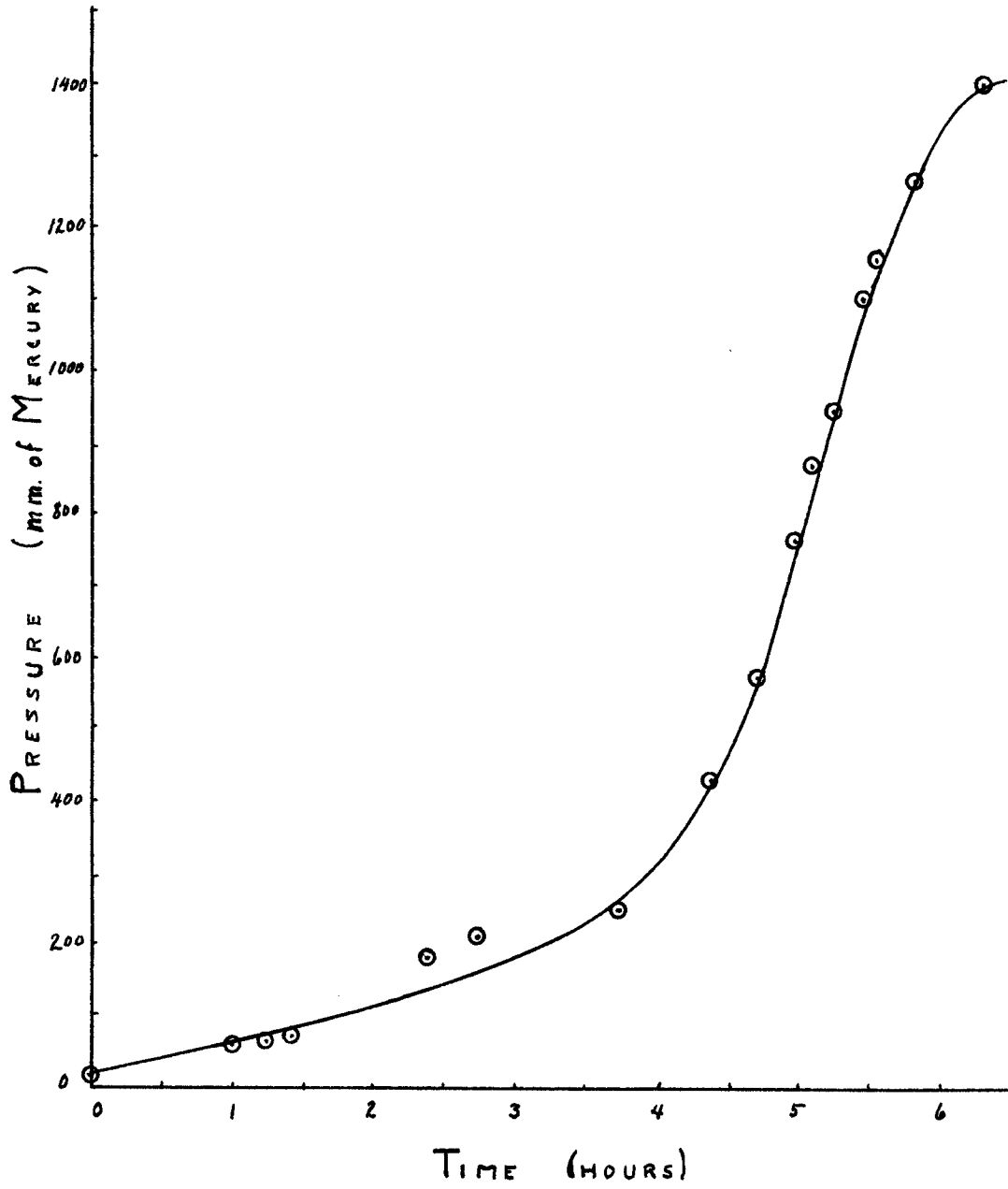
TABLE 2
 PHYSICAL CONSTANTS OF THE FRACTIONS FROM THE SECOND RUN

Frac- tions	Boiling Range @ 21 mm.	d_4^{20}	n_D^{20}	Refrac- tivity Intercept	Vol. ml.
1	55.8- 56.4	.7196	1.4080	1.0482	27.6
2	97.0	1.4189	0.2
3	107.8	1.4201	(3 drops)
4	121.3-122.0	.7772	1.4231	1.0345	0.2
5	152.2-155.4	.8111	1.4413	1.0358	0.2
6	158.7-159.0	1.4431	0.3
7	160.8-164.2	.8039	1.4452	1.0433	0.2
8	164.8-167.7	.8063	1.4452	1.0421	0.3
9	173.8-176.3	.8080	1.4472	1.0432	0.8
10	180.0-181.0	.8202	1.4508	1.0407	1.3
11	182.3-184.0	.8264	1.4524	1.0392	0.8
12	186.0-187.3	.8415	1.4570	1.0363	1.5
13*	187.8-188.8	.8557	1.4593	1.0315	0.9
14*	205.5-207.8	1.0264	1.4871	0.9559	2.8

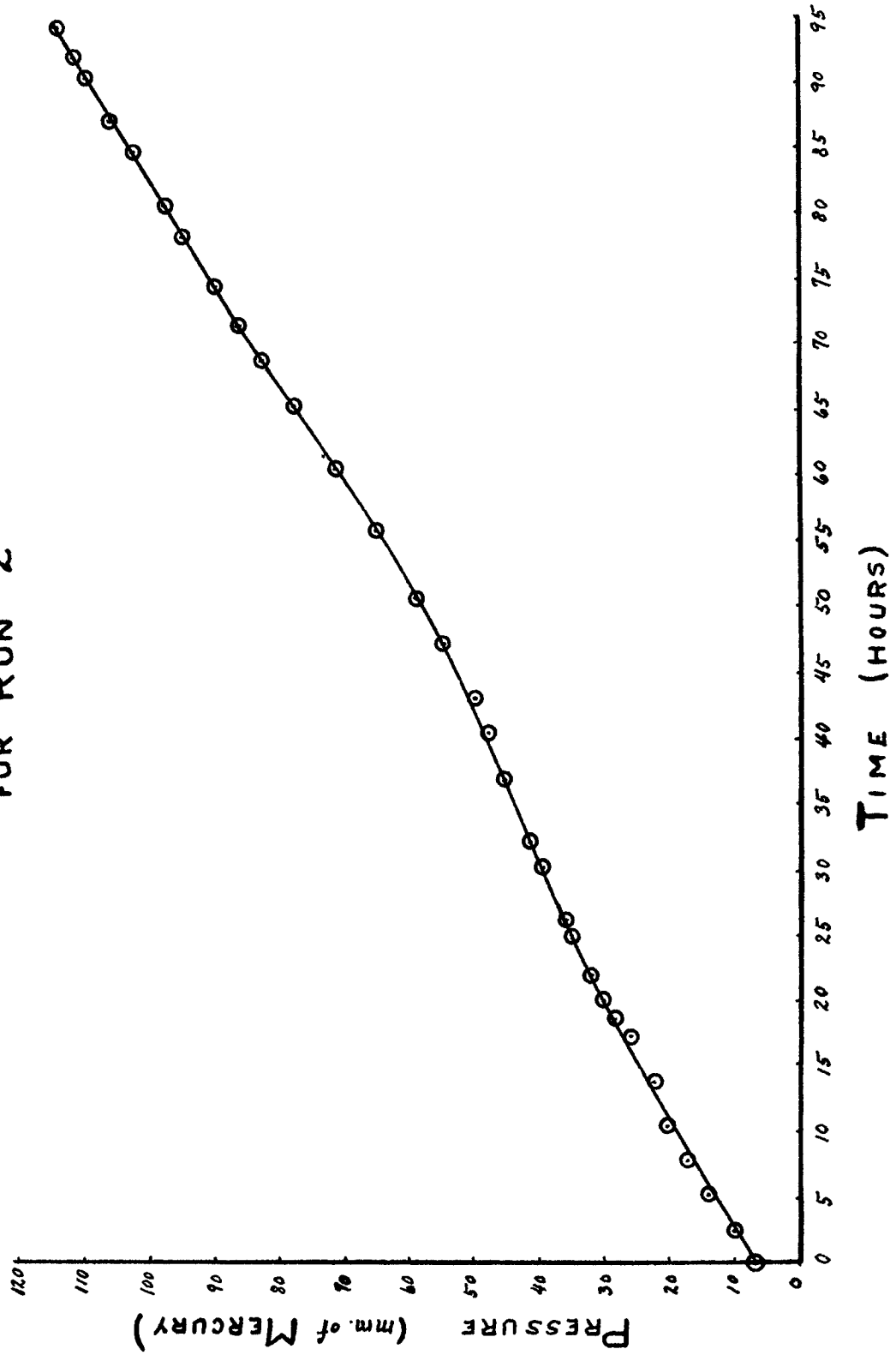
*Contains "chaser," dibutyl phthalate.

The progress of the runs was followed by recording the pressure developed in the system at regular intervals during the irradiation. In Figures 1 and 2 the increase in total pressure in mm. of mercury versus time of irradiation in hours is plotted for Runs One and Two respectively.

GRAPH OF PRESSURE VERSUS TIME FOR RUN # 1



GRAPH OF PRESSURE VERSUS TIME
FOR RUN #2



CHAPTER IV

CONCLUSIONS

The data obtained for Run One are not valid due to the effect of the air introduced into the system at the start of the run. Also, the sharp rise in the rate of pressure increase during the last half of the run was due to thermal as well as photochemical decomposition. It is impossible to differentiate between the products of the separate reactions, though from theoretical considerations the only high boiling products should result from a photochemical decomposition.

All of the fractions recovered from the liquid product of the second run had boiling points which were much higher than the original charge stock. In addition, the pressure-time curve for this run is linear, indicating a steady rate of pressure increase during the run, and the molecular weight of the permanent gases shows that hydrogen was the by-product of the reaction as predicted. These factors indicate that the products obtained were largely due to photochemical reaction.

An inspection of the refractivity intercepts reveals that the very high boiling products of Run Two are saturated monocyclic compounds. No evidence was found to indicate that any compound comparable to the expected 2,7,7,8,8,13-hexamethyltetradecane was formed. In fact, a negligible amount

of paraffinic compounds were isolated. A comparison of the physical constants of the fractions with the published values for hydrocarbons shows that the products are probably alkyl-substituted cyclohexanes. This could occur through the cyclization of the 2,7-dimethyloctenyl radical to an alkylated cyclohexane (which might react photochemically itself).

A further study of this reaction in a system in which higher yields of the products could be obtained should lead to more information concerning the nature of the products.

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