PART I

THE SYNTHESIS AND SOME PROPERTIES OF 1-PHENYL HEPTANE,
1-CYCLOHEXYL HEPTANE AND n-TRIDECANE

PART II

THE VAPOR PHASE OXIDATION OF HYDROCARBONS

BY

WILLIAM A. HORNE

UMI Number: DP70405

# UMI

Dissertation Publishing

UMI DP70405

# ProQuest

The University of Maryland assumes no
responsibility for the material herein presented.

# TABLE OF CONTENTS

## PART I

The Synthesis and some Properties of 1-Phenyl Heptane, 1-Cyclohexyl Heptane and n-Tridecane

## PART II

The Vapor Phase Oxidation of Hydrocarbons

# PART I

## THE SYNTHESIS AND SOME PROPERTIES OF 1-METHYL HEPTANE, 1-CYCLOHEXYL HEPTANE, AND n-TRIDECANE.

### A - INTRODUCTION

The purpose of this investigation was to prepare some hydrocarbons which would represent the heavy ends in the gasoline fraction and the low boiling kerosene fraction of petroleum, which were to be used in the following oxidation studies. The compounds were selected to represent three types of hydrocarbons found in petroleum; namely, straight chain paraffins, aromatics with paraffinic side chain and cyclo-paraffins with paraffin side chain. Also to determine some of the physical constants of the purified products.

## B. EXPERIMENTAL PART

### 1. The Synthesis of 1-Phenyl Heptane

1-Phenyl heptane has been prepared by Auger[1] by
the action of $AlCl_3$ on 1,1-dichloro heptane and benzene
at 40-50°C., by Braun and Deutsch[2] by the action of
sodium on 1-phenyl 7-chloro heptane in ether or benzene,
by Sabatier and Mailhe[3] by the reduction of n-hexyl
phenyl ketone with hydrogen over nickel at 300°C., and
by Eisenlohr and Schulz[4] by a Wolff reduction of n-hexyl
phenyl ketone. The physical properties of their product
vary to some extent.

The preparation of 1-phenyl heptane was carried
out by the following series of reactions:

$$Castor\ Oil \longrightarrow C_6H_{13}MgO$$
$$C_6H_5Br \longrightarrow C_6H_5MgBr$$
$$\longrightarrow C_6H_5CHOHC_6H_{13}$$
$$C_6H_5CH_2C_6H_{13} \longleftarrow C_6H_5CH=CHC_5H_{11}\ (?)$$
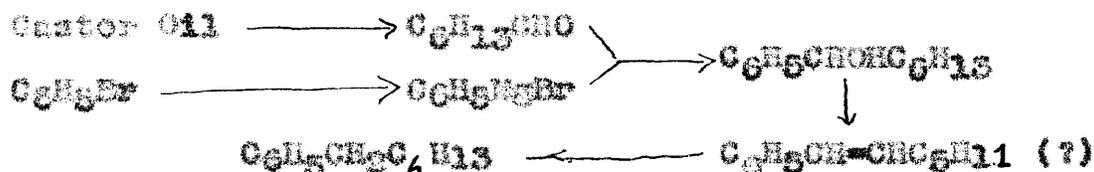
The castor oil was distilled according to the
method of Perkins and Cruz[5] as rapidly as possible, at
approximately 50 mm. pressure. Foaming was excessive
throughout the distillation. The product was fractionat-
ed at 20 mm. pressure, the fraction b.p. 50-52°C collected.
Phenyl magnesium bromide was prepared according to the

8

method in Organic syntheses[6] and to this was added the heptaldehyde in a manner similar to the method in Organic syntheses[7]. Fractionation yielded 41 grams of phenyl n-hexyl carbinol, b.p. 278-279°C. after a small forerun of biphenyl.

An attempt was made to dehydrate the carbinol by means of distillation with iodine. 100 grams of carbinol and 1 gram of iodine were slowly distilled through a 30 cm. unpacked column. A trace of water was produced, and 'popped'. A trace of water was dis— the dehydration was so slight that the method was dis— carried.

The dehydration was then tried using alumina as the catalyst. The alumina was prepared from potassium alum, washed free of sulfate ion and dried at 100°C. for one day and then pressed into pellets. A 40x1.8 cm. pyrex tube was packed for 10-15 cm. at the exit end with alumina such that a thermocouple well was approximately in the middle of the catalyst bed which was held in place by glass wool plugs. The tube was heated to 350 ± 10°C. and dry air drawn through the apparatus for 3 days to become anhydrous; temperature was determined by means of a chromel alumel thermocouple.

Twenty-five grams of the carbinol was allowed to flow into the tube from a dropping funnel at a rate of about one-half gram per minute maintaining the temperature

at 150°C. The reaction was slightly endothermic and water collected in the distilling flask which was used as a receiver. The water was separated and the product again passed over the catalyst forming more water; total volume 2.0 ml., or an apparent conversion of 57%. This indicated that dehydration was taking place sufficiently so the remainder of the carbinol was passed over the catalyst, but at a slightly slower rate. The combined product was distilled and the portion boiling above 250°C. was again passed over the catalyst.

The combined crude phenyl heptene was refluxed over sodium for 3 hours and fractionated, collecting the fraction b.p. 242-247°C. This was refractionated over sodium collecting the phenyl heptene fraction at 244-245°C.

An attempt was made to hydrogenate the olefin by means of a nickel catalyst prepared according to the method given in Gattermann and Heland[8]. Twenty-five gms. of phenyl heptene were allowed to flow into a tube similar to that described by Welsh[9] at a rate of about 1 drop every 4 seconds and hydrogen was allowed to pass in at a rate such that about 1 bubble per second was emitted after passage through the tube as evidenced by a bubble counter at the outlet end of the system. The tube was maintained at 300° C. ± 10°C., using chromel-alumel thermocouple.

The product (24 gms.) was hydrogenated only to a few percent as indicated by Erg addition method of McIllhiney[10].

Using Adkins "copper chromite" catalyst[11] under the same conditions as in the case of nickel, the product was about 70% saturated and could be raised no higher by further passage over the catalyst. This mixture was washed with syrupy phosphoric acid in an attempt to remove olefins, but after washing, drying and distilling from sodium the mixture still contained about the same amount of unsaturation, so it was washed lightly with cold concentrated $H_2SO_4$ several times, 10% $Na_2CO_3$ and $H_2O$ and distilled again from sodium. The olefins were reduced but some sulfonation of the aromatic nucleus also took place at the same time.

The phenyl heptane was filtered through a 40 cm. column of silica gel in a manner similar to that described by Mair and White[12]. The refractive index of the fractions indicated that the olefins were absorbed a little more than the phenyl heptane as the unsaturation decreased from 3% to 1.5%. The filtrate was distilled from sodium and passed through fresh silica gel two times and the refractive index of the product indicated that it was fairly pure. This filtered material was fractionated from sodium and the fraction, b.p. 243-244°C. at 755 mm. pressure was collected as pure phenyl heptane.

2. The Synthesis of 1-Cyclohexyl Heptane

The preparation of 1-cyclohexyl heptane has not been reported in the literature. Murat and Amouroux[13] have prepared dipropyl cyclohexyl methane by hydrogenation of a mixture of cyclohexyl heptenes using a nickel catalyst.

The preparation of 1-cyclohexyl heptane was carried out by the following series of reactions:

$$Castor\ oil \longrightarrow C_6H_{13}CHO \longrightarrow$$
$$C_6H_{11}OH \longrightarrow C_6H_{11}Br \longrightarrow C_6H_{11}MgBr \longrightarrow C_6H_{11}CHOHC_6H_{13}$$
$$\downarrow (7)$$
$$C_6H_{11}CH_2CH_2C_5H_{11} \longleftarrow C_6H_{11}CH = CHC_5H_{11}$$
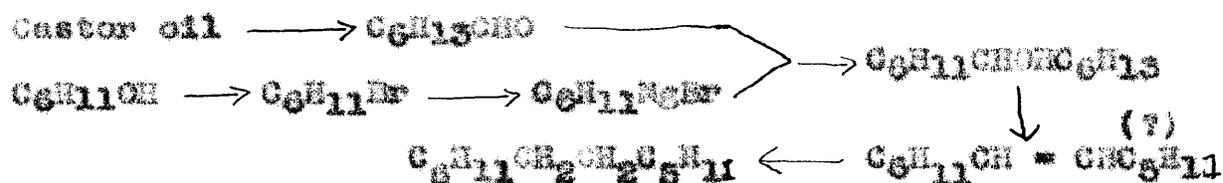
Heptaldehyde was prepared as given previously, cyclohexyl bromide was prepared according to the method in Organic Syntheses , the Grignard reagent prepared and the heptaldehyde added to it. The mixture decomposed with 30% sulfuric acid and extracted with ether. The combined ether extract was dried, the ether removed on a steam bath and the residual liquid distilled, collecting the fractions, b.p. 270-275°C., as crude cyclohexyl hexyl carbinol. This crude product was fractionated and the fraction, b.p. 272-272.5 (751 mm.), was collected as cyclohexyl hexyl carbinol.

Alumina dehydration of this carbinol did not seem to be satisfactory in a trial run so it was heated on a steam bath for 8 hours with a 50% excess of phosphorus pentoxide, extracted with ether, washed with $Na_2CO_3$ and water, then dried over anhydrous potassium carbonate. The ether was

removed on a steam bath and the residue distilled, collect-
ing the portion distilling in the range 242-243°C. There
was only a small forerun and practically no residue remain-
ing. The product was refluxed over sodium for 3 hours and
fractionated. The product collected distilled constantly
at 242.3° C. (760 mm.)

This dehydration should yield a mixture of two
olefins depending on the manner in which water splits out,
thus

but both should yield cyclohexyl heptane on hydrogenation.

The olefin was hydrogenated using Adkins' catalyst
at 150°C. and again hydrogenation was not complete as
indicated by bromine titration. The crude product was
washed with cold concentrated sulfuric acid, 10% sodium
carbonate and water, then dried over $CaCl_2$ and distilled
from sodium. The fraction of boiling range 243-244°C.,
was filtered through silica gel collecting the fraction
of constant refractive index and this material was passed
through fresh gel. This filtrate was refluxed over sodium
and fractionated, collecting the fraction, b.p. 243.5-244°C.
at 760 mm. pressure as pure 1-cyclohexyl heptane.

3.  The Synthesis of n-Tridecane.

n-Tridecane has been prepared by Krafft[14] by the action of phosphorus and hydriodic acid on tridecanoic acid and was isolated from a hydrogenated coconut oil by Ruhoff[15].

The preparation of n-tridecane was carried out by the following series of reactions:

$$C_4H_9OH \longrightarrow C_4H_9Br \longrightarrow C_6H_{13}OH \longrightarrow C_6H_{13}Br$$

$$C_6H_{13}CHOHC_6H_{13} \longleftarrow C_6H_{13}MgBr$$

$$C_6H_{13}CH=CHC_5H_{11} \longrightarrow C_6H_{13}CH_2CH_2C_5H_{11}$$
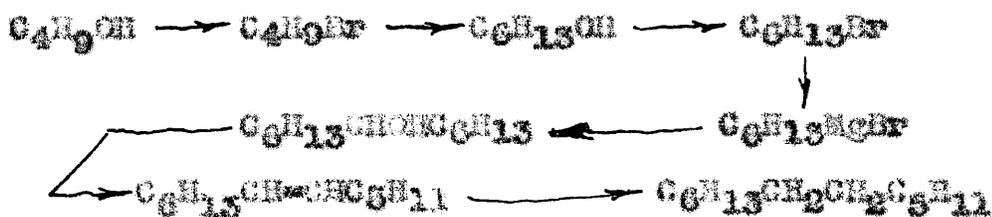
n-Butyl alcohol was brominated according to the method in Organic Syntheses[16] and from it n-hexyl alcohol was prepared by the method in Organic Syntheses[17]. n-Hexyl bromide was made using a hydrobromic-sulfuric acid mixture and the Grignard reagent prepared from the purified product, and to it was added heptaldehyde in a manner similar to that given in Organic Syntheses[7].

The product was extracted with ether, the extract dried with $K_2CO_3$, and the ether removed on a steam bath. The residue was distilled and the fraction, b.p. 263-266°C. collected as crude di-n-hexyl carbinol. This was fractionated, collecting the fraction distilling 264.5-265°C.

The carbinol was heated on the steam bath for 8 hours with 50% excess phosphorus pentoxide, the resulting pasty mass extracted with ether, washed with $Na_2CO_3$, and water, and the ether removed. The residue was distilled collecting the fraction b.p. 230-245°C. This was refluxed over sodium for 3 hours and fractionated from sodium, collecting the fraction, b.p. 232-232.2°C., as pure tridecene-6.

The dehydration of the tridecanol should yield a single olefin and not a mixture, for the molecule is symmetrical, thus:

$$C_6H_{11}CH_2CH - CHC_5H_{11} \longrightarrow C_6H_{13}CH = CHC_5H_{11}$$

$$C_6H_{11}CHCHCH_2C_5H_{11} \longrightarrow C_6H_{11}CH=CHC_6H_{13}$$
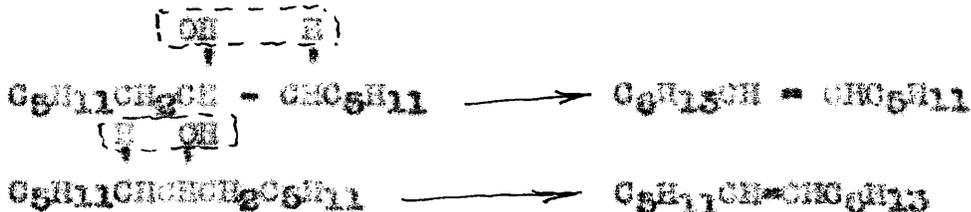
The tridecene was hydrogenated by passage over Adkins' catalyst at 200°C. as indicated by a reduction in the refractive index. The crude product was washed with cold concentrated sulfuric acid, 10% $Na_2CO_3$ and water and dried over $CaCl_2$. The product was refluxed over sodium 5 hours and fractionated, collecting the fraction, b.p. 234-235°C. This fraction was filtered through silica gel collecting the product of constant refractive index, and this was passed through fresh gel. The filtrate was fractionated from sodium and the fraction collected which boiled constantly at 234.2° C. at 760 mm. pressure. This was considered pure n-tridecane.

4.   The Synthesis of 2,2,4-Trimethyl Pentane.

The 2,2,4-Trimethyl pentane was prepared according to the method given by Edgar,[18] which is briefly as follows: Tertiary butyl alcohol was heated on a steam bath for 8 hours with a mixture of 50% by volume of $H_2SO_4$ and $H_2O$, cooled, separated, washed with water, dried over $CaCl_2$ and distilled from sodium, collecting the fraction, b.p. 98-110°C. This mixture of octylenes was passed over Adkins' catalyst, the product washed with cold concentrated sulfuric acid, 10% $Na_2CO_3$ and water, dried over $CaCl_2$ and fractionated from sodium collecting the fraction, b.p. 99-100°C. After one passage over silica gel, the product was distilled from sodium collecting the fraction, b.p. 99.0-99.5°C., as pure 2,2,4-trimethyl pentane.

Calibration of refractometer:

    $N_D$ distilled water              ------- 1.3325 at $25°C$.

    $N_D$ distilled water observed  ------- 1.3325 at $25°C$.

No correction applied.


## TABULATED PHYSICAL CONSTANTS

| Compound | B.P.($°C$.) | $n_D^{t °C}$. | $D_4^{t °C}$ |
|---|---|---|---|
| Phenyl n-hexyl carbinol | 278-279 (756) | $1.4994^{25}$ | $0.9439^{25}$ |
| Phenyl heptene (?) | 244.2 (760) | $1.4981^{25}$ | $0.8669^{25}$ |
| 1-Phenyl heptane | 243.0 (760) | $1.4875^{20}$ | $0.8631^{20}$ |
| Cyclohexyl n-hexyl carbinol | 272-272.5 (751) | $1.4621^{25}$ | $0.8834^{25}$ |
| Cyclohexyl heptene (?) | 242.3 (760) | $1.4790^{25}$ | $0.8626^{25}$ |
| 1-Cyclohexyl heptane | 243.9 (760) | $1.4710^{20}$ | $0.8424^{20}$ |
| di n-hexyl carbinol | 264.5-265 (758) | --- | --- |
| tridecone-6 | 232.2 (762) | $1.4360^{20}$ | $0.7869^{20}$ |
| n-tridecane | 234.7 (760) | $1.4258^{20}$ | $0.7577^{20}$ |
| 2,2,4-trimethyl pentane | 99.0-99.5 (760) | $1.3916^{20}$ | --- |

(?) denotes probably mixture

REPORTED PHYSICAL CONSTANTS

| Compound | B.P. °C (760) | $n_D^{20}$ | $D_4^{20}$ | Ref. |
|---|---|---|---|---|
| Phenyl n-hexyl carbinol | 275° | 1.501 | 0.946 | Colaciochi[19] |
| 1-Phenyl heptane | 235 | 1.4865 | 0.8570 | Auger[1] |
| | 236 | --- | --- | Braun & Deutsch[2] |
| | 240 | --- | --- | Sabatier & Mailhe[3] |
| | 245-245.2 | 1.4864 | 0.8604 | Eisenlohr & Schulz[4] |
| n-Tridecane | 234 | 1.4272 | 0.7571 | Krafft[14] |
| | 234 | $1.4230^{25}$ | 0.7543 | Ruhoff[15] |
| (from petroleum) | 226 | 1.4354 | 0.7834 | Mabery[20] |
| 2,2,4-trimethyl pentane | 99.3 | 1.3916 | 0.6918 | Laughlin & Whitmore[21] |

## C. SUMMARY

1-Phenyl heptane, 1-cyclohexyl heptane and n-tridecane have been prepared by the general method of condensation by means of a Grignard reaction of two suitably chosen radicals, one as the bromide and the other as aldehyde.  The resulting carbinol is dehydrated, and the resulting unsaturated hydrocarbon or hydrocarbons, hydrogenated.

The boiling point, refractive index, and density of the intermediates as well as the products have been determined and compared with recorded values if previously reported.

Fig. 1
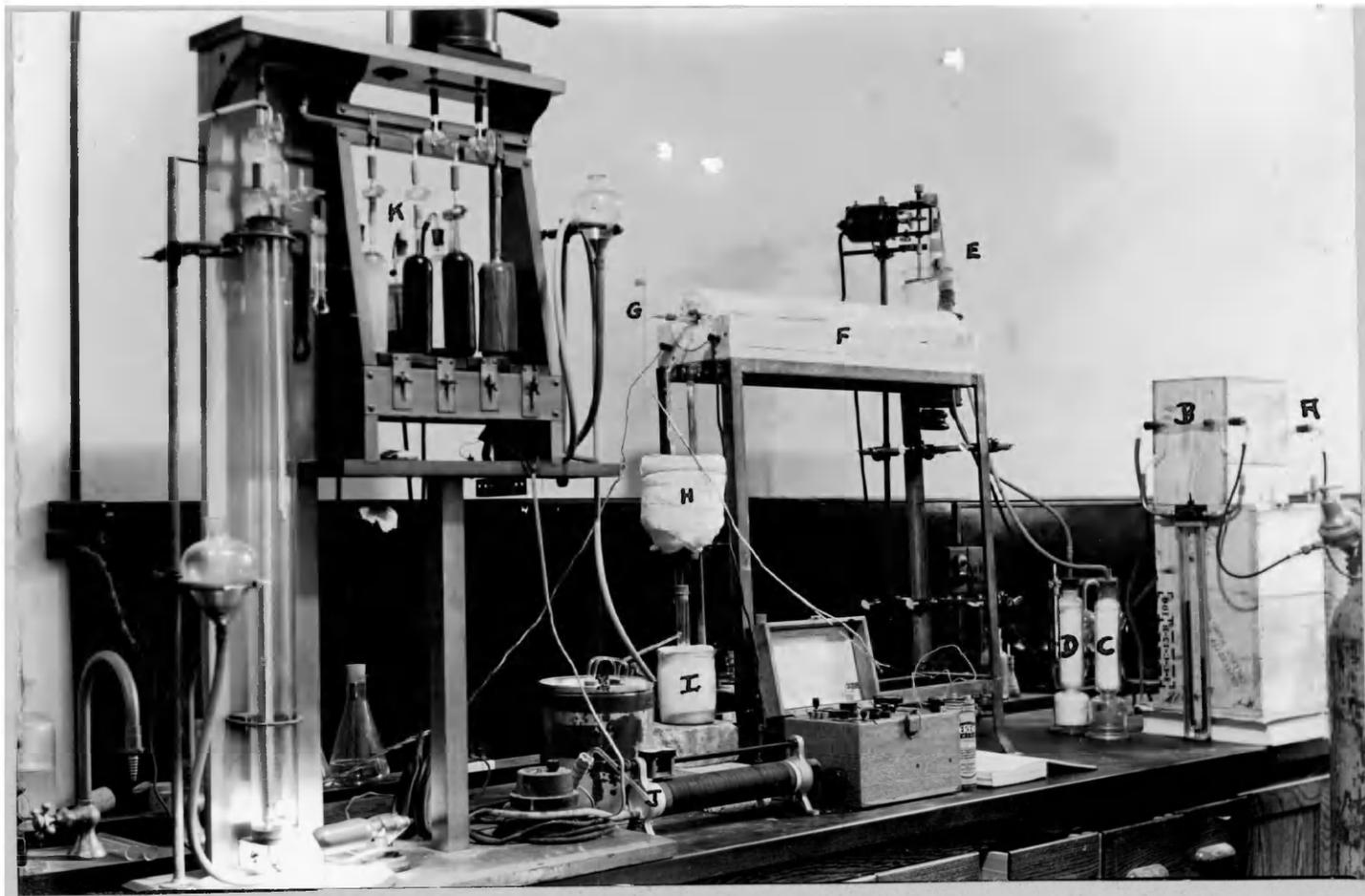
OXIDATION APPARATUS

A  -  Flow meter on oxygen line.

B  -  Flow meter on nitrogen line.

C & D Drying towers.

E  -  Vaporizing unit.

F  -  Furnace.

G  -  Thermocouple well.

H  -  Ice cooling bath.

I  -  $CO_2$-alcohol cooling bath.

J  -  Variable resistance.

K  -  Gas analysis outfit.

# Fig. 2
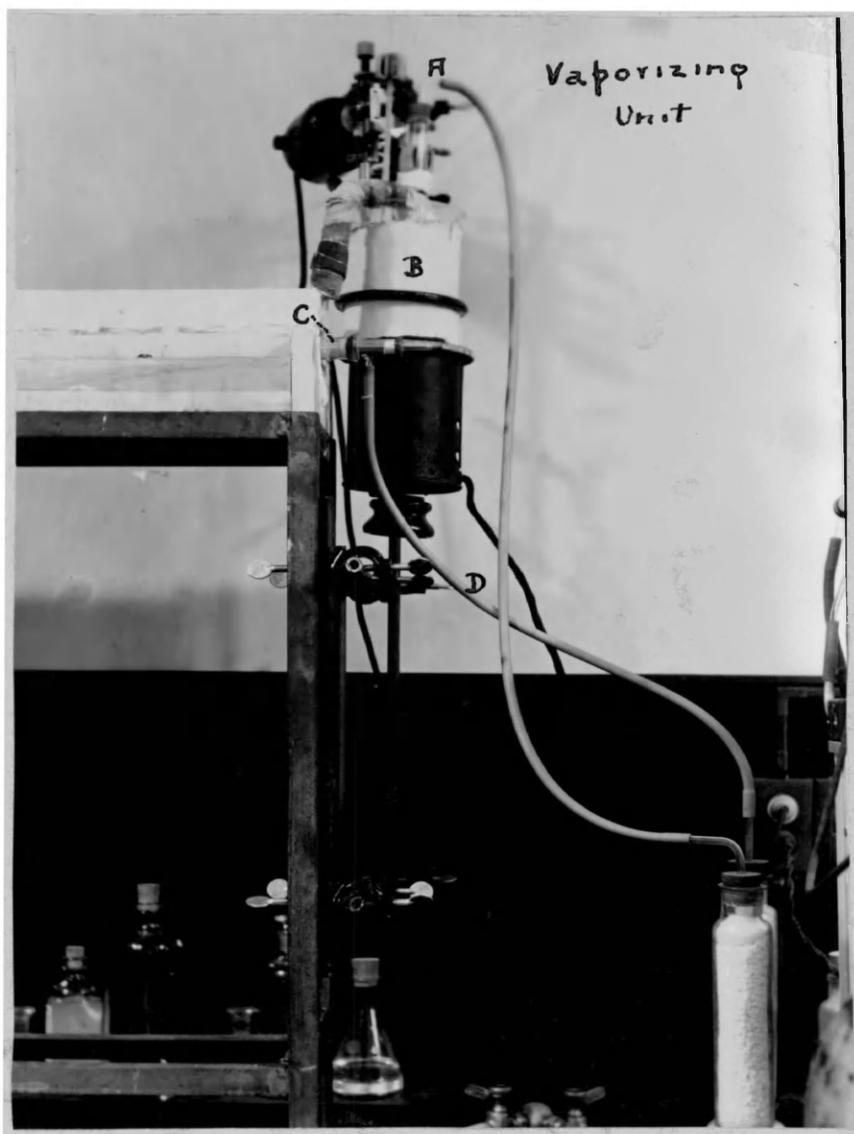


VAPORIZING UNIT

A — Nitrogen inlet.

B — Constant temperature.

C — Reaction tube.

D — Oxygen inlet.

O₂

N₂

CEMENT
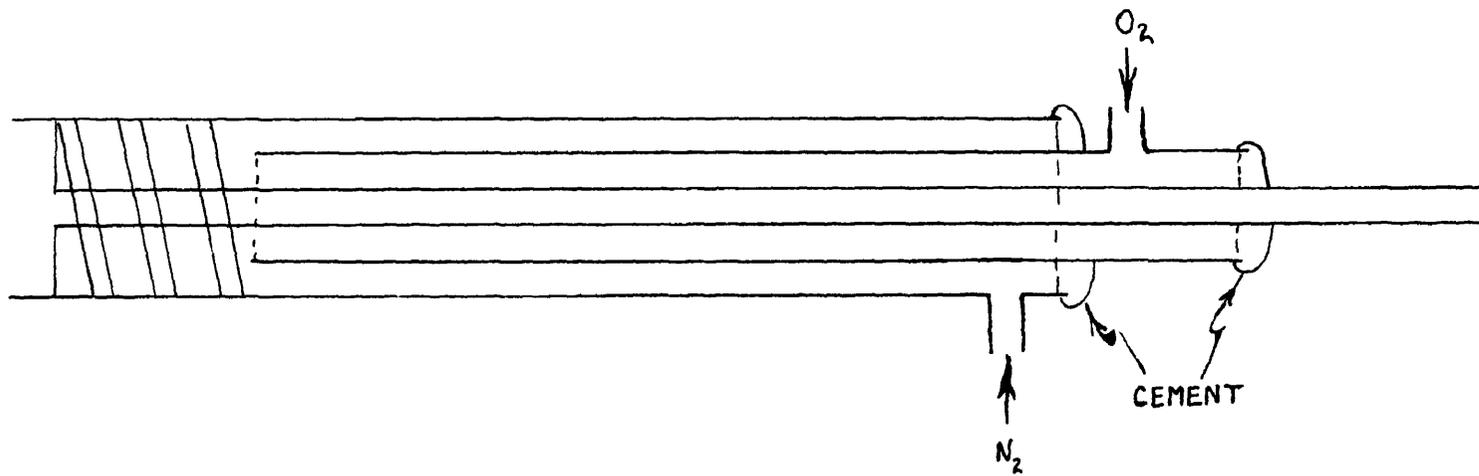
FIG. III

GAS MIXING DEVICE

PART II

The Vapor Phase Oxidation of Hydrocarbons.

A. INTRODUCTION

The atmospheric oxidation of hydrocarbons is extremely important from the viewpoint of the petroleum industry. Within the last decade there has been intensive chemical investigation on the oxidation mechanism, methods for its inhibition in some processes and acceleration in others.

The importance and scope of petroleum hydrocarbon oxidation is pointed out by Kalichevesky and Stagner;

---

Chemical Refining of Petroleum by Kalichevesky and Stagner, Chemical Catalog Co., Inc., 330 West 42nd St., New York, Chapter 9, Page 289.

---

"Although there is but little application of oxidation methods in the refining of petroleum, the subject of oxidation is, nevertheless, involved in practically all refining operations, ---------. The subject of complete and partial oxidation of the petroleum hydrocarbons is broad, and investigations are becoming more and more extensive in pure science and in industrial applications. It includes the control of complete oxidation under high pressure in engines to derive more of the potential energy of the fuel now only partly available because of detonation and other factors. It includes the partial oxidation and resulting deterioration of all petroleum products in use and in storage. It is involved in the manufacture of

asphalt and to some extent in other oxidation products, such as fatty acids, aldehydes, alcohols, etc."

For the past several years, this laboratory has been primarily interested in oxidation studies and inhibitors to prevent asphaltene formation in lubricating oils. Most petroleum products are used under relatively high temperatures in the presence of atmospheric oxygen and deterioration takes place under these conditions.

The addition of substances to inhibit this oxidation has been studied for a number of years with no satisfactory inhibitor being found, nor has the mechanism by which an inhibitor acts been determined conclusively. Before these questions can be explained it is necessary to determine on what component or components of an oil the inhibitor acts, and thus the oxidation mechanism and products formed.

The course of hydrocarbon oxidation has been studied for the lower members of the paraffin series. Experimental data and discussion of the oxidation mechanism of higher hydrocarbons is presented in this paper; the results may contribute to the interpretation of the behavior on oxidation of hydrocarbons of higher order.

## B. PROBLEM

"The Vapor Phase Oxidation of Hydrocarbons".
Specifically hydrocarbons which would represent components
of the lower kerosene or higher gasoline fraction of
petroleum, to be passed in the vapor phase through a
heated tube with a nitrogen-oxygen mixture of a composition
approximately as in the atmosphere. No catalysts are to be
present, or the tube packed in any way.

## C. INDICATIONS

1. Kerosene, n-tridecane, and 2,2,4-trimethyl pentane under the experimental conditions, in absence of oxygen, do not thermally decompose to yield gaseous products.

2. Kerosene, n-tridecane, and 2,2,4-trimethyl pentane oxidize under the experimental conditions to yield CO and $CO_2$ as gaseous products.

3. Kerosene, n-tridecane and 2,2,4-trimethyl pentane yield unidentified acids and aldehydes. No evidence of peroxide formation.

4. Oxidation of n-tridecane appears to take place by the same mechanism regardless of the hydrocarbon-oxygen ratio, but the extent of oxidation is greater, the larger the ratio.

5. The experimental results indicate that the mechanism of oxidation involves, primarily, the formation of aldehydes, and further that decomposition and oxidation of these intermediates yields CO, $CO_2$ and $H_2O$.

## D. EQUIPMENT AND PROCEDURE.

(a) Materials Used. The n-tridecane and 2,2,4-tri-methyl PENTANE were those whose preparation is described in Part I of this thesis. The hydrocarbon mixture was obtained by fractionation of a kerosene from sodium, collecting the fraction of boiling range, 230-238°C. at 758 mm. pressure. This fraction was washed thoroughly with Concentrated $H_2SO_4$, 10% $Na_2CO_3$, and water. The mixture was dried over anhydrous $K_2CO_3$, refluxed over sodium for three hours, and fractionated from sodium, again collecting the fraction, boiling range 230-238°C. The properties of the final fraction were as follows:

$$d_4^{20} = 0.8112$$

$$n_d^{20} = 1.4312$$

which indicate that it contains naphthenes as well as paraffins.

The nitrogen and oxygen were Southern Oxygen products, their analysis indicated that they were of high purity and were considered as 100% $N_2$ and 100% $O_2$ respectively.

(b) Oxidation Apparatus and Method. The complete oxidation apparatus is shown in the photograph, Figure I. Nitrogen from the tank was passed at a constant measured rate, as determined by the flowmeter (B), through a drying tower of $CaCl_2$ (C) and then to the vaporizing unit (E).

As it was necessary to preheat the hydrocarbon for vaporization, it was considered advisable to avoid exposure to oxygen until the desired experimental temperature was reached. In order to accomplish this, the hydrocarbon was vaporized into the nitrogen stream and then mixed with the oxygen when the furnace temperature had been reached.

The vaporizing unit is shown in the photograph, Figure II. It is composed of a 100 cc distilling flask with indentations directly over the bulb which support 1" of pyrex helices serving to remove any mist from the vapor stream. The nitrogen inlet tube (A) passes through the helices, and extends to the bottom of the flask, where it is drawn to a capillary opening. The flask is immersed in an electrically heated constant temperature bath (B). The nitrogen passes into the flask, bubbling through approximately a 2 cm. depth of hydrocarbon, and the mixture then passes out through the insulated side arm into the reaction tube, where it is mixed with the oxygen.

The mixing device is shown in the sketch, Figure III. The nitrogen-hydrocarbon is fed into the outer annular tube and the dried oxygen fed into the inner annular tube. Mixing takes place when the gases are diverted from their course and forced around the pyrex spiral at the end of the annular tubes.

The reaction tube is a 55 x 1.8 cm. pyrex tube of approximately 140 cc volume. It is placed in the furnace (F), Figure I, the temperature of which is controlled by

a chromel-alumel thermocouple (G) which extends to within 2" of the mixing device.

The emerging vapors pass through a spiral ice condenser (H), a 25 cc distilling flask immersed in a $CO_2$-alcohol bath (I) and thence through three other tubes cooled by $CO_2$-alcohol. Samples of the gases passing through the condensing system were collected over Hg directly and analyzed in the gas analysis outfit (K) for carbon dioxide, gases absorbed in fuming sulfuric acid, oxygen, and carbon monoxide. Occasional analyses were made for hydrogen and methane.

No determinations were made on the liquid products except the presence of aldehydes was shown when a red color was produced with fuchsin on addition to the aqueous product. Acids are also formed as the solution turns litmus red. Peroxides may be present for $I_2$ is liberated from KI, but this may be due to peroxides formed during the reaction or later oxidation of aldehydes to produce peroxides.

# 4. LITERATURE

The vapor phase oxidation of methane and ethane
has been studied extensively by Bone and co-workers. His
work is summarized by Ellis.

Chemistry of Petroleum Derivatives by Ellis, Chemical
Catalog Co., New York. Vol. I p. 346.

"A study of the oxidation mechanism of methane
made by Bone and Wheeler showed that, in the presence of
an excess of methane, the reaction between methane and
oxygen took place at temperatures below the ignition point.
In no case was there a preferential oxidation of either
element of the hydrocarbon molecule, inasmuch as neither
free carbon nor free hydrogen was observed at any stage
of the oxidation. In slow-oxidation experiments they
isolated formaldehyde as an intermediate oxidation pro-
duct. This evidence served as a basis for the hydroxy-
lation theory of oxidation. Briefly, this theory states that
oxidation proceeds through the successive conversion of the
hydrogen atoms (attached to a carbon atom) to hydroxyl
groups. Oxidation in the presence of a catalyst was held
to take place in exactly the same way, however, with this
difference: hydroxylation progressed with such velocity
that intermediate oxidation products could not be detected.
Only end-products such as the oxides of carbon and water
were obtained. Later work by Bone and Drugman with ex-
plosive mixtures of hydrocarbon gases indicated that this
same explanation, with some slight modification, was
also applicable."

The oxidation of ethane could be represented as follows:

$$C_2H_6 \rightarrow C_2H_5OH \rightarrow CH_3CH \begin{smallmatrix} OH \\ OH \end{smallmatrix} \rightarrow CH_3C \begin{smallmatrix} H \\ O \end{smallmatrix} \rightarrow CH_3C \begin{smallmatrix} O \\ OH \end{smallmatrix}$$

$$HOCH_2C \begin{smallmatrix} OH \\ O \end{smallmatrix} \rightarrow CH_3OH$$

$$H_2O + CO_2 \leftarrow H_2 + CO \leftarrow HC \begin{smallmatrix} H \\ O \end{smallmatrix} \rightarrow HC \begin{smallmatrix} OH \\ O \end{smallmatrix} \rightarrow HOC \begin{smallmatrix} OH \\ O \end{smallmatrix} \rightarrow CO_2 + H_2O$$
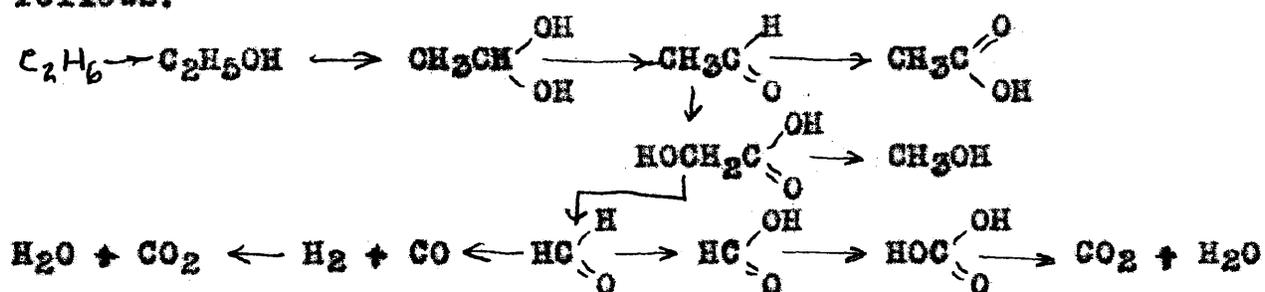
The mono and di-hydroxy derivatives of the hydrocarbons essential to the theory have not been found. Bone considers that they oxidize or decompose so rapidly that their presence would not be expected; but this is in contradiction with results obtained by other workers who find that both the hydrocarbon and corresponding aldehyde oxidize more readily than the alcohol under similar conditions. Also there is no evidence for the formation of glycols from alcohol oxidation.

Marek and Hahn in discussing the oxidation of hydrocarbons, have the following to say concerning the peroxidation theory:

---

Catalytic Oxidation of Organic Compounds in the Vapor Phase by Marek and Hahn, Chemical Catalog Co., New York. p. 305.

---

"Although considerable controversy has existed and still exists regarding the exact manner in which a hydrocarbon oxidizes, one fact stands out from the great mass of data that have accumulated and that is that aldehydes appear early and are prominent in the oxidation products. It has been recognized, however, that aldehydes are not the primary

products of the encounter between oxygen and hydrocarbon mole-
cules, and it has been proposed that the most probable
initial product is peroxidic in type.

The peroxide theory has developed largely from work
in the liquid phase or at low temperatures conducted
primarily in an attempt to solve some of the questions
regarding knocking phenomena. It has been assumed that the
evidence obtained in this manner would be directly appli-
cable to the high temperature vapor phase oxidation. It
has thus been assumed that the mechanism followed by the
oxidation at relatively low temperatures and at atmospheric
or low pressure is the same as, or sufficiently similar to
that at the high temperatures and higher pressures exist-
ing in an engine cylinder to make the results useful in
interpreting engine operation."

A number of workers have reported the presence of
peroxides in hydrocarbon oxidation, but it should be pointed
out that aldehydes on exposure to air form some type of
active oxygen compound which would replace iodine from
potassium iodide.

Pease has studied the oxidation of propane and the
two butanes. His results may be summarized as follows:

Pease, R.N., J.A.C.S. **51**, 1839 (1929).

The three main types of reactions appear to be:

(1) Unsaturates by dissociation:

$$C_4H_{10} \longrightarrow C_4H_8 + H_2$$
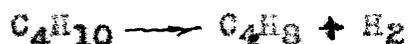
(2) Unsaturates by oxidation:

$$C_4H_{10} \longrightarrow (C_4H_8 + H_2) \longrightarrow C_4H_8 + H_2O$$

(3) Aldehyde reactions:

$$C_4H_{10} \longrightarrow C_2H_5CHO + CO + 2H_2O$$

$$C_2H_5CHO \longrightarrow CH_3CHO + CO + H_2O$$

Dissociations (1) and (2) need not give $H_2$ as the saturated product; methane or a higher hydrocarbon may occur instead, the oxidation product is then an aldehyde.

The reaction is strongly inhibited if the reaction tube is packed with broken pyrex glass, possibly deactivating excited molecules. If glass is coated with KCl, the reaction is further suppressed, but has little effect in an empty tube, which is independent of the nature of the tube walls. Coating in the packed tube probably inhibits a wall catalysis which has become important, or coating may increase efficiency in producing deactivations.

In a packed tube the reaction does not begin until the temperature of thermal decomposition of the hydrocarbon is reached. The total amount of hydrocarbon reaction is 2 or 3 times greater when $O_2$ is used than when $H_2$ is used, even reaction (1) (not involving oxidation) takes place more during oxidation than during thermal decomposition, which may be due to a temperature rise from the heat of oxidation but partly directly induced by excited molecules produced by the other reactions.

Oxidation of $C_3H_8$ in a packed tube began at about 575°C., in the empty tube at about 300°C. (mainly type 3). Packed tube greatly inhibts (3). The results follow no simple scheme. With 75% propane the reaction begins abruptly between 300°-325°C. and runs directly to completion. At lower temperatures the aldehyde reaction is dominant, out at 600°C (1) becomes more and more important until it finally accounts for 2/3 of the $C_3H_8$ reacting, probably largely due to the presence of excited molecules.

The inhibiting effect (negative temperature coefficient) of the dilutent gases increases in order $CH_4$, $N_2$, $CO_2$, $H_2$; reaction entirely stopped at 425° C. with $H_2$, but slightly retarded at 375°C.

Results indicate the aldehyde reactions involve a chain, and that excited molecules involved are capable of inducing reactions (1) and (2).

Similar results were obtained with $C_4H_{10}$, but the reaction occurs somewhat more readily, 400° for normal and 450° for isobutane. The aldehyde reaction occurs to a greater extent than with propane.

An investigation of the non-catalytic oxidation of octanes and heptaldehyde has been made by Pope, Dykstra, and Edgar:

---

Pope, Dykstra and Edgar, J.A.C.S. **51**, 1875,2203  (1929)

---

From analysis of gaseous products they conclude that the mechanism involves first the formation of aldehyde:

$$CH_3(CH_2)_6CH_3 + O_2 \longrightarrow CH_3(CH_2)_6CHO + H_2O$$
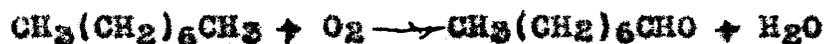
The aldehyde is then oxidized to heptaldehyde with libera-

tion of carbon monoxide or dioxide:

Main reaction: $CH_3(CH_2)_6CHO + O_2 \longrightarrow CH_3(CH_2)_5CHO + H_2O + CO$

Side reaction: $CH_3(CH_2)_6CHO + H_2O_2 \longrightarrow CH_2(CH_2)_5CHO + H_2O + CO_2$

The oxidation then continuing in similar steps, the

product each time being an aldehyde containing one carbon

atom less than the substance being oxidized.

At temperatures above 680° C. oxidation of n-octane to

carbon dioxide and water was found to take place so rapidly

that it was practically explosive. The luminescence asso-

ciated with carbon monoxide formation at the lower temperatures

was still seen. This indicated that the oxidation of aldehydes

to lower aldehydes, carbon monoxide and water also takes

place at the higher temperatures. The luminescence observed

during both low and high temperature oxidation, also

probably indicates the occurrence of chain reactions.

# DATA

## TABLE I

Oxidation of Kerosene

        Temperature of constant temperature bath 180°

        Nitrogen Rate  =  4.54 l./hr.

        Oxygen Rate   =  1.21 l./hr.

| Furnace Temp. (°C.) | Analysis of Exit Gases | | |
|---|---|---|---|
| | % $O_2$ | % $CO_2$ | % CO |
| 200 | 20.7 | 0.0 | 0.0 |
| 252 | 20.6 | 0.0 | 0.0 |
| 304 | 20.5 | 0.0 | 0.0 |
| 349 | 19.9 | 0.2 | 0.0 |
| 400 | 20.0 | 0.3 | 0.2 |
| 440 | 18.3 | 0.2 | 0.2 |
| 486 | 18.0 | 0.9 | 1.2 |
| 514 | 14.9 | 2.0 | 2.8 |
| 542 | 13.4 | 2.7 | 3.0 |
| 580 | 1.0 | 10.6 | 0.4 |

TABLE II

Oxidation of n-Tridecane

Bath Temperature = 105°C.

Nitrogen Rate    4.56 1./hr.

Oxygen Rate    1.21 1./hr

| Furnace Temp. (°C.) | Analysis of exit gases | | |
|---|---|---|---|
| | % $O_2$ | % $CO_2$ | % CO |
| 198 | 20.7 | 0.0 | 0.0 |
| 272 | 20.7 | 0.0 | 0.0 |
| 320 | 20.6 | 0.0 | 0.0 |
| 408 | 20.6 | 0.1 | 0.0 |
| 435 | 20.5 | 0.1 | 0.0 |
| 490 | 20.4 | 0.1 | 0.0 |
| 509 | 20.2 | 0.1 | 0.1 |
| 553 | 20.1 | 0.2 | 0.1 |
| 598 | 20.0 | 0.2 | 0.3 |
| 645 | 19.7 | 0.4 | 0.2 |

## TABLE III

### Oxidation of n-tridecane.

Furnace temperature = $600^0$ C.

Nitrogen Rate = 4.54 l./hr.

Oxygen Rate = 1.21 l./hr.

| Constant Temp. Bath (°C.) | Analysis of Exit Gases | | |
|---|---|---|---|
| | % $O_2$ | %$CO_2$ | % CO |
| 104 | 20.1 | 0.3 | 0.2 |
| 120 | 19.8 | 0.3 | 0.2 |
| 125 | 19.7 | 0.4 | 0.4 |
| 150 | 18.8 | 0.6 | 0.5 |
| 160 | 18.4 | 0.8 | 0.6 |
| 170 | 16.7 | 1.5 | 1.0 |
| 180 | 0.9 | 10.7 | 2.6 |

## TABLE IV

### Oxidation of n-Tridecane

Bath Temperature = 180°C.

Nitrogen Rate     4.54 l./hr.

Oxygen Rate       1.21 l./hr.

| Furnace Temp. (°C.) | Analysis of Exit Gases | | |
|---|---|---|---|
| | % $O_2$ | % $CO_2$ | % CO |
| 300 | 20.4 | 0.0 | 0.0 |
| 348 | 20.2 | 0.1 | 0.0 |
| 401 | 19.8 | 0.2 | 0.0 |
| 450 | 18.7 | 0.5 | 0.3 |
| 480 | 18.2 | 0.5 | 0.4 |
| 504 | 16.7 | 0.7 | 0.5 |
| 522 | 14.7 | 0.6 | 0.5 |
| 540 | 14.3 | 1.0 | 1.5 |
| 554 | 12.6 | 1.2 | 1.8 |
| 570 | 2.2 | 9.5 | 1.4 |
| 576 | 1.0 | 10.7 | 0.6 |
| 592 | 0.7 | 12.6 | 0.2 |
| 608 | 1.1 | 12.9 | 0.1 |
| 625 | 0.9 | 13.4 | 0.1 |

# TABLE V

## Oxidation of 2,2,4-Trimethyl Pentane

Bath Temperature = 7°C.

Nitrogen Rate = 4.54 l./hr.

Oxygen Rate = 1.21 l./hr.

| Furnace Temp. (°C.) | Analysis of Exit Gases | | |
|---|---|---|---|
| | % $O_2$ | % $CO_2$ | % CO |
| 348 | 20.7 | 0.0 | 0.0 |
| 404 | 20.6 | 0.0 | 0.0 |
| 450 | 20.5 | 0.2 | 0.0 |
| 509 | 19.4 | 0.2 | 0.1 |
| 549 | 15.7 | 0.6 | 1.0 |
| 578 | 6.4 | 1.0 | 3.3 |
| 609 | 0.6 | 7.3 | 0.2 |

Fig. IV

KEROSENE
△ OXYGEN
⊙ CARBON MONOXIDE
⊗ CARBON DIOXIDE

PERCENT BY VOLUME

FURNACE TEMPERATURE (°C)

FIG. V

N-TRIDECANE
△ OXYGEN
⊙ CARBON MONOXIDE
⊗ CARBON DIOXIDE

PERCENT BY VOL. (%)

BATH TEMPERATURE (°C)

FIG. VI

Percent by Volume (y-axis)

Furnace Temperature (°C) (x-axis)

N- Tridecane
△ Oxygen
⊙ Carbon Monoxide
⊗ Carbon Dioxide

FURNACE TEMPERATURE (°C)

PERCENT BY VOLUME

2,2,4-TRIMETHYL PENTANE

△ OXYGEN
⊙ CARBON MONOXIDE
⊗ CARBON DIOXIDE
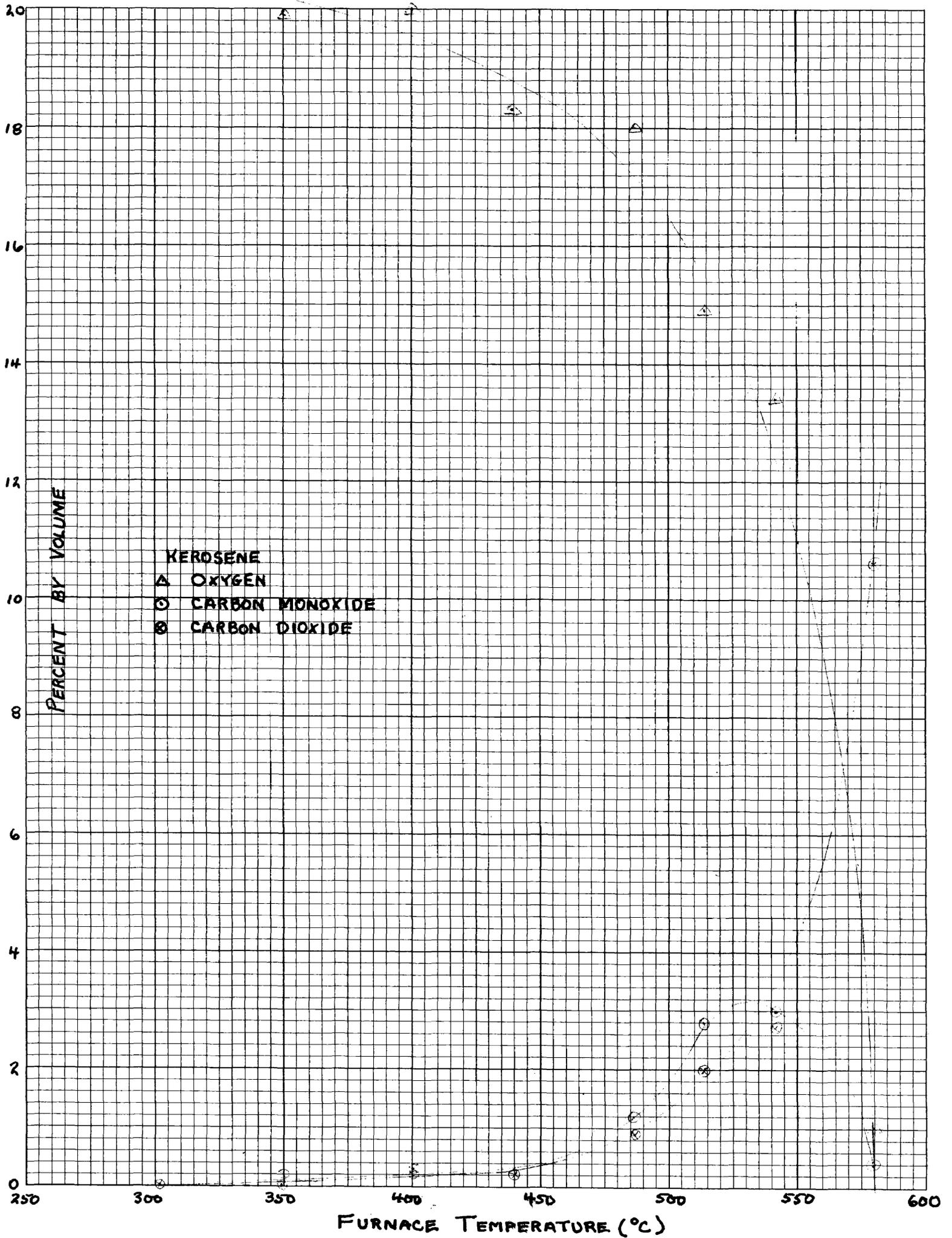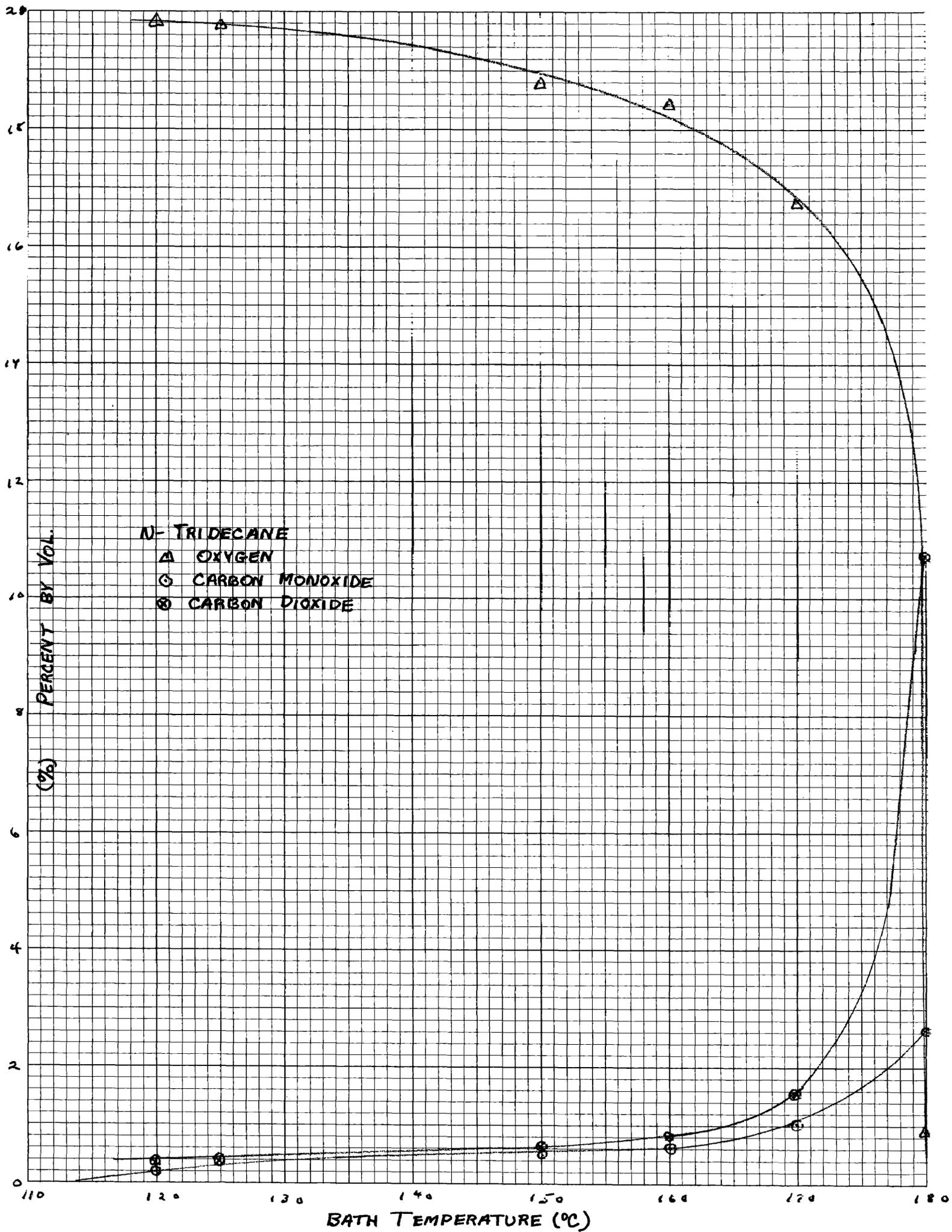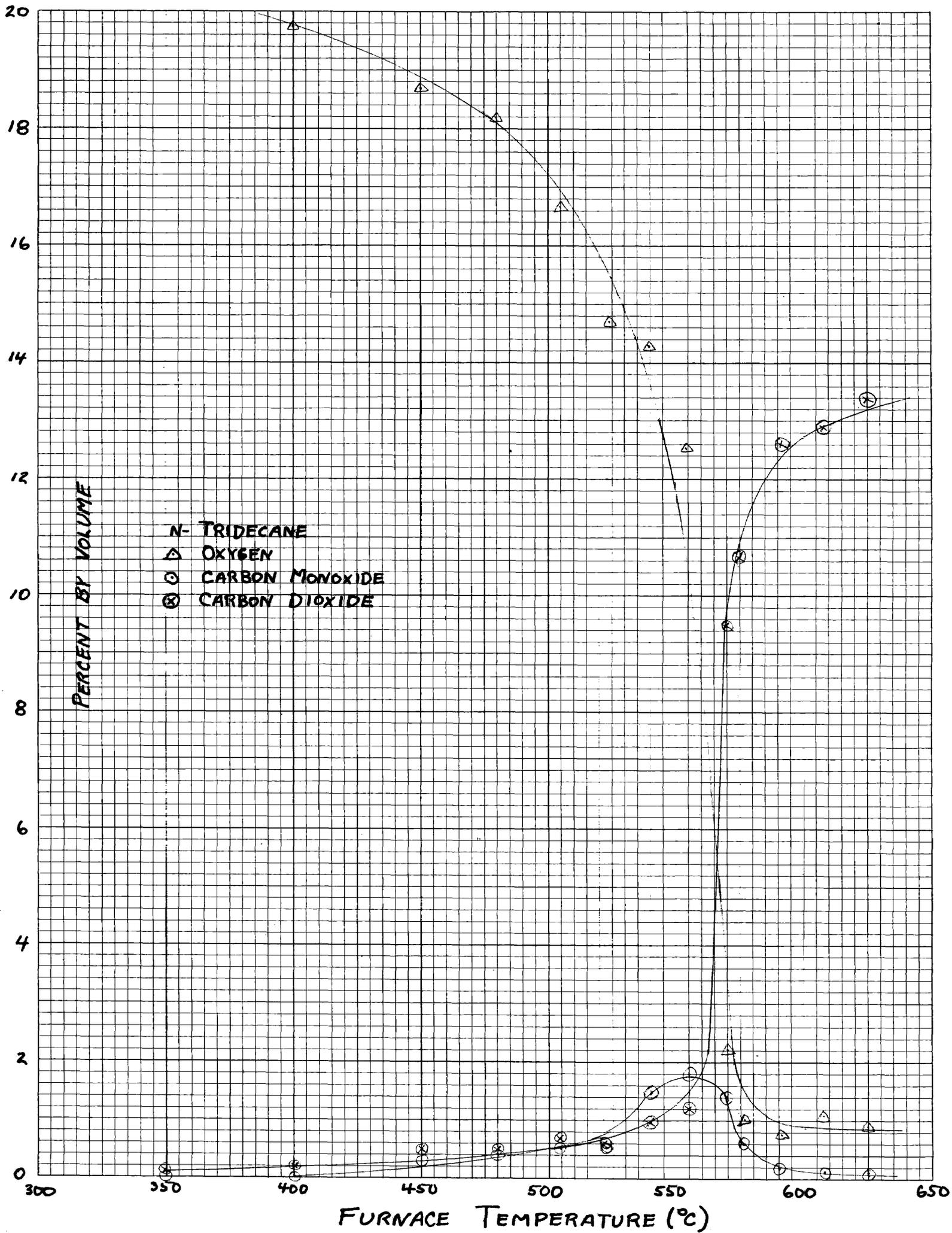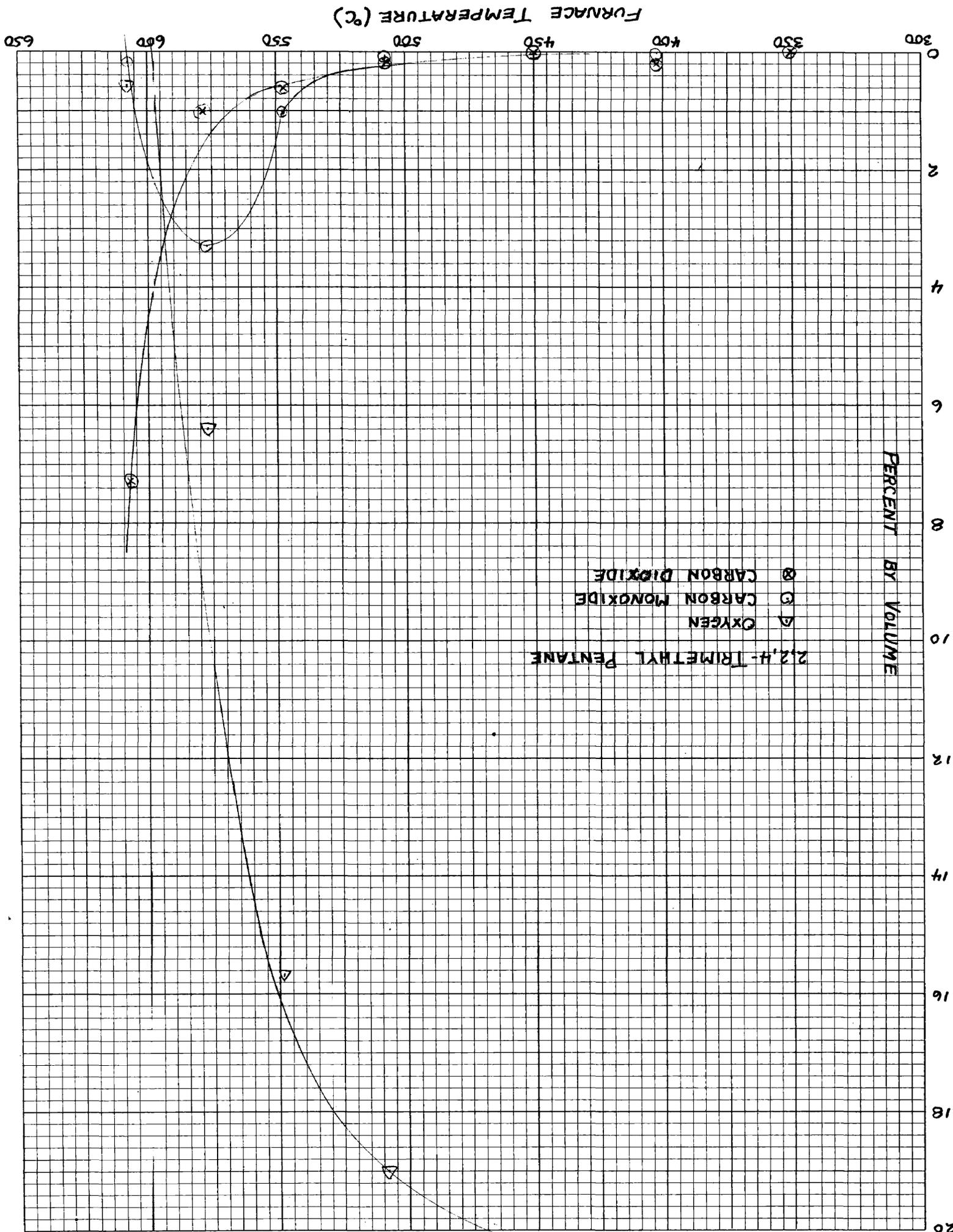
FIG. VII

## G. DISCUSSION OF RESULTS

The combined liquid products from a complete run were treated with litmus and in all cases there was an indication of acid formation. Similarly, a test with fuchsin produced a red color indicating that aldehydes were formed. The addition of potassium iodide solution and then starch gave a blue color, but as previously pointed out this may be due to aldehydes oxidizing to peroxides, and not to peroxides formed as intermediates.

When the varidus hydrocarbons were passed through the reaction tube in the absence of oxygen, there was no evidence of thermal decomposition. A slow combustion analysis for hydrogen and paraffin gas was made at 500°C on each sample, and the results indicate that if these are formed during the oxidation, they are further oxidized before leaving the reaction tube.

The gaseous oxidation products of the hydrocarbons are carbon monoxide, carbon dioxide, and a small amount of some gas absorbed by fuming sulfuric acid, the nature of which was not determined. Its amount were very small and possibly is composed of uncondensed organic compounds, such as an aldehyde vapor

Table IV and the graphical representation in Figure VI indicate that the n-tridecane oxidizes in a manner similar to n-octane as shown by Edgar. That is, the appearance of water and aldehydes, and the similarity of this curve with that formed for n-heptaldehyde and n-butyraldehyde strongly suggest that the

primary oxidation product is the aldehyde. The aldehyde then further oxidizes to form aldehydes of lower molecular weight, as given previously.

The small amounts of oxidation products shown in Table II indicate that the hydrocarbon-oxygen ratio was below that necessary to utilize the oxygen completely. In order to demonstrate that the increase in the ratio would increase proportionally the products formed, table III and figure V are included. It is observed that as the oxygen decreases, the carbon monoxide and dioxide increase in the same order of magnitude.

Table V and figure VII are given to illustrate the fact that the results for 2,2,4-trimethyl pentane agree with those found by Edgar. The curves agree as to general type with the additional data presented for higher temperatures.

In order to observe whether a hydrocarbon mixture would ox oxidize in the same manner, a kerosene fraction was oxidized, and the results presented in table I and figure IV, indicating that the general nature of hydrocarbon oxidation at least involves the formation of aldehydes at some intermediate stage and then the further oxidation of these aldehydes takes place.

# SUMMARY

Kerosene, n-tridecane, and 2,2,4-trimethyl pentane under the experimental conditions, in absence of oxygen, do not thermally decompose to yield gaseous products.

Kerosene, n-tridecane, and 2,2,4-trimethyl pentane oxidize under the experimental conditions to yield CO and $CO_2$ as gaseous products.

Kerosene, n-tridecane and 2,2,4-trimethyl pentane yield unidentified acids and aldehydes. No evidence of peroxide formation.

Oxidation of n-tridecane appears to take place by the same mechanism regardless of the hydrocarbon-oxygen ratio, but the extent of oxidation is greater, the larger the ratio.

The experimental results indicate that the mechanism of oxidation involves, primarily, the formation of aldehydes, and further that decomposition and oxidation of these intermediates yields CO, $CO_2$ and $H_2O$.

## BIBLIOGRAPHY

1. Bull. Soc. Chim. (2) **47**, 48 (1887)

2. Ber. **45**, 2180 (1912)

3. Compt. rend. **158**, 834 (1918)

4. Ber. **57B**, 1815 (1924)

5. J.A.C.S. **49**, 1070 (1927)

6. Org. Syn. Col. Vol. I, 221 (1932)

7. Org. Syn. **12**, 48

8. Gattermann and Wieland, 370 (1932)

9. Master Thesis, U. of Md. 15 (1936)

10. J.A.C.S. **21**, 1084 (1899)

11. J.A.C.S. **52**, 1092 (1931)

12. Natl. Bur. Stds., RP809, **15**, 52 (1936)

13. C. Zentrablatt, II, 104 (1912)

14. Ber. **15**, 1699 (1882)

15. J.A.C.S. **55**, 2399 (1923)

16. Org. Syn. Col. Vol. I, 26 (1932)

17. Org. Syn. Col. Vol. I, 299 (1932)

18. Ind. Eng. Chem. **19**, 146 (1927)

19. Att accad. Lincei **19**, II 601 (1910)

20. A.C.J. **28**, 170 (1902)

21. J.A.C.S. **55**, 2607 (1933)