

THE PYROLYSIS OF DIALLYL
AND
REACTIONS OF ALLYL RADICALS
WITH 1-BUTENE

by

DALIBOR J. RUZICKA

cand. mag. (University of Oslo) 1956

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in the Department
of
Chemistry

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

June, 1958

A B S T R A C T

A study has been made of the pyrolysis of 1,5-hexadiene (diallyl) and of the reactions of the allyl radicals thus produced with 1-butene.

The pyrolysis of 1,5-hexadiene was found to be first order and appears to proceed mainly by free radical reactions in the temperature range 460 - 520° C. However, molecular rearrangement in the formation of cyclohexene and benzene are possible. The over-all activation energy for the process was found to be 31.3 kcal/mole for an A factor of $10^{8.5} \text{ min}^{-1}$. The main products among the gaseous compounds were methane, ethane, ethylene, propylene, and 1-butene. The main liquid products were cyclopentene, cyclopentadiene, 1-hexene and benzene. Evidence was obtained for hydrogen abstraction by allyl and addition of the allyl radical to olefinic double bonds. Activation energies for the formation of methane, ethane, propane, ethylene, propylene and 1-butene were determined.

Addition of approximately 5 % by volume of 1,5-hexadiene was found to increase the rate of the pyrolysis of 1-butene about 6 - 7 times at 506° C. The formation of C_5 -cyclic products and methane was found to be proportional to $(\text{diallyl})^{1/2}$. This provides kinetic evidence that allyl radicals are involved directly in the formation of these products in the sensitized decomposition and also that the primary step in the pyrolysis of diallyl involves the formation of two allyl radicals. Mechanism for the pyrolysis of diallyl and for the reactions of allyl with 1-butene are discussed.

A brief study has also been made of the pyrolysis of 1-butene in the presence of acetaldehyde. The thermal decomposition of 1-butene sensitized by addition of 25 % by volume of acetaldehyde was carried out at 477° C.

The decomposition of acetaldehyde was found to be inhibited by the presence of 1-butene by a factor of more than two. 1-butene, which practically does not decompose at the above temperature by itself, decomposes appreciably in the presence of acetaldehyde.

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representative. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia

Vancouver 8, Canada

June 27, 1958

A C K N O W L E D G E M E N T S

This investigation was carried out under the direction of Dr. W.A. Bryce to whom the author is greatly indebted.

Thanks are due to Mr. S.A. Ryce for the use of his gas chromatographic apparatus as well as for many valuable discussions.

Mr. E.W.C. Clarke carried out the mass spectrometric analyses which was gratefully appreciated.

The author is also indebted to the Defence Research Board for financial assistance during the course of this work and to the British Columbia Sugar Refining Company Limited for a graduate scholarship (1957 - 1958).

T A B L E O F C O N T E N T S

| | Page |
|---|------|
| INTRODUCTION | 1 |
| GENERAL | 1 |
| HISTORICAL | 2 |
| EXPERIMENTAL | 4 |
| PYROLYSIS APPARATUS | 4 |
| METHOD OF PYROLYSIS | 6 |
| ANALYSES OF THE REACTION PRODUCTS BY GAS CHROMATOGRAPHY | 7 |
| Apparatus | 7 |
| Separation of the products | 9 |
| Product Identification | 10 |
| Quantitative determination of the products | 12 |
| Qualitative and quantitative determination of hydrogen | 13 |
| Analytical results | 14 |
| RESULTS | 17 |
| I. PYROLYSIS OF 1,5-HEXADIENE | 17 |
| Order of the reaction | 17 |
| Pressure increase in reaction system | 17 |
| Rate and over-all energy of activation for the pyrolysis of 1,5-Hexadiene | 17 |
| Rates of formation and over-all activation energies for the light hydrocarbons | 19 |
| Temperature and time dependence in the formation of products | 26 |
| II. PYROLYSIS OF 1-BUTENE IN THE PRESENCE OF DIALLYL | 32 |
| Introduction | 32 |

| | Page |
|--|------|
| Results for the decomposition of 1-butene sensitized by diallyl | 32 |
| III. PYROLYSIS OF n-BUTANE IN THE PRESENCE OF 1,5-HEXADIENE | 37 |
| IV. PYROLYSIS OF 1-BUTENE IN THE PRESENCE OF ACETALDEHYDE | 39 |
| DISCUSSION | 43 |
| PRECISION OF THE QUANTITATIVE DETERMINATIONS OF GAS CHROMATOGRAPHY | 43 |
| UNCERTAINTY IN THE VALUES OF THE KINETIC RATE CONSTANTS | 44 |
| THE OVER-ALL ACTIVATION ENERGY FOR THE DECOMPOSITION OF 1,5-HEXADIENE | 46 |
| MECHANISM OF THE PYROLYSIS OF 1,5-HEXADIENE | 48 |
| General | 48 |
| Reactions of the allyl radical | 49 |
| (1) Hydrogen abstraction by allyl | 49 |
| (2) Addition of allyl to double bond | 51 |
| (3) Combination of allyl with other radicals | 53 |
| The fate of the 1,5-hexadienyl radical | 54 |
| (1) Rearrangement | 54 |
| (2) Decomposition | 55 |
| (3) Combination with other radicals | 55 |
| Formation and reactions of other radicals | 55 |
| Mechanism for the formation of the pyrolysis products | 57 |
| MECHANISM OF THE THERMAL DECOMPOSITION OF 1-BUTENE SENSITIZED BY DIALLYL | 60 |
| (1) Addition to the double bond | 60 |
| (2) H-abstraction | 61 |
| DECOMPOSITION OF n-BUTANE SENSITIZED BY DIALLYL | 62 |

| | Page |
|---|------|
| BIBLIOGRAPHY | 64 |
| APPENDIX | |
| MASS SPECTROMETRIC IDENTIFICATION OF SOME OF THE PRODUCTS | 66 |

TABLES

| | Page |
|---|------|
| I. Products of 1,5-Hexadiene Pyrolysis (Mole %) at Various Temperatures | 15 |
| II. Rate Constants for the Over-all Decomposition of 1,5-Hexadiene | 20 |
| III. Rate Constants for the Over-all Decomposition of 1,5-Hexadiene for Different Reaction Times | 20 |
| IV. Rate Constants (min^{-1}) for the Formation of the Light Products | 23 |
| V. Energies of Activation and Frequency Factors for the Formation of the Light Products | 23 |
| VI. Decomposition Products of 1,5-Hexadiene Pyrolysis as a Function of Time at 501° C. | 31 |
| VII. Composition of the Reaction Mixture for Sensitized Decomposition of 1-Butene with 1,5-Hexadiene | 35 |
| VIII. Main Products of Pyrolysis of n-Butane and Sensitized Pyrolysis of n-Butane by Addition of Appr. 5 % by Volume of 1,5-Hexadiene at 506° C. Reaction Time 5 Minutes. | 38 |
| IX. Percentage of Decomposition of Acetaldehyde and 1-Butene at 477° C. | 40 |

FIGURES

| | Page |
|--|------|
| 1a. Pyrolysis Apparatus | 5 |
| 1b. Circuit Diagram of Furnace Heaters | 5 |
| 2a. Gas Chromatography Apparatus | 8 |
| 2b. Charcoal Trap System | 8 |
| 2c. U-Tube Trap | 8 |
| 3. Gas Chromatographic Separation of the Pyrolysis Products | 11 |
| 4. Pressure Change vs. Time for 1,5-Hexadiene | 18 |
| 5. Arrhenius Plot for Decomposition of 1,5-Hexadiene | 21 |
| 6. Arrhenius Plots for the Light Saturated Products in the Pyrolysis of 1,5-Hexadiene | 24 |
| 7. Arrhenius Plots for the Light Unsaturated Products in the Pyrolysis of 1,5-Hexadiene | 25 |
| 8. Light Products of the Pyrolysis of 1,5-Hexadiene vs. Temperature. Reaction Time 5 Minutes | 27 |
| 9a and 9b. Hydrogen and the Heavy Products of the Pyrolysis of 1,5-Hexadiene vs. Temperature. Reaction Time 5 Minutes. | 28 |
| 10. Products of the Pyrolysis of 1,5-Hexadiene vs. Time at 501° C. | 29 |
| 11. Heavy Products of the Pyrolysis of 1,5-Hexadiene vs. Time at 501° C. | 30 |
| 12. Pressure Change vs. Time at 506° C. Initial Pressure 200 mm. | 33 |
| 13. Products of Sensitized Decomposition of 1-Butene vs. (% Diallyl) ^{1/2} | 36 |
| 14. Extent of Decomposition at 477° C. Initial Pressure 200 mm. I. Acetaldehyde + Helium (1:3) II. Acetaldehyde + 1-Butene (1:3) | 41 |

INTRODUCTION

I N T R O D U C T I O N

GENERAL

Previous work on the thermal decomposition of 1-butene (4,12,19) provided very good evidence that the primary step in the process involves formation of methyl and allyl radicals. By studying the decomposition of 1-butene sensitized by methyl radicals from mercury dimethyl (10) it was further established that the methyl radicals play an important role in the mechanism of the subsequent decomposition.

It is to be expected that the allyl radical formed in the primary step would also participate in the mechanism of the decomposition. Little is known about the reactions of the allyl radical in hydrocarbon systems and therefore a study was undertaken of the fate of allyl in the pyrolysis of 1-butene by sensitizing the decomposition with the allyl radical.

Mercury diallyl and other metal-allyl compounds would be suitable sources of allyl radicals for the investigations. However, they are not available, nor are they mentioned in the literature. It was therefore necessary to use a hydrocarbon as a source of allyl.

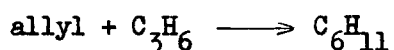
Lossing and co-workers (12) have observed allyl radicals to be the main radical products of the pyrolysis of 1,5-hexadiene (diallyl) in the temperature range 690 -890° C in a mass-spectrometer with a flow reactor. The decomposition of 1,5-hexadiene in a static system at temperatures around 500° C should thus most probably involve generation of allyl radicals in the primary step. It was therefore chosen as the source of allyl radicals for the present study.

A preliminary study of the pyrolysis of diallyl itself was undertaken to gain some insight into the mechanism of its decomposition before using it as a source of allyl radicals in reactions with 1-butene.

HISTORICAL

Very little is known about reactions of allyl radicals. Mooney and Ludlam (16) studied the pyrolysis of allyl bromide but radical mechanisms were not known at that time. This pyrolysis has been studied recently by Szwarc, Gosh and Sehon (23,24) using the toluene carrier technique. They ascribe the overall activation energy of 47.5 kcal to the dissociation of the allyl-Br bond in the primary step. Szwarc (22) has also obtained excellent kinetic evidence for the formation of allyl and hydrogen in the pyrolysis of propylene in a flow system at 680-870° C.

Taylor and Smith (25) mentioned that the resonance characteristics of the allyl radical result in a weak allyl-H bond in propylene. Hence in hydrocarbon systems the resonance stability of the allyl radical (2,5) would be expected to have a long life and to disappear by reactions such as methyl + allyl \longrightarrow 1-butene or by combination with itself to give diallyl. According to the authors the reaction:



may be involved in the polymerization of propylene sensitized by the photolysis of mercury dimethyl, and in the mercury-photosensitized reactions of propylene.

Hydrogen abstraction by allyl has been demonstrated by several workers:

Molera and Stubbs (15) have postulated that hydrogen abstraction by allyl takes place from isobutene in the pyrolysis of isobutene.

Very recently McNesby and Gordon (14) have studied the decomposition of cyclopentane in presence of acetone and found:

at 381° very little hydrogen abstraction by allyl takes place, allyl combines with CH_3 to give 1-butene.

at 453° 1-butene is still present in the system, but hydrogen abstraction by allyl both from cyclopentane and from CD_3COCD_3 takes place.

at 500° extensive abstraction of hydrogen by allyl takes place but also small amount of 1-butene is formed.

Some work has also been done on the reactions of allylic radicals in solution (1).

The information to date on the reactivity of allyl radicals in hydrocarbon systems can be summarized as follows:

- (1) the resonance stability of about 17 kcal/mole (average of values given by 2 and 5) leads to appreciable life-time of the allyl radical so that combination with other radicals may take place.
- (2) abstraction of hydrogen at temperatures above about 450° C takes place.
- (3) addition of allyl to olefinic double bonds may take place.

EXPERIMENTAL

EXPERIMENTAL

PYROLYSIS APPARATUS

The pyrolysis of 1,5-hexadiene was carried out in an all-glass static system (fig. 1a). V is a quartz vessel of a volume of about 300 ml placed in an electric furnace (F), A_1 to A_4 are reservoirs for the gases to be pyrolysed, P is a sampling pipette with a metal-teflon tap to avoid adsorption in stopcock grease. M_1 and M_2 are manometers.

The furnace was heated by means of three heating elements connected as shown in fig. 1b. The potentials across the three heating elements e_1 , e_2 , e_3 , were adjusted so that temperature gradient along the reaction vessel did not exceed 1°C.

Temperature measurements were made by means of two chromel-alumel thermocouples placed in position a and b. A rough calibration curve "applied voltage vs. furnace temperature" was constructed and used for approximate temperature setting. Fine temperature adjustments were obtained by switching the resistance r on or off. The heat capacity of the system was increased by filling the space between reaction vessel and furnace with sand. The purpose of this was to keep the temperature constant for sufficiently long periods of time to carry out a reaction even when strict steady state between the furnace and the surroundings was not reached. This technique proved satisfactory. It was possible to keep the furnace temperature constant during the pyrolysis experiments to within 1° C at 500° C.

In order to prevent condensation in the manometer M_1 and the adjacent capillaries, this part of the system was heated electrically to about 50 -

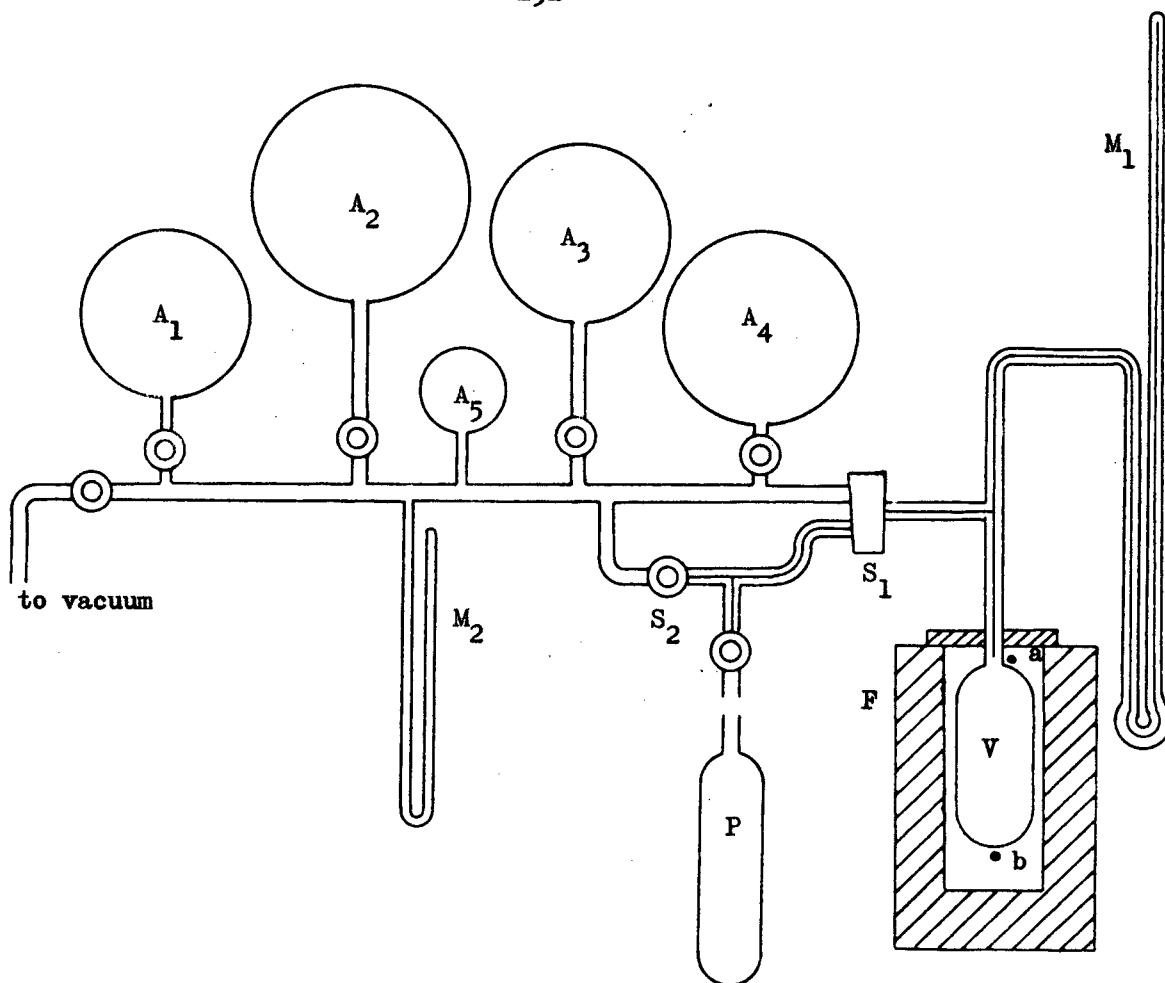


Fig. 1a Pyrolysis Apparatus

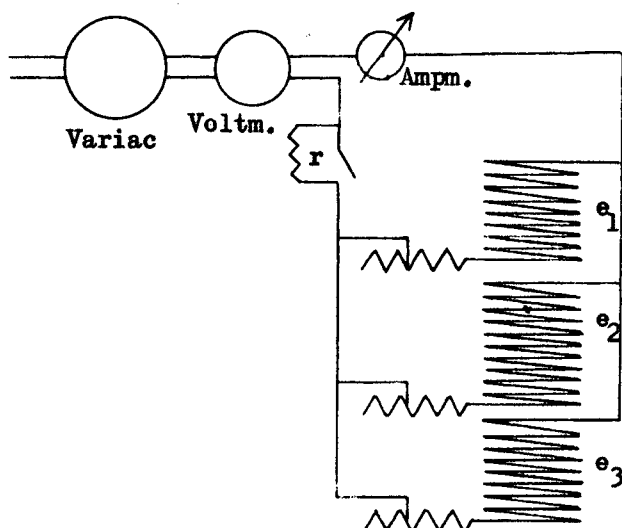


Fig. 1b Circuit Diagram of Furnace Heaters

60° C when necessary.

METHOD OF PYROLYSIS

When pyrolysis experiments are to be carried out in a static system there is the problem of admitting the reactant with a certain initial pressure in the reaction vessel. At the same time the starting point of the reaction should be reasonably well defined.

In order to satisfy both requirements, the volume of the system was increased by attachment of vessel A_5 . A pre-expansion volume was thus created. A calibration curve was constructed giving the dependence between the pressure in the pre-expansion volume (read on manometer M_2) and the pressure in the whole system (which is equal to the initial pressure in the reaction vessel) at different temperatures.

Before each experiment the system was pumped down to "black vacuum" which was tested with a Tesla coil. From the calibration curve the pressure in the pre-expansion volume corresponding to the desired initial pressure in the reaction vessel was read. The pre-expansion volume was filled with the gas or mixture of gases to be pyrolysed. In the case of a mixture 5 minutes was considered to be sufficient for the gases to mix completely. By opening the stopcock S_1 the reactant was admitted into the reaction vessel. The moment when the mercury column in manometer M_1 settled at a certain value was taken as the beginning of the reaction and the initial pressure was read. During the course of the reaction the pressure in the reaction vessel was read at 1 minute intervals. At the end of the reaction the stopcock S_1 was opened (S_2 was closed) such that the products expanded freely into the evacuated sampling pipette.

ANALYSES OF THE REACTION PRODUCTS BY GAS CHROMATOGRAPHY

Apparatus

The separation of the products of the pyrolysis of 1,5-hexadiene and of the allyl sensitized pyrolysis of 1-butene was effected by gas chromatography. A gas chromatograph constructed in the laboratory was available (fig. 2a).

With the exception of H_2 analyses where nitrogen was employed, helium was used as the carrier gas in all analyses. A self-compensating thermal conductivity cell (18) was the detector. Several gas chromatographic columns with different packings were available. The unbalance signal from the thermal conductivity cell mounted in a bridge circuit was recorded on a chart of a Speedomax recording potentiometer.

The existing gas chromatograph had to be modified for the present analysis:

- a) a second column furnace was built and attached to the apparatus so that two chromatographic columns, one for light hydrocarbons and the other for heavier hydrocarbons, could now be connected in parallel. This enabled a quick switch from one column to the other by merely turning the stopcocks S_3 and S_4 (fig. 2a).
- b) it was found that the amount of sample admitted into the bypass by free expansion from the sampling pipette was insufficient. A Toepler pump was therefore attached to the admission system. The efficiency of the pump was such that in the first pumping operation the pressure in the admission volume was increased more than four times.
- c) Moisture was shown to be not the only impurity in the helium carrier gas, and therefore the $CaCl_2$ purifying tower alone was not sufficient. Two charcoal traps were fitted to the apparatus as indicated in fig. 2b.

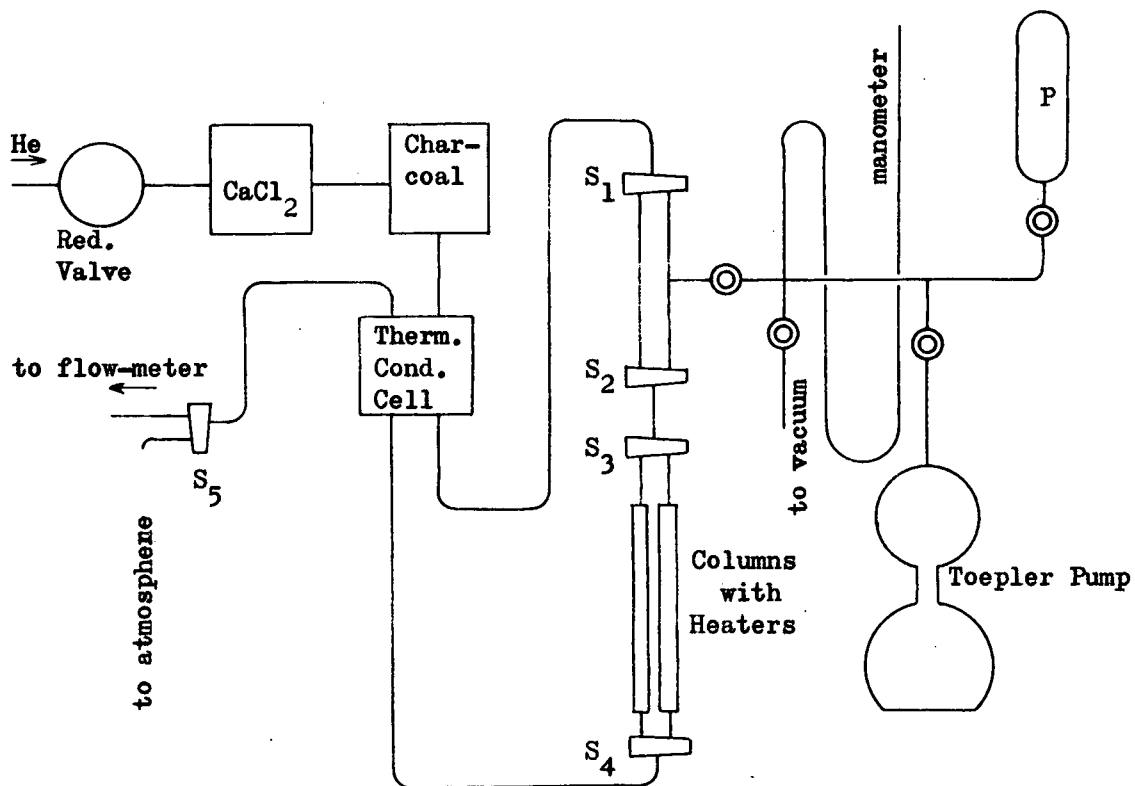


Fig. 2a Gas Chromatography Apparatus

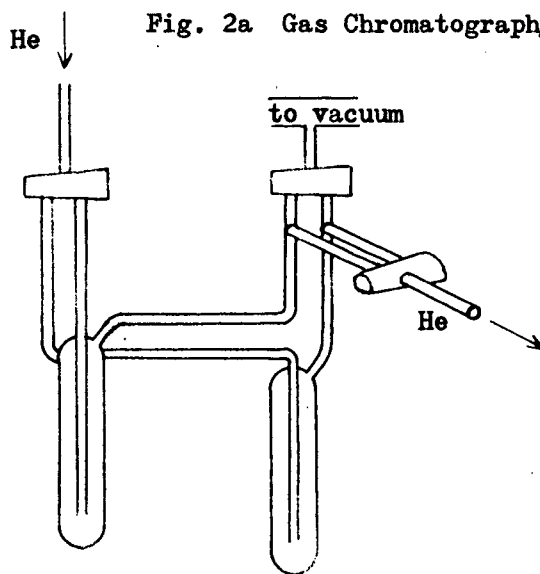


Fig. 2b Charcoal Trap System

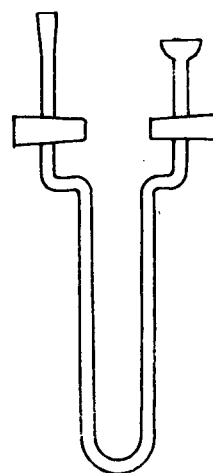


Fig. 2c U-Tube Trap

While one was being used as a purifier, the other was regenerated by evacuating and heating to about 300° C.

Separation of the products

Previous experience in this laboratory (9) had shown that two columns were necessary to separate the components of a mixture of products with such widely varying boiling points as that obtained from the decomposition of 1-butene. The light products, i.e. methane, ethane, etc., up to 1-butene had been successfully resolved on an alumina column (i.e. an adsorption-elution column). Products of higher boiling points than 1-butene were separated on a Tri Cresyl Phosphate (TCP) column (i.e. a partition elution column). Both columns had been operated with rising column temperature to decrease the elution times.

In the present work, however, it appeared desirable, with a view to quantitative measurements, to use one column only. While the TCP column had been found satisfactory to separate the products of boiling point higher than 1-butene (9), the lighter products were not satisfactorily resolved on this column.

An attempt was therefore made to separate all the products of the butene decomposition on a TCP column 12 feet long (i.e. twice the length of the column previously used for this kind of work in this laboratory). Fire brick was used as a support for the TCP to give a lower flow resistance (6) than that obtained with Celite.

The separation of the products was better on this column of double length. All the light products were in fact separated, except ethane and ethylene. The column was lengthened further to 18 feet (i.e. three

times the original length) but even this was not sufficient to separate ethane and ethylene. In the end it was found that a 6 foot alumina column was sufficient to separate all the products of the pyrolysis of 1,5-hexadiene if it was gradually heated to high enough temperature.

It was found important to purge the column from high boiling compounds previous to each run. A standard purging method was to heat the column to 210° C for about 30 minutes with the carrier gas flowing.

The separation of the products of the hexadiene pyrolysis are shown in the chromatogram (fig. 3). The light products are clearly separated. Although two pairs of the products following 1-butene are not completely resolved, the separation was sufficient for identification of the products and for their quantitative estimate.

Product Identification

All the light products were identified by comparison of present analysis charts with those previously obtained in this laboratory. An indication of the identity of the higher products was obtained by injection of a pure sample of a compound suspected to be present, together with the reaction products and thus obtaining re-inforcement of a particular peak. Re-inforcement of a particular peak is, however, merely a necessary but not sufficient condition to prove the presence of a compound. Positive identification was effected with a mass spectrometer.

The method adopted was to trap a particular peak. The mixture of the products was admitted onto the column as usual. The stopcock S₅ in fig. 2a was turned so that the gas stream was diverted from the flow meter directly into the atmosphere. A U-tube with two stopcocks (fig. 2c) was cooled in

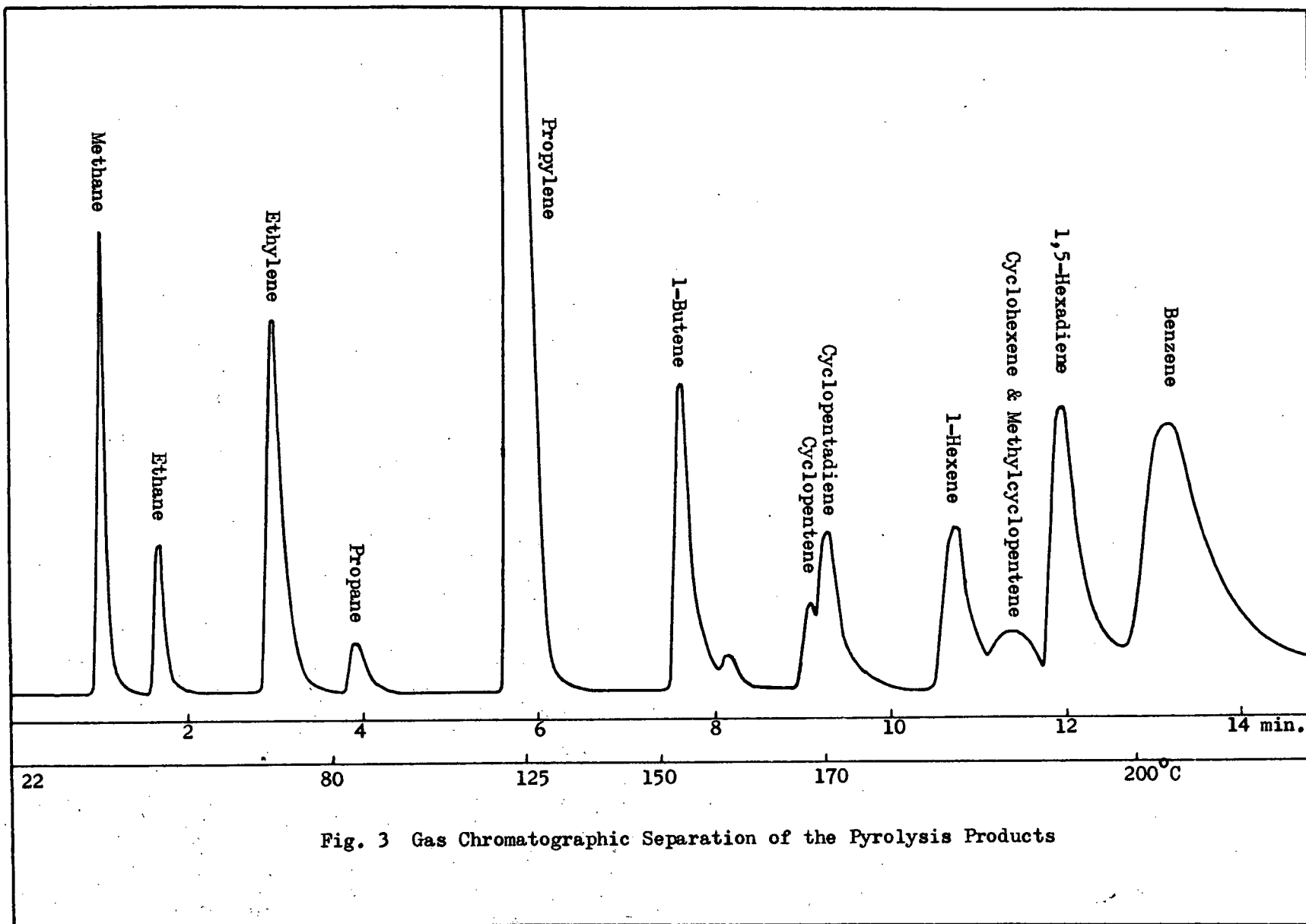


Fig. 3 Gas Chromatographic Separation of the Pyrolysis Products

liquid nitrogen and kept ready to be connected to the outlet from the thermal conductivity cell. As soon as the peak of the compound to be trapped appeared on the chart, the U-tube was attached to the outlet and the gas stream allowed to pass through. The trapped sample of the compound concerned was then analyzed with a mass-spectrometer as described in the Appendix.

Quantitative determination of the products

It has been shown that the peak areas in gas chromatograms are approximately proportional to the amount of the substance put through the column. (6) This relationship was made use of in the present quantitative determinations of the pyrolysis products, although some modifications had to be made because the column was not operated at constant temperature. Also since internal standards for all the reaction products were not available, approximations had to be used in some cases to determine the products quantitatively.

The procedure used was as follows: the pure compounds which were available were mixed in the following proportions:

| <u>Compound:</u> | <u>Percentage:</u> |
|------------------|--------------------|
| Benzene | 11.9 |
| 1,5-hexadiene | 13.9 |
| cyclopentene | 6.28 |
| Butene-1 | 8.28 |
| Propylene | 48.0 |
| Ethane | 12.6 |

The above mixture was run through the gas chromatographic column

under exactly the same conditions as the mixture of reaction products and the peak areas thus obtained were related to the amount of the particular compound.

The compounds for which no internal standards were available had to be determined quantitatively by an approximation. Raising the temperature causes the flow-rate of the carrier gas to decrease which in turn influences the peak areas. Therefore the variation of flow-rate of the carrier gas with column temperature (or time, since the temperature rise as a function of time was well reproducible) was determined. The thermal conductivity of the compound to be determined was assumed to be equal to the thermal conductivity of the internal standard with the closest retention volume. Assuming that the peak areas were inversely proportional to flow rate of the carrier gas (6), correction was then made for the variation of the flow-rate between the peak of the internal standard and the peak of the compound to be determined. The peak areas were measured with a planimeter.

In general two correction factors were applied in the quantitative determinations: correction for the variation in the cell current and in the cell temperature. It was found that a cell current of around 200 ma. of the peak area increased by approximately 1.7 % per ma. current increase. The peak area decreased by approximately 0.6 % when the cell temperature was increased by 1° C.

Qualitative and quantitative determination of hydrogen

Although no hydrogen peak was obtained when analyzing for the products of the pyrolysis of 1,5-hexadiene using alumina column and He as carrier gas it was suspected to be present because of the presence of certain other

compounds. An activated charcoal column was used to separate hydrogen from the other products. Injection of a mixture of hydrogen and methane indicated that these two gases are easily separated by the charcoal column at room temperature. Analyzing for hydrogen with helium as carrier gas, the sensitivity of the apparatus is greatly reduced as the thermal conductivities of hydrogen and helium differ by a factor of 2 only. Hence nitrogen was employed instead of helium. The analytical method was further slightly modified; because of the low heat conductivity of nitrogen (as compared to helium), less heat is removed from the detection filaments in the cell than when helium is used as carrier gas. The temperature of the filaments consequently increases. Since the sensitivity of the detector increases with temperature of the filaments, stability of the base line produced by the recorder was affected. The cell current had to be decreased from 200 ma. to 160 ma. The latter value was found sufficiently low to maintain the base-line stability.

Analytical Results

The composition of the reaction mixture from the pyrolysis of 1,5-hexadiene for 5 minutes at various temperatures is given in Table I. All initial pressures (P_{init}) were 70 mm. except for 506° C where P_{init} was 100 mm. The figures show percentage of sample withdrawn from the reaction vessel.

Table I

Products of 1,5-Hexadiene Pyrolysis (Mole %) at Various Temperatures

| Products | 5 minutes, $P_{init} \sim 70$ mm | | | | | | | |
|-------------------------------------|----------------------------------|-------|------|------|------|------|------|------|
| | <u>° C.</u> | | | | | | | |
| | 460 | 470.5 | 480 | 490 | 501 | 506 | 510 | 521 |
| Hydrogen | 1.0 | 2.0 | 3.3 | 4.5 | 6.3 | 6.5 | 7.0 | 7.8 |
| methane | 1.4 | 1.5 | 2.6 | 4.6 | 4.1 | 6.3 | 5.4 | 7.7 |
| ethane | 0.9 | 0.8 | 1.5 | 2.2 | 2.0 | 3.4 | 2.3 | 2.7 |
| ethylene | 4.7 | 4.2 | 6.7 | 9.2 | 9.2 | 9.2 | 8.4 | 10.3 |
| propane | 0.11 | 0.17 | 0.28 | 0.8 | 0.6 | 1.3 | 1.1 | 1.3 |
| propylene | 18.2 | 16.6 | 26.8 | 35.3 | 35.6 | 36.7 | 31.0 | 35.3 |
| 1-butene | 3.2 | 2.9 | 4.4 | 5.7 | 5.3 | 5.3 | 4.5 | 5.1 |
| cyclopentene | 1.7 | 1.3 | 1.3 | 2.3 | 0.9 | 0.8 | 0.85 | 1.0 |
| cyclopentadiene | 3.2 | 2.6 | 4.5 | 5.4 | 3.9 | 3.1 | 2.6 | 2.5 |
| 1-hexene | 1.7 | 1.5 | 2.4 | 2.7 | 2.2 | 1.6 | 1.9 | 2.2 |
| cyclohexene & methylcyclopentene | 1.4 | 1.4 | 1.6 | 2.1 | 0.7 | 1.0 | 0.6 | 0.7 |
| 1,5-hexadiene | 43.5 | 36.2 | 16.8 | 11.2 | 5.3 | 4.2 | 3.2 | 3.2 |
| benzene | 2.4 | 2.9 | 4.6 | 7.7 | 6.4 | 8.7 | 6.9 | 8.8 |
| Total mole % | 73.4 | 74.1 | 76.8 | 93.7 | 82.5 | 89.1 | 75.8 | 88.6 |

From the above table it can be seen that the analysis has accounted for approximately 70 - 90 % of the reaction products. There may be several reasons for this: (1) Uncertainty in the quantitative gas chromatographic determinations (discussed in a later chapter). (2) The sensitivities for those products for which no internal standards were available

(approximately one half of the products) had to be estimated from the values for similar compounds. (3) Some loss might possibly also be accounted for by assuming that some of the heavier products are so strongly adsorbed to the column that desorption does not take place.

From Table I it can be seen—at least qualitatively—that the "total mole%", i.e. products accounted for, increases with increased temperature. It has been mentioned earlier that the characteristics of the pressure-change vs. time curves for different temperatures (fig. 4) indicate that more of the heavier products are formed at low than at high temperatures. If this is the case the loss should be higher at lower temperatures than at higher temperatures.

Although some doubt exists regarding the absolute values of a few of the concentrations given in Table I, values for the compounds for which internal standards were available should be reasonably accurate. For the other compounds the relative concentrations at the different temperatures should be reliable and are of some considerable interest. On the average about 85% of the pyrolysis products have been accounted for. This should be sufficient to be able to make reasonable assumptions about the principal features of the mechanism of 1,5-hexadiene decomposition.

RESULTS

R E S U L T S

I. THE PYROLYSIS OF 1,5-HEXADIENE

Order of the reaction

The differential method was applied to determine the order of the pyrolysis of 1,5-Hexadiene. The reaction was first order but rose to higher values as extensive decomposition occurred.

Pressure increase in reaction system

In fig. 4 the relative pressure change in the reaction vessel as a function of time is given for temperatures between 460° and 521° C. The pressure dependence curves show a characteristic shape. At lower temperatures the curvature is convex to the time coordinate while at higher temperatures the curvature is concave to the time coordinate. This behaviour should indicate that more products of lower molecular weight than that of 1,5-hexadiene are formed at higher temperatures while relatively more products with higher molecular weight than that of hexadiene are formed at lower temperatures. The pressure change and the distribution of the products will be discussed later.

An attempt was made to make an estimation of the overall activation energy from the initial pressure change in the above mentioned temperature range. The relative pressure change after both 1/2 minute, 1 minute and 2 minutes of reaction was attempted, used for an Arrhenius plot but unsuccessfully.

Rate and overall energy of activation for the pyrolysis of 1,5-hexadiene

As was mentioned above, the kinetic order of the hexadiene pyrolysis

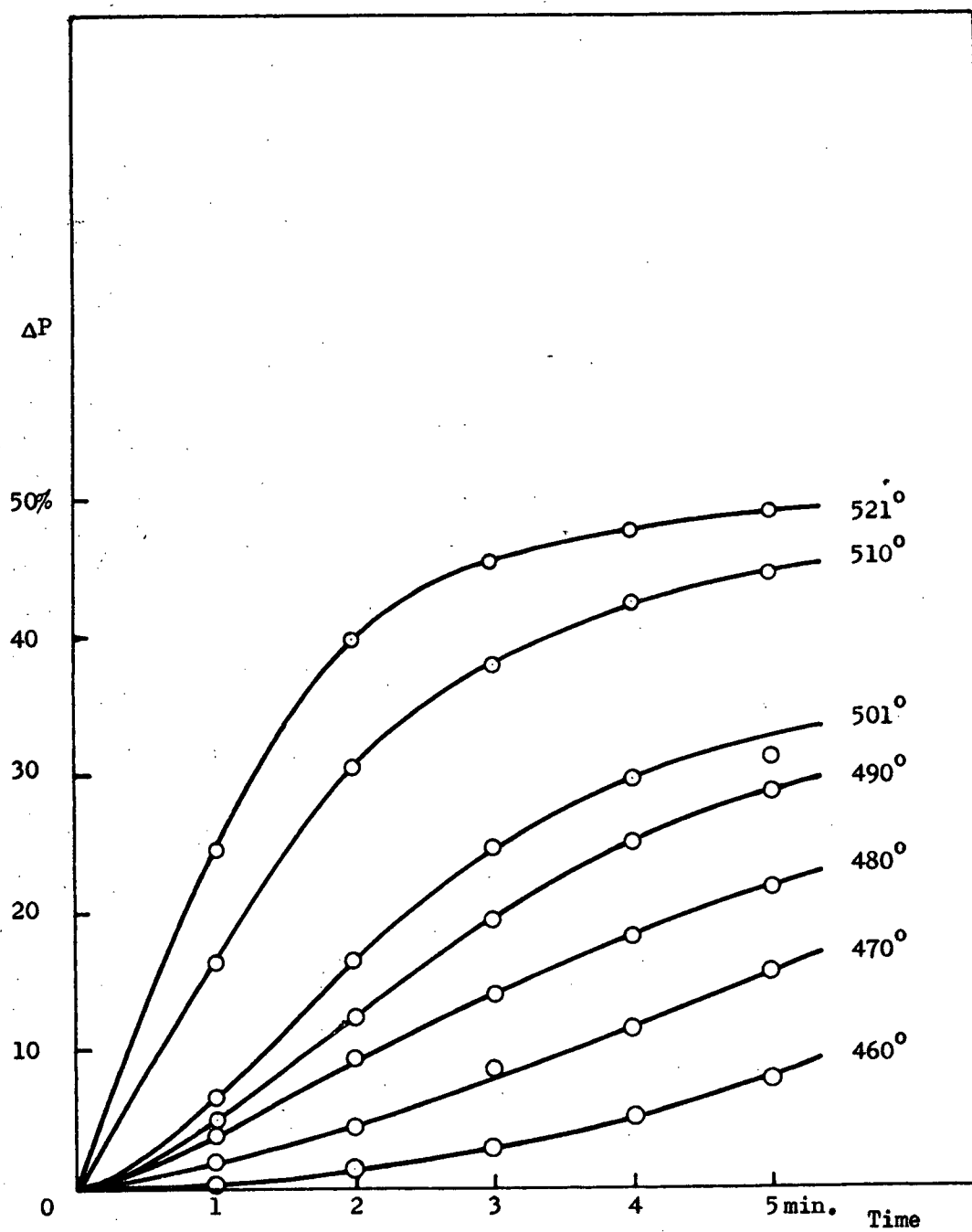


Fig. 4 Pressure Change vs. Time for 1,5-Hexadiene

is approximately first. First order rate constants were therefore calculated for reaction time 5 minutes at different temperatures and are given in table II.

Fig. 5 is the Arrhenius plot for the pyrolysis of 1,5-hexadiene. The activation energy obtained is 31.3 kcal/mole and the frequency factor found to be $10^{8.5} \text{ min}^{-1}$. As a check on the constancy of the rate constants with time several experiments were performed, the results of which are listed in table III. Using the values given in the table an activation energy of 32.6 kcal/mole was obtained for the decomposition of 1,5-hexadiene. This is approximately the same value as the one obtained using the rate constants for reaction time of 5 minutes.

Since the values at 1 and 3 minutes reaction time are considered more unreliable, both because of the high uncertainty in the reaction time and in the determination of the percentage of decomposition, only the values obtained for the reaction time of 5 minutes were used for the Arrhenius plot.

Rates of formation and overall activation energies for the light hydrocarbons

In order to calculate the kinetic rate constants for the formation of the light products from methane to 1-butene it was assumed that their formation is dependent upon the first power of (hexadiene). It has been previously shown (9) that the above dependence exists in the pyrolysis of 1-butene. As the products of the pyrolysis of 1,5-hexadiene are similar to those obtained in the pyrolysis of 1-butene, it was supposed that the mechanisms are very similar and the above assumption should be justified.

The mathematical expression for the rate constants for the formation

Table II

Rate Constants for the Over-all Decomposition of 1,5-Hexadiene

Reaction time 5 minutes. $P_{init} = 70$ mm.

| Temp. | | $1/T$ | % decomp. | $\ln \frac{P_i}{P_f}$ | k (min^{-1}) | $-\ln k$ |
|---------------------|---------------------|------------------|-----------|-----------------------|---------------------------|----------|
| $^{\circ}\text{C.}$ | $^{\circ}\text{K.}$ | $\times 10^{-3}$ | | | | |
| 460 | 733 | 1.365 | 50.5 | 0.705 | 0.141 | 1.960 |
| 470.5 | 743.5 | 1.345 | 61.7 | 0.960 | 0.192 | 1.73 |
| 480 | 753 | 1.328 | 69.5 | 1.19 | 0.238 | 1.44 |
| 490 | 763 | 1.311 | 79.0 | 1.56 | 0.312 | 1.17 |
| 501 | 774 | 1.291 | 89.6 | 2.27 | 0.454 | 0.790 |
| 510 | 783 | 1.278 | 92.6 | 2.60 | 0.520 | 0.653 |

Table III

Rate Constants for the Over-all Decomposition of 1,5-Hexadiene

for Different Reaction Times

| Temp. $^{\circ}\text{C.}$ | k (min^{-1}) | | | \bar{k} | $-\log_{10} k$ |
|------------------------------|---------------------------|--------|--------|-----------|----------------|
| | 1 min. | 3 min. | 5 min. | | |
| 510 | 0.539 | 0.543 | 0.520 | 0.534 | +0.273 |
| 501 | 0.554 | 0.545 | 0.454 | 0.517 | +0.287 |
| 490 | 0.307 | 0.275 | 0.312 | 0.298 | +0.526 |

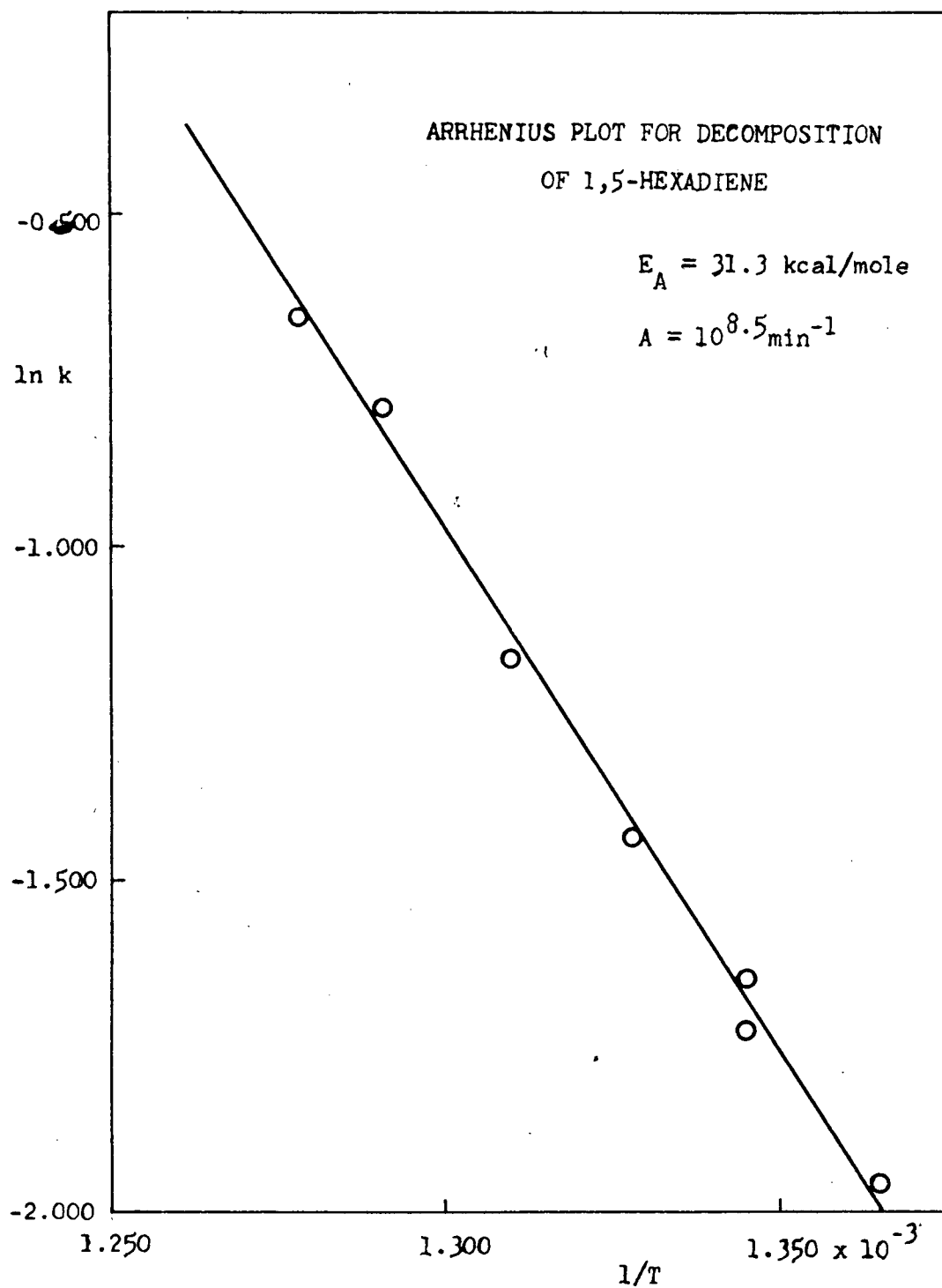


Fig. 5

of the products was derived as follows:

$$\begin{array}{ll} p_p = (\text{product}) & k_p = \text{rate const. for formation of } p. \\ p_h = (\text{hexadiene}) & k_h = \text{ " " " decomposition of hexadiene} \\ p_{ho} = (\text{hexadiene})_{\text{initial}} & \end{array}$$

$$\frac{dp_p}{dt} = k_p p_h \quad \text{where } p_h = p_{ho} e^{-k_h t}$$

$$\frac{dp_p}{dt} = k_p p_{ho} e^{-k_h t}$$

$$\int_0^{p_p} dp_p = \int_0^t k_p p_{ho} e^{-k_h t} dt$$

$$p_p = \frac{k_p}{k_h} p_{ho} (1 - e^{-k_h t})$$

No approximation can be used since $k_h t$ is neither small nor large.

From the above expression the rate constant for the formation of a product can be obtained:

$$k_p = k_h \frac{p_p}{p_{ho}} \frac{1}{1 - e^{-k_h t}}$$

By means of the above expression the rate constants were calculated and are given in Table IV.

Figs. 6 and 7 are the Arrhenius plots for the formation of the saturated and unsaturated light products respectively. Table V gives the energies of activation and the frequency factors obtained from the above graphs.

Table IV

Rate Constants (min^{-1}) for the Formation of the Light Products

| | 460° | 480° | 490° | 501° | 510° | 521° |
|-----------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Methane | 4.24×10^{-3} | 10.6×10^{-3} | 19.7×10^{-3} | 27.0×10^{-3} | 44.0×10^{-3} | 65.9×10^{-3} |
| Ethane | 3.05 | 6.38 | 9.28 | 13.0 | 18.3 | 22.7 |
| Propane | 0.336 | 1.17 | 3.38 | 4.0 | 9.15 | 11.4 |
| Ethylene | 14.3 | 27.7 | 39.3 | 60.8 | 68.1 | 87.8 |
| Propylene | 55.6 | 111.2 | 150.0 | 235.0 | 257.0 | 301 |
| 1-Butene | 9.65 | 18.1 | 24.1 | 34.8 | 36.6 | 43.2 |

Table V

Energies of Activation and Frequency Factors for the
Formation of the Light Products

| Product | E_a (kcal/mole) | A (min^{-1}) |
|-----------|-------------------|---------------------------|
| Methane | 50.1 | $10^{12.6}$ |
| Ethane | 39.1 | $10^{9.1}$ |
| Propane | 65.4 | $10^{16.1}$ |
| Ethylene | 32.8 | $10^{8.9}$ |
| Propylene | 36.0 | $10^{8.5}$ |
| 1-Butene | 33.9 | $10^{8.0}$ |

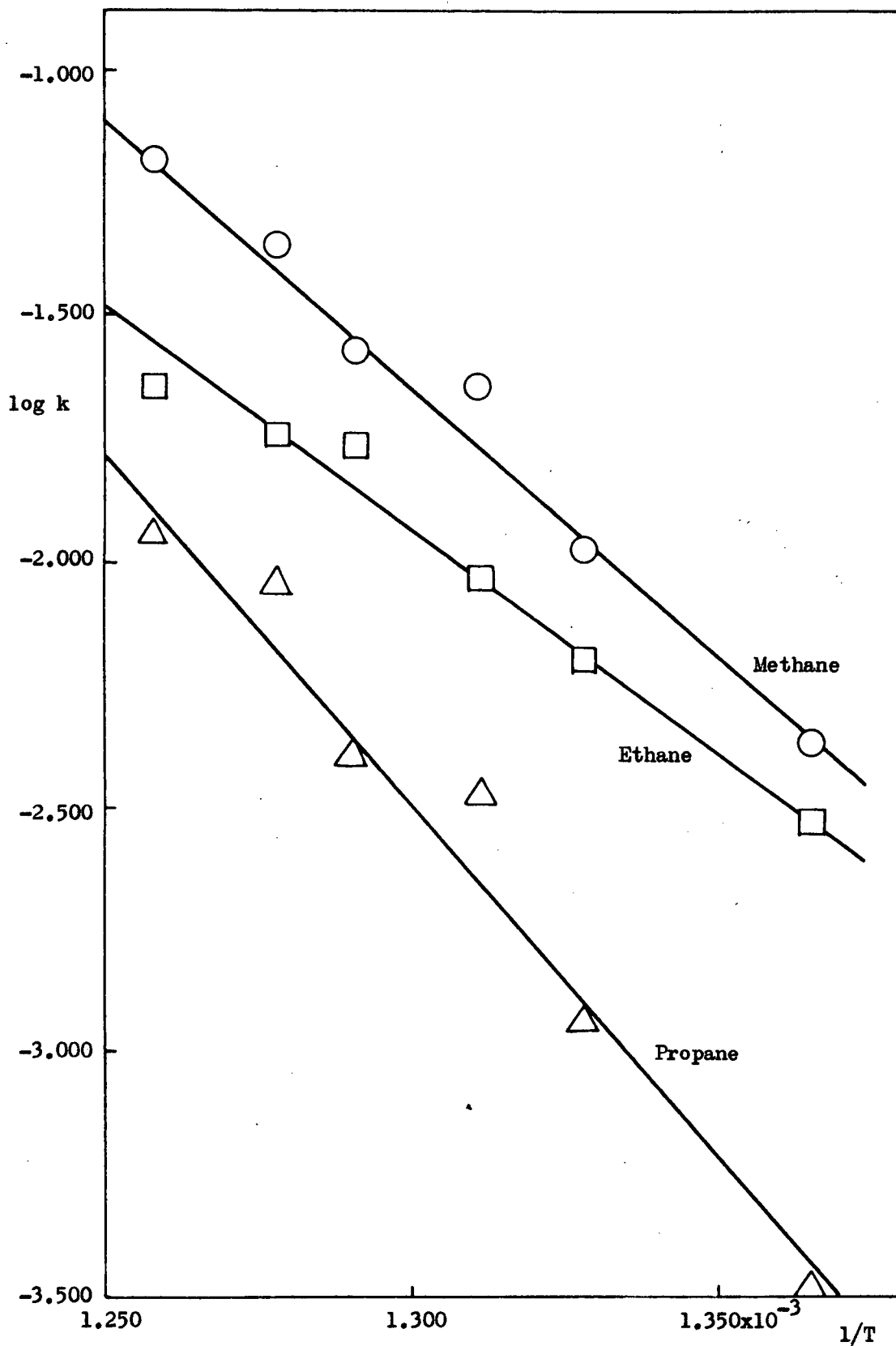


Fig. 6 Arrhenius Plots for the light saturated Products in the Pyrolysis of 1,5-Hexadiene

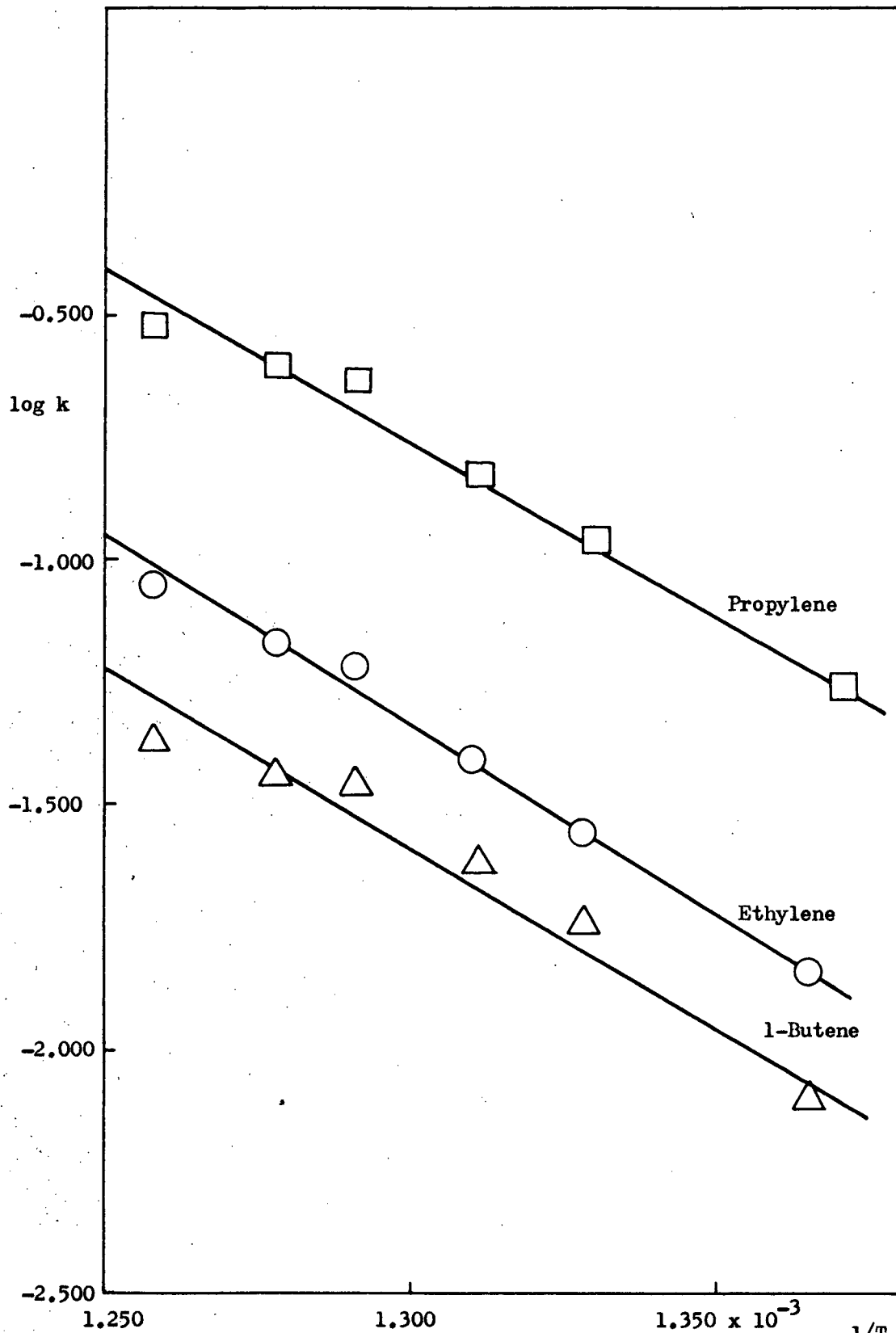


Fig. 7 Arrhenius Plots for the light unsaturated Products in the Pyrolysis of 1,5-Hexadiene

Temperature and time dependence in the formation of products

Table I [from quantitative determination of the products] was used to construct the graphs in figures 8, 9a, and 9b giving the concentrations of the different products at different temperatures after a reaction time of 5 minutes. It is seen that the concentrations of the saturated products increases with temperature while the concentrations of the unsaturated products increase to a certain point and then gradually decrease. This fact can be explained by decomposition (presumably attack by free radicals present in the system) of the unsaturated products formed. More attention will be paid to this fact in a later chapter.

Similarly the dependence of the concentration of the products at 501° C on the reaction time was plotted in figs. 10 and 11 using the values given in table VI. Also in this case there is an indication that the unsaturated products, both acyclic and cyclic, undergo decomposition in later stages of the reaction.

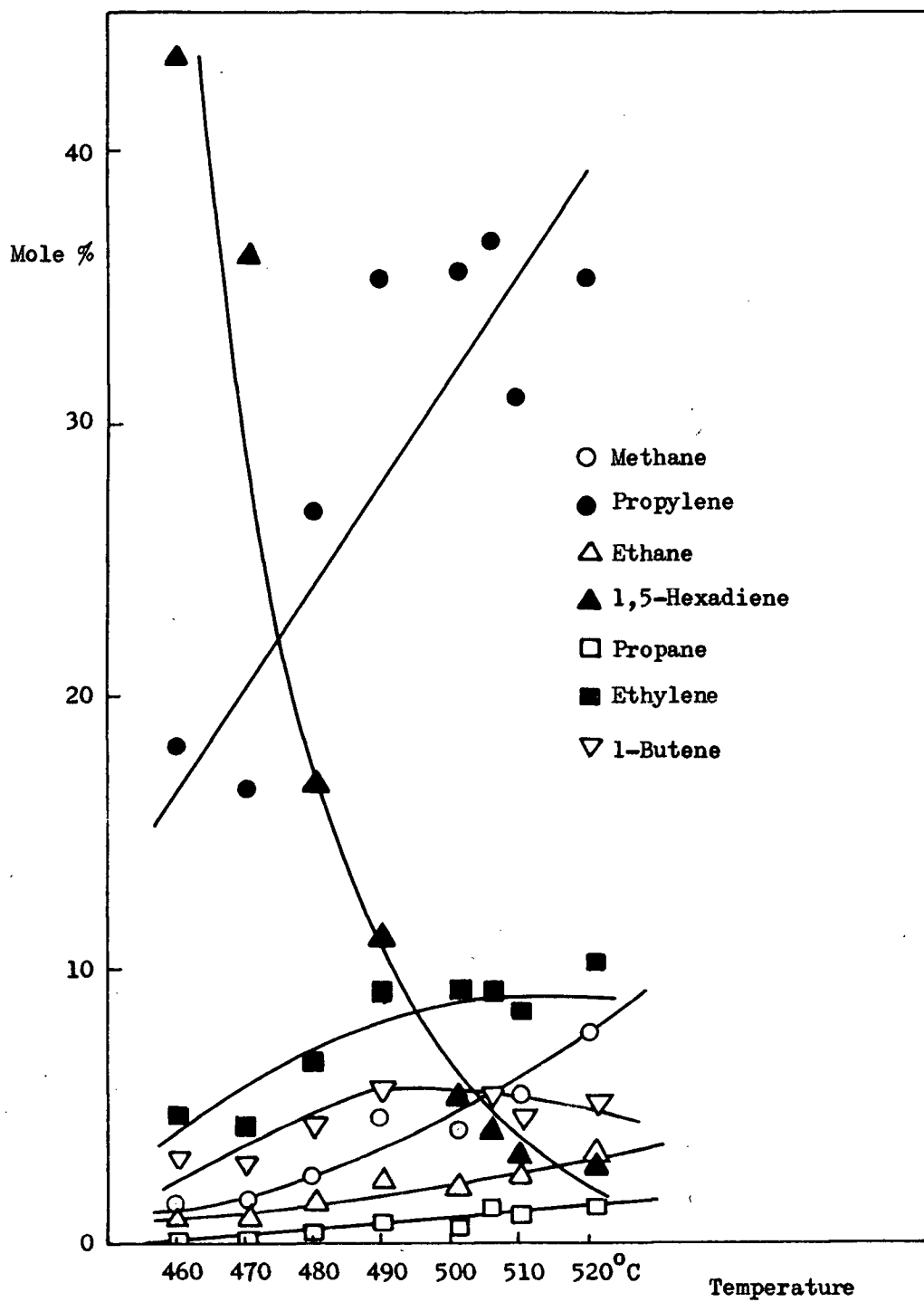


Fig.8 Light Products of the Pyrolysis of
1,5-Hexadiene vs. Temperature
Reaction Time 5 Minutes

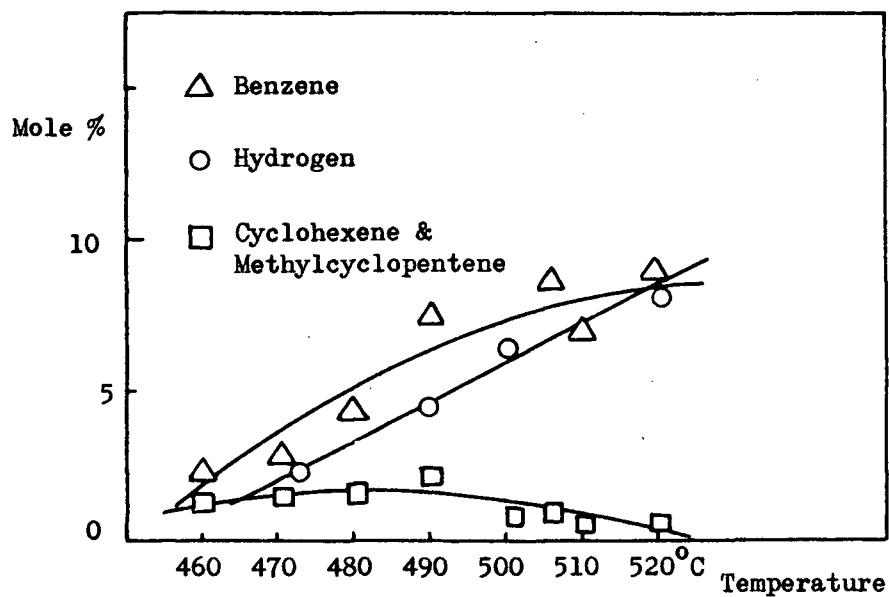


Fig. 9a

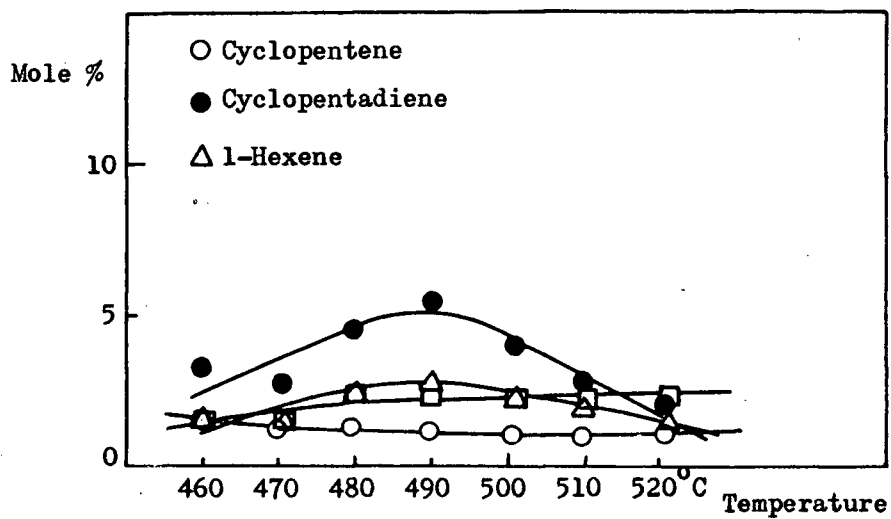


Fig. 9b

Fig. 9a and Fig. 9b Hydrogen and the heavy Products of the Pyrolysis of 1,5-Hexadiene vs. Temperature
Reaction Time 5 Minutes

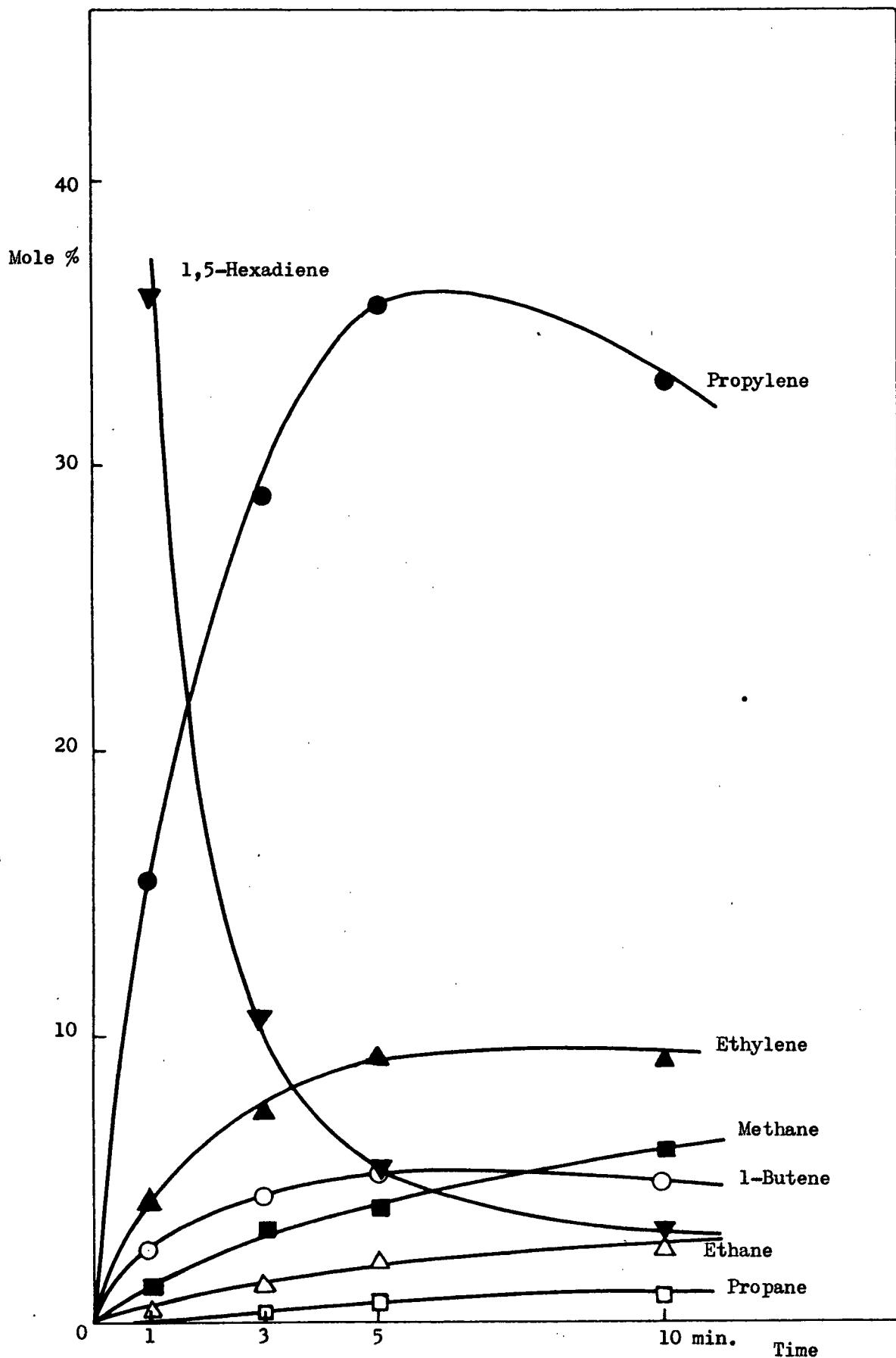


Fig. 10 Products of the Pyrolysis of 1,5-Hexadiene vs. Time at 501°C

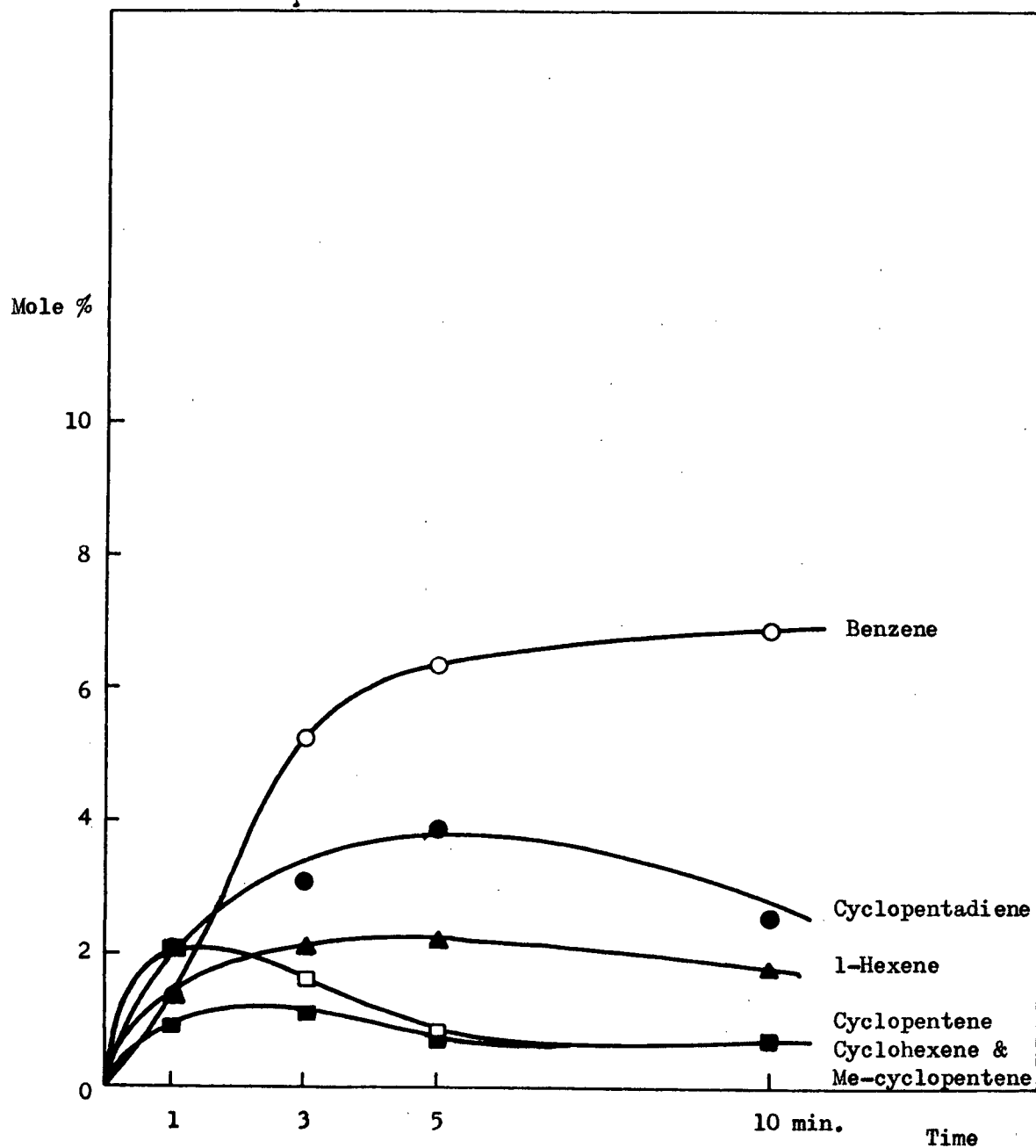


Fig. 11 Heavy Products of the Pyrolysis of 1,5-Hexadiene vs. Time at 501°C

Table VI

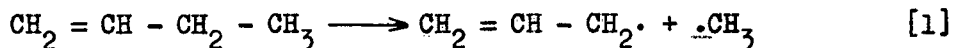
Decomposition products of 1,5-Hexadiene pyrolysis as a function of time
at 501° C.

| Product | 1 minute | 3 minutes | 5 minutes | 10 minutes |
|-------------------------------------|----------|-----------|-----------|------------|
| Methane | 1.2 % | 3.2 % | 4.1 % | 6.0 % |
| Ethane | 0.40 | 1.1 | 2.0 | 2.5 |
| Ethylene | 4.2 | 7.3 | 9.2 | 9.2 |
| Propane | 0.0 | 0.26 | 0.60 | 1.0 |
| Propylene | 15.5 | 28.9 | 35.6 | 33.0 |
| 1-Butene | 2.5 | 4.4 | 5.3 | 4.9 |
| Cyclopentene | 2.0 | 1.6 | 0.87 | 0.75 |
| Cyclopentadiene | 2.1 | 3.1 | 3.9 | 2.6 |
| 1-Hexene | 1.4 | 2.1 | 2.2 | 1.8 |
| Cyclohexene & methylcyclopentene | 0.93 | 1.1 | 0.68 | 0.76 |
| 1,5-Hexadiene | 35.9 | 10.7 | 5.3 | 3.2 |
| Benzene | 1.4 | 5.3 | 6.4 | 6.9 |

II. PYROLYSIS OF 1-BUTENE IN THE PRESENCE OF DIALLYL

Introduction

It has been shown (4) that the primary split in the pyrolysis of 1-butene in the temperature range round 500° C occurs in the following way:



It has also been shown that the addition of methyl radicals increases the rate of pyrolysis of 1-butene, increasing the amount of the light products. From that it was deduced that methyl radicals play an important part even in the unsensitized thermal decomposition of 1-butene and that its pyrolysis most probably proceeds by free radical chain reactions.

In the present work the fate of the allyl radical in the pyrolysis of 1-butene was taken up. The concentration of allyl radicals was increased by addition of 1,5-hexadiene, which on decomposition yields allyls in the primary step. The condition that a sensitizer should decompose much more readily than the substrate is satisfied in the case of 1,5-hexadiene, the difference of activation energies of 1-butene and 1,5-hexadiene being almost 35 kcal/mole. The product distribution for varying amounts of the sensitizer was determined by gas chromatography.

Results for the decomposition of 1-butene sensitized by diallyl

A preliminary run was made by decomposing 1-butene by itself at 506° C and the pressure change in the system studied. Then approximately 5 % by volume of 1,5-hexadiene was mixed with 1-butene and pyrolysis was carried out under the same conditions (total pressure: 200 mm). Fig. 12 gives the pressure increase with time in both cases. The slopes of

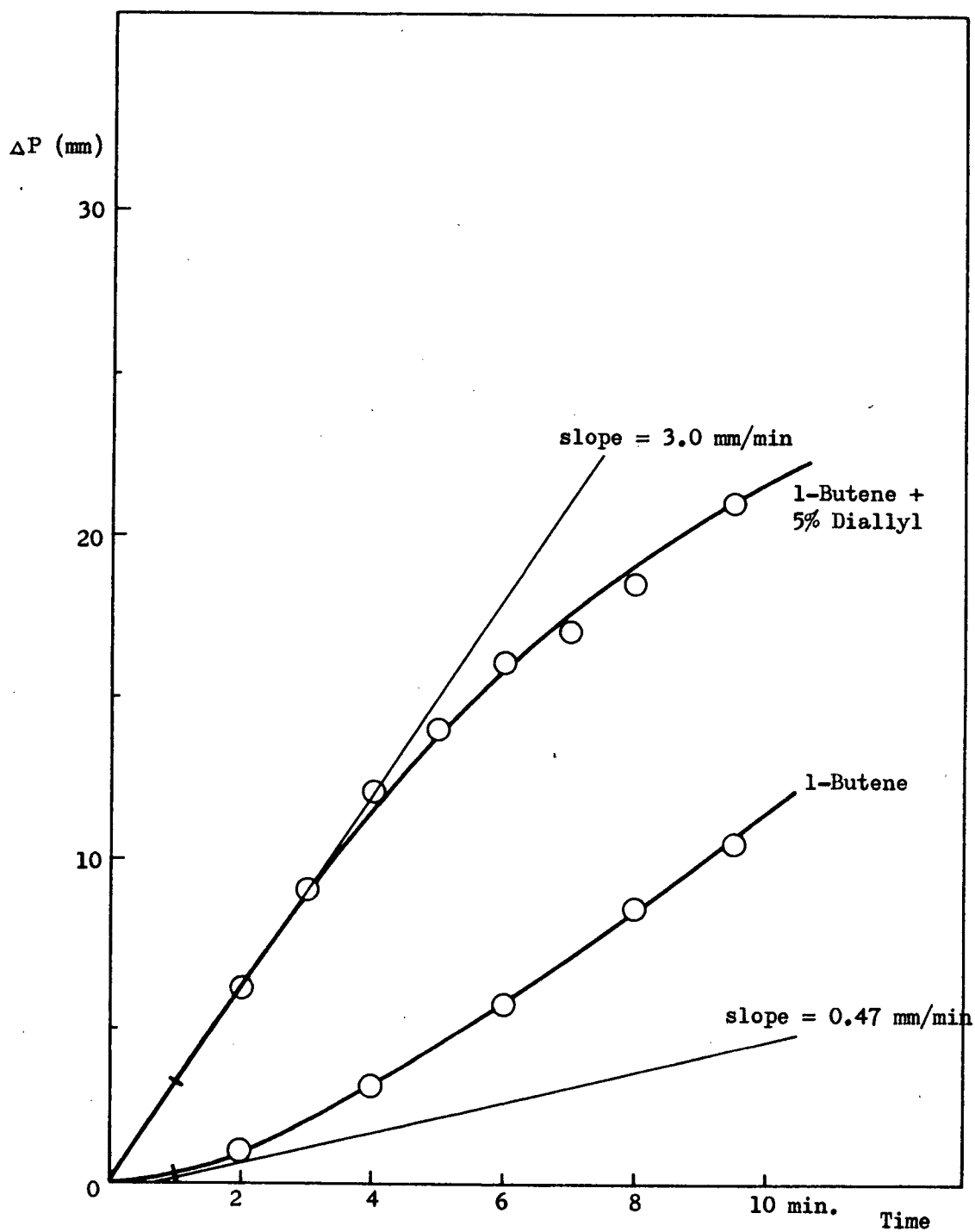


Fig. 12 Pressure Change vs. Time at 506°C. Initial Pressure 200 mm

tangents drawn to these curves should, at least in the early stages of the reaction, give an indication of the relative rates. Thus the ratio of the rates "sensitized to unsensitized" at the reaction time of 1 minute was found to be 6.5. This indicates that increase in concentration of allyl does increase the decomposition of 1-butene.

A series of pyrolyses with different concentrations of the sensitizer was carried out. The purpose of this was to relate the formation of the products to the concentration of allyl, which in turn should be proportional to (hexadiene)^{1/2} if the primary split in the 1,5-hexadiene pyrolysis is symmetrical. Table VII gives the concentrations of the products for the different concentrations of the sensitizer.

In fig. 13 the dependence of the formation of methane, cyclopentene, cyclopentadiene, cyclohexene and methylcyclopentene on the concentration of diallyl is given for reaction time of 5 min. It is seen that the rates of formation of the above products are roughly proportional to (diallyl)^{1/2}.

Table VII

Composition of the Reaction Mixture for Sensitized Decomposition of

1-Butene with 1,5-Hexadiene

5 min. at 506° C.

| Product | <u>Amounts of 1,5-hexadiene</u> | | | | | |
|----------------------------------|---------------------------------|-------|-------|-------|-------|--------|
| | 0 % | 3.1 % | 5.3 % | 6.7 % | 9.2 % | 11.4 % |
| Methane | 1.9 | 4.4 | 4.4 | 5.0 | 5.3 | 5.7 |
| Ethane | 0.7 | 2.0 | 2.4 | 2.4 | 2.6 | 2.8 |
| Ethylene | 1.2 | 2.8 | 3.5 | 4.2 | 4.2 | 5.2 |
| Propylene | 2.9 | 6.3 | 9.0 | 9.0 | 9.9 | 11.3 |
| 1-Butene | 52.2 | 31.4 | 33.6 | 31.1 | 32.6 | 29.8 |
| Cyclopentene | 0.7 | 0.9 | 1.3 | 1.1 | 1.4 | 1.2 |
| Cyclopentadiene | 1.0 | 1.8 | 2.0 | 2.0 | 2.2 | 2.4 |
| 1-Hexene | 0.0 | 0.5 | 0.7 | 0.5 | 0.9 | 1.0 |
| Cyclohexene & Me-cyclopentene | 0.0 | 0.3 | 0.4 | 0.4 | 0.5 | 0.6 |
| Benzene | 0.0 | 0.6 | 0.9 | 0.7 | 0.9 | 1.5 |

PRODUCTS OF SENSITIZED DECOMPOSITION OF 1-BUTENE
VS. $(\% \text{ DIALLYL})^{1/2}$

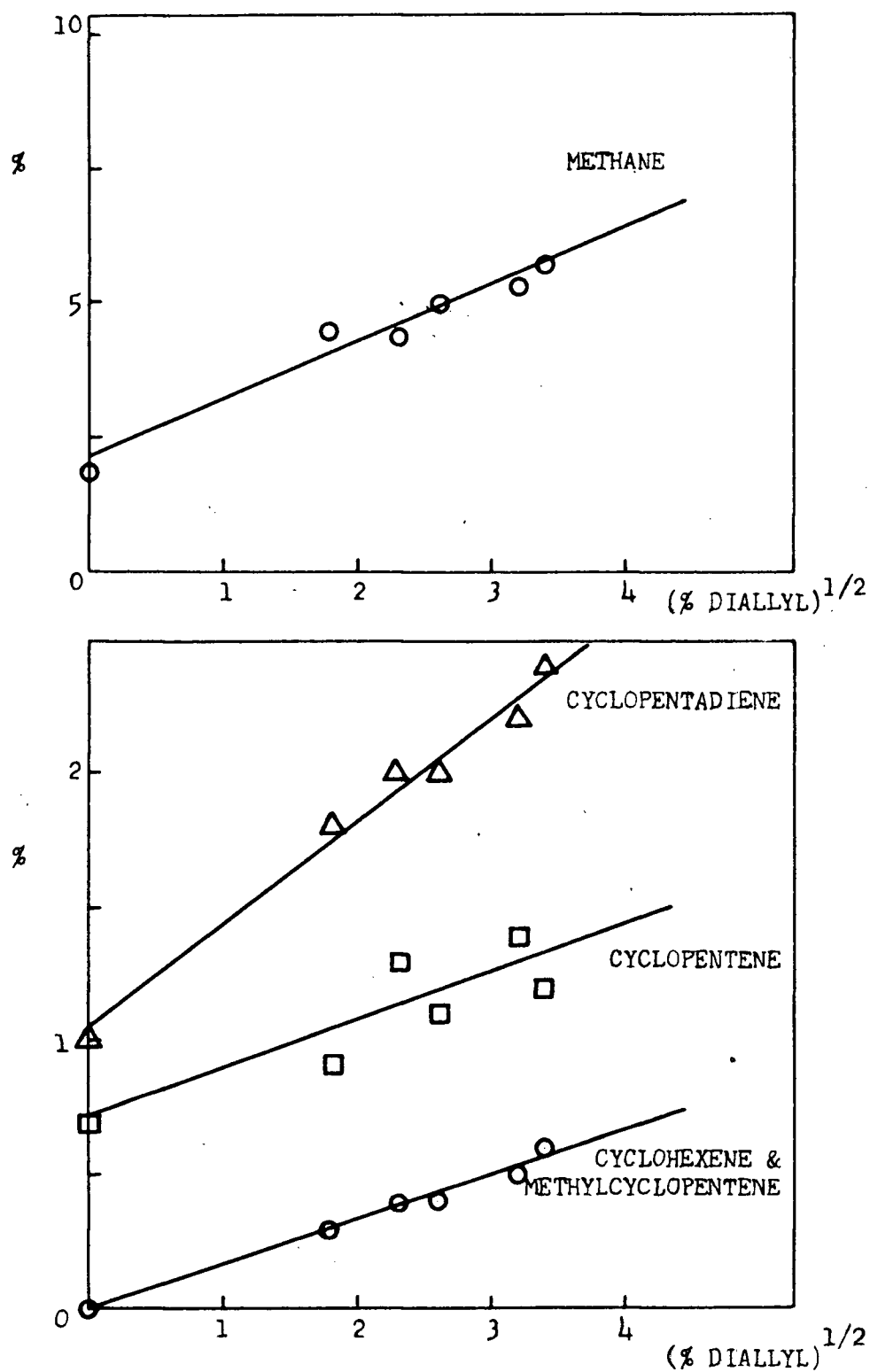


Fig. 13

III. PYROLYSIS OF n-BUTANE IN THE PRESENCE OF 1,5-HEXADIENE

In order to compare the reactivity of allyl with an olefin and a paraffin hydrocarbon, the sensitized decomposition of n-butane was studied in one experiment.

n-Butane was decomposed by itself and in presence of appr. 5 % by volume 1,5-hexadiene at 506° C. The products of the pyrolysis of n-butane had previously been determined (21). The pyrolysis of n-butane by itself at 506° C gave methane, ethane, ethylene and propylene as the principal products for a reaction time of 5 minutes (H_2 was not analyzed for).

The sensitization of the pyrolysis of n-butane with 1,5-hexadiene increases the amounts of products present when n-butane is decomposed by itself and in addition 1-butene and one compound with higher molecular weight than 1-butene are formed. The retention volume of the above compound appeared to be equal to the retention volume of 1-pentene and it is most probable that the compound concerned actually is 1-pentene. This may be expected since both allyl and ethyl radicals are present in the system and upon combination would yield 1-pentene.

Table VIII gives the products of the pyrolysis of n-butane and sensitized pyrolysis of n-butane by 1,5-hexadiene.

From the ratio sensitized/non-sensitized it can be seen that the formation of unsaturated products is favoured by the increase of concentration of allyl.

Table VIII

Main Products of Pyrolysis of n-Butane and Sensitized Pyrolysis of n-Butane
by Addition of Appr. 5 % by Volume of 1,5-Hexadiene at 506° C. Reaction

Time 5 Minutes. $P_{init} = 200 \text{ mm.}$

| | Non-sensitized | Sensitized | $\frac{\text{Sensitized}}{\text{Non-sensitized}}$ |
|-----------|----------------|------------|---|
| | % | % | |
| Methane | 2.0 | 4.9 | 2.5 |
| Ethane | 0.9 | 2.0 | 2.2 |
| Ethylene | 0.9 | 3.4 | 3.8 |
| Propylene | ? * | ? * | 3.5 |
| 1-Butene | negligible | 1.7 | |
| 1-Pentene | | 0.85 | |
| Benzene | | negligible | |

* Propylene and n-butane are not completely resolved on the alumina column so that the absolute values could not be obtained. Since the propylene peaks were extremely sharp, the ratio of the peak heights was taken as a measure of the rel. amount of propylene in the two runs.

IV. PYROLYSIS OF 1-BUTENE IN THE PRESENCE OF ACETALDEHYDE

It has been shown (4) that methyl radicals play an important role in thermal decomposition of 1-butene and that methyl radicals generated by pyrolysis of mercury dimethyl sensitize the decomposition of 1-butene. In order to show the effect of methyl radicals obtained from a source other than mercury dimethyl on 1-butene, and in order to get acquainted with the general method of pyrolysis of gases, pyrolysis of 1-butene in presence of acetaldehyde was carried out.

It is considered as well established that the thermal decomposition of acetaldehyde is a free radical chain process (11,17). Methyl radicals are formed in this reaction and have been detected by several workers (11,17). It would be therefore expected that reactions between these and 1-butene would take place in analogy with the work mentioned above.

From a pressure vs. temperature plot it was found that 1-butene starts to decompose at about 480° C. At 477° C there is essentially no decomposition of 1-butene while acetaldehyde was found to decompose appreciably at 440 - 450° C. The temperature of 477° C was therefore chosen as a suitable temperature and two series of experiments were performed:

I. acetaldehyde and helium in molar ratio 1:3

II. acetaldehyde and 1-butene in molar ratio 1:3.

The total initial pressure was 200 mm. in both cases.

The degree of decomposition of acetaldehyde was determined by taking the total amount of methane and carbon monoxide (20) as a measure of the decomposition. Percentage of 1-butene decomposed was estimated by gas chromatography from the amount of 1-butene which remained in the reaction

vessel after each reaction was completed.

The analytical results of the above pyrolyses are given in Table IX.

Table IX

Percentage of Decomposition of Acetaldehyde and 1-Butene at 477° C.

| | 1 minute | 3 minutes | 5 minutes |
|-----------------|----------|-----------|-----------|
| S e r i e s I | | | |
| Acetaldehyde | 8.2 | 11.8 | 24 |
| S e r i e s I I | | | |
| Acetaldehyde | 3.2 | 4.8 | 7.9 |
| 1-Butene | 8 | 11 | 19 |

The above experimental results are plotted in fig. 14. It can be seen that while the initial rate of decomposition of acetaldehyde in presence of helium is $6.0 \% \text{ min}^{-1}$, it is only $2.8 \% \text{ min}^{-1}$ when 1-butene is present. Thus acetaldehyde decomposes more than twice as fast in the former case. Suppression of the decomposition of acetaldehyde in later stages of the reaction in presence of 1-butene seems to be still more pronounced. 1-Butene, which practically does not decompose at the temperature of the experiments by itself, decomposes quite appreciably when acetaldehyde is present.

Since the thermal decomposition of acetaldehyde is known to be a free radical chain process, the decrease in rate of its decomposition in presence of 1-butene must be therefore caused by decrease in the steady state concentration of the free radicals which are the chain carriers. Thus

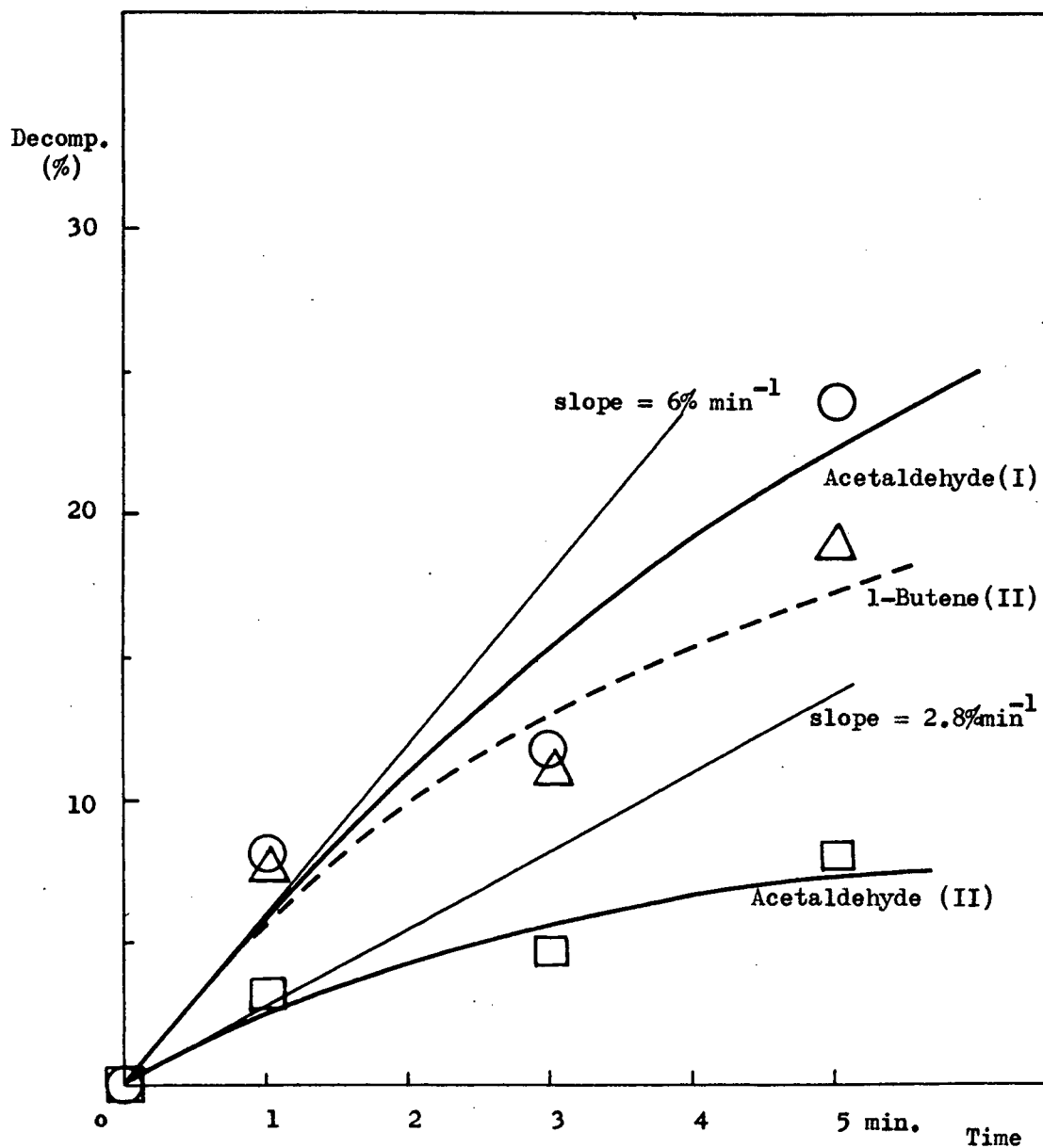


Fig. 14 Extent of Decomposition at 477°C. Initial Pressure 200 mm
 I. Acetaldehyde + Helium (1 : 3)
 II. Acetaldehyde + 1-Butene (1 : 3)

reactions of the free radicals formed must have taken place with 1-butene. Also, if 1-butene was inert to attack by methyl or/and other radicals, more decomposition of acetaldehyde would rather be expected in the presence of 1-butene than of helium. Molecules of 1-butene (being polyatomic molecules with a high number of degrees of freedom) would be expected to enable a far better energy transfer during the pyrolysis.

The nature of the products formed when 1-butene is attacked by the above free radicals was not determined in these preliminary experiments.

DISCUSSION

DISCUSSION

PRECISION OF THE QUANTITATIVE DETERMINATIONS BY GAS CHROMATOGRAPHY

There are several factors influencing the reproducibility of quantitative gas chromatographic determinations (6). The main ones have already been mentioned when the quantitative determination of the products was described: flow-rate of the carrier gas, column temperature (one of the factors determining the flow-rate), thermal conductivity, cell current and cell temperature. In addition to these variations in room temperature could produce variation in the amount of the gaseous sample admitted into the by-pass of the admission system. There is also uncertainty in determining the peak area with a planimeter.

The following are the estimated or assumed maxima of uncertainties in the above parameters:

| | |
|---|------------------------|
| 1) uncertainty in flow-rate (including the column temperature) | $\pm 3 \%$ |
| 2) uncertainty in cell current (after correction was applied) | $\pm 0.8 \%$ |
| 3) uncertainty in cell temperature (after correction was applied) | negligible |
| 4) uncertainty in room temperature | negligible |
| 5) uncertainty in planimeter measurements | $\pm 2 \%$ |
| | <hr/> |
| | $\pm 5.8 \% \sim 6 \%$ |

In addition to the above uncertainties there might be a number of factors leading to systematic errors which might have increased the maximum of the total error.

UNCERTAINTY IN THE VALUES OF THE KINETIC RATE CONSTANTS

The mathematical expression for the first order rate constant is:

$$k = \frac{1}{t} \ln \frac{p_0}{p} \quad [2]$$

where t is the reaction time (min in our case), p_0 initial pressure of reactant, p pressure of reactant at time t . If α is the degree of decomposition, ($0 < \alpha < 1$), then $p = (1 - \alpha) p_0$ and [2] will become:

$$k = \frac{1}{t} \ln \frac{1}{1-\alpha} \quad [3]$$

The kinetic constant is in this case dependent upon two variables the uncertainty in which will determine the total uncertainty of the value of the rate constant.

The maximum uncertainty in the degree of decomposition, α , is, in the best case, equal to the uncertainty in the quantitative gas chromatographic determinations. In cases where little decomposition took place the peak areas being subtracted from each other are of the same order of magnitude and consequently their difference will be of a higher degree of uncertainty than the peak areas themselves. Since normally two to four parallel analysis-runs were made and the results averaged, it should be reasonable to take the uncertainty in α equal to the uncertainty in the peak areas, or $\pm 6\%$.

The reaction time was 5 minutes in all the runs the data from which were used to calculate the rate constants. The difficulty in estimating the starting- and end-point of the reaction was found to lead to a maximum uncertainty in the reaction time of $\pm 5\%$.

The variation in the rate constant with t and α is given by:

$$\Delta k = - \frac{\Delta t}{t^2} \ln \frac{1}{1-\alpha} - \frac{1}{t} (1-\alpha) \Delta \alpha$$

and the maximum relative uncertainty by:

$$\begin{aligned} \frac{|\Delta k|_{\max}}{k} &= \pm \frac{\frac{|\Delta t|_{\max}}{t^2} \ln \frac{1}{1-\alpha} + \frac{1-\alpha}{t} |\Delta \alpha|_{\max}}{\frac{1}{t} \ln \frac{1}{1-\alpha}} \\ &= \frac{|\Delta t|_{\max}}{t} + \frac{(1-\alpha)}{\ln \frac{1}{1-\alpha}} \frac{|\Delta \alpha|_{\max}}{t} \end{aligned} \quad [4]$$

Putting: $\alpha = \frac{1}{2}$

$$|\Delta \alpha|_{\max} = \frac{1}{2} \times \frac{6}{100}$$

$$t = 5 \text{ (min)}$$

$$|\Delta t|_{\max} = 5 \times \frac{5}{100} \text{ min}$$

one gets: $\frac{|\Delta k|_{\max}}{k} = \pm 7 \%$

The above considerations were made on the assumption that there was no variation in the furnace temperature during a run. As was mentioned in the paragraph "Pyrolysis Apparatus", the furnace temperature (assumed to be equal to the temperature at which the reaction takes place) was kept constant to within $\pm 1^\circ \text{C}$. Considering the variation of temperature one obtains the following:

$$\begin{aligned} k &= A e^{-\frac{E_a}{RT}} \\ \Delta k &= A \frac{E_a}{R} e^{-\frac{E_a}{RT}} \frac{1}{T^2} \Delta T \end{aligned}$$

and $\left| \frac{\Delta k}{k} \right|_{\max} = \frac{E_a}{R} \frac{1}{T^2} |\Delta T|_{\max} \quad [5]$

Putting: $E_a = 32\,000 \text{ cal/mole}$

$R = 2 \text{ cal/mole-deg}$

$T = 773^\circ \text{ K}$

$|\Delta T|_{\text{max}} = 1^\circ \text{ K}$

it is obtained: $\left| \frac{\Delta k}{k} \right|_{\text{max}} = \pm 3 \%$

Considering uncertainty in both t , α , and T , the max. uncertainty in k is then $\pm 10 \%$. Consequently, most probably no more than two figures in the rate constants obtained are significant.

THE OVER-ALL ACTIVATION ENERGY FOR THE DECOMPOSITION OF 1,5-HEXADIENE

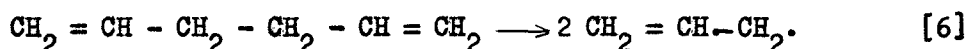
It was mentioned in a previous section that the attempt to determine the over-all activation energy for the pyrolysis of 1,5-hexadiene from the initial pressure changes at different temperatures was unsuccessful.

Although this method of determining the over-all activation energy had successfully been applied in the case of 1-butene (9) the negative result in the present work should not be surprising. A large number of products is formed in the pyrolysis and there is a considerable variation with temperature of the distribution with respect to their molecular weights (see Table I and Figs. 8, 9a and 9b). Consequently, the pressure change produced in the pyrolyses at different temperatures cannot be assumed as being proportional to the extent of the reaction in this system.

Furthermore, the initial pressure of the reactant in the reaction vessel was rather low (approx. 70 mm) so that the initial pressure changes involved were correspondingly small and the values obtained therefore uncertain.

The pressure change can be used as a measure of the extent of a reaction taking place in the gas-phase only if the distribution of the products is more or less constant with respect to temperature and if the pressures involved can be measured with sufficient accuracy.

The determination of the over-all activation energy from the gas chromatographic analyses yielded the value 31.3 kcal/mole. The dissociation energy for the central bond in 1,5-hexadiene had been estimated (22) to be around 42 kcal/mole. Taking the heat of formation of the allyl radical as 32.3 kcal/mole (13) and the heat of formation of diallyl as 20.6 kcal/mole (calculated from the heat of hydrogenation, -60.5 kcal/mole (3), and the heat of formation of n-hexane, -39.96 kcal/mole (8)) it can be calculated that the heat of the reaction:



is 44 kcal/mole.

The value obtained for the over-all activation energy is considerably lower than both of the above values. This fact indicates that reactions other than reaction [6] must take place, such as hydrogen abstraction by allyl radical and allyl addition to double bonds in the system.

Although the activation energies for these two processes are not known, it is certain that they are far below the bond dissociation energy for the central bond in diallyl. Thus the over-all value of 31.3 kcal/mole should not be surprising.

Conversely, the fact that the over-all activation energy found is considerably lower than the heat of reaction [6] could be used as an evidence that free radical processes take place.

It can be shown (7, p. 232) that for a mechanism involving a single

chain carrier with second-order termination, as follows

initiation $\longrightarrow R + \dots\dots$

propagation $R + \dots \longrightarrow R + \dots\dots$

termination $R + R \longrightarrow \dots\dots\dots$

if the activation energy for termination is non-zero or if chain termination is second order (as above) the apparent (over-all) activation energy may be significantly less than the activation energy for the initiation step.

MECHANISM OF THE PYROLYSIS OF 1,5-HEXADIENE

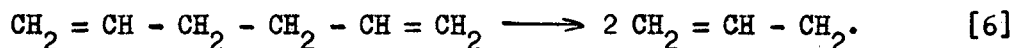
General

Three possibilities exist for the mechanism of pyrolysis of 1,5-hexadiene:

- (a) molecular mechanism
- (b) free radical mechanism
- (c) combined molecular and free radical mechanism.

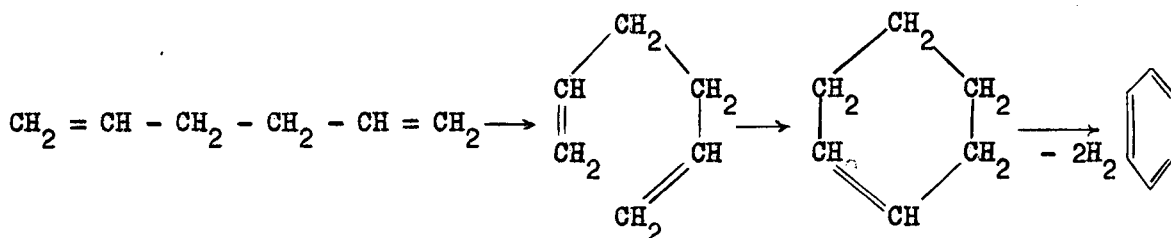
It was seen that a large number of both aliphatic and cyclic products is formed in the pyrolysis. Since such a large spectrum of products could not be expected if the mechanism was purely molecular, possibility (a) should thus be ruled out.

It has been shown (12) that at high temperatures (690 - 890° C) 1,5-hexadiene decomposes by splitting the central bond:



The results obtained in the present work also show that split of the central bond must have taken place. If the primary step in the pyrolysis at present conditions involved exclusively reaction [6], a pure free radical chain mechanism could be postulated.

On the other hand, cyclohexene, benzene and hydrogen have been found among the reaction products. As it is shown in the following chapter, the formation of cyclohexene and benzene can be explained on the basis of a free radical mechanism. But the presence of these products might equally well indicate that the following molecular rearrangement followed by dehydrogenation also takes place to some extent:



At this stage it can therefore be concluded that possibility (c) is most likely.

Reactions of the allyl radical

(1) Hydrogen abstraction by allyl

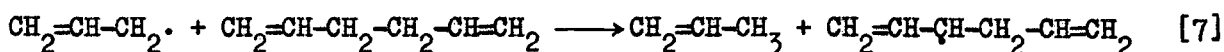
Since the decomposition of 1,5-hexadiene probably involves formation of two allyl radicals in the primary step, the allyl radical must play an important part in the over-all reaction mechanism.

Because of the resonance energy of 17 kcal/mole (2,5) the allyl radical would be expected to be rather unreactive in thermal reactions. However, it can be shown from thermochemical data (26) that the weakest bond in allyl (a C - H bond) has a strength of about 68 kcal. The life-time of allyl should thus be long enough to build up an appreciable steady state concentration and permit various reactions involving allyl to take place.

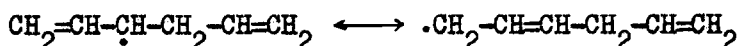
McNesby and Gordon have recently investigated the thermal decomposition

of cyclopentane-d₂ and cyclopentane-acetone-d₆ mixtures (14) and have shown that reactions of allyl radicals are involved. According to the authors appreciable H-abstraction, both from cyclopentane and from CD₃COCD₃ takes place at 453° and that the degree of H-abstraction is still higher at 500° C.

The main product of the pyrolysis of 1,5-hexadiene is propylene. This suggests that H-abstraction by allyl takes place readily in the present system. It would be expected to take place mainly by the reaction:



since a resonance stabilized radical is formed. It has the following two contributing forms:



Hydrogen abstraction by allyl would probably also take place from the products of the decomposition which, upon hydrogen abstraction, would yield resonance stabilized radicals.

The following products would be expected to undergo such reactions:

1-butene
cyclopentene
cyclopentadiene
1-hexene
cyclohexene
methyl-cyclopentene

Abstraction from propylene would also take place, but it would only produce back propylene and allyl.

The side reactions mentioned would be negligible in the early stages of the decomposition, but may be quite extensive in the later stages when

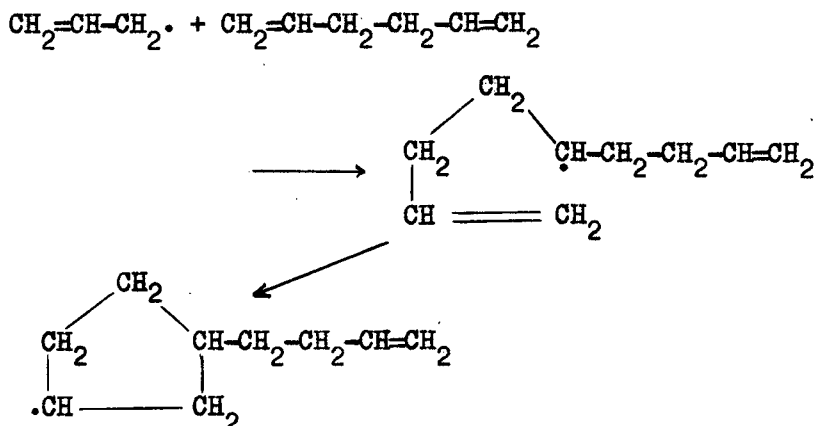
the concentrations of the products concerned are appreciable. Evidence for attack of the above products by allyl (and possibly other) radicals is indicated in figs. 10 and 11 where the concentration vs. time graphs for all the products listed above show a maximum.

There is also a drop in concentrations of these products with increased temperature at constant reaction time (see figs. 8, 9a and 9b). In the case of allyl radical, which in general reacts slower than the non-stabilized alkyl radicals, the extent of hydrogen abstraction would be expected to be quite temperature-dependent. Drop in concentrations of certain products from a certain temperature on may also be a good indication of increased hydrogen abstraction by allyl radical.

(2) Addition of allyl to double bond

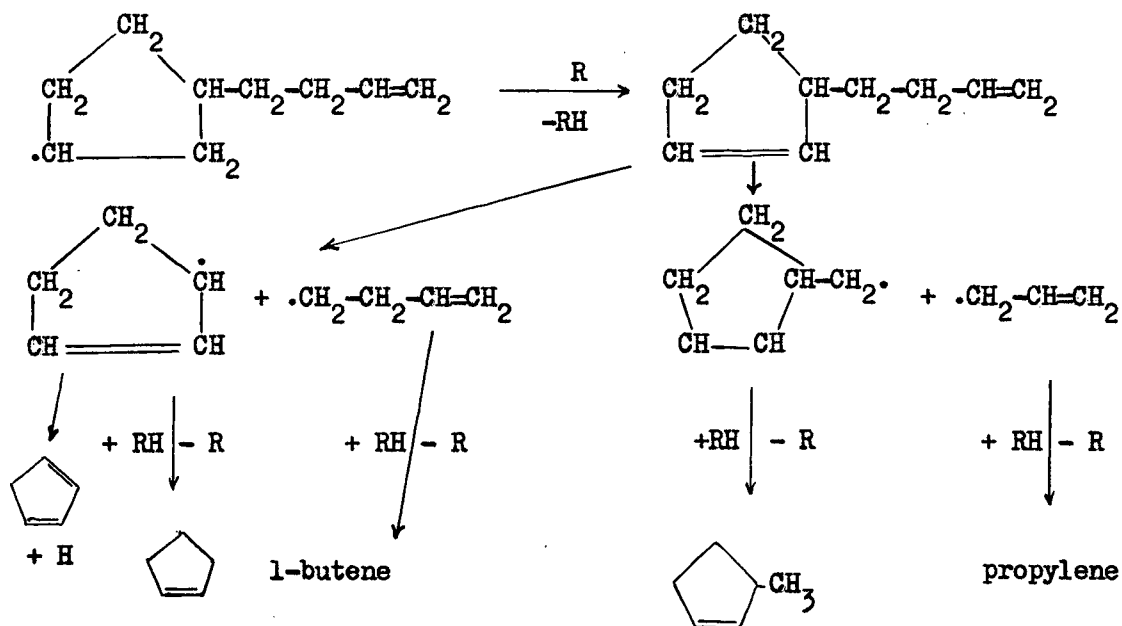
Addition of allyl radical to the double bond of olefins has not previously been reported. It appears, however, that such an addition must have taken place in the present system. The formation of cyclopentene, cyclopentadiene and methyl-cyclopentene is difficult to explain in any other way. In the present system there are two principal ways of addition to 1,5-hexadiene possible:

(a) addition to the terminal C-atom in diallyl:

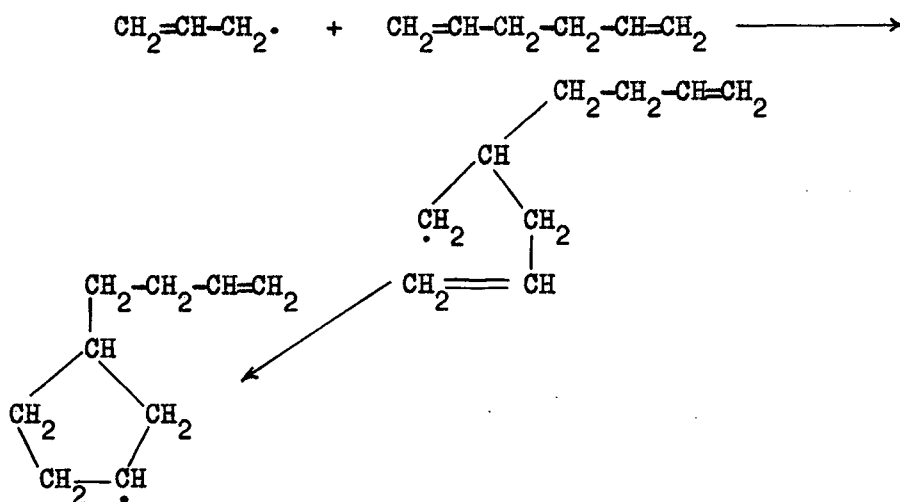


This large radical would likely be too unreactive to abstract hydrogen.

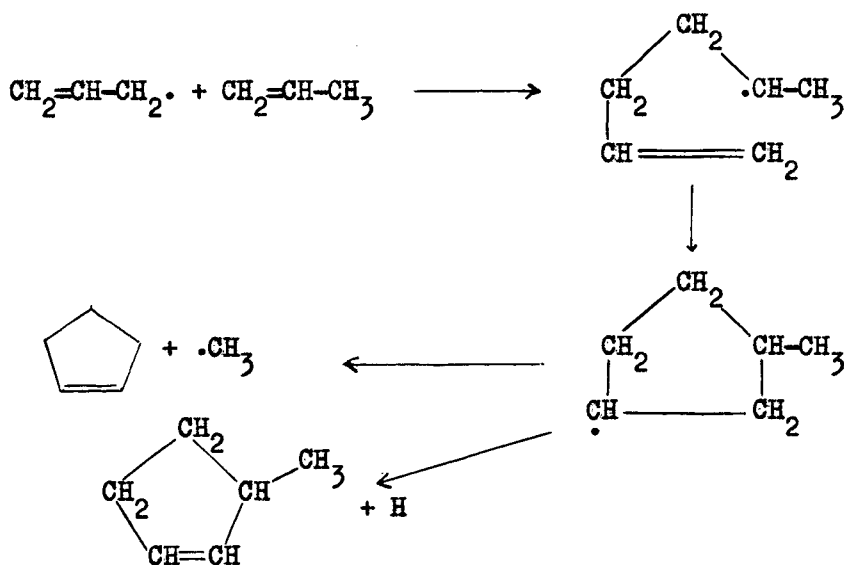
It seems rather more probable that its fate is the following:



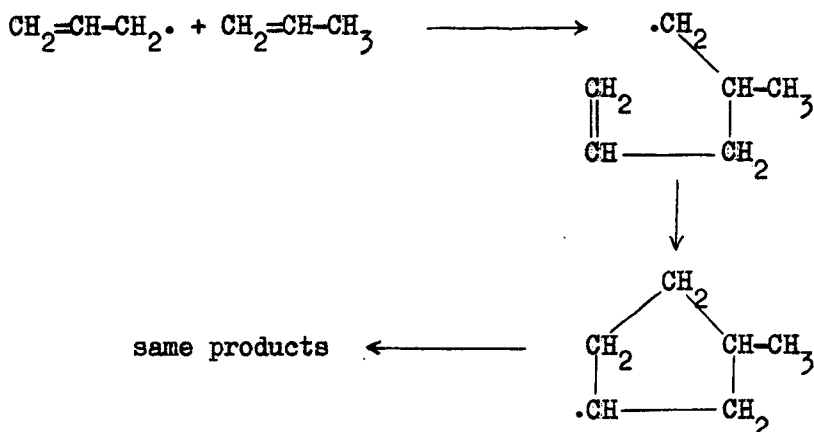
(b) addition to the non-terminal double bond in diallyl:



This radical is identical with the one obtained above. Addition of allyl to both double bonds of 1,5-hexadiene would yield products impossible to detect by the present method of analysis. Since the concentration of propylene is appreciable from the early stages of the reaction, addition of allyl radical to propylene has to be considered:



Addition to the non-terminal carbon atom would lead to the same products:



(3) Combination of allyl with other radicals

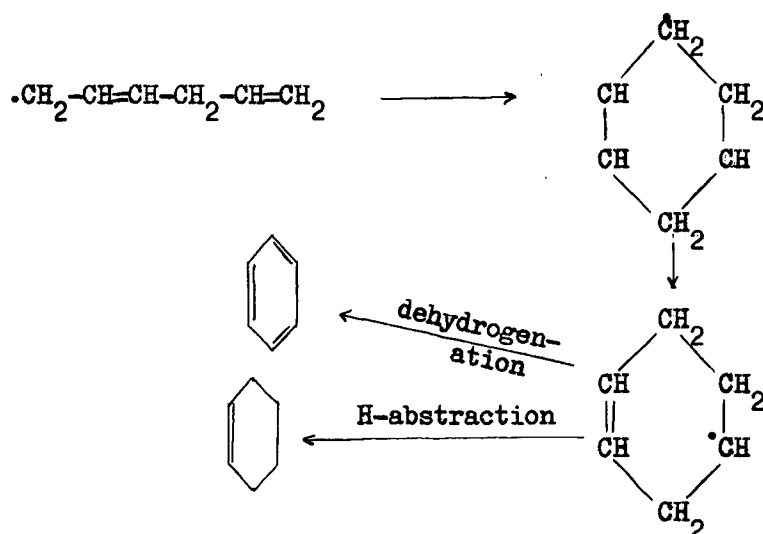
Apart from hydrogen abstraction and addition to the double bond the fate of the allyl radical may be combination with other radicals present. As will be indicated in a subsequent chapter, hydrogen atoms are assumed to be present in the system. Thus combination of an allyl with a hydrogen atom would yield a propylene molecule. Combination with a methyl would give a 1-butene molecule and recombination of two allyls would produce the parent, 1,5-hexadiene.

The fate of the 1,5-hexadienyl radical

Since both the allyl radical and unreacted 1,5-hexadiene are present in quite high concentrations in the beginning of the pyrolysis, the abstraction of hydrogen from hexadiene by allyl must be quite extensive. The rate of formation of 1,5-hexadienyl radical must consequently be rather high.

It seems that the hexadienyl radical formed may mainly disappear in three different ways:

(1) Rearrangement:



It may appear surprising that no cyclohexadiene, which would be expected to be the intermediate in the dehydrogenation process, has been found among the reaction products. The reason may be that the radical obtained upon hydrogen abstraction from cyclohexadiene has a high degree of resonance stabilization. Hydrogen abstraction from cyclohexadiene would thus readily take place because of the high resonance energy of the radical formed. Abstraction of hydrogen from this radical would be far more probable than hydrogen abstraction by the radical.

(2) Decomposition

There are several ways in which the 1,5-hexadienyl radical could be thought to decompose. It appears, however, that such decompositions would also necessarily lead to compounds like butadiene and allene which have not been found among the products. The resonance energy of the radical is probably sufficiently high that the life-time is appreciable and the radical rather undergoes re-arrangement as mentioned above.

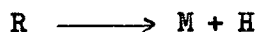
(3) Combination with other radicals

The third possibility for the disappearance of the 1,5-hexadienyl radical may be combination with other radicals to yield products which may be the ones that were suspected to suffer irreversible adsorption to the alumina column. Since the steady state concentration of the 1,5-hexadienyl radical is presumably quite high, the total amount of such addition products might have been appreciable.

Formation and reactions of other radicals

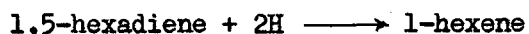
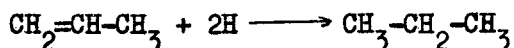
Hydrogen atoms:

formation: $\text{CH}_2=\text{CH}-\text{CH}_2 \longrightarrow \text{allyl} + \text{H} \quad (22)$

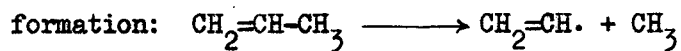


where M is an unsaturated molecule and R may be cyclopentenyl or cyclohexenyl.

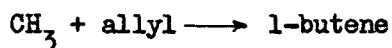
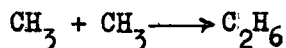
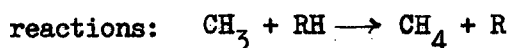
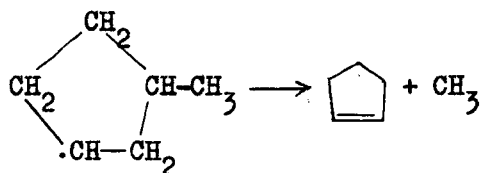
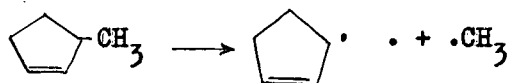
reactions: $\text{unsaturated product} + \text{H} \longrightarrow \text{saturated or partially saturated product}$



Methyl:

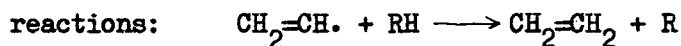
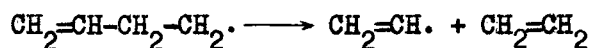
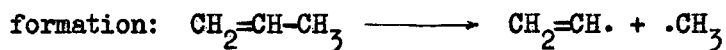


the following



Possibly addition to the double bonds of 1,5-hexadiene and some of the products giving compounds which have been adsorbed irreversibly to the alumina column.

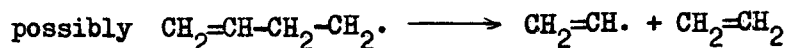
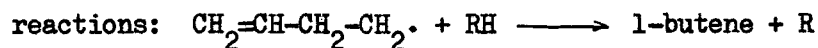
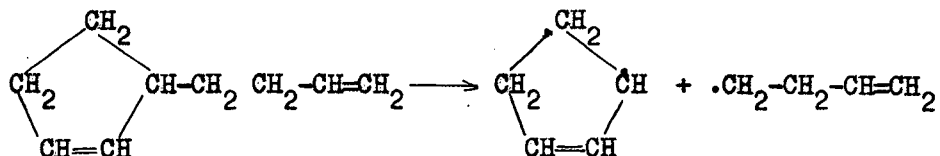
Vinyl:



possibly also addition to the double bonds.

Butenyl:

formation:



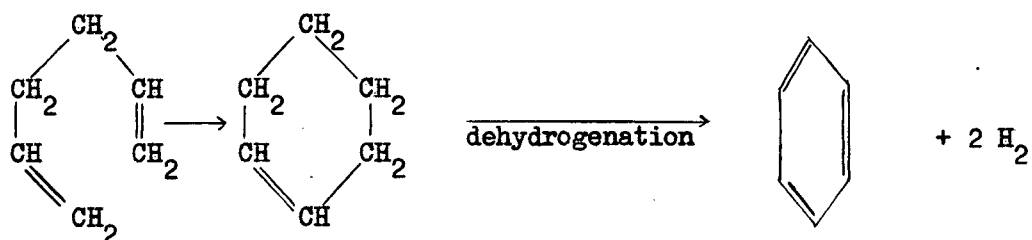
The cyclic radicals:

The cyclopentenyl and cyclohexenyl radicals probably expel H-atoms to yield unsaturated compounds. H-abstraction by the radicals also takes place to some extent to produce cyclopentene and cyclohexene respectively.

Mechanism for the formation of the pyrolysis products

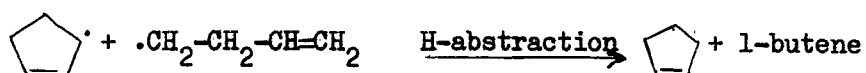
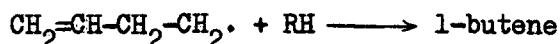
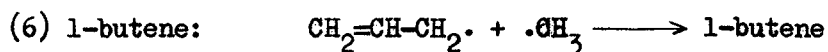
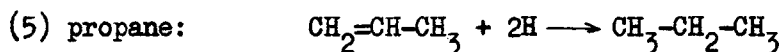
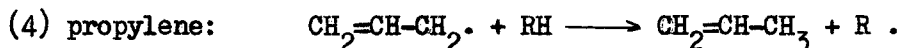
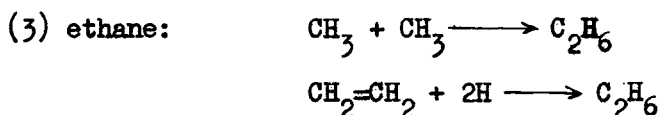
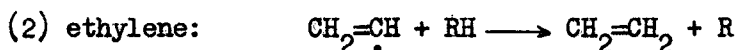
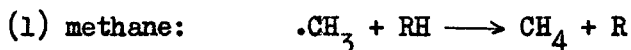
Summarizing the discussion of all the above mentioned elementary processes the mechanism of the pyrolysis of 1,5-hexadiene could be represented by the following scheme:

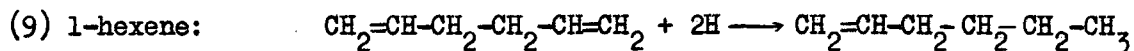
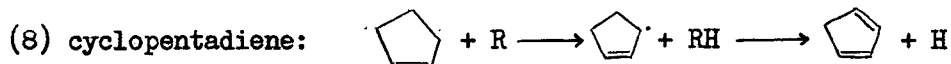
A. Molecular rearrangement



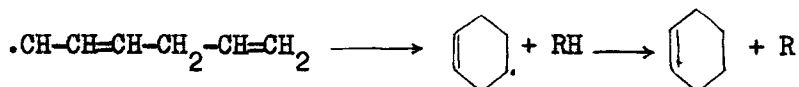
B. Free radical reactions

Formation of:

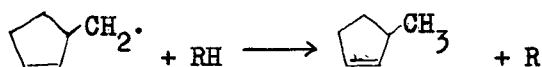
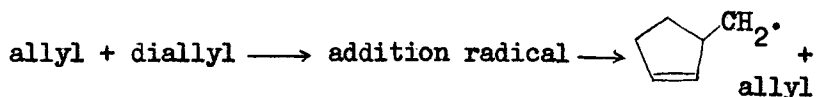




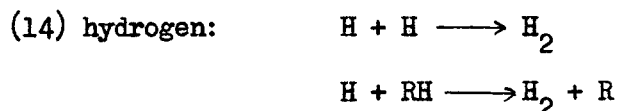
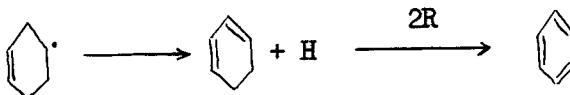
(10) cyclohexene:



(11) Me-cyclopentene:



(13) benzene:



The postulated mechanism of the pyrolysis of 1,5-hexadiene was mainly based upon the qualitative analyses of the products and upon their concentrations at different reaction times at 501° C. Some of the mechanisms for the formation of some of the products are rather speculative. However, a large variety of products is formed in the pyrolysis and the system is thus very complex and difficult to deal with. Nevertheless, the postulated mechanism should give an over-all picture of the reactions which may be expected in the system.

It would be desirable to isolate some of the elementary reactions assumed to take place in the system and obtain definite proof of their occurrence.

The most interesting feature of the mechanism is probably the addition of allyl radical to olefinic double bonds. Formation of five-membered cyclic products results. Since the formation of these products could not easily be explained in any other way, they should be sufficient evidence for addition reactions of the allyl radical with the 1,5-hexadiene.

Thermal decompositions taken to a much lower conversion than was the case in the present study might have simplified the mechanism of the reaction. However, such low-conversion pyrolyses would have involved much shorter reaction times in the temperature range studied and the reproducibility with the present system would consequently have been extremely poor.

The difficulty caused by the uncertainty in the reaction times could be overcome by decreasing the temperature of the pyrolyses and use of longer reaction times. However, in both cases there remains the problem of determining the percentage of conversion. Comparing peak areas on the chromatogram which are of the same order of magnitude leads necessarily to very serious errors and is thus not usable.

It is realized that it would have been desirable for the sake of comparison to have carried out pyrolyses at the different temperatures to approximately the same degree of conversion rather than use of constant reaction time. It would be possible to predict the reaction time at a certain temperature for a certain degree of conversion if the reaction time at a different temperature for the same degree of conversion was known. The following is the method of calculation. First order process is assumed.

If α = degree of conversion, 0 α 1

then $k = \frac{1}{t} \ln \frac{1}{1-\alpha} \quad \alpha \times \frac{1}{t}$ [3]

But we have also: $k = A e^{\frac{-E_a}{RT}}$

If t_1 is the reaction time at T_1

and t_2 is the reaction time at T_2 for α = constant

it is obtained:

$$\frac{k_1}{k_2} = \frac{t_2}{t_1} = \frac{e^{\frac{-E_a}{RT_1}}}{e^{\frac{-E_a}{RT_2}}}$$

or:

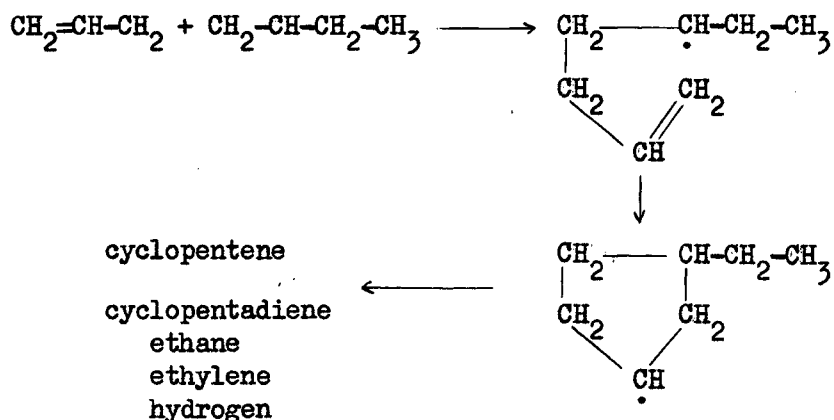
$$t_2 = t_1 e^{\frac{-E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$
 [8]

MECHANISM OF THE THERMAL DECOMPOSITION OF 1-BUTENE SENSITIZED BY DIALLYL

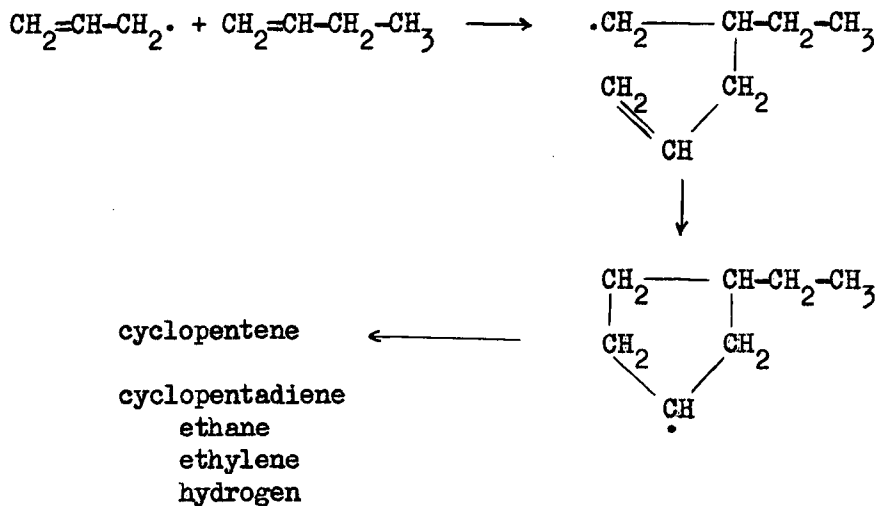
As was mentioned in a previous chapter a preliminary experiment clearly showed that addition of a small amount of diallyl to 1-butene accelerates the pyrolysis of the latter. The more detailed investigation involving variation in the diallyl concentration shows that formation of all the products of 1-butene pyrolysis is accelerated.

There are two reactions possible between the allyl radical and 1-butene:

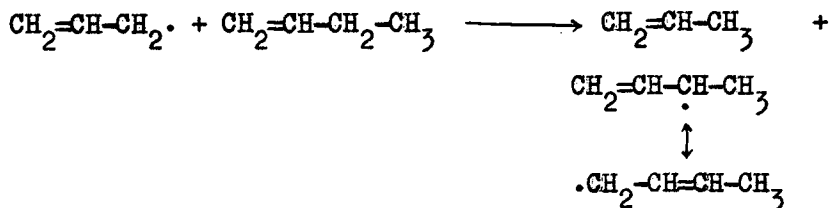
(1) Addition to the double bond:



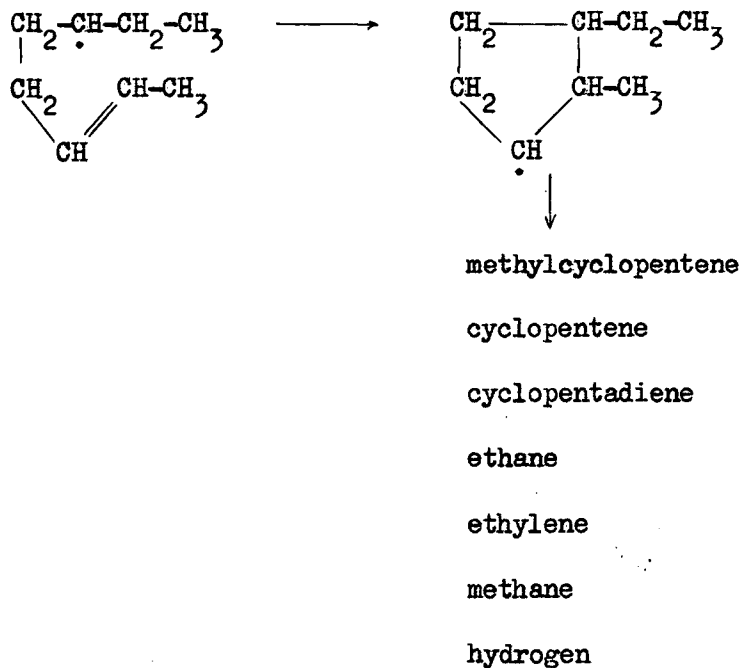
or:



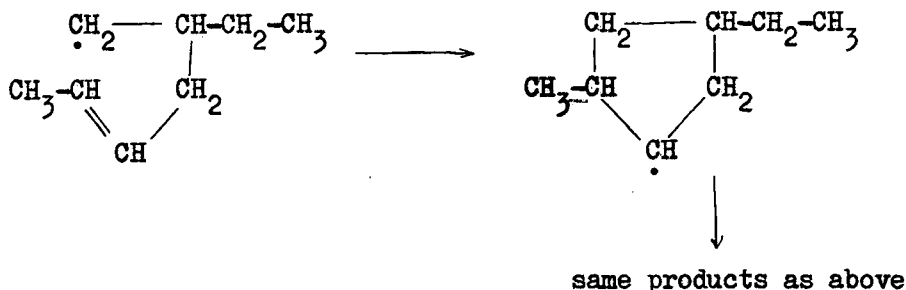
(2) H-abstraction to produce the resonance stabilized butenyl radical:



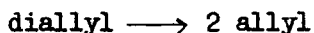
The butenyl radical may also add to the double bond of 1-butene:



or:



If the primary step in the diallyl decomposition is mainly



and if re-combination of two allyl radicals is also taken into consideration, the following is obtained:

$$\frac{(\text{allyl})^2}{(\text{diallyl})} = K$$

or

$$(\text{allyl}) \propto (\text{diallyl})^{1/2}$$

This means that the rate of formation of those products which result from attack of 1-butene by the allyl radical should be proportional to $(\text{diallyl})^{1/2}$. In fig. 13 it can be seen that the formation of methane, cyclopentadiene, cyclopentene, methylcyclopentene (and eventually but not necessarily cyclohexene) follows the above dependence within experimental error.

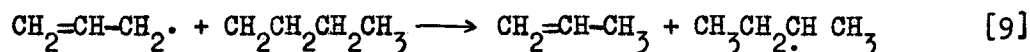
It can therefore be concluded that the above postulated mechanism for the reactions of allyl with 1-butene is correct. Furthermore, this should be an evidence that the primary step in the 1,5-hexadiene decomposition is mainly formation of two allyl radicals.

DECOMPOSITION OF n-BUTANE SENSITIZED BY DIALLYL

Earlier work has shown that it is possible to sensitize the thermal

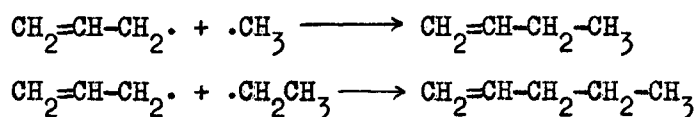
decomposition of n-butane by addition of small amounts of azomethane or ethylene oxide. It appears that the allyl radical is reactive enough at 506° C to sensitize the pyrolysis of 1-butene. It must be borne in mind, however, that in the case of 1-butene the hydrogen abstraction by allyl is eased by the formation of a resonance stabilized radical. No stabilized radical could be expected in the case of n-butane.

From the results obtained there does not seem to be any doubt that the allyl radical is capable of sensitizing the decomposition of n-butane. The rate of formation of the saturated products (methane and ethane) increased by a factor of 2 - 2.5 and the rates of formation of the unsaturated products increased by a factor of 3.5 - 4. It was not intended to postulate any mechanism for this sensitized decomposition, but it can at least be concluded that hydrogen abstraction takes place:



The activation energy for the decomposition of the radical formed is probably lower than that for the decomposition of n-butane. Therefore an over-all acceleration in the pyrolysis process results.

The formation of 1-butene and 1-pentene in the sensitized decomposition can be accounted for by:



It can be therefore concluded that the reactivity of the allyl radical at 506° C is sufficient to abstract hydrogen from secondary carbon atom in n-butane. More generally it might be concluded that the allyl radical is capable of abstracting hydrogen even from compounds which upon abstraction do not yield stabilized radicals.

BIBLIOGRAPHY

B I B L I O G R A P H Y

1. Bateman, L., Gee, G., Morris, A.L. and Watson, W.F., Disc. Faraday Soc., 10, 250 (1951)
2. Bolland, J.L., and Gee, Geoffrey, Trans. Farad. Soc., 42, 244 (1946)
3. Branch, G.E.K., and Calvin, Melvin, The Theory of Org. Chem., Prentice-Hall, Inc., New York, 1947, p. 275
4. Bryce, W.A., and Kebarle, Paul, Trans. Farad. Soc. (in press)
5. Coulson, C.A., Proc. Roy. Soc., A 164, 383
6. Dimbat, M., Porter, P.E., Stross, F.H., Anal. Chem., 28, 290 (1956)
7. Frost, A.A., and Pearson, R.G., Kinetics and Mechanism, John Wiley & sons, Inc., New York, 1953, p. 231
8. Handbook of Chem. and Physics, Chem. Rubber Publishing Co., 1956, p. 1772
9. Kebarle, Paul, Thesis, British Columbia 1957
10. Kebarle, Paul, and Bryce, W.A., Can. J. Chem., 35, 576 (1957)
11. Letort, M., Thesis, Paris, 1937
12. Lossing, F.P., Ingold, K.U., and Henderson, I.H.S., J. Chem. Phys. 22, 621 (1954)
13. McDowell, C.A., Lossing, F.P., Henderson, I.H.S., and Farmer, J.B. Can. J. Chem., 34, 345 (1956)
14. McNesby, J.R., and Gordon, A.S., J. Amer. Chem. Soc., 79, 4593 (1957)
15. Molera, M.J., and Stubbs, F.J., J. Chem. Soc., 381 (1952)
16. Mooney, R.B., and Ludlam, E.B., Proc. Roy. Soc., Edinburgh 49, (1929), 160
17. Rice, F.O., Johnston, W.R., and Evering, B.L., J. Amer. Chem. Soc., 54, 3529 (1932)
18. Ryce, S.A., Kebarle, Paul, And Bryce, W.A., Anal. Chem., 29, 1386 (1957)
19. Sehon, A.K., and Szwarc, M., Proc. Roy. Soc. (London), A 202, 263 (1950)

20. Steacie, E.W.R., Atomic and Free Radical Reactions, Reinhold Publishing Corporation, New York 1954, Vol I., p. 206
21. Steacie, E.W.R., and Puddington, I.E., Can.J. Research, B 16, 176 (1938)
22. Szwarc, M., J. Chem. Phys., 17, 284 (1949)
23. Szwarc, M., and Ghosh, B.N., J. Chem. Phys., 17, 744 (1949)
24. Szwarc, M., Ghosh, B.N., and Sehon, A.H., J. Chem. Phys., 18, 1142 (1950)
25. Taylor, H.S., and Smith, J.O., Jr., J. Chem. Phys., 8, 543 (1940)
26. Trotman-Dickenson, A.F., Gas Kinetics, Butterworths Scientific Publications, London 1955, p. 156

A P P E N D I X

A P P E N D I X

MASS SPECTROMETRIC IDENTIFICATION OF SOME OF THE PRODUCTS

As mentioned previously, it was necessary to identify some of the products formed in the pyrolysis of 1,5-hexadiene by means of a mass spectrometer. Definite proofs have not been obtained in all cases, but very good evidence in all cases. The procedures used are described in each individual case.

Cyclopentene: sample of pure cyclopentene was run through the mass spectrometer and its spectrum compared with the unknown. Definite proof was obtained.

Cyclopentadiene: pure substance was not available. From the value for the retention volume on alumina column it could be deduced that a C_5 hydrocarbon was present. The trapped sample was run at low electron energies and the mass number of the parent peak was thus obtained to be 66. The empirical formula is thus C_5H_6 . Since -ynic products are highly improbable, it must be concluded that cyclopentadiene is present.

1-Hexene: pure sample was not available. Presence of impurities made it difficult to compare the spectrum with that of 1-hexene published by the American Petroleum Institute. Mass spectrometric analyses at low electron energies showed that the parent peak had a mass number of 84. Retention volume on alumina column indicated that a C_6 hydrocarbon was present. From the cyclic compounds cyclohexane is the only one which might be considered. But its retention volume was different from the retention volume

of the unknown. Thus only a straight-chain hydrocarbon can be considered.

Conclusion: 1-hexene.

Cyclohexene and methyl-cyclopentene: these two products were not resolved on the alumina column. Mass spectrometric analyses carried out at low electron energies showed that there was only one parent peak and that was of mass number 82. Retention volume indicated a C_6 hydrocarbon. Thus C_6H_{10} . Comparison with the spectrum of pure cyclohexene showed that cyclohexene might be present but that also some other hydrocarbon C_6H_{10} was present. Methyl-cyclopentene seemed to be the most probable.