

T H E T H E R M A L D E C O M P O S I T I O N
O F
1 - B U T E N E A N D 1 - B U T E N E - 4 - d 3

by

PAUL KEBARLE

Dipl. Ing. Chem., E. T. H. (Zurich), 1952

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in the Department
of
Chemistry

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1957

A B S T R A C T

The thermal decomposition of 1-butene and 1-butene-4-d₃ was studied in the temperature range 490° to 560°C. in a static system. The majority of the reaction products were determined qualitatively and quantitatively by gas chromatography and mass spectrometry. The reaction products consisted of a gaseous and a liquid fraction at S.T.P. The main products in the gaseous fraction were methane, propylene, ethylene and ethane. The principal liquid products were cyclohexadiene, benzene, cyclopentene, cyclopentadiene, and toluene. The liquid fraction also contained a large number of other compounds in trace amounts. The concentrations of the methane, propylene, ethylene and ethane were found to increase almost linearly with the time of reaction over the temperature range. The rates of formation of these products were found to follow a first order dependence on the initial concentration of the butene. The overall activation energy for the butene decomposition was found to be approximately 66 kcal/mole. The overall activation energies for the formation of the individual gaseous hydrocarbons also were determined.

The thermal decomposition of the 1-butene-4-d₃ was found to be nearly identical with that of the 1-butene. The distribution of deuterium in the pyrolysis products was determined. The major components of the light hydrocarbons were: methanes, CHD₃; propylenes, C₃H₆, C₃H₅D, C₃H₃D₂; ethylenes, C₂H₄, C₂H₂D₂, C₂H₃D; ethanes, C₂H₆, C₂H₅D, C₂H₃D₂.

The addition of 5% by volume of mercury dimethyl to the initial 1-butene or 1-butene-4-d₃ was found to produce a large acceleration of the decomposition at 490° C. The products of these sensitized reactions were determined quantitatively and the deuterium distribution in the products from the 1-butene-4-d₃ experiment was obtained.

The results of this investigation provide strong evidence for the existence of complex free radical reactions. A mechanism is proposed which accounts at least qualitatively for the main features of the kinetics and predicts the observed distribution of deuterium isomers in the pyrolysis of the deuterated butene. A feature of the mechanism is the extensive use of disproportionation reactions in which disproportionation is assumed to occur by addition of a free radical to the double bond of the butene, followed by rapid subsequent decomposition of the addition product.

.

The mass spectrum of 1-butene-4-d₃ was measured in a 90° Nier-type mass spectrometer using 50-volt electrons. High resolution nuclear magnetic resonance measurements showed that the methyl group was fully deuterated and that there were no D atoms located elsewhere in the molecule.

A comparison of the mass spectrum with that of 1-butene shows that the total intensities of each group of C₄, C₃, C₂ and C₁ fragments are the same for both compounds. This indicates equal probabilities of C - C bond rupture in the dissociation

of the corresponding parent ions. The distribution of fragments within the groups in the deuterated compound shows, however, that extensive migration of the D atoms has occurred during ionization. Migration is also evident at much lower energies (approximately 15 e.v.)

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.

April 12, 1957

TABLE OF CONTENTS

	Page
INTRODUCTION	2
General	2
Survey of the Literature	4
Investigations of the Decomposition of 1-Butene	4
Primary Step in the Free Radical De- composition of 1-Butene	9
Summary	12
EXPERIMENTAL	15
Method of Pyrolysis	15
Apparatus and Materials	15
Furnace and Temperature Control	15
Description of a Typical Experiment	17
Methods of Analysis	18
Direct Mass Spectrometric Analysis	18
Low Temperature Fractionation and Sub- sequent Analysis of the Fractions with the Mass Spectrometer	19
Analysis by Gas Chromatography	23
Introduction	23
Apparatus and Procedure	25
General	25
Admission of Samples for Analysis into the Separating System	27
Separating Column and Heater	28
Thermal Conductivity Cell and Detection Circuit	29

	Page
System for Collecting the Separated Components	33
Analysis with Gradual Increase of the Column Temperature	34
Basis of the Quantitative Determinations	35
Results for the Pyrolysis of 1-Butene Obtained by Gas Chromatographic Analysis	39
Qualitative Determinations of the Light Hydrocarbons	39
Qualitative Determinations of the Polymers	40
Quantitative Determinations of the Light Hydrocarbons	42
Quantitative Determinations of the Polymers	42
Total Analysis and Material Balances	47
Conversion of the Analytically Determined Concentrations of the Reaction Mixtures to Concentrations in the Reaction Vessel	51
Kinetic Results for the Pyrolysis of 1-Butene	54
Kinetic Order of the 1-Butene Decomposition	54
Pressure Increase in Reaction System and Activation Energy From Pressure Change	56
Rate and Overall Activation Energy of Butene Decomposition	60
Rates of Formation and Overall Activation Energies for the Light Hydrocarbons	68
Time and Temperature Dependence in the Formation of the Polymer Products	72
Thermal Decomposition of 1-Butene Sensitized with Mercury Dimethyl	77
Thermal Decomposition of 1-Butene-4-d ₃	79
Comparison of the Pyrolyses of 1-Butene and 1-Butene-4-d ₃	79
Analytical Methods Used for the Identification of the Deuterated Reaction Products	81

	Page
Reaction Products from the Pyrolysis of 1-Butene-4-d ₃	82
Deutero-Methanes	82
Deutero-Ethanes	89
Deutero-Ethylenes	94
Deutero-Propylenes	98
Deutero-Butenes	102
Deuterium Distribution in the Polymers	105
DISCUSSION	110
Free Radical <u>versus</u> Molecular Mechanism	110
Primary Step of the Free Radical Decomposition of 1-Butene	112
Secondary Reactions in the 1-Butene Decomposition	115
Hydrogen Abstraction by Methyl Radicals	115
Addition of Methyl Radicals	122
Reactions of the Free Radicals Stabilized by Allyl-Type Resonance	132
Pyrolysis of 1,5-Hexadiene	140
Addition Reactions of Hydrogen Atoms	143
Mechanism of the Thermal Decomposition of 1-Butene and 1-Butene-4-d ₃	148
Significance of some of the Findings and Suggestions for Further Experimental Work	154
Pyrolysis of 1-Butene in the Presence of Deuterium	157
LITERATURE CITED	165
APPENDIX I: QUALITATIVE INVESTIGATION OF THE POLYMER PRODUCTS FORMED IN THE PYROLYSIS OF 1-BUTENE	169
Literature Cited	177

	Page
APPENDIX II: DEUTERIUM MIGRATION DURING THE IONIZATION OF 1-BUTENE-4-d ₃ BY ELECTRON IMPACT	179
Introduction	179
Experimental	180
Discussion	183
Literature Cited	190

TABLES

	Page
I Thermal Decomposition of 1-Butene (Wheeler and Wood)	5
II Results from Low Temperature Fractionation and Subsequent Mass Spectrometric Analysis of the Fractions	22
III Sensitivity of 1-Butene	38
IV Variation of Sensitivities of Light Hydrocarbons Over a Month's Period	39
V Analytical Results for Light Hydrocarbons	43
VI Analytical Results for Polymers	45
VII Total Composition of Reaction Mixtures in Volume %	48
VIII Mass Balances	49
IX Composition of Reaction Mixtures with Change in Initial Pressure of 1-Butene	55
X Activation Energy from Pressure Increase	58
XI Analyses of Reaction Mixtures -- Light Hydrocarbons (in Mole %)	61
XII Butene Decomposition, Variation of First Order Rate Constants with Reaction Time	64
XIII Activation Energies for the Butene Decomposition	65
XIV Rate Constants for the Formation of the Light Hydrocarbons	67
XV Activation Energies of the Light Hydrocarbons	68
XVI Thermal Decomposition of 1-Butene Sensitized with Mercury Dimethyl	76
XVII Increased Rate of Formation of Light Hydrocarbons in Sensitized Reaction	77
XVIII Light Hydrocarbons from the pyrolyses of 1-Butene and 1-Butene-4-d ₃	80
XIX Mass Spectra Used for Correction of the CH ₃ D Spectrum	83
XX Deutero-Methanes from the Pyrolysis of 1-Butene-4-d ₃	86

	Page
XXI Increased Rates of Formation of Deutero-Methanes in Reaction Sensitized with Mercury Dimethyl	89
XXII Deutero-Ethanes from the Pyrolysis of 1-Butene-4-d ₃	91
XXIII Increased Rates of Formation of Deutero-Ethanes in Reaction Sensitized with Mercury Dimethyl	94
XXIV Deutero-Ethylenes from the Pyrolysis of 1-Butene-4-d ₃	96
XXV Increased Rates for Formation of Deutero-Ethylenes in Reaction Sensitized with Mercury Dimethyl	98
XXVI Deutero-Propylenes from the Pyrolysis of 1-Butene-4-d ₃	100
XXVII Increased Rates of Formation of Deutero-Propylenes in Reaction Sensitized with Mercury Dimethyl	102
XXVIII Mass Spectra of Deutero-Butenes	103
XXIX Comparison of Normal and Sensitized Decomposition of 1-Butene-4-d ₃	104
XXX Deutero-Isomers of the Polymers from the Pyrolysis of 1-Butene-4-d ₃	106
XXXI Ratios of Total to Primary Decomposition of 1-Butene for 1 Minute Reaction Time	115
XXXII Abstraction of Hydrogen Atoms by Methyl Radicals (Trotman-Dickenson and Steacie)	117
XXXIII Addition of Methyl Radicals to Unsaturated Hydrocarbons (Mandelcorn and Steacie)	125
XXXIV Decomposition Reactions of the C ₅ H ₁₁ Radicals	128
XXXV Ratios of Polymer Formation to Primary Decomposition of the 1-Butene	136
XXXVI Ratios of Hydrogen Gas Plus Chemically Bound Hydrogen in Polymers to Chemically Bound Carbon in Polymers	138
XXXVII Hydrogen to Carbon Ratios in Polymer Products Resulting from Various Reactions	139

		Page
XXXVIII	Products from the Pyrolysis of 1,5-Hexadiene	142
XXXIX	Ratios of C_3H_5D to Total Molecular Hydrogen	147

APPENDIX I

I	Comparison of the Mass Spectrum of Fraction P_2 with that of Cyclopentene	171
II	Mass Spectra of Fraction P_3 , Trans-2-Pentene-4-yne, and Cyclopentadiene	173
III	Mass Spectrum of Fraction H_1	174
IV	Mass Spectra of Fractions H_2 , H_3 and 1,3-Cyclohexadiene	175
V	Mass Spectra of Fraction X_1 and O-Xylene	176

APPENDIX II

I	Variation of C_3 Ion Intensity with Electron Accelerating Potential for $CD_3CH_2CHCH_2$	185
II	Pyrolysis Products for the Two Butenes after 5.0 Min. at 552 °C	185
III	Variation of Ratio of the Sum of Masses 42, 43, and 44 to Mass 41 with Electron Energy	187

FIGURES

	Page
1a. Pyrolysis Apparatus	16
1b. Circuit Diagram of Furnace Heaters	16
1c. Furnace and Reaction Vessel with Thermocouples	16
2. Low Temperature Fractionation Apparatus	20
3. Gas Chromatographic Apparatus	26
4. Thermal Conductivity Cell	30
5. Diagram of Thermal Conductivity Recording Circuit	32
6. Gas Chromatographic Separation of the Light Hydrocarbons	36
7. Gas chromatographic Separation of the Polymers	41
8. Pressure Increase with Time	57
9. Activation Energy from Initial Rate of Pressure Increase	59
10. Butene Decomposition as a Function of Time	63
11. Overall Activation Energy of 1-Butene Decomposition	66
12. Time Dependence of Concentrations of Light Hydrocarbons	69
13. Activation Energies for the Formation of the Light Hydrocarbons	71
14. Time Dependence of Concentrations of Cyclohexadiene, Benzene and Toluene	73
15. Time Dependence of Concentrations of Cyclopentene and Cyclopentadiene	75
16. Comparison of Normal and Sensitized Decomposition of Butene-1	78
17. Composition of Deutero-Methanes as a Function of Temperature	88

	Page
18. Composition of Deutero-Ethanes as a Function of Temperature	93
19. Composition of Deutero-Ethylenes as a Function of Temperature	97
20. Composition of Deutero-Propylenes as a Function of Temperature	101
21. Deuterium Distribution in Polymers	108
22. Formation of CH_3D and CH_4 in the Pyrolysis of 1-Butene in the presence of Deuterium	159

APPENDIX II.

1a. NMR Absorption Spectrum of 1-Butene	181
1b. NMR Absorption Spectrum of 1-Butene-4- d_3	181
2. Mass Spectrum of 1-Butene	184
3. Mass Spectrum of 1-Butene-4- d_3	184
4. Normalized Spectra of 1-Butene (Black) and 1-Butene-4- d_3 (White) Showing the Relative Total Intensities for Each Group of Ions	184

ACKNOWLEDGMENT

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

The gas chromatographic apparatus was built jointly with Mr. S. A. Ryce whose cooperation is gratefully acknowledged.

The author is also indebted to the Defence Research Board for financial assistance during the course of this work and to the Standard Oil Company for a Graduate Scholarship (1953-54).

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

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

GENERAL

An experimental investigation in chemical kinetics generally involves the design and execution of experiments that provide appropriate data for the determination of the rates and mechanisms of the reactions concerned. In chemical reactions proceeding by radical chains, a special task arises in the determination of the elementary reactions involved in the mechanism. The thermal decomposition of hydrocarbons often proceeds largely by chain mechanisms. In this field, many investigations have been undertaken in which attempts were made to determine the chain mechanism by studying the overall thermal decomposition of the hydrocarbons. However, it has been gradually realized that most of the systems studied were prohibitively complex and that the information obtained was generally not sufficient for the establishment of the elementary steps occurring in the reaction mechanism. Therefore, in the last two decades, a change in approach has taken place. More of the investigations undertaken have been aimed at the study of isolated elementary reactions. Considerable knowledge, imagination and experimental skill are required for the design of a system by which an elementary reaction can be studied successfully.

Data on elementary reactions are of great importance because of their generality. Thus, a knowledge of the rate of recombination of methyl radicals can be applied to many

systems in which methyl radicals are produced. However, such a "carry over" of data from one reaction system to another is certainly not permissible in all cases. In some reaction systems, energetically excited "hot" radicals may be produced which behave quite differently from the normal species.

If the elementary reaction studied is the splitting of a molecule (or radical), the activation energy of the reaction can be identified with the dissociation energy of the bond broken, if the assumption is made that the activation energy of the reverse reaction is approximately zero. In this way, the study of elementary reactions can provide information about bond dissociation energies and conversely, bond dissociation energies determined by other means can be used in investigations of elementary reactions.

If a sufficient set of data on elementary reactions which might participate in the decomposition of a hydrocarbon (or in any other complex reaction) is available, the final test of the usefulness of these data is to attempt to use them to describe the kinetic behavior of the complex system. This final test often fails, as is illustrated by the thermal decomposition of ethane, about which considerable controversy still exists. This suggests that more reliable information about elementary reactions is required, and also that the "carry over" of information has to be done with caution.

In the light of the above considerations, the present

investigation, a study of the overall thermal decomposition of 1-butene, might appear to be somewhat out-dated. Yet, there are several justifications for undertaking it. No systematic investigation of the overall thermal decomposition of 1-butene is reported in the literature. This applies especially to the quantitative determination of the products formed. Subsequently, no reaction mechanism has been postulated or assumed. A considerable amount of information on elementary radical reactions is available in the literature. It was therefore believed that, if radical reactions are involved, it might be possible to correlate the available information with reliable analytical results for the products of butene decomposition in a way which would lead to a plausible mechanism for the overall reaction.

The thermal reactions of all higher olefins are not understood with any certainty. A better understanding of the thermal decomposition of 1-butene would throw some light on the thermal behavior of these olefins, since 1-butene can be considered as a good kinetic representative of this group of compounds.

SURVEY OF THE LITERATURE

INVESTIGATIONS OF THE DECOMPOSITION OF 1-BUTENE

The earliest investigation of the thermal decomposition of 1-butene was made by Wheeler and Wood.³⁶ 1-Butene was decomposed in a flow system in the temperature range between 600 and 700°C. The contact time varied with temperature from

20 seconds for the low temperature range to 10 seconds for the higher temperatures. At room temperature, the composition of the reaction mixtures obtained was: 88% gaseous products and 12% liquids, by weight.

The gas fraction was analysed separately. The unsaturated hydrocarbons were separated from the paraffins through bromination, and the bromides were identified further. The paraffins in the gas fraction were shown to be only methane and/or ethane, since no condensation occurred at the temperature of dry ice. The relative proportion of methane to ethane then was determined by combustion. The results obtained for the gaseous products are given in Table I.

TABLE I.

Thermal Decomposition of 1-Butene (Wheeler and Wood)

Temp.	Products in Volume % of Initial 1-Butene						
°C	C_4H_6	C_4H_8	C_3H_6	C_2H_4	H_2	CH_4	C_2H_6
600	0.9	54.0	7.6	3.2	0.8	8.1	1.9
650	1.7	20.0	24.5	14.2	6.2	37.2	7.1
700	1.4	2.1	19.6	22.3	11.9	62.1	10.6

The liquids in the reaction mixture were separated roughly by distillation, and the fractions were examined further. Cyclohexene, methyl-cyclohexene, cyclohexadiene, methyl-cyclohexadiene, benzene, and toluene were found to be some of the major products.

Wheeler and Wood assumed that three primary reactions

are responsible for the formation of the gaseous products. The first primary reaction considered is the rupture of the terminal bond of the 1-butene. This is followed by "hydrogenation of the radicals formed". Thus, the resulting products, methane and propylene, are formed in equal proportions, in approximate agreement with the analytical results for the lower temperatures. It is not clear whether or not Wheeler and Wood considered the products from the primary split to be free radicals. Since the work was done in 1930, one year before Paneth and Hofeditz positively proved the existence of free methyl radicals by the mirror technique, it must be assumed that the "radicals" referred to here were methane and allene. The subsequent hydrogenation was thought to be due to molecular hydrogen liberated from the second primary decomposition reaction of the butene, namely, the direct dehydrogenation of butene to butadiene. The third primary reaction considered is the decomposition of the butene to ethylene, some of the ethylene subsequently being hydrogenated to ethane.

The liquid hydrocarbons were believed to originate from the combination of the butadiene with an olefin; i.e., cyclohexene from ethylene and butadiene, and methyl-cyclohexene from propylene and butadiene, with subsequent dehydrogenation of the cyclic compounds so formed. To test this assumption, Wheeler and Wood heated mixtures of ethylene and butadiene. At 600°C, a mixture of 12.85% butadiene and 87.15% ethylene was prolysed under the same experimental conditions as was the butene. The formation of small amounts of cyclohexene

was observed. The dehydrogenation of the cyclohexene to form the more unsaturated products found, also was investigated by pyrolysing cyclohexene. At 600°C , approximately 9% of the original product was converted to benzene.

The molecular mechanisms assumed by Wheeler and Wood explain, in a general way, the formation of the main products. However, the experimental evidence clearly is insufficient to warrant an acceptance of the proposed reactions.

Hurd and Goldsby¹² have also studied the thermal decomposition of 1-butene. Analysis of the gaseous products was made by low temperature fractionation in an improved Podbielniak type distillation column. The analytical results obtained were similar to those of Wheeler and Wood. The authors were interested mainly in the isomerization of the 1-butene to 2-butene occurring at temperatures above 600°C , and therefore, a general reaction mechanism was not considered.

A more recent investigation is reported by Molera and Stubbs²² in a survey of the thermal behavior of a number of olefins in a static system. The initial pressure increase was found to be proportional to the initial pressure of 1-butene admitted, with a range of initial pressures from 50 to 500 mm. Hg. Therefore, an overall first order reaction was indicated. The activation energy for the overall reaction was determined by an Arrhenius plot of the initial rate obtained from pressure change measurements. The value found was $E=66.4$ kcal./mole, for the temperature range between 490 and 600°C . Unfortunately, activation energies

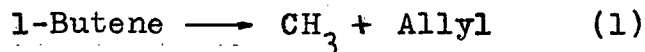
determined by following the initial pressure increase are difficult to interpret without a knowledge of the mechanism involved or of the reaction products formed.

Molera and Stubbs also investigated the effect of nitric oxide on the reaction. Addition of nitric oxide was found to produce an increase in the rate measured by the initial pressure increase.

The addition of nitric oxide in hydrocarbon pyrolysis has been used widely to test for the participation of free radicals. The nitric oxide is believed to be a very efficient inhibitor of free radical chains. Thus, a decrease in the decomposition rate in the presence of nitric oxide indicates that the reaction proceeds partly or exclusively by radical chains. Conversely, if the addition of nitric oxide has no effect, radical mechanisms do not appear to participate in the reaction. According to this concept, the slight increase in rate found by Molera and Stubbs should indicate that radical chains do not participate extensively in the reaction mechanism. However, some of the conclusions obtained with the use of the nitric oxide technique are open to doubt, and still subject to controversy. In the special case of 1-butene, an inhibitor of radical chains itself, the lack of inhibiting action of the nitric oxide cannot be considered as conclusive proof that free radicals do not participate in the reaction. This question will be dealt with in more detail in the discussion of the experimental results.

PRIMARY STEP IN THE FREE RADICAL DECOMPOSITION OF 1-BUTENE

For a number of years it has been recognized that the allyl radical is stabilized by high resonance energy. This has been substantiated on theoretical as well as on experimental grounds. The resonance energy of the allyl radical has been estimated theoretically by Coulson⁴ as 15.4 kcal./mole and by Orr (quoted by Bolland)³ as 18.7 kcal./mole. The high resonance energy of the allyl radical should manifest itself in a low value of the dissociation energy of the allyl-methyl bond as compared with the propyl-methyl bond in n-butane. The weakest bond in 1-butene is thus the allyl-methyl bond, and at sufficiently high temperatures, the thermal decomposition should proceed, at least partly, with the primary step (1), as follows:



The presence of methyl and allyl radicals in the pyrolysis of 1-butene has been detected directly with the aid of the mass spectrometer by Lossing, Ingold and Henderson.¹⁶ 1-Butene was decomposed at 1000°C in a fast flow system attached to a mass spectrometer. The nature of the apparatus requires relatively high concentrations of radicals for their positive detection. Since the contact time used in this method is also very short (about 0.8 milliseconds), the temperatures used are considerably higher than those of conventional kinetic investigations. The temperature range studied in the present investigation is lower by 400°C. The considerable difference

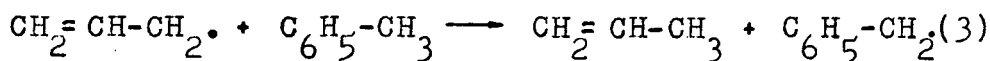
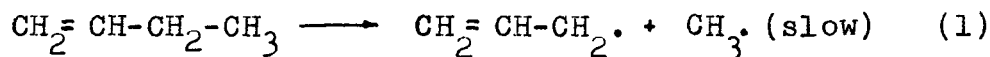
in temperature reduces the significance of Lossing's results for the present study, since the reaction might proceed by a different path at temperatures so much lower.

The primary step of the 1-butene decomposition has been studied at lower temperatures (650-770°C) by Sehon and Szwarc.²⁵ The investigation was based on the toluene carrier³⁰ technique. The main feature of the method is the use of toluene as a carrier gas. The radicals formed in the primary decomposition of the compound under investigation are removed by the fast reaction with toluene.

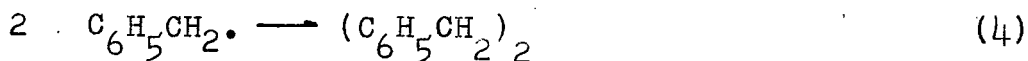


The relatively stable benzyl radicals dimerize eventually to dibenzyl. The toluene present in large excess thus acts as an effective chain inhibitor.

In the particular case of 1-butene, the idealized mechanism can be expressed by the equations:



and chain terminating steps like:



According to the above scheme the rate of formation of methane is equal to the rate of the primary decomposition. The rate of formation of methane can be conveniently measured by separation of the methane from the reaction products at the

temperature of liquid nitrogen. In the work described, the non-condensables contained, besides the expected methane, varying amounts of hydrogen (3% H_2 at $935^\circ K$ increasing to 26% H_2 at $1051^\circ K$). An Arrhenius plot of the rate of formation of non-condensables gave a straight line. The activation energy found was 61.5 kcal. and the frequency factor, $A = 10^{13} \text{ sec}^{-1}$. In separate experiments, it was shown that packing of the reaction vessel with silica wool had no influence on the rate, indicating a homogeneous reaction. The reaction also was shown to be of first order by a variation of the partial pressure of the butene by a factor of 6. The activation energy and frequency factor obtained were identified with those of the primary decomposition of 1-butene.

The results of Sehon and Szwarc provide the only quantitative data for the activation energy and frequency factor of the primary step in the free radical decomposition of 1-butene. However, it seems that the interpretation of the experimental results on the basis of the assumed mechanism was done without sufficient proof that the mechanism indeed represents the major reactions correctly. For example, a significant amount of hydrogen, not accounted for by the mechanism, was found in the methane fraction, the only gas fraction analysed. Also, the amount of dibenzyl, the only other product quantitatively determined, was considerably lower than the theoretically expected amount. The argument that the activation energy and frequency factor obtained represent values for the postulated primary step of the 1-butene decomposition

therefore must be accepted with caution.

SUMMARY

The investigations referred to above provide the only direct information on the thermal decomposition of 1-butene available in the literature. A large number of products apparently are formed in the reaction, but the information available was not sufficient to explain the modes of formation of these products satisfactorily. The important question concerning the reaction mechanism, whether or not radical chains participate, is also not answered with any certainty.

While there is positive evidence that free radicals are formed in the pyrolysis of 1-butene at 1000°C, the evidence available for the temperature range from 500 to 600°C was not sufficient to warrant a decision on this point. For this reason, possible secondary reactions of the free radicals produced by a primary split of the butene molecule will not be reviewed here, although such reactions have been studied. For example, the reactions of methyl radicals with 1-butene in systems where the methyl radicals were produced by the photolysis of acetone or by some other means have been investigated. The information about such reactions will be discussed later in relation to the experimental results from this work.

A major difficulty in past kinetic investigations has been the lack of convenient analytical methods capable of

providing adequate quantitative analyses. As a result, it has been a practice, in the past, to postulate mechanisms based on a minimum of quantitative information. In recent years, a number of excellent analytical methods especially suited for the analysis of very small quantities of complex mixtures of hydrocarbons have been developed. Some of these methods have been used in the present work.

The objective of the present study was the elucidation of the mechanism of the thermal decomposition of 1-butene. The investigation involved the following steps:

Choice of a suitable analytical method to provide sufficiently accurate analytical results.

Qualitative determination of the compounds present in the reaction mixtures.

Determination of the rates of formation of the products and the rate of butene decomposition as a function of temperature.

Specific testing to determine whether or not radical chains participate in the mechanism.

Tracing the origin of the products formed with the use of the deuterio-isomer 1-butene-4-d₃.

Correlation of the data and determination of the significant kinetic constants on the basis of a mechanism derived from the experimental results.

E X P E R I M E N T A L

EXPERIMENTAL

METHOD OF PYROLYSIS

APPARATUS AND MATERIALS

The 1-butene used was Phillips Research grade (99.8%). The method of preparation of the 1-butene-4-d₃ together with proofs of structure and purity are given in Appendix II.

The butenes were pyrolysed in a conventional static system. The apparatus used is represented in Fig. 1a. V₁ and V₂ are storage flasks for the 1-butene and 1-butene-4-d₃. M₁ and M₂ are mercury manometers. S is the silica reaction vessel (300 cc.). The reaction vessel was heated in an electric furnace. The system could be evacuated by a mercury diffusion pump.

FURNACE AND TEMPERATURE CONTROL

The heating arrangement is shown in Fig. 1c. The furnace consisted of a quartz tube around which three separate heating coils were wound. The tube was placed in a small steel barrel and insulated with asbestos wool. Two chromel-alumel thermocouples were fastened to the top and bottom of the reaction vessel. The current for the heating coils was supplied through a Sorensen voltage regulator and adjusted for a given temperature by a variable transformer (Fig. 1b). For finer manual adjustment and manual temperature control, the resistance R₁ was used. The current through the three separate heating coils could be adjusted by the resistances

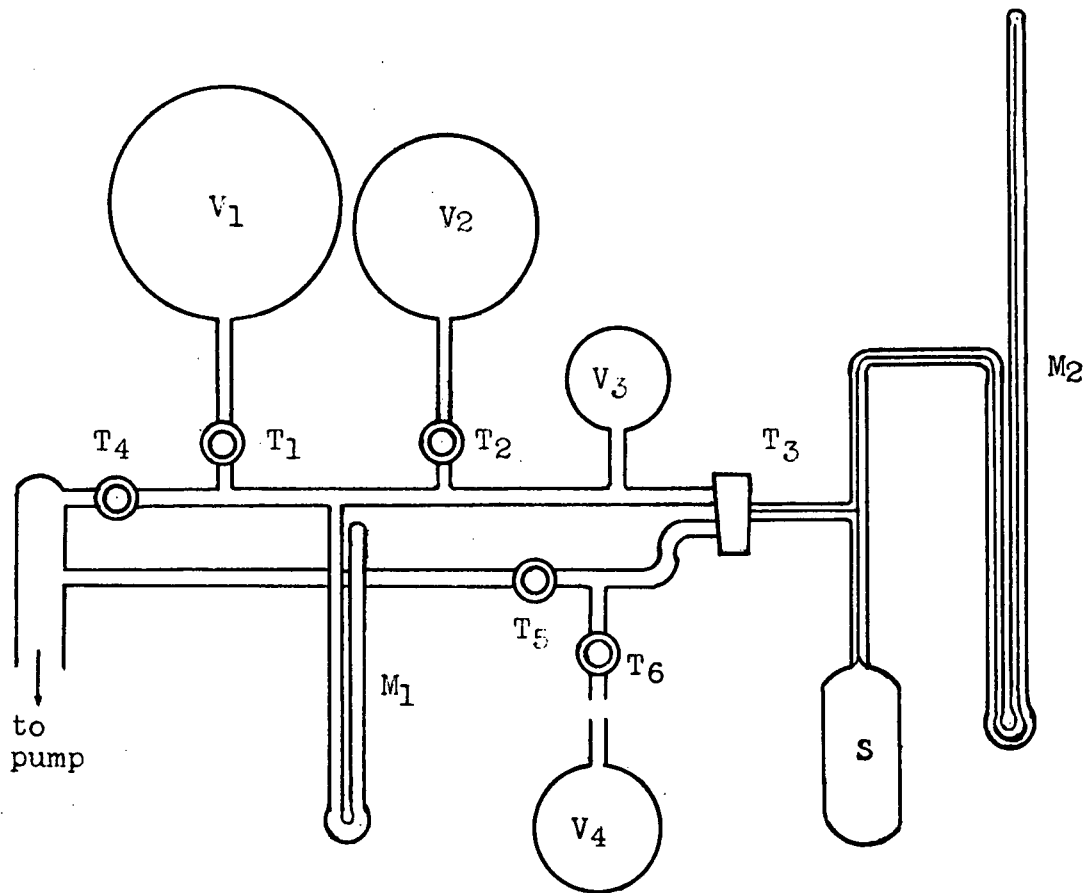


Fig.1a:Pyrolysis Apparatus

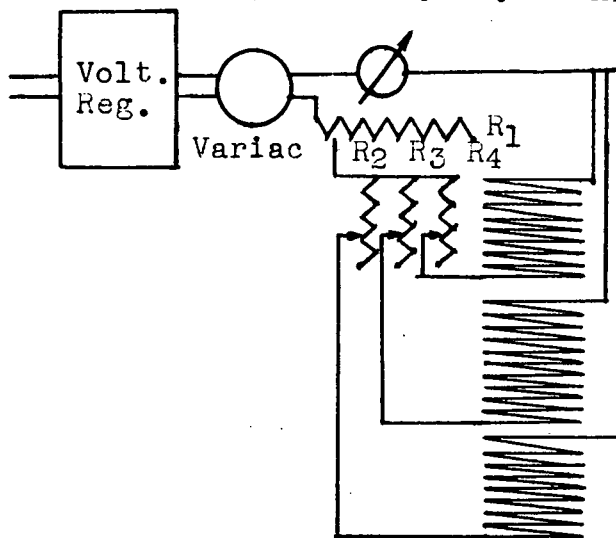


Fig.1b
Circuit Diagram of
Furnace Heaters.

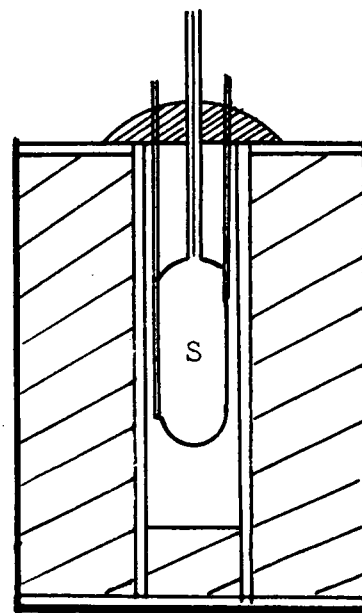


Fig.1c
Furnace and Reaction
Vessel with Thermo-
couples

R_2 , R_3 and R_4 to obtain the same reading on both thermocouples. It was possible to maintain the temperature of the reaction vessel constant to within 1°C .

DESCRIPTION OF A TYPICAL EXPERIMENT

To shorten the time for admission of a measured quantity of reactant gas into the heated reaction vessel, a pre-expansion volume V_3 was used. The pressure of butene admitted in V_3 (and read on manometer M_1), was so chosen as to produce a desired resultant pressure after expansion of the gas from V_3 into the reaction vessel. From V_3 , the gas was expanded into the reaction vessel by fully opening the connecting stopcock T_3 . After approximately 5 seconds, the pressure on the manometer M_2 having become stationary, stopcock T_3 was closed. The reaction time was measured from this moment. The pressure of the reaction system could be followed by readings on the mercury manometer M_2 .

After the desired reaction time (1-5 minutes) had elapsed, stopcock T_3 was opened to the lower gallery and the reaction mixture expanded through the open stopcock T_6 into the receiving volume V_4 . After a few seconds, T_6 was closed. The gas trapped in the receiving volume V_4 was used for analysis, while the remaining gas mixture in the reaction vessel was pumped out by opening T_5 .

The volume of the receiving pipette V_4 and its connection to the pyrolysis apparatus varied with the method and purpose

of the analysis. The individual variations will be mentioned in the discussion of the analytical methods.

METHODS OF ANALYSIS

DIRECT MASS SPECTROMETRIC ANALYSIS

The mass spectrometer used in all determinations was a 90° sector type instrument. Magnetic scanning and pen recording were employed. The sensitivity of recording was such that an ion current of 3×10^{-14} amps. gave a deflection of 1 cm. on the Leeds and Northrup Speedomax recorder. The ion source and electronic controls have been described by Lossing and Tickner,¹⁸ and by Graham, Harkness and Thode.¹¹ The instrument was of the same type as those used by Lossing and associates.

To obtain gas samples for analysis, a 300 cc. pipette (provided with stopcock) was attached by means of a ground glass joint to the outer end of stopcock T₆ of the pyrolysis apparatus. (See Fig. 1a.)

Direct mass spectrometric analysis showed that the reaction mixtures obtained at 490 - 550°C and 1-5 minutes reaction time contained; hydrogen, methane, ethane, ethylene, propylene, 1, 3-butadiene and unreacted butene, plus a great many compounds with masses higher than the molecular weight of butene. For convenience, pyrolysis products with a molecular weight greater than that of butene will be referred to as polymers. The molecular masses (parent masses) of the

polymers could be determined by scanning the higher mass range at low electron energies. The existence of a large number of possible isomers, and the lack of complete data on the mass spectra of hydrocarbons in the C_5 to C_8 range made the interpretation of the spectra very difficult. Furthermore, the quantitative determination of the lighter hydrocarbons was made uncertain by the contributions of the polymers to peaks in the lower mass range. For these reasons, the method of direct analysis was abandoned.

LOW TEMPERATURE FRACTIONATION AND SUBSEQUENT ANALYSIS OF THE FRACTIONS WITH THE MASS SPECTROMETER

Since mass spectrometric analysis could not be applied directly, a fractionation of the reaction mixture prior to mass spectrometric analysis was undertaken.

A LeRoy still¹⁵ was constructed for this purpose. The apparatus is represented in Fig. 2. It consisted of three main parts; sample pipette V (300 cc.), fractionation column F and Toepler pump T. The free end of the mercury cut-off C_1 was sealed to stopcock T_6 of the pyrolysis apparatus (see Fig. 1a). The amount of gas sample admitted into the calibrated volume of the pipette V could be determined by reading the pressure on the mercury manometer M. From pipette V, the gas sample was admitted into the fractionating column, which was cooled with liquid nitrogen. The gases not condensed after a short waiting period (hydrogen and methane) were removed. For this purpose, the mercury cut-off C_3 was opened and

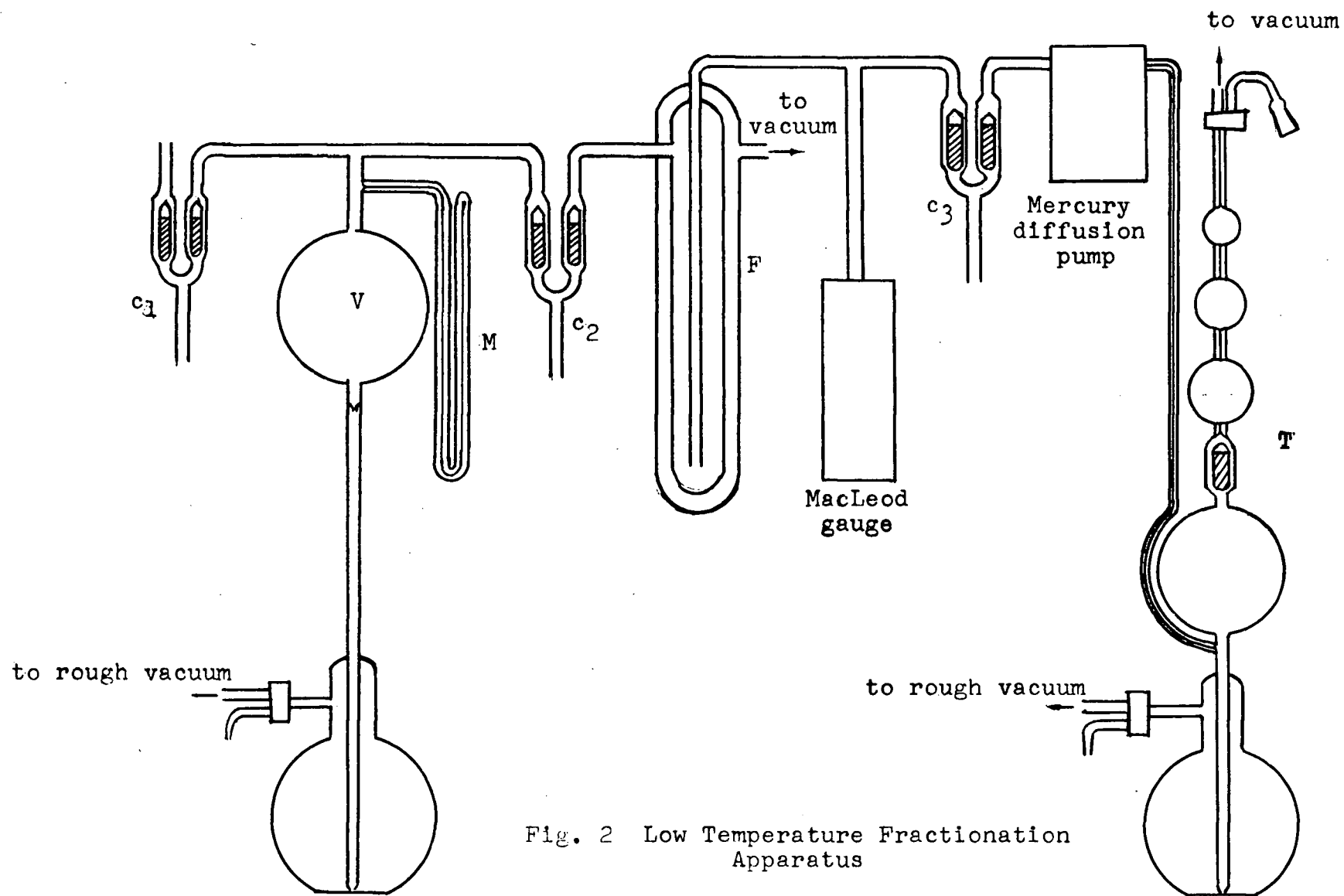


Fig. 2 Low Temperature Fractionation Apparatus

the gas pumped out by means of the auxiliary mercury diffusion pump and the Toepler pump. The amount of collected gas was measured in one of the calibrated volumes of the Toepler pump and then transferred into a pipette for mass spectrometric analysis. The fractionating column was then heated, by means of a built-in heating coil, to a slightly higher constant temperature. The column temperature was adjusted to produce the desired pressure of gas inside the column. The pressure was determined with the McLeod gauge. A pressure of 10-100 microns Hg generally was used, depending on the desired amount of fraction to be obtained. The fraction then was collected by means of the Toepler pump until the column pressure had fallen off to 1-10 microns Hg. In this way, a desired number of fractions, or "cuts", could be collected for mass spectrometric analysis.

The mass spectrometric results for the fractions of a typical run are reproduced in Table II.

A comparison of the values in Table II with values obtained later by gas chromatographic analysis (see Table V, reaction mixture 554.5°C - 4 min.) shows good agreement between the two methods.

The analysis by low temperature fractionation had some important disadvantages. The polymers could not be identified beyond their molecular masses, since the fractionation in the high molecular range was not efficient. Complete identification of the polymers was desirable for a better understanding of the reaction mechanism. Also, the results

Table II

Results from Low Temperature Fractionation and Subsequent
Mass Spectrometric Analysis of the Fractions

Analysed mixture produced by pyrolysis of 1-butene
(initial pressure 200 mm. Hg) for 4 minutes at 550°C.

Fraction No.	Amount of Fraction Volume %	Distribution of Compounds in Fraction Volume %
1	26.0	3.5 Hydrogen 22.5 Methane
2	7.3	0.3 Methane 6.5 Ethylene 0.5 Ethane
3	6.6	1.8 Ethylene 4.1 Ethane 0.5 Propylene 0.2 Butene
4	17.0	13.8 Propylene 1.0 Butadiene 0.8 Butene
5	36.7	0.3 Propylene 1.0 Butadiene 35.4 Butene
6	1.3	0.4 Butene 0.9 C ₅ H ₆ , C ₅ H ₈ , C ₅ H ₁₀
7 - 9	6.0	6.0 C ₆ H ₆ , C ₆ H ₈ , C ₆ H ₁₀ , C ₇ H ₈ , C ₇ H ₁₀ , C ₇ H ₁₂ , C ₈ H ₁₄
	<hr/> 99.6	<hr/> 99.6

Composition of Reaction Mixture in Vol. %

Hydrogen	3.5
Methane	22.8
Ethylene	8.3
Ethane	4.6
Propylene	14.6
1,3-Butadiene	2.0
Butene	36.8
Polymers	6.9
	<hr/> 99.5

in Table II show that the separation of the lighter hydrocarbons was not complete. For the mass spectrometric analysis of fractions from the pyrolysis of 1-butene, this is of little consequence. However, the analysis of the deuterated reaction products from 1-butene-4-d₃ would have been impossible under the same conditions. Another important disadvantage of the fractionation method is that it is very time-consuming.

Fortunately, the advent of gas chromatography coincided closely with the full realization of the drawbacks of the low temperature fractionation method.

ANALYSIS BY GAS CHROMATOGRAPHY

INTRODUCTION

A survey of this rapidly developing field will not be attempted here. Extensive bibliographies can be found in many recently published papers. 8, 9, 10

The separation of gaseous or liquid mixtures by the adsorption-elution and partition-elution methods is effected by passing the mixture in vapor form carried in a stream of an inert gas through a column filled with some "active" material. In the case of adsorption-elution chromatography, the "active" material is a solid, such as alumina, silica gel, charcoal, etc. The separation is then due to differential adsorption, as a result of which the different compounds travel through the column with different speeds, and

emerge from the end separately. In partition-elution chromatography, the active material in the column is a suitable liquid with low vapor pressure. The liquid is supported on the surface of particles of inactive material, such as cellite, glass powder, ground firebrick, etc., free passage of the carrier gas and a stationary liquid phase thus being achieved. The separation in this case is due to differential absorption of the compounds into the liquid phase, i.e., differences in the distribution coefficients of the components of the mixture.

The compounds leaving the end of the separating column can be detected in different ways. One of the methods commonly used employs a thermal conductivity cell mounted in a balanced bridge circuit. In this method, the detection is effected by passing the carrier gas alone through one channel of the cell (reference channel). The carrier gas leaving the separating column, carrying the separated compounds, is passed through the second channel of the cell (detection channel). The appearance of a compound other than the carrier gas in the detection channel causes an imbalance in the bridge circuit. Since the output of the bridge is fed into a recorder, the passage of each component of the gaseous mixture through the detection channel produces a peak on the recorder chart. The respective positions of the peaks can be used for qualitative identification of the compounds. The areas of the peaks are a measure of the amounts of the corresponding compounds in the sample.

APPARATUS AND PROCEDURE

General

The apparatus represented in Fig. 3 was constructed for the separation of the reaction mixtures obtained in the butene pyrolysis. It consisted of four main parts:

Sample admission section, for measuring samples and admitting them into the separating column.

Separating column with heater.

Thermal conductivity cell and detection circuit.

System for collecting the separated fractions.

Helium was used as the carrier gas. The carrier gas, supplied from a storage cylinder, passed through a reduction valve, a needle valve and a U-tube purifier filled with charcoal and silica gel into the reference channel of the thermal conductivity cell. From there, the gas was directed through either arm B_1 or B_2 of the bypass into the separating column. The gas leaving the column passed through the second (detection) channel of the thermal conductivity cell and then through any one of the traps t_1 to t_4 where the separated compounds could be collected. The gas then passed through stopcock S_{10} to the flow meter and finally out to the atmosphere. When collection of the fractions was not required, the gas leaving the detection channel of the conductivity cell was not directed through a trap, but bypassed to the flow meter by means of stopcock S_9 .

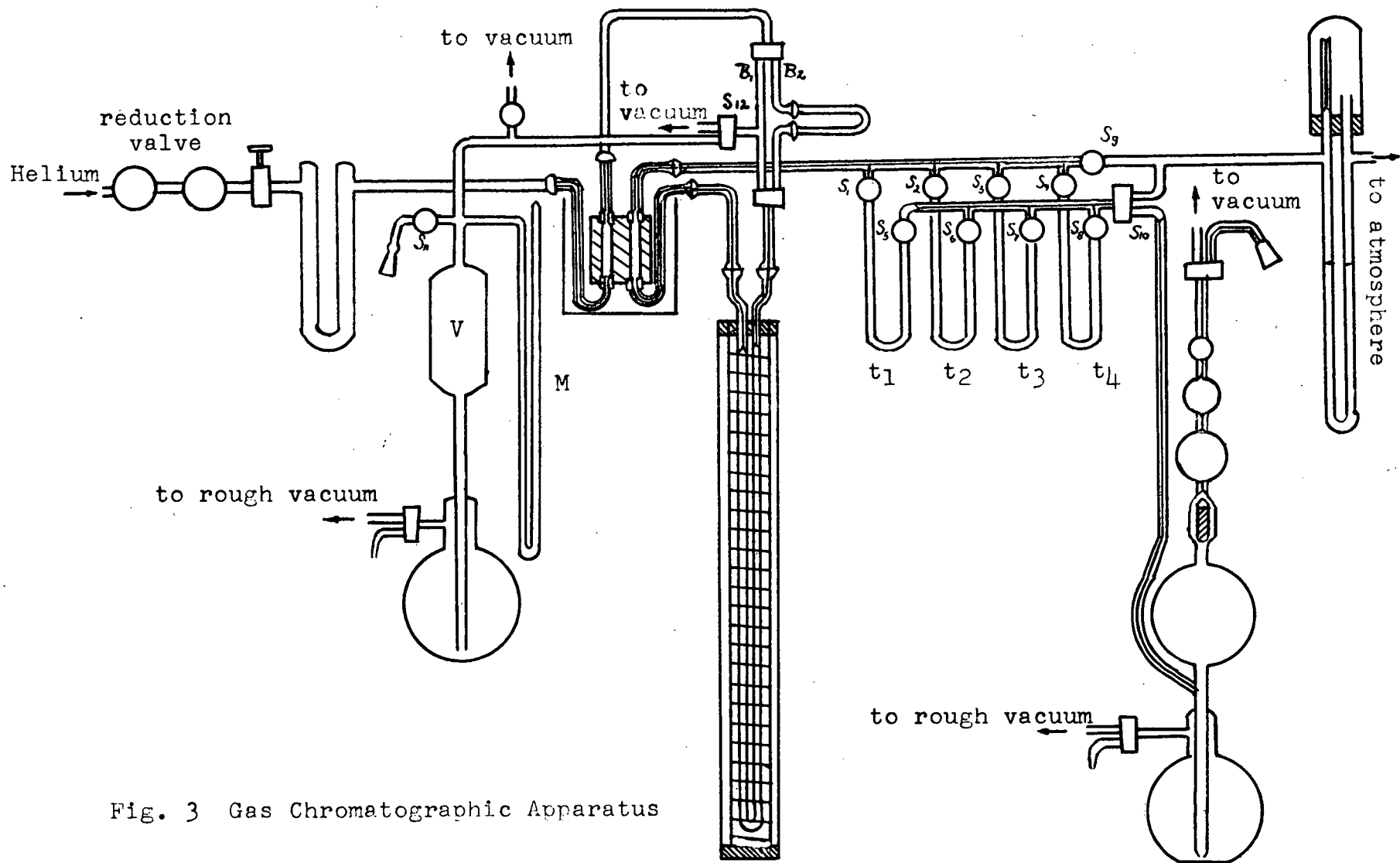


Fig. 3 Gas Chromatographic Apparatus

Admission of Samples for Analysis Into The Separating System

Samples for analysis could be admitted to the separating system in either gaseous or liquified form.

For admission of gaseous samples, the reservoir V and the bypass arm B_1 were used. The gas sample, withdrawn from the pyrolysis apparatus by means of a gas pipette, was admitted through stopcock S_{11} into the evacuated gas reservoir V and the bypass arm B_1 , the helium stream having been re-directed previously through bypass arm B_2 . Then, the pressure of the gas sample was adjusted to the desired value by raising or lowering the mercury level in V. After the pressure was read on the mercury manometer M, stopcock S_{12} was closed. The gas sample trapped in bypass arm B_1 was carried to the column by redirecting the helium stream through B_1 . The volume of the bypass arm B_1 (10.89 cc.), was known. After completion of the analysis, a new sample of the same gas could be admitted conveniently into bypass arm B_1 . After redirecting the helium stream through B_2 , B_1 was evacuated through the vacuum line connection on the two-way stopcock S_{12} . Then a new sample was admitted into B_1 , by connecting B_1 to the gas reservoir V. This arrangement was particularly useful, not only for repeated analyses of a particular gas mixture, but also for repeated determinations of the sensitivity of a standard gas. (See section entitled: Basis of the Quantitative Determinations.)

The admission of liquid samples by means of a syringe and a serum cap has become standard practice in gas

chromatography. A serum cap mounted on a short sidearm sealed to the upper part of bypass arm B_2 was used for this purpose. However, the method was used infrequently, i.e. only when an approximate value for the retention volume of a liquid standard substance under different analytical conditions was desired.

It was often necessary to admit large quantities of reaction mixture (containing hydrocarbons in the range $C_2 - C_7$) into the analytical apparatus. This was essential for the experiments in which compounds were trapped out and collected for mass spectrometric identification, and also for the quantitative determination of the polymers, which were present in relatively small amounts in the reaction mixture. For this purpose, the hydrocarbon mixture was liquified at the temperature of liquid nitrogen in a U-tube. The U-tube was then connected to the bypass arm B_2 . After the helium stream was directed through B_2 , the U-tube was heated rapidly, causing a rapid evaporation of the sample into the helium stream.

Separating Column and Heater

Glass columns with a total length of 150 cm. and an internal diameter of 5 mm. were used. Both ends of the column above the column packing were made of capillary glass tubing with 2 mm. internal diameter in order to avoid dead space. The column was joined to the gas line by means of two capillary ball-and-socket joints.

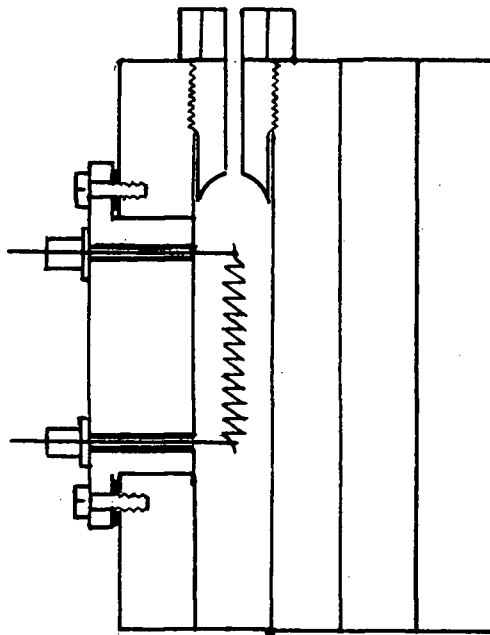
The column heater consisted of two concentric pyrex tubes which formed a closed jacket around the column. The heating wire was wound on the outer surface of the inner tube. The temperature was measured by means of a mercury thermometer, mounted beside the column. The current was supplied through a Sorensen voltage regulator and adjusted to the desired value by means of a variable transformer.

For the separation and quantitative determination of components in the reaction mixture ranging from methane up to and including butene, an alumina packing of the column was used. The aluminum oxide was graded to a particle size of 30-40 mesh.

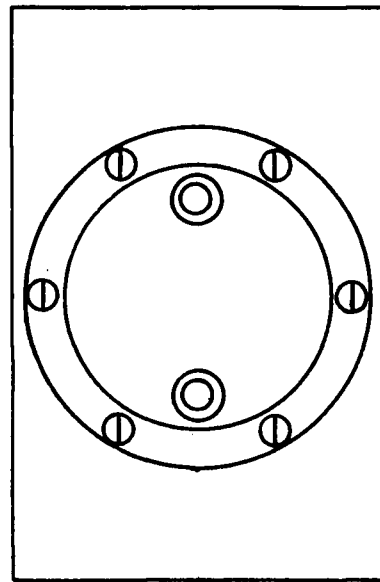
For the separation and quantitative determination of compounds in the reaction mixture with molecular weights higher than that of butene, a partition column with T.C.P. (tricresyl phosphate) on Celite was used. The ratio of Celite to T.C.P. was 2 to 1 by weight. The Celite (545 Johns-Manville Co.) was graded and mixed with the T.C.P. according to the method described by James and Martin.¹²

Thermal Conductivity Cell and Detection Circuit

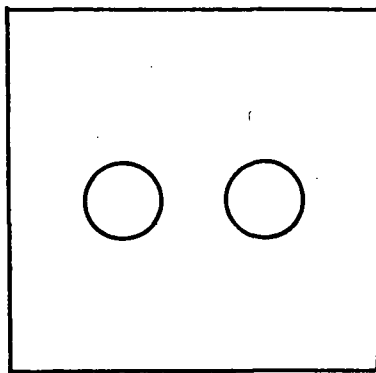
The thermal conductivity cell (Fig. 4) was constructed from a brass block. The conductivity elements were helices of platinum wire. The wire of each element had a diameter of 0.005 cm., a total length of 14 cm., and a total resistance of 7 Ohms. The ends of each platinum wire were silver-soldered to the projecting studs of two kovar seals which



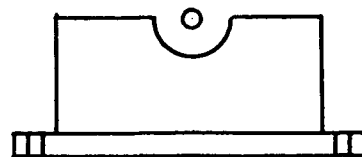
Cross-section



Side View



Top View



Side View of Brass
Plug Carrying
Conductivity Wire

Fig.4 Thermal Conductivity Cell
(actual size)

were soft-soldered to a removable brass plug. Two such brass plugs, one for each arm of the cell, fitted tightly into the brass block, completing the gas channels without obstructing them. Vacuum tight connections between the plugs and the cell were obtained by means of teflon gaskets. The connections to the gas line were made by copper capillary tubing soft-soldered to brass fittings carrying a gas thread of $1/8"$, and extending into the channel of the cell so as to reduce dead space.

The conductivity cell and the connecting copper capillary tubing were submerged in a thermostated oil bath.

The two platinum wires of the cell formed the two arms, C_1 and C_2 , of a conventional Wheatstone bridge. The circuit diagram is shown in Fig. 5. The current, supplied by a storage battery, was regulated to 200 m.A. by means of resistance R_3 .

Before the beginning of an experiment, when a steady stream of helium was established, the two reference points P_1 and P_2 were brought to equal potential by adjusting the two resistance boxes R_1 and R_2 to zero deflection of the galvanometer G. The output of the bridge (points P_1 and P_2) then was switched to the recorder. A Leeds and Northrup Speedomax recorder was used. The instrument provided variable sensitivity, from 1 to 20 m.v. for full scale deflection, and an adjustable "zero".

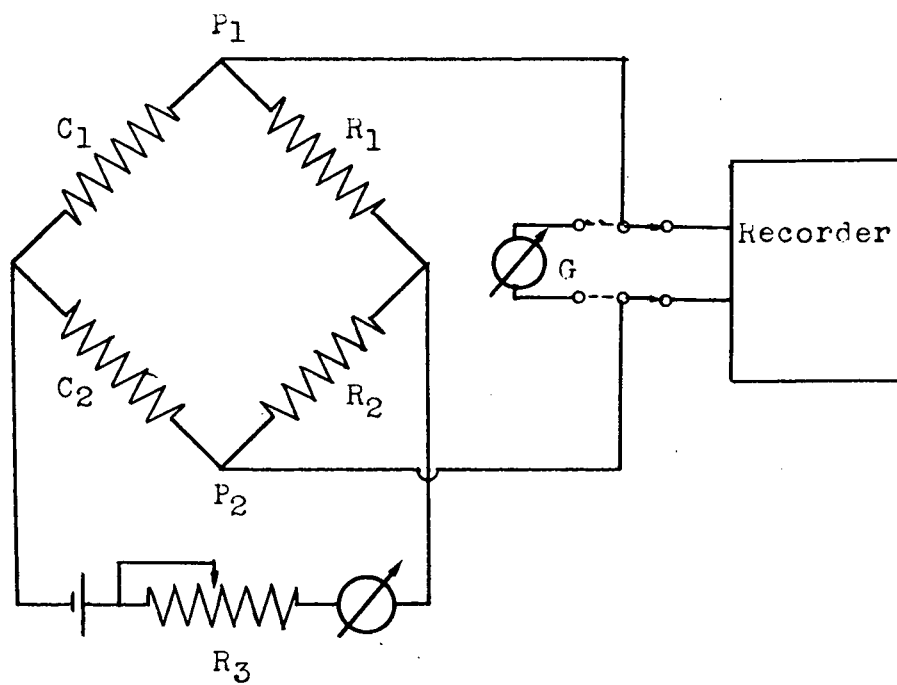


Fig.5 Diagram of Thermal Conductivity Recording Circuit

System for Collecting the Separated Components

The gas fractions leaving the column could be trapped out of the helium stream and transferred into pipettes for mass spectrometric analysis by means of a system of traps and a Toepler pump.

The following proved to be the most satisfactory procedure. Prior to the admission of the mixture to be analysed, helium was allowed to pass through all four traps, which were cooled with liquid nitrogen. Due to initial contraction of the helium gas in the traps, a substantial slowing down of the helium flow could be observed on the flow meter. After the flow had increased to normal, the helium stream was bypassed through stopcock S_9 (Fig. 3), and the traps were shut off. Then, the gas mixture to be separated was admitted to the system. In all trapping experiments, the gas mixtures were liquified previously in a U-tube and admitted into the helium stream in the way described earlier. In this way, the larger quantities of sample necessary for trapping could be handled. The gas chromatogram appearing on the Speedomax was observed, and the desired fraction trapped by directing the gas stream through one of the traps. The time lag between a signal on the recorder and the portion of gas which produced that signal reaching the trap was only about 1 to 2 seconds. Due to this fact, it was possible to trap any portion of a given peak accurately. A total of four samples could be collected in the four traps. To recover the trapped material, stopcock S_{10} was connected to the Toepler

pump, and the helium from a given trap was pumped out. The liquid nitrogen was removed, and the trap allowed to warm up. The gas was collected and measured by means of the Toepler pump, and then transferred into a pipette for mass spectrometric analysis.

Analysis with Gradual Increase of the Column Temperature

The variation of the retention volume* of hydrocarbons belonging to a given homologous series can be expressed by the approximate relation:

$$\log r_v = K.N_c$$

where: r_v retention volume
 N_c number of carbon atoms of compound
 K proportionality factor

For constant flow conditions, the relation can be expressed as:

$$\log r_t = k.N_c$$

where: r_t retention time
 k proportionality factor

The expressions hold for constant column temperature. The time of analysis thus increases exponentially with the molecular mass of the compounds (belonging to a homologous series) contained in the mixture to be analysed. The

* The retention volume of a compound is defined as the total volume of carrier gas that has passed through the detection cell from the onset of the analysis till the appearance of the compound in the detection cell.

resulting long duration of the analysis, undesirable in itself, is accompanied by a gradual spreading-out of the recorded peaks. The spreading-out is due to a gradual diffusion of the gas fractions into the carrier gas, and increases with the time spent by the fractions in the column. Low and drawn-out peaks reduce the value of the chromatogram obtained, with regard to qualitative and quantitative interpretation.

To obviate these difficulties it is necessary to reduce the time of the chromatographic separation. This can be done either by pre-separation of the mixture into two or three fractions or by a gradual increase of column temperature. The second method was adopted, since it appeared to be faster and less complicated. The temperature of the column was raised during the analysis by stepwise increases of the voltage across the column heater. This was done either manually or, for series of similar analyses, by a timeclock-relay system. The temperature increase could be reproduced within a few degrees in successive runs. The chromatogram of a reaction mixture taken under the described conditions with the alumina column is given in Fig. 6.

BASIS OF THE QUANTITATIVE DETERMINATIONS

The sensitivity, S_i , determined for the pure gas i can be defined as:

$$S_i = \frac{A_i}{n_i}$$

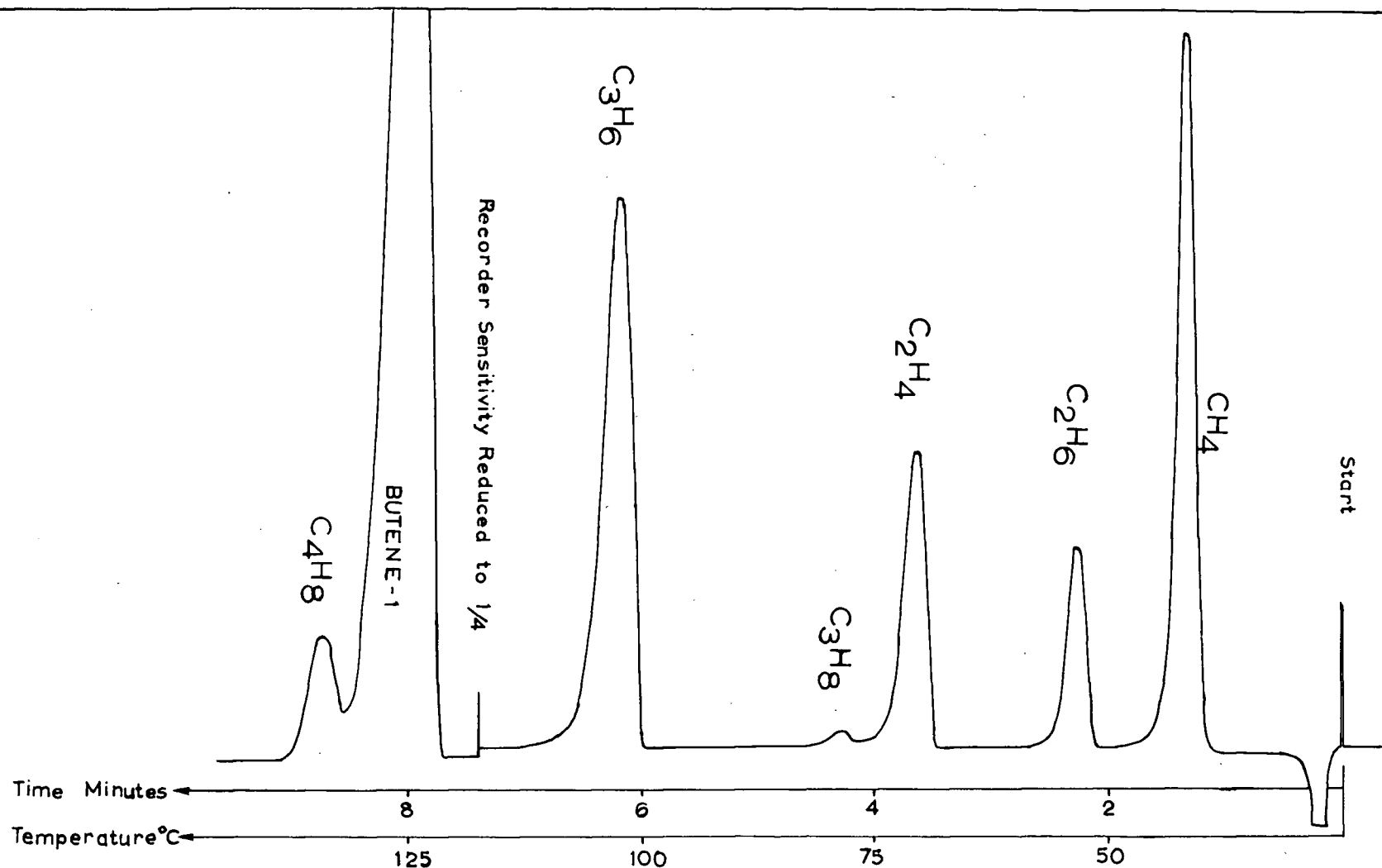


Fig.6 Gas chromatographic Separation of the Light Hydrocarbons

where:

A_i peak area produced by gas i on chromatogram

n_i number of moles of gas i .

For identical conditions of analysis (carrier gas flow, column temperature, etc.) S_i remains constant over a wide range of values of n_i . This forms the basis of the quantitative determination. The sensitivities of all components in a mixture are determined in separate experiments using the pure components (gas standards) alone. The amount of a component in a gas mixture then is obtained from:

$$n_i = \frac{A_i}{S_i}$$

where: n_i number of moles of i in gas mixture analysed

A_i peak area of gas i in the chromatogram of the gas mixture

S_i separately determined sensitivity of component i .

A discussion of the different methods for peak area determination and for computation of the results can be found in a recent paper by Dimbat and associates.⁸

The following procedures were used in the present investigation. The exact amount of sample admitted for analysis could be determined as described in the earlier section: Admission of Samples for Analysis into the Separating System. The peak areas were determined by cutting out the recorded peaks from the chart paper, and weighing them on an analytical balance. In preliminary experiments, a very satisfactory

constancy of the area/weight ratio of the chart paper (Leeds and Northrup) was established. The sensitivities of the constituent gases in the butene pyrolysis mixture were determined in preliminary experiments. All sensitivity determinations were done under the same conditions of helium flow (40 cc./min.) and controlled increase of the column temperature as were used in the analyses of the gas mixtures. Various amounts of each gas standard were used to check the constancy of the sensitivities in the range used in the analyses. The constancy of the sensitivity of 1-butene is demonstrated in Table III. Equally good constancy was obtained for the other components.

TABLE III

Sensitivity of 1-Butene

Amount Analysed (moles x 10 ⁵)	Sensitivity (arbitrary units)
5.3	14.8
3.5	14.5
1.47	14.8
0.9	14.55

Average sensitivity=14.67

Maximum deviation=14.8 - 14.5 = 0.3

Maximum error = $\frac{0.3 \times 100}{14.67} = 2.04\%$

The sensitivities required were redetermined at the beginning of each day of analytical work. The variation of the sensitivities of the light hydrocarbons determined over a period of a month is given in Table IV.

TABLE IV

Variation of Sensitivities of Light
Hydrocarbons over a Month's Period

<u>Compound</u>	<u>Sensitivity: in mg. of chart paper</u> <u>per micro-mole of</u> <u>compound</u>				
Methane	98	94	91	96	90
Ethane	136	134	135	135	136
Ethylene	125	125	120	124	120
Propylene	164	170	160	173	167
Butene	218	210	212	218	218

From the results in Table IV, it can be seen that there was little variation in the measured sensitivities over a long period of time. The relative increase in sensitivity from methane to butene is larger than the relative increase that could be expected on the basis of the increasing thermal conductivities of the compounds. The increase in column temperature produces a gradual decrease in carrier gas flow. The decrease in gas flow is responsible for the additional increase in the sensitivities of compounds emerging from the column after a longer time.

RESULTS FOR THE PYROLYSIS OF 1-BUTENE
OBTAINED BY GAS CHROMATOGRAPHIC ANALYSIS

QUALITATIVE DETERMINATIONS OF THE LIGHT HYDROCARBONS

The light hydrocarbons in the reaction mixture from the

1-butene pyrolysis were separated by gas chromatographic fractionation. Most of the compounds could be identified by retention volume measurements. In addition, all chromatographic fractions were collected and analysed in the mass spectrometer. The following compounds were identified positively:

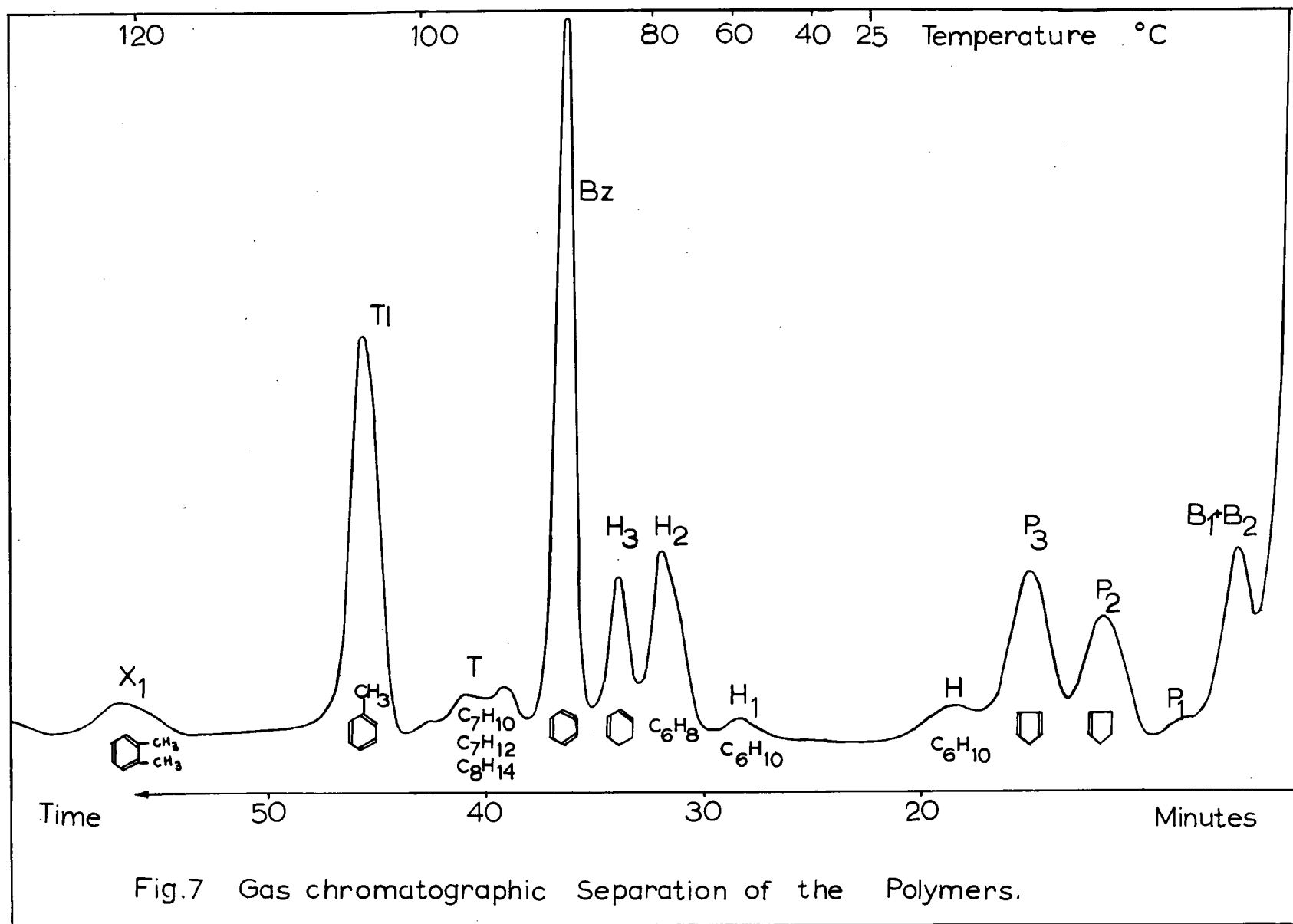
Methane	Propylene
Ethane	Butadiene
Ethylene	1-Butene
Propane (traces)	2-Butene

QUALITATIVE DETERMINATIONS OF THE POLYMERS

The chromatogram of the polymer compounds contained in a reaction mixture of 1-butene (pyrolysed at 550°C with a reaction time of 5 min.) is given in Fig. 7. A partition column with T.C.P. on Celite was used for the chromatographic separation. The peaks in the chromatogram have been indexed according to the nature of the compounds producing them:

B	C ₄	Hydrocarbons
P	C ₅	"
H	C ₆	"
Bz		Benzene
TI	C ₇	Hydrocarbons
X		Xylene

The compounds identified by mass spectrometric analysis of the fractions are given in Fig. 7 under the respective peaks. The mass spectrometric identification was difficult in some cases. Positively identified were:



Benzene
Toluene
Xylene (presumably orthoxylene)

Very good evidence, but not a positive proof, was obtained for the following compounds:

Cyclopentene
Cyclopentadiene
Cyclohexadiene.

The remaining compounds could not be identified beyond their molecular formulae.

The mass spectra of the isolated polymer fractions with a discussion of the mass spectrometric results are given in Appendix I at the end of this thesis.

QUANTITATIVE DETERMINATIONS OF THE LIGHT HYDROCARBONS

The gas chromatographic analysis of the light hydrocarbons was done with the alumina column. In all determinations, a gas sample of the reaction mixture of approximately 1.3 cc. at S.T.P. (10.89 cc. at 10 cm. Hg pressure) was analysed. The basis of the quantitative determinations was described earlier. The results for reaction mixtures produced under different experimental conditions are presented in Table V.

QUANTITATIVE DETERMINATIONS OF THE POLYMERS

The gas chromatographic analysis of the polymers was made with the T.C.P. column. In all determinations, the reaction mixture sample analysed was approximately 21 cc.

Table VAnalytical Results for Light Hydrocarbons

Time min.	Pressure of Reaction System mm. Hg	Volume %					
		Methane	Ethane	Ethylene	Propylene	1-Butene	Total

Temperature - 493°C

0	198.0					100	100.
1	198.6	0.20		0.10	0.15	97	97.5
2	199.0	0.62	0.13	0.30	0.44	98	99.5
3	199.8	1.25	0.27	0.50	0.74	95	98.3
4	200.0	1.72	0.40	0.77	1.14	94	97.0
5	200.2	2.10	0.56	1.11	1.67	94	99.5

Temperature - 509°C

0	197					100	100.
1	198	1.44	0.21	0.36	0.60	99	101.2
2	199	2.50	0.47	0.92	1.34	96	101.6
3	200	3.40	0.72	1.44	2.20	95	102.2
4	202	4.95	1.06	2.05	2.90	87	98.4
5	204	5.30	1.35	2.63	3.77	82	95.2

Temperature - 522.2°C

0	199					100	100.
1	201	2.2	0.4	0.7	1.3	93	97.7
2	207	4.1	0.9	1.7	2.7	86	94.8
3	209	6.2	1.4	2.5	4.0	82	95.7
4	211	8.5	1.7	3.4	5.7	76	95.3
5	213	11.0	2.3	3.9	6.8	69	82.6

Table V (Cont'd)

Time Pressure min. of	Reaction	Methane	Ethane	Ethylene	Propylene	1-Butene	Total
System							
mm. Hg							

Temperature - 540.6°C

0	202					100	100.
1	209	5.2	1.1	2.2	3.3	82	93.4
2	216	9.7	1.9	4.0	6.1	73	94.3
3	224	13.6	3.1	5.6	8.2	63	93.5
4							
5	234	20.0	4.6	7.9	11.5	47	91.0

Temperature - 546°C

0	202					100	100
1	211	8.0	1.3	2.7	4.5	71	87.7
2	222	12.3	2.7	5.3	8.3	55	84.1
3	234	16.1	3.7	6.9	10.6	47	84.2
4	242	18.4	4.4	7.4	12.1	39	81.6
5	250	22.4	4.8	8.7	13.6	33	82.5

Temperature - 554.5°C

0	202					100	100.
1	215	8.4	1.7	3.8	6.9	68	89.0
2	230	14.1	3.3	6.5	10.8	55	90.0
3	241	18.7	4.0	8.2	13.5	40	84.6
4	251	22.6	4.7	9.0	15.0	35	86.1
5	259	24.9	5.3	10.3	15.8	29	85.1

TABLE VI

Analytical Results for Polymers

Temp. °C		Volume %							
		500			512				
Time	min.	2	3	5	1	2	3	5	
B ₁	C ₄ H ₈	0.08	0.15	0.17	0.06	0.13	0.26	0.43	
B ₂	C ₄ H ₆	0.08	0.15	0.20	0.05	0.15	0.32	0.55	
P ₂	C ₅ H ₈	0.17	0.28	0.44	0.14	0.24	0.41	0.65	
P ₃	C ₅ H ₆		0.09	0.15			0.15	0.32	
H ₁	C ₆ H ₁₀	0.08	0.17	0.22		0.15	0.28	0.25	
H ₂	C ₆ H ₈	0.17	0.28	0.44		0.32	0.48	0.74	
H ₃	C ₆ H ₈	0.24	0.42	0.70	0.21	0.42	0.70	0.92	
Bz	C ₆ H ₆	0.09	0.22	0.35	0.07	0.19	0.34	0.63	
Tl	C ₇ H ₈	0.07	0.08	0.17	0.04	0.12	0.18	0.34	
Temp. °C		529				544			
Time	min.	1	2	3	5	1	2		
B ₁	C ₄ H ₈	0.14	0.30	0.48	0.45	0.33	0.42		
B ₂	C ₄ H ₆	0.17	0.40	0.50	0.65	0.48	0.62		
P ₂	C ₅ H ₈	0.32	0.50	0.70	0.93	0.50	0.78		
P ₃	C ₅ H ₆	0.12	0.31	0.48	0.88	0.31	0.58		
H ₁	C ₆ H ₁₀			0.22	0.15	0.21	0.17		
H ₂	C ₆ H ₈		0.36	0.75	0.92	0.55	0.66		
H ₃	C ₆ H ₈	0.48	0.70	0.84	0.85	0.66	0.82		
Bz	C ₆ H ₆	0.20	0.40	0.63	1.08	0.36	0.75		
Tl	C ₇ H ₈		0.20	0.41	0.87	0.20	0.50		

Table VI (Cont'd.)

Analytical Results for Polymers

Temp. °C	Time min.	Volume %					
		544		563			
		3	5	1	2	3	5
B ₁	C ₄ H ₈	0.60	0.68	0.54	0.52	0.50	0.30
B ₂	C ₄ H ₆	0.82	1.30	0.90	1.10	1.05	0.70
P ₂	C ₅ H ₈	0.91	1.31	0.88	1.05	0.86	0.76
P ₃	C ₅ H ₆	0.98	1.60	0.85	1.24	1.22	1.24
H ₁	C ₆ H ₁₀			0.20	0.18	0.19	0.19
H ₂	C ₆ H ₈	0.87	1.17	0.80	1.04	0.88	0.97
H ₃	C ₆ H ₈	0.84	0.55	0.77	0.60	0.35	0.30
Bz	C ₆ H ₆	1.36	2.67	1.10	2.45	2.90	3.70
Tl	C ₇ H ₈	0.95	1.98	0.80	1.62	1.95	2.35

at S.T.P. (325 cc. at 5 cm. Hg pressure). The amount of sample was measured volumetrically. Then, the sample was condensed with liquid nitrogen and analysed as described previously. The results obtained are presented in Table VI.

TOTAL ANALYSIS AND MATERIAL BALANCES

Since quantitative determinations of practically all components in the reaction mixtures were made, the overall accuracy of the determinations can be examined on the basis of the summation of the volume percentages of the components and, in more detail by the computation of material balances. The results for the summation of volume percent for several reaction mixtures are given in Table VII. The values for the light hydrocarbons and butene were taken directly from Table V. The data given for the polymers were based on Table VI. The data for the polymers were interpolated for all cases in which the reaction temperatures of the reaction mixtures used for the determinations in Table VI did not coincide with the temperatures used in the determinations of the light hydrocarbons. The results indicate a satisfactory overall accuracy, the sum total of the volume percent being within $\pm 3\%$ of 100 percent in all cases but one.

The computed material balances are given in Table VIII. The sources of basic data were the same as for Table VII. The values given for carbon represent the percentages of carbon contained in the respective products, with the total

Table VIITotal Composition of Reaction Mixtures
in Volume %

Temp. °C	Time reaction min.	Volume %				Total Vol. %
		Hydrogen	Light Hydro- carbons	1-Butene	Polymers	
509	2	0.25	5.20	96.4	1.6	103.45
	5	0.54	13.06	82.1	4.03	99.73
522.2	2	0.44	8.34	86.5	2.73	98.01
	5	1.33	14.01	68.6	6.36	90.30
540.6	2	1.20	21.70	72.6	4.88	100.38
	5	2.50	44.00	47.0	9.52	103.02
554.5	2	2.00	35.00	55.0	7.70	99.70
	5	4.23	56.33	28.8	11.06	100.42

TABLE VIII

Mass Balances

Reaction temp. °C	<u>509</u>		<u>522.2</u>	
Reaction time min.	2	5	2	5
<u>CARBON</u>	in % of Carbon as Initial Butene			
in light hydrocarbons	2.34	6.33	3.72	10.00
in polymers	2.27	5.75	4.56	9.18
total in reaction products	4.61	12.08	8.28	19.18
from reacted Butene	2.85	15.35	8.75	25.7
<u>CARBON %</u> accounted for	79	95	75	
<u>HYDROGEN</u>	in % of Hydrogen in Initial Butene			
in H ₂	0.006	0.014	0.116	0.36
in light hydrocarbons	3.08	8.09	5.94	15.51
in polymers	1.51	3.83	2.7	6.28
total in reaction products	4.60	11.93	8.76	22.15
from reacted Butene	2.85	15.35	8.75	25.7
<u>HYDROGEN %</u> accounted for	78	100	86	
<u>H/C RATIO IN PRODUCTS</u>	2.0	2.0	2.1	2.3

TABLE VIII (cont'd.)

Mass Balances

Reaction temp. °C	<u>540.6</u>		<u>554.5</u>	
Reaction time min.	2	5	2	5
<u>CARBON</u>	<u>in % of Carbon in Initial Butene</u>			
in light hydrocarbons	10.65	20.2	18.9	27.8
in polymers	7.10	15.47	12.23	19.8
total in reaction products	17.75	35.67	31.13	47.6
from reacted Butene	22.2	45.3	36.6	63.5
<u>CARBON %</u>				
accounted for	80	79	85	75
<u>HYDROGEN</u>	<u>in % of Hydrogen in Initial Butene</u>			
in H ₂	0.32	0.72	0.57	1.26
in light hydrocarbons	13.75	30.4	23.8	42.4
in polymers	4.77	9.86	7.89	12.34
total in reaction products	18.84	40.98	32.26	54.90
from reacted Butene	22.2	45.3	36.6	63.5
<u>HYDROGEN %</u>				
accounted for	85	90	88	86
<u>H/C RATIO IN</u>				
Products	2.1	2.3	2.0	2.3

carbon in the initially introduced 1-butene taken as 100.

The values for hydrogen were determined in the same way.

The material balance given as "carbon % accounted for" expresses the ratio:

$$\frac{\text{carbon found in the reaction products}}{\text{carbon in reacted butene.}} \times 100$$

The "hydrogen % accounted for" was similarly derived.

It can be seen that, on the average, only about 80% of the reacted carbon and 88% of the reacted hydrogen is accounted for by the products. The hydrogen to carbon ratio found in the products is close to the theoretical value, 2. Deviations from the theoretical value are more pronounced for reaction mixtures with longer reaction times. All deviations show values larger than 2.0, reflecting the higher percentage of hydrogen accounted for. The probable reason for the discrepancy between carbon and hydrogen accounted for and reacted carbon and hydrogen will be discussed in the next section, since it has a bearing on the analytical results and their specific use for kinetic purposes.

CONVERSION OF THE ANALYTICALLY DETERMINED CONCENTRATIONS OF THE REACTION MIXTURES TO CONCENTRATIONS IN THE REACTION VESSEL

The conversion of the analytically determined concentrations to the actual concentrations in the reaction vessel involves the assumption of ideal gas behaviour of the reaction mixtures between the temperature and pressure conditions in the reaction vessel and the conditions under which a sample of the reaction mixture is measured and admitted

for analysis. The volume percent data obtained from the analysis are based essentially on a determination of the partial pressure p_i of the component i in a gas sample of the reaction mixture with known total pressure p_{tot} :

$$\text{Vol. \% } i = \frac{p_i}{p_{tot}} \times .100$$

Under assumed ideal gas, or nearly ideal gas, behaviour of the reaction mixture:

$$\frac{p_i}{p_{tot}} = \frac{p_i}{p_{tot}}$$

for conditions for conditions
in reaction before analysis
vessel

and thus, the analytically determined volume percent also should express the concentration conditions in the reaction vessel. Under the above assumption, it is also possible to express the concentration of component i in the reaction vessel in mole percent of the originally admitted butene:

$$\text{Mole \% } i = \frac{p_o + \Delta p}{p_o} \cdot \text{Vol. \% } i$$

where p_o initial pressure of the
butene admitted in the re-
action vessel

Δp measured pressure increase
in the reaction vessel at time
of withdrawal of the reaction
mixture.

The percentage of reacted butene can be obtained in an analogous way:

$$\% \text{ Butene reacted} = \left(\frac{p_o - \text{Vol. \% Butene} \times (p_o + \Delta p) / 100}{p_o} \right) \times 100$$

These methods of computation were used for the results presented in Table VIII, giving the material balances. In the table, a certain consistent discrepancy between reacted and accounted material was pointed out. This discrepancy could be due to inaccuracies in the analytical determinations. Another factor responsible could be the formation in the reaction vessel, of polymer compounds with very low vapour pressures. These polymers would condense on the cold walls of the apparatus after expansion of the reaction mixture from the reaction vessel into the sampling pipette. The deposition of yellow tarry compounds on the walls of the tubing leading from the reaction vessel to the sampling pipette could be observed after the apparatus had been in use for several runs. If the discrepancy in the material balances is explained by the presence of involatile polymeric compounds, the assumption of ideal gas behaviour of the reaction mixture is unjustified, and therefore, all conversions from concentrations in the analytical sample to concentrations in the reaction vessel will be slightly in error. We believe that the error is not too serious. For kinetic purposes, only results from reactions in which the decomposition of the 1-butene had proceeded to but a few percent have real significance. The error due to polymer formation in these cases will be very small.

The difficulty in converting concentrations in analytical gas samples to concentrations in the reaction vessel, in cases where condensation of part of the reaction products

might be expected, is often obviated by the addition of known amounts of a reference gas. The reference gas must be inert to the reaction (generally one of the permanent gases is used), and its analytical detection should be possible with good quantitative accuracy. The quantitative determination of a permanent gas such as neon was not possible with the gas chromatographic arrangements used in this investigation. A separate mass spectrometric determination of the reference gas in the reaction mixture was possible, of course. This procedure was used in only a few preliminary experiments and, unfortunately, later discontinued in the belief that all compounds formed in the pyrolysis were detectable by the analytical methods previously described.

KINETIC RESULTS FOR THE PYROLYSIS OF 1-BUTENE

The methods of the qualitative and quantitative analysis were described in the previous sections, and some of the results obtained were given also. In the following sections, the results from the kinetic investigation of the pyrolysis of 1-butene will be given in their proper sequence.

KINETIC ORDER OF THE 1-BUTENE DECOMPOSITION

The order of the reaction was studied by admitting varying initial amounts of 1-butene into the reaction vessel, at a given temperature, and analysing the reaction mixtures

Table IXComposition of Reaction Mixtures with Change in InitialPressure of 1-Butene

Temperature of reaction 522°C

Time of reaction 1 minute

Initial pressure			
mm. Hg	96	200	415
$\Delta P/P$	0.0104	0.0104	0.011
Volume % Methane	2.20	2.40	2.50
" Ethane	0.38	0.42	0.45
" Ethylene	0.73	0.80	0.85
" Propylene	1.32	1.40	1.45
" 1-Butene	94.00	94.50	95.00

Temperature of reaction 556.5°C

Time of reaction 1 minute

Initial Pressure

mm. Hg	94	140	195	292	324	404
$\Delta P/P$	0.12	0.1	0.1	0.1	0.11	0.11
Volume % Methane	10.0	10.5	10.0	11.0	12.0	12.0
" Ethane	2.0	2.0	2.0	3.0	3.0	3.0
" Ethylene	4.5	5.0	4.5	5.0	6.0	5.0
" Propylene	8.5	8.5	7.5	8.5	8.5	8.5
" 1-Butene	65.0	60.0	65.0	60.0	60.0	60.0

obtained after one minute reaction time. The composition of reaction mixtures obtained at the temperatures 522° and 556.5°C for various initial concentrations of 1-butene are given in Table IX. The pressure increase for one minute reaction time is proportional to the initial pressure of the 1-butene for both temperatures studied. The concentration of each compound analysed is found to be nearly independent of the initial pressure of the 1-butene. The slight variations are quite at random, and must be taken to represent analytical inaccuracies or slight differences in the reaction temperature. The decomposition of the 1-butene and the formation of the light hydrocarbons show, therefore, a first order dependence on the initial concentration of the 1-butene. The dependence of the kinetic order with the time of reaction is complex, as will be seen in the subsequent sections.

PRESSURE INCREASE IN REACTION SYSTEM AND ACTIVATION ENERGY FROM PRESSURE CHANGE

The pressure change in the reaction system with time for several temperatures is given in Fig. 8. The pressure vs. time functions show a characteristic change with temperature. At low temperatures, the functions have a convex curvature to the time base. At higher temperatures, the convex curvature changes to straight lines and then, at still higher temperatures, the curves assume the regular, "first order" form. As will be seen later, this behaviour is paralleled by the concentration vs. time curves of the light

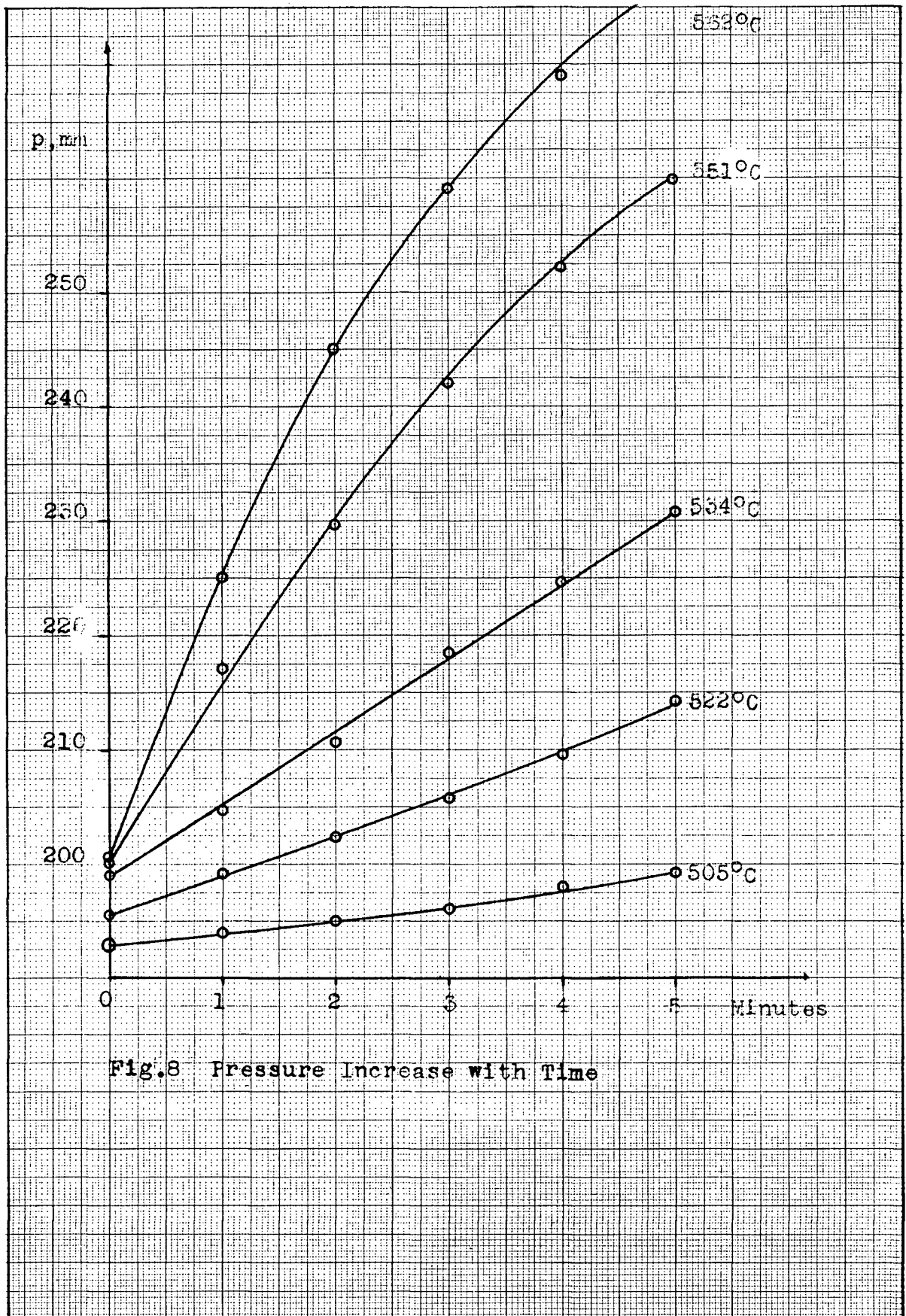


Fig.8 Pressure Increase with Time

Table XActivation Energy From Pressure Increase

P Initial Pressure of 1-butene 200 mm. Hg.

 ΔP Pressure increase after 1 minute.

$\frac{\Delta P}{P} \times 10^3$	$-\log. \frac{\Delta P}{P}$	$T^\circ \text{ K}$	$\frac{1}{T} \times 10^3$
----------------------------------	-----------------------------	---------------------	---------------------------

6.2	2.208	778.1	1.2851
7.18	2.144	781.4	1.2797
8.8	2.056	785.7	1.273
14.	1.855	792.1	1.2625
17.2	1.766	794.8	1.2582
18.85	1.725	798.2	1.2528
22.6	1.647	802.4	1.2462
31.	1.5095	807.	1.2391
41.	1.388	812.3	1.2311
51.2	1.292	818.8	1.222
61.	1.216	819.8	1.2198
75.	1.126	824.4	1.2130
91.4	1.06	828.15	1.207
125.5	0.902	835.7	1.197

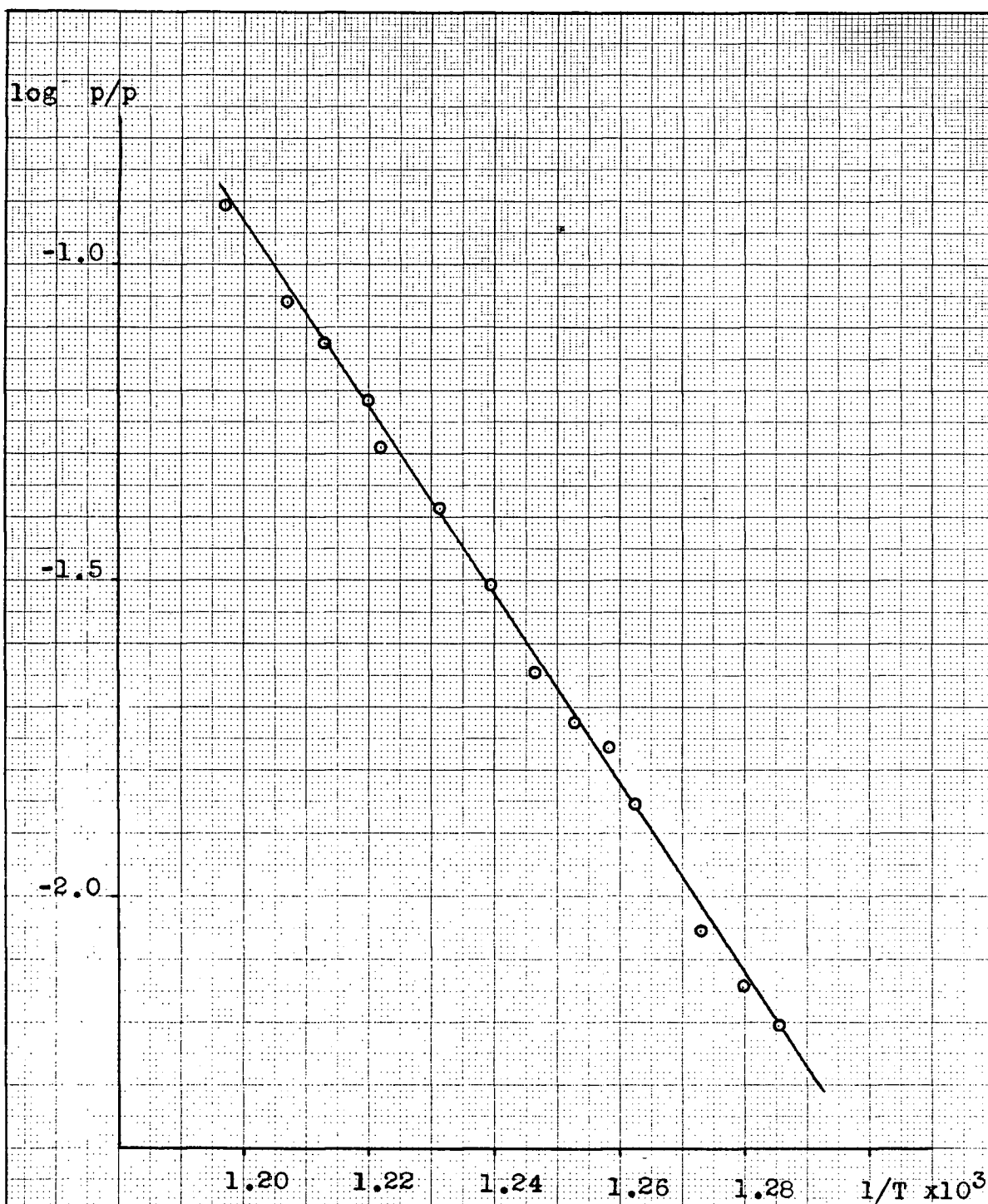


Fig.9 Activation Energy from Initial Rate
of Pressure Increase; E_A 67 kcal/mole

hydrocarbons.

The pressure increase in the reaction system was determined for a number of constant temperatures in the temperature range between 500 and 565⁰ C. The rates of initial pressure increase are given in Table X. The values in Table X were used in an Arrhenius plot for the determination of the activation energy from the initial rate of pressure increase (Fig. 9). The value obtained for this activation energy is 67 kcal/mole, which compares well with the value of 66.4 kcal obtained by Molera and Stubbs.²²

RATE AND OVERALL ACTIVATION ENERGY OF BUTENE DECOMPOSITION

The concentrations of the light hydrocarbons and the 1-butene as a function of time are given in Table XI. The values are in mole % of the originally admitted 1-butene and represent data from Table V, recalculated under the assumptions described in the section entitled: Conversion of the Analytically Determined Concentrations of the Reaction Mixtures to Concentrations in the Reaction Vessel. The percentage of butene decomposed as a function of time is shown in Fig. 10. The butene decomposition shows a dependence that could have been anticipated from the pressure increase curves. At low temperatures the decomposition is slow and shows an induction period, after which the decomposition increases relatively rapidly. At intermediate temperatures the decomposition is nearly proportional to the time of reaction and for the higher temperatures the curves show a concave

Table XI

Analyses of Reaction Mixtures -- Light Hydrocarbons

Components are given in mole % of the initially admitted 1-butene.

Temperature 493° C

Time min.	Methane	Ethane	Ethylene	Propylene	1-Butene
1	0.2	-	0.1	0.15	97.5
2	0.62	0.13	0.31	0.44	98.0
3	1.26	0.27	0.5	0.75	96.5
4	1.74	0.4	0.78	1.15	95.0
5	2.12	0.57	1.12	1.69	94.5

Temperature 509° C

Time min.	Methane	Ethane	Ethylene	Propylene	1-Butene
1	1.45	0.21	0.36	0.6	99.0
2	2.52	0.47	0.93	1.35	97.5
3	3.46	0.73	1.46	2.24	97.0
4	5.08	1.09	2.1	2.98	90.0
5	5.45	1.39	2.71	3.88	84.6

Temperature 522.2° C

Time min.	Methane	Ethane	Ethylene	Propylene	1-Butene
1	2.26	0.38	0.73	1.33	94.0
2	4.27	0.88	1.74	2.84	90.0
3	6.48	1.45	2.58	4.20	85.0
4	9.00	1.80	3.65	6.03	80.5
5	11.8	2.47	4.17	7.30	73.5

Table XI (Cont'd.)

Temperature 540.6°C

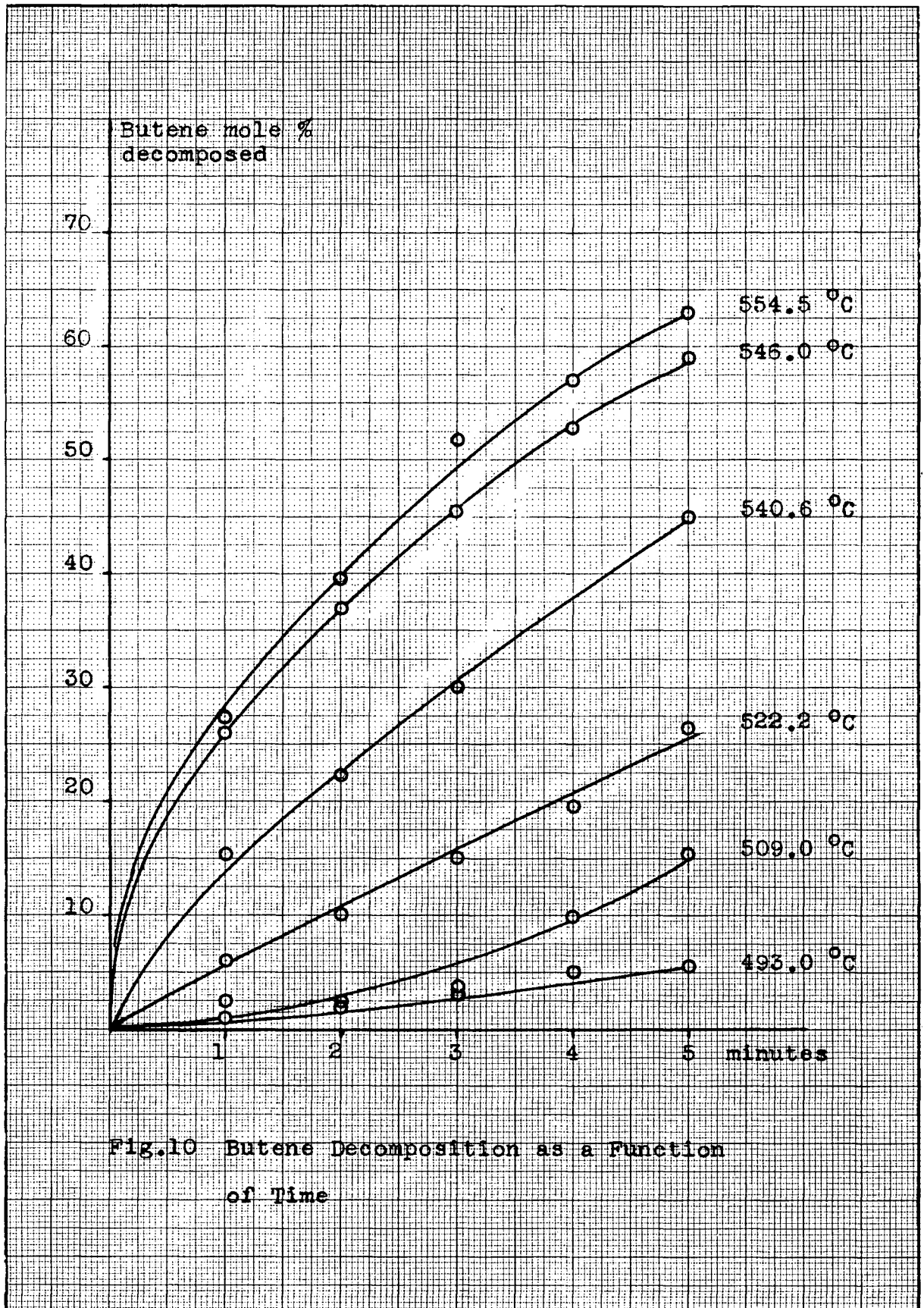
Time min.	Methane	Ethane	Ethylene	Propylene	1-Butene
1	5.4	1.12	2.29	3.46	84.6
2	10.4	2.03	4.28	6.53	77.7
3	15.1	3.44	6.22	9.1	70.0
5	23.2	5.35	9.2	13.4	55.0

Temperature 546°C

Time min.	Methane	Ethane	Ethylene	Propylene	1-Butene
1	8.3	1.33	2.81	4.7	74.5
2	13.6	2.94	5.8	9.1	60.4
3	18.7	4.32	8.0	12.3	54.5
4	22.1	5.23	8.92	14.5	47.2
5	27.8	6.00	10.8	16.9	41.0

Temperature 554.5°C

Time min.	Methane	Ethane	Ethylene	Propylene	1-Butene
1	8.93	1.83	4.1	7.45	72.6
2	16.1	3.78	7.4	12.3	63.1
3	22.4	4.85	9.9	16.2	48.1
4	28.1	5.88	11.2	18.7	43.0
5	32.0	6.85	13.25	20.3	37.0



curvature to the time base. First order rate constants were calculated using the expression:

$$k = \frac{1}{t} \log \left(\frac{100}{C_t} \right)$$

where t reaction time (sec.)

C concentration of butene after
t time t (mole %)

The results are summarized in Table XII.

Table XII

Butene Decomposition, Variation of First Order Rate
Constants with Reaction Time

Time (min.)	$k \times 10^4 (\text{sec.}^{-1})$					
	Temp. ($^{\circ}\text{K}$)					
	766 $^{\circ}$	782 $^{\circ}$	795 $^{\circ}$	814 $^{\circ}$	819 $^{\circ}$	827 $^{\circ}$
1	1.7	4.2	10.3	28	49	54
2	1.7	2.3	8.8	21	37	41
3	1.8	3.2	9.1	20	34	43
4	2.1	4.4	9.0	20	31	35
5	1.9	5.4	10.3	20	28	33
\bar{k} (averaged)	1.84	3.9	9.5	21.8	35.8	41.2

The rate constants show some lack of constancy for almost all experimental temperatures. This should be largely due to the fact that the decomposition does not follow a simple

first order behaviour, as was already evident from the shape of the decomposition versus time curves. An additional scatter in the values of the rate constants could be expected from errors in the quantitative determinations. In a previous section (Basis of the Quantitative Determinations), the accuracy of the butene analysis was estimated to be within 2% of the measurement. Since the "per cent butene decomposed" was obtained by subtracting the amount of butene found in the reaction products from the initially admitted butene, the analytical errors will have a relatively large effect on the rate constants in all cases where the per cent of decomposition was low.

An Arrhenius plot of the averaged rate constants is shown in Fig. 11. The activation energy obtained is 66 kcal/mole. Similar plots were constructed for the rate constants obtained for a given reaction time. The activation energies from these plots are given in Table XIII.

Table XIII

Activation Energies for the Butene
Decomposition
 E_A 's from Rate Constants for
t minutes

t (minutes)	E_A (kcal/mole)
1	72
2	70
3	69
4	64
5	60
E_A from Averaged Rate Constants	66

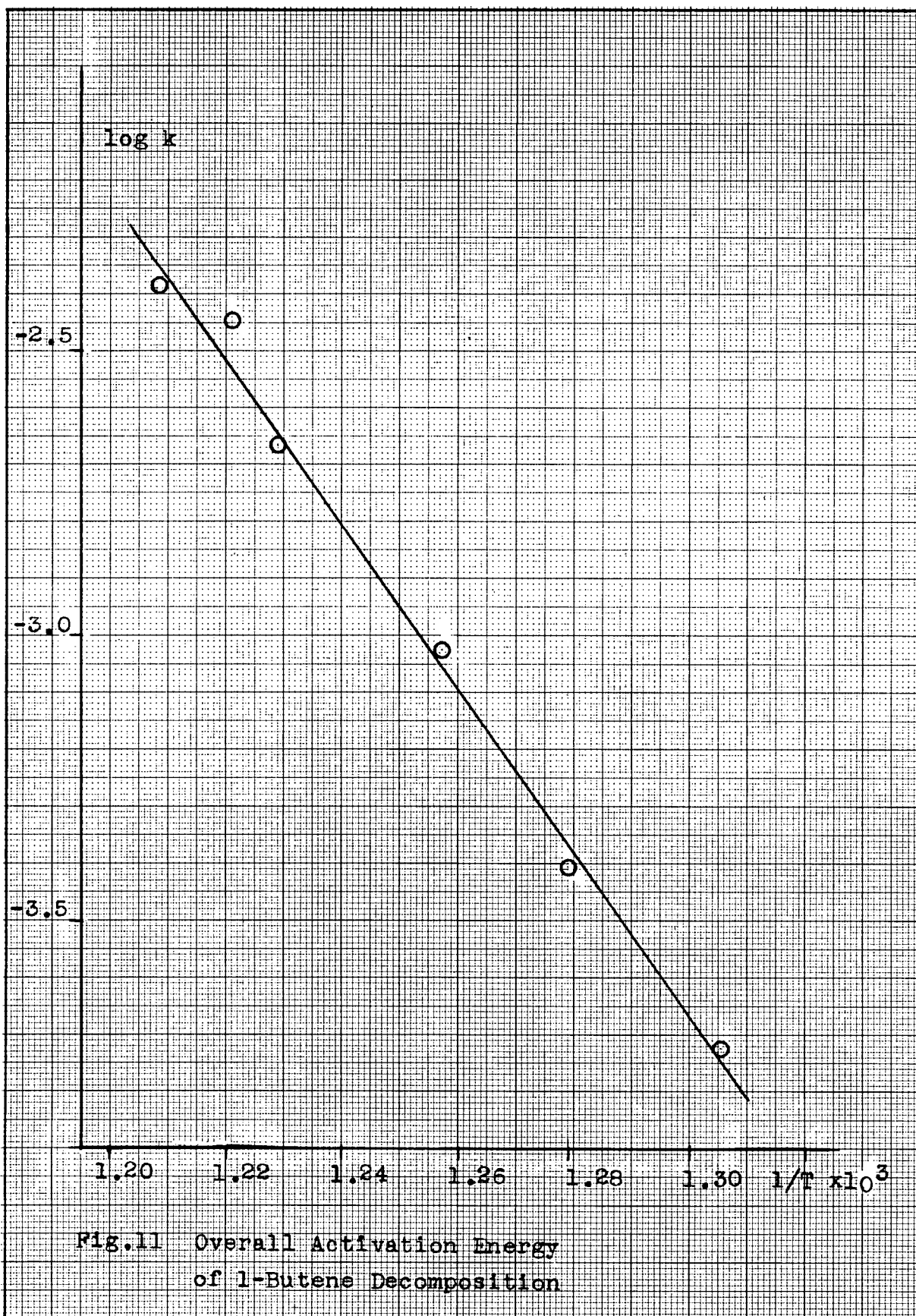


Table XIV

Rate Constants for the Formation of the Light Hydrocarbons

k rate constant sec.⁻¹ x 10⁵
 B initial concentration of 1-butene (molecules/cc. x 10⁻¹⁶)
 C concentration of light hydrocarbons for 60 sec. reaction
 time (molecules/cc. x 10⁻¹⁶)

<u>Methane</u>	<u>B</u>	<u>C</u>	<u>k</u>	<u>-log k</u>	<u>T</u>	<u>1/T</u>
	250	1.25	8.4	4.078	766.0	1.3055
	246	3.56	24.1	3.618	782.0	1.2787
	246	3.57	24.2	3.618	787.2	1.270
	241	5.51	38.1	3.419	795.2	1.2575
	241	13.04	90.2	3.046	813.7	1.229
	240	20.15	140.0	2.855	819.0	1.2210
	237	21.20	149.0	2.828	827.5	1.2085
	240	24.60	172.0	2.760	828.4	1.2075
<u>Ethane</u>						
	246	0.52	3.5	4.454	782.0	1.2787
	241	0.94	6.5	4.186	795.2	1.2575
	241	2.71	18.8	3.728	813.7	1.229
	240	3.19	22.2	3.656	819.0	1.2210
	237	4.32	30.4	3.518	827.5	1.2085
	240	5.50	38.8	3.412	828.4	1.2075
<u>Ethylene</u>						
	250	0.27	1.7	4.752	766.0	1.3055
	250	0.50	3.3	4.482	766.0	1.3055
	246	0.89	6.0	4.221	782.0	1.2787
	241	1.94	13.4	3.873	795.2	1.2575
	241	5.44	37.6	3.425	813.7	1.229
	240	6.74	46.8	3.331	819.0	1.221
	237	9.80	68.8	3.163	827.5	1.2085
<u>Propylene</u>						
	250	0.39	2.6	4.582	766.0	1.3055
	246	1.46	9.9	4.005	782.0	1.2787
	241	3.25	22.4	3.650	795.2	1.2575
	241	8.35	57.7	3.238	813.7	1.229
	240	11.90	82.6	3.084	819.0	1.2210
	237	17.60	124.0	2.908	827.5	1.2085

It should be mentioned that in all cases given in Table XIII, the estimated error is relatively large (of the order of 5 kcal) since the experimental points generally did not determine the slope of the straight line unambiguously.

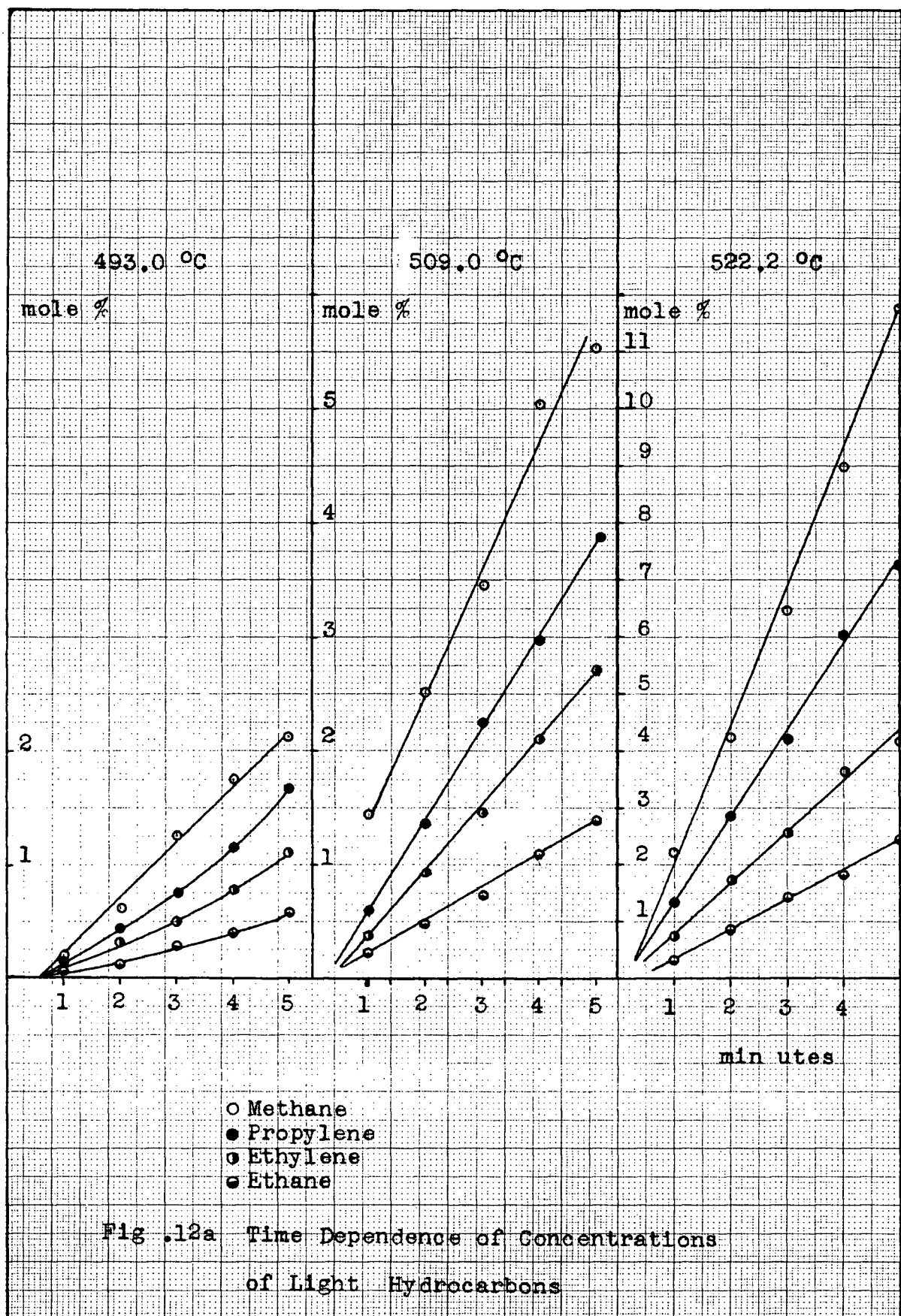
RATES OF FORMATION AND OVERALL ACTIVATION ENERGIES
FOR THE LIGHT HYDROCARBONS

The changes in concentration for the light hydrocarbons (methane, ethane, ethylene and propylene) with time are graphically represented in Fig. 12, on the basis of the values given in Table XI. The concentration curves of the light hydrocarbons follow the same regularities with increase in temperature as were pointed out for the pressure increase and for the butene decomposition.

The rate constants for the initial formation of the light hydrocarbons were calculated assuming first order dependence on the butene concentration. The results are given in Table XIV. The Arrhenius plots for the rate constants of the light hydrocarbons are shown in Fig. 13. The activation energies and pre-exponential factors obtained are given in Table XV.

Table XV
Activation Energies of Light Hydrocarbons

	\bar{A}	1/sec.	E kcal/mole
Methane	$10^{13.2}$		60.5
Ethane	$10^{13.8}$		63.6
Ethylene	$10^{15.7}$		71.6
Propylene	$10^{16.4}$		70.8



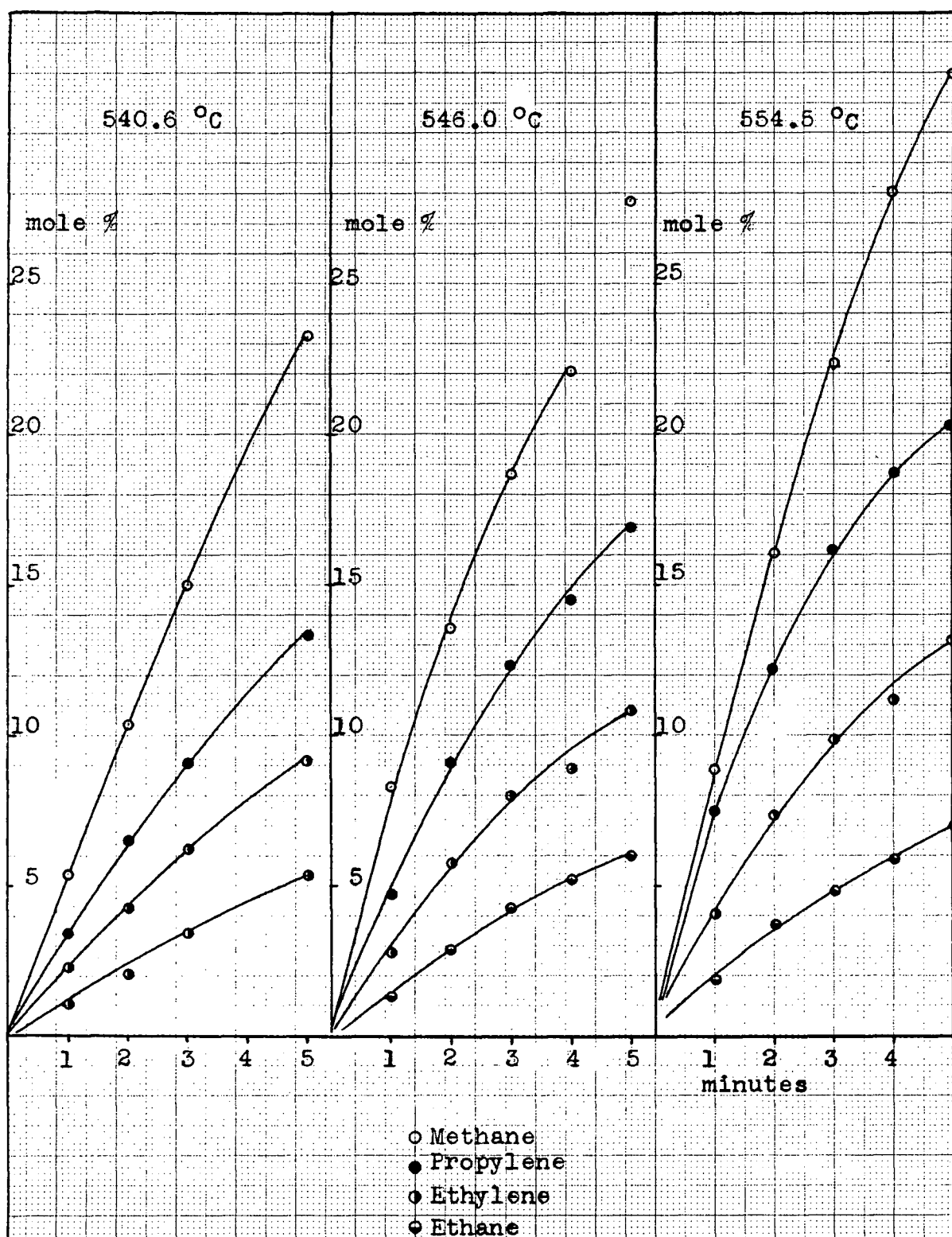


Fig.12b Time Dependence of Concentrations
of Light Hydrocarbons

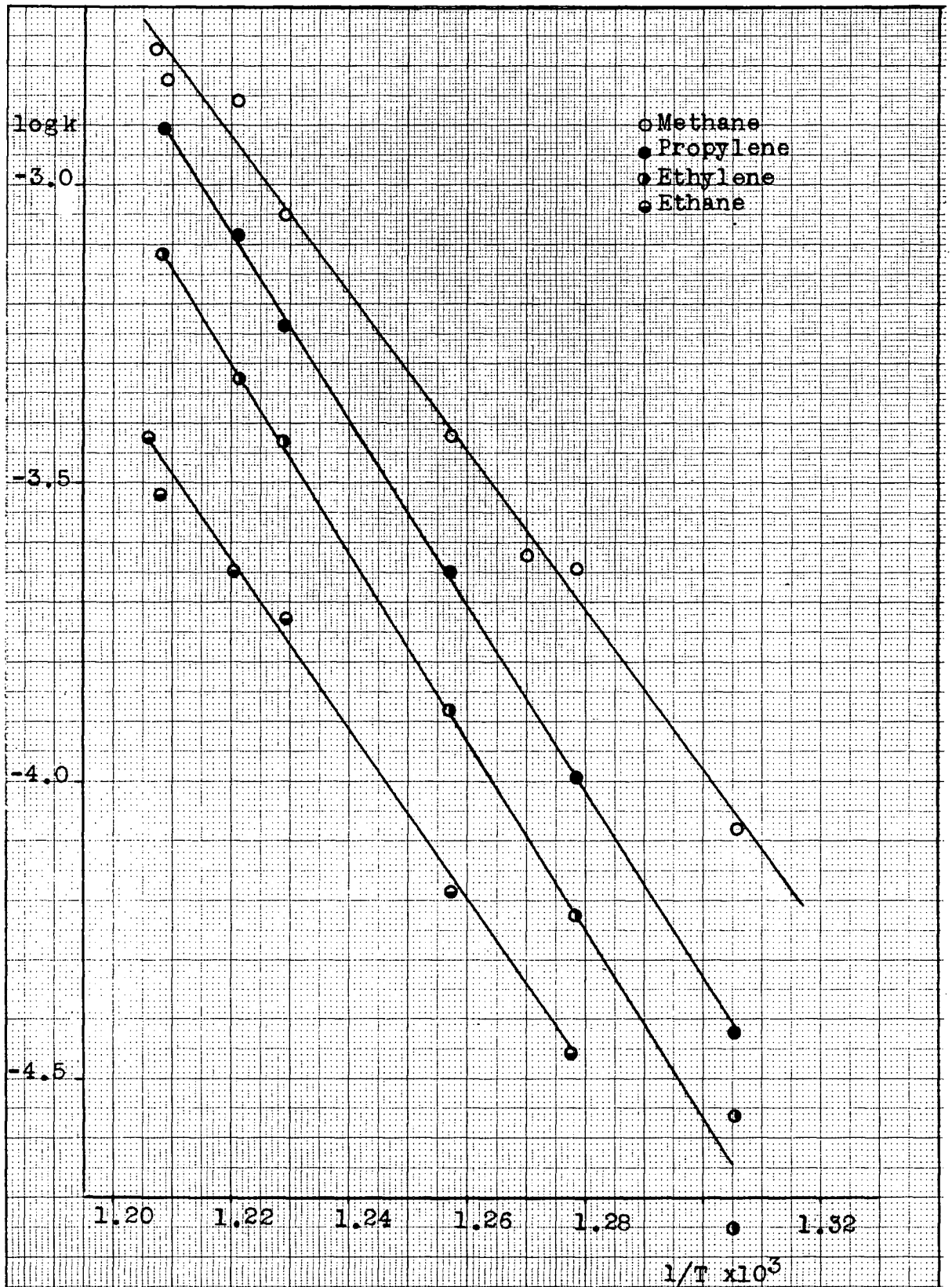
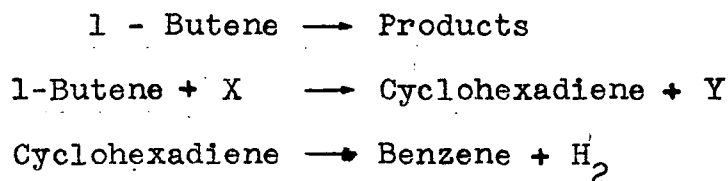


Fig.13 Activation Energies for the Formation of the Light Hydrocarbons

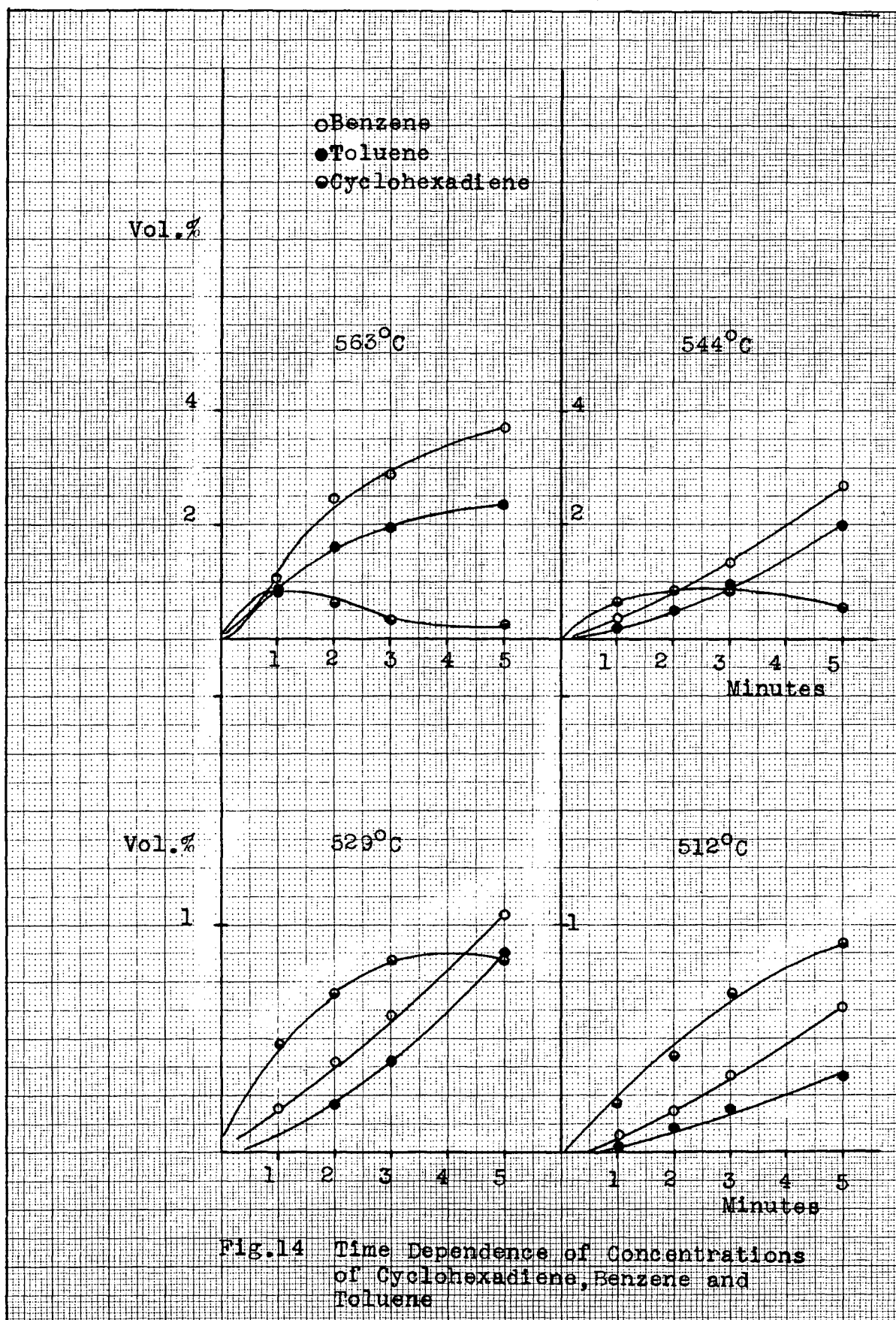
TIME AND TEMPERATURE DEPENDENCE IN THE FORMATION OF POLYMER PRODUCTS

The concentrations of the major polymer products as a function of time are given in Figures 14 and 15. The data for the plots were taken from Table VI: Analytical Results for Polymers.

The time dependence of the cyclohexadiene, benzene and toluene concentrations is given in Fig. 14. A definite relation between the concentration curves of the cyclohexadiene and benzene can be observed. The rate of formation of the benzene appears directly proportional to the concentration of the cyclohexadiene. The concentration curves of these two compounds follow, qualitatively at least, the relationships of a consecutive reaction that could be expressed by the following equations:



According to the above reaction sequence the rate of formation of the cyclohexadiene should decrease gradually with time, due to the decrease in the butene concentration, until a point is reached where the rate of formation of cyclohexadiene is equal to the rate of formation of benzene. This corresponds to the maximum of the cyclohexadiene concentration. Beyond this point the concentration of the cyclohexadiene should decrease, with a corresponding decrease in the rate



of formation of the benzene. The experimental curves at the highest temperature (563°C) show exactly this behaviour. The experimental curves obtained for the lower temperatures correspond qualitatively to the earlier stages of the process described. It is, therefore, reasonable to assume that the benzene is a direct product of some dehydrogenation reaction of the cyclohexadiene. The data available in Table VI are not sufficient to provide information as to whether or not the cyclohexene and cyclohexadiene form an analogous pair. The concentration of the cyclohexene is found to be much smaller than that of the cyclohexadiene, even for the shortest reaction time analysed. Thus, either the dehydrogenation of the cyclohexene to cyclohexadiene is a much faster reaction than the dehydrogenation of cyclohexadiene to benzene (in the butene system), or the cyclohexadiene is formed by a different mechanism not involving cyclohexene as an intermediate. The second alternative appears more probable.

The toluene concentration shows very much the same time dependence as does the benzene.

The concentrations of the cyclopentene and cyclopentadiene as a function of time are given in Fig. 15. The situation seems somewhat similar to that of the cyclohexadiene and benzene, with the difference that at the highest temperature, the cyclopentadiene curve flattens out: i.e., the compound participates in further reactions.

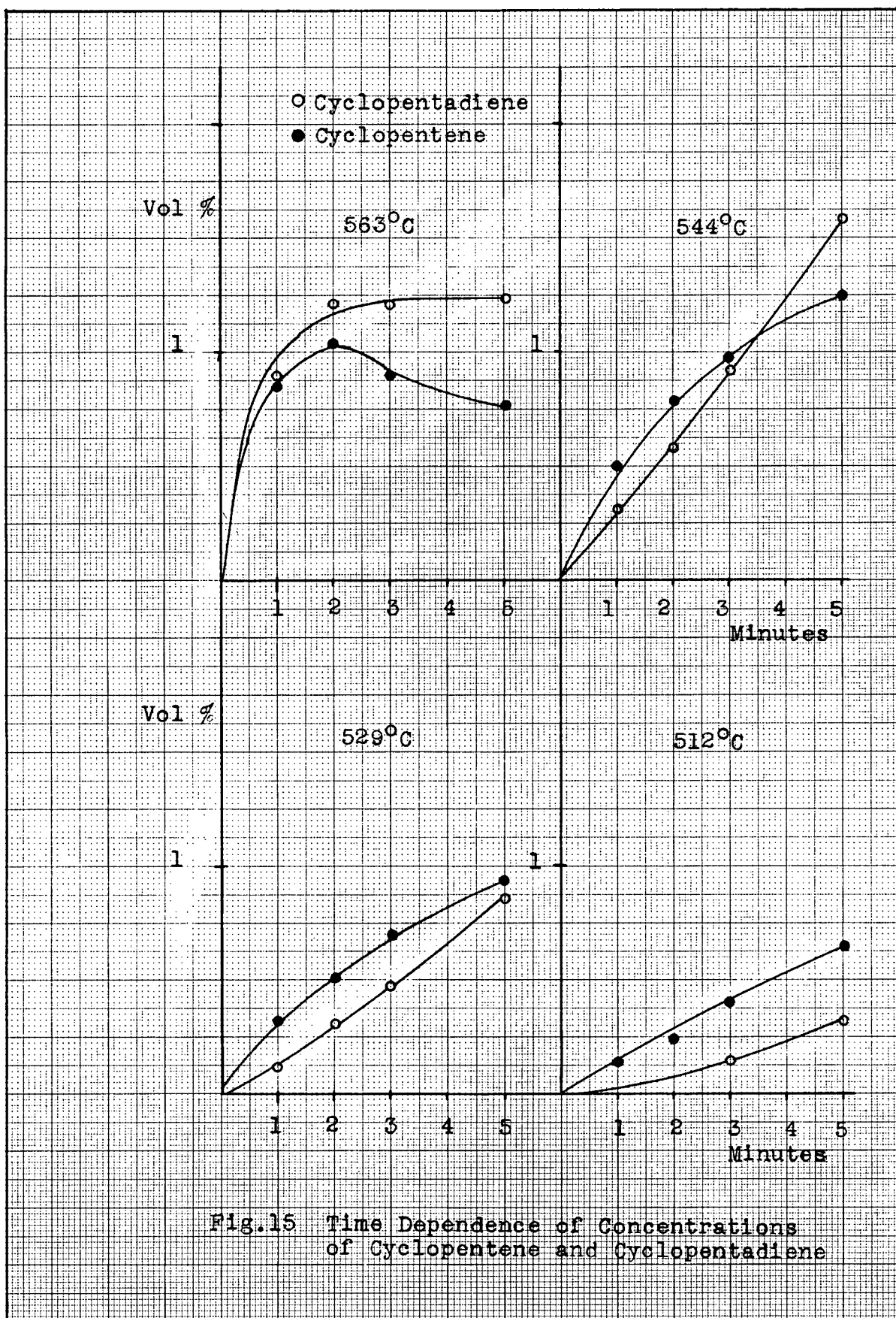


Fig.15 Time Dependence of Concentrations of Cyclopentene and Cyclopentadiene

THERMAL DECOMPOSITION OF 1-BUTENE
SENSITIZED WITH MERCURY DIMETHYL

Addition of a small amount (5%) of mercury dimethyl to the reactant 1-butene produced a substantial increase in the rate of the decomposition. The conditions of the experiment and the results are given in Table XVI, together with the results from a blank run containing only butene, pyrolysed and analysed under exactly the same conditions. Concentration versus time plots for both experiments are given in Fig. 16. The increase in rate of formation of the polymers was not studied. It can be seen that the addition of mercury dimethyl produces a substantial increase in the initial rate. The increase in initial rate of formation for the light hydrocarbons can be calculated from the results in Table XVI. A calculation based on the concentration after one minute reaction time is given in Table XVII.

Table XVII

Increased Rate of Formation of Light Hydrocarbons in
Sensitized Reaction

<u>Compound</u>	<u>Increased Rate</u>	
Methane	5.75/0.433	13.3
Ethane	0.95/0.083	11.4
Ethylene	1.4 /0.196	7.1
Propylene	2.2 /0.228	9.7

It is interesting that in the sensitized reaction, not only methane, but also ethane, propylene and ethylene show greatly

Table XVI

Thermal Decomposition of 1-Butene Sensitized with Mercury-dimethyl

Composition of mixture before reaction:

1-Butene	95%
Mercury dimethyl	5% (by volume)

Initial pressure in reaction vessel	209.8 mm. Hg
Reaction temperature	492°C

Composition of Reaction Mixtures

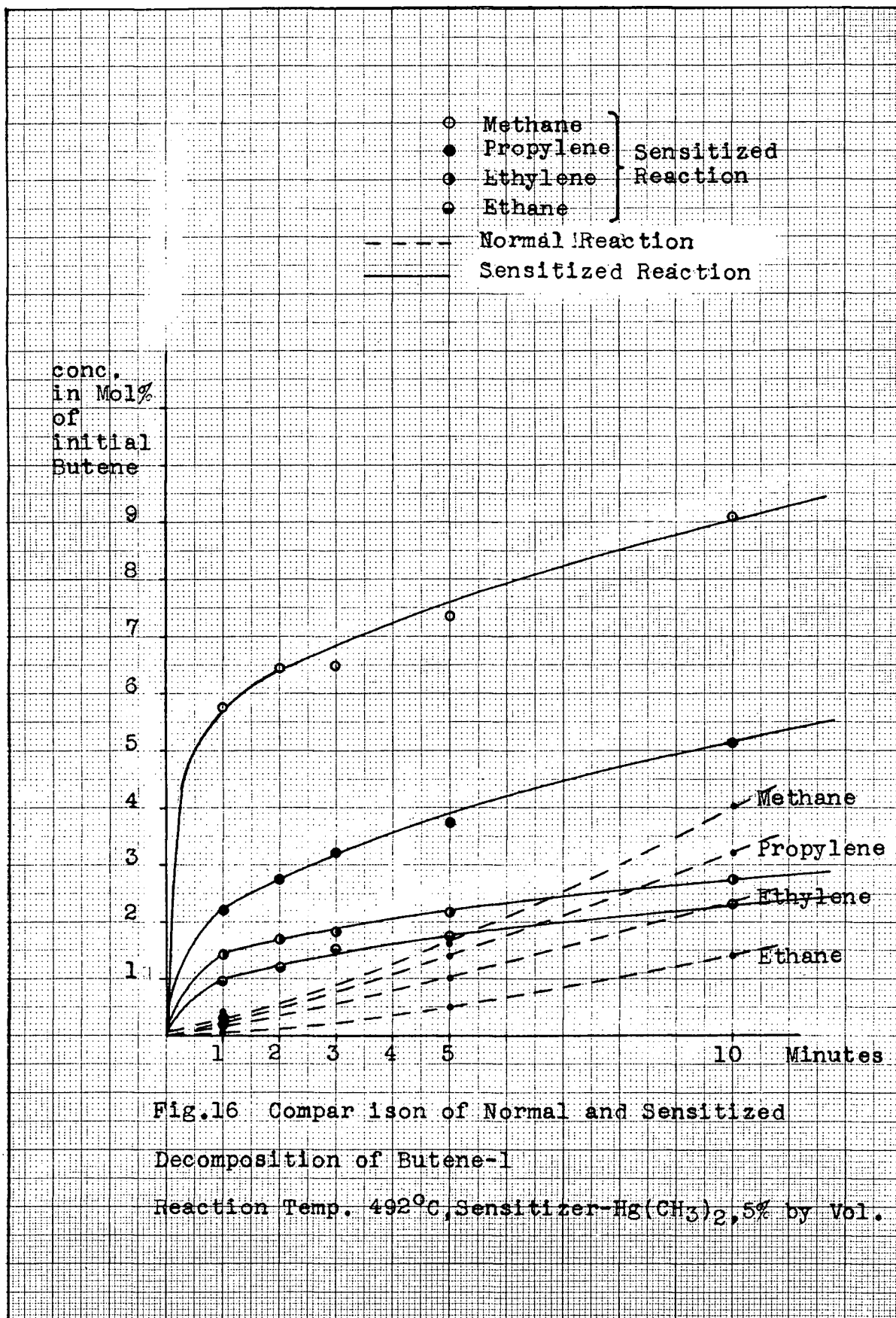
Amount of each reaction product is given in mole % of initial 1-Butene.

Reaction time min.	1	2	3	5	10
Pressure mm. Hg	214.8	216.9	217.9	218.5	220.9
Methane	5.75	6.45	6.45	7.35	9.1
Ethane	.95	1.2	1.5	1.6	2.3
Ethylene	1.4	1.7	1.8	2.15	2.75
Propylene	2.2	2.75	3.2	3.75	5.15
Butene	89.	88.2	85.5		78.6

Blank run with 1-Butene only, for comparison

Same temperature and initial pressure (199.5 mm. Hg)

Reaction time min.	1	2	3	5	10
Pressure mm. Hg	199.5	199.5	199.5	201.5	204.5
Methane	0.433			1.7	4.0
Ethane	0.083			0.5	1.45
Ethylene	0.196			1.0	2.35
Propylene	0.228			1.4	3.2
Butene	95.5			95.3	84.2



increased rates of formation.

The discussion of the results from the 1-butene decomposition will be postponed until the results from the pyrolysis of the 1-butene-4-d₃ have been described.

THERMAL DECOMPOSITION OF 1-BUTENE-4-d₃

The deuterated butene, CH₂=CH-CH₂-CD₃, used in this investigation was kindly prepared by Dr. L. C. Leitch of the National Research Laboratories, Ottawa. The method of preparation and the proof of structure are given in the experimental part of Appendix II: Deuterium Migration During the Ionization of 1-Butene-4-d₃ by Electron Impact. The prepared compound was found to contain 90% CH₂=CH-CH₂-CD₃ and 10% CH₂=CH-CH₂-CD₂H. The deuterated butene was pyrolysed in the same reaction system used for the 1-butene.

COMPARISON OF THE PYROLYSES OF 1-BUTENE AND 1-BUTENE-4-d₃

The thermal behaviour of the 1-butene-4-d₃ was very similar in all respects to that of 1-butene. All products formed in the 1-butene decomposition also were found in the reaction products of the deuterated butene. The pressure increase with time was identical for both compounds. The quantitative analysis of the reaction products formed in the pyrolysis of both compounds showed no detectable differences

in the rates of formation of the different compounds. The concentrations of the light hydrocarbons in the two reaction mixtures obtained and analysed under identical conditions are given in Table XVIII.

Table XVIII

Light Hydrocarbons from the Pyrolyses of 1-Butene
and 1-Butene-4-d₃ for 5 Minutes at 552°C

	CH ₃ .CH ₂ .CH=CH ₂	CD ₃ .CH ₂ .CH=CH ₂
	Vol. %	Vol. %
Methane	24.0	24.0
Ethane	5.3	5.2
Ethylene	8.3	9.0
Propylene	13.0	13.6

The value given for methane formed from the deuterated butene includes all deuterio-isomers of methane formed in the pyrolysis. The values for the remaining products of the pyrolysis of the deuterated butene are given on the same basis. It is seen that the differences in the compositions of the reaction mixtures are very small.

Differences in the kinetic behavior of the two compounds could be expected. Significant differences in the reaction rates of normal and deuterated compounds are generally observed in cases where the reaction involves processes in which the respective bonds R-H and R-D are formed and/or broken. The overall effect of such processes, if they occur

in the system under study, must produce changes in the rates of formation of the products which are smaller than the limit of detection obtainable with the analytical method used.

The pyrolysis of 1-butene-4-d₃ sensitized with 5% Hg(CH₃)₂ by volume, was studied in one experiment at 492°C with one minute reaction time. A substantial acceleration of the reaction was observed. The formation of the light hydrocarbons had increased by amounts essentially equal to those in the sensitized decomposition of the non-deuterated 1-butene.

ANALYTICAL METHODS USED FOR THE IDENTIFICATION OF THE DEUTERATED REACTION PRODUCTS

The reaction products of the pyrolysis were separated by gas chromatography. The techniques were analogous to those used for the separation of the 1-butene reaction mixtures. Separation of the individual deuterio-isomers* could not be achieved. Therefore, the deuterio-isomers of a given compound were collected in one fraction and analysed on the mass spectrometer. The clean separation of these fractions achieved was of great advantage in the interpretation of the mass spectrometric results. The mass spectra of the deuterio-isomers of even simple hydrocarbons often are not known.

* According to the meaning given here to the expression, CH₄ and CD₃H are deuterio-isomers.

Therefore, the mass spectrometric analysis of a sample containing a number of deuterio-isomers can present considerable difficulties. The molecular formulae of the deuterio-isomers contained in the fractions of propylene, butene, and other singly-or multiply-unsaturated hydrocarbons could be determined without great difficulty by scanning the mass range at low electron energies. The procedures used for the remaining compounds, deuterio-methanes, deuterio-ethanes and deuterio-ethylenes, varied from group to group and will be described with the results for these compounds.

REACTION PRODUCTS FROM THE PYROLYSIS OF 1-BUTENE-4-d₃
DEUTERO-METHANES

The mass spectra of the deuterio-methanes published by Dibeler and Mohler⁶ were used as standards for the computation of the analysis. Since mass spectra show variations from instrument to instrument, the spectra given by Dibeler were corrected before being used. The corrections were based on what is essentially a comparison of the methane (CH_4) spectrum obtained by Dibeler with the methane spectrum obtained with the mass spectrometer used in the present work. The method by which the corrections were applied will be illustrated by treating the case of CH_3D . The spectra necessary for the correction are given in Table XIX.

Table XIX

Mass Spectra Used for Correction of the CH_3D Spectrum

<u>Mass</u>	<u>Ion Intensity</u>			
	CH_3D (Dibeler)	CH_4 (Dibeler)	CH_4 (This Laboratory)	CH_3D (Corrected)
17	100			100
16	77.2	100	100	74.4
15	20.9	86.1	83	17.7
14	8.8	16.3	12.4	6.3
13	4.9	8.21	5.4	3.22
12	2.46	2.57	1.6	1.48

In the dissociation pattern of CH_3D , some of the mass peaks originate from two different ions. For example, the mass 14 peak is produced by CH_2^+ and CD^+ . For these cases, the relative abundances of each contributing ion were estimated by the method of Dibeler and Mohler. It was assumed that the probability of removing one atom, either H or D, is equal to the probability of removing one H from CH_4 ; the probability of removing two atoms is equal to that of removing two H atoms from CH_4 , and so forth. This assumption is consistent with the fact that the sums of the ions in CH_4 and in the deuterio-methanes are nearly equal. Starting with the low mass end of the CH_3D spectrum, the contribution of each type of ion is computed in the following manner: Mass 13 results from CH^+ only, and is equal to 4.90 (Table XIX). As CH^+ and CD^+ are both formed by the dissociation of three atoms, the CD^+ abundance can be calculated as the difference: CH^+ in CH_4 (8.21) minus CH^+ in CH_3D

(4.90) equals 3.31. Further, the total abundance of ions of mass 14 in CH_3D is 8.80. Consequently, the CH_2^+ abundance is given by $8.80 - 3.31 = 5.49$. Continuing in this manner, the abundances of all remaining ions were computed.

The correction to Dibeler's spectra then was applied by multiplying the abundance of each individual ion formed by the loss of i atoms, by the ratio:

$$\frac{\text{Abundance of } \text{CH}_{4-i}^+ \text{ (in Methane spectrum obtained in this laboratory)}}{\text{Abundance of } \text{CH}_{4-i}^+ \text{ (in Methane spectrum obtained by Dibeler)}}$$

The calculation of the corrected ion abundances in the lower mass range of the CH_3D spectrum is given below:

Mass	Ions	Corrected Ion Abundances
12	C^+	$2.46 \times \frac{1.6}{2.57} = 1.48$
13	CH^+	$4.9 \times \frac{5.4}{8.21} = 3.22$
14	$\text{CH}_2^+, \text{CD}^+$	$3.31 \times \frac{5.4}{8.21} + 5.49 \times \frac{12.4}{16.3} = 6.35$

and so on.

The complete corrected spectrum of CH_3D is given in the last column of Table XIX.

The spectra of all the deuterio-methanes were corrected in an analogous way. The analyses of the mass spectra of the deuterio-methanes from the 1-butene-4- d_3 pyrolysis were computed with the use of the corrected spectra. The method of computation consisted in successive subtraction of the ion contributions of the compounds present, starting with the compound with the highest mass (CD_4). In an ideal analysis,

no residual mass peaks would remain after the contributions of all compounds have been subtracted. The relative smallness of the residuals in a real analysis is a measure of its accuracy. The residuals from the computations of the deuterio-methanes were relatively small. Only the results for the mercury sensitized reaction are somewhat in doubt, since the sample contained small amounts of water which interfered with the analysis.

The results of the analyses are given in Table XX. The results for the deuterio-methanes from the pyrolyses of 1-butene-4-d₃ show only small variations with reaction time and reaction temperature. The main product, CD₃H, constitutes approximately 63% of the methanes. The CD₃H most certainly originates from the deuterated methyl group of the CH₂=CH-CH₂-CD₃ molecule. Since the deuterated butene also initially contained 10% CH₂=CH-CH₂-CD₂H, about $63 \times 10/90 = 7\%$ CD₂H₂ should have been formed together with the 63% CD₃H. It is seen from the analytical results that the percentage of CD₂H₂ found is much higher, close to 20% on the average. The methane originating from the deuterated methyl group of the butene can be estimated to be at least 75% of the methane total by adding an average value of 5% for the CD₄ to the corrected value for CD₃H:

$$\begin{array}{rcl}
 63\% & \text{CD}_3\text{H} & \\
 7 & \text{CD}_2\text{H}_2 & \text{proportional part from} \\
 & & \text{CH}_2:\text{CH}.\text{CH}_2.\text{CD}_2\text{H} \\
 5 & \text{CD}_4 & \\
 \hline
 75\% & \text{Total} &
 \end{array}$$

Table XX

Deutero-Methanes from the Pyrolysis of 1-Butene-4d₃

Reaction		Volume % of total of Methane					Total
Temp. °C	Time min.	CD ₄	CD ₃ H	CD ₂ H ₂	CDH ₃	CH ₄	
507	2	3.34	63.	24.7	2.1	6.95	100%
	4	4.6	64.	21.9	3.	6.65	"
524	2	4.9	62.5	23.4	3.8	5.5	"
	4	5.6	63.	22.1	3.1	5.5	"
550.7	2	6.4	60.4	22.9	4.8	5.6	"
	5	6.3	52.3	24.6	8.7	8.2	"

Deutero-Methanes from the Pyrolysis of 1-Butene-4d₃

Sensitized with Mercury-Dimethyl

Reaction		Volume % of total of Methane					Total
Temp. °C	Time min.	CD ₄	CD ₃ H	CD ₂ H ₂	CDH ₃	CH ₄	
492	1	1.34	29.4	14.7	2.	52.5	100%*
		1.36	30.	14.1	3.66	51.	"**

* 50 e.v.
** Low el. energies.

Extrapolated Values for Non-Sensitized Reaction

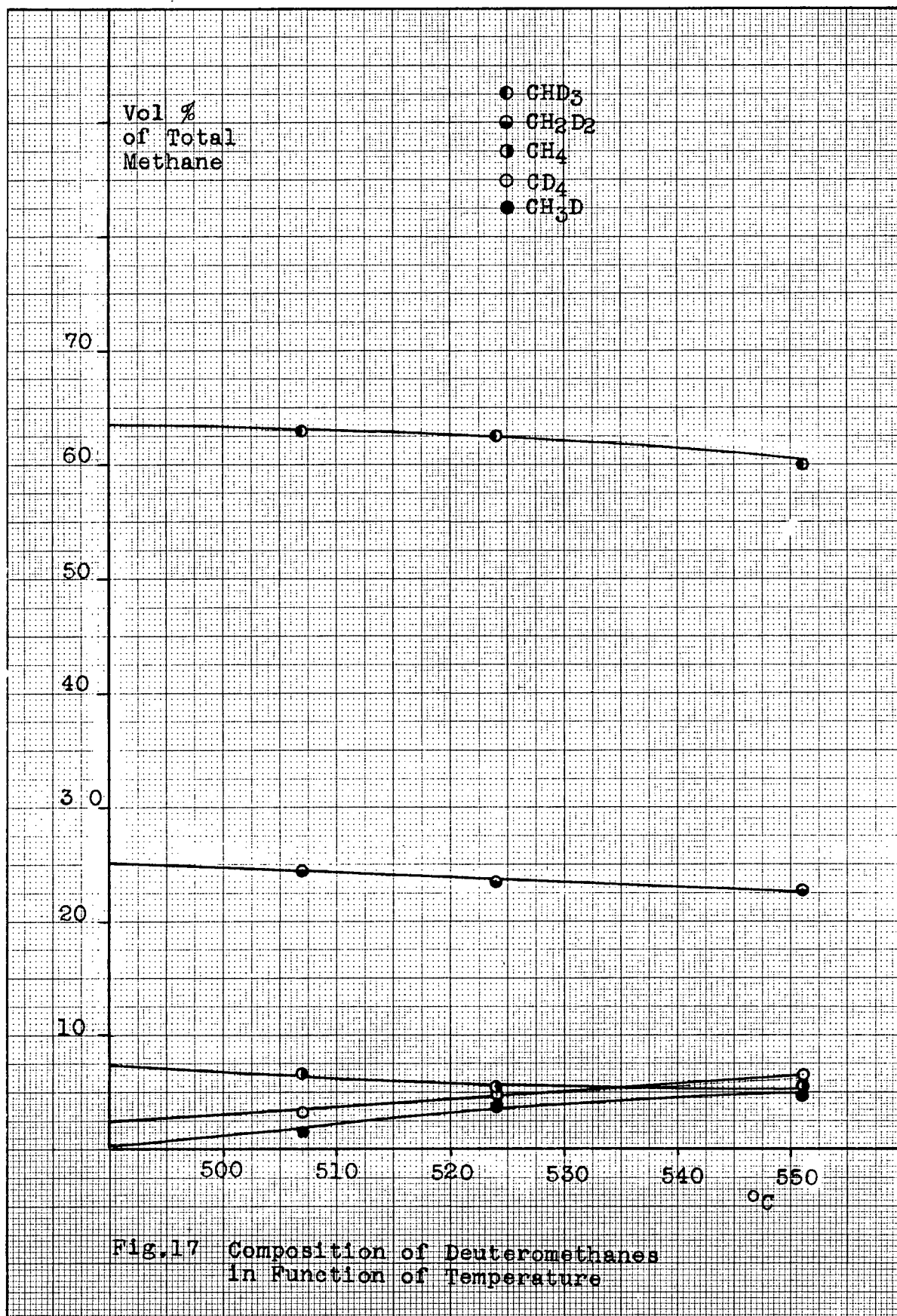
Temp. °C	Time min.	CD ₄	CD ₃ H	CD ₂ H ₂	CDH ₃	CH ₄	Total
492	1	2.5	64	25.2	1.3	7.0	100%

The main product from the mercury-dimethyl sensitized reaction is CH_4 , approximately 51% of the methanes. The CH_4 should originate predominately from the methyl groups of the sensitizer.

A determination of the concentrations of the deuterio-isomers in the reaction mixture of the 1-butene-4- d_3 decomposition under conditions of temperature and reaction time identical with those of the sensitized reaction was not made. The concentrations of the products of the non-sensitized reaction obtained for these conditions were so small that special procedures would have been necessary for the collection and subsequent mass spectrometric analysis of the separated products. The lack of direct comparative data is unfortunate. However, semi-quantitative estimates are possible by extrapolation of the concentrations of the deuterio-isomers in the non-sensitized reaction to the lower temperature of the sensitized reaction. The plotted concentrations of the deuterio-methanes as a function of temperature are given in Fig. 17. Since the variation of the concentrations with temperature is quite small, it is believed that no appreciable additional error is introduced by the extrapolation to 492°C . The extrapolated values obtained were corrected to total 100%.

The corrected values for the concentrations also are given in Table XX.

The concentrations of the deuterio-methanes for the normal and sensitized reactions were used to calculate the



relative increase in the rate of formation of the individual deuterio-methanes for the sensitized reaction. The total increase of methane formation was taken to be 13.3-fold for one minute reaction time on the basis of previous experiments on the sensitized reaction of 1-butene (Table XVII). The calculation is given in Table XXI.

Table XXI

Increased Rates of Formation of Deuterio-Methanes in Reaction Sensitized with Mercury Dimethyl

(13.3 fold increase for the total methanes

<u>Compound</u>	Ratio of Concentration from Sensitized Reaction to Concentration from Normal Reaction for 1 Min. Reaction Time
CD_4	$1.35 \times 13.3/2.5 = 7.2$
CD_3H	$30 \times 13.3/64 = 6.2$
CD_2H_2	$14.4 \times 13.3/25.2 = 7.6$
CDH_3	$2.8 \times 13.3/1.3 = 28.6$
CH_4	$51.7 \times 13.3/7 = 98.3$

It is seen that the rates of the CD_4 , CD_3H and CD_2H_2 have an approximately equal increase, while the increase of the CDH_3 has an intermediate value. The CH_4 shows a nearly 100-fold increase.

DEUTERO-ETHANES

The mass spectra of CH_3CD_3 , CH_3CHD_2 , and CH_3CH_2D obtained by Schissler, Thompson and Turkevich were used as

standards for the computation of the mass spectrometric analyses. The spectra of the remaining isomers of $C_2H_3D_3$ and $C_2H_4D_2$, are not known. Therefore, the analyses had to be computed on the assumption that the $C_2H_3D_3$ compound present was CH_3CD_3 and the $C_2H_4D_2$ was CH_3CHD_2 . The spectra of Schissler and associates were corrected before use, according to the method described in the analysis of the deuterio-methanes. The analyses then were computed by the same method used with the deuterio-methanes.

The mass spectra and the results of the analyses are given in Table XXII. The resolution of the spectra was not satisfactory. The residuals were considerable, indicating that the standard spectra used did not represent accurately the spectra of the compounds present in the mixture. Therefore, the analytical results are quite uncertain.

The main product found in the deuterio-ethanes is $C_2H_3D_3$, about 70% of the total volume of ethanes. The ratio:

$$C_2H_3D_3/C_2H_4D_2 = 14.7$$

Table XXII

Deutero-Ethanes from the Pyrolysis of 1-Butene-4-d₃

A. Mass spectra of the Ethane fraction.

							Sensitized with Mercury- dimethyl
Temp. °C	507	507	524	524	550.7	550.7	492.1
Time min.	2	4	2	4	2	5	1
Mass							
34	1.02	1.06	1.3	1.27	1.54	1.67	0.75
33	10.	10.	10.	10.	10.	10.	10.
32	11.4	10.75	10.9	10.4	10.3	10.8	10.5
31	18.4	17.8	15.9	19.3	18.9	18.6	17.5
30	56.	54.	55.6	55.1	54.	53.3	54.9
29	34.3	31.4	32.6	32.	28.6	30.3	30.5
28	34.7	28.3	37.	24.4	22.	22.8	39.5
27	13.	12.1	12.2	11.4	11.2	11.7	15.

B. Residuals after subtracting contributions by C₂H₄D₂, C₂H₃D₃, and C₂H₄D₂ so that peak heights of mass 34, 33, 32 = 0.

31	2.6	2.5	0	3.7	2.7	1.5	2.6
30	-1.6	-2.	-0.4	0.7	0.4	-2.	-2.
29	0	-1.	-0.2	-0.9	-2.	-2.	-1.
27	-0.5	-0.6	-0.6	-0.9	-0.9	-1.	-0.7
26	-0.9	-0.7	-0.7	-0.8	-1.	-1.	-0.7

C. Composition of Deutero-Ethanes in Volume % of total of Ethane.

	Volume %							
C ₂ H ₂ D ₄	4.7	5.	6.4	6.3	7.8	8.4	3.4	5.9*
C ₂ H ₃ D ₃	69.	71.5	70.	72.	70.6	69.	74.5	67.1*
C ₂ H ₄ D ₂	26.3	23.5	23.6	21.6	21.8	22.4	22.3	27.0*
	Total-100%							

* Extrapolated Values for Non Sensitized Reaction 492°C.

for 2 minutes reaction time at 507°C is approximately equal to, but slightly smaller than the ratio:

$$\text{CHD}_3/\text{CD}_4 = 18.8$$

obtained earlier. There are further similarities between the methanes and ethanes. The ratio of the tetradeuterated to the tri-deuterated compound increases with temperature for both groups. The ratio of $\text{C}_2\text{H}_4\text{D}_2/\text{C}_2\text{H}_3\text{D}_3$ is greater than the ratio expected on the basis of the deuterio-butenes pyrolysed, as was the case with the methanes.

The concentrations of the ethanes for two minutes reaction time as a function of temperature are plotted in Fig. 18. The extrapolated values for the temperature of 492°C obtained from these plots are given in Table XXII. A comparison of these values with those for the concentrations of the sensitized reaction shows great similarity. This is of particular interest, considering that the total increase in the ethanes formed in the sensitized reaction, over the ethanes formed in the normal reaction, was 11.4-fold, (Table XVII) i.e.:

$$10.4 \times 100/11.4 = 91\%$$

of the ethanes in the sensitized reaction are due to the action of the mercury-dimethyl.

On the basis of the approximate values available, the increase in rate for the individual deuterio-ethanes is calculated in Table XXIII.

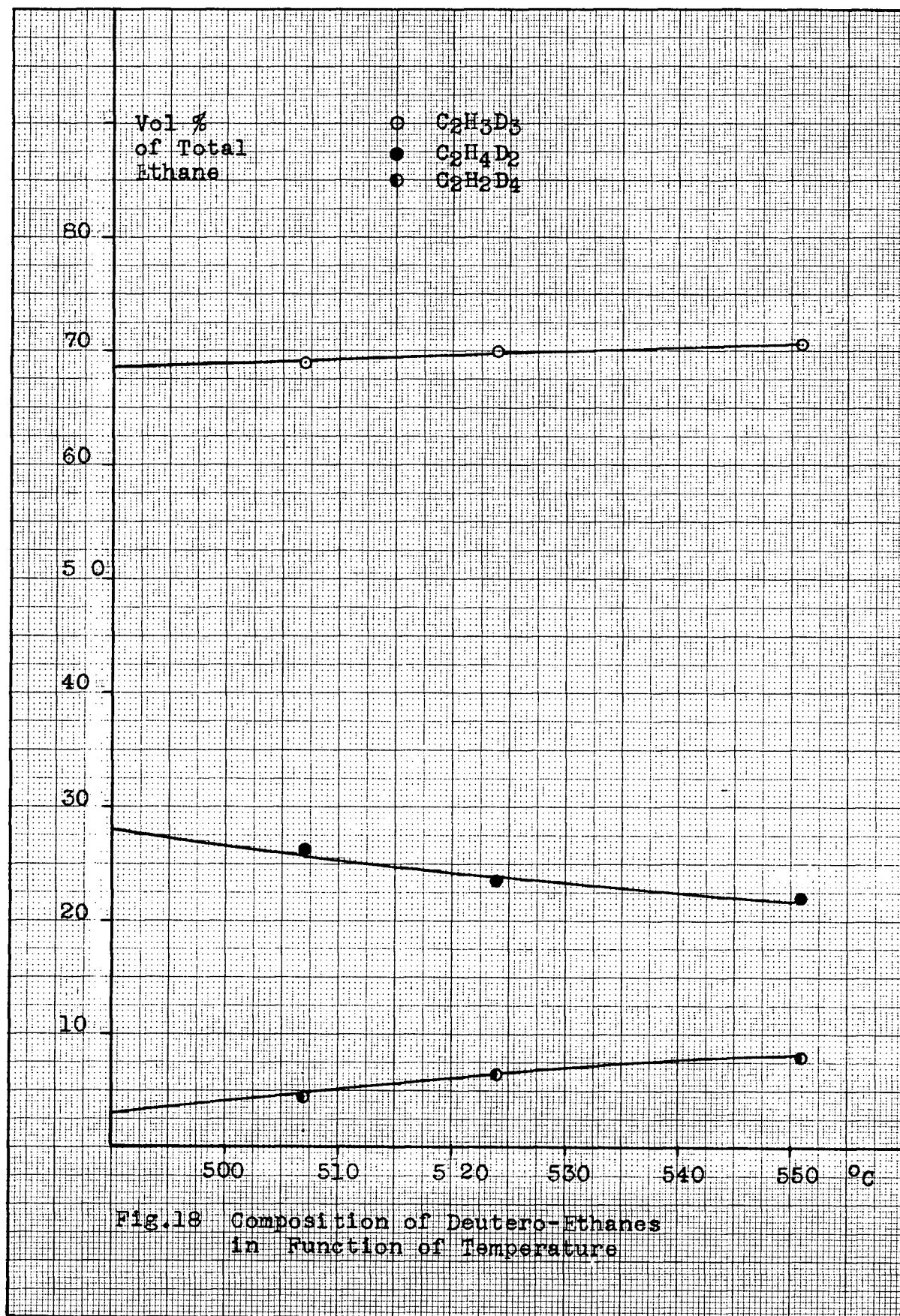


Table XXIII

Increased Rates of Formation of Deutero-Ethanes in
Reaction Sensitized
with Mercury Dimethyl

(11.4-fold increase for the total ethanes)

Compound	Ratio of Concentration from Sensitized Reaction to Concentration from Normal Reaction for 1 Min. Reaction Time.
$\text{C}_2\text{H}_2\text{D}_4$	$3.4 \times 11.4 / 5.9 = 6.6$
$\text{C}_2\text{H}_3\text{D}_3$	$74.5 \times 11.4 / 67.1 = 12.2$
$\text{C}_2\text{H}_4\text{D}_2$	$22.3 \times 11.4 / 27.0 = 9.4$

The increase in rate is seen to be roughly of the same order. It is questionable whether the variations are real or due to the approximate nature of the analytical determination.

DEUTERO-ETHYLENES

The mass spectra of the deutero-ethylenes published by Dibeler, Mohler and de Hemptinne⁷ were used as standards for the computation of the mass spectrometric analysis. The spectra were corrected before use according to the method described in the analysis of the deutero-methanes. Since the quantitative determination of the deutero-ethylenes is also possible by measurements of the parent (molecular) peaks at low electron energies, results were obtained by both methods. The satisfactory agreement between the two independent methods indicates good accuracy of the

results obtained. The results from both methods are represented in Table XXIV.

The main product found in the deuterio-ethylenes is $\text{CH}_2=\text{CH}_2$. Two other products formed in considerable and approximately equal amounts are $\text{C}_2\text{H}_2\text{D}_2$ and $\text{C}_2\text{H}_3\text{D}$. The ratios of $\text{C}_2\text{H}_2\text{D}_2/\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_3\text{D}/\text{C}_2\text{H}_4$ increase with temperature, the first ratio increasing faster. The concentrations of the deuterio-ethylenes for two minutes reaction time plotted in function of temperature are represented as a Fig. 19. The extrapolated concentrations for the temperature 492°C are given in Table XXIV. Comparison of these results with the concentrations for the sensitized reaction shows that the values are practically identical, as was the case with the deuterio-ethanes. Since the increase in the ethylene formation due to sensitization was approximately 7.1-fold (Table XVII), approximately

$$6.1 \times 100/7.1 = 86\%$$

of the ethylenes in the sensitized reaction are due to the action of the mercury dimethyl.

On the basis of the values available, the increase of rate for the individual deuterio-ethylenes is calculated in Table XXV.

The results indicate that the concentrations of all deuterio-ethylenes have increased in nearly equal proportions.

Table XXIV

Deutero-Ethylenes from the Pyrolysis of 1-Butene-4-d₃

Reaction		Volume % of total of Ethylene				Total	
Temp. °C	Time min.	C ₂ HD ₃	C ₂ H ₂ D ₂	C ₂ H ₃ D	C ₂ H ₄		
507	2	0.76	18.45	19.25	61.5	100%	50 e.v.
		0.7	18.8	18.8	61.6	"	low el. energies
	4	1.37	22.6	21.4	54.6	"	50 e.v.
		2.	22.7	21.4	54.	"	low el. energies.
524	2	1.3	23.9	22.	52.8	"	50 e.v.
		2.3	23.8	21.4	52.5	"	low el. energies
	4	1.89	26.4	22.6	49.	"	50 e.v.
		2.5	25.6	22.8	49.2	"	low el. energies
550.7	2	2.75	27.6	23.4	46.3	"	50 e.v.
		1.	28.6	22.6	48.	"	low el. energies.
	5	3.6	28.4	25.3	42.2	"	50 e.v.
		3.5	29.2	25.8	41.5	"	low el. energies.

Deutero Ethylenes from the Pyrolysis of 1-Butene-4-d₃Sensitized with Hg(CH₃)₂

Reaction		Volume % of total of Ethylene				Total	
Temp. °C	Time min.	C ₂ HD ₃	C ₂ H ₂ D ₂	C ₂ H ₃ D	C ₂ H ₄		
492	1	0.66	16.6	14.5	68.3	100%	50 e.v.
		"	19.	13.8	67.1		low el. energies.

Extrapolated Values for Non-Sensitized
Reactions

Temp. °C	Time min.	C ₂ HD ₃	C ₂ H ₂ D ₂	C ₂ H ₃ D	C ₂ H ₄	Total
492	2	0.4	14.7	16.5	68.5	100%

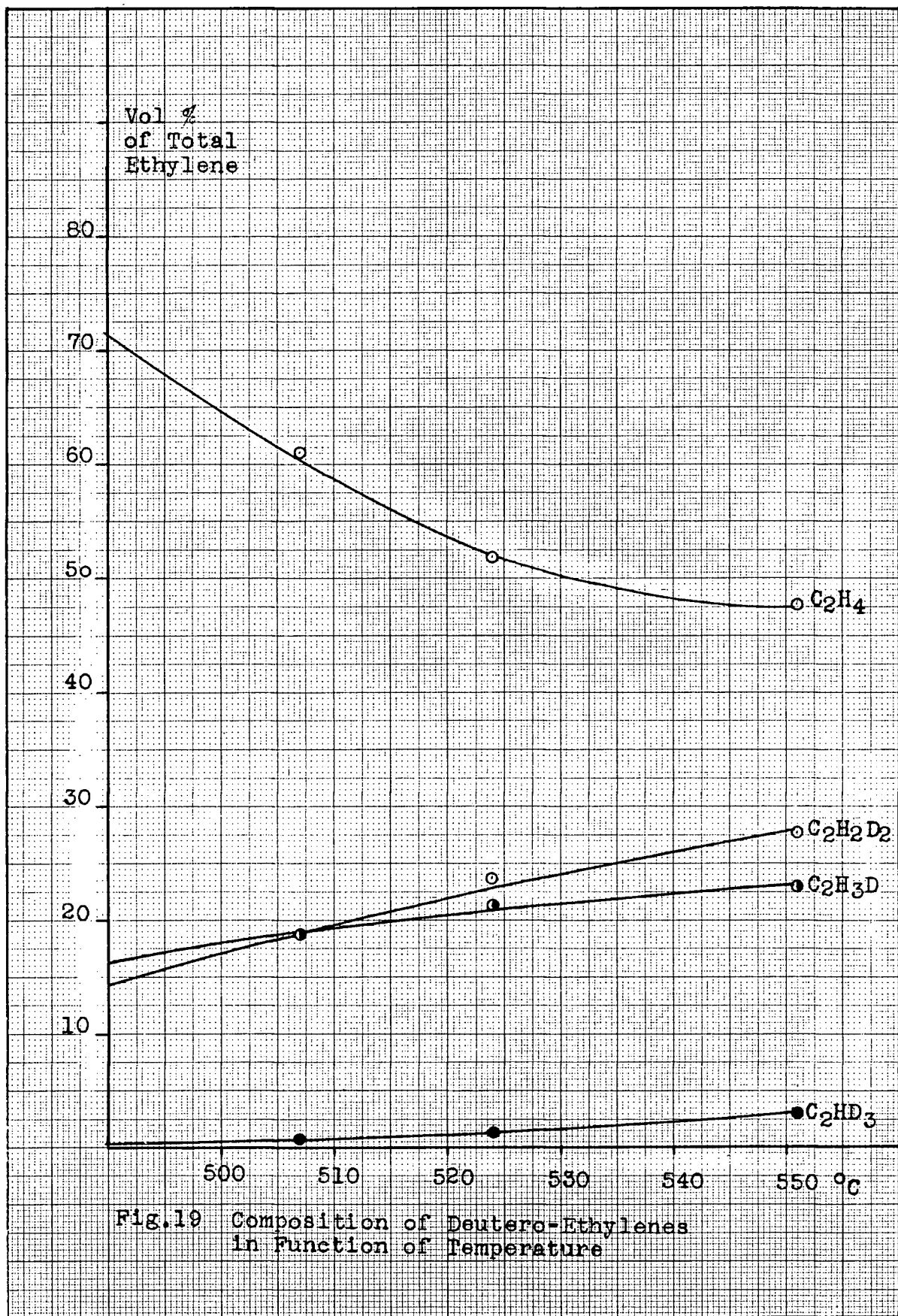


Table XXV

Increased Rates of Formation of Deutero-Ethylenes in the

Reaction Sensitized with Mercury Dimethyl

(7.1 fold increase for the total ethylenes)

Compound	Ratio of Concentration from Sensitized Reaction to Concentration from Normal Reaction for 1 Min. Reaction Time
$C_2H_2D_3$	$0.66 \times 7.1 / 0.49 = 9.3$
$C_2H_2D_2$	$16.6 \times 7.1 / 14.7 = 8.$
C_2H_3D	$14.5 \times 7.1 / 16.5 = 6.3$
C_2H_4	$68.3 \times 7.1 / 68.5 = 7.1$

DEUTERO-PROPYLENES

Due to lack of data on the spectra of the deutero-propylenes, the analysis was based on measurements of the parent (molecular) peaks at low electron energies. The quantitative estimation of deutero-isomers by measurements at low electron energies was proposed first by Stevenson and Wagner.²⁸ The accuracy of the method depends on the assumed equality of the ionization potentials of the deutero-isomers. It has been shown by Tickner, Bryce and Lossing³² that this method can lead to errors as great as 15% in the estimation of the relative concentrations of CH_4 and CD_4 . However, there is evidence that the ionization potentials of the deutero-isomers of higher hydrocarbons, and especially higher olefins, are sufficiently close to

allow quantitative determinations with good accuracy. In the case of the olefins, the electron removed at lowest electron energies is a π electron which can be expected to be little affected by the deuterium substitution. Thus, for both acetylene and ethylene, the ionization potential of the non-deuterated compound has been shown to be the same as that of the completely deuterated compound within 0.02 e.v.¹⁸ The relatively good agreement between the results from the normal and low electron energy analyses of the deuterio-ethylenes is a further proof for the reliability of the low electron energy method for the analysis of unsaturated deuterio-hydrocarbons.

The results obtained from the analyses of the deuterio-propylenes are represented in Table XXVI. The main products found are C_3H_6 , C_3H_5D and $C_3H_4D_2$. The concentrations of the deuterio-propylenes for two minutes reaction time plotted against temperature are represented in Fig. 20. The extrapolated concentrations for the temperature $492^\circ C$ are given in Table XXVI. Since the concentrations of the propylenes changed considerably with temperature, the values obtained by extrapolation must be considered as very approximate.

The increased rates of formation of the deuterio-propylenes in the mercury dimethyl sensitized reaction are given in Table XXVII. The $C_3H_4D_2$, $C_3H_3D_3$ and $C_3H_2D_4$ show increases of the same order as those observed for the CHD_3 , the CH_2D_2 , the deuterio-ethanes and the deuterio-ethylenes. The increase in concentration of the $C_3H_3D_3$ has an

Table XXVI

Deutero-Propylenes from the Pyrolysis of 1-Butene-4-d₃

Reaction		Volume % of total of Propylene					
Temp.	Time	C ₃ D ₄ H ₂	C ₃ D ₃ H ₃	C ₃ D ₂ H ₄	C ₃ DH ₅	C ₃ H ₆	Total
°C	min.						
507	2	3.9	13.2	7.9	58.	17.1	100%
	4	4.3	18.6	8.5	42.8	25.7	"
524	2	-	-	-	-	-	
	4	4.1	20.2	10.1	31.4	34.3	"
550.7	2	4.3	17.	8.6	30.4	39.6	"
	5	4.	16.	9.4	25.	47.	"

Deutero-Propylenes from the Pyrolysis of 1-Butene-4-d₃
Sensitized with Mercury-dimethyl

Reaction		Volume % of total of Propylene					
Temp.	Time	C ₃ D ₄ H ₂	C ₃ D ₃ H ₃	C ₃ D ₂ H ₄	C ₃ DH ₅	C ₃ H ₆	Total
°C	min.						
492	1	2.8	17.4	7.9	37.7	34.	100%

Extrapolated Values for Non-Sensitized
Reaction

Temp.	Time	C ₃ D ₄ H ₂	C ₃ D ₃ H ₃	C ₃ D ₂ H ₄	C ₃ DH ₅	C ₃ H ₆	Total
°C	min.						
492	2	3.2	6.0	7.3	77	7.1	100%

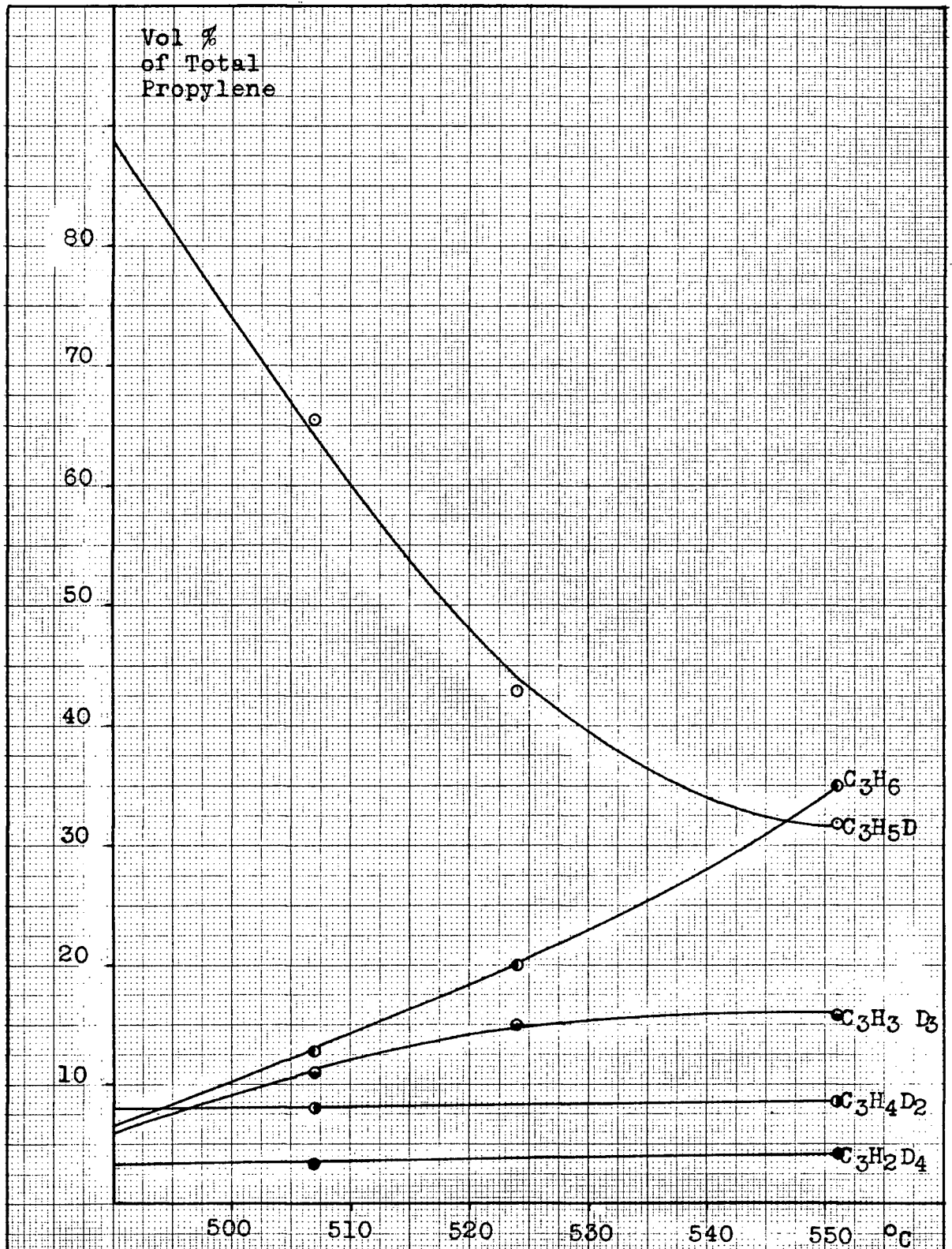


Fig.20 Composition of Deutero-Propylenes
in Function of Temperature

intermediate value and the high value for the C_3H_6 is second only to the increase of the CH_4 concentration.

Table XXVII

Increased Rates of Formation of Deutero-Propylenes in the
Reaction Sensitized with Mercury Dimethyl

(9.7-fold increase for the total propylenes (Table XVIII)

Compound Ratio of Concentration from Sensitized Reaction
to Concentration from Normal Reaction for 1
Min. Reaction Time.

$C_3H_2D_4$	$2.8 \times 9.7 / 3.2 = 8.5$
$C_3H_3D_3$	$17.4 \times 9.7 / 6. = 28$
$C_3H_4D_2$	$7.9 \times 9.7 / 7.3 = 10.5$
C_3H_5D	$37.7 \times 9.7 / 77. = 4.75$
C_3H_6	$34 \times 9.7 / 7.1 = 46.5$

DEUTERO-BUTENES

The deutero-butene fraction separated after pyrolysis of the 1-Butene-4- d_3 also was analysed on the mass spectrometer. The mass spectra obtained with 50 e.v. and low electron energies are given in Table XXVIII, together with the calculated percentages of the isomers found.

Unfortunately, no systematic investigation of the changes in deuterium distribution in the deuterated butene was made. The idea that the butene isolated after the reaction also should show detectable changes in the deuterium content occurred too late in the investigation. The

Table XXVIII

Mass Spectra of Deutero Butenes

Mass	Low el. energies			50 e.v.		
	A	B	C	A	B	C
60	4.8	4.8	11.	4.8	4.37	10.4
59	100.	100.	100.	100.	100.	100.
58	10.	10.	13.	39.	40.	45.
57	-	-	2.	15.4	15.5	20.9
56	-	4.2	-	7.5	10.9	12.

Composition of Deutero Butenes
in Volume % of total of Butene

	A	B		C
		Low el. en.	50 e.v.	
$C_4H_4D_4$	0	0	0	5.1
$C_4H_5D_3$	91.	87.5	88.2	82.6
$C_4H_6D_2$	9.	8.75	8.8	10.7
C_4H_7D	-	-	-	1.6
C_4H_8	-	3.68	3.	-
Total	100%	100%	100%	100%

A 1-Butene-4-d₃ standard

B Butene fraction isolated from reaction mixture obtained from pyrolysis of 1-Butene-4-d₃ sensitized with Mercury-dimethyl at 492°C, 1 minute reaction time.

C Butene fraction isolated from reaction mixture obtained from 1-butene-4-d₃ pyrolysed at 568°C, 3 minutes reaction time.

Table XXIX

Comparison of the Normal and Sensitized Decomposition
of 1-Butene-4-d₃

Compound	Concentration in Mole per cent (x 10) of Initial 1-Butene-4-d ₃		Concentration Ratio Sensitized to Unsensitized
	Unsensitized	Sensitized	
CD ₄	0.11	0.7	7
CD ₃ H	2.77	17.2	6
CD ₂ H ₂	1.09	8.3	8
CDH ₃	0.06	1.6	27
CH ₄	0.30	29.8	100
C ₂ D ₄ H ₂	0.05	0.3	6
C ₂ D ₃ H ₃	0.56	7.1	13
C ₂ D ₂ H ₄	0.22	2.1	10
C ₂ D ₃ H	0.10	0.9	9
C ₂ D ₂ H ₂	0.29	2.3	8
C ₂ DH ₃	0.32	2.0	6
C ₂ H ₄	1.34	9.5	7
C ₃ D ₄ H ₂	0.07	0.6	9
C ₃ D ₃ H ₃	0.14	3.8	27
C ₃ D ₂ H ₄	0.17	1.7	10
C ₃ DH ₅	1.75	8.3	5
C ₃ H ₆	0.16	7.5	47
C ₄ H ₈	-	27.0	

analysed deuterio-butene from the only fraction collected shows interesting changes. The production of isomers with 4, 2, and 1 deuterium atoms is indicated clearly. Considering the large concentration of the butene isolated from the reaction, the amounts of these isomers appear considerable.

The deuterio-butene isolated from the sensitized reaction contains C_4H_8 , presumably 1-butene.

.

The results from Tables XX -XXVIII concerning comparisons of the sensitized and normal reactions have been summarized in Table XXIX. The concentrations of the compounds are given in mole % of the initially admitted 1-butene.

DEUTERIUM DISTRIBUTION IN THE POLYMERS

No systematic investigation of the deuterio-compounds in the polymer fractions was made. The deuterio-isomers contained in several polymer fractions of only one reaction mixture were determined by mass spectrometric analysis of the separated fractions. The results of the analyses with low energy electrons are presented in Table XXX.

The results in Table XXX indicate the formation of a surprisingly large amount of deuterio-isomers for a given compound. There can be little doubt that the results are real, since special precautions were taken in all measurements to reduce the energy of the ionizing electrons below a value where all remaining peaks due to ion fragments

had completely disappeared. The parent peak with lowest mass measured under such conditions was always that of the completely non-deuterated compound. The concentrations of the deutero-isomers of a compound show a characteristic distribution around a maximum value. The concentrations of the deutero-isomers plotted against the number of deuterium atoms contained in the compound are shown in Fig. 21.

Table XXX

Deutero-Isomers of the Polymers from the Pyrolysis of
1-Butene-4-d₃

Temp. of Pyrolysis: 545°C Reaction time: 5 Min.

Deutero-isomers in Chromatographic Fraction P₃

P₃ was identified in the analysis of the pyrolysis mixtures from 1-butene as C₅H₆, most probably Cyclopentadiene,*

Mass	Compound	Vol. %
70	C ₅ H ₂ D ₄	4.08
69	C ₅ H ₃ D ₃	10.9
68	C ₅ H ₄ D ₂	25.8
67	C ₅ H ₅ D	32
66	C ₅ H ₆	<u>27.2</u>

Total 100%

* Appendix I: Qualitative Identification of the Polymers.

Table XXX (Cont'd)Deutero-Isomers in Chromatographic Fraction H₂

H₂ was identified in the analysis of the pyrolysis mixtures from 1-butene as C₆H₈, most probably Cyclohexadiene.*

Mass	Compound	Vol. %
87	C ₆ HD ₇	1.7
86	C ₆ H ₂ D ₆	3.7
85	C ₆ H ₃ D ₅	9.1
84	C ₆ H ₄ D ₄	18.3
83	C ₆ H ₅ D ₃	25.7
82	C ₆ H ₆ D ₂	18.6
81	C ₆ H ₇ D	14.3
80	C ₆ H ₈	<u>8.6</u>
		Total 100 %

Deutero-Isomers in Chromatographic Fraction Bz

Bz was identified in the analysis of the pyrolysis mixtures from 1-butene as C₆H₆- Benzene.*

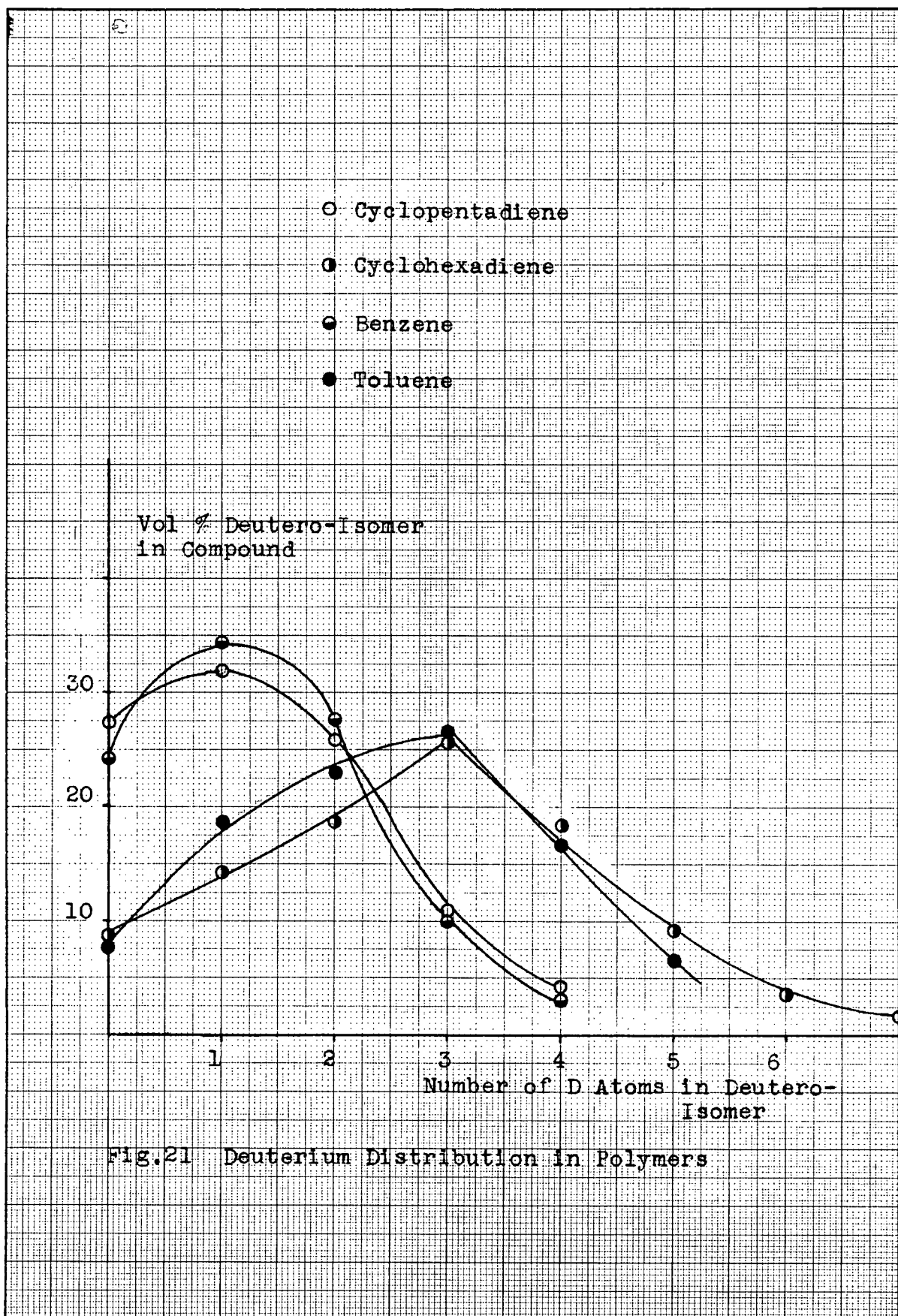
Mass	Compound	Vol. %
82	C ₆ H ₂ D ₄	3.4
81	C ₆ H ₃ D ₃	10.4
80	C ₆ H ₄ D ₂	27.6
79	C ₆ H ₅ D	34.5
78	C ₆ H ₆	<u>24.1</u>
		Total 100 %

Deutero-Isomers in Chromatographic Fraction Tl

Tl was identified in the analysis of the pyrolysis mixtures from 1-butene as C₇H₈- Toluene.*

Mass	Compound	Vol. %
97	C ₇ H ₃ D ₅	6.5
96	C ₇ H ₄ D ₄	16.8
95	C ₇ H ₅ D ₃	26.2
94	C ₇ H ₆ D ₂	23.4
93	C ₇ H ₇ D	18.7
92	C ₇ H ₈	<u>8.4</u>
		Total 100 %

* Appendix I: Qualitative Identification of the Polymers.



D I S C U S S I O N

DISCUSSION

FREE RADICAL VERSUS MOLECULAR MECHANISM

A decision as to whether the 1-butene pyrolysis proceeds largely by free radical mechanisms or by molecular mechanisms is of primary importance in the interpretation of the present results. Some of the experiments were designed specifically to provide information as to the nature of the mechanism.

It was found that the addition of approximately 5% by volume of mercury dimethyl to 1-butene and 1-butene-4-d₃ produced a large increase in the rate of the butene decomposition and in the rate of formation of the products. Mercury dimethyl is known to decompose with the formation of methyl radicals. Therefore, the acceleration of the butene decomposition must be due to the action of the methyl radicals from the sensitizer bringing about a "forced" free radical reaction.

If this is so, several points in a comparison of the results from the normal and sensitized reactions are significant:

The rate of formation of all light hydrocarbons was greatly accelerated in the sensitized reaction. For a reaction time of one minute at 493°C, the concentration of the light hydrocarbon products in the sensitized pyrolysis had increased 7 - to 13- fold over that in the non-sensitized pyrolysis.

In the normal and sensitized decomposition of 1-butene-4-d₃, the deuterio-ethanes and deuterio-ethylenes were produced in nearly equal relative proportions, although an estimated 90% of the deuterio-ethanes and 86% of the deuterio-ethylenes in the sensitized reaction resulted from the action of the mercury dimethyl. It is probable, therefore, that the deuterio-ethanes and deuterio-ethylenes were formed in both cases by analogous mechanisms, i.e. radical mechanisms. Thus, the deuterio-ethanes and deuterio-ethylenes appear to be products of radical chains started by the methyl radicals.

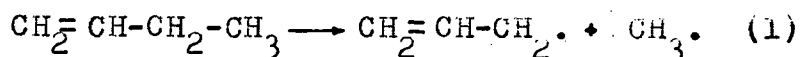
The increases in concentration of the remaining products in the sensitized reaction also show certain regularities. The concentrations of a large group of deuterio-isomers increased by approximately equal amounts, as did the deuterio-ethanes and deuterio-ethylenes. The remaining compounds showing a much larger increase were methane CH₄ and propylene C₃H₆, both containing no deuterium. (Table XXIX) It is, therefore, reasonable to assume that both these compounds were produced by fast reactions of the methyl radicals with the 1-butene-4-d₃. This is especially obvious in the case of CH₄.

A general inspection of the deuterated products from the normal 1-butene-4-d₃ decomposition shows that a wide variety of deuterio-isomers was formed. The formation of these products through molecular mechanisms appears improbable.

On the basis of these arguments, it can be concluded that, most probably, the decomposition of 1-butene and 1-butene-4d₃ proceeds largely by free radical mechanisms. Therefore, the present results will be interpreted on the basis of free radical reactions. The extent to which such reactions can explain the experimental results qualitatively and quantitatively will be a final test of the validity of this assumption,

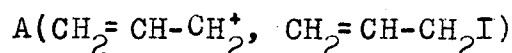
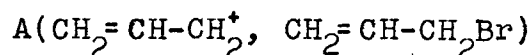
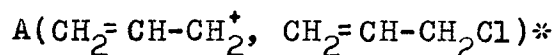
PRIMARY STEP OF THE FREE RADICAL DECOMPOSITION
OF 1-BUTENE

The primary step which is most probably involved in the free radical decomposition of 1-butene is:



The reasons for the expected weakness of the $\text{CH}_2:\text{CH}.\text{CH}_2-\text{CH}_3$ bond and evidence for the occurrence of reaction (1) at higher temperatures were given in the introduction. Also, it was mentioned that Sehon and Szwarc²⁶ obtained the values $E_1 = 61.5$ kcal/mole and $A_1 = 10^{13}$ 1/sec for reaction (1) by studying the pyrolysis of 1-butene with the toluene carrier technique. Some objections to the interpretation of the experimental results by which these values for E_1 and A_1 were obtained were pointed out. However, the value $E_1 = 61.5$ kcal has received recent confirmation by Lossing, Ingold and Henderson¹⁶ and by McDowell, Lossing, Henderson and Farmer.²⁰ These authors have measured the vertical ionization potential of the allyl radical by the electron

impact method. The heat of formation of the allyl radical was determined subsequently from appearance potential measurements of:



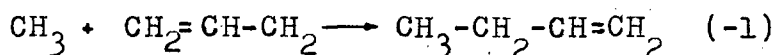
and the heats of formation of the allyl halides. The three values obtained in this way for the heat of formation of the allyl radical agreed within 1 kcal. The average value obtained was:

$$\Delta H_f^\circ (\text{CH}_2=\text{CH}-\text{CH}_2\cdot) = 32.3 \text{ kcal.}$$

The bond dissociation energy $D(\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3)$ can be calculated from the above value and the well-known heat of formation of the methyl radical³³ according to the equation:

$$\begin{aligned} D(\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3) &= \Delta H_f^\circ (\text{CH}_2=\text{CH}-\text{CH}_2\cdot) + \Delta H_f^\circ (\text{CH}_3\cdot) - \Delta H_f^\circ (\text{1-butene}) \\ &= 32.3 + 32.5 - (0.03)^1 \\ &= 64.8 \text{ kcal./mole.} \end{aligned}$$

Thus, since E_{-1} for the reverse reaction



should be equal or nearly equal to zero,

$$D(\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3) = E_{-1} = 64.8 \text{ kcal/mole.}$$

This value is in substantial agreement with the value obtained by Sehon and Szwarc $E_{-1} = 61.5$, considering the limits of error in both determinations.

* $A(\text{CH}_2=\text{CH}-\text{CH}_2^+, \text{CH}_2=\text{CH}-\text{CH}_2\text{Cl})$, means the appearance potential of the $\text{CH}_2=\text{CH}-\text{CH}_2^+$ ion in the mass spectrum of the $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ molecule.

From the agreement of these results, it would appear that the value for E_1 can be fixed within the limits of 61 to 65 kcal, and that A_1 should be in the neighbourhood of 10^{13} 1/sec. Using the above values, the percentage of decomposition of 1-butene due to the primary reaction only, can be calculated for several of the temperatures used in the present investigation, and the values obtained compared with the experimentally measured total decomposition of the 1-butene. The ratios Δc (total) to Δc (primary) obtained in this way are given in Table XXXI. Δc (total) refers to the percentage of total 1-butene decomposition as measured in the experiments for one minute reaction time (Table XI and Fig. 10). Δc (primary) is a calculated value for the percentage of primary decomposition under the assumption:

$E_1 = 61.5$ kcal, $A_1 = 10^{13}$ (column 2 of Table XXXI) and $E_1 = 64.8$ kcal/mole, $A_1 = 10^{13}$ (column 3 of the same table). The results obtained indicate that the ratio of total to primary decomposition is within the limits of 7.6 to 63.

In spite of the considerable uncertainty of the estimate and the wide variations between the values obtained, it appears that for each butene molecule decomposing by a primary split to methyl and allyl radicals, at least 8 molecules of butene are decomposed by secondary reactions initiated by the methyl and allyl radicals released in the primary reaction.

Table XXXI

Ratios of Total to Primary Decomposition
of 1-Butene for 1 Minute Reaction Time.

Temp. °C	$\frac{\Delta c \text{ (total)}}{\Delta c \text{ (primary)}}$	$\frac{\Delta c \text{ (total)}}{\Delta c \text{ (primary)}}$
	$E_I = 61.5 \text{ kcal}$	$E = 64.8 \text{ kcal}$
	$A_I = 10^{13}$	$A = 10^{13}$
493	5.9	50
509	5.9	53
522.2	8	69
540.6	8.6	73
546	9.0	71
554.5	8.2	62
Average	$\frac{\Delta c \text{ (total)}}{\Delta c \text{ (primary)}} 7.6$	63

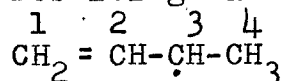
SECONDARY REACTIONS IN THE
1-BUTENE DECOMPOSITION

The secondary reactions occurring in the 1-butene decomposition should be initiated by the methyl and allyl radicals released by the primary decomposition. The possible reactions of the methyl radicals will be considered first, since the methyl radicals can be expected to have a greater reactivity than the resonance stabilized allyl radicals.

HYDROGEN ABSTRACTION BY METHYL RADICALS

In principle, methyl radicals can abstract hydrogen

atoms from any of the four carbon atoms in 1-butene. The weakness of the $\text{CH}_2 : \underset{\text{H}}{\text{CH}} \cdot \text{CH} \cdot \text{CH}_3$ bond due to resonance stabilization of the resulting radical:



suggests preferential abstraction from carbon atoms "3".

The bond dissociation energy $D(\text{CH}_2 = \underset{\text{H}}{\text{CH}} - \underset{\cdot}{\text{CH}} - \text{CH}_3)$ can be estimated on the basis of recent electron impact work by McDowell, Lossing, Henderson and Farmer.²⁰ The authors obtained the heat of formation of the $\underset{\cdot}{\text{CH}}_2 - \text{CH} = \text{CH} - \text{CH}_3$ radical from measurements of the vertical ionization potential of this radical produced by the pyrolysis of 1-iodo-but-2-ene and the appearance potential of the C_4H_7^+ ion from butene-2. The result obtained was:

$$\Delta H_f^\circ (\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3) = 26 \pm 3 \text{ kcal}$$

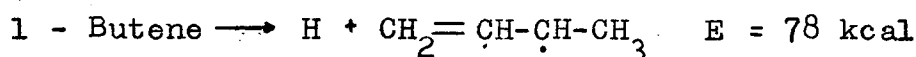
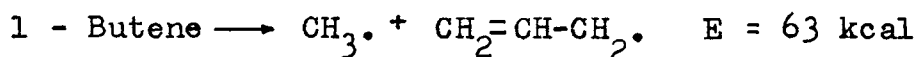
The $\underset{\cdot}{\text{CH}}_2 - \text{CH} = \text{CH} - \text{CH}_3$ radical and the $\text{CH}_2 = \text{CH} - \underset{\cdot}{\text{CH}} - \text{CH}_3$ radical differ only by the formally assigned electron distribution. The two formulae represent two forms of the same resonance hybrid. Therefore:

$$\Delta H_f^\circ (\underset{\cdot}{\text{CH}}_2 - \text{CH} = \text{CH} - \text{CH}_3) = \Delta H_f^\circ (\text{CH}_2 = \text{CH} - \underset{\cdot}{\text{CH}} - \text{CH}_3) = 26 \pm 3 \text{ kcal.}$$

The bond dissociation energy $D(\text{CH}_2 = \underset{\text{H}}{\text{CH}} - \underset{\cdot}{\text{CH}} - \text{CH}_3)$ then can be computed from the relation:

$$\begin{aligned} D(\text{CH}_2 : \underset{\text{H}}{\text{CH}} \cdot \text{CH} \cdot \text{CH}_3) &= \Delta H_f^\circ (\text{CH}_2 = \text{CH} - \text{CH} - \text{CH}_3) + \Delta H_f^\circ (\text{H}) - \Delta H_f^\circ (\text{1-butene})^1 \\ &= 26 + 52 - (-0.03) \\ &= 78 \text{ kcal.} \end{aligned}$$

The result obtained is of twofold interest. Firstly, there is an appreciable difference between the activation energies of the two possible primary reactions:



Secondly, the bond dissociation energy $D(\text{CH}_2=\text{CH}-\underset{\text{H}}{\text{CH}}-\text{CH}_3)$ is smaller by 15 to 20 kcal than a normal paraffinic C-H bond energy, thus confirming the expected preferential hydrogen atom abstraction from the carbon atom in position "3".

The rates of hydrogen abstraction by methyl radicals have been studied by Trotman-Dickenson and Steacie.³⁴ The methyl radicals were produced by the photolysis of acetone. In the actual determinations isotopically labelled, acetone-d₆ was used also. Some of the values obtained by the authors are reproduced in Table XXXII.

Table XXXII

Abstraction of Hydrogen Atoms by Methyl Radicals

33

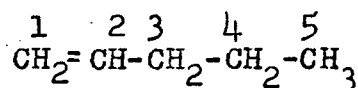
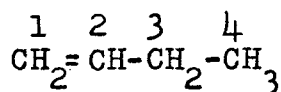
Trotman-Dickenson and Steacie

RH	E_{Ab} kcal	$k_{\text{Ab}} \times 10^6$ mole ⁻¹ .cc.sec ⁻¹ at 182°C	log A_{Ab}
----	-------------------------	-------------------------------------------------------------------------------------	---------------------

Ethane	10.4	2.	11.3
Ethylene	10.0	2.9	11.3
Propylene	7.7	12.	10.8
1-Butene	7.6	34.	11.2
1-Pentene	7.6	35.	11.2

The values in this table refer to the reaction of the methyl radicals with hydrogen atoms from the compound RH, i.e. with the sum of hydrogen atoms abstracted from any

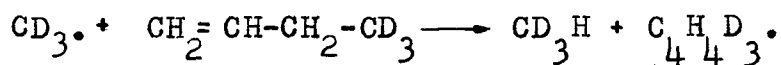
location in the molecule. Comparisons of the values obtained for the different compounds can be used to obtain information as to which hydrogen atoms in a given molecule are abstracted preferentially. Thus, a comparison of the results for ethane and ethylene with those for the rest of the compounds indicates that primary and vinylic hydrogens are abstracted with less ease, and that the difference is largely due to differences in the activation energies. The fact that the values for 1-butene and 1-pentene were practically identical indicates that it is the hydrogen atoms on carbon atom "3" (allylic hydrogen atoms) which are abstracted almost exclusively:



The temperature range in which Trotman-Dickenson and Steacie investigated the abstraction reactions was 180 to 340°C. The extension of these data to the present temperature range of 500 to 560°C introduces some uncertainty. The effect of differences in the activation energies will be reduced at higher temperatures, and abstraction of hydrogen atoms "at random" should become more probable.

The abstraction of hydrogen atoms by methyl radicals from unreacted butene can be considered to be the reaction responsible for the methane formation in the pyrolysis of 1-butene. The results from the pyrolysis of the 1-butene-4-d₃ showed that the deuterio-methane formed in largest amounts

was CD_3H , presumably originating by the reaction:

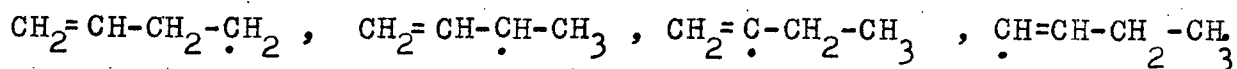


It was also found that small amounts of CD_4 were found, probably originating by the reaction:

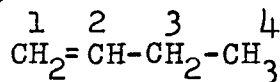


The methyl radicals necessary for the above reactions are supplied only partly by the slow primary decomposition of the butene. Most of the methyl radicals must originate from chain carrying reactions in which methyl radicals are generated. Possible reactions of this type will be discussed in subsequent sections. However, there are several points with regard to the abstraction reaction which will be considered here.

The positions from which hydrogen atoms are abstracted are of interest. Depending on the position from which a hydrogen atom is abstracted, four different C_4H_7 radicals can be formed. These are:



The four radicals can be expected to have different properties. An attempt to estimate the relative reaction velocities of the four abstraction reactions leading to these radicals can be made with the use of Trotman-Dickenson and Steacie's values. If the assumption is made that the primary hydrogen atoms of carbon atom "4".



behave towards abstraction in essentially the same way as do those in ethane, and the hydrogen atoms of carbon atoms "1" and "2", as do those in ethylene, the abstraction of hydrogen atoms from different locations of the 1-butene molecule can be estimated for the temperature 182°C from the values in Table XXXII.

$$\begin{array}{lcl} \text{Ethane} & k_{\text{Ab}} \times 10^6 = 2 \text{ per Hydrogen atom} & \frac{2}{6} = 0.33 \\ \text{Ethylene} & k_{\text{Ab}} \times 10^6 = 2.9 \text{ per Hydrogen atom} & \frac{2.9}{4} = 0.72 \end{array}$$

$$\text{Butene-1} \quad k_{\text{Ab}} \times 10^6 = 34$$

Since butene has three primary hydrogen atoms and three vinylic hydrogen atoms, the rate constants for abstraction of primary hydrogen atoms will be approximately

$$k_{\text{Ab}} \times 10^6 = 0.33 \times 3 = 1$$

and for vinylic hydrogen atoms

$$k_{\text{Ab}} \times 10^6 = 0.72 \times 3 = 2.16$$

The rate constant for total abstraction from 1-butene is $k_{\text{Ab}} \times 10^6 = 34$. The calculation leads to the result that only $\frac{3.16}{34} \times 100 = 9.3\%$ of the hydrogen atoms abstracted at 182°C are not allylic hydrogen atoms.

In order to estimate the relative rates of hydrogen abstraction from different locations of the 1-butene molecule at the temperature, 525°C (an average temperature in the range studied), the assumption was made that the values $E_{\text{Ab}} = 7.6$ kcal/mole and $A_{\text{Ab}} = 10^{11.2} \text{ mole}^{-1} \text{ .cc.sec.}^{-1}$ from

Table XXXII represent abstraction of allylic hydrogen atoms only. It was also assumed that the activation energies and pre-exponential factors for ethane and ethylene could be used

for the abstraction reactions of primary and vinylic hydrogen atoms respectively, after correcting for the appropriate number of hydrogen atoms. The values obtained by such a calculation for the temperature, 525°C are given below:

Calculated Rate Constants for the Abstraction of Hydrogen

Atoms from 1-Butene at 525°C.

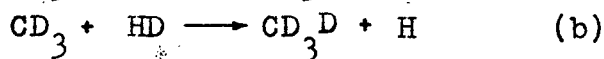
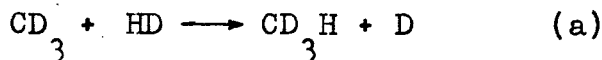
Hydrogen Atoms	k $\frac{Ab}{18}$	
Primary	0.33×10^{18}	mole ⁻¹ , sec. ⁻¹
Vinylic	0.63×10^{18}	"
Allylic	2.46×10^{18}	"

The very approximate nature of the estimate is of course well realized.

The results of the above calculation can be used to estimate the CD_3H/CD_4 ratio for the methanes formed in the decomposition of the 1-butene-4-d₃. If the difference in reactivity of the CH_3 and CD_3 radicals towards abstraction is neglected and if H and D atoms are assumed to be abstracted with equal ease by the CD_3 radicals, the ratio of CD_3H/CD_4 obtained is:

$$\frac{CD_3H}{CD_4} = \frac{2.46 + 0.63}{0.33} = 9.4$$

The abstraction of hydrogen atoms by CD_3 (or CH_3) radicals is known to be faster than the abstraction of deuterium atoms. For example, it has been found that the abstraction reaction (a)

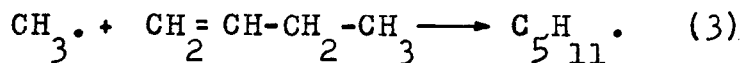


is approximately 1.7 times faster than (b) at 290°C.²⁶

Therefore, the calculated ratio $\text{CD}_3\text{H}/\text{CD}_4 = 9.4$ is certainly too low, and should be corrected upwards. The experimentally found ratio for 525°C is $\text{CD}_3\text{H}/\text{CD}_4 = 13$, (Table XVIII). The experimental value is well within the range predicted by the calculation.

ADDITION OF METHYL RADICALS

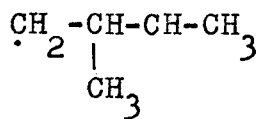
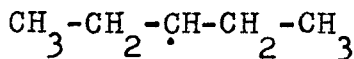
Methyl radicals, besides being capable of abstracting hydrogen from 1-butene, can add to the double bond.



The exothermicity of this reaction can be estimated, assuming a localization of the methyl group to one of the two carbon atoms participating in the double bond. The two resulting radicals are:

I

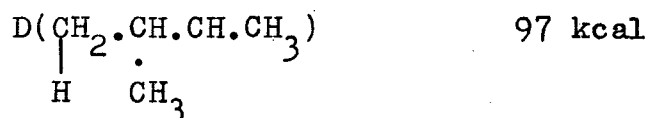
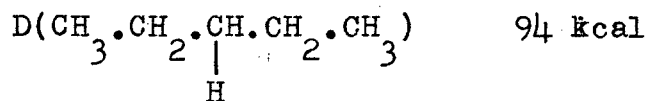
II



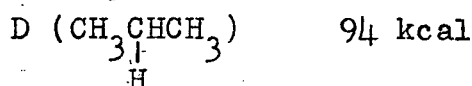
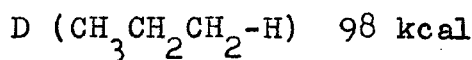
The exothermicity of reaction (3) is given by:

$$\Delta H_f^\circ(\text{CH}_3\cdot) + \Delta H_f^\circ(1\text{-butene}) - \Delta H_f^\circ(\text{I or II})$$

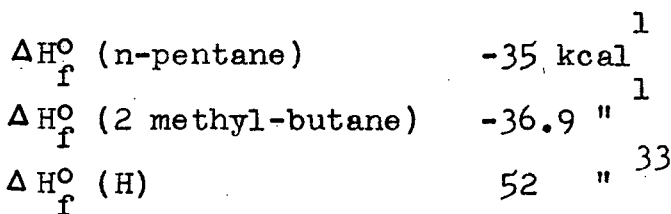
The bond dissociation energies necessary for the computation of $\Delta H_f^\circ(\text{I})$ and $\Delta H_f^\circ(\text{II})$ are not known. However, for the purpose of the estimate the following dissociation energies were assumed:



The dissociation energies were chosen on the basis of the known³³ dissociation energies of the lower hydrocarbons:



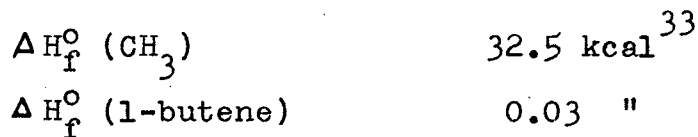
using:



one obtains:



The exothermicity of the reaction can then be obtained with the use of the known values for:



Exothermicity of reaction forming (I) 25.5 kcal

" " " " (II) 24.5 kcal

On addition of the activation energy of the methyl radical addition reaction of 2-5 kcal, (for the origin of this value see subsequent discussion) the excess energy contained in the

addition product C_5H_{11} . will be roughly 27 to 30 kcal.

The reverse decomposition of the addition product (C_5H_{11} .) will depend on the possibilities for distribution of the excess energy into the different degrees of freedom and de-activation by collision. At the elevated temperatures of the experiments (500-560°C), the life of the addition product will be very short, and the reverse reaction can be expected to take place with high probability. If this is exclusively the case, the addition reaction will not be important in the mechanism of the 1-butene decomposition. However, the possibility that the C_5H_{11} radicals also can decompose to form products different from methyl and 1-butene must be considered. Therefore, it is of interest to discuss some of the available information on the addition reaction itself, and also to consider some of the possible modes of decomposition of the addition product C_5H_{11} .

The addition reaction of methyl radicals to olefins has been subject to a number of investigations, most of which also deal with the subsequent polymerization of the olefins induced by methyl radicals. This work will not be considered here, since further polymerization of the addition product C_5H_{11} is highly improbable at the high temperatures used in the present investigation. However, the results from a recent study by Mandelcorn and Steacie²¹ in which only the addition reaction was studied (as far as this was possible) are relevant.

By comparing the experimental results obtained from the photolysis of acetone alone, and in the presence of an unsaturated hydrocarbon, Mandelcorn and Steacie were able to deduce the rate of addition of methyl radicals to the unsaturated hydrocarbon. Some of the values obtained by the authors are given in Table XXXIII. E_{Ad} is the activation energy for the addition reaction and E_2 is the activation energy for the recombination of the methyl radicals to ethane. Since $E_2 \sim 0$, $E_{Ad} - \frac{1}{2}E_2 \sim E_{Ad}$. P_{Ad} and P_2 refer to the steric factors for the addition and methyl radical recombination reactions.

Table XXXIII

Addition of Methyl Radicals to

Unsaturated Hydrocarbons - Mandelcorn and Steacie

Hydrocarbon	$E_{Ad} - \frac{1}{2}E_2$ kcal	$10^4 \times P_{Ad}/P_2^{\frac{1}{2}}$
C_2H_4	7	5
C_3H_6	6	3
C_2H_2	5.5	5

Unfortunately, experiments with 1-butene were not performed. However, propylene and 1-butene can be expected to behave very similarly towards addition. On the basis of these data and data for the abstraction reaction³⁴, a rough estimate can be made of the relative rates of the two competing reactions. The ratio of the rates for propylene at 500°C is given by:

$$\frac{R_{\text{Abstraction}}}{R_{\text{Addition}}} = \frac{3.e^{-7700/1.987 \times 773}}{3.e^{-6000/1.987 \times 773}} = 1/3$$

The ratio of the rates for 1-butene, assuming that 1-butene behaves identically like propylene towards addition, is then:

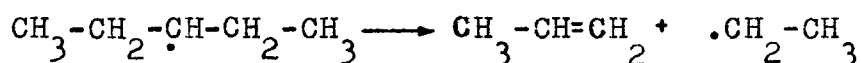
$$\frac{R_{\text{Abstraction}}}{R_{\text{Addition}}} = \frac{8.e^{-7600/1.987 \times 773}}{3.e^{-6000/1.987 \times 773}} = 1/1.1$$

The results indicate that the addition reaction will be about as fast as, or faster than the abstraction reaction in the temperature range around 500^o C. On the basis of these calculations, therefore, the addition reaction must be of importance for the mechanism of the butene decomposition, provided of course that the subsequent decomposition of the unstable addition product C₅H₁₁ also produces other species than the original methyl radicals and 1-butene.

There is an almost complete lack of direct kinetic data on the properties of the C₅H₁₁ radicals. Also, since the addition products in question are formed with an excess energy of the order of 30 kcal, their behaviour could not be predicted from a study of the properties of C₅H₁₁ radicals containing no excess energy. Therefore, the discussion must be limited to only one of the factors determining the possible decomposition reactions of the C₅H₁₁ radicals,

namely the bond dissociation energies involved in the various possible modes of decomposition. The modes of decomposition, together with calculated bond dissociation energies of the ruptured bonds, are summarized in Table XXXIV.

The reactions listed do not include modes of decomposition in which the products formed indicate that a re-arrangement has taken place. For example, reactions of the type:



were not considered. Although such reactions are possible, especially since the C_5H_{11} radical carries excess energy, they appear to be less likely than the straight decomposition reactions considered in Table XXXIV.

The activation energy of a decomposition reaction is equal to the bond dissociation energy of the bond ruptured plus the activation energy for the reverse reaction. Since in all cases considered in Table XXXIV the reverse reaction is the simple addition of a radical to the double bond of an olefin, the activation energy of the reverse reaction can be expected to be in the order of 3-6 kcal for all cases considered. Therefore, the bond dissociation energies given are a good measure of the activation energies for the decomposition reactions.

Table XXXIV

Decomposition Reactions of the C_5H_{11} Radicals

Radical Decomposition Reaction	Calculated Bond Dissociation Energy
(1a) $CH_3-CH_2-\dot{C}H-CH_2-CH_3 \longrightarrow CH_3-CH=CH-CH_2-CH_3 + H$	38 kcal
(1b) $----- \longrightarrow CH_3-CH_2-\dot{C}H=CH_2 + CH_3$	25.5
(11a) $CH_2-\underset{\substack{ \\ CH_3}}{\dot{C}H}-CH_2-CH_3 \longrightarrow CH_2=\underset{\substack{ \\ CH_3}}{C}H-CH_2-CH_3 + H$	35
(11b) $----- \longrightarrow CH_2=\dot{C}H-CH_2-CH_3 + CH_3$	24.5
(11c) $----- \longrightarrow CH_2=\dot{C}H-CH_3 + CH_3-\dot{C}H_2$	23

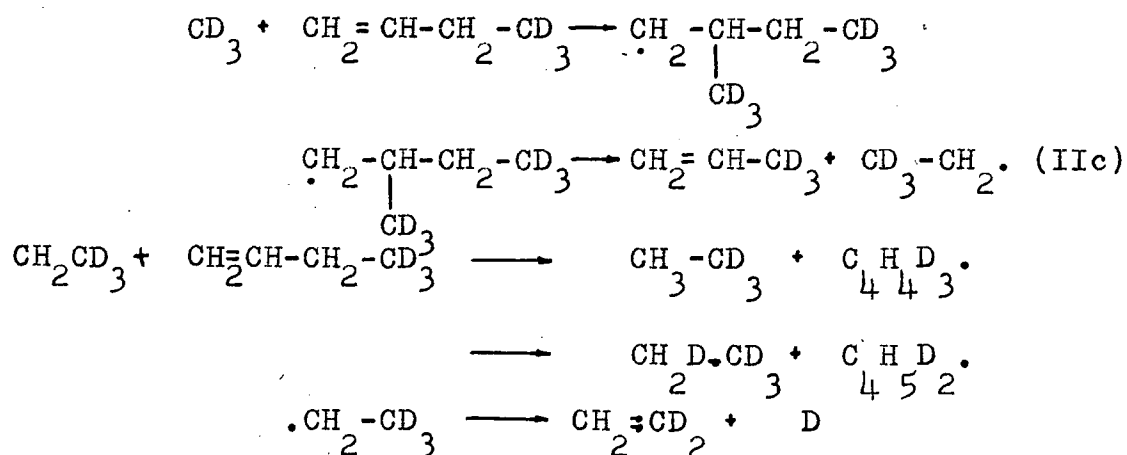
The bond dissociation energies and standard heats of formation used for the computed results in the table are listed below:

D (H-H)	104 kcal		
D(CH ₃ -H)	103 "	Currently	33
D(C ₂ H ₅ -H)	98 "	accepted values	
D(C ₂ H ₅ .CH.C ₂ H ₅)	94 "	Arbitrarily	
D(CH ₃ .CH ₂ .CH.C ₂ H ₅ -H)	97 "	chosen plausible values.	
		(see page 123)	

ΔH_f° methane	-17.9 kcal	at 25°C ¹
" ethane	-20.2 "	"
" propylene	4.9 "	"
" 1-butene	- 0.03 "	"
" n-pentane	-35 "	"
" 2-methyl-butane	-36.9 "	"
" 2-pentene	- 7 "	"
" 2-methyl-1-butene	- 8.7 "	"

The results in Table XXXIV show that reactions involving the elimination of a hydrogen atom require higher energy than those involving the elimination of an alkyl group. Thus, a prediction based on the activation energies only, indicates that reactions where the splitting of an alkyl group occurs will be faster. Reaction IIc is of particular interest, since in this case, the alkyl radical formed is not methyl. Therefore, if this reaction takes part in the mechanism of the 1-butene decomposition, propylene and ethyl radicals should be formed. The ethyl radicals can be expected to react further, either forming ethane by hydrogen abstraction from unreacted butene, or decomposing to ethylene and hydrogen atoms.

In the pyrolysis of 1-butene-4-d₃, the corresponding reactions would be:

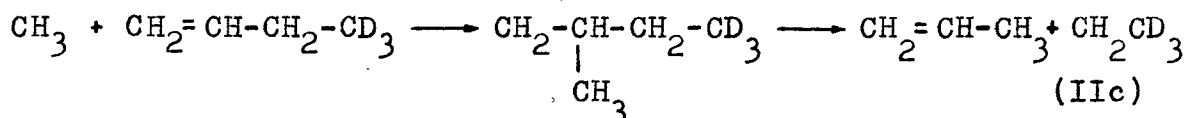
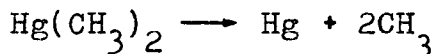


The above reactions can be used to explain the observed.

formation of propylene-d₃, ethane-d₃, ethane-d₄ and ethylene-d₂ in the pyrolysis of the 1-butene-4-d₃. According to the reaction sequence assumed above, the concentrations of the products should obey the equation:

$$C_2H_3D_3 + C_2H_2D_4 + C_2H_2D_2/C_3H_3D_3 = 1$$

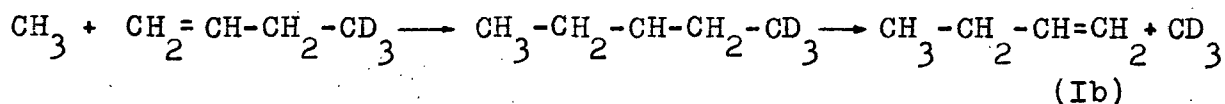
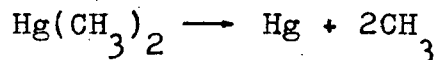
On examining the results for any given experimental conditions (Table XXVIII), it is found that the ratio for the concentrations considered is not equal to 1 but close to 2.4 on the average. Therefore, it must be concluded either that the proposed mechanism is not correct or that ethane-d₃ and -d₄ and ethylene-d₂ also are formed by some other reactions. The second alternative is considered more likely. On the basis of reaction (IIc) one should expect that in the sensitized decomposition of 1-butene-4-d₃ the formation of C₃H₆ should be greatly accelerated:



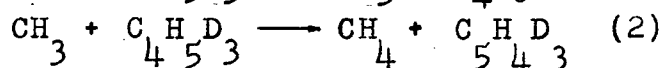
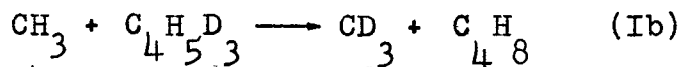
This, in fact, is the case. The increase of the C₃H₆ formation was found to be 47-fold, second only to the increase of the CH₄ formation (Table XXIX). The corresponding increase of the C₃H₃D₃ and C₂H₂D₂ formation was only 11 to 12-fold. This result can be explained if it is assumed again that the deuterio-ethane and deuterio-ethylene are formed not only as a result of reaction (IIc) but also by some other reactions, and that these reactions do not

receive such a direct enhancement in the sensitized decomposition as does reaction (IIc). Such reactions will be discussed in subsequent sections.

The formation of non-deuterated butene in the sensitized decomposition of 1-butene-4-d₃ (Table XXIX) can be explained on the basis of reaction (Ib) of Table XXXIV.



Since the formation of non-deuterated butene was observed only in the sensitized decomposition it is almost certain that this product must have been formed by the proposed mechanism. It is interesting to note that 2.7% C₄H₈ was formed. The non-deuterated butene together with CH₄ (2.9%) are the two products formed in by far the largest amounts in the sensitized reaction (Table XXIX). The results also indicate that reaction (Ib) is almost as fast as the hydrogen abstraction reaction by methyl radicals (2).

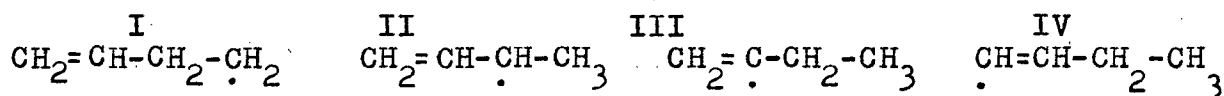


Besides explaining the formation of non-deuterated butene, reaction (Ib) indicates the main source of CD₃ radicals in the sensitized decomposition. Thus, the increased formation of CD₃H and CD₄ in the sensitized reaction should be due largely to hydrogen abstraction reactions of the CD₃ radicals released by (Ib).

The possible occurrence of reaction (Ic) and the almost certain occurrence of reaction (Ib) are considered as strong evidence that at higher temperatures the addition of a free radical to the double bond of an olefin is not invariably inactive for the mechanism: i.e., the addition product does not exclusively decompose to yield back the original radical and olefin. The newly formed bond in the addition might be retained and the addition product decompose with the splitting of a new bond leading to the formation of a new olefin and a new radical. Such disproportionation reactions might be of considerable importance in mechanisms of the thermal decomposition of olefins.

REACTIONS OF THE FREE RADICALS STABILIZED BY ALLYL-TYPE RESONANCE

It was noted earlier that as a result of hydrogen abstraction from 1-butene by free radicals, four different C_4H_7 radicals could be formed. These were:

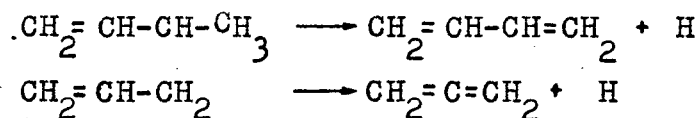


An approximate calculation indicated that about 70% of the abstraction reactions should lead to the formation of the resonance stabilized radical II. No evidence from the experimental results can be obtained for the formation of radicals III and IV, while the formation of I was indicated by the presence of relatively small amounts of CD_4 and

$C_2H_2D_4$ found in the 1-butene-4- d_3 pyrolysis.

Since the radicals I, III, and IV are formed only with low probability, the subsequent fate of these radicals in the butene system will not be considered further, on the assumption that the contribution of these reactions to the overall mechanism is relatively unimportant. The discussion will be limited to the possible fate of the resonance stabilized radical $CH_2=CH-CH-CH_3$ only. Since the allyl radical formed in the primary step of the 1-butene decomposition is also a stabilized radical, the reactions of these two free radicals will be treated together.

From the several possible modes of decomposition of the two radicals the following reactions appear most likely:



The bond dissociation energies of the bonds ruptured in the dissociation can be estimated from the heats of formation of the allyl and $CH_2=CH-CH-CH_3$ radical quoted earlier.

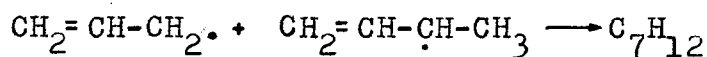
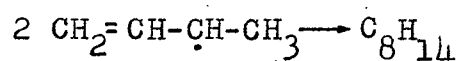
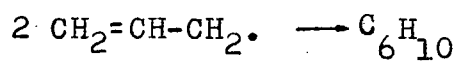
$$\begin{aligned} D(CH_2:CH.CH.CH_2-H) &= \Delta H_f^0 \text{ 1,3 Butadiene} + \Delta H_f^0 H \\ &\quad - \Delta H_f^0 CH_2:CH.CH.CH_3 \\ &= 26.3 + 52 - 26 \text{ kcal/mole} \\ &= 52.3 \text{ kcal/mole} \\ D(CH_2.C.CH_2) &= \Delta H_f^0 \text{ Allene} + \Delta H_f^0 H - \Delta H_f^0 CH_2:CH.CH_2 \\ &\quad | \\ &\quad H \\ &= 46 + 52 - 32 \text{ kcal/mole} \\ &= 66 \text{ kcal/mole} \end{aligned}$$

The activation energies for the decompositions considered above are equal to the bond dissociation energies plus the activation energies for the reverse reactions. The reverse reaction in both cases is the addition of a hydrogen atom to an unsaturated hydrocarbon, and therefore, of the order of a few kcal only. Thus, the bond dissociation energies can be taken as good representatives of the activation energy for the decomposition.

Since the frequency factors of the decomposition reactions are not known and can not be estimated, the rate constants can not be calculated. It is reasonable to assume that the reactions will have frequency factors of the same order of magnitude. If this is the case, the decomposition of the $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3$ radical should be faster than that of the allyl radical. Assuming that the frequency factors have a value in the neighbourhood of the "normal" value of 10^{13} 1/sec., the decomposition of the C_4H_7 radical will be sufficiently fast to constitute one of the reactions by which the $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3$ radical is removed from the reaction system, while the decomposition of the allyl radical will be much too slow to represent any appreciable fraction of the reactions of this radical.

Part of the allyl radicals will be eliminated by hydrogen abstraction reactions leading to the formation of propylene.

Since both radicals considered can be expected to be relatively unreactive due to their high degree of stabilization, it is reasonable to assume that their steady state concentration should be relatively high. Therefore, chain terminations should occur by recombination reactions of the allyl and $\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}-\text{CH}_3$ radical:



Cyclization and further dehydrogenation of the dimerization products could lead to the cyclic polymers identified in the experimental results. It is, therefore, of interest to establish if all, or at least an appreciable part, of the polymers found were formed as a result of the chain termination reactions considered above. Since the rate of primary decomposition of the 1-butene is not known, only a very uncertain estimate can be made. Assuming that the activation energy for the primary step is $E_1 = 61.5$ kcal/mole and the frequency factor is $A_1 = 10^{13}$ 1/sec., the rate of primary decomposition can be calculated and compared with the measured amount of polymers formed. Some of the values obtained in this way are given below. The amount of polymers formed after two minutes' reaction time is found to be larger than would be expected if the polymers were products of chain termination steps. This is particularly the case when it is considered that the

Table XXXVRatios of Polymer Formation to Primary Decomposition of the 1-Butene

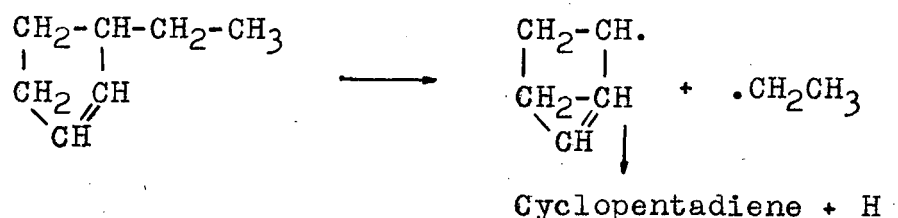
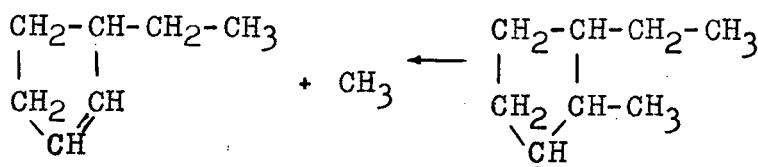
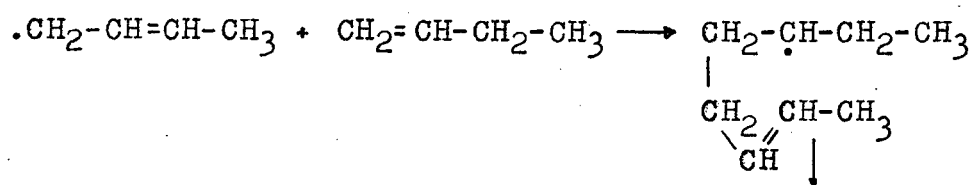
Temp. °C	Reaction Time (Minutes)	Calculated Primary Decomposition	Polymers Formed %	% Polymers %Primary De- composition
509	2	.54	1.6	3
522	2	1.49	2.7	1.93
540	2	3.55	4.9	1.38
554	2	6.61	7.7	1.16

calculated primary decomposition is a maximum value i.e. the primary reaction is, most probably, slower. (See Table XXXI). The gradual relative decrease in the polymer formation with increase in temperature is probably due to the decomposition of the polymer intermediates at the higher temperatures.

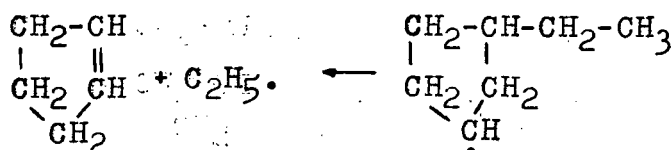
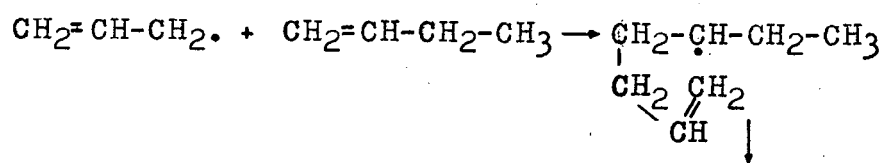
It appears that some of the polymer formation resulted from reactions other than free radical recombination followed by cyclization and dehydrogenation.

Some indication to the nature of these reactions is given by the fact that the polymers formed in largest amounts were identified as cyclic hydrocarbons: cyclopentene, cyclopentadiene, cyclohexadiene, benzene, toluene, etc. This suggests that reactions in which cyclization occurs as a natural consequence are involved. Polymerization reactions in which the intermediates have structures that are favourable for cyclization are the addition reactions of the allyl and $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3$ radical to unreacted

butene. For example, the following reactions are possible:



and:



etc.

In the above reactions cyclization occurs as an intramolecular addition reaction in which the free radical end adds to the double bond, both functional groups being on the same molecule.

Some of the results from the mass balance (Table VIII) can be used as support for mechanisms of this type. The ratio of the total hydrogen contained in the polymers plus the molecular hydrogen (H_2) to the total carbon contained in the polymers for different experimental conditions is

given below:

Table XXXVI

Ratios of Hydrogen Gas Plus Chemically Bound Hydrogen
in Polymers to Chemically Bound Carbon in Polymers.

Temp. C	Reaction Time Minutes	H/C
509	2	1.33
509	5	1.33
522	2	1.24
522	5	1.44
540.6	2	1.43
540.6	5	1.36
554.5	2	1.38
554.5	5	1.37

It is found that the H/C ratio remains relatively unaltered with the experimental conditions, the average ratio being about 1.4. Although the total hydrogen gas (H_2) found in the reaction mixtures is included in the above ratios, the ratios still fall far short of the H/C ratio of the reactant 1-butene, which is equal to 2. Since it also was found that the H/C ratio of the total products was close to the theoretical value 2, it follows that the low hydrogen content of the polymers is not compensated for by H_2 , but by the saturated hydrocarbon products, mainly methane and ethane. This then indicates that the unsaturated polymers were formed (from the original butene) by mechanisms in which very little molecular hydrogen was produced. Therefore, the formation of the polymers is limited to two types of reactions: either the (molecular) polymerization of some highly unsaturated products of the butene pyrolysis, e.g. acetylene, allene, etc., or reactions of the type (8) and (9) where effective

dehydrogenation of the cyclic polymer occurs mainly by the release of methyl and ethyl free radicals. The first alternative must be considered as very unlikely since no acetylene or allene were found in the products, even in concentrations below 0.1%.

The H/C ratios for the products of several a priori possible reactions are given in Table XXXVII.

Table XXXVII

Hydrogen to Carbon Ratios in Polymer Products Resulting from Various Reactions

	<u>H/C of Polymer Product</u>
a) $\text{CH}_2=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_2 \longrightarrow \text{C}_6\text{H}_{10}$	1.67
b) $2 \text{CH}_2=\text{CH}-\text{CH}_2 \cdot \longrightarrow \text{C}_6\text{H}_{10}$	1.67
c) $\text{CH}_2=\text{CH}-\text{CH}_2 \cdot + \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3 \longrightarrow \text{C}_7\text{H}_{12}$	1.72
d) $2 \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3 \longrightarrow \text{C}_8\text{H}_{14}$	1.75
e) $\text{CH}_2=\text{CH}-\text{CH}_2 \cdot + \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3 \longrightarrow \text{C}_6\text{H}_9 + \text{CH}_3$	1.50
f) $2 \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3 \longrightarrow \text{C}_6\text{H}_8 + 2\text{CH}_3$	1.34
g) $\text{CH}_2=\text{CH}-\text{CH}_2 \cdot + \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3 \longrightarrow \text{C}_5\text{H}_8 + \text{C}_2\text{H}_5$	1.6
$\longrightarrow \text{C}_6\text{H}_{10} + \text{CH}_3$	1.66
h) $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3 + \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3 \longrightarrow \text{C}_6\text{H}_9 + 2\text{CH}_3$	1.5
$\longrightarrow \text{C}_5\text{H}_7 + \text{CH}_3 + \text{C}_2\text{H}_5$	1.4

From the calculated H/C ratios it is evident that only reactions e, f, g, and h come close to the experimentally found ratio, H/C = 1.4. These results also suggest that the polymers were formed by allyl and $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3$ radical recombination reactions, and by reactions of the type (8) and (9), and that in both cases, free methyl,

and possibly ethyl radicals were released by the polymer molecules.

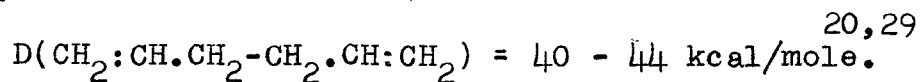
The assumed liberation of free methyl and ethyl radicals by the polymer intermediates also provides an explanation for the "induction" periods for the 1-butene decomposition and the formation of light hydrocarbons observed at the lower temperatures -- 490 to 510^o C (Fig. 10 and 12a,). The induction period can be considered to be a result of a gradual build-up of the concentration of polymer intermediates. Since the polymer intermediates react further, releasing free alkyl radicals, the rate of butene decomposition will increase in the induction period as the concentration of the polymer intermediates increases.

PYROLYSIS OF 1, 5-HEXADIENE

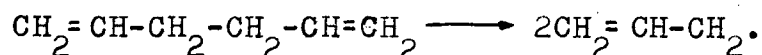
In the previous section it was suggested that the resonance stabilized allyl and $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_3$ radical, besides participating in chain termination reactions by radical recombination, might be involved in polymerization reactions with unreacted 1-butene, and also that in the course of the effective dehydrogenation of the polymers formed in this way, free alkyl radicals would be released. Since according to this view, the resonance stabilized radicals are capable of participating in a number of complex reactions, it was thought of interest to examine the

pyrolysis of 1,5-hexadiene, (di-allyl).

The dissociation energy of the central bond in 1,5-hexadiene has been estimated to be around 40 to 44 kcal/mole:



The weakness of the central bond suggests that the primary step in the pyrolysis should be the decomposition to free allyl radicals:



Indeed, the decomposition of 1,5-hexadiene to allyl radicals has been observed directly, with the use of the mass spectrometer. Lossing and co-workers¹⁶ detected a good yield of allyl radicals in the pyrolysis of 1,5-hexadiene at temperatures above 700°C. The high temperatures used are necessitated by the very short contact time of the flow system used by the authors and the relatively high concentrations of allyl radicals required for their positive identification. It appears reasonable to assume that at 550°C, also, 1,5-hexadiene will decompose by a free radical mechanism involving the formation of free allyl radicals in the primary step. Therefore, the pyrolysis of 1,5-hexadiene can be used to obtain some indications of the reactions of allyl radicals.

For this purpose, an experiment was performed in which 1,5-hexadiene at an initial pressure of 100 mm. Hg was pyrolysed at 550°C in the same static system as was used for the pyrolysis of the butenes. The products formed

after one minute reaction time are given in Table XXXVIII.

Table XXXVIII

Products from the Pyrolysis of 1,5-Hexadiene

Temperature, 550° C -- Reaction Time, 1 Minute
Initial Pressure of 1,5-Hexadiene, 100 mm. Hg

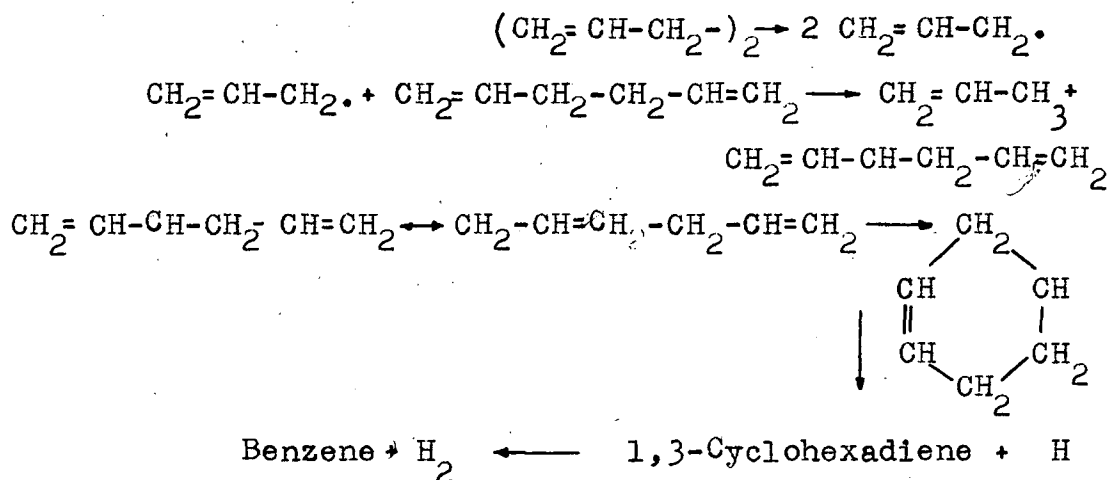
Composition of Reaction Mixture
Volume %

1,5-Hexadiene	15
Cyclohexene	1
Benzene	10
Toluene	2
Cyclohexadiene	4
C ₅ H ₆	4
Propylene	40
Ethylene	10
Ethane	1
Methane	7

The reaction mixture was analysed directly on the mass spectrometer without previous fractionation. Since some of the components (C₅H₆ and others in smaller quantities) could not be identified, the computation of the mass spectrometric results was only approximate. The quantitative results given should be considered as indicating the order of magnitude only. The analysis did not include a determination of the amount of hydrogen formed.

A comparison of the results for 1,5-hexadiene with the results of the 1-butene pyrolysis at 550°C shows that the overall decomposition of 1,5-hexadiene is much faster than that of the 1-butene. The large number of products observed in the reaction mixture of the 1,5-hexadiene pyrolysis indicates that the allyl radicals produced in the primary

step induce a number of secondary reactions. The mechanism appears to be complex. Some of the reactions can be suggested by analogy with the observations from the butene system. For example, the formation of propylene and benzene can be explained on the basis of the reactions:

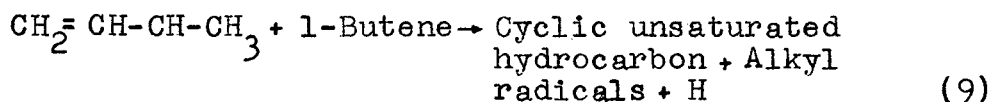
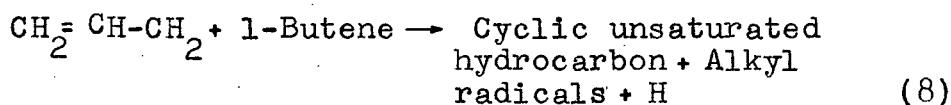
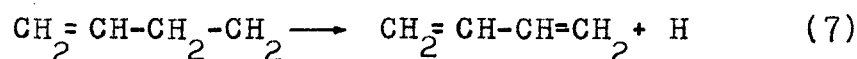
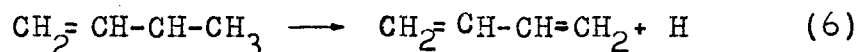
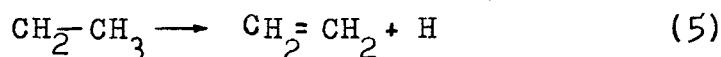


With regard to the 1-butene system, the following conclusions can be drawn from the 1,5 hexadiene pyrolysis experiment. At temperatures around 550°C and a pressure of the reactant gas of 100 mm. Hg, allyl radicals can engage in a number of complex reactions, leading to the formation of light hydrocarbons and unsaturated C₅, C₆ and C₇ hydrocarbons mainly of cyclic nature. The CH₂=CH-CH-CH₃ radical presumably can undergo analogous reactions. These conclusions are in agreement with the reactions proposed in the previous section.

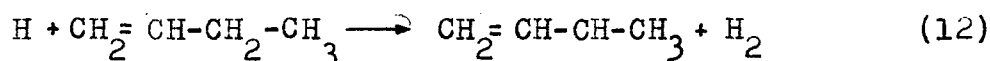
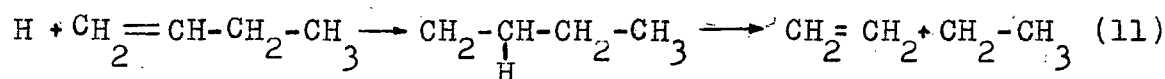
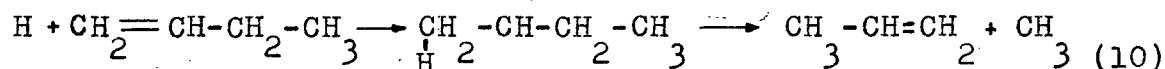
ADDITION REACTIONS OF HYDROGEN ATOMS

It was suggested in the previous sections that several

reactions could lead to the formation of hydrogen atoms. These were:



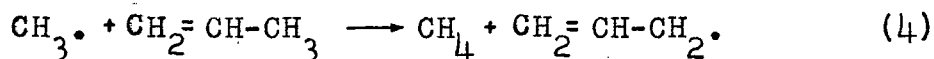
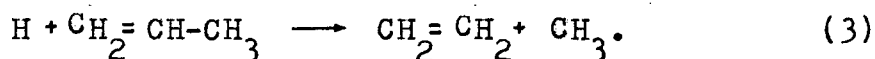
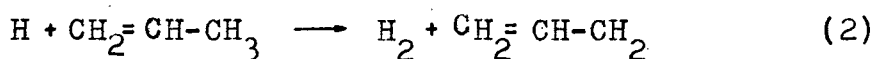
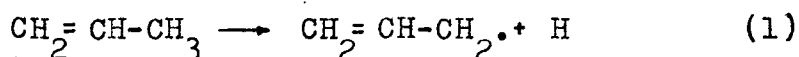
The hydrogen atoms produced by these reactions could react with the 1-butene according to the scheme:



In the corresponding reactions of 1-butene-4-d₃, deuterium atoms will be involved also. These should originate mainly from reactions (5) and (6). Reaction (10) in this case should lead to CD₃ radicals and CH₂D-CH=CH₂. The deuterio-propylenes isolated from the reaction mixtures of the 1-butene-4-d₃ pyrolysis contained considerable amounts of monodeutero-propylene (up to 60% of the total propylene at the low temperatures, falling off to 30% at the highest temperature). The observed formation of monodeutero-propylene thus suggests the possible occurrence of reaction (10). It should be mentioned here that the mass spectrometric analysis of

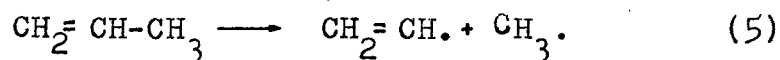
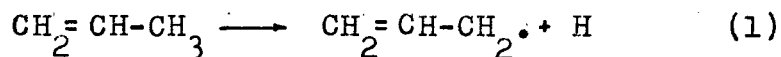
the molecular hydrogen obtained as a reaction product from the pyrolysis of the 1-butene-4-d₃ revealed the presence of varying amounts of HD besides the H₂. A quantitative estimate could not be made, due to the lack of gas standards (pure HD and D₂).

Support for the occurrence of disproportionation reactions of the type suggested (10) can be found in a study of similar systems. In an investigation of the pyrolysis of propylene, Szwarc^{29,31} found as major products of the reaction, methane and hydrogen, which were roughly in the ratio, 2:1. Other products formed in relatively large concentrations were ethylene and allene. Assuming that the primary process in the propylene decomposition is the formation of hydrogen atoms and allyl radicals, Szwarc explained the formation of methane according to the following reaction sequence:

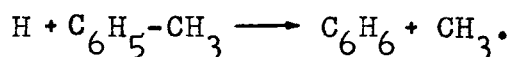


Reaction (3) is analogous to reaction (10) which is assumed to participate in the 1-butene pyrolysis. The two alternative mechanisms for the formation of methane are: a direct molecular decomposition of the propylene to methane and acetylene, or the direct primary split of the propylene to vinyl and methyl radicals, followed by reaction (4). The molecular decomposition to methane and acetylene appears improbable since the general

evidence presented by Szwarc strongly supports a free radical mechanism. Also, the formation of methyl radicals by a primary split of the propylene molecule could not account for all the methane formed, since reaction (1) should be considerably faster than (5):



Another example for the occurrence of a reaction analogous to reaction (10) is found in the pyrolysis of toluene:



The above reaction was proposed originally by Leigh¹⁴ and Szwarc, in an attempt to account for the observed formation of methane, and confirmed later by Blades² and Steacie.

On the basis of the evidence quoted, it seems justifiable to assume that hydrogen atoms can initiate disproportionation reactions of the discussed type and will generally do so in systems containing propylene, butene or other higher olefins.

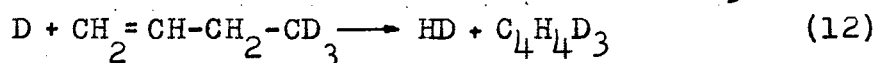
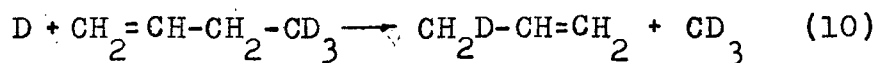
The occurrence of disproportionation reactions in the butene system will depend on the concentration of hydrogen or deuterium atoms. The ratios of monodeutero-propylene to total molecular hydrogen ($\text{H}_2 + \text{HD} + \text{D}_2$) formed under different experimental conditions in the pyrolysis of 1-butene-4-d₃ are given below.

Table XXXIX

Ratio of C_3H_5D to Total Molecular Hydrogen

Reaction Temp. °C	Reaction Time Min.	C_3H_5D
		Total Molecular Hydrogen
522	2	12
540	2	7.6
554	2	7.1

If it is assumed that all of the monodeutero-propylene was formed by the disproportionation reaction (10) in which deuterium atoms were involved, the ratios obtained would indicate that reaction (10) is more than seven times faster than the abstraction reaction (12):



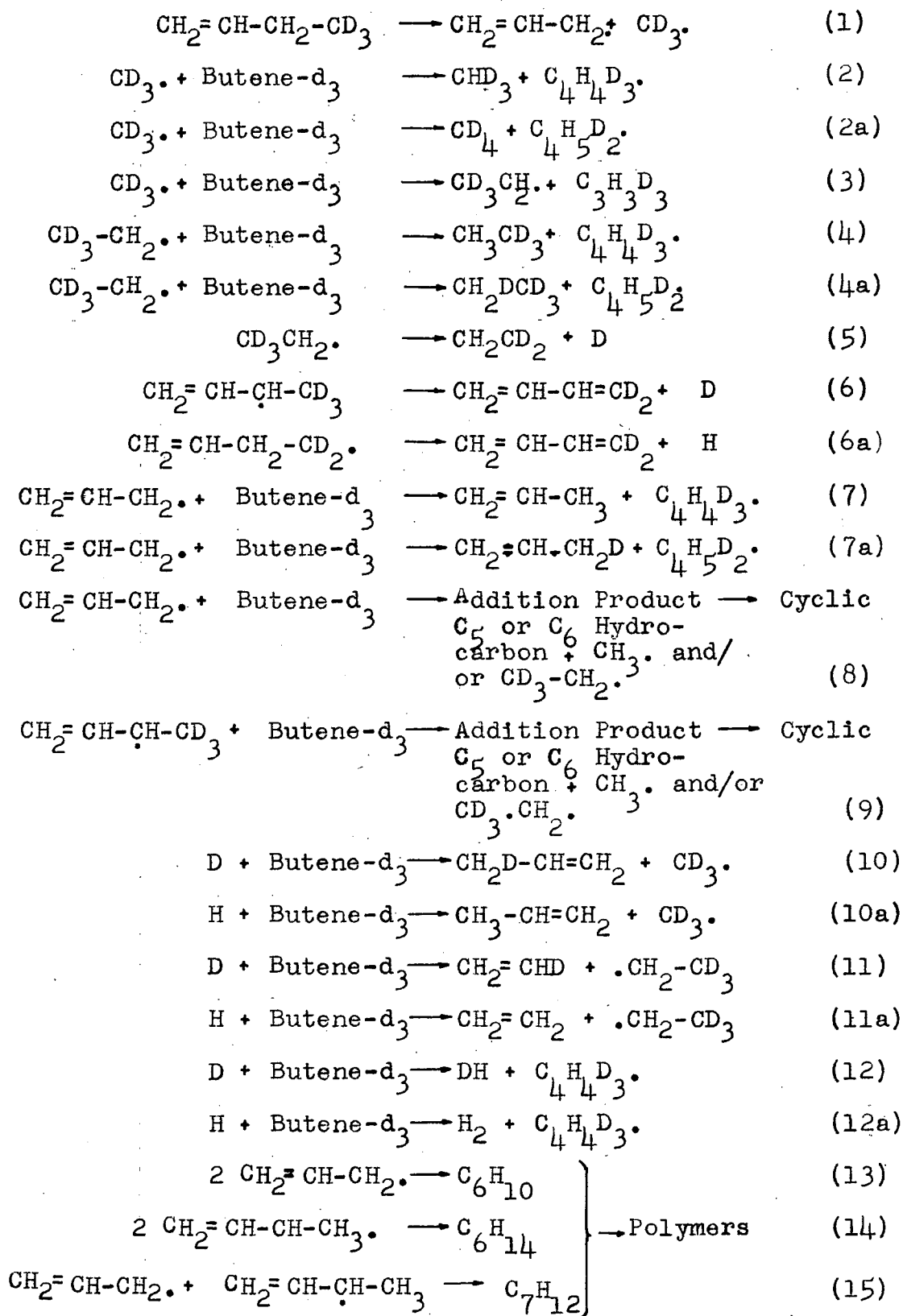
Although the relative rates of reactions (10) and (12) cannot be predicted with any certainty on theoretical grounds or from information available in the literature, it appears that the difference of the relative rates obtained is excessive. For example, Szwarc's results from the propylene pyrolysis, together with the interpretation represented by reactions (1) to (4), give the result that the disproportionation reaction is only about twice as fast as the abstraction reaction for the propylene system.

The disproportionation reaction (10) is difficult to reconcile with the large difference in the rates of formation of monodeutero-propylene and total hydrogen.

Therefore, although such a reaction seems very probable, the experimental evidence in the present work is not sufficient to establish its participation with certainty.

MECHANISM OF THE THERMAL DE-
COMPOSITION OF 1-BUTENE AND 1-BUTENE-4-d₃

The reactions discussed in the previous sections are summarized in a mechanism for the decomposition of 1-butene-4-d₃ given on the next page. The proposed mechanism has several important characteristics. The thermal decomposition is assumed to proceed by a complex free radical mechanism. The initiating reaction is considered to be the primary decomposition of the butene to methyl and allyl radicals. There are no long chains, but the secondary reactions are numerous. Methyl radicals are generated by several reactions: the primary decomposition (1), the release of methyl radicals in the effective dehydrogenation of the polymers (8) and (9), and the reaction of the hydrogen atoms with 1-butene (10). Ethyl radicals are generated by the methyl radical disproportionation reaction with 1-butene (3), the release of ethyl radicals in the effective dehydrogenation of the polymers (8) and (9), and the hydrogen atom disproportionation reaction with 1-butene (11). Finally, hydrogen atoms are generated by the unimolecular decomposition of the ethyl radicals



(5), the unimolecular decomposition of $\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}-\text{CH}_3$ and $\text{CH}_2=\text{CH}-\text{CH}_2-\dot{\text{C}}\text{H}_2$ radicals (6), and possibly, the dehydrogenation of the polymers.

Chain termination is assumed to occur by the recombination of the resonance stabilized allyl and $\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}-\text{CH}_3$ radicals.

A very large number of reactions has been included. The large number of reaction products and the deuterium distribution in the products can be explained only on the basis of a complex mechanism. Since the majority of the experimental results were obtained from pyrolysis experiments in which considerably more than 1 or 2% of the butene was decomposed, it can be argued that the complexity of the reaction products is largely due to secondary reactions involving the reaction products themselves. While this might be the case for these experiments, it should be noted that the reaction mixtures obtained from experiments in which only 1 or 2% of the original butene was decomposed showed the same large number of products, and the deuterio-isomers in the products were equally numerous. The decomposition of the butene, therefore, is certainly a complex reaction under the present conditions. The large number of proposed reactions therefore seems justified.

The reactions (1) to (15) were chosen on the basis of the discussion given in the previous sections. The arguments used were based mainly on a qualitative examination of the experimental results. Semi-quantitative or quantitative

support could be given for only some of the proposed reactions. Thus, the proposed mechanism requires further quantitative confirmation. Unfortunately, great difficulties are encountered in an attempt to verify the mechanism further. Some of these difficulties should be mentioned. The most useful procedure for the verification of a proposed mechanism with the experimental results is to compare the rates of formation of the products as a function of reaction time and temperature. Generally, the relative rates of formation for the reaction time $t \rightarrow 0$ are especially significant. The mechanism then can be verified by observing constant relations between the rates of formation of given compounds in accordance with the predictions of the mechanism. The use of this procedure for the system in question is made very difficult by the large number of products to be considered. The numerous reactions are so interconnected that a high uniform accuracy in the quantitative determinations of virtually all products, including the polymers, is required. Such accuracy cannot be expected considering the complex nature of the analyses. Moreover, in most of the relations the rates of formation of particular deuterio-isomers should be considered. However, it was noted earlier that the quantitative determinations of some of the deuterio-isomers were only approximate.

Some of the results from the quantitative analyses of the deuterium isomers which undoubtedly were accurate also have not been explained. For example, it was found that the deuterio-methanes from the 1-butene-4-d₃ contained CHD₃ and CH₂D₂ in the ratio:

$$\text{CHD}_3/\text{CH}_2\text{D}_2 = 3 \quad (\text{from Table XX})$$

Roughly the same result was found for the deuterio-ethanes:

$$\text{C}_2\text{H}_5\text{D}_3/\text{C}_2\text{H}_4\text{D}_2 = 3 \quad (\text{from Table XXII})$$

Since the 1-butene-4-d₃ was found to contain initially only 10% of bi-deuterated product (1-butene-4-d₂), the above ratios should have been expected to be not equal to 3, but equal to 10. The reason for the discrepancy is not understood.

The difficulties outlined above apply equally when attempts are made to interpret some of the kinetic constants obtained from the 1-butene pyrolysis. The overall activation energy of the butene decomposition was determined as well as the activation energies for the formation of the light hydrocarbons. If a steady state treatment could be applied to the proposed reaction mechanism, some kinetic significance possibly could be given to such results. However, the reactions assumed to participate in the mechanism are too numerous. Attempts to express even the essential features of the mechanism were not successful. Even if a steady state treatment

could be derived on the basis of the proposed mechanism, it is questionable whether the experimentally obtained figures for the activation energies, etc., should be associated with the derived expressions. Thus, the general results clearly indicate that some of the "primary" products formed in the decomposition are very reactive and participate further in the reactions. The effect of these products should be small at low temperatures and short reaction times since under such conditions their concentration is too low and still in the process of being built up. The induction period observed in the butene decomposition (Fig. 10) is an indication of such a process. At higher temperatures the effect of subsequent reactions of such products should be noticeable very soon; even during the first minute interval. Thus a change of kinetic pattern can be expected to take place for the different reaction temperatures influencing the composition of the reaction mixtures obtained even after the shortest sampling time (1 minute). To allow for such changes in a mathematical treatment would be a formidable task.

. . .

In view of the difficulties outlined above it seems that additional quantitative support for the proposed mechanism will be very difficult to obtain. Therefore, the reactions proposed represent, at best, a plausible mechanism for the complex decomposition of the 1-butene, providing a general qualitative picture of the processes involved.

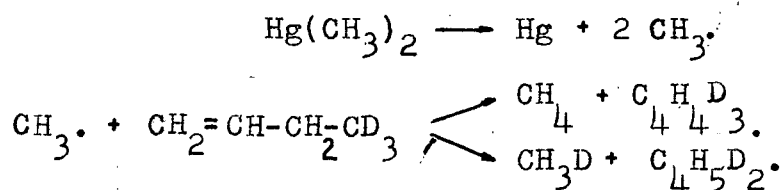
SIGNIFICANCE OF SOME OF THE FINDINGS
AND SUGGESTIONS FOR FURTHER EXPERIMENTAL WORK

The mechanism proposed to account for the major reactions of the 1-butene decomposition makes extensive use of two types of reactions, both involving free radicals and 1-butene. These are: the abstraction of hydrogen from the butene by free radicals and the addition of free radicals to the double bond of the butene followed by rapid decomposition of the addition product. The latter reaction results in disproportionation when the addition product decomposes to form products different from the initial radical and 1-butene. It was shown that at least qualitatively, a large number of reaction products observed can be explained on the basis of the addition-disproportionation reaction which should be characteristic of olefinic compounds. It must be mentioned that while the addition of free alkyl radicals, especially the methyl radical, to unsaturated hydrocarbons has been subject to considerable study at low temperatures (below 300°C), mechanisms involving addition products as intermediates have been considered to be of importance at higher temperatures only rarely. Since the occurrence of such reactions is strongly supported by the results of the present investigation, a complete proof for the extensive participation of such reactions in the mechanism of olefin decomposition certainly seems

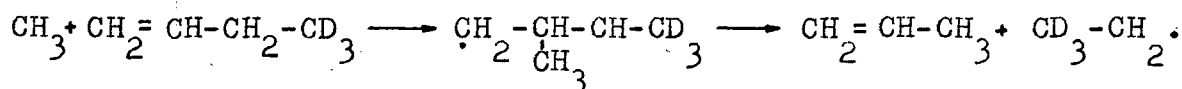
worthwhile. In this way, a class of reactions of seemingly great importance that hitherto has found little consideration will be established.

The following relatively simple experiments are suggested as a means for obtaining additional experimental evidence.

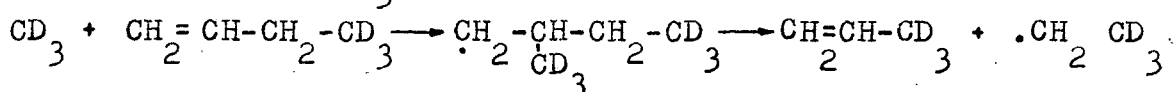
In the mercury-dimethyl sensitized decomposition of 1-butene-4-d₃, it was found that aside from the greatly increased formation of CH₄ and CH₃D, originating presumably by the reactions:



the formation of non-deuterated propylene also had received a great acceleration. This was explained by the reaction:

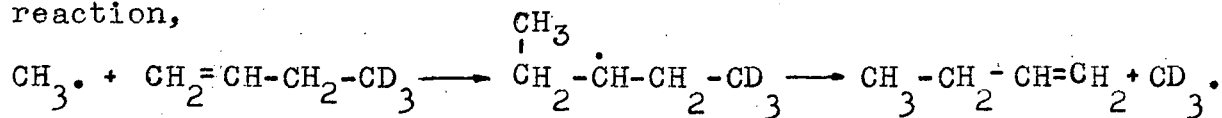


This reaction also was suggested by the formation of propylene-d₃ in the normal (non-sensitized) decomposition of the 1-butene-4-d₃:



The possible occurrence of this reaction could be investigated easily if the Hg(CD₃)₂ sensitized pyrolysis of CH₂=CH-CH₂-CH₃ were studied. According to the above assumed reactions, the formation of propylene-d₃ should be

observed. The suggested experiment also should lead to the formation of $\text{CD}_3\text{-CH}_2\text{-CH=CH}_2$ in analogy with the observed formation of $\text{CH}_2\text{=CH-CH}_2\text{-CH}_3$ in the $\text{Hg}(\text{CH}_3)_2$ sensitized reaction of the 1-Butene-4- d_3 for which the reaction,



was assumed. Thus, the $\text{Hg}(\text{CD}_3)_2$ sensitized decomposition of the $\text{CH}_2\text{=CH-CH}_2\text{-CH}_3$ should provide a definite answer regarding the reactions described above and possibly provide clues for some of the remaining reactions. Since $\text{Hg}(\text{CD}_3)_2$ is now readily available commercially, the experiment seems easily feasible, and involves only a duplication of the analytical techniques already used.

A qualitative study of the suggested mechanism leading to the cyclic polymers could be made if the pyrolysis of 1-butene or 1-butene-4- d_3 in the presence of small amounts of 1,5-hexadiene or mercury-diallyl²⁴ were studied. At temperatures around 490°C where the normal decomposition of the butene is very slow, the mentioned sensitizers should decompose appreciably under formation of allyl radicals. The increased supply of allyl radicals should lead to increased formation of the cyclic hydrocarbons such as cyclopentadiene and cyclohexadiene, with a simultaneous increase in the rate of butene decomposition. If 1-butene-4- d_3 is used, a simultaneous increase of the CHD_3 and $\text{CH}_3\cdot\text{CD}_3$ formation also should be observed, in accordance

with the proposed reactions (8) and (9).

A further extension of the investigation by means of further refinement of the accuracy of the analytical techniques does not seem worthwhile. The complex behaviour of the system under the conditions studied most probably would defeat any attempts for the derivation of significant kinetic constants such as pre-exponential factors and activation energies of the elementary reactions involved. It is certain that the reaction could be studied under conditions for which the mechanism is less complex. For example, the use of a flow system operated at very low percentages of total decomposition would be more suited for a further study of the butene pyrolysis, especially with the help of gas chromatographic analytical techniques.

PYROLYSIS OF 1-BUTENE IN THE
PRESENCE OF DEUTERIUM

The formation of methane in the pyrolysis of 1-butene in the presence of deuterium has been studied recently by Danby, Spall, Stubbs and Hinshelwood.⁵ Varying initial amounts of 1-butene were decomposed in the presence of D_2 at $560^\circ C$. The initial pressure of 1-butene was varied from 3 to 100 mm. Hg, while the initial pressure of the deuterium was kept constant at 100 mm. Hg in all experiments. The methane formed after 4

minutes reaction time was separated and analysed for deuterium content on the mass spectrometer. The methane was found to contain, besides CH_4 , varying amounts of CH_3D . A plot of the results obtained by Danby and co-workers is reproduced in Fig. 22. A gradual decrease of the $\text{CH}_3\text{D}/\text{CH}_4$ ratio with increase of the initial concentration of the 1-butene is a prominent feature in the results. The authors assumed that at 560°C , the temperature of their experiment, 1-butene decomposes by a molecular mechanism. The assumption was based mainly on the fact that nitric oxide has no inhibiting effect on the 1-butene decomposition, (Molera and Stubbs)²¹. The isotopic mixing, i.e. the CH_3D formed, was assumed to occur without the participation of free methyl radicals in the reaction. Therefore, as Danby and co-workers point out, the assumption in similar investigations^{23, 35} that isotopic mixing is an indication for the participation of free radicals in the reaction, is open to doubt.

However, since the results of the present investigation strongly favour a free radical mechanism, it is pertinent to show that the results obtained by Danby and co-workers can be interpreted on the basis of free radical reactions. A clue for the participation of methyl radicals in the 1-butene decomposition in the presence of deuterium as studied by Danby and co-workers is the observed gradual decrease of $\text{CH}_3\text{D}/\text{CH}_4$ with increase^{3 4}

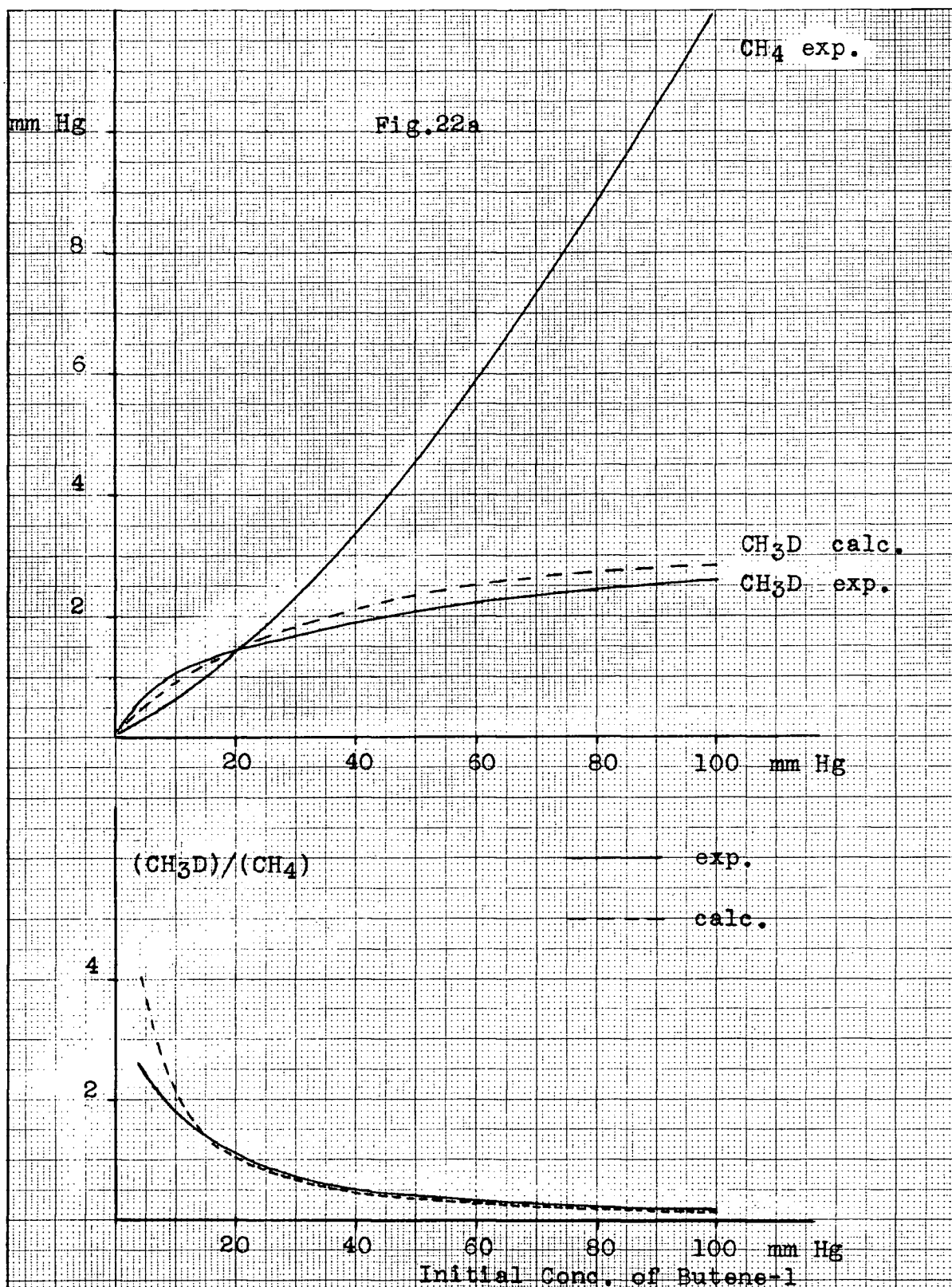
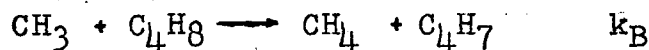
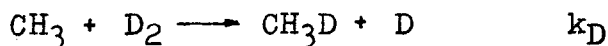


Fig. 22 Comparison of the Calculated Formation of CH₃D and CH₄ in the Pyrolysis of Butene-1 in the Presence of 100 mm D₂ with Experimentally Obtained Curves by Darby and Co-workers.

of the initial concentration of the pyrolysed 1-butene. This result can be interpreted on the basis of the two competing reactions:



If the methyl radical production is assumed to be proportional to the butene concentration, the following equations can be written:

$$\frac{d(\text{CH}_3\text{D})}{dt} = k_D(\text{CH}_3)(\text{D}_2)$$

$$\frac{d(\text{CH}_4)}{dt} = k_B(\text{CH}_3)(\text{B})$$

(where $(\text{B}) =$ concentration of 1-butene)

$$\frac{d(\text{CH}_3)}{dt} = k_1(\text{B}) - k_B(\text{CH}_3)(\text{B}) - k_D(\text{CH}_3)(\text{D}_2)$$

Assuming a steady state one obtains:

$$(\text{CH}_3) = \frac{k_1(\text{B})}{k_B(\text{B}) + k_D(\text{D}_2)}$$

and:

$$\frac{d(\text{CH}_3\text{D})}{dt} = \frac{k_D k_1(\text{B})(\text{D}_2)}{k_B(\text{B}) + k_D(\text{D}_2)}$$

$$\frac{d(\text{CH}_4)}{dt} = \frac{k_B k_1(\text{B})^2}{k_B(\text{B}) + k_D(\text{D}_2)}$$

If substitution $\frac{k_B}{k_D} = p$ is made:

$$\frac{d(\text{CH}_3\text{D})}{dt} = \frac{k_1(\text{B})(\text{D}_2)^{\frac{1}{p}}}{(\text{B}) + \frac{1}{p}(\text{D}_2)} \quad \text{I}$$

$$\frac{d(\text{CH}_4)}{dt} = \frac{k_1(\text{B})^2}{(\text{B}) + \frac{1}{p}(\text{D}_2)} \quad \text{II}$$

The ratios of $\text{CH}_3\text{D}/\text{CH}_4$ for the initial stages of the reaction in function of various initial concentrations of the 1-butene can be obtained from equations I and II if a plausible value for p is assumed. A value for $k_B/k_D = p$ can be estimated with the use of known data for the abstraction of hydrogen atoms from 1-butene and deuterium by methyl radicals. For the abstraction from butene, Trotman-Dickenson and Steacie³⁴ give:

$$k_B/k_2^{\frac{1}{2}} \times 10^{13} = 210 \text{ cc.}^{\frac{1}{2}} \text{ molecules}^{-\frac{1}{2}} \text{ sec.}^{-\frac{1}{2}} \text{ at } 253^\circ\text{C}$$

and $E_B = 7.6 \text{ kcal/mole}$

where k_2 refers to the methyl radical re-combination to ethane. For the abstraction from D_2 , Whittle and Steacie³⁷ give:

$$k_D/k_2^{\frac{1}{2}} = 44.9 \text{ cc.}^{\frac{1}{2}} \text{ molecules}^{-\frac{1}{2}} \text{ sec.}^{-\frac{1}{2}} \text{ for } 290^\circ\text{C}$$

and $E_D = 11.8 \text{ kcal/mole}$

Since $E_2 = 0$, the above data can be used for a calculation of k_B/k_D at 560°C . The result obtained is:

$$k_B/k_D = 2.5 \text{ at } 560^\circ\text{C}$$

Of course, the result is only approximate. Since the k_B obtained represents in essence only abstraction of allylic hydrogen atoms from the 1-butene, the value for k_B should be corrected upwards by a factor of at least 1.4. (See calculations of k_B on page 120). Thus, the calculation leads to a value for p in the order of:

$$p = k_B/k_D = 4$$

The value $p = 5$ was used in the subsequent calculations.

Substituting into equations I and II the values:

$p = 5$, $D_2 = 100$ mm. Hg, and varying initial pressures for B, values for the ratio of the initial rates, $r(\text{CH}_3\text{D})/r(\text{CH}_4)$ in function of the initial concentration of the butene were obtained. These values are plotted in Fig. 20(b), together with the experimental values for the ratio $\text{CH}_3\text{D}/\text{CH}_4$ found by Danby and co-workers after 4 minutes' reaction time. It can be seen that the calculated values for the relative initial concentrations approximate the experimental curve well. Thus, the experimentally found variation of $\text{CH}_3\text{D}/\text{CH}_4$ can be explained by a free radical mechanism.

The procedure of comparing the calculated initial rates $r(\text{CH}_3\text{D})/r(\text{CH}_4)$ with the ratio of the concentrations, $\text{CH}_3\text{D}/\text{CH}_4$ obtained after four minutes reaction time implies the unwarranted assumption that the concentration of the 1-butene has remained essentially unchanged. According to the experimental results described earlier in this work (for example, Fig. 10), more than half of the 1-butene is decomposed after 4 minutes at 550°C . Therefore, a refinement can be introduced in the calculation by taking account of the variation of the butene concentration with time. It was found that the 1-butene concentration decreases approximately by a first order law with time at temperatures around 550°C (Fig. 10). Therefore, one can write:

$$\frac{d(B)}{dt} = k_B \quad \text{and} \quad (B) = (Bo)e^{-kt}$$

(where (Bo) = initial concentration of the 1-butene).

If this time dependence of the butene concentration is introduced in equations I and II, one obtains:

$$\frac{d(CH_3D)}{dt} = \frac{k_1 (Bo)e^{-kt} (D_2)^{\frac{1}{p}}}{(Bo)e^{-kt} + (D_2)^{\frac{1}{p}}} \quad \text{I(a)}$$

$$\frac{d(CH_4)}{dt} = \frac{k_1 (Bo)^2 e^{-2kt}}{(Bo)e^{-kt} + \frac{1}{p}(D_2)} \quad \text{II(a)}$$

Upon integration of I(a) one obtains:

$$(CH_3D) = \frac{k_1 (D_2)}{k.p} \log \left[\frac{(Bo) + (D_2)^{\frac{1}{p}}}{(Bo)e^{-kt} + (D_2)^{\frac{1}{p}}} \right]$$

(after t seconds)

From the experimental results given in Table XII, an approximate value for k can be chosen:

$$k_{554^\circ C} = 33 \times 10^{-4} \text{ l/sec.} = k$$

Introducing the above value in the equation, the ratio $(CH_3D)/k_1$ can be calculated for a reaction time of four minutes, for different initial pressures of the 1-butene.

In order to compare the values thus arrived at with the experimental results obtained by Danby and co-workers, a value for the constant factor k_1 was calculated by putting:

$$(CH_3D)/k_1^* = (CH_3D)/k_1$$

where $(CH_3D)/k_1^*$ represents the number obtained from the calculation for four minutes' reaction time and an

initial concentration $B_0 = 20$ mm. Hg, and the CH_3D on the right hand side represents the experimentally obtained concentration of the CH_3D by Danby and co-workers for the pyrolysis of butene with 20 mm. initial pressure. The value for k_1 obtained in this way was:

$$k_1 = 7.78 \times 10^{-4} \text{ sec.}^{-1}$$

The values for CH_3D calculated by this second method are plotted in Fig. 20 (a). It can be seen that the calculated points follow the general trend of the experimental curve well.

Thus, the experimentally found variation of the CH_3D and CH_4 concentrations as a function of the initial butene concentration can be predicted on the basis of a free radical mechanism. Therefore, the conclusion of Danby and co-workers that isotopic mixing can occur to the extent observed in their experimental results without participation of free methyl radicals is open to doubt. It is also important to note that if the above conclusions are correct, the nitric oxide criterion for the existence of radical chains as used by Molera and Stubbs and Danby, Spall, Stubbs and Hinshelwood can not be applied to the 1-butene system.

L I T E R A T U R E C I T E D

1. AMERICAN PETROLEUM INSTITUTE, Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Pittsburgh, Carnegie Press, 1953.
2. BLADES, A. T. and STEACIE, E. W. R., Can. J. Chem., 32, 1142 (1954).
3. BOLLAND, J. L. and GEE, G., Trans. Faraday Soc., 45, 244 (1946).
4. COULSON, C. A., Proc. Roy. Soc. (London), A 164, 383 (1938).
5. DANBY, C. J., SPALL, B. C., STUBBS, F. J. and HINSHELWOOD, Sir Cyril, Proc. Roy. Soc. (London), A 228, 449 (1955).
6. DIBELER, V. H. and MOHLER, F. L., J. Research N.B.S., 46, 441 (1950).
7. DIBELER, V. H., MOHLER, F. L. and DE HEMPTINNE, M., J. Research N.B.S., 53, 107 (1954).
8. DIMBAT, Martin, PORTER, P. E. and STROSS, F. H., Analyt. Chem., 28, 290 (1956).
9. EGGERTSEN, F. T., KNIGHT, H. S. and GROENNINGS, S., Analyt. Chem., 28, 303 (1956).
10. FREDERICKS, E. M. and BROOKS, F. R., Analyt. Chem., 28, 297 (1956).
11. GRAHAM, R. L., HARKNESS, A. L. and THODE, H. G., J. Sci. Instr., 24, 119 (1947).
12. HURD, C. R. and GOLDSBY, A. R., J. Am. Chem. Soc., 56, 1812 (1934).
13. JAMES, A. T. and MARTIN, A. J. P., Biochem. Journal, 50, 681 (1951).
14. LEIGH, C. H. and SZWARC, M., J. Chem. Phys., 20, 403 (1952).
15. LEROY, D. J., Can. J. Research, B 28, 492 (1950).
16. LOSSING, F. P., INGOLD, K. U. and HENDERSON, I. H. S., J. Chem. Phys., 22, 621 (1954).

17. LOSSING, F. P., INGOLD, K. U. and HENDERSON, I. H. S.,
J. Chem. Phys., 22, 1489 (1954).
18. LOSSING, F. P. and TICKNER, A. W., J. Chem. Phys., 20,
907 (1952).
19. LOSSING, F. P., TICKNER, A. W. and BRYCE, W. A., J. Chem.
Phys.,
20. McDOWELL, C. A., LOSSING, F. P., HENDERSON, I. H. S. and
FARMER, J. B., Can. J. Chem., 34, 345 (1956).
21. MANDELCORN, L. and STEACIE, F. W. R., Can. J. Chem., 32,
474 (1954).
22. MOLERA, M. J. and STUBBS, F. J., J. Chem. Soc., 1952,
381.
23. RICE, F. O. and VARNERIN, R. E., J. Am. Chem. Soc., 76,
324 (1954).
24. ROTHSTEIN, Eugene and SAVILLE, R. W., J. Chem. Soc.,
1952, 2987.
25. SCHISLER, D. O., THOMPSON, S. O. and TURKEVITCH, J.,
Discussions Faraday Soc., 10, 40 (1951).
26. SEHON, A. H. and SZWARC, M., Proc. Roy. Soc. (London),
A 202, 263 (1950).
27. STEACIE, E. W. R., Atomic and Free Radical Reactions,
N.Y., Reinhold, 1954, p. 537.
28. STEVENSON, D. P. and WAGNER, C. D., J. Am. Chem. Soc.,
72, 5612 (1950).
29. SZWARC, M., J. Chem. Phys., 17, 284 (1949).
30. SZWARC, M., J. Chem. Phys., 17, 431 (1949).
31. SZWARC, M. and SEHON, A. H., J. Chem. Phys., 18, 237
(1950).
32. TICKNER, A. W., BRYCE, W. A. and LOSSING, F. P., J. Am.
Chem. Soc., 73, 5001 (1951).
33. TROTMAN-DICKENSON, A. F., Gas Kinetics, London,
Butterworths, 1955.
34. TROTMAN-DICKENSON, A. F. and STEACIE, E. W. R., J. Chem.
Phys., 19, 169 (1951).

35. WALL, L. A. and MOORE, W. J., J. Am. Chem. Soc., 73,
2840 (1951).
36. WHEELER, R. V. and WOOD, W. L., J. Chem. Soc., 1930,
1819.
37. WHITTLE, E. and STEACIE, E. W. R., J. Chem. Phys., 21,
993 (1953).

A P P E N D I X I

QUALITATIVE INVESTIGATION OF THE POLYMER PRODUCTS

FORMED IN THE PYROLYSIS OF 1-BUTENE

A P P E N D I X I

QUALITATIVE INVESTIGATION OF THE POLYMER PRODUCTS FORMED
IN THE PYROLYSIS OF 1-BUTENE

The reaction mixture from the pyrolysis of 1-butene contained a large number of compounds with molecular weights higher than that of butene. For convenience, these products are referred to as polymers. As was described in the main text, the polymers were separated by gas chromatography and the collected fractions analysed with the mass spectrometer. This appendix presents the results from the mass spectrometric investigation.

The mass spectrum of a given compound varies to a small extent from instrument to instrument. The observed variations are generally small, amounting to a few percent of the relative ion intensity for a given mass number. Thus, in the majority of cases, satisfactory identification of a pure compound can be achieved by a simple comparison of its experimentally-obtained spectrum with the published spectra of isomeric compounds. The polymer products were identified by comparing the experimentally-obtained mass spectrum of each gas chromatographic fraction with the mass spectra of compounds listed in the Catalogue of Mass Spectral Data published by the American Petroleum Institute.

All the mass spectra originating from this laboratory were taken with 50 e.v. energy of the ionizing electrons.

A typical gas chromatogram showing the fractions containing the polymer compounds is represented in Fig. 7 of the main text. In the following sections, the mass spectrometric results are given in the order in which the fractions appear in the chromatogram.

Fractions B, B₁ + B₂, P₁

Peak B results from unreacted 1-butene. Peak B₁ B₂ contains two hydrocarbons: 1,3 butadiene and a butene, presumably 2-butene. The identification of these hydrocarbons was effected using fractions separated in the alumina column, where peak B₁ + B₂ was resolved into the two peaks of the constituent gases, due to a better separation achieved with the alumina column in that range. No attempt was made to identify peak P₁.

Fraction P₂

A comparison of the mass spectrum of P₂ with that of cyclopentene is given in Table I. The spectrum of P₂ was recalculated on the basis:

Ion intensity for mass 68 (parent peak) = 41.

It can be seen that the two spectra fit quite closely except at mass 67. The mass spectra of 1,3-pentadiene,^{1(e)} 1,4-pentadiene,^{1(f)} 1-pentyne,^{1(d)} and 2 methyl-1,3 butadiene,^{1(c)} the only other mass spectra available for compounds with the molecular formula C₅H₈, give a much less satisfactory

Table I

Comparison of the Mass Spectrum of Fraction P₂ with
That of Cyclopentene

<u>Mass</u>	<u>Ion Intensity of Fraction P₂</u>	<u>Ion Intensity of Cyclopentene^{1(a)}</u>
69	2	2
68	41	41
67	83	100
66	5.7	7
65	7.6	5
64	0.3	0.5
63	2.5	2.6
62	1.6	1.8
61	0.8	1.08
54	1.3	1
53	24.3	23
52	1.7	1.4
51	3.2	2.8
50	2.1	1.8
49	0.3	0.35
42	11.6	8.4
41	22	19
40	16	16
39	30.2	30

correspondence. It is concluded, therefore, that the gas present in fraction P₂ is cyclopentene.

Fraction P₃

The mass spectrum of the fraction P₃ is given in column two of Table II. The recorded ion currents for masses 84 and 66 were identified as parent peaks by scanning at low electron energies. The spectrum at 50 electron volts also indicated the presence of two compounds: C₅H₆ (parent mass 66), present in large amounts, and C₆H₁₂ (parent mass 84),

present in trace amounts. The identity of the C_6H_{12} compound could not be established. The contributions of this compound to the spectrum were estimated on the basis of the spectrum for 1-hexene (column three of Table II). Since the spectra of all hexenes are quite similar, the error should not be large. In columns four and five of the table, the only two available spectra for compounds with the molecular formula C_5H_{12} are given. A comparison of the spectra, especially for masses where contributions from the hexenes are not to be expected (underlined), reveals a close similarity of the P_3 spectrum to that of cyclopentadiene. It is concluded, therefore, that the gas present in fraction P_3 is cyclopentadiene.

Fraction H

Attempts to identify the components in fraction H were not successful. This was due to the small amounts of fraction H present, and also to the proximity of fraction H to fraction P_3 . The mass spectrometric analysis showed that the compound present in the highest concentration had the molecular C_6H_{10} . The spectrum showed some resemblance to that of cyclohexene, but a positive identification could not be made.

Table II

Mass Spectra of Fraction P₃, Trans-2-pentene-4-yne

(CH₃-CH CH-C CH) and Cyclopentadiene

Mass	Ion Intensity of Fraction P ₃	Contributions of C ₆ H ₁₀ on the Basis of 1-Hexene	Ion Intensity of CH ₃ .CH:CH.C:CH	Ion Intensity of Cyclo- pentadiene ²
84	2.8	2.8		
70	0.15			
69	2.2	1.9		
68	1.27			
67	8.27		5.4	6.5
66	100		100	100
65	51		48	39.5
64	3.8		4.4	8
63	8.9		18	9.5
62	6		11	6.15
61	3.5		9	3.62
60	0.55		2.4	0.72
56	2.8	8.5		
55	10	5.5		
54	1			
53	1.58			0.72
52	0.318			0.36
51	3.18		11	3.62
50	1.9		10	2.18
42	5.5	7.4		
41	8.4	10	1.4	1.45
40	37	0.8	45	30.4
39	44.5	5	69	41.6
38	11.3		20	12.7
37	4.9		12	5.44

Fraction H₁

The mass spectrum of fraction H₁ is given in Table III.

Table III

Mass Spectrum of Fraction H₁

<u>Mass</u>	<u>Ion Intensity</u>	<u>Mass</u>	<u>Ion Intensity</u>	<u>Mass</u>	<u>Ion Intensity</u>
83	0.7	70	0.5	56	1.8
82	10.1	69	0.45	55	2.7
81	8.1	68	1.85	54	3.5
80	1.6	67	32.4	53	4.2
79	4	66	1.1	52	1.1
78	0.6	65	2.8	51	2.1
77	2.15			50	1.2
				etc.	

The only parent peak detected at low electron energies was at mass 82. The spectrum is obviously that of a hydrocarbon with molecular formula C₆H₁₀. The spectra of cyclohexene and 1, 5 hexadiene could not be fitted, either separately or in combination, to the spectrum of H₁.

Fractions H₂ and H₃

The mass spectra obtained for the separately collected and analysed fractions H₂ and H₃ are given in Table IV. For comparison, the spectrum of 1,3 cyclohexadiene is given in column four. The three compounds have very similar spectra. It is probable that a better agreement would have resulted but for the interference of compounds present in trace quantities in fractions H₂ and H₃.

Table IV

Mass Spectra of Fractions H₂ and H₃ and 1,3 Cyclohexadiene

<u>Mass</u>	<u>Ion Intensity of H₂</u>	<u>Ion Intensity of H₃</u>	<u>Ion Intensity of 1,3-cyclo- hexadiene 1(g)</u>
80	60	51	59
79	100	100	100
78	11.5	26.6	19
77	41	44	38
76	0.8	1	0.8
75	1.6	2.38	4.9
74	2.0	2.8	2.2
53	10	13	7
52	12.3	16	14
51	15.6	21	19
50	9.85	13.8	12

The presence of a compound with parent mass 82 (C₆H₁₀) in fraction H₂ and a compound with parent mass 96 (C₇H₁₂) in fraction H₃ could be detected easily by measurements at low electron energies. It is concluded that H₂ and H₃ are composed of cyclohexadienes; presumably the two isomers, 1,3 and 1,4 cyclohexadiene.

Fraction Bz

The trapped fraction, Bz, was positively identified with the mass spectrometer as benzene.

Fractions T

The three small peaks following the benzene peak were collected together. A resolution of the mass spectrum was not attempted. At low electron energies, the parent peaks for masses 96 (C₇H₁₂), 94 (C₇H₁₀), and 110 (C₈H₁₄), were found. By analogy with the benzene group, the C₇H₁₀ could be expected to be methyl cyclohexadiene.

Fraction T1

The mass spectrometric analysis of the T1 gave positive identification of Toluene. Trace quantities of a compound with parent mass 106(C_8H_{10}) also were found.

Fraction X₁

Table V gives a comparison of the upper mass spectrum of fraction X₁ with that of o-xylene. The spectrum of X₁ was recalculated on the basis:

ion Intensity for mass 106 = 51.

All three xylenes have similar spectra, but the spectrum of X₁ is most similar to that of o-xylene. It is concluded that fraction X₁ consists of xylene, most probably o-xylene.

Table V

Mass Spectra of Fraction X₁ and O-Xylene

<u>Mass</u>	Ion Intensity of X ₁	Ion Intensity of O-Xylene 1(b)
106	51	51
105	18	22
104	3	2.4
103	5	5
102	1.3	1.1

APPENDIX I

LITERATURE CITED

1. Catalogue of Mass Spectral Data,
American Petroleum Institute,
Mass spectrum serial numbers as follows:
 - (a) 127
 - (b) 178
 - (c) 242
 - (d) 271
 - (e) 330
 - (f) 331
 - (g) 436
 - (h) 936.
2. Lossing, F. P., National Research Council, Ottawa.
Private communication.

A P P E N D I X I I

DEUTERIUM MIGRATION DURING THE IONIZATION OF
1-BUTENE-4-d₃ BY ELECTRON IMPACT*

* Reproduction of paper by W. A. Bryce and Paul Kobarle:
Can. J. Chemistry, 34, 1249 (1956).

A P P E N D I X II

DEUTERIUM MIGRATION DURING THE IONIZATION

OF 1-BUTENE-4-d₃ BY ELECTRON IMPACT

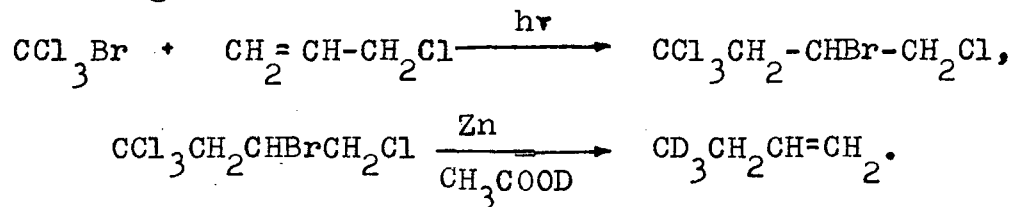
INTRODUCTION

Migration of hydrogen atoms along the carbon skeleton in ionized hydrocarbon molecules has been proposed to account for the appearance of such fragments as CH_4^+ in the mass spectrum of propane and CH_3^+ in the spectrum of cyclohexane. These peaks can not be accounted for by isotopic contributions from C^{13} . Evidence for rearrangement of hydrogens prior to dissociation of the corresponding molecule ions has been reported by several workers (1, 2, 8). Some migration of deuterium atoms is reported in a recent paper on the mass spectra of deuterated butanes (5). Migration of atoms and isomerization of ionized molecules has been referred to by McDowell (4) in an interpretation of mass spectra based on excited molecular states. Processes of this type are of special interest because of the insight they provide into the nature of bonding forces in molecular ionic states.

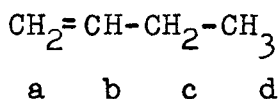
The present study of the mass spectrum of 1-butene-4-d₃ arose in connection with mass spectral analysis of the pyrolysis products of this compound and of the light isomer 1-butene.

EXPERIMENTAL

The 1-butene used for purposes of comparison was Research Grade (99.88%) obtained from the Phillips Petroleum Company, Bartlesville, Okla. The deuterated butene was kindly prepared for us by Dr. L. C. Leitch of the National Research Laboratories, Ottawa, according to the following method:



The product was shown by analysis to be almost 100% C=C hydrocarbon. A preliminary mass spectrometric analysis using 10 volt electrons gave an uncertain result but indicated that the sample was better than 90% 1-butene-4-d₃. Conclusive proof of the purity of the compound was obtained by analysis with a Varian high resolution nuclear magnetic resonance (NMR) spectrometer. The NMR spectrum of the 1-butene is shown in Fig. 1(a). The peaks labelled a, b, c, and d are proton resonance absorption peaks for the hydrogens located on the carbons as follows:



The theoretical relative intensities of the two groups of peaks for 1-butene can be expressed as

$$(a+b)/(c+d) = (2+1)/(2+3) = 3/5.$$

The actual ratio found by measuring the area under the

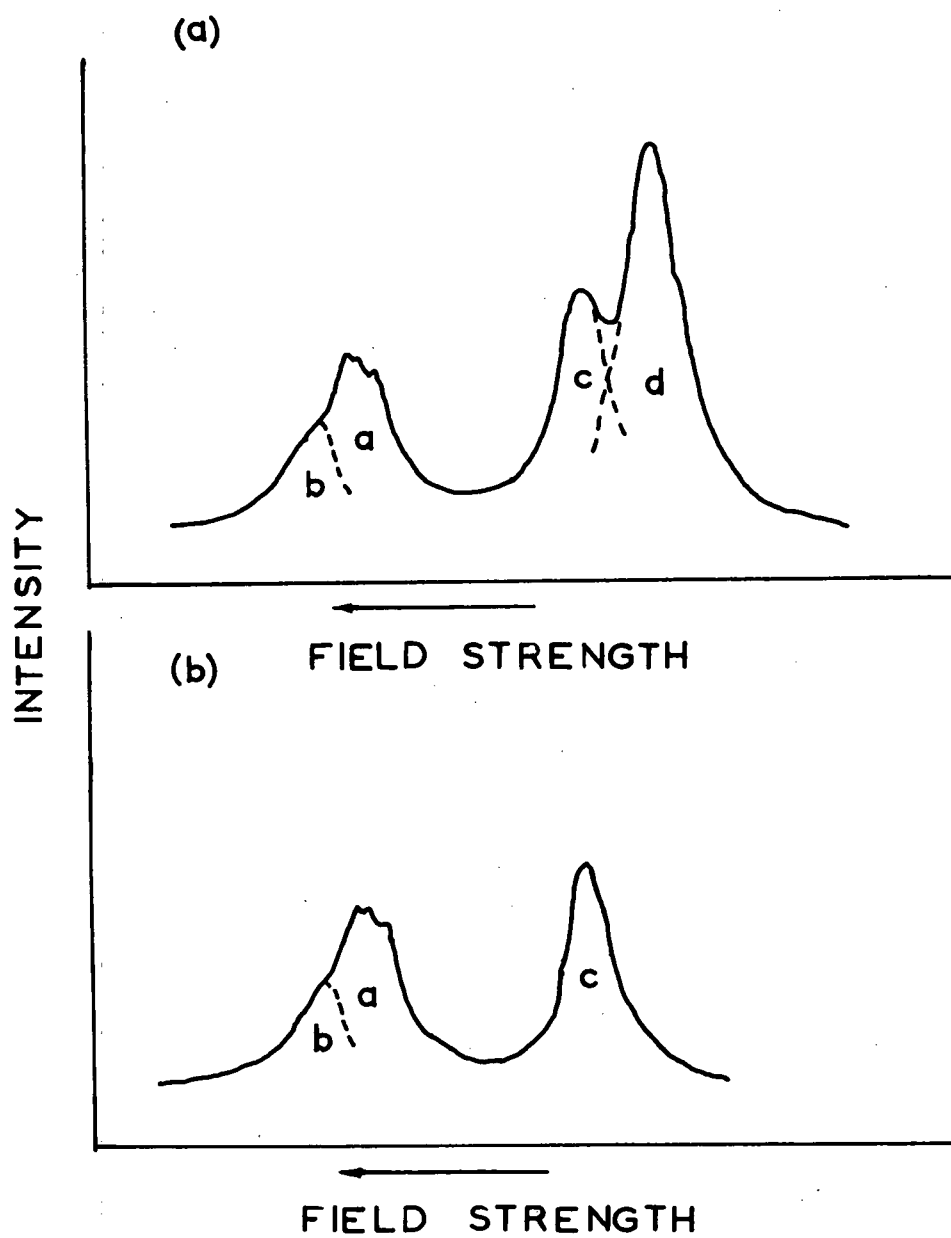


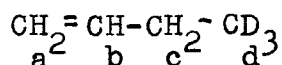
Fig.1a NMR Absorption Spectrum of 1-Butene

1b NMR Absorption Spectrum of 1-Butene-4-d₃

peaks was 3/5.8.

Fig. 1(b) shows the NMR spectrum of the deuterated butene. The identity of the a and b peaks with those shown in Fig. 1(a) is obvious. The d peak of the CH₃ group in 1-butene has completely disappeared in the deuterated compound.

Deuterium atoms, having an even number of nucleons, do not exhibit NMR absorption. The relative intensities of the groups in



should be

$$(a+b)/(c+d) = (2+1)/(2+0) = 3/2.$$

The observed ratio was 3/2.26. The complete absence of a 'd' branch in the spectrum of the deuterated compound was taken as conclusive evidence that the methyl group was completely deuterated, within the sensitivity of detection of the analytical method. The relative intensities of the a, b, and c branches demonstrate the absence of deuterium in the groups to which these peaks correspond.

As a check on the results obtained by NMR a comparison of the infrared spectra of the two butenes was made using a Perkin-Elmer double beam spectrophotometer. A complete interpretation of the spectra obtained has not yet been achieved but a preliminary band assignment confirms the results obtained by NMR.

The mass spectrum of the light butene is presented in Fig. 2 and that of the deuterated compound in Fig. 3. Fifty-volt electrons were used in obtaining these spectra. The intensity of the largest peak in each spectrum is assigned a value of 100 in the usual way. Normalized spectra for both compounds are presented in Fig. 4. Here the total ion intensities for the C_4 , C_3 , C_2 , and C_1 groups of ions are plotted on a scale such that the C_4 ion intensities are made equal. The solid peaks are for the undeuterated compound.

A detailed study of the fragmentation pattern of the deuterated butene at low electron energies was not made but a few preliminary results showing the intensities of various fragments as a function of electron energy are presented in Table I. The relative intensities at 50 electron volts are also shown.

Results obtained for the pyrolysis of the two butenes provided an interesting basis for comparison of the thermal and electron-impact modes of dissociation. The results given in Table II show the distribution of the principal products for the pyrolysis of 100 mm. of each hydrocarbon in a static system for 5 min. at 552°C . The analyses were performed by gas chromatography, using both adsorption-elution and partition-elution methods.

DISCUSSION

The mass spectrum of the light butene shows clearly that

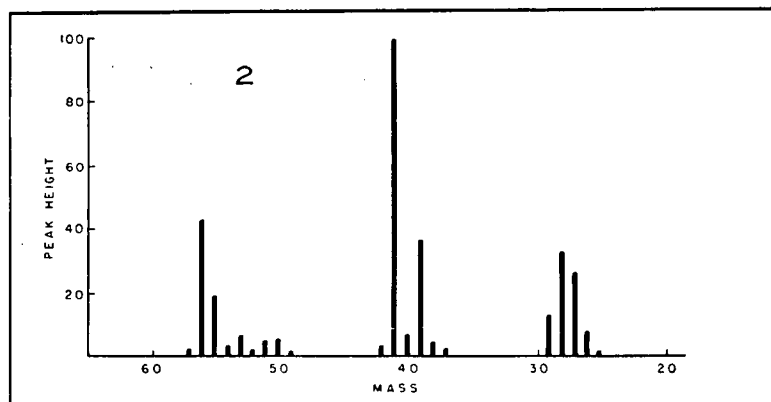


Fig.2 Mass Spectrum of 1-Butene

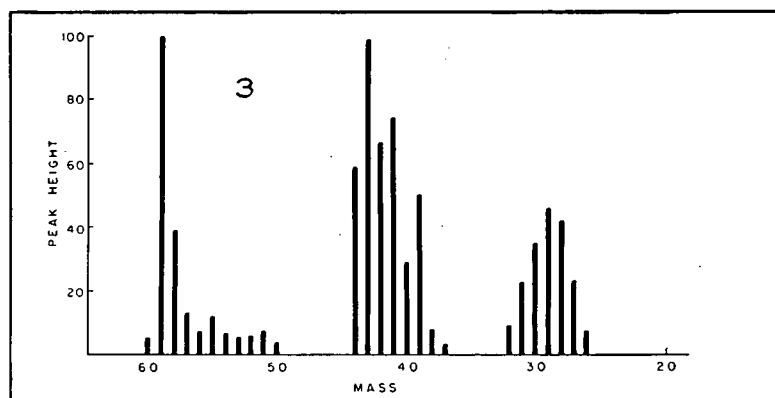


Fig.3 Mass Spectrum of 1-Butene-4-d₃

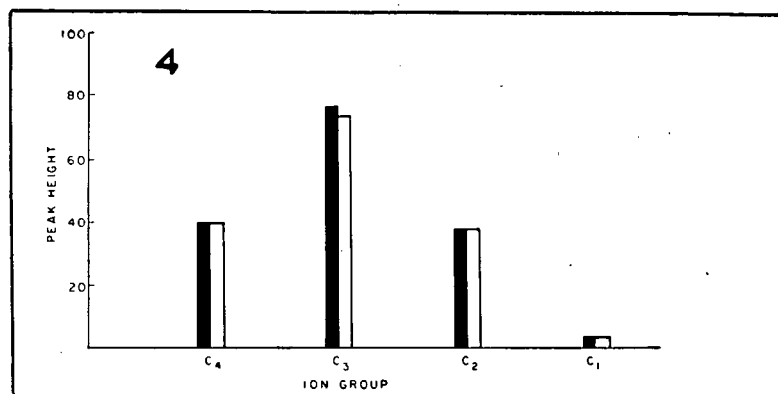


Fig.4 Normalized Spectra of 1-Butene (black) and 1-Butene-4-d₃ (white) Showing the Relative Total Intensities for Each Group of Ions

Table I

Variation of C_3 Ion Intensity with Electron Accelerating
Potential for $CD_3CH_2CHCH_2$.

Electron Accelerating Potential (volts)	Ion Intensity (Arbitrary Units)			
	41	42	43	44
13.0	1.0	3.0	5.0	2.0
15.0	4.0	8.0	14.0	6.0
17.0	12.0	20.5	32.0	16.0
50.0	74.3	67.0	99.3	59.0

Table II

Pyrolysis Products for the Two Butenes
After 5.0 Min. at 552° C.

	$CH_3CH_2CHCH_2$ (vol.%)	$CD_3CH_2CHCH_2$ (vol.%)
Methane	24.0	24.0
Ethane	5.3	5.2
Ethylene	8.3	9.0
Propylene	13.0	13.6

the most abundant fragment produced by electron impact is the $C_3H_5^+$ ion, formed presumably as a consequence of the preferred rupture of the $CH_3-CH_2CHCH_3$ bond. This ion would be expected to have the allyl structure, CH_2CHCH_2 , but by rearrangement could assume structures such as CH_2CH_2CH or CH_3CH_2C . A C_3H_3 fragment is also relatively abundant. The spectrum of the deuterated compound is markedly different from that of the light isotopic molecule. The chief difference is seen in the C_3 group of peaks.

The $C_3H_5^+$ ion (mass 41), which might well be expected to be the most abundant 3-carbon fragment, accounts for only 19% of the total ion intensity. The greater part of the C_3 ion intensity comes from higher masses. Several possible formulas can be written for each of these ions, but the contributions of some of these to the ionic intensities will be negligible. Since the 42 peak from 1-butene is only slightly greater than the C^{13} isotopic peak the contribution of ions equivalent to $C_3H_6^+$ can be neglected. This includes ions such as $C_3H_4D^+$ (mass 44) and $C_3H_5D^+$ (mass 43). In addition since the mass 40 peak from 1-butene is quite small, ions equivalent to $C_3H_4^+$ will make relatively small contributions to the low energy spectrum. Therefore, ions $C_3HD_3^+$ (mass 43), $C_3D_3^+$ (mass 42), and $C_3HD_2^+$ (mass 41) can be neglected. Thus, the greater part of the C_3 ion intensity comes from $C_3H_2D_3^+$ (mass 44), $C_3H_3D_2^+$ (mass 43), $C_3H_4D^+$ (mass 42), and $C_3H_5^+$ (mass 41). It is therefore apparent that migration of the deuterium atoms from the CD_3 group to the rest of the carbon skeleton must have occurred. Rearrangement of hydrogen atoms similar to the rearrangements observed in the deuterated butene will, of course, occur in the light compound but cannot be detected by the present method.

The relative intensities of the ions of masses 41 to 44 (Table I) provide some insight into the relationship between the energy of the ionizing electron and the

extent of the migration process. At the lowest electron energy the $C_3H_5^+$ ion makes a comparatively small contribution to the total C_3 ion intensity. The contribution increases markedly with increasing electron energy. This can be seen from Table III in which the variation of the $C_3H_4D^+$ (42) + $C_3H_3D_2^+$ (43) + $C_3H_2D_3^+$ (44) to $C_3H_5^+$ (41)

Table III

Variation of Ratio of the Sum of Masses 42, 43 and 44 to
Mass 41 with Electron Energy

Electron accelerating potential (volts)	$\frac{42 + 43 + 44}{41}$
13.0	10.0
15.0	7.0
17.0	5.7
50.0	3.0

intensity ratio is presented as a function of electron accelerating potential. It is apparent that deuterium migration is the less probable the higher the energy of the ionizing electron, a consequence presumably of the shorter lifetimes of ions in higher energy states. At lower electron energies the lifetimes of the ions are sufficient, perhaps several vibrations long, to permit extensive rearrangement of the atoms attached to the carbon skeleton.

The relative intensities of the ions of masses 42, 43, and 44 remain approximately constant for all electron energies. This indicates that the migration mechanism does not depend

on the energy of the ionizing electron but is the same for all energies once ionization of the molecule has occurred. The factor controlling the extent of migration is the lifetime of the ion, as suggested above.

It can be seen from Fig. 4 that the total intensities of the ions of a given carbon-number group are the same in the two butenes even though the distribution of intensities and the numbers of fragments observed within the groups are different. This similarity in group intensities shows that deuteration does not have any appreciable effect on the probability of C - C bond rupture. A similar lack of effect in the thermal decomposition of the parent molecule is shown by the distribution of pyrolysis products for the two isotopic compounds given in Table II.

The present work confirms the results reported by Stevenson and Wagner (8) and bears out their prediction that rearrangement of H and D atoms would be more extensive in olefinic than in paraffinic hydrocarbons. This is presumably a consequence of the less localized character of the bonding in the olefinic parent molecule-ion.

The variety of three-carbon fragments formed is evidence of the existence of a number of different modes of decomposition of the ionized molecules. The existence of such modes has been referred to by Rosenstock et al. (7) in attempting to calculate the mass spectra of polyatomic molecules from a statistical basis. Migration of deuterium

atoms, with the resulting changes in configuration, results in transitions between various close-lying energy levels of the given ionic state. Such transitions are equivalent to the crossing of the corresponding potential energy surfaces. The over-all decomposition pattern of the molecule-ions will depend on the distribution of the ions among the various accessible energy states. Information is not yet available to permit the evaluation of the probabilities of the transitions referred to above. Lennard-Jones and Hall (3) have considered the probability of excitation to various electron states in n-octane by calculating the density of positive charge over the octane ion but little is known about the probability of transition between close-lying configurational states in polyatomic molecules.

The extensive migration of isotopic hydrogens observed in the present work casts some doubt on the reliability of the "fragmentation indices" calculated by Magat and Viallard (6) to describe the probability of bond rupture in the dissociation of hydrocarbons by electron impact. The necessity for caution in interpreting the results of mass spectral analyses where deuterium migration can occur is obvious.

APPENDIX II

LITERATURE CITED

1. BRINTON, R. K. and BLACET, F. E. I., J. Chem. Phys., 17, 797 (1949).
2. LANGER, A., J. Phys. & Colloid Chem., 54, 618 (1950).
3. LENNARD-JONES, Sir J. and HALL, G. G., Trans. Faraday Soc., 48, 581 (1952).
4. McDOWELL, C. A., Applied Mass Spectrometry, Inst. of Petroleum (1954).
5. McFADDEN, W. H. and WAHRHAFTIG, A. L., J. Am. Chem. Soc., 78, 1572 (1956).
6. MAGAT, M. and VAILLARD, R. I., J. chim. phys., 48, 385 (1951). MAGAT, M., Discussions Faraday Soc., 10, 114 (1951).
7. ROSENSTOCK, H. M., WALLENSTEIN, M. B., WAHRHAFTIG, A. L., and EYRING, H., Proc. Natl. Acad. Sci. U.S., 38, 667 (1952).
8. STEVENSON, D. P. and WAGNER, C. D., J. Chem. Phys., 19, 11 (1951).