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**TOPPING, Joseph John, 1942-
THE PYROLYSIS-GAS CHROMATOGRAPHY
OF SELECTED LOW MOLECULAR WEIGHT
ALCOHOLS AND HYDROCARBONS.**

**University of New Hampshire, Ph.D., 1969
Chemistry, analytical**

University Microfilms, Inc., Ann Arbor, Michigan

THE PYROLYSIS-GAS CHROMATOGRAPHY
OF SELECTED LOW MOLECULAR
WEIGHT ALCOHOLS AND HYDROCARBONS

by

JOSEPH J. ^{PH}TOPPING

B.S., LeMoyne College, 1964

M.S., University of New Hampshire, 1967

A THESIS

Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of
Doctor of Philosophy

Graduate School
Department of Chemistry

July, 1969

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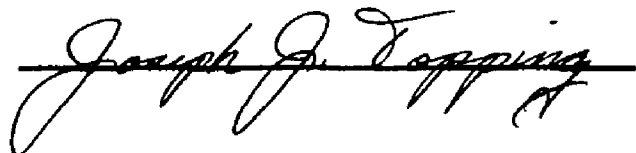
ACKNOWLEDGMENT

The author wishes to express his sincere gratitude and appreciation to Dr. Albert F. Daggett for his patient guidance and invaluable assistance throughout the course of this investigation and for his assistance in the preparation of this manuscript.

The author would like to thank Dr. David W. Ellis and Miss Rosemarie Russo for their assistance in the preparation of this manuscript. In addition, the author wishes to thank the members of his committee for their time and assistance.

Acknowledgment is due Mr. Robert M. Murphy and Mr. James Eberhardt for the use of their computer programs.

The author is indebted to the University of New Hampshire for granting a teaching assistantship and fellowship as well as a Summer Fellowship. Also, the author is grateful for the award of a Lester A. Pratt Fellowship.

A handwritten signature in cursive script, reading "Joseph J. Topping", is written over a horizontal line.

This thesis is dedicated to my wife, Lucille

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ABSTRACT

THE PYROLYSIS-GAS CHROMATOGRAPHY OF SELECTED LOW MOLECULAR WEIGHT ALCOHOLS AND HYDROCARBONS

by

JOSEPH J. TOPPING

The thermal decomposition of various organic compounds has been studied using the technique of pyrolysis-gas chromatography. The observed pyrolysis data were found to be consistent with first order kinetics. The distribution of the products of the thermal reaction was in agreement with the Kossiakoff-Rice Theory as well as with the results of other pyrolysis investigations. This indicates the potential utility of the method for qualitative analysis, in a manner analogous to mass spectrometry.

A pyrolysis-gas chromatograph, employing a continuous flow system, which is capable of causing decomposition of volatile organic compounds and of providing a means for qualitative and quantitative analysis of the products produced, has been designed and constructed. The furnace consisted of a quartz tube housed in a stainless steel block which could be heated to 700°C. The chromatographic columns were prepared from various types of Porapak and the pyrolysis was carried out in a helium carrier gas stream. Products were qualitatively characterized by comparison of retention times with known standards. Quantitative estimation was

based upon peak areas. Area measurement was accomplished using a Disc integrator. These areas were corrected for inequality of the thermal conductivity detector response using tables of weight factors.

Estimation of the time and temperature of the thermal decomposition was made using a suitable flow meter and thermocouples. This information, coupled with the amount of sample and product which was obtained from the recorder trace, was used to calculate values of the first order rate constants. These values were used in the Arrhenius equation to obtain energies of activation and estimates of the frequency factors. Suitable computer programs were employed to facilitate calculation and to perform regression analyses, which provided a measure of the error and lack of fit of the data to the proposed relationship. Variability in the data was explained in statistical terms.

Mechanisms accounting for the products observed were postulated, and various thermodynamic properties of activation were calculated.

The analytical utility of the technique was evaluated for the compounds studied and compared with mass spectral data for the same compounds. Structural isomers were found to produce pyrolysis patterns sufficiently different for qualitative analysis. Geometrical isomers yielded similar patterns; however, the percent conversion was somewhat higher for the cis form. This may be attributed to the greater strain present in the cis form. This effect was noted to

be much smaller for the C₆ isomers, when compared against the C₅ isomers.

Suggestions for future investigation were made.

INTRODUCTION

The term "reaction gas chromatography" was first used by Drawert in 1960.¹ The term may be broadly defined as the chemical alteration of an injected sample in a reaction zone with subsequent passage of the altered sample through a chromatographic column and detector to produce a chromatogram. Reaction gas chromatography is generally considered to be a single continuous unit. Systems where the reaction occurs previous to sample injection would not properly be termed reaction gas chromatography.

The earliest example of a process which may be called reaction gas chromatography was performed in 1955.² A micro-reactor containing a catalyst at elevated temperature was linked with a gas chromatograph and the catalytic decomposition of selected organic compounds was studied with respect to temperature and type of catalyst by observation of the products formed in the microreactor. This apparatus, in a modified form,^{3,4} is presently a useful device for studies of this type.

Beroza, in his review of reaction gas chromatography,⁵ has arbitrarily divided the area into seven general categories.

These are:

1. subtractive processes
2. elemental analysis
3. class reactions
4. kinetic and catalytic studies
5. hydrogen reactions
6. miscellaneous studies
7. pyrolysis reactions

A subtractive process involves the inclusion of one or more substances in the chromatographic flow system between the injector port and the column which will selectively retard the migration of one or more compounds or classes of compounds. A system of this type may be used to simplify a complex system or prove the presence or absence of certain compounds. Many examples of the use of this type of system are available in the literature.⁶⁻⁹ Subtractive processes have been used to retard alkanes,¹⁰ permanent gases,¹¹ olefins,¹² alcohols,¹³ and water.¹⁴

Elemental analysis by reaction gas chromatography may be viewed as extreme pyrolysis followed by catalytic conversion of the fragments to species which are easily separable and measurable. The most salient example of this type of process is automated CHN analysis. There are a multitude of publications dealing with this area, and several review articles have appeared.¹⁵⁻¹⁸

Class reactions are generally thought of in terms of functional group analysis. Reactions of this type, within a chromatographic system previous to the column, may cause the molecules to degrade to a different but related structure or effect the formation of a derivative. Either of these processes is able to supply valuable information pertaining to the qualitative identification of the organic compounds in question. Review papers¹⁶⁻²⁰ call attention to the majority of work that has been performed in this area.

Various classes of compounds which have been studied using class reactions in reaction gas chromatography are

alcohols,²¹ amino acids,²² aldehydes and ketones,²³ acids and esters,^{24,25} and those containing primary amino groups²⁶ and active hydrogen.²⁷ The techniques used in these cases generally may be classified as on-column derivative formation²⁸ or reaction in a vessel or syringe.²⁹

Several variations of the reaction gas chromatograph developed by Kokes, et al.² have been used in studies to determine the effects of various catalysts on chemical reactions.³⁰⁻³² A variety of specific applications has been reviewed by Beroza.⁵ This technique lends itself readily to the determination of relative rates of reactions, equilibrium constants, etc., due to the fact that product detection and identification are quite simple. Early efforts in this area were made by Juvet and Wachi³³ and the subject has been treated by Habgood.³⁴

The term hydrogen reactions in reaction gas chromatography actually includes three different processes. These are hydrogenation (the addition of hydrogen), dehydrogenation (removal of hydrogen), and hydrogenolysis (hydrogen addition following cleavage). The general technique involves the use of a precolumn and carrier gas specifically adapted to the type of process which one wishes to occur. Hydrogenation³⁵ has been used to determine olefins in the presence of saturated hydrocarbons. Dehydrogenation of various classes of compounds has been used for purposes of analysis.³⁶ Thermal catalytic cleavage, followed by hydrogenation has had wide utility in the determination of the chemical structure of a large number

of organic compounds.³⁷⁻³⁹

Reactions with varying degrees of utility and applicability have often been accidentally discovered. Unexpected reactions which occur due to exposure to high temperatures or to reactive or catalytic column packings during the course of gas chromatographic investigation are not uncommon. Methyl esters of fatty acids have been found to dehydrate, deacylate, and undergo cis-trans isomerization.⁴⁰ Various other examples of unique reactions may be found in Beroza's review.⁵

The last subdivision of reaction gas chromatography, pyrolysis reactions, is the type of investigation which is carried out in this thesis. This subject has been reviewed several times.⁴¹⁻⁴⁵ An excellent bibliography to the literature on pyrolysis-gas chromatography containing 205 references covering the period 1960-1963 has appeared.⁴⁶ In addition, a bibliography and index to the literature on gas chromatography covering the period January 1, 1963 - November 1, 1966 (available in four parts) containing many references to pyrolysis-gas chromatography has been published.⁴⁷⁻⁵⁰ Due to this fact, no attempt will be made here to include a complete treatment of previous publications. Rather, an effort will be made to point to representative examples of different types of instrumentation and areas of application. Most recent work in the specific area of this thesis will be cited in the statement of the problem. Since the time of the first publication dealing with pyrolysis-gas chromatography,⁵¹ several hundred papers have appeared concerning the various facets of this technique.

Three techniques of sample heating have been employed almost exclusively. They are (1) flash pyrolysis, utilizing a heated resistance wire, (2) thermal pyrolysis utilizing a hot tubular reaction chamber, and (3) pyrolysis induced by a high voltage electric arc.

The first technique involves placing the sample to be determined on a cold resistance wire followed by the passage of an electric current through the wire for a specific length of time causing a temperature rise and consequent pyrolysis of the sample. The pyrolysis may be conducted in the flowing carrier gas stream⁵² or in a sample loop,⁵³ the contents of which may be flushed into the chromatographic column. A modification of this technique, used to avoid possible catalytic effects of the metal filament, is the use of a sample boat (frequently porcelain) inserted within the helix of the filament.⁵⁴ As an alternate approach to resistance heating, induction heating of a ferromagnetic wire holding the sample to be pyrolyzed has been employed.⁵⁵

Experimentally, this type of procedure has many drawbacks. Accurate estimation of the pyrolysis temperature is practically impossible. Catalytic effects must be considered and the type of sample which one may study is somewhat limited. The assumption that pyrolysis takes place at the equilibrium temperature of the furnace has been attacked on theoretical grounds.⁵⁶

Pyrolysis within a tubular reaction chamber is a later and, in many respects, a more suitable method. The

temperature may be measured accurately and the extent of pyrolysis may be controlled by regulating the temperature, sample size, flow rate of carrier gas and volume and geometry of the reactor. By using different surfaces, the catalytic effect may be controlled. Both packed and unpacked reactors have been used. The sample may be injected as a gas or liquid using a micro-volume syringe, or a sample boat technique may be used. Depending on the design, the tube furnace may be used with a continuous carrier stream or as part of a sample loop. Due to its versatility many applications appear in the literature.⁵⁷⁻⁵⁹

Uncertainty in this technique arises primarily from the assumption that the sample temperature is approximately the same as the apparent temperature. The time of reaction is difficult to estimate in a continuous flow system. These problems will be treated in some detail in later sections of this work.

The electric discharge technique has been used rather infrequently. It is a difficult apparatus to fabricate and good precision of analysis has yet to be demonstrated. The pyrolysis is drastic and the fragmentation pattern resembles a mass spectrum. A large number of products of small molecular weight are formed. This is a disadvantage when viewed against a milder form of pyrolysis where the products are larger, less numerous, and as a result retain more of the structural components of the parent molecule. Large fragments reveal information concerning the position of substi-

tuent groups, location of multiple bonds, etc. Basic research in this area has been performed by Sternberg,^{60,61} and a commercial instrument has recently been introduced.

Following the convention of Beroza,⁵ pyrolysis techniques may be grouped according to the degree of degradation, based upon arbitrary temperature ranges:

- | | |
|------------------------|------------|
| 1. thermal degradation | 100- 300°C |
| 2. mild pyrolysis | 300- 500°C |
| 3. normal pyrolysis | 500- 800°C |
| 4. vigorous pyrolysis | 800-1100°C |

These classifications are approximate and may be modified by the experimental conditions (time, flow rate, stability of compounds, etc.). They are useful designations in bringing some order to the multitude of research papers in the area of pyrolysis-gas chromatography.

Thermal degradation has been used primarily to study unstable compounds. It generally produces molecular isomerization or dissociation into relatively large fragments. Frequently little or no modification of the gas chromatograph is needed; the injection port may serve as the pyrolysis unit if operated at an elevated temperature. Aliphatic amine salts,⁶² quaternary methyl amine chlorides,⁶³ quaternary ammonium salts,⁶⁴ dialkylphosphates,⁶⁵ and certain esters⁶⁶ offer but a few examples of the types of compounds which have been studied in this temperature range.

Mild pyrolysis is capable of causing cleavage of carbon-carbon bonds under most conditions. Generally the fragments formed are characteristic of the parent compound due to the fact that weaker carbon-carbon bonds are broken

whereas stronger bonds remain; however, the percent decomposition is generally quite small. Useful studies of the pyrolysis of certain amines,⁶⁷ carbohydrates⁶⁸ and metal carbonates and oxalates⁶⁹ have been conducted. Many classes of compounds show little or no fragmentation in this temperature interval, aromatics being a prime example.

Normal pyrolysis is perhaps the most suitable compromise between two extremes. High temperature pyrolysis produces large amounts of decomposition, but in doing so the resulting fragments are small enough to lose their ability to reveal their structural similarity to the parent molecule. At low temperatures, a greater structural similarity exists between the parent and fragment; however, the conversion is generally quite low and detection may become a problem. For this reason, most of the more recent work has concerned itself with the 500-800°C interval.

Polymers,⁷⁰ plastics,⁷¹ elastomers,⁷² ester plasticizers,⁷³ organosilicon polymers⁷⁴ and a host of similar compounds have been investigated, primarily for purposes of qualitative determination, with some success. A significant number of smaller organic compounds have been studied under conditions of normal pyrolysis. These will be referred to in the statement of the problem of this work.

Vigorous pyrolysis has been used less frequently than the other techniques. The experimental apparatus is more complex and control of experimental parameters more difficult. However, useful analyses have been obtained for several types

of compounds among which are oils,⁷⁵ paint pigments,⁷⁶ and soil humic acids.⁷⁷ Sternberg's electric discharge apparatus^{60,61} causes reactions which may be classified as vigorous pyrolysis.

Despite the fact that a large number of papers have been published in the area, much remains to be done from the standpoint of basic development of techniques as well as broadening the range of application of these techniques. In addition to qualitative analysis, which is the major area of application of pyrolysis-gas chromatography, the technique offers considerable promise as an approach to the study of bond energies, reaction rates, energies of activation and the determination of other fundamental knowledge as relates to kinetics and molecular structure. For these reasons, this work was undertaken.

STATEMENT OF PROBLEM

Previous investigations in the area of pyrolysis-gas chromatography of simple organic molecules have been limited to a few papers using varying techniques and experimental apparatus. Little effort has been made to relate the pyrolytic breakdown of molecules in a pyrolysis-gas chromatography setup to theory or to previous investigations using different techniques.

For the purpose of this work it was decided to design a method and apparatus for the study of the thermal decomposition of simple organic compounds which would meet the following criteria:

1. Be simple and efficient in design and construction.
2. Minimize catalytic effects.
3. Produce pyrolysis of five to fifty percent in the thermal range of "normal pyrolysis."
4. Allow for control and accurate estimation of both pyrolysis temperature and residence time in the reaction zone.
5. Produce the best resolution of products, allowing both qualitative and quantitative determination.

An instrument of this type should produce fragments characteristic of the parent molecule in sufficient amounts to be observed. Identification and quantitative estimation of all products would thus allow speculation as to the most probable pathways of decomposition and enable calculations to be made

relating the extent of decomposition to the experimental parameters. These relationships may be expressed in the form of rate constants for the thermal decomposition and associated energies of activation. The stability of various molecules may then be compared and related to the molecular structure. The molecules which were studied (alcohols and hydrocarbons) have been found by others to follow a first order rate expression:

$$C = C_0 e^{-kt}$$

where k = specific rate constant
 t = time of reaction
 C_0 = initial concentration of reactant
 C = final concentration of reactant

If t , C_0 , and C can be estimated from the pyrolysis conditions, the rate constant, k , may be calculated. Similarly, if k may be calculated for a series of reaction temperatures the two may be related by the Arrhenius equation:

$$k = k_0 e^{-E_a/RT}$$

where E_a = energy of activation
 R = molar gas constant
 T = reaction temperature
 k_0 = frequency factor

This relationship may be expressed graphically in such a fashion that the slope of the graph of $\ln k$ vs $1/RT$ is the energy of activation and the intercept is the frequency factor. Furthermore, the frequency factor and the energy of activation may be used to estimate thermodynamic properties of activation using the following expressions.

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta F^\ddagger}{T}$$

$$\Delta H^\ddagger = E_a - nRT$$

$$k_r = \frac{kT}{h} e^{-\Delta F^\ddagger/RT}$$

where

ΔS^\ddagger	=	change in entropy of activation
ΔH^\ddagger	=	change in enthalpy of activation
ΔF^\ddagger	=	change in free energy of activation
k_r	=	rate constant
k	=	Boltzmann's constant
h	=	Planck's constant.

Results obtained in this fashion may be compared to previous studies of thermal decomposition by other techniques.

Theories of unimolecular decomposition of hydrocarbons have been presented and theoretical product distributions have been calculated for several compounds.⁷⁸⁻⁸⁰ A comparison of experimental and theoretical product distribution would be valuable.

From a qualitative standpoint, the comparison of mass spectral data with pyrolysis fragmentation patterns would evaluate the potential of pyrolysis-gas chromatography as an analytical tool.

In order to make all data obtained as meaningful as possible, statistical methods of analysis will be used for purposes of handling and evaluating the data.

During the period of time that this research was in progress, several interesting papers appeared in the literature dealing with the pyrolysis of simple organic compounds and

the determination of kinetic parameters by pyrolysis-gas chromatography.⁸¹⁻⁸⁵ The results of these papers may be compared, in part, to some facets of this problem.

EXPERIMENTAL

Reagents

Compounds for Thermal Decomposition Study

<u>Compound</u>	<u>Source</u>	<u>Purity</u>
Methanol	Fisher Scientific Co.	99 Mole %
Ethanol	Commercial Solvents Co.	Absolute (200 Proof)
1-Propanol	Fisher Scientific Co.	99 Mole %
2-Propanol	Fisher Scientific Co.	99 Mole %
<u>n</u> -Pentane	Matheson, Coleman & Bell	99 Mole %
Isopentane	Matheson, Coleman & Bell	99 Mole %
1-Pentene	Matheson, Coleman & Bell	99 Mole %
<u>cis</u> -2-Pentene	K & K Laboratories	99 Mole %
<u>trans</u> -2-Pentene	K & K Laboratories	99 Mole %
<u>n</u> -Hexane	Chemical Samples Co.	99.9 Mole %
2-Methylpentane	Chemical Samples Co.	99 Mole %
1-Hexene	Chemical Samples Co.	99.9 Mole %
<u>cis</u> -2-Hexene	Chemical Samples Co.	96 Mole %
<u>trans</u> -2-Hexene	Chemical Samples Co.	99 Mole %
Cyclopentane	Matheson, Coleman & Bell	99 Mole %
Cyclohexane	Fisher Scientific Co.	99 Mole %

Compounds for Qualitative Identification

<u>Compound</u>	<u>Source</u>
Hydrogen	Air Reduction Co.
Carbon Monoxide	The Matheson Co.

Methane	J. T. Baker Co.
Ethane	J. T. Baker Co.
Ethylene	The Matheson Co.
Acetylene	Prepared by the reaction of CaC ₂ with H ₂ O
Propane	Instrumentation Lab., Inc.
Propylene	Prepared by the dehydration of <u>n</u> -propyl alcohol
Formaldehyde	J. T. Baker Co.
Acetaldehyde	Eastman Organic Co.
Isobutene	Prepared by the dehydration of 2-methylpropanol
Butane	J. T. Baker Co.
1- & 2-Butene	Prepared by the dehydration of <u>sec</u> -butyl alcohol with sulfuric acid
1,3-Butadiene	The Matheson Co.
Propionaldehyde	Eastman Organic Co.
Acetone	Fisher Scientific Co.
3-Methyl-1-Butene	K & K Laboratories
1,3-Pentadiene	Aldrich Chemical Co.
4-Methyl-1-Pentene	Aldrich Chemical Co.

Compounds for Thermocouple Calibration

<u>Compound</u>	<u>Source</u>	<u>Purity</u>
Water	Barnstead Still	99.9 Mole %
Tin metal	Matheson, Coleman & Bell	Reagent Grade
Lead metal	Mallinckrodt	Reagent Grade
Zinc metal	Fisher Scientific Co.	Reagent Grade

Materials and Apparatus

Design and Construction of Instrumentation

A Varian Aerograph Model A90-P-3 gas chromatograph equipped with a thermal conductivity detector was modified for use as a single-unit, continuous flow pyrolysis-gas chromatograph. The overall design of the apparatus is illustrated as a block diagram in Figure 1. The entire assembly, with the exception of the recorder and voltage regulator, was securely affixed to the benchtop using appropriate clamps and tripod stands. This served to prevent any movement of the apparatus which could damage the gas-tight seals or fracture the delicate quartz tube.

The carrier gas used throughout this work was helium, obtained from the Air Reduction Company. The inlet pressure of the carrier gas was controlled through the use of a reduction valve from Kim Products Company. The outlet pressure of the system was uncorrected atmosphere pressure. The carrier gas was routed from the reduction valve in a normal fashion through the reference side of the detector and through the injector port. The injector port was lined with a Pyrex glass sleeve (Aerograph part #69-000011-00). The port itself was removed from its normal position and mounted in front of the instrument using suitable clamps. This facilitated the insertion of the pyrolysis tube furnace directly between the injector port and the chromatographic column.

The furnace consisted of two concentric tubes, the

Figure 1
Pyrolysis-Gas Chromatograph

- A Carrier Gas
- B Reduction Valve
- C Thermal Conductivity Detector (Ref. Side)
- D Injector Port
- E Pyrolysis Tube
- F Chromatographic Column
- G Thermal Conductivity Detector (Spl. Side)
- H Recorder (Detector Output)
- I Injector Block
- J Cartridge Heater
- K Pyrolyzer Block
- L Cartridge Heater
- M 110-120 Volt Source
- N Regulated Power Supply
- O Variac
- P 4-Position Thermocouple Switch
- Q Recorder (Thermocouple Potential)
- R Precision Potentiometer
- S Electric Timer
- T Soap Bubble Flow Meter

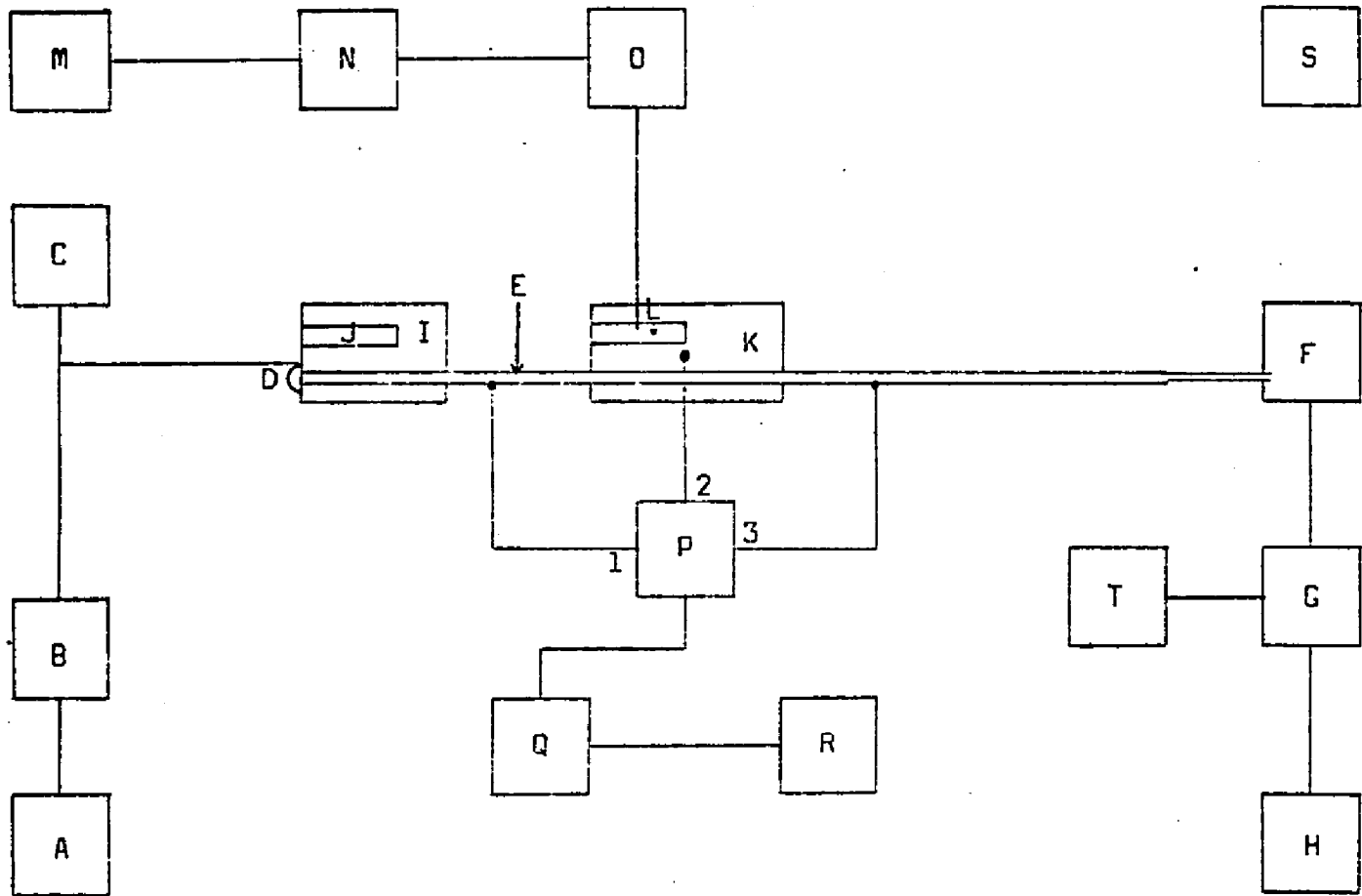


FIGURE 1

PYROLYSIS-GAS CHROMATOGRAPH

outer one being 13 inches in length. The outer tube, 0.25-inch outer diameter stainless steel, served as a mount for the inner quartz tube. The quartz tube had a 13.25 inch length, 0.12 inch outer diameter, and a 0.08 inch inner diameter. This tube was held securely in place by two silicone tubber O-rings which were placed at extreme ends between the quartz and steel tubes. The O-rings were located in zones where the temperature remained low enough so that degradation of the rubber would not be a problem.

A section of the tube, four inches in length, was surrounded by a stainless steel block (see Figure 2) in which a 150 watt, 115 volt Vulcan W7 cartridge heater was imbedded. The temperature of the cartridge heater was controlled by a Type 116 Powerstat (Superior Electric Company). Line voltage was stabilized using a Stabiline voltage regulator (Superior Electric Company), the output of which was fed directly to the Powerstat.

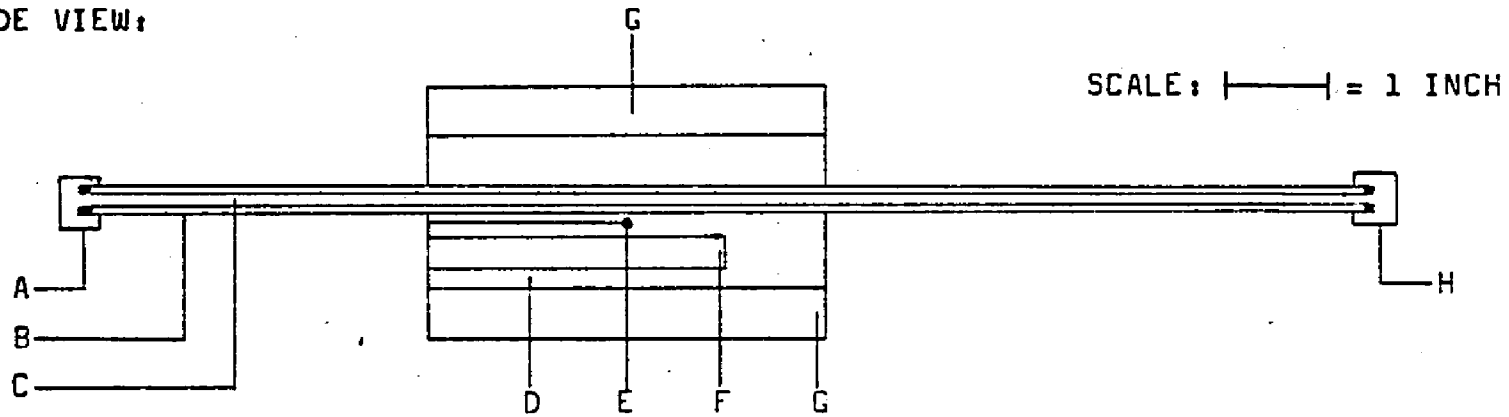
The pyrolysis reaction occurred within the four inch section of the quartz tube which was heated by the furnace block.

The temperature of the heated region of the pyrolysis tube was sensed by an Iron-Constantan thermocouple placed in the center of the block adjacent to the tube furnace. Two other thermocouples were placed at either end of the tube furnace. The thermocouple assembly was obtained from Varian Aerograph. A multi-position switch allowed each couple to be used individually with a single readout device.

Figure 2
Pyrolysis Tube Furnace

- A Swagelok Fitting to Injector Port
- B Stainless Steel Tube
- C Quartz Reaction Tube
- D Stainless Steel Heater Block
- E Thermocouple Seat
- F Cartridge Heater
- G Asbestos Insulation
- H Swagelok Union to Separation Column
- I Bore for Thermocouple
- J Bore for Tube Reactor
- K Bore for Cartridge Heater

SIDE VIEW:



FRONT VIEW:

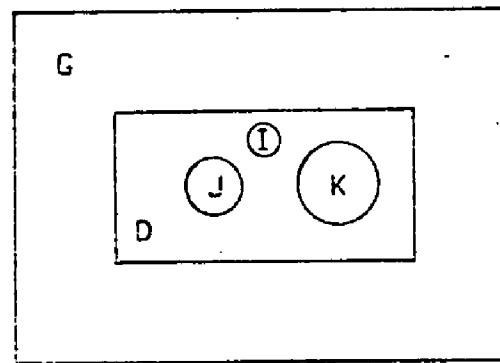


FIGURE 2

PYROLYSIS TUBE FURNACE

A Sargent Model SR recorder was used for all temperature measurements. The recorder was calibrated using pure metals of various melting points (see p 25) and a variable resistance (Helipot Precision Potentiometer, Model T-10-A) incorporated into the recorder circuit allowed continuous adjustment of the recorder range.

The tube furnace was joined to the injector port and the chromatographic column with Swagelok fittings (Crawford Fitting Co.). The design of the connections is shown in Figure 3. The use of the O-rings insured that the gas flow was through, not around, the quartz tube furnace.

The gas stream leaving the tube furnace entered directly into the separation column (for types of columns used, see p 26). From this point the apparatus resembled a conventional gas chromatograph. The output of the column led into the sample side of the thermal conductivity detector (tungsten filament) and was vented to the atmosphere. A soap-bubble flow meter was used in conjunction with an electric stopwatch (Macalaster Scientific Company, MSC2482) to determine the flow rate of gas at the exit port. The detector output was recorded by a Texas Instruments, Inc. Servo/riter II recording potentiometer equipped with a Model 231 Disc chart integrator (60 rpm motor) obtained from Disc Instruments, Inc.

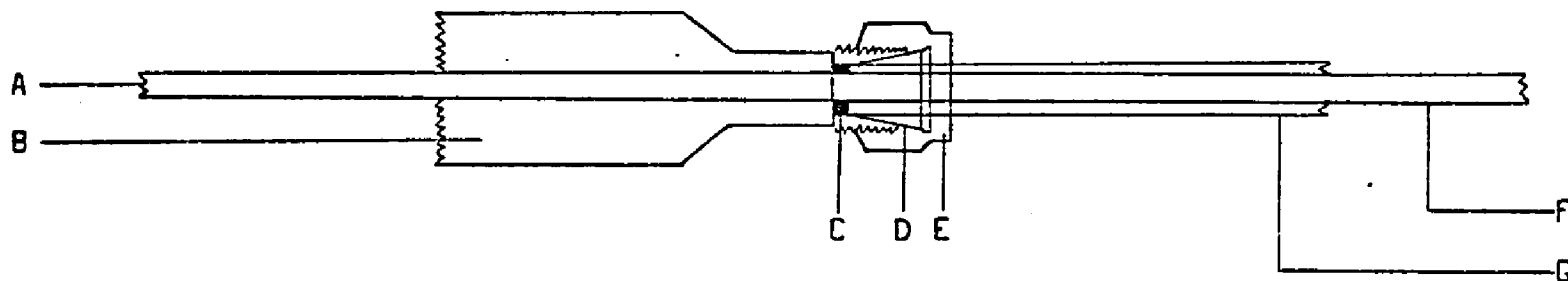
Calibration of Temperature Recorder

Initial adjustment. A standard voltage of 50 millivolts (Heath Voltage Reference Source) was fed into the recorder. The Helipot precision potentiometer was introduced

Figure 3
Detail of Tube Furnace Connectors

- A Pyrex Tube Insert
- B Injector Tube
- C Silicone O-Ring
- D Ferrule
- E Hexagonal Nut
- F Quartz Tube Furnace
- G Stainless Steel Tube
- H Swagelok Union
- I Separation Column
- J Column Packing

PYROLYSIS TUBE TO INJECTOR



PYROLYSIS TUBE TO SEPARATION COLUMN

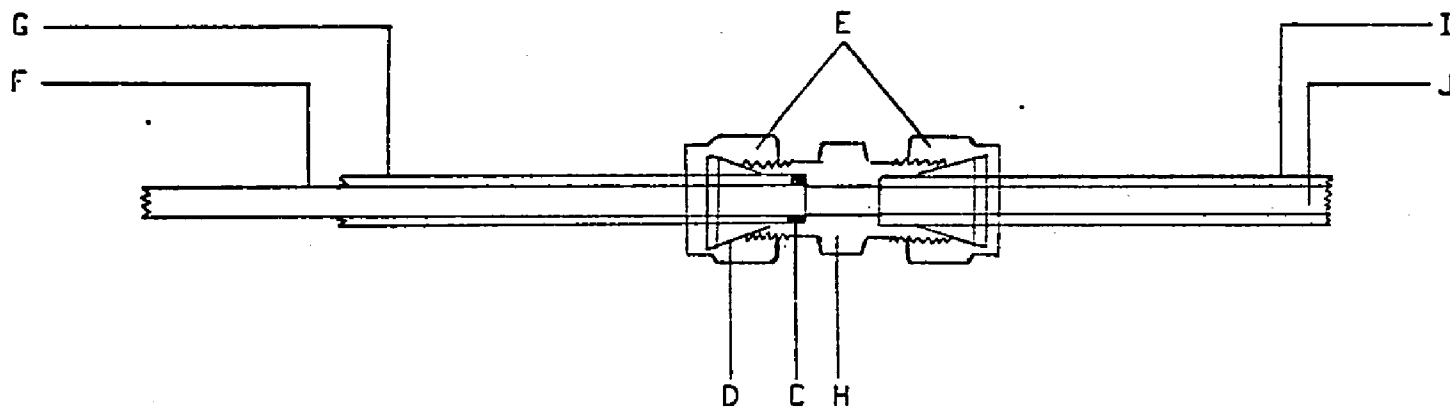


FIGURE 3

DETAIL OF TUBE FURNACE CONNECTORS

into the recorder circuit as an input voltage divider. The resistance was adjusted until the recorder pen was displaced full-scale. The potentiometer was then locked in this position, giving the recorder a range of 0-50 millivolts. Since the potential of the Iron-Constantan thermocouple was within this range for the temperature interval of interest in this work, a millivolt reading from the recorder chart would correspond to the temperature of the thermocouple. Correlation between temperature and thermocouple E.M.F. may be found in the literature.⁸⁶

Final calibration. In order to verify this correlation, the following procedure was used:

Pure samples of tin, lead, and zinc, whose melting points are accurately known, were obtained. A small amount of each metal was heated in a graphite crucible using a Meker burner. Each metal was heated well above its melting points ($\approx 100^\circ$). The crucible was then placed on an asbestos board under a five-sided asbestos box fitted with a $\frac{1}{4}$ inch diameter hole at the top. The box was fabricated from five 6" x 6" asbestos mats. The thermocouple, encased in 3 mm i.d. Pyrex tubing, sealed at the bottom, was placed through the hole in the top of the box into the molten metal. The cooling curve was then observed using the previously calibrated recorder. The resulting cooling curves gave a plateau indicative of the melting point of the metal. Low temperature calibration was made using boiling water and an ice-water mixture. This information correlated well with

the literature E.M.F. - temperature relationship. Therefore the temperature sensed by the thermocouple was determined from this point by reading the potential from the chart and determining the temperature from the above-mentioned relationship for an Iron-Constantan thermocouple.

Preparation of Chromatographic Columns

Two columns were used in this work, a relatively non-polar Porapak Q and a polar Porapak T. Both packing materials were obtained from Waters Associates. Each column was packed in the same manner, using a partial vacuum at one end and mechanical vibration. Each was fabricated to the following specifications:

Column Type	Stainless Steel
Packing Mesh Size	80-100
Length	5'
Outer Diameter	$\frac{1}{4}$ "

Procedure for Pyrolysis Studies

All samples were introduced using a Hamilton 10 μ l syringe. The overall operation was similar to normal chromatographic analysis. All conditions were set and allowed to reach equilibrium. Samples were randomized as much as possible to prevent systematic errors. Attenuation was controlled throughout the run in order to maintain each peak in the "pyrogram" on the recorder chart. Retention time, expressed in Kovat's Index form, was used as a means of qualitative identification. Quantitative analysis was accomplished using the Disc integration technique and corrections for baseline drift were made using #1291 Disc Drift Corrector.

RESULTS

Qualitative Product Identification

Procedure

The retention distance of each peak in the pyrolysis-gas chromatogram was measured to the nearest 0.01 inch for values less than 5 inches. For longer retention distances, the value was estimated to the nearest 0.1 inch. A chart speed of 0.50 inch/minute was used for all determinations, enabling conversion from retention distance to retention time.

While maintaining the same experimental conditions, chromatograms of all suspected products of the thermal decomposition were run. The retention times for the pure compounds were obtained and compared with those of the unknown products. Agreement of unknown and standard at two flow rates was considered positive proof of identity.

In order to put this information into a convenient form, the index system developed by Kovats⁶⁷ was used. This method takes advantage of the fact that a homologous series of reference compounds yields a straight line relationship between the logarithm of the adjusted retention time and the carbon number. By using aliphatic hydrocarbons (C₁-C₆) and assigning methane an index value of 100 (one carbon atom), ethane, index 200 (two carbon atoms), etc., a series of index values may be obtained by graphical interpolation. By virtue

of the fact that practically all of the pyrolysis-gas chromatograms contained two or more "index" compounds as products, a convenient internal standard was present in each analysis.

Experimental Conditions

The following conditions were maintained for all analyses which were performed:

Carrier Gas	Helium
Inlet pressure	31 psig.
Injector temperature	150°C
Detector temperature	190°C
Filament current	150 mA
Chart speed	0.5 inch/minute
Sample Size	1.0 μ l (unless otherwise stated)

Conditions which were varied in a systematic fashion for each analysis are:

Furnace temperatures	700°, 667°, 633°, 600°C
Flow rates	30 and 40 cc/min

Special conditions, in addition to those given above, are shown in Table 1. These will be referred to as Condition Ia, Condition Ib, etc., throughout this work.

Table 1

Special Conditions Used in Pyrolysis Studies

<u>Variable</u>	<u>Cond. Ia</u>	<u>Cond. Ib</u>	<u>Cond. IIa</u>	<u>Cond. IIb</u>
Column type	Porapak Q	Porapak Q	Porapak T	Porapak T
Column Temp.	115°C	115°C	150°C	150°C
Flow rate	30cc/min	40cc/min	30cc/min	40cc/min

Retention Times and Retention Indices

Retention distances were converted to retention times. These were adjusted for the dead volume of the furnace and column and converted to the Kovats Index system. The resulting values are listed for Conditions Ia, Ib, IIa, and IIb in Tables 2-5.

Table 2

Qualitative Results for Condition Ia

<u>Compound</u>	<u>T_r(min)</u>	<u>T_r adj(min)</u>	<u>Index No.</u>
Hydrogen	0.95	0.00	000
Methane	1.20	0.25	100
Ethylene	1.95	1.00	162
Acetylene	2.30	1.35	175
Ethane	3.30	2.35	200
Water	3.55	2.60	210
Propylene	4.95	4.00	289
Propane	5.20	4.25	300
Methanol	7.45	6.50	338
Acetaldehyde	9.65	8.70	363
Butane	13.6	12.6	400
1,3-Butadiene	13.6	12.6	400
1- & 2-Butene	15.4	14.4	411
Ethanol	16.5	15.5	415
Propionaldehyde	29.0	28.0	471
Acetone	30.3	29.3	476
2-Propanol	33.6	32.6	485
Isopentane	34.9	33.9	489
1-Pentene	35.0	34.0	491
<u>trans</u> -2-Pentene	37.7	36.7	495
<u>cis</u> -2-Pentene	38.7	37.7	499
<u>n</u> -Pentane	39.8	38.8	500
Cyclopentane	44.0	43.0	519
1-Propanol	48.0	47.0	520

Table 3

Qualitative Results for Condition Ib

<u>Compound</u>	<u>T_r(min)</u>	<u>T_r adj(min)</u>	<u>Index No.</u>
Hydrogen	0.72	0.00	000
Methane	0.95	0.23	100
Ethylene	1.60	0.88	165
Acetylene	1.80	1.08	175
Ethane	2.60	1.88	200
Water	2.70	1.98	210
Propylene	4.00	3.28	287
Propane	4.30	3.58	300
Methanol	5.85	5.13	335
Acetaldehyde	7.35	6.63	359
Butane	11.0	10.3	400
1,3-Butadiene	11.0	10.3	400
1- & 2-Butene	12.4	11.7	411
Ethanol	12.5	11.8	411
Propionaldehyde	22.7	22.0	471
Acetone	23.3	22.6	475
2-Propanol	25.5	24.8	483
Isopentane	28.1	27.4	491
1-Pentene	29.7	29.0	494
<u>trans</u> -2-Pentene	29.7	29.0	497
<u>cis</u> -2-Pentene	30.7	30.0	499
<u>n</u> -Pentane	30.9	30.2	500
Cyclopentane	38.1	37.4	520
1-Propanol	38.0	37.3	520

Table 4
Qualitative Results for Condition IIa

<u>Compound</u>	<u>T_r(min)</u>	<u>T_r adj(min)</u>	<u>Index No.</u>
Hydrogen	1.00	0.00	000
Methane	1.12	0.12	100
Ethane	1.65	0.65	200
Ethylene	1.65	0.65	200
Propane	3.10	2.10	300
Propylene	3.10	2.10	300
Formaldehyde	3.20	2.20	302
Water	5.50	4.50	381
Isobutene	5.65	4.65	385
Butane	6.50	5.50	400
1- & 2-Butene	6.50	5.50	400
Methanol	6.55	5.55	400
1,3-Butadiene	7.65	6.65	426
3-Methyl-1-butene	12.6	11.6	479
<u>n</u> -Pentane	14.0	13.0	500
1-Pentene	14.0	13.0	500
2-Pentene	16.0	15.0	517
1,3-Pentadiene	21.9	20.9	552
2-Methylpentane	27.4	26.4	581
4-Methyl-1-pentene	29.0	28.0	588
<u>n</u> -Hexane	32.1	31.1	600
1-Hexene	32.6	31.6	602
<u>trans</u> -2-Hexene	33.0	32.0	604
<u>cis</u> -2-Hexene	35.3	34.3	611
Cyclohexane	40.0	39.0	623

Table 5

Qualitative Results for Condition I Ib

<u>Compound</u>	<u>T_R(min)</u>	<u>T_R adj(min)</u>	<u>Index No.</u>
Hydrogen	0.75	0.00	000
Methane	0.85	0.10	100
Ethane	1.30	0.55	200
Ethylene	1.30	0.55	200
Propane	2.50	1.75	300
Propylene	2.50	1.75	300
Formaldehyde	2.60	1.85	305
Water	4.40	3.65	379
Isobutene	4.60	3.85	386
Butane	5.30	4.55	400
1- & 2-Butene	5.30	4.55	400
Methanol	5.25	4.50	400
1,3-Butadiene	6.30	5.55	427
3-Methyl-1-butene	10.2	9.4	483
<u>n</u> -Pentane	12.2	11.4	500
1-Pentene	12.2	11.4	500
2-Pentene	12.9	12.1	513
1,3-Pentadiene	17.7	16.9	549
2-Methylpentane	22.1	21.3	577
4-Methyl-1-pentene	24.2	23.4	586
<u>n</u> -Hexane	26.0	25.2	600
1-Hexene	27.2	26.4	602
<u>trans</u> -2-Hexene	27.5	26.7	605
<u>cis</u> -2-Hexene	30.0	29.2	611
Cyclohexane	33.0	32.2	621

Reproducibility of Pyrolysis Technique

Procedure

The reproducibility of pyrolysis under a typical set of operating conditions was studied. Ten replicate determinations were made at Condition Ib using a furnace temperature of 700°C and a sample size of 1 μ l of n-pentane. The attenuation was adjusted when necessary in order to keep all peaks on-scale. The area of each peak was estimated in Disc integrator counts and multiplied by the value of the attenuator to put all areas on the same basis. These values are given in Table 6.

The areas obtained in this manner were subsequently corrected for inequality of detector response using the appropriate thermal conductivity weight factors (Appendix I). The resulting values are shown in Table 7. Using these values, the percent decomposition was calculated using the standard normalization technique; the results are contained in Table 8.

Treatment of Data

The various statistical parameters were obtained in the following way:

a. Mean - Average of ten replicates.

$$\bar{x} = \frac{\sum_{i=1}^{i=n} x_i}{n}$$

Table 6

Reproducibility of Pyrolysis--Uncorrected Areas

<u>Product</u>	<u>Replicate No.</u>									
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Methane	772	772	760	700	668	640	700	680	640	624
Ethylene	1680	1700	1680	1680	1600	1480	1520	1500	1460	1520
Acetylene	668	704	640	600	560	500	520	580	560	600
Ethane	200	120	192	200	160	180	260	212	200	204
Propylene	1816	1900	1752	1808	1800	1620	1632	1600	1600	1680
Butane	724	804	720	768	864	840	808	640	640	884
<u>n</u> -Pentane*	38800	39160	37640	37632	38260	38240	38820	38180	38020	39060

*Undecomposed sample

Table 7

Reproducibility of Pyrolysis--Corrected Areas

<u>Product</u>	<u>Replicate No.</u>									
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>
Methane	347	347	342	315	301	288	315	306	288	281
Ethylene	991	1003	991	991	944	873	897	885	861	897
Acetylene	394	415	378	354	330	295	307	342	330	354
Ethane	118	71	113	165	94	106	153	125	118	120
Propylene	1180	1235	1139	1175	1170	1053	1061	1040	1040	1092
Butane	492	547	490	522	588	571	549	435	435	601
<u>n</u> -Pentane*	26772	27020	25972	25966	26399	26386	26788	26344	26234	26951
Total Product	3522	3618	3453	3422	3427	3186	3282	3133	3072	3345
Total Sample	30294	30638	29425	29488	29826	29572	30070	29477	29306	30272

*Undecomposed sample

Table 8

Reproducibility of Pyrolysis--Percent Decomposition

<u>Determination No.</u>	<u>Percent Decomposition</u>
1	11.63
2	11.81
3	11.73
4	11.94
5	11.49
6	10.77
7	10.91
8	10.63
9	10.48
10	11.05

- b. Median - Average of the two middle values, when the results are listed in order.
- c. Range - Difference between high and low values.
- d. Average deviation

$$\bar{d} = \frac{\sum_{i=1}^{i=n} |x_i - \bar{x}|}{n}$$

- e. Relative average deviation (parts per thousand)

$$\bar{d}^{\circ} = \frac{1000 \bar{d}}{\bar{x}}$$

- f. Standard deviation

$$s = \left[\frac{\sum_{i=1}^{i=n} |x_i - \bar{x}|^2}{n - 1} \right]^{\frac{1}{2}}$$

- g. Coefficient of variation

$$v = \frac{100 s}{\bar{x}}$$

Results

Table 9 contains the values obtained for these measures of variability for a series of replicate studies of the decomposition of n-pentane.

In addition, this data was used to compare the relative product distribution over a period of four months. The average relative distribution of products on two different dates are compared in Table 10. This was done in order to determine

Table 9

Reproducibility of Pyrolysis--Statistical
Analysis of Percent Decomposition

<u>Term</u>	<u>Value</u>
Mean	11.24%
Median	11.27%
Range	1.46%
Average Deviation	0.48%
Relative Average Deviation	42 ppt
Standard Deviation	0.536
Coefficient of Variation	4.77%

Table 10

Reproducibility of Pyrolysis--Comparison of
Product Distribution with Time

<u>Compound</u>	<u>5/1/68</u>	<u>8/26/68</u>
Hydrogen	0.0%	0.0%
Methane	9.3%	9.3%
Ethylene	28.2%	27.8%
Acetylene	11.6%	10.4%
Ethane	2.6%	3.6%
Propylene	33.7%	33.3%
Butane	14.7%	15.6%

whether any change was occurring due to contamination or alteration of the quartz surface with time and use.

Effect of Sample Size on Pyrolysis

Procedure

Replicate analyses of the thermal decomposition of n-pentane were made using approximate sample sizes of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 μ l. The conditions of analysis were similar to those used in the previous section for the reproducibility studies. The areas were measured in Disc integrator counts and the results are given in Table 11.

These areas were then corrected for the response of the detector using suitable weight factors (Appendix I) and are shown in Table 12. The percent thermal decomposition of each replicate was calculated and averaged.

Results

The relationship between the size of the sample taken for analysis and the resulting extent of thermal decomposition is shown in Figure 4. It may be seen that there is a small increase in the percent decomposition with an accompanying increase in the size of the sample.

A comparison of the relative amount of each product with respect to sample size is given in Table 13. The relative amounts, expressed as weight percent of total products, were calculated using the standard normalization technique.

Figure 4
Effect of Sample Size on Thermal Decomposition

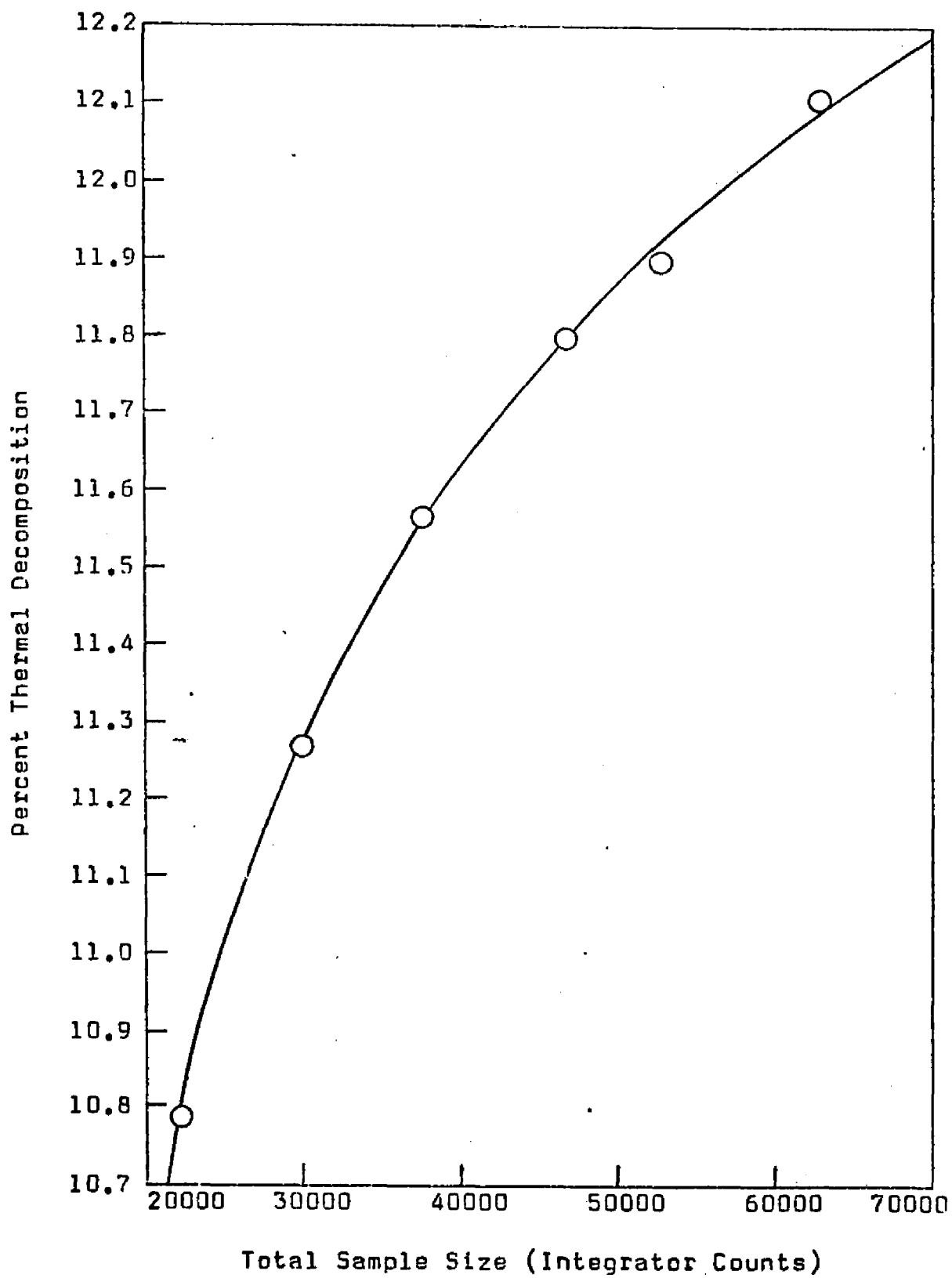


Table 11

Uncorrected Areas for Investigation of Effect of Sample Size

<u>Product</u>	<u>0.5-ul Spl.</u>		<u>1.0-ul Spl.</u>		<u>1.5-ul Spl.</u>	
	<u>Rep.#1</u>	<u>Rep.#2</u>	<u>Rep.#1</u>	<u>Rep.#2</u>	<u>Rep.#1</u>	<u>Rep.#2</u>
Methane	488	474	668	624	900	920
Ethylene	1170	1188	1600	1520	2000	1960
Acetylene	418	372	560	600	920	920
Ethane	150	200	160	204	140	176
Propylene	1232	1236	1800	1680	2288	2280
Butane	582	540	864	884	1008	992
<u>n</u> -Pentane*	28960	29300	38260	39060	48900	48160

*Undecomposed sample

Table 11
(Continued)

<u>Product</u>	<u>2.0-ul Spl.</u>		<u>2.5-ul Spl.</u>		<u>3.0-ul Spl.</u>	
	<u>Rep.#1</u>	<u>Rep.#2</u>	<u>Rep.#1</u>	<u>Rep.#2</u>	<u>Rep.#1</u>	<u>Rep.#2</u>
Methane	1000	1008	1344	1352	1600	1560
Ethylene	2400	2424	2640	2880	3200	3184
Acetylene	1120	1296	1560	1600	1856	1912
Ethane	120	120	80	80	104	176
Propylene	2832	2960	3344	3400	3984	3976
Butane	1376	1440	1288	1312	1824	1840
<u>n</u> -Pentane*	58620	60500	65993	68997	80624	79704

*Undecomposed sample

Table 12

Corrected Areas for Investigation of Effect of Sample Size

<u>Product</u>	<u>0.5-μl Spl.</u>		<u>1.0-μl Spl.</u>		<u>1.5-μl Spl.</u>	
	<u>Rep.#1</u>	<u>Rep.#2</u>	<u>Rep.#1</u>	<u>Rep.#2</u>	<u>Rep.#1</u>	<u>Rep.#2</u>
Methane	220	213	301	281	405	414
Ethylene	690	701	944	897	1180	1156
Acetylene	247	219	330	354	543	543
Ethane	89	118	94	120	83	104
Propylene	801	803	1170	1092	1487	1482
Butane	396	367	588	601	685	675
<u>n</u> -Pentane*	19982	20217	26399	26951	33741	33230
Total Product	2443	2421	3427	3345	4383	4374
Total Sample	22425	22638	29826	30272	38124	37604

*Undecomposed sample

Table 12
(Continued)

<u>Product</u>	<u>2.0-ul Spl.</u>		<u>2.5-ul Spl.</u>		<u>3.0-ul Spl.</u>	
	<u>Rep.#1</u>	<u>Rep.#2</u>	<u>Rep.#1</u>	<u>Rep.#2</u>	<u>Rep.#1</u>	<u>Rep.#2</u>
Methane	450	454	605	608	720	702
Ethylene	1416	1430	1558	1699	1888	1879
Acetylene	661	765	920	944	1095	1128
Ethane	71	71	47	47	61	104
Propylene	1841	1924	2174	2210	2590	2584
Butane	936	979	876	892	1240	1251
<u>n</u> -Pentane*	40448	41745	45535	47608	55631	54996
Total Product	5375	5623	6180	6400	7594	7648
Total Sample	45823	47368	51715	54008	63225	62644

*Undecomposed sample

Table 13

Relative Product Distribution for Various Sample Sizes

<u>Product</u>	<u>0.5-ul Spl.</u>		<u>1.0-ul Spl.</u>		<u>1.5-ul Spl.</u>		<u>2.0-ul Spl.</u>		<u>2.5-ul Spl.</u>		<u>3.0-ul Spl.</u>	
	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>
Methane	9.0	8.8	8.8	8.4	9.2	9.5	8.4	8.1	9.8	9.5	9.5	9.2
Ethylene	28.2	29.0	27.5	26.8	26.9	26.4	26.3	25.4	25.2	26.5	24.5	24.6
Acetylene	10.1	9.0	9.6	10.5	12.4	12.4	12.3	13.6	14.9	14.8	14.4	14.7
Ethane	3.6	4.9	2.7	3.6	1.9	2.4	1.3	1.3	0.8	0.7	0.8	1.4
Propylene	32.8	33.2	34.1	32.6	33.9	33.9	34.3	34.2	35.2	34.5	34.1	33.8
Butane	16.2	15.2	17.2	18.0	15.6	15.4	17.4	17.4	14.2	13.9	16.3	16.4

Effect of Rate of Flow and Temperature on Pyrolysis

Procedure

Sixteen aliphatic hydrocarbons and alcohols were chosen for a thorough study of their thermal decomposition as a function of pyrolysis temperature and rate of flow of the sample through the tube furnace.

The range of carrier flow rate which could be studied was somewhat limited by the requirements of the chromatographic column. If a flow rate lower than 30 cc/min was used, the quality of the resulting peak shapes was poor and the time of analysis became extremely long. If a flow rate greater than 40 cc/min was used, the resolution of the early, high boiling compounds suffered. A potential solution to the problem was the use of temperature programming of the column. Two disadvantages were noted in this method: the instrument used was operable only in a manual programming mode; this was not sufficiently reproducible for quantitative or qualitative analysis. In addition, when operating at the high sensitivities required for this work, the baseline drift during programming makes quantitative estimation of the peaks difficult and subject to error.

For these reasons, the two flow rates of 30 and 40 cc/min (measured at exit of detector) were chosen. The temperature region of "normal" pyrolysis was of primary interest and data was taken at 600°C, 633°C, 667°C, and 700°C for both rates of flow. Each determination was made in duplicate and replicates were run randomly in order to avoid systematic errors.

A blank was run on each compound as a check on its purity by lowering the furnace temperature to 200°C, a value sufficiently low to prevent any thermal decomposition. The compounds were all of high purity as claimed, and any small impurities were compensated for by subtraction of the area of the impurity from the pyrolysis-gas chromatogram.

All pyrolysis products were identified (see pp 27-33 of this work) and the areas were measured and corrected for detector response in the same manner as described on pp 34-40. In order to facilitate comparison of different sets of data, all areas were adjusted in such a way as to provide identical sample sizes upon normalization.

Experimental Data

Tables 14-29 contain the experimental data obtained from the analyses. The experimental Conditions, represented as Ia, Ib, IIa, and IIb, are given on page 28.

Tables 30-45 contain the corrected and adjusted data from the same investigation.

Table 46 contains a compilation of the percent pyrolysis for each of the sixteen compounds with respect to furnace temperature and flow rate. Replicate determinations for each Condition of analysis have been averaged to facilitate reporting of the data.

Table 14

Uncorrected Areas for the Pyrolysis of Methanol

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	30	40	20	15	0	0	0	0
Methane	35	45	30	25	10	10	5	5
Formaldehyde	525	500	280	275	168	174	76	65
Water*	353	335	288	275	275	274	265	260
Methanol**	203520	197760	200320	197760	203520	209600	200960	198720

<u>Compound</u>	Condition IIb							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	15	15	5	5	0	0	0	0
Methane	25	25	15	15	8	10	3	3
Formaldehyde	367	378	210	190	110	105	50	50
Water*	265	268	235	229	220	205	185	195
Methanol**	145926	147200	154240	151680	155520	140800	145280	149120

*Before correction for impurity; **Undecomposed sample

Table 15

Uncorrected Areas for the Pyrolysis of Ethanol

<u>Compound</u>	Condition Ia							
	<u>700°C Rep. #1</u>	<u>700°C Rep. #2</u>	<u>667°C Rep. #1</u>	<u>667°C Rep. #2</u>	<u>633°C Rep. #1</u>	<u>633°C Rep. #2</u>	<u>600°C Rep. #1</u>	<u>600°C Rep. #2</u>
CO/Hydrogen	1020	764	220	260	80	58	15	16
Methane	1480	1128	400	380	147	135	28	32
Ethylene	2464	2000	840	896	365	300	70	70
Acetylene	196	120	52	56	24	30	0	0
Water*	8160	6912	5912	6040	6700	6360	5344	5320
Acetaldehyde	10500	8684	4448	4420	2004	1540	800	900
Ethanol**	163856	144160	152768	160000	187040	176480	161120	159920

* Before correction for impurity

**Undecomposed sample

Table 15
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	528	420	120	140	60	36	22	24
Methane	880	700	240	232	140	88	26	52
Ethylene	1520	1400	500	640	296	220	90	127
Acetylene	72	40	40	32	24	16	0	0
Water*	5600	5600	4560	804	4300	4160	3952	4712
Acetaldehyde	6780	5900	2944	3280	1540	1280	584	720
Ethanol**	123600	122592	117760	124880	134576	117040	117696	138128

* Before correction for impurity

**Undecomposed sample

Table 16

Uncorrected Areas for the Pyrolysis of 1-Propanol

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	360	300	128	180	26	30	24	24
Methanol	2600	2280	1012	1320	440	520	250	260
Ethylene	1760	1320	600	700	230	250	150	140
Acetylene	400	400	152	212	110	160	48	46
Water*	4660	4320	4440	4860	3900	4160	3980	3780
Propylene	3920	3340	1660	1880	660	700	368	340
Methanol	600	540	208	320	40	40	0	0
Acetaldehyde	3940	3340	1700	2000	720	800	420	320
Propionaldehyde	440	440	240	240	96	140	0	0
1-Propanol**	118560	120420	152700	169360	148968	163840	152640	147480

* Before correction for impurity

**Undecomposed sample

Table 16

(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	200	200	50	60	30	18	28	24
Methane	1560	1720	720	740	420	270	260	240
Ethylene	960	1000	340	360	190	110	130	110
Acetylene	188	240	100	160	74	36	40	36
Water*	3640	3640	3160	3468	3614	2740	3100	3240
Propylene	2320	2480	1000	1000	588	370	360	288
Methanol	336	308	120	88	48	30	0	0
Acetaldehyde	2380	2492	1000	1328	634	384	380	400
Propionaldehyde	320	320	160	180	100	100	0	0
1-Propanol**	107728	108800	111440	125760	143760	107320	129440	132040

* Before correction for impurity

**Undecomposed sample

Table 17

Uncorrected Areas for the Pyrolysis of 2-Propanol

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	500	480	160	260	115	120	80	100
Methane	1964	1740	780	900	270	320	140	150
Ethylene	660	560	160	180	30	40	14	24
Acetylene	60	60	20	28	0	0	0	0
Water*	6140	5720	3920	4528	2560	3200	2240	2340
Propylene	8840	8260	4200	4840	1800	2220	1000	1080
Acetaldehyde	1392	1352	760	968	200	300	140	176
Acetone	22120	20480	12560	14400	6720	7000	3520	3160
2-Propanol**	141040	139696	153760	180280	150400	174520	150864	148320

* Before correction for impurity

**Undecomposed sample

Table 17
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	232	240	150	160	70	70	45	52
Methane	1140	1020	530	520	230	260	95	95
Ethylene	300	260	95	100	32	30	14	15
Acetylene	20	20	20	18	0	0	0	0
Water*	4000	3840	2870	2880	2202	2510	1620	1600
Propylene	5392	5200	3110	3110	1400	1590	600	600
Acetaldehyde	824	820	540	560	240	260	120	120
Acetone	13496	13680	9080	8960	4880	5880	2336	2400
2-Propanol**	109440	113760	114480	114640	127200	146480	108840	115840

* Before correction for impurity

**Undecomposed sample

Table 18

Uncorrected Areas for the Pyrolysis of n-Pentane

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1788	1720	300	320	126	121	30	37
Ethylene	3760	3868	650	710	257	254	52	55
Acetylene	1864	1748	340	358	224	199	60	60
Ethanol	660	520	230	225	299	291	240	238
Propylene	4388	4356	800	915	403	380	108	100
Butane	1812	1880	275	330	140	134	0	0
<u>n</u> -Pentane*	75248	75428	86925	86662	88071	88141	89030	89030

*Undecomposed sample

Table 18
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1120	1332	252	235	56	80	17	15
Ethylene	2580	3300	543	530	112	135	25	25
Acetylene	1060	1160	290	255	80	95	22	23
Ethane	240	340	175	140	152	200	148	150
Propylene	2800	3120	685	622	178	187	40	40
Butane	1164	1160	300	325	35	78	0	0
<u>n</u> -Pentane*	54540	53092	61259	61397	62891	62729	63252	63251

*Undecomposed sample

Table 19

Uncorrected Areas for the Pyrolysis of Isopentane

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1900	1680	560	520	314	295	80	75
Ethylene	1100	980	300	275	155	148	32	36
Acetylene	360	320	110	135	75	73	18	18
Ethane	172	188	205	225	320	318	250	260
Propylene	1800	1680	496	525	257	240	48	50
Butane	2472	2280	687	668	379	391	93	80
1- & 2-Butene	1680	1680	533	534	311	315	112	93
Isopentane*	82000	75680	67640	69400	76872	77568	78000	77980

*Undecomposed sample

Table 19
(Continued)

Condition 1b

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	740	1240	326	517	144	160	54	52
Ethylene	460	760	207	270	68	72	15	14
Acetylene	100	200	80	113	31	30	10	8
Ethane	208	220	185	152	291	240	220	214
Propylene	660	1180	323	473	138	109	22	19
Butane	972	1500	452	675	244	224	46	45
1- & 2-Butene	612	948	339	498	295	232	53	53
Isopentane*	35920	64900	50048	56168	60600	59860	62320	61260

*Undecomposed sample

Table 20

Uncorrected Areas for the Pyrolysis of 1-Pentene

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1064	440	520	252	194	145	58	40
Ethylene	5200	2592	1440	832	520	405	108	75
Acetylene	936	448	560	316	255	190	57	40
Ethane	280	384	168	160	38	80	35	480
Propylene	4260	2168	1248	696	512	382	95	65
Butane/1,3-Butadiene	5120	2588	2096	1176	930	725	192	147
1-Pentene*	36096	18440	51144	28920	52860	41128	57268	39504

*Undecomposed sample

Table 20
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	400	200	220	195	144	117	38	32
Ethylene	1920	1120	696	634	356	295	88	75
Acetylene	400	180	270	234	188	156	55	45
Ethane	400	200	270	43	48	37	95	197
Propylene	1600	1020	660	522	360	300	100	85
Butane/1,3-Butadiene	1728	1016	1160	965	670	606	206	137
1-Pentene*	20160	13960	22400	19880	49040	42092	37892	31900

*Undecomposed sample

Table 21

Uncorrected Areas for the Pyrolysis of cis-2-Pentene

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	3440	3760	1632	1644	440	480	186	232
Ethylene	860	920	208	212	70	80	20	21
Acetylene	720	720	280	296	80	85	41	56
Ethane	224	232	264	380	114	295	188	344
Propylene	1000	1120	332	336	94	111	30	30
Butane/1,3-Butadiene	9080	9240	3280	3400	1150	1157	444	568
<u>cis-2-Pentene*</u>	55156	60628	86880	90000	52060	59248	61632	76776

*Undecomposed sample

Table 21
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	2300	2000	1000	944	416	400	165	180
Ethylene	530	500	164	168	60	56	20	21
Acetylene	370	325	160	160	80	86	30	31
Ethane	332	370	220	208	310	336	90	101
Propylene	700	620	224	168	84	90	35	41
Butane/1,3-Butadiene	5925	5353	2440	2140	1034	1050	333	358
<u>cis-2-Pentene*</u>	53340	47160	61640	56904	59920	62040	45680	49928

*Undecomposed sample

Table 22

Uncorrected Areas for the Pyrolysis of trans-2-Pentene

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	3200	3200	1400	1128	322	305	45	52
Ethylene	820	812	188	152	46	44	5	10
Acetylene	580	536	256	188	67	63	10	13
Ethane	460	460	144	100	235	265	57	60
Propylene	1040	1024	288	200	62	56	10	10
Butane/1,3-Butadiene	8326	8220	3680	2952	811	790	155	165
<u>trans-2-Pentene*</u>	58720	58120	92480	77208	69260	65184	55560	59800

*Undecomposed sample

Table 22
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1800	1760	640	760	142	146	70	67
Ethylene	460	440	120	120	18	20	4	4
Acetylene	340	305	152	144	29	30	8	8
Ethane	252	225	180	128	200	195	15	17
Propylene	588	547	160	160	32	35	7	7
Butane/1,3-Butadiene	5280	4938	1600	1552	288	350	170	173
<u>trans-2-Pentene*</u>	50400	47480	59160	58500	54752	57008	45168	44280

*Undecomposed sample

Table 23

Uncorrected Areas for the Pyrolysis of Cyclopentane

Condition IIa

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	19	20	5	6	2	3	-	-
Ethane/Ethylene	577	600	135	105	30	31	-	-
Propane/Propylene	580	612	124	118	33	32	-	-
1- & 2-Butene	78	85	20	12	8	3	-	-
Cyclopentane*	175800	184400	163520	175360	161840	161280	-	-

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	15	18	6	5	2	2	-	-
Ethane/Ethylene	330	415	95	75	15	17	-	-
Propane/Propylene	330	412	85	70	13	12	-	-
1- & 2-Butene	32	40	10	7	0	0	-	-
Cyclopentane	110880	117600	119680	116800	122000	118800	-	-

*Undecomposed sample

Table 24

Uncorrected Areas for the Pyrolysis of n-Hexane

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	3520	3680	1560	1560	700	540	350	350
Ethane/Ethylene	9760	9600	3680	3760	1600	1360	670	700
Propane/Propylene	5600	5920	2520	2520	1080	1080	485	500
1- & 2-Butene/Butane	3700	3800	1665	1592	696	655	302	313
1,3-Butadiene	174	176	10	10	0	0	0	0
1-Pentene	1270	1320	580	595	280	310	89	115
<u>n</u> -Hexane*	123840	131520	141480	142240	143040	145600	157920	158080

*Undecomposed sample

Table 24
(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	2320	2400	1040	1200	400	420	200	200
Ethane/Ethylene	6240	6400	2680	2760	1000	1060	440	400
Propane/Propylene	3712	3840	1680	1720	680	740	240	265
1- & 2-Butene/Butane	2240	2560	1072	1120	540	530	160	155
1,3-Butadiene	40	43	0	0	0	0	0	0
1-Pentene	860	920	392	400	180	180	70	60
<u>n</u> -Hexane*	97480	102280	102480	103480	107280	100800	112000	115040

*Undecomposed sample

Table 25

Uncorrected Areas for the Pyrolysis of 2-Methylpentane

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	3200	3360	1160	1240	540	520	220	230
Ethane/Ethylene	5440	5760	2080	2240	1000	1000	345	365
Propane/Propylene	8960	9600	3680	4000	1840	1720	680	705
Isobutene	136	140	130	136	120	105	130	115
1- & 2-Butene/Butane	5420	5700	2350	2660	1200	1136	480	480
1,3-Butadiene	232	240	125	100	35	20	20	15
3-Methyl-1-butene	870	870	430	435	222	205	40	40
1- & 2-Pentene	2430	2500	1085	1090	450	445	104	80
2-Methylpentane*	112240	123360	131520	131440	149440	144800	151200	157440

*Undecomposed sample

Table 25
(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	2080	1920	720	896	260	288	130	145
Ethane/Ethylene	3840	3840	1520	1620	540	540	230	235
Propane/Propylene	6320	6240	2720	2960	1080	1060	409	445
Isobutene	144	136	105	90	100	90	83	70
1- & 2-Butene/Butane	3800	3800	1690	1800	708	718	279	270
1,3-Butadiene	176	180	60	50	5	24	0	0
3-Methyl-1-Butene	550	540	330	310	110	112	38	40
1- & 2-Pentene	1690	1600	764	785	240	275	101	70
2-Methylpentane*	96640	96400	102720	100720	105280	105120	105520	104400

*Undecomposed sample

Table 26

Uncorrected Areas for the Pyrolysis of 1-Hexene

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	5920	6080	3200	3120	1200	1040	410	360
Ethane/Ethylene	22400	23040	12480	12160	4400	4400	1300	1420
Propane/Propylene	22880	23520	12800	11520	4480	4400	1680	1680
Isobutene	200	220	200	184	230	210	245	238
1- & 2-Butene	8560	8800	4560	4400	1720	1610	650	645
1,3-Butadiene	8240	8640	5560	5000	2165	2080	880	900
3-Methyl-1-Butene	180	192	40	20	0	0	0	0
1-Pentene	4960	5440	3320	3240	1465	1460	590	600
1,3-Pentadiene	940	940	480	534	240	300	130	135
1-Hexene*	85480	85920	115880	115360	139840	142840	154000	155400

*Undecomposed sample

Table 26

(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	3520	3680	1600	1440	600	680	265	280
Ethane/Ethylene	15040	15040	6320	6080	2480	2640	935	976
Propane/Propylene	14400	15200	6400	6400	2480	2760	980	1000
Isobutene	160	120	120	110	135	162	170	185
1- & 2-Butene	5920	5960	2400	2340	970	1010	410	430
1,3-Butadiene	5600	5600	2890	2800	1230	1300	545	625
3-Methyl-1-Butene	60	20	16	14	0	0	0	0
1-Pentene	3400	3480	2020	2190	810	933	440	440
1,3-Pentadiene	500	540	400	406	140	145	50	72
1-Hexene*	65680	68640	94760	91120	103040	105280	106880	112000

*Undecomposed sample

Table 27

Uncorrected Areas for the Pyrolysis of cis-2-Hexene

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	9120	9280	4640	4640	1760	1840	600	600
Ethane/Ethylene	24896	25344	12160	12576	4160	4320	1200	1160
Propane/Propylene	6080	6240	2800	2800	760	800	220	260
1- & 2-Butene	6960	7264	4000	3900	1150	1180	270	277
1,3-Butadiene	16960	17760	7980	8160	3170	3304	950	930
3-Methyl-1-Butene	2700	2800	1440	1492	480	560	180	140
1- & 2-Pentene	6720	6680	2660	2744	820	890	60	70
1,3-Pentadiene	11860	12320	7860	7884	3450	3594	1088	936
4-Methyl-1-Pentene	2240	2240	1560	1420	750	800	180	182
<u>cis-2-Hexene*</u>	74040	74480	113840	112040	144400	144800	156240	157680

*Undecomposed sample

Table 27
(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	4864	5600	2480	2480	1000	1040	480	360
Ethane/Ethylene	16000	17280	6880	6720	2400	2416	800	760
Propane/Propylene	3840	4000	1360	1360	400	360	140	100
1- & 2-Butene	4920	4920	2080	2000	690	755	200	180
1,3-Butadiene	10400	10720	4720	4840	1720	1765	620	580
3-Methyl-1-Butene	1760	1780	790	750	305	298	130	100
1- & 2-Pentene	4300	4340	1500	1400	450	370	130	110
1,3-Pentadiene	7600	8200	4840	4816	2000	2130	780	755
4-Methyl-1-Pentene	1920	2080	940	960	300	350	83	90
<u>cis-2-Hexene*</u>	58440	58720	91760	88480	163000	107600	125150	117200

*Undecomposed sample

Table 28

Uncorrected Areas for the Pyrolysis of trans-2-Hexene

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	9056	8160	4448	4320	1840	1760	540	540
Ethane/Ethylene	23680	22400	10000	9840	3600	3560	1060	1000
Propane/Propylene	5760	5440	2240	2080	760	760	142	140
1- & 2-Butene	7520	6480	2880	2840	1050	1050	272	250
1,3-Butadiene	15420	14400	7360	6960	2770	2670	855	790
3-Methyl-1-Butene	2560	2360	1220	1200	520	500	145	140
1- & 2-Pentene	5360	5080	2120	2000	668	660	120	105
1,3-Pentadiene	11880	11120	7400	7060	3268	2980	1085	972
4-Methyl-1-Pentene	1520	1400	1080	1040	550	460	125	125
<u>trans-2-Hexene*</u>	77632	76560	121200	116240	139520	137760	161080	151640

*Undecomposed sample

Table 28
(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	6400	5760	2560	2880	800	1000	400	380
Ethane/Ethylene	16480	16000	6240	6880	1680	2400	660	680
Propane/Propylene	4000	3840	1600	1600	320	440	100	104
1- & 2-Butene	4800	4720	2000	2160	480	690	170	170
1,3-Butadiene	10560	10240	4400	4840	1280	1860	510	525
3-Methyl-1-Butene	1880	1840	800	888	200	360	85	120
1- & 2-Pentene	4400	3700	1330	1440	350	580	60	80
1,3-Pentadiene	9320	7900	4780	5180	1540	2180	670	665
4-Methyl-1-Pentene	1520	1360	720	720	300	325	75	72
<u>trans-2-Hexene*</u>	66000	62720	87280	89960	107040	110480	113600	114640

*Undecomposed sample

Table 29

Uncorrected Areas for the Pyrolysis of Cyclohexane

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	42	40	15	18	5	5	-	-
Ethane/Ethylene	715	710	215	194	40	45	-	-
Propane/Propylene	355	320	128	126	30	35	-	-
1- & 2-Butene	57	52	26	20	0	0	-	-
1,3-Butadiene	788	770	253	195	50	45	-	-
Cyclohexane*	138880	127680	145760	140160	134730	135680	-	-

*Undecomposed sample

Table 29
(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	33	30	10	10	2	3	-	-
Ethane/Ethylene	455	420	136	87	15	22	-	-
Propane/Propylene	220	205	66	51	10	15	-	-
1- & 2-Butene	38	30	13	12	0	0	-	-
1,3-Butadiene	500	428	147	94	20	20	-	-
Cyclohexane*	109880	105560	96480	102080	103720	103520	-	-

*Undecomposed sample

Table 30

Corrected Areas for the Pyrolysis of Methanol

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Hydrogen	32	45	22	17	0	0	0	0
Methane	8	11	7	6	3	3	1	1
Formaldehyde	183	180	100	99	57	59	27	24
Water	31	27	13	10	8	6	6	5
Methanol*	61514	61507	61627	61637	61701	61702	61734	61739
Total Pyrolysis	254	263	142	132	68	68	34	30
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 30
(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Hydrogen	16	16	5	5	0	0	0	0
Methane	6	6	3	3	2	3	1	1
Formaldehyde	127	129	69	63	36	38	18	17
Water	25	25	13	12	8	10	3	4
Methanol*	43645	43643	43728	43734	43772	43768	43797	43796
Total Pyrolysis	174	176	90	83	46	51	22	22
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 31

Corrected Areas for the Pyrolysis of Ethanol

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	355	303	79	92	19	12	0	0
Methane	355	310	109	99	34	33	8	8
Ethylene	774	720	301	307	109	96	24	25
Acetylene	62	43	19	19	7	10	0	0
Water	587	517	168	124	70	86	0	0
Acetaldehyde	3802	3602	1833	1743	693	565	324	367
Ethanol*	55835	56275	59260	59385	60837	60968	61412	61369
Total Pyrolysis	5935	5495	2509	2384	932	802	356	400
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 31
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	172	137	36	41	12	5	0	0
Methane	202	163	61	55	32	23	7	11
Ethylene	457	428	166	199	88	75	31	37
Acetylene	21	12	13	10	7	5	0	0
Water	292	318	129	120	0	40	0	0
Acetaldehyde	2350	2080	1123	1178	525	501	230	241
Ethanol*	40326	40678	42291	42215	43155	43169	43550	43528
Total Pyrolysis	3494	3138	1528	1603	664	649	268	289
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 32

Corrected Areas for the Pyrolysis of 1-Propanol

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	147	121	38	51	1	2	0	0
Methane	763	670	247	290	112	121	63	68
Ethylene	667	509	192	202	77	76	50	48
Acetylene	154	154	49	61	37	49	16	16
Water	508	388	162	143	55	18	57	38
Propylene	1662	1418	586	597	244	235	133	128
Methanol	227	204	66	91	13	12	0	0
Acetaldehyde	1748	1483	628	665	278	281	159	126
Propionaldehyde	192	193	87	79	36	49	0	0
1-Propanol*	55690	56629	59713	59590	60916	60927	61291	61347
Total Pyrolyzed	6078	5140	2055	2179	853	843	478	424
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 32
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	62	61	10	11	2	0	0	0
Methane	370	403	172	157	79	68	55	49
Ethylene	299	307	107	100	47	36	36	30
Acetylene	59	74	31	44	18	12	11	10
Water	231	218	97	72	6	20	0	0
Propylene	796	840	345	306	160	135	109	87
Methanol	103	93	37	24	12	10	0	0
Acetaldehyde	854	883	361	425	180	146	120	125
Propionaldehyde	113	112	57	57	28	38	0	0
1-Propanol*	40932	40826	42601	42622	43287	43352	43487	43518
Total Pyrolyzed	2887	2991	1217	1196	532	465	331	301
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 33

Corrected Areas for the Pyrolysis of 2-Propanol

<u>Compound</u>	Condition Ia							
	700°C	700°C	667°C	667°C	633°C	633°C	600°C	600°C
	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>
CO/Hydrogen	157	153	46	68	33	30	21	29
Methane	434	394	177	174	67	68	35	39
Ethylene	191	166	47	46	10	11	4	8
Acetylene	17	18	6	7	0	0	0	0
Water	1070	992	497	482	178	239	98	142
Propylene	2824	2700	1377	1355	638	680	363	399
Acetaldehyde	465	462	261	283	74	96	53	68
Acetone	7393	7003	4307	4218	2494	2243	1338	1222
2-Propanol*	49217	49880	55051	55134	58274	58401	59856	59863
Total Pyrolyzed	12551	11888	6718	6633	3494	3367	1912	1907
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 33
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
CO/Hydrogen	65	66	40	44	14	12	8	10
Methane	241	210	114	173	48	47	24	22
Ethylene	83	70	27	28	9	7	4	5
Acetylene	6	5	6	5	0	0	0	0
Water	617	546	342	344	139	133	72	55
Propylene	1650	1543	974	974	419	413	215	202
Acetaldehyde	264	255	177	183	75	71	45	43
Acetone	4319	4247	2975	2934	1528	1597	875	846
2-Propanol*	36573	36877	39162	39193	41586	41541	42575	42636
Total Pyrolysis	7245	6942	4656	4625	2232	2280	1243	1183
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 34

Corrected Areas for the Pyrolysis of n-Pentane

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	805	774	135	144	57	54	14	17
Ethylene	2218	2282	384	419	152	150	31	32
Acetylene	1100	1031	201	211	132	117	35	35
Ethane	389	307	136	133	176	172	142	140
Propylene	2852	2831	520	595	262	247	70	65
Butane	1237	1278	187	224	95	91	0	0
<u>n</u> -Pentane*	53173	53257	60206	60043	60895	60938	61477	61480
Total Pyrolysis	8596	8512	1563	1726	847	831	292	289
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 34

(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	504	599	113	106	25	36	8	7
Ethylene	1522	1947	320	313	66	80	15	15
Acetylene	625	684	171	150	47	56	13	14
Ethane	142	200	103	83	90	118	87	89
Propylene	1820	2028	445	404	116	122	26	26
Butane	792	789	204	221	24	53	0	0
<u>n</u> -Pentane*	38413	37571	42462	42541	43450	43353	43669	43667
Total Pyrolysis	5405	6247	1356	1277	368	465	149	151
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 35

Corrected Areas for the Pyrolysis of Isopentane

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	825	790	313	283	156	146	40	38
Ethylene	626	604	220	196	101	96	21	23
Acetylene	204	197	81	97	49	47	12	12
Ethane	97	116	150	161	210	207	164	170
Propylene	1129	1141	399	413	185	172	34	37
Butane	1622	1619	579	549	286	293	70	60
1- & 2-Butene	1086	1176	443	433	231	232	83	69
Isopentane*	56176	56125	59580	59636	60550	60575	61344	61357
Total Pyrolysis	5593	5644	2189	2133	1219	1194	425	412
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 35
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	525	491	195	246	65	73	24	23
Ethylene	427	395	146	168	40	43	9	8
Acetylene	93	104	56	71	18	18	6	5
Ethane	194	114	130	95	172	144	128	126
Propylene	676	675	251	324	90	72	14	12
Butane	1042	898	366	484	166	154	31	31
1- & 2-Butene	646	559	271	352	198	157	35	36
Isopentane*	40213	40577	42403	42076	43065	43155	43570	43573
Total Pyrolysis	3605	3241	1415	1742	753	663	248	245
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 36

Corrected Areas for the Pyrolysis of 1-Pentene

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	819	662	361	308	138	132	39	39
Ethylene	5243	5111	1311	1338	485	486	96	95
Acetylene	943	882	509	507	237	228	51	52
Ethane	282	759	153	256	35	95	32	32
Propylene	4732	4710	1250	1232	527	504	93	91
Butane/1,3-Butadiene	5951	5883	2197	2180	999	1002	197	216
1-Pentene*	43789	43763	55989	55948	59348	59322	61258	61245
Total Pyrolysis	17980	18006	5780	5821	2421	2447	511	524
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 36
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	431	322	242	245	79	75	27	27
Ethylene	2711	2366	1004	1041	256	247	84	84
Acetylene	565	379	389	384	135	131	52	51
Ethane	565	422	389	70	34	31	90	221
Propylene	2488	2373	1048	944	285	277	105	105
Butane/1,3-Butadiene	2811	2474	1877	1827	556	585	225	177
1-Pentene*	34248	35481	38869	39306	42471	42470	43234	43153
Total Pyrolysis	9570	8337	4949	4512	1347	1348	584	665
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 37

Corrected Areas for the Pyrolysis of cis-2-Pentene

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1968	1977	694	675	321	307	117	116
Ethylene	644	635	116	114	66	67	17	13
Acetylene	540	497	156	160	76	71	33	37
Ethane	168	160	148	204	108	248	155	227
Propylene	826	851	204	199	99	102	28	22
Butane/1,3-Butadiene	7847	7343	2109	2110	1266	1120	421	431
<u>cis-2-Pentene*</u>	49774	50308	58342	58309	59832	59856	61000	60921
Total Pyrolysis	11995	11461	3427	3460	1937	1913	769	848
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 37
(Continued)

<u>Compound</u>	Condition Ib							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1028	1008	426	436	187	174	99	99
Ethylene	311	330	92	102	35	32	16	15
Acetylene	217	215	89	96	47	49	24	22
Ethane	195	244	123	125	183	192	71	73
Propylene	452	451	138	112	55	57	31	33
Butane/1,3-Butadiene	4002	4076	1569	1493	704	691	302	297
<u>cis-2-Pentene*</u>	37613	30492	41383	41452	42607	42621	43275	43280
Total Pyrolysis	6205	6326	2435	2366	1211	1197	543	538
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 38

Corrected Areas for the Pyrolysis of trans-2-Pentene

<u>Compound</u>	Condition Ia							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1845	1865	593	574	189	190	33	35
Ethylene	620	620	104	102	35	36	5	9
Acetylene	438	409	142	125	52	51	10	12
Ethane	347	351	80	67	181	216	56	54
Propylene	866	862	176	147	52	50	12	11
Butane/1,3-Butadiene	7254	7238	2355	2269	719	744	173	172
<u>trans-2-Pentene*</u>	50401	50423	58319	58485	60539	60483	61481	61477
Total Pyrolysis	11368	11346	3450	3284	1230	1286	288	292
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 38
(Continued)

Condition Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	906	941	305	366	76	75	46	44
Ethylene	303	309	75	76	13	14	3	3
Acetylene	225	214	95	91	20	20	7	7
Ethane	167	158	112	81	139	130	13	15
Propylene	427	423	110	111	25	26	7	7
Butane/1,3-Butadiene	4016	3989	1152	1129	231	270	167	173
<u>trans-2-Pentene*</u>	37773	37786	41968	41962	43313	43283	43576	43576
Total Pyrolysis	6045	6032	1850	1856	505	535	242	242
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 39

Corrected Areas for the Pyrolysis of Cyclopentane

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	4	4	1	1	1	1	-	-
Ethane/Ethylene	165	164	42	30	10	10	-	-
Propane/Propylene	191	192	44	39	12	12	-	-
1- & 2-Butene	25	26	7	4	3	1	-	-
Cyclopentane*	61383	61383	61674	61694	61744	61747	-	-
Total Pyrolysis	385	386	94	74	26	24	-	-
Total Sample Size	61769	61769	61769	61769	61769	61769	-	-

*Undecomposed sample

Table 39
(Continued)

Condition I Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	4	4	2	1	0	1	-	-
Ethane/Ethylene	106	126	28	23	4	5	-	-
Propane/Propylene	122	144	29	25	4	4	-	-
1- & 2-Butene	11	13	4	3	0	0	-	-
Cyclopentane*	43574	43531	43755	43766	43810	43808	-	-
Total Pyrolysis	243	287	63	52	8	10	-	-
Total Sample Size	43818	43818	43818	43818	43818	43818	-	-

*Undecomposed sample

Table 40

Corrected Areas for the Pyrolysis of n-Hexane

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	967	958	412	410	189	144	87	87
Ethane/Ethylene	3517	3276	1276	1297	567	475	218	228
Propane/Propylene	2230	2232	965	960	423	417	175	180
1- & 2-Butene/Butane	1491	1450	646	614	276	256	110	114
1,3-Butadiene	71	69	39	39	0	0	0	0
1-Pentene	551	542	242	247	120	130	35	45
<u>n</u> -Hexane*	52942	53242	58189	58201	60192	60348	61142	61114
Total Pyrolysis	8827	8527	3580	3567	1575	1422	625	654
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 40
(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	590	582	270	308	103	114	50	49
Ethane/Ethylene	2082	2034	913	929	337	379	144	127
Propane/Propylene	1368	1349	632	640	253	292	86	93
1- & 2-Butene/Butane	836	911	409	422	203	212	59	55
1,3-Butadiene	15	16	0	0	0	0	0	0
1-Pentene	345	352	161	162	73	78	28	25
<u>n</u> -Hexane*	38581	38574	41433	41356	42850	42743	43451	43470
Total Pyrolysis	5236	5244	2385	2461	969	1075	367	347
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 41

Corrected Areas for the Pyrolysis of 2-Methylpentane

Condition IIa

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	919	884	320	340	136	136	56	57
Ethane/Ethylene	2049	1987	752	806	331	342	115	117
Propane/Propylene	3729	3660	1469	1590	673	649	251	250
Isobutene	59	56	55	57	46	42	50	43
1- & 2-Butene/Butane	2279	2200	950	1071	444	434	179	172
1,3-Butadiene	100	95	51	41	13	8	7	5
3-Methyl-1-butene	393	360	186	187	88	84	16	15
1- & 2-Pentene	1086	1023	466	465	177	181	41	30
2-Methylpentane*	51155	51504	57521	57213	59860	59894	61053	61079
Total Pyrolysis	10614	10265	4249	4557	1908	1876	715	689
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 41
(Continued)

Condition I Ib

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	509	471	181	229	66	73	34	38
Ethane/Ethylene	1232	1236	502	542	181	181	78	81
Propane/Propylene	2240	2219	992	1095	400	393	154	169
Isobutene	53	51	40	35	39	35	33	28
1- & 2-Butene/Butane	1363	1368	624	674	265	270	106	104
1,3-Butadiene	65	66	22	19	2	9	0	0
3-Methyl-1-butene	211	208	130	124	44	45	16	16
1- & 2-Pentene	643	655	299	312	95	110	41	28
2-Methylpentane*	37503	37544	41028	40789	42724	42702	43357	43354
Total Pyrolysis	6316	6274	2790	3030	1092	1116	462	464
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 42

Corrected Areas for the Pyrolysis of 1-Hexene

Condition IIa

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1430	1443	742	736	272	232	90	78
Ethane/Ethylene	7092	7169	3793	3759	1310	1287	371	402
Propane/Propylene	8005	8088	4300	3935	1474	1422	530	525
Isobutene	74	79	71	66	79	71	81	78
1- & 2-Butene	3032	3063	1551	1522	573	527	208	204
1,3-Butadiene	2980	3071	1930	1766	736	695	287	291
3-Methyl-1-butene	68	72	14	7	0	0	0	0
1-Pentene	1890	2037	1214	1205	525	514	203	204
1,3-Pentadiene	319	314	157	177	77	94	40	41
1-Hexene*	36879	36433	47997	48595	56724	56927	59959	59946
Total Pyrolysis	24890	25336	13772	13171	5046	4842	1810	1823
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 42
(Continued)

<u>Compound</u>	Condition I Ib							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	834	841	350	326	134	148	59	60
Ethane/Ethylene	4672	4509	1813	1807	725	753	274	273
Propane/Propylene	4943	5035	2029	2102	801	869	317	309
Isobutene	57	42	40	38	46	54	58	60
1- & 2-Butene	2057	1999	770	778	317	322	134	134
1,3-Butadiene	1987	1917	947	950	411	423	182	199
3-Methyl-1-butene	22	7	5	5	0	0	0	0
1-Pentene	1271	1255	697	783	285	320	155	148
1,3-Pentadiene	167	174	123	129	44	44	16	22
1-Hexene*	27806	28039	37043	36900	41055	40885	42624	42614
Total Pyrolysis	16010	15779	6774	6918	2763	2933	1195	1205
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 43

Corrected Areas for the Pyrolysis of cis-2-Hexene

<u>Compound</u>	Condition IIa							
	700°C	700°C	667°C	667°C	633°C	633°C	600°C	600°C
	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>	<u>Rep. #1</u>	<u>Rep. #2</u>
Methane	2301	2283	1120	1131	405	421	136	135
Ethane/Ethylene	8143	8174	3850	4019	1256	1297	358	342
Propane/Propylene	2203	2224	980	989	254	266	72	85
1- & 2-Butene	2553	2621	1417	1394	388	396	90	92
1,3-Butadiene	6353	6543	2887	2979	1094	1133	323	314
3-Methyl-1-butene	1061	1082	546	571	174	201	64	50
1- & 2-Pentene	2614	2556	999	1041	294	317	21	25
1,3-Pentadiene	4172	4263	2670	2703	1174	1157	348	297
4-Methyl-1-pentene	934	918	628	577	288	305	68	69
<u>cis</u> -2-Hexene*	31436	31105	46673	46365	56468	56275	60289	60360
Total Pyrolysis	30334	30664	15097	15404	5300	5493	1480	1409
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 43
(Continued)

Condition IIb

<u>Compound</u>	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1206	1351	568	568	233	233	97	78
Ethane/Ethylene	5200	5468	2066	2082	735	709	212	215
Propane/Propylene	1379	1399	451	466	135	117	41	31
1- & 2-Butene	1789	1741	699	693	236	248	59	57
1,3-Butadiene	3862	3875	1619	1713	601	592	188	187
3-Methyl-1-butene	685	675	284	278	112	105	41	34
1- & 2-Pentene	1658	1629	534	515	163	129	41	37
1,3-Pentadiene	2650	2784	1559	1601	657	670	222	229
4-Methyl-1-pentene	793	837	359	378	117	131	28	33
<u>cis-2-Hexene*</u>	24595	24059	35679	35504	40828	40885	42890	42917
Total Pyrolysis	19222	19759	8139	8312	2989	2934	929	901
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 44

Corrected Areas for the Pyrolysis of trans-2-Hexene

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	2376	2234	1131	1145	476	463	129	138
Ethane/Ethylene	8145	8041	3335	3419	1221	1226	333	334
Propane/Propylene	2190	2158	825	799	285	290	50	52
1- & 2-Butene	2893	2602	1075	1104	399	405	95	93
1,3-Butadiene	6059	5905	2804	2763	1074	1051	307	301
3-Methyl-1-butene	1055	998	488	499	212	207	55	56
1- & 2-Pentene	2187	2164	839	824	269	270	45	42
1,3-Pentadiene	4384	4283	2648	2632	1190	1101	366	348
4-Methyl-1-pentene	665	639	458	459	238	201	50	53
<u>trans-2-Hexene*</u>	31816	32745	48165	48125	56406	56556	60339	60352
Total Pyrolysis	29954	29024	13603	13644	5364	5214	1430	1417
Total Sample Size	61769	61769	61769	61769	61769	61769	61769	61769

*Undecomposed sample

Table 44
(Continued)

<u>Compound</u>	Condition IIb							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	1514	1446	659	712	198	235	97	91
Ethane/Ethylene	5112	5266	2107	2229	546	740	209	213
Propane/Propylene	1371	1396	597	573	115	150	35	36
1- & 2-Butene	1666	1738	755	783	175	238	60	60
1,3-Butadiene	3742	3850	1697	1792	475	656	184	188
3-Methyl-1-butene	699	726	324	345	78	133	32	45
1- & 2-Pentene	1619	1445	533	554	135	212	23	30
1,3-Pentadiene	3102	2790	1731	1801	537	721	228	224
4-Methyl-1-pentene	599	568	309	297	124	128	30	29
<u>trans-2-Hexene*</u>	24394	24594	35107	34733	41436	40604	42920	42902
Total Pyrolysis	19424	19225	8712	9086	2383	3213	898	916
Total Sample Size	43818	43818	43818	43818	43818	43818	43818	43818

*Undecomposed sample

Table 45

Corrected Areas for the Pyrolysis of Cyclohexane

<u>Compound</u>	Condition IIa							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	11	12	4	5	1	1	-	-
Ethane/Ethylene	252	272	73	68	15	17	-	-
Propane/Propylene	144	142	50	51	12	15	-	-
1- & 2-Butene	23	22	10	8	0	0	-	-
1,3-Butadiene	317	337	98	78	21	19	-	-
Cyclohexane*	61022	60984	61534	61558	61719	61717	-	-
Total Pyrolysis	747	785	235	210	49	52	-	-
Total Sample Size	61769	61769	61769	61769	61769	61769	-	-

*Undecomposed sample

Table 45
(Continued)

<u>Compound</u>	Condition IIb							
	<u>700°C</u> <u>Rep. #1</u>	<u>700°C</u> <u>Rep. #2</u>	<u>667°C</u> <u>Rep. #1</u>	<u>667°C</u> <u>Rep. #2</u>	<u>633°C</u> <u>Rep. #1</u>	<u>633°C</u> <u>Rep. #2</u>	<u>600°C</u> <u>Rep. #1</u>	<u>600°C</u> <u>Rep. #2</u>
Methane	8	8	3	3	1	1	-	-
Ethane/Ethylene	144	139	49	30	5	7	-	-
Propane/Propylene	81	78	28	20	4	6	-	-
1- & 2-Butene	13	11	6	5	0	0	-	-
1,3-Butadiene	181	161	61	37	7	7	-	-
Cyclohexane*	43391	43422	43672	43724	43801	43796	-	-
Total Pyrolysis	427	397	147	95	17	21	-	-
Total Sample Size	43818	43818	43818	43818	43818	43818	-	-

*Undecomposed sample

Table 46

Percent Pyrolysis as Function of Temperature and Flow Rate

<u>Compound</u>	<u>700°C</u> <u>30cc/min</u>	<u>700°C</u> <u>40cc/min</u>	<u>667°C</u> <u>30cc/min</u>	<u>667°C</u> <u>40cc/min</u>	<u>633°C</u> <u>30cc/min</u>	<u>633°C</u> <u>40cc/min</u>	<u>600°C</u> <u>30cc/min</u>	<u>600°C</u> <u>40cc/min</u>
Methanol	0.42	0.40	0.22	0.20	0.11	0.11	0.06	0.05
Ethanol	8.76	7.57	3.96	3.58	1.41	1.50	0.62	0.64
1-Propanol	8.58	6.71	3.43	2.76	1.37	1.14	0.73	0.73
2-Propanol	19.79	16.19	10.81	10.60	5.56	5.15	3.10	2.77
<u>n</u> -Pentane	13.84	12.34	2.66	3.01	1.40	0.95	0.47	0.34
Isopentane	9.10	7.81	3.50	3.22	1.96	1.61	0.68	0.56
1-Pentene	29.12	20.43	9.39	10.79	3.94	3.07	1.31	1.42
<u>cis</u> -2-Pentene	18.99	14.30	5.57	5.48	3.12	2.75	1.31	1.23
<u>trans</u> -2-Pentene	18.39	13.80	5.45	4.23	2.04	1.19	0.47	0.56
Cyclopentane	0.62	0.60	0.14	0.13	0.04	0.02	-	-
<u>n</u> -Hexane	14.05	11.96	5.79	5.53	2.43	2.33	1.04	0.82
2-Methylpentane	16.90	14.37	7.63	6.65	3.07	2.52	1.14	1.06
1-Hexene	40.66	36.28	21.82	15.63	8.01	6.50	2.94	2.74
<u>cis</u> -2-Hexene	49.39	44.48	24.69	18.77	8.74	6.76	2.34	2.09
<u>trans</u> -2-Hexene	47.74	44.10	22.06	20.31	8.56	6.39	2.31	2.07
Cyclohexane	1.24	0.94	0.36	0.28	0.08	0.05	-	-

Determination of Kinetic Parameters

Rate Constants

From the pyrolysis data obtained at various temperatures and flow rates, the rate constants and activation energies may be obtained. The first order expression for the rate constant:

$$k = (\ln C_0/C)/t \quad (1)$$

is readily evaluated if the initial and final concentrations of reactant and the reaction time are known.

The initial concentration (C_0) and final concentration (C) of reactant were obtained from Tables 30-45, on the assumption that the areas are proportional to concentration.

The estimation of the residence time (t) was, however, more difficult. The volumetric flow rate at the exit of the pyrolysis-gas chromatograph was easily measured using a soap bubble flow meter. If the temperature were uniform throughout the system, the residence time would be adequately represented by the expression:

$$t_r = V/v \quad (2)$$

where t_r = residence time (sec)
 V = volume of tube furnace (cc)
 v = volumetric flow rate (cc/sec)

In order to compensate for the fact that the tube furnace section of the flow system was being operated at a considerably higher temperature than any other part, this equation had to be modified to take into account changes

in volume due to this temperature difference. The residence time expression, with the Charles' Law dependence, is as follows:

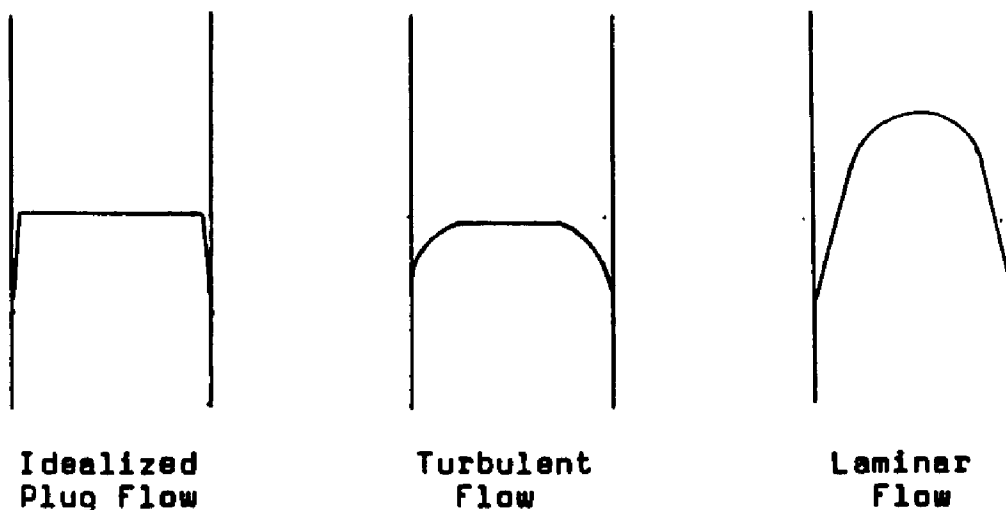
$$t_r = (V/v)(T_1/T_2) \quad (3)$$

where T_1 = temperature at which flow rate was measured
 T_2 = temperature of tube furnace reactor

This equation is based upon the assumption that a "plug flow" exists. This is an idealized state of flow which conforms to the following specifications:

1. Over any cross-section perpendicular to the motion of flow, the mass flow rate and the fluid properties are uniform.
2. Any diffusion is negligible relative to the bulk flow.

In reality, the validity of the plug flow assumption varies with the type of flow present within the tube furnace reactor:



It may be seen that the greatest deviation from plug flow in an unpacked tube is the case of laminar flow.

In order to determine whether the flow in this application was laminar or turbulent, the Reynolds Number was calculated.

The Reynolds Number is represented by the following expression:

$$Re = dv\rho/\mu \quad (4)$$

where Re = Reynolds Number
 d = tube diameter
 v = average linear velocity of the molecule
 ρ = density of the moving phase
 μ = viscosity of the moving phase

These parameters were estimated in the following way:

- a) The tube diameter (d) was 0.3 cm
- b) The linear velocity of a molecule is represented by the expression:

$$v = v/\pi r^2 \quad (5)$$

where v = volumetric flow rate
 r = radius of the tube furnace

Assuming a 1 μ l sample size of density 0.78 g/ml (corresponding to a 7×10^{-4} gram sample) and a flow rate of 30 cc/min, the linear velocity was found to be 7.0 cm/sec.

- c) The density (ρ) of the moving phase may be estimated from the modified ideal gas law:

$$\rho = PM/RT \quad (6)$$

where P = pressure (3 atm)
 M = molecular weight (assume = 70)
 R = gas constant (82.05 ml atm/degree mole)
 T = temperature (assume 973^oK)

substituting:

$$\rho = 2.6 \times 10^{-3}$$

d) The viscosity of the moving phase was assumed to be the viscosity of the helium which is 4.5×10^{-8} g/cm-sec.

Substituting these values in eq (4), the Reynolds Number was found to be 12. This very small value clearly indicates that the flow is laminar. This means that a significant residence time distribution exists. The exact dimension of this distribution is difficult to obtain either theoretically or experimentally. Therefore, the residence time calculated from eq (3) was used. If a normal distribution exists, this will be a good estimate of the most probable residence time due to the fact that the mean of the distribution will correspond to the average residence time, which eq (3) yields. The values obtained in this manner are given in Table 47.

Table 47
 Calculated Residence Times for
 Various Pyrolysis Temperatures

<u>Temperatures (°C)</u>	<u>t_r (sec) for Condition Ia & IIa</u>	<u>t_r (sec) for Condition Ib & IIb</u>
700	0.453	0.340
667	0.469	0.352
633	0.486	0.365
600	0.504	0.379

The rate constants calculated on the basis of these considerations are given in Table 48. All calculations were made using a suitable computer program which is reproduced in Appendix II. The rate constants $k_1 - k_4$ and k_{av} represent the following:

k_1 = rate constant for flow rate
of 30 cc/min (1st replicate)

k_2 = rate constant for flow rate
of 30 cc/min (2nd replicate)

k_3 = rate constant for flow rate
of 40 cc/min (1st replicate)

k_4 = rate constant for flow rate
of 40 cc/min (2nd replicate)

k_{av} = average of k_1 , k_2 , k_3 , and k_4 .

Table 48

First Order Rate Constants for Thermal Decomposition

a. Methanol

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	9.1×10^{-3}	9.4×10^{-3}	11.6×10^{-3}	11.8×10^{-3}	10.5×10^{-3}
667°C	4.9×10^{-3}	4.6×10^{-3}	5.8×10^{-3}	5.5×10^{-3}	5.2×10^{-3}
633°C	2.3×10^{-3}	2.2×10^{-3}	2.9×10^{-3}	3.1×10^{-3}	2.6×10^{-3}
600°C	1.1×10^{-3}	1.0×10^{-3}	1.2×10^{-3}	1.3×10^{-3}	1.2×10^{-3}

b. Ethanol

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	2.2×10^{-1}	2.1×10^{-1}	2.4×10^{-1}	2.2×10^{-1}	2.2×10^{-1}
667°C	8.8×10^{-2}	8.8×10^{-2}	1.0×10^{-1}	1.1×10^{-1}	9.3×10^{-2}
633°C	3.1×10^{-2}	2.7×10^{-2}	4.2×10^{-2}	4.1×10^{-2}	3.5×10^{-2}
600°C	1.1×10^{-2}	1.3×10^{-2}	1.6×10^{-2}	1.8×10^{-2}	1.5×10^{-2}

Table 48
(Continued)

c. 1-Propanol

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	2.3×10^{-1}	1.9×10^{-1}	2.0×10^{-1}	2.1×10^{-1}	2.1×10^{-1}
667°C	7.2×10^{-2}	7.7×10^{-2}	8.0×10^{-1}	7.9×10^{-1}	7.7×10^{-1}
633°C	2.9×10^{-2}	2.8×10^{-2}	3.3×10^{-2}	2.9×10^{-2}	3.0×10^{-2}
600°C	1.5×10^{-2}	1.4×10^{-2}	2.0×10^{-2}	1.8×10^{-2}	1.7×10^{-2}

d. 2-Propanol

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	5.0×10^{-1}	4.7×10^{-1}	5.3×10^{-1}	5.1×10^{-1}	5.0×10^{-1}
667°C	2.5×10^{-1}	2.4×10^{-1}	3.2×10^{-1}	3.1×10^{-1}	2.8×10^{-1}
633°C	1.2×10^{-1}	1.2×10^{-1}	1.4×10^{-1}	1.5×10^{-1}	1.3×10^{-1}
600°C	6.2×10^{-2}	6.2×10^{-2}	7.6×10^{-2}	7.2×10^{-2}	6.8×10^{-2}

Table 48
(Continued)

e. n-Pentane

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	3.3×10^{-1}	3.3×10^{-1}	3.7×10^{-1}	3.3×10^{-1}	3.4×10^{-1}
667°C	—	—	8.9×10^{-2}	8.4×10^{-2}	8.7×10^{-2}
633°C	2.9×10^{-2}	2.8×10^{-2}	2.3×10^{-2}	2.9×10^{-2}	2.7×10^{-2}
600°C	9.4×10^{-3}	9.3×10^{-3}	9.0×10^{-3}	9.1×10^{-3}	9.2×10^{-2}

f. Isopentane

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	2.1×10^{-1}	2.1×10^{-1}	2.5×10^{-1}	2.3×10^{-1}	2.3×10^{-1}
667°C	7.7×10^{-2}	7.5×10^{-2}	9.3×10^{-2}	1.1×10^{-1}	8.9×10^{-2}
633°C	4.1×10^{-2}	4.0×10^{-2}	4.7×10^{-2}	4.2×10^{-2}	4.3×10^{-2}
600°C	1.4×10^{-2}	1.3×10^{-2}	1.5×10^{-2}	1.5×10^{-2}	1.4×10^{-2}

Table 48
(Continued)

g. 1-Pentene

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	7.6×10^{-1}	7.6×10^{-1}	7.2×10^{-1}	6.2×10^{-1}	7.2×10^{-1}
667°C	2.1×10^{-1}	2.1×10^{-1}	3.4×10^{-1}	3.1×10^{-1}	2.7×10^{-1}
633°C	8.2×10^{-2}	8.3×10^{-2}	8.6×10^{-2}	8.6×10^{-2}	8.4×10^{-2}
600°C	1.6×10^{-2}	3.6×10^{-2}	3.5×10^{-2}	4.0×10^{-2}	3.2×10^{-2}

h. cis-2-Pentene

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	4.8×10^{-1}	4.5×10^{-1}	4.5×10^{-1}	4.6×10^{-1}	4.6×10^{-1}
667°C	1.2×10^{-1}	1.2×10^{-1}	1.6×10^{-1}	1.6×10^{-1}	1.4×10^{-1}
633°C	6.6×10^{-2}	6.5×10^{-2}	7.7×10^{-2}	7.6×10^{-2}	7.1×10^{-2}
600°C	2.5×10^{-2}	2.7×10^{-2}	3.3×10^{-2}	3.2×10^{-2}	2.9×10^{-2}

Table 48
(Continued)

i. trans-2-Pentene

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	4.5×10^{-1}	4.5×10^{-1}	4.4×10^{-1}	4.4×10^{-1}	4.5×10^{-1}
667°C	1.2×10^{-1}	1.2×10^{-1}	1.2×10^{-1}	1.2×10^{-1}	1.2×10^{-1}
633°C	4.1×10^{-2}	4.3×10^{-2}	3.2×10^{-2}	3.4×10^{-2}	3.8×10^{-2}
600°C	9.2×10^{-3}	9.4×10^{-3}	1.5×10^{-2}	1.5×10^{-2}	1.2×10^{-2}

j. Cyclopentane

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	1.4×10^{-2}	1.4×10^{-2}	1.6×10^{-2}	1.9×10^{-2}	1.6×10^{-2}
667°C	3.3×10^{-3}	2.6×10^{-3}	4.1×10^{-3}	3.4×10^{-3}	3.4×10^{-3}
633°C	8.3×10^{-4}	7.3×10^{-4}	5.0×10^{-4}	6.2×10^{-4}	6.7×10^{-4}
600°C	-	-	-	-	-

Table 48
(Continued)

k. n-Hexane

<u>Temperature</u>	<u>k₁</u>	<u>k₂</u>	<u>k₃</u>	<u>k₄</u>	<u>k_{av}</u>
700°C	3.4 × 10 ⁻¹	3.3 × 10 ⁻¹	3.7 × 10 ⁻¹	3.7 × 10 ⁻¹	3.5 × 10 ⁻¹
667°C	1.3 × 10 ⁻¹	1.3 × 10 ⁻¹	1.6 × 10 ⁻¹	1.6 × 10 ⁻¹	1.5 × 10 ⁻¹
633°C	5.3 × 10 ⁻²	4.8 × 10 ⁻²	6.1 × 10 ⁻²	6.8 × 10 ⁻²	5.8 × 10 ⁻²
600°C	2.0 × 10 ⁻²	2.1 × 10 ⁻²	2.2 × 10 ⁻²	2.1 × 10 ⁻²	2.1 × 10 ⁻²

l. 2-Methylpentane

<u>Temperature</u>	<u>k₁</u>	<u>k₂</u>	<u>k₃</u>	<u>k₄</u>	<u>k_{av}</u>
700°C	4.1 × 10 ⁻¹	4.0 × 10 ⁻¹	4.6 × 10 ⁻¹	4.5 × 10 ⁻¹	4.3 × 10 ⁻¹
667°C	1.5 × 10 ⁻¹	1.6 × 10 ⁻¹	1.9 × 10 ⁻¹	2.0 × 10 ⁻¹	1.8 × 10 ⁻¹
633°C	6.5 × 10 ⁻²	6.3 × 10 ⁻²	6.9 × 10 ⁻²	7.1 × 10 ⁻²	6.7 × 10 ⁻²
600°C	2.3 × 10 ⁻²	2.2 × 10 ⁻²	2.8 × 10 ⁻²	2.8 × 10 ⁻²	2.5 × 10 ⁻²

Table 48
(Continued)

m. 1-Hexene

<u>Temperature</u>	<u>k₁</u>	<u>k₂</u>	<u>k₃</u>	<u>k₄</u>	<u>k_{av}</u>
700°C	1.14	1.17	1.34	1.31	1.24
667°C	5.4 × 10 ⁻¹	5.1 × 10 ⁻¹	4.8 × 10 ⁻¹	4.9 × 10 ⁻¹	5.1 × 10 ⁻¹
633°C	1.8 × 10 ⁻¹	1.7 × 10 ⁻¹	1.8 × 10 ⁻¹	1.9 × 10 ⁻¹	1.8 × 10 ⁻¹
600°C	5.9 × 10 ⁻²	5.9 × 10 ⁻²	7.3 × 10 ⁻²	7.4 × 10 ⁻²	6.6 × 10 ⁻²

n. cis-2-Hexene

<u>Temperature</u>	<u>k₁</u>	<u>k₂</u>	<u>k₃</u>	<u>k₄</u>	<u>k_{av}</u>
700°C	1.49	1.51	1.70	1.76	1.62
667°C	5.9 × 10 ⁻¹	6.1 × 10 ⁻¹	5.8 × 10 ⁻¹	6.0 × 10 ⁻¹	6.0 × 10 ⁻¹
633°C	1.8 × 10 ⁻¹	1.9 × 10 ⁻¹	1.9 × 10 ⁻¹	1.9 × 10 ⁻¹	1.9 × 10 ⁻¹
600°C	4.8 × 10 ⁻²	4.6 × 10 ⁻²	5.6 × 10 ⁻²	5.5 × 10 ⁻²	5.1 × 10 ⁻²

Table 48
(Continued)

o. trans-2-Hexene

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	1.46	1.40	1.72	1.70	1.56
667°C	5.3×10^{-1}	5.3×10^{-1}	6.3×10^{-1}	6.6×10^{-1}	5.9×10^{-1}
633°C	1.8×10^{-1}	1.8×10^{-1}	1.5×10^{-1}	2.1×10^{-1}	1.8×10^{-1}
600°C	4.6×10^{-2}	4.6×10^{-2}	5.5×10^{-2}	5.6×10^{-2}	5.1×10^{-1}

p. Cyclohexane

<u>Temperature</u>	<u>k_1</u>	<u>k_2</u>	<u>k_3</u>	<u>k_4</u>	<u>k_{av}</u>
700°C	2.7×10^{-2}	2.8×10^{-2}	2.9×10^{-2}	2.7×10^{-2}	2.8×10^{-2}
667°C	8.1×10^{-3}	7.3×10^{-3}	9.5×10^{-3}	6.1×10^{-3}	7.8×10^{-3}
633°C	1.7×10^{-3}	1.7×10^{-3}	1.1×10^{-3}	1.4×10^{-3}	1.5×10^{-3}
600°C	-	-	-	-	-

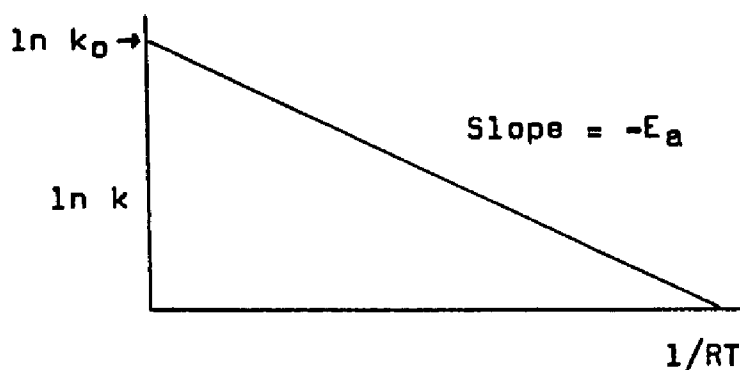
Energies of Activation

Through the use of the Arrhenius equation and knowledge of the rate constant at several temperatures, the energy of activation and frequency factor of the overall first order decomposition may be obtained. This equation, in its most useful linear form, is as follows:

$$\ln k = \ln k_0 - E_a (1/RT)$$

where k = rate constant (sec^{-1})
 k_0 = frequency factor (sec^{-1})
 E_a = energy of activation (kcal/mole)
 R = gas constant (cal/deg. mole)
 T = temperature ($^{\circ}\text{K}$)

A graphical representation of this equation is given below:



The best least squares fit of the data was made through substitution of the proper values of k , R and T in the Arrhenius equation for each condition of analysis using a suitable computer program (see Appendix III). The program was run on an IBM 360 computer. In addition to providing an estimate of the slope ($-E_a$) and the intercept ($\ln k_0$),

it provided terms which enabled a statistical evaluation of the slope in the form of a regression analysis. The essential output from the computer is given in Table 49.

The regression mean square represents the variability which was removed from the data through the fitting of the constant b_0 in the linear equation:

$$y = b_0x + b_1$$

The residual mean square is a measure of the variability remaining in the system after the linear relationship has been fitted. The ratio of these terms, the F value, provides a number which may be compared with a table value at a selected probability level. If the calculated F value exceeds the table value, the slope is considered significant with respect to the amount of variability remaining in the system at the selected probability level. This, in effect, serves as a measure of the adequacy of the linear relationship.

A 99% probability level was chosen and the F values corresponding to this level are as follows:

For a system of 6 data points $F_{.99} = 21.20$

For a system of 8 data points $F_{.99} = 13.74$.

Since all the calculated values (Table 49) exceed the critical F value, the slope is significantly different from zero, and the linear representation of the data is adequate for each data set.

In order to determine whether the slopes obtained at different flow rates are homogeneous, a t test was performed according to the method outlined by Volk.⁸⁸

Table 49

Computer Output for Least Squares Fit and Regression Analysis

<u>Run No.*</u>	<u>No. Obs.</u>	<u>ln k₀ Intercept</u>	<u>-E_a Slope</u>	<u>Regression Mean Square</u>	<u>Residual Mean Square</u>	<u>F Ratio</u>	<u>Residual Sum of Squares</u>
001	8	14.47399	37058	5.33600	0.00252	2113.5	0.01515
002	8	14.53498	36750	5.24744	0.00312	1680.3	0.01874
003	8	23.82465	49126	9.37695	0.00888	1056.2	0.05327
004	8	21.54692	44523	7.70213	0.00205	3765.5	0.01227
005	8	22.77605	45379	8.00119	0.02528	316.5	0.15167
006	8	19.29077	40638	6.41660	0.03200	200.5	0.19197
007	8	17.30731	34951	4.74382	0.00274	1729.9	0.01645
008	8	16.81004	33705	4.41399	0.00337	1308.6	0.02024
009	6	30.29929	60823	13.23411	0.00765	1729.0	0.03062
010	8	30.68063	61644	14.76498	0.02991	493.6	0.17947
011	8	21.63748	44982	7.86197	0.01434	548.4	0.08602
012	8	22.67731	46599	8.43740	0.00875	963.9	0.05252
013	8	29.13199	57065	12.65268	0.06273	201.7	0.37641
014	8	25.78105	50565	9.93462	0.02359	421.1	0.14156
015	8	23.22900	46798	8.50948	0.04520	188.2	0.27122
016	8	21.67087	43654	7.40462	0.01244	595.1	0.07466

Table 49
(Continued)

<u>Run No.*</u>	<u>No. Obs.</u>	<u>ln k₀</u> <u>Intercept</u>	<u>-E_a</u> <u>Slope</u>	<u>Regression</u> <u>Mean Square</u>	<u>Residual</u> <u>Mean Square</u>	<u>F</u> <u>Ratio</u>	<u>Residual</u> <u>Sum of Squares</u>
017	8	32.35185	64210	16.01952	0.01170	1369.7	0.07018
018	8	28.96783	57914	13.03223	0.04087	318.9	0.24520
019	6	34.67920	75490	8.23646	0.02179	378.0	0.08717
020	6	43.14827	91201	12.02158	0.01592	755.0	0.06369
021	8	23.12425	46963	8.56959	0.00515	1665.3	0.03088
022	8	23.92966	48144	9.00597	0.00262	3439.6	0.01571
023	8	24.17931	48554	9.16015	0.00195	4692.3	0.01171
024	8	23.85539	47676	8.83174	0.00207	4273.9	0.01240
025	8	26.51849	50924	10.07605	0.00355	2835.5	0.02132
026	8	25.50169	48906	9.29315	0.00505	1841.3	0.03028
027	8	30.89813	58827	13.44600	0.00796	1688.4	0.04778
028	8	30.55069	58049	13.09297	0.00052	25268.0	0.00311
029	8	30.24742	47732	12.95018	0.00577	2245.2	0.03461
030	8	30.97188	58822	13.44390	0.01037	1296.3	0.06223
031	6	34.34764	73354	7.77699	0.00264	2945.8	0.01056
032	6	39.21455	82655	9.87432	0.04553	216.9	0.18213

Table 49
(Continued)

*To simplify the reporting of the data, the various experimental sets of data have been coded in the following way:

<u>Run No.</u>	<u>Compound</u>	<u>Condition</u>
001	Methanol	IIa
002	Methanol	IIb
003	Ethanol	Ia
004	Ethanol	Ib
005	1-Propanol	Ia
006	1-Propanol	Ib
007	2-Propanol	Ia
008	2-Propanol	Ib
009	<u>n</u> -Pentane	Ia
010	<u>n</u> -Pentane	Ib
011	Isopentane	Ia
012	Isopentane	Ib
013	1-Pentene	Ia
014	1-Pentene	Ib
015	<u>cis</u> -2-Pentene	Ia
016	<u>cis</u> -2-Pentene	Ib
017	<u>trans</u> -2-Pentene	Ia
018	<u>trans</u> -2-Pentene	Ib
019	Cyclopentane	IIa
020	Cyclopentane	IIb

Table 49
(Continued)

<u>Run No.</u>	<u>Compound</u>	<u>Condition</u>
021	<u>n</u> -Hexane	IIa
022	<u>n</u> -Hexane	IIb
023	2-Methylpentane	IIa
024	2-Methylpentane	IIb
025	1-Hexene	IIa
026	1-Hexene	IIb
027	<u>cis</u> -2-Hexene	IIa
028	<u>cis</u> -2-Hexene	IIb
029	<u>trans</u> -2-Hexene	IIa
030	<u>trans</u> -2-Hexene	IIb
031	Cyclohexane	IIa
032	Cyclohexane	IIb

In order to do this, the pooled estimate of the standard deviation was calculated for each pair of data sets using the following expression:

$$S \hat{y}_p = \left[\frac{(n_1-2) S^2 \hat{y}_1 + (n_2-2) S^2 \hat{y}_2}{(n_1-2) + (n_2-2)} \right]^{\frac{1}{2}}$$

where $S \hat{y}_p$ = pooled estimate of the standard deviation

n_1 = number of observations at flow rate = 30cc/min

n_2 = number of observations at flow rate = 40cc/min

$S^2 \hat{y}_1$ = variance of data set at flow rate = 30 cc/min

$S^2 \hat{y}_2$ = variance of data set at flow rate = 40 cc/min.

The expression for the \underline{t} test is:

$$\underline{t} = \frac{b_1 - b_2}{S \hat{y}_p \left[\frac{1}{Ex_1^2 - \frac{(Ex_1)^2}{n_1}} + \frac{1}{Ex_2^2 - \frac{(Ex_2)^2}{n_2}} \right]^{\frac{1}{2}}}$$

Calculated \underline{t} values are compared with $t_{\alpha=0.05}$ values in Table 50 for $(n_1 + n_2 - 4)$ degrees of freedom.

From Table 50 it may be seen that since the table \underline{t} value exceeds the calculated \underline{t} value for each pair of data sets with the exception of those for cyclopentane and cyclohexane, these slopes may be pooled for they are considered homogeneous, that is, representing the same function.

Table 50Values of t for the Comparison of Slopes

<u>Set</u>	<u>t_{calc.}</u>	<u>t_{α=0.05}</u>
001-002	0.256	2.179
003-004	2.146	2.179
005-006	1.235	2.179
007-008	0.985	2.179
009-010	0.245	2.228
011-012	0.664	2.179
013-014	1.379	2.179
015-016	0.816	2.179
017-018	1.712	2.179
019-020	4.837	2.306
021-022	0.855	2.179
023-024	0.864	2.179
025-026	1.356	2.179
027-028	0.527	2.179
029-030	0.535	2.179
031-032	2.534	2.306

In the case of cyclopentane and cyclohexane, the disparity is most probably due to the small % conversion, which makes accurate analysis very difficult. For the purpose of this work, these values will also be pooled, bearing in mind the fact that this data has less justification than the other work. Pooling these values can be justified only by going to a smaller α value ($\alpha = 0.001$). At this level of probability a table t (5.041) is larger than the calculated t .

The data obtained under two different flow rate conditions were then pooled and calculated in the same way as the individual sets. The results of interest from the computer are given in Table 51. Using the same reasoning given for the individual sets of data, the calculated F values may be compared with critical F values given below:

For a system of 12 data points $F_{.99} = 10.04$

For a system of 14 data points $F_{.99} = 9.33$

For a system of 16 data points $F_{.99} = 8.86$.

All calculated values far exceed the critical values, consequently the linear expression is adequate.

In order to more meaningfully report the energies of activation, confidence limits for the slope (which represents the energy of activation) were assigned using the expression:

$$b_1 \pm tSy/[Ex^2 - (Ex)^2/n]^{1/2}$$

where

b_1 = the experimental slope

t = standard value at $\alpha = 0.01$

$S\hat{y}$ = square root of the residual mean square

Ex^2 = sum of squares of $1/RT$ values

Table 51

Computer Output for Least Squares Fit and Regression Analysis (Pooled Data)

<u>Run No.*</u>	<u>No. Obs.</u>	<u>ln k₀ Intercept</u>	<u>-E_a Slope</u>	<u>Regression Mean Square</u>	<u>Residual Mean Square</u>	<u>F Ratio</u>	<u>Residual Sum of Squares</u>
033	16	14.50446	36904	10.58346	0.01741	607.8	0.24377
034	16	22.68578	46824	17.03792	0.02330	731.3	0.32616
035	16	20.53339	43008	14.37413	0.03065	468.9	0.42912
036	16	17.05867	34323	9.15485	0.01184	773.0	0.16580
037	14	30.43372	61139	28.06003	0.01895	1461.1	0.22734
038	16	22.15736	45791	16.29427	0.01733	940.1	0.24265
039	16	27.45647	53815	22.50520	0.05385	417.9	0.75395
040	16	22.44991	45226	15.89490	0.03317	479.2	0.46435
041	16	30.65976	61062	28.97473	0.02879	1006.4	0.40306
042	12	38.91362	83345	20.07965	0.03377	594.6	0.33772
043	16	23.52695	47554	17.57285	0.01092	1609.1	0.15289
044	16	24.01730	48115	17.99036	0.00874	2059.4	0.12230
045	16	26.01006	49915	19.36128	0.00630	3071.8	0.08824
046	16	30.72435	58438	26.53777	0.00540	4910.9	0.07565
047	16	30.60963	58277	26.39180	0.01187	2223.9	0.16614
048	12	36.78102	78005	17.58878	0.02953	595.6	0.29529

Table 51
(Continued)

*The experimental sets of data (pooled) are coded in the following way:

<u>Run No.</u>	<u>Compound</u>
033	Methanol
034	Ethanol
035	1-Propanol
036	2-Propanol
037	<u>n</u> -Pentane
038	Isopentane
039	1-Pentene
040	<u>cis</u> -2-Pentene
041	<u>trans</u> -2-Pentene
042	Cyclopentane
043	<u>n</u> -Hexane
044	2-Methylpentane
045	1-Hexene
046	<u>cis</u> -2-Hexene
047	<u>trans</u> -2-Hexene
048	Cyclohexane

$(Ex)^2$ = sum of $1/RT$ values squared

n = number of degrees of freedom.

The numerical values of t are 3.169 for data sets having 10 degrees of freedom, 3.055 for data sets having 12 degrees of freedom, and 2.977 for data sets having 14 degrees of freedom. The number of degrees of freedom for each data set is defined as the number of data points - 2. The energies of activation and their confidence limits are reported in Table 52.

Frequency Factors

According to the Arrhenius equation, the frequency factor is defined as the value of k when $1/RT$ approaches zero and is represented as k_0 . The computer output (Table 51) lists values for the intercept $\ln k_0$. From this value, the k_0 may be found for each compound studied. In the same manner as used for energies of activation, confidence limits were calculated for the frequency factor using the expression:

$$\hat{y}_1 \pm tS\hat{y} \left[(1/N) + \frac{(\bar{x}-x_1)^2}{Ex^2 - \frac{(Ex)^2}{n}} \right]^{\frac{1}{2}}$$

where \hat{y}_1 = estimated value of the frequency factor
 t = standard value at $\alpha = 0.01$
 $S\hat{y}$ = square root of the residual mean square
 n = number of degrees of freedom
 \bar{x} = average value of $1/RT$
 x_1 = value of $1/RT$ at the y intercept

Table 52
Energies of Activation Determined
from the Arrhenius Expression

<u>Compound</u>	<u>E_a (kcal/mole)</u>
Methanol	36.9±4.6
Ethanol	46.8±5.1
1-Propanol	43.0±5.9
2-Propanol	34.3±3.7
<u>n</u> -Pentane	61.1±4.9
Isopentane	45.8±4.4
1-Pentene	53.8±7.8
<u>cis</u> -2-Pentene	45.2±6.1
<u>trans</u> -2-Pentene	61.1±5.7
Cyclopentane	83.3±6.2
<u>n</u> -Hexene	47.6±3.6
2-Methylpentane	48.1±3.2
1-Hexene	49.9±2.7
<u>cis</u> -2-Hexene	58.4±2.5
<u>trans</u> -2-Hexene	58.3±3.7
Cyclohexene	78.0±5.8

Chosen t values correspond to those in the calculation of confidence limits for the energies of activation (page 136). The final data are given in Table 53.

Error Analysis

The F ratios reported in Table 51 indicate that the linear fit is a reasonable one. These values were computed as the ratio of the variability (expressed as the mean square associated with the slope) removed by fitting a linear relationship to the data to the residual variability of the system. The residual may be considered to be composed of variability due to two sources, random experimental error and systematic inability of the data to fit the chosen (linear) functional relationship. It is possible to calculate an F value comparing these two sources of variability according to the following expression:

$$F = \frac{\text{Mean Square Due to Lack of Fit}}{\text{Mean Square Due to Error}}$$

Significance of F at a chosen probability level would indicate that some variability still exists which cannot be explained by random error alone.

The sum of squares associated with random error is found using the following expression:

$$SS \text{ error} = \sum (y_1 - y_2)^2 / 2$$

where SS error = sum of squares associated with error

y_1 = ln k for 1st replicate

y_2 = ln k for 2nd replicate

Table 53
Frequency Factors Determined
from the Arrhenius Expression

<u>Compound</u>	<u>k_0</u>
Methanol	$2.0 \times 10^6 \pm 1.1 \times 10^1$
Ethanol	$0.7 \times 10^{10} \pm 1.6 \times 10^1$
1-Propanol	$0.8 \times 10^9 \pm 2.5 \times 10^1$
2-Propanol	$0.3 \times 10^8 \pm 0.7 \times 10^1$
<u>n</u> -Pentane	$1.6 \times 10^{13} \pm 1.4 \times 10^1$
Isopentane	$0.4 \times 10^{10} \pm 1.1 \times 10^1$
1-Pentene	$0.8 \times 10^{12} \pm 7.2 \times 10^1$
<u>cis</u> -2-Pentene	$0.6 \times 10^{10} \pm 2.9 \times 10^1$
<u>trans</u> -2-Pentene	$2.1 \times 10^{13} \pm 2.3 \times 10^1$
Cyclopentane	$7.9 \times 10^{16} \pm 2.8 \times 10^1$
<u>n</u> -Hexane	$0.2 \times 10^{11} \pm 0.7 \times 10^1$
2-Methylpentane	$0.3 \times 10^{11} \pm 0.6 \times 10^1$
1-Hexene	$0.2 \times 10^{12} \pm 0.4 \times 10^1$
<u>cis</u> -2-Hexene	$2.2 \times 10^{13} \pm 0.4 \times 10^1$
<u>trans</u> -2-Hexene	$1.9 \times 10^{13} \pm 0.7 \times 10^1$
Cyclohexane	$9.4 \times 10^{16} \pm 2.2 \times 10^1$

From this, the mean square due to error may be represented by

$$M.S.error = SS_{error} / n$$

where n is the number of degrees of freedom associated with error.

The mean square due to lack of fit is found by difference:

$$M.S.l.o.f. = M.S.residual - M.S.error$$

The residual mean square values are listed in Table 51. The calculated F values are given in Table 54, along with the critical F value at the 95 percent confidence level. It may be seen that in all cases except cyclopentane and trans-2-hexene the calculated F value exceeds the critical value. At the 95 percent confidence level, it may be said that there does exist variability other than random experimental error. The sources of this variability will be considered in a later discussion.

Determination of Thermodynamic

Properties of Activation

Procedure

Having obtained values for the energy of activation and frequency factor, the thermodynamic properties of activation may be calculated for each decomposition reaction using the following expression:

Table 54

F Value for Comparison of Lack of Fit and Random Error

<u>Run No.</u>	<u>Compound</u>	<u>F_{calc}, $\alpha = 0.05$</u>	<u>F_{crit}, $\alpha = 0.05$</u>
033	Methanol	13.363	3.581
034	Ethanol	11.653	3.581
035	1-Propanol	13.369	3.581
036	2-Propanol	40.367	3.581
037	<u>n</u> -Pentane	6.832	3.972
038	Isopentane	7.188	3.581
039	1-Pentene	11.892	3.581
040	<u>cis</u> -2-Pentene	86.590	3.581
041	<u>trans</u> -2-Pentene	111.540	3.581
042	Cyclopentane	3.939	4.120
043	<u>n</u> -Hexane	12.410	3.581
044	2-Methylpentane	18.943	3.581
045	1-Hexene	22.869	3.581
046	<u>cis</u> -2-Hexene	24.197	3.581
047	<u>trans</u> -2-Hexene	3.026	3.581
048	Cyclohexane	5.903	4.120

$$\Delta H^\ddagger = E_a - nRT$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T}$$

$$\Delta G^\ddagger = \left(\frac{kT}{h}\right) e^{-\Delta F^\ddagger/RT}$$

where

ΔH^\ddagger = change in enthalpy of activation (kcal/mole)

ΔS^\ddagger = change in entropy of activation (e.u.)

ΔG^\ddagger = change in free energy of activation (kcal/mole)

E_a = energy of activation (kcal/mole)

n = # moles

R = molar gas constant

T = temperature ($^{\circ}\text{K}$)

k = Boltzmann's constant

h = Planck's constant

All calculations were carried out for a temperature of 973°K .

Results

Values for ΔH^\ddagger , ΔG^\ddagger , and ΔS^\ddagger were calculated for the thermal decomposition of each of the sixteen compounds studied. These values are given in Table 55.

Table 55

Thermodynamic Properties of Activation at 973°K

<u>Compound</u>	<u>ΔH^\ddagger (kcal/mole)</u>	<u>ΔG^\ddagger (kcal/mole)</u>	<u>ΔS^\ddagger (e.u.)</u>
Methanol	35.0	68.2	-34.1
Ethanol	44.9	62.3	-17.9
1-Propanol	41.1	62.6	-22.2
2-Propanol	32.4	60.7	-29.1
<u>n</u> -Pentane	59.2	61.6	- 2.5
Isopentane	43.9	62.3	-18.9
1-Pentene	51.9	60.0	- 8.4
<u>cis</u> -2-Pentene	43.3	61.1	-18.3
<u>trans</u> -2-Pentene	59.1	61.1	- 2.0
Cyclopentane	81.4	67.4	+14.4
<u>n</u> -Hexene	45.6	61.4	-16.2
2-Methylpentane	46.2	61.0	-15.2
1-Hexene	48.0	58.9	-11.3
<u>cis</u> -2-Hexene	56.5	58.3	- 1.9
<u>trans</u> -2-Hexene	56.3	58.4	- 2.1
Cyclohexane	76.1	66.2	+10.1

Relative Distribution of Products

Procedure

The areas obtained for products of the thermal decomposition reaction, when corrected using the thermal conductivity weight factors, represent the relative weights of the various compounds present. It is then possible, using a normalization technique, to obtain the weight percent of the total amount decomposed for each product according to the following expression:

$$\text{Weight \% of A} = \frac{\text{Corrected Area of A} \times 100}{\text{Sum of Corrected Areas of Products}}$$

When the weight % is known, the relative number of moles of each product formed may be found:

$$\text{Relative \# Moles} = \frac{\text{Weight \% of A}}{\text{Molecular Weight of A}}$$

Results

Weight percent values were calculated for the decomposition of the sixteen compounds studied. These numbers are listed in Table 56 as a function of temperature and flow rate for each compound. To facilitate consideration as an analytical tool, the values at 700°C and a flow rate of 30 cc/min were converted to a series of bar graphs reflecting the relative number of moles of each product. This was accomplished by adjusting the relative number of moles in

such a way that the largest value in a particular decomposition had an arbitrary "intensity" of 100 units. These data are presented in Appendix IV.

Table 56

Relative Product Distribution (Weight Percent of Total Amount Decomposed)
as a Function of Temperature and Flow Rate

a. Methanol

<u>Product</u>	<u>700°C</u> <u>Cond.</u> <u>Ia</u>	<u>700°C</u> <u>Cond.</u> <u>Ib</u>	<u>667°C</u> <u>Cond.</u> <u>Ia</u>	<u>667°C</u> <u>Cond.</u> <u>Ib</u>	<u>633°C</u> <u>Cond.</u> <u>Ia</u>	<u>633°C</u> <u>Cond.</u> <u>Ib</u>	<u>600°C</u> <u>Cond.</u> <u>Ia</u>	<u>600°C</u> <u>Cond.</u> <u>Ib</u>
CO/Hydrogen	15.4	9.1	14.6	5.7	0.0	0.0	0.0	0.0
Methane	3.9	3.4	5.1	3.4	4.4	6.1	3.1	4.5
Formaldehyde	69.9	73.1	73.0	75.9	85.3	75.5	81.2	81.8
Water	11.2	14.3	8.0	14.9	10.3	18.4	15.6	13.6

b. Ethanol

<u>Product</u>	<u>700°C</u> <u>Cond.</u> <u>Ia</u>	<u>700°C</u> <u>Cond.</u> <u>Ib</u>	<u>667°C</u> <u>Cond.</u> <u>Ia</u>	<u>667°C</u> <u>Cond.</u> <u>Ib</u>	<u>633°C</u> <u>Cond.</u> <u>Ia</u>	<u>633°C</u> <u>Cond.</u> <u>Ib</u>	<u>600°C</u> <u>Cond.</u> <u>Ia</u>	<u>600°C</u> <u>Cond.</u> <u>Ib</u>
CO/Hydrogen	5.8	4.7	3.5	2.5	1.8	1.4	0.0	0.0
Methane	5.8	5.5	4.3	3.7	3.9	4.3	2.1	3.2
Ethylene	13.1	13.4	12.4	11.7	11.9	12.5	6.6	12.1
Acetylene	0.9	0.5	0.8	0.8	1.0	0.9	0.0	0.0
Water	9.6	9.2	6.0	8.0	8.9	3.0	0.0	0.0
Acetaldehyde	64.8	66.8	73.1	73.5	72.5	78.1	91.5	84.6

Table 56
(Continued)

c. 1-Propanol

Product	700°C Cond. Ia	700°C Cond. Ib	667°C Cond. Ia	667°C Cond. Ib	633°C Cond. Ia	633°C Cond. Ib	600°C Cond. Ia	600°C Cond. Ib
CO/Hydrogen	2.4	2.1	2.1	0.9	0.2	0.2	0.0	0.0
Methane	12.8	13.2	12.7	13.7	13.8	14.8	14.6	16.4
Ethylene	10.6	10.3	9.3	8.6	9.1	8.4	10.8	10.4
Acetylene	2.7	2.3	2.6	3.1	5.1	3.0	3.5	3.5
Water	8.0	7.7	7.2	7.0	4.4	2.6	10.6	0.0
Propylene	27.5	27.8	28.0	27.0	28.3	29.7	29.0	31.0
Methanol	3.9	3.3	3.7	2.6	1.5	2.2	0.0	0.0
Acetaldehyde	28.8	29.6	30.6	32.6	33.0	32.7	31.7	38.9
Propionaldehyde	3.4	3.8	3.9	4.7	5.1	6.6	0.0	0.0

Table 56
(Continued)

d. 2-Propanol

<u>Product</u>	<u>700°C</u> <u>Cond.</u> <u>Ia</u>	<u>700°C</u> <u>Cond.</u> <u>Ib</u>	<u>667°C</u> <u>Cond.</u> <u>Ia</u>	<u>667°C</u> <u>Cond.</u> <u>Ib</u>	<u>633°C</u> <u>Cond.</u> <u>Ia</u>	<u>633°C</u> <u>Cond.</u> <u>Ib</u>	<u>600°C</u> <u>Cond.</u> <u>Ia</u>	<u>600°C</u> <u>Cond.</u> <u>Ib</u>
CO/Hydrogen	1.3	0.9	0.9	0.9	0.9	0.6	1.3	0.7
Methane	3.4	3.2	2.6	2.4	2.0	2.1	1.9	1.9
Ethylene	1.5	1.1	0.7	0.6	0.3	0.4	0.3	0.4
Acetylene	0.2	0.1	0.1	0.1	0.0	0.0	0.0	0.0
Water	8.4	8.2	7.3	7.4	6.1	6.0	6.3	5.3
Propylene	22.6	22.5	20.5	21.0	19.2	18.4	19.9	17.2
Acetaldehyde	3.8	3.7	4.1	3.9	2.5	3.2	3.2	3.6
Acetone	58.9	60.4	63.9	63.7	69.0	69.3	67.0	70.9

Table 56
(Continued)

e. n-Pentane

<u>Product</u>	700°C Cond. <u>Ia</u>	700°C Cond. <u>Ib</u>	667°C Cond. <u>Ia</u>	667°C Cond. <u>Ib</u>	633°C Cond. <u>Ia</u>	633°C Cond. <u>Ib</u>	600°C Cond. <u>Ia</u>	600°C Cond. <u>Ib</u>
Methane	9.2	9.3	8.5	8.3	7.0	7.4	5.2	4.7
Ethylene	26.3	28.2	24.4	24.0	17.6	17.5	11.0	10.0
Acetylene	12.5	11.6	12.5	12.2	14.6	12.5	12.0	9.3
Ethane	4.1	2.6	8.1	7.1	20.3	24.9	48.5	58.7
Propylene	33.2	33.7	33.9	32.2	29.2	28.3	23.4	17.3
Butane	14.7	14.7	12.5	16.1	10.8	9.4	0.0	0.0

Table 56
(Continued)

f. Isopentane

<u>Product</u>	<u>700°C Cond. Ia</u>	<u>700°C Cond. Ib</u>	<u>667°C Cond. Ia</u>	<u>667°C Cond. Ib</u>	<u>633°C Cond. Ia</u>	<u>633°C Cond. Ib</u>	<u>600°C Cond. Ia</u>	<u>600°C Cond. Ib</u>
Methane	14.4	14.8	13.8	13.8	12.5	9.8	9.4	9.8
Ethylene	10.9	12.0	9.6	9.9	8.2	5.9	5.3	3.7
Acetylene	3.6	2.9	4.1	4.0	4.0	2.5	2.9	2.4
Ethane	1.9	4.5	7.2	9.2	17.3	22.4	40.0	51.6
Propylene	20.2	19.8	18.8	17.8	14.8	11.5	8.6	5.3
Butane	28.9	28.4	26.1	26.0	24.0	22.7	15.6	12.6
1- & 2-Butene	20.1	17.6	20.3	19.2	19.2	25.2	18.2	14.6

Table 56
(Continued)

g. 1-Pentene

<u>Product</u>	<u>700°C Cond. Ia</u>	<u>700°C Cond. Ib</u>	<u>667°C Cond. Ia</u>	<u>667°C Cond. Ib</u>	<u>633°C Cond. Ia</u>	<u>633°C Cond. Ib</u>	<u>600°C Cond. Ia</u>	<u>600°C Cond. Ib</u>
Methane	4.1	4.2	5.8	5.2	5.5	5.7	4.8	4.3
Ethylene	28.8	28.4	22.8	21.6	20.0	18.7	11.9	13.5
Acetylene	5.1	5.3	8.8	8.2	9.6	9.9	6.4	8.3
Ethane	2.9	5.5	3.5	4.9	2.7	2.4	39.9	25.0
Propylene	26.2	27.2	21.4	21.1	21.2	20.9	11.4	16.8
Butane/1,3- Butadiene	32.8	29.5	37.7	39.2	41.1	42.4	25.6	32.2

Table 56
(Continued)

h. cis-2-Pentene

<u>Product</u>	700°C Cond. <u>Ia</u>	700°C Cond. <u>Ib</u>	667°C Cond. <u>Ia</u>	667°C Cond. <u>Ib</u>	633°C Cond. <u>Ia</u>	633°C Cond. <u>Ib</u>	600°C Cond. <u>Ia</u>	600°C Cond. <u>Ib</u>
Methane	16.8	16.2	19.9	18.0	16.3	15.0	14.5	18.3
Ethylene	5.5	5.1	3.3	4.0	3.5	2.8	1.9	3.0
Acetylene	4.4	3.4	4.6	3.9	3.8	4.0	4.3	4.3
Ethane	1.4	3.5	5.1	5.2	9.2	15.6	23.6	13.3
Propylene	7.2	7.2	5.9	5.2	5.2	4.7	3.1	5.9
Butane/1,3- Butadiene	64.6	64.5	61.3	63.8	62.0	58.0	52.7	55.6

Table 56
(Continued)

1. trans-2-Pentene

<u>Product</u>	<u>700°C Cond. Ia</u>	<u>700°C Cond. Ib</u>	<u>667°C Cond. Ia</u>	<u>667°C Cond. Ib</u>	<u>633°C Cond. Ia</u>	<u>633°C Cond. Ib</u>	<u>600°C Cond. Ia</u>	<u>600°C Cond. Ib</u>
Methane	16.3	15.3	17.3	18.1	15.1	14.6	11.7	18.3
Ethylene	5.5	5.1	3.1	4.1	2.9	2.7	2.4	1.2
Acetylene	3.7	3.6	4.0	5.0	4.1	3.8	3.8	2.8
Ethane	3.1	2.7	2.2	5.2	15.8	26.0	19.0	5.7
Propylene	7.6	7.0	4.8	6.0	4.1	5.0	4.1	2.8
Butane/1,3- Butadiene	63.8	66.3	68.7	61.6	58.2	48.3	59.7	69.1

Table 56
(Continued)

j. Cyclopentane

<u>Product</u>	<u>700°C Cond. IIa</u>	<u>700°C Cond. IIb</u>	<u>667°C Cond. IIa</u>	<u>667°C Cond. IIb</u>	<u>633°C Cond. IIa</u>	<u>633°C Cond. IIb</u>	<u>600°C Cond. IIa</u>	<u>600°C Cond. IIb</u>
Methane	1.0	1.5	1.2	3.4	4.0	11.1	-	-
Ethane/Ethylene	42.7	43.8	42.9	44.8	40.0	55.5	-	-
Propane/Propylene	49.7	50.2	50.0	46.6	48.0	44.4	-	-
1- & 2-Butene	6.7	4.5	7.1	6.9	8.0	0.0	-	-

k. n-Hexane

<u>Product</u>	<u>700°C Cond. IIa</u>	<u>700°C Cond. IIb</u>	<u>667°C Cond. IIa</u>	<u>667°C Cond. IIb</u>	<u>633°C Cond. IIa</u>	<u>633°C Cond. IIb</u>	<u>600°C Cond. IIa</u>	<u>600°C Cond. IIb</u>
Methane	11.1	11.2	11.5	11.9	11.1	10.7	13.6	14.0
Ethane/Ethylene	39.1	39.3	36.0	38.0	34.8	35.0	34.8	38.1
Propane/Propylene	25.7	25.9	26.9	26.2	28.0	26.7	27.8	25.2
1- & 2-Butene/ Butane	17.0	16.7	17.6	17.2	17.7	20.4	17.5	16.0
1,3-Butadiene	0.8	0.3	1.1	0.0	0.0	0.0	0.0	0.0
1-Pentene	6.3	6.7	6.9	6.9	8.3	7.4	6.3	7.3

Table 56
(Continued)

1. 2-Methylpentane

<u>Product</u>	<u>700°C</u> <u>Cond.</u> <u>Ila</u>	<u>700°C</u> <u>Cond.</u> <u>Iib</u>	<u>667°C</u> <u>Cond.</u> <u>Ila</u>	<u>667°C</u> <u>Cond.</u> <u>Iib</u>	<u>633°C</u> <u>Cond.</u> <u>Ila</u>	<u>633°C</u> <u>Cond.</u> <u>Iib</u>	<u>600°C</u> <u>Cond.</u> <u>Ila</u>	<u>600°C</u> <u>Cond.</u> <u>Iib</u>
Methane	8.6	7.8	7.5	7.0	7.2	6.3	8.1	7.8
Ethane/Ethylene	19.3	19.6	17.7	17.9	17.8	16.4	16.5	17.3
Propane/Propylene	35.4	35.4	34.7	35.9	34.9	36.0	35.8	35.0
Isobutene	0.6	0.8	1.3	1.3	2.3	3.4	6.7	6.7
1- & 2-Butene/ Butane	21.5	21.7	23.0	22.3	23.2	24.3	25.1	22.7
1,3-Butadiene	0.9	1.0	1.0	0.7	0.6	0.5	0.9	0.0
3-Methyl-1- butene	3.6	3.3	4.2	4.4	4.5	4.1	2.3	3.5
1- & 2-Pentene	10.1	10.3	10.6	10.5	9.5	9.3	5.1	7.6

Table 56
(Continued)

m. 1-Hexene

<u>Product</u>	700°C	700°C	667°C	667°C	633°C	633°C	600°C	600°C
	<u>Cond.</u> <u>Iia</u>	<u>Cond.</u> <u>Iib</u>	<u>Cond.</u> <u>Iia</u>	<u>Cond.</u> <u>Iib</u>	<u>Cond.</u> <u>Iia</u>	<u>Cond.</u> <u>Iib</u>	<u>Cond.</u> <u>Iia</u>	<u>Cond.</u> <u>Iib</u>
Methane	5.7	5.3	5.5	4.9	5.1	5.0	4.6	5.0
Ethane/Ethylene	28.4	28.9	28.0	26.4	26.3	25.9	21.3	22.8
Propane/Propylene	32.0	31.4	30.6	30.2	29.3	29.3	29.1	26.1
Isobutene	0.3	0.3	0.5	0.6	1.5	1.8	4.4	4.9
1- & 2-Butene	12.1	12.8	11.4	11.3	11.1	11.2	11.3	11.2
1,3-Butadiene	12.0	12.3	13.7	13.9	14.5	14.6	15.9	15.9
3-Methyl-1-butene	0.3	0.1	0.1	0.1	0.0	0.0	0.0	0.0
1-Pentene	7.8	7.9	9.0	10.8	10.5	10.6	11.2	12.7
1,3-Pentadiene	1.3	1.1	1.2	1.8	1.7	1.5	2.3	1.6

Table 56
(Continued)

n. cis-2-Hexene

<u>Product</u>	700°C Cond. <u>Ila</u>	700°C Cond. <u>Iib</u>	667°C Cond. <u>Ila</u>	667°C Cond. <u>Iib</u>	633°C Cond. <u>Ila</u>	633°C Cond. <u>Iib</u>	600°C Cond. <u>Ila</u>	600°C Cond. <u>Iib</u>
Methane	7.5	6.6	7.4	7.0	7.7	7.9	9.4	9.6
Ethane/Ethylene	26.8	27.4	25.8	25.2	23.7	24.4	24.2	23.4
Propane/Propylene	7.3	7.1	6.5	5.6	4.8	4.3	5.5	3.9
1- & 2-Butene	8.5	9.1	9.2	8.5	7.3	8.2	6.3	6.3
1,3-Butadiene	21.1	19.9	19.2	20.3	20.6	20.2	22.1	20.5
3-Methyl-1-butene	3.5	3.5	3.7	3.4	3.5	3.7	3.9	4.2
1- & 2-Pentene	8.5	8.4	6.7	6.4	5.7	4.9	1.6	4.3
1,3-Pentadiene	13.8	13.9	17.6	19.2	21.3	22.4	22.4	24.7
4-Methyl-1-pentene	3.0	4.2	4.0	4.5	5.5	4.2	4.8	3.4

Table 56
(Continued)

o. trans-2-Hexene

<u>Product</u>	700°C Cond. <u>Ila</u>	700°C Cond. <u>Iib</u>	667°C Cond. <u>Ila</u>	667°C Cond. <u>Iib</u>	633°C Cond. <u>Ila</u>	633°C Cond. <u>Iib</u>	600°C Cond. <u>Ila</u>	600°C Cond. <u>Iib</u>
Methane	7.8	7.7	8.4	7.7	8.9	7.8	9.4	10.4
Ethane/Ethylene	27.4	26.9	24.8	24.4	23.1	23.0	23.5	23.3
Propane/Propylene	7.4	7.2	6.0	6.6	5.4	4.8	3.6	4.0
1- & 2-Butene	9.3	8.8	8.0	8.6	7.6	7.4	6.6	6.6
1,3-Butadiene	20.3	19.6	20.4	19.6	20.1	20.2	21.3	20.5
3-Methyl-1-butene	3.5	3.7	3.6	3.8	4.0	3.8	3.9	4.3
1- & 2-Pentene	7.4	7.9	6.1	6.1	5.1	6.2	3.1	3.0
1,3-Pentadiene	14.7	15.2	19.4	19.8	21.7	22.5	25.1	24.9
4-Methyl-1-pentene	2.2	3.0	3.4	3.4	4.2	4.5	3.7	3.3

Table 56
(Continued)

p. Cyclohexane

<u>Product</u>	<u>700°C Cond. IIa</u>	<u>700°C Cond. IIb</u>	<u>667°C Cond. IIa</u>	<u>667°C Cond. IIb</u>	<u>633°C Cond. IIa</u>	<u>633°C Cond. IIb</u>	<u>600°C Cond. IIa</u>	<u>600°C Cond. IIb</u>
Methane	1.6	1.9	2.2	2.5	2.0	5.3	-	-
Ethane/Ethylene	34.2	34.5	31.8	33.1	31.4	31.5	-	-
Propane/Propylene	18.7	19.4	22.9	19.8	27.5	26.3	-	-
1- & 2-Butene	3.0	2.9	4.0	5.0	0.0	0.0	-	-
1,3-Butadiene	42.7	41.5	39.5	40.5	39.2	36.8	-	-

DISCUSSION

The work which has been accomplished here has evaluated the utility of pyrolysis-gas chromatography as a method for the study of thermal decomposition reactions. These reactions, in turn, produced chromatograms which were useful for purposes of qualitative analysis. It has been demonstrated that the decomposition patterns which have been observed here were in agreement with theoretical predictions. In addition, these pyrolysis studies yielded product distributions which were similar to those obtained using various types of flow systems. This indicates that experimental disagreement among different laboratories may be less serious than previously expected.

In this section the theoretical predictions and experimental results are compared. The kinetics and mechanism of the decomposition reactions is examined and various kinetic parameters are calculated. The reproducibility of the method and its utility as an analytical tool are considered. Suggestions for further improvement of the technique are made.

Theories of Thermal Decomposition

The mechanisms by which simple organic compounds thermally decompose are not well understood. A large quantity of conflicting data, dating back into the 1860's with the work of Berthelot,⁸⁹ has been published in the chemical literature. Part of the difficulty is due to the fact that a

large number of different experimental setups have been used for the investigation of similar systems. Little effort has been made to correlate or compare these data on a common basis. In addition, the basic theory is still uncertain. The existence of a free-radical mechanism is felt to be more probable than a molecular one; however, this has not been conclusively proven. No single theory has been developed which is successful in explaining the thermal decomposition of a series of homologous compounds, let alone a significant fraction of unimolecular, first order decompositions which have been experimentally studied.

Due to the fact that a free-radical mechanism appears to be more probable, the basic concepts of this process will be considered first.

Free radicals are formed from stable molecular species most commonly through the homolytic cleavage of a carbon-carbon bond, a carbon-oxygen bond or a carbon-hydrogen bond. The electronic configuration of the resulting species is unstable, and the resulting radical is strongly electrophilic and, therefore, quite reactive. The existence of organic free radicals was first demonstrated by Gomberg⁹⁰ in 1900. Subsequent discovery of alkyl free radicals⁹¹ in 1929 stimulated interest in the theory and practice of free-radical reactions. Rice⁷⁸ attempted to formulate a decomposition mechanism for organic compounds in terms of free-radical reactions. Later, Rice and Herzfeld⁷⁹ made certain modifications of the original theory. In 1943, Kossiakoff and

Rice⁸⁰ expanded and modified the early theory.

A brief summary of each of these areas of development is given below:

1. Rice's Theory⁷⁸

This theory is based upon the observed results of the thermal decomposition of various saturated hydrocarbons. It is, as all other decomposition theories are, an attempt to explain and correlate experimental observations in a consistent manner. The basic points of Rice's development are as follows:

- a. The initial step in the decomposition is the dissociation of the compound into two radicals. Due to the greater strength of the C-H bond (93.3 kcal vs C-C bond energy of 71 kcal), the C-C bond rupture predominates almost exclusively.
- b. If the overall decomposition is small (<50%), the probability of the radicals colliding is small. Therefore the radicals formed may either decompose or react with a surrounding parent compound.
- c. Free radicals may dissociate because a single bond becomes a double bond in the process. This releases energy which may be used to break a C-H bond or another C-C bond.
- d. The process of decomposition is a chain. A free radical or atomic hydrogen may combine with a hydrogen atom of another molecule. The radical thus created then may decompose to a stable compound and another radical or hydrogen atom which continues the chain.
- e. By estimating the strengths of various bonds, it is possible to estimate the final composition of products.

Using the above reasoning, Rice was able to obtain satisfactory explanation for the observed products of the thermal decomposition of ethane, propane, isobutane, n-butane,

n-pentane, isopentane and neopentane.

2. Rice - Herzfeld Theory⁷⁹

Approximately three years later, Rice and Herzfeld published an extension of the original theory. Essentially, it enabled the original Rice mechanisms to be consistent with the observed kinetics and the calculated activation energy for a series of thermal decompositions. It involved the writing of the mechanism as a series of free-radical steps: radical formation, chain initiation, chain propagation, and chain termination. A purely arbitrary, though hopefully reasonable, energy of activation was then assigned to each step. Through application of the proper kinetic equations, suitable values were found for several systems. The overall treatment is quite involved and lengthy and may be found in the original papers.

3. Kossiakoff - Rice Theory⁸⁰

Kossiakoff and Rice, in 1943, introduced additional postulates to the original theory in order to make the theory more compatible with the large number of experimental observations on various systems. These modifying postulates may be summarized as follows:

- a. Hydrocarbon free radicals are stabilized by resonance. This stabilization decreases in the order: tertiary radical > secondary radical > primary radical. This may account for differences in energy required to remove a primary, secondary, and tertiary hydrogen atom.
- b. This approach, resonance stabilization, enables the predication of the relative rates of formation and decomposition of these radicals.
- c. Long chain radicals may isomerize unimolecularly. This would account for the formation of isomers.

The use of these refinements has resulted in an adequate explanation of the experimental results for some compounds, while it has given little or no improvement for others.

An alternate approach to pyrolysis mechanisms for simple organic molecules is a purely molecular scheme. Many variations have been proposed; however, the basic reasoning is as follows: The molecule obtains sufficient energy for heterolytic bond cleavage forming two (or more) stable products. This energy is generally believed to result from collision, either with a hot wall or another excited molecule. When the molecule obtains sufficient energy through these collisions, it spontaneously ruptures and forms two stable products.

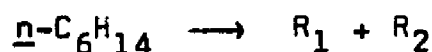
Mechanism of Thermal Decomposition

As was mentioned previously, no absolute proof exists as to the exact mechanism of decomposition. The pyrolysis technique affords information as to product quantity and identity. Rate and energy of activation information can be obtained from this. No information as to the presence or absence of free radicals is possible with the present apparatus. A few generalizations may be made, however. The energies of activation are too low to suspect a purely molecular mechanism. The values of the rate constants also support a free-radical mechanism. The products formed may be accounted for by either mechanism.

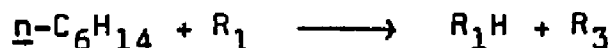
The case of n-hexane will be treated below from the standpoint of both a free-radical and molecular mechanism to illustrate the difference and similarities.

Free-Radical Mechanism for n-Hexane

The initiation reaction is the decomposition of the n-hexane into two radicals, R_1 and R_2 .



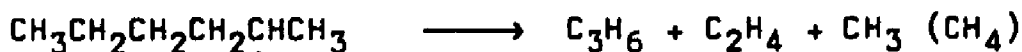
Either of the radicals formed may then abstract a proton from the parent molecule to form a stable product and a new free radical R_3 .



R_3 may be any of these three forms:

1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$
2. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}\cdot\text{CH}_3$
3. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}\cdot\text{CH}_2\text{CH}_3$

R_3 may then decompose rapidly and unimolecularly in certain definite ways.

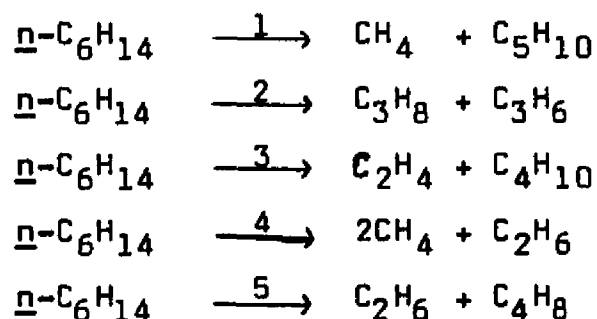


The species given in parentheses is the protonated form of

the radical, which is the most probable stable compound produced. These steps successfully account for all products formed by pyrolysis-gas chromatography except for small amounts of butane and 1,3-butadiene.

Molecular Mechanism for n-Hexane

This may be written as a series of steps leading to stable products. The series of steps is given below:



It may be seen that the experimental results can be explained by either theory with respect to the products formed. The decomposition of the sixteen compounds which were studied is represented below as a series of balanced equations. These equations represent logical processes by which the presence of the various products in the pyrolysis-gas chromatogram may be explained. It must be understood that, in many cases, various other pathways may also account for the observed products; however, only the most straightforward steps have been included. Without direct evidence of intermediates, the justification of one process over another is impossible. Since pyrolysis-gas chromatography affords only information on stable products, a detailed

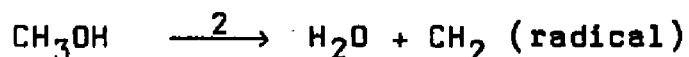
consideration of the reaction mechanism is unwarranted.

Methanol

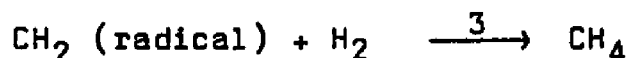
The primary decomposition process in methanol is that of dehydrogenation:



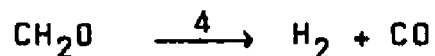
Dehydration is also observed, to a lesser extent:



The postulated carbene radical may react with hydrogen formed from the first reaction, producing methane.

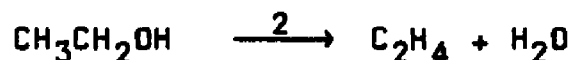
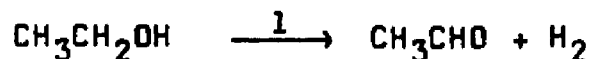


In addition, the carbene may react in various ways to yield stable products. Due to the fact that formaldehyde is known to be quite thermally unstable, it may dissociate in the following way:

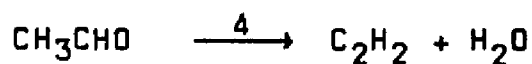
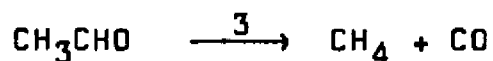


Ethanol

The degree of thermal degradation of ethanol is much greater than that observed for methanol. However, the same processes of dehydrogenation and dehydration predominate.

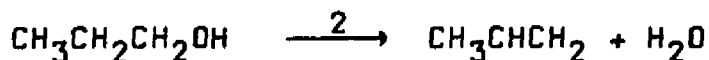
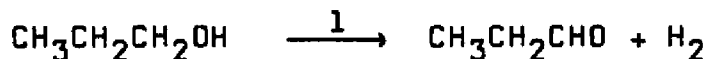


The acetaldehyde formed from reaction (1) may in turn react in the following ways:

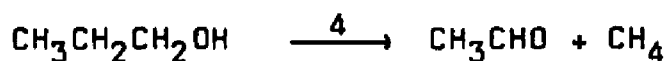
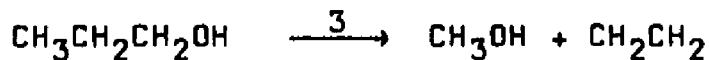


1-Propanol

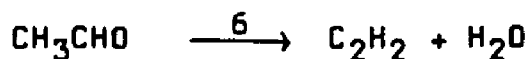
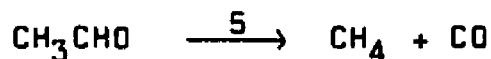
The extent of pyrolysis of 1-propanol is comparable to that of ethanol, with two important processes once again being the loss of water and hydrogen.



Processes which occur to a great extent involve carbon-carbon bond cleavage to form methanol and acetaldehyde.



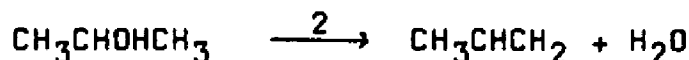
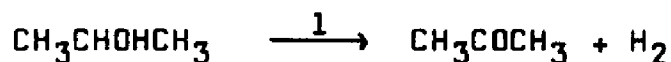
Large amounts of acetaldehyde formed may then react in the following manner:



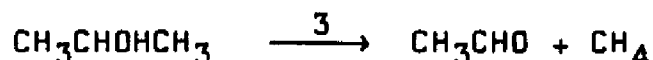
2-Propanol

This compound, a secondary alcohol, thermally degrades to a much greater extent than the primary alcohol, and has a correspondingly lower energy of activation. Common to all the

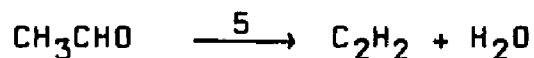
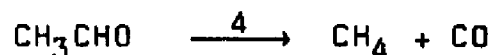
alcohols studied, dehydrogenation and dehydration are important paths of decomposition.



Carbon-carbon bond cleavage produces acetaldehyde,



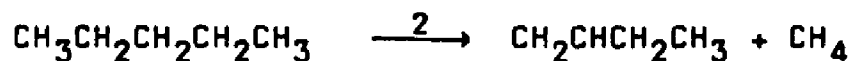
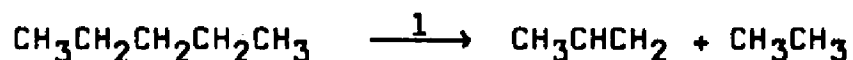
which may itself decompose in the following way:



These processes account for all products formed except ethylene, which is present in very small quantities, and most probably results from some type of secondary reaction of low yield.

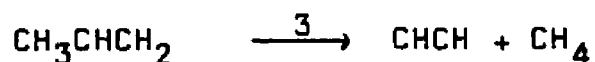
n-Pentane

Thermal decomposition results primarily in the formation of both a saturated and an unsaturated hydrocarbon with the cleavage of any carbon-carbon bond having approximately the same probability.



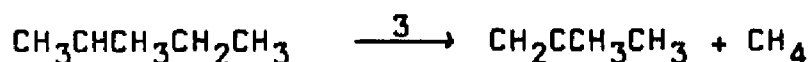
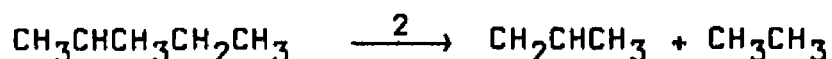
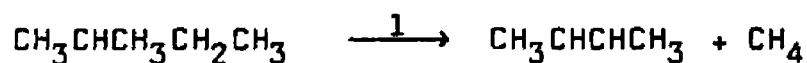
Products formed from the first two steps can react in the

following ways:

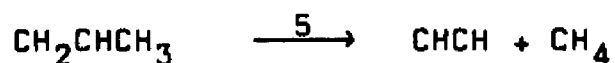
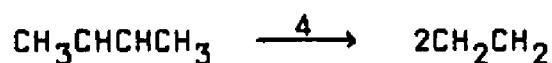


Isopentane

The energy of activation for the decomposition of isopentane is less than that for n-pentane. Generally a branched hydrocarbon is less stable than a straight chain hydrocarbon. As in the case of n-pentane, the formation of both a saturated and an unsaturated product through carbon-carbon bond cleavage predominates.



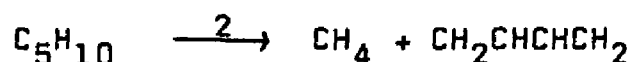
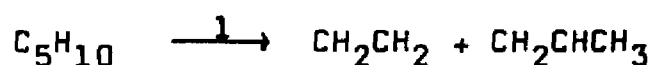
Products formed from these reactions tend to form smaller unsaturated hydrocarbons.



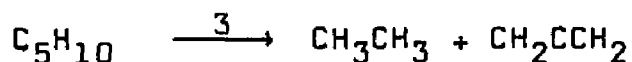
1-Pentene, cis-2-Pentene, and trans-2-Pentene

All of these compounds yield the same products under similar pyrolysis conditions. The relative product distribution is quite similar for the cis-trans species, but different from that of 1-pentene. Although both processes occur

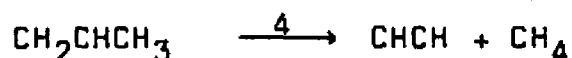
in both 1- and 2-pentene, process (1) is favored for 1-pentene, and process (2) is favored for 2-pentene (cis and trans).



This is reasonable due to the fact that bond rupture at the allylic position would be most favored and the products formed result from this bond breakage. All three substances also appear to undergo the reaction:



Large amounts of propylene formed from process (1) can decompose in this way:

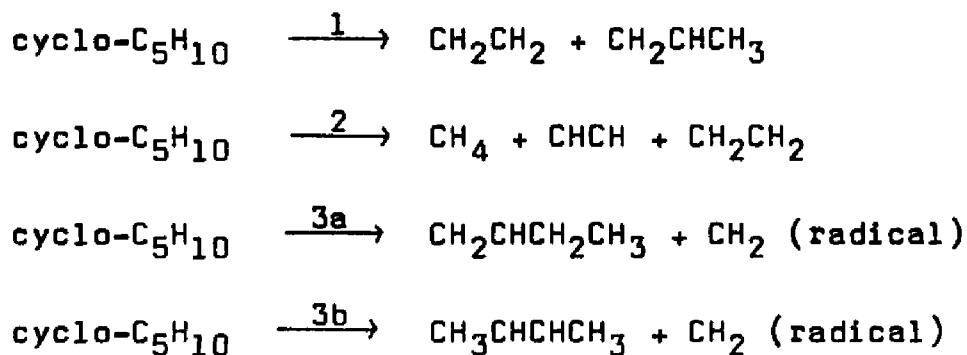


The most thermally unstable compound of these three is the 1-pentene which decomposes approximately thirty percent at the most drastic conditions. Cis- and trans-2-pentene decompose to about the same extent, yielding approximately eighteen percent conversion under the same conditions. The percent decomposition of the cis species is greater at lower temperatures, and the activation energy is also lower. This is most probably due to the greater strain present in the cis isomer.

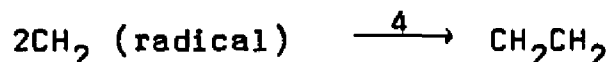
Cyclopentane

This compound, due to its ring structure, possesses

a much greater stability than any of its straight chain C_5H_{10} isomers. The energy of activation is correspondingly higher (by 20-40 kcal/mol). Processes which would form the observed products are as follows:

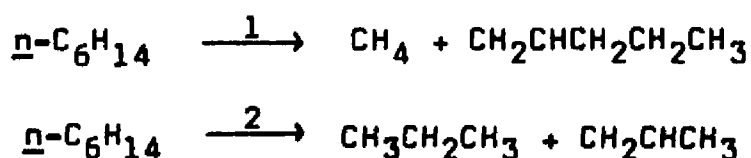


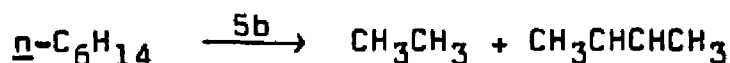
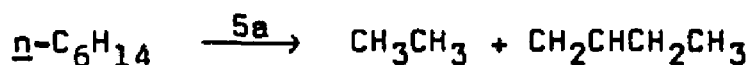
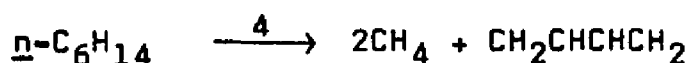
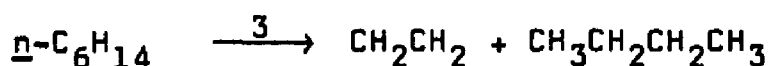
A radical recombination may account for the presence of ethylene:



n-Hexane

As the number of carbon atoms increases from five to six, the number of products increases. In the same way, the number of processes which could explain their formation greatly increases. There are more bonds available for scission and the resulting larger fragments are prone to undergo thermal decomposition themselves. Consequently, the following steps represent logical although not exclusive paths leading to the observed products:

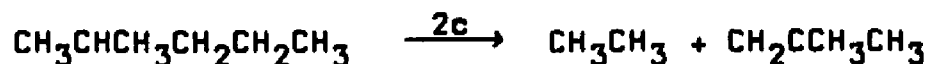
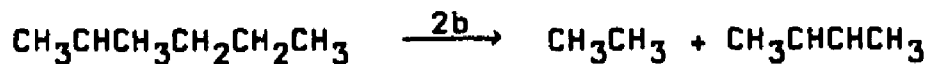
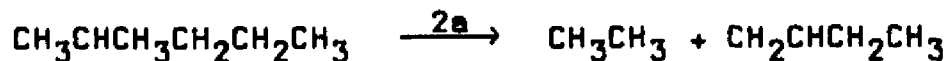
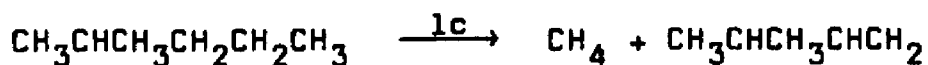
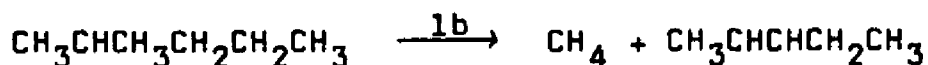


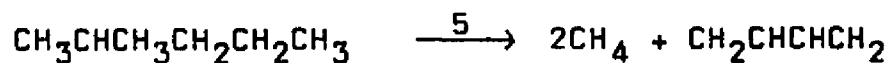
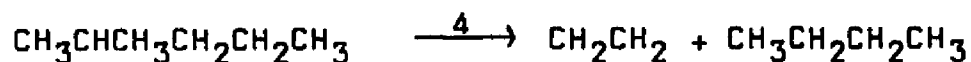
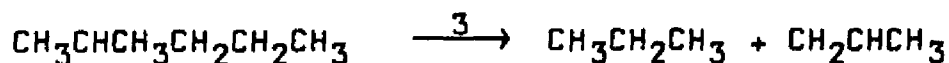


The most predominant products contain one, two, or three carbon atoms. The formation of both a saturated and unsaturated fragment from the parent compound is, as in the case of the five-carbon compound, a common characteristic of most of the postulated decomposition routes.

2-Methylpentane

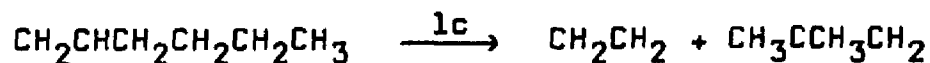
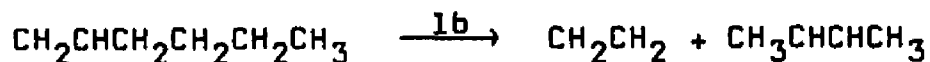
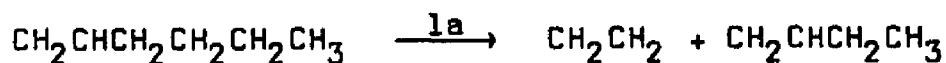
Products formed from the pyrolysis of this compound are similar, but the product distribution varies appreciably from that observed for n-hexane. The energies of activation are statistically indistinguishable whereas, in the smaller n-pentane and isopentane, the energy difference is larger. Most probable processes accounting for the products found are:



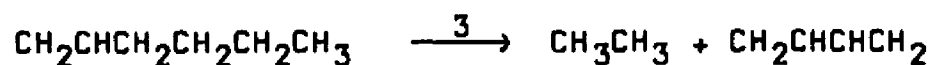
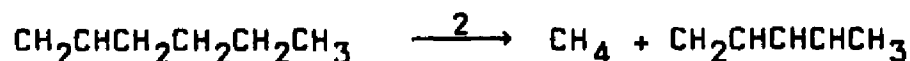


1-Hexene

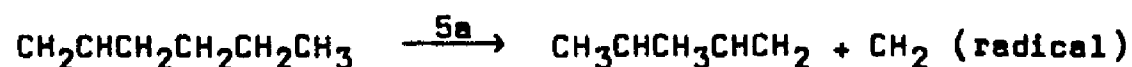
Unlike the analogous five-carbon isomer, this compound breaks down in a slightly different way than the 2-hexenes. The energy of activation is lower than that for the 2-hexenes but the total decomposition is also lower. This may be accounted for only by postulating that the steric factor or probability of forming an activated complex is lower. Three different C_4 alkene isomers are formed in the following ways:

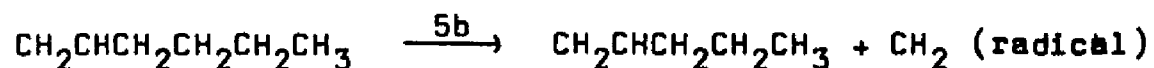


In addition, the following carbon-carbon bond cleavages occur:



Five-carbon isomers appear to be formed by radical cleavage:



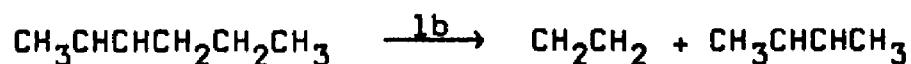
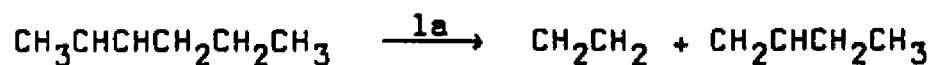


These radicals may recombine or enter into other reactions. Due to the complexity of the overall reaction, no attempt has been made to account for all possibilities.

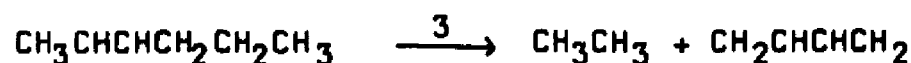
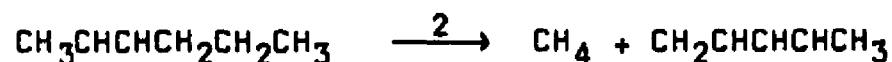
cis-2-Hexene and trans-2-Hexene

Both of these compounds yield the same products under similar pyrolysis conditions. The relative amounts of the various products are, for all practical purposes, identical; furthermore, the energies of activation are statistically indistinguishable.

Although three butene isomers are formed from 1-hexene, only two of these are observed for cis- and trans-2-hexene. Isobutene was not detected in the latter cases. The formation of isobutene is most readily explained by postulation of a cyclic intermediate. This indicates that 1-hexene may be more prone to form a cyclic intermediate than either of its straight chain isomers.

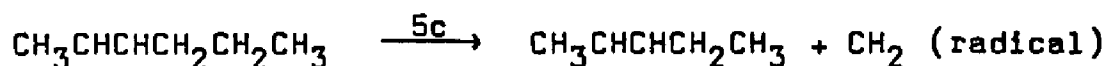
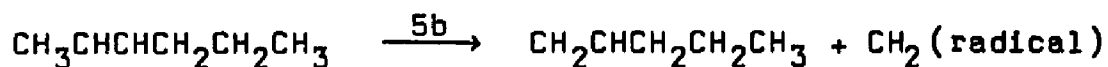
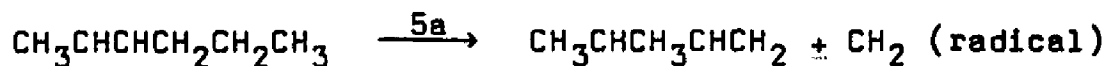


Simple carbon-carbon bond cleavage is similar to that observed in 1-hexene:

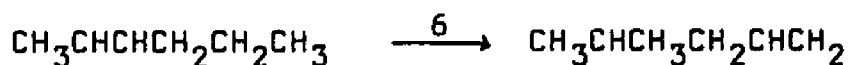




Radical cleavage forms three pentene isomers; only two are produced from 1-hexene.



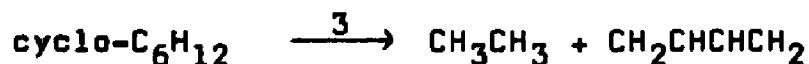
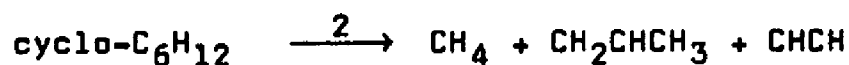
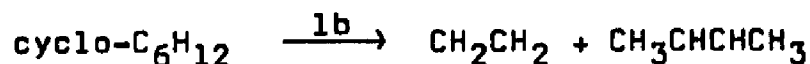
In addition trace amounts of the product of a molecular isomerization are observed:



Small yields of this compound are expected; a larger yield would be more characteristic of a decomposition at lower temperatures.

Cyclohexane

The stability of this compound was similar to cyclopentane, due to the stabilizing ring structure. The products formed are somewhat analogous and may be accounted for in the following ways:



The foregoing has included a general treatment of the mechanistic aspect of the pyrolysis studies. For an accurate estimation of the relative number of products formed in each reaction, the reader is referred to Appendix IV where the relative number of moles of product formed (as a function of the index number of the product) is given in bar graph form.

Comparison of Theoretical and
Experimental Product Distribution

It would be of value at this point to compare the relative product distribution obtained in this work with values calculated using the Kossiakoff-Rice Theory for a number of the compounds studied. In addition, the results of pyrolysis studies from other laboratories obtained using different apparatus are compared where possible. The relative number of moles of product is given below for the various compounds being considered. Relative amounts were recalculated on the basis of largest amount being assigned a value of 100 where necessary.

n-Pentane

Kossiakoff-Rice Theory⁸⁰

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	34
C ₄	15

Kossiakoff-Rice experimental results⁸⁰

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	45
C ₄	22

Experimental results of this work

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	37
C ₄	12

IsopentaneKossiakoff-Rice Theory⁸⁰

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	29
C ₄	71

Kossiakoff-Rice experimental results⁸⁰

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	32
C ₄	61

Experimental results of this work

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	32
C ₄	58

n-HexaneKossiakoff-Rice Theory⁸⁰

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	22
C ₄	17
C ₅	6

Experimental results (other laboratories)

<u>Carbon #</u>	<u>Ref. 8</u>	<u>Ref. 85</u>	<u>Ref. 92</u>
C ₁ + C ₂	100	100	100
C ₃	30	33	40
C ₄	15	19	21
C ₅	4	6	5

Experimental results of this work

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	29
C ₄	15
C ₅	4

2-MethylpentaneKossiakoff-Rice Theory⁸⁰

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	61
C ₄	31
C ₅	25

Experimental results of this work

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	68
C ₄	33
C ₅	15

cis-2-Hexene

No theoretical values are available

Experimental results (other laboratories)

<u>Carbon #</u>	<u>Ref. 81</u>	<u>Ref. 85</u>
C ₁ + C ₂	100	100
C ₃	12	12
C ₄	32	47
C ₅	27	46
C ₆	0	0

Experimental results of this work

<u>Carbon #</u>	<u>Relative Amount</u>
C ₁ + C ₂	100
C ₃	12
C ₄	38
C ₅	26
C ₆	3

The above information indicates that the pyrolysis patterns for these compounds are reproducible from laboratory to laboratory, even though the design of the apparatus

is different, as long as all of the data are calculated on a common basis. In addition, the experimental results are in good agreement with theory. This means, first of all, that it should be possible to use pyrolysis-gas chromatography for qualitative analysis, if the patterns are sufficiently different. In addition, useful kinetic information may be obtained since the decomposition appears to follow a theoretical mechanism. These two points will be considered in detail in the following sections.

The Utility of Pyrolysis-Gas Chromatography
for the Study of the Kinetics of Chemical Reactions

The Calculation of Rate Constants

In order to calculate the rate constant of a particular reaction, one must be able to measure the concentration of the reactant(s) and products of the reaction. In addition, an accurate estimation of both the temperature and time of the reaction must be made. The estimation of each of these quantities from the standpoint of the pyrolysis-gas chromatograph used in this work is given below.

Concentration. All of the reactions which are studied here have been reported to be first order unimolecular decompositions. The rate constant for reactions of this type is independent of concentration for a particular reaction temperature. The term $\ln (C_0/C)$ of the first order rate equation

$$kt = \ln (C_0/C)$$

remains constant regardless of the initial concentration due to the fact that the fractional conversion remains the same. For this reason pyrolysis-gas chromatography may be used for the calculation of first order kinetic properties. The relative amounts of sample and products can be estimated quite accurately from the resulting gas chromatogram.

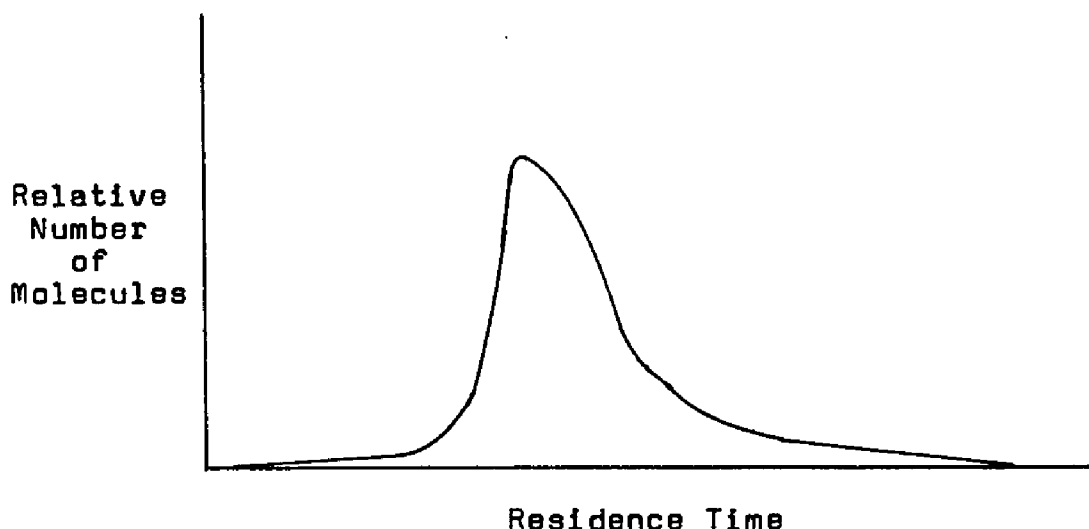
The situation is quite different for reactions which are other than first order, however. The performance of the tube furnace reactor and its ability to represent the true kinetic processes which are occurring are dependent upon the extent of mixing between the carrier and the sample and the point in time at which this mixing takes place. In short, the complexity of the system, both kinetically and hydrodynamically, is such that the problem becomes insoluble. Dankwerts⁹³ alludes to this complexity in his discussion of the efficiency of tube furnace reactors.

At the moment there is no method whereby the history of the molecules flowing through an arbitrarily chosen reactor can be determined and the results formulated in such a way that the output could be predicted for a reaction of known kinetics.

Due to the complexity of such systems no attempt was made to study any reaction which was suspected to follow anything other than first order kinetics.

Reaction time. In order to calculate meaningful rate constants, the reaction time must be known. On p112-113 of the results, it is noted that the residence time of a single molecule in the hot zone of the reactor (corresponding to the reaction time) is estimated from the conventional residence time expression corrected for the Charles'

Law dependence of volume on temperature. These calculations are done assuming a plug flow reactor. Calculation of the approximate Reynolds Number indicates that the flow through the tube is laminar. This implies that there exists a residence time distribution of the form:



The assumption is made that the calculated residence time is the average value of the distribution. This assumption is most valid when the distribution is gaussian, and becomes progressively worse as the curve becomes more skewed. Very little information can be obtained pertaining to the form of this distribution. Consequently there is uncertainty as to the exact value of the reaction time, but the approximations made appear valid enough to accept the calculated value.

Reaction temperature. The temperature of the reaction is given as the temperature of the pyrolysis oven at the point of the hot junction of the thermocouple. This is consistent with most of the pyrolysis-gas chromatography

studies using a flow system. However, this is actually only an approximation of the temperature of the decomposing molecule. In reality a temperature gradient exists throughout the length of the reaction chamber. In order to properly evaluate this gradient, temperature sensing devices would be needed within the flow system at regular intervals throughout its length. Such an arrangement was not attempted due to the fact that: 1) the construction would be difficult, 2) the presence of thermocouples would alter the flow pattern and hopelessly confound the calculation of a reasonable reaction time, and 3) the presence of a series of thermocouples may cause undesirable metal catalysis of the thermal decomposition being studied. For these reasons the apparent temperature, which is easily controlled and which proved to be quite reproducible, is used in the calculation of the kinetic parameters.

Under these conditions, the rate constants for each decomposition are calculated. The values obtained are quite reproducible and appear reasonable when viewed against rate constants calculated for the decomposition of similar compounds using other experimental techniques. The agreement of the rate constants at two different reaction times is relatively good, substantiating the observations of other researchers who state that these are first order decompositions. The error in the calculation of k increases appreciably for low fractional conversions (<1%). This is due to the fact that the ratio (C_0/C) is most sensitive to change at very high and very low values.

The Calculation of Energies of Activation

The values for the energy of activation are obtained from the slope of the graph of $\ln k$ vs $1/RT$ in accordance with the Arrhenius equation:

$$\ln k = \ln k_0 - E_a (1/RT)$$

Data for each compound at each flow rate were analyzed using the least squares technique. The slopes of the lines at each flow rate were compared and found to be statistically similar at the 95 percent confidence level. The data were then pooled and the slopes were calculated. Ninety-five percent confidence intervals were placed around each value. The computation, using the computer program in Appendix III, allowed the statistical estimation of the ratio of the variability removed by fitting a straight line to the data (correlation) to the residual variability.⁹⁴ These ratios (F ratios) indicated that the linear functional relationship was an adequate one. By virtue of the fact that duplicate runs were made of each experimental point, another F test could be used to assess the residual variability. In other words, it can answer the question: is the remaining variability due solely to experimental error, or is there some functional non-linearity present? This test compared the lack of fit with random experimental error. In every case, with the exception of cyclopentane and trans-2-hexene, the lack of fit term was found to be significant at the 95 percent level of confidence. This indicated the presence

of some significant inability of the linear equation to represent the experimental data. This non-linearity may arise from the following sources:

- a. The inadequacy of the Arrhenius equation to represent the kinetics of the decomposition.
- b. Erroneous estimation of the reaction time.
- c. Inaccurate assignment of the temperature at which the reaction was taking place.

Of the three possible explanations, the last two appear most logical. The variation is quite small when compared to the overall fit of the data to the Arrhenius function. Earlier, it was stated that both the time and temperature of the reaction were educated approximations, close to the true value but not likely to be exact. This small amount of non-linearity appears, in all probability, to be associated with experimental error in these estimations.

It must be emphasized here that the confidence intervals for the energies of activation are based upon the residual error, that is, the combination of random experimental error and lack of fit. This suggests that the precision could be improved through a better estimation of the time and temperature factors.

The literature for non-catalyzed thermal decompositions of these compounds and calculation of energies of activation is scanty. Therefore comparison of data is difficult. However, trends of stability qualitatively agree with the trends found in this work. One would expect high values for the cyclic hydrocarbons. The values for n-hexane

appear somewhat low, values about 10 kcal/mole higher being reported in the literature. The methanol value is impossibly low. One would expect a value about twice as great as that which was found. It may be possible that methanol decomposes according to an order other than one. The other three alcohols are in agreement with other work,⁹⁵ the stability decreasing in the order ethanol, 1-propanol, 2-propanol. The cis-2-pentene was found to have a lower activation energy than the trans form. This is due to the fact that the cis configuration is more strained than the trans. This effect apparently decreases as the carbon chain becomes longer; the analogous C₆ alkenes have activation energies which are statistically indistinguishable.

The Calculation of Frequency Factors

These values are obtained by extrapolation of the linear relationship of $\ln k$ and $1/RT$ to a value of $1/RT = 0$. This is a conventional method of obtaining experimental values for the frequency factor from rate studies. A normal value for a first order reaction is in the vicinity of 10^{13} (10^{11} - 10^{15}). This has been found to be generally true for all hydrocarbons which were studied. Cyclic compounds would be expected to have frequency factors greater than 10^{13} and this fact is borne out here. Cyclopentane has a k_0 equal to 7.9×10^{16} and for cyclohexane, the k_0 is 9.4×10^{16} . The values for the alcohols, on the other hand, are somewhat lower, suggesting either a different mechanism or a low

probability factor, indicating a greater difficulty in forming the activated species. A greater insight may be obtained here through the investigation of the thermodynamic properties of activation, particularly the entropy term.

Thermodynamic Properties of Activation

Knowing the energy of activation (E_a) and the frequency factor for each of the reactions, it is possible to obtain values for the change in enthalpy of activation, the change in free energy of activation, and the change in entropy of activation. The change in enthalpy of activation can be found from:

$$\Delta H^* = E_a - nRT \quad (1)$$

The free energy of activation is related to the rate constant by the following expression:

$$k_T = (kT/h) e^{-\Delta G^*/RT} \quad (2)$$

or

$$\ln k_T = \Delta G^*/RT + \ln (kT/h) \quad (3)$$

Solving for ΔG^* we find

$$\Delta G^* = [\ln (kT/h) - \ln k_T] RT \quad (4)$$

By substituting a $\ln k_T$ value at a particular temperature from the Arrhenius graph, along with the proper constant, ΔG^* may be obtained. The entropy of activation is expressed as:

$$\Delta S^\ddagger = (\Delta H^\ddagger - \Delta G^\ddagger)/T \quad (5)$$

and this may be solved through the substitution of proper values obtained from equations (1) and (4). Symbols in equations (1) through (5) refer to the following:

ΔH^\ddagger = change in enthalpy of activation

E_a = energy of activation (kcal/mole)

n = number of moles

R = molar gas constant (cal/°K mole)

T = temperature (°K)

k_r = specific rate constant

k = Boltzmann's constant

h = Planck's constant

ΔG^\ddagger = change in free energy of activation

ΔS^\ddagger = change in entropy of activation.

The values that were obtained are based upon, and therefore include, the error associated with the frequency factors and activation energies. For this reason, these figures must be viewed with some caution. Indeed, all calculations of these parameters which are based upon empirical observation are subject to error, both theoretical and experimental.

Cyclopentane and cyclohexane give high positive values for the entropy of activation while all other compounds yield negative values. Rice predicts that the decomposition of a ring compound should be accompanied by a larger entropy value. A positive ΔS^\ddagger value corresponds to a more probable activated complex and means that the

reaction is faster than normal. A negative ΔS^\ddagger indicates a less probable activated complex, and consequently a slower rate.⁹⁶ A "normal" rate constant is defined here as

$$k_r = 10^{13} e^{-E_a/RT}$$

The alcohols all have large negative ΔS^\ddagger values; cis- and trans-2-hexene, and trans-2-pentene have values of approximately -2, and similar energies of activation. Cis-2-pentene, however, has a large negative ΔS^\ddagger and a lower E_a value. 1-Pentene and 1-hexene have similar values. The saturated hydrocarbons have similar values except n-pentane whose ΔS^\ddagger is much less negative. The reasons for these observations are not clear and would involve the determination of the mechanism and a detailed study of its complexities. If the values for ΔS^\ddagger are correct, one can only interpret them as a measure of the probability of the formation of the activated complex (or complexes).

Analytical Potential of Pyrolysis - Gas Chromatography

The use of pyrolysis-gas chromatography as an analytical tool has, for the most part, been restricted to studies of compounds which are not sufficiently volatile or do not possess the necessary thermal stability for conventional gas chromatographic analysis. Only a few important papers have appeared dealing with the analytical implications of this technique for the analysis of volatile, stable organic

compounds. The purpose of this work has been to substantiate and extend work which has already been done.

As a necessary antecedent to analysis, the experimental system which has been developed here has been characterized with respect to the effect of various parameters and the reproducibility of the technique.

As expected, the extent of pyrolysis is a function of the temperature of pyrolysis and the length of time the sample spends in the "hot zone" of the unit. This length of time is proportional to the carrier gas flow rate. As discussed previously, provisions were made for estimation of both of these factors. The fractional conversion of the sample is dependent to a small extent on the size of the sample used. For a true first order reaction no dependence upon sample size would be expected. In fact, this effect is most likely due to a change in residence time with variation of sample quantity. This is not unusual, due to the extreme sensitivity of the residence time distribution to small changes in the input flow concentration.

The separation column chosen is dependent upon the nature (polarity, boiling point, molecular weight) of the sample and its products. With the tremendous variety of column materials available, the types of compounds which may be studied are numerous. For this work Porapak Q and T, porous polymer bead structures, were chosen because of their adequate compromise between suitable separation of low molecular weight products and reasonable retention

times for the higher molecular weight samples being studied.

The overall percent decomposition due to pyrolysis has a coefficient of variation of less than five percent. The relative amounts of various products are quite constant among repetitive samples. In addition, this product distribution does not vary greatly with temperature although the total amount of product decreases as the temperature becomes lower.

Due to the facts that the process is reproducible, the product distribution is only moderately temperature dependent, and the pyrolysis appears to follow a theoretical decomposition path, it offers promise as an analytical tool.

Referring to the bar graphs depicting the distribution of products of pyrolysis (Appendix IV), it may be seen that pyrolysis is comparable to mass spectrometry for qualitative identification. Levy and Paul⁹² have recently constructed a pyrolysis analog of gas chromatography-mass spectrometry. It consists of a conventional gas chromatograph which is connected directly to a pyrolysis-gas chromatograph. The greatest advantage of pyrolysis-gas chromatography over mass spectrometry in this respect is cost and ease of operation.

It has been found experimentally that a difference in the structure of isomers produces a sufficiently distinct pattern to be used for qualitative identification. For geometrical isomers, the patterns are similar due to the fact that the structures are the same. The percent decomposition varies, but not sufficiently for qualitative

analysis, in the case of the C₅ isomers. The C₆ isomers do not statistically differ in their percent decomposition, rendering identification impossible. This is undoubtedly due to the lessening of strain in the cis-2-hexene caused by the longer carbon chain.

This approach appears to have considerable promise for qualitative identification of organic structural isomers, but more detailed experimentation with a large number of compounds will be required.

Suggestions for Further Work

Pyrolysis-gas chromatography as a means for determining kinetic and mechanistic properties of certain thermal reactions appears feasible. In order to obtain more precise and meaningful data, other systems, which may allow a more accurate estimation of time and temperature of the reaction, should be studied. Specifically, this would include a closed loop, where a particular temperature could be maintained for a specified time interval. This would also alleviate the dependence of the reaction time on the carrier flow rate in the separation column.

The use of C¹⁴ labeling and a suitable counting device monitoring the column effluent could provide valuable information as to the mechanism of thermal decomposition. Such a system would be easy to design and at the same time be relatively inexpensive.

The technique of pyrolysis-gas chromatography for qualitative identification could be extended to other classes

of compounds and higher molecular weight compounds. Non-volatile solids may perhaps be studied in a volatile solution. Some work in this area has been done by Burke,⁵⁷

SUMMARY

The thermal decomposition of various organic compounds has been studied using the technique of pyrolysis-gas chromatography. The observed pyrolysis data were found to be consistent with first order kinetics. The distribution of the products of the thermal reaction was in agreement with the Kossiakoff-Rice Theory as well as with the results of other pyrolysis investigations. This indicates the potential utility of the method for qualitative analysis, in a manner analogous to mass spectrometry.

A pyrolysis-gas chromatograph, employing a continuous flow system, which is capable of causing decomposition of volatile organic compounds and of providing a means for qualitative and quantitative analysis of the products produced, has been designed and constructed. The furnace consisted of a quartz tube housed in a stainless steel block which could be heated to 700°C. The chromatographic columns were prepared from various types of Porapak and the pyrolysis was carried out in a helium carrier gas stream. Products were qualitatively characterized by comparison of retention times with known standards. Quantitative estimation was based upon peak areas. Area measurement was accomplished using a Disc integrator. These areas were corrected for inequality of the thermal conductivity detector response using tables of weight factors.

Estimation of the time and temperature of the thermal decomposition was made using a suitable flow meter and thermocouples. This information, coupled with the amount of sample and product which was obtained from the recorder trace, was used to calculate values of the first order rate constants. These values were used in the Arrhenius equation to obtain energies of activation and estimates of the frequency factors. Suitable computer programs were employed to facilitate calculation and to perform regression analyses, which provided a measure of the error and lack of fit of the data to the proposed relationship. Variability in the data was explained in statistical terms.

Mechanisms accounting for the products observed were postulated, and various thermodynamic properties of activation were calculated.

The analytical utility of the technique was evaluated for the compounds studied and compared with mass spectral data for the same compounds. Structural isomers were found to produce pyrolysis patterns sufficiently different for qualitative analysis. Geometrical isomers yielded similar patterns; however, the percent conversion was somewhat higher for the cis form. This may be attributed to the greater strain present in the cis form. This effect was noted to be much smaller for the C₆ isomers, when compared against the C₅ isomers.

Suggestions for future investigation were made.

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Appendix I
LIST OF THERMAL CONDUCTIVITY
WEIGHT FACTORS FOR QUANTITATIVE
AREA NORMALIZATION

<u>Compound</u>	<u>Weight Factor</u>
Hydrogen	2.08 ^a
Methane	0.45
Ethylene	0.585
Acetylene	0.59 ^b
Ethane	0.59
Water	0.55
Formaldehyde	0.67 ^b
Propylene	0.652
Propane	0.68
Methanol	0.58
Acetaldehyde	0.68
Isobutene	0.683
Butane	0.68
1,3-Butadiene	0.674
1- & 2-Butene	0.67 ^c
3-Methyl-1-butene	0.707
Ethanol	0.64
Propionaldehyde	0.67 ^b
Acetone	0.68
2-Propanol	0.71
Isopentane	0.707
1-Pentene	0.710
<u>trans</u> -2-Pentene	0.673
<u>cis</u> -2-Pentene	0.710
<u>n</u> -Pentane	0.69

<u>Compound</u>	<u>Weight Factor</u>
Cyclopentane	0.720
1-Propanol	0.72
1,3-Pentadiene	0.63 ^b
2-Methylpentane	0.714
4-Methyl-1-pentene	0.75
<u>n</u> -Hexane	0.70
1-Hexene	0.76 ^b
<u>trans</u> -2-Hexene	0.80
<u>cis</u> -2-Hexene	0.70
Cyclohexane	0.735

^aEstimated from relative response value given
in: Technical Bulletin, Fisher Sci. Co., TD-146

^bEstimated from thermal response of similar compounds

^cAverage of 2 values

All others: Dietz, W. A., J. Gas Chromatog., 5,
68 (1967)

Appendix II
A WATFOR FORTRAN IV
PROGRAM FOR THE CALCULATION
OF FIRST ORDER RATE CONSTANTS

```
WRITE(3,2)
10 READ(1,1)C1,C,T
   AK=ALOG(C1/C)/T
   BK=ALOG(AK)
   WRITE(3,3)AK,BK
1  FORMAT(I5,I6,F6.3)
2  FORMAT(32H          AK          BK          )
3  FORMAT(2E16.8)
   GO TO 10
END
```

Appendix III
A FORTRAN IV PROGRAM
FOR THE POLYNOMIAL
REGRESSION ANALYSIS


```

    DIMENSION X(660),DI(100),D(66),B(10),E(10),SB(10),T(10),XBAR(11),
    1STD(11),COE(11),SUMSQ(11),ISAVE(11),ANS(10),P(120)
    1 FORMAT(A4,A2,I5,I2,I1)
    2 FORMAT(2F10.6)
    3 FORMAT(27H1POLYNOMIAL REGRESSION.....A4,A2/)
    4 FORMAT(23H0NUMBER OF OBSERVATIONS,I6//)
    5 FORMAT(32H0POLYNOMIAL REGRESSION OF DEGREE,I3)
    6 FORMAT(12H0 INTERCEPT,F15.5)
    7 FORMAT(26H0 REGRESSION COEFFICIENTS/(10E15.5))
    8 FORMAT(1H0/24X,24HANALYSIS OF VARIANCE FOR,I4,19H DEGREE POLYNOMI
    1AL/)
    9 FORMAT(1H0,5X,19HSOURCE OF VARIATION,7X,9HDEGREE OF,7X,6HSUM OF,9X
    1,4HMEAN,10X,1HF,9X,20HIMPROVEMENT IN TERMS/33X,7HFREEDOM,8X,7HSQUA
    2RES,7X,6HSQUARE,7X,5HVALUE,8X,17HOF SUM OF SQUARES)
    10 FORMAT(20H0 DUE TO REGRESSION,12X,I6,F17.5,F14.5,F13.5,F20.5)
    11 FORMAT(32H DEVIATION ABOUT REGRESSION ,I6,F17.5,F14.5)
    12 FORMAT(8X,5HTOTAL,19X,I6,F17.5///)
    13 FORMAT(17H0 NO IMPROVEMENT)
    14 FORMAT(1H0//27X,18HTABLE OF RESIDUALS//16H OBSERVATION NO.,5X,7HX
    1VALUE,7X,7HY VALUE,7X,10HY ESTIMATE,7X,8HRESIDUAL/)
    15 FORMAT(1H0,3X,I6,F18.5,F14.5,F17.5,F15.5)
100 READ(1,1) PR,PR1,N,M,NPLOT
    WRITE(3,3)PR,PR1
    WRITE(3,4)N
    L=N*M
    DO 110 I=1,N
    J=L+I
110 READ(1,2) X(I),X(J)
    CALL GDATA (N,M,X,XBAR,STD,D,SUMSQ)
    MM=M+1
    SUM=0.0
    NT=N-1
    DO 200 I=1,M
    ISAVE(I)=I
    CALL ORDER (MM,D,MM,I,ISAVE,DI,E)
    CALL MINV (DI,I,DET,B,T)
    CALL MULTR (N,I,XBAR,STD,SUMSQ,DI,E,ISAVE,B,SB,T,ANS)
    WRITE(3,5)I
    IF(ANS(7)) 140,130,130
130 SUMIP=ANS(4)-SUM
    IF(SUMIP) 140,140,150
140 WRITE(3,13)
    GO TO 210
150 WRITE(3,6) ANS(1)
    WRITE(3,7) (B(J),J=1,I)
    WRITE(3,9)
    SUM=ANS(4)
    WRITE(3,10) I,ANS(4),ANS(6),ANS(10),SUMIP
    NI=ANS(8)
    WRITE(3,11) NI,ANS(7),ANS(9)

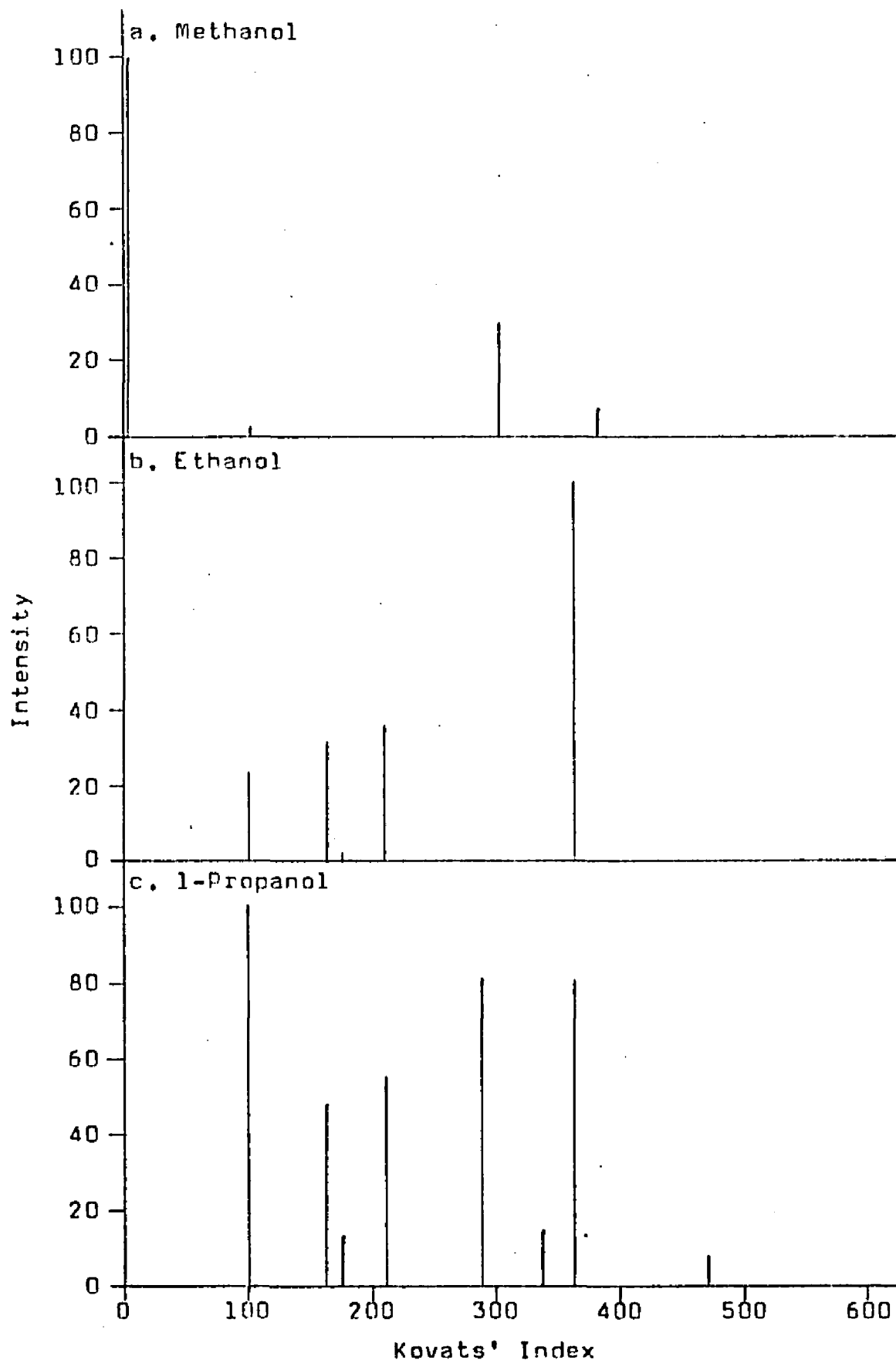
```

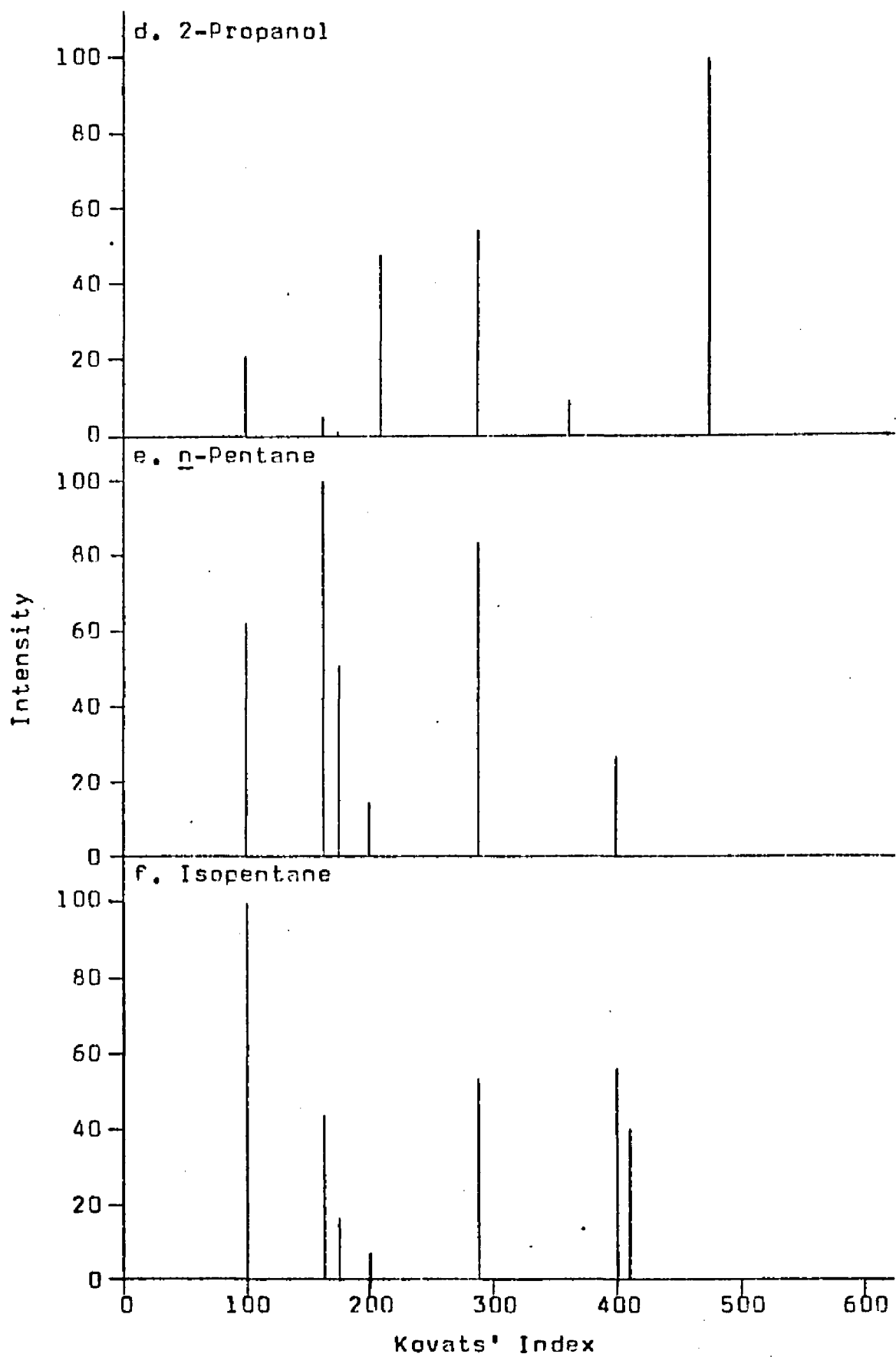
```

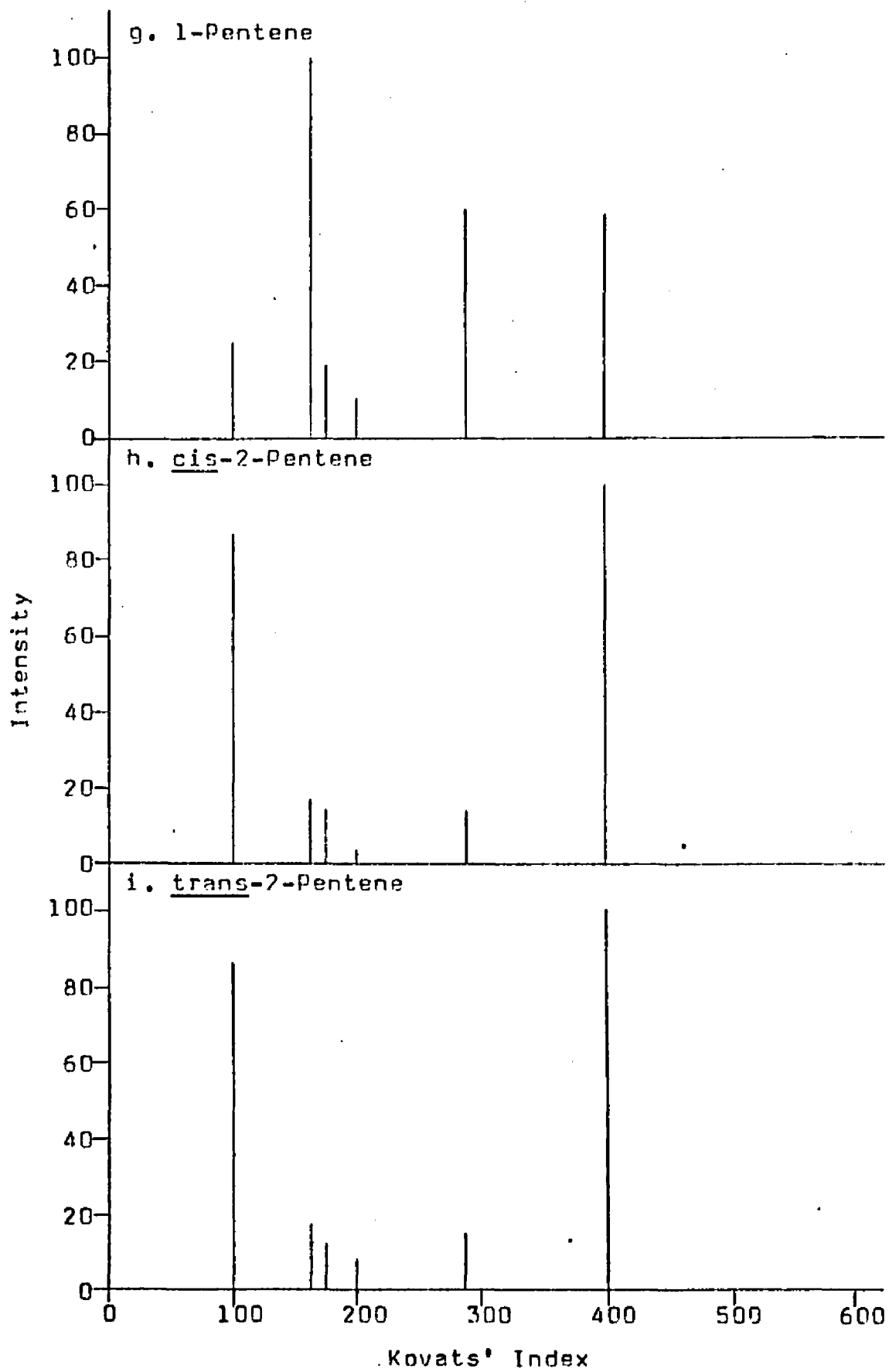
        WRITE(3,12) NT,SUMSQ(MM)
        COE(1)=ANS(1)
        DO 160 J=1,I
160    COE(J+1)=B(J)
        LA=I
200    CONTINUE
210    IF(NPLOT) 100,100,220
220    NP3=N+N
        DO 230 I=1,N
        NP3=NP3+1
        P(NP3)=COE(1)
        L=I
        DO 230 J=1,LA
        P(NP3)=P(NP3)+X(L)*COE(J+1)
230    L=L+N
        N2=N
        L=N*M
        DO 240 I=1,N
        P(I)=X(I)
        N2=N2+1
        L=L+1
240    P(N2)=X(L)
        WRITE(3,3)PR,PRI
        WRITE(3,5)LA
        WRITE(3,14)
        NP2=N
        NP3=N+N
        DO 250 I=1,N
        NP2=NP2+1
        NP3=NP3+1
        RESID=P(NP2)-P(NP3)
250    WRITE(3,15) I,P(I),P(NP2),P(NP3),RESID
        CALL PLOT (LA,P,N,3,0,1)
        GO TO 100
        END

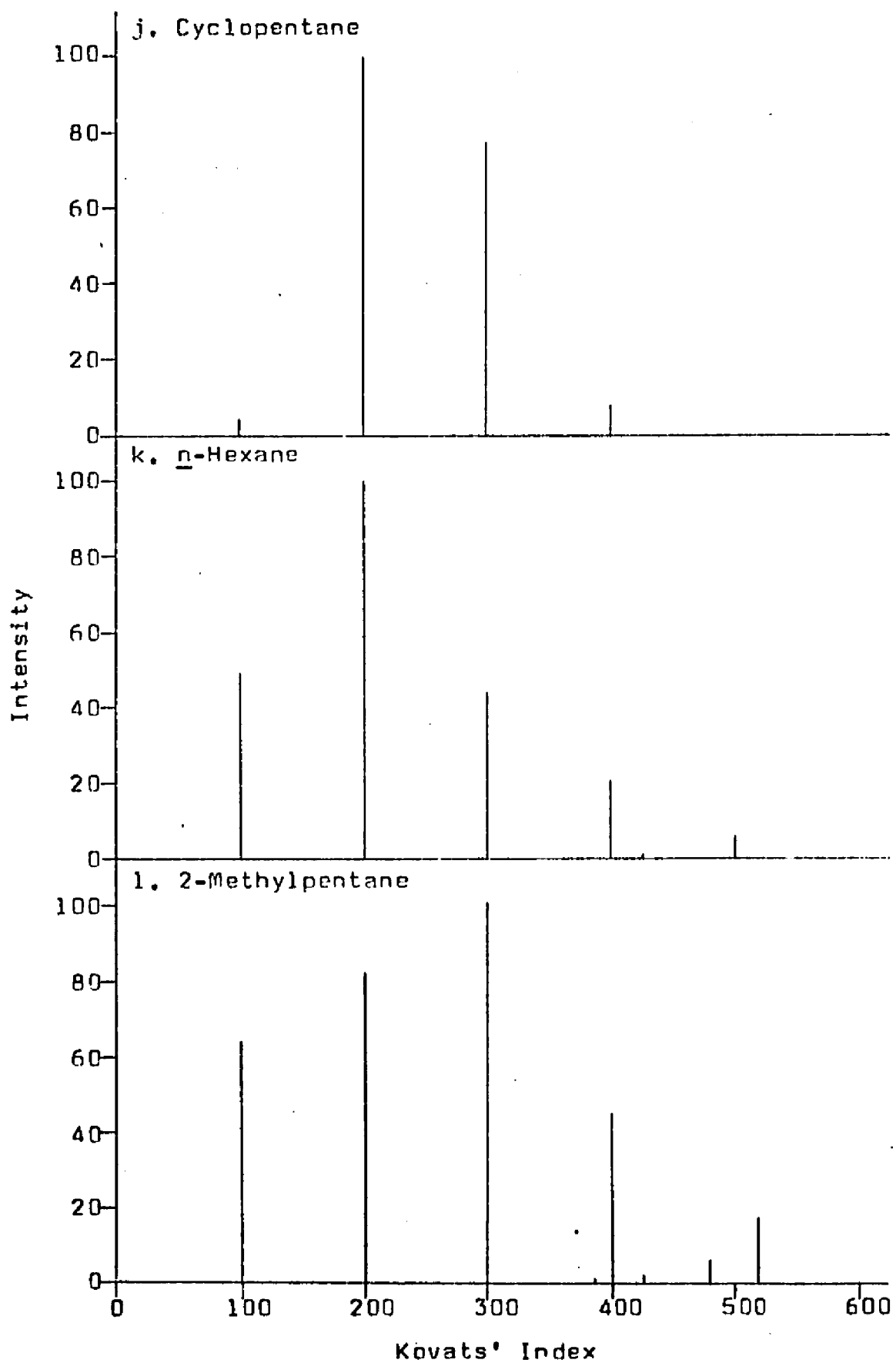
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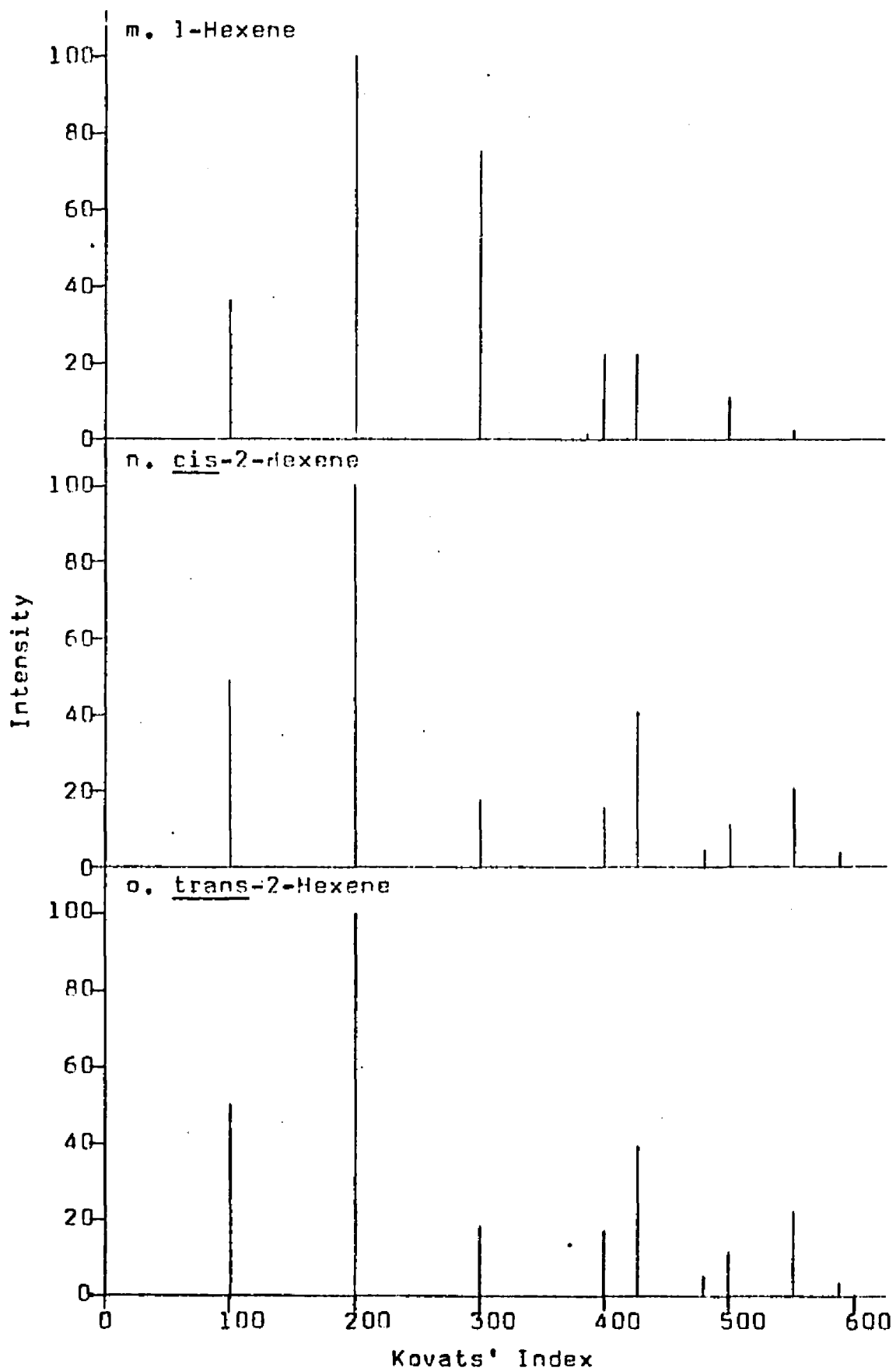
Appendix IV
RELATIVE NUMBER OF
MOLES OF PRODUCTS FORMED
BY PYROLYSIS

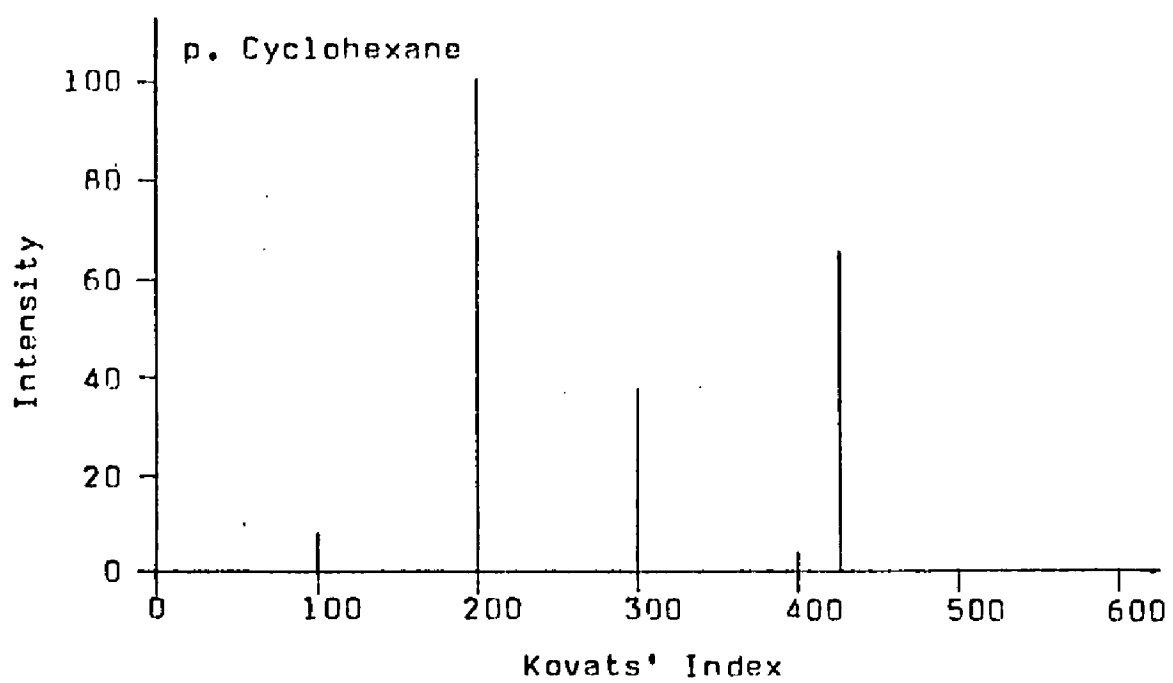






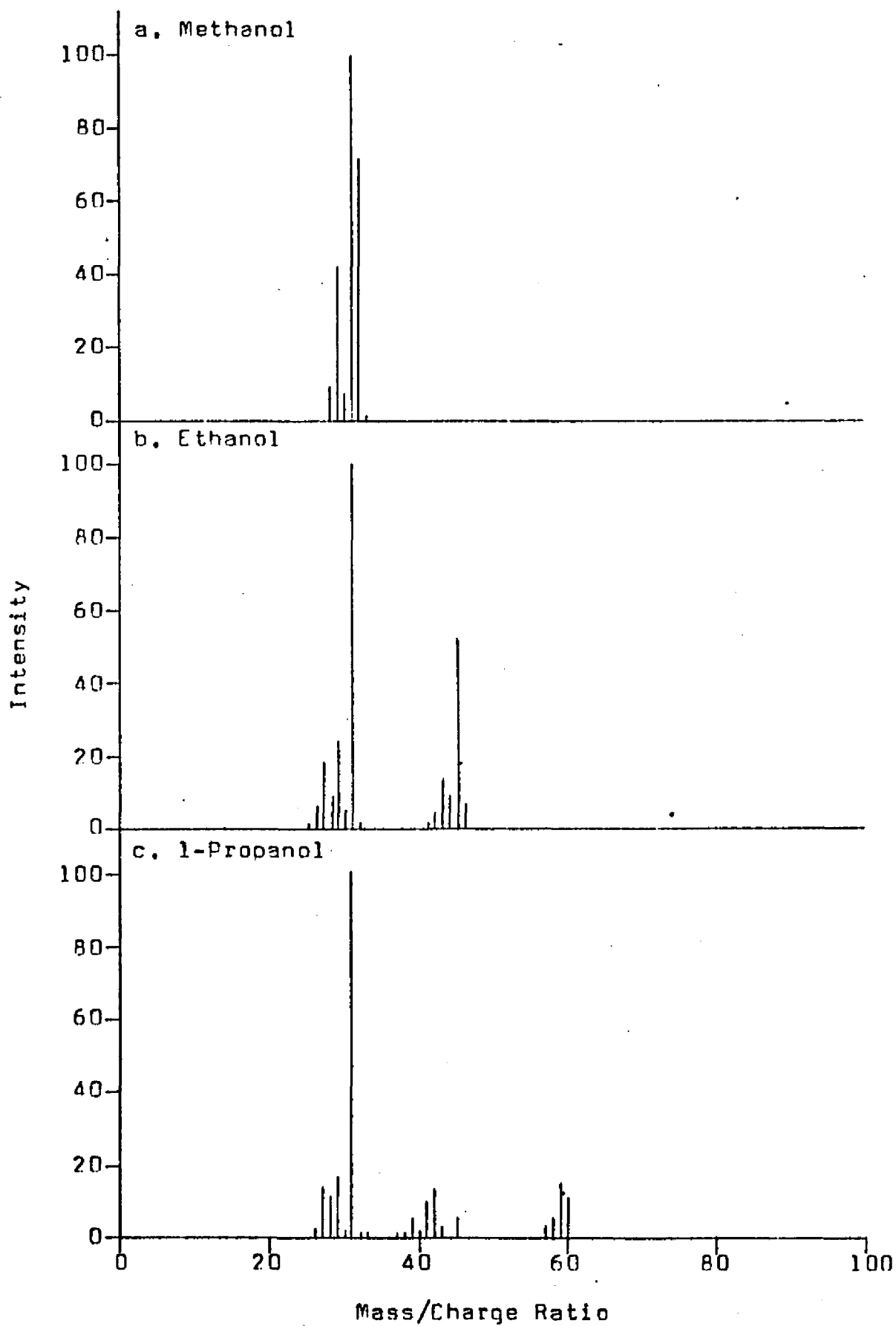


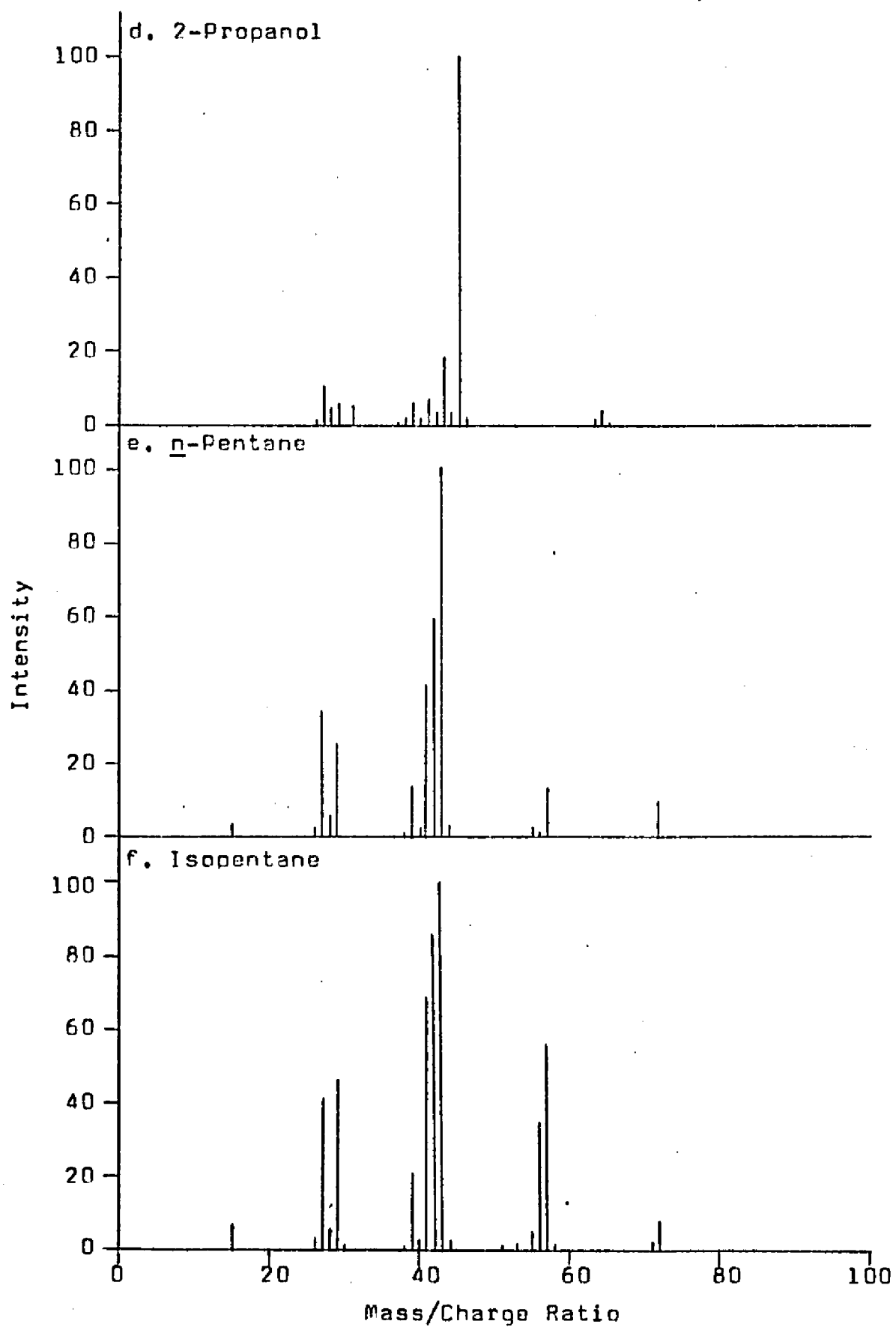


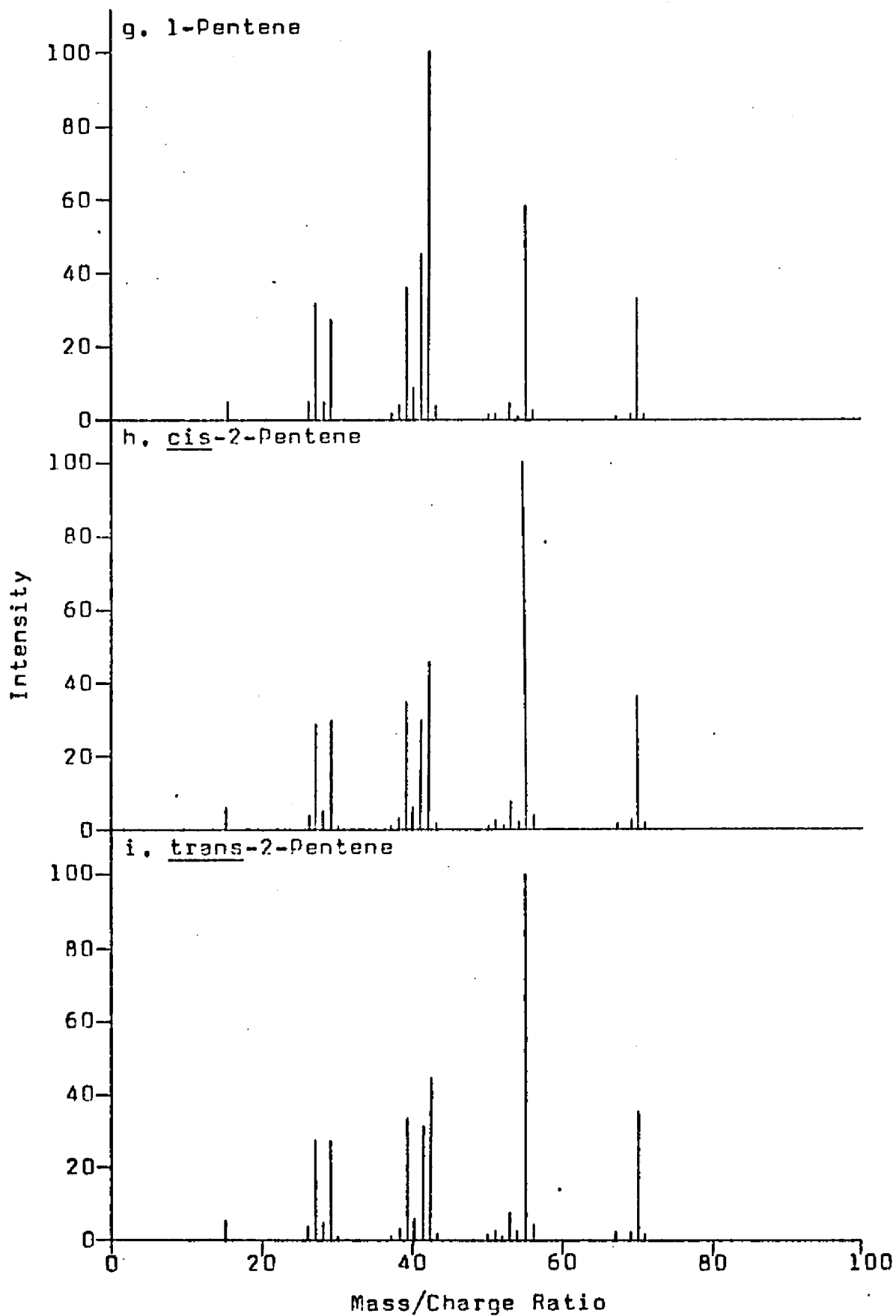


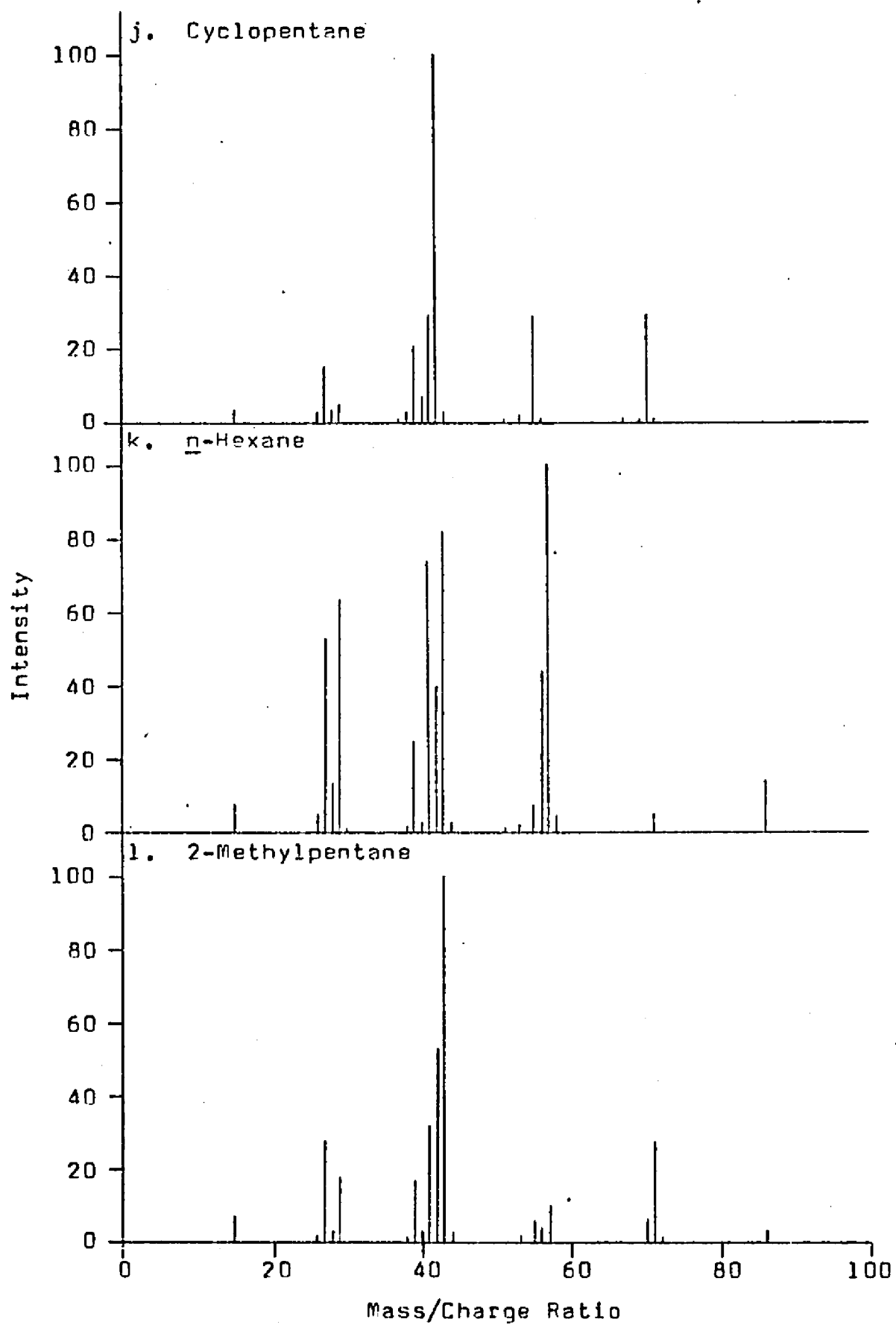
Appendix V
MASS SPECTRAL DATA FOR EACH COMPOUND
WHOSE PYROLYSIS WAS STUDIED

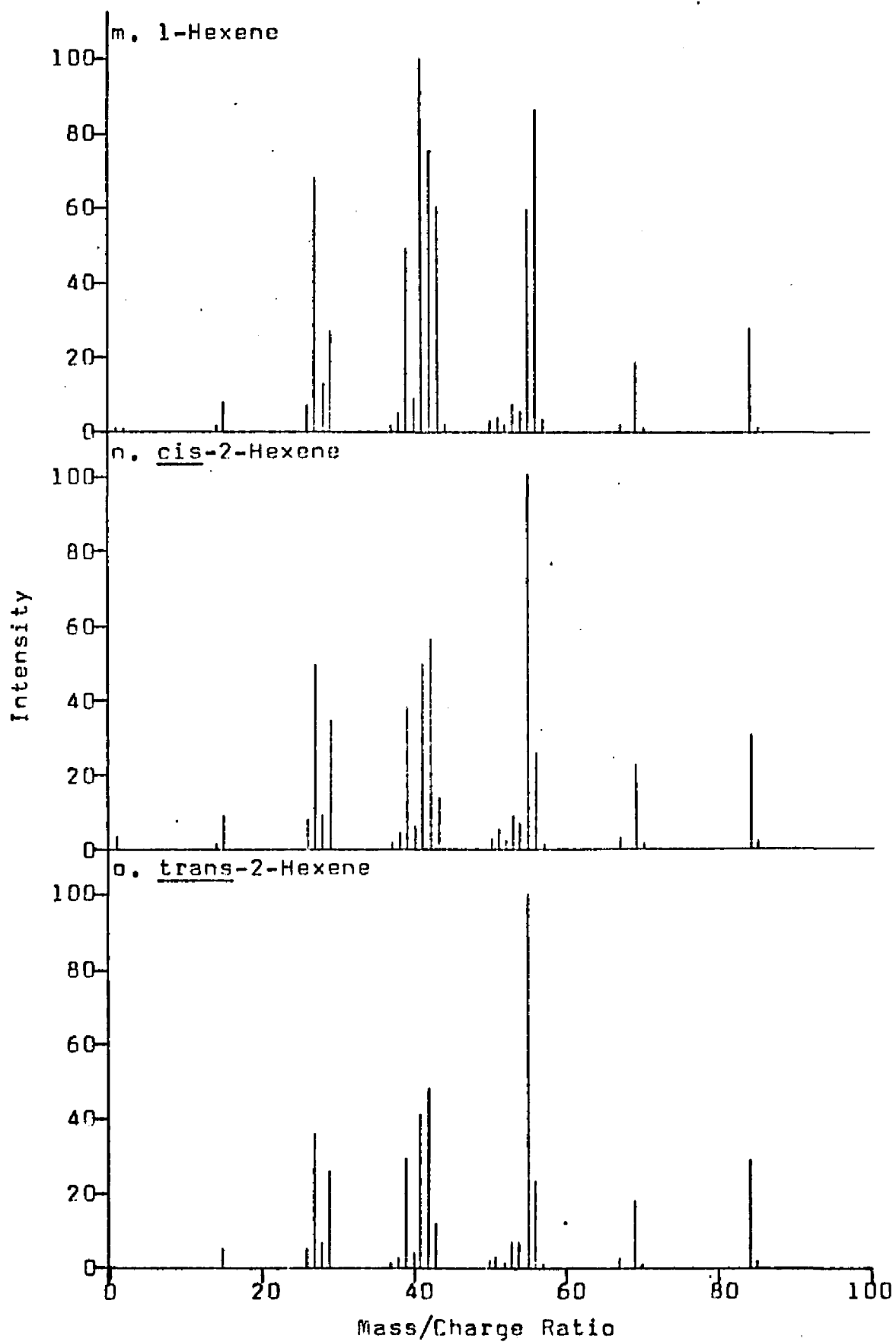
(Obtained from American Petroleum
Institute Research Project 44)

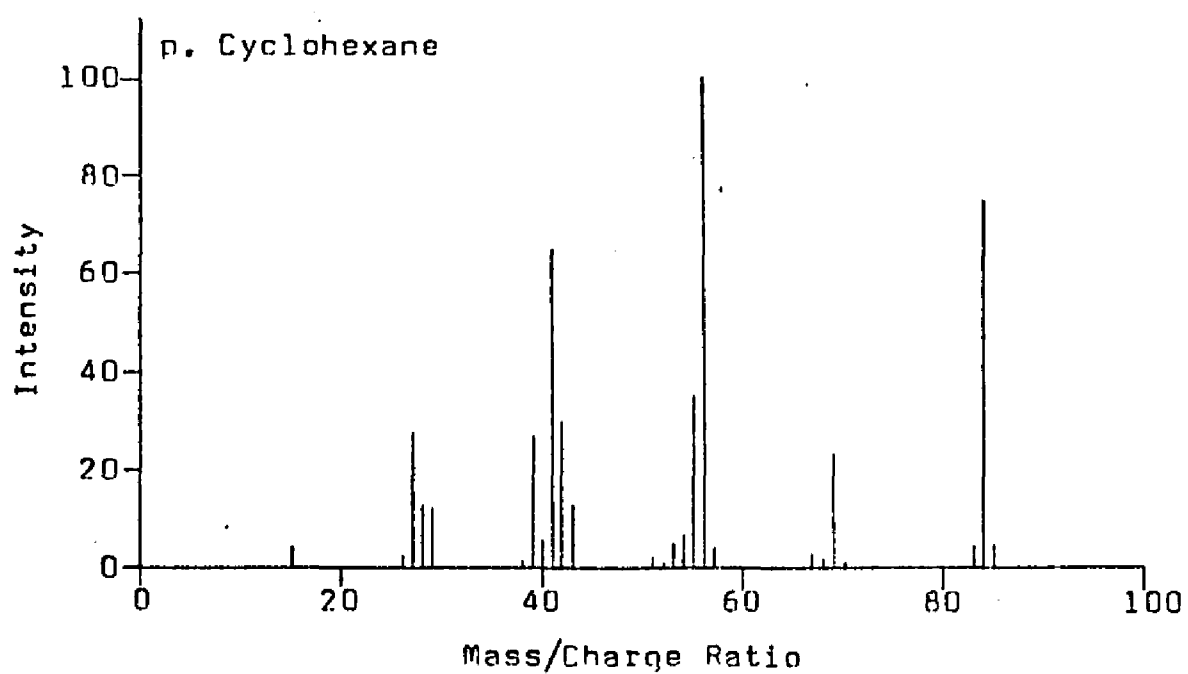












BIOGRAPHICAL DATA

Name	Joseph John Topping	
Date of Birth	October 9, 1942	
Place of Birth	Amsterdam, New York	
Secondary education	St. Mary's Institute Amsterdam, New York	
Collegiate Institutions attended	Dates	Degree
LeMoyne College	1960-1964	B.S.
University of New Hampshire	1964-1967	M.S.
University of New Hampshire	1967-1969	