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STUDIES IN GAS CHROMATOGRAPHY AND THE REACTION OF METHYL RADICALS WITH BUTENE-1

ABSTRACT

Studies in the general field of gas chromatographic analysis have been made and some of the methods developed have been applied to a kinetic investigation of the reactions of methyl radicals with butene-1.

An all-metal thermal conductivity cell with platinum sensing elements was designed to serve as the detector in the glass chromatographic investigation.

Relative retention volumes of eluted compounds in gas partition chromatography were related to dipole-dipole and dipole-induced dipole interactions between the stationary and moving phases.

An ionization gauge detector for gas chromatography was developed. Sensitivities from 100 to 500 times those of thermal conductivity cells were observed.

Chromatographic separations without the use of a carrier gas were achieved.

The products from the reaction of methyl radicals with butene-1 at temperatures near 200°C were identified by gas chromatographic and mass spectrometric analysis as: methane, ethane, 3-methyl-butene-1, pentene-2, n-pentane, isopentane, and 3-methyl-pentane. A mechanism accounting for the formation of these compounds is supported by kinetic evidence.

Butenyl and pentyl radicals formed in the reaction were found to be stable near 200°C. The energy of activation for the formation of 3-methyl-butene was found to be about 4 kcal/mole higher than for the formation of pentene-2. Hydrogen abstraction by pentyl radicals from butene-1 gave n-pentane and isopentane.

From material balances it followed that 60 to 80% of the butenyl, and 7 to 30% of the pentyl radicals are removed from the system by reactions other than combination with methyl and hydrogen abstraction in the case of pentyl.

At temperatures near 500°C the main product of the reaction between methyl and butene-1 was butene-2. It is shown that at these temperatures the isomerization to butene-2 in the unsensitized pyrolysis of butene-1 is a chain process with chain length increasing with temperature reduction.

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GRADUATE STUDIES

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STUDIES IN GAS CHROMATOGRAPHY

AND THE REACTION OF METHYL

RADICALS WITH BUTENE - 1

by

Stephen Alan Ryce

B.A. University of British Columbia, 1955

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A B S T R A C T

Studies in the general field of gas chromatographic analysis have been made and some of the methods developed have been applied to a kinetic investigation of the reactions of methyl radicals with butene-1. In Part I the developments in the field of gas chromatography are described.

An all-metal thermal conductivity cell with platinum sensing elements has been designed and constructed. Excellent compensation for the resulting changes of flow rate of the carrier gas was attained in analyses with rising column temperature. The use of thermistors as sensing elements in such cells was also studied.

The influence of polarity of the stationary phase on relative retention volumes in gas partition chromatography was investigated in conjunction with the analysis of a complex mixture of organic sulfur compounds. Satisfactory separations of hydrogen sulfide, methyl mercaptan, ethyl mercaptan, methyl sulfide, propyl mercaptan, ethyl sulfide, thiophene and dimethyl disulfide were obtained. Isopentane and n-pentane were included for purposes of comparison. Irregularities were observed in relating retention volumes to boiling points for some of these compounds. Reversal of normal elution order within groups of compounds with different columns was related to the polarity of the column and the polarisability of the eluents.

A high-sensitivity ionization gauge detector for gas chromatography was developed. By keeping the grid potential below the ionization potential of helium the device is sensitive only to the eluted compounds in the gas stream. Sensitivities from 100 to 500 times greater than

those of thermal conductivity cells were observed. Only a small fraction of the gas stream emerging from the column is sufficient for detection purposes, and the device is insensitive to temperature and flow rate changes.

Significant advantages may be obtained from the application of the newly developed ionization gauge detector to displacement chromatography because of the possibility of distinguishing between isomeric organic compounds.

Results obtained with gas chromatographic methods without the use of a carrier gas are reported. A partial separation of a mixture of volatile organic compounds was obtained. The ionization gauge detector may be useful in the development of this method.

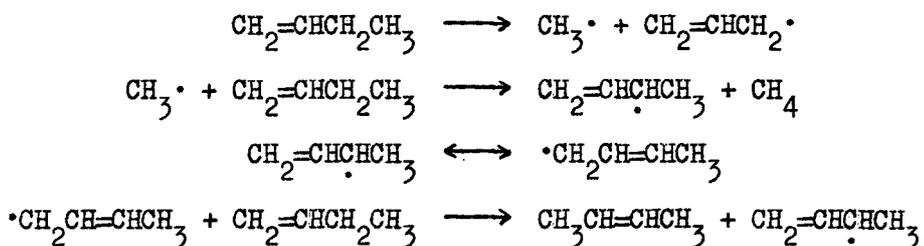
In Part II the results obtained from the reaction of methyl radical with butene-1 are described. Alumina, squalane-pelletex, and tricresyl phosphate columns were used for the gas chromatographic analysis. Mass spectrometric identification of products was done where necessary.

In the temperature range 160 to 220°C with di-t-butyl peroxide as the methyl source the following reaction products were identified: methane, ethane, 3-methyl-butene-1, pentene-2, n-pentane, isopentane, 3-methyl-pentane, and acetone. A mechanism accounting for the formation of these products and supported by kinetic evidence is presented. The butenyl and pentyl radicals formed in the reaction are stable near 200°C. Butenyl radical does not abstract hydrogen from butene-1 near 200°C, but combines with methyl to yield pentene-2 and 3-methyl-butene-1. The energy of activation for the formation of 3-methyl-butene-1 is from 2 to 4 kcal/mole higher than for the formation of pentene-2. Hydrogen

abstraction by pentyl radicals from butene-1 gives n-pentane, and isopentane. The reactivity of the branched radical $\cdot\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{CH}_3$ in hydrogen abstraction is twice as great as that of the straight chain radical $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3\cdot$.

From material balances obtained it was found that 60 to 80% of butenyl, and from 7 to 30% of pentyl radicals are removed from the system by reactions other than combination with methyl and hydrogen abstraction in the case of pentyl. The disproportionation of pentyl radicals to pentane and pentene was unimportant in the present system.

At 450 and 492°C methyl radicals do not sensitize the formation of the cyclic reaction products which were observed by other workers in the unsensitized pyrolysis of butene-1 at temperature near 500°C. The main reaction product of methyl with butene-1 at 450 and 492°C was found to be butene-2. The isomerization to butene-2 in the unsensitized reaction is a chain process with chain length increasing with temperature reduction. The mechanism of the chain reaction of isomerization is postulated to be:



The chain length at 450°C was found to be 12.6, and at 492°C as 2.3.

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

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P R E F A C E

Previous investigations in this laboratory¹²(Part II) had shown that the reaction of methyl radicals with butene-1 yields a complex mixture of hydrocarbon products. Before the advent of gas chromatography the only reliable method for the analysis of such complex mixtures was mass spectrometry, often preceded by low temperature fractionation. The mass spectrometric method remains unexcelled for the identification of a single hydrocarbon or for the analysis of simple mixtures but it cannot be applied readily to complex mixtures because of the overlapping of fragmentation peaks and because of similarities in the mass spectra of isomeric compounds.

At the beginning of the present investigation the technique of gas chromatography was still very much in its infancy. Relatively few publications dealing with the gas chromatographic analysis of the higher hydrocarbons had appeared. In addition, no commercial apparatus was available except for a displacement-type instrument which required comparatively large amounts of sample, and a thermal conductivity cell which did not perform satisfactorily when used in research-type instruments.

Some studies in the field of gas chromatography were therefore undertaken to develop apparatus and techniques appropriate to the present investigation, and as a contribution to knowledge generally on the subject.

A description of the studies in gas chromatography is presented in Part I of this thesis. Part II contains the results of a study of the reactions of methyl radicals with butene-1. Gas chromatography was the principal analytical method used in this latter work.

PART I

STUDIES IN GAS CHROMATOGRAPHY

INTRODUCTION

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

Chromatographic techniques, which today are an indispensable tool in almost every chemical laboratory, originated in 1906 with the investigations of the Russian botanist Tswett. His work was largely neglected until it was rediscovered by Kuhn, Winterstein and Lederer in the 1930's who applied it to the separation of carotenes and xanthophylls.

A number of early attempts were made to separate gases and vapours by chromatographic methods using stationary solid adsorbents and a moving gaseous phase. However, the occurrence of non-linear adsorption isotherms prevented clear-cut separations, and the technique remained undeveloped for many years.

Following the displacement technique introduced by Claesson¹ in 1946, gas chromatography received its greatest impetus from the introduction by James and Martin² in 1952 of the gas-liquid partition method, which had been suggested in 1941 by Martin and Synge³.

At the beginning of the present investigation, in the summer of 1955, relatively few publications existed concerning gas chromatography generally, and only very few dealing with the aspects of the analysis of hydrocarbons. By 1958 a bibliography published by a commercial firm⁴ lists no fewer than 260 publications in the field. This wide-spread interest in gas chromatography is chiefly due to the much higher resolving power in analytical separations than that of the best distillation methods. A striking example is the separation of ortho- and para-hydrogen recently reported by Moore and Ward⁵.

Apart from its use in analysis, gas chromatography has been applied

to the determination of certain physical quantities, such as heats of solution⁶, and heats and entropies of adsorption⁷, and to the preparative isolation of components from mixtures⁸. However, the interest in the present investigation was centred in the application of gas chromatography to the analysis of the complex mixtures of hydrocarbons obtained from such pyrolyses as the thermal decomposition of butene-1⁹.

In discussing the application of gas chromatography to hydrocarbon analysis it is appropriate to refer to other methods available for the same purpose.

Before the advent of gas chromatography, mass spectrometry was virtually the only technique available for the analysis of the small samples obtained from the thermal decomposition of hydrocarbons in a static system. However, the results obtained in the mass spectrometric analysis of complex mixtures are often very difficult to interpret. This is due to the fact that a relatively simple hydrocarbon such as butene-1 will not only show a parent peak at 56, i.e. its molecular mass, but will also give rise to fragmentation peaks at intervals down to mass 12. The analysis of a mixture of such compounds can be simplified by reducing the energy of the electrons in the ionization chamber of the mass spectrometer to a value such that parent ions only are formed, but this procedure results in a large loss of sensitivity. Moreover, the 'cracking pattern' is the main basis of identification of a molecule in the mass spectrometer. The mass spectra of most, if not all hydrocarbons encountered in chemical kinetic studies have been tabulated¹⁰. Due to the overlapping of fragmentation peaks, the unravelling of mass spectra of complex mixtures, especially those containing unsaturated compounds,

is a difficult task. A particular disadvantage in research work is that due to this overlapping of peaks, substances present in trace quantities may be lost. Commercial oil firms, which in some instances control the output of their fractionation columns by mass spectrometric analysis, use electronic computers for the interpretation of the complex spectra obtained. However, for the positive identification of a single hydrocarbon a mass spectrum is as yet unsurpassed.

Other methods for the analysis of hydrocarbons and their mixtures are infra-red absorption and distillation. Both these methods use comparatively large samples, and are useful primarily in conjunction with flow systems where large amounts of products can be accumulated. Distillation has been used extensively to reduce the complexity of hydrocarbon mixtures before mass spectrometric analysis.

The application of liquid chromatography to the resolution of hydrocarbon mixtures^{11,12} suffers from relative insensitivity and slowness of operation. The column effluents are monitored here by such techniques as refractive index measurement. One of the main advantages of gas chromatography over liquid chromatography is the sensitivity of the detection devices available for the former. As little as 10^{-8} moles¹³ can be detected readily. The advantages of gas chromatography in analytical separations with regard to sharpness of separation, speed, and sensitivity, have led to its application to substances with boiling points of 300°C and above, provided that they are not thermo-labile.

Gas Chromatographic Methods

In principle gas- and liquid chromatography are very similar. The

difference is that in gas chromatography the mobile phase is a gas instead of a liquid, and that instead of a solvent, a permanent gas is used to carry the mixture past the stationary medium, which is usually contained in a column. Separation takes place as a consequence of the fact that each component travels through the column at a different rate. The analytical separation depends on the differential adsorption or absorption of the components of the flowing mixture by the stationary medium.

Two principal techniques of gas chromatography exist. These require rather different experimental set-ups, and a choice has to be made as to which method is preferable for the problem in hand.

In the displacement analysis introduced by Claesson¹ and developed by Phillips and co-workers^{8,14}, the mixture of gases is first adsorbed on the top portion of a column filled usually with charcoal. The mixture is then moved along the column by saturating the carrier gas with a constant concentration of a vapour more strongly adsorbed than any of the components of the mixture. This method removes the various fractions from the column in order of their increasing affinities for the column material. This is usually in order of their boiling points, the most volatile components emerging first. If the effluent gas stream is passed through a thermal conductivity cell connected to a high speed pen recorder, the compounds appear on the recorder chart as a series of steps, the height of which is characteristic of the component, and the length proportional to the amount present.

In the elution technique, associated with the names of James and Martin², the mixture to be analysed is inserted into the carrier gas

stream which moves the individual components through the column at different rates depending on the extent to which they are retained by the column material. A chromatogram appears in this case as a series of peaks. The peak location is characteristic of the component, and the peak area is a direct measure of the amount present. The column material in the elution technique can be an adsorbent, or a solid such as kieselguhr or powdered fire-brick coated with a high boiling liquid. In the latter technique referred to as 'partition-elution chromatography', the volatile components emerge from the columns at rates proportional to their respective vapour pressures over the column liquid. The chromatographic process here is analogous to fractional distillation, and the efficiency of such columns can be described in terms of the number of theoretical plates. The best analytical fractional distillation columns have 10 to 20 theoretical plates per meter. With partition-elution columns efficiencies of 1000 theoretical plates per meter are attainable². This high efficiency explains the success of the chromatographic method of resolving components of almost identical physical and chemical properties.

A comparison of the relative merits of displacement and elution method shows that the former cannot easily distinguish isomers of hydrocarbons which are displaced one after the other¹⁵. Such isomers have usually very similar thermal conductivities, and although resolved by the column, appear as one step in the displacement chromatogram. With the elution technique on the other hand, two substances with similar conductivities, if resolved, give quite separate peaks.

Because of the more complete separation of components the elution

technique is preferred for analyses of an exploratory nature. Partition-elution and adsorption-elution chromatography has been used in the investigations described in the following chapters, and also for the analyses in Part II. However, a more critical comparison of displacement and elution techniques is presented in the last chapter of Part I, in which some further developments in gas chromatography have been considered.

Comprehensive investigations into all the practical and theoretical aspects of gas chromatography have been reported by Desty¹⁶, Keulemans¹⁷, and Phillips¹⁸. An extensive survey of the literature will not be given here. The present studies arose in connection with the application of gas chromatography to analytical problems of interest in this laboratory. They include the design of a thermal conductivity cell with a high degree of stability¹⁹, an investigation of polarity interactions between column liquid and sample components which led to a satisfactory analytical separation of a complex mixture of organic sulfur compounds²⁰, and the development of a highly sensitive ionization gauge detector for gas chromatography^{21,22}. Other preliminary studies are also reported on briefly.

CHAPTER I

C H A P T E R I

THERMAL CONDUCTIVITY CELL FOR GAS CHROMATOGRAPHY

An important part of the apparatus in all types of gas chromatography is the device required for detecting the presence of components in the effluent carrier gas stream. Most sensing devices which have been suggested for this purpose are of the differential type, i.e. they indicate a momentary change in the properties of the effluent gas. Integral detector types which record the integrated value of a property of the effluent gas have so far not found any important application in gas chromatography.

A large number of differential detection devices have been suggested which respond to a change in some property of the carrier gas caused by the eluant. Physical properties which are of use in this connection include: thermal conductivity, density²³, viscosity¹⁴, heats of combustion²⁴, and surface potential¹⁴. Other methods employing beta-ray ionization²⁵, and ionization by glow discharge²⁶, have been used.

The suitability of a detection device based on one or the other of the above physical properties depends very largely on the particular application. However, it is generally agreed, that thermal conductivity cells afford the best compromise in meeting most of the requirements of a detector. These are: adequate sensitivity, rapid response, applicability to a wide range of compounds with approximately constant sensitivity, linear response with concentration, insensitivity to flow rate changes, and ease of construction and maintenance of auxiliary equipment.

Various types of thermal conductivity cells have been used in gas analysis, and have been described by Berl²⁷ and Daynes²⁸. Their use in gas chromatography is credited originally to Claesson¹. Such cells consist essentially of a fine metal wire or thermistor, heated by a constant electric current. The effluents from the column are led past this wire, and provided the composition of the gas stream does not vary, the rate of loss of heat by the wire, and hence its electrical resistance, will be constant. A change in composition of the gas stream will cause a change in heat loss, and thus in resistance. By connecting this wire in a Wheatstone Bridge, any change of resistance of the wire caused by a change in composition of the gas stream generates an 'imbalance' signal from the bridge, which can be recorded on a high speed pen recorder.

A thermal conductivity cell can be compared with a platinum resistance thermometer, the temperature of which is changed by the differing thermal conductivities of gases flowing past it. Such a thermometer of very low heat capacity is, of course, sensitive not only to ambient temperature changes but also to the slightest change in the flow rate of the carrier gas, as the flow rate determines largely the rate of heat loss from the wire. To overcome the sensitivity of thermal conductivity cells to temperature and flow changes without affecting their detecting sensitivity, the resistance in the opposing arm of the bridge is replaced by a sensing element identical with that in the measuring channel. This arrangement provides compensation for changes in flow rate and temperature. For maximum compensation both elements should experience the same temperature and gas flow changes.

A thermal conductivity cell described by Phillips and co-workers⁸

consisted of a thermostated glass envelope containing a fine platinum wire. The performance of this cell was found unsatisfactory for the present purposes, presumably due to a lack of flow rate and temperature compensation.

Patton, Lewis, and Kaye²⁹ designed an all metal conductivity cell, in which both measuring and compensating elements were placed in adjoining bores of a metal block. Such an arrangement could be expected to give excellent compensation to ambient temperature changes. However, these authors chose a channel geometry in which the compensating element was placed in a diffusion cavity, with the measuring element only exposed to the full gas flow. A commercial instrument (Gow-Mac Instrument Company) employed the same geometry.

Preliminary experiments with systems of interest in the present investigation had shown that the temperature of the column would have to be increased progressively during an analysis to expedite the elution of the higher boiling components of the samples. Therefore a marked change in flow rate had to be taken into account in cell design. One would expect maximum compensation to changes in flow rate with an arrangement in which the geometry of both channels is identical. A 'straight through' flow design seemed to offer the advantage of most rapid response. The alternative, even more flow insensitive, of having both sensing elements in a diffusion cavity, has been reported³⁰ as having a response time greater by a factor of twenty.

Design of Cell

The cell described in the following is inexpensive to construct,

and has performed satisfactorily for nearly three years in almost continuous operation, during which time it has never been disassembled.

The construction details of the cell are shown in fig. 1. The body is a brass block through which channels containing the detecting and reference filaments are drilled. Excellent temperature compensation was achieved with this metal cell, as compared to a glass system previously tried. The use of brass as the cell material did not interfere with the determination of even such chemically active compounds as hydrogen sulfide and mercaptans (see Chapter II).

The filaments were mounted on brass plugs which are sealed to the body of the cell with rubber O-rings. Gaskets with greater heat resistance can be used at elevated temperatures. The filaments are helices of 0.3 cm diameter containing 14 cm of 0.005 cm platinum wire. They are silver-soldered to the ends of Kovar terminals through which the external electrical connections are made. The operating temperature of the filaments was approximately 100°C at a current of 200 ma. This temperature is sufficiently low to avoid pyrolysis of thermo-labile compounds on the filament. The entire stream from the column can, therefore, pass through the detecting channel without the use of a bypass system³¹ if collection of the separated sample components is desired (see Part II). The reference and detecting channels are symmetrical, with both filaments located in the center of the gas stream.

The external features of the cell are shown in fig. 2. Connection with the column and sample inlet system is made with metal-glass ball-and-socket joints. Bakelite rods are tapped into the block for mounting purposes. Electrical connections are made through a terminal block.

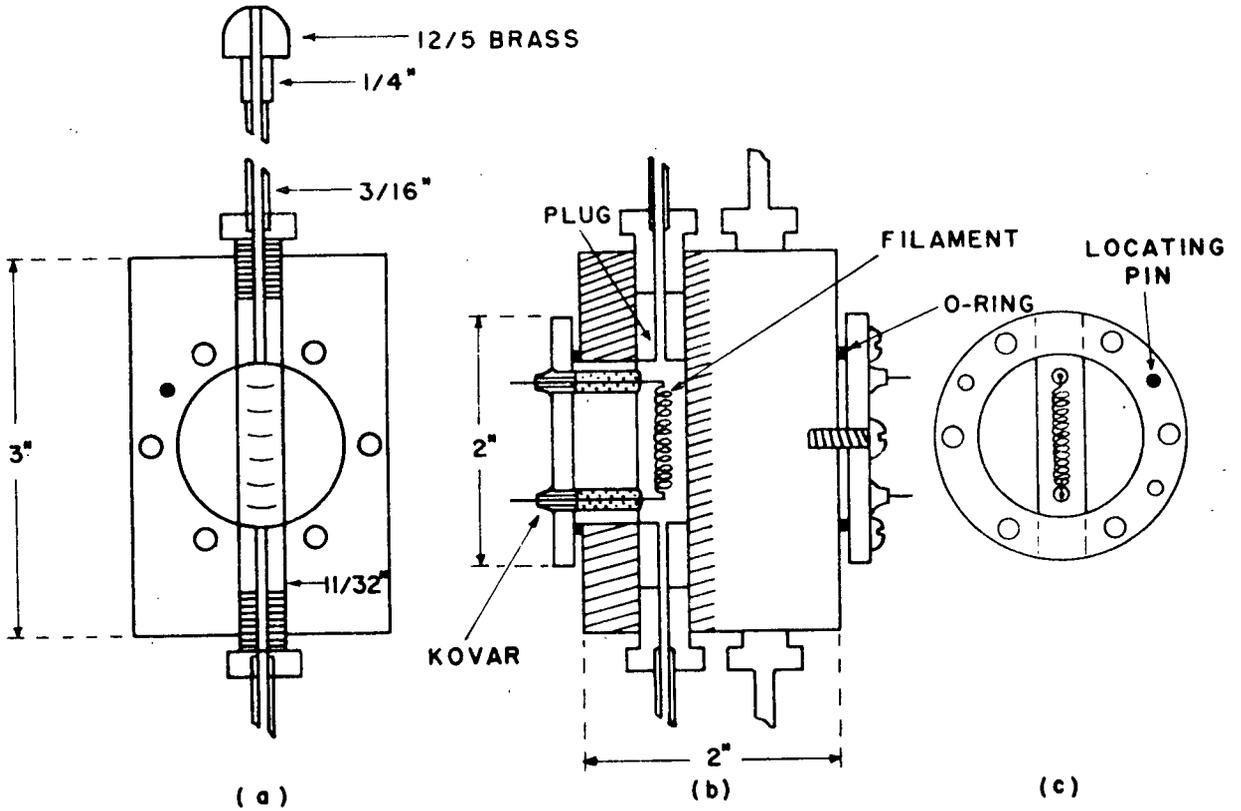


Fig. 1. Thermal conductivity cell

- a. Frontal section
- b. Side section showing detail of one channel only
- c. Detail of filament support

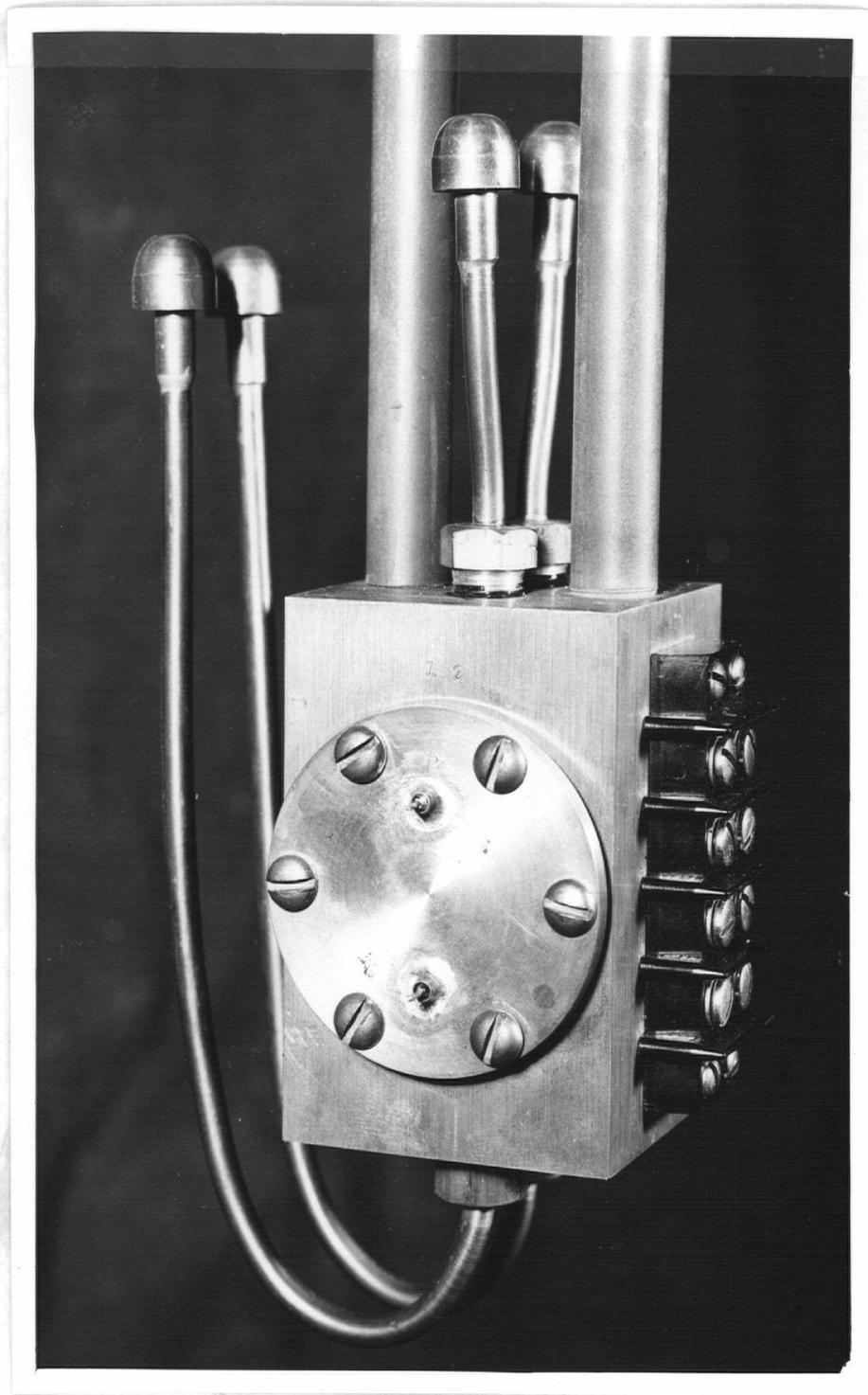


Fig. 2. Exterior view of cell

Performance

Compensation for changes in ambient temperature was sufficient to eliminate the need for thermostating the cell, unless a high degree of reproducibility was desired over an extended period of time. In experiments described in the next chapter a flow rate change from 50 - 30 ml per minute of helium had no effect on the base line setting of the Leeds & Northrup Speedomax recorder (sensitivity 1 - 20 mv full scale). The minimal noise level was insignificant at maximum sensitivity. The minimal amount of material detectable with this cell was approximately 10^{-8} mole of a hydrocarbon. The sensitivity in terms of the sensitivity parameter "S" suggested by Dimbat, Porter, and Stross³⁰, was calculated to be 60 ml x mv per mg. Values as high as $S = 300$ have been reported by other authors³⁰. However, higher sensitivities usually necessitate higher filament temperatures with the resulting danger of pyrolysis of the eluted compounds.

Thermistors in Thermal Conductivity Cells

An alternative to the use of metal filaments as sensing elements in thermal conductivity cells are thermistors³². Certain semi-conductors have a very much larger temperature coefficient of resistance than any known metals or alloys. The coefficient is negative in this case. A matched thermistor pair obtained from the Victory Engineering Corporation, Springfield Road, Union, New Jersey, was mounted in an identical manner to the platinum filaments in the same brass block as described previously.

It was found that the inherent sensitivity of the thermistor cell

was superior to the one achieved with platinum filaments by a factor of 5 - 10. However, the sensitivity to ambient temperature changes was much larger, and rapid drift of the baseline occurred. The reason for this undesirable behaviour appears to be that the degree of matching of thermistors changes much more rapidly with temperature than is the case with metal filaments. Hence, to remain matched, the thermistor beads must be kept virtually at a constant temperature. This requirement is a technical impossibility in experiments where changes of flow rate of the carrier gas occur. It is interesting to note that the use of thermistors in thermal conductivity cells of commercially available gas chromatographs has now been abandoned by almost all companies.

CHAPTER II

C H A P T E R I I

POLARITY INTERACTIONS BETWEEN GAS AND LIQUID PHASE

IN PARTITION CHROMATOGRAPHY

General

In gas partition chromatography separation of the components of the moving phase is effected by a column packed with a solid, porous material of large surface area coated with a thin film of a non-volatile liquid. Celite 545 (Johns Manville) is a suitable solid for this purpose. Components in the mobile phase will be partitioned between the gas and the liquid phase. The difference in the partition coefficient for each component provides the basis for separation.

To a first approximation components are eluted from partition columns in the order of their boiling points, providing that there is no molecular interaction between the column liquid and eluants. In this case separations are based on the difference in vapour pressures of the components, and such differences are usually sufficient to effect separations in a homologous series. However, it is often desired to separate substances of closely similar boiling points. It was realized early in the development of gas-liquid chromatography that molecular interaction between the components of the mobile phase, and the stationary column liquid could have a strong influence on the partition coefficients, and thus on the resolution of components of a mixture.

Such molecular interactions causing selective retardation on columns have been ascribed to hydrogen bonding, polarity of the column liquid,

and others.

James and Martin³³ reported that primary, secondary and tertiary amines could be distinguished by comparing their elution times from two columns having different hydrogen bonding tendencies.

The selectivity of the stationary liquid in gas chromatography has been investigated by Keulemans, Kwantes, and Zaal³⁴. A variety of high boiling compounds ranging from transformer oil to dimethyl formamide were tried as column liquids, and their polarity linked with their increasing selectivity for the separation of olefins from paraffins, and for saturates from aromatics.

A separation of butene-1 from isobutene (boiling points - 6.3 and - 6.9°C respectively) was achieved by Bradford, Harvey and Chalkley¹⁵ with a column liquid consisting of a saturated solution of silver nitrate in glycol. It is claimed that the forces of attraction between metal ions and unsaturated hydrocarbons made the separation of these closely similar olefins possible. These forces are of a higher magnitude, and are more specific due to steric effects, than hydrogen bonding.

In the following report interactions between column liquid and mobile gas phase are considered which are ascribed not only to dipole-dipole interactions but also to polarizability effects. These effects were observed during the analysis of a mixture of volatile organic sulfur compounds. The apparatus and techniques used here are described in some detail, as they are identical to those applied to the analysis of hydrocarbon mixtures in Part II of this thesis.

Analysis of Volatile Organic Sulfur Compounds by Gas Partition

Chromatography

Analytical methods for the quantitative determination of hydrogen sulfide, mercaptans, and alkyl sulfides and disulfides in the presence of each other are of importance in a number of investigations. Because of similarities in chemical behavior of these compounds, chemical procedures³⁵⁻⁴⁰ are usually difficult, and the results may be unreliable. The success achieved by gas chromatography as an analytical tool has suggested the application of the technique, based on physical rather than chemical differences, to the analysis of sulfur compounds. Hydrocarbons virtually identical in their properties have been separated by this means, and it was felt that separation of sulfur compounds, which differ greatly in volatility, should be possible.

The system chosen for investigation was one that had been encountered in work on the pyrolysis of dimethyl disulfide³⁹. It contained hydrogen sulfide, methyl, ethyl, and propyl mercaptans, dimethyl and diethyl sulfides, dimethyl disulfide, and thiophene.

Experimental

The hydrogen sulfide was prepared in the laboratory. The other compounds were standard grade, obtained from Eastman Kodak Co., Rochester, N.Y.

The choice of a suitable chromatographic system was governed by experience gained in this laboratory in hydrocarbon analysis⁹ and by the nature of the compounds studied. Adsorption methods using activated alumina or silica gel columns were avoided, as the acidic nature of some

of the sulfur compounds might lead to irreversible adsorptions. A preliminary investigation showed that suitable separations could be accomplished by using a partition-elution column with tricresyl phosphate as the liquid phase on a Celite column.

The apparatus is illustrated in fig. 3.

Helium was used as the carrier gas because of its low viscosity and the large difference between its thermal conductivity and those of the compounds being analyzed. The sample inlet system was designed for admission of vapor samples by the convenient syringe and serum-cap technique. The less volatile components of the mixture were admitted at partial pressures not exceeding their vapor pressures at room temperature, to avoid condensation in the apparatus. Air was also present in the vapor samples of these compounds. The column was a 4-foot borosilicate glass U-tube of 5-mm internal diameter, mounted in a heating jacket by means of which the column temperature could be increased rapidly. The column was filled with a mixture of tricresyl phosphate (Eastman Kodak technical grade) and Celite 545 (Johns Manville) in proportion 30 to 70 by weight, according to the method described by James and Martin².

The thermal conductivity cell¹⁹ has been described in the previous chapter. The fact that the cell body was made from brass did not affect the determination. The sensitivity of the cell remained unaltered during the investigation and no reaction with the sulfur compounds was observed.

The two filaments of the cell were mounted in the usual manner in opposing arms of a bridge circuit and carried a current of approximately 200 ma. Any imbalance in the bridge circuit caused by the appearance

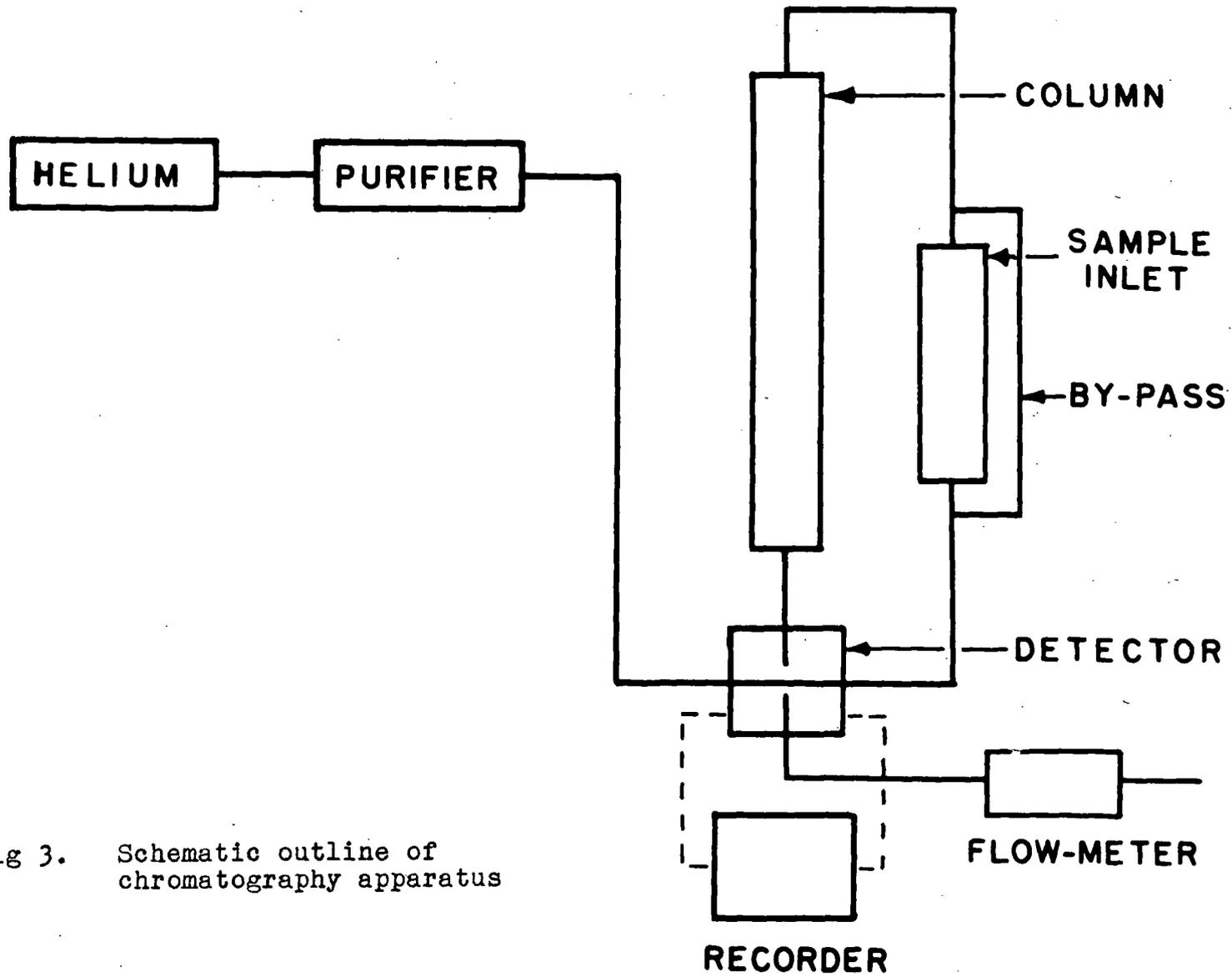


Fig 3. Schematic outline of chromatography apparatus

of a substance other than the carrier gas in the detecting channel of the cell was displayed on a Leeds & Northrup Speedomax recorder of adjustable sensitivity (1 - 20 mv full scale).

The time required for elution of a group of compounds differing greatly in boiling points can be reduced sharply by gradual increase of column temperature during the analysis. This procedure has been used successfully by other workers³¹. Lower boiling components of a mixture, which move through the column with relatively high velocities, can be resolved at or near room temperature. The rate at which the higher boiling compounds pass through the columns is greatly increased at elevated temperatures⁴¹. A reproducible heating rate was used in all analyses.

Owing to the increase in gas viscosity with rising temperature, the flow rate through the columns decreases markedly. In order to maintain the carrier gas flow at the initial rate, the pressure differential should be increased with the temperature. However, such an increase would affect only the compensating filament in the conductivity cell, causing it to operate like a Pirani gauge, with resulting deviations in the base line of the recorder. Hence, it is necessary to keep the pressure differential constant and accept the considerable change in flow rate. For example, at a pressure differential of 3 pounds per square inch, the flow rate changed from 50 ml per minute at 19°C to 33.5 ml per minute at 112°C. The reproducibility of these figures suggests that the change in flow rate is a better measure of the true column temperature than that indicated by a thermometer placed inside the heated column jacket.

Results and Discussion

A chromatogram, showing the separation of the components of a mixture containing hydrogen sulfide, methyl mercaptan (methanethiol), ethyl mercaptan (ethanethiol), methyl sulfide, propyl mercaptan (propanethiol), ethyl sulfide, thiophene, and dimethyl disulfide, is presented in fig. 4. Normal pentane and isopentane were added to the mixture to relate the relative retention volumes of hydrocarbons to those of the sulfur compounds. The compounds were identified by their retention volumes and by reinforcing the peaks with the pure substances.

Satisfactory separation of the hydrogen sulfide from the air present in the syringe and of the pentanes and methyl mercaptan was obtained with a reasonable elution rate at room temperature. After methyl mercaptan appeared, the temperature of the column was raised to speed up elution of the remaining compounds. Lower temperatures result in sharper separations but greatly increase the retention volumes for substances of relatively low volatility^{31,42}. Ethyl mercaptan and dimethyl sulfide were separated at approximately 70°C and the column temperature was allowed to rise to approximately 120°C to accelerate the elution of dimethyl disulfide.

Water vapour, introduced with the sample, appeared as a peak between dimethyl sulfide and propyl mercaptan. It could be eliminated by placing a drying agent like sodium sulfate between the inlet point and the column. The air peak could also be eliminated by using sample collecting and admission systems in which air is excluded. In the syringe technique, the sharp peaks due to the pressure differential during the insertion of the sample, served as a convenient reference point from which to determine

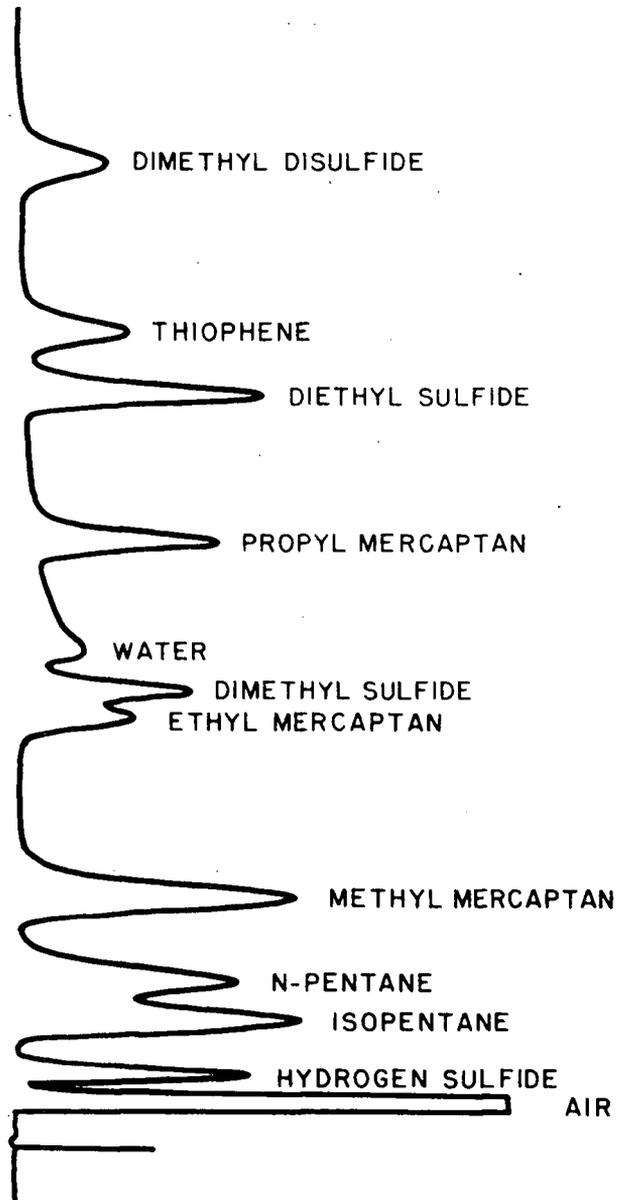


Fig. 4. Separation of volatile sulfur compounds plus pentanes with tricresyl phosphate column

retention volumes.

Fig. 5 further demonstrates the separation of a hydrocarbon and a related sulfur compound and the effect of column temperature on the separation. Thiophene and benzene could not be completely resolved at 115°C but were satisfactorily separated at 77°C.

To show the separation of mercaptans and the corresponding alcohols, a mixture containing methanol, ethanol, and methyl and ethyl mercaptans was passed through the column, while the column temperature was increased gradually to approximately 100°C. The resulting chromatogram is shown in fig. 6. Normal pentane was again added to show the relative position of the hydrocarbons.

Quantitative Aspects

In quantitative analysis by gas chromatography, peak areas are customarily used as a measure of the amount of substance placed on the column^{29,30}. Measurements of this type depend on experimental parameters such as carrier gas flow rate, sensitivity of the thermal conductivity cell to the compound at a particular cell temperature, and recorder sensitivity and chart speed. However, the method is capable of a high degree of accuracy if experimental conditions are standardized carefully. In the present study the peak areas were directly proportional to the amounts of the substances placed on the column.

In dealing with compounds like alkyl sulfides and mercaptans, it is difficult to admit micromole quantities of the pure substances into the apparatus to determine sensitivities, an operation that should be repeated with each analysis. A method was devised which permits rapid

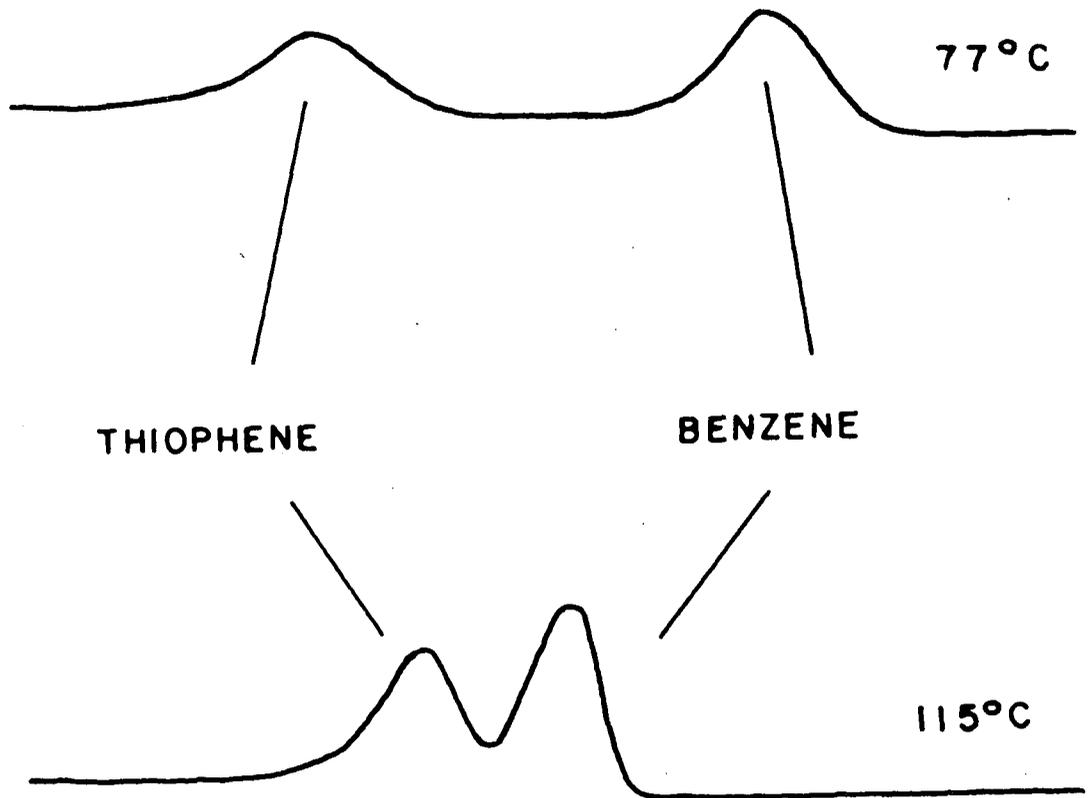


Fig.5. Effect of temperature on separation of thiophene and benzene with tricresyl phosphate column

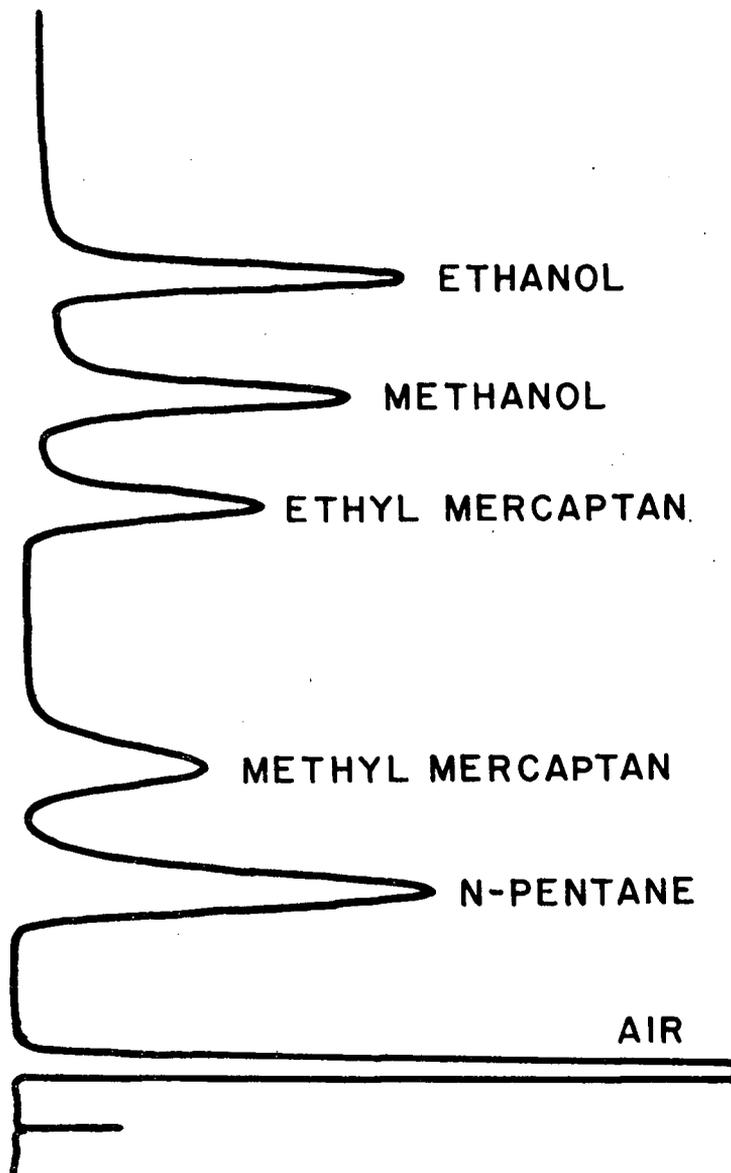


Fig. 6. Elution order for mercaptans, alcohols, and hydrocarbon with tricresyl column

determination of the sensitivity of the apparatus to a particular compound by means of a calibration involving a mixture of the compound and air. The method is illustrated with ethyl mercaptan (boiling point 34.7°C) and is applicable to all volatile substances having a reasonably high vapour pressure.

A few drops of the mercaptan are placed in a polyethylene bag fitted with a serum cap. A volume, V_1 , of the air-mercaptan vapour mixture is withdrawn with a syringe and injected into the apparatus. Peak areas, A_1 for the mercaptan and A_2 for air, are measured. In a second experiment, the same amount of air-mercaptan vapour is withdrawn from the bag and an additional volume V_2 , of air is then drawn into the syringe. Injected into the apparatus, this yields the same peak area for the mercaptan - i.e. A_1 - and a larger peak, A_3 , for air. Assuming that the ideal gas laws are applicable, the unknown volume of mercaptan V_x in V_1 is :

$$V_x = V_1 - \left(\frac{A_2}{A_3 - A_2} \right) \times V_2$$

With a column temperature of 78°C and a helium flow rate of 50 ml per minute, the elution time for the mercaptan was 2.5 minutes. It was therefore possible to obtain a reliable average value within a reasonable period. By using the same syringe for admitting both standards and samples for analysis, errors in syringe calibration are largely eliminated. The method becomes inaccurate if V_1 and V_2 are very dissimilar or if the vapour pressure of the substance being analyzed is low. It is important to saturate the syringe lubricant with the compound, to avoid errors due to absorption. This can be done by purging the syringe several times with the vapour.

Sensitivity

The volume, V_x , is then converted to micromoles and the sensitivity of the apparatus is calculated in, for instance, square centimeters of peak area per micromole. In an experiment with ethyl mercaptan, V_1 was 0.60 ml and V_2 was 0.30 ml. The sensitivity of the apparatus to this compound was 1.44 sq.cm. per micromole at a chart speed of 1 inch per minute. A 0.03-sq.cm. peak, the limit of quantitative estimation in the present work, therefore, corresponded to 2×10^{-8} mole of ethyl mercaptan.

The Influence of Polarity and Polarizability on Retention Volumes

A logarithmic relationship between the peak retention volume of a substance and its vapour pressure at a given temperature has been reported by several investigators^{6,41}. In the present work the situation is complicated by the temperature increase during the analysis, but the elution order for the organic sulfur compounds in fig. 4 agrees qualitatively with the general relationship.

The influence of the polarity of the compound on its retention volume can be seen in the relative positions of the hydrocarbons and the mercaptans. The pentanes, with boiling points of 28° to 36°C and a molecular weight of 72, have a smaller retention volume than has methyl mercaptan with a boiling point of 7.6°C and a molecular weight of 48. The dipole moments of n-pentane and methyl mercaptan are 0 and 1.26, respectively⁴³. The more polar mercaptan presumably interacts more strongly with the highly polar tricresyl phosphate phase on the column than does the non-polar hydrocarbons.

The elution order for thiophene and benzene conforms to the usual pattern; the less volatile, more polar thiophene has the larger retention volume.

However, the elution order for thiophene and diethyl sulfide, fig. 4, is different from that predicted by boiling points or dipole moments. The sulfide (boiling point 92°, dipole moment 1.51⁴³) has a smaller retention volume than thiophene (boiling point 84°C, dipole moment 0.6⁴³). The observed reversal of elution order is presumably due to an electron interaction effect. Thiophene, because of its aromatic character, is strongly polarized by the polar tricresyl phosphate, causing an induced dipole-dipole interaction which is greater than that for the less polarizable diethyl sulfide. The thiophene is therefore retained to a greater extent on the column. Evidence to support this contention is presented in fig. 7. The top chromatogram shows again the elution order with a tricresyl phosphate column. The remaining chromatograms are for a thiophene-diethyl sulfide mixture and for thiophene and the sulfide separately, all done with a column in which paraffin oil replaced tricresyl phosphate as the liquid phase. With a non-polar liquid on the column, the more volatile thiophene has the smaller retention volume.

In further work⁴⁴ three columns of different polarity were used. The column liquids were paraffin, di-n-butyl phthalate (DNBP) and tricresyl phosphate (TCP), with dipole moments of 1, 1.2, and 1.5 debye respectively. The relative retention volumes of five systems of 3-7 compounds each were compared on these columns. Included were alcohols, ketones, ethers, esters, unsaturated cyclics, and halogenated compounds. By taking also into account hydrogen bonding, when this was reasonable,

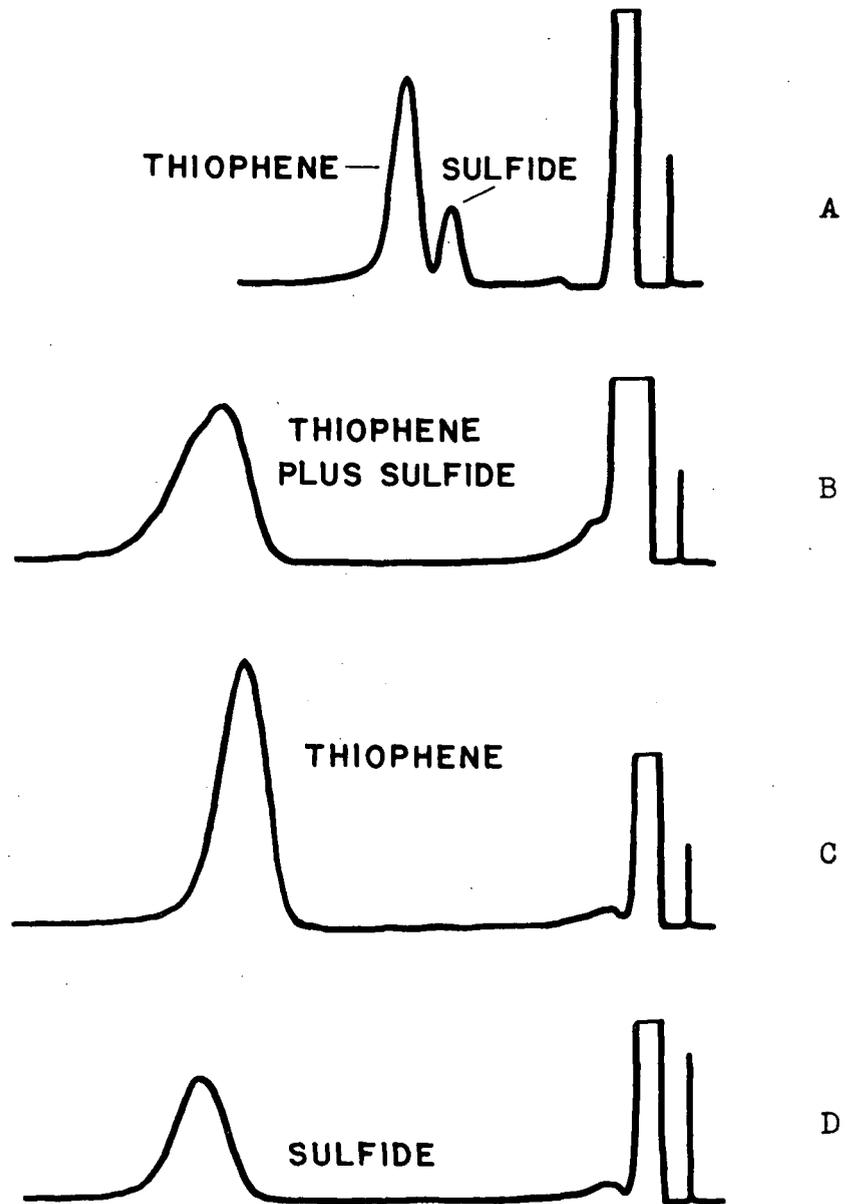


Fig. 7. Effect of nature of column liquid on order of elution of thiophene and diethyl sulfide

- A. TCP
- B. Paraffin
- C. Thiophene only with paraffin column
- D. Diethyl sulfide only with paraffin

the results were consistent in every case with dipole interactions.

Particularly interesting with regard to the dipole-induced dipole interaction between tricresyl phosphate and thiophene postulated in a previous paragraph, were the ratios of the relative retention volumes found for 1,3-butadiene and butene-1 on the three columns.

T A B L E I

Ratio of Retention Volumes of 1,3-Butadiene/
Butene-1 on Paraffin, DNBP, and TCP Columns

Paraffin .0 debye	DNBP 1.2 debye	TCP 1.5 debye
1.07	1.12	1.14

Considering that the butene-1 has a small dipole moment (0.3 debye), and the symmetrical butadiene has none, the increase of the ratio of the retention volumes with increasing column polarity is contrary to the trend expected on the basis of dipole-dipole interaction alone. However, butadiene has two π bonds which are polarizable, whereas butene-1 has only one π bond. Therefore, the observed facts may be explained, as in the case of thiophene, by invoking the dipole-induced dipole effect.

It seems that it should be possible to separate any mixture of volatile compounds by the use of two or more columns of differing polarity. It should also be possible qualitatively to predict the elution order of the components of a mixture on different columns, and the trend of the ratios of their retention volumes.

CHAPTER III

C H A P T E R I I I

AN IONIZATION GAUGE DETECTOR FOR GAS CHROMATOGRAPHY

Introduction

In Chapter I, it was pointed out that thermal conductivity cells afford a good compromise in meeting most of the common requirements for a gas chromatographic detector. A further requirement in some analytical procedures is that the separated material should not be destroyed or altered by the detection device. This requirement is met by the gas density balance²³, but not by thermal conductivity cells unless they are operated at low sensing element temperatures, or unless only part of the effluent gas from the column passes through the cell³¹, a condition which reduces cell sensitivity.

For analyses such as the determination of trace compounds in gaseous systems, high sensitivity is undoubtedly the most important single requirement. The "sensitivity" of a detector is not always clearly defined in the literature. Dimbat, Porter, and Stross³⁰ have proposed a "sensitivity parameter" which takes into account recorder sensitivity, chart speed, and carrier gas flow rate, according to the following relationship:

$$S = \frac{A C_1 C_2 C_3}{w} \text{ ml.mv./mg.}$$

S = sensitivity parameter

A = peak area, cm²

C₁ = recorder sensitivity, mv. per cm. of chart

C_2 = reciprocal chart speed, minutes per cm.

C_3 = flow rate at exit of column, ml. per minute, corrected to column temperature and atmospheric pressure

w = weight of sample introduced at head of column, mg.

These authors suggest that the noise level (in millivolt) should be given along with the reported sensitivity in describing the performance of a detector.

In this connection a distinction should be made between "high frequency" noise (i.e. more than 2 cycles per second) due to vibration of the sensing elements, etc., and base line drift. The latter may be thought of as noise of a very low frequency. Noise of a frequency greater than about 2 cycles per second can usually be eliminated by increasing the time constant of the amplifier circuit without any significant effect on response to the bridge signal.

In the present author's experience the factor limiting the sensitivity of thermal conductivity cells is not the noise level, but the drift of the base line caused at high sensitivities by minute temperature changes in the thermostated cell and by changes in flow rate. Large-scale drifting, consistently to one side of the base line, may be encountered during experiments with rising column temperature when the flow rate changes markedly, or if the pressure differential in the compensating and detecting arms of the cell is altered. The ultimate sensitivity of thermal conductivity cells may depend upon the degree of matching of the filaments or thermistors with regard to electrical properties and geometrical positioning in the channels. In the gas density balance²³ the difficulty in precise matching of detecting and reference

columns would be a limiting factor for the sensitivity, especially in experiments with rising column temperature.

The sensitivity of the detectors referred to above appears to be limited by the fact that they measure the change in a physical property of the gas stream caused by the addition of a minute amount of the eluted material. It seemed desirable, therefore, to develop a detector which would be sensitive to the eluted compound only, and would be independent of the relative amount of carrier gas. Differences in ionization potentials were utilized for this purpose. The ionization potential of helium is much greater than that for all other volatile compounds (Table II). The highest ionization potential among the hydrocarbons is that of methane (14.5 volts).

T A B L E I I

Ionization Potentials for Various Volatile Substances⁴⁵

Substance	Ionization Potential (volts)
He	24.5
Ne	21.5
O ₂	12.5
N ₂	15.5
CO ₂	14.4
CH ₄	14.5
CS ₂	10.4
C ₆ H ₆	9.6

$C_6H_5CH_3$	8.5
CH_2O	11.3
CH_3Br	10.0

Experimental

In initial experiments an ionization gauge (RCA 1949) was modified to serve as a means of utilizing the relatively low ionization potentials of other compounds in detecting them in a stream of helium^{21,22}. The apparatus is shown in fig. 8. A very small fraction of the gas stream from a standard chromatographic column is diverted through an adjustable leak into the ionization gauge. The potential difference between the filament and grid of the gauge is adjusted to approximately 18 volts, a value not sufficient to produce ions when helium only is flowing, and consequently there is no plate current. When a substance of lower ionization potential is carried into the gauge, ions are formed. The ion current is amplified in the usual manner and recorded on a Leeds and Northrup Speedomax recorder (sensitivity 1 - 20 mv. full scale).

For convenience in operation, a metal valve with a Teflon diaphragm was placed between the gauge and the leak. The flow rate and pressure in the gauge could be varied by means of a needle valve located downstream from the gauge. The pressure was measured with a McLeod gauge protected by a dry ice - acetone trap. It was observed that mercury vapor greatly reduced ionization efficiency.

The adjustable leak was made by enlarging the channel of an ordinary Hoke needle valve and drilling a 5/16 inch hole in the body opposite the

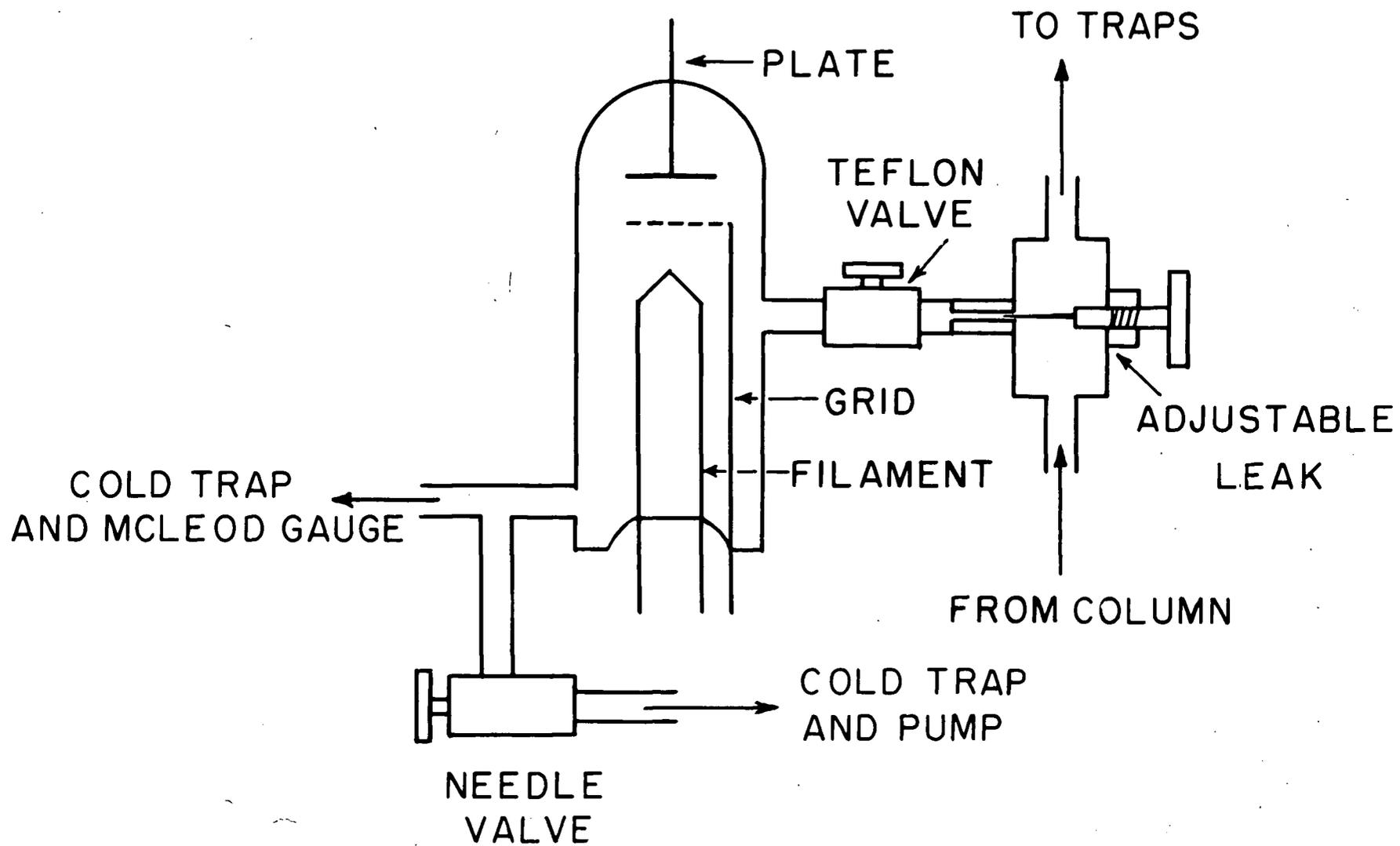


Fig 8. Schematic diagram showing ionization gauge and adjustable leak

tip of the needle. A brass tube, containing a brass plug with a center hole or leak 0.7 mm. in diameter, was soldered into the hole. The "cone" of the original needle was replaced by a sewing needle, the tapered end of which fitted into the leak.

The ionization gauge control unit was a balanced d-c. amplifier with an emission stabilizer. The circuit diagram is given in fig. 9. Grid and plate potentials for the gauge were supplied by batteries to avoid the use of additional stabilized circuits.

Operating Conditions

Over a pressure range in the gauge of from 0.02 to 1.5 mm. of mercury there was a fairly linear relationship between peak height and pressure. The flow rate through the gauge was varied from 13% of the flow through the column (38 ml./minute) to 0.5% at a constant gauge pressure of 0.7 mm. The peak areas were unaffected by the change in flow rate and therefore the ion current seems to depend only on the steady-state pressure in the gauge. At the lower flow rate, tailing of the peaks became noticeable.

The grid potential was found to be the chief factor affecting the sensitivity of the gauge. The variation of peak height with grid potential is shown in fig. 10_a for a typical hydrocarbon. Although the ionization potential of helium is 24.46 volts, grid potentials much less than this value had to be used to avoid ionization of the helium due to the high energy electrons occurring in the Maxwellian distribution with which the electrons leave the filament. The maximum grid potential that could be used was 18 volts. Higher grid potentials might be used at lower filament temperatures where the fraction of high energy electrons is

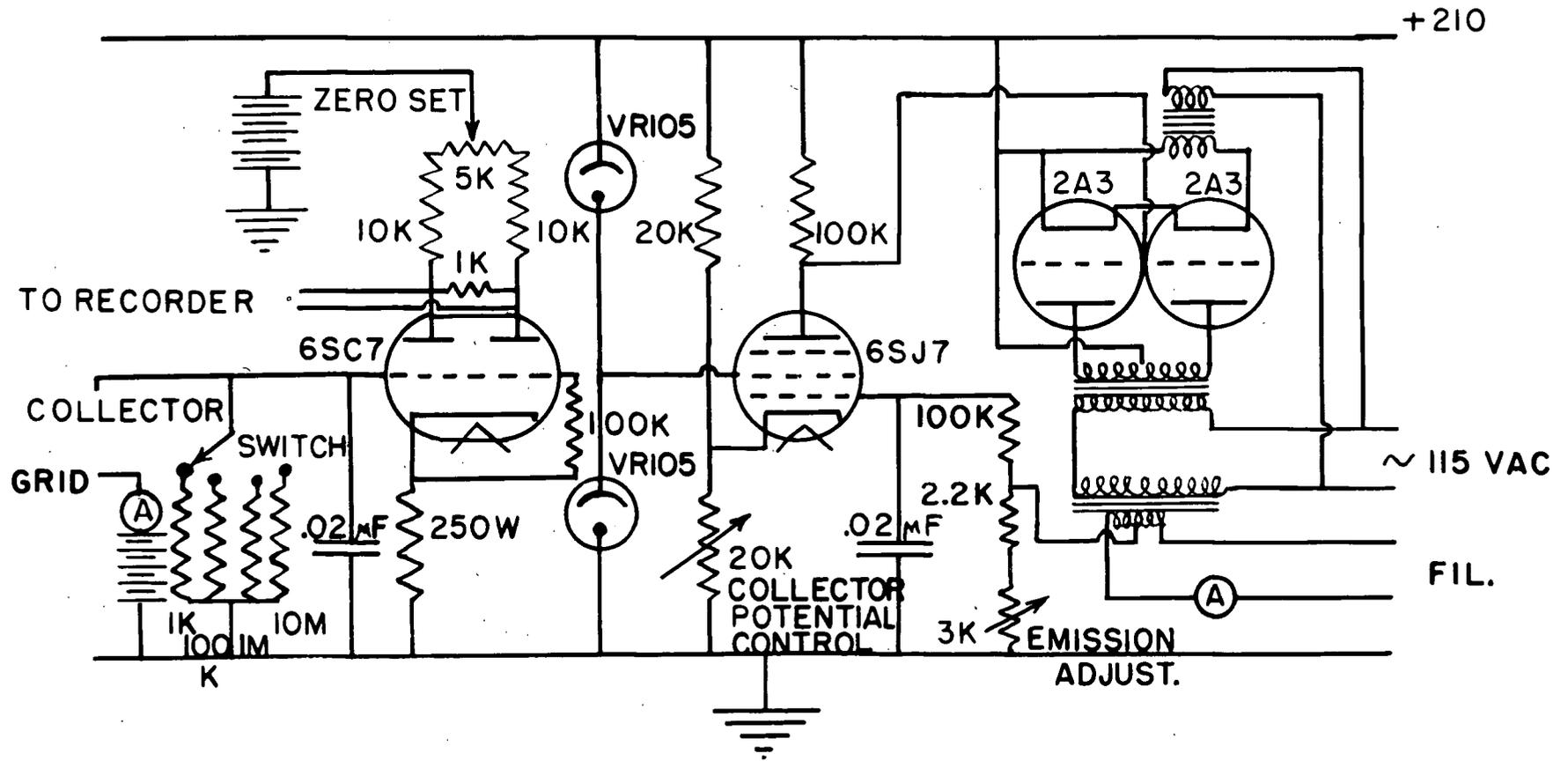
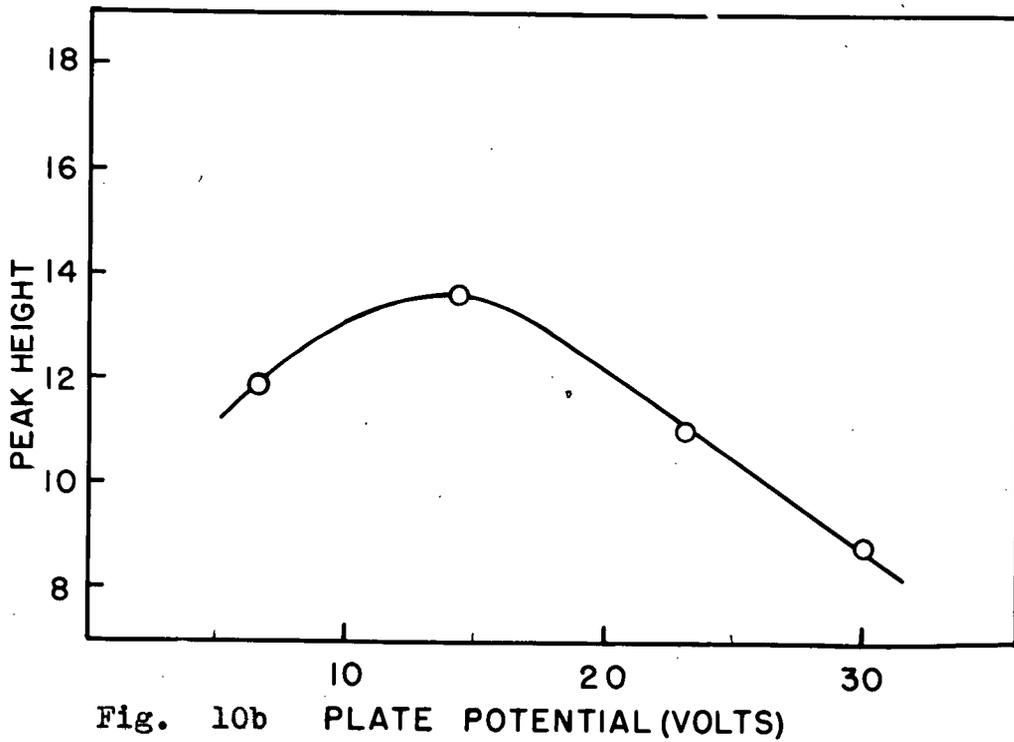
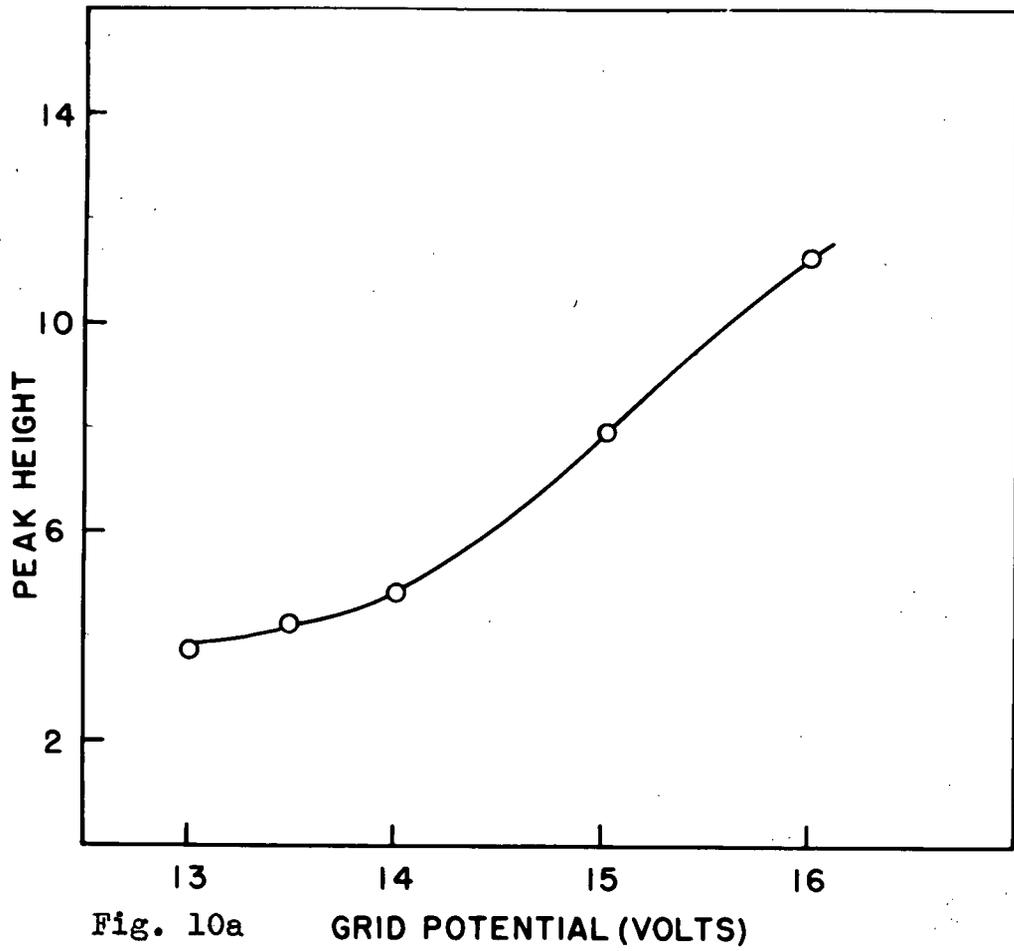


Fig. 9. Circuit diagram of ionization gauge control unit



reduced. The maximum grid potential, and hence the sensitivity, depends also on the purity of the helium. Impurities such as oxygen, nitrogen, and hydrocarbons increase the background ionization in the gauge. The helium was purified before entering the chromatographic system by passing it through a charcoal trap cooled in dry ice - acetone.

The variation of sensitivity with plate potential is shown in fig. 10_b. The observed maximum is presumably due to emission of secondary electrons, penetration of the field into the filament-grid space, and space charge effects.

The sensitivity of the gauge was calculated in terms of the sensitivity parameter³⁰ on the basis of the following experimental conditions: gauge pressure 0.7 mm. mercury; filament current 2.7 ma.; grid potential +15 volts; collector potential -15 volts. S for the ionization gauge was found to be 32,500. Values of 312 for a thermal conductivity cell and 60 for a platinum filament cell operated at low filament temperature have been reported^{30,19}. The noise level on the base line was imperceptible under the above operating conditions. The fraction of the effluent gas stream from the column can be reduced to 0.5% without loss of sensitivity or effect on base line stability. The limit of detection for a typical hydrocarbon was approximately 5×10^{-11} moles (3 mm.² peak area).

Discussion

It is anticipated that a further increase in sensitivity may be achieved by operating at higher gauge pressure and by replacing the tungsten filament with an iridium filament, thus minimizing the change

in work function that occurs when oxygen and hydrocarbons come in contact with the filament. An additional increase may result from further purification of the helium with consequent increase in base line stability.

The speed of response of the gauge depends chiefly on the velocity with which the eluted compound passes between the electrodes. The cross-sectional area of the gauge as presently constituted is very much greater than that of the main gas stream, but because of the reduction in pressure that occurs on passing through the leak, the flow rate through the gauge is more than 10 times the rate in the main gas stream. Thus only a very small fraction of the effluent gas stream need be used for detection, even though the dead volume of the gauge is large. The volume could be reduced markedly by altering the shape of the envelope and the arrangement of the gauge components.

The gauge is completely insensitive to temperature changes and thus it can be located close to the exit end of the column. This is not desirable with thermal conductivity cells used in experiments with rising column temperature, as the gases must enter the cell at the same temperature as the cell.

At the present stage of development, the ionization gauge detector is useful where it is desired to combine very high sensitivity and rapid response with almost complete independence of changes in flow rate, pressure, or temperature. Its use also eliminates the possibility of pyrolysis of the eluted compounds in the detector after elution from the column. The extent to which sensitivity is related linearly to sample size and is independent of the effect of surface reactions on the filament has not been fully established. More recent work indicates that the

stability of the device was substantially increased by the use of an ionization gauge with an iridium filament⁴⁶.

CHAPTER IV

C H A P T E R I V

FURTHER DEVELOPMENTS IN GAS CHROMATOGRAPHY

A Comparison of Displacement and Elution Methods

It was mentioned in the Introduction to Part I of this thesis that elution chromatography is preferred for most analyses due to its ability to distinguish between compounds of equal or nearly equal thermal conductivities, such as hydrocarbon isomers. Although resolved by the displacement column such compounds may give rise to one step only in a displacement chromatogram.

This would imply that compounds are displaced from the column in equal concentrations for a given concentration of the displacer. This is only true if the adsorption isotherms of the compounds are similar. For the general case of dissimilar adsorption isotherms the following conditions apply¹:

Let a_i be the amount of solute i adsorbed per gram of adsorbent at equilibrium with a concentration c_i of the solute, and let a_d be the corresponding quantity for the displacer. Then the adsorption isotherms may be represented as

$$a_i = f_i(c_i)$$

and

$$a_d = f_d(c_d)$$

In order that the component i should travel with the same speed as the displacer d , the condition must exist that

$$\frac{a_i}{c_i} = \frac{a_d}{c_d}$$

or

$$\frac{f_i(c_i)}{c_i} = \frac{f_d(c_d)}{c_d}$$
$$c_i = \frac{f_i(c_i)}{f_d(c_d)} \times c_d \quad (ii)$$

Hence for a given displacer concentration c_d the concentration c_i is proportional to the ratio of the adsorption isotherms. In displacement gas chromatography the factor $f_i(c_i)/f_d(c_d)$ usually decreases with the order of displacement, and therefore successive components will emerge from the column with successively lower concentrations. If the detection device gave a signal dependent on the concentration only the chromatogram would consist of a number of diminishing steps. Actually, the detector, such as a thermal conductivity cell, gives a signal which is determined not only by the concentration but also by a property of the compound displaced, in this case the thermal conductivity. With successive displacement the difference in thermal conductivities between the compounds and the carrier gas usually increases. The latter factor is predominant over the concentration factor, and therefore a displacement chromatogram presents an overall picture of increasing steps. In certain cases the two factors may compensate each other. For instance pyridine and o-xylene on charcoal⁴⁷ give rise to one step only. It follows from the above that the disadvantage of equal step-height for successively displaced compounds may not be confined to closely related isomers only.

This difficulty can be overcome by the insertion of a 'marker' of intermediate displacement, causing a step of different height in the chromatogram. Chlorobenzene can be used to distinguish between pyridine and o-xylene. Another possibility is to evaluate the actual step heights

in the chromatogram. These can be calculated from a knowledge of the respective thermal conductivities and adsorption isotherms. The latter can be measured conveniently by the method of frontal analysis⁴⁸. However, these methods are tedious and time consuming.

Another disadvantage of the displacement method is that the column must be replaced or regenerated after each run when it has become saturated with the displacer. Also the time taken for a displacement analysis is that necessary to saturate the adsorbent with the displacer. This time may be longer than for many elution analyses, in which the same column may be used over and over again.

On the other hand, displacement chromatography has some fundamental advantages over the elution method. Firstly, in a displacement chromatogram the step length is a measure of the quantity of component present as compared to the peak area in the elution chromatogram. This step length is entirely independent of the sensitivity of the detection device, and is influenced by changes of flow rate and displacer concentration only. In the elution method the peak area is very much dependent on the sensitivity of the detection device, and not only on changes of flow rate as such, but on the changes of sensitivity brought about by a change of sensing element temperature in a thermal conductivity cell if the flow rate changes.

This is reflected in the accuracies claimed for both methods. A figure of $\pm 1\%$ has been claimed for the elution method²⁹. Such accuracies may be attainable within repetitive runs, but a figure of $\pm 5\%$ postulated by other workers⁴⁹ is perhaps more realistic. According to Phillips⁸ accuracies of better than 1% can be obtained readily with the

displacement method.

The most important advantage of displacement columns is their self-sharpening property. As almost all adsorption isotherms are concave with respect to the pressure axis, a disturbance travelling in front of a band in a displacement column is automatically corrected as low concentrations travel more slowly than high ones. Elution columns on the other hand, have no self-sharpening properties. Diffuseness once obtained cannot be remedied, and in fact is increased along the length of the column by diffusion effects in the gas and liquid phase. It is a well known phenomenon in elution chromatography that the peak base widens progressively with the time a compound stays on the column. This effect makes the measurement and even the detection of components with fairly long retention volumes uncertain. The width of a peak-base of a trace component in elution chromatography is on a time scale, at least as long as the time taken to introduce the whole of the sample into the carrier gas stream.

In any investigation in which products are analyzed by gas chromatography it is of importance that the reactants are 'gas-chromatographically' pure. Often for mass spectrometric work purification of substances by gas chromatography is also desirable. Large amounts of sample can be easily dealt with by means of displacement columns consisting of sections of decreasing diameter with which very sharp fronts are maintained⁸. Elution columns suitable for preparative work have been mentioned³⁰, but their dimensions and packing requirements make them more cumbersome and more inefficient.

It is unlikely that an elution technique can be evolved which will either have self-sharpening properties or which will give inherently the

same quantitative accuracy as the displacement method. It is then perhaps useful to consider whether it would be possible to overcome some of the disadvantages of the displacement technique which may be less fundamental than those of the elution method.

The problem of equal step height of two successively displaced substances is really not due to the displacement column as such, but to the inability of the thermal conductivity cell to distinguish between such compounds. The ionization gauge as described in Chapter III may have here a useful application as a detection device. The ionization potentials of even isomeric hydrocarbons differ by at least a fraction of a volt⁵⁰, and it can be expected that this would result in a considerable difference of step height. It is reasonable to assume that a certain value of grid potential exists for the ionization gauge detector which would give a maximum step difference between two compounds. To overcome the difficulty of carrying out several runs to establish this optimum potential, it should be possible to fairly rapidly vary this potential between +8 and +18 volts for instance (see Table II). Under these conditions the grid potential should pass twice for each cycle through the 'optimum step potential', and it would then be extremely unlikely that two hydrocarbons should produce the same ion current.

The ionization potential of unsaturated compounds is usually less than that of saturated ones of the same number of carbon atoms, and the ionization potentials of aromatic compounds are even lower (see Table II). It can be expected therefore that step heights between for instance a hexane, a hexene, and benzene which would be displaced near or next to each other would vary tremendously, as compared to the difference in step

height between two hexanes or two hexenes. It is therefore possible that the ionization gauge detector used in conjunction with displacement chromatography would not only detect components, but would also provide some information as to their molecular structure.

The disadvantage of renewing the column after each run is only a technical detail. The construction of a regenerating unit where columns would be desorbed under heat and low pressure would present no difficulty. Contrary to the opinion expressed in Keulemans' book¹⁷ (p. 194), Phillips states¹⁸ (p. 89) that the packing requirements of displacement columns are not critical. It has also been the experience in the present work that elution columns have to be 'purged' after analyzing a reaction mixture containing high boiling constituents.

The time required for a displacement analysis in which the whole column has to be saturated with the displacer is to a great extent dependent on the amount of adsorbent in the column. The columns employed by Phillips and co-workers⁸ were capable of handling gram quantities of material. With better detection devices developed since then it is thought that columns of much smaller capacity could be employed, and this would materially reduce the time taken for the displacement analysis.

Gas Chromatography without Carrier Gas

The ionization gauge shares with the infra-red analyser recommended by A.E. Martin and Smart⁵¹ the advantage over most other detection devices including the thermal conductivity cell that it is in principle sensitive to the eluted compounds only, and is independent of the amount of carrier gas. However, as has been pointed out in Chapter III, a background ion

current occurs even with very pure helium due to the Maxwellian distribution with which the electrons leave the filament of the gauge. The conflicting requirements for the operation of the ionization gauge exist that the grid potential should be as high as possible from the point of view of ionization efficiency, and thus sensitivity of the device to the eluted compounds. On the other hand, as the grid potential is raised towards the ionization potential of helium (24.5 volts), the gain in ion current obtained from hydrocarbon ions, for instance, is off-set by the rapid increase of helium ions formed. At, or near, 24.5 volts the current due to the hydrocarbon would be swamped out by the current due to the helium ions. Thus it appears that the sensitivity of the ionization gauge is limited by the formation of helium ions.

One way to overcome this would be to have mono-energetic electrons such as photo-electrons of just under 24.5 volts. However, it is known from mass spectrometry where mono-energetic electrons are often desirable, that only very low electron intensities can be obtained in this fashion. Furthermore, photo-electric surfaces are extremely sensitive to contamination.

Another possibility is to consider whether a gas chromatographic scheme could not be devised which would operate without a carrier gas. The detection device in such a method could be an ionization gauge operated under 'ordinary' conditions, i.e. conditions when the gauge is used as a pressure measuring device. In this case ionization gauges are usually run with grid potentials of 50 - 120 volts. Ionization efficiencies are then very high, and the sensitivity of an ionization gauge operated under these conditions to a compound suddenly introduced

into its glass envelope should surpass by far that of the ionization gauge mentioned in Chapter III.

In devising a gas chromatography without a carrier gas the elution technique seems to be ruled out almost by definition. A displacement technique has been tried and is described in the following.

Description of Apparatus

The column consisted of a 7 mm o/d Pyrex glass tube about 3 ft long which was filled with activated charcoal (e.g. 208C, BSS 30-40 mesh, supplied by Sutcliffe Speakman, Leigh, Lancashire, England). The entrance to the column had two branches. One branch lead via a stopcock to a small vessel containing the displacer. The other branch lead also via a stopcock to a globe containing the mixture of compounds to be analysed. Between the latter and the column a small expansion volume (about 1 ml) was situated, also contained between stopcocks. The exit of the column was connected via a cold trap to a mercury diffusion pump. A Pirani gauge was placed between the end of the column and the cold trap, and served as the detection device. The glass envelope of the Pirani was modified to 'straight through' flow conditions. A Leeds & Northrup Speedomax recorder (sensitivity 1 - 20 mv full scale) was connected across the terminals of the meter indicating the pressure of the Pirani.

Operating Conditions

The displacer was ethyl acetate kept at 0°C. The composition of the mixture with approximate molecular weights and boiling points is shown in Table III.

T A B L E I I I

Composition of Mixture for Analysis by Displacement
Chromatography without Carrier Gas

Compound	Molecular Weight	Boiling Point
isopentane	72	28
n-pentane	72	36
methylene chloride	85	40
methyl iodide	142	43
chloroform	119	61
n-hexane	86	69
carbon tetrachloride	154	76
ethyl acetate (displacer)	88	77

It was to be expected that if any chromatographic separation would take place at all, the compounds would be displaced in the order of their boiling points. Considering the rule that thermal conductivities are approximately inversely proportional to molecular weights, it was hoped that carbon tetrachloride, for instance, would give a higher step than the displacer, and thus make a separation more convincing than a series of progressive steps.

Description of a Typical Experiment

The column and expansion volume were pumped down until a minimum reading was obtained on the Pirani meter, and the base line on the recorder

stopped drifting. During the pumping the column was fanned with a flame to aid desorption. Both displacer and mixture containers were cooled with liquid nitrogen, and air pumped away. Then the temperature of both was allowed to rise to 0°C.

Vapour from the globe holding the mixture was allowed to expand, successively, first into the expansion volume, and from there on to the upper part of the column, where it was adsorbed by the charcoal.

After closing off the expansion volume the stopcock of the displacer containing globe was opened, and the ethyl acetate was allowed to flow freely on to the column under its own vapour pressure at 0°C.

Results and Discussion

The chromatogram obtained (fig. 11) does not show a clear cut separation of the seven components of the mixture, but four steps are clearly recognizable. As hoped for one of the steps is higher than that of the displacer.

The experiments described were of a very preliminary nature only, but they seem to demonstrate that in principle a gas chromatographic process of separation can be carried out without the use of a carrier gas. Further work would show whether separations could be improved by altering such parameters as nature and division of the adsorbent, temperature and shape of columns, nature and 'flow rate' of displacer, and also the nature of the detection device.

As was mentioned previously, elution chromatography without a carrier gas is almost a contradiction of terms. The difficulty exists here that

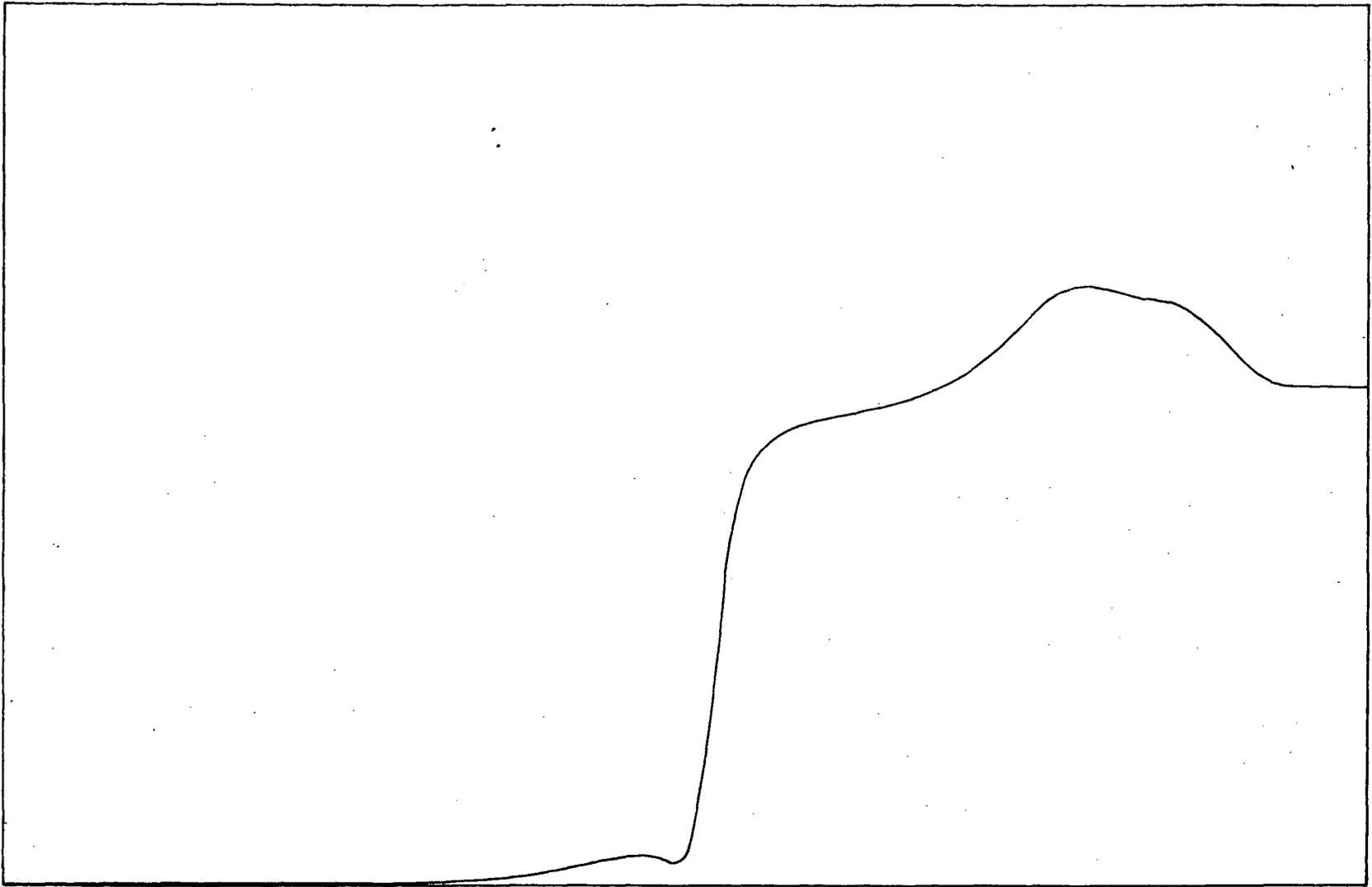


Fig. 11. Chromatogram obtained in the analysis of a synthetic mixture by displacement chromatography without carrier gas

whether conditions of viscous or molecular flow exist, the rate of travel of a gas through a tube is proportional to the pressure differential existing at any time between the two ends of the tube⁵². Thus if a quantity of a gas is introduced at one end of a previously evacuated column, it would travel, or rather expand, towards the other end, the latter being maintained at a low pressure all the time. But as the pressure decreases, severe tailing could be expected.

To test the feasibility of the method a further experiment was carried out. The charcoal column in the apparatus described above was replaced by one filled with 30-40 mesh activated alumina granules. Working now without a displacer, a mixture of air and butene-1 was expanded on to the column. Two 'elution' peaks resulted, which are clearly separated, see fig. 12. Whether the separation has taken place here by a chromatographic process is not certain. It is possible that a diffusion effect came into play⁵², for which the whole length of the alumina column can be considered as a 'porous plug'. However, the symmetry of the first peak, probably air, is surprising. Whether such a method has any practical possibilities as an analytical tool is difficult to decide without further investigations. The compound emerging first should be pure, and should be detectable with ultra high sensitivity by an ionization gauge operated with 50 - 100 volts grid potential.

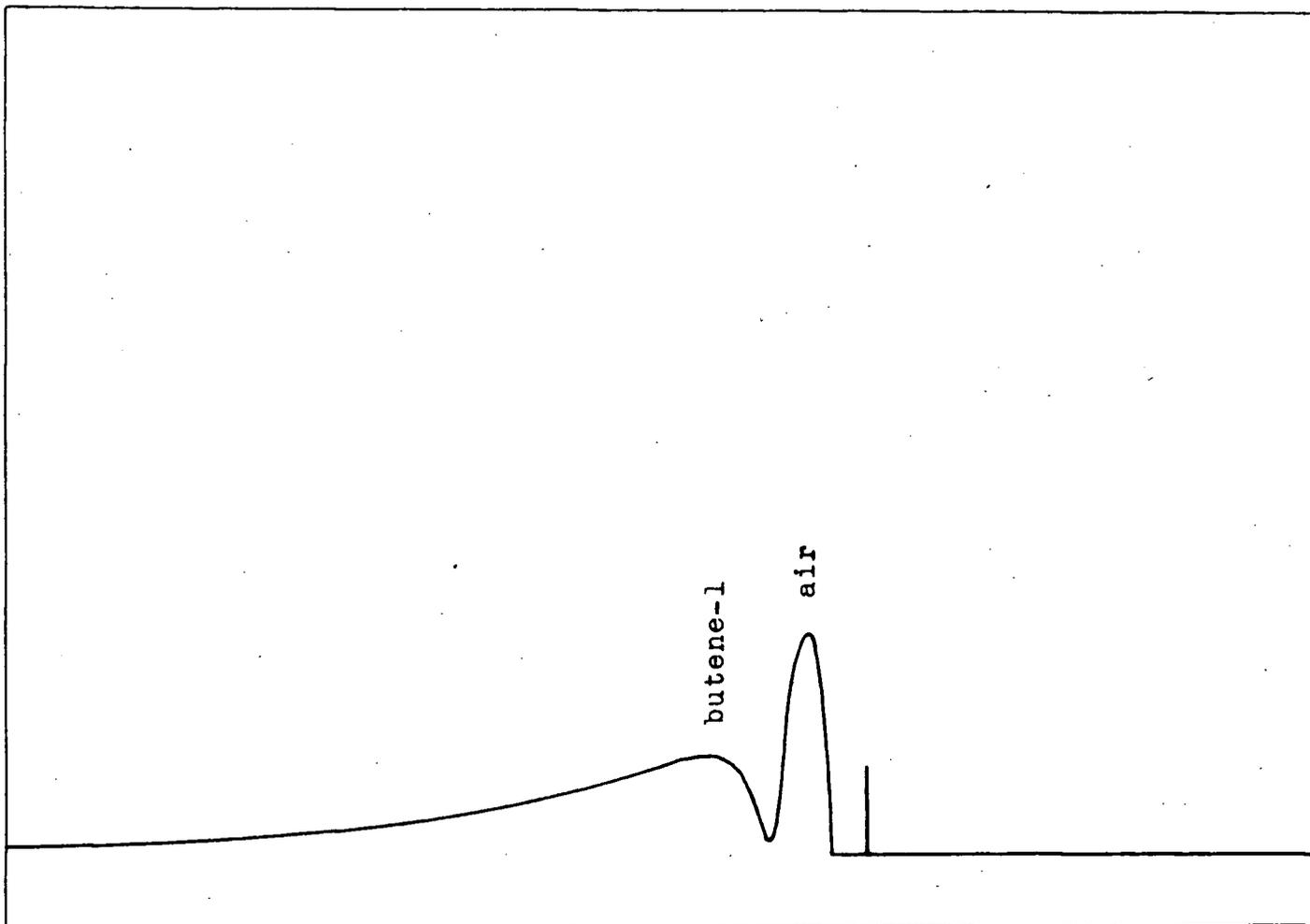


Fig. 12. Chromatogram obtained in the analysis of a butene-air mixture by elution chromatography without carrier gas

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PART II

THE REACTION OF METHYL RADICALS

WITH BUTENE - 1

INTRODUCTION

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WITH BUTENE - 1

INTRODUCTION

The thermal decomposition of a large number of organic compounds has been studied in the gas phase during the past thirty years. Many of these decompositions have been shown to proceed by free radical mechanisms. In such processes the reactions of the radicals are considered to be elementary steps. It is an important objective of a kinetic study of such mechanisms to gain as much information as possible about such reactions. This includes not only the identification of all reaction products but also, if possible, the evaluation of the corresponding rate constants, activation energies and entropy of 'A' factors. Because of their high reactivity and corresponding very short lives, it is often difficult to obtain reliable kinetic results for the reactions of hydrocarbon radicals in the gas phase. Various experimental techniques have been used in attempts to obtain such results.

In 1928 Paneth and Hofeditz¹ demonstrated the existence of short-lived alkyl free radicals, and measured their half-lives by the formation and removal of metallic mirrors obtained by the pyrolysis of metal alkyls.

The direct study of free radicals with a mass spectrometer was pioneered by Eltenton² in 1942. Radicals produced by pyrolysis in a

flow system were diverted through a molecular leak into a mass spectrometer.

The rotating sector technique^{3,4} involves photolysis using intermittent illumination which allows one to measure the lifetime of radicals with a reasonable degree of accuracy.

Electron spin resonance has been used to study the behaviour of free radicals^{5,6}. Unfortunately, this method is not capable of dealing with radicals encountered in the gas phase, as before microwaves can be applied to induce resonance the radicals have to be frozen out in a matrix at low temperatures.

By their very nature, the techniques mentioned above are not applicable to many systems, and moreover require elaborate apparatus. In most cases the participation of free radicals in a reaction has been deduced on the basis of more indirect evidence. There are a number of experimental observations which indicate the presence of free radicals during a reaction: a high quantum yield indicates a chain reaction involving free radicals; a large number of substrate molecules decompose for each quantum of light absorbed, or each radical released. The converse is not true, i.e. the absence of a chain reaction does not rule out a free radical mechanism. A reliable indication that radicals are involved in the decomposition of a particular substance is the initiation by that substance of a chain reaction in a substrate which is known to proceed by a free radical mechanism⁷.

The toluene carrier technique developed by Szwarc⁸ relies on the ease with which hydrogen is abstracted from toluene by a radical being studied to give the relatively unreactive benzyl radical. The amount of dibenzyl

formed by benzyl recombination is a measure of the concentration of the abstracting radical.

Other indications of free radical reactions include the partial inhibition of a reaction by the addition of nitric oxide⁹, and deuterium exchange between deuterated and undeuterated molecules during pyrolysis.

A convenient method for the study of the behaviour of free radicals, and one which was adopted in this investigation, is the production of radicals from a 'source' with subsequent reaction of the radicals either with themselves or with a substrate. Two principal methods of generating radicals are available: photolysis and pyrolysis.

Acetone is often used as a photolytic source of methyl radicals:



Common pyrolytic sources of methyl radicals are di-t-butyl peroxide, azomethane, and mercury dimethyl. The peroxide is useful between 170 - 220°C, the mercury dimethyl between 350 - 500°C, and the azomethane in the intermediate range.

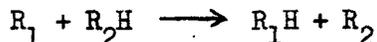
The photolytic generation of radicals has the advantage that the rate of release of radicals is controlled over a considerable temperature range by the intensity of the incident radiation only. However, disadvantages of this method are the possible production of "hot" radicals, and the possibility that the reaction products and the substrate may be photosensitive. These disadvantages do not exist with radicals from pyrolytic sources. On the other hand the complication arises in pyrolysis that the rate of radical release is now a function of temperature. Thus it is more difficult to correlate experiments carried out at different

temperatures, and also the same source of radicals can only be employed over a comparatively narrow temperature range. The lower limit is the temperature at which too few radicals are released during a convenient reaction time, and the upper limit is a temperature at which the half-life of the source is of the same order of magnitude as the time of admission of the mixture to a reaction vessel.

For both pyrolytic and photolytic radical generation, the source itself and the molecular products of the decomposition must be considered with respect to their influence on the reaction mechanism, or their participation in the reaction itself.

Reactions of Free Radicals in the Gas Phase

In the presence of a substrate free radicals can react in a variety of ways. The best understood of these are hydrogen abstraction:



and radical recombination:



A large body of information is available on hydrogen abstraction reactions. The recombination reaction for which the third-body restriction may apply is also well understood due to the quantitative investigation of Gomer and Kistiakowsky¹⁰ who applied the rotating sector technique to the recombination reaction of methyl radicals. An excellent summary of these reactions is contained in the Liversidge Lecture in 1955 by Steacie¹¹.

Far less is known about the fate of hydrocarbon free radicals of three and more carbon atoms which are formed when hydrogen is abstracted from a substrate by radicals such as methyl. Such large radicals can

stabilize themselves, apart from abstracting hydrogen or recombining with another radical, by decomposition, e.g.



Another important radical reaction is addition to the double bond of an olefin. The present study is concerned principally with this type of reaction, about which comparatively little information is available in the literature. The behaviour of the higher radicals formed by the addition of methyls to the double bond of olefins such as butene-1 has received very little attention by previous investigations.

The reaction of methyl with butene-1 was chosen for this study because of interest in the pyrolysis of butene-1 in which this reaction plays an important part¹². Also, methyls are conveniently produced by pyrolysis, and are of course the simplest, and perhaps best understood hydrocarbon radicals. Butene-1 can be considered as a good kinetic representative of an olefin. It is not symmetrical, and hence the addition of the radicals may be expected to take place at either end of the double bond. Further, it had been shown^{12,13} that hydrogen abstraction by methyl from butene-1 is largely confined to the allylic position in the molecule resulting in a resonance stabilized radical which can be represented as having two different canonical forms. The next lower unsymmetrical olefin, i.e. propylene, yields on hydrogen abstraction the resonance stabilized allyl radical which, however, has identical canonical resonance structures.

SURVEY OF THE LITERATURE

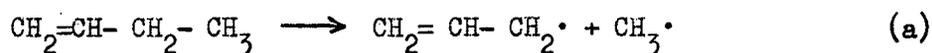
The addition of radicals to the double bond of an olefin has been postulated in a number of early investigations.

Danby and Hinshelwood¹⁴ found that the addition of methyls to butene-1 occurs readily.

Raal and Danby¹⁵ established that the abstraction of hydrogen from acetaldehyde by methyl is about three times as fast as the addition of methyl to the various butenes at 300°C.

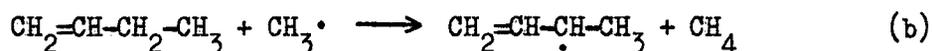
Volman and Graven^{16,17} studied the photolysis of di-*tert*-butyl peroxide and of acetone in the presence of large quantities of butadiene. They showed that methyl radicals add to butadiene more rapidly than do the C₅H₉ radicals which are formed by the addition of methyls to butadiene.

Bryce and Kebarle^{12,18} postulated in their investigation of the thermal decomposition of butene-1 in a static system between 490 and 560°C that the primary step of decomposition of the olefin was



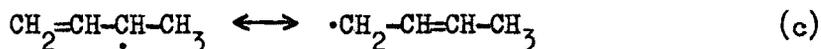
i.e. allyl and methyl radicals were formed. The methyl radicals were found to attack the parent butene-1 in two ways, i.e. hydrogen abstraction and addition to the double bond.

Hydrogen abstraction was considered to take place almost exclusively from the allylic position



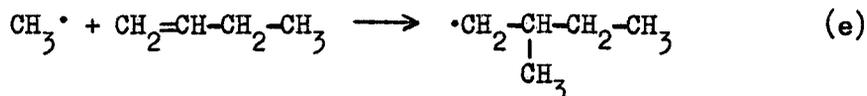
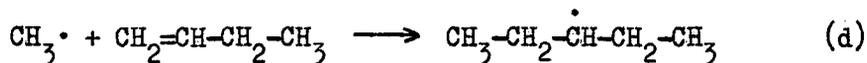
The reason for this is the low activation energy for the abstraction of hydrogen from this position, which was found by Trotman-Dickenson and

Steacie¹⁹ to be 7.6 kcal. The energy of activation for the abstraction of hydrogen from the other carbon atoms is about 5 kcal higher. Reaction (b) results in the resonance stabilized butenyl (methallyl) radical

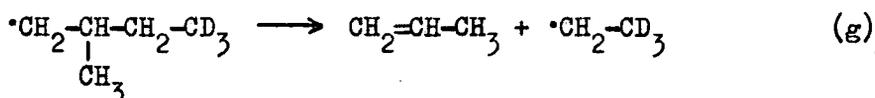
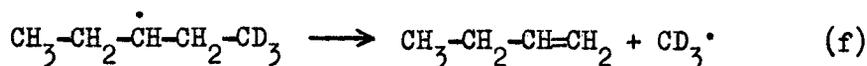


The authors claim that the butenyl radical would disappear through hydrogen abstraction, decomposition or recombination with other radicals.

Addition of methyl was postulated to take place at both ends of the double bond, giving two types of pentyl radicals

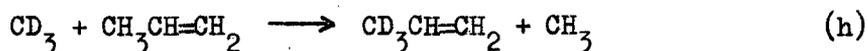


From thermochemical data Bryce and Kebarle estimated that reactions (d) and (e) were exothermic and that the pentyl radicals would contain an excess energy of about 27 - 30 kcal. It was thought that at the temperature of their experiments, i.e. about 500°C, the lifetime of these radicals would be very short, and that the reverse of reactions (d) and (e) could be expected to take place easily. However, the possibility was considered that the pentyl radicals could also decompose so as to form products different from methyl and butene-1. By sensitizing their reaction with 5% mercury dimethyl, a source of methyl radicals at these temperatures, and using 1-butene-4-d₃ instead of ordinary butene-1 the same workers²⁰ were able to show from the distribution of the deuterated products that at the temperatures in question pentyl radicals would decompose:



The net result of reactions (d), (e), (f) and (g), in which methyl adds to one end of a double bond, is the expulsion of a radical from the other end of the addition product. E.g. the amount of CD_3CH_3 formed by reaction (g) was increased by a factor of 27 in the decomposition of 1-butene-4- d_3 sensitized by methyl. Furthermore the large amount of undeuterated butene-1 observed provided direct evidence of reaction (f).

A similar mechanism of radical displacement has been postulated by Varnerin²¹ for the reaction between methyl and propylene at 550°C



Varnerin took into account the possibility that the propylene- d_3 could also have been formed by the successive abstraction of deuterium from his CD_3 source, i.e. from CD_3DO . However, one would then expect that the amount of propylene- d_2 would be larger in the reaction products than propylene- d_3 , but this was not so.

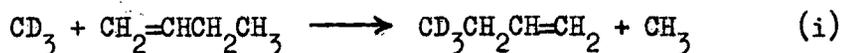
More recently Pitts and co-workers^{22,23} have reported free radical displacement processes in the reactions of methyl with trans-methyl propenyl ketone, and crotonaldehyde at about 150°C. The methyl radicals were obtained from the photolysis of acetone. The reaction postulated in the case of trans-methyl propenyl ketone is:



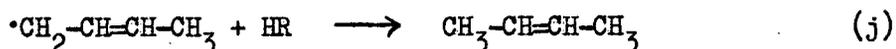
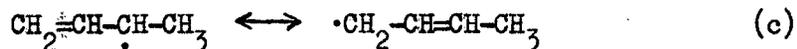
By using CD_3 Pitts and co-workers were able to confirm a displacement mechanism for this reaction.

McNesby and Gordon¹³ allowed CD_3 obtained from the photolysis of acetone- d_6 to react with the four butenes, i.e. butene-1, cis-butene-2, trans-butene-2, and isobutene, in a temperature range between 220 and 500°C. For butene-1 they confirmed the radical displacement mechanism

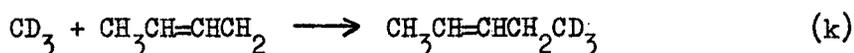
at temperatures as low as 375°C on the basis of the occurrence of 1-butene-4-d₃ due to the following reaction:

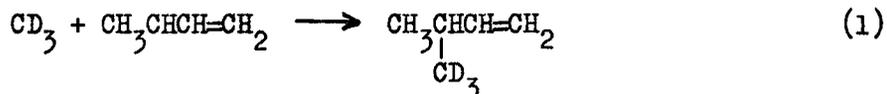


By assuming that the reverse of reactions (d) and (e) take place at equal rates McNesby and Gordon calculated the relative frequency of CD₃ addition to the terminal and non-terminal end of the double bond in butene-1 as 7.3 : 1 . at 400°C. The corresponding value obtained from the data of Bryce and Kebarle¹² is 4 : 1 at about 500°C. McNesby and Gordon arrived at this ratio from the product distribution of reactions (f) and (g) which in their case yielded CH₂=CH-CH₂-CD₃ and CD₃CH=CH₂ respectively. The same authors also found that the resonance stabilized butenyl radical does not abstract hydrogen at 375°C but does so readily at 503°C. Hence the mechanism of isomerization from butene-1 to butene-2 was thought to be the following



They state that at 503°C only 9% of the butene-2 found was marked with deuterium, indicating that the abstraction by butenyl from acetone-d₆ is relatively unimportant. Some results for the photochemical and the thermal reaction of acetone-d₆ and butene-1 from McNesby and Gordon's paper are given in Table IV. Gas chromatography was used for the analyses. Although McNesby and Gordon list 3-methyl-butene-1 as one of the products of their reaction its identity and that of the other pentene, and the hexane was not established. The authors suggest that the pentenes are formed by the following reactions





and are therefore pentene-2, and 3-methyl-butene-1.

T A B L E I V

Per Cent Composition of Products of the Photochemical and
the Thermal Reaction of Acetone-d₆ and Butene-1
(McNesby and Gordon¹³)

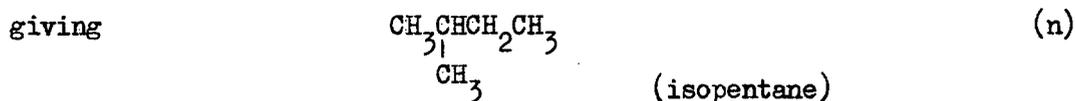
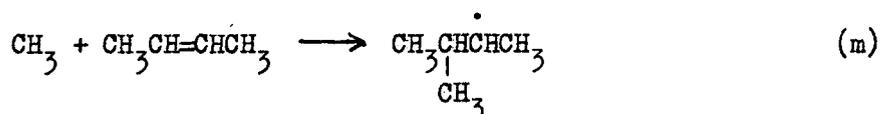
T, °C	220	400	504
CO	61.5	29.0	2.7
Methane	31.0	49.7	32.1
Ethylene	1.7	4.9	11.5
Ethane	1.7	3.3	9.1
Propylene	0.0	7.7	20.1
Propane	0.3	0.9	0.8
Butene-2	0.0	2.2	21.8
3-Me-Butene-1	1.0	1.2	0.4
Pentene	0.4	1.0	1.4
Hexane	2.5	0	0
% Reacted	3	5	10

Some of the higher molecular weight products were not identified. The percentages have a precision of about 5%.

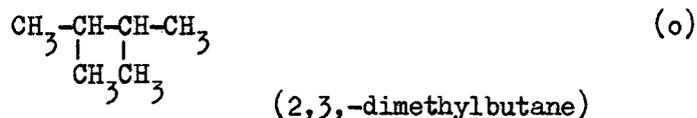
Rust, Seubold and Vaughan²⁴ investigated the products of the reactions of methyl radicals, obtained from the pyrolysis of di-tertiary butyl peroxide, with propylene, butene-2, and isobutene in a flow system at

235°C. The analysis was carried out by infra-red absorption. Rust and co-workers did not study butene-1. However, with isobutene the products indicate terminal as well as non-terminal addition to the double bond. The mechanism proposed for butene-2 is of interest as it relates to the results of the present investigation.

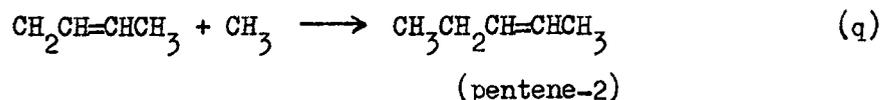
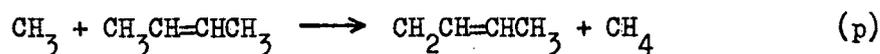
Addition of methyl to the double bond is followed by hydrogen abstraction by the pentyl radical



Recombination with a methyl can occur to give



Abstraction of hydrogen from the end of the butene-2 molecule is followed by recombination with methyl to give pentene-2



Abstraction of hydrogen from carbon 2 was also observed with the corresponding products. The recombination of higher radicals has also been considered by these authors. The above hydrocarbons were the only reaction products found.

Mandelcorn and Steacie²⁵ deduced the rate of addition of methyl radicals to various olefins by comparing the experimental results obtained from the photolysis of acetone alone and in the presence of the unsaturated

hydrocarbon. Unfortunately butene-1 was not included in their investigation. Some of the values obtained by Mandelcorn and Steacie are reproduced in Table V. E_{Ad} is the activation energy for the addition reaction, and E_2 is the activation energy for the recombination of the methyl radicals to ethane. As $E_2 \cong 0$, $E_{Ad} - 1/2 E_2 \cong E_{Ad}$. P_{Ad} and P_2 refer to the steric factors for the addition and recombination reactions respectively.

T A B L E V

Addition of Methyl Radicals to Unsaturated Hydrocarbons
(Mandelcorn and Steacie)

Hydrocarbon	$E_{Ad} - 1/2 E_2$ kcal	$10^4 P_{Ad} / P_2^{1/2}$
Ethylene	7	5
Propylene	6	3
Acetylene	5.5	5

Bryce and Kebarle¹² assumed that the behaviour of butene-1 toward methyl addition would be identical to that of propylene. They used values for the activation energy and P factor found by Trotman-Dickenson and Steacie¹⁹ for the abstraction of hydrogen by methyl from butene-1, i.e. $E_{Ab} = 7.6$ kcal and $P_{Ab} = 8 \cdot 10^{-4}$, and calculated the ratio

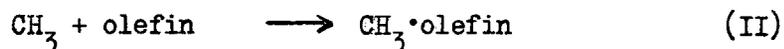
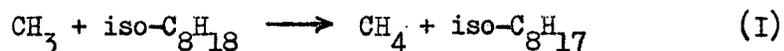
$$\frac{R_{\text{Abstraction}}}{R_{\text{Addition}}} = \frac{1}{1.1} \quad \text{at } 500^\circ\text{C}$$

Through the work of Szwarc and his co-workers²⁶⁻²⁹ a large body of information is available on methyl reactions with olefins in the liquid

phase. Methyl radicals were obtained in this work from the thermal decomposition of acetylperoxide. It was shown that this decomposition, if carried out in a highly diluted solution of the peroxide in isooctane, yields carbon dioxide, methane and ethane in quantities which obey the relation

$$(\text{CH}_4 + 2 \text{C}_2\text{H}_6) / \text{CO}_2 = 1$$

The addition of an olefinic compound to such a solution decreases the amount of methane formed, without affecting the yields of carbon dioxide or of ethane produced by the decomposition. The following two reactions appear to compete for methyl radicals:



where $\text{CH}_3 \cdot \text{olefin}$ denotes the initial intermediate addition product.

The ratio of the bimolecular rate constants $k_{\text{II}} / k_{\text{I}}$ was measured. The relative rates of addition were denoted as methyl affinities and were determined for a large number of substrates which included olefins, dienes and aromatics. The methyl affinities were related to the degree of conjugation and hyperconjugation of the substrate, and to the blocking effect of substituent groups. However, conditions in gas and liquid phases differ so much, that results obtained in one can only be applied with great reservation to the other. An example is the constancy of the ethane formation, referred to above, which is independent of the amount of substrate added. This is attributed in the liquid phase to a 'cage' reaction. Also in the liquid phase the probability that a methyl radical will recombine with a solvent radical, formed in reaction (I), is much lower than the probability of its reaction with a solvent molecule. In

the gas phase, methyl recombination with radicals formed in similar reactions to (I) and (II) is important. On the other hand, a system of methyl affinities may be applicable to gas phase reactions, when more olefinic substrates have been investigated.

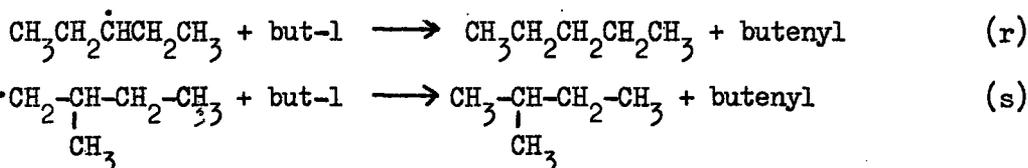
EVALUATION OF LITERATURE SURVEY

The results summarized in the foregoing pages indicate that the reaction of methyl with butene-1 in the temperature range 200 to 500°C involves two competing reactions.

- 1) hydrogen abstraction by methyl from the allylic position in the butene-1 molecule, reaction (b), with an activation energy of 7.6 kcal and a P factor of 8×10^{-4} . The resulting butenyl radical is considered to be resonance stabilized, reaction (c), and will undergo recombination with methyls at low temperatures, reactions (k) and (l). At temperatures above 375°C butenyl will also abstract hydrogen to give butene-2, reaction (j);
- 2) addition of methyl to either end of the double bond, reactions (d) and (e), resulting in two forms of pentyl radical, which may decompose at temperatures near 500°C by reactions (f) and (g).

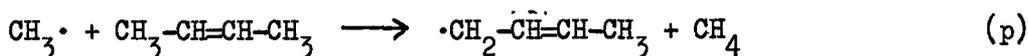
Beyond this, several important questions concerning the reaction of CH_3 with the olefin remain unanswered, and a number of inconsistencies seem to exist in results cited: no mention is made by McNesby and Gordon of the fate of the pentyl radicals at 220°C. According to Table IV no pentanes were found, although one would expect that by analogy with

reaction (n), postulated by Rust and co-workers, the pentyl radicals would be stable at 220° and would abstract hydrogen to give n-pentane and isopentane:



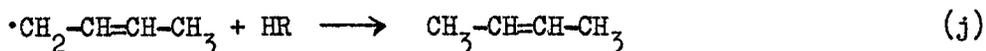
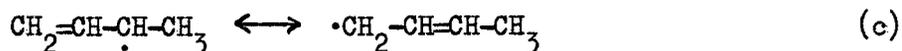
According to Table IV McNesby and Gordon found a considerable amount of ethylene in their products, increasing from 1.7% at 220° to 11.5% at 504°C. No explanation is offered for the occurrence of this compound. It is reasonable to assume that the ethylene must originate from the decomposition of a radical. This would be surprising at 220° considering that Rust and co-workers did not find any ethylene or C₃'s in their work at the same low temperature, with admittedly, however, not the same substrate.

An examination of reaction (p) postulated by Rust and co-workers

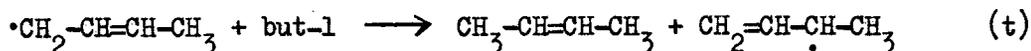


indicates that the resulting radical is one of the resonance forms of the butenyl radical. Hence one would expect that in addition to pentene-2 given by reaction (q), 3-methyl-butene-1 should have also been formed by reaction (l) postulated by McNesby and Gordon.

Bryce and Kebarle did not positively identify butene-2 in their analysis. A relatively small peak in their chromatograms following butene-1 was considered to be butene-2. On the other hand, McNesby and Gordon found that butene-2 was one of the major products of their reaction at 504°C. As cited previously, the latter authors presented the mechanism for the isomerization to butene-2 as follows



If one completes the right hand side of equation (j) and inserts butene-1 for HR it becomes apparent that this isomerization can be a chain reaction as a new butenyl radical is formed for each abstraction step



If this is so, then extensive isomerization to butene-2 should also take place in the straight pyrolysis of butene-1, where methyl radicals resulting from the primary split (a) should initiate the chain.

OBJECTIVES OF THE INVESTIGATION

It is apparent from the foregoing that our understanding of the reactions of CH_3 with olefins is incomplete. It was therefore decided to investigate the reactions in more detail.

The lower temperature range near 200°C appeared to be more attractive for initial studies, as the reaction at 500°C is apparently complicated by the decomposition of the pentyl radicals, reactions (f) and (g), and the primary split of the butene-1 itself to allyl and methyl. Bryce and Kebarle¹² had identified cyclic compounds, among the reaction products at these temperatures, e.g. cyclopentadiene, cyclohexadiene, benzene, and toluene, all of which might interfere with the analysis of the pentenes, pentanes, and hexanes formed by the reaction of methyl with higher hydrocarbon radicals. However, experiments at the higher temperatures are also of interest, especially with a view to studying the isomerization reaction (t).

It was therefore decided to attempt the identification of all the reaction products between methyl radicals and butene-1 in the gas phase at temperatures near 200°C. From the product distribution it should be possible to draw conclusions about the behaviour of the various butenyl and pentyl radicals formed, and to gain an understanding of the mechanism involving these radicals. The variation of the product distribution with pressure and temperature should provide additional useful information.

At the low temperature di-t-butyl peroxide can be used as a methyl source. This has the advantage that one acetone molecule is formed for each methyl generated and since acetone can be conveniently estimated by gas chromatography in the presence of hydrocarbon products, a material balance of the products with respect to the total methyl supplied should be possible. Thus, it was hoped that with the help of a complete kinetic scheme, a measure of the activation energy of the addition of methyl to the double bond should be obtainable.

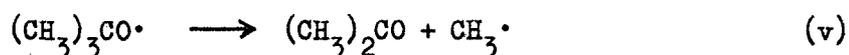
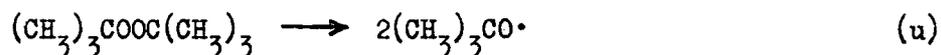
A static pyrolysis system was chosen so that the results could be related to those previously obtained in this laboratory. Furthermore, temperature measurements in a flow system are considerably less accurate than in a static system.

For the analysis of the products the gas chromatograph was available which has been described in Part I of this thesis.

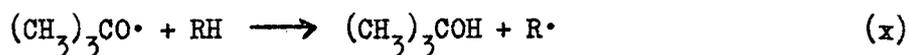
Di-t-butyl peroxide and mercury dimethyl were chosen as methyl radical sources for the temperature ranges near 200 and 500°C respectively. A brief discussion of the mechanism of the thermal decomposition of these compounds is therefore of interest.

The Thermal Decomposition of Di-t-Butyl Peroxide

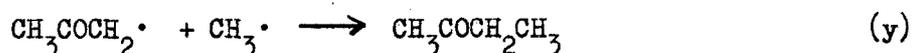
The di-t-alkyl peroxides have been reported by Milas and Surgenor³⁰ and George and Walsh³¹, to undergo clean-cut decompositions in the vapour phase to a ketone and hydrocarbon. For the di-t-butyl peroxide the mechanism proposed is as follows



The above mechanism was further supported by the extensive studies of Raley, Rust and Vaughan³², who showed that the decomposition of di-t-butyl peroxide in various organic solvents resulted in the formation of some t-butyl alcohol, formed by



The kinetics of the thermal decomposition of the di-t-butyl peroxide have been investigated³³ and it was found that reaction (u) is the rate determining step. It has also been established that, in the gas phase, all the butoxy radicals decomposed according to equation (v). On the other hand methyl radicals were removed not only by reaction (w), but also by reaction with acetone according to reactions (x) and (y)



However, the amount of methyl radicals reacting with acetone ranged from 5-10 percent only. The reaction was found to be homogeneous, and first order. The unimolecular rate constant was independent of the initial pressure of peroxide which was varied from 50 - 380 mm Hg. No inhibition was observed when nitric oxide or propylene was added. From the temperature

dependence of the rate constants between 140 - 160°C the activation energy was computed as 39 kcal/mole with a frequency factor of $3.2 \times 10^{16} \text{ sec}^{-1}$.

The high A factor reported by the above authors induced Murawski, Roberts and Szwarc³⁴ to reinvestigate the decomposition over a wider temperature range, i.e. 120 - 280°C. Owing to technical difficulties a static method had to be used below 170°C. The well known toluene carrier flow technique^{8,35,36} was used above this temperature. The activation energy found by Szwarc was 36 ± 1 kcal/mole corresponding to a frequency factor of the order of 4 to $7 \times 10^{14} \text{ sec}^{-1}$.

The rates of decomposition obtained by Szwarc are in fair agreement with the rates reported by Raley, Rust and Vaughan. Although the latter authors found a higher frequency factor their activation energy is also higher.

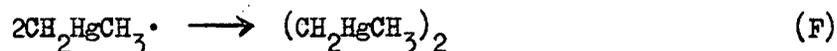
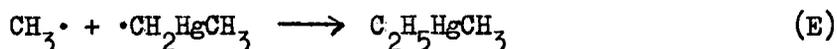
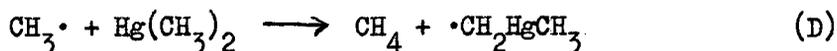
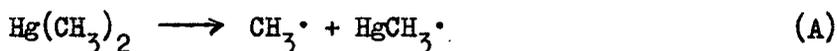
The Thermal Decomposition of Mercury Dimethyl

Far less reliable data are available for the pyrolysis of mercury dimethyl than for di-t-butyl peroxide.

Cunningham and Taylor³⁷ found no appreciable decomposition below 290°C in a static system. At 348°C the gaseous products were about 3 CH₄ to 1 C₂H₆ in short runs, and up to 5 or 6 to 1 in long runs. About 40 per cent of the carbon remained unaccounted for in the gaseous products.

Gowenlock, Polanyi and Warhurst³⁸ studied the pyrolysis of mercury dimethyl in a flow system. The toluene-carrier technique was also applied. The reaction was followed by analysis of the mercury produced, as well

as by gas analysis for methane, ethane and ethylene. With CO₂ as carrier gas methane was measured by pressure difference in a known volume, after CO₂ and all other hydrocarbons were removed by cooling to liquid nitrogen temperature. With N₂ and H₂ as carrier gases, methane was determined from the overall pressure increase in the apparatus. Ethane and ethylene were trapped together with CO₂ at -148°C. CO₂ was taken off by KOH, and ethylene was then determined by hydrogenation. At 492°C the light hydrocarbon fraction consisted of methane and ethane only. Small amounts of ethylene were found from about 550°C upwards. The mechanism suggested by Gowenlock, Polanyi and Warhurst for the decomposition of mercury dimethyl is



Reaction (F) is thought to be negligible. Steacie³⁹ considers the activation energy of 51.5 kcal/mole reported by these authors for reaction (A) as good to within 3 to 4 kcal only, and rejects the assumption that as the A factor was found as 1.0×10^{13} the reaction is necessarily a unimolecular change.

With a mass spectrometric method Lossing and Tickner⁴⁰ found methyl radicals to be the major product of the decomposition of mercury dimethyl. They report an over-all activation energy of 42 kcal.

It is regrettable that so little is known about the decomposition

of this compound. On page 86, fig. 14, a gas chromatogram of the products obtained from the thermal decomposition of mercury dimethyl obtained by the author of this thesis is shown. Although the mercury dimethyl available was impure (see later under "Purity of Materials"), the spectrum of hydrocarbons obtained suggests that the mechanism (A) to (F) proposed by Gowenlock and co-workers does not describe the reaction fully.

EXPERIMENTAL

EXPERIMENTAL

Pyrolysis Apparatus

The reactions were carried out in an all-glass static system which is shown schematically in fig. 13. It was evacuated by the usual combination of an oil- and mercury diffusion-pump. S is the quartz reaction vessel of about 300 cc volume. P is a pre-expansion vessel in which mixing of the methyl source and butene-1 was effected before admission to the reaction vessel. V_1 , V_2 and V_3 are globes which served as reservoirs for the gaseous reactants. B_1 and B_2 are bulbs in which the di-t-butyl peroxide and the mercury dimethyl were kept. Except during the time of an actual experiment these bulbs were kept cooled with dry ice, to avoid dissolution of the grease of stopcocks T_1 and T_2 . In the case of di-t-butyl peroxide a fluorocarbon grease was used (KEL-F, M.W. Kellogg Company, Jersey City, New Jersey).

Owing to the great toxicity of mercury dimethyl precautions were taken to avoid venting it into the laboratory. The exhaust of the oil pump was connected to a cylinder of about 3" internal diameter and about 18" long filled with gas-mask charcoal. In turn, the exhaust from this adsorption was led out a window.

To facilitate the admission of gaseous reactants to the storage globes V_1 to V_3 , the latter were fitted with cold fingers, which are not shown in fig. 13. To admit butene-1 a plastic tube was fitted to the steel cylinder containing the olefin, and connected via a B 10 cone and socket to tap T_3 . After careful expansion into one of the previously pumped out storage globes V, the butene-1 was frozen in the cold finger

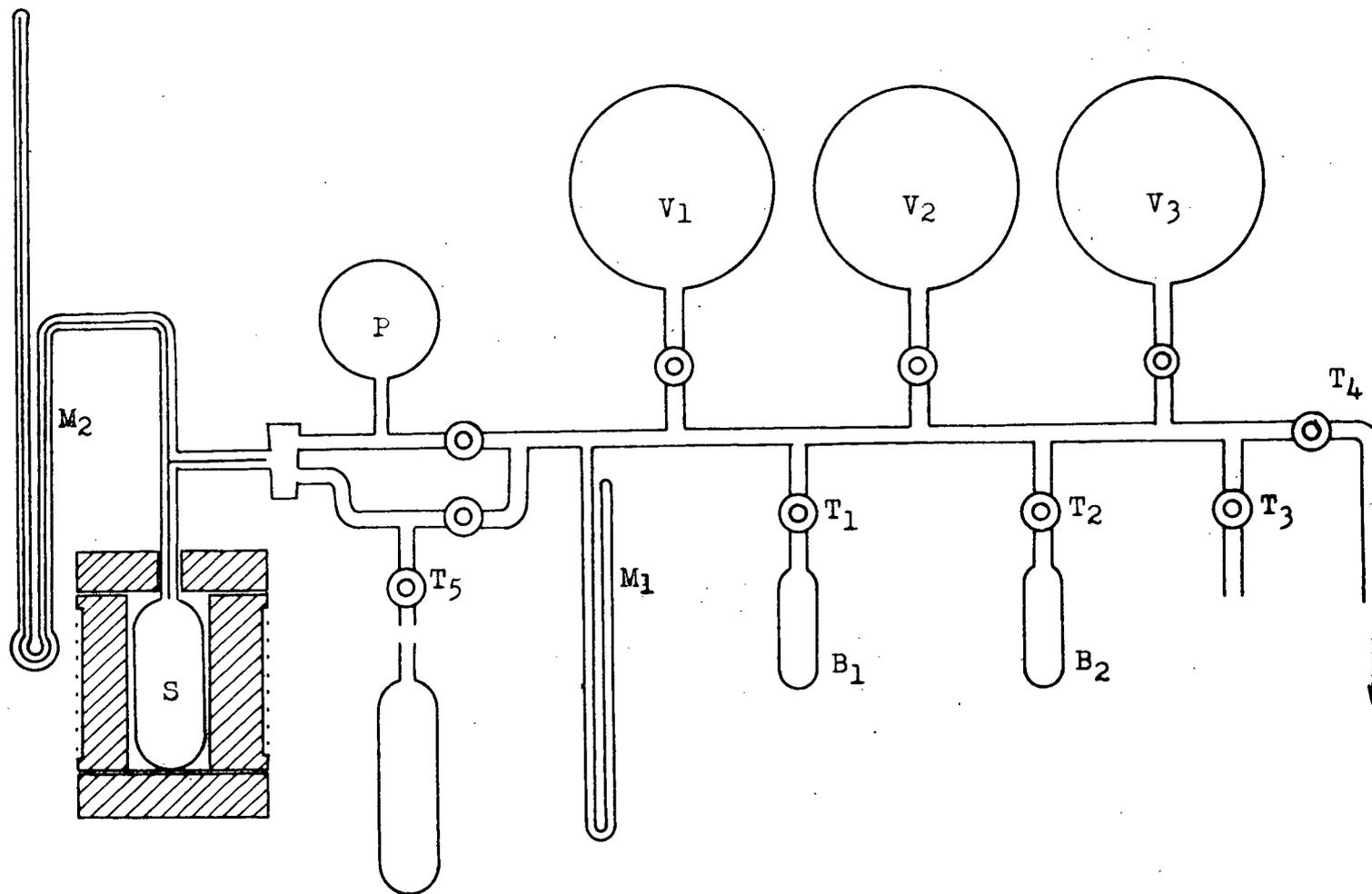


Fig. 13. Schematic outline of thermal decomposition apparatus

by immersing the latter in liquid nitrogen. This made it possible to pump away any air entering the system during admission. Mercury dimethyl and the peroxide were handled in a similar manner, except that cold fingers were not necessary as the storage bulbs themselves could be conveniently immersed in liquid nitrogen. When pumping away air over the cooled reactants, care was taken to cool the trap situated between T_4 and the mercury diffusion pump in liquid nitrogen instead of the customary dry ice, to avoid back-diffusion of substances from the trap to colder parts of the system.

Furnace and Temperature Control

The furnace consisted of a cylinder of Tobin bronze of 4" outside diameter, 5" long and weighing about 20 lbs. The internal diameter of this cylinder was bored to about 65 mm to accommodate the reaction vessel with a few mm clearance on either side. Lids of the same material one inch thick closed the cylinder on both ends. The top lid was drilled in the center for the passage of the capillary of the reaction vessel, and was cut into halves for easy assembly. The lids were screwed to the main body of the cylinder. The heater was 18 gauge nichrome wire wound around the cylinder with the interposition of a thin asbestos sheet. The 34 windings had a cold resistance of about 17 ohms. This assembly, coated with a 1/4" layer of fireclay, and with the capillary of the reaction vessel facing upwards, was placed in the centre of a 5 gall metal drum supported from below and the sides by fire bricks. Expanded vermiculite was then poured into the interstices. 150 Watts only was sufficient to maintain the furnace at 500°C.

Power was supplied through a Solar constant voltage transformer. The voltage was adjusted for a given temperature by a variable transformer. A finer adjustment was possible by a variable resistance in the circuit.

Two chromel-alumel thermocouples were placed in drill-holes in the bronze body of the furnace, at half the length and in the lid. With the very good heat insulation, and the substantial metal body the temperature of the two couples differed by less than 1° near 500°C. The E.M.F. of the thermocouples was measured with a potentiometer (Rubicon Company, No. 2732, Philadelphia, Pa., U.S.A.).

A Series 156 C Honeywell Electronic Millivolt Controller was available for the control of temperatures above 350°C. This instrument was actuated by the chromel-alumel thermocouple, and working on a potentiometer principle gave precise and accurate temperature control at 500°C to within 1°. The advantage of the millivolt controller is that it can be used with thermocouples of differing type, and that temperature settings can be made by adjusting a dial on a millivolt scale, eliminating the need for a calibration. The current capacity of the instrument fitted with a mercury switch was 30 amp., permitting rapid predetermined temperature changes even with a large furnace. Unfortunately, a conversion kit for the use of the instrument for temperatures below 350° was not available in time, and the lower temperatures were controlled manually to within 1°C.

Description of a Typical Experiment

After pumping the reaction vessel, gallery, and pre-expansion volume

to "black" vacuum, the substance being used as a source of methyls was admitted to the latter. The gallery was pumped down again and butene-1 was then admitted. The total pressure of gases in the pre-expansion volume, as shown by manometer M_1 was chosen so as to produce a desired final pressure, read on manometer M_2 , after expansion of the gas into the reaction vessel. As there was no difference in the analysis of test runs obtained with 5 min and 10 min mixing time in the pre-expansion volume, it was assumed that complete mixing had taken place in 10 min. By admitting the much smaller amount of the methyl source first it was assumed that a better mixing would occur when admitting the butene-1, than by carrying out the admission procedure in the reverse order.

It was desirable to be able to analyze the samples from a series of pyrolysis runs together, to reduce the change of experimental parameters on the gas chromatograph to a minimum (Part I, p. 44). Hence the storage of reaction products was of importance.

Lubricated stock cocks were ruled out as it has been observed⁴¹ that substances like ethylene dissolve readily in Apiezon grease and other similar lubricants.

Break-seals for storage of samples were found unsuitable. Preliminary experiments had shown that three gas chromatographic columns had to be used for the analysis. Thus it would have been necessary to switch columns on the chromatograph for each sample, once the seal was broken, instead of being able to analyze all samples on one column, then all on the next, etc. Furthermore analysis of a sample of pure butene-1 sealed in a break-seal with the greatest care possible showed that approximately 1% of the butene was decomposed during the sealing of the

side-arm. Most of the products were substances having vapour pressures above atmospheric at room temperature, and hence it was not feasible to cool the break-seal in liquid nitrogen during sealing for fear of building up excessive pressures on warming up to room temperature.

The sampling method finally adopted was to draw the products of the thermal decomposition into pipettes of about 300 ml volume attached to the apparatus by a B 10 cone and socket at T_5 (fig. 13). The pipettes were fitted with metal valves made of brass with a sealing diaphragm of Teflon. These valves were an adaptation of a valve produced by the Metropolitan Vickers Co. The valves were tested by evacuating the pipettes and analyzing the "contents" by gas chromatography after several days. No leakage of air was found.

Purity of Materials

The butene-1 was "Research Grade" supplied by Phillips Petroleum Company, Bartlesville, Oklahoma, U.S.A. A gas chromatographic analysis of one sample showed two impurities to be present, about 1% of a C_5 - and about 0.25% of a C_3 -hydrocarbon. A test of another cylinder showed no detectable impurities within the limits of the analytical method. This sample of butene-1 was used in all experiments.

Di-t-butyl peroxide was obtained from A.D. Mackay Inc., 198 Broadway, New York 38, N.Y. After bulb-to-bulb distillation under reduced pressure on the vacuum line of the pyrolysis apparatus, no detectable impurity was found in the material. Repeated tests of the thermal decomposition of di-t-butyl peroxide at 20 mm Hg pressure between 180 and 220°C showed that the sole reaction products of this pyrolysis were ethane and acetone. No

methane was detected, and it was therefore considered that the abstraction by methyl from acetone reported by Raley and co-workers³³ was negligible at low peroxide pressures.

The mercury dimethyl, supplied by Delta Chemical Works Inc., 23 West 60th, New York 23, N.Y., contained three impurities, which together constituted approximately 8% of the material. The chromatogram shown in fig. 14 shows the analysis of the reaction mixture obtained from the pyrolysis of mercury dimethyl by itself. It appears that the amounts of compounds--presumably hydrocarbons judging from the peak-shapes--obtained other than the expected methane and ethane is significant.

Analytical Procedures

For the analysis the gas chromatograph described in Part I of this thesis was available. However, the syringe technique previously described for admission of samples was no longer appropriate and was replaced by a by-pass system (fig. 15a).

Free expansion from the sampling pipette into the evacuated by-pass was found initially to provide an insufficient quantity of sample in some cases. A Toepler pump was therefore attached with which the pressure in the by-pass could be raised by a factor of four.

A system of stopcocks permitted the use of two different analytical columns, both of which were contained in a heated air jacket.

The helium was rigidly purified by a system of two charcoal traps shown in Fig. 15b. These traps could be regenerated alternately.

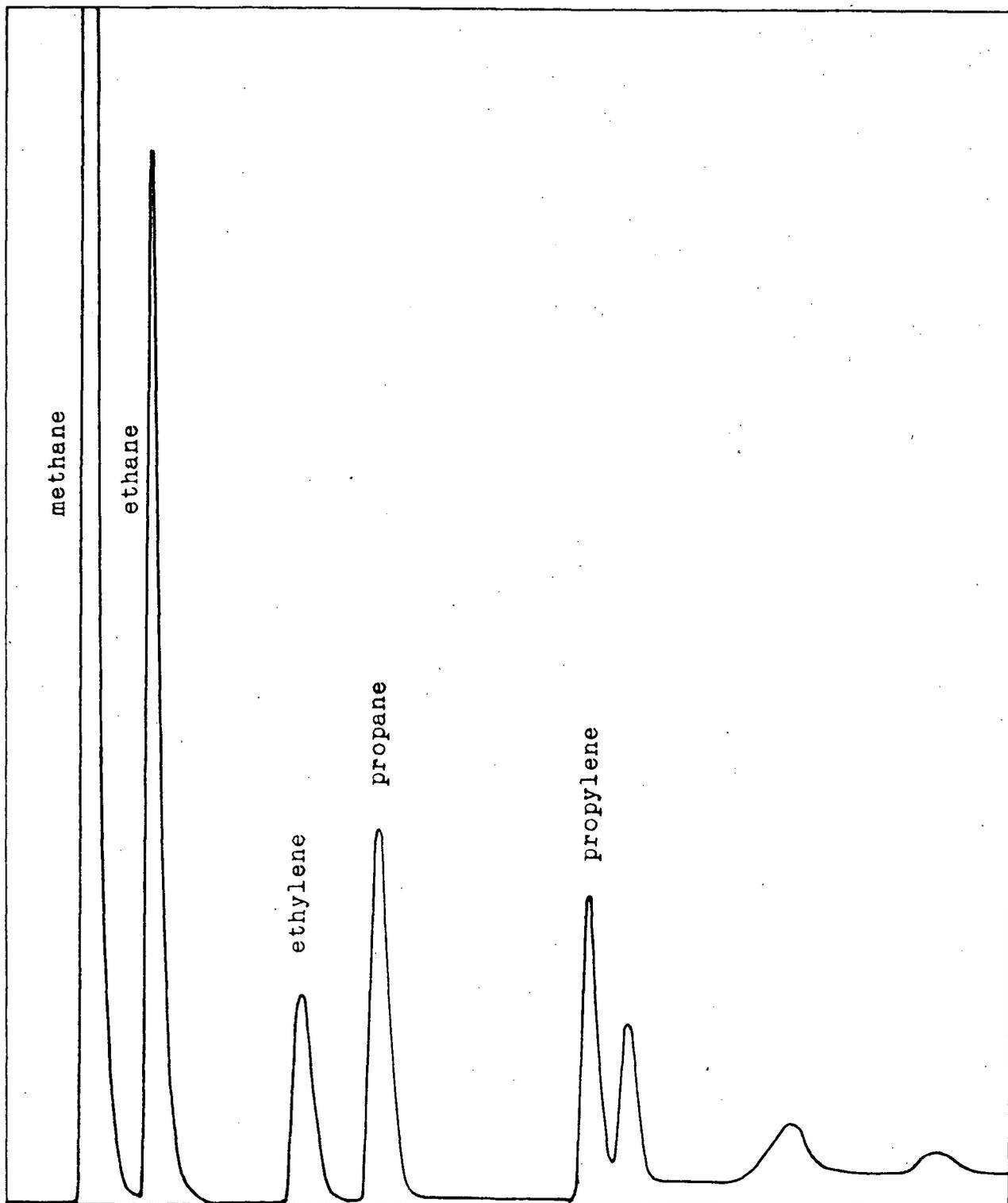


Fig. 14. Chromatogram with alumina column of products obtained from the pyrolysis of mercury dimethyl at 492°C for 1 minute

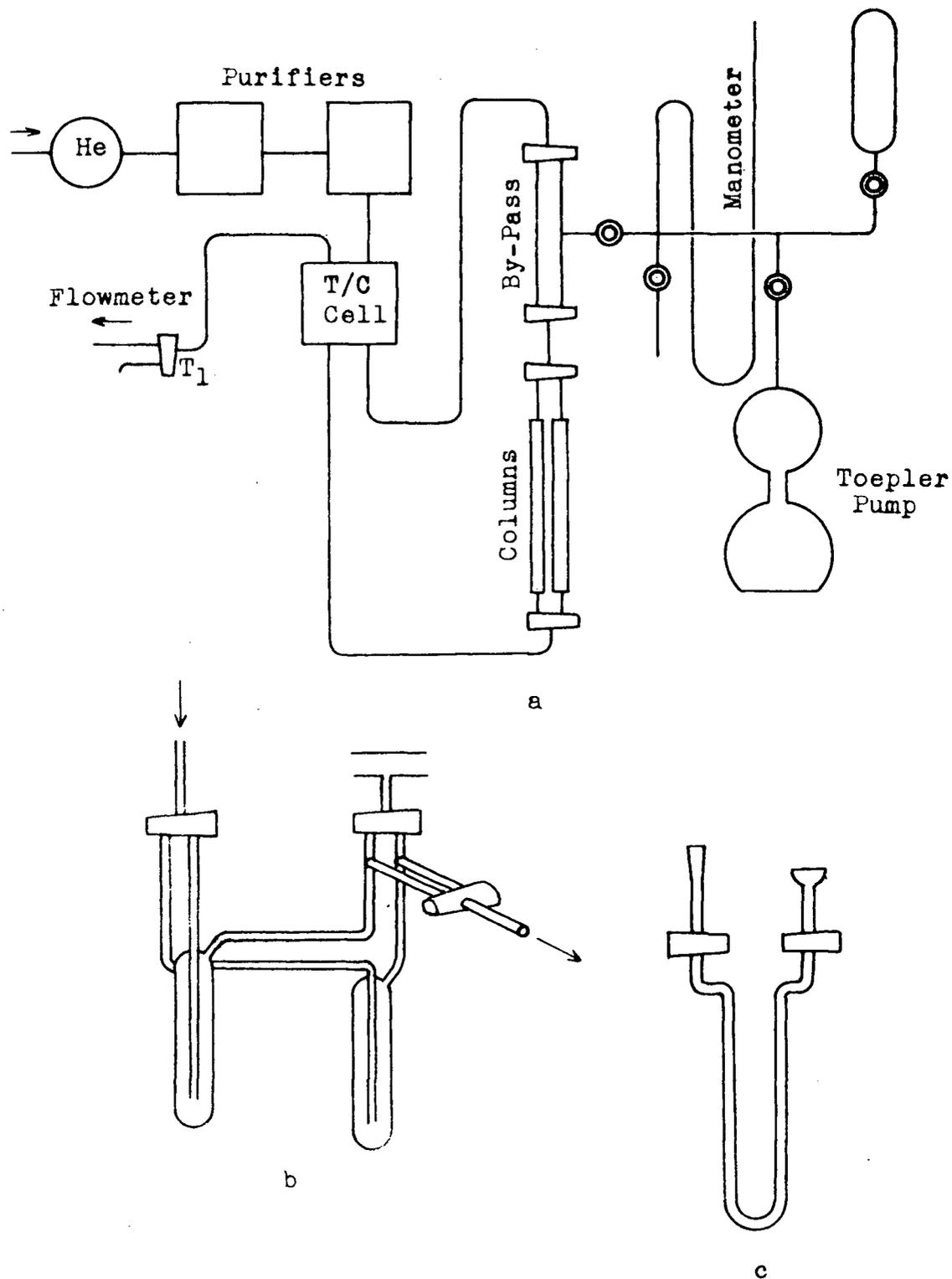


Fig. 15. a) Schematic outline of chromatography apparatus
b) System of carbon traps for helium purification
c) U-tubes for trapping of components

Chromatographic Columns

A 12 ft. column with 1.5% squalane on carbon black (Pelletex) has been used by McNesby and Gordon¹³. Bryce and Kebarle¹² used an alumina column and a tricresyl phosphate (TCP) column, with controlled temperature rise during each analysis to accelerate the elution of higher boiling components of the samples.

The original 6 ft. columns used by the latter authors were available, and it was shown that neither the alumina, nor the TCP column would separate butene-1 and butene-2. Nor would they separate butene-1 from 3-methylbutene-1 and from isopentane.

The 12 ft. squalane-pelletex column, referred to in the following as 'SP column', failed to resolve pentene-2 and n-pentane, and would separate butene-1 and butene-2 only, when run at 0°C. Separation of methane and ethane was incomplete on this column at 0°C. The latter two compounds were even less well resolved with the TCP column. The SP column had also the disadvantage of producing a very strongly tailing peak for acetone, the determination of which was desirable in experiments involving di-t-butyl peroxide as a source of methyls. Tailing peaks cannot be used as a quantitative measure of the substance that produces them.

To analyze the reaction mixture completely it was found necessary to use all three columns. Although rather tedious, this method had the advantage that it obviated the use of rising column temperatures. The latter type of analysis has, a priori, less accuracy than an analysis carried out with constant column temperature.

The separations achieved on the three columns in the analysis of a sample of reaction mixture from the pyrolysis of a particular di-t-butyl

peroxide - butene-1 system are shown in figs. 16, 17 and 18.

The methane and ethane analyses were obtained with the alumina column.

The SP column separated butene-2, 3-methyl-butene-1, isopentane, 3-methyl-pentane, and gave a combined peak for pentene-2 and n-pentane.

The TCP column resolved pentene-2, 3-methyl-pentane, and acetone.

It follows from the above that n-pentane had to be estimated by deducting the value found for pentene-2 with the TCP column from the pentene-2 + n-pentane peak obtained with the SP column. The separation of n-pentane from butene-1 shown in fig. 18 on the TCP column was considered insufficient for a direct estimation of this compound.

It is interesting that acetone shows such a strongly tailing peak on the SP column. The 1.5% squalane, a branched hydrocarbon of high molecular weight obtained by the hydrogenation of shark liver oil, is supposed to straighten the adsorption isotherms of compounds on the carbon black (Pelletex)⁴², and thus give symmetrical peaks in the chromatogram. The tailing peak of the acetone indicates a strongly curved adsorption isotherm. A brief test showed that aldehydes and ethers produced tailing peaks on the SP column also. It appears then that squalane is ineffective in straightening the adsorption isotherms of these compounds. If it can be shown that the action of squalane is confined to hydrocarbons only, then an SP column might be used to distinguish between hydrocarbons and ketones, aldehydes and ethers, the compound type being indicated by the shape of the peak. The distinction would most probably be between polar and non-polar compounds. It should be observed in this respect that an adsorption column like

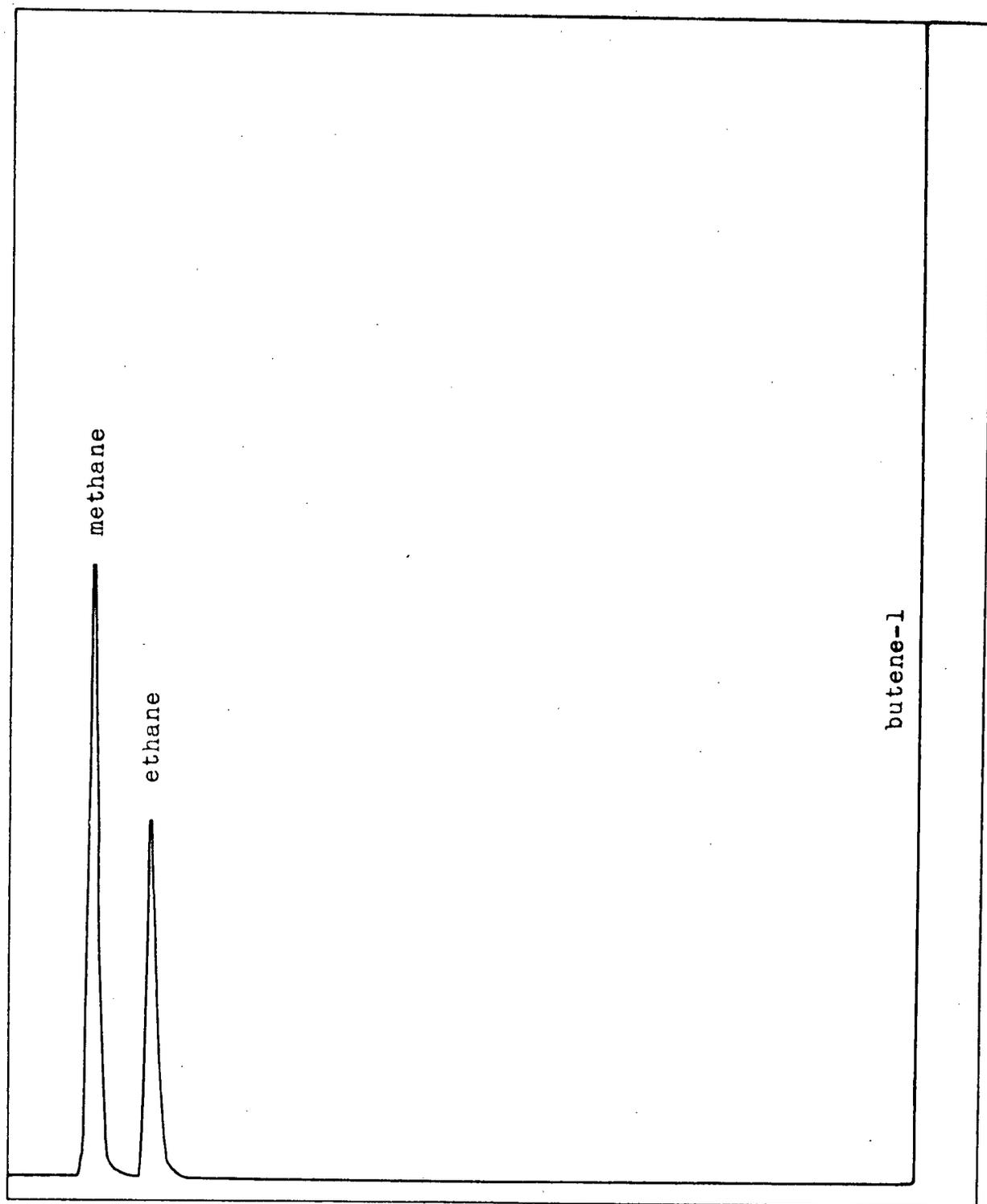


Fig. 16. Chromatogram with alumina column of product mixture from reaction of methyl with butene-1 at 205°C

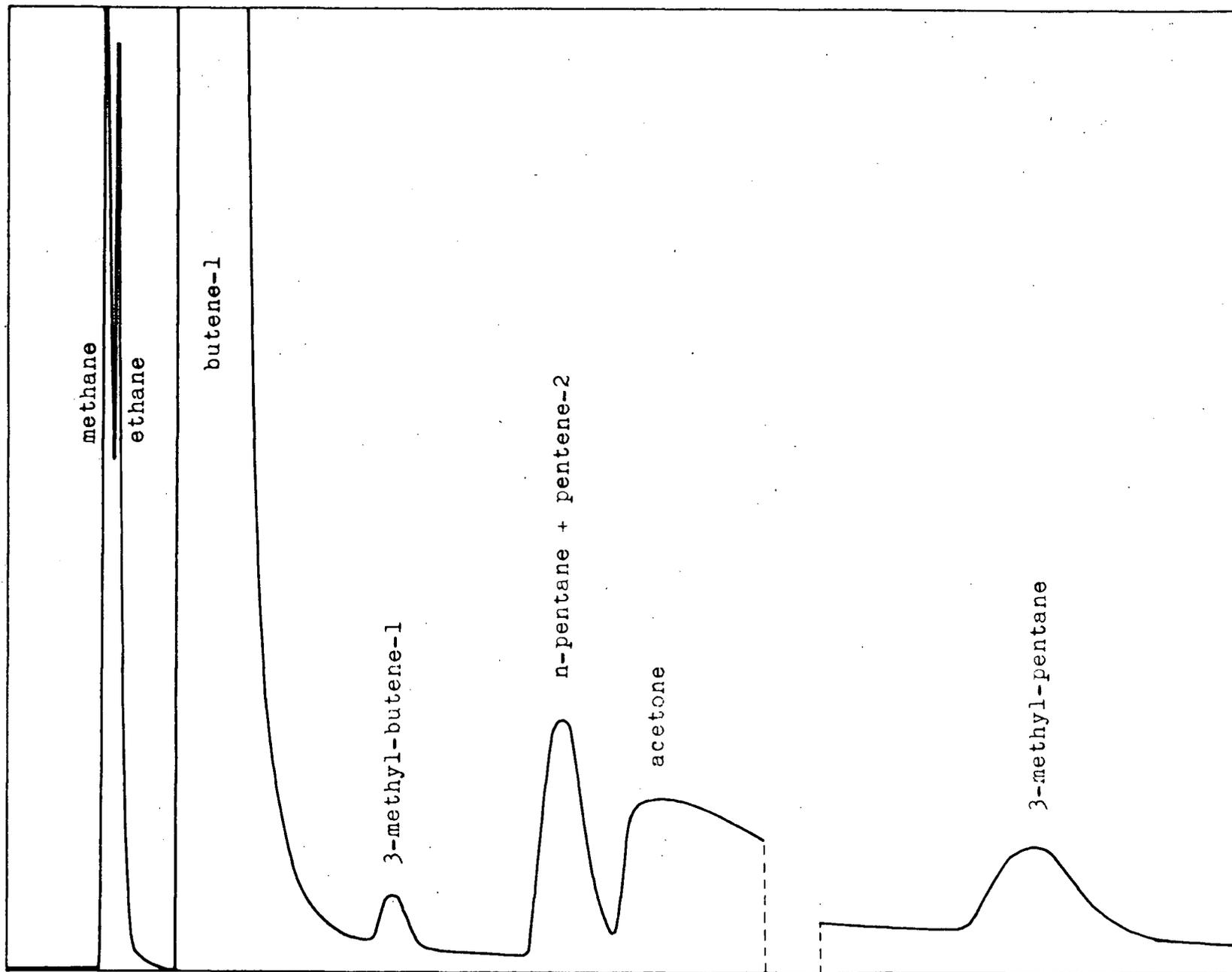


Fig. 17. Chromatogram with squalane-pelletex column of product mixture from reaction of methyl with butene-1 at 205°C

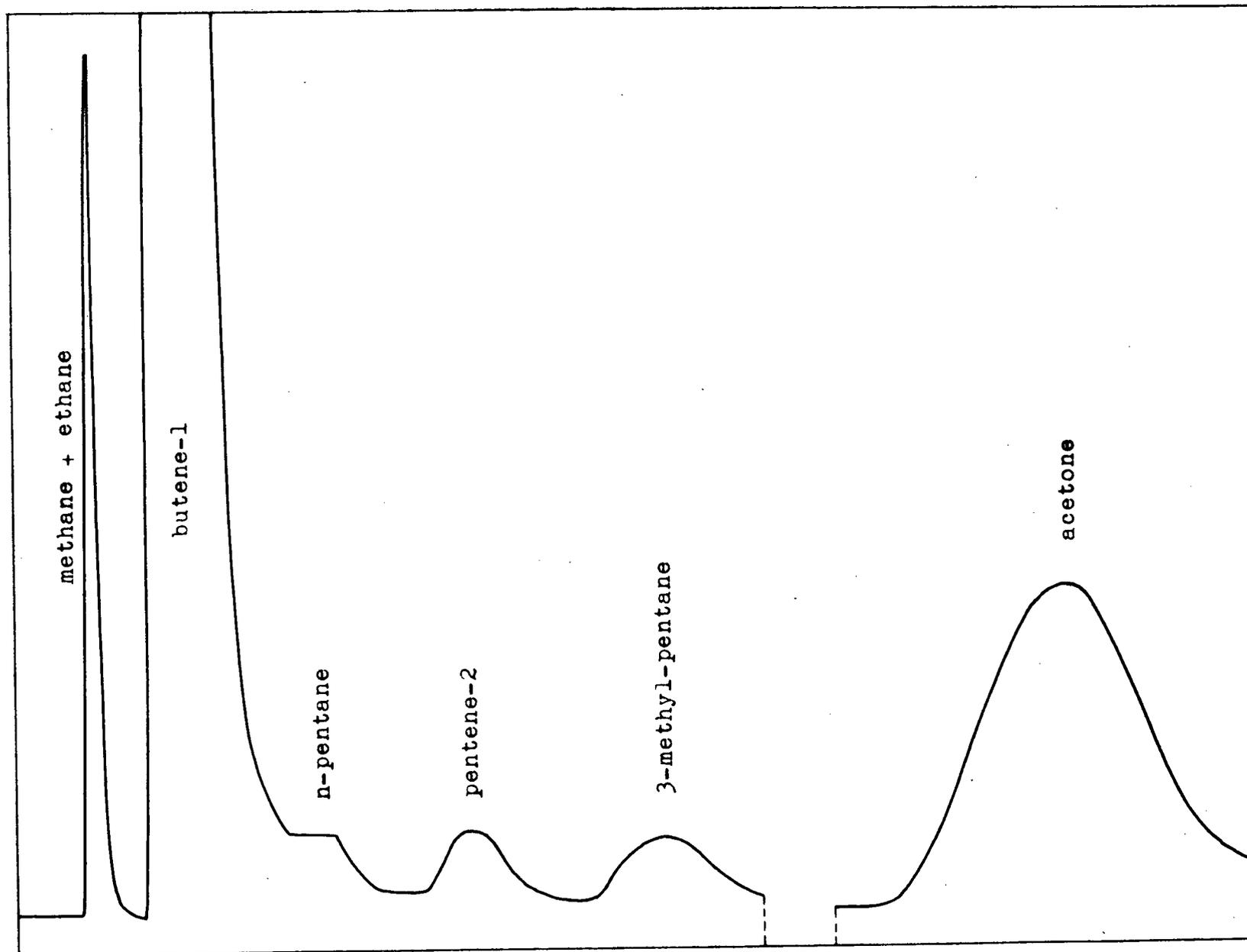


Fig. 18. Chromatogram with tricresyl phosphate column of product mixture from reaction of methyl with butene-1 at 205°C

alumina gives tailing peaks for all compounds including hydrocarbons. On a partition column like TCP even acetone gives a symmetrical peak.

The alumina and TCP columns consisted of 8 mm o.d. Pyrex U-tubes of an effective length of about 6 ft. Both columns were operated at 26°C. The SP column was prepared according to reference⁴². The 1/4" copper tubing was filled and then coiled into a spiral which fitted into a Dewar vessel. Its operating temperature was either 0° or 23°C according to whether or not it was desired to test for the presence of butene-2, which was only separated from butene-1 at the lower temperature. The flow-rate of the carrier gas, helium, was 50 ml/min for all three columns.

It is practically impossible to obtain two columns with exactly equal flow resistance. Hence, when switching from one column to another, the pressure of the carrier gas has to be adjusted to obtain the same flow. For instance, it was found that the SP column had a much lower flow resistance than the TCP column. To avoid the necessity of re-setting the carrier gas pressure, the SP column was fitted at its entrance with a Hoke valve, which was so adjusted that the combined flow resistance of valve and column equalled that of the TCP column.

The exhaust precautions described for the thermal decomposition apparatus were taken with the pumps and flow meters due to the presence of mercury dimethyl.

Product Identification

Light products such as methane, ethane, etc., were identified by peak reinforcement and by comparison with chromatograms previously obtained

in this laboratory.

An indication of the identity of the higher products, i.e. compounds with a molecular weight greater than butene-1, was obtained by peak re-inforcement, which is produced by injection of a pure sample together with the reaction products. Peak re-inforcement is a necessary but not a sufficient condition to establish the presence of a particular compound, and positive identification was obtained with a mass spectrometer.

For the trapping of a particular peak a U-tube fitted with stopcocks at both ends (fig. 15c) was immersed in liquid nitrogen, and attached at T_1 (fig. 15a). Mass spectra of compounds identified by this method are reproduced in the Appendix. The efficiency of trapping carried out in this manner was very low. The contents of a U-tube re-admitted for analysis after trapping into the gas chromatograph, yielded a peak the area of which was only about 5% of the original peak.

Quantitative Determination

Peak areas, measured with a planimeter were taken as representative of the amount of compound present⁴³ after calibrating the chromatograph with a synthetic blend of compounds (see also Chapter II, Part I).

Precision of the Quantitative Determinations

By taking the uncertainties in flow-rate of the carrier gas, cell current, cell temperature, column temperature, room temperature, and planimeter measurements into account, Ruzicka⁴⁴, working with the identical chromatograph in this laboratory, estimated that the error involved in equating the peak areas to the amounts of substances present

is $\pm 6\%$. By allowing also for uncertainties in furnace temperature and time of reactions (5 min) the over-all error was thought to be $\pm 10\%$. However, it is reasonable to assume that a number of experimental parameters such as flow-rate, cell current, room temperature, etc., remained virtually constant during the time chromatograms were obtained. In the present work relative rate constants were used in calculations and these were obtained from the ratios of peak areas measured in one chromatogram, and hence errors would largely cancel.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

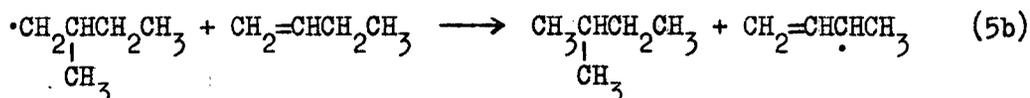
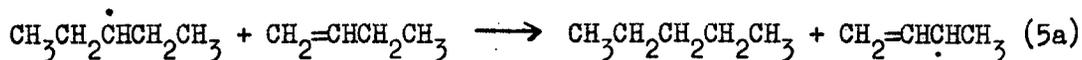
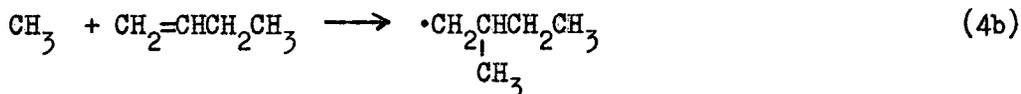
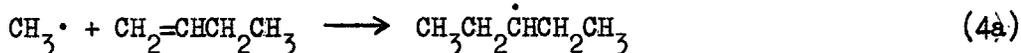
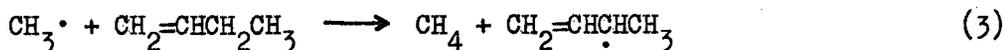
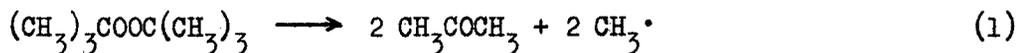
I THE REACTION OF METHYL RADICALS FROM DI-t-BUTYL
PEROXIDE WITH BUTENE-1 IN THE TEMPERATURE RANGE

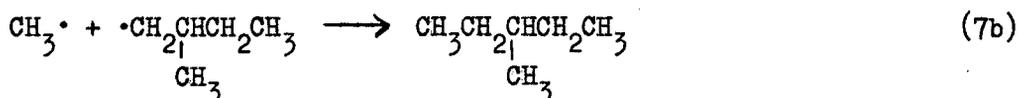
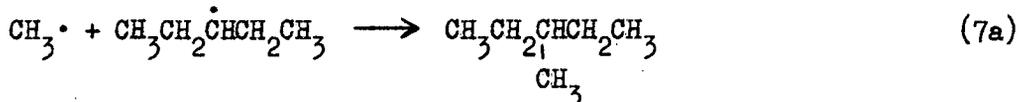
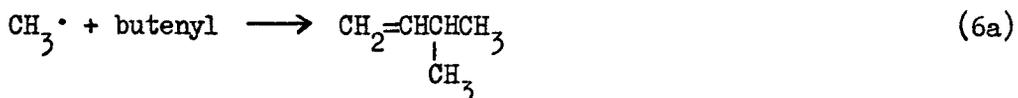
160 - 220°C

A typical mixture containing 10% di-t-butyl peroxide pyrolysed at a representative temperature of 180°C yielded the following products:

methane
ethane
3-methyl-butene-1
pentene-2
n-pentane
isopentane
3-methyl-pentane
acetone

The following mechanism for their formation is postulated:





The above mechanism accounts for all the products identified, i.e.

reaction (3) yields methane

"	(2)	"	ethane
"	(6a)	"	3-methyl-butene-1
"	(6b)	"	pentene-2
"	(5a)	"	n-pentane
"	(5b)	"	isopentane
"	(7a)	"	3-methyl-pentane
"	(7b)	"	3-methyl-pentane
"	(1)	"	acetone

In subsequent discussions a number of abbreviations have been introduced as follows:

Pentyl radical resulting from reaction (4a) = pentyl A

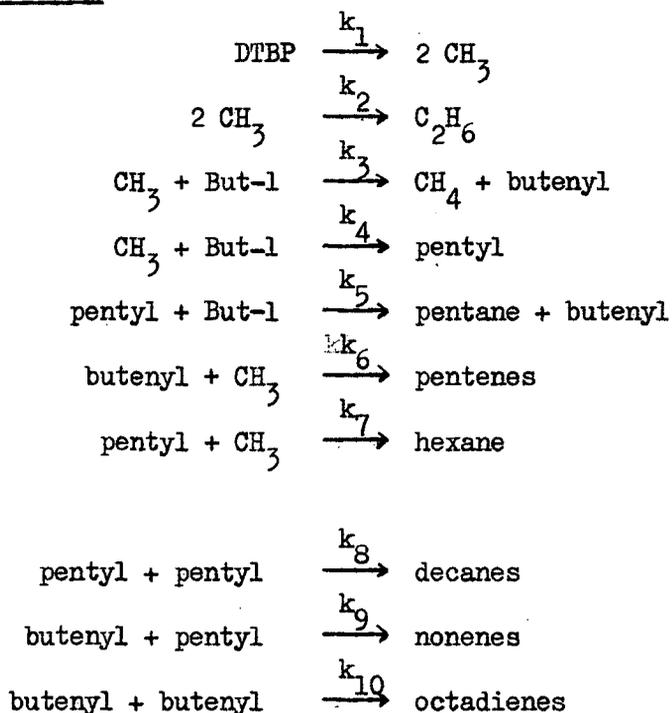
Pentyl radical resulting from reaction (4b) = pentyl B

Collectively these radicals will be called "pentyl".

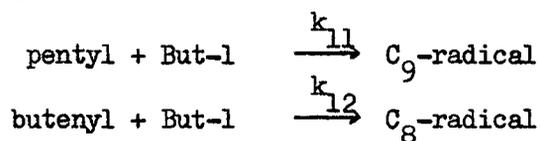
3-methyl-butene-1 and pentene-2 will be referred to collectively as pentenes, n-pentane and isopentane as pentanes, and 3-methyl-pentane as hexane.

Di-t-butyl peroxide and butene-1 will be referred to as DTBP and But-1 respectively.

Kinetic Scheme



Also possible are the addition of pentyl and butenyl to the double bond of butene-1



The higher molecular weight products resulting from reactions (8) to (12) were not identified.

Product Distribution

The distribution of hydrocarbon products having a molecular weight greater than butene-1 is shown in Table VI for an experiment at 160°C.

T A B L E V I

Relative Concentrations of Higher Hydrocarbon Products

Experimental Conditions: 18% DTBP; Total Pressure

111 mm Hg; 30 min at 160°C

pentene-2	72.7
n-pentane	27.3
3-methyl-pentane	93.0
isopentane	2.5
3-methyl-butene-1	7.0

The Reaction of Methyl with Butenyl Radical

The product distribution given in Table VI shows that the ratio of pentene-2 / 3-methyl-butene-1 is $72.7 / 7 \cong 10$. The formation of these products has been accounted for in the mechanism by reactions (6a) and (6b). The products may suggest that both electronic structures of the butenyl radical are actually present and react as such



Such an interpretation would be incorrect. According to molecular orbital theory, the unpaired electron occupies an orbital of lower energy than those which would be representative of either of the two canonical structures. In approaching the hybrid molecular orbital the methyl radical may form activated complexes, the relative concentrations of which will be a function of the energy change involved in their formation. The energy changes in the formation of the complexes are related to the localisation energy of the electron as given by the two canonical forms

in which the hybrid can be represented.

If no activation energy were involved in the reaction butenyl + methyl, as is probably the case with the reaction of pentyl + methyl discussed later, one could then attribute the factor of 10 found in the relative concentrations of pentene-2 and 3-methyl-butene-1 to steric factors. However, it is reasonable to assume that the resonance energy of the butenyl is considerable by analogy with the allyl radical. For the latter the value of the resonance energy has been estimated theoretically by Coulson⁴⁵ as 15.4 kcal/mole, and by Orr (quoted by Bolland)⁴⁶ as 18.7 kcal/mole. The fact that butenyl does not abstract hydrogen from butene-1 below 375°C¹³ suggests that the resonance energy of this radical should be of the same magnitude as allyl.

Using the value of 10 obtained for the pentene ratio, a calculation of the energy difference can be made.

$$2.3 \log 10 = \frac{\Delta E}{RT} \quad T = 160^\circ\text{C}$$

$$\Delta E_{\text{calc}} = 2 \text{ kcal/mole}$$

Further confirmation that an energy term is involved can be obtained by determining the temperature dependence of the product rates according to the relationship

$$\log \frac{\text{pentene-2}}{\text{3-methyl-butene-1}} = \frac{\Delta E}{2.3 RT}$$

Hence the temperature dependence of the pentene ratio should yield a value for ΔE by plotting the log of the ratio against $1/T$ in the usual manner. The necessary data are given in Table VII, and the Arrhenius plot is shown in fig. 19.

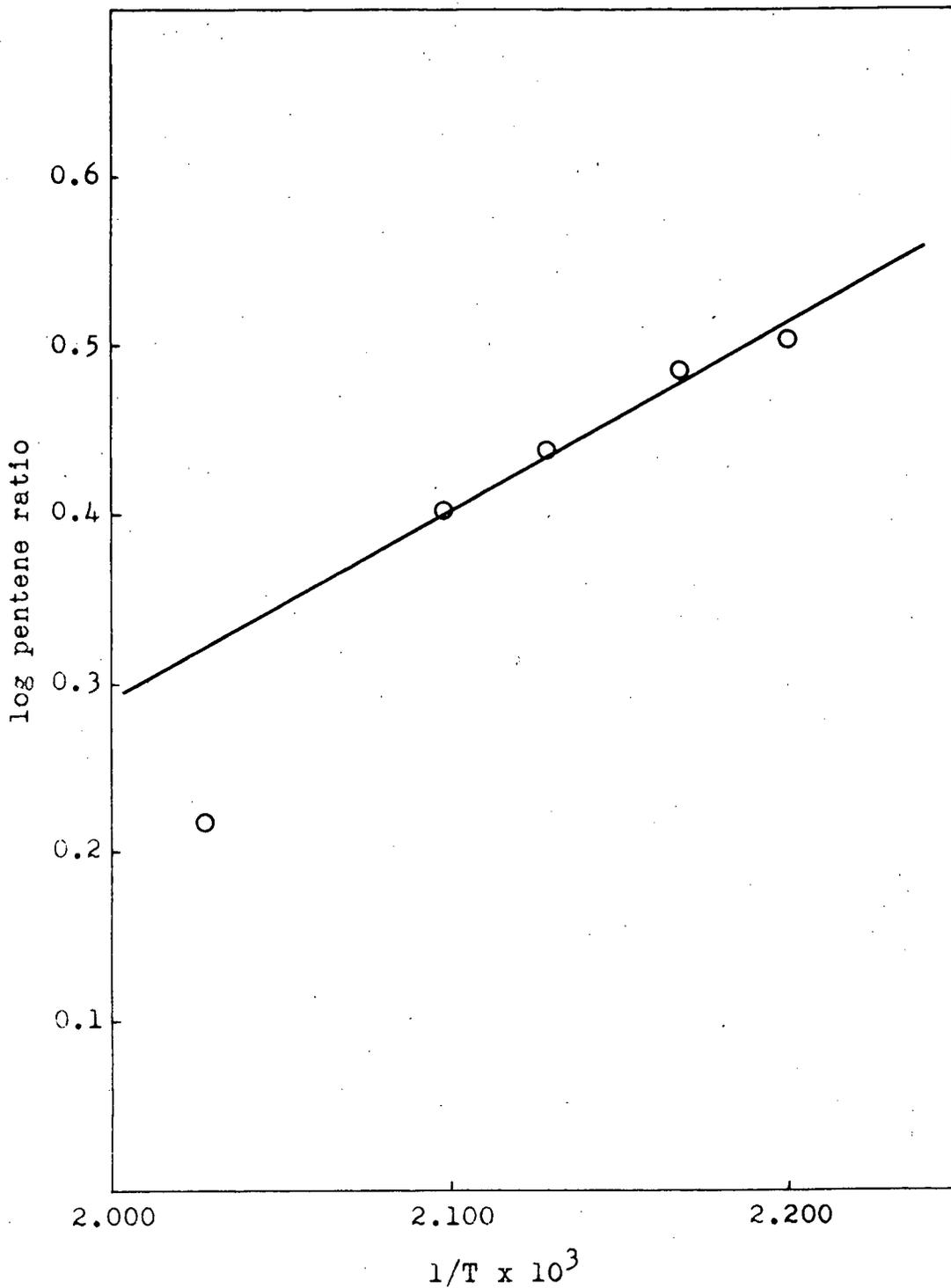


Fig. 19. Arrhenius plot of pentene ratio

T A B L E V I I

Temperature Dependence of the Pentene-2 / 3-Methyl-Butene-1 Ratio

20% DTBP ; Total Pressure 100 mm Hg

T°C	$\frac{1}{t^{\circ}\text{K}} \times 10^3$	Pentene Ratio	log Pentene Ratio
220	2.028	1.65	0.219
203	2.099	2.52	0.402
197	2.129	2.74	0.438
188	2.167	3.05	0.484
181	2.200	3.18	0.502

The slope of the Arrhenius plot is 1×10^3 deg, therefore

$$\Delta E = 2.3 \times R \times 10^3 = 4 \text{ kcal/mole}$$

If E_a is the localization energy of the electron in the activated complex leading to the formation of 3-methyl-butene-1, and E_b that leading to the formation of pentene-2, then

$$E_a - E_b = \Delta E$$

as $\Delta E > 0$, $E_a > E_b$. This is in agreement with the fact that more pentene-2 is produced than 3-methyl-butene-1, assuming that the entropy changes for the corresponding reactions are the same.

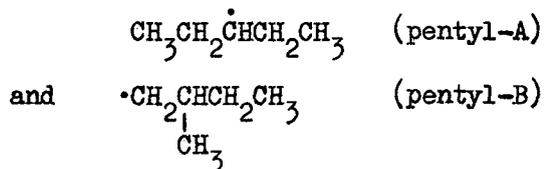
The figure of 4 kcal/mole has an uncertainty of approximately ± 0.4 kcal. The experimental point for 220°C was left out in drawing the line, because at this temperature the half-life of DTBP is of the order of 5 sec only, which is about the time of admission to the reaction vessel. If this point is included then ΔE is calculated as 7 kcal/mole with an uncertainty of 3 kcal.

The pentene ratio in Table VI is much higher than the values given

in Table VII. The value obtained from Table VI was for the lower temperature of 160°C, and the ratio decreases with increasing temperature. Also, the value in Table VI was determined from the mass spectrometric analysis of a trapped chromatographic peak which contained not only pentene-2, but also n-pentane. The results in Table VII are considered more reliable, as they were obtained from a complete chromatographic resolution of the sample.

The Reaction of Methyl with Pentyl Radicals

Normal-pentane and isopentane are the products of reactions (5a) and (5b), i.e. hydrogen abstraction from butene-1 by two different pentyl radicals:



The pentyl radicals in turn are produced by reactions (4a) and (4b), i.e. the terminal and non-terminal addition of methyl to the double bond of butene-1.

If one knew the relative concentrations of pentyl-A and pentyl-B, one could estimate the relative reactivities of these radicals with respect to hydrogen abstraction, from the observed n-pentane / isopentane ratio. This ratio, for the pentanes, is 27.3 / 2.5 (Table VI). The ratio of the rates of methyl addition to the terminal and non-terminal position of the double bond of butene-1 was found by McNesby and Gordon¹³ to be 7.3 : 1. This value should be applicable to the interpretation of the present results, as its elucidation was based not on the reaction of

the pentyl radicals with a substrate, but rather on the decomposition of these radicals. Using these figures:

$$\frac{k_{5b}}{k_{5a}} = \frac{27.3}{2.5 \times 7.3} = 1.5$$

The results obtained by Bryce and Kebarle¹² yield a value of 4 for the relative rates of addition to the terminal and non-terminal carbon in butene-1. This result gives a k_{5b}/k_{5a} ratio of 2.7.

It appears that the reactivity of pentyl-A is approximately twice that of pentyl-B. The higher reactivity of the branched radical may be due to a difference in steric factors, as the non-branched radical is probably puckered, and the approach to the orbital of the unpaired electron would be hindered by the ethyl groups on either side.

Reactions of Butenyl Radical with Species other than Methyl

The kinetic scheme represented by reactions (1) to (7) involves the formation and disappearance of the butenyl radical. If one assumes a steady state condition of this radical, i.e.

$$\frac{d [\text{butenyl}]}{dt} = 0$$

one can write, if methane, pentanes, and pentenes are formed by reactions (3), (5) and (6) respectively:

$$k_3 [\text{CH}_3][\text{butene-1}] + k_5 [\text{pentyl}][\text{butene-1}] - k_6 [\text{butenyl}][\text{CH}_3] = 0$$

therefore methane = pentenes - pentanes

If the observed results do not conform to this last equation the difference should be a measure of the reactions of butenyl with species other than methyl as indicated by reactions (9), (10) and (12). This balance should depend upon the partial pressure of butene-1 in the system,

with the partial pressure of DTBP kept constant, as the steady state concentration of methyl is decreased if more butene-1 is available to the same number of methyls. This pressure dependence is shown in Table VIII.

T A B L E V I I I

Pressure Dependence of Reactions of Butenyl Radical with Species Other than Methyl

20 mm Hg of DTBP; 5 min at 206°C

Part.Press. But-1, mm Hg	CH ₄	Pentenenes	Pentanes	Pentenenes -Pentanes	Non-Methyl Reactions (%)
78	3.36	1.48	0.19	1.29	61.6
131	3.04	1.22	0.20	1.02	66.5
176	3.01	1.13	0.22	0.91	70.0
224	2.58	0.82	0.25	0.57	77.8
269	2.48	0.78	0.28	0.50	79.8

In figure 20 results in the last column in Table VIII have been plotted against the partial pressure of butene-1. The dependence appears to be nearly linear over the range investigated.

The result indicates that only 20 - 40% of the butenyl formed disappears through recombination with methyl. As butenyl does not abstract hydrogen at these low temperatures, one must conclude that butenyl is removed from the system by reactions (9), (10) or (12).

Material Balance Based on Total Methyl Supplied

From the kinetic scheme :

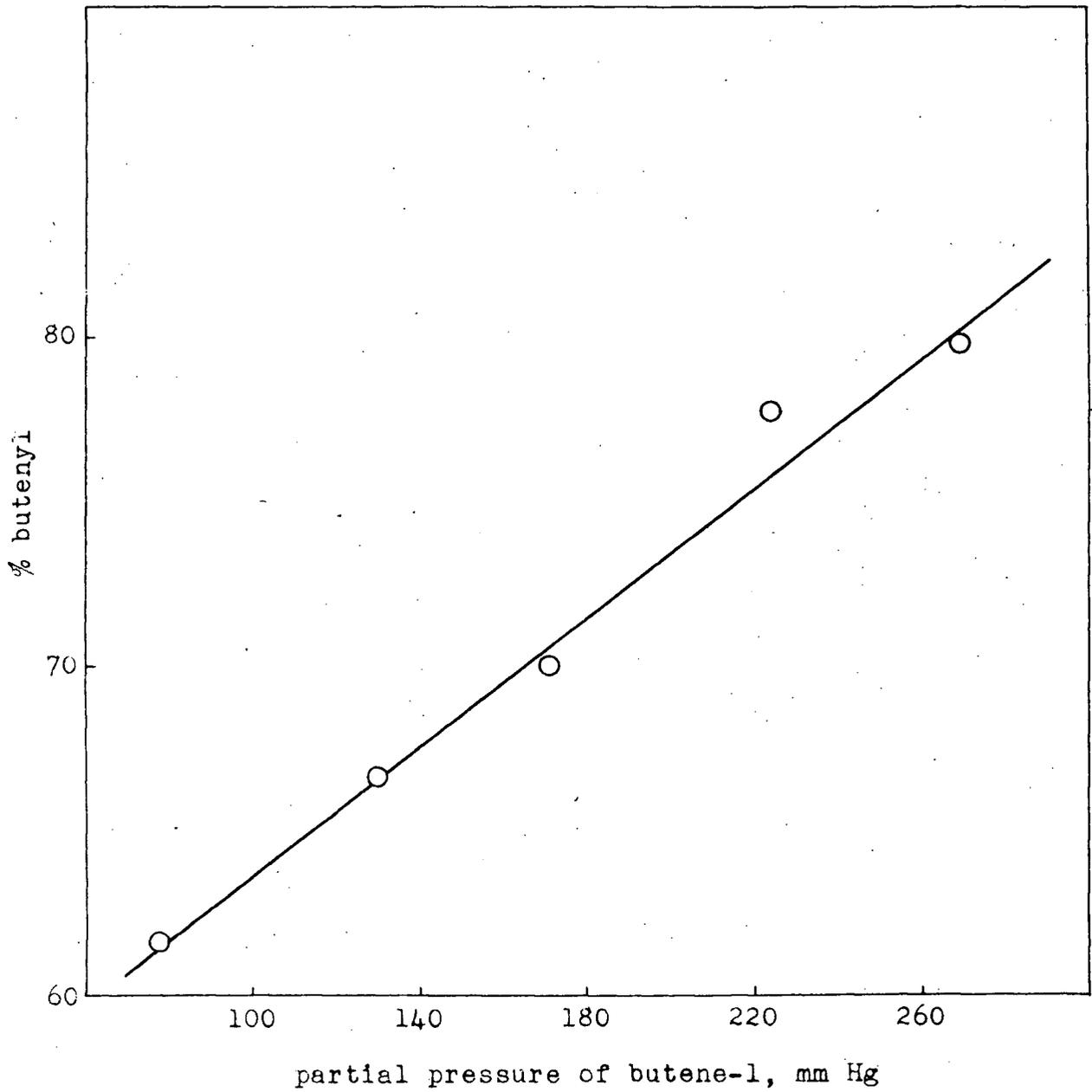


Fig. 20. Pressure dependence of reactions of butenyl with species other than methyl

$(\text{CH}_3)_{\text{total}} = \text{methane} + 2 \text{ ethane} + \text{pentenes} + \text{pentanes} + 2 \text{ hexane}$

but, $(\text{CH}_3)_{\text{total}} = 2 \text{ DTBP decomposed} = \text{acetone}$

Hence, the amount of acetone should be equal to the sum of the products as above.

A chain reaction would be indicated in the system if the sum of methane, ethane, etc. is larger than the amount of acetone found. If, however, the sum is smaller than the amount of acetone, then the difference is a measure of reactions (8), (9) and (11), i.e. recombination of higher radicals involving at least one pentyl.

In Table IX the pressure dependence of this balance is presented.

T A B L E I X

Variation of Material Balance Based on Total Methyl

Supplied with Partial Pressure of Butene-1

20 mm Hg of DTBP; 5 min at 206°C

Partial Pressure Butene-1, mm Hg	Acetone	Sum of Products = $(\text{CH}_3)_{\text{total}}$	% Pentyl Reacting by (8),(9),(11)
78	27.24	25.35	6.9
131	18.40	15.88	13.7
176	14.69	12.44	15.2
224	11.92	8.78	26.3
269	10.38	7.32	29.5

The results contained in the last column in Table IX are plotted against the partial pressure of butene-1 in fig. 21.

The fraction, 7 - 30%, of pentyls removed by recombination of higher

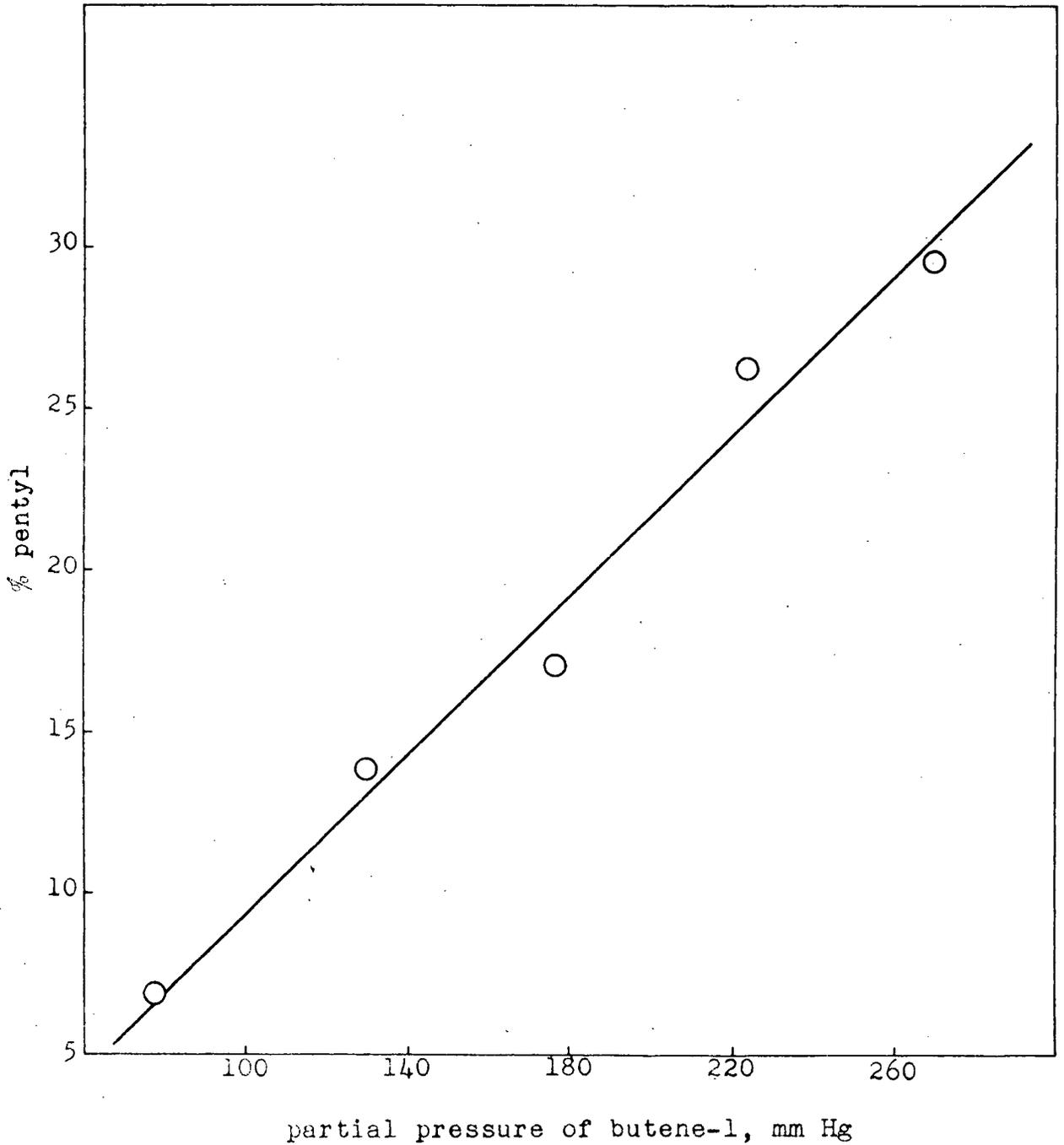


Fig. 21 Variation of material balance based on total methyl supplied with partial pressure of butene-1

radicals differs markedly from the fraction for butenyl (Table VIII), which varies from 60 - 80%. This difference in the behaviour of the two radicals can be attributed to the fact that pentyl, apart from recombination with methyl can also disappear by hydrogen abstraction, while butenyl cannot do so at 206°C. With increasing partial pressure of butene-1 the steady state concentration of methyl decreases, and hence the rate of reactions (7) also decreases. The rate of reaction (5) increases, i.e. the abstraction of hydrogen by pentyl from butene-1.

Pressure Dependence of other Reaction Products

The effect of pressure on the overall product distribution was considered. The results are given in Table X.

T A B L E X

Dependence on the Partial Pressure of Butene-1
of Per Cent Hydrocarbons Formed with Respect to

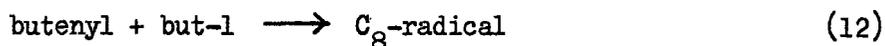
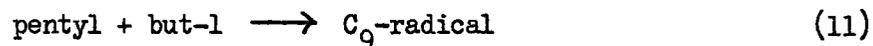
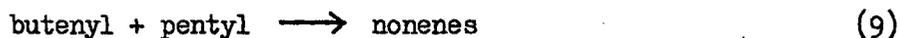
Total Methyl Supplied. 20 mm Hg DTBP; 5 min at 206°C

Part.P. But-1	methane	ethane	3-me ⁺ but-1	pentene-2	n-pentane	3-me- pentane
78	12.3	28.8	1.7	5.5	2.3	7.7
131	16.5	20.6	1.9	4.7	3.8	9.1
176	21.0	16.5	2.0	5.7	4.9	9.0
224	21.6	11.5	1.9	5.0	6.0	8.1
269	23.9	9.7	1.7	5.8	5.1	7.3

Note: isopentane was not included as the amounts produced were insignificant under these conditions.

The product distribution is plotted as a function of the partial pressure of butene-1 in fig. 22. The shape of the curves appears to support the postulated mechanism for the formation of these compounds. Methane increases, and ethane decreases, with increasing butene-1 pressure, as a smaller fraction of the methyls reacts by recombination, and a larger one with the more abundant butene-1. The pentenes and the hexane formed by recombination of butenyl and pentyl with methyl stay about constant for, although the steady state concentration of methyls is decreased with increasing butene-1 pressure, more of the higher radicals are produced also. The amount of pentane formed increases as less methyl becomes available for hexane formation, and the hydrogen abstraction by pentyl from butene-1 increases with increasing pressure of the latter.

The material balances indicate that from 60 to 80% of butenyl (Table VIII), and from 7 to 30% of pentyl (Table IX) were removed from the system by reactions of type (8) - (12). Reactions at the wall should also occur. Considerable tar formation was observed. An analysis of the higher molecular weight products would be necessary for a completely satisfactory interpretation of the results. But it is interesting to consider which reactions are more likely for butenyl and for pentyl.



The activation energy for radical combination reactions is generally

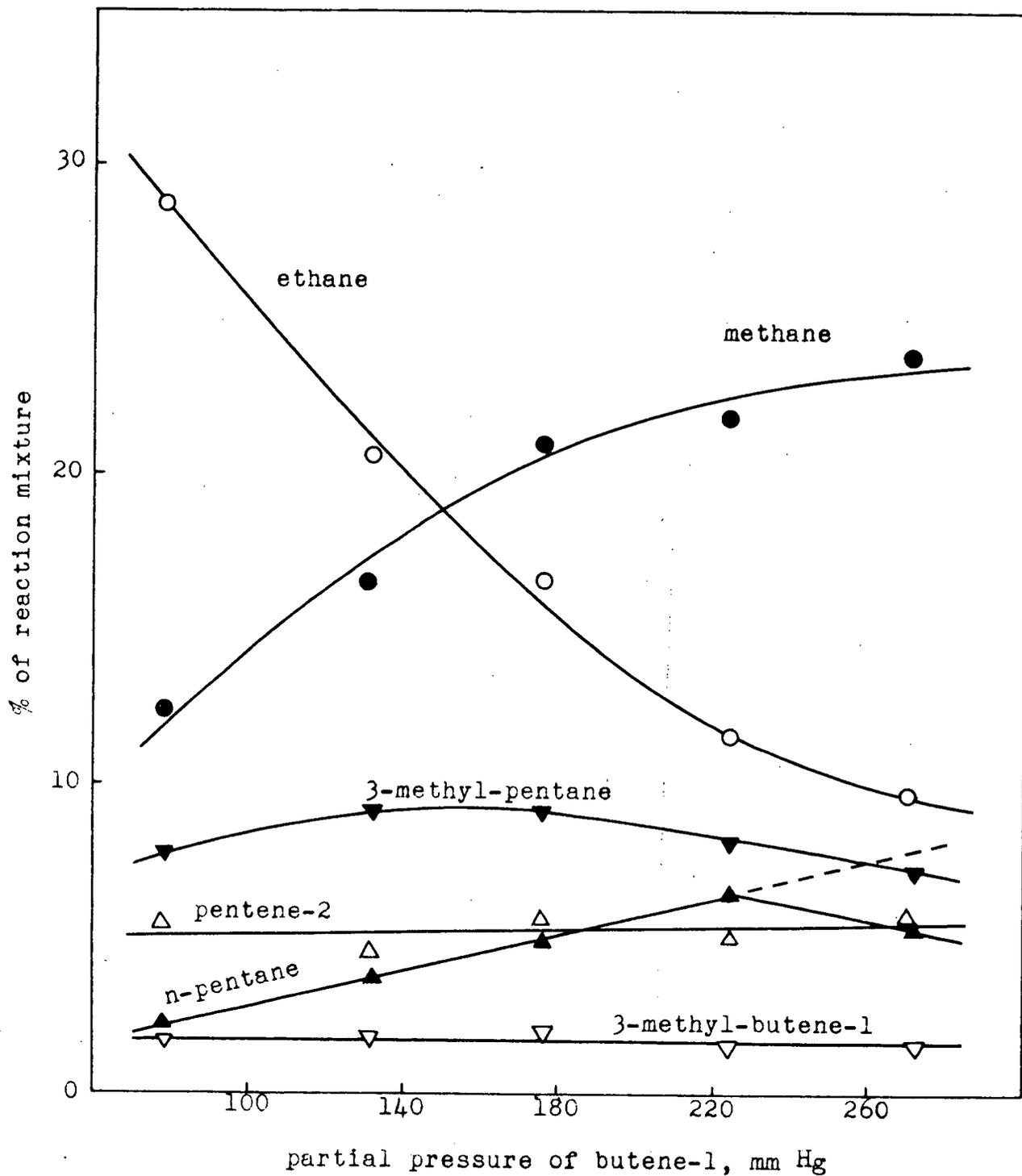


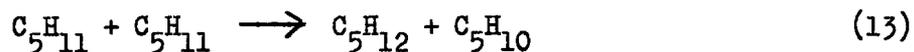
Fig. 22. Variation of hydrocarbon products with partial pressure of butene-1

accepted to be zero. But it is not certain whether this is true also if a resonance stabilized radical like butenyl is involved. It was shown (p. 102) that the difference in the activation energies of reactions (6a) and (6b) is about 4 kcal/mole. This leaves the possibility open that $E_{6b} = 0$; similarly E_9 and E_{10} may be zero. But it is reasonable to assume that the activation energies of the reactions (8) to (12) rise in the same order.

The steady state concentration of butenyl in the system should rise considerably with decrease of steady state concentration of methyl, i.e. with increasing butene-1 pressure. Hence reaction (9) could well become competitive with reaction (5) in removing pentyl radicals from the system. This would help to explain the observation that, with increasing butene-1 pressure, more pentyls are removed from the system by reactions other than (5) and (7).

The pentyl can disappear by reactions (8), (9) and (11). Of these reaction (8), i.e. the recombination of two pentyls, has the lowest activation energy. On the other hand the rate of reaction (8) is proportional to the square of the pentyl concentration. This concentration may be low and therefore reaction (8) is probably not important.

Another reaction involving pentyl radicals should be taken into account here, i.e. the disproportionation of two pentyl radicals to form a pentane and a pentene:



Such reactions have been reported by Kraus and Calvert⁴⁷ for the t-butyl, iso-butyl, and sec-butyl radicals. These radicals were obtained from the photolysis of the corresponding di-butyl ketones. The ratios of

the rate constants for the disproportionation (k_{13}) and combination reaction (k_8) near 100°C are given in Table XI.

T A B L E X I

Rate Constants for the Disproportionation (k_{13})
and Combination Reaction (k_8) for the Butyl
Radicals near 100°C. (Kraus and Calvert)

Radical	k_{13} / k_8
t-C ₄ H ₉	4.5 ₉
iso-C ₄ H ₉	0.41 ₈
sec-C ₄ H ₉	2.2 ₇

Averages of the best published estimates cited by Kraus and Calvert of k_{13} / k_8 at 25°C for various other radicals are presented in Table XII.

T A B L E X I I

Rate Constants for the Disproportionation (k_{13})
and Combination Reaction (k_8) for Various
Radicals at 25°C.

Radical	k_{13} / k_8
C ₂ H ₅	0.12
n-C ₃ H ₇	0.13
iso-C ₃ H ₇	0.52
sec-C ₄ H ₉	0.61

These studies also showed that $E_{13} - E_8 \cong 0$

Kraus and Calvert's results indicate that with increasing complexity of the radical the disproportionation reaction becomes more important, and its influence on the present investigation must be considered.

Reaction (13) does not affect the material balances based either on the steady state concentration of the butenyl or on the total methyl supplied. In the former case

$$\text{methane} = \text{pentenes} - \text{pentanes}$$

As reaction (13) produces equal amounts of pentenes and pentanes its effect cancels. In the other case the following relationship

$$(\text{CH}_3)_{\text{total}} = \text{methane} + 2 \text{ ethane} + \text{pentenes} + \text{pentanes} + 2 \text{ hexane}$$

Again, reaction (13) does not impair the validity of this balance.

The amounts of pentanes and pentenes formed by the disproportionation reaction (13) should increase with the square of the pentyl steady state concentration. An increase of the pentene formation with increase of the partial pressure of butene-1 was not observed (Table X). It can be seen from fig. 22 that the amount of n-pentane formed does increase with increase of partial pressure of butene-1. However, an explanation for this was put forward on p. 109 without invoking reaction (13).

The interpretation of the product formation trends is complicated further by the possibility mentioned on p. 112 that reaction (9), p. 110, may remove pentyl radicals from the system.

It appears that in the present investigation there is no way to assess the extent of a pentyl radical disproportionation reaction.

Temperature Dependence of the Reaction

An attempt was made to evaluate the activation energy of methyl addition to the double bond of butene-1. It follows from the kinetic scheme proposed earlier (reaction 1 - 10) that

$$\frac{k_3 [\text{CH}_3] [\text{butene-1}]}{k_4 [\text{CH}_3] [\text{butene-1}]} = \frac{\text{CH}_4}{\text{pentanes} + \text{hexanes} + \text{recombination product of pentyls}}$$

'Recombination product of pentyls' refers to reactions (8), (9), and (11).

A measure of this pentyl recombination can be obtained from the material balance based on total methyl supplied:

$$(\text{CH}_3)_{\text{total}} = \text{acetone} = \text{methane} + 2 \times \text{ethane} + \text{pentenes} + \text{pentanes} + 2 \times \text{hexane}$$

as shown in Table IX.

An Arrhenius plot of $\log k_3/k_4$ vs. $1/T$ should yield a value for $E_4 - E_3$. E_4 is the energy of activation for the addition reaction. But E_3 , the activation energy for the abstraction of hydrogen by methyl from butene-1, is known to be 7.6 ± 0.4 kcal/mole from the photochemical work of Trotman-Dickenson and Steacie¹⁹.

Experimental values for the temperature dependence of the above product ratio are given in Table XIII.

An Arrhenius plot of the results in the last two lines of Table XIII is shown in fig. 23. The points are obviously irregular, and no attempt to connect them has been made. A series of experiments using a higher butene-1 pressure (289 mm Hg), gave equally inconsistent results.

T A B L E X I I I

Temperature Dependence of Product Distribution.

20 mm DTBP and 80 mm Butene-1.

Expressed as Percentage Methyl Supplied

Compound	Temperature °C.					
	220	212	203	197	188	181
methane	9.4	12.3	12.4	18.2	19.0	20.9
2 x ethane	81.6	54.3	51.6	46.1	40.4	37.4
3-me-butene-1	0.9	1.4	1.5	1.2	1.5	1.3
pentene-2	1.1	3.1	2.7	3.3	4.1	4.4
pentane	2.4	2.3	3.1	4.5	4.3	4.5
2 x hexane	5.4	12.5	9.9	13.0	14.9	14.7
Sum of above	100.8	85.9	81.2	86.3	84.2	83.2
Pentyl re- combination: (100 - above) -	0.8	14.1	18.8	13.7	15.8	16.8
pentane	2.4	2.3	3.1	4.5	4.3	4.5
hexane	2.7	6.3	5.0	6.5	7.5	7.4
Sum	4.3	9.7	26.9	24.7	27.6	28.7
CH ₄ /Sum	2.18	1.23	0.462	0.682	0.688	0.728
log CH ₄ /Sum	0.338	0.09	-0.436	-0.160	-0.156	-0.138
1/T°K	2.028	2.061	2.099	2.129	2.167	2.200

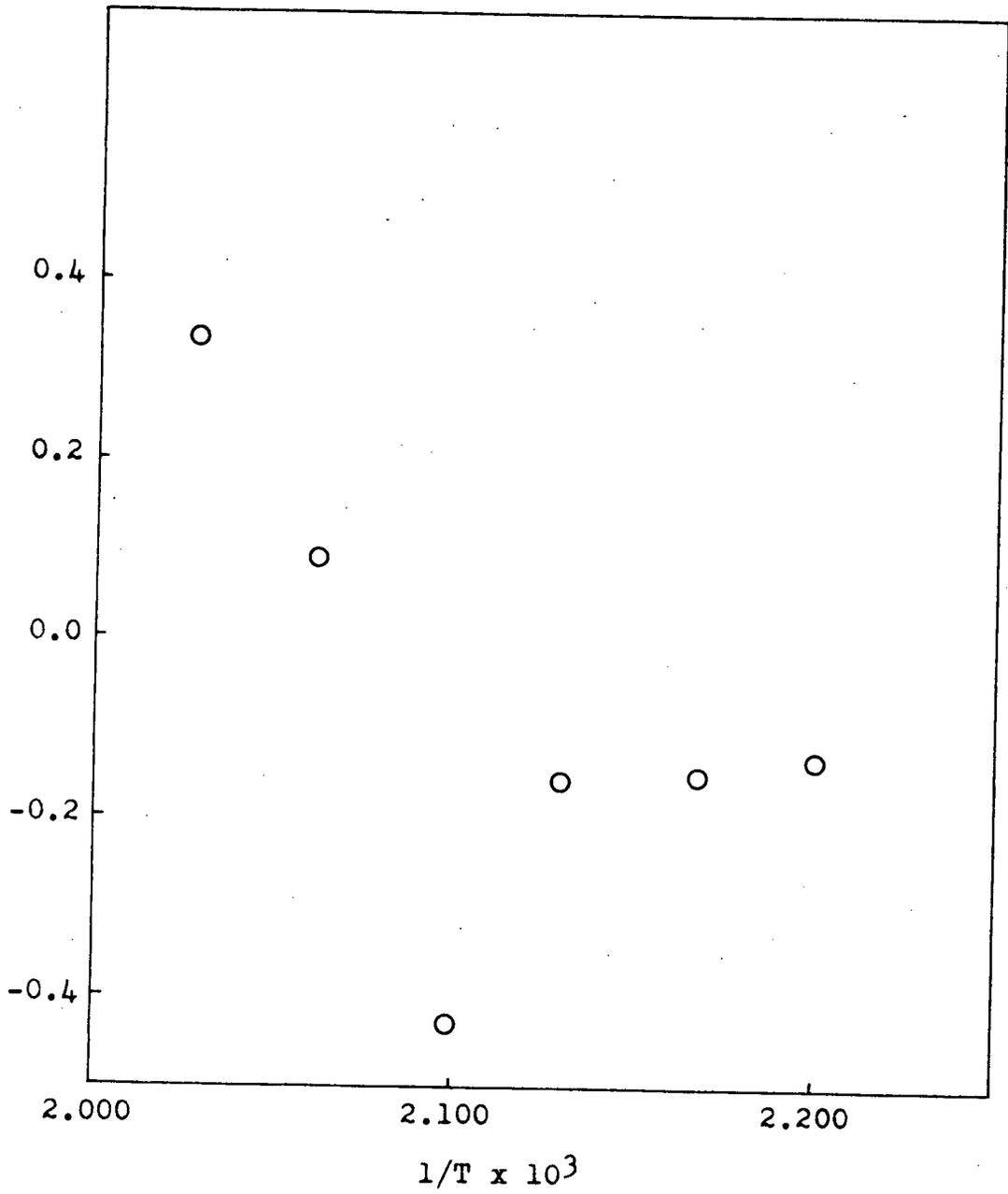


Fig. 23. Arrhenius plot of product distribution

In comparing the pressure effect on the 'pentyl recombination' (Table IX) with the results for temperature variation (Table XIII), it is surprising that, although a steady trend was observed in the pressure studies (fig. 21), the results for the temperature runs are so erratic. This inconsistency is believed to have two causes:

The temperature range for the reaction is limited at the upper end by the half-life of the peroxide. A few values for this half-life are given in Table XIV which was compiled by inserting the kinetic constants found by Raley and co-workers³³ for the first order decomposition of the peroxide into the expression

$$t_{1/2} = 0.693/k \text{ sec}$$

The value of $t_{1/2}$ for DTBP is given by

$$\frac{0.693}{3.2} \times 10^{16} \times \exp \frac{-39,100}{RT}$$

T A B L E X I V

Half-life of DTBP at Temperatures between 160 - 220°C

<u>T°C</u>	<u>t_{1/2} sec</u>
160	1,170
170	429
180	157
190	62
200	25
210	11
220	4.6

According to Table XIV the half-life of DTBP at 220°C is less than

5 sec. The danger then arises that during admission of the reactants to the reaction vessel a significant portion of the peroxide will decompose at an effectively lower temperature than that of the furnace. This effect may explain the very wide variance of the experimental points obtained for 220, 212, and 203°C.

The second effect to be considered is, that with a pyrolytic methyl source, as compared to a photolytic one, the rate of radical release is a function of the temperature, and changes moreover during the course of each experiment. To eliminate the latter uncertainty, one would have to operate under conditions of very small conversion of DTBP, so that the rate of methyl release would remain virtually constant within one experiment. However, this was not possible in the present system as the amount of product formed would have been too small for reliable analysis. As the reaction had been shown earlier to be sensitive to the methyl concentration the failure to obtain a linear Arrhenius plot can be attributed to this cause.

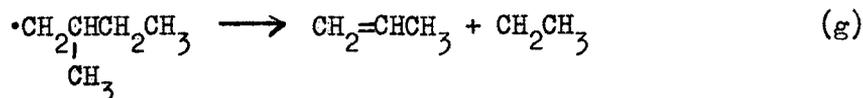
In spite of the negative result to obtain with a pyrolytic methyl source a value for the activation energy of methyl addition to the double bond of butene-1, the arguments for its evaluation were included. With a photolytic methyl source, and using the same kinetic scheme, a reliable value of the activation energy should be obtainable.

II THE REACTION OF METHYL RADICALS WITH BUTENE-1
AT TEMPERATURES OF 450 AND 492°C

The reactions of methyl with butene-1 at these higher temperatures were studied on an exploratory and semi-quantitative basis only, mainly with the intention of studying the isomerization reaction of butene-1 to butene-2. This reaction was observed by McNesby and Gordon¹³, but was not considered in any detail by Bryce and Kebarle¹².

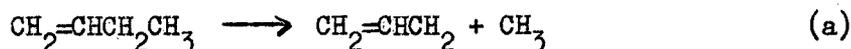
In these experiments the reaction mixture contained 5 - 20% mercury dimethyl at a total pressure of 200 mm Hg. The reaction times were varied from 1 - 15 min at temperatures of 450 and 492°C.

In agreement with Bryce and Kebarle¹² it was found that the light hydrocarbon products were: methane, ethane, ethylene, and propylene. Methane and ethane can be the products of hydrogen abstraction and recombination of methyl radicals at low temperatures. Ethane and propylene are formed at these higher temperatures by decomposition of a pentyl radical (see Introduction), i.e. by



Methyl recombination can also occur.

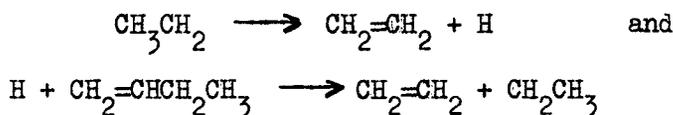
The possibility must be taken into account that propylene could also result from the primary split of butene-1, i.e.



Subsequent hydrogen abstraction by allyl radicals thus formed, would give propylene. However, the reaction of methyl radicals with butene-1 at 450°C yielded a substantial amount of propylene, and at this temperature

reaction (a) is negligible.

The mechanism proposed by Bryce and Kebarle¹² to account for the presence of ethylene is:



A chromatogram from a SP column run at 0°C giving the products is shown in fig. 24. The experiment was done with 50 mm Hg mercury dimethyl and 150 mm Hg butene-1 at 450°C. Only two products of greater molecular weight than butene-1 were observed, and were present in such small amounts that they do not show in fig. 24. These higher products were not identified. The retention volume of one, on the SP column, agreed exactly with that of pentene-2.

By far the most abundant product was butene-2. The amount of butene-2 formed appeared to confirm the idea expressed in the introduction, that this isomerization is a chain reaction.

This assumption was experimentally tested by the pyrolysis of butene-1 in the absence of a methyl source. The results from the chromatograms obtained with a SP column run at 0°C are presented in Table XV.

T A B L E X V

Distribution of the Pyrolysis Products; 200 mm Hg
Butene-1; 15 min at 450 and 492°C

	450°C	492°C
methane	1.2 ₅	3.4
ethane + ethylene	0.6	3.0
propylene	0.5	2.9
butene-2	15.8	7.9

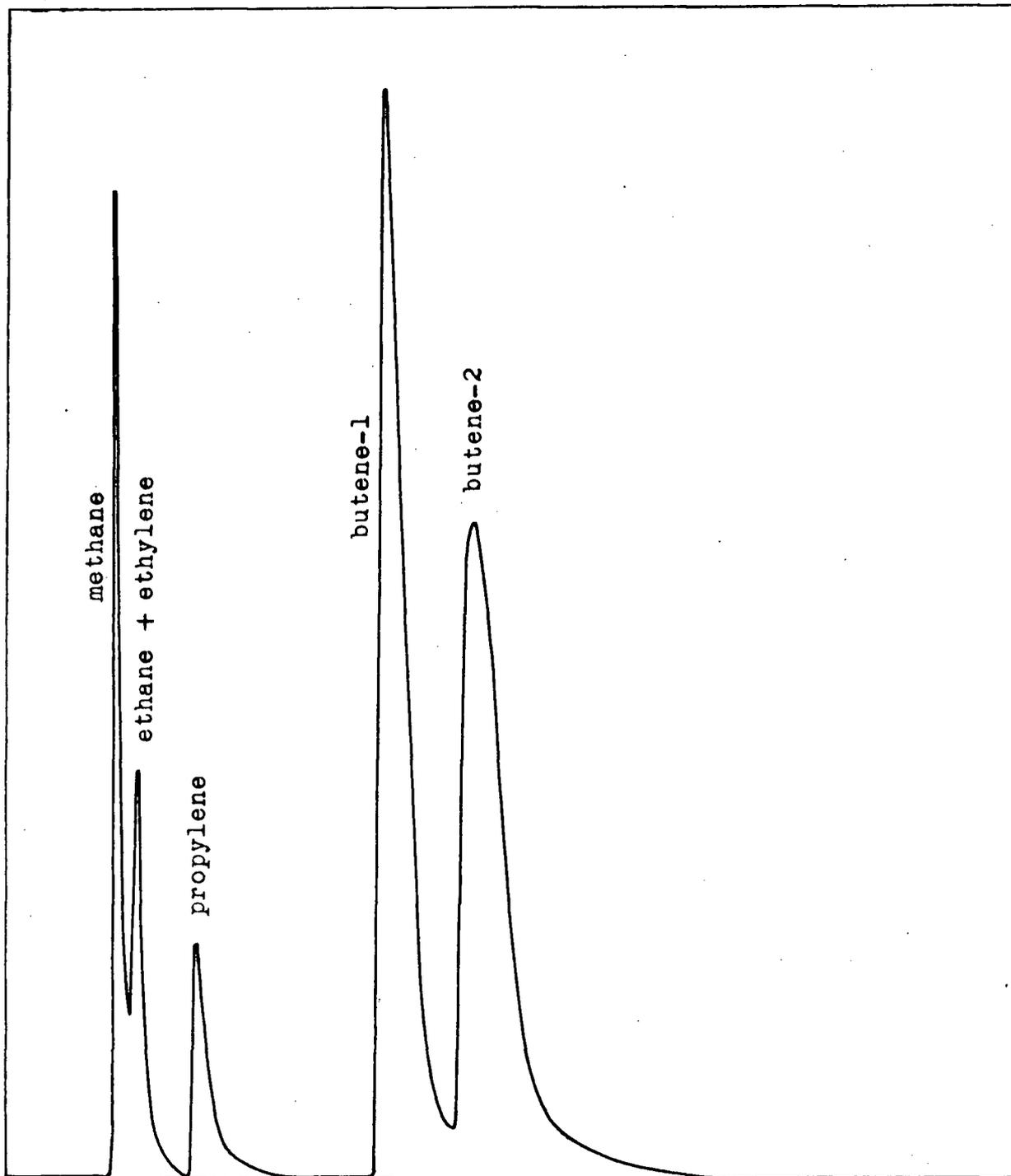
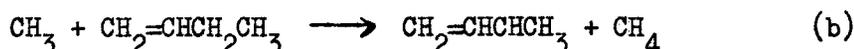
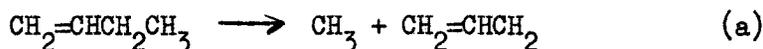


Fig. 24. Chromatogram showing the isomerization to butene-2 in the reaction of methyl with butene-1 at 450°C

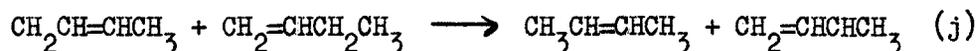
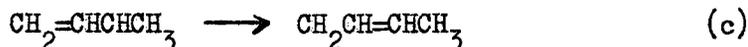
The results in Table XV show that the butene-2 formation is actually less at the higher temperature, but that the amount of light hydrocarbons is greater.

Methyl radicals resulting from the primary split of butene-1 could abstract hydrogen from the parent molecule:



Thus for the isomerization, reaction (b) is the chain initiation step.

The reaction proceeds then via the alternate form of the butenyl radical



Hence butenyl is the chain carrier. Termination of the chain would take place by reactions of butenyl other than hydrogen abstraction from butene-1. Such termination reactions would no doubt involve recombination of butenyl with other radicals, i.e. methyl and allyl radicals resulting from the primary split. Hence it is to be expected that chains will be longer at 450°C where the concentration of methyl and allyl is small but sufficient to initiate the chain, while at 492°C the chains will be shortened by the now more abundant methyl and allyl radicals through recombination with butenyl.

If the chain length is defined as the number of successful chain-propagation steps resulting from a single original chain carrier, then each methane formed in reaction (b) produces such an original chain carrier. Thus the ratio of butene-2 to methane at 450°C and at 492°C should be a measure of the chain length at these two temperatures. These ratios calculated from the results in Table XV were found to be:

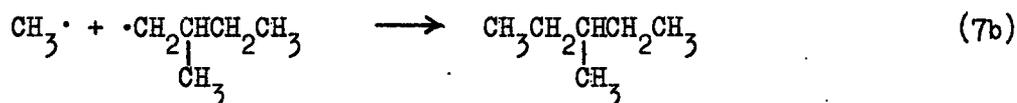
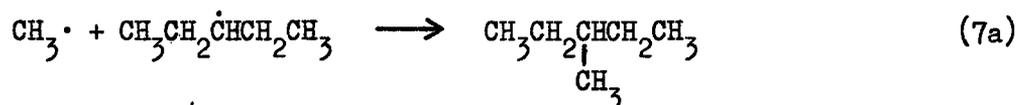
12.6 at 450°, and 2.3 at 492°C.

C O R R E L A T I O N W I T H P R E V I O U S
W O R K

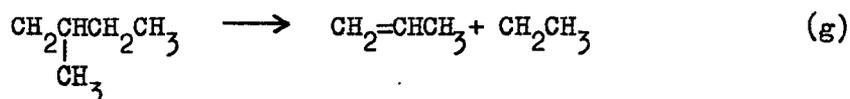
It was pointed out in the Evaluation of the Literature (p. 71) that a number of inconsistencies exist in the results reported by previous workers. The fate of the pentyl radicals was not considered fully and the origin of ethylene in the reaction mixture has not been explained by McNesby and Gordon. Rust and co-workers failed to detect 3-methyl-butene-1. Although McNesby and Gordon reported butene-2 as a major product, it was not considered to be important in the mechanism proposed by Bryce and Kebarle.

It has been shown in this study that the pentyl radicals $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{CH}_3$ and $\cdot\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, resulting from the terminal and non-terminal addition of methyl to the double bond of butene-1 by reaction (4a) and (4b) are both stable at 220°C. It appears that the products n-pentane and isopentane, resulting from hydrogen abstraction by these radicals have been missed by McNesby and Gordon¹³ as these authors used a squalane-pelletex column only for their gas chromatographic analysis. These columns will not separate n-pentane and pentene-2. Isopentane may have been overlooked as it is the end-product of the non-terminal addition of methyl to the double bond, and is produced in much smaller amounts.

It is reasonable to assume that the unidentified hexane reported by McNesby and Gordon¹³ (Table IV) is identical with our 3-methyl-pentane. The latter is the product of recombination of both pentyl radicals with methyl by reactions (7a) and (7b)



No hexane was found at 400°C, and it is therefore concluded that pentyl radicals are unstable at this temperature. This is in agreement with the fact that no propylene was present at 220°C, but 7.7% were found at 400°C probably formed by reaction (g)



The fact that no propylene was found may be considered as additional evidence that pentyl radicals are stable at 220°C.

Another difference between the present results and those of McNesby and Gordon¹³ is that these authors found as much as 1.7% ethylene at 220°C, while none at all was found at this temperature in the present investigation. The alumina column used in this work does separate ethylene completely from the other light hydrocarbons. McNesby and Gordon found more ethylene (1.7%) than pentene (0.4%), and almost as much as the hexane (2.5%). The peaks in the present chromatograms for the hexane and pentene-2 were several square centimeters. Hence it is certain that if ethylene was formed at all in the present investigation near 220° this could have amounted to trace quantities only, which were below the detection limit of the gas chromatograph. McNesby and Gordon¹³ do not put forward a mechanism to account for the presence of ethylene.

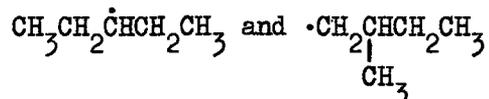
McNesby and Gordon used a medium pressure Hanovia mercury arc in their experiments. In these arcs the 2537 Å line is completely quenched. Hence the possibility is excluded that the formation of ethylene is a

consequence of energy transfer by excited mercury atoms to some species in the system.

The rate of methyl radical release is higher in the present investigation than in the experiments by McNesby and Gordon. This is reflected in the greater ethane/methane ratio observed by us (compare Table X, p. 109 and Table IV, p. 67). It is very unlikely that the less rapid release of methyl radicals should lead to the formation of ethylene.

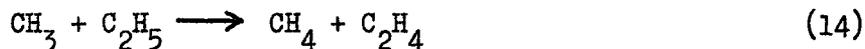
That butenyl radical should be the precursor of ethylene is hardly possible, considering that this radical is stable enough at 504°C to form large amounts of butene-2 (see Table IV, p. 67).

The direct formation of ethylene by the decomposition in some manner of the pentyl radicals

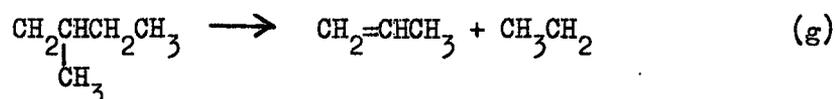


is also unlikely. This would involve the formation of an equivalent amount of propyl radical (1.7%). Only 0.3% of propane is reported by McNesby and Gordon. Some of the remaining propyl would undoubtedly combine with methyl to yield butane, a compound not observed in the products.

Another possibility would be a disproportionation reaction between methyl and ethyl, i.e.



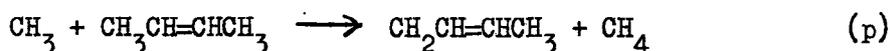
However, the only possible source of ethyls in the system is reaction (g)



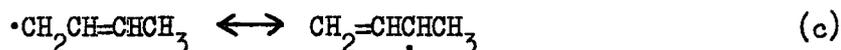
This involves the production of an equivalent amount of propylene, and according to Table IV no propylene was observed.

The present investigation remains irreconcilable with McNesby and Gordon's work with respect to the large amount of ethylene found by these authors at 220°.

It has been pointed out that Rust and co-workers²⁴ did not find 3-methyl-butene-1, although the radical formed in their reaction (p):



is one of the resonance forms of the butenyl radical:



The present investigation has shown that two products result from the reaction of methyl with butenyl each corresponding to one of the electronic structures given in (c). As shown in Table VI the ratio of pentene-2 to 3-methyl-butene-1 is about 10 : 1. The latter compound has apparently been missed by Rust and co-workers in their analysis by infrared absorption.

Bryce and Kebarle¹² did not identify butene-2 as a major product in the methyl sensitized reaction, nor in the straight pyrolysis of butene-1. This was probably because of the fact that at the time of their investigation columns⁴² for the separation of these isomers were not available.

SUMMARY OF PART II

SUMMARY OF PART II

The Reaction of Methyl Radicals and Butene-1 at
Temperatures near 200°C

All products except those due to higher radical recombination have been identified. A mechanism accounting for the formation of the products at these temperatures agrees with mechanisms postulated by other workers using similar substrates. This mechanism is supported by the pressure dependence of the reaction products.

Both pentyl and butenyl radicals have been found to be stable near 200°C. Pentyl radicals can stabilize themselves by hydrogen abstraction from butene-1 in addition to recombination. The butenyl radical does not abstract hydrogen in this low temperature range.

At 200 mm Hg of di-t-butyl peroxide, and with butene-1 pressures varying from 80 - 270 mm Hg, 7 to 30% of pentyl radicals react by radical recombination other than with methyl, while under the same conditions 60 to 80% of the butenyl radicals do so.

The reactivity of $\cdot\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{CH}_3$ in hydrogen abstraction from butene-1 is twice as great as $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{CH}_3$, presumably because of steric effects.

The Arrhenius energy of activation for the reaction of the butenyl radical with methyl to form 3-methyl-butene-1 is from 2 to 4 kcal greater

than the energy for the reaction forming pentene-2.*

The Reaction between Methyl Radicals and Butene-1
at 450° and 492°C

The product distribution for the light hydrocarbons supports the result of earlier work.

Methyl radicals do not sensitize the formation of cyclic compounds below 500°C.

The isomerization to butene-2 is a chain reaction, with the chain length increasing as the temperature is reduced. The chain length leading to butene-2 formation is

12.6 at 450°, and 2.3 at 492°C.

* It may appear as an inconsistency to accept this value of 2 - 4 kcal obtained from the temperature dependence of the pentene ratio, since it was argued earlier that a value for the energy of activation of methyl addition to the double bond cannot be obtained from a similar temperature dependence with a pyrolytic methyl source. However, in the former case the reaction of methyl with one species only is involved, i.e. the butenyl hybrid, and a change in the methyl concentration would cancel in its effect on the ratio of the pentenes. In fact this argument can be turned around to say that, as a satisfactory Arrhenius plot was obtained, this supports the assumption that the energy term, and not steric factors, determines the pentene ratio.

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APPENDIX

A P P E N D I X

QUALITATIVE INVESTIGATION OF COMPOUNDS OF HIGHER
MOLECULAR WEIGHT THAN BUTENE-1 BY MASS SPECTROMETRY

The mass spectrum of a given compound varies from instrument to instrument. The variations are generally small, amounting to a few per cent of the relative ion intensity for a given mass number. Thus in the majority of cases satisfactory identification of a pure compound can be achieved by a simple comparison of its experimentally-obtained spectrum with the published spectra of isomeric compounds.

The peaks following butene-1 in the chromatogram shown in fig. 17, p.91, were trapped, and their mass spectra, obtained with a 60° Nier-type instrument, were compared with the mass spectra listed in the Catalogue of Mass Spectral Data published by the American Petroleum Institute.

A comparison of the mass spectrum of the peak labelled '3-methyl-butene' in fig. 17, and the published data is given in Table XVI.

T A B L E X V I

Comparison of Mass Spectra of 3-Methyl-Butene-1
(70 e.v.)

Mass	Measured	Published
72	1.48	0.03
71	2.04	1.47
70	26.2	26.2
69	2.4	2.46
68	0.18	0.12
57	12.1	0.08
56	29.0	4.50
55	99.2	100
54	4.8	2.70
53	11.3	8.10
52	1.9	1.09
51	5.6	3.25
50	5.0	2.64
49	1.3	0.53
44	6.3	0.10
43	19.3	3.44
42	36.8	26.8
41	94.0	20.8
40	8.2	3.59
39	43.5	25.6
37	2.2	2.86

The main discrepancies between the measured and the published spectrum occur at mass 57, 56, 43, 42, 41, 40, and 39. It can be seen from the chromatogram, fig. 17, p. 91, that the 3-methyl-butene-1 peak is situated on the 'shoulder' of the large butene-1 peak. Also, isopentane follows 3-methyl-butene-1 closely, although the amount of isopentane formed was usually small, and for instance insufficient to cause a noticeable peak in the chromatogram in fig. 17. It must therefore be expected that the sample of 3-methyl-butene-1 was contaminated with butene-1 and possibly also with some isopentane. The relative ion intensities for butene-1 and isopentane are reproduced from published data in Table XVII for

those peaks where discrepancies occurred in Table XVI.

T A B L E X V I I

Ion Intensities for Butene-1 and Isopentane from
Published Data (70 e.v.)

Mass	Butene-1	Isopentane
57	1.63	54.0
56	37.0	16.8
43	0.10	100
42	3.47	86.0
41	100	67.3
40	6.41	3.38
39	34.5	21.5

Table XVII shows that the combined contribution of butene-1 and isopentane is large for all masses where the ion intensities in Table XVI do not agree. Scanning with low electron energy showed the parent peak at mass 70. It was concluded that the compound in question was 3-methyl-butene-1. This conclusion agreed also with the gas chromatographic re-inforcement test.

Scanning with low electron energy of the peak labelled 'n-pentane + pentene-2' in the chromatogram in fig. 17, p. 91, gave parent peaks at mass 72 and mass 70. The measured ion intensities for this peak with 50 volt electrons are given in Table XVIII together with the published values for n-pentane and trans-pentene-2.*

* The mass spectra of trans- and cis-pentene-2 are virtually identical.

T A B L E X V I I I

Comparison of Mass Spectrum of 'n-pentane + pentene-2'
with Published Values for Normal Pentane and Pentene-2
(50 e.v.)

Mass	'n-pentane + pentene-2'	n-pentane	pentene-2
72	12	8.84	0.05
71	8	0.5	1.87
70	142	0.11	34.7
69	9	0.06	2.44
68	2	0.03	0.33
67	8	0.08	1.93
57	17	12.7	0.08
56	28	2.2	4.39
55	355	2.94	100
54	11	0.22	2.89
53	29	0.91	7.65
52	3	0.18	1.08
51	9	0.55	2.92
50	6	0.34	1.91
44	13	3.35	0.05
43	128	100	2.05
42	234	59	43.8
41	171	41.2	30.8
40	35	2.46	5.82
39	117	13.8	32.6
38	10	1.08	3.63

As the contribution of pentene-2 to mass 72 would be practically zero, the column for n-pentane in Table XVIII was multiplied by a factor 12/8.84. The resultant values were deducted from the figures in the 'n-pentane + pentene-2' column. These results were then multiplied by a factor such that the relative ion intensity for mass 55 equalled 100. The comparison of this final result with published data for pentene-2 is given in Table XIX.

T A B L E X I I X

Measured and Published Mass Spectra for Pentene-2
(50 e.v.)

Mass	Measured	Published
72	0	0.05
71	2.0	1.87
70	39.1	34.7
69	2.5	2.44
68	0.6	0.33
67	2.2	1.93
57	0.05	0.08
56	7.2	4.39
55	100.0	100.0
54	3.0	2.89
53	8.0	7.65
52	0.8	1.08
51	2.4	2.92
50	1.6	1.91
44	2.4	0.05
43	0.1	2.05
42	46.8	43.8
41	34.8	30.8
40	9.4	5.82
39	29.3	32.6
38	2.4	3.63

The agreement between the spectra is satisfactory. The possibility has been taken into account that the substance present could have been pentene-1. However, pentene-1 has a peak of 100 at mass 42, and a peak of 57.7 at mass 55. Also the possibility that the pentane was isopentane and not n-pentane was excluded on the basis of the gas chromatographic retention volumes. The mass spectra of these two isomers are closely similar. The above example demonstrates the power of a combined mass spectrometric and gas chromatographic analysis.

The measured ion intensities for the peak labelled '3-methyl-pentane' in fig. 17, p. 91, are compared with published values in Table XX.

T A B L E X X

Comparison of the Mass Spectra of 3-Methyl-Butene-1
(70 e.v.)

Mass	Measured	Published
87	0.3	0.19
86	5.0	3.03
85	0.8	0.64
84	0.2	0.03
73	0.1	0.02
72	0.3	0.28
71	6.2	5.39
70	2.5	1.47
69	1.1	0.56
68	0.04	0.04
67	0.5	0.23
65	0.2	0.18
59	0.1	0.06
58	4.7	4.26
57	100	100
56	82.3	75.7
55	8.6	7.86
54	1.0	0.76
53	2.3	2.59
52	0.4	0.52
51	1.1	1.57
50	0.8	1.07
44	2.0	1.23
43	24.7	28.4
42	4.9	5.53
41	34.9	63.5
40	2.0	2.46
39	12.3	18.1
38	0.8	1.41

A parent peak was obtained for mass 86. The mass spectra of all other hexanes are sufficiently different to identify the compound as 3-methyl-pentane.

Ionization Gauge Detector for Gas Chromatography

THE development of high-sensitivity detectors for the chromatographic analysis of gaseous mixtures is of importance in the determination of substances present in very small amounts. A sensitive ionization gauge detector has been developed in this laboratory which makes use of the fact that the ionization potential of the helium carrier gas (24.5 volts) is very much greater than that of most other volatile substances. The ionization potentials for hydrocarbons, for example, range from 8 to 14-volts.

The gauge and adjustable metal leak associated with it are shown in Fig. 1. A very small fraction of the gas stream from the chromatographic column passes through the leak into an R.C.A. 1949 ionization gauge with the glass envelope modified so that the gas flows between the gauge components. The potential difference between the filament and the grid is adjusted to approximately 18 volts, a value not sufficient to produce ions when helium only is flowing through the gauge and consequently there is no plate current. When a substance of lower ionization potential is carried into the gauge, ions are formed. The ion current from the plate is amplified in the usual manner and recorded on a Leeds and Northrup 'Speedomax' recorder.

Typical operating conditions for the gauge are: pressure in the envelope, 0.2 mm. mercury; filament emission 5 m.amp.; grid potential + 18 volts; plate potential - 27 volts.

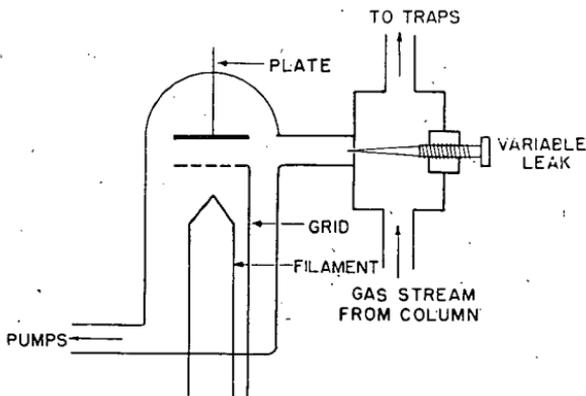


Fig. 1. Schematic diagram of gauge and leak

The sensitivity obtained so far is at least 200 times that given by a thermistor-type thermal conductivity cell, and compares favourably with the value reported recently by Harley and Pretorius¹. This sensitivity has been achieved by using only a very small fraction (less than 0.5 per cent) of the gas stream emerging from the column, thus leaving almost all the effluent stream unchanged and available for subsequent trapping and identification if this is desired. A significant feature of the gauge is that its performance is insensitive to ambient temperature changes and also to changes in pressures and flow-rate in the main gas stream. This latter factor is of great importance in analyses done with rising column temperature during which marked reductions in flow-rate occur.

It may be possible to increase the sensitivity of the gauge by incorporating screen and suppressor grids. A further increase should be obtained by replacing the tungsten filament with an iridium filament to increase the stability of the emission.

A detailed report will be published later. We are grateful to Messrs. D. C. Frost and E. W. C. Clarke for advice and assistance.

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Jan. 2.

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AN IONIZATION GAUGE DETECTOR FOR GAS CHROMATOGRAPHY¹

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ABSTRACT

An ionization gauge has been modified to serve as a detector for gas chromatography. A small fraction of the effluent gas from the column is diverted into the gauge through an adjustable leak. The gauge is operated under conditions such that ionization of the eluted compound only occurs, and not of the helium carrier. The ion current is amplified and displayed on a pen recorder. The gauge combines very high sensitivity and rapid response with almost complete independence of changes in flow rate, pressure, or temperature.

INTRODUCTION

Thermal conductivity cells with either hot wire or thermistor sensing elements are used extensively as detectors in gas chromatography. They afford a good compromise in meeting most of the following requirements (4): adequate sensitivity (i.e. large signal to noise ratio), rapid response, applicability to a wide range of compounds with approximately constant sensitivity, linear response with concentration, and insensitivity to flow-rate changes. A further requirement in some analytical procedures is that the separated material should not be destroyed or altered by the detection device. This requirement is met by the gas density balance (5), but not by thermal conductivity cells unless they are operated at low sensing element temperatures, or unless only part of the effluent gas from the column passes through the cell (2), a condition which reduces cell sensitivity.

For analyses such as the determination of trace compounds in gaseous systems, high sensitivity is undoubtedly the most important single requirement. The "sensitivity" of a detector is not always clearly defined in the literature. Dimbat, Porter, and Stross (1) have proposed a "sensitivity parameter" which takes into account recorder sensitivity, chart speed, and carrier gas flow rate, according to the following relationship:

$$S = AC_1C_2C_3 \text{ (ml. mv.)}/w \text{ (mg.)};$$

S = sensitivity parameter,

A = peak area, cm.^2 ,

C_1 = recorder sensitivity, mv. per cm. of chart,

C_2 = reciprocal chart speed, minutes per cm.,

C_3 = flow rate at exit of column, ml. per minute, corrected to column temperature and atmospheric pressure,

w = weight of sample introduced at head of column, mg.

These authors suggest that the noise level (in millivolts) should be given along with the reported sensitivity in describing the performance of a detector. In this connection a distinction should be made between "high frequency" noise (i.e. more than 2 cycles per second) due to vibration of the sensing elements, etc., and base line drift. The latter may be thought of as noise of a very low frequency. Noise of a frequency greater than about 2 cycles per second can usually be eliminated by increasing the time constant of the amplifier circuit without any significant effect on response to the bridge signal.

In the authors' experience the factor limiting the sensitivity of thermal conductivity cells is not the noise level, but the drift of the base line caused at high sensitivities by minute temperature changes in the thermostatted cell and by changes in flow rate. Large-scale drifting, consistently to one side of the base line, may be encountered during

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Contribution from the Department of Chemistry, University of British Columbia, Vancouver, British Columbia.

experiments with rising column temperature when the flow rate changes markedly, or if the pressure differential in the compensating and detecting arms of the cell is altered. The ultimate sensitivity of thermal conductivity cells may depend upon the degree of matching of the filaments or thermistors with regard to electrical properties and geometrical positioning in the channels. In the gas density balance (5) the difficulty in precise matching of detecting and reference columns would be a limiting factor for the sensitivity, especially in experiments with rising column temperature.

The sensitivity of the detectors referred to above appears to be limited by the fact that they measure the change in a physical property of the gas stream caused by the addition of a minute amount of the eluted material. It seemed desirable, therefore, to develop a detector which would be sensitive to the eluted compound only, and would be independent of the relative amount of carrier gas. Differences in ionization potentials were utilized for this purpose. The ionization potential of helium is much greater than that for all other volatile compounds (Table I). The highest ionization potential among the hydrocarbons is that of methane (14.5 volts).

TABLE I
IONIZATION POTENTIALS FOR VARIOUS VOLATILE SUBSTANCES (3)

Substance	Ionization potential (volts)
He	24.5
Ne	21.5
O ₂	12.5
N ₂	15.5
CO ₂	14.4
CH ₄	14.5
CS ₂	10.4
C ₆ H ₆	9.6
C ₆ H ₅ CH ₃	8.5
CH ₂ O	11.3
CH ₃ Br	10.0

EXPERIMENTAL

An ionization gauge (RCA 1949) has been modified to serve as a means of utilizing the relatively low ionization potentials of other compounds in detecting them in a stream of helium (6). The apparatus is shown in Fig. 1. A very small fraction of the gas stream from a standard chromatographic column, is diverted through an adjustable leak into the ionization gauge. The potential difference between the filament and grid of the gauge

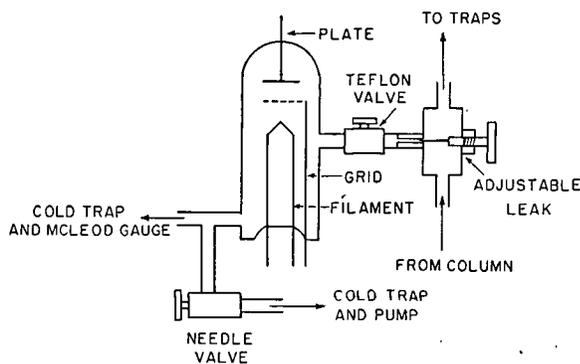


FIG. 1. Schematic diagram showing ionization gauge and adjustable leak.

energy electrons is reduced. The maximum grid potential, and hence the sensitivity, depends also on the purity of the helium. Impurities such as oxygen, nitrogen, and hydrocarbons increase the background ionization in the gauge. The helium was purified before entering the chromatographic system by passing it through a charcoal trap cooled in dry ice - acetone.

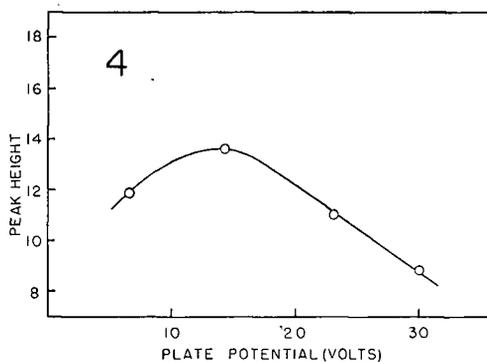
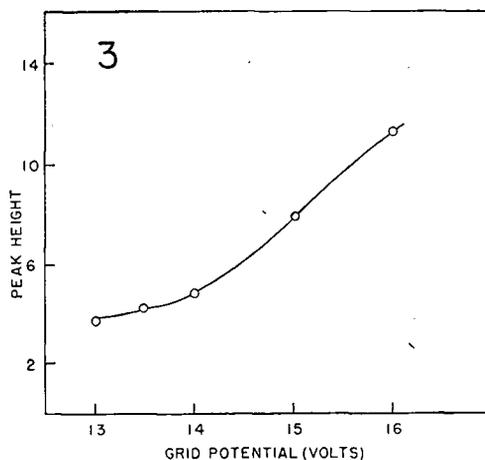


FIG. 3. Variation of peak height with grid potential.
FIG. 4. Variation of peak height with plate potential.

The variation of sensitivity with plate potential is shown in Fig. 4. The observed maximum is presumably due to emission of secondary electrons, penetration of the field into the filament-grid space, and space charge effects.

The sensitivity of the gauge was calculated in terms of the sensitivity parameter (1) on the basis of the following experimental conditions: gauge pressure, 0.7 mm. mercury; filament current, 2.7 ma.; grid potential, +15 volts; collector potential, -15 volts. S for the ionization gauge was found to be 32,500. Values of 312 for a thermistor thermal conductivity cell and 60 for a platinum filament cell operated at low filament temperature have been reported (1, 7). The noise level on the base line was imperceptible under the above operating conditions. The fraction of the effluent gas stream from the column can be reduced to 0.5% without loss of sensitivity or effect on base line stability. The

limit of detection for a typical hydrocarbon was approximately 5×10^{-11} moles (3 mm.² peak area).

DISCUSSION

It is anticipated that a further increase in sensitivity may be achieved by operating at higher gauge pressure and by replacing the tungsten filament with an iridium filament, thus minimizing the change in work function that occurs when oxygen and hydrocarbons come in contact with the filament. An additional increase may result from further purification of the helium with consequent increase in base line stability.

The speed of response of the gauge depends chiefly on the velocity with which the eluted compound passes between the electrodes. The cross-sectional area of the gauge as presently constituted is very much greater than that of the main gas stream, but because of the reduction in pressure that occurs on passing through the leak, the flow rate through the gauge is more than 10 times the rate in the main gas stream. Thus only a very small fraction of the effluent gas stream need be used for detection, even though the dead volume of the gauge is large. The volume could be reduced markedly by altering the shape of the envelope and the arrangement of the gauge components.

The gauge is completely insensitive to temperature changes and thus it can be located close to the exit end of the column. This is not desirable with thermal conductivity cells used in experiments with rising column temperature, as the gases must enter the cell at the same temperature as the cell.

At the present stage of development, the ionization gauge detector is useful where it is desired to combine very high sensitivity and rapid response with almost complete independence of changes in flow rate, pressure, or temperature. Its use also eliminates the possibility of pyrolysis of the eluted compounds in the detector after elution from the column. The extent to which sensitivity is related linearly to sample size and is independent of the effect of surface reactions on the filament has not been fully established. It is anticipated that an iridium filament will substantially reduce this latter effect.

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Thermal Conductivity Cell for Gas Chromatography

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DEVICES used for detecting eluted substances in the carrier gas stream in gas chromatography (3, 5, 8) usually measure the change in some physical property of the gas stream caused by the presence of the eluate in the carrier gas. Properties of use in this connection include thermal conductivity, density, viscosity, infrared absorption, and heat of adsorption. Measurement of change in thermal conductivity has proved to be a reliable and sensitive method, involving standard electrical equipment which will operate with great stability over long periods of time.

Various types of thermal conductivity cells have been used in gas chromatography (1-9). Several models are available commercially. The cell described in the present report is inexpensive to construct and has performed satisfactorily for 18 months for both partition-elution and adsorption-elution chromatography.

The construction details of the cell are shown in Figure 1. The body is a brass block through which channels containing the detecting and reference filaments are drilled. Excellent temperature compensation was achieved with the metal cell. The use of brass as the cell material did not interfere with the determination of even such chemically active compounds as hydrogen sulfide and mercaptans (9).

The filaments are mounted on brass plugs which are sealed to the body of the cell with rubber O-rings. Gaskets with greater heat resistance can be used at elevated temperatures. The filaments are helices of 0.3-cm. diameter containing 14 cm. of 0.005-cm. platinum wire. They are silver-soldered to the ends of Kovar terminals through which the external electrical connections are made. The operating temperature of the filaments was approximately 100° C. at a current of 200 ma. This temperature is sufficiently low to eliminate pyrolysis of thermolabile compounds on the filament. The entire stream from the column can, therefore, pass through the detecting channel without the use of a bypass system (4) if collection of the separated sample components is desired.

The reference and detecting channels are symmetrical with both filaments located in the center of the gas stream. In certain commercial models the compensating filament is situated in a

diffusion cavity, an arrangement which offers practically no flow-rate compensation (?). This latter factor is of great importance in operations in which a rising column temperature is used. In experiments described elsewhere (9) with the present cell a flow-rate change from 50 to 30 ml. per minute over 20 minutes had no effect on the base-line setting of the recorder. The minimal amount of material detectable with the cell was approximately 10^{-8} mole. The noise level was insignificant at maximum sensitivity.

Compensations for changes in ambient temperature are sufficient to eliminate the need for thermostating the cell, unless a high degree of reproducibility is desired over an extended period of time.

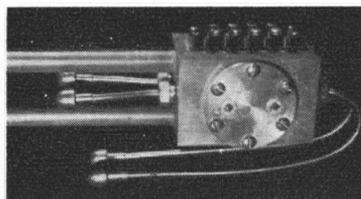


Figure 2. Exterior view of cell

The external features of the cell are shown in Figure 2. Connection with the column and sample inlet system is made with metal-glass ball-and-socket

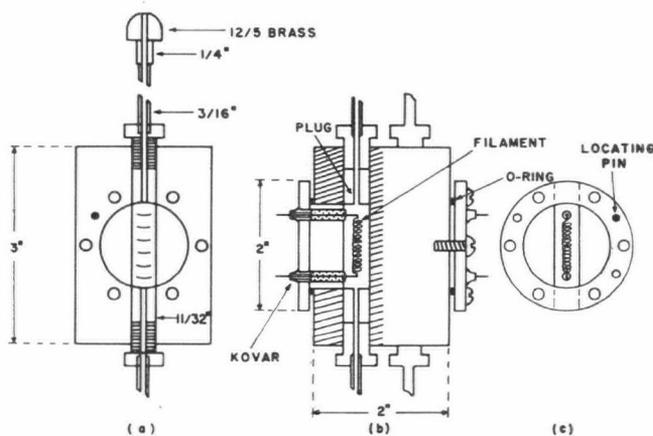


Figure 1. Thermal conductivity cell

- Frontal section
- Side section showing detail of one channel only
- Detail of filament support

joints. Bakelite rods are tapped into the block for mounting purposes. Electrical connections are made through a terminal block.

ACKNOWLEDGMENT

The authors are grateful to Frank Sawford for assistance in the construction of the cell.

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Analysis of Volatile Organic Sulfur Compounds by Gas Partition Chromatography

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► A method is described for the analysis by gas partition chromatography of a sample containing hydrogen sulfide, methyl, ethyl, and propyl mercaptans, dimethyl and diethyl sulfides, dimethyl disulfide, and thiophene. The sulfur compounds have also been separated from light hydrocarbons and from methanol and ethanol. Benzene and thiophene were also separated. A method is outlined for determining the sensitivities of the

instrument to vapor samples containing air. The relationship among retention volume, polarity of the column liquid, and polarizability of the gases being analyzed is discussed.

ANALYTICAL METHODS for the quantitative determination of hydrogen sulfide, mercaptans, and alkyl sulfides and disulfides in the presence of each other are of considerable importance in

industrial laboratories and in fundamental investigations. Because of similarities in chemical behavior of these compounds, chemical procedures (1-6) are usually difficult and the results may be unreliable. The success achieved by gas chromatography as an analytical tool has suggested the application of this technique, based on physical rather than chemical differences, to the analysis of sulfur compounds. Hydrocarbons virtually identical in their properties

have been separated by this means, and it was felt that separation of sulfur compounds, which differ greatly in volatility, should be possible.

The system chosen for investigation was one that had been encountered in work on the pyrolysis of dimethyl disulfide (5). It contained hydrogen sulfide, methyl, ethyl, and propyl mercaptans, dimethyl and diethyl sulfides, dimethyl disulfide, and thiophene.

EXPERIMENTAL

The hydrogen sulfide was prepared in the laboratory. The other compounds were standard grade, obtained from Eastman Kodak Co., Rochester, N. Y.

The choice of a suitable chromatographic system was governed by experience gained in this laboratory in hydrocarbon analysis (11) and by the nature of the compounds studied. Adsorption methods using activated alumina or silica gel columns were avoided, as the acidic nature of some of the sulfur compounds might lead to irreversible adsorptions. A preliminary investigation showed that suitable separations could be accomplished by using a partition-elution column with tricresyl phosphate as the liquid phase on a Celite column.

The apparatus is illustrated in Figure 1.

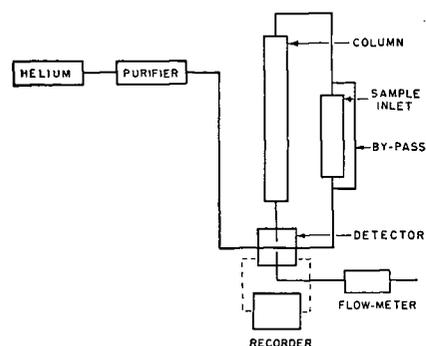


Figure 1. Schematic outline of chromatography apparatus

Helium was used as the carrier gas because of its low viscosity and the large difference between its thermal conductivity and those of the compounds being analyzed. The sample inlet system was designed for admission of vapor samples by the convenient syringe and serum-cap technique. The less volatile components of the mixture were admitted at partial pressures not exceeding their vapor pressures at room temperature, to avoid condensation in the apparatus. Air was also present in the vapor samples of these compounds. The column was a 4-foot borosilicate glass U-tube of 5-mm. internal diameter, mounted in a heating jacket by means of which the column temperature could be increased rapidly. The column was filled with a mixture of tricresyl phosphate (Eastman Kodak technical grade)

and Celite 545 (Johns Manville) in the proportions 30 to 70 by weight, according to the method described by James and Martin (9).

The thermal conductivity cell (14) contained detecting and compensating filaments, mounted in channels drilled in a brass block. The cell gave excellent temperature compensation and much better flow-rate compensation than some commercially available cells in which the compensating filament is not placed in the gas stream but sits in a diffusion cavity. The fact that the cell was made from brass did not in any way affect the determination. Its sensitivity remained unaltered during the investigation and no reaction with the sulfur compounds was observed.

The two filaments of the cell were mounted in the usual manner in opposing arms of a bridge circuit and carried a current of approximately 200 ma. Any imbalance in the bridge circuit caused by the appearance of a substance other than the carrier gas in the detecting channel of the cell was displayed on a Leeds & Northrup Speedomax recorder of adjustable sensitivity (1 to 20 mv. full scale).

The time required for elution of a group of compounds differing greatly in boiling points can be reduced sharply by gradual increase of column temperature during the analysis. This procedure has been used successfully by other workers (7). Lower boiling components of a mixture, which move through the column with relatively high velocities, can be resolved at or near room temperature. The rate at which the higher boiling compounds pass through the columns is greatly increased at elevated temperatures (8). An exactly reproducible heating rate was used in all analyses.

Owing to the increase in gas viscosity with rising temperature, the flow rate through the columns decreases markedly. In order to maintain the carrier gas flow at the initial rate, the pressure differential should be increased with the temperature. However, such an increase would affect only the compensating filament in the conductivity cell, causing it to operate like a Pirani gage, with resulting deviations in the base line of the recorder. Hence, it is necessary to keep the pressure differential constant and accept the considerable change in flow rate. For example, at a pressure differential of 3 pounds per square inch, the flow rate changed from 50 ml. per minute at 19° C. to 33.5 ml. per minute at 112° C. The reproducibility of these figures suggests that the change in flow rate is a better measure of the true column temperature than that indicated by a thermometer placed inside the heated column jacket.

RESULTS AND DISCUSSION

A chromatogram, showing the separa-

tion of the components of a mixture containing hydrogen sulfide, methyl mercaptan (methanethiol), ethyl mercaptan (ethanethiol), methyl sulfide, propyl mercaptan (propanethiol), ethyl sulfide, thiophene, and dimethyl disulfide, is presented in Figure 2. *n*-Pentane and isopentane were added to the mixture to relate the relative retention volumes of hydrocarbons to those of the sulfur compounds. The compounds were identified by their retention volumes and by reinforcing the peaks with the pure substances.

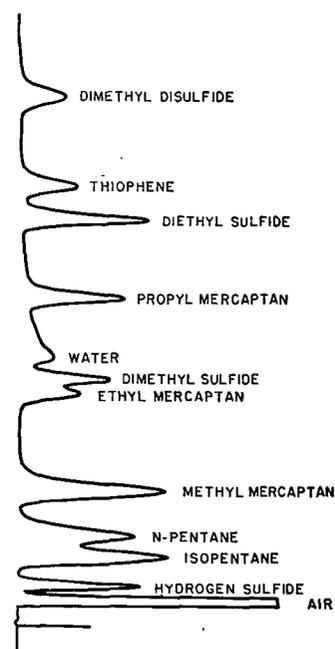


Figure 2. Separation of volatile sulfur compounds plus pentanes with tricresyl phosphate column

Satisfactory separation of the hydrogen sulfide from the air present in the syringe and of the pentanes and methyl mercaptan was obtained with a reasonable elution rate at room temperature. After methyl mercaptan appeared, the temperature of the column was raised to speed up elution of the remaining compounds. Lower temperatures result in sharper separations but greatly increase the retention volumes for substances of relatively low volatility (7, 10, 16). Ethyl mercaptan and dimethyl sulfide were separated at approximately 70° C. and the column temperature was allowed to rise to approximately 120° C. to accelerate the elution of dimethyl disulfide.

Water vapor, introduced with the sample, appeared as a peak between dimethyl sulfide and propyl mercaptan. It could be eliminated by placing a drying agent like sodium sulfate between the inlet point and the column. The air peak could also be eliminated by using

sample collecting and admission systems in which air is excluded. In the syringe technique, the sharp peaks due to the pressure differential during the insertion of the sample served as a convenient reference point from which to determine retention volumes.

Figure 3 further demonstrates the separation of a hydrocarbon and a related sulfur compound and the effect of column temperature on the separation. Thiophene and benzene could not be completely resolved at 115° C. but were satisfactorily separated at 77° C.

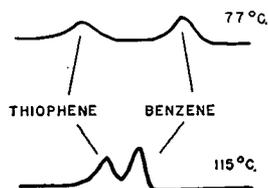


Figure 3. Effect of temperature on separation of thiophene and benzene with tricresyl phosphate column

To show the separation of mercaptans and the corresponding alcohols, a mixture containing methanol, ethanol, and methyl and ethyl mercaptans was passed through the column, while the column temperature was increased gradually to approximately 100° C. The resulting chromatogram is shown in Figure 4. *n*-Pentane was again added to show the relative position of the hydrocarbons.

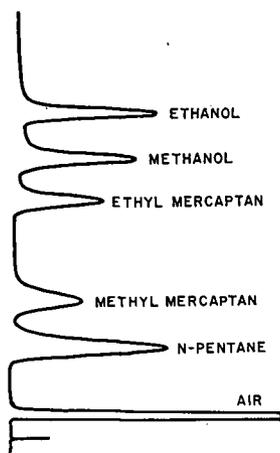


Figure 4. Elution order for mercaptans, alcohols, and hydrocarbon with tricresyl column

In quantitative analysis by gas chromatography, peak areas are customarily used as a measure of the amount of substance placed on the column (13). Measurements of this type depend on experimental parameters such as carrier

gas flow rate, sensitivity of the thermal conductivity cell to the compound at a particular cell temperature, and recorder sensitivity and chart speed. However, the method is capable of a high degree of accuracy if experimental conditions are standardized carefully. In the present study the peak areas were directly proportional to the amounts of the substances placed on the column.

In dealing with compounds like alkyl sulfides and mercaptans, it is difficult to admit micromole quantities of the pure substances into the apparatus to determine sensitivities, an operation that should be repeated with each analysis. A method was devised which permits rapid determination of the sensitivity of the apparatus to a particular compound by means of a calibration involving a mixture of the compound and air. The method is illustrated with ethyl mercaptan (boiling point 34.7° C.) and is applicable to all volatile substances having a reasonably high vapor pressure.

A few drops of the mercaptan are placed in a polyethylene bag fitted with a serum cap. A volume, V_1 , of the air-mercaptan vapor mixture is withdrawn with a syringe and injected into the apparatus. Peak areas, A_1 for the mercaptan and A_2 for air, are measured. In a second experiment, the same amount of air-mercaptan vapor is withdrawn from the bag and an additional volume, V_2 , of air is then drawn into the syringe. Injected into the apparatus, this yields the same peak area for the mercaptan—i.e., A_1 —and a larger peak, A_3 , for air. Assuming that the ideal gas laws are applicable, the unknown volume of mercaptan V_x in V_1 is

$$V_x = V_1 - \left(\frac{A_2}{A_3 - A_2} \right) V_2$$

With a column temperature of 78° C. and a helium flow rate of 50 ml. per minute, the elution time for the mercaptan was 2.5 minutes. It was therefore possible to obtain a reliable average value within a reasonable period. By using the same syringe for admitting both standards and samples for analysis, errors in syringe calibration are largely eliminated. The method becomes inaccurate if V_1 and V_2 are very dissimilar or if the vapor pressure of the substance being analyzed is low. It is important to saturate the syringe lubricant with the compound, to avoid errors due to adsorption. This can be done by purging the syringe several times with the vapor.

The volume, V_x , is then converted to micromoles and the sensitivity of the apparatus is calculated in square centimeters of peak area per micromole. In an experiment with ethyl mercaptan, V_1 was 0.60 ml., and V_2 was 0.30 ml. The sensitivity of the apparatus to this compound was 1.44 sq. cm. per micromole at a chart speed of 1 inch per minute. A

0.03-sq. cm. peak, the limit of quantitative estimation in the present work, therefore, corresponded to 2×10^{-8} mole of ethyl mercaptan.

A logarithmic relationship between the peak retention volume of a substance and its vapor pressure at a given elution temperature has been reported by several investigators (8, 12). In the present work the situation is complicated by the temperature increase during the analysis, but the elution order for the organic sulfur compounds in Figure 2 agrees qualitatively with the general relationship.

The influence of the polarity of the compound on its retention volume can be seen in the relative positions of the hydrocarbons and the mercaptans. The pentanes, with boiling points of 28° to 36° C. and a molecular weight of 72, have a smaller retention volume than has methyl mercaptan with a boiling point of 7.6° C. and a molecular weight of 48. The dipole moments of *n*-pentane and methyl mercaptan are 0 and 1.26, respectively (15). The more polar mercaptan presumably interacts more strongly with the highly polar tricresyl phosphate phase on the column than does the nonpolar hydrocarbons.

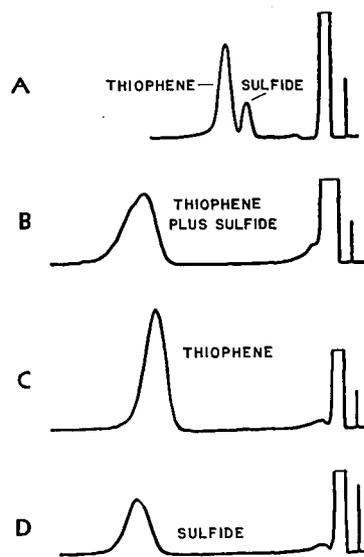


Figure 5. Effect of nature of column liquid on order of elution of thiophene and diethyl sulfide

- A. TCP
- B. Paraffin
- C. Thiophene only with paraffin column
- D. Diethyl sulfide only with paraffin

The elution order for thiophene and benzene conforms to the usual pattern; the less volatile, more polar thiophene has the larger retention volume.

However, the elution order for thiophene and diethyl sulfide (Figure 2) is different from that predicted by boiling

points or dipole moments. The sulfide [boiling point 92° C., dipole moment 1.51 (15)] has a smaller retention volume than thiophene [boiling point 84° C., dipole moment 0.6 (15)]. The observed reversal of elution order is presumably due to an electron interaction effect. Thiophene, because of its aromatic character, is strongly polarized by the polar tricresyl phosphate, causing an induced dipole-dipole interaction which is greater than that for the less polarizable diethyl sulfide. The thiophene is therefore retained to a greater extent on the column. Evidence to support this contention is presented in Figure 5. The top chromatogram shows again the elution order with a tricresyl phosphate column. The remaining chromatograms are for a thiophene-diethyl disulfide mixture and for thiophene and the sulfide separately, all done with a column in which paraffin oil replaced tricresyl phosphate as the liquid phase. With a

nonpolar liquid on the column, the more volatile thiophene has the smaller retention volume.

These results provide an additional illustration of the technique of separating two compounds which on one column appear together, by altering the nature of the column liquid. Furthermore, they indicate that gas partition chromatography may be a useful tool for investigation of dipole-dipole interactions between molecules.

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