

ELECTRIC DISCHARGE REACTION

OF

CARBON WITH HYDROGEN

by

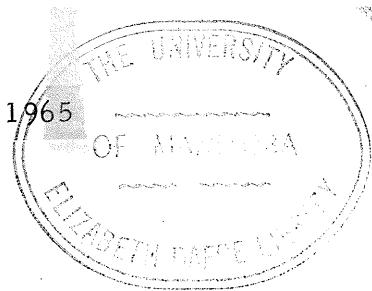
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A thesis submitted to the Faculty of Graduate  
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in partial fulfillment of the requirements for  
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From the Parker Chemistry Laboratory  
of the University of Manitoba  
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INTRODUCTION

Hydrogen, under normal conditions, is unreactive towards carbon in the chemical sense. The absence of chemical reactivity of hydrogen and carbon extends to most of the elements under normal conditions. Hydrogen and oxygen mixed in the ratio two to one respectively, can be stored, without a reaction occurring, until the mixture is exposed to a spark or a flame and under these conditions the mixture reacts with explosive violence.

The reaction of hydrogen with oxygen is generally expressed by equation (1).



As the equation is written, this process would require a three body collision, and some process for instantaneously breaking three bonds and forming four others. This process, although possible, is not probable from general consideration. The three body collisions as previously mentioned must occur to some extent in the gas mixture though no products are formed. The products are only formed when energy is supplied to the mixture. The energy supplied to the system must therefore create some reactive species which cause the reaction to occur. These reactive species are now firmly established to be of atomic or

radical form.

### HYDROGEN ATOMS

Evidence for the existence of hydrogen atoms was demonstrated by Wood, who showed that these species could be produced in a discharge tube (1).

Hydrogen atoms can be produced by several other methods, however, the basic principle of their production is the same. Hydrogen atom production depends on the ability of supplying sufficient energy to the hydrogen molecule, to increase its vibrational energy. If the energy supplied to the molecule is equal to or greater than the bond dissociation energy, then the molecule bond will break and as a result, atomic species will be formed.

The energy which must be supplied to the hydrogen molecule may originate from different sources. These sources of energy could be heat, light, electron impact, microwave, photosensitization by atoms etc..

Regardless how these hydrogen atoms are produced, they are relatively short-lived due to their reactivity, either with themselves, resulting in recombination or with other atoms or radicals, resulting in compound formation. The recombination process occurs mainly on the walls of the apparatus in which they are produced. Recombination may be minimised to some extent by poisoning the walls, that

is, by coating the walls with a thin layer of some chemical which does not act as a catalytic agent for the atomic recombination process. In the case of hydrogen atoms, a poisoning effect is obtained by coating the walls with orthophosphoric acid or its various sodium salts.

By minimising the recombination process, it is possible, then, to pump these hydrogen atoms from their source into another part of the apparatus where their reactions can be studied.

The reactions which the hydrogen atoms can undergo, are generally of two types;

- a) Abstraction
- b) Addition

To demonstrate the two types of reactions with specific examples, only the compounds containing hydrogen and carbon will be considered, as these pertain directly to the present study, though similar processes can be extended to other systems.

### Abstraction Reactions

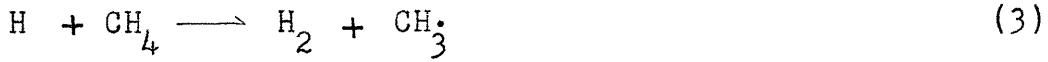
Abstraction reactions are reactions in which a hydrogen atom abstracts another hydrogen atom from a molecule. The generalized expression is given by equation (2).



where H is the hydrogen atom, HR is the hydrocarbon,  $H_2$  is a hydrogen molecule, and R is a hydrocarbon with one unshared electron, termed radical.

### Hydrogen Atoms With Methane

The activation energy for the reaction



has been controversial for many years, however, reaction (3) was thought to be the primary step (2).

In 1937, Steacie (3) investigated this reaction using deuterium atoms, and although the exact mechanism of the reaction was undecided, he concluded that the initial step was an abstraction reaction



In 1953, Berlie and Le Roy (4) indicated that an abstraction reaction is probably correct.

In 1964, Jamieson and Brown (5) reported ethane as their product from a reaction of hydrogen atoms (generated in an electric discharge) with methane above  $500^{\circ} C$ . The amount of methane reacted under these conditions, approached very closely the amount of hydrogen atoms capable of reacting. The amount of ethane formed was half of the

amount of methane reacted indicating that reaction (3) probably occurred to give  $\text{CH}_3$  species, which participated in ethane formation.

### Hydrogen Atoms With Ethane

As with methane, the controversy over the hydrogen atom ethane reaction lasted for several years (2). Steacie and Phillips (6) from their study of deuterium atoms with ethane, suggested reaction (5) to take place.



Berlie and Le Roy (7) concluded from their investigation of H atoms, produced by a hot filament, with ethane that reaction (5) does occur. The reaction of hydrogen atoms with propane has also been investigated (8). The results from this study indicated that the abstraction reaction is also operative. From these and other studies, it is indicative that the abstraction may occur with any hydrocarbon which has an abstractable hydrogen.

### Addition Reaction

Hydrogen atoms react with unsaturated hydrocarbons by the addition to the double bond. This reaction can be shown by the following equation:

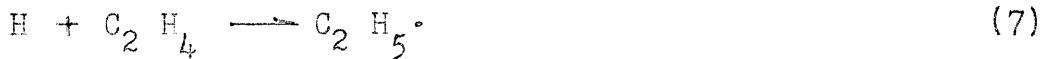


The radical produced in reaction (6), is itself very reactive, and can undergo further reactions. The reactions of radicals will be discussed later in the thesis.

Specific examples of hydrocarbons which undergo hydrogen atom addition reaction are ethylene and acetylene.

#### Hydrogen Atoms With Ethylene

The reaction of hydrogen atoms with ethylene gives ethyl radicals as the intermediate radical product;



Reaction (7) was first investigated by Von Waterburg, and Schultze (9), whose results indicated the process as given in reaction (7) to occur. Other workers (2) (10) (11) verified that addition to double bonds does occur.

#### Hydrogen Atoms With Acetylene

The reaction of hydrogen atoms with acetylene, in the early stages of investigation, appeared to be non-existent. It was shown by Geib and Steacie (2), in their study of deuterium atoms with acetylene, that a reaction did occur,

as they obtained as their reaction products deuterated acetylene. From their results they suggested the following mechanism which would explain why no reaction was observed by other workers using hydrogen atoms.



Le Roy and Steacie (12), studied the reaction of hydrogen atoms at low and high concentration with acetylene, and have shown that at low hydrogen atom concentration ethylene was formed. From their results they concluded that the formation of the vinyl radical ( $\text{C}_2\text{H}_3$ ) is a necessary step before further hydrogenation can take place to give ethylene as a product.

#### Hydrogen Atoms With Carbon

The reaction of hydrogen atoms with elemental carbon, in a form of soot, was shown to occur at  $100^\circ\text{ C.}$  from independent studies by Avramenko (13) and Harris and Tickner (14). Avramenko reported that the reaction showed an emission band at  $4317 \text{ \AA}^0$  indicating C-H radicals to be present. The report of Harris and Tickner indicated that hydrocarbons were actually formed and methane was the chief

product with small amounts of C<sub>2</sub> to C<sub>5</sub> hydrocarbons.

More recent studies of hydrogen atoms with carbon, indicated that the C<sub>2</sub> species were generally ethane and ethylene(15,16).

Shahin (15) in his work on hydrogen atom reaction (produced by microwave discharge) with solid graphite reported acetylene to be present among his products. King and Wise (16) reported acetylene to be only important as a product at higher temperatures, although hydrocarbons up to C<sub>7</sub> were observed by these investigators.

#### ATOMIC CARBON

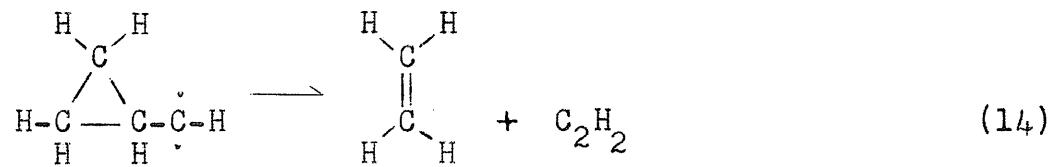
The reaction of atomic carbon (produced by a nuclear process) was studied with several hydrocarbons. McKay and Wolfgang (17) reacted atomic carbon with methane, ethane, propane, cyclopropane, and propylene. The reaction products from these hydrocarbons showed that acetylene was the major constituent, and ethylene was generally secondary in abundance. The authors were able to explain their high yields of acetylene on assumption that the carbon atom inserted into the C-H bond of the hydrocarbon. The generalized form for this reaction, as given by the authors, is;



The carbene (the product from reaction (12)), thus formed, may be collisionally de-excited to a singlet state (as the atomic carbon is assumed to react in the triplet state), causing decomposition by the following process;



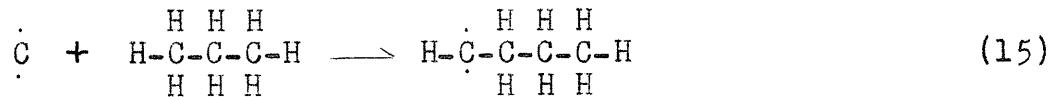
It is also possible, as the authors have suggested, that the process may involve a direct rupture of two C-C bonds, if sufficient energy is available, by the insertion process. The carbene formation can only arise from carbon insertion into the hydrocarbon C-H bond. In the case where the hydrocarbon is cyclopropane, the carbene formed, should favor acetylene formation, as simple electronic rearrangement can form stable products, as is shown by the reaction;



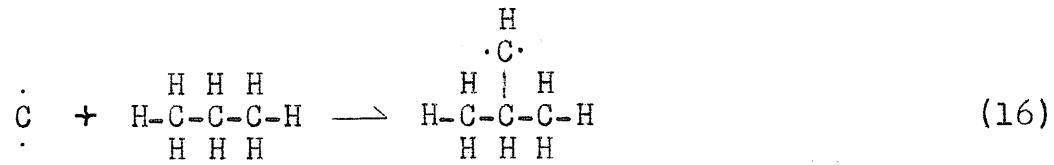
In confirmation to this process, the amount of

acetylene formed from this reaction was found to be approximately twice the quantity obtained from the reaction with other hydrocarbons.

The reaction of carbon atoms with propane yield ethylene, propylene, allene, methylacetylene, and butadiene. The small yields of butene-1 and isobutene from this reaction, as explained by the authors, arose from the deactivation of the intermediate carbene without decomposition. The carbon atom can insert into propane in two different positions as is shown by the following equation;



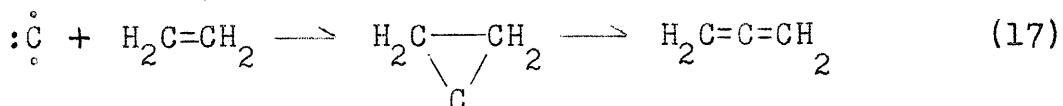
or



Deactivation of the intermediate carbene from equation (15) would form butene-1. Similiarly deactivation of the intermediate carbene from equation (16) could form isobutene.

### Reaction Of Carbon Atoms With Ethylene

The reaction of carbon atoms with ethylene has been studied by McKay et al. (18). The major products from this reaction were found to be acetylene and allene. Acetylene formation could result from atomic carbon insertion into the ethylene C-H bond as was mentioned previously. The formation of allene can be rationalized by carbon atom attack on the double bond of ethylene forming  $\pi$  bonded species which then can rearrange to allene. The reaction is illustrated as follows:



These results were supported by Dubrin, McKay and Wolfgang (19), who had studied  $\text{C}^{11}$  carbon atom reactions with equimolar mixtures of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$ . These authors have also studied the reactions of carbon atoms with ethane and found that the product was propylene. The reaction was believed to involve the insertion of the carbon atom into the C-H bond of ethane forming an intermediate which could be deactivated in different ways giving rise to several products in the same way as was postulated earlier (17).

RADICALS AND THEIR REACTIONS IN THE GAS PHASE

The reaction of hydrogen atoms and carbon atoms have been briefly reviewed. These atomic species characterize the behaviour of free radicals and are considered by some to be radicals. Generally, free radicals are short-lived intermediates, with life times in the order of milli or microseconds depending on the radical and its environment. It is possible however, to extend their life times to hours and days by freezing techniques (20) (21).

The historical approach to the discussion will not be given, since it is only desired to emphasise certain radicals and their reactions which are pertinent to the present study.

Carbon Species

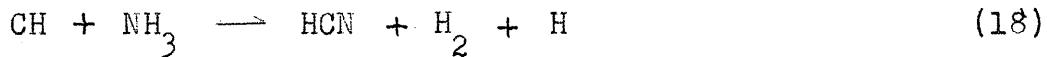
Studies of the evaporation of graphite indicate that at elevated temperatures the vapours of graphite are composed of  $C$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_5$ ,  $C_6$ , and  $C_7$  fragments (22). Baun and Fischer (23) have reported positive ions of carbon up to  $C_{28}$ , in a high frequency spark between graphite electrodes. The abundance of these species, as measured with a mass spectrometer, sharply decreases as the molecular weight of the species increase.

Although C<sub>1</sub> species have been briefly discussed, very little is known about the higher molecular weight fragments.

### Carbon Hydrogen Radicals

#### CH Radical

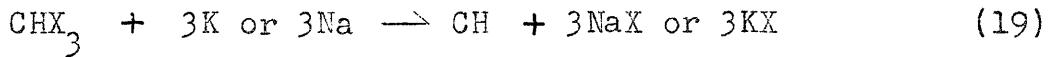
The simplest of the carbon hydrogen radicals is the CH radical. The presence of these radicals was identified by spectroscopy. In the work done by Safrany, Reeves, and Harteck (24), it was postulated that the CH radicals were involved in the HCN formation, when NH<sub>3</sub> was added upstream from the acetylene and active nitrogen reaction flame. This reaction is shown by equation (18);



Palmer and Miller (25), while studying the reaction of Na and K vapors with organic halides, observed a visible emission spectra, not due to the alkali metal atoms. Using CHCl<sub>3</sub> and CHBr<sub>3</sub>, and other organic halides, predominantly the Swan bands of C<sub>2</sub> species were observed. From the interpretation of the spectra, the authors concluded that the C<sub>2</sub> formation was due to the C atoms reacting with CH or CCl radicals. Since the dominant stable product was ethylene and no halogenated products were observed, the

process must include the following steps;

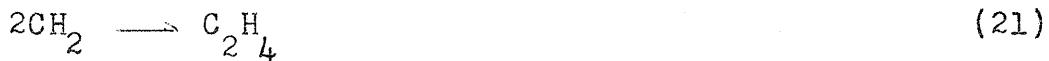
a) the first step is the stripping of the halogen atoms from the haloform by the alkali metal, leaving the CH radical;



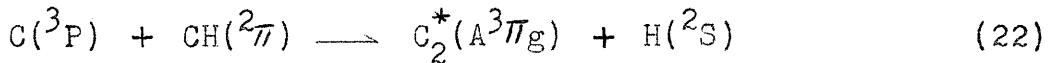
b) the second step is disproportionation of the CH radicals;



The formation of ethylene could be explained by recombination of the  $\text{CH}_2$  radicals;



The  $\text{C}_2$  species can be formed by the following reaction;



The  $\text{C}_2^*$  refers to the electronically excited  $\text{C}_2$  species which can lose the excess energy by emission of visible light; - the observed Swan bands.

The CH radicals are believed to be present as intermediate species in many reactions involving flames, and high temperature systems containing carbon and hydrogen.

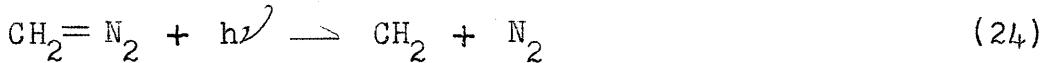
### $C_2H$ Radical

$C_2H$  radicals have been detected spectroscopically. Very little is known about them, although these are believed to exist in carbon-hydrogen-acetylene equilibrium at elevated temperatures (26), and as intermediates in hydrogen atom-acetylene reaction (12).

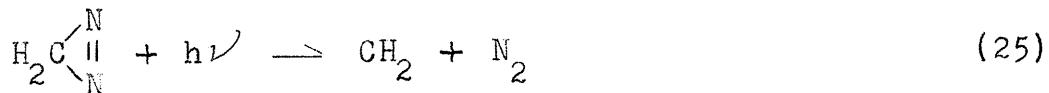
### $CH_2$ (Methylene) Radical

The existence of methylene is well established, and extensive studies have been performed, to determine the chemical behaviour of this biradical sometimes termed carbene.

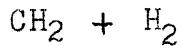
Methylene can be produced by photolysis of ketene or diazomethane. These processes are illustrated by the following two reactions;



Frey and Stevens (27) have also studied methylene reactions produced by photolysis of diazirine (cyclo-diazomethane). The photolysis step is shown by equation (25);



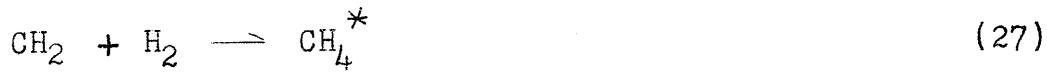
From equations (23), (24), and (25), it can be seen that the photolysis products are methylene and a stable molecule either CO or N<sub>2</sub>. It should be noted that methylene can be formed in two electronic states, the triplet state, where the electrons are unpaired (CH<sub>2</sub><sup>↑↑</sup>) or in the singlet state where the electrons are paired (CH<sub>2</sub><sup>↑↓</sup>). The ground state of methylene is now believed to be the triplet state. The electronic state of methylene plays an important role in the reactivity and product formation as will be shown shortly.



The reaction of methylene with hydrogen or deuterium has been studied by several workers. The study of Gesser and Steacie (28), had shown that the reaction of methylene with hydrogen is an abstraction reaction of the type;



In disagreement with this, Chanmugan and Burton (29), and Bell and Kistiakowsky (30), have postulated that the reaction of methylene with hydrogen is an insertion reaction as is shown by reaction (27);

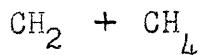


where  $\text{CH}_4^*$  is an excited methane molecule, which if not collisionally stabilized, can then undergo decomposition into a methyl radical and a hydrogen atom.



The slight difference in the mechanism proposed, or in the products observed by Chanmugan and Burton, and by Bell and Kistiakowsky, can be rationalized, if the source of methylene is considered (31), as the former used ketene, and the latter used diazomethane as their source of methylene. The discordance with Gesser and Steacie's results is not quite so simple. Bell and Kistiakowsky would like to explain this discrepancy by the former's poor analytical techniques - a most unsatisfactory explanation. The author supports an alternative explanation, suggested by Demchuk and Gesser (32), which observes the difference in the type of irradiation used in the two cases. Gesser and Steacie used a narrow band of frequencies ( $2700 \text{ \AA}^0$ ), whereas Bell and Kistiakowsky used a full mercury arc. The difference in the irradiation used could very well explain the formation of methylene possessing different amounts of energy, therefore, a different reaction mechanism could result.

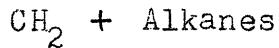
The reaction of methylene with hydrogen is not certain, and further work seems necessary.



This reaction is also controversial, with no definite conclusion, though it appears that insertion reaction may exist as is shown by equation (29);

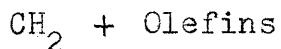


where  $\text{C}_2\text{H}_6^*$  indicates an excited species which may be deactivated by a third body M to give ethane as a product.

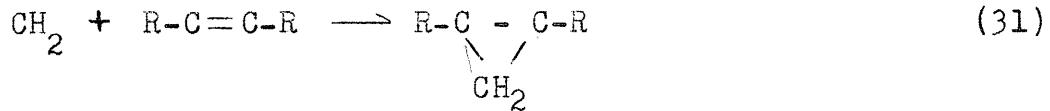


Methylene can react with alkanes and olefins. In the reaction with the alkanes, the methylene inserts into the CH bond of the alkane to give as a product the next higher alkane. Methylenes produced from diazomethane photolysis seems to be more reactive and less selective in the insertion reaction than methylene produced from ketene photolysis, attacking primary, secondary, and tertiary C-H bonds indiscriminately and almost statistically. A

study of methylene produced from diazomethane, in the presence of inert gas, shows the radical to have more vibrational (or electronic) energy than methylene from ketene photolysis (33). When this extra energy is removed the methylene from diazomethane behaves similarly to that produced from ketene.

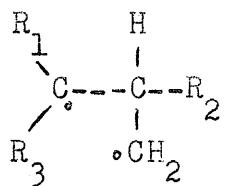


Methylene reacts directly with olefinic double bonds. The reaction products depend greatly on the state of methylene. In the study of Rabinovitch and Setser (34), on the thermal decomposition of diazomethane, stereospecific addition of the  $\text{CH}_2$  to the olefinic double bond was observed. The stereospecific addition would necessitate a singlet  $\text{CH}_2$ , as the bond in the olefin must have its electrons paired, (spin conservation must be observed). The  $\text{CH}_2$  adds directly to the olefin system as is shown by the following reaction;



The excited product formed in reaction (31) may be stabilized by collision to give a cyclopropane.

The  $\text{CH}_2$  triplet also attacks the olefinic bond, however direct addition in this case is not possible if spin conservation is to be observed. As the consequence of this, the  $\text{CH}_2$  triplet addition to olefinic bonds gives products which are nonstereospecific. To account for this, Duncan and Cvetanovic (35) proposed an intermediate which is able to rotate about a C-C bond thus leading to the formation of nonstereospecific products. This triplet addition complex (a biradical) is shown.

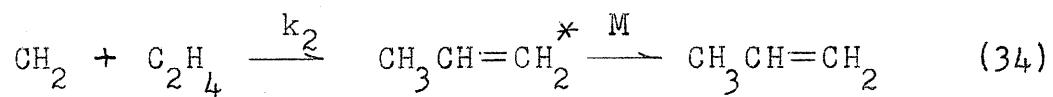
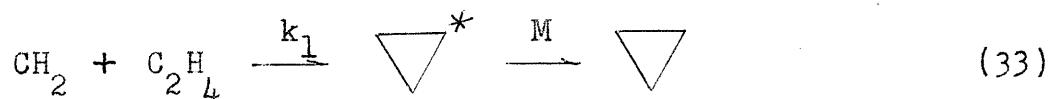


(32)

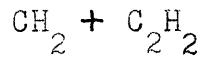
The biradical may also rearrange via H or  $\text{CH}_3$  migration to give other stable reaction products. For the olfins studied by these authors, this rearrangement scheme is consistent.

Generally the reaction of  $\text{CH}_2$  with a double bond leads to the formation of an excited adduct, which may undergo either deactivation, isomerization or dissociation. From the previous discussion it can be seen that the singlet methylene in the reaction with ethylene forms, in the primary step, an active cyclopropane, which may be

collisionally deactivated, (to form a cyclopropane), rearrange to give an olefin, or may decompose to smaller fragments. Setser and Rabinovitch (36) studied the reaction of methylene with ethylene and found as their major products cyclopropane and propene. The reaction scheme as given by the authors is;

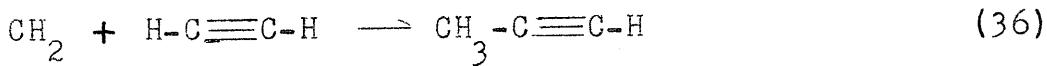
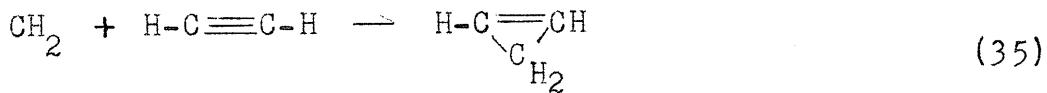


The side products were found to increase at lower pressures and could indicate the increase in decomposition of intermediate excited molecules into smaller fragments. It should be mentioned that the side products found were ethane, propane, butane, and butene-1.



Another pertinent reaction to the present study is the reaction of methylene with acetylene. This study was done by Terao, Sakai and Shida (34) using ketene as their source of methylene. The reaction products, methyl-acetylene, allene and a polymer, confirmed the earlier observations by Frey (37). The former authors indicated that the reaction of methylene with acetylene can occur in two different

parallel paths as shown by reactions (35) and (36).



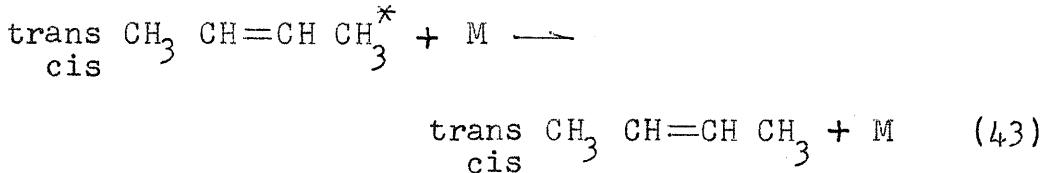
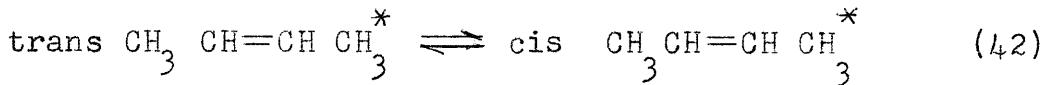
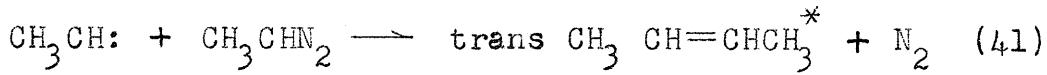
The failure to obtain cyclopropene in their reaction products was explained by the authors (Terao, Sakai, and Shida) that cyclopropene, being a very unstable molecule, upon formation, instantly isomerized to methyl-acetylene and allene.

### $\text{CH}_3\text{CH:}$ (Ethyldene) Radical

The ethyldene radical is next higher in the homologous series to the methylene radical. Very little study has been done on this radical. The ethyldene radical can be prepared by photolysis of diazoethane, or methylketene.

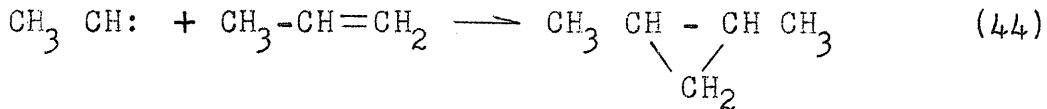
Frey (38), photolyzed diazoethane and found that the products consisted of ethylene, acetylene and cis and trans-butene-2. To account for the products Frey postulated the following mechanism:





In qualitative agreement Frey found that the yield of ethylene rose and the yield of cis and trans butene-2 fell with the decrease in pressure.

The reaction of ethylidene with propylene gave cis and trans 1, 2-dimethyl-cyclopropane as the major product.



Thus ethylidene undergoes only an addition reaction. The mechanism as proposed by Frey (reactions 37-43) was supported by Chong and Kistiakowsky (39) who studied the ethylidene reaction by photolysing methylketene.

### Alkyl Radicals

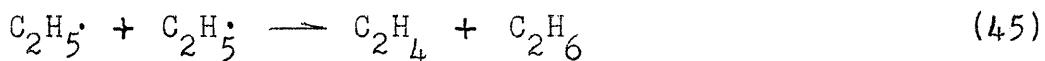
The alkyl radicals will be discussed very briefly.

The reactions of these radicals have been studied in some detail (2,40), and they appear to undergo three main types of reactions.

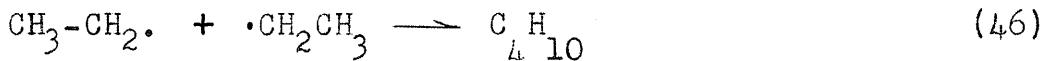
- 1) abstraction
- 2) recombination
- 3) disproportionation

The abstraction and recombination reaction have already been discussed in the case of hydrogen atoms, and the analogy can be extended to the alkyl radicals.

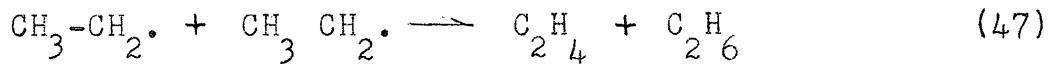
Disproportionation reaction involves two radical, as does the recombination. In the disproportionation reaction, one radical donates a hydrogen atom to the other radical, resulting in the formation of two stable molecules, an alkane and an olefin. This is illustrated by reaction (45) where the ethyl radical is used as a typical alkyl radical.



This type of reaction always accompanies the recombination reaction. The recombination reaction occurs where the two radicals are tail-to-tail (40);



and the disproportionation reaction occurs when the two radicals are head-to-tail (40).



The disproportionation reaction could be thought to be a form of abstraction reaction.

### Discharge Phenomena

There are basically three types of electric discharge.

- 1) silent discharge
- 2) glow discharge
- 3) arc discharge

The electric discharge depends on three variables, the potential E, the pressure P, and the current density. By properly adjusting these variables one type of discharge may be converted into another.

The silent discharge is operative under high potential differences between the electrodes, and high gas pressures. The discharge is self sustained, due to residual ionization of the gas in the discharge tube. The silent discharge may be classified into two types, depending on conditions. With increase of potential, and in non homogeneous electric field, corona discharge is observed. This type of discharge is characterized by a glowing layer close to the electrode. An increase in current density converts the corona discharge into a spark discharge. Spark discharge is characterized by its disruptive nature. The

discontinuity of discharge is due to the fall of resistance of the discharge gap, after the discharge has begun. The fall of resistance causes a redistribution of potential, which leads to a decrease of potential difference at the electrodes, making the potential insufficient to support the discharge. After the discharge has stopped, the potential again redistributes itself and the discharge can occur again, and this process is repeated.

The glow discharge is observed at low pressures and is characterized by the presence of light and dark regions along the discharge tube. These regions are attributed to electron impact with the gas molecules, resulting in excitation of the gas to luminescence and to ionization.

An increase of current, therefore an increase in the electrode temperature, transforms the glow discharge into an arc discharge. This type of discharge generally involves intense evaporation of electrode material. The arc may be of the A.C. or the D.C. type. The D.C. arc may be altered by use of a spark gap in series and a condenser in parallel just before the discharge tube to give an interrupted D.C. arc. The importance of the D.C. interrupted arc lies in the ability of obtaining higher energies and the ability of measuring the energy imparted with each discharge. The electrical diagram of this type

of circuitry will be given later.

The processes which occur in the discharge are very complex (41,42,43) and their discussion is beyond the scope of this thesis. It should be mentioned however, that the species present in a discharge may be ionic (positively or negatively charged) neutral species, and species electronically excited to various degree. The shape and size of the discharge tube, the gas, the electrodes, the pressure, the voltage, and the temperature are all variables, affecting directly or indirectly the formation of the species which may exist in the discharge tube.

#### SYNTHESIS OF HYDROCARBONS FROM THE ELEMENTS

The synthesis of hydrocarbons from their elements by arcing carbon electrodes in a hydrogen atmosphere was first investigated by Berthelot(44), who was able to produce acetylene in this way. The study of Lepsius and Bone and Jerdan followed (44), thus establishing the formation of acetylene by this method. A more detailed study of acetylene formation was done by Fischer and Pichler (45) in 1938. By cooling the apparatus with water and using 110 v. D.C., a current of 3 amps and  $H_2$  at atmospheric pressure, they were able to produce 2.2% acetylene 0.8% ethylene and 1.3% saturated hydrocarbons (mostly methane)

along with residual hydrogen. Resorting to liquid air as the coolant and H<sub>2</sub> pressure at 66 mm, they were able to produce 93.4% acetylene and 6.6% of saturated hydrocarbons. Under these conditions H<sub>2</sub> was totally converted. From the acetylene formation in methane reaction between carbon electrodes at 8mm. Hg., they showed the following over all reaction to take place.



In 1942, Kudnig and Briner (44) studied the reaction of hydrogen between carbon and graphite electrodes under the influence of high and low frequency A.C. discharge. Their chief interest was to determine the feasibility of acetylene formation in grams of acetylene per k.w.h. They reported the presence of other hydrocarbons, but only specified methane in some cases. Other work done on hydrogen reaction with carbon has already been mentioned in the discussion of hydrogen atoms (13,14,15,16). Thermal reactions of graphite with hydrogen was also studied in the range of 360-800° C.(46) and in the range 1100° - 2600° C. (47).

The reaction products reported by various workers vary slightly, though methane was reported in every case. Acetylene was reported in all cases except in the study of the thermal reaction hydrogen with graphite in the range

360-800°<sup>o</sup>C. (46). Ethane was reported in all cases except the thermal study in the range 1100°-2600°<sup>o</sup>C. (47). Ethylene was also reported in all cases except in the reaction of hydrogen atoms with carbon films (16).

The purpose of the present study is twofold. The primary purpose was to determine what products are formed in a high voltage A.C. discharge of hydrogen at low pressures and high flow rates through graphite electrodes and to analyse for major and minor products since generally only the major products were reported.

The secondary purpose was to determine what effect the variation of voltage and flow rate had on the reaction. By studying these effects it was hoped that something could be learned of the reaction process and the intermediates present.

EXPERIMENTALMATERIALS

Commercial grade hydrogen was obtained from Linde Company. It was purified in three stages.

1) The hydrogen was passed through a hot copper furnace maintained at  $410^{\circ}$  -  $420^{\circ}$  C. to remove any oxygen present.

2) The second purification stage was composed of two traps in series maintained at liquid nitrogen temperature to remove all the condensable impurities.

3) Third purification stage was a silica gel trap maintained at liquid nitrogen temperature to remove all non condensable gases such as nitrogen (48).

The graphite used for the electrodes was spectroscopically pure grade (obtained from United Carbon Products Inc.,). Any impurities which may have arisen in its handling, were removed by subjecting the electrodes to high voltage discharge in an atmosphere of hydrogen, and allowing them to heat up to an orange colour. This temperature was maintained intermittently for five or ten minutes, after which the system was evacuated to approximately 0.5 micron pressure.

The gaseous hydrocarbons, except acetylene, which were used for retention time determination were obtained from

Matheson. The hydrocarbons and their purities are given below.

| <u>Hydrocarbon</u>                  | <u>Grade</u> | <u>Purity (%)</u> |
|-------------------------------------|--------------|-------------------|
| CH <sub>4</sub>                     | C P          | 99.0              |
| C <sub>2</sub> H <sub>4</sub>       | C P          | 99.5              |
| C <sub>2</sub> H <sub>6</sub>       | C P          | 99.0              |
| C <sub>3</sub> H <sub>6</sub>       | C P          | 99.0              |
| cyclo-C <sub>3</sub> H <sub>6</sub> |              | 99.5              |
| C <sub>3</sub> H <sub>8</sub>       | Inst.        | 99.5              |
| iso-C <sub>4</sub> H <sub>8</sub>   | C P          | 99.0              |
| C <sub>4</sub> H <sub>8</sub> -1    | C P          | 99.0              |
| n C <sub>4</sub> H <sub>10</sub>    | C P          | 99.0              |

Acetylene (commercial grade) was obtained from Linde.

i-Pentane (B.P. 27.5 - 28.5) and n-pentane (practical grade) were obtained from Matheson Coleman and Bell.

Hexamethylphosphoramide was obtained from Aldrich Chemical.

2,5 Hexanedione was obtained from Eastman Organic Chemicals.

Silica gel (mesh < 60) was obtained from Fisher Scientific.

Firebrick (60/80 regular) was obtained from Wilkins Instrument and Research Inc.

## THE APPARATUS

A description of the apparatus will be divided into two parts;

- 1) the reaction part
- 2) the analysis part

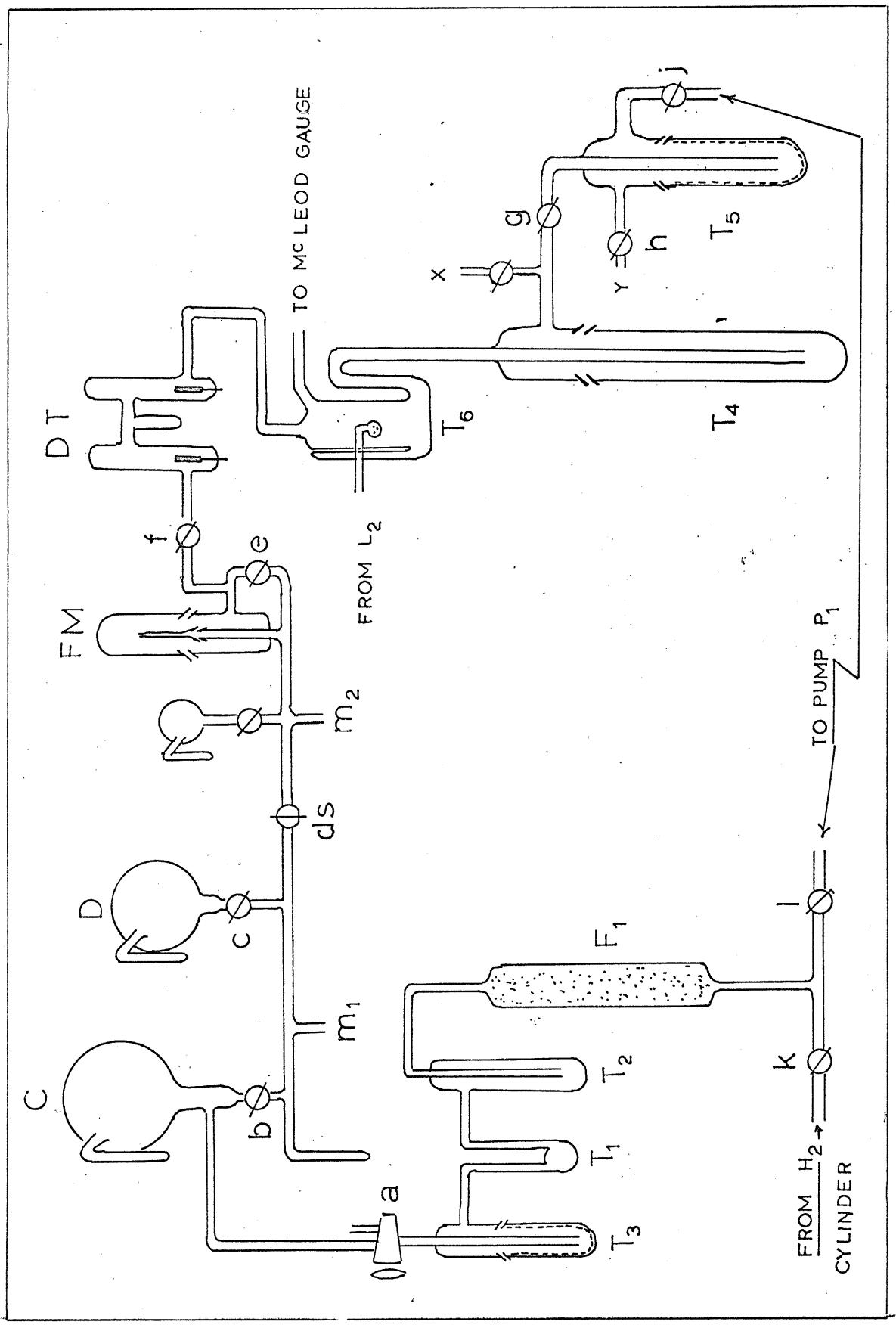
### The Reaction Apparatus

The reaction part, shown in Figure 1, was a typical fast flow, low pressure apparatus, constructed entirely of pyrex except for the discharge tube which was constructed from quartz. To add versatility to the apparatus, two lines instead of one were constructed, that is, the apparatus was duplicated up to the discharge tube. Only one of the lines ( $L_1$ ) is shown, in Figure 1. All volumes were calibrated from PV relations.

#### Method of Introducing Hydrogen Into The Storage Bulbs C and D

An electric heated furnace operating at  $184^{\circ}\text{C}$ . was placed around the silica gel trap,  $T_5$ , of Figure 1 as the line  $L_1$  up to the stopcock "a" was evacuated by means of the mechanical 1402B, 2 stage, V. E. Welsh Duo-SEAL pump (by having all the stopcocks b,c,ds, e,f,g, and j open and stopcock a shut off to both lines  $L_1$  and  $L_2$ ). The pressure

FIGURE 1  
Diagram of the reaction apparatus



was constantly checked with a McLeod gauge. When the pressure had dropped down to 0.5 microns or less, stopcocks d, f, and j, were closed. The furnace operating at  $184^{\circ}\text{C}$ . was now removed from the silica gel trap  $T_5$ , and placed around the silica gel trap  $T_3$  as the copper furnace  $F_1$  (capable of operating at  $410^{\circ} - 420^{\circ}\text{C}$ .) was turned on. Stopcocks k and l were now opened, so that evacuation of the purification system (traps  $T_1, T_2, T_3$ , the copper furnace  $F_1$  and the line leading to the hydrogen cylinder) could be possible. After evacuating for a period of 15-20 minutes, stopcock j was opened in order that the pressure of the purification system could be determined with the McLeod Gauge. After obtaining a pressure of approximately 0.5 microns, stopcocks l and j were closed and stopcock a was opened to line  $L_1$ . Having removed the electric furnace from trap  $T_3$ , traps  $T_1, T_2$ , and  $T_3$  were cooled down to liquid nitrogen temperature. Hydrogen from the cylinder, was now allowed to pass very slowly through a reducing valve, a needle valve, the three traps ( $T_1, T_2, T_3$ ) and into the storage bulbs C and D. The pressure in the system was determined with the manometer  $m_1$ . After a desired pressure of hydrogen had been reached, the valves of the hydrogen cylinder, and stopcock a were closed. From the known volumes, the temperature and pressure of the system and by

using the Ideal Gas Law,

$$PV = nRT \quad (49)$$

it was possible to calculate the number of moles of hydrogen admitted.

#### Introduction of Hydrogen Into The Reaction Zone At A Desired Pressure

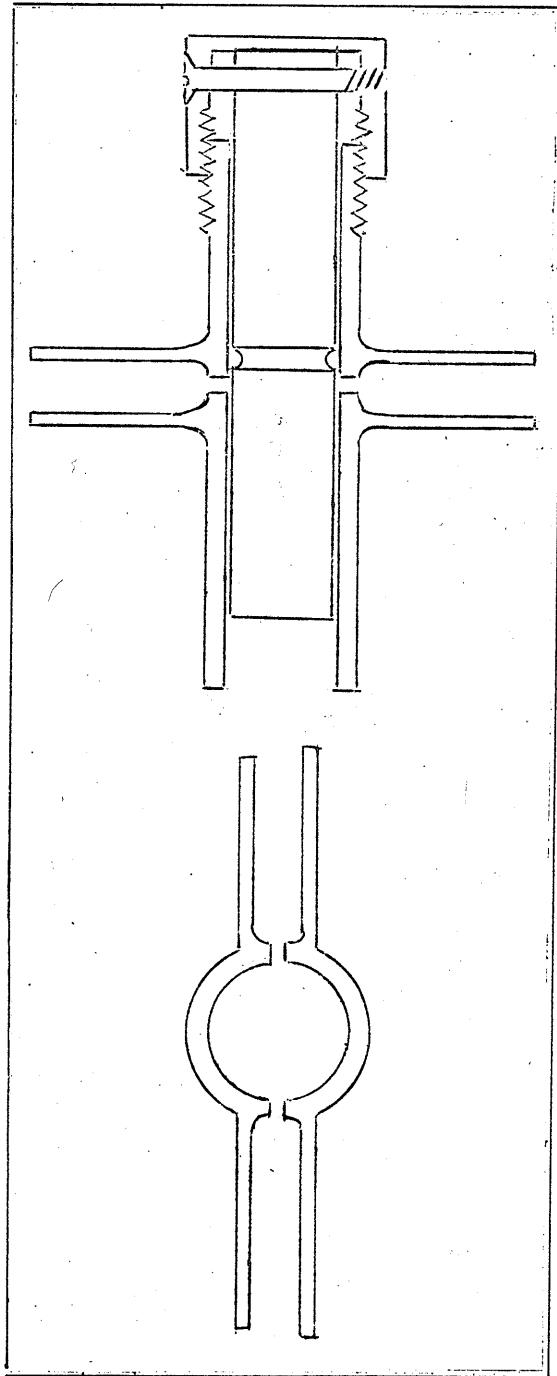
The stopcock ds was different from the other stopcocks and served a dual purpose. Its function was not only to cut off a part of a line, but also to allow a small leak of gas to pass from the storage bulbs to the reaction zone (the discharge tube designated as DT in Figure 1). Instead of using the conventional scratched stopcock, a regulation valve was used. The physical description is shown in Figure 2. This regulation valve had some advantage over the scratched stopcock, for example;

- 1) A much finer flow control
- 2) Lesser tendency of erratic behaviour, as scratched stopcocks have when the scratches become partially filled with stopcock grease.

After the line from stopcock ds to the pump  $P_1$ , had been evacuated to a pressure of 0.5 microns or less, stopcock e was closed so that the gas when allowed to flow was forced to pass through a constriction in a flow meter

FIGURE 2

The front view and the side view of the regulation valve ds.



(FM) before entering the reaction zone. The pressure in the section between ds and FM was determined with the manometer  $m_2$ . The absolute pressure in the reaction zone was determined with the McLeod Gauge. A direct relationship exists between the pressure as observed on the manometer  $m_2$  and the absolute pressure in the reaction zone, so it is possible, by regulating the pressure observed on the manometer  $m_2$  by means of the valve ds, to regulate the absolute pressure in the reaction zone. Under experimental conditions the pressure as shown by manometer  $m_2$  was kept within  $\pm 0.2$  cm, resulting in a variation of pressure in the reaction zone of  $\pm 0.02$  mm.

#### The Discharge Tube

The discharge tube was constructed from quartz so that higher temperatures could be attained. The design of the discharge tube is given in Figure 3. The graphite electrodes were machined in such a manner that if any heating was to occur during the reaction, it would occur mostly at the ends, away from the tungsten supports. The electrodes are illustrated in Figure 4.

#### The Power Supply

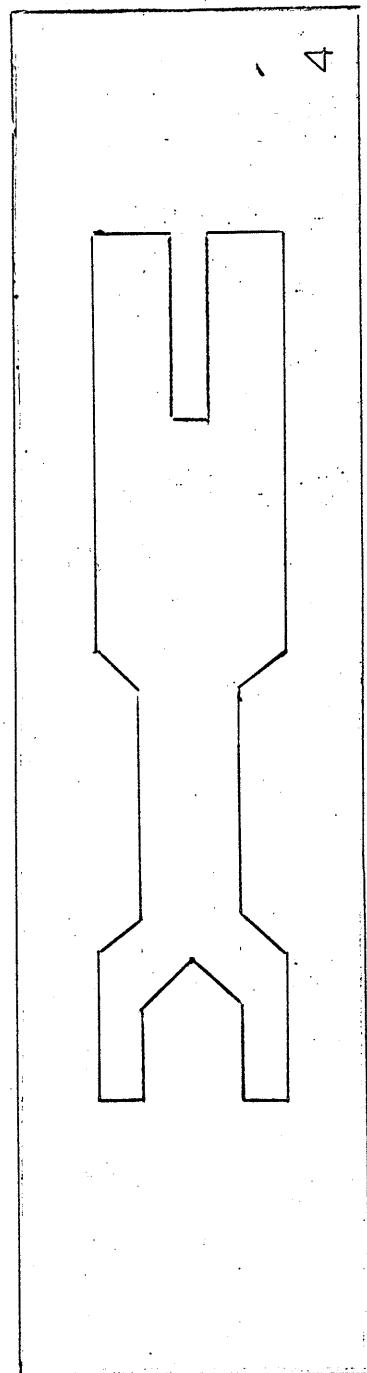
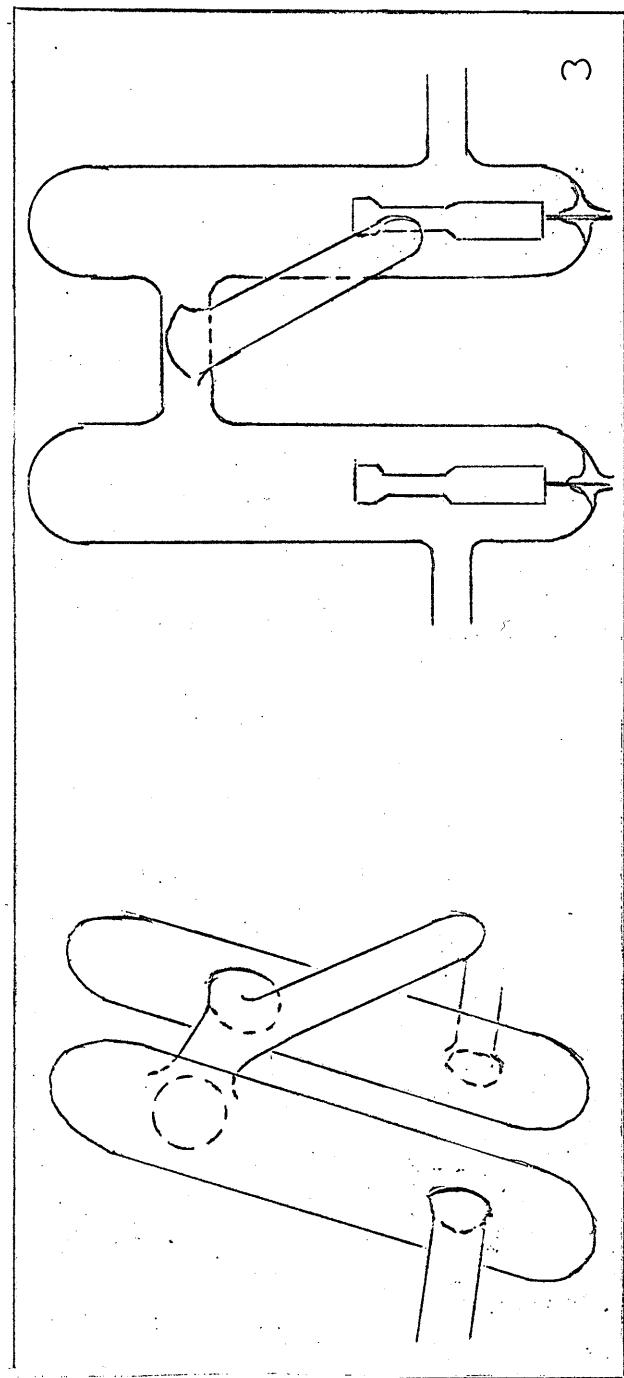
The high voltage power supply to the discharge tube was designed such that either high voltage A.C. or high

FIGURE 3

Diagram of the discharge tube.

FIGURE 4

The shape of the graphite electrode.



voltage condensed D.C. discharge could be obtained by simply rearranging a few high voltage wires. The schematic diagram of the high voltage power supply is shown in Figure 5. By disconnecting lines at points indicated by X, by connecting together points marked Z, and by shorting out the spark gap SG, the system could be converted from a condensed D.C. discharge to an A.C. discharge. The voltage appearing at the electrodes of the discharge tube was regulated by the variable autotransformer  $T_3$ , Figure 5.

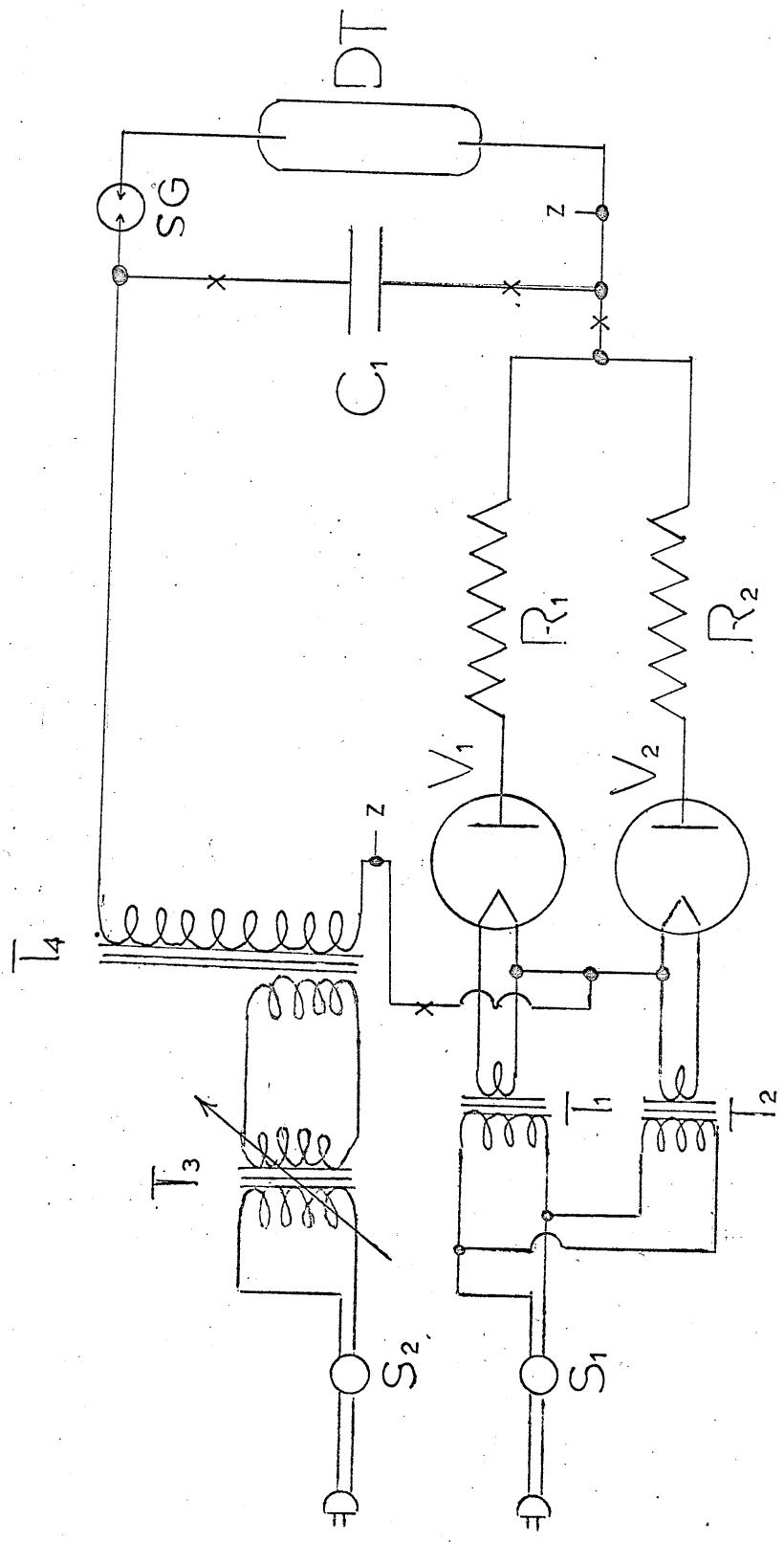
#### Reaction Procedure

After having degassed the silica gel trap  $T_5$  in Figure 1, at  $184^{\circ}\text{C}.$ , and the pressure lowered to 0.5 microns or less, the main trap  $T_4$  and the silica gel trap  $T_5$  were cooled to liquid nitrogen temperature. The hydrogen gas was then introduced into the reaction zone in a manner already described. When a desirable steady pressure was attained (indicated by manometer  $m_2$  in Figure 1), a stopwatch and the power to the discharge tube were turned on simultaneously. Immediately following, the initial hydrogen pressure (in the storage system) was read on manometer  $m_1$ . During the reaction the pressure in the discharge tube was checked periodically with the McLeod Gauge. A steady pressure in the zone ds to FM was

FIGURE 5

Schematic diagram of the power supply.

|            |  |
|------------|--|
| $S_1, S_2$ | dpdt switches                                |
| $T_1, T_2$ | step down transformers                       |
| $T_4$      | step up transformer 4,000 v. at 220 v. input |
| $T_3$      | variable autotransformer                     |
| $V_1, V_2$ | 866A mercury rectifier tubes                 |
| $R_1, R_2$ | 10,000 ohm plate resistors                   |
| $C_1$      | 8 $\mu$ f condensor                          |
| DT         | discharge tube                               |
| SG         | variable spark gap                           |



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maintained by manipulation of the regulation valve ds.

After the reaction had gone for the desirable length of time, the reaction was terminated by simultaneously shutting off the power and the regulation valve ds. The final hydrogen pressure was then read on the manometer  $m_1$ .

Stopcock f was turned off in order that a pressure of 0.5 microns could be attained sooner. When the pressure had fallen to 0.5 microns or less, stopcocks g and j were closed in order to isolate the products in the two traps.

#### Product Trapping

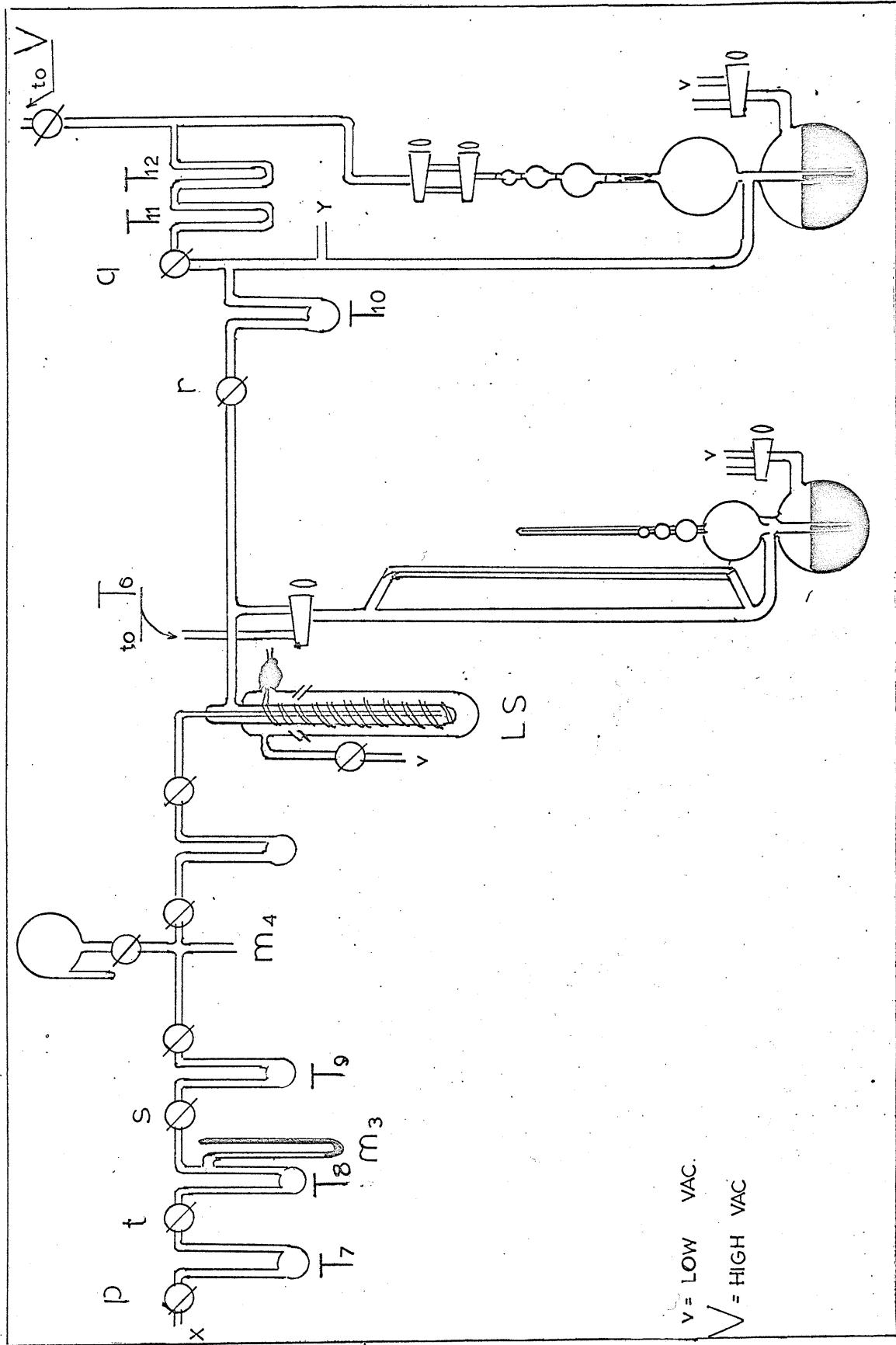
The products formed during the reaction, along with hydrogen, were pumped out of the reaction zone through trap  $T_6$ , the main trap  $T_4$ , and the silica gel trap  $T_5$  in Figure 1. All the products which were condensable at liquid nitrogen temperature were trapped in the main trap  $T_4$ , and all the other gases passed through this trap. All the non-condensable gases, for example methane, were trapped in the silica gel trap (48). Hydrogen being noncondensable in either of the two traps (48), passed through them and was pumped out of the system.

#### ANALYSIS APPARATUS

The analysis apparatus was constructed entirely of pyrex and is shown in Figure 6. The purpose of traps  $T_7$ ,

FIGURE 6

Diagram of the analysis apparatus.



$T_8$ , and  $T_9$ , was to separate the condensable products from the main trap into three fractions; - those condensing at  $0^\circ$  C., -  $90^\circ$  C., and  $-196^\circ$  C.. In the early stages of experimentation it was observed that there were no products condensing at  $0^\circ$  C., therefore trap  $T_7$  was no longer used. There was only a small quantity of products condensing at  $-90^\circ$  C., which upon compression liquified, therefore, it was not possible to use the McLeod gauge and the Toepler pump for determining the pressure-volume data. In order to measure the pressure-volume data of the  $-90^\circ$  C. fraction, trap  $T_8$  was modified. This modification included a decrease in the trap volume and an addition, to one of the side arms of the trap, a manometer constructed from tubing of small inside diameter, as shown in Figure 6. The quantity of products collected in this trap could now be measured as the volume, the temperature, and the pressure were all attainable. To assure that no products were in the condensed form when the pressure was determined, the products could be allowed to expand into the adjacent trap  $T_7$ . From the change in pressure it would have been possible to determine whether all the constituents, if more than one were present, were in the vapour phase.

The LeRoy still was found to be good for fractionation of components which have a considerable difference in their

vapour pressure at a specific temperature. However for compounds such as ethylene and ethane, whose vapour pressure is quite similar at a given temperature, fractionation by using the LeRoy still was not possible. Many of the compounds found among the reaction products were in small quantities. It became obvious that identification of compounds from their vapour pressure data would be a major problem giving rise to unreliable results. For example, it would be difficult to determine whether a vapour pressure exerted at a certain temperature was due to one or several compounds.

For these and other reasons vapour pressure methods of identification and separation of products for quantitative determination was abandoned, and attention was turned to identification by gas chromatography. With a proper column it should have been possible to determine how many products were present in the product mixture, their relative amounts and their identity.

#### Analysis By Chromatography

A chromatograph must essentially have a good column and a good detector. The choice of which is determined by the problem.

##### The Detector

The detector chosen for this problem was a gas density balance detector manufactured by Gow-Mac Instrument Co., having two matched thermistors as the detectors. The sensitivity of this detector is comparable to that of a thermistor conductivity cell, requiring no amplification at room temperature. The added advantage of using a gas density balance, lies in the possibility of determining molecular weights of the products, as will be shown later.

The gas density balance detector was mounted in one of the two compartments of a transite enclosure. The other compartment was provided to contain two gas preheater coils and the column. Transite was chosen since it has low thermal conductivity and high thermal stability. Both of the compartments could be heated individually by means of flat electric heaters (two in each compartment). The temperature of each compartment could be regulated by means of a variable autotransformer. The entire enclosure was set on three leveling screws in order that the detector could be levelled. The two thermistors of the gas density balance were incorporated into the arms of the Wheatstone bridge shown in Figure 7.

#### Principles Of The Gas Density Balance

The schematic diagram of the gas density balance is

FIGURE 7

Schematic diagram of the bridge used with the gas density balance detector.

|                 |                               |
|-----------------|-------------------------------|
| $T_1, T_2$      | thermistors                   |
| M               | milli ammeter                 |
| $R_1$           | current adjust resistor       |
| $R_2$           | bridge 'zero' adjust resistor |
| $R_3, R_4, R_5$ | resistors (bridge components) |
| $R_6$           | sensitivity control resistor  |

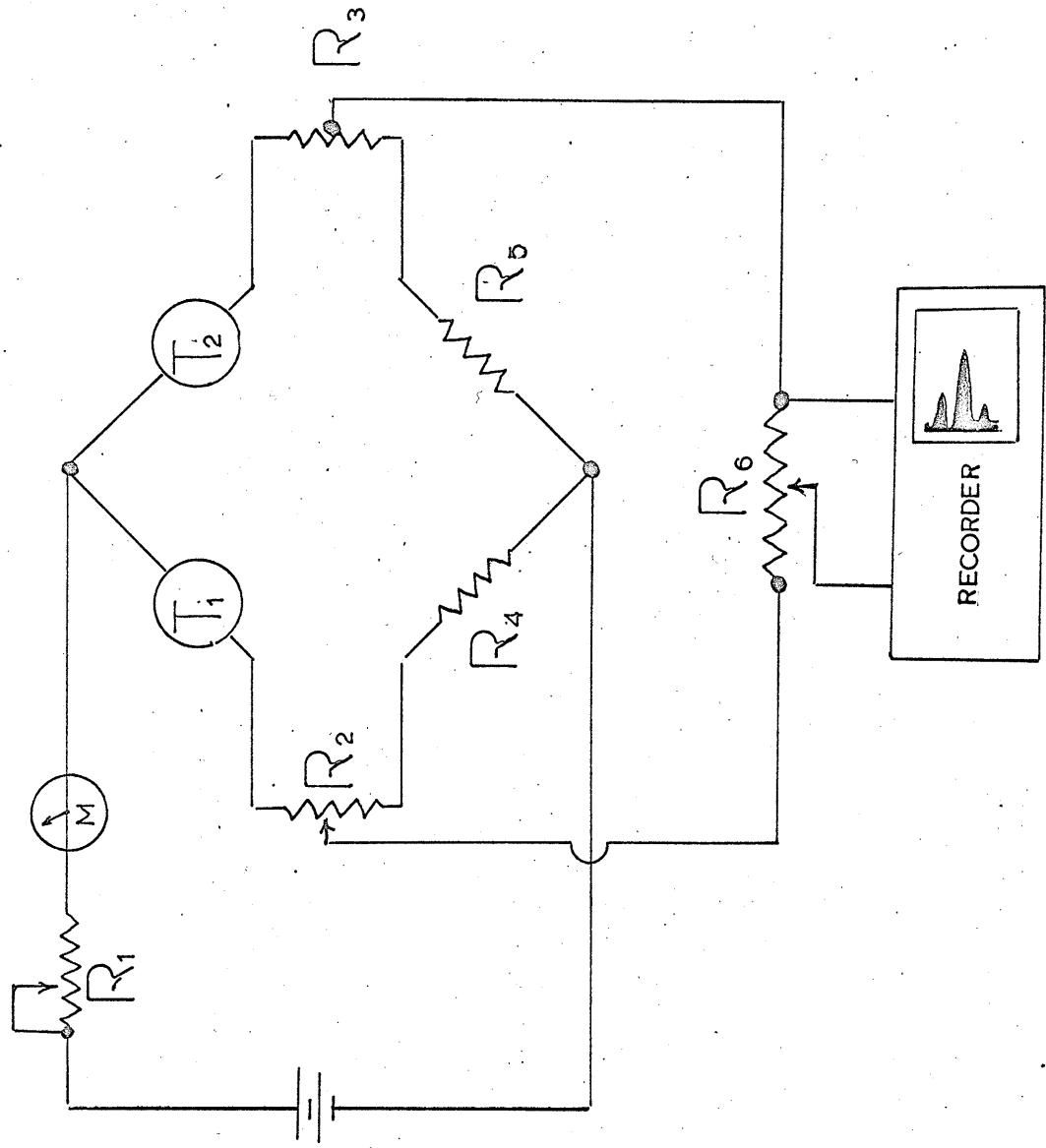
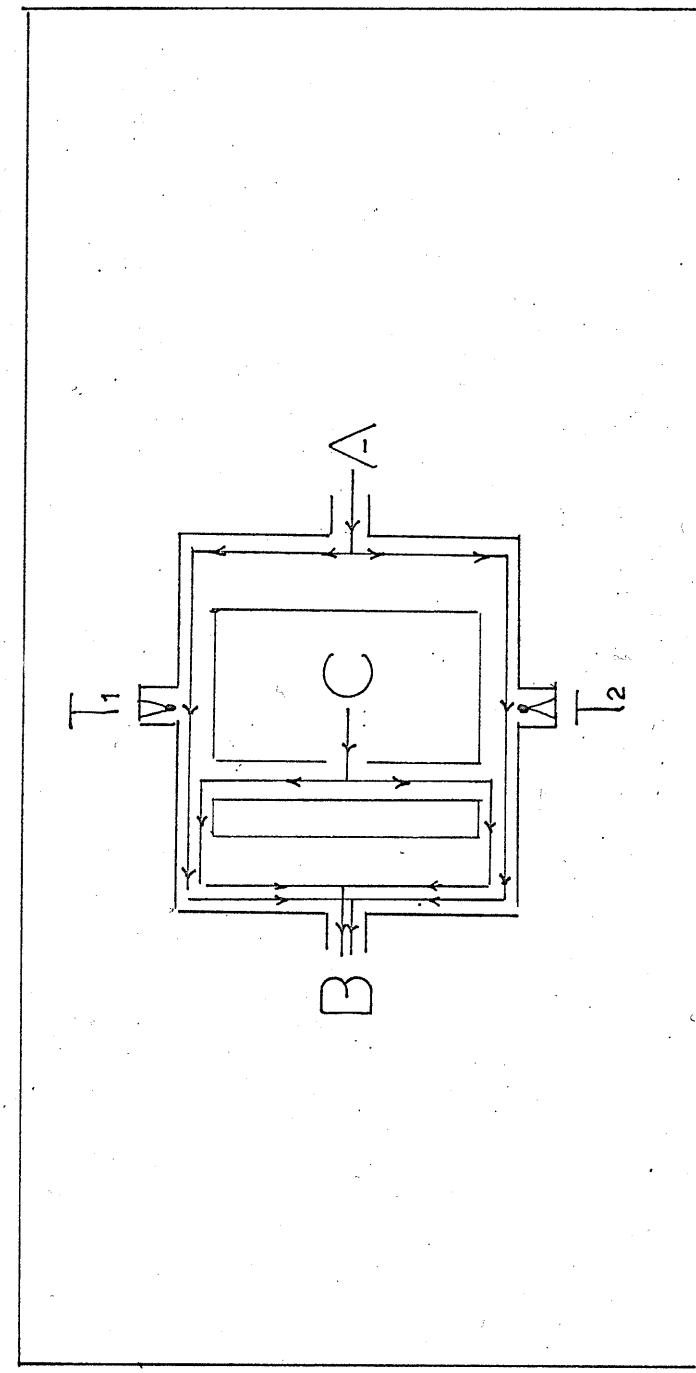


FIGURE 8

Diagrammatic representation of the gas density balance.



shown in Figure 8.

The gas density balance detector requires two streams of gases. One of the streams, the reference gas, enters the detector at point A Figure 8, and is split into an upper and a lower stream, and then exits the detector at point B. The thermistors  $T_1$  and  $T_2$  are placed in the detector such that one is in the upper and the other is in the lower stream of the reference gas. When the flow of the reference gas through the upper and the lower stream is balanced, the thermistors, which are a matched pair, are equally cooled, and there is no off balance in the bridge. The other stream which passes through the chromatographic column, enters the detector in the chamber C, is similarly split into two streams, exits the detector at point B, and is termed as the carrier gas.

When the sample gas (from the chromatographic column) leaves the chamber C, it will also be split into two streams, however, the splitting may occur in three different ways.

- 1) If the sample gas is lighter than the reference and the carrier gas, then the majority of the sample gas will rise and will exit at B via the top loop.
- 2) If the sample gas is of the same density as the reference and the carrier gas, the sample gas will split equally into two streams, and equal amounts of gas will

exit at B via the top and the bottom loop.

3) If the sample gas is heavier than the reference and the carrier gas, the sample gas will split into two streams such that majority of the sample gas will exit B via the lower loop.

In the first case, the rising sample gas will obstruct the flow of the reference gas through the top loop thus forcing more of the reference gas to exit via the bottom loop. For this reason, the top thermistor  $T_1$  will experience heating and the bottom thermistor  $T_2$  will experience cooling. The heating and cooling of thermistors  $T_1$  and  $T_2$  respectively, causes the bridge to become off balance. The degree of the off balance, which is proportional to the sample size and the molecular weight, is measured by the recorder.

A similar situation arises when the sample gas is heavier than the reference and carrier gases. In this case however, thermistor  $T_1$  will cool and thermistor  $T_2$  will heat giving rise to the bridge off balance but in the opposite direction to that of the previous case. As can be seen, positive and negative chromatographic peaks are possible.

In the case where the sample gas is of the same density as the reference and the carrier gas, there will be no

unbalance of the reference stream, and therefore there will be no response from the recorder.

It should be noted that in all three cases mentioned, the sample is never in contact with the detectors.

#### Chromatographic Columns

Of the three columns tried, the 2,5, hexanedione, the hexamethylphosphoramide, and the porous glass, the best columns for the separation of the hydrocarbons were found to be the hexamethylphosphoramide and the porous glass.

#### The Porous Glass Column (50)

The porous glass column was found to be very good for the separation of the lightest hydrocarbons, such as methane, ethane, and ethylene. With the heavier hydrocarbons it was observed that as the molecular weight of the hydrocarbon increased, the peaks broadened, and the retention times became very long. Hydrocarbons such as ethylene but especially acetylene showed considerable tailing. In order to minimize the retention times and the tailing, shorter columns and higher column temperatures were used, but unfortunately under these conditions the separation efficiency of the column was greatly reduced, and the peaks of the majority of the hydrocarbons were found to be too

narrow for accurate area measurements.

#### The Hexamethylphosphoramide (HMPA) Column (51)

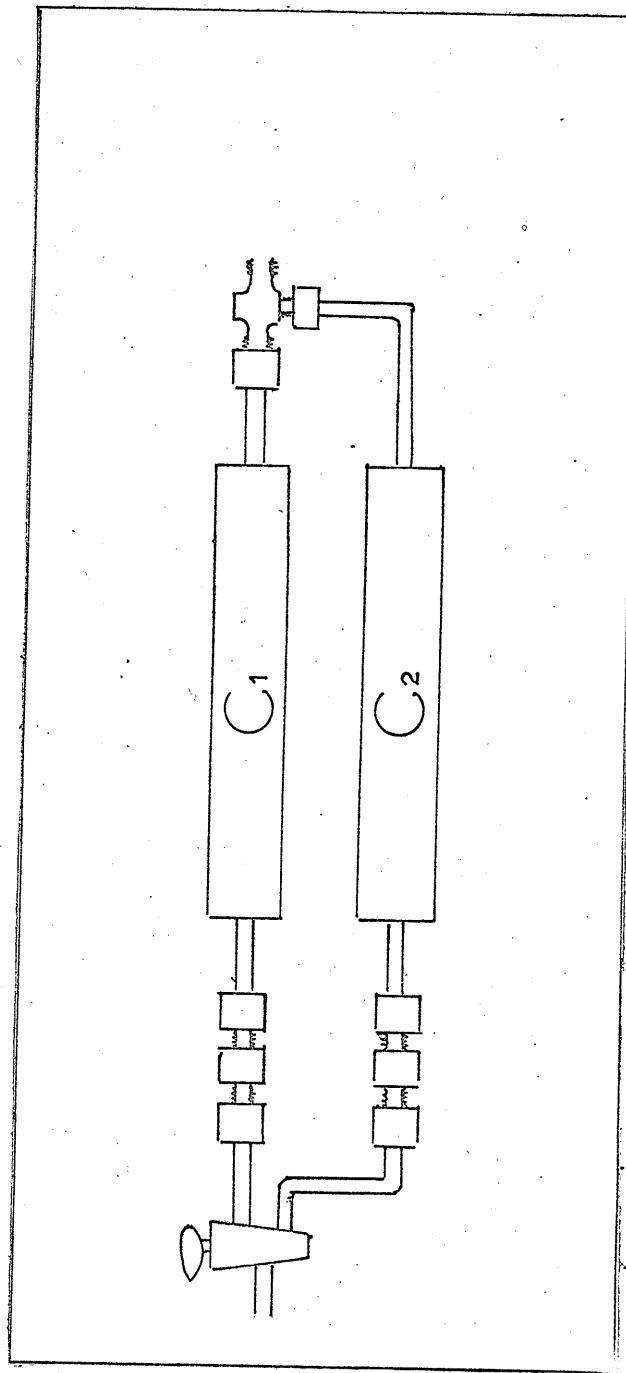
The HMPA column was found to be very good, surpassing the porous glass column. The retention times for all the hydrocarbons were found to be quite reasonable, and the separation was very good for all hydrocarbons except ethane and ethylene. With this column ethane and ethylene generally gave a single peak with a double tip if the concentration of ethane was comparable to that of ethylene or conversely.

After doing some experimentation with the porous glass and the HMPA column, in their additive and mixed properties, it was realized that the best approach to this problem would be to use both of the columns independantly. The HMPA column was therefore used for the separation of all the compounds other than ethane and ethylene, and the porous glass column was used in the separation of ethane and ethylene.

To minimize time consumption by continuously replacing one column by the other, a switching device was devised which is shown in Figure (9). The carrier gas can be made to flow into the three-way stopcock which could select either of the two columns  $C_1$  or  $C_2$  (one being the HMPA column

FIGURE 9

The column switching device.



and the other the porous glass column). The unions between the glass stopcock and the copper tubing of the column were made with Swagelok unions. In order to obtain a better seal between the glass-copper union, teflon front ferrules were used rather than the brass type. These types of unions were found to be excellent, and no leaks were detected up to 50 psig. The columns were joined together at the other end with a Swagelok three-way union, of which the third opening served as a connection between the columns and the detector.

#### Column Specifications

##### 1) The HMPA column

|               |                                     |
|---------------|-------------------------------------|
| Column length | 20 feet                             |
| Tubing size   | 1/4 in. copper                      |
| Packing       | 30% HMPA on 60/80 regular firebrick |

##### 2) The porous glass column

The porous glass obtained from Corning Glass Works, was subjected to heating at  $450^{\circ}$  -  $500^{\circ}$  C. for periods of 1/2 to 1 hour, for degassing purposes.

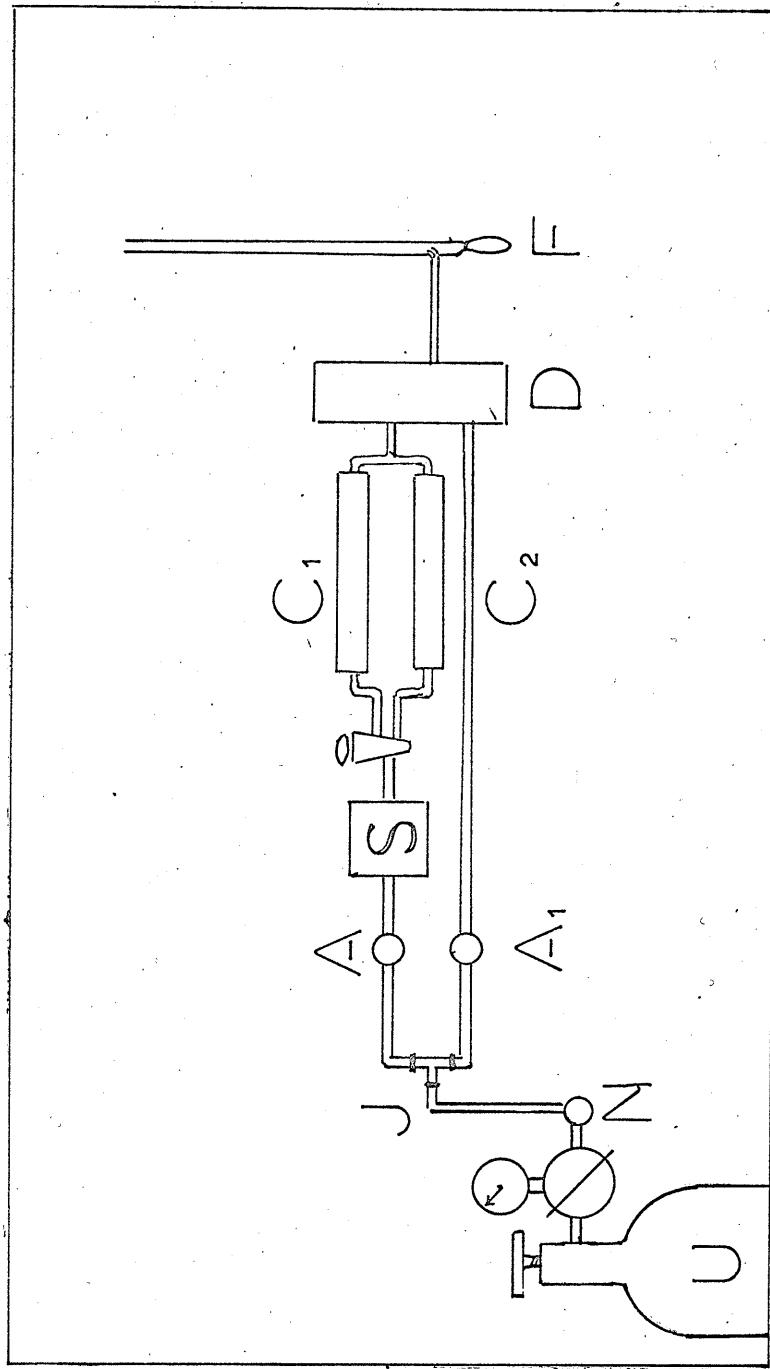
|               |                         |
|---------------|-------------------------|
| Column length | 2 feet                  |
| Tubing size   | 3/16 in.                |
| Packing       | 60/80 mesh porous glass |

The chromatographic system including all the major components is shown in Figure 10.

The carrier and the reference gas used was helium (obtained from Linde Gas). A better choice of gas for this type of detector would have been nitrogen, however, since ethylene has the same molecular weight as nitrogen, nitrogen was not used. Helium gas was passed out of the cylinder through a reducing valve, a needle valve, and into the  $1/8$  inch copper tubing. The copper tubing led to junction J in Figure 10, where the helium stream was split into the carrier and the reference streams. The flow through each stream was regulated very precisely by two Nupro B-2M micrometer needle valves ( $A$ ,  $A_1$ ). The flow through each stream was determined with a soap film flowmeter (F) in the following manner. At first one of the needle valves was turned off completely, and the other needle valve was used to adjust the flow in one of the streams. Having obtained a desired flow rate in that stream as indicated by the soap film flow meter, the other stream was then opened and adjusted to a predetermined flow rate. By knowing the flow rate in one of the streams and the total flow rate through both streams, the flow rate in the other stream could be calculated.

FIGURE 10

Diagram showing the complete chromatographic system.

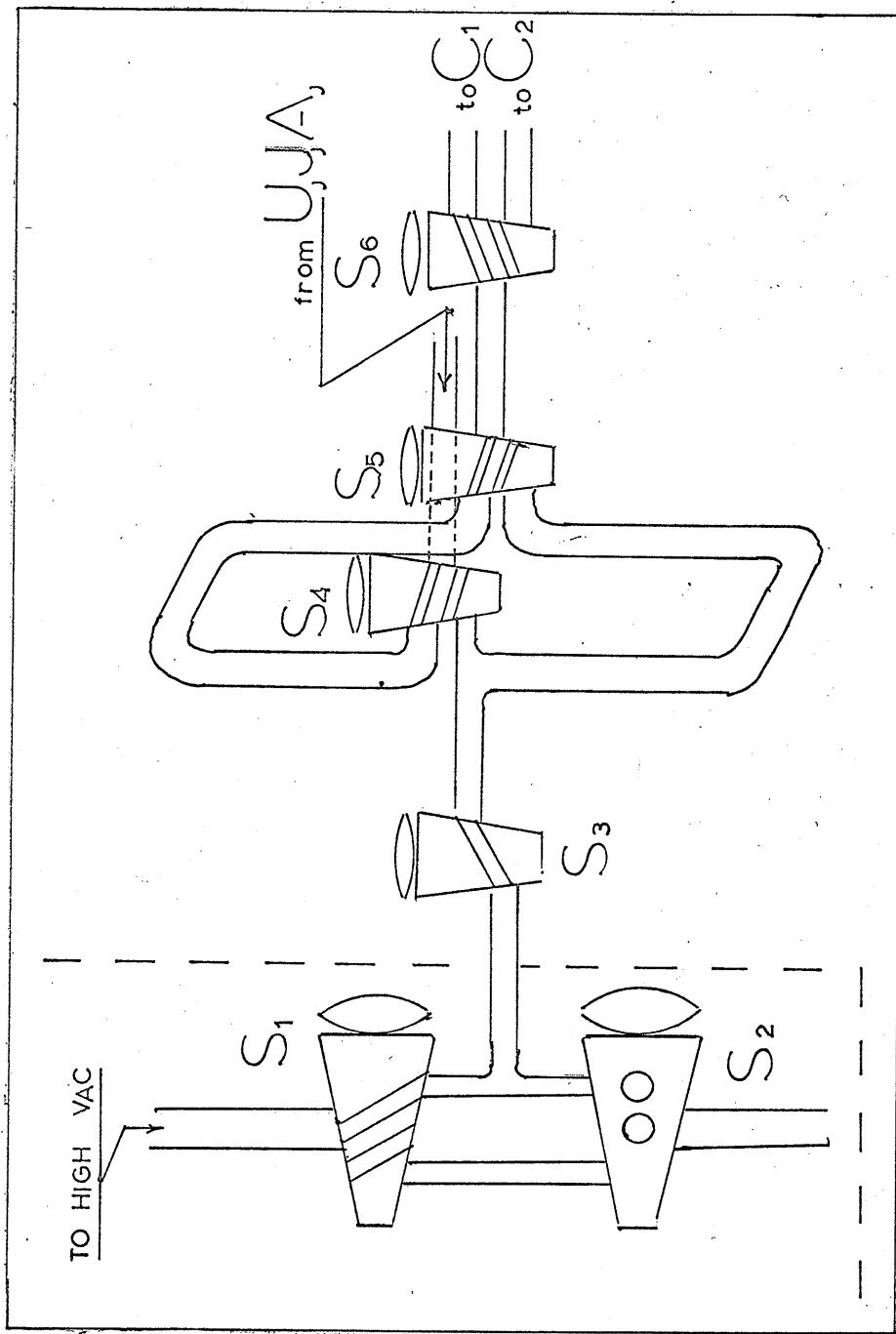


### Sample Injection Method

The sample injection system is shown in Figure (11). The section designated by dashes is part of the Toepler pump of the analysis apparatus. The stopcocks  $S_1$ ,  $S_2$ ,  $S_4$ ,  $S_5$ , and  $S_6$ , are all three way stopcocks. As the stopcocks are positioned in Figure 11, helium carrier gas entered stopcock  $S_4$ , passed through the top loop, left via stopcock  $S_5$ , and entered column  $C_1$ . Stopcock  $S_2$  was in a neutral position. Any gas present in the lower loop was evacuated via stopcocks  $S_1$  and  $S_3$ . After complete evacuation of the lower loop, stopcock  $S_1$  was turned to a neutral position. Stopcock  $S_2$  made it possible to introduce the sample, contained in the Toepler pump, directly into the lower loop. The amount of sample gas was controlled by the Toepler pump. It was possible to introduce all of the condensable sample from the Toepler pump into the lower loop by cooling the lower loop to liquid nitrogen temperature. After a desired quantity of sample had been introduced into the lower loop stopcocks  $S_2$  and  $S_3$  were turned off. By simultaneously switching stopcocks  $S_4$  and  $S_5$  into a  $180^\circ$  position, the carrier gas was rerouted from the upper loop, to the lower loop, and in the process the sample was swept out of the lower loop, through the stopcock  $S_5$  and into the column  $C_1$ .

FIGURE 11

The sample injection system.



or C<sub>2</sub>, depending on the position of stopcock S<sub>6</sub>.

This method of sample injection was found to be excellent. Sample sizes could be reproduced, if desired, by means of the Toepler pump. The sample gas never suffered the possibility of being lost or contaminated, as it was contained in the apparatus up to the time of injection. Provisions were also made for retrapping the sample, but this technique was seldom used.

#### Typical Method Of Analysis

After the reaction had been completed in a manner previously described and the products were isolated in the two traps, the liquid nitrogen was removed from the two traps, and the furnace operating at 184° C. was placed around the silica gel trap T<sub>5</sub> Figure 1. After the analysis apparatus had been evacuated to less than 0.5 microns (generally 0.1 microns), dry ice-acetone slush was placed around trap T<sub>8</sub> and liquid nitrogen was placed around the trap T<sub>10</sub> Figure 6. Stopcock q Figure 6 was then closed and stopcock p was opened. All the other stopcocks in the analysis line were left open such that the line was opened between the main trap T<sub>4</sub> Figure 1 and the stopcock q Figure 6. To insure that no loss of products occurred the products from the main trap were not pulled through the analysis line by opening stopcock q to the high vacuum, but

were allowed to expand into the analysis line up to stopcock q. The products condensable at dry ice-acetone temperature were trapped in trap  $T_8$ , while all the other products passed through trap  $T_8$  and were condensed in trap  $T_{10}$ . The pressure in the main trap (including the reaction zone and the analysis line) was constantly checked with the McLeod gauge. When the pressure in both regions had become negligible (less than a micron) stopcocks p, r, s, and t, were closed. Dry ice-acetone mixture and the liquid nitrogen were removed from the two traps. After a sufficient time was allowed for the products in trap  $T_{10}$  to come to room temperature, the products were then pumped into the Toepler pump where their total pressure-volume data was determined. To insure homogeneity in the product mixture, the products were vigorously expanded and compressed several times in the Toepler pump. A sample of the product mixture was then introduced into the chromatograph using the HMPA column in a manner already described. After all the chromatographic peaks had been obtained, the carrier gas flow was then rerouted into the porous glass column. After base line stability was achieved, a sample was injected into the chromatograph.

The products from the silica gel trap could not be condensed with liquid nitrogen. After evacuation of the trap  $T_{10}$  Figure 6, stopcocks r and q were closed and

stopcock h in Figure 1 was opened. The products in the silica gel trap were allowed to expand through stopcock h, through the line indicated by the letter y in Figures 1 and 6, into trap T<sub>10</sub> and the line of the Toepler pump. The products were then pumped into the Toepler pump where their total pressure-volume data was determined. After mixing of the products, two samples were injected into the chromatograph, one through the HMPA column and one through the porous glass column.

RESULTS AND DISCUSSION

It will be shown shortly, that in order to determine the relative amount of each constituent present in the product mixture, the molecular weight of every constituent must be known. Therefore, before any experimental data could be obtained, it was necessary to identify all the constituents present in the product mixture.

INTERPRETATION OF THE CHROMATOGRAPHIC PEAKS

The chromatograms of the reaction products revealed that approximately eighteen different compounds were present. The relative amounts of the individual constituents fell into three classes:

- a) major
- b) minor
- c) trace

Identification of the Products

The identification of the products was performed in two different ways.

One way was the direct identification; - a comparison of retention times to that of known hydrocarbons. This method was used to identify  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ ,  $n\text{-C}_4\text{H}_{10}$

and iso -  $C_4H_8$ .

An alternative but a more tedious method was the identification by molecular weight determination. The molecular weights were determined with the gas density balance using two different carrier (and reference) gases.

This method will now be described.

The area of the peak (A) multiplied by an area factor

$$\frac{M}{M-C} \quad (50)$$

(where M is the molecular weight of the sample gas, and C is the molecular weight of the carrier gas,) is proportional to the amount of the constituent present in the sample.

For n constituents:

$$\sum_{i=1}^n \frac{M_i A_i}{M_i - C} \quad (51)$$

is proportional to the amount of all constituents.

For any constituent r

$$\frac{\frac{M_r A_r}{M_r - C}}{\sum_{i=1}^n \frac{M_i A_i}{M_i - C}} \times 100 = \% \text{ of constituent } r \text{ in the sample} \quad (52)$$

From expression (50) it is obvious that for n moles of constituent r the following relation holds;

$$\frac{Mr \text{ Ar}}{Mr-C} = nk \quad (53)$$

where k is the proportionality constant.

Similarly, for the same sample size but a different carrier gas,  $C_1$ , the following expression will hold;

$$\frac{Mr \text{ Ar}'}{Mr-C_1} = nk \quad (54)$$

It should be noticed that the two areas represented by Ar and  $\text{Ar}'$ , are different for the two different carrier gases. Since both expressions (53) and (54) are equal to nk, then they can be equated to give the following expression;

$$\frac{Mr \text{ Ar}'}{Mr-C_1} = \frac{Mr \text{ Ar}}{Mr-C} \quad (55)$$

If the sample size in the case of carrier gas C contains n moles of constituent r, and if the sample used with the carrier gas  $C_1$  is K times the size of the former sample, then the number of moles of constituent r present in the latter sample is Kn moles, if both samples have identical composition. The relation (55) then becomes;

$$\frac{Mr \text{ Ar}'}{Mr-C_1} = K \frac{Mr \text{ Ar}}{Mr-C} \quad (56)$$

A similar relationship exists for any constituent i.

By knowing the molecular weight of any one of the n

constituents, and the areas for the two different carrier gases, it is possible to evaluate K. Once K has been obtained the molecular weights of all the other constituents can be determined, since  $A_i$ ,  $A_i'$ , C,  $C_1$ , and K are all known quantities. Other methods of molecular weight determination have been described by Phillips and Timms (52).

In the present study the two sets of carrier gases used were;

|    |       |       |
|----|-------|-------|
| 1) | He    | $C_1$ |
|    | $N_2$ | C     |
| 2) | He    | $C_1$ |
|    | Ar    | C     |

The best results were obtained when He and Ar were used as C and  $C_1$  respectively.

After a reaction had been completed the products from the main trap were transferred to the Toepler pump where they were mixed by recirculation through traps  $T_{10}$ ,  $T_{11}$ , and  $T_{12}$  of Figure 6, to insure homogeneity of the product mixture. Although identical sample sizes could have been introduced into the chromatograph using two different carrier gases, this was found to be disadvantageous. It was observed that the detector showed a much greater response to samples with argon as the carrier gas than with helium as the carrier gas. A certain size sample, which gave reasonable peak areas using argon as the carrier gas,

gave peak areas which were very small and too unreliable for molecular weight determination when helium was used as the carrier gas. If the sample size was increased to improve the peak areas in the helium case, the peaks associated with argon were found to be so large that the majority of them were off scale. This problem was solved by using different sized samples for the two carrier gases.

Although it is possible to determine the molecular weights using the gas density balance, it is not possible, however, to distinguish between isomeric forms of various compounds. Even if exact molecular weight determinations were possible, the question would still arise as to which compound or isomer is a certain molecular weight associated with. For example, two different compounds such as methyl-acetylene and allene have the same molecular weight of 40 grams/mole, and the three isomers of butene have a molecular weight of 56 grams/mole. To differentiate between compounds of the same molecular weight, methods other than molecular weight determination had to be employed. One method was the direct identification by comparison of retention times to known compounds.

Samples of isobutylene, butene-1, cyclopropane, and n-butane were injected into the chromatograph, in order to determine by direct comparison whether the reaction products contained any of these compounds. From the

chromatograms of the above mentioned compounds, it was observed that cyclopropane had almost the same retention time as n-butane, and that butene-1 had almost the same retention time as isobutylene. Although the four compounds gave only two double tipped peaks, it was observed that cyclopropane had a slightly shorter retention time than n-butane and that butene-1 had a slightly shorter retention time than isobutylene. A chromatogram of the reaction products showed that there existed a peak in the cyclopropane - n-butane position marked \* in Figure 12, and that there existed a peak in the butene-1 - isobutylene region marked \*\* in Figure 12.

To complicate matters, it was observed that the HMPA column had a tendency to age, that is, it gave longer retention times with use.

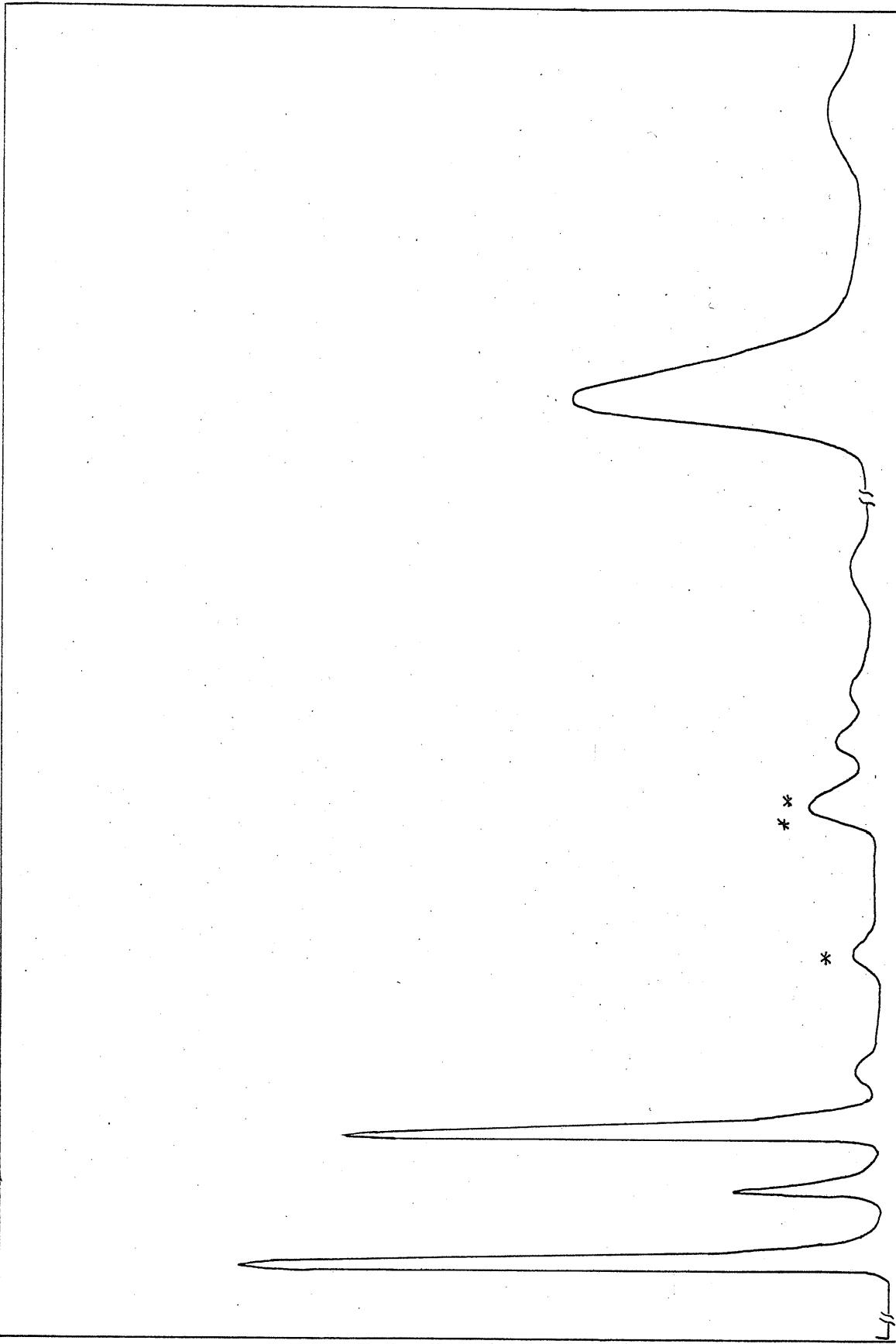
The peak associated with the cyclopropane - n-butane region, did not coincide with either cyclopropane nor with n-butane but was found to be somewhere between the two peaks. A similiar situation was found to exist in the butene-1 - isobutylene region.

The problem was resolved in the following way;

#### Cyclopropane - n-butane Region

When larger sample sizes were used it was observed that the single peak was preceded by a very small peak which

FIGURE 12  
Chromatogram of the main trap products.



with smaller samples was not observed. The slight difference between the retention times of the two peaks was comparable to the difference between the retention times of cyclopropane and n-butane peaks. The smaller peak was assigned to be cyclopropane on the following grounds:

- a) the position relative to n-butane peak
- b) when argon was used as the carrier gas, this peak

had almost vanished, thus indicating a molecular weight very close to 40 grams/mole

The large peak was assigned to be n-butane on the following grounds:

- a) from the comparison of retention time with a known sample
- b) from the comparison of the relative retention time to that obtained by McEwen (51)
- c) the molecular weight determination using the gas density balance, showed this compound to have a molecular weight of 56 grams/mole.

#### Butene-1 - Isobutylene Region

Similarly, by using larger samples, a small peak was observed, which preceded the large peak and the difference of the retention time was comparable to the difference of retention time of butene-1 and isobutylene as

found from the known sample. The small peak was assigned to be butene-1 and the large peak was assigned to be iso-butylene.

The identification of the remaining constituents was performed in the following manner. First of all the molecular weights were determined with the gas density balance. The molecular weights calculated in this way are given in Table 1. The numbers corresponding to the peaks are shown in Figure 13.

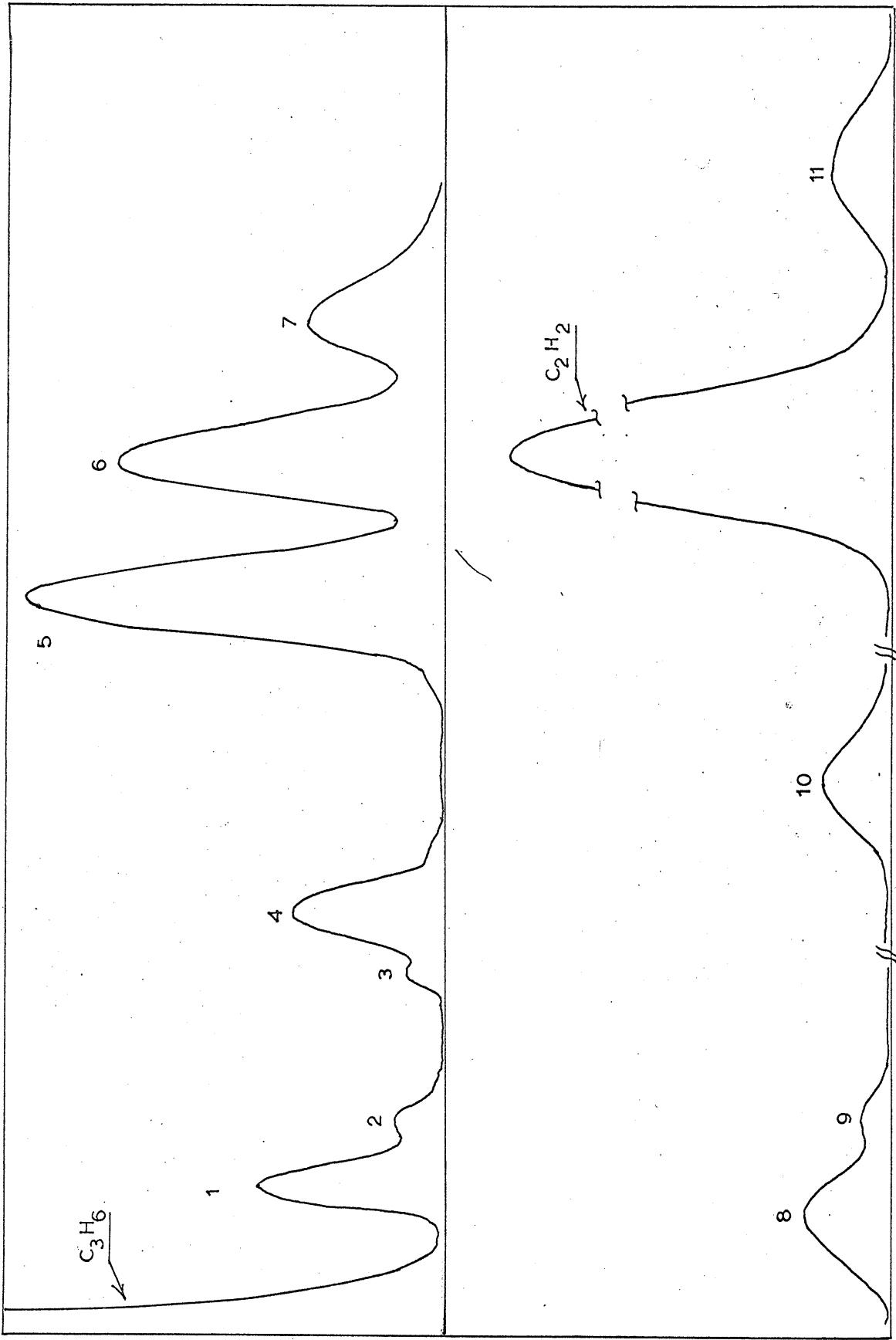
TABLE 1  
Calculated molecular weights

| Peak No. | Area *<br>He Carrier | Area *<br>Ar Carrier | Molecular Weight<br>(grams/mole) |
|----------|----------------------|----------------------|----------------------------------|
| 1        | 45                   | 107                  | 60                               |
| 2        | 12                   | 37                   | 72                               |
| 3        | 12                   | ~0                   | ~40                              |
| 4        | 51                   | 106                  | 56                               |
| 5        | 260                  | 525                  | 56 **                            |
| 6        | 174                  | 0                    | 40                               |
| 7        | 65                   | 95                   | 50                               |
| 8        | 41                   | 89                   | 57                               |
| 9        | 20                   | 67                   | 77                               |
| 10       | 89                   | 139                  | 51                               |

\* Arbitrary units    \*\* Isobutylene as standard Mol. Wt.

## FIGURE 13

Portion of a chromatogram showing the peaks whose molecular weights have been determined with the gas density balance.



The reference peak used for the evaluation of the molecular weights of the other constituents was that of isobutylene. This constituent had been previously identified and it was found to yield the largest peak of the minor constituents, with both the Ar and He carrier gases. A large peak area is desirable with both carrier gases, as this minimizes the error in the calculation of the proportionality constant K.

The method of identification with reference to Figure 13 will now be given.

#### Peak #3

This peak was previously determined to be cyclopropane. The molecular weight as calculated was found to be 40 grams/mole which agrees quite reasonably with the actual value of 42 grams/mole.

#### Peak #4

This peak was previously determined to be n-butane, and the molecular weight as calculated was found to be 56 grams/mole which agrees quite reasonably with the actual value of 58 grams/mole.

#### Peak #1

From the relative retention times as reported by McEwen (51), this peak appeared to be i-butane. The calculated molecular weight for this compound was found to be 60 grams/mole which confirms this peak to be i-butane.

It should be mentioned that this peak of necessity must be i-butane, as no other hydrocarbons of C<sub>2</sub> or C<sub>3</sub> except allene are possible in this region. From the characteristics of the HMPA column, it was observed that the branched compounds always preceded the linear compounds, and the cyclic compounds, for example cyclopropane, were found to follow the linear compounds. Since there are only two non-cyclic butanes possible, this peak would have to correspond to i-butane.

#### Peak #6

This peak has a molecular weight of 40 grams/mole. When He was used as the carrier gas the area of this peak was found to be approximately 0.7 times the size of the isobutylene peak area. However, when Ar was used as the carrier gas, this peak had entirely disappeared. This would require the compound to be C<sub>3</sub>H<sub>4</sub>. The only three possibilities are cyclopropene, allene, and methyl-acetylene. Since cyclopropene is not stable at room temperature, this possibility was eliminated. It was observed that acetylene was one of the last peaks in the chromatogram, therefore, methylacetylene could not be the constituent associated with peak #6. The only remaining possibility is allene, and therefore peak #6 was assigned to be allene.

### Peak #7 and #8

From the relative retention time comparison with the work done by McEwen, these two peaks were determined to be trans-butene-2 and cis-butene-2 respectively. The molecular weight of 56 grams/mole, as was determined with the gas density balance, indicated that peak #8 was a butene. However, a calculated molecular weight of 50 grams/mole for peak #7, did not agree that this compound was a butene. To determine whether the peaks #7 and #8 were the two butenes, a small quantity of the two compounds was prepared by dehydration of sec-butyl alcohol (53). The prepared butenes were injected into the chromatograph. Although the concentrations were very small, their retention times agreed very well with the retention times of peaks #7 and #8, and with the relative retention times obtained by McEwen. From these observations, peaks #7 and #8 were assigned to be trans-butene-2 and cis-butene-2 respectively. The discrepancy in the determined molecular weight associated with peak #7 is not obvious.

### Peak #9

The molecular weight of 77 grams/mole as determined with the gas density balance, indicated this peak to be a pentane. A comparison of relative retention times with McEwen's work showed that this peak could be due to i-pentane. A comparison of retention times with a known

sample of i-pentane showed that the two retention times were not quite the same. Although there was a strong possibility that this peak was due to i-pentane, no assignment was made, as this constituent was only of trace quantity and did not appear in normal chromatograms. In order to clarify the term normal chromatograms, the author wishes to point out that in the molecular weight determination process, large samples were used and that peaks due to ethane-ethylene mixture, propane, and propylene were all off scale. A normal chromatogram refers to a chromatogram in which no peaks are off scale, and with which quantitative calculations were made.

#### Peak #10

A comparison of relative retention times of this peak with relative retention times obtained by McEwen, indicated this peak to be either n-pentane or 1, 3-butadiene since McEwen was not able to separate those two compounds. A comparison of the retention time of this peak with a retention time obtained from a sample of n-pentane, showed that peak #10 had longer retention time than n-pentane. The following two facts indicated that peak #10 was due to 1,3 butadiene;

- a) The retention time of peak #10 is not that of n-pentane

b) The molecular weight 51 grams/mole indicates a C<sub>4</sub> rather than C<sub>5</sub> species, and agrees reasonably well with the actual molecular weight of 1,3-butadiene which is 54 grams/mole.

#### Peak #2

Molecular weight calculation showed this compound to have a molecular weight of 72 grams/mole. The only pentane possible in this region is 2,2-dimethylpropane. The peak #2 appears just past i-butane, and 2,2-dimethylpropane appears just past n-butane, therefore, peak #2 could not be 2,2-dimethylpropane. Since this product was only a trace quantity, and did not appear in normal chromatograms, no further work was done to determine its positive identity.

#### Peak #11

The last peak observed on the chromatogram was established to have a molecular weight of 40 grams/mole. from other work using He and N<sub>2</sub> as the carrier gases. Its position in the chromatogram was just past acetylene. With the aging of the column, the acetylene peak drifted towards peak #11 until in the last phases of work, the acetylene peak completely overshadowed peak #11. From its close relation to acetylene and from its calculated molecular weight of 40 grams/mole, peak #11 was assigned to be methyl-acetylene.

A product which was found in a quantity too small to

be measured individually was obtained from the dry ice-acetone trap. This product was collected from every reaction so that enough could be obtained for its identity. Chromatographic and I.R. analysis both proved this product to be cyclohexane.

Other products in trace quantity were found to be;

- a) 2,2-dimethylpropane
- b) 1-pentene

Products of sub-trace quantities were not identified.

#### QUANTITATIVE DETERMINATION OF THE PRODUCTS

From each reaction the quantity of products found in the silica gel trap and in the main trap was calculated from the pressure - volume data, using the Ideal Gas Equation;

$$PV = nRT \quad (49)$$

where  $n$  in this case represented the total number of moles; that is for  $m$  constituents

$$\sum_{i=1}^m n_i = n \quad (58)$$

The total number of moles of the products formed during the reaction is the sum of the number of moles found in the silica gel trap plus the total number of moles found in the main trap.

It was found that the main trap contained all the compounds except methane. In order to determine how much of each compound was present, the following procedure was used:

a) After all the compounds had been identified, it was then possible to determine the area factors ( $\frac{M}{M-C}$ ) for each compound.

b) All peak areas were then measured very carefully with a planimeter.

c) By knowing  $n$  (eqn (58)) it was possible to determine the quantity of each constituent by the following equation;

$$\frac{\frac{Mr}{Mr-C}}{\sum \frac{Mi}{Mi-C} Ai} xn = n_r \quad (59)$$

where  $n_r$  is the number of moles of constituent  $r$  present in the main trap.

The rate of formation of compound  $r$  was obtained by the following expression;

$$n_r/t = n'_r \quad (60)$$

where  $t$  is the duration of the experiment in minutes, and  $n'_r$  is expressed in  $\mu\text{moles}/\text{min.}$

## Silica Gel Trap Products

The only product expected in the silica gel trap was methane, however, ethane and ethylene were also found. The quantities of ethane and ethylene found in the silica gel trap were much greater than that found in the main trap. Table 2 shows the ethane and the ethylene distribution in the two traps.

TABLE 2

Ethane and Ethylene distribution between the Silica Gel and the Main trap

| Reaction | $C_2H_4$  |            | $C_2H_6$  |            |
|----------|-----------|------------|-----------|------------|
|          | Main Trap | Silica Gel | Main Trap | Silica Gel |
| 1        | 290       | 470        | 87        | 190        |
| 2        | 77        | 1710       | 540       | 370        |
| 3        | 370       | 2340       | 940       | 500        |
| 4        | 1040      | 3060       | 1730      | 780        |

Units -  $\mu$ moles  $\times 10^3$ /min.

The reason for such a large carry over is not clear since care was always taken to insure sufficient cooling of the main trap prior to reactions. Insufficient cooling is definitely not the answer. The possibility that the liquid nitrogen was contaminated with some oxygen giving rise to liquid air of slightly higher temperature was excluded on

the grounds of observed temperatures as indicated by a low temperature thermometer, however, the accuracy of the thermometer could be questioned. Other workers (54, 55) did not observe any carry over of ethane from their main trap into the silica gel trap even when they used hydrogen flow rates which were over ten times greater than those used in the present work.

The same degree of carry over was observed when traps  $T_6$  and the main trap were cooled to liquid nitrogen temperature. However, by cooling the main trap to solid nitrogen temperature, no carry over was observed.

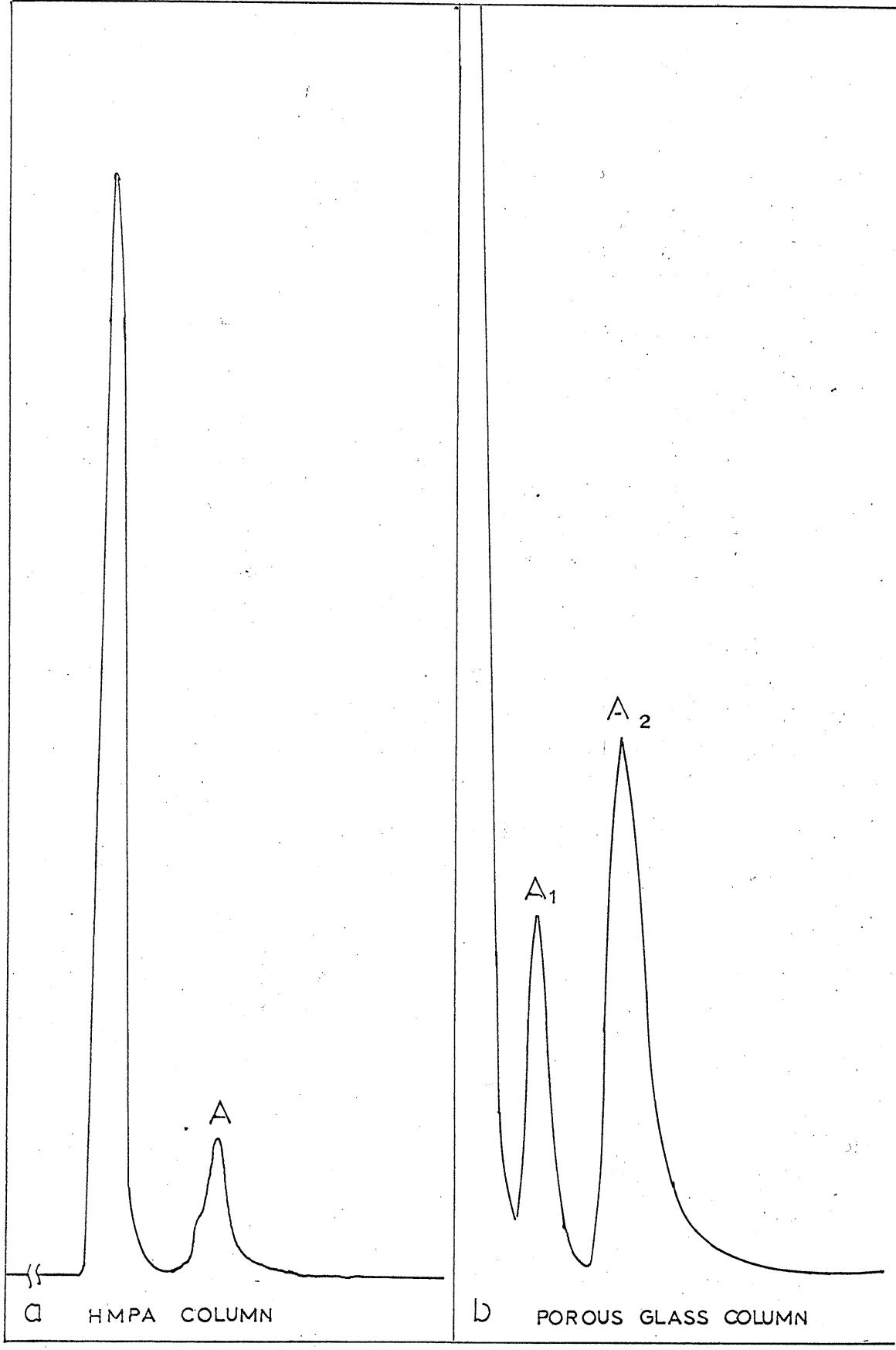
One point still remains to be clarified. As was mentioned previously, the inability of the HMPA column to separate ethane and ethylene was compensated by the use of the porous glass column. As ethane and ethylene were found in both traps, each experiment would have associated with it four chromatograms. The determination of the quantity of ethane and ethylene in each experiment was carried out by the following procedure (with reference to the products in the silica gel trap, however, similar procedure was followed for the main trap products).

From the chromatogram, using the HMPA column, Figure 14a, the combined peak area of  $C_2H_6$  and  $C_2H_4$  was determined and was designated by a value A. From the chromatogram using the porous glass column, Figure 14b individual peak areas

FIGURE 14

Chromatograms of the silica gel products

- a) HMPA column
- b) Porous glass column.



of  $C_2H_6$  and  $C_2H_4$  were determined and were designated by values  $A_1$  and  $A_2$  respectively. From the values of  $A_1$  and  $A_2$  it was possible to determine the peak area value of  $C_2H_6$  and  $C_2H_4$  in A by the following equations:

$$(A_1/A_1+A_2) \times A = A(C_2H_6) \quad (61)$$

$$(A_2/A_1+A_2) \times A = A(C_2H_4) \quad (62)$$

From values obtained by equations (61) and (62) it was then possible to determine the quantities of  $C_2H_6$  and  $C_2H_4$  from the following equation:

$$\frac{\frac{M(C_2H_6)}{M(C_2H_6)-C} \times A(C_2H_6) \times n}{\sum \frac{Mi}{Mi-C} \times Ai} = n(C_2H_6) \quad (63)$$

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$$\frac{\frac{M(C_2H_4)}{M(C_2H_4)-C} \times A(C_2H_4) \times n}{\sum \frac{Mi}{Mi-C} \times Ai} = n(C_2H_4) \quad (64)$$

where  $M(C_2H_6)$  and  $M(C_2H_4)$  refer to molecular weight of  $C_2H_6$  and  $C_2H_4$  respectively,  $A(C_2H_6)$  and  $A(C_2H_4)$  are the evaluated areas from (61) and (62) of  $C_2H_6$  and  $C_2H_4$  respectively, C is the molecular weight of the carrier gas. Quantities  $n(C_2H_6)$  and  $n(C_2H_4)$  refer to the number of moles of  $C_2H_6$  and  $C_2H_4$  found in the silica gel trap.

Similarly the values  $n'(C_2H_6)$  and  $n'(C_2H_4)$  were determined for the main trap. Summation of  $n(C_2H_6) + n'(C_2H_6)$  and of  $n(C_2H_4) + n'(C_2H_4)$  gave the total amount of  $C_2H_6$  and  $C_2H_4$  respectively found in the reaction products.

#### FLOW RATE VARIATION

The first set of reactions (#1-4) were done with a constant voltage and varying flow rates of hydrogen. The voltage across the electrodes, as calculated, was approximately 1,090 volts A.C. The hydrogen flow rate study was limited to a rather small range. This range was governed at the lower end by the hydrogen pressure below which no discharge would take place, and the upper range limit was governed by the transition of silent discharge to an arc discharge.

The data from the four experiments are tabulated in Table 3. From first observation it is possible to see that the total number of products/min increases with the hydrogen flow rate. A plot of total number of moles of products/min against the hydrogen flow rate, Figure 15, shows that the increase is not directly proportional. However, a plot of total number of moles of products against the square root of hydrogen flow rate (Figure 16) shows a more direct dependance. It should be pointed out that the relation of the total number of moles/min to the

TABLE 3  
Hydrogen Flow Rate Variation Experiments

| Exp.<br>No.                        | 1                             | 2                            | 3                             | 4                             |
|------------------------------------|-------------------------------|------------------------------|-------------------------------|-------------------------------|
| H <sub>2</sub> Flow                | 9.25x10 <sup>2</sup>          | 18.75x10 <sup>2</sup>        | 30.80x10 <sup>2</sup>         | 49.86x10 <sup>2</sup>         |
| H <sub>2</sub> Pres.               | 0.432 mm.                     | 0.700 mm.                    | 0.995 mm.                     | 1.463 mm.                     |
| Total<br>Prod.                     | 5,242                         | 16,924                       | 26,394                        | 39,672                        |
| React.<br>Time                     | 20 min.                       | 12.37 min.                   | 8 min.                        | 5 min.                        |
| Product                            | umoles<br>(x10 <sup>3</sup> ) | Rel.%<br>(x10 <sup>3</sup> ) | umoles<br>(x10 <sup>3</sup> ) | umoles<br>(x10 <sup>3</sup> ) |
| CH <sub>4</sub>                    | 2,770                         | 52.85                        | 9,491                         | 56.08                         |
| C <sub>2</sub> H <sub>2</sub>      | 982                           | 18.73                        | 2,713                         | 16.03                         |
| C <sub>2</sub> H <sub>4</sub>      | 501                           | 9.56                         | 1,784                         | 10.54                         |
| C <sub>2</sub> H <sub>6</sub>      | 274                           | 5.23                         | 906                           | 5.35                          |
| C <sub>3</sub> H <sub>4</sub>      | 65                            | 1.24                         | 154                           | 0.91                          |
| CH <sub>3</sub> -C <sub>2</sub> H  | 86                            | 1.64                         | 288                           | 1.70                          |
| C <sub>3</sub> H <sub>6</sub>      | 264                           | 5.04                         | 748                           | 4.42                          |
| C <sub>3</sub> H <sub>8</sub>      | 86                            | 1.64                         | 276                           | 1.63                          |
| i C <sub>4</sub> H <sub>8</sub>    | 86                            | 1.64                         | 254                           | 1.50                          |
| t C <sub>4</sub> H <sub>8</sub> -2 | 28                            | 0.53                         | 71                            | 0.42                          |
| c C <sub>4</sub> H <sub>8</sub> -2 | 26                            | 0.49                         | 71                            | 0.42                          |
| i C <sub>4</sub> H <sub>10</sub>   | 16                            | 0.30                         | 58                            | 0.34                          |
| n C <sub>4</sub> H <sub>10</sub>   | 43                            | 0.81                         | 91                            | 0.54                          |
| 1,3 C <sub>4</sub> H <sub>6</sub>  | 16                            | 0.30                         | 21                            | 0.12                          |
|                                    |                               |                              | 154                           | 0.58                          |
|                                    |                               |                              | -                             | -                             |

\* umoles/min

With reference to Table 3;

i - iso

t - trans

c - cis

n - normal

The total products as given in Table 3, are in units  $\mu\text{moles} \times 10^{-3}/\text{min}$ . The values given are the calculated values having a maximum deviation of  $\pm 80 \mu\text{moles} \times 10^{-3}/\text{min}$ .

The maximum percent deviation for all the constituents was calculated to be  $\pm 0.04\%$ .

FIGURE 15

A plot of the rate of the total products formation  
versus the hydrogen flow rate.

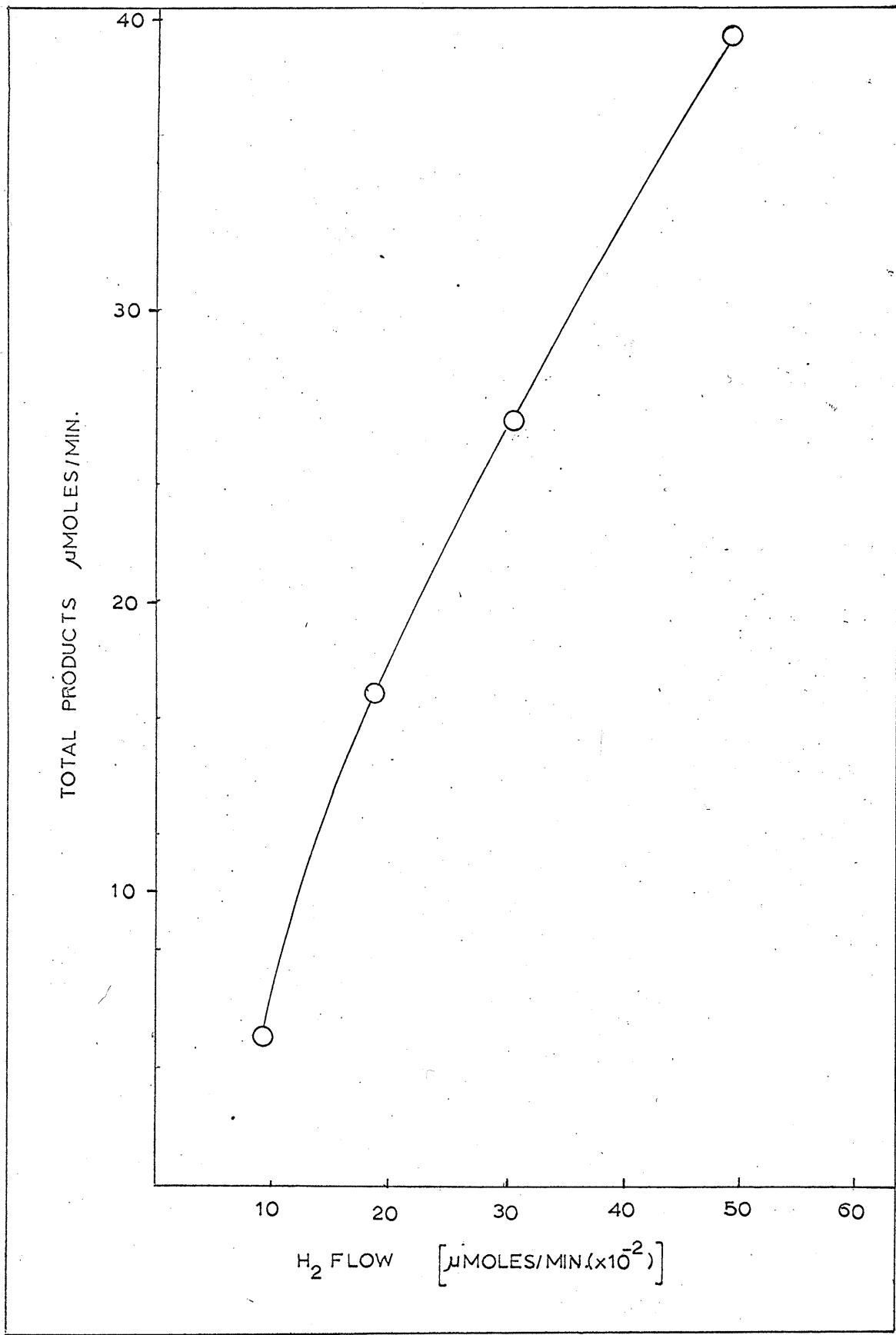
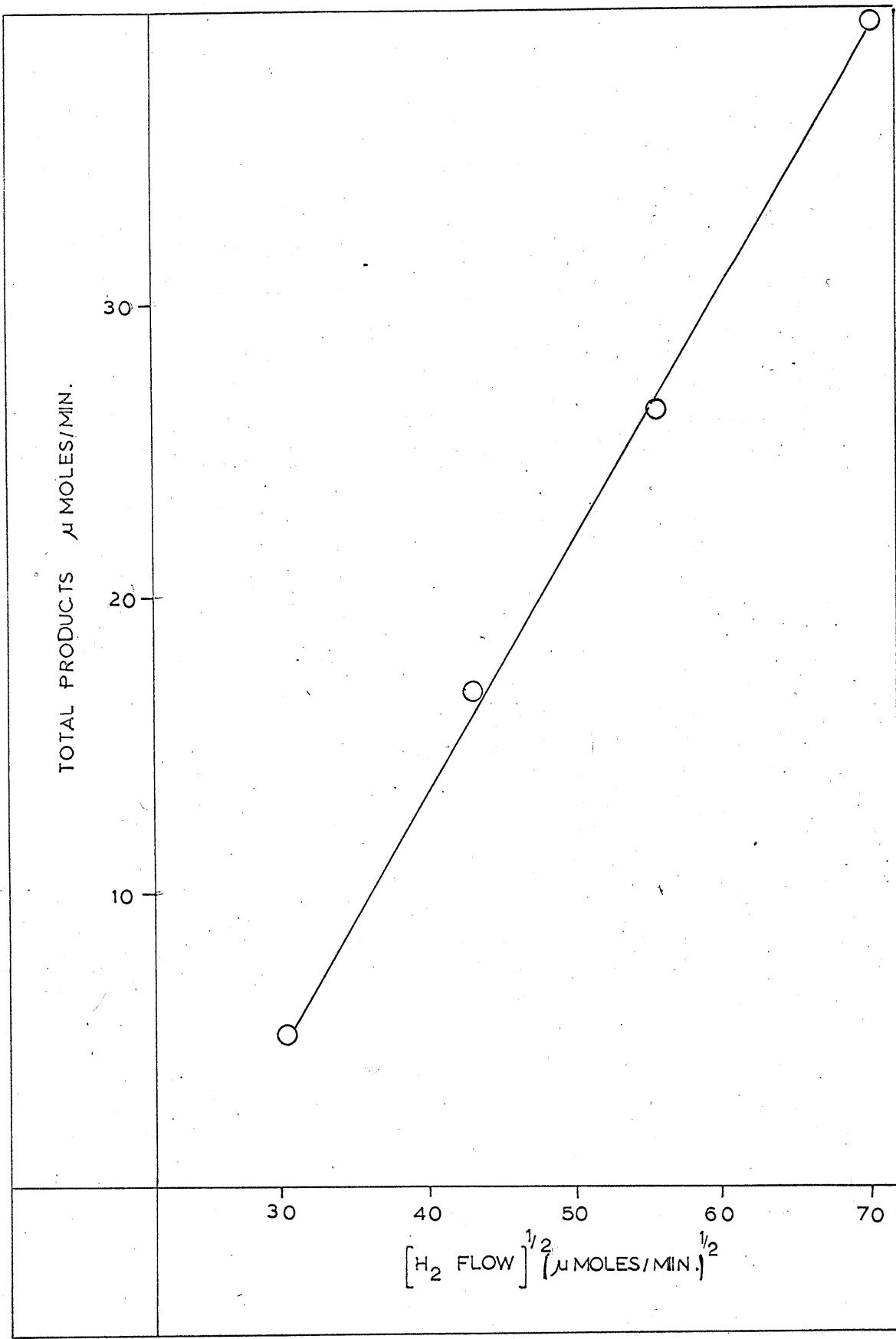


FIGURE 16

A plot of the rate of the total products formation  
versus the square root of the hydrogen flow rate.



hydrogen flow rate, will be strongly biased by the methane, and its relation to the hydrogen flow rate, as methane was found to be the major product exceeding 50%.

At this point it was found convenient to designate the rate of formation of constituent r by  $R(r)$ , and from now on,  $R(r)$  will refer to the number of moles of constituent r per minute.

A plot of  $R(CH_4)$  against  $H_2$  flow rate, Figure 17, gives a similiar relationship as Figure 15. The plot of  $R(CH_4)$  against square root of hydrogen flow rate gives a straight line plot, Figure 18. The square root relation is not obvious. It is possible that the variation of hydrogen flow rate does not directly affect the rate of methane formation. The observed relation between the rate of hydrogen flow rate and the rate of methane formation may be due to a relation between hydrogen flow rate and the rate of formation of some reactive species which undergo further reactions to give methane as the final product. If these reactive species are carbon atoms, then their formation could be rationalized in two ways.

- 1) Carbon atoms arising from graphite due to the vapour pressure of graphite.
- 2) Carbon atom formation arising from impact of electrodes, or some highly energetic hydrogen species on the graphite electrodes.

FIGURE 17

A plot of the rate of methane formation  
versus the hydrogen flow rate.

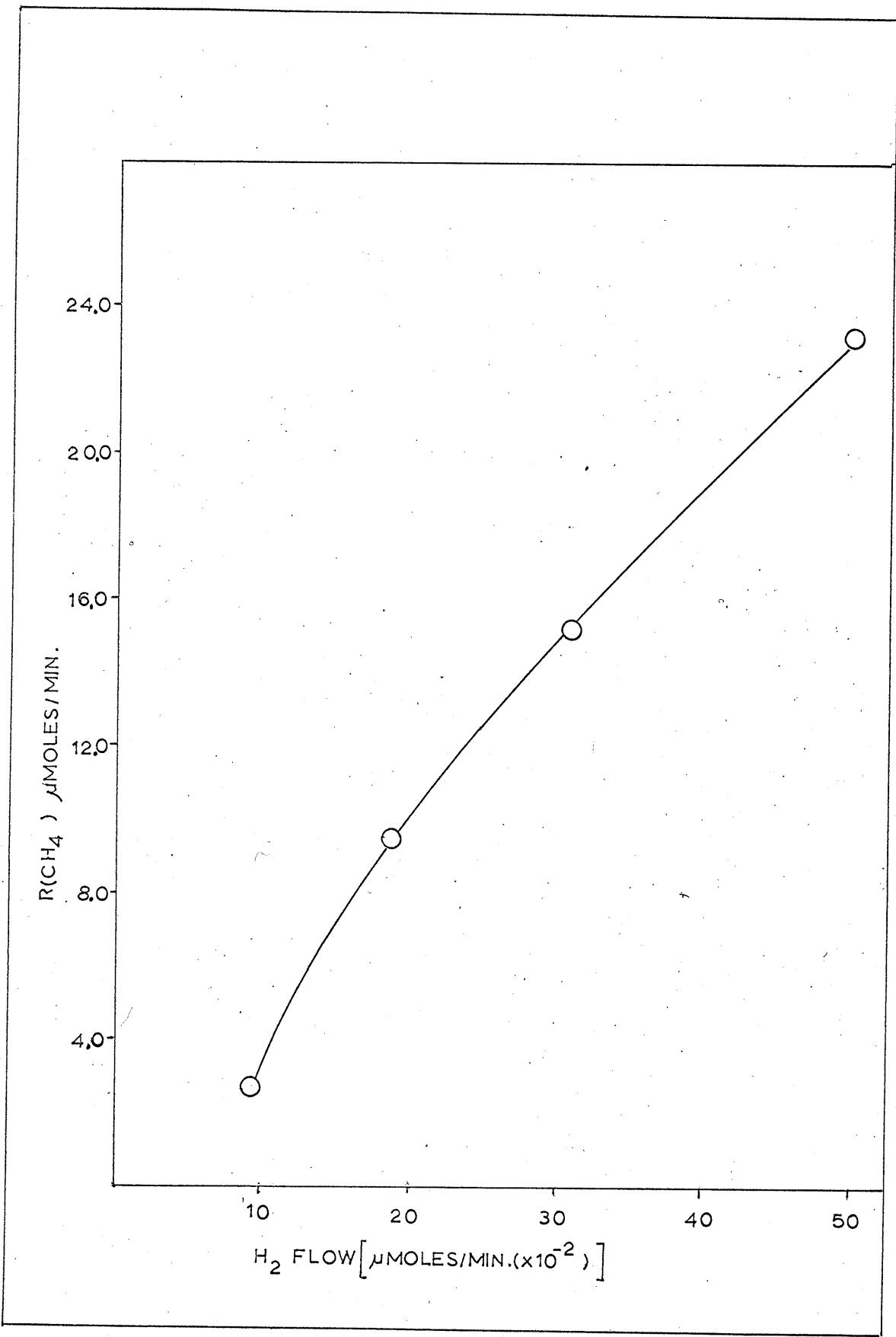
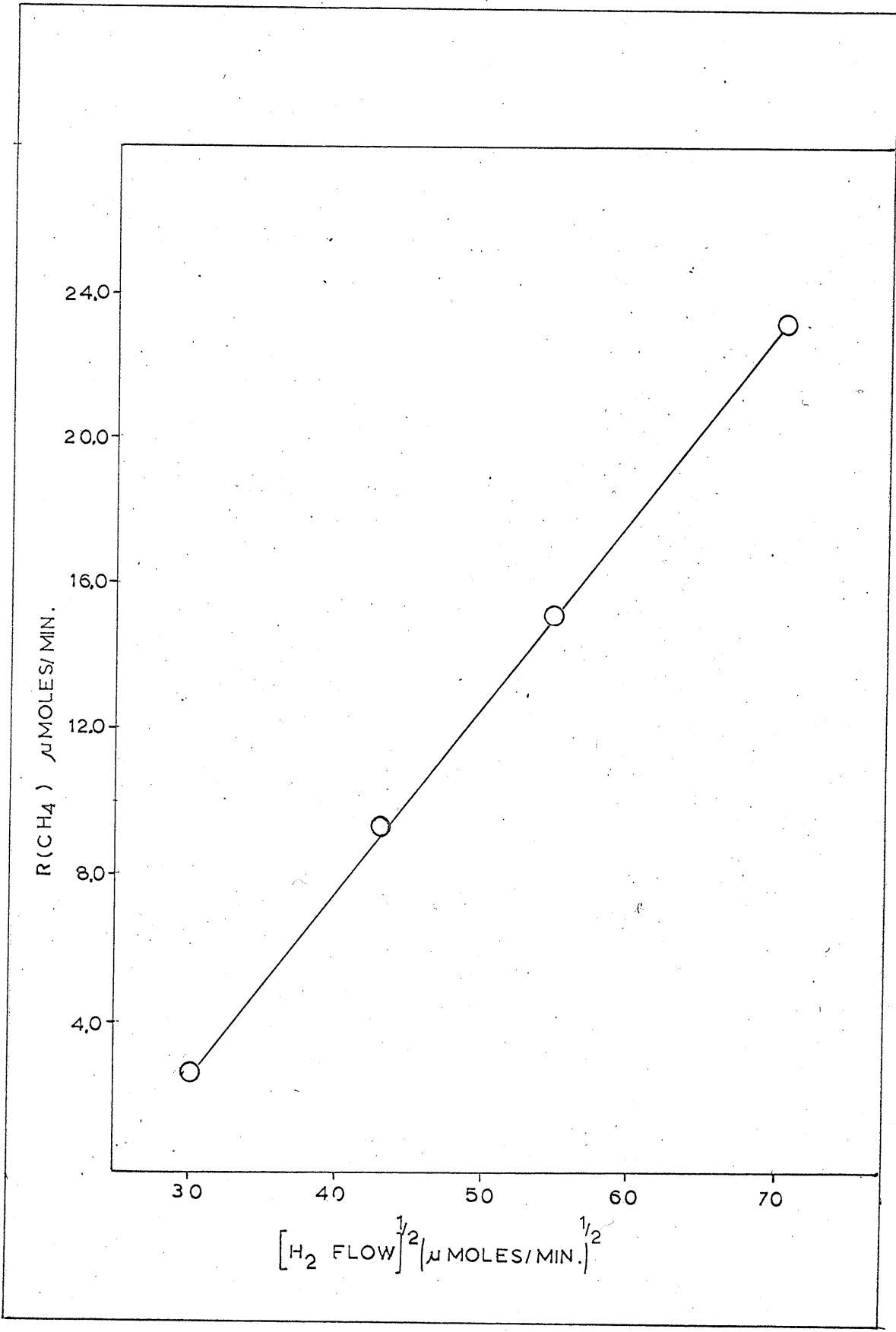


FIGURE 18

A plot of the rate of methane formation  
versus the square root of the hydrogen flow rate.



Carbon atom formation due to graphite evaporation is not likely since a temperature of approximately  $3000^{\circ}$  C is required to give graphite a vapour pressure of 1 mm. (56). Since the maximum temperatures of graphite attained were in the neighbourhood of  $1,200^{\circ}$  to  $1,300^{\circ}$  C, the amount of products formed can not be accounted for by vapourization of graphite electrodes.

Carbon atom or some carbon species formation due to impact of electrons or highly energetic species of hydrogen on the graphite electrodes fits more closely to the observed facts. When helium was discharged between the graphite electrodes, large deposits of carbon were observed to form on the walls of the discharge tube in the direction of pumping. Observations similar to this were reported by Shahin (15), when a graphite rod was placed in a microwave discharge of helium under conditions similar to those used in the present study. It was also noticed in the present study that the temperature of the graphite rods, as was observed by their glow, increased with increasing hydrogen flow rate. However, no such heating was observed when helium was discharged between the electrodes at flow rates greater than that used for hydrogen.

It has been reported (15), that hydrogen atoms produced in a microwave discharge can only react with solid carbon when the carbon is placed in the hydrogen plasma.

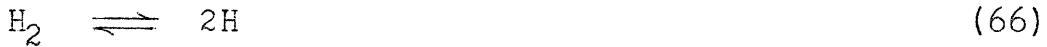
The position of the carbon rod with respect to the center of plasma had a great effect on the amounts of products produced. This would indicate, as Shahin had suggested, that a collision of positive ions with the surface of the carbon is necessary for reaction to take place. In the present study, the formation of methane as the largest constituent would indicate that monatomic carbon species are formed to a large degree in the discharge tube.

It was previously pointed out that the observed change in  $R(CH_4)$  with respect to change of hydrogen flow rate, need not be directly related to the mechanism of  $CH_4$  formation, but could indicate the dependance of  $R(C)$  formation on the hydrogen flow rate, (where C is some form of monatomic carbon). It should be also pointed out that the flow rates used were approximately 100 times the rate at which the total of products were formed. This would mean that  $-\frac{d}{dt} [H_2] \approx 0$ , or in other words the hydrogen concentration could be considered to be constant due to its large excess.

The straight line dependence of the rate of change of  $R(CH_4)$  with the square root of the hydrogen flow rate could be explained, by postulating the existance of an equilibrium between hydrogen molecules and some excited or energetic hydrogen species.



where  $H^*$  refers to some excited or energetic hydrogen species. The formation of the  $H^*$  species could possibly involve the following steps;



The equilibrium constant  $K^*$  for the process would be

$$K^* = \frac{[H^*]^2}{[H_2]} \quad (68)$$

In a continuous discharge at a constant hydrogen concentration such an equilibrium should be possible. It is also believed that an impact of these energetic species with the graphite electrode is responsible for the production of the monatomic carbon species as shown by reaction (69), and (70).



G in equations (69) and (70) refers to the graphite electrodes. The concentration of the monatomic carbon species is dependant on the  $H^*$  species by the following relationship;

$$[C] = k [H]^{\frac{1}{2}} \quad (71)$$

From equation 68, it can be shown that;

$$[H]^{\frac{1}{2}} = \sqrt{k} [H_2] \quad (72)$$

or upon combining (71) and (72) it can be shown that;

$$[C] = k k^{\frac{1}{2}} [H_2]^{\frac{1}{2}} \quad (73)$$

It is possible to see why the rate of methane formation could be dependant on the square root of the hydrogen flow rate. This is speculative, but nevertheless could serve as an explanation.

It was previously mentioned that the heating of the electrodes was only observed when hydrogen was discharged through the graphite electrodes. This heating effect could be attributed to a surface reaction since no heating was observed in the helium case. The heating effect could not have been due to the hydrogen atom recombination on the graphite surface. From the design of the discharge tube, hydrogen entered the discharge tube at one of the electrodes and exited past the second electrode. During the reaction, the hydrogen atoms formed in the main body of the discharge tube would have to pass over the second electrode on their way out, as this was the direction of hydrogen flow. This electrode could very well serve as a

surface on which hydrogen atoms could recombine and therefore the heating of this electrode should be expected. It was observed, however, that the heating occurred at both electrodes and to the best estimation, to the same degree. Equal heating of the electrodes can be explained by some interaction of charged species with the graphite electrodes.

Shahin (15) observed a flow rate dependence of the  $R(CH_4)/(C_2H_2)$  ratio. With increasing hydrogen flow rate he observed that  $R(C_2H_2)$  decreased while  $R(CH_4)$  increased, and  $R(C_2H_4)$  and  $R(C_2H_6)$  remained constant. In the present study it can be seen from Table 3 that both  $R(CH_4)$  and  $R(C_2H_2)$  were found to increase with increasing hydrogen flow rate. However, if the molar percents, as defined by equation (52), of  $CH_4$  and  $C_2H_2$  are plotted against the hydrogen flow rate, Figure 19, the same effect is observed as was reported by Shahin. For comparison Shahin's values are plotted in Figure 20.

The fact that Shahin observed an increase of  $R(CH_4)$  and fall off of  $R(C_2H_2)$  with increasing hydrogen flow rate while this author observed a percent increase of  $CH_4$  and percent decrease of  $C_2H_2$  with increasing pressure can be explained by a pressure effect. Shahin, by regulating his pumping speeds was able to maintain a constant hydrogen

FIGURE 19

A plot of percent methane and percent acetylene  
versus the hydrogen flow rate.

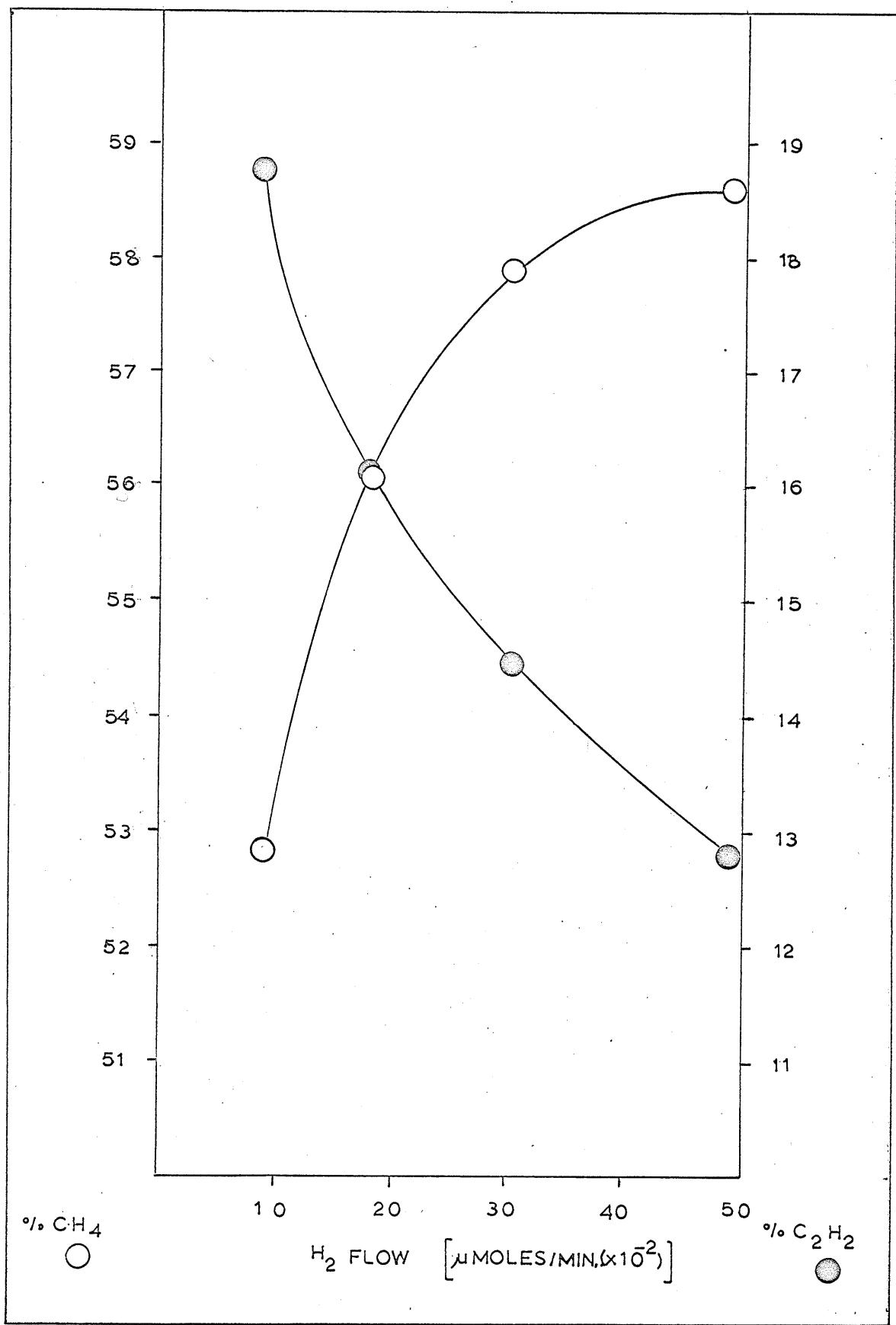
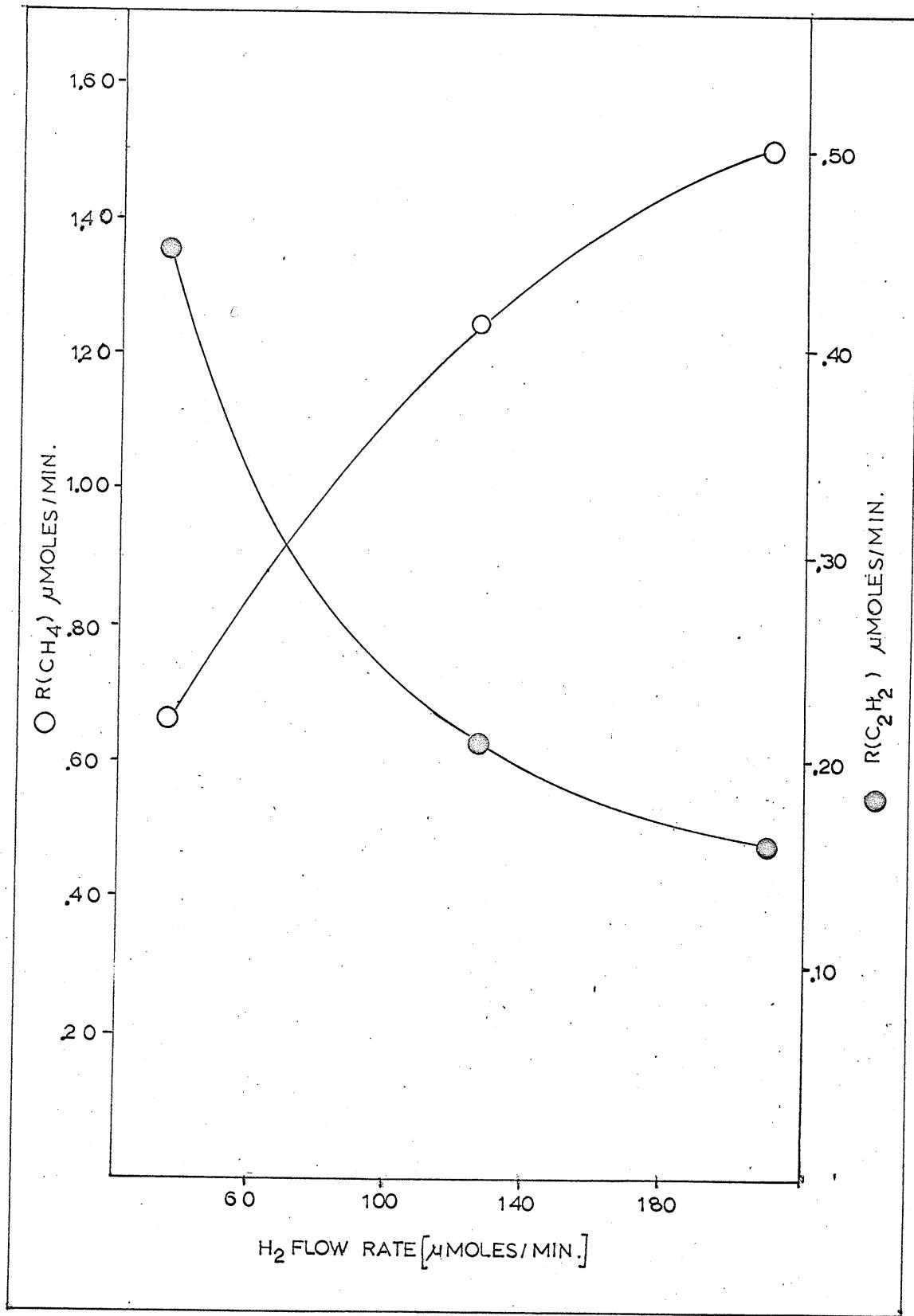


Figure 20

A plot of the data of methane formation  
and the rate of acetylene formation  
versus hydrogen flow rate from data reported by Shahin.

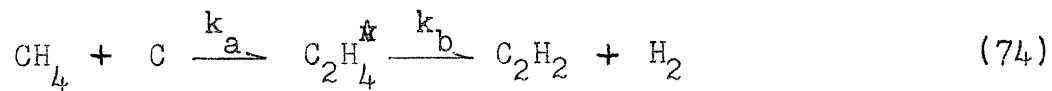


pressure of 0.57 mm. Hg. as he varied the flow rates. In the present study the pumping speed was maintained approximately constant therefore, the hydrogen pressure increased with increasing flow rate.

The pressure effect would support the proposed equilibrium  $H_2 \rightleftharpoons 2H^*$ , since an increase in pressure would increase the concentration of the  $H^*$  species, which then in turn would increase the concentration of the carbon species, and the final result would be an increase in  $R(CH_4)$  as well as  $R(C_2H_2)$ . The increase of  $R(CH_4)$  and  $R(C_2H_2)$  with increasing hydrogen flow rate was observed in the present study.

The flow rate, on the other hand, would affect the duration of time a molecule or a radical spends in the reaction zone. From the present study and from the study done by Shahin, it is indicative that  $R(CH_4)$  favors a shorter duration in the reaction zone and  $R(C_2H_2)$  favors longer duration in the reaction zone.

Shahin had suggested that the inverse  $R(C_2H_2)$  relation to  $R(CH_4)$  may be due to carbon atom insertion into the newly formed methane molecule. If this is the case then;



$$\frac{d}{dt}[C_2H_2] = k_b[C_2H_4^*] = k_a[C][CH_4] \quad (75)$$

but  $\text{CH}_4 \propto R(\text{CH}_4)$ , and if  $[C] \propto \sqrt{H_2}$   
then;

$$R(\text{C}_2\text{H}_2) = k_a R(\text{CH}_4) \sqrt{H_2} \quad (76)$$

or

$$\frac{R(\text{C}_2\text{H}_2)}{R(\text{CH}_4) \sqrt{H_2}} = k' \quad (77)$$

From the experimental data, it was found that the ratio as given in equation (77), was not constant but was found to increase very rapidly with increasing hydrogen flow rate.

Another possibility for the  $R(\text{CH}_4)$  and  $R(\text{C}_2\text{H}_2)$  percent dependance on the hydrogen flow rate, is that there exists a competition between hydrogen molecules and carbon atoms for some species such as  $\text{CH}_2^*$ .



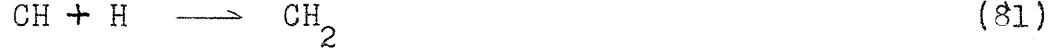
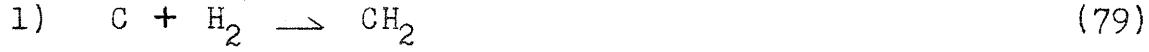
This would give qualitatively the observed variations with the hydrogen flow rate. Other schemes could also be proposed, but they all seem less plausible.

Hydrogen atom reactions with carbon films have been studied by King and Wise (16). The major products found by these workers were methane and ethane, with acetylene becoming important at higher temperatures. Both ratios

$C_2H_2/C_2H_6$  and  $C_2H_6/CH_4$  were found to increase with increasing temperature and increasing hydrogen atom concentration. In the present study although the ratio  $C_2H_6/CH_4$  remained relatively constant the ratio of  $C_2H_2/C_2H_6$  was found to decrease with increasing hydrogen flow rate and therefore with increasing temperature. This would seem to indicate that the same mechanism is not operative in the two studies.

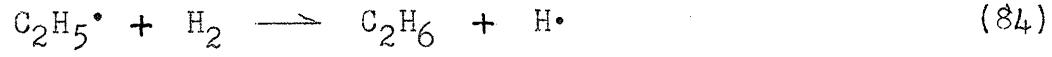
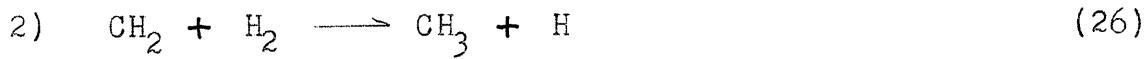
It is possible to rationalize the formation of all products if certain radicals and reactions are assumed. The products and the reactions leading to their formation will now be given.

#### Methane

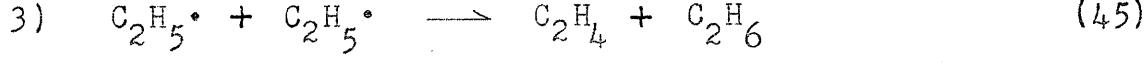
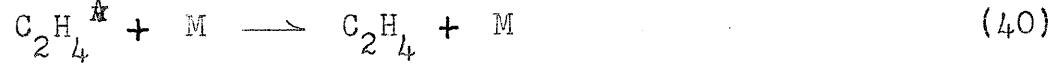




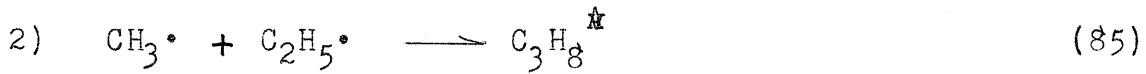
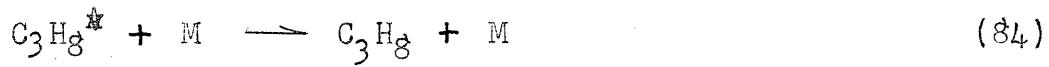
## Ethane



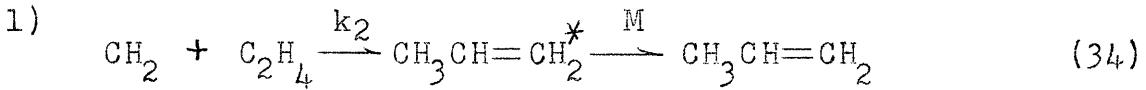
## Ethylene



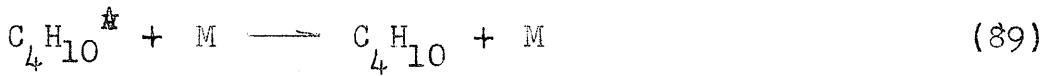
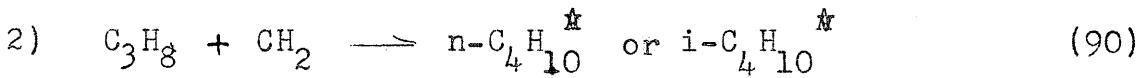
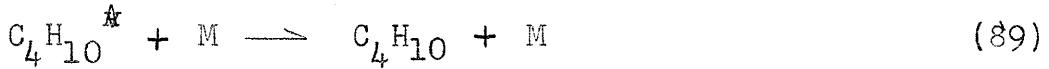
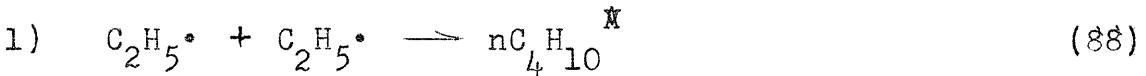
## Propane



## Propylene

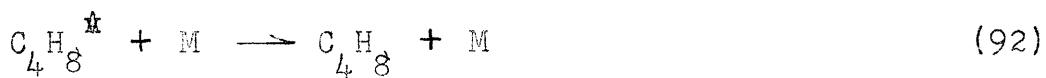


## Butane

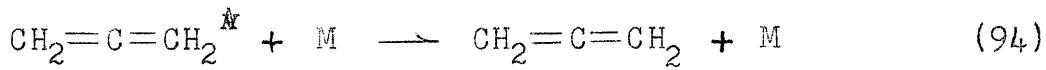
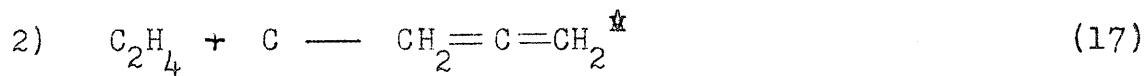
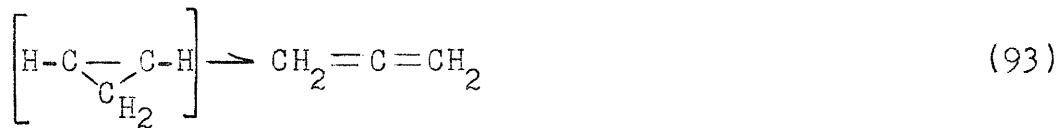
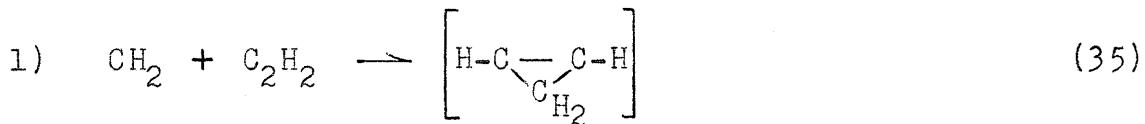


## Butenes

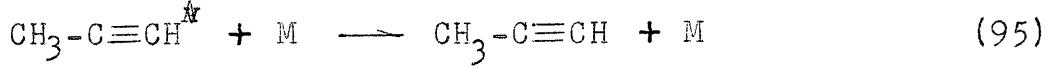
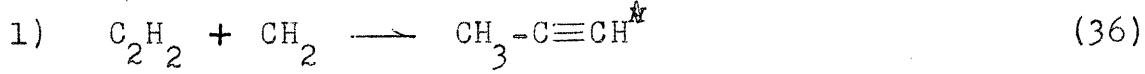




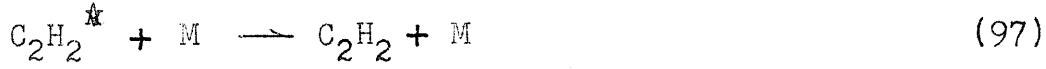
Allene

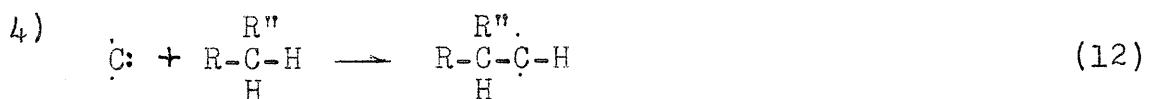


Methylacetylene



Acetylene





Qualitatively all products can be rationalized, though quantitatively no relationships can be obtained. It is difficult for example to explain why  $R(C_2H_6)$  and  $R(C_2H_4)$  are directly proportional to  $R(CH_4)$ , or why  $R(C_2H_2)$  is directly proportional to the log of the hydrogen flow rate. If  $CH_2$  species are present, and ethylene was found to be one of the major products, then why is cyclopropane only formed in trace quantities. If  $CH_2$  radicals were in trace quantity, what would account for the relatively large formation of methylacetylene, if methylacetylene is considered to be formed from the reaction of methylene with acetylene? This discrepancy could be resolved if the relative rates of reaction of methylene with ethylene and with acetylene under these conditions were known.

#### VOLTAGE VARIATION

In this set of reactions, the hydrogen flow rate was maintained constant. In order to be able to study a wider range of voltages, hydrogen flow rate was maintained quite low, thus eliminating arcing at the high voltages. The data

from these experiments is tabulated in Table (4). All the products which were found in the hydrogen flow rate variation experiments, were also found in the voltage study.

A plot of total number of moles formed per minute against the primary voltage is shown in Figure 21. From this plot it is easily seen that the R(total products) first increases and then decreases with increasing voltage.

The  $R(CH_4)$  and  $R(C_2H_2)$  are plotted against voltage in Figure 22. From the two plots in this figure, it can be seen that both curves have a maximum and a fall-off. Figure 23 shows the percent plots of  $CH_4$  and  $C_2H_2$  against the voltage. A comparison of plots for methane in Figure 22 and Figure 23, will show that although  $R(CH_4)$  reaches a maximum and then drops off, the percent plot shows a continuous, though not constant, increase with increasing voltage. The acetylene percent plot against voltage has a maximum at approximately 1,600 volts followed by a rather sharp fall-off at higher voltages. This behavior could indicate that the following two processes may be occurring:

- 1) methane is formed in an energetic state, the energy of which is related to the voltage appearing across the electrodes.
- 2) acetylene, to a large degree, is formed from a stable methane.

If methane is formed by the reaction of the initiating species with hydrogen molecules, then the amount of energy

TABLE 4  
Voltage Variation Experiments

| Exp.<br>No.                        | 1                              | 5                             | 6                              | 7                             |                                |                               |                                |       |
|------------------------------------|--------------------------------|-------------------------------|--------------------------------|-------------------------------|--------------------------------|-------------------------------|--------------------------------|-------|
| Volt<br>prim.                      | 60                             | 90                            | 120                            | 160                           |                                |                               |                                |       |
| Volt<br>Sec.                       | 1,090                          | 1,630                         | 2,180                          | 2,910                         |                                |                               |                                |       |
| H <sub>2</sub> Flow                | 9.25x10 <sup>2</sup>           | 9.50x10 <sup>2</sup>          | 9.24x10 <sup>2</sup>           | 9.98x10 <sup>2</sup>          |                                |                               |                                |       |
| H <sub>2</sub> Pres.               | 0.432 mm.                      | 0.462 mm.                     | 0.460 mm.                      | 0.448 mm.                     |                                |                               |                                |       |
| Total<br>Prod.                     | 5,242                          | 13,500                        | 17,100                         | 15,030                        |                                |                               |                                |       |
| React.<br>Time                     | 20 min.                        | 12 min.                       | 8 min.                         | 6 min.                        |                                |                               |                                |       |
| Product                            | μmoles<br>(x10 <sup>-3</sup> ) | Rel.%<br>(x10 <sup>-3</sup> ) | μmoles<br>(x10 <sup>-3</sup> ) | Rel.%<br>(x10 <sup>-3</sup> ) | μmoles<br>(x10 <sup>-3</sup> ) | Rel.%<br>(x10 <sup>-3</sup> ) | μmoles<br>(x10 <sup>-3</sup> ) | Rel.% |
| CH <sub>4</sub>                    | 2,770                          | 52.85                         | 7,452                          | 55.18                         | 9,750                          | 57.01                         | 9,441                          | 62.84 |
| C <sub>2</sub> H <sub>2</sub>      | 982                            | 18.73                         | 2,883                          | 21.35                         | 3,051                          | 17.84                         | 2,423                          | 16.13 |
| C <sub>2</sub> H <sub>4</sub>      | 501                            | 9.56                          | 1,622                          | 12.01                         | 1,769                          | 10.34                         | 582                            | 3.87  |
| C <sub>2</sub> H <sub>6</sub>      | 274                            | 5.23                          | 855                            | 6.33                          | 1,075                          | 6.29                          | 1,102                          | 7.33  |
| C <sub>3</sub> H <sub>4</sub>      | 65                             | 1.24                          | 133                            | 0.98                          | 144                            | 0.84                          | 141                            | 0.94  |
| CH <sub>3</sub> -C <sub>2</sub> H  | 86                             | 1.64                          | 246                            | 1.82                          | 280                            | 1.64                          | 191                            | 1.27  |
| C <sub>3</sub> H <sub>6</sub>      | 264                            | 5.04                          | 604                            | 4.47                          | 594                            | 3.47                          | 317                            | 2.11  |
| C <sub>3</sub> H <sub>8</sub>      | 86                             | 1.64                          | 155                            | 1.15                          | 208                            | 1.22                          | 253                            | 1.68  |
| i C <sub>4</sub> H <sub>8</sub>    | 86                             | 1.64                          | 158                            | 1.17                          | 175                            | 1.02                          | 105                            | 0.69  |
| t C <sub>4</sub> H <sub>8</sub> -2 | 28                             | 0.53                          | 43                             | 0.32                          | 52                             | 0.30                          | 68                             | 0.45  |
| c C <sub>4</sub> H <sub>8</sub> -2 | 26                             | 0.49                          | 43                             | 0.32                          | 48                             | 0.28                          | 68                             | 0.45  |
| i C <sub>4</sub> H <sub>10</sub>   | 16                             | 0.30                          | 29                             | 0.21                          | 44                             | 0.26                          | 56                             | 0.37  |
| n C <sub>4</sub> H <sub>10</sub>   | 43                             | 0.81                          | 43                             | 0.32                          | 44                             | 0.26                          | 278                            | 1.85  |
| 1,3 C <sub>4</sub> H <sub>6</sub>  | 16                             | 0.30                          | 34                             | 0.25                          | 48                             | 0.28                          | ~ 0                            | ~ 0   |

With reference to Table 4;

\*  $\mu$ moles/min

i - iso

t - trans

c - cis

n - normal

The total products as given in Table 4, are in units  
 $\mu$ moles  $\times 10^{-3}$ /min. The values given are the calculated  
values having a maximum deviation of  $\pm 80 \mu$ moles  $\times 10^{-3}$ /min.

The maximum percent deviation for all the constituents  
was calculated to be  $\pm 0.04\%$ .

FIGURE 21

A plot of the rate of total products formation  
versus the primary voltage.

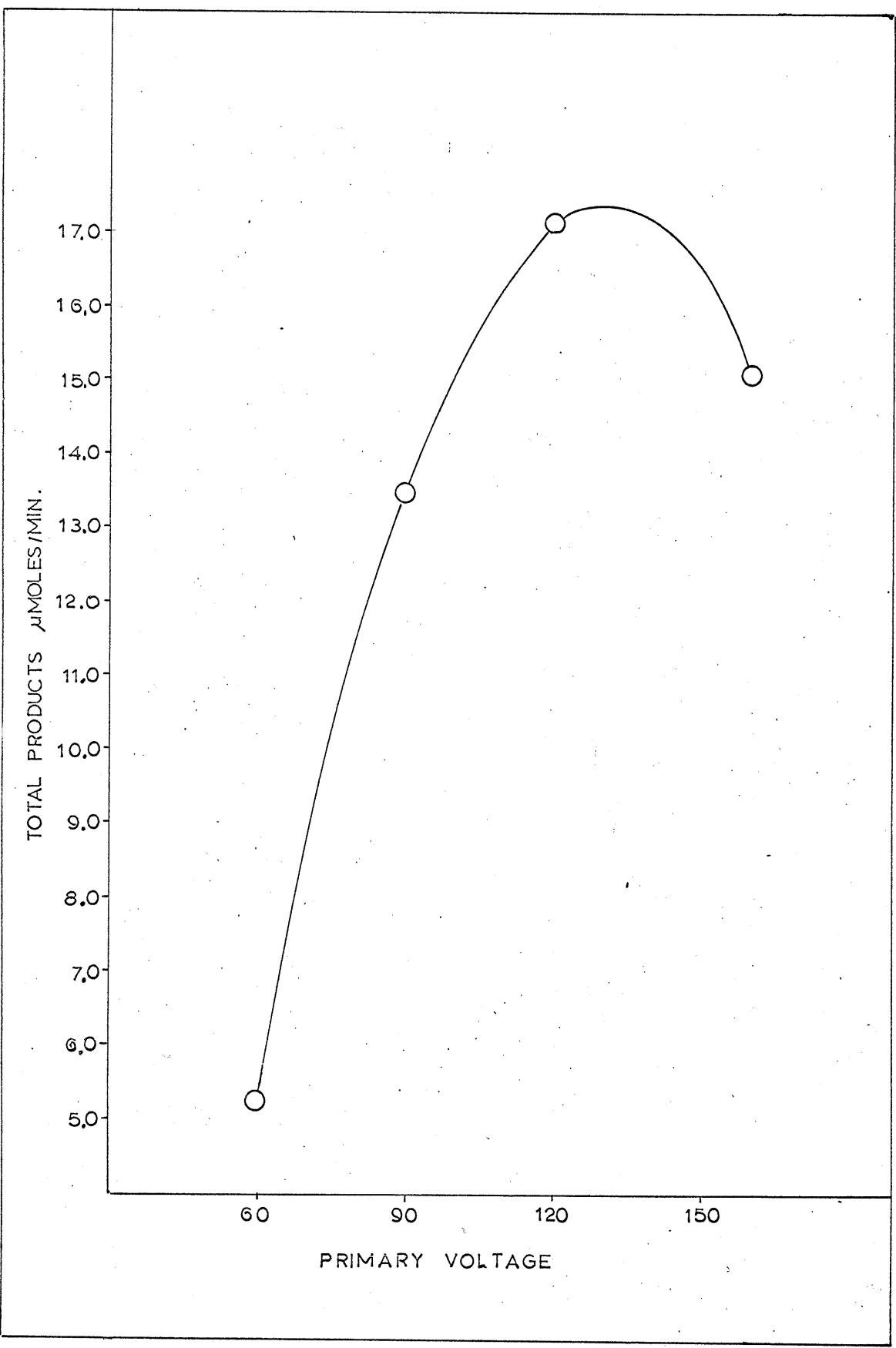


FIGURE 22

A plot of the rate of methane formation and the  
rate of acetylene formation versus the primary voltage.

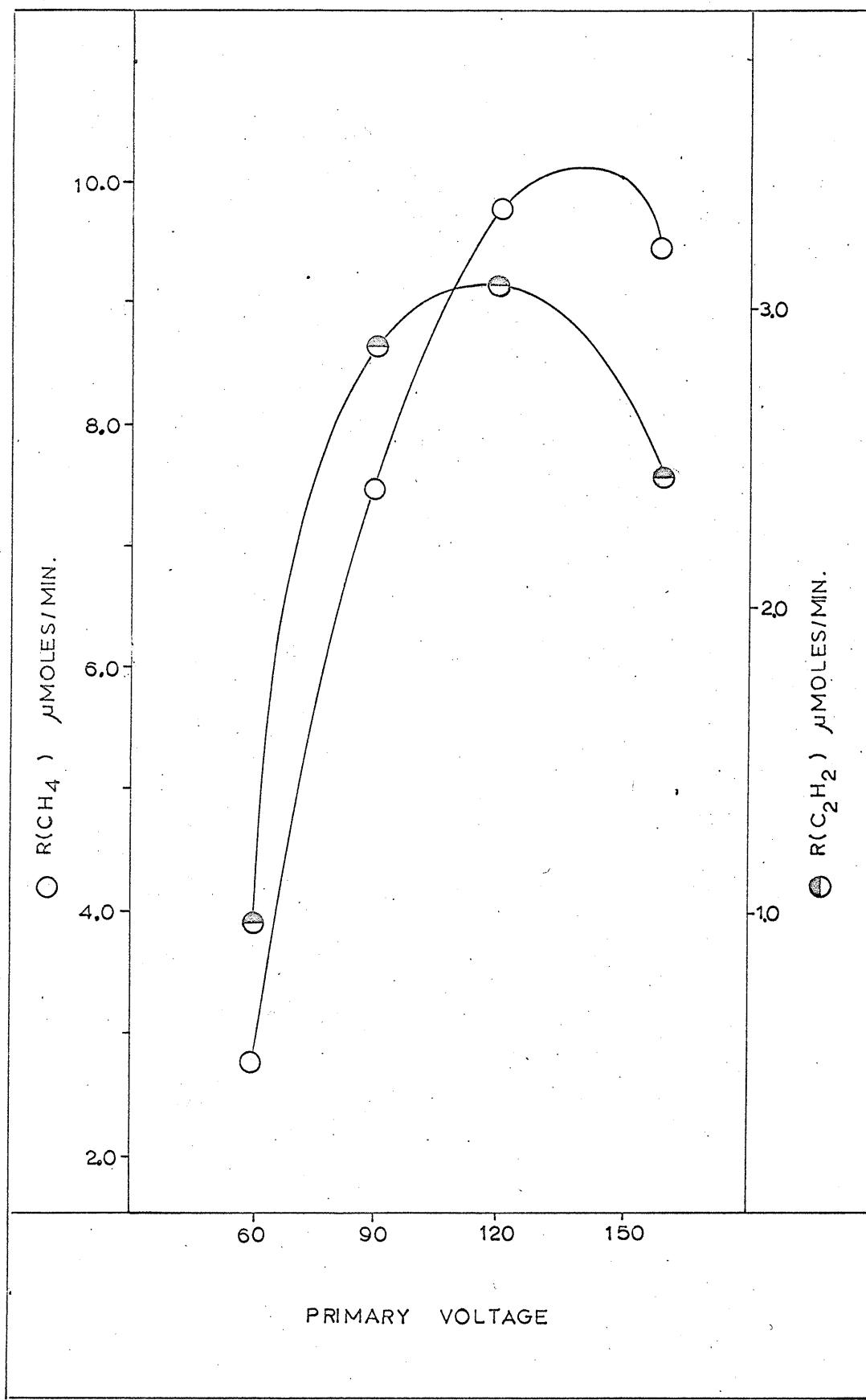
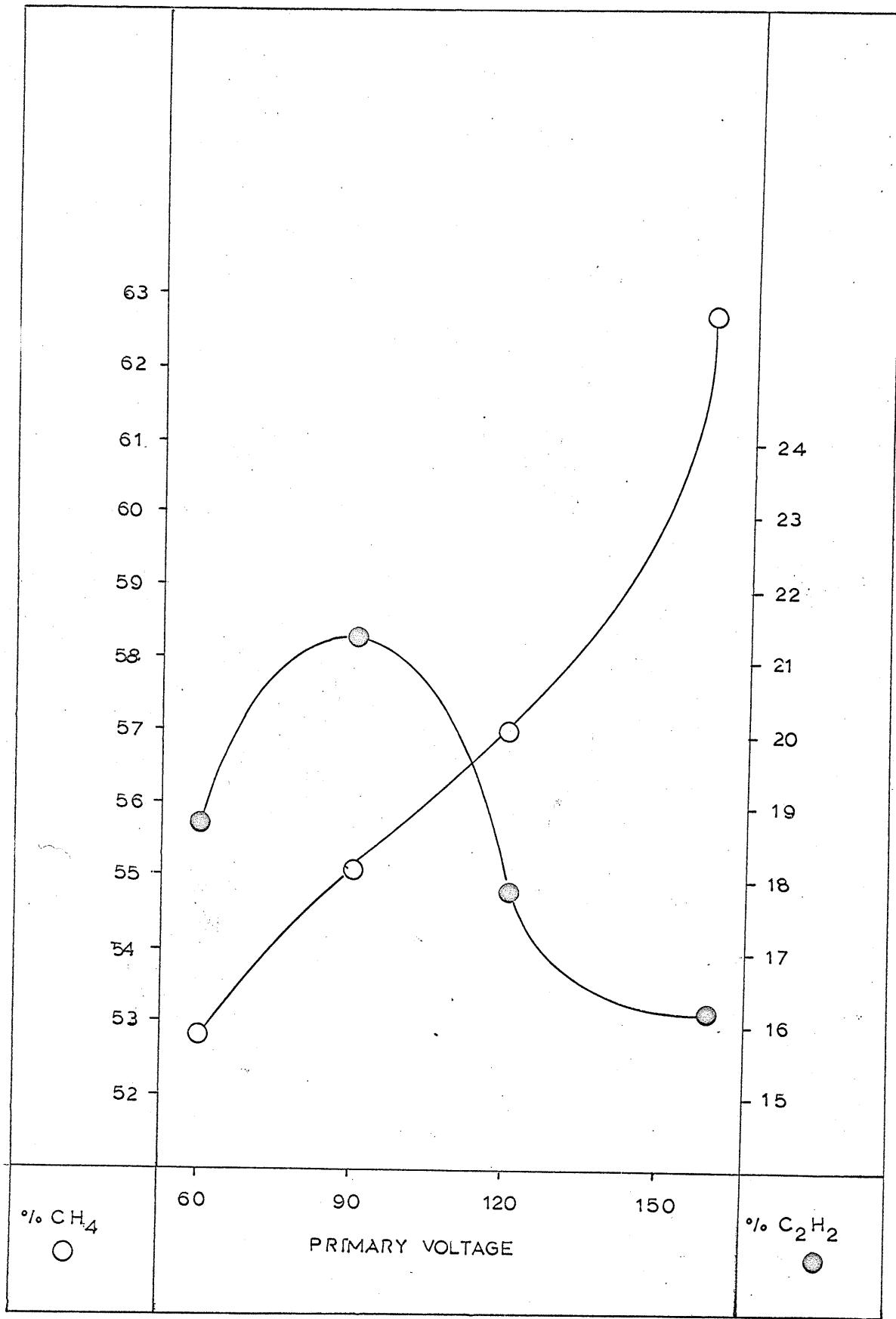


FIGURE 23

A plot of the percent of methane and the percent acetylene versus the primary voltage.



the newly formed methane will possess will be related to the energetic state of the reacting species. The fate of the newly formed methane will be governed by one of the following steps:

- 1) Deactivation
- 2) Further excitation arising from;
  - a) absorption of U.V. radiation
  - b) collisional energy transfer
- 3) Reaction of the stable methane molecule

(consequence of step 1) with some form of carbon to give, directly, or indirectly, acetylene.

Deactivation can be brought about from two different sources, namely; - collisional deactivation by the hydrogen molecules and collisional deactivation by the walls. At lower voltages the newly formed methane would be expected to have a relatively small amount of excess energy, and deactivation could be achieved by either of the two processes already mentioned. With increasing voltage the energy associated with the newly formed methane could also increase. Since hydrogen is known to be a poor acceptor of energy in a collisional process (57) deactivation of excited methane molecules at higher voltages by hydrogen molecules will become less significant and deactivation by the walls of the apparatus will become important.

Deactivation by the walls can occur in two different regions of the apparatus. Should the deactivation take place within the discharge tube, the stable methane molecule formed is subject to further excitation by the absorption of U.V. radiation or by collisional energy transfer from other molecules, atoms, or ions. Deactivation could also occur outside the discharge tube. In this case, the stabilized methane molecule would be pumped away from the discharge tube and would be trapped in the silica gel trap. From what has been said it can be seen that the amount of stable methane within the discharge tube should decrease with increasing voltage. If the methane molecule within the discharge tube may undergo reaction with some carbon species to give acetylene, then the amount of acetylene formation should decrease with increasing voltage. The reaction of an excited methane molecule with the carbon species would, form a very energetic intermediate which probably would immediately decompose into radicals, and no stable products should be expected. The reaction of methane with the carbon species should only occur when the participating methane molecule is stable or has very little excess energy. At low voltages the formation of acetylene within the discharge tube is possible, but at higher voltages where the methane molecule depends on the walls outside the discharge tube for deactivation, acetylene form-

ation should drop since if the molecule is deactivated then it is no longer in the discharge region and therefore cannot undergo any further reaction.

Up to now nothing has been said about the amounts of methane or acetylene formed, but only the relative quantities have been discussed. The relative amounts (the relative percents), especially at higher voltages, Figure 23, appear to validate the preceding discussion. The increase of both,  $R(CH_4)$  and  $R(C_2H_2)$  with increasing voltage in the lower voltage region, may be explained by the increase in the equilibrium constant  $K^\ddagger$  for the equilibrium  $H_2 \rightleftharpoons 2H^\ddagger$ . The fall off of  $R(CH_4)$  at the highest voltages used, may be due to one of the following reasons:

- a) destruction of the initiating species by transformation to some non-reactive species.
- b) formation of methane molecules which are very rich in energy and which;
  - i) decompose instantaneously
  - ii) have life-times too short for a deactivation process.
- c) the initiating species are formed to a lesser degree if the fall off is a thermal rather than a voltage effect.

If the fall off is a thermal effect, then it could be

related to hydrogen adsorption on the graphite electrodes. It has been shown that hydrogen is adsorbed on graphite to a considerable extent even at temperatures up to  $2000^{\circ}\text{C}$ . (58). In these studies it has been shown that the quantity of hydrogen adsorbed per gram of graphite first increases, reaches a maximum and then decreases with increasing temperature. The position of the maximum, with respect to temperature, was shown to be dependant on the pressure of the system. For example, at 1 mm. Hg. the maximum was found to be at approximately  $1350^{\circ}\text{C}$ ., and at 10 mm. Hg. the maximum was found to be at approximately  $1080^{\circ}\text{C}$ .

In the present study no measurements were made of the temperature of the graphite electrodes. However, from the colour of their glow it could be estimated that the highest temperature reached was in the vicinity of  $1250^{\circ}\text{C} \pm 100^{\circ}\text{C}$ . If the hydrogen adsorption on the graphite electrodes is responsible for the formation of the initiating species then the number of initiating species formed will be proportional to the hydrogen adsorbed. Should the adsorption maximum correspond with the maxima observed in the present study then the increase and the fall off of the product formation with the increase in voltage can be explained.

It must be mentioned that the foregoing discussions are speculative, and their validity is subject to further

experimentation.

#### FURTHER EXPERIMENTS

Other experiments performed on the same apparatus will now be briefly described.

One of the studies was to determine whether carbon species (if formed in the reaction), were able to react directly with the hydrogen molecules. To study this, fast flows of helium were discharged between graphite electrodes, as hydrogen was bled into trap T<sub>6</sub> Figure 1 at a very slow rate to prevent back diffusion. Upon analysis of the products, only small quantities of nitrogen, carbon dioxide, and smaller quantities of unidentified compounds were found. The quantities of products as found, could be very easily explained as impurities in the helium used. Although the helium was passed through the same purification system as was used for hydrogen, perfect trapping of the impurities was not accomplished, perhaps because the flow of helium through the purification system was too fast. Though carbon deposits were observed at a considerable distance from the discharge tube it was concluded that the carbon species were short lived, and the distance between the exit of the discharge and the trap T<sub>6</sub> Figure 1, was too long.

To minimise the distance, the discharge tube was

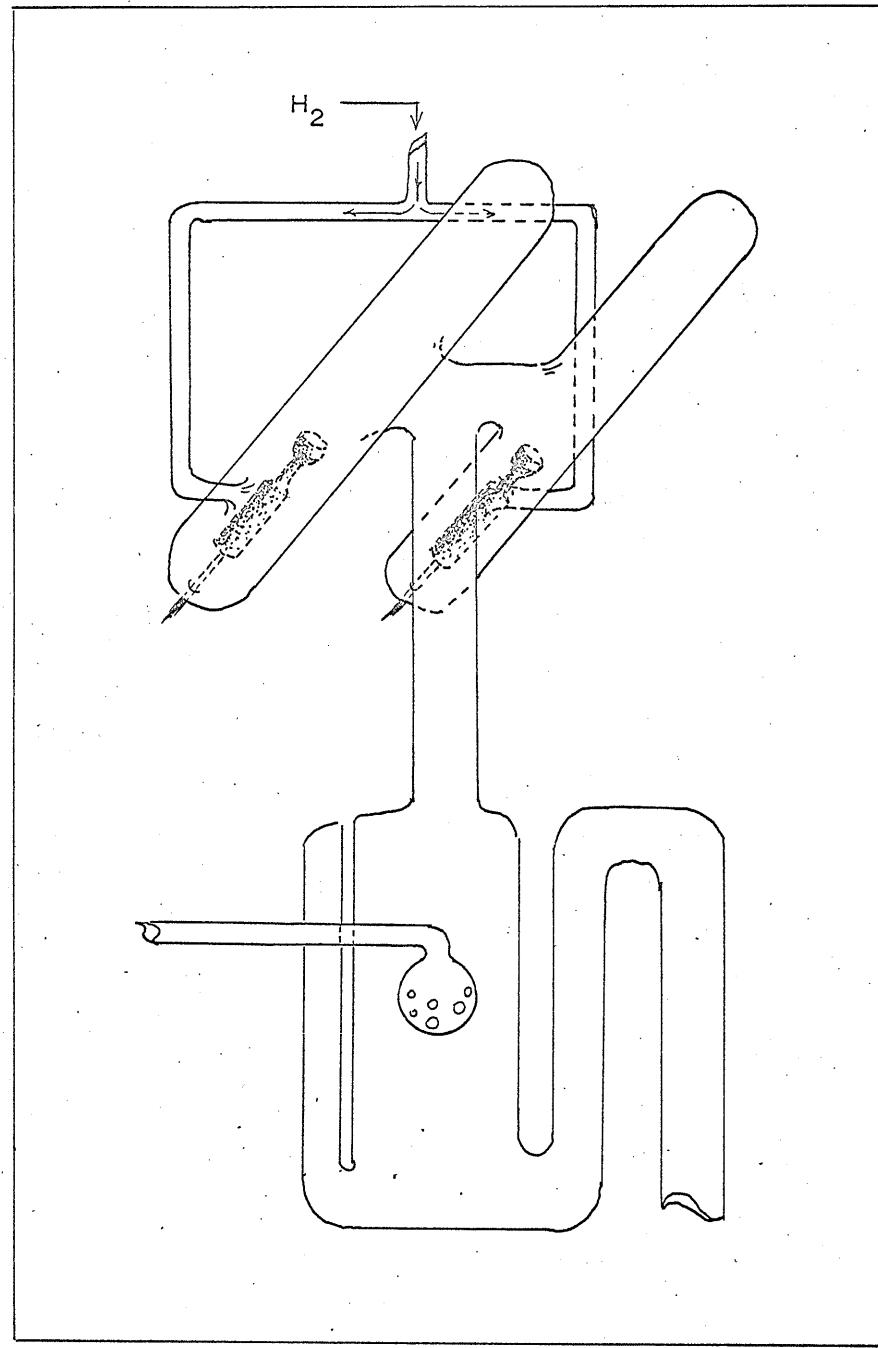
slightly altered such that the gas was allowed to enter at both electrodes and exit through the tube between the electrodes straight down into trap T<sub>6</sub>. A physical description of the modified discharge tube is given in Figure 24.

It was decided that methane rather than hydrogen should be bled into trap T<sub>6</sub>, as this could have shown whether the carbon species could be pulled out of the discharge tube, and whether the reaction of carbon atoms with methane would give ethylene or acetylene in this system. The experiment was performed under conditions similiar to those when hydrogen was used. The products from this reaction were ethane and carbon dioxide. The yield of carbon dioxide was much greater than that of ethane. The products could have been formed from water which may have been absorbed on the graphite electrodes during the alteration of the discharge tube. As no other products were found, and as it was observed that the amount of carbon deposition in the discharge tube had decreased very considerably from that observed before the discharge tube was altered, it was concluded that this reaction could not be properly studied with this system,- the study was terminated.

The object of the final study was to determine what effect the design of the discharge tube which was used in experiments 1 to 7, had on the product formation. From Figure 1 it can be seen that if any products were formed in

FIGURE 24

Diagram of the modified discharge tube.



the body of the discharge tube during a reaction, they were subject to decomposition or further reaction as their exit out of the discharge tube included;

- a) their passage through the discharge plasma
- b) their passage over one of the graphite electrodes.

With the alteration of the discharge tube, as shown in Figure 24, it was possible to study what effects (a) and (b) had on the product formation.

In experiment 10 the conditions of experiment 1 were duplicated such that a direct comparison could be made. The data for the two experiments is given in Table 5.

TABLE 5  
Comparison of results obtained in experiments 1 and 10.

|   | Experiment 1 | Experiment 10 |
|---|--------------|---------------|
| H <sub>2</sub> Flow(μmoles/min.)            | 925          | 963           |
| H <sub>2</sub> Pressure (mm.)               | 0.434        | 0.436         |
| Total products (μmoles/min.)                | 5.24         | 8.54          |
| CH <sub>4</sub> (μmoles/min.)               | 2.77         | 6.30          |
| C <sub>2</sub> H <sub>2</sub> (μmoles/min.) | 0.98         | 1.21          |
| CH <sub>4</sub> %                           | 52.85        | 74.36         |
| C <sub>2</sub> H <sub>2</sub> %             | 18.73        | 14.00         |
| Other products (μmoles/min.)                | 1.49         | 1.02          |
| Other products %                            | 28.42        | 11.64         |

By comparison of the results from these two experiments it can be seen that  $R(\text{total products})$  is greater in experiment 10 than in experiment 1. The yield of methane and acetylene was also found to be greater than that found in experiment 1. Although the  $R(\text{C}_2\text{H}_2)$  in experiment 10 was found to be greater than in experiment 1, the percent of  $\text{C}_2\text{H}_2$  was found to decrease.

A comparison of the data of the two experiments seems to indicate that;

- a) methane was destroyed in experiment 1
- b) the destruction of methane results in the formation of the heavier products as well as decomposition into the elements
- c) acetylene formation arises to a considerable degree from the destruction of methane
- d) methane is initially formed within the discharge plasma.

CONCLUSION

Hydrogen under low pressures and fast flow rates was discharged between the graphite electrodes. The products obtained from this reaction were identified and were found to range from C<sub>1</sub> to C<sub>6</sub> in their carbon content. The quantity of the respective compounds was observed to decrease with increasing carbon number. This type of behaviour could arise from hydrogenation of carbon fragments of appropriate size or from monatomic carbon fragments which initially form methane followed by the reaction of methane with other radicals or fragments to give rise to the heavier compounds. The formation of the heavier products from methane appears to exist to some degree as the results from experiments 1 and 10 have indicated.

Qualitatively all products may be accounted for by reactions which have been previously postulated. Quantitatively no mechanism scheme was obtained as it was found that no kinetic expression appeared to fit the variations observed. This discrepancy can be explained if one considers that the formation of any one of the products could arise from several different reactions.

In order to determine the process which may be occurring during the reaction one must study not only the variations observed in the end products as a function of either the hydrogen flow rate, the voltage or the electrode

temperature, but also one must determine the nature of the reacting species and their variation as a function of the above mentioned variables. The latter study could be carried out to some extent by the use of absorption or emission spectra techniques.

It should be possible to study the kinetics of the hydrogen-carbon reaction, however, static systems must be used. With a static system an A.C. or a repeated condensed D.C. discharge cannot be used as this would result in discharging, along with hydrogen, the compounds already formed. The reaction apparatus which would be more suitable for the kinetic studies, would be basically a small discharge tube of known volume. Hydrogen under known pressure would be allowed to fill the discharge tube. The reaction would be initiated with a single pulse discharge. The power supply which should be used in this system should be a condensed ( $10\mu$ f), high voltage (15,000 - 50,000 v.) D.C. discharge. If the single pulse discharge does not produce sufficient quantity of products for analysis, then the reaction may be repeated several times and the products collected out of the discharge tube after each reaction. The collection of products after each reaction would not necessitate complete evacuation of the discharge tube if a small silica gel trap was to be attached to the discharge tube by means of a stopcock.

In the pulse discharge reaction the initiating species can only be formed during the pulse. As the pulse is expected to have a time duration of 1-10  $\mu$ sec., it should not have any influence on further reactions or on the products formed. It is believed that by using the pulse discharge along with spectra studies, and by varying the hydrogen pressure and the voltage, much can be learned about the reaction of hydrogen with carbon.

In conclusion the author wishes to say that although the present study could not establish a concrete scheme for the reaction of hydrogen with carbon, it did however, indicate the complexity of the reaction and made it possible to see how this reaction may be studied in the future.

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