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A THESIS

entitled

STUDIES OF FREE RADICAL REACTIONS

LEADING TO CARBON FORMATION

submitted by

JOHN VICTOR SHEPHERD

for the Degree of Doctor of Philosophy

in the City University

1973

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Abstract

In the Introduction, evidence is presented in support of the view that acetylene is a key intermediate in the production of carbon by the burning and pyrolysis of hydrocarbons. It is also pointed out that recent investigations of the decomposition of acetylene show that polyalkynes are the main products formed prior to carbon formation and that there is a need for kinetic information regarding the reactions of unsaturated radicals (mainly the ethynyl radical) with alkynes.

The Experimental Section describes the construction of a static vacuum apparatus. This comprises a quartz reactor which can be irradiated by a low-pressure mercury vapour lamp. Ethynyl radicals may be generated by the photolysis of monobromoethyne at 253.7 nm and the gaseous products formed in the reactor can be analysed by on-line gas chromatography.

The Results Section shows how the photolysis of monobromoethyne is affected by variations in photolysis time, initial pressure of monobromoethyne and pressures of added nitric oxide and inert gases. A description is also given of analytical measurements on the primary products formed by the reaction of ethynyl radicals with both alkanes and alkynes.

The Discussion Section shows that the ethynyl radical can react with an alkyne either by addition to a triple bond:

$$C_2H + C_nH_2 \longrightarrow C_{n+2}H_3$$

or by hydrogen abstraction:

$$C_2H + C_nH_2 \longrightarrow C_2H_2 + C_nH$$

or by hydrogen displacement forming the next higher polyalkyne

$$C_2H + C_nH_2 \longrightarrow C_{n+2}H_2 + H$$

The kinetic results indicate that all these reactions have low activation

energies whilst hydrogen displacement reactions probably have activation energies and A factors of about 3 kcal.mole^{-1} and 10^8 l.mole^{-1}sec^{-1} respectively. Using the data obtained from these experiments a new mechanism for acetylene pyrolysis is proposed and an outline is given of the probable role which the ethynyl radical plays in the reactions leading to carbon formation.

ACKNOWLEDGEMENTS

I would like to thank Professor C.F. Cullis and Dr. D.J. Hucknall for their considerable help and encouragement during this project. I would also like to thank my colleagues for providing a congenial atmosphere in which to work.

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March 1973 J.V.S.

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INTRODUCTION

1 Introduction

1.1 General

Interest in the formation of carbon as a product of the pyrolysis and combustion of hydrocarbons extends back into the nineteenth century, when such eminent scientists as Faraday[1] and Berthelot[2] speculated as to the nature of the chemical processes involved. Nevertheless, it is only within the last ten years or so that some of the elementary precursors of carbon have been unambiguously identified.

Industrially, carbon is of importance in various contexts. For example, carbon black is used for reinforcing rubber, and carbon films are used in electrical resistors[3]. However, carbon can be a costly nuisance when formed, for instance, during the cracking of hydrocarbons in catalytic reactors[4] and in the exhausts of aircraft engines. It is obviously desirable, then, to exert control over carbon forming systems, even if the carbon is a desirable product. For this reason, it is important that quantitative kinetic information, i.e. rate constants, A-factors and activation energies, should be available for the supposed elementary reactions involved in carbon formation. These data are of intrinsic as well as practical value, since the chemical information may be considered in the wider context of the reactions of carbon-containing radicals such as C_2H_3, CH_3 and C_2H_5.

1.2 Production of carbon from hydrocarbons

The large quantity of literature published on the production of carbon from hydrocarbons reflects its industrial importance and several recent reviews[5-9] have dealt with various aspects of this subject. Carbon is formed both during the pyrolysis of hydrocarbons and in hydrocarbon flames. In both systems, the carbon produced has similar physical and chemical properties and alterations to the conditions under

which carbon appears tend merely to change the extent of its formation.

Carbon formed by the pyrolysis of hydrocarbons is produced both in the gas phase and on the surface of the reactor. Depending on the conditions of the pyrolysis (e.g. temperature, reactant concentration and contact time) the nature of the material produced in the gas phase can vary greatly. Thus, at low temperatures, "polymeric" substances are formed, although both small carbon particles (d = 100Å) and large aggregates, consisting of particles of 5000Å diameter, can be produced at higher temperatures[10].

The surface deposits of carbon formed during the pyrolysis of gaseous organic compounds have been extensively studied by Kinney et al[11]. The results of these investigations may be summarized as follows. In the temperature range 900 to 1400°C, four different types of carbon may be observed. A-type carbon ("thin film" carbon) is hard, brittle and metallic in appearance and adheres well to surfaces. Type B is soft and sooty, adhering poorly to surfaces. Type C is a mixture of A and B. Type D ("thick film" carbon) is feathery and grey and appears to grow out of deposits of type A. A further type (designated type E) is usually associated with type D. It is, however, distinguished by its brownish colour, sponge-like character and formation downstream of type D carbon. The starting hydrocarbon has little effect on the nature of the final carbon and merely determines the relative extents of production of the different types of carbon.

It has been found that the ability of a hydrocarbon to form pyrolytic carbon varies with its molecular structure. Thus Brooks, Hesp and Rigby[12] arranged certain hydrocarbons in order of their decreasing tendency to give carbon. This order was found to be:

aromatics > cycloalkanes > alkanes

The carbon formed from flames has been shown by electron microscopy to consist of a chain of bead-like particles, the diameter of which may vary between 100 and 2000Å. An average carbon particle contains perhaps 10^5 to 10^6 carbon atoms arranged in about ten thousand crystallites. These crystallites consist of between five and ten sheets of carbon atoms and each sheet has a length and breadth of between 20 and 30Å. The empirical formula of the carbon is roughly C_8H, indicating that the particles contain hydrogen and indeed chloroform extracts from such particles have indicated the presence of a number of polycyclic aromatic hydrocarbons[13-20].

Flames can be divided into premixed flames and diffusion flames. In a premixed flame a homogeneous mixture of a hydrocarbon and oxygen is formed prior to the flame reaction zone; in a diffusion flame, oxygen is supplied by a process of diffusion from the surrounding atmosphere. (A bunsen burner used with the air-hole open is a common example of a premixed flame. Closure of the air-hole produces a diffusion flame.) In a premixed flame, the hydrocarbon is in contact with oxygen in the preheating zone just prior to the flame front; in a diffusion flame the fuel is separated from the oxygen by a wedge of combustion products. In a premixed flame the residence time in the reaction zone is of the order of 10^{-3} sec; in a diffusion flame it is considerably longer.

Both types of hydrocarbon flame have been extensively studied and the effects of pressure, molecular structure, additives and electric fields have been elucidated. In addition, for premixed flames, the initial oxygen/fuel ratio is known and the stoichiometry can be determined. Now if the species within such flames are in thermodynamic equilibrium, carbon should be liberated by a flame only if the O/C ratio is less than unity[22]. However, the critical O/C ratio when carbon first appears is invariably greater than unity, varying from 2.4 in the case of the

methylnaphthalenes to 1.2 for acetylene[23].

The precise interpretation of these results is difficult because several factors vary between flames of the same stoichiometry. Chief among these differences are the products of combustion, the temperature of the carbon-forming region and the value of the O/C ratio at the site of carbon formation as distinct from its initial value. Variation of this ratio has, for a given stoichiometry, been minimised by obtaining results in a reactor under well-stirred conditions[21]. Here the critical O/C ratio was found to be 10-20% lower than values obtained in premixed flames, but was still greater than unity.

For premixed flames the critical O/C ratio is virtually independent of the pressure of the reactant gases. However, if the flame is sooting, then an increase in pressure increases the extent of carbon formation[24,25].

With diffusion flames of acetylene and air at sub-atmospheric pressures, carbon formation ceases below 25 mm.Hg.[26,27], whereas an increase in pressure to 140 mm.Hg. yields a normal sooting flame. The effect of pressures up to 11 atmospheres have been studied for diffusion flames involving several hydrocarbons[28]. The maximum flow of hydrocarbon fuel required to give a smoke-free flame was determined at a given pressure and it was found that the required flow decreased with increasing pressure.

It has been found that, in both diffusion and premixed flames, the structure of a hydrocarbon affects the ease with which it will yield carbon. In hydrocarbon diffusion flames the order of decreasing tendency to form carbon is benzenes > dialkenes > monoalkenes > alkanes[29,30]. Similarly the propensity to carbon formation from hydrocarbons in a premixed flame decreases in the order naphthalenes > benzenes > alkanes > alkenes > alkynes[23].

In general, additives present in small quantities have little effect

on the sooting properties of either diffusion or premixed flames. One exception is, however, sulphur trioxide. If this is added to a premixed coal gas-oxygen flame at a concentration of 0.1%, the tendency of the flame to soot is greatly increased[33]. The same additive, however, apparently decreases carbon formation in a diffusion flame[34]. Naphthalene has been found to increase carbon formation in diffusion flames[35]. On the other hand, carbon formation in diffusion flames is strongly inhibited by nitrosocompounds[36,37] and tert-butylhydroperoxide[37].

It has been found that many carbon particles in a flame have a positive charge and Weinberg and his co-workers (see for instance references 38, 39 and 40) have investigated this phenomenon in some detail. The negative electrode of a field applied to a sooting flame collects carbon at a much greater rate than a similar plate with an applied positive charge[38,39]. It appears that, on average, there is one positive charge per 10^4 carbon atoms in a particle. The mechanism by which a particle acquires its charge still requires elucidation. Experiments on the particles in a propane-oxygen flame indicate that agglomeration occurs prior to the attainment of the observed charge[41]. On the other hand, in the presence of an applied electric field, the size of the particles collected can be altered by varying the field strength. This suggests that the particles are charged when they are small and before they form large aggregates[40].

The work described above has tended to concentrate on the phenomenological aspects of carbon formation. However, in various systems involving the pyrolysis or combusition of hydrocarbons, acetylene is formed in substantial quantities and early studies by Tropsch and Egloff[42] and Egloff, Schoad and Lawry[43] suggested the following scheme of overall reactions for both ethane pyrolysis and ethane/oxygen flames:

$$\begin{array}{ccccc} C_2H_6 & \longrightarrow & C_2H_4 & \longrightarrow & C_2H_2 \\ & & + & & + \\ & & H_2 & & H_2 \end{array}$$

This viewpoint was consistent with the observed increase in stability of acetylene relative to other hydrocarbons at temperatures above 1100K [44,45]. Studies of the pyrolysis of hydrocarbons at high temperatures have demonstrated the importance of acetylene, not only as a final product but also as an intermediate involved in the reactions within such systems[46-52]. Indeed pyrolysis of hydrocarbons both in conventional furnaces[53] and in plasma jets[54,55] is an important commercial source of acetylene. Similarly, despite its high reactivity in flames, several studies have indicated the important role played by acetylene in the formation of carbon in flames and allied systems. For example, mass spectrometric analysis has shown the presence of acetylene in methane-oxygen and propane-oxygen flames[56,57,58] whilst the technique of flash photolysis has indicated that acetylene is the principal intermediate involved in the formation of carbon from ketene[59,60,61]. Such observations led Porter to suggest that acetylene is a major precursor in the reactions leading to carbon formation in flames[59,60,61] and have initiated a considerable amount of research into the formation of carbon from acetylene. Similarly, the industrial importance of "acetylene black" has made acetylene pyrolysis the subject of many experimental studies[62-65].

1.3 Carbon formation from acetylene

1.3.1 Carbon formation in acetylene/oxygen flames

Early work with acetylene-oxygen flames tended to rest on observations of their physical behaviour and some of the results obtained with such flames have already been described. Thus Street and Thomas[23] when they determined the critical O/C ratio for a series of premixed hydrocarbon-air flames, included an acetylene flame in their experiments and found that it had the lowest critical O/C ratio of the series. Parker and Wolfhard[26] and Milberg[27] determined the effect of pressure on an

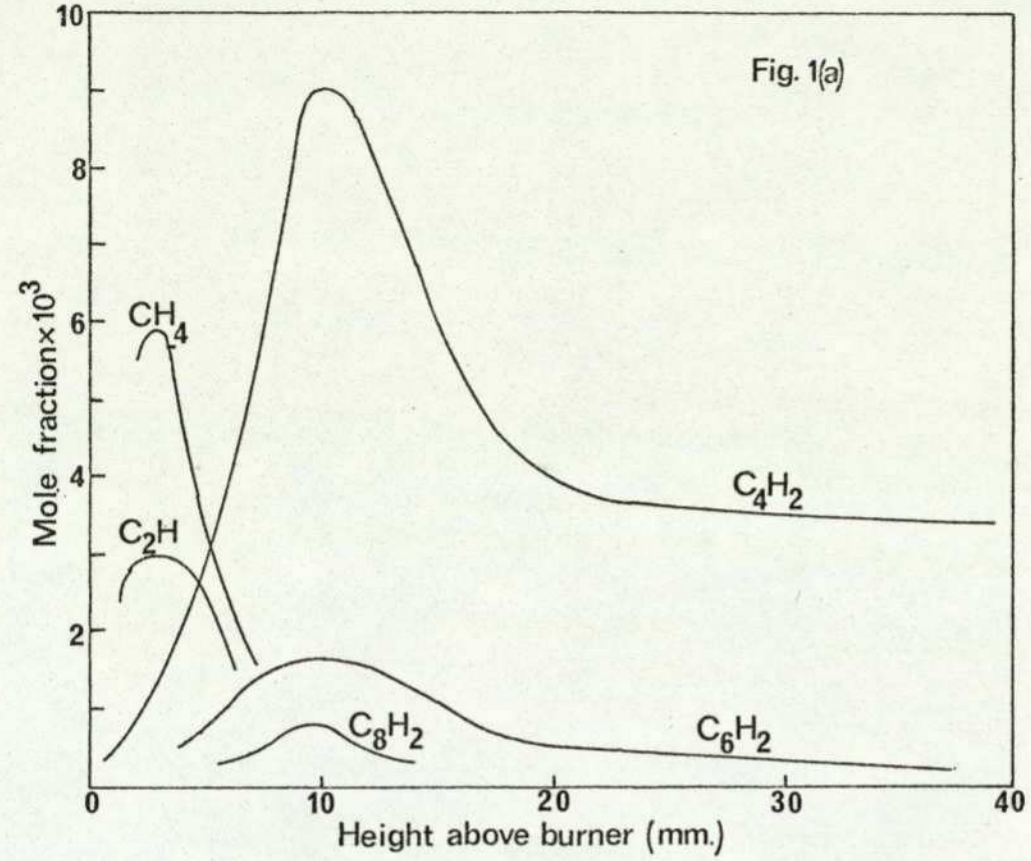
acetylene-air diffusion flame.

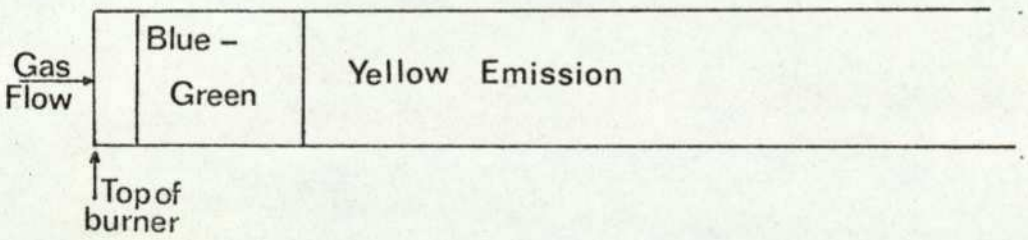
It was found that some transient intermediates present in the flame, such as C_2, could be observed using spectroscopic methods. Gaydon and Fairbairn[66] found a high concentration of C_2 in carbon-forming acetylene-oxygen flames, whilst isotopic tracer work by Ferguson[121] with similar flames established that radiating C_2 is randomized; in other words, this species does not originate by stripping off hydrogen atoms from acetylene.

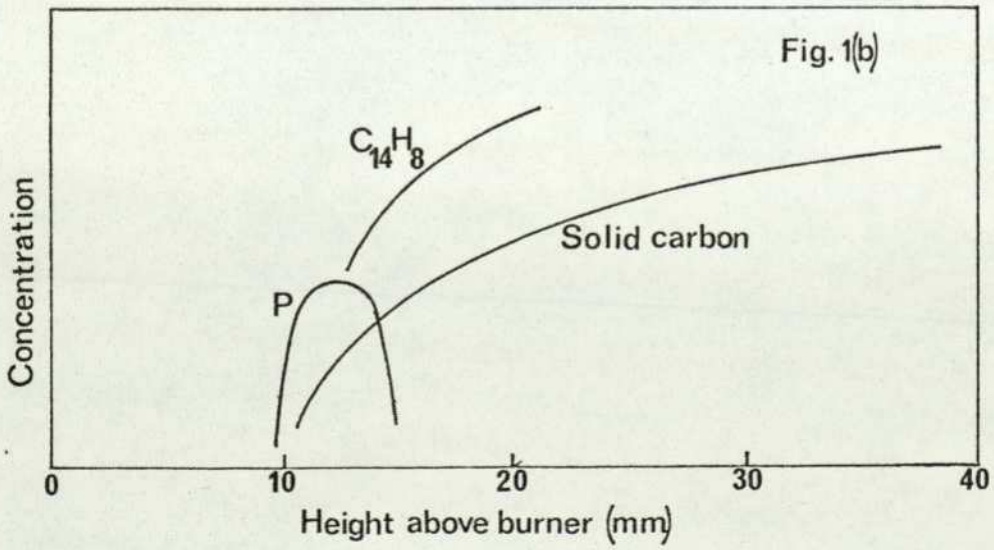
Extremely interesting results have recently been reported by Bonne , Homann and Wagner[67] in the course of an investigation of the chemical species present in acetylene-oxygen premixed flames burning under conditions where carbon is or is nearly formed. Using a flat-flame burner and working under reduced pressures (20 mm.Hg.) to facilitate sampling, constituents in the flame were analysed by mass spectrometry and optical spectroscopy. Figure 1.1(a) shows concentration profiles for the low molecular weight hydrocarbons and radicals detected in the flame. The diagram also indicates the usual appearance of the flame at various heights above the burner. (The blue-green/yellow dividing line marks the end of the oxidation zone and the beginning of the carbon-forming zone within the flame.) Bonne et al[67] observed that butadiyne was the principal hydrocarbon product formed in the initial stages of the flame although this compound was preceded by relatively large amounts of methane. Hexatriyne (C_6H_2) and octatetrayne (C_8H_2) were also found together with butadiyne, and in very fuel-rich flames $C_{10}H_2$ and $C_{12}H_2$ were also detected. A continuous increase in polyalkyne concentration was observed on passing from a carbon-free flame to one which yielded soot, whilst the concentrations of other low molecular weight species became immeasurably small before the start of the yellow carbon-forming zone.

Figures 1(a) and 1(b)

The variation in the concentration of various chemical species at different heights above a low pressure acetylene-oxygen premixed flame (ref. 67)







Work on an acetylene-oxygen flame at somewhat higher pressures (240 mm.Hg.) by Fenimore andJones[68] indicated a similar profile for butadiyne and hexatriyne, although limitations of sensitivity precluded measurements of the concentrations of higher polyalkynes. Furthermore, the temperature of the flame in the region of polyalkyne formation was about 1800K, some 100K higher than the flame at 20 mm.Hg.

From the results of Bonne, Homann and Wagner[67], it appears that the ethynyl radical (C_2H) is the most abundant of the free radicals present. Other hydrogen-containing radicals present were CH_3, C_4H_3 and C_3H_3, although their concentrations were not recorded. C_2 was detected by its emission spectrum; its absolute concentration was not determined but the maximum relative concentration was recorded at ca. 7 mm above the burner. The concentration then decreased rapidly, until little of this species was present at a height of 20 mm and beyond.

Jessen and Gaydon[69] measured the concentration of C_2 in an oxyacetylene flame burning at one atmosphere pressure. It was found that C_2 had a high concentration throughout the flame, although its concentration in the early stages exceeded that of the equilibrium value calculated from the amount of solid carbon present in the flame. Beyond the reaction zone the concentration gradually fell to the equilibrium value. The flames studied by Jessen and Gaydon[69] were not strictly comparable with those investigated by Bonne et al[67]. The difference in pressure is large and this affects the temperature. The high pressure flame had a temperature above 3000K whereas the maximum temperature in the low pressure flame was between 1650 and 1700K. Pressure may also affect the reactions of the reactant molecules and radicals; the low-pressure flame presumably allows a longer half life for the participating radicals than the flame at atmospheric pressure and due to the extended, low-temperature reaction zone, the reactions in the low-pressure flame

may have some of the characteristics of reactions in a diffusion flame.

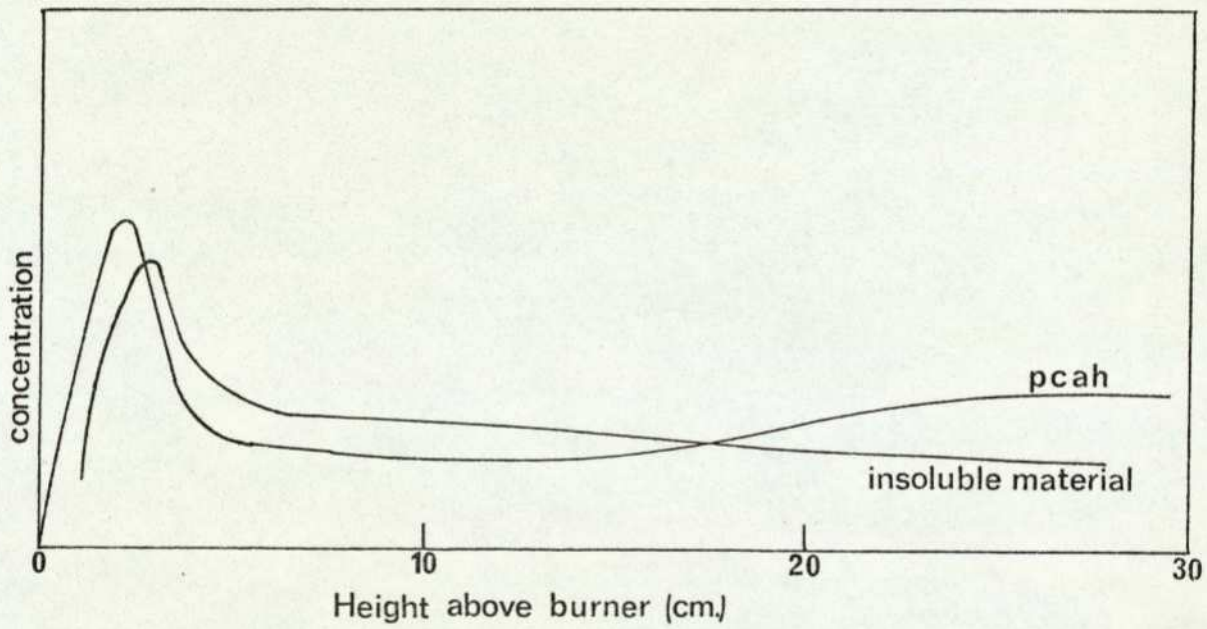
In a later paper, Homann and Wagner[70] examined the formation of polycyclic aromatic hydrocarbons (p.c.a.h.) through an acetylene-oxygen flame. Naphthalene, acenaphthalene, phenanthrene, pyrene and coronene were among the p.c.a.h. found in the flame. Figure 1.1(b) shows the concentration profile of a typical p.c.a.h. together with a profile (not to scale) of carbon formed throughout the flame. The p.c.a.h. were produced at the same time as carbon and their concentrations increased steadily during carbon formation. The total concentration of p.c.a.h. in the burnt gas was found to be 10^{-2} mole per cent.

Tompkins and Long[71] have given a detailed description of the flux of polycyclic aromatic hydrocarbons in low pressure acetylene-oxygen flames. The results differ from those of Homann and Wagner[70] and are shown in Figure 1.2. The height above the burner is measured in cm. The flux of p.c.a.h. shows a maximum concentration just before the maximum concentration attained by the carbonaceous material collected in the flame. The concentration of p.c.a.h. then passes through a minimum value before gradually rising to another maximum ca. 35 cm above the burner. The discrepancy between the two sets of results in the region 12 to 40 mm above the burner may, however, be due to the different analytical techniques used. Tompkins and Long[71] indicate that sampling in the lower region of the flame may not have been as accurate as in the method used by Bonne et al[67]. However, the general trend of consumption of p.c.a.h. in the higher parts of the flame is fairly clear. The gradual growth of p.c.a.h. after the minimum concentration is attributed to pyrolysis of residual acetylene.

Homann and Wagner[70] have also monitored the concentration of what are termed "precursors of carbon"; these correspond to P in Figure 1.1(b). These precursors are hydrocarbons of molecular weight between 250 and 550.

Figure 1.2

Flux of polycyclic aromatic hydrocarbons (p.c.a.h.) and insoluble residues in a low pressure acetylene-oxygen flame (ref. 71).



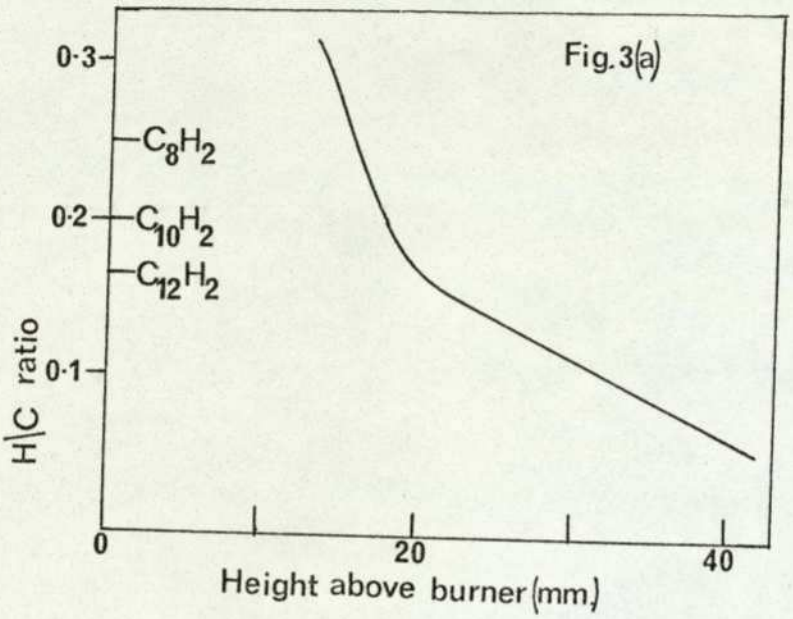
They are not apparently aromatic, show a maximum concentration between 12 and 14 mm above the burner and are rapidly consumed in the carbon-forming region. Tompkins and Long[71] collected solid material at various heights above the burner, and at a position in the flame corresponding to the region of precursor formation observed by Homann and Wagner[70] noted the deposition of a continuous smooth translucent yellow film. When sampling was carried out at various points higher in the flame, a gradual change in the nature of the deposit was observed until, at 6.4 cm above the burner, fluffy black carbon was formed.

Homann and Wagner[7] also plotted the H/C ratio of carbon particles against their location (height above the burner) and their results are shown in Figure 1.3(a). The comparable graph obtained by Tompkins and Long[71] is shown in Figure 1.3(b). There is a rather large discrepancy between the two sets of results but this was neither explained nor discussed in the later paper[71]. To obtain the graph illustrated in Figure 1.3(b), Tompkins and Long used chloroform to extract the soluble component of the carbonaceous particles collected. It is possible that an explanation for the discrepancy lies in this pretreatment of samples.

Homann and Wagner[7] presented profiles of concentration of carbon, rate of carbon formation and rate of growth of particle radii (Figure 1.4). The size was found to increase continuously up to a point ca. 50 mm above the burner, although the total number of particles decreased in this range. The yield of carbon remained constant above 50 mm. However, Tesner et al[72] working with acetylene-oxygen diffusion flames found that particle concentration attained a constant maximum value. On account of the differences in conditions and units involved in references 7, 70, 71 and 72 it is difficult to compare the rates of carbon formation in the different systems.

Figures 1.3(a) and 1.3(b)

Variation of H/C ratio with height above the burner of a low pressure acetylene-oxygen flame. (refs. 7 and 71 respectively)



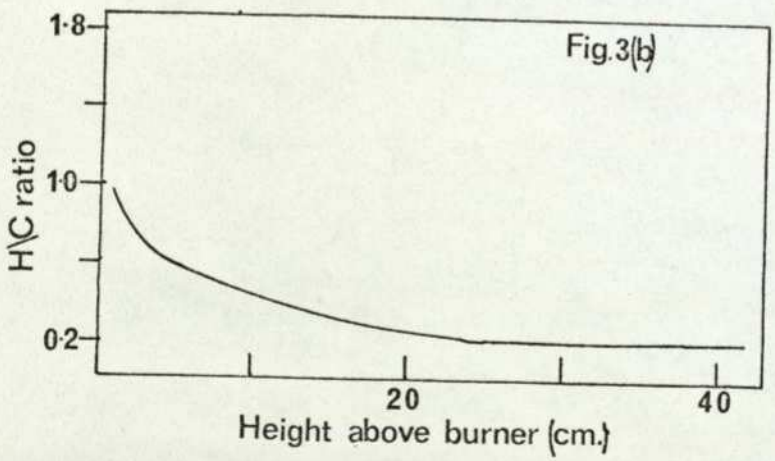
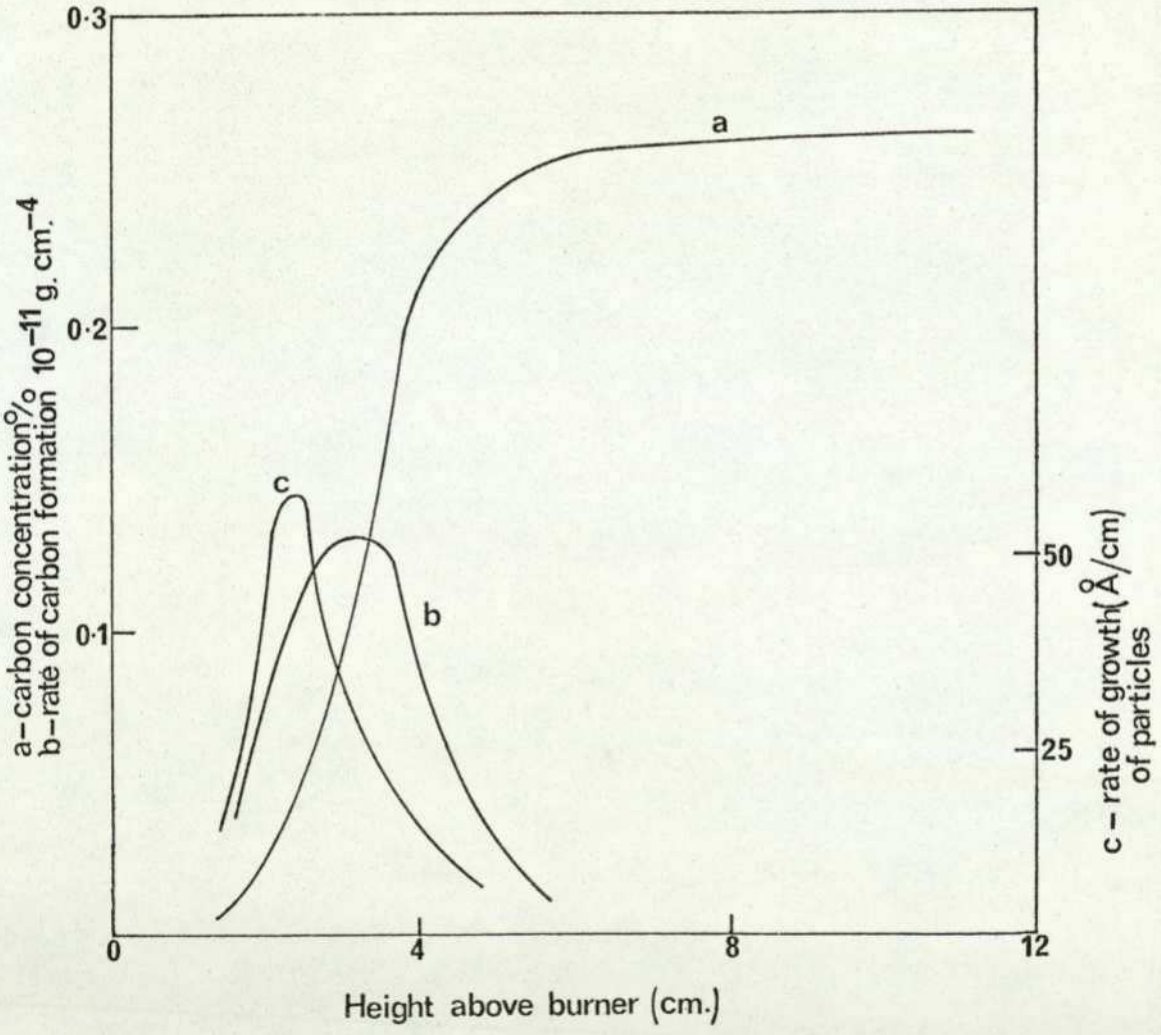


Figure 1.4

Carbon concentration, rate of carbon formation and rate of particle growth in a low pressure acetylene-oxygen flame (ref. 7)



1.3.2 Carbon formation in the pyrolysis of acetylene

The decomposition of acetylene has been extensively studied in the range 400°C to 2500°C. Somewhat remarkably the kinetics are second order in acetylene throughout the whole of this temperature range. Nevertheless, the product spectrum shows a significant change with temperature as will be seen below.

(i) 400 - 600°C

No carbonaceous solid is deposited at these temperatures. A liquid "polymeric" product is formed which contains several polycyclic aromatic hydrocarbons and the principal gaseous products are ethylene and methane[73,74]. Benzene has also been detected in low yield[73]. The experiments carried out in this temperature region do not allow the primary products to be distinguished unambiguously.

(ii) 600 - 800°C

Cullis and Franklin[75] suggest that, in this region, butenyne is the sole primary product. In the later stages of the pyrolysis butadiyne becomes the principal product. Other abundant gaseous products are propyne, ethylene, methane and butadiyne. Polycyclic aromatic hydrocarbons are again formed[75,76] and these include chrysene, pyrene, phenanthrene, 1,2-benzpyrene and 3,4-benzpyrene. Benzene is also found as was earlier shown by Berthelot[77].

As the temperature is varied from 600 to 800°C, there is a transition from a light yellow liquid formed at lower temperatures to solid carbon[78,79]. The empirical formula of the "carbon" formed at 800°C is C_8H_4.

(iii) 800 - 2400°C

Up to 1000°C butenyne is again the primary product and the aliphatic and aromatic products are the same as those found between 600 and 800°C. Above 1000°C the p.c.a.h. seem to become less important and their presence is not always recorded.

In the range 1000°C - 1500°C the primary product changes from butenyne to butadiyne[80,81]. Gay et al[81] have established that butadiyne is the primary product of the shock-heated decomposition of acetylene throughout the whole of the temperature range 1325 to 2125°C. The appearance of butadiyne is preceded by the formation of the radical species C_4H_3. Butadiyne is followed by hexatriyne and octatetrayne and the build up of these polyalkynes (Figure 5) bears a strong resemblance to the growth of polyalkynes prior to carbon formation in the low-pressure premixed acetylene-oxygen flame investigated by Bonne et al[67] (Figure 1(a)).

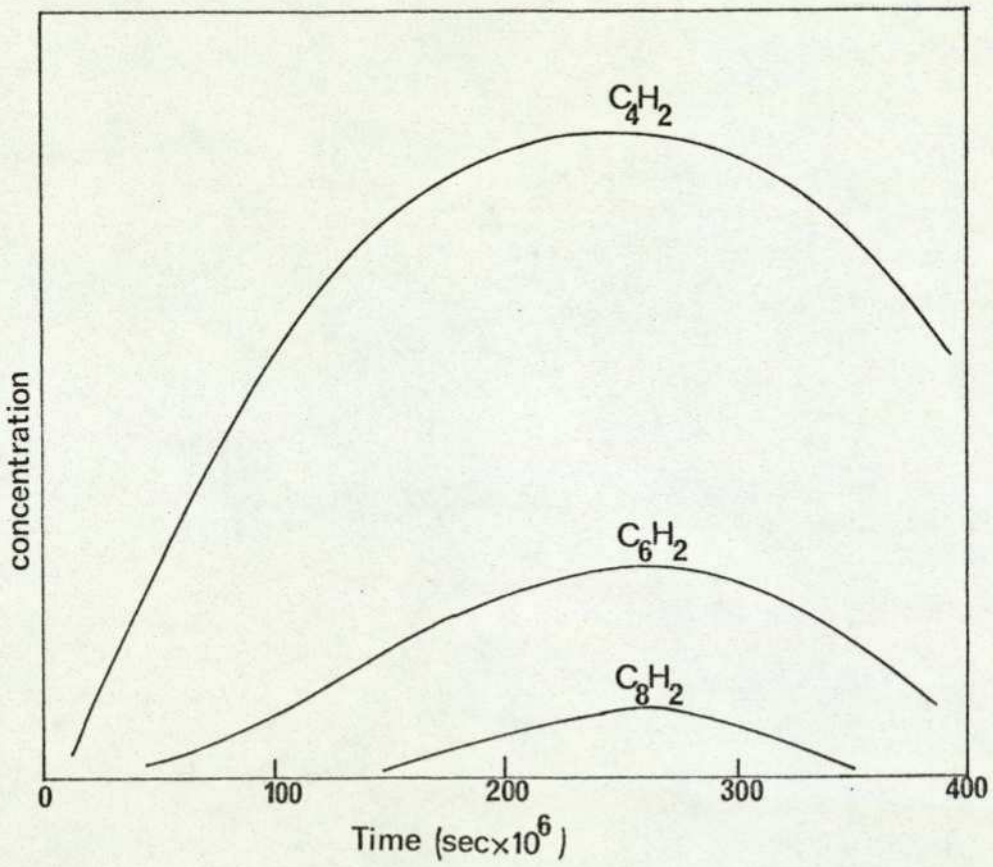
Tesner[62,82] studied carbon formation in the region 800 - 1700°C and found two distinct types of carbon[62]. A "polymeric" type containing up to 50% of volatile material predominated at lower temperatures, and a "pyrocarbon" became prominent at higher temperatures. "Acetylene black", produced at the very high temperatures of a plasma jet, is the purest form of carbon black so far obtainable.

1.3.3 Similarities between carbon formation in systems involving acetylene and other hydrocarbons

Bonne et al[67] showed that acetylene and polyalkynes are formed in fuel-rich flames of ethane and propane. Acetylene formation preceded the appearance of polyalkynes and, as in an acetylene flame, the polyalkyne concentration passed through a maximum in the later stages of the oxidation zone. Subsequently the polyalkynes were consumed in the carbon-forming region. In experiments involving ethylene flames, Fenimore and Jones[68] found a similar build up of acetylene, butadiyne and hexatriyne prior to the carbon-forming region. Homann and Wagner[70] found, perhaps not surprisingly, that with a benzene flame aromatic species were present in higher concentration than in an acetylene flame. Under these conditions polyalkynes were found in relatively low concentration. Unfortunately,

Figure 1.5

Variation of polyalkyne concentration with pyrolysis time for shock heated acetylene at 2200K (ref. 81)



no time-resolved studies have been carried out of the concentrations of acetylene and polyalkynes which are formed as intermediates in the pyrolysis of hydrocarbons.

Earlier, it has been mentioned that acetylene is a principal product of the high temperature pyrolysis of hydrocarbons and is itself readily transformed into carbon at these temperatures. Furthermore, pyrolysis of acetylene has been shown to proceed through the formation of polyalkynes. It is difficult, therefore, to escape the conclusion that the role of acetylene in hydrocarbon pyrolysis is similar to that which it plays in hydrocarbon flames.

1.4 Mechanisms of carbon formation

If hydrocarbons are heated to a sufficiently high temperature in the absence of oxygen, they form carbon particles containing relatively small amounts of hydrogen. Hydrocarbon flames yield similar carbon particles even when there is more than enough oxygen present to react with the carbon in the original fuel. The reactions which lead to carbon must therefore be those of addition and dehydrogenation. The formation of carbon seems to be a very rapid process; in premixed flames, for example, carbon particles containing 10^4 to 10^5 carbon atoms are produced within a millisecond. The process appears to be extremely efficient, and Thomas[83] has calculated that the "average collisional efficiency" is about one in ten. Thus carbon formation involves rapid polymerization reactions which occur at temperatures normally associated with the decomposition and fragmentation of molecules.

Cullis and Palmer[5] have reviewed most of the theories of carbon formation but only those mechanisms which are applicable to the pyrolysis and burning of acetylene will be mentioned here. Acetylene frequently appears as a product of the flames and pyrolysis of other hydrocarbons

and, even if carbon formation via acetylene plays only a minor role in the production of carbon from more complex molecules, an understanding of the mechanism of the formation of carbon from acetylene would be of considerable value.

One theory of the growth of carbon particles involves decomposition of hydrocarbons on C_2 nuclei initially formed in the reaction. The C_2 particles, it is thought, grow rapidly by adding on parent hydrocarbon molecules which simultaneously undergo dehydrogenation. This theory was first put forward by Gaydon and Fairbairn[66] and recently Jessen and Gaydon[69] have found high concentrations of C_2 in premixed acetylene-oxygen flames. Tesner[82] introduced the same idea as a basis for a mathematical model for carbon formation during the pyrolysis of acetylene. Later studies by Tesner and co-workers on both acetylene-oxygen flames[72] and acetylene pyrolysis[62] indicated that this mechanism takes place at temperatures above 1600°C. Hudson and Heicklen[84] used a similar mechanism in developing a sophisticated (but, as yet, untested) mathematical model. The active nucleus was not specified but it was suggested that this might be C_2, C_2H or C_2H_2.

Yet another theory introduces the idea of simultaneous dehydrogenation and polymerization of acetylene. According to this, acetylene molecules and derived free radicals add to one another by hydrogen displacement reactions to form "polymers" which subsequently grow sufficiently to form carbon particles. This view was first introduced by Porter[59] and has recently received strong support from the analytical work of Bonne, Homann and Wagner[67] on premixed acetylene-oxygen flames. The build-up of polyalkynes just prior to carbon formation in this system has already been described. These compounds are produced via free radicals derived from acetylene. For example, the ethynyl radical may react initially with acetylene, and then with more complex alkynes, in the following way:

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H$$

$$C_2H + C_4H_2 \longrightarrow C_6H_2 + H$$

The polyalkynes produced are envisaged as active intermediates to which unsaturated radicals can readily add, forming the high molecular weight precursors of carbon observed by Bonne et al. Polyalkynes were observed in the low pressure flames at temperatures in the region of 1400°C but this temperature is well below that of the flames studied by Jessen and Gaydon[69] and also below that favoured by Tesner[62] in his postulation of the C_2 mechanism.

Gay et al[81] have described the time-resolved analysis of the products of acetylene pyrolysis in the temperature range 1325 to 2125°C. The concentration/time profiles for the growth of butadiyne, hexatriyne and octatetrayne (Figure 1.5) are similar to those for polyalkynes found by Bonne et al[67] and this may indicate that the process of carbon formation is the same during acetylene pyrolysis at these temperatures as it is in the acetylene-oxygen flame. Unfortunately, there are no time-resolved data on the fate of high molecular weight compounds in acetylene pyrolysis.

Polycyclic aromatic hydrocarbons (p.c.a.h.) are formed during the pyrolysis and burning of hydrocarbons and, since these compounds are frequently found together with the carbon collected in these systems, a further theory suggests their involvement in the formation of carbon. It is difficult to assess whether or not polycyclic compounds are unreactive stable co-products or intermediates which can undergo dehydrogenation and combination to form carbon. The evidence is ambiguous. Results from the low-pressure oxygen-acetylene flames of Long and Tompkins[71] indicate that p.c.a.h. are consumed in the carbon-forming region of the flame. Bonne et al, on the other hand, show that there is a rising concentration of p.c.a.h. in this region (see Figures

1.1(b) and 1.2). The rapid decline in p.c.a.h. concentration found by Long and Tompkins[71] may be due to carbon formation or merely to oxidation of the p.c.a.h.

In the pyrolysis of acetylene, p.c.a.h. occur in the lower temperature region 400-1000°C but above 1000°C their relative concentration falls off rapidly. Badger and co-workers (see for instance reference 76) have established that p.c.a.h. are formed in the highest yield in the region 600-900°C. Carbon formation begins to occur at 700°C and becomes important above 800°C. This could mean that the carbon-forming reactions are sufficiently fast to compete with the production of p.c.a.h. or that the p.c.a.h. once formed are consumed to form carbon.

In summary, it can be seen that all the principal theories of carbon formation rely for evidence on the identification of the postulated intermediate just before and during the carbon-forming region. The process of carbon formation is, however, extremely fast and the very fact that these intermediates are identified in appreciable quantities before, during and after carbon formation could indicate that they are stable co-products rather than precursors. Identification of a given intermediate is suggestive but insufficient to establish a mechanism with any certainty.

A general mechanism for carbon-formation is difficult to establish for two reasons. Firstly the present analytical techniques are inadequate to identify the potential precursors of carbon of molecular weight in the range from about 600 up to that of the first carbon particles identified by the electron microscope. Thus it is impossible to follow all stages of carbon formation analytically.

Secondly, and more fundamentally, the mechanism of pyrolysis of many unsaturated compounds and particularly that of acetylene is still not fully known. It is probable that the mechanism of carbon formation will remain uncertain at least until the mechanism of acetylene pyrolysis is understood and information is available regarding the kinetics of

radical reactions involving not only such species as C_2, C_2H and C_2H_3 but also their higher homologues.

1.5 Mechanisms of acetylene pyrolysis

It has already been seen (Section 1.3.2) that the thermal decomposition of acetylene is second order over the whole of the temperature range 673-2773K. From 673 to 2450K the second order rate constant has been found to increase with temperature according to the equation[81]:

$$\log k(\text{l.mole}^{-1}\text{sec}^{-1}) = (10.8 \pm 0.11) - [(41{,}610 \pm 620)/4.58T].$$

The primary product over the region 1200-2450K is butadiyne. Below 900K a considerable quantity of polymer is found. None of the gaseous products found are believed to be primary products in this temperature region. Reaction is preceded by an induction period at all temperatures, the maximum rate being between two and four times the initial rate. Reaction is inhibited by nitric oxide. At lower temperatures there are marked surface effects and reaction vessels need to be conditioned before reproducible results can be obtained. Indeed some workers find evidence for a separate heterogeneous unimolecular reaction[80,85]. The striking similarity in the overall kinetics and in the values of the Arrhenius parameters have stimulated continued efforts to base the mechanism on a single initiation step which operates over the entire temperature range in question.

In acetylene, the C≡C bond strength is 230 k.cal mole^{-1} and the strength of the C-H bond is about 114 k.cal mole^{-1}. These values greatly exceed the overall activation energy for the breakdown of acetylene and hence initiation by a homogeneous unimolecular reaction appears to be unlikely.

A mechanism has been suggested to overcome this difficulty,

however, and this involves the formation of triplet acetylene by the bimolecular collision of two acetylene molecules:

$$2C_2H_2 \longrightarrow C_2H_2^* + C_2H_2 \qquad (1)$$

where $C_2H_2^*$ denotes the triplet state of acetylene. This excited species can then add to another acetylene molecule:

$$C_2H_2^* + C_2H_2 \longrightarrow C_4H_4^* \qquad (2)$$

or alternatively suffer deactivation:

$$C_2H_2^* + C_2H_2 \longrightarrow C_2H_2 + C_2H_2 \qquad (3)$$

The excited $C_4H_4^*$ biradical can undergo rearrangement to yield butenyne in a chain-propagating step:

$$C_4H_4^* + C_2H_2 \longrightarrow C_4H_4 + C_2H_2^* \qquad (4)$$

or it can add to a molecule of acetylene to form higher polymeric products:

$$C_4H_4^* + C_2H_2 \longrightarrow \text{Products} \qquad (5)$$

Formation of butadiyne via the heterogeneous decomposition of butenyne is suggested:

$$C_4H_4 \longrightarrow C_4H_2 + H_2 \qquad (6)$$

The operation of this mechanism is very difficult to test both experimentally and theoretically. Little is known about the triplet states of acetylene, although the energy of the lowest lying triplet state has recently been estimated to be between 60 and 108 k.cal mole^{-1} [86]. Since the overall activation energy of the reaction is ca. 41.6 k.cal mole^{-1}, the reaction must proceed via a long chain involving step (4) and the rate of deactivation by step (3) should be low. It seems unlikely that this mechanism could be effective in the region accessible to shock-tube measurements (1600-2400K), since butadiyne is a primary product and there is no contribution from heterogeneous processes under these conditions.

Further, the radical species C_4H_3 has been directly observed in such systems[81]. A further mechanism has been postulated, involving the free mono-radicals, C_2H_3 (vinyl) and C_2H (ethynyl). Their formation in acetylene-containing systems is presumed to involve the reaction:

$$C_2H_2 + C_2H_2 \longrightarrow C_2H + C_2H_3 \qquad (1a)$$

Alternatively, a butenynyl radical (C_4H_3) and a hydrogen atom can be produced:

$$C_2H_2 + C_2H_2 \longrightarrow C_4H_3 + H \qquad (1b)$$

Back[87] has recently suggested a complete mechanism for acetylene pyrolysis based on initiation step (1a). In the high-temperature region, the vinyl radical is assumed to be largely dissociated into acetylene and a hydrogen atom:

$$C_2H_3 \longrightarrow C_2H_2 + H \qquad (2)$$

Butadiyne, the sole reaction product on the basis of this mechanism, is assumed to be formed via the following reaction sequence:

$$C_2H + C_2H_2 \longrightarrow C_4H_3 \qquad (3)$$

$$C_4H_3 \longrightarrow C_4H_2 + H \qquad (4)$$

$$H + C_2H_2 \longrightarrow H_2 + C_2H \qquad (5)$$

$$2C_2H \longrightarrow C_4H_2 \qquad (6)$$

A steady-state treatment of reactions (1a) and (2) - (6) yields the following equation for the rate of formation of butadiyne:

$$\frac{d[C_4H_2]}{dt} = [k_1 + k_3(\frac{k_1}{k_6})^{\frac{1}{2}}] [C_2H_2]^2$$

Back, however, tacitly assumes that

$$k_3\left(\frac{k_1}{k_6}\right) \gg k_1$$

so that the above equation becomes

$$\frac{d[C_4H_2]}{dt} = k_3\left(\frac{k_1}{k_6}\right)^{\frac{1}{2}} [C_2H_2]^2$$

The validity of this assumption is critically dependent on the pre-exponential factors chosen for k_1, k_3 and k_6. If it is assumed that the activation energy for reaction (1) is about 70 k.cal mole^{-1} [87,88], then the rate constant for reaction (1a) may be written in the form

$$k_1 = A_1 \, e^{\frac{-70,000}{RT}} = A_1 \, 10^{\frac{-70,000}{2.303RT}}$$

Unfortunately, the energy of activation for reaction (3) is harder to estimate. The activation energy for the addition of unsaturated radicals to acetylene is estimated to be 6.5 k.cal mole^{-1} [87]. If this value for reaction (3) is accepted and the activation energy of reaction (6) is zero, then:

$$k_3\left(\frac{k_1}{k_6}\right)^{\frac{1}{2}} = A_3\left(\frac{A_1}{A_6}\right)^{\frac{1}{2}} e^{\frac{-(E_3+E_1)/RT}{2}}$$

$$= A_3\left(\frac{A_1}{A_6}\right)^{\frac{1}{2}} e^{\frac{-41,500}{RT}}$$

$$= A_3\left(\frac{A_1}{A_6}\right)^{\frac{1}{2}} 10^{\frac{-41,500}{2.303RT}}$$

Hydrocarbon radical combination reactions invariably have A factors of $10^{10 \pm 0.5}$ l.mole^{-1}sec^{-1} [89]. Thus $A_6 \simeq 10^{10 \pm 0.5}$ l.mole^{-1}sec^{-1} and $A_{(1a)}$ has been estimated from thermochemical data to be $10^{12.7}$ l.mole^{-1} sec^{-1} [87]. Back[87] also estimates a value of $10^{8.8}$ for the pre-exponential factor for the addition of unsaturated free radicals to acetylene. If

an identical value is assumed for A_3 in the expression for $A_3(\frac{A_1}{A_6})^{\frac{1}{2}}$, then:

$$A_3(\frac{A_1}{A_6})^{\frac{1}{2}} = 10^{8.8}\ (10^{12.7} - 10)^{\frac{1}{2}}\ \text{l.mole}^{-1}\text{sec}^{-1}$$

$$= 10^{8.8 + 1.35}\ \text{l.mole}^{-1}\text{sec}^{-1}$$

$$= 10^{10.15}$$

and

$$A_1 = 10^{12.7}\ \text{l.mole}^{-1}\text{sec}^{-1}$$

whence

$$k_3(\frac{k_1}{k_6})^{\frac{1}{2}} = 10^{10.15 - 41.5/\phi}\ \text{l.mole}^{-1}\text{sec}^{-1}$$

and $$k_1 = 10^{12.7 - 70/\phi}\ \text{l.mole}^{-1}\text{sec}^{-1}$$

where ϕ = 2.303 RT in units of k cal.mole^{-1}. Thus, for the high temperature region with T = 2.0, ϕ = 2.303 x 1.98 x 2 = 9 and

$$k_3(\frac{k_1}{k_6})^{\frac{1}{2}} = 10^{10.15 - 4.6} = 10^{5.55}$$

$$k_1 = 10^{12.7 - 7.8} = 10^{4.9}$$

Thus, $k_3(\frac{k_1}{k_6})^{\frac{1}{2}} \simeq \frac{k_1}{4.5}$

Hence the value of $k_3(k_1/k_6)^{\frac{1}{2}}$ is comparable with k_1 at these temperatures if the above A factor values are used.

The estimate of the A factors are of course tentative. In order to make the mechanism reasonable in the high temperature region, an alteration by a factor of 10^2 would be required in the value of $A_3(A_1/A_6)^{\frac{1}{2}}$.

The assumption that C_2H_3 is mainly dissociated at these temperatures is also open to question. Benson and Haugen[90] estimate that the rate constant of reaction (2) is $10^{11.9 - 31.5/\phi}$ $l.mole^{-1}sec^{-1}$. If the rate constant for the addition of C_2H_3 to C_2H_2 is again[87] given by:

$$k_a = 10^{8.8 - 6.5/\phi} \ l.mole^{-1}sec.^{-1}$$

then when $T = 2.0K \times 10^3$

$$\phi = 1.98 \times 2 \times 2.303 = 9.1$$

$$k_2 = 10^{11.9 - 3.46} = 10^{8.4} \ l.mole^{-1}sec.^{-1}$$

and $$k_a = 10^{8.8 - 0.72} = 10^{8.1} \ l.mole^{-1}sec.^{-1}$$

Thus the rate of dissociation of C_2H_3 could be comparable with the rate of the addition reaction

$$C_2H_3 + C_2H_2 \longrightarrow C_4H_5 \qquad (7)$$

and substantial amounts of C_4H_5 might then decompose to form a hydrogen atom and butenyne:

$$C_4H_5 \longrightarrow C_4H_4 + H \qquad (8)$$

Back[87] proposes that these reactions (7 and 8) occur only at the lower temperatures associated with the formation of butenyne via the ethynyl radical, viz.

$$C_2H_3 + C_2H_2 \longrightarrow C_2H_4 + C_2H \qquad (9)$$

$$C_4H_3 + C_2H_2 \longrightarrow C_4H_4 + C_2H \qquad (10)$$

This would require the co-formation of ethylene in comparable quantities to and simultaneously with butenyne. This is not, in fact, the case. Ethylene appears only at very high conversions. Back suggests that the change in the primary products may be due to a change in the

concentrations of C_2H and C_2H_3 radicals but concludes that this cannot be ascertained without more exact knowledge of the rate constants for the elementary reactions involved.

The initiation reaction proposed by Gay et al[81] and Cullis and Read[88],

$$C_2H_2 + C_2H_2 \longrightarrow C_4H_3 + H \qquad (1b)$$

has an enthalpy change of 46 k.cal mole^{-1} [81,88]. It may therefore have an activation energy close to that for the overall value for acetylene pyrolysis. It is significant that the C_4H_3 radical formed in reaction (1b) has two possible structures:

$$H_2C = \dot{C} - C \equiv CH \qquad (A)$$

$$H\dot{C} = CH - C \equiv CH \qquad (B)$$

Structure (A) is, presumably, more stable by virtue of resonance:

$$H_2C = \dot{C} - C \equiv CH \longleftrightarrow H_2C = C = C = \dot{C}H$$

$H^{\circ}F$ for this radical has been calculated to be 103 k.cal mole^{-1} [91] and this is the value which has been used for the determination of the heat of reaction for reaction (1b). Structure (B) is probably similar to that of the radical formed when C_2H adds to acetylene and it may well be more endothermic than (A). In the case of structure (A) the reaction

$$C_4H_3 \longrightarrow C_4H_2 + H \qquad (4)$$

has been estimated to be endothermic by 61 kcal.mole^{-1} [91]. Hydrogen atom elimination from (B) may be energetically more favourable and an estimate of 40 k.cal mole^{-1} has been made for the activation of this reaction[87]. If initiation takes place via reaction (1b) then chain-propagation may take place as follows:

$$C_2H_2 + H \longrightarrow C_2H + H_2 \qquad (11)$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad (12)$$

In the studies of Gay et al[81], the C_4H_3 radical had a very high steady state concentration and this could mean that the C_4H_3 radical is indeed a relatively stable entity (structure (A)) and that acetylene decomposition occurs principally by a chain mechanism involving reactions (11) and (12).

In summary it can be seen that there is a marked contrast between the relative simplicity of the mechanism of pyrolysis of saturated hydrocarbons where initiation takes place by scission of a carbon-carbon bond and the much greater complexity of the pyrolysis of acetylene where several initiation steps seem energetically possible. Detailed treatment of the subsequent chain reactions is difficult both on account of the multiplicity of possible reactions and because only approximate estimates can be made for the appropriate Arrhenius parameters.

The simplest free radical which features in the acetylene system is the ethynyl radical. Unfortunately technical difficulties make this radical impossible to detect in the shock tube studies of Gay et al[81], although Bonne, Homann and Wagner[67] have observed it in acetylene-oxygen flames.

Little is known about the kinetics of reactions of the ethynyl radical. No account of its reactions with alkynes has been published. The energetics of such reactions are difficult to estimate not least because of the divergence of opinion as to the bond strengths in acetylene. Thus, although the C-H bond strength has been studied on several occasions[91,92,93] the values recorded lie in the range 112 to 128 k.cal mole^{-1}

1.6 The ethynyl radical and its reactions

The ethynyl radical appears to have special significance, not only in the carbon-forming reactions occurring in flames and pyrolysis, but also in the mechanisms of both the high- and low-temperature oxidation

of acetylene[94]. The participation of the ethynyl radical in pyrolysis and related reactions has already been discussed, but in this Section, after a brief discussion of its role in acetylene oxidation, a review is given of studies in which the ethynyl radical has been generated and detected and information regarding the kinetics of its reactions has been obtained.

The oxidation of acetylene provides good indirect evidence for the existence of the ethynyl radical. Thus Minkoff and Tipper[95] and Stevenson and Tipper[96] believe that in the low temperature (200-450°C) oxidation of acetylene initiation occurs via the reaction:

$$OH + C_2H_2 \longrightarrow C_2H + H_2O$$

Indeed Hay and Lyon[97] have recently detected C_2HD in studies of the co-oxidation of C_2H_2/C_2D_2 mixtures and have attributed its formation to reactions such as

$$C_2H_2(C_2D_2) + OH \longrightarrow C_2H(C_2D) + H_2O(HDO)$$

$$C_2H + C_2D_2 \longrightarrow C_2HD + C_2D$$

$$C_2D + C_2H_2 \longrightarrow C_2HD + C_2H$$

At temperatures in excess of 450°C, the ethynyl radical is also an important species and the high-temperature oxidation of acetylene is initiated by pyrolysis of the hydrocarbons. For example, from shock-tube experiments, Kistiakowsky and his co-workers[98-105] proposed the following reactions as part of a more comprehensive scheme:

$$OH + C_2H_2 \longrightarrow H_2O + C_2H$$

$$O + C_2H_2 \longrightarrow OH + C_2H$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H$$

In fuel-lean mixtures, the oxidation of the ethynyl radical takes place via the reaction:

$$C_2H + O_2 \longrightarrow 2CO + H$$

Studies of the oxidation of acetylene have enabled rate constants and Arrhenius parameters to be derived mainly for reactions involving the formation of C_2H but also for its subsequent oxidation. These data are summarized in Table 1.1.

Investigations in which direct observations of the ethynyl radical has been reported are rare. This species has been observed by Homann and Wagner[106] and Jones and Boyes[107] in mass spectrometric measurements on acetylene-oxygen flames. The ethynyl radical has also been detected by e.s.r. in the high temperature reaction of hydrogen atoms with acetylene[108] and in the low temperature photolysis of acetylene[109].

Thermochemical data for the ethynyl radical and its parent molecule, acetylene, are still uncertain. However, Tables 1.2 and 1.3 list the published data for the bond dissociation energy and $H^{o}f$ of acetylene and C_2H. The difference between the highest and lowest values given for the dissociation energy of the C-H bond in acetylene is some 18 k.cal.mole^{-1}. When it is remembered that an uncertainty in activation energy of 18 kcal mole^{-1} leads to an uncertainty in rate constant of about 10^6 l.mole^{-1}sec.$^{-1}$ at 500°C, it can be seen that thermochemical estimates for the rate constants of reactions involving ethynyl radicals which employ such bond dissociation energies are liable to a considerable margin of error. Nevertheless, because the C-H bond in C_2H_2 is so strong, it might be expected that the ethynyl radical would be potentially a very reactive entity. This indeed appears to be the case. Thus Brown et al[122] have obtained A-factor values of 10^{10} l.mole^{-1}sec^{-1} (E = 7 kcal.mole^{-1}) for the reactions of ethynyl radicals with oxygen molecules and oxygen

Table 1.1

Estimates of the kinetic parameters of reactions involving the ethynyl radical

Reaction	A $cm^3 mole^{-1} sec^{-1}$	E $kcal.mole^{-1}$	Temp. K	Ref.
$OH + C_2H_2 \rightarrow H_2O + C_2H$	1.4×10^{13}	7	1700–2000	129
	6×10^{12}	7	1000–1700	122
	6×10^{11}	–	300	130
$O + C_2H_2 \rightarrow OH + C_2H$	10^{14}	14	1920–2380	128
	$3.2 \times 10^{15} \times T^{-0.6}$	17	1000–1700	122
	2×10^{14}	14	–	131
$C_2H_2 + H \rightarrow H_2 + C_2H$	2×10^{14}	11	1000–1700	122
$C_2H + O_2 \rightarrow 2CO + H$	10^{13}	7	1000–1700	122
$C_2H + O \rightarrow CH + CO$	5×10^{13}	0	1000–1700	122

Table 1.2

Thermochemical Data for Acetylene

$H^{o}f$ ($kcal.mole^{-1}$)	$D(HC \equiv CH)$ ($kcal.mole^{-1}$)	$D(HC_2 - H)$ ($kcal.mole^{-1}$)	Reference
54.3	-	-	123
54.2	-	-	124
-	-	114	91
-	150	110	92
-	-	128	93
-	-	112	87
-	230 ± 2	114 ± 7	94
-	-	117	125

Table 1.3

Heat of formation of the ethynyl radical

$H^{o}f$ ($kcal.mole^{-1}$)	Reference
130 ± 3	93
114 ± 7	94
123	126
122	127
112	92

atoms respectively. In their review of the combustion and oxidation of acetylene, Williams and Smith[94] suggest that the ethynyl radical should be even more reactive towards hydrogen abstraction than it is in the reactionswith oxygen. This means that the reactivity of the ethynyl radical compares very favourably in ease of hydrogen abstraction to that of H, OH and O (see table 1.1).

Very few studies have been reported where the reactions of the ethynyl radical have beenspecificallȳ examined. The main problem appears to be to find a radical source which generates ethynyl radicals but will not decompose added reactants. Thus mercury-photosensitized decomposition of acetylene is probably initiated by the production of an ethynyl radical and hydrogen atom[110-114].

$$Hg^* + C_2H_2 \longrightarrow Hg + C_2H + H$$

The excited mercury atom would also decompose other hydrocarbons added to the system and the resulting reaction mixture would be unsuitable for a kinetic study of the reaction of the ethynyl radical with the added hydrocarbon. The photolytic decomposition of acetylene also appears to yield an ethynyl radical[115,109] but may proceed via an excited state mechanism[115,116]. Wyatt and Stafford[93] have generated the ethynyl radical by passing hydrogen over graphite heated to about 2000K. The data obtained yielded values for the heat of formation of the ethynyl radical but the apparatus would not be easily adaptable for the study of subsequent reactions. Tarr, Strausz and Gunning[118] have shown that monochloroethyne and monobromoethyne decompose photolytically to give an ethynyl radical as the primary step:

$$C_2HX + h\nu \longrightarrow C_2H + X$$

A mixture of monobromoethyne and nitric oxide irradiated at 253.7 nm

produces carbon monoxide, bromocyanogen, acetylene and butadiyne as primary products. The following reaction mechanism was therefore proposed[118]:

$$C_2HBr + h\nu \longrightarrow C_2H + Br \quad (1)$$

$$NO + Br + C_2HBr \longrightarrow HBr + BrCN + CO \quad (2)$$

$$C_2H + C_2HBr \longrightarrow C_4H_2 + Br \quad (3)$$

$$C_2H + C_2H \longrightarrow C_4H_2 \quad (4)$$

$$C_2H + C_2HBr \longrightarrow C_2H_2 + C_2Br \quad (5)$$

Nitric oxide was added to scavenge the bromine atom and thus minimise polymerization. Reaction (2) is an example of a general mechanism whereby cleavage of a triple bond occurs in the presence of a radical and nitric oxide[119]. The yields of acetylene and butadiyne did not decrease with added nitric oxide. It appeared that nitric oxide was not scavenging the ethynyl radical. Added inert gas had only a small effect on the yields of the hydrocarbon products and this indicated that an excited state was not involved.

It was shown that reaction (3) was the principal source of butadiyne. The evidence for this was quite convincing. Variation of the light intensity of photolysis by a factor of 1000 did not alter the ratio $[CO]/[C_2H_2]$ by a factor of more than 2. It hardly varied the ratio $[C_4H_2]/[C_2H_2]$. This was not pointed out by Tarr et al[118] but does provide strong evidence for reaction (3). If reaction (4) were dominant, then

$$\frac{[C_4H_2]}{[C_2H_2]} = \frac{k_4[C_2H]^2}{k_5[C_2H][C_2HBr]} = \frac{k_4[C_2H]}{k_5[C_2HBr]}$$

The steady-state of ethynyl radicals would increase with increasing light

intensity and thus the ratio $[C_4H_2]/[C_2H_2]$ would rise at higher light intensities. This does not, in fact, occur (Table 1.4). Instead the constant ratio $[C_4H_2]/[C_2H_2]$ is consistent with reaction (3) being the sole source of C_4H_2. It was also shown that the reaction of the propynyl radical (CH_3C_2) with chloroethyne gave the product C_5H_4 (penta-1,3-diyne):

$$CH_3C_2 + C_2HCl \longrightarrow CH_3C_4H + Cl$$

Tarr, Strausz and Gunning[118] found that the ethynyl radical could abstract hydrogen from alkanes and alkenes as well as from monobromoethyne.

$$RH + C_2H \longrightarrow R + C_2H_2 \qquad (6)$$

The rate of reaction (6) for several alkanes were measured relative to reaction (3) and Table 1.5 shows some of the values obtained. Tarr et al[120] also did some work on the addition of ethynyl radicals to alkenes and found that these radicals could displace as well as abstract hydrogen atoms forming enynes. For example, when ethylene was added to a mixture of monobromoethyne and nitric oxide, butenyne was one of the principal products:

$$C_2H + C_2H_4 \longrightarrow C_4H_4 + H$$

The reaction of the ethynyl radical with propane gave five displacement products, viz. butenyne, cis and trans pent-1-en-3-yne, pent-1-en-4-yne and 2-methylbutenyne;

$$C_2H + CH_3 - CH = CH_2 \longrightarrow CH_2 = CH - C \equiv CH + CH_3$$

$$\longrightarrow CH_3 - CH = CH - C \equiv CH + H$$

(cis and trans)

$$\longrightarrow CH_2 = CH - CH_2 - C \equiv CH + H$$

$$\longrightarrow HC_2 - C(CH_3) = CH_2 + H$$

Table 4

The value of the ratio $[C_4H_2]/[C_2H_2]$ with different light intensities (reference 118)

Relative light intensity	$\frac{[C_4H_2]}{[C_2H_2]}$
1	6.4
100	3.4
120	6.8
1000	6.1

Table 1.5

Relative rates of reaction (6) to reaction (3):

$$C_2H + BrC_2H \longrightarrow C_4H_2 + Br \qquad (3)$$

$$C_2H + RH \longrightarrow C_2H_2 + R \qquad (6)$$

from the data of Tarr, Strausz and Gunning (reference 118).

RH	k_6/k_3
n-butane	0.99
isobutane	1.25
methane	0.020
ethane	0.40
neopentane	1.1
tetramethylbutane	1.2

and their rates of formation relative to reaction (3) were 1.05, 0.07, 0.06, 0.13 and 0.01 respectively. Further proof of hydrogen atom displacement was obtained when the ethynyl radical reacted with ethylene D_4 and the product C_4D_3H was identified indicating that the ethynyl radical had displaced a deuterium atom from C_2D_4.

1.7 The present work

Recent analytical work on the pyrolysis of acetylene and on acetylene-oxygen flames identified some of the intermediate species present in such systems but it has also given rise to new and complex problems. In particular it has pinpointed the need for a better understanding of the reactions of unsaturated radicals with alkynes. Hitherto investigations of aliphatic free-radical reactions have been almost exclusively confined to studies of saturated species and it has only recently become so apparent that reactions of unsaturated radicals are of considerable importance in the decomposition of acetylene.

In the present work a study has been made of the reactions of the ethynyl radical with alkynes. The results of these investigations help to elucidate the mechanism of high-temperature reactions of acetylene, some of which are of importance in carbon formation.

EXPERIMENTAL

2. Experimental Technique

2.1 Apparatus

2.1.1 Static vacuum apparatus

A mercury-free static vacuum apparatus was constructed from Pyrex glass and is shown in Figure 2.1 and Plate 1. A pressure of 5×10^{-4} mm. Hg. could be obtained in about 10 minutes using an oil diffusion pump connected to a rotary backing pump. The gas storage bulbs and gas handling section of the apparatus were fitted with either Rotaflow greaseless taps or Kel F-lubricated taps and cones (as shown in Figure 2.1). Sections of the apparatus likely to contain photosensitive compounds were blackened, either by painting the glass with matt black paint or by wrapping with aluminium foil. The apparatus also contained facilities for gas purification by trap-to-trap distillation.

2.12 Reactor

The cylindrical reactor, constructed of quartz and shown in Figure 2.2 had a diameter of 7 cm and a length of 5 cm; its volume was ca. 125 cm^3. The face opposite to the photolytic source was an optical flat. The reactor was attached to the apparatus by a greaseless ball joint enabling it to be removed for cleaning. A vacuum of 10^{-4} to 10^{-5} mm. Hg. could be maintained in the reactor for several hours. In the course of photolytic experiments a coating formed within the reactor; this was removed either after five photolyses lasting about 2 min each, or immediately after any photolysis exceeding 10 min. It was found that rinsing the reactor thoroughly with three 50 ml aliquots of AnalaR methanol was usually sufficient to restore optical transparency. Photolysis of mixtures not containing nitric oxide produced a more tenacious coating which could be removed only with fuming nitric acid.

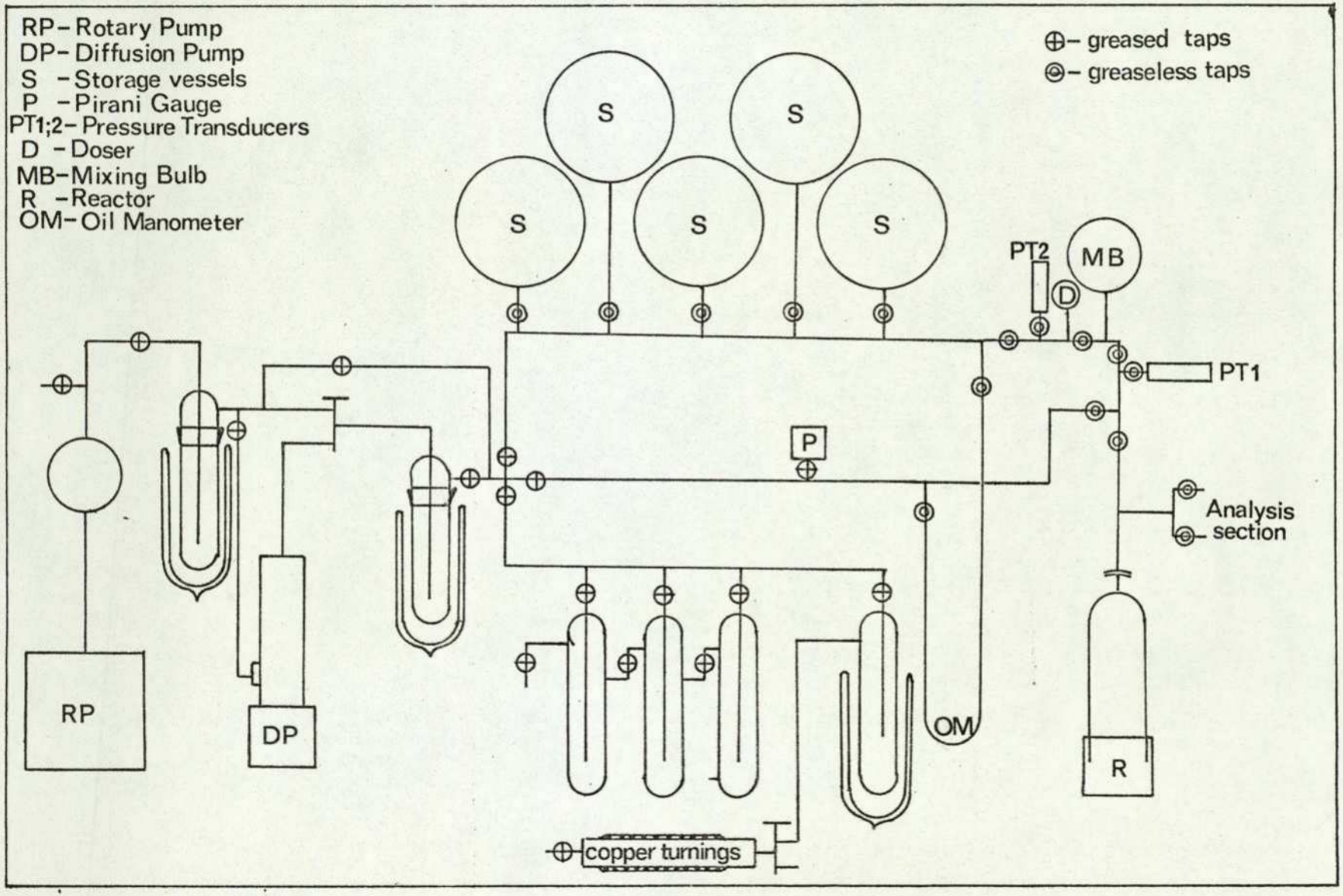


Figure 2.1

Vacuum Apparatus

PLATE 1

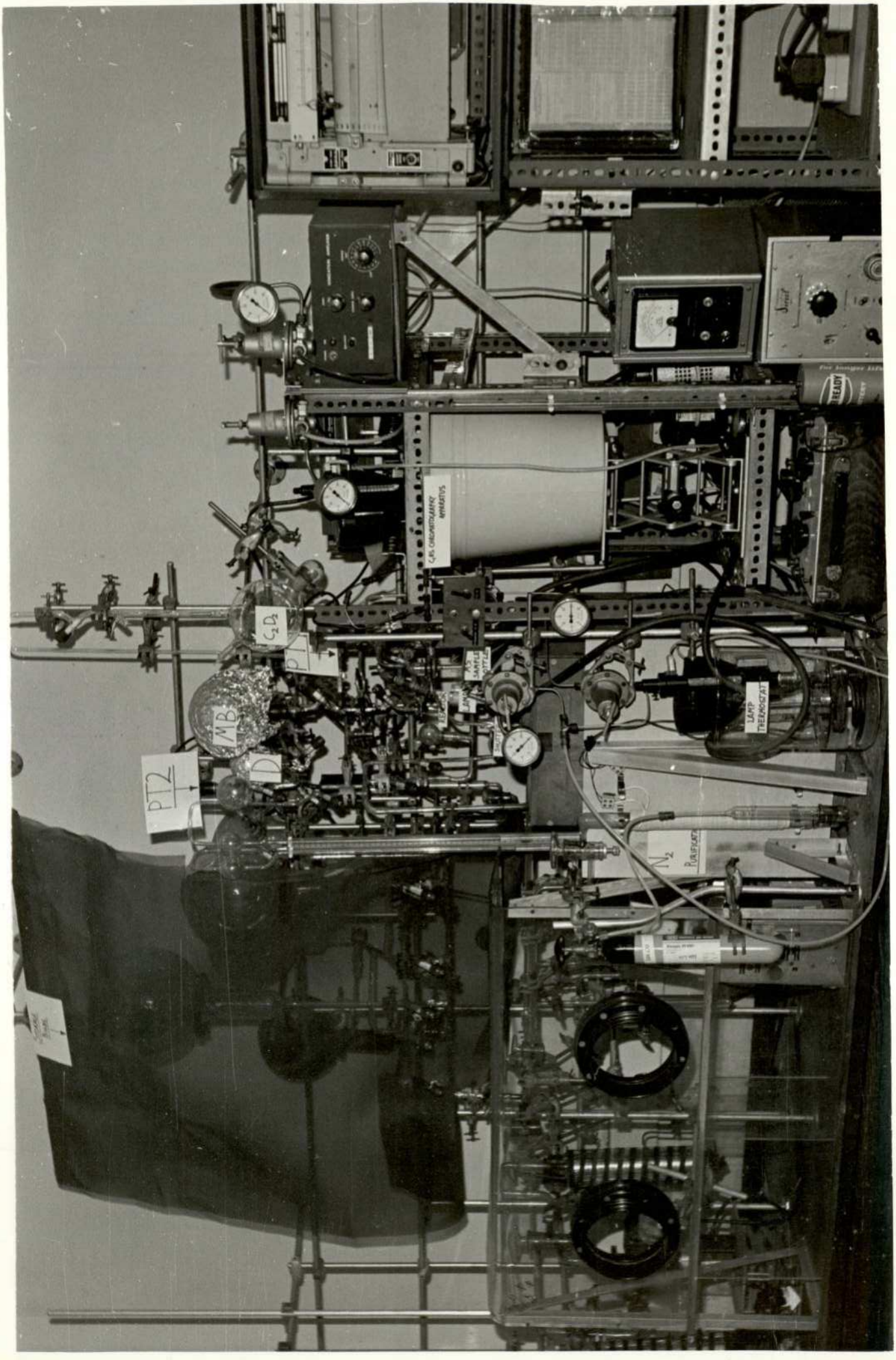
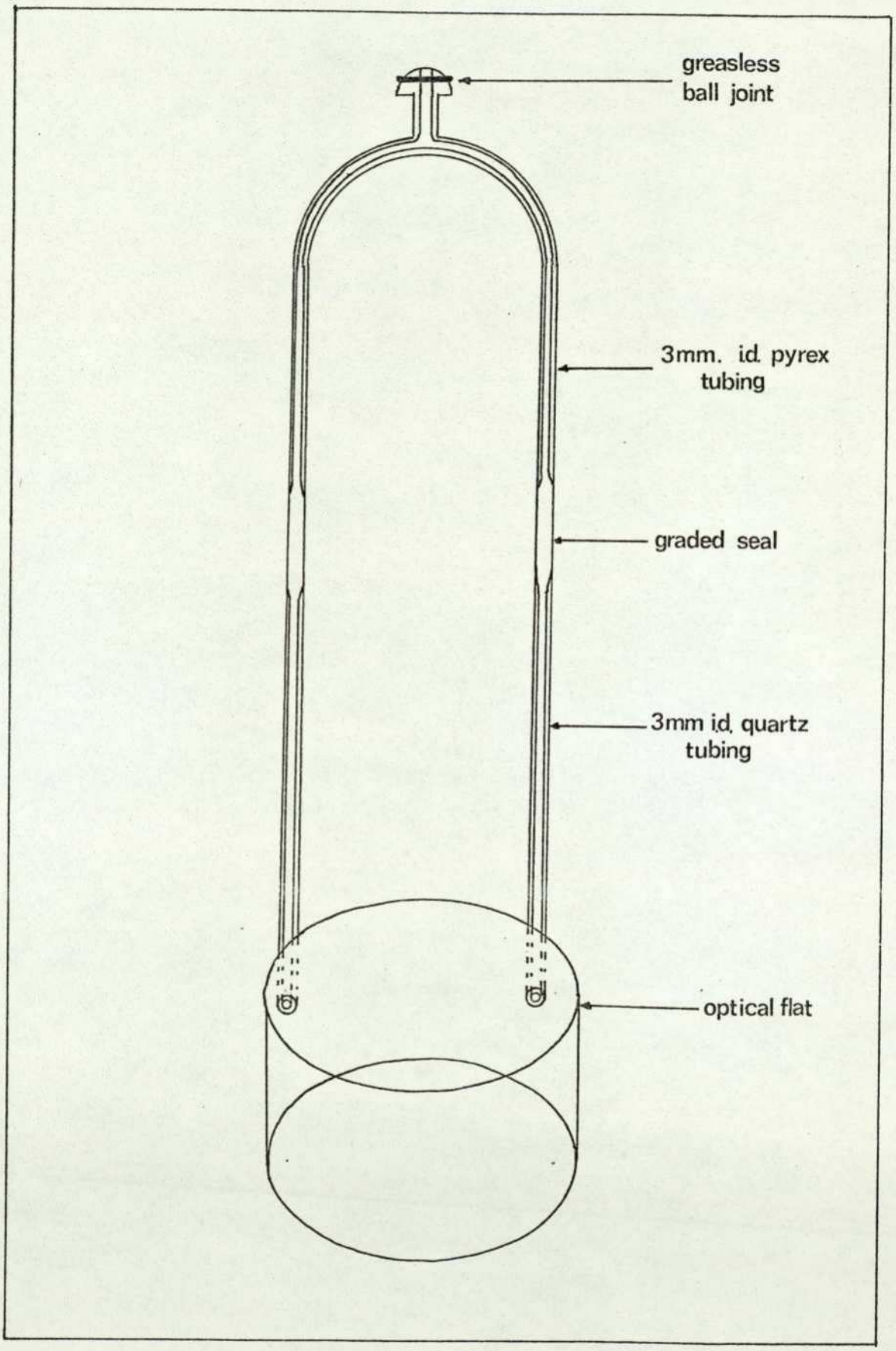


Figure 2.2

Quartz Reactor



2.1.3 Furnace

The reactor, shutter and lamp were located in a vertical furnace. The furnace consisted of an inner vitrosil tube of length 30 cm and internal diameter 9 cm. The temperature of the furnace was controlled by a Sirect Mark II temperature controller. The temperature within the furnace was measured with a calibrated chromel/alumel thermocouple, with its cold junction immersed in ice water at $0^{\circ}C$; the e.m.f. developed was measured to $\pm$ 0.01 mv on a thermocouple potentiometer. The temperature inside the furnace could be maintained to within $\pm 0.5^{\circ}C$ of the required temperature.

Initially, the temperature control unit was set to give a temperature of about $200^{\circ}C$ and a temperature distribution was obtained along the central axis and side of the furnace using a probing thermocouple. This temperature distribution is shown in Figure 2.3. The reactor was positioned within the region of minimum temperature deviation over which the temperature variation was $\pm \frac{1}{2}^{\circ}C$.

2.1.4 Pressure transducers

Reactant gas pressures were measured using Bell and Howell pressure transducers. These were activated by a Bell and Howell d.c. stabilised mains transformer and the outputs were displayed on a Comark millivoltmeter. Zero could be adjusted using the device shown in Figure 2.4. One transducer measured pressures between the doser and mixing bulbs (0 - 15 p.s.i. range, PT2 in Figure 2.1); the other measured the final pressure in the reactor (0 - 25 p.s.i. range, PT1 in Figure 2.1).

The pressure transducers were calibrated against a silicone oil manometer. (The density of the degassed oil is 1.053 $g.cm.^{-3}$ at $22.5^{\circ}C$.) The pressure on the manometer could be read to better than $\pm$ 0.035 mm.Hg. A typical calibration graph covering the range 0 to 18.5 mm.Hg. is shown

Figure 2.3

Temperature distribution of furnace

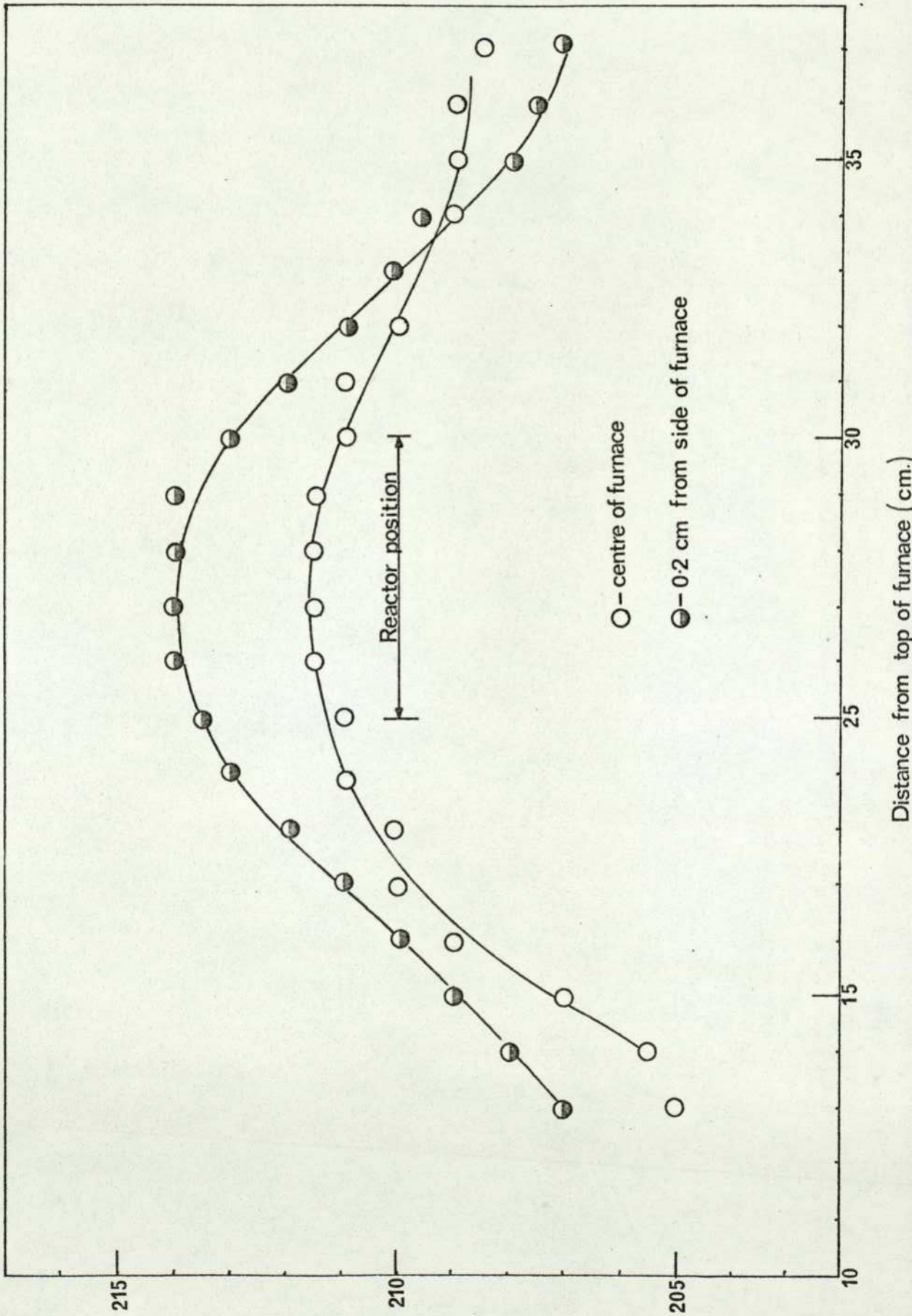
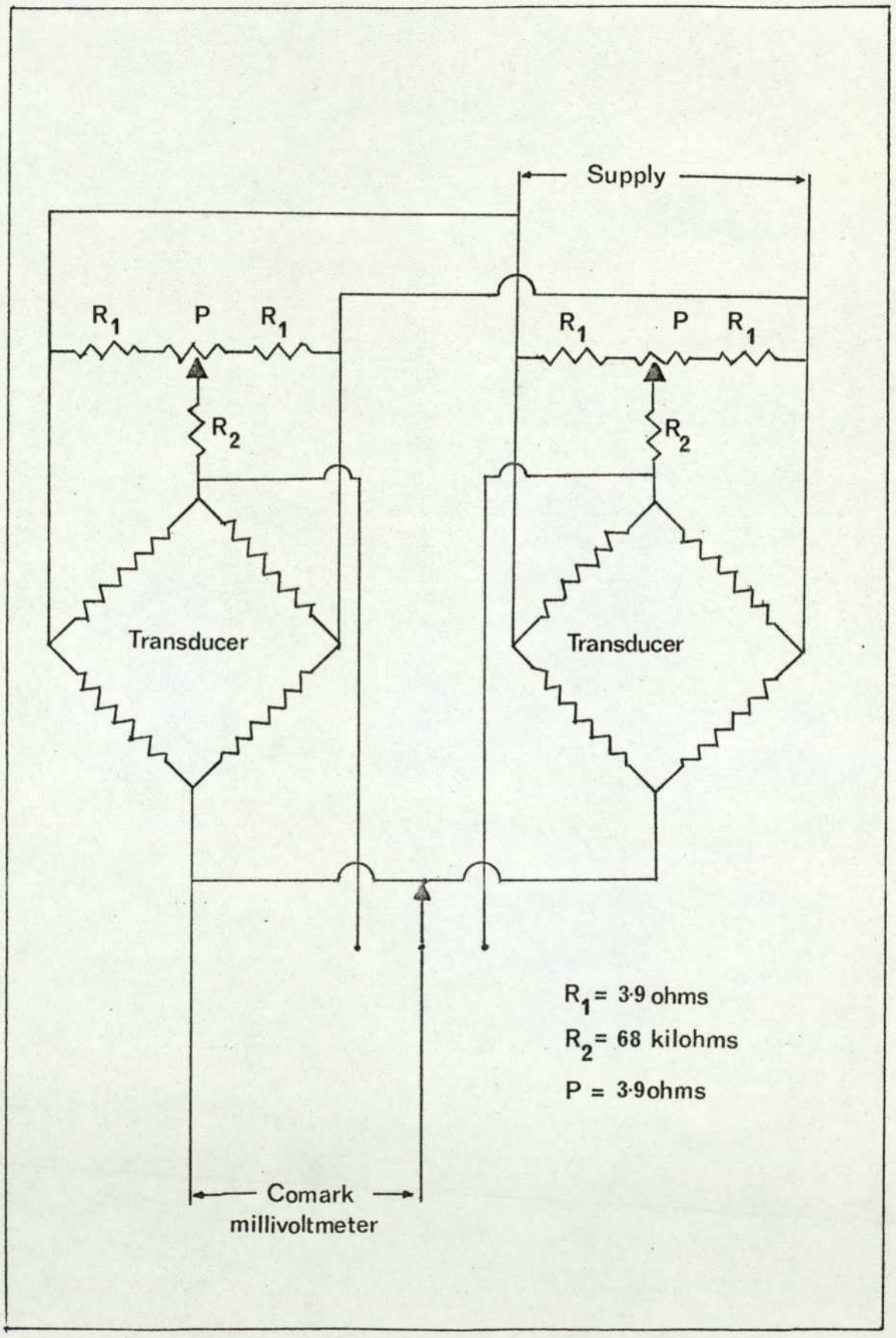


Figure 2.4

Transducer zero-setting circuit



in Figure 2.5. The reproducibility of the initial calibration graphs obtained was checked every three months and found to be within ± 3% in the range 3 to 70 mm.Hg.

2.1.5 Measurement of vacuum

The vacuum in the system was monitored by an Edwards Hi-Vac Pirani gauge. This was periodically standardised against an ion gauge which had a threshold sensitivity of 10^{-4} mm.Hg. This instrument was not good for measuring the absolute vacuum and was used primarily as a leak detector. If a section of line was free from leaks it was found that pumping for about 15 min. would produce a vacuum of 10^{-5} mm.Hg.

2.1.6 Photolysis apparatus

Low pressure mercury vapour lamp

Mixtures of reactants were photolysed at 253.7 nm with light from a modified Hanovia flat spiral low-pressure mercury vapour lamp. The lamp can be seen in plate 2 and Figure 2.6. One modification made to the lamp consisted of increasing the length between the spiral and electrodes to 11 cm; this allowed the electrodes to remain outside the furnace. The other modification involved surrounding the electrodes themselves by a water jacket, maintained at 35°C by means of a Circotherm unit. The lamp spiral was located 8 cm above the upper face of the reactor and the shutter was placed between the two (see Figure 2.6). The lamp was energised by a 30 milliamp step-up Hanovia transformer.

Shutter

The lamp reached maximum,constant light output only when it had been switched on for a few minutes. In order to overcome this problem, a shuttering device was inserted between the reactor and the lamp. This enabled the reactor to be irradiated only after the lamp had "warmed up"

Figure 2.5

Pressure Transducer calibration curve

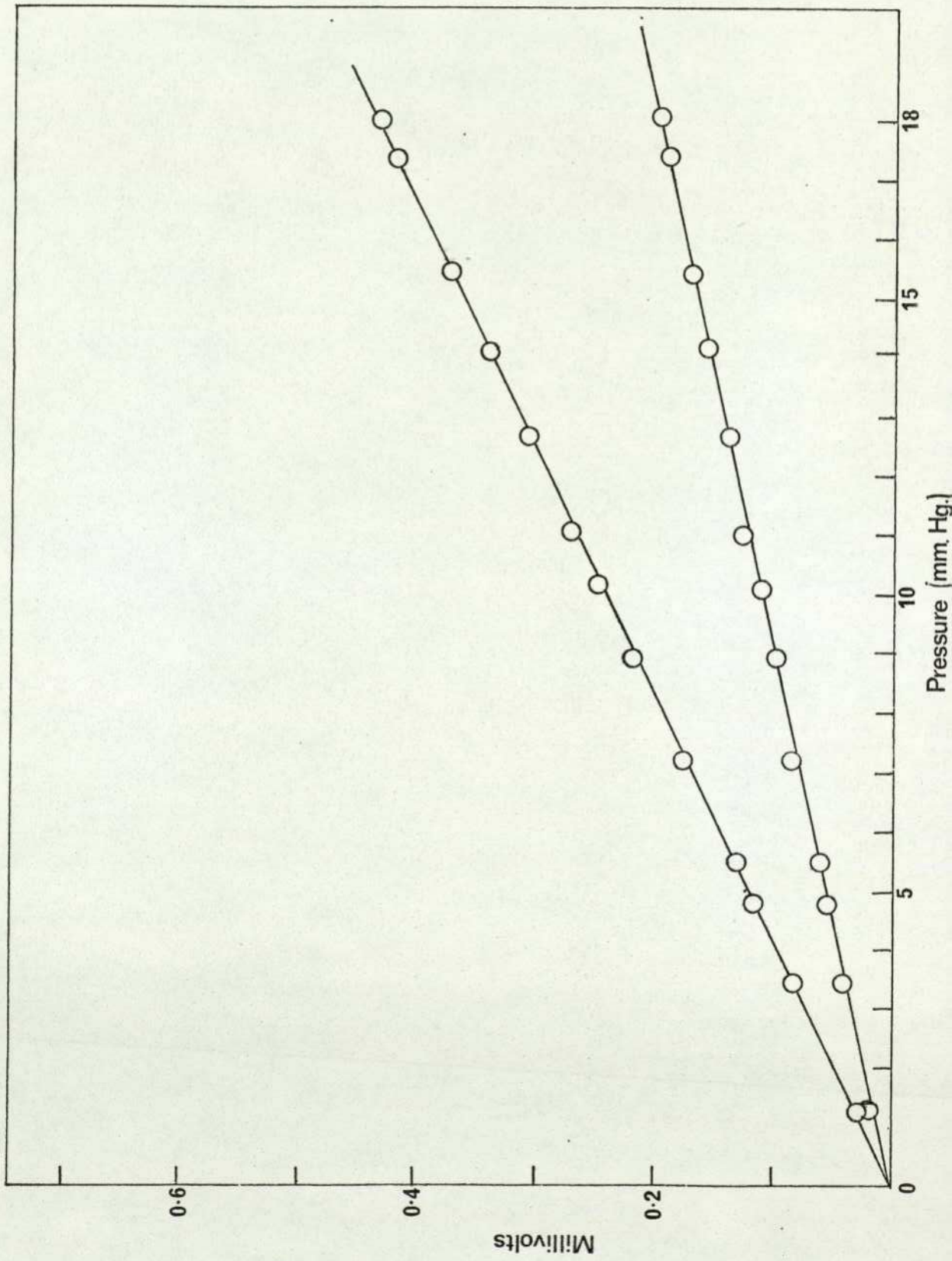


Figure 2.6

Reactor, L.P.M.V. lamp and shutter positioned in the furnace

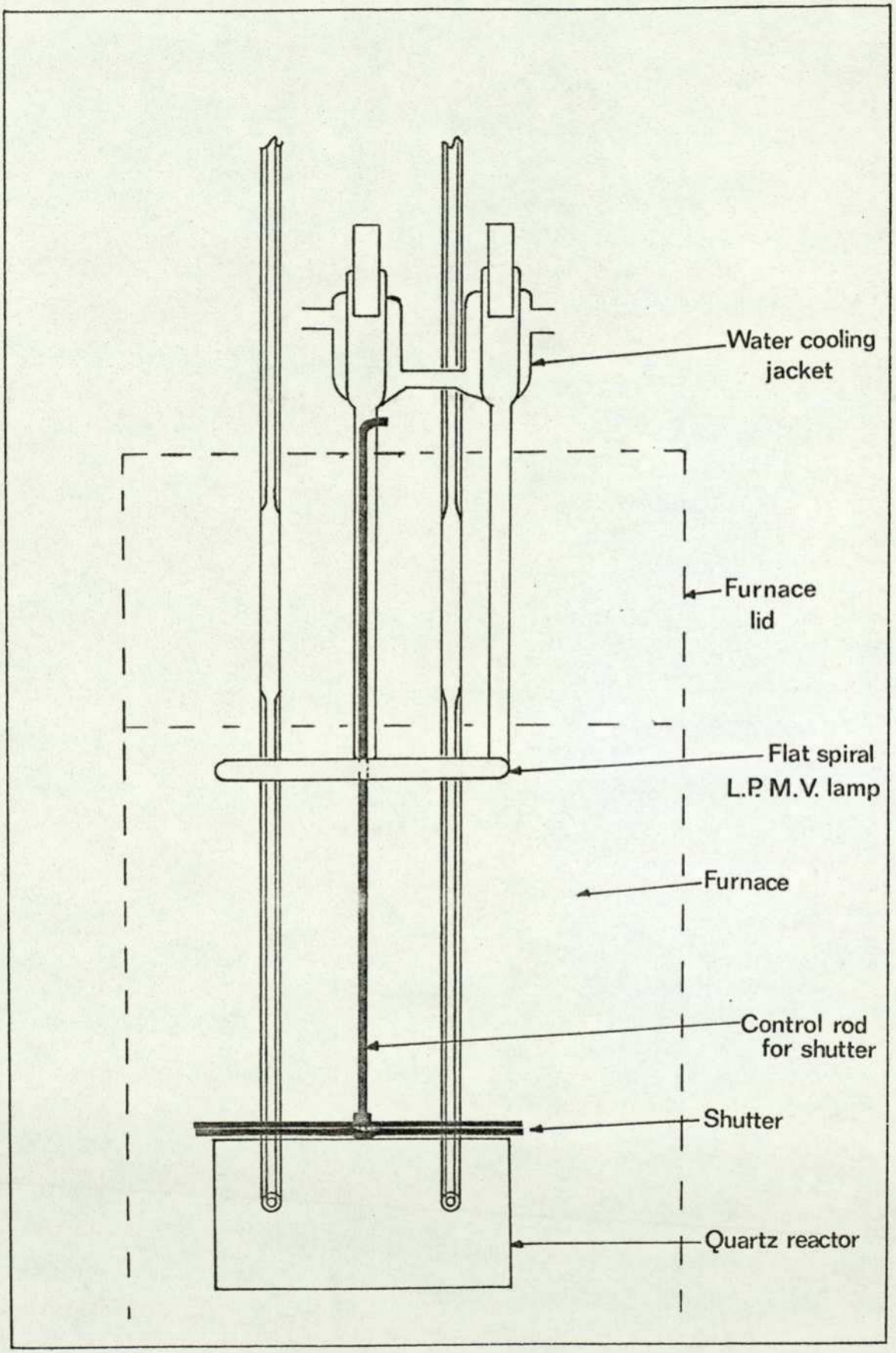
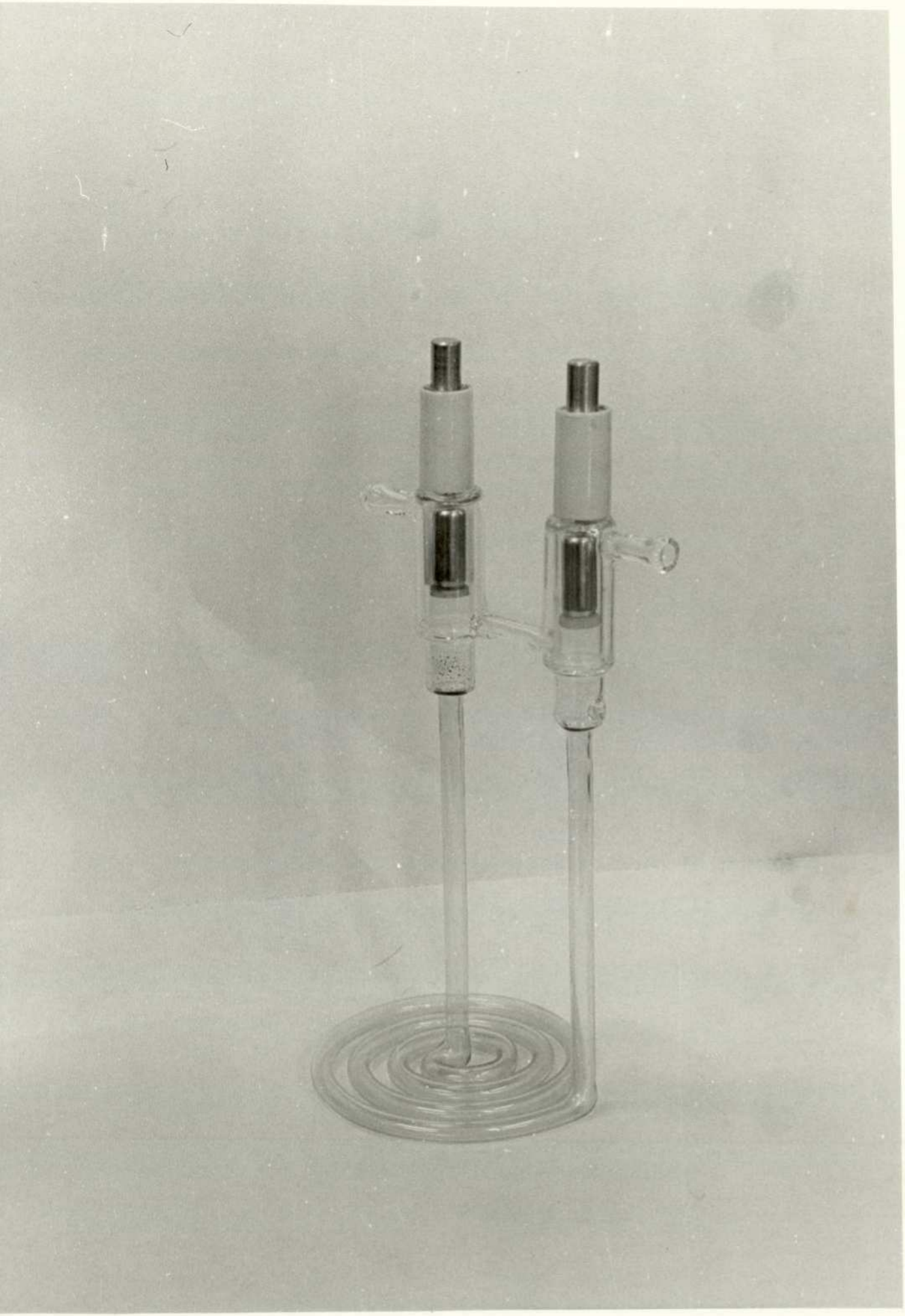


PLATE 2



sufficiently to emit its maximum light intensity. This device comprised of two coaxial and coplanar aluminium discs having a diameter 1 cm. greater than that of the reactor. The lower disc was fixed, whereas the upper disc could be rotated by means of a handle positioned outside the furnace. Both discs were perforated in such a way that light passed to the reactor only when the handle was in the "on" position. The shutter is shown in Figure 2.7.

2.2 Reagents

2.2.1 Monobromoethyne (C_2HBr)

Monobromoethyne was prepared by the method of Oppenheim and Shorr[132]. The apparatus consisted of a 250 ml three-necked flask fitted with a nitrogen inlet, 0 - 300°C thermometer, dropping funnel and double surface condenser. A modified Volman trap (Figure 2.8), cooled in liquid nitrogen, was attached to the top of the condenser. Potassium hydroxide (10.25 g, 0.182 mole) and water (1 g) were placed in the flask. After the apparatus had been flushed with dry nitrogen gas for ten minutes, the contents of the flask were heated to 180°C. The collection trap was cooled with liquid nitrogen, and 1,2-dibromoethylene (20.5 g, 0.11 mole) was slowly added to the molten potassium hydroxide over a period of $2\frac{1}{2}$ hr., the temperature being maintained above 120°C. After the addition had been completed the contents of the reaction flask were allowed to cool and the nitrogen flow was then interrupted and the collection trap was isolated. The contents of the trap were transferred to the purification line by low temperature vacuum distillation. The main impurities were acetylene and butadiyne. These were removed by successively distilling very small top fractions of the monobromoethyne (ca. 0.01% of the total product) into a trap cooled by liquid nitrogen. Some 11 "top fraction" distillations removed nearly all the acetylene

Figure 2.7

Shutter

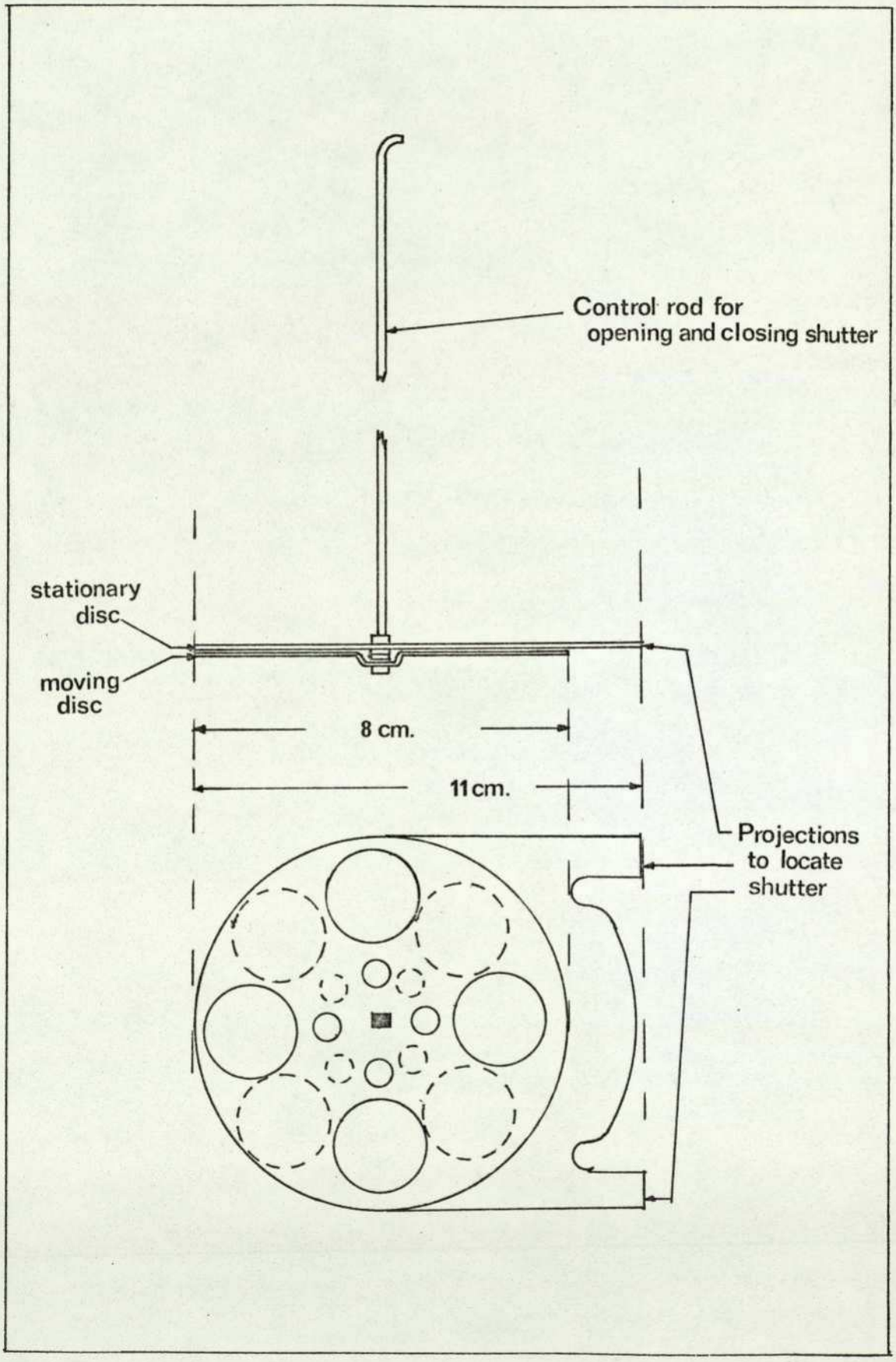
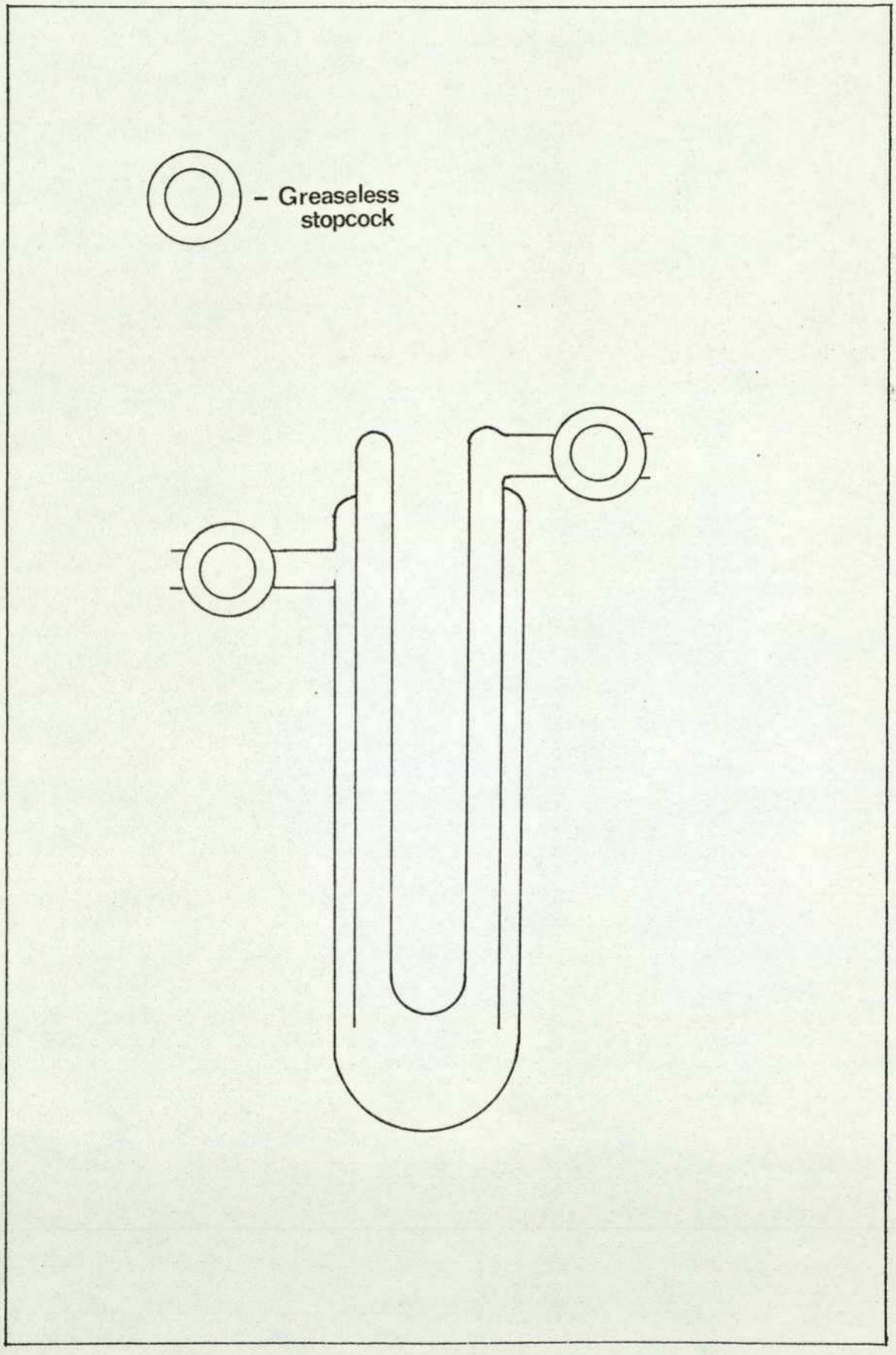


Figure 2.8

Low temperature collection trap used in preparations



and butadiyne. 90% of the remaining monobromoethyne was then transferred to a blackened storage bulb on the line. The only impurity left was 0.02% of the dibromoethylene. The resulting product corresponded to 60% yield. The monobromoethyne was identified by its gaseous infrared spectrum (i.r. spec. no. 1) which was identical to the published spectrum[133]. No decomposition was apparent over three months.

Monobromoethyne is an extremely unstable compound exploding on contact with air or oxygen[136]. For this reason elaborate safety precautions should be taken in preparing and handling it.

2.2.2 Preparation of butadiyne (C_4H_2)

Butadiyne was prepared by a method described by Armitage, Jones and Whiting[134]. 1,4-dichlorobut-2-yne (12.2 g, 0.099 mole) was added to a solution of potassium hydroxide (12 g, 0.214 mole) in water (120 ml) and contained in a 250 ml flask fitted with a nitrogen inlet, stirrer and reflux condenser connected to the collection trap described in Section 2.2.1. The mixture was slowly heated to reflux with stirring. The gaseous products were swept over calcium chloride and then into the collection trap cooled by liquid nitrogen. After the reaction mixture had been refluxed for 15 min. it was allowed to cool and the trap was isolated. The products were transferred to the purification line by vacuum distillation. The major impurities (acetylene and 1,4-dichlorobut-2-yne) were removed by pumping the product from a trap at -62°C through a trap at -115°C into one at -196°C and retaining the contents of the -115°C trap. This removed all the acetylene and left ca. 1% of the 1,4-dichlorobut-2-yne. The yield was 50%. The product was identified by comparison of its gaseous infrared spectrum (i.r. spec. no. 2) with a published spectrum[135].

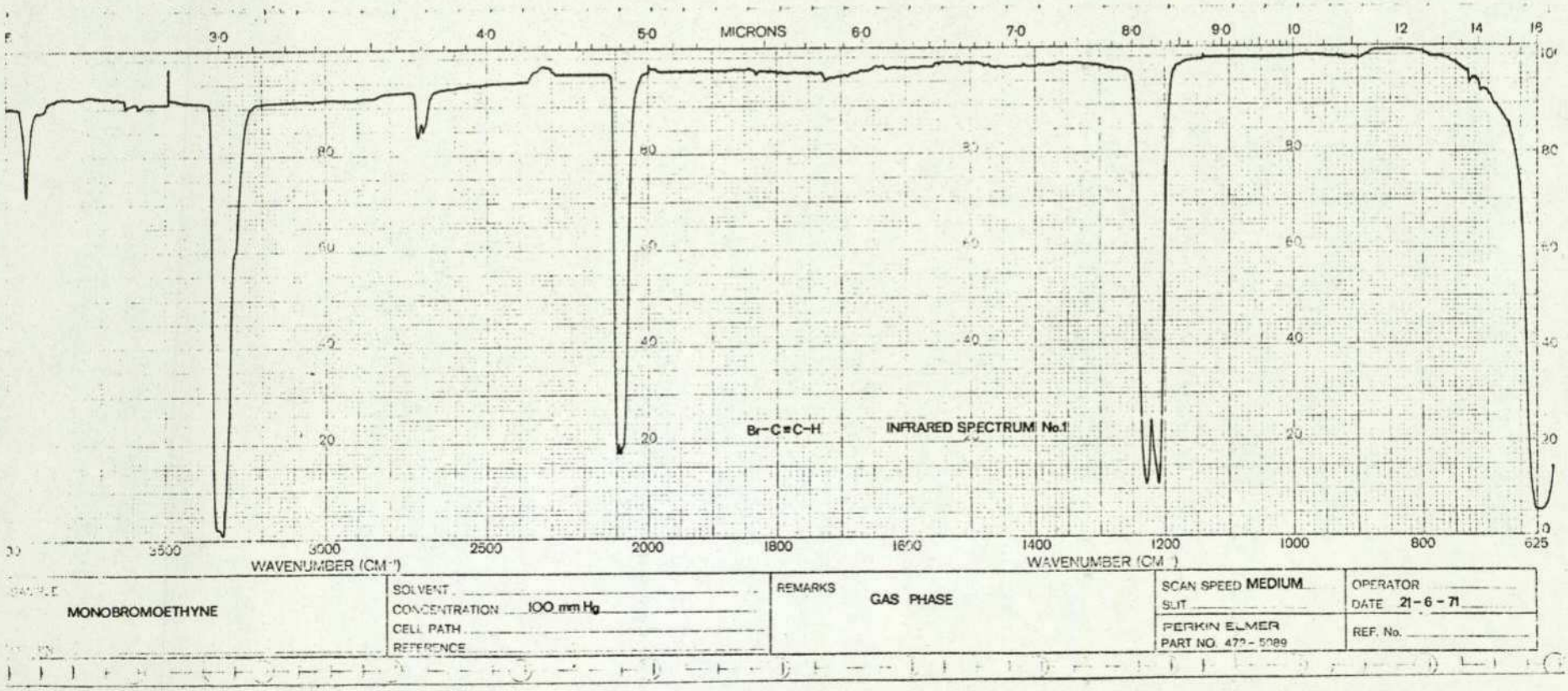
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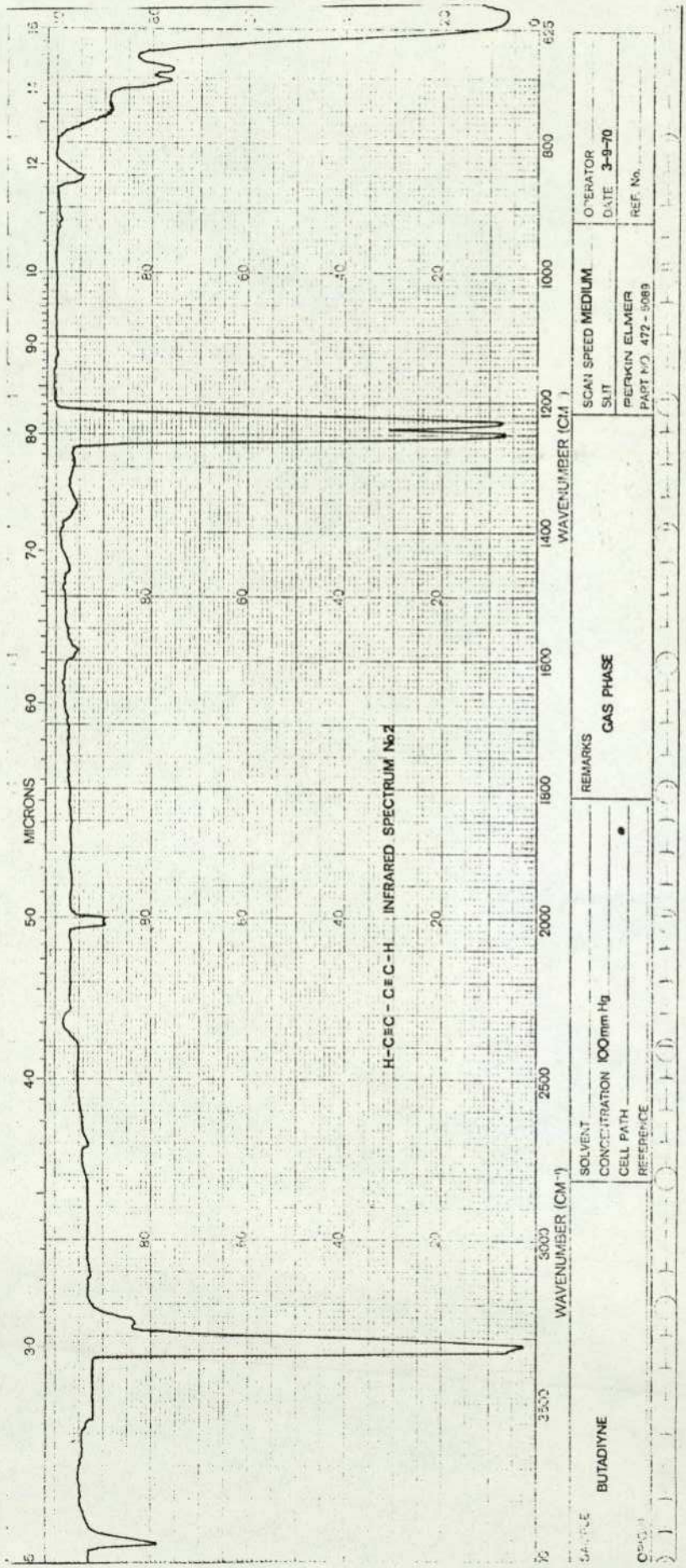
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IR. SPECTRUM No.1



IR. SPECTRUM No.2

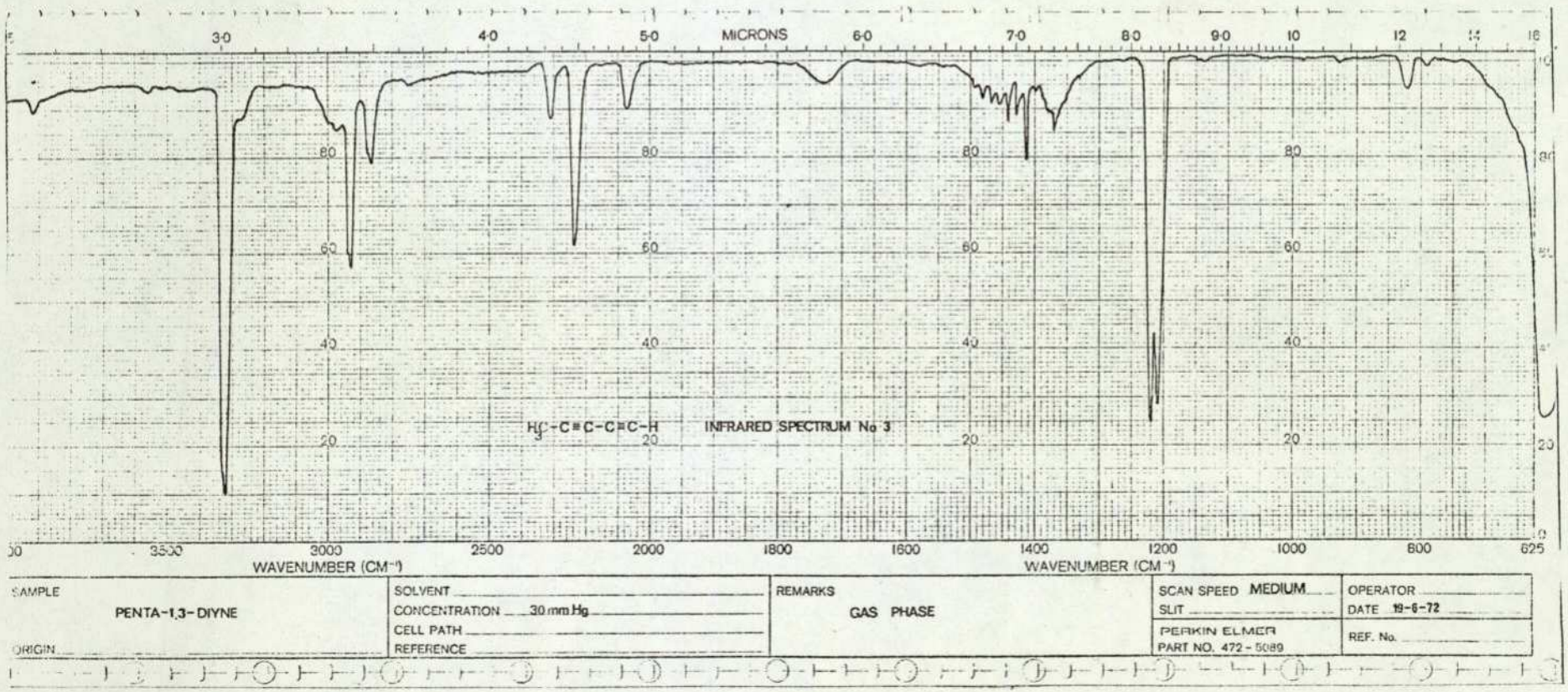


2.2.3 Preparation of penta-1,3-diyne (C_5H_4)

This compound was prepared by the method of Armitage, Jones and Whiting[137]. Liquid ammonia (200 ml) was transferred to a 350 ml silvered Dewar and ferric nitrate (0.05 g) was added. Sodium (8.3 g, 0.296 mole) was reduced to small pellets, each of which was washed in petroleum ether and methanol and finally added to the liquid ammonia. 1,4-dichlorobut-2-yne (14.8 g, 0.120 mole) was slowly added to the resulting sodamide solution. After 5 min. methyl iodide (17 g, 0.12 mole) was added and the mixture was stirred for three hours. It was left for 15 hr. and the resulting concentrated solution was extracted with six (15 ml) butane aliquots. The butane extract was reduced in volume using a 100 ml flask attached to a condenser maintained at $-10^{\circ}C$ and this was then transferred to the purification line by low temperature vacuum distillation. The product was unstable both in the condensed and gaseous phases, depositing a brown polymer in the handling system. Successive distillations gave a pure product identified by gas chromatography and its gaseous infrared spectrum. The spectrum of this compound does not appear to have been published and the one obtained is shown in i.r. spec. no. 3.

It can be seen that there are several absorption bands which identify this compound as a polyalkyne. The band at 3325 cm^{-1} is due to an alkyne C-H stretch, the band at 2235 cm^{-1} may be attributed to a C≡C stretch, the doublet centered at 1230 cm^{-1} is a combination band (cf. the spectrum of butadiyne) and the strong absorption at 620 cm^{-1} indicates an alkyne C-H band. The methyl group exhibits two groups of absorption bands. The bands centered at 2930 cm^{-1} are due to CH_3 stretch and the absorption centered at 1400 cm^{-1} is due to asymmetric and symmetric bending of the CH_3 group. This is not an exhaustive interpretation as there are several peaks which are difficult to identify and may even be due to impurities. However, the above assignments taken together with

IR. SPECTRUM No.3



SAMPLE PENTA-1,3-DIYNE ORIGIN	SOLVENT CONCENTRATION 30 mm Hg CELL PATH REFERENCE	REMARKS GAS PHASE	SCAN SPEED MEDIUM SLIT PERKIN ELMER PART NO. 472-5089	OPERATOR DATE 19-6-72 REF. No.

gas chromatographic analysis showing only one peak are sufficient evidence for the product being penta-1,3-diyne.

2.2.4 Preparation of hexatriyne (C_6H_2)

Hexatriyne was prepared by the method of Armitage et al[138], which involved a three-stage synthesis. Firstly hexa-2,4-diyne-1,6-diol was prepared; this was then chlorinated to give 1,6-dichlorohexa-2,4-diyne which was finally dehydrochlorinated to give hexatriyne.

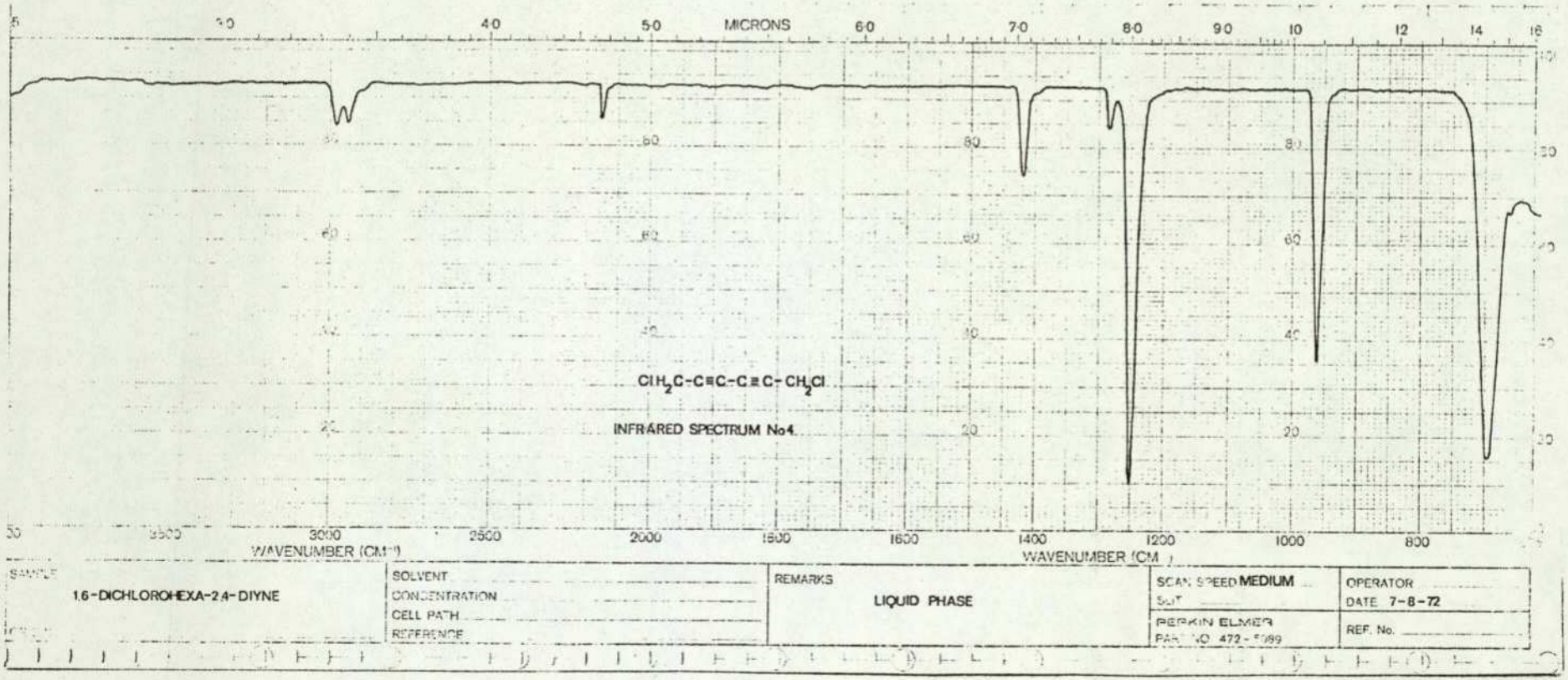
Preparation of hexa-2,4-diyne-1,6-diol[139]

A solution of cuprous chloride (20 g) and ammonium chloride (50 g) in water (160 ml) was added to a solution of propyne-1-ol (21.36 ml, 20.2 g, 0.361 mole) in water (50 ml) contained in a 500 ml flask. Oxygen was bubbled through the solution for 12 hr. The solution was then extracted with 15 x 30 ml of diethyl ether. The solid which was left after boiling off the ether was recrystallised once from petroleum ether. It had a m.p. of 112-114°C (literature value = 111-112°C). Comparison of its i.r. spectrum with that of an authentic sample supplied by Fluka showed that it was the same compound; Yield = 13.5 g (30%).

Preparation of 1,6-dichlorohexa-2,4-diyne[138]

Hexa-2,4-diyne-1,6-diol (19.2 g, 0.175 mole) was dissolved in pyridine (30 ml) contained in a 250 ml flask. Thionyl chloride (30.9 ml) was added over a period of 3¼ hr. with stirring and the temperature maintained below 15°C. After addition of thionyl chloride, the mixture was allowed to warm to room temperature and stirred overnight. Ice was then added and the reactants were extracted with 5 x 30 ml of ether. After an initial flash-distillation to remove ether, the extract was distilled under vacuum. The fraction boiling at 34°C, 0.07 mm.Hg. pressure was collected. (Literature value[138] 54°C, 0.1 mm.Hg.). The i.r. spectrum of the liquid is shown in i.r. spectrum no. 4. The product was obtained in 20% yield.

IR. SPECTRUM No4



Preparation of Hexatriyne[138]

Liquid ammonia (150 ml) was placed in a 250 ml flask fitted with a dropping funnel, thermometer (10-150°C), nitrogen inlet and glass stirrer. Sodium (4.6 g), washed in petroleum ether and methanol, was slowly added to the liquid ammonia. The flask was then cooled to -70°C and 1,6-dichlorohexa-2,4-diyne (7.4 g, 0.05 mole) was added dropwise over a 10 min period. After a further 5 min, ammonium chloride (8 g) was added and the solution was allowed slowly to warm to -33°C. After about 1 hr. the reaction mixture had concentrated to 60 ml and was extracted with 10 x 15 ml butane. The extracts were combined in a flask maintained at -70°C and the bulk of the butane was distilled off under vacuum. The concentrated extract was transferred to the line via a low temperature trap. It was found to be unstable, rapidly giving an involatile brown polymer near room temperature. In order to obtain a sufficiently high vapour pressure for gas chromatographic calibration and infrared analysis it was necessary to warm hexatriyne to room temperature. Even then the vapour pressure was found to be only about 7 mm.Hg. The gaseous i.r. spectrum is shown in i.r. spec. no. 5; this agrees with the recently published spectrum[117]. The half-life of the compound in the gas phase appeared to be about 3 hr.

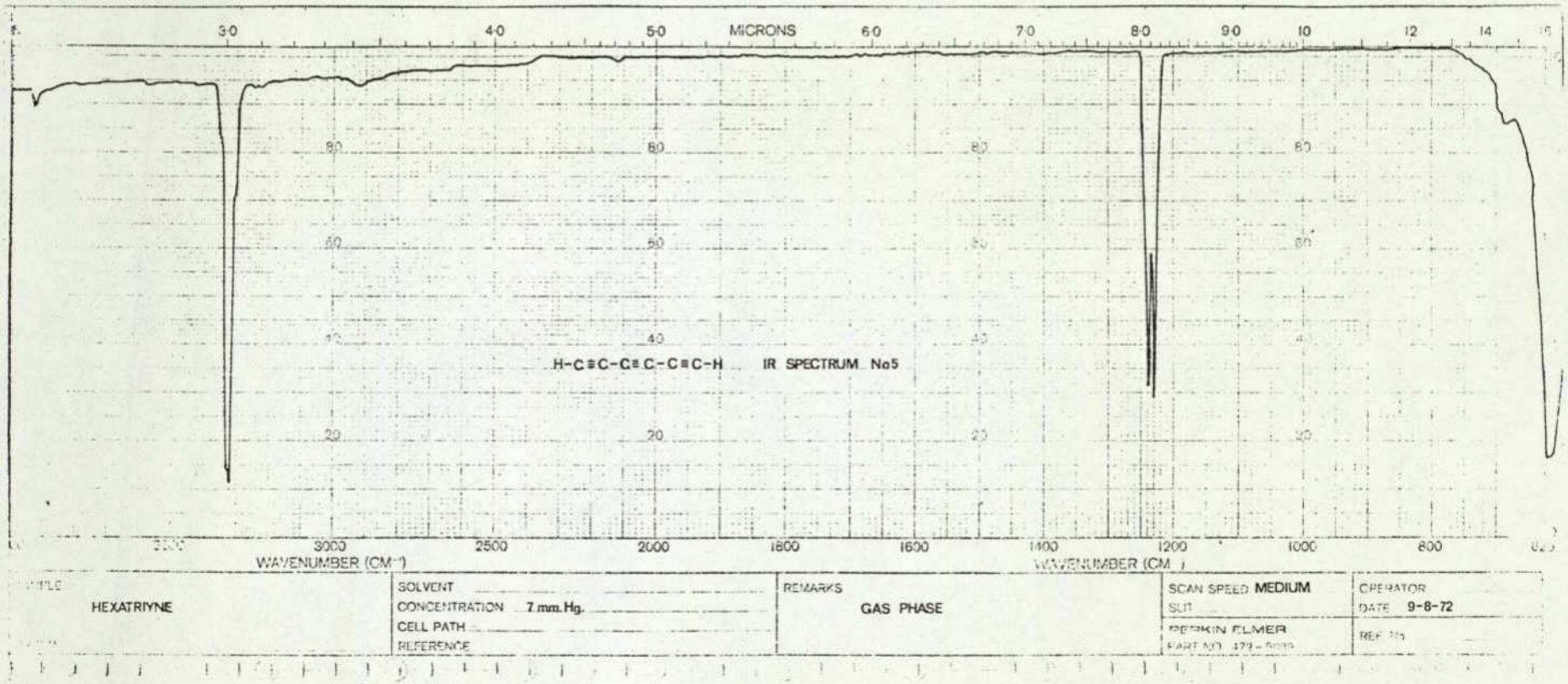
2.2.5 Purification of gases obtained from commercial gas cylinders

Nitrogen B.D.H. nitrogen (stated purity 99.999%) was further purified by passing over copper turnings at 600°C to remove traces of oxygen. It was then admitted to the reactor via a liquid nitrogen cooled trap.

Nitric oxide B.D.H. nitric oxide (stated purity 99%) was purified by three trap-to-trap distillations.

Carbon monoxide B.D.H. carbon monoxide was passed over copper turnings at 600°C before use. The stated purity of the bottled gas was better

IR. SPECTRUM No.5



than 99.98%.

Acetylene Matheson's acetylene was purified by trap-to-trap distillation to remove acetone, the only impurity detectable by gas chromatography.

Propyne B.D.H. propyne (stated purity 98%) was found to contain acetylene as the major impurity and this proved very difficult to remove. The most effective purification procedure was found to be pumping for 4-5 hr. on the propyne maintained at -110°C through a trap cooled in liquid nitrogen.

2,2-dimethylpropane and ethane These compounds were obtained from B.D.H. lecture bottles and had stated purities of 99%. They were degassed and distilled once, the middle fraction being retained.

Methane B.O.C. methane was purified by condensation into a cold-trap at -196°C followed by sublimation of the required pressure of methane from the trap. The methane thus obtained contained no detectable impurities.

2.3 Experimental Procedure

2.3.1 Measurement of reactant pressures

Reactant pressures greater than 4 mm.Hg. were measured directly on the pressure transducers. Pressures of less than 4 mm.Hg. were measured using a doser technique. This involved admission of the required gas at relatively high pressure into a small doser volume (D in Figure 2.1). This pressure was measured on PT2 and then further expansion into an evacuated mixing bulb, where other gases could be added. The expansion ratio between the doser and the mixing bulb was previously determined and had a value of 8.58:1.

2.3.2 Procedure in a typical photolysis

An equimolar mixture of monobromoethyne and nitric oxide was made up in the mixing bulb. 14 mm.Hg. of this mixture were introduced into the

reactor using PT1 to measure the pressure. If required, additional reactant gas could be added direct from the appropriate storage bulb, care being taken that the pressure measured on PT1 was in excess of 28 mm.Hg. before the reactor stopcock was opened. 672 mm.Hg. of purified nitrogen were then introduced into the reactor. The shutter was closed and the u.v. lamp was switched on. After five minutes the shutter was opened and the reactants were irradiated for the required time. The lamp was switched off and the contents of the reactor were analysed by gas chromatography.

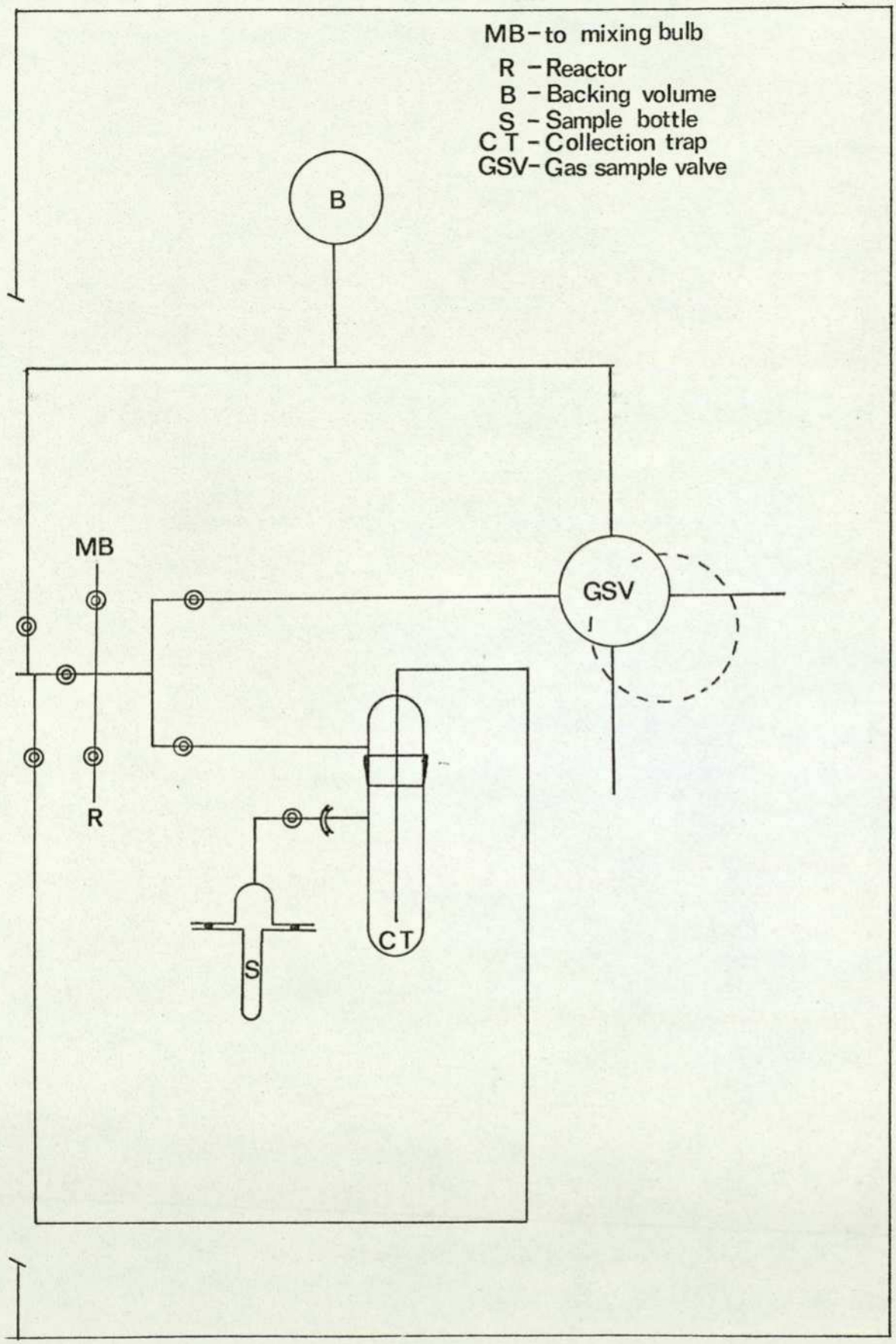
2.3.3 Analysis by gas chromatography

The contents of the reactor were allowed to expand into a previously evacuated sample-loop (5 ml) on the gas sample valve for 6 sec. and were then injected onto the column. The sample loop had a backing volume (50 ml) attached to it, so that a representative sample of the irradiated mixture could then be obtained. The sampling system is shown in Figure 2.9. In the majority of cases, analysis was carried out using a Perkin Elmer F11 flame ionization detector. Hydrogen and compressed air supplies to the flame were pre-purified by passage through molecular sieve 5A. Gas flows from the cylinders were controlled using Watts (0-45 p.s.i.) pressure regulators. The detector response was amplified with a Perkin Elmer ionization amplifier and finally displayed on a Honeywell 0 - 2.5 mv potentiometric recorder.

In earlier work, a Servomex katharometer had been used. The detector was particularly useful for the identification of carbon monoxide and bromocyanogen (BrCN) formed during the photolysis of C_2HBr/NO mixtures. The katharometer was activated at 6V d.c. using a Solartron stabilized voltage supply, and the out-of-balance currents were displayed on the Honeywell recorder via an attenuator.

Figure 2.9

Gas sampling apparatus for mass spectrometic and gas chromatographic analysis



Separation of the product and reactant gases was achieved by means of a column-switching system, which utilizes a method of external pressure compensation to direct flow along the required column. The apparatus is shown schematically in Figure 2.10. This method has three advantages over the more conventional method which uses multi-port sliding-rotor valves. The first advantage is that switching is performed outside the oven; the second is that the gases do not have to be diverted through a valve, thus minimising dead space; and the third is that the whole system is inexpensive, consisting only of two pressure gauges, two pressure regulators and two close off valves. The gas sample valve injects a sample from the reactor onto the first column A. The function of this column is to separate the gases to be analysed into two groups, each of which can be completely analysed on either column B or column C. As the first group of compounds emerges from column A, it is diverted down the column appropriate for its complete separation, say, column B. This means that close-off valve, F_1, is closed while F_2 is open. The pressure due to pressure regulator 2 had previously been adjusted so that the flow through the close-off value F_2 was sufficient to divert the effluent flow away from column C down column B, at the same time producing a compensating flow through column C. By opening F_1 and closing F_2, the second group of compounds emerging from A can be diverted down column C. The specifications of columns A, B and C are shown in table 2.1. In the present work the gases to be analysed were carbon monoxide, nitric oxide, hydrogen cyanide, bromocyanogen, monobromoethyne, propyne, butadiyne, hexatriyne, penta-1,3-diyne, 2,2-dimethylpropane, ethane and methane. Column A separated carbon monoxide, nitric oxide, acetylene, propyne and the alkanes into one group and hydrogen cyanide, bromocyanogen and the polyalkynes into another. Porapak Q-S (column B) was used to separate nitric oxide, acetylene, propyne and the alkanes. Carbon monoxide could

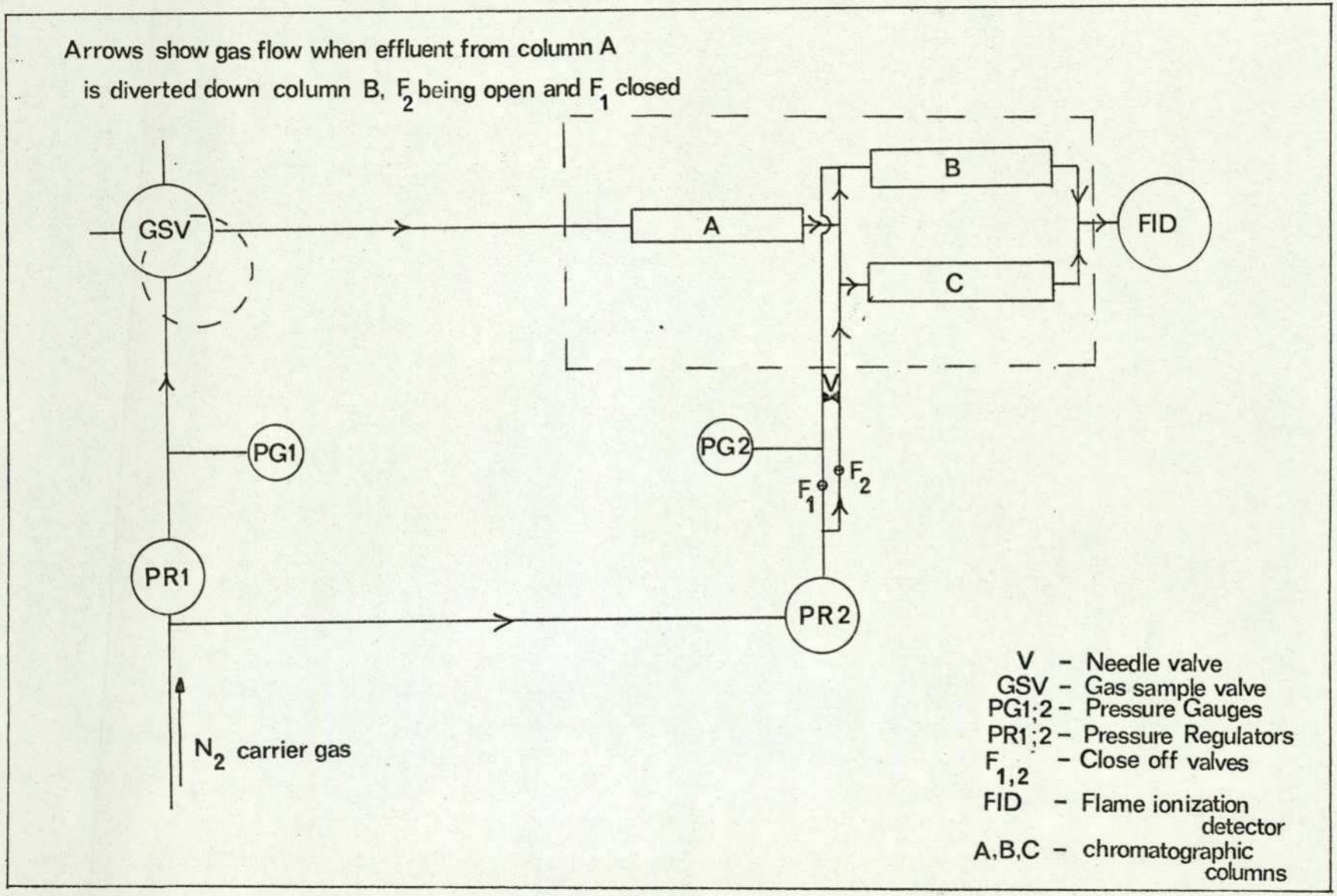


Figure 2.10

Column switching system

Table 2.1

Specification of columns for gas chromatography

Column	A	B	C i	C ii	B'
Solid phase	Chromosorb W, 60/80 mesh	Porapak Q-S, 80/100 mesh	Polypak	Chromosorb P, 60/80 mesh	Molecular sieve 5A
Liquid phase	1,2,3 tris (cyano-ethoxy) propane	-	1,2,3 tris (cyano-ethoxy) propane	1,2,3 tris (cyano-ethoxy) propane	-
% wt. loading	20	-	20	5	-
Column material	Nylon	Stainless steel	Nylon	Nylon	Stainless steel
o.d. of column (ins)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$
Length of column (ft)	12	8	0.17	10	10
Weight of column packing (g)	2.4	3.3	0.07	5	8.5
Conditioning temp (°C)	120	180-200	120	110	400
Conditioning time (hr.)	3	2	3	4	2

not be separated from nitric oxide on this column and in order to establish its presence as a product the Q-S column was replaced by a molecular sieve column (column B' in table 2.1). This was used solely to separate carbon monoxide qualitatively. Column C separated hydrogen cyanide, bromocyanogen and the polyalkynes. The columns were maintained at 63 $\pm$ 0.5°C in a thermostatic oil bath. The retention times of the various gases analysed are listed in table 2.2 together with the operating conditions used. Calibration curves were obtained for the pure components of a mixture covering all ranges of gas concentration encountered in the work. The system was calibrated for very low pressures of acetylene, butadiyne and penta-1,3-diyne (0.5 to 10 x 10^{-2} mm Hg) by means of the following procedure. The alkyne (usually in a 10:1 mixture with nitrogen) was admitted to the evacuated doser to give the required pressure. This mixture was then expanded into the mixing bulb where a further known pressure of nitrogen was added. Finally a measured pressure of the gas mixture was admitted into the evacuated reactor and the contents were then expanded into the sample loop of the gas sample valve and thence onto the column. The area of the peak thus obtained on the recorder was calibrated by triangulation, and plotted against the pressure of the alkyne in the reactor. All calibration curves were linear and independent of the amounts of diluent, of the mixing time (provided that this was greater than 5 sec) and of the expansion time into the reactor (provided this was greater than 2 sec). Figure 2.11 shows a typical calibration graph for butadiyne.

Compounds containing bromine form hydrogen bromide within the F.I.D. and continual exposure to this gas can alter the detector response so that frequent checks (monthly) were made of the calibrations throughout the work. Table 2.3 gives the response of the F.I.D. (amplifier attenuation = 50 x 1) in mm Hg per unit peak area for all the product

Table 2.2

Retention times of the gases on the gas chromatographic system

Gas	Columns	Retention Time (min.)
bromocyanogen	A - B	32
nitric oxide	A - B	3.17
	A - B'	17.5
carbon monoxide	A - B'	35.25
acetylene	A - B	5.67
methane	A - B	3.67
ethane	A - B	6.0
2,2-dimethylpropane	A - B	110
butadiyne	A - C	10
monobromoethyne	A - C	7.25
propyne	A - B	19.0
1,3-pentadiyne	A - C	30
hexatriyne	A - C	64

temperature of columns = 63°C

settings of the pressure regulators: PR1 = 30 p.s.i.g.
PR2 = 25 p.s.i.g.

flow rate through column B = 22.7 $cm^3 min^{-1}$

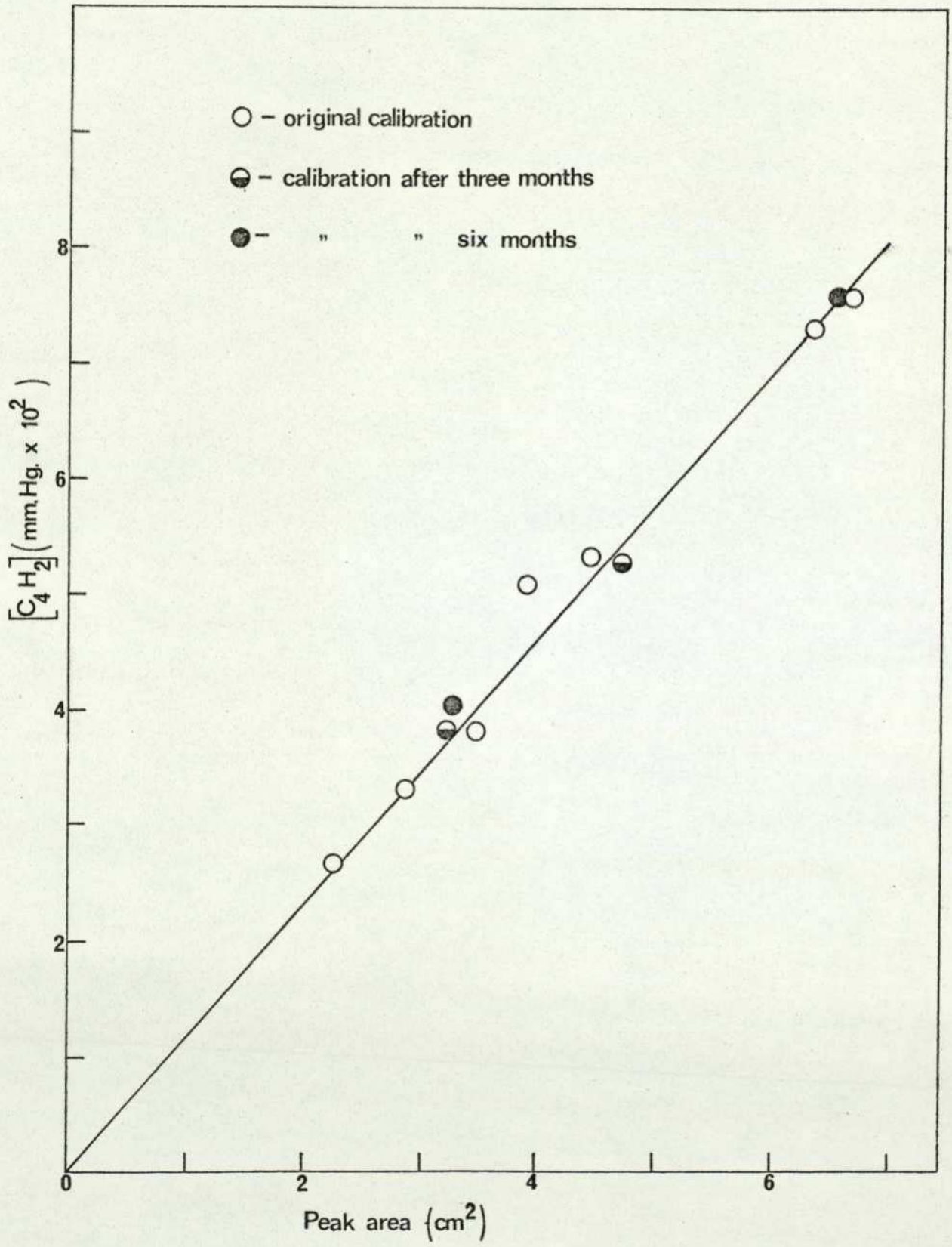
flow rate through column C = 25.3 $cm^3 min^{-1}$

time of switch from column B to column C = 5 minutes after injection

for specifications of the columns see table 2.1

Figure 2.11

Calibration curve for butadiyne (amplifier attenuation = 50 x 1)



gases investigated. Particular difficulty was experienced during the calibration of hexatriyne. Due to its instability, this gas could not be diluted as above and hence it was calibrated in the range of pressures which could be measured on the pressure transducers. The result was then extrapolated linearly to the lower attenuations required for experiments involving hexatriyne. The error in extrapolation probably does not exceed 10%. The calibrations were not found to alter with the temperature of the reactor.

2.3.4 Analysis by mass spectrometry

In mass spectrometric analysis samples of the reactant mixture were collected using the apparatus shown in Figure 2.9. The contents of the reactor were drawn into the collection trap, cooled in liquid nitrogen, by means of the rotary pump. The contents of the collection trap were then transferred to a sample bottle by initially evacuating the trap and sample bottle and then, after isolation of the collection system, cooling the sample bottle with liquid nitrogen and allowing the collection trap to warm to room temperature. The collection system was then brought to atmospheric pressure using purified nitrogen. The sample bottle, still cooled with liquid nitrogen, was transferred to an all-glass inlet system of an A.E.I. MS20 mass spectrometer and the mass spectrum of the reactor contents was recorded. By this method the products from the reaction between the ethynyl radical and acetylene-d_2 were determined.

In the spectrum obtained, peaks with m/e values of 27, 50 and 51 were ascribed to C_2HD, C_4H_2 and C_4HD respectively and, for a given partial pressure in the reactor, the heights of the parent peaks of C_2H_2, C_2D_2 and C_4H_2 were equal. One difficulty encountered in quantitatively estimating relative concentrations of the various deuterated alkynes was the fact that acetylene -d_2 contained C_2HD as a detectable impurity. It was impossible

Table 2.3

Response of the flame ionization detector to various alkynes*

Compound	F.I.D. Response ($mm.Hg.cm^{-2} \times 10^2$)
Hexatriyne	1.09
Butadiyne	1.15
1,3-Pentadiyne	1.01
Acetylene	1.71

* for a chart speed of 15 in. per hr. and an amplifier attenuation of 50 x 1

to assess the quantity of this impurity by reference to the parent peak of C_2D_2 (m/e = 28), since this mass number coincides with that for nitrogen which was always present in the ionization chamber. As an alternative the height of the peak at m/e = 26 (C_2D fragment) was measured relative to the impurity peak at m/e = 27 and, since the peak at m/e = 26 is some 50 times greater than the product peaks, it remained comparatively unaffected by the appearance of acetylene (parent peak m/e = 26) during a photolysis. Thus by measuring its height in a photolysed sample it was possible to estimate the proportion of the peak at m/e = 27 which was due to impurity. The value of the height due to C_2HD produced during the reactions was calculated by subtracting this proportion from the total height.

RESULTS

3. Results

3.1 Preliminary Experiments

Experiment has shown that at room temperature monobromoethyne consumption occurs only in the presence of light of wavelength 253.7 nm. For example, no detectable reaction occurred in monobromoethyne/nitric oxide mixtures which were allowed to stand in the reactor for one hour. As the temperature was increased monobromoethyne at first remained stable but at 210°C thermal decomposition occurred to a small extent (5% consumption in 1 hr.). In experiments requiring photolysis at higher than ambient temperatures, therefore, reactants were never left in the reactor for more than five minutes; decomposition was thus minimised even at 210°C (the maximum temperature investigated).

During the photolysis of monobromoethyne it was found that apart from the gaseous products[118] a polymeric material was deposited on the reactor surface. With monobromoethyne alone, this material was brown in colour and difficult to remove, but in the case of monobromoethyne/nitric oxide mixtures the polymer was yellow and quite easy to remove.

The gaseous products formed during the photolysis of monobromoethyne/nitric oxide mixtures are diverse and include C_4H_2, C_2H_2, BrCN, HCN, HBr and CO. The analysis of such a mixture is a complex problem and the method suggested by Tarr et al[118] was unsatisfactory when applied to the present work. For this reason a column-switching system was constructed which enabled quantitative analysis of the products to be carried out from one reaction sample (see Section 2.3.3).

Accurate analytical work required good initial separation of acetylene from carbon monoxide and nitric oxide, complete separation of butadiyne from monobromoethyne and the elution of bromocyanogen within a reasonable time ($<$ 60 min). Numerous experiments showed that it was

impossible to meet all these requirements. For example, many columns were constructed in an attempt to find a pre-column which would separate alkynes from carbon monoxide and nitric oxide; the two groups thus formed could then be completely separated on two subsequent columns. However, columns which separated nitric oxide from acetylene sufficiently well to allow switching retained monobromoethyne indefinitely and columns which eluted monobromoethyne did not completely separate acetylene from nitric oxide. Table 3.1 gives details of some of the columns investigated in these experiments. Eventually the separation of carbon monoxide and nitric oxide was sacrificed and a column system was developed which made possible the quantitative estimation of acetylene, monobromoethyne and butadiyne as well as the separation of hydrogen cyanide and bromocyanogen. As mentioned in Section 2.3.3, a molecular sieve column was used in early experiments to separate nitric oxide from carbon monoxide allowing the latter compound to be detected among the reaction products of the photolysis of nitric oxide/monobromoethyne mixtures. However, this column was later discarded and the columns used in subsequent experiments were those described in Section 2.3.3.

3.2 Photolysis of C_2HBr/NO mixtures

3.2.1 Products

The products from the photolysis of a 1:1 monobromoethyne/nitric oxide mixture in the temperature range 295 to 483K were butadiyne, acetylene, bromocyanogen, hydrogen cyanide and carbon monoxide. Addition of inert gas did not alter the nature of the products formed but did change the relative amounts produced. Although no accurate measurement was made of the amounts of bromocyanogen and carbon monoxide formed, these compounds did appear in somewhat greater quantities than acetylene and butadiyne. Tarr et al[118] had found that acetylene, butadiyne, bromocyanogen and

Table 3.1

Specifications of columns used to separate NO/CO from the acetylenes

Length of column (m.)		1	3	1	1	1	1	1	1	1.5	1
Solid phase		Porapak Q	Chromasorb P	Alumina	Polypak	Polypak	Polypak	Polypak	Polypak	Polypak	Porapak P
Liquid phase		-	squalene	squalene	-	squalene	squalene	squalene	T.C.E.P.	T.C.E.P.	-
% loading		-	30	15	-	10	5	2.5	10	20	-
Retention times (min.)	NO/CO	2.3	2.9	3.6		2.25	2.25	2.6	2.4	4	2.4
	C_2H_2	3.75	3	15	7.4	3	3.4	4	3.4	5.5	3
	C_2HBr		7.8	not eluted	60	15	20	30	24.8	39.5	15
	C_4H_2							36		49	

All columns were used as pre-columns in a three column switching system and the products eluted through a column of uncoated Chromasorb P

Inlet pressure = 21 p.s.i.g.
Temperature = 63°C

carbon monoxide were all primary products, whilst hydrogen cyanide was a secondary product. In the present work a plot of acetylene and butadiyne concentrations against photolysis time (Figure 3.1) shows that these compounds are indeed primary products and for monobromoethyne conversions of up to 5% (photolysis time 600 sec) between one quarter and one third of the monobromoethyne consumed is converted to butadiyne and acetylene.

3.2.2 Reproducibility

As indicated in Section 2.1.2 the reactor was cleaned after every five runs (duration of each run $\leq$ 2 min) by washing with AnalaR methanol. After such treatment, a standard photolysis mixture comprising monobromoethyne (7 mm.Hg.), nitric oxide (7 mm.Hg.) and nitrogen (686 mm.Hg) was irradiated for 120 sec and analysed for acetylene and butadiyne. The deviation in the concentration of these acetylenes in such runs was $[C_2H_2] = 2.3 \pm 0.3 \times 10^{-3}$ mm.Hg. and $[C_4H_2] = 1.8 \pm 0.2 \times 10^{-2}$ mm.Hg. throughout.

3.2.3 Influence of monobromoethyne concentration on the formation of acetylen and butadiyne

Reaction mixtures were prepared containing varying amounts of monobromoethyne (3 - 18.2 mm.Hg.) together with 7 mm.Hg. of nitric oxide and the total pressure was made up to 700 mm.Hg. by the addition of nitrogen. Such mixtures were photolysed for up to 120 sec and, as a measure of the rate of formation of butadiyne and acetylene, the respective amounts formed were divided by the photolysis time. Figure 3.2 shows a plot of the rate of formation of acetylene against the square root of the rate of formation of butadiyne times the initial concentration of monobromoethyne. A graph of the rate of formation of acetylene against the

Figure 3.1

Variation of the concentrations of monobromoethyne, acetylene and butadiyne with photolysis time (reaction mixture: monobromoethyne (7 mm.Hg.); nitric oxide (7 mm.Hg.) and nitrogen (686 mm.Hg.))

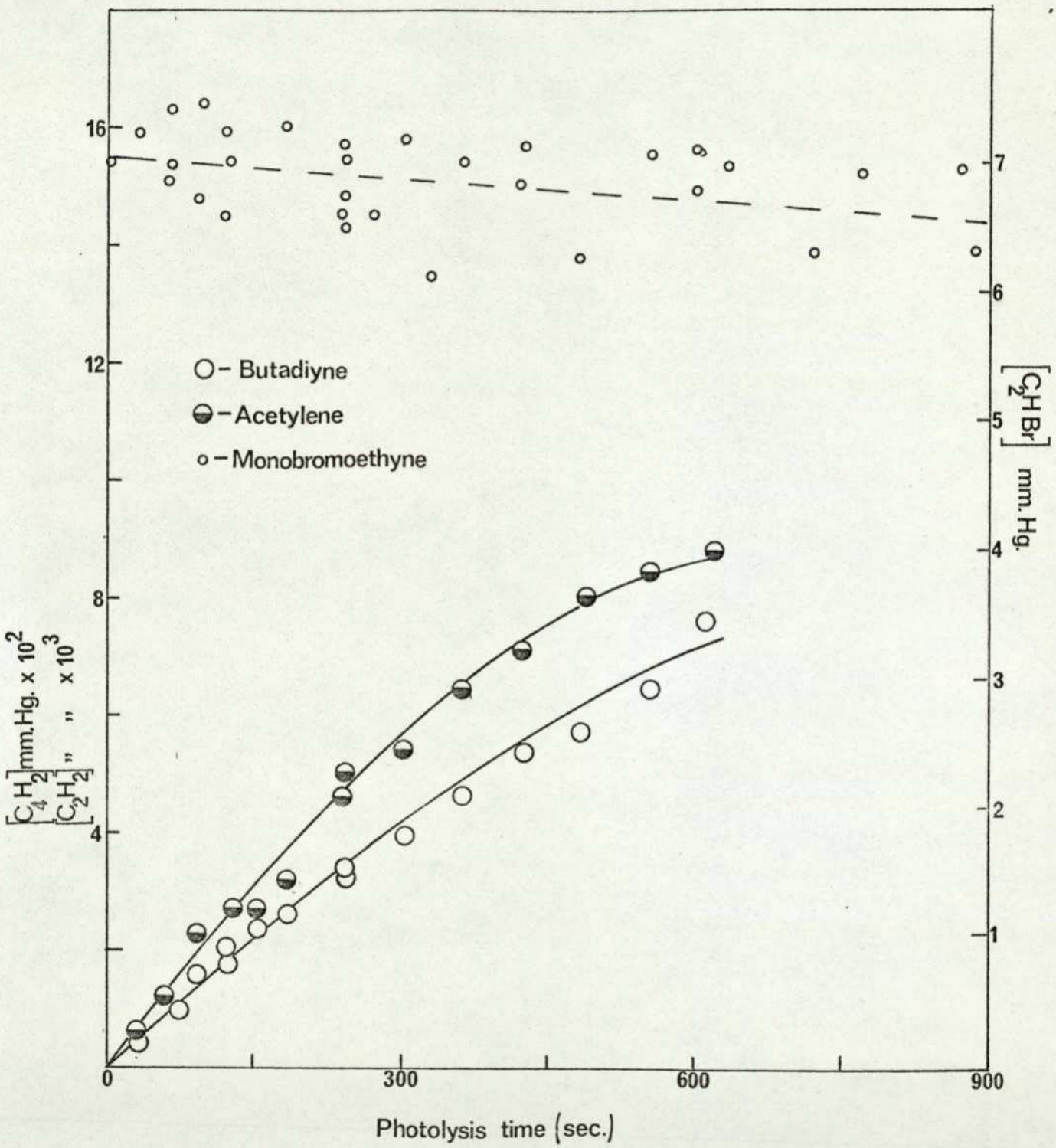
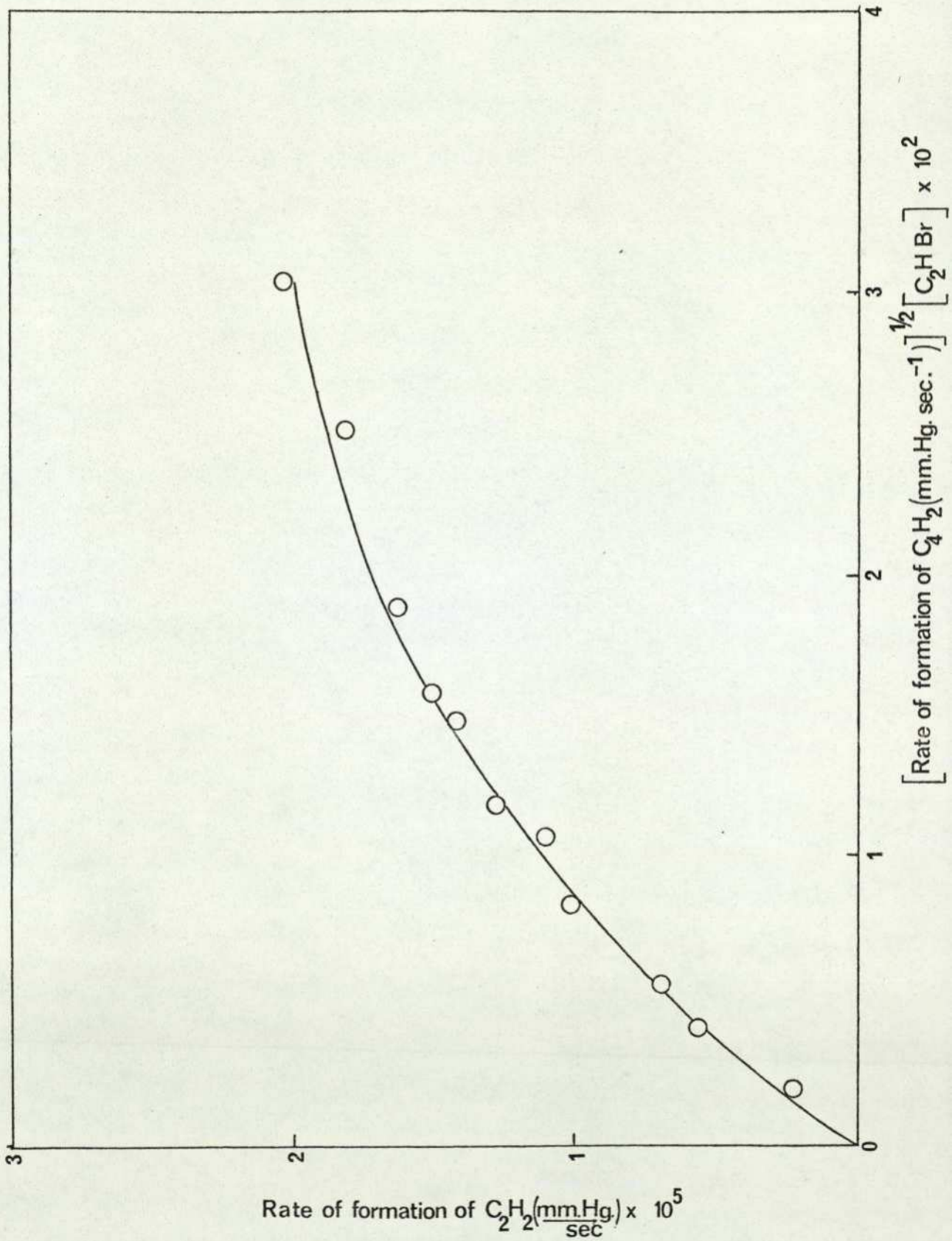


Figure 3.2

Graph of the square root of the rate of formation of butadiyne times the concentration of monobromoethyne against the rate of formation of acetylene



rate of formation of butadiyne gave the straight line shown in Figure 3.3.

It is convenient, here, to assume the conclusion reached in the Discussion (Section 4.1.2) that these results confirm the reaction

$$C_2H + C_2HBr \longrightarrow C_4H_2 + Br \qquad (3)$$

to be the only significant source of C_4H_2.

3.2.4 Influence of nitric oxide on the formation of acetylene and butadiyne

Monobromoethyne (7 mm.Hg.) was photolysed for 90 sec in the presence of varying amounts of nitric oxide made up to a final total pressure of 700 mm.Hg. by the addition of nitrogen. It was found that the rates of formation of acetylene and butadiyne diminished with increasing nitric oxide concentration (Figures 3.4 and 3.5). The variation of $[C_4H_2]/[C_2H_2]$ with the concentration of nitric oxide is shown in Figure 3.6.

3.2.5 Influence of inert gas on the ratio $[C_4H_2]/[C_2H_2]$

Photolysis of 1:1 monobromoethyne/nitric oxide mixtures (C_2HBr and NO = 7 mm.Hg.) in the presence of inert gas showed that, at low conversions of monobromoethyne (<2%), the ratio $[C_4H_2]/[C_2H_2]$ increased with increasing pressures of inert gas. Only two inert gases (nitrogen and carbon dioxide) were tested but Figure 3.7 shows that carbon dioxide had a similar effect to nitrogen, $[C_4H_2]/[C_2H_2]$ tending to a limiting value for partial pressures of these gases greater than 600 mm.Hg.

3.2.6 The effect of temperature on the ratio $[C_4H_2]/[C_2H_2]$

Experiments had shown that, for periods of up to ten minutes,

Figure 3.3

Graph of the rate of formation of acetylene against the rate of formation of butadiyne for varying concentrations of monobromoethyne

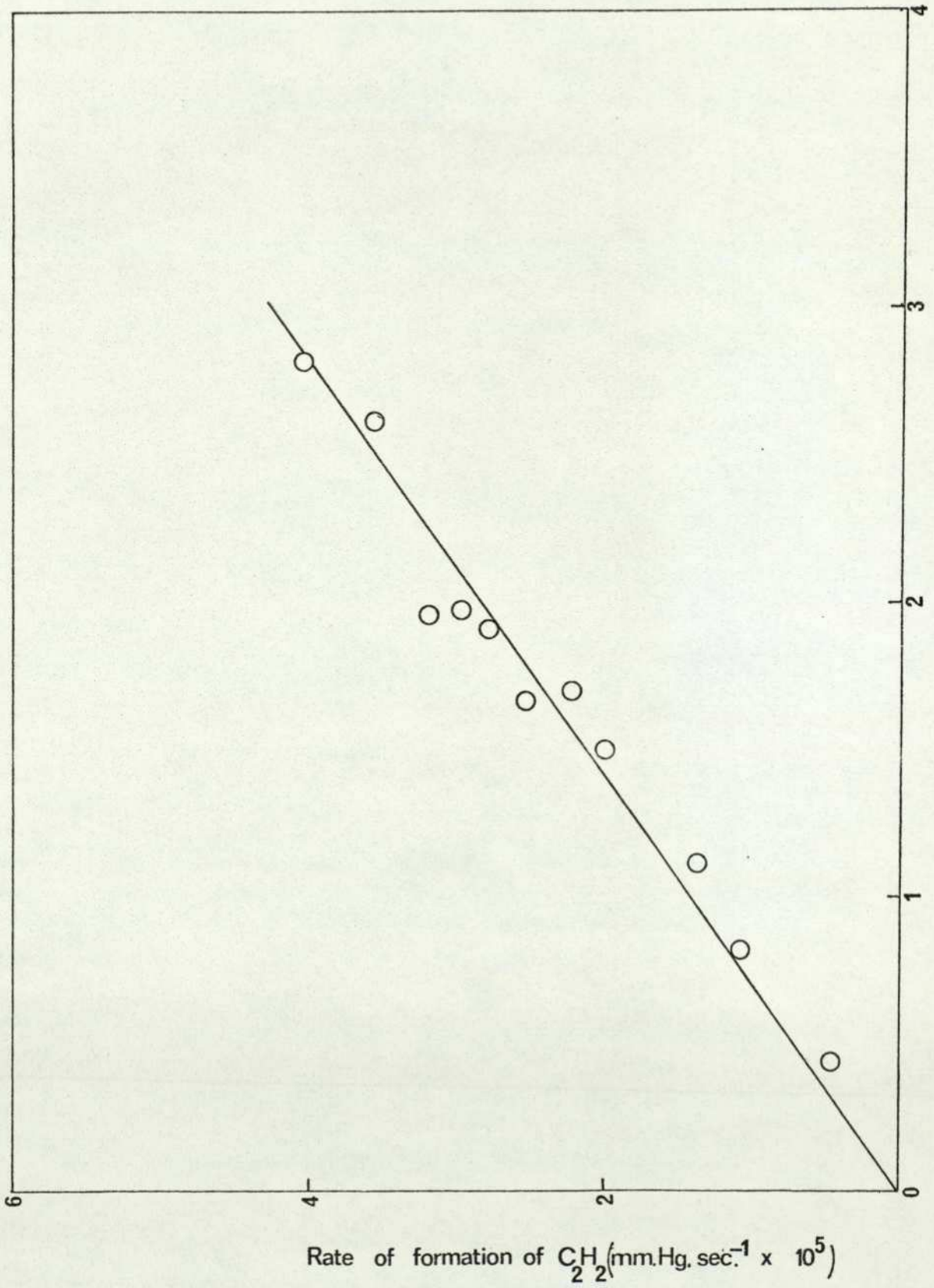


Figure 3.4

Graph of the rate of formation of butadiyne against pressure of added nitric oxide in the photolysis of monobromoethyne (7 mm.Hg.) and nitrogen (added to make total pressure 700 mm.Hg.)

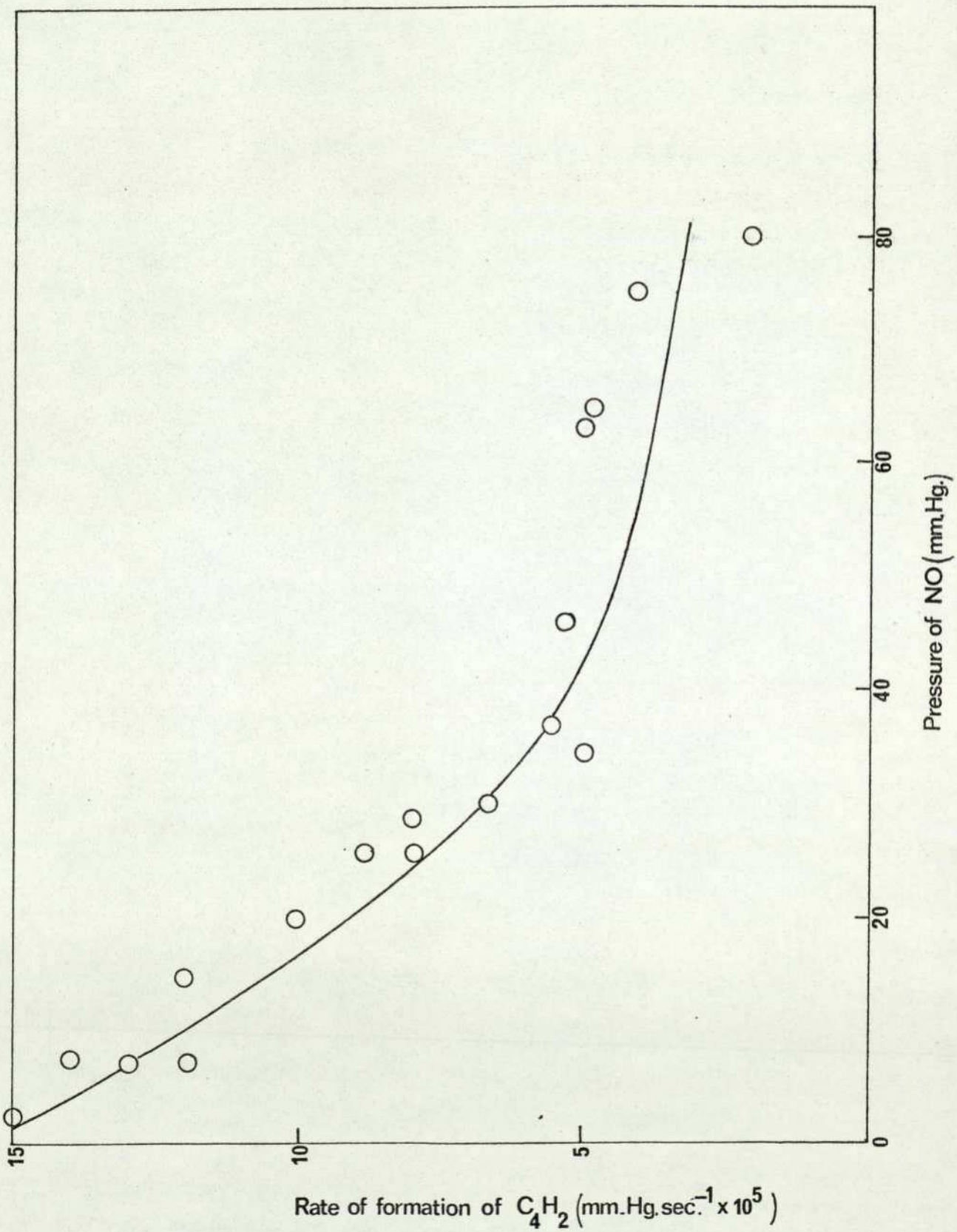


Figure 3.5

Graph of the rate of formation of acetylene against presence of added nitric oxide in the photolysis of monobromoethyne (7 mm.Hg.) and nitrogen (added to make total pressure 700 mm.Hg.)

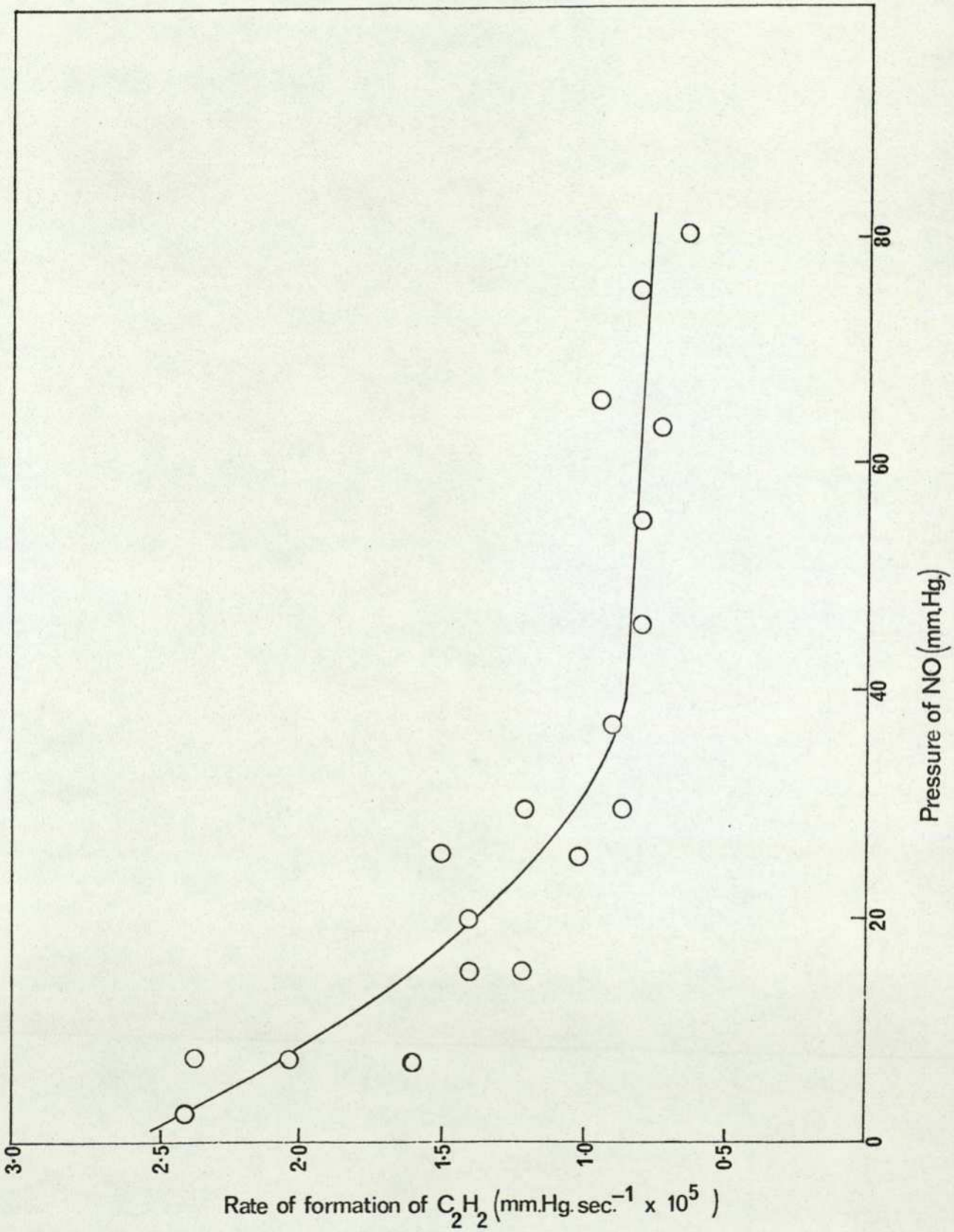


Figure 3.6

The variation of the ratio $[C_4H_2]/[C_2H_2]$ with added nitric oxide in the photolysis of monobromoethyne (7 mm.Hg.) and nitrogen (added to make total pressure (700 mm.Hg.)

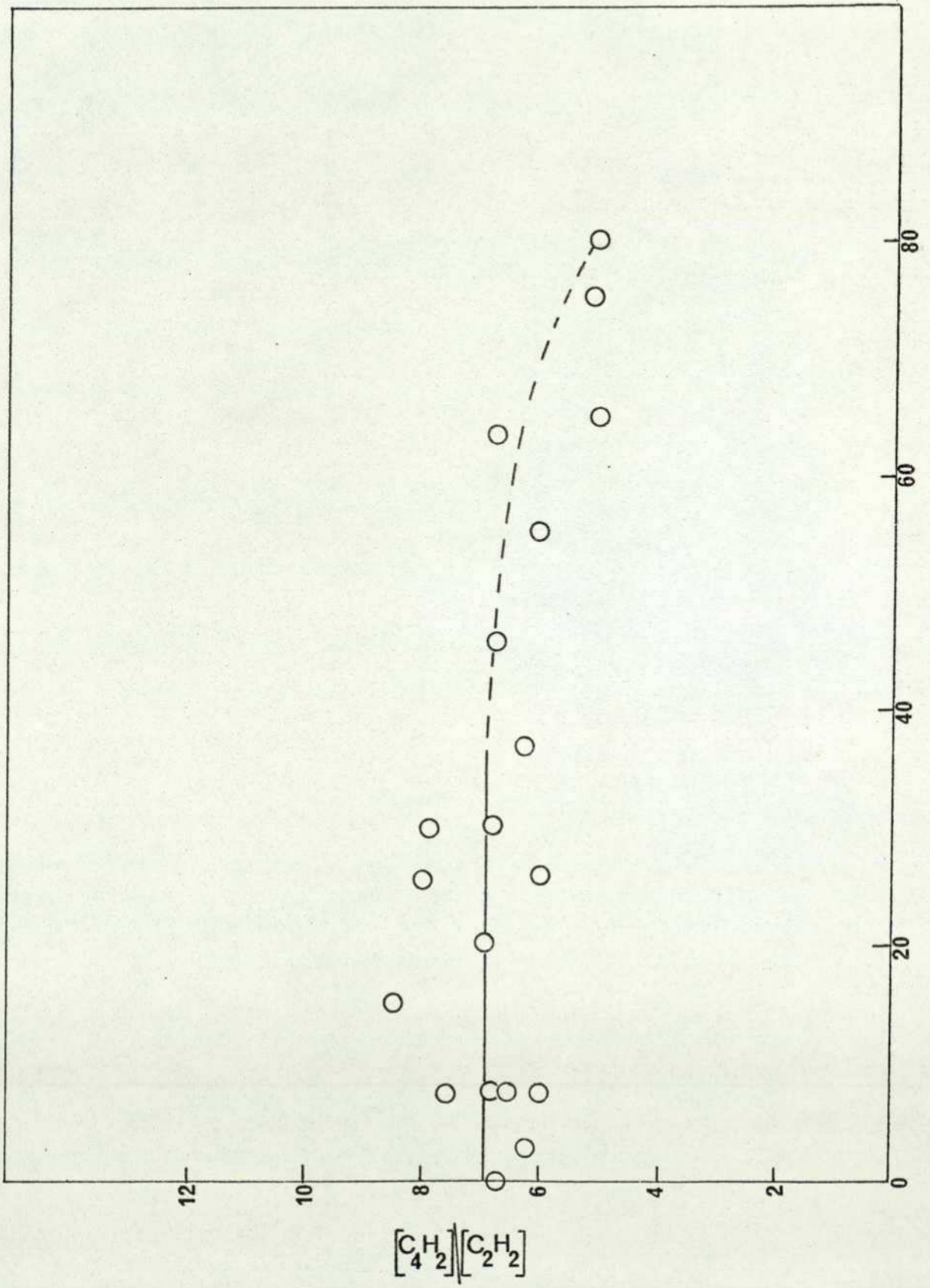
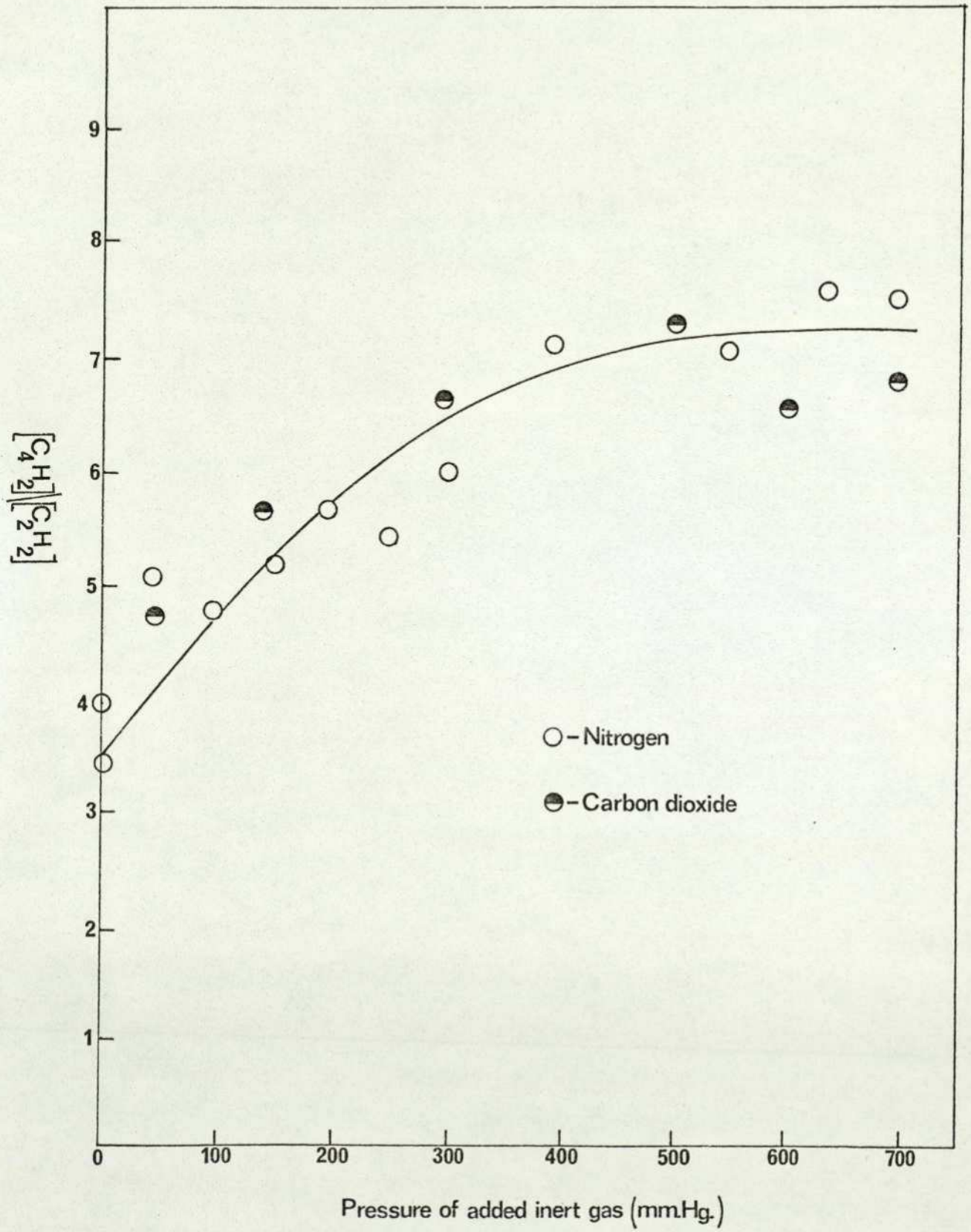


Figure 3.7

Graph of the change of the ratio $[C_4H_2]/[C_2H_2]$ with varying amounts of inert gas (CO_2 or NO_2) added to a photolysis mixture of monobromoethyne (7 mm.Hg.) and nitric oxide (7 mm.Hg.)



bromoethyne/nitric oxide/nitrogen mixtures (7:7:686) were thermally stable up to 210°C and data were obtained when such mixtures were photolysed (photolysis time 60-120 sec) at temperatures in the range 23 to 210°C. Arrhenius plots for the variation of $[C_4H_2]/[C_2H_2]$ with temperature are shown in Figure 3.8.

3.3 Photolysis of C_2HBr/NO mixtures in the presence of added alkanes

Alkanes were added in order to define the radical system more accurately. Tarr et. al. have determined relative rates for monobromoethyne/nitric oxide mixtures in the presence of alkanes and in view of certain differences between their findings and those reported in this work (notably concerning the influence of inert gases and nitric oxide) it was necessary to re-determine the relative rates in the present system.

In experiments with added alkanes, a standard mixture of nitric oxide (7 mm.Hg.) and monobromoethyne (7 mm.Hg.) was employed, and in each experiment the total pressure was adjusted to 700 mm.Hg. with added nitrogen. Such mixtures were photolysed for periods between 120 and 180 sec.

3.3.1 Experiments with added ethane, 2,2-dimethylpropane and methane

When alkanes were added to the standard photolysis mixture, an increase was observed in the yield of acetylene relative to butadiyne. This is due to the hydrogen-abstraction reaction

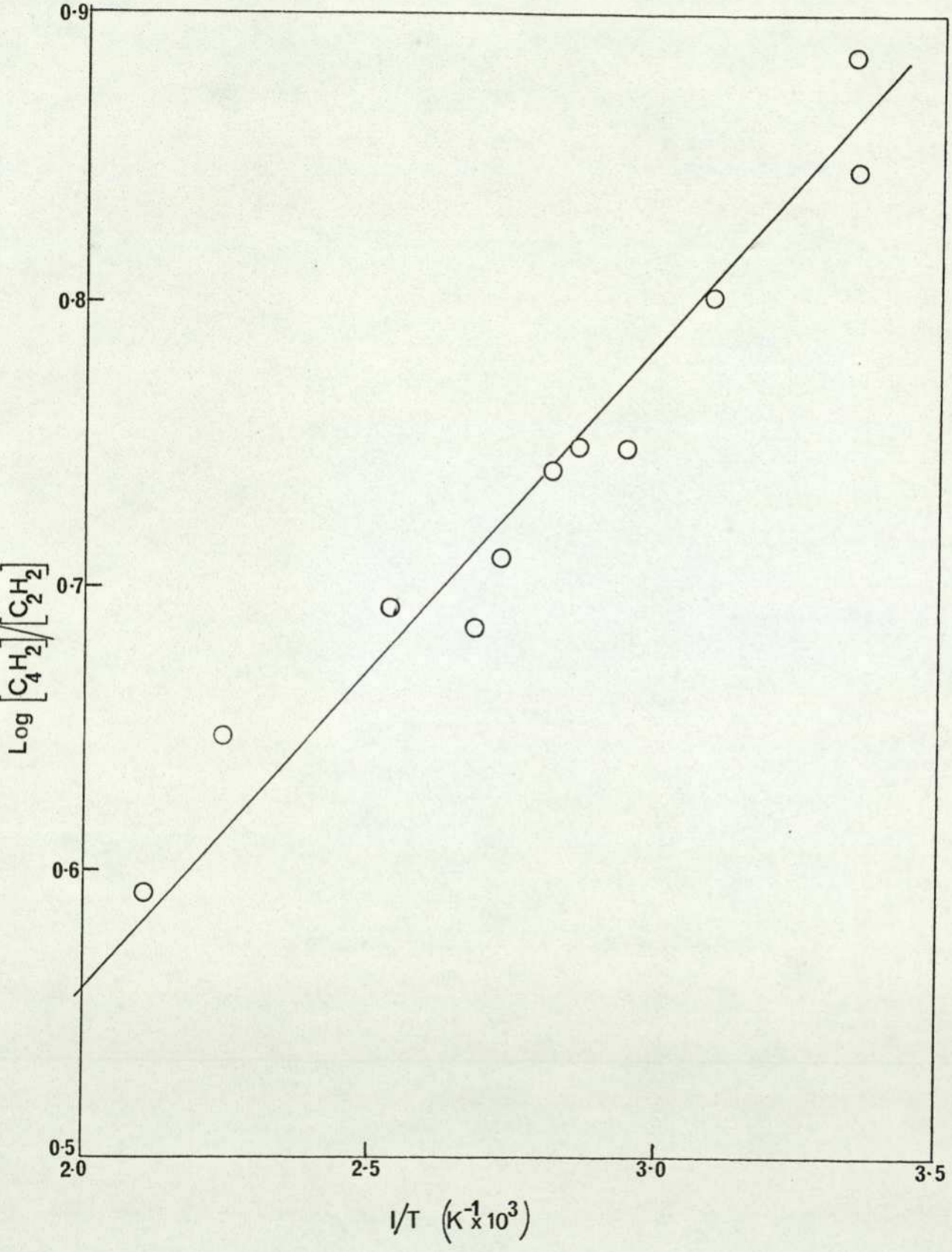
$$C_2H + RH \longrightarrow C_2H_2 + R \qquad (6)$$

Without added alkane acetylene is produced by the abstraction reaction,

$$C_2H + C_2HBr \longrightarrow C_2H_2 + C_2Br \qquad (5)$$

Figure 3.8

Graph of log $[C_4H_2]/[C_2H_2]$ against reciprocal temperature (K)



Experiments previously described have shown that in the absence of alkane the ratio $[C_4H_2]/[C_2H_2]$ is 7 ± 0.5. Therefore, the contribution of reaction (6) to the total amount of acetylene formed in the presence of alkane can be calculated by subtracting $^1/_7$ of the amount of butadiyne from the total concentration of acetylene. The results are shown in tables 3.2 and 3.3.

In the case of methane, the amount of acetylene formed in the reaction

$$C_2H + CH_4 \longrightarrow C_2H_2 + CH_3$$

was low and comparatively large amounts of methane (60 mm.Hg.) had to be added to the mixtures to produce any accurately measurable decrease in the ratio $[C_4H_2]/[C_2H_2]$. The results of these addition experiments are shown in tables 3.2 and 3.3.

3.3.2 The effect of temperature on the yields of acetylene in alkane-containing systems

The yields of acetylene and butadiyne produced by the photolysis, at 478K, of monobromoethyne/nitric oxide/nitrogen mixtures containing either 2,2-dimethylpropane or methane are given in table 3.4. At this temperature the ratio $[C_4H_2]/[C_2H_2]$ is 4.0 ± 0.5 in the absence of added alkane and in order to calculate the amount of acetylene produced from reaction (6), one-quarter of the total butadiyne formed was subtracted from the amount of acetylene produced.

Runs with 60 mm.Hg. of added methane were carried out in the temperature range 25-200°C. The yield of acetylene formed by reaction of the ethynyl radical with methane was calculated by subtracting the proportion formed from reaction (5), at a given temperature, from the total yield of acetylene. The amount of acetylene formed from reaction (5),

Table 3.2

Product yields from the photolysis of monobromoethyne (7 mm.Hg.), nitric oxide (7 mm.Hg.) and nitrogen (to make total pressure 700 mm.Hg.) with added alkanes.

Alkane	Photolysis time (sec.)	[RH] mm.Hg.	$[C_4H_2]$ mm.Hg.x10^{-2}	$[C_2H_2]$ mm.Hg.x10^{-2}	$[C_2H_2] - [C_4H_2]/7$ mm x 10^{-2}	k_6/k_3 Result	k_6/k_3 Average	k_6/k_3 Ref.(118)
Ethane	180	7	2.1	1.51	1.21	0.58	0.54	0.4
	120	7	1.47	0.93	0.72	0.5		
2,2-dimethyl-propane	120	7	0.81	0.75	0.64	0.8	0.94	1.1
	180	7	1.09	1.29	1.15	1.05		
Methane	120	60	1.24	0.35	0.173	0.016	0.015(5)	0.02
	120	60	1.17	0.32	0.153	0.015		

Table 3.3

Comparison of product yields with and without added alkanes under standard conditions*

Alkane	[RH] (mm.Hg.)	$[C_4H_2]$ (mm.Hg.x10^{-2})	$[C_2H_2]$ (mm.Hg.x10^{-2})	$[C_4H_2]+[C_2H_2]$ (mm.Hg.x10^{-2})
	0	1.6	0.22	1.82
2,2-di-methylpropane	7	0.81	0.75	1.56
Ethane	7	1.47	0.93	2.4
Methane	60	1.24	0.35	1.59

* Photolysis mixture = C_2HBr (7 mm.Hg.) + NO (7 mm.Hg.) + nitrogen to make total pressure 700 mm.Hg.

Photolysis time = 120 sec

Room temperature

Table 3.4

Yields of acetylene and butadiyne from the photolysis at 478K of mixtures of monobromoethyne, nitric oxide and nitrogen

Alkane	2,2-dimethylpropane	methane
Photolysis time (sec)	180	150
Pressure of monobromo-ethyne (mm.Hg.)	11.1	5.5
Pressure of nitric oxide (mm.Hg.)	11.1	5.5
Pressure of N_2 (mm.Hg.)	667	629
Pressure of added alkane	11.1	60.0
$[C_4H_2]$ (mm.Hg. x 10^{-2})	2.97	0.91
$[C_2H_2]$ (mm.Hg. x 10^{-2})	3.54	1.07
$[C_2H_2] - \frac{1}{4}[C_4H_2]$ (mm.Hg. x 10^{-2})	2.80	0.83
$\frac{k_6}{k_3}$	0.97	0.10
$\frac{k_6}{k_3}$ at room temperature	0.94	0.016

relative to the amount of butadiyne formed from reaction (3), had previously been established in a separate relative rate-temperature plot (section 3.2.6). A plot of log $[C_4H_2]/[C_2H_2]$ against 1/T was drawn using the corrected yield of acetylene formed from methane (Figure 3.9).

3.4 Photolysis of C_2HBr/NO mixtures in the presence of added alkynes

Experiments with added alkynes were usually performed using a mixture of monobromoethyne (7 mm.Hg.), nitric oxide (7 mm.Hg.) and a total pressure of 700 mm.Hg. If the pressure of monobromoethyne was altered the total pressure was kept constant at 700 mm.Hg. by adding nitrogen. A few runs were carried out without added nitric oxide (section 3.5). The thermal stability of reactant mixtures was found to be unaltered by the addition of the alkyne. Trial photolyses performed on mixtures containing the alkyne, nitric oxide and nitrogen showed that, under these conditions, all the mixtures used were stable except those containing butadiyne. Butadiyne suffered slight photolytic decomposition, but even then no acetylen was formed in the reaction and no other gaseous products were detected. A brown polymer was, however, formed which could only be removed from the reactor by rinsing with fuming nitric acid.

3.4.1 Added propyne (methylacetylene)

Photolysis of mixtures of monobromoethyne (7 mm.Hg.), nitric oxide (7 mm.Hg.), propyne (7 mm.Hg.) and nitrogen (to make total pressure 700 mm.Hg.) yielded butadiyne, acetylene and penta-1,3-diyne (C_5H_4). A photolysis time-concentration plot for these gases is given in Figure 3.10. Further experiments showed that the ratios $[C_5H_4]/[C_2H_2]$ and $[C_5H_4]/[C_4H_2]$ varied with propyne concentration and with temperature in the range 25 to 210°C.

Figure 3.9

Graph, $\log [C_4H_2]/[C_2H_2]$ against reciprocal temperature in the presence of added methane

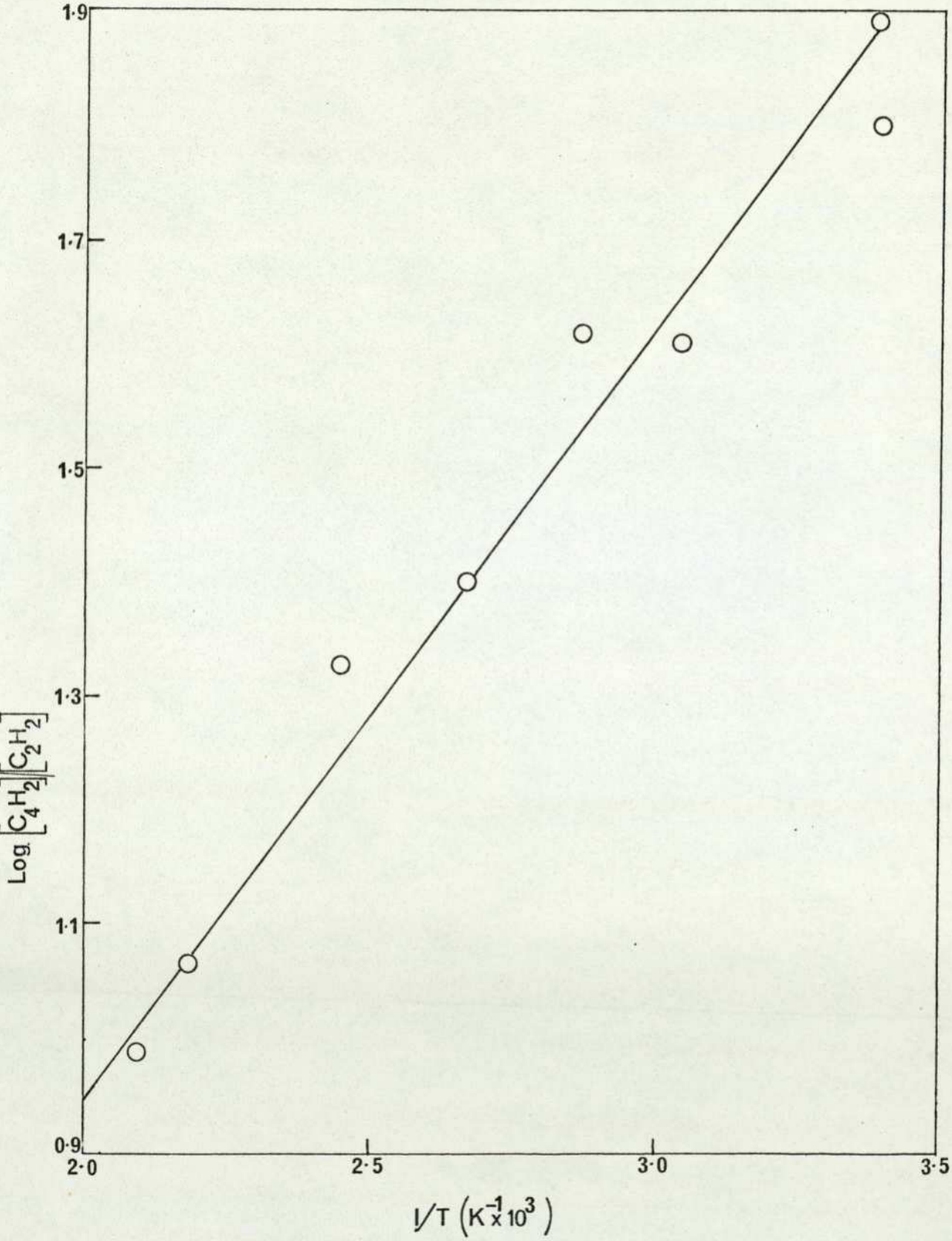
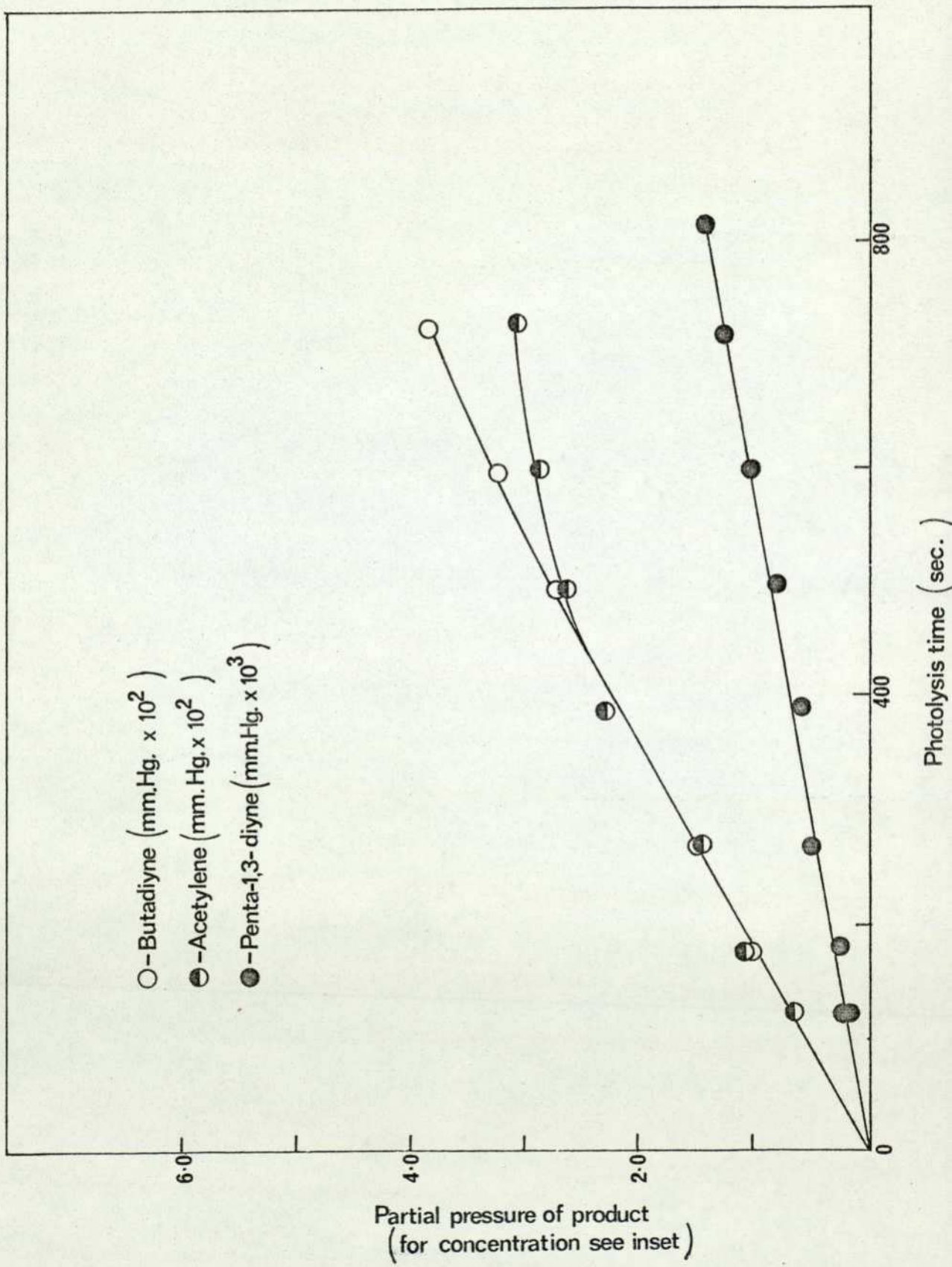


Figure 3.10

Variation of the concentration of acetylene, butadiyne and penta-1,3-diyne with photolysis time. (Reaction mixture: monobromoethyne (7 mm.Hg.) nitric oxide (7 mm.Hg.) propyne (7 mm.Hg.) and nitrogen (679 mm.Hg.)



3.4.2 Addition of acetylene

Acetylene was introduced in varying quantities to mixtures of propyne (7mm monobromoethyne (7 mm.Hg.), nitric oxide (7 mm.Hg.) and nitrogen added to a total pressure of 700 mm.Hg. Photolysis of these mixtures for periods not exceeding 300 sec showed that the ratio $[C_4H_2]/[C_5H_4]$ increased with acetylene concentration.

3.4.3 Addition of acetylene $-d_2$

Runs with added acetylene were performed using mixtures of acetylene $-d_2$ (2 mm.Hg.), monobromoethyne (2 mm.Hg.) and nitrogen (700 mm.Hg.) No nitric oxide was added because hydrogen cyanide formed in the photolysis produced a peak at m/e = 27, thus obscuring the acetylene $-d_1$ peak at this mass number. Low partial pressures of reactants were used to facilitate sampling. During photolyses acetylene $-d_1$, butadiyne and butadiyne $-d_1$ were formed. Table 3.5 shows the ratios $[C_4HD]/[C_2HD]$ and $[C_4H_2]/[C_4HD]$ determined after various photolysis times.

3.4.4 Addition of butadiyne (diacetylene)

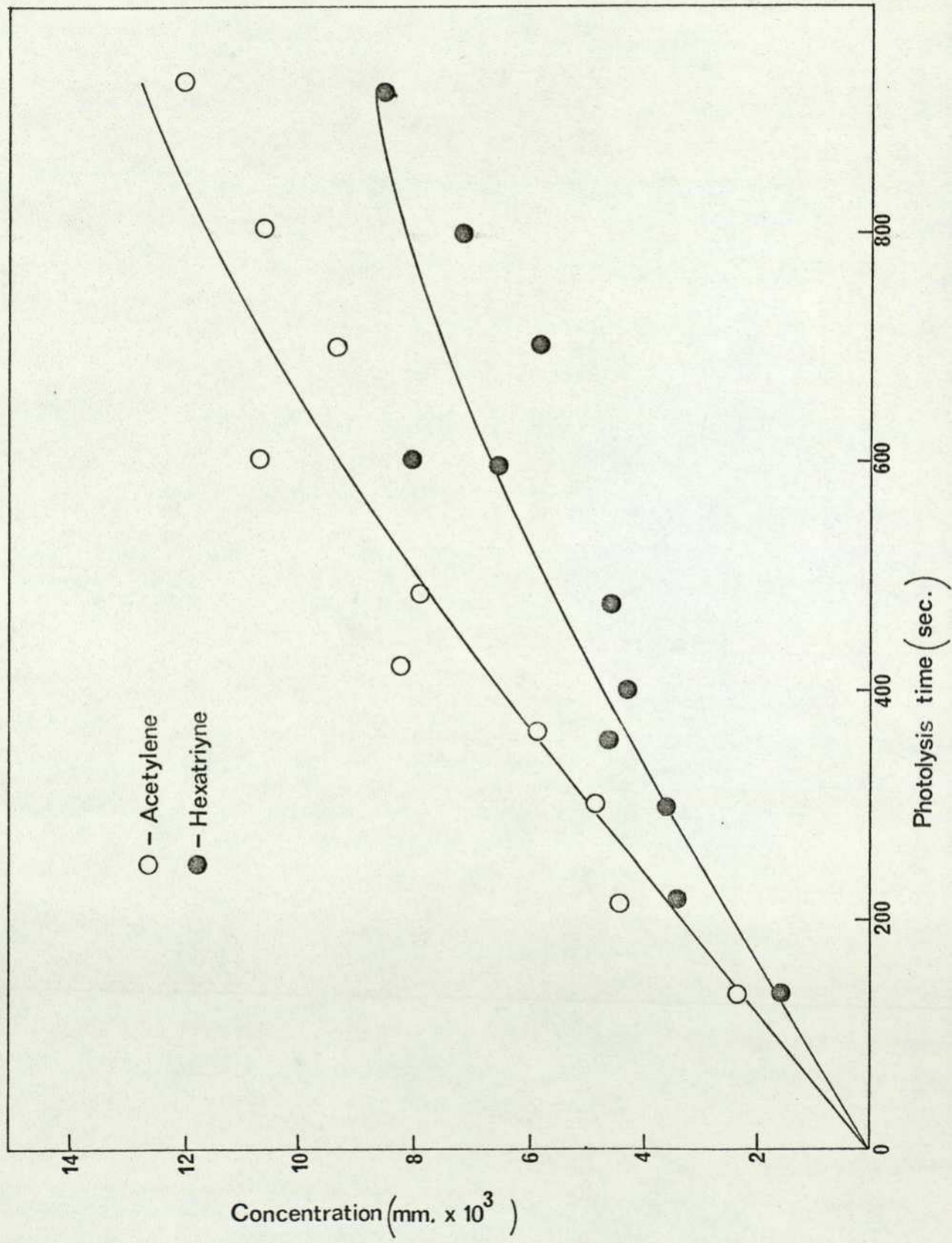
Photolysis of a mixture of monobromoethyne (7 mm.Hg.), butadiyne (7 mm.Hg.), nitric oxide (7 mm.Hg.) and nitrogen (to a total pressure of 700 mm.Hg.) gave acetylene and hexatriyne as products. A photolysis time - concentration curve for these products is shown in Figure 3.11. An increase in the partial pressure of monobromoethyne was found to increase the ratio $[C_2H_2]/[C_6H_2]$.

3.5 Photolysis of monobromoethyne in the presence of alkynes but without added nitric oxide

A limited number of experiments were performed in which monobromo-

Figure 3.11

Variation of the concentration of acetylene and hexatriyne with photolysis time (Reaction mixture: butadiyne (7 mm.Hg.) monobromoethyne (7 mm.Hg.) nitric oxide (7 mm.Hg.) and nitrogen (686 mm.Hg.))



ethyne/ alkyne mixtures were photolysed in the absence of nitric oxide. The alkynes used were butadiyne and propyne and the mixtures consisted of alkyne (7 mm.Hg.), monobromoethyne (7 mm.Hg.) and nitrogen (686 mm.Hg.). The yields of products with and without added nitric oxide, together with relative rates, are listed in Tables 3.6(a) and 3.6(b).

Table 3.5

The ratios $[C_4HD]/[C_2HD]$ and $[C_4H_2]/[C_4HD]$ determined after the photolysis of mixtures of acetylene $-d_2$ (2 mm.Hg.), monobromoethyne (2 mm.Hg.) and nitrogen (700 mm.Hg.)

Photolysis time (sec)	$\frac{[C_4HD]}{[C_2HD]}$	$\frac{[C_4H_2]}{[C_4HD]}$
600	0.63	1.15
450	2.04	1.1
720	1.48	1.6
180	5.76	1.8
300	6.21	1.2
200	0.58	1.7
Average	2.7(8)	1.4(8)

Table 3.6a

The yields of products formed from monobromoethyne, propyne and nitrogen (7 + 7 + 686 mm.Hg.) with and without added nitric oxide.

NO (mm.Hg.)	Photolysis time	$[C_5H_4]$ (mm.Hg.x10^3)	$[C_2H_2]$ (mm.Hg.x10^3)	$\frac{[C_2H_2]}{[C_5H_4]}$
0	300 sec	0.6	14.2	23·(6)
7	300 sec	0.56	15.3	27·(3)

Table 3.6b

The yield of products formed from monobromoethyne, butadiyne and nitrogen (7 + 7 + 686 mm.Hg.) with and without added nitric oxide.

NO (mm.Hg.)	Photolysis time	$[C_2H_2]$ (mm.Hg.x10^3)	$[C_6H_2]$ (mm.Hg.x10^3)	$\frac{[C_2H_2]}{[C_6H_2]}$
0	300 sec	3.12	2.25	1.38
7	300 sec	3.3	2.15	1.5

D I S C U S S I O N

4. Discussion

4.1 Photolysis of monobromoethyne

4.1.1 Monobromoethyne as a source of ethynyl radicals

Several criteria must be satisfied before a compound may be considered a satisfactory photolytic source of radicals[157]. Among these are the following:

(i) The compound should have a high vapour pressure and should be decomposed by light in an accessible spectral region.

(ii) Only one type of free radical should ideally be produced

(iii) The radicals produced should not react with the parent compound

(iv) The excited electronic states of the compound should neither react with added substrates nor photosensitise their decomposition

(v) The primary photolytic decomposition should produce not only radicals but also a non-radical compound which acts as a measure of the number of radicals produced.

(vi) Any non radical primary products should be inert.

Tarr, Strausz and Gunning[118] have studied halogeno-acetylenes as suitable sources of the ethynyl radical and, although neither criterion (ii) nor criteria (iii) and (v) are satisfied, monobromoethyne appears to be a reasonably convenient source of ethynyl radicals.

Since the energy of the C-Br bond in monobromoethyne is probably no more than 80 kcal.mole^{-1} [118], photolytic decomposition is likely to proceed by the initial fission of this bond to produce an ethynyl radical and a bromine atom.

$$C_2HBr + h\nu\ (253.7\ nm) \longrightarrow C_2H + Br$$

These and subsequent reactions suggested by Tarr et al[118] accounted for the primary products observed in the presence of nitric oxide

$$Br + NO + C_2HBr \longrightarrow BrCN + CO + HBr \qquad (2)$$

$$C_2H + C_2HBr \longrightarrow C_4H_2 + Br \quad (3)$$

$$2C_2H \longrightarrow C_4H_2 \quad (4)$$

$$C_2H + C_2HBr \longrightarrow C_2H_2 + C_2Br \quad (5)$$

The only likely alternative to this mechanism would be the production of a triplet state of bromoethyne by absorption of light:

$$C_2HBr + h\nu \longrightarrow C_2HBr^* \longrightarrow \text{products}$$

The triplet state would be liable, however, to suffer collisional deactivation by a third body:

$$C_2HBr^* + M \longrightarrow C_2HBr + M$$

It might therefore be expected that an increase in the concentration of inert gas would decrease the quantities of primary products produced in a given photolysis time.

There is, in fact, no direct experimental proof for the existence of ethynyl radicals in the photolytic decomposition of monobromoethyne. Nevertheless several observations suggest that such radicals are formed in the present system. For example, the addition of increasing quantities of nitric oxide was found to diminish the yields of acetylene and butadiyne (Figures 3.4 and 3.5), indicating that free radical reactions produce both these products. When monobromoethyne/nitric oxide mixtures were photolysed in the presence of alkanes for 120 sec, the total concentration of acetylene and butadiyne produced was constant ($2 \pm 0.4 \times 10^{-2}$ mm.Hg.) and did not differ substantially from that found without added alkane. The yield of acetylene increased, however, when alkane was added and there was a corresponding decrease in the yield of butadiyne (Table 3.3). This observation is consistent with the occurrence of the reaction:

$$C_2H + RH \longrightarrow C_2H_2 + R \quad (6)$$

This would remove some of the ethynyl radicals which would otherwise form butadiyne via reactions (3) and (4).

Finally, the formation of bromocyanogen and carbon monoxide is satisfactorily explained by reaction (2). Its occurrence indicates the presence of bromine atoms which are presumably formed in the primary process (1). The sum of the concentrations of acetylene and butadiyne produced after a photolysis lasting 90 sec remained approximately constant at 0.016 mm.Hg., irrespective of the presence of inert gas. These products are thus unlikely to be produced via a triplet state radical.

4.1.2 Reactions of the ethynyl radical with monobromoethyne

The results of Tarr et al[118] indicate that the ethynyl radical can abstract a hydrogen atom from monobromoethyne to produce acetylene:

$$C_2H + C_2HBr \longrightarrow C_2H_2 + C_2Br \qquad (5)$$

and also yield butadiyne by displacement of a bromine atom:

$$C_2H + C_2HBr \longrightarrow C_4H_2 + Br \qquad (3)$$

(The evidence for this reaction was summarised in Section 1.6.) The further possibility that two ethynyl radicals may combine to form butadiyne:

$$2C_2H \longrightarrow C_4H_2 \qquad (4)$$

was also suggested[118]. In order to determine the significance of reaction (4) in the present system, the concentration of monobromoethyne was varied as described in Section 3.2.3.

If butadiyne is produced exclusively from reaction (3), then:

$$\frac{d[C_4H_2]}{dt} = k_3[C_2H][C_2HBr]$$

and $$\frac{d[C_2H_2]}{dt} = k_5[C_2H][C_2HBr]$$

whence $$\frac{[C_4H_2]}{[C_2H_2]} = \frac{k_3[C_2H][C_2HBr]}{k_5[C_2H][C_2HBr]}$$

This equation predicts that the ratio $[C_4H_2]/[C_2H_2]$ should not vary with monobromoethyne concentration. A plot of the rate of formation of butadiyne against the rate of formation of acetylene for varying concentrations of monobromoethyne should thus be linear with a slope of k_3/k_5. This plot is shown in Figure 3.3 and is indeed a straight line with a slope of 7.

If reaction (4) were the only source of butadiyne, then the analogous expressions would be:

$$\frac{d[C_4H_2]}{dt} = k_4[C_2H]^2$$

whence $$\left(\frac{d[C_4H_2]}{dt}\right)^{\frac{1}{2}} = k_4^{\frac{1}{2}}[C_2H]$$

and $$\frac{(d[C_4H_2]/dt)^{\frac{1}{2}}}{d[C_2H_2]/dt} = \frac{k_4^{\frac{1}{2}}[C_2H]}{k_5[C_2H][C_2HBr]}$$

$$= \frac{k_4^{\frac{1}{2}}[C_2H]}{k_5[C_2H][C_2HBr]}$$

$$= \frac{k_4^{\frac{1}{2}}}{k_5[C_2HBr]}$$

A plot of $(d[C_4H_2]/dt)^{\frac{1}{2}}[C_2HBr]$ against $d[C_2H_2]/dt$ should, therefore, be a straight line. This plot is shown in Figure 3.2 and is curved, showing that the principal source of butadiyne is reaction (3). Neither of the plots in Figures 3.2 and 3.3 prove that reaction (4) does not occur but they do suggest that it is a minor reaction. For this reason, it has been

neglected in the present discussion. From Figure 3.3, $k_3/k_5 = 7 \pm 1$ at a total pressure of 700 mm.Hg. (nitrogen or carbon dioxide).

In the present investigation, the ratio $[C_4H_2]/[C_2H_2]$ was found to decrease with decreasing partial pressure of inert gas (Figure 3.7), indicating that the addition of inert gas favoured reaction (3) relative to reaction (5). A possible explanation for this behaviour is that reaction (3) has a third body requirement:

$$C_2H + C_2HBr + M \longrightarrow C_4H_2 + Br + M$$

At total pressures approaching 600 mm.Hg., however the ratio $[C_4H_2]/[C_2H_2]$ attained a limiting value, and thereafter remained constant. This observation is difficult to explain if only one reaction has a third body requirement. A relatively simple explanation of this behaviour is that during photolysis, ethynyl radicals produced in the absence of inert gas have excess translational energy and, probably, enhanced reactivity. It is typical of systems containing "hot" radicals that addition of inert gas modifies the rates of reactions involving them[140]. The extra energy required for the formation of "hot" ethynyl radicals is supplied by the excess energy of the absorbed light over the energy needed to break the carbon-bromine bond in monobromoethyne. The energy needed to break this carbon-bromine bond probably does not exceed 80 kcal.mole^{-1} [118] but the energy corresponding to the absorption of light at 253.7 nm is about 112 kcal.mole^{-1}. The excess energy is thus approximately 34 kcal.mole^{-1} and is divided between the bromine atom and the ethynyl radical in inverse proportion to their molecular weights. The ethynyl radical might therefore be expected to have about 24 kcal.mole^{-1} excess energy. The ethynyl radical has few vibrational or rotational degrees of freedom and most of the energy would be dissipated as translational energy. The "hot" ethynyl radical is more reactive and less selective than a

similar "thermalised" radical and the ratio $[C_4H_2]/[C_2H_2]$ would thus be smaller with relatively large quantities of "hot" radicals present. As the inert gas pressure is increased, there are proportionately less "hot" radicals reacting to form acetylene and butadiyne and the increase in the ratio $[C_4H_2]/[C_2H_2]$ reflects the change in selectivity of the "thermalised" ethynyl radical compared with "hot" radicals. A limiting value of $[C_4H_2]/[C_2H_2]$ is reached when all the ethynyl radicals are thermalised before reacting and this ratio is a measure of k_3/k_5 at pressures greater than 600 mm.Hg. All subsequent experiments were performed with a total pressure of 700 mm.Hg. under conditions which were unaffected by changes in pressure.

In the presence of increasing amounts of nitric oxide, the rates of formation of acetylene and butadiyne decreased the rates tending to a minimum value at $p_{NO} > 35$ mm.Hg. (Figures 3.4 and 3.5). The ratio $[C_4H_2]/[C_2H_2]$ remained approximately independent of nitric oxide pressure up to about 60 mm.Hg. thereafter the ratio decreased slightly (Figure 3.6). The likely explanation is that the inhibition mechanism is identical for both reactions (3) and (5), at least for the addition of the first 60 mm.Hg. of nitric oxide. The inhibition of reactions (3) and (5) can be explained in terms of the scavenging of the ethynyl radical by nitric oxide:

$$C_2H + NO \longrightarrow C_2HNO \qquad (i)$$

Since the addition of nitric oxide does not, however, completely inhibit the reactions of the ethynyl radical but merely produces a minimum in the rate of reactions (3) and (5), the inhibition must involve reactions in addition to (i). Methyl radicals, produced during the photolysis of methyl iodide, have been found to react with nitric oxide to form nitrosomethane[142]:

$$CH_3 + NO \longrightarrow CH_3NO$$

This latter compound can also react further with nitric oxide to regenerate the original methyl radical[141,142], the overall reactions becoming:

$$CH_3NO + 2NO \longrightarrow CH_3 + N_2 + NO_3$$

$$NO_3 + NO \longrightarrow 2NO_2$$

If a similar mechanism occurred during the photolysis of monobromoethyne, the nitrosoethyne formed by reaction (i) could decompose by further reaction with nitric oxide:

$$C_2H + NO \longrightarrow C_2HNO \qquad (i)$$

$$C_2HNO + 2NO \longrightarrow C_2H + N_2 + NO_3 \qquad (ii)$$

and the concentration of ethynyl radicals available to react by reactions (3) and (5) would be determined by the relative rates of reactions (i) and (ii). Unfortunately, there are no rate data available for reactions (i) and (ii). However, for inhibition to take place, reaction (ii) would have to be slower than reaction (i) at low concentrations of nitric oxide. A limit would be reached when the rate of (i) was equal to that of (ii) i.e. when

$$k_{(i)}[NO][C_2H] = k_{(ii)}[NO]^2[C_2HNO]$$

In the present work it was found that the rate of formation of butadiyne continued to decrease with increasing partical pressures of nitric oxide, even when the rate of formation of acetylene had almost attained a minimum (Figures 3.4 and 3.5). This caused the ratio $[C_4H_2]/[C_2H_2]$ to decrease slightly (Figure 3.6). A possible explanation is that the transition state adduct between the ethynyl radical and monobromoethyne which leads to butadiyne is also scavenged by nitric oxide:

$$C_2H + C_2HBr \longrightarrow [\,H\dot{C} = C(C_2H)(Br)\,]$$

$$\downarrow NO$$

$$HCN + HC_2(Br)C = O \leftarrow [\,H(NO)C = C(C_2H)(Br)\,]$$

This reaction is analogous to the general reaction described by Sherwood and Gunning[119] wherein a radical (Y), in the presence of nitric oxide, breaks the carbon-carbon triple bond:

$$Y + XC_2Z \longrightarrow \begin{matrix} Y \\ X \end{matrix}\!\!>\!C = C\!<\!\!\begin{matrix} \\ \end{matrix}^{Z}$$

$$\downarrow \quad NO$$

$$\begin{matrix} X \\ Y \end{matrix}\!\!>\!C = O + ZCN$$

The mechanism of inhibition by nitric oxide is still under discussion[143,144] and no attempt has therefore been made in the present work to clarify what may be an extremely complex reaction sequence. All experiments with added hydrocarbon were carried out, however, with no more than 7 mm.Hg. of nitric oxide present and this had no effect on the relative rates of the reaction under discussion. These results differ considerably from those of Tarr et al[118] who found no evidence for scavenging of the ethynyl radical by nitric oxide. The present work was performed at a constant initial pressure of 700 mm.Hg. whereas the total pressure used in the previous work[118] varied with the amount of nitric oxide added although it is difficult to see how this could affect detection of an inhibiting effect. Indeed, it is difficult to explain this difference in the results, although it may be due to the relatively insensitive analytical methods used by Tarr, Strausz and Gunning[118].

The variation of $[C_4H_2]/[C_2H_2]$ with temperature (Section 3.2.6) has enabled the relative Arrhenius parameters of reactions (3) and (5) to be estimated. Thus, if $[C_4H_2]/[C_2H_2] = k_3/k_5$ and k_3 and k_5 are expressed in the form $k = Ae^{-E/RT}$ then $k_3/k_5 = A_3/A_5\, e^{E_5-E_3/RT}$ whence $\log k_3/k_5 = \log A_3/A_5 + E_5 - E_3/4.58T$. It has been found that a plot of $\log [C_4H_2]/[C_2H_2]$ against $1/T$ (Figure 3.8) gives a straight line

of slope $E_5 - E_3/2.303R$ and an intercept of $\log A_3/A_5$. E_5-E_3 and A_3/A_5 are found to be 1.0 ± 0.2 kcal.mole^{-1} and 1.2 ± 0.5 respectively. It is of interest that there is little difference between the activation energies of reaction (3) and (5) particularly since reaction (3) could be exothermic by up to 40 kcal.mole^{-1} whilst reaction (5) is probably thermoneutral. Both reactions proceed easily at room temperature accounting for between one-quarter and one-third of the monobromoethyne consumed and probably have relatively low activation energies. The possible absolute values for the activation energies and A factors of these reactions are discussed at the end of the following section.

4.2 The reaction of the ethynyl radical with alkanes

The observation that, although the yield of acetylene increased in the presence of alkanes the total amount of acetylene and butadiyne produced remained constant, is consistent with the occurrence of the reaction:

$$C_2H + RH \longrightarrow R + C_2H_2 \qquad (6)$$

Values of the ratio k_{6/k_3} for methane, ethane and 2,2-dimethylpropane are given in Table 3.2. These ratios are in good agreement with similar values obtained by Tarr, Strausz and Gunning[118]. The hydrogen atoms in both ethane and 2,2-dimethylpropane are in the primary position and have similar bond dissociation energies. The rates of abstraction per hydrogen atom relative to the rate of reaction (3) are 0.09 and 0.08 for ethane and 2,2-dimethylpropane respectively. At 478K, the ratio k_{6/k_3} for 2,2-dimethylpropane has a value of 0.97 which is very close to that obtained at room temperature (Table 3.4); this suggests that reactions (3) and (6) have the same activation energy when (6) involves abstraction of a primary hydrogen.

k_6/k_3 for methane has a value of 0.015 and this ratio varies substantially with temperature, the value at 478K being 0.1 (Table 3.4). In the presence of added methane the ratio of butadiyne to acetylene produced by reaction (6) was measured at various temperatures and a plot of log k_3/k_6 against $1/_T$ produced a straight line (Figure 3.9) of slope $E_6-E_3/2.303R$ and intercept log A_3/A_6. From this graph (E_6-E_3) = 3.04 ± .4 kcal.mole^{-1} and A_3/A_6 = 0.54 ± 0.25. The C-H bond in methane has a dissociation energy of about 105 kcal.mole^{-1} [89] and it might be expected that reaction (6) for methane would be exothermic by at least 5 kcal.mole^{-1}. However, this reaction has a substantially higher activation energy than reaction (5) even though the value of $D(CH_3-H)$ is probably lower than that for the fission of an acetylenic hydrogen atom by at least 5 kcal.mole^{-1}.

The activation energy of the reverse of reaction (6)

$$CH_3 + C_2H_2 \longrightarrow CH_4 + C_2H \qquad (-6)$$

has been measured in the case of CD_3 radicals.[145] If a similar value is assumed for $D(CD_3-H)$ and $D(CH_3-H)$, then the activation energy for reaction (-6) should be 14 kcal.mole^{-1}. If $D(C_2H-H)$ and $D(CH_3-H)$ are 114 and 105 kcal.mole^{-1} respectively[89,94], then the heat of reaction (-6) is about 9 kcal.mole^{-1}. The activation energy of reaction (6) can now be estimated by subtracting the heat of reaction from the activation energy of (-6). In this case a value of 5 kcal.mole^{-1} is found for E_6. The strength of the C-H bond in acetylene is still uncertain and literature values for the dissociation energy range from 110 to 128 kcal.mole^{-1} (Table 1.2). This means that the activation energy for reaction (6) could be as high as 9 kcal.mole^{-1} or be close to zero, although this latter alternative seems unlikely since reactions (3) and (5) have even lower activation energies than reaction (6). Thus it is reasonable to select a value of 5 ± 4 kcal.mole^{-1} for the activation energy of

reaction (6) and, since E_6-E_3 is 3.0 ± 0.4, then $E_3 \simeq 2$ kcal.mole^{-1} with an upper limit of about 6 kcal.mole^{-1} and a lower limit of zero. $E_5-E_3 = 1.0 \pm 0.2$ kcal.mole^{-1}, so that $E_5 \simeq 3$ kcal.mole^{-1} with an upper limit of about 7 kcal.mole^{-1} and a lower limit again of zero.

The A factor for reaction (-6) is difficult to estimate to better than an order of magnitude, but reactions involving hydrogen abstraction by methyl invariably have A factor values of the order of 10^8 l.mole^{-1}sec^{-1} [146] If the entropy change in reaction (-6) can be estimated, it is possible to assess the order of magnitude of the reverse reaction (reaction 6) by means of the expression:

$$\frac{A_{(-6)}}{A_{(6)}} = \exp \Delta S^\circ/R$$

(This formula has been extensively used by Benson and his co-workers[89] and is derived simply from the thermodynamic expression $-RT \ln K = \Delta H^\circ - T\Delta S^\circ$ where K is the equilibrium constant of a given reaction and RT, ΔH° and ΔS° have their usual meanings.) Taking values for the standard entropies of CH_4, C_2H_2, C_2H and CH_3 as 44.5, 48, 49.6 and 46.1 gibbs mole^{-1} respectively[89]

$$\Delta S^\circ_{(-6)} = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$
$$= 44.5 + 49.6 - 46.1 + 48$$
$$= 94.1 - 94.1 = 0$$

i.e. $A_{(-6)} = A_6$. This indicates that the pre-exponential factor for reaction (6) must be about 10^8 l.mole^{-1}sec^{-1}. It has also been found that $A_3/A_6 = 0.5 \pm 0.25$ and hence it may be concluded that all the reactions of the ethynyl radical so far discussed have A factor values of about 10^8 l.mole^{-1}sec^{-1}.

The activation energy differences and A factor ratios which can be obtained using reaction (3) as a standard are summarised in table 4.1

and estimates of the absolute values of the activation energies are summarised in table 4.2.

With these data, it becomes possible to compare the reactivity of the ethynyl radical with that of other highly reactive radicals, namely H, OH and CH_3. These species readily abstract hydrogen from ethane and table 4.3 lists the Arrhenius parameters obtained for the reaction:

$$X + C_2H_6 \longrightarrow XH + C_2H_5$$

where X is either CH_3, H, OH or C_2H. The ethynyl radical emerges as the most reactive species, thus fully confirming the expectations alluded to in the Introduction (Section 1.6).

4.3 The reaction of the ethynyl radical with alkynes

4.3.1 The reaction of the ethynyl radical with propyne

The primary products found in the reaction of the ethynyl radical with propyne are acetylene, butadiyne and penta-1,3-diyne (Section 3.4.1). The work of Tarr, Strausz and Gunning[120] has shown that ethynyl radicals react with alkenes in three ways, namely by hydrogen abstraction, hydrogen atom displacement and alkyl radical displacement; examples of these reactions were given in Section 1.6. The ethynyl radical might be expected to react in a similar way with alkynes. Acetylene can be formed by the hydrogen-abstraction reaction

$$C_2H + C_3H_4 \longrightarrow C_2H_2 + C_3H_3 \qquad (7)$$

whilst methyl radical displacement reaction gives butadiyne:

$$C_2H + CH_3C_2H \longrightarrow C_4H_2 + CH_3 \qquad (8)$$

Hydrogen atom displacement gives penta-1,3-diyne:

$$C_2H + CH_3C_2H \longrightarrow CH_3C_4H + H \qquad (9)$$

Table 4.1

Activation energy differences ($E_x - E_3$) and A factor ratios (A_3/A_x) obtained in the temperature range 273-478K (where x is the appropriate reaction number)

x (reaction number)		$E_x - E_3$ (kcal.mole^{-1})	A_3/A_x
5		1.0 ± 0.2	1.2 ± 0.5
	ethane	0	1.85 ± 0.15
6	2,2-dimethylpropane	0	1.05 ± 0.2
	methane	3.04 ± 0.4	0.54 ± .25

Table 4.2

Estimated values of activation energies (A factor values are of the order 10^8 $l.mole^{-1}sec.^{-1}$ - see text)

Reaction	Activation Energy ($kcal.mole^{-1}$)
3	2 (6) *
5	3 (7) *
6 (methane)	5 ± 4

* Value in parenthesis indicates upper limit, the lower limit being zero.

Table 4.3

Comparison of Arrhenius parameters for the abstraction of hydrogen from ethane in the reaction: $X + C_2H_6 = XH + C_2H_5$

Radical (X)	Activation energy ($kcal.mole^{-1}$)	log A factor ($l.mole^{-1}sec^{-1}$)	Temp. (K)	Ref.
CH_3	10.8	8.5	420	147
H	9.7	11.1	300 - 1100	148
OH	9.0	14.54	754 - 1254	156
C_2H	2 (6) [a]	8 ± 1	300 - 480	b

a - value in parenthesis represents upper limit

b - estimation based on the present work (tables 4.1 and 4.2)

In reaction (7) it is probably a methyl hydrogen atom which is abstracted, not only because the C-H bond of a methyl group is weaker than that in acetylene but also because of the formation of a resonance-stabilised radical:

$$\dot{C}H_2 - C \equiv CH \quad \longleftrightarrow \quad CH_2 = C = \dot{C}H$$

The H_3C-C_2H bond for propyne has been estimated to have a dissociation energy of 100-116 kcal.mole^{-1} [92,126] and the HC_2-C_2H bond strength for butadiyne has been measured as 122 and 143 kcal.mole^{-1} [92,126]. From these data reaction (8) is exothermic by between 6 and 43 kcal.mole^{-1}. Probably reaction (9) is also exothermic by a few kcal.mole^{-1} unless the highest value for the acetylenic C-H dissociation energy is used. A further hydrogen displacement could take place forming penta-1,2-diene-4-yne:

$$C_2H + CH_3C_2H \quad \longrightarrow \quad H_2C = C = CH - C \equiv CH + H$$

This is thermochemically at least as favourable as reaction (9). However, no attempt was made to detect the dienyne in the present work.

Due to the possible participation of reactions (7) and (8) in the formation of acetylene and butadiyne, it is not possible to estimate the relative rates of reactions (7), (8) and (9) by direct measurement of the ratios of the primary products. However, if reactions (7) and (8) contribute significantly to the production of acetylene and butadiyne, and if reaction (9) is the only source of penta-1,3-diyne then simple relationships can be derived which allow the relative rates of the above reactions to be determined. Considering reactions (5), (7) and (9) then

$$\frac{[C_5H_4]}{[C_2H_2]} = \frac{k_9[C_2H][C_3H_4]}{k_5[C_2H][C_2HBr] + k_7[C_2H][C_3H_4]}$$

or

$$\frac{[C_5H_4]}{[C_2H_2]} = \frac{k_9[C_3H_4]/[C_2HBr]}{k_5 + k_7[C_3H_4]/[C_2HBr]}$$

If $[C_5H_4]/[C_2H_2] = R_1$ and $[C_3H_4]/[C_2HBr] = r$

then

$$R_1 = \frac{k_9 r}{k_5 + k_7 r}$$

$$k_5 + k_7 r = k_9\left(\frac{r}{R_1}\right)$$

$$\left(\frac{r}{R_1}\right) = \frac{k_7}{k_9}.r + \frac{k_5}{k_9} \qquad (A)$$

A linear relationship was indeed found between r and r/R_1 (Fig. 4.1), demonstrating that reactions (7) and (9) represent important modes of interaction of the ethynyl radical with propyne. An alternative route to the formation of penta-1,3-diyne involves the following reaction sequence:

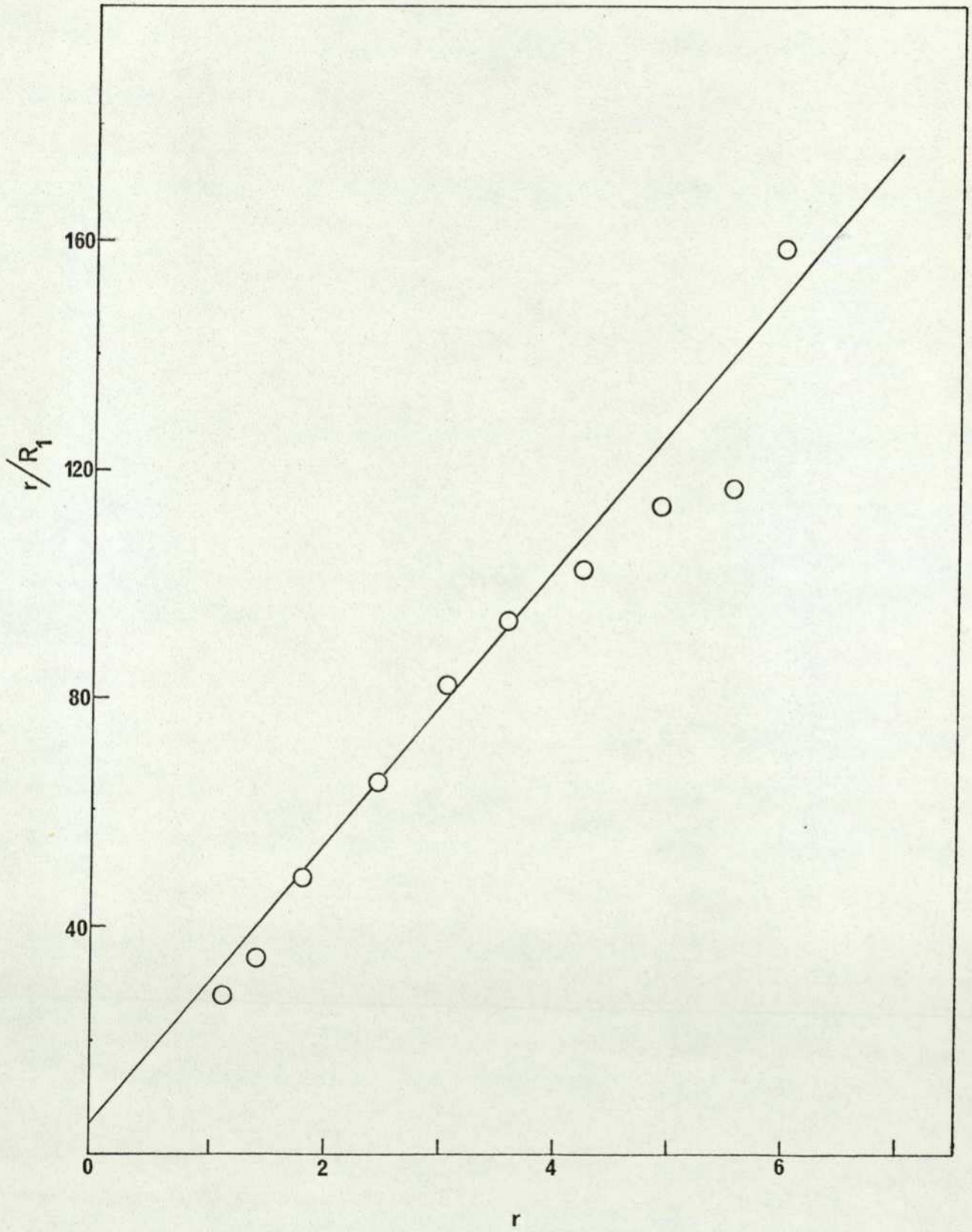
$$C_2H + CH_3C_2H \longrightarrow C_2H_2 + CH_3C_2 \qquad (7a)$$

$$CH_3C_2 + C_2HBr \longrightarrow CH_3C_4H + Br \qquad (9a)$$

Reaction (9a) is quite feasible, being analogous to reaction (3) and the relative amounts of penta-1,3-diyne produced will depend on the values of k_9 and k_{9a} and on the relative concentrations of the ethynyl and propynyl radicals. Reaction (7a) is probably the least favoured hydrogen abstraction reaction, since apart from the thermochemical consideration mentioned earlier there is only one hydrogen attached to an acetylenic carbon in comparison with three hydrogens attached to the methyl carbon. Therefore the concentration of propynyl radicals is probably much smaller than that of ethynyl radicals although it is not possible with the present data to calculate the relative concentrations of the two radicals to within an order of magnitude. Undoubtedly, the best demonstration that (9a) is an insignificant source of penta-1,3-diyne in this system is the

Figure 4.1

Graph of r/R_1 against r, where $r = [C_3H_4]/[C_2HBr]$ and $R_1=[C_5H_4]/[C_2H_2]$



linearity of the plot in Figure 4.1. If reaction (9a) were significant there would be a pronounced curvature in this plot; this is due to the relative increase in the concentration of propynyl radicals with increasing concentration of propyne. Similar evidence comes from the variation of the ratio $[C_5H_4]/[C_4H_2]$ with propyne concentration. Considering reactions (8) and (9), then

$$\frac{[C_5H_4]}{[C_4H_2]} = \frac{k_9[C_2H][C_3H_4]}{k_3[C_2H][C_2HBr] + k_8[C_2H][C_3H_4]}$$

If $$\frac{[C_5H_4]}{[C_4H_2]} = R_2$$

and $$\frac{[C_3H_4]}{[C_2HBr]} = r$$

then $$R_2 = \frac{k_9 r}{k_3 + k_8 r}$$

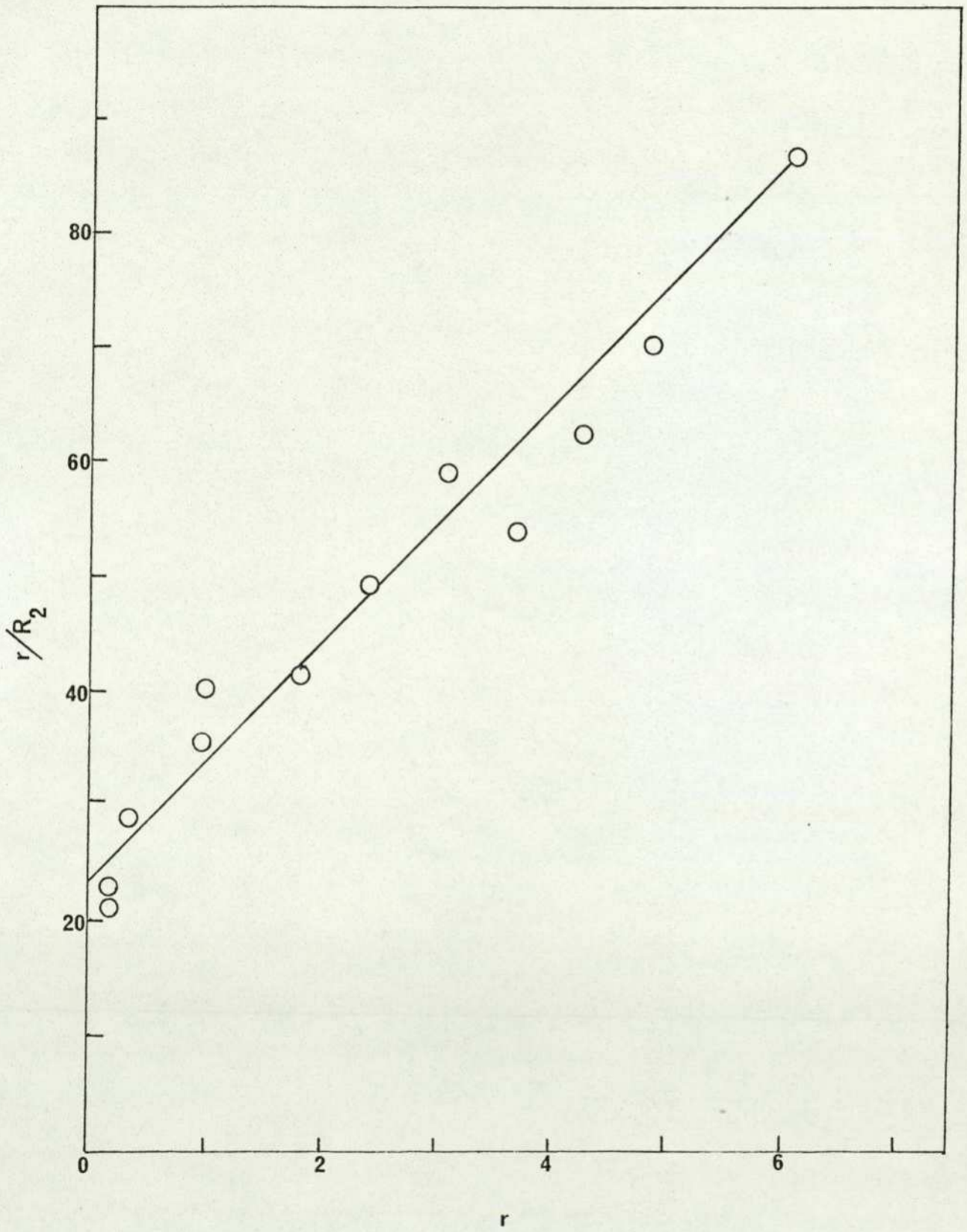
or $$k_9/k_8\left(\frac{r}{R_2}\right) = r + \frac{k_3}{k_8}$$

$$\frac{r}{R_2} = \frac{k_8}{k_9} r + \frac{k_3}{k_9} \qquad \text{(B)}$$

Figure 4.2 shows a plot of r/R_2 against r which is again found to be linear. Both the plots in Figures 4.1 and 4.2 allow various rate constant ratios to be determined. Figure 4.1, based on equation (A) has a slope corresponding to the ratio k_7/k_9 and an intercept equal to k_5/k_9 and from this graph $k_7/k_9 = 25 \pm 3$ and $k_5/k_9 = 5 \pm 2$. Similarly from Figure 4.2 and from equation (B), $k_8/k_9 = 9.9 \pm 1$ and $k_3/k_9 = 23 \pm 3$. As a cross check on these values, the ratio k_3/k_5 can be determined by dividing k_3/k_9 by k_5/k_9 and this gives a value of 4.6 ± 2. This is rather low in comparison with the value obtained by direct measurement, (7 ± 1) but

Figure 4.2

Graph of r/R_2 against r, where $r = [C_3H_4]/[C_2HBr]$ and $R_2 = [C_5H_4]/[C_4H_2]$



nevertheless a reasonably self-consistent picture emerges.

The fate of the methyl radicals and hydrogen atoms produced during displacement reactions (8) and (9) must now be considered. Possible reactions involve either addition to triple bonds of propyne and monobromoethyne or reaction with nitric oxide. The scavenging of hydrogen atoms by nitric oxide is known to take place[149,150] and is thought to involve the following reactions:

$$H + NO + M \longrightarrow HNO + M$$

$$H + HNO \longrightarrow H_2 + NO$$

The first reaction, which is rate-determining, is very fast at room temperature with a rate constant of 4.8×10^{15} cm^6 $mole^{-2}sec^{-1}$ [149,150]. Hydrogen atoms may also add to acetylene to form the vinyl radical:

$$H + C_2H_2 \longrightarrow C_2H_3$$

but, at room temperature do not abstract hydrogen from acetylene[151,152]. At room temperature the addition reaction to give vinyl radicals has a rate constant of 2.4×10^{10} $cm^3mole^{-1}sec^{-1}$ [152] and probably does not compete effectively with scavenging by nitric oxide. A previously unconsidered reaction of hydrogen atoms is that with propyne to form acetylene[153]:

$$H + CH_3C_2H \longrightarrow CH_3 + C_2H_2$$

This reaction will probably not, however, contribute significantly to the production of acetylene in this system in view of the low relative rate of reaction (9) and the efficiency of scavenging of hydrogen by nitric oxide.

The methyl radical is efficiently scavenged by nitric oxide[142,154,15] and, at room temperature the reaction

$$CH_3 + NO = CH_3NO$$

has a rate constant of 2.6×10^9 $l.mole^{-1}sec^{-1}$ [154]. This is about

one-tenth of the rate of the combination reaction[154]:

$$2CH_3 \longrightarrow C_2H_6$$

However, since the concentration of nitric oxide is at least 10^3 times that of the methyl radical the formation of ethane in this system is probably small, and this compound was not detected among the reaction products. The methyl radical can also add to the triple bond in acetylene[145], although the rate constant does not appear to have been determined. The rate of addition of methyl radicals to triple bonds probably does not exceed that of the corresponding addition of hydrogen atoms and the principal reaction of methyl radicals generated in the system thus probably involves their addition to nitric oxide.

The variation of the ratios $[C_5H_4]/[C_2H_2]$ and $[C_4H_2]/[C_5H_4]$ with changing concentrations of propyne was measured at various temperatures in the range 300 to 480K and plots of r/R_1 and r/R_2 against r yielded a series of straight lines. In this way, the ratios of k_7/k_9, k_5/k_9, k_8/k_9 and k_3/k_9 determined at various temperatures. The values obtained are recorded in table 4.4. k_5/k_9 does not appear to vary with temperature and k_8/k_9 varies only a small amount, indicating that E_8 has a value close to E_9. Both k_7/k_9 and k_3/k_9 vary substantially with temperature. A plot of log k_7/k_9 against 1/T (Figure 4.3) gives a straight line, the slope of which corresponds to a value for E_9-E_7 of 1.07 ± 0.3 kcal.mole^{-1}, and for A_7/A_9 of 4.1 ± 2. Similarly, a plot of log k_3/k_9 against 1/T (Figure 4.4) yields a straight line giving a value for E_9-E_3 of 1.1 ± 0.3 kcal.mole^{-1} for A_3/A_9 of 3.35 ± 2. Using reaction (3) as a standard, activation energy differences and A-factor ratios can now be estimated and are listed in table 4.5. All the activation energies of reactions (3), (5), (7), (8) and (9) are close to each other. Reaction (5) and reaction (9) have almost the same activation energies showing that the displacement of an acetylenic hydrogen is as favourable as its abstraction. The

Figure 4.3

Graph of log k_{7/k_9} against reciprocal temperature (Date from Table 4.4)

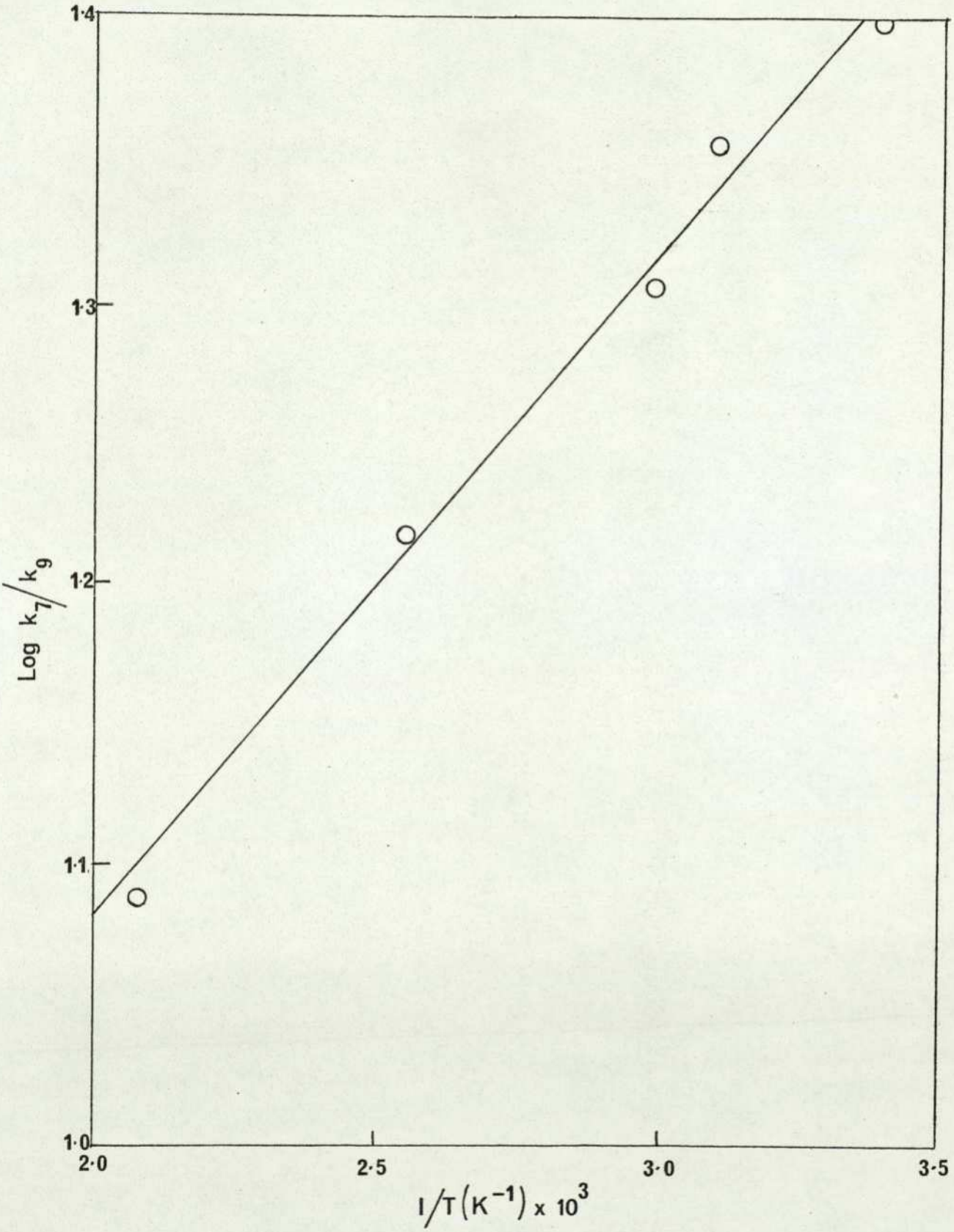


Figure 4.4

Graph of log k_3/k_9 against reciprocal temperature (Data from Table 4.4)

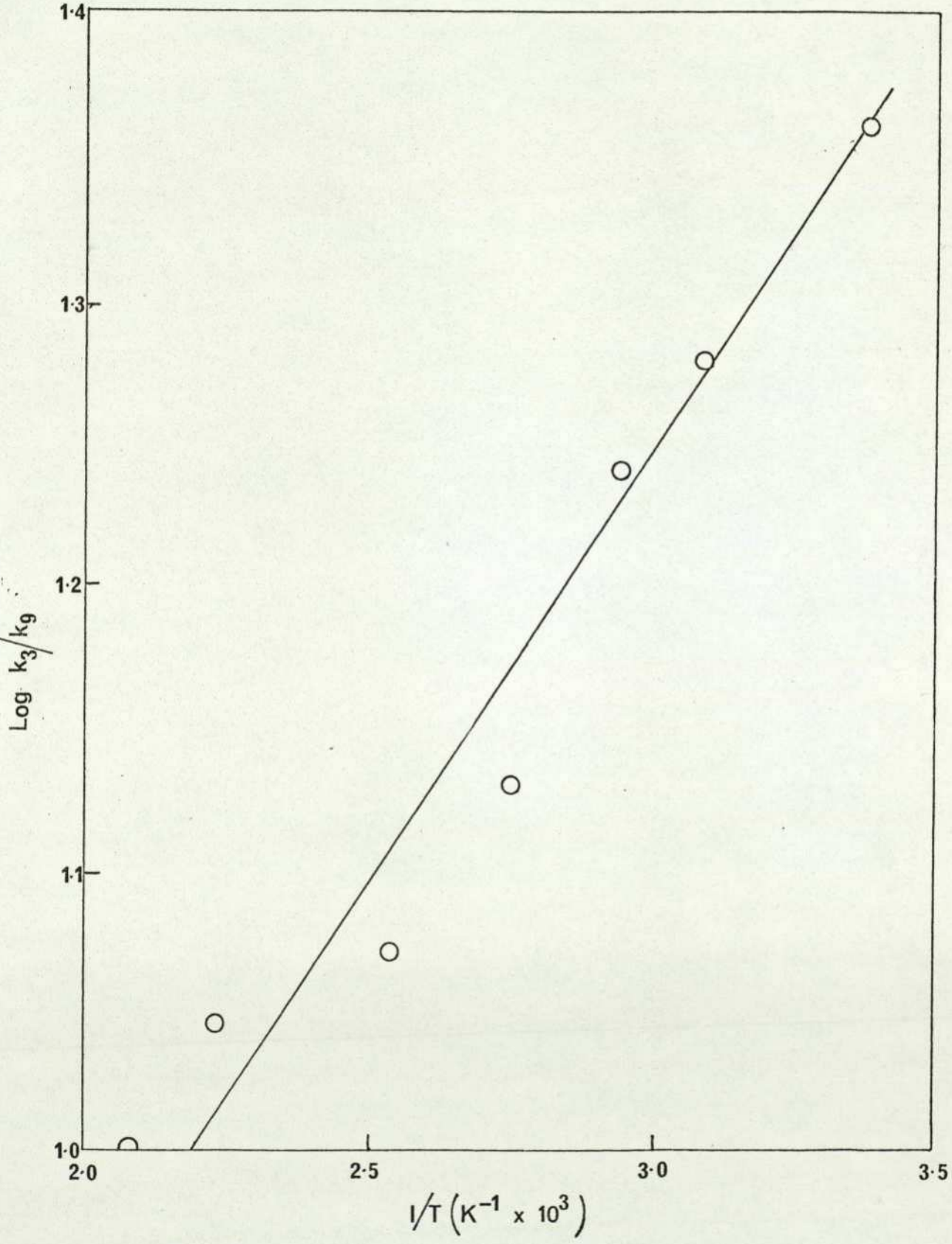


Table 4.4

Relative rates of reaction of the ethynyl radical with propyne at various temperatures.

Temperature (K)	k_7/k_9	k_5/k_9	k_8/k_9	k_3/k_9
298	25	5	9.9	23
323	22.6	2.2	12	16
343	20.1	5	10.4	14.2
363	-	-	11.5	13.5
393	16.4	6	13	11.8
448	-	-	14	11
483	12.2	5	10.6	10

Table 4.5

Activation energy differences and A-factor ratios using reaction (3) as a standard.

Reaction number (x)	$E_x - E_3$ kcal.mole^{-1}	A_3/A_x
5	1.0 ± 0.2	1.2 ± 0.5
7	ca. 0	0.92 ± 0.1
8	ca. 1.1 ± 0.3	0.34 ± 0.1
9	1.1 ± 0.3	3.35 ± 2

ethynyl radical may also add to the triple bond in propyne and produce a radical which will then undergo further reactions in the system:

$$C_2H + C_3H_4 \longrightarrow CH_3 - C = C(H) - C \equiv CH$$

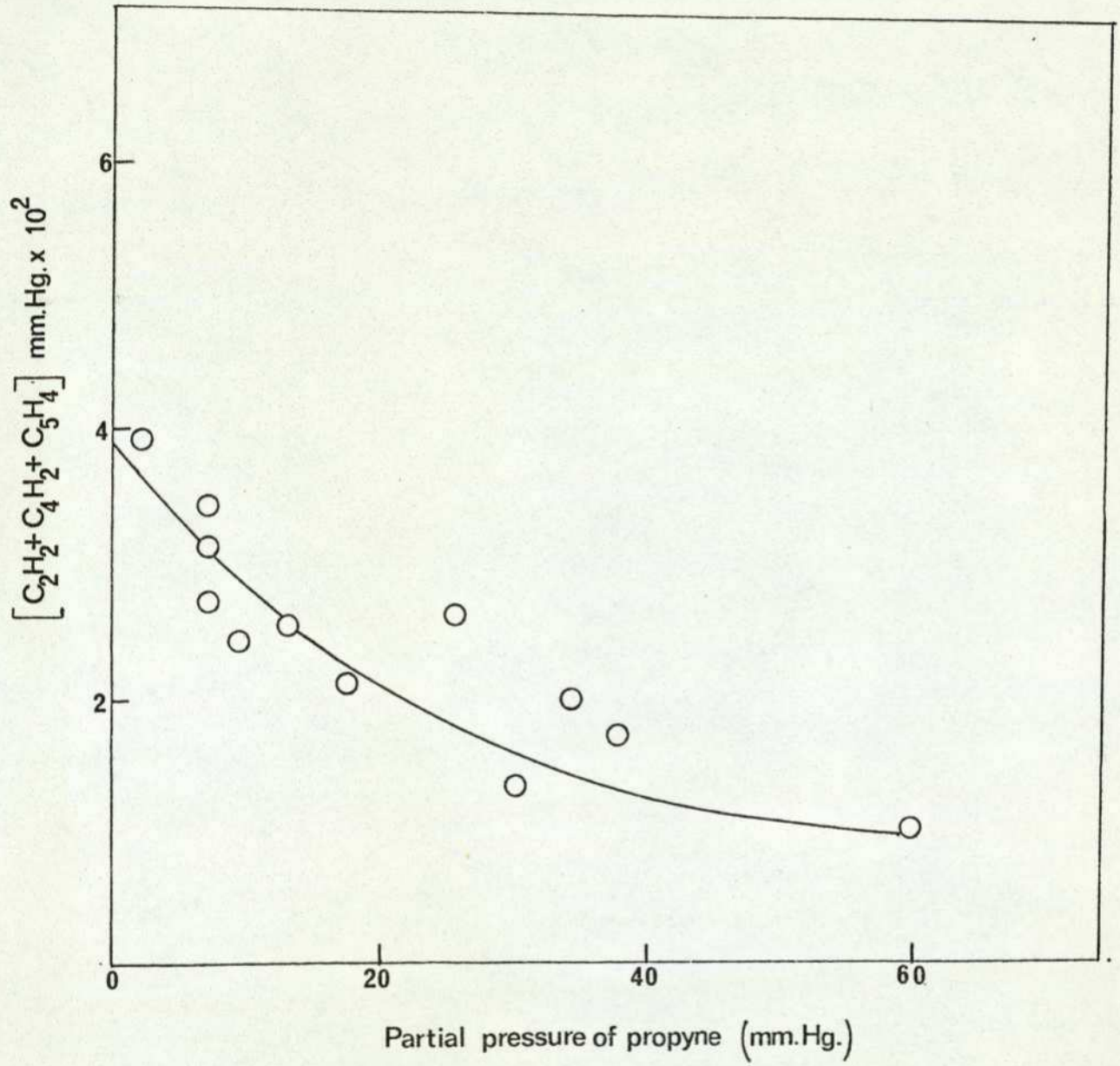
or

$$CH_3 - C(C \equiv CH) = CH \qquad (a)$$

Since the radical formed by this addition will probably undergo several different reactions, including further addition reactions, it is very difficult to determine the relative rate of reaction (a). One effect of this addition reaction will be to remove ethynyl radicals from reaction with monobromoethyne. If enough propyne is added then nearly all the ethynyl radicals will react with propyne by reactions (7), (8) and (9) or by the addition reaction. Thus if a graph is drawn of the concentration of propyne against the sum of the concentrations of the acetylene, butadiyne and penta-1,3-diyne, there should be a limit at which the concentrations of these products become independent of propyne concentration. A plot of this type is shown in Figure 4.5 and indicates that the limit may be about 1×10^{-2} mm.Hg. being reached after approximately 60 mm.Hg. of propyne has been added. With no propyne present the total yield of butadiyne and acetylene (from reactions (3) and (5)) is about 4×10^{-2} mm.Hg. If it is assumed that in the absence of propyne the majority of ethynyl radicals react to form acetylene and butadiyne, then the difference between the amount of these products produced at a fixed time without propyne and the total amount of penta-1,3-diyne, butadiyne and acetylene produced at the limit (Figure 4.5) is equal to the proportion of ethynyl radicals taking place in addition reactions yielding:

Figure 4.5

Graph of the sum of the concentrations of acetylene, butadiyne and penta-1,3-diyne against pressure of propyne added to a mixture of monobromoethyne (7 mm.Hg.), nitric oxide (7 mm.Hg.) and nitrogen (added to make total pressure 700 mm.Hg.)



$$\frac{k_a}{k_7 + k_8 + k_9} \simeq \frac{3}{1}$$

and $$\frac{k_a}{k_7} \simeq \frac{3k_7}{k_7} + \frac{3k_8}{k_7} + \frac{3k_9}{k_7}$$

$$\frac{k_a}{k_7} \simeq 3 + 3 \times 0.1 + 3 \times 0.05$$

$$\simeq 3.5$$

and since $$\frac{k_7}{k_3} \simeq 1$$

$$\frac{k_a}{k_3} \simeq 3.5$$

Obviously this estimate is subject to large errors, since the ethynyl radical probably undergoes a variety of reactions apart from those outlined above. However, it is probable that the estimated figure for k_a/k_3 represents the lower limit and hence

$$k_a/k_3 \geqslant 3.5$$

4.3.2 The reactions of the ethynyl radical with acetylene

The ethynyl radical reacts with acetylene by either abstracting or displacing a hydrogen atom:

$$C_2H + C_2H_2 \longrightarrow C_2H_2 + C_2H$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad (10)$$

If unlabelled acetylene is used, the abstraction reaction does not alter the system in any way and it has not therefore been numbered. Because a mixture of monobromoethyne and nitric oxide containing added acetylene would give insufficient data, propyne was also added to such mixtures, thus producing penta-1,3-diyne.

Under these conditions

$$\frac{[C_4H_2]}{[C_5H_4]} = \frac{k_3[C_2H][C_2HBr] + k_{10}[C_2H][C_2H_2] + k_8[C_2H][C_3H_4]}{k_9[C_3H_4][C_2H]}$$

If $[C_2H_2]/[C_2HBr] = r_1$

and $[C_4H_2]/[C_5H_4] = R_3$

$$R_3 = \frac{k_3 + k_{10}r_1 + k_8[C_3H_4]/[C_2HBr]}{k_9[C_3H_4]/[C_2HBr]}$$

If the concentration of propyne is kept equal to that of monobromoethyne and only the acetylene concentration is varied, then

$$R_3 = \frac{k_{10}r_1 + k_3 + k_8}{k_9}$$

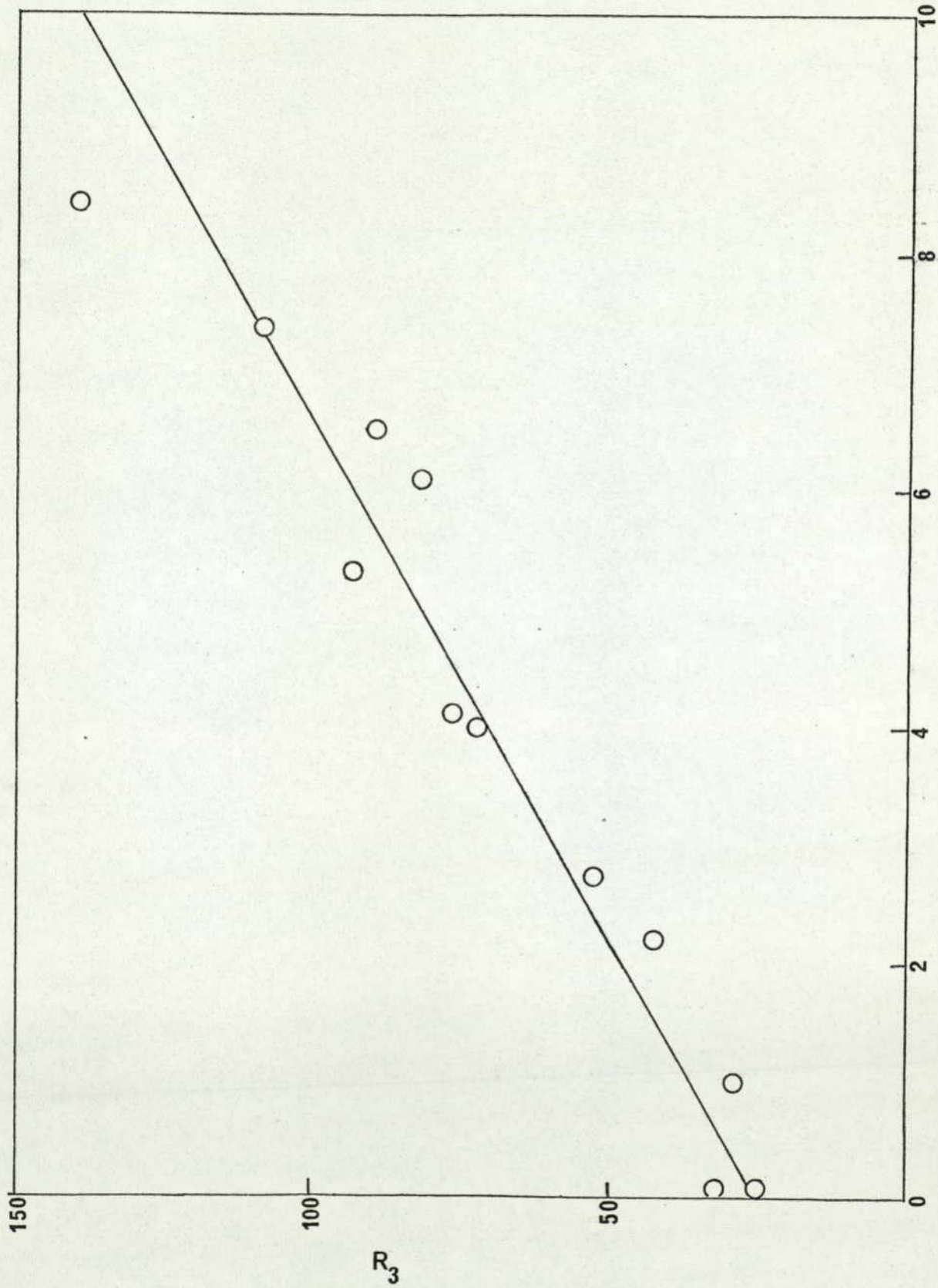
$$\text{or } R_3 = \frac{k_{10}}{k_9} r_1 + \frac{k_3 + k_8}{k_9}$$

A plot of R_3 against r_1 is shown in Figure 4.6. The resulting straight line has a slope which directly yields a value for k_{10}/k_9 of 12 ± 3. From previous data $k_3/k_9 = 23 \pm 3$ and $k_8/k_9 = 9.9 \pm 1$ giving $(k_3+k_8)/k_9 = 32.9 \pm 4$. The intercept in Figure 4.6, which should also correspond to $k_3 + k_8/k_9$ is 27 ± 4 and this shows reasonable self-consistency with the previous results. The results of acetylene addition can be seen to offer conclusive proof that displacement of alkyne C-H bonds do in fact take place, for only the acetylene concentration was altered during these experiments. If reaction (10) did not occur, then the ratio $[C_4H_2]/[C_5H_4]$ should not alter with increasing acetylene concentration. However, since this ratio does alter under these conditions, reaction (10) must occur.

Addition of acetylene $-d_2$ to monobromoethyne (Section 3.4.3) gave acetylene $-d_1$ and butadiyne $-d_1$ as products:

Figure 4.6

Graph of R_3 against r_1 where $R_3 = [C_4H_2]/[C_5H_4]$ and $r_1 = [C_2H_2]/[C_2HBr]$



$$C_2H + C_2D_2 \longrightarrow C_2HD + C_2D \quad (11)$$

$$C_2H + C_2D_2 \longrightarrow C_4HD + D \quad (12)$$

The ratios of $[C_4HD]/[C_2HD]$ and $[C_4H_2]/[C_4HD]$ were determined after various photolysis times (Table 3.5). There was found to be a large, apparently random, scatter in the results but the rate constant ratios k_{12}/k_{11} and k_3/k_{12} (Table 3.5) were obtained from the mean of the values: in this way values for k_{12}/k_{11} and k_3/k_{12} of 2.8 ± 2.5 and 1.5 ± 0.3 respectively were obtained. The rate of reaction (12) is comparable with that of reaction (10) and it was found that $k_{10}/k_9 = 12 \pm 3$ and $k_3/k_9 = 23 \pm 3$ whence $k_3/k_{10} = 2 \pm 0.7$ and $k_{10}/k_{12} = 1.3 \pm 0.6$. Thus the rates of reactions (10) and (12) have similar values and there appears to be little or no detectable isotope effect. Comparing the rate of the hydrogen abstraction reaction (5) with that of the deuterium abstraction reaction (11), it is found that from the values obtained for k_{12}/k_{11} and k_3/k_{12}, k_3/k_{11} can be calculated as 4.1 ± 2.8 whilst k_3/k_5 is 7 ± 1 whence $k_5/k_{11} = 0.6 \pm 0.4$. This indicates that reaction (11) is slightly faster than reaction (5). Reactions (11) and (5) are both probably thermoneutral since the bond being broken during abstraction is essentially the same as the bond being made and slight differences in rate may be due to subtle electronic effects rather than the simple thermochemical differences between reactants and products.

4.3.3 The reaction of the ethynyl radical with butadiyne

The ethynyl radical reacts with butadiyne to form acetylene and hexatriyne as primary products (Section 3.4.4, Figure 3.11). Acetylene is formed by reactions (5) and (13),

$$C_2H + C_2HBr \longrightarrow C_2H_2 + C_2Br \quad (5)$$

$$C_2H + C_4H_2 \longrightarrow C_2H_2 + C_4H \quad (13)$$

whilst hexatriyne is formed by the displacement reaction (14):

$$C_2H + C_2H_2 \longrightarrow C_6H_2 + H \qquad (14)$$

Considering reactions (5), (13) and (14)

$$\frac{[C_2H_2]}{[C_6H_2]} = \frac{k_5[C_2H][C_2HBr] + k_{13}[C_2H][C_4H_2]}{k_{14}[C_2H][C_4H_2]}$$

Putting $[C_2H_2]/[C_6H_2] = R_4$

and $[C_2HBr]/[C_4H_2] = r_2$

then

$$R_4 = \frac{k_5 r_2 + k_{13}}{k_{14}}$$

or $$R_4 = k_5/k_{14} \cdot r_2 + k_{13}/k_{14}$$

A plot of R_4 against r_2 was linear (Figure 4.7) with a slope of 0.57 ± 0.1 and an intercept of 1.05 ± 0.2. This leads directly to the ratios $k_{5/k_{14}} = 0.57 \pm 0.1$ and $k_{13/k_{14}} = 1.05 \pm 0.2$. From these data, the ratio $k_{5/k_{13}}$ may be calculated and has the value 0.54 ± 0.2 whilst $k_{3/k_{14}}$ is 4 ± 1.

4.3.4 Results without added nitric oxide

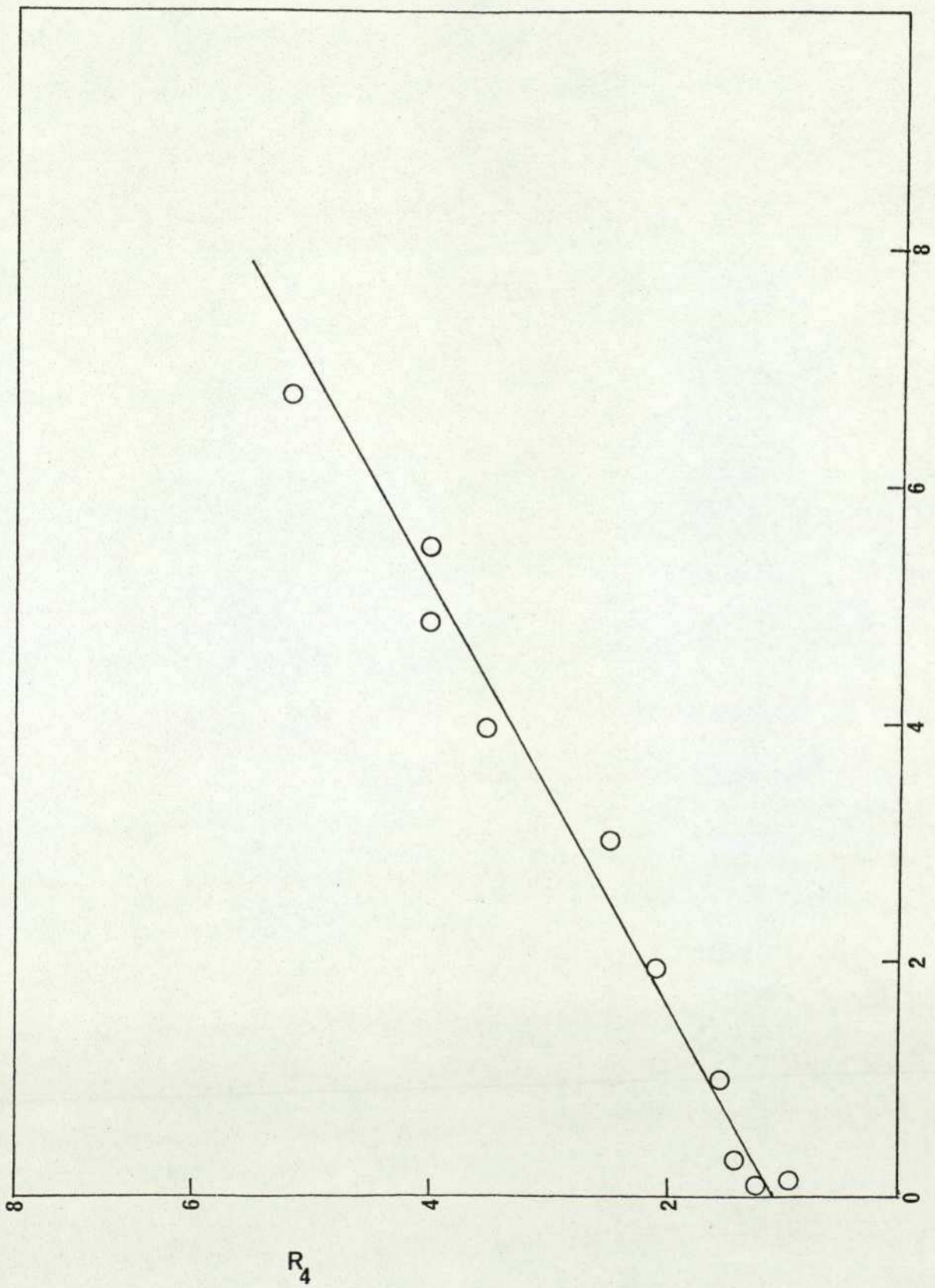
The results of experiments performed in the absence of nitric oxide appear in tables 3.6(a) and 3.6(b). Nitric oxide has little effect on the reaction of the ethynyl radical with either propyne or butadiyne. The yields of products seem to be almost unaffected by the addition of nitric oxide and, most important, the relative yields of products were found to be the same.

4.3.5 Comparison of the relative rates and activation energy differences of the reactions of the ethynyl radical with propyne, acetylene, acetylene -d_2 and butadiyne

The rates of the following hydrogen displacement reactions relative to that of reaction (3) can now be calculated:

Figure 4.7

Graph of R_4 against r_2, where $R_4 = [C_2H_2]/[C_6H_2]$ and $r_2 = [C_2HBr]/[C_4H_2]$



$$C_2H + C_3H_4 \longrightarrow C_5H_4 + H \qquad (9)$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad (10)$$

$$C_2H + C_2D_2 \longrightarrow C_4HD + D \qquad (12)$$

$$C_2H + C_4H_2 \longrightarrow C_6H_2 + H \qquad (14)$$

and the values are shown in table 4.6. Reaction (9) is appreciably slower than reactions (10), (12) and (14). One reason for the increased rate of these reactions compared with that of reaction (9) is that there are two hydrogen (or deuterium) atoms available for displacement in acetylene, acetylene-d_2 and butadiyne. If the relative rates of reaction per hydrogen atom displaced are calculated, the largest ratio is 7.5 ± 2 $(= \frac{k_{12}}{k_9})$, corresponding to an activation energy difference of about 1 kcal.mole^{-1} on the assumption that the A factors for reactions (9) and (12) are the same. The possibility that the activation energies of reactions (9) and (12) may differ by as much as 1 kcal.mole^{-1} is difficult to explain, especially as a C-H bond is weaker than a C-D bond. However, the activation energy difference for reactions(9) and (3) is 1.1 ± 0.3 kcal.mole^{-1}, and since the C-Br bond broken in reaction (3) has a dissociation energy at least 20 kcal.mole^{-1} less than the C-H bond broken in reaction (9) it becomes clear that bond dissociation energies have little influence on the magnitude of the various activation energies.

The value of the activation energy of reaction (3) has been estimated as approximately 2 kcal.mole^{-1} with an upper limit of 6 kcal.mole^{-1} (Table 4.2). Thus reaction (9) has an activation energy of about 3 kcal.mole^{-1} (with an upper limit of about 7 kcal.mole^{-1}) and reactions (10), (12) and (14) have activation energies between those of reactions (3) and (9). The value of A_3/A_9 has been found to be $3.3(5) \pm 2$ and thus

Table 4.6

Rates of the hydrogen and deuterium displacement reactions of the ethynyl radical relative to reaction (3):

$$C_2H + C_2HBr \longrightarrow C_4H_2 + Br \qquad (3)$$

Reaction	Relative rate ($k_3 = 1$)
9	0.044 ± 0.005
10	0.5 ± 0.14
12	0.67 ± 0.15
14	$0.25 \pm .1$

reactions (3), (9), (10), (12) and (14) all have A-factors of the same order of magnitude which, from the earlier A-factor estimation for (3) is 10^8 l.mole sec^{-1}. There appears to be only one other estimation of the Arrhenius parameters for a comparable hydrogen displacement reaction and this is for the reaction between the vinyl radical and ethylene to form buta-1,3-diene[90]:

$$C_2H_3 + C_2H_4 \longrightarrow C_4H_6 + H \qquad (15)$$

From thermochemical considerations E_{15} was estimated to be 7.3 kcal.$mole^{-1}$ and A_{15} to be $10^{8.7}$ l.$mole^{-1}sec^{-1}$. The A factors reported here for the displacement of hydrogen from an alkyne show reasonable agreement with the A factor evaluated for the above reaction. E_{15} is greater than the estimated values for (9), (10), (12) and (14) indicating that the vinyl radical is less reactive than the ethynyl radical.

Again if reaction (3) is taken as an internal standard, the rates of the following hydrogen and deuterium abstraction reactions can be compared:

$$C_2H + C_2HBr \longrightarrow C_2H_2 + C_2Br \qquad (5)$$

$$C_2H + CH_4 \longrightarrow C_2H_2 + CH_3$$
$$C_2H + C_4H_{12} \longrightarrow C_2H_2 + C_4H_{11} \qquad (6)$$

$$C_2H + C_3H_4 \longrightarrow C_2H_2 + C_3H_3 \qquad (7)$$

$$C_2H + C_2D_2 \longrightarrow C_2HD + C_2D \qquad (11)$$

$$C_2H + C_4H_2 \longrightarrow C_2H_2 + C_4H \qquad (13)$$

Table 4.7 lists the rates of reactions (5), (6), (7), (11) and (13) relative to the rate of reaction (3), together with the calculated activation energy differences. The abstraction of acetylenic hydrogen (or deuterium) in reactions (5), (11) and (13) has a similar value if an allowance is made for the two hydrogen atoms available for abstraction in reactions (11) and (13) as opposed to the one hydrogen atom available in

Table 4.7

Rates of ethynyl radical hydrogen abstraction reactions relative to rate of reaction (3) and their activation energy differences.

Reaction number		Rate relative to reaction (3)	$E_x - E_3$
5		0.14 ± 0.02	1.0 ± 0.2
6	methane	0.015(5)	3.0 ± 0.4
	2,2-dimethyl-propane	0.94	0
7		1.0 ± 0.1	0
11		0.36 ± 0.3	1.0
13		0.26 ± 0.1	1.0

reaction (5). It is therefore reasonable to assume that reactions (5), (11) and (13) have similar activation energies. This shows that for all reactions so far studied, the abstraction of an acetylenic hydrogen atom is as favourable as its displacement. The abstractions of hydrogen from propyne and 2,2-dimethylpropane have similar activation energies; this is presumably because the ethynyl radical preferentially attacks the three primary "methyl group" hydrogens in propyne which will have similar bond-dissociation energies to the primary hydrogens on 2,2-dimethylpropane. The abstraction of hydrogen from methane requires the highest activation energy of the abstraction reactions studied. This is surprising since the methane C-H bond is weaker than the acetylenic C-H bond and hence reactions (5), (11) and (13) might be expected to have higher activation energies than reaction (6) for methane.

4.4 Conclusions

In the case of alkynes the ethynyl radical has been shown to react by hydrogen abstraction, hydrogen and alkyl radical displacement and by addition reactions. These reactions have relatively low activation energies and similar A factors. The most significant result in the present work has been to show that the ethynyl radical can react with acetylene to form butadiyne:

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad (10)$$

and with butadiyne to form hexatriyne:

$$C_2H + C_4H_2 \longrightarrow C_6H_2 + H \qquad (14)$$

The activation energies of such reactions are about 3 kcal.mole^{-1} and the A-factors are of the order of 10^8 l.mole^{-1}sec^{-1}. It seems likely that these reactions are concerted, i.e. they do not proceed via a stabilised adduct:

$$C_2H + C_2H_2 \longrightarrow C_4H_3$$

which may then undergo further decomposition:

$$C_4H_3 \longrightarrow C_4H_2 + H$$

The latter decomposition reaction may have an activation energy of between 40 and 60 kcal.mole^{-1} [125,87] and presumably has an A-factor of the same order of magnitude as unimolecular decompositions, i.e. about 10^{14} sec^{-1}. Since the C_4H_3 adduct can probably add further to the triple bond in acetylene with relative ease, one would expect very little butadiyne to be formed at room temperature in the present system. As the rate determining step is the decomposition of the C_4H_3 radical, the activation energy and A factors measured should have far greater values than those actually observed. Further, it would be expected that such decompositions would depend very much on the strength of the bond being broken and thus reactions involving the displacement of bromine atoms and methyl radicals:

$$C_2H + C_2HBr \longrightarrow C_4H_2 + Br \qquad (3)$$

$$C_2H + CH_3C_2H \longrightarrow C_4H_2 + CH_3 \qquad (8)$$

should proceed much faster than those involving hydrogen atom displacement. In fact, despite bond strength differences of at least 30 kcal.mole^{-1}, reactions (8), (10) and (14) have nearly the same activation energies whilst the activation energy of reaction (3) is only about 1 kcal. less.

4.4.1 The role of the ethynyl radical in the pyrolysis of acetylene

The kinetics and products of the pyrolysis of acetylene have been described in Section 1.5. Briefly the thermal decomposition of acetylene has a second order rate constant of ($10^{10.8-41.6/\theta}$) l.mole^{-1}sec^{-1}. In the high temperature region (above 2000K) the sole primary product is butadiyne, whilst at lower temperatures (below 1200K) butenyne is initially the most important product. From the present work butadiyne can be

produced by the reaction of an ethynyl radical with acetylene:

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H$$

At temperatures associated with the thermal decomposition of acetylene, the hydrogen atoms thus produced could then abstract hydrogen from acetylene in a chain-propagating step:

$$H + C_2H_2 = H_2 + C_2H$$

If initiation proceeds via the bimolecular disproportionation reaction having the lowest activation energy[88,94], then butenynyl radicals will be produced:

$$2C_2H_2 \longrightarrow C_4H_3 + H$$

Thus a simple chain mechanism which will account for the production of butadiyne above 2000K can be written:

$$2C_2H_2 \longrightarrow C_4H_3 + H \qquad (1)$$

$$C_4H_3 \longrightarrow C_4H_2 + H \qquad (2)$$

$$H + C_2H_2 \longrightarrow C_2H + H_2 \qquad (3)$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad (4)$$

$$2C_2H \longrightarrow C_4H_2 \qquad (5)$$

(The numbering of these reactions differs from that in other sections.)

A steady-state treatment for reactions (1) - (5) gives:

$$-d[C_2H_2]/dt = [4k_1 + 2k_4(\frac{k_1}{k_5})^{\frac{1}{2}}][C_2H_2]^2$$

k_1 has been estimated as $10^{11-44.3/\theta}$ l.mole^{-1}sec^{-1} [81]. k_3 has been estimated as $10^{11.3-19/\theta}$ whilst the present work yields $k_4 = 10^{3-8/\theta}$. k_5 can be estimated as 10^{10} l.mole^{-1}sec^{-1} (Section 1.5). The rate of decomposition of acetylene can now be expressed as

$$\frac{-d[C_2H_2]}{dt} = [4 \times 10^{11-44.3/\theta} + 2 \times 10^{8-3/\theta}(\frac{10^{11-44.3/\theta}}{10^{10}})^{\frac{1}{2}}][C_2H_2]^2$$

$$= [4 \times 10^{11-44.3/\theta} + 2 \times 10^{8.5-25.2/\theta}] [C_2H_2]^2$$

The change of the rate constant for decomposition with reciprocal temperature is shown by curve 'A' in Figure 4.8. This also includes some of the rate constants determined by other workers at other temperatures. Curve 'A' agrees reasonably well with the results of experiments down to temperatures of about 1900K ($\frac{1}{T} = 5.3 \times 10^{-4}$). However, below this temperature the rate of reaction predicted by this simple chain mechanism becomes too great by one or two orders of magnitude. This means that other reactions are beginning to compete for the radicals available, thus shortening the chain made up of reactions (3) and (4). Hydrogen atoms will add to acetylene

$$H + C_2H_2 \longrightarrow C_2H_3$$

and butenynyl radicals may abstract hydrogen from acetylene to produce butenyne:

$$C_4H_3 + C_2H_2 \longrightarrow C_4H_4 + C_2H$$

A more complex reaction scheme including chain and non-chain reactions which produce butadiyne, butenyne and also buta-1,3-diene (which can be an important product[158]) can be written:

$$2C_2H_2 \longrightarrow C_4H_3 + H \qquad (1)$$

$$C_4H_3 \longrightarrow C_4H_2 + H \qquad (2)$$

$$H + C_2H_2 \longrightarrow C_2H + H_2 \qquad (3)$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad (4)$$

$$C_4H_3 + C_2H_2 \longrightarrow C_4H_4 + C_2H \qquad (6)$$

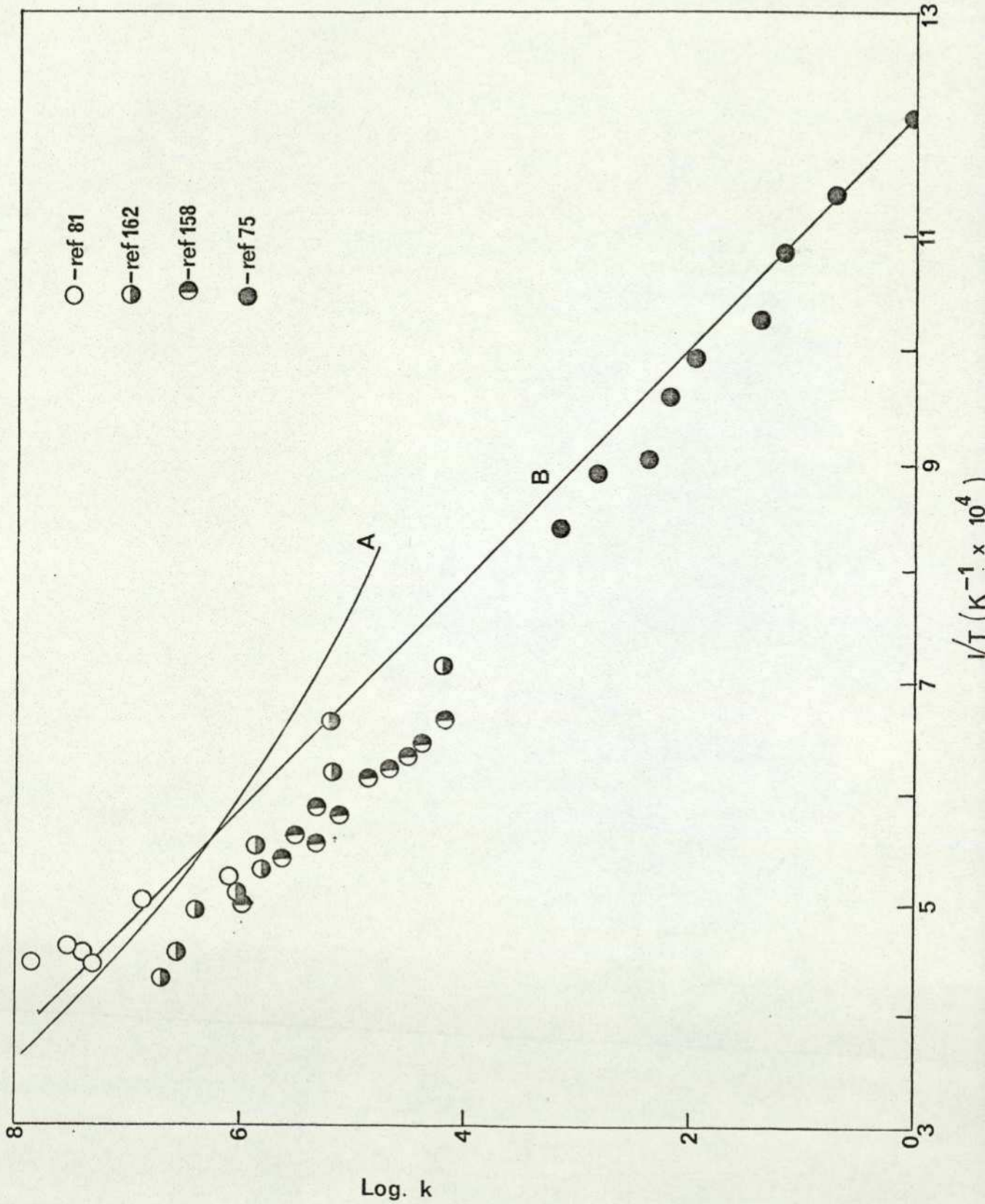
$$H + C_2H_2 \longrightarrow C_2H_3 \qquad (7)$$

$$2C_2H_3 \longrightarrow C_4H_6 \qquad (8)$$

A steady-state treatment of reactions (1) to (4) and (6) to (8) yields:

Figure 4.8

Graph of the rate constant for the pyrolytic decomposition of acetylene against reciprocal temperature: (i) as predicted by two mechanisms (see text) and (ii) from the data of various workers.



$$\frac{-d[C_2H_2]}{dt} = k_1\left(4 + \frac{4k_3}{k_7} + \frac{2k_6[C_2H_2]}{k_2+k_6[C_2H_2]}\right)[C_2H_2]^2$$

This expression shows that the rate of decomposition of acetylene involves the competition of two pairs of reactions: reactions (3) and (7) represented by the expression (k_{3/k_7}) and k_2 and k_6 represented by the expression $(2k_6[C_2H_2]/k_2 + k_6[C_2H_2]$. (3) and (7) are the two possible reactions of hydrogen with acetylene. The hydrogen abstraction reaction (reaction (3)) has been estimated to have a rate constant of $10^{11.3-19/\theta}$ 122

The addition of hydrogen to ethylene:

$$H + C_2H_4 \longrightarrow C_2H_5$$

has a rate constant which has been measured as $10^{11.1-9.7/\theta}$ $l.mole^{-1}sec^{-1}$ 148 and it seems reasonable to suppose that hydrogen addition to acetylene might have similar Arrhenius parameters. However Benson and Haugen[90] have estimated that the activation energy for the latter reaction is 15 $kcal.mole^{-1}$ whilst the A factor is $10^{7.9}$ $l^2.mole^{-2}sec^{-1}$. (A third-body requirement is included in this treatment but has been omitted from the present mechanism.) The rate constant for the addition of hydrogen atoms to acetylene has been measured as 2.4×10^7 $l.mole^{-1}sec^{-1}$ 152 whilst the expression of Benson and Haugen[90] would predict a rate constant of about 10^{-2} $l^2mole^{-2}sec^{-1}$. The value $10^{10-6.5/\theta}$ $l.mole^{-1}sec^{-1}$ seems a reasonable compromise between the various possible values and this would give $k_{3/k_7} = 10^{11.3-19/\theta}/10^{10-6.5/\theta}$ or $10^{1.3-12.5/\theta}$. Using this value then, at 2000K, $k_{3/k_7} \simeq 1$ indicating that at this temperature as many hydrogen atoms abstract hydrogen from acetylene as add to the triple bond. Below this temperature $k_{3/k_7} < 1$ and below 1500K the term $4k_{3/k_7}$ can be ignored in the general expression for the decomposition of acetylene. The competition between reactions (2) and (6) described in the expression $(2k_6[C_2H_2]/k_2 + k_6[C_2H_2])$ must now be considered. Reaction

(2) probably has an activation energy of 60 kcal.mole^{-1} [125] and possibly an A-factor similar to that for a unimolecular decomposition i.e. about 10^{14} sec^{-1}. k_6 may have an A factor of the same magnitude as many hydrogen abstraction reactions (10^8 l.mole^{-1}sec^{-1})[146] and an activation energy of at least 10 kcal.mole^{-1} (the approximate difference between the strengths of an olefinic C-H bond and an acetylenic C-H bond). If the concentration of acetylene is about 10^{-3} mole.l^{-1} then

$$2k_6[C_2H_2]/k_2 + k_6[C_2H_2] = \frac{10^{8.3-10/\theta}.10^{-3}}{10^{14-60/\theta} + 10^{8.0-10/\theta}.\ 10^{-3}}$$

$$= \frac{10^{5.3-10/\theta}}{10^{14-60/\theta} + 10^{5.0-10/\theta}}$$

Above 1400K this expression is small in comparison with $4 + 4(k_3/k_7)$ and hence is unimportant in the overall expression. Below 1400K the value tends to unity. If the expressions contained in the relationship derived for the decomposition of acetylene are now combined, then the composite rate constant is approximately $10^{11.7-44.3/\theta}$ in the range 2500 to 1000K and this is represented by curve 'B' in Figure 4.8. This curve is in agreement with observed data to better than an order of magnitude. It also predicts a change in the relative concentrations of butadiyne and butenyne. Thus for small conversions of acetylene:

$$\frac{[C_4H_2]}{[C_4H_4]} = \frac{(1+2k_3/k_7)(k_2 + k_6[C_2H_2])}{k_6[C_2H_2]}$$

If the value of $[C_4H_2]/[C_4H_4]$ is plotted against temperature for a concentration of acetylene of 10^{-3} mole.l^{-1}, then the curve shown in Figure 4.9 results. This shows that there is a rapid change in the relative concentrations of butadiyne and butenyne in the temperature range 1200 to 1400K with the concentration of butadiyne becoming equal to that of butenyne at 1200K. However, experimental evidence suggests that there is

a complete change over to butenyne at temperatures below 1300K and this reveals an inadequacy in the present mechanism. It seems possible that butenyne may also be produced from a reaction between the vinyl radical and acetylene:

$$C_2H_3 + C_2H_2 \longrightarrow C_4H_4 + H$$

and, of course, there is also the possibility that the triplet state of acetylene may be involved in its decomposition. Nevertheless, the mechanism derived here shows that the rate constant for acetylene pyrolysis can be predicted to reasonable accuracy using the initiation reaction:

$$2C_2H_2 \longrightarrow C_4H_3 + H$$

The major initial products can be accounted for in the subsequent reaction scheme. A more detailed discussion would consider many other reactions including several quadratic terminations and a more detailed examination of the rate constants with allowances being made for the effect of temperature on the A factors.

4.4.2 The role of the ethynyl radical in carbon formation

Homann[8] has suggested that polyalkynes are key intermediates in the production of carbon in acetylene flames and the present work has shown that the ethynyl radical can add to alkynes, displacing hydrogen and producing the next higher polyalkyne:

$$C_2H + C_nH_2 \longrightarrow C_{n+2}H_2 + H$$

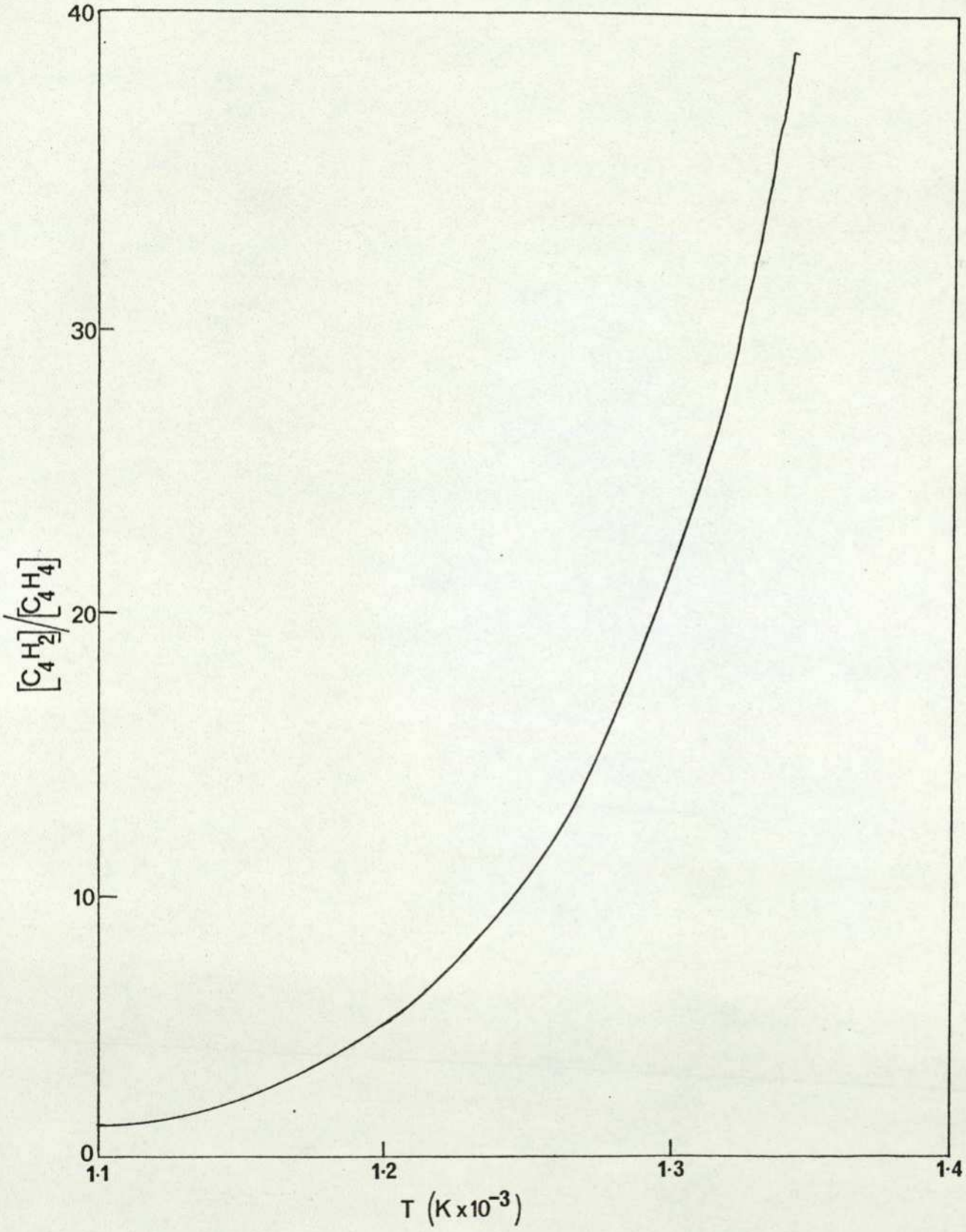
At room temperature this reaction is somewhat slower than the simple addition reaction (section 4.3.1):

$$C_2H + C_nH_2 \longrightarrow C_{n+2}H_3$$

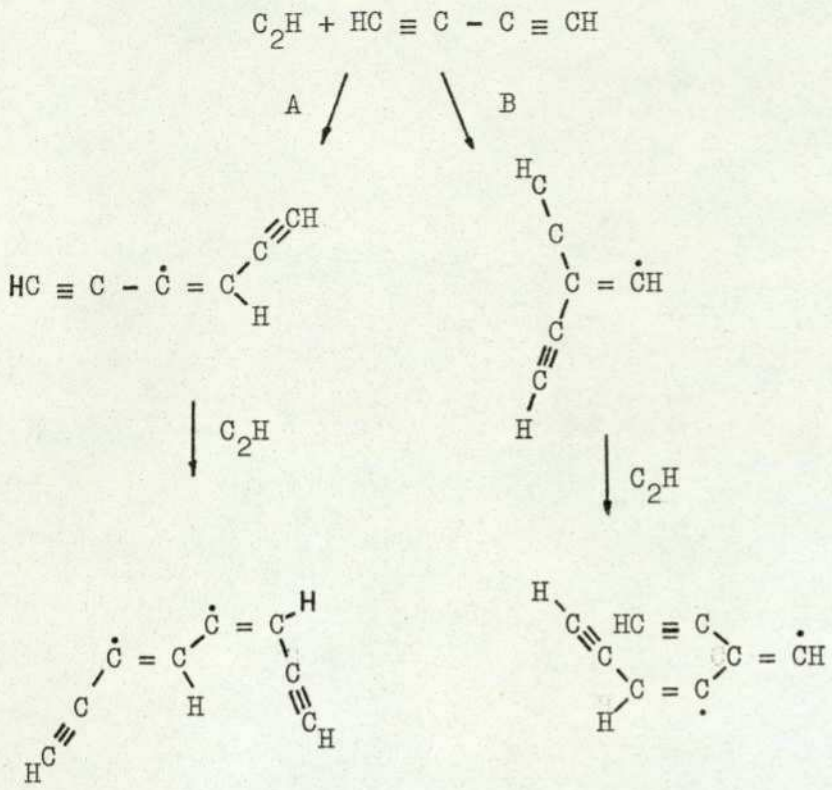
However, as the temperature is increased, the displacement reaction will presumably, increase relative to the addition reaction and fom a rapid route to the higher alkynes. It has also been shown that the ethynyl

Figure 4.9

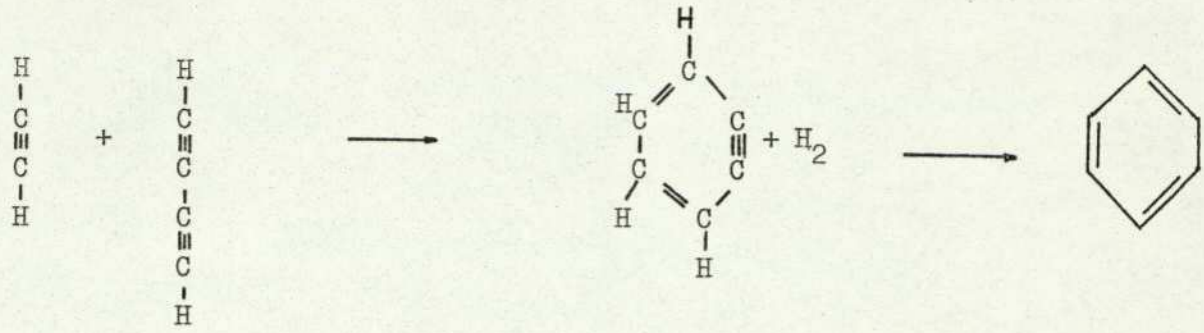
Variation of the predicted ratio of $[C_4H_2]/[C_4H_4]$ against temperature



radical will not only displace hydrogen but also alkyl radicals (the particular example here was the displacement of the methyl group in propyne) thus increasing the carbon content of any substituted unsaturated compound. There seems to be the further possibility that the ethynyl radical may displace other unsaturated radicals such as the vinyl radical, although this has not yet been investigated. The present work indicates that, at the temperatures associated with carbon formation from acetylene (1000K and above), both displacement and addition reactions will have rate constants of about 10^8 $l.mole^{-1}sec^{-1}$. Thus evidence is provided that polyalkynes are active intermediates and not stable byproducts in high temperature carbon-forming systems. Hence carbon formation may proceed first by the build up of polyalkynes which act as highly reactive nuclei for the addition of other radicals. This produces substituted polyalkynes and the saturated or alkylenic substituents either undergo dehydrogenation or are displaced by a highly unsaturated radical such as the ethynyl radical. This leads to an increase in the relative carbon content of the nucleus. It seems possible that, due to the rigidity of the polyalkynes and because addition of radicals inevitably leads to some reduction in the conjugation in an unsaturated molecule, the resulting nuclei will be highly branched but will be unlikely to undergo ring closure to form polyaromatics. Taking the simplest example of the successive addition of ethynyl radicals to butadiyne:



None of the above structures readily lends itself to aromatic-ring closure and although the structures remain reactive they will probably grow mainly by addition, displacement and combination reactions. These intermediates correspond with the carbon precursors of molecular weight 250-550 found by Homann and Wagner[7]. They are not polycyclic aromatic compounds and their concentration peak runs parallel with those of 'young' carbon particles (see section 1.3.1). Homann and Wagner also indicate that polycyclic aromatic compounds are formed at the same time as these precursors but are not subsequently consumed in the region of carbon formation. This might mean that the growth of p.c.a.h. occurs by a separate, largely non-radical process, possibly involving Diels Alder condensation:



4.4.3 Suggestions for future work

Since the ethynyl radical may be an important intermediate in the oxidation of acetylene, it would be useful to determine its reactions with oxygen. However, bromoethyne is unstable towards oxygen and a new source of ethynyl radicals will have to be found. One source might be monoiodoethyne photolysed at the appropriate wavelength. This compound combines relative stability with ease of preparation[159].

Section 4.5.1 suggests that the decomposition of acetylene may involve the reaction of hydrogen atoms and of vinyl and butenynyl as well as ethynyl radicals. Thus an investigation of the reactions of these species with alkynes is of importance. Vinyl radicals have been generated by the mercury-photosensitized decomposition of monochloroethylene[160]. A more convenient source might be for the addition of hydrogen atom to acetylene in an excess of inert gas[151,152]. Similarly butenynyl might be generated by the addition of ethynyl radicals to acetylene (present in excess):

$$C_2H + C_2H_2 \longrightarrow C_4H_3$$

If methane-d_4 was added to this reaction mixture, then the rates of reactions of the butenynyl radical relative to the reaction

$$C_4H_3 + CD_4 \longrightarrow C_4H_3D + CD_3$$

could be measured. It also appears that the reactions of the hydrogen atom with acetylene have not been studied quantitatively above room

temperature and thus a study of this kind would give information as to the possible competition between the two reactions

$$H + C_2H_2 \longrightarrow H_2 + C_2H$$

$$H + C_2H_2 \longrightarrow C_2H_3$$

The reverse of the former reaction (i.e. the reaction of the ethynyl radical with hydrogen) might also be studied.

The reactions of the triplet state of acetylene may also be important but it seems difficult to identify a source of triplet acetylene which is free from possible free mono-radical reactions. Burton and Hunziker[86] generated triplet acetylene by the mercury photosensitized decomposition of acetylene and found other products were either non condensables or materials without substantial vapour pressures.

If the decomposition of acetylene occurs by a free radical mechanism even at relatively low temperatures, then it may be possible to identify the radicals involved by a radical-trapping technique using CD_4. Since methane does not begin to decompose thermally until about 900°C, its addition to a decomposing mixture of acetylene below this temperature should enable the deuterated derivatives of any free radicals present to be identified. Thus acetylene-d_1 would be produced from the ethynyl radical:

$$C_2H + CD_4 \longrightarrow C_2HD + CD_3$$

Suggestions about future work on carbon formation are more difficult. However, it appears almost certain that carbon particles are built up by a series of radical addition reactions to triple bonds. Thus the rate of addition of both radicals and atoms to triple bonds may form an important area of research.

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