A THESIS

entitled

THE PYROLYSIS OF ACETYLENE AND RELATED COMPOUNDS

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ABSTRACT

This thesis describes some work on the thermal decomposition of acetylene and vinylacetylene. The Introduction surveys the earlier work on the pyrolysis of these and related compounds and describes also some of the important properties of carbons formed in both pyrolytic systems and flames. Special attention is paid to the ways in which the properties of pyrolytic carbons depend on the conditions under which carbon formation occurs, and the various mechanisms by which carbon may be formed are discussed.

The Experimental Section describes both the static system used for the study of the pyrolysis of acetylene and vinylacetylene, and also the gas chromatographic, electron diffraction and radio-assay techniques employed for the analysis of the reaction products.

In the Results Section data are presented on the reactions of pure vinylacetylene and of vinylacetylene/acetylene mixtures. At sub-atmospheric pressures, and temperatures below about 500°C, the pyrolysis of vinylacetylene follows second-order kinetics and results mainly in the formation of polymers, the overall activation energy of the reaction being 28 kcal. $mole.^{-1}$. At higher temperatures, however, the pyrolysis is complex and results in the formation of large amounts of acetylene, ethylene, hydrogen, methane and soot. Only traces of diacetylene and methylacetylene can be detected among the products. Studies of the pyrolysis of mixtures of vinylacetylene with ^{14}C-acetylene show that vinylacetylene is not an intermediate in the

formation of surface carbon from acetylene. The Results Section presents data also on the variation with temperature of the properties of the carbonaceous deposits formed in these reactions. The steady increase with temperature of the atomic carbon:hydrogen ratio contrasts with the more complex dependence of crystallite size on temperature.

In the Discussion Section these results are related to previous data, and a critical analysis of the possible reaction steps which may be involved leads to a postulated mechanism which accounts for the principal features of the pyrolysis of both compounds. The variations with temperature of formation of the dimensions of the carbon crystallites are accounted for in terms of the relative rates of carbon deposition and ordering, but it is shown that simple quantitative relationships between the crystallite diameter and the atomic carbon: hydrogen ratio are unlikely to be valid except under very restricted conditions. The importance of these results in relation to the overall mechanism of carbon formation is also discussed and it is concluded that vinylacetylene is not an important intermediate in the formation from acetylene of either diacetylene, methylacetylene or carbon. Finally, suggestions are made for possible lines of future work.

CONTENTS

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1. INTRODUCTION

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1.1 General

At high temperatures all organic compounds are thermodynamically unstable and their decomposition often results in the formation of carbon, a phenomenon which was first observed by Berthelot over 100 years ago [1]. Berthelot observed that, at ca. 400°C, acetylene decomposed slowly to form a tarry residue and a little free carbon. In a porcelain tube at bright-red heat the acetylene decomposed rapidly to give mainly carbon and hydrogen. The formation of carbon is not, however, confined to gaseous pyrolytic systems. It occurs also in the solid and liquid phases (as in the charring of sugars and of aromatic hydrocarbons such as anthracene), and it can take place in both premixed and diffusion flames. Coal is the result of similar processes occurring in past geological ages.

Today, the decomposition of organic compounds is the basis of the industrial manufacture of many different types of carbon, each having specific properties and uses. Compact pyrolytic carbons are deposited at high temperatures on insulating substrates for use as resistors [2], and petroleum cokes are widely used in the production of "graphite" rods for use in nuclear reactors [3]. Carbons formed during the combustion of gaseous and liquid hydrocarbons are used extensively by the rubber industry, for the manufacture of printing inks, and, more recently, for the manufacture of lubricants containing colloidal graphite.

On the other hand, carbon formation is sometimes an inconvenience. The formation of carbonaceous deposits in internal combustion engines results in decreased efficiency and requires the use of more costly fuels having higher octane numbers [4]. It also adds significantly to the degree of air pollution in large cities and can be responsible for the poisoning of certain catalysts [5].

Carbon formation has, therefore, assumed widespread industrial and theoretical importance and in recent years there has been considerable interest in the mechanism of the process. This Section summarises the present state of knowledge concerning carbon formation and shows in particular how studies of the pyrolysis of vinylacetylene can lead to an improved understanding of the mechanism of the reactions concerned.

1.2 The structure of synthetic carbons

1.2.1 Types of synthetic carbons

Several types of carbon can be obtained from the thermal decomposition of organic compounds. The distinctions between them depend principally on whether the carbon is formed from a solid, liquid or gas, and whether, in the case of gases, the carbon is formed in the gas phase or as a result of an essentially heterogeneous process on a surface. Those carbons formed by the charring or 'coking' of solid or liquid compounds are massive products of low density and high porosity, and usually there is a marked tendency for such carbons to retain the morphology of the initial compound. The carbons formed by homogeneous reactions during the combustion or pyrolysis of gases are usually referred to as soots or carbon blacks. These are more or less finely powdered materials and, like chars and cokes, they have a low density and high porosity. On the other hand, the carbon deposits formed from gases by heterogeneous reactions are compact, grey, lustrous materials and are comparatively dense and non-porous.

There is also a group of synthetic carbons of industrial importance which are formed during the combustion of liquid droplets. As might be expected, these carbons, sometimes referred to as lamp blacks, have properties intermediate between the chars formed in the liquid phase and the carbon blacks formed from gases. Their formation falls outside the scope of the present work, however, and they will not therefore be considered further. Similarly, the formation of carbons by the charring of solids and liquids will not be considered in detail.

1.2.2 The structure of carbons formed from gases

Unlike near-ideal graphite, synthetic carbons have grossly defective structures and in some cases, their structure is so imperfect that graphite is not in fact a particularly useful model for describing them. X-ray powder photographs of these carbons show, with varying degrees of distinctness, only diffuse bands corresponding to the (00ℓ) reflections and the two-dimensional (hk) bands in graphite [6]. White and Germer [7], and Biscoe and Warren [8] found that synthetic carbons consist of small crystallites, about 20 to 50 Å in diameter, embedded in a mass of amorphous material. In each crystallite the carbon atoms are hexagonally arranged in planes as they are in graphite, but successive parallel atomic layers (of which there are only a few) are displaced so that no other regularities are apparent. Franklin termed this type of disorder "turbostratic"[9].

Carbon formed in the gas phase, either by pyrolysis or in premixed or diffusion flames is composed of crystallites aggregated into approximately spherical particles which have diameters ranging from 100 to 5,000 Å[10]. The particles cling together in crooked chains and under the electron microscope they resemble beads on a necklace. The crystallites appear to be evenly embedded in the mass of amorphous material with their basal planes oriented approximately parallel to the surface of the particles near the surface, but more or less randomly at the centre[11,12].

Surface carbons are formed mainly in pyrolytic systems and in contrast to gas-phase carbons, they display no particulate structure. The crystallites are, however, larger, and have smaller interlayer spacings than those of gas-phase carbons[13,14]. They are also denser and less porous than gas-phase deposits and it would appear that there is relatively little amorphous carbon between the individual crystallites which are all oriented more or less parallel to the substrate on which they are formed; they display, in other words, a strong preferred orientation.

Carbonaceous deposits are sometimes formed on surfaces present in combustion systems, but it is not always clear whether the carbon adhering to the surface is a direct result of reactions taking place thereon. Often the deposits formed in internal combustion engines and on surfaces placed in flames are found to consist of dense agglomerates of spherical particles [4,15], and as such it would seem that they are best regarded as gas-phase deposits resulting simply from the impingement of a sooting flame onto a relatively cool surface. Bonne, Homann & Wagner [15] did find, however, that the carbon which was deposited on a quartz thread at the end of the oxidation zone of a premixed acetylene-oxygen flame was a typical surface deposit, but further downstream the deposit changed to a typical gas-phase carbon.

1.3 The properties and extent of formation of synthetic carbons

Each carbon crystallite contains about 10^3 atoms, and in the case of gas-phase carbons there are approximately 10^4 crystallites per particle. Thus the fundamental problem in carbon formation is the elucidation of the mechanism whereby simple fuel molecules containing only a few carbon atoms are converted into aggregates containing as many as 10^7 atoms. The process obviously involves the polymerisation and dehydrogenation of the fuel and since the size of the particles formed in pyrolysing gases is a function of their residence time in the gas [10], carbon formation must also involve growth stages in which further carbon is deposited on initially formed nuclei. Cyclisation and ordering processes must occur too if crystallites of roughly graphitic structure are to be formed.

The kinetics of these processes play an important role in determining the extent of formation and the properties of synthetic carbons and thus an important aspect of the study of carbon formation has been the investigation of the way in which experimental conditions influence properties such as the structure, the density and the chemical composition of the carbons formed. Of course, the thermal and electrical properties of carbons also depend upon the conditions under which carbon formation occurs, but such properties are determined largely by the structure and chemical composition of the deposits, and are thus only indirectly related to the process of carbon formation.

1.3.1 Carbon formation by pyrolysis

Despite the fact that the carbon formed in gaseous pyrolytic systems is of two main types depending principally on whether it is formed in the gas phase or on a surface, most of the studies of pyrolytic carbon have been concerned only with the properties of surface deposits. Such deposits are sometimes the only ones to be formed, but often they occur together with gas-phase material and Kinney and his co-workers [14,16] have been able to distinguish as many as four different types of deposit. Kinney pyrolysed a variety of organic compounds in a flow system at temperatures from 900 to 1400°C and found that the relative amounts of the two main types of carbon deposited at a given temperature and concentration depended quite markedly on the nature of the starting material. Anthracene, for example, showed a great tendency to form gas-phase carbon whilst under identical conditions methane tended to give surface carbon. Pressure and temperature also influenced the relative amounts of the two carbons; low pressures of reactant favoured the formation of surface carbon, whilst low temperatures favoured the formation of gas-phase carbon.

Experimental conditions which affect the relative amounts of surface and gas-phase carbons also influence the size of the particles and the dimensions of the constituent crystallites. Johnson and Anderson[10] carried out an electron microscope study of the carbon particles formed in the gas phase by the pyrolysis of acetylene, vinylacetylene and a wide variety of other hydrocarbons. The sizes of the particles were investigated as functions of the nature and concentration of the hydrocarbon fuel, and of the temperature of pyrolysis. The size of the particles was found to be independent of the hydrocarbon fuel but to increase with increasing temperature and concentration. It was also shown that carbon formation was time-dependent and that the particle size increased with increasing contact time. The rate of growth of carbon particles has in fact been the subject of several investigations but a review of this aspect of carbon formation is reserved for later discussion (see Section 1.4.2).

The effect of temperature of pyrolysis on the structure of pyrolytic carbons has been studied by many workers [13,16-19], and there is general agreement that the degree of perfection of surface carbons increases quite markedly with temperature; the sizes of the crystallites and their degree of preferred orientation increase, while the interlayer spacing decreases correspondingly. On the other hand, the crystallite dimensions of gas-phase carbons are relatively little affected by the temperature of pyrolysis. The size of the crystallites and their degree of preferred orientation are, however, decreased by an increase in the partial pressure of the starting material [14].

The extent to which the structure of the deposited carbon depends on the nature of the starting compound has received comparatively little attention. In general, it would appear that the structure of the deposit depends little on the nature of the starting compound provided that this contains only carbon and hydrogen [13,14,16], but on the other hand, the presence of chlorine in the starting compound has been found to have a quite pronounced effect. Cullis, Manton, Thomas and Wilman studied the formation of surface carbon from methane, methylchloride, methylene dichloride, chloroform and carbon tetrachloride at 932°C [19] and found that, as the number of chlorine atoms in the starting compound was increased, so the size of the crystallites and their degree of preferred orientation were reduced. A few of the results obtained for the effect of molecular structure and temperature on carbon formation are shown in Tables 1 and 2.

Since pyrolytic carbons have very defective structures, it is not surprising that their density is lower than that of natural graphite. The X-ray density of a perfect single crystal of graphite is 2.265 $g.cm.^{-3}$ [21], but pyrolytic carbons rarely have densities greater than about 2.20 $g.cm.^{-3}$, and in most cases the bulk density is much lower due to the fact that pyrolytic carbons are porous and have a large number of voids. Most of the pores are accessible to fluids such as methanol and hexane or, better still, to gaseous helium, and these are called "open pores". In some cases, however,

Table 1

The effect of molecular structure on carbon formation [16,20]

Compound	Temperature of formation: 1200°C					
	Surface Carbon			Gas-phase Carbon		
	d_c (Å)	L_c (Å)	L_a (Å)	d_c (Å)	L_c (Å)	L_a (Å)
Benzene	3.49	33	56	3.66	11	48
Toluene	3.48	29	-	3.61	14	-
Anthracene	3.52	28	51	3.71	12	36
Naphthalene	3.50	20	56	3.68	13	40
Methane	3.48	32	47	3.61	14	-

Compound	Temp. of formation: 932°C		
	Surface Carbon		
	Preferred Orientation	L_c (Å)	L_a (Å)
Methane	Strong	>100	>200
Methyl chloride	Slight	100	150
Methylene dichloride	Nil	30	100
Chloroform	Nil	20	100

Table 2

The effect of temperature on carbon formation [16,18]

Temperature of formation (°C)	Compound: Benzene					
	Surface Carbon			Gas-phase Carbon		
	d_c (Å)	L_c (Å)	L_a (Å)	d_c (Å)	L_c (Å)	L_a (Å)
900	3.56	15	49	3.60	13	44
1200	3.48	30	73	3.61	13	41
1400	3.43	40	110	3.62	15	46

Compound: Methane	
Temperature of formation (°C)	Surface Carbon d_c (Å)
1600	3.425
1700	3.427
1800	3.415
1900	3.410
2000	3.362
2050	3.361
2150	3.356

as much as 20% of the volume may consist of inaccessible or "closed pores" and then the helium density is still lower than the crystallographic density. The helium density is lowest for chars and highest for surface carbons. Some typicalvalues are: sugar carbon, 1.54 $g.cm.^{-3}$; acetylene black, 2.04 $g.cm.^{-3}$; surface carbon deposited from methane at 2000°C, 2.20 $g.cm.^{-3}$ [17,21].

In the case of surface carbons, several systematic studies have been made of the effect of temperature of formation and of pressure of reactant [17,18,22-25]. Brown and Watt [17] studied the deposition of carbon from methane onto a heated graphite rod and found that above 2000°C the density of the carbon, as determined by a flotation technique using bromoform and ethanol, was about 2.2 $g.cm.^{-3}$. At lower temperatures, however, it was found that the density was lower and showed a minimum at 1700°C of only 1.18 $g.cm.^{-3}$. The density was independent of the nature of the fuel (either methane, propane or benzene), but was found to be a function of the initial pressure. An increase in the initial pressure of the fuel tended to increase the density of the deposit and shift the minimum to lower temperatures.

These results have been confirmed by Blackman,Saunders and Ubbelohde, by Rappeneau and his co-workers, and by Diefendorf [18,23,25], and in addition, Diefendorf found that if the pressure of methane was reduced to 1.7×10^{-2} mm.Hg, the density of the carbon was 2.2 $g.cm.^{-3}$ irrespective of the temperature of deposition. The reason for the low density of the carbons deposited at around 1700°C is, however, far from clear. Diefendorf and Rappeneau et al. suggest that it is purely a physical effect due to the incorporation of gas-phase carbon into the surface deposit but, on the other hand, both Brown and Watt, and Ubbelohde and his co-workers consider that it is more likely to be a kinetic effect. The fact that surface carbon has a high density when formed at 2000°C is to be expected from the general increase in the diffusion rates of carbon atoms at high temperatures. On the other hand, at very low temperatures or pressures, the rate of carbon deposition may well be the rate-determining step so that the density is again high. At intermediate temperatures, however, the rate of adding on fresh atoms could be faster than the rate of rearrangement of lattice defects, and in such circumstances, the carbons would contain a greater proportion of amorphous material and their density would be lower.

1.3.2 Carbon formation in flames

Carbon formation occurs in both premixed and diffusion flames, and in both cases investigations have been made of the extent of carbon formation and the properties of the carbons formed. In general, however, the properties of flame carbons are independent of the type of flame or the nature of the fuel, and in many ways these carbons are remarkably similar to the gas-phase carbons formed in pyrolytic systems. It is perhaps for this reason that most of the work on carbon formation in flames has dealt only with the extent of carbon formation. Nor is it surprising that the properties of the gas-phase carbons formed in the two systems are similar. In diffusion flames particularly, favourable conditions exist for the formation of carbon by processes which are similar to those occurring in pyrolytic systems since mixing of the fuel and oxygen or air takes place only in the combustion region.

In premixed flames, the extent of soot formation depends upon the air to fuel ratio. If the fuel is progressively diluted with air, soot formation is reduced and indeed premixing of the fuel with sufficient air can eventually suppress carbon formation completely. Work on carbon formation in premixed flames has, therefore, been directed primarily towards establishing the critical air:fuel ratio under which carbon formation can just occur. Unfortunately there is no comparable fundamental property of diffusion flames, and the only measurements related to carbon formation in these flames are the luminosity due to the presence of hot carbon particles, and the flame height at which soot formation can just be detected. The luminosity of a flame is however somewhat dependent on flame temperature and thus, although it is only an empirical measure, the flame height at which carbon formation occurs is a much more convenient indication of sooting tendency [26].

In diffusion flames, the tendency of hydrocarbons to form soot is determined in a standard type of lamp known as a Factor lamp, and several workers [27-31] have made measurements of the "smoke point" of various fuels as a function of their molecular structure. In general it is found that the tendency to carbon formation increases with increasing molecular weight and degree of unsaturation of the hydrocarbon. It also increases with increasing extent of branching of the fuel, although the actual position of the branching appears to make little difference. Some typical results [30] show that the tendency for carbon to be formed decreases in the order:

naphthalenes $>$ benzenes $>$ di-olefins $\gtrsim$ acetylenes $>$ mono-olefins $>$ paraffins, and 3ry.paraffins $>$ 2ry.paraffins $>$ 1ry.paraffins.

Street and Thomas[32] studied the influence of molecular structure of fuels on their tendency to form carbon in premixed flames, and at first sight their results appear to conflict with those obtained by workers using diffusion flames. Street and Thomas burnt fuel:air mixtures on the top of a Bunsen-type burner fitted with an outer jacket to prevent the entrainment of secondary air. Under these conditions the air:fuel ratio was adjusted so that carbon formation was just observed or just disappeared. The results were expressed in terms of the critical mixture strength as defined by the amount of air needed to prevent carbon formation divided by the amount required to convert all the carbon to carbon dioxide. The order of decreasing tendency to carbon formation was found to be:

naphthalenes $>$ benzenes $>$ paraffins $>$ olefins $>$ acetylenes.

However, the data can also be expressed on the basis of the number of oxygen atoms per molecule of hydrocarbon required to suppress carbon formation [33] and in these terms the tendency of fuels to form carbon in premixed flames is found to depend on molecular structure in exactly the same way as is found for diffusion flames.

Street and Thomas also performed a few experiments in which the fuel:air mixtures were preheated to 400°C. They found that the preheated mixtures showed a greater tendency to form carbon and since the effect of preheating is to raise the flame temperature, they concluded that carbon formation is directly dependent upon temperature. This effect was confirmed in a much more elegant investigation of the effect of flame temperature made by Millikan [34] using a porous plate burner, where the burnt gas temperature is dependent on the gas flow rate but independent of the air:fuel ratio. It was possible to show by variation of the flow rate that the critical air:fuel ratio for ethylene/air flames was inversely proportional to the burnt gas temperature.

The tendency of various fuels to form carbon has also been investigated over a fairly wide range of pressures, and in both premixed and diffusion flames it is found that, as the pressure is increased, soot formation increases also. In premixed flames there is a critical pressure at which soot formation is first observed, which is strongly dependent on mixture strength; the higher the pressure, the greater the oxygen to fuel ratio needed to suppress carbon formation [35,36]. There is also a critical pressure associated with carbon formation in diffusion flames. Thus both Parker and Wolfhard[37], and Milberg [38] studied the behaviour of acetylene/air flames on concentric tube burners and found that no soot formation takes place at pressures below about 150 mm.Hg. At higher pressures however, the rate of soot formation is proportional to the pressure [38] and the maximum rate at which fuel can be burnt without carbon formation decreases with increasing pressure. Plots of the maximum "smoke-free" fuel flow versus the reciprocal of the pressure are linear for a variety of fuels [31].

Many studies have been made of the influence of additives on carbon formation in flames. Most organic additives have only a small effect on carbon formation but benzene and naphthalene promote the formation of soot in diffusion flames [39], and bromine and organic bromides enhance carbon formation in premixed and diffusion flames to quite a marked extent [32,40,41]. On the other hand, hydrogen, nitrogen oxides, organic nitro-compounds and tert-butylhydroperoxide decrease carbon formation [32,42-44]. Sulphur trioxide also slightly reduces carbon formation in diffusion flames but, surprisingly, its effect on premixed flames is quite the opposite; even in 0.1% concentration there is a marked increase in the luminosity of the flame [45,46].

1.4 The mechanism of carbon formation

1.4.1 Nucleation and growth - the nature of the intermediates

It is now quite certain that carbon formation involves initially the formation of nuclei which then grow by reaction with other species. However, the exact nature of the nuclei, the way in which they are formed and the species with which they react are still the subject of controversy. This is to some extent understandable, since the number of radicals and relatively stable molecules which can be detected in flames and pyrolysing gases is extremely large. It is difficult to decide whether, for example, a particular intermediate product is involved in nucleation or in growth, or whether it is best regarded as a reactive side-product. It is even difficult to ascertain the extent to which the original fuel molecule is involved. If it is assumed that nuclei grow very rapidly once they are formed in a pyrolysing gas, then the observation of induction periods during the formation of carbon behind shock waves in acetylene [47-49] proves that something more complicated than the original fuel molecule is required to produce nuclei. On the other hand, the observation of an induction period provides no clue as to whether or not the original fuel molecule is involved in growth.

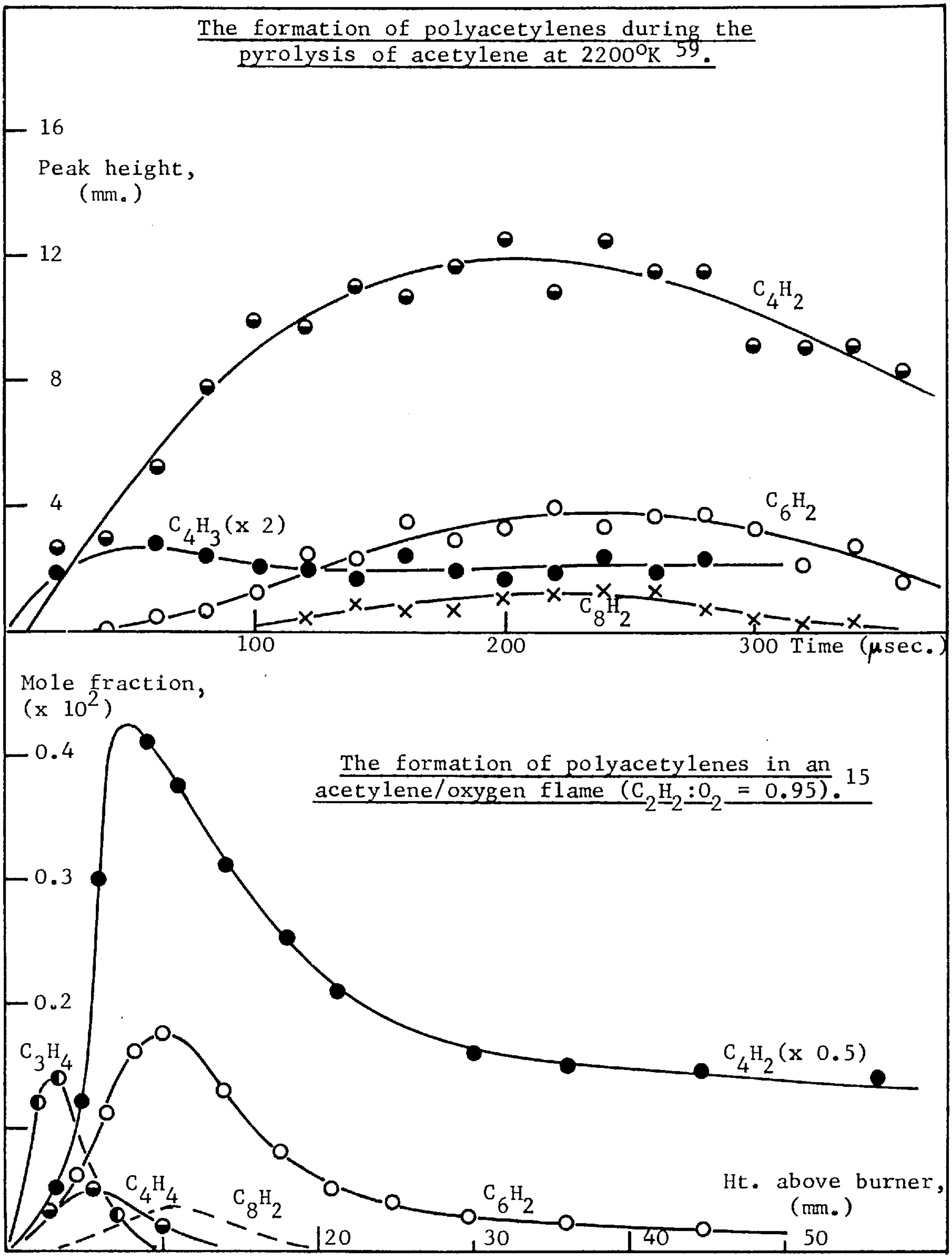
The overall process of carbon formation obviously involves polymerisation and dehydrogenation of the fuel, and several early theories of carbon formation tended to favour the view that one of these processes was a distinct preliminary to the other. Thus Smith, for example, [35] suggested that dehydrogenation occurred first giving rise to C_2 radicals which then polymerised, whereas Rummel and Veh [50], and Parker and Wolfhard [37] believed that polymerisation occurred first and was <u>followed</u> by dehydrogenation to yield carbon as the end product. According to more recent theories, however, the two processes, dehydrogenation and polymerisation, are not truly independent and neither occurs as a distinct preliminary to the other. Thus, Porter [51] has suggested that initially the fuel is degraded to acetylene and that carbon is formed from this compound by a series of rapid reactions involving "simultaneous" polymerisation and dehydrogenation. Acetylene is certainly a common product of hydrocarbon pyrolysis reactions -

studies of the pyrolysis of ethane, ethylene, and n-butane for example show that it occurs as a significant product in every case [52-58] - and recently the concept of simultaneous polymerisation and dehydrogenation has been greatly clarified by Bonne, Homann and Wagner [15], and by Kistiakowsky and his co-workers [59]. It would appear that carbon formation from acetylene takes place via the intermediate formation of polyacetylenes.

Bonne, Homann and Wagner studied the formation of carbon in premixed acetylene/oxygen flames, whilst Kistiakowsky and his co-workers investigated the pyrolysis of acetylene in shock-waves. Even though the two systems are very different, the results obtained are remarkably similar (Fig. 1) and in each case it was possible to identify and follow the concentrations of C_2H_2, C_4H_2, C_6H_2, C_8H_2 and $C_{10}H_2$ throughout the entire course of the reaction. In acetylene pyrolysis it was found that there is an initial induction period during which the concentrations of polyacetylenic species increase but that, after the growth period, all species tend to equilibrate. Later an abrupt decrease in the concentration of polyacetylenes occurs and the characteristic times for this decrease correspond quite well to the induction periods for carbon growth measured by Hooker [49].

Bonne, et al. detected a great many species (including C_2) in the oxidation zone of the acetylene/oxygen flame but the majority had in fact disappeared almost completely by the end of the reaction zone and only C_2, CH and polyacetylenes were present. It was found, however, that it is precisely at this point that the concentration of poly-

Figure 1



The formation of polyacetylenes during the pyrolysis of acetylene at 2200°K [59].

The formation of polyacetylenes in an acetylene/oxygen flame ($C_2H_2:O_2 = 0.95$).[15]

acetylenes reaches a maximum and carbon formation is first detected. In the carbon-forming zone, the polyacetylenes disappear rapidly, but the concentrations of C_2 and CH remain roughly constant. The results suggest that in both flames and pyrolytic systems nuclei are formed from acetylene via polyacetylenes and that growth occurs by decomposition of these species on growing carbon nuclei.

In addition to observing the formation and disappearance of polyacetylenic species, Kistiakowsky and his co-workers [59] were able to detect the presence of the radical $C_4H_3^\bullet$. This radical apparently exists in a steady state concentration throughout the entire course of the pyrolysis. It is believed that the $C_4H_3^\bullet$ radical is formed from acetylene by a reaction such as

$$2C_2H_2 \longrightarrow C_4H_3^\bullet + H^\bullet$$

and that, subsequently, polyacetylenes are formed by the reactions:

$$\begin{aligned} &C_4H_3^\bullet \ (+ M) \longrightarrow C_4H_2 + H^\bullet \ (+ M) \\ &C_4H_2 + C_2H_2 \longrightarrow C_6H_3^\bullet + H^\bullet \\ &C_6H_3^\bullet \ (+ M) \longrightarrow C_6H_2 + H^\bullet \ (+ M) \qquad \text{etc.} \end{aligned}$$

Bonne, et al. propose a very similar mechanism. It differs only in that the formation of higher polyacetylenes is thought to occur via the reaction of acetylene with $C_4H_3^\bullet$ and $C_6H_3^\bullet$ radicals rather than with the polyacetylenes themselves:

$$\begin{aligned} &C_2H_2 + C_2H^\bullet \longrightarrow C_4H_3^\bullet \\ &C_4H_3^\bullet \ (+ M) \longrightarrow C_4H_2 + H^\bullet \ (+ M) \\ &C_4H_3^\bullet + C_2H_2 \longrightarrow C_6H_3^\bullet + H_2 \end{aligned}$$

$$C_6H_3^{\bullet} \ (+ \ M) \longrightarrow C_6H_2 + H^{\bullet} \ (+ \ M)$$

$$C_6H_3^{\bullet} + C_2H_2 \longrightarrow C_8H_3^{\bullet} + H_2 \qquad \text{etc.}$$

There is, however, one difficulty arising out of Wagner's work on acetylene/oxygen flames. The composition of the earliest particles detected seems to correspond to the empirical formula CH, and it is only very much later in the reaction that the carbon has a composition C_8H typical of carbon blacks. One way of reconciling the importance of polyacetylenes with this fact is to assume that the sequence of addition reactions leading to the formation of nuclei is slightly different to that controlling later growth. A sequence of polymerisation reactions starting with $C_2H^{\bullet}$ and acetylene could lead to nuclei with a composition very close to CH in the large radical limit if hydrogen were not split out during the course of the additions. If it is assumed that the particles first detected are these large radicals and that they grow by addition of polyacetylenes then, as carbon formation progresses, the carbon:hydrogen ratio of the particles will increase.

Because of the importance of the polymerisation and dehydrogenation reactions of acetylene, much attention has also been paid to the kinetics of the pyrolysis of this compound and to some of the products derived from it, particularly diacetylene. Extensive kinetic studies of the pyrolysis of acetylene have been carried out over a wide range of temperatures, and the most striking feature of the results is that the reaction appears to be second order in acetylene over the entire range from 400 to 2500°C [47-49,52,59,60-69]. An

Arrhenius plot of the second order constants covering the whole temperature range fall on a single straight line and show only slight random scatter. The line of best fit is given by the equation

$$\log_{10}k = -10.01\ (\pm\ 0.11) - \frac{41{,}600\ (\pm\ 620)}{4.58T}$$

where k is in cm.^{3} molecule.$^{-1}$ sec.$^{-1}$ and the uncertainties are standard deviations [59].

An induction period is often observed [47-49,61,63,66,68,70] but the addition of compounds such as diacetyl and ethylene oxide, which break down to give free radicals has a pronounced accelerating influence; the induction period is eliminated and the maximum rate is acquired immediately [66]. On the other hand, nitric oxide and halogen compounds act as inhibitors and prolong the induction period [61-63,66,71-73].

There is good agreement as to the nature of the intermediate and final products which are hydrogen, methane, ethane, ethylene, methylacetylene, vinylacetylene, diacetylene and benzene. Benzene is the major aromatic hydrocarbon (except at the highest temperatures) but a large number of other aromatic compounds are also formed. Ultimately, methane is the predominant gaseous product and at the highest conversions almost 50 mole % of the acetylene is converted to methane; this means that almost all the hydrogen appears as methane [68]. Both methane and hydrogen are stable products, but benzene and ethylene undergo secondary reactions at high temperatures and vinylacetylene and diacetylene are reactive even at low temperatures.

In contrast to the effect of additives such as nitric oxide, many of the products of the reaction have no influence on the decomposition of acetylene. Thus the addition of small amounts of hydrogen, methane, ethane, ethylene or methylacetylene gives rise to very little change in either the product distribution or the rate of reaction [68]. On the other hand, when vinylacetylene and diacetylene are used as additives in the pyrolysis of acetylene, the rate of disappearance of acetylene is considerably enhanced [74]. It would appear that, once formed, products such as hydrogen, methane and ethane do not react with further acetylene, but that, in contrast vinylacetylene and diacetylene may play an important role in the overall process.

Unfortunately, there is conflicting evidence as to the role of vinylacetylene and diacetylene in the pyrolysis of acetylene. From work at high temperatures it would appear that diacetylene is the important intermediate [15,48,49], but recent work at temperatures from 600 to 1000°C [68] suggests that vinylacetylene is the sole primary product and that it is not until later in the reaction that other products such as diacetylene begin to be formed.

Relatively few kinetic studies have been made of the pyrolysis of diacetylene and vinylacetylene. Diacetylene is known to form carbon very much faster than acetylene [75-78] and the principal products at 1200°C are acetylene, methane, polymeric material and carbon; a little ethylene and traces of vinylacetylene are also formed. The decomposition appears to be second order in diacetylene and has an activation energy of about 40 kcal.mole^{-1} [78]. The pyrolysis of vinylacetylene at temperatures from 400 to 900°C has been studied by Stehling, Frazee and Anderson [74]. It was found that the principal products were hydrogen, methane, ethylene, benzene and carbon. It is not possible, on the basis of this information, to decide the precise roles of vinylacetylene and diacetylene in carbon formation from acetylene, and it is perhaps for this reason that there is no general agreement as to the mechanism of acetylene pyrolysis.

Despite the obvious importance of acetylene in carbon formation, it would appear, however, that it is not always an essential intermediate. Cole and Minkoff [79], and Tesner, Robinovitch and Rafalkes [39] found that, although acetylene was always present in diffusion flames of methane, ethane and ethylene, the addition of acetylene to the fuel caused no change in the brightness of the carbon zone, and the amount of soot formed did not increase. Similarly, Ferguson found that the carbon formed in premixed propane-2-^{13}C/air flames did not arise preferentially from a fragment containing two carbon atoms. In both cases it was concluded that acetylene could not be an essential intermediate in carbon formation. The same would also appear to be true in the case of carbon formation from benzene. The predominant reactions of benzene at high temperatures are ring opening and fragmentation to form $C_2H\cdot$ and $C_4H_3\cdot$ radicals [81], and the remarkable ease with which carbon is formed in benzene flames is almost certainly due to its initial degradation to $C_4H_3^{\cdot}$.

Although these degradation reactions are undoubtedly important at high temperatures, the pyrolysis of benzene at low temperatures results also in the formation of substantial amounts of biphenyl and other polynuclear aromatic compounds [82,83]. For this reason it has often been suggested that polycyclic aromatic hydrocarbons are important intermediates in carbon formation [37,84,85]. A wide variety of such compounds are found among the products of pyrolysis reactions [86,87] and these also occur in diffusion flames [88-91]. Lindsay, for example,[91] studied the formation of polycyclic compounds in the diffusion flames of a wide variety of aliphatic and aromatic hydrocarbons and found that, although no systematic trends were apparent, the same polycyclic compounds were formed irrespective of the nature of the fuel. A similar observation was made by Hadzi [87] in a study of aromatic hydrocarbon formation in pyrolytic systems, and it was concluded that aromatic compounds are involved in the reaction partly as precursors of carbon and partly as the products of side reactions. Thomas has pointed out [92] that the isolation of polybenzenoid compounds does not necessarily imply that they are intermediates in carbon formation. On the other hand, such products may be the result of premature chain termination processes and, although the isolation of these substances often means that they are not sufficiently reactive to form soot, their structure may be an important guide to the reaction route.

Lewis and Edstrom [93] have studied the thermal behaviour of a wide variety of polycyclic aromatic compounds using differential thermal analysis and found that the ease with which they carbonise in the liquid phase is markedly dependent on their structure. Kinney and DelBel reached the same conclusion from a more limited study of carbon formation in the gas phase [85]. If the amounts of polymer products formed during the pyrolysis of acetylene at 700°C [86] are compared with their reactivity, it is found that the amounts isolated increase with decreasing reactivity (Table 3). It would seem, therefore, that major polymeric products such as benzene and naphthalene are best regarded as side products, but that those which are isolated only in small amounts may well be intermediates in carbon formation at least at low temperatures.

Evidence that benzene and naphthalene are not important as intermediates is shown also in the work of Stehling, Frazee and Anderson [74]; the presence of small amounts of benzene or naphthalene was found not to influence the rate of disappearance of acetylene during pyrolysis.

For the sake of completeness it is necessary to mention briefly the suggestion put forward by Smith [35], that carbon formation occurs via the intermediate production of C_2 radicals. However, whilst it appears that conditions which favour the formation of C_2 radicals do indeed favour the formation of soot (the intensity of the C_2 emission bands is highest in fuel rich mixtures [95-97]), it is now quite certain that carbon formation does not in fact occur by this route. Gaydon and Wolfhard investigated the total amount of light emitted by hydrocarbon/air flames and concluded that the concentration of C_2

Table 3

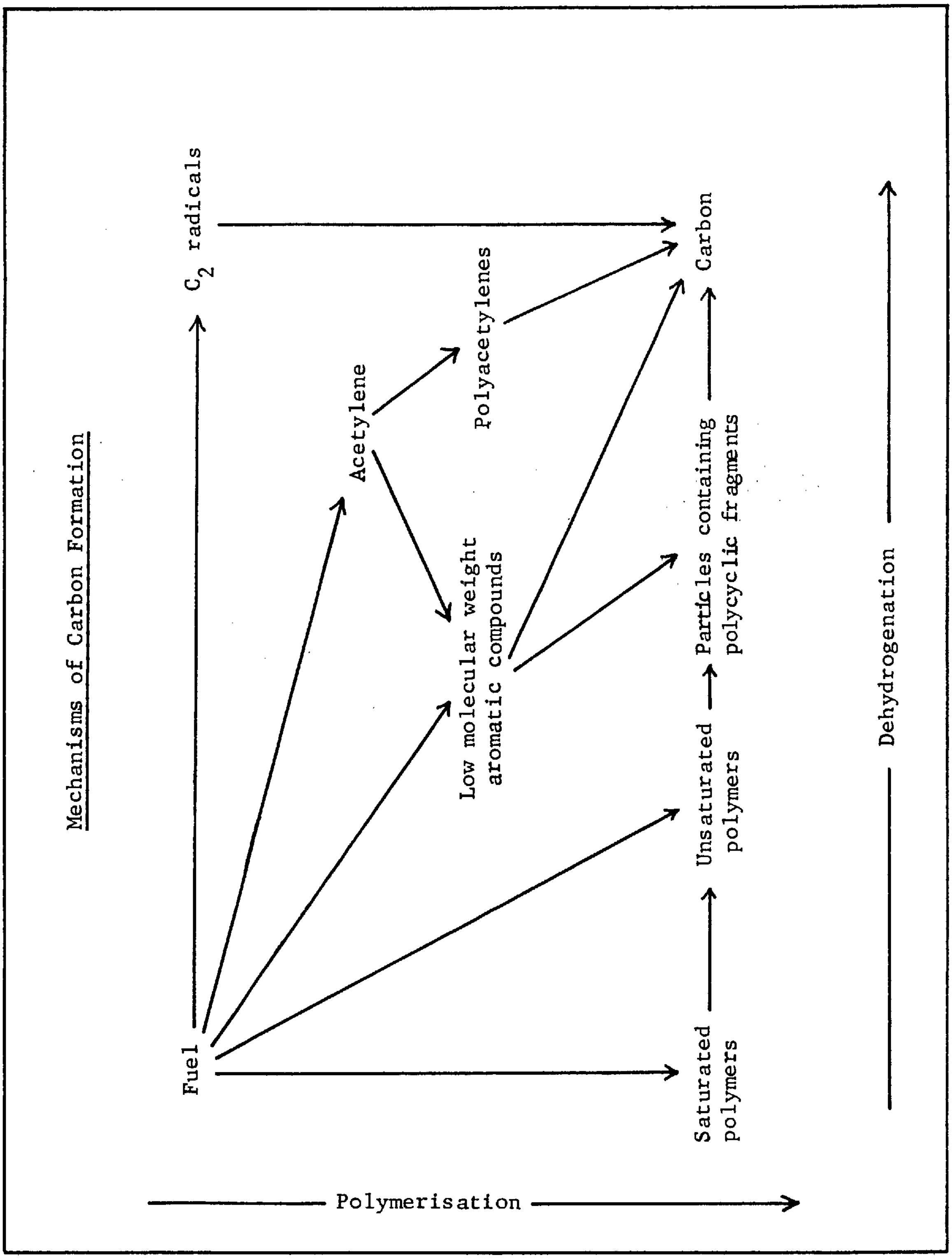
Compound	Methyl affinity [94]	Reactivity by DTA [93]	% yield of carbon at 800°C [85]	% w/w isolated from C_2H_2 pyrolysis at 700°C [86]
Benzene	1	No	2	28
Naphthalene	22	No	3	12
Phenanthrene	27	No	-	13
Crysene	57	No	13	0.5
Pyrene	125	No	15	6.5
Fluorene	300	No	-	4.5
Fluoranthene	-	No	-	3.7
1,2 Benzanthracene	515	Slightly	-	0.4
Anthracene	820	Fairly	70	Trace
Naphthacene	9250	Very	-	Not detected

radicals was quite insufficient to account for the formation, in the time available, of carbon particles having diameters of about 500Å. This result is not, in itself, very meaningful since the concentration of the radicals could be low simply because they polymerise rapidly. However, the concentration of C_2 radicals is higher in carbon-forming flames than in flames which produce no carbon, and thus polymerisation of these radicals does not occur.

Gaydon and Wolfhard also suggested [93,98] that the C_2 radicals did not originate from the stripping of hydrogen atoms from acetylene and this has now been proved conclusively by tracer studies using ^{13}C-acetylene. In both acetylene/oxygen flames [99] and in the pyrolysis of acetylene in shock-waves [100] the C_2 products are randomised and it would seem, therefore, that the C_2 radicals are formed in side reactions involving single carbon fragments such as $CH^\bullet$, $CH_2^{\bullet}$ or $CHO^\bullet$. Their exact mode of formation is, however, still very obscure.

It seems that no one theory of carbon formation can account for all the observed features of the nucleation process, and it is more probable that the process can occur in several ways depending on the nature of the fuel and the conditions under which carbon formation is taking place. Street and Thomas [32] attempted to account for carbon formation in this way and a diagram showing the interrelationships among the possible routes to carbon is shown in Fig. 2. It can be seen that all three theories discussed in this Section fall into place quite naturally although, of course, the relative importance of the various routes is not indicated.

Figure 2



Mechanisms of Carbon Formation

1.4.2 The Kinetics of growth

Whilst the nature of the intermediates involved in nucleation and growth are still something of a mystery, the kinetics of growth have proved more amenable to study, and it is well established that the two processes have quite different kinetic features. The differences are apparent from several observations: Tesner [96], for example, has found that the temperature required for nucleation in the gas phase is always significantly higher than that required for subsequent growth, and both Tesner [102] and Palmer [78,81] have observed that carbon deposition onto surfaces can occur at concentrations below the lower limit of sooting. The conclusion seems to be that growth is a simpler process than nucleation and is kinetically of a lower order; in fact it is generally agreed that the rate of deposition onto a carbon surface is directly proportional to the concentration of hydrocarbon. This appears to be true for both gas-phase and surface carbons.

Tesner and his co-workers [101,103-105] made an electron microscope study of the growth of carbon particles suspended in the gas phase and found that the rate of growth in methane, acetylene or benzene was first order in the concentration of hydrocarbon. Grisdale, Pfister and van Roesbroeck [2], and Brown and Watt [17], on the other hand, studied the rate of deposition of surface carbon; it was again shown that the deposition rate was directly proportional to the concentration of hydrocarbon. In the case of carbon deposition from methane, Grisdale et al. found that the activation energy of the process was

107 kcal.mole^{-1}. Brown and Watt, however, reported an activation energy of only 32 kcal.mole^{-1} for the same process, but it is difficult to assess the significance of these values since their apparatus was not isothermal and consisted of a resistance-heated graphite rod placed centrally in a chamber through which cold methane was pumped.

In an effort to make some well controlled measurements, Palmer and his co-workers [106-108] measured isothermal deposition rates from methane, benzene and toluene in an annular flow reactor at 900 to 1100°C using a large excess of helium as the carrier gas. The deposition rates were calculated from measurements of the resistance of the deposit on a portion of a centrally placed porcelain rod. A steady state treatment was developed which related the deposition rate to the rate of gas-phase decomposition of the starting material. It was found that the deposition rate was first order in hydrocarbon and, in the case of methane, the values of the rate of decomposition calculated from the rate of carbon deposition agreed well with other data on methane pyrolysis in shock tubes, the value of the activation energy being 102 kcal.mole^{-1}.

Unfortunately, the kinetic data provide no clues as to the identity of the species which actually decompose on the surface. The rate-determining step in carbon deposition from methane can quite clearly be identified as the first step in methane pyrolysis, at least at temperatures around 1000°C, since otherwise the deposition rate would not be related so simply to the rate of gas-phase decomposition of methane. The initial steps in methane pyrolysis are probably

$$CH_4 \longrightarrow CH_3^{\bullet} + H\bullet$$

and

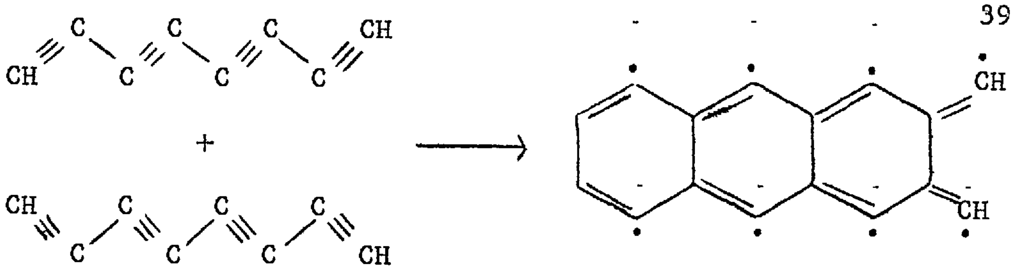
$$CH_4 \longrightarrow CH_2^{\bullet} + H_2$$

However, it is not possible to determine from the kinetics the extent to which radicals such as $CH_3^{\bullet}$ and $CH_2^{\bullet}$ are important in the deposition process. A further difficulty is that, although in the case of methane, the starting material does not appear to decompose directly on the carbon surface, it is not known to what extent this is true of other hydrocarbons. Tesner [101] has advocated strongly the importance of reactions of this type, and it would be particularly interesting to know whether acetylenic compounds decompose directly on carbon surfaces.

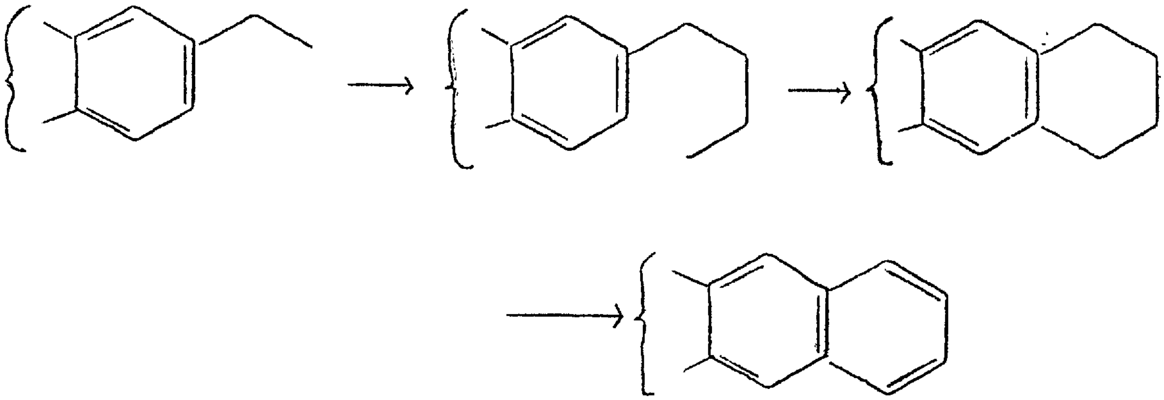
1.4.3 Cyclisation and ordering

The process of carbon formation involves the formation of small crystallites which have a roughly graphitic structure. The crystallites are embedded in a mass of amorphous material and in fact do not have a true graphitic structure in so far as they possess no three-dimensional symmetry. Nevertheless, they are composed of layers of carbon atoms arranged hexagonally as in graphite and at some stage in carbon formation therefore, a cyclisation or ordering process must occur.

Stehling, Frazee and Anderson [109] suggested that cyclisation might occur by the cross-linking of compounds such as octatetrayne:



The multiradical systems so formed were envisaged as combining to give graphite-like arrays of carbon atoms. There is, however, no positive evidence to support this mechanism and indeed it seems rather improbable from both energy and steric considerations. It would seem more likely that ring-closure occurs during growth and that the crystallites are built up in a way similar to that which Badger et al. have suggested for the formation of polycyclic aromatic compounds [110]:



Of course, there is no direct evidence to suggest that this concept is correct but at least it would appear to be more probable sterically.

There is, however, one point which does seem to be important. It is almost certain that the initial formation of crystallites is a separate process from that which occurs during graphitisation at elevated temperatures. Graphitisation is a process by which the carbon crystallites grow at the expense of the amorphous material surrounding them. However, this process, which presumably involves the migration of carbon atoms and perhaps even small lattice layers [111], is significant only at temperatures above about 1800°C, and thus must be considered as separate from that in which the original crystallites are formed.

1.5 The present work

In the foregoing pages of this Section a review has been given of the published work on carbon formation, and it is readily apparent that there are still many aspects of the process about which little is known. Of these there are two which are perhaps of outstanding interest. The first, and one which has so far received only scant attention, is the role of vinylacetylene in carbon formation from acetylene. The second is the way in which the experimental conditions of pyrolysis influence the properties and extent of formation of carbon deposits. It is clear that the two principal types of carbon which can be formed, namely gas-phase carbon and surface carbon, are in fact produced in different ways. Unfortunately, however, many workers have, in the past, failed to distinguish adequately between the two types and there is a particular dearth of information concerning the properties of pyrolytic carbons formed in the gas phase.

The present work was carried out with three principal objects. The first was to obtain information about the gaseous reaction products of vinylacetylene pyrolysis. The second was to elucidate the role of vinylacetylene in the formation of carbon from acetylene. The third was to make a comparative study of the gas-phase and surface carbons formed during the pyrolysis of acetylene and vinylacetylene, determining in each case the structure and chemical composition of the deposits. In this way it was hoped to elucidate the roles of vinylacetylene and acetylene in carbon formation and also to obtain a greater understanding of the mechanisms of formation of gas-phase and surface carbons.

2. EXPERIMENTAL

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2. EXPERIMENTAL

2.1 Apparatus

2.1.1 General construction

The vacuum system, which was constructed of pyrex glass, is illustrated diagrammatically in Figs. 3 and 4. Fig. 3 shows that part of the system associated with the purification and storage of reactants, while Fig. 4 illustrates the apparatus used for the collection and analysis of the reaction products.

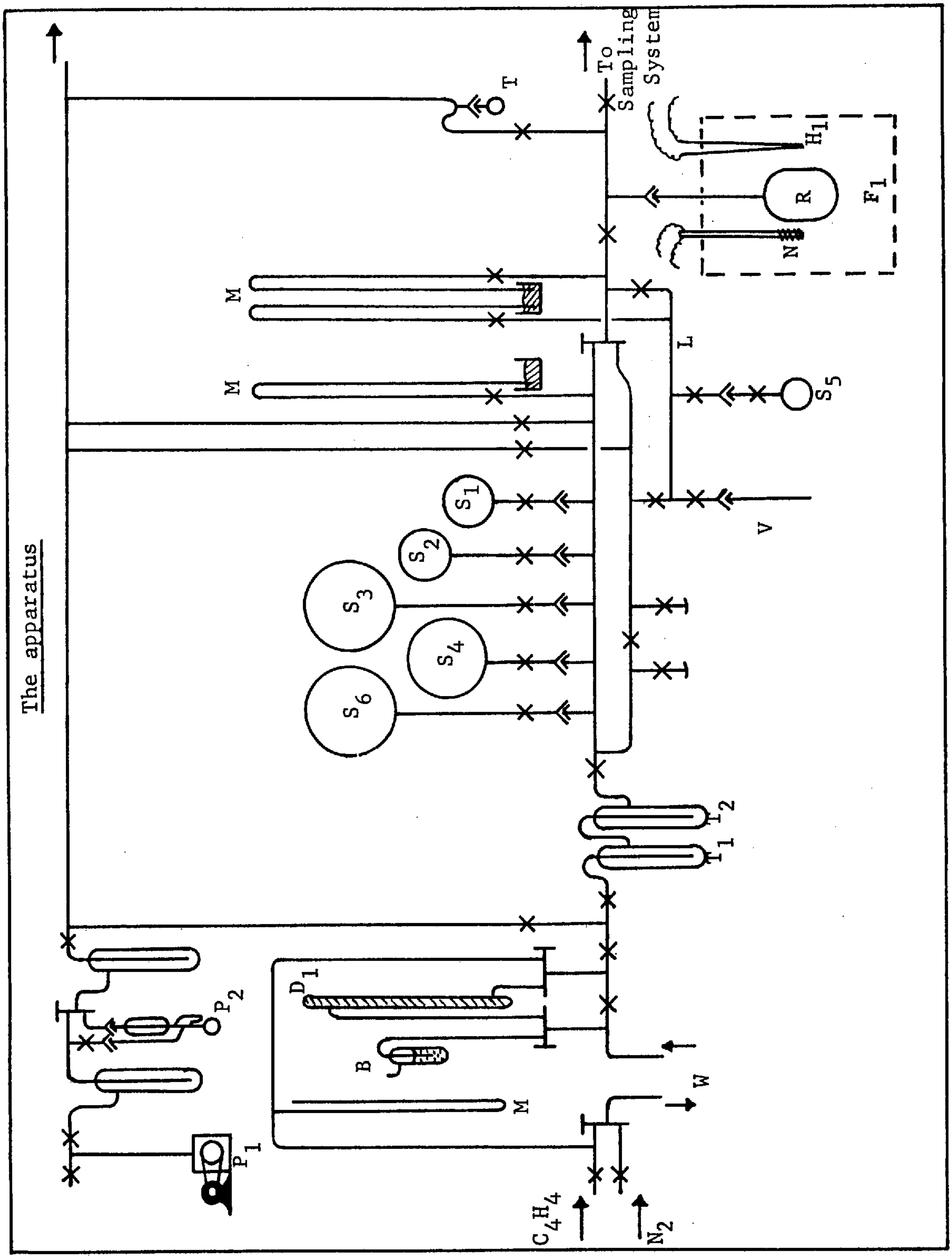
Gases entering the system were, if necessary, passed through a purification train (W) and then through a drying column containing anhydrous magnesium perchlorate (D). The gases could be condensed in cold traps (T_1, T_2) for final purification by distillation and were stored in 5 litre vessels (S_3, S_4 ... etc.). The reactant gases were admitted to the reaction vessel (R) from dosing vessels S_1 and S_2. The dosing vessel S_5 was used to prepare mixtures of vinylacetylene with ^{14}C-labelled acetylene.

Samples of the reaction products, for gas-chromatographic analysis were collected in the U-tube (U) or were condensed in cold traps (T_3, T_4). The reaction products could be trapped out individually as they were eluted from the gas-chromatographic columns and, after being transferred to vessel G, where they were mixed with oxygen, could be oxidised to carbon dioxide and water by pumping through a heated reaction tube containing cupric oxide (O). The water was absorbed by anhydrous magnesium perchlorate, and the carbon dioxide

Key to Figure 3

B	Blow-off
D_1	Drying column
F_1	Furnace
H_1	Thermocouple
L	Vacuum line for ^{14}C-acetylene/vinylacetylene mixtures
M	Manometers
N	Platinum resistance thermometer (for temperature controller)
P_1	Rotary pump
P_2	Diffusion pump
R	Reaction vessel
S_1 - S_6	Storage vessels
T	Polymer collection vessel
T_1, T_2	Cold traps
V	Calibrated volume
W	Purification train

Figure 3

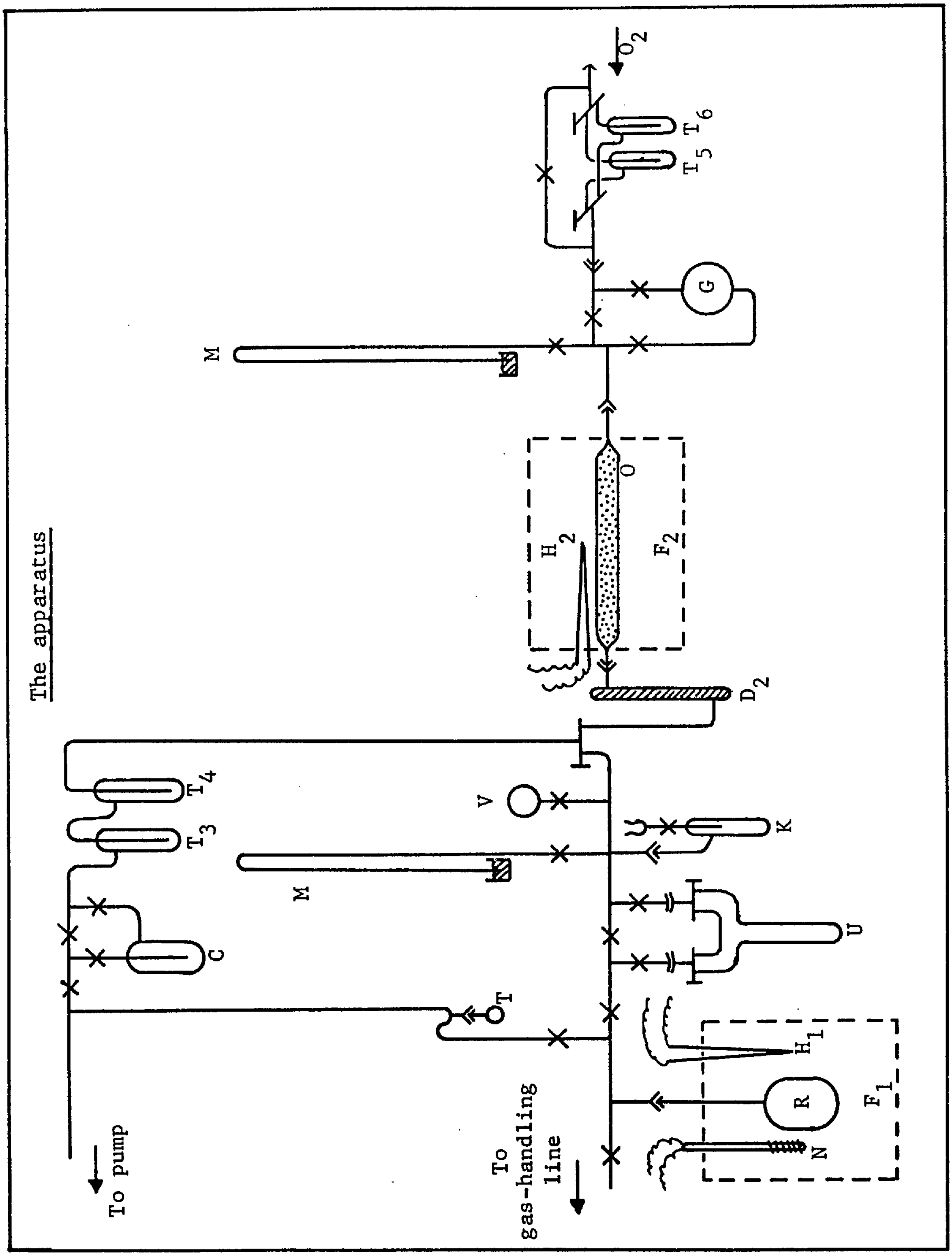


The apparatus

Key to Figure 4

C	Flow restrictor
D_2	Drying tube
F_2	Furnace
G	Mixing vessel
H_2	Thermocouple
K	Carbon dioxide uptake vessel
M	Manometers
O	Reaction tube containing cupric oxide
R	Reaction vessel
T	Polymer collection vessel
T_3, T_4	Cold traps
T_5, T_6	Cold traps from G.L.C. apparatus
U	U-tube for sample collection
V	Calibrated volume

Figure 4



The apparatus

was condensed in cold traps (T_3 and T_4).

At various points the system was connected to mercury manometers and to a high vacuum line which was maintained by a two-stage mercury diffusion pump (P_2) backed by a rotary oil pump (P_1). The taps and joints in the system were lubricated with Edwards Silicone High-Vacuum grease.

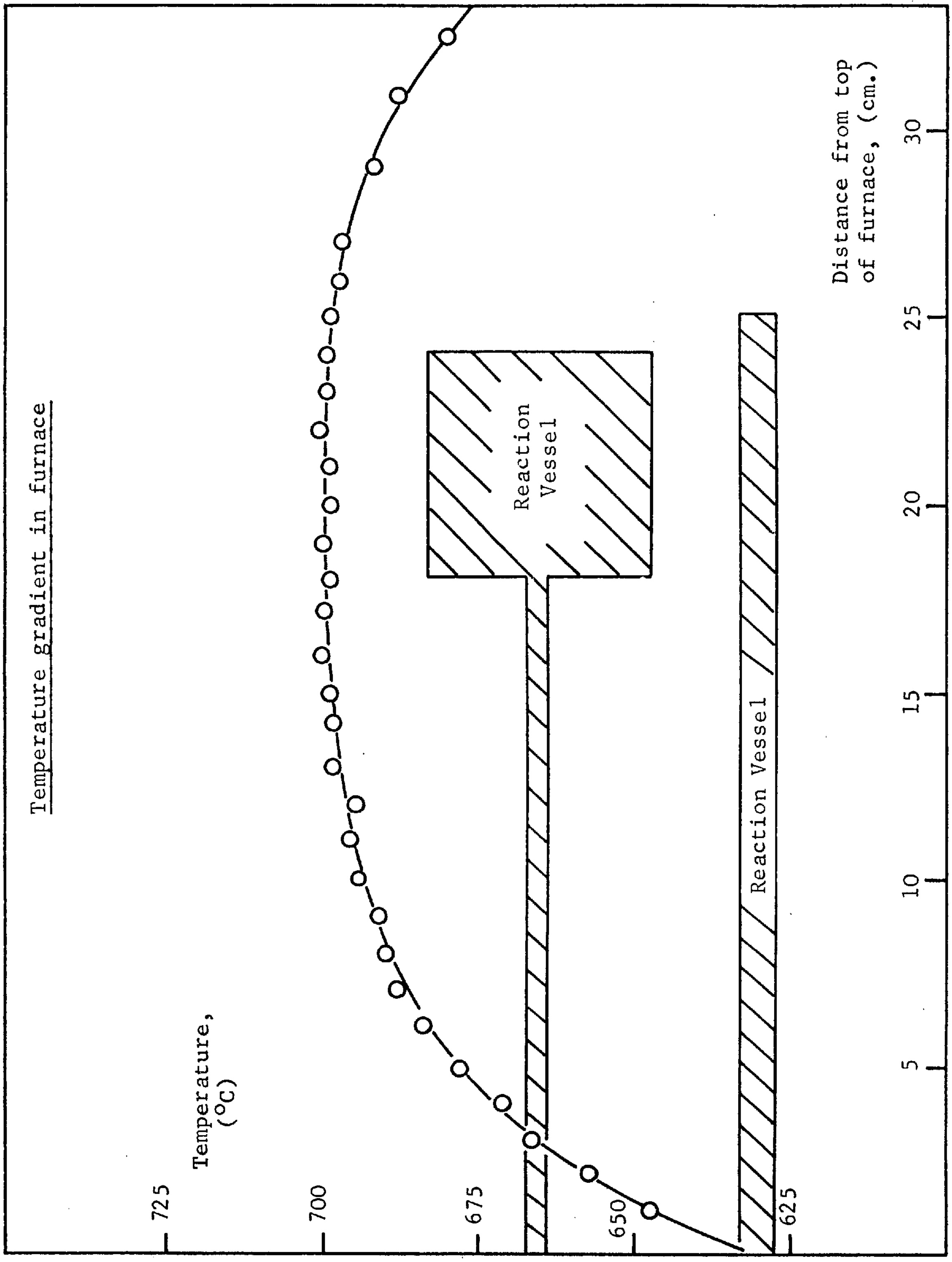
2.1.2 Reaction vessels

The reaction vessels were manufactured in transparent silica by Quartz Fused Products, Ltd. They were of two types - the first, a cylindrical vessel 6 cm. long and 6 cm. in diameter (volume ca. 200 cm.^{3}), was closed at one end and was attached to the vacuum system via a narrow neck and a B10 standard joint, while the second, also cylindrical in shape, was 35 cm. long and 1 cm. in diameter (volume ca. 25 cm.^{3}) and was attached to the vacuum system directly by means of a B14 standard joint.

2.1.3 Furnaces

The furnace in which the reaction vessels were placed was a vertical electric furnace and consisted essentially of a vitreosil tube, height 34 cm., diameter 11.5 cm., and wound with 18 s.w.g. nichrome wire to give a total resistance of ca. 40 ohms at room temperature. The furnace tube was lined internally with a 1/16 in. mild steel sheath in order to improve the temperature distribution along the length of the furnace. A typical example of the temperature gradient along the furnace tube is shown in Fig. 5.

Figure 5



Temperature gradient in furnace

The reaction tube containing copper oxide was heated using another Gallenkamp electric furnace, length 32.5 cm., diameter 3.2 cm.

2.1.4 Temperature control and measurement

The vertical furnace was powered and controlled via an A.E.I. RTR3 temperature controller, but since accurate control was not required for the other furnace, this was controlled by a Variac transformer type 100RM. In both cases, however, the temperature was measured using platinum/87% platinum-13% rhodium thermocouples supported in twin bore mullite tubes. Each thermocouple was inserted into the furnace in such a way that the hot junction was at the same depth as the mid-point of the side of the reaction vessel. With the cold junction maintained at the temperature of melting ice, the e.m.f. was measured on a Doran thermocouple potentiometer and the corresponding temperature was read from standard tables.

2.1.5 Line heating

The vacuum line connecting the reaction vessel to its associated manometer and to the sampling tube and the connection to the pumping line were wound with nichrome heating wire (15 ohms/yard) and lagged with asbestos rope. The heating wire was connected in series with a 200 ohm rheostat and an ammeter, and was powered by a Variac V6HMTF transformer. The current was adjusted so as to maintain this section of the line at about 120°C.

2.2 Preparation and purification of materials

2.2.1 Vinylacetylene

Vinylacetylene (kindly supplied by the Du Pont Co. (U.K.) Ltd.) was obtained from a cylinder containing a 50% solution of the gas in xylene with a small amount of p-tert butyl catechol added as stabiliser. Solutions of vinylacetylene are in fact rather unstable and can be kept for only about one month, but the gas itself can be stored for longer periods provided that oxygen is carefully excluded. In order to ensure that this condition was always satisfied, the vinylacetylene was passed through a purification train to remove oxygen. The purification train consisted of three bubblers: the first two contained 30% sodium hydrosulphite and 2% indigo carmine in 10% potassium hydroxide solution, and the third, water, and prior to admission of the vinylacetylene they were flushed for 30 min. with "oxygen-free" nitrogen.

After purification, the vinylacetylene was dried first over anhydrous calcium chloride and then over anhydrous magnesium perchlorate and was finally condensed in cold traps immersed in liquid nitrogen, prior to fractional distillation and storage. The vinylacetylene was shown, by gas chromatography, to have a purity of about 99%. The main impurity was identified as butadiene, but no xylene could be detected.

2.2.2 Acetylene

This compound was obtained from a cylinder and purified in a manner similar to that used for vinylacetylene. In addition, however, acetone was removed by first passing the acetylene through two bubblers containing saturated sodium bisulphite solution [112].

2.2.3 Hydrogen, oxygen and methane

These gases were obtained directly from cylinders and prior to storage, each gas was passed slowly through two cold traps immersed in either liquid nitrogen or oxygen. Liquid nitrogen was used in the case of hydrogen and methane, and liquid oxygen in the case of oxygen.

2.2.4 Nitrogen

"Oxygen-free" nitrogen was obtained directly from a cylinder and was purified by passage through the oxygen removal train described previously, and then through a cold trap immersed in liquid nitrogen.

2.2.5 Ethane, ethylene, propylene and methylacetylene

Each gas in turn was obtained from its respective cylinder and passed into the static line where it was frozen in a cold trap immersed in liquid nitrogen. After purification by distillation, it was transferred to an appropriate storage vessel.

2.2.6 Diacetylene

Since diacetylene was not obtainable commercially, a sample for gas chromatographic purposes was prepared by the pyrolysis of acetylene at 650°C [113]. Acetylene was introduced at an initial pressure of 20 cm.Hg. into a silica reaction vessel and after 5 sec. the contents of the vessel were pumped out again through a cold trap immersed in liquid nitrogen. The liquid nitrogen surrounding the cold trap was then replaced by an acetone/cardice mixture and pumping was continued for a few minutes to allow the more volatile products such as hydrogen, methane, ethane and ethylene to be pumped off. The trap was then isolated and allowed to warm up to room temperature. Analysis of the contents of the trap by gas chromatography (see Section 2.3.3) revealed the presence of three major products in addition to unchanged acetylene. Two of these were positively identified as benzene and vinylacetylene. The third compound, which was eluted slightly later than vinylacetylene was taken to be diacetylene.

2.2.7 Benzene

Pure benzene (crystallisable), obtained from May and Baker Ltd., was used without further purification.

2.2.8 Attempts to prepare ^{14}C-vinylacetylene

Several attempts were made to prepare specifically labelled ^{14}C-vinylacetylene. The overall yields were, however, too small to be practicable, and the details of the methods tried are not, therefore, appropriate to this Section. They are, however, described in an Appendix (see p. 142).

2.3 Experimental procedure

2.3.1 Gas handling

Five litre globes provided the means of bulk storage of vinylacetylene and acetylene, and from these the gases were transferred as required to a 500ml. dosing vessel. When the furnace had reached a steady temperature, the reaction vessel and associated manometer were evacuated, and the reactant was shared from the dosing vessel into the reaction vessel. The pressures of reactant in the dosing vessel both before and after 'sharing' were measured, and following the determination of the volumes of the dosing vessel, the reaction vessel and the various sections of line by reference to a standard volume, the initial pressure of the gas introduced into the reaction vessel was calculated. The subsequent change with time of the pressure of gases in the reaction vessel was followed manometrically.

Mixtures of vinylacetylene with acetylene or gaseous additives were prepared by evacuation of a dosing vessel, admission of the additive to a known pressure and then addition of vinylacetylene from a storage globe until the required total pressure for the mixture was attained in the smaller vessel. The storage globes contained vinylacetylene at pressures much greater than the required total pressure (500-700 mm.Hg compared with 100-200 mm.Hg) and this minimised the possibility of back-diffusion of the additive into the storage globe. The gases were allowed to mix for a minimum of 30 min. before use.

2.3.2 Sampling

In addition to following the course of the pyrolysis manometrically, samples were withdrawn from the reaction vessel and analysed by gas-chromatography; for this part of the work a reaction vessel having a volume of about 200 ml. was chosen. Three methods of sampling were used depending on the nature and the concentration of the compound being analysed.

(i) At a given time during the reaction, the pressure of gases in the reaction vessel (P_r) was measured and the gases were then pumped through a cold trap immersed in liquid nitrogen. Hydrogen and methane did not condense in the cold trap, and part of the polymeric material formed during the reaction condensed out in the vacuum line between the reaction vessel and the cold trap. The trapped gases were allowed to warm up to room temperature, were expanded into a known volume, and were then shared with an evacuated U-tube also of known volume. The contents of the U-tube were analysed by gas-chromatography, and by measurement of the pressure of gases both before and after sharing (P_1 and P_2 respectively), it was possible to calculate "sharing factors" and hence the concentration and pressure in the reaction vessel of each identifiable constituent. It was also possibe to calculate (from P_1) the pressure in the reaction vessel (P_c) equivalent to the total amount of condensable products. The difference between P_c and the total pressure of identifiable constituents was taken to be the pressure of polymer which was gaseous at room temperature, while the value of (P_r-P_c) was taken to be the pressure of polymer which had condensed out in the vacuum line, plus the pressures of hydrogen and methane. Determination of the amounts of hydrogen and methane present enabled the total amount of polymer formed to be calculated.

(ii) For the analysis of minor products, the contents of the reaction vessel were pumped through a U-tube immersed in liquid nitrogen, the whole of the condensate being used for analysis. It was assumed that total condensation of the various components occured as the condensate was invariably found only in the inlet side of the tube.

(iii) In order to analyse for hydrogen and methane, samples were obtained by sharing the contents of the reaction vessel with an evacuated U-tube of known volume. This procedure was, however, complicated by the partial condensation of the polymeric material. The samples were representative not of the reaction mixture as a whole, but only of that part which was gaseous at room temperature. To take this into account, it was necessary to calculate the concentrations of hydrogen and methane as follows:

The total pressure in the reaction vessel of compounds which are gaseous at room temperature and which are, therefore, shared with the U-tube, is equal to $(P_{H_2} + P_{CH_4} + P_c)$, where P_{H_2} and P_{CH_4} are the pressures of hydrogen and methane respectively and P_c is as defined in method (i). Thus, if the number of moles of hydrogen and methane in a sample of pressure P_s in a volume V_s at a temperature T_s (^{o}K) are x_{H_2} and x_{CH_4} respectively, then

$$P_{H_2} = x_{H_2} . \frac{T_s R}{P_s V_s} [P_c + P_{H_2} + P_{CH_4}] \qquad 1.$$

and $$P_{CH_4} = x_{CH_4} . \frac{T_s R}{P_s V_s} [P_c + P_{H_2} + P_{CH_4}] \qquad 2.$$

where R is the gas constant.

Thus $$\frac{P_{H_2}}{P_{CH_4}} = \frac{x_{H_2}}{x_{CH_4}} \qquad 3.$$

Combining equations 1 and 3, and 2 and 3, and setting $\frac{T_s R}{P_s V_s} = K$

$$P_{H_2} = Kx_{H_2}\left[P_c + P_{H_2} + \frac{P_{H_2} x_{CH_4}}{x_{H_2}}\right]$$

and $$P_{CH_4} = Kx_{CH_4}\left[P_c + P_{CH_4} + \frac{P_{CH_4} x_{H_2}}{x_{CH_4}}\right]$$

$$\therefore \quad P_{H_2} = \frac{Kx_{H_2} P_c}{1 - K\left(x_{H_2} + x_{CH_4}\right)} \qquad 4.$$

and $$P_{CH_4} = \frac{Kx_{CH_4} P_c}{1 - K\left(x_{H_2} + x_{CH_4}\right)} \qquad 5.$$

From equation 4, the concentration of hydrogen in the reaction vessel $[H_2]$ is given by

$$[H_2] = \frac{Kx_{H_2} P_c}{1 - K\left(x_{H_2} + x_{CH_4}\right)} \cdot \frac{1}{RT_r}$$

whence $$[H_2] = \frac{x_{H_2} P_c T_s}{T_r\left[P_s V_s - T_s R\left(x_{H_2} + x_{CH_4}\right)\right]}$$

and similarly $$[CH_4] = \frac{x_{CH_4} P_c T_s}{T_r\left[P_s V_s - T_s R\left(x_{H_2} + x_{CH_4}\right)\right]}$$

where T is the reaction temperature (^{o}K).

The validity of these equations was demonstrated by analysis of the reaction mixture for residual vinylacetylene using all three methods. The results obtained differed by less than 5%.

2.3.3 Gas chromatography

The gas-flow system of the instrument used for this purpose is shown in Fig. 6. "Oxygen-free" nitrogen was used as the carrier gas and was admitted to the system via a pressure controller and a needle valve. A suitable flow rate of nitrogen was achieved by incorporating a further needle valve, a 15 l. buffer volume and a rotary pump at the outlet of the system, the buffer volume being used to obtain smoother pumping. The carrier-gas flow rate was measured using a rotameter and the inlet and outlet pressures were measured on mercury manometers.

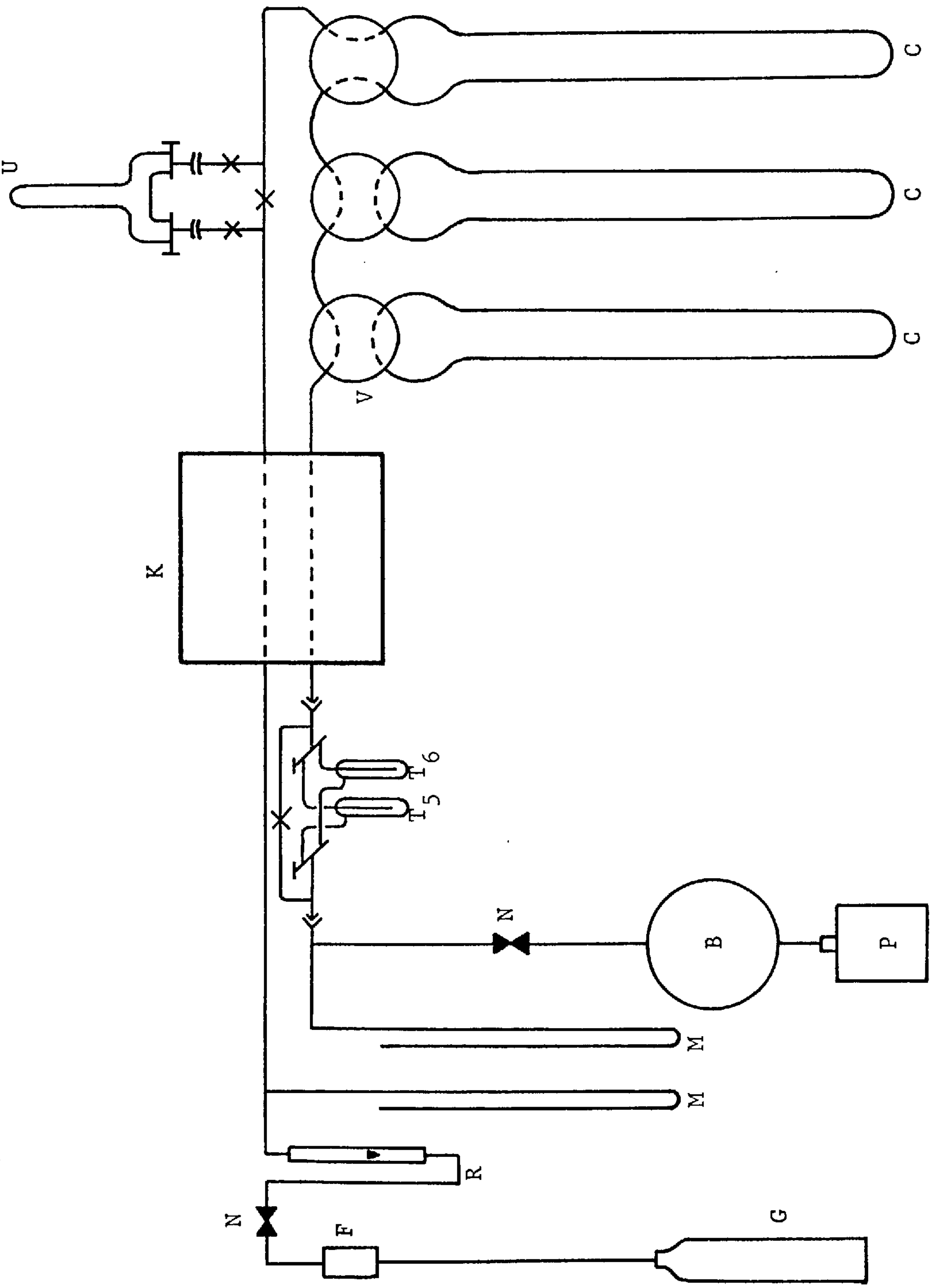
Three columns were incorporated into the unit using Circle Seal P4-418 selector valves, the connections between the columns and the selector valves being made in stainless steel tubing with a teflon-sleeved standard B10 cone at one end and a stainless steel coupling at the other. The columns were maintained at 56°C by vapour jackets supplied from a vapour generator containing acetone. The flow system also incorporated two traps for sample collection, and a Pye katharometer detector. The katharometer was enclosed in an asbestos filled Sindanyo box and was maintained at a temperature of 60°C by a heating mantle powered from a Variac V6HMTF transformer.

The detector formed part of a Wheatstone bridge network powered by a Belix TSS65 transistorised power supply (see Fig. 7). The output from the bridge was fed into a Pye D.C. Amplifier

Key to Figure 6

B	15 l. buffer volume
C	Columns
F	Pressure regulator
G	Carrier-gas cylinder
K	Katharometer
M	Manometers
N	Needle valves
P	Pump
R	Rotameter
T_5, T_6	Cold traps
U	Sample U-tube
V	Column selector valves

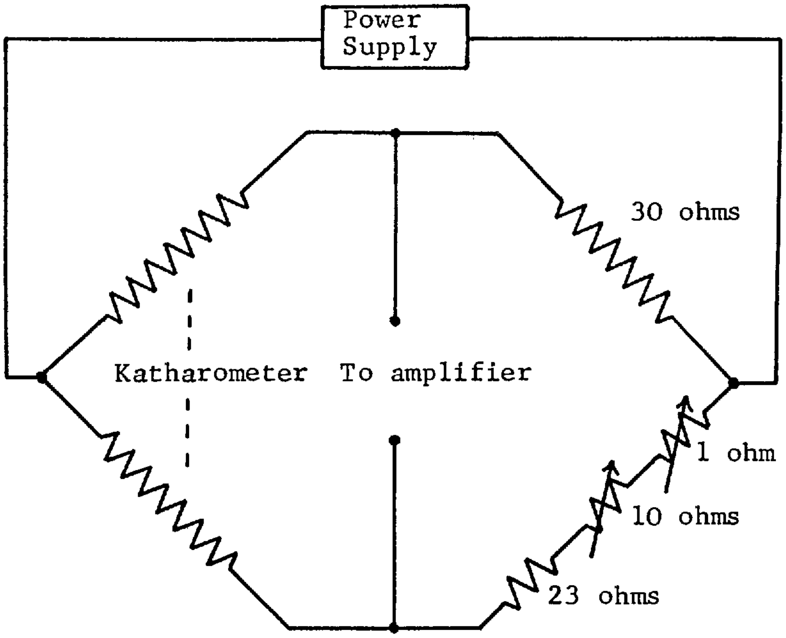
Figure 6



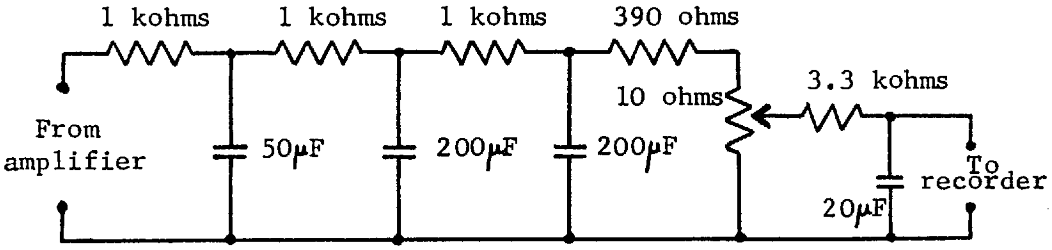
The gas chromatograph

Figure 7

Bridge circuit



Coupling circuit



(Type 11340/S) and the resulting signal was displayed on a Sunvic 10mV. potentiometric recorder. The coupling between the amplifier and the recorder incorporated an attenuator and a fast-response filter network to reject A.C. noise (Fig.7).

Partition columns containing MS 550 silicone oil and polyethylene glycol (Mol.wt 400) were used for the analysis of acetylenic hydrocarbons and of benzene respectively, and a silica gel adsorption column was used for the analysis of hydrogen, methane, ethane and ethylene. In each case, the carrier-gas flow rate was adjusted to give optimum resolution, the height equivalent of a theoretical plate (H.E.T.P.) being used as the criterion for this. The H.E.T.P. is given by the expression: [114]

$$\text{H.E.T.P.} = \frac{L}{5.54}\left[\frac{\text{Peak breadth at } \frac{1}{2} \text{ height}}{\text{Retention distance}}\right]^{\frac{1}{2}}$$

A typical plot of the H.E.T.P. versus flow rate is shown in Fig. 8, and the operating conditions for each column are summarised in Table 4. The detector response was shown to vary linearly with sample size and details of the sensitivity to each of the gases analysed are shown in Table 5.

2.3.4 The extent of carbon formation

The estimation of the carbon deposits was completed by assay of the carbon as carbon dioxide. In order to produce sufficient amounts of carbon for accurate analysis, however, it was necessary to oxidise the carbon produced from ten similar experiments in the same

Figure 8

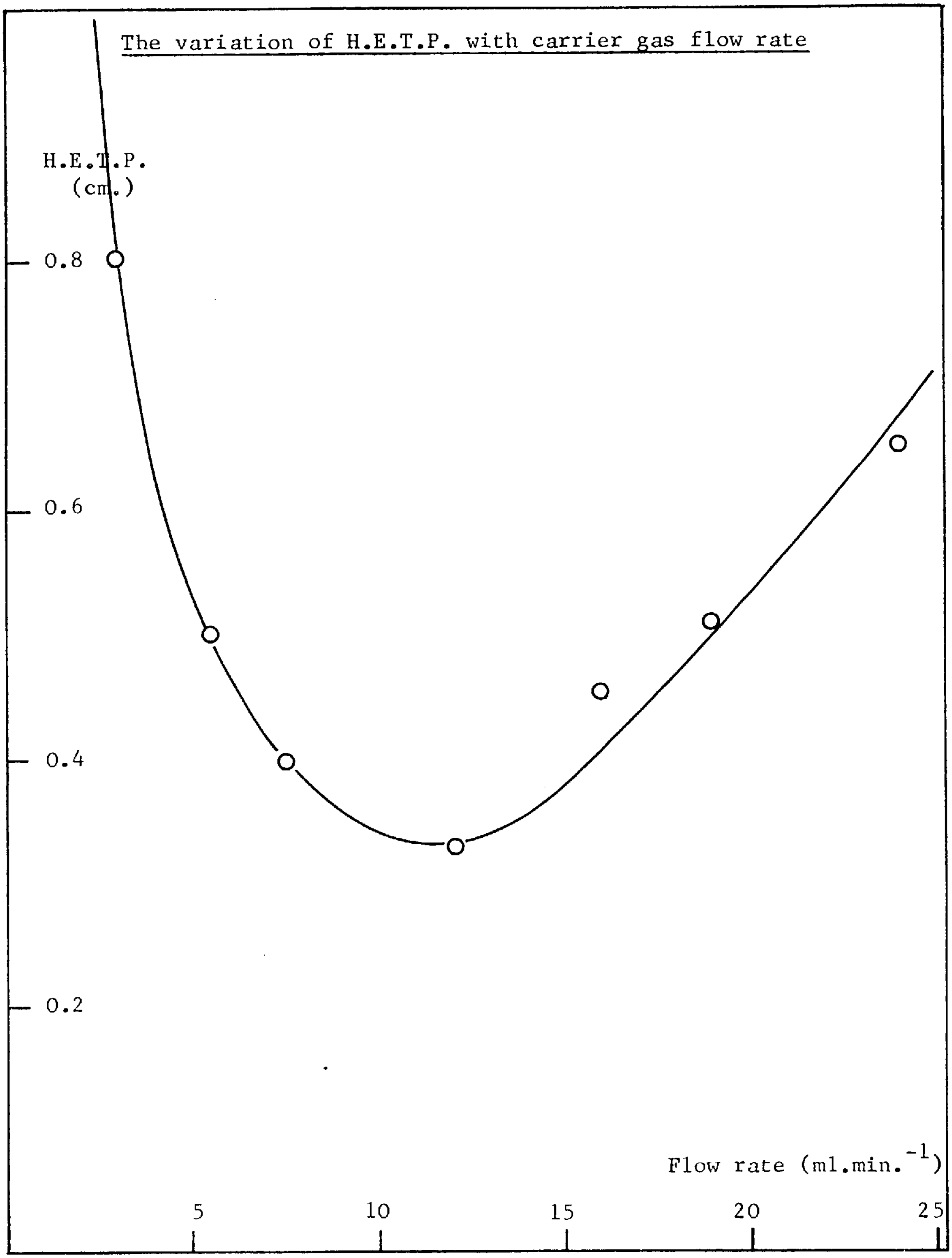

The variation of H.E.T.P. with carrier gas flow rate
H.E.T.P. (cm.)
0.8
0.6
0.4
0.2
Flow rate (ml.min.$^{-1}$)
5
10
15
20
25

Table 4

Gas chromatography specifications

Column	1	2	3
Carrier gas	"Oxygen-free" nitrogen		
Column temperature (°C)	56		
Bridge current (ma.)	196		
Katharometer block temperature (°C)	60		
Composition	20% w/w Silicone oil (MS 550) on 40-60 mesh Embacel.	20% w/w P.E.G. (Mol. wt = 400) on 40-60 mesh Embacel.	Davidson U.S. Grade Silica gel, 30-60 mesh.
Length (ft.)	14	4	6
Inlet pressure (mm. Hg)	828	808	822
Outlet pressure (mm. Hg)	656	748	686
Flow rate (ml. min.$^{-1}$)	12	15	12

Table 5

Response of the detection system to various substances

Compound	Retention time (min.)	Sensitivity (cm.^{2}g.mole.$^{-1}$)
Hydrogen	2.0	3.45×10^7
Methane	3.3	3.30×10^6
Ethane	9.2	3.90×10^5
Ethylene	13.5	1.35×10^5
Acetylene	4.6	1.53×10^6
Propylene	7.0	-
Methylacetylene	7.5	5.25×10^6
Vinylacetylene	10.2	5.50×10^6
Diacetylene	12.0	-
Benzene	10.0	3.90×10^6

vessel. After the carbon had been deposited, the furnace was allowed to cool to room temperature, the reaction vessel was removed and the polymer was cleaned from its neck. The vessel was then reconnected to the vacuum line, evacuated, heated to 750°C, and flushed twice with oxygen (ca. 70 cm. Hg pressure; 10 min. residence time). The carbonaceous deposits were found to be quantitatively converted to carbon dioxide which was removed to a cold-trap immersed in liquid oxygen. The oxygen was pumped off and the carbon dioxide was allowed to expand into a calibrated volume where the pressure of the gas was measured at room temperature.

2.3.5 The nature of the carbonaceous deposits

In order to obtain samples of the carbonaceous deposits suitable for microanalysis, and for electron microscopy and electron diffraction, a reaction vessel (30 cm. long and 1 cm. in diameter) having a wide neck was chosen. The reactant gas was introduced, in the normal way, at a pressure of 200 mm. Hg, and when decomposition was apparently complete, the reaction vessel was pumped out and the reactant gas was again admitted to the same pressure. This procedure was repeated until a sufficiently thick carbon deposit had been obtained. The reaction vessel was then allowed to cool under vacuum and was removed from the vacuum line. The carbon deposit was carefully scraped from the sides of the reaction vessel with a glass spatula. Two types of carbon, viz. a shiny surface deposit and a fluffy black powder, could usually be clearly distinguished and wherever possible samples of the two types of deposit were carefully separated by hand. Before the reaction vessel was reconnected to the vacuum line for collection of the next carbon deposit, it was strongly heated in a current of air to remove all traces of residual carbon.

The carbon samples, collected and separated as described above, were washed in chloroform by ultrasonic vibration and dried at 100°C in vacuo. One portion of each sample was submitted to the Microanalytical Laboratory of the Chemistry Department of Imperial College, where it was analysed for carbon and hydrogen; another portion was examined by electron microscopy and electron diffraction.

2.3.5.1 Electron microscopy and electron diffraction

The carbon deposits were examined in a Siemens Elmiskop-1 electron microscope. Each sample was dusted on to a standard copper grid which had been made tacky by immersion in a solution obtained by treating cellulose adhesive tape with chloroform. It was usually necessary first to grind surface-carbon samples into dust by lightly rubbing them between filter paper.

In addition to taking straightforward electron-microscope photographs of selected areas, so that the particle sizes of the gas-phase carbons could be determined, two types of electron diffraction pattern were obtained. For the first, the electron microscope was used as a simple diffraction camera with all lenses except the two condensers switched off; for the second, a 750μ diameter intermediate aperture was used, and a selected area diffraction pattern was thus obtained. No significant difference was observed between the two types of diffraction patterns taken from the same sample, provided that a sufficiently large selected area aperture was used. Too small an aperture gave rise to marked intensity and breadth variations around the Debye-Scherrer rings, indicating that insufficient carbon was contributing to the diffraction pattern.

The crystallite dimensions, L_{002} and L_{10} (the height and diameter respectively), were obtained from the breadths of the three-dimensional (002) reflection and the two-dimensional (10) reflections respectively, which were measured from diametral microdensitometer traces. The angular breadth of a diffraction ring, B, is related to the mean crystallite diameter, L, by the equation:

$$L = \frac{K\lambda}{B\cos\theta}$$

where λ is the electron wavelength and θ is the Bragg angle, which, for electron diffraction, is so small that $\cos\theta \approx 1$. The crystallographic direction of L is perpendicular to the planes giving rise to the reflection and the value of K is 1.0 for three-dimensional and 1.84 for two-dimensional reflections [6].

The angular breadth of a diffraction ring is also related to the linear half-breadth, Δr, by the equation:

$$RB = \Delta r$$

where R is the camera-length. Since, however,

$$R = \frac{rd}{\lambda}$$

where r is the ring radius and d is the interplanar spacing,

$$B = \frac{\Delta r\lambda}{rd}$$

and $$L = \frac{Krd}{\Delta r}$$

For the (10) reflection, $d = 2.13$Å, and for the (002) reflection $d \approx 3.55$Å. d_{002} varies between 3.45 and 3.65Å in gas-phase carbons, but the error introduced by assuming a value of 3.55Å is less than 3%.

2.3.6 Pyrolysis of vinylacetylene/^{14}C-acetylene mixtures

2.3.6.1 Gas handling

Mixtures of vinylacetylene with ^{14}C-labelled acetylene (obtained from the Radiochemical Centre, Amersham) were prepared in the dosing vessel S_5 (see Fig. 3) and were pyrolysed in a reaction vessel having a volume of ca. 200 ml. in exactly the same manner as has been described for the pyrolysis of vinylacetylene itself (Section 2.3.1.). Prior to carrying out each run using the vinylacetylene/^{14}C-acetylene mixture, the vessel was however first coated with carbon by carrying out nine pyrolysis experiments using a mixture of vinylacetylene and unlabelled acetylene having exactly the same composition as the labelled mixture. Each of these runs was carried out under the same conditions and with the same residence time as was used subsequently for the run using labelled material.

At a known stage in the reaction, the products of pyrolysis were withdrawn from the reaction vessel and trapped in a capillary U-tube surrounded by liquid nitrogen. The products were separated by gas chromatography using a silicone oil column and the residual acetylene and vinylacetylene were trapped out individually in cold traps immersed in liquid nitrogen.

2.3.6.2 The method of radioassay

The method adopted for the radioassay of the residual acetylene and vinylacetylene involved the complete combustion of these compounds to carbon dioxide, the absorption of this carbon dioxide in a suitable reagent, and radioassay of the resulting solution in a windowless proportional counter.

The oxidation was achieved by passing the gases over cupric oxide at 750°C in the presence of a large excess of oxygen. In each case, the trapped gas was allowed to warm up to room temperature and shared with a previously evacuated globe of about one litre capacity (see Fig. 4). Dry, carbon dioxide-free oxygen was then admitted to the trap and globe until a total pressure of about one atmosphere was attained. The remaining sections of the apparatus, including the reaction tube containing the cupric oxide were flushed with oxygen for 30 min. to remove any impurities present, and the contents of the trap and globe were then pumped over the hot cupric oxide, the rate of pumping being controlled by a flow restrictor. The water formed in the oxidation was absorbed by passing the gas over anhydrous magnesium perchlorate, and the carbon dioxide was collected in two cold traps immersed in liquid oxygen.

The carbon dioxide was transferred to a calibrated volume, where its pressure at a known temperature was measured, and absorbed in a known amount of a 40% solution of potassium hydroxide in ethylene glycol. This reagent was chosen because it has a low volatility and absorbs carbon dioxide both quantitatively and irreversibly [115]. The extent of uptake of carbon dioxide by the reagent was followed manometrically, and in order to ensure that all the ^{14}C-carbon dioxide was absorbed, the two cold-traps and the calibrated volume were flushed with about 5 cm.Hg of inactive carbon dioxide and this also was absorbed in the reagent solution.

Samples of the solution were assayed in the counter using nickel planchettes 25 mm. in diameter and 2 mm. deep; about 0.3 ml. of solution was used for each sample. It has been found that samples of this size have 'infinite' thickness when placed in planchettes 25 mm. in diameter, and thus, for a sample of given activity no increase in count rate can be observed even if sample volumes greater than 0.3 ml. are used. Each determination was corrected for background count rate, which was measured using an empty planchette in the counter chamber.

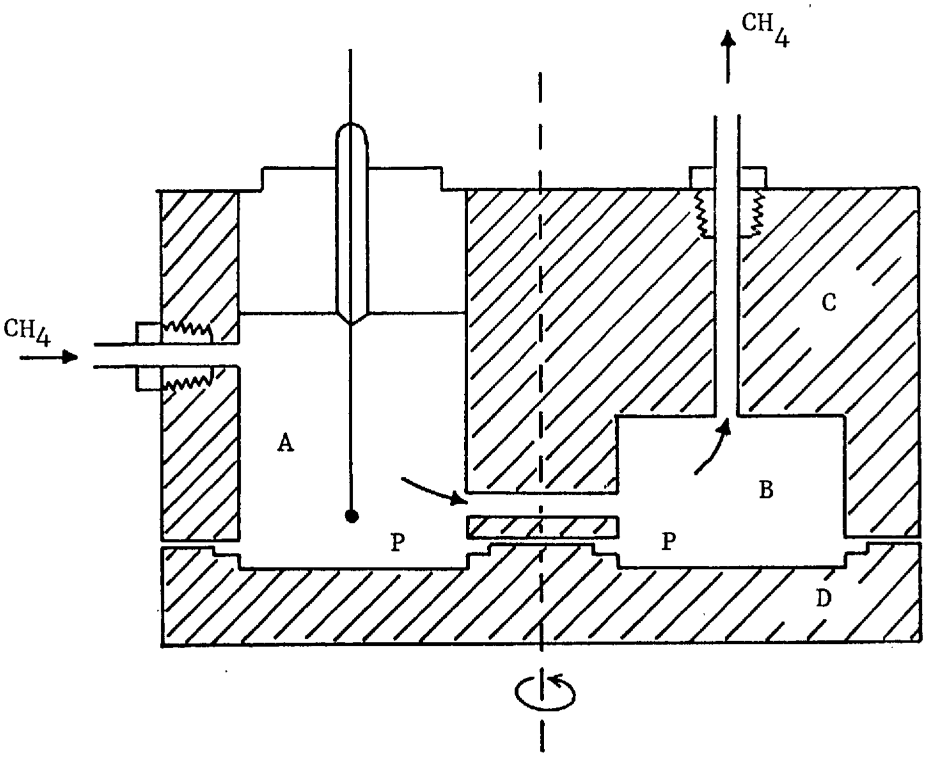
The carbon deposits formed during the pyrolysis were also assayed as carbon dioxide. The carbon was converted to carbon dioxide using the method described in Section 2.3.4., and the carbon dioxide was assayed in the same manner as described above.

2.3.6.3 The radioassay equipment

Since the radioactive decay of carbon-14 results in soft β-rays with a maximum energy of only 0.15 MeV. [116], it is necessary to employ a windowless counter if a high counting efficiency is to be obtained. The instrument used in the present work [117] is shown schematically in Fig. 9. It consisted essentially of two brass cylindrical blocks C and D. The lower block held the planchettes (P)

Figure 9

Sectional view of counter



A	Counting chamber
B	Pre-flushing chamber
C	Fixed block
D	Rotating block
P	Planchettes

and could be rotated so as to bring the planchettes successively into the pre-flushing chamber B and the counting chamber A. The apparatus was enclosed in a lead casing 2 in. thick, and was continuously flushed with 99% methane from which carbon dioxide and water had been removed by passage over soda-lime and anhydrous magnesium perchlorate respectively.

A positive collecting potential of 2.75 kV was applied to the centre wire of the counter, and the output pulses were fed into a H.F. head amplifier and a linear amplifier. The linear amplifier was operated at 20 dB below maximum gain and with time constants of differentiation and integration of 0.15 and 0.5 microseconds respectively. The output pulses from the amplifier were then fed into a decatron scaler, a discriminator level of 12v. being used to suppress interference. The scaler had a paralysis time of 5 microseconds and thus, in the present work where count rates were always less than 3×10^5 counts/min., no coincidence correction was necessary. An operating potential of 2.75 kV was chosen so that the counter was operating in the proportional region, i.e. the pulse height was proportional to the magnitude of the initial ionizing event.

3. RESULTS

3. RESULTS

3. RESULTS

3.1 The pyrolysis of vinylacetylene

3.1.1 General features

Appreciable thermal decomposition of vinylacetylene was found to occur at temperatures above about 300°C, and manometric measurements showed that, over the temperature range studied (300 to 800°C), the reaction in a static system always resulted in an overall decrease in pressure. Typical plots of pressure versus time for various temperatures are shown in Fig. 10. The initial rate of pressure decrease was found, however, to be a complex function of temperature, and to exhibit a maximum at about 500°C.

The two temperature régimes exhibited marked differences as regards the nature of the products. At 550°C, the pyrolysis of vinylacetylene gave rise to polymers and to both surface carbon and soot; at 478°C, however, no soot formation could be detected. It was found also, by gas chromatographic analysis, that although the formation of low molecular weight products such as hydrogen, methane, ethylene and acetylene was significant at 550°C, this was not the case at 478°C.

3.1.2 The nature and extent of formation of the gaseous products

The formation of gaseous products was studied in detail at both 478°C and 550°C. Figs. 11 and 12 show plots of the concentrations of the identifiable products and of residual vinylacetylene as a function of time for each temperature. In addition to hydrogen, methane,

Figure 10

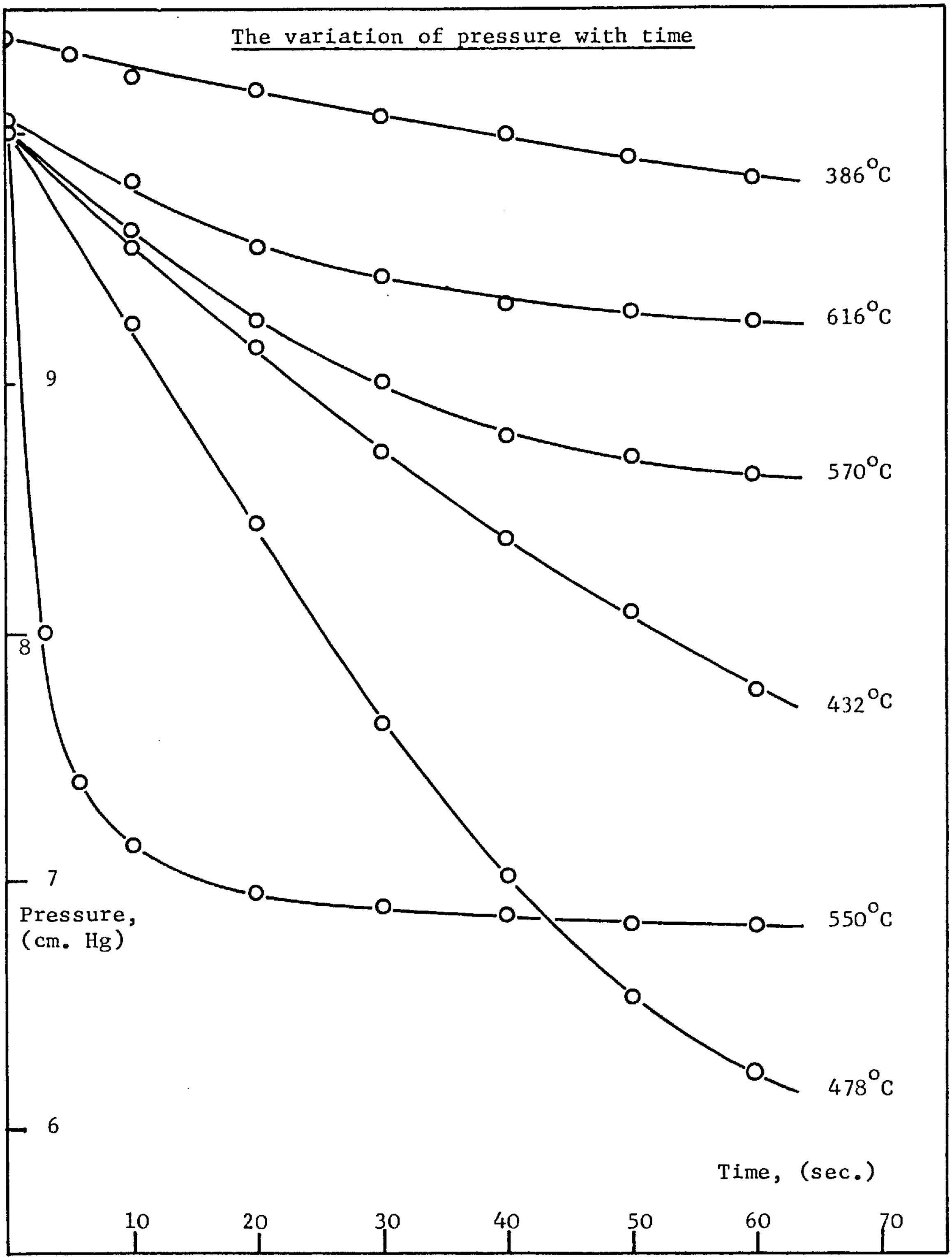

The variation of pressure with time
386°C
616°C
570°C
432°C
550°C
478°C
9
8
7
6
Pressure, (cm. Hg)
Time, (sec.)
10
20
30
40
50
60
70

Figure 11

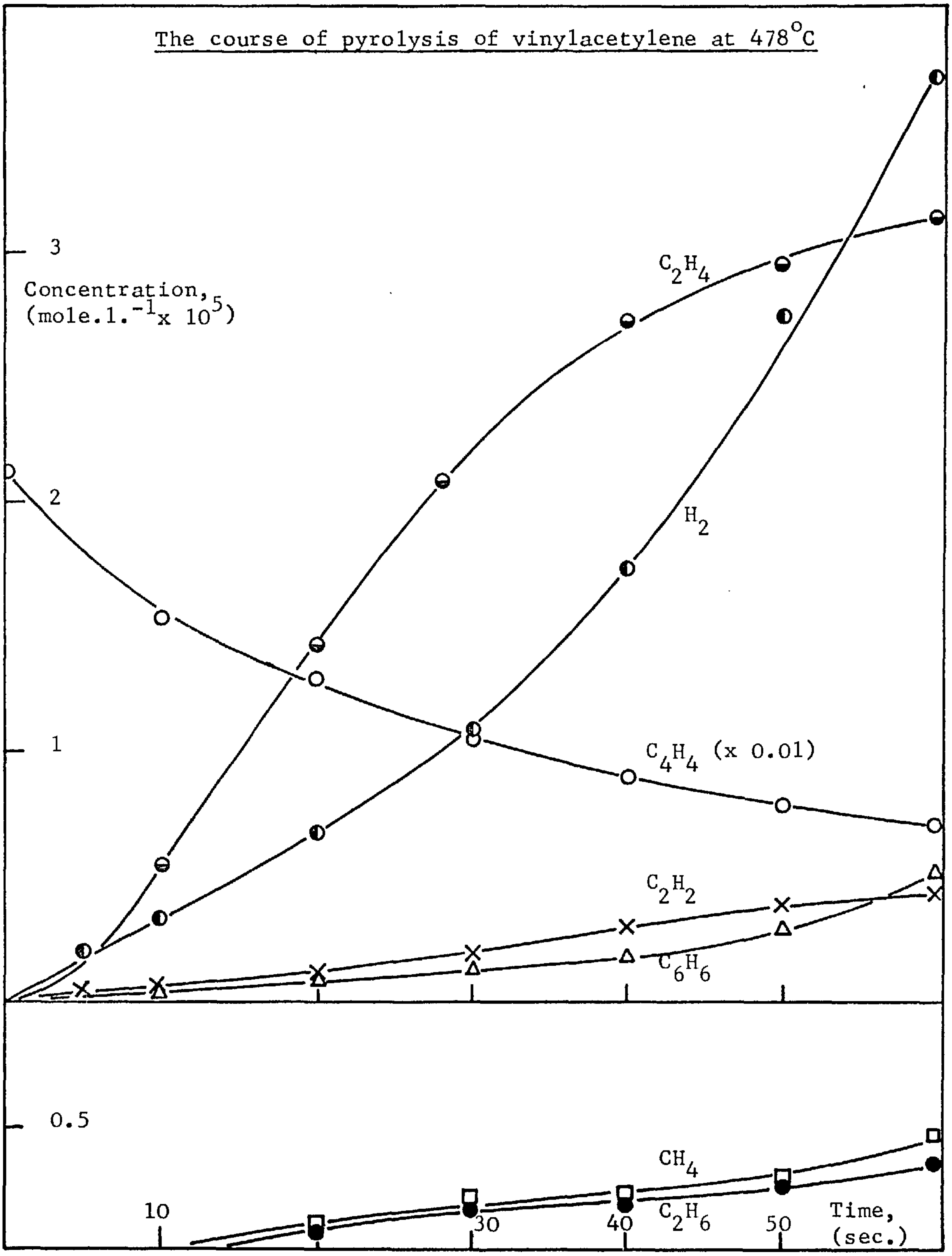
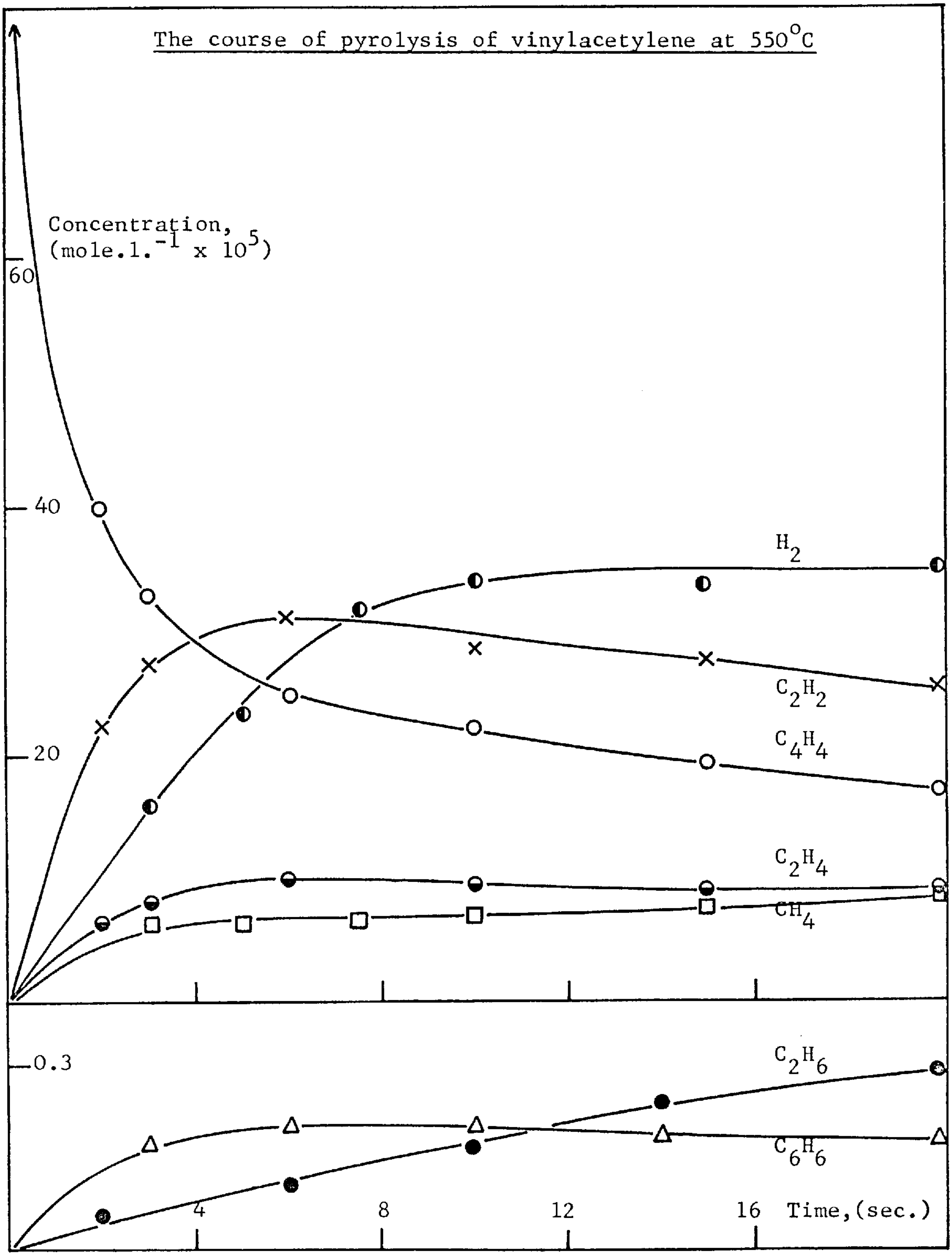

The course of pyrolysis of vinylacetylene at 478°C
Concentration, (mole.l.$^{-1}$x 10^5)
3
2
1
0.5
C_2H_4
H_2
C_4H_4 (x 0.01)
C_2H_2
C_6H_6
CH_4
C_2H_6
10
30
40
50
Time, (sec.)

Figure 12



The course of pyrolysis of vinylacetylene at 550°C ethane, ethylene, acetylene and benzene, traces of propylene, methylacetylene, diacetylene and an unknown C_5 compound were also identified but in amounts insufficient to enable accurate determinations to be made.

From a knowledge of the measured pressure of gases in the reaction vessel, and the total pressure of identifiable products and residual vinylacetylene present after various residence times, it was possible to calculate the total concentration of polymers formed in the reaction. These results (shown graphically in Fig. 13), together with the values of the carbon and hydrogen balances at the same residence times, enabled the apparent average molecular composition of the polymers to be determined. The composition was found to increase with time from about C_8H_8 to about $C_{11}H_{11}$ (Table 6).

3.1.3 The kinetics of the decomposition

The analytical results showed that, at 478°C, the gaseous products accounted for only a very small proportion of the vinylacetylene consumed, and that the major part of the reacted vinylacetylene was converted to polymers. Furthermore, the initial composition of the polymers suggested that at least in the early stages it might be possible to represent the reaction by the simple equation

$$2\ C_4H_4 \longrightarrow C_8H_8$$

If the reaction is second order with respect to vinylacetylene, then

$$- d \frac{[C_4H_4]}{dt} = k\ [C_4H_4]^2$$

Figure 13

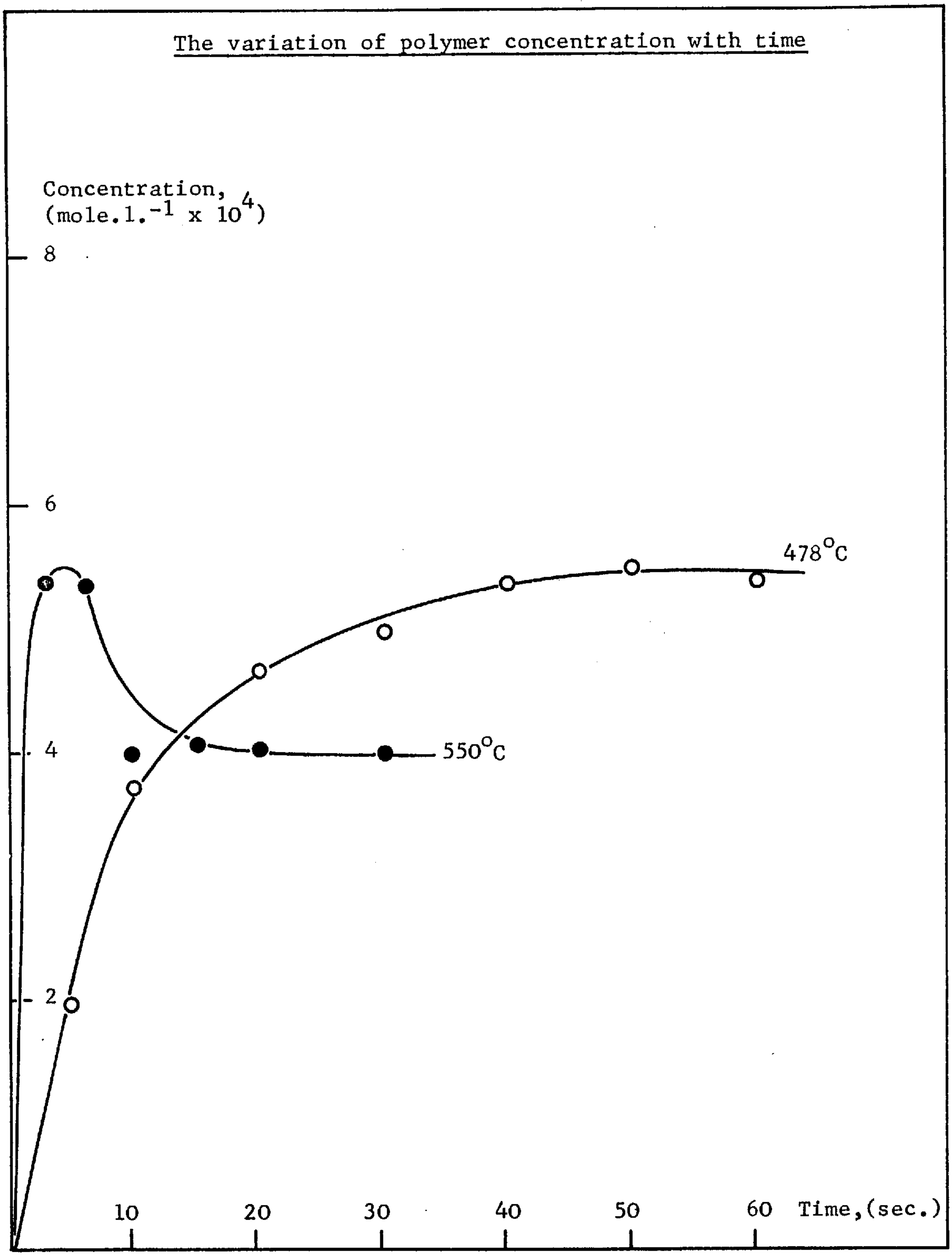

The variation of polymer concentration with time
Concentration,
(mole.1.$^{-1}$ x 10^4)
8
6
4
2
10
20
30
40
50
60
Time,(sec.)
478°C
550°C

Table 6

The variation of the average molecular composition of the polymers with residence time at 478 and 550°C

Temperature: 478°C		Temperature: 550°C	
Time (sec.)	Composition	Time (sec.)	Composition
10	C_7H_7	5	C_8H_6
20	C_7H_7	10	$C_{10}H_8$
30	C_8H_8	15	$C_{11}H_8$
40	C_9H_9	20	$C_{11}H_8$
50	$C_{10}H_{10}$	30	$C_{12}H_9$
60	$C_{11}H_{11}$		

where k is the rate constant. Integration of this equation gives

$$\frac{1}{[C_4H_4]} = kt + \text{Constant}$$

so that a plot of the reciprocal of the vinylacetylene concentration versus time should be linear and of slope k. For a second order reaction, the rate constant can, therefore, be determined from measurements of the reactant concentration as a function of time. The most satisfactory method of determining the concentration of reactant is by direct analysis, but it was hoped that it might also be possible to determine the concentration of vinylacetylene from manometric measurements.

For a dimerisation reaction, the total pressure at time t (p_t) will be given by

$$p_t = p_{C_4H_4} + p_{C_8H_8}$$

where $p_{C_4H_4}$ and $p_{C_8H_8}$ are the partial pressures of vinylacetylene and the dimer respectively. Since however,

$$p_{C_8H_8} = \frac{p_o - p_{C_4H_4}}{2}$$

where p_o is the initial pressure,

$$p_{C_4H_4} = 2p_t - p_o$$

and

$$[C_4H_4] = \frac{2p_t - p_o}{RT}$$

where R is the gas constant and T is the absolute temperature.

A comparison of the results obtained by analysis and from manometric measurements at 386 and 478°C is shown in Fig. 14. It can be seen that, in the initial stages of the reaction, the degree of correlation is very satisfactory.

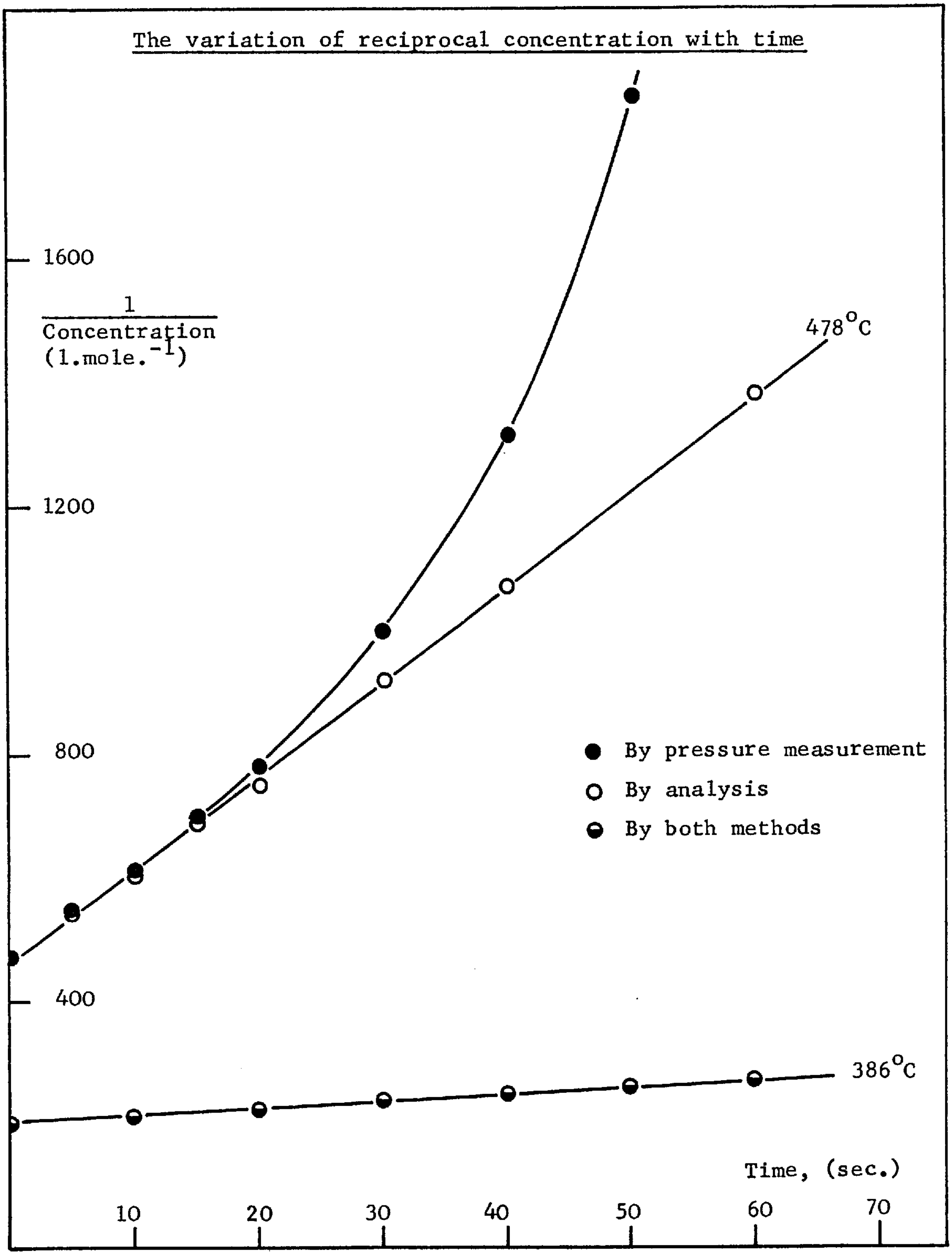
Values of the second order rate constants have been determined over a range of temperatures from 336 to 478°C. The results are given in Table 7 and are shown on an Arrhenius plot in Fig. 15. The Arrhenius plot yields an overall activation energy for the disappearance of vinylacetylene of 28 kcal.mole.$^{-1}$ over the temperature range studied. Above 550°C the rate of disappearance of vinylacetylene was found to be extremely high. Unfortunately, however, the rate could not be determined accurately since pressure measurements could not be used, and analysis of the reaction mixture after residence times of only ca. 1 sec. could not be achieved in the static system.

The independence of the rate constant at a given temperature on the initial pressure of vinylacetylene is shown in Table 8.

3.1.4 The kinetics of carbon formation

At 478°C, the pyrolysis of vinylacetylene resulted in the deposition of surface carbon, and a study was made of the extent and rate of formation of this product at this temperature. At lower temperatures, the amount of surface carbon was unfortunately too small to permit accurate assay, and at higher temperatures, soot was also formed. A significant proportion of this soot remained suspended in the gas phase and was lost when the reaction vessel was evacuated.

Figure 14



The variation of reciprocal concentration with time

Figure 15

The variation of rate constant with temperature

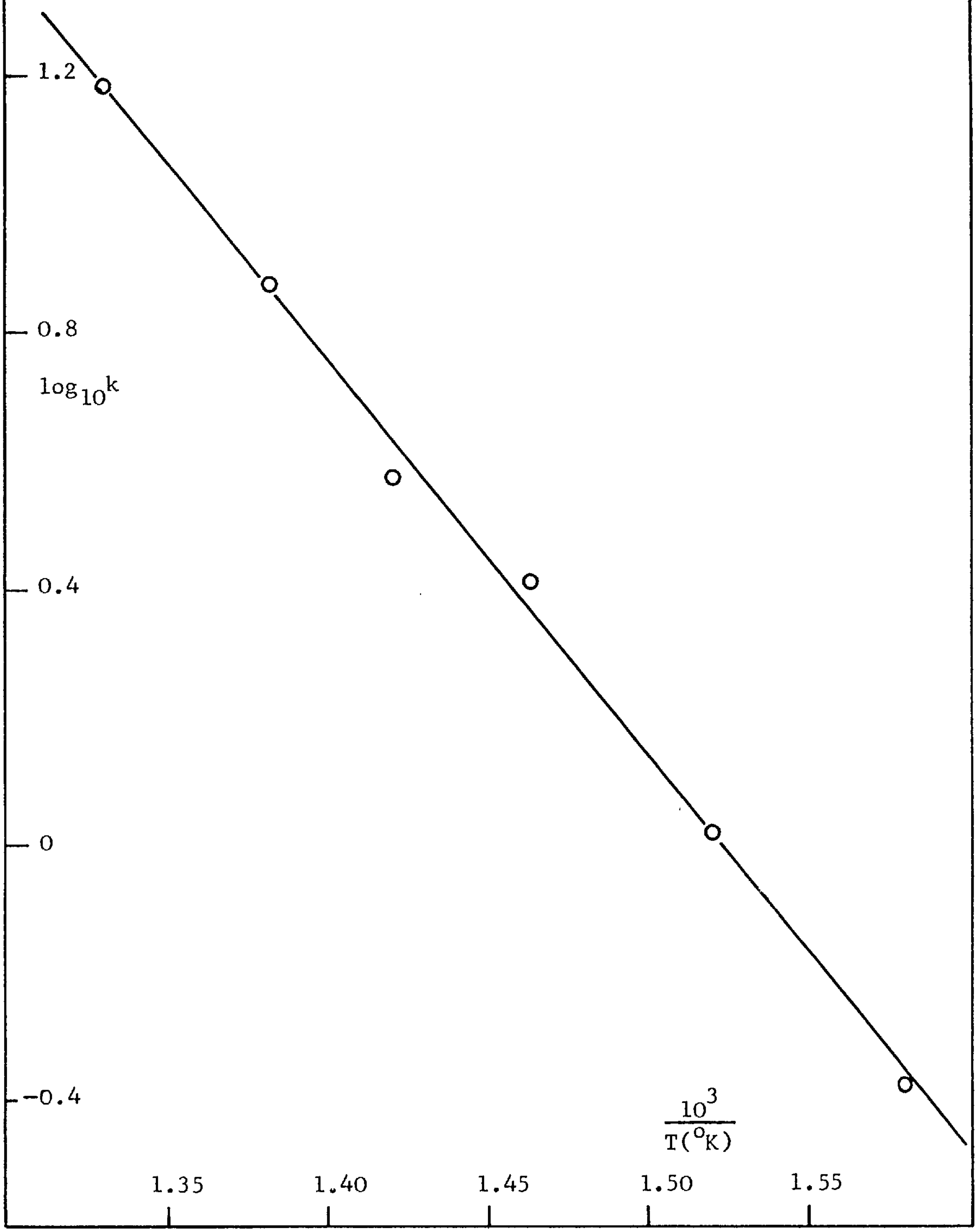


Table 7

Variation of rate constant with temperature

Temperature (^{o}C)	Rate constant (k) ($l.mole.^{-1}sec.^{-1}$)
336	0.296
360	0.417
386	1.04
410	2.60
432	3.76
450	7.54
478	15.40

Table 8

Variation of rate constant with initial pressure

Temperature: 386°C		Temperature: 478°C	
Initial pressure (cm.Hg)	Rate constant (l.mole.$^{-1}$sec.$^{-1}$)	Initial pressure (cm.Hg)	Rate constant (l.mole.$^{-1}$sec.$^{-1}$)
33.7	1.18	10.0	16.09
29.0	1.19	7.5	15.63
24.9	1.16	5.0	14.85
22.3	1.18	3.0	15.40
20.0	0.98	2.0	13.90
17.6	1.13		
15.7	0.98		
13.8	1.15		
12.0	1.09		
10.4	0.96		
7.0	0.91		

The results at 386°C were obtained manometrically; those at 478°C were obtained by analysis

The amount of surface carbon deposited was estimated by measurement of the amount of carbon dioxide formed from its combustion. The method was tested by determining the amount of carbon dioxide formed from the combustion of a weighed amount of carbon which had been added to a clean reaction vessel; the accuracy of the method was found to be ± 5%.

Experiments were first carried out to determine whether or not the amount of carbon deposited depended on the state of the reaction vessel. A number of runs was carried out in the reaction vessel each with an initial pressure of vinylacetylene of 10 cm.Hg, and at the same residence time (60 sec.), and the total amount of carbon deposited was determined. A plot of the amount deposited against the number of runs carried out is shown in Fig. 16 from which it is apparent that for six or more consecutive runs, the amount of carbon deposited is a linear function of the number of runs. Initially, however, the amount of carbon deposited per run is significantly higher.

A study was also made of the amount of carbon deposited in ten consecutive runs at the same initial pressure and residence time. The results are summarised in Fig. 17. For curves A, B, D and E each determination was made using an initially "carbon-free" reaction vessel. For each point on curve C, however, the reaction vessel was first coated with 1.7 mg. carbon (obtained from ten pyrolyses, each at an initial pressure of 10 cm.Hg and a residence time of 60 sec.). The rate of carbon deposition appears to be independent of the presence of a carbon surface; it is, however, dependent on the initial pressure

Figure 16

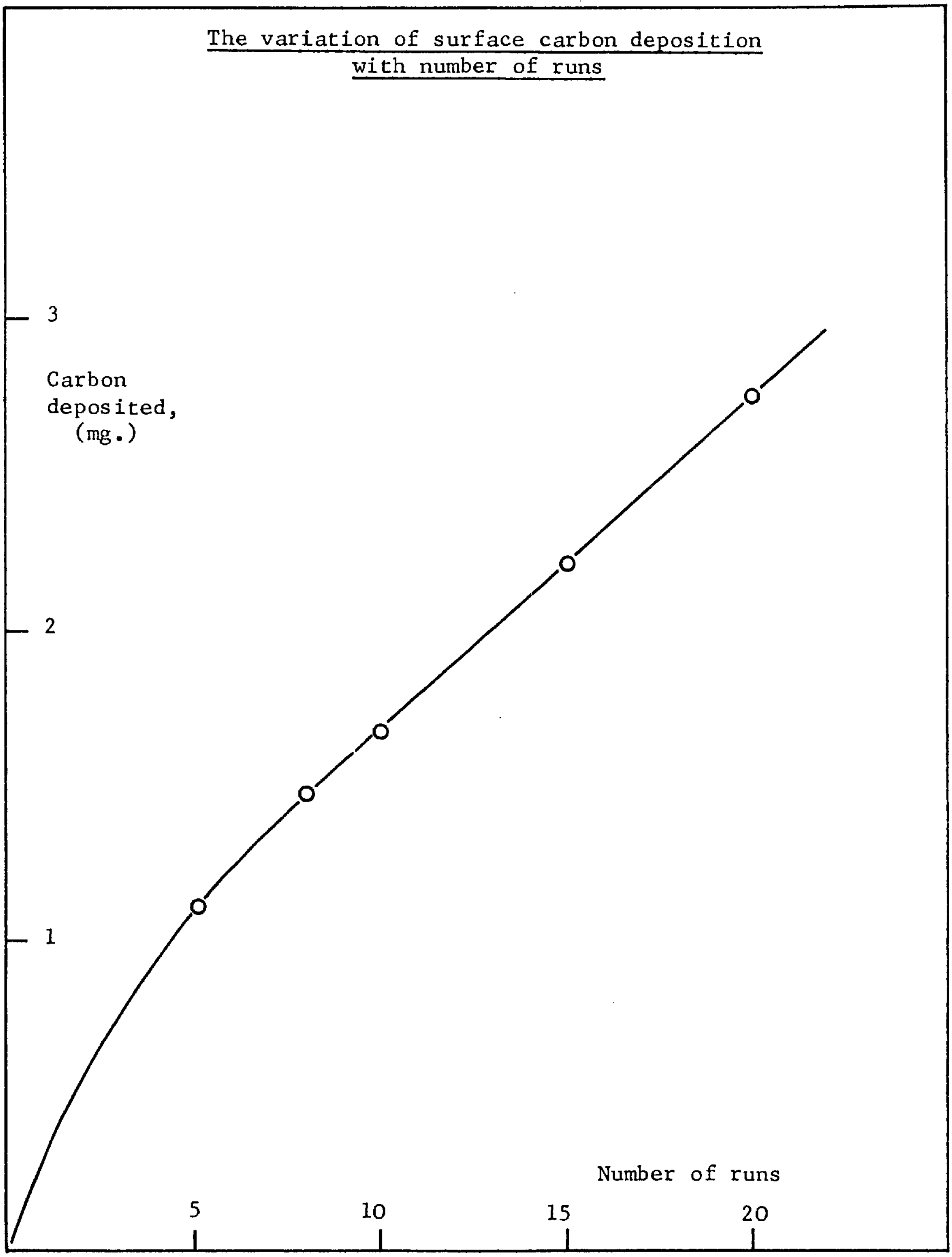
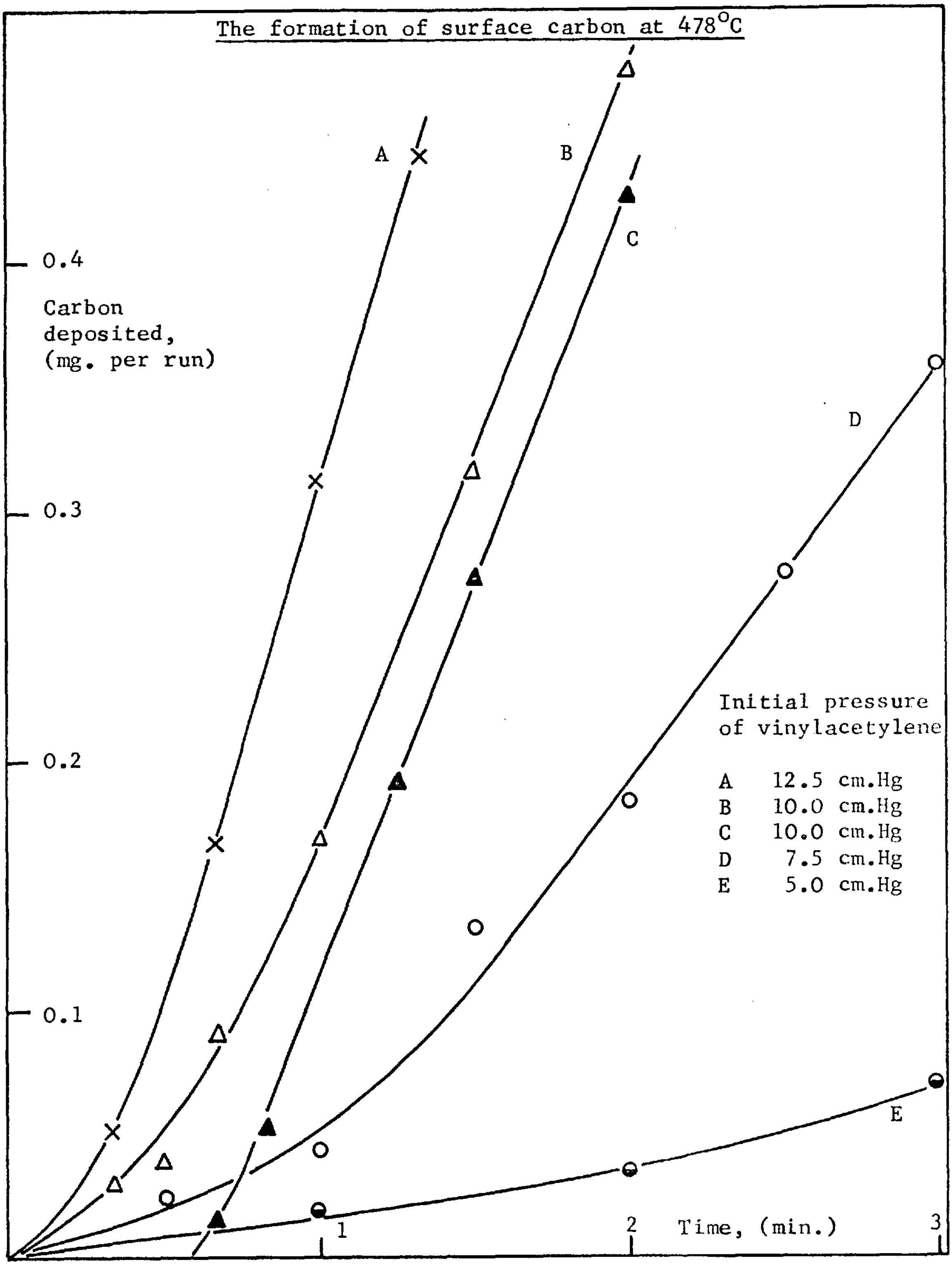

The variation of surface carbon deposition with number of runs
3
Carbon deposited, (mg.)
2
1
Number of runs
5
10
15
20

Figure 17



The formation of surface carbon at 478°C of vinylacetylene.

If the rate of surface carbon formation ($^{dC}/dt$) is given by

$$\frac{dC}{dt} = k'[C_4H_4]_o^n$$

where n is the order of the reaction with respect to vinylacetylene, $[C_4H_4]_o$ is the initial pressure of vinylacetylene and k' is the rate constant, then

$$\log\left(\frac{dC}{dt}\right) = n \log [C_4H_4]_o + \log k$$

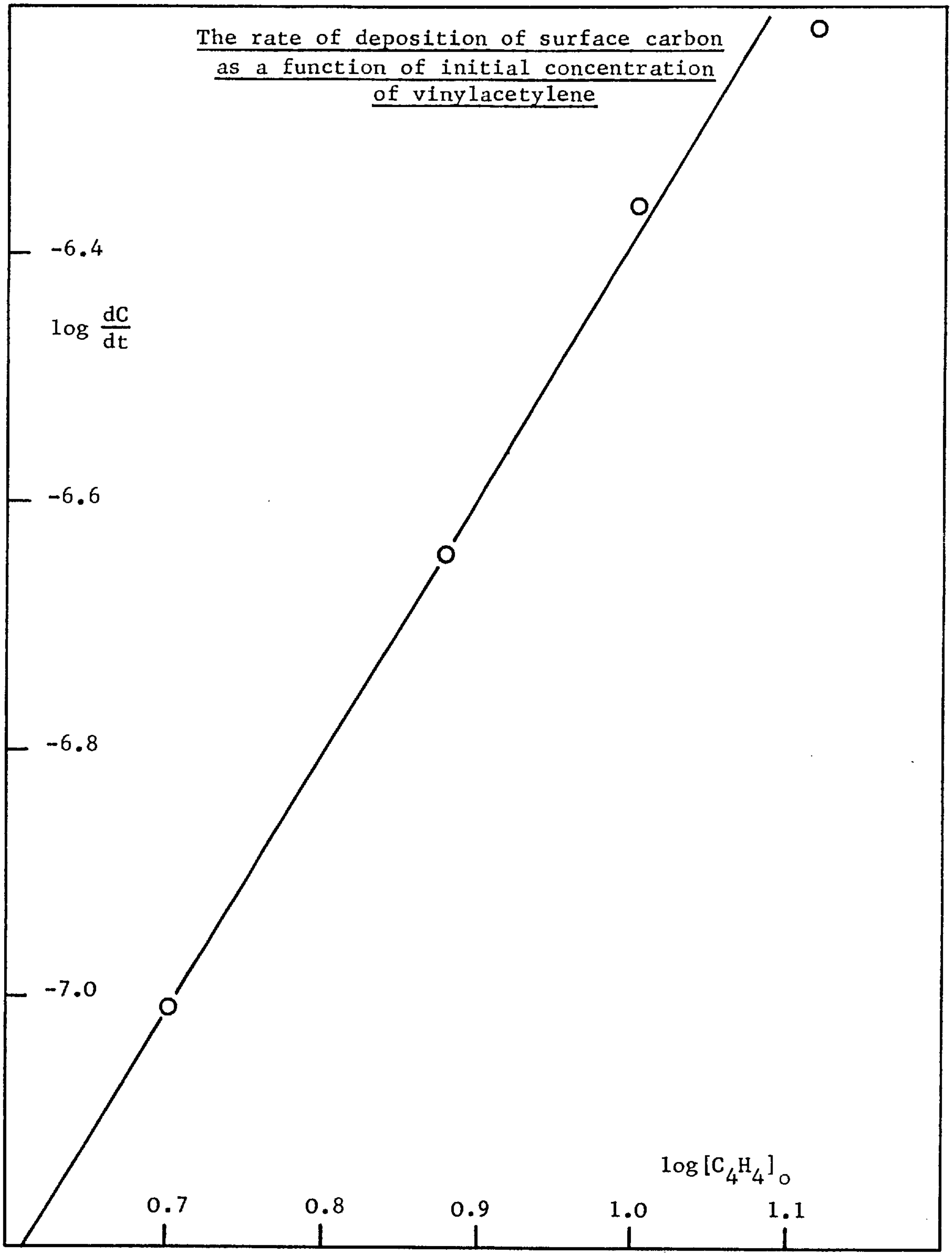
and a plot of log ($^{dC}/dt$) versus log $[C_4H_4]_o$ should be linear and of slope n (Fig. 18). The value of n, the apparent order of reaction for carbon formation, is two. The rate of formation of carbon as a function of the initial pressure of vinylacetylene is shown in tabular form in Table 9. The results show that k' = 4.1×10^{-9} g.atom. cm. Hg^{-2} $sec.^{-1}$ or 2×10^{-5} g.atom.$l.^{2}$$mole.^{-2}$$sec.^{-1}$.

3.1.5 The nature of the carbonaceous deposits

3.1.5.1 Electron microscopy

The gas-phase and surface carbons formed during the pyrolysis of vinylacetylene were readily distinguishable. The former were fluffy black deposits whereas the latter consisted of grey, lustrous platelets which adhered well to the surface of the reaction vessel. Under the electron microscope, the surface carbons were found to consist of platelets about 5000Å thick. The platelets were quite smooth on the side adjacent to the surface of the reaction vessel, but the other side was invariably covered with spherically shaped growths of diameter

Figure 18



The rate of deposition of surface carbon as a function of initial concentration of vinylacetylene

Table 9

Variation of rate of surface carbon formation with initial pressure at 478°C

Initial pressure (cm.Hg)	Rate of C formation (g.atom.sec.$^{-1}$)	$\log [C_4H_4]_o$	$\log \left(\frac{dC}{dt}\right)$
5.0	1.02×10^{-7}	0.699	-6.992
7.5	2.29×10^{-7}	0.875	-6.640
10.0	4.36×10^{-7}	1.000	-6.361
12.5	6.03×10^{-7}	1.097	-6.219

varying from 0.1 to 1.5μ. The gas-phase deposits were found to consist of spherical particles having diameters ranging from 1000 to 2500Å.

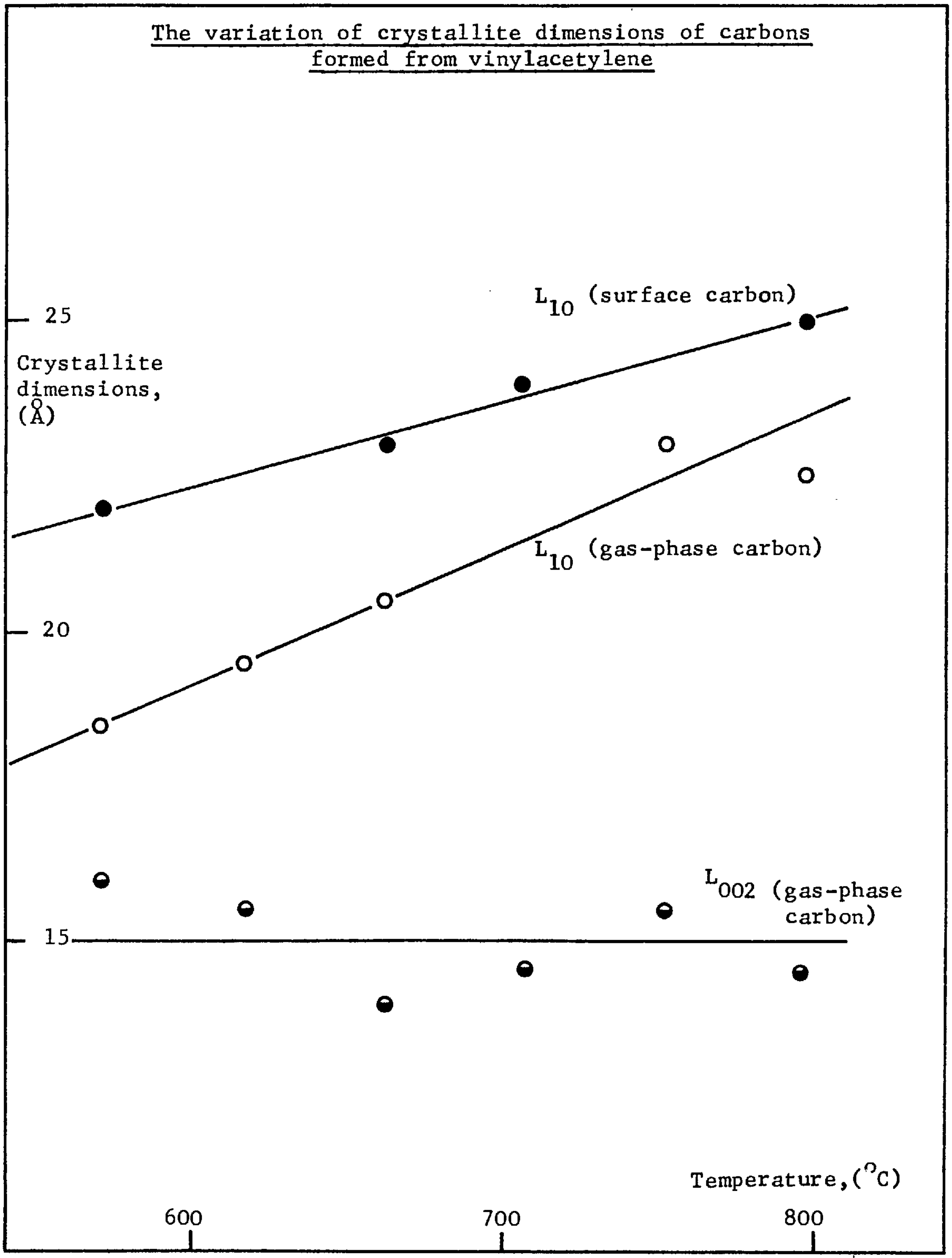
3.1.5.2 Electron diffraction

The gas-phase carbons gave rise to diffraction patterns consisting of three main rings corresponding to the (002) three-dimensional reflection and the (10) and (11) two-dimensional reflections. The (002) ring was always absent from the surface carbon diffraction patterns indicating that the electron beam was perpendicular to the basal plane of the crystallites. Since the beam was also perpendicular to the plane of the platelets, the crystallite basal plane must be parallel to this plane and hence to the surface on which the platelets were deposited. This orientation is typical of pyrolytic surface deposits.[13,14]

Values of the crystallite dimensions were calculated from the (002) and (10) reflections for both types of deposit. The (11) reflection was not used since it proved to be rather diffuse and ill-defined.

The variation with temperature of formation of the crystallite dimensions of the carbons was studied over the temperature range 550 to 800°C, and the results are shown in Fig. 19. The crystallite diameters of both the surface and gas-phase carbons increased with temperature of formation. The height of the crystallites in the gas-phase carbons was approximately independent of the temperature of formation. Each reported crystallite dimension is in fact the mean of at least twelve separate determinations of the peak breadth and ring diameter for a

Figure 19



The variation of crystallite dimensions of carbons formed from vinylacetylene given sample, and when sufficient material was available, diffraction patterns were also obtained from a number of separate samples. The results were always found to agree within the limits of experimental error ($\pm$ 1Å).

3.1.5.3 Elemental analysis

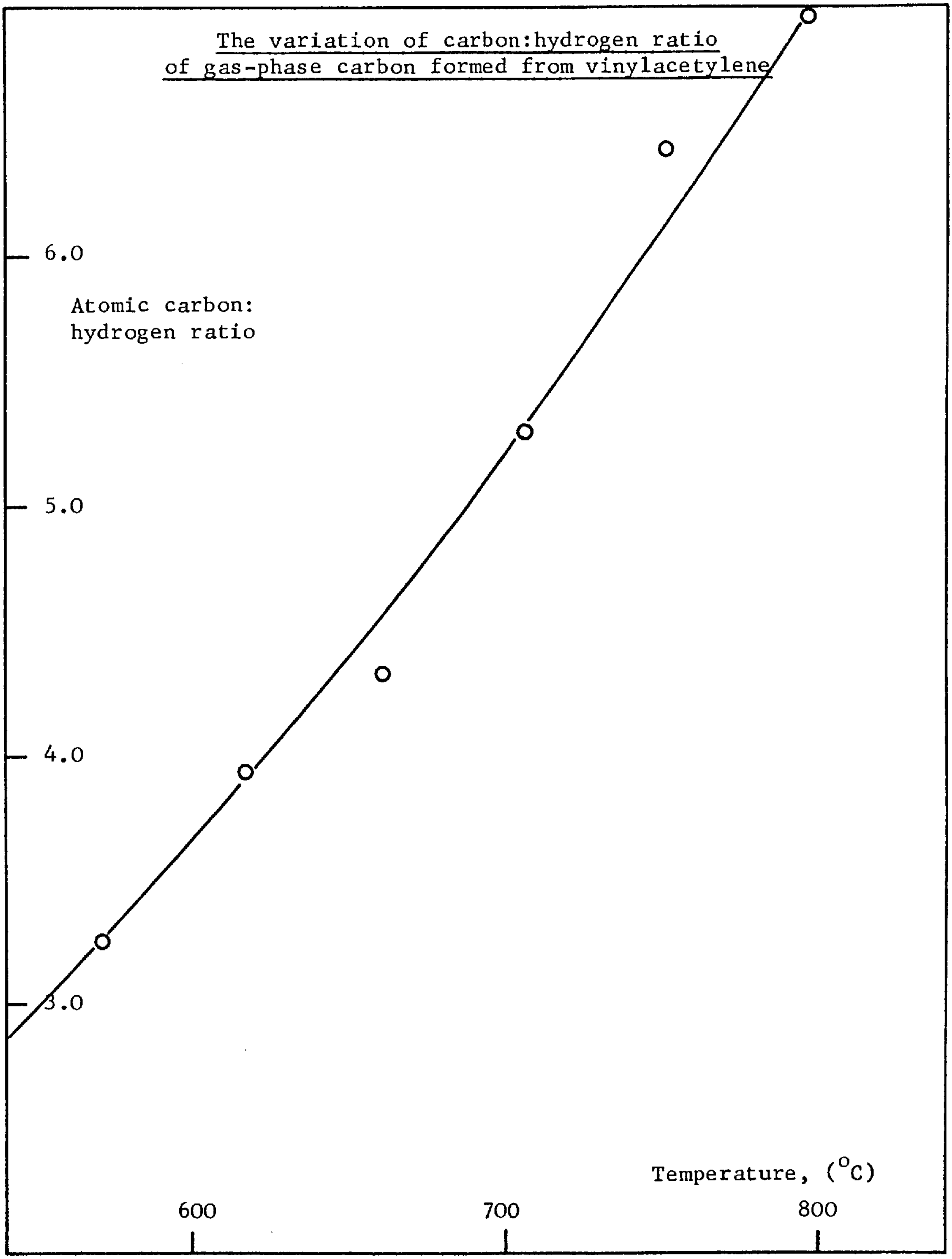
Unfortunately, in the case of the surface carbons, sufficient material for analysis (ca. 4 mg.) was not available. For the gas-phase carbons, however, it was possible to study the variation of carbon: hydrogen ratio with the temperature of formation. The results in Fig. 20 show that the carbon:hydrogen ratio increases steadily with temperature of carbon formation.

3.2 The nature of the carbonaceous deposits formed from acetylene

In view of the possible importance of vinylacetylene as an intermediate in carbon formation from acetylene, it was decided to make a comparative study of the carbonaceous deposits formed from each compound. To obtain sufficient carbon from acetylene, it was necessary, however, to pyrolyse this compound at higher temperatures than had been used for vinylacetylene. The formation of carbon from acetylene was very slow at temperatures below about 700°C and significant amounts of carbon were formed only at temperatures above 750°C.

The pyrolysis of acetylene resulted in the formation of both gas-phase and surface carbons, and under the electron microscope the two types of carbon showed strong resemblance to the carbons formed from vinylacetylene. The gas-phase carbons consisted of spherical

Figure 20

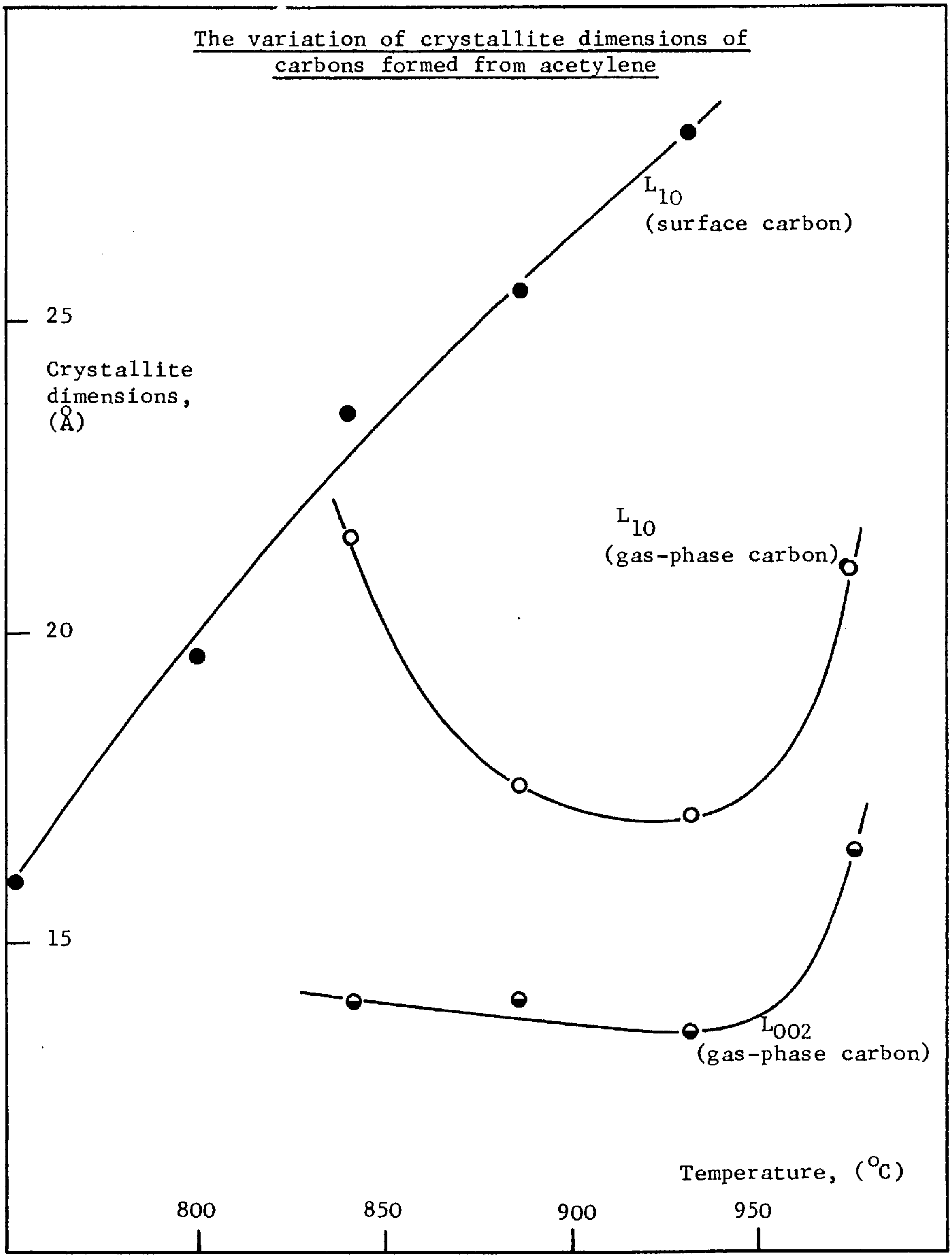


The variation of carbon:hydrogen ratio of gas-phase carbon formed from vinylacetylene particles having diameters ranging from 1000 to 8000Å, and the surface carbons were again characterised by the formation of spherical growths of varying size (0.1 to 1.5μ in diameter) which were apparently attached to the main deposit.

The variation of the crystallite dimensions of these carbons with temperature of formation was studied over the temperature range 750 to 975°C, and the results are shown in Fig. 21. The diameters of the crystallites in the surface carbons formed from acetylene increased with increasing temperature of formation in the same way as those in the surface carbons formed from vinylacetylene. On the other hand, the crystallite diameters of the gas-phase deposits at first decreased with increasing temperature of formation but, after passing through minimum values at about 930°C, increased again quite markedly as the temperature of formation was further raised.

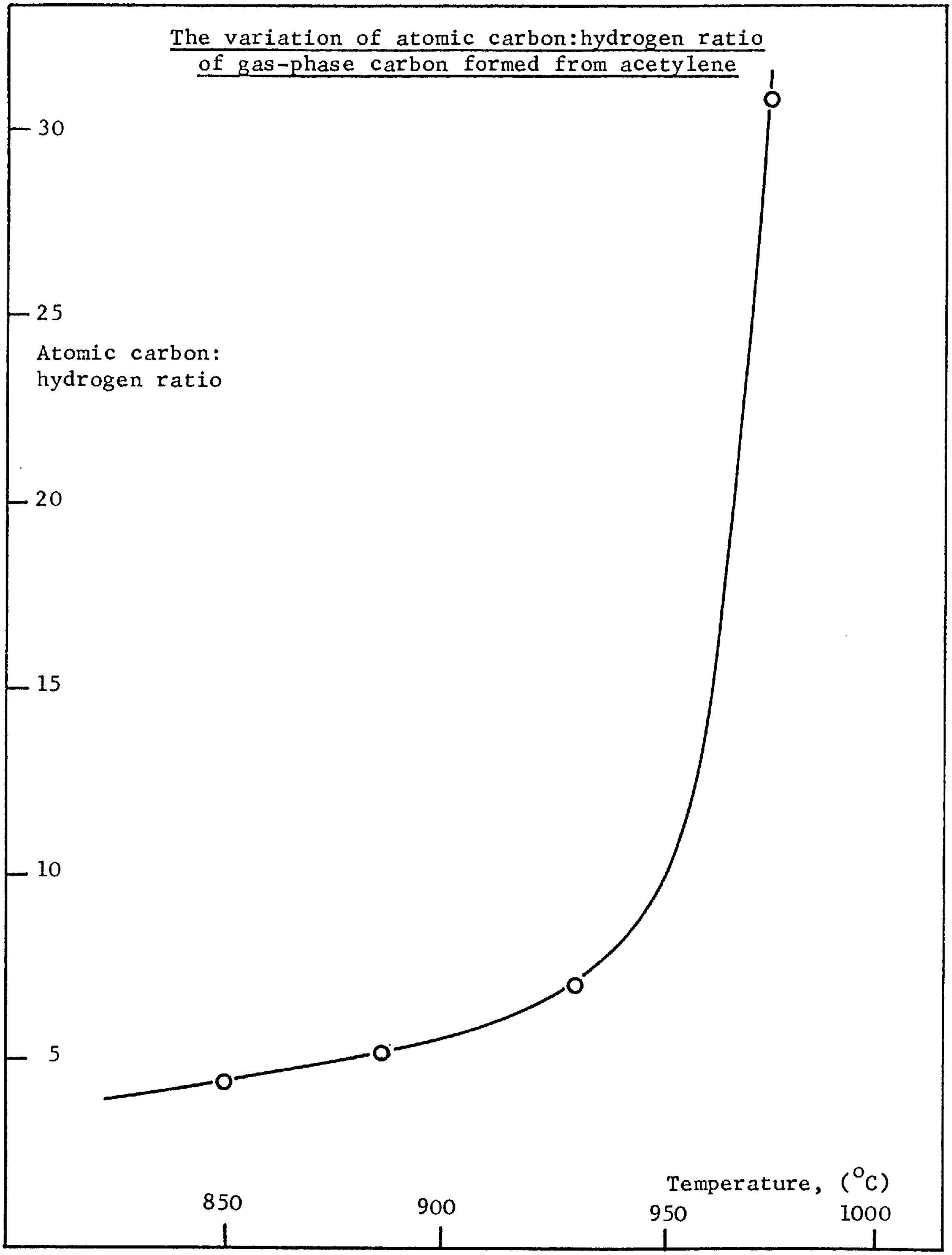
This increase in the crystallite dimensions over the temperature range 930 to 975°C was found to be paralleled by a similarly marked increase in the carbon:hydrogen ratio. Over the temperature range 840 to 930°C, the carbon:hydrogen ratio of the gas-phase carbons was found to increase slowly from 4.2 to 7. The gas-phase carbon formed at 975°C was found, however, to have a carbon:hydrogen ratio of 30.8 (Fig. 22). In the case of the surface carbons formed from acetylene, it was not possible to detect the presence of hydrogen. Since the limit of detection for the method of analysis used was 0.1% by weight, the atomic carbon:hydrogen ratio in these carbons must be greater than 80.

Figure 21



The variation of crystallite dimensions of carbons formed from acetylene

Figure 22



The variation of atomic carbon:hydrogen ratio of gas-phase carbon formed from acetylene

3.3 The influence of acetylene on the pyrolysis of vinylacetylene

3.3.1 The pyrolysis of vinylacetylene/acetylene mixtures

An investigation was made of the influence of acetylene on the pyrolysis of vinylacetylene at 478°C. Experiments were performed to determine whether or not the acetylene influenced either the rate of polymerisation of the vinylacetylene or the extent of formation of surface carbon. In the first instance, vinylacetylene mixtures containing 5% and 28.75% acetylene were pyrolysed at an initial pressure of 10.5 cm.Hg, and samples of the reaction mixture, taken after residence times of either 60 or 120 seconds, were analysed by gas chromatography for residual vinylacetylene and acetylene. Each hydrocarbon was also pyrolysed individually at an initial pressure equal to its partial pressure in the mixture and the concentrations of acetylene and vinylacetylene present after 60 or 120 seconds were again determined.

The total amounts of acetylene and vinylacetylene present when each gas was pyrolysed individually were compared with the amounts obtained on pyrolysis of the mixture. The results are presented in Tables 10 and 11 and it can be seen that the presence of acetylene does not influence the pyrolysis of vinylacetylene to any appreciable extent. It is also apparent that, under these conditions, the pyrolysis of acetylene is very slow.

The effect of acetylene on the formation of surface carbon from vinylacetylene was investigated by direct comparison of the amounts of carbon deposited during the pyrolysis of vinylacetylene

Table 10

The effect of acetylene on the pyrolysis of vinylacetylene at 478°C
Pyrolysis of mixture containing 5% acetylene

	Pyrolysis of vinylacetylene	Pyrolysis of acetylene	Pyrolysis of mixture (5% acetylene)
Initial concn. vinylacetylene (mole.l.$^{-1}$ x 10^4)	21.36	-	21.36
Initial concn. acetylene (mole.l.$^{-1}$ x 10^4)	-	1.12	1.12
Concn. of vinylacetylene after 60 sec. (mole.l.$^{-1}$ x 10^4)	6.87	0	6.89
Concn. of acetylene after 60 sec. (mole.l.$^{-1}$ x 10^4)	0.04	1.12	1.08

Table 11

The effect of acetylene on the pyrolysis of vinylacetylene at 478°C Pyrolysis of mixture containing 28.75% acetylene

	Pyrolysis of vinylacetylene	Pyrolysis of acetylene	Pyrolysis of mixture (28.75% acetylene)
Initial concn. vinylacetylene (mole.l.$^{-1}$ x 10^4)	16.02	-	16.02
Initial concn. acetylene (mole.l.$^{-1}$ x 10^4)	-	6.47	6.47
Concn. of vinylacetylene after 120 sec. (mole.l.$^{-1}$ x 10^4)	4.05	0.012	3.92
Concn. of acetylene after 120 sec. (mole.l.$^{-1}$ x 10^4)	0.02	6.47	6.49

with that deposited under similar conditions during the pyrolysis of vinylacetylene/acetylene mixtures. The initial pressure of the hydrocarbon mixture was again such that the partial pressure of vinylacetylene in the mixture was equal to the initial pressure of vinylacetylene used in experiments on this hydrocarbon alone. The amounts of carbon deposited were compared directly since it was found that the amount of carbon formed during the pyrolysis of acetylene was very small. For each hydrocarbon or hydrocarbon mixture, determinations were made of the total amount of carbon deposited from 10 runs each at the same initial pressure and with the same residence time.

The results obtained are presented in Table 12. It was found that the presence of 5% acetylene in vinylacetylene had no effect on the amount of carbon deposited. When 28.75% acetylene was present, however, a significant reduction in the amount of carbon deposited was observed.

3.3.2 The pyrolysis of vinylacetylene/^{14}C-acetylene mixtures

In order to obtain further information about the formation of surface carbon during the pyrolysis of vinylacetylene/acetylene mixtures, it was decided to repeat the experiments described in the previous section using ^{14}C-labelled acetylene in place of unlabelled acetylene. Radioassay of the surface carbon would thus enable determinations to be made of the amount of surface carbon formed from acetylene under these conditions. It was hoped also that further information would be obtained about the role of vinylacetylene as an intermediate in the formation of carbon from acetylene.

Table 12

The effect of acetylene on the formation of surface carbon from vinylacetylene at 478°C

Initial concentration (mole.l.$^{-1}$ x 10^4)		Residence time (μsec.)	Total amount of carbon from 10 runs (mg.)
Vinylacetylene	Acetylene		
21.36	0	60	1.68
21.36	1.12		1.68
16.02	0	120	1.82
16.02	6.47		1.63

For accurate assay of the deposited carbon it was, of course, necessary to carry out a total of ten similar runs in the same reaction vessel, and furthermore it had been found earlier (see Section 3.1.4.) that the amount of carbon deposited during the pyrolysis of vinylacetylene was a function of the nature of the surface. Prior to carrying out each experiment using the labelled material, the reaction vessel was, therefore, precoated with carbon from nine identical runs using unlabelled material, and preliminary experiments were carried out to determine, by difference, the amount of carbon deposited in the tenth of a series of ten runs.

The pyrolysis of vinylacetylene/^{14}C-acetylene mixtures was investigated using two mixtures, the first containing 5% acetylene and the second 28.75% acetylene. After each series of experiments the residual vinylacetylene and acetylene were separated by gas-chromatography, converted to carbon dioxide and subjected to radioassay; for this purpose the carbon dioxide was dissolved in a potassium hydroxide/ethylene glycol solution, and a windowless proportional counter was used. The total deposit of carbon was converted to carbon dioxide and assayed in the same way. Each measurement was corrected for the background count rate, which was 10.7 count.min.$^{-1}$. The measurements made are summarised in Tables 13 and 14. It can be seen that the amounts of products were similar in both inactive and active experiments, indicating that the polymerisation of vinylacetylene induced by β-radiation was not important. This conclusion was borne out by the observation that no chemical change could be detected when

Table 13

The pyrolysis of vinylacetylene in the presence of 5% ^{14}C-labelled acetylene at 478°C

Initial concentration of vinylacetylene	21.36×10^{-4} mole.l.$^{-1}$
Initial concentration of acetylene	1.12×10^{-4} mole.l.$^{-1}$
Residence time	60 sec.
Amount of carbon deposited in 9 runs	1.58 mg.
Amount of carbon deposited in 10 runs	1.68 mg.

	Total carbon deposited	Residual vinylacetylene	Residual acetylene
Amount of compound expected	1.68 mg.	1.47×10^{-4} moles	2.56×10^{-5} moles
Amount of carbon dioxide expected (moles)	1.40×10^{-4}	5.88×10^{-4}	5.12×10^{-5}
Amount of carbon dioxide actually found (moles)	1.43×10^{-4}	5.79×10^{-4}	5.87×10^{-5}
Weight of ethylene glycol/potassium hydroxide solution (g.)	3.132	2.261	2.177
Count rate (counts.min.$^{-1}$)	199	1361	2.428×10^{5}

Table 14

The pyrolysis of vinylacetylene in the presence of 28.75% ^{14}C-labelled acetylene at 478°C

Initial concentration of vinylacetylene	21.36×10^{-4} mole.l.$^{-1}$
Initial concentration of acetylene	6.47×10^{-4} mole.l.$^{-1}$
Residence time	120 sec.
Amount of carbon deposited in 9 runs	1.53 mg.
Amount of carbon deposited in 10 runs	1.63 mg.

	Total carbon deposited	Residual vinylacetylene	Residual acetylene
Amount of compound expected	1.63 mg.	8.34×10^{-5} moles	1.38×10^{-4} moles
Amount of carbon dioxide expected (moles)	1.36×10^{-4}	3.35×10^{-4}	2.76×10^{-4}
Amount of carbon dioxide actually found (moles)	1.33×10^{-4}	3.51×10^{-4}	2.43×10^{-4}
Weight of ethylene glycol/ potassium hydroxide solution (g.)	3.296	3.872	3.770
Count rate (counts.min.$^{-1}$)	105	541	7.053×10^{4}

vinylacetylene was left in contact with ^{14}C-acetylene for one week at room temperature.

3.3.2.1 Treatment of results

If x is the number of counts recorded per minute, and m is the number of moles of carbon dioxide dissolved in z g. of ethylene glycol/potassium hydroxide solution, then the specific molar activity of the carbon dioxide (in counts.min.$^{-1}$g.mole.$^{-1}$g.soln.(a)) is given by

$$a = \frac{xz}{m}$$

and the specific activity of the carbon deposited in the run with labelled acetylene (in counts.min.$^{-1}$g.atom.$^{-1}$g.soln.(a_c)) is given by

$$a_c = \left(\frac{m_{10}}{m_{10} - m_9}\right)\frac{xz}{m}$$

where m_9 and m_{10} are the total amounts of carbon deposited in 9 and 10 runs, respectively.

If $a_{C_2H_2}$ and $a_{C_4H_4}$ are the specific activities of the carbon dioxide formed from the residual acetylene and vinylacetylene respectively, then the percentage of carbon derived from acetylene is approximately equal to $\frac{100a_c}{a_{C_2H_2}}$. The number of g.atoms of carbon formed from acetylene is given by

$$\frac{a_c}{a_{C_2H_2}}\left(\frac{m_{10} - m_9}{12}\right),$$

and the percentage of acetylene converted to carbon is given by

$$\frac{a_c}{a_{C_2H_2}} \left(\frac{m_{10} - m_9}{12}\right) \cdot \frac{1}{2} \; \frac{100}{X_{C_2H_2}}$$

where $X_{C_2H_2}$ is the number of moles of acetylene present initially. The number of g.atoms of carbon formed from vinylacetylene is approximately equal to

$$\frac{m_{10} - m_9}{12} \left(1 - \frac{a_c}{a_{C_2H_2}}\right)$$

and hence the percentage of vinylacetylene converted to carbon is given by

$$\frac{m_{10} - m_9}{12} \left(1 - \frac{a_c}{a_{C_2H_2}}\right) \frac{1}{4} \cdot \frac{100}{X_{C_4H_4}}$$

where $X_{C_4H_4}$ is the number of moles of vinylacetylene present initially.

The results obtained using this treatment are summarised in Table 15. A small amount of surface carbon is, in fact, formed from acetylene, but the most significant finding is that the specific activity of the carbon formed is about ten times that of the residual vinylacetylene. Thus, only a small proportion of the radioactive carbon can be formed via vinylacetylene.

3.3.2.2 Accuracy of results

The accuracy of the results presented above is dependent on several factors. Errors are associated with the determinations of the amounts of surface carbon and of residual acetylene and vinylacetylene, and they can also arise due to the statistical nature of the counting data and the influence of isotopic effects.

Table 15

The pyrolysis of vinylacetylene in the presence of ^{14}C-labelled acetylene at 478°C

% Acetylene in mixture	5	28.75
Specific activity of CO_2 formed from acetylene (counts.min.$^{-1}$.g.mole.$^{-1}$ g.soln.)	9.01×10^9	1.09×10^9
Specific activity of CO_2 formed from vinylacetylene (counts.min.$^{-1}$ g.mole.$^{-1}$ g.soln.)	5.32×10^6	5.97×10^6
Specific activity of CO_2 formed from surface carbon (counts.min.$^{-1}$ g.mole.$^{-1}$ g.soln.)	7.32×10^7	4.24×10^7
Percentage carbon derived from acetylene	0.81	3.88
Percentage acetylene converted to carbon	0.13	0.12
Percentage vinylacetylene converted to carbon	0.45	0.59
$\frac{\text{Specific activity of } CO_2 \text{ formed from carbon}}{\text{Specific activity of } CO_2 \text{ formed from vinylacetylene}}$	13.8 (±3.3)	7.1 (±1.7)

Since radioactive disintegration is a random process in which individual nuclei decay independently of one another, it can be treated by the usual laws of probability and it can be shown that the error in the average number of counts detectable in a given time interval, $\bar{n}$, is $\sqrt{\bar{n}}$. In the present work, the number of counts recorded varied from about 6400 to 400,000 per interval, and were thus subject to errors of between 80 (1.25%) and 632 (0.16%) counts respectively.

Errors due to the influence of isotope effects are difficult to estimate. Examination of the results obtained with ^{14}C-labelled compounds shows, however, that the effect is quite small. Frey, Danby and Hinshelwood [118] concluded from a study of the thermal decomposition of ^{14}C-labelled propanes that ^{12}C-^{12}C bonds are ruptured about 6% more frequently than ^{12}C-^{14}C bonds, and it has been calculated that the isotope effect between ^{14}C-H and ^{12}C-H is considerably less [119]. It is not known to what extent isotope effects may be important in the present work, but errors arising from this cause are unlikely to exceed ±5%.

By combination of the possible error arising from isotope effects with the "counting" errors and errors associated with the determinations of the amounts of carbon, acetylene and vinylacetylene, it is found that the limits of accuracy of the specific activities recorded in Table 15 are ±12%. The possible error in the ratio of the activities of the carbon deposits and residual vinylacetylene is thus about ±24%.

4. DISCUSSION

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4.1 Introduction

The pyrolysis of vinylacetylene could conceivably occur via a radical or a molecular mechanism, but since the pyrolysis of acetylene undoubtedly involves the formation of free radicals, it is likely that vinylacetylene too breaks down by a free radical mechanism. Indeed similar mechanisms could well account for the pyrolysis of both compounds. Unfortunately, however, the mechanism of acetylene pyrolysis has not yet been firmly established and many different mechanisms have, from time to time, been postulated. It is profitable, therefore, to examine first of all the various mechanisms proposed for the pyrolysis of acetylene in order to establish which is the most probable.

4.2 The pyrolysis of acetylene

4.2.1 The initiation reaction

Studies of the pyrolysis of acetylene have been carried out over a wide range of temperatures, and perhaps the most striking feature of the results is that the reaction appears to be second order in acetylene over the entire range from 400 to 2500°C. An Arrhenius plot of the second order rate constants covering the whole range gives a single straight line which shows only slight random scatter. The line of best fit is given by the equation [59]:

$$\log_{10}k = 11 - \frac{41{,}600}{4.58T}$$

where k is the rate constant expressed in $\mathrm{l.mole.^{-1}sec.^{-1}}$ and T is the absolute temperature.

The initiation steps which have been proposed are:

1. $C_2H_2 \longrightarrow C_2H\cdot + H\cdot \qquad \Delta H = 115 \text{ kcal.mole.}^{-1}$
2. $C_2H_2 + C_2H_2 \longrightarrow C_4H_3\cdot + H\cdot \qquad \Delta H = 46 \text{ kcal.mole.}^{-1}$
3. $C_2H_2 + C_2H_2 \longrightarrow C_2H\cdot + C_2H_3\cdot \qquad \Delta H = 75 \text{ kcal.mole.}^{-1}$
4. $C_2H_2 + M \longrightarrow C_2H_2^{*} + M \qquad \Delta H = 46 \text{ kcal.mole.}^{-1}$
5. $C_2H_2 \xrightarrow{\text{surface}} C_2H_2^{*} \qquad \Delta H = 46 \text{ kcal.mole.}^{-1}$

The asterisk is used to denote an acetylene molecule in its triplet state configuration, $\dot{C}H = \dot{C}H$, and the heats of reaction, ΔH, are calculated from the data of Cowperthwaite and Bauer [120], and Bowman and Miller [121].

Now if the initiation reaction is slower than all subsequent reaction steps and does not result in the setting up of propagating chains, its rate will be equal to that of the overall reaction. A mechanism which satisfies these criteria was proposed recently by Palmer and Dormisch [69] :

4,-4 $C_2H_2 + C_2H_2 \rightleftarrows C_2H_2^{*} + C_2H_2$
6 $C_2H_2^{*} + C_2H_2 \longrightarrow C_4H_4^{*}$
7 $C_4H_4^{*} + C_2H_2 \longrightarrow$ non-radical products

On the assumption that the steady state approximation holds, the rate of disappearance of acetylene is given by

$$- d \frac{[C_2H_2]}{dt} = \frac{3k_4k_6}{k_{-4} + k_6} \cdot [C_2H_2]^2$$

and if $k_6 \gg k_{-4}$

$$-d\frac{[C_2H_2]}{dt} \approx 3k_4[C_2H_2]^2$$

This mechanism can be shown to be improbable, however. The activation energy of the overall reaction is in fair agreement with the heat of reaction 4 since the reverse reaction will have only a small activation energy, but it is doubtful whether the frequency factor for this reaction is as large as that of the overall reaction. The frequency factor of the overall reaction is about as large as the collisional frequency, but the excitation of an acetylene molecule to its triplet state will involve an electronic transition which is forbidden by the Wigner-Witmer spin conservation rule. Although this rule cannot be applied rigidly to polyatomic species [122], nevertheless the probability factor would be expected to be about 10^{-5} [123]. Furthermore, unless acetylene is a much more efficient third body for the excitation than are other third bodies, it would be expected that the rate of consumption of acetylene would be proportional to the total pressure and to only the first power of the acetylene concentration.

Reaction mechanisms which involve other initiation steps but which, nevertheless, satisfy the original criteria concerning the rate of initiation and the absence of propagating chains, are also unlikely. Reactions 1 and 3 cannot apply since they are much too endothermic, and furthermore, reaction 1 is unlikely to result in second order kinetics. Reaction 5 is also unlikely to result in second order kinetics and would not, in any case, be expected to be significant in shock tubes. The activation energy of reaction 2 may be close to that of the overall reaction but, in this case, the pre-exponential factor will almost certainly be too low by a factor of between 100 and 1000 [124]. It must be concluded, therefore, that none of the initiation reactions participate in acetylene pyrolysis in a rate controlling way, and the high rate of consumption of acetylene is probably due to chain propagation reactions.

If the initiation results in the setting up of propagating chains, then the overall rate of reaction may be less directly related to the rate of initiation. In such circumstances, it is difficult to assess the relative importance of each initiation reaction. Reactions 1 and 5 are improbable, since the overall order of the reaction with respect to acetylene is unlikely to be 2, but, on the other hand, initiation by reactions 2, 3 and 4 can result in the observed dependence on acetylene concentration and on this basis all three reactions are equally probable. Reaction 2 is, however, likely to be faster than reactions 3 and 4. It may be postulated, therefore, that initiation occurs mainly via the reaction

2. $C_2H_2 + C_2H_2 \longrightarrow C_4H_3\cdot + H\cdot$

and that it results in the setting up of propagating chains.

4.2.2 The propagation and termination reactions

One simple scheme for the formation of diacetylene during the pyrolysis of acetylene is:

8. $H\cdot + C_2H_2 \longrightarrow H_2 + C_2H\cdot$ $\Delta H = 11$ kcal.mole.$^{-1}$

9. $C_2H\cdot + C_2H_2 \longrightarrow C_4H_2 + H\cdot$ $\Delta H = -7$ kcal.mole.$^{-1}$

There are, of course, other reactions which can be postulated, but many of them will be slower than the above reactions. Both the addition of hydrogen atoms to acetylene:

$$H\cdot + C_2H_2 + M \longrightarrow C_2H_3\cdot + M \qquad \Delta H = -39 \text{ kcal.mole.}^{-1}$$

and the formation of diacetylene from $C_4H_3\cdot$:

$$C_4H_3\cdot \longrightarrow C_4H_2 + H\cdot \qquad \Delta H = 61 \text{ kcal.mole.}^{-1}$$

will be slow, since the former requires a third body to remove the excess energy of the $C_2H_3\cdot$ radical and the latter is strongly endothermic. Polymerisation reactions such as:

10. $C_2H\cdot + C_2H_2 \longrightarrow C_4H_3\cdot$

and 11. $C_4H_3\cdot + C_2H_2 \longrightarrow C_6H_5\cdot$

must undoubtedly occur, however, since the formation of polymers occurs to a significant extent even in the early stages of the pyrolysis of acetylene. Hydrogen transfer reactions could also take place, and it may well be that vinylacetylene is formed in this way:

12. $C_4H_3\cdot + C_2H_2 \longrightarrow C_4H_4 + C_2H\cdot$ $\Delta H = 25$ kcal.mole.$^{-1}$

There are, in addition, several reactions which would be expected to assume greater importance as pyrolysis continues, e.g.

13. $H\cdot + C_4H_2 \longrightarrow C_4H\cdot + H_2$

14. $C_4H\cdot + C_2H_2 \longrightarrow C_6H_2 + H\cdot$

and then:

15. $H\cdot + C_6H_2 \longrightarrow C_6H\cdot + H_2$

16. $C_6H\cdot + C_2H_2 \longrightarrow C_8H_2 + H\cdot$

These reactions may well account for the observation that the various polyacetylenes seem to equilibrate with one another in the later stages of the reaction at high temperatures [15,59].

The available data do not, unfortunately, provide any information as to the nature of the possible termination reactions. The rates of the various propagation reactions are unknown and it is not possible, therefore, to calculate the relative concentrations of the intermediate radicals. All that may safely be said is that the termination reactions are probably bimolecular. If termolecular reactions such as the recombination of hydrogen atoms were involved, then the rate of the overall reaction would be expected to show some dependence on total pressure. This effect is not observed [68].

4.3 The pyrolysis of vinylacetylene

4.3.1 The formation of gaseous products

One of the most striking features of the pyrolysis of vinylacetylene is the marked difference between the products formed at 478°C and at 550°C (compare Figs. 11 and 12). At 478°C, the reaction appears to be essentially a second-order polymerisation process. Vinylacetylene is converted almost entirely to low molecular weight polymers, where the primary product is probably the dimer C_8H_8. Small amounts of other products are indeed formed, but these account for only a very small fraction of the vinylacetylene consumed (ca. 2%). At 550°C, however, the rate of disappearance of vinylacetylene is about two orders of magnitude higher, and while the formation of polymers is still important, the reaction gives rise to large amounts of ethylene, acetylene, methane, hydrogen and soot. (The yields of gaseous products at 7.5 sec., expressed as moles of product per mole of vinylacetylene decomposed x 100, are 8%, 25%, 5% and 25%, respectively). Unfortunately, it was not possible, in the static system, to measure accurately the rate of so fast a reaction and it is not known with certainty, therefore, whether the reaction mechanism remains the same. It may be that, at 550°C, the disappearance of vinylacetylene and the formation of gaseous products are controlled by processes which are unimportant below about 500°C. There is a certain amount of evidence to suggest that this is indeed the case. Firstly, the initial rate of pressure decrease shows a complex dependence on temperature (Fig. 10), and secondly, at 478°C, the ratio $[C_2H_4]/[C_2H_2]$ is ca. 8 whereas at 550°C it is approximately 0.3. It is reasonable to assume that neither ethylene nor acetylene reacts appreciably at these temperatures; indeed, it was found experimentally that at 478°C acetylene does not influence the pyrolysis of vinylacetylene. Thus a change in the ratio of the amounts of ethylene and acetylene represents a change in the relative rates of formation of these two compounds.

If it is assumed that the pyrolysis of vinylacetylene parallels that of acetylene, then one possible initiation reaction is:

17. $C_4H_4 + C_4H_4 \longrightarrow C_8H_7\cdot + H\cdot$

The hydrogen atoms may either add to vinylacetylene, giving $C_4H_5\cdot$ radicals:

18. $C_4H_4 + H\cdot \longrightarrow C_4H_5\cdot$

or abstract hydrogen from vinylacetylene, giving molecular hydrogen:

19. $C_4H_4 + H\cdot \longrightarrow C_4H_3\cdot + H_2$

It is difficult to assess the relative importance of reactions 18 and 19. The rate constants for the corresponding reactions of hydrogen atoms with ethylene:

20. $H\cdot + C_2H_4 \longrightarrow C_2H_5\cdot^{(v)}$

and 21. $H\cdot + C_2H_4 \longrightarrow C_2H_3\cdot + H_2$

are $10^{10.7}e^{-3\overset{000}{\cancel{x}}/RT}$ and $10^{10.5}e^{-7\overset{000}{\cancel{x}}/RT}$ $l.mole.^{-1}sec.^{-1}$ respectively [125]. It might be expected, therefore, that the addition reaction would be favoured. Unfortunately, however, it is not possible to make such a straightforward comparison, since reaction 20 results in the formation of ethyl radicals in a vibrationally excited state. If reaction 18 results in the formation of vibrationally excited $C_4H_5\cdot$ radicals, then the net rate of formation of ground state radicals may well be much lower and, as a consequence, reaction 19 may be the faster. This indeed appears to be the case. The formation of $C_4H_5\cdot$ radicals would be expected to lead to the formation of butadiene:

$$C_4H_5\cdot + C_4H_4 \longrightarrow C_4H_6 + C_4H_3\cdot$$

Since this reaction would be expected to be about as fast as the addition reaction [126]:

$$C_4H_5\cdot + C_4H_4 \longrightarrow C_8H_9\cdot$$

and since butadiene is not detected among the products of the pyrolysis, it must be concluded that $C_4H_5\cdot$ radicals are not important intermediates in the reaction.

The $C_4H_3\cdot$ and $C_8H_7\cdot$ radicals will lead to further polymerisation, e.g.

22. $C_4H_3\cdot + C_4H_4 \longrightarrow C_8H_7\cdot$

23. $C_8H_7\cdot + C_4H_4 \longrightarrow C_{12}H_{11}\cdot$

Hydrogen transfer reactions, leading to the formation of stable polymeric molecules, may also occur, e.g.

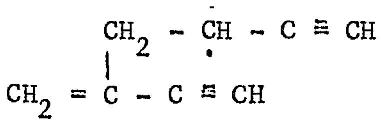
24. $C_8H_7\cdot + C_4H_4 \longrightarrow C_8H_8 + C_4H_3\cdot$

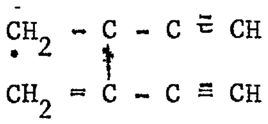
The setting up of such propagating chains may readily account for the rapid polymerisation of vinylacetylene and explain the fact that the polymers formed initially have an average composition corresponding to C_8H_8. In fact these reactions may constitute the major steps in the pyrolysis of vinylacetylene at low temperatures. It is evident, however, that this is not the case at 550°C. At this temperature considerable amounts of hydrogen, methane, acetylene and ethylene are formed.

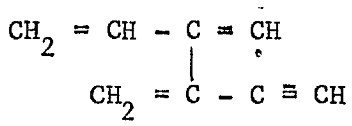
It is possible to account for the production of hydrogen, acetylene and ethylene if it is postulated that the $C_8H_7\cdot$ radicals can undergo unimolecular decomposition at higher temperatures with the elimination of hydrogen atoms, or $C_2H\cdot$ or $C_2H_3\cdot$ radicals. The $C_4H_3\cdot$ radical which is the most stable, and the one which is therefore most likely to be formed in reaction 24, has the structure [120] :

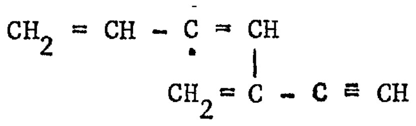
$$CH_2 = \dot{C} - C \equiv CH \qquad \Delta H_f^o = 103 \text{ kcal.mole.}^{-1}$$

If it is assumed that this radical may add on to vinylacetylene (Reaction 22) at each of the four positions in the molecule, then the $C_8H_7\cdot$ radical so formed may have one of four structures


(A)


(B)


(C)

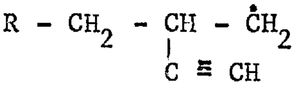

(D)

Loss of an acetylenyl and a vinyl radical from (B) and (C) respectively will result immediately in stable C_6 species. In the case of radicals (A) and (D), the radicals may decompose, with the loss of a hydrogen atom, to form a stable molecule directly, or may lose an acetylenyl radical. In the latter case, intramolecular hydrogen transfer in the resulting biradical would result in the formation of a molecular product. Reactions such as these are indeed possible. Tarr, Strauss and Gunning have shown [127,128] that the reaction:

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

is faster at room temperature than the alternative reaction:

$$C_2H\cdot + C_2H_4 \longrightarrow C_2H_2 + C_2H_3\cdot$$

Moreover, their results indicate that for substituted ethylenes, the decomposition of the radical  $R - CH_2 - \underset{\displaystyle C \equiv CH}{\underset{|}{CH}} - \dot{C}H_2$ occurs by carbon-carbon bond scission rather than carbon-hydrogen bond scission.

The radicals resulting from the decomposition of $C_8H_7\cdot$ radicals will abstract hydrogen from vinylacetylene to give $C_4H_3\cdot$ and either hydrogen, acetylene or ethylene:

19. $H\cdot + C_4H_4 \longrightarrow C_4H_3\cdot + H_2$

25. $C_2H\cdot + C_4H_4 \longrightarrow C_2H_2 + C_4H_3\cdot$

26. $C_2H_3\cdot + C_4H_4 \longrightarrow C_2H_4 + C_4H_3\cdot$

It may be that the establishment of this alternative chain propagation reaction gives rise to the change in the product distribution at about 500°C.

It is interesting to note that the loss of an acetylenyl radical from the $C_8H_7\cdot$ radical of structure (A) results in the formation of 1,5-hexadiyne

$$CH \equiv C - CH_2 - CH_2 - C \equiv CH$$

1,5-hexadiyne is thermally unstable at these temperatures and rearranges to yield benzene [129]. C_3 radicals could also be formed from 1,5-hexadiyne by carbon-carbon bond scission at the weak allylic bond[130], and once formed, these radicals could participate in further reactions leading to propylene and methylacetylene which are observed as minor products. Many other C_6 and C_8 species could conceivably take part in cyclisation reactions, and for this reason it is not possible to define the mechanism of benzene formation in more detail. Unfortunately this uncertainty applies also to the other minor products formed in the pyrolysis of vinylacetylene. Methane is presumably formed at least in part via the reaction:

$$CH_3\cdot + RH \longrightarrow CH_4 + R\cdot$$

but the data do not, however, allow any reasoned suggestions as to the way in which the methyl radicals are formed. Ethane could perhaps be formed via the hydrogenation of ethylene.

The mechanism outlined above for the early stages of the pyrolysis of vinylacetylene can thus accommodate qualitatively the majority of the observed facts. To define the mechanism more closely would, however, require either more specific information about the rates of the individual steps or evidence of the type which can be obtained using ^{14}C-compounds specifically labelled in one or more positions. It had been hoped, originally, that information of the second type might have been obtained from the use of ^{14}C-vinylacetylenes but unfortunately synthesis of such compounds could not be achieved.

4.3.2 The kinetics of surface carbon formation

The pyrolysis of vinylacetylene at 478°C results in the formation of small amounts of surface carbon, but no gas-phase carbon. If a number of pyrolyses are carried out at this temperature with the same initial pressure of vinylacetylene and for the same residence time, then the total amount of carbon deposited is a linear function of the number of runs, provided that this number is greater than about 6 (Fig. 16). If fewer than 6 runs are carried out, however, the amount of carbon deposited per run is significantly higher. This result can be interpreted in two different ways. Either the rate of deposition of carbon is faster on a silica surface than it is on a carbon surface, or there is an induction period which increases as the surface becomes coated with carbon. To distinguish between these two possibilities a further experiment was performed in which the variation with time of the amount of carbon deposited in an initially clean vessel during ten consecutive runs was compared with that when the deposition occurred in a vessel which had been pre-coated with carbon (Fig. 17). It was found that the average rate of carbon deposition per run was identical in the two cases. The 'apparent' induction period was however greater when the pre-coated vessel was used, and the plot of average weight of carbon deposited per run versus residence time was linear to much smaller amounts of carbon. This result suggests strongly that the rate of deposition of carbon is not affected by the nature of the surface, but that the induction period in the presence of a silica surface is shorter than that in the presence of a carbon surface. Unfortunately, the measured values of the induction period in an initially clean vessel have little significance, since each point on the curves represents the average weight of carbon deposited over 10 consecutive runs. The rate of carbon formation, on the other hand, is probably a true value, since in this case the nature of the surface is unimportant. The rate of deposition is dependent on the square of the vinylacetylene concentration and it appears, therefore, that surface carbon formation involves an intermediate which builds up to a critical concentration in the gas phase during the induction period and then reacts further to give carbon by a heterogeneous reaction. The second order kinetics observed for this reaction are somewhat surprising in view of the fact that carbon deposition from methane is first order in methane.[2,17,106-108] The data do not provide any information as to the nature of the intermediate in either case, but the reason for the differing kinetics in the two systems may lie in the different modes of formation of the intermediates. The kinetics of the pyrolysis of vinylacetylene show a second order dependence on the vinylacetylene concentration. On the other hand, the initiation reaction in the pyrolysis of methane is first order, and, in view of the high activation energy of this reaction (103 kcal.mole.^{-1}), is probably rate-determining. It may well be, therefore, that the rate of formation of surface carbon is dependent not on the rate of deposition, but on the rate of formation of some specific intermediate.

Whilst the pyrolysis of vinylacetylene at 478°C resulted only in the formation of surface carbon, at 550°C both surface carbon and gas-phase carbon were formed. This result is in agreement with other studies [96] where it was found that the temperature required for nucleation in the gas phase is always higher than that required for nucleation on the surface. Unfortunately, however, the formation of both types of carbon precluded a study of the kinetics of surface carbon deposition at the higher temperature.

4.4 The nature of the carbonaceous deposits

At temperatures above 550°C, the pyrolysis of vinylacetylene resulted in the formation of significant amounts of both gas-phase and surface carbon, and it was possible, therefore, to study the variation with temperature of formation of the crystallite dimensions and carbon/hydrogen ratios of each type. The results obtained for vinylacetylene can be compared with those obtained for acetylene even though higher temperatures had to be used for the pyrolysis of the latter compound, owing to its greater thermal stability.

4.4.1 The variation of crystallite size with temperature

With gas-phase carbons from acetylene, the crystallite diameter at first decreases with increasing temperature of formation but, after passing through a minimum value at about 950°C, it increases again as the temperature is further raised. In contrast, the diameters of the crystallites in the gas-phase carbons formed from vinylacetylene increase continuously with temperature. The crystallite diameters of the surface carbons from both compounds also increase with increasing temperature. It was not possible to measure the heights of the crystallites in the surface carbons due to their strong preferred orientation but in the gas-phase carbons the crystallite height was found to be virtually independent of temperature. Only with acetylene at temperatures above 950°C was a significant increase in crystallite height observed.

The fact that the dependence on temperature of the crystallite diameter is different from that of the crystallite height is not surprising since the valency forces between the carbon atoms in the layer planes are much stronger than the predominantly physical forces which hold adjacent layers together[131]. Growth of the crystallites along the layer planes will be much more probable than the formation of new layers, and over a limited range of temperatures the average number of layers will not vary significantly.

The increase with temperature of formation of the crystallite diameters of the gas-phase carbons from vinylacetylene and the contrasting decrease, from 850 to 950°C, for the gas-phase deposits from acetylene can readily be accounted for by the different kinetic characteristics of the two competing processes involved in the production of a crystallite. These two processes are the rate of deposition of "carbon" on the growing nucleus and the rate at which the newly deposited material adopts a configuration which is ordered with respect to the lattice on which the deposition occurs, i.e. the rate of ordering. Both these processes are of course complex. The rate of deposition may in fact be controlled by the rate of pyrolysis - indeed this may well be the case for vinylacetylene (see Section 4.3.2) - and certainly the intermediates involved in growth are not carbon radicals as such. They are probably highly unsaturated hydrocarbons or hydrocarbon radicals and will contain a certain amount of hydrogen. The ordering process will, therefore, involve both dehydrogenation and cyclisation. If the rate of deposition is high and the rate of ordering is low, then the crystallites will be small; if the converse is true then the crystallites will be large. The relative rates of these processes will change with temperature and if the rate of ordering is more temperature-dependent than the rate of deposition, then, as the temperature is increased, the crystallites will become progressively more highly ordered and larger. If the reverse is true, then at high temperatures the carbon will be deposited as smaller, less ordered crystallites. However, unless the carbons from acetylene and vinylacetylene originate entirely from the same intermediate species, there is no reason to suppose that the rates of deposition will be similar, although for deposits formed on like surfaces the rates of ordering may well be comparable. Thus the increase with temperature of the crystallite diameters of the gas-phase deposits from vinylacetylene may be attributed to a rate of ordering which increases faster with temperature than does the rate of deposition. In contrast, with gas-phase carbons from acetylene, the reverse evidently holds over the range 850-950°C. The crystallite diameters of the surface carbons formed from both acetylene and vinylacetylene increase with temperature more rapidly than do the crystallite diameters of the corresponding gas-phase carbons. This may be due to a promoting effect of the surface on the ordering process.

The marked increase in both the diameter and the height of the crystallites in the gas-phase carbon formed from acetylene at 975°C is rather surprising. A similar phenomenon has been found for the variation with temperature of the density of surface carbon deposited from methane [17,18], but in this case the minimum occurred at much higher temperatures (ca. 1700°C). The high density at low temperatures was accounted for in terms of the relative rates of deposition and ordering, but it was postulated that the high density observed at 2000°C was the result of graphitisation. A similar explanation may be advanced to account for the observed minimum size of the crystallites in gas-phase carbon formed from acetylene at 975°C. It is, however, doubtful whether graphitisation is a significant process at temperatures below 1000°C.

4.4.2 The variation of carbon : hydrogen ratio with temperature

The continuous decrease with increasing temperature of formation of the hydrogen content of gas-phase carbons from acetylene and vinylacetylene contrasts with the more complex variation of crystallite dimensions. In the case of the gas-phase carbons from vinylacetylene, the carbon:hydrogen ratio increases with crystallite size (Figs. 19 and 20). For gas-phase carbons from acetylene, however, the observed increase in carbon:hydrogen ratio contrasts with a decrease in crystallite size as the temperature of formation is raised from 840 to 940°C (Figs. 21 and 22). The amount of hydrogen present in pyrolytic deposits will, however, be expected to be a function not only of the size of the crystallites but also of the extent of cross-linking between adjacent crystallites. Indeed, in the case of gas-phase carbons from acetylene, the extent of cross-linking appears to be the more important factor. This is certainly true for surface carbons; the very small quantity of hydrogen found in such deposits (carbon:hydrogen ratio $\geqslant$ 80) is to be expected in view of their strong preferred orientation and the comparative ease with which cross-linking may occur. It is also consistent with the suggestion that the gas-phase carbon formed from acetylene at 975°C undergoes lattice reorganisation; the carbon:hydrogen ratio in this carbon is significantly higher than that in the corresponding carbons formed at lower temperatures (Fig. 22).

If the atomic carbon:hydrogen ratio in pyrolytic carbons were a function solely of the crystallite dimensions, then a fairly simple direct relationship might be expected between crystallite diameter and chemical composition. Such a quantitative relationship has indeed recently been proposed by Digonskii and Krylov [132]. Each layer plane in the carbon crystallites was assumed to be circular and to consist essentially of a large polycyclic aromatic structure, the average diameter, d, being given by:

$$d = (4KS/\pi)^{\frac{1}{2}}$$

where S is the surface area of a single benzene ring, and K is the number of benzene rings in the layer. It can be shown, however, that for a circular structure

$$K = 1 + 3n(n - 1)$$

where n is the atomic carbon:hydrogen ratio. It was proposed, therefore, that the diameter of the crystallites is related to the carbon:hydrogen ratio by the expression:

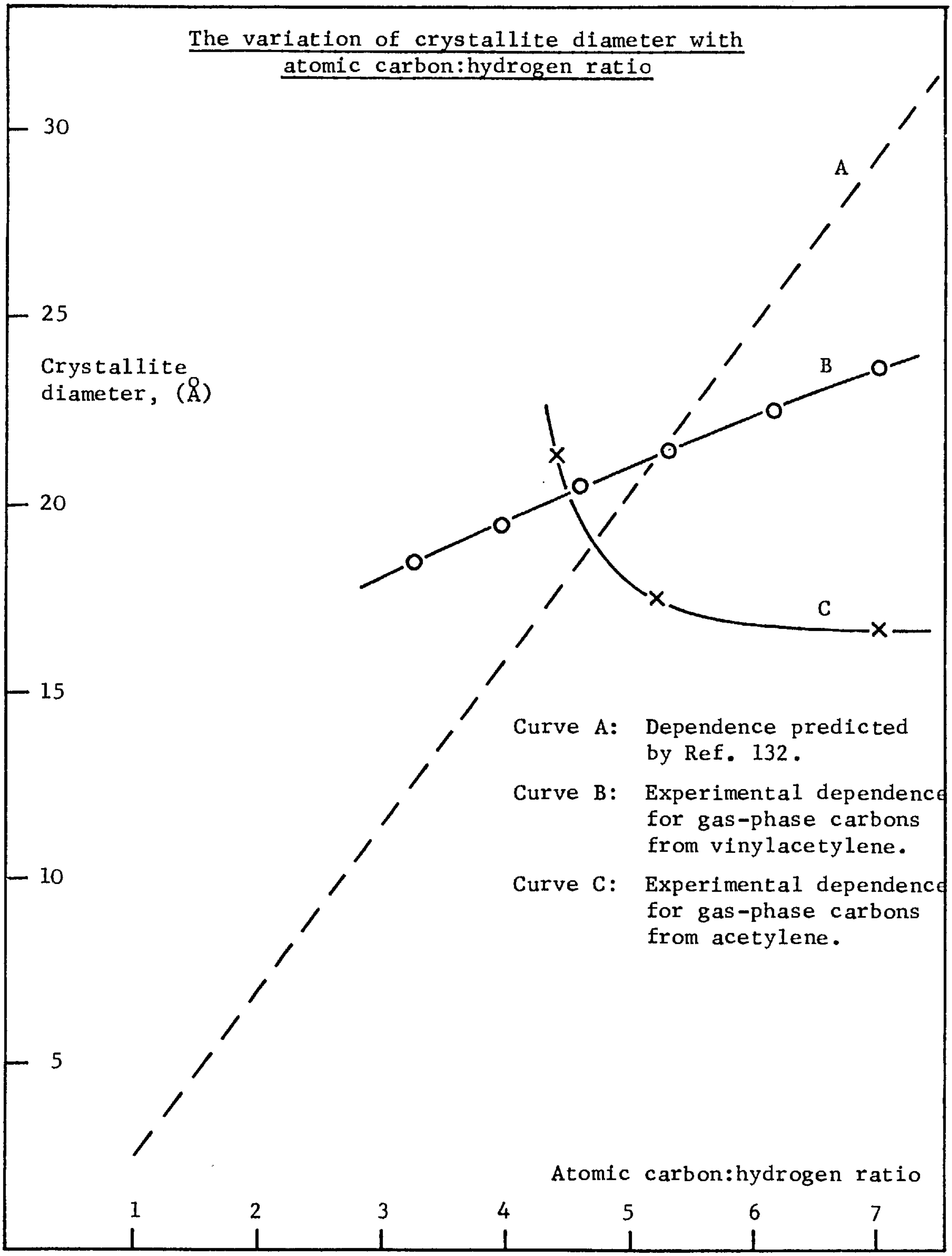
$$\underline{d^2 = \frac{4S}{\pi}[1 + 3n(n - 1)]}$$

On the assumption that the area of a single benzenoid unit in graphite is 5.217Å [13,132], then

$$d = 2.58\,[1 + 3n(n - 1)]^{\frac{1}{2}}$$

where d is measured in Ångstrom units. A plot of the variation of crystallite diameter with carbon:hydrogen ratio predicted by this equation is shown in Fig. 23 (Curve A), while the experimental variations for gas phase carbons from vinylacetylene and acetylene are given by curves B and C. Although the equation predicts the correct order of

Figure 23



The variation of crystallite diameter with atomic carbon:hydrogen ratio

Curve A: Dependence predicted by Ref. 132.

Curve B: Experimental dependenc for gas-phase carbons from vinylacetylene.

Curve C: Experimental dependenc for gas-phase carbons from acetylene.

magnitude for the crystallite diameters, the experimental values of this parameter are clearly far less dependent on carbon:hydrogen ratio than would be expected. Furthermore, curves B and C cross curve A (at a carbon:hydrogen ratio of ca. 5) showing that, at C/H ratios greater than 5, the structure contains less hydrogen than that required to satisfy the free valencies at all the peripheral sites around the layer planes, in other words cross-linking must take place.

4.5 The role of vinylacetylene in carbon formation from acetylene

One of the significant features of the present results is that the products formed from the pyrolysis of vinylacetylene differ markedly from those formed during the pyrolysis of acetylene. The most important differences occur in the case of diacetylene and methylacetylene. In both the present study of the pyrolysis of vinylacetylene and in other investigations [74], these two compounds were found only in trace amounts. Since it has already been shown, however, that in the pyrolysis of acetylene under similar conditions [68], they are present in large amounts and, together with vinylacetylene, have a significant lifetime, neither can be formed from acetylene via vinylacetylene.

A consideration of the formation of surface carbon from acetylene at 478°C leads to a similar conclusion. Radio-assay of the carbon deposited from mixtures of acetylene and vinylacetylene (Table 15) shows that the activity of the carbon is greater than that of the residual vinylacetylene, and hence only a small proportion of the radioactive carbon can be formed via vinylacetylene. In fact, the ratio of the activities indicates that, at the most, only about 10% of the carbon formed from acetylene can arise via the intermediate production of vinylacetylene. Vinylacetylene is, therefore, the sole primary product of the pyrolysis of acetylene at low temperatures [68], but it is not an important intermediate in the formation of either diacetylene, methylacetylene, or surface carbons. Indeed, it appears probable that at low temperatures as well as at high temperatures carbon formation from acetylene occurs mainly via the formation of diacetylene.

4.6 Conclusions

(i) The pyrolysis of vinylacetylene at temperatures below 500°C is essentially a free-radical polymerisation reaction. The reaction is second order with respect to vinylacetylene and has an overall activation energy of 28 kcal.mole.^{-1}. Surface carbon is formed in small amounts but at these low temperatures nucleation in the gas phase does not occur. The formation of surface carbon shows a second order dependence on the concentration of vinylacetylene and it may well be that the rate of formation of surface carbon is dependent not on the rate of deposition, but on the rate of formation of some critical intermediate. At temperatures above 550°C the pyrolysis of vinylacetylene becomes more complex; large amounts of acetylene and hydrogen are formed and gas-phase carbon is also deposited. The proposed mechanism of the pyrolysis is consistent with that suggested for the pyrolysis of acetylene.

(ii) While the properties of the surface and gas-phase carbons are strongly dependent on the conditions under which they are produced, they are nevertheless typical of the carbons formed in other pyrolytic systems and in flames. The most important differences depend on whether the carbon is formed in an essentially homogeneous reaction in the gas phase or by some process involving deposition on to a solid surface. The crystallite dimensions of the gas-phase carbons show a dependence on temperature different from that of the surface carbons. The latter also show strong preferred orientation and have very much higher carbon:hydrogen ratios. A quantitative relationship between crystallite size and hydrogen content which is based on a simple geometrical model is, however, unlikely to be valid unless due allowance is made for the extent of cross-linking between adjacent crystallites.

(iii) Although both vinylacetylene and diacetylene are products of the pyrolysis of acetylene and can give rise to the formation of gas-phase and surface carbons, the formation of surface carbon from acetylene at low temperatures appears to involve diacetylene rather than vinylacetylene. Furthermore, diacetylene is not a significant product of the pyrolysis of vinylacetylene, and its formation during acetylene pyrolysis does not therefore occur via the intermediate production of vinylacetylene. Diacetylene thus appears to be the more important intermediate in carbon formation from acetylene at low temperatures as well as at high temperatures.

(iv) There is already a considerable wealth of experimental findings concerning the pyrolysis of acetylene and mechanisms involving many different individual reaction steps have, from time to time, been postulated. The absolute rates of these individual steps have, however, been measured only in a few instances and it is still not possible to test conclusively the validity of any of the proposed mechanisms. It would be of the utmost value to know the absolute rates of reactions such as

(20) $C_2H\cdot + C_2H_4 \longrightarrow C_4H_4 + H\cdot$

and (7) $C_2H\cdot + C_2H_2 \longrightarrow C_4H_2 + H\cdot$

Recent work at room temperatures [128], has shown that reaction 20 is faster than the reaction

(21) $C_2H\cdot + CH_4 \longrightarrow C_2H_2 + CH_3\cdot$

but in the present context such relative rates are of only limited usefulness.

Of equal interest would be a study of the kinetics of the pyrolysis of vinylacetylene at temperatures above 550°C. The present work, whilst offering an outline of the reactions involved at these temperatures, was limited in its value by the experimental method employed. The use of a flow system, under carefully controlled conditions might well provide data which would indicate the extent to which the reaction mechanism changes as the temperature is increased.

APPENDIX

APPENDIX

Synthesis of ^{14}C-vinylacetylene

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Synthesis of ^{14}C-vinylacetylene

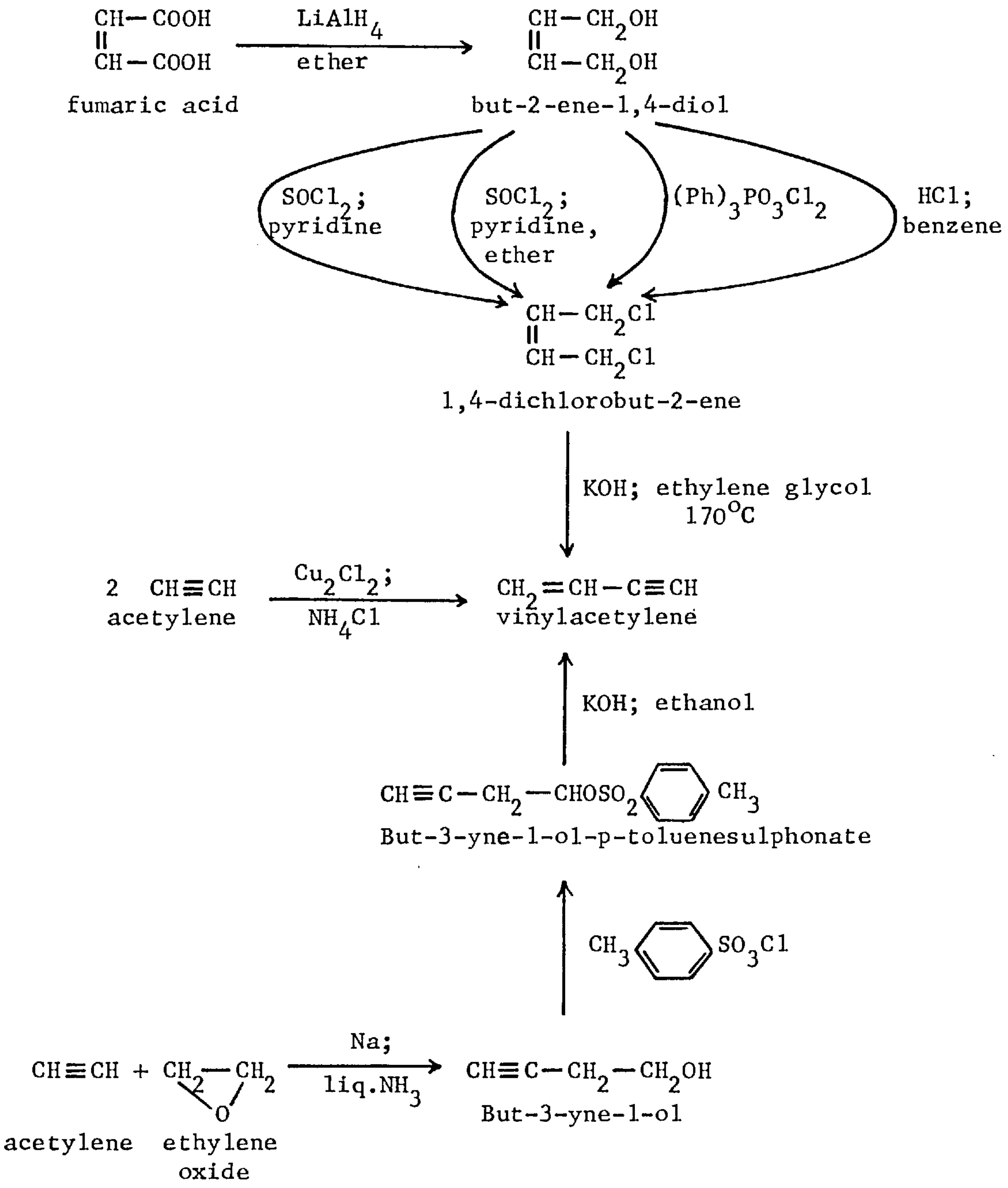
A.1 Introduction

There are two possible routes for the preparation of ^{14}C-vinylacetylene, one starting with ^{14}C-fumaric acid and the other with ^{14}C-acetylene (Fig. 24). In the first case, reduction of the fumaric acid to give the corresponding but-2-en-1,4-diol [133] is followed by halogenation to give the 1,4-dichlorobut-2-ene [134-136] and then dehydrohalogenation to give vinylacetylene [137]. The second route involves either the dimerisation of acetylene to give vinylacetylene directly [138], or its condensation with ethylene oxide, using sodium in liquid ammonia, giving but-3-yne-1-ol [139]; this latter compound can then be dehydrated to give vinylacetylene via the p-toluenesulphonate.[140]

Although the data reported in the literature indicate that the highest overall yields of vinylacetylene are obtained via the condensation of acetylene and ethylene oxide (yield = 30%), it was decided to investigate the route starting with fumaric acid. The overall yield in this case is reported to be slightly lower (ca. 20%), but the method appeared to be more attractive since firstly the vinylacetylene could be obtained labelled specifically in either the 1,4 or 2,3 positions, and secondly, it is less easy, practically, to handle isotopically-labelled gases. The investigation was initially carried out using unlabelled materials, but on a semi-micro scale, so that conditions approximated closely to those which would have been

Figure 24

Synthetic routes to vinylacetylene



required when labelled compounds were used.

The reduction of fumaric acid to but-2-en-1,4-diol was accomplished in 40% yield using lithium aluminium hydride in diethyl ether, but the conversion of the diol to the corresponding 1,4-dichlorobut-2-ene proved more troublesome. The usual Darzen's procedure using carefully purified thionyl chloride in the presence of dry pyridine resulted in a tarry mixture from which it was impossible to isolate the product (even in crude form) with a yield greater than about 30%. A modification of this procedure, in which ether was added to the mixture and the precipitated pyridine hydrochloride was filtered off [134], did not increase the yield significantly and it was concluded that the thionyl chloride itself was responsible for the formation of the tar. A more satisfactory method for the preparation of the dichlorobutene involved the addition of the diol to triphenylphosphite dichloride [135] and in this reaction the yield was 45%. The synthesis of 1,4-dichlorobut-2-ene was found, however, to be most readily achieved by passing dry hydrogen chloride into a vigorously stirred mixture of the diol and benzene at 80°C [136]. This reaction leads to the formation of dichlorobutene and water, the water being continuously removed as an azeotropic mixture with benzene; this procedure prevents the addition of hydrogen chloride to the double bond. The yield of 1,4-dichlorobut-2-ene was 55%.

Dehydrohalogenation of 1,3-dichlorobut-2-ene using potassium hydroxide in ethylene glycol at 170°C is reported to give vinylacetylene in 45% yield [137]. Even with the most careful attention to detail, however, it was found impossible to prepare vinylacetylene from the isomer, 1,4-dichlorobut-2-ene, in yields greater than 10%, and thus the overall yield for the synthesis of vinylacetylene from fumaric acid was only 2.5%. Such a yield was too low to be practicable for use with labelled compounds.

A.2 Experimental procedures

A.2.1 Reduction of fumaric acid

60 ml. of anhydrous ether were placed in a 100 ml. three-necked flask fitted with a mechanical stirrer, a nitrogen inlet and a Soxhlet extractor fitted with a drying tube containing anhydrous calcium chloride. An atmosphere of nitrogen was provided and 1.6g. of lithium aluminium hydride were dissolved in the ether, the mixture being stirred for three hours. When solution was complete, 2g. of fumaric acid were placed in the thimble of the extractor, and the ether was refluxed for 24 hours.

The excess lithium aluminium hydride was then carefully decomposed with water, and the lithium aluminium organo intermediate was decomposed with excess 20% sulphuric acid. The two layers were separated, and the aqueous layer was continuously extracted with ether. Ferrous sulphate was added to the aqueous layer to prevent the formation of ether peroxide. After drying with anhydrous sodium sulphate, and treatment with potassium carbonate to remove any unchanged fumaric acid, the ether was removed by distillation. The resulting but-2-ene-1,4-diol boiled at 126-130°C. The yield was 0.6g. (40%).

A.2.2 Preparation of 1,4-dichlorobut-2-ene

A.2.2.1 - 2.3g. of but-2-ene-1,4-diol were dissolved in 4 ml. of dry pyridine contained in a 25 ml. three-necked flask fitted with a mechanical stirrer, a dropping funnel and a thermometer. 4.6 ml. of freshly distilled thionyl chloride were then added dropwise, with stirring and cooling, the temperature being maintained at 10-20°C. The mixture was allowed to warm to room temperature and after stirring for fifteen hours, was treated with crushed ice. The product was extracted with ether (3 x 5 ml.), and the ether extract was washed with saturated sodium bicarbonate solution, dried with anhydrous sodium sulphate, and fractionally distilled. The yield of crude product was 1.0g. (30%).

A.2.2.2 - 2.4g. of but-2-ene-1,4-diol were treated with a solution containing 4.4 ml. of pyridine in 10 ml. of ether, and the resulting mixture was placed in a 25 ml. three-necked flask fitted with a mechanical stirrer, a dropping funnel and a thermometer. The flask was then cooled to -10°C in an ice-salt freezing mixture, and 2ml. of thionyl chloride were added dropwise. The resulting solution was filtered from the precipitated pyridine hydrochloride, and the ether was removed by distillation. The residue was treated with 2 ml. of thionyl chloride and then refluxed for one hour. The excess thionyl chloride was finally distilled off to leave a residue of about 0.7g. of crude 1,4-dichlorobutene.

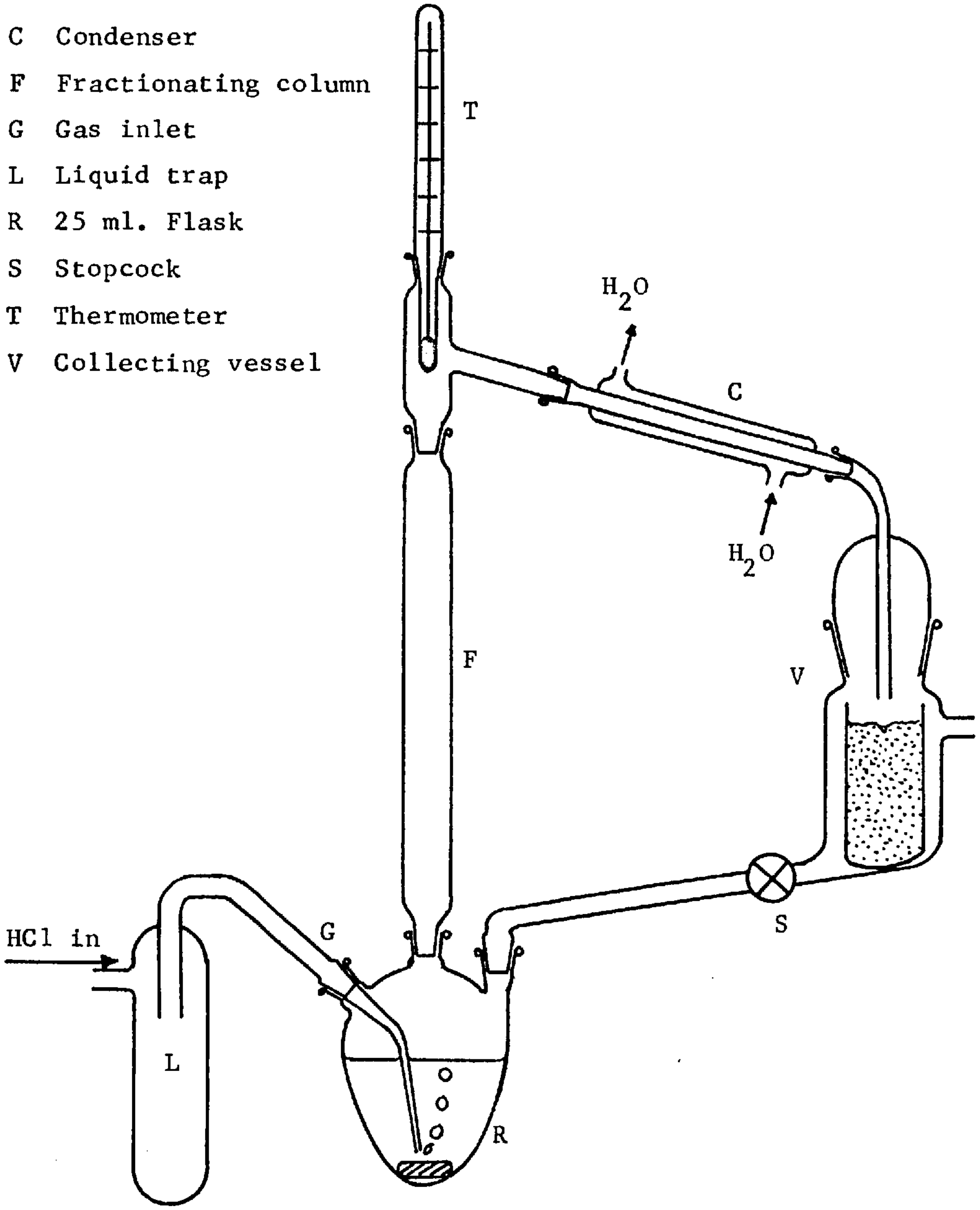
A.2.2.3 - 16g. of anhydrous triphenylphosphite were placed in a 25 ml. three-necked flask fitted with a mechanical stirrer, a dropping funnel and a gas inlet, and chlorine was passed in until the contents of the flask had increased in weight to 19.8g., corresponding to the formation of triphenylphosphite dichloride. The mixture became solid as the reaction proceeded due to the formation of the dichloride. 2.2g. of but-2-ene-1,4-diol were then added dropwise, and stirring was recommenced as soon as possible. After the reaction had subsided, the mixture was distilled under reduced pressure to yield a mixture of phenol and 1,4-dichlorobut-2-ene. The crude dichlorobutene was dissolved in 5 ml. of ether, and the phenol was extracted by treatment with saturated sodium carbonate solution. The ethereal solution was then dried with anhydrous sodium sulphate, and the ether was removed by distillation. The resulting 1,4-dichlorobut-2-ene boiled at 150-165°C. Yield = 1.4g. (45%).

A.2.2.4 - The synthesis of 1,4-dichlorobut-2-ene from but-2-ene-1,4-diol using dry hydrogen chloride, was carried out in the apparatus shown in Fig. 25. A 25 ml. three-necked flask (R) was fitted with a gas inlet (G), and a short fractionating column (F) leading to a downward condenser (C) and a collection vessel (V) containing a sintered glass thimble (T). The distillate could be returned to the reaction flask via a stopcock (S).

8g. of but-2-ene-1,4-diol were dissolved in an equal quantity of sodium-dried benzene and placed in the 25 ml. flask, together with a drop of silicone fluid to prevent foaming. 15g. of anhydrous potassium carbonate were placed in the thimble, and the solution was heated to about 90°C so that benzene gently distilled over into the collection vessel. Dry hydrogen chloride was then admitted at a rate

Figure 25

Apparatus for the preparation of 1,4-dichlorobut-2-ene



C	Condenser
F	Fractionating column
G	Gas inlet
L	Liquid trap
R	25 ml. Flask
S	Stopcock
T	Thermometer
V	Collecting vessel

of about 100 $cm.^3 min.^{-1}$, and as the reaction proceeded, the water which was formed distilled off as an azeotropic mixture with benzene. After being dried in the collection vessel, the benzene was returned, at intervals, to the reaction flask. The reaction was allowed to proceed for 12 hours and the benzene was then distilled off completely. The residue was fractionally distilled to yield 6.25g. (55%) of pure 1,4-dichlorobut-2-ene (b.p. 160-165°C).

A.2.3 Preparation of vinylacetylene

6.5g. of potassium hydroxide and 10 ml. ethylene glycol were placed in a 25 ml. three-necked flask fitted with a gas inlet, a reflux condenser and a dropping funnel. The top of the condenser was connected to a trap immersed in an acetone/dry-ice mixture for collection of the product, and thence to a calcium chloride drying tube. The system was swept with a stream of nitrogen for 15-20 min. while the temperature of the flask was raised to 165 to 170°C. The flow of nitrogen was then reduced to a rate just sufficient to maintain an atmosphere of nitrogen in the system. 2g. of 1,4-dichlorobut-2-ene were added dropwise to the reaction mixture over a period of about 5 min., and the reaction mixture was stirred vigorously for about 1 hour, the resulting vinylacetylene being collected in the cold trap. The yield of crude product was ca. 0.08g. (10%).

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