THE PHOTOLYSIS OF SOME

SELECTED OLEFINS

A THESIS

by

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ABSTRACT

Studies have been made on the photolytic decompostion of but-1-ene, isobutene and cis pent-2-ene. A number of decomposition products were found in each case and the effects of time, added gas pressure, reactant pressure and temperature on the product yields was studied. The yields of the products increased linearly with time up to about 30 mins and thereafter the rate of production decreased due to polymer formation on the cell window. Temperature had no general effect on the product yields, whereas increasing the pressure of the reactant, added inert gases or oxygen caused a general decrease in the product yields. The yields of many of the products were eliminated by the addition of oxygen and were therefore taken to be of free radical origin, whereas thoseproducts whose yields are only affected by oxygen to the same extent as they were by nitrogen say, were classified as molecular fragmentation products.

From the results of the above experiments primary reaction schemes have been proposed for the decomposition of the olefins studied, the major reaction in each case being of free radical nature. In but-1-ene and cis pent-2-ene this is the cleavage of a C-C bond in the β position to the double bond and in isobutene it is the cleavage of a corresponding C-H bond. The quantum yields of the primary reactions are estimated after consideration of the fate of the free radicals produced.

But-1-ene

$$C_4H_8 - 1 \xrightarrow{h\nu} CH_3{\cdot} + {\cdot}CH_2 - CH = CH_2 \qquad \phi = 0.51$$
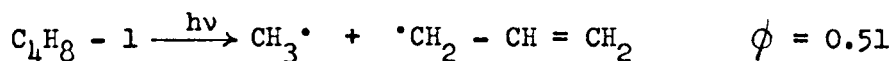
In addition five more primary reactions are postulated and their total quantum yield, $\phi = 0.213$

Isobutene

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} C = CH_2 \xrightarrow{h\nu} \begin{array}{c} {\overset{\cdot}{C}H_2} \\ \diagdown \\ \diagup \\ CH_3 \end{array} C = CH_2 + H{\cdot} \qquad \phi = 0.476$$
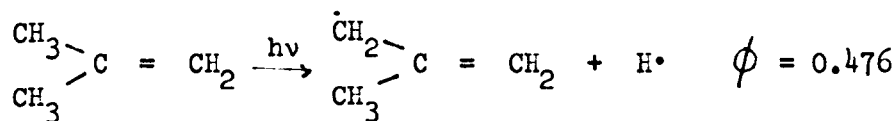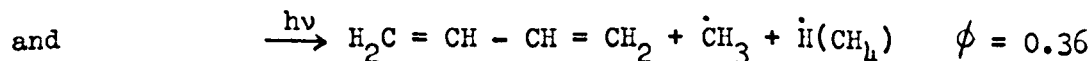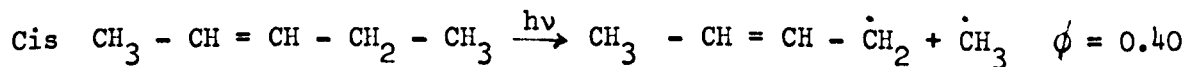
Similarly five more primary reactions are postulated to account for the products and their relative yields, the total quantum yield of these being 0.309.

Cis Pent-2-ene

The two major primary reactions suggested are:-

Cis $CH_3 - CH = CH - CH_2 - CH_3 \xrightarrow{h\nu} CH_3 - CH = CH - \overset{\cdot}{C}H_2 + \overset{\cdot}{C}H_3 \quad \phi = 0.40$

and $\xrightarrow{h\nu} H_2C = CH - CH = CH_2 + \overset{\cdot}{C}H_3 + \overset{\cdot}{H}(CH_4) \quad \phi = 0.36$

with a further three primary reactions of minor importance (total $\phi = 0.034$).

The decrease in the product yields with pressure is thought to be due to the collisional deactivation of an excited state intermediate; in the case of cis pent-2-ene this is the first excited singlet Rydberg

state on the basis that collisional deactivation did not give rise to isomerisation. The presence of a second excited state for cis pent-2-ene is postulated which is arrived at by a self-quenching or energy transfer process, this state gave rise to isomerisation rather than decomposition.

Estimates have been made of the decomposition lifetimes of the excited state intermediate in each of the three olefins and these are compared with the radiative lifetimes of the first excited singlet state obtained from spectral data.

CONTENTS

1. INTRODUCTION

1.1 Preliminary Remarks

The interaction of light with certain molecules may cause physical and chemical changes to take place and the study of this process is known as photochemistry. More than a century ago Grotthus put forward the first law of photochemistry and in 1912-13 Stark and Einstein formulated the second law. Since this time much work has been done and the early results have been shown more recently by the advent of mass spectrometry and gas chromatography to have been very accurate in view of the difficulties of product analysis confronting early workers. Light plays an important role in all forms of life since it is necessary in many biological reactions. One such process is the photochemical cis-trans isomerisation which plays an essential part in the mechanism of vision. The rods on the retina of the eye contain a visual pigment, rhodopsin, which is a combination of retinene (Vitamin A, aldehyde) and a protein (opsin). The retinene is in the 11-cis configuration and the absorption of light converts it all to the all-trans form. This isomerisation triggers off a chain of processes which eventually lead to visual excitation.[1]

Even though the process of photochemical cis-trans isomerisation is of basic importance little is known of the exact nature of the

mechanism. With this in mind James[2] set out to study the cis-trans
isomerisation of a simple olefin at 1849 Å, but-2-ene, in order to
gain some knowledge of the excited state intermediate involved.
Although some cis-trans isomerisation was induced the major process
involved appeared to be the dissociation of the butene leading to a
variety of products. Following this previous work but-1-ene and isobutene
were studied in order that the mechanism of photodecomposition may be
elucidated more fully, since both these compounds have similar
absorption spectra to those of the but-2-enes but the nature of the bonds
differ slightly. But-1-ene has C-C bonds in a β-position to the double
bond whereas the three other isomeric butenes have only C-C bonds in the
α-position. In an effort to pursue the mechanism of cis-trans isomerisa-
tion the photolysis of cis-pent-2-ene was studied and the results
examined in the light of the previous work on cis and trans but-2-ene.

The introduction to this thesis includes a discussion of the
various absorption spectra related to the compounds under examination
which provide information on the excited states involved by the
absorption of light. Some knowledge may also be gained with regard to
the various bond strengths of the olefins by thermal dissociation, and
thus an indication of which bond will dissociate first which is of prime
importance in establishing the reaction mechanism. Consideration is also
given to previous studies of olefinic photodecomposition using light of
various wavelengths.

1.2 Absorption Spectra

The absorption spectra of ethylene has been well studied and the discussion is therefore centred about ethylene[3,4] and may be then extended to include the substituted ethylenes.

The spectrum may be divided into several zones:-

(a) A series of diffuse bands of rapidly rising intensity, from 2069 Å (weak) to 1750 Å.

(b) A series of intense sharp bands, beginning at 1744 Å, and decreasing in intensity to shorter wavelengths.

(c) A broad continuum underlying the sharp bands, and rising to a maximum at 1630 Å.

(d) Three further series of sharp bands beginning at 1520 Å, 1440 Å and 1370 Å, underlain by another continuum.

The spectrum is associated with absorption by the π-electrons of the C=C bond, but the nature of the spectrum indicates that more than one type of electronic transition is involved.

The sharp bands beginning at 1744 Å have been assigned to a Rydberg transition by Price.[5] The banded structure is attributed to the excitation of the ν_2 (C=C stretching) and the ν_4 (twisting) vibrations in the Rydberg state, other vibrational modes being unexcited. The further banded series beginning at 1520 Å, 1440 Å and 1370 Å are also assigned to Rydberg transitions,[3,6] all three series converging to the same ionisation potential.

Figure 1.1
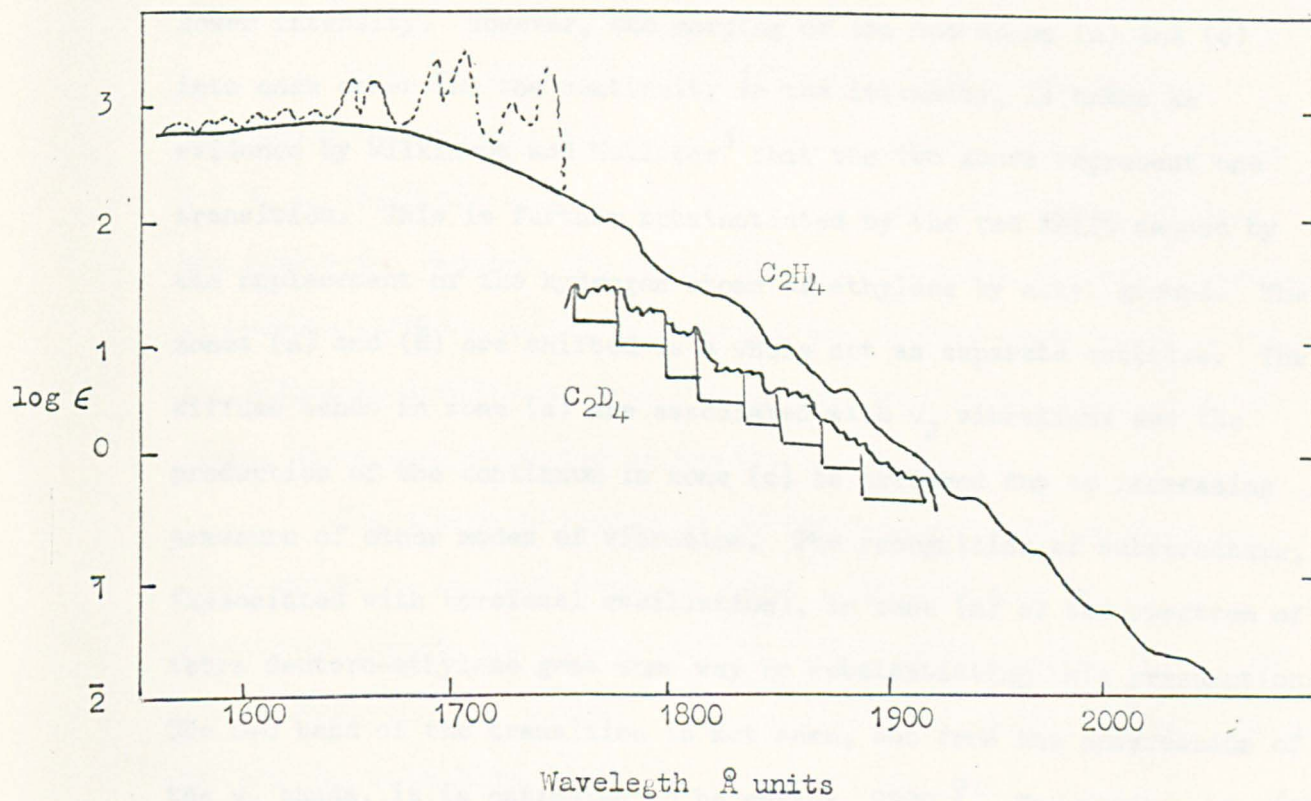
Absorption Spectra of C_2H_4 and C_2D_4 from 1550 to 2050 Å.
The dashed and solid curves correspond to the R←N and
V←N transitions respectively.[2]

The broad continuum (c) and the series of diffuse bands (a) are considered by Craig[7] to represent two different transitions, both singlet-singlet, but the latter one symmetry-forbidden and hence of lower intensity. However, the merging of the two zones (a) and (c) into each other and the continuity in the intensity, is taken as evidence by Wilkinson and Mulliken[3] that the two zones represent one transition. This is further substantiated by the red shift caused by the replacement of the hydrogen atoms of ethylene by alkyl groups. The zones (a) and (c) are shifted as a whole not as separate entities. The diffuse bands in zone (a) are associated with ν_2 vibrations and the production of the continuum in zone (c) is presumed due to increasing pressure of other modes of vibration. The recognition of substructure, (associated with torsional oscillation), in zone (a) of the spectrum of tetra deutero-ethylene goes some way to substantiating this presumption. The 0-0 band of the transition is not seen, but from the progression of the ν_2 bands, it is estimated to be approx. 2500 Å. The maximum at 1630 Å is associated with some twenty quanta of stretching vibrations, corresponding to a C=C bond length of 1.69 Å in the excited state, compared with a C= C bond length of 1.35 Å in the ground state.[8]

Thus two transitions are seen to occur. These are designated R ← N and V ← N in Mulliken's terms,[9] where N represents the singlet ground state, R represents the Rydberg state with one of the π-electrons transferred to a Rydberg orbital, undergoing a change in principal quantum number, and V represents the first upper excited singlet state, with one

of the π-bonding electrons transferred to an antibonding orbital. Price and Tutte[10] considered that the first Rydberg orbital is itself somewhat antibonding, since it occurs at a shorter wavelength than predicted.

Snow and Allsop[11] originally believed the weak diffuse absorption bands below 2069 Å to be due to singlet-triplet transition T ← N, in which the spin of the electron in the antibonding orbital was reversed. However, the use of long path lengths of liquid ethylene,[11] or gaseous ethylene in the presence of one hundred atmospheres of oxygen,[13] has helped to distinguish weak absorption bands in the 2600 - 3500 Å region which are attributed to the T ← N transition.

The effect of replacing the hydrogen atoms of ethylene by alkyl groups is to shift both the R ← N transition and the V ← N transition towards the visible region, although the former is shifted much further than the latter. These effects have been carefully studied by Carr and co-workers.[14,15,16]

The shift in the Rydberg bands depends solely upon the number of hydrogen atoms which have been replaced, and not upon the position of the hydrogens which are replaced. This is so since the energy of the transition is due to the effective nuclear charge on the central carbon atoms.[15] On the other hand the V ← N transition is a charge transfer transition, and thus depends on the effective dipole vector of the molecule. Therefore it is dependent on the positions of the hydrogen atoms replaced.[16,17]

The absorption spectra of but-1-ene and isobutene are shown in figures 1.2 and 1.3[18] and the positions of the first Rydberg bands and the band maxima are shown in Table 1.1.

Table 1.1

Olefin	Band Max. cm^{-1} (V ← N)	1st Rydberg band cm^{-1} (R ← N)
But-1-ene	57,100	53,390
Isobutene	53,100	49,750

Similar work was carried out on the isomeric pentenes,[16] the absorption spectra of cis-pent-2-ene, trans-pent-2-ene, and 2Me-butene being shown in figure 1.4.

The figures for the band maxima and first Rydberg bands are shown in Table 1.2.

Figure 1.2

Figure 1.3

BUT-1-ENE

log ϵ

WAVE NUMBER X 10^{-3} CM^{-1}

ISOBUTENE

log ϵ

WAVE NUMBER X10^{-3} CM^{-1}

Figure 1.4

Epsilon X 10^{-3}

WAVE NUMBER X 10^{-3} cm^{-1}
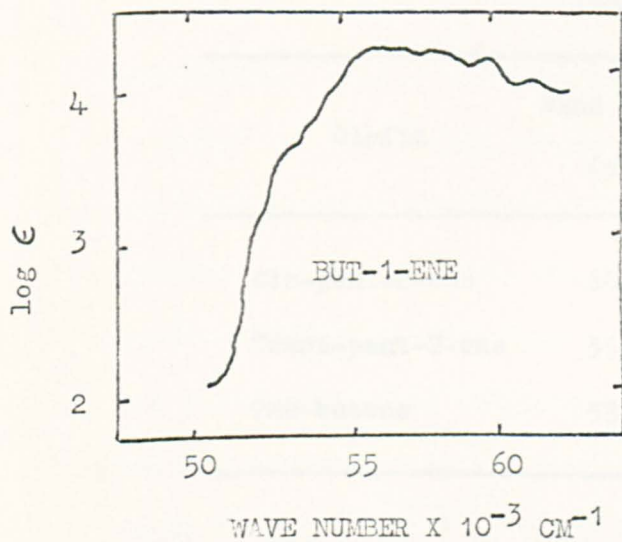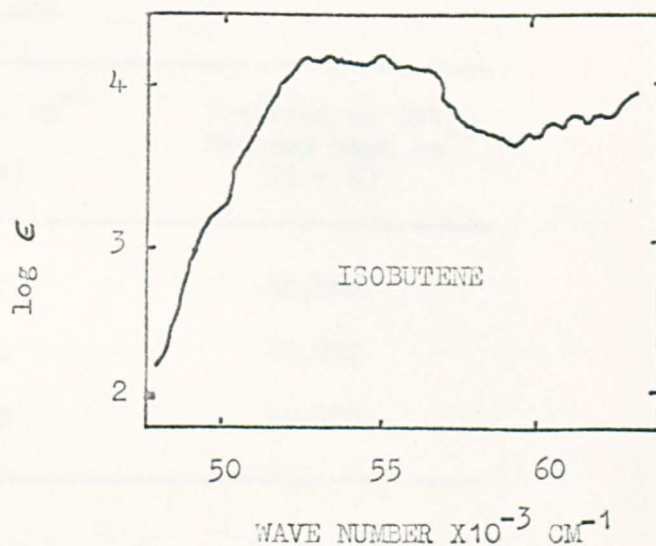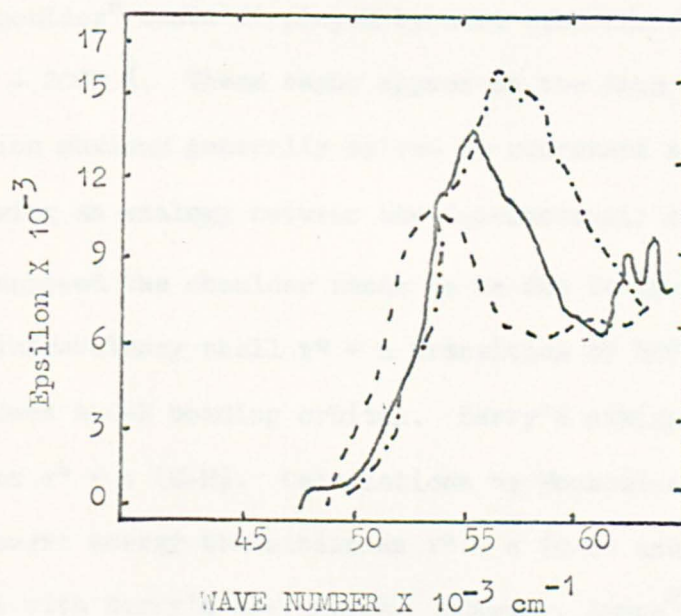
- - - Trans Pent-2-ene.

—— Cis Pent-2-ene.

—.—. 2 Me- But-1-ene.

Table 1.2

Olefin	Band Max. cm^{-1} (V ← N)	Position of 1st Rydberg band cm^{-1} (R ← N)
Cis-pent-2-ene	56,600	48,800
Trans-pent-2-ene	55,500	49,800
2Me-butene	53,200	49,800

Numerous conflicting assignments have been put forward for the weak "shoulder" bands displayed by most ethylene derivatives in the region 2500 - 2000 Å. These bands appear on the long wavelength side of the absorption maximum generally agreed to represent the V ← N transition. Berry[19] drawing an analogy between the isoelectronic molecules HCHO and C_2H_4, has supposed the shoulder bands to be due to the analogue of the well-known intravalency shell $\pi^* \leftarrow n$ transition of HCHO. In C_2H_4 the "n" orbital becomes a C-H bonding orbital. Berry's assignment may thus be symbolised as $\pi^* \leftarrow \sigma$ (C-H). Calculations by Moskowitz and Harrison[20] yield the lowest energy transition as $\pi^* \leftarrow \sigma$ (C-H) and the next as $\pi^* \leftarrow \pi$ in agreement with Berry's assignment. However, Evans[21] found a pronounced effect of nitrogen under pressure on the bands, in tetramethyl ethylene and cyclohexane, which is a strong indication that they are Rydberg bands. In agreement the $\pi^* \leftarrow \pi$ transition is found to be little affected by

nitrogen. It seems clear that the orbital to which an electron is transferred is not the same in the shoulder bands as in the $\pi^* \leftarrow \pi$ transition. Robin, Hart and Kuebler[22] assign the bands to a σ (C-H)$^* \leftarrow \pi$ transition, where the σ (C-H)* stands for an antibonding C-H orbital which is unoccupied in the ground state and has considerable Rydberg character. Robin et. al., seem to assume that the shoulder bands correspond to the Snow and Allsop bands of ethylene,[11] but these are much weaker than originally supposed and Evans[13] finds no evidence for any transition in the ethylene spectrum in the region 2500 - 2000 $\overset{o}{A}$ other than the "tail" of the V $\leftarrow$ N transition. Similarly in the same region, the spectrum of a single crystal of ethylene shows[23] only bands apparently analogous to the V $\leftarrow$ N transition in the gas phase. It does not seem to rule out that the shoulder bands of ethylene derivatives simply correspond to the well-known 1744 $\overset{o}{A}$ Rydberg bands of ethylene itself, as originally supposed by Carr and Stucklen.[15] In this connection it should be remembered that the origin of the V $\leftarrow$ N transition lies at lower energy than the origin of the 1744 $\overset{o}{A}$ transition, even though the order of the vertical transition energies is reversed. The shoulder bands have been called the "mystery" bands; the mystery does not yet appear to have been cleared up.

Gary and Pickett and also Jones and Taylor[24] measured the extinction coefficient (ϵ) for the butenes and the oscillator strengths for the bands were determined using the formula:

$$f = 4.32 \times 10^{-9} \int_{\nu_1}^{\nu_2} \epsilon d\nu \qquad 1.I$$

where the value of the integral was evaluated from the product of the maximum value of ϵ and the band width at half the maximum value.[25] Table 1.3 shows the values obtained for the butenes.[18]

Table 1.3

Olefin	f value
But-1-ene	0.39
Isobutene	0.39
Trans But-2-ene	0.32
Cis But-2-ene	0.59

and Table 1.4 those obtained for the pentenes.[16]

Table 1.4

Olefin	f value
Cis Pent-2-ene	0.45
Trans Pent-2-ene	0.32
2Me Butene	0.38

The spectra of the above olefins show that the V ← N and R ← N are superimposed in the region of 1849 $\overset{o}{A}$ and certainly the mystery band is in easy "striking" distance, one therfore may expect that excitation with light of 1849 $\overset{o}{A}$ may produce ~~either~~ any of the above three or indeed a mixture.

1.3 Excited States

By international convention the symbol for the upper state is always written first and that for the lower state last regardless of whether the process is absorption or emission.[26] In the enumerative notation, singlet states are labelled S_o, S_1, S_2 etc., in order of increasing energy with S_o the ground state. Triplets[27] are labelled T_1, T_2, T_3 etc., Mulliken[25,28] employs different capital letters to represent states, N (normal) being the ground state and V, R, for example, referring to excited states.

One can also describe electronic transitions in terms of the initial and final orbitals occupied by the single electron involved in the transition.[29] A relatively simple system but less precise than say symmetry notation.

As stated previously the olefins under study may undergo transitions of the V ← N and R ← N types from consideration of the absorption spectrum. The V ← N transition involves promotion of one electron from a bonding M.O. to an antibonding M.O. and in the case of an olefin is designated as $\pi^* ← \pi$ transition. In Rydberg transitions, R ← N, a change in the principal quantum number of the electron occurs.

The electron is promoted from a bonding M.O. to a M.O. which is essentially atomic in character. This being illustrated by the fine structure superimposed on the olefin absorption spectrum. The excited state responsible for the "mystery" band is also a possible state to be considered but conflicting assignments make it difficult to name one in particular, but an extension of the Rydberg bands is strong possibility, and calculations of the type made by Mulliken and Wilkinson[3] on the barrier to rotation about the double bond in the Rydberg state, would yield much useful information. A value of 0.1 ev for the barrier to rotation of the double bond in the Rydberg state has been calculated from the work of Mulliken and Wilkinson, which is much lower than that of the ground state (2.66 e.v.) thus isomerisation from an excited Rydberg is likely, but less so than say the V state (upper singlet).[103] The triplet state for ethylene has been shown to lie at 3600 - 2500 $\overset{o}{A}$ for ethylene[13] but being spin-forbidden is only very low in intensity.

Once an excited singlet V state has been produced by the electronic transition from a bonding π-orbital to an antibonding π^*-orbital, the energy gained from the exciting light may be lost by the following processes,[29] as illustrated with a Jablonski diagram. Figure 1.5.

1. Dissociation of a vibronic state to yield photochemical products.

2. Collisional deactivation of a vibronic state.

3. Fluorescence: radiative conversion to the ground state.

Figure 1.5
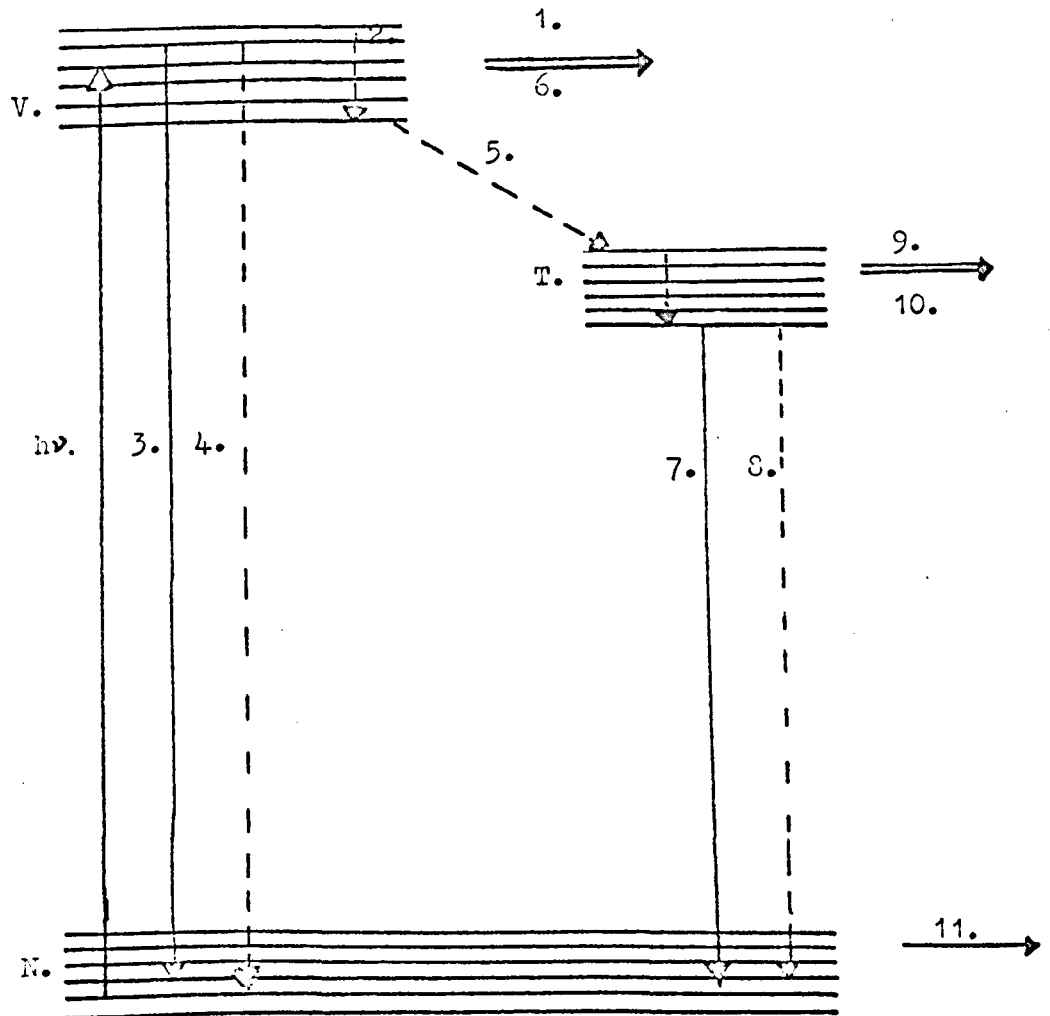
Full lines represent radiative processes, and broken
lines represent non-radiative processes.

4. Internal Conversion: non-radiative conversion to the ground state.

5. Intersystem Crossing: non-radiative transition which involves a spin intercombination to the triplet state, which is then vibrationally deactivated.

6. Energy transfer non-radiatively to a neighbouring molecule.

   The triplet state produced in (5) will lose its energy by:-

7. Phosphorescence: radiative intercombination with the ground state.

8. Internal conversion: non-radiative intercombination with the ground state.

9. Photochemical dissociation from the triplet state.

10. Triplet-Triplet energy transfer: non-radiative transfer of electronic energy to a neighbouring molecule.

The ground state molecule produced by internal conversions (4) and (8) may be highly vibrationally excited, and may lose its energy by:-

11. Dissociation of the vibrationally excited ground state to yield photochemical products.

If an excited molecule is not deactivated or does not decompose, it will return to the ground state after a certain time with emission of radiation (3). If A_m is the average number of transitions per

atom per sec. between upper state n and lower state m, the mean life

of state n is defined as:

$$\tau = {}^1\!/A_{nm} \qquad\qquad 1.II[30]$$

A_{nm} is the Einstein transition probability of spontaneous emission, and

governs the intensity of emission from the upper state. Hence each

excited state has a mean life τ, and if the molecule is to undergo

reaction in the excited state the rate constant for the reaction must be

shorter than the mean life. The mean life is also inversely proportional

to the absorption strength of the excited state. The Beer-Lambert Law[31]

states that the integrated fraction of light absorbed by an assembly of

molecules is proportional to the number of absorbing systems in the light

path, viz.

$$\log ({}^I\!o/_I) = \epsilon\,cl \qquad\qquad 1.III$$

where I_o and I are the incident and transmitted intensities respectively,

l the path length in cm. and c the concentration in moles/litre. The ϵ is

the molar extinction coefficient in litres/mole/cm. The mean lifetime and

ϵ are related by:-

$$\int_{\nu_1}^{\nu_2} \epsilon\,d\nu = \frac{\lambda_o^2}{8\pi} \cdot \frac{N_o}{\tau} \qquad\qquad 1.IV[32]$$

where λ_o is the wavelength of the maximum of the absorption band, N_o is Avogadro's number and ν_1 and ν_2 the limits of the absorption band, are in units of frequency. The value of $\int \epsilon d\nu$ may be taken as $\epsilon_{max.}$ times the peak width at half peak height.

In the near u.v. this can be approximated to

$$\tau = 10^{-4}/\epsilon_{max.} \qquad\qquad 1.V^{32}$$

Thus for V ← N transition in olefins, where $\epsilon_{max.}$ is of the order 10,000, τ is of the order 10^{-8} sec.; while for T ← N transitions, which are spin-forbidden, $\epsilon_{max.}$ is less than 10, so that $\tau \sim 10^{-5}$ sec. Consequently, triplet states are much more likely to be influenced by environment in view of the longer mean lifetime.

The mean radiative lifetime of the V state of the isomeric butenes as calculated from the spectral measurements of Gary and Pickett[18] using the formula 1.I to calculate the value of the integral are shown in Table 1.5.

Table 1.5

Olefin	τ rad. (sec)
But-1-ene	1.19×10^{-9}
Cis-but-2-ene	1.09×10^{-9}
Trans-but-2-ene	1.93×10^{-9}
Isobutene	1.37×10^{-9}

These mean lifetimes must be considered in relation to a vibrational period of 10^{-13} sec., a rotational period of 10^{-10} sec., and a collision frequency in the vapour phase of 2×10^{11} litres moles^{-1} sec.$^{-1}$ (calculated using a value of 6.5 Å for butene[34] in the relationship

$$Z_o = \frac{2 N_o}{1000} \sigma^2 \left(\frac{\pi RT}{M}\right)^{\frac{1}{2}} \qquad \qquad 1.VI[35]$$

where σ is the collision diameter and M the molecular weight of butene).

From the above one might expect that deactivation of the V state may yield a mixture of cis and trans isomers of say cis pent-2-ene whereas deactivation of the R state (shown to have a potential barrier to rotation about the C=C) would yield only the original isomer. The state responsible for the "mystery" band would behave as a Rydberg state if it too has a potential barrier or the V state if it is found not to have such a barrier to rotation.

1.4 Pyrolysis

Thermal decomposition of olefins serves as a useful comparison with photochemical decompositions, especially when deciding which bond is most likely to break first. This section describes briefly work which has been performed on some olefins.

The pyrolysis of propylene has been studied in some detail between 550 and 870°C,[36-39] and a long chain free radical mechanism proposed in which reactions of the 1-methyl-4-pentenyl radical is of prime importance.[40] The main chain termination reaction was found to be

combination of methyl and allyl radicals. Very extensive studies of the kinetics of the reaction were made possible with the use of gas chromatography and mass spectrometry. The most probable initiation steps are:-

$$C_3H_6 \rightarrow H\cdot + C_3H_5\cdot \qquad 1.VII$$

$$C_3H_6 \rightarrow CH_3\cdot + C_2H_3\cdot \qquad 1.VIII$$

$$2C_3H_6 \rightarrow C_3H_5\cdot + C_3H_7\cdot \qquad 1.IX$$
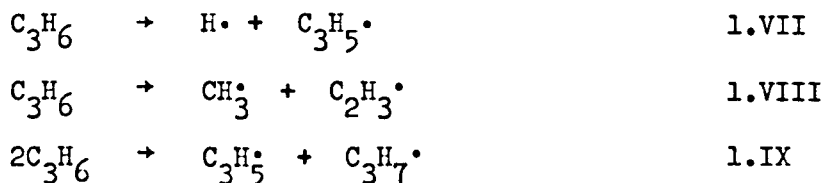
The rates of these reactions have been compared on a theoretical basis[41] and supported by experimental work,[42,43,44] the conclusion has been drawn that reaction 1.VIII is the prime initiation step.

Swarc and Sheon[45] examined the results of the pyrolysis of but-1-ene by a flow method using toluene as carrier gas between 935 and $1046^\circ K$. The decomposition was measured by the rate of formation of methane which was found as a non-condensable gas with hydrogen. They proposed the cleavage of the C-C bond β to the double bond as the major reaction,

$$CH_3-CH_2-CH=CH_2 \xrightarrow{\Delta} CH_3\cdot + \overset{\cdot}{C}H_2-CH=CH_2 \qquad 1.X$$
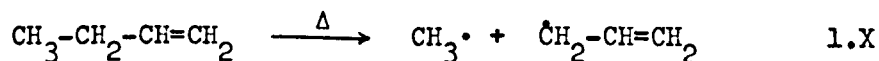
this being homogeneous and of 1st order.

The products from the pyrolysis of isobutene[46] were found to include hydrogen, methane and allene. The experimental results were

explained in terms of a chain mechanism the initiating step being

decomposition of isobutene into a hydrogen atom and a C_4 radical,

$$\begin{array}{c} CH_3 \\ {}^{\backslash}\!C = CH_2 \\ {}_{/} \\ CH_3 \end{array} \xrightarrow{\Delta} H\cdot + \begin{array}{c} \overset{\bullet}{C}H_2 \\ {}^{\backslash}\!C = CH_2 \\ {}_{/} \\ CH_3 \end{array} \qquad 1.XI$$
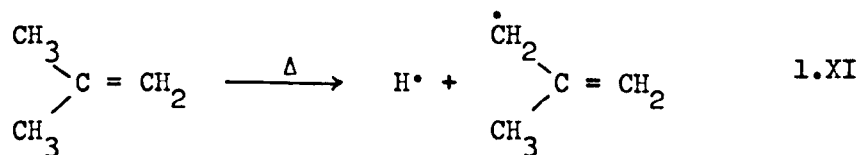
the value of D(C—H) in isobutene given as 76 kcal/mole corresponding to

the C—H bond β to the double bond. Rice and Haynes[47] supported a chain

mechanism but they suggested that the initiating step was the cleavage

of the α C—C bond:-

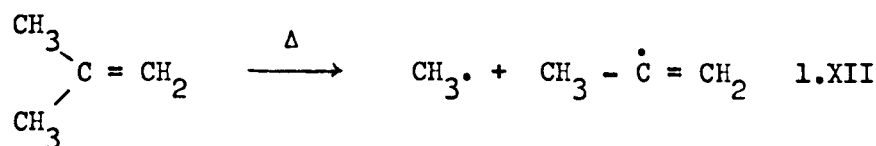$$\begin{array}{c} CH_3 \\ {}^{\backslash}\!C = CH_2 \\ {}_{/} \\ CH_3 \end{array} \xrightarrow{\Delta} CH_3\cdot + CH_3 - \overset{\bullet}{C} = CH_2 \qquad 1.XII$$

When ethylene is heated to moderately high temperatures

decomposition takes place, at the same time some polymerisation is also

found.[48,49] As is the case of most thermal decompositions it is not

possible to separate the two reactions and hence the mechanism becomes

very complex. Hague and Wheeler[48] concluded that butadiene was the most

important product in the polymerisation but the result was complicated

by much decomposition.

The thermal decomposition of pentene[50] also illustrates the weakness of the β C-C and β C-H bonds in olefinic molecules. With this in mind one might say that cleavage of the C-C bond β to the double bond is of prime importance in thermal decomposition reactions, this being concluded after consideration of the product distribution.

The thermal decomposition of radicals[51,52] is also important when one sets out to formulate a mechanism for the photodecomposition of olefins since radicals are formed and their disappearance will give rise to products. The decomposition of the sec-butyl radical, formed say by the addition of a hydrogen atom to but-1-ene,

$$\text{sec.} \quad CH_3\text{-}\overset{\bullet}{C}H\text{-}CH_2\text{-}CH_3 \quad \rightarrow \quad CH_3\cdot \ + \ C_3H_6 \qquad \text{1.XIII}$$
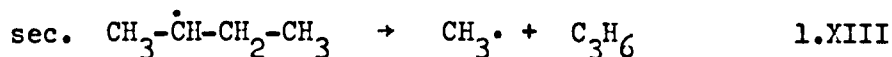
into propylene and a methyl radical has an activation energy of 23.5 kcal/mole.[51]

Studies on the i-butyl[53] radical show that for the same decomposition a value of 31 ± 2 kcal has been calculated for the activation energy.

1.5 <u>Photosensitisation</u>

Certain elements have excited states with resonance levels of sufficient energy that collision with many types of molecules leads to

primary photochemical processes. Those that also have vapour pressures of about 10^{-3} mm. or more at temperatures where the molecule is stable, and are capable of being excited in a low pressure discharge to give an intense resonance line or lines, may be effective sensitisers for inducing decomposition of a wide variety of molecules which are transparent to the incident resonance radiation itself. Several of these are tabulated in Table 1.6.[54]

<div align="center">Table 1.6</div>

	Metal			
	Hg	Cd	Zn	Ca
Principal quantum number, n:	6	5	4	4
Singlet-Singlet				
$n(^1P_1) \rightarrow n(^1S_0) + h\nu$				
wavelength; Å	1849	2288	2139	4227
Energy, kcal/einstein:	154.6	125.0	133.7	67.6
Radiative lifetime, sec:	1.3×10^{-9}	1.2×10^{-9}	$< 10^{-7}$	3.5×10^{-9}
Triplet-Singlet				
$n(^3P_1) \rightarrow n(^1S_0) + h\nu$				
wavelength: Å	2537	3261	3076	6537
Energy, kcal/einstein:	112.7	87.7	92.9	43.7
Radiative lifetime, sec:	1.1×10^{-7}	2×10^{-6}	-	-

If one is to study on the other hand a 'direct' photolysis then one must be very careful to exclude any traces of metallic sensitisers from the system. Pertol[55] noted that the direct photolysis of C_2H_4 at 1849 Å gave different results than the Hg ($^1P_1$) sensitised reaction.

Ley Roy and Steacie[56] proposed that for ethylene (and it is now agreed for olefins generally)[57] the primary act is triplet energy transfer to produce a relatively long-lived excited state intermediate of the olefin.
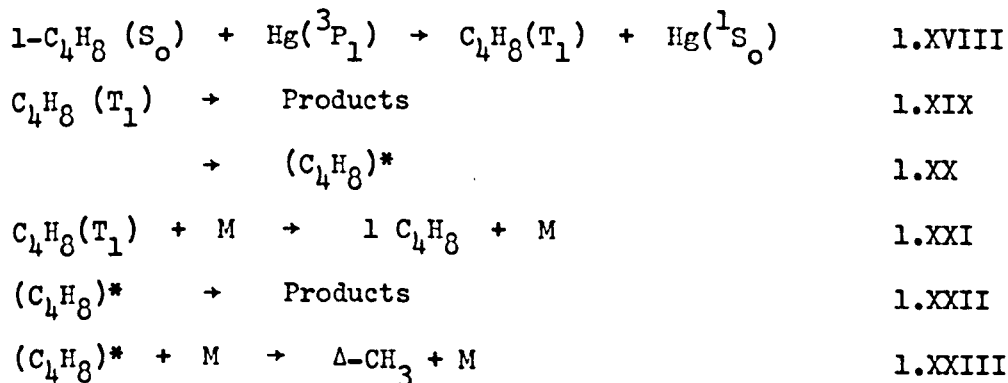
Hydrogen and acetylene are the major products from the mercury sensitised decomposition of ethylene, which has been studied extensively. The quantum yields of these products were found to decrease with increasing pressure of ethylene or added inert gas.[58,59] These facts are indicative of an excited state intermediate and Cvetanovic and Callear[60] verified this using mixtures of ethylene and deuterated ethylene. They found that the product did not contain any HD or mixed acetylenes, though some evidence for vinyl and H radical split has been found.[58] Later, Cvetanovic and Callear[61] suggested a mechanism that incorporated two electronically and vibrationally excited states of approximately equal lifetime, both were subject to collisional deactivation but only one decomposed.

Evidence to support this two-excited states proposal was gained by using cis-ethylene d_2. Not only were D_2, HD, and H_2 (in the ratio 1:6:2) and the corresponding acetylenes formed, but there was also extensive isomerisation to the trans isomer and the unsymmetrical

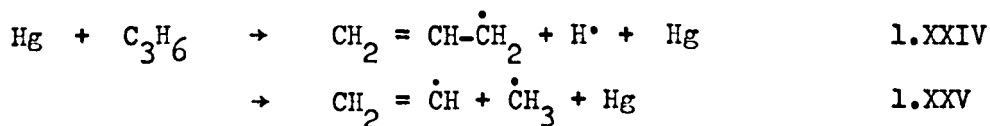isomer, $H_2C = CD_2$. Similar experiments using the trans isomer gave a very similar result.[62]

Cis-trans isomerisation using mercury as a sensitiser has been illustrated using the but-2-enes.[63,64] On prolonged irradiation a 1:1 mixture of trans and cis was found to result, and at pressures above 30 mm. $\emptyset_{c-t} = \emptyset_{t-c} = 0.5$.[65] Using mass spectrometry it was found that at low reactant pressures CH_3 and H radicals were formed but the major reaction was cis/trans isomerisation.[66]

Cleavage of C-C bonds is of great importance in but-1-ene, and in general the higher olefins. The relatively weak β-C-C bonds in but-1-ene facilitate dissociation and the ratio of β-C-C to the β-C-H bond cleavage was calculated to be 1.3 - 1.6 to 1.[63] Isomerisation to but-2-ene was also found[67] but it was of minor importance, whereas the isomerisation to methyl cyclopropane was of importance.[63] The thirty-three products found were shown to decrease in yield with pressure but the isomerisation to methylcyclopropane rose to a maximum at 65 mm. and then dropped off at 230 mm. Thus two excited states are proposed in the mechanism.

$$1\text{-}C_4H_8 \ (S_o) + Hg(^3P_1) \rightarrow C_4H_8(T_1) + Hg(^1S_o) \qquad \text{1.XVIII}$$

$$C_4H_8 \ (T_1) \rightarrow \text{Products} \qquad \text{1.XIX}$$

$$\rightarrow (C_4H_8)^* \qquad \text{1.XX}$$

$$C_4H_8(T_1) + M \rightarrow 1 \ C_4H_8 + M \qquad \text{1.XXI}$$

$$(C_4H_8)^* \rightarrow \text{Products} \qquad \text{1.XXII}$$

$$(C_4H_8)^* + M \rightarrow \Delta\text{-}CH_3 + M \qquad \text{1.XXIII}$$

The importance of the β bond cleavage in the pentenes was also illustrated by Majer and Robb,[67] α-bond cleavage was not totally ruled out but was only of minor importance.

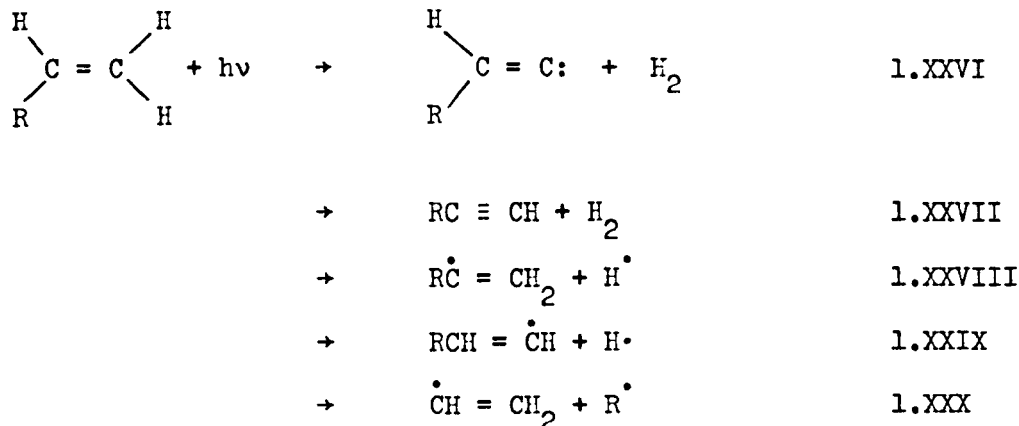Propylene decomposes into free radicals by two reactions on mercury photosensitisation.[102]

$$Hg \; + \; C_3H_6 \quad \rightarrow \quad CH_2 = CH\text{-}\overset{\bullet}{C}H_2 + H^{\bullet} + Hg \qquad \text{1.XXIV}$$

$$\rightarrow \quad CH_2 = \overset{\bullet}{C}H + \overset{\bullet}{C}H_3 + Hg \qquad \text{1.XXV}$$

The ratio of the two reactions being about 9:1 in preference to the C-H bond split.

Mercury photosensitisation (input 112 kcal.mole^{-1}) results mainly in the cleavage of the weak bonds β to the double bond,[63,67] yielding resonance stabilised allylic radicals. With compounds able to exhibit cis-trans isomerisation the main reaction is in fact the isomerisation, and workers[63,64,65] have found that the two isomers are formed in equal amounts. Thus it is also concluded that deactivation of the triplet state of but-2-ene would yield both isomers with equal probability.

1.6 Direct Photolysis

As noted earlier several possible excited states may be intermediates in any reaction of olefins which may be excited by light. Excitation within the first singlet-singlet absorption band may be

followed by a variety of fragmentation steps involving H_2 molecule and hydrogen atom and radical formation,

$$\underset{R}{\overset{H}{\diagdown}}C = C\underset{H}{\overset{H}{\diagup}} + h\nu \quad \rightarrow \quad \underset{R}{\overset{H}{\diagdown}}C = C: \ + \ H_2 \qquad \text{1.XXVI}$$

$$\rightarrow \quad RC \equiv CH + H_2 \qquad \text{1.XXVII}$$

$$\rightarrow \quad R\overset{\bullet}{C} = CH_2 + \overset{\bullet}{H} \qquad \text{1.XXVIII}$$

$$\rightarrow \quad RCH = \overset{\bullet}{CH} + H\cdot \qquad \text{1.XXIX}$$

$$\rightarrow \quad \overset{\bullet}{CH} = CH_2 + \overset{\bullet}{R} \qquad \text{1.XXX}$$
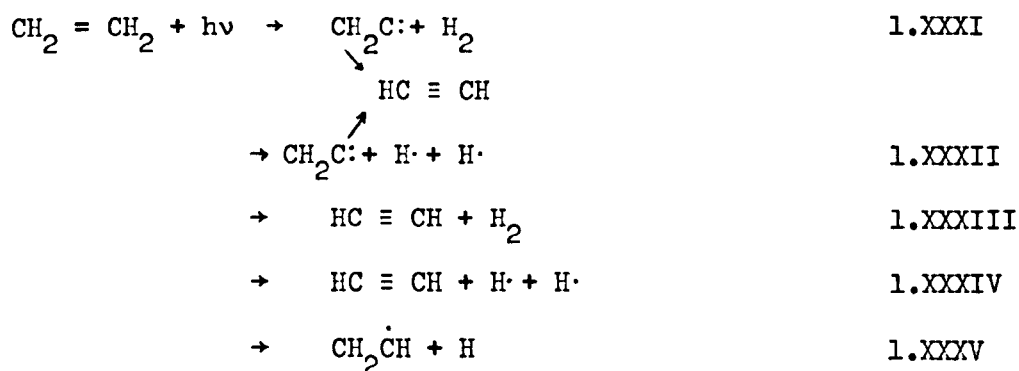
Alternatively the major result of excitation, particularly in solution may be isomerisation of the original olefin.

In the remainder of this section some of the direct olefin photolysis studies will be reviewed.
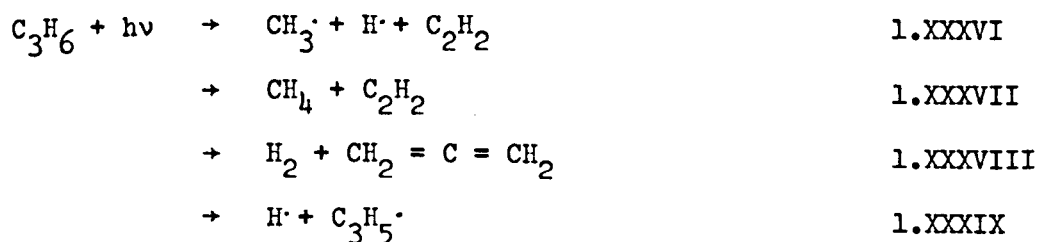
Early investigations of the photolysis of ethylene did not distinguish very clearly between the direct photochemical reaction and the mercury sensitised reaction. The most definite information about the direct photoreaction was obtained by Mooney and Ludlam,[68] who found that ethylene did not absorb light of wavelength greater than 2130 Å to any appreciable extent, and concluded that nothing was to be expected from investigations using lamps not capable of emitting light less than 2000 Å. Mooney and Ludlam used an aluminium spark with a high intensity at 1860 Å and found that acetylene was formed. Qualitative observations by Lind and
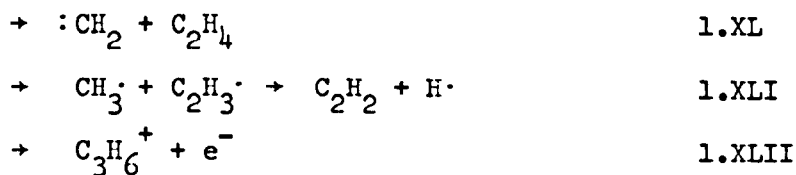
Livingston[69] are in agreement with these results. Taylor and Emeleus[70] showed that a polymer was formed on irradiating ethylene by 1849 $\overset{o}{A}$ light from a mercury arc, in the absence of mercury vapour. McDonald and Norrish[71] reinvestigated the reaction using a hydrogen lamp source and fluorite apparatus and were thus able to use shorter wavelengths. Hydrogen, a polymer and a condensable gas were formed under these conditions. More recently[72,73] at 1236, 1470 and 1849 $\overset{o}{A}$ investigations suggest the mechanism

$$CH_2 = CH_2 + h\nu \rightarrow CH_2C: + H_2 \qquad \text{1.XXXI}$$
$$\searrow$$
$$HC \equiv CH$$
$$\nearrow$$
$$\rightarrow CH_2C: + H\cdot + H\cdot \qquad \text{1.XXXII}$$
$$\rightarrow HC \equiv CH + H_2 \qquad \text{1.XXXIII}$$
$$\rightarrow HC \equiv CH + H\cdot + H\cdot \qquad \text{1.XXXIV}$$
$$\rightarrow CH_2\dot{C}H + H \qquad \text{1.XXXV}$$

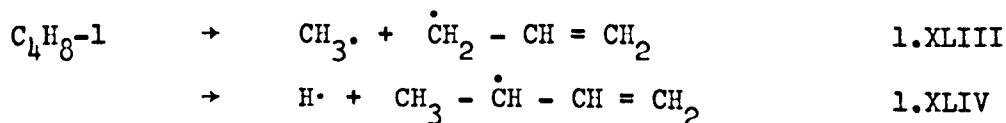to account for the products and the possible cis/trans isomerisation with deuterated ethylene.

Six reactions have been suggested for the photolysis of propylene[74,75] at 1470 $\overset{o}{A}$ and a further reaction XLII for that at 1236 $\overset{o}{A}$.

$$C_3H_6 + h\nu \rightarrow CH_3\cdot + H\cdot + C_2H_2 \qquad \text{1.XXXVI}$$
$$\rightarrow CH_4 + C_2H_2 \qquad \text{1.XXXVII}$$
$$\rightarrow H_2 + CH_2 = C = CH_2 \qquad \text{1.XXXVIII}$$
$$\rightarrow H\cdot + C_3H_5\cdot \qquad \text{1.XXXIX}$$

$$\rightarrow \; :CH_2 + C_2H_4 \qquad\qquad\qquad 1.XL$$

$$\rightarrow \; CH_3\cdot + C_2H_3\cdot \rightarrow C_2H_2 + H\cdot \qquad 1.XLI$$

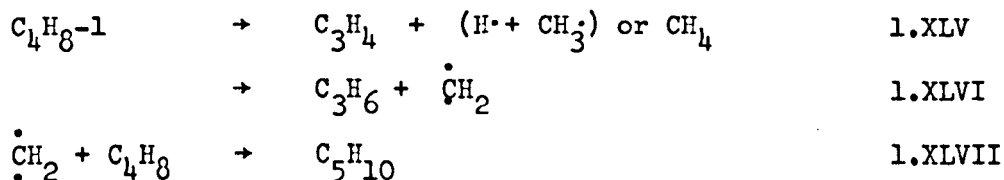$$\rightarrow \; C_3H_6^+ + e^- \qquad\qquad\qquad 1.XLII$$

Arai et. al.[76] photolysed propylene at 1849 Å and found some fifteen products and a solid polymer. The yields of the products were found to be practically independent of propylene pressure (10 - 70 mm.) though a slight possible linear increase was reported. This being quite different from the mercury photosensitised results. They accounted for the products and their relative yields by C-C and C-H bond cleavage reactions, which occur to a comparable extent. Very few results were reported and the effect of propylene pressure appears inconclusive.

Previous studies on but-1-ene at 1849 Å[77] showed that some twenty products were formed and the yields said to be independent of but-1-ene pressure. The pressure range quoted was 1.7 - 125 mm. Hg but as before[76] few experimental results were listed and in fact a pressure dependence was indeed found in several products. The two major reactions suggested were free radical reactions,

$$C_4H_8\text{-}1 \qquad \rightarrow \qquad CH_3\cdot + \overset{\bullet}{C}H_2 - CH = CH_2 \qquad 1.XLIII$$

$$\rightarrow \qquad H\cdot + CH_3 - \overset{\bullet}{C}H - CH = CH_2 \qquad 1.XLIV$$
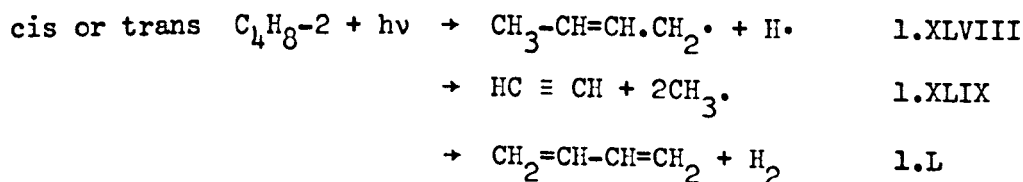
The ratio of the C-C bond split to the C-H bond split was put at about 7 to 1, thus indicating the weakness of the C-C bond β to the double bond. Okabe et. al.[78] confirmed the preference for β C-C split
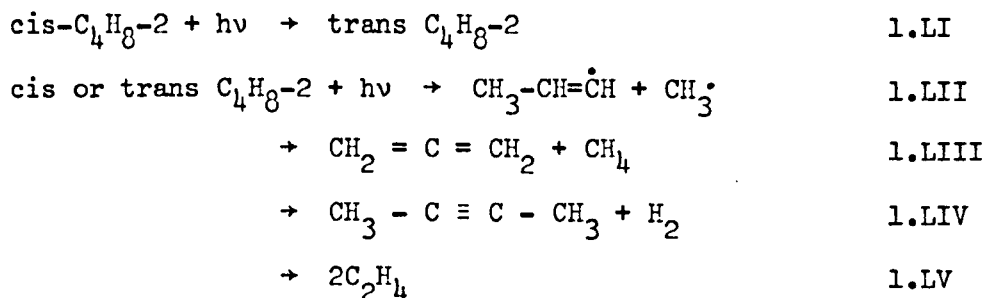
and from their mass spectrometric measurements proposed that the following reactions were also of importance in the photolysis of but-1-ene at 1849 $\overset{\circ}{A}$.

$$C_4H_8\text{-}1 \quad \rightarrow \quad C_3H_4 + (H\cdot + \overset{\bullet}{C}H_3) \text{ or } CH_4 \qquad \text{1.XLV}$$

$$\rightarrow \quad C_3H_6 + \overset{\bullet}{C}H_2 \qquad \text{1.XLVI}$$

$$\overset{\bullet}{\underset{\bullet}{C}}H_2 + C_4H_8 \quad \rightarrow \quad C_5H_{10} \qquad \text{1.XLVII}$$

The preferential C-C bond split can be explained on the basis of the bond energy difference $D(C_2H_3 - C_2H_5) - D(C_3H_5 - CH_3)$ of 28 kcal/mole.[79]

In isobutene[80] and the but-2-enes[2,82,83] the major reaction is cleavage of the C-H bond β to the double bond since no β C-C bond exists. Borrell and James[2] reported the presence of hydrogen and thirty-two hydrocarbon products in the gas phase and also a solid polymer. The yields of the products were said to decrease with pressure except those of the geometric isomer and but-1-ene. A mechanism was suggested in which eight possible primary reactions account for the products. Only the reaction involving the isomer is pressure independent, all the others being quenched by increasing the pressure or adding foreign gases.

$$\text{cis or trans } C_4H_8\text{-}2 + h\nu \quad \rightarrow \quad CH_3\text{-}CH\text{=}CH.CH_2\cdot + H\cdot \qquad \text{1.XLVIII}$$

$$\rightarrow \quad HC \equiv CH + 2CH_3\cdot \qquad \text{1.XLIX}$$

$$\rightarrow \quad CH_2\text{=}CH\text{-}CH\text{=}CH_2 + H_2 \qquad \text{1.L}$$

$$cis\text{-}C_4H_8\text{-}2 + h\nu \rightarrow trans\ C_4H_8\text{-}2 \qquad\qquad\qquad 1.LI$$

$$cis\ or\ trans\ C_4H_8\text{-}2 + h\nu \rightarrow CH_3\text{-}CH\text{=}\overset{\bullet}{C}H + CH_3\overset{\bullet}{} \qquad 1.LII$$

$$\rightarrow CH_2 = C = CH_2 + CH_4 \qquad\qquad 1.LIII$$

$$\rightarrow CH_3 - C \equiv C - CH_3 + H_2 \qquad\qquad 1.LIV$$

$$\rightarrow 2C_2H_4 \qquad\qquad\qquad\qquad 1.LV$$

The first reaction accounts for half the observed reaction and the ratio of this to the fourth gives a value of 7 to 1 which corresponds to the ratio of the C-H to C-C split.

Recent studies using flash photolysis techniques[95] have illustrated the importance of the β C-C bond cleavage in but-1-ene by the presence of the absorption spectra of the free allyl radical in the product mixture. Similarly the methyl allyl radical absorption spectra was seen on flashing but-2-ene, isobutene and cis pent-2-ene, illustrating the importance of the β C-H bond cleavage in but-2-ene and isobutene where no β C-C bond exists and the β C-C bond cleavage is cis pent-2-ene.

1.7 Summary of Available Information

The results from pyrolysis, mercury photosensitisation and direct photolysis seem to suggest that, when present, it is the C-C bond β to the double bond which breaks first when energy is added to the system. If a C-C in the β position is not present then it is the C-H bond in a β position to the double bond which breaks first. In the case of photo-sensitisation at 2537 Å a definite pressure quenching effect is noted;

presumably from an excited triplet state, whereas the effect in
the unsensitised studies is not clear since conflicting reports have
been made. The excited state responsible for the unsensitised
decompositions is not yet resolved, much support being given to the
theory of the first excited singlet Rydberg state being the intermediate
for decomposition whereas the V state is responsible for isomerisation
wherever possible. These possibilities being suggested after
consideration of pressure effects remembering that the first excited
singlet Rydberg state has a potential barrier to rotation about the
double bond.

Experiments were then performed on selected olefins to
determine the effects of several parameters – not least that of pressure,
thus the above postulations may be examined further and perhaps some
support for the suggestion of the excited state intermediate gained.

2. EXPERIMENTAL

2.1 Introduction

Known pressures of but-1-ene, isobutene or cis pent-2-ene were admitted to the reaction cell via a mercury-free vacuum system. After allowing the system to equilibriate the gas was irradiated by light of 1849 $\overset{o}{A}$ from a low pressure mercury lamp. Ethylene was used as an actinometer to measure the number of quanta of light entering the cell. After allowing time to mix the product gas was analysed using gas chromatography.

2.2 Materials

But-1-ene and isobutylene were obtained from Phillips Petroleum Company and were research grade materials. But-1-ene was 99.98% pure the impurities being propylene and propane, isobutene was also 99.98% pure the impurities being propylene and propane plus a little isobutane.

Cis pent-2-ene was obtained from Koch Light and was purified first by distillation under vacuum to separate it from the hydroperoxide and then by preparative gas chromatography. A Pye 105 preparative gas chromatograph was used incorporating a 30 ft. column packed with silver nitrate/ethylene glycol on a celite solid support (60 - 80 mesh). The column temperature was set at $40^{\circ}C$ and nitrogen used as carrier gas the flow rate being 100 mls./min. The cis pent-2-ene obtained from this source was found by gas chromatography (using column O at $35^{\circ}C$ and flow rate 60 mls./min.) to be about 0.01% in the trans isomer. Ethylene was an Air Products Special Gas and was distilled under vacuum before use, the purity being better than 99.9%.

Carbon dioxide, argon, nitrogen and oxygen were obtained from cylinder gases.

Nitrous oxide was also a cylinder gas of research grade obtained from B.O.C., and was stored after vacuum distillation, the purity being 99.95%.

Perfluorocyclobutane was a gift from Dr. R.B. Cundall of Nottingham University.

Materials for quantitative calibration and qualitative analyses were either Matheson Research Grade gases or pure liquid samples from British Petroleum Co. (C_5 hydrocarbons) and Gulf Petroleum Co. (C_6 - C_8 hydrocarbons).

2.3 Apparatus

2.3.1 Vacuum System

The high vacuum apparatus is represented by Figure 2.1.

An oil diffusion pump was used in order to exclude any mercury from the system. The pump was of the three stage type and charged with 150 mls. of Edwards No. 704 Silicone oil. This diffusion pump was backed by an Edwards Speedivac Rotary Oil Pump (type 1.S.50) and with the use of a liquid nitrogen trap a working vacuum of 10^{-5} mm. mercury was readily obtained.

Pure gases were introduced into the system at A liquified in B and stored in a one litre bulb C which were fitted with freeze-arms to assist recovery of the gases from the vacuum line. Liquids were introduced at the trap B and cooled with liquid nitrogen whilst pumped down, after boiling they were stored as before.

The system of taps at D provided alternate routes from the storage bulbs to the reaction cell.

Pressure measurements were made with Edwards Absolute Dial Gauges at F, which were calibrated using a butyl phthalate manometer.[2]

Gaseous samples are introduced into the gas chromatograph via the U-tube at G. In Figure 2.2, taps I and II were double oblique bore taps and III was a single straight through tap. A sample was taken for analysis by the following procedure:-

Figure 2.1

The vacuum system
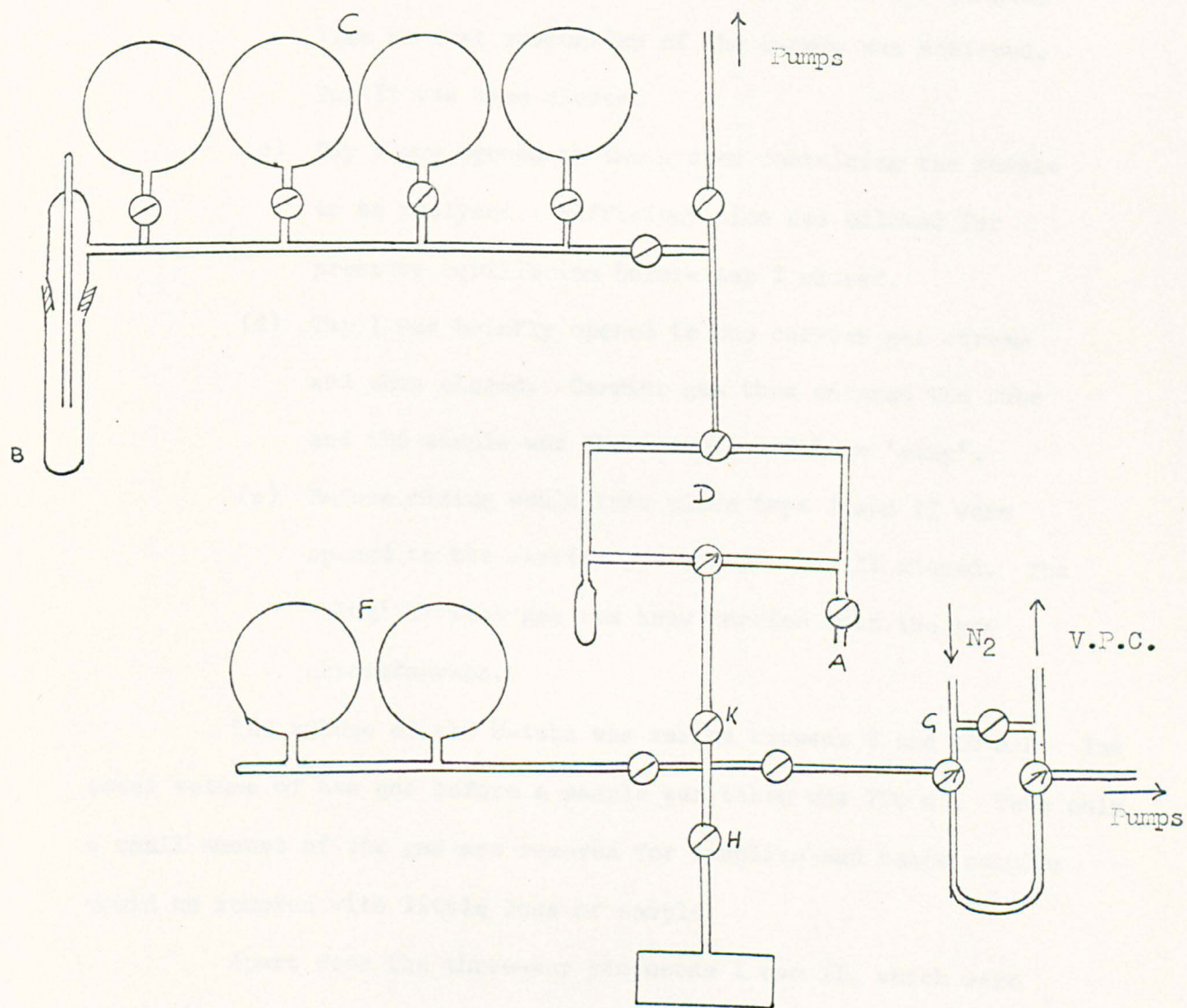
(a) Tap III remained open to allow unimpeded flow of carrier gas to the chromatograph.

(b) With tap I closed, tap II was opened to the pumping line so that evacuation of the U-tube was achieved. Tap II was then closed.

(c) Tap I was opened to the system containing the sample to be analysed. Sufficient time was allowed for pressure equilibrium before tap I closed.

(d) Tap I was briefly opened to the carrier gas stream and then closed. Carrier gas thus entered the tube and the sample was thus compressed to a 'slug'.

(e) Before mixing could take place taps I and II were opened to the carrier gas stream and III closed. The 'slug' of test gas was thus carried into the gas chromatograph.

The volume of the U-tube was varied between 8 and 10 mls. The total volume of the gas before a sample was taken was 720 ml. Thus only a small amount of the gas was removed for sampling and hence samples could be removed with little loss of sample.

Apart from the three-way stopcocks I and II, which were lubricated with silicone grease, all stopcocks which reactant and product gases came into contact were greaseless Springham Valves with fluorocarbon (Viton A) diaphragms. These do not absorb paraffin or

Figure 2.2

Gas sampling tube for vapour phase chromatography
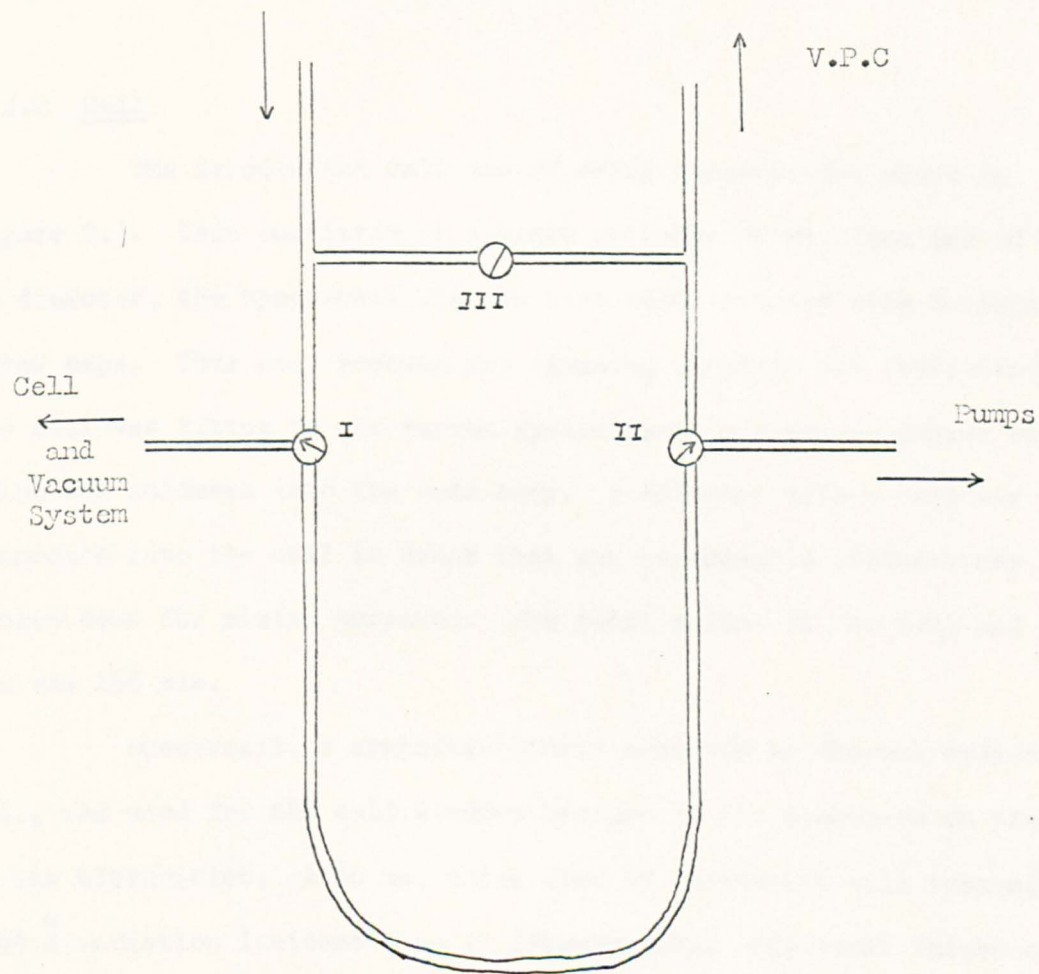
Volume of U-tube = 10ml

olefinic hydrocarbons. All other stopcocks in the system were

lubricated with silicone high vacuum grease.

2.3.2 Cell

The irradiation cell was of metal construction shown in

Figure 2.3. This consisted of a brass cylinder 80 mm. long and 50 mm.

in diameter, the Spectrosil windows were held in place with O-rings and

screw caps. Thus easy removal for cleaning purposes was facilitated.

The cell was fitted to the vacuum system using a glass to copper seal

which was soldered into the cell body. A side-arm with a bulb was

connected into the cell in order that any condensable products may be

frozen down for mixing purposes. The total volume of the cell and side-

arm was 158 mls.

Spectrosil, a synthetic quartz produced by Thermal Sydicate

Ltd., was used for the cell windows because of its transmission properties

in the ultraviolet. A 10 mm. thick disc of Spectrosil will transmit $\sim 90\%$

1849 $\overset{o}{A}$ radiation incident upon it (Figure 2.4). The total thickness of

Spectrosil traversed by the 1849 $\overset{o}{A}$ radiation before reaching the cell was

<5 mm.

2.3.3 Thermostat

The cell was enclosed in an air thermostat constructed of

Syndanyo, (compressed asbestos cement) Figure 2.5. The total volume was

24 litres. The thermostat was heated by a 1.5 kw. spiral heater and the

gas circulated by means of an electrically driven high speed fan. The

Figure 2.3

Vapour phase cell

To vacuum system

Bulb for freezing
reaction products

Screwcap

Cell window

5 cm

Rubber o-ring

8 cm
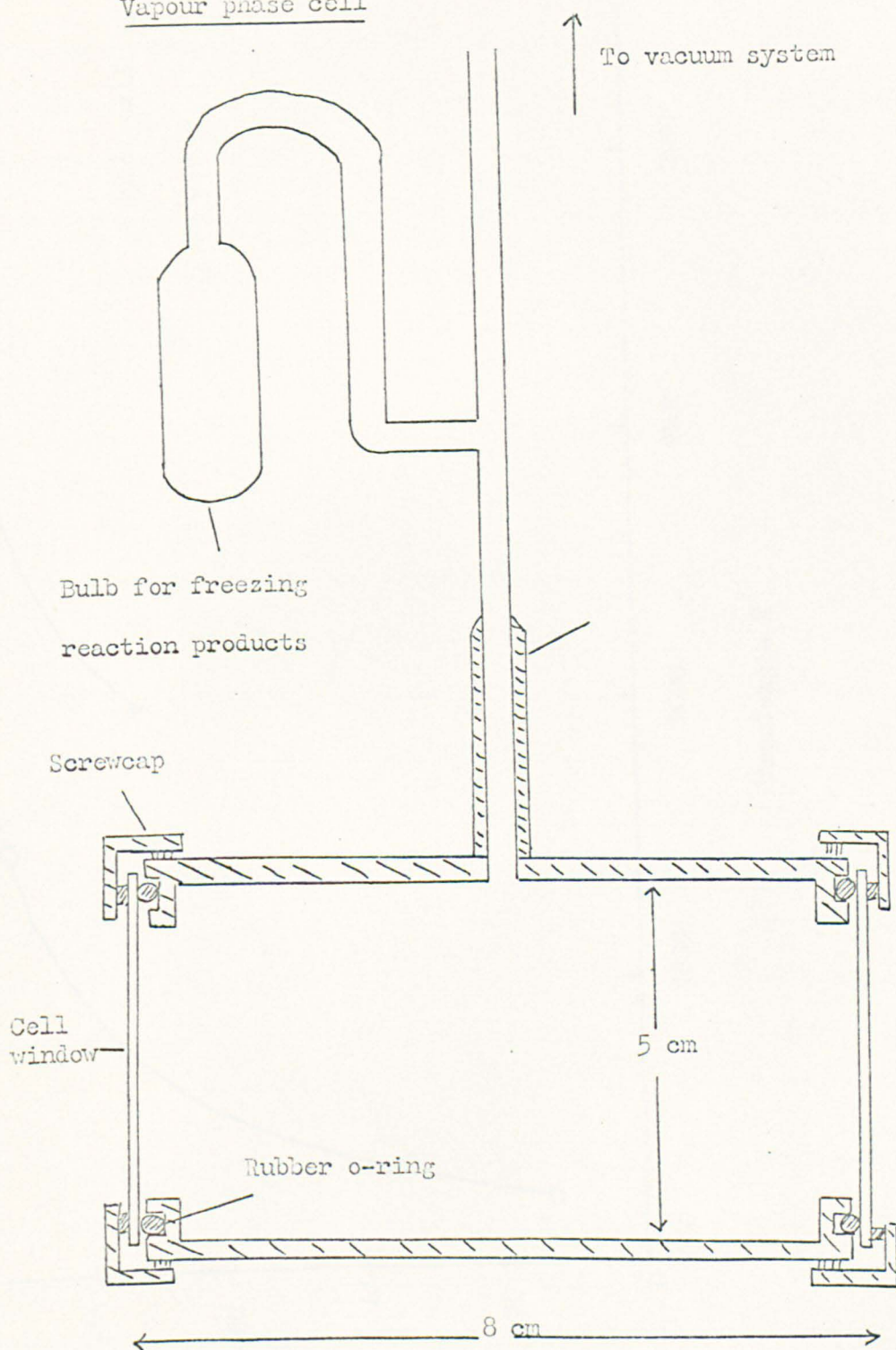
Volume of cell + side arm = 158 ml.

Figure 2.4

Comparison of the transmission of Spectrosil

and Quartz in the ultraviolet
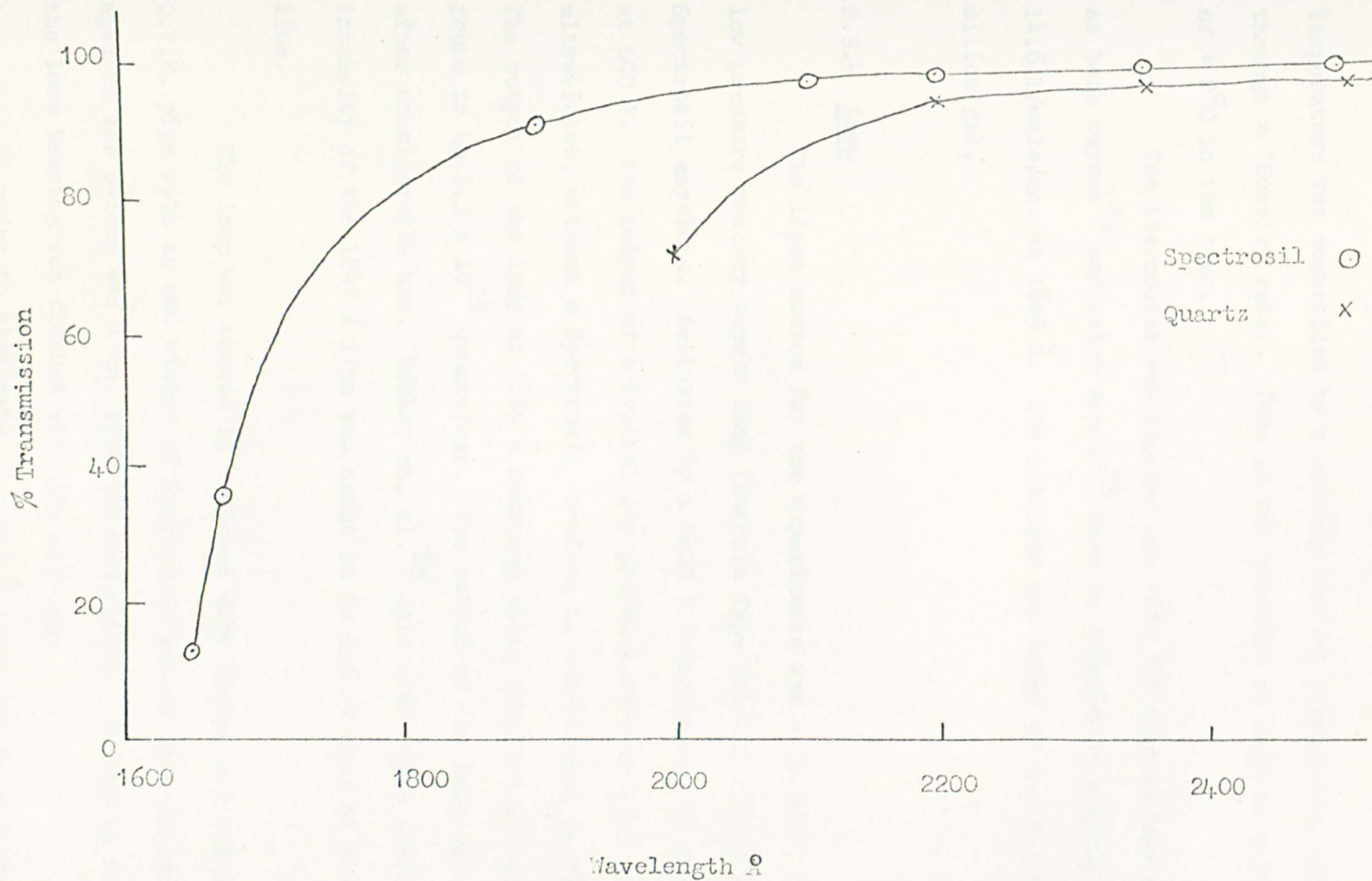
temperature was controlled by a mercury contact thermometer acting through a 'Sunvic' relay. Thus it was possible to achieve a temperature of $\pm 2^{\circ}C$ in the oven.

The thermostat was flushed out with dry oxygen-free nitrogen, as both oxygen[83] and water vapour[84] have an absorption coefficient of 14.6 l/mole/cm. at 1849 $\overset{\circ}{A}$. The nitrogen was dried by passing the gas over silica gel.

2.3.4 Lamp

The light source for the experiments was a 15 watt, 24" U-tube low pressure mercury vapour lamp (Hanovia Type 766/63) fitted with a Spectrosil envelope. Activated by a 2000 V transformer, it drew 30 mA at 600 V. The output of a typical low pressure mercury lamp in the ultraviolet, without a Spectrosil envelope is illustrated in Figure 2.6.[85] The output of the lamp at 1849 $\overset{\circ}{A}$ measured using ethylene actinometry was found to be 2.3 x 10^{15} quanta/sec. The output of the lamp did not change after considerable use. Beckey et. al.[88] said that for a similar lamp the intensity of the 1849 $\overset{\circ}{A}$ line was about 10 to 15% of that of the 2537 $\overset{\circ}{A}$ line.

The lamp was housed in a closed tube Figure 2.7 constructed of a Q.V.F. pipe with an end window of Spectrosil sealed with Araldite. The apex of the U-lamp was 1 cm. from the end-window. During an irradiation the lamp housing was flushed with dry nitrogen.

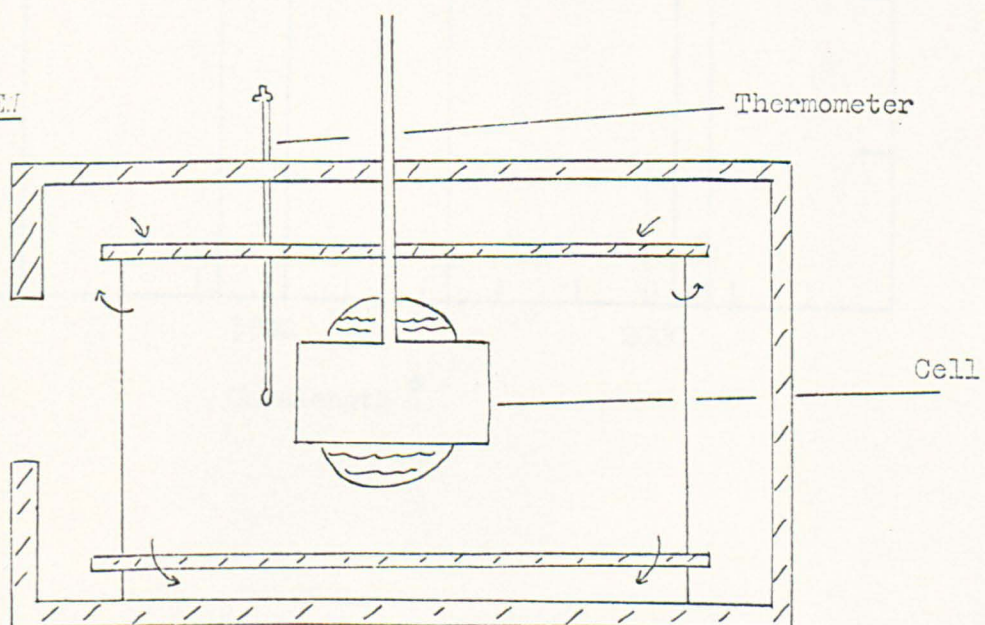In order to eliminate the 1849 $\overset{\circ}{A}$ radiation to test for

Figure 2.5

The air thermostat
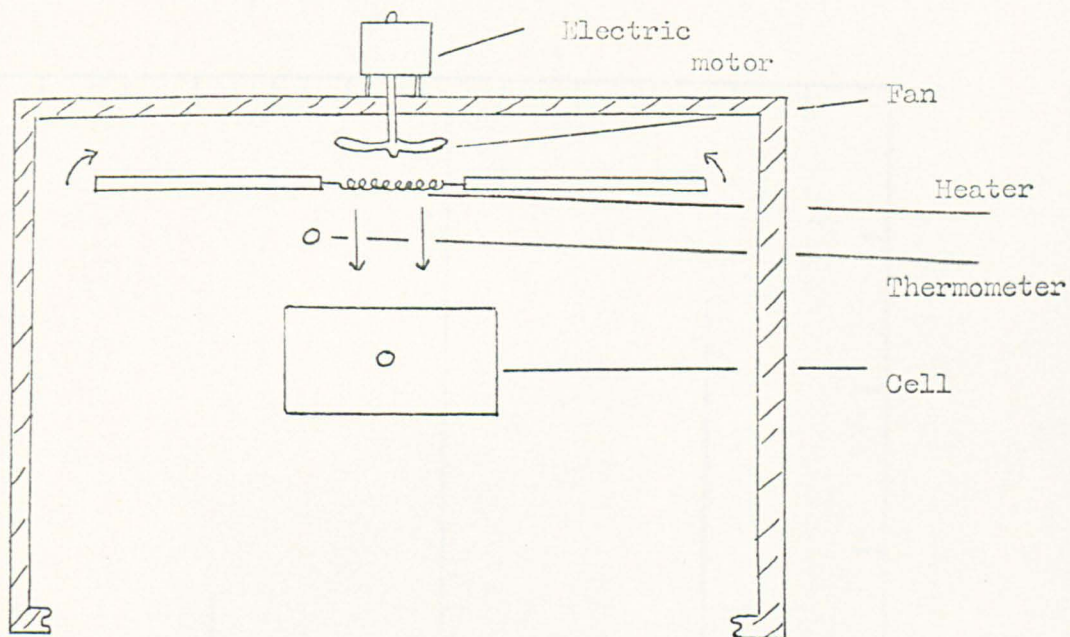
Arrows indicate direction of air flow.

Figure 2.6

Relative intensities of the emission lines

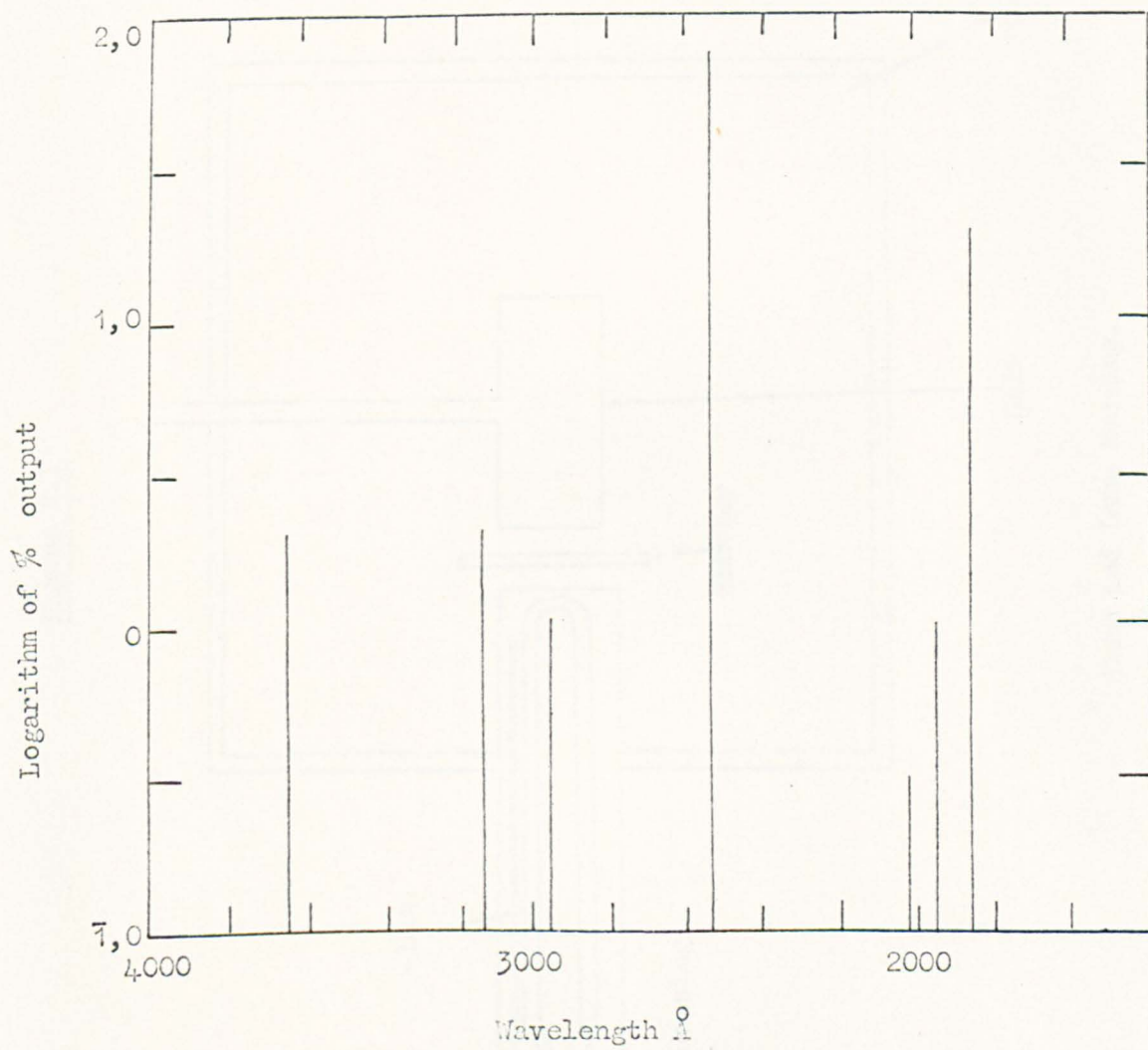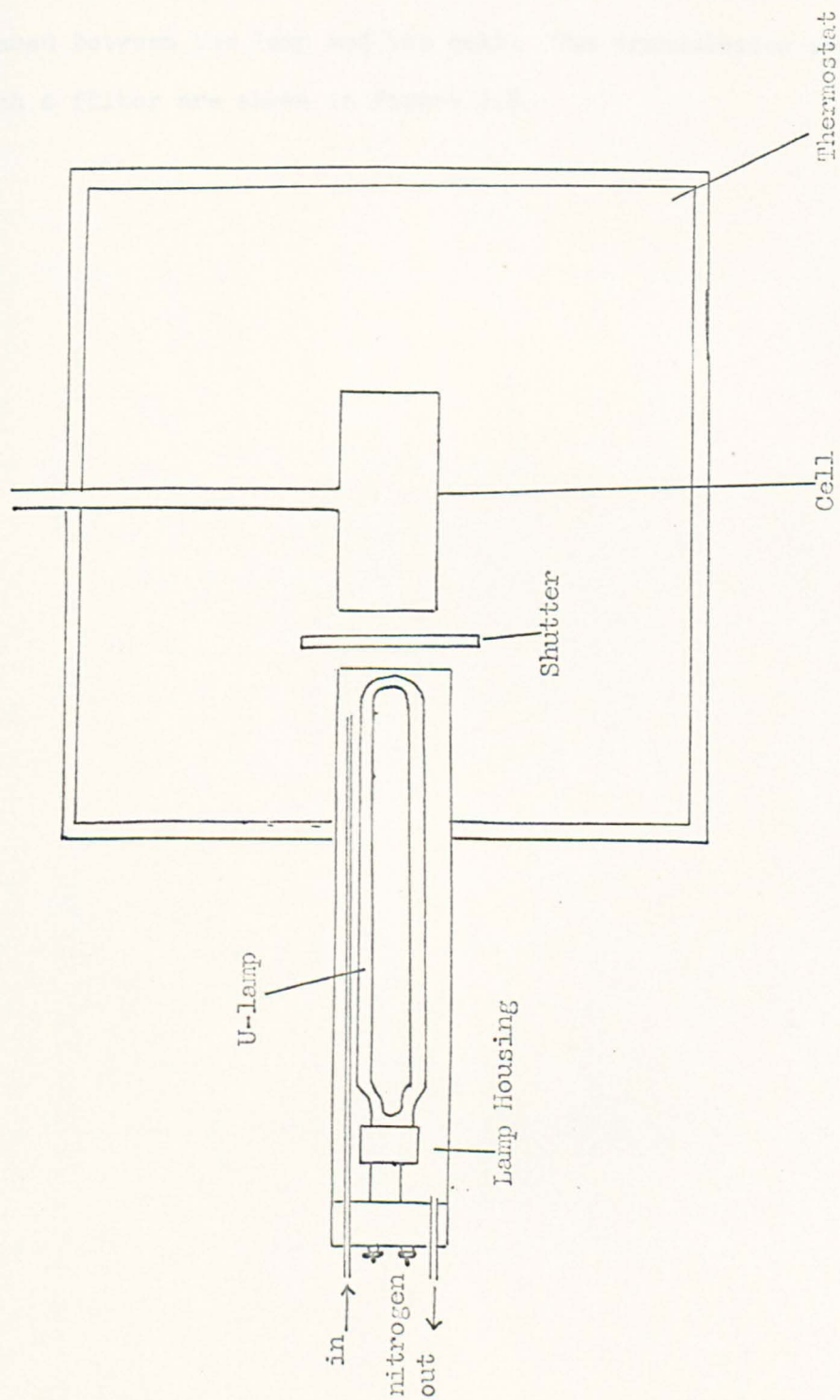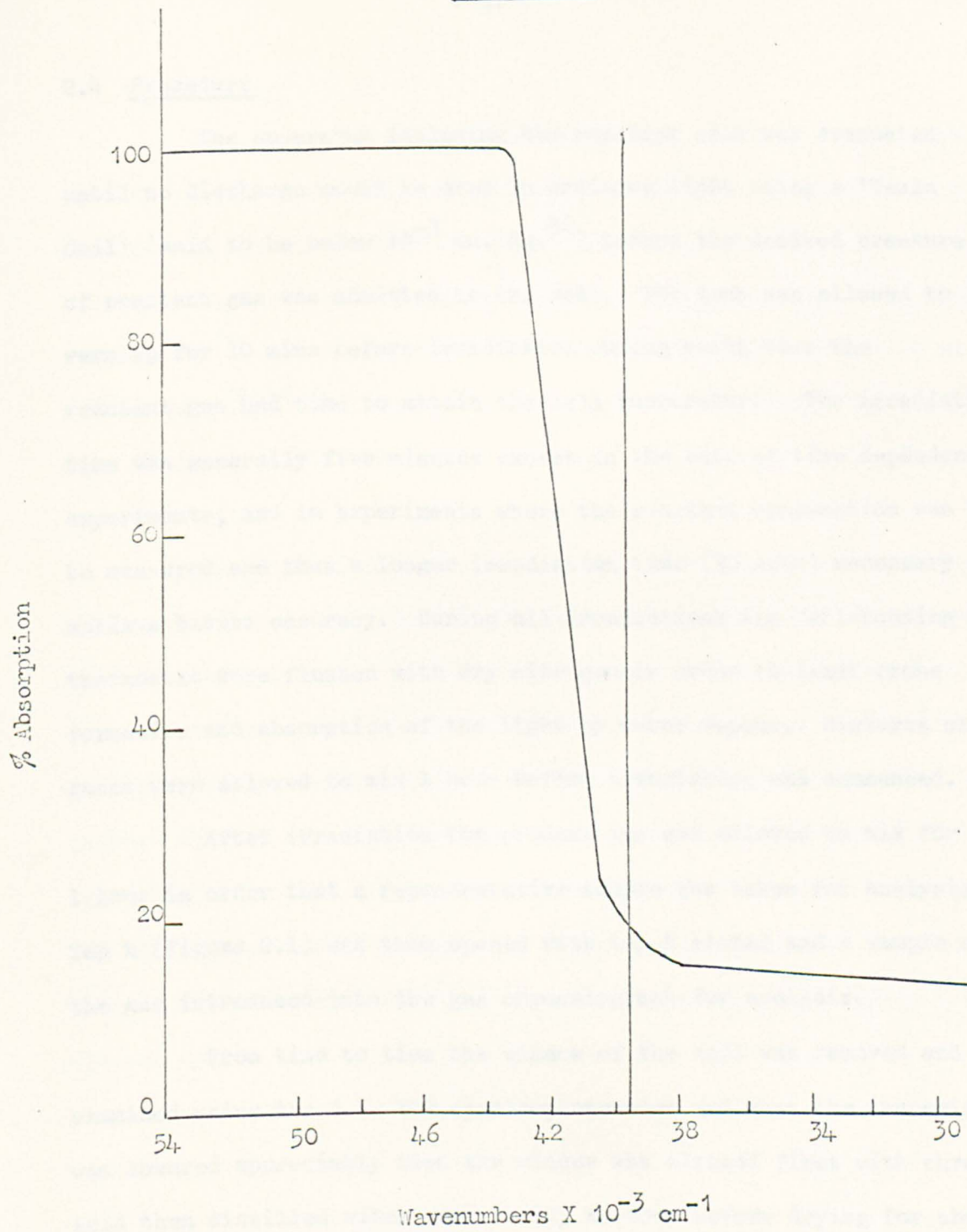of a low pressure mercury lamp.

Figure 2.7

Lamp and Lamp Housing.

photosensitisation a 1 cm. thick 2% acetic-acid solution filter was placed between the lamp and the cell. The transmission properties of such a filter are shown in Figure 2.8.

Figure 2.8

100

80

60

% Absorption

40

20

0

54   50   46   42   38   34   30

Wavenumbers X 10^{-3} cm^{-1}

2.4 Procedure

The apparatus including the reaction cell was evacuated until no discharge could be seen in ordinary light using a 'Tesla Coil' (said to be below 10^{-3} mm. Hg.[86]) before the desired pressure of reactant gas was admitted to the cell. The lamp was allowed to warm up for 10 mins before irradiation during which time the reactant gas had time to attain the cell temperature. The irradiation time was generally five minutes except in the case of time dependence experiments, and in experiments where the reactant consumption was to be measured and thus a longer irradiation time (30 mins) necessary to achieve better accuracy. During all irradiations the cell-housing and thermostat were flushed with dry nitrogen in order to limit ozone formation and absorption of the light by water vapour. Mixtures of gases were allowed to mix 1 hour before irradiation was commenced.

After irradiation the product gas was allowed to mix for 1 hour in order that a representative sample was taken for analysis. Tap H (Figure 2.1) was then opened with tap K closed and a sample of the gas introduced into the gas chromatograph for analysis.

From time to time the window of the cell was removed and examined using the S.P. 700 spectrophotometer and when the transmission was lowered appreciably then the window was cleaned first with chromic acid then distilled water, and lastly acetone before drying for about 20 mins in an oven at 100°C.

2.5 Actinometry

The output of the lamp at 1849 $\overset{o}{A}$ was measured using ethylene as a chemical actinometer. The quantum yields for the formation of acetylene (1.0) and hydrogen (0.8 ± 0.1) were originally given to us by Dr. H. Rommel[87] and subsequently published by Beckey, Groth, Okabe and Rommel.[88] The values were determined using nitrous oxide as an actinometer.[89,90,91] Due to the importance of the figure for the $\emptyset H_2$ from ethylene it was decided to remeasure this using nitrous oxide as an actinometer.

Several steady state experiments were carried out with nitrous oxide and ethylene in order to determine the yields of nitrogen and hydrogen respectively. In each case 100 mm. of gas was irradiated and after allowing 1 hour for the products to mix they were analysed by gas chromatography using a 6 metre column packed with silicone grease on celite (60 - 80 mesh) for hydrogen and a 2 metre column packed with a molecular sieve (5A) for nitrogen. At 100 mm. pressure of either gas all the light was absorbed in the cell (see Section 2.6). The results from these experiments are shown in Table 2.1 for ethylene and Table 2.2 for nitrous oxide.

Table 2.1 (Ethylene)

Run No.	Irradiation Time (mins)	Hydrogen Yield Moles x 10^7
1	10	1.43
2	"	1.43
3	"	1.49
4	"	1.43
5	20 hours	0.117

Analytical Conditions:

Column 'O' (silicone grease); Temperature, 35°; Nitrogen Carrier gas flow rate, 60 mls/min.; Detector, Hot-wire.

Table 2.2 (nitrous oxide)

Run No.	Irradiation Time (mins)	Nitrogen Yield Moles x 10^7
1	10	3.34
2	"	3.34
3	"	3.46
4	"	3.36
5	20 hours	0.263

Analytical Conditions:

Column, molecular sieve (5A); Temperature, Room Temp.; Hydrogen Carrier gas flow rate, 60 mls/min.; Detector, Hot-wire.

The first four runs were conducted using the usual cell arrangement while in run 5 the lamp was withdrawn from the cell and viewed through a small aperture so that the effect of the intensity and also the geometry of the cell on the quantum yield could be tested. The results shown in Tables 2.1 and 2.2 show that the quantum yield was unaltered throughout the runs, a figure of 0.60 ± 0.02 being calculated in each case using the results as numbered. A steady state experiment was also performed to determine the ratio $\emptyset C_2H_2/\emptyset H_2$ and the result found to be the same as that quoted by Rommel.

It was therefore decided to use the figure of 0.60 ± 0.02 for $\emptyset H_2$ to calculate the product yields later in this thesis since the optical system used to arrive at this figure was well defined, and with a path length of 8 cm. more than 96% of the light is absorbed. If less light were to be absorbed then, because of the difference in molar absorbtivity between ethylene and nitrous oxide, a higher value for $\emptyset H_2$ would be obtained. The path length used by the previous workers[88] was less than 8 cm.

2.6 Measurement of Molar Extinction coefficient - A Photochemical Method

During the study of the use of ethylene as an actinometer at 1849 Å a possible method for the measurement of the extinction coefficient (ϵ) was seen, using a modification of the Beer-Lambert Absorption Law:

$$I = I_o \, e^{-kcl}$$

where I_o and I are the incident and transmitted light intensities respectively, k is the molar absorption coefficient, c the concentration in moles/litre and l the path length of the cell in cm.

$$\text{then } I_{abs} = I_o (1 - e^{-kcl})$$

if $\emptyset$ is the quantum yield of product then the rate $= I_{abs} \emptyset$

$$\therefore \text{Rate} = I_o \emptyset (1 - e^{-kcl})$$

$$= R_o (1 - e^{-kcl})$$

where R_o is the rate of production when all the light is absorbed, calculated from figure 2.9 for nitrous oxide and figure 2.10 for ethylene.

$$\text{then } -\ln (1 - {}^R/R_o) = kcl$$

$$\text{and } -\log (1 - {}^R/R_o) = \varepsilon cl$$

where $k = 2.303 \varepsilon$.

A plot of $-\log (1 - {}^R/R_o)$ versus c in moles per litre would therefore have a slope equal to εl. Thus ε may be calculated by irradiating various pressures of the gas under investigation and calculating the product yield. The results for ethylene (table 2.3) and nitrous oxide (table 2.4) are summarised below and illustrated in figures 2.11 and 2.12.

Figure 2.9

Rate of formation of nitrogen as a
function of nitrous oxide pressure.
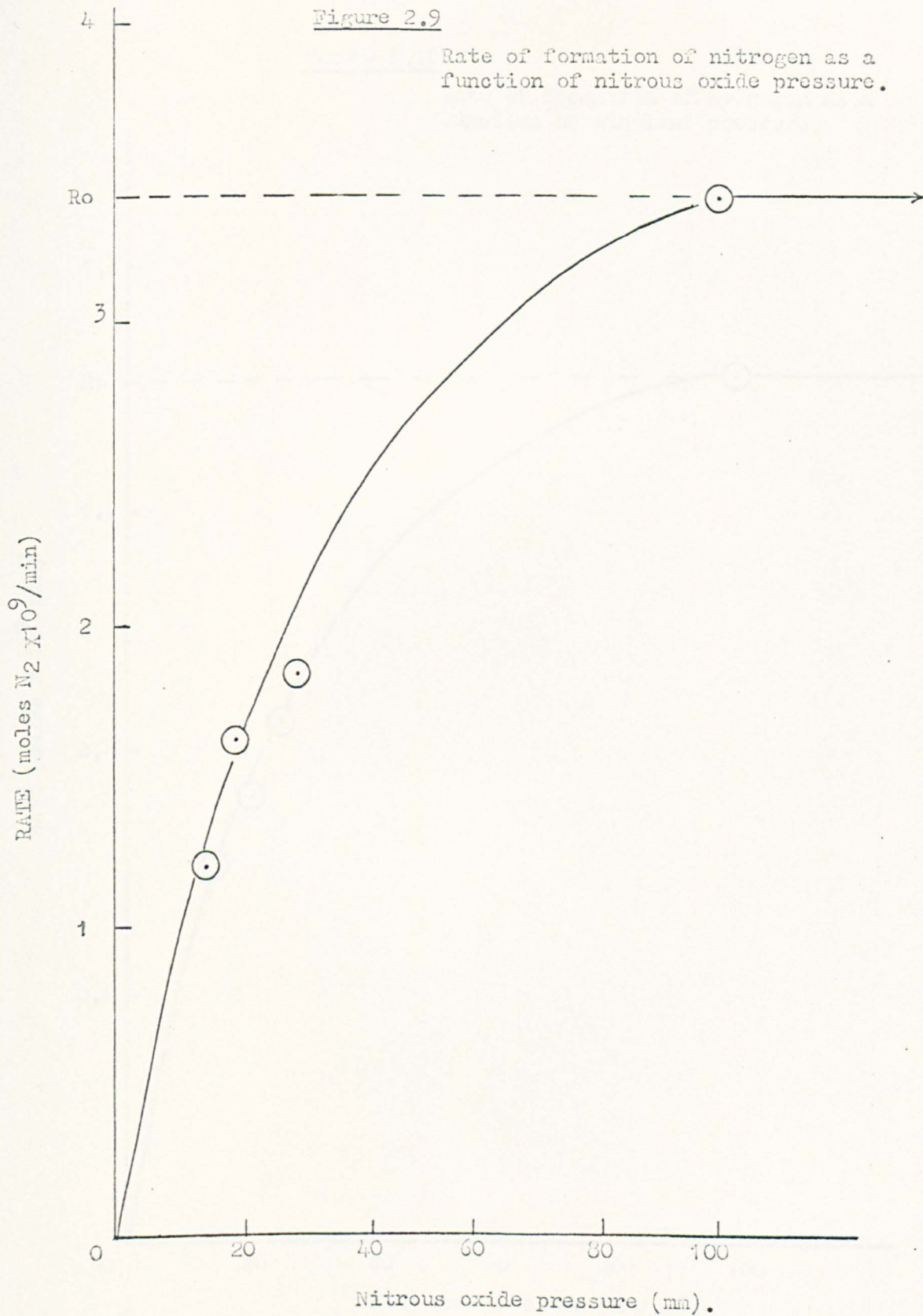
Figure 2.10

Rate of formation of hydrogen as a
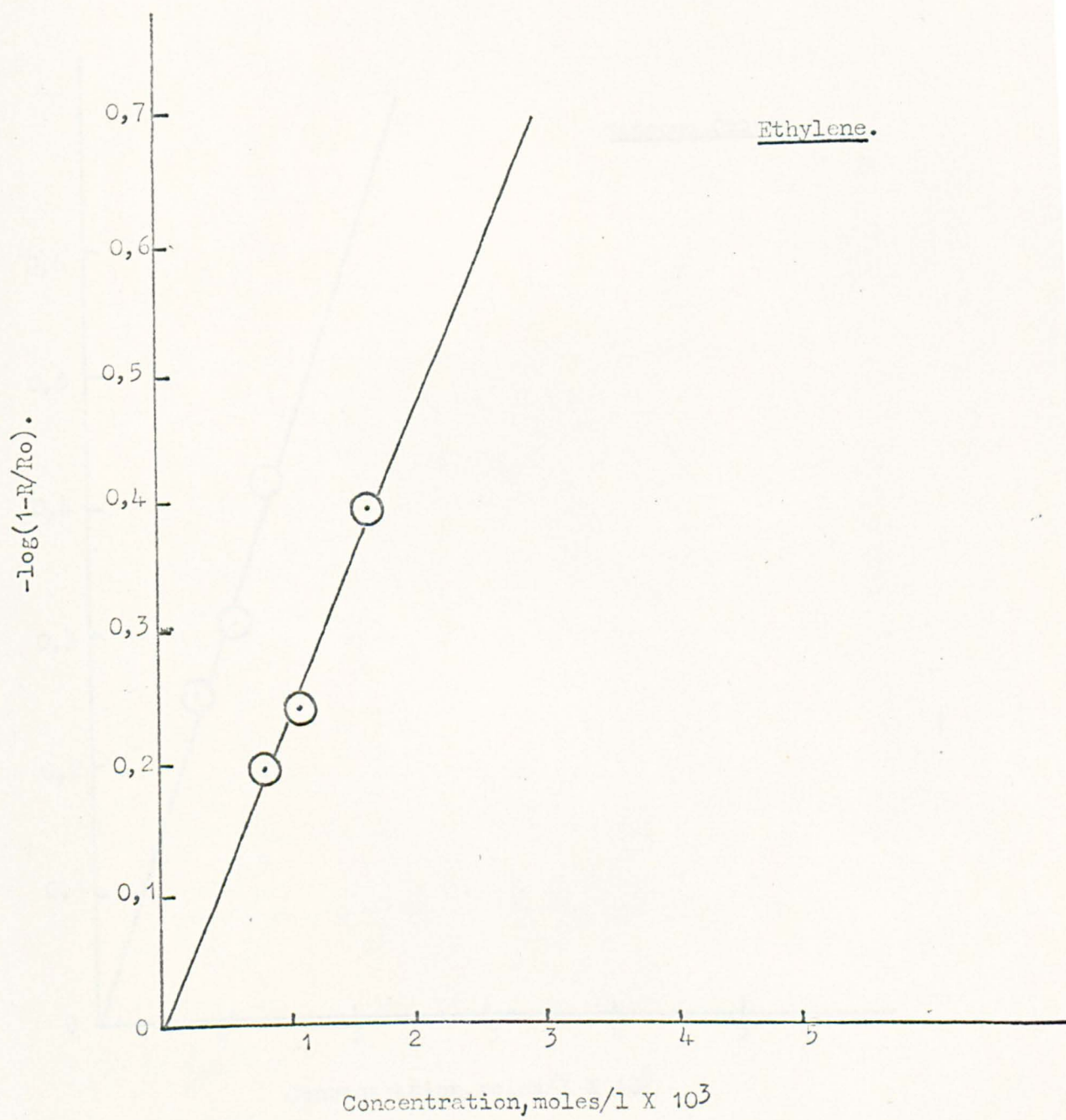function of ethylene pressure.

Figure 2. 11

Ethylene.

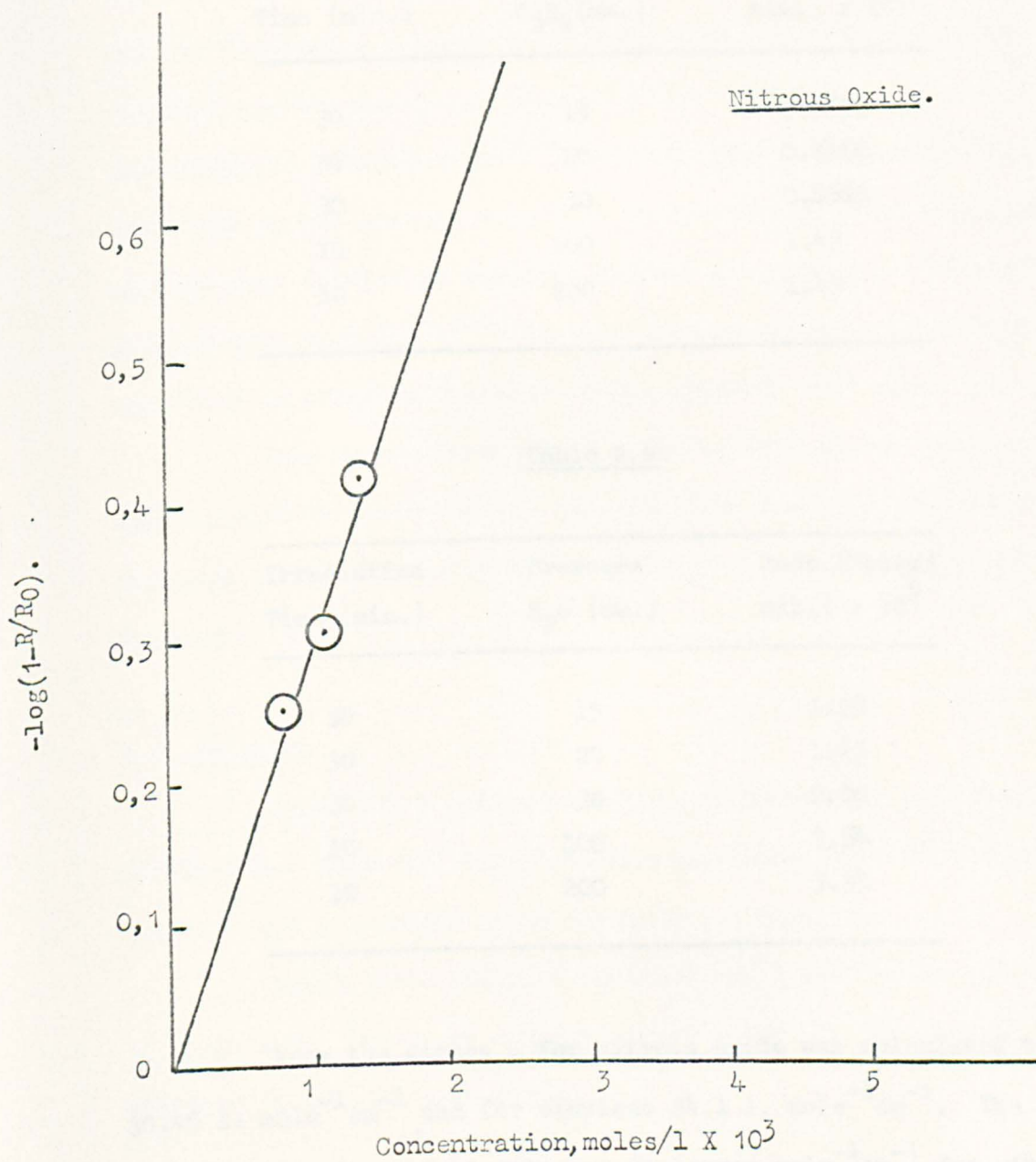y-axis: $-\log(1 - R/Ro)$.

x-axis: Concentration, moles/l $\times$ 10^3

Figure 2. 12

Nitrous Oxide.
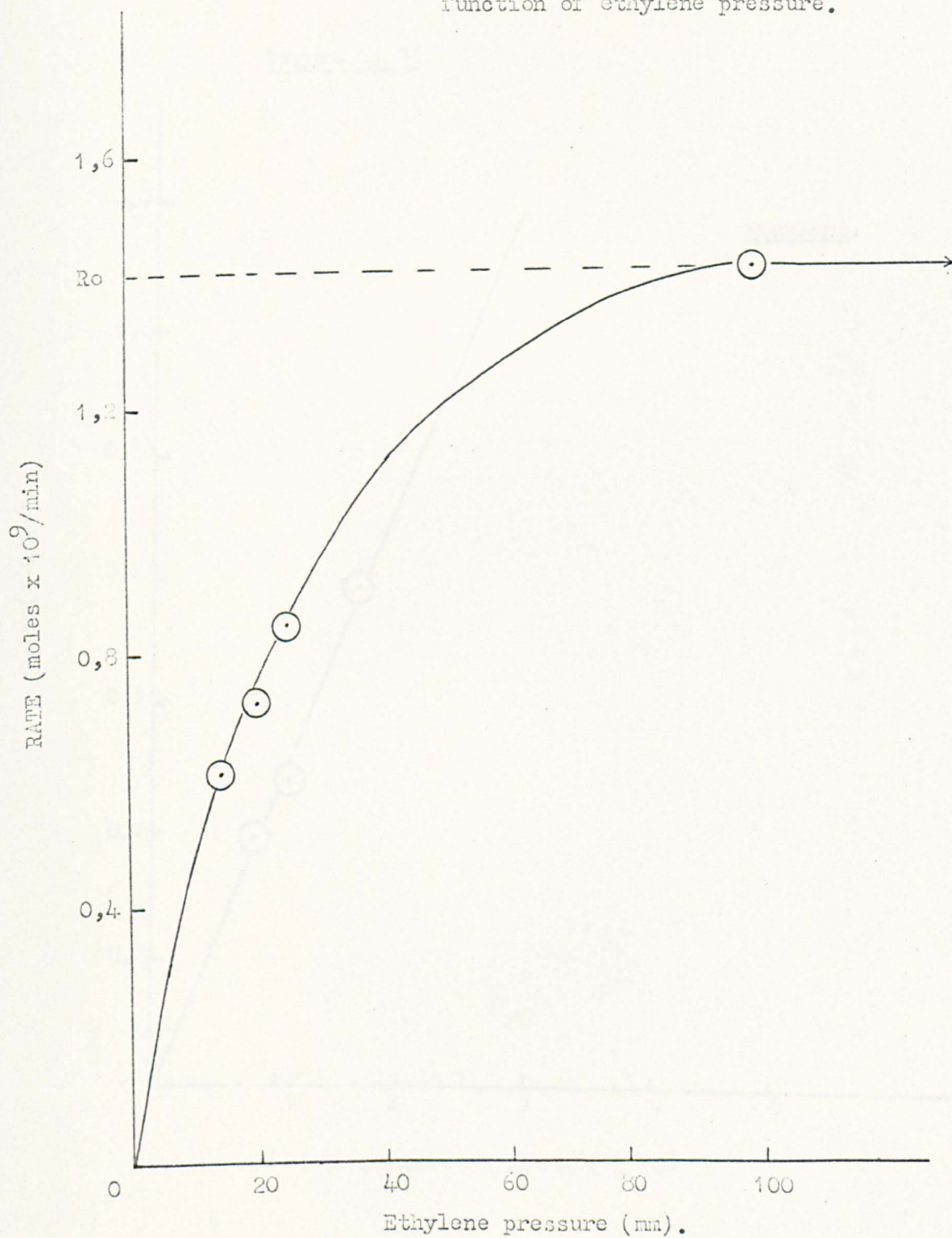
Table 2.3

Irradiation Time (min.)	Pressure C_2H_4 (mm.)	Rate (Moles/ min.) x 10^9
30	15	0.6333
30	20	0.7166
30	30	0.8666
10	100	1.43
10	200	1.43

Table 2.4

Irradiation Time (min.)	Pressure N_2O (mm.)	Rate (Moles/ min.) x 10^9
30	15	1.23
30	20	1.45
30	30	2.05
10	100	3.34
10	200	3.35

From the slopes ε for nitrous oxide was calculated to be 30.49 l. mole^{-1}cm^{-1} and for ethylene 34.1 l. mole^{-1}cm^{-1}. The values calculated from spectral data are 99 litres mole^{-1}cm^{-1} for ethylene,[3,24] and 29 litres mole^{-1}cm^{-1} [92] or 35 litres mole^{-1}cm^{-1} [83] for nitrous oxide.

The agreement for nitrous oxide demonstrates the validity of the method for a compound with a continuous spectrum.

The spectrum of ethylene shows some structure in this region and the difference between the results obtained from this method and the spectral results may be attributed to the bandwidths used. In the photoelectric determination[3,24] the bandwidth was approximately 1Å. The bandwidth in the present work will be determined by the width of the mercury line emitted by the low pressure arc, it is not likely to be greater than 0.05 Å.[93,100] Clearly this measurement will be more sensitive to detailed features of the spectrum than those made previously.

This method then offers a way of determining absorption coefficients in photochemical systems where a narrow emission line is produced by the light source; in this case a monochromator is not required.

2.7 Analysis

Qualitative and quantitative analyses were performed on a Perkin-Elmer Model 452 Gas Chromatograph fitted with both a hot-wire detector and a hydrogen flame ionisation detector.

Qualitative analyses were made on a variety of columns listed in Table 2.5. The inert support material for all Perkin-Elmer column fillings is 60 - 80 mesh Celite.

Table 2.5

Perkin-Elmer Classification	Column Stationary phase	Length (metres)	Running Temp. $^{\circ}$C	Carrier gas flow rate mls/min.
H	Silver nitrate on ethylene glycol	2 9(Preparative)	35 40	60 100
O	Silicone grease	6	35 80	65 140
S	Silica gel + diethylhexyl sebacate	2	80	135
-	Poropak 'R'	2	100	60
EA	Bis methoxyethyl-adiptate	2	35	65
I	Molecular sieve (5A)	2	Room Temp.	60

The product retention times were compared with authentic samples.

Column O separated by boiling points and from boiling point-log retention time curves[94] the boiling points of products for which no authentic samples were available could be determined to within ± 2°C.

Quantitative analyses were made on column O, S and I, C_1 - C_5 hydrocarbons

on column 0 at $35^{\circ}C$, C_6 to C_8 hydrocarbons on column 0 at $80^{\circ}C$, nitrogen on column I at room temperature. Calibration was made using mixtures of the authentic sample with nitrogen. Table 2.6 shows the relationship between the peak height or peak area, recorded on a Honeywell high gain high impedance recorder with a 0-2.5 mV range, and the molar quantities of C_1 - C_8 hydrocarbons.

Table 2.6

Peak height or peak area with detector at full
sensitivity corresponding to 10^{-9} moles.
(Column 0 at $35^{\circ}C$)

Hydrocarbon	Peak Height (ins)	Hydrocarbon	Peak Area (ins^2)
Methane	7.0	3 Me-butene	2.52
Ethylene	10.5	Iso pentane	2.65
Ethane	11.0	n-Pentane	2.1
Acetylene	14.0	Trans Pent-2-ene	2.4
Propylene	18.0	Cis Pent-2-ene	2.37
Allene	11.9	2 Me-butene	1.0
But-1-ene	4.0		
Isobutane	7.0	Col. 0 80°C	
Isobutene	4.5		
Cis-but-2-ene	9.4	n-Hexane	0.5
Trans-but-2-ene	9.0	Cis Hept-2-ene	0.25
Butadiene	4.0	Oct-1-ene	0.52

Infrared spectra were recorded on a Perkin-Elmer Model 221 I.R. Spectrometer, and ultra-violet transmission data and spectra were recorded on a Unicam Model S.P. 700.

3. RESULTS: But-1-ene

Irradiation of known pressures of but-1-ene using a low pressure mercury lamp with a 1 cm. thick filter containing 2% acetic acid solution interposed between the lamp and the cell resulted in no photochemical products. The filter which absorbs 1849 $\overset{o}{A}$ radiation (Section 2.3 Figure 2.8) proved that the exciting radiation was that of the 1849 $\overset{o}{A}$ resonance line. Thus it was concluded that no sensitisers, such as mercury, were present in the system, since the olefins under study are transparent to 2537 $\overset{o}{A}$ radiation which is the main component of the light emitted from a low pressure mercury lamp (Section 2.3 Figure 2.6).

After irradiation without such a filter more than twenty-five hydrocarbons, hydrogen and a solid polymer were found to be present. The products were analysed by gas chromatography using column 0 at $35^{o}C$ for $C_1 - C_5$ hydrocarbons and column 0 at $80^{o}C$ for $C_6 - C_8$, no hydrocarbons higher than C_8 were detected after thorough examination. Table 3.1 illustrates the relative yields of the products from a 5 min. irradiation compared with ethane, which is taken as 10 (equivalent to 2.7×10^{-7} moles).

Table 3.1

Relative amounts of Products formed by Photolysis of
But-1-ene at 1849 A with reference to C_2H_6 = 10
(equivalent to 2.7×10^{-7} moles)

Time of Irradiation 5 min.; $p(C_4H_8\text{-}1)$ = 6 mm.;
Temperature = $20^\circ \pm 2^\circ C$

H_2	0.002	C_3H_4	1.64	But-2-yne	trace
CH_4	2.52	Iso-butane	0.2	Cis Pent-2-ene	1.08
C_2H_4	5.34	Cis but-2-ene	0.76	Trans Pent-2-ene	0.08
C_2H_6	(10.0)	Trans but-2-ene	0.34	Pent-1-ene	1.0
C_2H_2	0.76	3He-butene	0.92	(C_6)	10.66
				(C_7)	2.85
C_3H_6	2.28	Iso-Pentane	2.62	(C_8)	0.75
C_3H_8	1.84	n-Pentane	1.1		

(C_6), (C_7), (C_8) represent the total approximate values for
several peaks. Individual hydrocarbons were not identified and therefore
are grouped together as (C_6) (C_7) or (C_8) after consideration of their
retention times.

In order to establish which products are formed by molecular fragmentation reactions and which are formed by free radical reactions steady state experiments were carried out to determine the effect of the following parameters on the product yields:

(1) Irradiation Time

(2) Added Gas Pressure

(3) Reactant Pressure

(4) Temperature

The irradiation time was generally 5 minutes which give rise to about 1% conversion of the butene present. The yield of the products was thus small and a hydrogen flame ionisation detector was needed to measure the yields accurately. But-1-ene contained propylene and propane as impurities (0.02%) but this level of impurity presented no analytical difficulty at low but-1-ene pressures. At higher butene pressures the yields of propylene and propane were so small that the amount present as impurity became a serious problem. Measurement of the product yields (C_5 hydrocarbons) which had a longer retention time than but-1-ene became increasingly difficult as the pressure of but-1-ene was increased, due to severe tailing of the butene peak. The pressure of but-1-ene ($\varepsilon \sim 10,000$)[17] in the cell was always sufficient to absorb > 99% of the radiation. All the light being absorbed in the first 2 cm. length of the cell.

In the figures referring to section 3.1 the product yields are quoted in moles and in sections 3.2, 3.3 and 3.4 quantum yields are

used to show the effect on the product yield where,

$$\emptyset_{product} = \frac{\text{moles of product produced per minute}}{\text{quanta light used per minute}}$$

the amount of light used being determined by ethylene actinometry (section 2.5).

3.1 Effect of Irradiation Time

The effect of varying the irradiation time on the rate of formation of the C_1 to C_5 hydrocarbon products is shown in Table 3.2 and illustrated by Figures 3.1 to 3.14. It can be readily seen that the yields of the products increase linearly with time up to about 20 minutes thereafter the rate of formation decreases due to the formation of a solid polymer on the cell window during long irradiations. Later experiments were therefore carried out using 5 minutes irradiation time. The polymer was not found to build up on the cell window during consecutive 5 minute irradiations.

Table 3.2

Product Yields in Moles x 10^7 as a function of Irradiation Time

$p(C_4H_8-1) = 6$ mm; temperature $= 20^{\circ} \pm 2^{\circ}C$

Analytical Conditions: Flame Ionisation Detector; Column: 0;
Temperature: $35^{\circ}C$; N_2 pressure: 12 lb/sq. in.

Time Mins.	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_8	C_3H_4	t-b-2	c-b-2	3Me-butene	iso-pentane	n-pentane	t-p-2	c-p-2
0					trace	trace								
1	0.04	0.16	0.32	0.02	0.12	0.08	0.08	–	0.02	0.02	–		0.03	0.05
2	0.12	0.32	0.64	0.04	0.24	0.16	0.16	0.03	–	0.02	–	0.08	–	0.08
3	0.24	0.39	1.26	0.08	0.36	0.24	0.24	–	0.03	0.04	0.06	–	0.09	0.11
5	0.4	0.70	3.20	0.16	0.68	0.53	0.40	0.08	–	0.32	0.06	0.16	0.18	0.16
7	0.52	1.05	3.85	0.19	0.77	0.71	0.52		0.35	–	–	–	0.24	0.24
10	0.96	1.60	6.70	0.36	0.92	1.04	0.76	0.13	0.48	0.35	0.08	0.20	0.26	0.30
12	1.08	–	–	–	1.24	1.15	0.79	–	–	0.64	–	0.28	0.32	0.42
15	1.35	2.55	9.90	0.71	1.80	1.23	1.13	–	0.60	–	0.12	–	–	0.56
20	1.76	3.24	–	–	2.28	1.56	1.48	0.34	0.76	0.64	0.16	0.48	0.58	0.67
30	2.40	4.68	16.50	1.08	2.70	2.13	1.80	–	0.96	1.02	0.27	–	–	–
40	2.68	6.00	21.60	1.20	3.60	2.72	2.52	–	1.32	1.21	0.40	0.88	0.70	–
60	4.68	7.56	50.4	2.76	5.04	3.96	3.60	1.83	1.86	3.24	3.6	–	2.19	1.34
90	7.20	11.70	63.0	3.42	9.27	4.86	6.66	–	2.79	3.78	4.32	3.15	2.25	1.46
120	7.44	13.68	75.6	4.20	11.04	9.00	8.28	3.66	2.88	4.32	5.52	4.20	–	1.70

Figure 3.1

Variation of methane yield with irradiation time.
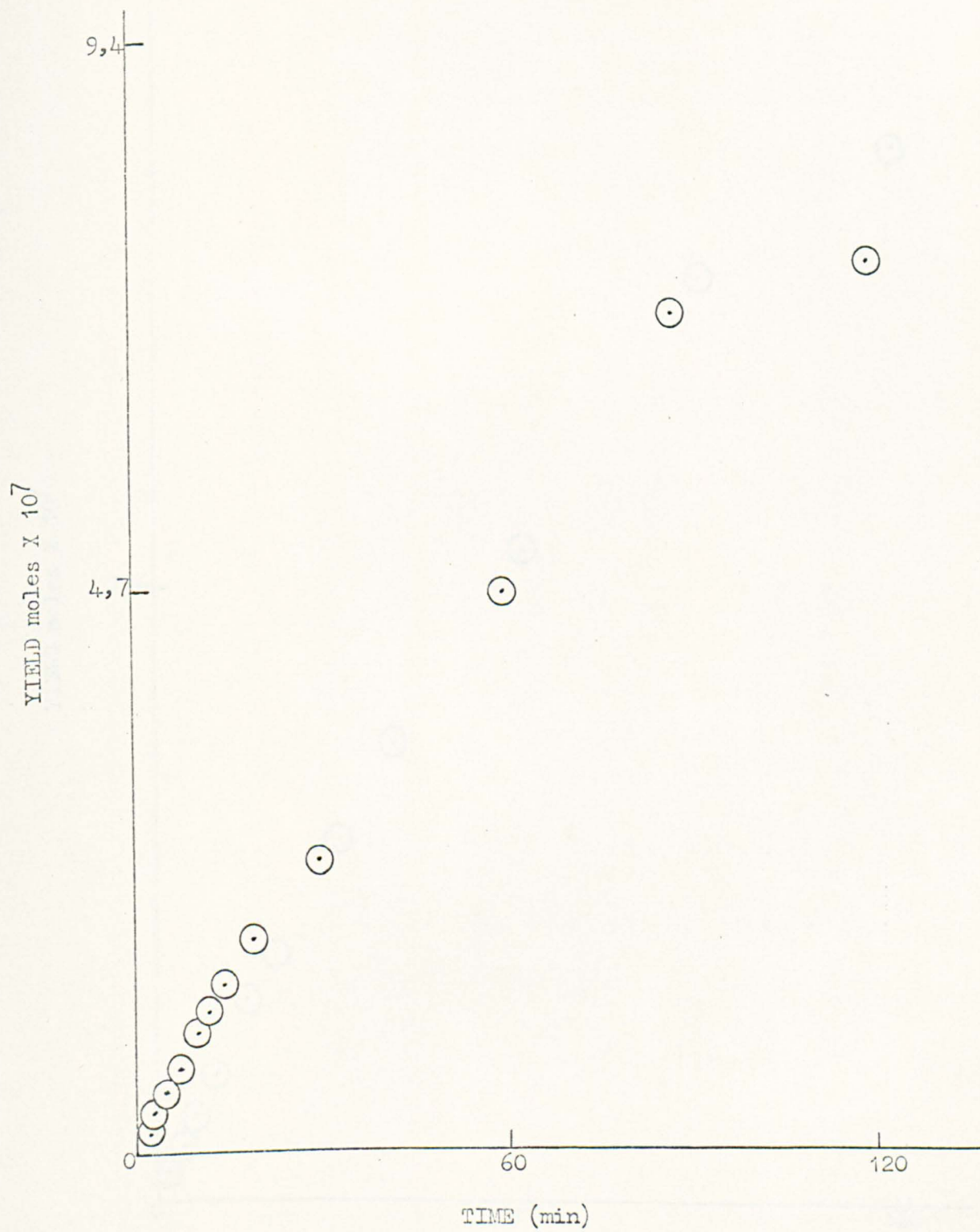
Figure 3.2

Variation of ethylene yield with irradiation time.
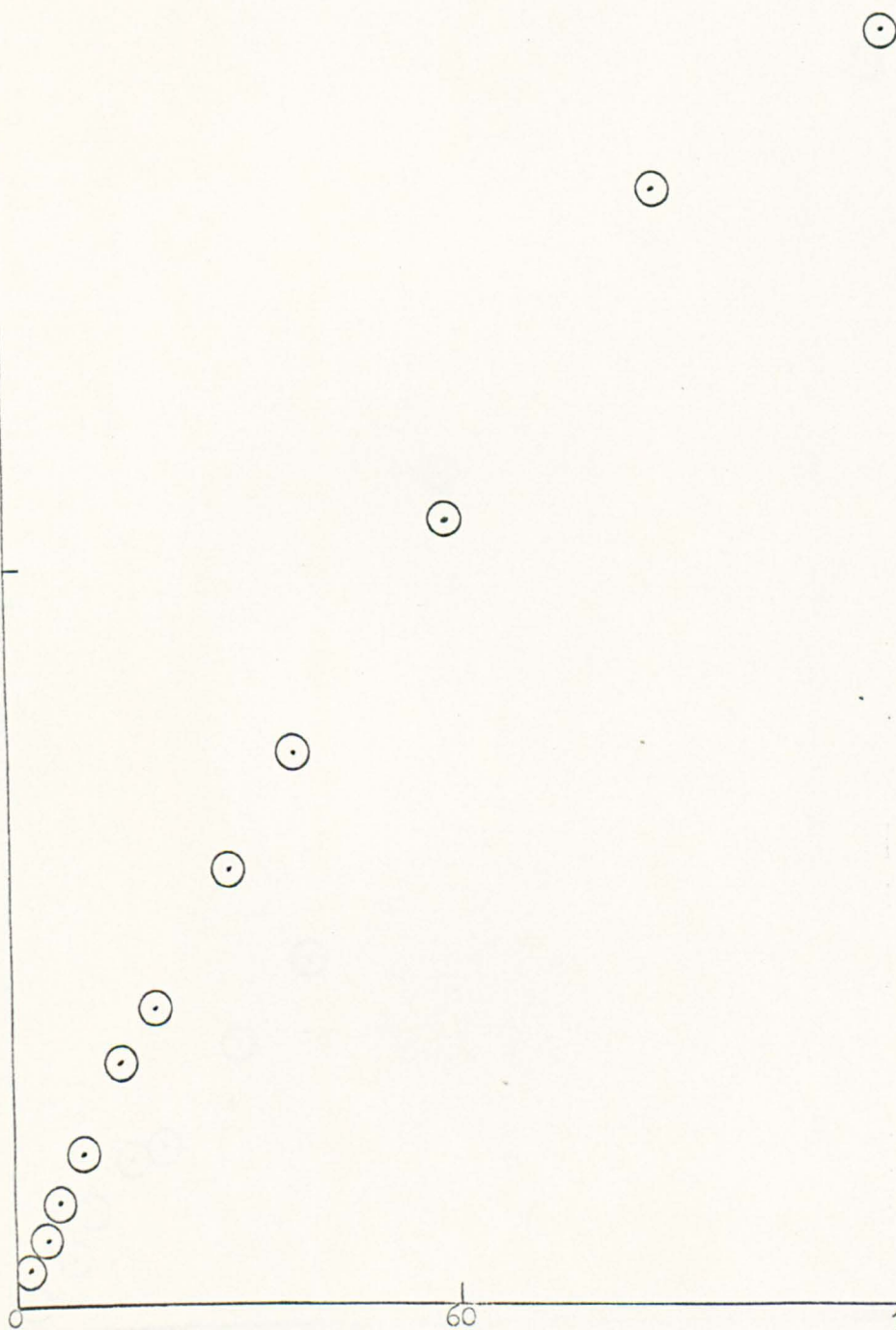
Figure 3.3

Variation of ethane + acetylene yield with irradiation time.

Figure 3.4

Variation of propylene yield with irradiation time.
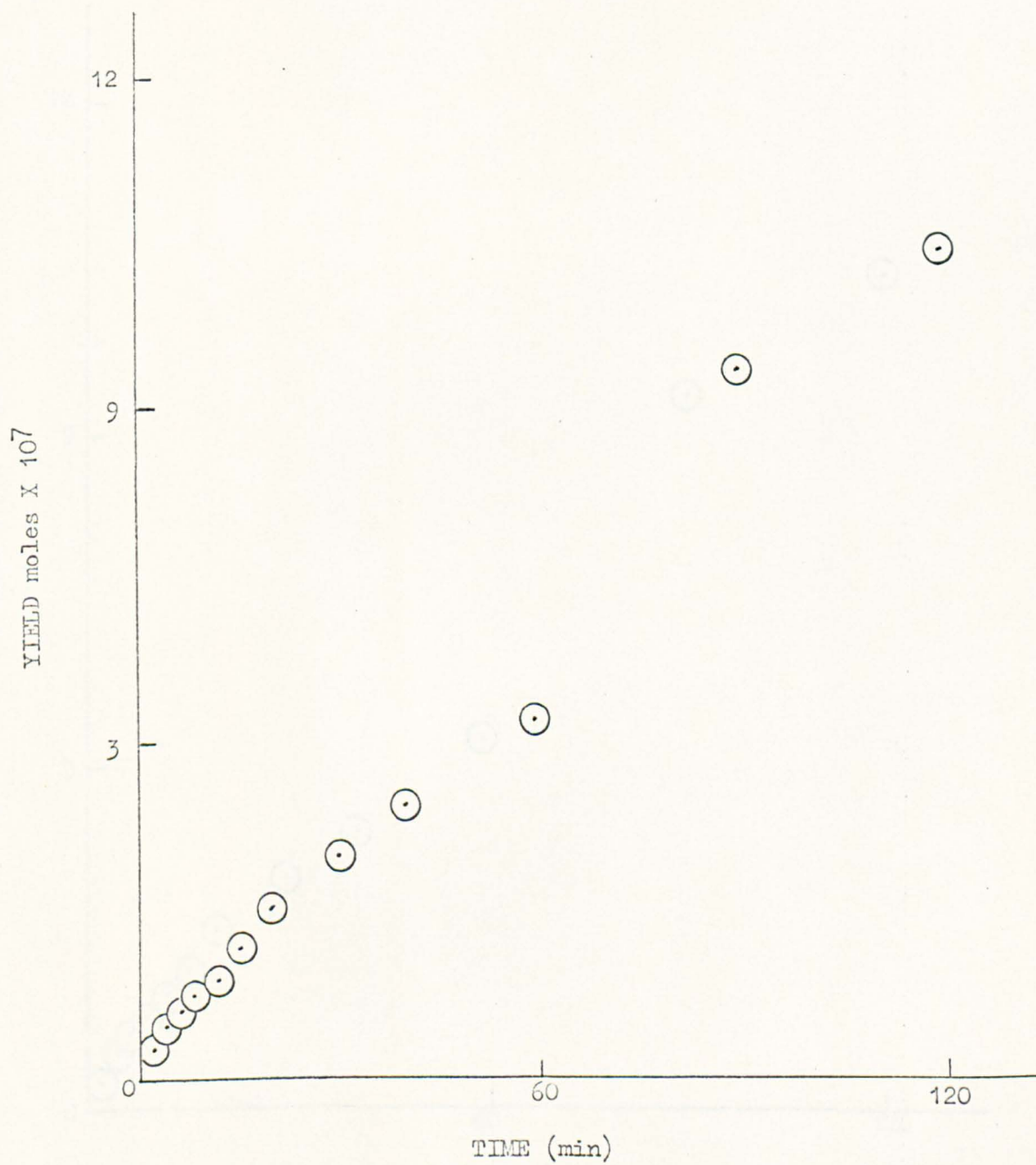
Figure 3.5

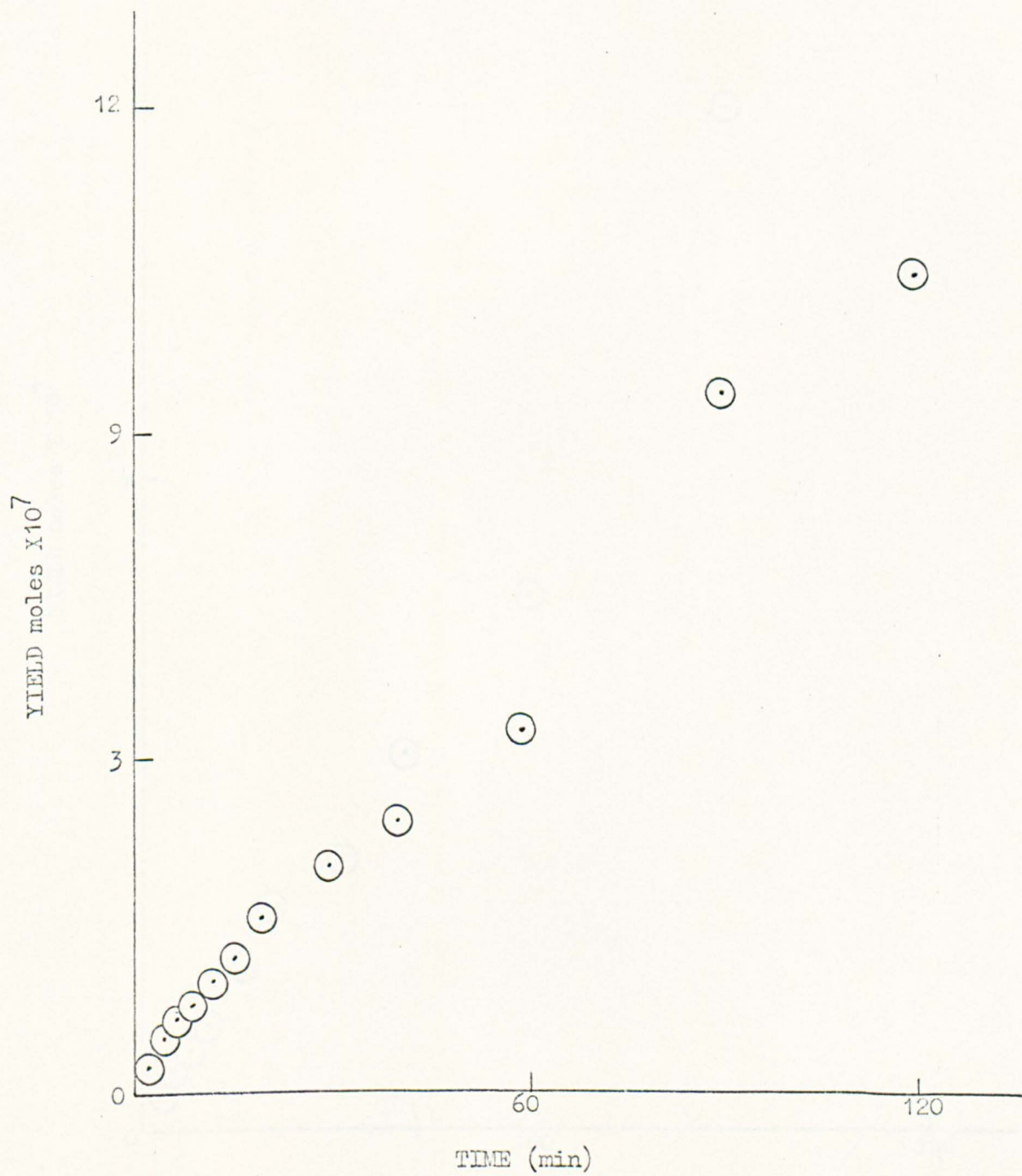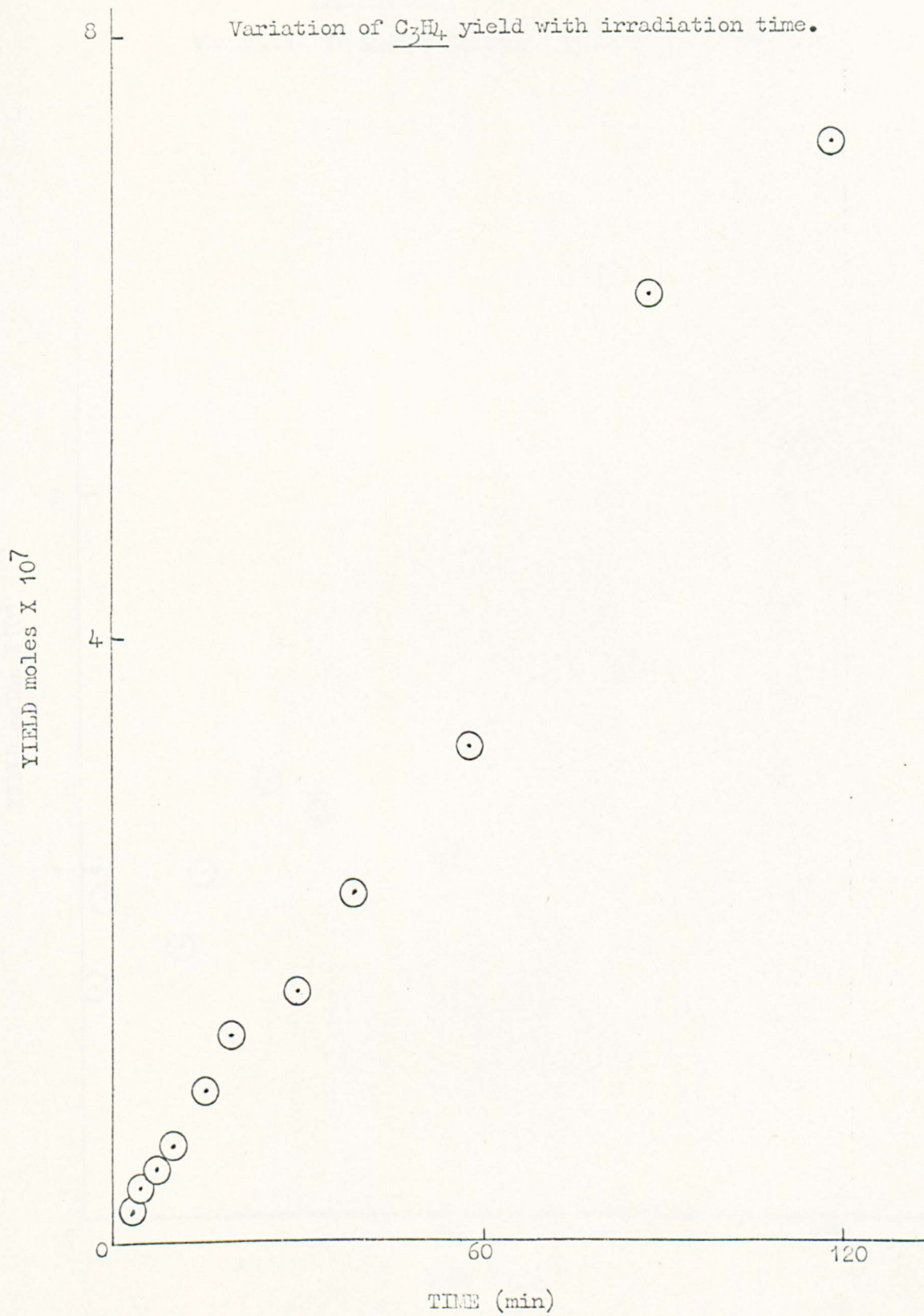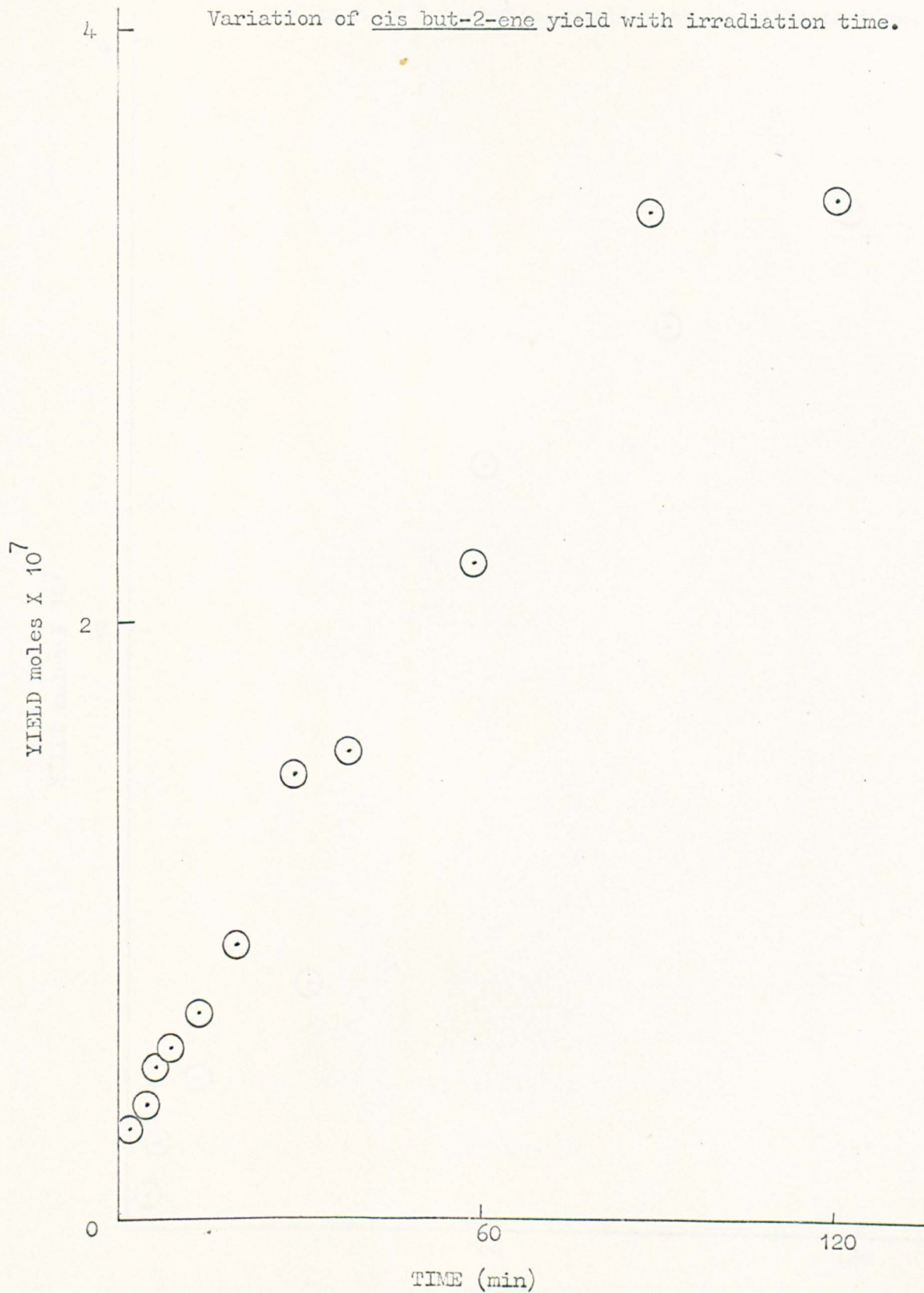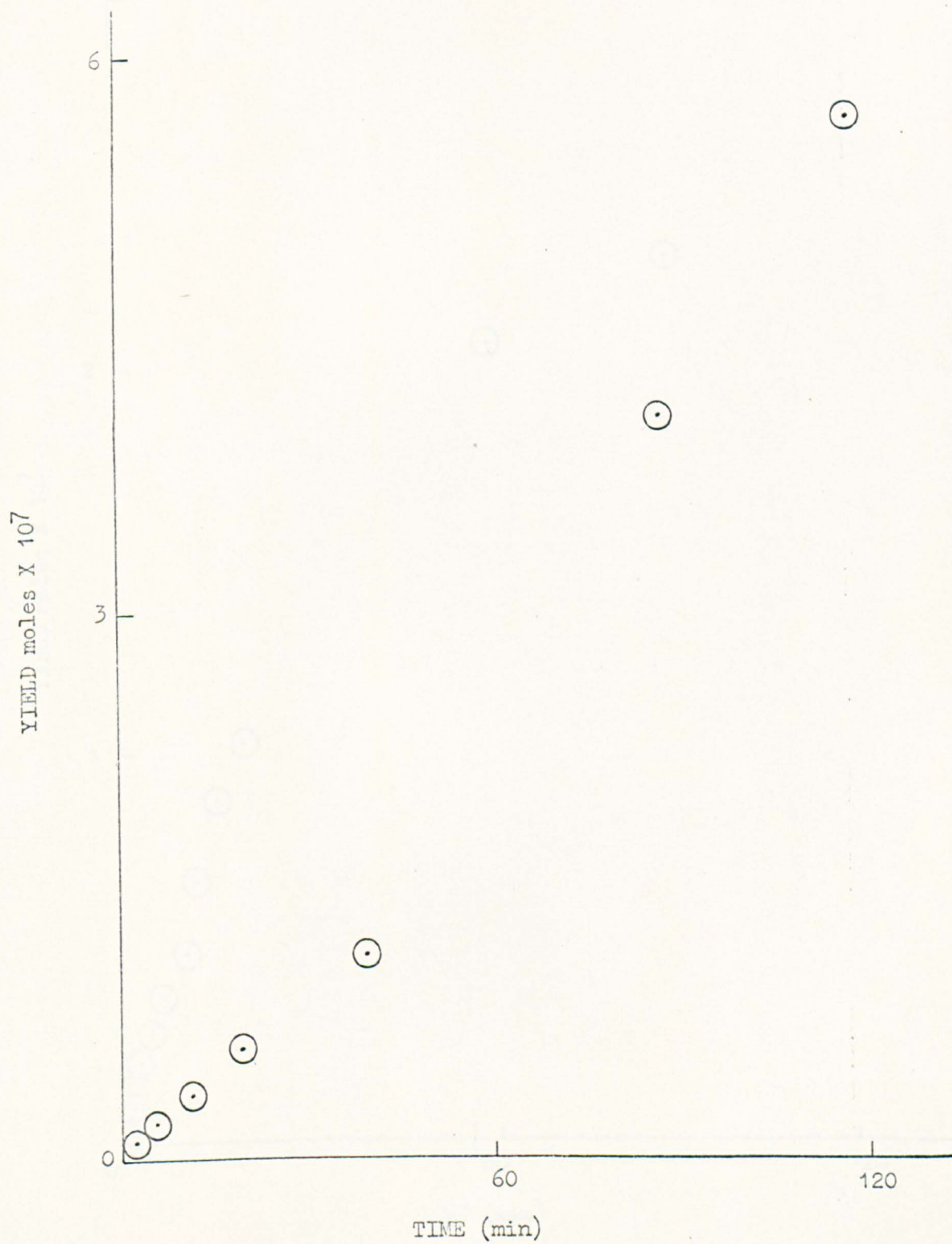Variation of propane yield with irradiation time.

Figure 3.6

Variation of C_3H_4 yield with irradiation time.

Figure 3.7

Variation of _isobutane_ yield with irradiation time.

Figure 3.8

Variation of trans but-2-ene yield with irradiation time.

Figure 3.9

Variation of cis but-2-ene yield with irradiation time.

Figure 3.10

Variation of 3-me-butene yield with irradiation time.

Figure 3.11

Variation of isopentane yield with irradiation time.

Figure 3.12

Variation of n-pentane yield with irradiation time.

Figure 3.13

Variation of cis pent-2-ene yield with irradiation time.

Figure 3.14

Variation of *trans* pent-2-ene yield with irradiation time.
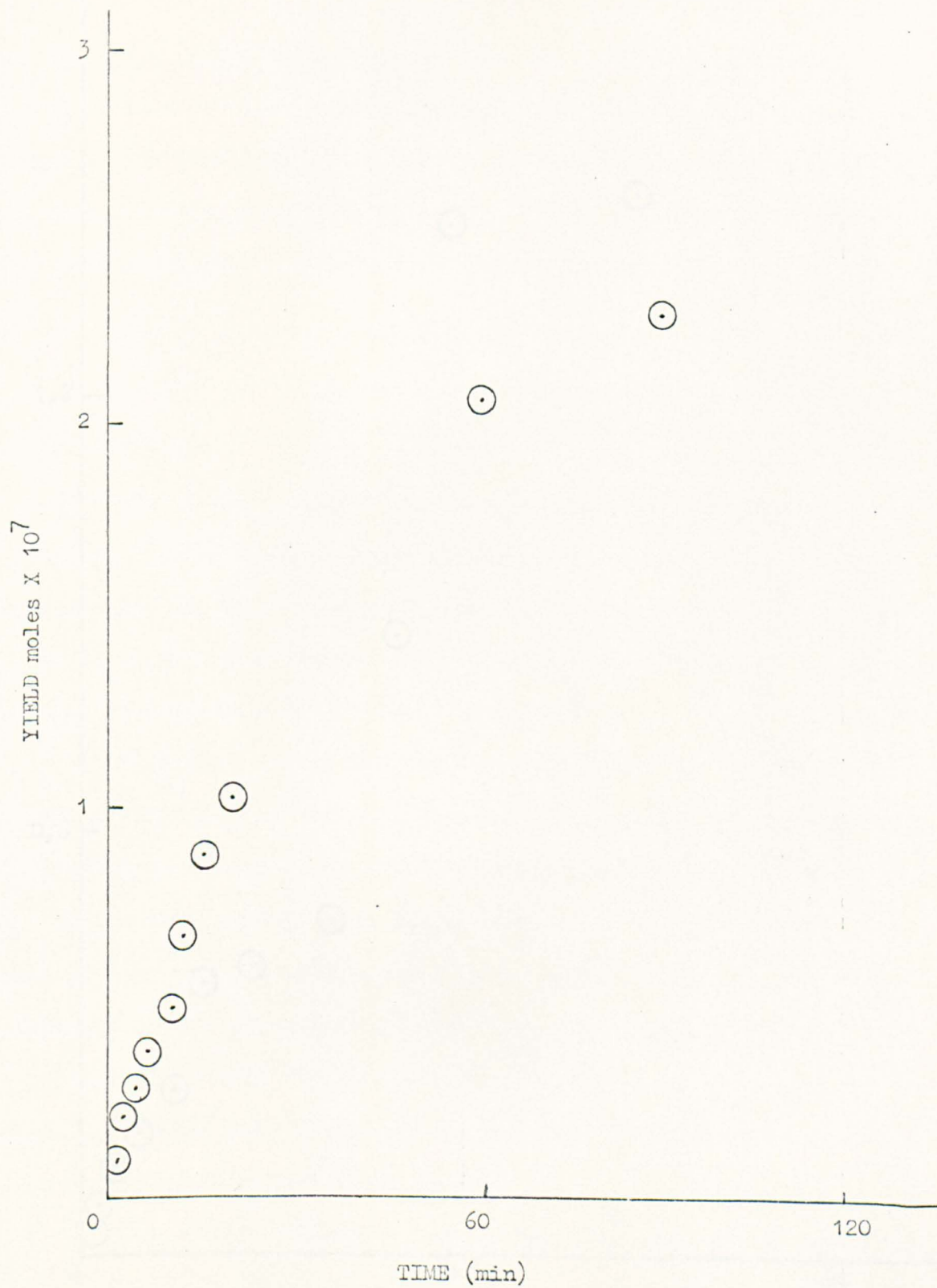
3.2 Effect of Added Gas Pressure

In order to determine which products are formed by molecular fragmentation reactions in the primary reactions and which are formed via free radicals, the effect of adding various gases was investigated. The added gases may be divided into two categories:

(a) Inert gases

(b) Radical Scavengers,
(oxygen taken as an example)

The effect of inert gases on the product yields is shown in Table 3.3, 3.4 and 3.5 for argon, nitrogen and carbon dioxide respectively, and the results are also illustrated by Figures 3.15a to 3.27a. A general decrease in the quantum yields is noted and the effect of all three inert gases is seen to be the same.

In order to determine whether quenching of the excited state is in fact taking place further experiments were performed to determine the consumption of the but-1-ene as a function of nitrogen pressure. The results are illustrated in Figure 3.28, it must be noted that the error in each point is greater than in the other figures since each point represents a small difference between two large numbers (equivalent to 5% decomposition of the but-1-ene). Clearly, in spite of this the figure shows that quenching of an excited state intermediate is taking place to yield the starting material.

The effect of adding oxygen on the product yields is shown in

Table 3.6 and illustrated by Figures 3.15b to 3.22b. Those products

whose yields are completely eliminated by oxygen are not illustrated

by any figure (C_5 - C_8 hydrocarbons). It was noted that oxygen affected

the yields of some products much more than the inert gases did and

eliminated the higher products immediately, these products are formed

via free radical processes. The products whose yields are only affected

the same by oxygen as they were by the inert gases are formed in the

primary reactions by molecular fragmentation. The question now arises

as to whether oxygen just quenches the excited state intermediate as well

as reacting with radicals or whether it also reacts with the excited

state. Experiments were conducted to determine the consumption of

but-1-ene in the presence of oxygen and are illustrated in Figure 3.29,

the accuracy of the points is the same as in Figure 3.28. The consumption

of but-1-ene was seen to rise as oxygen was added but then appears

constant up to about 250 mm., indicating that oxygen is reacting

chemically with the butene in addition to other reactions with the

excited molecule.

Effect of Added Gases

Experimental Conditions:

p(But-1-ene) = 6 mm; temperature = $20^\circ \pm 2^\circ C$;

irradiation time = 5 mins.

Analytical Conditions:

Column, 0; temperature, $35^\circ C$;

flame ionisation detector; N_2 pressure, 12 lb/sq.in.

Key to Figures:

The following notation is used in Figures 15 to 27.

⊙ Argon;   ✕ Carbon dioxide;

△ Oxygen   ▽ Nitrogen

The yields of the products are quoted as quantum yields and signified by ϕ.

Table 3.3

Effect of Argon on the C_1 to C_5 Product Yields

(Moles x 10^9 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_2	C_2H_6	C_3H_6	C_3H_8	C_3H_4	c-b-2	3Me butene	iso-pentane	n-pentane	t-b-2	c-b-2
0	12.6	26.7	3.8	50.2	11.4	9.2	8.2	3.8	4.6	13.1	5.5	5.4	4.0
20	12.0	20.2	3.4	48.0	8.7	7.1	6.0	3.6	4.1	11.5	4.4	4.2	3.5
50	10.9	16.4	3.3	45.8	7.1	6.0	4.9	3.3	3.8	10.9	3.0	3.7	3.2
100	8.7	13.6	2.7	39.3	6.0	4.4	3.3	-	2.9	9.3	2.4	2.6	2.7
200	8.2	9.3	2.8	39.3	4.4	3.0	2.0	2.9	2.9	9.3	2.2	2.4	2.6
300	8.2	9.3	2.8	39.3	4.4	3.0	1.6	2.7	2.7	9.2	1.5	2.4	2.4

Table 3.4

Effect of Nitrogen on the C_1 to C_5 Product Yields

(Moles x 10^9 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_2	C_2H_6	C_3H_6	C_3H_8	C_3H_4	c–b–2	3Me butene	iso-pentane	n-pentane	t–b–2	c–b–2
0	12.6	26.7	3.8	50.2	11.4	9.2	8.2	3.8	4.6	13.1	5.5	5.4	4.0
25	12.5	25.1	3.8	50.0	9.1	5.5	5.2	3.8	4.4	9.6	3.8	5.0	3.8
50	10.9	22.4	3.3	43.6	6.9	4.9	4.9	3.7	4.0	8.7	3.7	4.7	3.7
100	8.2	18.5	3.3	43.0	5.5	3.1	4.6	3.5	3.9	8.0	3.3	4.1	3.3
200	7.5	10.9	2.7	39.3	4.7	1.3	3.1	3.1	3.7	7.1	2.6	3.8	2.8
300	7.5	9.3	2.6	32.7	4.1	1.2	3.1	3.1	3.5	7.1	2.6	3.8	2.5

Table 3.5

Effect of Carbon Dioxide on the C_1 to C_5 Product Yields

(Moles x 10^9 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_2	C_2H_6	C_3H_6	C_3H_8	C_3H_4	c-b-2	3Me butene	iso-pentane	n-pentane	t-b-2	c-b-2
0	12.6	26.7	3.8	50.2	11.4	9.2	8.2	3.8	4.6	13.1	5.5	5.4	4.0
20	10.6	16.4	3.5	44.5	8.0	6.6	3.0	2.9	3.7	9.6	3.3	4.2	3.2
50	10.3	12.5	3.3	43.5	5.8	4.4	2.7	2.9	3.5	8.9	2.2	3.7	2.9
100	9.5	9.8	2.9	40.0	4.8	3.8	2.2	2.5	2.9	8.2	2.0	3.5	2.5
200	9.3	5.5	2.5	33.0	4.2	3.1	1.1	2.2	2.8	7.1	1.1	1.9	1.5
300	8.2	3.4	2.5	33.0	4.2	3.1	0.6	2.4	2.7	6.8	1.4	2.2	2.0

Table 3.6

Effect of Oxygen on C_1 to C_5 Product Yields

(Moles x 10^9 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_2	C_2H_6	C_3H_6	C_3H_8	C_3H_4	c-b-2	3Me butene	iso- pentane	n- pentane	t-b-2	c-b-2
0	12.6	26.7	3.8	50.2	11.4	9.2	8.2	3.8	4.6	13.1	5.5	5.4	4.0
25	10.3	22.9	3.7	12.8	4.9	3.8	5.7	3.7	-	-	-	-	-
50	9.3	16.9	3.3	12.5	2.7	2.5	4.9	3.7	-	-	-	-	-
100	7.1	15.8	3.2	12.0	2.0	1.1	4.6	3.0	-	-	-	-	-
220	7.6	9.8	2.6	10.1	1.1	0.9	2.5	1.5	-	-	-	-	-
300	7.6	9.3	2.5	9.3	1.1	0.9	2.5	1.5	-	-	-	-	-

Figure 3.15a

Variation of product yield with added gas pressure.
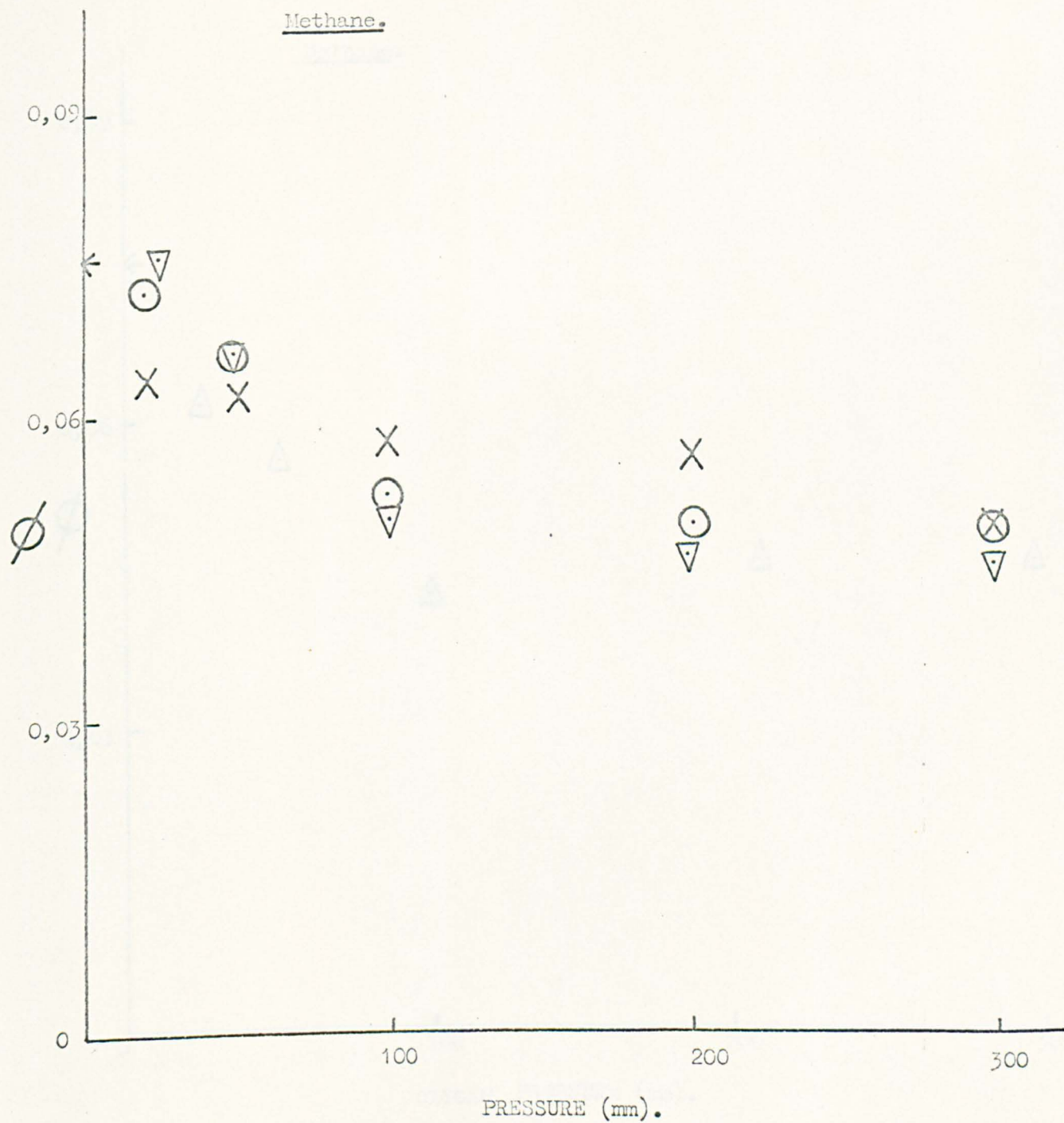
Figure 3.15b

Variation of product yield with oxygen   pressure.
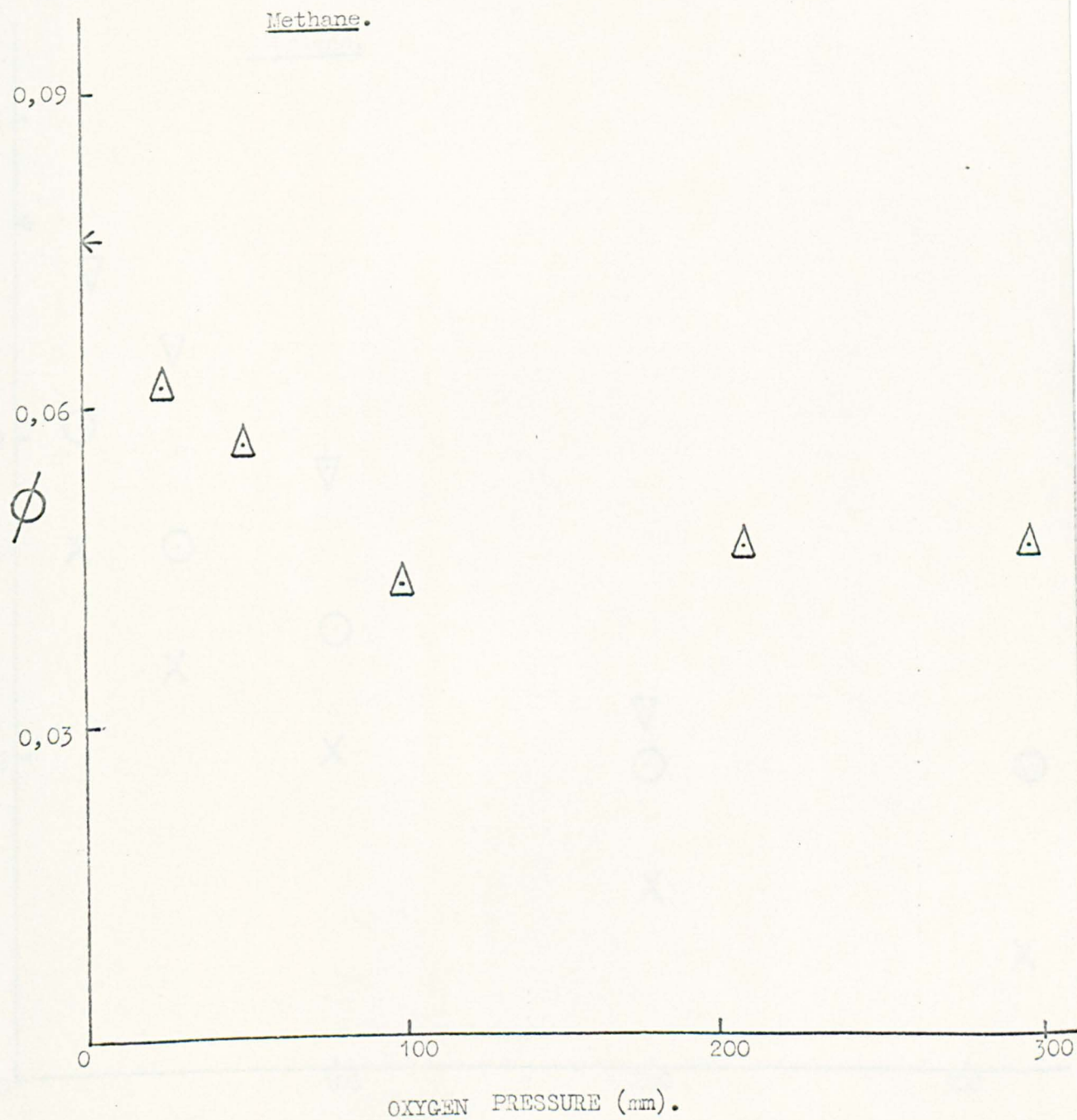
Figure 3.16a

Variation of product yield with added gas pressure.

Ethylene.
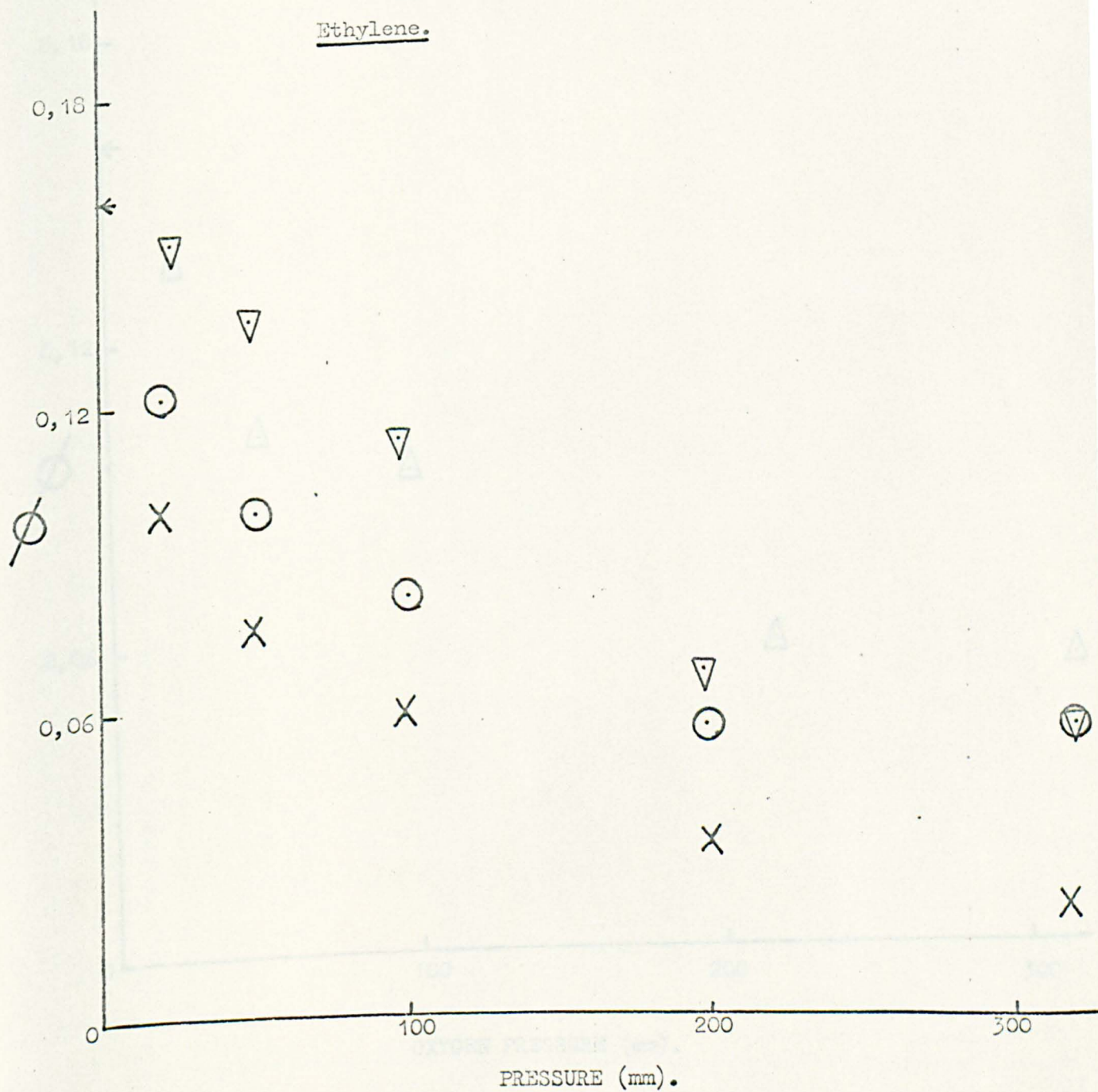
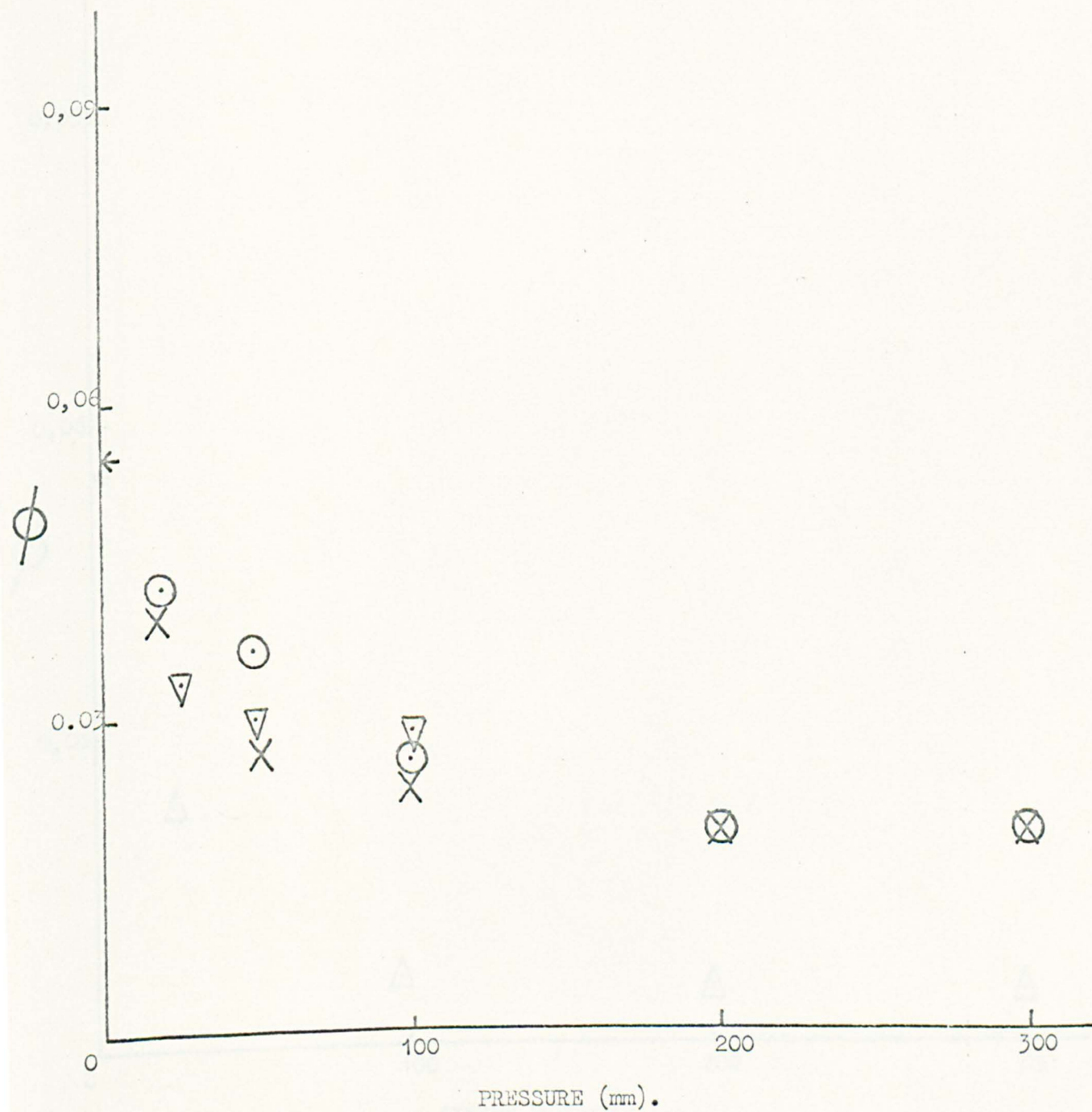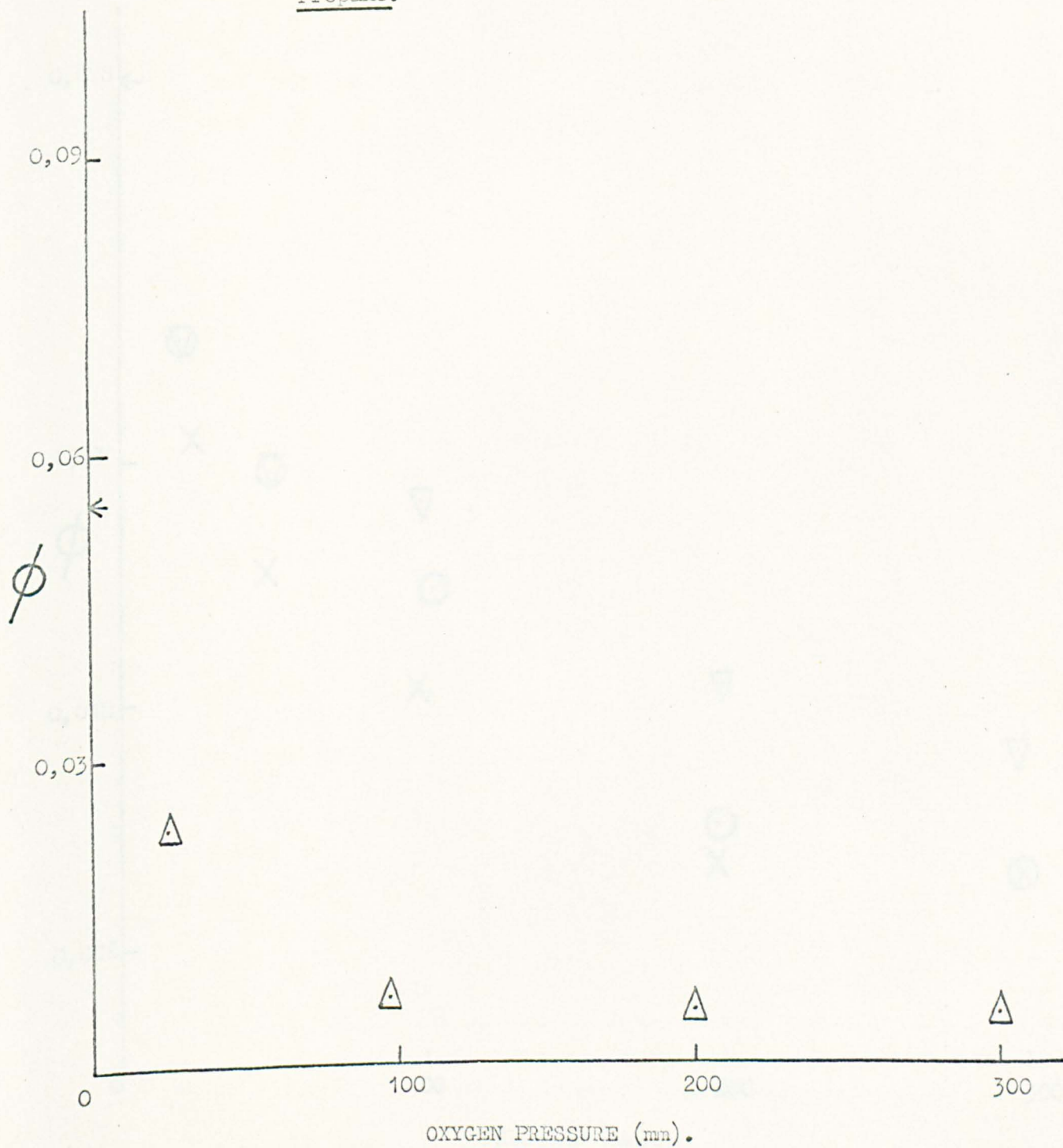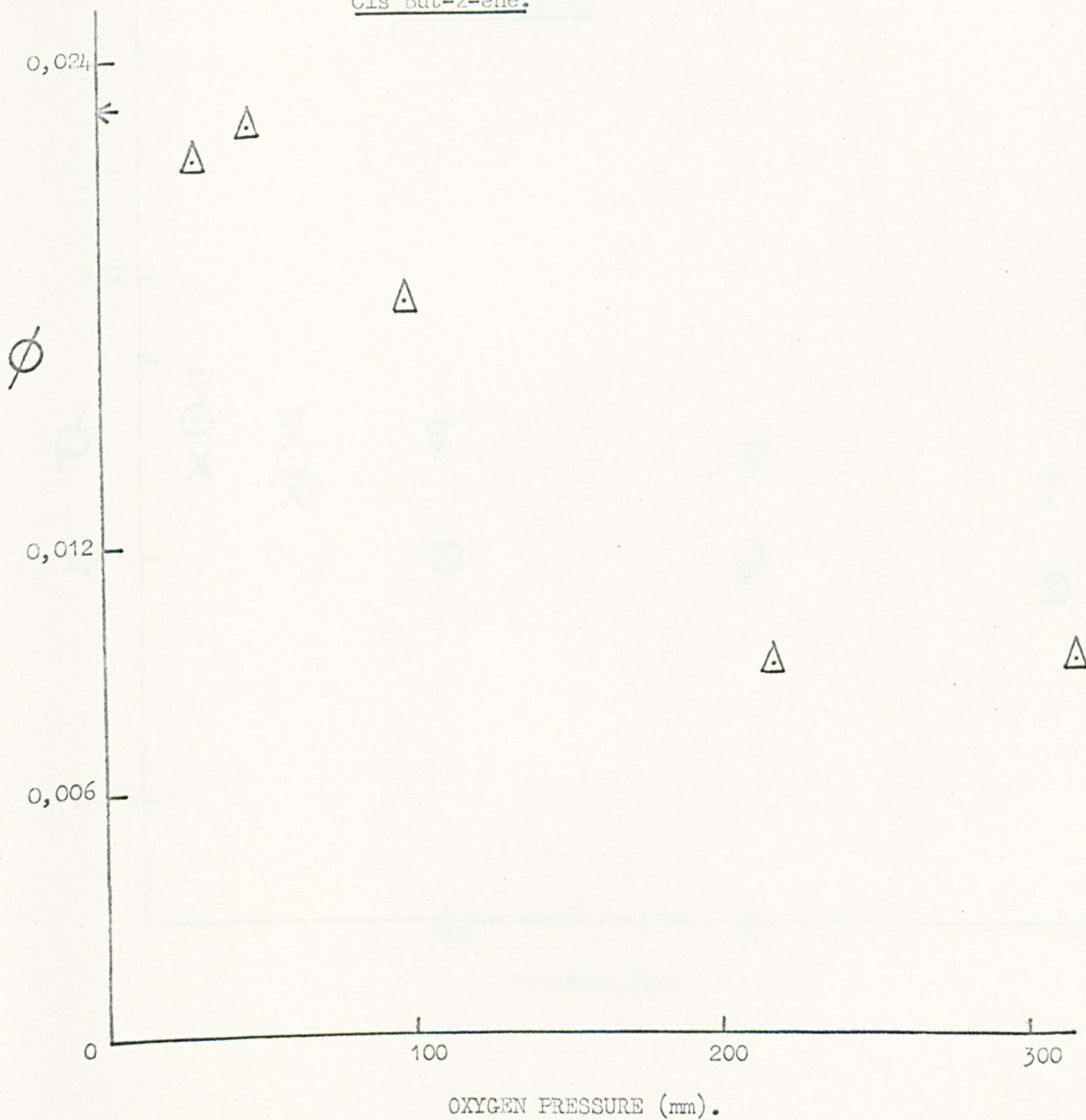PRESSURE (mm).

Figure 3.16b

Variation of product yield with oxygen pressure.

Ethylene.
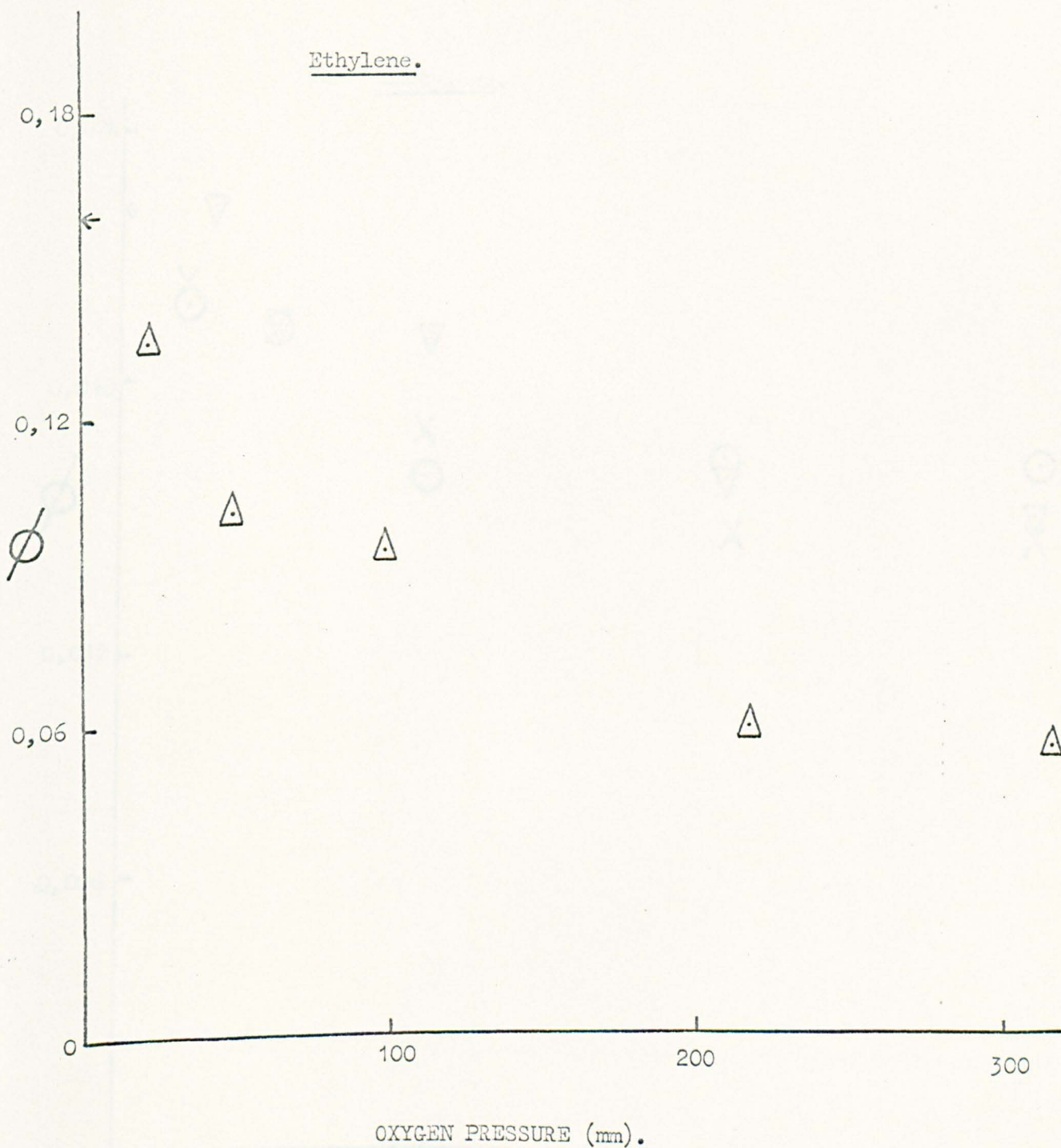
Figure 3.17a

Variation of acetylene yield with added gas pressure.

Acetylene.
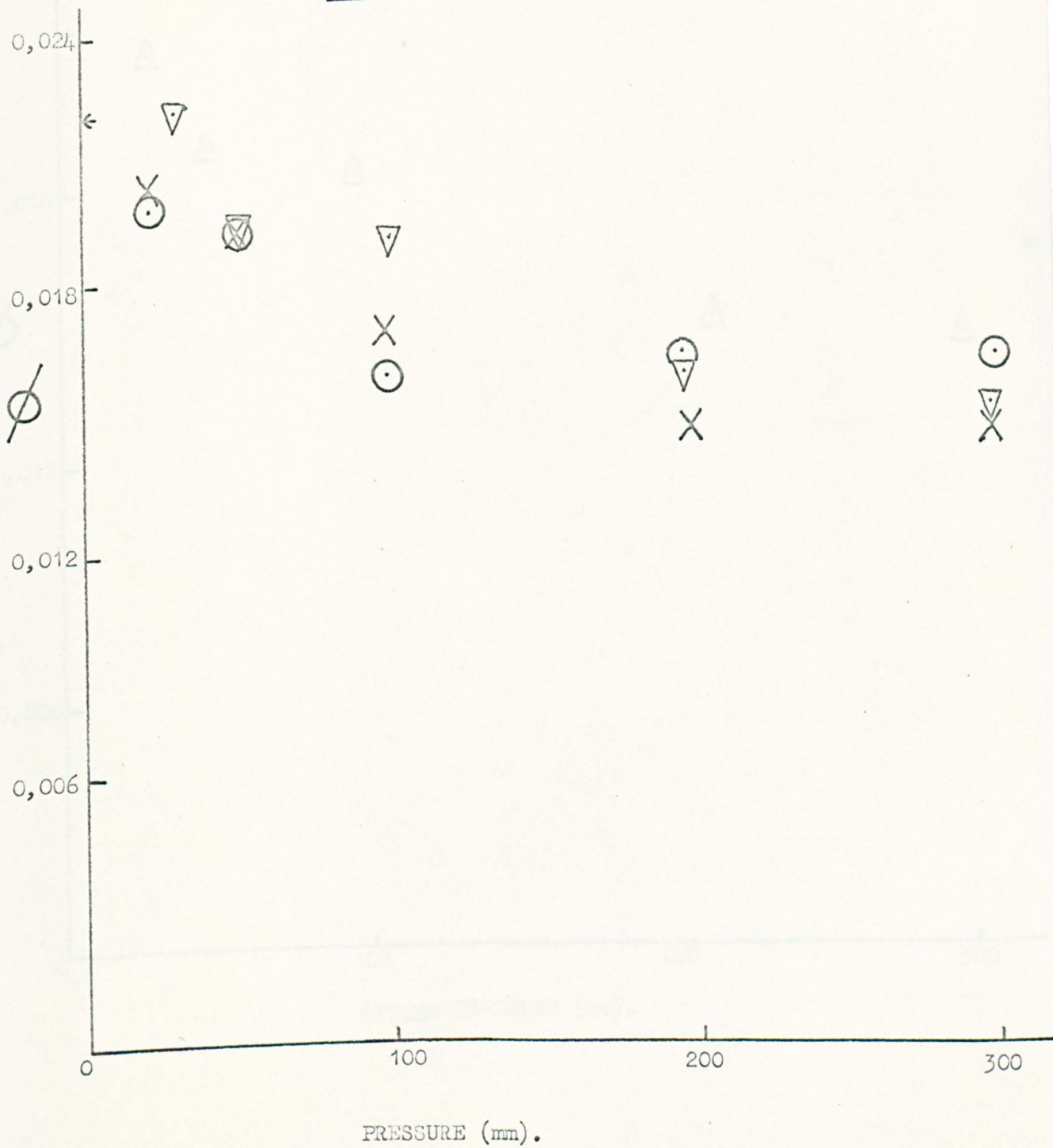
Figure 3.17b

Variation of acetylene yield with oxygen pressure.
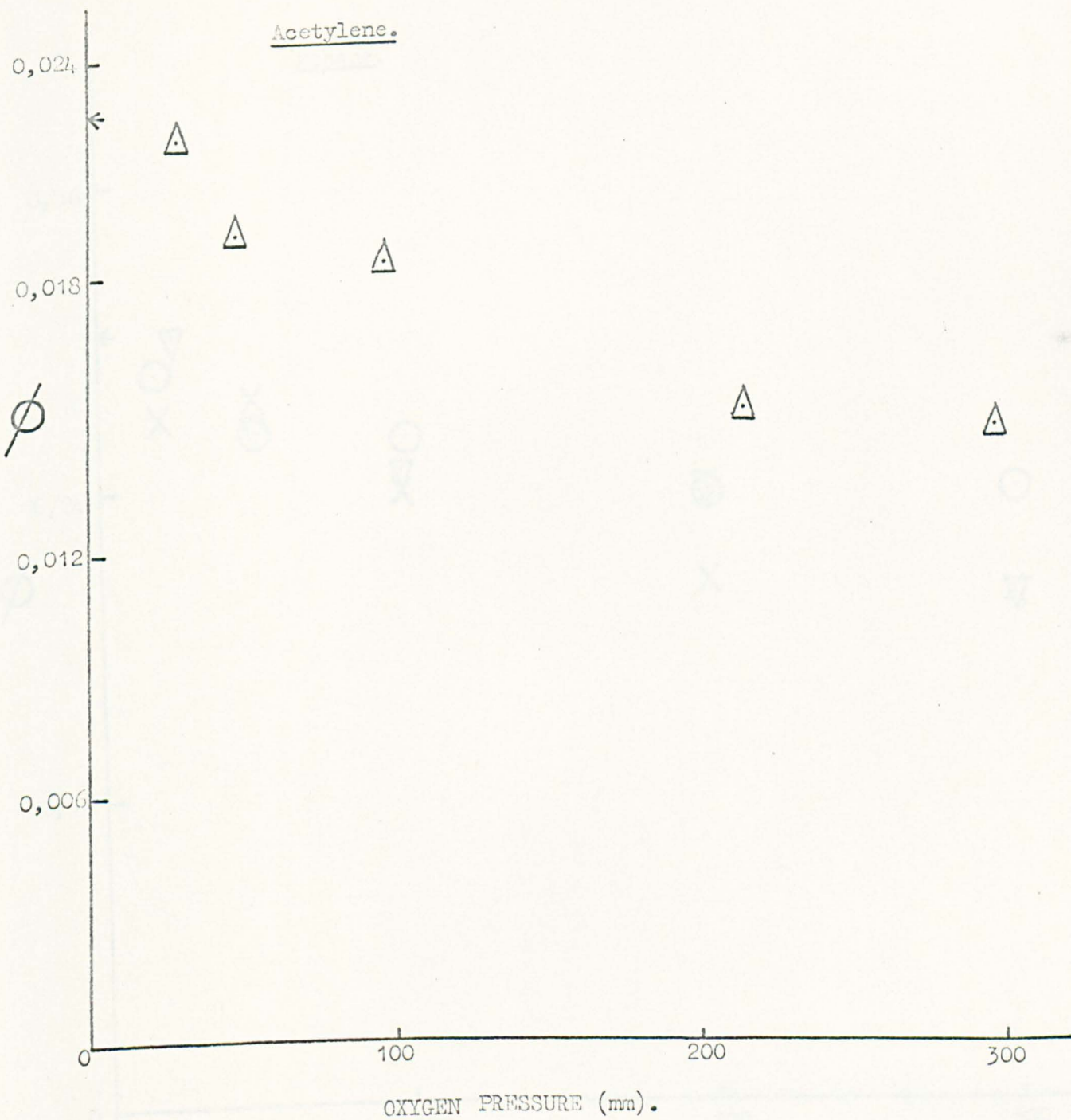
Figure 3.18a

Variation of product yield with added gas pressure.

Ethane.
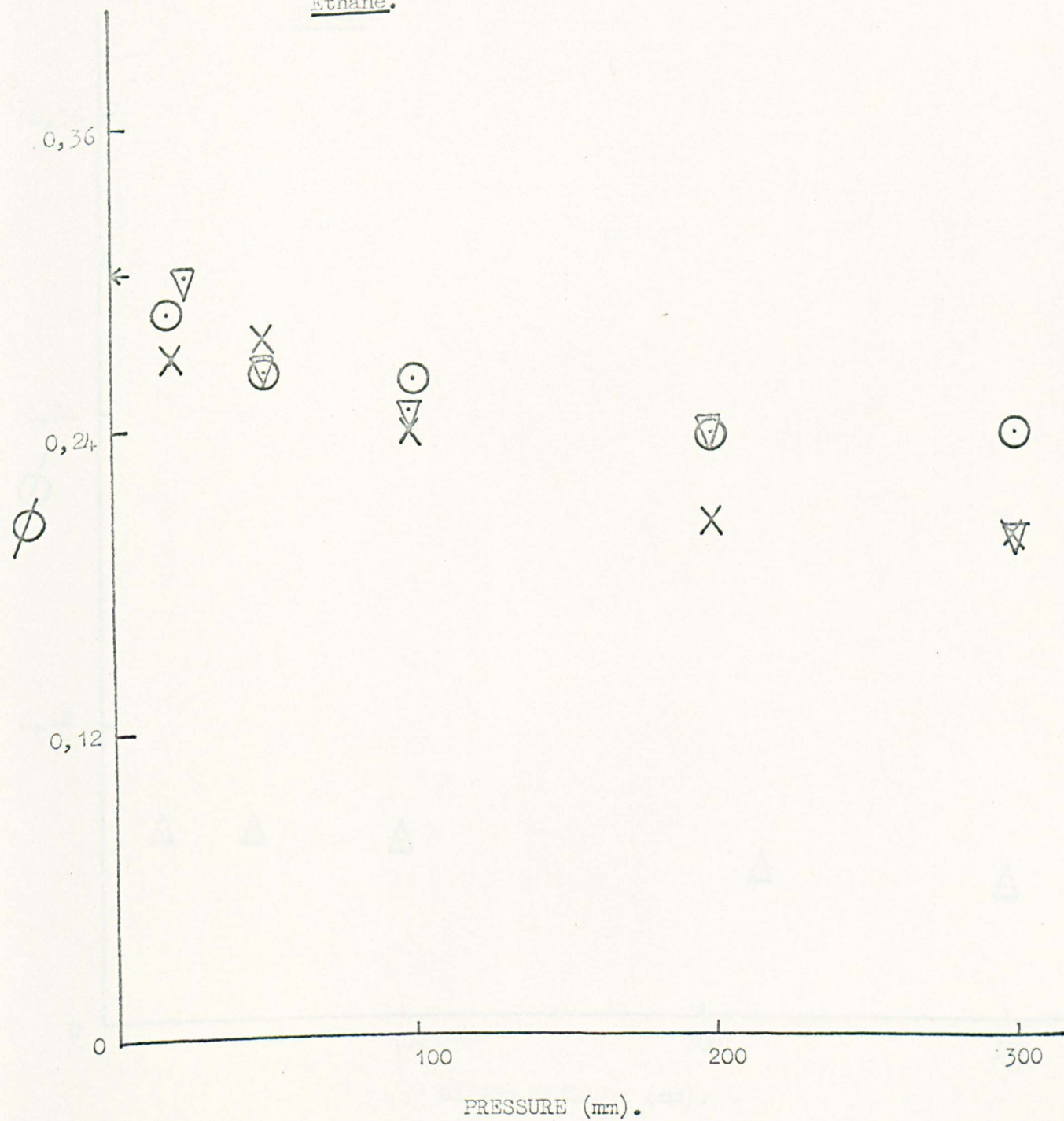
Figure 3.18b

Variation of product yield with oxygen pressure.

Ethane.
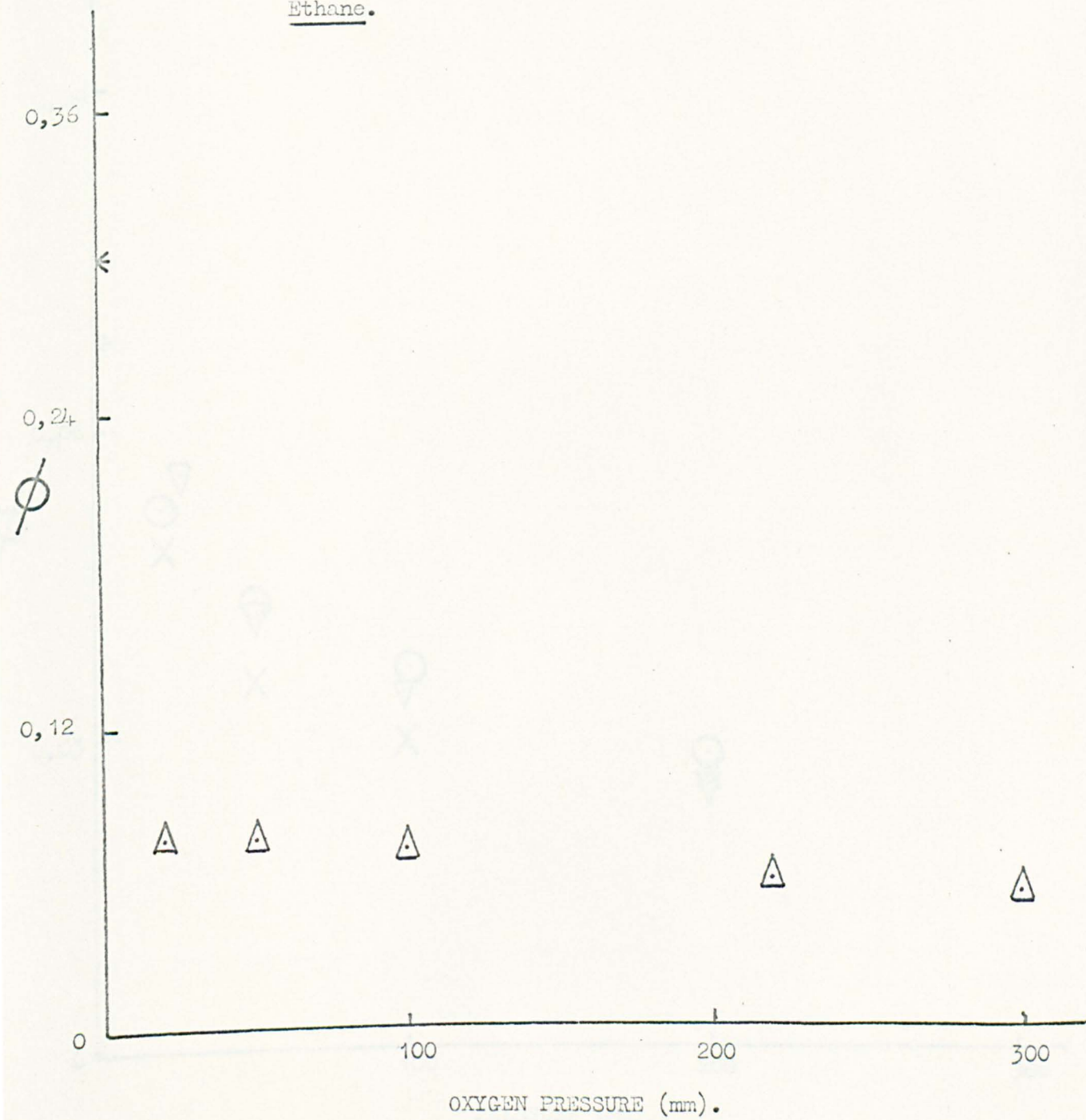
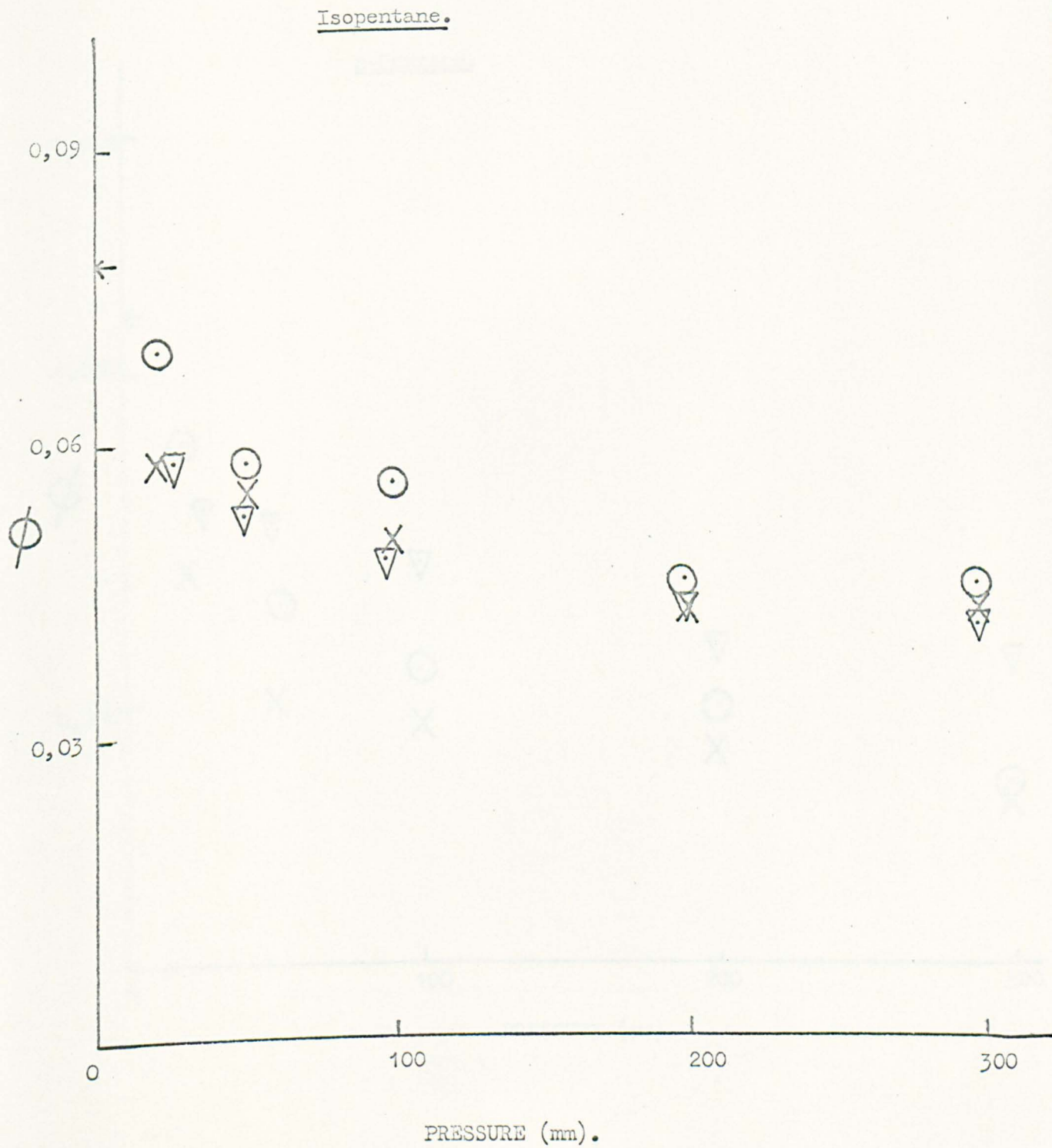Figure 3.19a

Variation of product yield with added gas pressure.

Propylene.
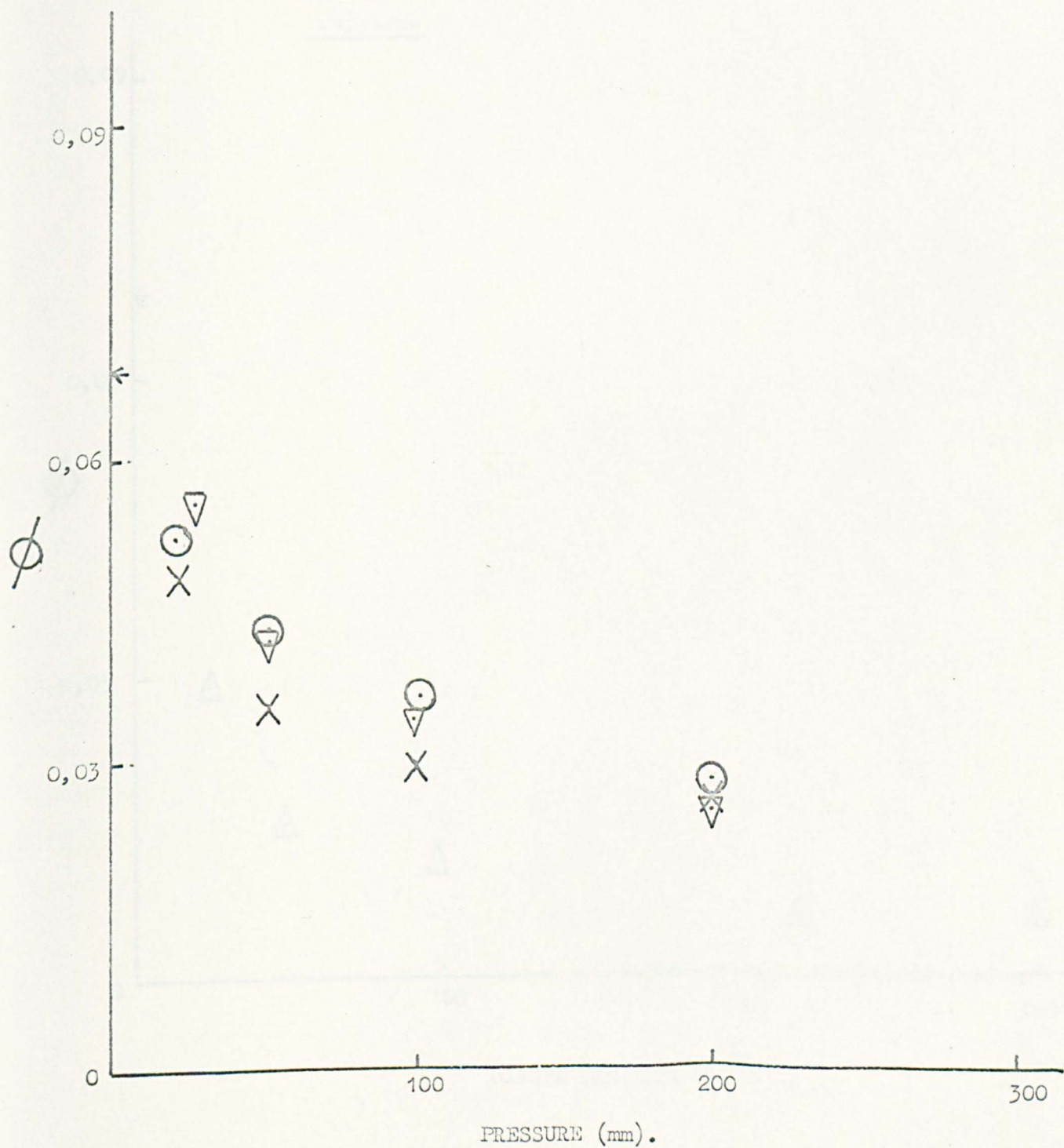
Figure 3.19b

Variation of product yield with oxygen pressure.

Propylene.
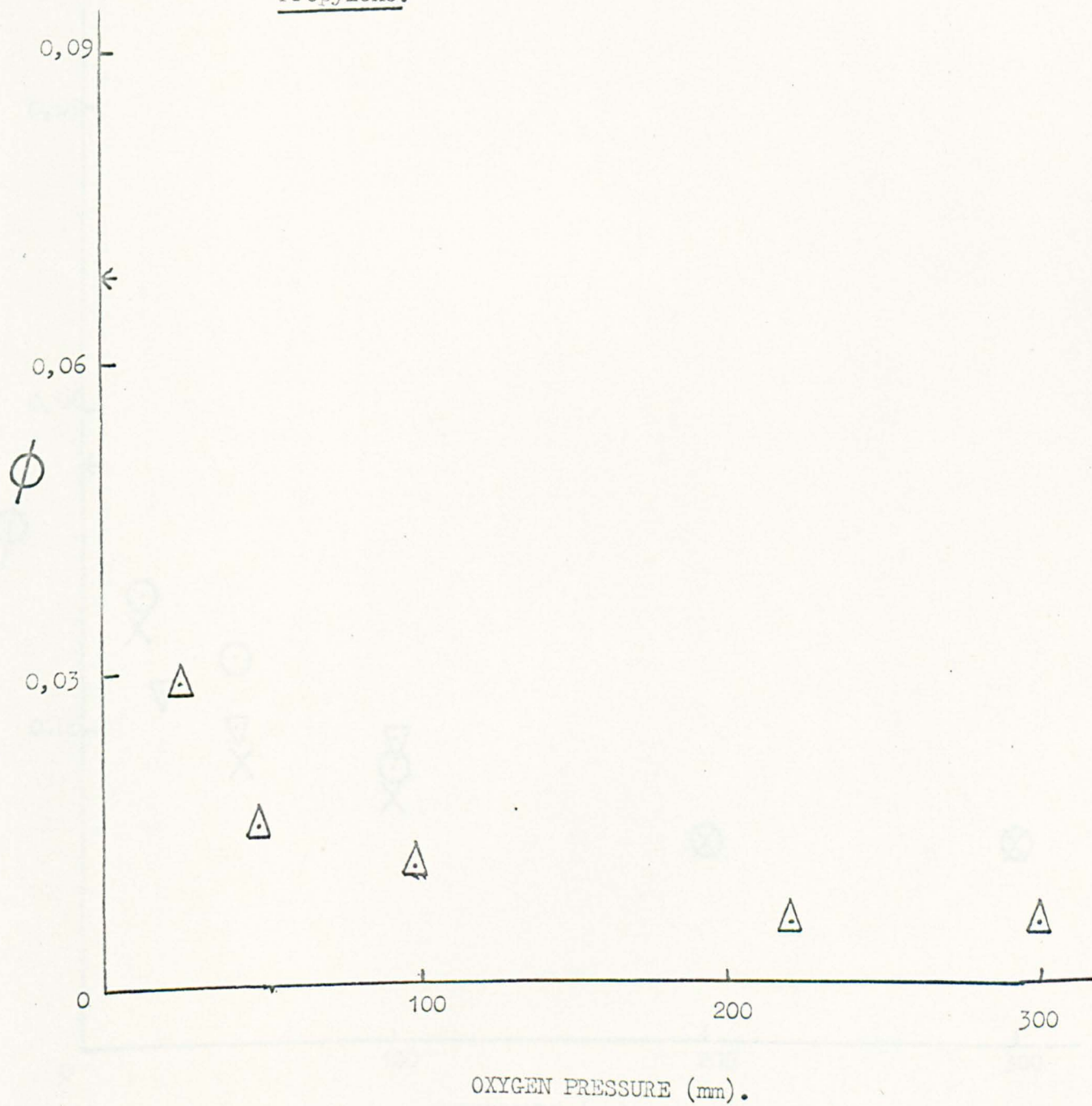
Figure 3.20a
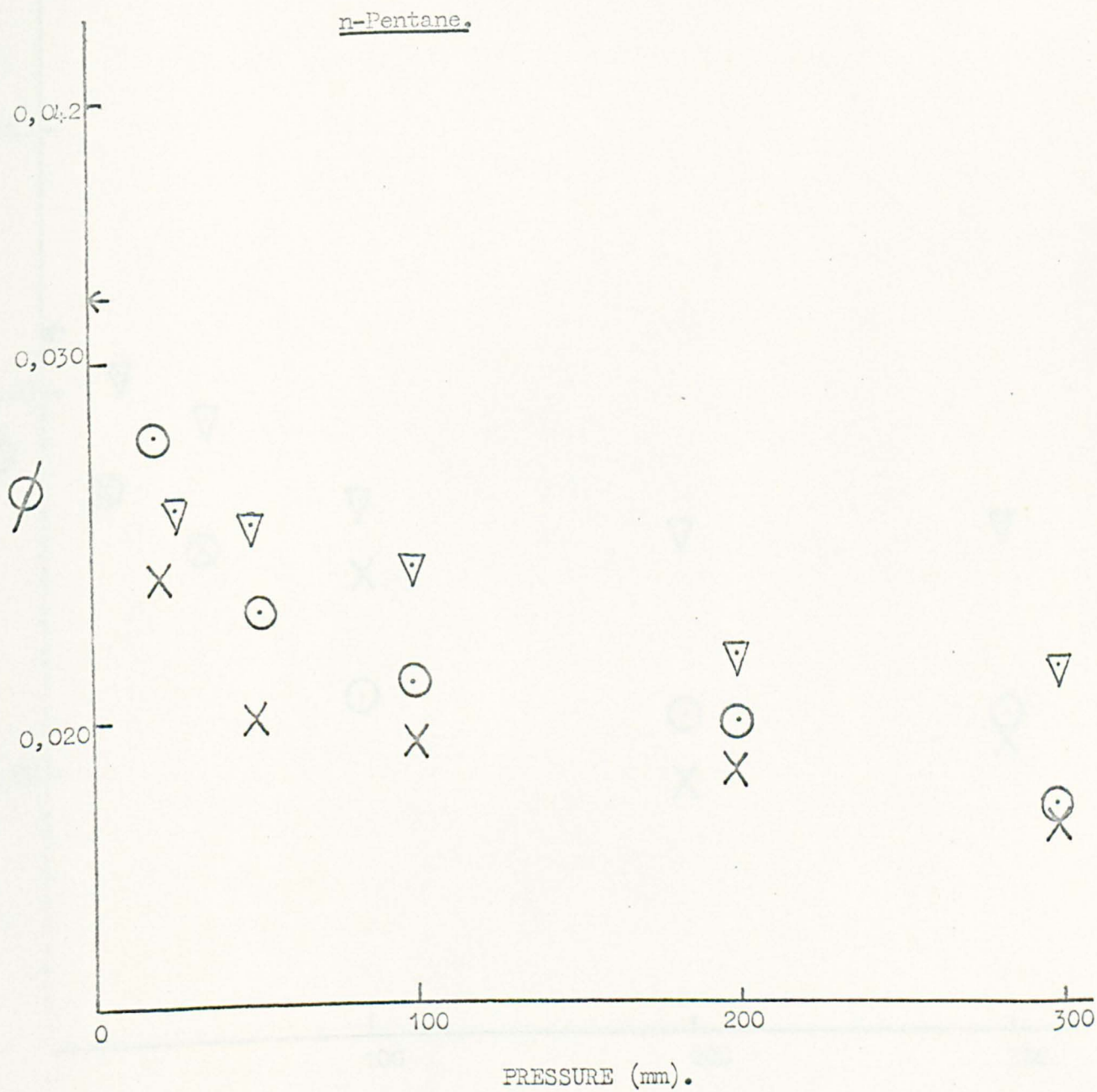
Variation of product yield with added gas pressure.

Propane.

Figure 3.20b

Variation of product yield with oxygen pressure.

Propane.

Figure 3.21a

Variation of product yield with added gas pressure.

C_3H_4.

Figure 3.21b

Variation of product yield with oxygen pressure.

C_3H_4.

Figure 3.22a

Variation of product yield with added gas pressure.

Cis But-2-ene.

PRESSURE (mm).

Figure 3.22b

Variation of product yield with oxygen pressure.

Cis But-2-ene.

Figure 3.23a

Variation of product yield with added gas pressure.

3-Methyl-Butene.

Figure 3.24a

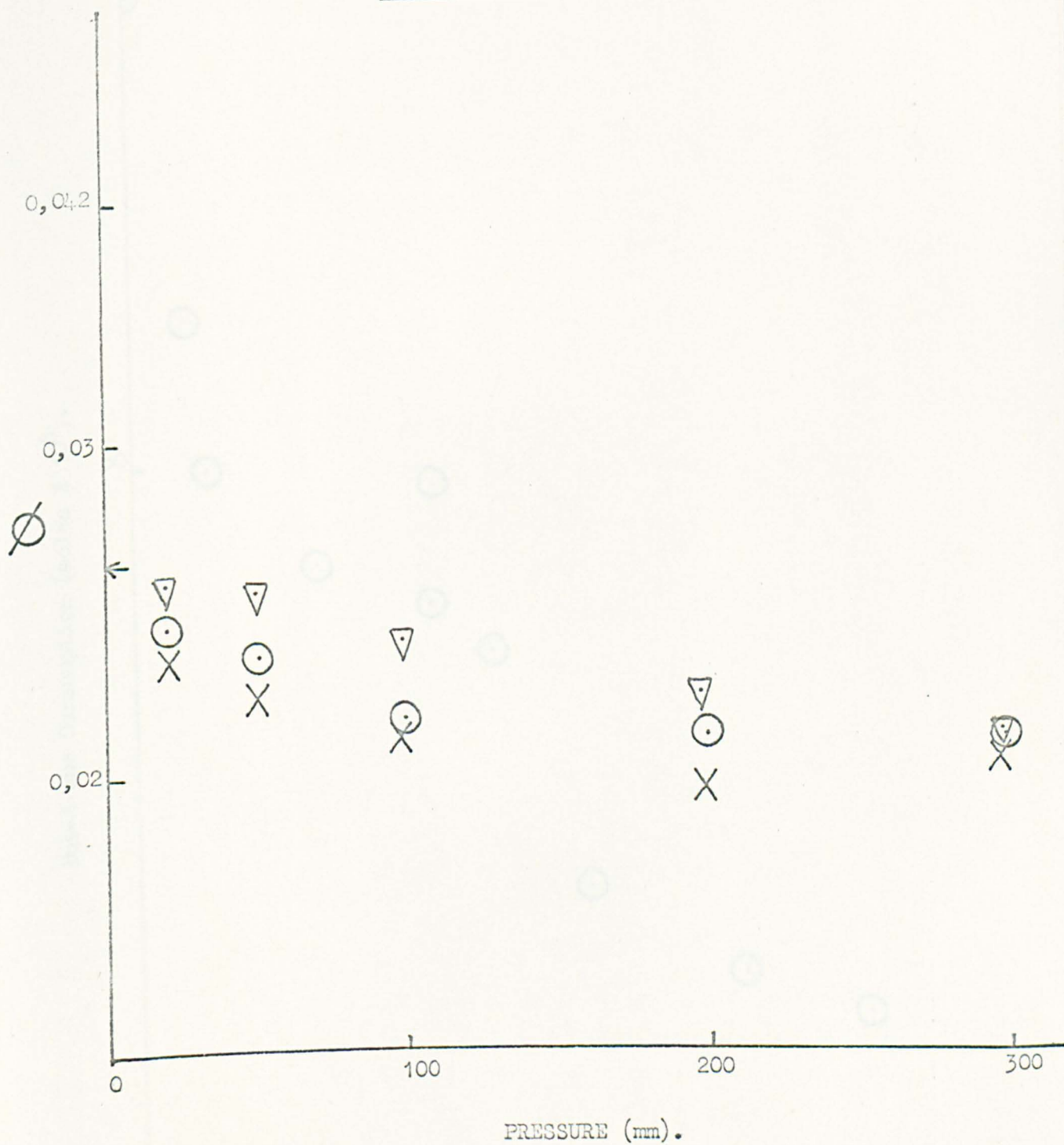Variation of product yield with added gas pressure.

Isopentane.

Figure 3.25a

Variation of product yield with added gas pressure.

n-Pentane.

Figure 3.26a

Variation of product yield with added gas pressure.

Trans Pent-2-ene.

Figure 3.27a

Variation of product yield with added gas pressure.
Cis Pent-2-ene.

Figure 3.28

Consumption of but-1-ene as a function of nitrogen pressure.

Figure 3.29

Consumption of but-1-ene as a function of oxygen pressure.

But-1-ene consumption moles x 10^6

OXYGEN PRESSURE (mm)
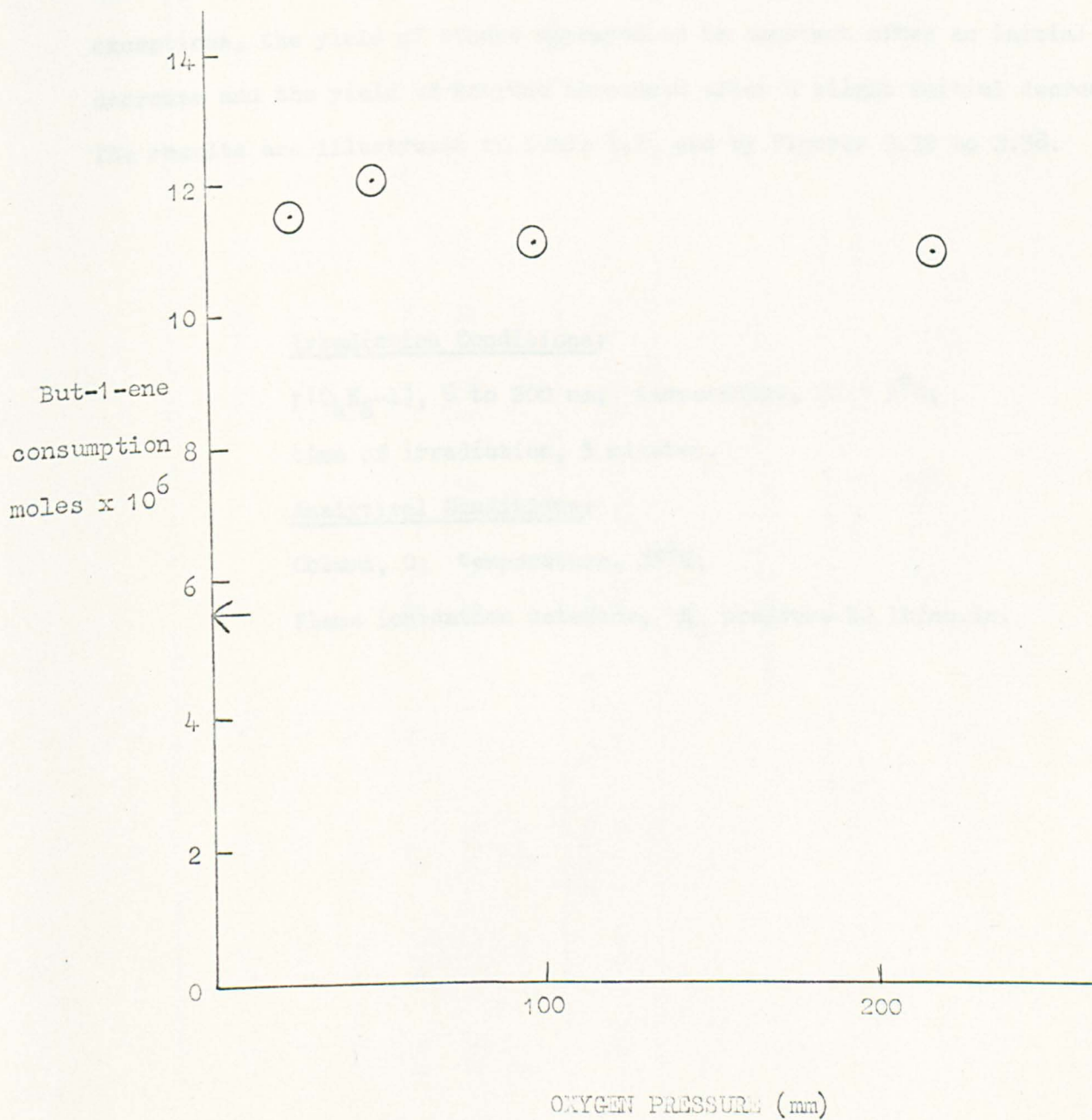
3.3 Effect of Reactant Pressure

On increasing the pressure of but-1-ene the yields of
the majority of the products were decreased as before with two
exceptions, the yield of ethane appeared to be constant after an initial
decrease and the yield of methane increased after a slight initial decrease.
The results are illustrated in Table 3.7, and by Figures 3.30 to 3.38.

Irradiation Conditions:

$p(C_4H_8\text{-}1)$, 6 to 200 mm; temperature, $20 \pm 2^\circ C$;

time of irradiation, 5 minutes.

Analytical Conditions:

Column, 0; temperature, $35^\circ C$;

Flame ionisation detector; N_2 pressure 12 lb/sq.in.

Table 3.7

Effect of Reactant Pressure on Product Yields

(Moles x 10^9 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_2	C_2H_6	C_3H_4	c-b-2	3Me butene	iso-pentane	n-pentane	t-p-2	c-p-2
6	12.0	26.7	3.7	50.2	8.2	3.8	4.6	13.1	5.5	5.4	3.8
12	-	23.0	3.5	38.0	6.3	3.7	4.4	10.4	4.2	5.1	3.7
20	11.0	20.0	3.4	44.0	5.2	-	4.2	9.6	3.9	4.9	3.7
50	13.0	17.0	3.2	42.0	4.9	-	-	8.7	3.7	4.7	3.2
90	24.0	15.0	2.6	44.0	4.6	-	-	8.1	3.4	4.0	2.8
200	34.0	11.0	2.5	38.0	3.1	-	-	7.1	2.6	3.7	2.4

Figure 3.30

Variation of methane yield with reactant pressure.

METHANE.

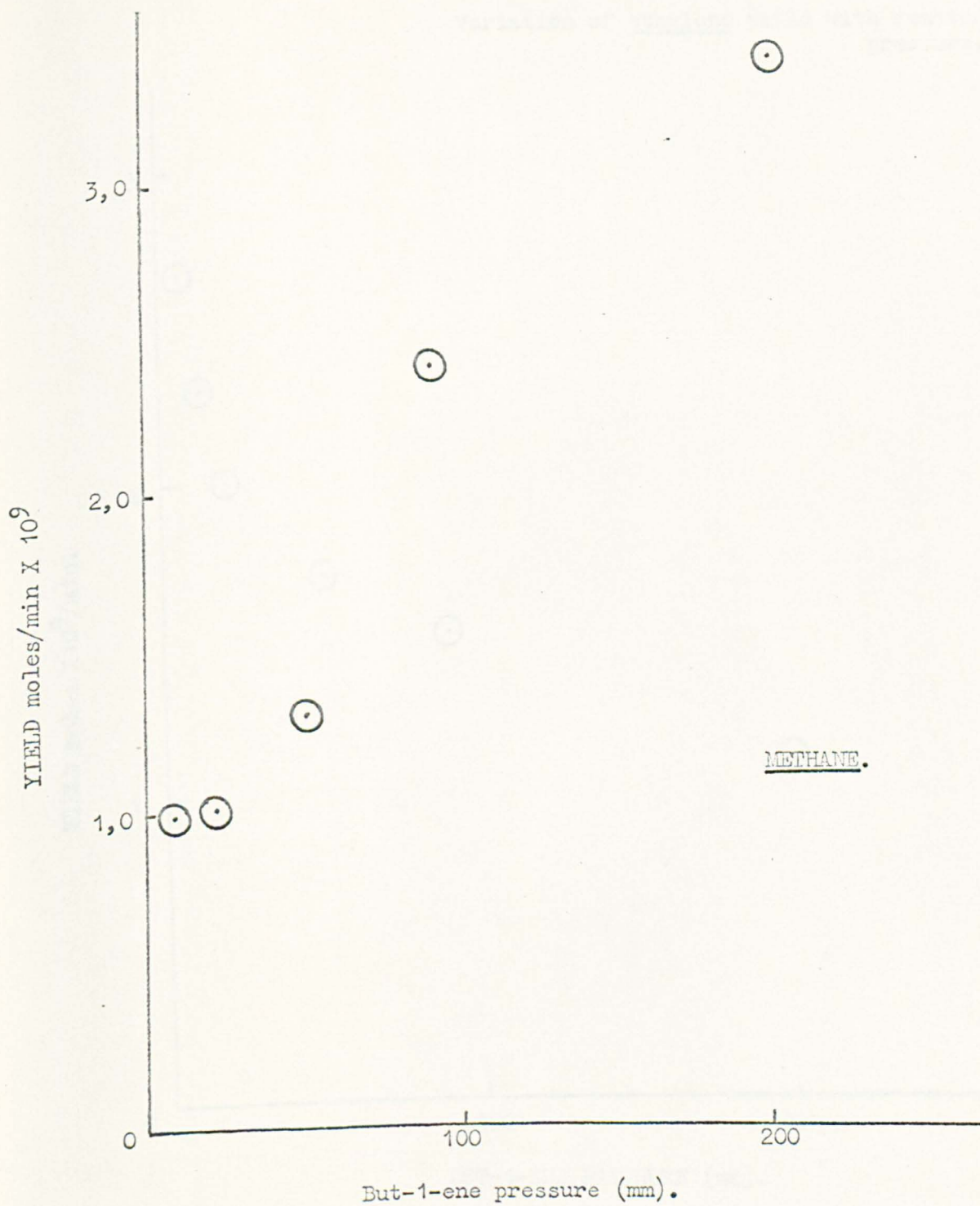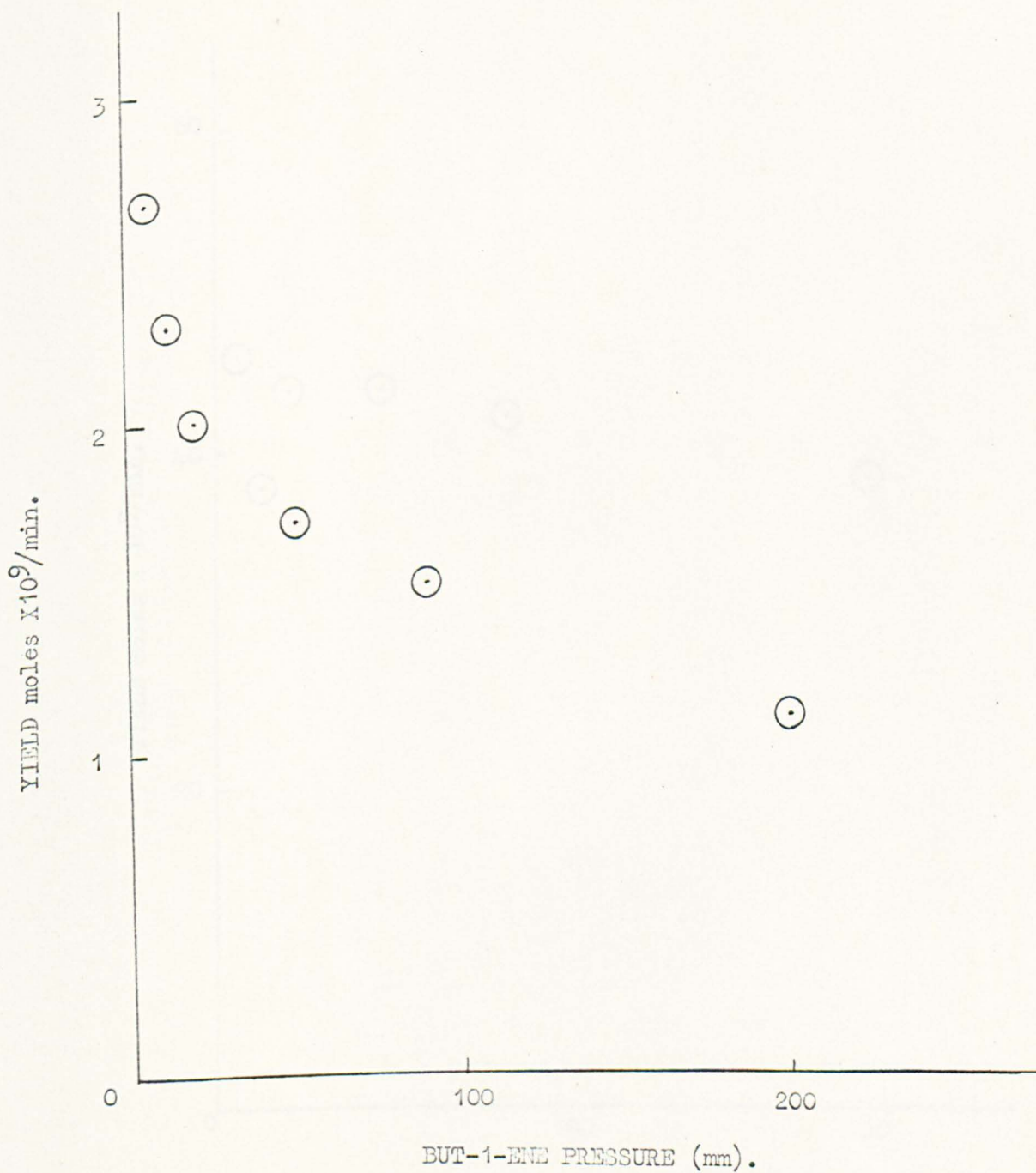YIELD moles/min X 10^9

But-1-ene pressure (mm).

Figure 3.31

Variation of ethylene yield with reactant
pressure.

Figure 3.32   Variation of ethane yield with reactant pressure.

Figure 5.33

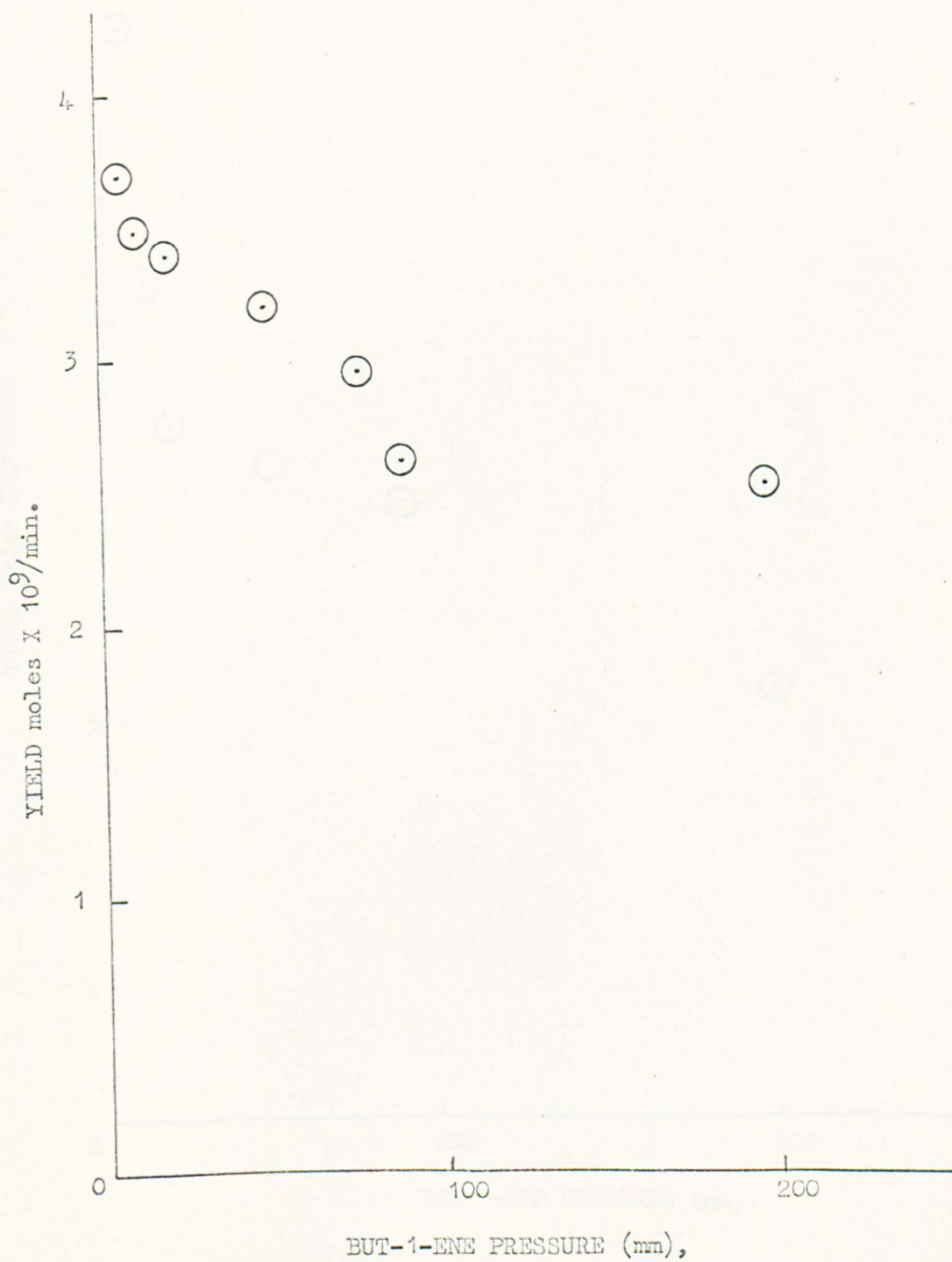Variation of acetylene yield with reactant pressure.

YIELD moles X 10^9/min.

BUT-1-ENE PRESSURE (mm),

Figure 3.34 Variation of C_3H_4 yield with reactant pressure.
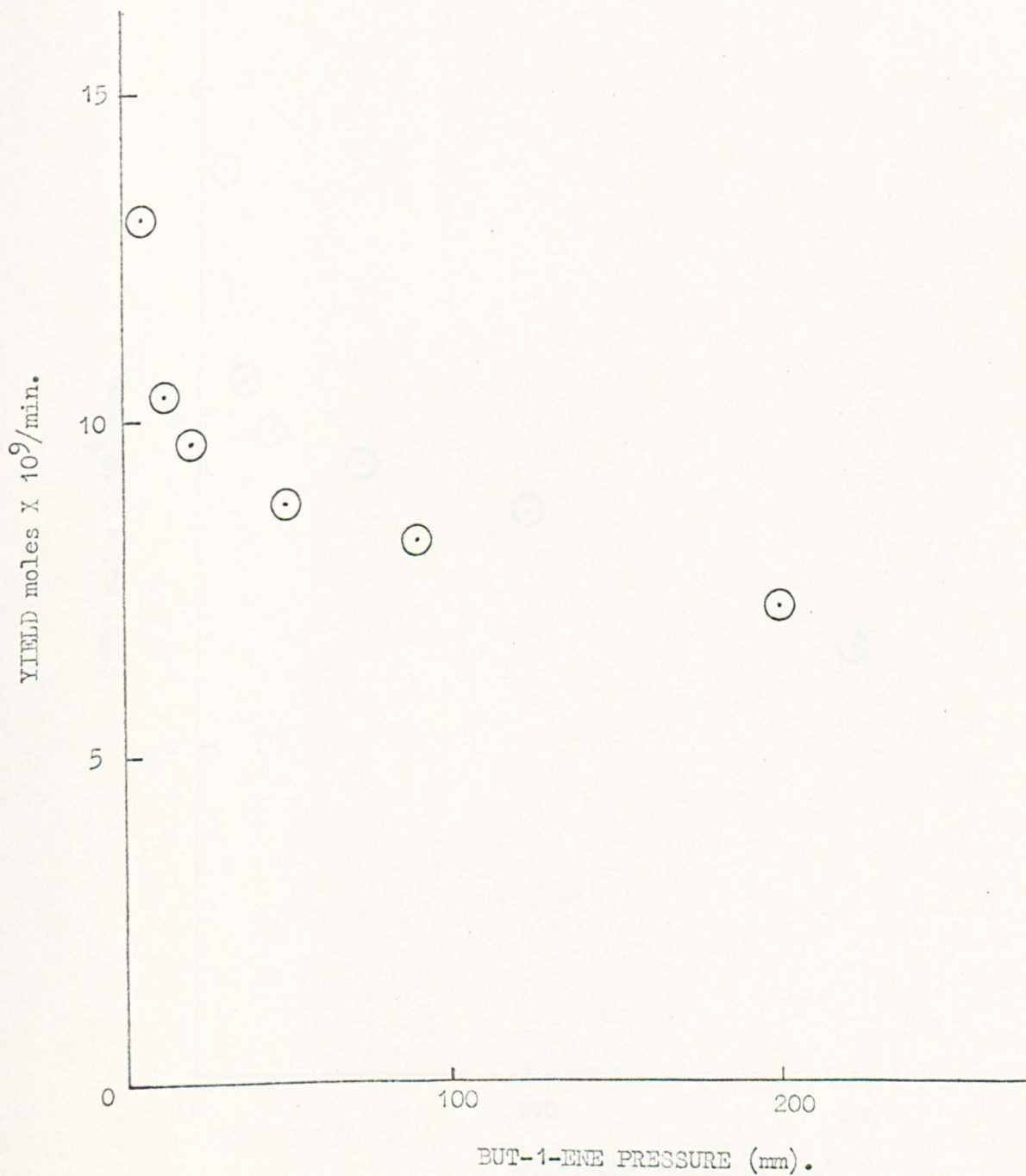
YIELD moles $X10^9$/min.

BUT-1-ENE PRESSURE (mm).

Figure 3.35

Variation of _isopentane_ yield with reactant pressure.

Figure 3.36

Variation of n-pentane yield with reactant pressure.
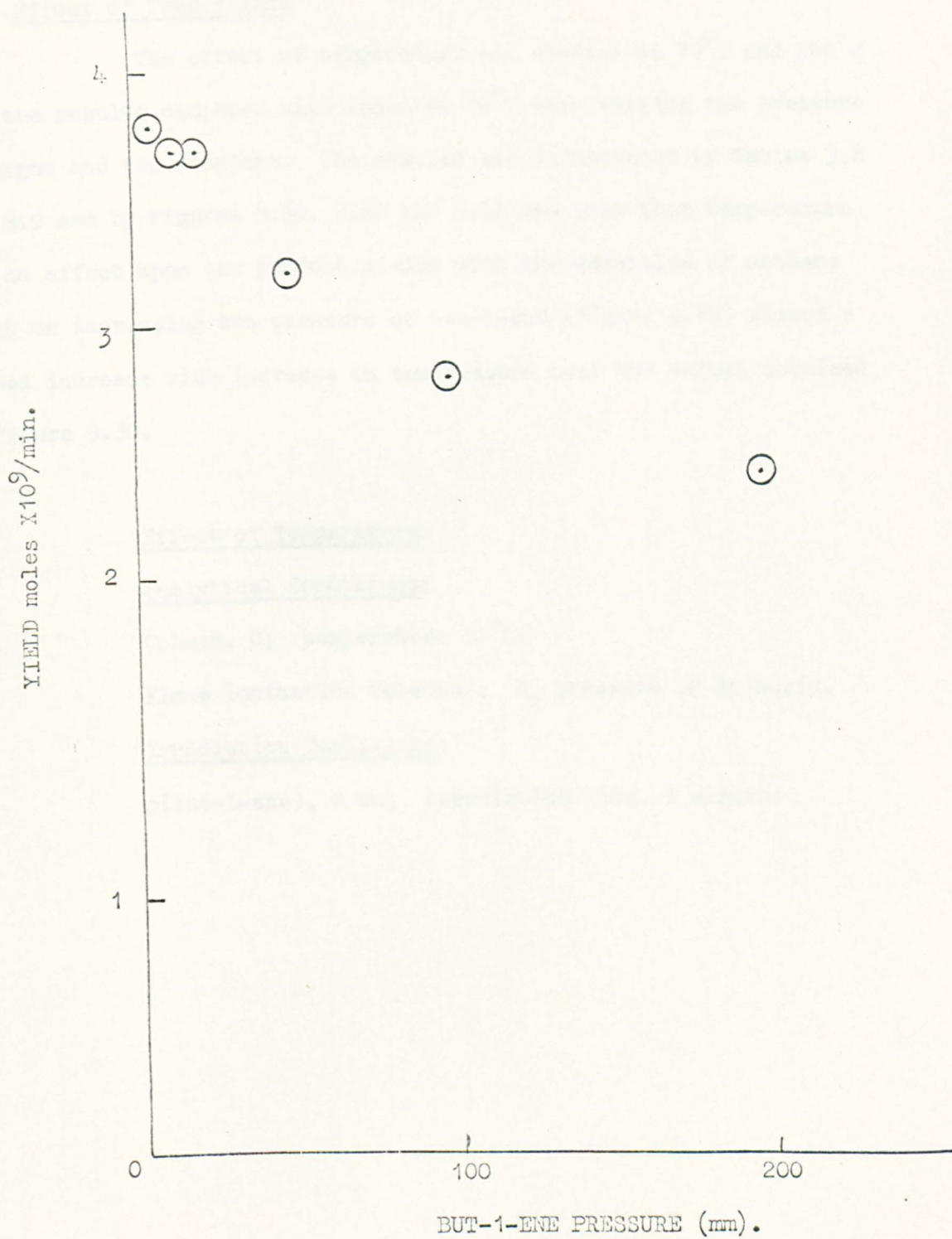
YIELD moles X 10^9/min.

BUT-1-ENE PRESSURE (mm).

Figure 3.37

Variation of trans pent-2-ene yield with reactant pressure.

Figure 3.38

Variation of cis pent-2-ene yield with reactant pressure.

YIELD moles X10^9/min.

BUT-1-ENE PRESSURE (mm).

3.4 Effect of Temperature

The effect of temperature was studied at 70°C and 140°C and the results compared with those at 20°C when varying the pressure of argon and the reactant. The results are illustrated by Tables 3.8 and 3.9 and by Figures 3.39, 3.40 and 3.41 and show that temperature had no effect upon the product yields with the exception of methane which on increasing the pressure of but-1-ene (Figure 3.40) showed a marked increase with increase in temperature over the values obtained in Figure 3.30.

Effect of Temperature

Analytical Conditions:

Column, 0; temperature 35°C;

Flame ionisation detector; N_2 pressure 12 lb/sq.in.

Irradiation Conditions:

p(but-1-ene), 6 mm; irradiation time, 5 minutes

Table 3.8

Effect of Argon on Product Yields as a Function of Temperature

$$(\text{Moles} \times 10^9/\text{min})$$

Pressure mm	Temp. °C	CH_4	C_2H_4	*C_2H_6 C_2H_2	*C_3H_2 C_3H_8	C_3H_4	c-b-2	3Me butene	iso-pentane	n-pentane	t-p-2	c-p-2
0	140	12.6	26.7	44	13.4	8.2	3.8	4.6	13.1	5.5	5.4	4.0
	70	12.6	26.6	44	13.4	8.2	3.8	4.6	13.2	5.3	5.3	4.1
	20	12.6	26.7	44	13.4	8.1	3.8	4.6	13.2	5.4	5.3	4.1
25	140	12.0	25.1	40	11.5	6.0	3.5	4.1	11.5	4.2	4.3	3.5
	70	12.0	25.0	40	11.4	6.0	3.5	4.0	11.4	4.2	4.1	3.6
	20	12.0	25.0	40	11.4	6.0	3.5	4.1	11.5	4.2	4.2	3.5
100	140	8.7	16.0	34	9.1	4.9	3.2	3.8	10.8	3.7	3.7	3.2
	70	8.6	16.0	33	9.1	5.0	3.3	3.8	10.6	3.6	3.7	3.2
	20	8.5	16.0	33	9.1	5.0	3.2	3.8	10.7	3.6	3.7	3.2
200	140	8.2	9.6	20	5.4	3.3	2.9	2.9	9.2	2.4	2.6	2.7
	70	8.2	9.6	21	5.4	3.3	2.9	2.9	9.5	2.4	2.5	2.3
	20	8.2	9.6	21	5.4	3.3	2.9	2.9	9.4	2.3	2.6	2.5
300	140	8.2	9.3	19	4.8	2.0	2.8	2.9	9.2	2.4	2.4	2.1
	70	8.2	9.2	19	4.9	2.0	2.9	2.9	9.0	2.4	2.3	2.3
	20	8.2	9.2	19	4.9	2.0	2.8	2.9	9.1	2.4	2.3	2.2

* Expressed as peak heights.

Table 3.9

Effect of Reactant Pressure on the Product Yields as a Function of Temperature

(Moles x 10^9 per minute)

Pressure mm	Temperature $^\circ$C	CH_4	C_2H_4	*C_2H_6 C_2H_2	iso-pentane	n-pentane	t-p-2	c-p-2
6	20	12.0	26.7	50.2	13.1	5.5	5.4	3.8
	70	12.0	26.7	50.2	13.1	5.3	5.4	3.8
	140	12.4	26.6	50.6	13.1	5.5	5.5	4.0
12	20	-	23	38.0	10.4	4.2	5.1	3.7
	70	11.5	23	38.0	10.6	4.2	5.0	3.7
	140	12.0	22	38.0	10.5	4.3	5.0	3.6
18	20	11.0	20	42.0	9.6	3.9	4.9	3.7
	70	12.1	21	42.0	9.7	3.9	4.9	3.7
	140	15.0	21	47.0	9.6	3.9	4.8	3.8
100	20	13.0	17	44.6	8.7	3.7	4.7	3.2
	70	30.0	14.7	44.0	8.7	3.6	4.1	2.8
	140	60.0	14.5	44.0	8.7	3.6	3.9	2.8
170	20	24.0	15	39.0	8.1	3.4	3.6	2.1
	70	40.0	12.1	38.0	8.2	2.6	3.7	2.3
	140	63.0	12.1	39.0	8.2	2.6	3.7	2.5

* Yields quoted as peak heights.

Figure 3.39

Yield of METHANE versus pressure of argon as a
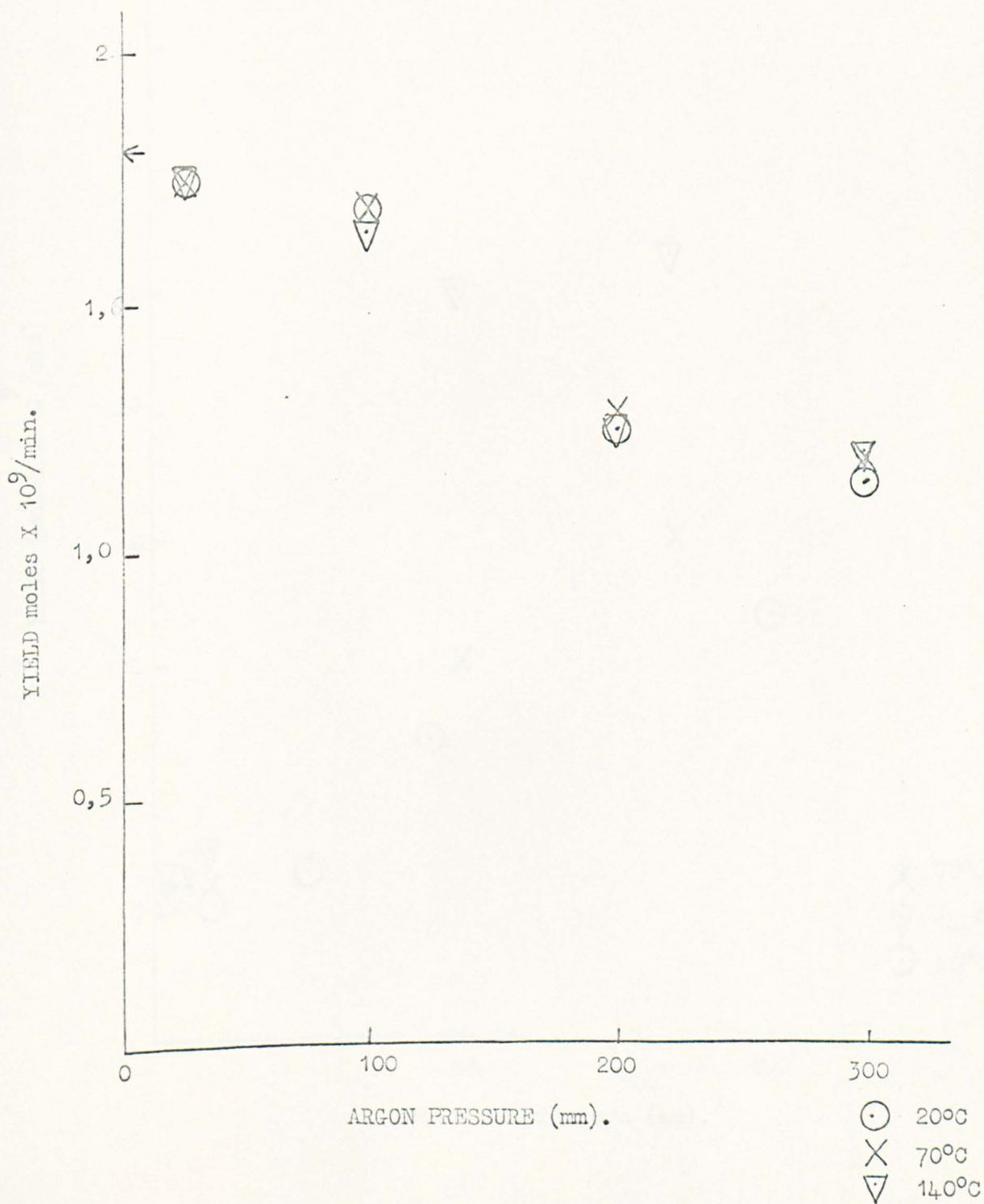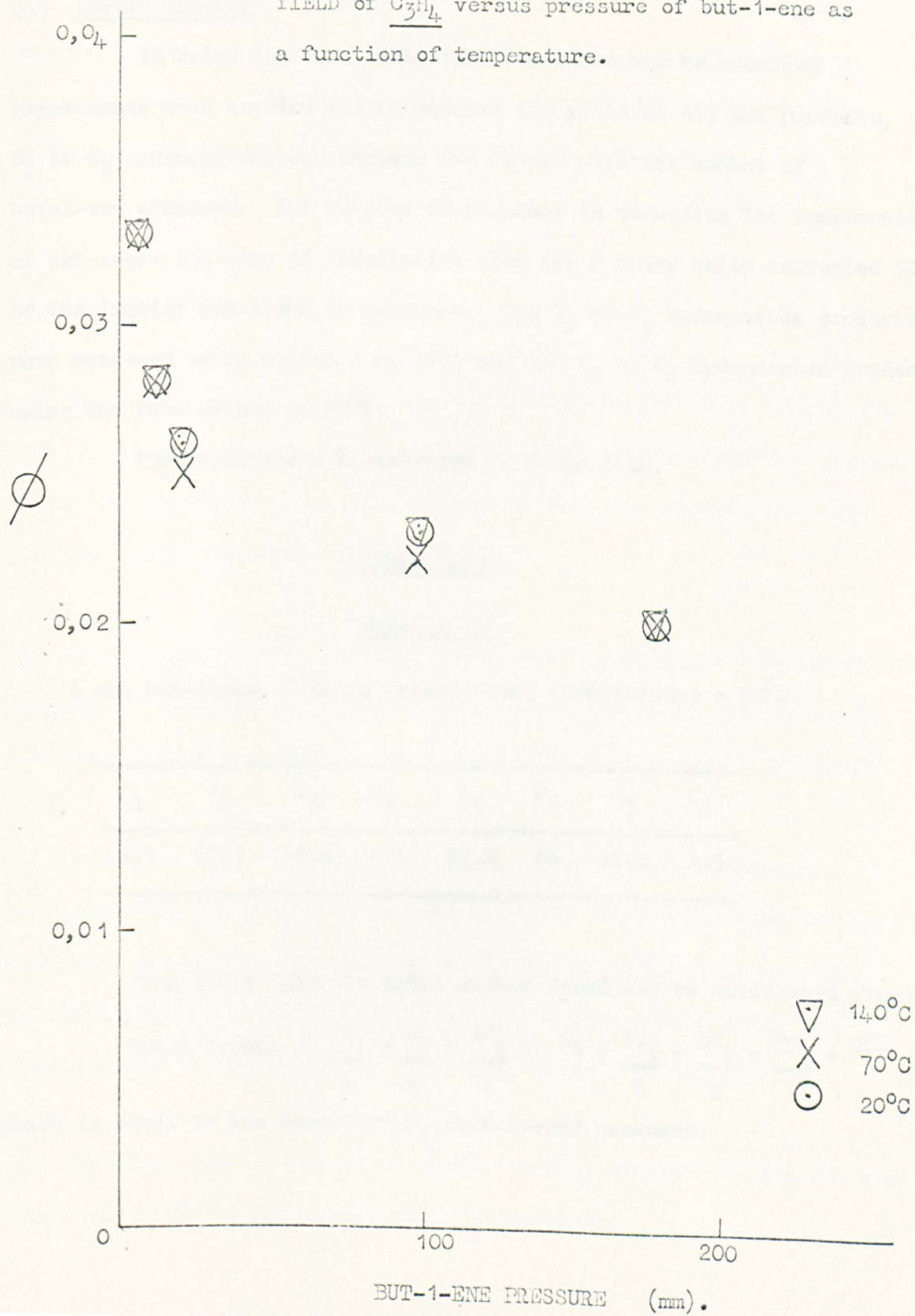function of temperature.

Figure 3.40

Variation of methane yield with reactant pressure as a function of temperature.

Figure 3.41

YIELD of C_3H_4 versus pressure of but-1-ene as a function of temperature.

∇ 140°C
✕ 70°C
⊙ 20°C

BUT-1-ENE PRESSURE (mm).

3.5 Carbon Balance

In order that the analytical technique may be examined experiments were carried out to measure the yield of all the products, C_1 to C_8 hydrocarbons, and compare the result with the amount of but-1-ene consumed. For reasons of accuracy in measuring the consumption of but-1-ene the time of irradiation used was 2 hours which converted 50% of the initial but-1-ene to products. The C_1 to C_5 hydrocarbon products were measured using column O at 35°C and the C_6 to C_8 hydrocarbon products using the same column at 80°C.

The results are illustrated in Table 3.10.

Table 3.10

Moles x 10^7

6 mm. but-1-ene, 2 hours irradiation; temperature = 20°C

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
6.5	87.7	13.3	2.1	17.2	64	17.1	4.5

From Table 3.10 the total carbon found may be calculated from:

$$\text{Total butene} = \frac{C_1}{4} + \frac{C_2}{2} + \frac{3C_3}{4} + C_4 + \frac{5C_5}{4} + \frac{3C_6}{2} + \frac{7C_7}{4} + 2C_8$$

which is equal to the amount of C_4 (but-1-ene) consumed.

It was calculated that 270×10^{-7} moles of but-1-ene were used and from Table 3.10 the accumulated products accounted for 212×10^{-7} moles but-1-ene. Taking into account the polymer formed in a long run, the two figures show a good product recovery.

3.6 Summary of But-1-ene Results

(1) The yields of the products increased linearly with the irradiation time until about 20 mins, after which time the rate of formation decreased due to the formation of a solid polymer on the cell window which cut down the amount of light entering the cell.

(2) The majority of the product yields were decreased on increasing the pressure of the reactant except methane which showed an increase with increased but-1-ene pressure, and ethane which was virtually unchanged.

(3) Oxygen reduced the yields of all the products and completely eliminated the C_5 hydrocarbons. The yields of CH_4, C_2H_4, C_3H_4 and C_2H_2 were only affected to the same extent by oxygen as by nitrogen. The yields of ethane and propylene and the but-2-enes are affected to a greater extent by oxygen, but are not completely eliminated.

(4) The inert gases argon, nitrogen and carbon dioxide reduced the yields of all the products with increasing gas pressure.

(5) Temperature had little effect on the product yields with the exception of methane and in runs where the pressure of but-1-ene was increased the results showed an increase at 70° and $140^{\circ}C$ over those at $20^{\circ}C$.

4. RESULTS: Isobutene

Experiments were performed as in Section 3 to establish if any sensitisation was taking place and these experiments proved negative.

On irradiating isobutene with light of 1849 $\overset{o}{A}$ hydrogen, thirty-one hydrocarbons and a solid polymer were found. The gaseous products were analysed by gas chromatography as in Section 3.

Steady state experiments were conducted to determine the effects of:

1. Irradiation time

2. Isobutene pressure

3. Added gases

In subsections 2 and 3 the irradiation time was generally 5 minutes which gave rise to about 2% decomposition of the isobutene present. The isobutene contained propylene, propane and a small amount of isobutane as impurities therefore at high reactant pressures the yields of these products were obscured. Difficulties were also experienced in measuring the product yields which were eluted from the column immediately after the isobutene due to tailing of the isobutene peak.

Table 4.1

Product Yields from the Photolysis of Isobutene

Irradiation Conditions:

Time of irradiation, 5 mins; p(isobutene), 6 mm;
temperature, $20^{\circ} \pm 2^{\circ}C$

Moles x 10^{8}

H_2	0.12	isobutane	16.65	Cis pent-2-ene	0.08
CH_4	12.50	Cis but-2-ene	trace	pent-1-ene	0.31
C_2H_4	0.40	Trans but-2-ene	6.25	(C_6)	3.75
C_2H_6	7.75	3-Me-butene	trace	(C_7)	13.75
C_2H_2	3.35	isopentane	trace	(C_8)	2.5
C_3H_6	6.00	2-Me-butene	21.15		
C_3H_4	9.20	Trans pent-2-ene	0.16		

(C_6), (C_7) and (C_8) represent total approximate values for several peaks.

Analytical Conditions:

Column, O; flame ionisation detector;

N_2 pressure, 12 lb/sq.in; temperature 35°C.

4.1 Effect of Irradiation Time

On increasing the irradiation time the yields of the products increased linearly up to about 25 minutes and then the rate fell off, due again to the formation of a solid polymer on the cell window after long irradiation times. The results for the C_1 to C_5 hydrocarbon products are shown in Table 4.2 and illustrated by Figures 4.1 to 4.12.

Irradiation Conditions:

p(isobutene), 6 mm; temperature, $20^{\circ} \pm 2^{\circ}C$.

Analytical Conditions:

Column, 0; temperature, $35^{\circ}C$;

N_2 pressure 12 lb/sq.in.; flame ionisation detector.

Table 4.2

Effect of Irradiation Time on the Product Yields

(Moles x 10^8)

| Time mins	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_4	iso-butane	t-b-2	c-b-2	3Me-butene	iso-pentane	2Me-butene	t-p-2	c-p-2
1	3.6	0.13	2.2	1.0	2.2	1.8	4.8	0.91	trace	–	trace	6.5	trace	trace
3	11.6	0.2	6.3	3.2	5.9	5.3	13.8	–	"	0.1	"	19.2	0.2	"
5	16.7	0.4	9.6	4.7	8.3	8.2	20.5	4.2	"	0.1	"	27.5	0.6	0.4
7	22.5	0.6	13.5	6.6	11.5	11.4	30.3	4.4	"	–	"	40.6	–	0.6
11	39.3	1.6	20.9	11.0	18.1	18.9	44.2	12.1	"	2.1	"	86.5	0.7	0.8
20	78.9	3.9	36.3	18.0	33.1	35.6	82.0	33.5	"	–	"	108	1.2	1.4
30	91.2	4.0	52.8	26.1	39.5	43.5	105.7	43.7	10.5	2.7	1.5	155	2.0	2.1
60	153.5	10.2	90.7	42.9	65.7	80.7	168.0	58.2	15.8	3.5	2.5	225	2.8	3.9
120	258.1	10.2	171.5	84.9	95.4	87.5	257.0	106.0	23.4	8.0	8.2	269	–	–

Figure 4.1

Variation of methane yield with irradiation time.

Figure 4.2   Variation of ethylene yield with irradiation time.
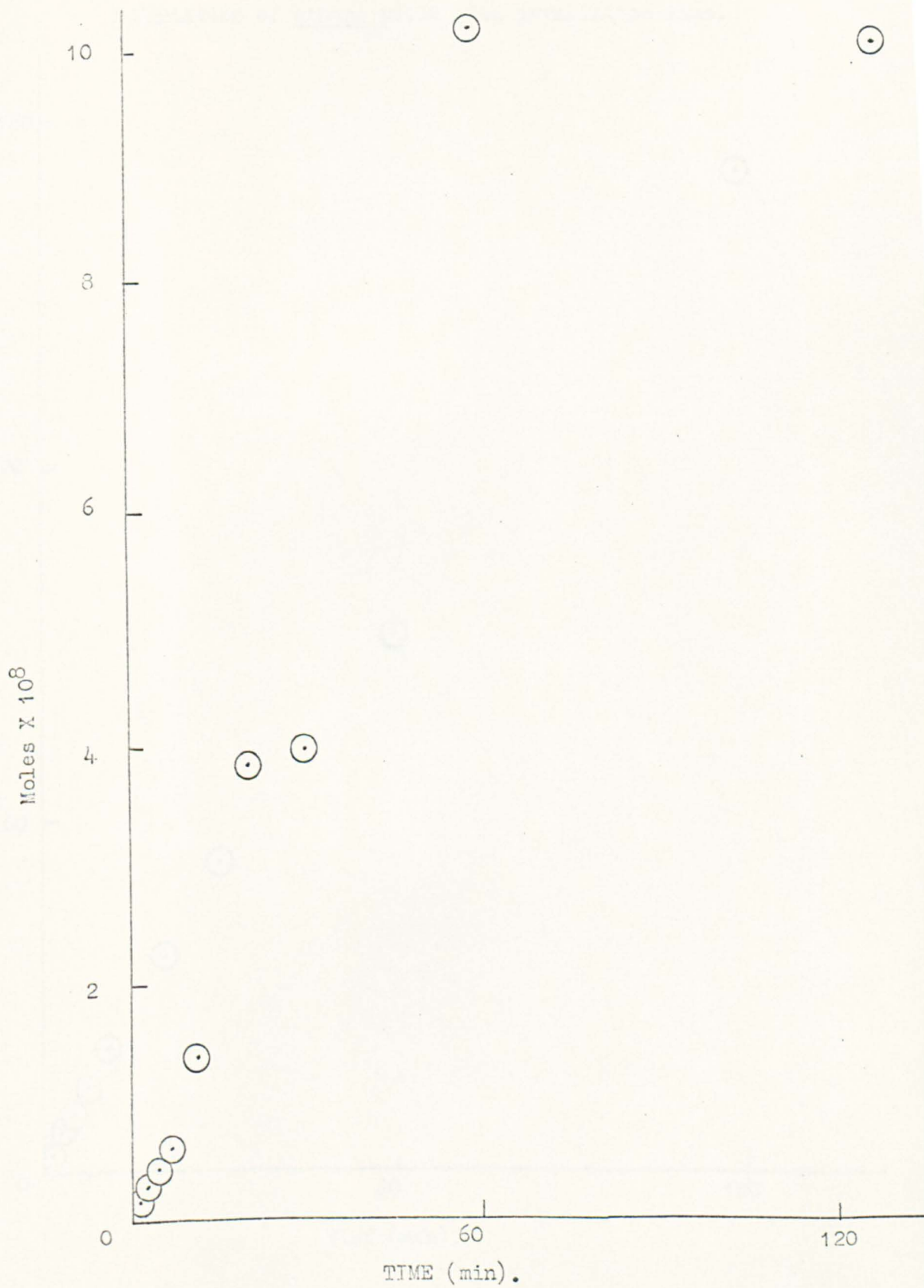
Figure 4.3

Variation of ethane yield with irradiation time.
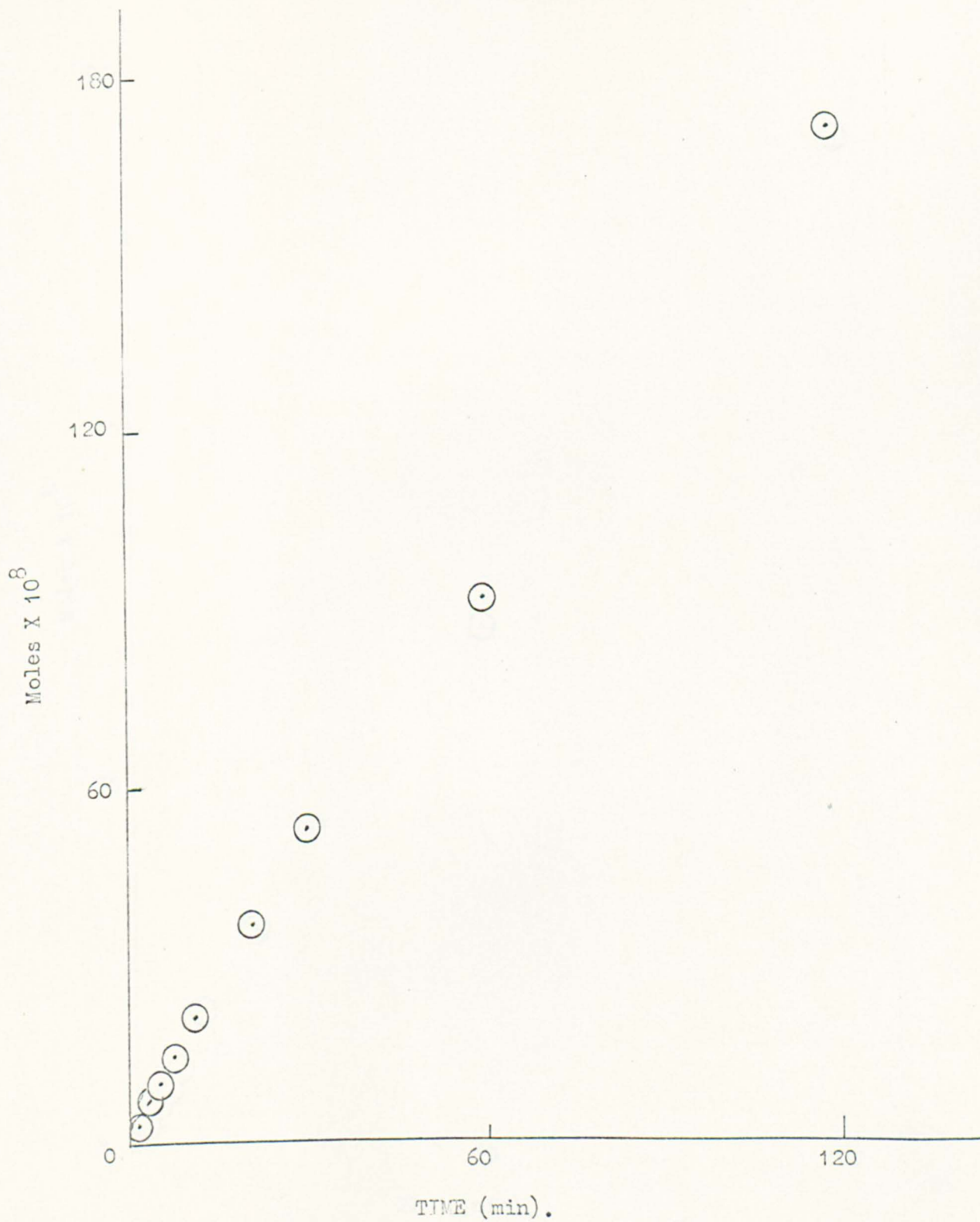
Figure 4.4

Variation of acetylene yield with irradiation time.

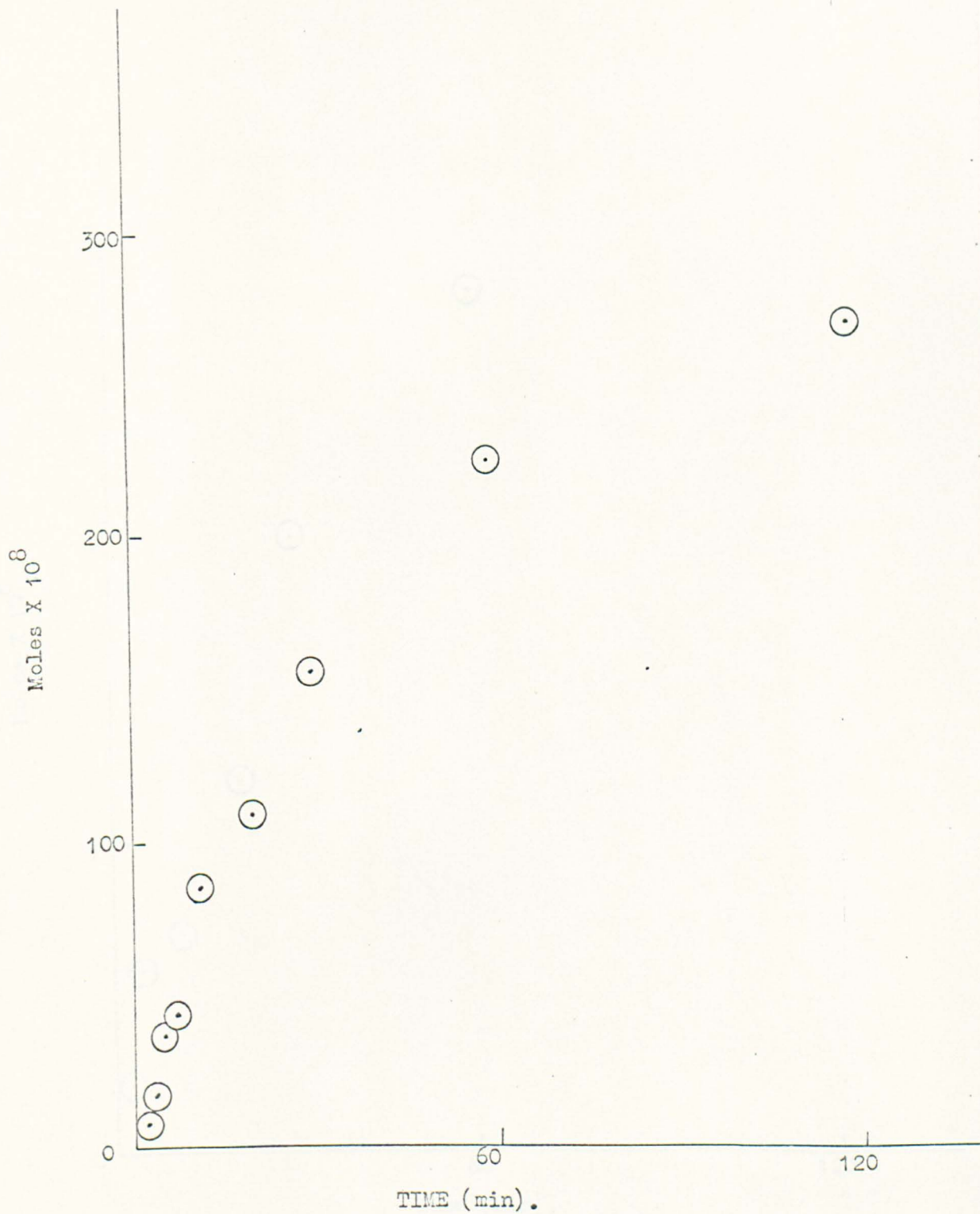Figure 4.5
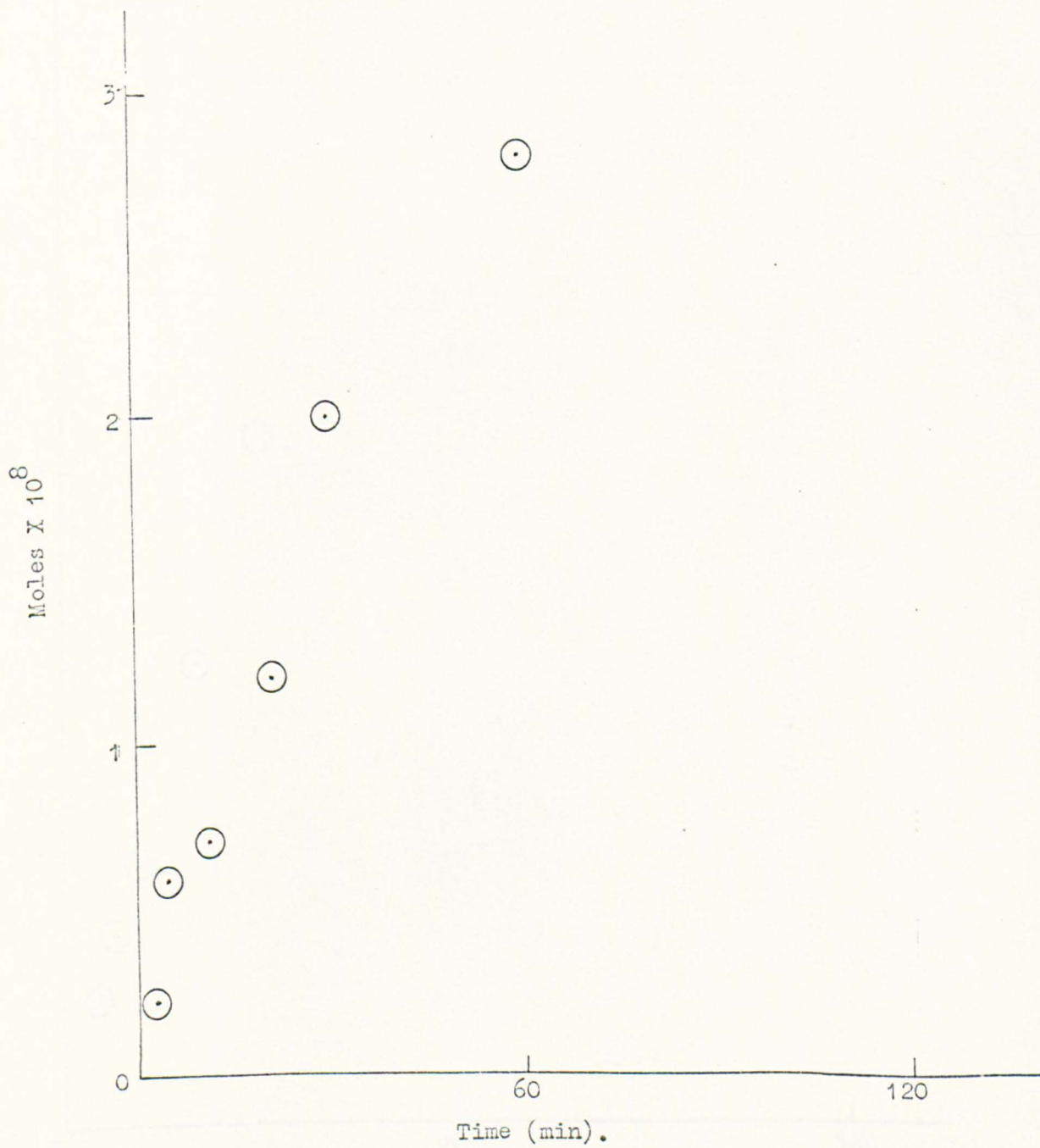
Variation of propylene yield with irradiation time.

Figure 4.6

Variation of *allene* yield with irradiation time.

Figure 4.7

Variation of isobutane yield with irradiation time.
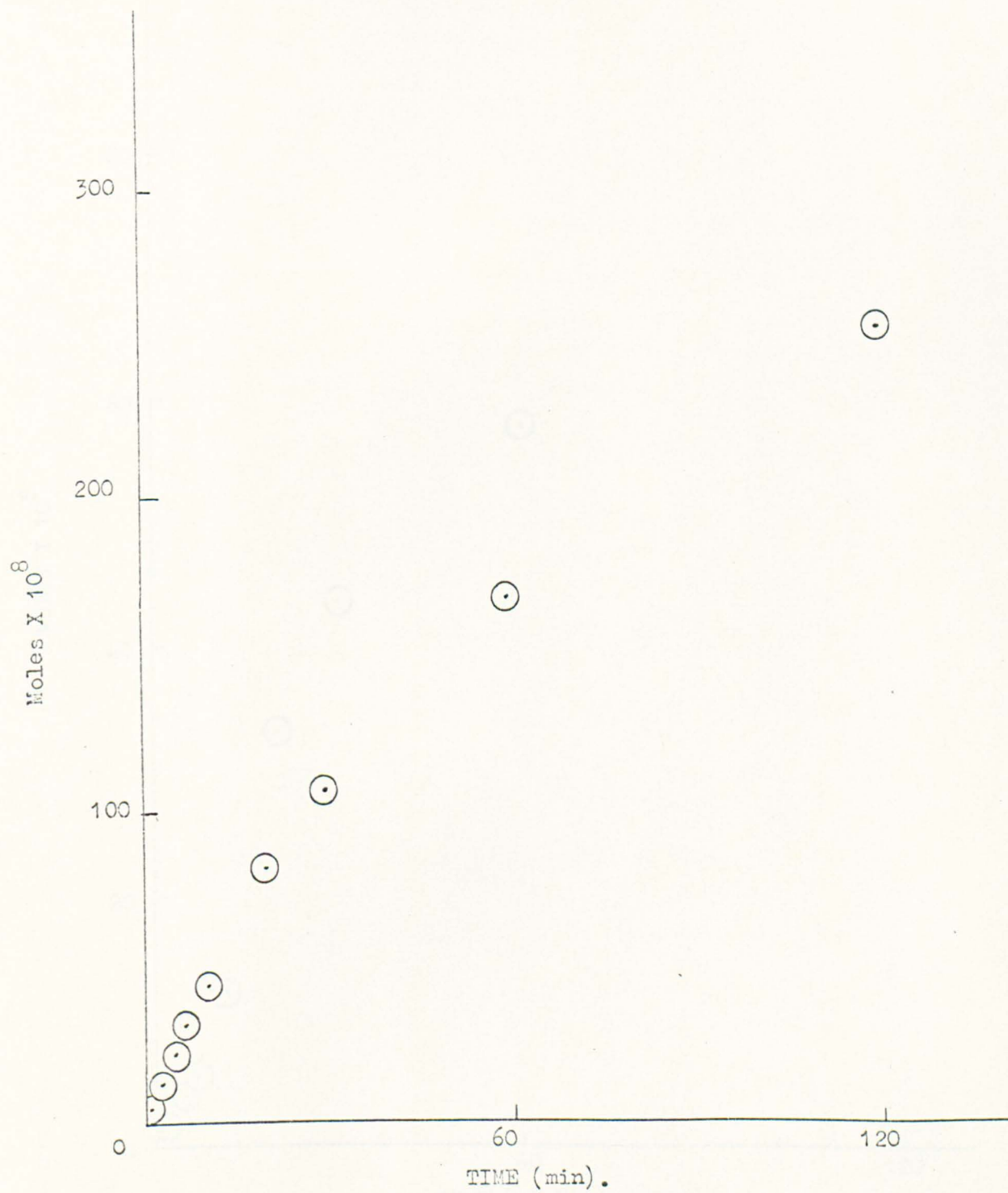
Figure 4.8

Variation of trans but-2-ene yield with irradiation time.
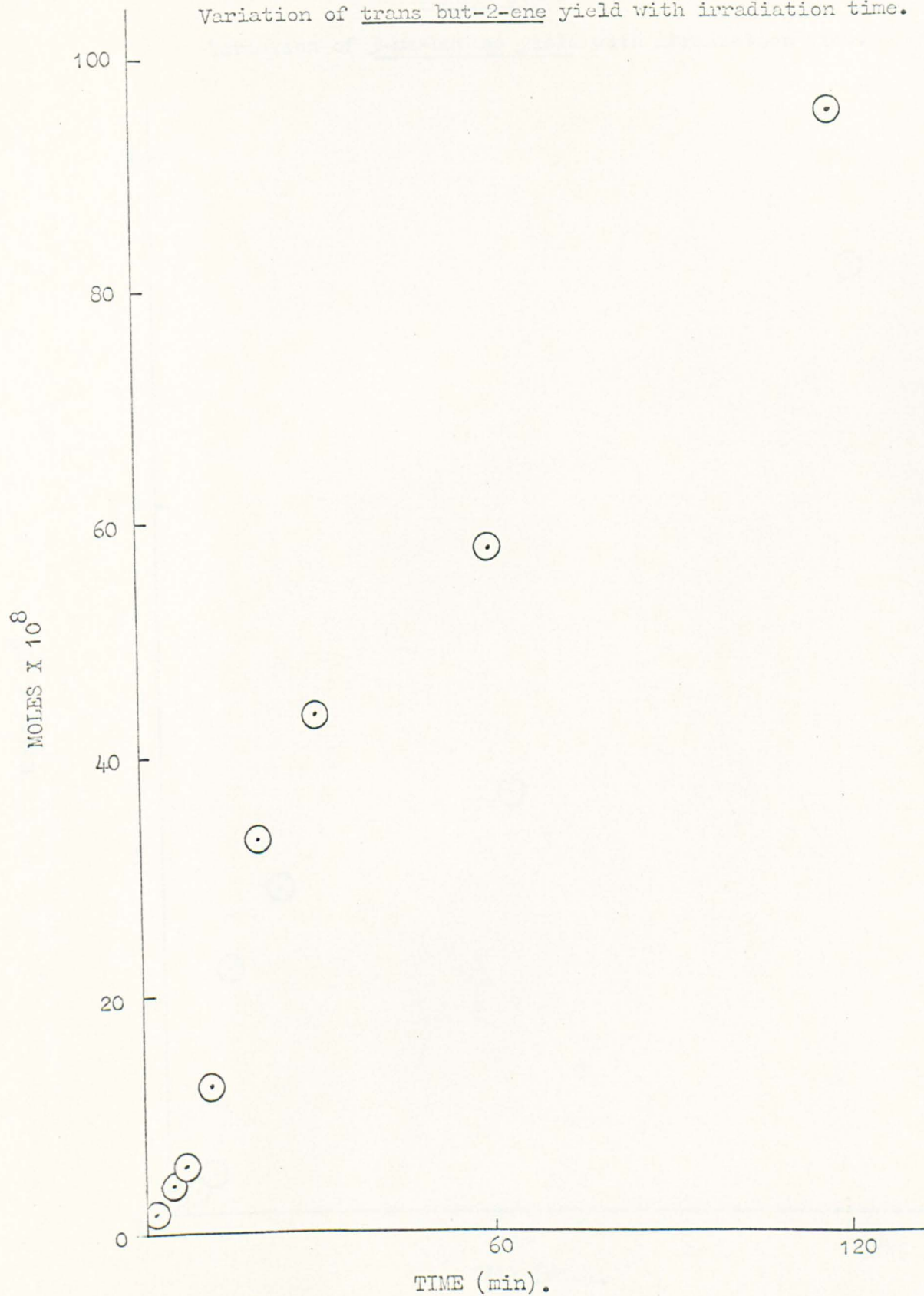
Figure 4.9

Variation of 3-me-butene yield with irradiation time.

Figure 4.10

Variation of 2-me-butene yield with irradiation time.

Figure 4.11

Variation of trans pent-2-ene yield with irradiation time.

Figure 4.12

Variation of cis pent-2-ene yield with irradiation time.

Moles X 10^8

Time (min).
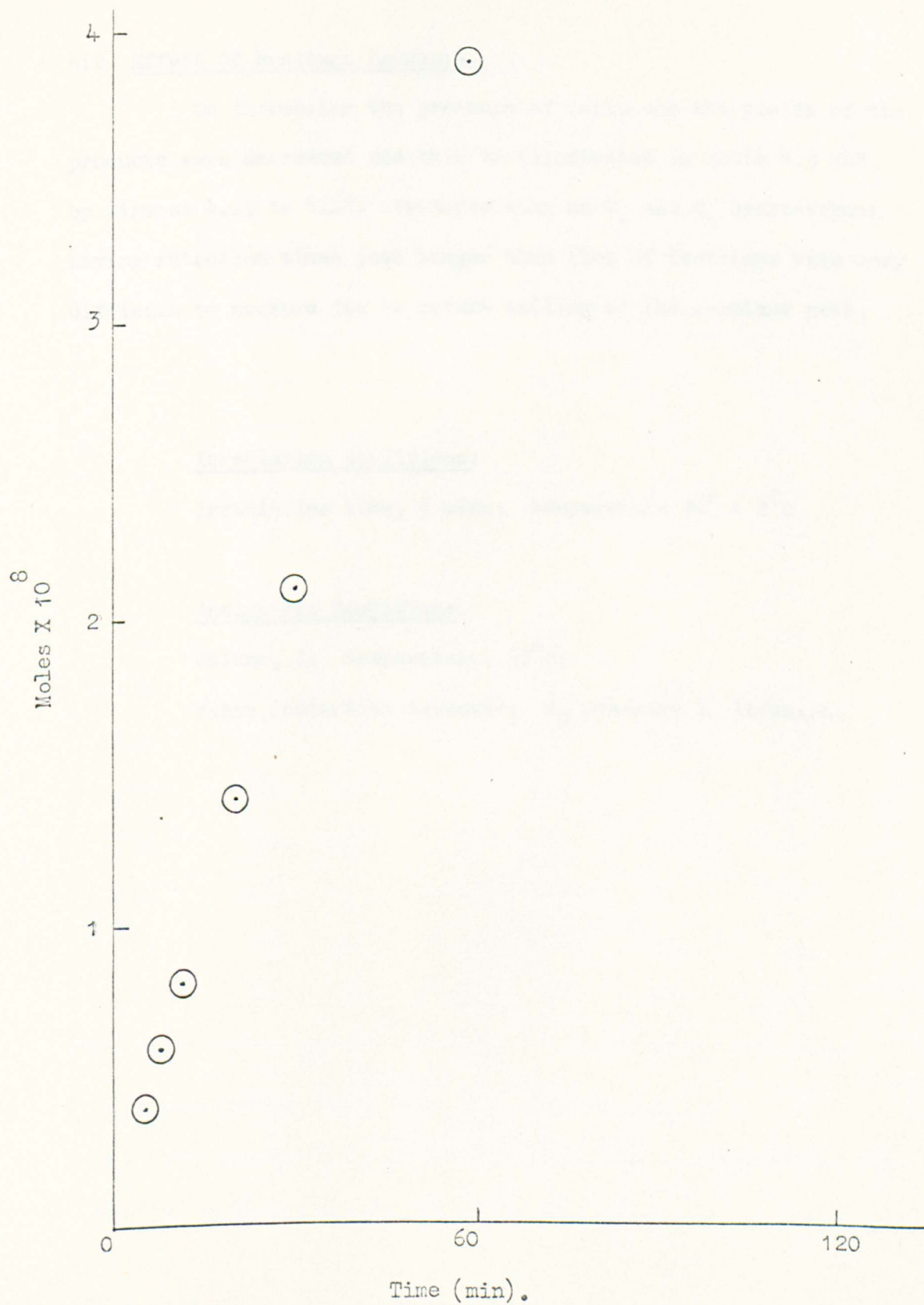
4.2 Effect of Reactant Pressure

On increasing the pressure of isobutene the yields of the products were decreased and this is illustrated in Table 4.3 and by Figures 4.13 to 4.17. Products such as C_4 and C_5 hydrocarbons having retention times just longer than that of isobutene were very difficult to measure due to severe tailing of the reactant peak.

Irradiation Conditions:

Irradiation time, 5 mins; temperature $20^{\circ} \pm 2^{\circ}C$

Analytical Conditions:

Column, 0; temperature, $35^{\circ}C$;

flame ionisation detector; N_2 pressure 12 lb/sq.in.

Table 4.3

Effect of Isobutene Pressure

(Moles x 10^8 per minute)

Pressure mm	CH_4	C_2H_6	C_2H_2	C_3H_4	*iso- butane	2Me- butene
2	1.9	1.3	0.5	1.4	1.8	2.8
4	2.1	1.3	0.6	1.6	2.5	2.9
6	2.0	1.6	0.7	1.8	3.3	4.2
10	2.4	1.4	0.8	1.6	3.4	4.5
15	2.4	1.4	0.5	1.4	3.4	4.5
20	2.1	1.3	0.6	1.1	2.7	2.9
50	1.4	0.8	0.4	0.5	1.8	2.8
100	1.8	1.0	0.5	0.2	2.3	2.3
120	1.7	0.8	0.4	0.3	-	2.9
200	1.1	0.6	0.3	0.1	1.8	1.7
220	1.4	0.7	0.4	0.2	-	2.0
280	1.2	0.6	0.3	0.2	-	1.5
380	0.3	0.3	0.1	0.1	1.7	0.9

* Isobutane was an impurity in the starting material.

The remaining products are not tabulated due to 'tailing' of the

reactant peak and the levels of impurity.

Figure 4.13

Variation of methane yield with reactant pressure
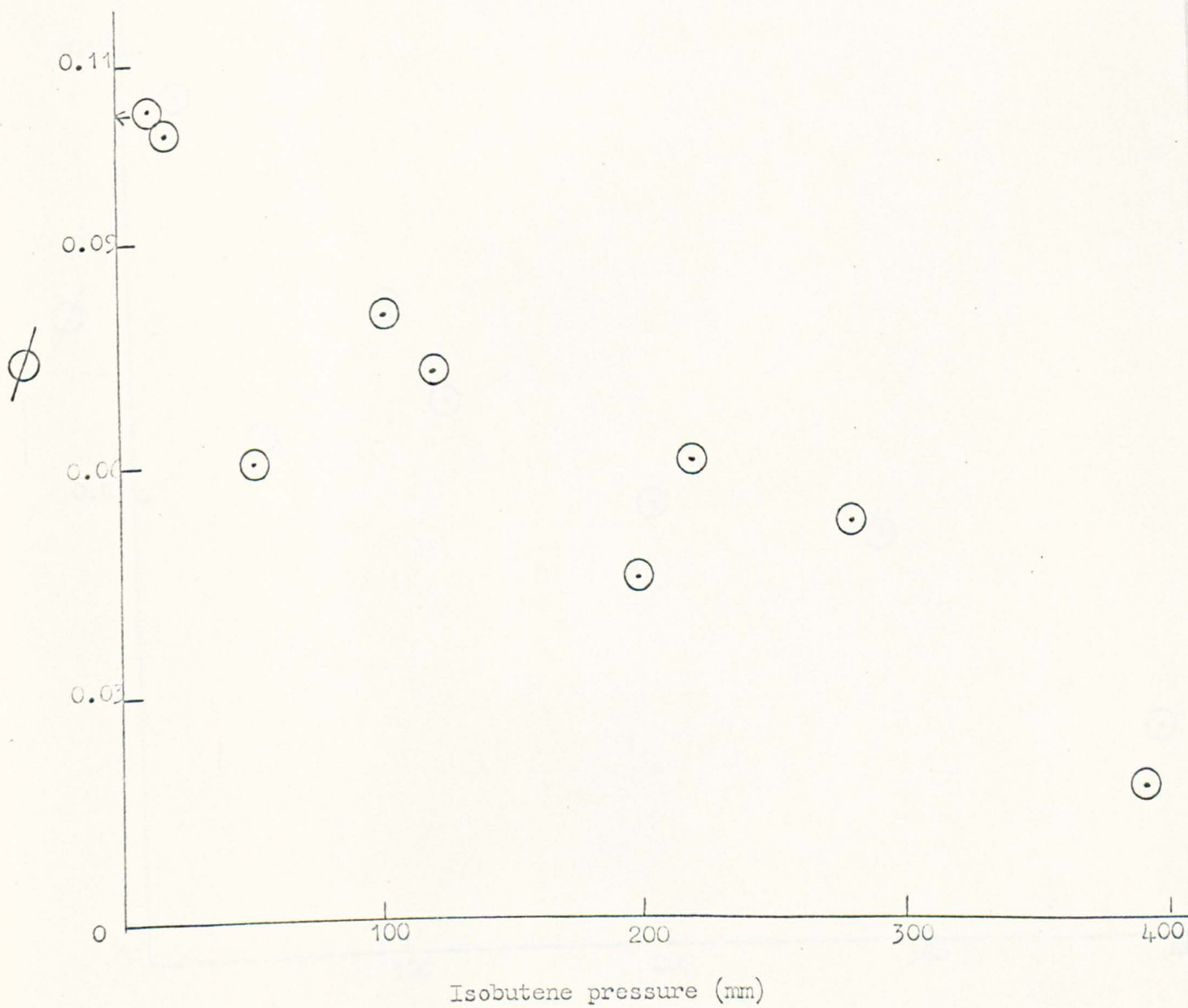
Figure 4.14

Variation of ethane yield with reactant pressure

Isobutene pressure (mm)
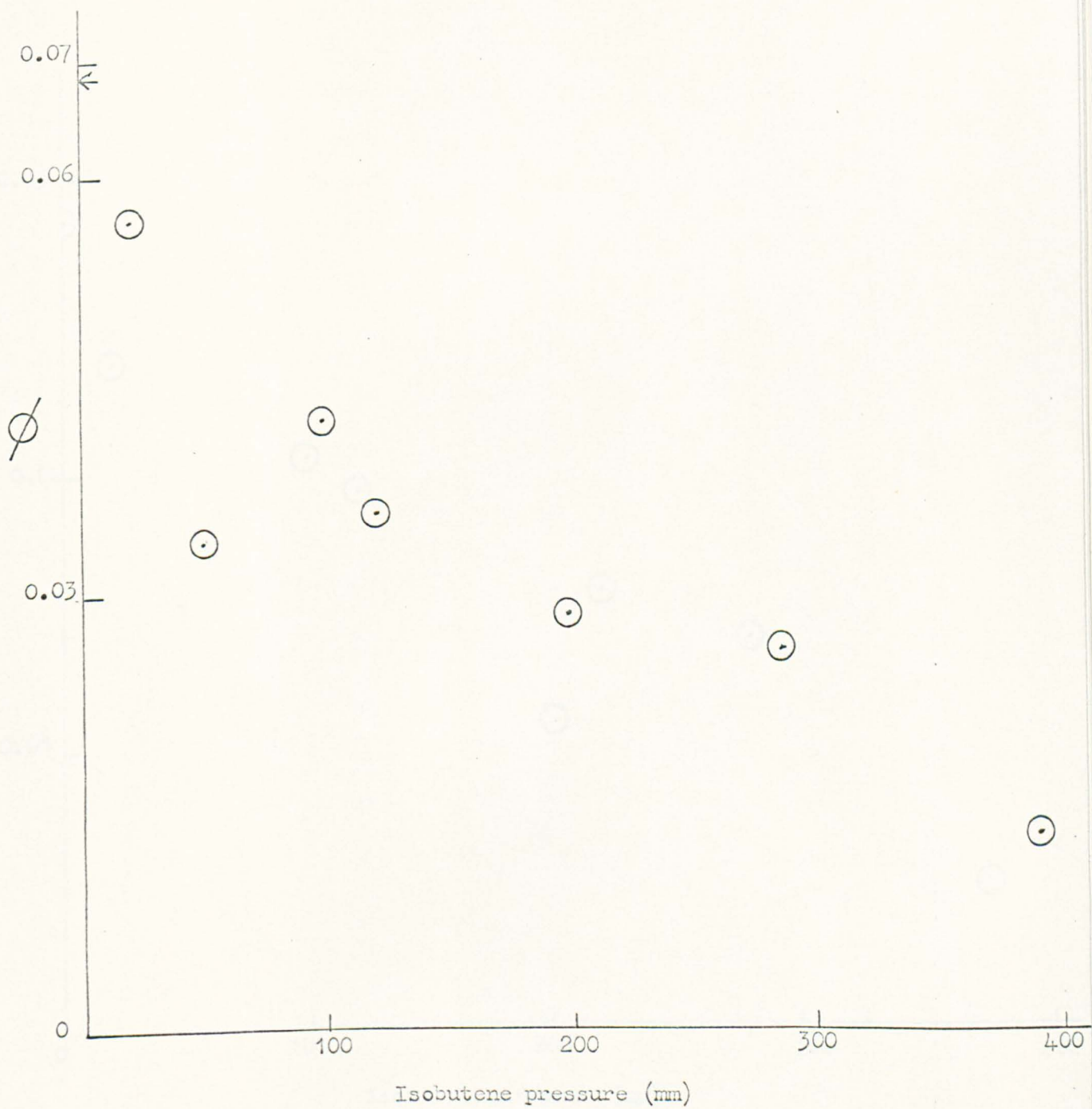
Figure 4.15

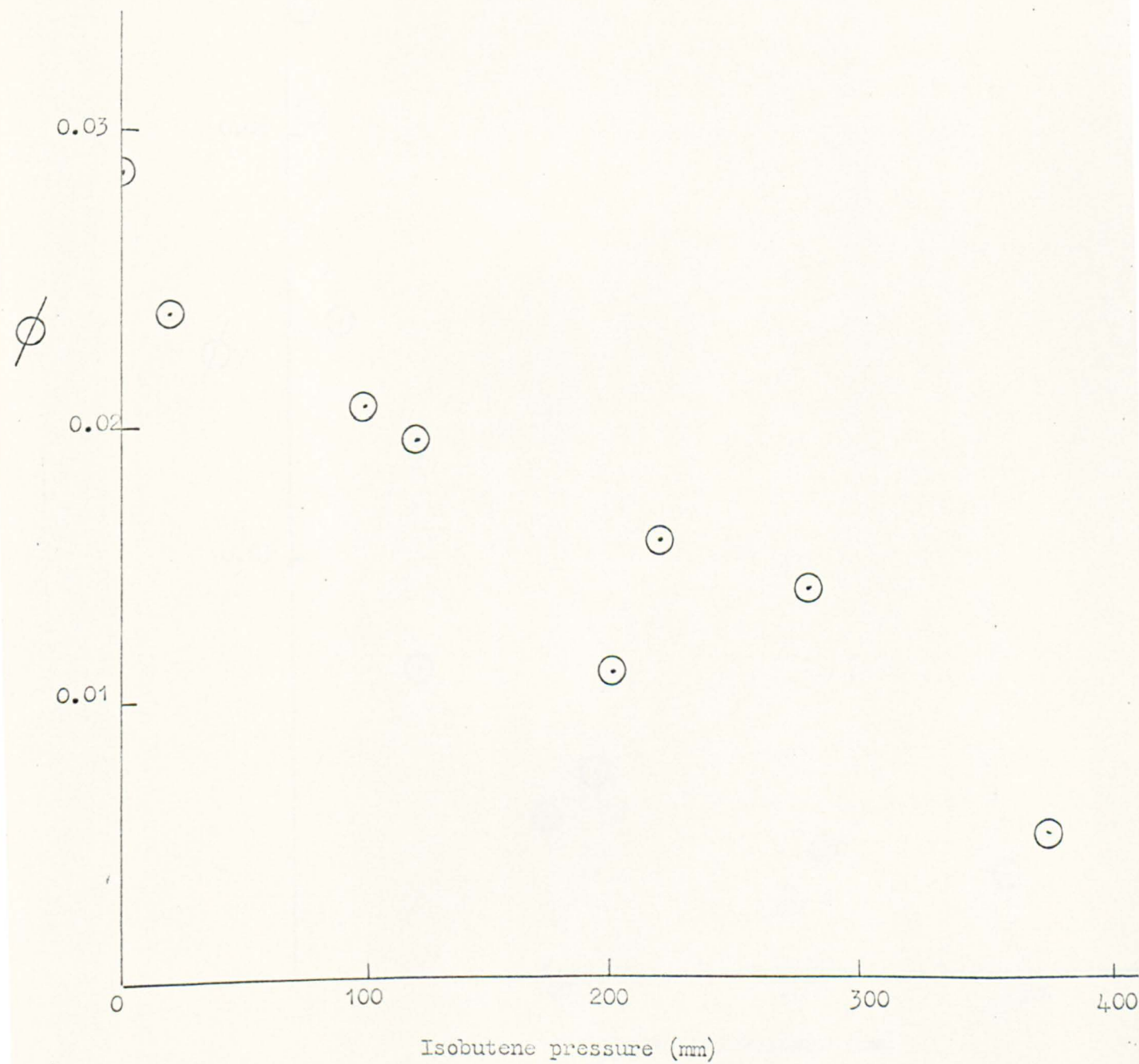Variation of acetylene yield with reactant pressure

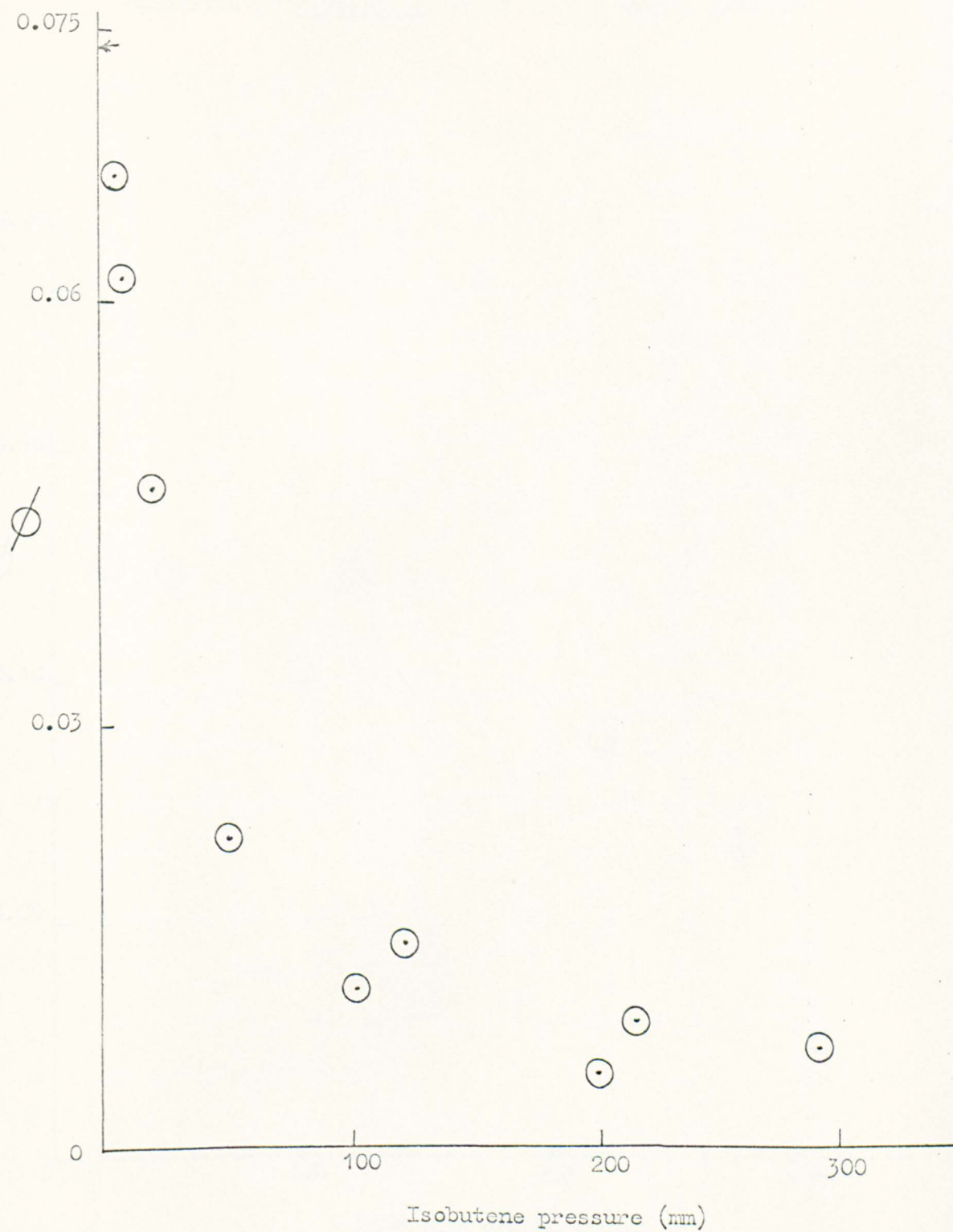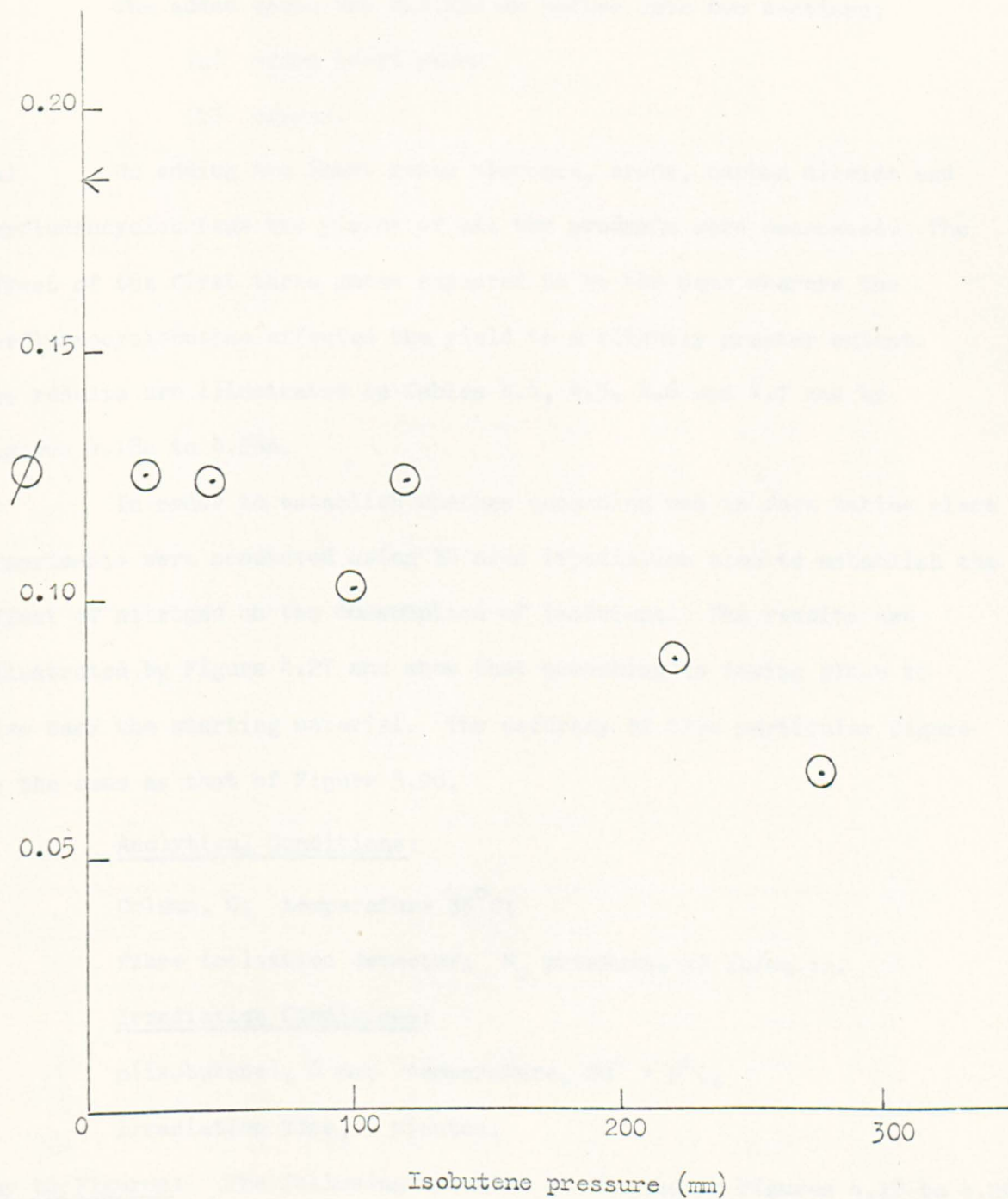Figure 4.16   Variation of allene yield with reactant pressure

Figure 4.17

Variation of 2-me-butene yield with reactant pressure

4.3 <u>Effect of Added Gases</u>

The added gases are divided as before into two sections;

(a) added inert gases

(b) oxygen.

(a) On adding the inert gases nitrogen, argon, carbon dioxide and perfluorocyclobutane the yields of all the products were decreased. The effect of the first three gases appeared to be the same whereas the perfluorocyclobutane affected the yield to a slightly greater extent. The results are illustrated in Tables 4.4, 4.5, 4.6 and 4.7 and by Figures 4.18a to 4.26a.

In order to establish whether quenching was in fact taking place experiments were conducted using 30 mins irradiation time to establish the effect of nitrogen on the consumption of isobutene. The results are illustrated by Figure 4.27 and show that quenching is taking place to give back the starting material. The accuracy of this particular figure is the same as that of Figure 3.28.

<u>Analytical Conditions</u>:

Column, O; temperature $35^{\circ}C$;

flame ionisation detector; N_2 pressure, 12 lb/sq.in.

<u>Irradiation Conditions</u>:

p(isobutene), 6 mm; temperature, $20^{\circ} \pm 2^{\circ}C$;

irradiation time, 5 minutes.

<u>Key to Figures</u>: The following notation is adopted in Figures 4.18 to 4.26:

⊙ Argon;   ✗ CO_2;   △ Oxygen;   ▽ Nitrogen;

● Perfluorocyclobutane.

Table 4.4

Argon

(Moles x 10^8 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_4	iso-butane	t-b-2	2Me butene
0	2.5	0.08	1.6	0.7	1.2	1.8	3.3	1.3	4.2
20	2.2	0.07	1.4	0.63	1.0	1.3	3.2	1.1	4.16
50	2.0	0.06	1.2	0.58	0.96	1.1	2.7	1.0	3.5
100	1.8	0.05	1.0	0.47	0.92	1.0	2.5	0.9	3.3
200	1.6	0.04	0.95	0.43	0.83	0.7	1.9	0.6	2.67
300	1.6	0.04	0.95	0.42	0.87	0.6	2.1	0.6	2.55
400	1.5	0.03	0.92	0.42	0.73	0.4	1.7	0.4	2.5

Table 4.5

Nitrogen

(Moles x 10^8 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_4	iso-butane	t-b-2	2Me butene
0	2.5	0.08	1.55	0.67	1.2	1.84	3.33	1.25	4.2
20	2.33	0.07	1.5	0.67	1.05	1.33	3.0	0.88	4.1
60	2.25	0.07	1.4	0.58	1.02	1.25	2.92	0.9	3.5
100	2.0	0.06	1.38	0.5	1.0	0.92	2.33	0.87	3.2
200	1.6	0.05	1.12	0.5	0.77	0.58	1.5	0.43	2.6
300	1.5	0.04	0.91	0.42	0.75	0.5	1.2	0.42	2.5
400	0.67	0.04	0.75	0.33	0.5	0.49	0.33	0.30	1.7
560	0.6	0.04	0.7	0.32	0.48	0.3	0.25	0.30	1.5

Table 4.6

Carbon Dioxide

(Moles x 10^8 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_4	iso-butane	t-b-2	2Me butene
0	2.5	0.08	1.55	0.67	1.2	1.8	3.3	1.25	4.2
50	2.0	0.06	1.4	0.65	0.93	1.2	2.5	1.0	3.8
100	1.7	0.04	1.3	0.57	0.91	0.9	1.6	0.9	3.2
200	1.6	0.03	0.9	0.48	0.85	0.7	1.5	0.6	2.8
300	1.5	0.02	0.8	0.38	0.8	0.6	1.4	0.4	2.6
400	1.6	-	0.8	0.39	-	-	-	0.3	-

Table 4.7

Perfluorocyclobutane

(Moles x 10^8 per minute)

Pressure mm	CH_4	C_2H_4	C_3H_4	iso-butane	t-b-2	2Me butene
0	2.6	0.08	1.8	3.3	1.3	4.2
25	1.9	0.06	1.3	2.9	0.8	4.0
80	1.5	0.05	0.7	2.1	0.7	3.4
180	1.3	0.03	0.4	1.8	0.6	2.9
250	0.8	0.01	0.4	1.1	0.4	1.7

(b)   On adding oxygen the yields of all the products were decreased and the yields of C_5 hydrocarbons were completely eliminated since they cannot be formed by any other method than by free radicals. Those product yields which were affected more by added oxygen than by the inert gases were also formed mainly from free radicals. The results are illustrated in Table 4.8 and by Figures 4.18b to 4.23b.

Addition of Oxygen

Irradiation Conditions:

p(isobutene), 6 mm; temperature, $20^{\circ}C$;

time of irradiation, 5 minutes.

Analytical Conditions:

Column, O; temperature, $35^{\circ}C$;

flame ionisation detector; N_2 pressure 12 lb/sq.in.

Table 4.8

Oxygen

(Moles x 10^8 per minute)

Pressure mm	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_4	iso-butane	t-b-2	2Me butene
0	2.5	0.08	1.55	0.67	1.2	1.84	3.3	1.25	4.23
20	0.22	0.07	Nil	0.15	0.13	1.2	0.07	Nil	Nil
50	0.20	0.06	"	0.09	0.12	1.0	0.07	"	"
100	0.20	0.06	"	0.13	0.11	0.9	Nil	"	"
200	0.07	0.05	"	0.08	0.10	0.6	"	"	"
300	0.05	0.04	"	0.07	0.09	0.4	"	"	"
400	0.02	0.04	"	0.05	0.09	0.4	"	"	"

Figure 4.18a

Variation of <u>methane</u> yield with added gas pressure

Added gas pressure (mm)

Figure 4.18b

Variation of <u>methane</u> yield with oxygen pressure
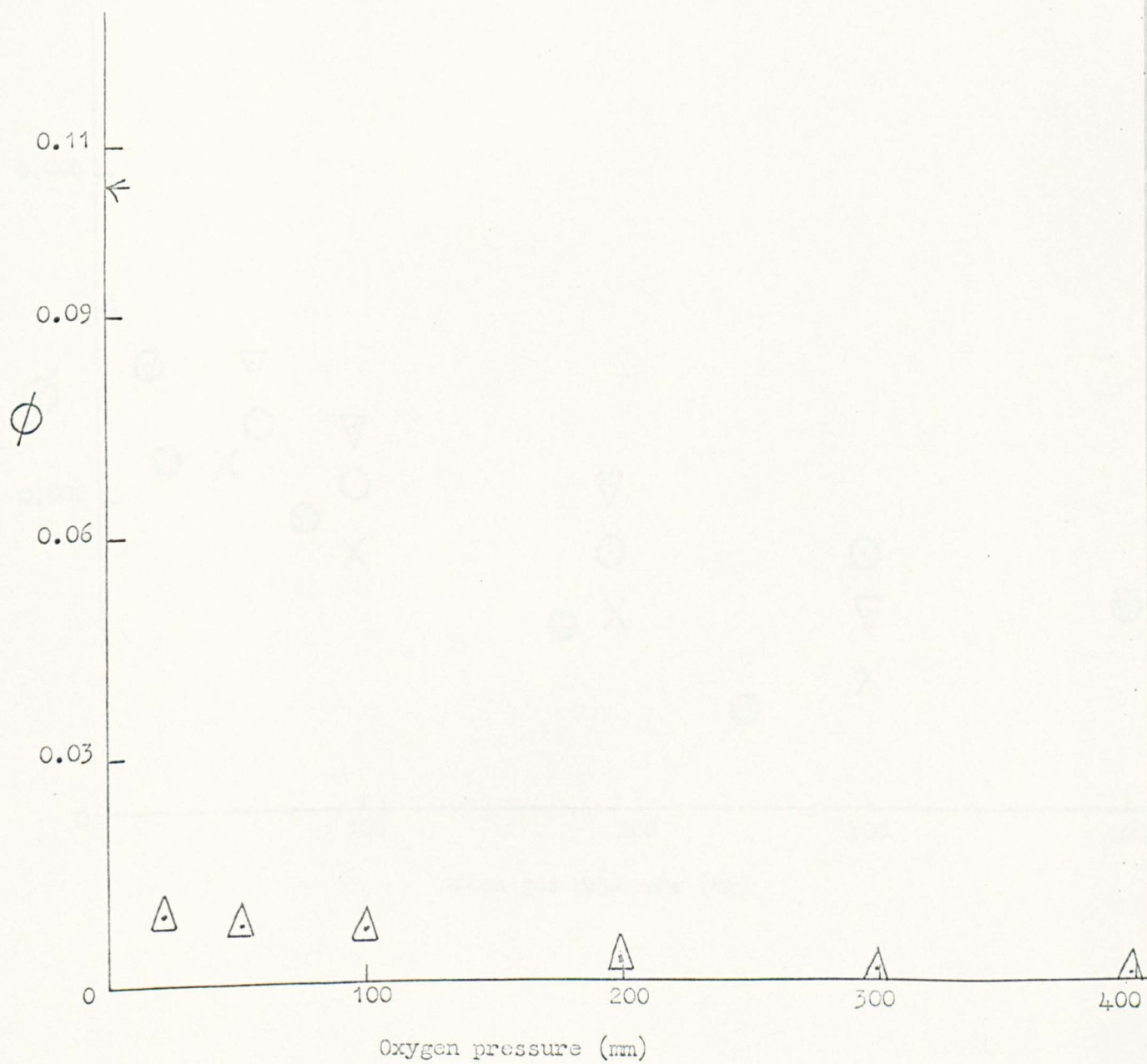
Oxygen pressure (mm)

Figure 4.19a

Variation of ethylene yield with added gas pressure
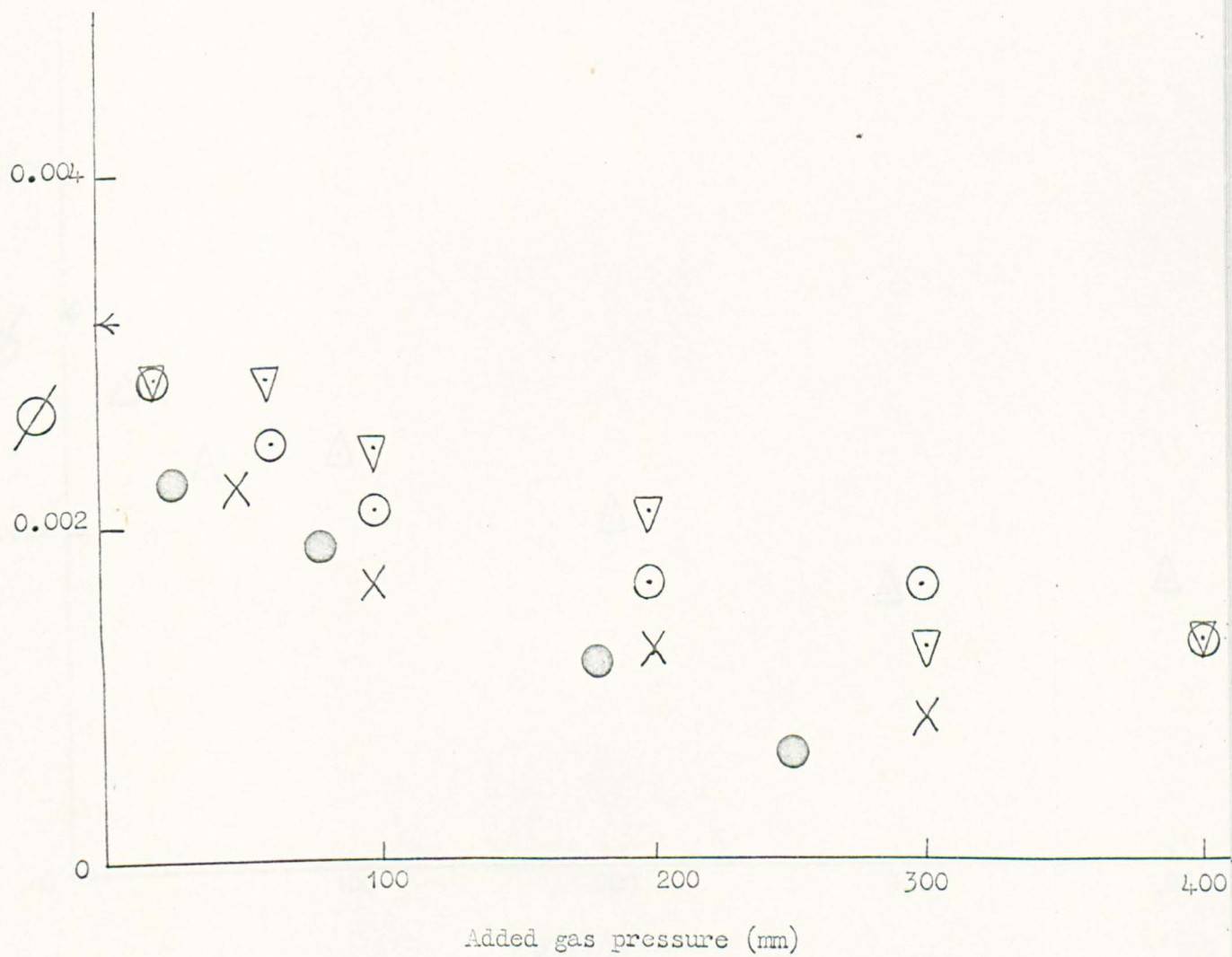
Figure 4.19b

Variation of ethylene yield with oxygen pressure
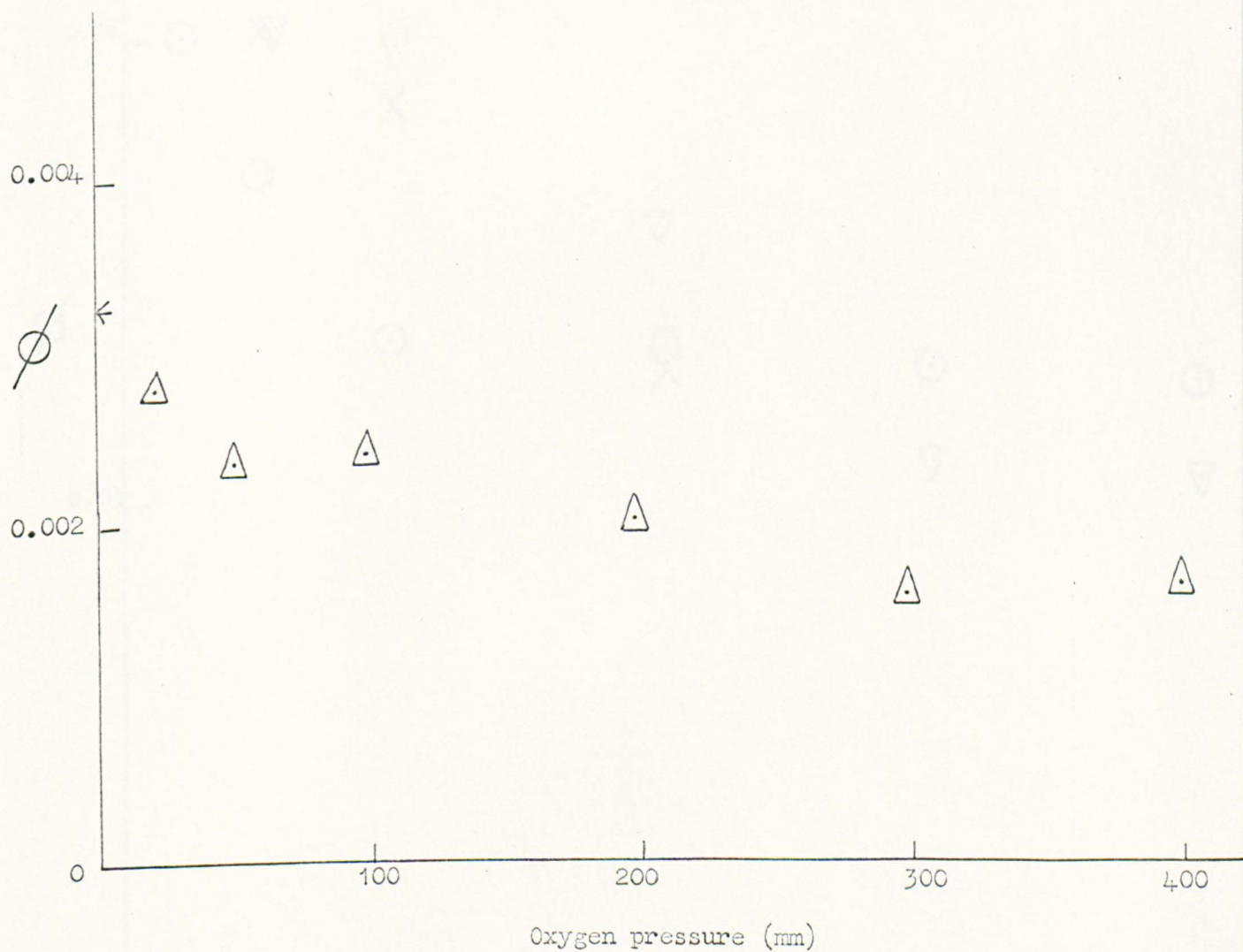
Figure 4.20a

Variation of ethane yield with added gas pressure
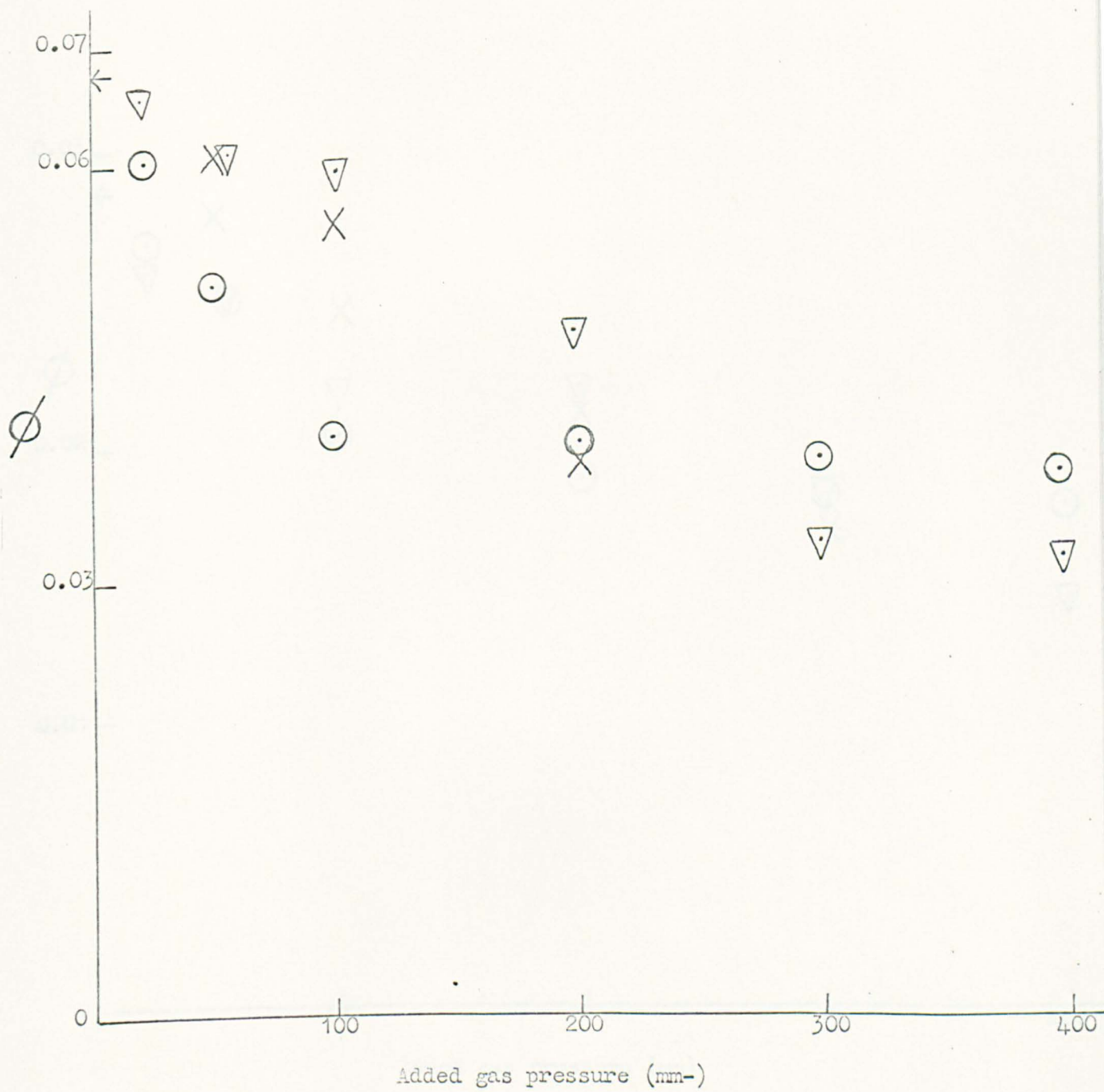
Figure 4.21a
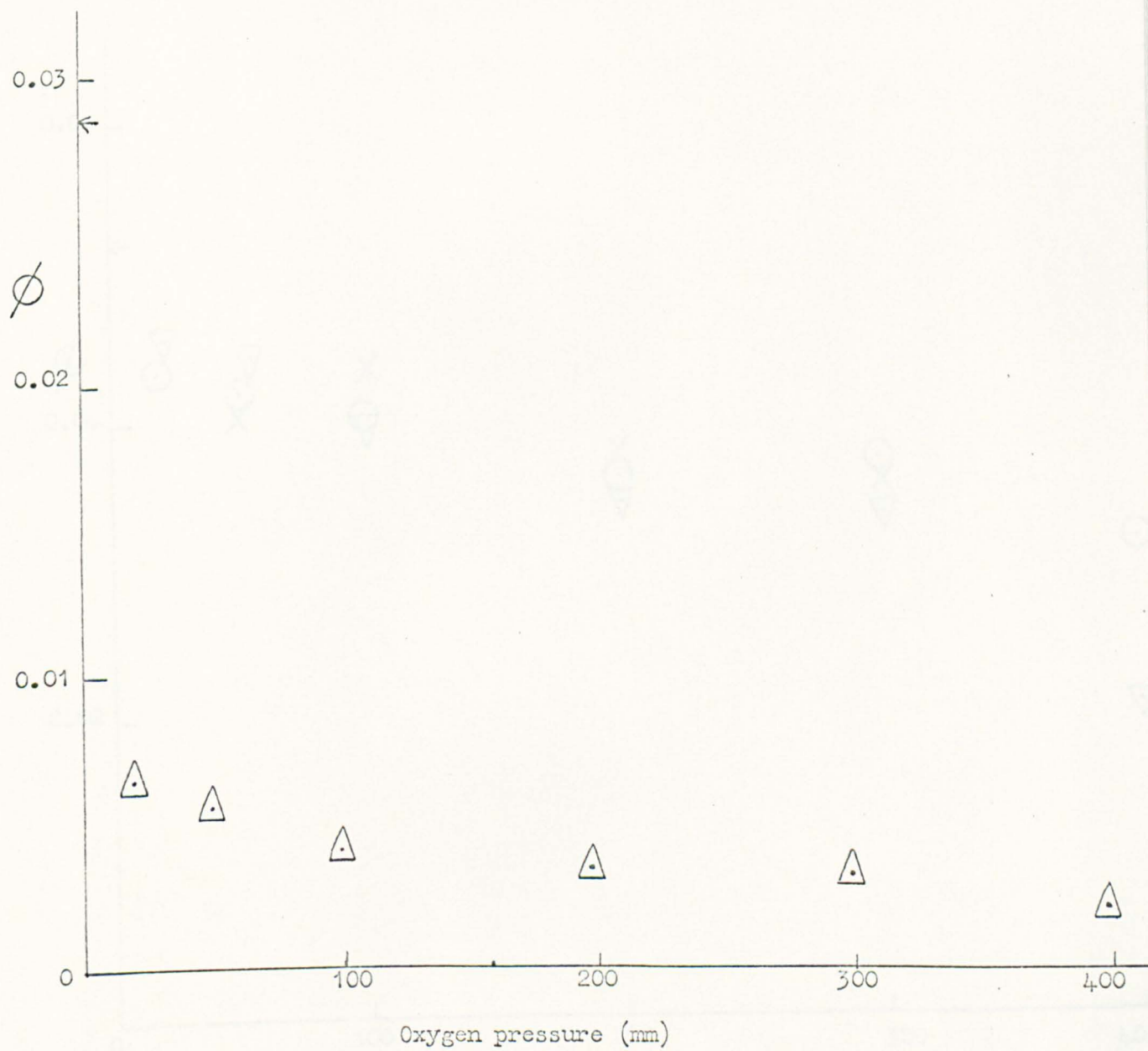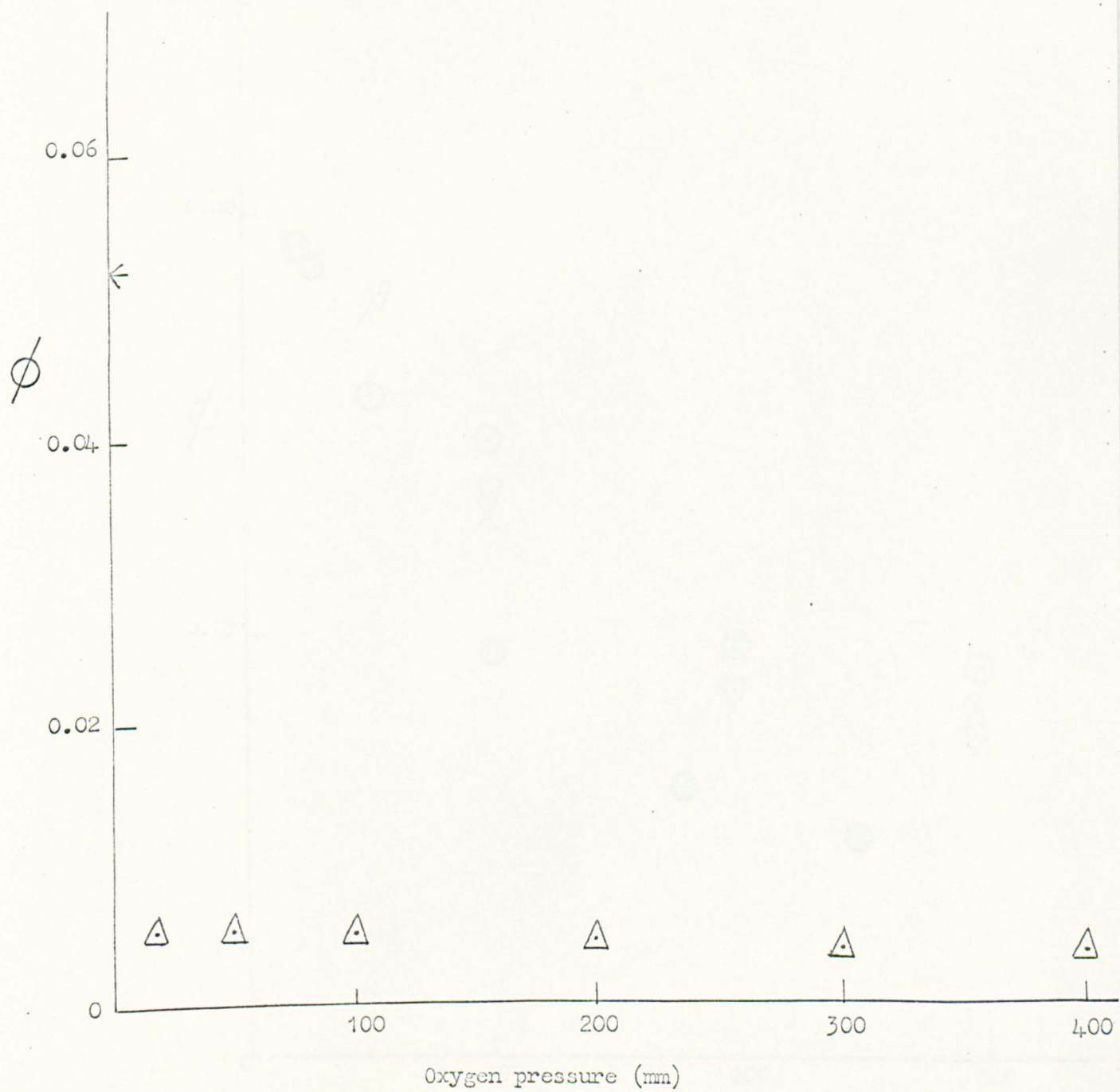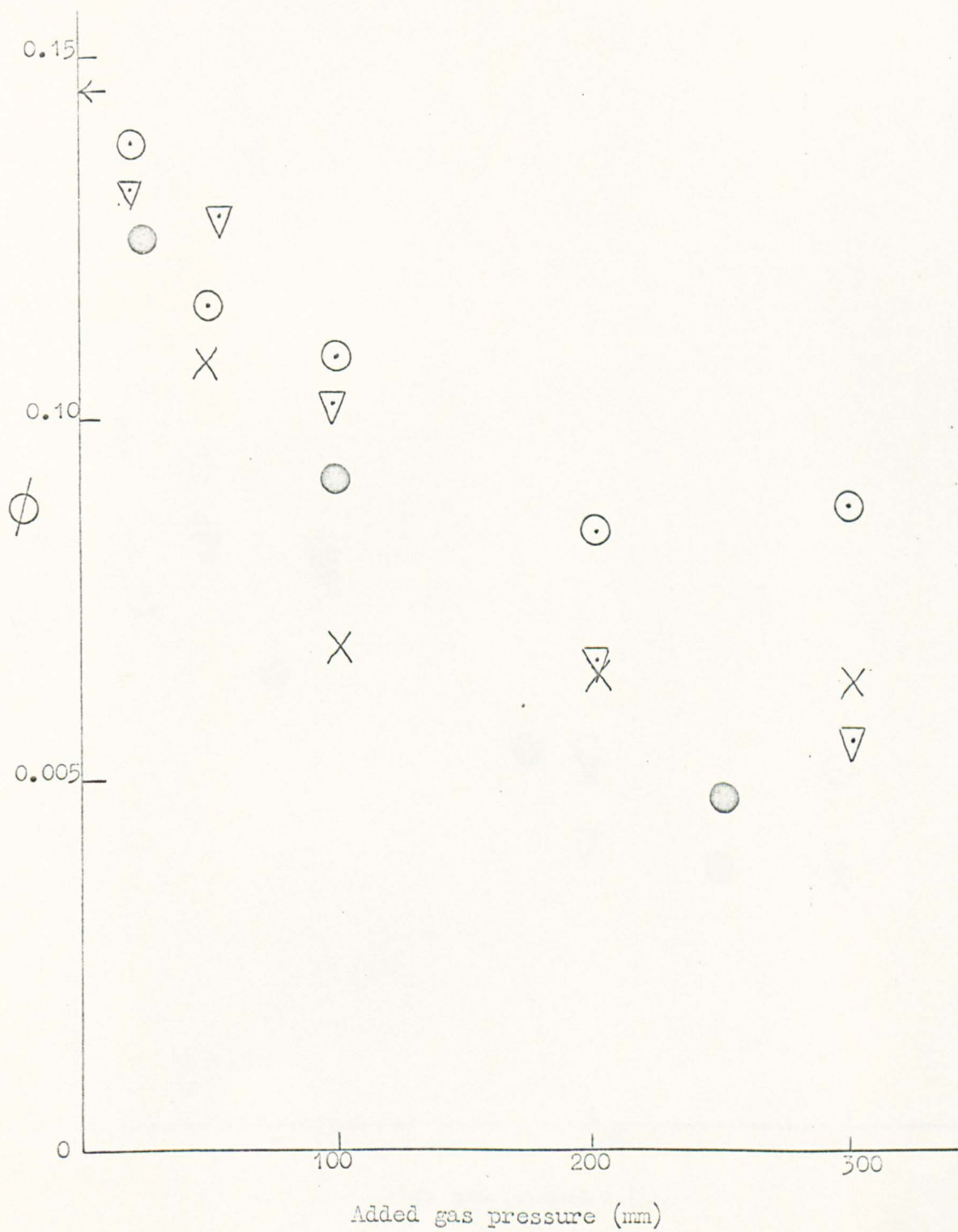
Variation of acetylene yield with added gas pressure
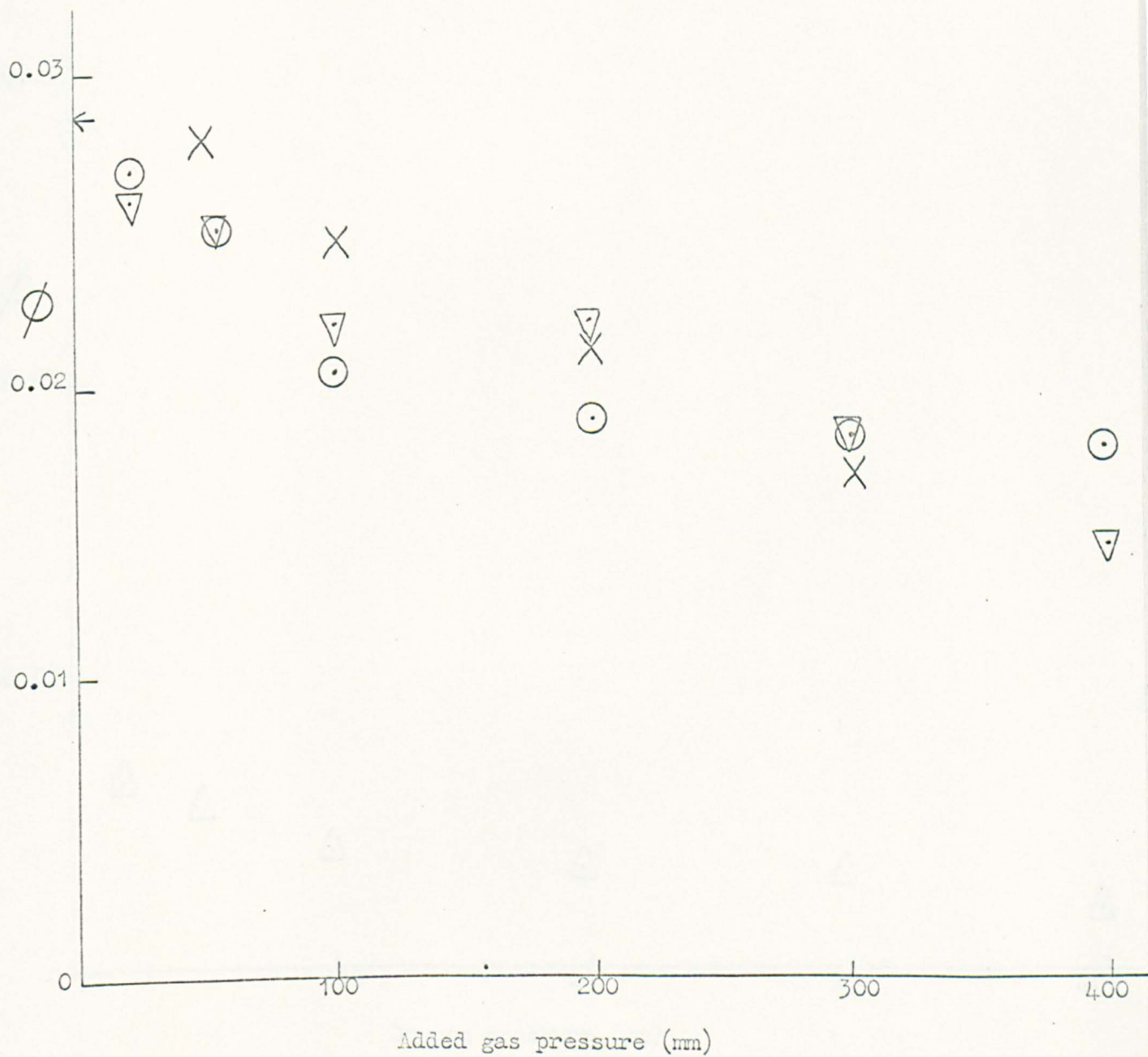
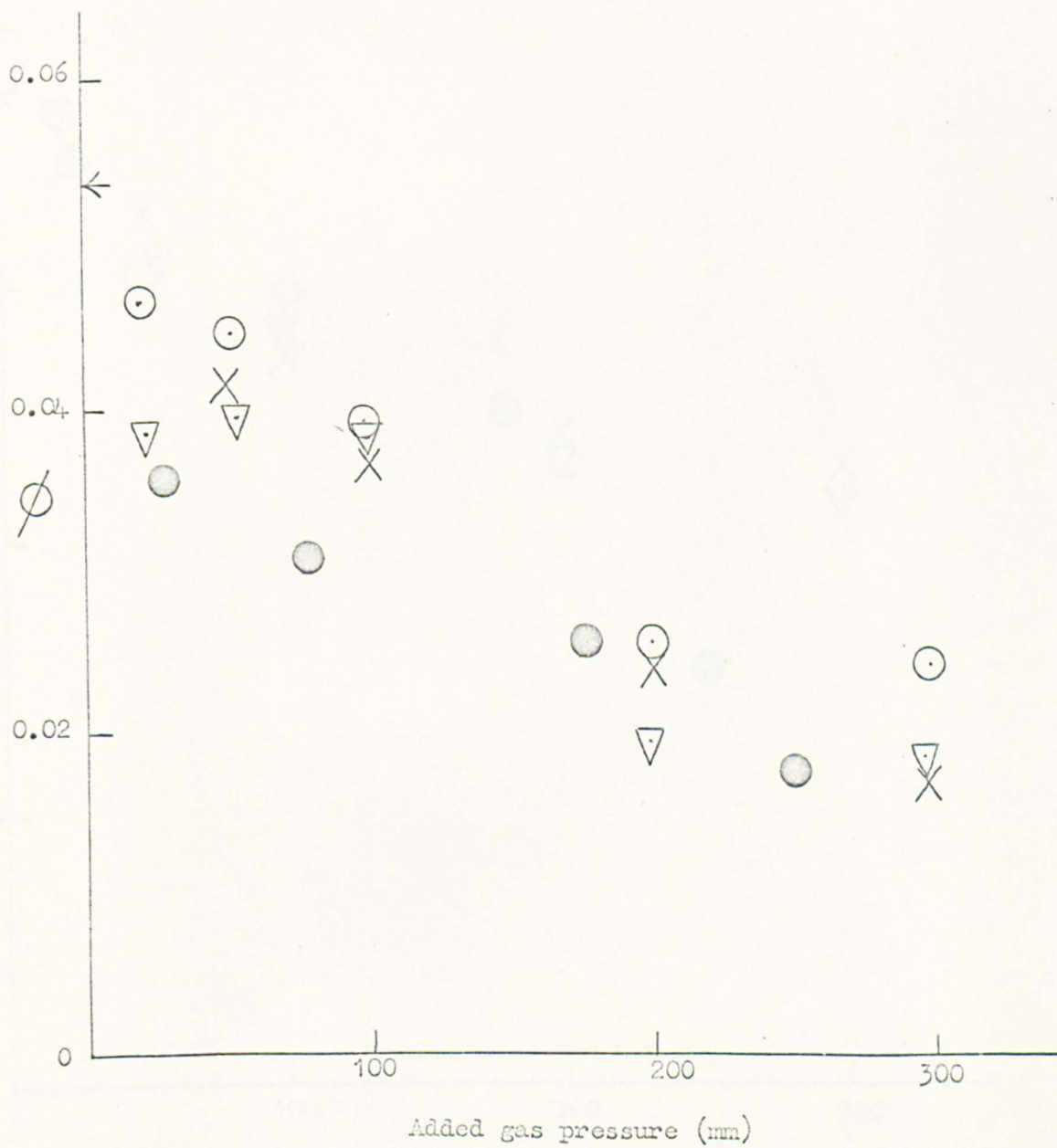# Figure 4.21b

Variation of acetylene yield with oxygen pressure

Figure 4.22a

Variation of propylene yield with added gas pressure

Figure 4.22b

Variation of propylene yield with oxygen pressure

Figure 4.23a

Variation of allene yield with added gas pressure

Added gas pressure (mm)

Figure 4.23b

Variation of allene yield with oxygen pressure

Oxygen pressure (mm)

Figure 4.24a

Variation of isobutane yield with added gas pressure

Figure 4.25a

Variation of trans but-2-ene yield with added gas pressure

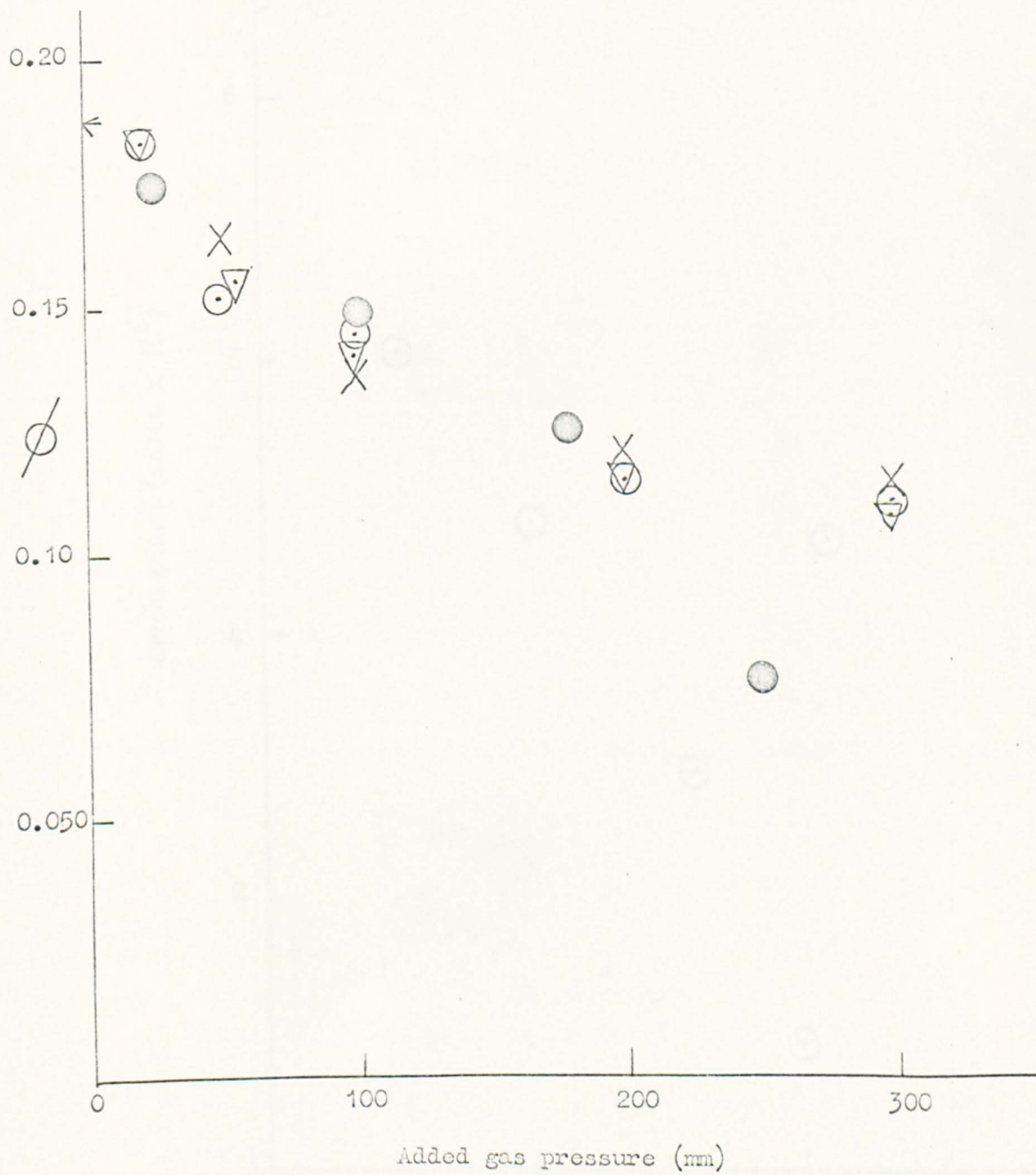Figure 4.26a
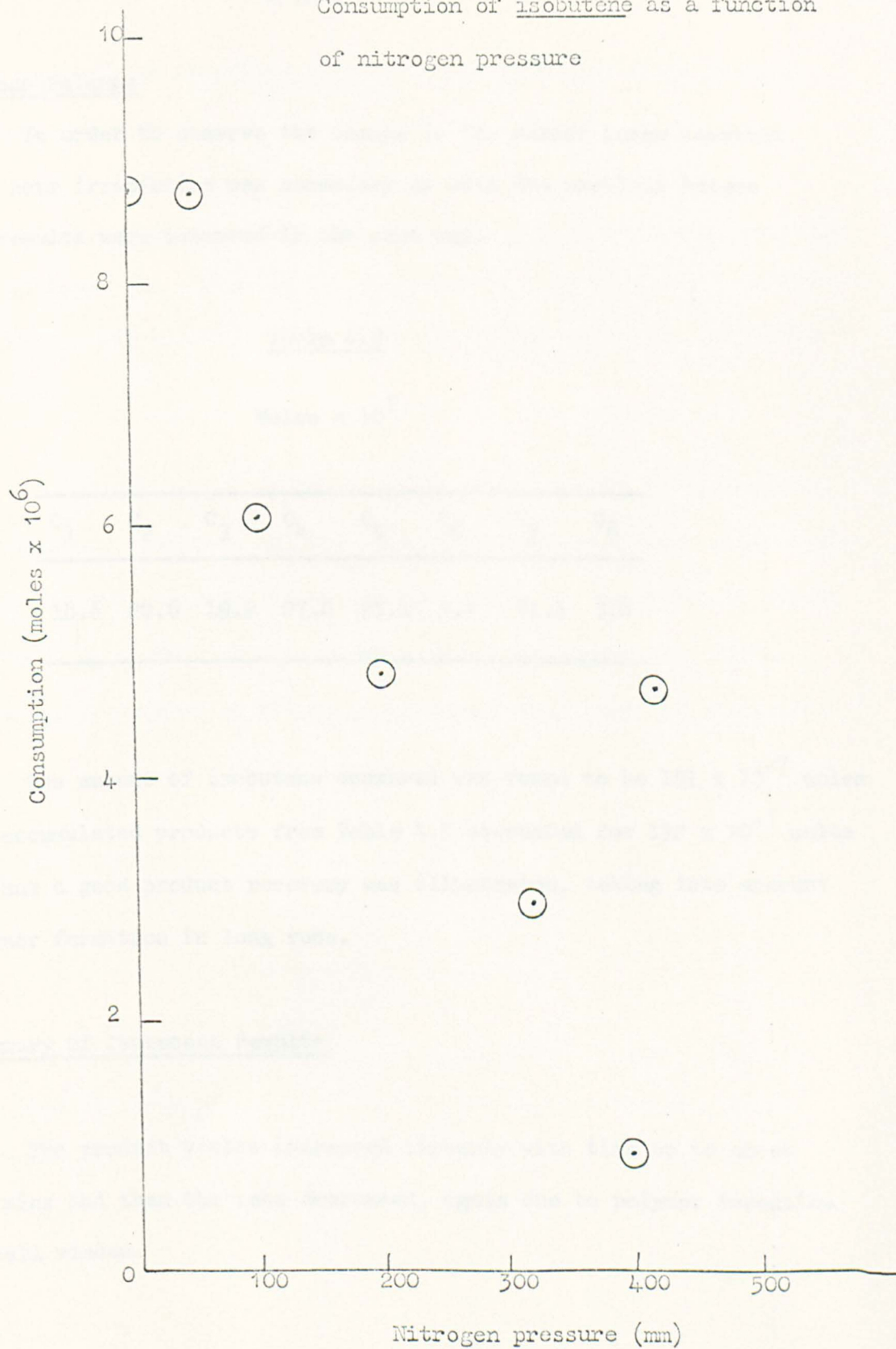
Variation of 2-me-butene yield with added gas pressure

Added gas pressure (mm)

Figure 4.27

Consumption of isobutene as a function of nitrogen pressure

4.4 Carbon Balance

In order to observe the change in the rather large reactant peak a 2 hour irradiation was necessary as with the previous butene and the results were measured in the same way.

Table 4.9

Moles x 10^7

c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8
18.6	20.6	19.2	27.8	25.1	5.4	21.1	3.8

The amount of isobutene consumed was found to be 191×10^{-7} moles and the accumulated products from Table 4.9 accounted for 152×10^{-7} moles butene thus a good product recovery was illustrated, taking into account the polymer formation in long runs.

4.5 Summary of Isobutene Results

(1)   The product yields increased linearly with time up to about 25 - 30 mins and then the rate decreased, again due to polymer formation on the cell window.

(2)   The yields of all the products were decreased by an increase
in reactant pressure.

(3)   Inert gases nitrogen, argon, carbon dioxide and perfluorocyclo-
butane decreased the yields of all the products. It was noted that the
last foreign gas appeared to decrease the yields more than the former
three gases.

(4)   On adding oxygen to the reaction system the yields of ethane,
C_5 hydrocarbons, isobutane and the but-2-enes were completely eliminated.
The yields of the remainder of the products with the exception of allene
and ethylene were affected to a greater extent by oxygen than by the
inert gases, the yields of allene and ethylene only being affected the
same.

5. RESULTS: Cis Pent-2-ene

The cis pent-2-ene was stored as a gas in a 1 litre bulb and on irradiating known pressures with light of 1849 $\overset{o}{A}$ wavelength the product mixture was found to contain hydrogen and twenty three hydrocarbons. A solid polymer was also found to build up on the cell window after long periods of irradiation. The products were analysed by gas chromatography using column O at 35°C for the C_1 to C_5 hydrocarbons and column O at 80°C for the higher compounds. No products were found after C_8 hydrocarbons. Table 5.1 shows the product yields from a typical 5 minute irradiation.

Steady state experiments were conducted to categorise the products in the same way as for but-1-ene and isobutene, the effect of the following parameters investigated.

(1) Time of irradiation

(2) Pressure of Cis pent-2-ene (reactant)

(3) Pressure of added gases

The irradiation time used was generally 5 minutes which gave rise to about 5% decomposition of the cis pent-2-ene which was at a pressure of 3 mm. for experiments in Sections 5.1 and 5.3.

The extinction coefficient of cis pent-2-ene was about 12,000 l.moles^{-1}cm^{-1} [18] and therefore more than 99% of the incident light

was absorbed in the cell at pressures greater than 2 mm. of cis

pent-2-ene.

Irradiation Conditions:

p(c-p-2), 3 mm; temperature, $20^\circ \pm 2^\circ C$;

irradiation time, 5 mins.

Analytical Conditions:

Column O; temperature, $35^\circ C$ and $80^\circ C$;

N_2 pressure, 12 lb/sq.in. and 20 lb/sq.in.;

flame ionisation detector.

Table 5.1

Product Yields from a Typical 5 minute Run Quoted
in moles x 10^8

H_2	5.7	C_3H_4	0.2	2Me butene	8.0
CH_4	4.2	But-1-ene	7.8	trans pent-2-ene	7.9
C_2H_4	4.4	Butadiene	38.2	(C_6)	1.8
C_2H_6	39.1	trans but-2-ene	trace	(C_7)	0.5
C_2H_2	1.0	cis but-2-ene	0.2	(C_8)	1.7
C_3H_6	2.1	3Me butene	7.6	1-3 pentadiene	3.2
C_3H_8.	2.1	(18.3 mins)	∽4.8		

(C_6) (C_7) and (C_8) represent total approximate values for several peaks.
Individual identification of these higher products was not made and the
presence of (C_7) compounds was not established beyond doubt.

5.1 Effect of Irradiation Time

The rate of production of all products increased linearly with time to about 30 mins thereafter the rate decreased due to the formation of a solid polymer on the cell window. The presence of the polymer was confirmed spectrophotometrically and after a long irradiation (2 h.) was clearly visible with the naked eye. Later experiments were conducted using an irradiation time of 5 minutes, therefore limiting the effect of the polymer. After longer irradiations the cell window was cleaned with chromic acid and then water and finally acetone before drying at $100^{\circ}C$ for 20 minutes.

The results are illustrated by Table 5.2 and Figures 5.1 to 5.13.

Analytical Conditions:

Column 0; temperature, $35^{\circ}C$;

N_2 pressure, 12 lb/sq.in.; flame ionisation detector.

Table 5.2

(Moles x 10^8)

Time mins	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_8	C_3H_4	But-1-ene	Buta-diene	t-b-2	c-b-2	3Me butene	*18.3 min.	2Me butene
5	4.2	4.4	39.1	1.0	2.1	2.1	0.2	7.8	38.2	trace	0.2	7.6	30	4.0
7	5.0	5.4	46.8	1.1	2.3	2.4	0.2	8.8	42.8	"	0.2	8.3	45	5.2
15	12.1	14.9	104	2.6	5.6	5.7	0.9	21.3	84.4	"	0.8	19.5	52	8.3
20	15.4	19.7	136	3.4	7.2	7.4	0.9	28.4	114	"	1.3	27.6	60	9.9
30	21.6	28.3	205	5.1	10.3	10.5	1.2	40.0	147	1.4	2.0	41.3	80	14.4
60	33.1	50.2	308	7.7	15.1	15.4	3.0	57.7	173	2.9	5.2	51.5	90	17.4
100	55.1	89.0	482	12.1	24.0	24.4	3.8	87.0	195	5.6	7.9	60.5	97.5	20.3
120	60.6	102.3	514	12.8	27.2	27.6	5.3	92.3	200	8.4	9.7	63.8	100	21.1

* The yield of the unidentified product is quoted as a peak area.

Figure 5.1   Variation of methane yield with irradiation
time.

Figure 5.2 Variation of ethylene yield with irradiation time
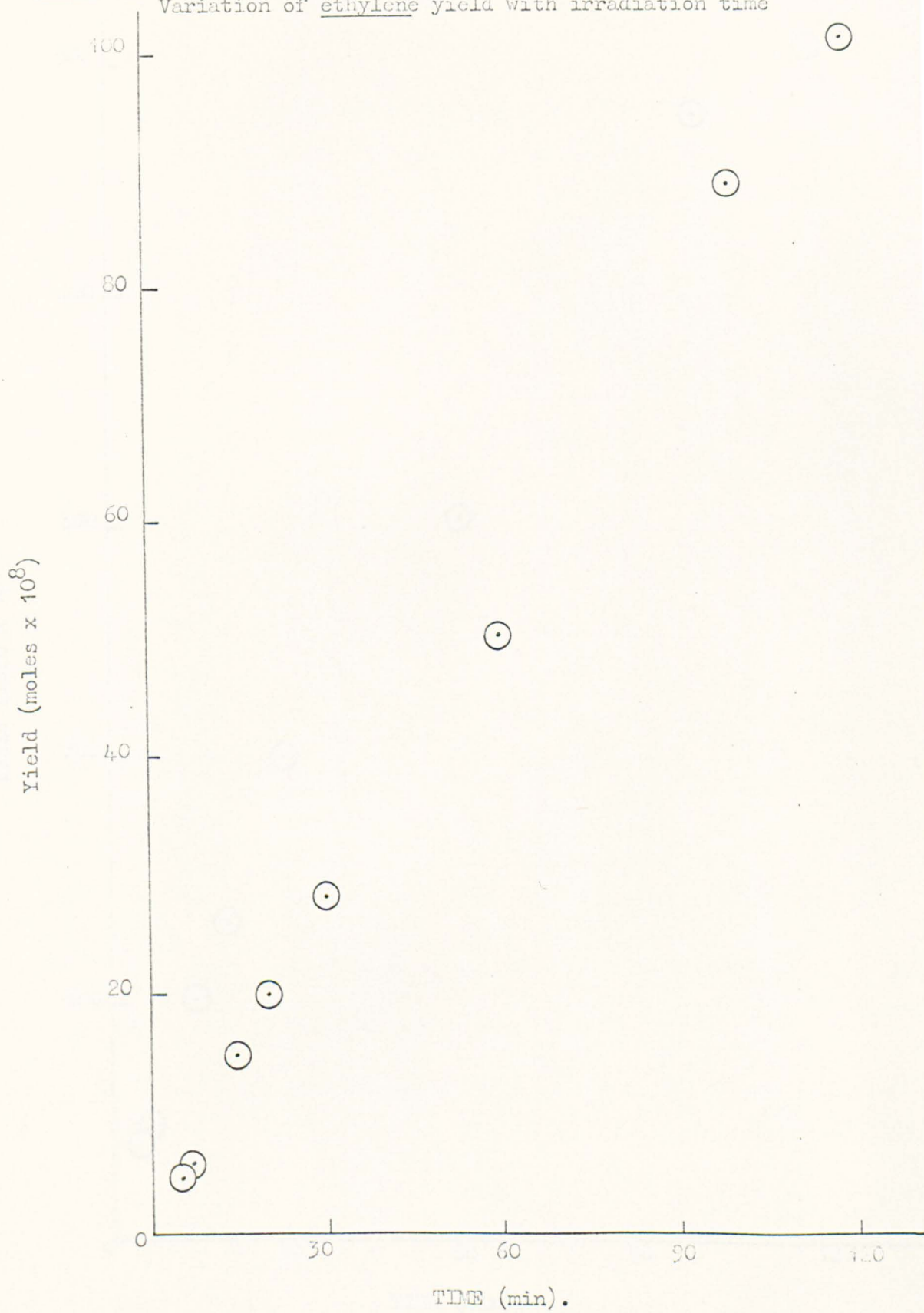
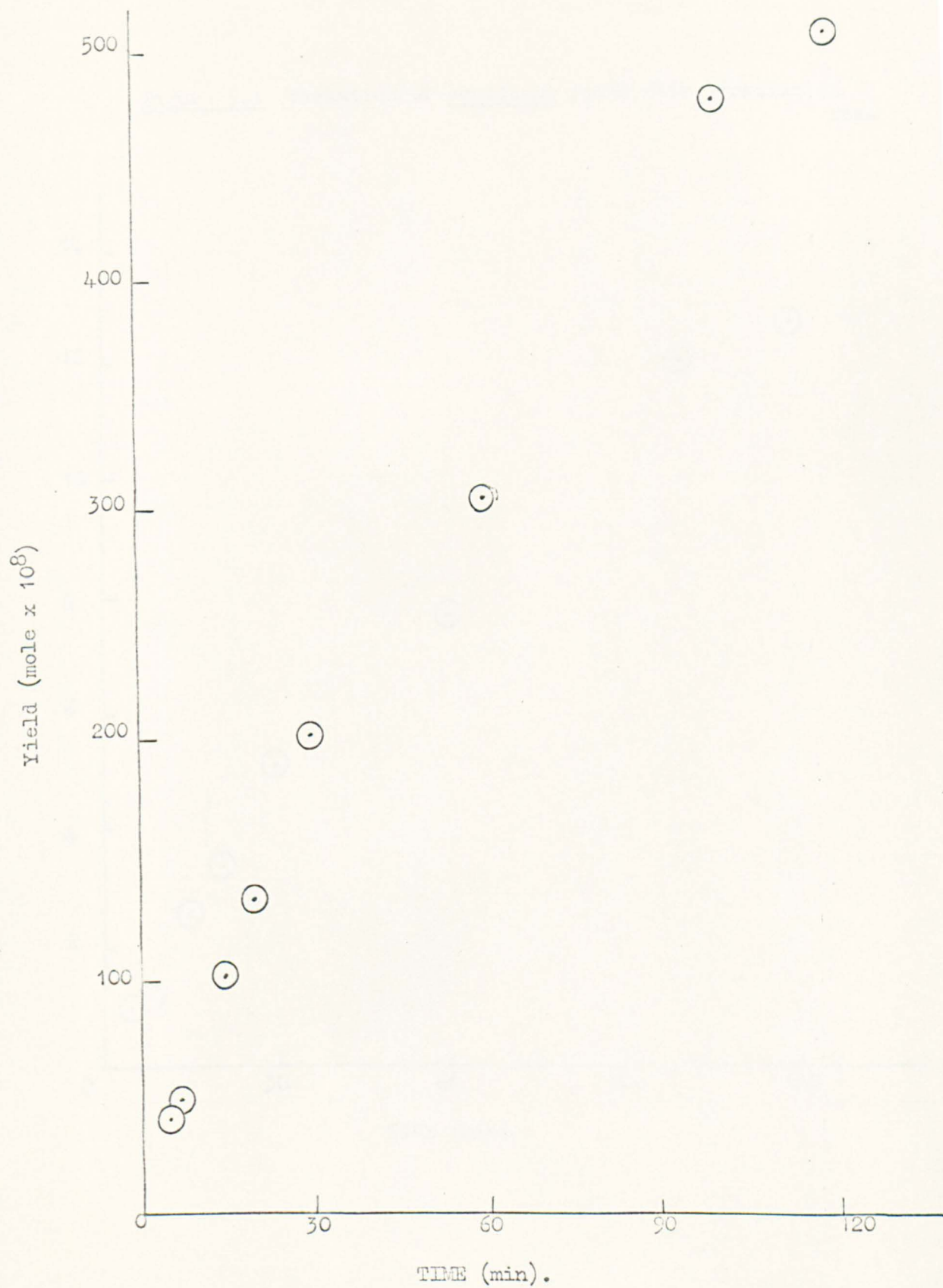Figure 5.3 Variation of ethane yield with irradiation time

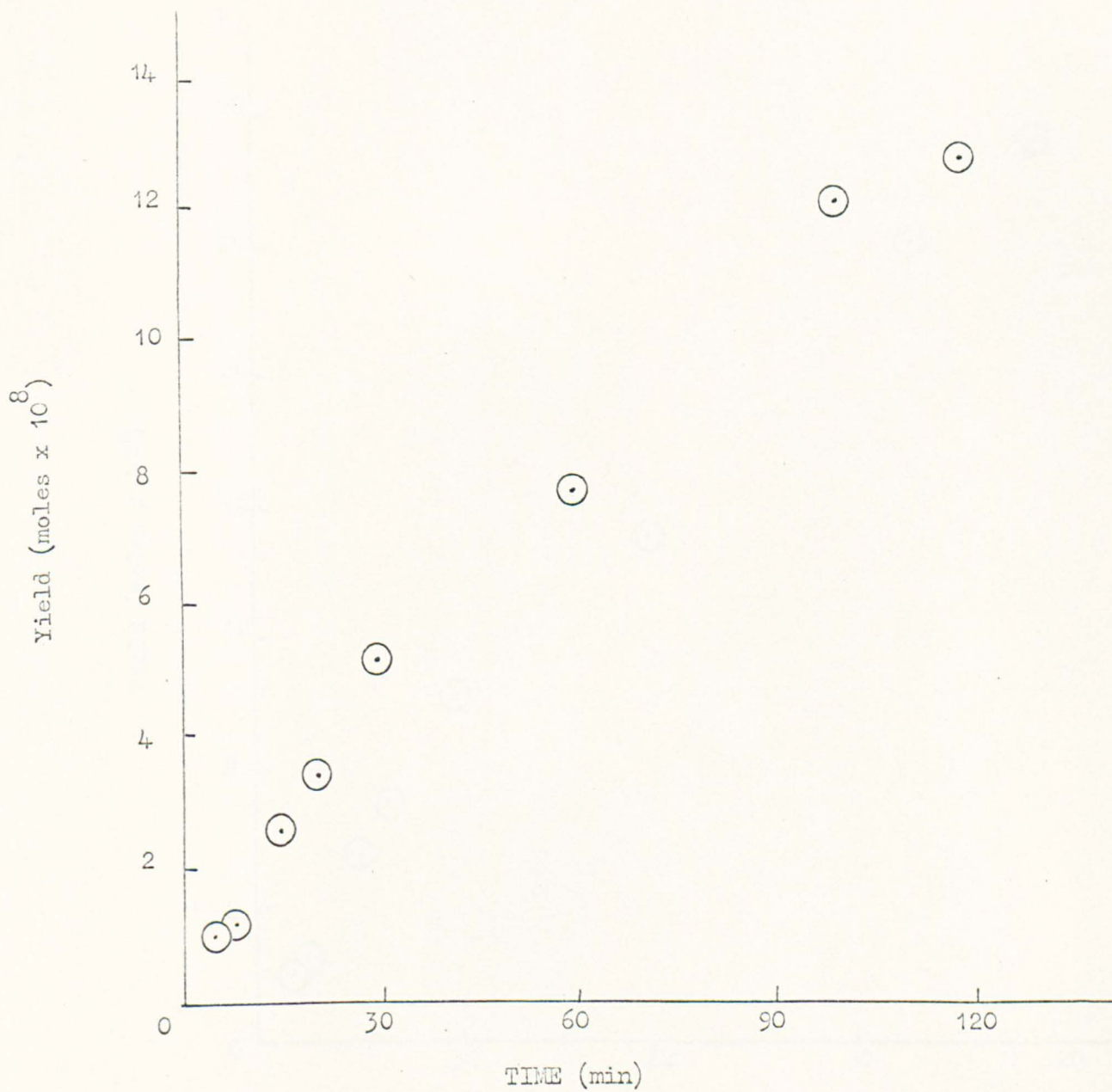Figure 5.4 Variation of acetylene yield with irradiation time

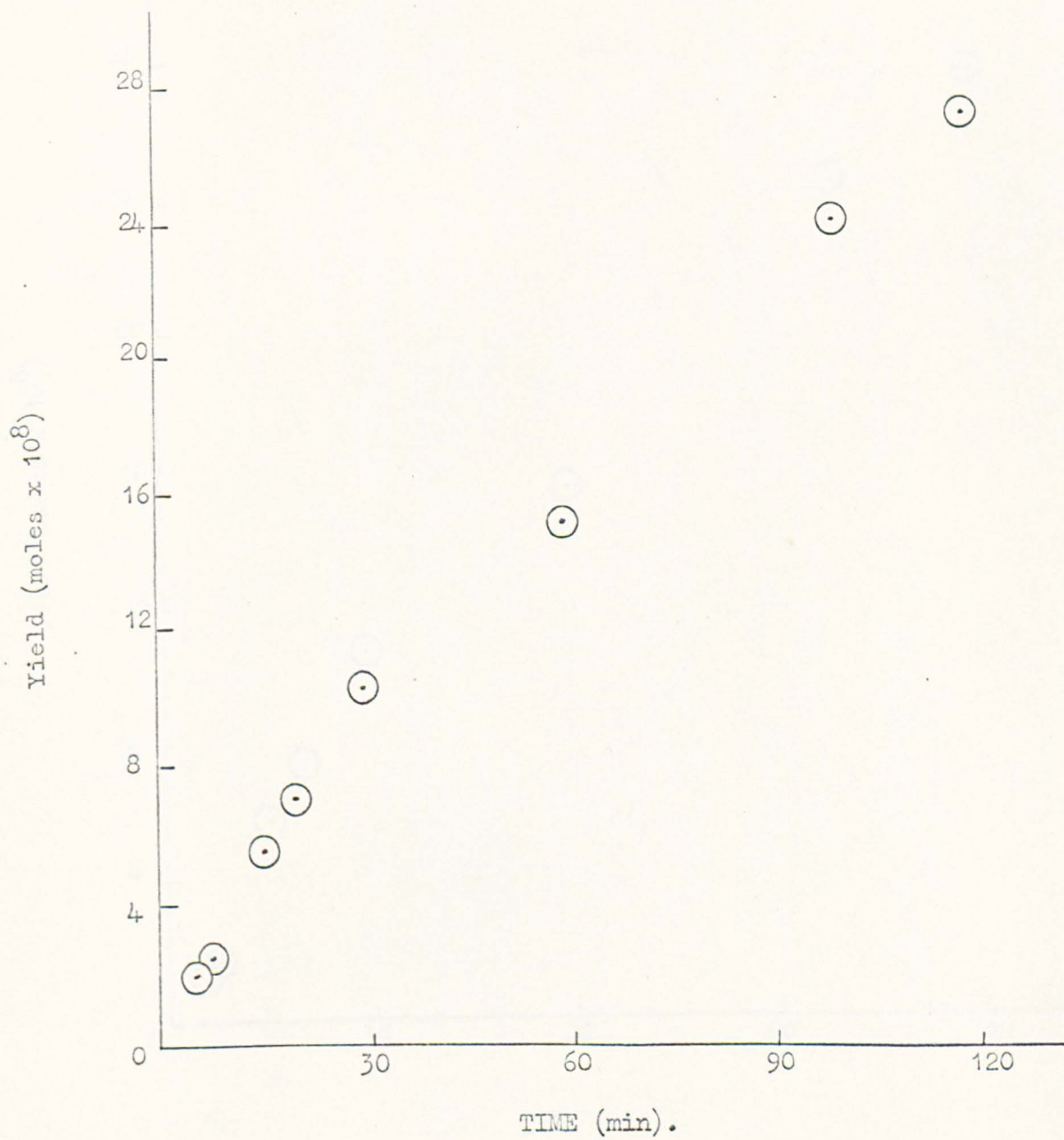Figure 5.5   Variation of propylene yield with irradiation time

Figure 5.6

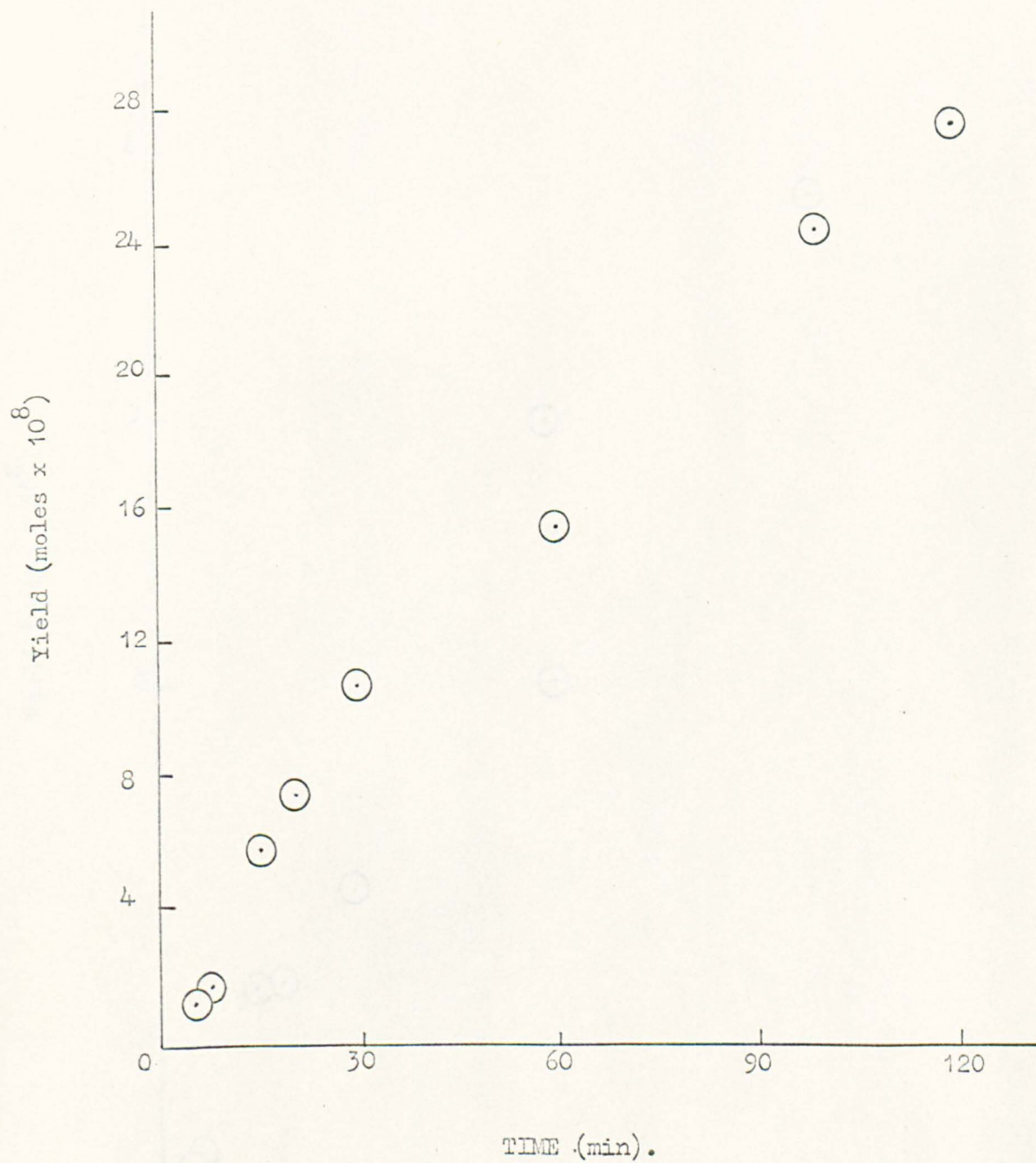Variation of propane yield with irradiation time

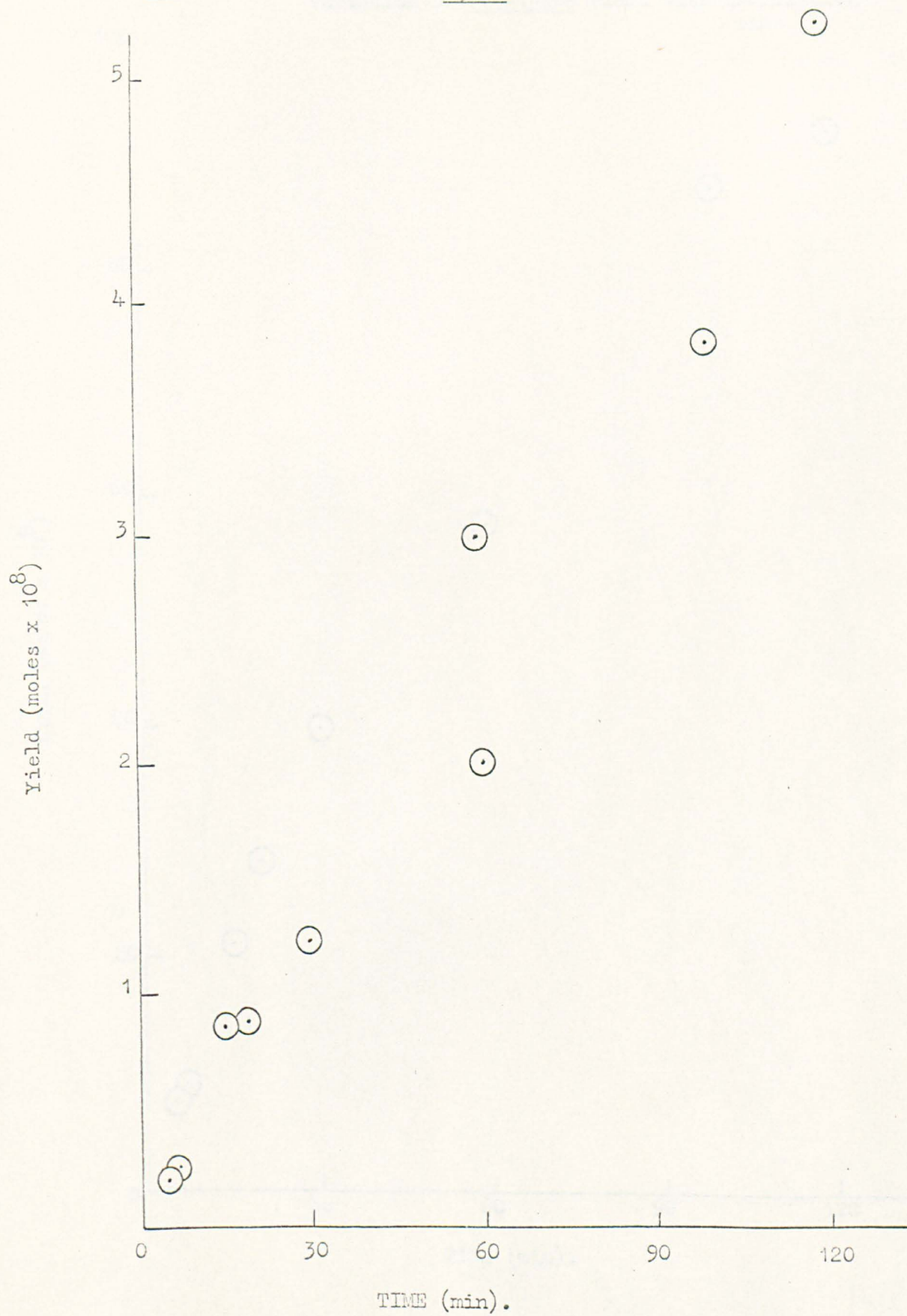Figure 5.7 Variation of C_3H_4 Yield with irradiation time

Figure 5.8
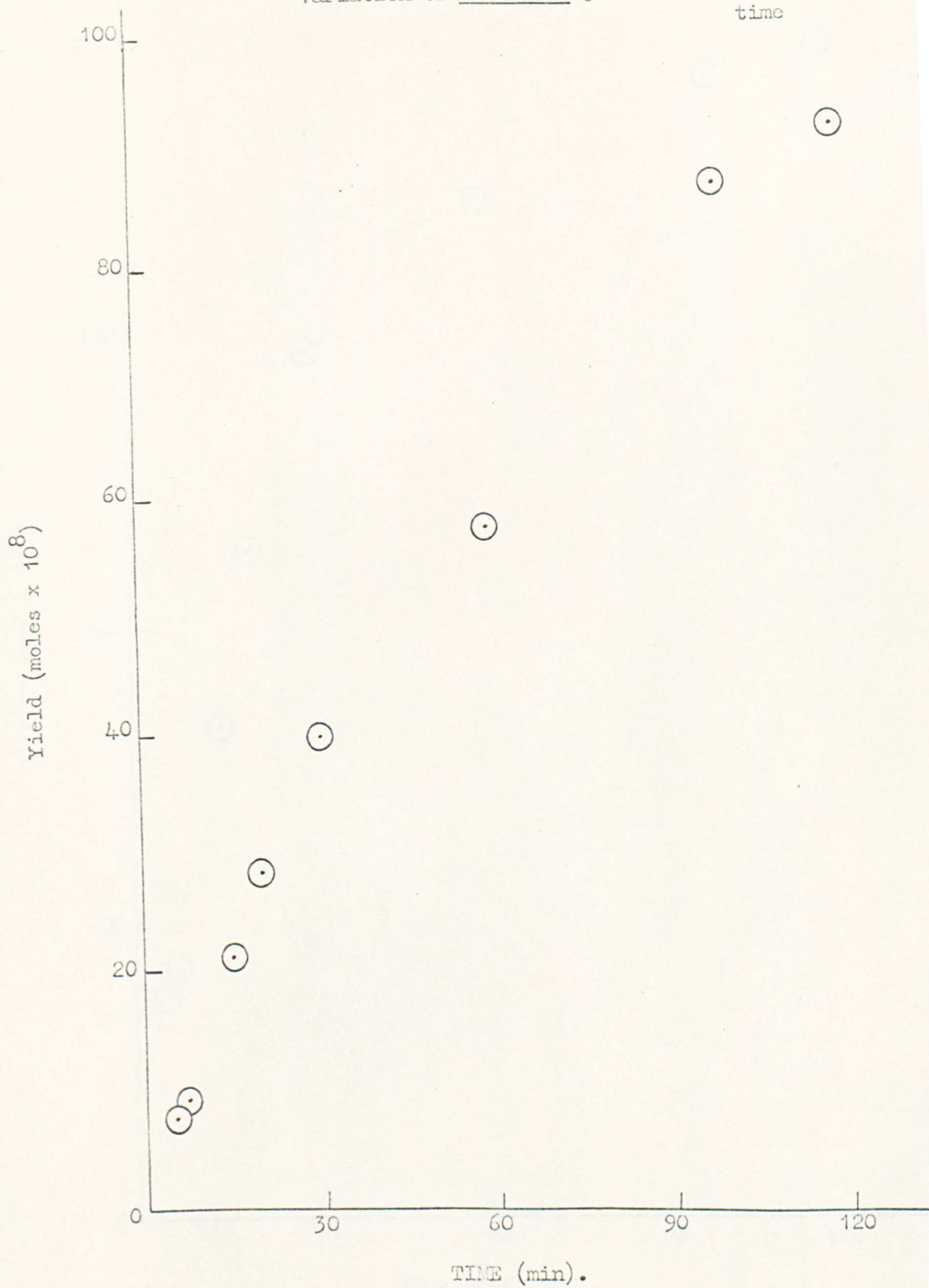
Variation of but-1-ene yield with irradiation time

Figure 5.9 Variation of butadiene yield with irradiation time

Figure 5.10   Variation of but-2-ene (cis) yield with irradiation time

Yield (moles x 10^8)

TIME (min).

Figure 5.11

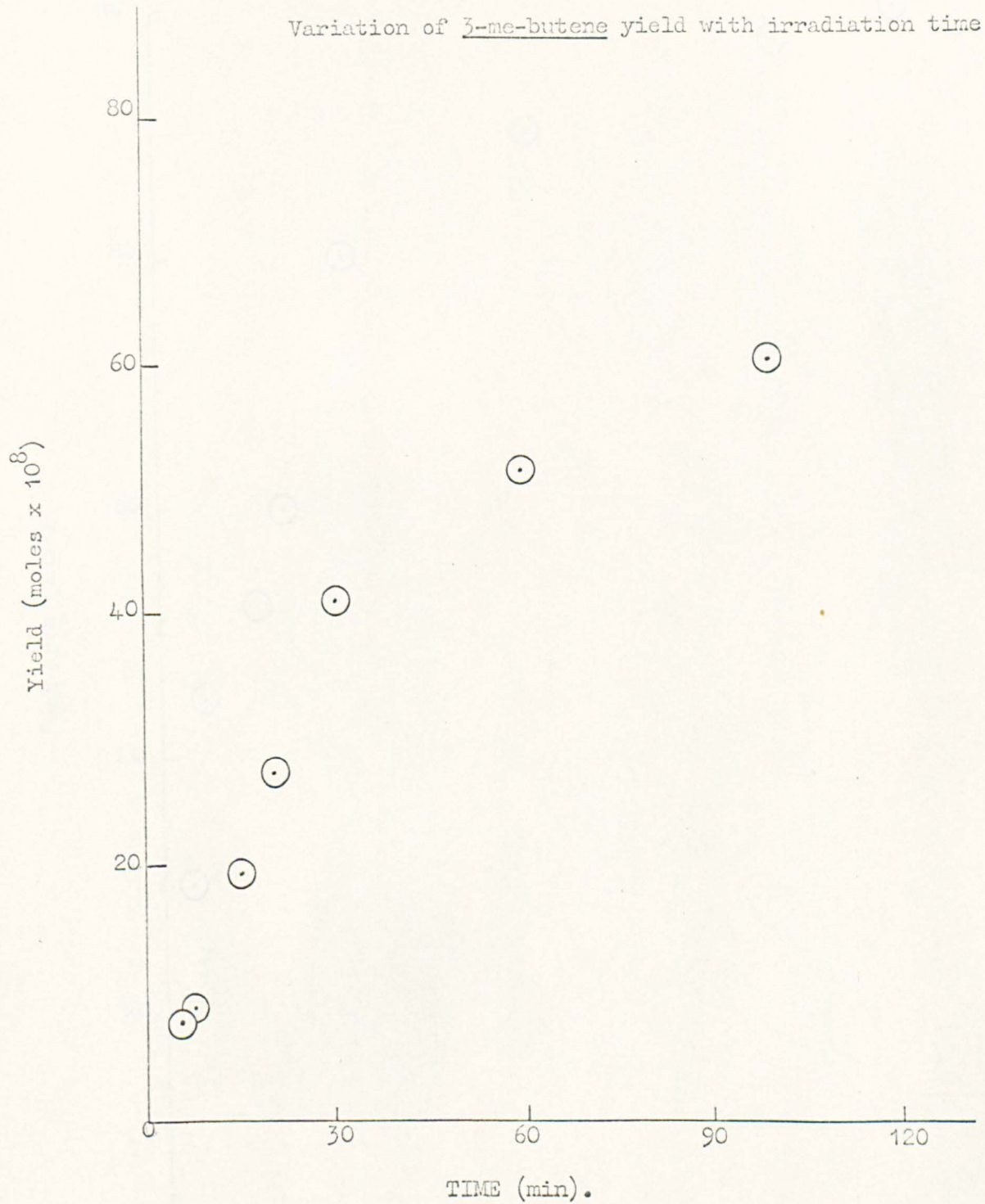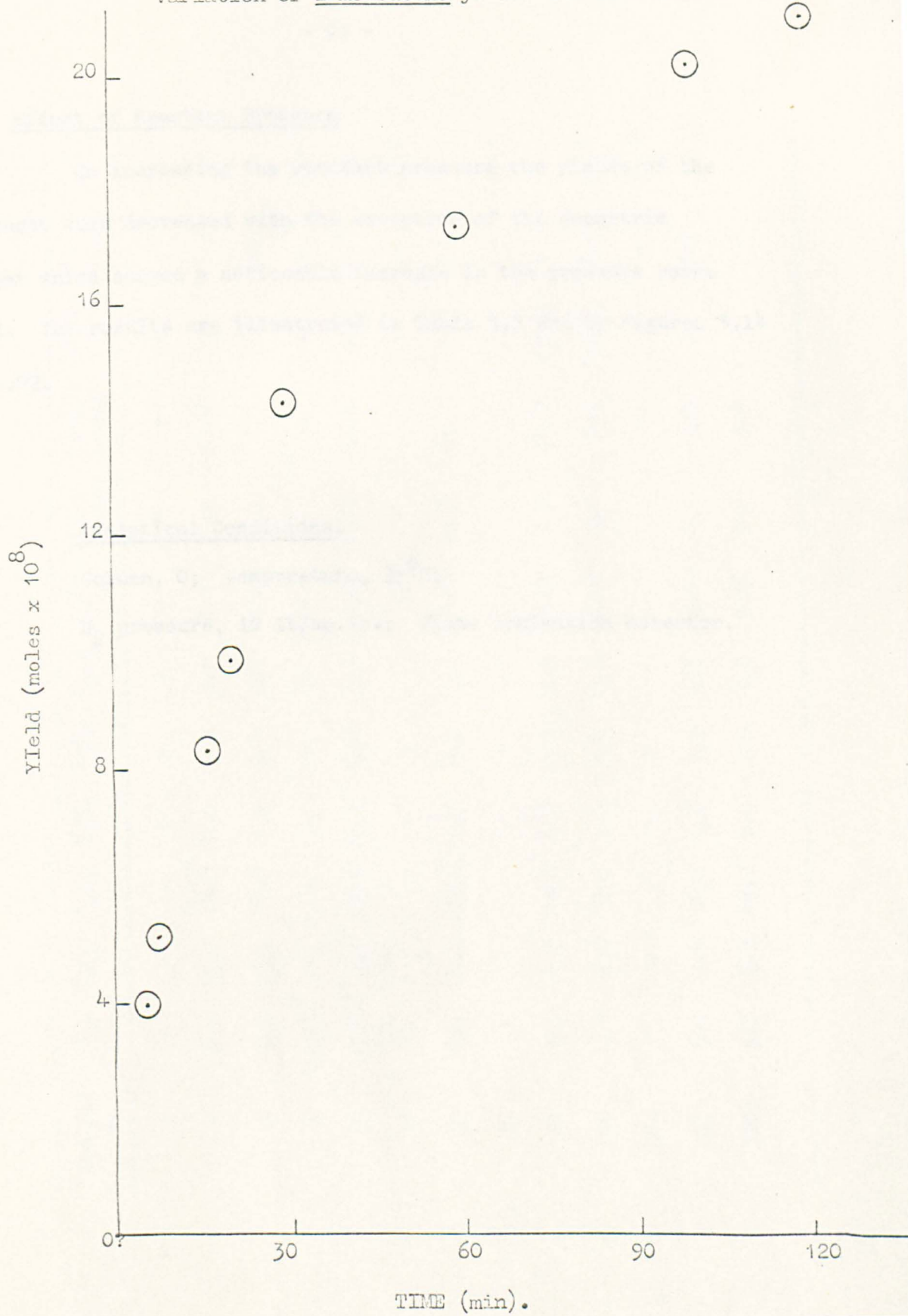Variation of 3-me-butene yield with irradiation time

Figure 5.12

Variation of the peak area of product with retention time
18·3 mins against irradiation time

Figure 5.13

Variation of 2-me-butene yield with irradiation time

Yield (moles x 10^8)

20

16

12

8

4

0

30   60   90   120

TIME (min).

5.2 Effect of Reactant Pressure

On increasing the reactant pressure the yields of the products were decreased with the exception of the geometric isomer which showed a noticeable increase in the pressure range used. The results are illustrated in Table 5.3 and by Figures 5.14 to 5.23.

Analytical Conditions:

Column, O; temperature, $35^{\circ}C$;

N_2 pressure, 12 lb/sq.in.; flame ionisation detector.

Table 5.3

(Moles x 10^9 per minute)

| Pressure mm	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_8	C_3H_4	but--1-ene	buta-diene	c-b-2	3Me butene	t-p-2
2	-	-	-	-	-	-	-	-	-	-	-	15.7
3	9.5	13.2	78.2	2.0	5.2	5.2	0.13	18.8	72.9	0.4	13.3	-
5	8.2	8.1	78.2	2.0	3.4	3.4	0.05	14.1	67.3	0.4	14.5	-
8	-	-	-	-	-	-	-	-	-	-	-	21.0
11	7.6	6.7	79.0	2.1	3.4	3.4	0.04	14.1	48.6	0.3	17.5	-
15	-	-	-	-	-	-	-	-	-	-	-	25.2
20	7.1	5.3	78.2	2.0	3.2	3.2	0.03	12.8	30.4	0.2	17.2	-
35	-	-	-	-	-	-	-	-	-	-	-	42.4
60	6.6	3.0	67.3	1.7	2.3	2.3	0.03	9.3	10.0	trace	13.1	-
100	6.6	3.0	55.1	1.3	2.1	2.1	0.03	8.0	6.1	trace	12.3	82.4
160	-	-	-	-	-	-	-	-	-	-	-	84.0
200	6.0	1.9	48.1	1.2	2.1	2.1	0.02	8.0	4.4	-	12.5	-
300	5.7	1.2	24.3	0.6	1.0	1.0	0.02	3.5	2.8	-	5.1	-

Figure 5.14 Variation of methane yield with reactant pressure
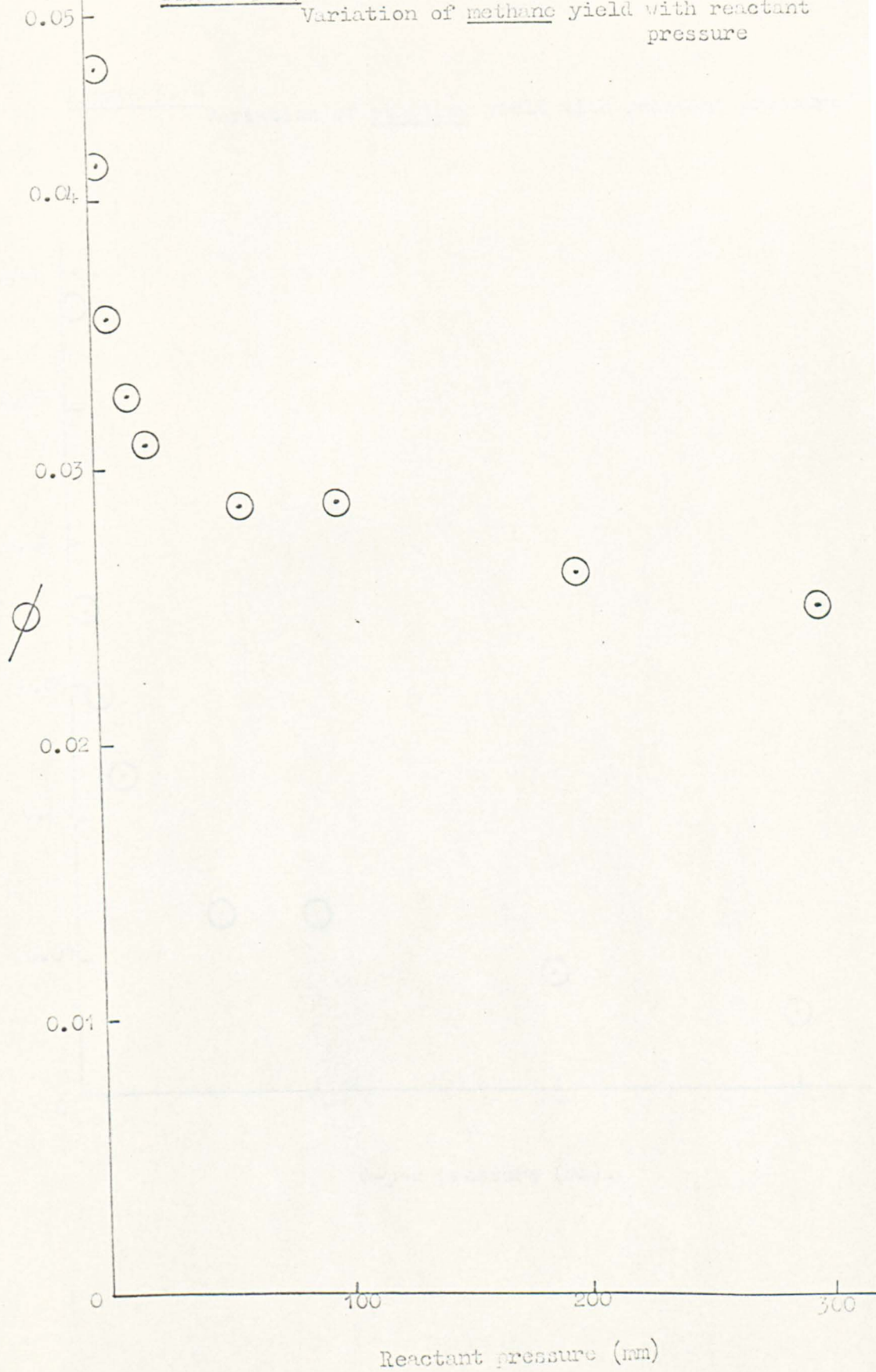
Figure 5.15   Variation of ethylene yield with reactant pressure
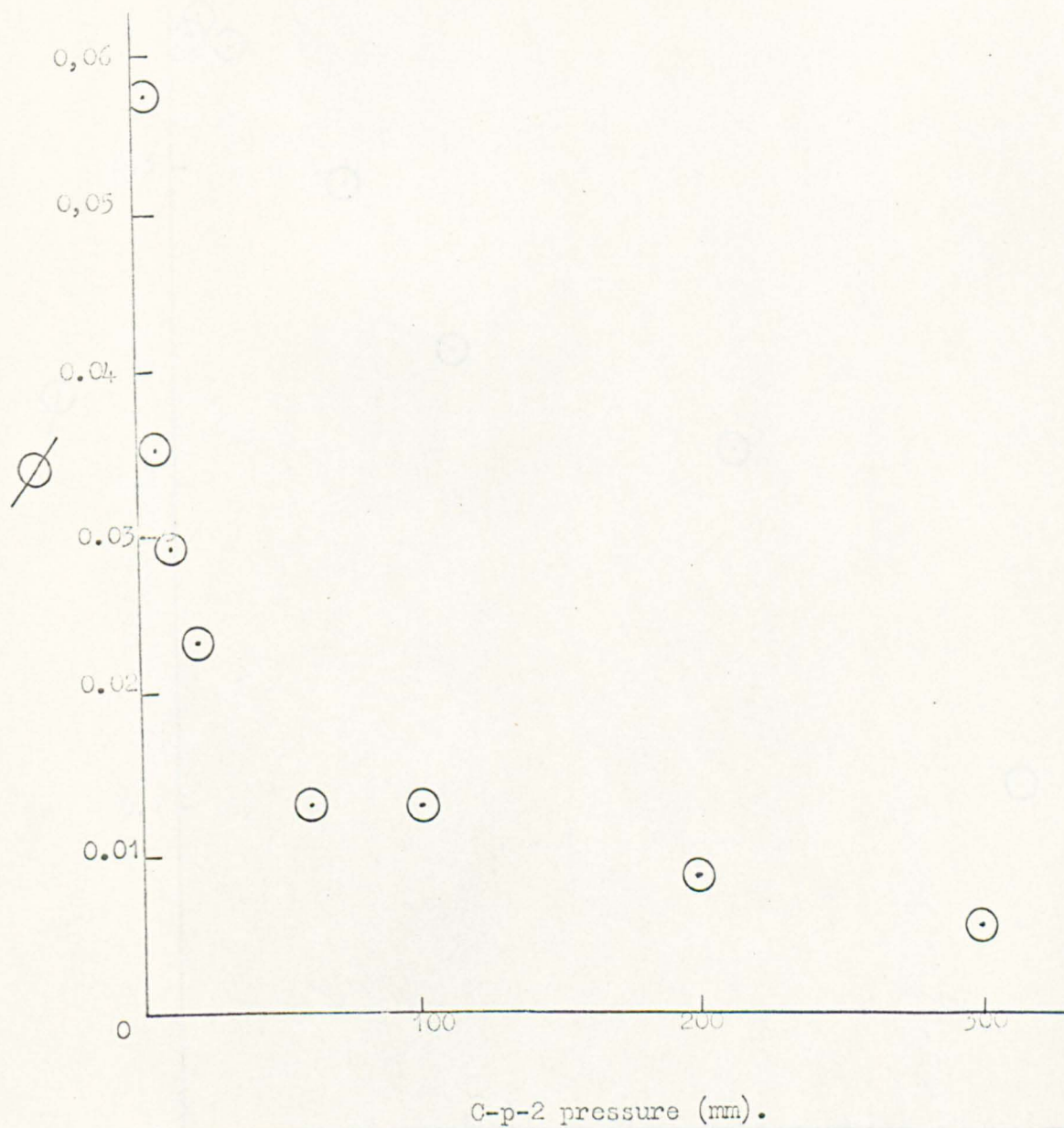
Figure 5.16
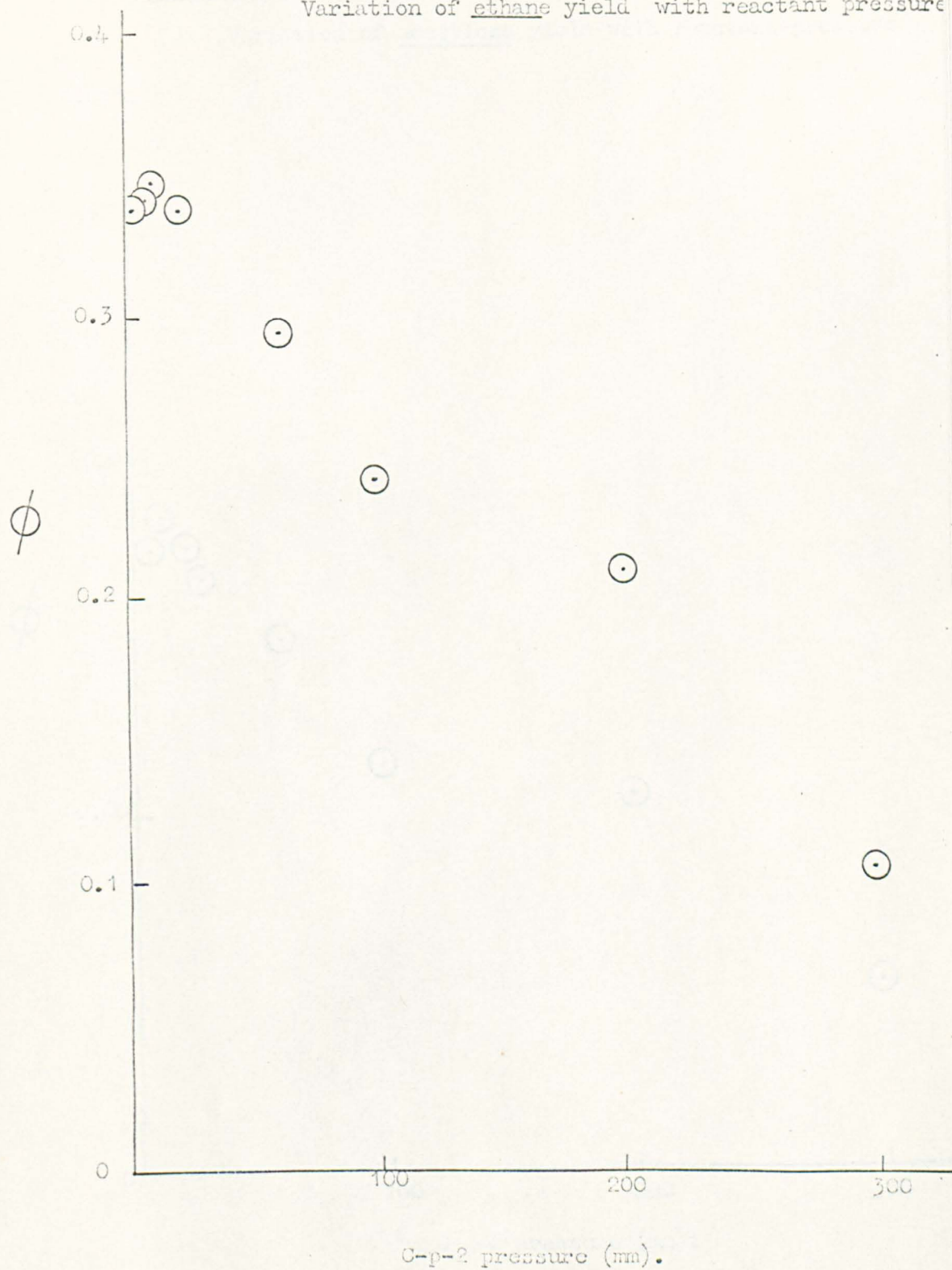

Variation of ethane yield with reactant pressure

Figure 5.17

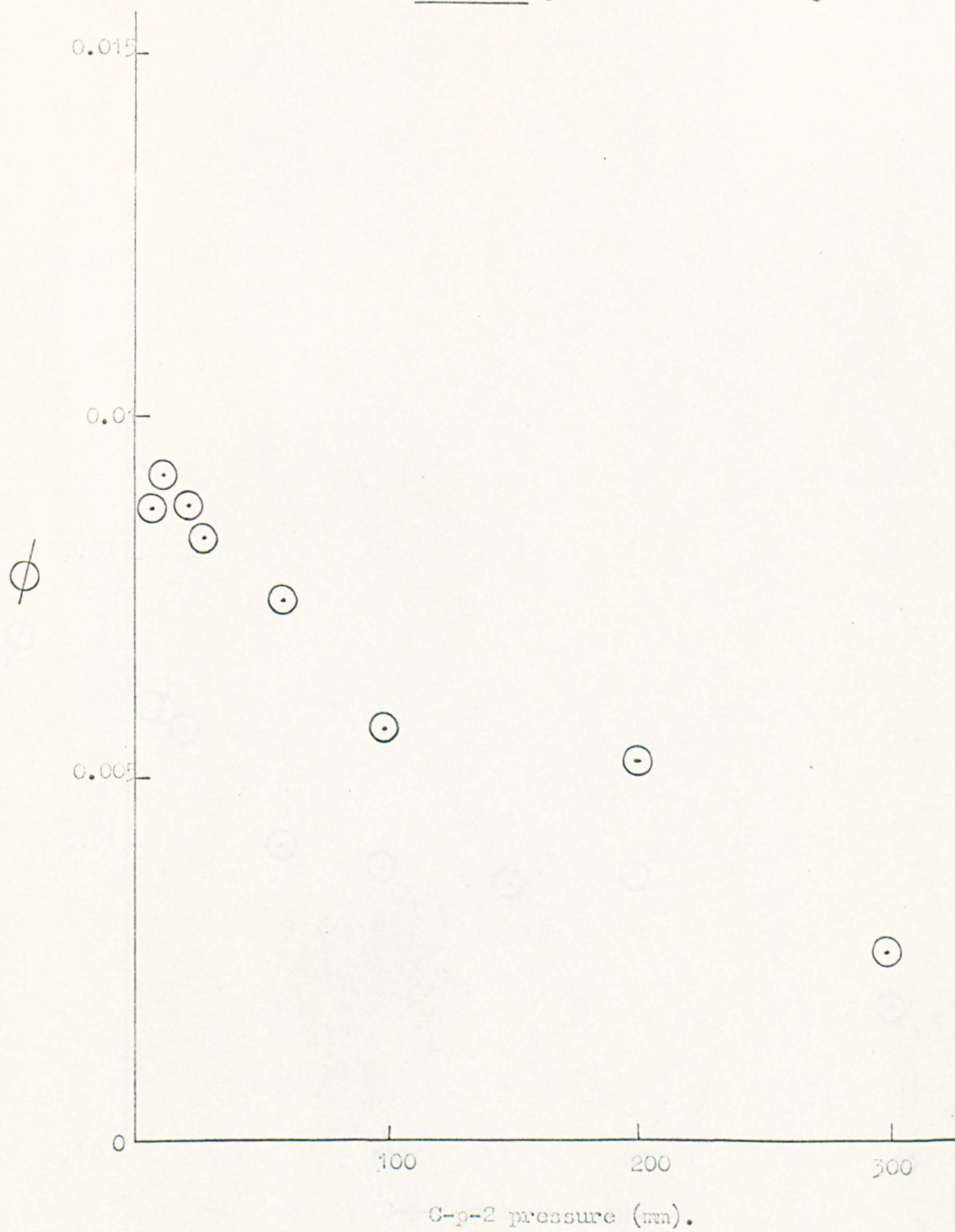Variation of acetylene yield with reactant pressure

C-p-2 pressure (mn).

Figure 5.18

Variation of propylene yield with reactant pressure
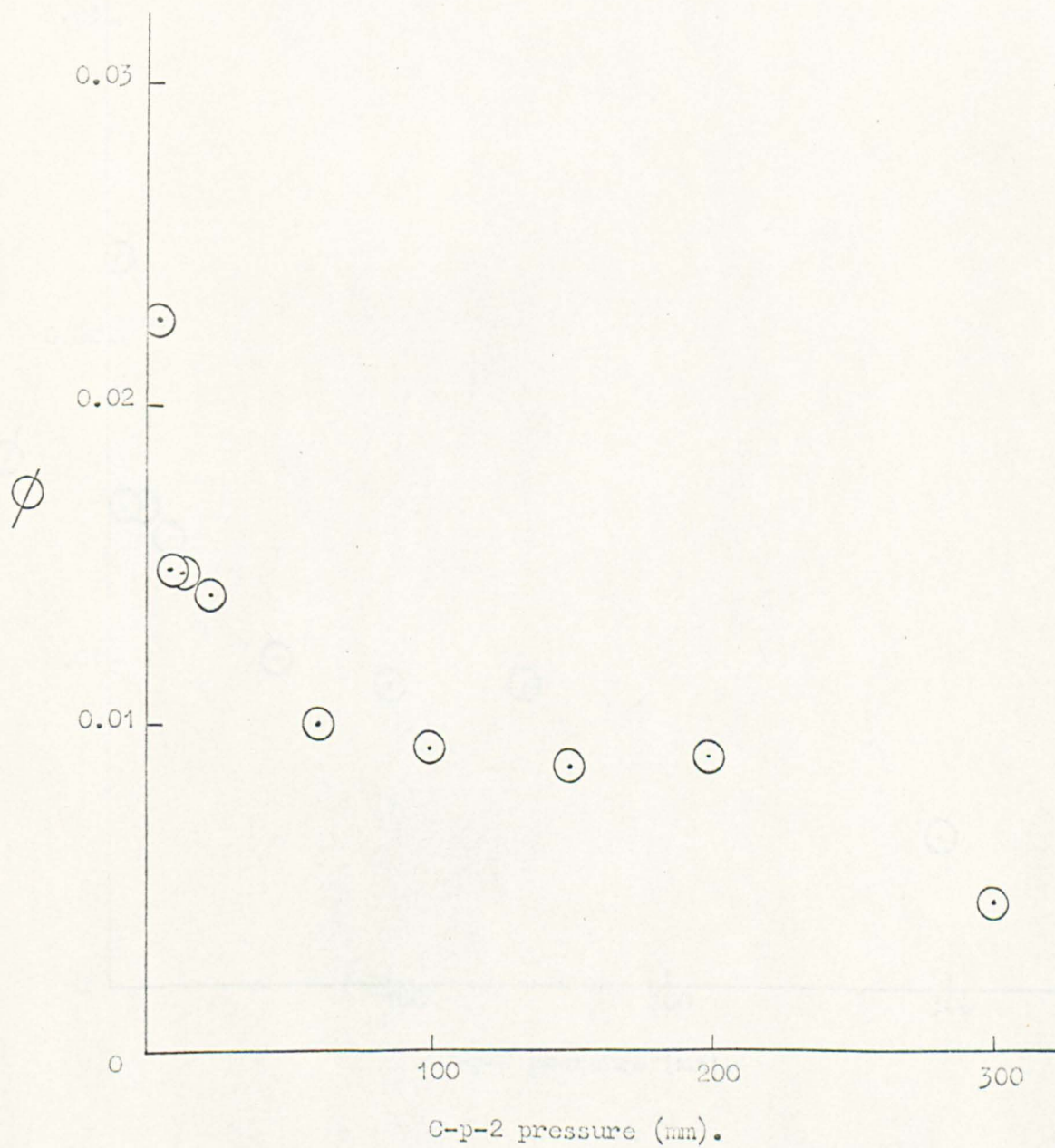

C-p-2 pressure (mm).

Figure 5.19

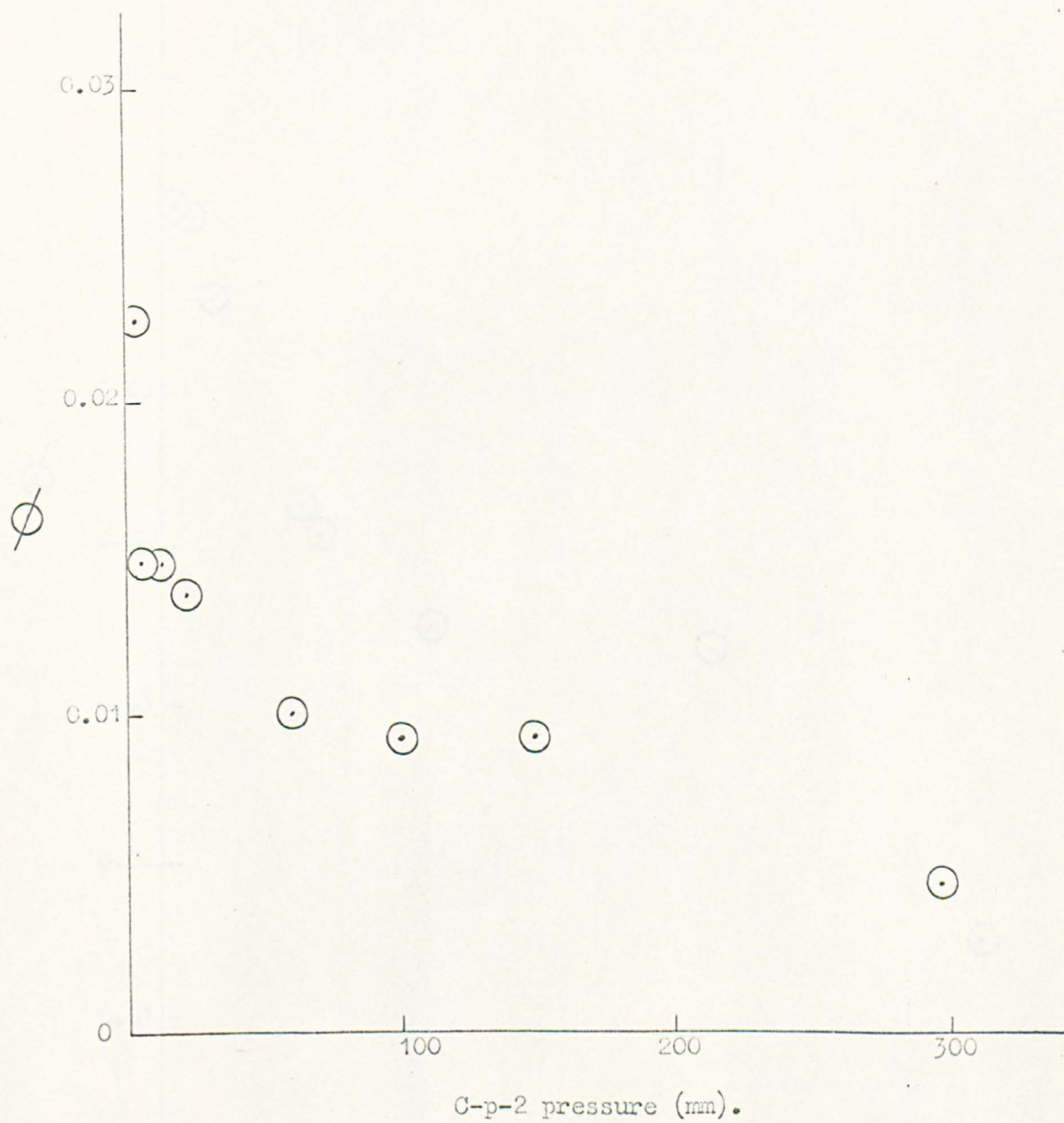Variation of propane yield with reactant pressure

Figure 5.20 Variation of but-1-ene yield with reactant pressure

Figure 5.21

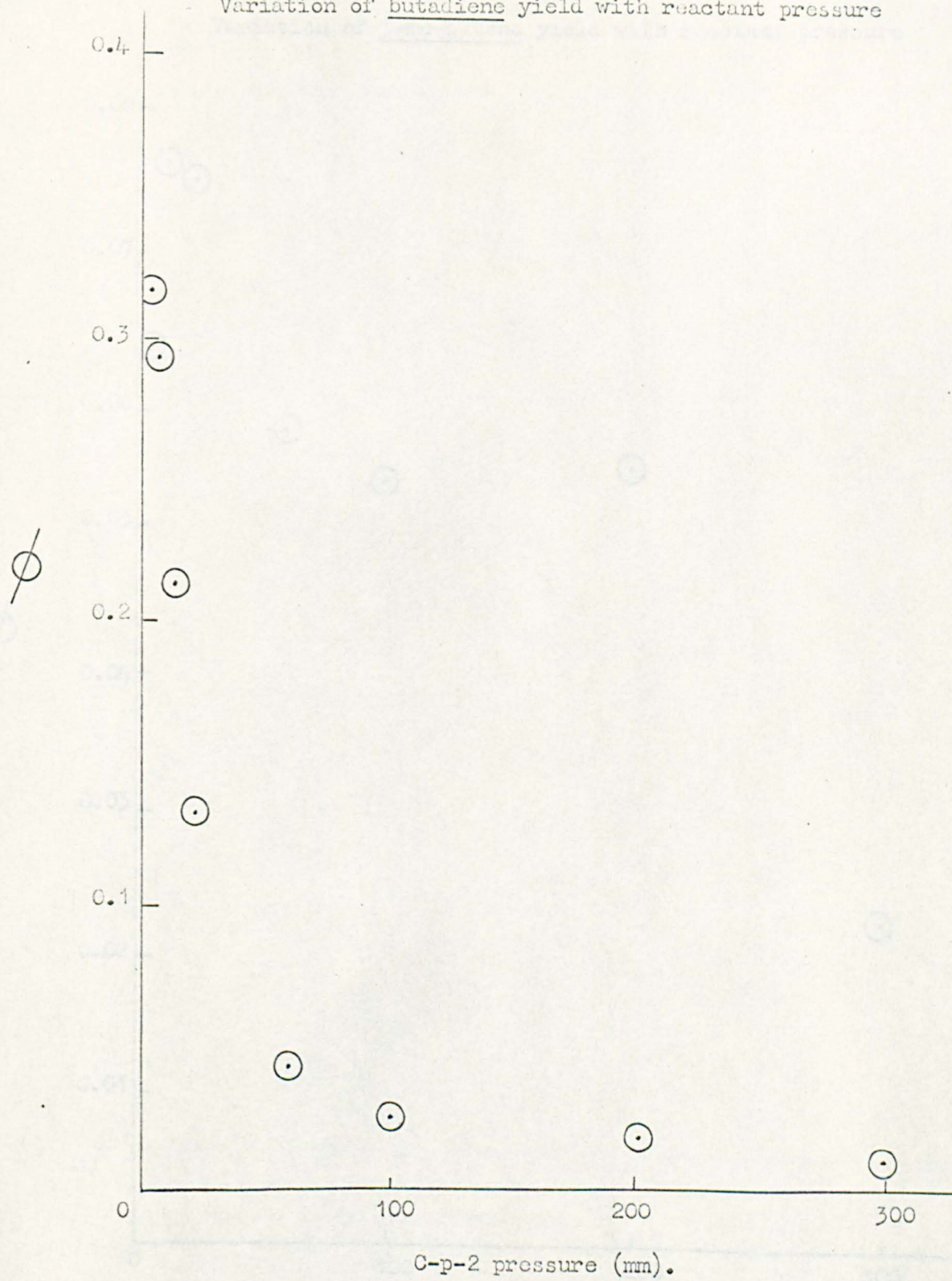Variation of butadiene yield with reactant pressure

Figure 5.22

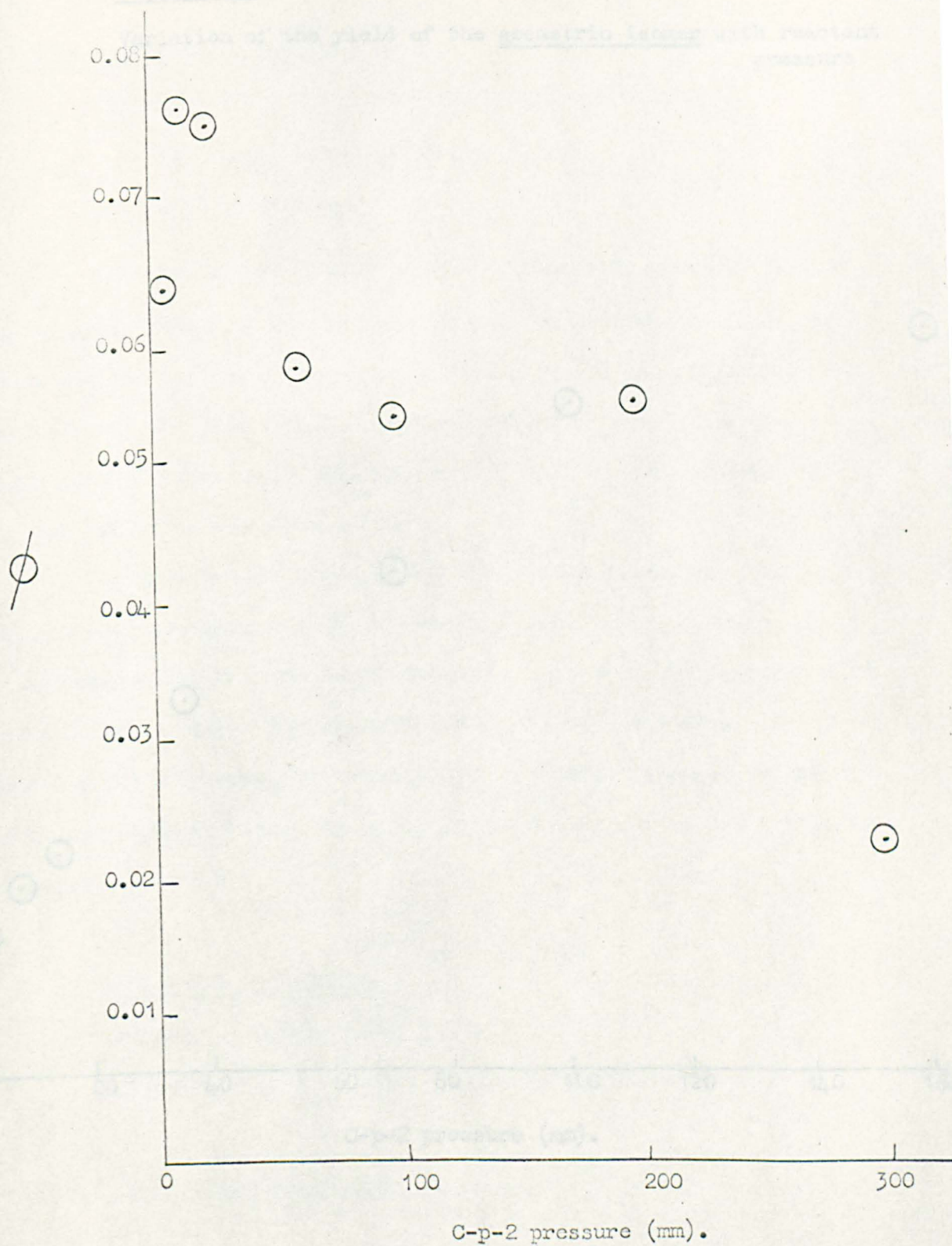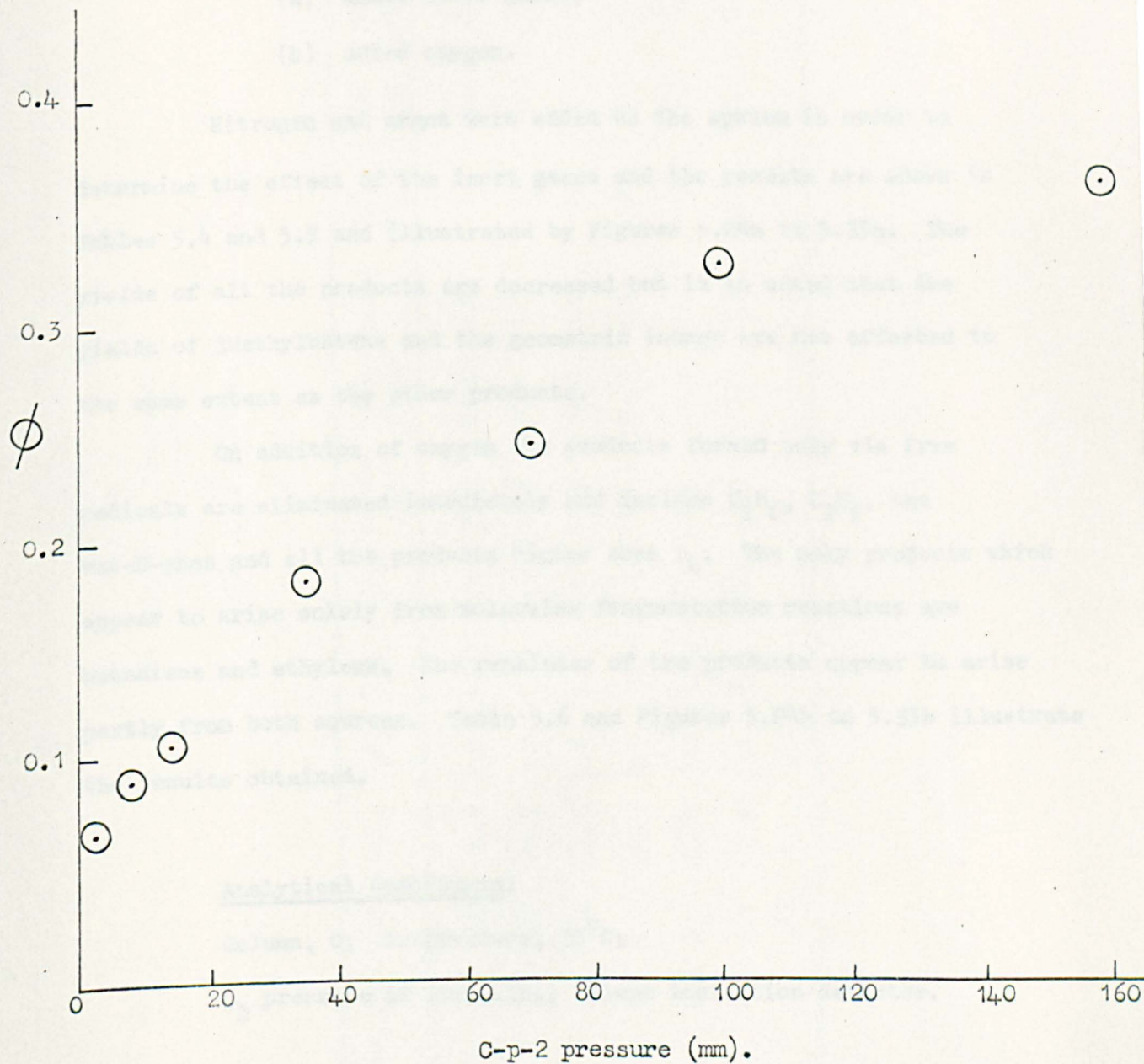Variation of 3-me-butene yield with reactant pressure

C-p-2 pressure (mm).

Figure 5.23

Variation of the yield of the geometric isomer with reactant pressure

ϕ

C-p-2 pressure (mm).

5.3 Effect of Added Foreign Gases

The added gases are divided into two subsections:

(a) added inert gases,

(b) added oxygen.

Nitrogen and argon were added to the system in order to determine the effect of the inert gases and the results are shown in Tables 5.4 and 5.5 and illustrated by Figures 5.24a to 5.35a. The yields of all the products are decreased but it is noted that the yields of 3Methylbutene and the geometric isomer are not affected to the same extent as the other products.

On addition of oxygen the products formed only via free radicals are eliminated immediately and include C_2H_6, C_2H_2, the but-2-enes and all the products higher than C_4. The only products which appear to arise solely from molecular fragmentation reactions are butadiene and ethylene. The remainder of the products appear to arise partly from both sources. Table 5.6 and Figures 5.24b to 5.31b illustrate the results obtained.

Analytical Conditions:

Column, 0; temperature, $35^{\circ}C$;

N_2 pressure 12 lb/sq.in.; flame ionisation detector.

Key to Figures 5.24 to 5.35

⊙ Argon,   ▽ Nitrogen,   △ Oxygen.

Table 5.4

Effect of Nitrogen

(Moles x 10^9/minute)

Pressure mm	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_8	but-1-ene	buta-diene	c-b-2	*18.3 mins	3Me butene	2Me butene	t-p-2
0	8.4	9.7	78.2	2.0	4.0	4.0	15.6	83.5	0.40	26	13.4	8.0	15.7
25	7.6	9.0	76.9	1.9	3.3	3.3	13.4	50.0	0.33	25	12.7	7.3	14.9
50	6.3	5.2	63.6	1.6	2.0	2.1	8.9	32.0	0.23	20	12.0	5.3	13.5
100	5.5	4.4	60.0	1.5	1.9	2.0	7.6	19.9	0.22	18	11.7	4.3	12.7
220	4.2	2.7	51.0	1.3	1.6	1.8	6.4	10.2	0.20	15	10.2	3.0	12.1
300	4.0	2.5	51.2	1.3	1.5	1.7	6.0	7.9	0.17	14	10.1	2.7	11.4

Table 5.5

Effect of Argon

$(Moles \times 10^9/minute)$

Pressure mm	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_8	but-1-ene	buta-diene	c-b-2	*18.3 mins	3Me butene	2Me butene	t-p-2
0	8.4	9.7	78.2	2.0	4.0	4.0	15.6	83.5	0.40	26	13.4	8.0	15.7
20	7.7	9.0	76.8	1.9	3.3	3.3	13.6	51.0	0.32	26	12.7	7.4	15.4
60	6.1	5.2	62	1.6	2.1	2.1	9.0	31.0	0.22	18	12.0	5.4	14.6
120	5.3	4.3	59	1.5	1.8	1.8	7.6	19.5	0.23	16	11.6	4.3	13.9
230	4.2	2.7	49	1.2	1.6	1.7	6.1	10.3	0.20	15	10.1	3.0	12.2
320	3.9	2.5	49	1.2	1.4	1.6	6.0	7.9	0.18	14	10.0	2.6	11.5

Table 5.6

Effect of Oxygen

(Moles x 10^9/minute)

Pressure mm	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_8	C_3H_4	but-1-ene	buta-diene	c-b-2	3Me butene	*18.3 mins	2Me butene	t-p-2
0	8.4	9.7	78.2	2.0	4.0	4.0	0.12	15.6	83.5	0.4	13.4	26	8.0	15.7
25	1.4	6.8	–	–	0.61	0.62	0.06	–	40.0	–	–	–	–	–
50	1.2	4.4	–	–	0.40	0.41	0.03	–	21.7	–	–	–	–	–
100	0.9	4.6	–	–	0.37	0.37	0.03	–	20.0	–	–	–	–	–
200	0.9	2.7	–	–	0.33	0.34	–	–	7.3	–	–	–	–	–
300	0.5	1.7	–	–	0.28	0.29	–	–	6.2	–	–	–	–	–

Figure 5.24a

Variation of methane yield with added inert gas pressure

Figure 5.24b
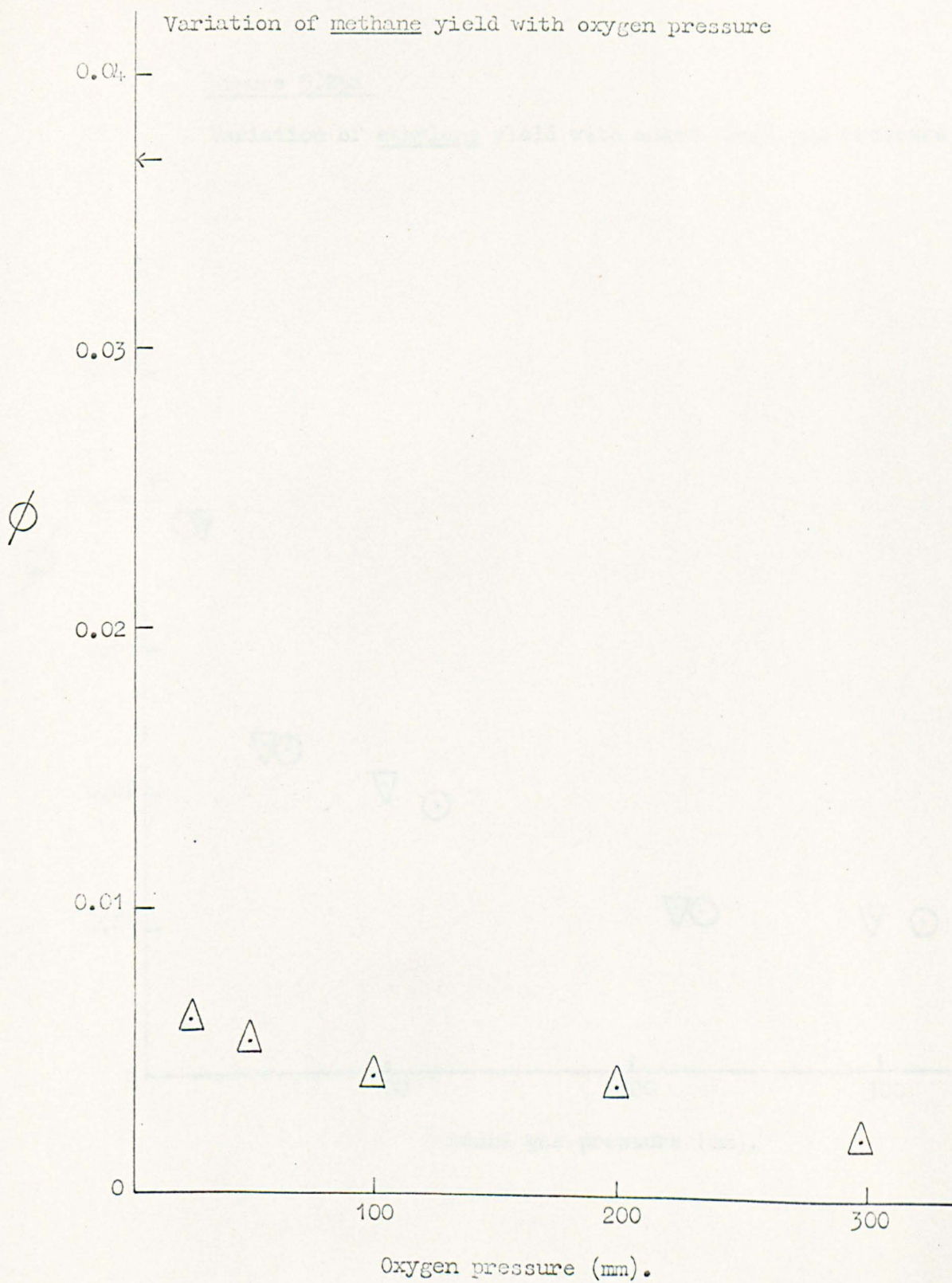
Variation of methane yield with oxygen pressure

Figure 5.25a

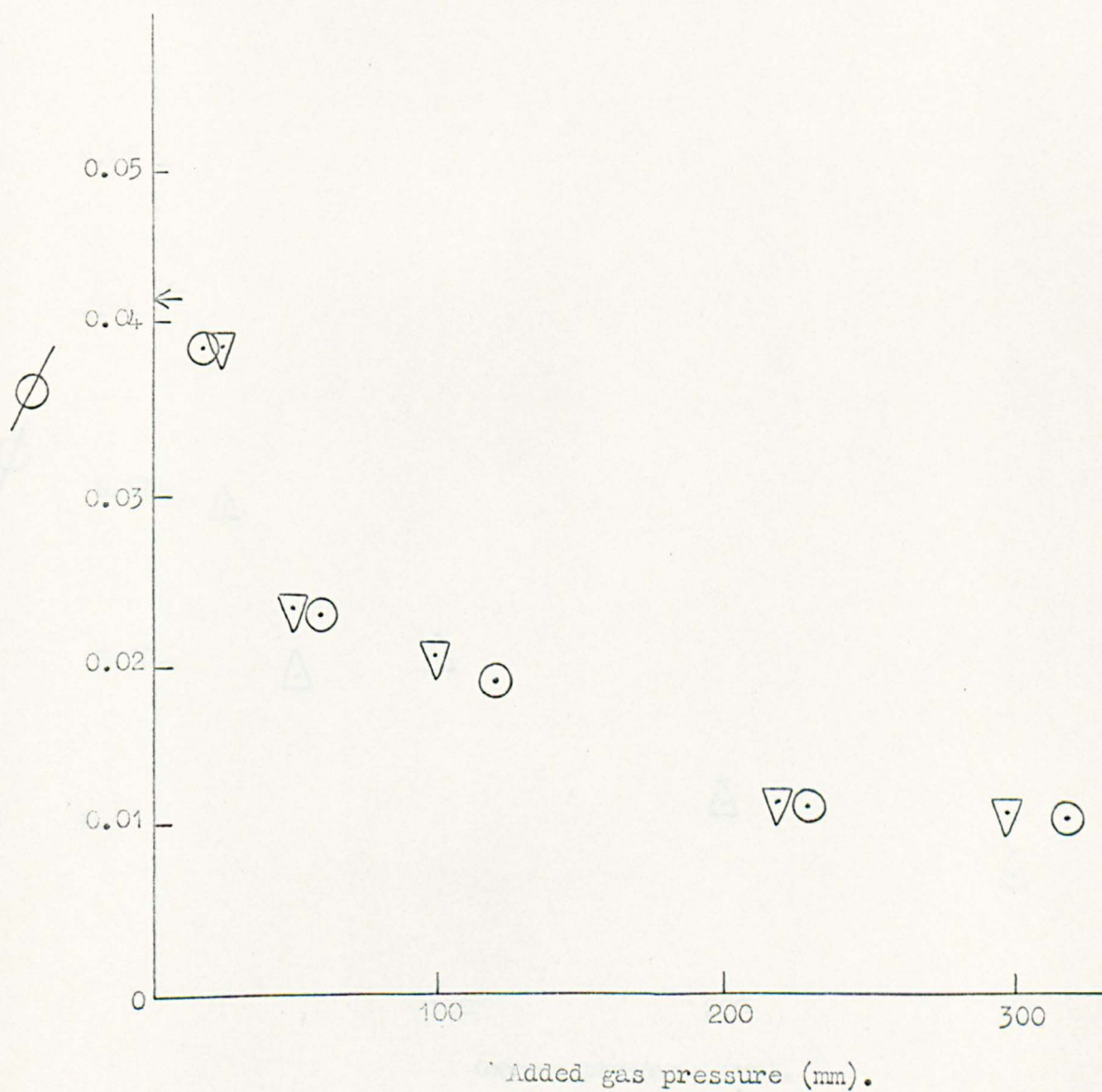Variation of ethylene yield with added inert gas pressure

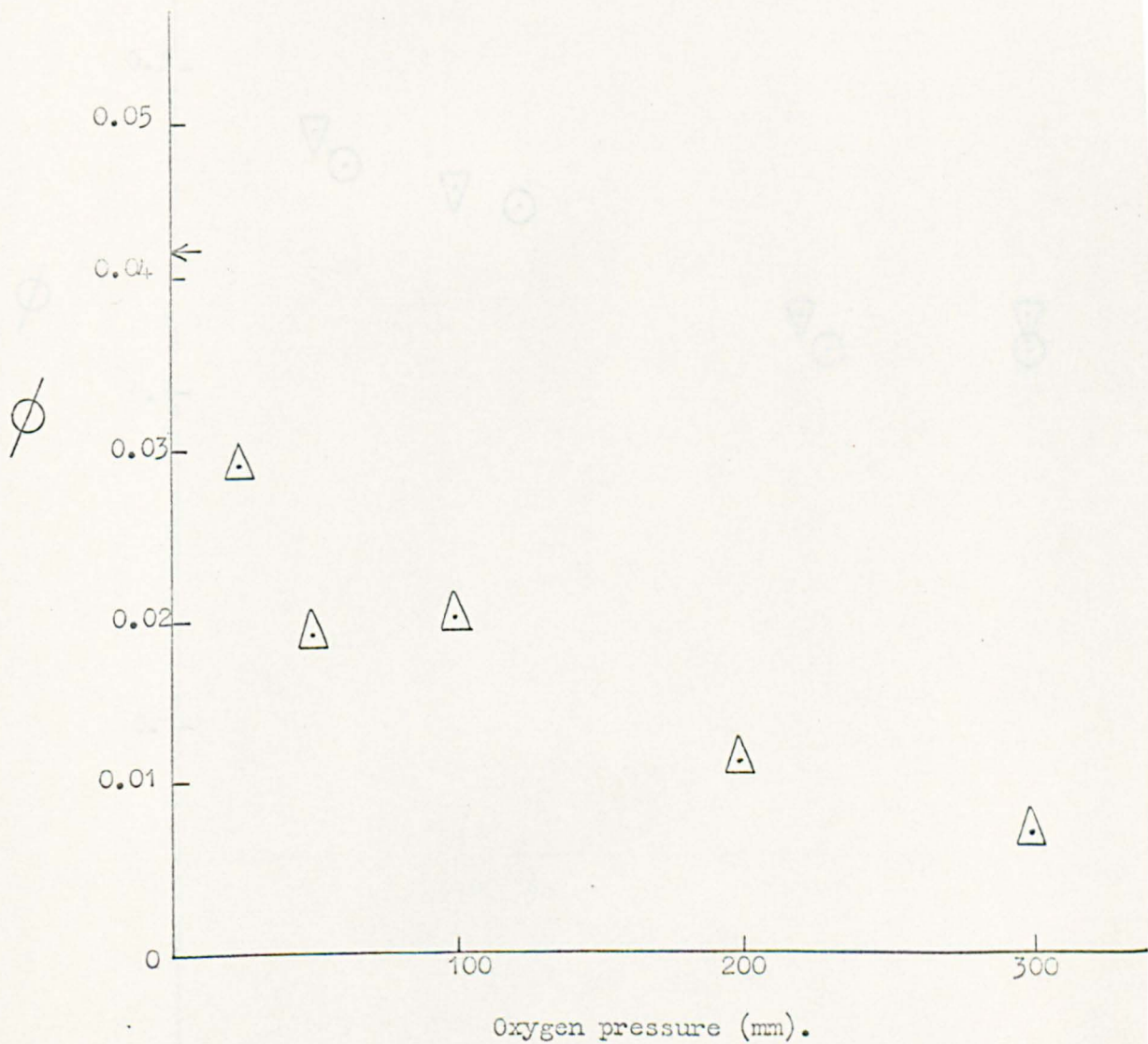Figure 5.25b

Variation of ethylene yield with oxygen pressure

Figure 5.26a

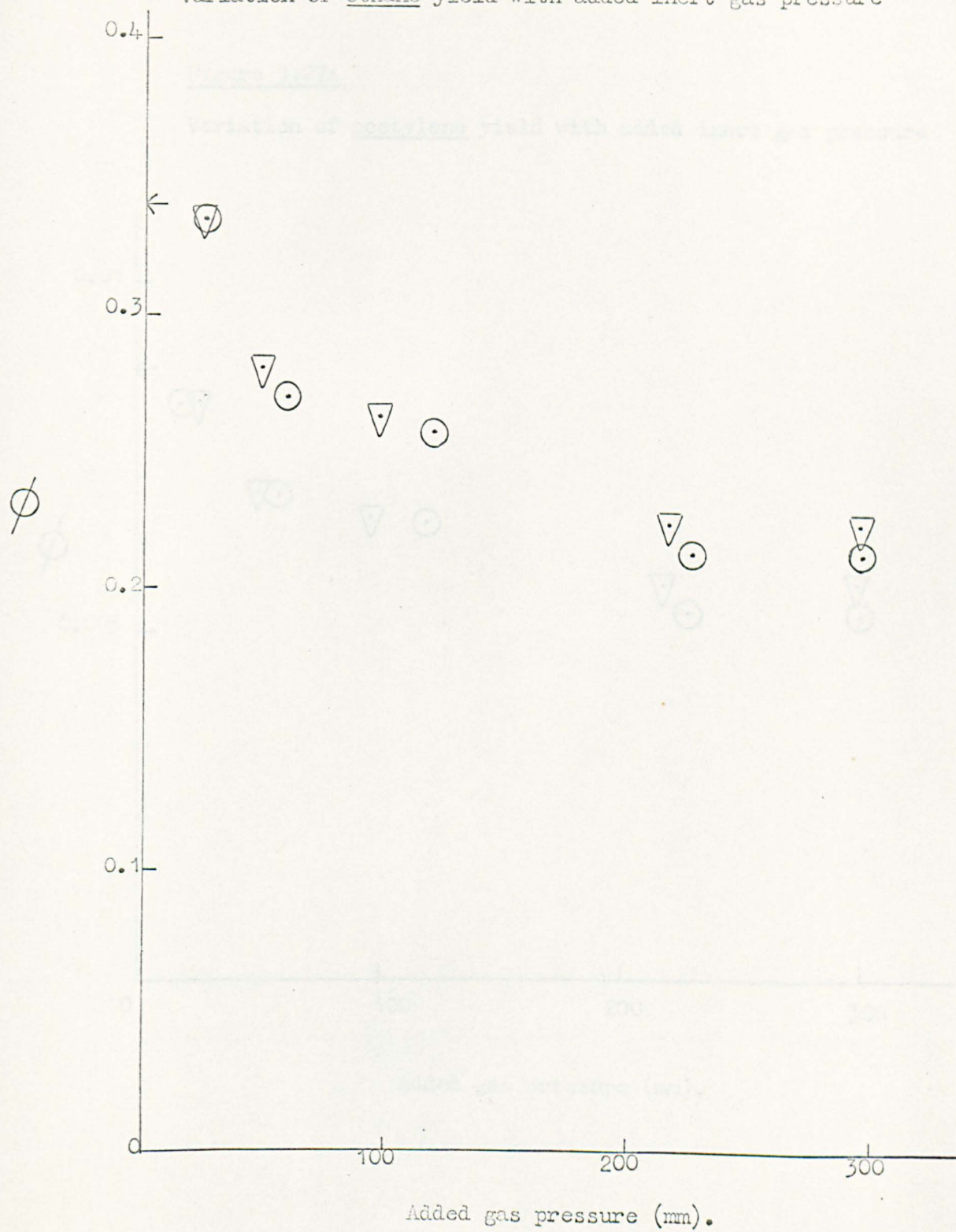Variation of _ethane_ yield with added inert gas pressure

Added gas pressure (mm).

Figure 5.27a

Variation of acetylene yield with added inert gas pressure

Figure 5.28a

Variation of propylene yield withadded inert gas pressure

Added gas pressure (mm).

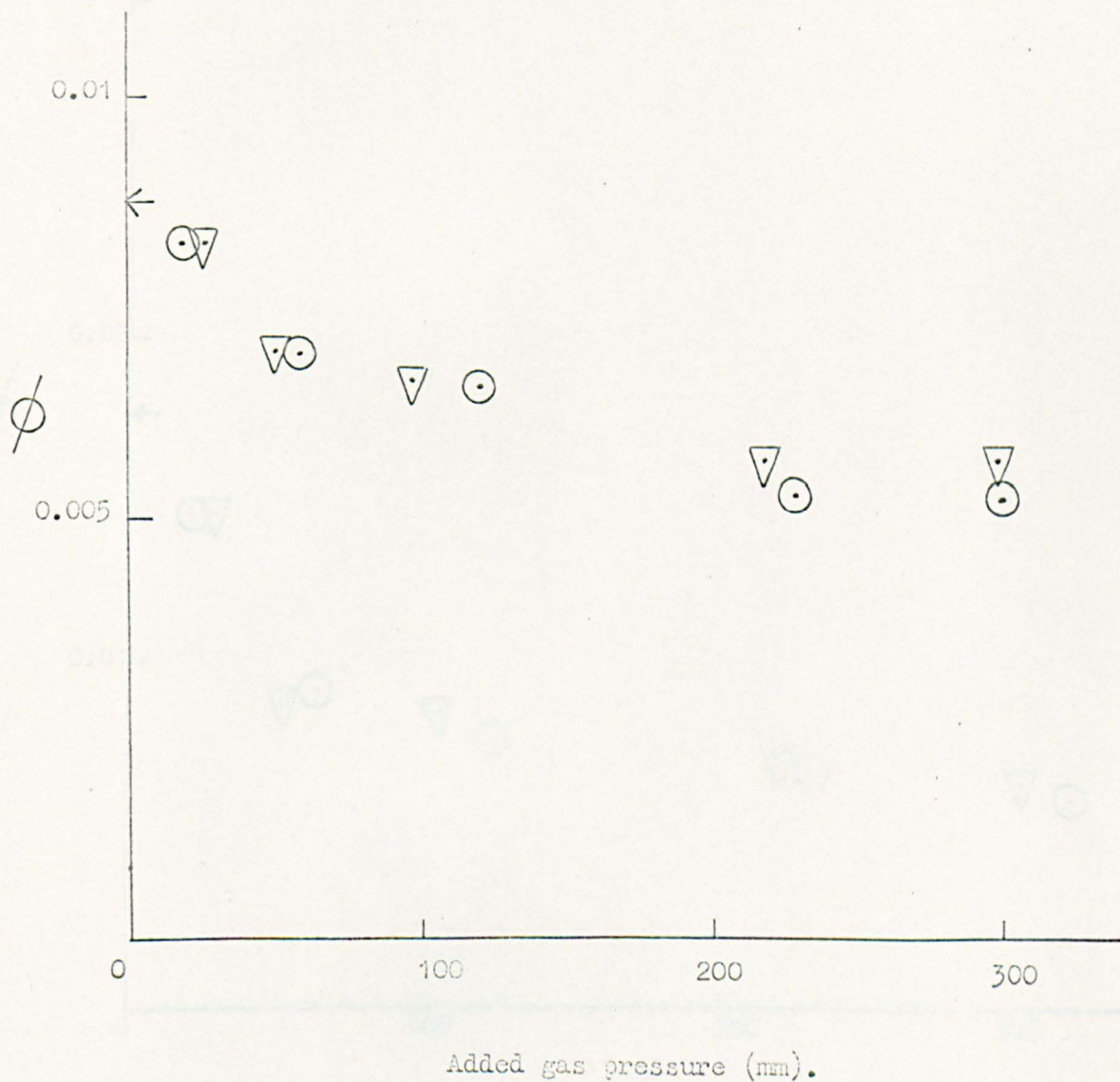Figure 5. 28b

Variation of propylene yield with added oxygen
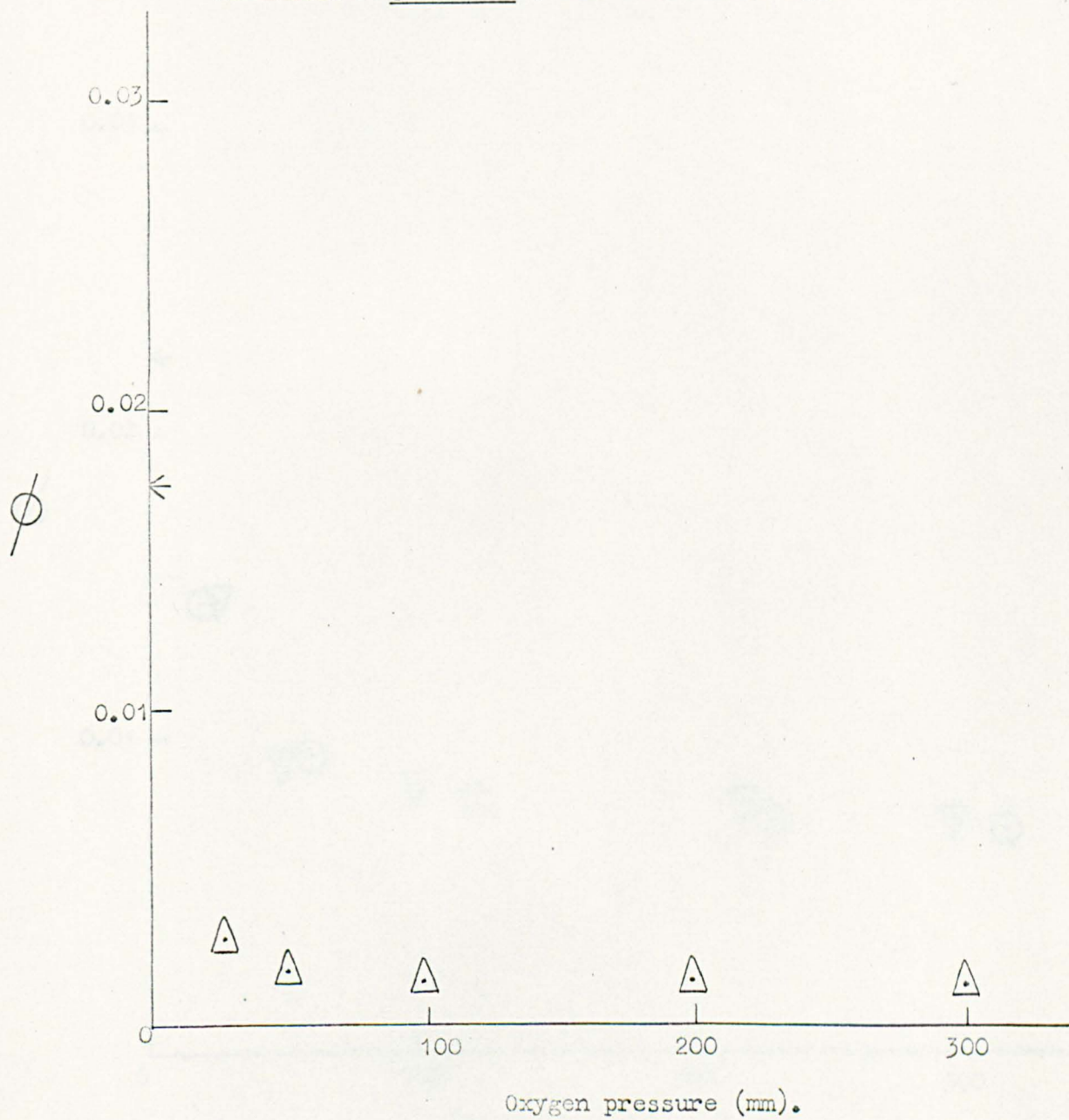
Figure 5.29a

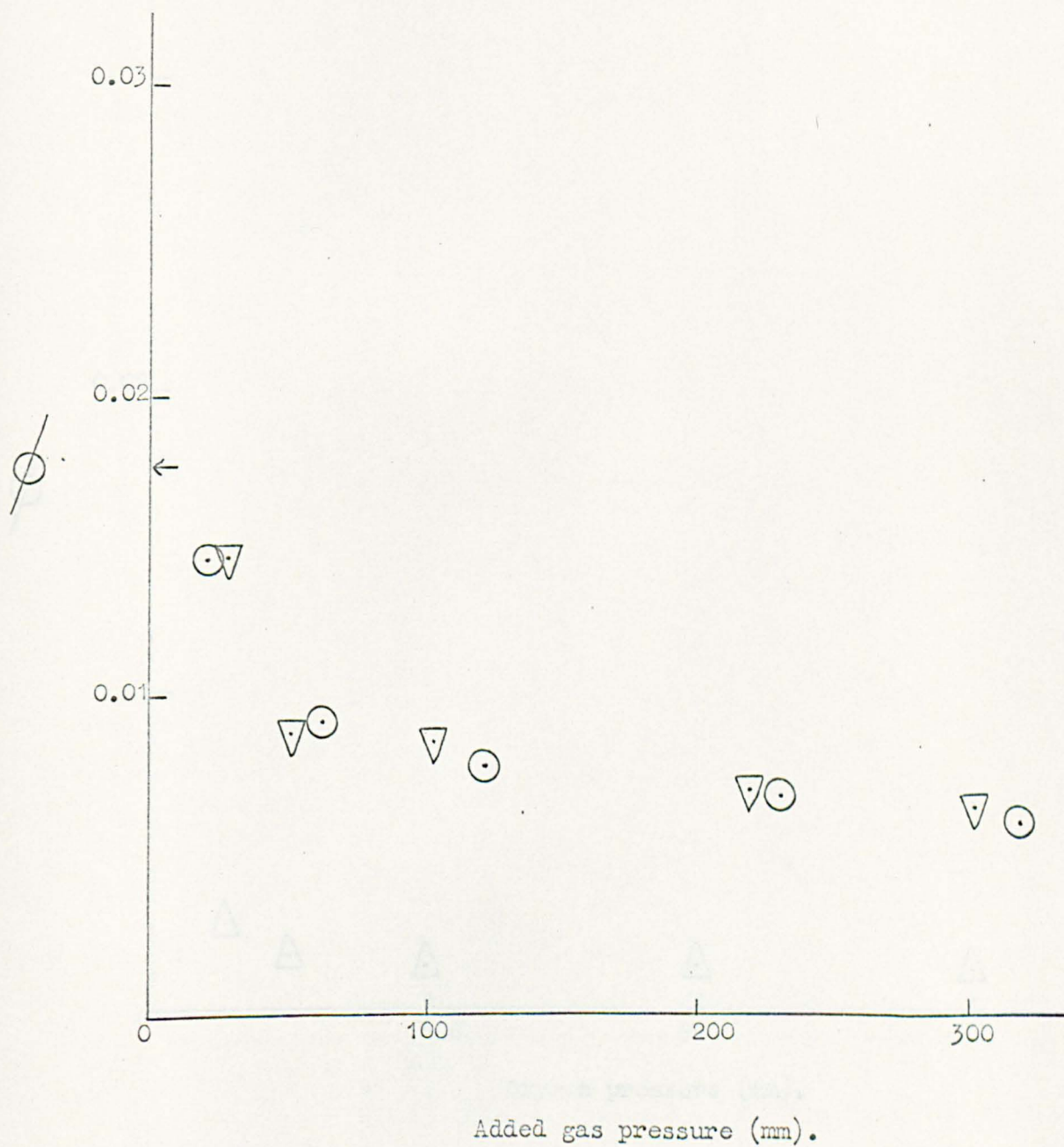Variation of propane yield with added inert gas pressure
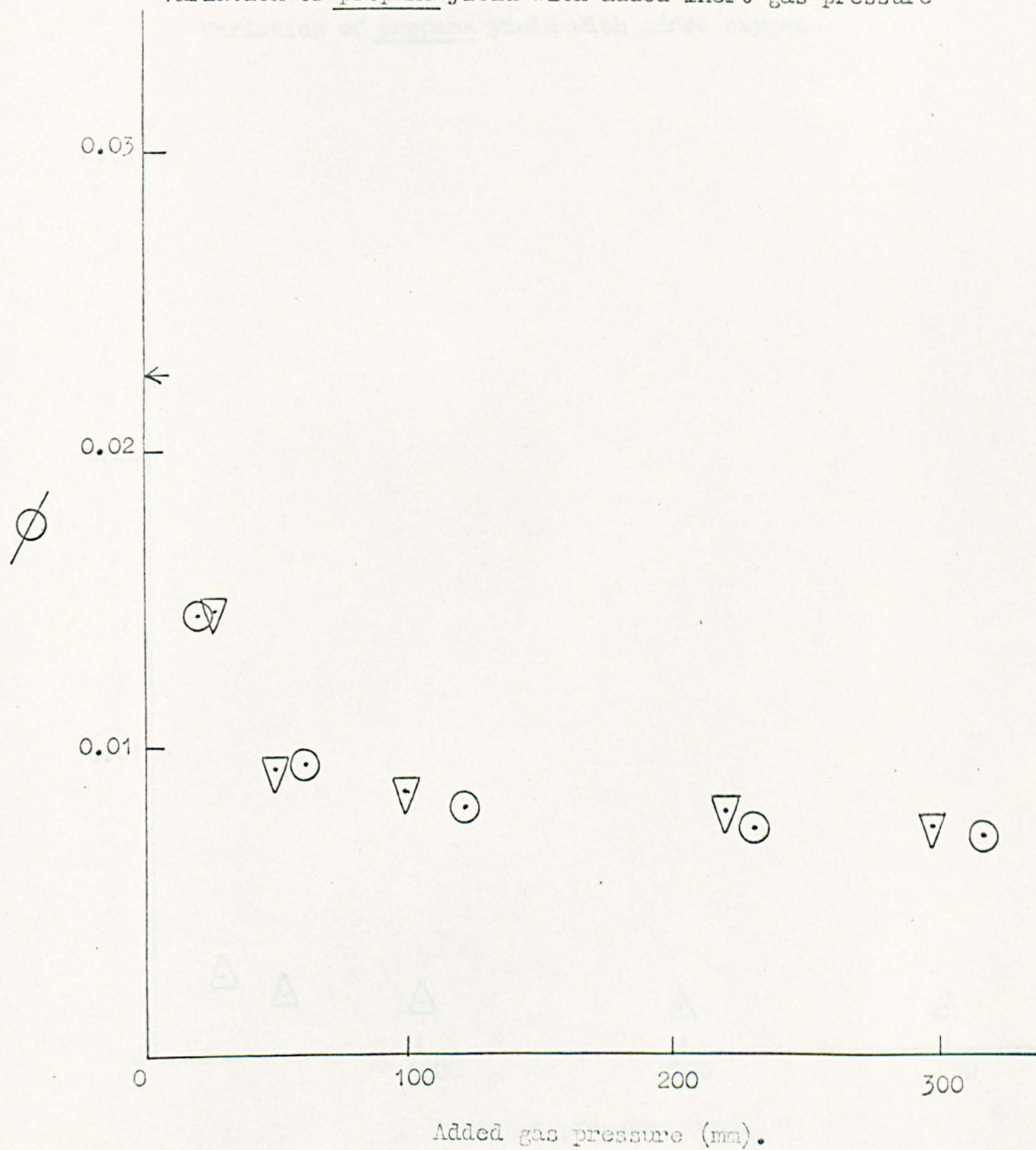
Figure 5.29b

Variation of propane yield with added oxygen
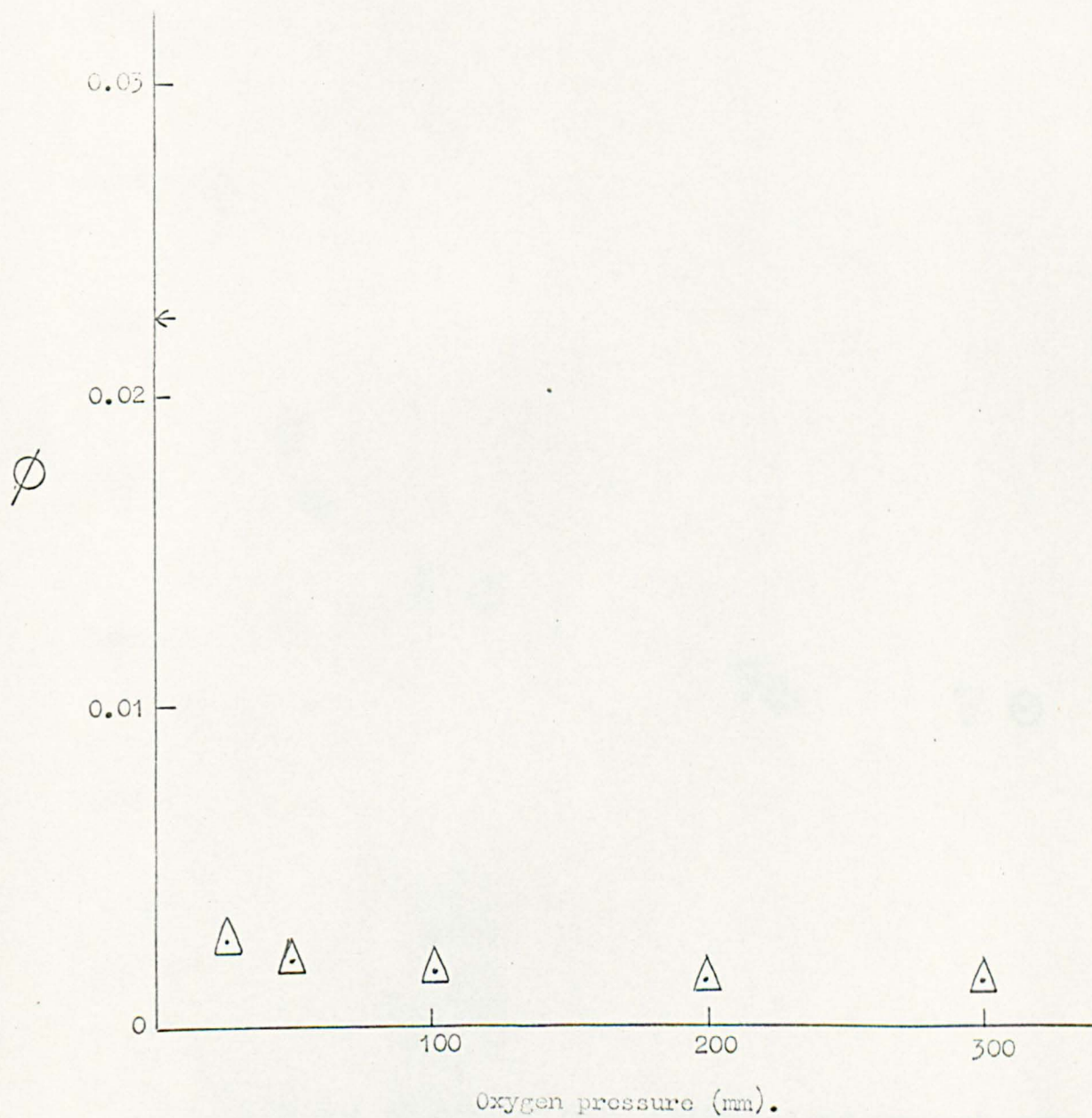
Figure 5.30a

Variation of but-1-ene yield with added inert gas pressure
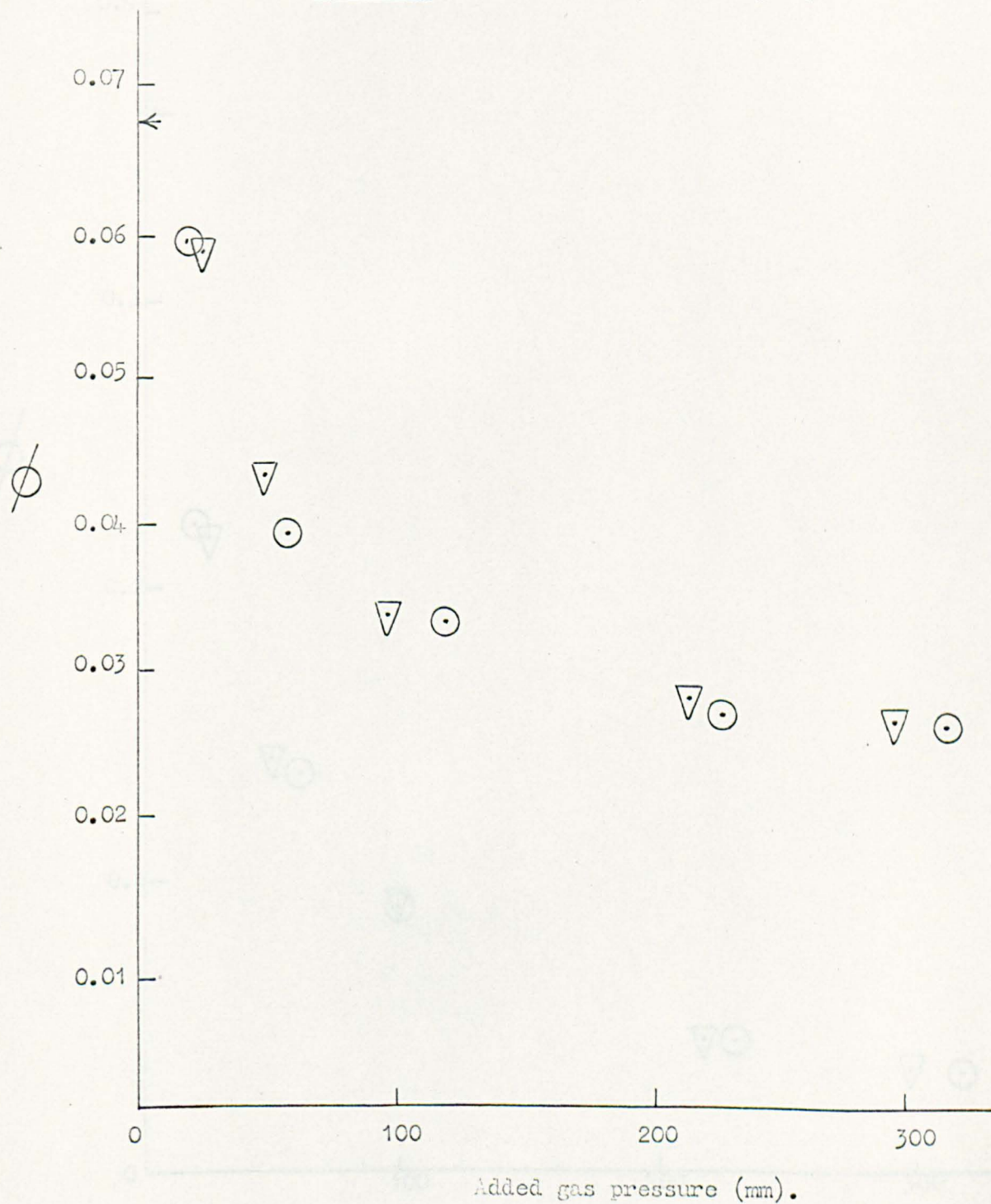
Figure 5.31a

Variation of butadiene yield with added inert gas pressure

Added gas pressure (mm).

Figure 5.31b

Variation of butadiene yield with added oxygen pressure

Oxygen pressure (mm).

Figure 5.32a

Variation of 3-me-butene yield with added inert gas pressure
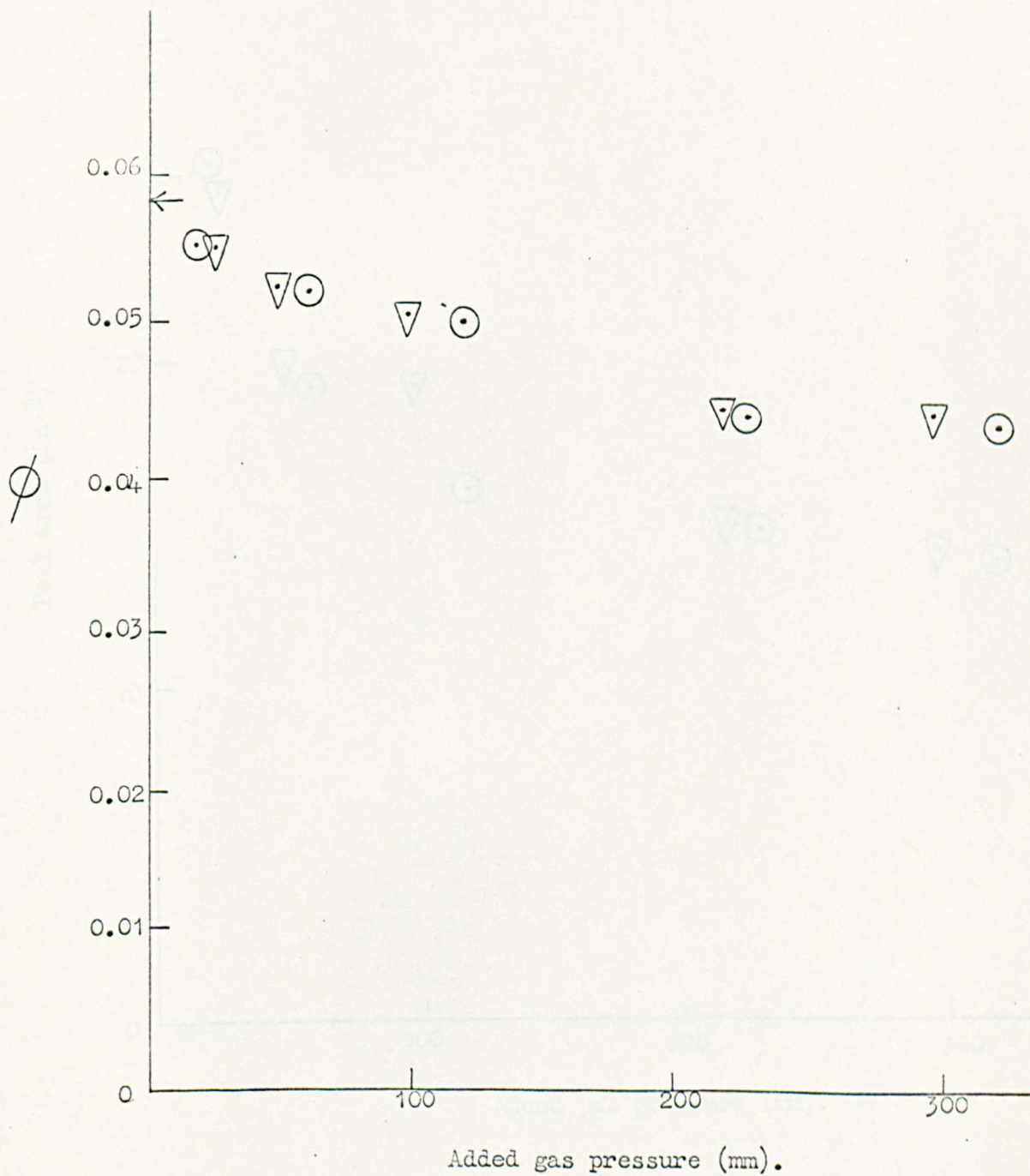
Figure 5.33a

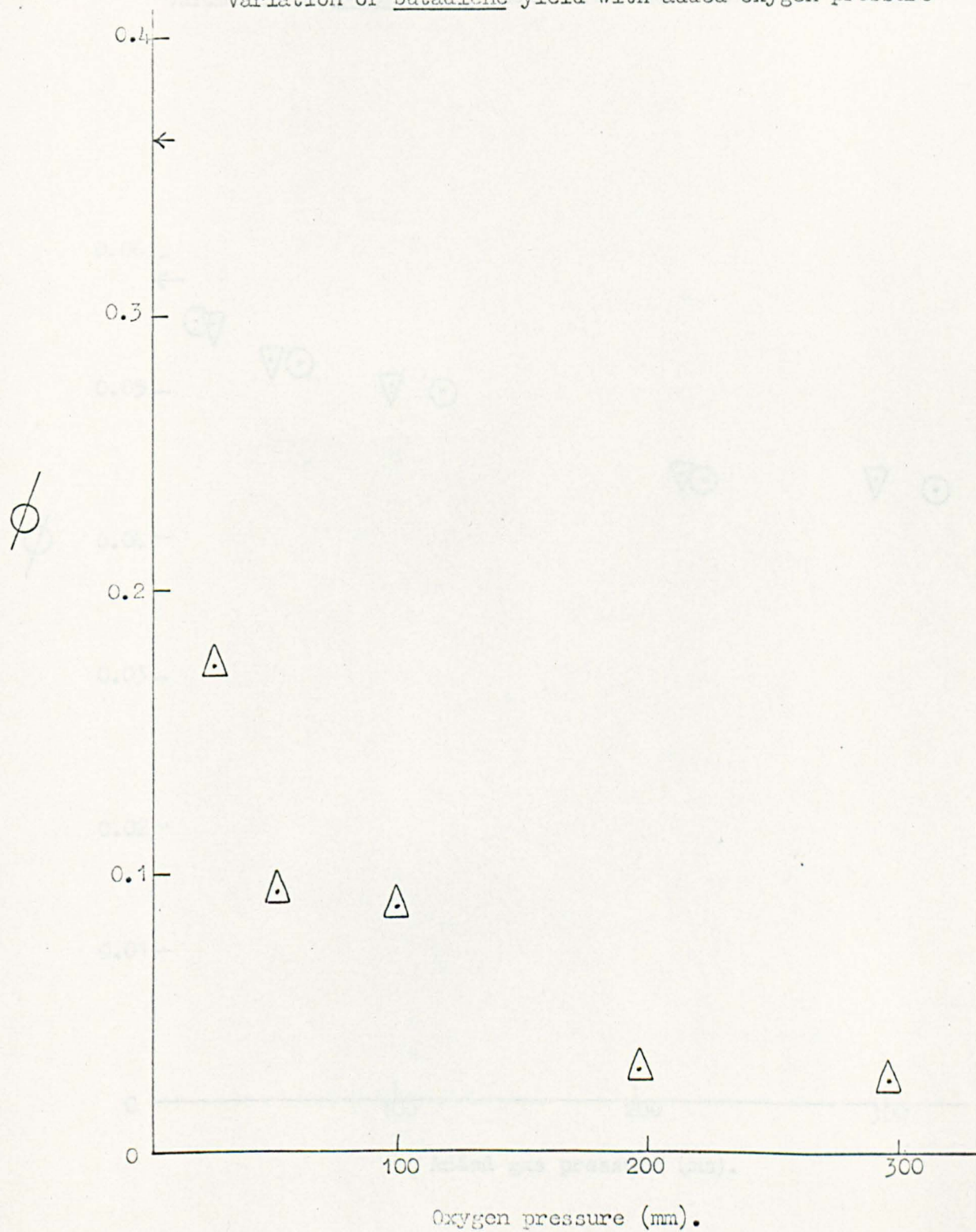Variation of the peak area of the product of retention time 18·3 mins with added gas pressure
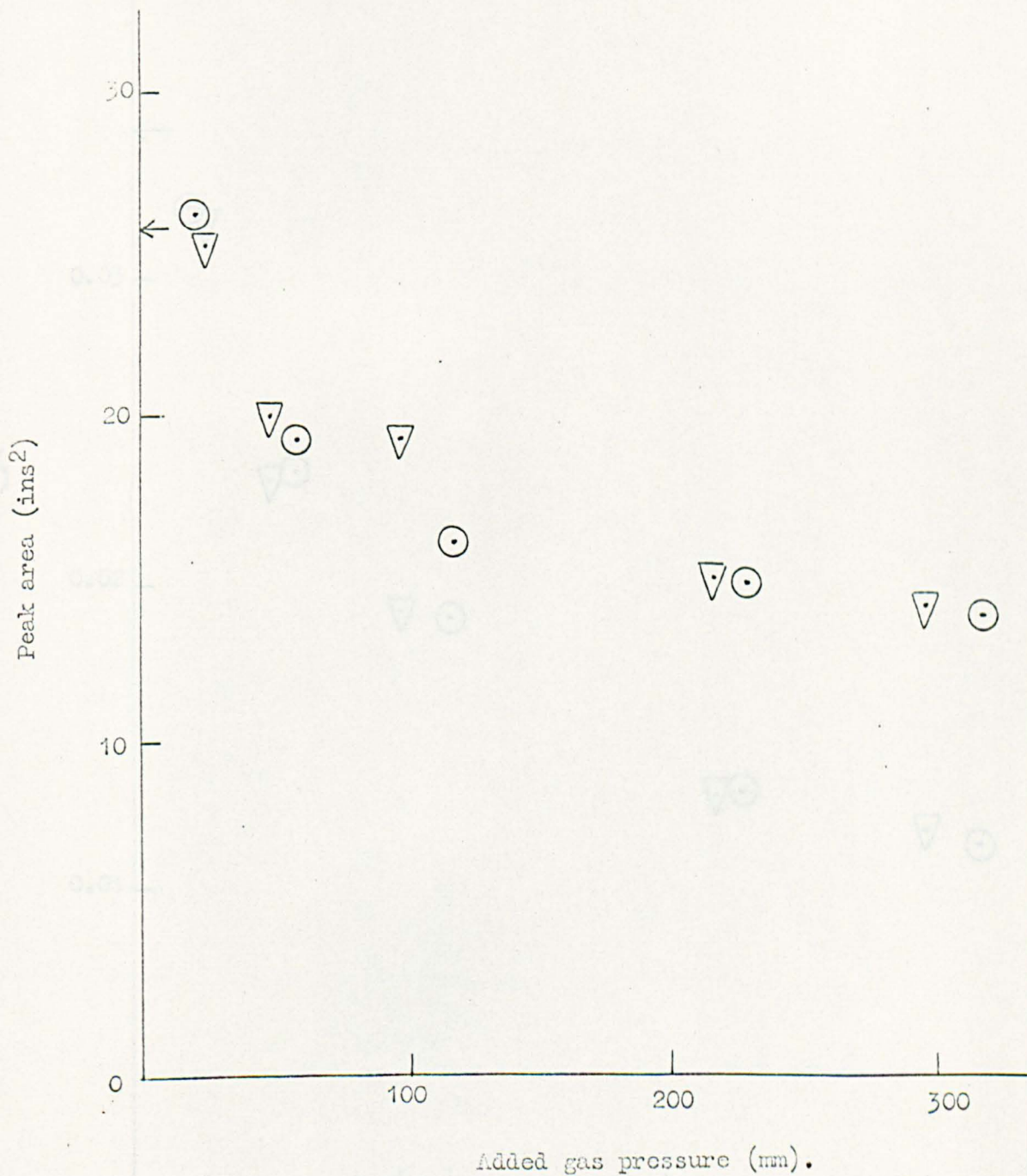
Figure 5. 34a

Variation of 2-me-butene yield with added inert gas pressure

Added gas pressure (mm).

Figure 5.35a

Variation of geometric isomer yield with added inert gas pressure

Added gas pressure (mm).
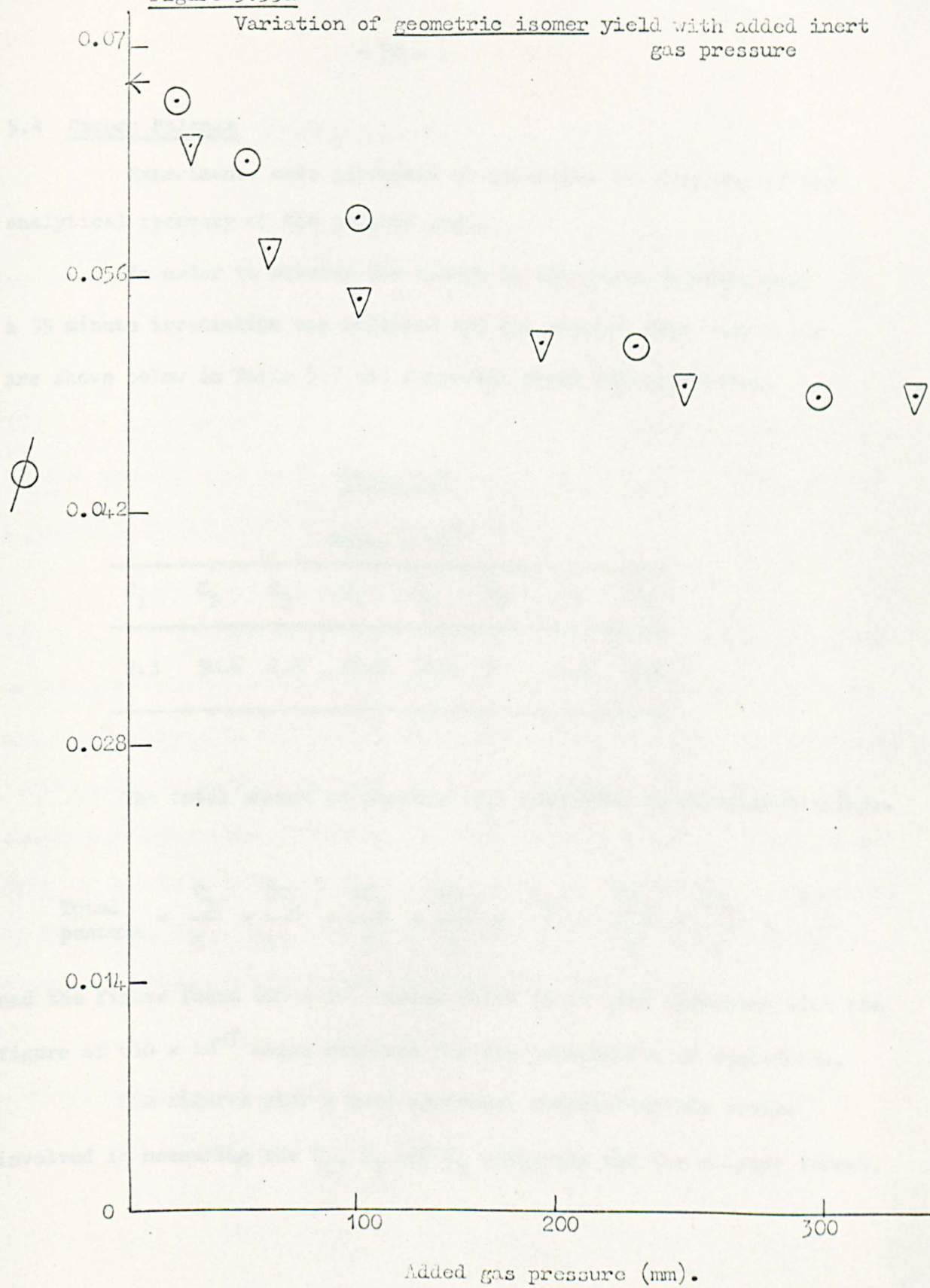
5.4 Carbon Balance

Experiments were performed to determine the accuracy of the analytical recovery of the pentene used.

In order to observe the change in the large reactant peak a 35 minute irradiation was required and the results from such a run are shown below in Table 5.7 and represent about 60% conversion.

Table 5.7

Moles x 10^7

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
2.3	30.6	2.4	20.2	10.6	5	4.4	6.4

The total amount of pentene (C_5) recovered is calculated using:-

$$\text{Total pentene} = \frac{C_1}{5} + \frac{2C_2}{5} + \frac{3C_3}{5} + \frac{4C_4}{5} + C_5 + \frac{6C_6}{5} + \frac{7C_7}{5} + \frac{8C_8}{5}$$

and the figure found 600×10^{-7} moles which is in good agreement with the figure of 610×10^{-7} moles obtained for the consumption of pent-2-ene.

The figures show a good agreement considering the errors involved in measuring the C_6, C_7 and C_8 compounds and the polymer formed.

5.5 Summary of Cis Pent-2-ene Results

(1)   The yields of all the products increased linearly with time up to 30 minutes thereafter the rate decreased due to the formation of a solid polymer on the cell window.

(2)   On increasing the reactant pressure the yields of all but one of the products were decreased, the yield of the geometric isomer showed a marked increase with cis pent-2-ene pressure.

(3)   The addition of foreign gases to the system decreased the yield of the products and on adding oxygen the yields of C_2H_6, C_2H_2, but-1-ene and the C_5 compounds were eliminated illustrating that these products were formed wholly from free radical reactions. Ethylene and butadiene were shown to arise solely from molecular fragmentation reactions since oxygen only had the same effect as nitrogen or argon on their yields. The yields of CH_4, C_3H_4, C_3H_6, C_3H_8 were affected more by oxygen than they were by nitrogen or argon but they were not completely eliminated.

6. DISCUSSION: But-1-ene

6. Discussion of But-1-ene Results

The results from the experiments (Section 3) enable the products to be divided into two categories; those whose yields are affected equivalently by inert gases and by oxygen, being formed by molecular fragmentation processes in the primary reactions; and those whose yields are severely reduced by oxygen are formed via free radical reactions.

Methane (at 6 mm. but-1-ene pressure), ethylene, allene, acetylene and to some extent ethane, propylene and the but-2-enes are examples of products formed by molecular fragmentation processes, whereas the C_5 products cannot be formed in any other way than from free radical reactions. From the number of products formed and their relative yields it is concluded that a number of primary reactions are operative in their formation. The reactions postulated are shown below in their probable order of importance, each reaction is discussed in detail also.

6.1 Primary Reactions

			$\emptyset^{\neq}$
1) C_4H_8-1*	$\longrightarrow$	$CH_3\cdot + \cdot CH_2\text{-}CH\text{=}CH_2$	0.51
2)	$\longrightarrow$	$H\cdot + CH_3\text{-}\overset{\bullet}{C}H\text{-}CH\text{=}CH_2$	0.09
3)	$\longrightarrow$	$2C_2H_4$	0.07
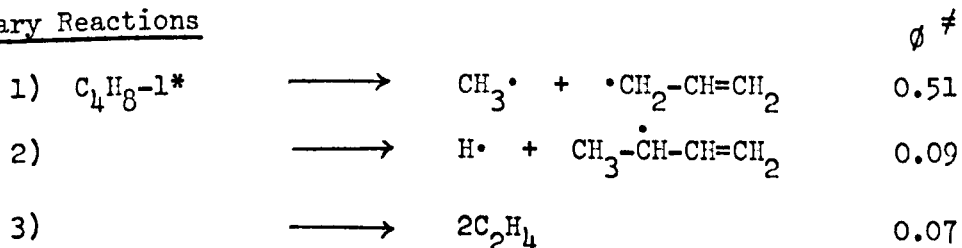
4)	$\longrightarrow$	$CH_4 + C_3H_4$	0.031
5)	$\longrightarrow$	$C_2H_6 + C_2H_2$	0.008
6)	$\longrightarrow$	$:CH_2 + C_3H_6$	0.007
7)	$\longrightarrow$	C_4H_8-2 (cis/trans)	0.007

$\neq$ The quantum yields for reactions 1) and 2) are estimated after consideration of the yields of the secondary products and can only be regarded as minimum values (see later). The quantum yields of the remainder of the reactions are estimated after extrapolating the product yield to zero pressure.

The most important reaction is 1) the cleavage of the C-C bond β to the double bond, this being 5.7 times greater than 2) the cleavage of the C-H bond β to the double bond. No evidence was found for any α C-C bond cleavage to yield ethyl and vinyl radicals. This is in accordance with estimates for the relative bond dissociation energies, the C-C bond in the β position being 28 kcal/mole less energetic than the corresponding α C-C bond.[79] Other workers have also observed this preferential cleavage at 1849 $\overset{o}{A}$.[77] Mercury sensitised at 2537 $\overset{o}{A}$ studies yielded a figure of 1.3 to 1.6 to 1 for the same ratio.[57]

The remainder of the reactions are molecular fragmentations. Reaction 3) is postulated since there seems to be no other processes which account for the similarity of the effect of oxygen and added inert gases on the yield of ethylene. On the same basis reaction 4) accounts for the rough equivalence of the methane yield with that of allene, the
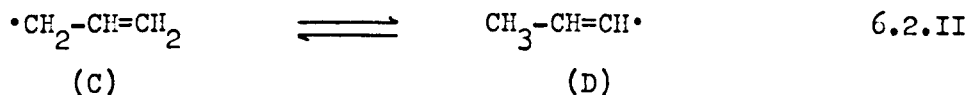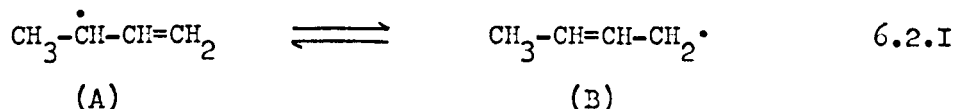
slight excess of methane being readily attributed to hydrogen abstraction by methyl radicals from the reactant (Figure 3.30). Reaction 5) accounts for both acetylene and the small fraction of ethane which is of molecular rather than free radical origin. Reaction 6) is suggested after consideration of the work of Okabe, Beckey and Groth,[78] using a Field Ion Mass Spectrometer, who found evidence for the presence of methylene radicals. This reaction would account for the 20% (maximum) of the propylene yield which is not eliminated by oxygen.

Reaction 7) is of interest since there seems to be some specificity, for more cis but-2-ene is formed than the trans isomer. This is not in accordance with the observations of Harumiya, Shida and Arai.[77] An even greater specificity has been observed in the photolysis of isobutene (see Table 4.1 for ratio trans/cis).

Measurements were not undertaken to categorise the hydrogen produced since it is a very minor product and estimation using a hot-wire detector is much less accurate than using the flame ionisation detector (see Table 3.1 for relative yield).

6.2 Secondary Reactions

The primary reactions give rise to five free radicals $H\cdot$; $\dot{C}H_3$; $\dot{C}H_2-CH=CH_2$; $CH_3-\dot{C}H-CH=CH_2$ and $\dot{C}H_2$. The last radical, methylene, will almost certainly react with the but-1-ene to produce pentene. The two larger radicals probably equilibriate with their isomers.

$$CH_3-\overset{\bullet}{CH}-CH=CH_2 \quad \rightleftharpoons \quad CH_3-CH=CH-CH_2\bullet \qquad 6.2.I$$

$$(A) \qquad\qquad\qquad\qquad (B)$$

$$\bullet CH_2-CH=CH_2 \quad \rightleftharpoons \quad CH_3-CH=CH\bullet \qquad 6.2.II$$

$$(C) \qquad\qquad\qquad\qquad (D)$$

Reaction of (A) with $CH_3\bullet$ would yield 3-Methylbutene. (B) by reaction with methyl radicals gives rise to the pent-2-enes (c,t). Combination of either two together would yield the C_8 compounds.

Reaction of $CH_3\bullet$ with (D) would give rise to but-2-enes (c,t), whereas reaction of (C) with methyl radicals would give back the starting material.

The products may be mainly accounted for by radical recombination reactions i.e. $C_3 + C_3 = C_6$ etc. (activation energy $\sim$ zero[96]) rather than radical-olefin addition reactions (E_A for alkyl radical + C = C $\sim$ 5kcal/mole[97]), and in the temperature range studied radical disproportionations are insignificant compared with radical combination reactions. A possible exception in the secondary butyl radical which will be formed immediately ($E_A \sim$ 2kcal/mole) by addition of the hydrogen atom formed in 2) with but-1-ene.[97,98]

$$H\bullet + C_4H_8\text{-}1 \longrightarrow C_4H_9{}^* \qquad 6.2.III$$

which may decompose or be collisionally deactivated

$$C_4H_9* \longrightarrow CH_3\cdot + C_3H_6 \qquad 6.2.IV$$

$$C_4H_9* + M \longrightarrow C_4H_9\cdot + M \qquad 6.2.V$$

$$2C_4H_9\cdot \longrightarrow C_8H_{18} \text{ etc.} \qquad 6.2.VI$$
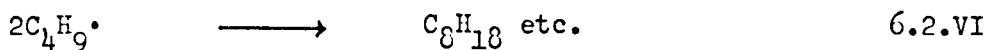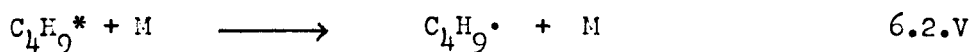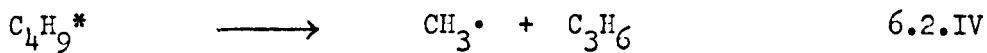
Reaction 6.2.IV would account for the remainder of the propylene yield and the greater effect of added gases on the propylene yield.

Hydrogen abstraction by H· radicals is unlikely[101] but evidence was found of the hydrogen abstraction by methyl from the but-1-ene to yield methane at higher reactant pressures. This was confirmed by temperature runs thus illustrating that there is an activation energy needed for the reaction:

$$CH_3\cdot + C_4H_8\text{-}1 \longrightarrow CH_4 + C_4H_7\cdot \qquad 6.2.VII$$
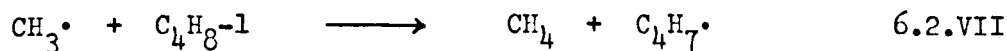
6.3 Primary Quantum Yields

The primary quantum yields of reactions 1) and 2) are estimated after consideration of the fate of the free radicals. The allyl and propenyl radicals from reactions 1) and 6.2.II can recombine with the radicals present to give C_4, C_6 and C_7 products. The difficulty is of course that but-1-ene will be reformed from methyl and allyl radicals and therefore will not be estimated. The increase in CH_4 yield with increasing but-1-ene pressure may be attributed to methyl radicals which would otherwise have reformed but-1-ene since no other product was found to

decrease proportionately. Consequently it is only possible to estimate a minimum value for $\emptyset_1$ from:

$$\emptyset_1 \text{ (minimum)} = 2 \emptyset (C_6) + \emptyset (C_7) \qquad 6.3.I$$

The value is probably 25% low, if the increase in methane yield with but-1-ene pressure is taken as a measure of the loss.

Reaction 2) with 6.2.I, 6.2.III and 6.2.IV gives rise to propylene and C_4 radicals which may form C_5, C_7 and C_8 products. $\emptyset_2$ is then given by:

$$\emptyset_2 = \tfrac{1}{2} \emptyset (C_3H_6) + \emptyset (C_5) + \emptyset (C_7) + 2\emptyset (C_8) \qquad 6.3.II$$

The quantum yields of the molecular fragmentation reactions are estimated by extrapolating the product yields to zero pressures.

The sum of the primary quantum yields given is 0.72, but this is a minimum value. With the errors of estimating C_6, C_7 and C_8 products it is within experimental error, unity.

A check on the scheme proposed is to sum the yields which contribute to the formation of methyl radicals, and compare this with the figure obtained from the products formed by methyl radicals.

Methyl radicals produced in 1) and 6.2.IV

$$R(CH_3) = R_1 + \frac{4}{5} R (C_3H_6) \qquad 6.3.III$$

Methyl radicals form intercombination products ethane (^{4}/5 total yield) and C_5 hydrocarbons

$$R(CH_3) \ = \ 2 \ C_2H_6 \ + \ C_5 \qquad\qquad 6.3.IV$$

The two figures obtained for $R(CH_3)$ are 145×10^{-7} moles and 124×10^{-7} moles which are in moderate agreement considering the complexity of the mechanism postulated.

Reaction 2) could possibly give four different butenyl radicals by detachment of a hydrogen atom. There is no way to distinguish between these possibilities and the presence of various C_5 olefins suggests that the major primary reaction breaks the weakest bond in the molecule and that the ratio of the β C-C to the β C-H split is at least 5.7 to 1, a value somewhat greater than that recorded in sensitised studies.

6.4 Excited State Intermediates

The decrease in product yield with increasing pressure of but-1-ene, inert gases and oxygen may be attributed to the collisional deactivation of an excited state intermediate. The observation is again in conflict with Harumiya, Shida and Arai[77] who reported no major variation of product yields within the pressure range 5 - 170 mm. Hg.
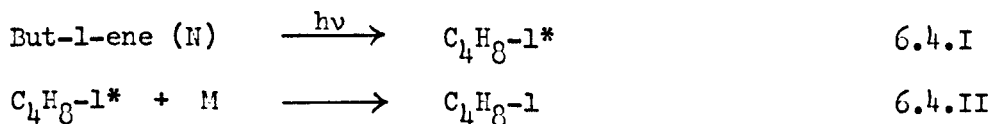
There are three possible excited states which may be intermediates in the reaction: first the (π, π^*) state responsible for the broad maximum in the absorption spectrum at 1751 Å attributed to the V ← N transition.[14]

The second is the excited singlet Rydberg state, the first absorption band in the spectrum attributed to an R ← N transition being at 1873 $\overset{o}{A}$ for but-1-ene.[14] The third suggested by Professor S.F. Mason[99] is the state responsible for the "Mystery Band" described by Berry.[19] There is a strong possibility however[15,23] that these bands found in substituted ethylenes ~~ethylenes~~ are in fact a continuation of the Rydberg bands.

Borrell and James[2] suggested that it was in fact the first excited Singlet Rydberg state which was the intermediate after observing that quenching only produced the original isomer and this is in accordance with the potential barrier to rotation which exists in the Rydberg state. In but-1-ene there are no cis/trans isomers therefore distinction becomes impossible on these grounds. The question also arises as to whether a potential maximum exists for the state responsible for the "Mystery Band".

Berry, who assigned the mystery band to a $\pi_z^* \leftarrow \pi_y^1$ transition and also Robin, Hart and Kuebler[22] who disagreed with the assignment suggested that α bond cleavage should be observed if this state gives rise to photochemical decomposition. Although this would seem to give a guide to the intermediates involved, Berry's conclusion seems to be based on a misinterpretation of the work of Majer, Mille and Robb[67] and therefore does not help.

The following reaction scheme illustrates the fate of the but-1-ene; $C_4H_8-1^*$ is the unspecified intermediate.

$$\text{But-1-ene (N)} \xrightarrow{h\nu} C_4H_8-1^* \qquad 6.4.\text{I}$$

$$C_4H_8-1^* + M \longrightarrow C_4H_8-1 \qquad 6.4.\text{II}$$

and/or

$$C_4H_8\text{-}1^* \longrightarrow \text{products via reactions 1) to 7)} \quad 6.4.\text{III}$$
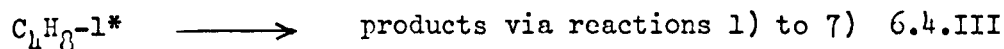
Assuming steady state conditions we may write:-

$$1/(\text{Rate}) = \frac{1}{I\phi_i} + \frac{k_{II}}{k_{III}} \frac{M}{I\phi_i} \qquad 6.4.\text{IV}$$

where ϕ_i is the quantum yield at zero pressure.

Stern-Volmer plots have been made for three of the products and are shown in Figure 6.1, from which the decomposition lifetime for the excited state was found to have values between 2.6 and 6.4 x 10^{-10} sec (k_{III}^{-1}). These were calculated using a value of 2 x $10''$ l.mole^{-1}sec^{-1} for k_{II} assuming that deactivating reactions take place at each collision. Cvetanovic and Doyle[63] estimated the decomposition lifetime of presumably the triplet state in the mercury sensitised studies of but-1-ene at 2537 $\overset{o}{A}$ to be 6.3 x 10^{-9} sec, assuming a value of 10^{-10} molecules^{-1} cc. sec^{-1} for the deactivation rate constant.

The radiative lifetime of the V state has been calculated to be 1.08 x 10^{-9} sec, using the spectral data of Gary and Pickett[17] (Section 1.3). That for the Rydberg state will be somewhat longer so that the fate of the but-1-ene intermediate will be decomposition, and at higher pressures it may be collisionally deactivated. It is concluded that no fluorescence would be observed.
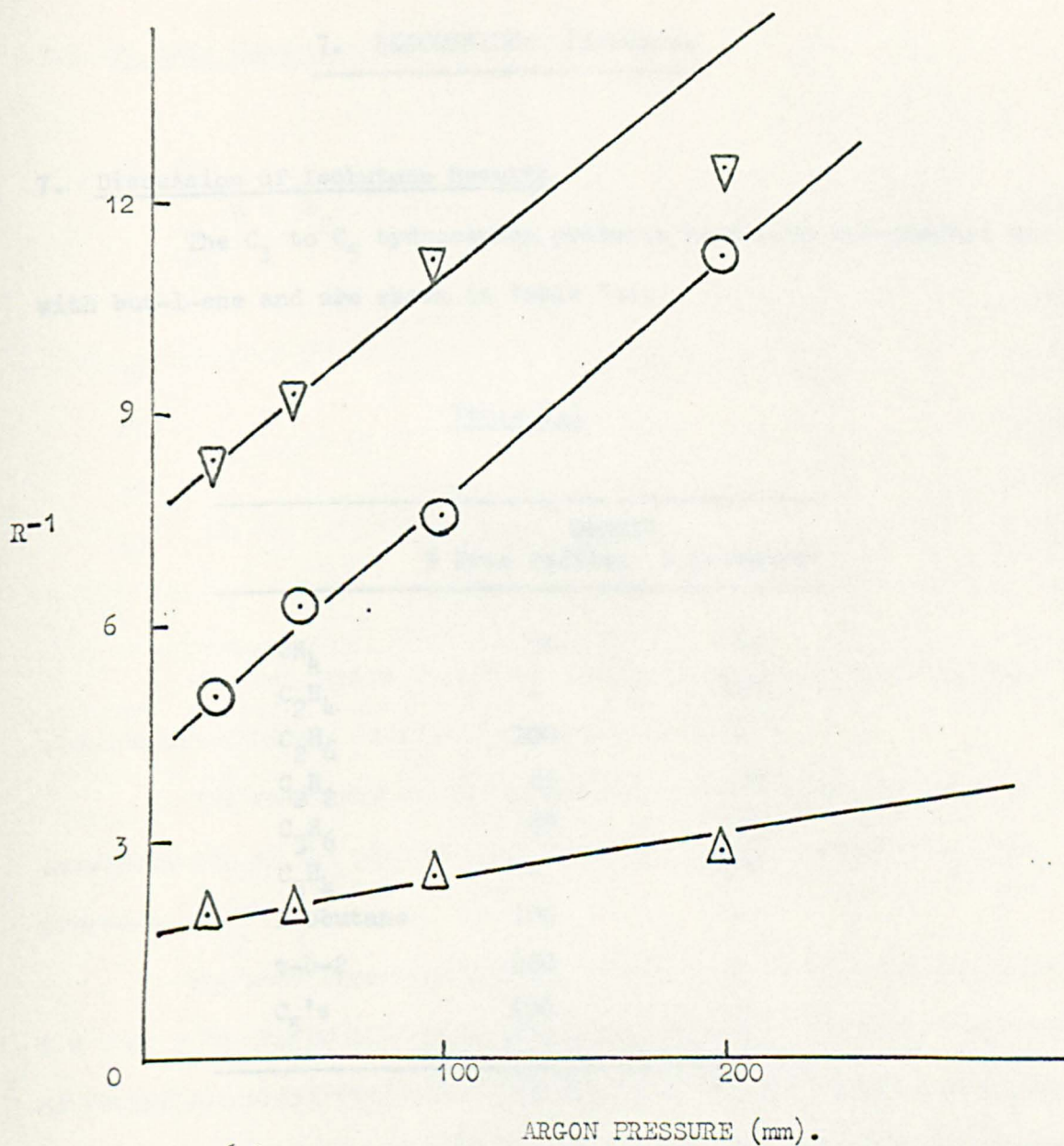
<u>Figure 6.1</u>

The reciprocal of the rate of formation

of several products as a function of

argon pressure.

(R^{-1} in arbitrary units)

▽	METHANE
⊙	ETHYLENE
△	ETHANE

7. DISCUSSION: Isobutene

7. Discussion of Isobutene Results

The C_1 to C_5 hydrocarbon products have been categorised as with but-1-ene and are shown in Table 7.1.

Table 7.1

	ORIGIN	
	% Free radical	% Molecular
CH_4	75	25
C_2H_4	-	100
C_2H_6	100	-
C_2H_2	85	15
C_3H_6	80	20
C_3H_4	-	100
Isobutane	100	-
t-b-2	100	-
C_5's	100	-

One must therefore account for the ethylene and allene yields in the primary reactions and also to some extent the CH_4, C_2H_2 and C_3H_6 yields. The primary reactions postulated are shown below in their probable order of importance.

7.1 Primary Reactions

$$\emptyset^{\neq}$$

1)
$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \quad C = CH_2{}^* \\ CH_3 \end{array} \longrightarrow \begin{array}{c} \dot{C}H_2 \\ \diagdown \\ \diagup \quad C = CH_2 + H\cdot \\ CH_3 \end{array} \qquad 0.476$$

2) $\longrightarrow CH_3 - \dot{C} = CH_2 + CH_3\cdot \qquad 0.203$

3) $\longrightarrow C_3H_4 + \dot{C}H_3 + H\cdot \ (CH_4) \qquad 0.088$

4) $\longrightarrow C_3H_6 + \dot{C}H_2 \qquad 0.011$

5) $\longrightarrow C_2H_2 + 2CH_3\cdot \qquad 0.005$

6) $\longrightarrow 2C_2H_4 \qquad 0.002$
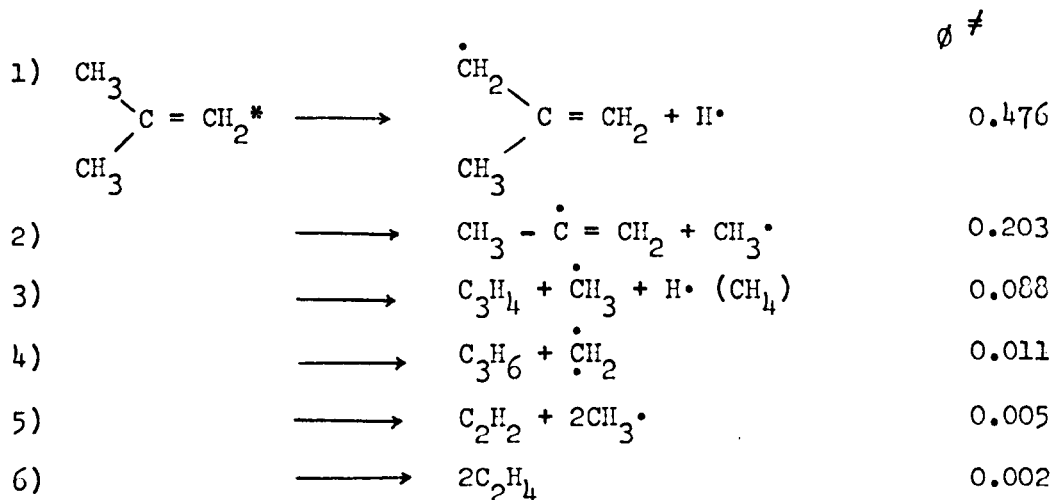
$\neq$ The quantum yields of reactions 1) and 2) are estimated after consideration of the yields of secondary products.

The remainder of the quantum yields are estimated by the extrapolation of the portion of the product yield concerned to zero pressure.

The most important primary reaction is 1) the cleavage of the C–H bond β to the double bond, this being about 2.4 times 2) the production of methyl and allyl radicals. The remainder of the primary reactions account for the similarity of the effects of oxygen and the inert gases on the product yields. Reaction 3) is suggested to account for the allene produced which appears to be wholly of molecular origin, and the small amount of methane which is not eliminated by the addition of oxygen. Similarly reactions 4) and 5) account for the small remaining yields of propylene and acetylene respectively, after the addition of oxygen to the system. Reaction 6) accounts for the ethylene yield which appears to be

wholly of molecular origin.

7.2 Secondary Reactions

The four free radicals $H\cdot$, $CH_3\cdot$, $CH_3-\overset{\bullet}{C}=CH_2$ and $\underset{CH_3}{\overset{\overset{\bullet}{CH_2}}{\diagdown}}C=CH_2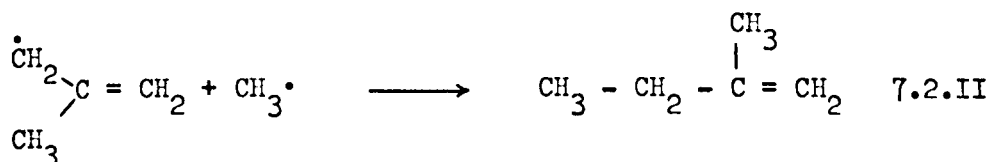$ produced may now take part in a number of secondary reactions. The C_3 radical produced in 2) may equilibriate with its isomer:

$$CH_3 - \overset{\bullet}{C} = CH_2 \quad \rightleftharpoons \quad CH_3 - CH = \overset{\bullet}{CH} \qquad 7.2.I$$
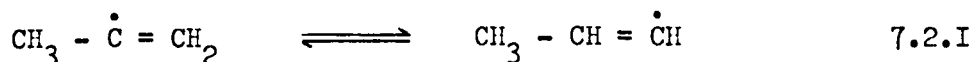
The C_4 radical does not isomerise as the C_4 radical from the other isomeric butenes did and therefore there is a noticeable change in the distribution of the C_5 products (see Table 4.1). By far the major C_5 product is 2Methyl-butene which is presumably formed by the addition of a methyl group to the C_4 radical thus,

$$\underset{CH_3}{\overset{\overset{\bullet}{CH_2}}{\diagdown}}C = CH_2 + CH_3\cdot \quad \longrightarrow \quad CH_3 - CH_2 - \overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C} = CH_2 \qquad 7.2.II$$

The relatively high quantum yield of the C_7 hydrocarbons would account for the excess of C_3 radicals left after combination with the $CH_3\cdot$ available to yield 2Methyl-butene.

The fate of the hydrogen atom is almost certainly in combination with the isobutene which is present in great excess to form an excited tertiary butyl radical. Little information is available on the reactions of the tertiary butyl radical. It seems likely however that the tertiary

butyl radical would behave in a similar way to the secondary butyl
radical reported in Section 6 since one must account for 80% of
the propylene which is produced from free radicals. Abstraction of
hydrogen by allyl radicals from isobutene is ruled out on the basis
that one would expect to see an increase in propylene yield with
increase in isobutene pressure. Even though propylene is present as
an impurity in the isobutene after subtraction of the level of impurity
its yield showed a decrease with isobutene pressure to at least the same
extent as the other product yields.

From the above arguments the following scheme of reactions is
put forward to illustrate the fate of the excited tertiary butyl radical.

$$\text{iso } C_4H_8 + H\cdot \longrightarrow t\text{-}C_4H_9^* \qquad 7.2.\text{III}$$

$$t\text{-}C_4H_9^* \longrightarrow CH_3\cdot + C_3H_6 \qquad 7.2.\text{IV}$$

$$\xrightarrow{+M} t\text{-}C_4H_9\cdot \qquad 7.2.\text{V}$$

$$2t\text{-}C_4H_9\cdot \longrightarrow C_8H_{18} \text{ etc.} \qquad 7.2.\text{VI}$$

$$\longrightarrow C_4H_{10} + \text{iso } C_4H_8 \qquad 7.2.\text{VII}$$
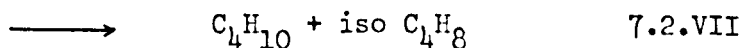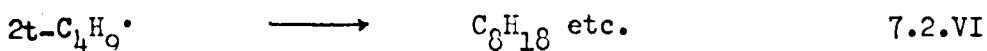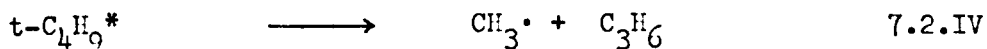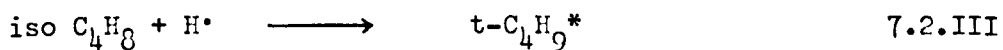
Reaction 7.2.IV would account for the propylene yield which is
of free radical rather than molecular origin.

The ratio of the isobutane/C_8 (Table 4.1) is a measure of k_{VII}/k_{VI}
and it is noted that there is a greater tendency for the $t\text{-}C_4H_9\cdot$ to
disproportionate than to recombine which is opposite to that found in the
case of the but-2-enes.[2]

The free radicals thus produced would recombine or disproportionate

to yield the products listed. However disproportionation reactions of the type listed below would yield the starting material and thus will not be accounted for in the calculations.

$$\begin{matrix} \overset{\bullet}{C}H_2 \\ \quad \diagdown \\ \qquad C = CH_2 \ + \ t\text{-}C_4H_9{}^\bullet \\ \quad \diagup \\ CH_3 \end{matrix} \longrightarrow \quad 2 \begin{matrix} CH_3 \\ \diagdown \\ \ \ C = CH_2 \\ \diagup \\ CH_3 \end{matrix} \qquad 7.2.VIII$$
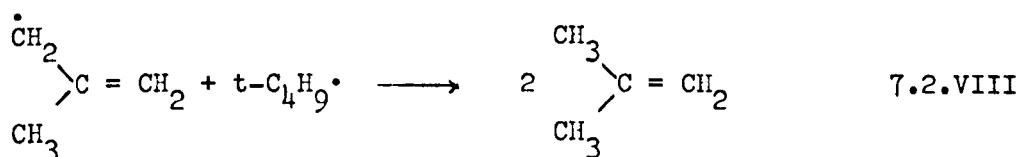
Hydrogen abstraction or addition to isobutene by the remaining radicals at room temperatures is unlikely.[101]

7.3 Primary Quantum Yields

The primary quantum yields of the two major reactions are estimated after consideration of the fate of the free radicals produced. It is taken that the C_4 radicals produce C_5, C_3, C_7 and C_8 hydrocarbons and by summation of the necessary quantum yields.

$$\emptyset_1 = \tfrac{1}{2} (\emptyset \, C_5 + 2 \, \emptyset \, C_8 + \emptyset \, C_7 + {}^4\!/5 \, (C_3H_6) + 2 \, \emptyset \left[i\text{-}C_4H_{10} \right])$$

which is a minimum value since disproportionations to yield isobutene is not accounted for (reaction 7.2.VIII).

Similarly $\emptyset_2 = 2 \, \emptyset \, C_6 + \emptyset \, C_7$

The sum of the quantum yields is 0.785 and is a minimum value due to the 'unaccountable' reformation of isobutene.

A check on the scheme proposed is again to sum the yields of the products which give rise to methyl radicals and to compare this figure with that obtained from those products which are formed from methyl radicals.

Methyl radicals are produced in reactions 2), 3), 5) and 7.2.IV.

$$\therefore \ R \ \overset{\bullet}{C}H_3 \ = \ (C_2H_2) + C_3H_4 + R_2 + \frac{4}{5} \ C_3H_6$$
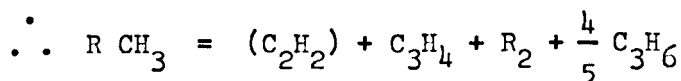
Consumption of methyl radicals takes place in the formation of ethane and C_5 products.

$$\therefore \ R \ \overset{\bullet}{C}H_3 \ = \ 2 \ C_2H_6 + C_5$$
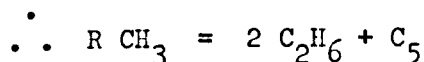
The values of $R \ \overset{\bullet}{C}H_3$ were found to be 42 and 37 x 10^{-8} moles respectively which is in fair agreement for such a complex mechanism.

7.4 Excited State Intermediates

The general decrease in product yields with increasing pressure is taken to be an indication of the presence of an excited state intermediate.

Once again three possible excited state intermediates must be considered, the second and third probably being of the same origin.

Firstly, there is the π,π^* state responsible for the broad maximum in the absorption spectrum at 1883 $\overset{o}{A}$ attributed to the V ← N transition.[14] The second is the excited singlet Rydberg state, the first absorption band in the spectrum assigned to a Rydberg transition (R ← N) being at 2010 $\overset{o}{A}$ for isobutene.[14] The third possibility is again the state responsible for the mystery band at wavelengths longer than 2000 $\overset{o}{A}$ found in substituted ethylenes, but as explained in the but-1-ene discussion this may just be an extension of the Rydberg bands which are superimposed on the band maximum and extend to shorter wavelengths.

There is no possibility at the moment of distinguishing between these possibilities but since the excited state intermediate gives rise to photochemical products it is possible to determine the decomposition lifetime using a Stern Volmer plot, illustrated for two products by Figure 7.1, and applying steady state conditions as before. If one assumes deactivation takes place at each collision for simplicity, the values of the decomposition lifetime of the excited state intermediate are found to be 2.7 and 3.7 x 10^{-10} secs.

The radiative lifetime of the V state was found to be 1.37 x 10^{-9} secs from the spectral data of Gary and Pickett.[17] Thus the fate of the isobutene is again decomposition and at higher pressures deactivation.

Figure 7.1

The reciprocal of the rate of formation of two
products as a function of nitrogen pressure

(R^{-1} in arbitrary units)
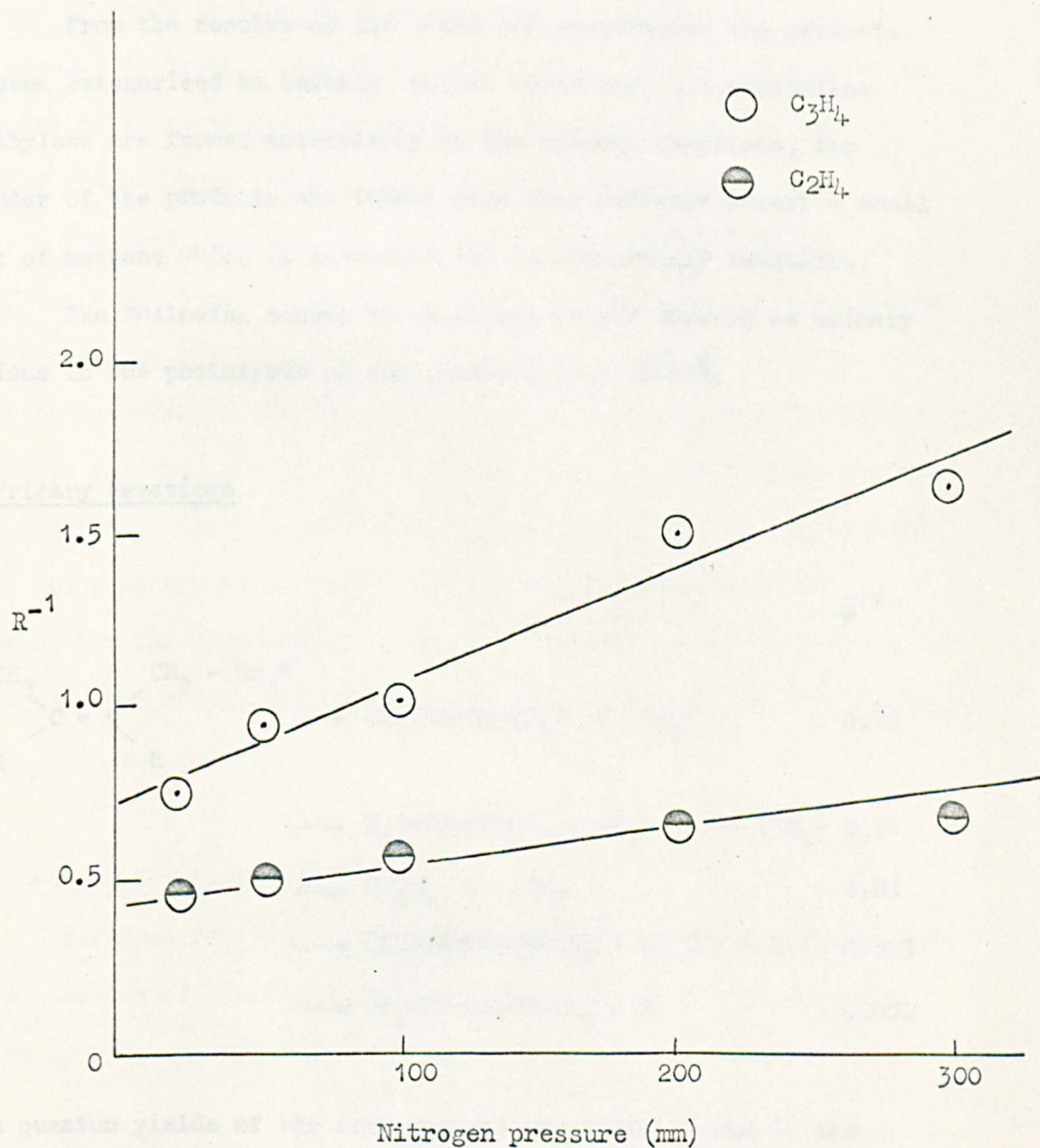
8. DISCUSSION: Cis pent-2-ene

From the results of the added gas experiments the products have been categorised as before: whilst butadiene, 1.3.pentadiene and ethylene are formed molecularly in the primary reactions, the remainder of the products are formed from free radicals except a small amount of methane which is accounted for in the primary reactions.

The following scheme of reactions is put forward as primary reactions in the photolysis of cis pent-2-ene at 1849 $\overset{o}{A}$.

8.1 Primary Reactions

$$\emptyset^{\neq}$$

1) CH_3, $CH_2 - CH_3{}^*$
   $>C = C<$ $\longrightarrow$ $CH_3-CH=CH-CH_2\cdot$ + $CH_3\cdot$ 0.40
   H   H

2) $\longrightarrow$ $H_2C=CH-CH=CH_2$ + $CH_3\cdot$ + H· (CH_4) 0.36

3) $\longrightarrow$ $2C_2H_4$ + $:CH_2$ 0.03

4) $\longrightarrow$ $CH_3-CH=CH-CH=CH_2$ + H_2 (H· + H·) 0.003

5) $\longrightarrow$ $CH_3-CH=CH-\overset{\bullet}{CH}-CH_3$ + H·   0.001
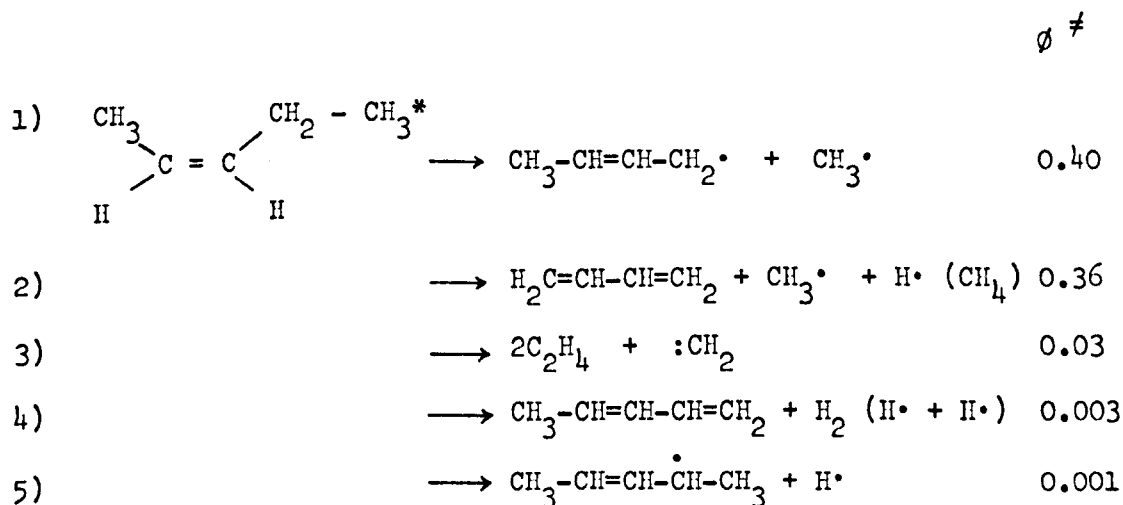
$\neq$ The quantum yields of the free radical reactions 1) and 5) are estimated after consideration of the secondary reactions. The quantum yields of molecular fragmentation reactions are calculated

after consideration of the particular product yield.

Reaction 2) is suggested to account for the butadiene formed, the yield of which is only affected the same by oxygen as it was by the inert gases. Similarly reaction 3) and 4) are suggested to account for the yields of ethylene and 1.3.pentadiene respectively which are of molecular fragmentation origin rather than free radical.

The most important reaction is 1), the cleavage of the C-C bond in the β position to the double bond, this being 400 times greater than the cleavage of the C-H bond in the weak β position (Reaction 5)). This is in accordance with the recent flash photolysis work of Callear and Lee who observed the presence of the methylallyl absorption spectra in the flashed cis pent-2-ene[95] and Chesick[81] who found no evidence to support the cleavage of a C-H bond in the direct photolysis of cis hex-2-ene, but the possibility cannot be ruled out in the case of cis pent-2-ene. The absence of C_9 or C_{10} compounds is indicative of the small quantum yield for reaction 5).
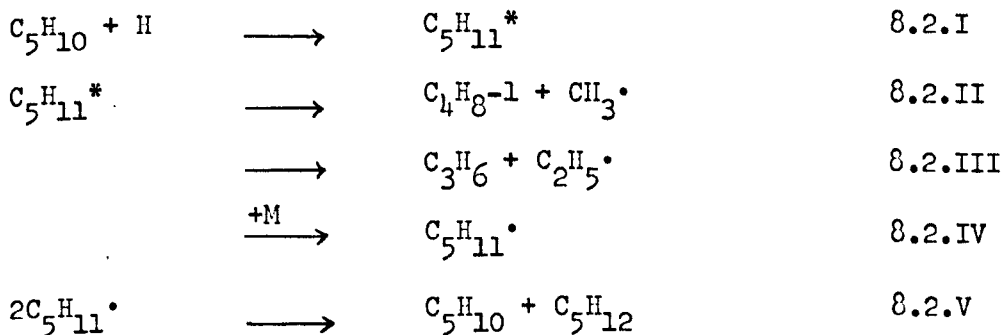
8.2 Secondary Reactions

The free radicals formed in the primary reactions may now take part in a number of secondary reactions. The C_4 radical produced in reaction 1) will equilibriate with its isomer.

$$CH_3 - CH = CH - \overset{\bullet}{CH_2} \rightleftharpoons CH_3 - \overset{\bullet}{CH} - CH = CH_2$$

(A)   (B)

Reaction of (A) or (B) with methyl radicals would yield the pent-2-enes or 3Me-butene respectively. Assuming equal probability of forming cis and trans pent-2-ene from (A) it is seen from Table 5.1 that the ratio of (A) to (B) is 2 to 1.

The C_5 radical produced in 5) would mainly give rise to C_6 compounds and the hydrogen atoms react with the cis pent-2-ene to give excited pentyl radicals which would decompose or recombine and disproportionate as the excited butyl radicals did.

Thus the following reactions are thought to be operative.

$$C_5H_{10} + H \longrightarrow C_5H_{11}^* \qquad 8.2.I$$

$$C_5H_{11}^* \longrightarrow C_4H_8\text{-}1 + CH_3^{\bullet} \qquad 8.2.II$$

$$\longrightarrow C_3H_6 + C_2H_5^{\bullet} \qquad 8.2.III$$

$$\overset{+M}{\longrightarrow} C_5H_{11}^{\bullet} \qquad 8.2.IV$$

$$2C_5H_{11}^{\bullet} \longrightarrow C_5H_{10} + C_5H_{12} \qquad 8.2.V$$

The absence of C_{10} hydrocarbons which may be formed by the straightforward recombination reaction of the pentyl radicals again confirms the low value for ϕ_5.

Reaction 8.2.IV is put forward to account for the possibility of C_7 products which could not be ruled out on analysis - thus $C_2 + C_5 \rightarrow C_7$. It would also account for the propylene yield which is mainly formed via free radicals.

8.3 Primary Quantum Yields

The C_4 radicals formed in reaction 1) will give rise to the C_5 and C_8 hydrocarbons and by disproportionation the butenes.

$$\therefore \ \phi_1 \ = \ \phi \ C_5 \ + \ 2 \ \phi \ C_8 \ + \ \phi \ C_4$$

which is a minimum value; and similarly

$$\phi_5 \ = \ \tfrac{1}{2} \ \phi \ C_6 \ + \ \phi \ C_7$$

The sum of the primary quantum yields is 0.794 which is a minimum value since recombination to yield back cis pent-2-ene is not accounted for. If the probability of $C_1 + C_4 = C_5$ were the same for both cis and trans pentene then the value would be about 17% low and therefore the primary quantum yield is taken to be unity within the limits of experimental error.

The methyl radicals used and produced are again compared to check the mechanism suggested.
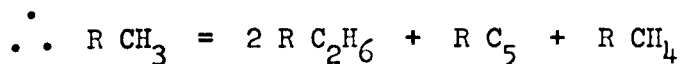
Methyl radicals are produced in reactions 1), 2) and 8.2.II.

$$\therefore \ R \ CH_3 \ = \ R_1 \ + \ R_2 \ + \ R \ C_4H_8\text{-}1$$

The last term may be neglected since the quantum yield of but-1-ene from this source will only be equivalent to ϕ_5 and thus is very small.

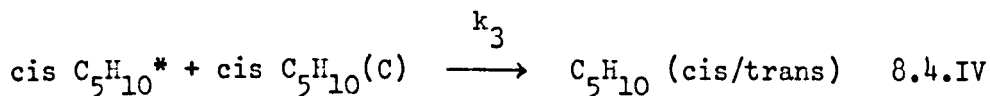Methyl radicals are used to produce the C_5 hydrocarbons, ethane

and methane.

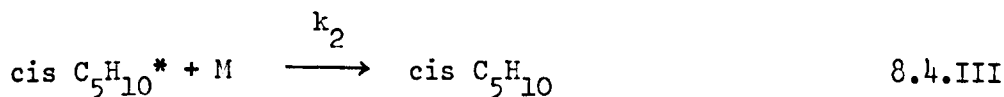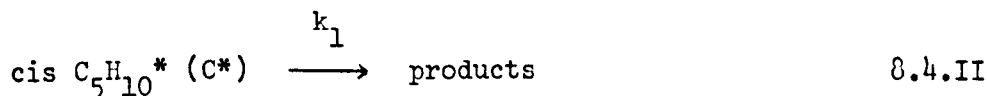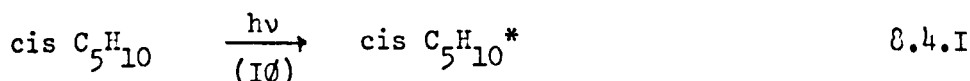$$\therefore \ \dot{R} \ CH_3 \ = \ 2 \ R \ C_2H_6 \ + \ R \ C_5 \ + \ R \ CH_4$$

The two figures for $R \ CH_3$ are 90 and 120 x 10^{-8} moles respectively,
which in view of the complexity of the mechanism is in fair agreement.

8.4 Excited States

As in the case of the butenes a decrease in the yields of the
products was found on increasing the pressure of the system either by
adding gases or by increasing the reactant pressure itself. This fact
was taken to be indicative of the quenching of an excited state inter-
mediate to yield the reactant, though experiments to measure the
consumption of cis pent-2-ene versus nitrogen pressure were abortive, but
on the other hand no increase in any product yield was seen with added
gases. The behaviour of the yield of the geometric isomer was anomalous
in that it increased with an increase in reactant pressure, whereas a
decreased yield was noted with added gases. The increase was sharp at
first but then levelled off at a quantum yield around 0.4.

This latter fact may be explained on an energy transfer basis,
the first excited pentene is quenched by more pentene to yield a second
excited state of pentene which does not decompose but is able to isomerise.
At 3 mm. cis pent-2-ene pressure the yield of the trans isomer is decreased
on adding inert gases to the system and was eliminated by the addition of
oxygen, this was not so in the but-2-enes[2] where the yield of the geometric
isomer was unaffected by pressure.

Since a mixture of cis and trans isomers is not formed on
quenching the first excited state of pentene it is suggested that the
first excited singlet Rydberg state is the most likely intermediate
in the decomposition. The first absorption band attributed to an R ← N
transition being at 2049 Å for cis pent-2-ene[16] (Section 1.2). Excitation
through the V state would yield a mixture of the isomers.[2] At this
juncture the 'mystery bands' are taken to be an extension of the Rydberg
bands and would therefore be a similar intermediate. The second excited
state reached by energy transfer yields cis or trans isomers therefore
does not possess a potential barrier to rotation thus may be the V state
(V ← N transition at 1767 Å)[16] or indeed a triplet state. The exact
assignment is not clear at this stage and the following scheme is put
forward to illustrate the fate of the excited pentene.

$$\text{cis } C_5H_{10} \quad \xrightarrow[(I\emptyset)]{h\nu} \quad \text{cis } C_5H_{10}^* \qquad\qquad 8.4.I$$

$$\text{cis } C_5H_{10}^* \ (C^*) \quad \xrightarrow{k_1} \quad \text{products} \qquad\qquad 8.4.II$$

$$\text{cis } C_5H_{10}^* + M \quad \xrightarrow{k_2} \quad \text{cis } C_5H_{10} \qquad\qquad 8.4.III$$

$$\text{cis } C_5H_{10}^* + \text{cis } C_5H_{10}(C) \quad \xrightarrow{k_3} \quad C_5H_{10} \ (\text{cis/trans}) \quad 8.4.IV$$

Applying steady state conditions as in Section 6 to the above

scheme, for the decomposition products we get

$$\frac{1}{(\text{Rate})} = \frac{1}{I\emptyset_i} + \frac{k_2}{k_1} \cdot \frac{M}{I\emptyset_i} \qquad \qquad 8.4.\text{V}$$

where $\emptyset_i$ is the quantum yield at zero pressure.

Stern Volmer plots have been made for ethylene and butadiene, Figure 8.1, and from these the ratio k_1/k_2 calculated to be 1.0×10^2 mm., and the decomposition lifetime ($1/k_1$) of the first excited pent-2-ene estimated to be 3.5×10^{-9} and 8.9×10^{-10} secs respectively. These were estimated using a value of 2×10^{11} l. mole^{-1} sec^{-1} for k_2 which assumes a similar collision diameter for cis pent-2-ene to that of the butenes and that deactivation takes place on each collision.

If similar treatment is now given to the trans isomer alone which is a product of equation 8.4.IV.

Now

$$\text{Rate trans (Rt)} = \tfrac{1}{2} k_3 (C^*)(C) \qquad \qquad 8.4.\text{VI}$$

$$\frac{dc^*}{dt} = I\emptyset - k_1 C^* - k_2 C^* M - k_3 C^* C = 0 \qquad \qquad 8.4.\text{VII}$$

assuming steady state conditions

$$\therefore \quad C^* = \frac{I\emptyset}{k_1 + k_2 M + k_3 C} \qquad \qquad 8.4.\text{VIII}$$

Figure 8.1

The reciprocal of the rate of formation of two products as a function of nitrogen pressure (R^{-1} in arbitrary units)
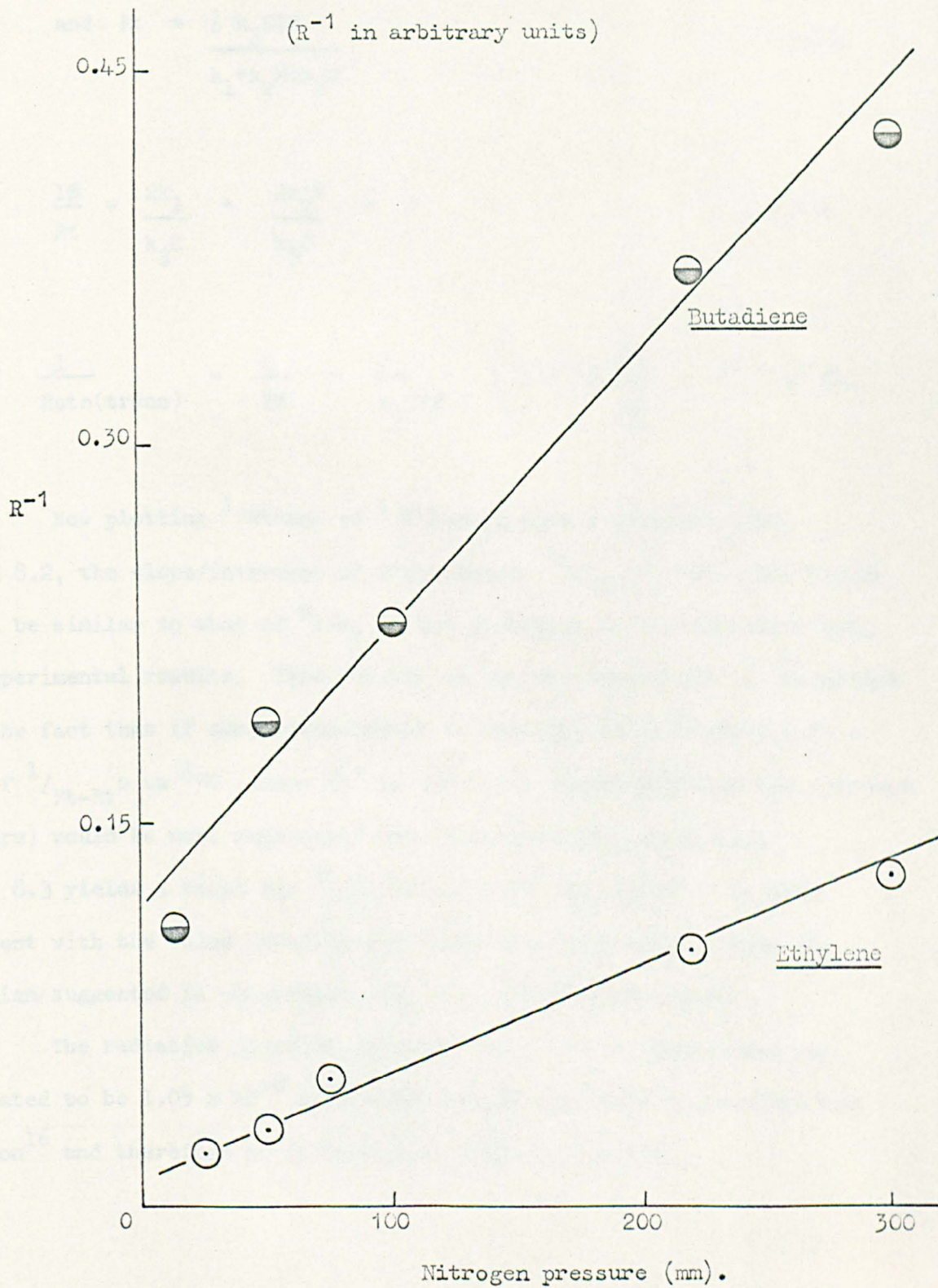
and   Rt $= \dfrac{\frac{1}{2}\,k_3 CI\emptyset}{k_1 + k_2 M + k_3 C}$ 8.4.IX

$\dfrac{I\emptyset}{Rt} = \dfrac{2k_1}{k_3 C} + \dfrac{2k_2 M}{k_3 C} + 2$ 8.4.X

$\dfrac{1}{\text{Rate(trans)}} = \dfrac{2}{I\emptyset} + \dfrac{2}{k_3 CI\emptyset}\left(k_1 + k_2 M\right)$ 8.4.XI

Now plotting $1/\text{Rtrans}$ vs $1/C$ should give a straight line,
Figure 8.2, the slope/intercept of which equals k_1/k_3 (M = 0). The figure
should be similar to that of k_1/k_2 if the mechanism is in accordance with
the experimental results. This was not so but the result may be reconciled
with the fact that if some trans isomer is produced in reaction 8.4.II a
plot of $1/_{Rt-Rt}{}^o$ vs $1/C$ (where Rt^o is the trans isomer yield at low reactant
pressure) would be more consistent with the mechanism postulated.
Figure 8.3 yields a value for k_1/k_3 of 1.1×10^2 mm. which is in good
agreement with the value obtained for k_1/k_2 from Figure 8.1. Thus the
mechanism suggested is consistent with the experimental results.

The radiative lifetime of the V state for cis pent-2-ene was
calculated to be 1.05×10^{-9} secs from the spectral data of Semenhow and
Harrison[16] and therefore no fluorescence would be observed.

Figure 8.2

The reciprocal of the rate of formation of trans pent-2-ene
as a function of the reciprocal of the cis pent-2-ene pressure
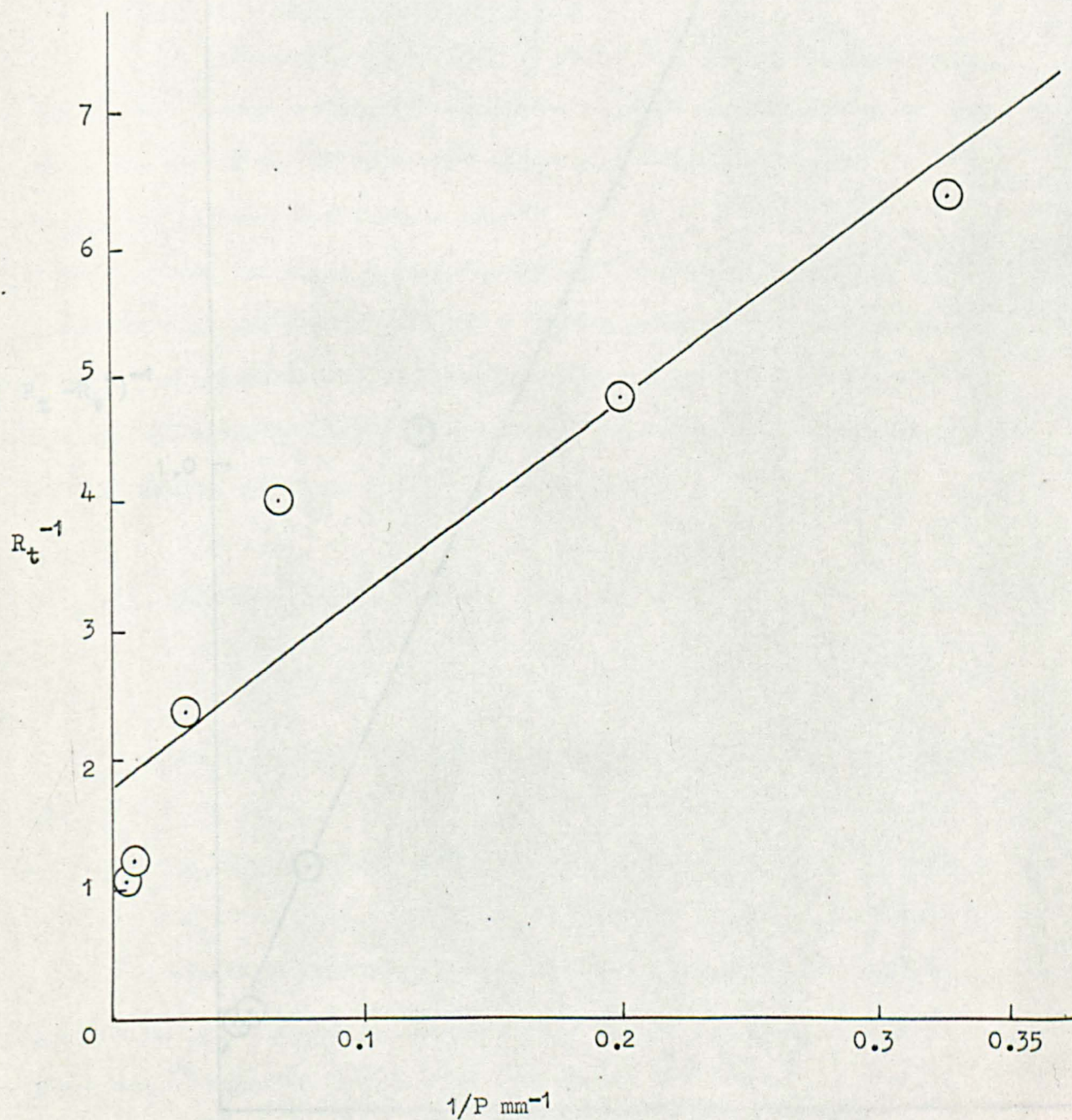
(R^{-1} in arbitrary units)

Figure 8.3

The reciprocal of the corrected rate of formation of _trans_ pent-2-ene vs 1/P

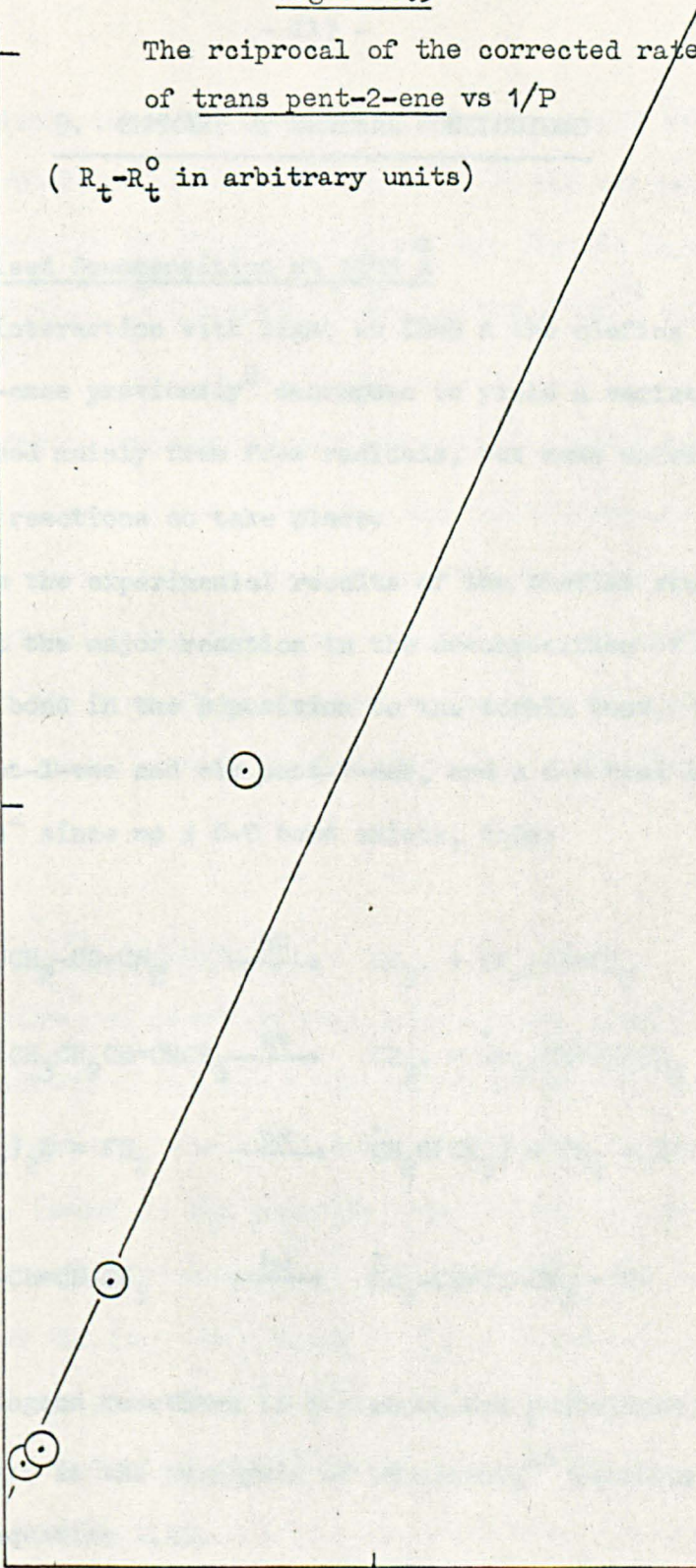($R_t - R_t^o$ in arbitrary units)

2.0

$(R_t - R_t^o)^{-1}$

1.0

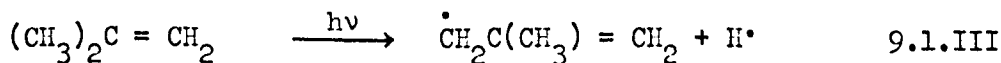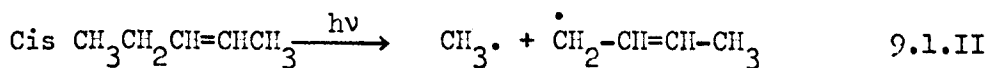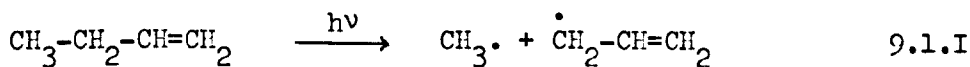0   0.1   0.2
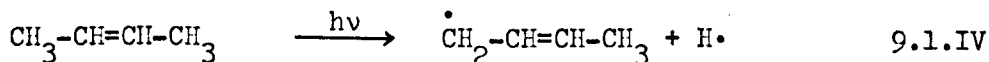
$1/P \ mm^{-1}$

9. SUMMARY OF GENERAL CONCLUSIONS

9.1 Unsensitised Decomposition at 1849 $\overset{o}{A}$

On interaction with light at 1849 A the olefins studied here, and the but-2-enes previously[2] decompose to yield a variety of products which are formed mainly from free radicals, but some molecular fragmentation reactions do take place.

From the experimental results of the olefins studied it is concluded that the major reaction in the decomposition of olefins is cleavage of a bond in the β position to the double bond. This being a C-C bond in but-1-ene and cis pent-2-ene, and a C-H bond in isobutene and the but-2-enes[2] since no β C-C bond exists, thus:

$$CH_3-CH_2-CH=CH_2 \xrightarrow{h\nu} CH_3\cdot + \overset{\bullet}{C}H_2-CH=CH_2 \qquad 9.1.I$$

$$\text{Cis } CH_3CH_2CH=CHCH_3 \xrightarrow{h\nu} CH_3\cdot + \overset{\bullet}{C}H_2-CH=CH-CH_3 \qquad 9.1.II$$

$$(CH_3)_2C=CH_2 \xrightarrow{h\nu} \overset{\bullet}{C}H_2C(CH_3)=CH_2 + H\cdot \qquad 9.1.III$$

and

$$CH_3-CH=CH-CH_3 \xrightarrow{h\nu} \overset{\bullet}{C}H_2-CH=CH-CH_3 + H\cdot \qquad 9.1.IV$$

Analogous reactions to the above are postulated as prime initiation steps in the pyrolysis of but-1-ene,[45] equation 1.X, and Isobutene,[46] equation 1.XI.

Similarly in mercury sensitised studies (2537 Å) for but-1-ene;[61,63] propylene,[102] equation 1.XXIV; but-2-enes[64,65] and cis pent-2-ene.[67]

The results of direct photolysis are also in agreement; but-1-ene (1849 Å),[77,78] equation 1.XLIII; Isobutene[80] and the but-2-enes.[82,83]

The recent work by Callear and Lee[95] on the flash photolysis of but-1-ene, cis pent-2-ene, Isobutene and the but-2-enes showed the presence of the methylallyl radical absorption spectrum in the product mixture after flashing the last three olefins, and on flashing but-1-ene the presence of the free allyl absorption spectrum was noted. Thus the weakness of the bonds, especially C-C, β to the double bond has been well established.

9.2 Excited State Intermediates

Definite assignment of the excited state intermediate involved in the decomposition of but-1-ene and isobutene was not possible but since ▄ deactivation of the first excited state of cis pent-2-ene did not yield the trans isomer it was concluded that the first excited singlet Rydberg state was participating in the decomposition of cis pent-2-ene. This is based on the fact that there exists a barrier to rotation in the excited singlet Rydberg state but no such barrier exists in the singlet V state. Previous work on the but-2-enes[2] brought this point to light. Evidence for a further excited state was also found for cis pent-2-ene which gives rise to isomerisation rather than decomposition but this was

not definitely assigned due to lack of information. The weight of
evidence seems to be in favour of the first singlet Rydberg state
participating in the decomposition of olefins at 1849 $\overset{\text{o}}{\text{A}}$ with a further
intermediate for the isomerisation wherever possible.

REFERENCES

1. G. Wald, Light and Life, W.D. McElroy and B. Glass; Editors.
    John Hopkins press, Baltimore, 1961, p.724.

2. C.F. James, Ph.D. Thesis, 1965, Keele University.
    P. Borrell, C.F. James, Trans. Farad. Soc., 62, 2542, 1966.

3. P.G. Wilkinson, R.S. Mulliken, J. Chem. Phys., 23, 1895, 1955.

4. A.D. Walsh, Anal. Rep. Chem. Soc., 63, 44, 1966.

5. W.C. Price, Phys. Rev., 47, 444, 1935.

6. P.G. Wilkinson, Can. J. Phys., 34, 643, 1956.

7. D.P. Craig, Proc. Roy. Soc. Lond., A.200, 272, 1950.

8. W.S. Galway, E.F. Barker, J. Chem. Phys., 10, 88, 1942.

9. R.S. Mulliken, Revs. Mod. Phys., 14, 265, 1942.

10. W.C. Price, W.F. Tutte, Proc. Roy. Soc. Lond., A.174, 207, 1940.

11. C.P. Snow, C.B. Allsop, Trans. Farad. Soc., 30, 93, 1934.

12. C. Reid, J. Chem. Phys., 18, 1299, 1950.

13. D.F. Evans, J. Chem. Soc., 1735, 1960.

14. (a) E.P. Carr, M.P. Walker, J. Chem. Phys., 4, 751, 1936.
    (b) E.P. Carr, G.F. Walter, J. Chem. Phys., 4, 756, 1936.
    (c) E.P. Carr, H. Stucklen, J. Chem. Phys., 4, 760, 1936.

15. E.P. Carr, H. Stucklen, J. Chem. Phys., 7, 631, 1939.

16. D. Semenhow, A.J. Harrison, E.P. Carr, J. Chem. Phys., 22, 638, 1954.

17. J.T. Gary, L.W. Pickett, J. Chem. Phys., 22, 1266, 1954.

18. J.T. Gary, L.W. Pickett, J. Chem. Phys., 22, 599, 1954.

19. R.S. Berry, J. Chem. Phys., 38, 1934, 1963.

20. J.W. Moskowitz, M.C. Harrison, J. Chem. Phys., 42, 1726, 1964.

21. D.F. Evans, Proc. Chem. Soc., 378, 1963.

22. R.R. Hart, M.B. Robin, Theoret. Chim. Acta., 3, 374, 1965.
    M.B. Robin, R.R. Hart, N.A. Kuebler, J. Chem. Phys., 44, 1803,
    1966.

23. A. Lubezky, R. Kopelman, J. Chem. Phys., 45, 2526, 1966.

24. L.C. Jones, L.W. Taylor, Anal. Chem., 27, 228, 1955.

25. R.S. Mulliken, J. Chem. Phys., 7, 14, 1939.

26. Photochemistry, J.G. Calvert, J.N. Pitts, Jnr., Wiley and Sons,
    Inc., N.Y., p.246.

27. There is a tendency to consider triplet molecules to be diradicals.
    This is NOT correct. Triplet molecules are not automatically
    diradicals. Paramagnetism is symptomatic of, but does not of itself
    confer all the properties we associate with diradical behaviour. The
    ultimate diradical possesses the following properties:

    (a) Paramagnetism

    (b) The charge densities of the two odd electrons are
         spatially separate

    whilst triplets possess property (a) they do not always have (b) and
    when they do the singlet state has also. - S.P. McGlynn, F.J. Smith,
    G. Silento, Photochem. and Photobiol., 3, 269, 1964.

28. R.S. Mulliken, C.A. Rieke, Rept. Progress in Phys., 8, 231, 1941.

29. M. Kasha, Discussions Farad. Soc., 9, 14, 1950.

30. G. Herzberg, Spectra of Diatomic Molecules. 2nd Ed. Van Nostrand,
    New York, 1959, p.21.

31. Beer, Ann. Phys. Chem., 163, (Dritte Reihe 86) 78, 1852.

32. A.C.G. Mitchell, M.W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge Press, 1961, p.96.

33. S.F. Mason, Quart. Rev., 15, 287, 1961.

34. R.B. Cundall, T.F. Palmer, Trans. Farad. Soc., 56, 1211, 1960.

35. S. Glasstone, Textbook of Physical Chemistry, 2nd Edn., Macmillan, London, 1948, p.277.

36. R.V. Wheeler, W.L. Wood, J. Chem. Soc., 1819, 1930.

37. K.U. Ingold, F.J. Stubbs, J. Chem. Soc., 1794, 1951.

38. K.J. Laidler, B.W. Wojciechowski, Proc. Roy. Soc., A.259, 257, 1961.

39. A. Amano, M. Uchiyama, J. Phys. Chem., 68, 1133, 1964.

40. A.S. Kallend, J.H. Purnell, B.C. Shurlock, Proc. Roy. Soc., A.300, 120, 1967.

41. R.M. Marshall, J.H. Purnell, B.C. Shurlock, Canad. J. Chem., 44, 2778, 1966.

42. R.J. Ellis, H.M. Frey, J. Chem. Soc., 5578, 1964.

43. K.W. Egger, D.M. Golden, S.W. Benson, J. Amer. Chem. Soc., 86, 5420, 1964.

44. J.W. Simons, B.S. Rabinovitch, F.H. Dorer, J. Phys. Chem., 70, 1076, 1966.

45. M. Swarc, A.H. Sheon, J. Chem. Phys., 18, 237, 1950.

46. M. Swarc, J. Chem. Phys., 17, 292, 1949.

47. F.O. Rice, W.S. Haynes, J. Amer. Chem. Soc., 70, 964, 1948.

48. E.N. Hague, R.V. Wheeler, J. Chem. Soc., 378, 1929.

49. R.V. Wheeler, W.L. Wood, J. Chem. Soc., 1819, 1930.

50. G. Egloff, C.I. Parris, Chem. Rev., 19, 145, 1936.

51. M.C. Linn, K.J. Laidler, Can. J. Chem., 45, 1315, 1967.

52. M.C. Linn, K.J. Laidler, Can. J. Chem., 44, 2927, 1966.

53. D.H. Slater, S.C. Collier, J.G. Calvert, J. Amer. Chem. Soc., 90, 268, 1968.

54. Photochemistry, J.G. Calvert, J.N. Pitts, Jnr., John Wiley and Sons, Inc., New York, 1966.

55. R. Pertel, Abstracts Sixth Informal Photochemistry Conference, University of California, Davis, June 1964.

56. D.J. Le Roy, E.W.R. Steacie, J. Chem. Phys., 9, 829, 1941.

57. R.J. Cvetanovic, H.E. Gunning, E.W.R. Steacie, J. Chem. Phys., 31, 573, 1959.

58. D.J. Le Roy, E.W.R. Steacie, J. Chem. Phys., 10, 676, 1942.

59. D. Line, D.J. Le Roy, J. Chem. Phys., 13, 307, 1945.

60. R.J. Cvetanovic, A.B. Callear, J. Chem. Phys., 23, 1182, 1955.

61. A.B. Callear, R.J. Cvetanovic, J. Chem. Phys., 24, 873, 1956.

62. D.W. Setser, B.S. Rabinovitch, D.W. Placzeck, J. Amer. Chem. Soc., 85, 862, 1963.

63. R.J. Cvetanovic, L.C. Doyle, J. Chem. Phys., 37, 543, 1962.

64. R.B. Cundall, T.F. Palmer, Trans. Farad. Soc., 56, 1211, 1962.

65. R.B. Cundall, Progress in Reaction Kinetics, Vol. II, ed. by G. Porter, Macmillan Co., New York, 1964, p.167.

66. P. Kebarle, M. Avrahami, J. Chem. Phys., 38, 700, 1963.

67. J.R. Majer, B. Mille, J.C. Robb, Trans. Farad. Soc., 57, 1336, 1961.

68. R.B. Mooney, E.B. Ludlam, Trans. Farad. Soc., 25, 442, 1929.

69. S.C. Lind, R. Livingston, J. Amer. Chem. Soc., 55, 1036, 1933.

70. H.S. Taylor, H.J. Emeleus, J. Amer. Chem. Soc., 53, 562, 3370, 1931.

71. R.D. McDonald, R.G.W. Norrish, Proc. Roy. Soc. (London), A.157, 480, 1936.

72. M.C. Sauer, Jnr., L.M. Dorfman, J. Chem. Phys., 35, 497, 1961.

73. H. Okabe, J.R. McNesby, J. Chem. Phys., 36, 601, 1962.

74. D.A. Becker, H. Okabe, J.R. McNesby, J. Phys. Chem., 69, 538, 1965.

75. J.A.R. Samson, F.F. Marmo, K. Watanabe, J. Chem. Phys., 36, 783, 1962.

76. S. Arai, S. Shida, T. Nishikawa, Bull. Chem. Soc. Japan, 39, 2548, 1966.

77. N. Harumiya, S. Shida, S. Arai, Bull. Chem. Soc. Japan, 38, 142, 1965.

78. H. Okabe, H.D. Beckey, W. Groth, Z. Naturforschg., 21a., 135, 1966.

79. Calculated from the table by A.F. Trotman-Dickenson, Gas Kinetics, Academic Press, Inc., New York, 1955. p.15.

80. W.F. Keifer, J.P. Howe, J. Amer. Chem. Soc., 64, 1, 1942.

81. J.P. Cheswick, J. Chem. Phys., 45, 3934, 1966.

82. Y. Hatano, S. Shida, Bull. Chem. Soc. Japan, 39, 456, 1966.

83. K. Watanabe, E.C.Y. Inn, M. Zelikoff, J. Chem. Phys., 21, 1026, 1953.

84. K. Watanabe, M. Zelikoff, J. Opt. Soc. Am., 43, 753, 1953.

85. Hanovia information.

86. Experimental Methods in Gas Reactions, H. Melville, B.G. Gowenlock, Macmillan & Co., London, 1964, p.102.

87. H. Rommel, Private Communication.

88. H.D. Beckey, W. Groth, H. Okabe, H.J. Rommel, Z. Naturforschg., 19a, 1511, 1964.

89. W.A. Noyes, J. Chem. Phys., 5, 807, 1937.

90. M. Zelikoff, L.M. Aschenbrand, J. Chem. Phys., 22, 1685, 1954.

91. N.R. Greiner, J. Chem. Phys., 47, 4374, 1967.

92. J. Romand, J. Mayence, Compt. Rend., 228, 998, 1949.

93. A.C.G. Mitchell and M.W. Zemansky, "Resonance Radiation and Excited Atoms", Cambridge University Press, 1961.

94. H. Purnell, Gas Chromatography, Wiley, New York, 1962.

95. A.B. Callear, H.K. Lee, Trans. Farad. Soc., 64, 308, 1968.

96. E.W.R. Steacie, Atomic and Free Radical Reactions, 2nd Edn., American Chemical Society Monograph Series No. 102, New York, 1954.

97. B.S. Rabinovitch, D.W. Sester, Advances in Photochemistry, 3, 62, 1964.

98. R.F. Kubin, B.S. Rabinovitch, R.E. Harrington, J. Chem. Phys., 37, 937, 1962.

99. Professor S.F. Mason, Private Communication.

100. P. Borrell, Private Communication.

101. K.R. Jennings, R.J. Cvetanovic, J. Chem. Phys., 35, 1233, 1961.

102. M. Avrahami, P. Kebarle, J. Phys. Chem., 67, 354, 1963.

103. R.S. Mulliken, C.C.T. Roothaan, Chem. Revs., 41, 219, 1947.