PHOTOCHEMICAL STUDIES OF
CIS- AND TRANS-BUT-2-ENE

A THESIS

by

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Submitted to the UNIVERSITY OF KEELE in
partial fulfilment of the requirements
for the degree of Doctor of Philosophy.

University of Keele
November, 1965.

All the work reported in this thesis was carried out by the author, under the supervision of Dr. P. Borrell.

ACKNOWLEDGMENTS

In presenting this thesis I should like to thank Professor H. D. Springall, who made facilities available for this work.

I would particularly like to thank my supervisor, Dr. P. Borrell, for his invaluable guidance and stimulating encouragement throughout this work, Mr. N. D. Stewart for numerous helpful discussions, Miss L. Whitwam for help in drawing the diagrams, and Miss J. Bateman who patiently typed this thesis.

I would also like to thank the Science Research Council for a maintenance grant, 1962-65.

ERRATA

p.17	line 6	For converted read connected.
p.27	line 12	For iodine read ferric chloride.
p.44	line 20	For appiezon read apiezon.
p.77	line 14	For is read was.
p.105	line 11	For Hertzberg read Herzberg.

ABSTRACT

A study has been made of the vapour phase photolysis of cis- and trans-but-2-ene at 1849 Å. The pressure quenching effects of butene or added gases on the yields of the products suggest that absorption of light at 1849 Å produces either the Rydberg (R) state or the first excited singlet $\pi - \pi^*$ (V) state of but-2-ene, in the ratio ~8:1.

The V state leads solely to isomerisation, while the R state may decompose by seven primary reactions. The effect of radical scavengers oxygen or nitric oxide helps to distinguish five molecular and two radical primary reactions.

$$C_4H_8\text{-}2 + h\nu \rightarrow \mathrm{V} \text{ or } \mathrm{R}$$

	ϕ
$\mathrm{V} \rightarrow$ isomer (cis from trans, trans from cis)	0·085
$\mathrm{R} \rightarrow H\cdot + \cdot CH_2 - CH = CH - CH_3$	0·6
$\mathrm{R} \rightarrow HC \equiv CH + 2\ \cdot CH_3$	0·23
$\mathrm{R} \rightarrow CH_2 = CH - CH = CH_2$	0·11
$\mathrm{R} \rightarrow \cdot CH_3 + \cdot CH = CH - CH_3$	0·085
$\mathrm{R} \rightarrow CH_4 + CH_2 = C = CH_2$	0·05
$\mathrm{R} \rightarrow CH_3 - C \equiv C - CH_3 + H_2$	0·007
$\mathrm{R} \rightarrow 2\ H_2C = CH_2$	0·007

Recombination reactions of the radicals formed in the primary reactions explain the full range of products C_1 to C_8 and the solid polymer formed in the photolysis. Photolysis of but-2-ene in the liquid phase at 1849 Å suggests that only the V state is formed, for the products consist almost entirely of the geometric isomer.

A third excited state, the triplet state of but-1-ene is formed by crossover from the excited but-2-ene states, and results in the formation of but-1-ene.

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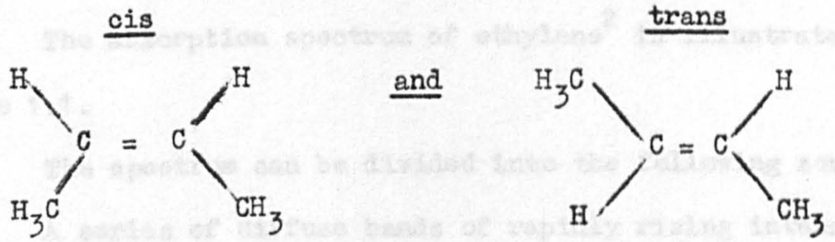
1. INTRODUCTION

1.1 Preliminary Remarks

Photochemical processes are of fundamental importance in nature, for the conversion of light energy into chemical energy is essential to many biological activities. One such conversion process is photochemical cis-trans isomerisation, which plays an important role 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 absorption of light converts it to the all-trans form. This isomerisation triggers off a chain of processes which eventually lead to visual excitation.[1]

Although photochemical cis-trans isomerisation is of such basic importance, very little is known about the nature of the process. The present study, using a simple olefin, was initiated to gain more understanding of the intermediate excited states involved in photochemical cis-trans isomerisation. It was found that on photoexcitation of the olefin, there was competition in the excited state between isomerisation and dissociation, with the latter process predominating. So, although the original intent was to study photochemical cis-trans isomerisation, the scope was extended to include a study of photodissociation.

But-2-ene was chosen for the study, for it is the simplest undeuterated olefin which exists in two geometrical isomeric forms,



and has the advantage of being a gas at room temperature. Consequently, the photolysis can be studied in the vapour phase where interactions between neighbouring molecules are at a minimum, and solvent effects do not have to be considered.

The introduction to this thesis includes a discussion of the absorption spectra of olefins which provide information on the nature of the excited states produced by absorption of light. The various theories of cis-trans isomerisation are considered in terms of the excited states involved, and a discussion is given of the relationship between isomerisation and breakdown of excited olefins produced by several different methods.

1.2 Absorption Spectra

The absorption of simple olefins, particularly ethylene, in the ultraviolet has been the subject of considerable practical investigation and theoretical interpretation. As the absorption spectra of all simple olefins are qualitatively similar, the discussion can be centred on ethylene, and then extended to incorporate but-2-ene and other olefins.

The absorption spectrum of ethylene[2] is illustrated in Figure 1.1.

The spectrum can be divided into the following zones:-

(a) A series of diffuse bands of rapidly rising intensity, from 2069 Å (very weak absorption) to at least 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 intensity at 1620 Å.

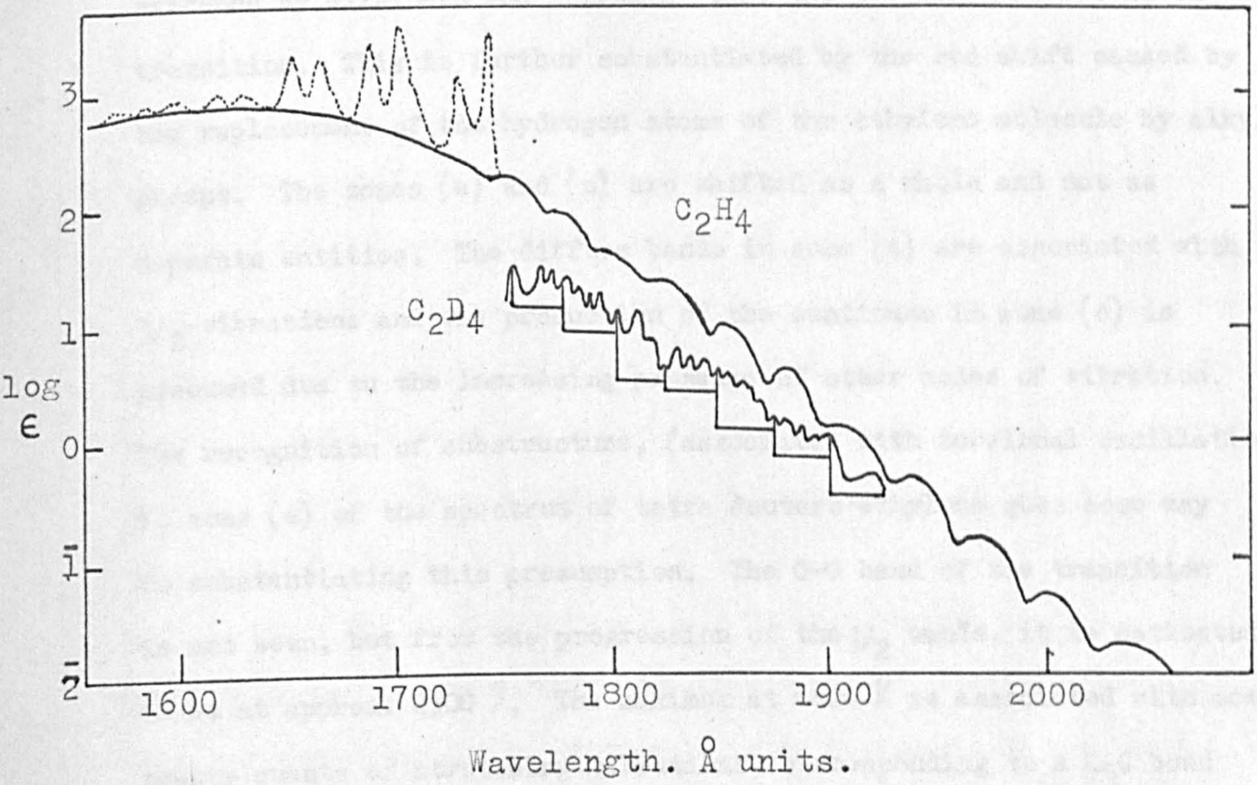
(d) Three further series of sharp bands beginning at 1520 Å, 1440 Å, and 1370 Å, underlain by another continuum.

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.[3] The banded structure is attributed to 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 at 1370 Å are also assigned to Rydberg transitions,[2,4] all three series converging to the same ionization potential.

The broad continuum (c) and the series of diffuse bands (a)

Figure 1.1



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

are considered by Craig[5] 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[2] that the two zones represent one transition. This is further substantiated by the red shift caused by the replacement of the hydrogen atoms of the ethylene molecule by alkyl groups. The zones (a) and (c) are shifted as a whole and 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 the increasing presence 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 at approx. 2500 Å. The maximum at 1620 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 1.353 Å in the ground state.[6]

Thus two transitions are seen to occur. These are designated R ← N and V ← N in Mulliken's[7] terms, where N represents the singlet ground state, R represents the Rydberg state with one of the π-bonding electrons transferred to a Rydberg orbital, and V represents the first upper excited singlet state, with one of the π-bonding electrons transferred to an anti-bonding orbital. Price and Tutte[8] consider that the first Rydberg orbital is itself somewhat anti-bonding, since it occurs at a shorter wavelength than predicted.

Snow and Allsopp[9] originally believed the weak diffuse absorption bands below 2069 Å to be due to a singlet - triplet transition T ← N, in which the spin of the electron in the anti-bonding orbital was reversed. However, the use of long path-lengths of liquid ethylene,[10] or gaseous ethylene in the presence of one hundred atmospheres of oxygen,[11] 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.[12,13,14]

The shift of the Rydberg bands depends solely upon the number of hydrogen atoms which have been replaced, and not upon their position. This is because the energy of transition is due to the effective nuclear charge on the central carbon atoms.[13] Thus the Rydberg bands of cis-but-2-ene and cyclohexene are almost coincident.

Since the V ← N transition is a charge transfer transition, the shift depends upon the dipole vector of the molecule. Therefore the V ← N shift is dependent upon molecular shape, and hence upon the position of replacement , rather than upon the number of hydrogen atoms replaced.[14,15] The direction of the dipole governs whether the maximum of the V ← N absorption is displaced to longer or shorter wavelengths than the molecule with no effective dipole. This is illustrated for the isomeric butenes in Table 1.1

Table 1.1

Olefin	cis-but-2-ene and but-1-ene	trans-but-2-ene	2-methylpropene
Effective Dipole	Perpendicular to C=C	None	Along C=C
λ_{max} V ← N absorption	1754 Å cis- 1750 Å but-1-ene	1780 Å	1883 Å

The absorption spectra of cis- and trans-but-2-ene are given in Figures 1.2 and 1.3.[16]

The 0-0 band for the R ← N transition is an intense band for each isomer at 2066 Å (cis-) and 2021 Å (trans-). The ν_2 (C=C stretching) frequency is ~1680 cm.$^{-1}$ from infrared and Raman measurements,[17] and is comparable with the moderately strong bands at 2004 Å (cis-) and 1959 Å (trans-). The remaining bands observed before the R ← N absorption is submerged below the V ← N absorption are attributed to other vibrational modes of the molecule, which are comparable with similar

Figure 1.2

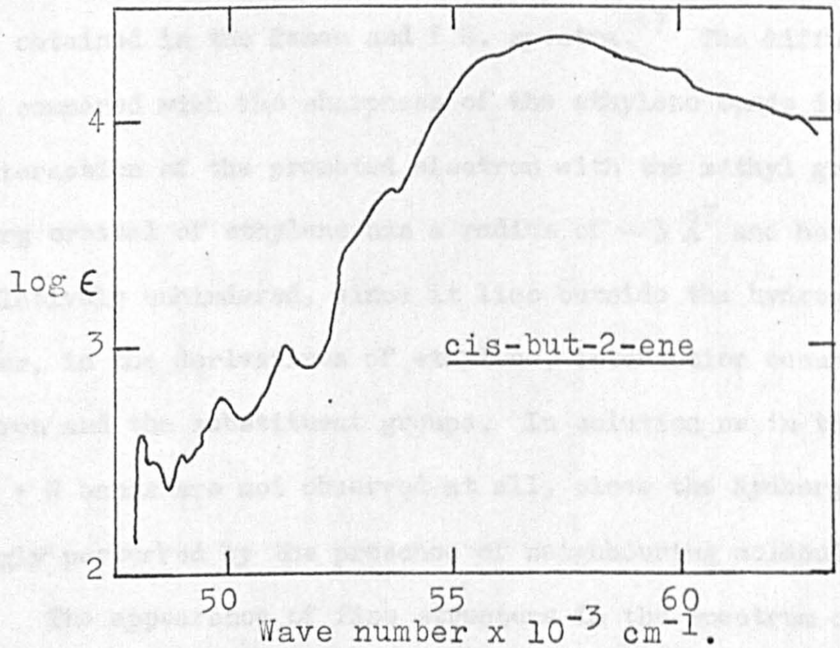
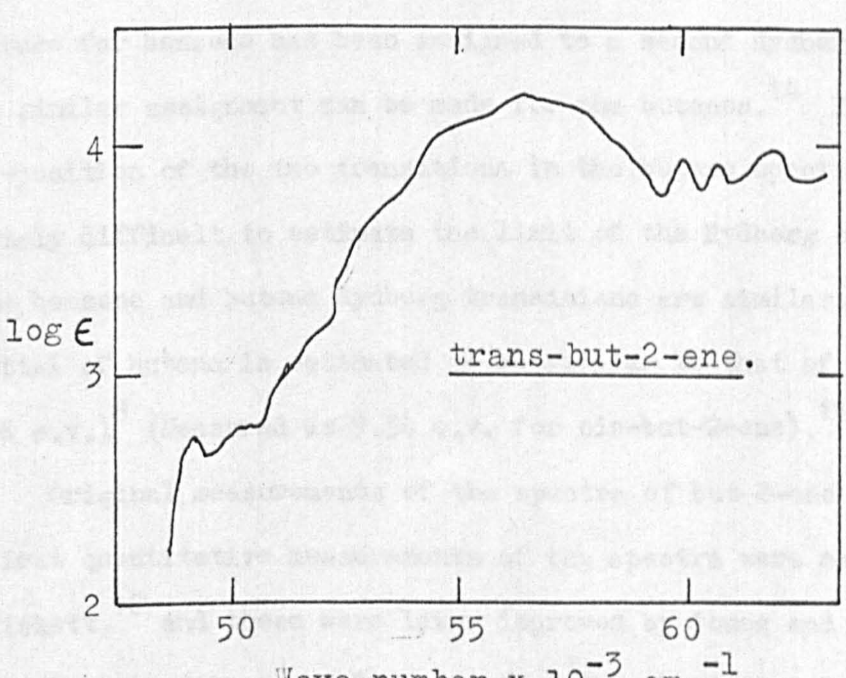


Figure 1.3



Absorption spectra of cis- and trans-but-2-ene.

bands obtained in the Raman and I.R. spectra.[17] The diffuseness of the bands compared with the sharpness of the ethylene bands is believed due to interaction of the promoted electron with the methyl groups. The Rydberg orbital of ethylene has a radius of ~3 Å[7] and hence the electron is relatively unhindered, since it lies outside the hydrogen atoms. However, in the derivatives of ethylene, interaction occurs between the electron and the substituent groups. In solution or in the solid phase, the R ← N bands are not observed at all, since the Rydberg orbital is strongly perturbed by the presence of neighbouring molecules.[18]

The appearance of fine structure in the spectrum of isobutene, which is not quite so well marked in cis- and trans-but-2-ene, has been compared to similar structure in benzene. Benzene can be considered for this purpose as ethylene with two cis-hydrogens replaced. The fine structure for benzene has been assigned to a second Rydberg transition,[19] and a similar assignment can be made for the butenes.[14] In view of the super-position of the two transitions in the butene spectrum it is extremely difficult to estimate the limit of the Rydberg series. However, as the benzene and butene Rydberg transitions are similar, the Ionization Potential of butene is estimated to be similar to that of benzene (~9.6 e.v.).[8] (Measured as 9.34 e.v. for cis-but-2-ene).[111]

Original measurements of the spectra of but-2-ene were qualitative.[12a] The first quantitative measurements of the spectra were made by Gary and Pickett,[16] and these were later improved by Jones and Taylor[20] using a photoelectric detector. Both measured the absorption intensities of the broad V ← N absorption. The results are given in Table 1.2.

Table 1.2

	Gary and Pickett		Jones and Taylor	
	λ_{max} Å	ϵ_{max} cm.$^{-1}$	λ_{max} Å	ϵ_{max} cm.$^{-1}$
cis	1754	21,900	1740	16,000
trans	1777	14,100	1780	13,000

The oscillator strengths for the bands were determined using the formula

$$f = 4.32 \times 10^{-9} \int_{\nu_1}^{\nu_2} \epsilon \, d\nu \qquad 1.I.^{21}$$

where the area of the band is taken as ϵ_{max} times the band width at half peak height. For cis f = 0.59, and for trans f = 0.32.[16]

The spectra of both butenes show that at 1849 Å the two transitions V ← N and R ← N are superimposed, the former being the most intense. Thus irradiation by light of 1849 Å may produce either the V state of butene, or a mixture of both V and R states.

1.3 Excited States

Mulliken[7,22] has discussed in theoretical terms the form of the excited states of ethylenic molecules which are produced by the absorption of ultraviolet light.

The Rydberg state maintains the planar form of the ground state molecule, although with a greatly reduced resistance to twisting. The barrier to rotation in the Rydberg state is put as low as 0.1 e.v. (cf. 2.66 e.v. in the ground state).[2] The sharpness of the absorption bands imply that the ground state structure is retained. However, in the upper singlet state V, the most stable form of the molecule is with the planes of the two CH_2 groups mutually perpendicular. The rotation is taken to account for the extended wavelength range of the $V \leftarrow N$ spectrum. The perpendicular nature of the excited state is further indicated by the pronounced shoulder on the long wavelength side of the spectrum, particularly noticeable in solution when the $R \leftarrow N$ bands are absent. This shoulder is due to molecules in the ground state occupying the first or second torsional vibration levels. Consequently, less energy is required to produce the 90° form from these levels, and absorption occurs at longer wavelengths. At 77°K the shoulder disappears, for almost all molecules are then in the zeroth vibrational level.[18]

Associated with singlet states V and R are triplet states T and R_T in which the spin of the electron has been reversed. The work of Evans[11] has shown that the $T \leftarrow N$ transition of ethylene lies at 2500 - 3600 Å, and is of very low intensity since it is spin-forbidden.

Although there is no experimental evidence on the structure of the T state of olefins, Walsh[23] suggests that triplet ethylene may have two non-planar groupings, and Mulliken and Roothaan[31] have estimated that the perpendicular form of the T state of ethylene would be more stable than the planar form by approximately 20 kcal.

No information is available on the state R_T, although comparing it with the relationship of state T to state V, the $R_T \leftarrow N$ transition would be expected to occur at longer wavelengths than the $R \leftarrow N$ transition.

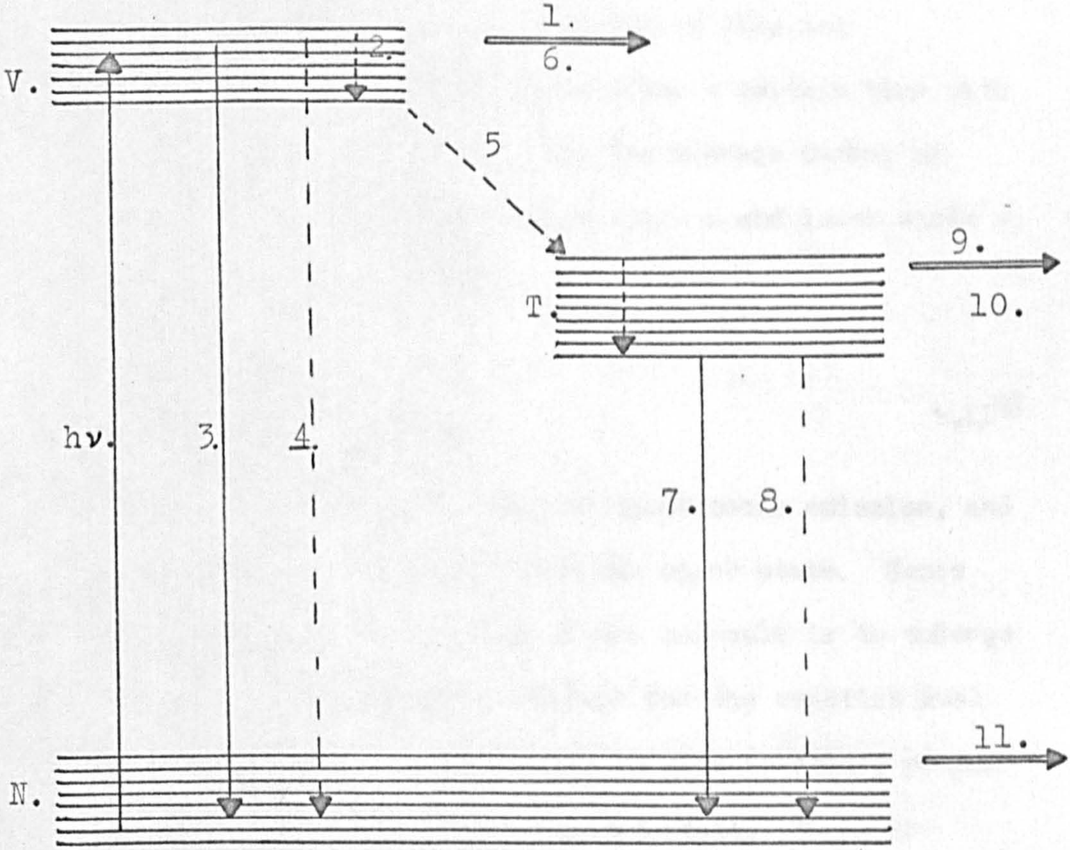
Once an excited singlet state V has been produced by absorption of radiation, the molecule can lose its energy by the following processes,[24] as illustrated on the Jablonski diagram in Figure 1.4.

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.
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.

Figure 1.4



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

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 (process 3). If A_{nm} is the average number of transitions per atom per second between upper state n and lower state m, the mean life of state n is defined as

$$\tau = {}^{1}/_{A_{nm}} \qquad 1.\text{II}^{25}$$

A_{nm} is the Einstein transition probability of spontaneous emission, and is related to 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-Bouguer-Lambert[26] law 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.

$$\log \left({}^{I_o}/_{I}\right) = \epsilon cl \qquad 1.\text{III}$$

where I_o and I are the intensities of entrant and emergent light respectively, with a path length l of absorbing species at a concentration of c moles/litre. The constant ϵ is the molar extinction coefficient and is a measure of the strength of absorption. The mean life τ, and ϵ are related by the expression

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

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

In the near ultraviolet this can be approximated to

$$\tau = 10^{-4}/\epsilon_{\text{max.}} \qquad 1.\mathrm{V}$$[28]

Thus for V ← N transitions in olefins, where $\epsilon_{\max}$ is of the order 10,000, τ is of the order of 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 life.

The mean life of the V state of butene as calculated from the spectral measurements of Gary and Pickett[16] is as follows:-

	cis-but-2-ene	trans-but-2-ene
τ	5.1×10^{-10} secs	1.5×10^{-9} secs

These mean lifetimes must be considered in relation to a vibrational period of $\sim 10^{-13}$ sec., a rotational period of $\sim 10^{-10}$ sec., and a collision frequency in the vapour phase of 2×10^{11} litres moles^{-1} sec.^{-1} (Calculated using a collision diameter of 6.5 Å for butene[29] in the relationship

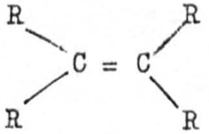
$$Z_o = \frac{2.N_o}{1000} \sigma^2 \left(\frac{\pi RT}{M}\right)^{\frac{1}{2}} \qquad [30] \quad 1.VI$$

where σ is the collision diameter and M the molecular weight of but-2-ene).

In view of the mutually perpendicular form of the CR_2 groups adjacent to the C=C bond in the V and T states of but-2-ene, deactivation of these states may be expected to lead to either cis- or trans-isomer, while deactivation of the R or R_T states would be expected to yield the original isomer.

1.4 Cis-Trans Isomerisation

The variation in energy of the N, V, R and T states of a simple olefin



as a function of the angle between the planes of the two CR_2 groups is given in Figure 1.5.[31]

However, when the olefin linkage is part of a conjugated system, the energy variations can be much more complicated, as is seen with stilbene[32] and azobenzene.[33]

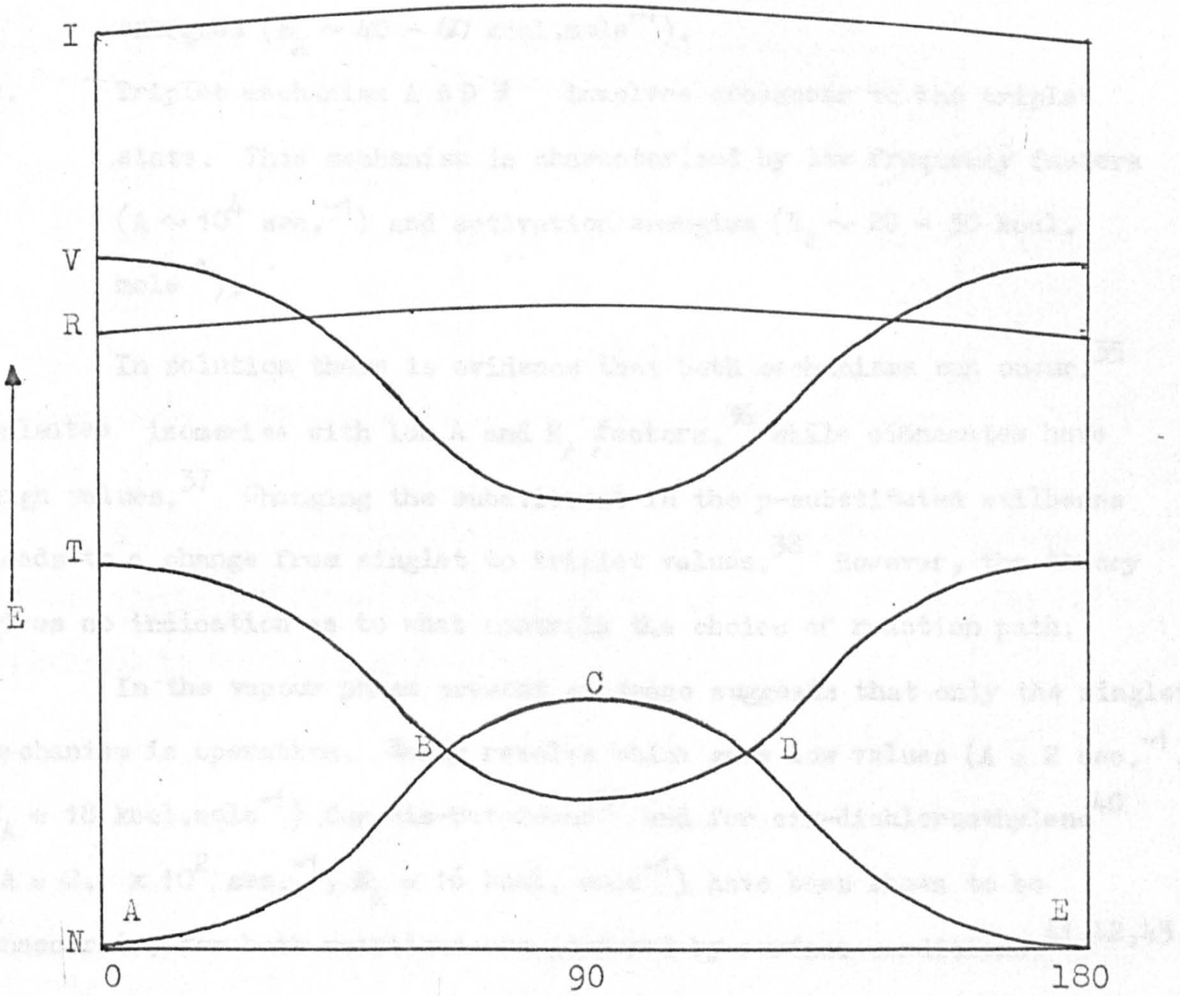
The pathway by which cis-trans isomerisation proceeds depends upon the energy that is put into the molecule. Thus thermal isomerisation would be expected to proceed via the N state, while photochemical isomerisation would proceed via the V, T or possibly R state.

1.4.1 Thermal Isomerisation

Figure 1.5 shows that in the perpendicular configuration the triplet state has lower energy than the ground state. This presents two possible pathways for isomerisation,[34] a purely singlet mechanism, or a mechanism involving transfer from the singlet state to the triplet state and vice versa.

1. The singlet mechanism A C E involves the formation of an activated complex, C. Enhanced stabilisation in the 90° form is attributed to resonance, due to the interaction between two equivalent

Figure 1.5



Variation in energy of states I,V,R,T and N with rotation about the C = C bond of a simple olefin.[31]

structures. The singlet mechanism is characterised by high (normal) frequency factors ($A \sim 10^{13}$ sec.$^{-1}$) and activation energies ($E_A \sim 40 - 60$ kcal.mole^{-1}).

2. Triplet mechanism A B D E involves crossover to the triplet state. This mechanism is characterised by low frequency factors ($A \sim 10^4$ sec.$^{-1}$) and activation energies ($E_A \sim 20 - 30$ kcal. mole^{-1}).

In solution there is evidence that both mechanisms can occur.[35] Maleates isomerise with low A and E_A factors,[36] while cinnamates have high values.[37] Changing the substituent in the p-substituted stilbenes leads to a change from singlet to triplet values.[38] However, the theory gives no indication as to what controls the choice of reaction path.

In the vapour phase present evidence suggests that only the singlet mechanism is operative. Early results which gave low values ($A = 2$ sec.$^{-1}$, $E_A = 18$ kcal.mole^{-1}) for cis-but-2-ene[39] and for cis-dichloroethylene[40] ($A = 2.1 \times 10^2$ sec.$^{-1}$, $E_A = 16$ kcal. mole^{-1}) have been shown to be inaccurate, for both reactions are governed by surface conditions.[41,42,43] When the surface effects were counteracted by 'conditioning', high A and E_A values were obtained. However, the values for but-2-ene were still considered low,[44] and Lifshitz, Bauer and Resler[45] extended the work up to a temperature of 1250°K, using a single-pulse shock tube, to reduce the errors obtained working over a limited temperature range. The best values for the thermal isomerisation of but-2-ene and the conditions they were obtained under are listed in Table 1.3.

Table 1.3

Temp. °C	Press. range mm.	A sec.$^{-1}$	E kcal.	Ref.
391 – 443	200 – 400	10^{11}	52	46
413 – 503	3×10^{-3} – 445	6.1×10^{13}	62.8	41
410 – 476	1.7×10^{-2} – 401	10^{14}	62.4	42
727 – 977	30 – 160	3.5×10^{14}	65	45

A further mechanism involving tunneling through the potential barrier between the two singlet states was considered to be of negligible importance by Magee, Shand and Eyring.[34]

1.4.2 Photochemical

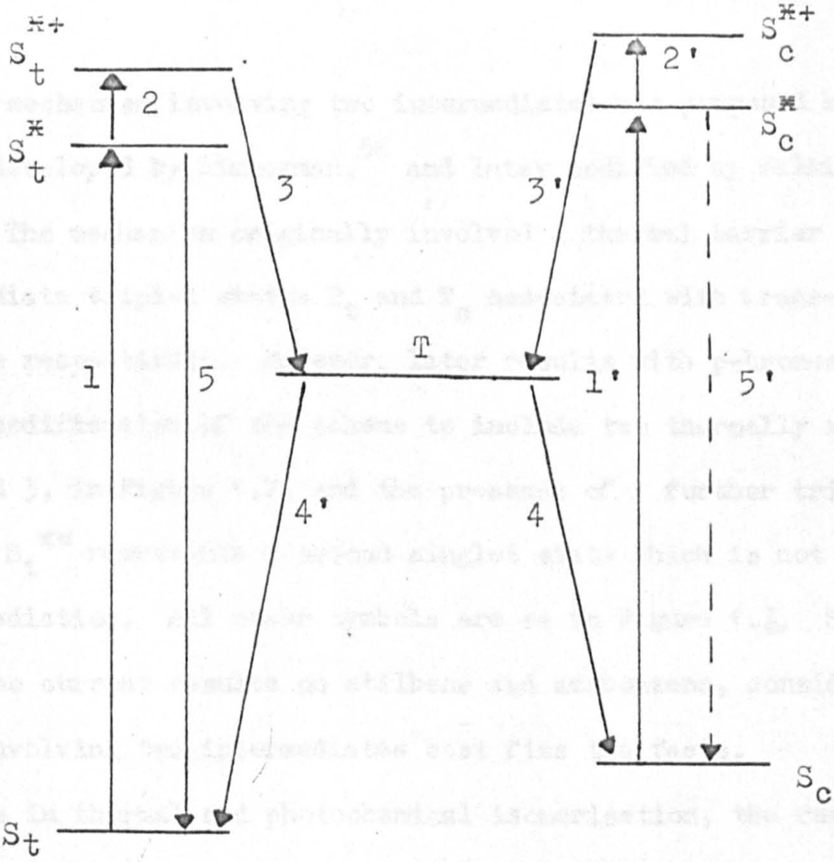
Although there is very little information on the direct photochemical isomerisation of simple olefins, conjugated compounds, particularly stilbene and azobenzene have been extensively investigated. Various theories have been proposed to explain the mechanism of cis-trans isomerisation, many being discarded as improved techniques have brought new facts to light. Olson,[47] basing his conclusions on the limited results available at the time, considered cis-trans isomerisation as occurring by rotation in an excited state common to both isomers, produced directly by absorption. However, a number of features, particularly concerning stilbene, were not explained by this mechanism.

viz. The fluorescence of the trans-isomer and not the cis-; the definite structure of the absorption spectrum of the trans-isomer, while the cis-isomer has a continuous absorption with no discrete levels. Lewis, Magel and Lipkin[48] interpreted the results in terms of the "loose bolt" theory,[49] in which the electronic energy of excitation of the cis-isomer is very rapidly connected to vibrational and rotational energy of the ground state. The molecule in this highly vibrationally excited state can then undergo cis-trans isomerisation. The cis-trans isomerisation of stilbene and substituted stilbenes is further complicated by the quantum yield of trans → cis conversion being dependent upon concentration, solvents, and very strongly dependent on temperature,[50] and by the formation of the side-product phenanthrene.[51] The discovery of an emission which was originally thought to be due to phosphorescence,[52] but was later shown to be caused by impurities,[53] led to the proposal of theories involving the triplet state as intermediate in the cis-trans isomerisation. There are two major schools of thought on the mechanism, one believing that a common triplet intermediate is involved, and the other postulating two triplet intermediates with a thermal barrier between them.

The single intermediate mechanism is supported by Schülte-Frohlinde[50] and by Dyck and McClure.[54] The reaction scheme is represented by Figure 1.6.

S_t, S_t^*, S_c, S_c^* are ground and 1st excited singlet states of trans- and cis-stilbene respectively. S_t^{*+} is a vibrationally excited level of the S_t^* state. The vibrational or rotational energy is equal

Figure 1.6



Mechanism of cis - trans isomerisation involving a single intermediate state.[50,54].

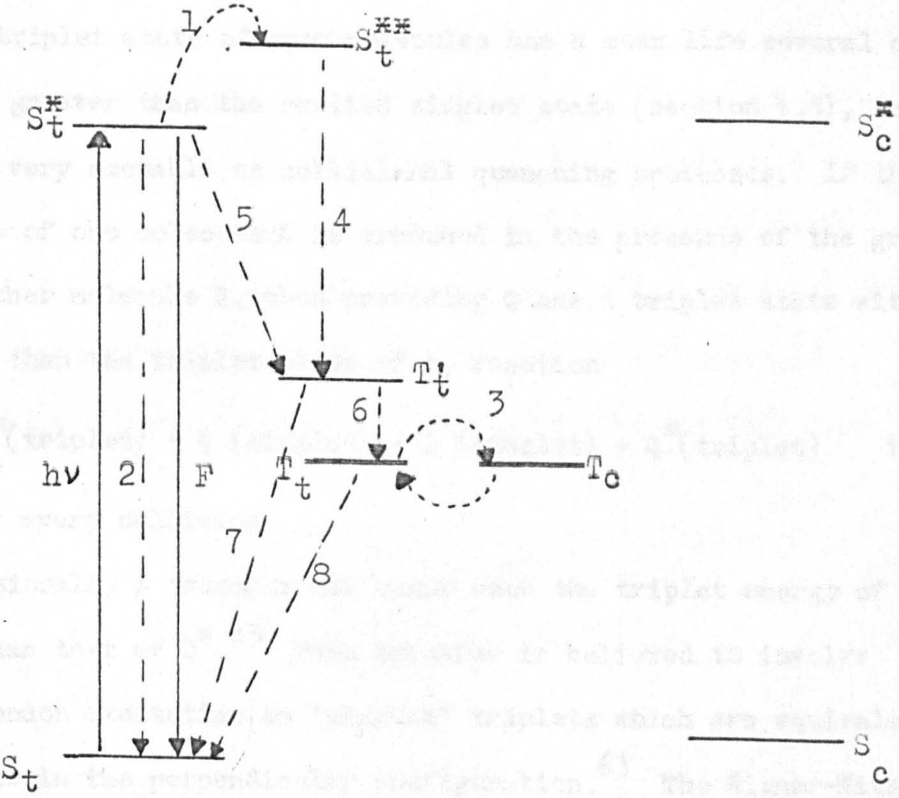
to the activation energy of the thermally activated singlet → triplet transition.

Isomerisation trans → cis involves 1, 2, 3, 4, and cis → trans involves 1', 2', 3', 4'. 5 represents fluorescence from the trans state, while 5' represents a possible radiationless combination with the ground state. Only processes 2 and 2' are considered to be thermally activated.

The mechanism involving two intermediates was proposed by Förster,[55] developed by Zimmerman,[56] and later modified by Malkin and Fischer.[57] The mechanism originally involved a thermal barrier between two intermediate triplet states T_t and T_c associated with trans- and cis-stilbene respectively. However, later results with p-bromostilbene[58] required a modification of the scheme to include two thermally activated steps, 1 and 3, in Figure 1.7, and the presence of a further triplet state T'_t. S_t^{**} represents a second singlet state which is not obtained by direct radiation. All other symbols are as in Figure 1.6. Stegemeyer,[59] reviewing the current results on stilbene and azobenzene, considers that the model involving two intermediates best fits the facts.

Thus in thermal and photochemical isomerisation, the reaction path includes the lowest possible energy states of the reactant molecules. Viz. the N and T states. The following review will cover other methods of inducing cis-trans isomerisation, considering, where possible, the nature of the excited states involved.

Figure 1.7



Mechanism of photochemical cis - trans isomerisation involving two intermediate states.

1.5 Photosensitisation

The process of photosensitisation involves the absorption of light energy by a strongly absorbing substance, the photosensitiser, and its transfer by collision to another substance which does not absorb in the spectral region employed. The non-absorbing molecule then quenches the energy of the excited molecule.

The triplet state of most molecules has a mean life several orders of magnitude greater than the excited singlet state (section 1.3), and is consequently very amenable to collisional quenching processes. If the triplet state of one molecule A is produced in the presence of the ground state of another molecule Q, then providing Q has a triplet state with energy lower than the triplet state of A, reaction

$$A^{*}(\text{triplet}) + Q\ (\text{singlet}) \rightarrow A\ (\text{singlet}) + Q^{*}(\text{triplet}) \qquad 1.\text{VII}$$

will occur at every collision.

Occasionally a transfer can occur when the triplet energy of A^{*} is less than that of Q^{*}.[63] This transfer is believed to involve non-Franck-Condon excitation to 'phantom' triplets which are equivalent to the T state in the perpendicular configuration.[63] The Wigner-Witmer rule[60] states that a change of multiplicity of Q must occur for the process to be spin-allowed. This process has been shown to occur in the solid,[61] liquid[62,63] and vapour[35,64] phases. For photosensitisation in the vapour phase, particularly in the ultraviolet region, the vapours of some metals have proved most useful. Steacie[66] defines a suitable sensitiser as a metal with a sufficiently high vapour pressure at a reasonably low temperature, and an excitation energy of the right order of magnitude. These requirements narrow down the choice for the u.v. region to mercury, cadmium and zinc. Of these, mercury has been the most extensively used.[35,64]

1.5.1 Mercury as Photosensitiser

Triplet state mercury has been used to transfer energy to both paraffinic and olefinic hydrocarbons. With paraffins a sufficiently low-lying triplet state is not available for process 1.VII to occur, so that the reaction is spin-forbidden. Quenching then results in the rupture of a C-H bond of the paraffin. With olefins a low-lying triplet state is available ($\sim 70 \pm 5$ kcals.[66] for but-2-ene c.f. 112.2 kcal. for mercury) and reaction 1.VII occurs at every collision, producing a vibrationally excited olefin triplet. This triplet can either decompose or be collisionally deactivated to the ground state by a radiationless intercombination. These processes are represented by the following sequence:-

$$\mathrm{Hg}\ 6(^1S_0) + h\nu \quad (\lambda\ 2537\ \text{Å}) \longrightarrow \mathrm{Hg}\ 6(^3P_1) \qquad 1.\mathrm{VIII}$$

$$C_nH_{2n} + \mathrm{Hg}\ 6(^3P_1) \longrightarrow C_nH_{2n}^{*+} + \mathrm{Hg}\ 6(^1S_0) \qquad 1.\mathrm{IX}$$

$$C_nH_{2n}^{*+} \longrightarrow \text{products} \qquad 1.\mathrm{X}$$

$$C_nH_{2n}^{*+} + M \longrightarrow C_nH_{2n}^{*} + M \qquad 1.\mathrm{XI}$$

$$C_nH_{2n}^{*} \rightsquigarrow C_nH_{2n} \qquad 1.\mathrm{XII}$$

where * represents triplet electronic excitation and $^+$ represents vibrational excitation.

The mercury sensitised photolysis of ethylene has been extensively studied and the mechanism is quite well understood. The production of

acetylene and hydrogen by an intramolecular decomposition was recognised by early workers,[67] although the possibility of a free radical mechanism[68] was not finally discounted until Cvetanovic and Callear[69] photolysed mixtures of C_2H_4 and C_2D_4. Kinetic studies of the decomposition required the existence of two excited states of ethylene, with approximately equal lifetimes, both of which could be collisionally deactivated but only one of which could decompose.[64] The sensitisation of cis-CHD:CHD[70] yielded the trans isomer, and also $CD_2:CH_2$, a reaction which again required the existence of two intermediate excited states:-
a) The triplet state of CHD:CHD which on deactivation could yield either cis- or trans-CHD:CHD. b) A triplet ethylidene formed by the migration of H or D, which could either decompose or be collisionally deactivated to yield $CD_2:CH_2$. Similarly in the sensitisation of but-1-ene, a 1,2 or 1,4 hydrogen atom shift in the excited state can explain the formation of methyl cyclo propane,[71] - which was originally thought to be but-2-ene.[72,73]

Mercury photosensitisation (input 112 kcal.mole^{-1}) results in the rupture of weak bonds β to the double bond,[74] yielding resonance stabilised allylic radicals. Cvetanovic and Doyle[71] discovered over thirty products formed by the combination and disproportionation reactions of the radicals formed by β-bond cleavage in but-1-ene. The ratio of C-C to C-H cleavage was found to be ~ 1.6 - 1.3. Although there are no β-bonds in ethylene, C-H cleavage does occur at room temperature, and becomes of increasing importance as the temperature is raised to 350°C.[75]

With but-2-ene the principle photosensitised reaction is cis-trans isomerisation,[72,76,29] with very little formation of other products except at lowest reactant pressures.[29] Cvetanovic, Gunning and Steacie,[76] working at 60 mm pressure of but-2-ene, obtained approximately equimolar mixtures of the two isomers after prolonged irradiation. Thus the excited triplet state gives either isomer with equal probability on deactivation. Cundall and Palmer[29] obtained a limiting value for the fraction of trans-isomer as 0.53 - 0.54. The small difference from 0.5 was considered due to different quenching efficiences of the two isomers. Below 30 mm pressure the rate of isomerisation was pressure dependent, and from the pressure effect the lifetime of the vibrationally excited triplet state of but-2-ene was calculated as 3.3×10^{-9} sec.[29] (c.f. but-1-ene 6.3×10^{-9} sec.;[71] methyl cyclopropane 4.7×10^{-9} sec.;[71] ethylene and ethylidene $\sim 4 \times 10^{-9}$ sec.[64]). At low pressure of but-2-ene Lossing, Marsden and Farmer,[74] showed, using the technique of a mass spectrometer coupled directly to the reaction vessel, that β C-H bond cleavage occurred to yield the γ-methylallyl radical $CH_3.CH{=}CH.\dot{C}H_2$ in considerable amounts. Other products were butadiene and hydrogen, possibly formed by molecular decomposition, some propylene and allene, and a dimer. Kebarle and Avrahami[77] working at a pressure of 2μ cis-but-2-ene mixed with 10 mm helium at a temperature of 55°C, used a similar technique to Lossing, Marsden and Farmer, and discovered that even at such low pressure the main fate of the excited triplet butene molecule was collisional deactivation, the ratio of deactivated to decomposed being approximately 3:2. A large number of products C_1 to C_8 were obtained which could be explained by two primary processes:- β C-H bond cleavage and also a rearrangement of the excited triplet to give methyl and allyl radicals.

$$\text{cis } (C_4H_8\text{-}2)^* \longrightarrow \cdot CH_2{:}CH.CH_2 + \cdot CH_3 \qquad 1.XIII$$

The methylallyl radical is considered to be a mesomer of the two forms

$$CH_2{=}CH{-}\dot{C}H{-}CH_3 \rightleftharpoons \cdot CH_2{-}CH{=}CH{-}CH_3 \qquad 1.XIV$$

and its recombination with other radicals would be expected to lead to two distinct products. The direct elimination of hydrogen to form butadiene is considered unlikely, since no direct elimination occurs in the mercury photosensitised decomposition of propylene.[78] Thus the transfer of energy from mercury (112 kcal.mole^{-1}) to but-2-ene yields a vibrationally excited triplet state of butene. At high pressures (> 30 mm) this is deactivated to yield either isomer with approximately equal probability, while at low pressures the excited molecule has sufficient energy to undergo β C-H bond cleavage. The production of both isomers on deactivation indicates that the triplet state involved is T (Figure 1.5). Deactivation of the Rydberg triplet state R_T would be expected to yield only the original isomer.

1.5.2 Other photosensitisers

1.5.2.a. Metals and Inorganic Sensitisers

Cadmium Cd $5(^3P_1)$ (87.3 kcal.mole^{-1}) has been successfully used to photosensitise the isomerisation of but-2-ene,[79] although the rate is slower than with mercury. Although zinc Zn 4($^3P_1$) (92.5 kcal.mole^{-1}) has not been used, it should equally well cause isomerisation. However, sodium Na 3(^2P) (48 kcal.mole^{-1}) has insufficient energy to cause isomerisation.[80]

Photoexcited sulphur dioxide[81] has been discovered to transfer energy to olefins in the vapour phase, and transfer to but-2-ene[29] results in isomerisation. This has been taken as an indication that the lowest triplet state of sulphur dioxide (73.4 kcal.mole^{-1})[82]is involved in the transfer.

1.5.2.b Organic sensitisers

A variety of organic compounds, and in particular benzene, has been used to photosensitise but-2-ene. The cis-trans isomerisation reaction sensitised by benzene has recently been followed by I.R. spectroscopy.[83] The value for the photostationery state cis/trans has been reported as 1.37[84] and 1.0.[85] The results for a range of sensitisers investigated by Cundall and c0-workers are given in Table 1.4.

Table 1.4

Sensitiser	Triplet state energy kcal.mole^{-1}	Resulting cis-trans isomerisation of but-2-ene	Ref.
Benzene	85	Yes	84,29
Pyridine	85	"	84
Pyrrol	83	"	84
Toluene	83	"	35
Fluorobenzene	85	"	35
cis-dichloroethylene	?	"	35
Formic Acid	?	"	35
Cyclopentanone	?	"	35
Acetone	~78	"	35,29
Benzophenone	68.5	"	35
Styrene	62	No	84
Acrylonitrile	?	"	35
Vinyl Acetate	?	"	35
Biacetyl	54.9	"	29
Cyclopentanone	?	"	35

The difference in the photostationary states that are obtained are attributed to the different quenching cross-sections of the butene isomers in the interaction with the sensitisers.[35]

Thus, in order to induce isomerisation of but-2-ene the sensitiser must have a triplet state energy in excess of ~ 65 kcal.mole^{-1}. This is a good indication that the triplet state energy of but-2-ene is $\geqslant$ 65 kcal.mole^{-1}. The sole products from the triplet state are either the cis- or trans-isomer, unless the triplet state is highly vibrationally excited, when C-H bond cleavage can occur.

1.6 Radiation Sensitised Isomerisation

The radiation-sensitised isomerisation of but-2-ene is in essence the same as the photosensitised isomerisation. The triplet state of the sensitiser which is produced by the γ-radiation, transfers its energy to the butene.

$$\text{Benzene (singlet)} \overset{\gamma}{\rightsquigarrow} \text{Benzene (triplet)} \qquad 1.\text{XV}$$

$$\text{Benzene (T)} + \text{trans-but-2-ene (S)} \longrightarrow \text{but-2-ene (T)} + \text{Benzene (S)} \qquad 1.\text{XVI}$$

$$\text{But-2-ene (T)} \longrightarrow \text{cis- or trans-but-2-ene} \qquad 1.\text{XVII}$$

However, the production of ions, free electrons and free radicals as well as the excited states, may be expected to complicate the reactions. In benzene solution free radical scavengers iodine[86] and ferric chloride,[87] when present in low concentration, have no effect upon the isomerisation. However, when iodine is present in sufficient concentration to deactivate the triplet state,[88] the isomerisation is reduced. Side products, which constitute less than 5% of the products, are substantially reduced by the radical scavengers. Further evidence for a triplet state mechanism is obtained from the addition of naphthalene and anthracene[87] which have lower triplet state energies (61 and 42 kcal. mole^{-1} respectively) than benzene (85 kcal.mole^{-1}) and but-2-ene ($\sim$ 65 - 70 kcal.mole^{-1}), and oxygen,[87] which quenches the triplet state. The additions lead to a reduction in the amount of isomerisation.

In the vapour phase benzene, toluene and acetone[89] all sensitise the isomerisation, although free radical products are also formed.

Inorganic sensitisers nitric oxide[90] and sulphur dioxide[90] transfer triplet energy although the latter leads to some formation of sulphinic acid and polymer, probably by a free radical mechanism.[89]

Thus, although there is clear evidence for a triplet state mechanism the radiation-sensitised reaction similar to that in the photosensitised reaction, the products are complicated by the presence of free radicals in the system.

1.7 Radical Isomerisations

The addition of a radical to the double bond of an olefin requires very little energy. (H + C=C $E_A \sim 2$ kcal./mole;[91] $CH_3\cdot$ or $C_2H_5\cdot$ + C=C $E_A \sim 5$ kcal./mole[65]). Hence olefins act as efficient scavengers of radicals in a system. The resultant adduct radical is vibrationally excited with the energy of the newly formed bond, and its lifetime is sufficient for it to undergo rotation about the C-C bond and also for it to be involved in further collisions. Consequently, there is a competition between isomerisation, which involves expulsion of the original radical after rotation, and addition which results from vibrational deactivation of the adduct radical. The competition is best illustrated by the reactions of but-2-ene with halogen-[89,92,93,87] or sulphur-[94,89,45] containing radicals, produced either thermally,[93] photolytically[92,94] or radiolytically.[87,89,95] Initially, a π-complex is formed between the radical and olefin,[96] held together by charge transfer processes. With all halogens except iodine this π-complex rapidly collapses to a σ-complex[97] (free radical).

X(halogen or, S-radical) + A (olefin) $\rightarrow$ π-complex $\rightarrow$ σ-complex[35] 1.XVIII

The adduct radical deactivated by collision abstracts from the halogen or sulphur radical source, yielding a dihalide or disulphide. In all cases the isomerisation reaction predominates over the addition reaction.

Addition of hydrogen atoms to but-2-ene results in cis-trans isomerisation, but the mechanism is not necessarily the same as with halogen- or sulphur-containing radicals. Positional isomerisation is also obtained by exchange reactions of the hydrogen atom,[89] while Rabinovitch[98] and co-workers, have found that sec-butyl radicals, formed by the addition of H to cis-but-2-ene, dissociate and do not isomerise;

$$C_4H_9^{*} \longrightarrow CH_3\cdot + C_3H_6 \qquad 1.XIX$$

and hence they explain the cis-trans isomerisation as resulting from disproportionation between sec-butyl radicals and decomposition of secondary n-butyl radicals.

Thus the presence of free radicals in a system containing but-2-ene can lead to isomerisation possibly by a variety of reactions.

1.8 Radiolysis

The bombardment of olefins by high energy electrons produced by a Van de Graaff accelerator, or by γ-rays from a Co^{60} source, results in the formation of excited states, ion-molecules and free radicals. The final products of radiolysis are a compromise between the reactions of these various species.

The radiolysis of ethylene has received considerable attention, largely because there is much information available for comparison from mass spectrometry, photosensitisation and photochemistry. Initial excitation produces the ion-molecule $C_2H_4^+$ and an excited state which dissociates to yield either molecular hydrogen and acetylene, or atomic hydrogen and the sequent free radicals.

In the vapour phase below 150 mm[99] $C_2H_4^+$ possibly dissociates yielding acetylene and hydrogen, while above 150 mm,[99,100] and also in the liquid[101] and solid[102] phases, $C_2H_4^+$ participates in condensation reactions of the type:-

$$C_2H_4^+ + C_2H_4 \longrightarrow C_4H_8^+ \qquad 1.XX$$

$$C_4H_8^+ + C_2H_4 \longrightarrow C_6H_{12}^+ \text{ etc.} \qquad 1.XXI$$

Polymers up to C_{18}, mainly branched chain mono-olefins, have been detected in the solid phase,[102] while lack of polymers above the trimer in the liquid phase has been accounted for by more rapid electron neutralisation, and hence chain termination.[101]

Elimination of molecular hydrogen has been detected in all three phases,[103] two modes of splitting being demonstrated by use of deuterated ethylenes.

$$CD_2 = CH_2 \longrightarrow :C = CH_2 + D_2 \qquad 1.XXII$$

$$CD_2 = CH_2 \longrightarrow CD \equiv CH + HD \qquad 1.XXIII$$

The vinylidene radical rapidly rearranges to acetylene. The acetylene yield in the vapour phase accounts for only 10% of the ethylene used up,[99] the remainder yielding condensation products.

The importance of radicals has been demonstrated particularly in the liquid phase,[101] where $G_{\text{radical products}} \approx G_{\text{molecular products}}$.[104] The radical products can be almost totally accounted for by the presence of ethyl, vinyl and methyl-allyl radicals.

$$C_2H_4 \rightsquigarrow C_2H_3\cdot + H\cdot \qquad 1.XXIV$$

$$H\cdot + C_2H_4 \rightarrow C_2H_5\cdot \qquad 1.XXV$$

$$C_2H_3\cdot + C_2H_4 \rightarrow C_4H_7\cdot \qquad 1.XXVI$$

The participation of ions and free radicals has been demonstrated in the radiolysis of propylene,[105] the butenes[106] and higher olefins.[107]

Although the geometric isomer is the major product of the radiolysis of cis- or trans-but-2-ene,[104,108,109] little information is available on the mechanism of formation, for attention has been centred on the reactions of the molecule-ion $C_4H_8^+$. In the liquid phase condensation of the ion leads to a number of branched chain dimers

(80% mono-olefins) and unspecified higher polymers.[106] Alternatively, the ion may undergo the reaction:-

$$C_4H_8^{+} + C_4H_8 \longrightarrow C_4H_9^{+} + \cdot C_4H_7 \quad ^{108} \qquad 1.XXVII$$

which may be considered as proton transfer or hydrogen atom abstraction. The 1-methyl allyl radicals so formed are mainly the cis isomers from cis-but-2-ene, and almost exclusively the trans isomer from trans-but-2-ene. The carbonium ion $C_4H_9^{+}$ after neutralisation yields an excited sec-butyl radical which may decompose:-

$$C_4H_9^{*} \longrightarrow \cdot CH_3 + C_3H_6 \qquad 1.XXVIII$$

abstract hydrogen to form n-butane:-

$$C_4H_9^{*} + C_4H_8 \longrightarrow C_4H_{10} + \cdot C_4H_7 \qquad 1.XXIX$$

or stabilise to sec-butyl radicals. Thus the only radicals present are 1-methyl allyl, sec-butyl and methyl.[108] Elimination of the radicals by p-benzoquinone and iodine, which are more effective scavengers than cis-but-2-ene, indicates that hydrogen, acetylene and propylene, and most of the geometric (trans) and positional (but-1-ene) isomers are formed by a molecular mechanism.[109]

The neutralisation of the $C_4H_8^{+}$ ion is believed to yield an excited molecule $C_4H_8^{*}$ which produces a mixture of singlet and triplet molecules. Cis-trans isomerisation would then occur in the triplet state.[109]

$$\text{Cis}^{+} + e \longrightarrow \text{Cis}^{*} \qquad 1.\text{XXX}$$

$$\text{Cis}^{*} \longrightarrow \tfrac{1}{4}\ \text{cis (singlet)} \qquad 1.\text{XXXI}$$

$$\longrightarrow \tfrac{3}{4}\ \text{cis (triplet)} \longrightarrow \tfrac{3}{8}\ \text{trans} \qquad 1.\text{XXXII}$$

$$\longrightarrow \tfrac{3}{8}\ \text{cis}$$

The addition of naphthalene and anthracene which have lower ionisation potentials (8.12 and 7.23 e.v.[110]) than cis-but-2-ene (9.34 e.v.[111]) results in charge transfer to the additive, and hence in a reduction of isomerisation:-

$$\text{Cis}^{+} + \text{M} \longrightarrow \text{Cis} + \text{M}^{+} \qquad 1.\text{XXXIII}$$

The formation of the geometric isomer in the vapour phase has been reported as the major product,[106] but also as not important.[87] A significantly larger amount of fragmentation products (hydrogen $C_1 - C_3$ hydrocarbons) are produced compared with the liquid phase. This is due to increased collisional deactivation of the excited molecules in the liquid phase, while in the vapour phase dissociation readily occurs.

Thus, in the direct radiolysis of but-2-ene, although geometrical isomerisation does occur, a large number of other products are produced due to the interactions of ion-molecules, excited states and free radicals.

1.9 Photolysis

Finally, a discussion of the few studies of the direct photolysis of olefins.

Decomposition of ethylene by light of 1470 Å[112] produces hydrogen both molecularly and atomically.

$$C_2H_4 \longrightarrow C_2H_2 + H_2 \quad \phi_1 \qquad 1.XXXIV$$

$$C_2H_4 \longrightarrow C_2H_2 + 2H\cdot \quad \phi_2 \qquad 1.XXXV$$

For these reactions $\phi_1 \approx \phi_2$. It is unlikely that the reaction

$$C_2H_4 \longrightarrow C_2H_3 + H \qquad 1.XXXVI$$

occurs, for no products characteristic of vinyl radicals are produced. The hydrogen atoms are scavenged by ethylene to produce ethyl radicals.

Variation of the exciting wavelength results in an increase in the proportion of atomic hydrogen to molecular hydrogen as the wavelength is shortened[113] (C_2H_2/H_2 is 2.8 ± 0.2 at 1236 Å,[113] 2.01 ± 0.1 at 1470 Å[112] and 1.2 ± 0.1 at 1849 Å[114].).

Similarly, atomic and molecular elimination of hydrogen is exhibited on photolysis of propylene, at 1470 Å and 1236 Å[115] although molecular elimination of methane is also important:-

$$\text{atomic:} \qquad CH_3 - CH = CH_2 \rightarrow CH_3\cdot + H\cdot + C_2H_2 \qquad 1.XXXVII$$

$$\text{molecular:} \quad \begin{cases} CH_3 - CH = CD_2 \rightarrow H_2 + CH_2 = C = CD_2 & 1.XXXVIII \\ CH_3 - CH = CH_2 \rightarrow CH_4 + C_2H_2 & 1.XXXIX \end{cases}$$

However, a further three primary reactions have been invoked to reasonably explain the final distribution of products.

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

$$C_3H_6 \rightarrow :CH_2 + C_2H_4 \qquad 1.XLI$$

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

The photolysis of 2-methyl-propene at 1900 Å has given rise to free radicals from an excited state which is pressure quenched,[116] while pressure has no effect on the majority of the products formed in the photolysis of but-1-ene at 1849 Å.[117] Although polymerisation occurs with 2-methyl-propene, only a trace of C_8 hydrocarbons have been detected from but-1-ene. The photolysis of the latter is explained by two primary reactions

$$C_4H_8 - 1 \rightarrow \cdot CH_3 + \cdot C_3H_5 \qquad 1.XLIII$$

$$C_4H_8 - 1 \rightarrow \cdot H + CH_2 = CH - \underset{\cdot}{C}H - CH_3 \qquad 1.XLIV$$

followed by recombination of these various radicals.

Finally, Cundall has attempted the photolysis of but-2-ene with light from an aluminium spark (1860 - 1920 Å) and has obtained high molecular weight products and some associated isomerisation, but he has not investigated the reaction in any detail.[35]

Summary

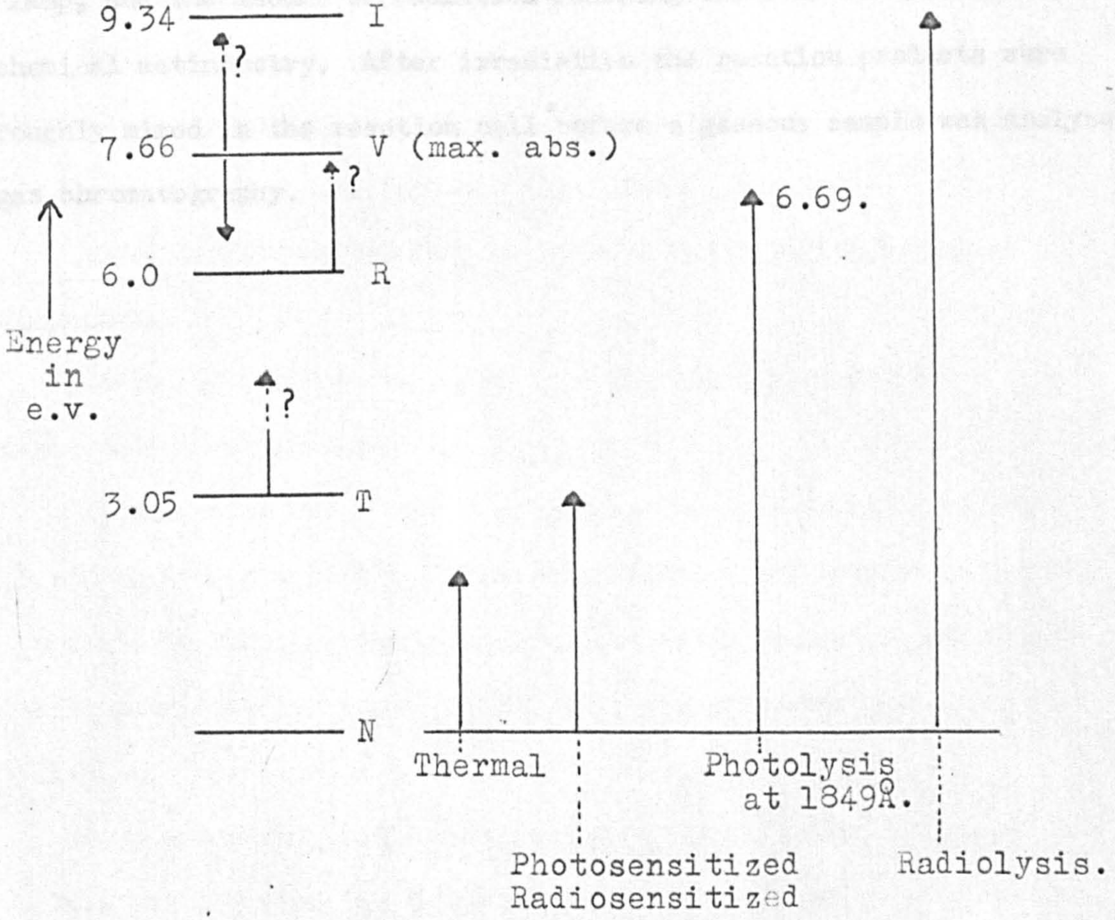
Figure 1.8 represents the energies of the various excited states of cis-but-2-ene, and the order of the energy put into the molecule in the reactions described in the preceeding sections.

Low energy input (thermal, photosensitised and radiosensitised) results almost solely in cis-trans isomerisation reactions. High energy input (radiolysis) results not only in cis-trans isomerisation, but in atomic and molecular elimination reactions from excited states or molecular ions. Increasing energy of photolysing radiation of ethylene, produces an increase of atomic elimination relative to molecular elimination.

Irradiation by 1849 Å radiation will possibly produce a mixture of the R and V states of butene, the former planar, and the latter twisted with the CH_3-C-CH planes mutually perpendicular. If both states are produced, then the products may be expected to be a compromise between the reactions of both excited states. In fact, on irradiation of but-2-ene at 1849 Å, a large number of hydrocarbon products, as well as the geometrical isomer, are formed, and these can only be explained by postulating the presence in the system of a mixture of excited states.

Figure 1.8

Comparison of the energy levels of the excited states of but-2-ene with the input energies of the processes discussed in section 1.



2. EXPERIMENTAL

2.1 Introduction

Cis- or trans-but-2-ene, at a known pressure, was introduced into the thermostated reaction cell via a mercury-free vacuum system. The gas was irradiated for a known period of time with a low pressure mercury vapour lamp. 1849 Å was the activating radiation emitted by the lamp, and the amount of radiation reaching the cell was measured by chemical actinometry. After irradiation the reaction products were thoroughly mixed in the reaction cell before a gaseous sample was analysed by gas chromatography.

2.2 Materials

Cis- and trans-but-2-ene were Phillips Research Grade materials. The cis-but-2-ene contained less than 0.05% of the trans isomer, and the trans-but-2-ene contained less than 0.10% of the cis isomer, butane and propylene. The gases were used without further purification.

Ethylene was originally prepared by the action of zinc and methanol on ethylene dibromide. It was purified by repeated distillation in vacuum. Matheson Research Grade ethylene was used in later experiments.

Hydrogen bromide was prepared by the action of bromine on tetralin (tetrahydronaphthalene)[118] and collected as a white solid at 77°K. Purification was by repeated distillation in vacuum.

Ammonia was obtained from a cylinder and purified by vacuum distillation.

Carbon dioxide was obtained from the solid material by repeated vacuum sublimation.

Nitric oxide was prepared by the action of moderately dilute sulphuric acid on a solution of potassium nitrite and potassium iodide,[119] and purified by bubbling through strong potassium hydroxide and concentrated sulphuric acid. Final purification was achieved by vacuum distillation.

Oxygen was obtained from a cylinder, liquified at 77°K and the middle portion from the third distillation retained.

Oxygen-free nitrogen was obtained from a cylinder, dried over silica-gel and then stored in a bulb cooled at 77°K, for several hours before use. Argon was obtained from a cylinder and purified by repeated vacuum distillation.

Materials for quantitative calibration and qualitative analyses were either Matheson Research Grade gases (methane, ethane, propylene, ethylene, but-1-ene, buta-1,3-diene) or pure liquid samples obtained from British Petroleum Co. (C_5 hydrocarbons) and Gulf Petroleum Co.(C_6 - C_8 hydrocarbons).

2.3 Apparatus

The high vacuum apparatus is represented by Figure 2.1.

A conventional mercury diffusion pump could not be used in the system because of the importance of keeping the system mercury-free. The presence of mercury in the reaction cell would result in:-

a) preferential absorption of the radiation by the mercury, resulting in the production of excited mercury atoms, and b) photosensitisation of the but-2-ene by the excited mercury atoms. Consequently, an oil diffusion pump (Figure 2.2) was used.

The pump was a three stage oil diffusion pump filled with a charge of 150 mls. Edwards No. 704 Silicone Oil, and it was backed by an Edwards Speedivac Rotary Oil Pump (Type 1.S.50). This combination, pumping through a trap cooled in liquid nitrogen, was capable of producing a vacuum of 10^{-5} mm. Hg.

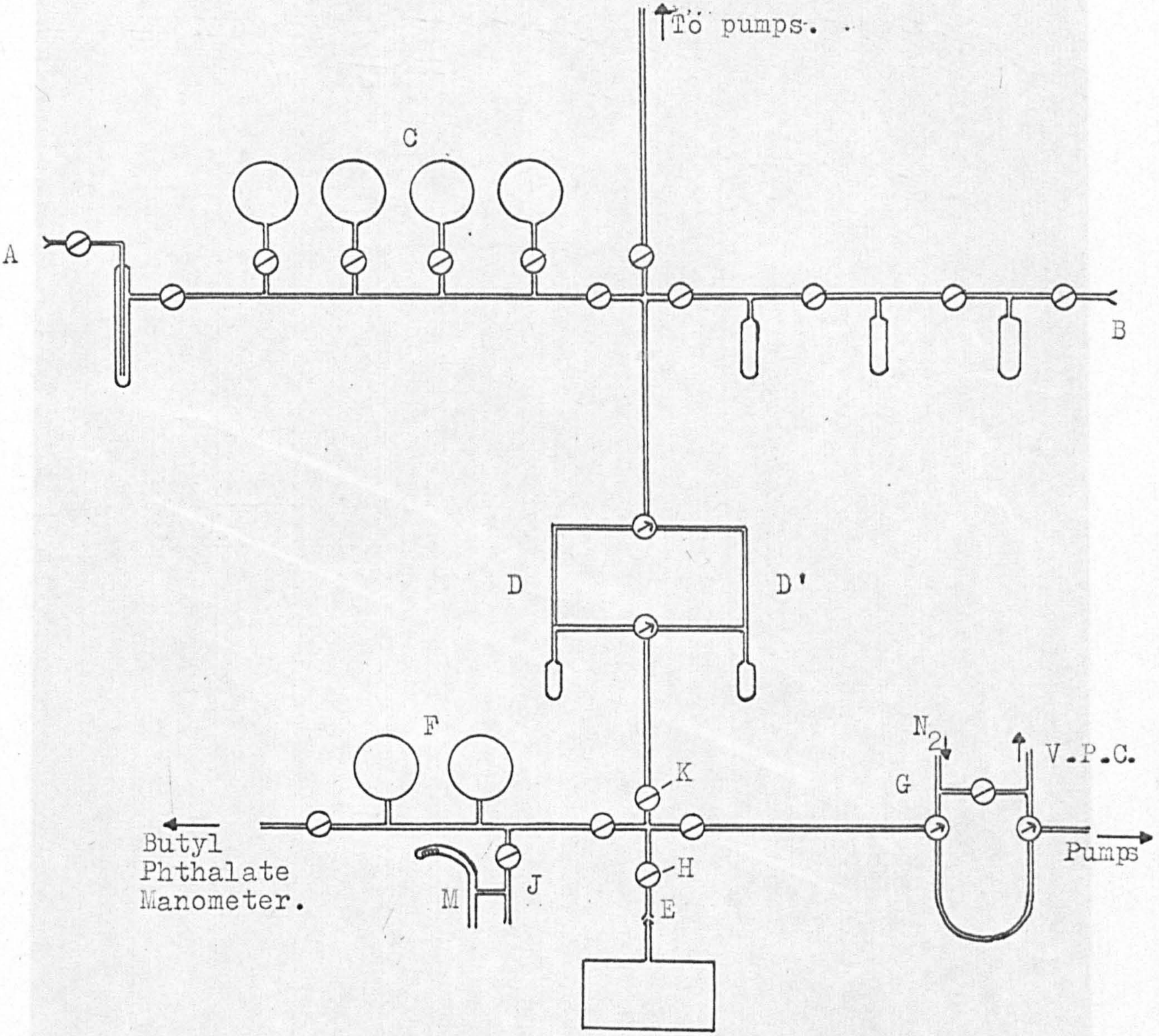
Pure gases were introduced into the system via inlet A, liquified in cooled traps and then degassed before use or storage. Impure gases were introduced at B, and purified by bulb to bulb distillation along the distillation train. Gases were stored in one litre bulbs, C, which were fitted with freeze-arms to assist recovery of the gases from the vacuum line.

The reaction cell was attached to the system at E, via a B.10 ground-glass joint which was lubricated with Edwards High Vacuum Silicone Grease. This joint provided for easy removal of the cell when necessary.

D and D' provided alternate routes for the gases from the storage

Figure 2.1

The Vacuum System.



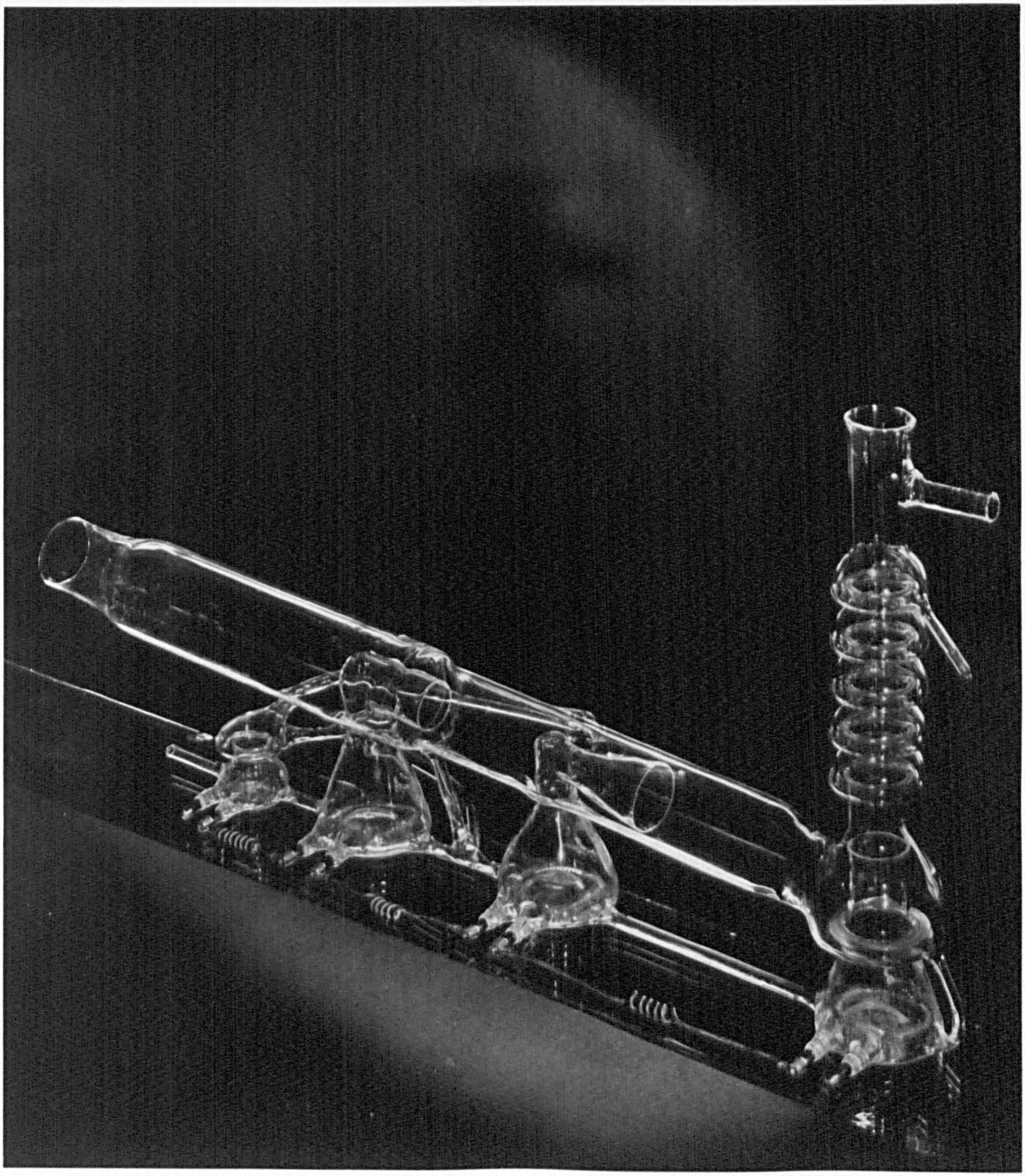


Figure 2.2

Oil Diffusion Pump.

bulbs to the reaction cell, and also any one section provided a useful 'siding' for holding gases before mixing, or before introduction into the cell.

Pressure measurements were made on Edwards Absolute Dial Gauges (Type C.G.3.) at F, calibrated 0-20 mm. and 0-760 mm., and on a butyl phthalate manometer. It was necessary to check the calibration of the gauges against the mercury manometer of an independent vacuum system. The gauges and mercury manometer were separated by a trap cooled in liquid nitrogen to prevent mercury distilling into the vacuum system. Immediately after calibration the mercury manometer and trap were sealed off from the vacuum system. The calibration charts for the two gauges are given in Figures 2.3 and 2.4. The 0-20 mm. gauge was accurate, while the 0-760 mm. gauge had a zero error of 26 mm. The butyl phthalate manometer was used for measuring pressures in the range 20-40 mm.

Gaseous samples were introduced into the gas chromatograph through the U-tube at G. In diagram 2.5, taps I and II were three-way glass stopcocks, while III was a straight-through stopcock. A sample was taken for analysis by the following procedure:-

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 the U-tube was evacuated. Tap II was then closed.

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

Figure 2.3

Calibration of 0-20mm. Dial Gauge against a mercury manometer.

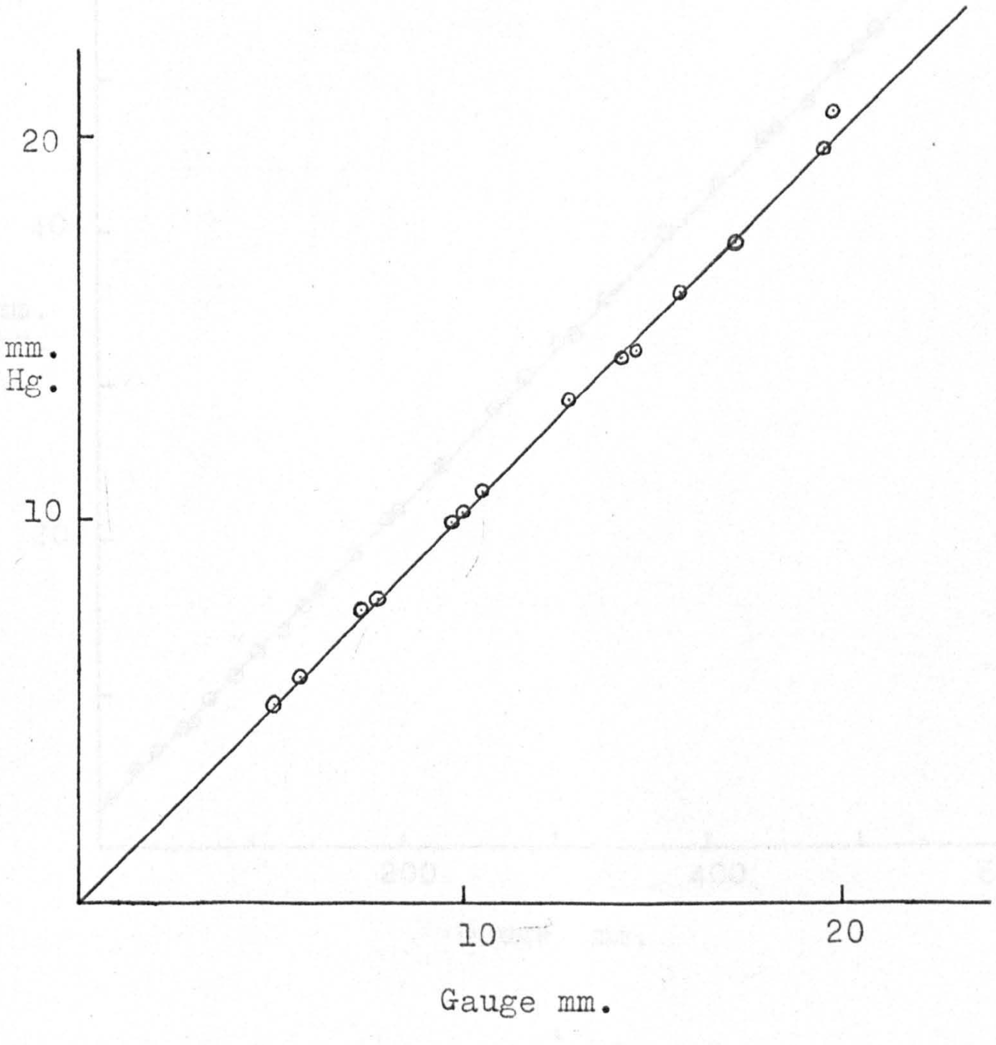


Figure 2.4

Calibration of 0-760 mm. Dial Gauge against a mercury manometer.

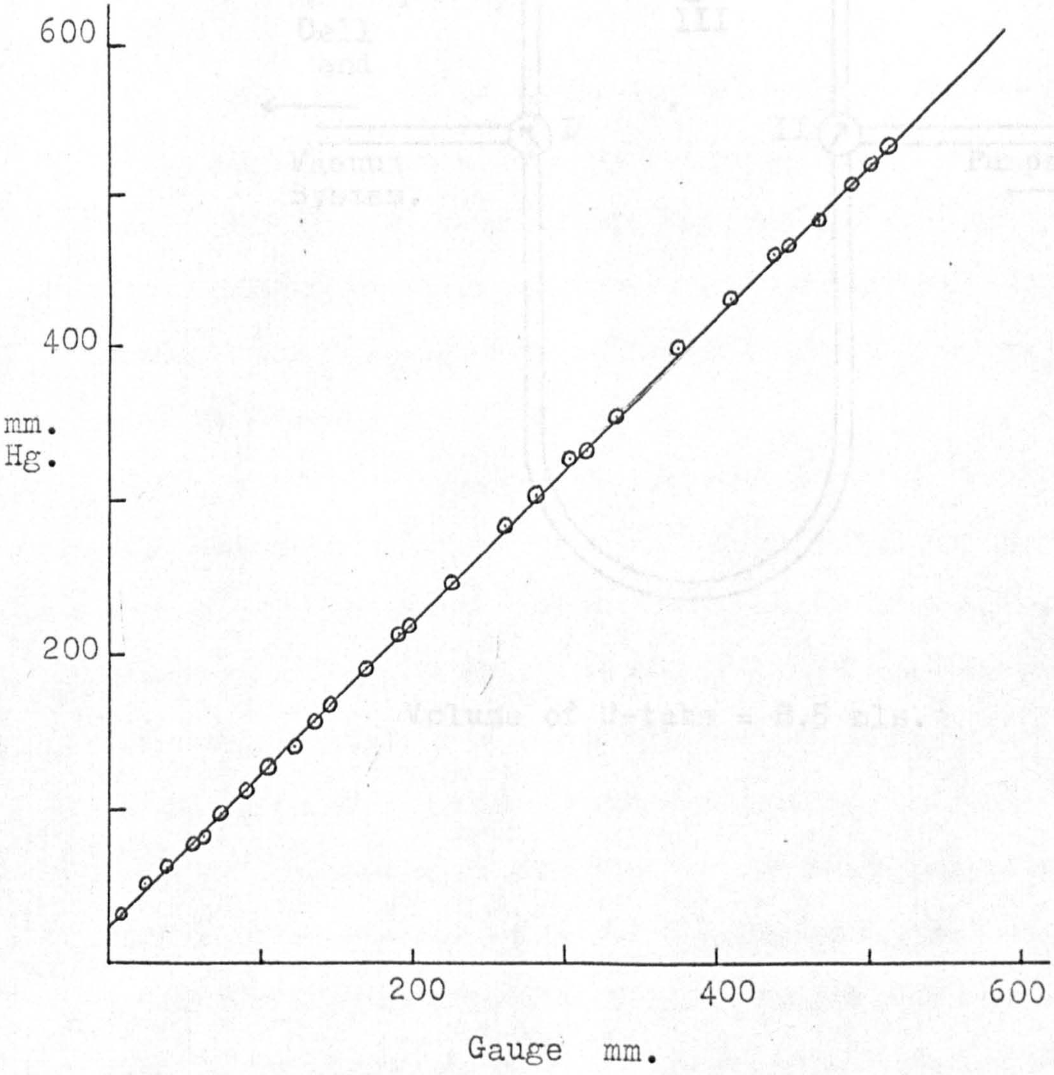
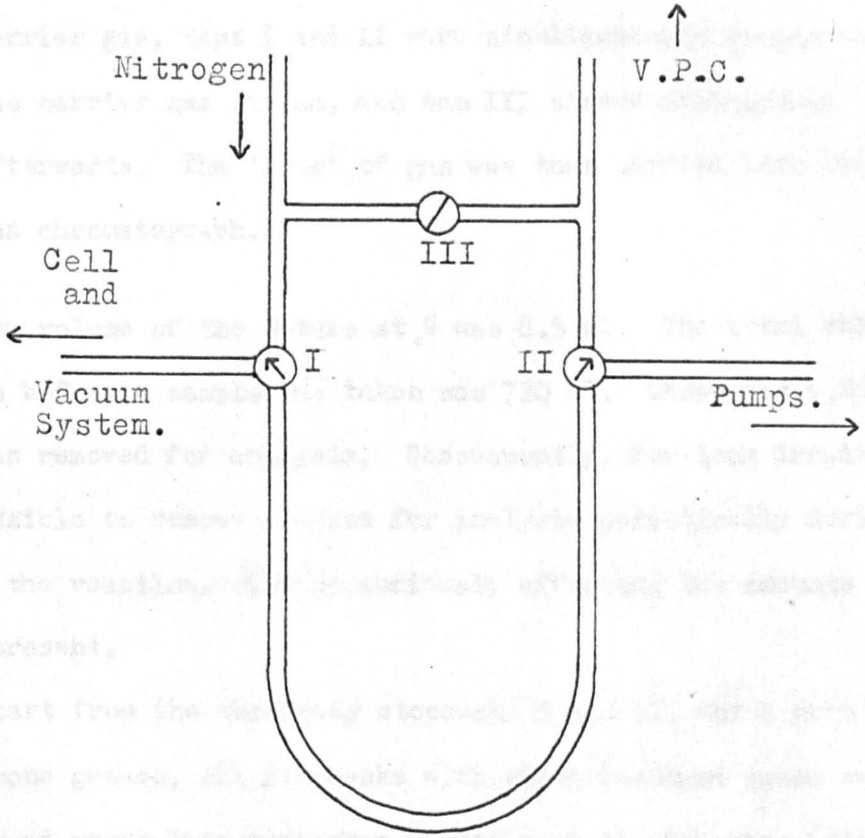


Figure 2.5

Gas sampling tube for vapour phase chromatography.



Volume of U-tube = 8.5 mls.

d) Tap I was briefly opened to the carrier gas stream and then closed. Carrier gas entered the U-tube and forced the gas to be analysed into a 'slug' against tap II.

e) Before the gaseous 'slug' had time to diffuse through the carrier gas, taps I and II were simultaneously opened to the carrier gas stream, and tap III closed immediately afterwards. The 'slug' of gas was then carried into the gas chromatograph.

The volume of the U-tube at G was 8.5 ml. The total volume of the gas before a sample was taken was 720 ml. Thus only 1.2% of the gas was removed for analysis. Consequently, for long irradiations, it was possible to remove samples for analysis periodically during the course of the reaction, without seriously affecting the amounts of material present.

Apart from the three-way stopcocks I and II, which were lubricated with silicone grease, all stopcocks with which reactant gases came into contact, were greaseless Springham Valves with fluorocarbon (Viton A) diaphragms. These do not absorb paraffin or olefin hydrocarbons, and are resistant to attack by hydrogen bromide and bromine. All other stopcocks in the system were lubricated with Appiezon L grease.

On completion of the experiments with trans-but-2-ene, great difficulty was experienced in removing final traces of butene from the vacuum system, even after all the stopcocks had been regreased, the fluorocarbon diaphragms replaced, and the system continuously pumped for several days. The continued presence of butene in $10^{-7} - 10^{-8}$ molar concentration was attributed to adsorption of the gas on the walls of the vacuum system. It could only finally be removed by a thorough flaming down of the whole system.

2.4 Reaction Cells

2.4.1 Vapour Phase

2.4.1.a. Cell

Originally the reaction cell was a Pyrex clyinder, 80 mm. long and 50 mm. in diameter with a side arm connecting it to the vacuum system through a B.10 joint at E. The end windows were of Spectrosil and were sealed on with Araldite. However, this arrangement proved unsatisfactory because:-

i) During irradiation, a polymer formed on the cell window which could only be removed by chromic acid or concentrated nitric acid. The acid, however, also attacked the Araldite, breaking the vacuum-tight seal. It was then necessary to remove all the hardened Araldite and recement the windows to the cell.

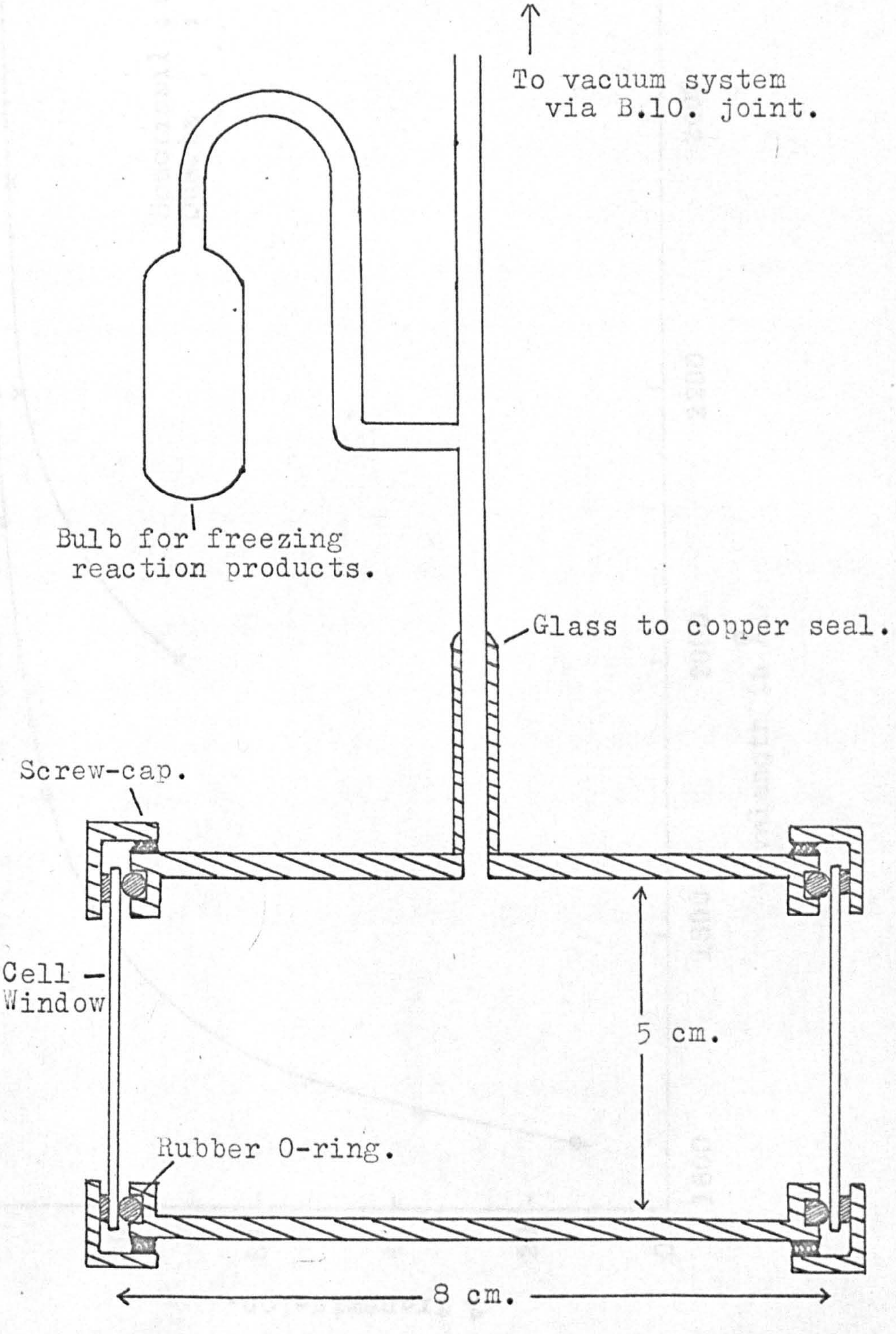
ii) The Araldite itself was photodecomposed, and was also attacked by the bromine formed in the actinometric photolysis of hydrogen bromide.

These difficulties were overcome by use of the metal cell illustrated in Figure 2.6. It consisted of a brass cylinder of the same dimensions as the pyrex cell, with the Spectrosil windows held on by O-rings and screw caps. These provided for easy removal of the windows when they became coated in polymer.

The side arm was attached to the cell via a glass to copper junction, the copper tube being soldered into the wall of the cell. Connection with the vacuum line was via the B.10 joint at E. The bulb

Figure 2.6

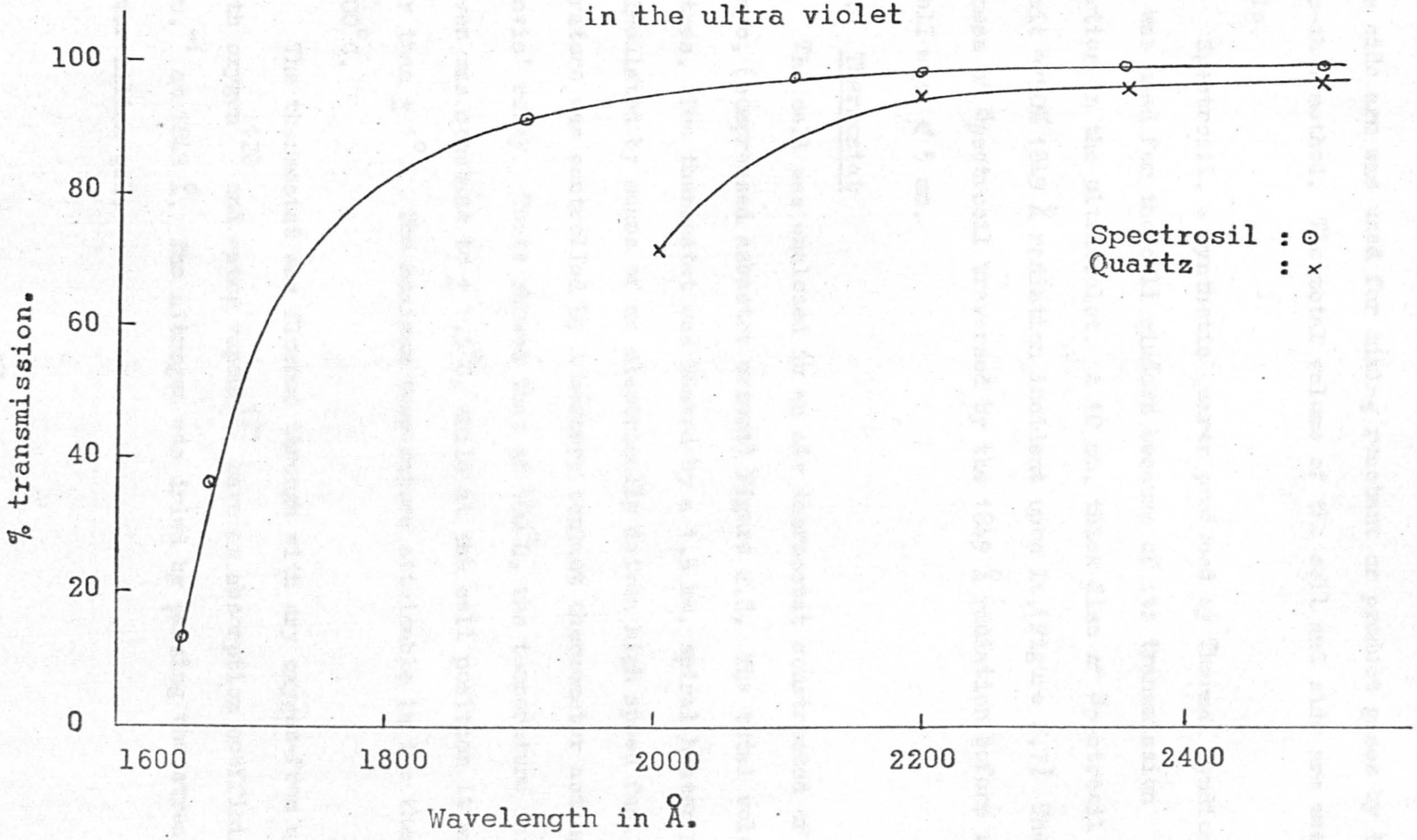
Vapour Phase Cell.



Volume of cell + side-arm = 155 mls.

Figure 2.7

Comparison of the transmission data of spectrosil and quartz in the ultra violet



on the side arm was used for mixing reactant or product gases by the freeze-thaw method. The total volume of the cell and side arm was 155 mls.

Spectrosil, a synthetic quartz produced by Thermal Syndicate Ltd., was used for the cell windows because of its transmission properties in the ultraviolet. A 10 mm. thick disc of Spectrosil will transmit ~90% 1849 Å radiation incident upon it,(Figure 2.7). The total thickness of Spectrosil traversed by the 1849 Å radiation before reaching the cell was $<$ 5 mm.

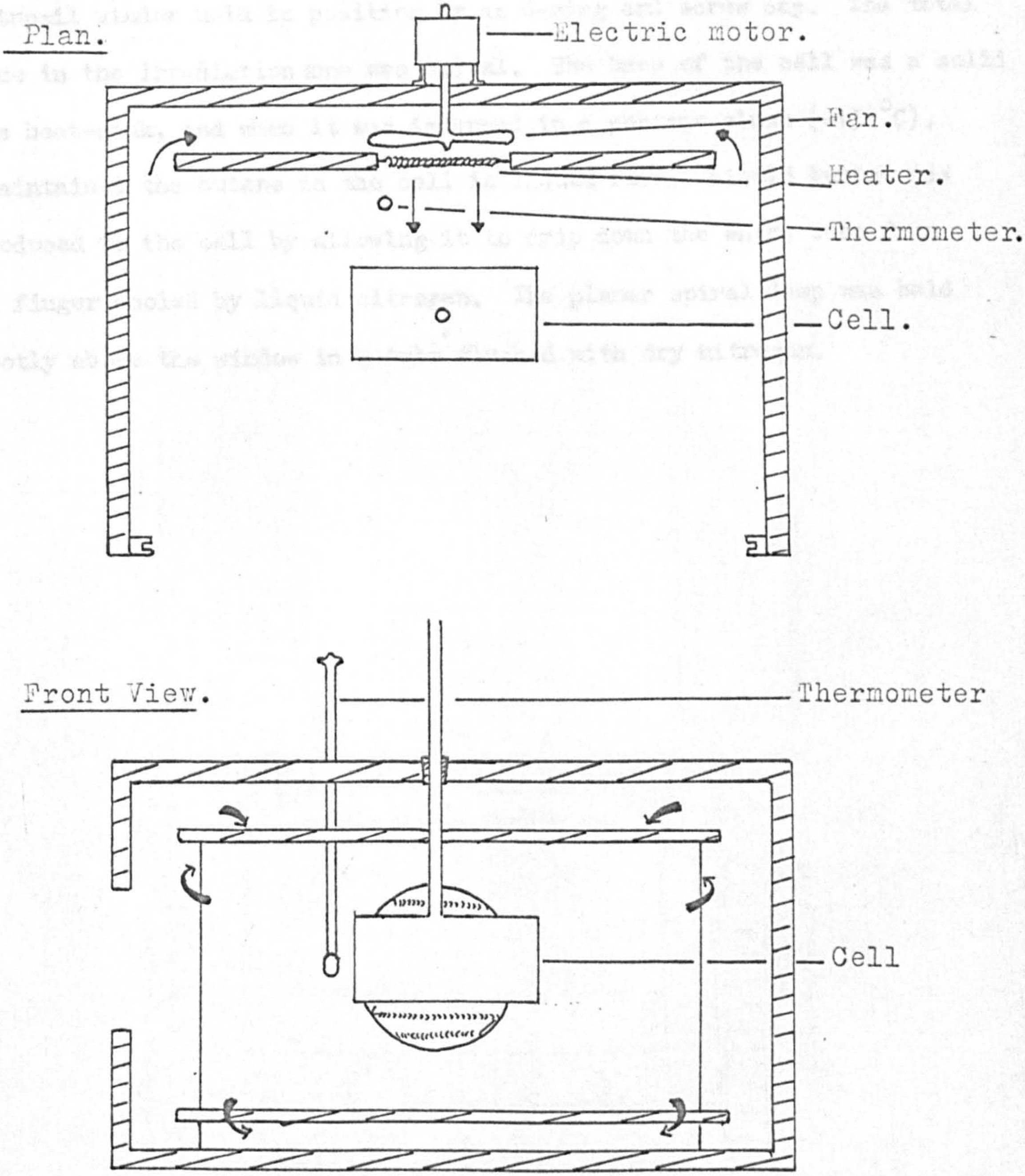
2.4.1.b Thermostat

The cell was enclosed in an air thermostat constructed of Sindanyo, (compressed asbestos cement) Figure 2.8. 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 temperature was controlled by a mercury contact thermometer acting through a 'Sunvic' relay. Tests showed that at 100°C, the temperature throughout the oven was constant to ± 1.5°C, while at the cell position it was better than ± 1°C. The maximum temperature attainable in the thermostat was 200°C.

The thermostat was flushed through with dry oxygen-free nitrogen, as both oxygen[120] and water vapour[121] have an absorption coefficient of 1.5 cm.^{-1} at 1849 Å. The nitrogen was dried by passing the stream of gas over silica gel.

Figure 2.8

The Air Thermostat.



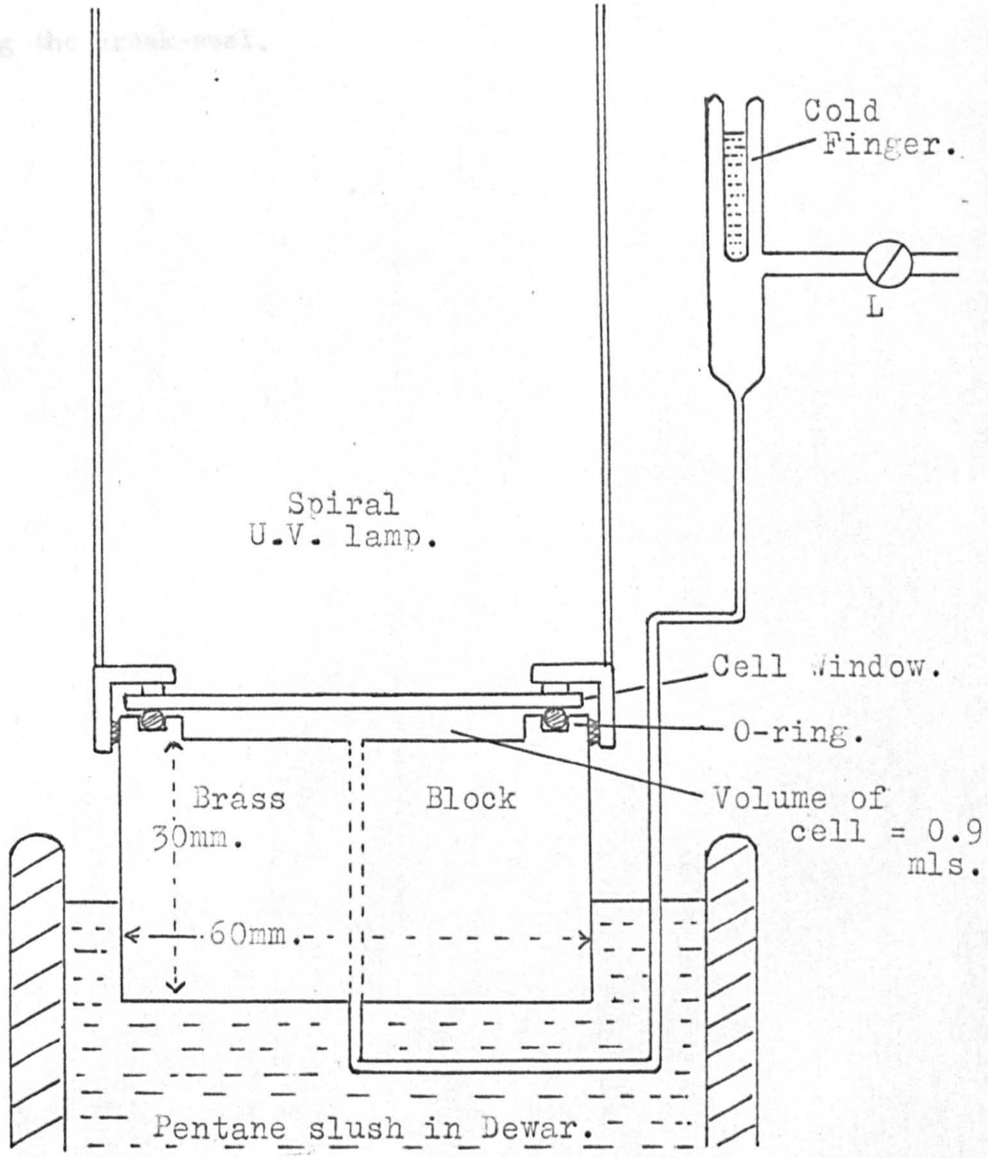
Arrows indicate direction
of air flow.

2.4.2 Liquid Phase

The cell is illustrated in Figure 2.9. It was connected to the vacuum line at J (Figure 2.1.). It was constructed of brass with a Spectrosil window held in position by an O-ring and screw cap. The total volume in the irradiation zone was 0.9 ml. The base of the cell was a solid brass heat-sink, and when it was immersed in a pentane slush (-131 °C), it maintained the butene in the cell in liquid form. Liquid butene was introduced to the cell by allowing it to drip down the entry tube from a cold finger cooled by liquid nitrogen. The planar spiral lamp was held directly above the window in a tube flushed with dry nitrogen.

Figure 2.9

Liquid Phase Cell

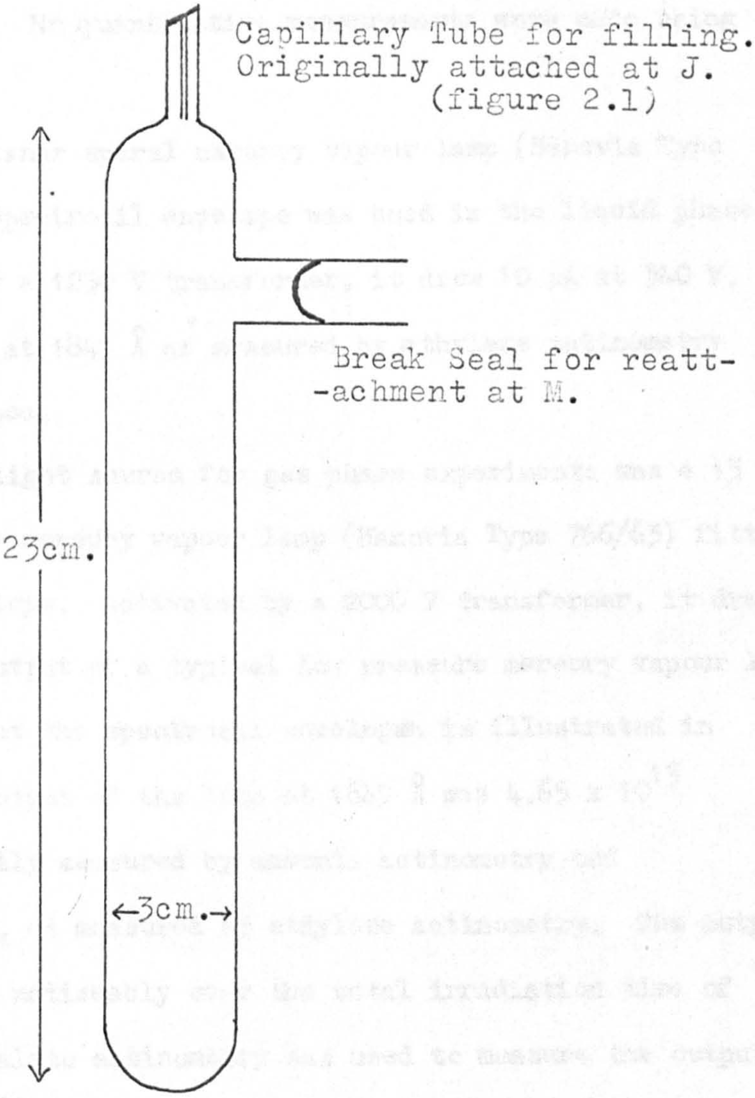


2.4.3 Radiolysis Cell

The cell is illustrated in Figure 2.10. It consisted of a Pyrex cylinder of total volume 75 mls. connected to the vacuum system via a capillary arm at J (Figure 2.1). For irradiation the capillary was sealed and the cell removed from the vacuum system. Following irradiation the cell was reconnected to the vacuum system at M (Figure 2.1) via the side arm containing the break-seal.

Figure 2.10

The Radiolysis Cell



2.5 Light Sources

2.5.1 Ultraviolet

Preliminary experiments were conducted using a Phillips 4 watt Ozonising lamp (Type 024W) which had ∼5% of its output at 1849 Å (5×10^{14} quanta/sec.). No quantitative measurements were made using this lamp.

A 2 watt 12" planar spiral mercury vapour lamp (Hanovia Type 752/62) fitted with a Spectrosil envelope was used in the liquid phase photolysis. Powered by a 1250 V transformer, it drew 10 μA at 340 V. The output of the lamp at 1849 Å as measured by ethylene actinometry was 2.8×10^{15} quanta/sec.

The principal light source for gas phase 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 vapour lamp in the ultraviolet, without the spectrosil envelope, is illustrated in Figure 2.11.[123] The output of the lamp at 1849 Å was 4.65×10^{15} quanta/sec. as originally measured by ammonia actinometry and 3.54×10^{15} quanta/sec. as measured by ethylene actinometry. The output at 1849 Å did not fall noticeably over the total irradiation time of ∼ 800 hrs. Uranyl oxalate actinometry was used to measure the output at 2537 Å as 1.45×10^{16} quanta/sec. The output of the two minor lines at 1942 Å and 2020 Å was found to be less than 10% of the 1849 Å line in a similar lamp.[122]

The lamp was housed in a closed tube (Figure 2.12), constructed of

Figure 2.11

Relative intensities of the emission lines of a low pressure mercury lamp.

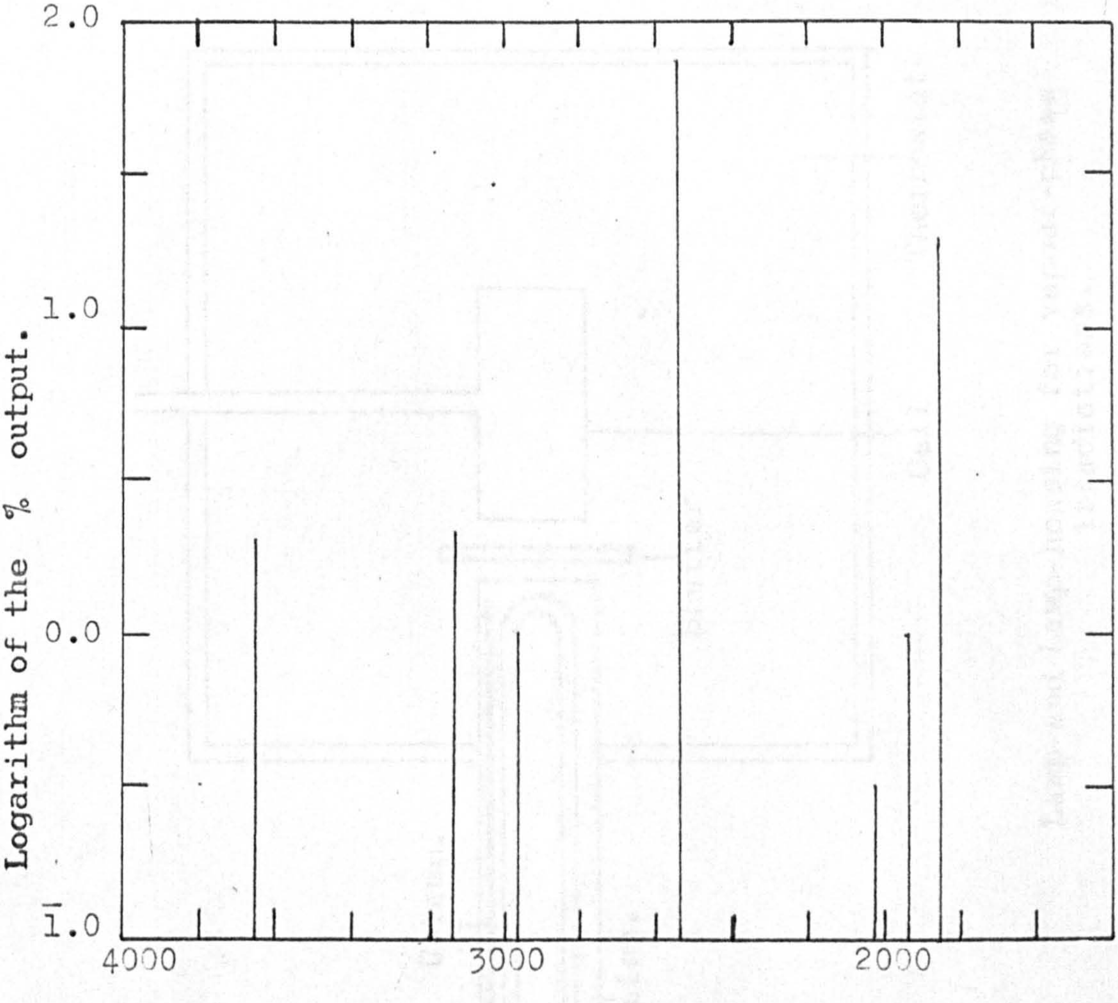
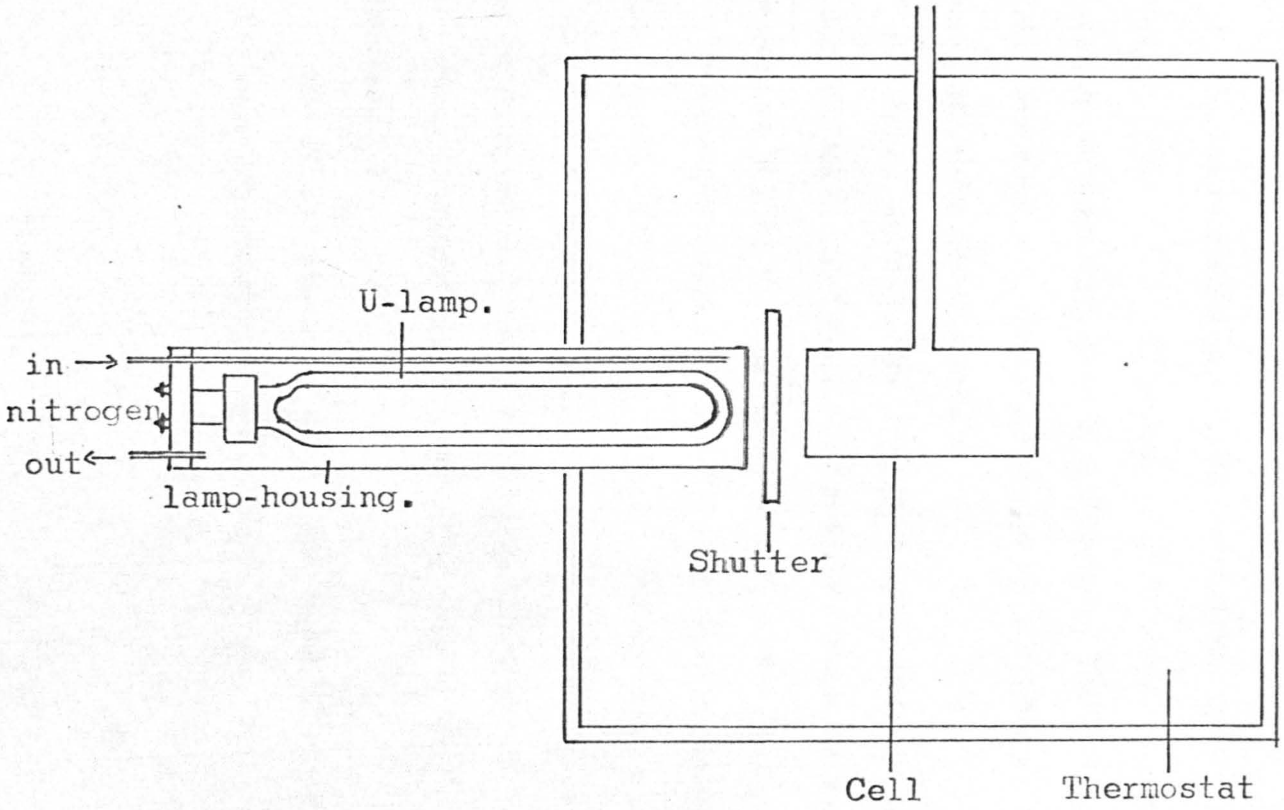


Figure 2.12



Lamp and Lamp-housing for vapour-phase irradiations.

Q.V.F. pipes, with an end window of Spectrosil sealed on with Araldite. The apex of the U-lamp was 1 cm. from the end-window. During an irradiation the lamp-housing was flushed through with dry nitrogen.

2.5.2 Optical System

Originally, an attempt was made to focus the 1849 Å radiation at a point near the centre of the cell using a 50 mm. diameter f.1 lens of Spectrosil. However, the lens was found to absorb almost all of the 1849 Å radiation and was therefore discarded.

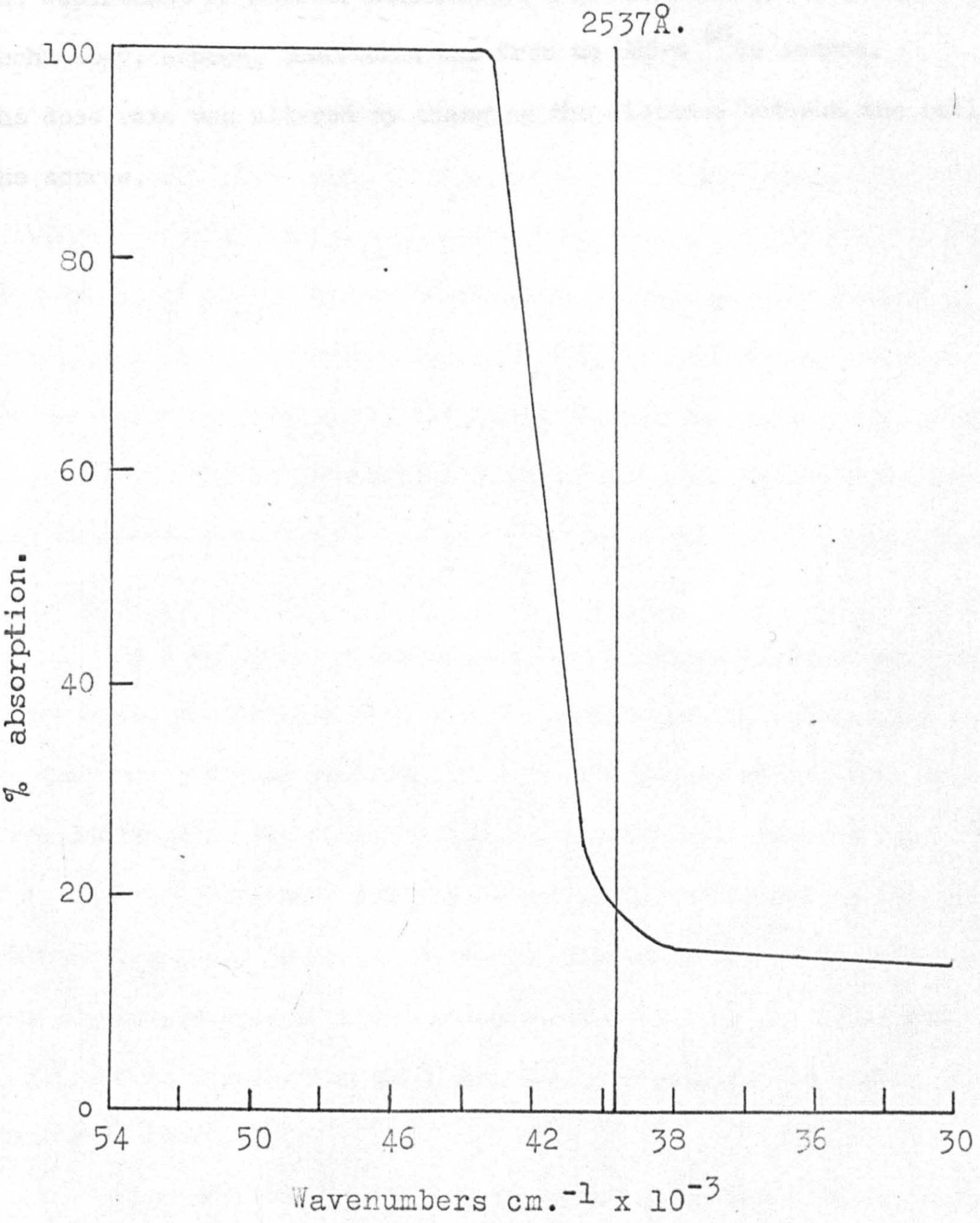
The lamp-housing was fixed so that the apex of the U-lamp was 1.5 cm. from the cell, the thick walls of the brass screw cap of the cell acting to some extent as a collimater. The distance between the lamp and cell was kept to a minimum because of the inverse square relationship between intensity and distance.

A metal shutter, operated by a pull-cord, separated the lamp-housing and cell. To insert the intensity stops or the filter, the lamp-housing had to be withdrawn 2 cm. from the cell.

Intensity stops were constructed of metal gauze of various gauges, coated with black matt paint. The geometry was fixed by holding the stop in a short metal cylinder (Fig. 2.13), and the position of the stops between the lamp and the cell was fixed by the lugs, on the foot of the stop, fitting into corresponding sockets on the base of the thermostat.

The filter consisted of a 1 cm. thick 2% acetic acid solution. The transmission properties are given in Figure 2.14.

Figure 2.14



Absorption spectrum of a 2% solution acetic acid.

2.5.3 Radiolysis

Radiolysis experiments were conducted by Dr. P. G. Clay of the Department of Nuclear Technology, Imperial College of Science and Technology, London. Radiation was from an 825-c ^{60}Co source. The dose rate was altered by changing the distance between the cell and the source.

2.6 Procedure

2.6.1 Vapour Phase

The reaction cell was pumped under high vacuum for a period of half an hour prior to introducing a known pressure of but-2-ene into the cell. After admission of the gas tap H (Figure 2.1) was closed, and the gas given sufficient time to attain the cell temperature. The lamp was allowed a warm-up period of ten minutes, before irradiation was commenced by removal of the shutter. Irradiation periods were in general of six minutes or less, although occasionally of several hours, and were terminated by switching off the lamp. During the warm-up and irradiation periods both the lamp-housing and thermostat were flushed through with dry nitrogen, a stream of the gas playing on the space between the lamp and cell.

On completion of irradiation, the reaction products were mixed by three rapid freeze-thaw cycles, alternately cooling and warming the bulb on the cell side-arm with liquid nitrogen and hot water. The products were then admitted to the pressure measuring section by opening tap H (Figure 2.1) with tap K closed, and a gaseous sample introduced to the gas chromatograph for analysis. When irradiation of but-2-ene was carried out in the presence of a non-condensable additive, the gases were given $\frac{1}{2}$ hr. before irradiation and 1 hr. after irradiation to enable thorough mixing to occur.

When the transmission of the cell window had been decreased by formation of a polymer, the window was removed and washed in firstly concentrated nitric acid or chromic acid for several hours, secondly distilled water and lastly acetone. Then the window was dried and the transmission at 1849 Å measured on the S.P. 700 spectrometer. After insertion of a clean window the cell was pumped for several hours under high vacuum before irradiations were recommended

2.6.2 Liquid Phase

The reaction cell was immersed in a pentane slush ($-131\,^{\circ}C$) and pumped under high vacuum for $\frac{1}{2}$ hr. prior to introduction of the but-2-ene sample. When the pressure of the butene had been measured, the gas was frozen unto the cold finger and tap L (Figure 2.9) closed. As the cold finger was slowly warmed, the butene dripped down into the reaction cell. Irradiations were commenced and terminated by switching the lamp on and off. After an irradiation, tap L was opened, and the products evaporated into the pressure-measuring section. A gaseous sample was then introduced to the gas chromatograph for analysis.

2.6.3 Radiolysis

Prior to introduction of a sample the cells were pumped under high vacuum for several hours. A known pressure of but-2-ene was admitted to the cell, and the capillary tube sealed off with the cell cooled in liquid nitrogen. Following irradiation the cell was reconnected to the vacuum system at M, (Figure 2.1) the break-seal broken by a small metal rod, and the products admitted to the pressure-measuring section and a sample analysed as above.

2.7 Actinometry

The output of the lamp at 1849 Å was measured by chemical actinometry. The essential characteristic of an actinometer is that the quantum yields of the products of photolysis are accurately known for particular wavelengths. The photolysis must be essentially simple, and the rate of reaction proportional to the first power of the intensity. At 1849 Å, few materials had been sufficiently studied for use as actinometers, viz. Hydrogen bromide, ammonia, ethylene and nitrous oxide. They all had the advantage of being gases, and could therefore be used in the same cell as butene. Consequently, they would be subjected to the same intensity of radiation as the butene, and no correction would be necessary for absorption by the windows or for the distance traversed by the radiation.

Three actinometric gases were used in this study - hydrogen bromide, ammonia and ethylene. The first two had to be discarded, because of complications on photolysis, while ethylene was found to be successful. No measurements were made using nitrous oxide because of lack of a suitable means of accurately estimating the nitrogen yield.

2.7.1 Hydrogen bromide

Hydrogen bromide has an absorption coefficent at 1849 Å of 470 $\mathrm{cm.}^{-1}$.[124] Warburg[125] initially studied the vapour phase photolysis of hydrogen bromide at 2090 Å and 2530 Å, obtaining $\phi_{\mathrm{decomp.\ HBr}}$ as 2.08 and 2.01 at the respective wavelengths. Later workers used the value $\phi = 2.00$ for actinometric work,[122,126,127] and measured the pressure of hydrogen formed: $\phi_{H_2} = 1.00$.

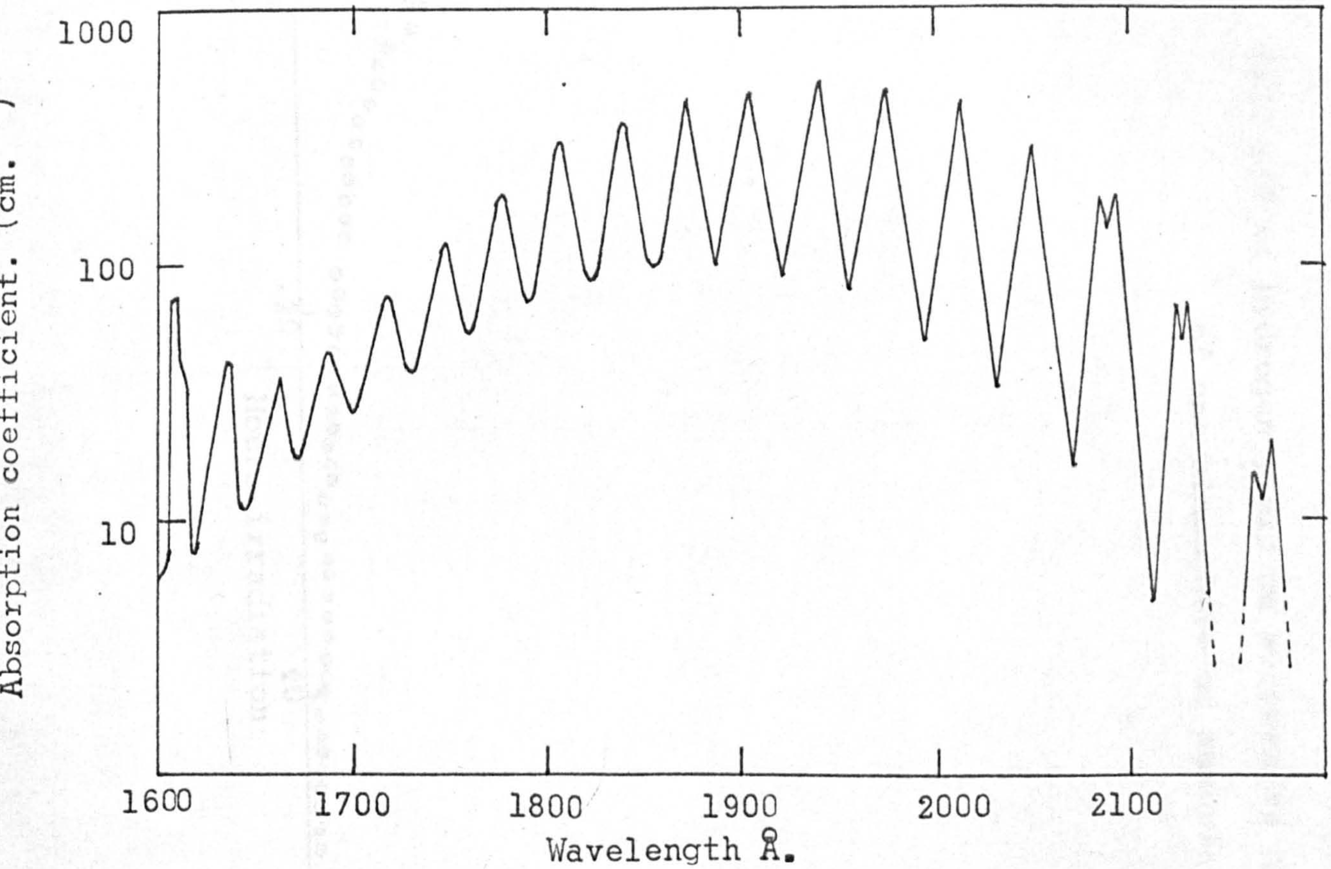
The photolysis of hydrogen bromide was attempted in the original Pyrex cell. 50 mm. of hydrogen bromide were irradiated for 1 hr., yielding a mixture of bromine and hydrogen. The bromine immediately attacked the Araldite window cement, and also the metal of the dial gauges, preventing accurate pressure measurements. Consequently, the photolysis of hydrogen bromide was abandoned in favour of:-

2.7.2 Ammonia

The absorption spectrum of ammonia is given in Figure 2.15, showing an absorption coefficient at 1849 Å of 150 cm.$^{-1}$.[128] Warburg[129] again initially studied the photolysis and later work was summarised by Welge and Beckman.[130] Due to the build-up of hydrazine in the reaction zone the $\phi_{\text{decomp. NH}_3}$ in a flow system was shown to be twice that in a static system.[131] The accepted value for ϕ_{NH_3} at 2100 Å is 0.16.[132] This is in fact a compromise between three earlier values (0.14,[133] 0.16,[126] 0.18[127]). The value of ϕ at 1849 Å was assumed to be the same as at 2100 Å,[132] and was found to be dependent upon pressure, cell size and temperature.

The photolysis of 760 mm. ammonia was conducted in the Pyrex cell. Reproducible results were not obtained until the cell had been 'conditioned' by irradiating for upwards of forty hours. During this time the hydrogen yield fell off exponentially with time, Figure 2.16, and even after 40 hrs. was still falling slowly. The window became coated with a solid material during the irradiation. Such 'conditioning' is in accord with previous measurements.[127,130] However, when the cell was finally conditioned it was found that the window would transmit very little 1849 Å radiation. The photolysis of ammonia was therefore abandoned in favour of:-

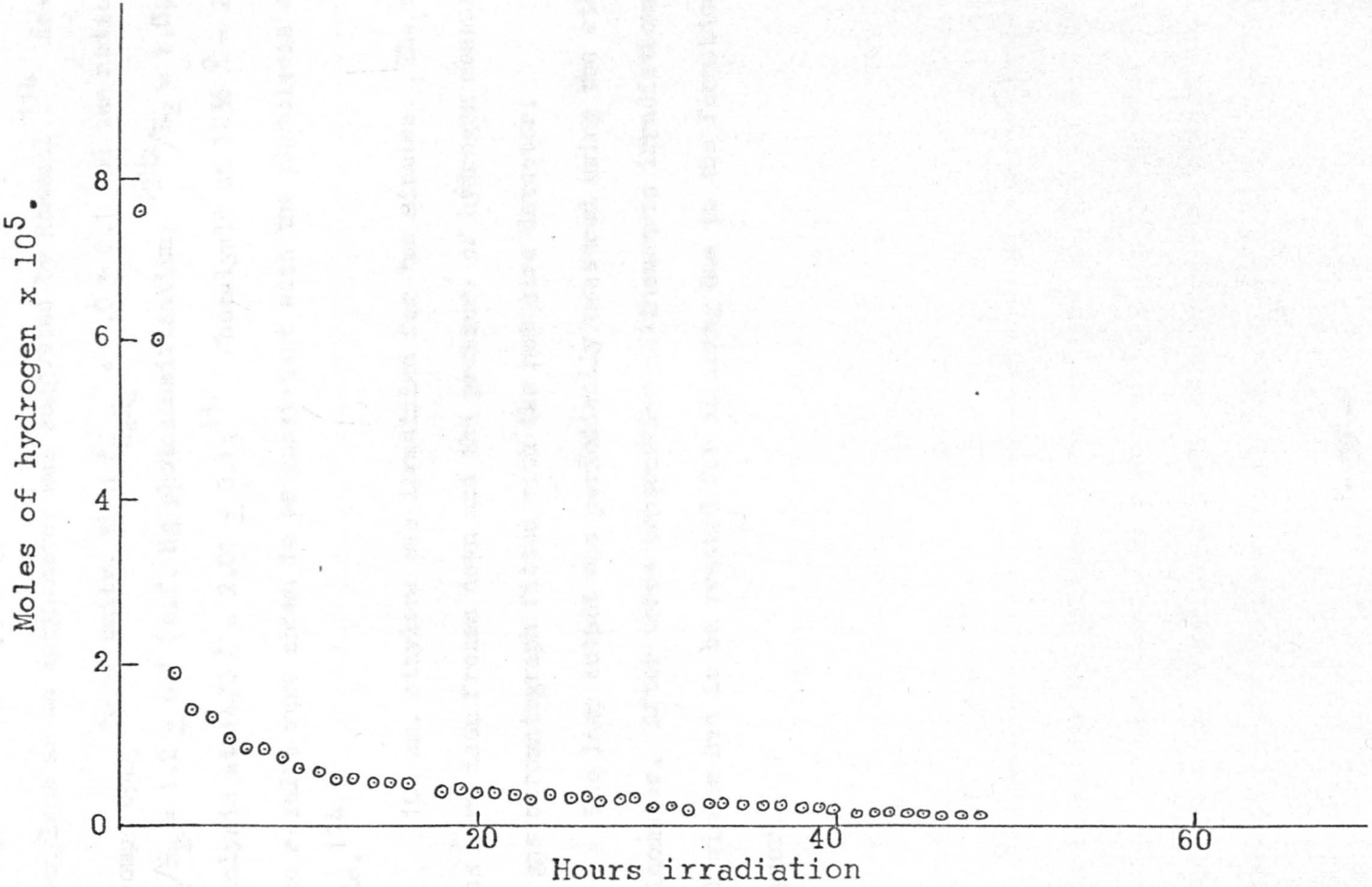
Figure 2.15



Absorption spectrum of ammonia.

Figure 2.16

Fall off of hydrogen yield on successive hourly irradiations of one atmosphere of ammonia.



2.7.3 Ethylene

The absorption spectrum of ethylene is given in Figure 1.1, showing an absorption coefficient at 1849 Å of ~ 10 cm.$^{-1}$. The use of ethylene as an actinometer was suggested by Rommell.[114] Assuming $\phi_{\mathrm{decomp.}\ C_2H_4}$ to be unity, then $\phi_{C_2H_2} = 1.0 \pm 0.1$ and the ratio $C_2H_2/H_2 = 1.2 \pm 0.1$ (c.f. Hg photosensitisation, $C_2H_2/H_2 = 1.0$;[69] Photolysis at 1470 Å = 2.01 ± 0.1;[112] Photolysis at 1236 Å = 2.8 ± 0.2[113]). These results were shown to be consistent with the photolysis of nitrous oxide.[114]

100 mm. ethylene was irradiated for ten minutes. The condensable gases were then frozen down and the pressure of hydrogen measured using the gas chromatograph fitted with the hot wire detector.

The lamp output was periodically measured using the ethylene actinometer. After three consecutive actinometric irradiations, the cell window had to be removed for cleaning due to the formation of a polymer.

2.8 Analysis

Product analyses were made on a Perkin Elmer Model 452 Gas Chromatograph using either a hot-wire detector or a hydrogen flame ionization detector.

Initial qualitative analyses were made using a variety of columns, listed in Table 2.1.

TABLE 2.1

Perkin Elmer Classification	Column Stationary Phase	Length Metres	Running Temp. °C	Nitrogen Carrier gas flow rate in mls./min.
C	Silicone Oil DC 200/50	2	35	110
H	Silver nitrate on ethylene glycol	2	35	110
EA	Bis methoxy ethyl adipate	2	35	170
BMEA	Bis methoxy ethyl adipate	100 Capillary	25	150
O	Silicone grease	6	35 and 80	170
S	Silica gel + diethylhexyl sebacate	2	80	270

The inert support material on all columns is 60 - 80 mesh Celite.

Columns were used singly or in pairs and product retention times compared with authentic samples, when these were available. The retention times for four sets of colums are listed in Table 2.2.

TABLE 2.2

Retention time in minutes

Material	Columns C + H 35°C Flow 170 ml/min	Columns H + EA 35°C Flow 170 ml/min	Column BMEA 25°C 150 ml/min	Column S 80°C 270 ml/min
Methane	2.2	2.4	11.0	0.8
Ethane	2.7	2.6	11.25	1.3
Ethylene	3.4	3.6	11.05	1.7
Propane	3.6	2.9	11.3	2.1
Propylene	4.7	4.4	11.35	4.0
Acetylene	–	3.6	11.4	3.5
n-Butane	6.4	4.0	11.5	4.0
Butene-1	–	7.4	–	8.5
Cis-2-butene	9.7	8.5	11.7	11.8
Trans-2-butene	7.4	5.9	11.65	11.0
Isobutene	7.1	6.2	11.6	–
Allene	–	5.6	–	5.7
Neopentane	–	3.8	11.5	––
Isopentane	–	5.4	11.8	6.6
n-Pentane	–	6.4	11.95	7.1
3-Methyl butene-1	–	8.2	–	
Cis-2-pentene	15.6	10.4	12.4	–
Trans-2-pentene	19.0	14.0	12.6	–
Pentene-1	–	11.6	–	–
2-Methyl butene-1	15.7	11.6	12.3	–
2-Methyl butene-2	16.8	11.5	12.8	–

Columns 'C' and 'O' separated by boiling point, and boiling point - log retention time[134] curves are given in Figures 2.17 Column 'C' at 35°C; 2.18 Column 'O' at 35°C; Figure 2.19, Column 'O' at 80°C. The boiling points of products for which no authentic samples were available could then be estimated with an accuracy of ± 2°C.

Quantitative analyses were made using column 'O' or Column 'S' at 35°C (for C_1 to C_5 hydrocarbons) and Column 'O' 80°C (for C_6 to C_8 hydrocarbons). Quantitative calibration curves were constructed for the major products using measured samples of authentic gases mixed with nitrogen. The relationship between peak height or peak area and molar quantities of C_1 to C_5 hydrocarbons is given in Table 2.3.

TABLE 2.3

Peak height or peak area with detector at full sensitivity corresponding to 10^{-7} mole

Column O at 35°C

Material	Height (1" divisions)	Material	Area (small squares)
Methane	10.5	3-methyl-but-1-ene	125
Ethylene	10.9	iso-pentane	135
Ethane	9.4	n-pentane	135
Propylene	9.4	trans-pent-2-ene	125
Allene	8.0	cis-pent-2-ene	120
Acetylene	8.0		
But-1-ene	6.6	Column O at 80°C	
n-Butane	6.6		
Trans-but-2-ene	5.8	n-hexane	140
Cis-but-2-ene	5.4	cis-hept-2-ene	110
Butadiene	5.4	oct-1-ene	95

Figure 2.17

Log. retention time vs. boiling point
Column "C" 35°C

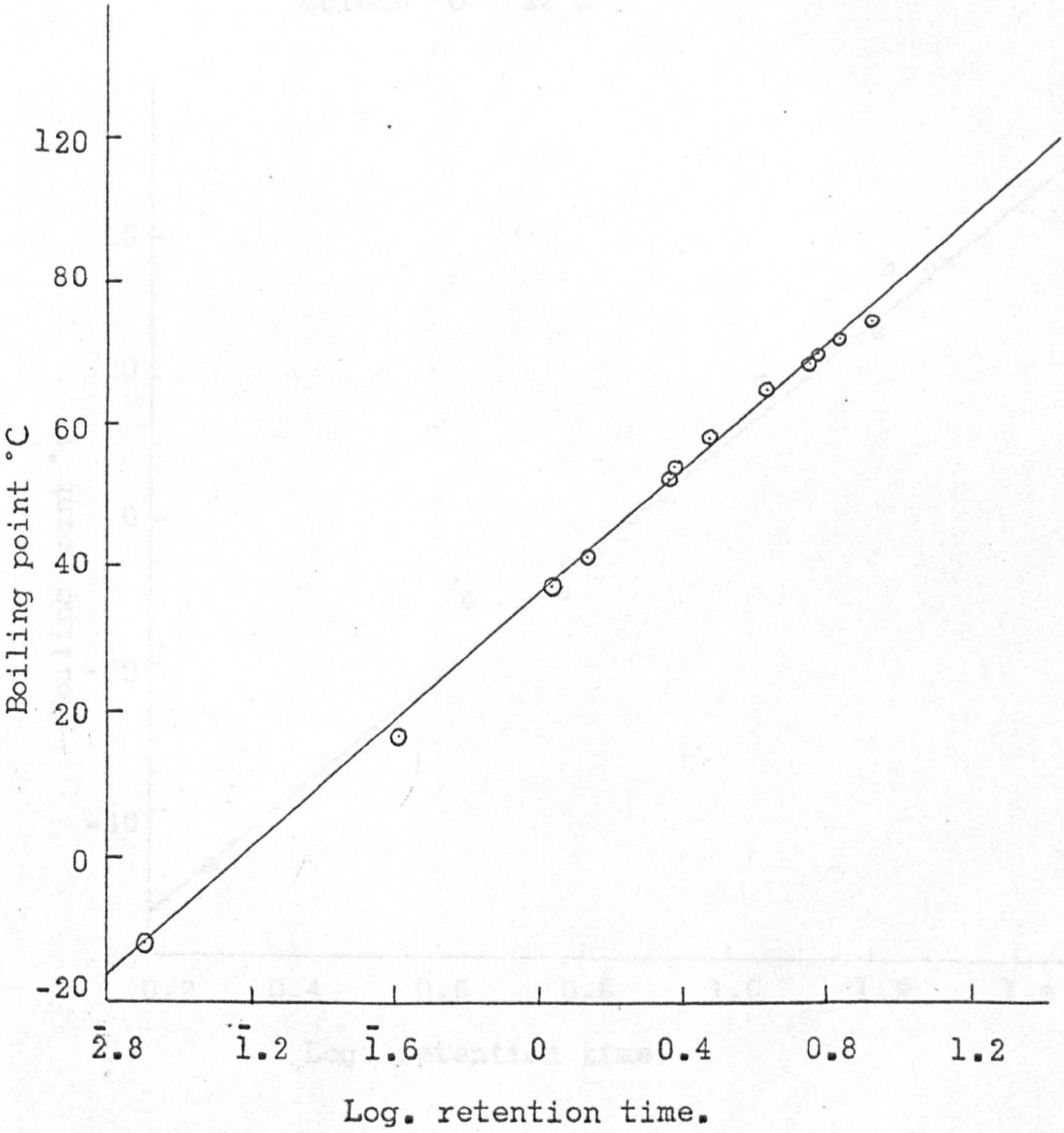


Figure 2.18

Log retention time vs. boiling point

Column 'O' 35°C

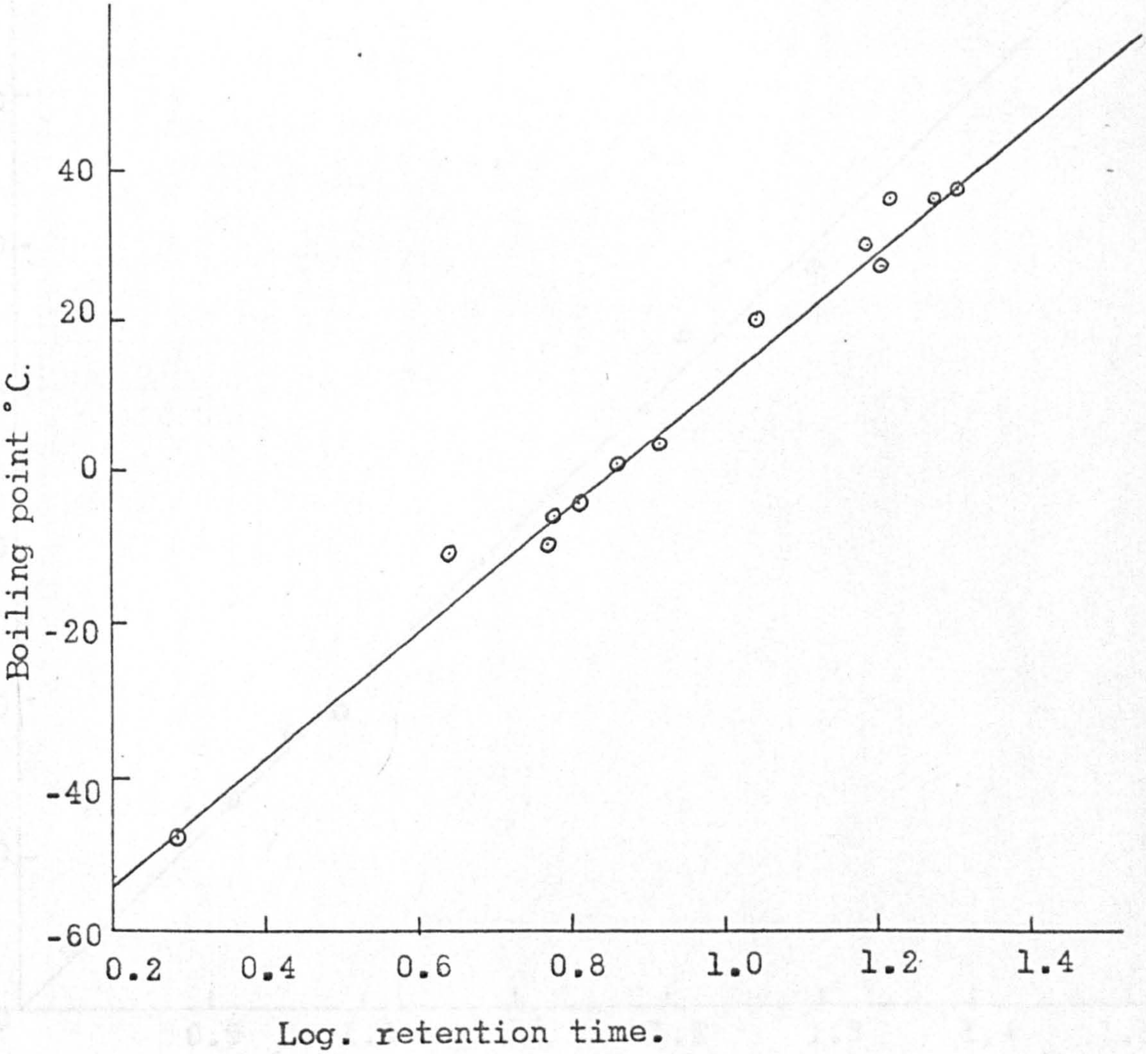
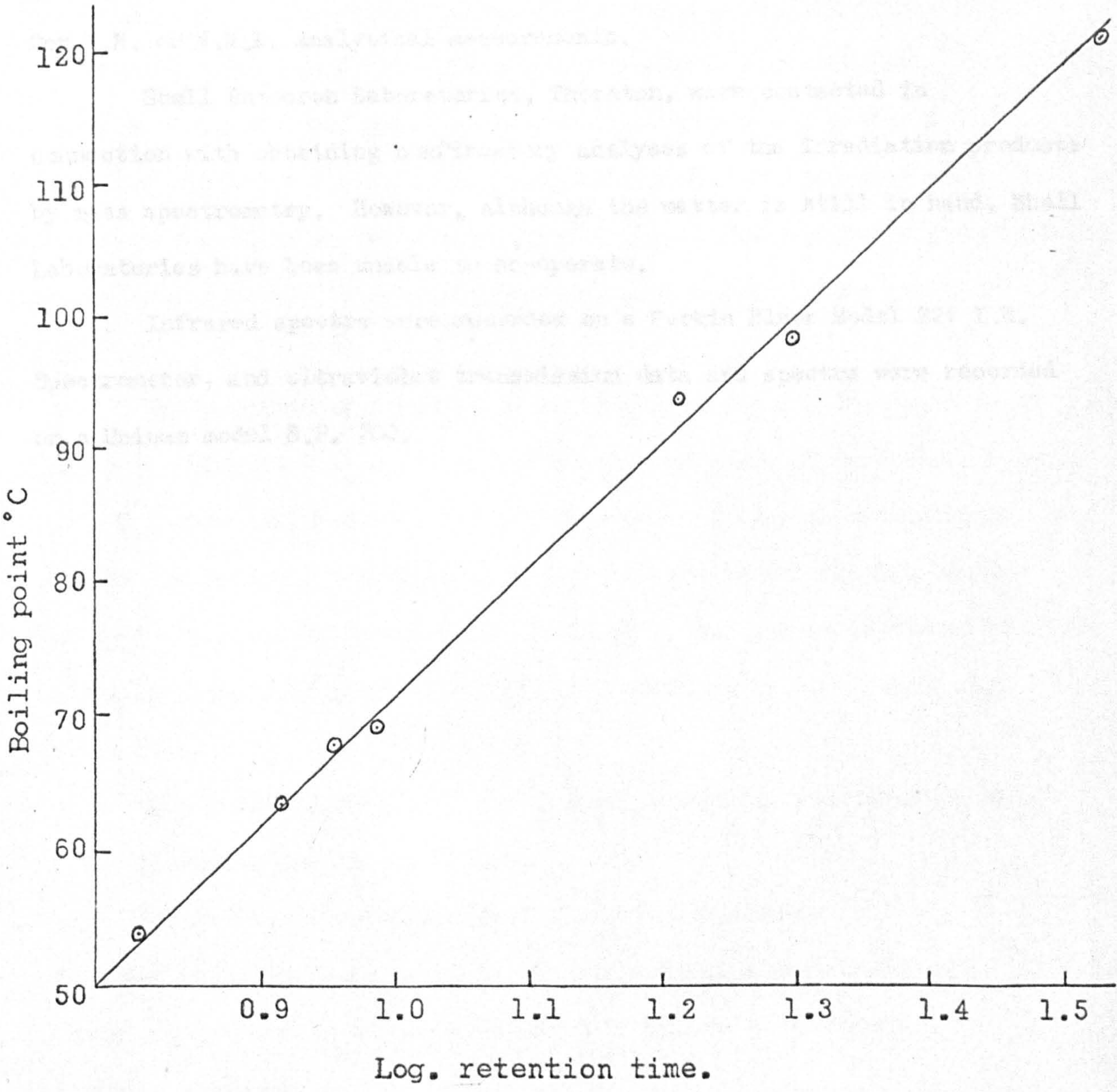


Figure 2.19

Log. retention time vs. boiling point

Column "O" 80°C



Chromatograms were recorded on a Honeywell high gain high impedance recorder with a 0-25 m.V. range.

An attempt was made to collect samples of eluent from the Gas Chromatograph by passing the gas stream through a number of traps cooled in liquid nitrogen. However, insufficient material could be collected for I.R. or N.M.R. analytical measurements.

Shell Research Laboratories, Thornton, were contacted in connection with obtaining confirmatory analyses of the irradiation products by mass spectrometry. However, although the matter is still in hand, Shell Laboratories have been unable to co-operate.

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

3. RESULTS

3.1 Vapour Phase

Irradiation of a sample of either cis- or trans-but-2-ene with a filter of 2% acetic acid interposed between the lamp and the cell, resulted in no photochemical reaction, whereas without the filter in position, a large number of photochemical products were obtained. The presence of the filter, which absorbs 1849 Å radiation (section 2.5.2), indicated that 1849 Å was the exciting radiation, and also that no mercury was present in the system. Mercury would have produced geometrical isomerisation of the but-2-ene by mercury photosensitisation (section 1.5.1).

The products of irradiation at 1849 Å included hydrogen, at least thirty two hydrocarbons C_1 to C_8 and a solid polymer. Hydrocarbons from C_9 to C_{12} were searched for, but not detected. A typical chromatogram showing the product distribution after six minutes irradiation of cis-but-2-ene is given in Figure 3.1. Products C_1 to C_5 were separated on Column '0' (silicone grease) at 35°C, and products C_6 to C_8 on Column '0' at 80°C.

The relative yields of the C_1 to C_5 products from irradiation of 10 mm. cis-but-2-ene are as follows:

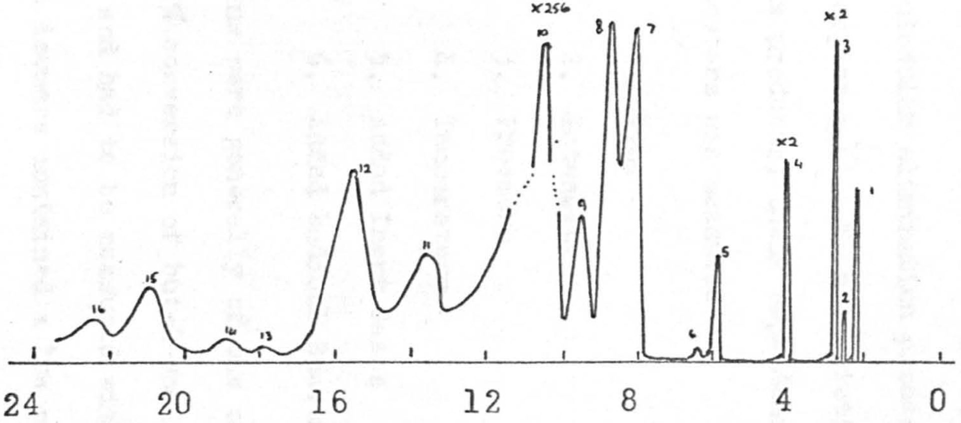
Acetylene > but-1-ene > hydrogen > butadiene > propylene = isopentane > ethane > cis and trans pent-2-ene = 3-methyl-but-1-ene > trans-but-2-ene > n-butane > methane > allene > ethylene.

Figure 3.1

Elution times of products.

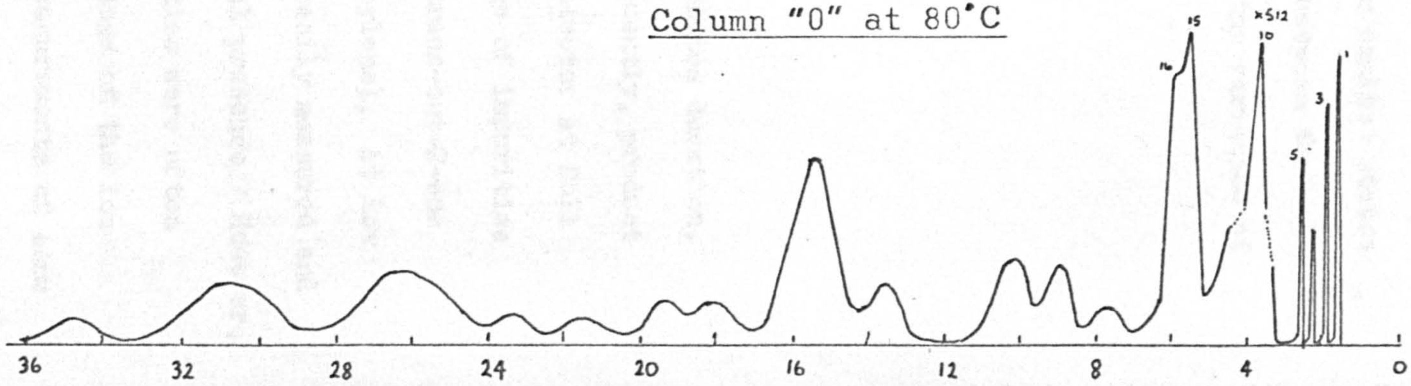
1. methane + hydrogen.
2. ethylene
3. acetylene + ethane.
4. propylene + propane.
5. allene.
6. isobutane.
7. but-1-ene.
8. n-butane + butadiene.
9. trans-but-2-ene.
10. cis-but-2-ene.
11. 3-methyl but-1-ene.
12. isopentane.
13. n-pentane.
14. but-2-yne.
15. trans-pent-2-ene.
16. cis-pent-2-ene.

Column "0" at 35°C



Elution time in minutes.

Column "0" at 80°C



Clearly, in the formation of such a large number of products, both free radical and molecular elimination processes from excited states can be involved (section 1.5). To help distinguish between the modes of formation of the products, their dependence upon the variation of the following parameters was measured:

1. Time
2. Intensity
3. Pressure
4. Temperature
5. Added Inert Gases
6. Added Radical Scavengers

Irradiations were generally of one or two minutes duration, resulting in $<$ 0.1% conversion of but-2-ene. Consequently, product yields were small and had to be measured with the detector at full sensitivity. Both isomers contained a low percentage of impurities (cis-but-2-ene contained $<$ 0.05% trans-but-2-ene; trans-but-2-ene contained $<$ 0.1% cis-but-2-ene, but-1-ene, and propylene). At low pressure of reactant but-2-ene the impurities were easily measured and the product distribution corrected for their original presence. However, at high pressures of reactant but-2-ene, the impurities were often an order of magnitude greater than the product, because of the low conversions used. Consequently, the quantitative measurements of some of the products at high reactant pressures of but-2-ene are subject to considerable error. Also at high reactant pressures of but-2-ene it was not possible to measure the products above C_4, for their peaks were swamped by the large but-2-ene peak. The pressure of but-2-ene in the reaction cell was always sufficient to cause > 99% absorption of the 1849 Å radiation.

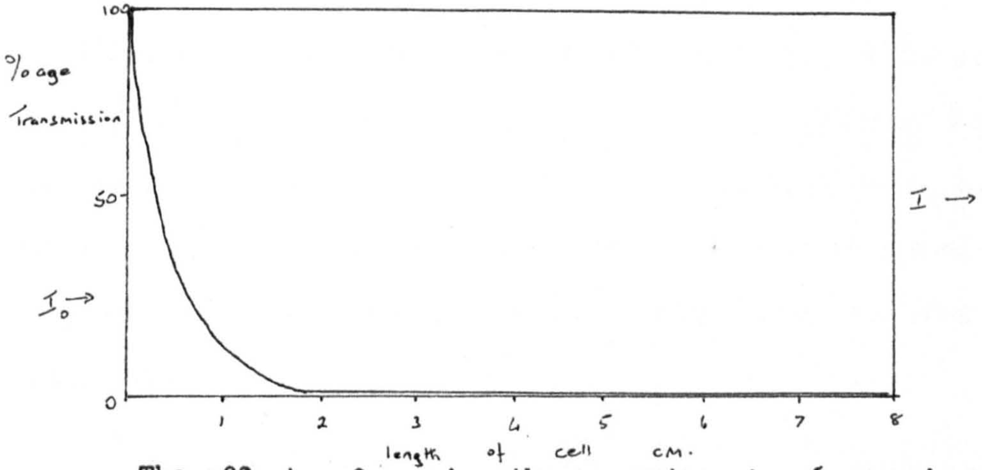
$$\log \frac{I_o}{I} = \epsilon \text{ c.d.}$$

at 10 mm. pressure, $C = \frac{10}{22.4 \times 760} \times \frac{150}{1000}$ moles/litre,

d = 8 cm., and $\epsilon = 6{,}300 \text{ cm.}^{-1}$ (cis) and $10{,}000 \text{ cm.}^{-1}$ (trans).

Thus $\log \frac{I_o}{I} = 4.4$ (cis) and 7.05 (trans)

The absorption profile in the cell was then:



The effects of varying the parameters 1 - 6 are given in Sections 3.1.1 to 3.1.6.

In sections 3.1.1 and 3.1.2 product measurements are in terms of rate of formation in moles per minute. In Sections 3.1.3 to 3.1.6 product measurements are in terms of quantum yield of formation ϕ, where

$$\phi = \frac{\text{No. of molecules formed per second}}{\text{Amount of light absorbed per second}}$$

and the amount of light absorbed was determined by ethylene actinometry (section 2.5.1). When no quantitative calibration data for particular products had been determined, the product measurements are in terms of peak areas.

3.1.1 The effect of Time Variation

Originally the hot wire detector was used to analyse the products of irradiation. Using the detector at full sensitivity it was necessary to irradiate a sample for ten minutes before a dependable analytical measurement could be made. The variation with irradiation time of the rates of formation of hydrogen and ethane are given in Figures 3.2 and 3.3. The rate of formation of hydrogen was apparently linear for one hour, while that of ethane was linear with time for only twenty minutes. Beyond these times the rates of formation of the products were progressively reduced. Examination of the cell window revealed that on long irradiations, a solid polymeric material was produced which coated the window and reduced the transmission of 1849 Å radiation. Consequently, it was considered desirable to irradiate for much shorter periods of time, and to use the flame ionization detector for product analyses. Figures 3.4 to 3.14 show that products C_1 to C_5 have linear rates of formation with irradiation time for at least 4 minutes. No polymer could be detected on the cell window after four minutes irradiation.

Variation of Time

Irradiation Conditions:

Pressure of trans-but-2-ene : 6.1 mm.

Temperature : 25°C.

Analytical Conditions

Detector	Hot wire	Flame ionization
Column	EA + H	O
Temperature °C	35	35
N_2 pressure lb/sq.in.	12	12

Figure 3.2

Variation of hydrogen yield with irradiation time.

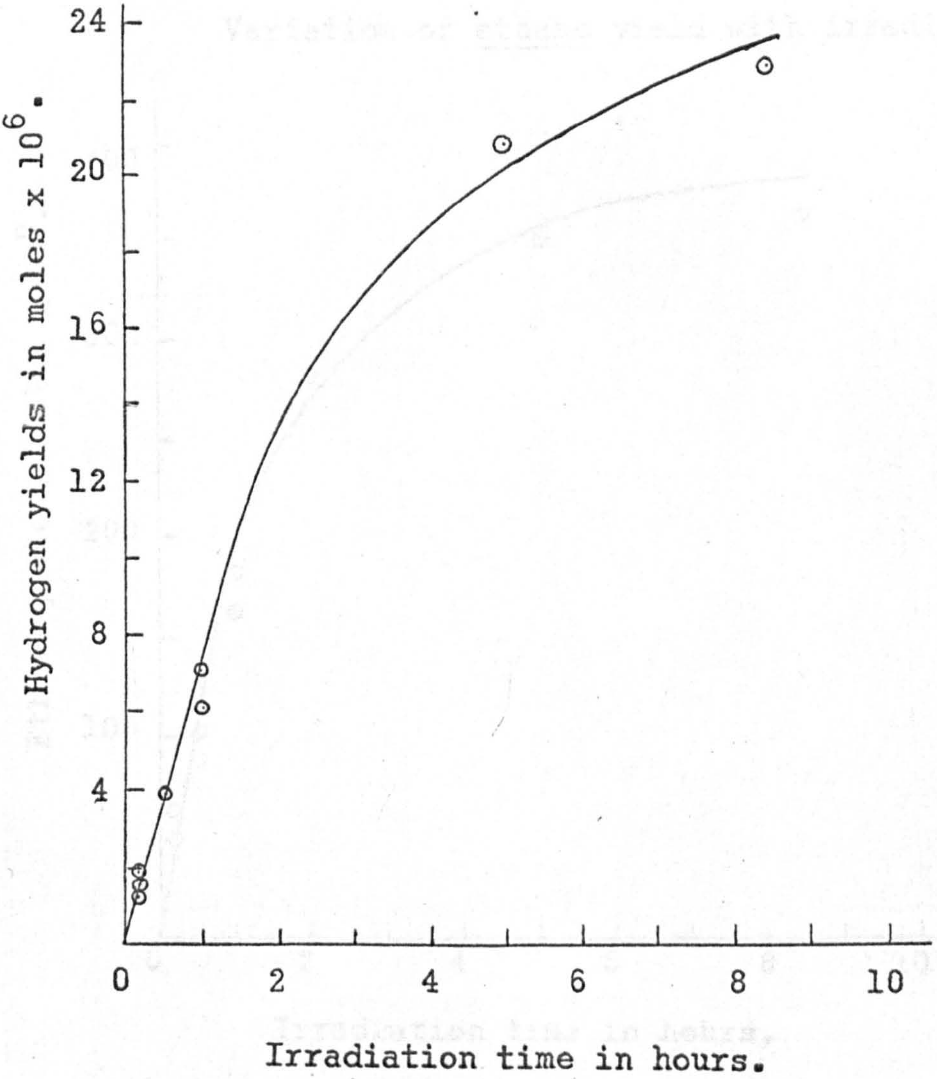


Figure 3.3

Variation of ethane yield with irradiation time.

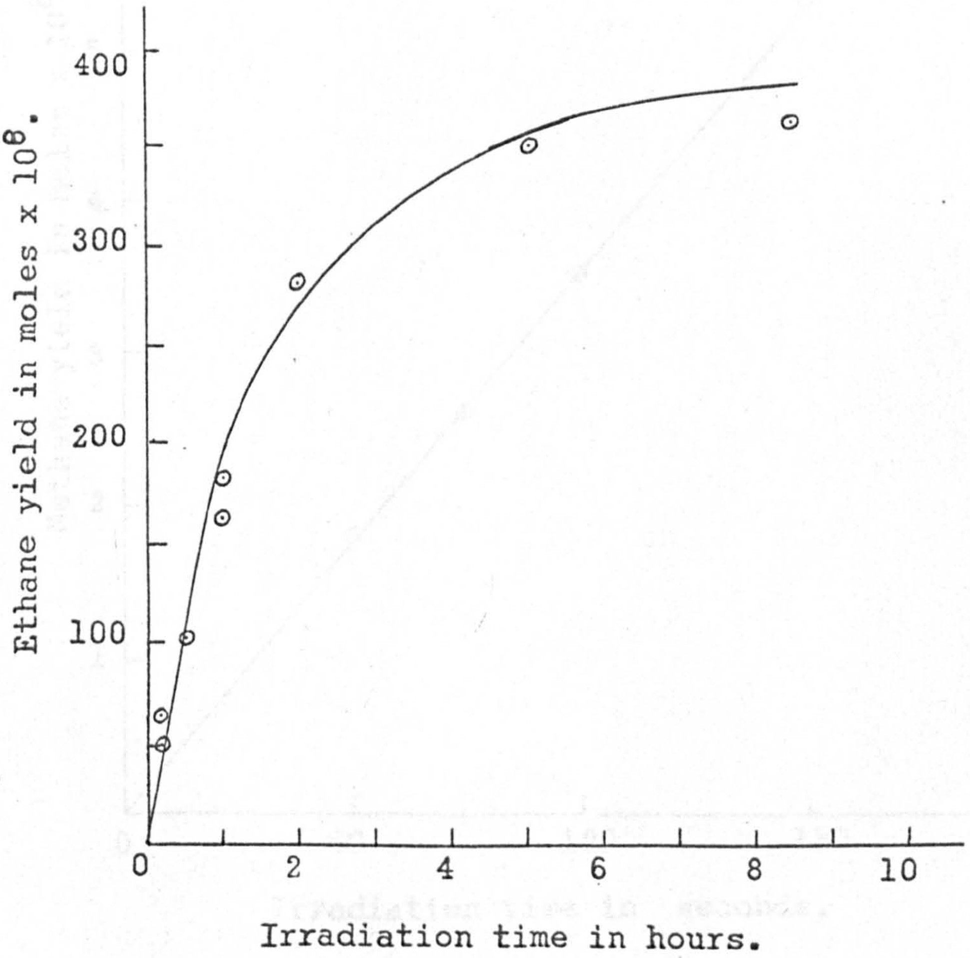


Figure 3.4

Variation of methane yield with irradiation time.

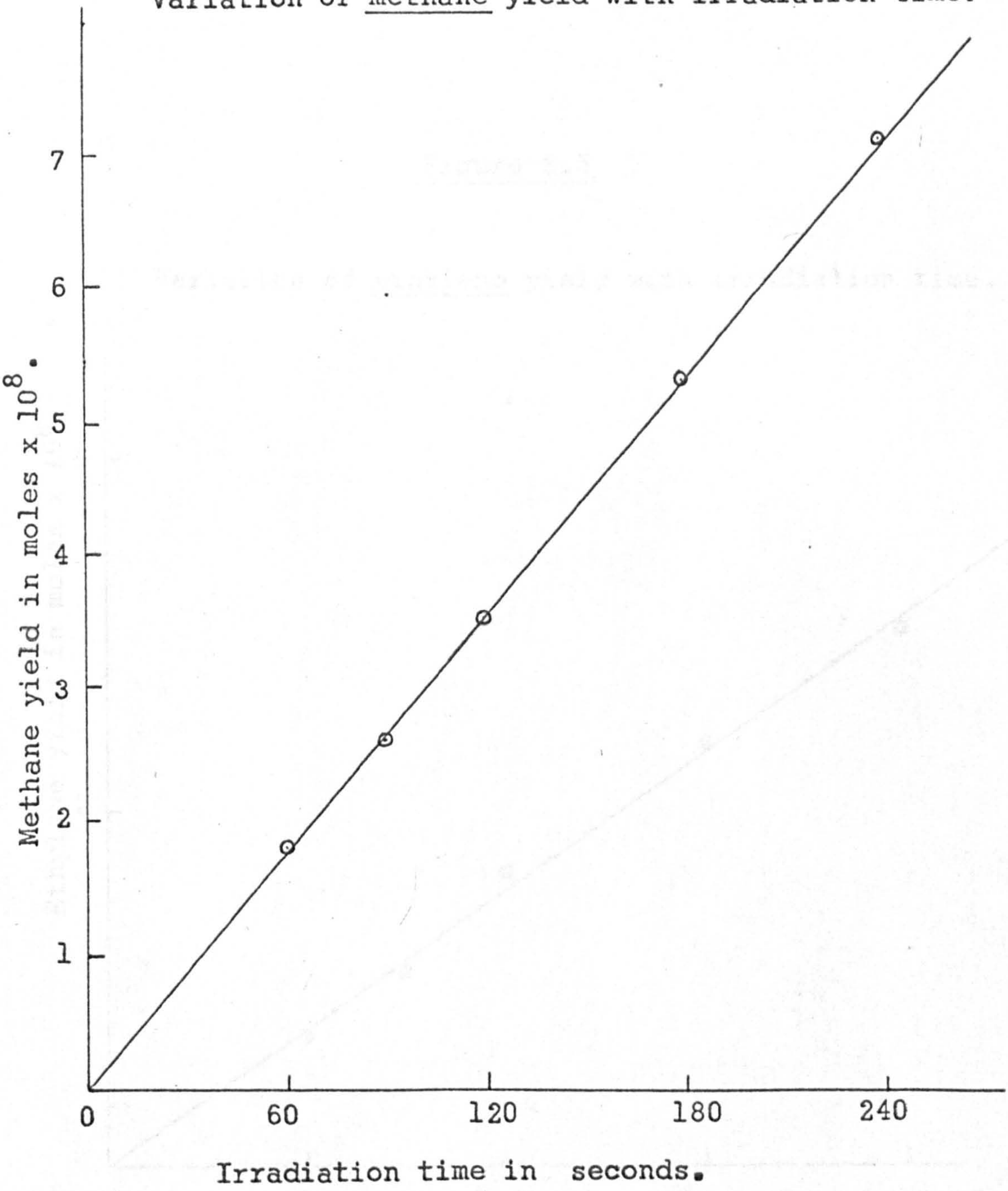


Figure 3.5

Variation of ethylene yield with irradiation time.

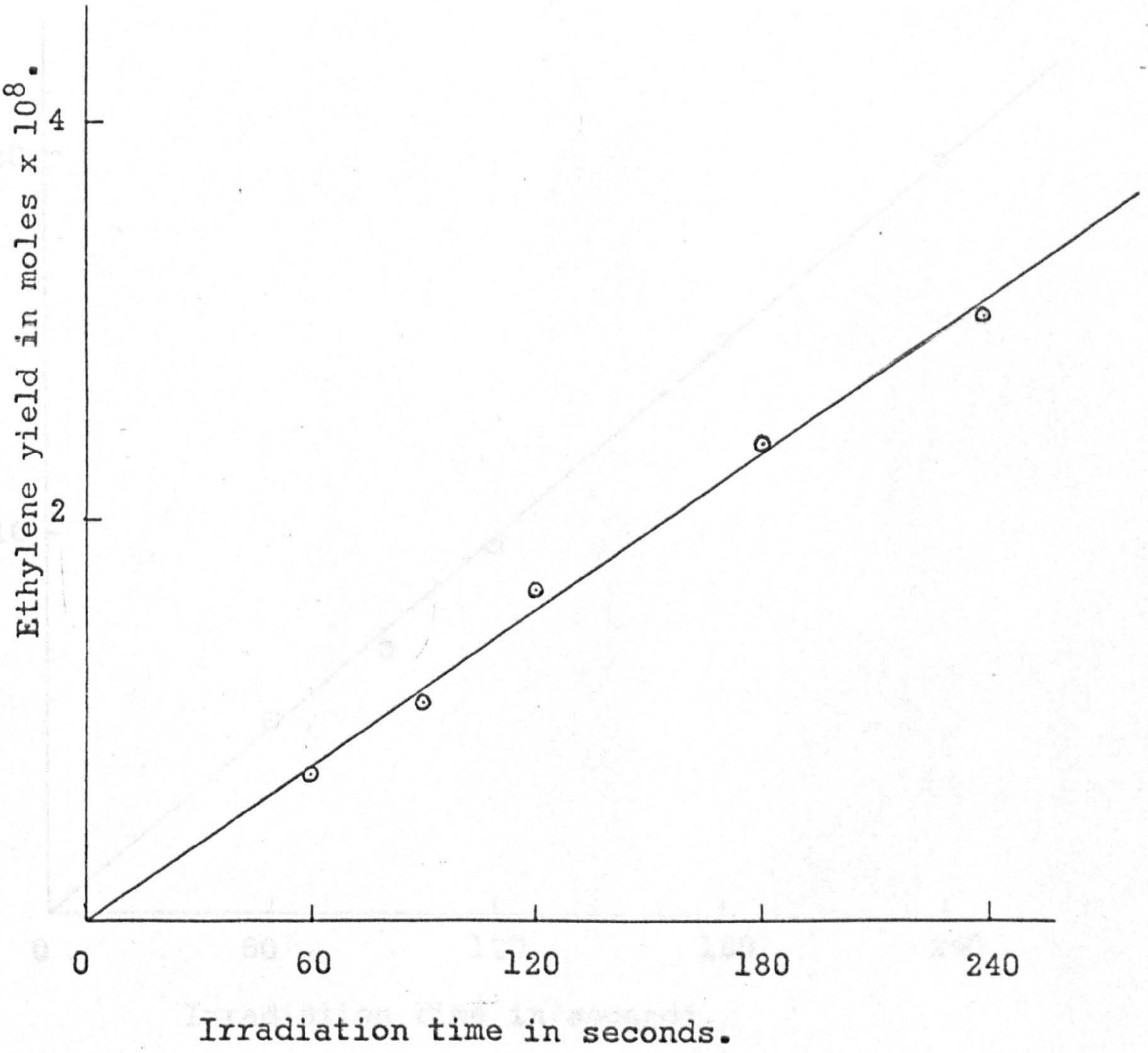


Figure 3.6

Variation of ethane yield with irradiation time.

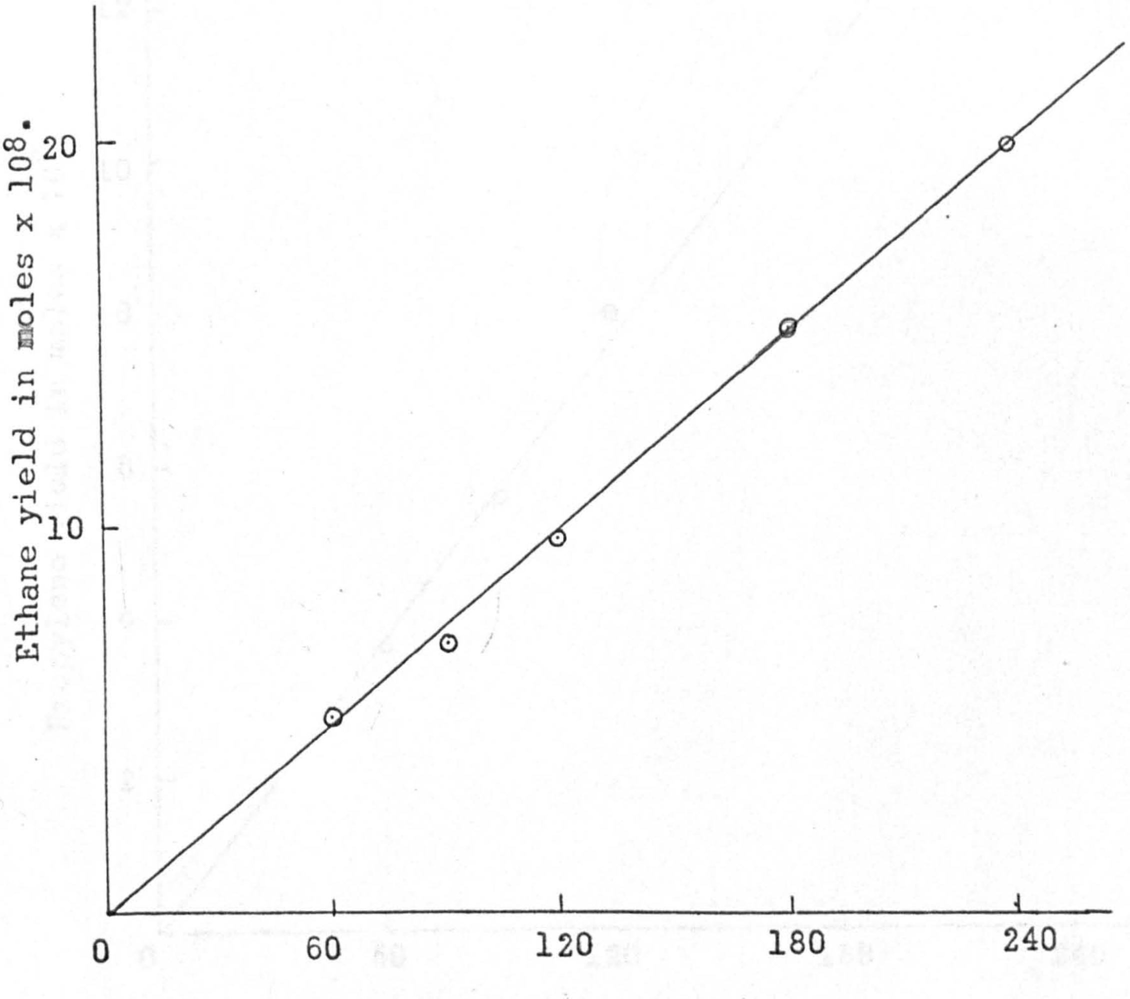


Figure 3.7

Variation of propylene with irradiation time.

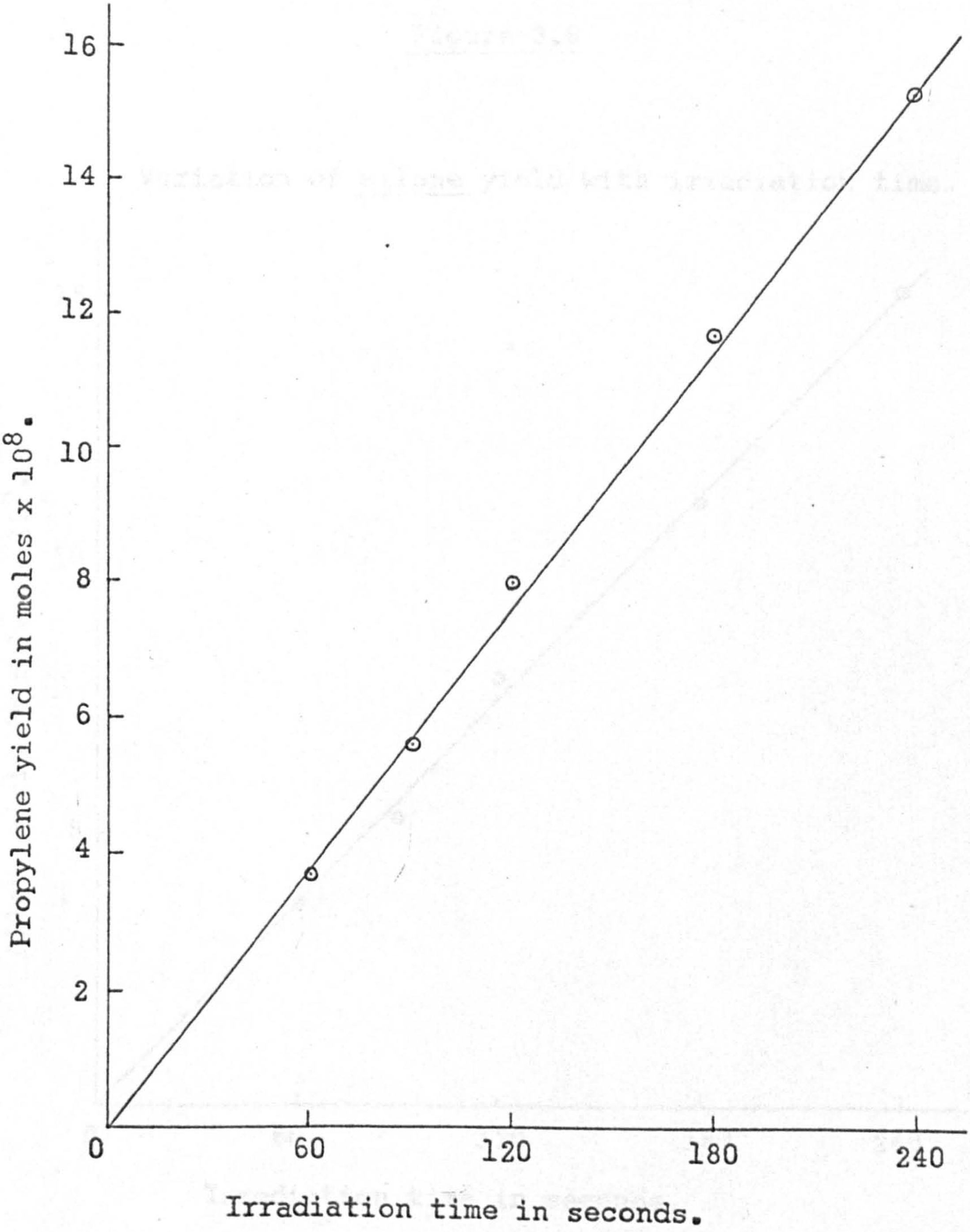


Figure 3.8

Variation of allene yield with irradiation time.

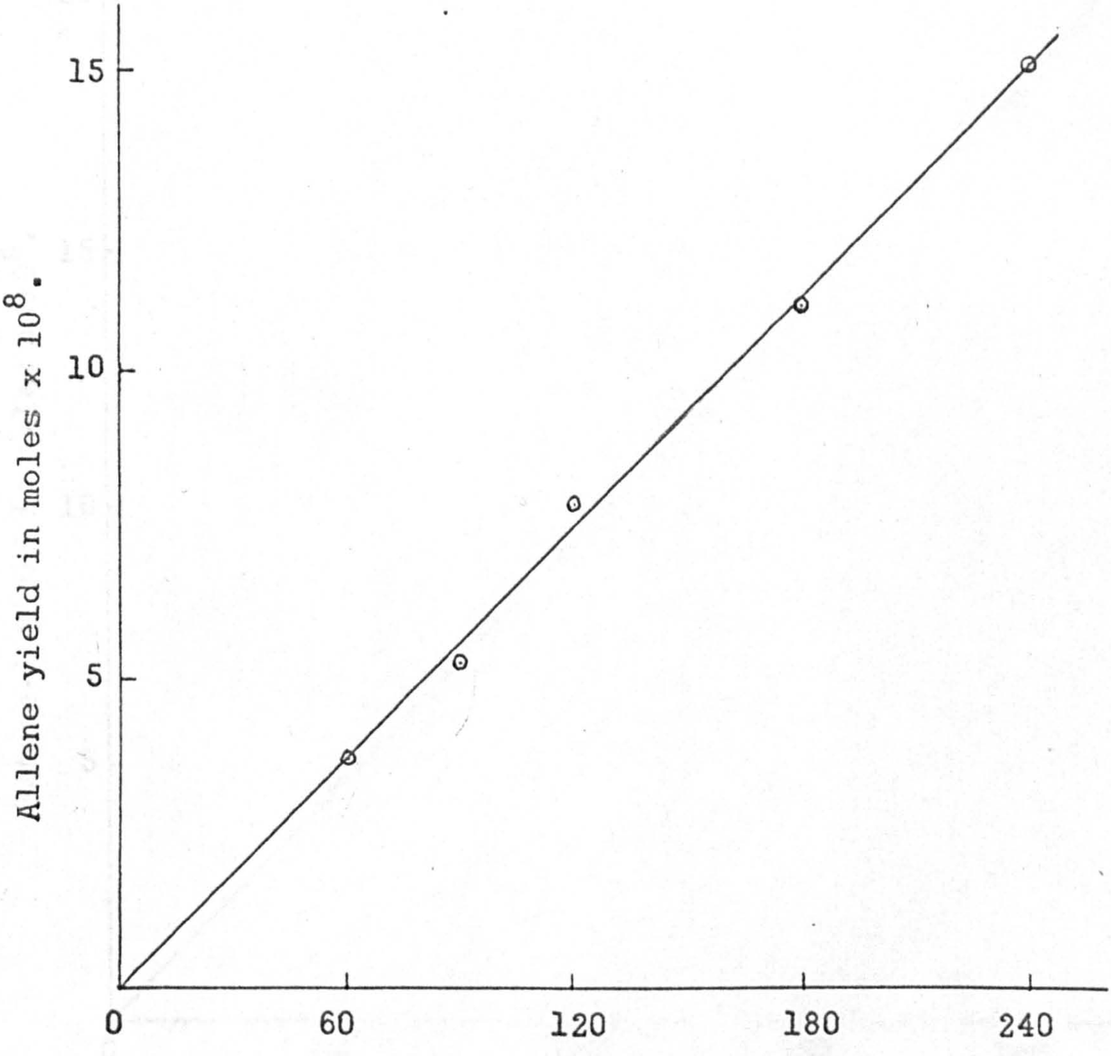


Figure 3.9

Variation of butene-1 yield with irradiation time.

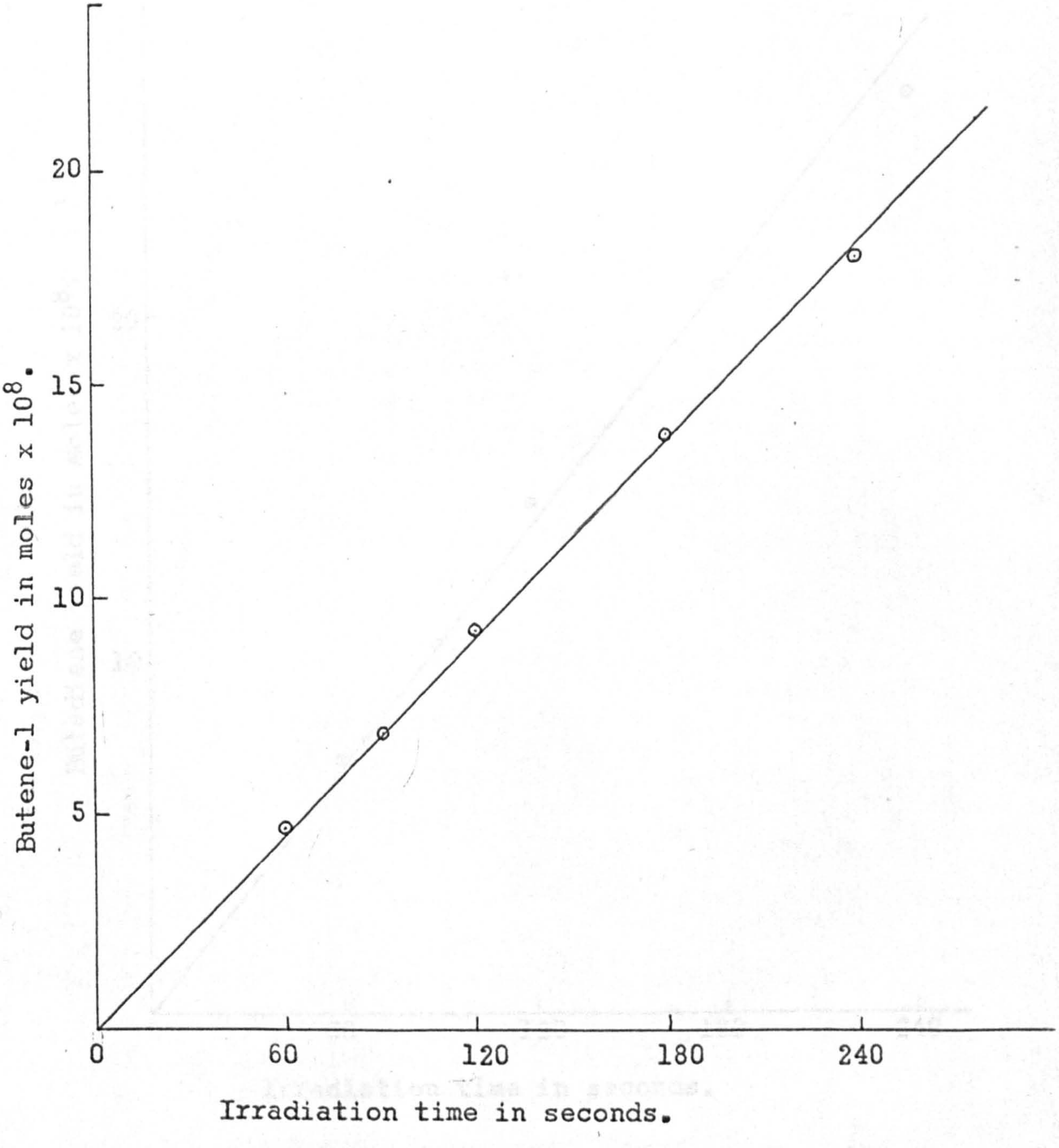


Figure 3.10

Variation of butadiene yield with irradiation time.

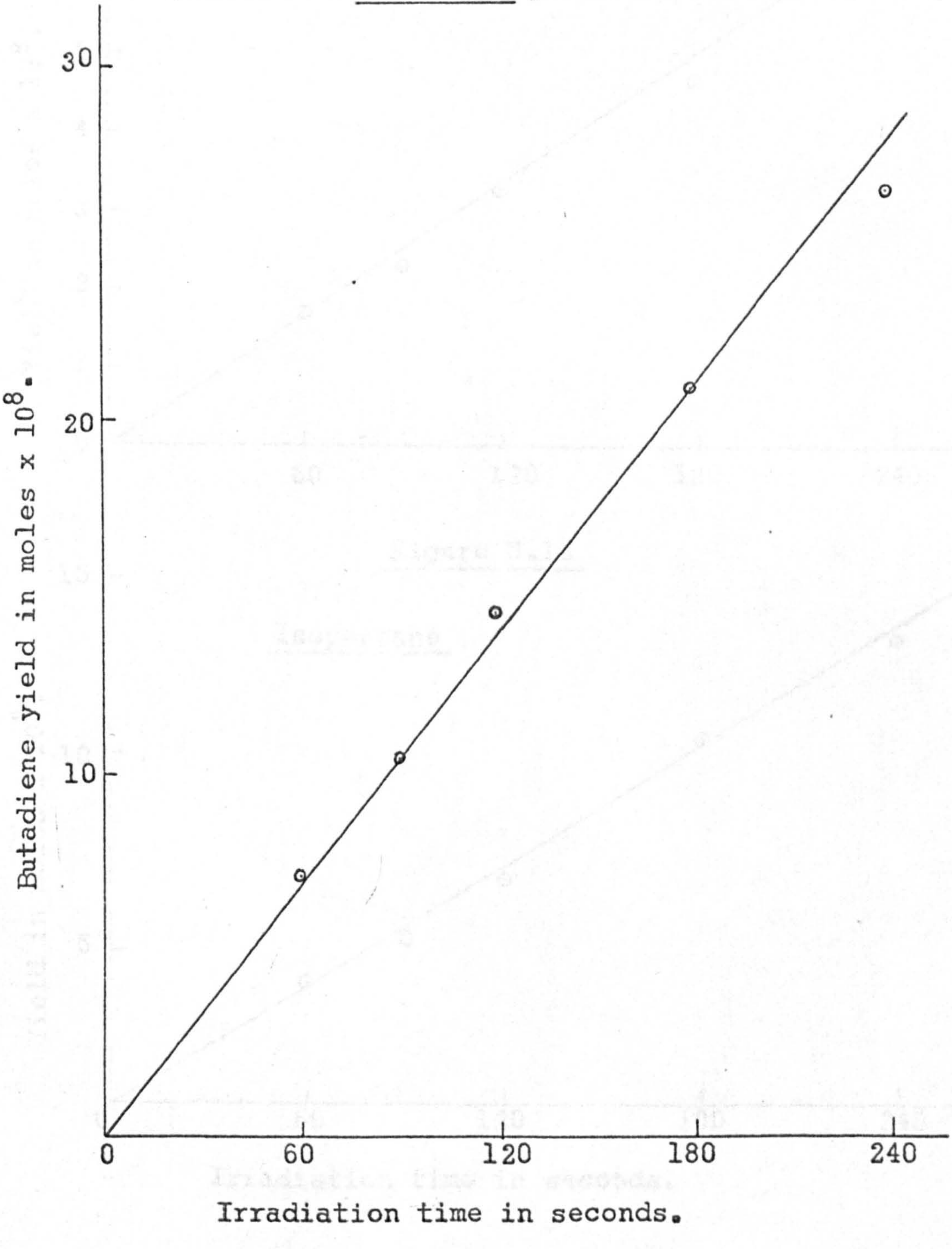


Figure 3.11

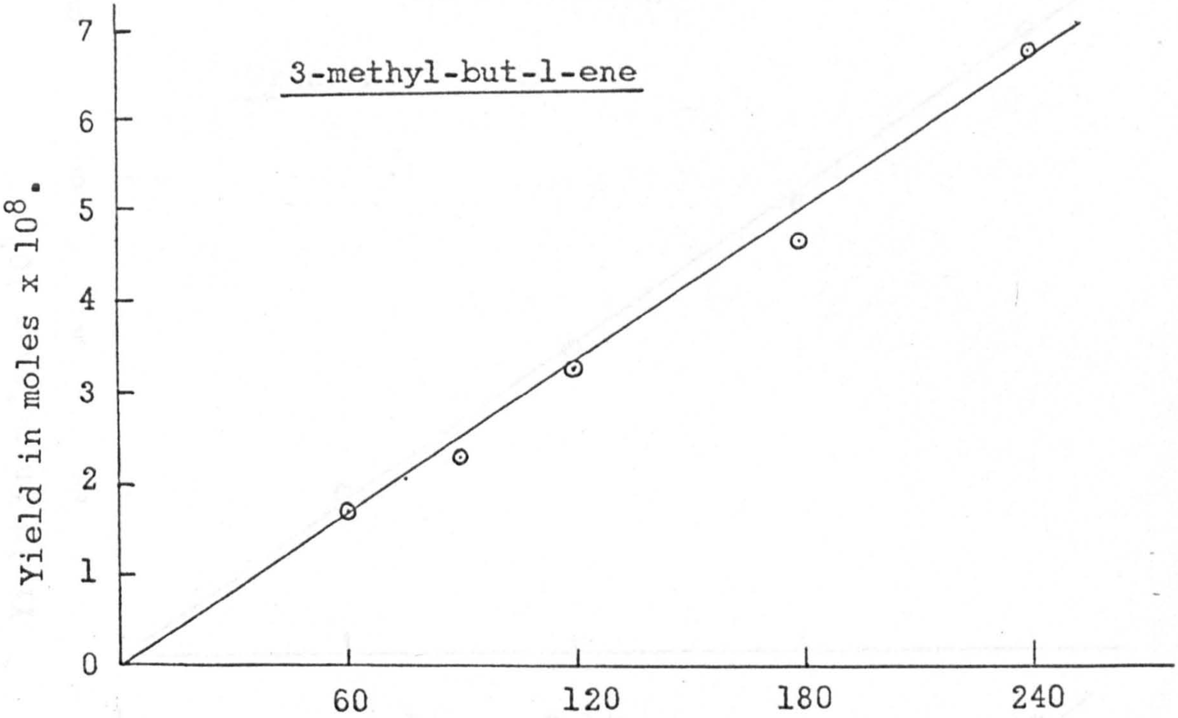
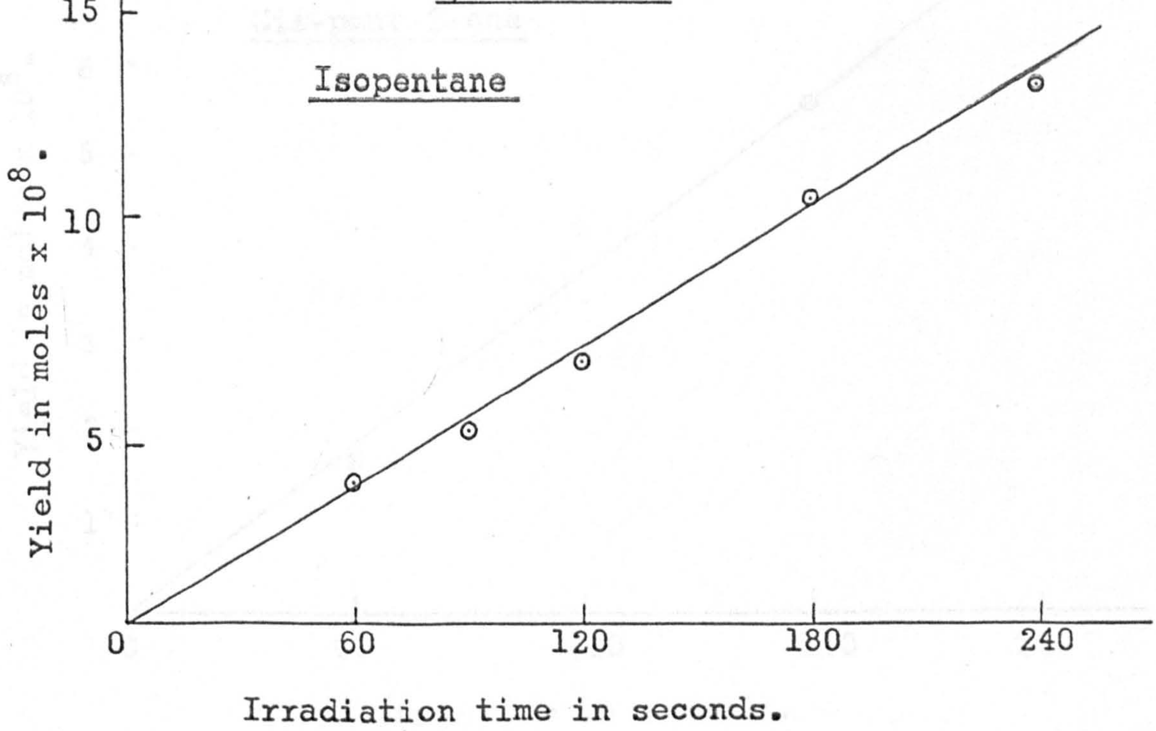


Figure 3.12



Variation of 3-methyl-but-l-ene and isopentane yields with irradiation time.

Figure 3.13

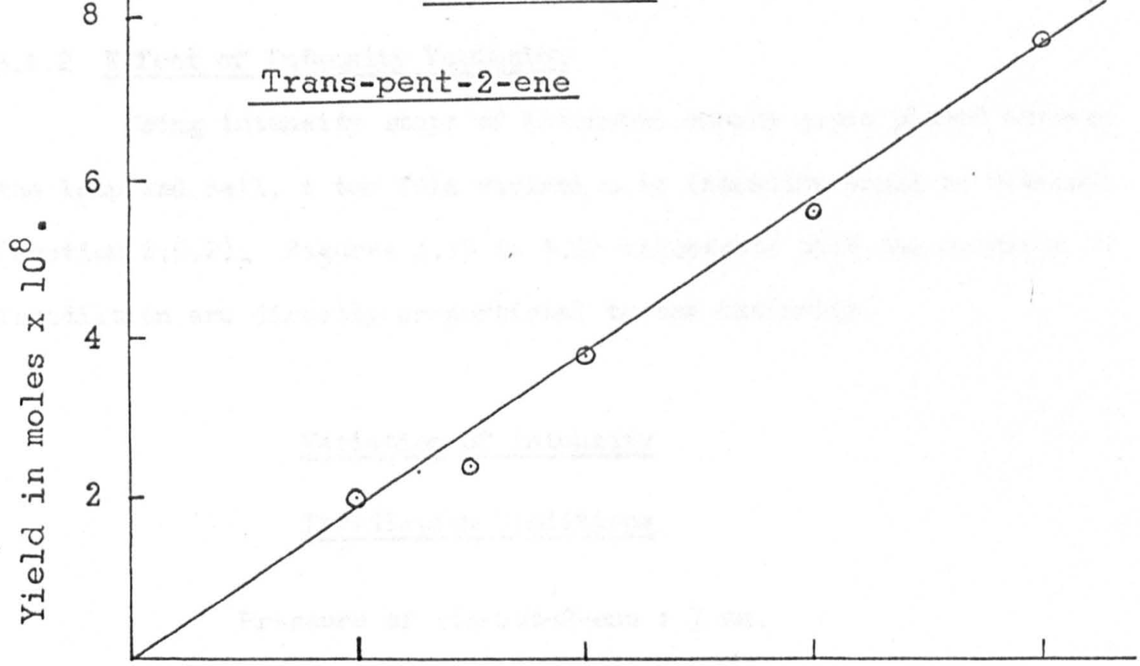
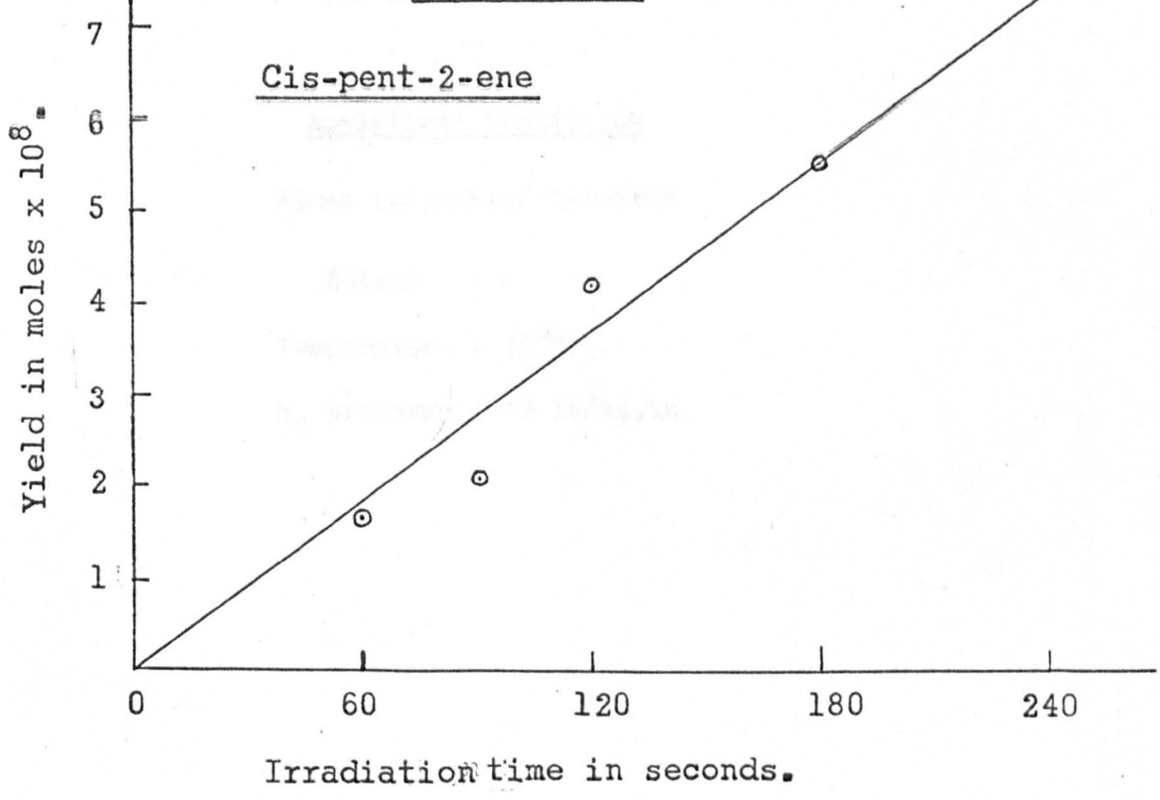


Figure 3.14



Variation of trans-pent-2-ene and cis-pent-2-ene yields with irradiation time.

3.1.2 Effect of Intensity Variation

Using intensity stops of blackened copper gauze placed between the lamp and cell, a ten fold variation in intensity could be obtained (Section 2.5.2). Figures 3.15 to 3.22 illustrate that the products of irradiation are directly proportional to the intensity.

Variation of Intensity

Irradiation Conditions

Pressure of cis-but-2-ene : 7 mm.

Temperature : 25°C

Irradiation Time : 10 minutes

Analytical Conditions

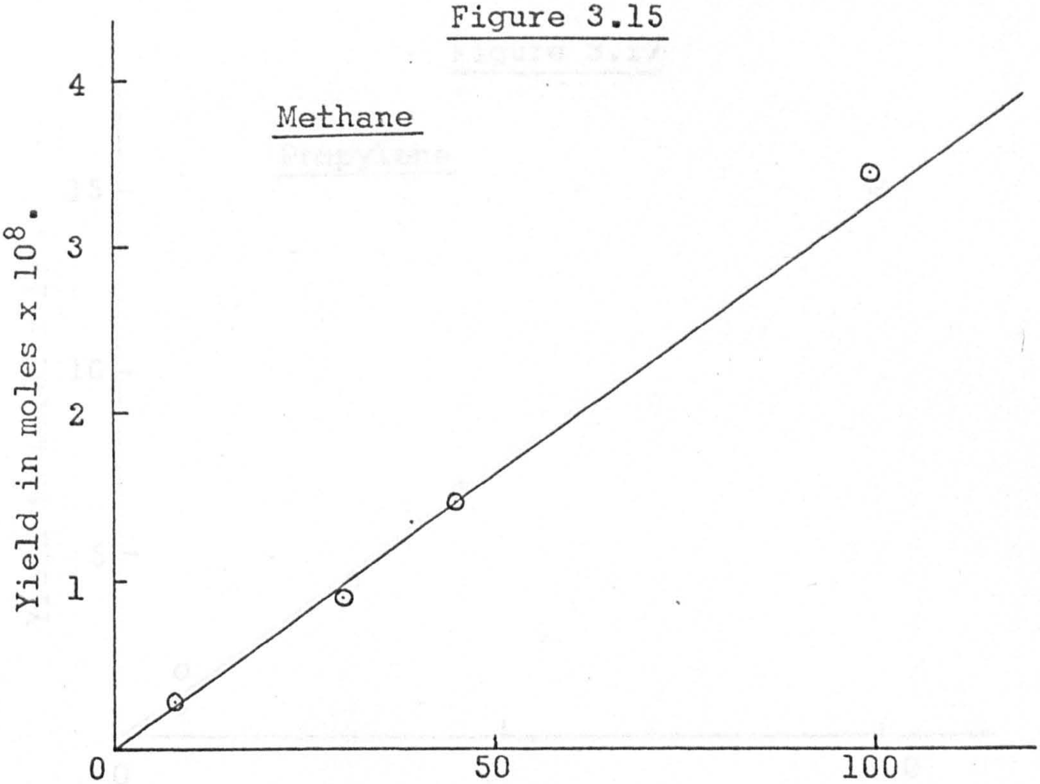
Flame Ionization Detector

Column : 0

Temperature : 35°C

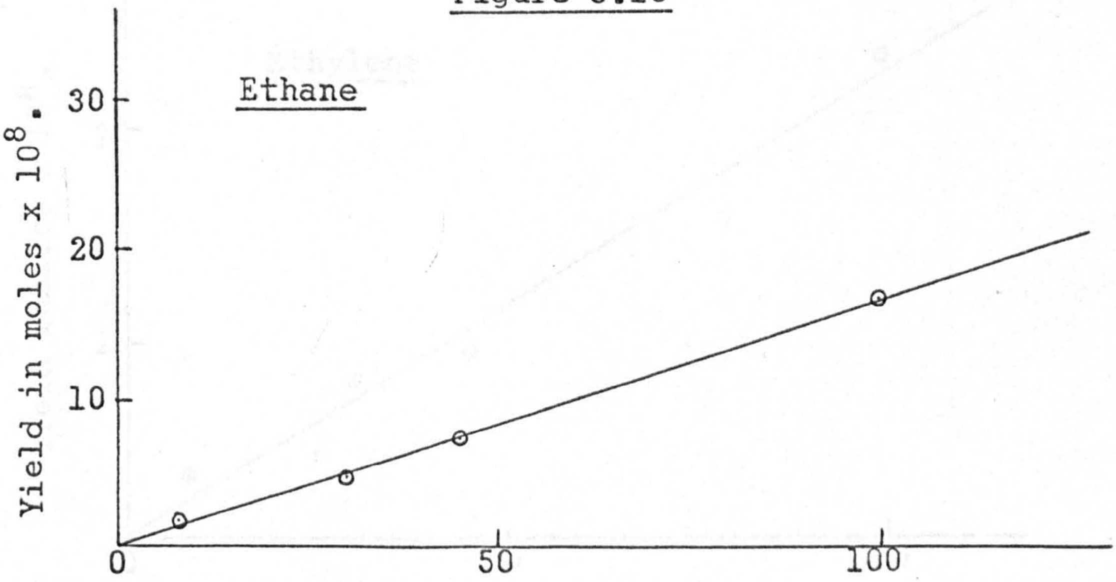
N_2 pressure : 12 lb/sq.in.

Figure 3.15



% intensity.

Figure 3.16



% intensity

Variation of methane and ethane yields with intensity of irradiation.

Figure 3.17

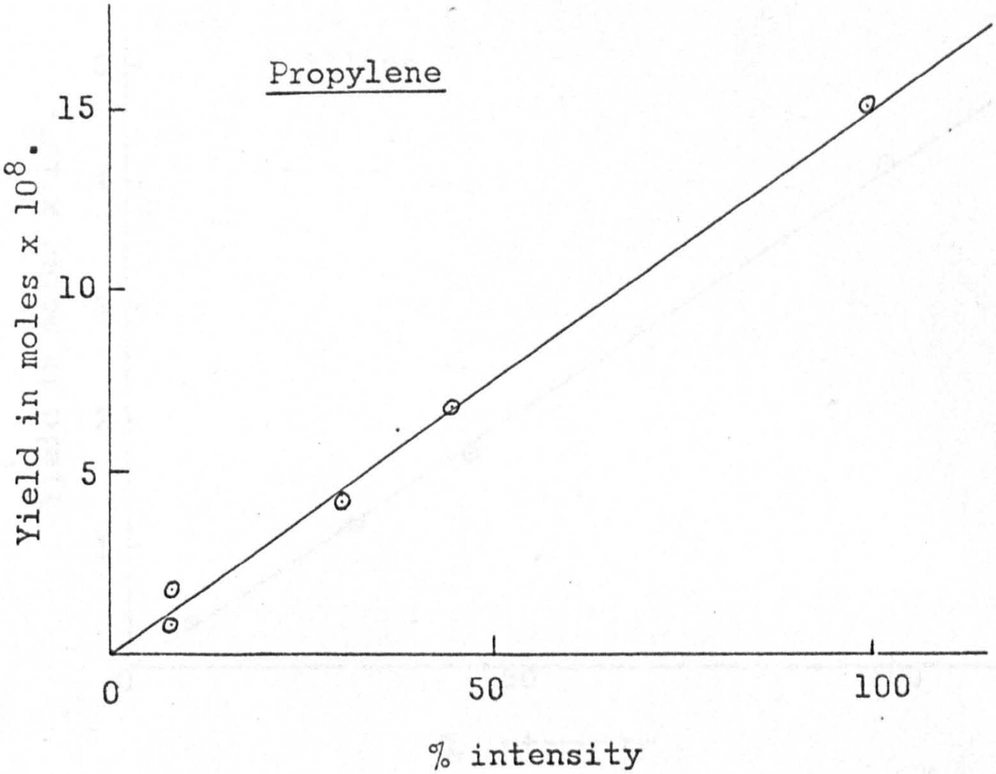
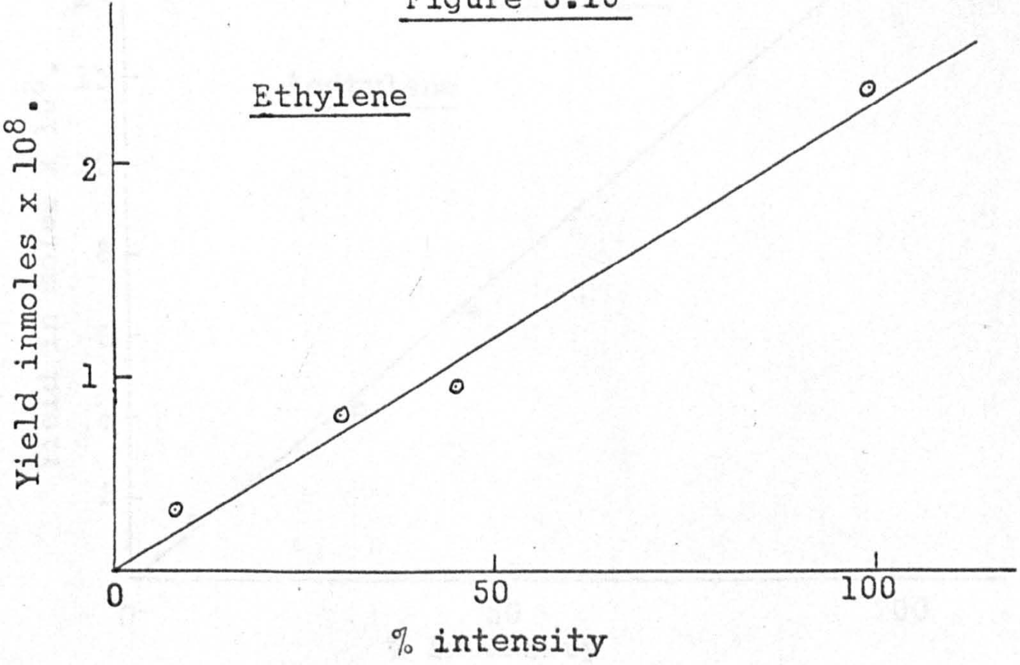


Figure 3.18



Variation of propylene and ethylene yields with intensity of irradiation.

Figure 3.19

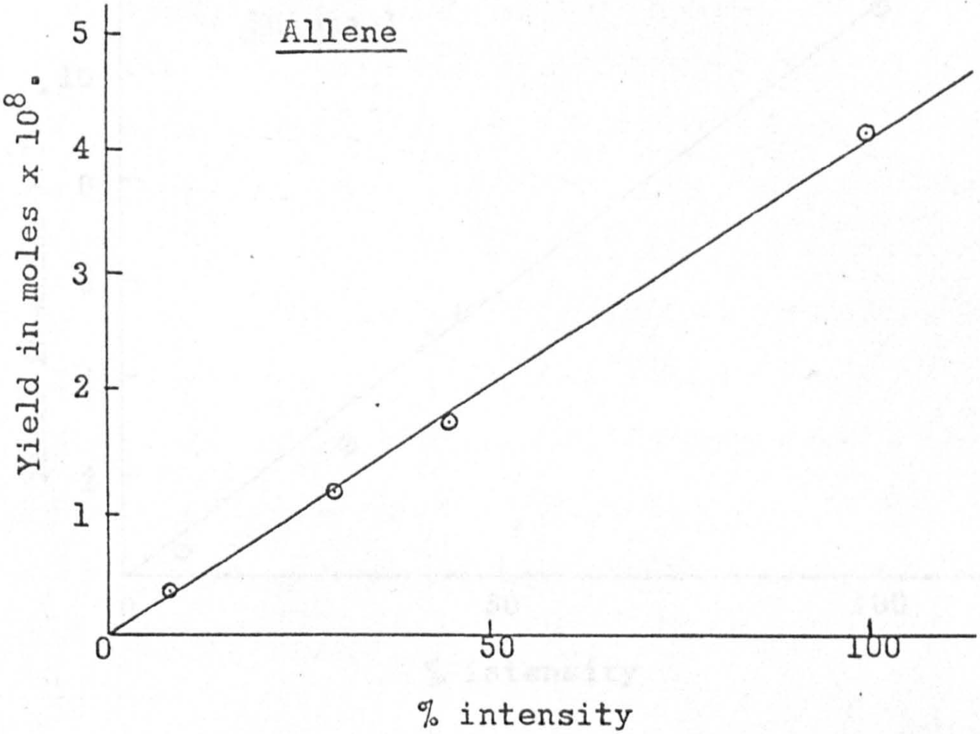
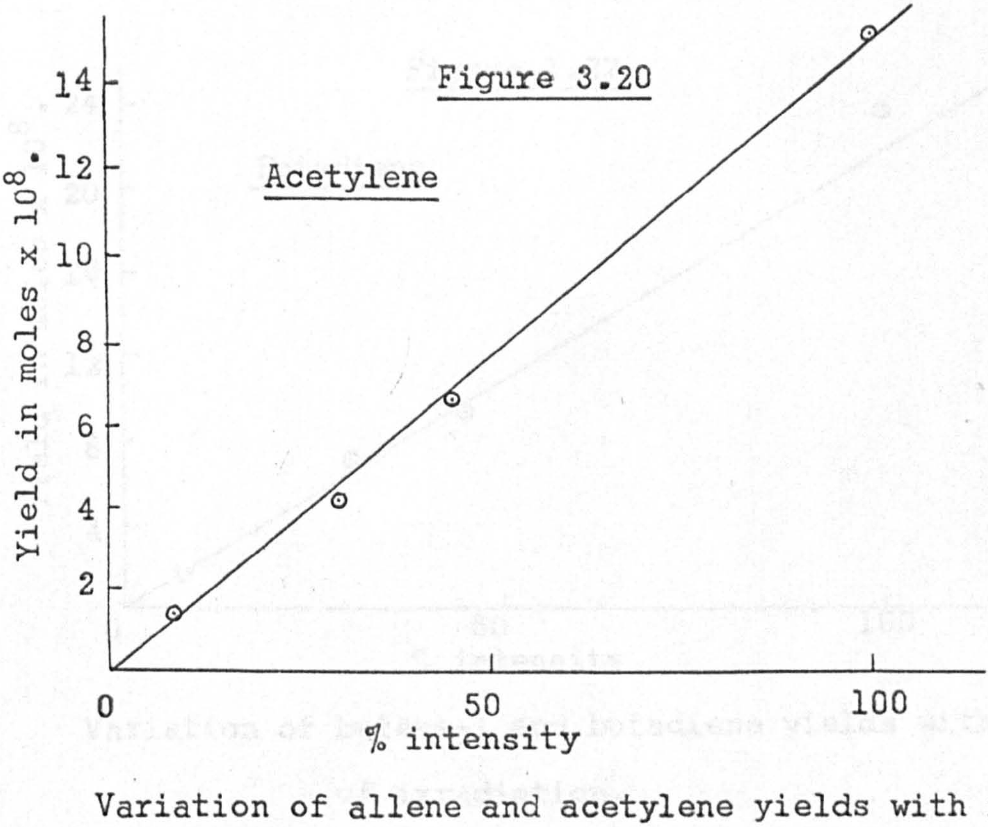


Figure 3.20



Variation of allene and acetylene yields with intensity.

Figure 3.21

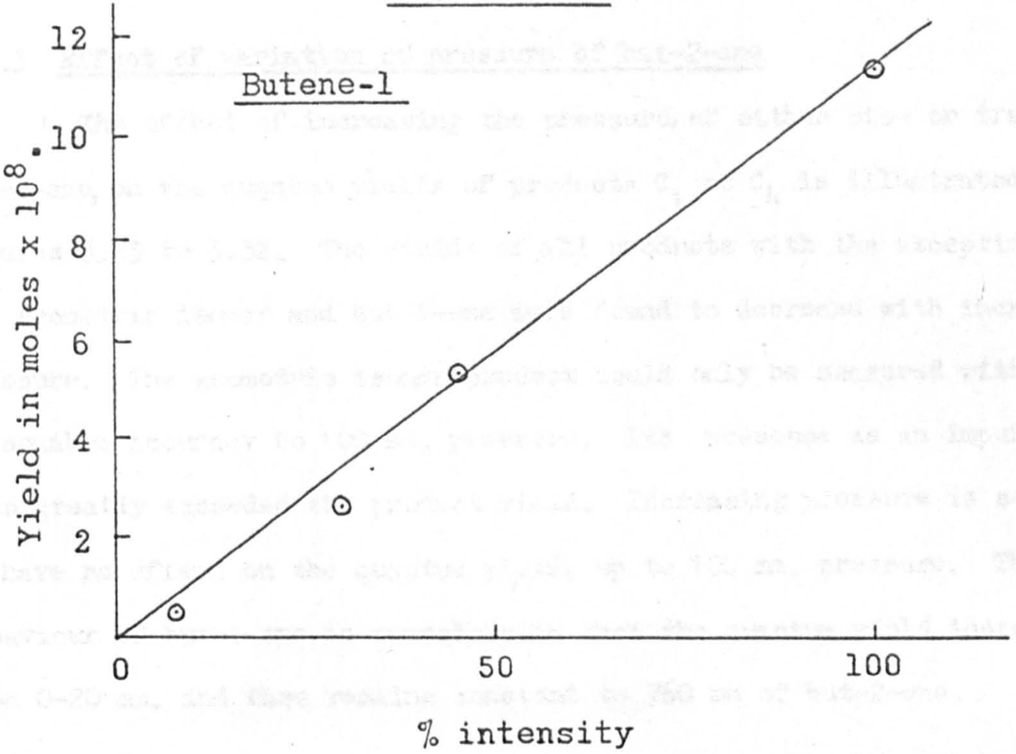
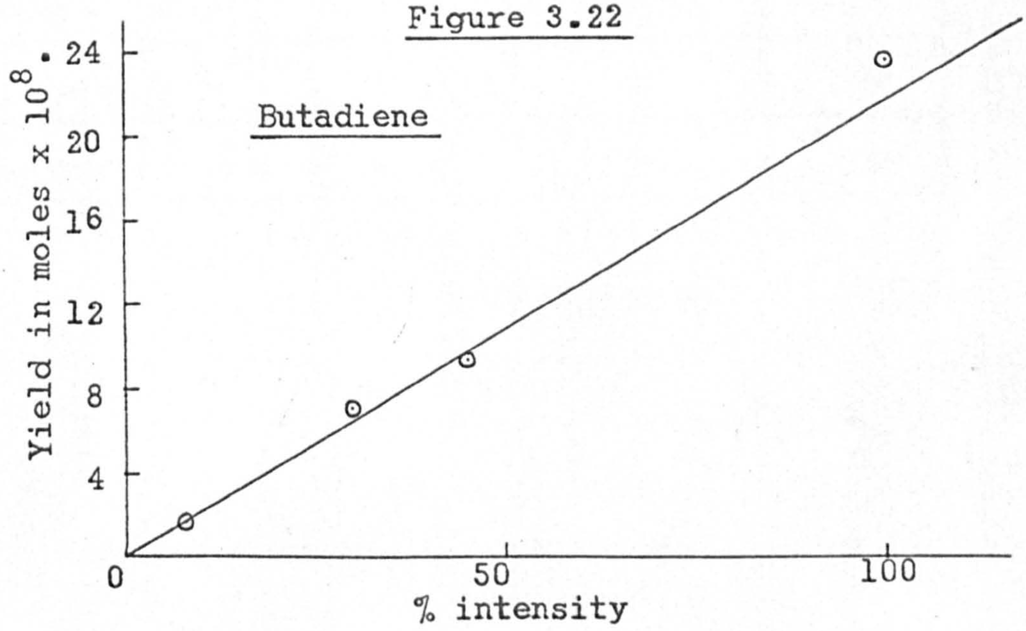


Figure 3.22



Variation of butene-1 and butadiene yields with intensity of irradiation.

3.1.3 Effect of variation of pressure of but-2-ene

The effect of increasing the pressure, of either cis- or trans-but-2-ene, on the quantum yields of products C_1 to C_4 is illustrated in Figures 3.23 to 3.32. The yields of all products with the exception of the geometric isomer and but-1-ene were found to decrease with increasing pressure. The geometric isomer product could only be measured with reasonable accuracy to 100 mm. pressure. Its presence as an impurity then greatly exceeded the product yield. Increasing pressure is seen to have no effect on the quantum yield, up to 100 mm. pressure. The behaviour of but-1-ene is anamolous in that the quantum yield increases from 0-20 mm, and then remains constant to 760 mm of but-2-ene.

Variation of but-2-ene pressure

Conditions of Irradiation:

Temperature : 25°C

Irradiation time : from one to five minutes

Analytical Conditions

Flame ionization detector:

Column	H	O	S
Temperature °C	35	35	80
N_2 pressure lb./□"	12	12	20

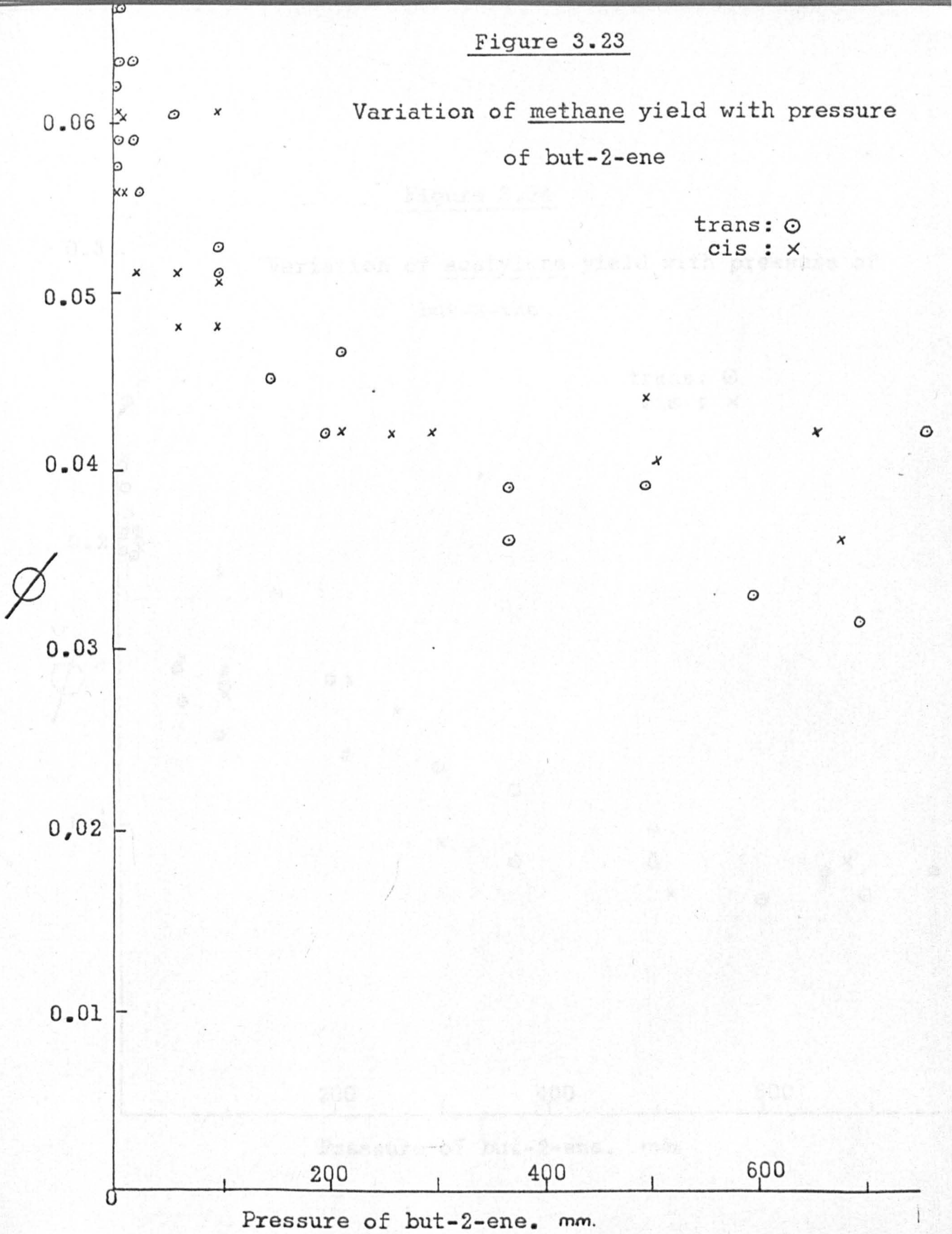
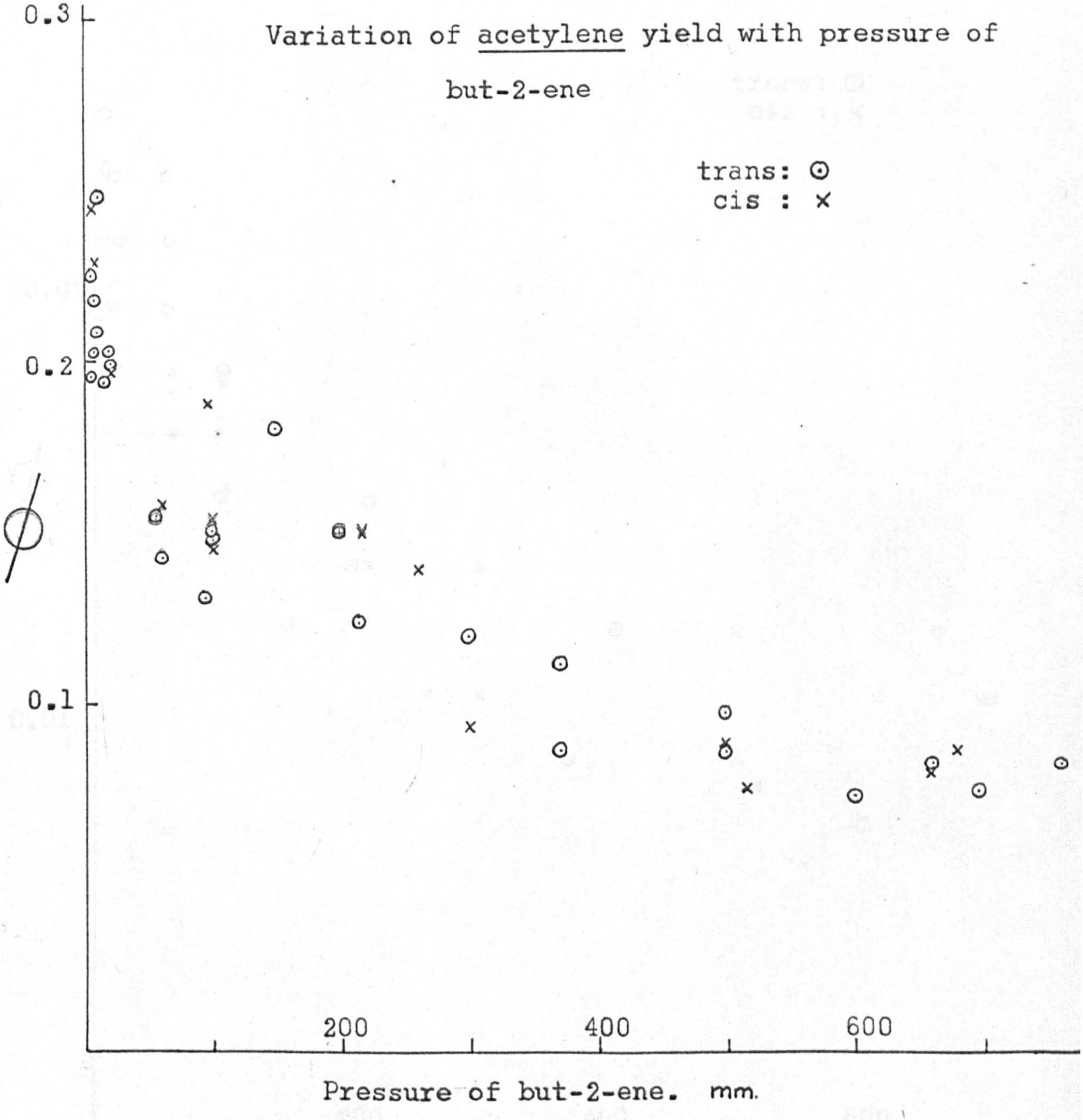


Figure 3.23

Variation of methane yield with pressure of but-2-ene

Figure 3.24



Variation of acetylene yield with pressure of but-2-ene

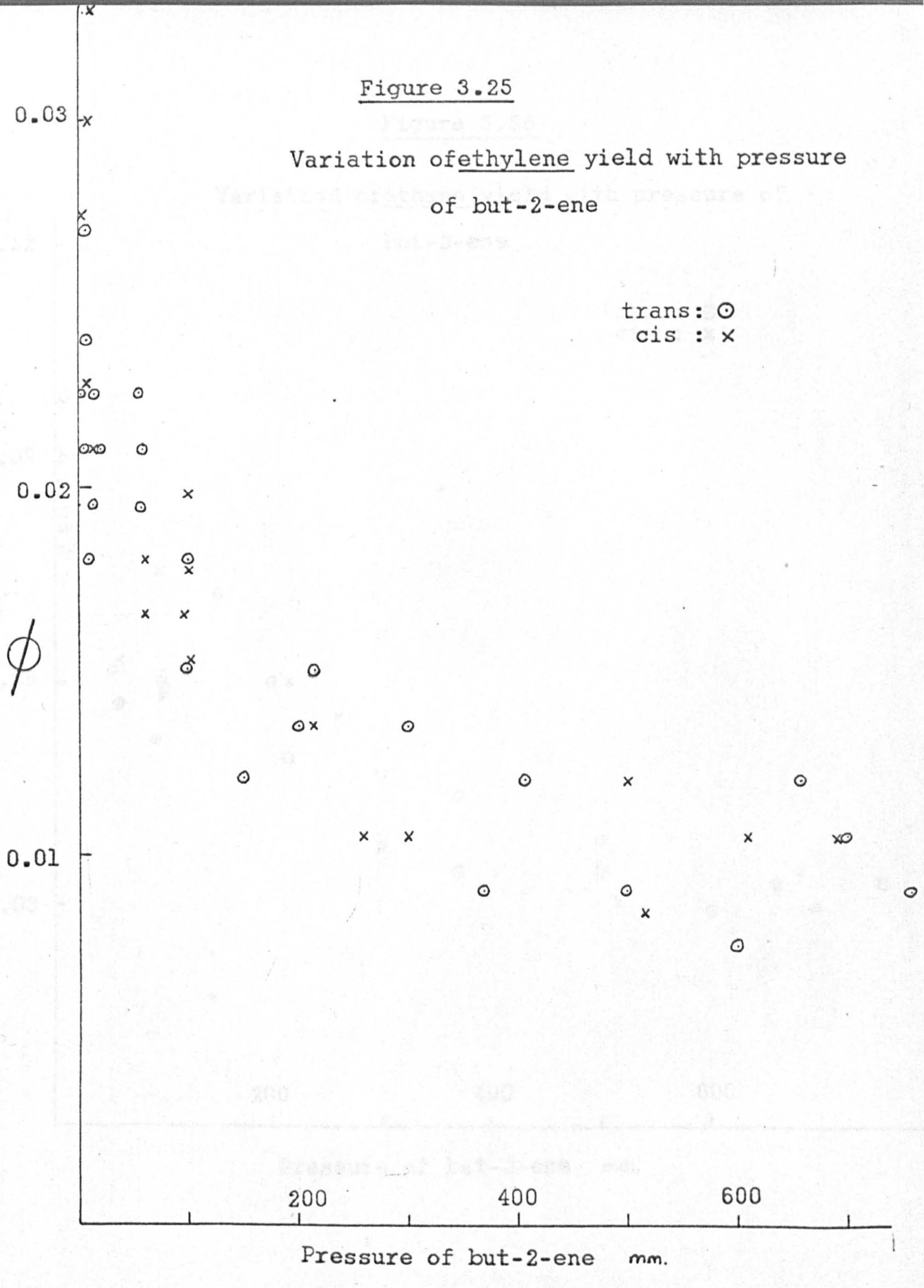


Figure 3.25

Variation of ethylene yield with pressure of but-2-ene

Figure 3.26

Variation of ethane yield with pressure of but-2-ene

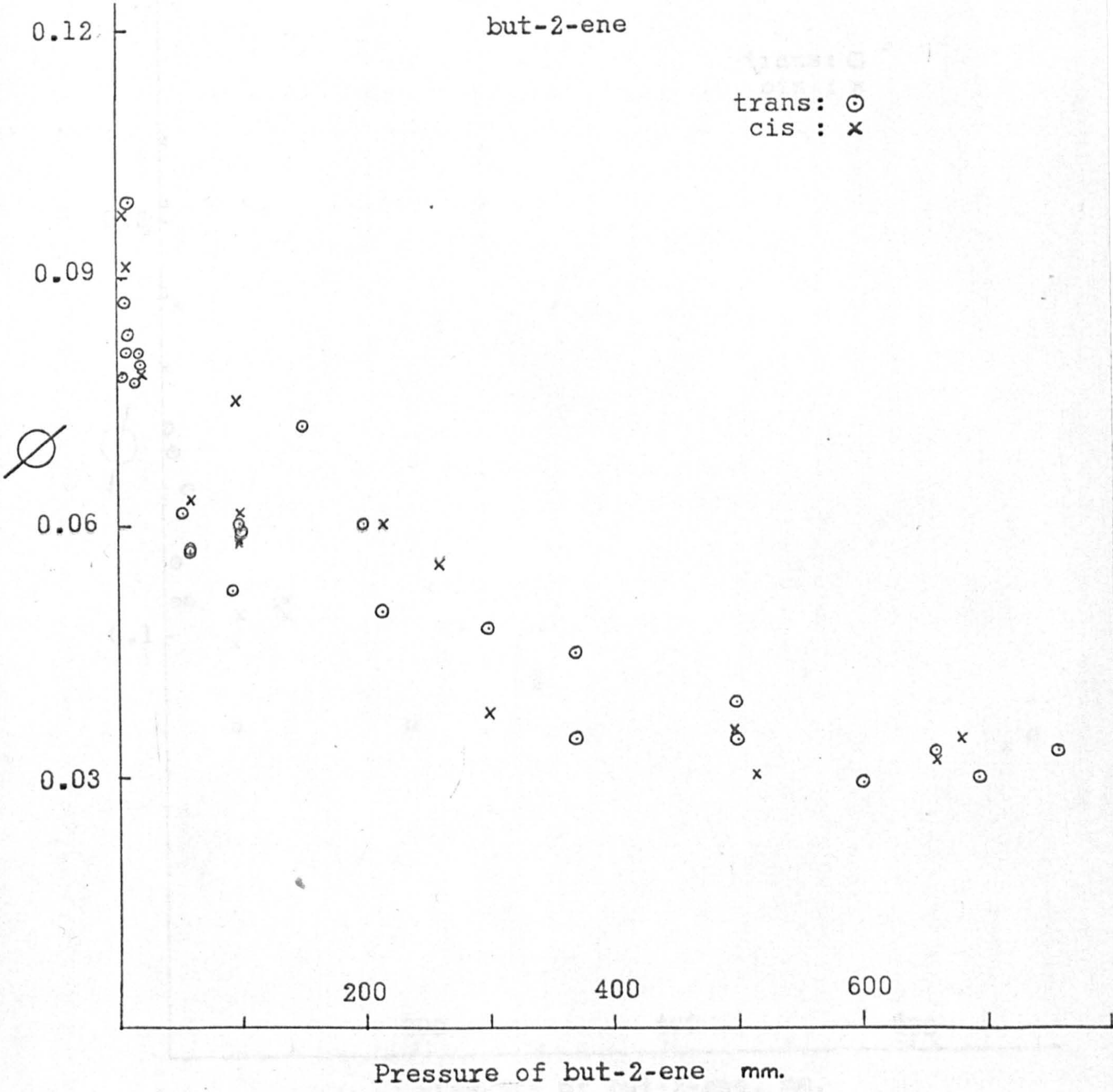
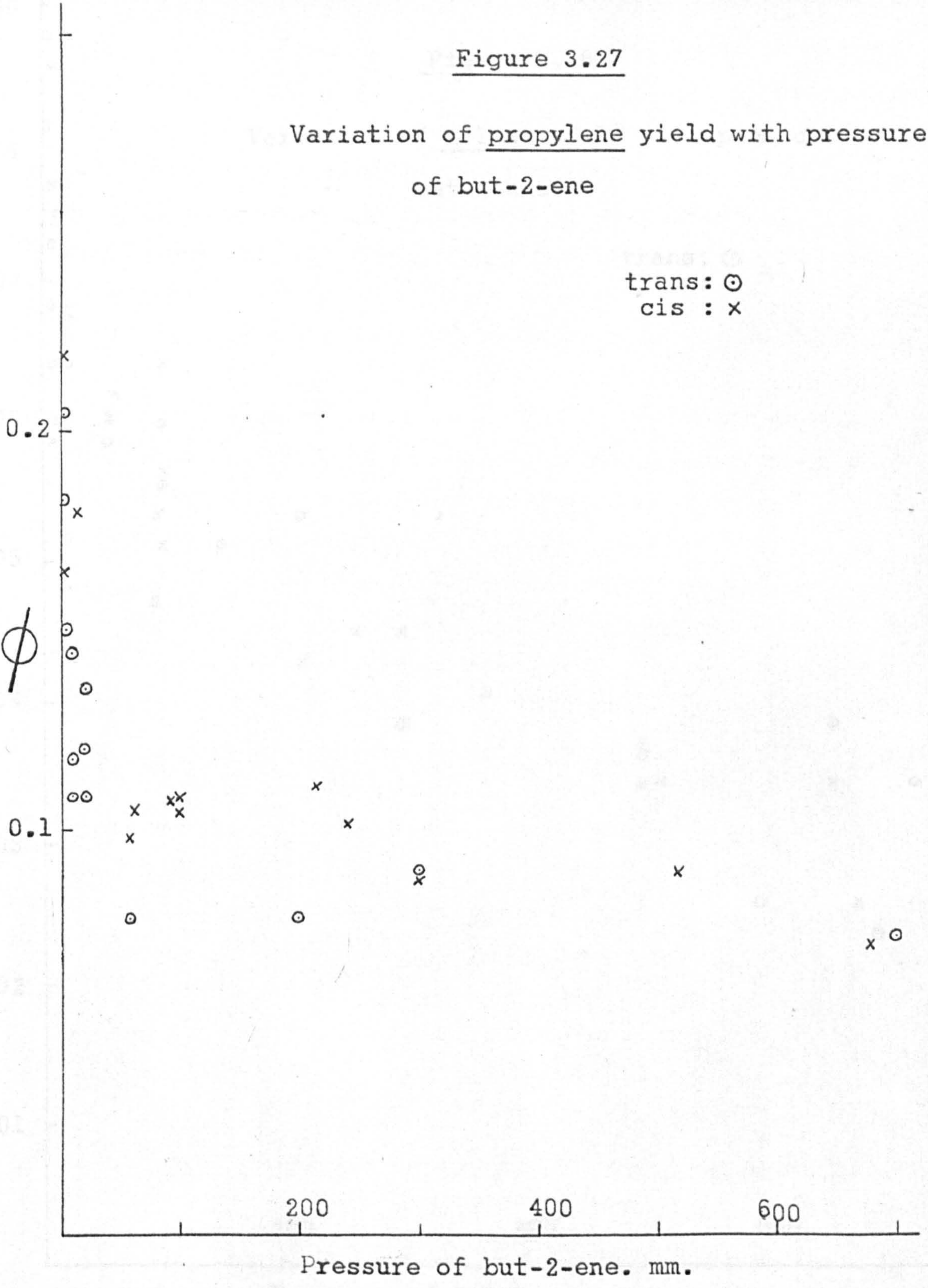


Figure 3.27

Variation of propylene yield with pressure of but-2-ene



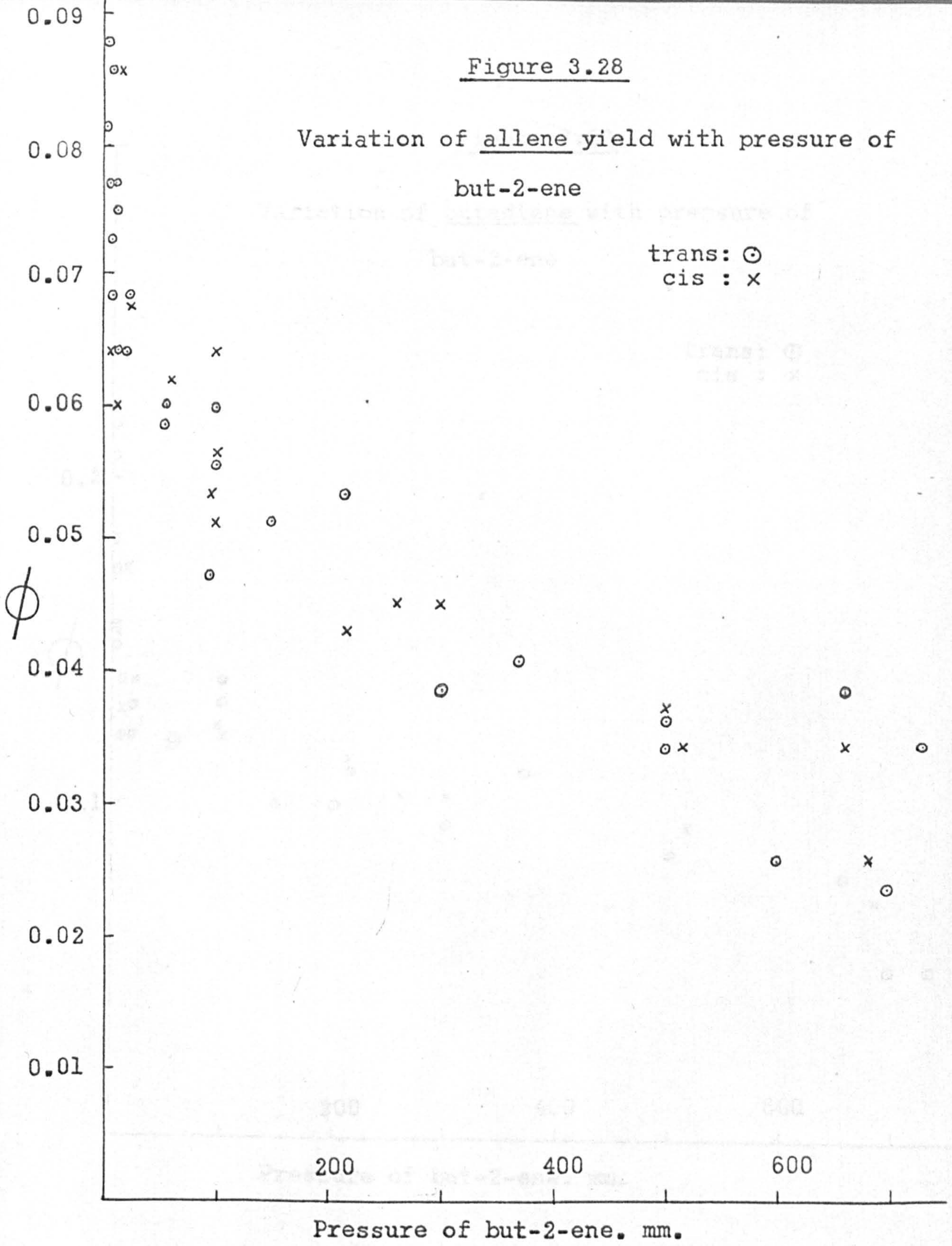


Figure 3.28

Variation of allene yield with pressure of but-2-ene

Figure 3.29

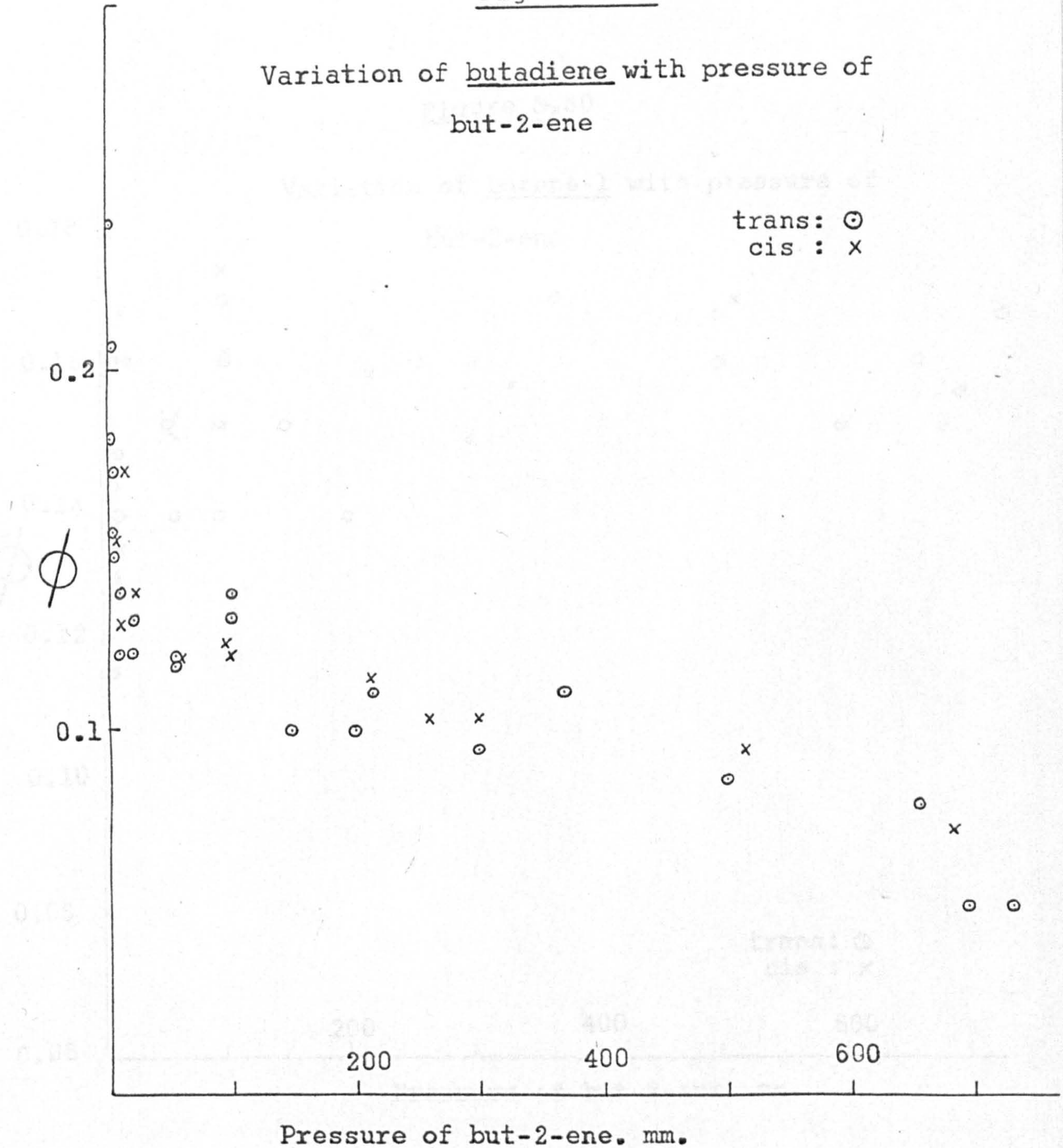

Variation of butadiene with pressure of but-2-ene
trans: ⊙
cis : x
0.2
0.1
ϕ
200
400
600
Pressure of but-2-ene. mm.

Figure 3.30

Variation of butene-1 with pressure of but-2-ene

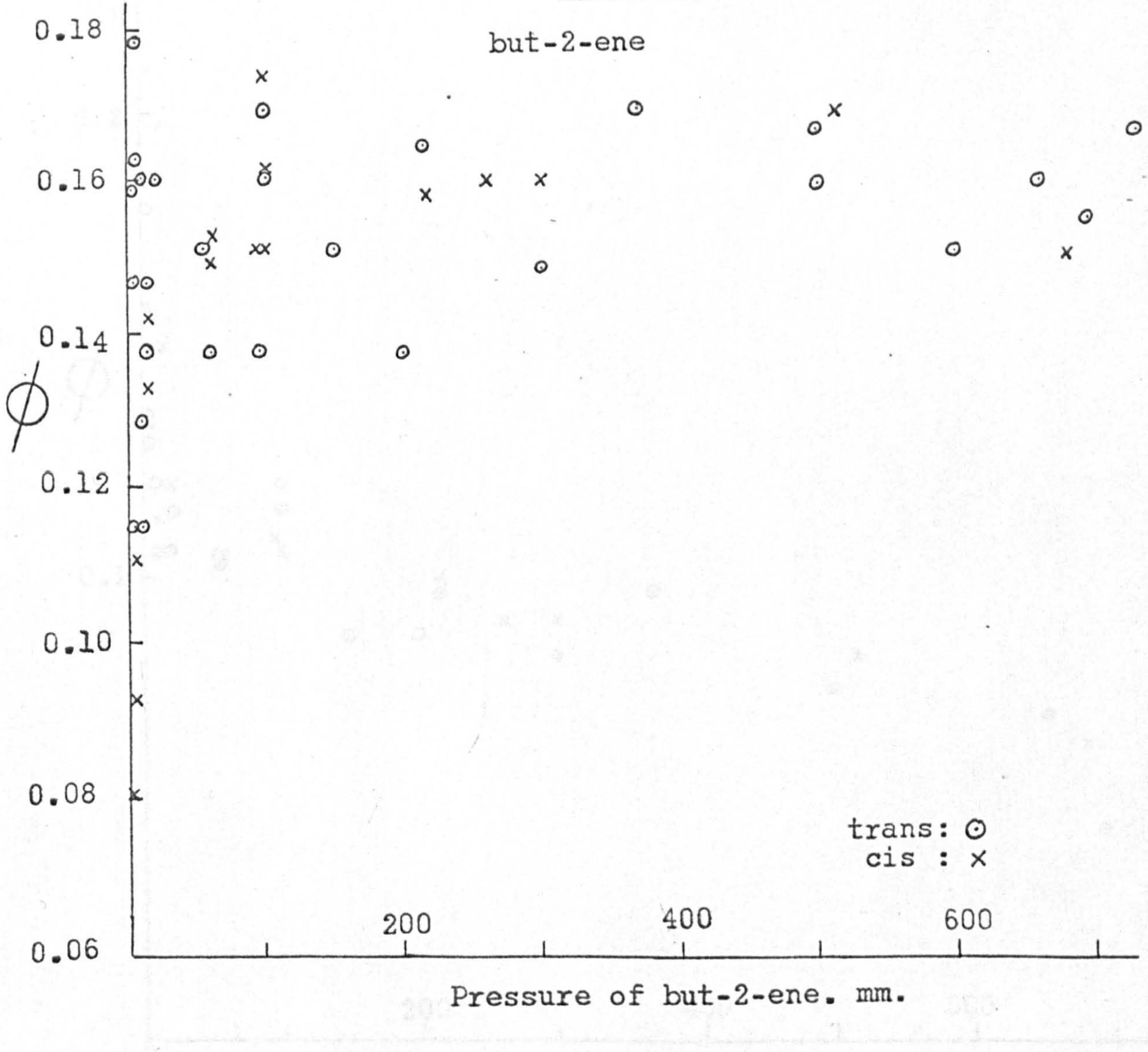


Figure 3.31

Variation of n-butane with pressure of but-2-ene

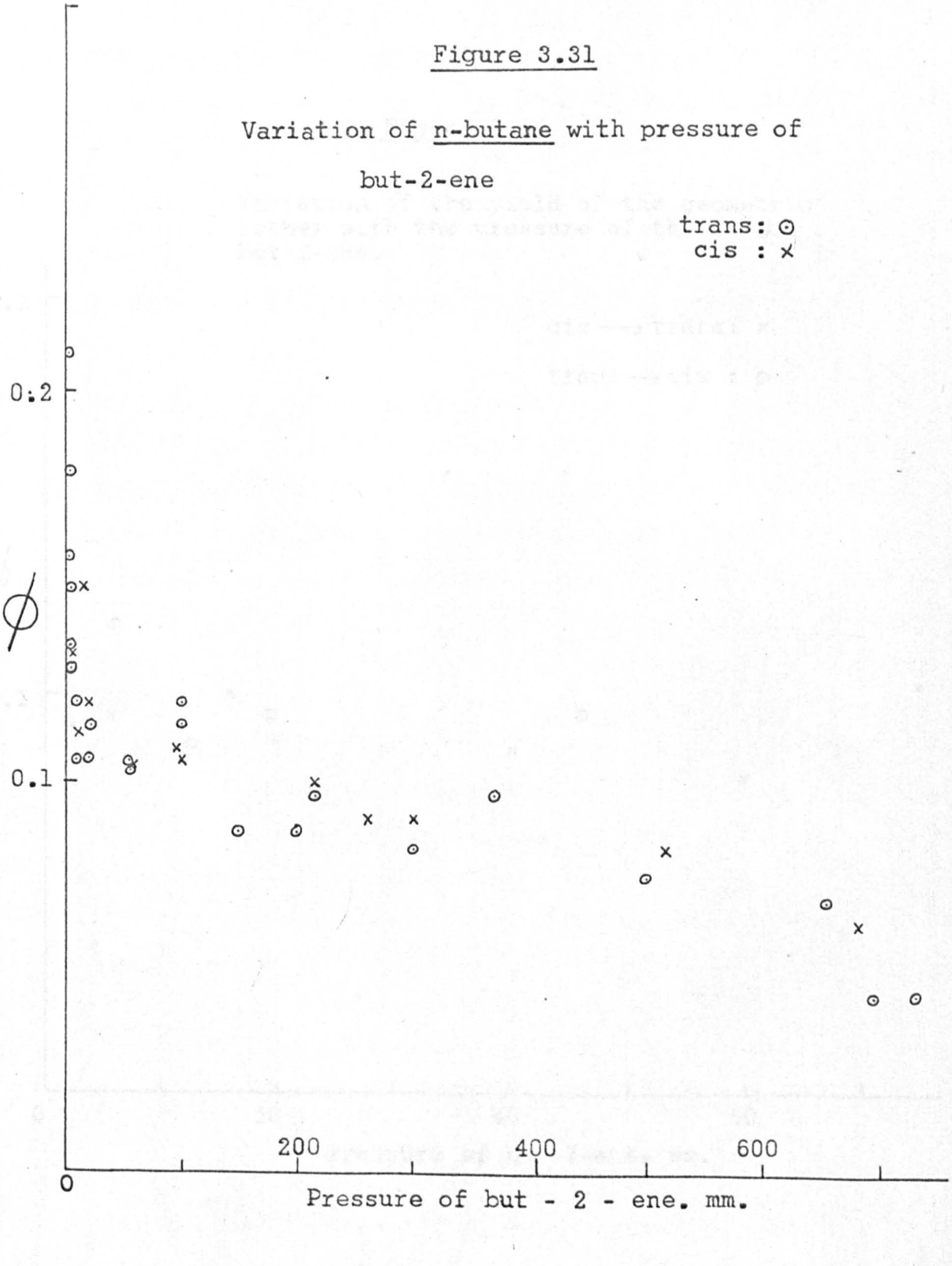
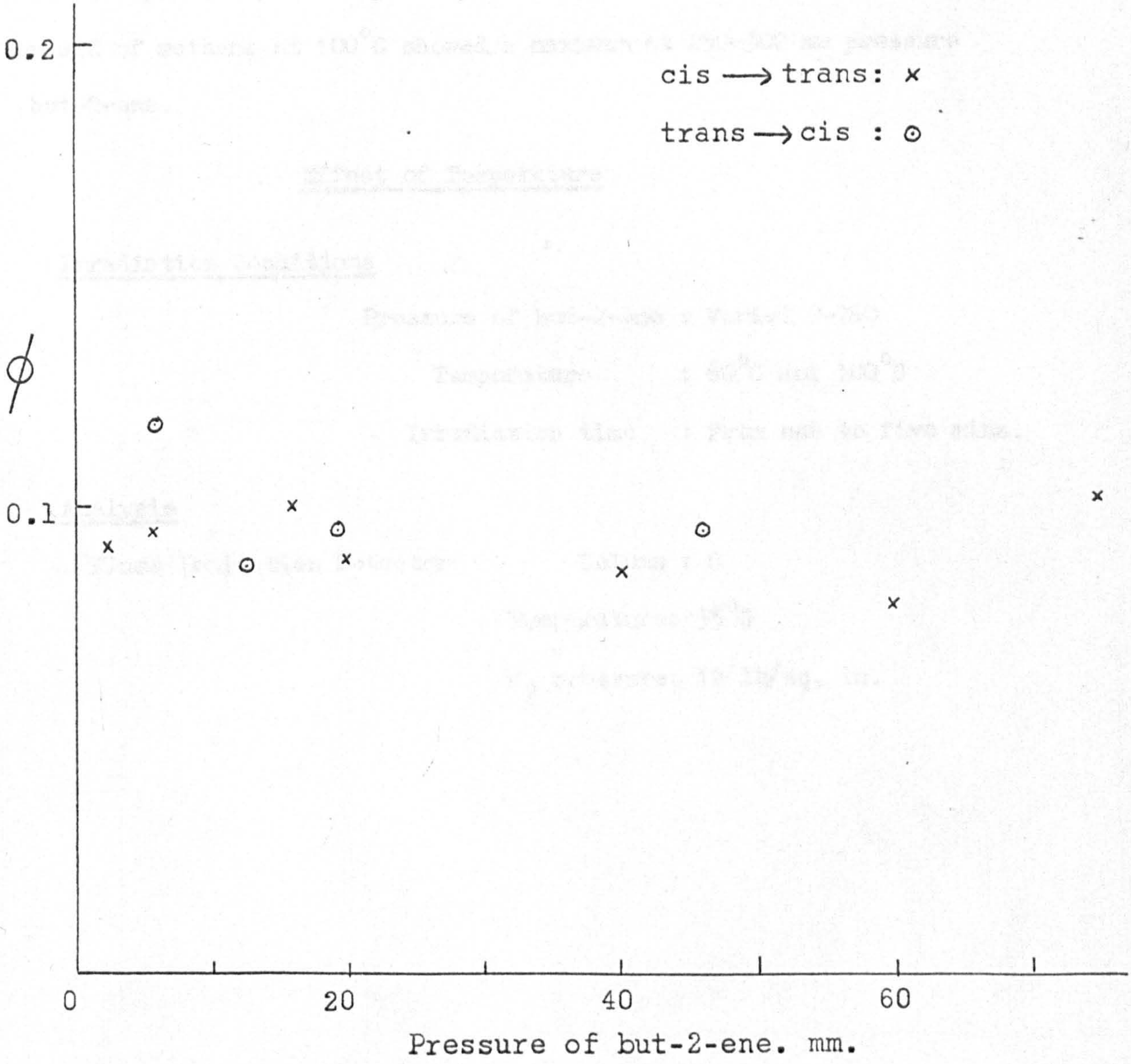


Figure 3.32

Variation of the yield of the geometric isomer with the pressure of the initial but-2-ene.



3.1.4 Effect of Temperature Variation

Irradiations were carried out at three temperatures, 25, 60 and 100°C. Comparison of the results obtained in section 3.1.3 with Figures 3.33 to 3.41 show that in the range studied temperature had no effect upon the products, with the exception of methane. The quantum yield of methane at 100°C showed a maximum at 250-300 mm pressure but-2-ene.

Effect of Temperature

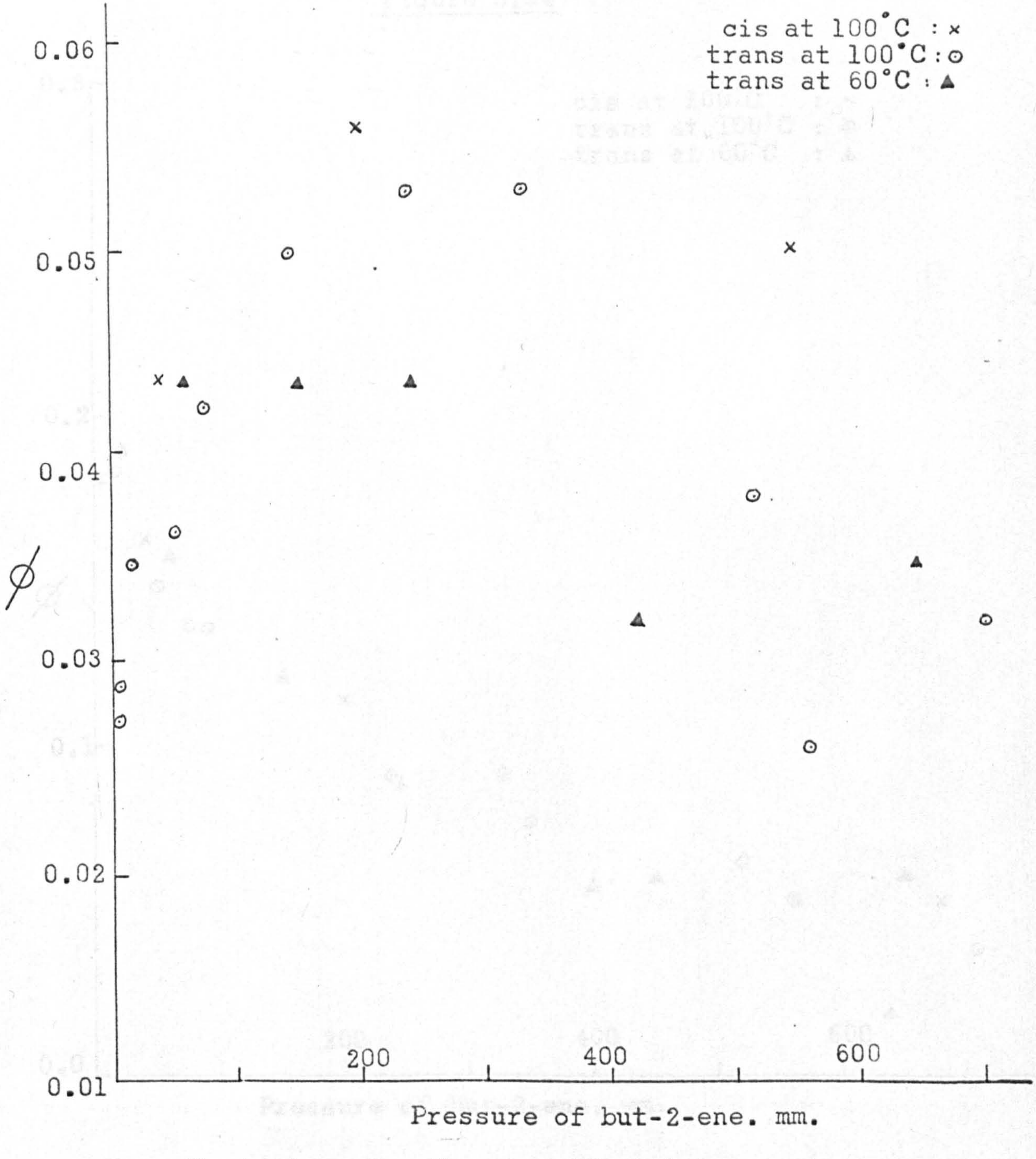
Irradiation Conditions

Pressure of but-2-ene : Varied 0-760
Temperature : 60°C and 100°C
Irradiation time : From one to five mins.

Analysis

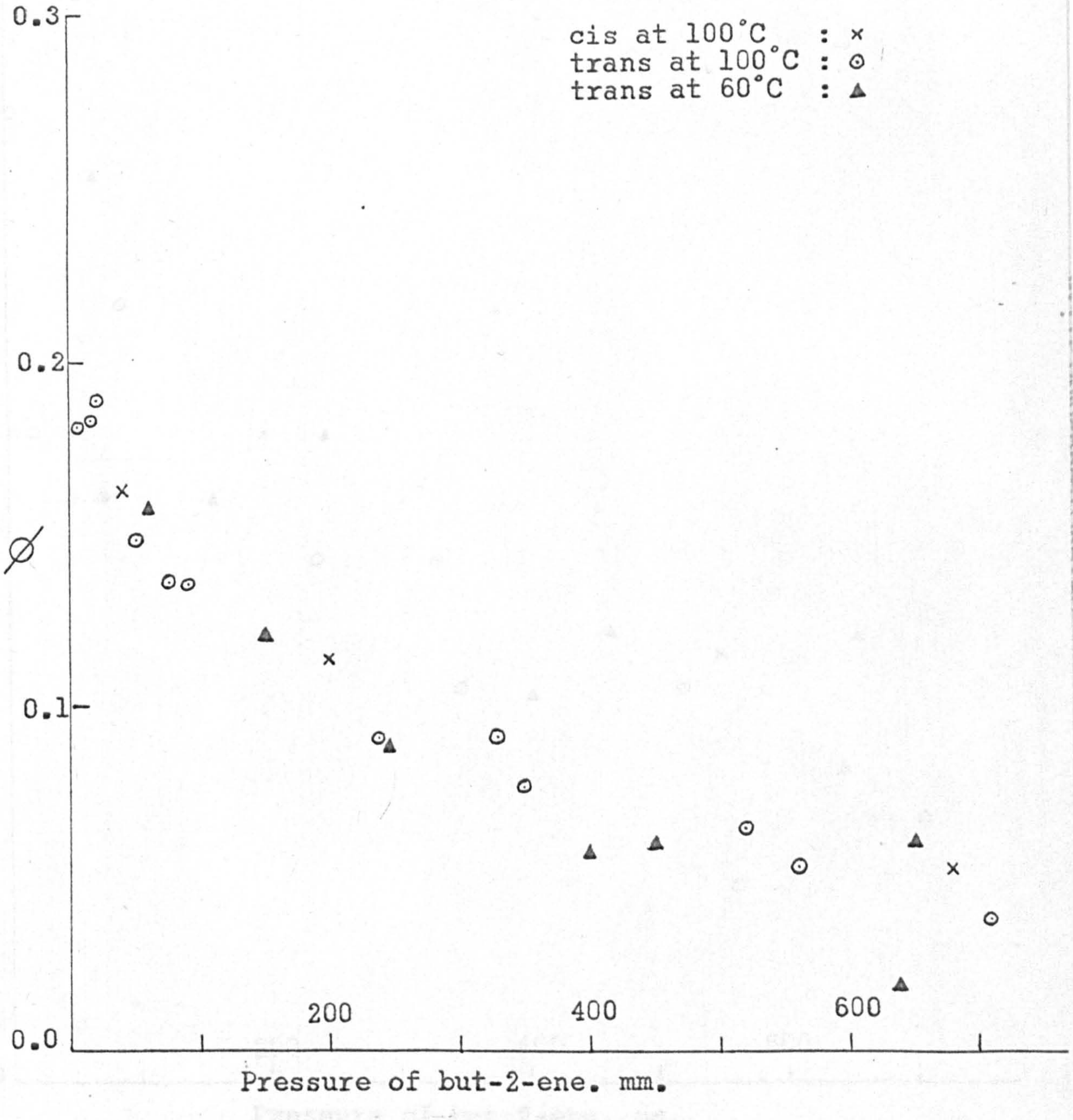
Flame Ionization Detector
Column : 0
Temperature: 35°C
N_2 pressure: 12 lb/sq. in.

Figure 3.33



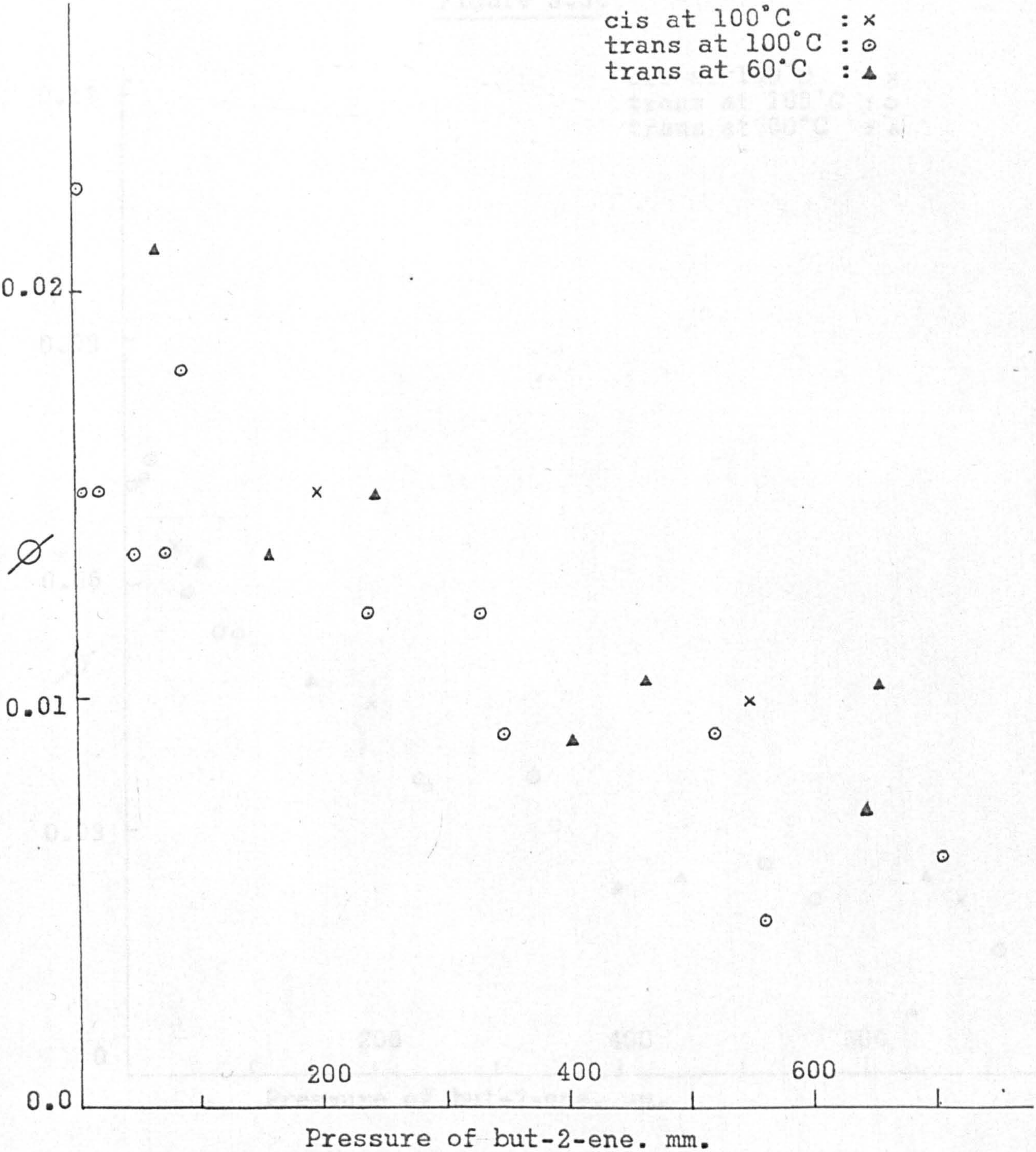
Variation of methane yield with temperature.

Figure 3.34



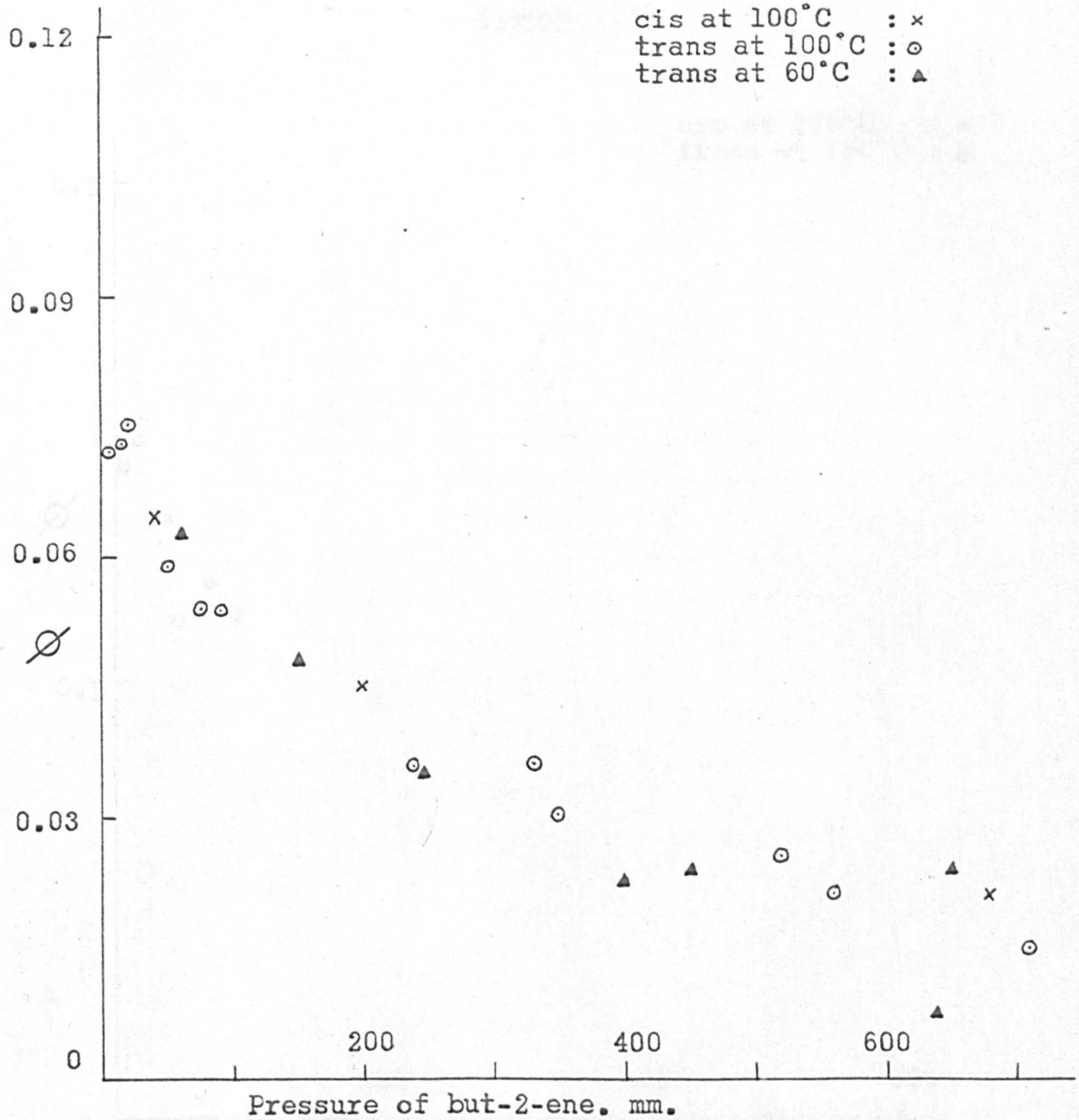
Variation of acetylene yield with temperature.

Figure 3.35



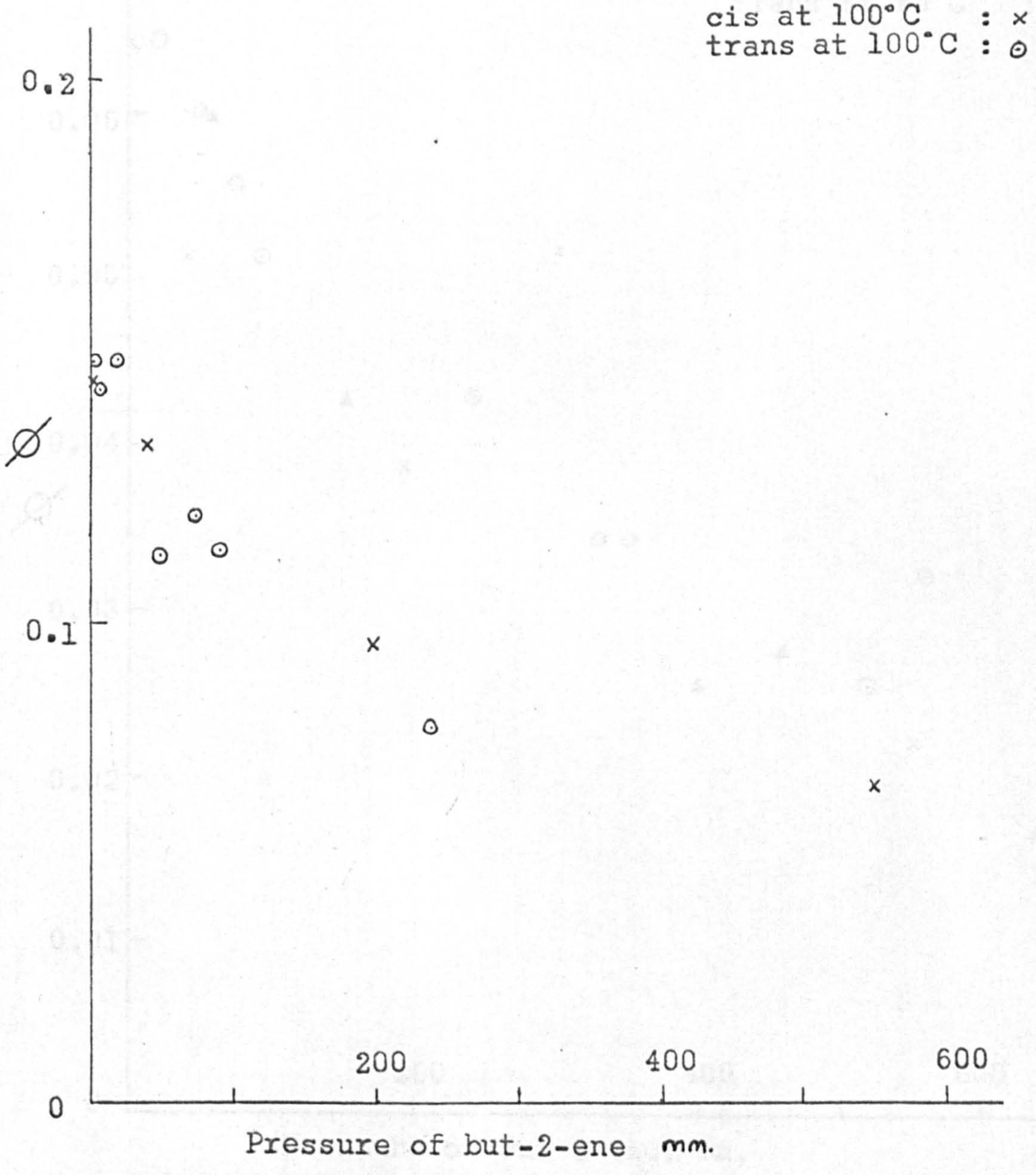
Variation of ethylene yield with temperature.

Figure 3.36.



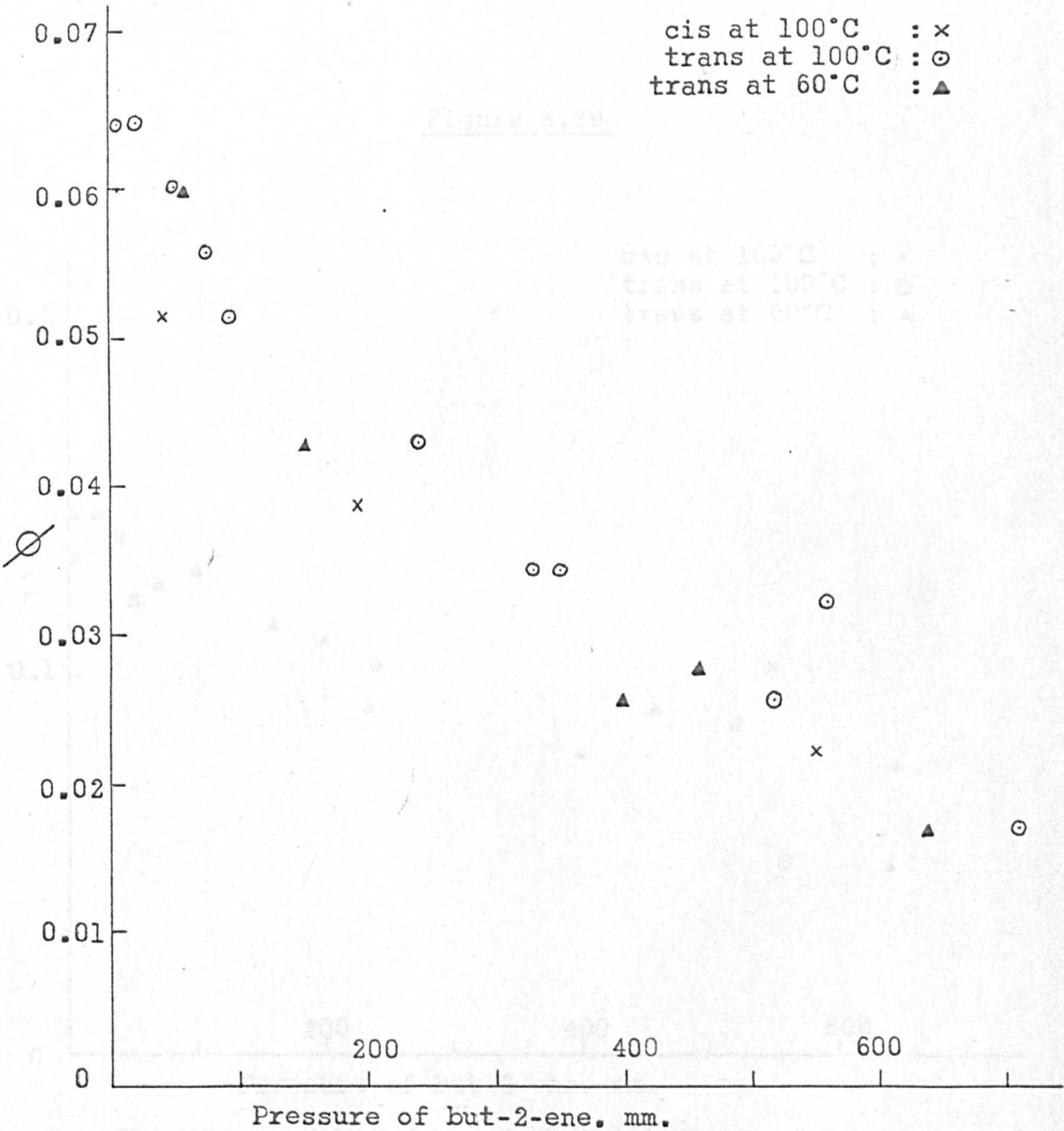
Variation of ethane yield with temperature.

Figure 3.37



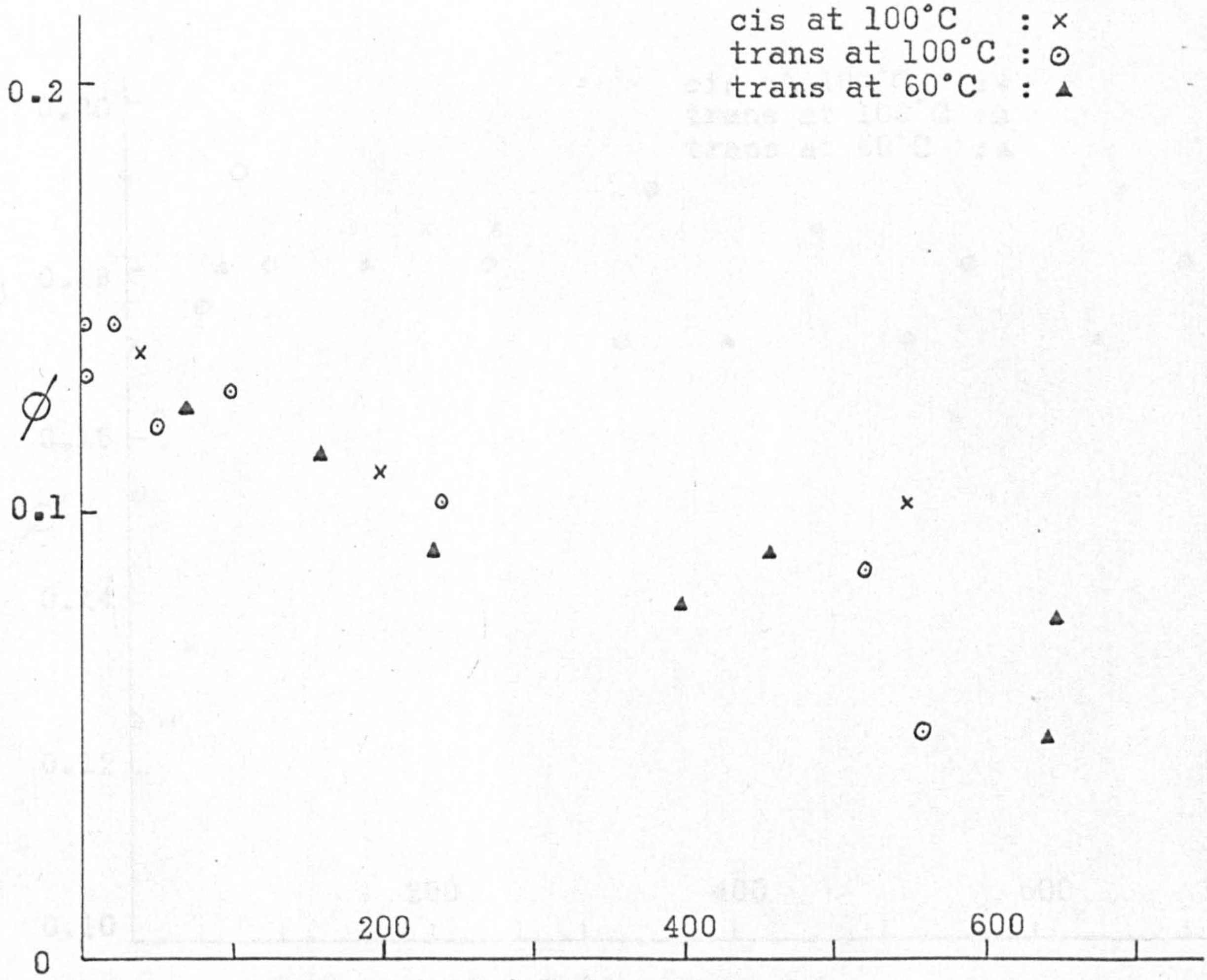
Variation of propylene yield with temperature.

Figure 3.38



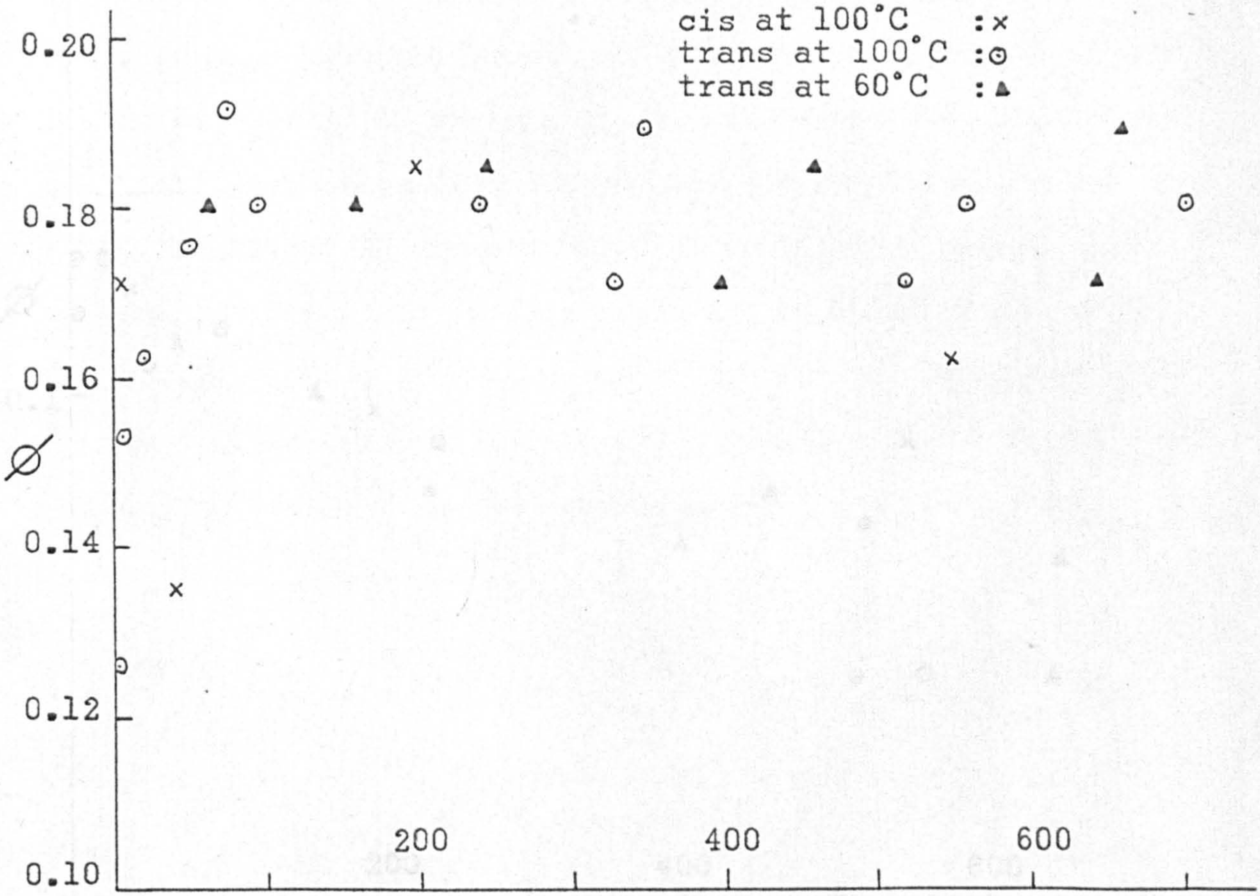
Variation of allene yield with temperature.

Figure 3.39



Variation of butadiene yield with temperature.

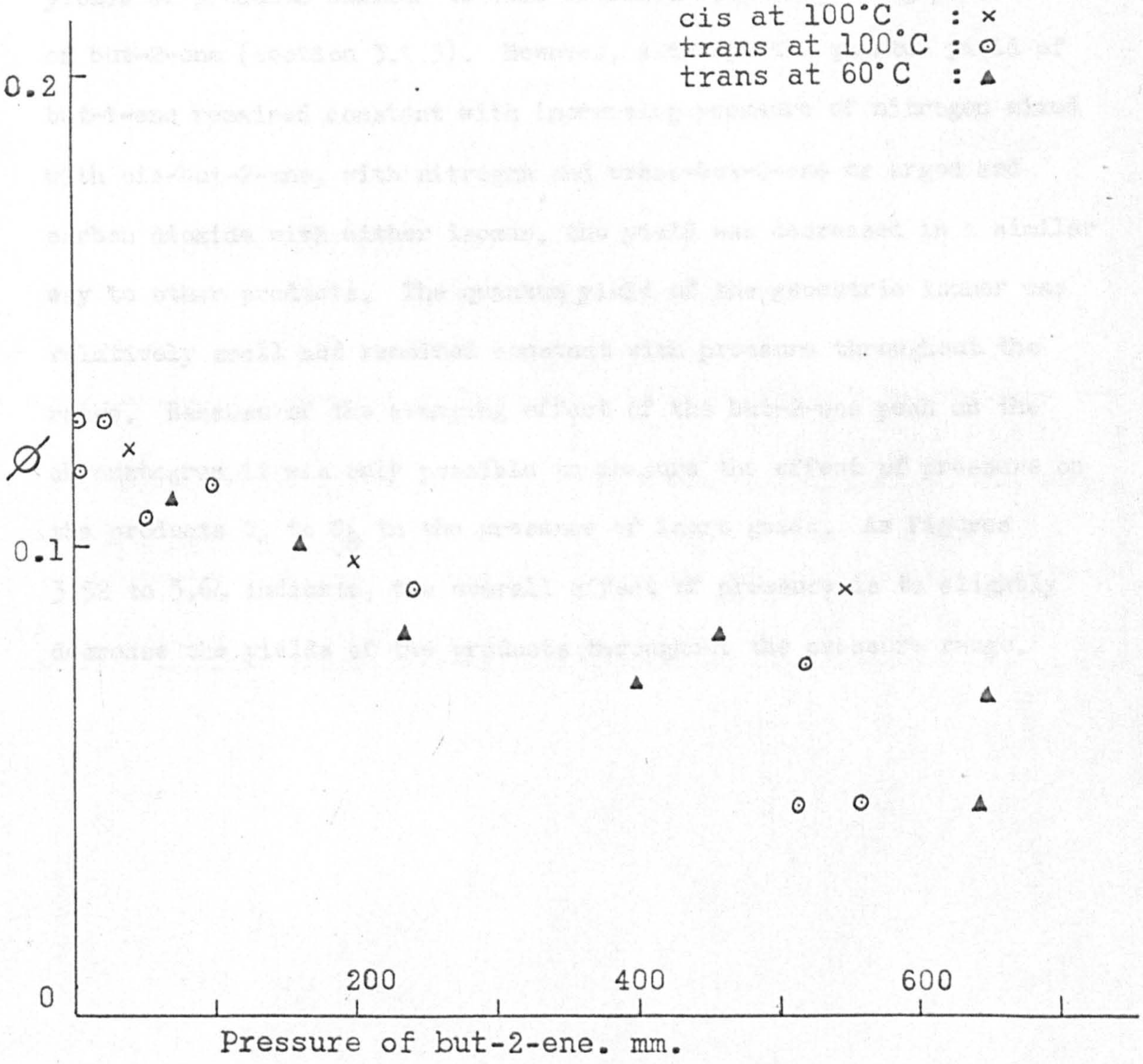
Figure 3.40



Pressure of but-2-ene. mm.

Variation of but-1-ene yield with temperature.

<u>Figure 3.41</u>



Variation of <u>n-butane</u> yield with temperature.

3.1.5 Effect of the presence of added inert gases

The effect of adding differing pressures of nitrogen, carbon dioxide and argon to a fixed pressure of either cis- or trans-but-2-ene is illustrated in Figures 3.42 to 3.64. The result of increasing the pressure of additive gas was a reduction in the quantum yields of products similar to that obtained with increasing pressure of but-2-ene (section 3.1.3). However, although the quantum yield of but-1-ene remained constant with increasing pressure of nitrogen mixed with cis-but-2-ene, with nitrogen and trans-but-2-ene or argon and carbon dioxide with either isomer, the yield was decreased in a similar way to other products. The quantum yield of the geometric isomer was relatively small and remained constant with pressure throughout the range. Because of the swamping effect of the but-2-ene peak on the chromatogram, it was only possible to measure the effect of pressure on the products C_5 to C_8 in the presence of inert gases. As Figures 3.52 to 3.64 indicate, the overall effect of pressure is to slightly decrease the yields of the products throughout the pressure range.

Effect of Added Gases

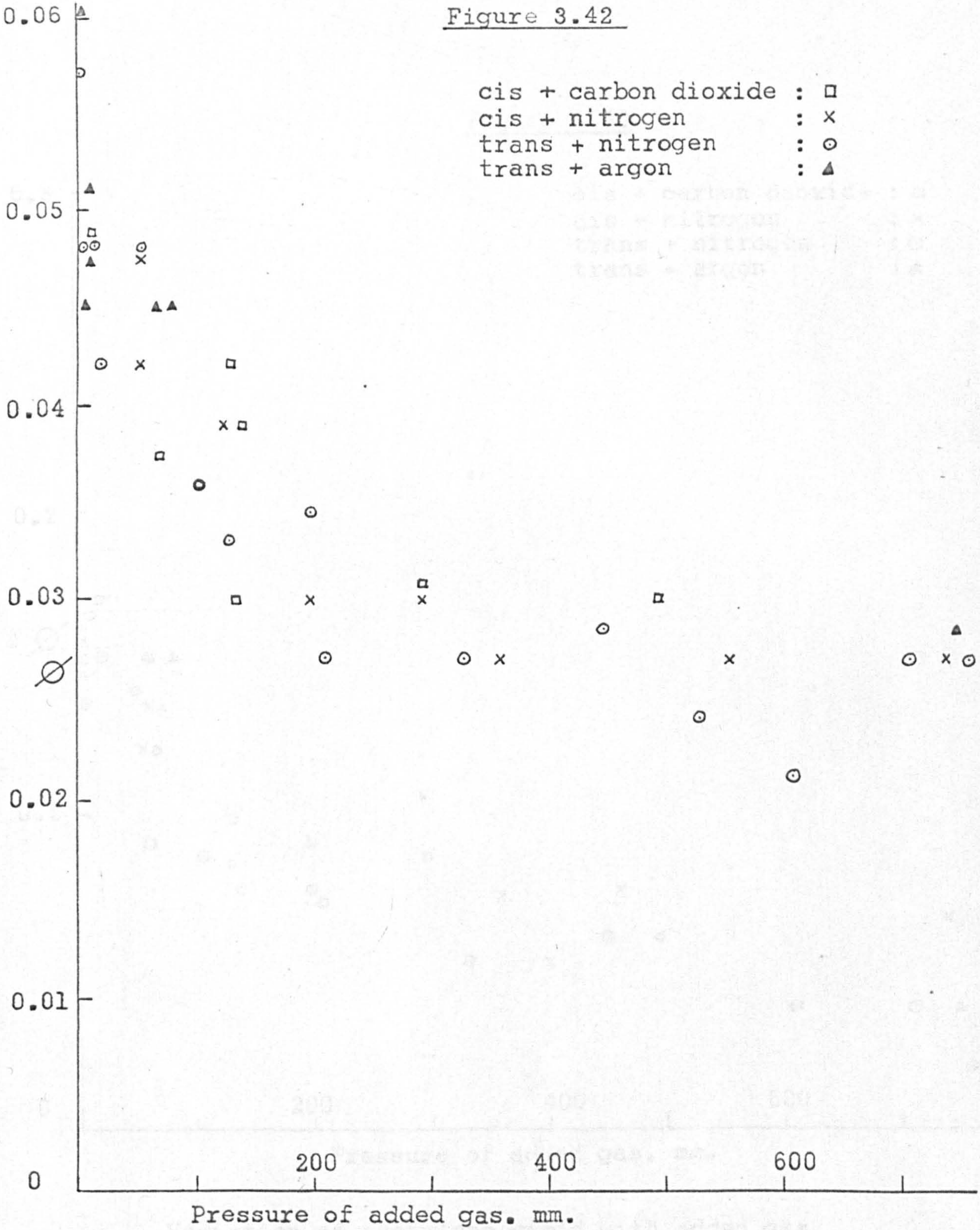
Irradiation Conditions:

Pressure of but-2-ene : 10 mm
Temperature : 25°C
Irradiation time : one to six minutes

Analysed Conditions:

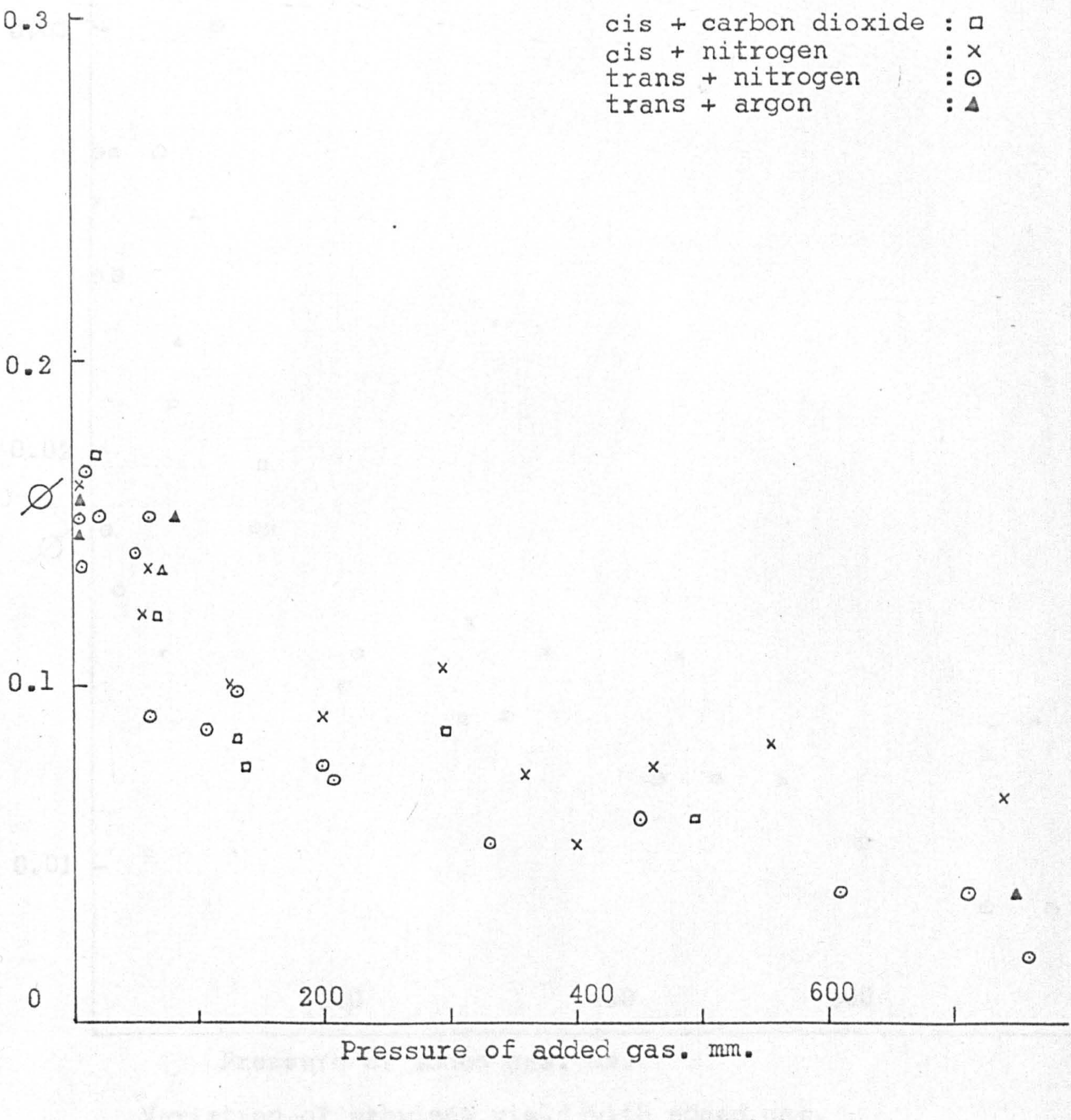
Flame ionization detector

Column	0	0	S
Temperature	35°C	80°C	80°C
N_2 pressure	12 lb/sq. in	20 lb./□"	20 lb./□"



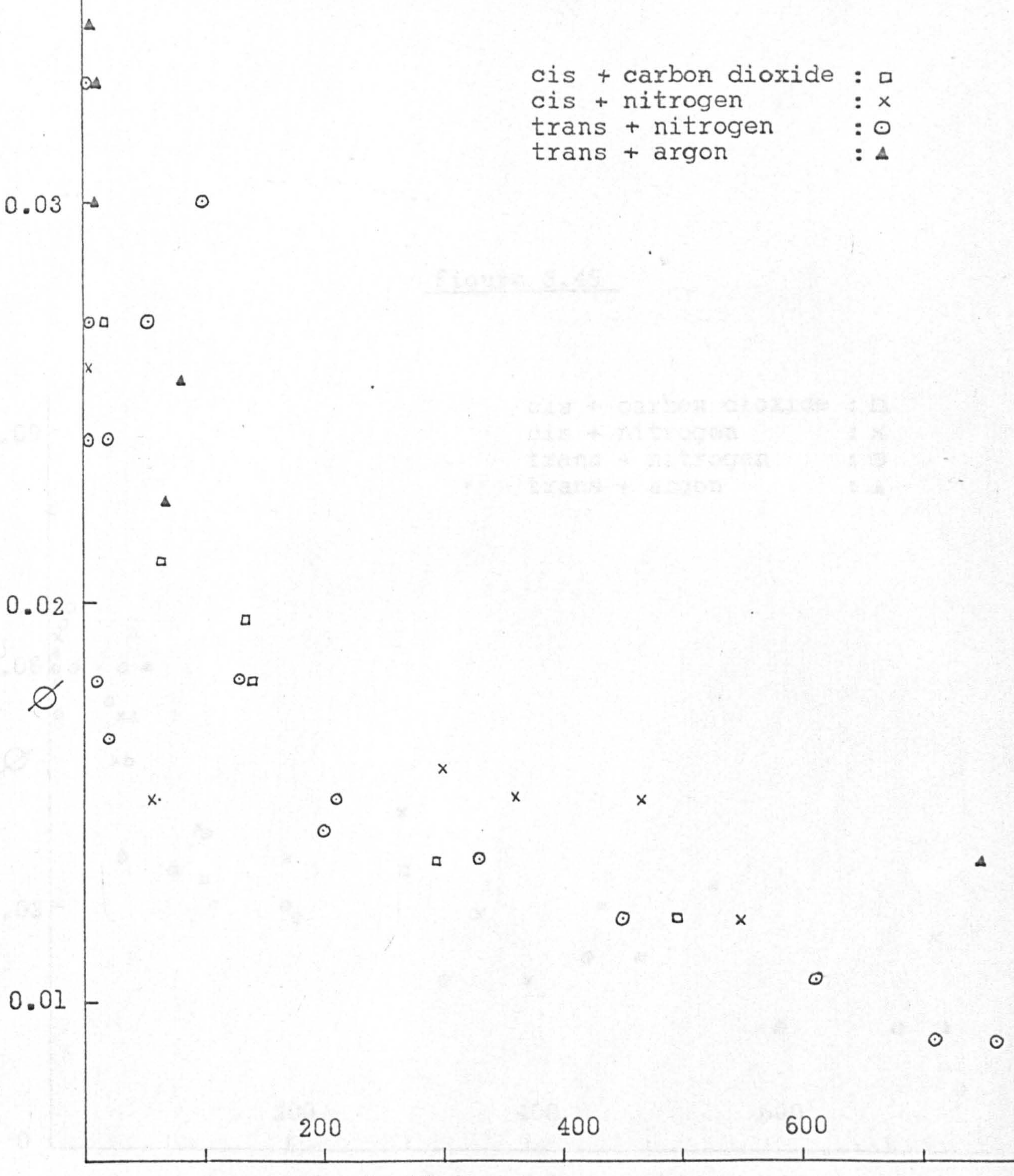
Variation of methane yield with added gas.

Figure 3.43



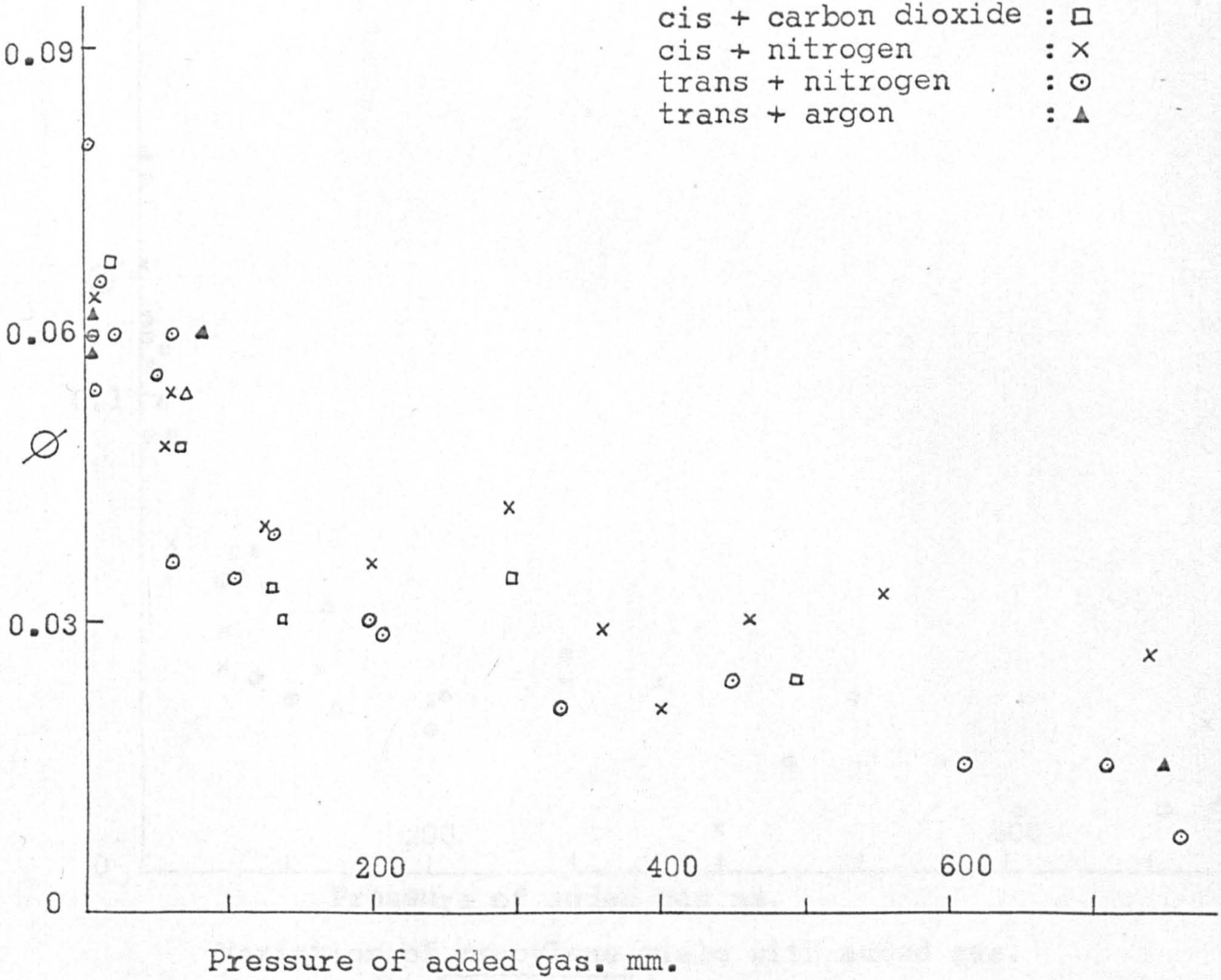
Variation of acetylene yield with added gas.

Figure 3.44



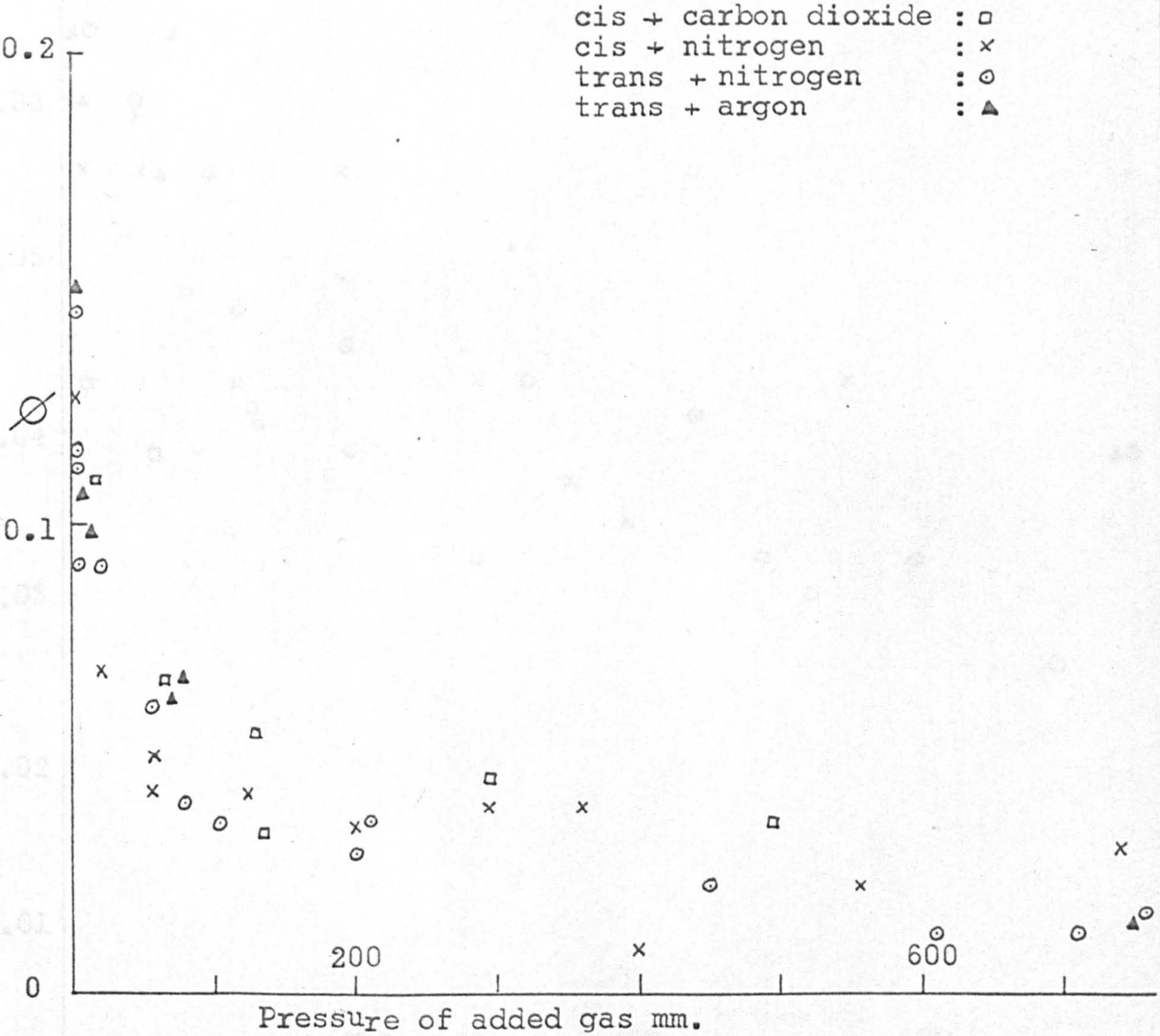
Variation of ethylene yield with added gas.

Figure 3.45



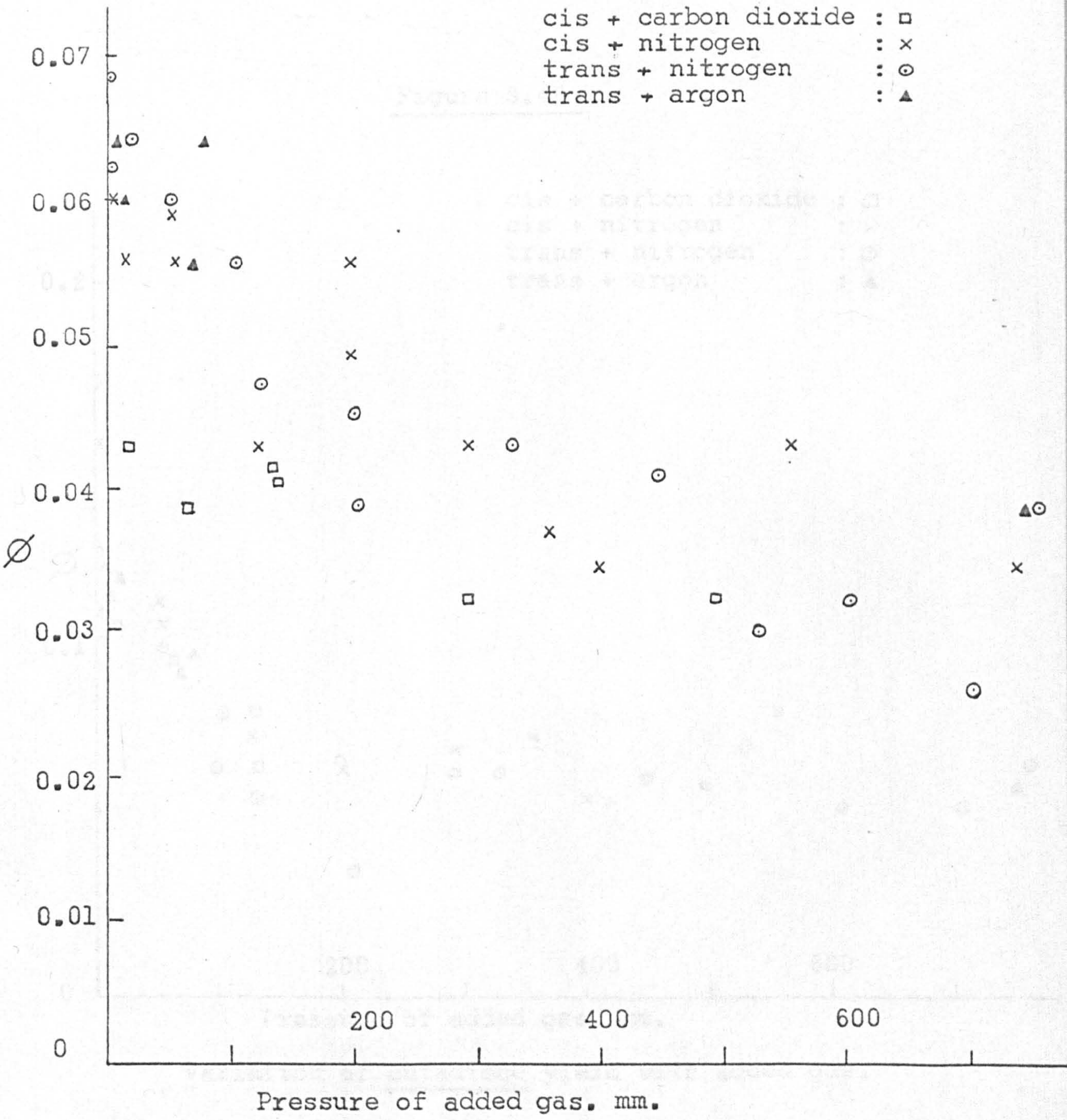
Variation of ethane yield with added gas.

Figure 3.46



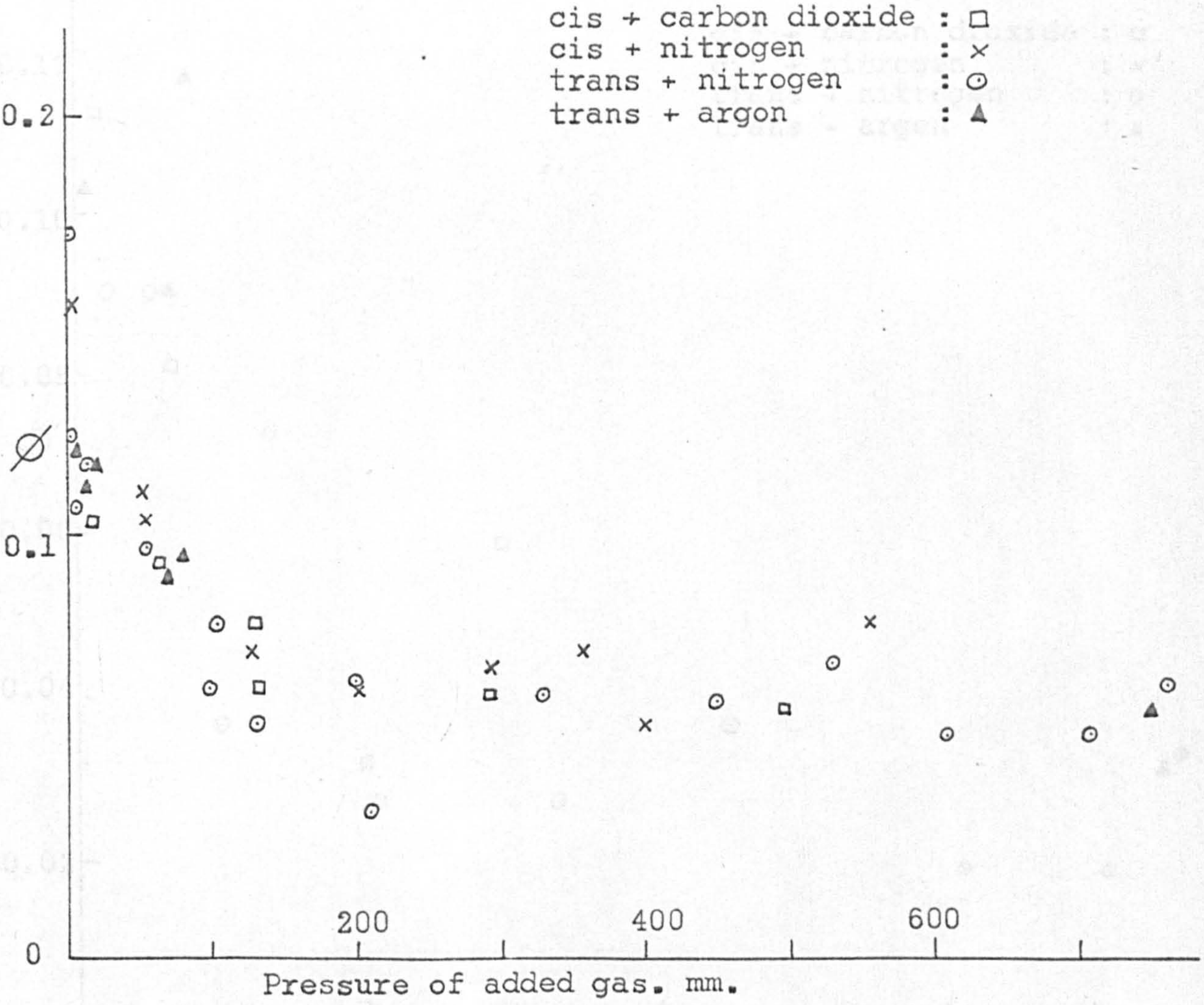
Variation of propylene yield with added gas.

Figure 3.47



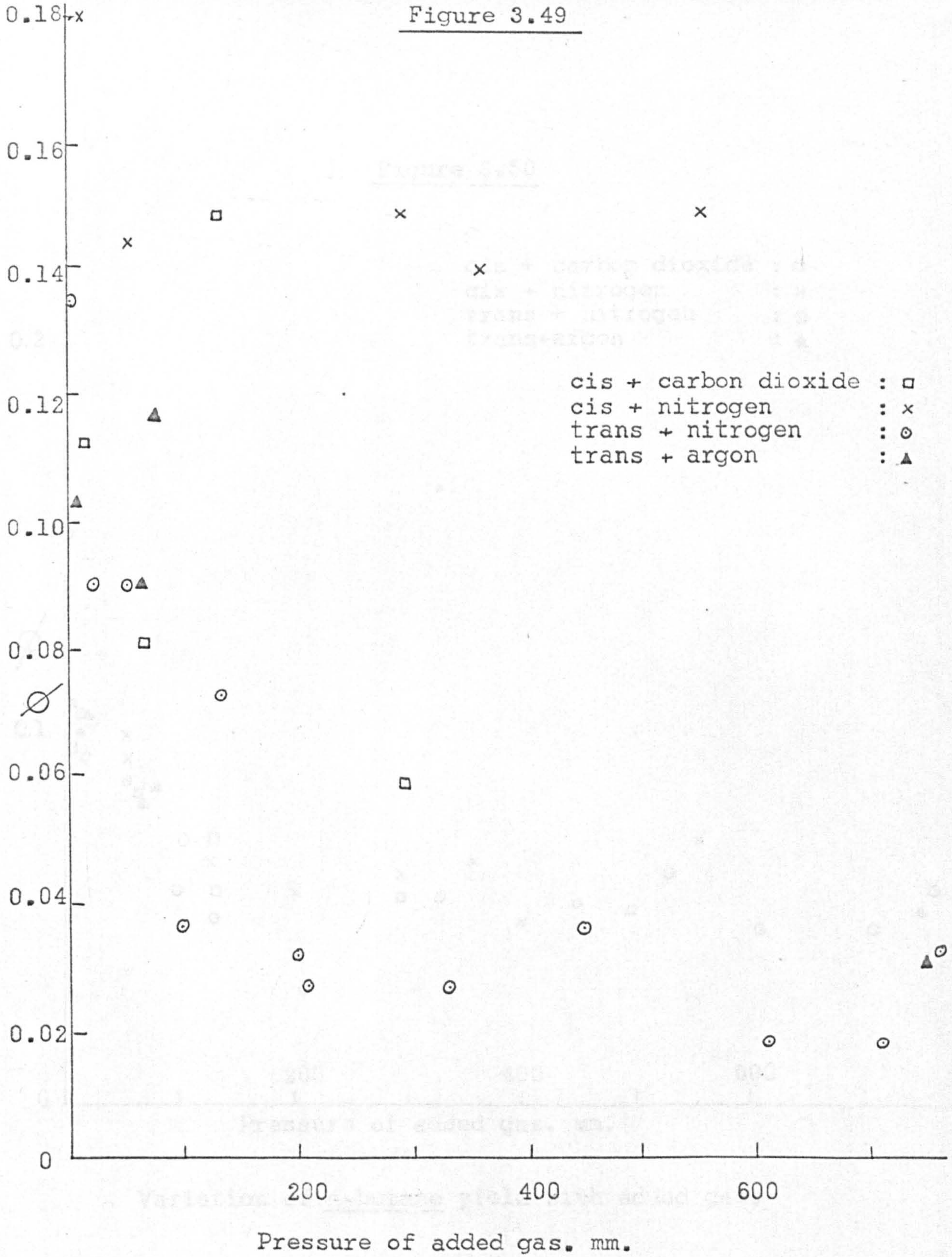
Variation of allene yield with added gas.

Figure 3.48



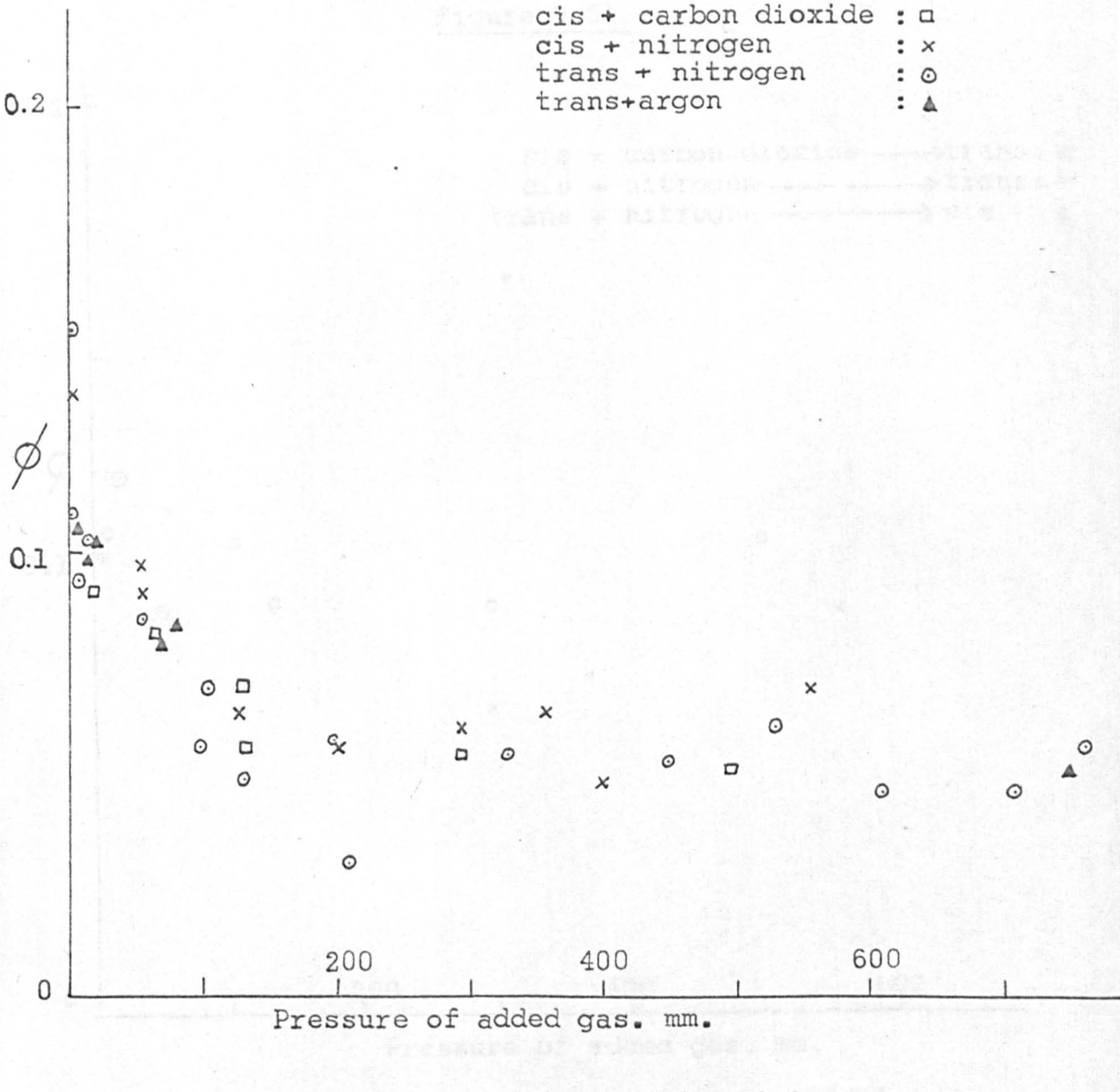
Variation of <u>butadiene</u> yield with added gas.

Figure 3.49



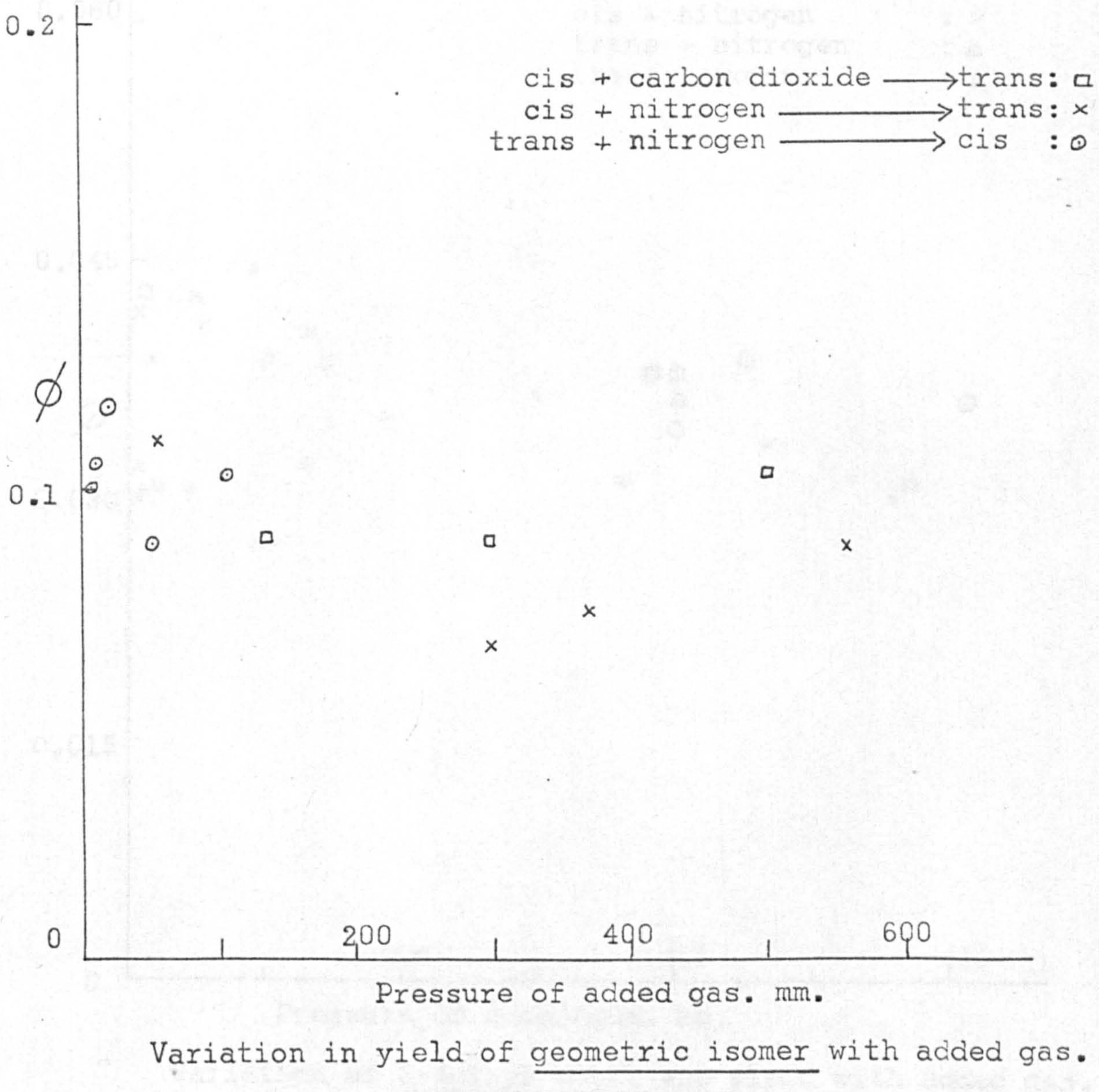
Variation of but-1-ene yield with added gas.

Figure 3.50



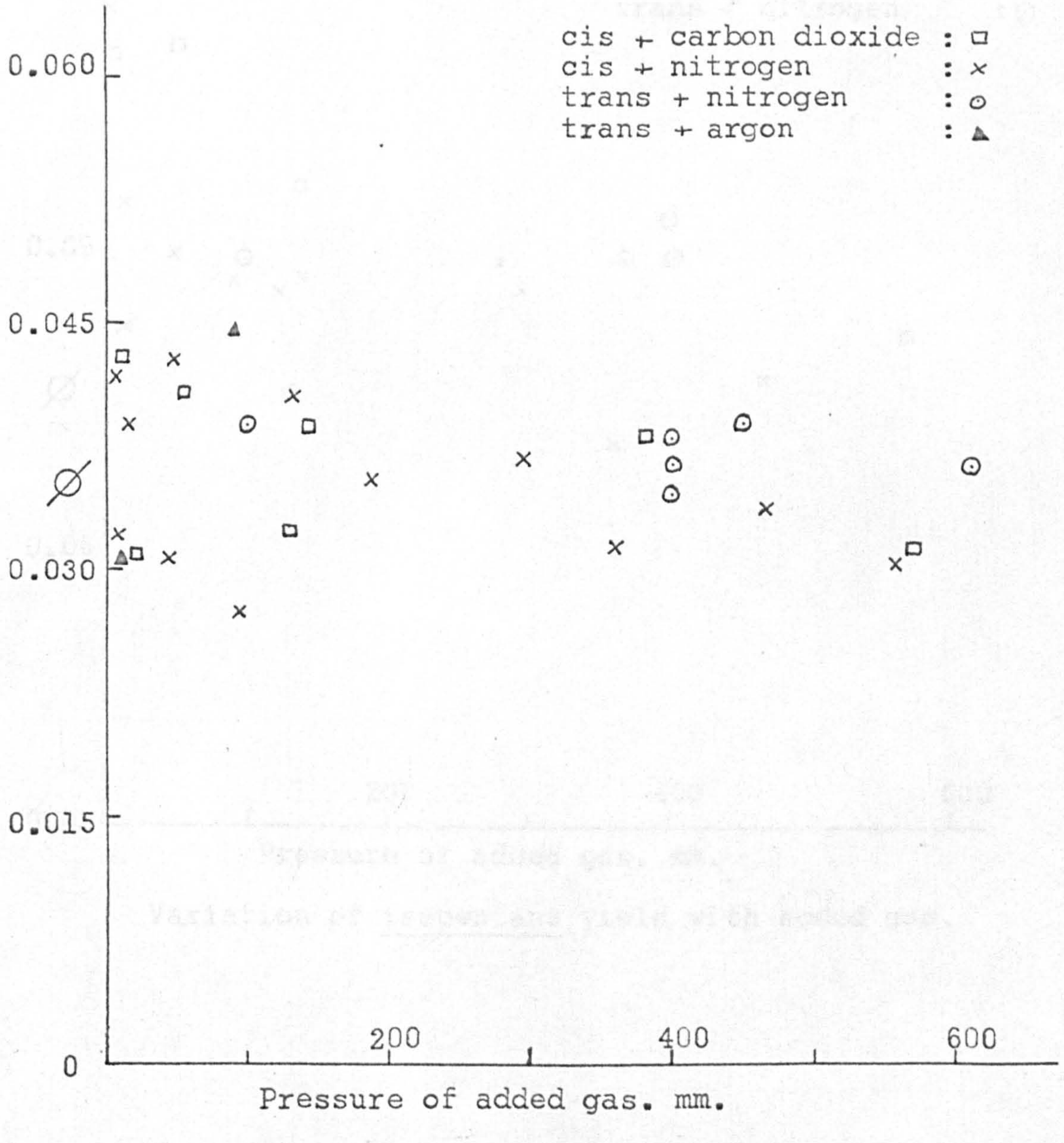
Variation of n-butane yield with added gas.

Figure 3.51



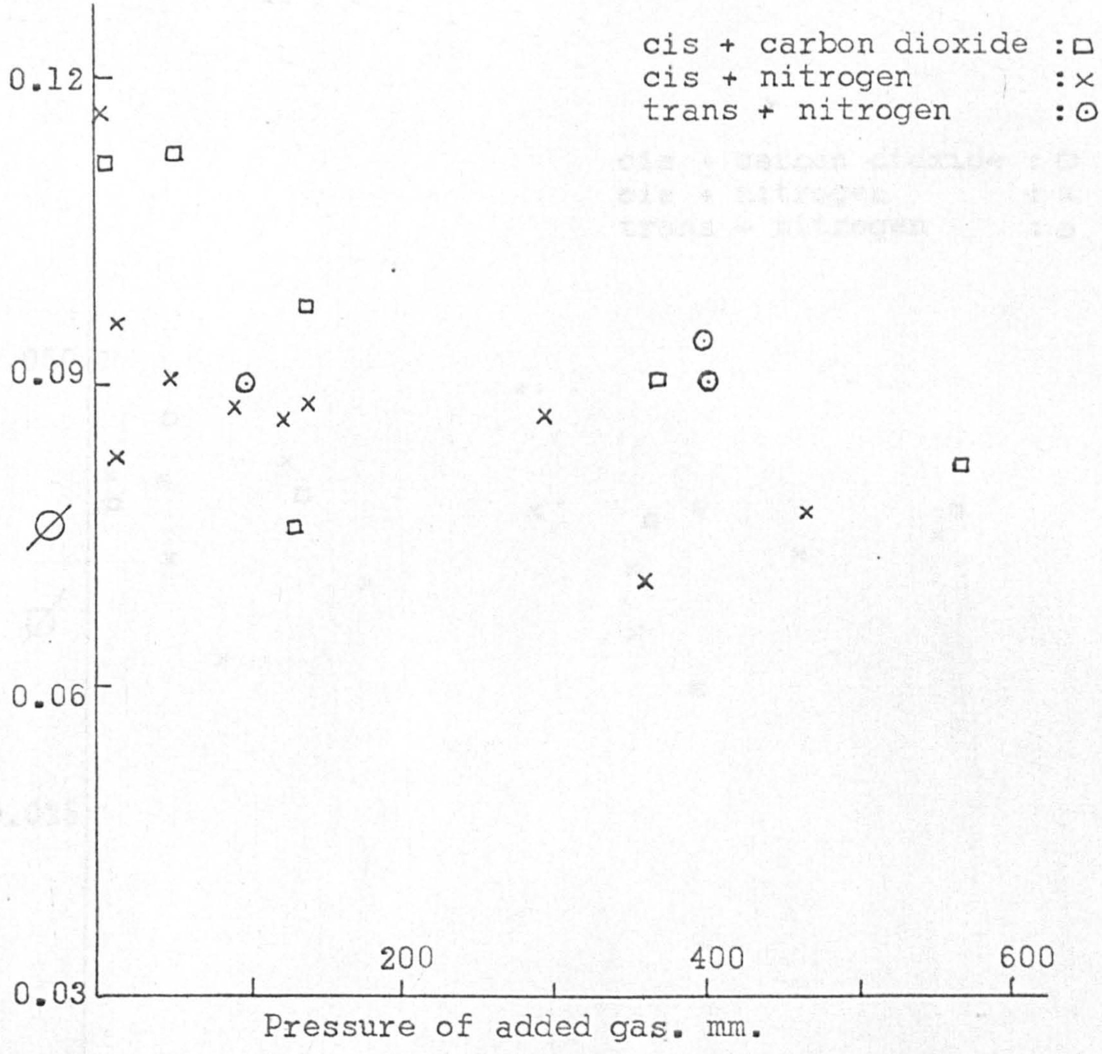
Variation in yield of geometric isomer with added gas.

Figure 3.52



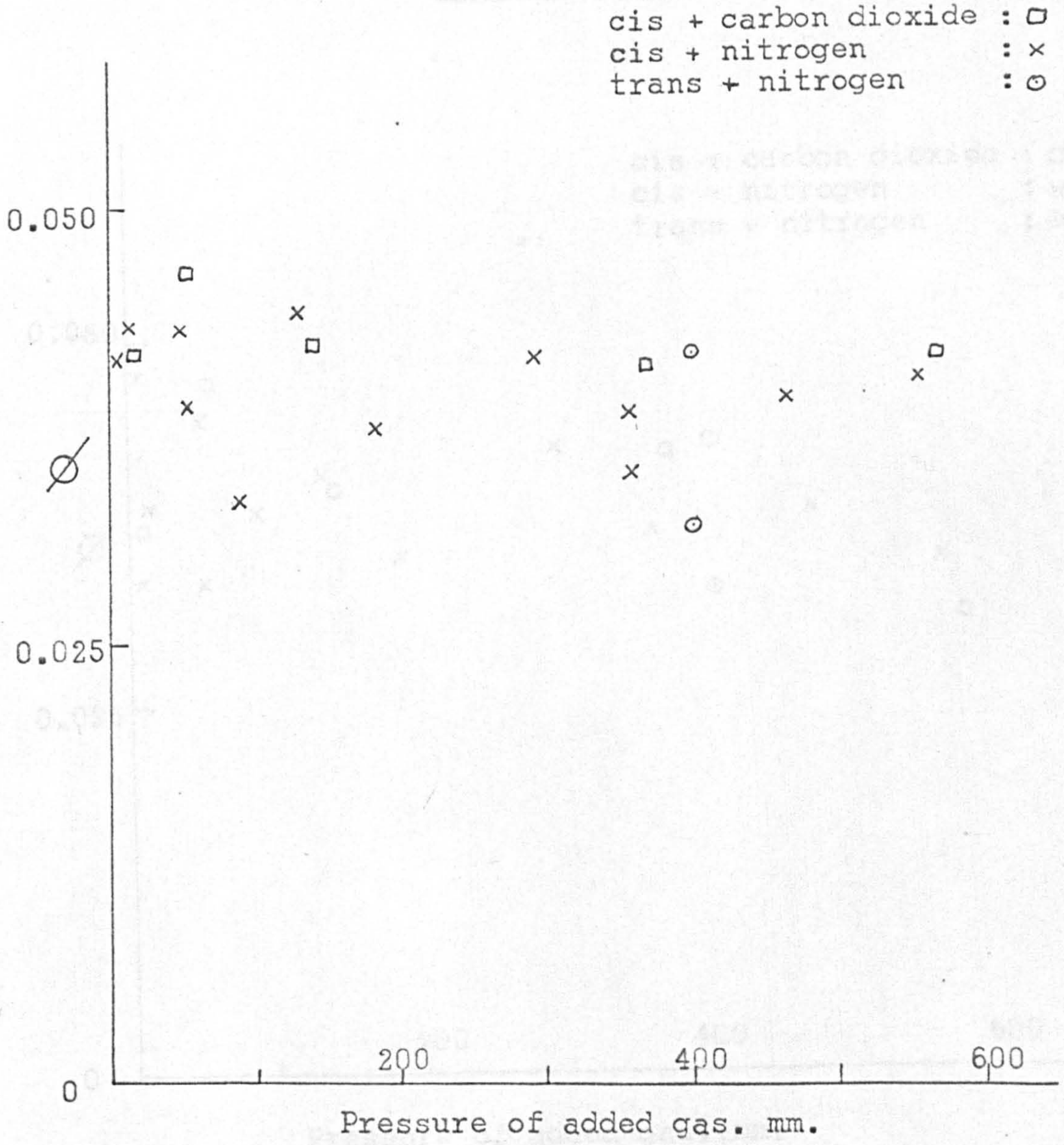
Variation of 3-methyl but-1-ene yield with added gas.

Figure 3.53



Variation of isopentane yield with added gas.

Figure 3.54



Variation of trans-pent-2-ene yield with added gas.

Figure 3.55

Variation of cis-pent-2-ene yield with added gas.

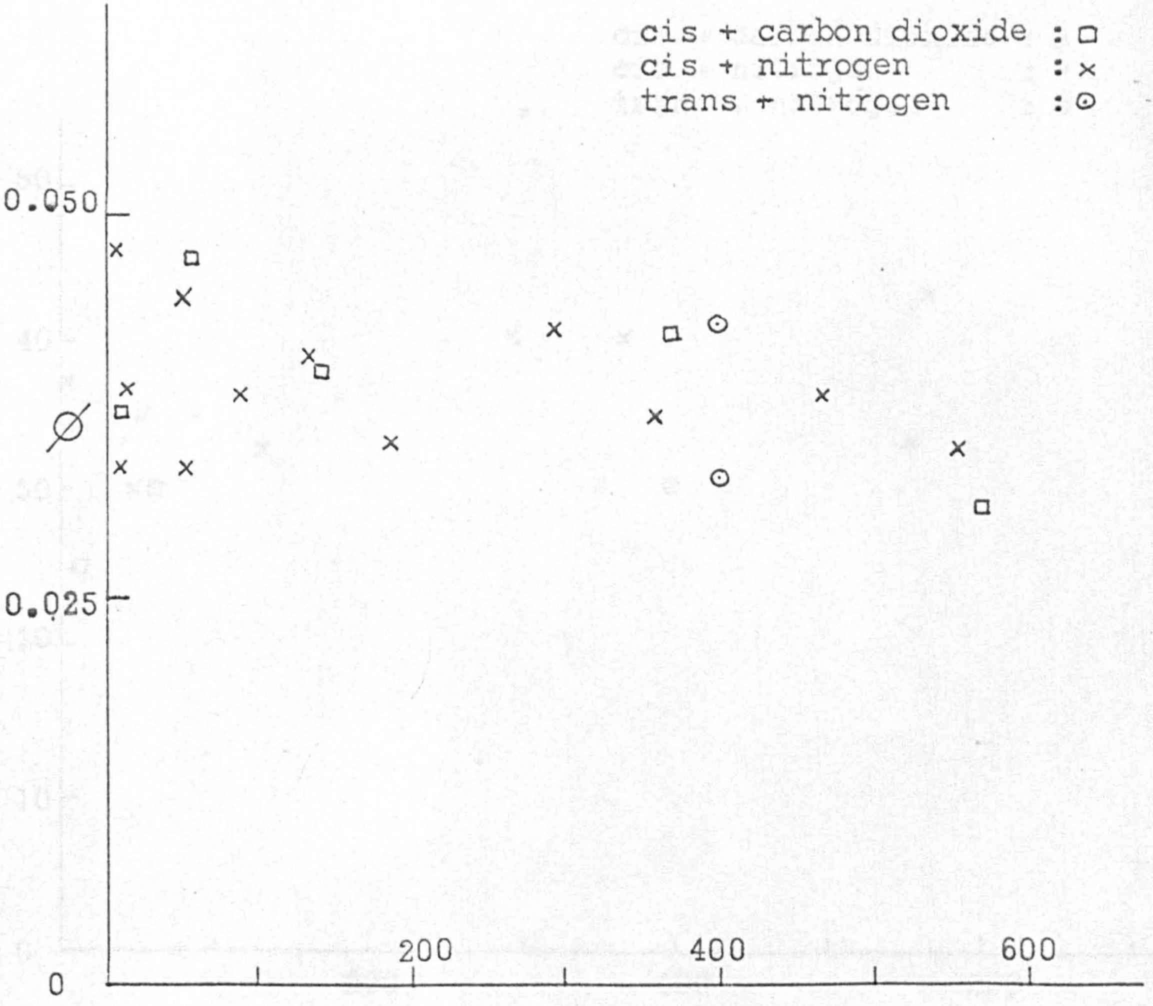


Figure 3.56

Variation with pressure of the peak area of the product with b.p. ~57°C

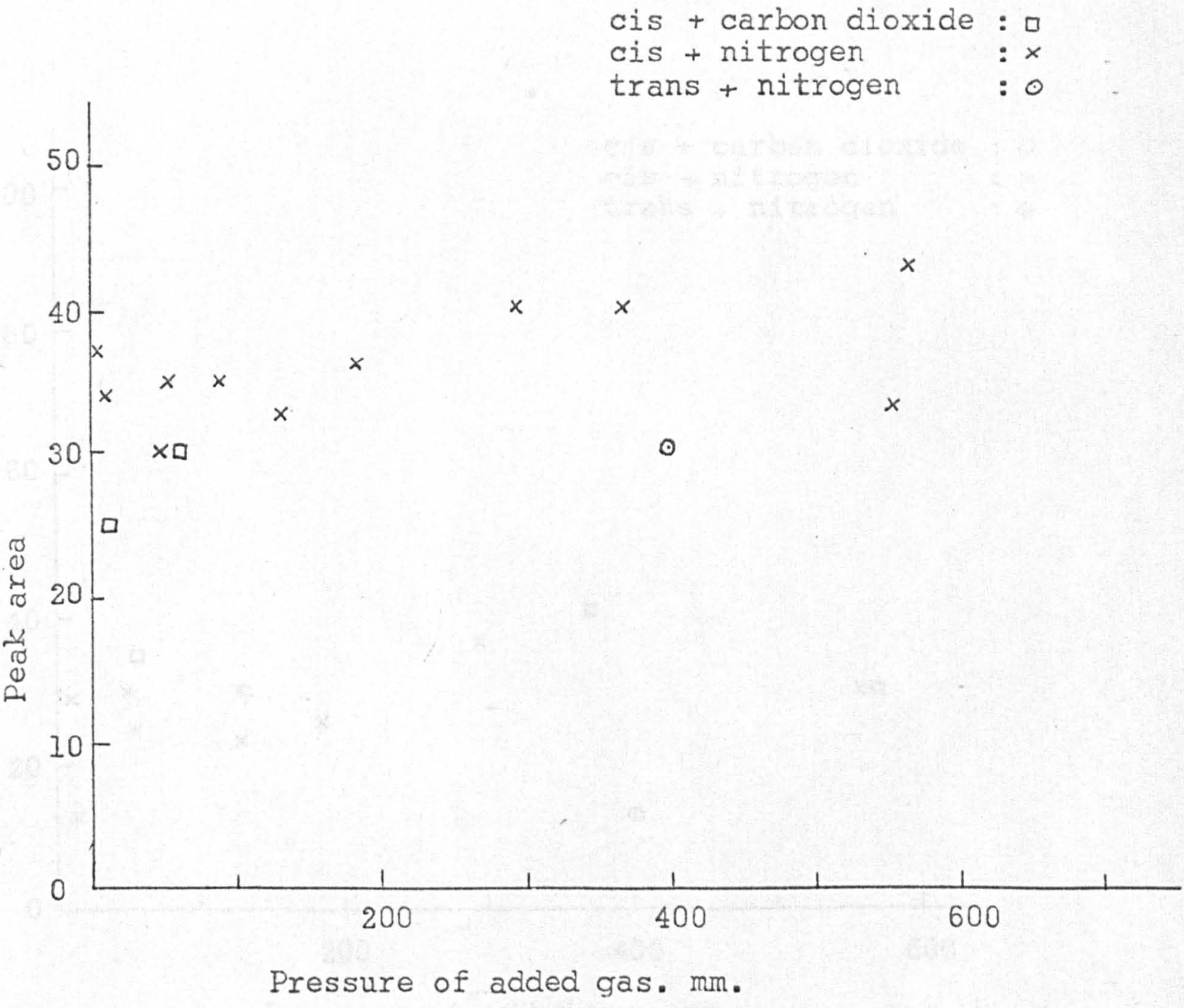
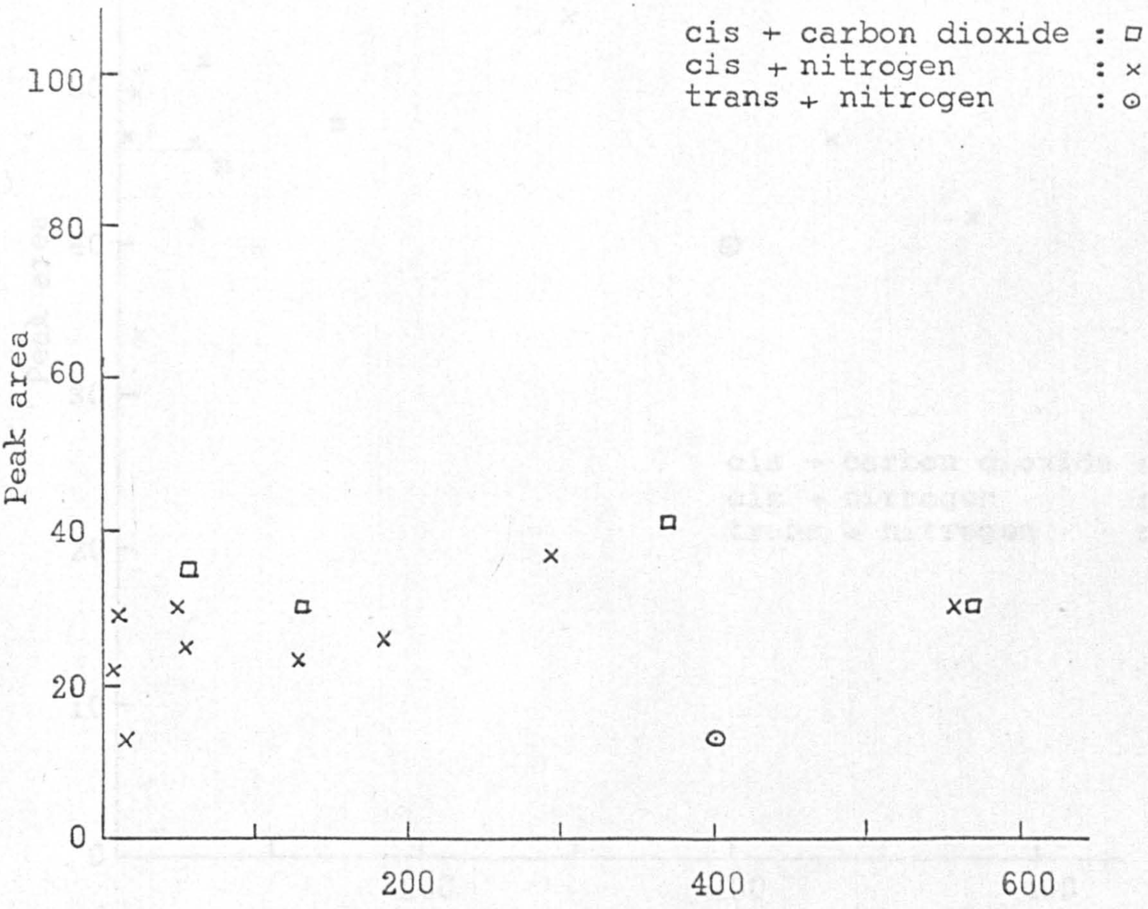


Figure 3.57

Variation with pressure of the peak area of the product with b.p. ~ 68°C



Pressure of added gas. mm.

Figure 3.58

Variation with pressure of the peak area of the product with b.p. ~ 81°C

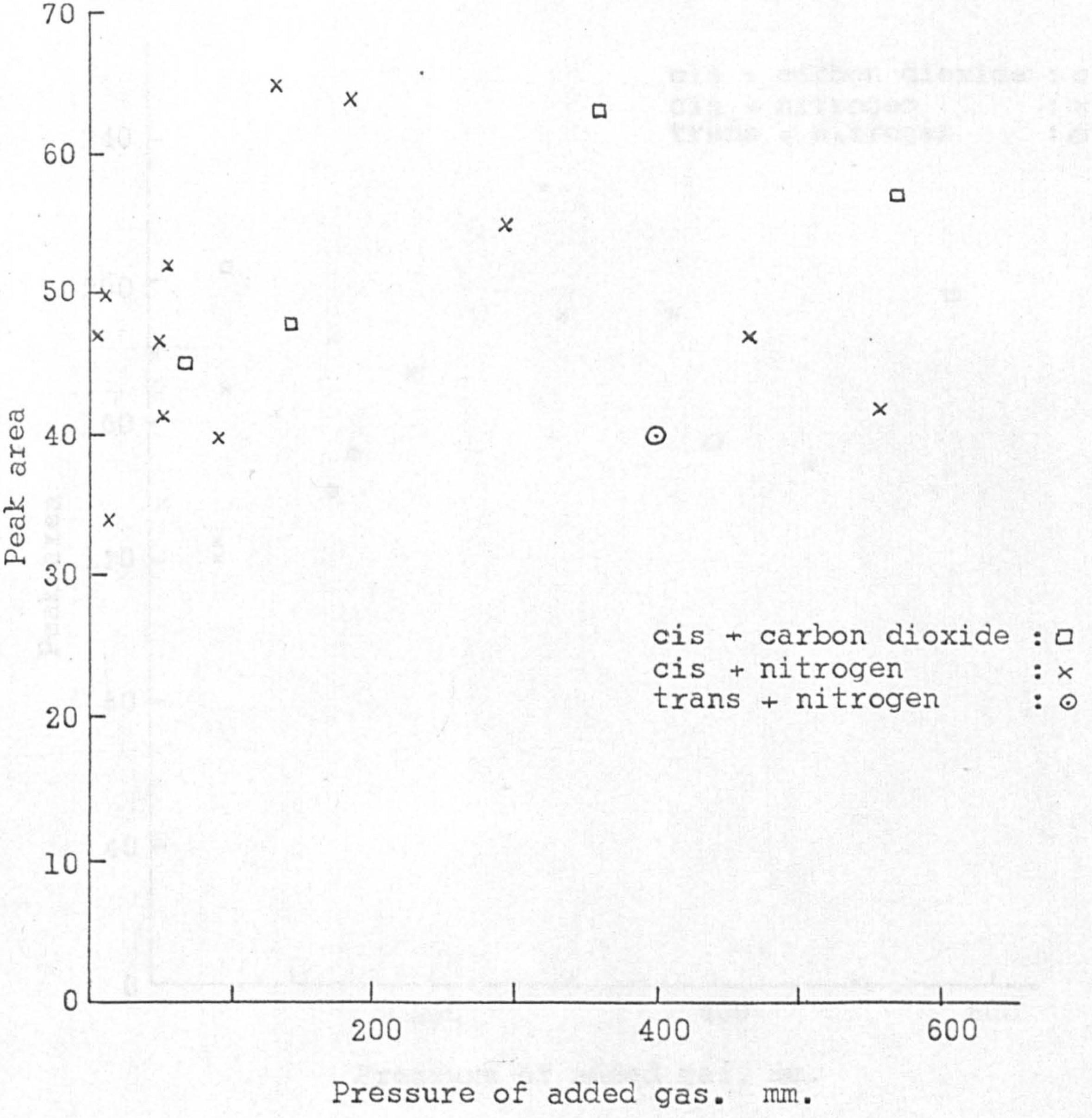


Figure 3.59

Variation with pressure of the peak area of the product with b.p. ~ 87°C

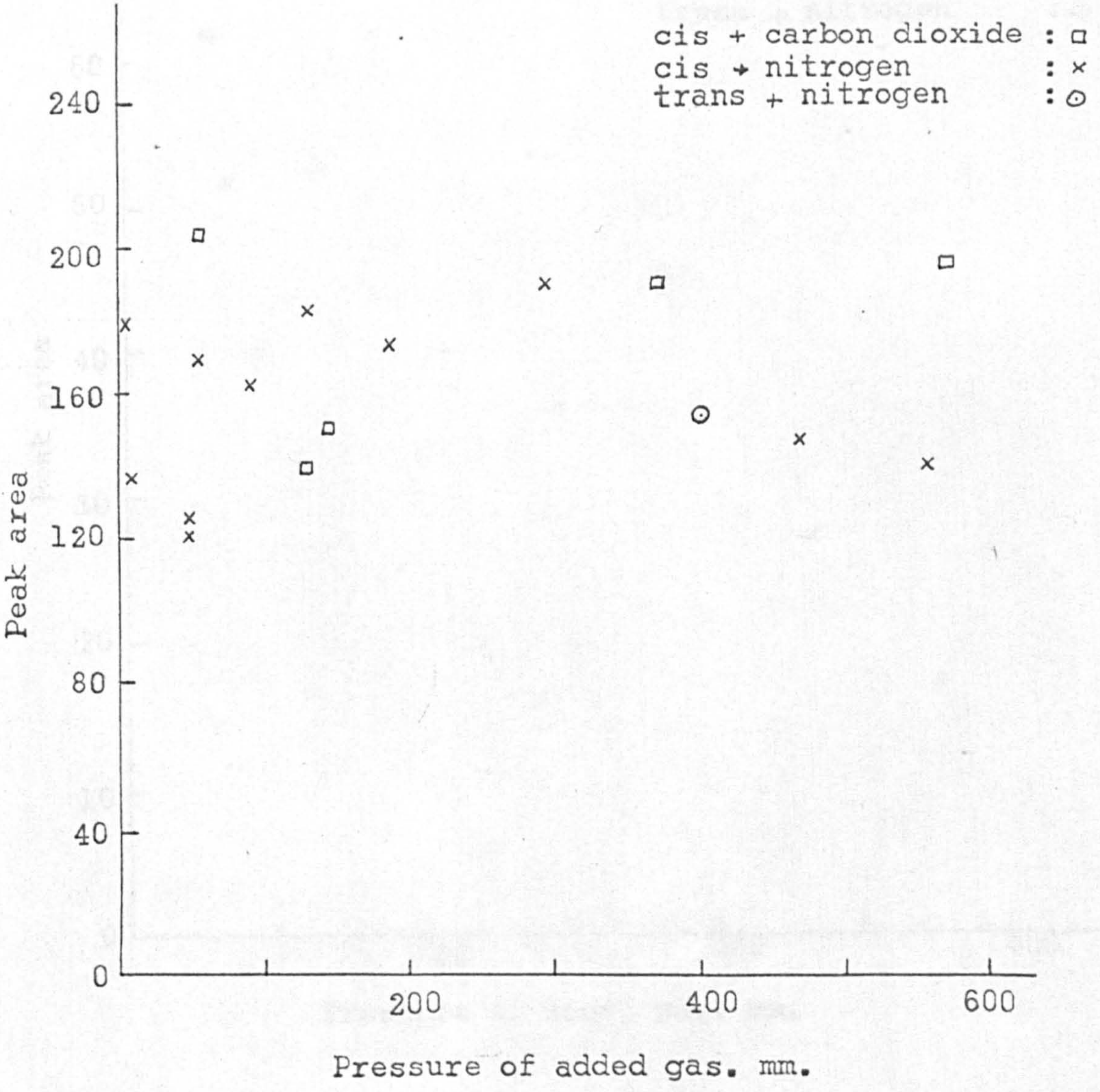


Figure 3.60

Variation with pressure of the peak area of the product with b.p. ~ 96°C

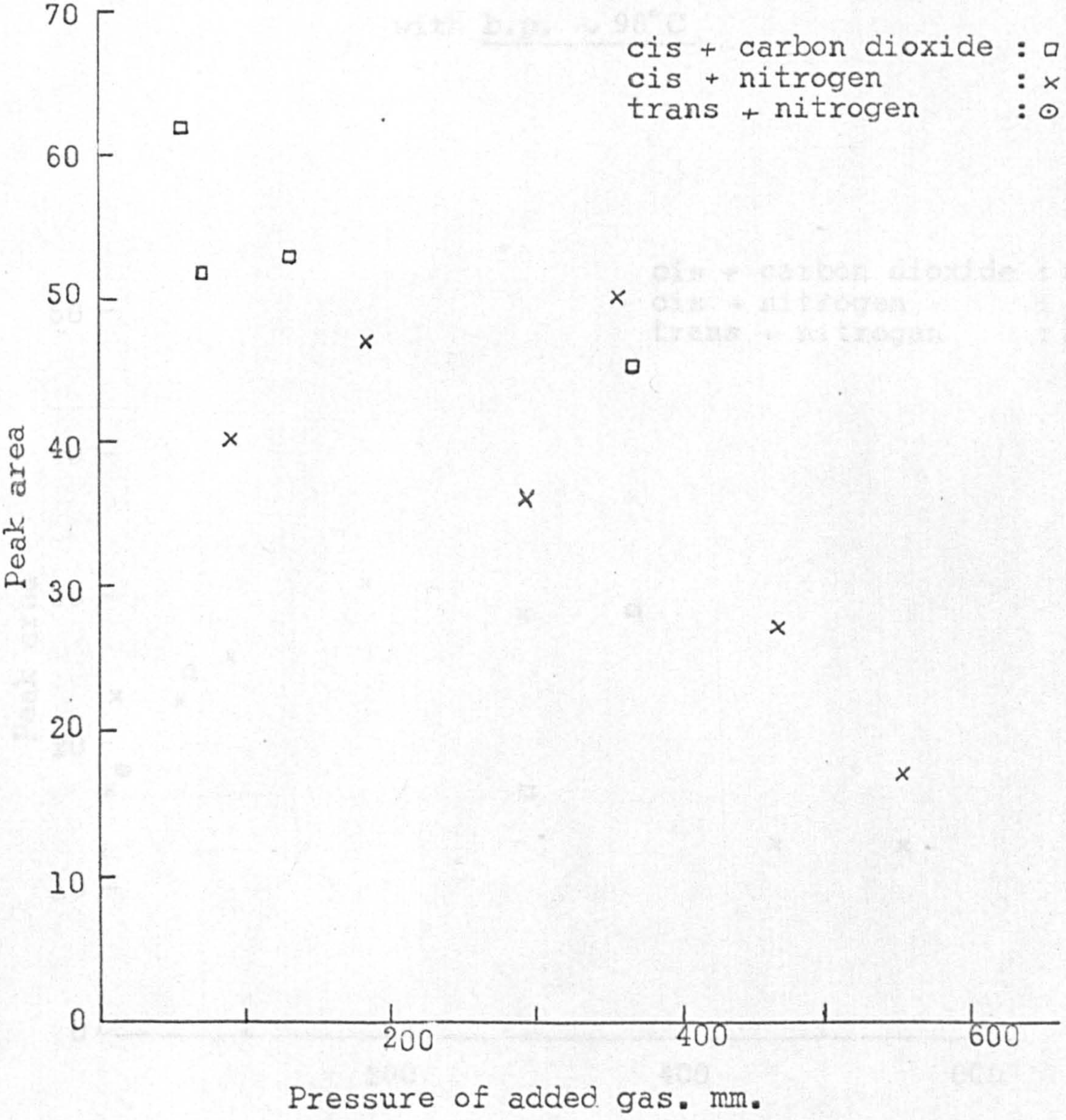


Figure 3.61

Variation with pressure of the peak area of the product with b.p. ~ 98° C

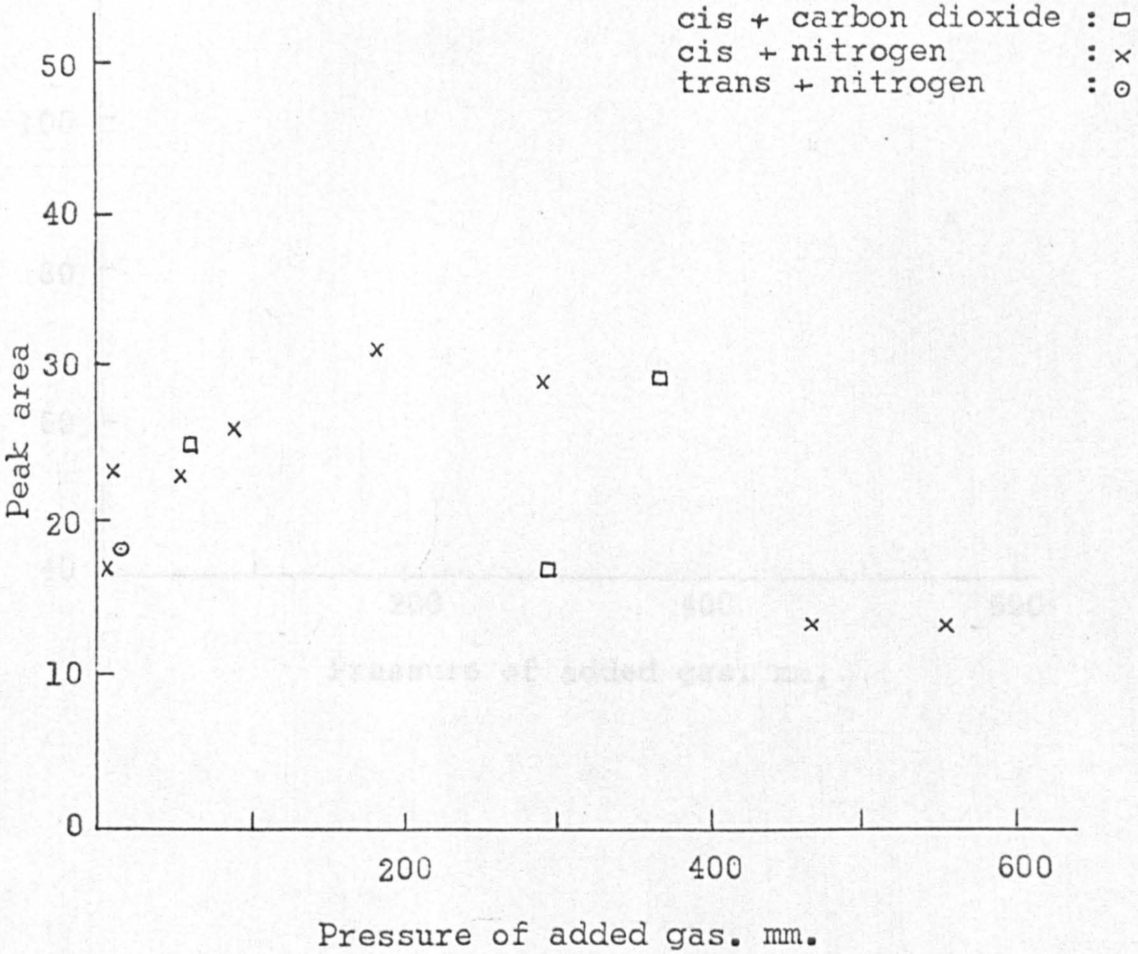


Figure 3.62

Variation with pressure of the peak area of the product with b.p. ~111°C

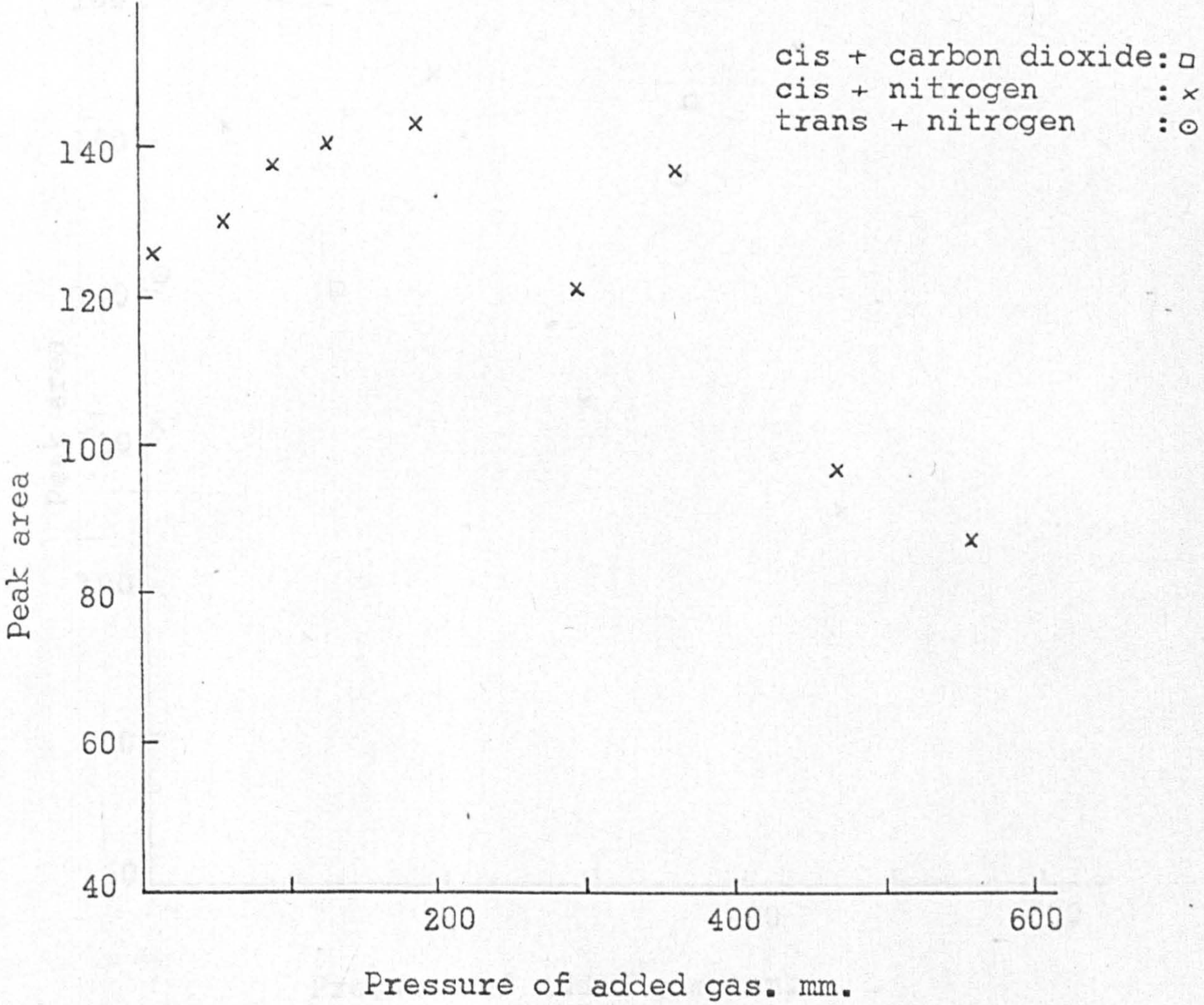
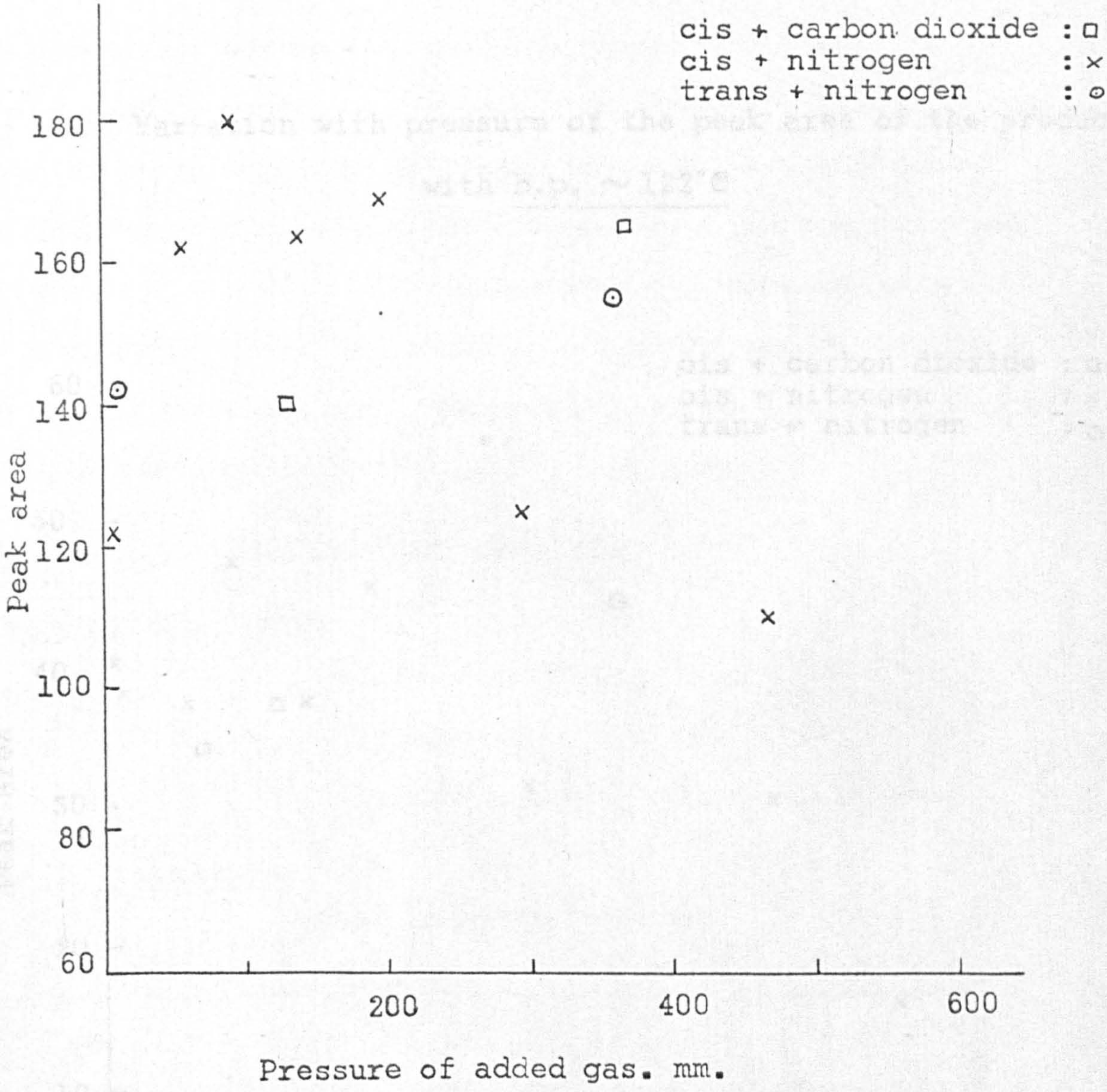


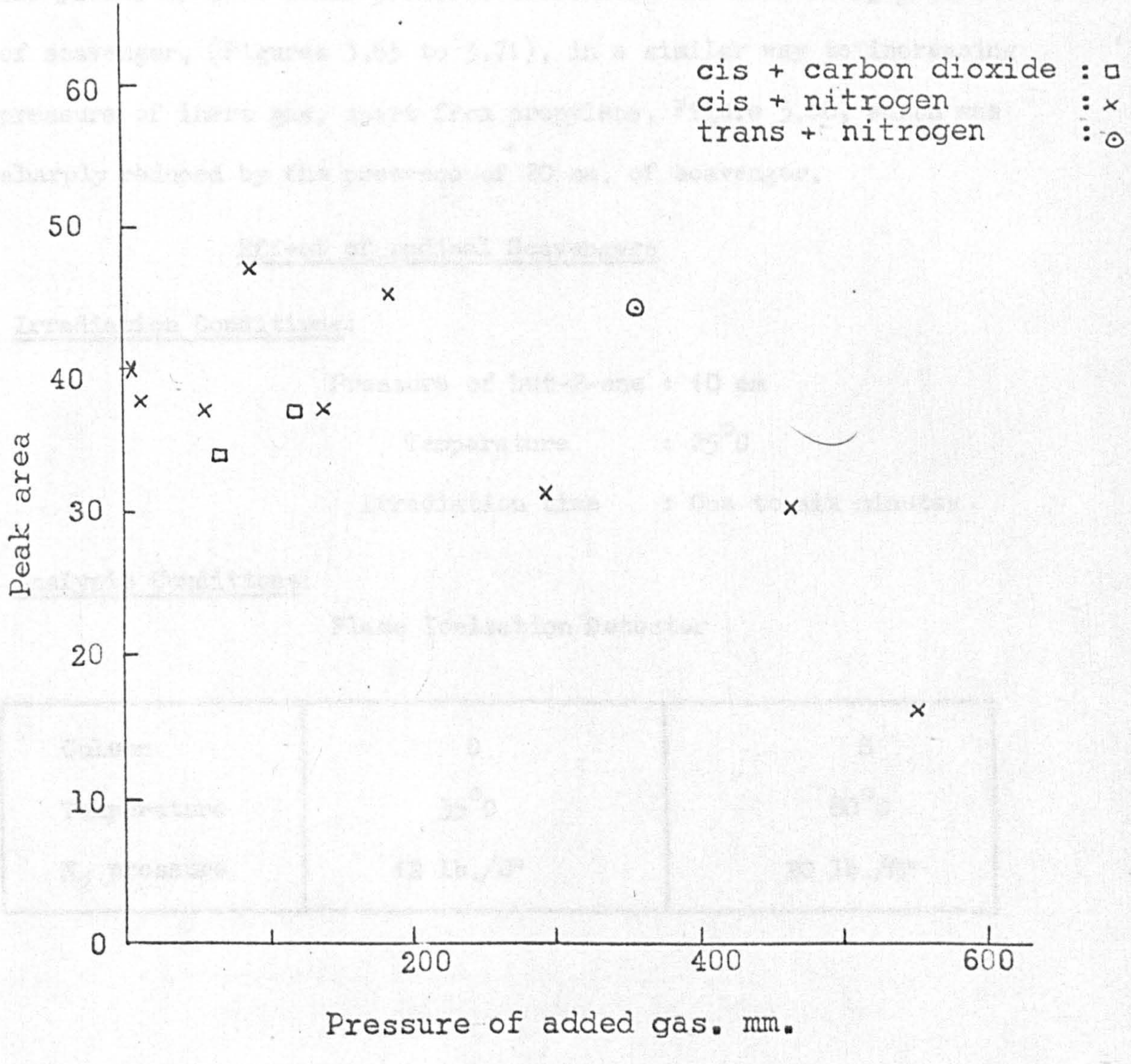
Figure 3.63



Variation with pressure of the peak area of the product with b.p. ~ 117°C

Figure 3.64

Variation with pressure of the peak area of the product with b.p. ~122°C



3.1.6 Effect of radical scavengers

The addition of nitric oxide or oxygen, gases which have been used as radical scavengers in similar systems,[117,35] resulted in the almost complete removal of ethane, n-butane, isobutane and all products with carbon number greater than four. But-1-ene was totally removed by the presence of 1% oxygen, while the geometric isomer was unaffected. The yields of most other products decreased with increasing pressure of scavenger, (Figures 3.65 to 3.71), in a similar way to increasing pressure of inert gas, apart from propylene, Figure 3.68, which was sharply reduced by the presence of 20 mm. of scavenger.

Effect of radical Scavengers

Irradiation Conditions:

Pressure of but-2-ene : 10 mm
Temperature : 25°C
Irradiation time : One to six minutes

Analysis Conditions:

Flame Ionization Detector

Column	0	S
Temperature	35°C	80°C
N_2 pressure	12 lb./□"	20 lb./□"

Figure 3.65

Variation in methane yield with pressure of added radical scavenger

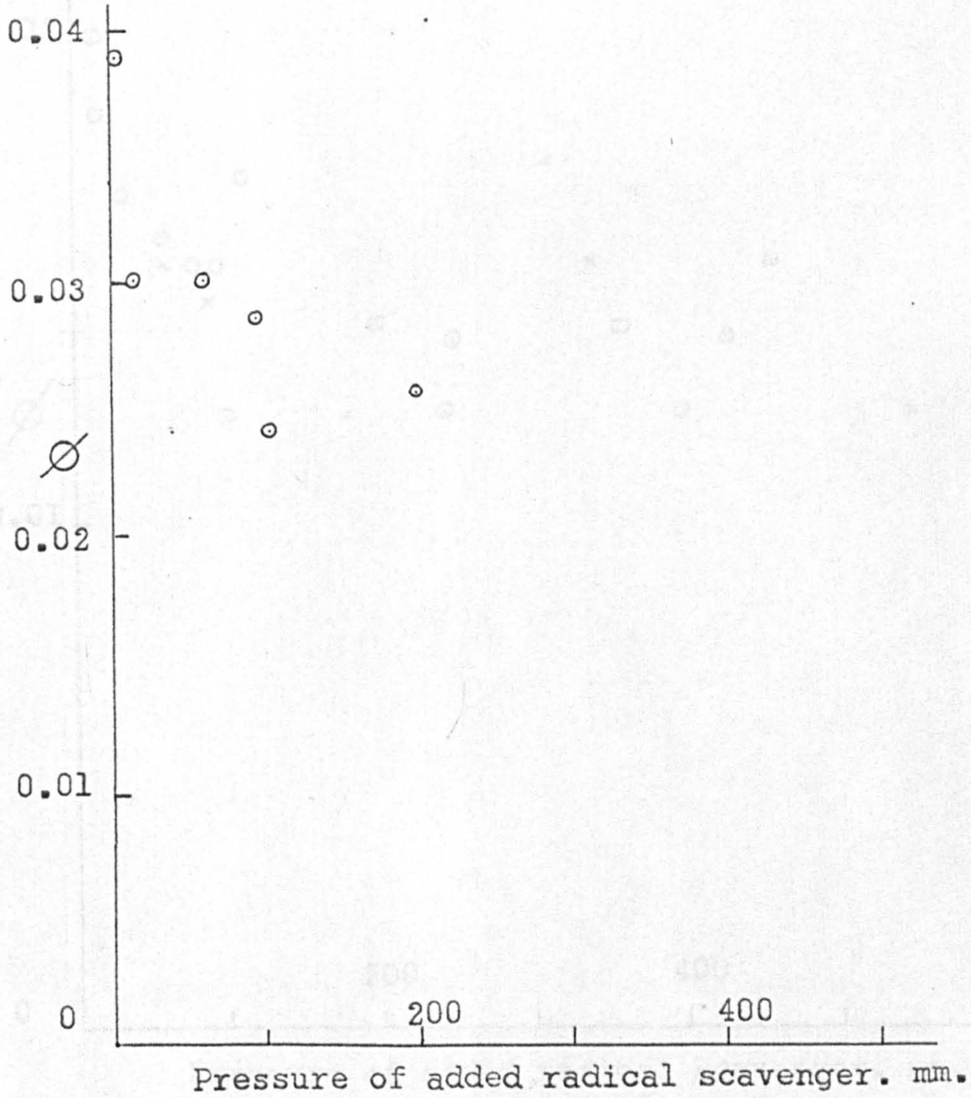


Figure 3.66

Variation of ethylene yield with pressure of added radical scavenger

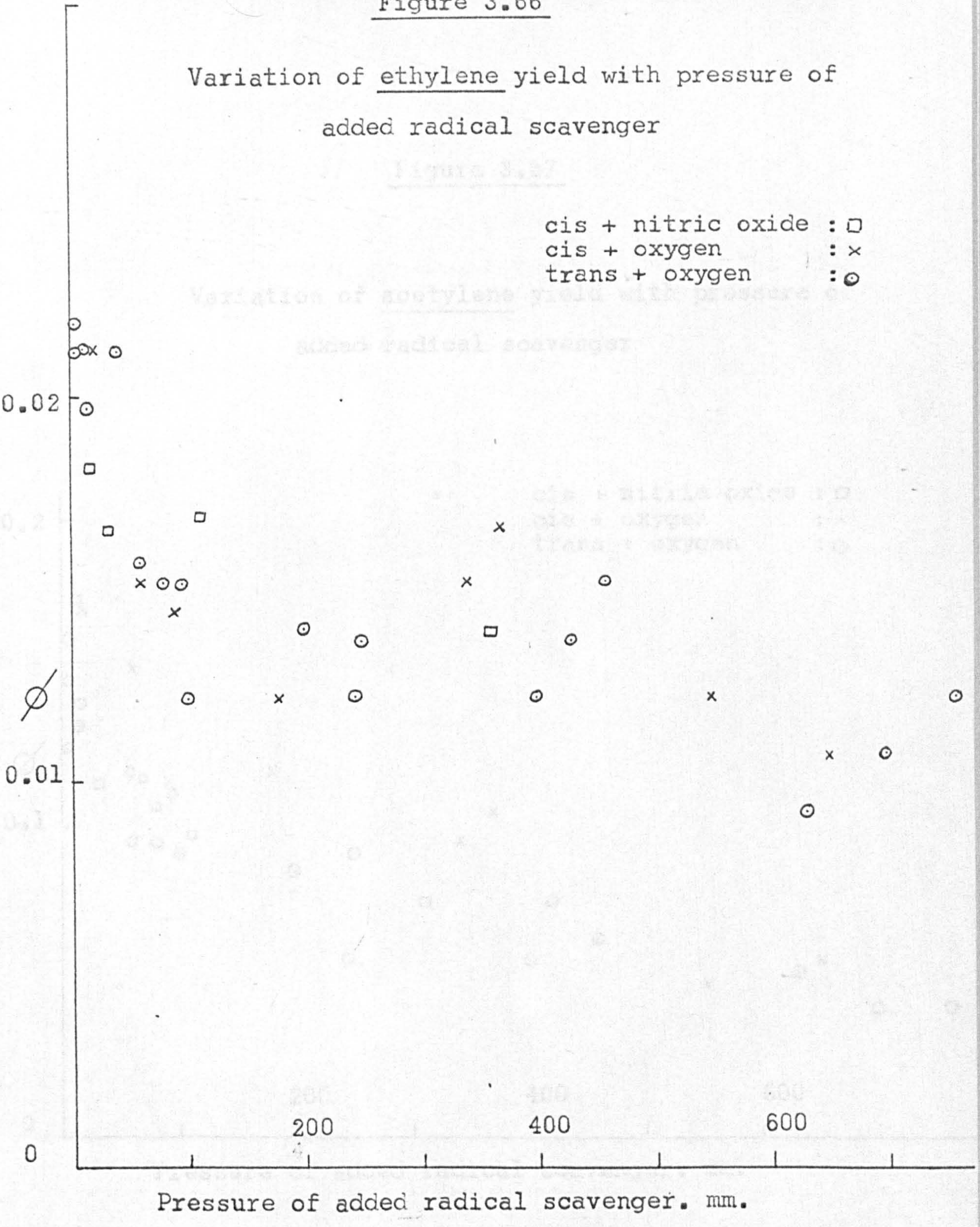


Figure 3.67

Variation of acetylene yield with pressure of added radical scavenger

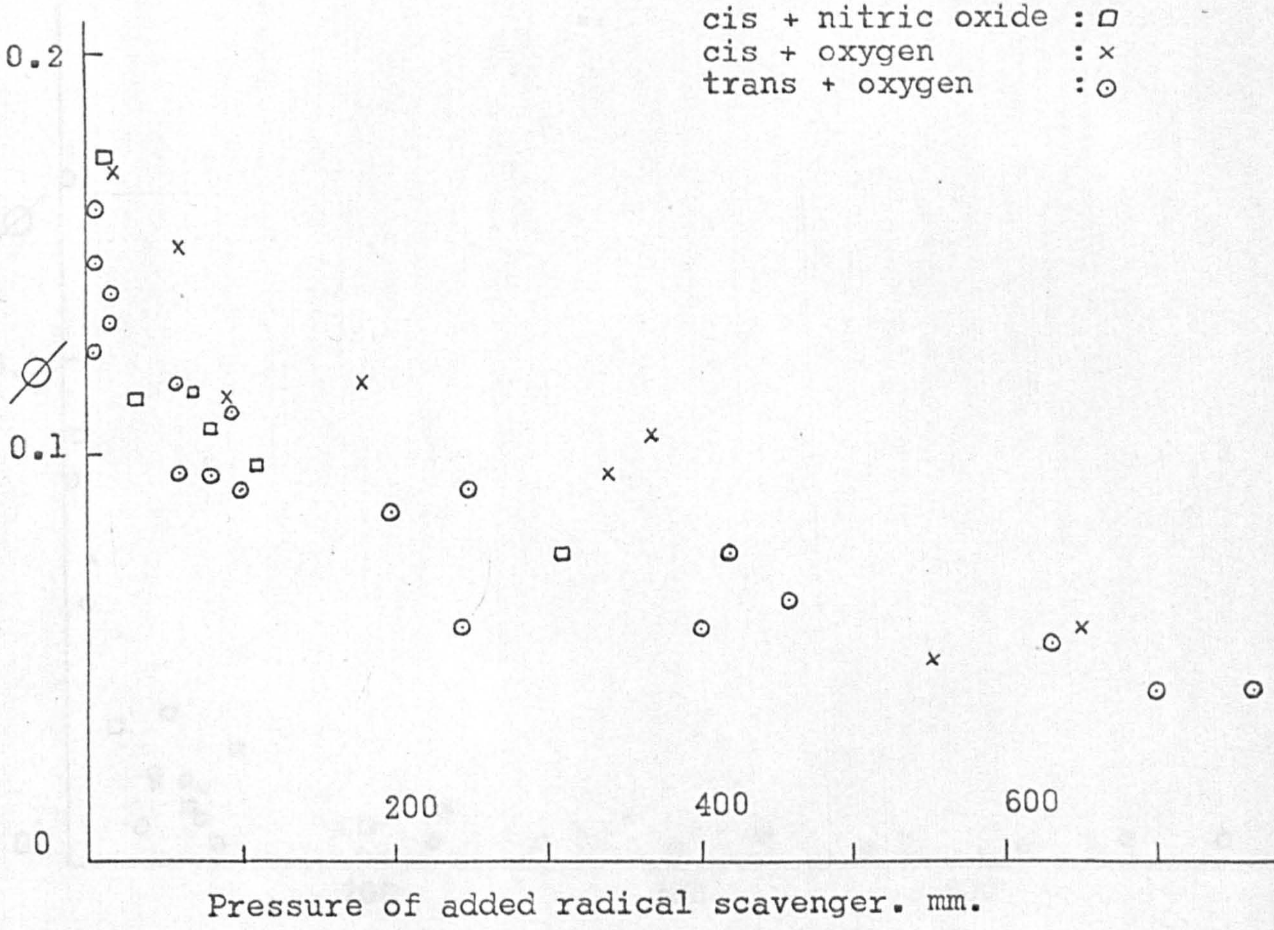


Figure 3.68

Variation of propylene yield with pressure of added radical scavenger.

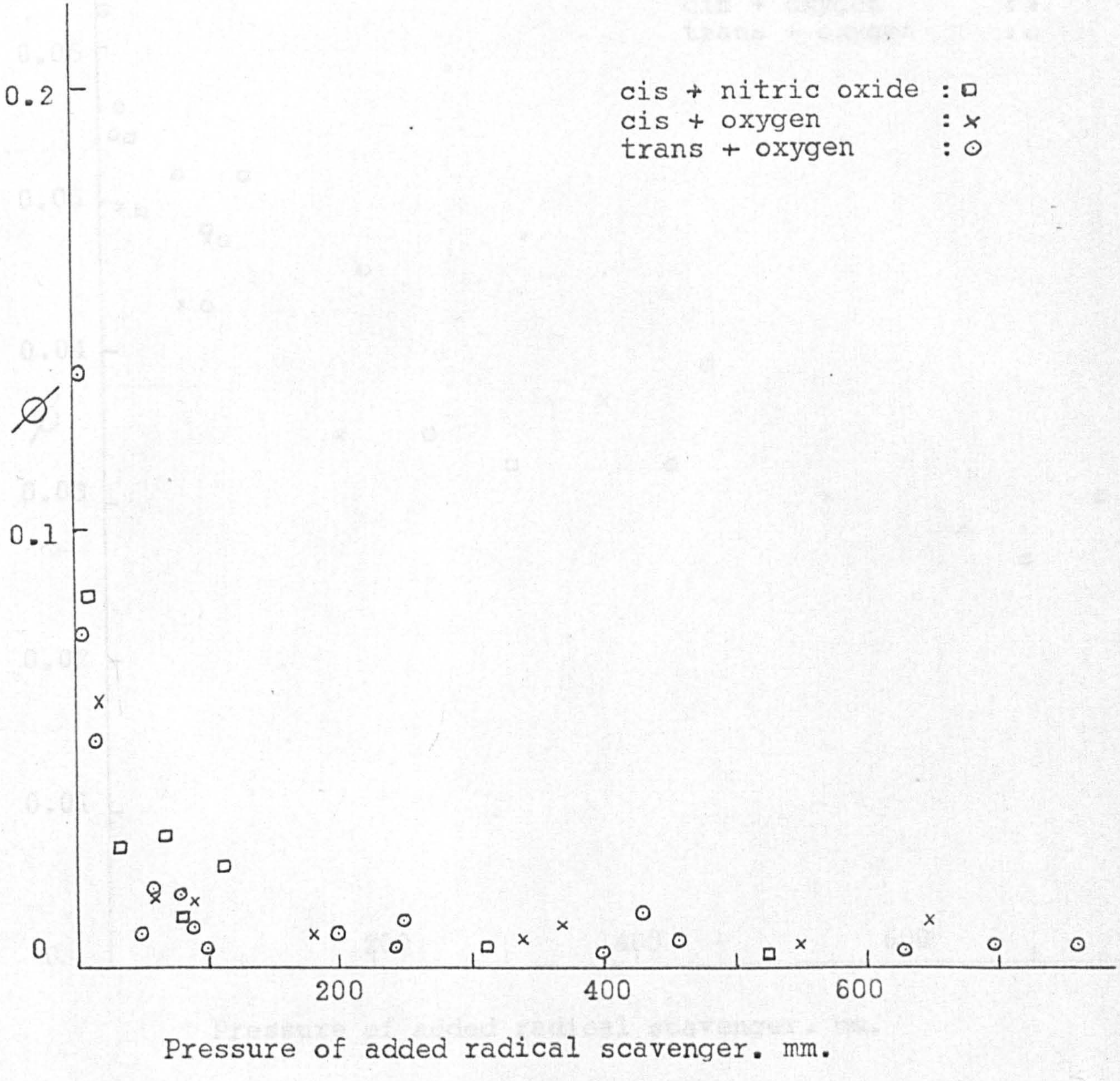
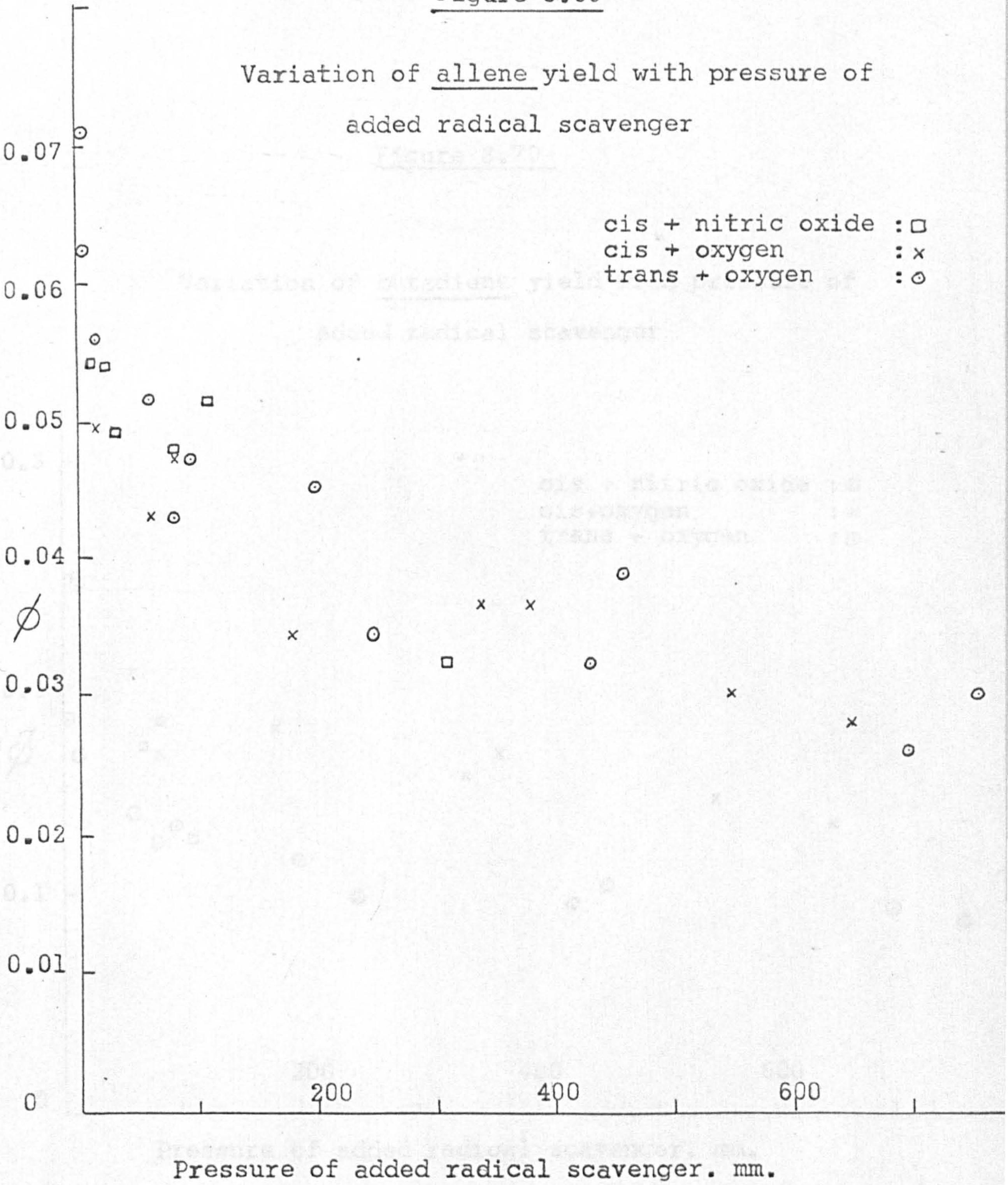


Figure 3.69



Variation of allene yield with pressure of added radical scavenger

Figure 3.70

Variation of butadiene yield with pressure of added radical scavenger

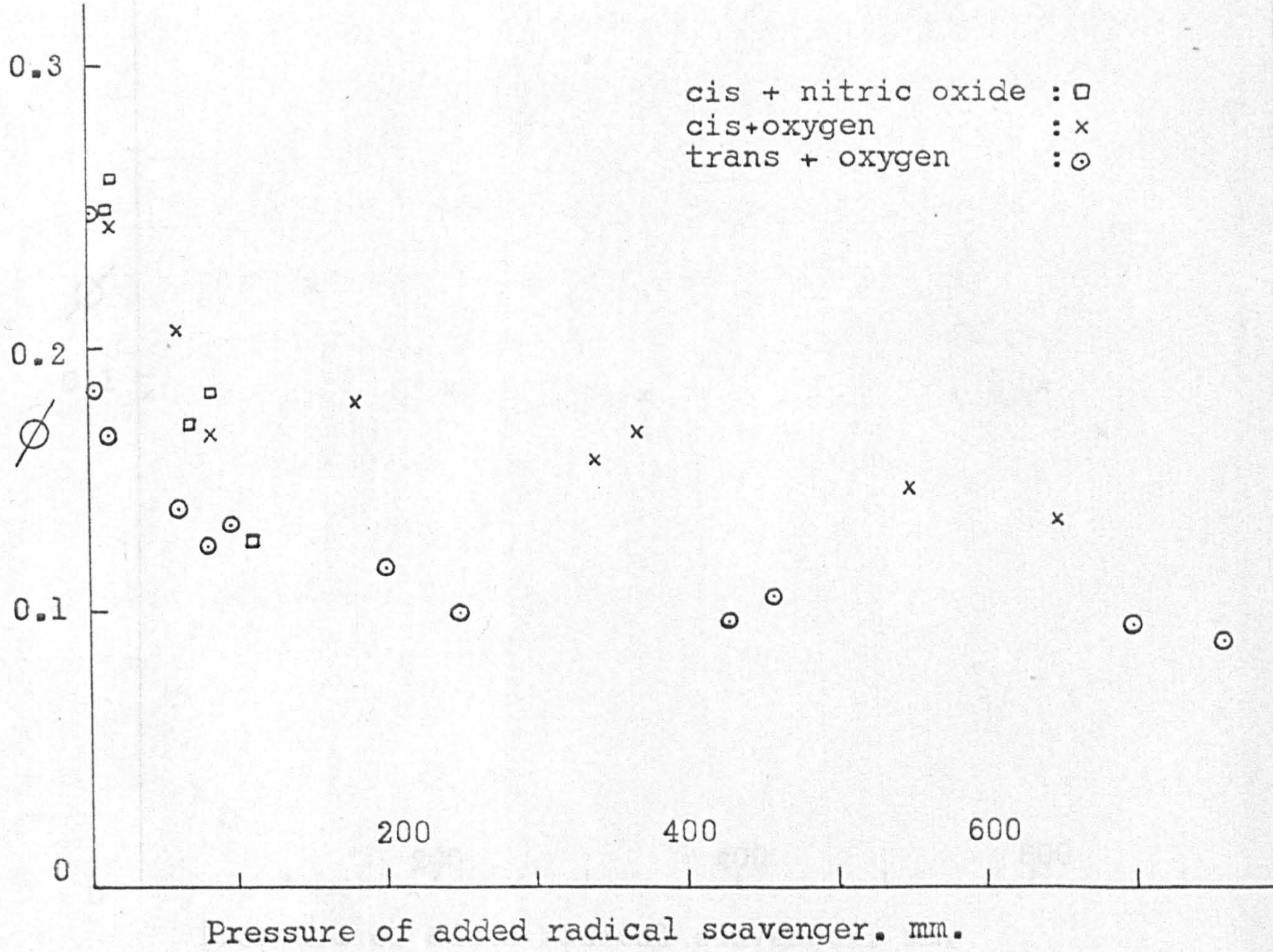
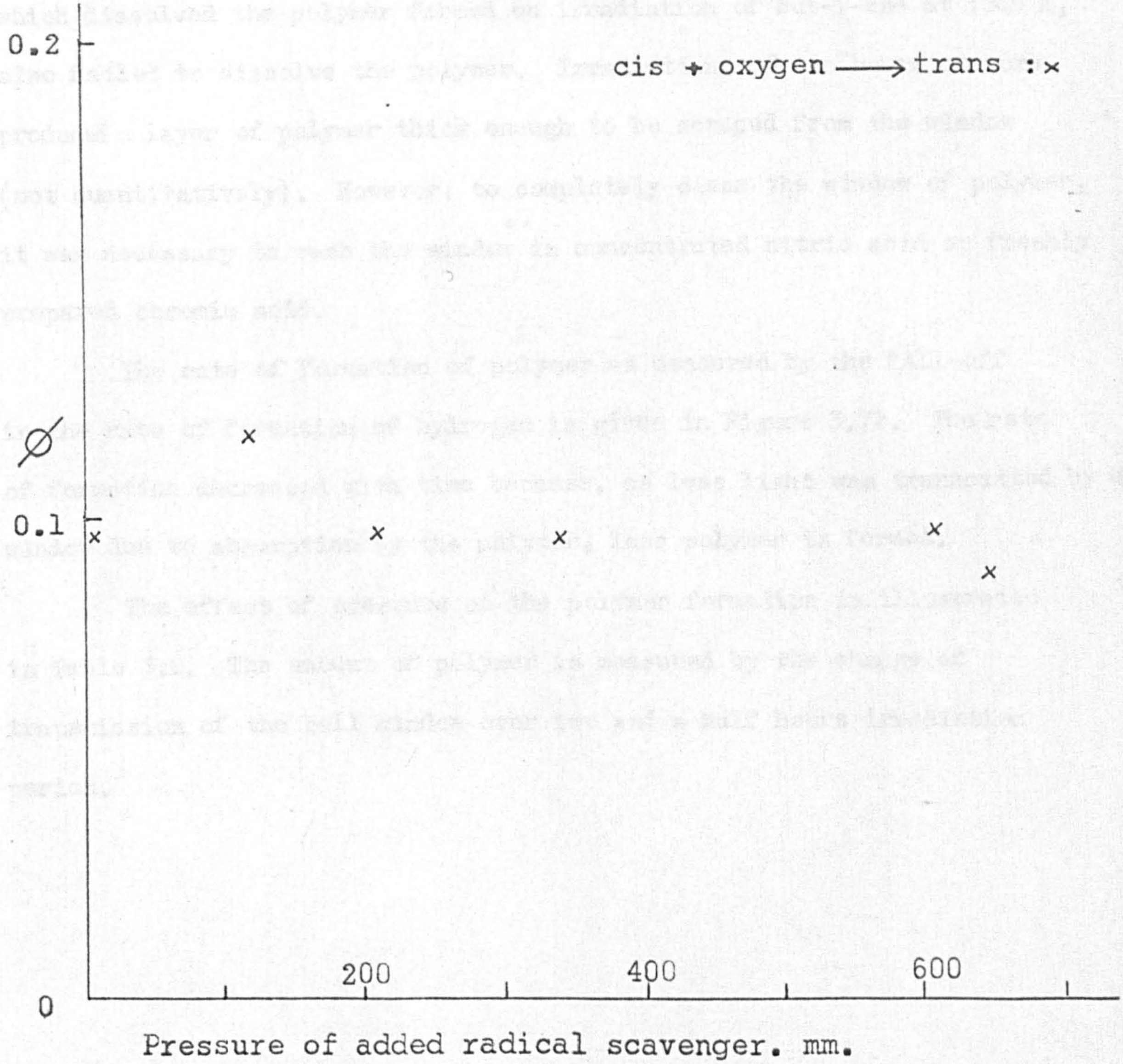


Figure 3.71

Variation of yield of geometric isomer with added radical scavenger



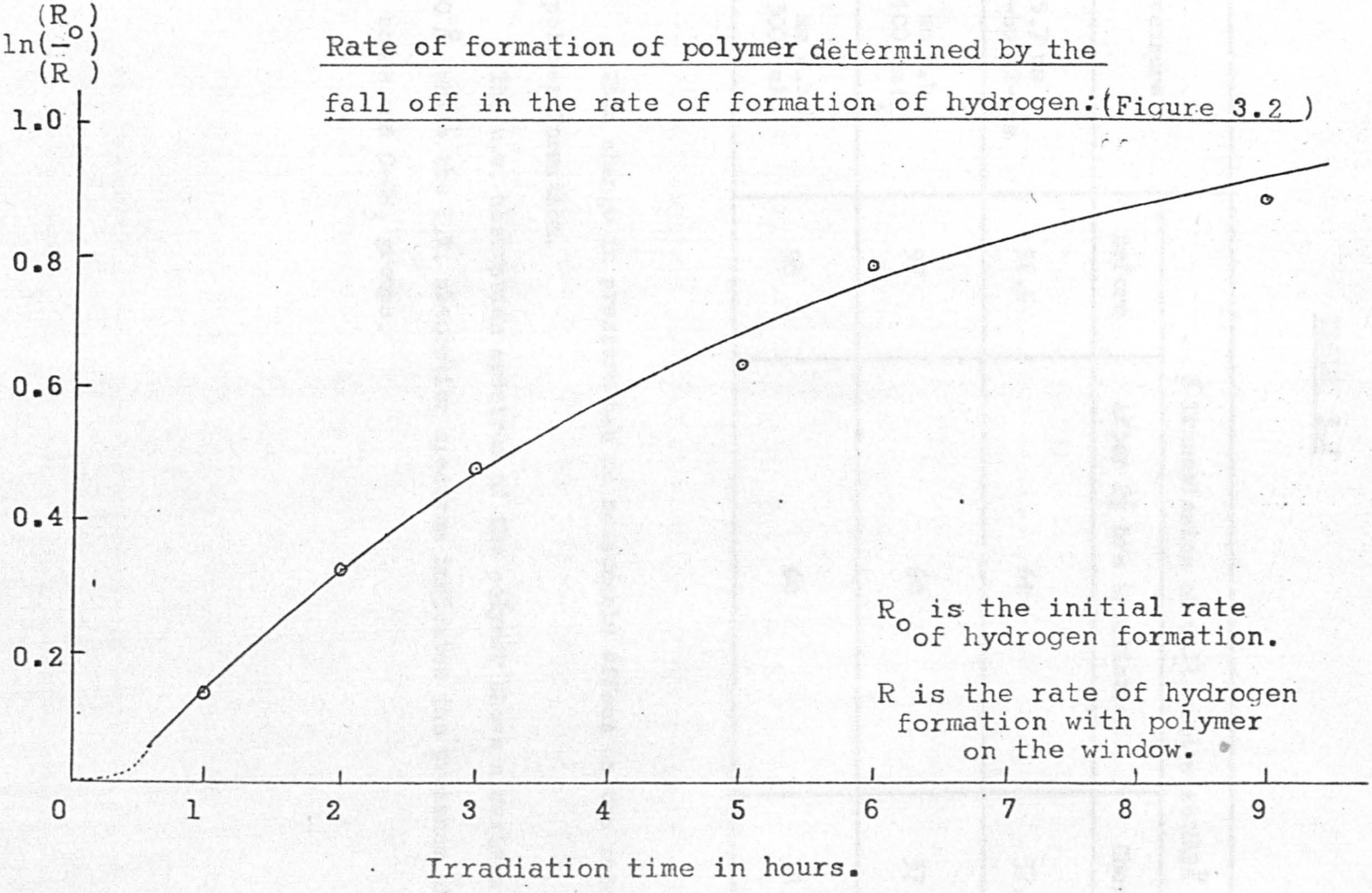
3.1.7 Polymer Formation

Irradiations of longer than 20 minutes resulted in the formation of a solid polymer of but-2-ene that coated the cell window and absorbed the 1849 Å radiation. The polymer proved insoluble in all available hydrocarbon solvents, including benzene, toluene, xylene, hexane and heptane. Acetone, which dissolved the polymer formed on irradiation of but-1-ene at 1849 Å,[117] also failed to dissolve the polymer. Irradiations of ten hours or more produced a layer of polymer thick enough to be scraped from the window (not quantitatively). However, to completely clear the window of polymer, it was necessary to wash the window in concentrated nitric acid or freshly prepared chromic acid.

The rate of formation of polymer as measured by the fall-off in the rate of formation of hydrogen is given in Figure 3.72. The rate of formation decreased with time because, as less light was transmitted by the window due to absorption by the polymer, less polymer is formed.

The effect of pressure on the polymer formation is illustrated in Table 3.2. The amount of polymer is measured by the change of transmission of the cell window over two and a half hours irradiation period.

Figure 3.72


Rate of formation of polymer determined by the fall off in the rate of formation of hydrogen: (Figure 3.2)

R_o is the initial rate of hydrogen formation.

R is the rate of hydrogen formation with polymer on the window.

TABLE 3.2

Pressure	% Transmission of Cell window at 1849Å		
	Before	After $2\frac{1}{2}$ hrs irradiation	Change
5.7 mm cis-but-2-ene	98.5	61	37.5
5.8 mm c.b.2 + 100 mm N_2	97	60	37
5.7 mm c.b.2 + 300 mm N_2	98	60	38

Thus change in pressure has no measurable effect on the rate of polymer formation.

The u.v. absorption spectrum of the polymer shows a maximum near 1850 Å, while the I.R. absorption spectrum indicates the presence of C=C bonds and $C-CH_3$ groups.

3.1.8 Carbon Balance

The product yields of a typical run are given in Table 3.3.

TABLE 3.3

Yields in moles x 10^{-8}

Hydrogen	18	Propylene	20	t-but-2-ene	12	t-pent-2-ene	12
Methane	8	Allene	7	3-Me-but-1-ene	11	c-pent-2-ene	11
Ethylene	2	But-1-ene	30	Isopentane	27	C_6	3
Ethane	13	Butadiene	16	n-pentane	1	C_7	6
Acetylene	34	n-Butane	17	but-2-yne	1	C_8	30

Unfortunately, at such low conversions, it was not possible to measure the fall off in the reactant cis-but-2-ene with any accuracy, because of the small change in the large chromatograph peak of the cis-but-2-ene. Consequently, it was necessary to irradiate for a period of two and a half hours to obtain a reasonable decrease of but-2-ene, so that an estimate of the carbon balance could be made. The products obtained after 2½ hrs. irradiation are given in Table 3.4.

TABLE 3.4

2½ hrs. irradiation 10 mm. cis-but-2-ene Yield in moles x 10^{-7}

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
10	50	25	52	56	5	6	30

The C_6 to C_8 hydrocarbons in Tables 3.3 and 3.4 are only roughly estimated quantitatively.

Converting the yields in Table 3.4 to C_4, the total yield is equivalent to $\sim$ 245 x 10^{-7} moles of cis-but-2-ene. The actual amount used up in the experiment was $\sim$ 285 x 10^{-7} moles. The difference of $\sim$ 40 x 10^{-7} moles can be accounted for by the formation of the solid polymer, and by the inaccuracy of estimation of the yields of the C_6 to C_8 hydrocarbon products.

3.2 Liquid Phase

Two runs were conducted with cis-but-2-ene in the liquid phase to compare the results with irradiations in the vapour phase.

0.01 mole cis-but-2-ene was admitted to the liquid cell and irradiated for a period of one hour. The product yields were as follows:

Methane	1.1×10^{-8} moles
Ethane	1.4×10^{-8} moles
But-1-ene	8.6×10^{-8} moles
Butadiene	6.5×10^{-8} moles
Trans-but-2-ene	170×10^{-8} moles

Higher molecular weight products could not be measured because of the large cis-but-2-ene peak on the chromatogram.

Thus, in the liquid phase, the geometrical isomer is the major product.

3.3 Radiolysis

Two radiolysis experiments were conducted on cis-but-2-ene to compare the results with those obtained by Kaufman.[106] The major product from both radiolyses was the trans isomer. Evidence of decomposition was obtained by the presence of C_1 to C_4 hydrocarbons. C_8 hydrocarbons were detected but not measured quantitatively. Radiolysis results are given in Table 3.5.

TABLE 3.5

Radiolysis Results

Total dose is approximately 10^7 rads.
Yields are in moles x 10^{-7}

Press. cis-but-2-ene	CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_4	iso C_4H_{10}	C_4H_8-1	n C_4H_{10}	C_4H_6	t-C_4H_8
370 mm	10	10	5.5	12.5	9.3	7	0.15	7	9	5.5	47
650 mm	5	5	2.6	6.3	6.6	3.5	0.15	11.7	13	8.8	76

Thus, as in Kaufman's work,[106] the geometric isomer is the major product in the vapour phase. However, there is apparently a pressure dependence of the products which was not found by Kaufman.

3.4 Summary

1. Photolysis of either cis- or trans-but-2-ene at 1849 Å produces at least thirty four products, among which the geometric isomer is not of major importance.

2. The product yields were directly proportional to irradiation time for four minutes. On longer irradiations the product yields fell off due to formation of polymer on the cell window.

3. All product yields were directly proportional to the intensity of irradiation.

4. All product yields were decreased by increasing the pressure of reactant but-2-ene, except the yield of the geometric isomer, which remained constant to at least 100 mm. pressure, and the yield of but-1-ene, which after an initial increase, remained constant to one atmosphere.

5. Temperature over the range 25°C to 100°C had no effect upon the product yields except for the yield of methane which showed a maximum at 100°C.

6. The pressure effect of added gases nitrogen, carbon dioxide and argon was similar to that of increased pressure of but-2-ene, except that the yield of but-1-ene was decreased by argon, carbon dioxide and nitrogen with the trans isomer but not by nitrogen with the cis isomer. The yield of the geometric isomer was constant to one atmosphere.

7. The effect of addition of radical scavengers was

   a: To remove but-1-ene completely, at low scavenger %age.

   b: To almost completely remove ethane, n-butane, isobutane and products above C_4 at low scavenger %age.

c. To reduce propylene substantially in the range 0-20 mm scavenger addition.

d. To have little effect on the remainder of the C_1 to C_4 products, including the geometric isomer.

8. The major product in the liquid phase photolysis was the geometric isomer.

9. The major product on radiolysis was the geometric isomer.

In the discussion of this thesis an attempt is made to weld these facts into the framework of previous experience discussed in the introduction.

4. DISCUSSION

The number and variety of the products formed by the photolysis of either cis- or trans-but-2-ene at 1849 Å, and their differing dependences upon the addition of inert gases and radical scavengers, suggests that a number of primary processes are operative in their formation. The pressure dependence of the yields of the majority of the products suggests that some common excited state precursor is being influenced, while the pressure independence exhibited by the yields of the geometric isomer and but-1-ene suggests that these products may be formed from some other excited state(s), different to the state that yields the majority of products.

The addition of the free radical scavengers oxygen and nitric oxide to the system helps to distinguish two modes of product formation - molecular and free radical. The products that show little difference in yield when produced in the presence of oxygen or nitrogen, viz. the geometric isomer, butadiene, allene, acetylene, ethylene, hydrogen and methane, may be attributed to molecular primary reactions. The products that have their yields substantially reduced by the presence of scavengers may be attributed to the reactions of radicals. The anomolous behaviour of the product but-1-ene with respect to pressure, and its total removal by 1% of oxygen, suggest a different mode of formation to the other products.

The following primary reactions are proposed to account for the nature and distribution of the products.

4.1 Molecular Reactions

4.1.1 Formation of the cis- or trans-isomer

$$\text{cis} - C_4H_8\text{-}2 \; + \; h\nu \dashrightarrow \text{trans-}C_4H_8\text{-}2 \qquad 4.\text{Ia}$$

$$\text{trans} - C_4H_8\text{-}2 + \; h\nu \longrightarrow \text{cis} - C_4H_8\text{-}2 \qquad 4.\text{Ib}$$

The rate of formation of the geometric isomer is uninfluenced by pressure or by the presence of free radical scavengers. These facts indicate a unique molecular mode of formation in the system, which can be attributed to the presence of an excited state which leads principally to cis-trans isomerisation (Section 4.5).

4.1.2 Formation of acetylene

Acetylene is one of the major products of the photolysis, and the reaction for its formation is suggested as

$$H_3C - CH = CH - CH_3 \; + h\nu \rightarrow HC \equiv CH + 2 \; {\cdot}CH_3 \qquad 4.\text{II}$$

This reaction is analogous to that observed in the photolysis of propylene, where a methyl radical and a hydrogen atom are eliminated (Reaction 1.XXXVII).[115] The possibility of molecular elimination of ethane accompanying the formation of acetylene is discounted because of the influence of radical scavengers on the ethane yield.

4.1.3 Formation of butadiene and but-2-yne

The formation of butadiene and but-2-yne is accounted for by molecular elimination of hydrogen from but-2-ene

$$H_3C - CH = CH - CH_3 + h\nu \rightarrow CH_2 = CH - CH = CH_2 + H_2 \qquad 4.III$$

$$\rightarrow CH_3 - C \equiv C - CH_3 + H_2 \qquad 4.IV$$

Although no accurate measurement of the yield of but-2-yne has been made, it is estimated to be approximately 10% of the yield of butadiene. Reactions 4.III and 4.IV require the yield of hydrogen to equal that of butadiene + but-2-yne. This is seen to be so from Table 3.3. The formation of but-2-yne is analogous to the formation of acetylene in the photolysis of ethylene.[112,113] At the same time as acetylene is formed from ethylene, hydrogen is eliminated both atomically and molecularly, the ratio depending upon the wavelength of irradiation. At 1849 Å the hydrogen elimination from ethylene is mainly molecular,[114] and the correspondence between the yields of hydrogen and butadiene + but-2-yne indicates that the hydrogen yield from but-2-ene is similarly mainly molecular.

4.1.4 Formation of methane and allene

The formation of methane and allene is accounted for by the process

$$CH_3 - CH = CH - CH_3 + h\nu \rightarrow CH_4 + H_2C = C = CH_2 \qquad 4.V$$

This reaction is analogous to that proposed for the molecular elimination of methane from propylene[115] (Reaction 1.XXXIX). From Table 3.3 the yields of allene and methane are seen to be approximately equal. However, the occurrence of a maximum in the graph of quantum yield of methane against pressure of but-2-ene at 100°C (Figure 3.33) suggests that methane is also formed by some other process at this temperature - possibly a disproportionation reaction involving methyl radicals.

4.1.5 Formation of ethylene

The formation of ethylene is postulated as occurring by the process

$$CH_3 - CH = CH - CH_3 + h\nu \rightarrow 2\ CH_2 = CH_2 \qquad 4.VI$$

although such a rearrangement has not previously been suggested for olefin decomposition. Initial formation of ethylidene radicals cannot be discounted, although rearrangement of the radicals to ethylene would necessarily have to be faster than the collision frequency to account for the lack of effect by radical scavengers.

4.2 Radical Reactions

Although the effect of radical scavengers indicates that a large number of the products owe their origin to the presence of free radicals, it is only necessary to postulate two primary reactions which form free radicals.

4.2.1 C-H bond cleavage

The weak C-H bond β to the C=C bond is readily split (c.f. photosensitisation of but-2-ene[77] and photolysis of but-1-ene at 1849 Å [117])

$$CH_3 - CH = CH - CH_3 + h\nu \rightarrow H\cdot + H_2\dot{C} - CH = CH - CH_3$$

$$\Updownarrow$$

$$H_2C = CH - \dot{C}H - CH_3 \qquad 4.VII$$

The products are a hydrogen atom and a resonance stabilised γ-methyl allyl radical. The hydrogen atom would be expected to react immediately with the but-2-ene ($E_A \sim 2$ kcal.mole^{-1} [91]) to produce an excited sec-butyl radical,[136] $C_4H_9^*$.

$$H + C_4H_8 \xrightarrow{k_2} C_4H_9^* \qquad 4.VIII$$

The disproportionation reaction:-

$$H + C_4H_8 \xrightarrow{k_1} H_2 + C_4H_7\cdot \qquad 4.IX$$

is unlikely to occur, as the ratio $\frac{k_1}{k_2}$ is only 0.076 for trans-but-2-ene, and 0.023 for cis-but-2-ene.[135]

The excited radical $C_4H_9^*$ may either decompose to yield propylene and a methyl radical:-

$$C_4H_9^* \rightarrow C_3H_6 + \cdot CH_3 \qquad 4.X$$

or be collisionally deactivated to yield a sec-butyl radical.

$$C_4H_9^* + M \rightarrow C_4H_9\cdot + M \qquad 4.XI$$

The yield of the product propylene shows a greater decrease in yield when formed in the presence of oxygen (Figure 3.68) than when formed in the presence of other gases (Figure 3.46). This is attributed to the combined effect of pressure quenching and interaction of oxygen with the excited sec-butyl radical.

4.2.2 C-C bond cleavage

C-C bond cleavage was found to occur in the mercury photosensitisation of but-2-ene,[77] and a similar reaction is postulated here.

$$CH_3 - CH = CH - CH_3 + h\nu \rightarrow \cdot CH_3 + \cdot CH = CH - CH_3 \qquad 4.XII$$

The propenyl radical formed in reaction 4.XII is likely to rearrange to the more stable allyl radical $\cdot CH_2 - CH = CH_2$, as was found in the photosensitisation of but-2-ene.[77]

4.2.3 Secondary Reactions

The radicals formed in primary reactions 4.VII and 4.XII may then undergo a series of secondary reactions. Radical recombination reactions ($\sim$ zero activation energy[65]) are likely to predominate over radical-olefin addition reactions (E_A for alkyl radical + C = C $\sim$ 5 kcal.mole^{-1} [91]), and in the temperature range studied radical disproportionation reactions are likely to be insignificant in comparison with radical recombination reactions. A possible exception is the interaction of sec-butyl radicals where $\frac{k_1}{k_2}$ has been reported as 1.5[137] and 0.98[98] at 25°C (k_1 = rate constant for disproportionation, k_2 for recombination). Consequently, the disproportionation reaction must be considered of importance.

The products of the recombination reactions of the radicals formed in the primary processes are given in Table 4.1, using the numbering system given below.

$CH_3\cdot$ (1); $\dot{C}H_2 - CH = CH - CH_3$ (2); $H_2C = CH - \dot{C}H - CH_3$ (3);

$\cdot CH_2 - CH = CH_2$ (4); $H_3C - CH_2 - \dot{C}H - CH_3$ (5).

	1	2	3	4	5
1	Ethane				
2	Pent-2-ene (c, t)	2,6-octadiene (c-c, c-t, t-t)			
3	3-methyl but-1-ene	3-Me-1,5-heptadiene (c,t)	3,4-Dimethyl-1,5-hexadiene		
4	But-1-ene	1,5-heptadiene (c,t)	3-methyl-1,5-hexadiene	1,5-hexadiene	
5	Isopentane	5-methyl hept-2-ene (c, t)	3,4-Dimethyl-hex-1-ene	4-methyl hex-1-ene	3,4-Dimethyl hexane

Disproportionation of 5 + 5 yields n-butane + but-1-ene.

The ratio of cis/trans-pent-2-ene formed by the combination of the γ-methyl allyl radical, produced by C-H bond cleavage (4.VII), and a methyl radical, is the same (0.9) no matter whether the γ-methyl allyl radicals are formed from cis- or trans-but-2-ene. This indicates that the γ-methyl allyl radicals do not retain their original configuration, which contrasts with the work of Holroyd and Klein[108] who suggest that the γ-methyl allyl radicals formed on the radiolysis of but-2-ene do retain their original configuration. The ratio of 3-methyl but-1-ene/pent-2-ene (cis + trans) in the present work is 0.47 (Table 3.3) which is in good agreement with the findings of Kubin, Rabinovitch and Harrington, who obtained 0.4.[136]

Although the majority of high molecular weight products could not be positively identified, the number of peaks on the chromatogram corresponded to the number of possible products formed by these recombination reactions. If the whole product sample was frozen down into the sampling U-tube, and then passed through the chromatograph, a number of other minor products were detected. These may be attributed to the disproportionation reactions of the radicals (1) to (4). These products are present in such small quantities as to be undetectable under regular sampling conditions.

Assuming that all C_8 hydrocarbons result from the C-H split (reaction 4.VII), all C_6 hydrocarbons result from the C-C split (4.XII), and that the C_7 hydrocarbons can be attributed equally to C-H and C-C split, an estimation of the products C_6 to C_8 gives the ratio of C-H to C-C cleavage as ∼ 5.5:1 (Table 3.3). This compares with a ratio of ∼5:1 obtained in the mercury photosensitisation of but-2-ene.[77] When the product yields in Table 3.3 are converted to a percentage of the total products formed by molecular and free radical reactions, the relative importance of the postulated primary reactions can be estimated.

Reaction	No. of moles x 10^{-8}	% of total
1. Formation of methane + allene	8	5
2. Formation of acetylene	34	20
3. Formation of butadiene	16	10
4. Formation of but-2-yne	1	0·5
5. Formation of ethylene	1	0·5
6. C-H split $\frac{1}{2}\sum[\text{pentenes}] + 2[C_8]$ $+ [C_7] + [C_3H_6] + [n\text{-}C_4H_{10}] + [\equiv C_4H_8\text{-}1] + [\text{iso}C_5H_{12}]$	95	57
7. C-C split $[C_7] + 2[C_6]$	11	7

It is seen that primary reactions involving the formation of free radicals are slightly more important than primary molecular elimination reactions.

4.2.4 Formation of Polymer

The polymer formed on the cell window is a yellowish transparent solid that is thick enough to show second order diffraction colours after six hours irradiation. The insolubility of the polymer suggests a high degree of cross linking, and the U.V. and I.R. absorption spectra suggest the presence of C=C bonds.

The polymer is almost certainly formed by radicals reacting with the but-2-ene to form higher molecular weight radicals. This process will continue until a chain breaking step occurs - reaction with another radical, or abstraction of hydrogen from another molecule.

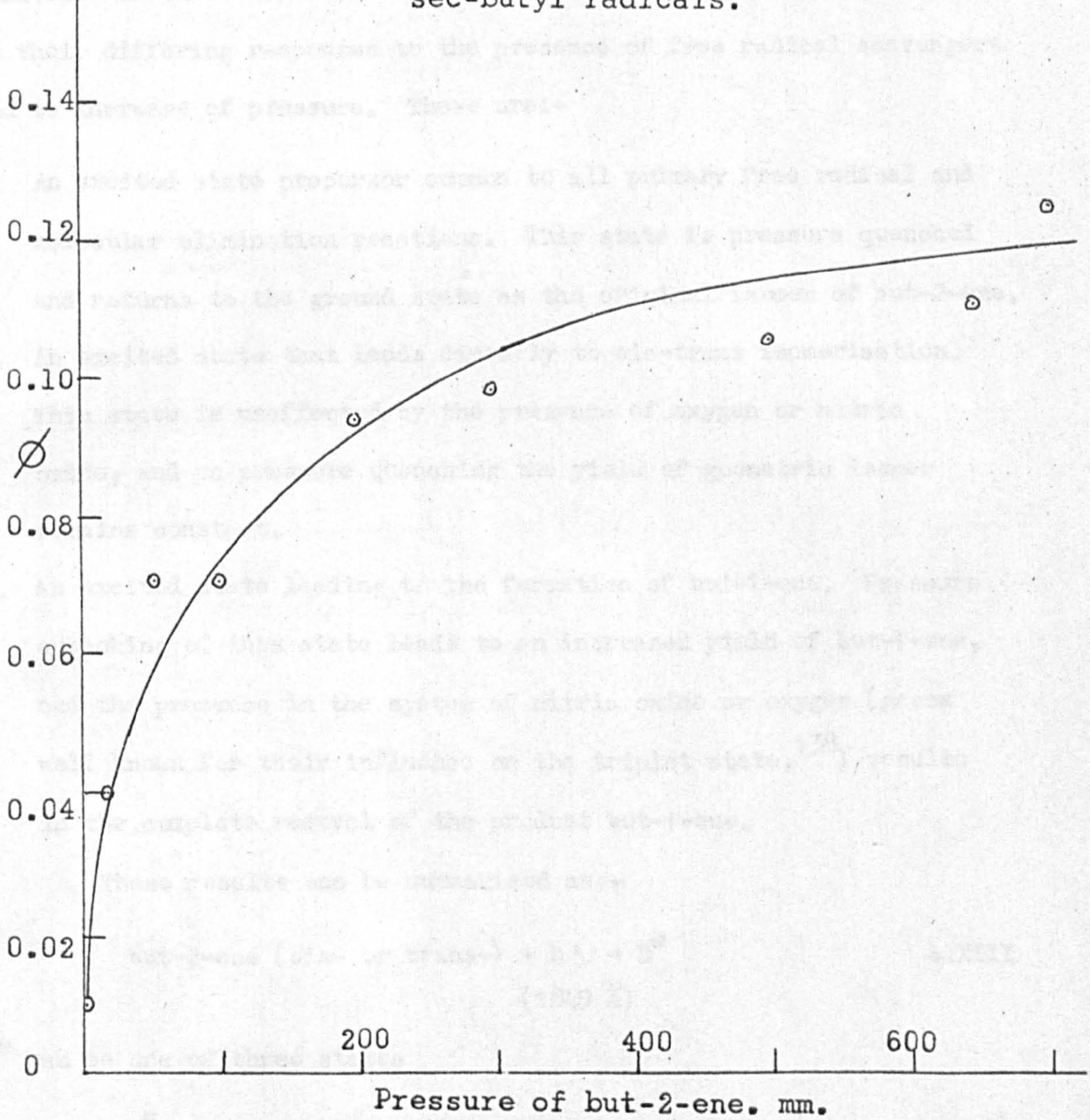
The rate of formation of the polymer is illustrated in Figure 3.72. The initial induction period of half an hour before polymer formation becomes noticeable is suggestive of catalytic action on the cell window. Until sufficient high molecular weight products are present at the window, formation of the solid polymer cannot commence. This was confirmed by the polymer formed after only short irradiations. Irradiations of but-2-ene for a few minutes followed by replacement with fresh but-2-ene, and reirradiation, yielded very little polymer even after a total irradiation time of several hours. Thus, the polymer formation would seem to be dependent upon the build up of high molecular weight radicals which interact with each other and with the but-2-ene.

4.3 Formation of but-1-ene

It was suggested earlier that the anomolous effect of pressure on the yield of but-1-ene was due to the presence of a different excited state in the system, which yielded but-1-ene. If it is assumed that the butene formed by the disproportionation of sec-butyl radicals is primarily but-1-ene (lack of radical scavenger effect on the yield of but-2-ene), then the but-1-ene yield should equal that of n-butane (considering the yield of but-1-ene formed by the recombination of methyl and allyl radicals to be small). Subtracting the n-butane yield from the total yield of but-1-ene results in a yield of but-1-ene that increases with pressure, Figure 4.1. This suggests that the but-1-ene is being formed from some state that is being stabilised by increasing pressure. The effect of oxygen is not only to remove the but-1-ene formed by the disproportionation of sec-butyl radicals, but also to remove the but-1-ene formed by this second process. The pressure effect and the effect of oxygen suggest that a triplet state may play a role in the formation of but-1-ene.

Figure 4.1

Total yield of but-1-ene, minus the yield of but-1-ene formed by disproportionation of sec-butyl radicals.



4.4 Excited States

The preceeding discussion has drawn attention to the possible existence of three different excited states in the system, distinguished by their differing responses to the presence of free radical scavengers and to increase of pressure. These are:-

1. An excited state precursor common to all primary free radical and molecular elimination reactions. This state is pressure quenched and returns to the ground state as the original isomer of but-2-ene.
2. An excited state that leads directly to cis-trans isomerisation. This state is unaffected by the presence of oxygen or nitric oxide, and on pressure quenching the yield of geometric isomer remains constant.
3. An excited state leading to the formation of but-1-ene. Pressure quenching of this state leads to an increased yield of but-1-ene, and the presence in the system of nitric oxide or oxygen (gases well known for their influence on the triplet state,138) results in the complete removal of the product but-1-ene.

These results can be summarised as:-

$$\text{but-2-ene (cis- or trans-)} + \underset{(1849\ \text{Å})}{h\nu} \rightarrow B^* \tag{4.XIII}$$

B^* can be one of three states

$$B_1^* \rightarrow \text{products (free radicals and molecular)} \tag{4.XIV}$$

$$B_1^* + M \rightarrow \text{original isomer} \tag{4.XV}$$

$$B_2^* \rightarrow \text{geometric isomer} \tag{4.XVI}$$

$$\begin{matrix} B_1^* \\ \text{or} \\ B_2^* \end{matrix} \rightarrow B_3^* \rightarrow \text{but-1-ene} \tag{4.XVII}$$

The pressure quenching effect on B_1^* can be used to estimate the lifetime of the excited state B_1^*

$$B + h\nu \rightarrow B_1^* \text{ --------- } k_1 \qquad 4.\text{XIX}$$

$$B_1^* \rightarrow \text{products --------- } k_2 \qquad 4.\text{XX}$$

$$B_1^* + M \rightarrow B + M \text{ --------- } k_3 \qquad 4.\text{XXI}$$

The rate of product formation R is

$$R = k_2[B_1^*] \qquad 4.\text{XXII}$$

From equations 4.XIX to 4.XXI

$$\frac{d[B_1^*]}{dt} = I\emptyset - k_2[B_1^*] - k_3[B_1^*][M] \qquad 4.\text{XXIII}$$

where I is the intensity of irradiation, and Ø is the quantum yield of formation of B_1^*.

For steady state conditions

$$\frac{d[B_1^*]}{dt} = 0 \qquad 4.\text{XXIV}$$

Then
$$[B_1^*] = \frac{I\emptyset}{k_2 + k_3 M} \qquad 4.\text{XXV}$$

Hence the rate of product formation from 4.XXII is

$$R = \frac{k_2 I\emptyset}{k_2 + k_3[M]} \qquad 4.\text{XXVI}$$

This expression can be rearranged to

$$\frac{1}{R} = \frac{1}{I\emptyset} + \frac{k_3}{k_2} \cdot \frac{[M]}{I\emptyset} \qquad 4.\text{XXVII}$$

From a Stern-Volmer graph of $\frac{1}{R}$ against [M], where [M] is the pressure of gas in mm., the ratio k_3/k_2 can be calculated as the ratio slope/intercept. The rate constant k_3 for binary collisions, was calculated as 2×10^{11} litres moles.^{-1} sec.^{-1} (using a collision diameter of 6.5 Å for but-2-ene, Section 1.3). Hence, the lifetime of the excited state B_1^* may be determined from the first order rate constant k_2 providing it is assumed that deactivation occurs on every collision.

Figure 4.2 represents Stern-Volmer graphs of the products methane, ethane, allene and butadiene, and Figure 4.3 consists of Stern-Volmer graphs of allene formed from 10 mm. trans-but-2-ene in the presence of nitrogen, oxygen and trans-but-2-ene itself. The graphs are straight lines indicating that the assumption that deactivation occurs on every collision is a reasonable one. The values for the mean lifetime of B_1^* calculated from the Stern-Volmer graphs of Figures 4.2 and 4.3 are all in the range $1 - 2.5 \times 10^{-10}$ secs. These values are a minimum in view of the assumption of quenching occurring on every collision, and they compare with the values of 5.1×10^{-10} sec. (cis) and 1.5×10^{-9} sec (trans) calculated for the lifetimes of state V (Section 1.3).

A Stern-Volmer graph of the product but-1-ene consisting of two points - the rate of formation of but-1-ene from 10 mm. trans-but-2-ene, and the rate of formation in the presence of $\nless$ 1% of oxygen - indicate a lifetime for state B_3^* of 5×10^{-9} secs. This compares with the triplet state lifetimes of but-2-ene (3.3×10^{-9} secs.[29]) and but-1-ene (6.3×10^{-9} secs.[71]) obtained by mercury photosensitisation (Section 1.5.1).

Figure 4.2

Stern-Volmer plots of the products methane, ethane, allene and butadiene formed on photolysis of trans-but-2-ene.

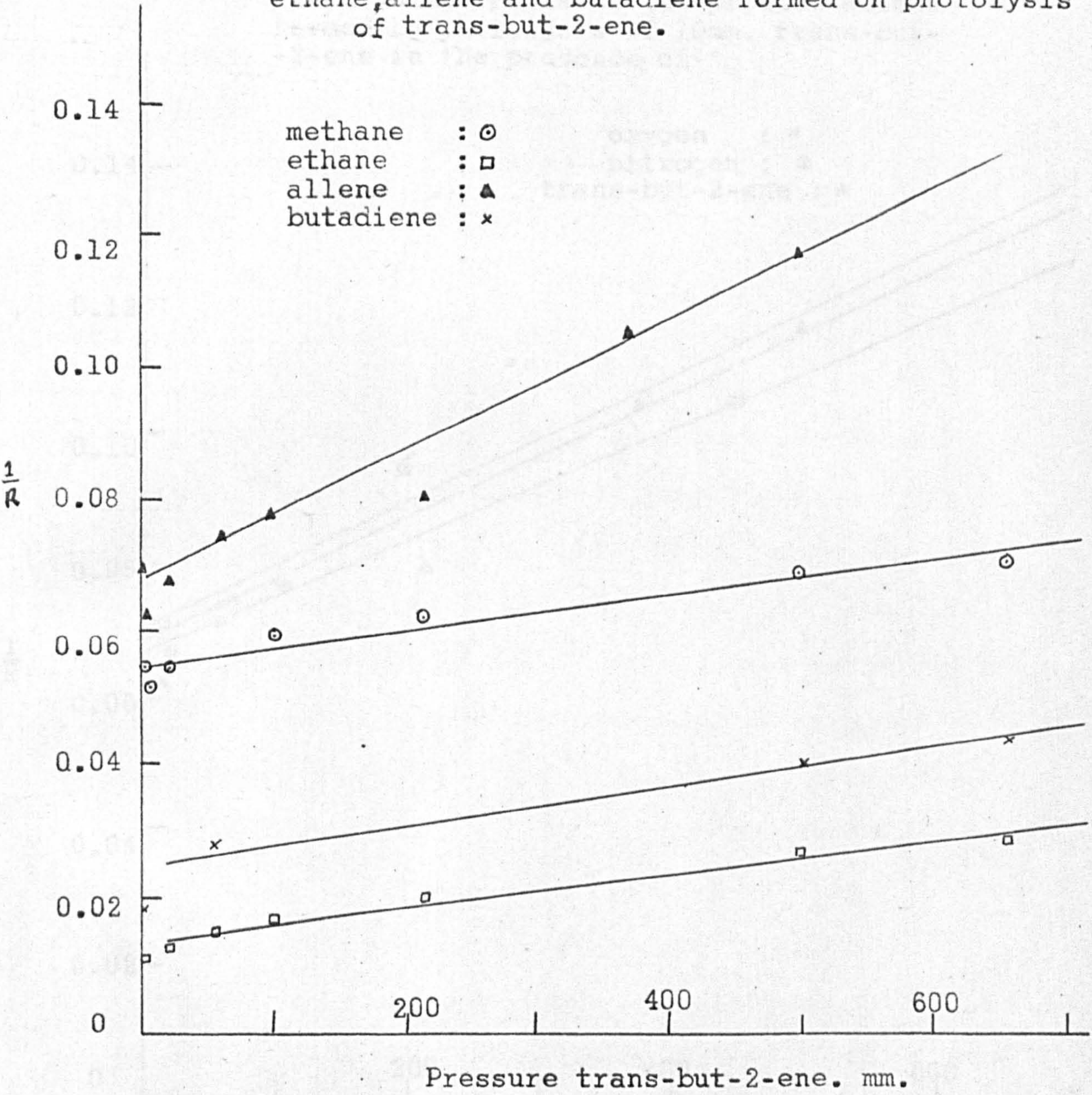
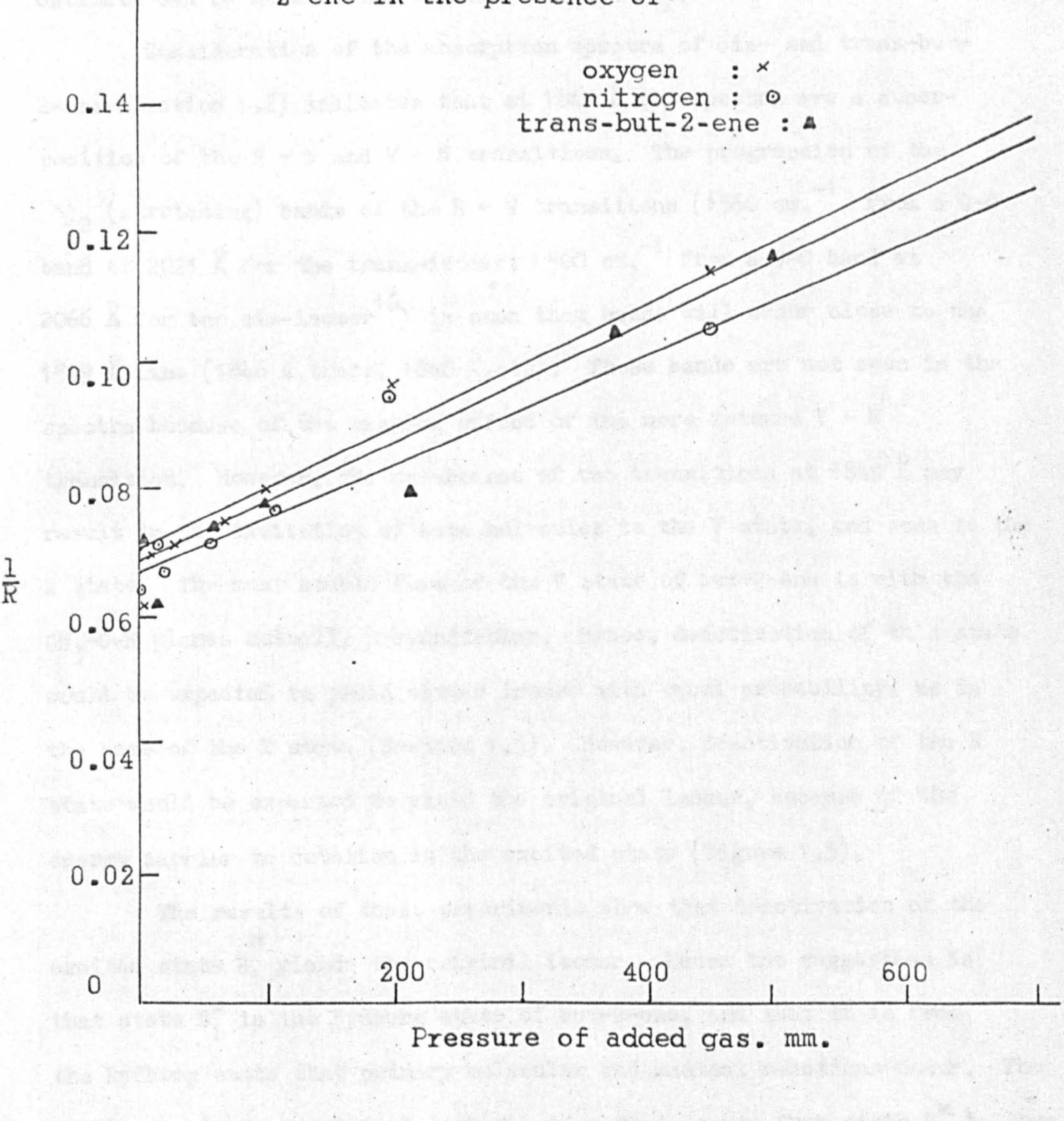


Figure 4.3

Stern-Volmer plots of the product allene formed by photolysis of 10mm. trans-but-2-ene in the presence of:-



As the yield of the geometric isomer is unaffected by pressure, no estimate can be made of the lifetime of state B_2^*.

Consideration of the absorption spectra of cis- and trans-but-2-ene (Section 1.2) indicates that at 1849 Å the spectra are a superposition of the R ← N and V ← N transitions. The progression of the ν_2 (stretching) bands of the R ← N transitions (1560 cm.$^{-1}$ from a 0-0 band at 2021 Å for the trans-isomer; 1500 cm.$^{-1}$ from a 0-0 band at 2066 Å for the cis-isomer[16]) is such that bands will occur close to the 1849 Å line (1846 Å, trans; 1840 Å, cis). These bands are not seen in the spectra because of the masking effect of the more intense V ← N transition. However, the occurrence of two transitions at 1849 Å may result in the excitation of some molecules to the V state, and some to the R state. The most stable form of the V state of but-2-ene is with the $CH_3-\ddot{C}-H$ planes mutually perpendicular. Hence, deactivation of this state would be expected to yield either isomer with equal probability, as in the case of the T state (Section 1.5). However, deactivation of the R state would be expected to yield the original isomer, because of the energy barrier to rotation in the excited state (Figure 1.5).

The results of these experiments show that deactivation of the excited state B_1^* yields the original isomer. Hence the suggestion is that state B_1^* is the Rydberg state of but-2-ene, and that it is from the Rydberg state that primary molecular and radical reactions occur. The small amount of geometrical isomerisation that occurs from state B_2^* is then considered to result from the upper singlet state V. Deactivation of this state produces either isomer with equal probability.

Confirmation of this analysis is obtained from irradiations in the liquid phase (Section 3.2), where the trans-but-2-ene constitutes 90% of the products $C_1 - C_4$ detected in the photolysis of cis-but-2-ene (cf. 6.3% in the vapour phase, Table 3.3). In the liquid phase R ← N transition bands cannot be detected, because the Rydberg orbital is highly perturbed by the presence of neighbouring molecules.[18] Consequently, absorption at 1849 Å can only produce the V ← N transition, and hence geometrical isomerisation far outweighs the formation of other products.

The product but-1-ene is peculiar in the system in that its yield increases with increasing pressure, and that it is removed by oxygen. These facts suggest that a triplet state is involved in the formation of but-1-ene, and it is postulated that an excited triplet state of but-1-ene is formed from either the V or R state of but-2-ene

$$C_4H_8\text{-}2^{*} \longrightarrow C_4H_8\text{-}1^{*}(T) \qquad 4.XXVIII$$

The triplet state of but-1-ene can either decompose or be collisionally deactivated to yield but-1-ene. The selective deactivation by nitrogen on the triplet state produced from cis-but-2-ene (Section 3.1.5) is difficult to understand, although the deactivation by both isomers of but-2-ene is explicable in terms of the larger collision diameters of but-2-ene relative to those of argon or carbon dioxide.

4.5 Summary of Conclusions

The vapour phase photolysis of cis- or trans-but-2-ene at 1849 Å results in the formation of hydrogen, at least thirty two hydrocarbons C_1 to C_8, including the geometric isomer, and a solid polymer. The varying effects that the pressure of but-2-ene or of added gases have on the yields of these products indicates the existence of two different excited states B_1^* and B_2^* in the system. Absorption of light at 1849 Å can produce either the B_1^* state, or the B_2^* state, and once formed, they can undergo reaction or be pressure quenched. Pressure quenching of B_1^* results in reformation of the original isomer while quenching of B_2^* produces the geometric isomer. These facts help to equate states B_1^* and B_2^* with the Rydberg (R) and first excited singlet (V) states of but-2-ene respectively. The V state results solely in isomerisation, while the R state can decompose by seven primary reactions. The effect of radical scavengers helps distinguish two modes of decomposition - molecular and free radical.

$$C_4H_8\text{-}2 + h\nu \rightarrow B_1^* \text{ or } B_2^*$$

% decomposition of B_1^*	ϕ		
	0·085	$B_2^* \rightarrow$ geometric isomer	4.I a,b
57	0·6	$B_1^* \rightarrow H\cdot + \cdot CH_2 - CH = CH - CH_3$	4.VII
20	0·23	$B_1^* \rightarrow HC \equiv CH + 2\ \cdot CH_3$	4.II
10	0·115	$B_1^* \rightarrow CH_2 = CH - CH = CH_2 + H_2$	4.III
7	0·085	$B_1^* \rightarrow \cdot CH_3 + \cdot CH = CH \cdot CH_3$	4.XII
5	0.05	$B_1^* \rightarrow CH_4 + CH_2 = CH = CH_2$	4.V
0·5	0.007	$B_1^* \rightarrow CH_3 - C \equiv C - CH_3 + H_2$	4.IV
0·5	0·007	$B_1^* \rightarrow 2\ H_2C = CH_2$	4.VI

The ratio of the quantum yields of decomposition to isomerisation indicates that the R and V states are formed in the ratio 8:1 in the vapour phase. Confirmation of the correct designation of these excited states is suggested by the liquid phase photolysis at 1849 Å, where cis-trans isomerisation is almost the sole reaction. This must occur in the V state, for the R state does not exist in the liquid phase. Further confirmation could be obtained by use of deuterated butenes which shift the R ← N and V ← N absorption spectra relative to each other. Photolysis at 1849 Å would then be expected to produce a different ratio of excited states, and hence a different proportion of

$$C_4H_8\text{-}2 + h\nu \rightarrow B_1^* \text{ or } B_2^*$$

% decomposition of B_1^*	ø		
–	0.1	$B_2^* \rightarrow$ geometric isomer	4.I a,b
46	0.26	$B_1^* \rightarrow H\cdot + \cdot CH_2 - CH = CH - CH_3$	4.VII
26	0.2	$B_1^* \rightarrow HC \equiv CH + 2\ \cdot CH_3$	4.II
12	0.15	$B_1^* \rightarrow CH_2 = CH - CH = CH_2 + H_2$	4.III
8	0.06	$B_1^* \rightarrow \cdot CH_3 + \cdot CH = CH \cdot CH_3$	4.XII
6	0.05	$B_1^* \rightarrow CH_4 + CH_2 = CH = CH_2$	4.V
1	0.01	$B_1^* \rightarrow CH_3 - C \equiv C - CH_3 + H_2$	4.IV
1	0.01	$B_1^* \rightarrow 2\ H_2C = CH_2$	4.VI

The ratio of the quantum yields of decomposition to isomerisation indicates that the R and V states are formed in the ratio 8:1 in the vapour phase. Confirmation of the correct designation of these excited states is suggested by the liquid phase photolysis at 1849 Å, where cis-trans isomerisation is almost the sole reaction. This must occur in the V state, for the R state does not exist in the liquid phase. Further confirmation could be obtained by use of deuterated butenes which shift the R ← N and V ← N absorption spectra relative to each other. Photolysis at 1849 Å would then be expected to produce a different ratio of excited states, and hence a different proportion of isomerisation to decomposition. Deuterated butenes would also be useful in determining more accurately the nature of the primary reactions.

An interesting consequence of the pressure quenching of the excited states is that if they fluoresce, this should also show a pressure quenching effect. Such an observation would provide a useful confirmation of the mechanisms.

A third excited state B_3^* found to exist in the system is pressure quenched to yield but-1-ene, and is equated with the triplet state of but-1-ene, formed by an intersystem crossing from the excited but-2-ene.

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