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A T H E S I S

entitled

The VAPOUR-PHASE POLYMERISATION and
OXIDATION of STYRENE

by

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Submitted for the
Degree of Doctor of Philosophy
of The City University

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ABSTRACT

Studies have been made of vapour-phase reactions of styrene both in the absence and presence of oxygen at subatmospheric pressures and at temperatures ranging from 180–580°C. Special attention has been paid to the influence of polymerising liquid styrene on the vapour-phase oxidation of this compound.

In the Introduction, the liquid-phase polymerisation of styrene and related monomers is discussed in detail. The limited amount of work which has been carried out on the vapour-phase polymerisation of styrene is also described. Finally a review is given of the vapour-phase oxidation of aromatic hydrocarbons with special reference to the behaviour of styrene.

The Experimental Section describes the apparatus and procedures used in this work. Reactions were followed by virtue of the accompanying pressure and temperature changes, which were measured with a strain-gauge pressure transducer and a microthermocouple respectively. The principal reaction products were identified and determined by gas chromatography.

In the Results Section, it is shown that no appreciable polymerisation of styrene takes place in the vapour-phase at pressures below atmospheric. Furthermore, the presence of 1–5% oxygen does not significantly enhance such polymerisation. Styrene remains stable in the absence of oxygen up to temperatures of ca. 550°C. However, in the presence of 1–5% oxygen, decomposition occurs at temperatures as low as 320°C.

Studies of the vapour-phase oxidation of styrene have shown that no cool flame region is observed and that only slow oxidation

takes place at temperatures below 465°C . At higher temperatures, ignition occurs.

Experiments carried out at ca. 570°C in which polymerising liquid styrene was introduced into a reacting styrene-air vapour mixture, have shown that the liquid monomer facilitates ignition. At higher initial pressures, however, temperature measurements indicate that a cooling effect takes place when the relatively cold monomer is introduced into the vapour mixture. This cooling effect tends to 'mask' the influence of polymerising liquid styrene in promoting ignition.

Finally, in the Discussion, the significance and implications of the experimental results are considered and deductions are made as to the probable mechanisms involved in the vapour-phase reactions of styrene.

CONTENTS

	Page No.
ABSTRACT	2
ACKNOWLEDGEMENTS	5
SECTION 1 INTRODUCTION	6
SECTION 2 EXPERIMENTAL	60
SECTION 3 RESULTS	86
SECTION 4 DISCUSSION	146
REFERENCES	167

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SECTION 1

INTRODUCTION

SECTION 1

		Page No.
1.1	<u>Introduction</u>	9
1.2	<u>Storage of styrene-type monomers</u>	13
1.2.1	Polymerisation aspects of storage	13
1.2.2	Flammability aspects of storage	16
1.3	<u>Liquid-phase polymerisation of styrene and related monomers</u>	18
1.3.1	Uncatalysed thermal polymerisation of styrene	18
1.3.1.1	Bimolecular initiation theories	22
1.3.1.2	Termolecular initiation theories	24
1.3.2	Polymerisation in the presence of air	26
1.4	<u>Vapour-phase polymerisation of styrene and related monomers</u>	27
1.5	<u>Pyrolysis of styrene and saturated aromatic hydrocarbons</u>	30
1.6	<u>Vapour-phase oxidation of saturated aromatic hydrocarbons</u>	32
1.6.1	Vapour-phase oxidation of benzene	34
1.6.2	Vapour-phase oxidation of alkylbenzenes	35
1.6.2.1	Combustion phenomena	35

	Page No.
1.6.2.2	Structure and reactivity 42
1.6.2.3	Effect of methyl groups in the benzene nucleus 44
1.6.2.4	Effect of chain length in monoalkylbenzenes 45
1.6.2.5	Effect of branched side chains in monoalkylbenzenes 45
1.6.2.6	Effect of positional isomerism in diakylbenzenes 46
1.6.3	Products of slow oxidation 47
1.6.3.1	Side-chain oxidation 47
1.6.3.2	Nuclear oxidation 51
1.7	<u>Oxidation of styrene</u> 51
1.7.1	Liquid-phase studies 51
1.7.1.1	Rate of oxidation of styrene as a function of reactant concentration 52
1.7.1.2	Initiation of oxidation of styrene by styrene peroxide 53
1.7.1.3	Effect of various other additives on the rate of oxidation of styrene 53
1.7.2	Vapour-phase studies 56
1.8	<u>Present work</u> 58

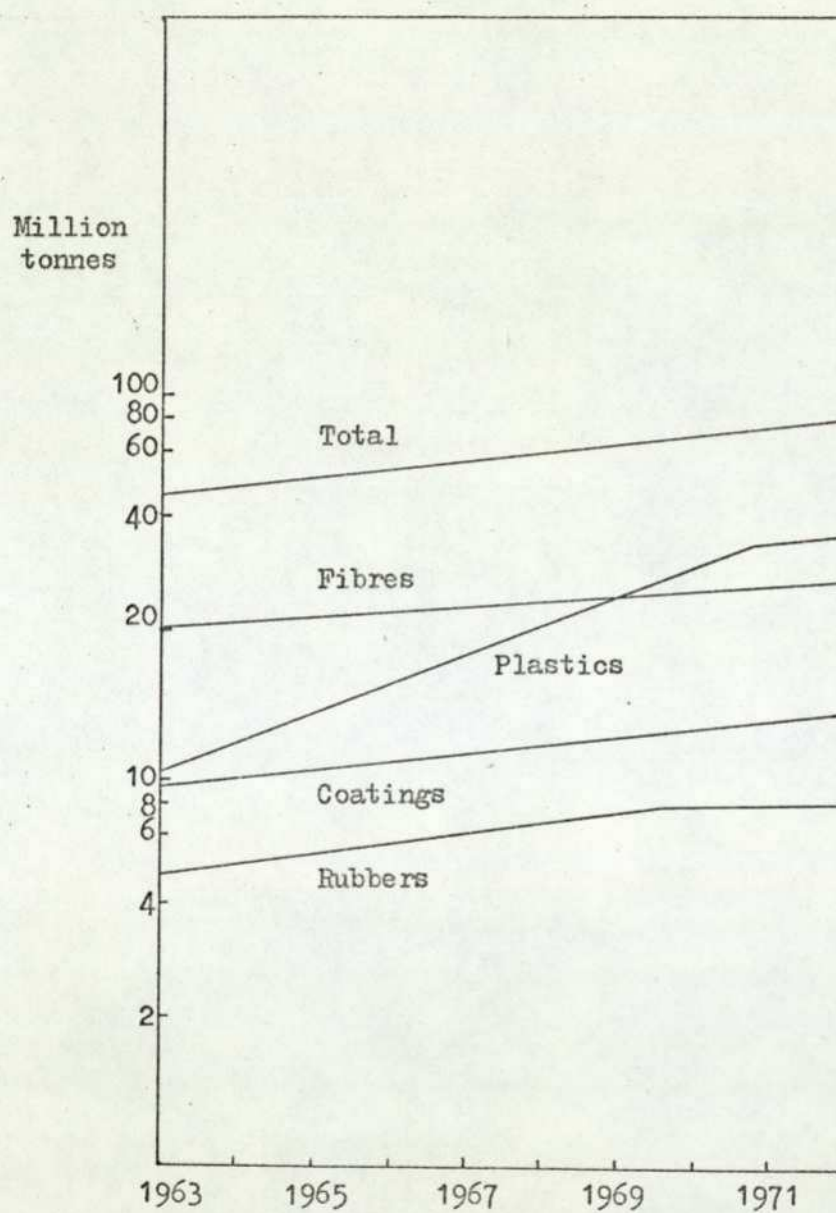
1.1

Introduction

Expansion of the chemical and chemical-processing industries over the last two decades has proceeded at a rate much higher than that for many other sections of industry. Production of polymers for example has grown steadily over the last ten years (Figure 1.1).¹ Styrene-type monomers, including styrene, vinyltoluene, α -methylstyrene and divinylbenzene, have been used in ever-increasing quantities in the synthesis and manufacture of plastics, coatings, resins, latexes and rubbers. As a result too of appreciable advances in polymer technology and of the competitive nature of industry, there has been a dramatic increase in the scale of plant and in the complexity of associated processes. In consequence, considerably larger quantities of chemicals involved in polymer production are being stored and this in turn has led to a rise in potential hazards, foremost among which is perhaps that of fire and explosion, as indicated by the frequency and cost of accidents in the chemical process industry generally.

Explosion of unconfined vapour clouds produced by the evaporation or dispersion of flammable liquids or vapours is a growing problem, mainly on account of the increasing extent of spillages in recent years. Unchecked explosions of combustible gases or gas mixtures inside or outside buildings and installations continue to cause substantial damage. Strehlow² has shown that damage due to the explosion of unconfined gas clouds is increasing.

On 4th January, 1966, at Feyzin in France, a 2 in. valve on a large liquid butane tank became stuck in the open position. Explosion and subsequent fire burned fire-fighters 330 yards away. Seventeen people were killed and refinery damage was extensive³.

Figure 1.1World Polymers Production

At Crescent City, Illinois, a train containing ten 33,000-gallon tank cars was derailed in the town on 2nd June, 1970. A vapour-cloud explosion initiated a fire and subsequent explosions effectively destroyed the business section. No fatalities were reported⁴.

On 22nd January, 1972, at East St. Louis, Illinois, a tank car containing propylene was pierced during humping operations. There was at least a 5-minute delay prior to ignition. However the resulting blast caused an estimated 6.5 million dollars damage to railroad property.

Other incidents have been reported subsequent to the publication of Strehlow's review². One of the more notable of these was the explosion which took place at the Shell Refinery at Pernis, Holland, on 28th January, 1968. Two people were killed, nine were admitted to hospital and 76 were slightly injured. The explosion and fire caused considerable damage to neighbouring installations at the nearby towns of Vlaardingen and Hoogrliet⁶.

The cost of losses in life and property in the United Kingdom has, over the last twenty years, increased in proportion to the square of the growth of the National Product⁷. This is exemplified by the Flixborough disaster in 1974. Twenty-eight people were killed and thirty-six others received serious injuries. Outside the Works, injuries and damage were widespread but no one was killed. Property damage extended over a wide area and a preliminary survey showed that 1,821 houses and 167 shops and factories had suffered to some extent⁸.

Clearly, the presence of highly flammable liquids and vapours in manufacturing processes constitutes a major risk in industry. Offord⁹ has pointed out that the actual area potentially at risk in any particular works will generally depend upon the following factors:

- (i) The physical characteristics of the liquids and gases stored and used.
- (ii) The conditions of storage and usage.
- (iii) The likelihood of spillage or leakage taking place during normal storage and working operations.
- (iv) The presence of hazards in an adjacent process or storage area.

These factors have to be taken into account in order to be able to make an initial yet realistic assessment of hazard areas.

1.2 Storage of styrene-type monomers

Styrene has become one of the most important materials employed in plastics and coatings. However, the same chemical reactivity and chemical constitution, which allow styrene monomer to polymerise readily into a desirable end-product, also creates certain problems in its handling and storage.

1.2.1 Polymerisation aspects of storage

Styrene polymerises readily at elevated temperatures and it therefore tends to become viscous on storage. The time scale involved may vary from a month to several years, depending on the ambient temperature and on the amount of air in contact with the monomer. For this reason, phenolic inhibitors, such as p-tert-butylcatechol (T.B.C.), are added in order to prevent polymerisation during shipment and subsequent storage. The monomer usually contains 10-15 ppm of such inhibitors.

Inhibitors of the above type are sensitive to oxygen. A small amount of oxygen usually activates the inhibitor and results in a larger polymerisation-free storage time. However, excess oxygen eventually destroys the inhibitor and results in increased aldehyde and peroxide formation. Table 1.1 shows induction periods for styrene monomer containing 5 and 10 ppm T.B.C. at different elevated temperatures. The induction periods represent the length of time taken for the viscosity of styrene to increase by 1% due to the formation of polystyrene.¹⁰

Table 1.2 shows the formation of polymer and aldehyde in the styrene monomer stored at room temperature under air and nitrogen with and without inhibitor present. From this table it is evident that T.B.C. provides adequate protection against polymerisation of styrene under most shipment and storage conditions, and also reduces the formation of aldehydes.¹⁰

Table 1.1

Effect of inhibitors on styrene polymerisation
at various temperatures

Temperature (°C)	Induction period (min)		
	No inhibitor	5 ppm TBC	10 ppm TBC
60	50-55	4200-4800	-
80	7-12	355	450
100	2-4	20-23	70-75
120	0-4	4-7	5-7

Table 1.2Stability of Styrene Monomer in Storage

(a) Stored under nitrogen at 25°C

Time in Days	% Polymer		% Aldehyde	
	No Inhibitor	50 ppm TBC	No Inhibitor	50 ppm TBC
2	0.6	--	0.010	0.010
4	--	--	0.010	0.010
6	--	--	0.010	0.010
8	1.0	--	0.010	0.010
10	1.6	--	0.010	0.010
12	1.6	--	0.010	0.010
14	--	--	0.010	0.010
16	4.0	--	0.010	0.010
18	--	--	0.010	0.010
20	5.0	0.2	0.010	0.010
25	5.2	0.3	0.020	0.020
(b) Stored under air at 25°C				
2	0.6	--	0.040	0.010
4	1.0	--	0.080	0.010
6	1.6	--	0.100	0.010
8	2.0	--	0.110	0.010
10	2.9	--	0.140	0.010
12	4.2	--	0.160	0.010
16	6.9	--	0.210	0.010
20	11.0	--	0.240	0.010
25	16.0	0.2	0.320	0.010

Vinyltoluene monomer also polymerises readily at elevated temperatures. It has a greater absolute rate of polymerisation at 100°C than styrene. The presence of the methyl group lowers the activation energy of the polymerisation process (71 - 79 kJ mole⁻¹ for vinyltoluene compared with ca. 88 kJ mole⁻¹ for styrene)¹¹.

α - Methylstyrene differs from styrene in its polymerisation behaviour. This compound does not polymerise readily in the presence of radical-producing initiators such as heat, light, or peroxides. However ionic initiators will successfully induce polymerisation e.g. sulphuric acid, stannic chloride, metal powders and sodium to name a few. Usually, 10 ppm T.B.C. are added to the monomer for shipment and storage purposes¹¹.

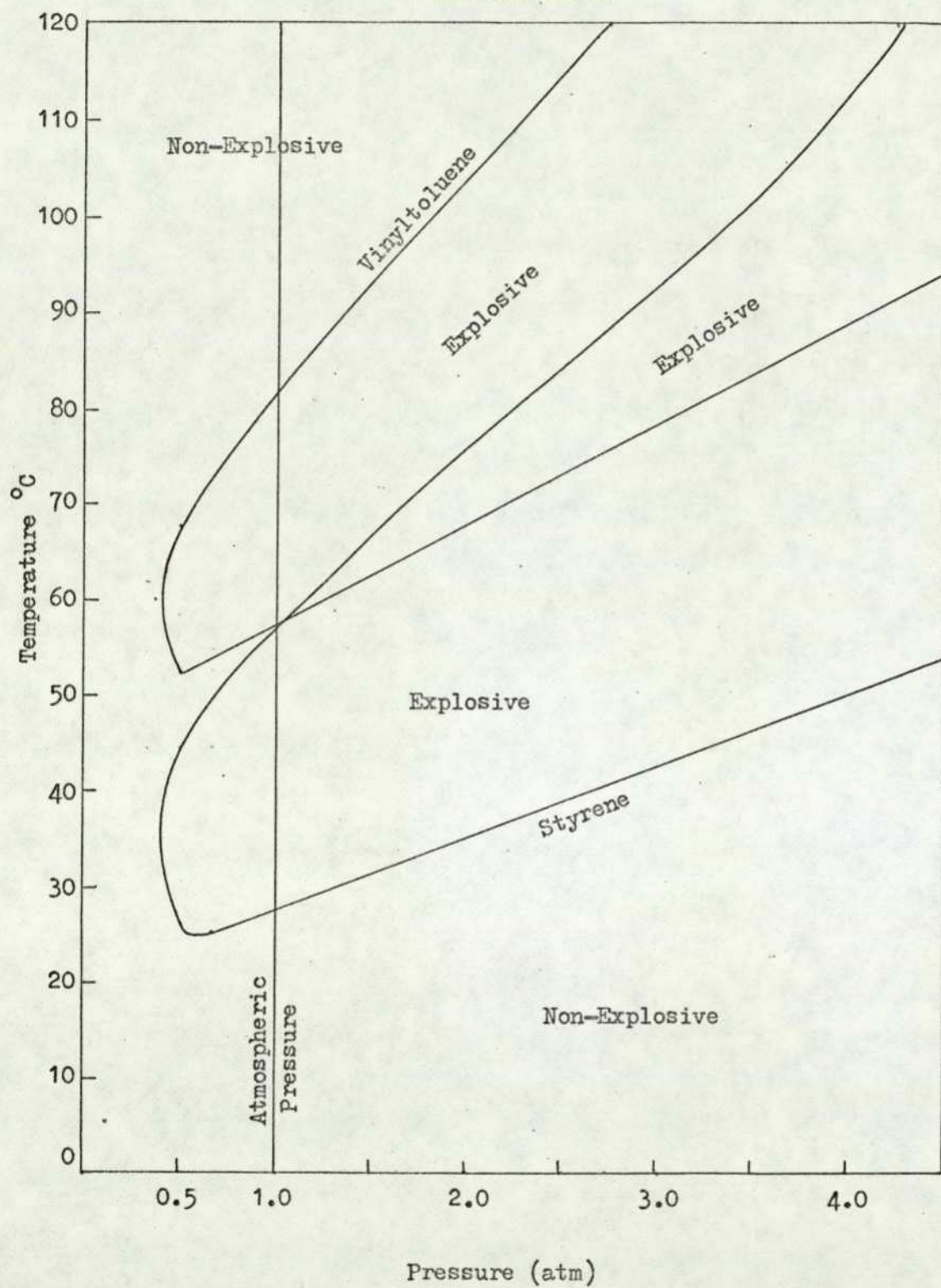
Divinylbenzene is appreciably less stable than styrene. For this reason it contains about 1000 ppm T.B.C. which is claimed to be sufficient for storage and handling for up to thirty days at temperatures below 32°C. Dissolved oxygen is required for the effective inhibition of polymerisation and, owing to the high reactivity of divinylbenzene, this monomer is usually stored under refrigerated conditions¹².

1.2.2 Flammability aspects of storage

Styrene is the only one of the styrene-type monomers which will form explosive mixtures at room temperature. Thus the danger of fire and explosion are, in many real situations, greatest with this compound. Figure 1.2 shows the approximate explosive limits of styrene and vinyltoluene over a range of pressures and temperatures which could be encountered during vacuum and pressure-impregnating operations.¹² While the actual operating conditions may lie outside the explosive limits, the vapour system may pass through the explosive region in reaching the desired operating conditions. The lower explosive limit is 1.1% by volume and the upper limit is 6.1% by volume, both in air. The percentage of styrene present in air at various

Figure 1.2

Approximate Explosion Limits of Styrene
and Vinyltoluene



temperatures and pressures is given in Table 1.3. The dotted lines in this table indicate approximate explosion limits. At pressures below 0.4 atmospheres, explosive mixtures would not be likely to be formed at any concentration of styrene vapour.¹⁰ The explosive limits of styrene in air are fairly similar to those of related aromatic hydrocarbons as shown in Table 1.4.¹⁰

The higher boiling points and lower vapour pressures of vinyltoluene and divinylbenzene make it difficult to produce explosive mixtures of these compounds with air at room temperature. Tables 1.5 (a) and (b) list data pertinent to the safe handling of these two monomers.¹⁰

1.3 Liquid-phase polymerisation of styrene and related monomers

Various reasons, such as its ready availability, commercial importance and reproducible polymerisation kinetic behaviour, have resulted in styrene being probably the most extensively studied monomer. The results of the first systematic kinetic investigations of the uncatalysed polymerisation of styrene were published in 1937.¹³

Although studies of the polymerisation kinetics of compounds related to styrene would have been of interest, the difficulties involved in the preparation of the pure compounds, together with their relatively low industrial importance, are mainly responsible for the fact that only two such monomers have been the subject of detailed study, viz. p-methoxystyrene¹⁴ and 4-vinylpyridine.¹⁵

1.3.1 Uncatalysed thermal polymerisation of styrene

During the late 1930's and 1940's, a number of investigations were reported which described the spontaneous polymerisation of vinyl and diene monomers.¹⁶ In many cases, however, the observed polymerisation was initiated by traces of peroxide formed in contact with air, or by

Table 1.3

Volume Percent Styrene Vapour in Air at Various
Temperatures and Pressures

Temperature		Absolute Pressure in Atmospheres					
°C	°F	0.25	0.50	1.0	2.0	4.0	8.0
0.0	32.0	0.68	0.34	0.17	0.085	0.043	0.021
10.0	50.0	1.37	0.68	0.34	0.17	0.086	0.042
20.0	68.0	2.58	1.29	0.65	0.32	0.16	0.080
29.3	85.0	4.40	2.20	1.10	0.55	0.27	0.14
30.0	86.0	4.52	2.26	1.13	0.56	0.28	0.14
40.0	104.0	7.84	3.92	1.96	0.98	0.49	0.25
50.0	122.0	12.9	6.44	3.22	1.61	0.81	0.40
60.0	140.0	20.5	10.3	5.13	2.57	1.28	0.64
63.5	146.3	24.4	12.2	6.10	3.05	1.53	0.77
70.0	158.0	32.2	16.1	8.03	4.02	2.01	1.00
80.0	176.0	49.6	24.8	12.4	6.20	3.10	1.55
90.0	194.0	71.6	35.8	17.9	8.95	4.47	2.24
100.0	212.0	100.0	50.4	25.2	12.6	6.30	3.16

NOTE: Region inside dotted lines represents approximate explosion limits.

Table 1.4Explosive Limits in Air for Styrene Monomer and Related Materials

<u>Fuels</u>	Explosive Limits (% volume in air)	
	Lower	Upper
Benzene	1.4	8.0
Toluene	1.27	7.0
Ethylbenzene	1.2*	6.8*
Styrene	1.1	6.1

* Approximate values

Table 1.5

(a) Properties of vinyltoluene pertinent to its safe handling

Boiling Point (101.3 kNm^{-2})	171.88°C
Flash Point	65°C
Fire Point	68.3°C
Explosive limits in air ($@ 70^{\circ}\text{C}$)	1.9%
lower limit % volume	
Vapour Pressure ($\text{Nm}^{-2} @ 20^{\circ}\text{C}$)	147 Nm^{-2}
Inhibitor: p-tert-butylcatechol	10-15 ppm

(b) Properties of divinylbenzene (DVB) pertinent to its safe handling

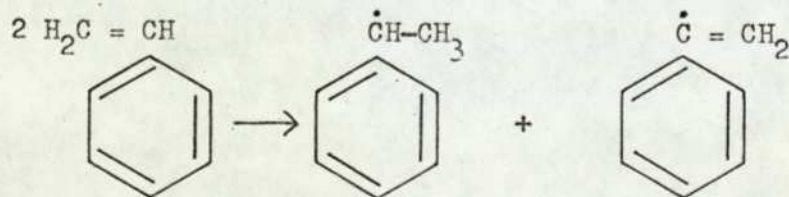
	m-DVB	p-DVB
Boiling Point (101.3 kNm^{-2})	180°C	195°C
Flash Point	57°C	73.89°C
Fire Point	57°C	76.67°C
Explosive limits in air ($@ 65^{\circ}\text{C}$)	1.1-1.5%	1.2-1.6%
lower limit % volume		
Vapour Pressure ($\text{kNm}^{-2} @ 75^{\circ}\text{C}$)	1.3 kNm^{-2}	4 kNm^{-2}
Inhibitor: p-tert-butylcatechol	1000 ppm	1000 ppm

other impurities present in the monomer. In only one instance was there unequivocal evidence for a reproducible rate of thermal polymerisation, and this was found for styrene.^{13,17-21} The work of Foord²² and others showed that the polymerisation was free-radical in character. Despite a phenomenal number of investigations of the thermal polymerisation of styrene, there is still some doubt as to the mechanism of initiation of this polymerisation. Most of the work carried out before 1966 has been summarised by George.²³ The various initiation theories which have been proposed have recently been critically reviewed by Ebdon.²⁴

1.3.1.1 Bimolecular initiation theories

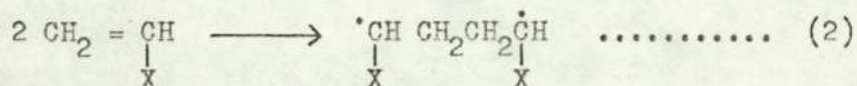
Investigations of the rates of thermal polymerisation of styrene in various solvents over a range of concentrations have shown that the overall rate is second order with respect to the monomer.^{18,19,21} However, an apparent first-order dependence was observed for the bulk polymerisation of styrene.¹⁷ This latter finding has been attributed either to a lowered reactivity of the monomer in the polymerising system²⁵ or to the occurrence of a slight gel effect.²⁶

Bimolecular formation of two monoradicals from two styrene molecules²⁷ has not been seriously considered as a possible mode of initiation of thermal polymerisation.²³



Such a reaction, while being energetically feasible²⁷, would involve the transfer of a hydrogen atom from the α -position of a styrene molecule. However, no evidence of a primary isotope effect has been obtained in the thermal polymerisation of α -deuterostyrene.^{28,29}

Flory³⁰ has proposed the bimolecular formation of a tail-to-tail biradical as the initiation step. The biradical was expected to propagate from both ends to yield polymer of high molecular weight:



(X = C₆ H₅ for styrene)

Walling²⁷ estimated that such a reaction would be exothermic by as much as 41.8 kJ mole⁻¹ in the case of styrene, owing to a considerable resonance stabilisation of the resulting biradical. The theory of biradical initiation and propagation has however come under considerable criticism.

Evidence against biradical propagation, with termination by recombination, has been obtained from measurements of the molecular weight distribution of thermally prepared polystyrenes.³³ Propagation and termination reactions of this type (in the absence of cyclisation and appreciable chain-transfer) should produce radical-ended polymer chains which have a very broad and flat molecular weight distribution.³⁴ Such distributions are not found in practice. A normal molecular weight distribution would be produced only if termination of biradical chains occurred by disproportionation.³⁴ However, disproportionation is not the main mode of termination in the conventional monoradical-initiated polymerisation of styrene and there is no evidence to suggest that propagating styrene biradicals would behave differently.

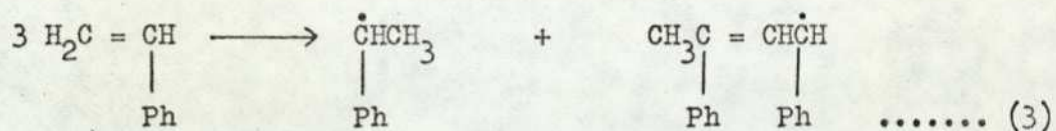
Whilst biradicals may not be involved in the propagation of styrene polymerisation, they may nevertheless be formed initially and then undergo transfer reactions to give pairs of monoradicals. Several attempts have been made to initiate the polymerisation of styrene with compounds yielding biradicals on decomposition. Among the compounds investigated have been cyclic peroxides³⁵⁻³⁷, cyclic azo compounds³⁸⁻⁴⁰, cyclic

disulphides⁴¹ and polysubstituted hydrocarbons.⁴² Most have proved to be poor initiators, while those which were found to be efficient (cyclic peroxides, such as dihydroascaridole⁴³ and cyclohexanone peroxide^{36,43}) decompose to give pairs of monoradicals. Prevailing evidence thus points to the fact that biradicals do not participate in either the initiation or propagation steps of styrene polymerisation.

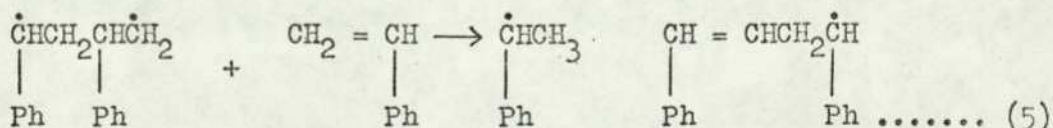
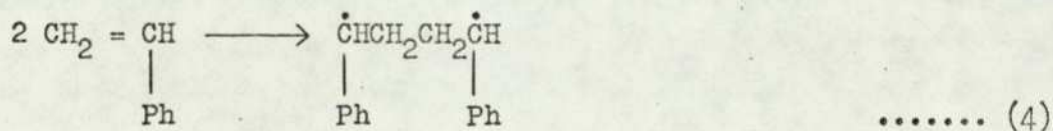
1.3.1.2 Termolecular initiation theories

Other theories of styrene initiation have been based on the rates of thermal polymerisation in solutions containing various concentrations of the monomer in refluxing bromobenzene. Mayo⁴⁴ isolated two major products from the reaction. One was a polymer of high molecular weight, for which the overall order of formation was $5/2$; the other was a low molecular weight oligomer. Previous estimates^{18,19,21} of an overall order of 2 were attributed to a failure to recognise the existence of the two types of product.

An order of $5/2$ suggests that the initiation step is third order with respect to the monomer. Mayo⁴⁴ thus proposed the formation of monoradicals from three molecules of styrene:

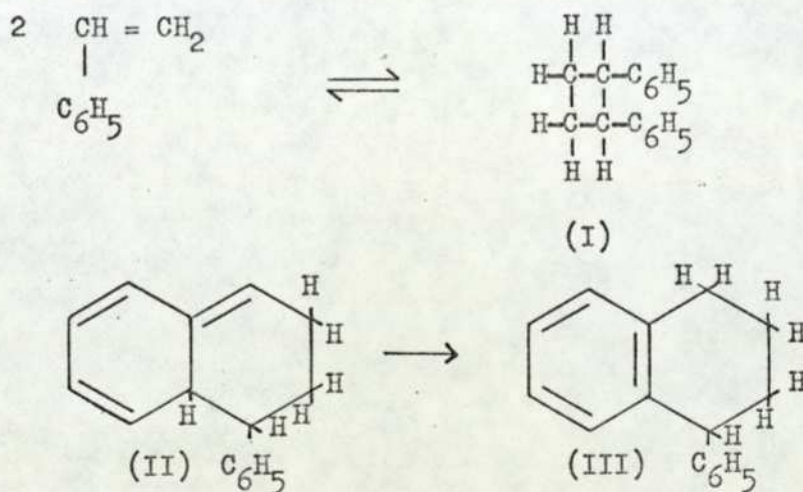


However, termolecular reactions are rare⁴⁵ and a more reasonable assumption is that initiation is a two-step process involving reversible inefficient bimolecular formation of a biradical followed by a rapid transfer reaction:



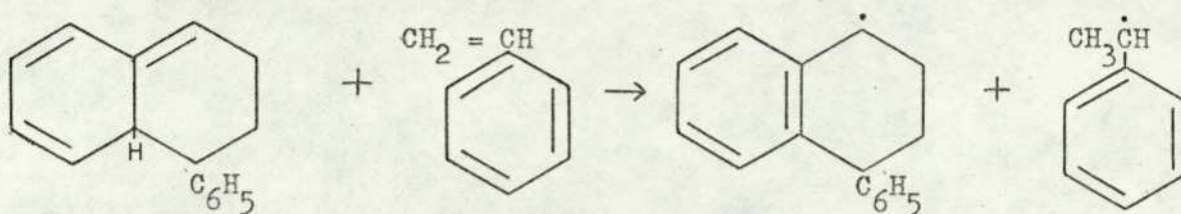
Both these schemes have come under criticism. Mayo's scheme⁴⁴ involves the transfer of a hydrogen atom from the α - position of a styrene molecule, but rate measurements with α - deuterostyrene do not support this.^{28,2} The second mechanism involves the transfer of hydrogen from the β - position of a styrene molecule. This has also not been justified by experiments involving isotopically labelled styrene.^{29,46} For this latter mechanism, the biradical would have to possess specially high reactivity towards styrene, because the rate of transfer to the monomer of polystyryl radicals is only about 10^{-5} times the rate of propagation.

A recent proposal regarding the thermal initiation of styrene polymerisation is based on characterisation of the low molecular weight products formed concurrently with the polymer both in bulk⁴⁹ and in bromobenzene solution.⁴⁸ The low molecular weight fraction consists mainly of two dimeric products: 1,2-diphenylcyclobutane (I) and 1-phenyltetralin (III). Mayo proposed the following dimerisation reactions:



The 1-phenyltetralin was believed to be formed by aromatisation of a previously formed bicyclic triene (II), which in turn was assumed to take part in the initiation of polymerisation.^{47,48} The reaction sequence postulated is shown below (only the ring hydrogen involved in the transfer

step is shown for clarity):



Such a process satisfies the apparent termolecular nature of the initiation step and does not require the prior formation of a biradical. This mechanism has been supported by the observation that the rate of initiation of the thermal polymerisation of 2,4,6- trideutero-styrene is markedly lower than that of styrene.^{28,29}

The controversy over initiation mechanisms involving biradicals is by no means finished. Variations of the original theory have recently been reported.²³ However no firm substantiation of the occurrence of biradical initiation has yet been obtained.

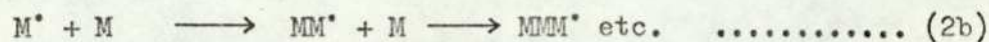
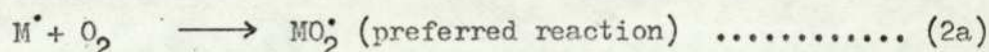
1.3.2 Polymerisation in the presence of air

When compared with polymerisation in the absence of air or oxygen, results with air-contaminated monomer have shown that (i) induction periods were shorter, (ii) higher rates of polymerisation were observed, (iii) polymers of lower chain-length were formed in the initial stages of polymerisation, and (iv) higher chain-length polymers were generated in the later stages.⁵⁰

Barnes⁵¹ related the catalytic action of oxygen to peroxide formation. The presence of peroxides in many vinyl compounds had been observed previously by various investigators.^{52,53} Moureu and Dufraisse^{54,55} established that it was combined oxygen rather than oxygen itself which catalysed the polymerisation of acrolein. In the complete absence of

oxygen, many vinyl monomers either fail to polymerise altogether or do so very slowly.⁵⁴

However, during photopolymerisation, oxygen exercises an inhibiting action. Barnes⁵¹ explained this by assuming that peroxide formation occurs in preference to polymerisation in accordance with the following scheme:



where M represents the monomer molecule, $M^{\bullet}$ is the corresponding free radical and $MO_2^{\bullet}$ is a peroxide. It was further assumed that the peroxide catalyses the reaction by generating $M^{\bullet}$ and that these molecules exhibit preferential reactivity towards oxygen.

1.4 Vapour-phase polymerisation of styrene and related monomers

The earliest investigation of dimerisation in the vapour-phase, namely that of ethylene, was carried out by Pease,⁵⁶ who found that at temperatures of 350–500°C and pressures of 202.6–1013 kNm⁻², butadiene was formed. The volume of this product was somewhat smaller than half that of the ethylene consumed, so that some higher polymers were also formed.

Compounds containing conjugated double bonds have been found to dimerise more readily than ethenoid compounds, but the products assume a variety of structures depending on the conditions of polymerisation.

Polymers formed in the reactions involving ethenoid gases were found to be of low molecular weight. This was attributed⁵⁷ to the fact that the high activation energy of the interaction of free radicals and hydrocarbon molecules prevents the formation of long chains before the

radicals are destroyed. Various methods for the promotion of reactions included photochemical and free-radical initiation, but purely thermal polymerisation could not be induced.

The most important factor in vapour-phase polymerisation is that the reactions, which are initially homogeneous, quickly become heterogeneous since, as polymers grow in size, they start to constitute a new phase in the system. Thus, instead of the monomer molecules simply colliding with the growing polymer, they are "absorbed" into the polymer particle, within which reaction subsequently takes place. In addition, the mechanism of termination is more complex. The amount of quantitative information available is therefore limited.

Studies⁵⁸ of vapour-phase polymerisation have been carried out in static systems by following pressure changes and occasionally analysing the products. Vinyl acetate decomposes at about 360°C but measurable polymerisation was observed at pressures below atmospheric. Methylacetylene does not polymerise readily even at 475°C at which appreciable decomposition starts to occur. Styrene is stable up to about 400°C, at which temperature slow reaction starts to occur accompanied by a decrease in pressure. The reaction apparently ceases after a small pressure change. At a slightly higher temperature, 420°C, an increase in pressure is observed, indicating the predominance of decomposition. No explanation has been given for the initial decrease in pressure.⁵⁸

A subsequent study of the vapour-phase polymerisation of styrene was reported by Mark and Breitenbach.⁵⁹ These workers found that gaseous styrene polymerised between 220 and 311°C. With increasing temperature, dimerisation apparently became more important. At 311°C, the polymerisate consisted entirely of unsaturated dimers. Table 1.6 shows the

Table 1.6Vapour-phase polymerisation of styrene

Temp ($^{\circ}\text{C}$)	Initial Pressure (kNm^{-2})	Pressure drop $\text{kNm}^{-2}/\text{hr}$
150	97	2.7
	115	9.3
175	97	1.5
	133	3.1

pressure changes observed at 150 and 175°C for various initial pressures of monomer vapour. Even above atmospheric pressure, vapour-phase polymerisation was relatively slow.⁵⁹

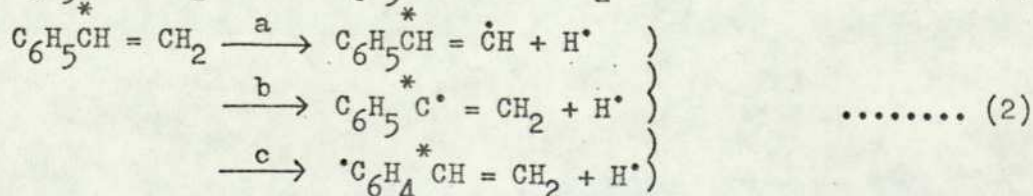
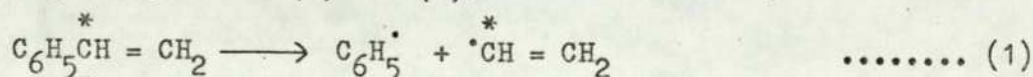
1.5 Pyrolysis of styrene and saturated aromatic hydrocarbons

During combustion at high temperatures, many fuel molecules tend to decompose before reacting with oxygen. Pyrolytic processes are therefore often relevant to high temperature oxidation reactions.

Berthelot⁶⁰ found that styrene gave acetylene and benzene when passed through a red-hot porcelain tube. Subsequent investigations⁶¹ showed that a 99% recovery of styrene is obtained following heating at 550°C and a 95.3% recovery after heating at 625°C.

Badger and Buttery⁶² decomposed styrene by passing the vapour mixed with nitrogen through a silica tube at 710°C. The major products included benzene (6.4), toluene (3.3), ethylbenzene (1.6), indene (0.4), naphthalene (6.1), diphenyl (1.6), dibenzyl (0.9), fluorene (1.3), stilbene (1.3), phenanthrene (11.1), anthracene (0.3) and 2-phenylnaphthalene (2.5), the values in brackets representing percentage yields by weight. Contrary to the findings of Berthelot⁶⁰, no acetylene was detected. It was proposed that the high temperature reaction leading to these products were predominantly free radical in nature.⁶²

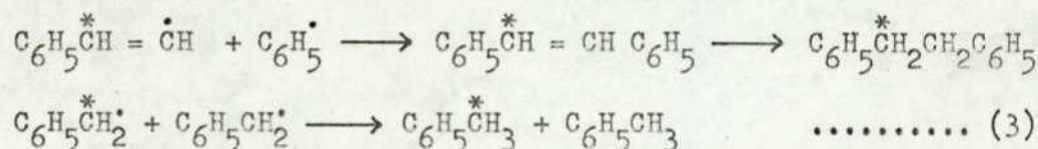
Subsequently, Badger et al.⁶³ further investigated the pyrolysis of styrene at 710°C using 1-¹⁴C styrene. It was suggested that the primary free radicals formed in the decomposition of styrene arose by random C-H scission in the side-chain and ring, and by C-C bond cleavage in the side chain, according to equations (1) and (2).



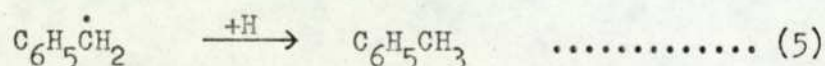
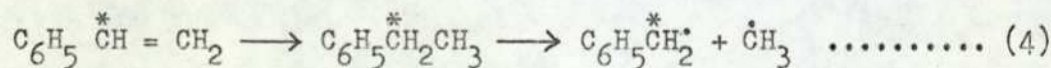
The bonds broken have comparable bond dissociation energies and the random formation of free radicals is thus feasible.

Benzene was a major constituent of the pyrolysate.⁶³ Its formation may be accounted for by assuming C-C bond fission in accordance with equation (1) followed by abstraction of hydrogen by the phenyl radical.

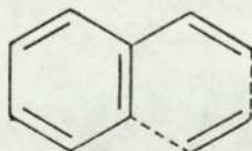
Toluene, which was also a major product,⁶² was thought to be formed by the reaction between a styryl radical and a phenyl radical followed by hydrogenation to dibenzyl, and subsequent cleavage to two benzyl radicals (equation 3).



An equally plausible suggestion⁶³ involved hydrogenation of styrene to ethylbenzene, followed by cleavage to a benzyl radical and a methyl radical (equation 4) and subsequent abstraction of hydrogen according to equation (5).



Among the polynuclear hydrocarbons, naphthalene was found⁶³ to be a major product of the pyrolysate. This compound is probably formed by a reaction between the styryl radical, $\text{C}_6\text{H}_5\dot{\text{C}}\text{H} = \dot{\text{C}}\text{H}$ and either ethylene or a vinyl radical, $\text{CH}_2 = \dot{\text{C}}\text{H}$, followed by ring closure and dehydrogenation (I)



(I)

Other investigations have also been carried out on the formation of arenes from other aliphatic and aromatic hydrocarbons.^{64,65} Generally,

mechanisms involving radical recombination and chain propagation have been used to explain product formation.⁶³⁻⁶⁷

More recent work⁶⁸ on the pyrolysis of stable aromatic systems containing the $\text{Ph} - \text{CH} = \text{CH}-$ structure, has shown that the products obtained from the pyrolysis of styrene are similar to those reported by Badger.^{62,63} Styrene was pyrolysed in the range $500 - 900^\circ\text{C}$ ⁶⁸ and the results in Table 1.7 indicate that this compound is relatively stable up to 700°C . Table 1.7 also shows the nature and complexity of the decomposition products.

1.6 The vapour-phase oxidation of saturated aromatic hydrocarbons

Investigations into the vapour-phase oxidation of aromatic hydrocarbons have not been as extensive as those carried out with aliphatic hydrocarbons. Early investigations by Fort and Hinshelwood,⁶⁹ and later by Amiel,^{70,71,72} showed that the slow combustion of benzene bore a general resemblance to that of ethylene. Fort and Hinshelwood⁶⁹ concluded that benzene is oxidised by a chain mechanism, the chains being initiated predominantly in the gas phase.

Newitt and Burgoyne⁷³ carried out a comparative study of the slow oxidation of benzene, toluene and ethylbenzene at high pressures with a view to determining the relative reactivities of the side chain and nucleus. The results suggested that, whilst in the case of benzene the formation of a single series of hydroxy-intermediates preceded the breakdown of the ring, with toluene and ethylbenzene, both nuclear and side-chain reactions occurred simultaneously. The phenyl group in ethylbenzene appeared to increase the reactivity towards oxygen of the α -carbon atom of the side chain.⁷³

Burgoyne⁷⁴ later studied the oxidation of benzene and a series of its derivatives at subatmospheric pressures. Comparative investigations

Table 1.7

Relative Concentrations, (wt %) of the Products
of Pyrolysis of Styrene

Products	700°C	800°C	900°C
Benzene	0.40	2.44	8.90
Toluene	0.31	3.50	2.41
Ethylbenzene	0.21	2.54	0.34
Styrene	95.31	68.22	28.05
Indene	0.06	1.02	2.38
Napthalene	0.15	3.05	16.14
Biphenyl	0.01	0.82	8.65
Diphenylmethane	0.02	0.25	0.69
Acenaphthalene		0.35	0.88
Fluorene	0.11	1.46	3.28
Dibenzyl	0.15	1.10	
trans - Stilbene	0.87	3.32	1.36
Phenanthrene	0.40	5.65	14.79
1-Phenylnaphthalene	0.28	1.75	2.54
Fluoranthene		0.05	0.77
Pyrene		0.11	1.05
1,2-Benzofluorene		0.10	0.11
Chrysene		0.33	1.26
Grams of neutrals/ grams of pyrolysand	0.72	0.40	0.35

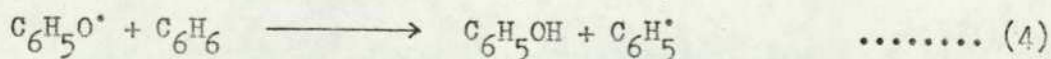
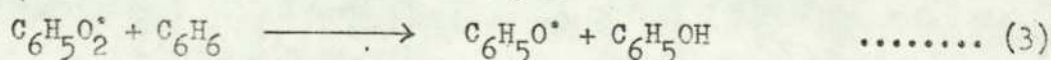
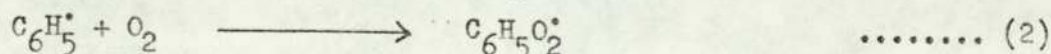
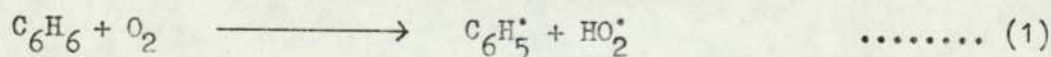
were carried out on benzene, toluene, ethylbenzene, n-propylbenzene, n-butylbenzene, o-, m- and p-xylenes and mesitylene. The results obtained confirmed the view that chain mechanisms are involved, but the kinetic characteristics of benzene oxidation were found to be somewhat different from those of its alkyl derivatives.⁷⁴

1.6.1 Vapour-phase oxidation of benzene

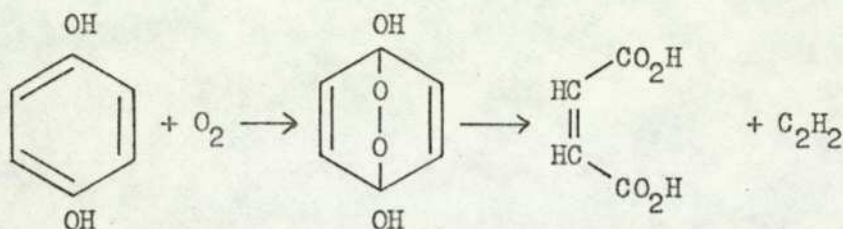
At a pressure of about 50 atm. benzene was found to react readily with oxygen at temperatures as low as 280°C. The principal products formed from mixtures containing an excess of hydrocarbon were phenol, oxides of carbon and steam.⁷³ Hydroquinone, quinone, maleic acid and formaldehyde were also found in smaller quantities. At higher temperatures, tarry products, together with free carbon, were deposited in the reaction vessel and gaseous products included hydrogen and methane; higher molecular weight - hydrocarbons such as diphenyl were also found.⁷³

The oxidation of benzene, unlike that of the aliphatic hydrocarbons, was not preceded by a marked induction period, but began almost immediately the mixture entered the reaction vessel. Ageing of the reaction vessel had relatively little effect.⁷³

At subatmospheric pressures, slow combustion occurred only above 450°C and the products included diphenyl, p-dihydroxybenzene, maleic acid, formaldehyde, formic acid, acetylene, ethylene, methane and hydrogen.^{73,75-77} It has been suggested that benzene undergoes successive hydroxylation followed by ring rupture. Norrish and Taylor⁷⁷ proposed a mechanism involving phenyl and phenylperoxy radicals, viz.



Phenol is then converted to dihydroxybenzenes by a similar mechanism, which is suggested by the results of a study of its oxidation.⁷⁸ The dihydroxy-compound formed then undergoes oxidation which leads to decomposition:



Further oxidation of acetylene leads to formaldehyde and formic acid and the reaction of the aldehyde with oxygen then gives rise to chain-branching. It has been suggested that diphenyl, which is formed in appreciable amounts, is unlikely to result from the reaction between phenyl radicals and benzene, since hydrogen atoms would be produced and the yield of hydrogen is quite small,⁷⁵⁻⁷ except at high temperatures. It was therefore proposed that phenyl radicals preferentially dimerised in the system and thus reacted much more slowly with oxygen than alkyl radicals.

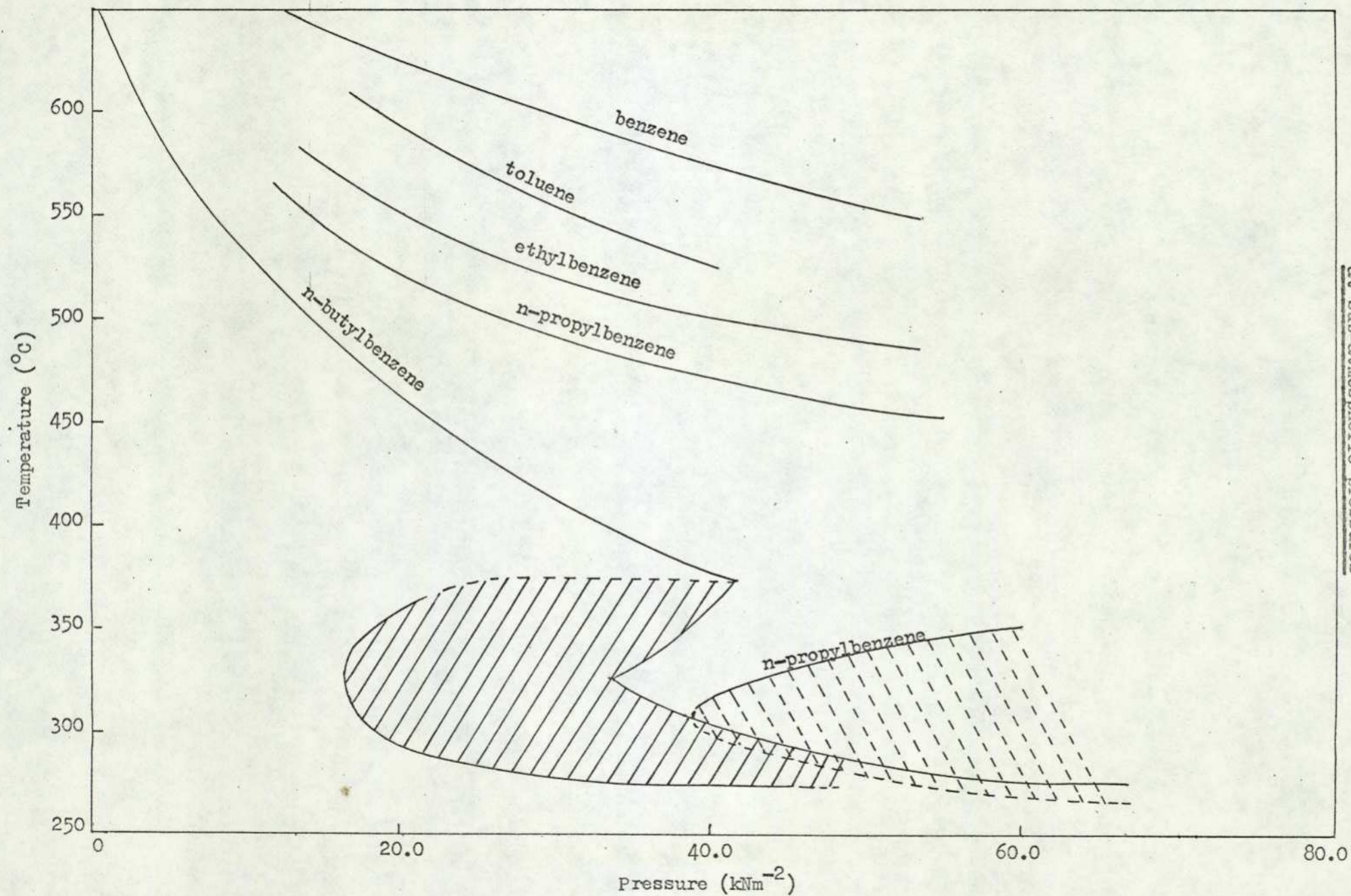
1.6.2 Vapour-phase oxidation of alkylbenzenes

1.6.2.1 Combustion phenomena

Burgoyne^{74,75,79,80} found that, in general, the kinetics of the oxidation of alkylbenzenes resembles that of alkanes, especially if the side-chain contains more than two carbon atoms. The oxidation of aromatic hydrocarbons (other than benzene) resembles that of aliphatic hydrocarbons in taking place by two distinct chain mechanisms, one predominant below 300°C and the other above 400°C. In the intervening range of temperature, the two mechanisms proceed concurrently. Intensification of the low-temperature reaction results in cool flames while at high temperatures, a chain-thermal ignition may occur. Figure 1.3, shows typical ignition

Figure 1.3

Ignition profiles of aromatic hydrocarbons
at sub-atmospheric pressures



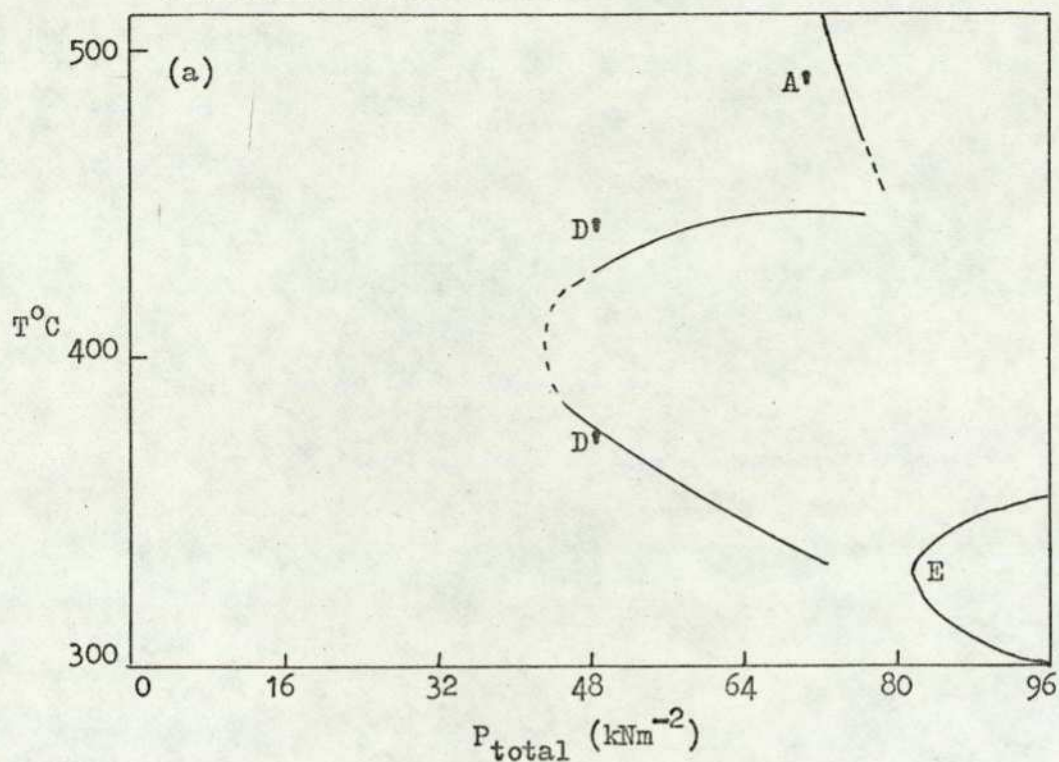
profiles obtained for some aromatic hydrocarbons including benzene.⁸⁰ The ignition profiles for benzene, toluene and ethylbenzene are of the same general shape as that for methane, the ignition temperature decreasing steadily with increasing pressure in each case. On the other hand the ignition profiles for n-propyl and n-butylbenzenes differ from those of the lower homologues due to the existence of a low-temperature peninsula.⁸⁰

Burgoyne, Tang and Newitt,⁸⁰ did not succeed in finding cool flames for benzene, toluene and ethylbenzene. However, all the aromatic hydrocarbons, except benzene, possessed a region of negative temperature coefficient. Norrish and Taylor⁸¹ later studied the oxidation of toluene and ethylbenzene under both static and flow conditions in the temperature range 285–425°C. Cool flames were observed during the oxidation of both these hydrocarbons. Such flames were recorded in mixtures containing 4 parts of hydrocarbon to 1 part of oxygen. Faint luminescence was observed even for a 2:1 hydrocarbon-oxygen mixture. Figure 1.4 shows the cool flame phenomena reported for toluene and ethylbenzene and, for comparative purposes, the region of cool flame oxidation for ethane has been included.⁸¹ The cool flame region of the aromatic hydrocarbons is shifted to somewhat higher temperatures and no periodic cool flame phenomena are observed. With toluene, the luminescence was reported to be considerably weaker than for the alkanes (except ethane) and with ethylbenzene the flash was found to be considerably brighter than for toluene.

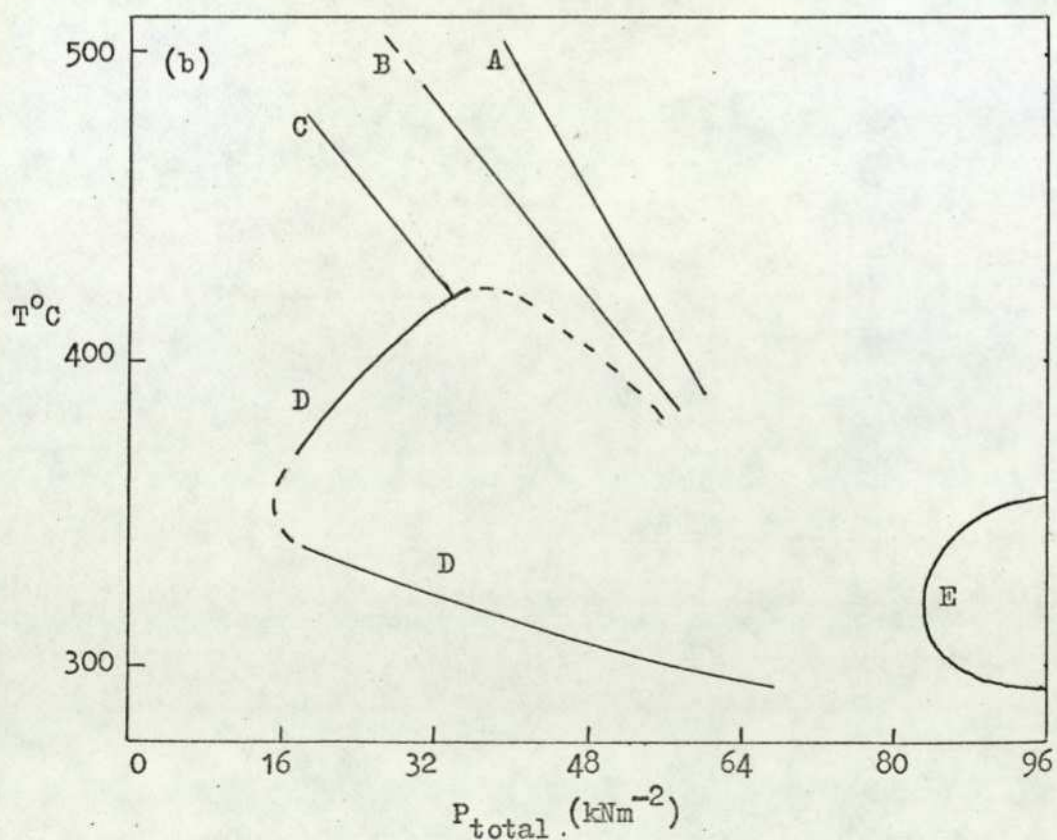
Results have shown that, at high pressures, benzene ignites with more difficulty than any of its derivatives or indeed methane.⁸⁰ Figure 1.5 shows ignition profiles for standard mixtures with air of benzene, toluene, ethylbenzene and n-propylbenzene. Corresponding data

Figure 1.4

Ignition profiles for (a) toluene and (b) ethylbenzene



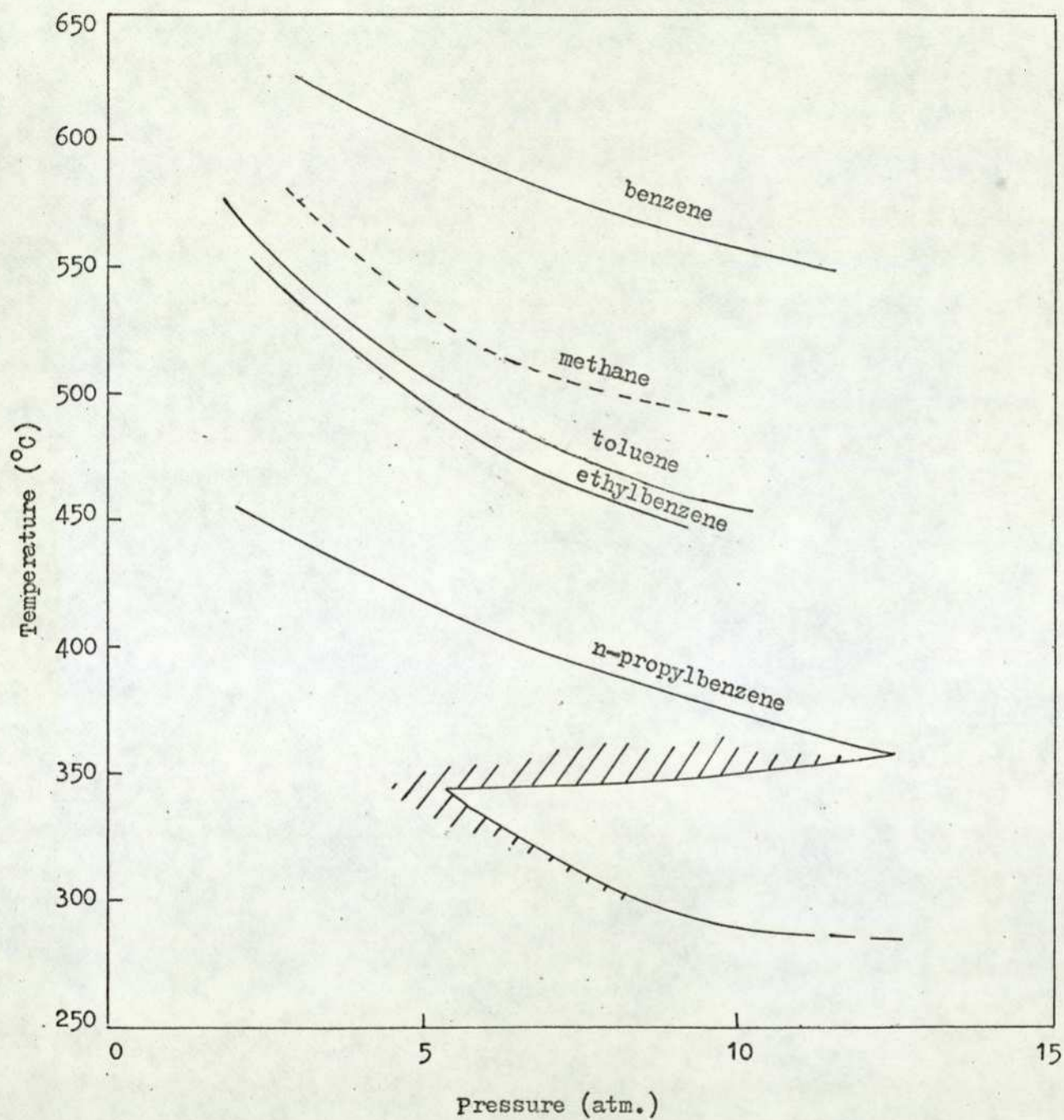
(a) A* : boundary of ignition region; D* : boundary of cool flame spontaneous ignition region; E : boundary of cool flame spontaneous ignition region of ethane



(b) A : boundary of spontaneous ignition region; B : boundary of the blue flame region and spontaneous ignition; C : boundary of blue flame region; D : boundary of cool flame spontaneous ignition; E : boundary of cool flame spontaneous ignition region for ethane

Figure 1.5

Ignition profiles of aromatic hydrocarbons at
high pressures



for a 15% methane-air mixture are included for comparative purposes.

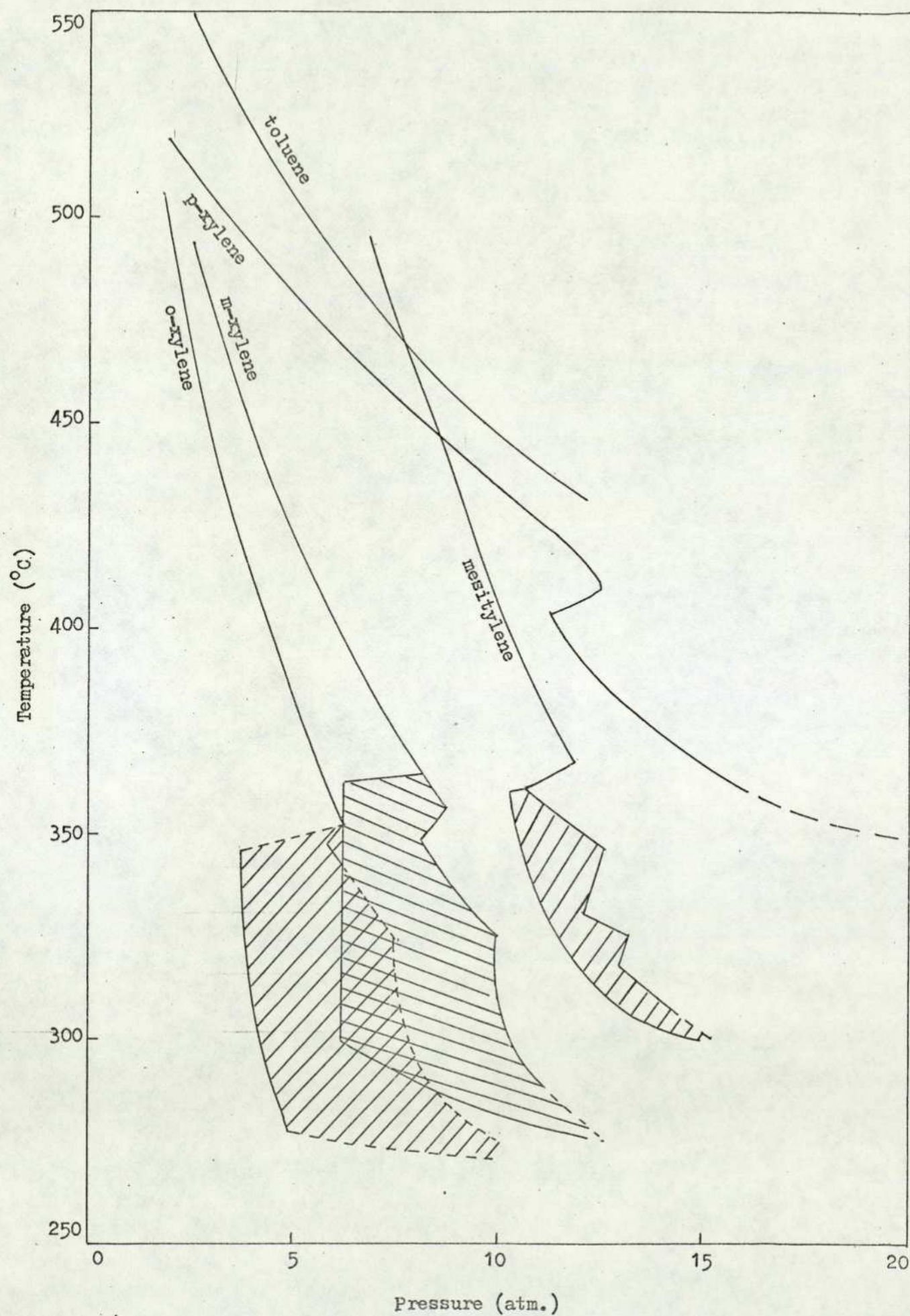
Clearly, the order of reactivity of the different compounds is the same as that observed at subatmospheric pressures. Except with n-propylbenzene, the ignition temperatures fall progressively with increasing pressure.

n-Propylbenzene exhibits characteristics which are associated with the higher alkanes. Figure 1.5 shows that this hydrocarbon has both upper and lower temperature ignition mechanisms. Evidence was also obtained for the passage of feeble cool flames but the boundaries of the cool flame zone were not established.⁸⁰

In an attempt to relate structure and reactivity, the ignition characteristics of o-, m- and p-xylenes were compared with one another and with that of the isomeric ethylbenzene.⁸⁰ The order of increasing reactivity was found to be para- < meta- ~ ortho-xylene. o- and m-xylenes possessed well-defined cool flame regions, whilst p-xylene exhibited no cool flames. Figure 1.6 shows the ignition profiles for the xylenes, mesitylene and toluene.⁸⁰ The low-temperature ignition regions of o- and m-xylene have two pressure minima, whilst p-xylene exhibits one pressure minimum and this at high temperature.

The gaseous oxidation of p-xylene was later investigated at low pressures by Barnard and Hawtin.⁸² Studies were carried out in a static system at temperatures between 460 and 512°C and no low-temperature ignition phenomena were reported.⁸² Subsequently, an extensive investigation of the preflame and ignition characteristics of 17 aromatic hydrocarbons was carried out by Salooja⁸³ using a flow system. The results for the extent of preflame reaction with all the fuels were presented in terms of the formation of carbon monoxide but it was suggested that the same general pattern would have been obtained if the criterion chosen had been formation

Figure 1.6

Ignition characteristics of dialkylbenzenes

of carbon dioxide or consumption of oxygen. Some typical results for benzene, o-xylene, isopropylbenzene and n-butylbenzene are shown in Figure 1.7. From the data obtained, relationships between the ease of combustion and molecular structure have been proposed.⁸³

1.6.2.2 Structure and reactivity

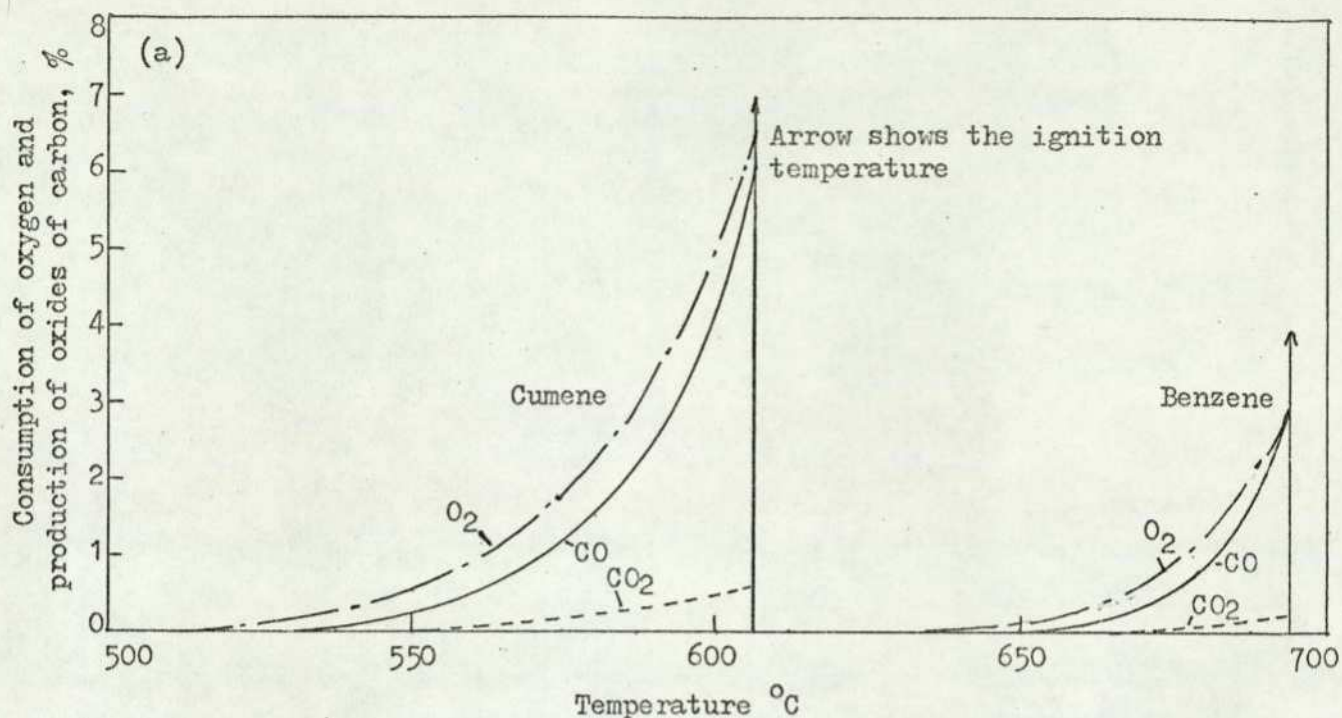
Results obtained by Burgoyne and Newitt⁷³ showed that the slow oxidation of benzene involved the formation of a single series of hydroxy-intermediates preceding the cleavage of the ring. With toluene and ethylbenzene, however, both nuclear and side-chain oxidations took place concurrently. Furthermore, it appeared that the phenyl group in ethylbenzene exposed the α -carbon atom of the side-chain to attack by oxygen.

In a subsequent investigation by Burgoyne, Tang and Newitt,⁸⁰ the ignition curves of aromatic hydrocarbons were shown to be analogous to those of the alkanes. Since all the aromatic fuels had saturated side-chains, there was some analogy with the behaviour of the alkanes, but little or no correlation with that of the alkenes. It was found that, with aromatic hydrocarbons, the transition between the high- and low-temperature ignition regions occurred at a temperature lower than that observed for the higher alkanes. The upper temperature limit of the cool flame zone was about 30° lower with the aromatic hydrocarbons. No generalisations were made with regard to the minimum pressure limits of ignition and the lower cool flame boundary since these were strongly dependent upon the nature of the fuel.⁸⁰

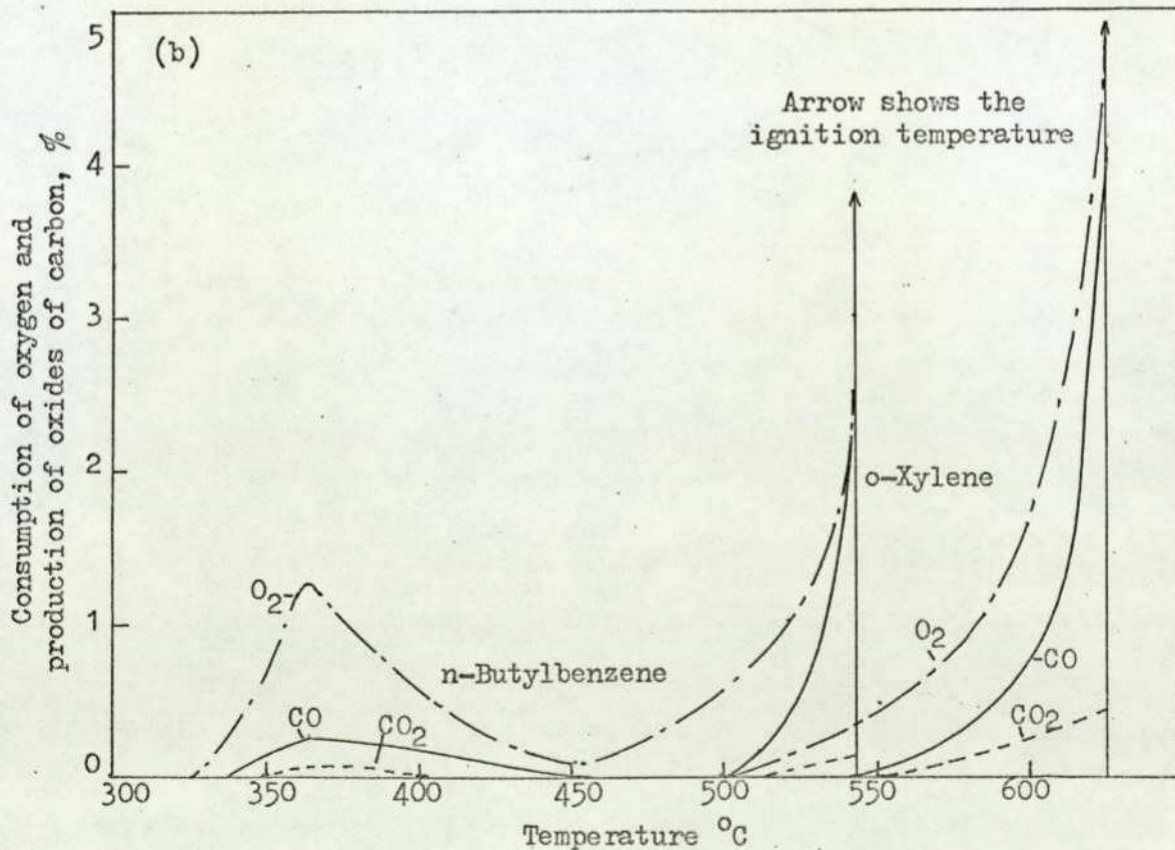
The occurrence of cool flame phenomena during hydrocarbon combustion is generally believed to be associated with the accumulation and subsequent reaction of a relatively stable intermediate species.

Figure 1.7

Production of carbon oxides during preflame processes leading to ignition

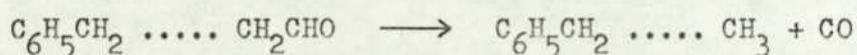


- (a) Relative consumption of oxygen and production of oxides of carbon at various temperatures up to ignition point. Benzene, twice stoichiometric hydrocarbon-air mixture; cumene, stoichiometric hydrocarbon-air mixture.



- (b) Relative consumption of oxygen and production of oxides of carbon at various temperatures up to ignition point. o-Xylene, 1.5 times stoichiometric hydrocarbon-air mixture; n-Butylbenzene, 3.0 times stoichiometric hydrocarbon-air mixture.

It has been suggested that, in the combustion of aromatic hydrocarbons, the intermediate or its predecessor, is comparatively unstable. This would account for the fact that the low-temperature ignition systems of aromatic hydrocarbons do not persist at such high temperatures as in the case of higher alkanes and that the cool flame region is generally less extensive in the former case. As an example, the cool flame region of n-propylbenzene is ill-defined compared with that of propane.⁸⁰ Furthermore, the higher aromatic aldehydes are comparatively unstable, decomposing at quite low temperatures to the next lower hydrocarbon:⁸⁰

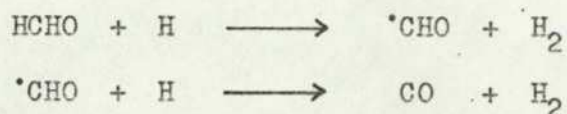


In view, therefore, of the known participation of higher aldehydes in the low-temperature combustion regime,⁸⁴ this reaction is of significance in establishing differences in behaviour between aromatic and aliphatic hydrocarbons.

1.6.2.3 Effect of methyl groups in the benzene nucleus

Despite the presence of other substituents in the benzene nucleus, the introduction of a methyl group lowers the temperature at which oxidation begins and also increases the extent of reaction during the subsequent stages. However, even though the methyl group tends to promote oxidation, the resistance to ignition has been shown to increase⁸³ and this is manifested in some cases (e.g. with toluene, m-xylene, p-xylene and mesitylene) by an increase in the ignition temperature with the concentration of fuel.

The inductive influence of the benzene nucleus is thought to lower the bond dissociation energy of the C-H bond in the methyl group⁸⁵ and thereby facilitate oxidation. The inhibiting effect on ignition was accounted for by reaction of formaldehyde, a reaction intermediate, with the labile hydrogen atoms to produce carbon monoxide and hydrogen:



This reaction would occur instead of oxidative degradation to produce, besides carbon monoxide, reactive $\cdot\text{OH}$ and $\text{HO}_2\cdot$ radicals which could eventually lead to the promotion of ignition.

1.6.2.4 Effect of chain length in monoalkylbenzenes

In general, the alkylbenzenes resemble the alkanes as regards the kinetics of their oxidation, particularly if the side chain contains more than two carbon atoms. An increase in the chain length invariably increases the ease of slow oxidation but not always the ease of ignition.

An increase in the length of the side-chain from methyl to ethyl results in a marked increase in the ease of both oxidation and ignition. A further increase in the chain length to n-propyl has been found to increase the ease of oxidation to an extent such that reactions will take place in the cool flame region. At high temperatures, the ease of oxidation is also enhanced but the resistance to ignition increases. With n-butylbenzene, both ease of oxidation and ignition are increased.⁸³

1.6.2.5 Effect of branched side chains in monoalkylbenzenes

Isopropylbenzene has been found to be unreactive in the cool flame region and this compound does not start to be oxidised until higher temperatures are attained.⁸³ With increasing temperature, isopropylbenzene is oxidised faster than the straight-chain isomer and eventually ignites at a lower temperature.

The difference in reactivity of n-propylbenzene and isopropylbenzene can be understood by analogy with branching of the carbon chain in alkanes.⁸⁶ Investigations on isomeric hexanes have shown that no cool flames are observed in the absence of secondary C-H bonds. However, at high temperatures, the

presence of tertiary C-H bonds instead of secondary C-H bonds is conducive to greater ease of ignition. It has been suggested that oxidation at secondary C-H positions results in the formation of aldehydes which are highly reactive in the cool flame region whereas oxidation at tertiary C-H positions results in the production of ketones which are relatively stable.⁸³

At high temperatures, both aldehydes and ketones are prone to oxidative degradation, and this is dependent upon the strength of the C-H bonds. Hydrocarbons containing relatively low strength tertiary C-H bonds in general ignite more readily than hydrocarbons with stronger secondary C-H bonds.

Of the butylbenzenes, only the n-isomer has been found to undergo considerable reaction in the cool flame region.⁸³ Slight oxidation occurs with sec-butylbenzene but the other isomers barely react in the cool flame region.⁸³ At high temperatures, the order of decreasing ease of oxidation and ignition is: n-butylbenzene > sec-butylbenzene > isobutylbenzene > tert-butylbenzene. This is in agreement with the expected effect of branched side-chains in alkanes. n-Butylbenzene, with the largest number of reactive secondary C-H bonds, is the most reactive isomer while tert-butylbenzene with neither secondary nor tertiary C-H bonds, is relatively unreactive. Both sec- and isobutylbenzene, have the same number of primary, secondary and tertiary C-H bonds. The greater ease of combustion of sec-butylbenzene is probably due to the greater tendency of the derived peroxy radicals to undergo intramolecular reaction with relatively reactive secondary hydrogen atoms.⁸³

1.6.2.6 Effect of positional isomerism in dialkylbenzenes

o-Xylene has been shown to be by far the most reactive of these isomers and to ignite at the lowest temperature; m- and p-xylenes differ

only slightly in their ease of oxidation.⁸³ With o-xylene, the effect of the fuel concentration on ignition temperature was much greater than in the case of the m- and p- isomers.

Burgoyne, Tang and Newitt,⁸⁰ as well as Wright,⁸⁷ showed that o-xylene is far more reactive than the m- and p- isomers but their results differed from those of Salooja⁸³ who found that p-xylene was less reactive than m-xylene. According to Szwarc,⁸⁵ the dissociation energy of the C-H bond in m-xylene is slightly greater than that in p-xylene. Wright⁸⁷ determined the lifetime of the degenerate branching intermediate and found that the intermediate for m-xylene oxidation was the most stable. These observations support the results of Salooja.⁸³ The higher reactivity of o-xylene compared with that of m- and p-xylenes has been attributed to the greater ease of intramolecular reaction between the peroxy radical first formed and the methyl group in the adjacent ortho position. On the basis of molecular models, the probability of intramolecular reaction for the m- and p-isomers has been shown to be remote.⁸³

1.6.3 Products of slow oxidation

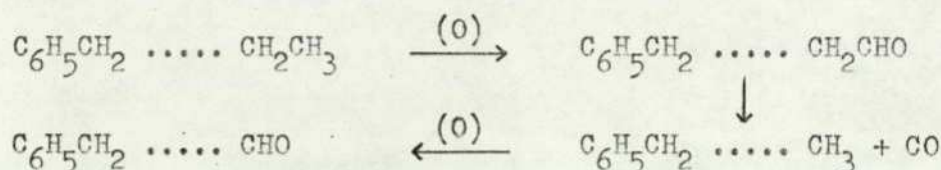
Products formed during the oxidation of benzene and alkylbenzenes fall into three groups: those resulting from oxidation of the side chain e.g. acetophenone, benzaldehyde; those arising by oxidation of the ring, e.g. phenols; and those formed through ring cleavage e.g. acetylene, maleic acid.

1.6.3.1 Side-chain oxidation

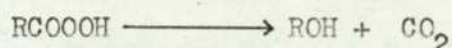
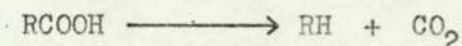
Burgoyne⁷⁵ suggested that the higher alkyl derivatives of benzene are primarily attacked at the α -carbon atom but this theory could not be substantiated owing to the instability of the higher aldehydes and carboxylic acids and the insensitivity of the analytical tests. It was

assumed that oxidation of the end carbon atom results in the formation of a primary alcohol, aldehyde and acid, although the latter compounds may not be formed owing to the instability of the aldehydes.

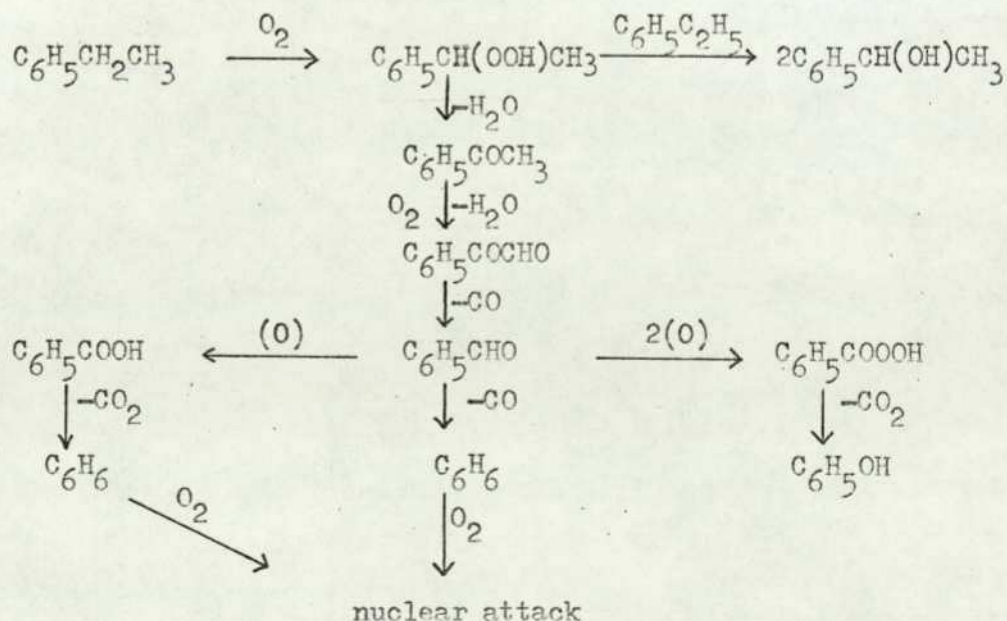
Thus the proposed combustion mechanism was based on the degradative sequence:



Other possible mechanisms proposed include the decarboxylation of acids and peracids resulting in the formation of a member of the next lower series:



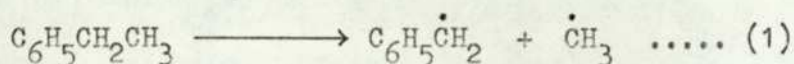
Oxidation at the α -carbon atom results in the formation of a secondary alcohol and a ketone. Once the ketone stage is reached, the end carbon atom is attacked and degradation through ketonic aldehydes leads ultimately to the formation of benzaldehyde, which may subsequently decompose to give benzene. In the case of ethylbenzene, the following scheme has been suggested:⁷⁵



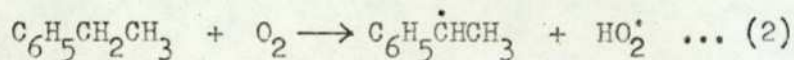
Subsequently, Kröger and Bigorajski^{88,89}, in the light of the results obtained in a static system at 310–410°C, discussed the mechanisms of oxidation of various hydrocarbons, including ethylbenzene and styrene.

With ethylbenzene, preliminary studies were carried out in the absence of oxygen at 380°C.⁸⁹ Analysis showed that the principal products (expressed as mole %) were benzene 1.45, toluene 0.49, styrene 15.22 and ethylbenzene 82.84.

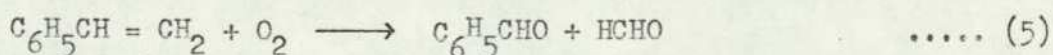
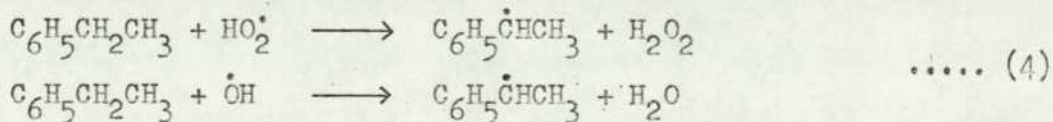
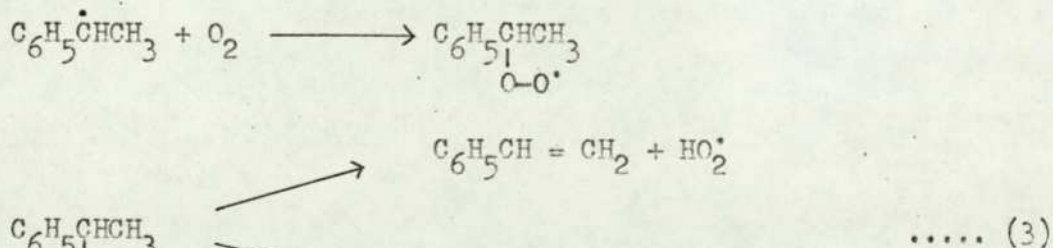
On the basis of bond dissociation energies, the most likely initiation step is:



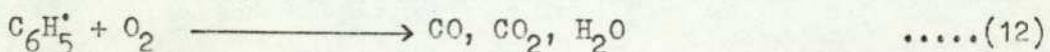
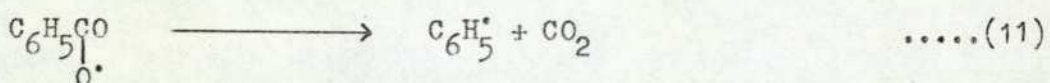
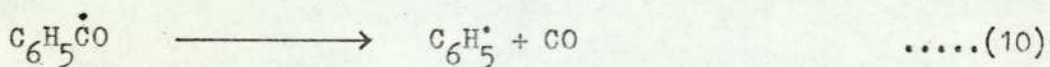
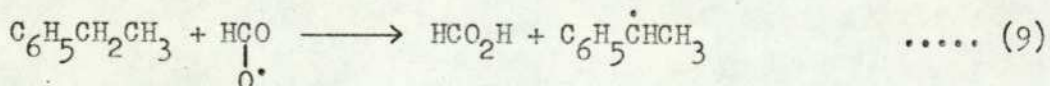
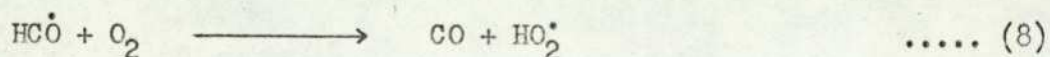
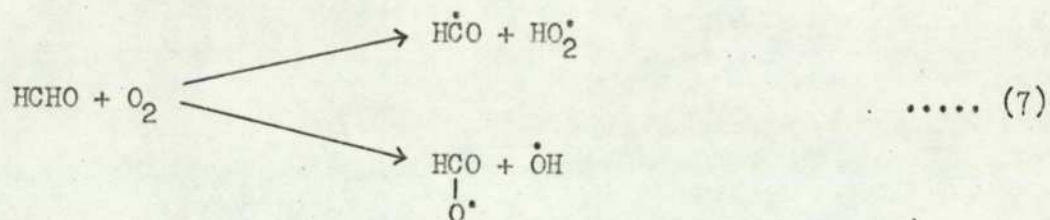
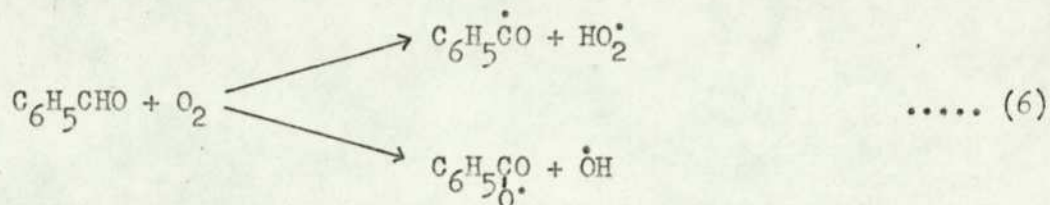
In the presence of oxygen, the initiation reaction presumably involves attack by oxygen at the resulting free α -carbon atom:



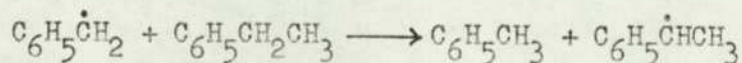
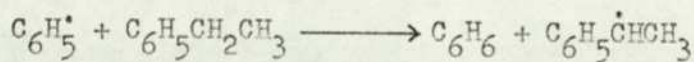
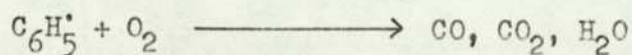
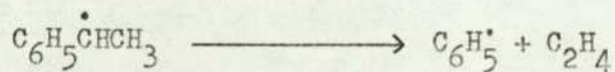
Liquid-phase oxidation studies⁹⁰ at low temperatures have indicated that the breakdown of peroxides plays an important part in promoting the branching reaction. In the gas phase, the corresponding aldehyde probably plays an important role above 300°C, as a degenerate branching agent. The overall mechanism of ethylbenzene oxidation has thus been outlined as:⁸⁹



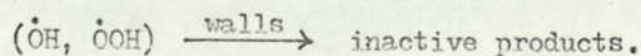
The branching reactions are as follows:



Reaction (12) involves attack of the benzene nucleus. The primary reactions leading to benzene and toluene are as follows:

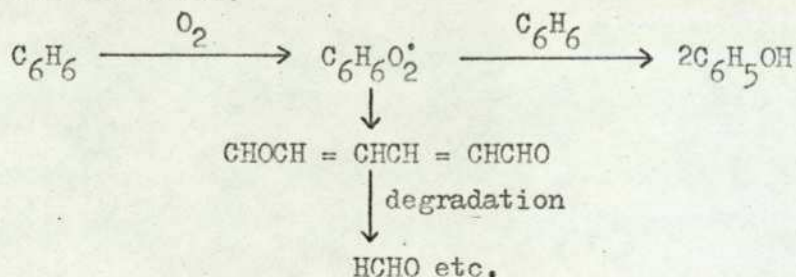


Chain breaking is believed to occur at the walls:



1.6.3.2 Nuclear oxidation

Initial attack of benzene by oxygen is thought to lead to an active centre which is not necessarily peroxidic in nature.⁷⁵ On reaction with an oxidisable molecule, the active centre may be converted to a phenol. Alternatively, it may undergo ring rupture to give a higher aliphatic aldehyde, which undergoes rapid degradation in oxygen to yield formaldehyde, formic acid, oxides of carbon and steam:^{84,91}



The ratio of CO/CO_2 has been taken to indicate the course of combustion under varying conditions, carbon monoxide resulting from degradation at the aldehyde stage and carbon dioxide from degradation of acids and peracids. At high temperatures, the above ratio was greater than 2, showing that, in general, degradation via aldehydes is the preferred reaction. At lower temperatures, however, the amount of carbon monoxide formed decreases and the reaction thus takes place predominantly via the acid. At very low temperatures, peracids are found in the products, and the amount of carbon dioxide increases as a result of the decomposition of these compounds.⁷⁵

1.7 Oxidation of styrene

1.7.1 Liquid-phase studies

Most of the early work on the oxidation of unsaturated hydrocarbons was concerned with compounds containing double bonds which were relatively unreactive with respect to polymerisation.⁹² Such compounds react with peroxy radicals to give substituted allyl radicals and later the corresponding allyl hydroperoxides. Much less attention has been paid to unsaturated compounds with reactive double bonds.

The relationship between the oxidation and polymerisation of styrene was shown by the work of Medvedev and Tseitlin.⁹³ Styrene oxidation proceeded two and a half times as rapidly as its polymerisation at 80°C, resulting in the formation of benzaldehyde and formaldehyde. Small quantities of benzyl alcohol were also detected. However, no accumulation of peroxidic compounds in the oxidised styrene was reported.⁹³

Mayo and Miller⁹⁴ suggested a mechanism involving copolymerisation of styrene to form a polyperoxide followed by cleavage of the latter to give carbonyl compounds. Both the composition of the copolymer and the fraction of styrene converted to aldehydes were found to depend on the oxygen pressure.

The styrene-oxygen copolymer, $(-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)-\text{O}_2-)_n$, of molecular weight about 5000, had previously been prepared by polymerisation of styrene in the presence of oxygen, first, in emulsion by Bovey and Kolthoff,⁹⁵ and subsequently in bulk by Barnes, Elofson and Jones.⁹⁶

1.7.1.1 Rate of oxidation of styrene as a function of reactant concentration

Mayo and Miller⁹⁴ investigated the effects of the concentrations of styrene and the initiator on the rate of oxygen absorption by the monomer at 101.3 kNm⁻² pressure. Rates were measured up to about 5% conversion and were found to be reproducible under these conditions. The rate of oxidation was proportional to the first power of the styrene concentration and to the square root of the concentration of the initiator (α, α' -azobisisobutyronitrile).

Experiments were also carried out with oxygen pressures ranging from subatmospheric to about 405 kNm⁻² and it was shown that the rate was almost independent of oxygen concentration in this region. The rate of formation of polyperoxide decreased and the rate of production of benzaldehyde increased as the oxygen pressure was reduced. Although the rate of formation of peroxide is about 17 times greater than that of aldehyde at 101.3 kNm⁻² of

oxygen, these rates were nearly equal at 3.3 kNm^{-2} pressure. At constant oxygen pressure, aldehyde formation increased with temperature. Figure 1.8 shows the conversion of styrene to polyperoxide and benzaldehyde at 80°C in the absence of an initiator.

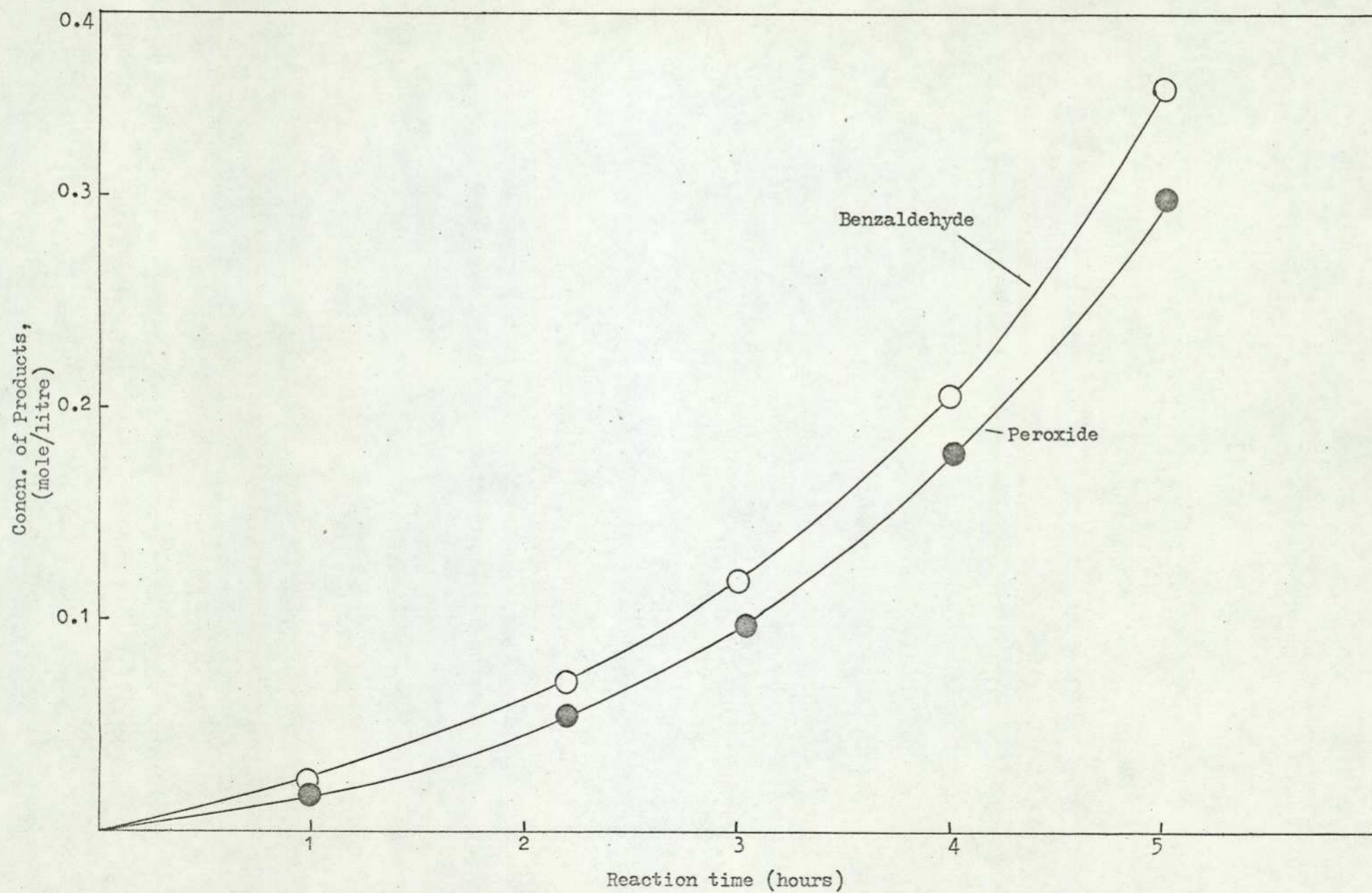
As the oxygen pressure is reduced, styrene radicals have a greater chance either of reacting with styrene molecules or of rearranging. At the same time, copolymerisation with oxygen becomes less important. Thus above about 0.13 kNm^{-2} oxygen pressure, the reaction of peroxy radicals with styrene is rate-determining. However, as the oxygen pressure is lowered, the rates of reaction of styrene radicals with styrene, of styrene radicals with oxygen and of peroxide radicals with styrene, become approximately equal to each other. As the oxygen pressure approaches zero, other products disappear and the composition of the polymer approaches that of polystyrene.⁹⁷

1.7.1.2 Initiation of oxidation of styrene by styrene peroxide

Studies have been carried out using styrene polyperoxide (shown by analysis to be $[(\text{C}_8\text{H}_8)_{1.13}\text{O}_2]_n$ as an initiator for styrene oxidation.⁹⁴ However, at 50°C , the rate of oxidation in the presence of 0.1M styrene peroxide was only 1.7 times that of the uncatalysed reaction, whilst a similar concentration of α, α' -azobisisobutyronitrile caused reaction to proceed 55 times faster than normal.

1.7.1.3 Effect of various other additives on the rate of oxidation of styrene

Isotopic tracer studies of styrene oxidation were carried out by Dutka and Gal.⁹⁸ Medvedev and Tseitlin⁹³ had previously shown that benzaldehyde catalyses styrene oxidation. It was assumed that, initially, benzaldehyde reacts with oxygen to form a labile peroxide, which then acts as a chain initiator. Oxidations carried out in the presence of benzaldehyde resulted in the production of a considerable quantity of benzoic acid.⁹³



Concurrent oxidation of styrene to peroxide and benzaldehyde

Figure 1.8

Subsequently Dutka and Gal⁹⁸ reported that benzaldehyde, which was not freshly purified, acted as an inhibitor. However, when freshly purified benzaldehyde was used, a promoting effect was observed, although inhibition still occurred at the beginning of the reaction. The extent of this inhibition depended on the benzaldehyde concentration as did the promoting effect. It was assumed that at the start of reaction, benzaldehyde undergoes more rapid oxidation than styrene and, only after the inhibition period, does the rate of oxidation of styrene become appreciable. This assumption was supported by the observation that, when benzaldehyde was introduced into the system at a later stage, it had no influence on the rate of oxidation.⁹⁸

Generally speaking, promoters and inhibitors play an important role in autoxidation processes. The promoting and inhibiting effects of a large number of compounds have therefore been investigated.

Moureu et al.⁹⁹ investigated the effect of 83 nitrogen compounds on the oxidation of styrene. The majority of these exerted an inhibiting influence, but some, e.g. dimethylaniline, accelerated oxygen uptake. In addition to the nitrogen compounds, the effects of compounds containing sulphur,¹⁰⁰ phosphorus,¹⁰¹ antimony, arsenic, bismuth and vanadium¹⁰² were also studied. Most of these additives promoted oxidation but phenols, hydroquinone and related compounds acted as inhibitors.¹⁰³

Subsequently, Dutka and Gal¹⁰⁴ investigated the effects of amines and amine salts on styrene oxidation. Aniline inhibited the reaction, while methylamine hydrochloride and aniline hydrochloride acted as promoters. When benzaldehyde was introduced into the system together with these compounds, an inhibiting effect was observed from the outset, which was attributed to primary reaction between the amine hydrochloride and benzaldehyde.¹⁰⁴

1.7.2

Vapour-phase studies

"Kroger and Bigorajski^{89,90} studied the slow oxidation of styrene in a static system at 310–340°C and at pressures below atmospheric. It was found that the activation energy for styrene oxidation was 103.7 kJ mole⁻¹ compared with values of 279, 202.7 and 165 kJ mole⁻¹ for benzene, toluene and ethylbenzene respectively. With styrene, the reproducibility was not as good as with ethylbenzene and it was suggested that, during styrene oxidation, the walls of the vessel become coated with polymer. Supporting evidence for this was provided by the finding that the rate of oxidation of ethylbenzene increases in a vessel which has previously been used for the oxidation of styrene (Figure 1.9).⁸⁹

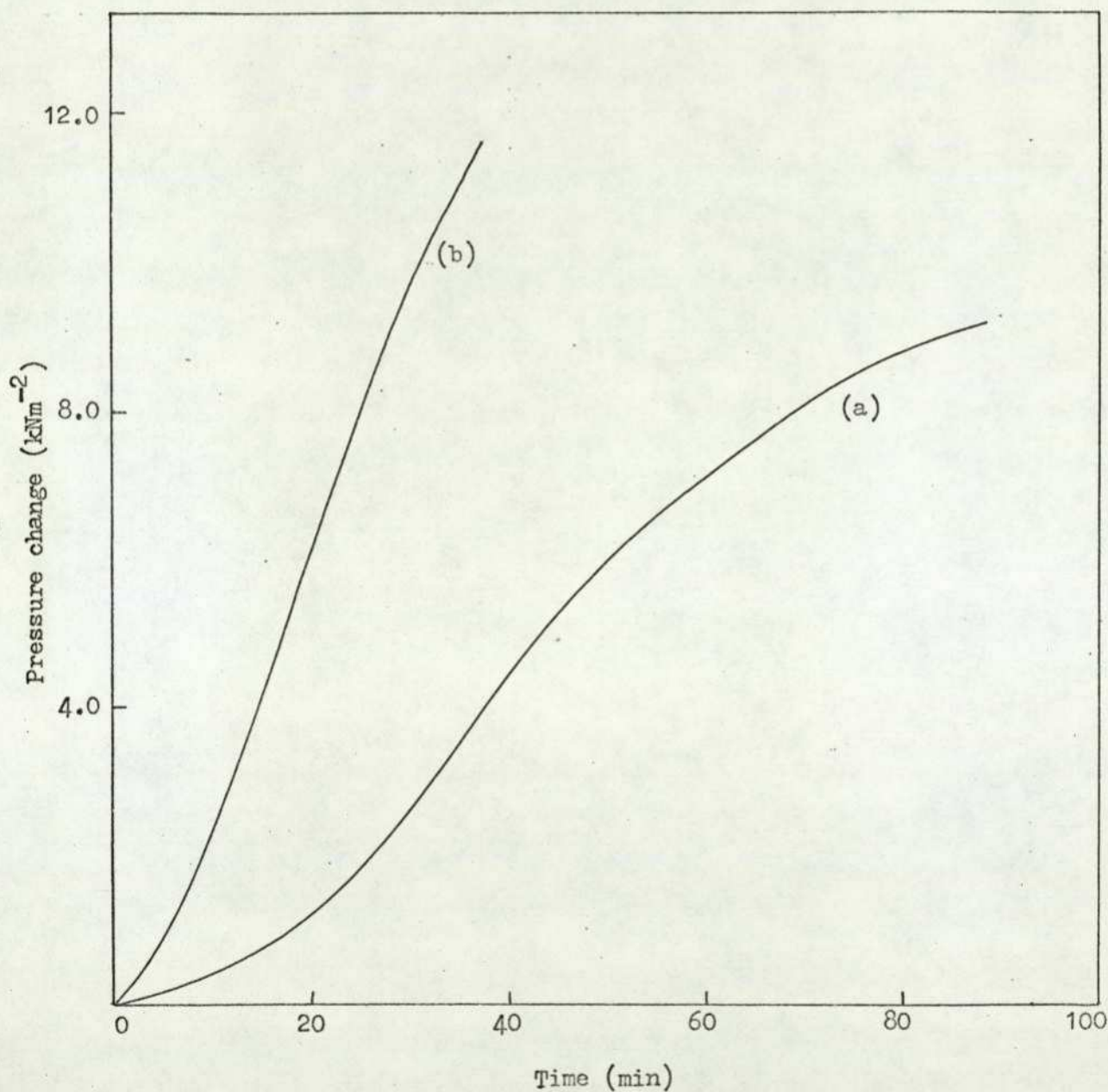
Earlier studies by Chamberlain and Walsh¹⁰⁵ established that various aromatic compounds, including styrene, inhibited the slow oxidation of diisopropylether. Kende and Gal¹⁰⁶ subsequently studied the vapour-phase oxidation of hexane in a static system. Styrene had a strong inhibiting effect which was proportional to its concentration. Using styrene labelled with carbon-14 on the α -carbon atom, it was shown that styrene also undergoes oxidation during the reaction. Various aldehydes and carbon dioxide were found to be derived from the α -carbon atom.¹⁰⁷

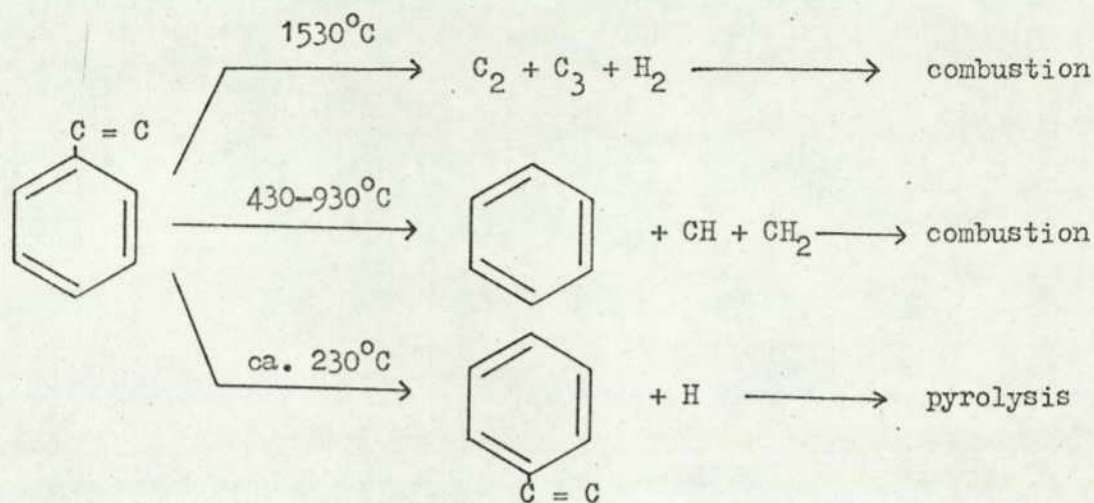
The combustion of styrene monomer has recently been investigated by kinetic spectroscopy under a variety of conditions.¹⁰⁷ The reaction was found to be complex, its course depending on both the reactant mixture composition and the temperature. It was concluded that the pyrolysis and ultimately the combustion of styrene follow at least three different paths according to the temperature and temperature limits were arbitrarily set for the three regimes. The proposed pyrolysis and combustion mechanisms are as follows:

Figure 1.9

(a) Slow oxidation of ethylbenzene at 360°C

(b) Slow oxidation of ethylbenzene at 360°C in a reaction vessel
previously used for styrene oxidation





The cracking is minimal at temperatures of about 230°C and combustion involves primarily attack by oxygen of the monomer itself or of the monomer minus one or more chain hydrogens.

At intermediate temperatures, 430-930°C, the styrene molecule undergoes C-C bond fission to give a phenyl radical and CH and CH₂ fragments. The latter then undergo combustion cleanly to CO and CO₂, depending on the concentration of oxygen present.

At temperatures approaching 1600°C, much more extensive breakdown of the styrene molecule occurs with loss of hydrogen to form C₂, C₃ and larger fragments. The latter combine to form soot as the hydrogen is burnt to steam. No analytical data were obtained in this investigation and a more detailed mechanism was not therefore proposed.¹⁰⁷

1.8

Present work

From the preceding literature survey it can be seen that, although detailed investigations have been carried out of the polymerisation and oxidation of styrene in the liquid-phase, very little work has been done on the reactions of this compound in the vapour-phase. Furthermore, recent incidents, in which vapour clouds of styrene escaping from a storage tank have apparently undergone spontaneous ignition, seem to suggest that

the vapour-phase polymerisation and oxidation of this compound may be strongly promoted by the presence of polymerising liquid styrene. Clearly then, more detailed studies of the vapour-phase reactions of styrene are required.

SECTION 2
EXPERIMENTAL

SECTION 2

	Page No.
2.1 <u>Apparatus</u>	63
2.1.1 The vacuum system	63
2.1.2 Furnace and line heating	67
2.1.3 Solenoid valve and timing circuit	68
2.1.4 Pressure-recording equipment	72
2.1.5 Modified reactor for liquid-phase studies	72
 2.2 <u>Materials</u>	 74
2.2.1 Styrene	74
2.2.2 Polystyrene	74
2.2.3 Oxygen and Nitrogen	74
2.2.4 Benzoyl peroxide	74
2.2.5 α, α -Azobisisobutyronitrile	75
 2.3 <u>General Procedures</u>	 75
2.3.1 Calibration of pressure transducer	75
2.3.2 Preparation of reactant mixtures	75
2.3.3 Introduction of reactants into the reaction vessel	75
2.3.4 Conditioning of reaction vessel	76
2.3.5 Measurement of kinetic parameters	76
2.3.6 Temperature measurements	78
2.3.7 Product sampling	79

	Page No.
2.4 <u>Analytical Procedures</u>	81
2.4.1 <u>Gas chromatographic analysis</u>	81
2.4.1.1 The gas chromatograph	81
2.4.1.2 Preparation of columns	81
2.4.1.3 Operating conditions for columns	81
2.4.1.4 Introduction of samples	83
2.4.1.5 Identification of products	83
2.4.2 <u>Colorimetric analysis</u>	83
2.4.2.1 The spectrophotometer	83
2.4.2.2 Analysis for formaldehyde	84
2.4.3 <u>Infrared spectrophotometric analysis</u>	84
2.4.3.1 The spectrophotometer	84
2.4.3.2 Analysis for polymeric styrene in styrene monomer	85

2.1 Apparatus

2.1.1 The vacuum system

The vacuum apparatus was constructed principally from Pyrex glass and is shown schematically in Figure 2.1 (see also Plate 2.1). The section of the vacuum line used for handling the reactants and products was kept completely greaseless by incorporating Teflon 'Rotaflo' taps.

Permanent gases were introduced through tap T1 and passed through a drying column containing Linde 5A molecular sieve and subsequently purified by condensation and fractionation between traps TP1 and TP2, which were cooled in liquid nitrogen. The manometer M1 was used as a pressure safety valve during fractionation of gases. Subsequently, the purified gases were stored in globes S1, S2, S3 and S4.

Liquid styrene was stored in a 50 cm³ flask FV, which was attached to the line by a cylindrical joint with Viton 'O' rings.

The reactant premixing vessels, PM1 and PM2, were encased in metal boxes as a protection against possible explosion. Gaseous fuel-air mixtures were stored in the heated premixing vessel PM1, while oxygen and nitrogen were premixed in the unheated vessel PM2.

The heated reaction section of the line was made as short as possible in order to minimise dead space. The introduction of the reactants into the reaction vessel was controlled by a 240 volt a.c. solenoid-activated valve and a similar valve was incorporated between the reaction vessel and the gas-sampling section for control of the withdrawal of reaction products. Each of the valves was operated by a time-variable electronic circuit (Section 2.1.3).

The cylindrical quartz reaction vessel, RV, the volume of which was ca. 308 cm³, was washed with hydrofluoric acid and baked in air at 450°C for 24 hours prior to use. The vessel was attached to the line

Key to figure 2.1

I	= Inlet for permanent gases
$T_1 - T_3$ and $T_{32} - T_{35}$	= Stopcocks (greased)
$T_4 - T_{31}$	= Rotaflo greaseless stopcocks
DT	= Drying column
TP1 - TP4	= Cold traps
M1, M2	= Mercury manometers
S1 - S4	= Storage vessels
FV	= Liquid fuel storage vessel
PM1, PM2	= Premixing vessels (1 litre and 5 litre)
RSV	= Reactant solenoid valve
PT1, PT2	= Pressure transducers
BV	= Baffle-valve
RV	= Reaction vessel
PSV	= Product solenoid valve
CV	= Calibration vessel
ST	= Sample trap
PG	= Pirani gauge
DP	= Diffusion pump
RP	= Rotary oil pump

Figure 2.1

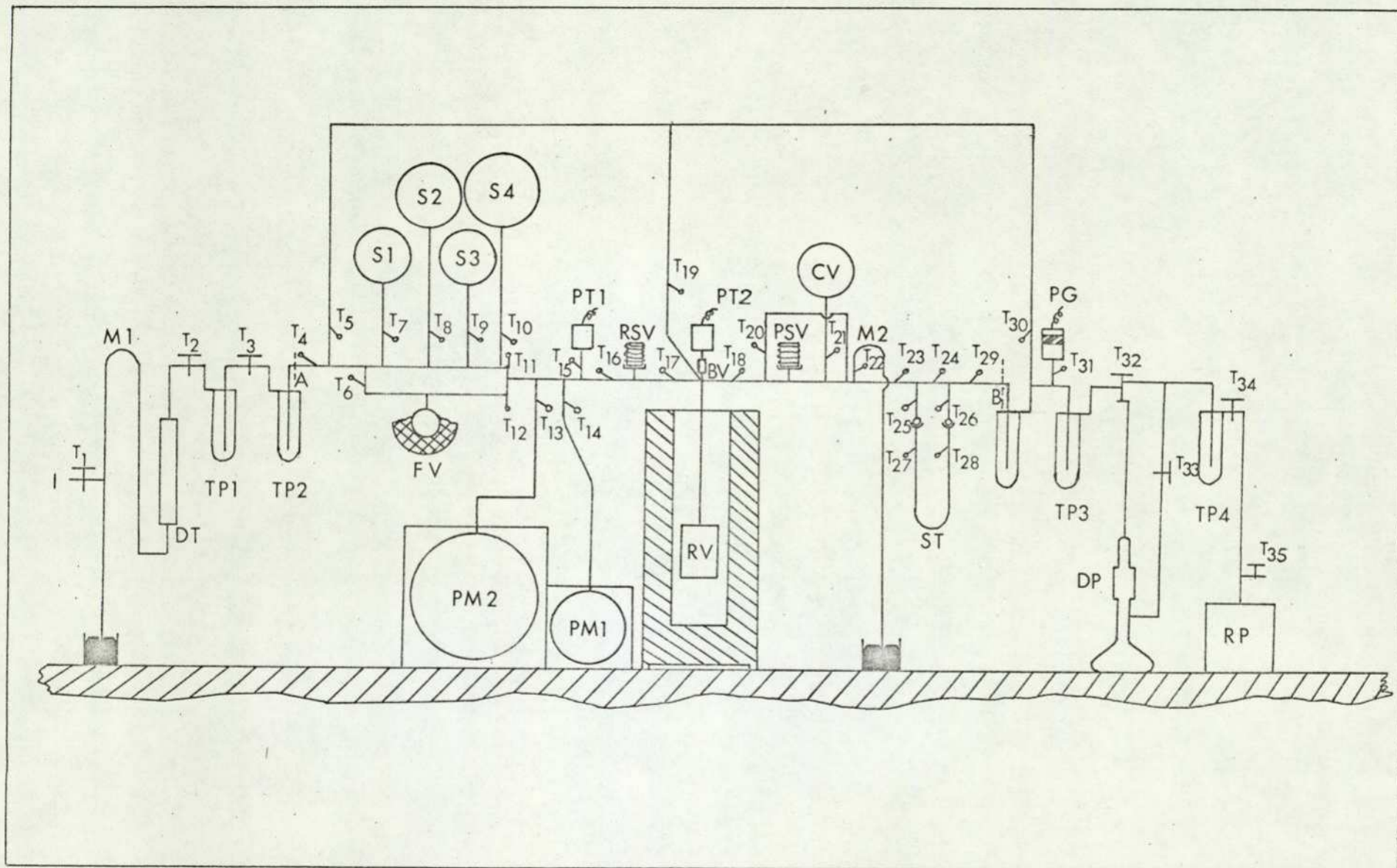
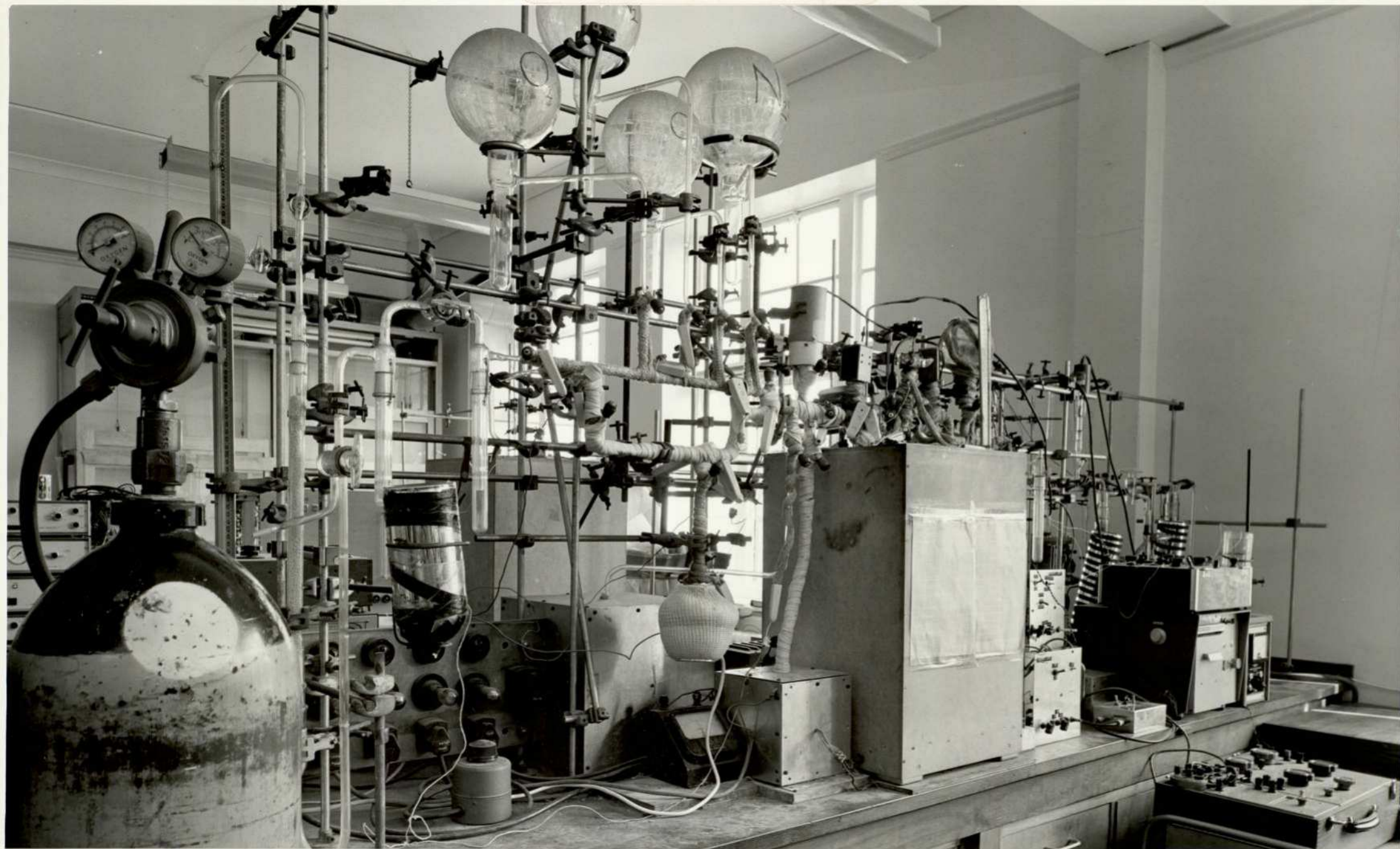


PLATE 21
The Static Vacuum Apparatus



by a greaseless ball-and-cup connection and suspended in the required position (Section 2.1.2) in an electrically heated furnace.

The Pyrex ball-joint was connected to the neck of the quartz vessel by means of a quartz-to-Pyrex graded seal. A baffle-valve BV was incorporated directly above the reaction vessel in order to prevent the pressure transducer, which was connected to the valve, from being damaged in the event of explosion in the reaction vessel.

The reaction section of the line was completed by a manometer M2, a calibration vessel CV of ca. 600 cm³ volume and a detachable sampling trap ST, which was joined by greaseless ball-and-cup connections and held in place by spring clips.

A vacuum of at least 1.33×10^{-5} kNm⁻² Hg was attained by means of a single-stage mercury diffusion pump, DP, backed by a rotary oil pump RP. Liquid nitrogen-cooled traps, TP3 and TP4, protected the diffusion pump from contamination by combustion products and also prevented mercury vapour diffusing into the by-pass line or the rotary pump. The vacuum was measured by an Edwards Pirani Gauge, PG (Figure 2.1).

2.1.2 Furnace and line heating

The furnace was capable of maintaining a temperature of up to 600°C to within $\pm 1^\circ\text{C}$ over a length of 9 cm. The current to the furnace was controlled by an A.E.I. RT3R/Mk2 proportional temperature controller and power regulator with temperature feedback from an A.E.I. PRT4 platinum resistance thermometer.

The temperature distribution of the vertical tube furnace was measured using a chromel-alumel thermocouple, which had been calibrated against a standard platinum/87% platinum + 13% rhodium thermocouple. The cylindrical quartz reaction vessels employed were placed in the central region of the furnace, the temperature distribution of which is shown

in Figure 2.2.

In order to prevent condensation of reactants and products, the section of the line (AB) was maintained at ca. 70°C using Electrothermal heating tape and a Variac voltage regulator to control the mains voltage supply. The premix vessel PM1 was independently maintained at a temperature of ca. 110°C by means of 3 in. heating tape, and was covered with glass-fibre lagging. Chromel-alumel thermocouples were placed at various points along the surface of the vessel, and measurements confirmed that there were no hot-spots and that the temperature was uniform.

The styrene storage vessel, FV, was heated by an isomantle connected to a Sunvic energy regulator (see Figure 2.1).

2.1.3 Solenoid valve and timing circuit

The solenoid valve is shown diagrammatically in Figure 2.3. The valve was constructed from two 'push-pull' Pyrex sockets sealed together by two Viton O-rings. When the solenoid coil was activated, a magnetic field was induced which lifted the metal rod from the glass cup and allowed the gas to flow through the valve. When the solenoid coil was isolated from the current supply, the metal rod dropped back into its cup seating under the combined action of gravity and a coiled spring, thus renewing the seal which was made between the rod and a silicone O-ring.

The time for which the 240 volt a.c. solenoid coil was activated, was controlled by an electronic timing circuit (see Figure 2.4). The time interval, during which the valve remained open, was dependant upon which capacitor in the timing circuit was allowed to discharge across the terminals of an a.c. relay. The capacitor discharge current was amplified by a transistor circuit involving an OC200 and an OC72 and hence enabled the relay to operate. The contacts on the relay closed the circuit between the mains voltage and the solenoid coil, which then operated the

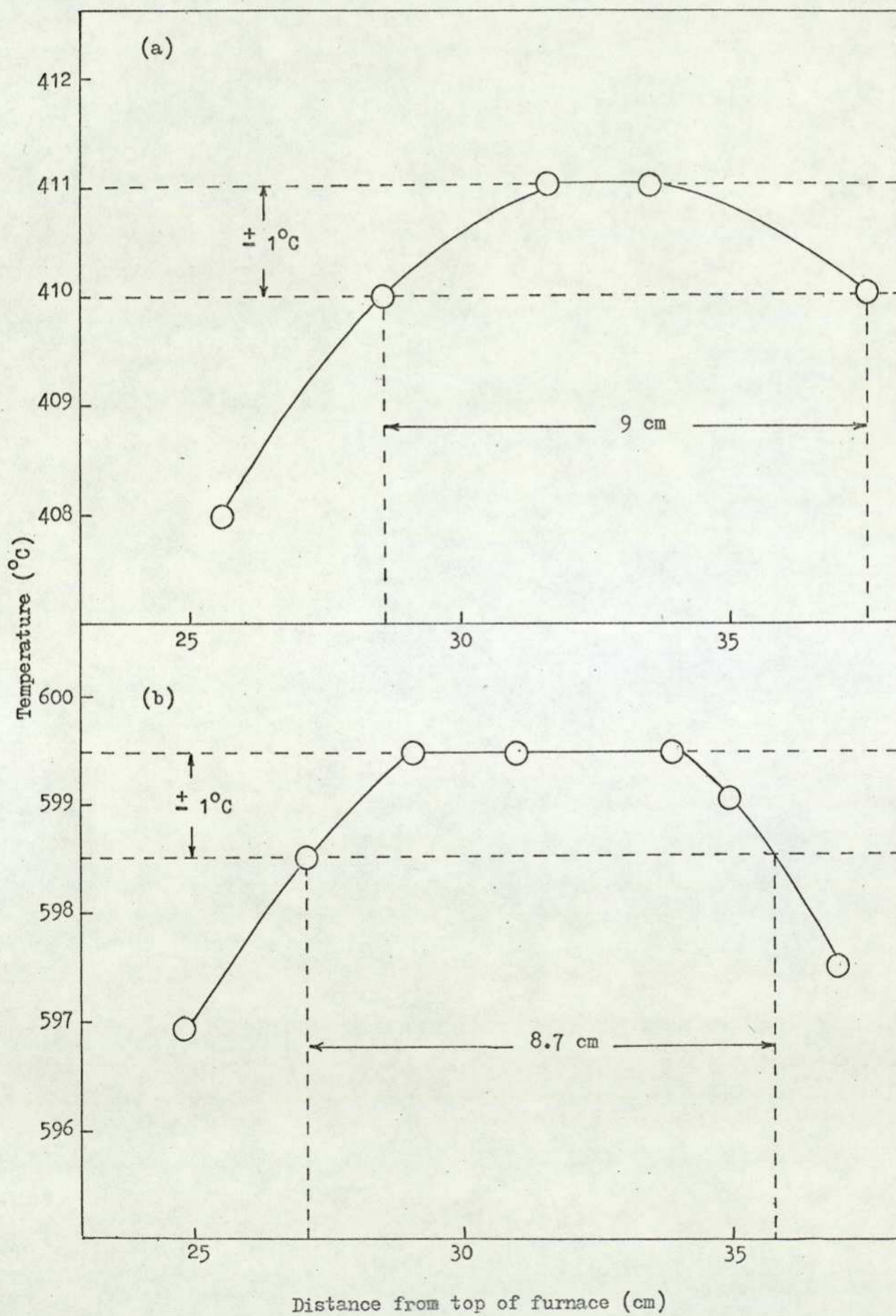
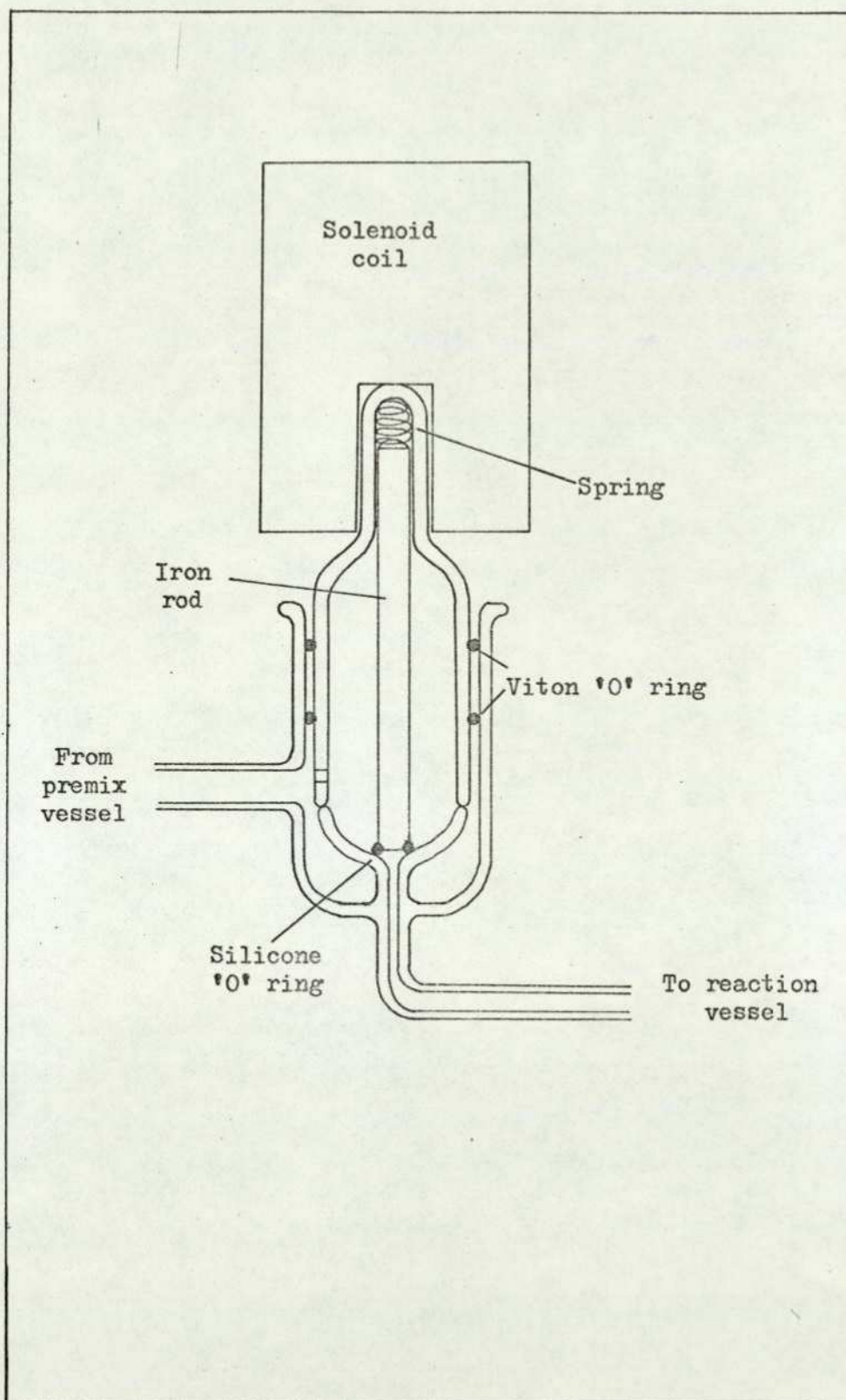
Figure 2.2Furnace temperature profiles at (a) 411°C and (b) 599°C

Figure 2.3The solenoid activated valve

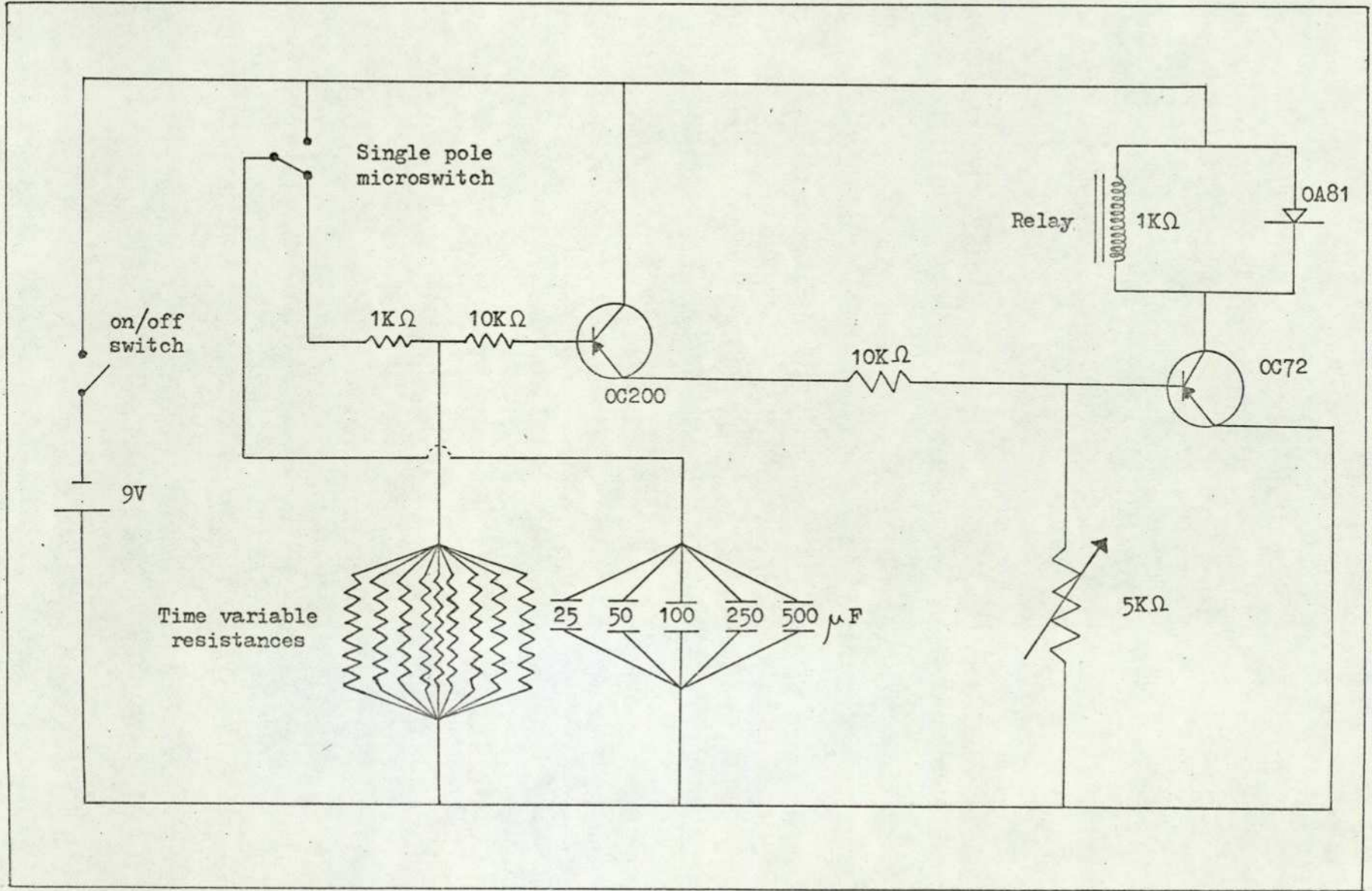


Figure 2.4
The solenoid valve timing circuit

valve. This arrangement made it possible for the valve to be operated for time intervals from 0.1 second to several seconds.

2.1.4 Pressure-recording equipment

Pressure changes occurring during the course of reaction were followed by means of a 0-50 p.s.i.a. unbonded strain-gauge transducer (Bell and Howell type : 4-366-0002-01M0-0). The 10 volt d.c. required for excitation of the transducer bridge was obtained from a Bell and Howell stabilised power pack (type : 3-142-2). The output signal from the transducer was amplified by a Fylde differential d.c. amplifier (type FE-151-BD/C) and subsequently recorded by an ultraviolet oscillograph (Honeywell type 1706 Visicorder). The galvanometer used for pressure recording was a Honeywell BB500A mirror galvanometer.

2.1.5 Modified reactor for liquid-phase studies

The modified reaction vessel used is shown in Figure 2.5. The slug of polymerising styrene monomer was introduced into the reaction vessel through an inlet tube connected by means of a quartz-to-Pyrex graded seal, S, to a heated compartment consisting of the volume between ground-glass stopcocks T1 and T2. The compartment was heated by Electro-thermal heating tape, and a Variac transformer was used to vary the mains supply voltage. In order to check the temperature within the compartment, two fine chromel-alumel thermocouples were inserted and connected into two hollow glass inlets positioned opposite each other (Figure 2.5a).

The glass capsules containing liquid monomer were constructed from melting-point tubes and were ca. 6 cm long. One end of the tube was sealed and a given quantity of styrene monomer was introduced by means of a microlitre syringe. Subsequently, the open end of the capsule was sealed and the tube was inserted into the heated compartment by opening stopcock T1 with stopcock T2 in the closed position (Figure 2.5b). After heating for a given time, stopcock T1 was closed thereby breaking the capsule seal. Stopcock

Figure 2.5

Modified Reactor for Introduction of a Polymerising Liquid Phase
into a Reacting Vapour Phase

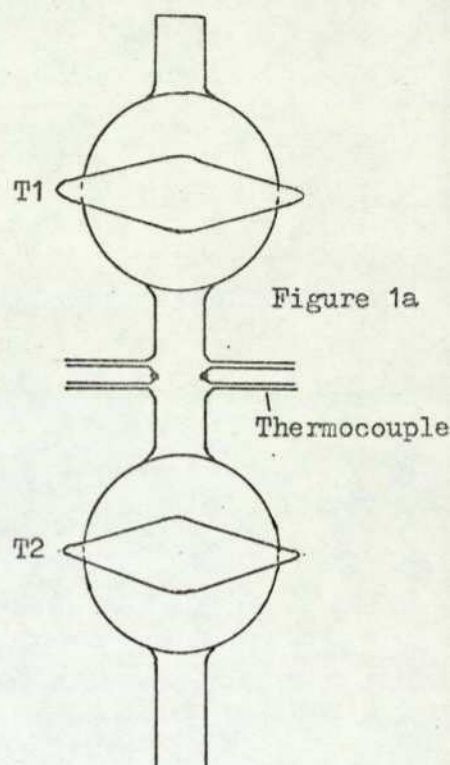
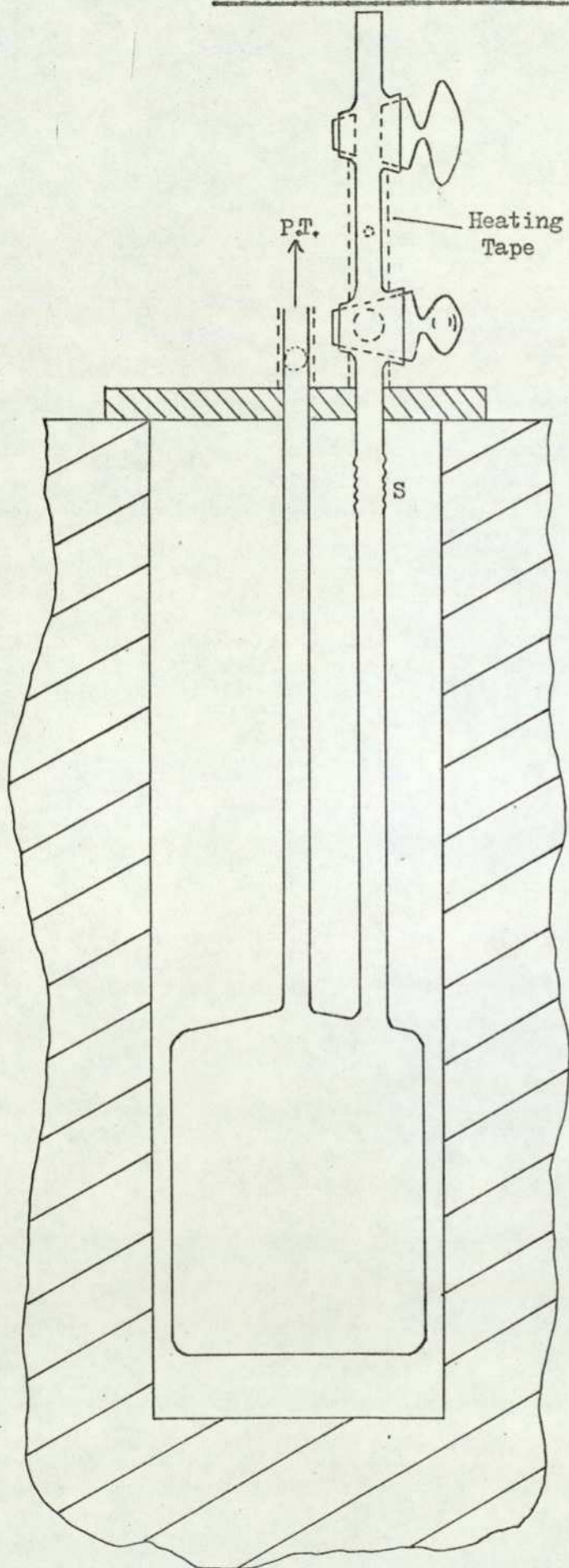


Figure 1a

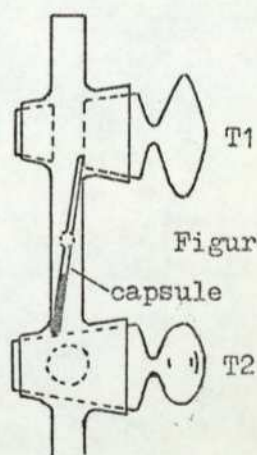


Figure 1b

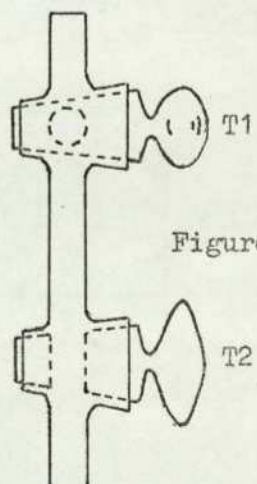


Figure 1c

T2 was then opened as quickly as possible (Figure 2.5c) and the broken capsule containing the polymerising monomer, together with the air trapped within the compartment was admitted to the reaction vessel containing the reacting styrene-air mixture.

2.2 Materials

2.2.1 Styrene

Styrene monomer, stabilised with 10-15 p.p.m. p-tert-butylcresol, was obtained from Ralph N. Emanuel Limited and was shown by gas chromatography to be at least 99% pure. The main impurities present were ethylbenzene (0.32%), isopropylbenzene (0.34%), n-propylbenzene (0.09%) and α -methylstyrene (0.25%).

2.2.2 Polystyrene

Finely ground polystyrene was obtained from Monsanto Chemicals Limited.

2.2.3 Oxygen and Nitrogen

Oxygen and 'white spot' nitrogen (at least 99.98% pure) were obtained from cylinders supplied by the British Oxygen Company. Oxygen was condensed in a liquid nitrogen-cooled trap and the middle fraction was allowed to evaporate into a storage globe, considerable head and tail fractions being pumped off. Oxygen-free nitrogen from the cylinder was dried by passage through a molecular sieve column and stored similarly.

2.2.4 Benzoyl peroxide

Benzoyl peroxide, (moistened with water), was obtained from Hopkin and Williams Ltd. and was incorporated into the monomer without removal of the water.

2.2.5 α,α' -Azobisisobutyronitrile

α,α' -Azobisisobutyronitrile, quoted as being $\geq 97\%$

pure, was obtained from Koch-Light Laboratories Ltd. and was used without further purification.

2.3 General Procedures

2.3.1 Calibration of pressure transducer

The output signal from the transducer was calibrated against a mercury manometer using dry nitrogen. The deflection of the Visicorder galvanometer at a particular amplification was recorded for various pressures of nitrogen and it was found that the transducer had a linear response from 0 to 93.3 kNm^{-2} .

2.3.2 Preparation of reactant mixtures

Gaseous reactant mixtures were prepared on a partial pressure basis, the component with the lowest pressure being admitted first into the premix vessel PM1 (see Figure 2.1). In these mixtures, the ratio of oxygen to nitrogen was 1:4 (i.e. almost the same as in air). Pressure measurements during the preparation of the reactant mixture were made with a 0-25 psia Bell and Howell type 4-366 general-purpose transducer PT1, which was calibrated with dry nitrogen and shown to have a linear response (see Figure 2.1). The output from the transducer was measured with a Croydon Type P3 Precision Potentiometer.

Prepared reactant mixtures were allowed to stand for 30 minutes at a temperature of 110°C to ensure homogeneity. Gas chromatographic analysis was carried out on mixtures which had been stored in the premix vessel for 1 hour and this confirmed that no apparent reaction had occurred between the styrene and oxygen.

2.3.3 Introduction of reactants into the reaction vessel

The reactants were introduced into the reaction vessel from

the heated premix vessel by first isolating the premix and reaction sections by closing stopcocks T11, T12, T18 and T19, then opening stopcocks T14, T16 and T17 and finally activating the reactant solenoid gate (see Figure 2.1). By pre-selecting the opening period of the solenoid gate, the required pressure of the reactants in the reaction vessel could be obtained by choice of suitable premixed reactant pressures. A gate opening period of 0.5 sec. was used for the majority of runs.

2.3.4 Conditioning of reaction vessel

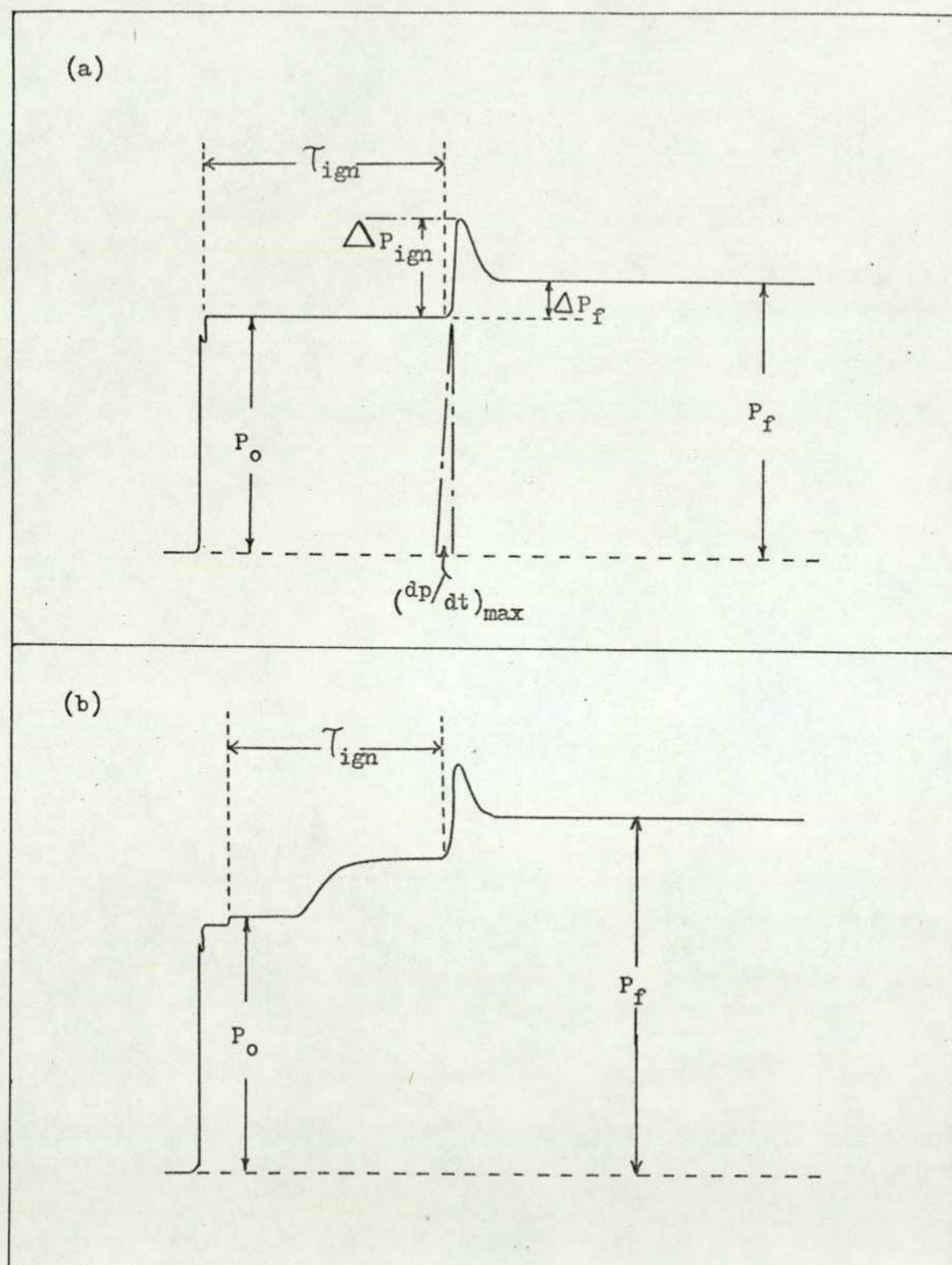
Prior to determination of the temperature/pressure ignition profile, about 50 slow combustion and ignition reactions were carried out in order to establish reproducible kinetic behaviour. Single-stage ignitions deposited a fine layer of carbon on the vessel surface which thereafter gave reproducible kinetic results. Even though the reaction vessel had been "conditioned", it was necessary to carry out at least three ignition reactions daily in order to maintain reproducibility.

2.3.5 Measurement of kinetic parameters

Two separate sets of kinetic studies were carried out. Initially, measurements were made of the temperature/pressure ignition profile for styrene-air mixtures with a molar ratio of 1:5. Subsequently, slugs of polymerising monomer were introduced into the reaction vessel and further measurements of the ignition characteristics were then carried out.

Figure 2.6(a) shows a standard pressure-time trace under conditions of temperature and pressure where single-stage ignition occurs. The trace relates to the studies where only vapour mixtures were introduced into the reaction vessel. P_f is the final pressure

Figure 2.6

Measurement of Kinetic Parameters

and P_0 is the initial pressure of the reactants admitted to the reaction vessel. ΔP_{ign} , the maximum pressure rise associated with the propagation of ignition, was measured as the difference between the maximum pressure at the ignition and the pressure prior to its propagation.

The induction period preceding ignition was measured as the time interval between the introduction of the reactant mixture into the vessel and the onset of the pressure rise associated with the passage of ignition.

Figure 2.6 (b) shows a typical pressure-time trace for a reaction where ignition occurs following the introduction of a slug of liquid monomer. In this case, P_0 corresponds to the overall initial pressure measured at the instant when the capsule compartment is opened to the reaction vessel in order to admit the polymerising monomer.

The induction period preceding ignition was measured as the time interval from the point of introduction of the slug into the reaction vessel to the onset of ignition.

2.3.6. Temperature measurements

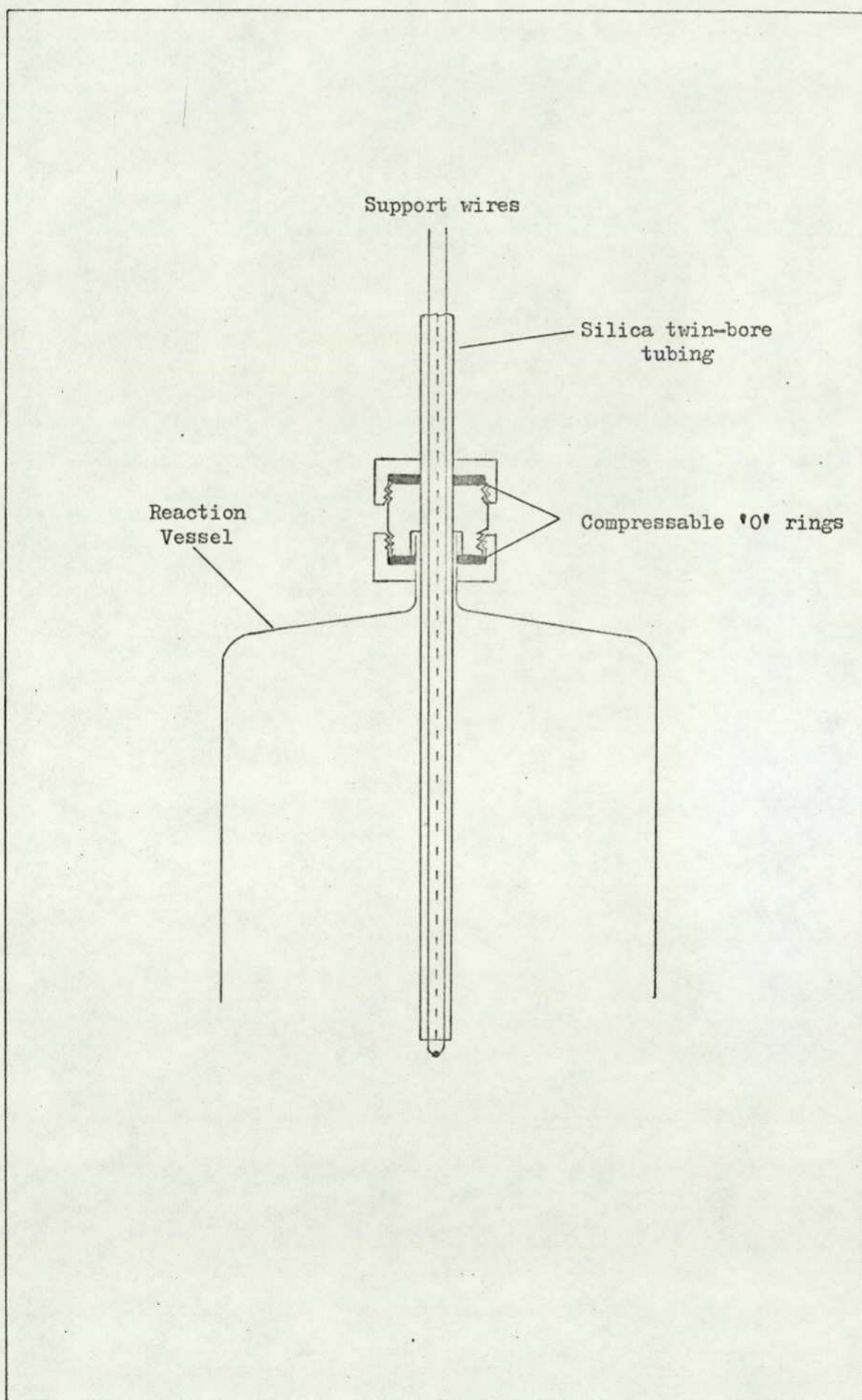
Temperature changes occurring on introduction of capsules of polymerising monomer into the reacting styrene-air vapour mixture were followed by using a 0.025 mm platinum/87% platinum + 13% rhodium thermocouple. The thermocouple junction was spot-welded and had a bead diameter of ca. 0.04 mm. The junction was supported on 0.25 mm wires of the same material seated in a twin-bore capillary silica tube. The tube was arranged so as to act as a probe which could be adjusted to any chosen position on the vertical length of the

cylindrical reaction vessel and the arrangement is shown in Figure 2.7. Finally, Kaskan's method¹⁰⁸ was used to deposit a thin layer of silica on the exposed thermocouple wires and thus prevent catalysis of combustion reactions. A similar thermocouple was maintained at a constant temperature of 0°C and was used as a reference.

Output signals from the thermocouple were recorded in exactly the same manner as for pressure changes (Section 2.1.4).

2.3.7 Product sampling

Sampling of the reacting gases was usually carried out during the induction period in order to avoid secondary reactions. Samples for analysis for major hydrocarbons and oxygenates were obtained as follows. The tap T20 (Figure 2.1) was closed and taps T21 and T23 were opened, thereby allowing the sampling operation to be controlled by the product solenoid valve PSV. The gas sample was withdrawn into an evacuated glass trap ST which had a volume of 34.75 cm³ and was maintained at a temperature of ca. 100°C. The final pressure achieved in the trap was noted on the manometer M2. This would allow calculation of the total products in the reaction vessel, after the contents of the trap had been analysed. In order to ensure that the small quantity of reactants between taps T17, T18 and T19 did not interfere with the sampling, the calibration vessel CV was included in the line. Thus, when the product gate was operated, the reaction mixture was allowed to expand into a volume of approximately 600 cm³ and a representative sample was obtained. After admission of the products into the trap, taps T25-T28 were closed, the trap was removed and the sample was analysed by gas chromatography.

Figure 2.7The micro-thermocouple

2.4 Analytical Procedures

2.4.1 Gas chromatographic analysis

2.4.1.1 The gas chromatograph

A Perkin-Elmer F11 Gas Chromatograph was used throughout the analytical work. This was fitted with a dual flame-ionisation detector. The output signal from the detector amplifier was recorded on a single-channel Hitachi - Perkin Elmer 159 chart recorder.

2.4.1.2 Preparation of columns

Two different column packings were employed as shown in Table 2.1. The packing for column II was purchased from Perkin-Elmer and the packing for column I was prepared as follows. A known weight of Chromosorb P, (60-80 mesh), was made into a slurry with as little acetone as possible. The weighed 1,2,3-tris (2-cyanoethoxy) propane was added to the same solvent and thoroughly mixed with the slurry. The solvent was then evaporated slowly on a rotary evaporator and the material was dried for 24 hours at 110°C under vacuum.

Stainless steel tubing, previously cleaned with dilute nitric acid, distilled water and acetone, was dried by passing dry nitrogen and was then packed by gravity feed. The complete columns were finally conditioned by passing nitrogen carrier gas through them for 24 hours whilst they were mounted in the chromatograph oven, which was maintained at 20°C above the normal column working temperature.

2.4.1.3 Operating conditions for columns

Column I was found to be suitable for separation of C_6-C_{10} aromatic hydrocarbons with saturated and unsaturated side-chains. However, column I was unsuitable for resolving higher-boiling hydrocarbons and oxygenates such as naphthalene, benzaldehyde and acetophenone.

Table 2.1Gas-Liquid chromatography column specifications

Column No.	I	II
Liquid phase	1,2,3-tris (2-cyanoethoxy) propane (TCEP)	Apiezon L
Support	Chromosorb P 60-80 mesh	Chromosorb P 80-100 mesh
% w/w liquid phase loading	5	15
Carrier gas flow (nitrogen, $\text{cm}^3 \text{min}^{-1}$)	24	23
Temperature of operation ($^{\circ}\text{C}$)	90	70, 90
Detector	F.I.D.	F.I.D.
Column dimensions	3m X 3 mm O.D.	2m X 3 mm O.D.

Column II was therefore used for separation of these higher-boiling materials. The composition of the columns and the conditions used are shown in Table 2.1.

2.4.1.4 Introduction of samples

A four-port Perkin Elmer gas sampling valve was used to inject the samples. In the 'off' position the carrier gas passed directly to the column, but in the 'on' position, the nitrogen swept through the sampling loop, carrying the sample onto the column in the form of a plug. Liquid samples were injected directly into the carrier gas stream through a silicone-rubber septum. The valve and any gas lines outside the chromatograph oven were heated by sheathed nichrome wire to prevent any condensation of products.

2.4.1.5 Identification of products

The products were identified by comparison of their retention times with those of model compounds obtained commercially. The comparisons were usually carried out on the two columns for confirmation of the identification.

A flame-ionisation detector was used throughout the investigation and as a consequence carbon oxides, water and hydrogen peroxide were not detected. Other possible products such as acids were too polar to be eluted from the column within a reasonable time.

2.4.2 Colorimetric analysis

2.4.2.1 The spectrophotometer

A Perkin-Elmer model 137 ultra-violet spectrophotometer with a range from 200-750 nm was used for the determination of formaldehyde. Matched quartz cells (1 cm.), were used to determine the absorption of the formaldehyde-chromotropic acid complex at 570 nm..

2.4.2.2 Analysis for formaldehyde

Formaldehyde was determined using the technique developed by Bricker and Johnson.¹⁰⁹

A solution of chromotropic acid (1,8 - dihydroxynaphthalene - 3,6 - disulphonic acid) was prepared by dissolving 2.5 g of the dry powder in 25 cm³ of distilled water. This solution gradually changed colour on standing, although it has been reported to be perfectly stable for about two weeks.

The method of sample preparation was similar to that used in the gas chromatographic investigations (Section 2.4.1.4). However, in this case, the reaction products were passed through the sampling trap immersed in liquid nitrogen. The sample was dissolved in water and made up to 50 cm³ in a volumetric flask. 1 cm³ of this solution was transferred to a glass-stoppered test tube and 0.5 cm³ of the chromotropic acid solution were added. 5 cm³ of concentrated sulphuric acid were then poured slowly into the test tube accompanied by continuous shaking. The test tube was stoppered and placed in a beaker of boiling water for 30 minutes. It was then cooled and after dilution and further cooling, made up to 50 cm³ in a volumetric flask. The transmission of the coloured solution was then read against a reagent blank at 570 nm.

2.4.3 Infrared spectrophotometric analysis

2.4.3.1 The spectrophotometer

A Perkin-Elmer model 457 infrared grating spectrophotometer was used for the determination of polymeric styrene in styrene monomer. KBr and NaCl cells of path length 0.1 mm were used with air as reference. The instrument has a range from 2.5 μm (4000 cm⁻¹) to 16 μm (625 cm⁻¹).

2.4.3.2 Analysis for polymeric styrene in styrene monomer

The extent of polymerisation of the liquid monomer in the capsule, at a given temperature, was monitored by infrared spectroscopy. The infrared transmission spectrum of styrene monomer in the region of 2.5 to 14 μm shows several characteristic bands such as those due to the $=\text{CH}_2$ of the vinyl group and the $=\text{CH}$ of the benzene ring, both at 3.25 μm . The vinyl $\text{C}=\text{C}$ band at 6.15 μm and the aromatic $\text{C}=\text{C}$ band at 6.35 μm are also characteristic. During polymerisation, a new band caused by $-\text{CH}_2-$ appears at 3.4 μm .

SECTION 3

RESULTS

SECTION 3

		Page No.
3.1	<u>Vapour-phase polymerisation of styrene</u>	90
3.1.1	Measurements in absence of oxygen	90
3.1.2	Measurements in presence of oxygen	90
3.2	<u>Pyrolysis of styrene</u>	91
3.2.1	Measurements in absence of oxygen	91
3.2.2	Measurements in presence of oxygen added initially	91
3.2.3	Measurements in presence of oxygen added subsequently	91
3.3	<u>Vapour-phase oxidation of styrene</u>	93
3.3.1	<u>Slow combustion</u>	93
3.3.1.1	Kinetic behaviour of styrene-oxygen mixtures	93
3.3.1.2	Products of reaction of styrene-oxygen mixtures	101
3.3.2	<u>Spontaneous ignition</u>	107
3.3.2.1	Measurements with styrene-oxygen mixtures	107
3.3.2.2	Measurements with styrene-air mixtures	110
3.3.2.3	Induction periods preceding hot ignition	110
3.3.2.4	Maximum accompanying pressure rise	110
3.3.2.5	Maximum rate of pressure rise accompanying hot flame	116
3.3.2.6	Residual pressure after passage of hot flame	116
3.3.2.7	Products of ignition of styrene-air mixtures	116

3.4	<u>Influence of polymerising styrene upon the ignition tendency of styrene-air vapour mixtures</u>	120
3.4.1	Polymerisation of liquid styrene in the capsules	120
3.4.2	Effect of inhibited monomer	122
3.4.3	Effect of inhibitor-free monomer	126
3.4.4	Effect of initiator-containing monomer	126
3.4.5	Effect of solid polystyrene	130
3.4.6	Cooling effects	133
3.4.7	Effect of polymerising styrene on product distribution	136
3.5	<u>Temperature measurements</u>	136
3.5.1	Temperature changes in reacting styrene-air mixtures	136
3.5.2	Temperature changes accompanying addition of solid polystyrene	139
3.5.3	Temperature changes accompanying addition of polymerising liquid styrene	141

Glossary

P_o	initial pressure
ΔP_{ign}	pressure rise accompanying the hot flame
P_f	residual pressure after passage of the hot flame
ΔP_f	residual pressure change
τ_{ign}	induction period of ignition
$(dP/dt)_{max}$	maximum rate of pressure rise accompanying the hot flame
ΔT_{ign}	temperature change accompanying the hot flame

3.1 Vapour-phase polymerisation of styrene

3.1.1 Measurements in absence of oxygen

The course of polymerisation was followed by pressure measurements and by periodic gas chromatographic analysis of the reactants and products. Experiments were carried out in the temperature range 180–300°C. From a handling viewpoint, initial partial pressures of styrene of ca. 10 kNm⁻² were found to be most convenient. Mixtures of styrene and oxygen-free nitrogen were also used in order to investigate reactions at higher total pressures.

Runs were carried out at 20° intervals within the above temperature range and, at each temperature, the reactant gases were left in the reaction vessel for a period of one hour and pressure measurements were recorded at ten minute intervals. The total initial pressures ranged from 10 to 24 kNm⁻². Below the depolymerisation temperature (ca. 300°C), no pressure change was observed and gas chromatographic analysis verified that no reaction had occurred after one hour.

3.1.2 Measurements in presence of oxygen

Experiments were also carried out in the same temperature and pressure ranges with the addition of 1–5% oxygen. Here again, no significant pressure change was observed and analysis of the products showed no evidence of chemical reaction. At 225°C, for example, a mixture containing 5% oxygen was left in the reaction vessel for 3 hours. A sample was then withdrawn for analysis but this showed no evidence of polymerisation. From these observations, it seems that oxygen does not initiate the vapour-phase polymerisation of styrene below 300°C.

3.2 Pyrolysis of styrene

3.2.1 Measurements in absence of oxygen

Experiments, similar to those described previously, were carried out at temperatures ranging from 300 to 500°C. However, no pressure changes were observed and gas chromatographic analysis showed that the extent of pyrolysis was extremely small even after two hours at 550°C. Between eight and twelve products were found in small amounts in the temperature range 500-550°C. Of these only the more volatile major components have been identified and are listed in Table 3.1.

These experiments thus show conclusively that, in the absence of oxygen and at the pressures and temperatures employed, styrene is stable up to 500°C although decomposition begins to occur to an increasing extent above this temperature.

3.2.2 Measurements in presence of oxygen added initially

Experiments were carried out with oxygen added at the start of reaction using the same initial reactant pressures as in the previous studies. One to five per cent oxygen was then added and measurements were carried out in the temperature range 300-500°C. In the presence of 5% of added oxygen, decomposition occurred at relatively low temperatures. After a styrene-oxygen mixture had been left in the reaction vessel at 320°C for 4 hours, the resulting mixture was sampled and six products were detected, although all were present in very low yields. At temperatures up to 550°C, some twelve products were detected in the presence of added oxygen. However, no appreciable pressure changes were observed.

3.2.3 Measurements in the presence of oxygen added subsequently

Experiments were carried out in the temperature range 500-550°C, in which 1-3% oxygen was added 30-50 minutes after the styrene had been introduced into the reaction vessel at an initial pressure of 10.7 kNm⁻². In each case, analysis was carried out one hour after introduction of the

Table 3.1Products identified resulting from the pyrolysis of styrene at ca. 500°C

Stationary phase	Column temp.(°C)	Products	Retention time (min)
TCEP	90	Benzene	1.9
		Toluene	2.7
		Ethylbenzene	3.7
		Styrene	7.3
		Naphthalene	67.9
Apiezon L	70	Benzene	1.3
		Toluene	2.3
		Ethylbenzene	4.6
		Styrene	6.3
	90	Styrene	3.5
		Naphthalene	21.3

oxygen. However, no pressure changes were detected following this later addition of oxygen and no change in the product distribution was observed.

3.3 Vapour-phase oxidation of styrene

3.3.1 Slow combustion

The vapour-phase oxidation of styrene has been studied using 1:1, 1:3, 1:5 and 1:10 styrene-oxygen mixtures in the temperature range 260-465°C. Rates of reaction were measured mainly by pressure change but with some supporting analysis of the principal products.

3.3.1.1 Kinetic behaviour of styrene-oxygen mixtures

No perceptible pressure change could be detected after one hour with any of the mixtures studied below 300°C.

At 309°C, pressure changes were observed with 1:3, 1:5 and 1:10 mixtures but not with the 1:1 mixture. At 317°C, a very slow reaction preceded by an induction period of ca. 30 minutes was observed for the 1:1 mixture. Figures 3.1 and 3.2 show pressure-time curves for various styrene-oxygen mixtures maintained at different temperatures. In all cases, after a preliminary acceleration, the rate of pressure change remained substantially constant until the reaction was about two-thirds complete.

The variation with time and pressure change of the rate of oxidation of different styrene-oxygen mixtures is shown in Figures 3.3 and 3.4 respectively. The maximum rate of oxidation is generally attained at ca. 40% conversion.

Figure 3.5 shows the variation with increasing partial pressure of oxygen of (a) the maximum rate of oxidation and (b) the reciprocal induction period. Both these quantities increase continuously with oxygen pressure.

Figures 3.6 and 3.7 show the pressure-time curves for the slow oxidation, at somewhat higher temperatures, of each of the mixtures studied.

Figure 3.1

Slow oxidation of (a) 1:3 and (b) 1:1 styrene-oxygen

mixtures at low temperatures

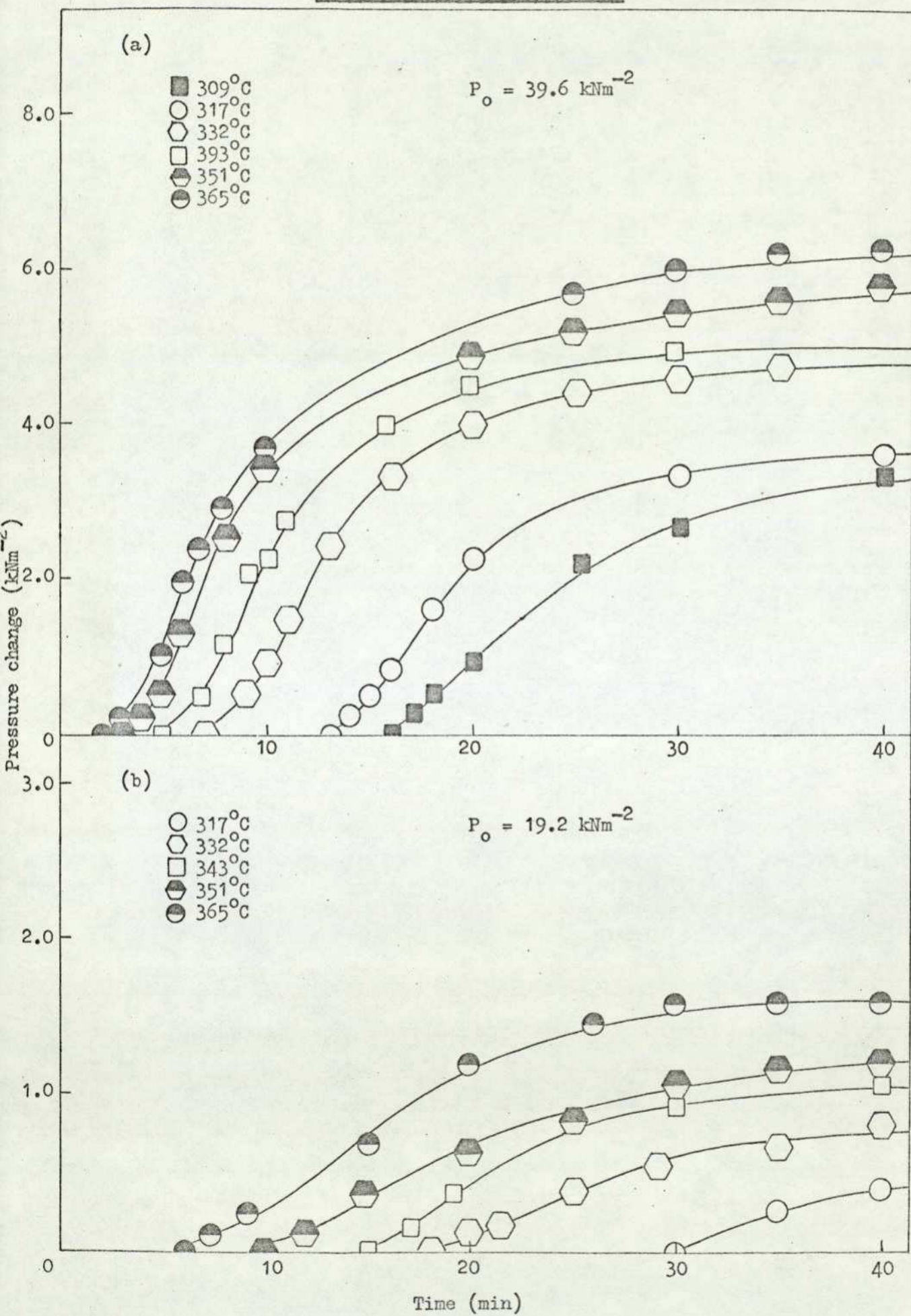
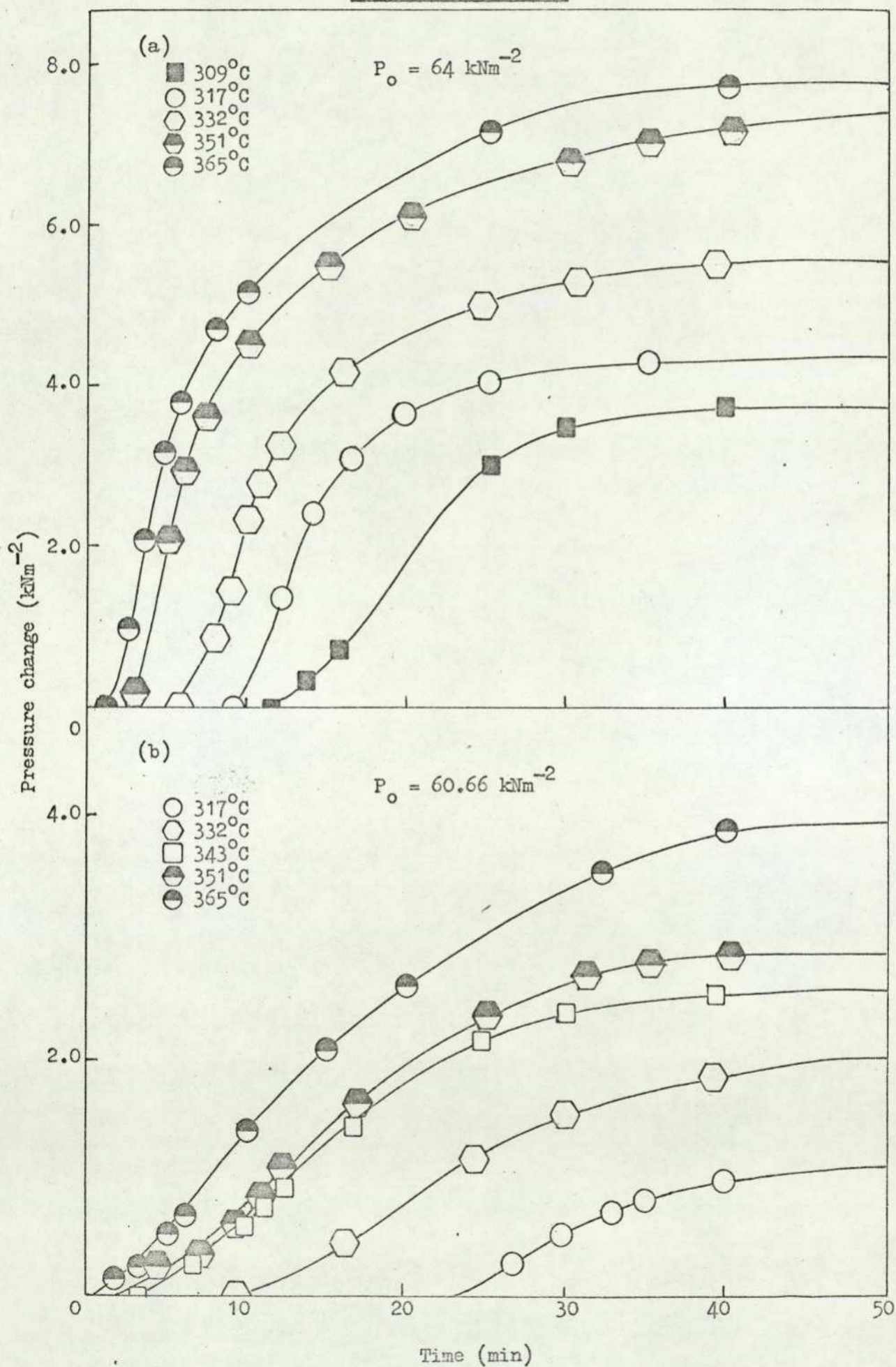
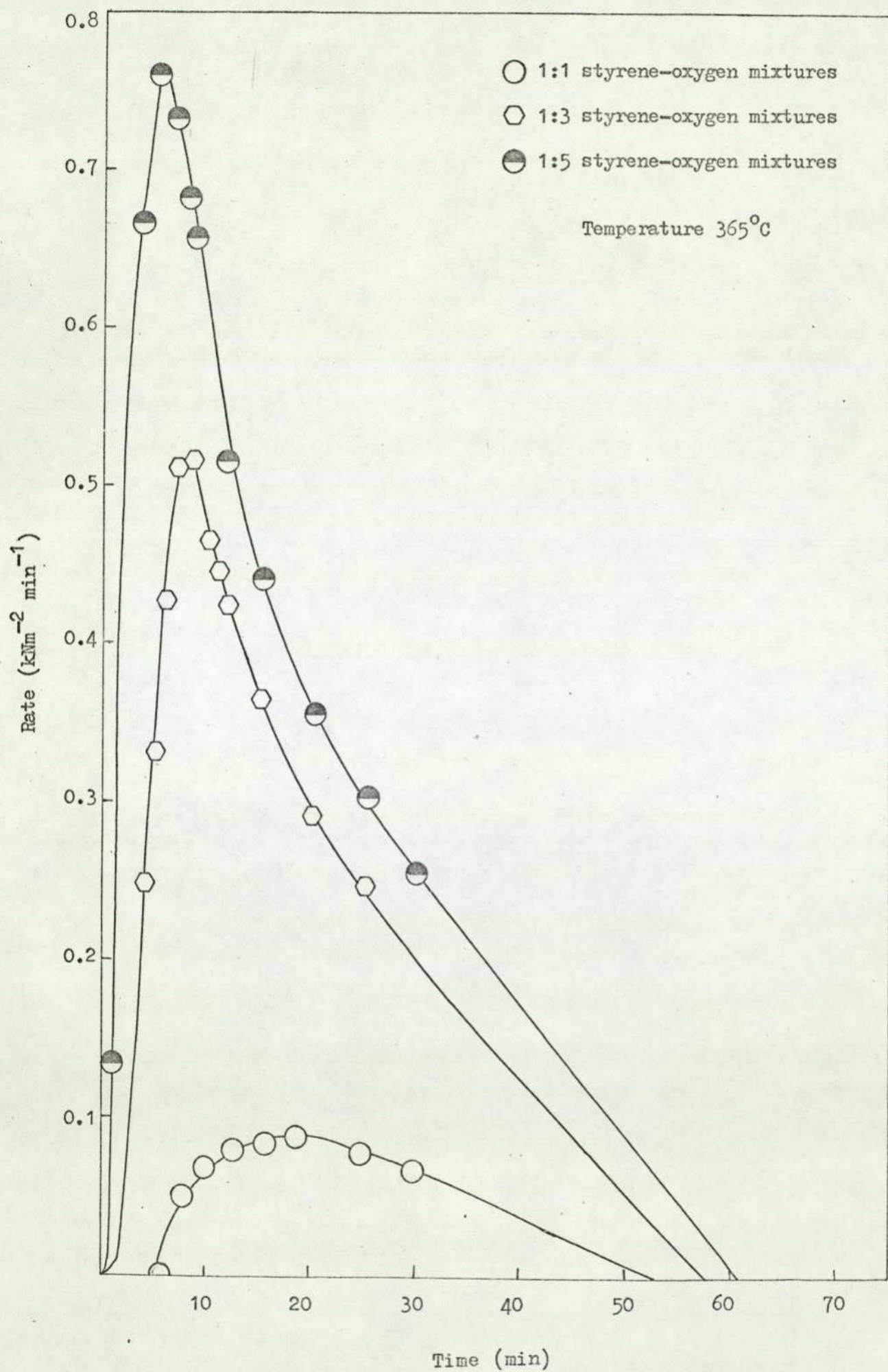


Figure 3.2

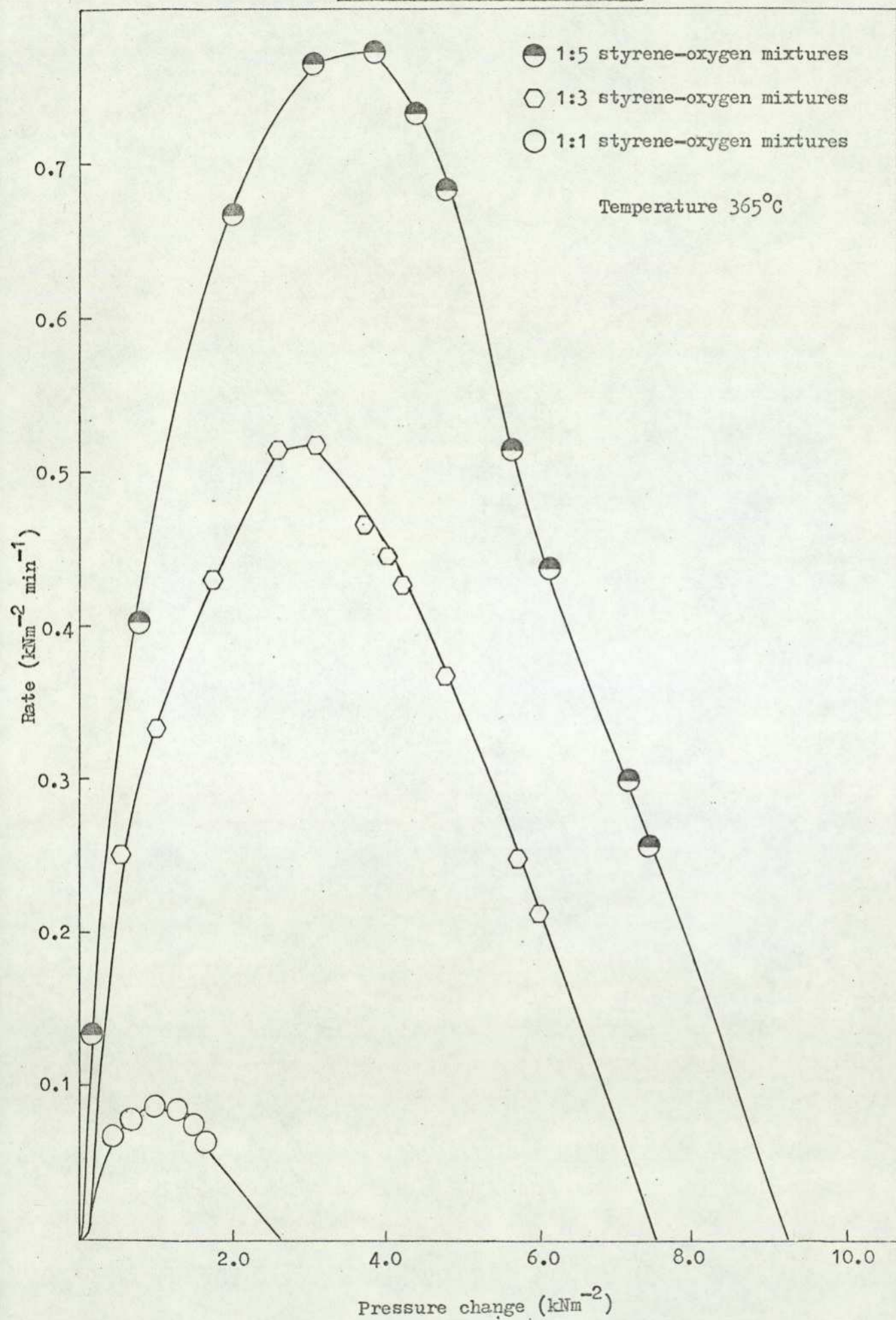
Slow oxidation of (a) 1:5 and (b) 1:10 styrene-oxygen mixtures

at low temperatures



Variation of reaction rate of styrene oxidation with time

Variation with accompanying pressure increase of the
rate of oxidation of styrene



Variation of (a) maximum rate of oxidation and
(b) the reciprocal of the induction
period with oxygen pressure

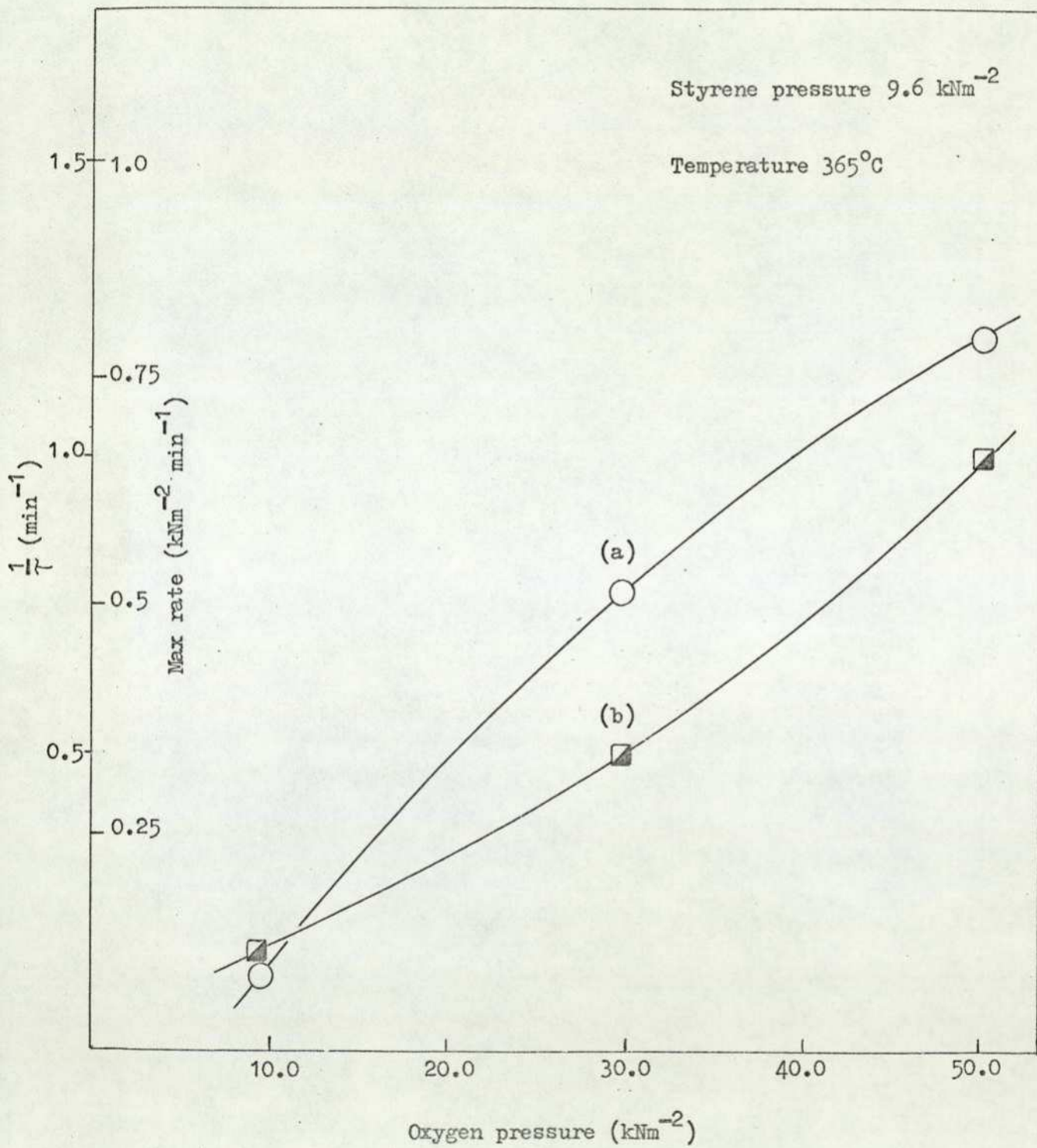
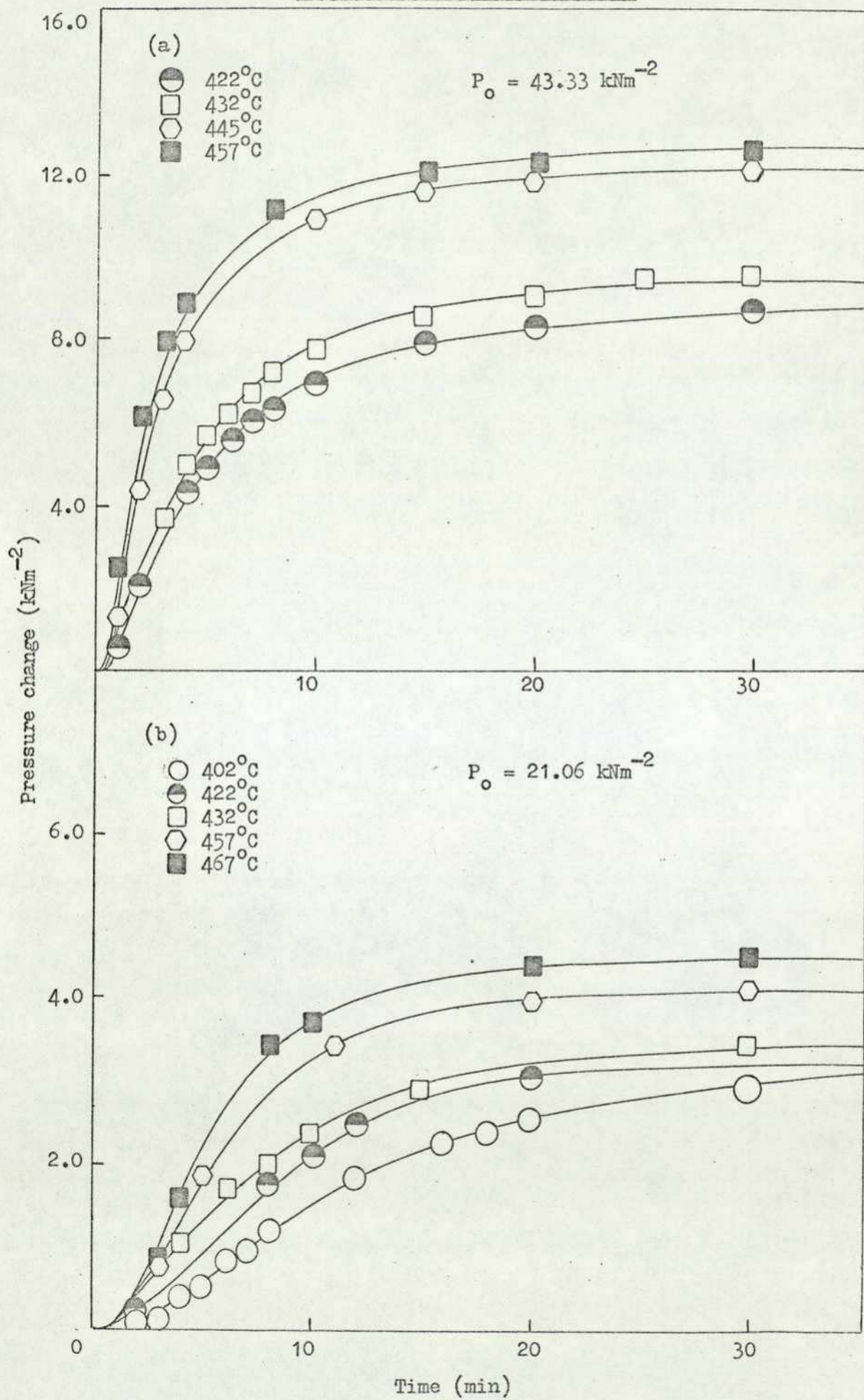


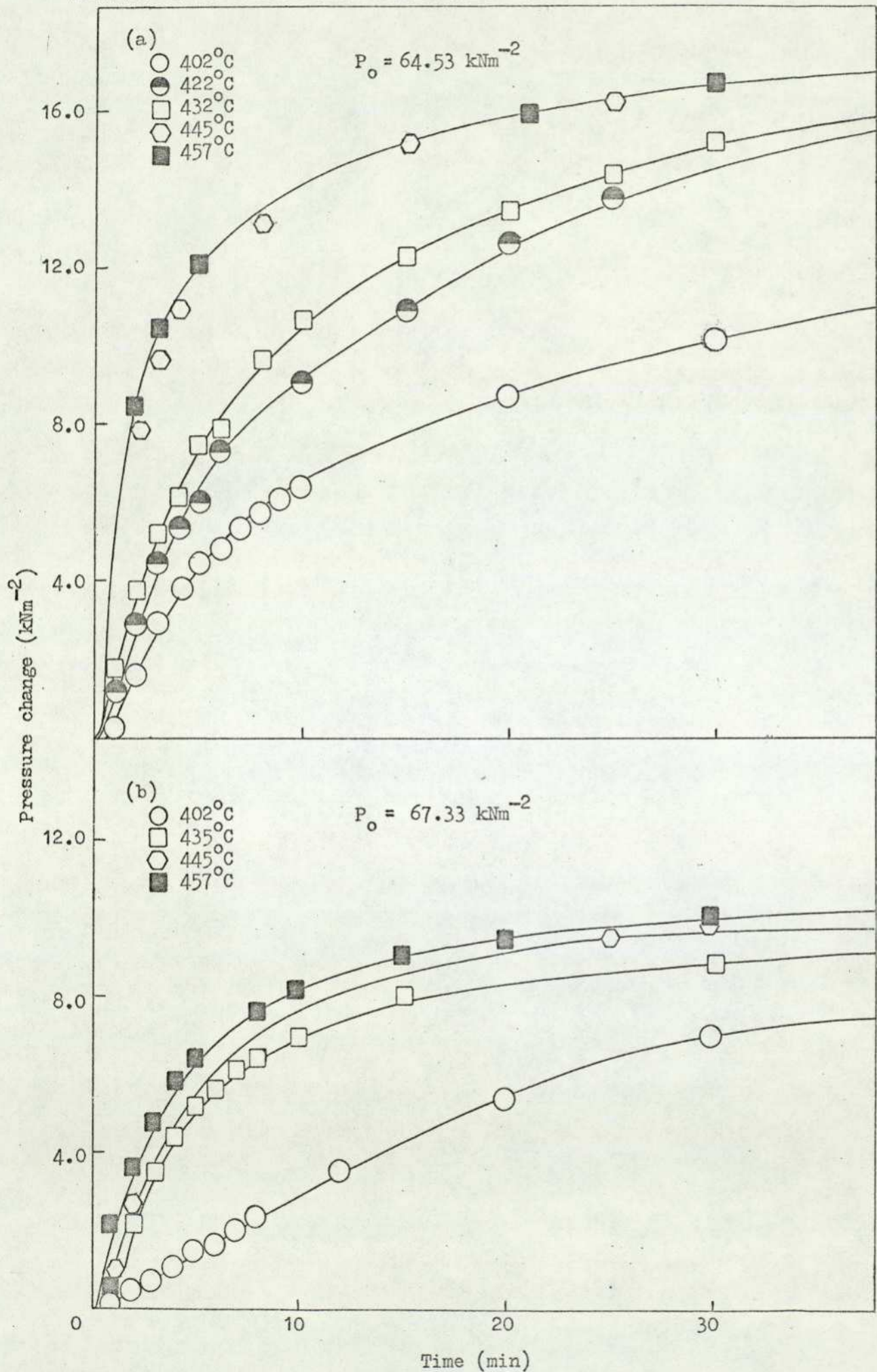
Figure 3.6

Slow oxidation of (a) 1:3 and (b) 1:1 styrene-oxygen

mixtures at high temperatures



Slow oxidation of (a) 1:5 and (b) 1:10 styrene-oxygen mixtures at high temperatures



Induction periods were considerably shorter than those observed at lower temperatures. Nevertheless, in this higher temperature region, induction periods of several seconds were still observed before the start of slow oxidation.

The variation in rate of oxidation at 457°C with time and initial pressure is shown in Figures 3.8 and 3.9 respectively for various styrene-oxygen mixtures. As at lower temperatures, the maximum rate of oxidation is observed quite early in the reaction. Whereas at lower temperatures the maximum rate of oxidation is generally found at 40% conversion for all mixtures, at higher temperatures the maximum rate is displaced towards the start of reaction as the partial pressure of oxygen is increased. Thus the maximum rate of oxidation occurs at 50% conversion for 1:1 styrene-oxygen mixtures, 43% conversion for 1:3 mixtures and 28% conversion for 1:5 mixtures.

The variation with temperature of the maximum reaction rate is shown in Figure 3.10 for 1:1 and 1:10 styrene-oxygen mixtures; there is no negative temperature coefficient of rate in either case.

Figure 3.11 shows that, with a 1:3 styrene-oxygen mixture, the final pressure increase after 30 minutes, ΔP_{30} , varies linearly with temperature.

3.3.1.2 Products of reaction of styrene-oxygen mixtures

Gas chromatographic analysis of the products of slow oxidation of styrene was carried out using an Apiezon L column exclusively; this limited the resolution of other products which might have been identified by use of a variety of back-up columns. Nevertheless, some 10 products were recorded for the slow oxidation of 1:1, 1:3 and 1:10 styrene-oxygen mixtures. Table 3.2 shows the product distribution for a 1:1 styrene-oxygen mixture analysed after 20 minutes. The principal product formed

Figure 3.8

Variation with time of the rate of oxidation
of styrene

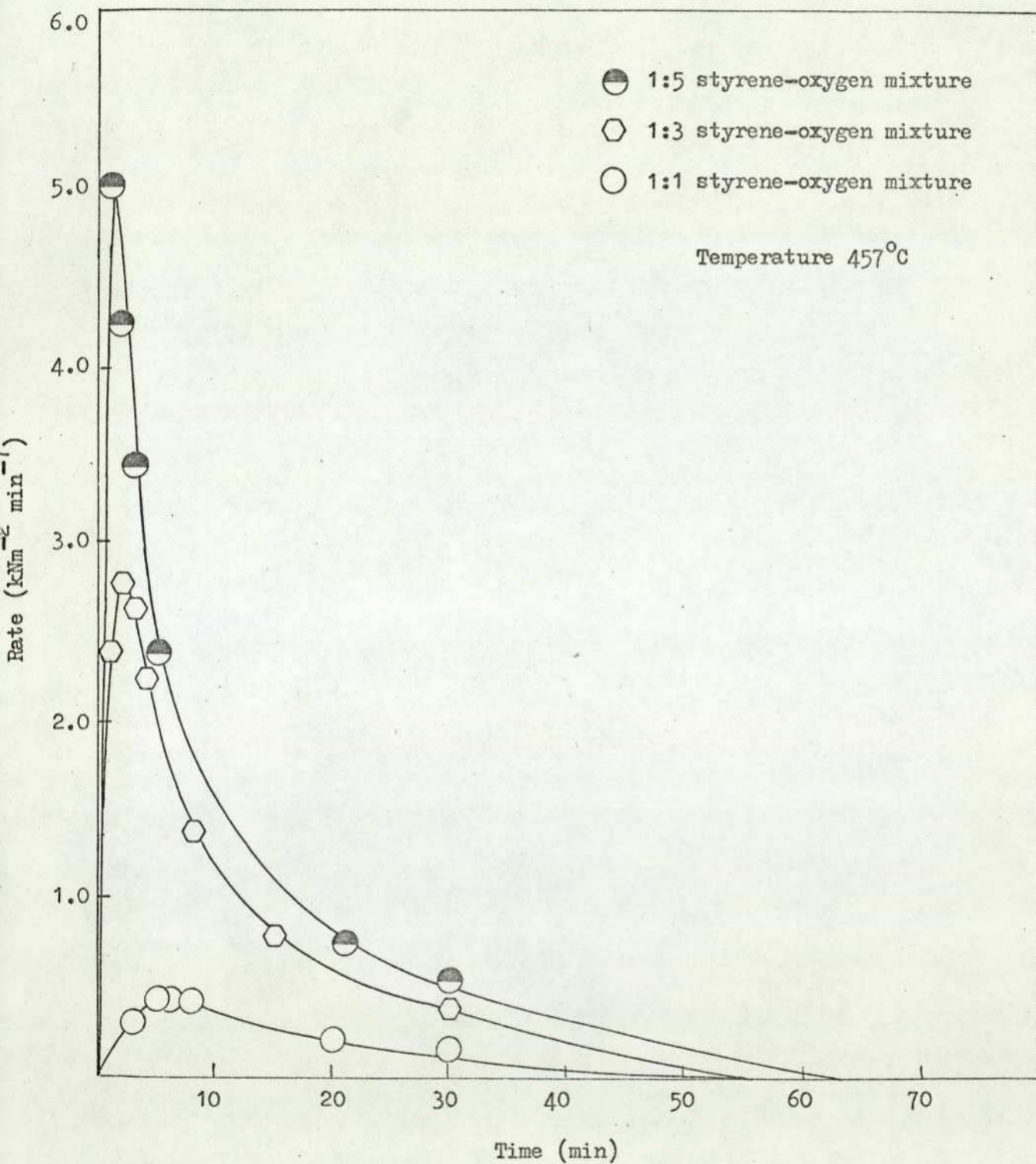


Figure 3.9

Variation of the rate of oxidation of styrene with
change in pressure

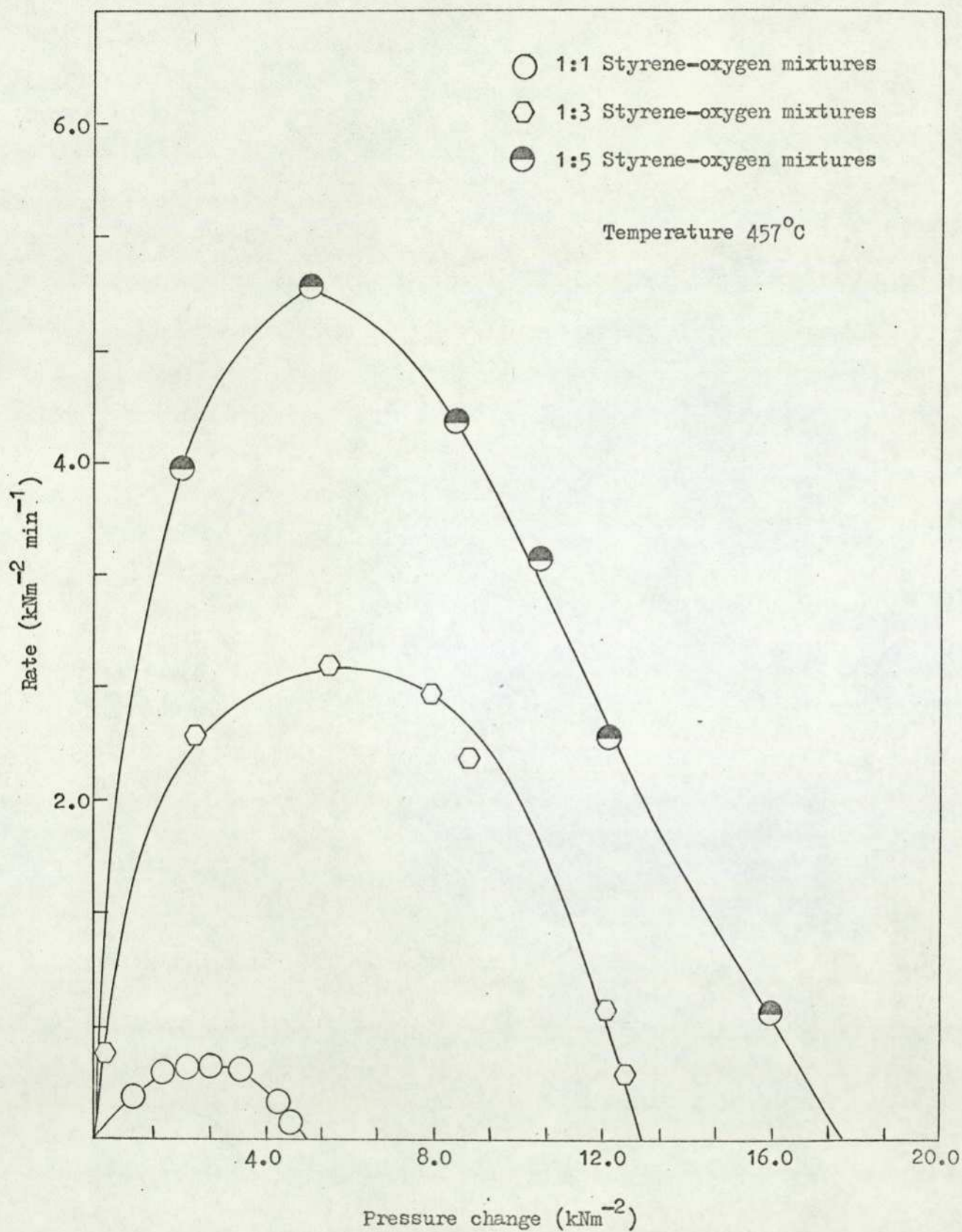


Figure 3.10

Variation of maximum rate of oxidation with temperature

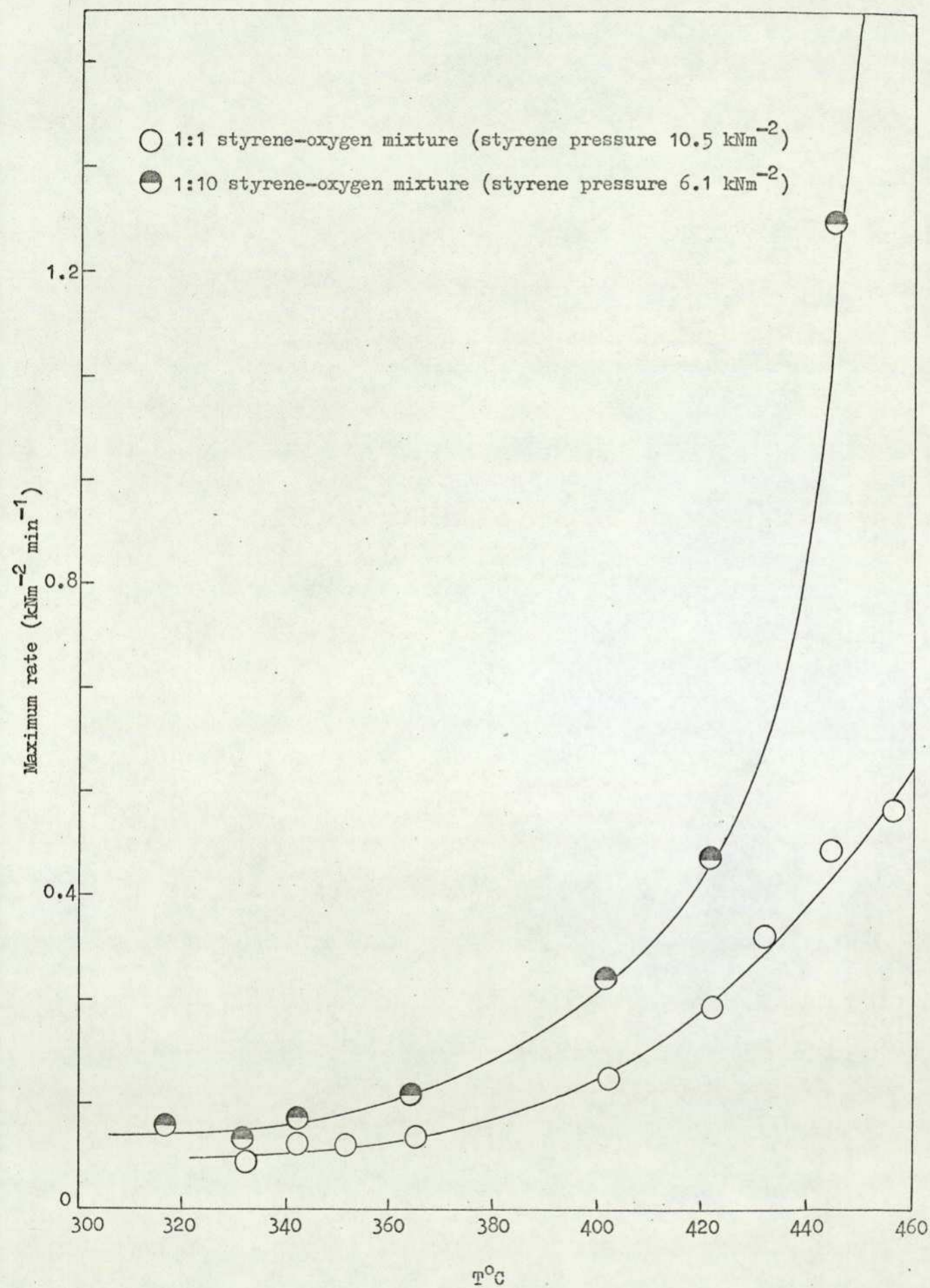


Figure 3.11

Variation of pressure increment expressed as a percentage of
initial pressure with temperature for a 1:3 styrene-oxygen mixture

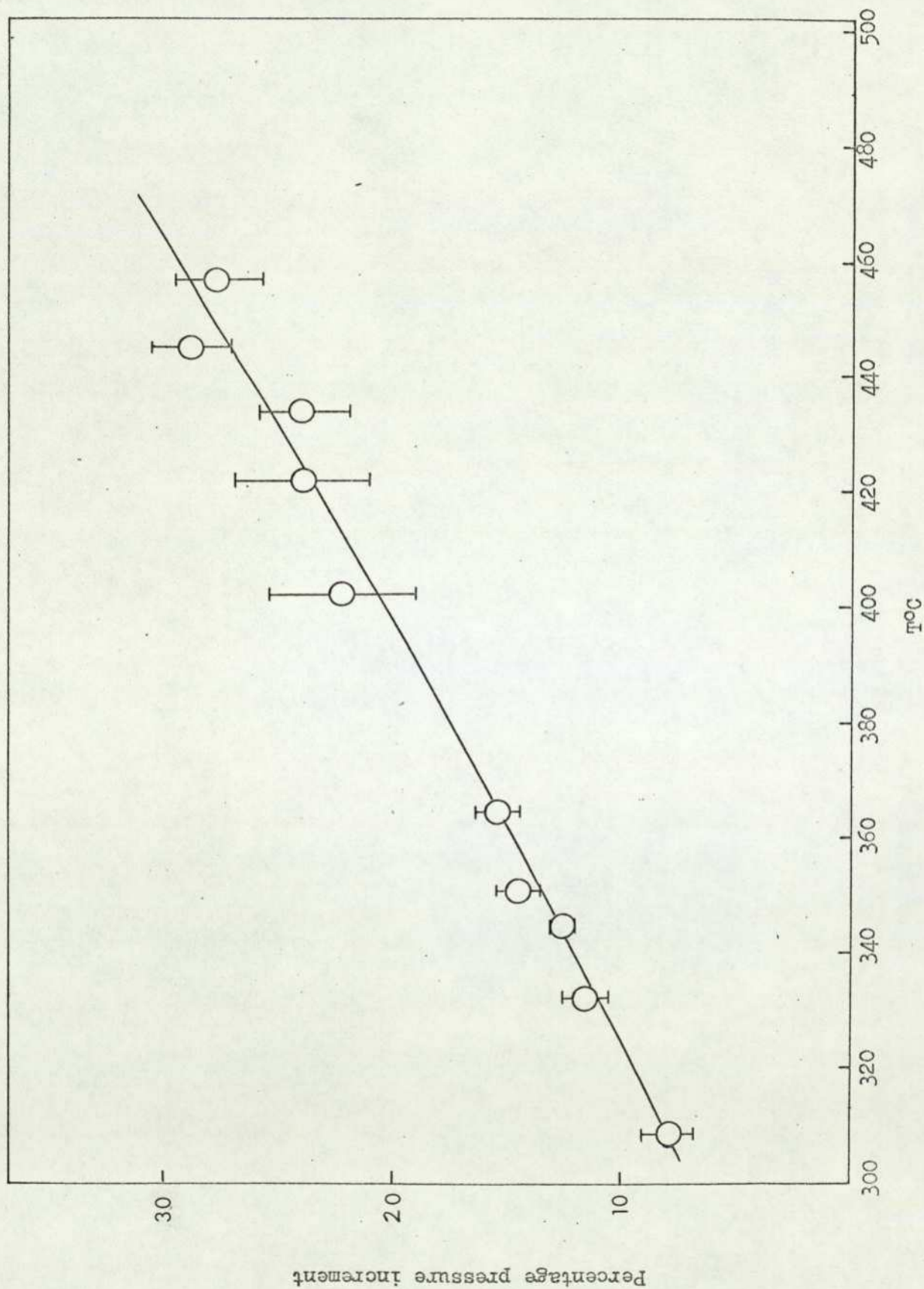


Table 3.2

Products of slow oxidation of equimolar styrene-oxygen mixtures at a
reaction temperature of 351°C

Analysis time: 20 min after introduction of reactants into the reaction
vessel

Pressure change, after 20 min: 667 Nm^{-2}

Initial pressure of reactants: 19.2 kNm^{-2}

Peak No.	Reaction Product	Retention time (min)
1	Unidentified	0.67
2	Benzene	1.17
3	Toluene	1.95
4	Ethylbenzene	3.42
5	Styrene	4.21
6	Unidentified	6.10
7	Benzaldehyde	7.38
8	Unidentified	13.07
9	Unidentified	28.83

from each of the mixtures was benzaldehyde and, in the case of a 1:1 styrene-oxygen mixture, at least twice as much of this compound was formed as any of the other individual products identified.

In the case of 1:3 and 1:10 styrene-oxygen mixtures, analysis showed the presence also of acetophenone, although this was the least abundant of the products identified.

3.3.2 Spontaneous ignition

Figure 3.12 shows typical pressure-time traces observed during the ignition of styrene-oxygen and styrene-air mixtures. With styrene-oxygen mixtures, the characteristic 'infinite' pressure rise is observed during ignition and an audible 'click' is heard. With styrene-air mixtures, on the other hand, ignition is a much milder phenomenon. Thus, for example, during the propagation of a hot flame through a 1:5 styrene-air mixture, (Figure 3.12 (b) (i)) ΔP_{ign} is small so that the final pressure, P_f , following passage of the flame is not very different from the initial pressure. The magnitude of both ΔP_{ign} and P_f increases with the initial pressure (Figure 3.12 (b) (ii)).

3.3.2.1 Measurements with styrene-oxygen mixtures

At subatmospheric pressures ignition was not observed in styrene-oxygen mixtures below 465°C. Figure 3.13 shows the variation with initial pressure of the induction period preceding ignition for a 1:5 styrene-oxygen mixture; it can be seen that relatively long induction periods are found at lower pressures.

No further experiments were carried out on styrene-oxygen mixtures in the ignition region, since copious carbon formation always accompanied ignition and the reaction vessel had to be 'burnt out' after each experiment. At higher pressures and temperatures, too, the reactions were too violent to be safely studied in a glass apparatus.

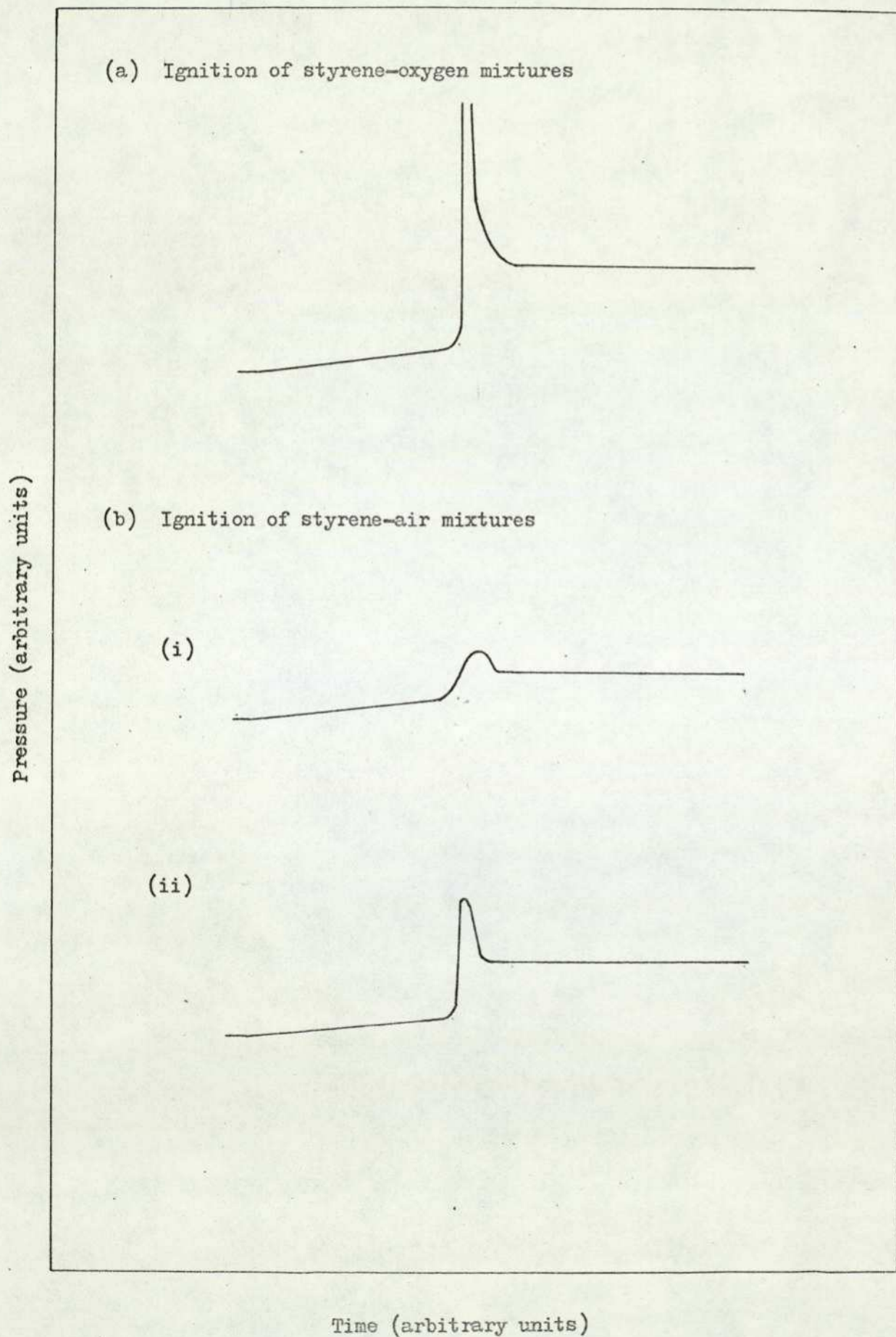
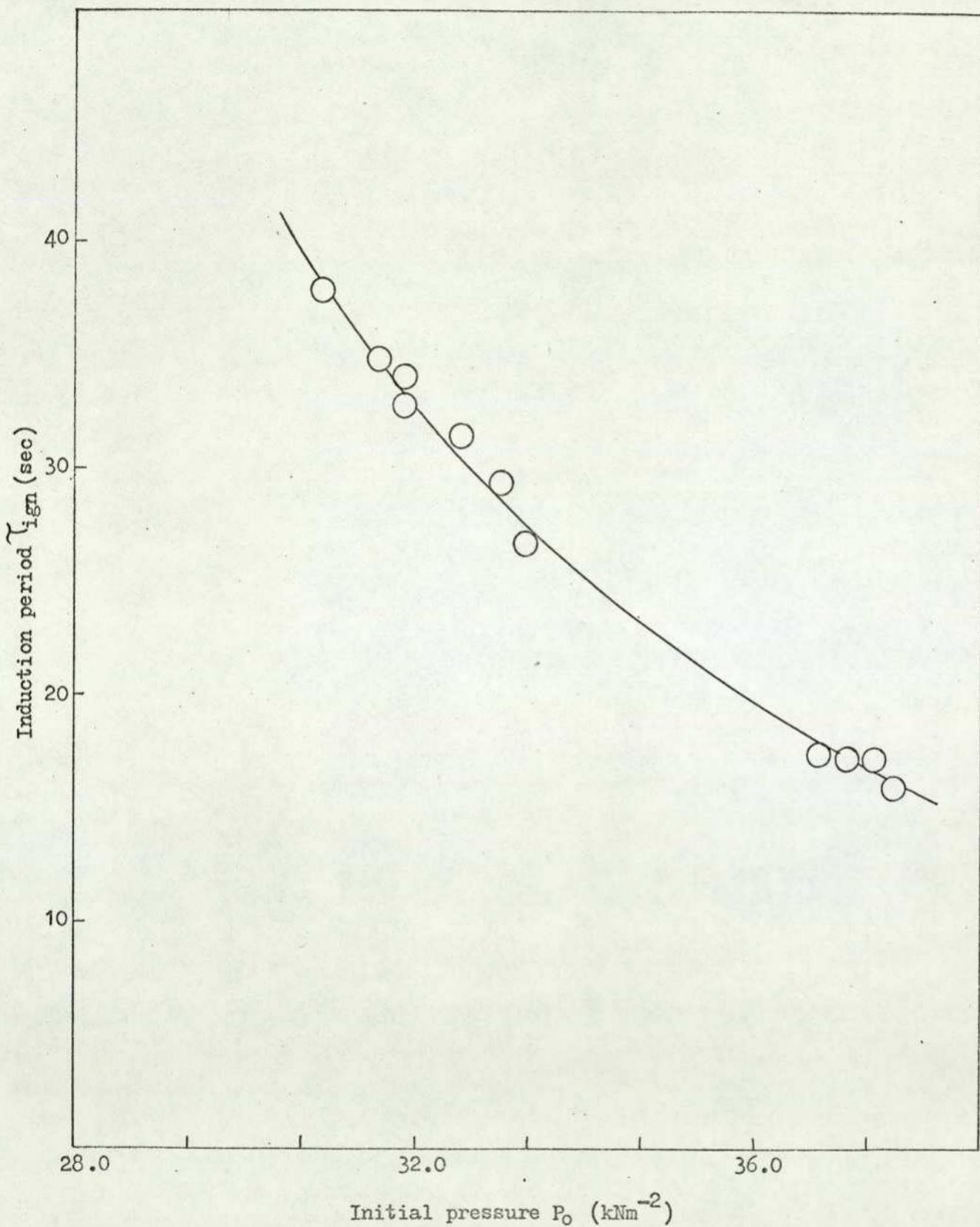
Figure 3.12Non-isothermal phenomena

Figure 3.13

Variation of induction period, τ_{ign} , with
initial pressure, P_0 , for a 1:5 styrene-oxygen
mixture at 465°C



3.3.2.2 Measurements with styrene-air mixtures

The conditions under which ignition was observed for a 1:5 styrene-air mixture have been used to construct a temperature/pressure ignition profile as shown in Figure 3.14. This profile is divided into two distinct regions. Throughout the range 300-510°C and at initial pressures of ca. 67 kNm⁻², only slow combustion occurs, but between 520 and 580°C and at pressures somewhat less than 60 kNm⁻², the initial slow reaction is followed by hot ignition. Similar temperature/pressure profiles have been reported for benzene, toluene and ethylbenzene at subatmospheric pressures.

3.3.2.3 Induction periods preceding hot ignition

Figure 3.15 shows the variation with initial pressure of the induction period preceding the hot flame (τ_{ign}). The induction periods vary from ca. 20 to 4 sec and it can be seen that, at all temperatures, the relationship

$$\tau_{\text{ign}} = kP_0^{-n}$$

holds for styrene-air mixtures. Figure 3.16 shows that $\log \tau_{\text{ign}}$ varies linearly with $\log P_0$.

3.3.2.4 Maximum accompanying pressure rise

The propagation of a hot flame is accompanied by an increase in pressure of between 3 and 22 kNm⁻². The magnitude of this pressure rise, ΔP_{ign} , is a function of both temperature and initial pressure, P_0 . Figure 3.17 shows the variation of ΔP_{ign} with P_0 at three initial temperatures. It can be seen that

$$\Delta P_{\text{ign}} = mP_0 - c$$

where m and c are constants, the values of which become independent of temperature above ca. 555°C. The logarithmic relationship between ΔP_{ign} and P_0 is shown in Figure 3.18.

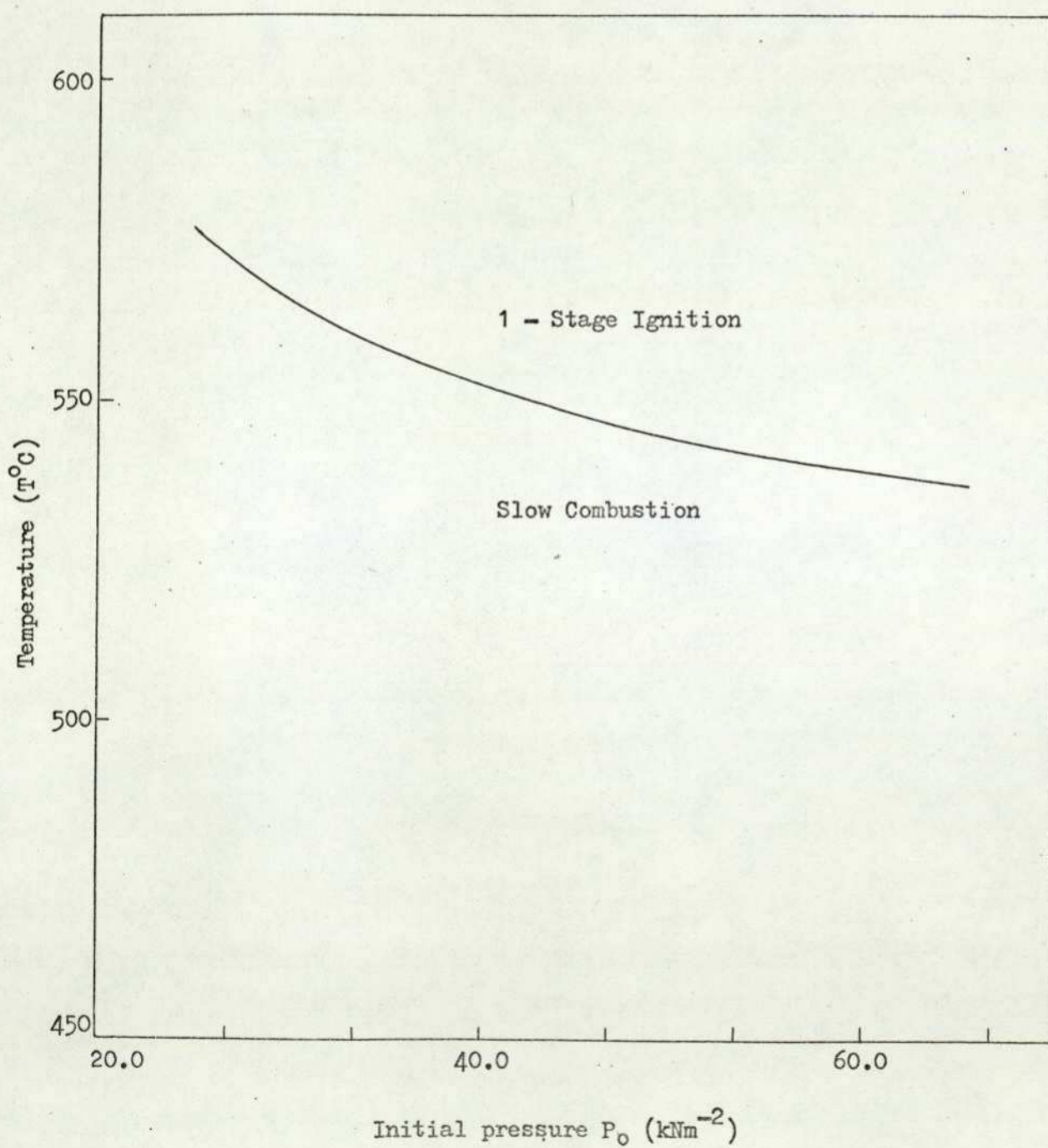
Figure 3.14IGNITION PROFILE FOR 1:5 STYRENE AIR MIXTURES

Figure 3.15

Induction periods for ignition of a styrene-air (1:5) mixture as a function of initial pressure at various temperatures

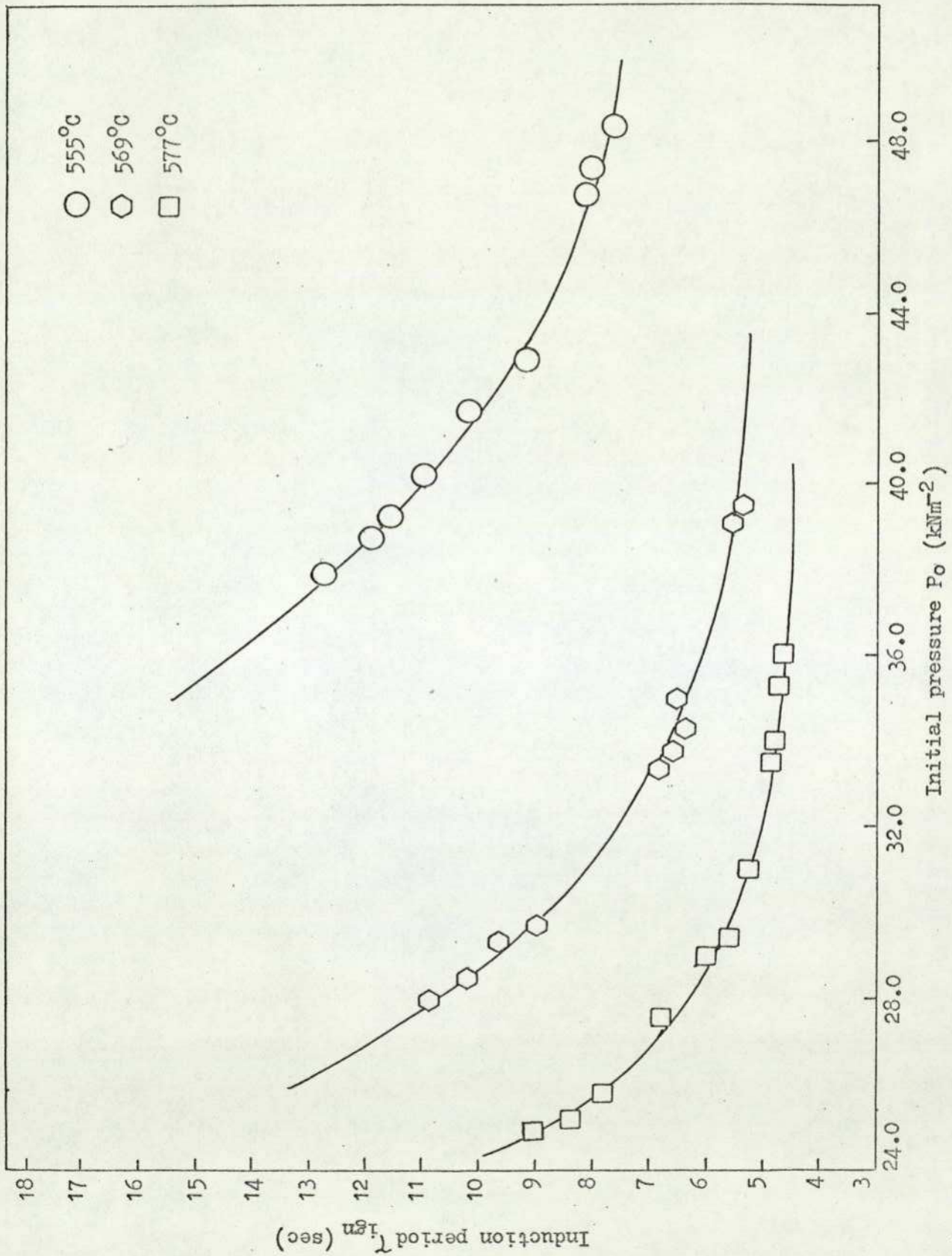


Figure 3.16

Logarithmic relationship between initial pressure and induction period

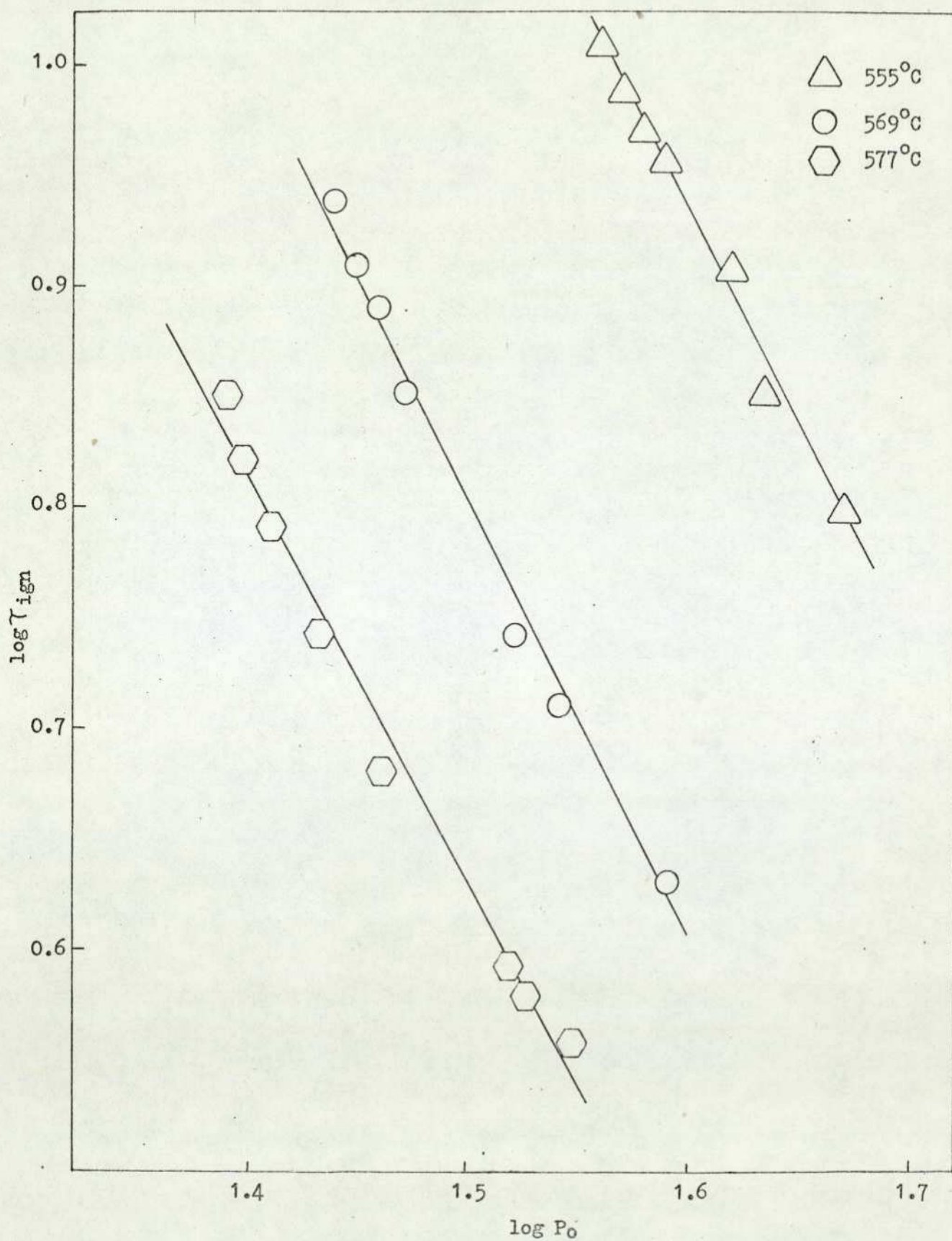


Figure 3.17

Variation of ΔP_{ign} with P_o

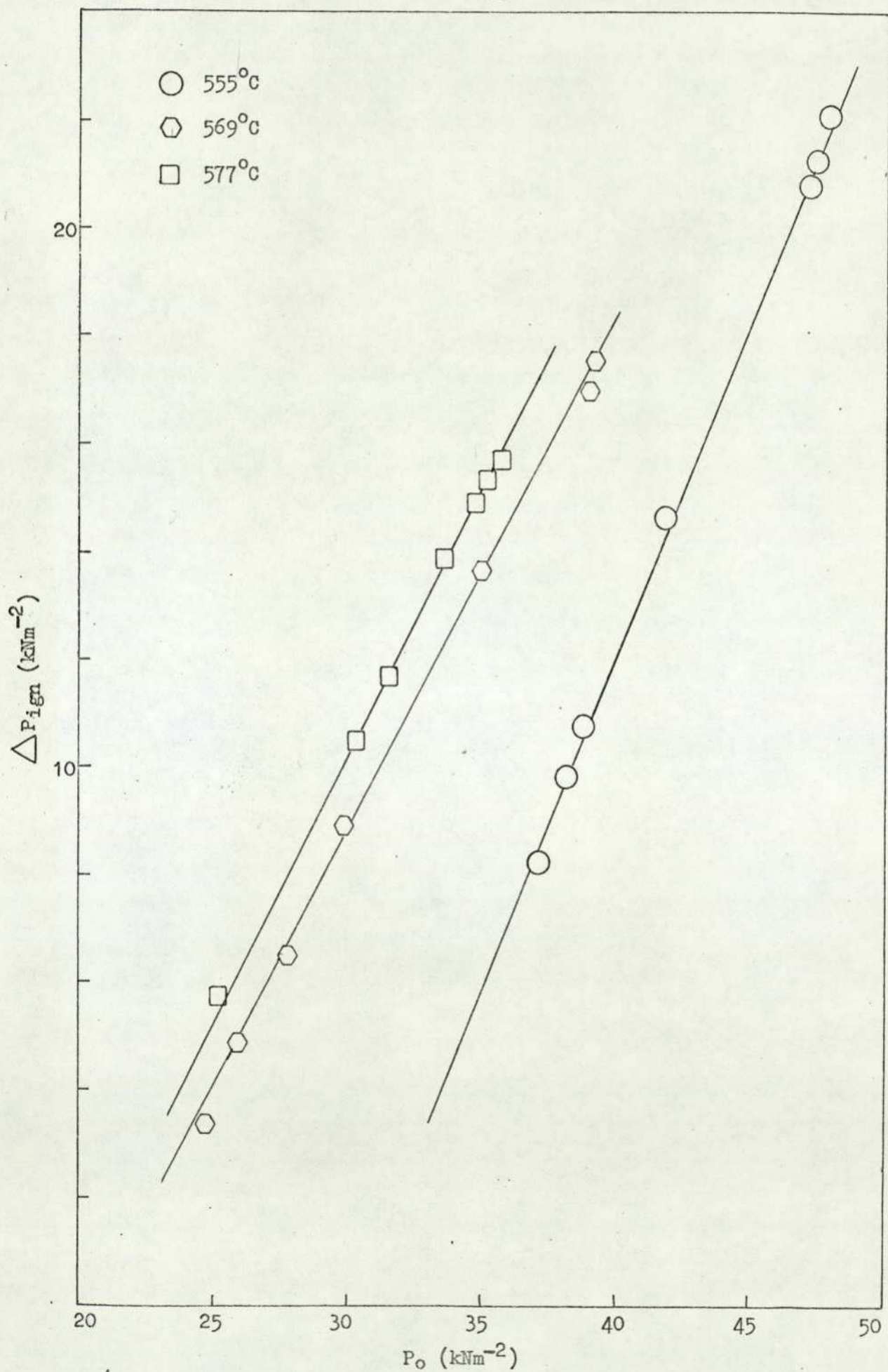
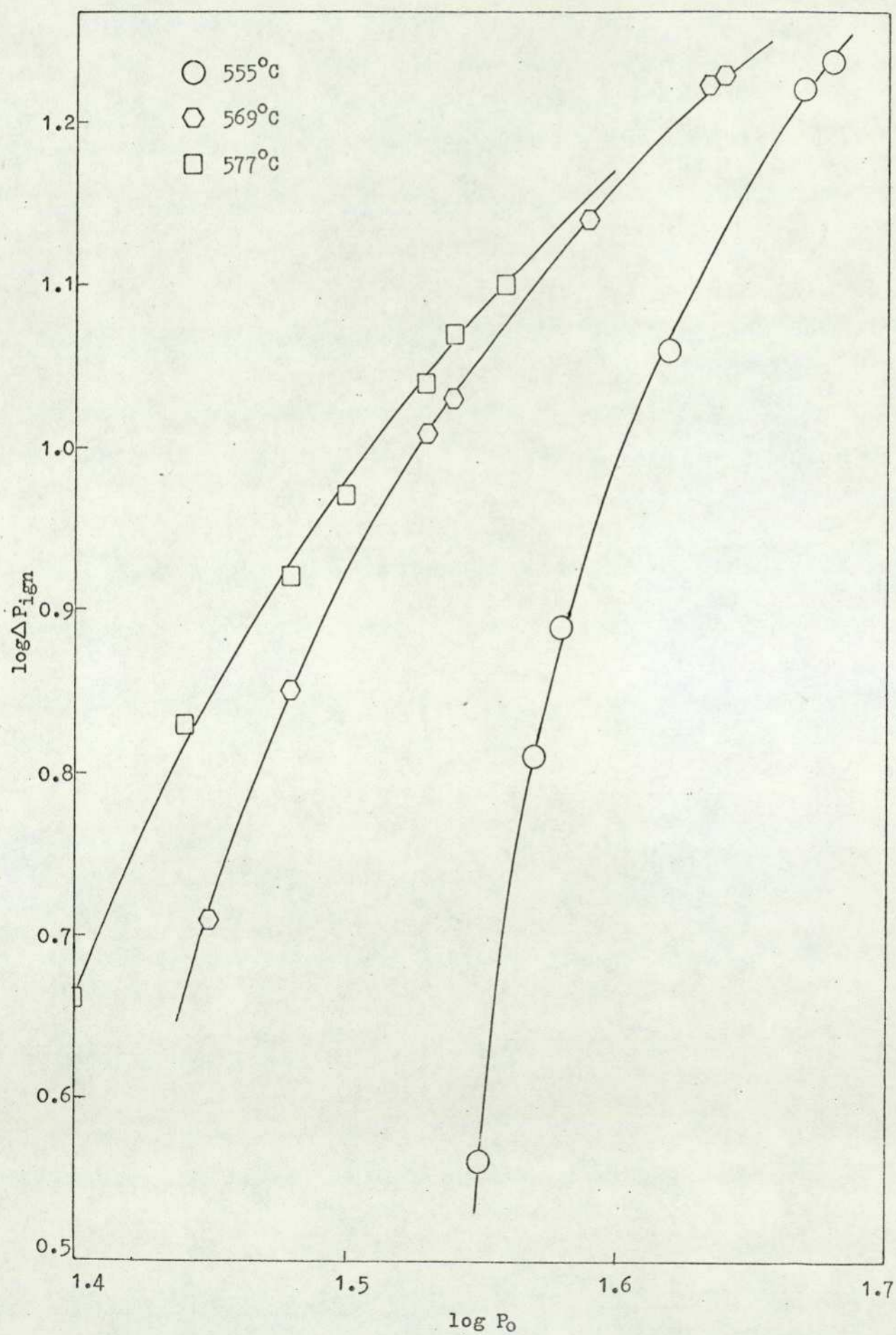


Figure 3.18

Logarithmic relationship of ΔP_{ign} with P_0 for the hot flame



3.3.2.5 Maximum rate of pressure rise accompanying hot flame

The maximum rate of pressure rise accompanying the passage of a hot flame, $(dP/dt)_{\max}$, is a measure of the maximum rate of chemical reaction associated with its propagation. The value $(dP/dt)_{\max}$ ranges from ca. 10 to 80 $\text{kNm}^{-2} \text{sec}^{-1}$, its value increasing with both the initial pressure and temperature (Figure 3.19).

3.3.2.6 Residual pressure after passage of hot flame

As can be seen from Figure 3.20 (a), the residual pressure, P_f , increases linearly with initial pressure but is independent of initial temperature. The ratio P_f/P_0 is usually about 1.1 over the range of pressure and temperature investigated.

Figure 3.20 (b) shows the variation with initial pressure of the residual pressure increase, ΔP_f , (expressed as a percentage of the total initial pressure). At lower initial pressures and at the slow-combustion/ignition boundary, the rise in pressure accompanying a hot flame, ΔP_{ign} , is small and ΔP_f is also small. However, from Figure 3.20 (b) it can be seen that, over a narrow range of initial pressures of ca. 13 kNm^{-2} , the value of ΔP_f increases rapidly by ca. 14%. This same behaviour is observed at each of the three temperatures studied.

3.3.2.7 Products of ignition of styrene-air mixtures

Table 3.3 shows the products formed during the slow combustion process leading to ignition. The principal products identified are virtually the same as those found in the oxidation of styrene at lower temperatures, the only 'new' product being benzyl alcohol. Furthermore, as at lower temperatures, benzaldehyde again appears to be the main product at the temperature of ignition, ca. 570°C.

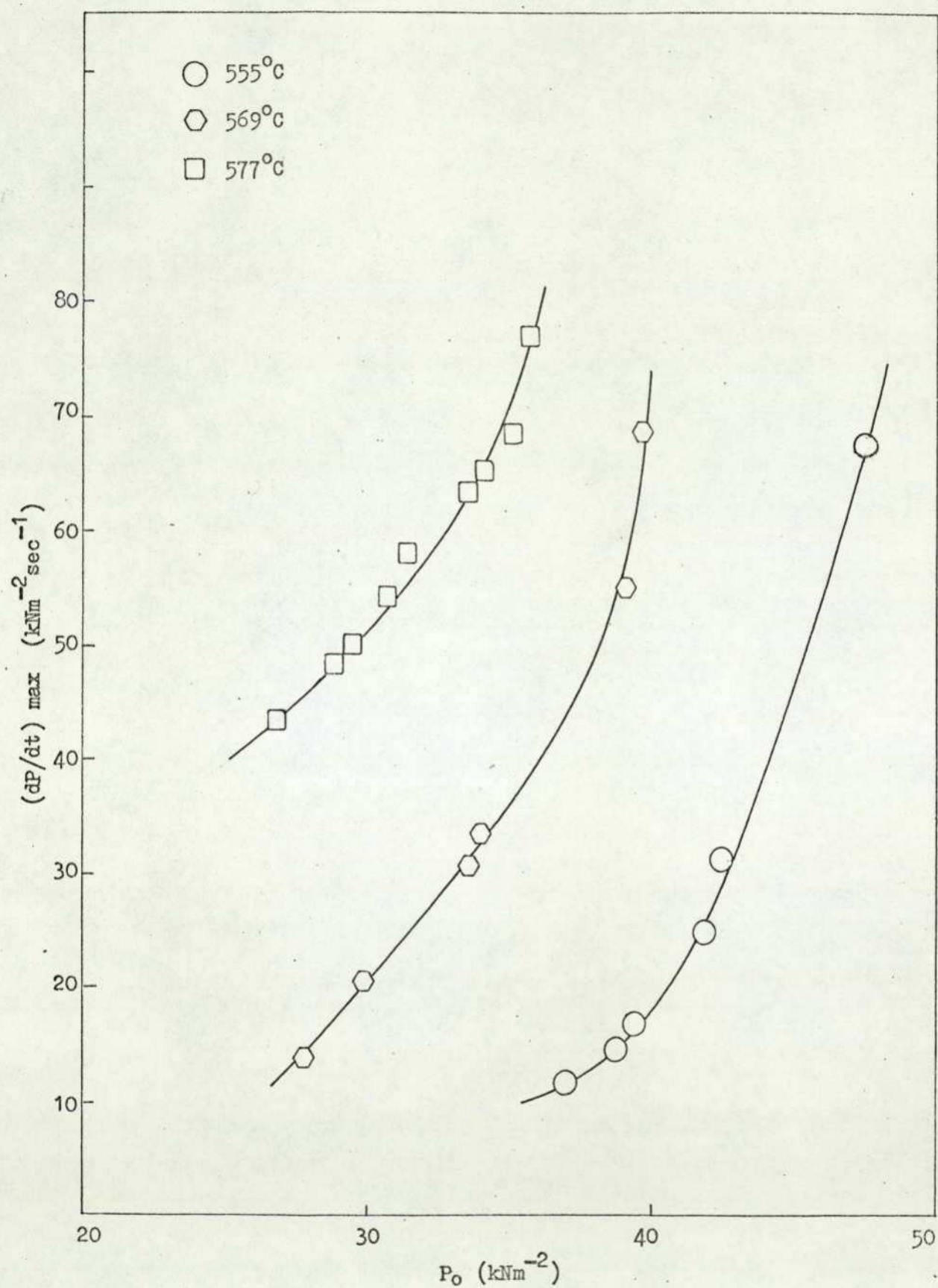
Figure 3.19Variation of $(dP/dt)_{\max}$ with P_0 for the hot flame

Figure 3.20

Variation of (a) P_f with P_o and (b) percentage pressure increment ΔP_f with P_o

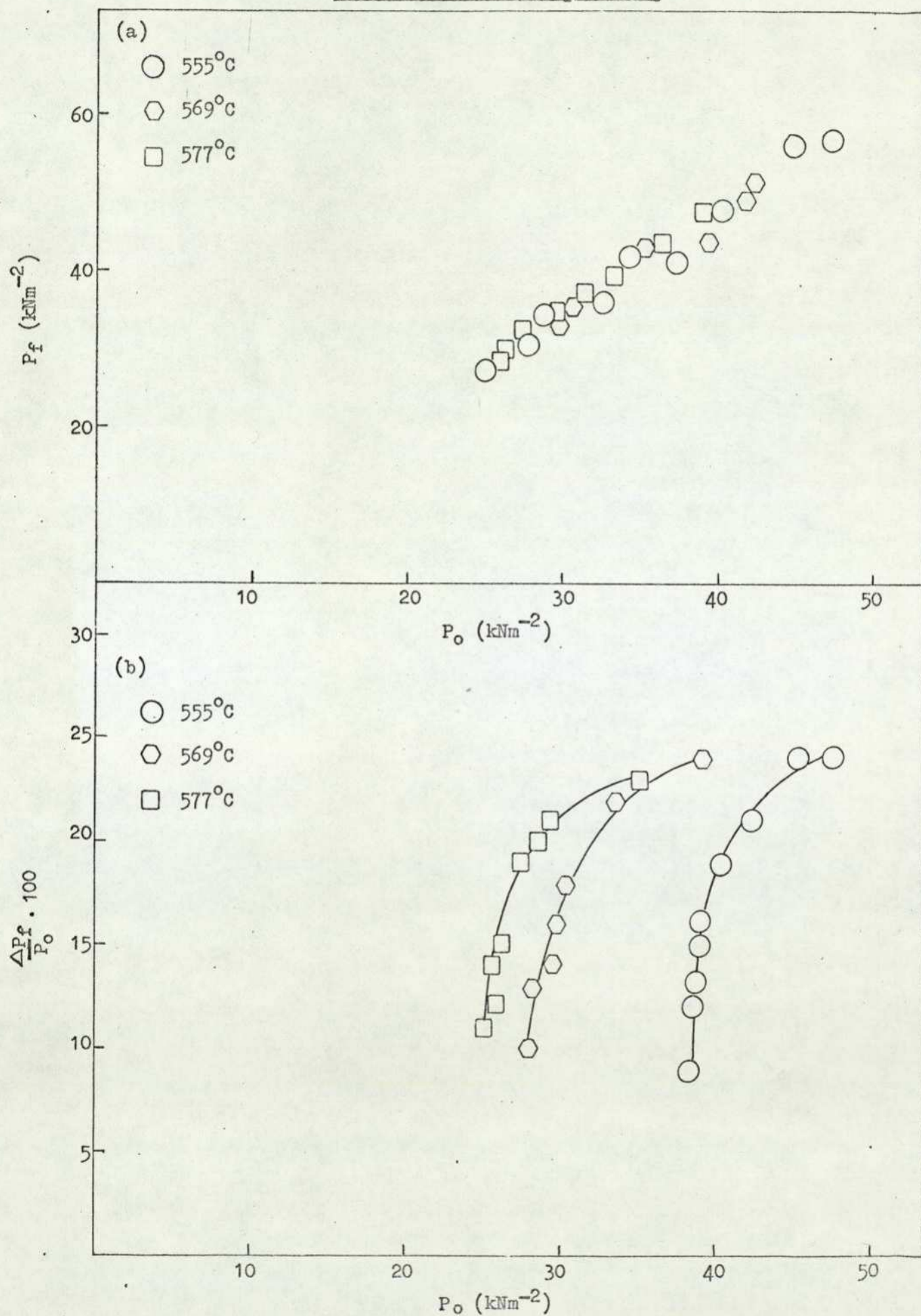


Table 3.3

Products formed during pre-flame stages of ignition of 1:5 styrene-air mixtures

Reaction temperature:- 569°C

Time of sampling during induction period:-

- (i) at initial pressure $P_0 = 35.2 \text{ kNm}^{-2}$,
sampling time = 3.08 sec.
- (ii) at initial pressure $P_0 = 47.36 \text{ kNm}^{-2}$,
sampling time = 2.00 sec.

Peak No.	Reaction Product	Retention time (min)	
		$P_0 = 35.2 \text{ kNm}^{-2}$	$P_0 = 47.36 \text{ kNm}^{-2}$
1	Ethylene	2.50	2.25
2	Unidentified	2.83	2.92
3	Unidentified	3.17	3.25
4	Benzene	4.92	5.02
5	Toluene	7.47	7.58
6	Ethylbenzene	11.00	11.17
7	Styrene	13.27	13.37
8	Benzaldehyde	17.15	17.33
9	Unidentified	21.00	21.33
10	Benzyl alcohol	23.45	24.42
11	Acetophenone	28.92	29.50

The products detected at the two pressure limits studied are shown in Table 3.3. In each case, these were formed in the same relative proportions, suggesting no significant change in the chemistry of the pre-flame process within the pressure range investigated.

As with analysis carried out during slow oxidation at lower temperatures (Section 3.3.1.2), the products were detected with an Apiezon L column exclusively. Resolution of the other products might have been achieved using various supporting columns.

3.4 Influence of polymerising styrene upon the ignition tendency of styrene-air mixtures

3.4.1 Polymerisation of liquid styrene in the capsules

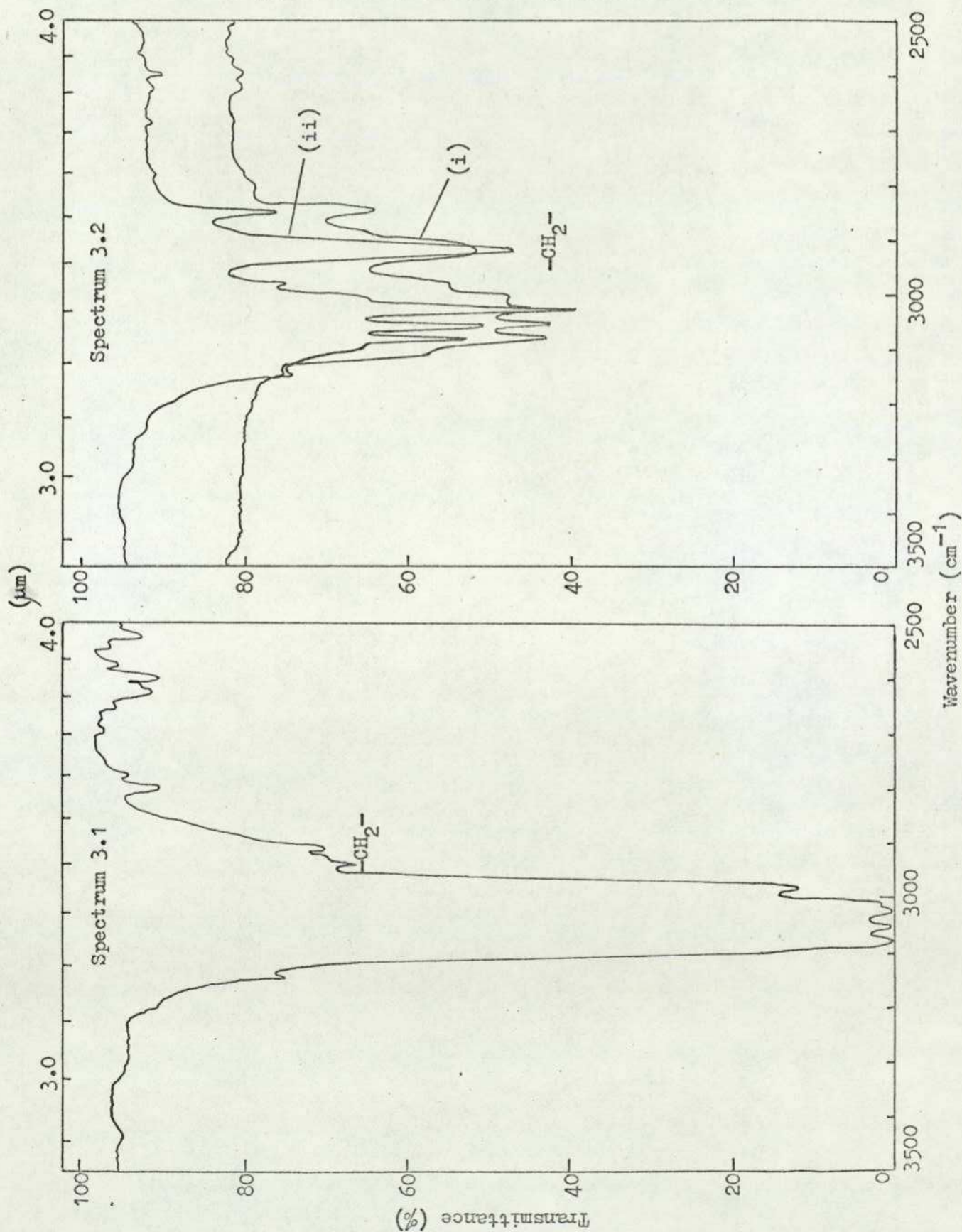
In order to ensure that the monomer was being introduced into the vessel as a polymerising medium, preliminary investigations were carried out to determine semi-quantitatively the extent of polymerisation of the monomer at a given temperature and reaction time.

Initially, tests were carried out on $30\mu\text{l}$ aliquots of inhibited and inhibitor-free monomer contained in sealed capsules which were left in the heated capsule compartment for 15 minutes at temperatures ranging from $60-240^{\circ}\text{C}$. Each capsule was then withdrawn from the compartment and the infrared spectrum of the polymerising monomer was obtained in the region $3370-2700\text{ cm}^{-1}$. The extent of polymerisation was indicated by the intensity of the absorption peak at 2905 cm^{-1} caused by the presence of $-\text{CH}_2-$ bonding in the polymer.

Spectrum 3.1 shows the extent of polymerisation after $30\mu\text{l}$ aliquots of both inhibited and inhibitor-free monomer had been heated at 108°C for 15 minutes. The extent of polymerisation is negligible, in each case, as indicated by the absence of an absorption peak at 2905 cm^{-1} .

Spectrum 3.1 : Effect of heating both inhibited and inhibitor-free styrene at 108°C for 15 minutes

Spectrum 3.2 Polymerisation of (i) inhibited and (ii) inhibitor-free styrene after heating for 15 minutes at 184°C



At higher temperatures of preheating, 184 and 210°C, Spectra 3.2 and 3.3 show evidence of appreciable polymerisation in both inhibited and inhibitor-free samples.

Additional tests were carried out with 30 μ l quantities of monomer containing 1-5% w/w benzoyl peroxide and 1-5% w/w α, α' -azobisisobutyronitrile as polymerisation initiators. Spectrum 3.4 shows that, after the monomer has been preheated in the presence of 1% w/w benzoyl peroxide at 103°C for 15 minutes, polymerisation occurs to an appreciable extent. When benzoyl peroxide was not added to the inhibitor-free monomer, the extent of polymerisation was appreciably smaller.

Spectrum 3.5 shows the extent of polymerisation of monomer containing 1% w/w α, α' -azobisisobutyronitrile heated for 15 minutes at 66°C with the appearance of only a weak band at 2905 cm^{-1} . At higher temperatures of preheating, e.g. 147°C, polymerisation takes place at an appreciable rate as shown in Spectrum 3.6.

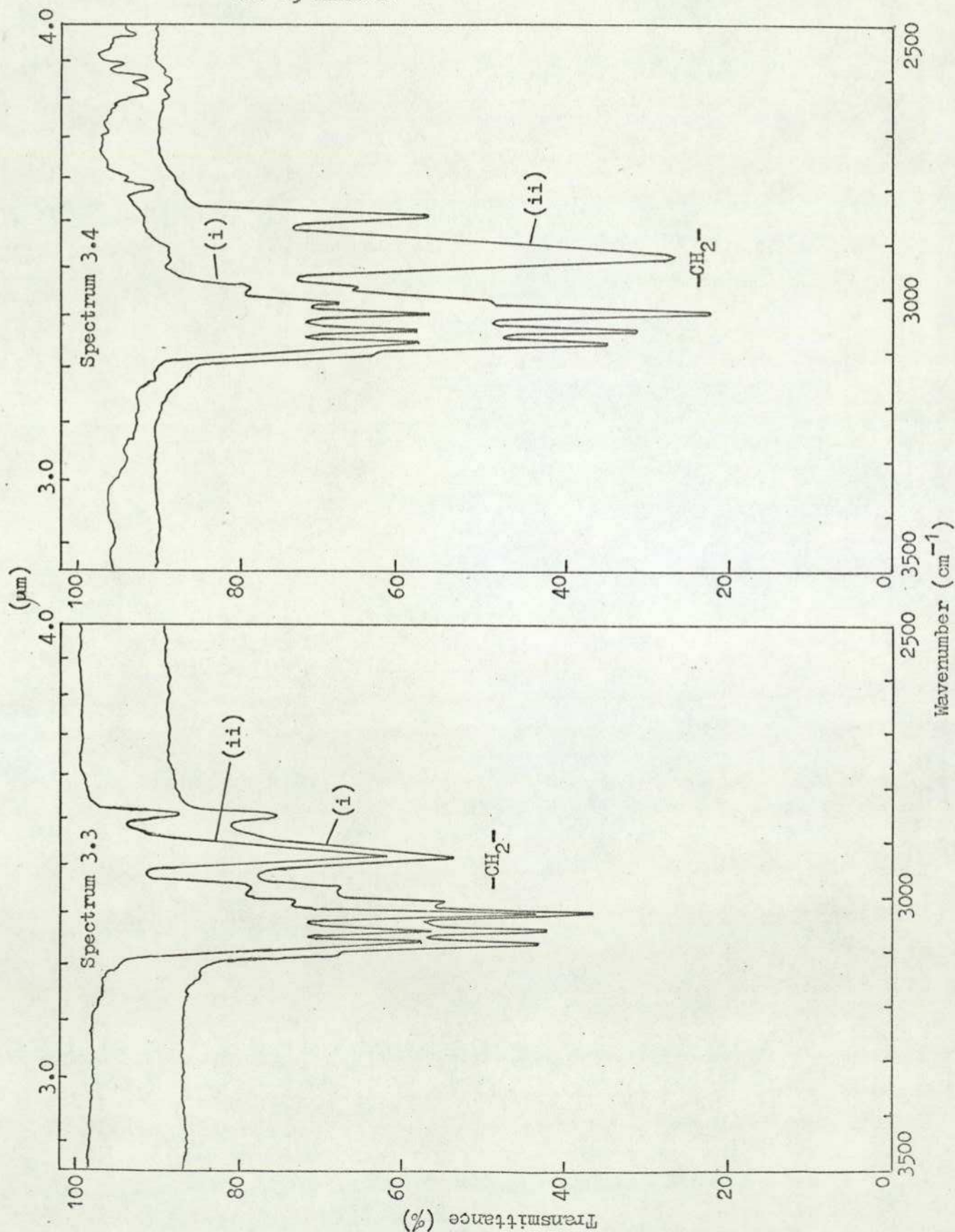
For investigations involving the addition of polymerising monomer to the reacting vapour mixtures, freshly prepared monomer was used daily to avoid discrepancies which could have arisen due to oxidative conversion of monomer to polymer in solutions more than one day old. This applies particularly to experiments where an initiator was added to the inhibitor-free monomer.

3.4.2 Effect of inhibited monomer

Experiments have been carried out with 10 and 30 μ l of monomer containing 10-15 ppm of p-tert-butylcatechol as inhibitor. Figure 3.21 shows the variation of induction period with total initial pressure for 1:5 styrene-air mixtures in the presence of 30 μ l of polymerising liquid monomer preheated for 15 minutes. Runs were carried out at different

Spectrum 3.3 : Polymerisation of (i) inhibited and (ii) inhibitor-free styrene after heating at 210°C for 15 minutes

Spectrum 3.4 : Polymerisation of (i) inhibitor-free and (ii) 1% w/w peroxide-containing styrene after heating at 103°C for 15 minutes



Spectrum 3.5 : Polymerisation of styrene containing 1% w/w AIBN
following heating for 15 minutes at 66°C

Spectrum 3.6 : Polymerisation of styrene containing 1% w/w AIBN
(spectrum (ii)) after heating for 15 minutes at 147°C.
Spectrum (i) represents unheated styrene containing
1% w/w AIBN

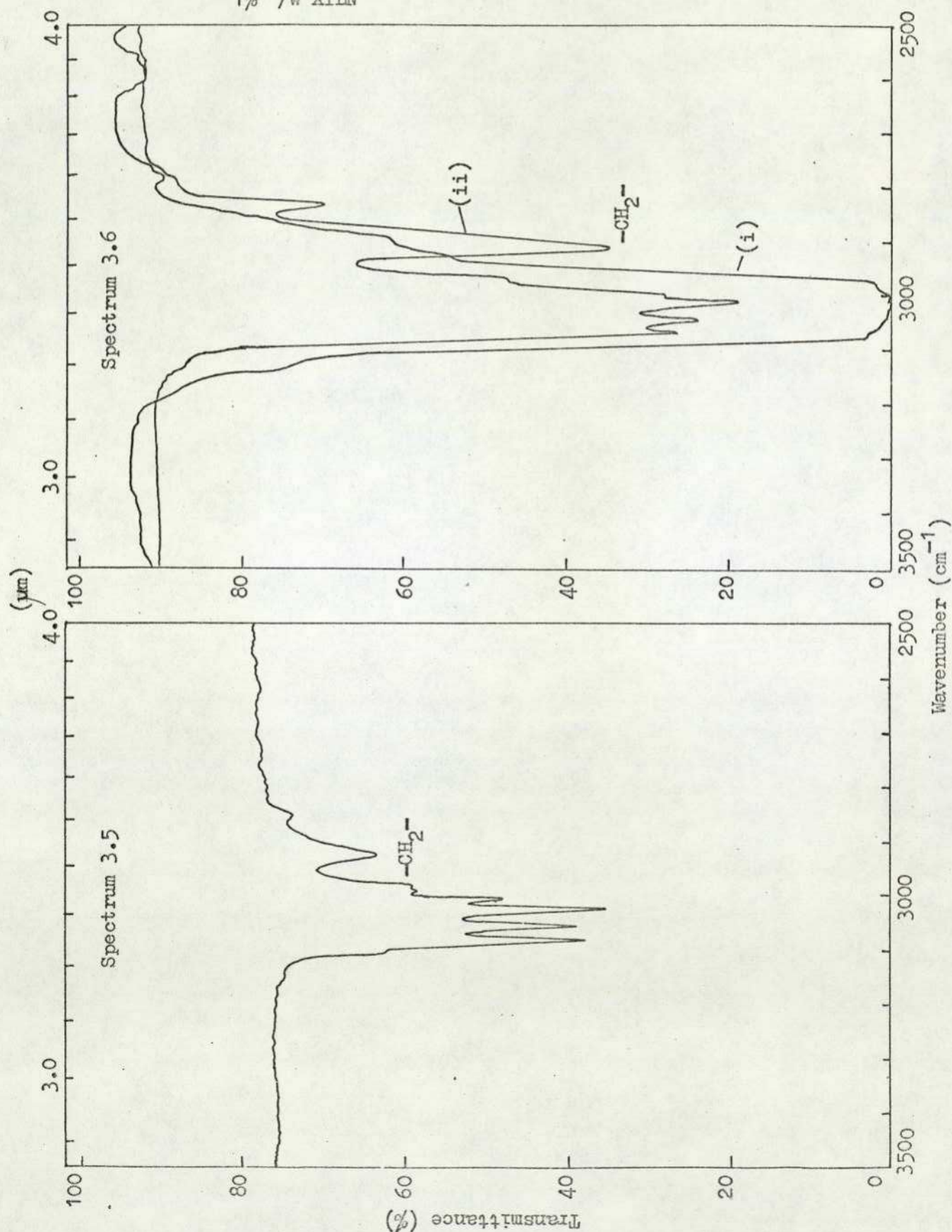
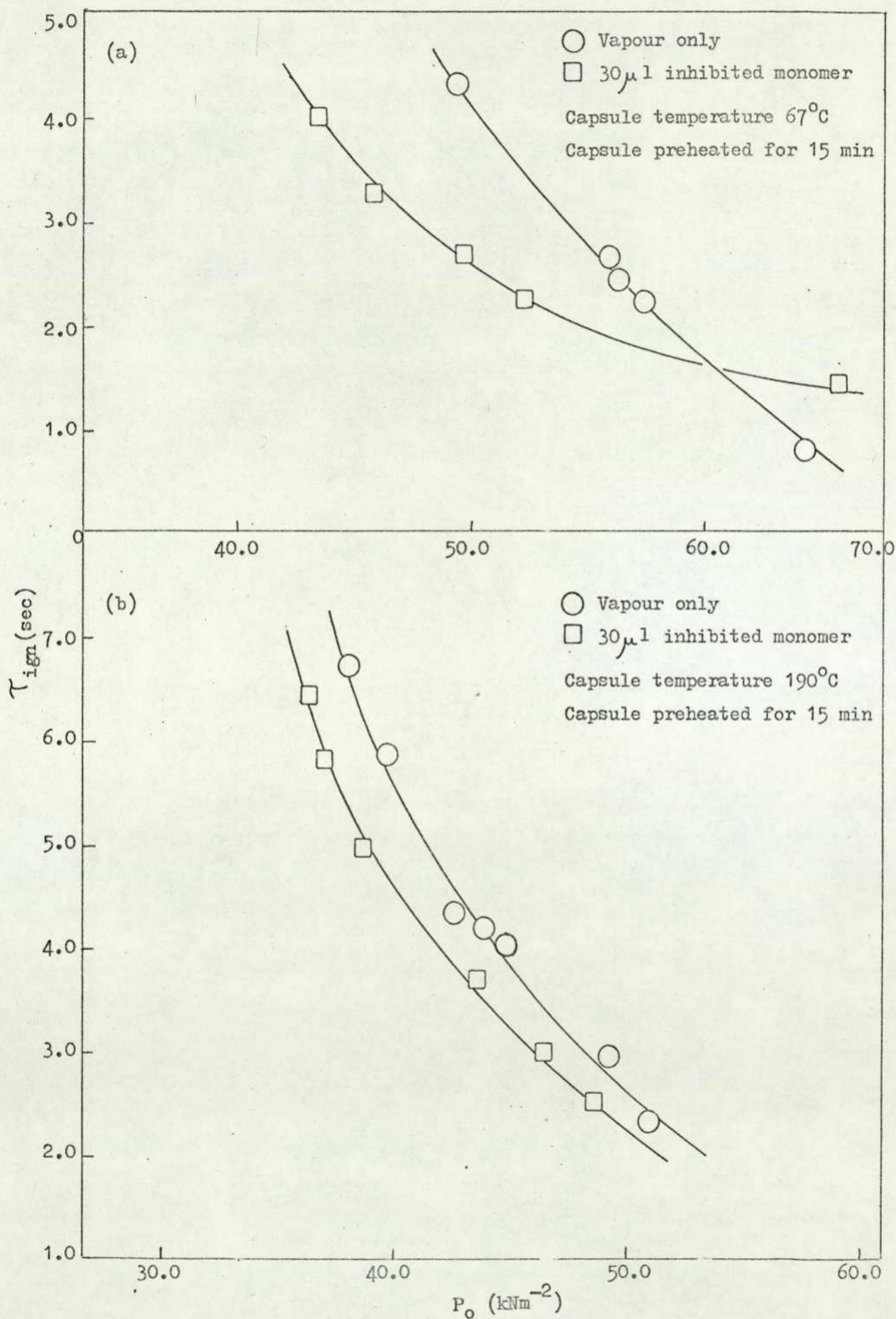


Figure 3.21

Effect of polymerising liquid styrene on the
induction period preceding vapour phase ignition



temperatures, firstly in order to observe the effect of different rates of polymerisation on the ignition tendency, and secondly, to provide an explanation for the convergence and, in some cases, intersection of the curves at higher pressures (Figure 3.21 (a)). In subsequent experiments, where capsules of liquid monomer were subjected to higher temperatures, the curves did not intersect but nevertheless converged at higher initial pressures (Figure 3.21 (b)).

Each curve relates to $30\mu\text{l}$ of inhibited monomer. Induction periods following introduction of polymerising liquid styrene were compared with those for purely vapour-phase ignitions at each of the initial pressures studied. Figure 3.21 (b) shows that, the higher the temperature to which the liquid monomer was preheated, the greater is the effect of the polymerising medium in shortening the induction period.

3.4.3 Effect of inhibitor-free monomer

Figure 3.22 shows the induction period - pressure curves for systems involving the addition of inhibitor-free monomer which had been preheated at two temperatures, viz. 67 and 190°C . In agreement with previous experiments in which inhibited monomer was introduced (Section 3.4.2), ignition was enhanced to an extent dependent on the temperature to which the liquid monomer was preheated. In general, inhibitor-free monomer is more effective than inhibited monomer in increasing the ignition tendency (Figures 3.21 (b) and 3.22 (b)). Figure 3.23 shows that the ignition tendency of a given styrene-air mixture increases also with the volume of polymerising liquid monomer added.

3.4.4 Effect of initiator-containing monomer

Experiments were carried out with 10 and $30\mu\text{l}$ samples of inhibitor-free monomer, to which $1-5\%$ benzoyl peroxide had been added. Figure 3.24 shows the influence on the induction period when 10 and $30\mu\text{l}$

Effect of polymerising liquid styrene on the induction
period preceding vapour phase ignition

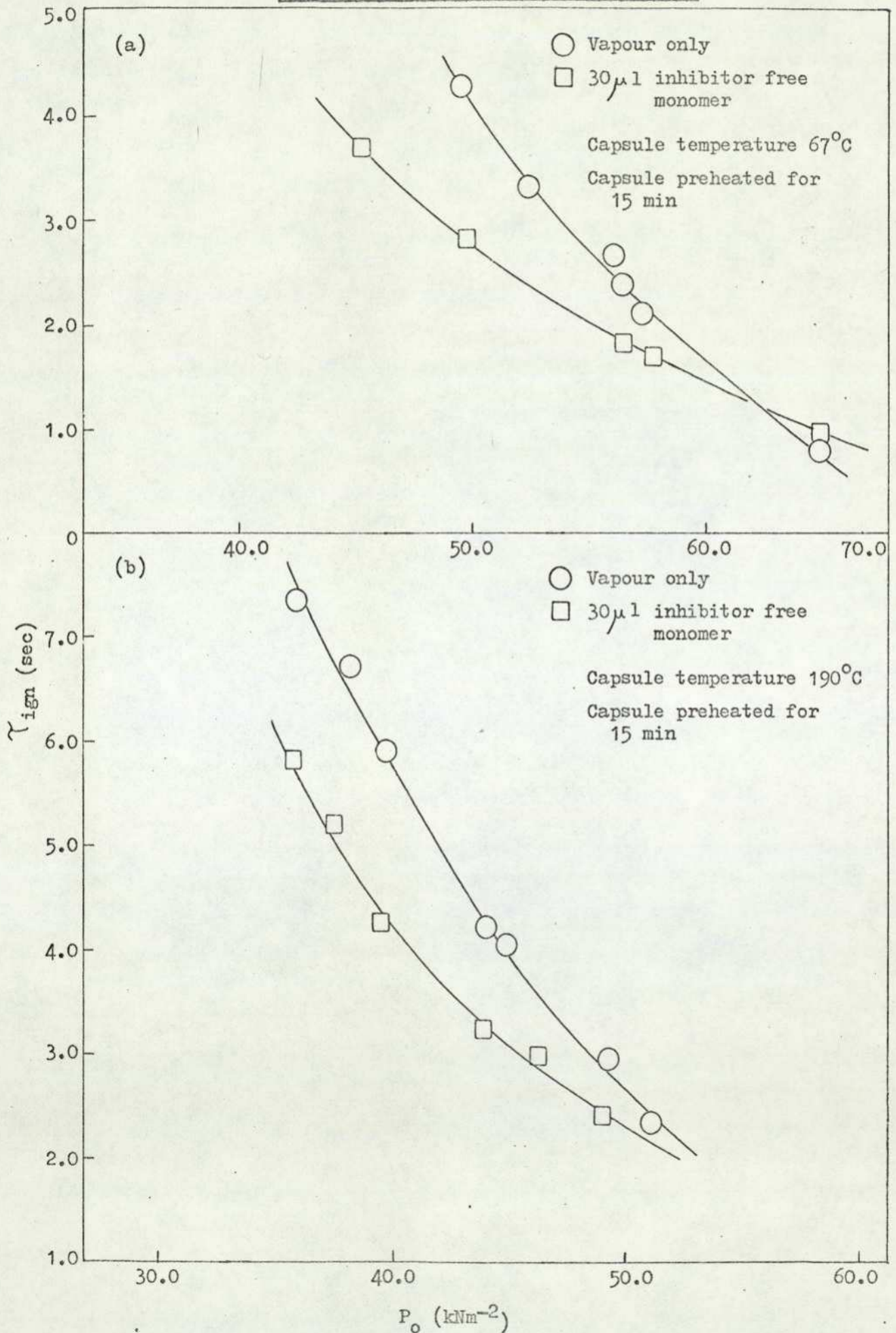
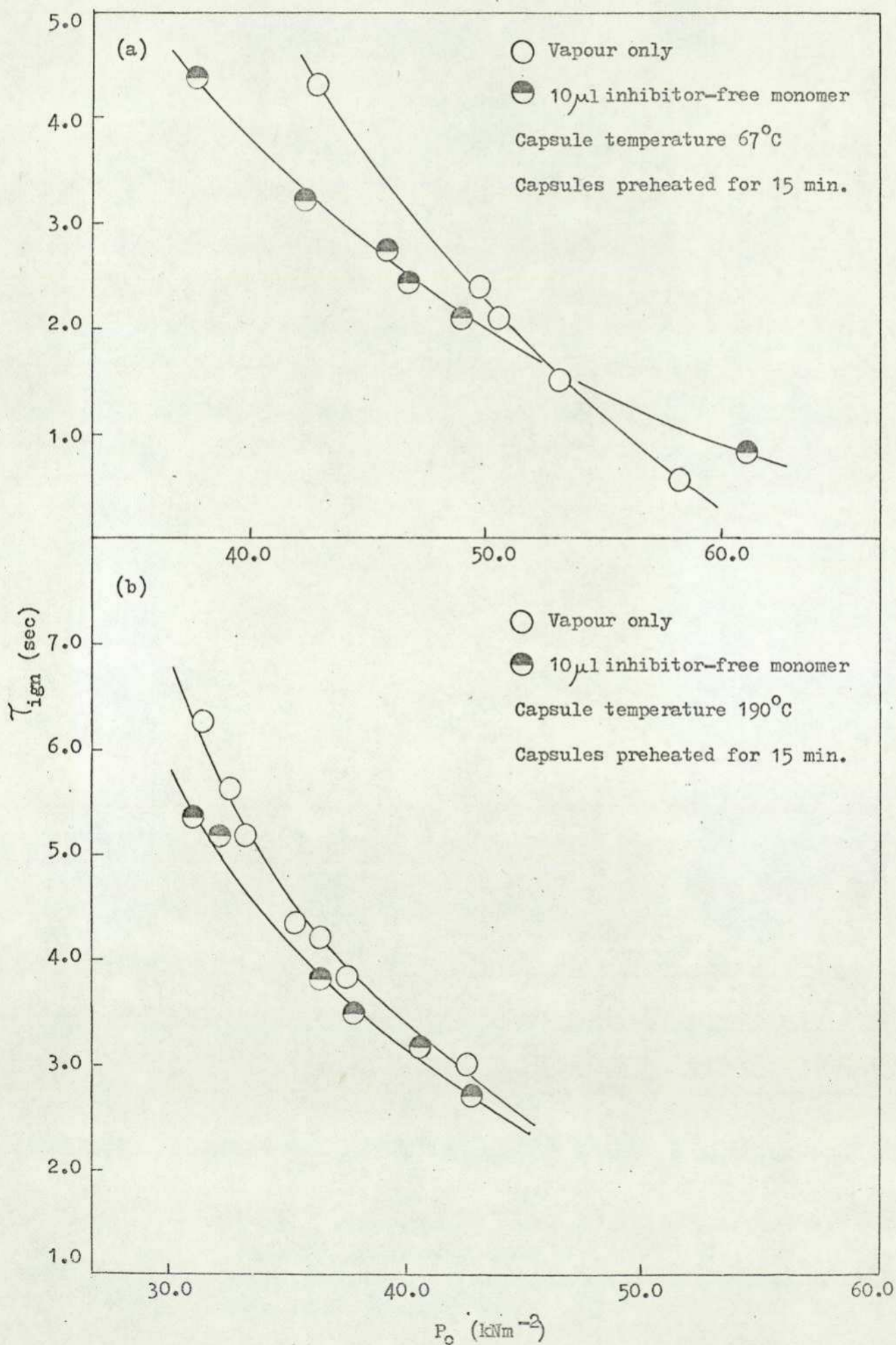
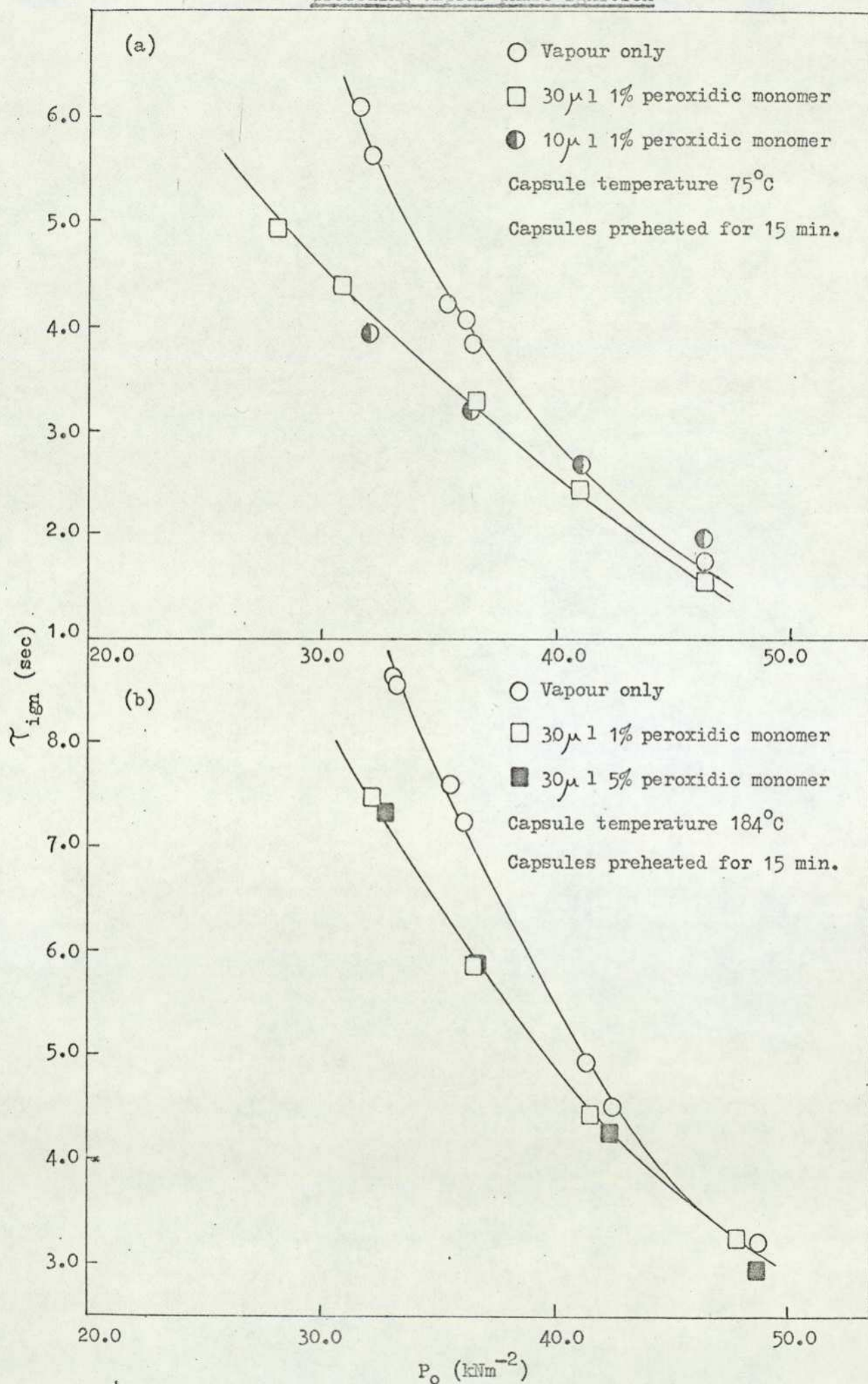


Figure 3.23

Effect of polymerising liquid styrene on the
induction period preceding vapour-phase ignition



Effect of polymerising liquid styrene on the induction period
preceding vapour-phase ignition



samples of monomer containing 1% benzoyl peroxide are introduced into the hot vapour mixture. At the lower temperature of preheating, ca. 75°C, the curves just intersect in the case of 10 μ l capsules but, in experiments where 30 μ l capsules were used, no intersection occurred. Comparison with experiments where the monomer was polymerised without an initiator present (Figures 3.22 (a) and 3.23 (a)), suggests that an increase in the rate of polymerisation shortens the induction period and this is further emphasised by the observation that in Figure 3.24 (a) the curves tend to converge rather than intersect at higher pressures. An increase in the concentration of benzoyl peroxide up to 5% w/w caused a corresponding increase in the rate of polymerisation.

Similar effects were observed in experiments in which α, α' -azobisisobutyronitrile was added to the monomer, (Figure 3.25), although this initiator appeared to be, on the whole, more effective than benzoyl peroxide.

3.4.5 Effect of solid polystyrene

Some experiments were carried out involving the addition of solid polystyrene to the reacting styrene-air vapour mixture with a view to determining whether depolymerisation of the solid polymer would enhance the ignition tendency of the vapour mixture. In each experiment, ca. 10 mg of finely granulated polystyrene were placed in capsules which were then sealed and heated at 66°C for 15 minutes prior to being introduced into the reaction vessel. Figure 3.26 shows that, over the range of pressure investigated, the effect on the induction period is extremely small. However, even when the solid polymer was heated only at 66°C, intersection of the curves did not occur at higher pressures, the polymer-additive curve being parallel to the solely vapour-phase ignition curve.

Figure 3.25

Effect of polymerising liquid styrene on the induction period
preceding vapour-phase ignition

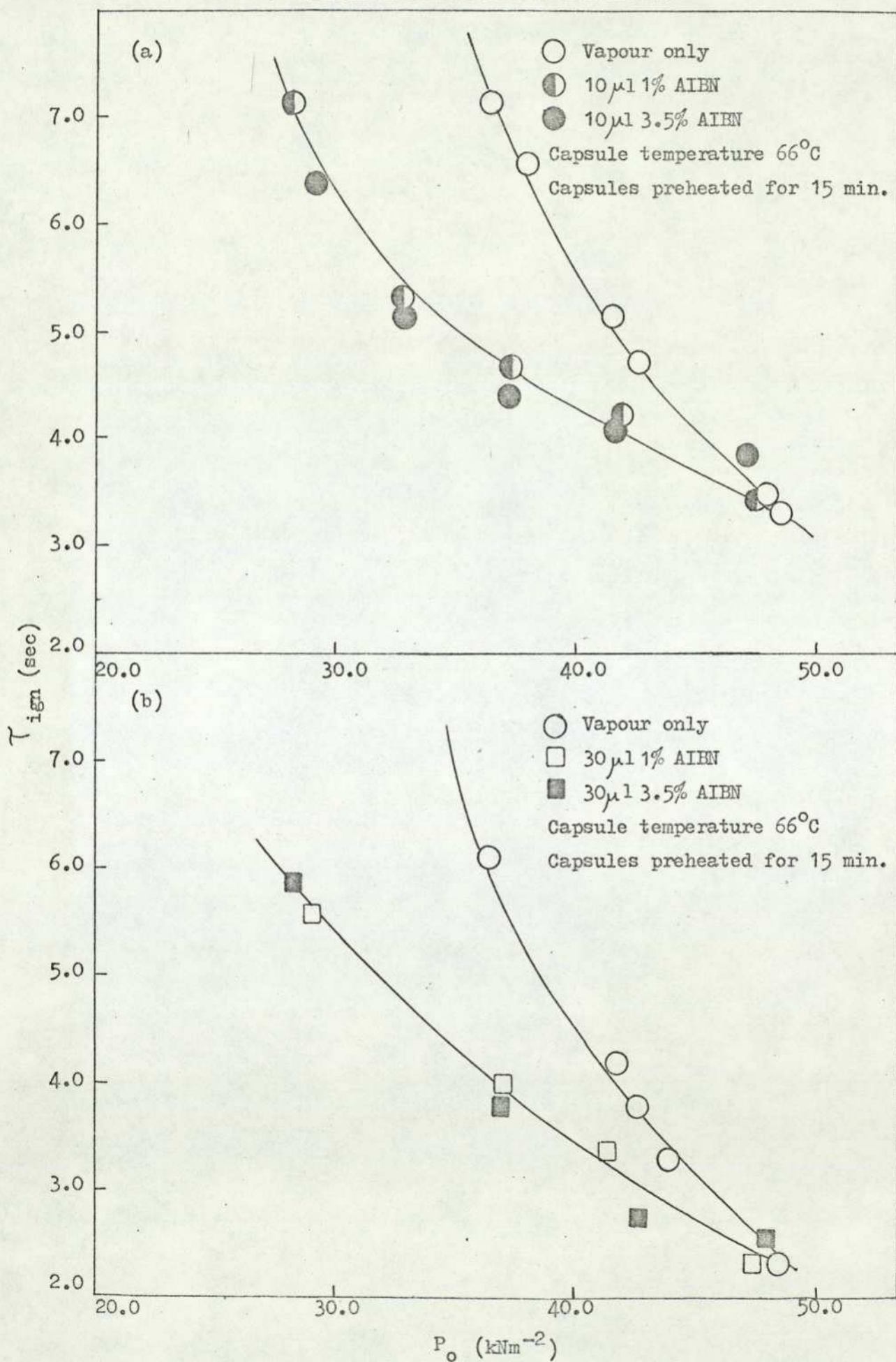
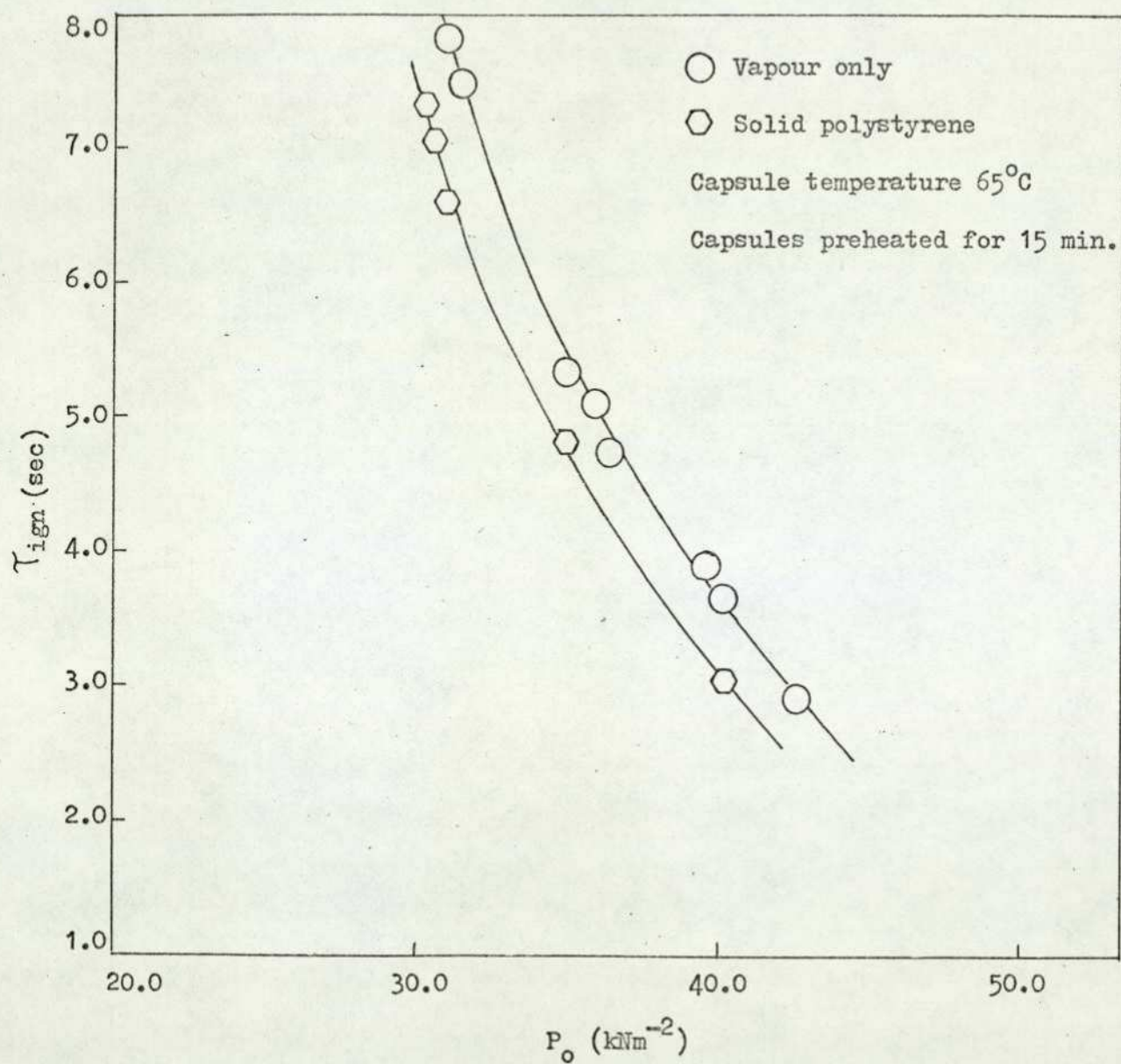


Figure 3.26

Effect of solid polystyrene on the induction period
preceding vapour-phase ignition



Studies with solid polystyrene thus suggest that polymerisation plays a much more important role than depolymerisation in increasing the ignition tendency.

3.4.6 Cooling effects

Experiments to investigate further the effects of adding 30 μ l quantities of relatively 'cold' liquid monomer to a hot vapour mixture were carried out using initially capsules of inhibitor-free monomer.

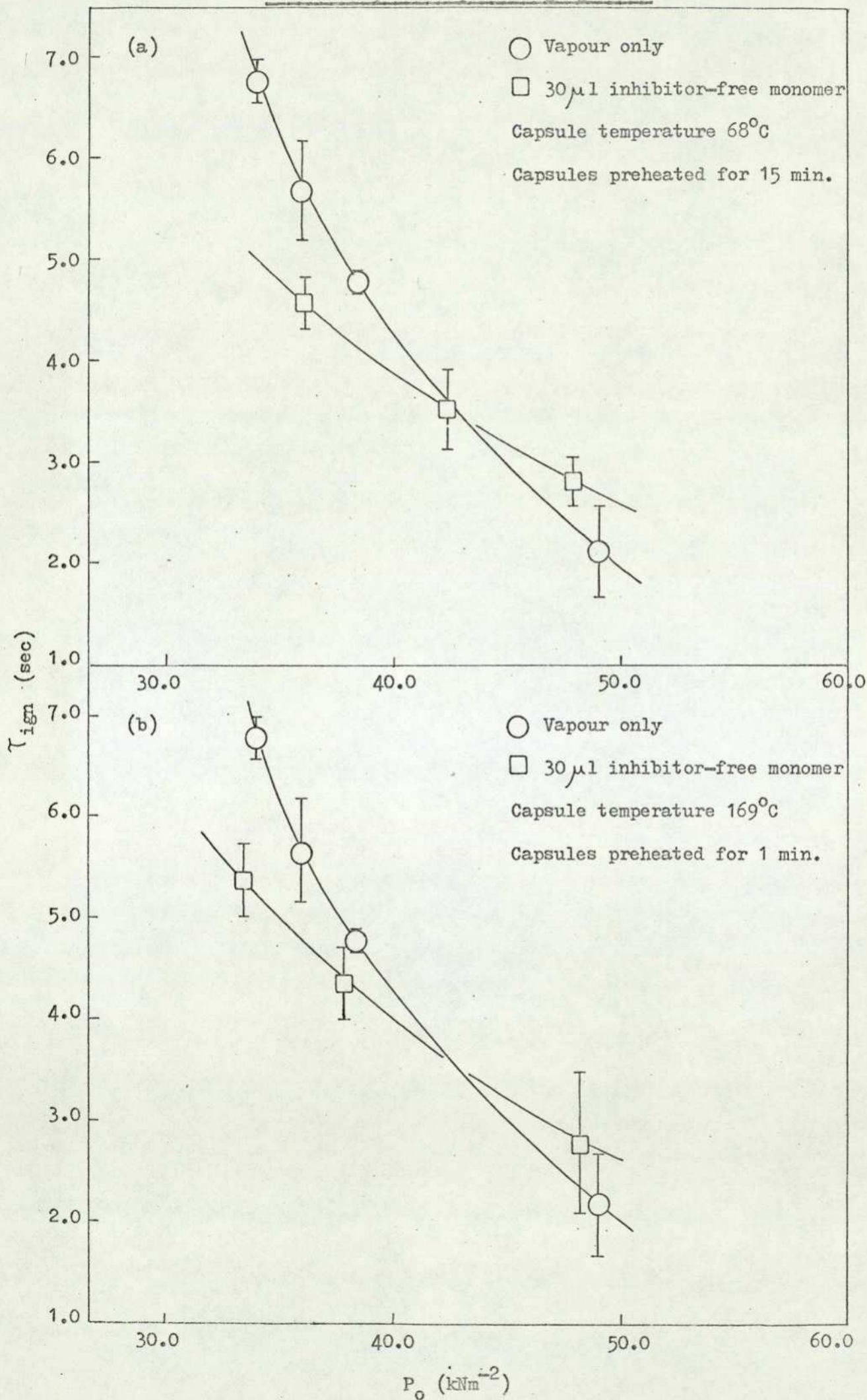
A large number of experiments were carried out in order to establish whether there are significant differences in the induction period over the range of pressures investigated.

Figure 3.27 shows that the induction period-pressure curves of pure vapour and vapour-liquid systems intersect so that differences in induction periods become more marked at higher pressures. At lower initial pressures, it is clear that the shortening of induction periods in the presence of polymerising liquid styrene becomes more significant.

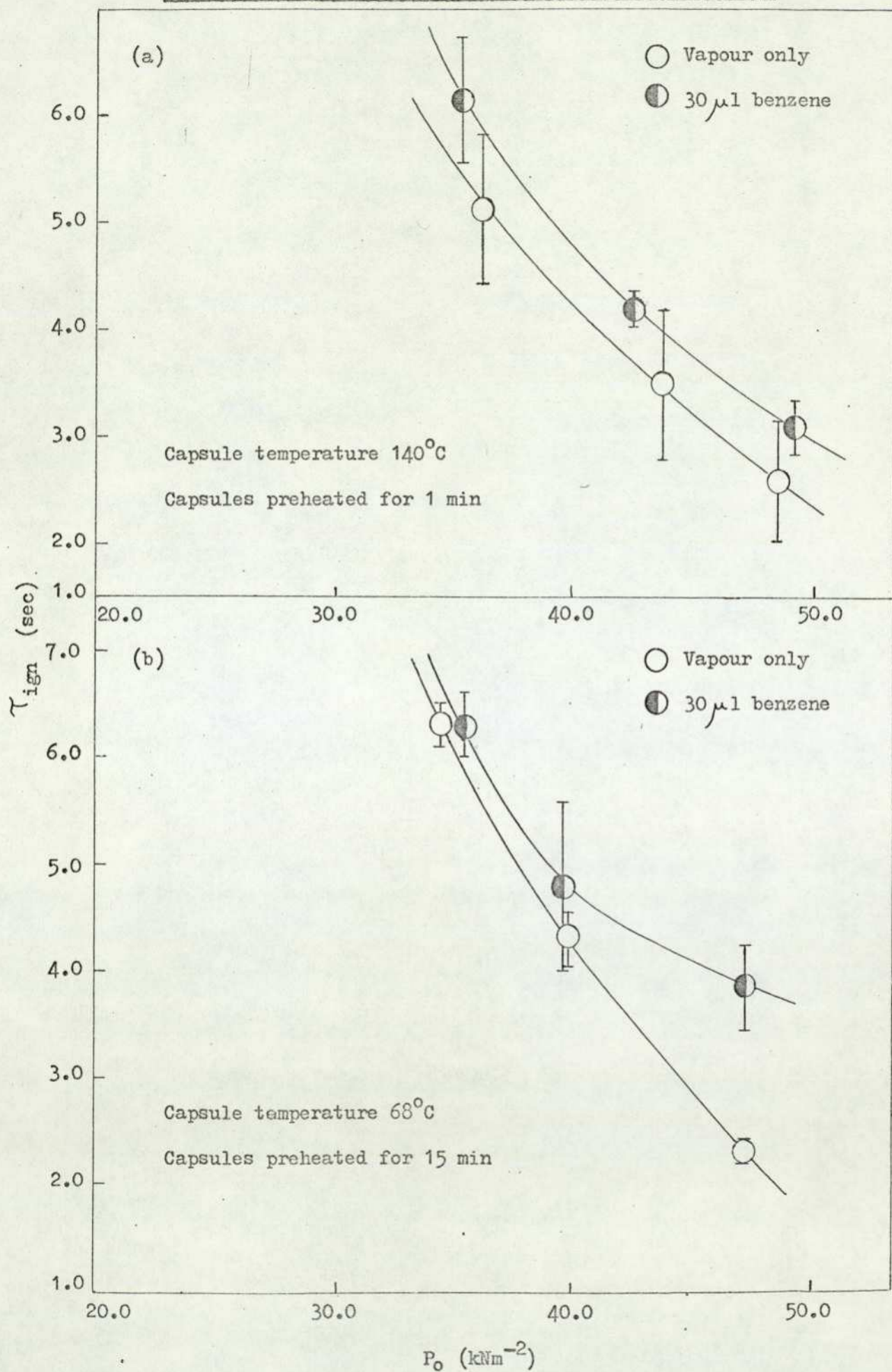
Blank experiments using relatively inert liquid benzene instead of liquid styrene were also carried out. Figure 3.28 shows the results obtained when the capsules of benzene were preheated at different temperatures. At the lower temperatures of preheating, subsequent addition of liquid benzene causes a significant lengthening of induction period at higher initial pressures. On the other hand, at lower initial pressures, the benzene curve tends to approximate to that for ignition taking place solely in the vapour-phase (Figure 3.28 (a)).

Since the preheating temperature of ca. 140°C is appreciably higher than the boiling point of benzene (80°C at 101.3 kNm⁻²), the period of preheating was restricted to 1 minute. When the seal of the capsule was broken, most of the liquid benzene vaporised immediately so

The significance of polymerising liquid styrene in shortening
induction periods preceding ignition



The effect of (a) strongly heated and (b) relatively cold liquid benzene on induction periods preceding ignition



that this compound entered the reaction vessel as vapour. Hence there was no significant cooling effect on the reacting styrene-air vapour mixture.

3.4.7 Effect of polymerising styrene on product distribution

Table 3.4 shows that the same number of products was detected during pre-flame stages of ignition as in experiments involving solely vapour-phase ignition (Table 3.3). Analysis of products obtained in experiments involving the addition of polymerising liquid monomer was carried out both at high and low initial pressures. Since there is no apparent difference in the nature of the products formed in the two series of experiments, it would appear that no marked change occurs in the chemistry of the pre-flame reactions as a result of the addition of polymerising liquid styrene.

Only qualitative gas chromatographic analysis was carried out using the Apiezon L column. No back-up columns were used so that only a partial resolution of the products was obtained.

3.5 Temperature measurements

3.5.1 Temperature changes in reacting styrene-air mixtures

Figure 3.29 shows typical temperature-time traces recorded at the centre of the reaction vessel for slow combustion and ignition reactions at an initial temperature of 569°C.

Temperature changes accompanying hot flame phenomena at different initial reactant pressures are shown in Figures 3.29 (a)-(e). Figure 3.29 (d) indicates the temperature change accompanying slow oxidation on the ignition boundary. Thus the maximum temperature change, ΔT_{ign} , increases with initial pressure, as does the maximum pressure change, ΔP_{ign} .

Figure 3.29 (e) shows a typical temperature-time trace obtained

Table 3.4

Effect of polymerising styrene on product distribution during pre-flame stages of ignition of 1:5 styrene-air mixtures

Reaction temperature:- 569°C

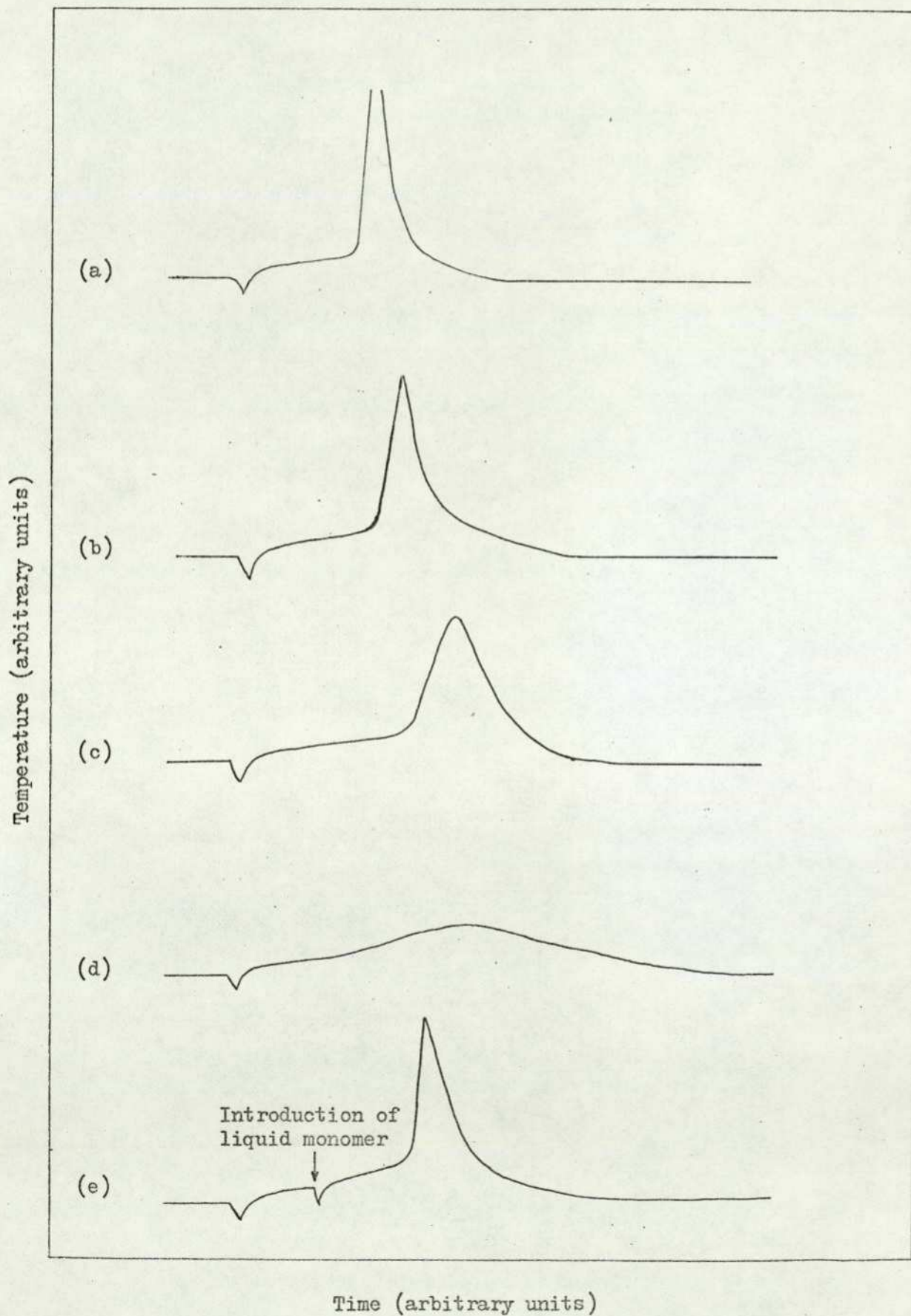
Time of sampling during induction period:-

(i) at initial pressure, $P_o = 35.6 \text{ kNm}^{-2}$,
sampling time = 4.7 sec.

(ii) at initial pressure, $P_o = 47.5 \text{ kNm}^{-2}$,
sampling time = 2.08 sec

Peak No.	Reaction Product	Retention time (min)	
		$P_o = 35.6 \text{ kNm}^{-2}$	$P_o = 47.5 \text{ kNm}^{-2}$
1	Ethylene	2.12	2.19
2	Unidentified	2.42	2.42
3	Unidentified	2.80	2.95
4	Benzene	4.88	4.92
5	Toluene	7.22	7.50
6	Ethylbenzene	10.80	11.17
7	Styrene	13.20	13.33
8	Benzaldehyde	17.08	17.17
9	Unidentified	21.45	21.29
10	Benzyl alcohol	23.71	24.27
11	Acetophenone	29.75	29.25
12	Unidentified	+	69.33

⁺ The sensitivity of the gas chromatograph was too low to resolve this product.

Figure 3.29Typical temperature-time recordings for ignition of styrene-air mixtures

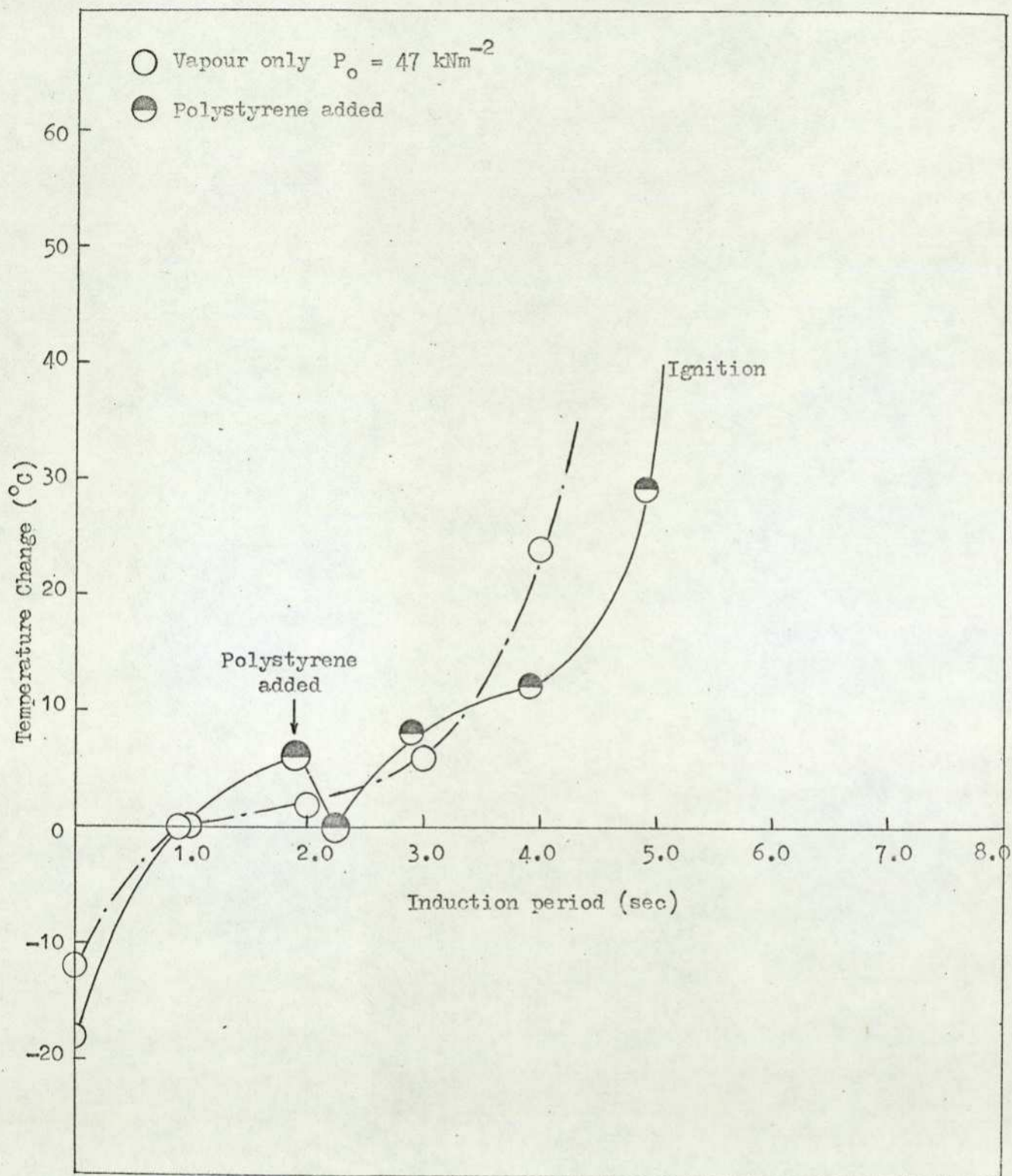
when a capsule of polymerising liquid styrene is introduced into the reaction vessel. The addition of a capsule is followed by a sharp fall in temperature which ranges from $3-10^{\circ}\text{C}$ depending upon the capsule temperature, the initial pressure in the reaction vessel and the extent of polymerisation of the liquid monomer.

3.5.2 Temperature changes accompanying addition of solid polystyrene

Figures 3.30 and 3.31 show temperature-time profiles for the pre-flame stages of high-temperature ignition in experiments involving the addition of capsules containing solid polystyrene, preheated at 66°C .

Figure 3.30 shows the effect on the induction period of the introduction of ca. 10 mg solid polystyrene. After a brief fall in temperature as the relatively cold styrene-air mixture enters the reaction vessel, the temperature rises above that of the reaction vessel. This initial cooling occurs ca. 0.1 sec after admission of the vapour mixture into the reaction vessel and is a feature common to all the temperature-time traces for ignition of styrene-air mixtures. When solid polystyrene is introduced (together with the air within the capsule compartment), a further cooling of ca. 6°C occurs so that the temperature of the reaction mixture is lowered to the reaction vessel temperature. This cooling occurs ca. 0.3 sec after the capsule is introduced into the reaction vessel. Subsequently the temperature of the reaction mixture rises and the rate of heating increases exponentially, resulting in a maximum rate of temperature change at ignition.

For comparative purposes, the temperature-time profile for a vapour-phase ignition is also shown in Figure 3.30. In this case, after the initial brief cooling, the temperature of the reacting mixture rises above the vessel temperature, and the rate of temperature change increases

Figure 3.30Temperature changes following addition of solid polystyrene

exponentially to a maximum value on ignition. No noticeable cooling is observed when the air within the capsule compartment is admitted to the reaction vessel.

Figure 3.31 shows the effect on the induction period of the addition of solid polystyrene to a fuel-air vapour mixture at a pressure of 33 kNm^{-2} . Following the initial cooling, the temperature starts to rise and, on introduction of the polymer, a further small cooling of $\text{ca. } 2^{\circ}\text{C}$ occurs. This takes place $\text{ca. } 0.1 \text{ sec}$ after the capsule is introduced into the reaction vessel and is 4°C smaller than that observed at higher initial pressures (Figure 3.30). As in previous experiments, the cooling is followed by an exponential increase in temperature rise leading to a maximum rate of temperature rise at ignition.

3.5.3 Temperature changes accompanying addition of polymerising liquid styrene

Figures 3.32 and 3.33 show the effect on the induction period of adding $30 \mu\text{l}$ of inhibitor-free monomer, preheated for 2 minutes at 170°C . In Figure 3.32, the polymerising monomer was added to a styrene-air vapour mixture at an initial pressure of $\text{ca. } 47 \text{ kNm}^{-2}$. Introduction of the monomer leads to a cooling of $\text{ca. } 10^{\circ}\text{C}$. Similar behaviour is observed in experiments at an initial pressure of $\text{ca. } 33 \text{ kNm}^{-2}$ (Figure 3.33).

Similar temperature changes were observed when polymerising liquid styrene was preheated at $\text{ca. } 66^{\circ}\text{C}$ (Figure 3.34). The polymerising liquid monomer, which is relatively cold, causes a cooling of 12°C about 0.6 sec after introduction of the liquid monomer. Subsequently, the temperature again rises above the temperature of the reaction vessel, leading to the maximum rate of temperature change on ignition.

Figure 3.31

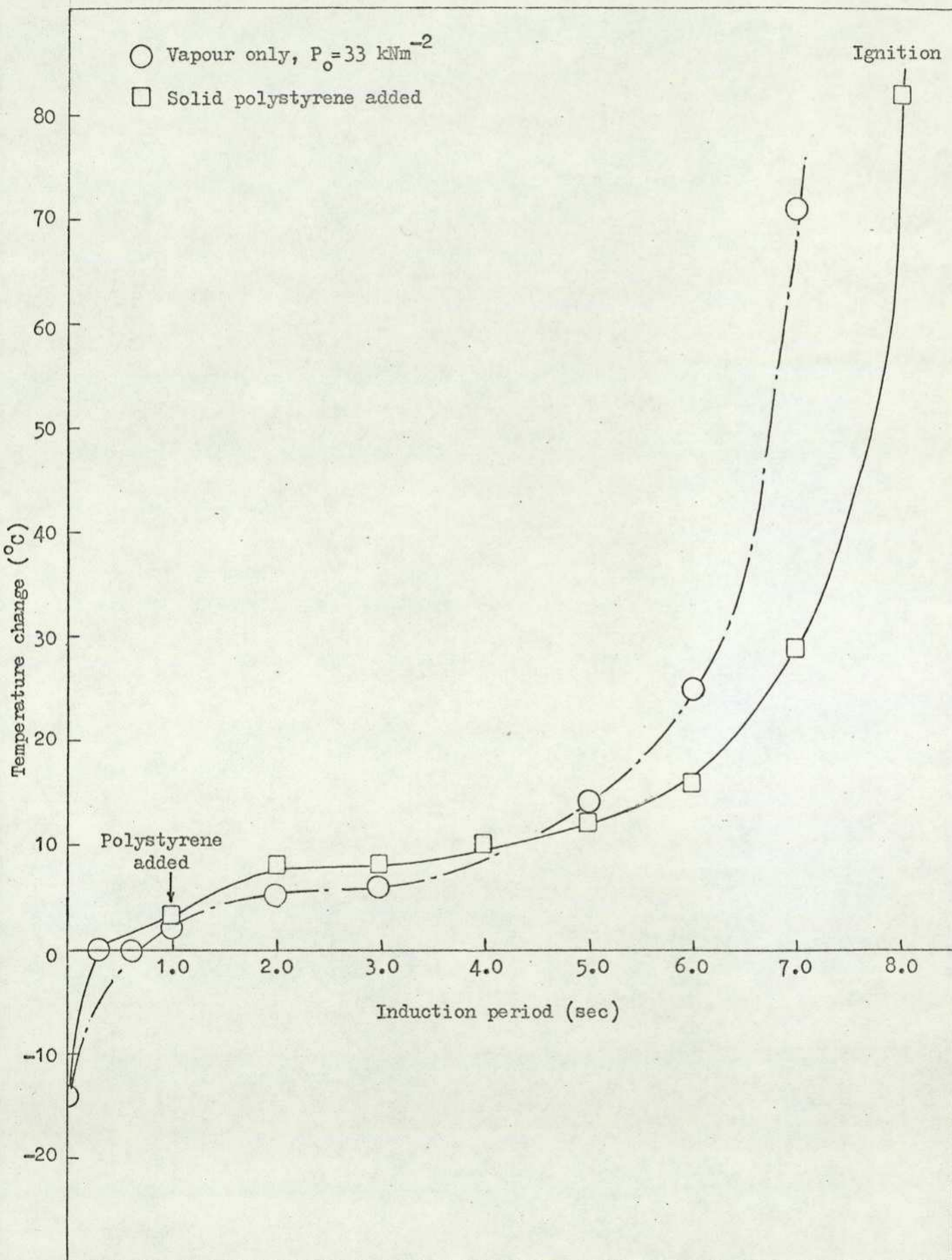
Temperature changes following addition of solid polystyrene

Figure 3.32

Temperature changes following addition of polymerising
liquid styrene

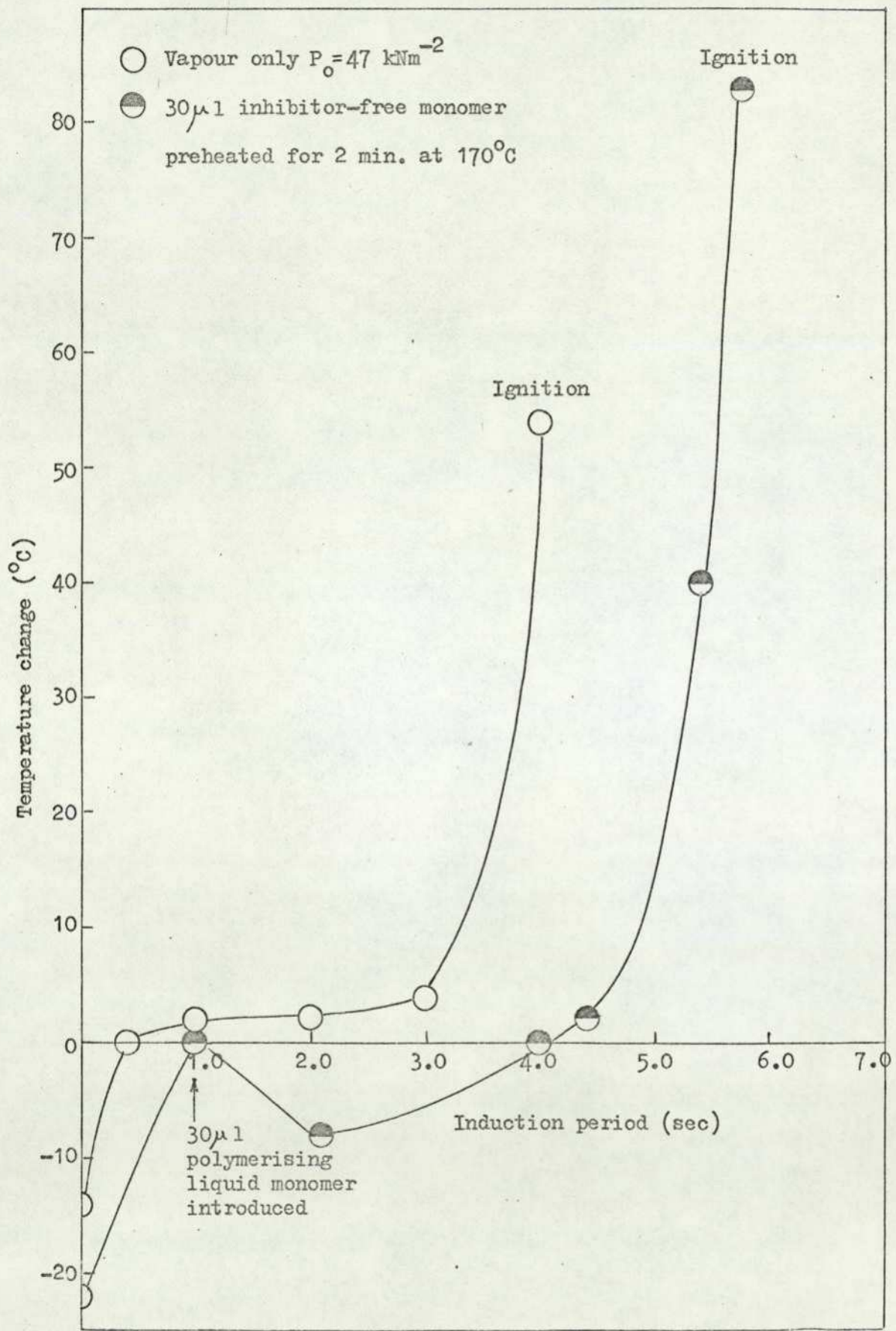


Figure 3.33

Temperature changes following addition of polymerising liquid styrene

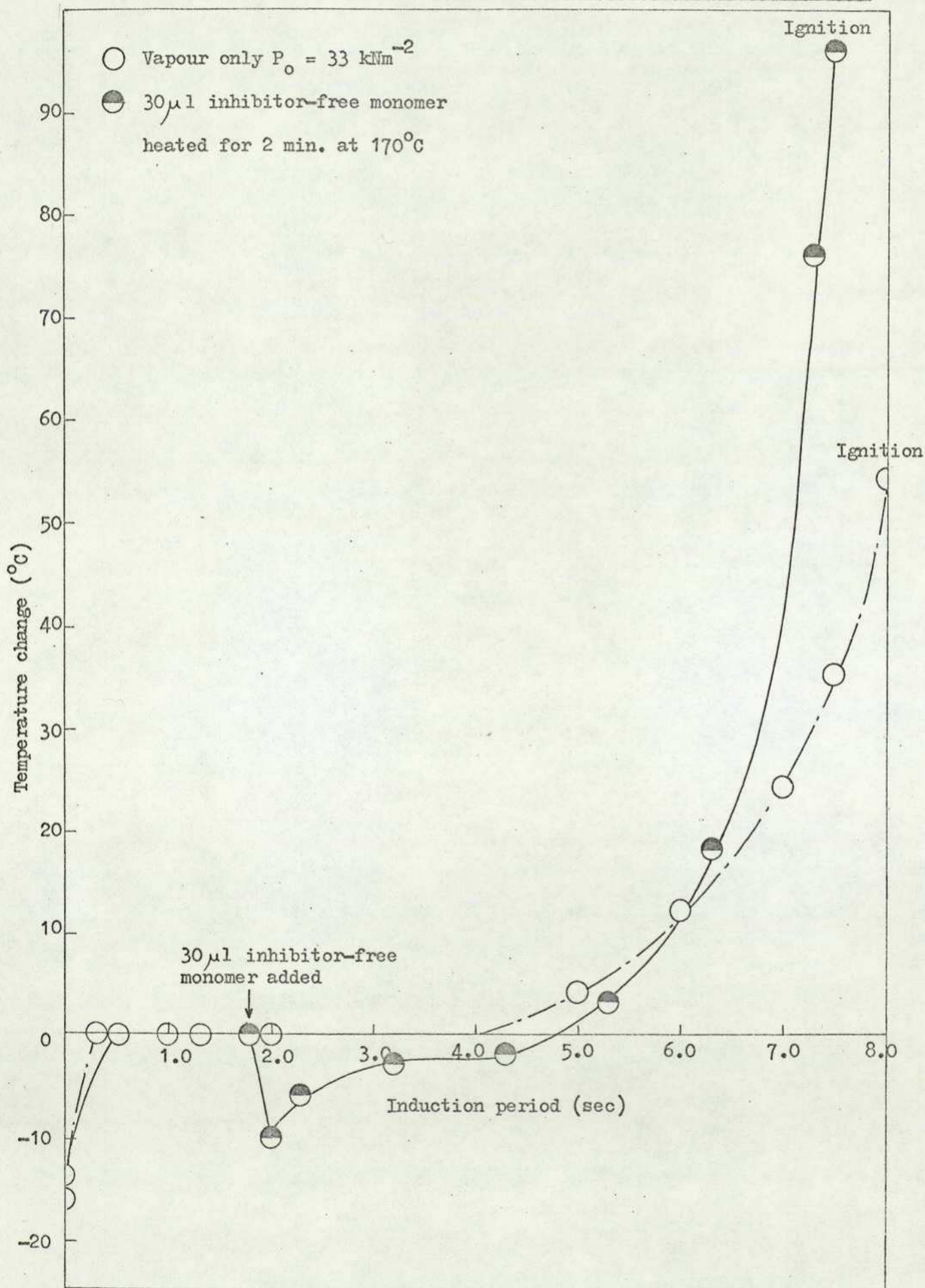
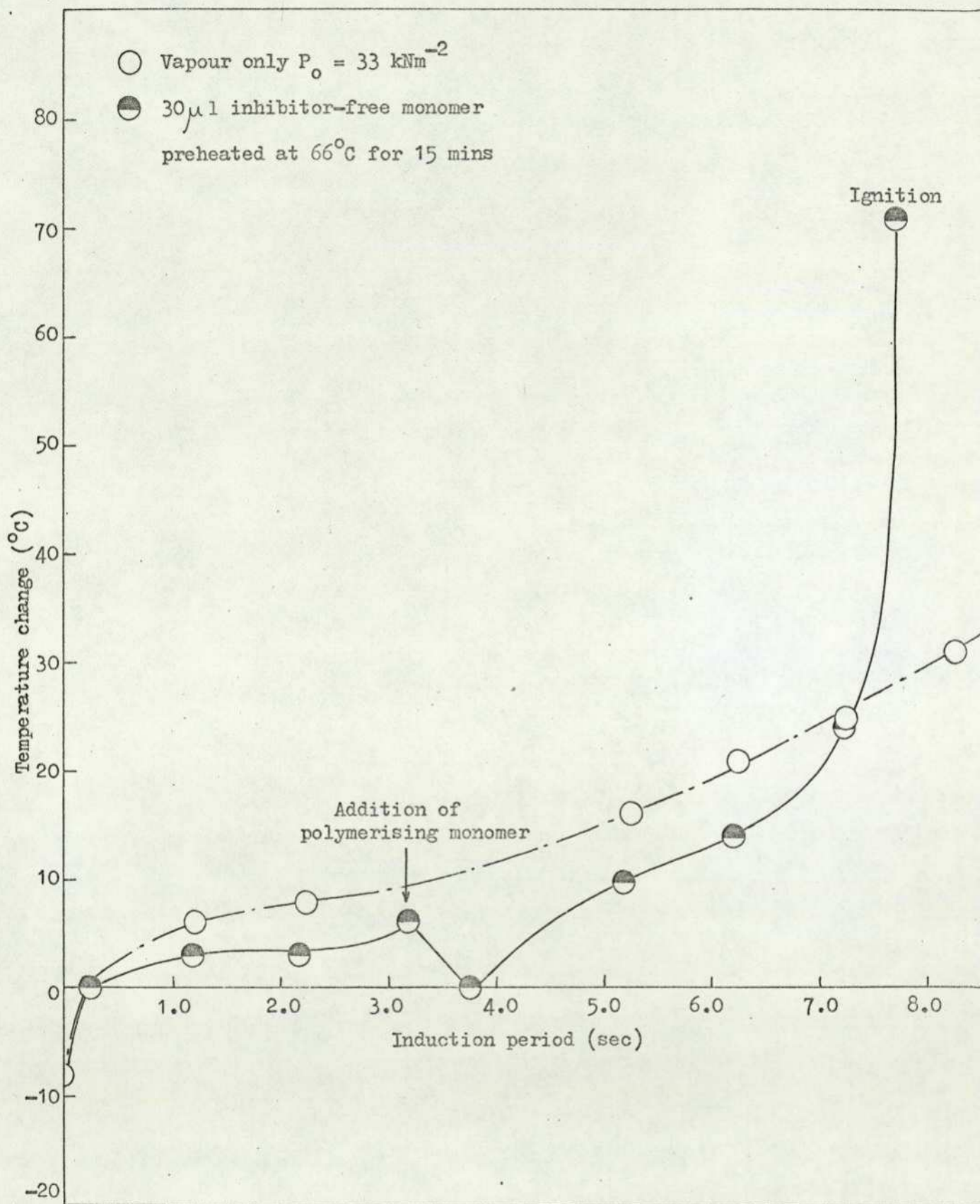


Figure 3.34

Temperature changes following addition of polymerising liquid styrene



SECTION 4

DISCUSSION

Section 4

	Page No.
4.1 <u>Vapour-phase polymerisation and decomposition of styrene</u>	148
4.1.1 Vapour-phase polymerisation	148
4.1.2 Thermal stability of styrene monomer	148
4.2 <u>Kinetics of the vapour-phase oxidation of styrene</u>	150
4.2.1 Slow combustion	150
4.2.2 The temperature-pressure ignition profile	153
4.2.3 The kinetic properties of the hot flame	155
4.2.4 Product formation during pre-flame stages of ignition	157
4.3 <u>Influence of polymerisation and depolymerisation on vapour-phase ignition</u>	160
4.3.1 Ignition characteristics	160
4.3.2 Factors promoting ignition	160
4.3.3 Factors inhibiting ignition	162
4.3.4 Product formation	163
4.4 <u>Conclusions</u>	165

4.1 Vapour-phase polymerisation and decomposition of styrene

4.1.1 Vapour-phase polymerisation

Studies of the vapour-phase polymerisation of monomers at pressures somewhat less than atmospheric have shown that no measurable polymerisation occurs with vinyl acetate, methylacetylene or styrene.⁵⁸ Significant measurements of the rate of polymerisation of styrene in the vapour-phase have been made only at pressures above atmospheric⁵⁹ and, even at these higher pressures, the reaction is relatively slow. Thus, the absence of measurable polymerisation at 180–300°C and at an initial pressure of ca. 10 kNm⁻² is not surprising and agrees well with previous observations.⁵⁸ Attempts to study the dimerisation of molecules which can be made to form long-chain polymers, such as styrene, have been unsuccessful. Even in the case of photochemical polymerisation, many monomers will not react in the vapour-phase as a result of direct irradiation but will do so only when a photosensitizer such as acetone is present. Such monomers include styrene, acrylonitrile and vinyl chloride.⁵⁷ In the present work, experiments carried out at the same temperatures and pressures have shown that no vapour-phase polymerisation of this monomer occurs even in the presence of small quantities of oxygen.

4.1.2 Thermal stability of styrene monomer

Earlier studies of the vapour-phase decomposition of styrene have indicated that this compound is stable at least up to 550°C. All these investigations were carried out under flow conditions in the presence of nitrogen. Recoveries of styrene monomer in the pyrolysis products ranged from 99% at 550°C to 95.3% at 625°C. Few attempts have been made to investigate the decomposition of styrene at higher temperatures, the only notable exception being that of Badger and co-workers^{62,63} who carried out detailed studies at 710°C, again using a flow system.

The present studies have indicated, in agreement with previous observations, that, in the absence of oxygen, styrene monomer is stable up to at least 500°C. Examination of the pyrolysis products formed at ca. 550°C shows that the major components are benzene, toluene, ethylbenzene, styrene and naphthalene, with unchanged styrene being by far the most abundant constituent (Table 3.1).

Consideration of the bond dissociation energies of the C - H and C - C bonds in styrene shows that the C - H bonds all have dissociation energies of the order of 418 kJ mole⁻¹. The approximate value for the dissociation energy of a C = C bond is of the order of 585 kJ mole⁻¹ and the C - C bond between the ethylenic group and the benzene ring has a dissociation energy of ca. 460 kJ mole⁻¹. There is thus little difference in the energy required to break any C - H bond and C - C bond. However, much greater energy is needed to break the C = C bonds in the ethylenic group or in the aromatic ring. Thus Badger⁶³ has pointed out that the radicals most likely to be formed initially are $\text{C}_6\text{H}_5^\bullet$, $\dot{\text{C}}\text{H} = \text{CH}_2$, $\text{C}_6\text{H}_5\dot{\text{C}}\text{H} = \dot{\text{C}}\text{H}$, $\text{C}_6\text{H}_5\dot{\text{C}} = \text{CH}_2$ and $\dot{\text{C}}_4\text{H}_6\text{CH} = \text{CH}_2$.

The various products resulting from the decomposition of styrene can be accounted for by the reaction pathways outlined in Section 1.5. In the present investigations, decomposition of styrene was also followed in the presence of small quantities of oxygen (1-5%). Oxygen appears to induce decomposition at temperatures as low as 320°C and the same products are detected in its presence as in its absence. However, as the oxygen pressure is increased, oxygen-catalysed pyrolysis gradually changes to oxidation, whereupon the reaction presumably involves the usual oxidation steps.

The methods mentioned hitherto for the study of pyrolysis reactions have their limitations. Minkoff and Tipper¹¹⁰ have pointed

out the disadvantages of the flow method. A relatively large amount of fuel is required, and it is more difficult to obtain kinetic results than from a static system. Furthermore, for slow combustion reactions preceded by a long induction period, it is necessary to work at much higher temperatures than if the system is at constant volume, since residence times in the tube cannot be made much greater than 1 minute. Oxidation rates cannot be obtained directly from flow systems, the course of reaction having to be followed by analysis of the exit gases at a series of increasing residence times.

While the static system used in the present investigations offers the most controllable conditions of temperature and reaction times, it is nevertheless susceptible to surface effects both for pyrolysis and oxidation reactions. However, the effects of the nature and extent of the surface on the pyrolysis and oxidation of styrene have not been examined in the present work.

4.2 Kinetics of the vapour-phase oxidation of styrene

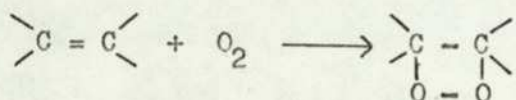
4.2.1 Slow combustion

Below atmospheric pressure, oxidation of styrene occurs only above 300°C and the region of slow oxidation extends to about 540°C for styrene-air mixtures. In the case of styrene-oxygen mixtures, the slow combustion region extends to about 460°C . No region of negative temperature coefficient of reaction rate has been observed for either styrene-air or styrene-oxygen mixtures. Similar observations have been reported for benzene, ethylene and p-xylene. Since styrene is made up of a benzene nucleus linked to an ethylenic group, it seems reasonable to expect this monomer to show oxidative characteristics similar to those of ethylene and benzene.

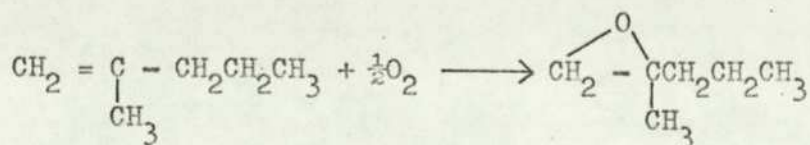
Below ca. 400°C, the slow oxidation of styrene exhibits long induction periods and a slow acceleration in reaction rate implying that the chain branching reaction is infrequent. Benzene, on the other hand, has been found to exhibit no appreciable induction period in a static system. As with benzene, the slow oxidation of styrene results in little ageing of the reaction vessel.

At about 300°C, the reaction of excess ethylene with oxygen commences with a decrease in pressure, whereas with excess oxygen or at higher temperatures, (> 400°C), the pressure-time curves are of the usual S - shape.¹¹¹ In contrast, the slow oxidation of styrene-oxygen mixtures, in ratios of 1:1 to 1:10, is not accompanied by a pressure decrease. The pressure-time curves for styrene-oxygen mixtures tend invariably to be S - shaped.

Other alkenes¹¹²⁻¹¹⁴ have also been found to exhibit an initial pressure decrease during slow oxidation at low temperatures, especially where fuel-rich mixtures are involved. This behaviour, which is not exhibited by alkane or alkylaromatic hydrocarbon - oxygen mixtures, is believed to be due to addition of oxygen across the double bond of the alkene. It has been proposed¹¹⁵ that this involves the formation of moderately stable peroxidic intermediates:-



Recently however, it has been suggested that the formation of an oxiran would also account for the pressure decrease.¹¹⁶



Since no initial decrease in pressure is observed for styrene-oxygen mixtures, when oxygen is present in 1-5% concentration, it appears that no appreciable amounts of such intermediates are formed during the oxidation of this compound.

Below 400°C, the maximum rate of oxidation of styrene is attained at ca. 40% conversion, whereas at higher temperatures the maximum rate of oxidation depends on the oxygen concentration. As the concentration of oxygen is increased at high temperatures, the maximum rate is displaced towards the start of reaction as compared with the usual oxidation behaviour of hydrocarbons, where the maximum rate is attained at ca. 50% conversion. At low temperatures, the maximum rate of reaction does not vary significantly with oxygen concentration.

Figure 3.11 shows a curve relating the final pressure increase for a 1:3 styrene-oxygen mixture (expressed as a percentage of the initial total pressure) to the reaction temperature. In this case the initial pressure was 41.5 kNm^{-2} , but since $\Delta P/P_0$ is constant at a given temperature, the curve should apply equally well to any 1:3 styrene-oxygen mixture. Over the temperature range, 310-460°C, the graph is linear, indicating a uniform course of reaction. Similar relationships between final pressure increment and reaction temperature have been reported for equimolar benzene-oxygen and toluene-oxygen mixtures.⁷⁵ However, with n-propylbenzene, the graph is linear above 400°C and this also appears to be the case below 300°C. However, a transition is observed at about 350°C, where ΔP is independent of temperature. This transition occurs in the region of negative temperature coefficient.⁷⁵ With styrene, the maximum rate of oxidation increases continuously with temperature for all the mixtures studied. No negative

temperature coefficient of reaction rate is observed. Styrene may thus be classed with methane, ethylene and benzene. However, especially at temperatures below 400°C , the rate of slow oxidation of styrene is somewhat sensitive to surface effects and is not very reproducible. This observation is in agreement with those of Kröger and Bigorajski,⁸⁸ who found that experiments with styrene-oxygen mixtures at $310\text{--}340^{\circ}\text{C}$ are not as reproducible as those for ethylbenzene. Generally, for other alkylaromatic hydrocarbons, no difficulty has been experienced in obtaining reproducible pressure-time curves, the rate of reaction being far less sensitive to surface effects than with the alkanes. Kröger and Bigorajski⁸⁸ suggested that, during the course of styrene oxidation, the walls of the vessel become coated with polymeric products which might help to account for the difficulty in obtaining reproducible pressure-time curves. These workers showed that the rate of oxidation of ethylbenzene was greater in a vessel which had been used previously for the oxidation of styrene. However, in the present work, no further evidence was obtained to substantiate the suggestion that the vessel walls become coated with polymer.

4.2.2 The temperature-pressure ignition profile

As with ethylene and benzene, a smooth ignition curve is obtained for styrene-air mixtures within the limits of pressure investigated. Monoalkylbenzenes generally exhibit a cool flame region as do aliphatic hydrocarbons, while at high temperatures ($>400^{\circ}\text{C}$) chain thermal ignition occurs. With styrene, only a high temperature chain thermal ignition has been observed.

Multistage ignition of benzene has been reported¹¹⁸ at pressures ranging from $500 - 600 \text{ kNm}^{-2}$ with fuel-rich mixtures. However, no subsequent evidence has been found for multistage ignition with this

compound. In the present work with styrene, no fuel-rich mixtures were studied in detail. The ignition tendency is however markedly affected by changes in the fuel-oxygen ratio. With a 1:5 styrene-air mixture, ignition is observed only above 540°C . Furthermore, ignitions with styrene-oxygen mixtures were too violent to be studied safely in glass apparatus, whereas with styrene-air mixtures ignition was a much milder phenomenon. Previous investigations of the ignition behaviour of styrene were confined to the determination of its spontaneous ignition temperature by a hot vessel method.¹¹⁷ This involved dropping liquid styrene into a quartz vessel through which a slow stream of air or oxygen was passed. Uniform fuel-air mixtures of known composition were not attained under these conditions.

The present studies of the vapour-phase oxidation of styrene have been restricted to pressures somewhat lower than atmospheric and it would clearly be desirable to extend the present work to higher pressures.

With benzene, for example, Burgoyne and Newitt⁷³ found that, at pressures of about 5066 kNm^{-2} , this compound reacted readily with oxygen at ca. 280°C , whereas at subatmospheric pressures slow oxidation occurred only above 450°C . Furthermore, in view of the observations of both Salooja⁸³ and Sokolik¹¹⁸ that the ignition tendency for benzene is increased by the presence of excess fuel, it may be worthwhile to investigate the ignition behaviour of styrene under fuel-rich conditions, both at high and low pressures.

Studies of the influence of molecular structure on the ease of oxidation of aromatic hydrocarbons with saturated side chains have shown that oxidation is facilitated by increasing carbon chain length. With styrene, however, oxidation is not as fast or as

reproducible as with ethylbenzene. The spontaneous ignition temperature of ca. 540°C at an initial pressure of ca. 59 kNm^{-2} is therefore not a surprising value and agrees fairly well with the reported temperature of 490°C for ignition in air at atmospheric pressure.

4.2.3 The kinetic properties of the hot flame

It has been found that the relationship

$$\tau_{\text{ign}} = kP_0^{-n}$$

holds for the high temperature oxidation of styrene (see Section 3.3.2.3).

The values of n and k have been evaluated at three temperatures and are listed in Table 4.1. It can be seen that n does not vary markedly with temperature, although k tends to increase towards a constant value at higher temperatures.

The increase in the value of k suggests that there is a change in mechanism above 555°C . Evidence for the existence of more than one mode of reaction is also provided by the relationship between ΔP_{ign} and P_0 , which is of the form

$$\Delta P_{\text{ign}} = mP_0 - c$$

m and c are constants which are not appreciably dependent on the initial temperature above 555°C (see Figure 3.17). At temperatures below 555°C , however, and at pressures approaching atmospheric, it is likely that m and c are dependent on the temperature as suggested by the curve at 555°C shown in Figure 3.18.

The maximum rate of pressure increase accompanying passage of a hot flame, $(dP/dt)_{\text{max}}$, increases continuously with P_0 and is also dependent on the initial temperature (see Figure 3.19). At the high temperatures involved, the rate of pressure increase is related not only to a possible intensification of chain branching, but also to an increase in the rate of heat liberation and to the appearance of thermal

Table 4.1Values of n and k

$T^{\circ}\text{C}$	n	k
555	1.82	1.12×10^5
569	2.00	4.68×10^5
577	1.88	4.97×10^5

autoacceleration of the reaction. Thus the most likely explanation for the dependence of the maximum rate of pressure increase on temperature, is that the reaction is chain thermal in nature.

A characteristic feature of the hot flame of styrene-air mixtures is the high residual pressure, P_f , which is established after equilibration of the temperatures of the reaction vessel and its contents and corresponds to an increase in the number of molecules formed during the reaction. In this flame, P_f/P_0 is usually about 1.1 (where P_0 is the initial pressure). The considerable increase in the number of molecules due to chemical reaction is related to the nature of these flames. Above initial pressures of ca. 33 kNm^{-2} , the residual pressure increase, ΔP_f , (expressed as a percentage of the total initial pressure), becomes independent of the initial pressure (see Figure 3.20).

4.2.4 Product formation during pre-flame stages of ignition

The products formed during the induction period preceding ignition were virtually the same as those of the slow oxidation of styrene at low temperatures. The principal oxygenated products were benzaldehyde and acetophenone, the former being by far the most abundant at both high and low temperatures. During the pre-flame stages of ignition, a relatively small amount of benzyl alcohol was also detected. Oxygen therefore preferentially attacks the α -carbon atom in the vinylic side chain. There is no evidence for reaction at the β -carbon atom, since no 2-phenylethanol was detected among the products.

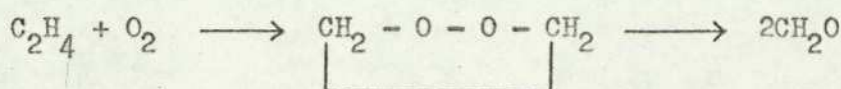
Similar observations have been made for ethylbenzene. At high pressures, oxygen attacks the α -carbon atom to a considerable extent with little indication of reaction at the β -position. Thus 2-hydroxyethylbenzene and acetophenone are important products and the aldehydic and acidic constituents consist almost entirely of benzaldehyde

and benzoic acid.

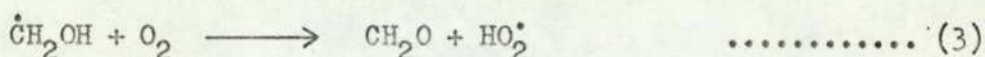
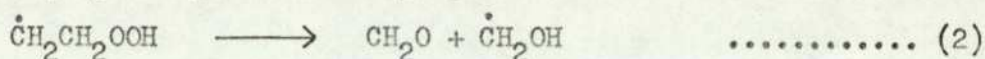
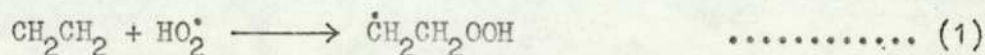
Although small quantities of peroxide have been detected during the slow oxidation of styrene at low temperatures (310–340°C)⁸⁹, no appreciable amounts of peroxides have ever been found during high temperature reactions. Thus analysis for peroxides was not carried out during the pre-flame stages of ignition.

Generally, the combustion of aromatic hydrocarbons involves both side chain and nuclear attack. Addition of an alkyl group to the benzene ring facilitates oxidation both because the nucleus is activated and because the alkyl group itself is readily attacked. Nuclear attack involves, in all cases, ultimate cleavage of the ring resulting in straight-chain products. The only such compound formed during the pre-flame stage of ignition of styrene was ethylene. Products from the oxidation of aromatic hydrocarbons fall into three general groups: those from oxidation of the side chain; those from oxidation of the ring and those from breakdown of the ring. With alkylaromatic hydrocarbons, increase of pressure and reduction of temperature reduces ring rupture (which produces CO, CO₂, aliphatic acids etc.) and increases the yield of products derived from oxidation of the side chain e.g. benzaldehyde.

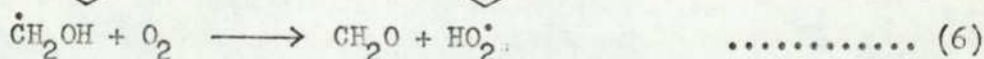
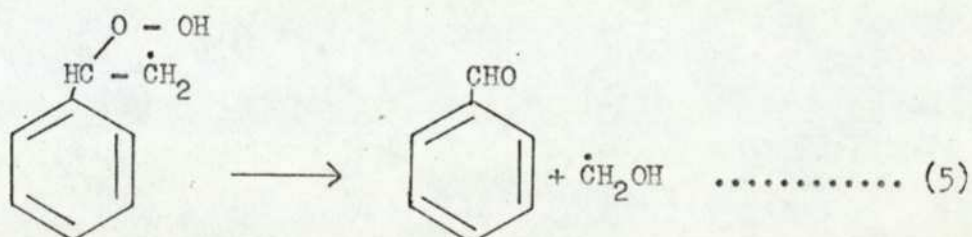
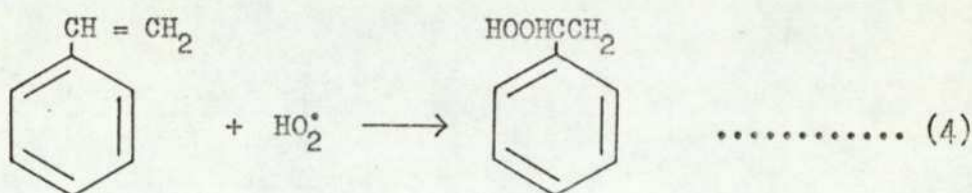
In terms of bond energies, styrene, which possesses only vinylic hydrogen atoms, ought to be an analogue of ethylene. Knox and Wells¹¹⁹ have studied the slow oxidation of the latter compound at ca. 360°C. Initial products were ethylene oxide, formaldehyde and acetaldehyde, while secondary products included methanol, ethanol, carbon monoxide and carbon dioxide. Formaldehyde was the principal product, its formation being attributed to the addition of an oxygen molecule across the double bond to give a four-membered ring peroxide which subsequently decomposed:



It is suggested that this reaction would explain the initial pressure decrease observed and was based on the assumption that the cyclic peroxide had appreciable thermal stability. Knox and Wells¹¹⁹ subsequently proposed a mechanism for olefin oxidation:



This mechanism may however also be applied to styrene:



The phenylethyl radical could be converted to ethylbenzene, which is one of the principal products formed from styrene at both high and low temperatures.

Neither styrene oxide nor products arising from oxidation of the benzene ring were detected. Kröger and Bigorajski⁸⁹ reported that, at 310–340°C, benzaldehyde was the main intermediate product and no products derived from ring oxidation were formed. Thus the present results are in good agreement with those previously obtained for the low temperature oxidation of styrene.

4.3 Influence of polymerisation and depolymerisation on vapour-phase ignition

4.3.1 Ignition characteristics

Some hydrocarbons start giving rise to cool flames well below their normal ignition temperature, while others react only to a small extent before igniting. Styrene appears to fall in the latter category. The temperature at which a hydrocarbon first starts to react, and the extent of reaction which it undergoes before ignition, are as much characteristic features of each hydrocarbon as are the ignition temperature and related properties. Salooja⁸³ found that, in general, richer fuel-air mixtures undergo a greater amount of pre-flame reaction than do weaker ones. Yet the ignition temperatures, while lowered in some cases, are raised markedly in others in spite of the higher rates of reaction.

4.3.2 Factors promoting ignition

In the present studies with a 1:5 styrene-air mixture, the introduction of polymerising liquid monomer into the reacting vapour mixture generally results in a shortening of the induction period preceding ignition.

Ignition of styrene-air mixtures was found to be promoted to an extent which increased with the temperature to which the liquid monomer was preheated. Generally, inhibitor-free monomer was slightly more effective in promoting ignition than was inhibited monomer. This suggests that it is the rate of polymerisation which is responsible for shortening the induction period. The volume of polymerising monomer introduced into the vapour mixture also influences the ignition tendency; the greater the volume of polymerising monomer added, the greater the promotion of ignition.

At about 300°C, polystyrene starts to depolymerise yielding largely the monomer. In the present situation, depolymerisation can occur only when the polymer actually enters the reaction vessel which is maintained at ca. 570°C. Once the depolymerisation process is initiated, it proceeds rapidly. Each bond broken produces two free radicals which react readily either with other polymer chains or with oxygen if present. In view of this, it is perhaps somewhat surprising that the introduction of solid polystyrene into the reacting vapour mixture has virtually no effect in promoting ignition. One possible explanation for this 'neutral' result is that the introduction of relatively cold polymer into the hot reacting vapour system exerts a cooling effect, thereby countering the tendency to promote ignition (see Section 4.3.3.).

In the case of liquid monomer polymerising in the capsule prior to its introduction into the reaction vessel, the free radicals generated have a limited survival time, but nevertheless grow in concentration as the rate of initiation is increased. When the capsule is introduced into the vessel, these free radicals may be present in sufficient concentration to promote the reactions leading to ignition. An increase in the volume of polymerising monomer introduced also results in an increase in the concentration of radicals generated.

Addition of initiators to the liquid styrene enables polymerisation to take place at relatively low temperatures. Introduction of initiator-containing monomer into the vapour mixture proved more effective in shortening the induction period. This accentuated shortening of the induction period was observed for monomer containing both benzoyl peroxide and α,α' -azobisisobutyronitrile, although the latter proved more effective. However, no further promotion of ignition was observed when larger amounts of these initiators were present. In addition to catalysing

polymerisation of the liquid styrene, some unchanged initiator may enter the reaction vessel and thereby promote reaction in the vapour-phase leading to ignition.

4.3.3 Factors inhibiting ignition

Comparison of the ignition characteristics of styrene-air vapour mixtures with those of similar mixtures into which polymerising liquid monomer has been introduced indicates that ignition is generally promoted by the introduction of the liquid. However this promoting effect tends to decrease with increasing initial pressure of the vapour mixture, suggesting that there are two counter-balancing factors in operation, one of which increases in relative importance at elevated pressures. The apparent inhibiting effect may be connected with the fact that a given decrease in temperature decreases the rate of vapour-phase polymerisation reaction to an extent dependent on the pressure. Blank experiments using liquid benzene instead of liquid styrene have also shown that the introduction of a relatively cool unreactive liquid decreases the ignition tendency to an extent which increases with the initial pressure of the gaseous reactant mixture.

In order to investigate further this cooling effect, direct measurements were made of temperature changes taking place within the reaction vessel during slow combustion preceding ignition. This was carried out both for purely vapour-phase ignition and for ignition following addition of the polymerising liquid styrene. These experiments have shown that the presence of the cold liquid, which needs not only to be vaporised but also heated to the temperature of the reaction vessel, does indeed suppress the temperature increase normally observed during slow combustion preceding vapour-phase ignition.

The rate of heating plus vaporisation of the liquid monomer was assessed directly from the pressure-time curves which showed that, with both 10 and 30 μ l aliquots of liquid, complete pressure equilibration occurred within one second as the liquid entered the reaction vessel.

Account must also be taken of the fact that, when the liquid styrene is volatilised, it increases the fuel-air ratio. Richer mixtures generally exhibit shorter induction periods and indeed the increase in the fuel air ratio consequent on the introduction of a given amount of liquid will be greatest at low pressures. It is precisely under these conditions that the promoting effect of the liquid polymer is most apparent.

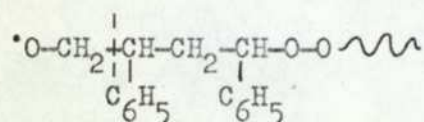
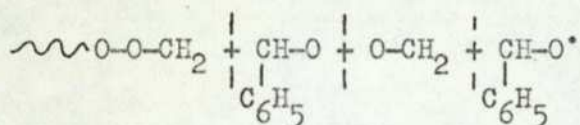
However, to summarise, probably the most important factor countering the normal promotion of ignition by the polymerising liquid monomer is the cooling effect caused by the addition of a relatively cold liquid to the reacting vapour mixture.

4.3.4 Product formation

The liquid monomer was polymerised prior to its introduction into the reaction vessel in sealed tubes. However the headspace inside these tubes contained trapped air, so that any subsequent polymerisation was initiated in the presence of air.

Miller and Mayo⁹⁴ showed that, at 50°C and in the presence of AIBN, styrene polyperoxide and benzaldehyde are formed concurrently. The rate of formation of polyperoxide decreases and that of benzaldehyde increases as the pressure of oxygen is decreased. The rate of peroxide formation was some 17 times greater than that of aldehyde at 101 kNm⁻² of oxygen, whereas these rates were nearly equal at 3.3 kNm⁻² oxygen pressure. At constant oxygen pressure, the proportion of aldehydes formed was found to increase with temperature.

In view of these observations, the products generated during the induction period preceding ignition were expected to differ to some extent from those formed during the pre-flame stages of purely vapour-phase ignition. When the monomer is heated in the capsule at 60-70°C, for example, styrene polyperoxide together with benzaldehyde and formaldehyde may well be formed concurrently. At higher temperatures of preheating, the rate of decomposition of the polyperoxide, which is known to explode above 100°C, will increase. Its principal reaction is cleavage of the O-O bonds to give two alkoxy radicals. These then lose alternately benzaldehyde and formaldehyde units in an exothermic chain reaction which may be interrupted by a chain end, an extra styrene unit in the chain or another radical:



As the principal products of decomposition of styrene polyperoxide are benzaldehyde and formaldehyde, it may be desirable in future work to determine more precisely the amounts of these aldehydes formed in the presence and absence of polymerising monomer.

4.4

Conclusions

Under the conditions used, styrene like acrylonitrile, vinyl acetate and vinyl chloride, does not appear to polymerise in the vapour-phase, although such polymerisation has been reported to occur with styrene at pressures above atmospheric.

In the absence of oxygen, styrene is stable up to ca. 500°C , but above this temperature, pyrolysis starts to occur. The presence of small quantities of oxygen (1-5%) does, however, induce decomposition at temperatures as low as 320°C .

The vapour-phase oxidation of 1:3, 1:5 and 1:10 styrene-oxygen mixtures starts to take place at about 300°C . Slow oxidation of a 1:1 styrene-oxygen mixture becomes measurable at 320°C . The partial ignition profile for a 1:5 styrene-air mixture shows two distinct regions of combustion, viz. slow oxidation at temperatures from $300-540^{\circ}\text{C}$ and hot ignition at higher temperatures. No cool flame region or negative temperature coefficient of reaction rate is found.

The introduction of polymerising liquid styrene generally promotes ignition in the vapour-phase. Thus, induction periods preceding ignition were shortened by introduction of the polymerising liquid monomer into the vapour system. This promoting effect is somewhat surprising in being more pronounced at lower initial pressures. Indeed at higher pressures this effect may be reversed. The main reason for this anomalous behaviour is probably the cooling effect exerted by the introduction of relatively cold polymerising monomer into the hot reacting vapour mixture. Results of blank experiments with liquid benzene (instead of liquid styrene) have shown a similar effect. Introduction of a comparatively cold and relatively unreactive compound into reacting styrene-air vapour mixtures at ca. 570°C lengthened the induction periods preceding ignition to an

extent which increased with the initial pressure of the vapour mixture. Furthermore, direct measurements of the temperature changes within the reaction vessel during the induction period preceding ignition have shown that the addition of a relatively cool liquid into the reacting vapour mixture suppresses at least partly the temperature rise normally observed during the induction period of a purely vapour-phase ignition. The temperature to which the liquid monomer is preheated (prior to introduction to the reaction vessel), influences the effectiveness of the polymerising monomer in promoting ignition. In general, the higher the temperature of initial preheating, the more effective is the polymerising medium in shortening the induction period. Inhibitor-free monomer is slightly more effective than inhibited monomer and the ignition tendency increases with the quantity of polymerising monomer. Addition of initiators to the inhibitor-free monomer enables polymerisation to occur at lower preheating temperatures with a consequent decrease in induction period. Thus the rate of initiation of polymerisation appears to be an important factor in enhancing ignition in the vapour-phase.

The process of polymerisation appears to be more important than that of depolymerisation in exercising a promoting effect on ignition in the vapour-phase. This is to some extent substantiated by comparative experiments involving the introduction of solid polystyrene into the reacting styrene-air vapour mixture. The addition of solid polymer has virtually no effect on ignition tendency.

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