FINAL REPORT

of

"STUDY OF SPONTANEOUS AND SPARK-INDUCED IGNITION CHARACTERISTICS OF HYDROCARBONS AT ATMOSPHERIC PRESSURE. PHASE III"

carried out under

AGREEMENT No. AT/2090/032 DR Ships

between

THE MINISTRY OF DEFENCE, PROCUREMENT EXECUTIVE

and

THE CITY UNIVERSITY, LONDON

during the period

1st AUGUST 1975 TO 31st JULY 1978

A THESIS

entitled

STUDIES OF THE COMBUSTION OF DECANE

by

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submitted for the

Degree of Doctor of Philosophy

of

The City University

1979

ABSTRACT

Much research has been carried out on the combustion of hydrocarbons containing up to about eight carbon atoms. In contrast the gas-phase oxidation of higher molecular weight hydrocarbons has received almost no attention. This is ascribable partly to the experimental problems associated with the gas-phase handling of compounds of low volatility and partly to the difficulties of obtaining and interpreting the extremely complex analytical data for the product distributions formed from large fuel molecules. Nevertheless, from the technological point of view, the combustion of larger hydrocarbons, such as decane, is of great significance as these compounds are important constituents of numerous practical liquid fuels. Decane is also of special interest as it is the lowest member of the alkane series whose uncatalysed oxidation can be studied in both the gas phase and the liquid phase at similar temperatures.

The Introduction (Section 1) outlines the general features of hydrocarbon combustion. Currently postulated mechanisms are reviewed and compared with those which are generally accepted to account for the observed kinetic and analytical features of the liquid-phase oxidation of hydrocarbons.

The Experimental Section (Section 2) describes the different apparatuses involved in this study. Initially a standard "premix" vacuum system was constructed and used but this was found to give unreliable results on account of the rapid oxidation of decane in the "premix" vessel. A "metal-free" apparatus was therefore built in order to obtain information about the peroxidic intermediates formed during the slow combustion of

the hydrocarbon, at lower temperatures, while a "liquid injection" apparatus was used at higher temperatures in order to ensure rapid mixing without the use of a "premix" vessel. The analytical techniques for identifying the complex mixtures of reaction products are also outlined. High-pressure liquid chromatography, with a post-column reactor, was used to detect and analyse peroxides, while the numerous other products were identified and determined using gas chromatography/mass spectroscopy.

The Results Section (Section 3) gives the temperature/pressure ignition profiles obtained for decane/air mixtures and describes the effects of several high molecular weight fuel additives on the slow combustion/cool flame boundary. The variation with time of the concentrations of the individual products is also presented. At low temperatures, decyl monohydroperoxides are formed in significant amounts but, as the temperature is raised through the slow combustion region, dihydroperoxides replace them as the main initial products. In the cool-flame region the yields of peroxides and carbonyl compounds containing less than ten carbon atoms are somewhat lower, while there is a concurrent increase in the yields of O-heterocyclic compounds and decenes. It is shown that the addition of hydrogen bromide to the reaction mixture decreases sharply the net amounts of hydroperoxides formed but at the same time increases the yields of decanones. An increase in the initial oxygen concentration in the reaction mixture is shown to increase the yields of dihydroperoxides and of carbonyl compounds with less than ten carbon atoms but to decrease the amounts of monohydroperoxides and O-heterocyclic compounds. Changes in the initial concentration of decane are shown to have little effect on the product distribution.

Finally, in the Discussion Section (Section 4), the ignition profiles of decane-air mixtures obtained in the "liquid injection" apparatus are shown to be in good agreement with previous results obtained in a "premix" apparatus. The mechanism of decane combustion at reasonably low temperatures is shown to involve the formation of decylperoxy radicals. Some of these abstract a hydrogen atom to form decyl monohydroperoxides which, in the liquid phase, is their almost exclusive fate. In contrast to the behaviour observed in the liquid phase, however, decylperoxy radicals in the gas phase may also isomerise and subsequently form dihydroperoxides and O-heterocycles. During slow combustion, carbonyl compounds with less than ten carbon atoms are shown to be formed mainly by the decomposition of the dihydroperoxides, the measured yields being in excellent agreement with those predicted. In the cool flame region, the rate of isomerisation of decylperoxy radicals and the subsequent formation of O-heterocycles increases rapidly, while at the temperatures involved, radical-radical reactions also become important. Decenes are formed in the cool flame region by the abstractive reaction of oxygen with decyl radicals, but above 623 K the main reaction of decyl radicals is their oxygen-catalysed cracking to form lower alkenes. The random initial attack on decane which occurs even at low temperatures suggests that, in contrast to the behaviour observed during the oxidation of some lower molecular weight alkanes, the main chain-propagating species are hydroxyl radicals rather than alkylperoxy radicals.

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Acknowledgements

The research for this thesis was carried out under the direction of Professor C.F. Cullis in the Combustion Research Laboratory of The City University. I would like to thank my colleagues for providing a congenial atmosphere in which to work.

My special thanks go to Professor Cullis for the help and guidance he has given me throughout this work and in many other ways, and to [redacted] for the interest he has shown in this work.

I am most grateful to the Ministry of Defence for the financial support given to this work.

Finally, I would like to thank [redacted], for her patience and for the help and encouragement which she has given me throughout.

SECTION 1

INTRODUCTION

SECTION 1 INTRODUCTION

1.1 General background

From a technological and economic point of view, the oxidation of hydrocarbons is probably the most important chemical reaction in modern society. It is not surprising, therefore, that the gas-phase and liquid-phase oxidation of these compounds has received considerable attention over the years.

Due to its importance with regard to the production of useful chemicals by selective oxidation and to its role in abnormal combustion phenomena such as "knock" and "run on" in the internal combustion engine, the combustion of hydrocarbons in the temperature range 450 to 900 K has been the most widely studied mode of oxidation.

Before 1970, the production of crude oil and its subsequent refining to petroleum fractions was carried out on such a large scale that there tended to be a surplus of these products on the world market. During this period, research into hydrocarbon oxidation was directed, therefore, towards finding alternative uses for this excess such as cracking and selective oxidation to lower molecular weight feedstocks for the chemical and plastics industries.

Since the fuel crisis of 1973, which led to vast increases in crude oil prices, and the subsequent realisation that there were finite oil reserves, there has been a change of emphasis in the use of hydrocarbons. One result has been the necessity to use higher molecular weight hydrocarbons as fuels. Previous research into hydrocarbon combustion has tended to be limited to low molecular weight fuels and it is apparent that there are gaps in our understanding of the oxidation mechanisms of higher molecular weight hydrocarbons.

1.2 Spontaneous ignition of hydrocarbons

The reaction of a hydrocarbon with oxygen at sub-atmospheric pressures and at temperatures between 400 and 750 K may be described by reference to figure 1.1 which shows a typical temperature-pressure ignition diagram. This figure shows that there are four basic physical phenomena in hydrocarbon combustion. These are slow combustion, cool flames, two-stage ignition and hot or true ignition[1]. The particular type of combustion behaviour which is observed depends on the initial reaction conditions and the nature of the fuel. It is also dependent, to a lesser degree, on the size, shape and surface of the reaction vessel and on the type of experimental system being used. These physical phenomena are usually followed by means of pressure transducers, fast-response micro-thermocouples[2] or photomultipliers[3].

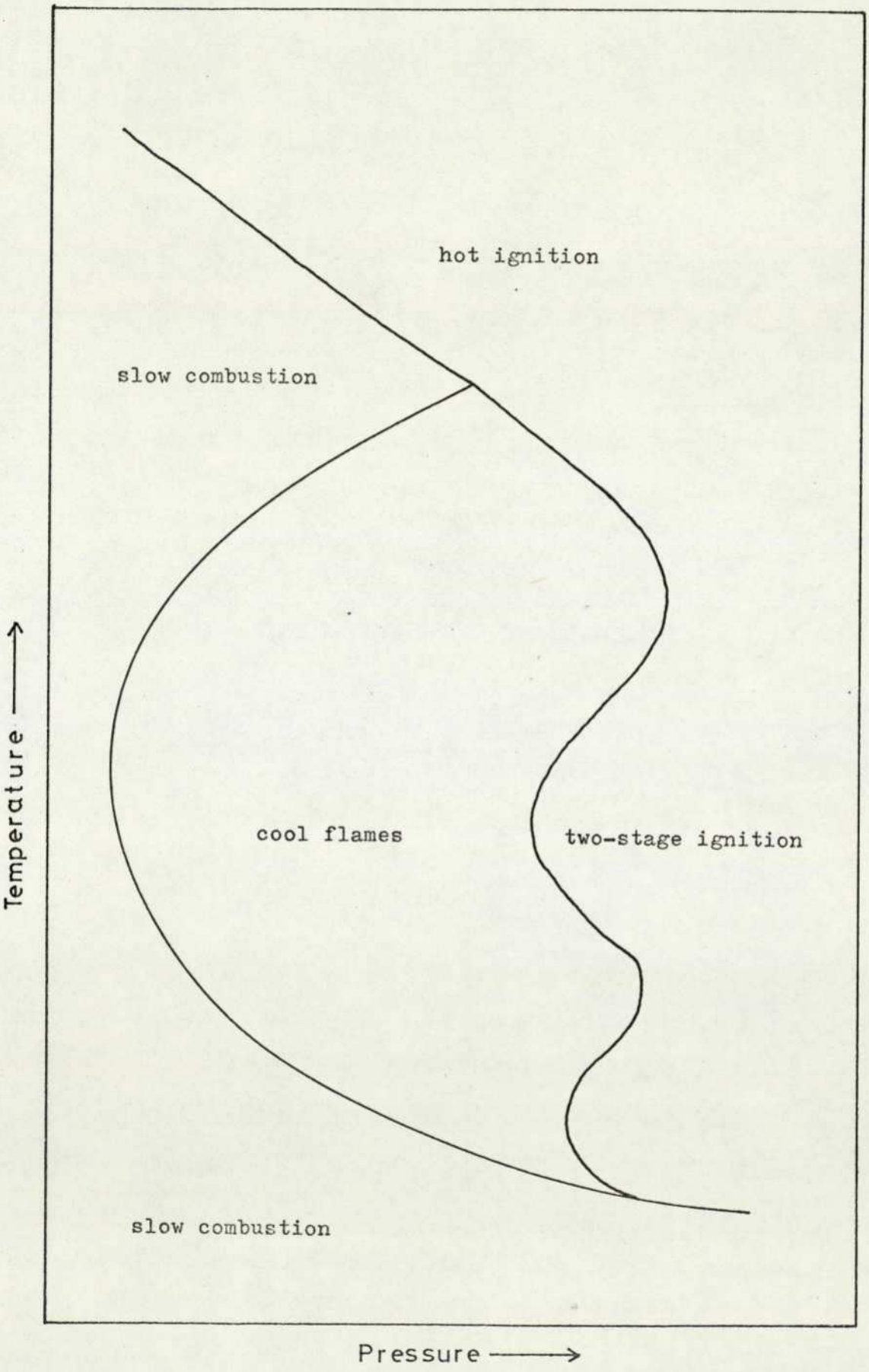
1.2.1 Slow combustion

Slow combustion is usually characterised by a sigmoidal pressure-time curve and is sometimes accompanied by a small transient temperature rise and a very faint luminosity which persists until the reaction is nearly complete[4].

The exponential pressure rise during slow combustion is often preceded by a long induction period and Semenov[5] suggested that hydrocarbon oxidation could best be considered as a degenerate branched-chain reaction. Branching is due to the presence of a relatively stable intermediate product, M, which is formed by a non-branching chain process. M can then react either to give inert products or radicals which can initiate the primary chain. The rate of reaction, w, is given by the following

Figure 1.1

Typical ignition profile for hydrocarbon/air mixtures



equation

$$w = a \exp(\phi t)$$

where a is a constant, t is the time and ϕ is the net branching factor i.e. the number of active centres which lead to branching minus those which lead to termination.

Later on, Knox pointed out[6,7] that the observed kinetics may be explained by an alternative mode of branching. In this case the intermediate, M, is formed in only a small fraction of the primary chain steps but every molecule of it reacts further to produce degenerate branching.

The slow combustion of hydrocarbons usually shows a region of negative-temperature coefficient between about 550 and 700 K, where the rate of reaction actually decreases with increasing temperature. It is generally agreed[8] that the negative temperature region is caused by a decrease in the rate of the branching reaction, although there is some disagreement about the nature of the branching agent.

1.2.2 Cool flames

The propagation of cool flames in a reacting mixture of hydrocarbon and oxygen is accompanied by a substantial pressure pulse (up to 9 kPa) and transient temperature rise (up to 200° C). It has been shown for a number of alkanes[9,10] that at a given temperature the relationship between ΔP_{cf}, the pressure rise associated with the cool flame and P_o, the initial pressure approximates to the following equation

$$\Delta P_{cf} = A P_o^{m}$$

where A is a constant and m has values between 1 and 3.

In addition to the transient pressure and temperature rises, the passage of a cool flame is also accompanied by a pale blue luminosity[4], which is thought to be due to excited formaldehyde[11,12].

Cool flames occur after a finite induction period, τ, following the introduction of the reactants into the reaction vessel. For a given hydrocarbon, the induction period increases as the initial pressure, P_o, is decreased and the induction period is related to the initial pressure by the following equation

$$\tau = kP_o^{-n} + c$$

where k, n and c are constants at constant temperature. This equation has been shown to hold at both low and high pressures in the oxidation of 2-methylpentane, n-heptane and isooctane[13-16].

At constant pressure, an Arrhenius relationship holds between the induction period and initial temperature. From the variation of the induction period with reciprocal temperature, the effective activation energy of the reaction has been calculated[15,16]. It has been shown that a linear relationship holds between the octane number of a hydrocarbon and the effective activation energy[10]. However, the large number of reactions occurring concurrently in hydrocarbon oxidation precludes any correlation of these activation energies with any particular chemical process[17].

Many workers have reported the occurrence of multiple cool flames and these non-isothermal events take place at intervals during an otherwise isothermal oxidation reaction. Various theories have been proposed to account for the self-quenching and periodicity of cool flames. One of the first was suggested by Lotka[18] and developed by Frank-Kamenetskii[19]. The reaction

sequence may be represented by the following steps:

$$A + X \rightarrow B + 2X$$

$$X + Y \rightarrow B + 2Y$$

$$A + Y \rightarrow B$$

where A is the reactant, B is an inert final product and X and Y are intermediates which are formed autocatalytically from A and X respectively.

An alternative mechanism, proposed by Salnikov[20], suggested that hydrocarbon combustion occurred as a two-stage process

$$A \rightarrow X \rightarrow B$$

Oscillations in the rate of reaction will be observed when the activation energy of the second stage is higher than that of the first and, if this second stage is exothermic, these oscillations may appear as cool flames.

In order to expain the negative temperature coefficient, this type of reaction scheme has been developed to include a second intermediate which leads either to the branching agent or to the final products[21]. These oscillatory reactions have recently been reviewed by Gray and Sherrington[22].

1.2.3 Ignition

The pressure-temperature locus of the limiting condition for ignition of hydrocarbons is often a complex diagram. As the temperature is increased, the necessary pressure for ignition passes through several minimum and maximum values. At temperatures above 630 K and at sufficiently high pressures, single-stage or hot ignition occurs. This manifests itself by a very rapid increase in pressure, a high transient temperature rise and a bright orange flame. At lower temperatures two-stage ignition

may occur, in which the hot ignition is preceded by one or more cool flames.

The two stage ignition limit curve (figure 1.1) may be divided into three principal lobes designated L_1, L_2 and L_3 respectively with increasing temperature[23]. A recent theory proposes that these lobes may be related to the molecular structure of the hydrocarbon and are associated with changes in the mechanism of cool-flame propagation[24].

Hydrocarbon oxidation, which involves a degenerately branched chain reaction, is unlikely to produce an isothermal branched-chain explosion since the increase in the number of chains is small[5]. Thus a theoretical treatment of cool flames and hot ignitions requires the introduction of a thermal factor. For a reaction whose rate is dependent on temperature, thermal instability will occur when the rate of heat release of the reaction exceeds the rate of heat removal from the system. During slow combustion self heating is small and the rate of heat dissipation will exceed the rate of heat release but when heat production is faster than its dissipation the system becomes thermally unstable and an explosion will occur. Application of this thermal ignition theory has been used successfully to predict the minimum initial temperature required to cause auto-ignition[25]. However, this treatment assumes that there is purely conductive heat transfer in the reacting gases and more recent studies have shown that convection may be important[2].

1.2.4 Effect of additives

The spontaneous ignition temperature of hydrocarbons in air or oxygen may be considerably modified by the presence of additives. Thus increasing amounts of a chemically inert substance in a flammable gas mixture causes the limits of flammability of the mixture to approach and ultimately to meet, i.e. the mixture becomes non-flammable. Examples of such inert substances listed in decreasing order of effectiveness are carbon dioxide, helium, nitrogen and argon[26].

Chemically reactive additives are often used to alter the ignition characteristics of hydrocarbon fuels in internal combustion engines. The occurrence of 'knock' in a spark-ignition engine, which has been shown to arise from spontaneous ignition in the last part of the unburnt charge, limits both the power output and economy of the engine[27]. Tetraethyl lead was found to possess tremendously effective 'anti-knock' properties in ca. 1918 and its use has continued to the present day. It is believed that tetraethyl lead acts by delaying or suppressing the second stage of two-stage ignition[28].

Aniline and its derivatives are also effective anti-knock agents[29] although studies of the 'anti-knock' action of aromatic amines have shown that all the anilines in which both hydrogen atoms of the $-NH_2$ group are replaced by alkyl groups have no effect on the tendency to 'knock'[30].

Aliphatic amines also possess significant inhibiting properties. The slow gaseous oxidation of acetaldehyde was found to be considerably more inhibited by the secondary and tertiary bases than by the primary amines[31]. Conversely, trimethylamine was found to have a marked promoting effect on

the two-stage ignition of cyclohexane and n-heptane, whereas primary and secondary amines (and NH_3) retarded both stages of two-stage ignition[32].

The oxides of nitrogen have also been reported to have both a promoting and inhibiting effect on gaseous oxidation reactions[33].

Halogen compounds promote the low-temperature oxidation of hydrocarbons by enhancing chain initiation, chain propagation or chain branching[34]. In contrast they exert a marked inhibiting effect on combustion processes at high temperatures where flame propagation takes place[35]. For many years halogen compounds have been used in fire extinguishers and it has been found that the effectiveness of the inhibitor increases as the number of halogen atoms in the molecule increases[36].

1.3 Chemical mechanism of hydrocarbon combustion

The first theory of hydrocarbon combustion was proposed at the beginning of the twentieth century[37]. This theory, the hydroxylation theory, stated that the intermediates in the oxidation could be accounted for by the replacement of successive C-H bonds by C-OH bonds. It was able to explain the formation of both aldehydes and acids, but the alcohols which should have deen the principal intermediates could not be detected.

It is now generally agreed that hydrocarbon combustion proceeds via a complicated free radical chain mechanism which also involves degenerate branching[5]. The following general reactions may be taken as a representative mechanism, where R represents an alkyl group.

initiation

$$RH + O_2 \rightarrow R^{\bullet} + HO_2 \qquad (1.1)$$

propagation

$$RH + X^{\bullet} \rightarrow R^{\bullet} + XH \qquad (1.2)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \qquad (1.3)$$

$$R^{\bullet} + O_2 \rightarrow \text{alkene} + HO_2^{\bullet} \qquad (1.4)$$

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (1.5)$$

$$RO_2^{\bullet} \rightarrow \text{products} + \text{radical} \qquad (1.6)$$

$$RO_2^{\bullet} \rightarrow {}^{\bullet}ROOH \qquad (1.7)$$

$${}^{\bullet}ROOH \rightarrow \text{products} + \text{radical} \qquad (1.8)$$

$${}^{\bullet}ROOH + O_2 \rightarrow {}^{\bullet}OOROOH \qquad (1.9)$$

branching

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (1.10)$$

$$H_2O_2 + M \rightarrow 2{}^{\bullet}OH + M \qquad (1.11)$$

termination

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow \text{chain termination} \qquad (1.12)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (1.13)$$

Any mechanism for the oxidation of a particular hydrocarbon must explain not only the nature and sequence of product formation, but also the different ignition phenomena, such as the negative temperature coefficient of reaction rate and the occurrence of single and multiple cool flames. The existence of such different phenomena indicates that the dominant reaction mechanism will change substantially with temperature.

1.3.1 Chain initiation

Chain initiation (reaction 1.1) which involves the abstraction of a hydrogen atom by molecular oxygen to yield an alkyl radical and a hydroperoxy radical was first suggested by Cullis and Hinshelwood[39]. Such abstraction reactions are highly endothermic with high activation energies which have been estimated to be between 185 and 210 kJ $mole^{-1}$. They therefore proceed slowly and selectively and, as would be expected from the C-H bond strengths, tertiary C-H bonds are the most readily attacked and primary bonds the least.

Owing to the high reactivity of the initial combustion products, this primary initiation reaction is rapidly masked by secondary processes such as reaction (1.2). The abstracting radical, X, will be either a hydroxyl radical, a hydroperoxy radical, or an alkylperoxy radical. The kinetic parameters suggested by Walker[40] for these reactions involving attack by primary, secondary and tertiary bonds have been listed in table 1.1 It is apparent

Table 1.1

Kinetic parameters for radical attack at primary, secondary and tertiary bonds

Bond broken	Primary C-H		Secondary C-H		Tertiary C-H	
Reaction	A l mole^{-1} s^{-1}	E kJ mole^{-1}	A l mole^{-1} s^{-1}	E kJ mole^{-1}	A l mole^{-1} s^{-1}	E kJ mole^{-1}
$^{\bullet}OH$ + RH	6.15×10^{8}	6.9	1.4×10^{9}	3.6	1.25×10^{9}	-0.8
$HO_2^{\bullet}$ + RH	1×10^{9}	81.0	1×10^{9}	71.3	1×10^{9}	60.3
$RO_2^{\bullet}$ + RH	1×10^{9}	81.0	1×10^{9}	71.3	1×10^{9}	60.3

that the attack by hydroperoxy and alkylperoxy radicals will be selective and will lie in the same order as for attack by oxygen. However, attack of the hydrocarbon by hydroxyl radicals, which has a low activation energy, will be relatively unselective.

1.3.2 Chain propagation

Below 500 K, the alkyl radicals initially generated will usually react exclusively with oxygen to form alkylperoxy radicals (reaction 1.3). However, as this reaction is reversible, the position of equilibrium plays an important part in determining the mechanism in the temperature range 500-750 K. Direct bimolecular reactions, such as reaction (1.4) forming the conjugate olefin, may become important as the temperature is raised above 500 K.

At temperatures above 650 K, cracking of alkyl radicals by C-C bond scission to yield an alkene and a lower alkyl radical (reaction 1.14) will begin to compete with conjugate alkene formation by reaction with oxygen.

$$R^{\bullet} \rightarrow \text{alkene} + R'^{\bullet} \qquad (1.14)$$

1.3.2 (a) $R + O_2 \rightarrow$ Alkene

Analytical studies of the oxidation of many hydrocarbons, especially those containing up to five carbon atoms, have shown that the main initial product is often the conjugate alkene. Thus in the oxidation of ethane[41], propane[42] and isobutane[43] the conjugate alkene accounted for up to 80% of the product formed in the early stages of the reaction between 570 and 720 K. These results led Knox[44] to propose that the primary oxidation process for alkyl radicals with oxygen was abstractive:

$$C_nH_{2n+1}^{\bullet} + O_2 \rightarrow C_nH_{2n} + HO_2^{\bullet} \qquad (1.4)$$

It was also suggested that, as the conjugate alkene concentration reached a kinetically controlled stationary value, it must play an important role in the intermediate and later stages of alkane oxidation.

Since the composition of the minor products varied with the nature of the reaction vessel wall, Knox[44] further concluded that these must be produced by the heterogeneous decomposition of a stable unknown intermediate, Z, which was formed from alkylperoxy radicals (reaction 1.15)

$$C_nH_{2n+1}OO^{\bullet} \rightarrow Z \rightarrow \text{minor products} \qquad (1.15)$$

In order to complete the chain cycle and explain the observed decrease in selectivity as the combustion proceeds, the following reaction sequence was proposed for the conversion of $HO_2^{\bullet}$ radicals to the more reactive $^{\bullet}OH$ radicals.

$$HO_2^{\bullet} + C_nH_{2n} \rightarrow HOOC_nH_{2n}^{\bullet} \qquad (1.16)$$

$$HOOC_nH_{2n}^{\bullet} + O_2 \rightarrow HOOC_nH_{2n}OO^{\bullet} \qquad (1.17)$$

$$HOOC_nH_{2n}OO^{\bullet} + HO_2 \rightarrow HOOC_nH_{2n}OOH + O_2 \qquad (1.18)$$

$$HOOC_nH_{2n}OOH \rightarrow HO^{\bullet} + R'{=}O + R''{=}O + {}^{\bullet}OH \qquad (1.19)$$

However, experiments involving the addition of small quantities of ^{14}C-labelled but-1-ene and but-2-ene during the combustion of n-butane[45] showed that butenes play an important but not overwhelming role in the mechanism. It was shown that 1-butylperoxy radicals could be formed only by direct addition of oxygen to 1-butyl radicals and were not produced at all via 1-butene.

Fish[46] suggested that below 725 K the dominant mode of formation of the conjugate alkene is not via the direct bimolecular reaction (1.4) but from the isomerised alkylperoxy radical:

$$R\text{-}CH_2\text{-}CH_2^{\bullet} + O_2 \rightarrow R\text{-}CH_2\text{-}CH_2(^{\bullet}O\text{-}O) \qquad (1.3)$$

$$R\text{-}CH_2\text{-}CH_2(^{\bullet}O\text{-}O) \rightarrow R\text{-}\dot{C}H\text{-}CH_2(HO\text{-}O) \qquad (1.7)$$

$$R\text{-}\dot{C}H\text{-}CH_2(HO\text{-}O) \rightarrow R\text{-}CH{=}CH_2 + HO_2 \qquad (1.20)$$

However, from a recent study of the addition of n-butane and of cis-but-2-ene to slowly reacting mixtures of hydrogen and oxygen, firm evidence was obtained[47] to show that hydroperoxy-alkyl radicals are not a major source of the conjugate alkene.

More recently, Cullis and Hirschler[38] have shown that during pentane combustion at 588 K only 30% of the pentane consumed was converted to pentenes. It was suggested that the predominant reaction of pentyl radicals, under the conditions used, was to add on oxygen to form pentylperoxy radicals, the direct decomposition of these radicals providing an alternative route for the formation of the conjugate alkenes

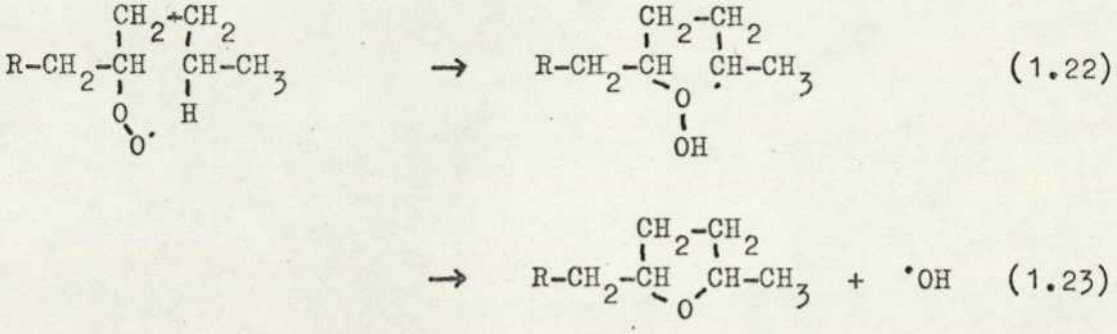
$$RO_2^{\bullet} \rightarrow \text{conjugate alkene} + HO_2^{\bullet} \qquad (1.21)$$

Walker[40] has argued, however, that the formation of the conjugate alkene is best considered a direct bimolecular process (reaction 1.4) at all reasonable temperatures.

1.3.2 (b) <u>R + O_2 → O-heterocycles</u>

O-heterocycles have been found in the combustion products of every alkane studied with four or more carbon atoms and their yields are often considerable, particularly under cool-flame conditions[48]. It is generally agreed[49,50,51], that O-heterocycles are formed by the homogeneous formation and subsequent isomerisation

of alkylperoxy radicals, followed by decomposition of the hydroxyperoxyalkyl radical:

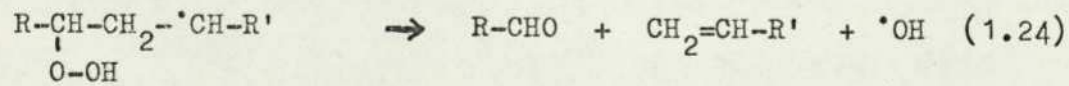


(1.22)

(1.23)

The relative importance of the various heterocycles produced is determined by the strength of the C-H bond from which internal hydrogen abstraction occurs and also the ring strain involved in the transition state. Values of 27-33, 0, 27 and 42 kJ mole^{-1} have been suggested for 5-, 6-, 7- and 8- membered rings respectively[52,53]. Thus, the formation of oxetans from β-hydroperoxyalkyl radicals will be preferred, since this involves effectively no strain.

Fish[50] has suggested that formation of the other reaction products from the combustion of alkanes may also be explained by alternative decomposition reactions of the isomerised alkylperoxy radicals involving C-C bond fission. Thus, the production of carbonyl compounds and lower alkenes in pairs may be accounted for qualitatively by C-C bond fission of β-hydroperoxyalkyl radicals.



(1.24)

1.3.2 (c) Radical-radical reactions

Radical-radical reactions have long been accepted as termination steps in hydrocarbon oxidation. However, it is only recently that such reactions have been postulated as propagation processes[54]. As the temperature is raised from 550 to 700 K, the equilibrium position of reaction (1.3), the addition of oxygen to alkyl radicals, moves increasingly to the right. Thus, there will be a large concentration of alkylperoxy radicals, neccessary for self-reaction, since reactions (1.5) and (1.7), the formation of hydroperoxides and the isomerisation of alkylperoxy radicals, have high activation energies and proceed relatively slowly.

The important radical-radical propagation reactions give rise to alkoxy radicals:

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow 2RO^{\bullet} + O_2 \qquad (1.25)$$

$$RO_2^{\bullet} + R^{\bullet} \rightarrow 2RO^{\bullet} \qquad (1.26)$$

$$RO_2^{\bullet} + HO_2^{\bullet} \rightarrow RO^{\bullet} + {}^{\bullet}OH + O_2 \qquad (1.27)$$

The subsequent disproportionation of the alkoxy radicals formed in reactions (1.25 - 1.27) has been successfully used to explain the product distribution which occurs during the cool-flame combustion of butane[54].

1.3.3 Evidence for the participation of hydroperoxides

Alkyl monohydroperoxides have long been known to participate in the liquid-phase oxidation of hydrocarbons and the detection of peroxy species in hydrocarbon combustion products has led to the assumption that monohydroperoxides also participate in gas-phase reactions. However, there is little conclusive proof for this assumption as low molecular weight peroxides are relatively unstable at the temperatures involved and are difficult to detect.

The formation of alkyl monohydroperoxides and their participation as the degerate branching agent in hydrocarbon combustion was first proposed by Ubbelohde[55]. Many attempts have been made to detect their presence in oxidation products, although the results obtained have seldom been unequivocal[56]. The analytical techniques used in many studies were often not selective enough to distinguish between the different peroxide classes. Iodometric titrations, the most common early method for determining the concentration of peroxides, give a total peroxide yield. The quantity of reaction product obtained from gas-phase oxidation is seldom sufficient to allow reduction of the peroxide present to the alcohol and its subsequent analysis by gas chromatography as in the liquid phase.

The assumption that the peroxides detected were alkyl monohydroperoxides, which was based on the fact that the addition of alkyl monohydroperoxides to the reaction mixture decreased the induction period of the cool flame[57], was rather unwarranted. Since such compounds decompose thermally to yield two radicals (reaction 1.10), it is inevitable that the rate of the oxidation reaction will be increased.

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (1.10)$$

Possibly the first positive identification of the peroxides present in hydrocarbon oxidation products was made by Cartlidge and Tipper. A paper-chromatographic technique was developed for the separation and identification of small amounts of organic peroxides[58] and was used to analyse the products of hydrocarbon slow combustion[59]. Using a flow system, it was found that with propane at 600 K and 2,2,3-trimethylbutane at 638 to 658 K the products contained only traces of hydrogen peroxide and its addition compounds with aldehydes. With n-butane between 583 and 618 K and cyclohexane between 563 and 589 K approximately 10-20% of the hydrocarbon oxidised appeared as peroxides. These consisted of hydrogen peroxide, monohydroperoxides and their addition compounds with aldehydes. With n-heptane between 513 and 583 K the yield of peroxide in the product was also considerable ($\sim$ 20% of the hydrocarbon reacted) and consisted mainly of dihydroperoxyheptane and its addition compounds with aldehydes. Much smaller amounts of monohydroperoxide, hydrogen peroxide, diheptylperoxide and possibly trihydroperoxyheptane were also formed. It was suggested that the dihydroperoxyheptane resulted from the internal abstraction of a hydrogen atom in the heptylperoxy radical from a methylene group β or γ to the point of original attack rather than from the monohydroperoxide. Dihydroperoxides have also been suggested as important intermediates responsible for many of the products formed in pentane combustion[60].

Paper chromatography was also used in a study of isobutane combustion[61] and it was reported that the monohydroperoxide was detected. This hydrocarbon is unique in that it contains

nine primary hydrogen atoms and only one tertiary hydrogen atom. This latter atom is the initial point of attack and subsequently leads to tertiary-butylhydroperoxide which has a high thermal stability.

Cullis and Fersht[62], however, failed to detect the simple monohydroperoxides in isopentane combustion between 613 and 673 K. Using gas-liquid chromatography they found that the products contained substantial amounts of peroxidic compounds, none of which was the simple monohydroperoxide even though separate experiments show this compound to be stable at the temperature used.

1.3.4 Chain branching

Degenerate chain branching accounts for the auto-catalytic nature of hydrocarbon oxidation and there has been considerable controversy concerning the identity of the branching intermediate. The two agents thought to be the most likely candidates are aldehydes and peroxides.

The thermal decomposition of an alkyl monohydroperoxide yields an alkoxy radical and a hydroxyl radical.

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (1.10)$$

Dihydroperoxides may also give rise to chain branching as they decompose by fission of both O-O bonds to yield two carbonyl compounds and two hydroxyl radicals.

$$HOOROOH \rightarrow R'{=}O + R''{=}O + 2{}^{\bullet}OH \qquad (1.19)$$

As the oxidation proceeds chain branching may occur by the abstraction by an oxygen molecule of a labile hydrogen atom from an intermediate oxidation product such as an aldehyde [63,64].

$$RCHO + O_2 \rightarrow RC^{\bullet}O + HO_2^{\bullet} \qquad (1.28)$$

An increase in temperature will favour the decomposition of alkylperoxy radicals by isomerisation or radical-radical reactions rather than the formation of alkylmonohydroperoxides. It is reasonable to suppose, therefore, that the aldehyde chain-branching mechanism will tend to take place at higher temperatures and the peroxide mechanism at low temperatures[24].

Hydrogen peroxide which will be formed by reaction (1.29)

$$RH + HO_2^{\bullet} \rightarrow R^{\bullet} + H_2O_2 \qquad (1.29)$$

may also decompose to give two hydroxyl radicals and therefore lead to chain branching.

$$H_2O_2 + M \rightarrow 2^{\cdot}OH + M \qquad (1.11)$$

As this reaction requires an activation energy of ca. 188 kJ mole^{-1} it probably becomes important only at high temperatures[28].

1.3.5 Chain termination

Termination may occur by either homogeneous or heterogeneous processes. Radicals may react together in the gas phase yielding products which are inactive as chain propagating species. The main radical disproportionation reactions are

$$2C_nH_{2n+1}O_2^{\cdot} \rightarrow C_nH_{2n+1}OOH + C_nH_{2n} + O_2 \qquad (1.30)$$

$$C_nH_{2n+1}OO^{\cdot} + HO_2^{\cdot} \rightarrow C_nH_{2n+1}OOH + O_2 \qquad (1.31)$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (1.13)$$

Heterogeneous termination occurs by the diffusion of chain carriers and branching agents to the reaction vessel walls and their subsequent destruction at the surface to inactive products.

1.3.6 Effect of additives

Chemically reactive additives influence the overall rate of hydrocarbon combustion by their effect on individual initiation, propagation and branching reactions; i.e. their action may be explained in terms of altering the rate of introduction of fresh radicals into the system or of reaction with active centres to give radicals which propagate the chains more or less efficiently.

It has been suggested that tetraethyl lead acts as an 'anti-knock' agent by forming a fog of solid particles of lead monoxide whose surface is particularly effective in destroying hydrogen peroxide, thus reducing the concentration of the high temperature branching agent[28,29]. An alternative suggestion[65] is that the tetraethyl lead decreases the concentration of hydroxyl radicals which are chain carriers.

$$PbO + {}^{\bullet}OH \rightarrow PbO(OH)$$

followed by

$$PbO(OH) + {}^{\bullet}OH \rightarrow PbO_2 + H_2O$$

The lead dioxide is then converted back to lead monoxide by reaction with alkyl radicals

$$PbO_2 + R^{\bullet} \rightarrow PbO + RO^{\bullet}$$

The inhibiting and 'anti-knock' role of primary amines is also believed to be due to their effect on branching reactions and a two-stage process has been proposed[66]. Firstly, a condensation reaction with acetaldehyde competes effectively with the oxidation of the aldehyde, thus preventing the formation of the branching agent.

$$C_2H_5NH_2 + CH_3CHO \rightarrow C_2H_5N{=}CHCH_3 + H_2O$$

Secondly, subsequent hydrogen abstraction from the imine produces a resonance-stabilised radical which is unable to propagate the reaction chain

$$RO_2^{\bullet} + CH_3CH_2N{=}CHCH_3 \rightarrow CH_3\dot{C}HN{=}CHCH_3 \leftrightarrow CH_3CH{=}N\dot{C}HCH_3 + ROOH$$

Tertiary amines do not readily form adducts with aldehydes in the same way as primary and secondary amines. They therefore have little effect on the induction period preceding a cool flame.

The inhibiting effect of nitrogen dioxide at low temperatures has been explained[33] by assuming that a molecule of NO_2 acts as a free radical and tends to combine with other free radicals to form a relatively stable complex $(NO_2)R$. During cool flames this complex can dissociate giving an increase in radical concentration and thus leading to the observed promotion of two-stage ignition.

It has been found that organic bromine compounds have a pronounced influence on the slow combustion and spontaneous ignition of hydrocarbons only under conditions where they themselves are converted to hydrogen bromide or bromine[34]. Thus the halogen compounds which promote cool-flame combustion dissociate to give halogen atoms which increase the rate of initiation.

$$RH + Br^{\bullet} \rightarrow R^{\bullet} + HBr$$

Chain propagation in the presence of halogen compounds generally involves either donation or abstraction of hydrogen atoms, the hydrogen halides providing an additional mode of

formation of alkylhydroperoxides.

$$RO_2^{\bullet} + HBr \rightarrow ROOH + Br^{\bullet}$$

As a result of this reaction the isomerisation of alkylperoxy radicals is suppressed and the dihydroperoxide cannot be formed by the further reaction of the hydroperoxyalkyl radical:

$$ROO^{\bullet} \rightarrow {}^{\bullet}ROOH \xrightarrow{O_2} {}^{\bullet}OOROOH \xrightarrow{AH} HOOROOH$$

Thus, dihydroperoxides have been identified in the oxidation products of n-heptane at 510 K[59], whereas only monohydroperoxides were detected in the presence of hydrogen bromide at 460 K[67].

In a detailed study of the effect of hydrogen bromide on the products of the cool-flame combustion of n-pentane, Bastow and Cullis[60] found that the main effect of adding hydrogen bromide was to increase dramatically the yields of C_5 ketones at the expense of almost all the other products. Control experiments on the homogeneous breakdown of pentane-2-monohydroperoxide, in the presence of hydrogen bromide, showed that the principal decomposition product is pentan-2-one thus confirming the importance of monohydroperoxides as intermediates in the hydrogen-bromide promoted reaction.

The inhibiting effect of organic halogen compounds on hydrocarbon flames is also believed to be due to the participation of the hydrogen halide in the reaction. It is thought that inhibition takes place by the removal of chain-propagating radicals by the hydrogen halide[36] viz:

$$^{\bullet}OH + HX \rightarrow H_2O + X^{\bullet}$$

Similar reactions will also occur for other radicals.

1.4 Comparison of gas-phase and liquid-phase oxidation of hydrocarbons

The liquid-phase oxidation of hydrocarbons has been extensively studied and Emmanuel[68] has shown that a hydroperoxide chain mechanism accounts satisfactorily for the oxidation of a wide variety of organic compounds at temperatures below 440 K. The main reactions may be listed as follows:

initiation

$$RH + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet} \qquad (1.1)$$

$$2RH + O_2 \rightarrow 2R^{\bullet} + H_2O_2 \qquad (1.40)$$

propagation

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \qquad (1.3)$$

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (1.5)$$

branching

$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH \qquad (1.10)$$

$$2ROOH \rightarrow RO_2^{\bullet} + H_2O + RO^{\bullet} \qquad (1.41)$$

termination

$$RO_2^{\bullet} + R'CHOO^{\bullet}R'' \rightarrow ROH + R'COR'' + O_2 \qquad (1.42)$$

$$RO_2^{\bullet} + R^{\bullet} \rightarrow ROOR \qquad (1.43)$$

$$R^{\bullet} + R^{\bullet} \rightarrow R\text{-}R \qquad (1.44)$$

It can be seen that many of the above reactions which occur in liquid-phase oxidation are similar to those in the gas phase. However, experimental comparisons between gas and liquid-phase oxidations have previously been limited to relatively low molecular weight hydrocarbons such as butane[69] and isobutane[70]. The slow reaction of these compounds at the low temperatures required for liquid-phase studies has necessitated the use of artificial initiators.

1.4.1 Elementary steps

As in the gas phase, initiation of the oxidation of hydrocarbons in the liquid phase involves the production of alkyl radicals. In an uncatalysed system, these may be formed either by reaction (1.1)[71] or (1.40)[72]

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet} \qquad (1.1)$$

$$2RH + O_2 \longrightarrow 2R^{\bullet} + H_2O_2 \qquad (1.40)$$

Reaction (1.1) is similar to that which is believed to occur during gas-phase combustion. However, there appears to be no evidence for a third body initiation step, such as reaction (1.40), occurring in the gas phase.

In both phases, however, secondary initiation, which involves the abstraction of a hydrogen from the fuel molecule by a radical, rapidly becomes more important even in the early stages of the oxidation.

$$RH + X^{\bullet} \longrightarrow R^{\bullet} + XH \qquad (1.2)$$

It has been shown (Section 1.3.1) that the initial products formed in the gas phase depend on the nature of the abstracting radical, X, in reaction (1.2). Thus if the abstracting species is a hydroxyl radical, unselective attack on the original fuel molecule will occur and products formed from primary alkyl radicals will be detected in the reaction mixture. At low temperatures in the gas phase, the abstracting radicals are usually either alkylperoxy or hydroperoxy radicals which are selective in the position which they attack. In the liquid phase the same species is believed responsible for initial hydrogen abstraction. Low yields of products formed from the primary alkyl radical will therefore be expected in both phases.

In gas-phase oxidation, the reaction of alkyl radicals with oxygen can be either additive, forming alkylperoxy radicals, or abstractive, forming the conjugate alkene. The abstractive reaction requires a high activation energy and therefore usually occurs only at higher temperatures. Thus at low temperatures (ca. 373 K) in both phases the main reaction of butyl radicals with oxygen was found to be additive[69,70]. No butenes were detected in either phase, although at higher temperatures in gas-phase oxidation they are known to be the main product[44].

The addition of oxygen to an alkyl radical, reaction reaction (1.3)

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \qquad (1.3)$$

has zero activation energy in the liquid phase[73,74] and, as in the gas phase, is therefore rapid provided that the oxygen concentration is sufficiently large.

1.4.2 Propagation and branching

The important propagating step in liquid-phase oxidation is the abstraction of a hydrogen atom by an alkylperoxy radical to form an alkyl monohydroperoxide.

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (1.5)$$

It has been shown (Section 1.3.3) that there is little conclusive evidence for the formation of alkyl monohydroperoxides in uncatalysed gas-phase combustion. This is partly due to the thermal instability of peroxides at the temperatures involved. In the artificially initiated oxidation of butane and isobutane at 373 K similar yields of the monohydroperoxide were found in both phases[69,70].

A major reaction of alkylperoxy radicals during

gas-phase combustion is their isomerisation and susequent decomposition to yield O-heterocycles or scission products. It has also been postulated[60] that at low temperatures the isomerised alkylperoxy radicals may be further oxidised to form dihydroperoxides which have been found during the combustion of heptane at 570 K[59]. One example of intramolecular hydrogen abstraction in the liquid phase is provided by the work of Rust[75] with dimethylalkanes. 2,4-dimethylpentane and 2,5-dimethylhexane gave high yields of the 2,4- and 2,5-dihydroperoxide, respectively, when oxidised at about 120° C; this has been attributed to the abstraction by tertiary alkylperoxy radicals of the other tertiary hydrogen atom in these radicals, followed by oxidation of the hydroperoxyalkyl radicals so formed. The reaction is energetically feasible, even at low temperatures, on account of the relative positions of the two tertiary hydrogen atoms. In contrast, no evidence for intramolecular hydrogen abstraction was found in the liquid-phase oxidation of 2-methylhexadecane at temperatures up to 500 K[76], suggesting that alkylperoxy radical isomerisation is negligible in the liquid phase except in cases where there is a conveniently situated tertiary hydrogen atom.

More recently, Van Sickle[77] studied the liquid-phase oxidation of 2,4,6-trimethylheptane at 373 K. It was found that the yield of the trihydroperoxide was approximately 80 % with only small amounts of mono- and dihydroperoxide present at any time. The addition of tetralin hydroperoxide, which is a very effective transfer agent for peroxy radicals[78] did not prevent the trihydroperoxide from becoming the main oxidation product, although the relative yields of mono- and dihydroperoxide were

increased. This indicates that, when the original fuel is 1.3 methyl substituted, intramolecular propagation is, in fact, faster than the intermolecular transfer reaction. In a later paper on the liquid-phase oxidation of n-pentane and n-octane[79], only a very small yield of bifunctional compounds was found. As the yields of these compounds were an erratic function of conversion, and the oxidation was artificially initiated, it is not conclusive that intramolecular hydrogen abstraction was occurring with these straight chain hydrocarbons.

Cyclic ethers have been detected in the products of the liquid-phase oxidation of n-dodecane at 473 K[80]. However, the authors suggested that these compounds were more likely to be formed as a result of vapour-phase reactions occurring above the liquid.

1.4.3 Radical-radical reactions

Radical-radical reactions, such as the disproportionation of alkylperoxy radicals, are now believed to be important chain-propagating processes during gas-phase oxidation provided that there is a sufficiently high concentration of radicals[54]. This usually occurs during cool-flame combustion. In liquid-phase oxidation, radical-radical reactions also occur quite readily due the 'cage effect'. They tend, however, to lead to termination.

The self-reaction of alkylperoxy radicals in the gas phase usually gives rise to alkoxy radicals which then decompose by C-C bond fission to yield products containing a smaller number of carbon atoms than the original fuel molecule. However, in the liquid phase, the disproportionation of alkylperoxy radicals leads either to dialkylperoxides or to products with the

same carbon skeleton as the original fuel molecule:

$$2RO_2^{\bullet} \rightarrow \underset{\text{cage}}{[ROO\text{---}OOR]} \nearrow ROOR + O_2 \qquad (1.45)$$

$$\underset{\text{cage}}{[ROO\text{---}OOR]} \searrow ROH + R{=}O + O_2 \qquad (1.46)$$

1.5 The present work

The preceding discussion has shown that there is general agreement about many aspects of hydrocarbon oxidation. However, it is apparent that the main theories for the mechanism of hydrocarbon combustion have been proposed on the basis of results obtained with relatively low molecular weight hydrocarbons, i.e. those containing up to eight carbon atoms. It is intended, therefore to study the oxidation of a higher molecular weight hydrocarbon, namely decane, which is also of technological importance as it is a constituent of many practical liquid fuels.

Previous studies of the combustion of decane[82,83] were concerned with the determination of its ignition limits in air and it was shown[82,84] that the results are in good agreement with the predictions of thermal ignition theory. The data obtained made possible the development of a computer model which was used to predict the spontaneous ignition limits of decane under other experimental conditions as well as the behaviour of other alkanes. Predictions of the behaviour of higher molecular weight hydrocarbon fuels assumes, however, that the mechanism of combustion of these compounds is similar to that involved in the case of lighter fuels. In order to determine whether this is so, a more chemically-orientated study of the combustion of decane is required.

The initial stages of the low temperature combustion of decane will be examined, where the reaction rates are relatively low and further reactions of the primary products do not complicate the system. With the advent of new analytical techniques, such as high-pressure liquid chromatography, it is hoped to identify conclusively the peroxidic species present

in the combustion products and thus resolve the controversy surrounding this subject.

It is intended to study the effect of additions of hydrogen bromide to the reaction mixture, as changes in the product distribution produced by the presence of a source of labile hydrogen atoms should aid the elucidation of the combustion mechanism.

High molecular weight additives are often blended with commercial fuels in order to alter their physical properties. A direct 'liquid-injection' apparatus will be developed to examine the effect on the spontaneous ignition limits of three such additives, viz: a biocide, a static dispersant agent and a fuel system icing inhibitor.

Since decane is possibly the lowest member of the alkane series whose uncatalysed oxidation can be studied in both the liquid and the gas phase at similar temperatures, it is also intended to complement the study of its combustion with an investigation of its oxidation in the liquid phase in order to ascertain what effect a change in phase has on the oxidation mechanism.

SECTION 2

EXPERIMENTAL

SECTION 2 EXPERIMENTAL

2.1 Materials

Decane was kindly supplied by the British Petroleum Company and was purified before use by fractional distillation under vacuum with a nitrogen bleed. It was shown by gas chromatography to have a purity greater than 99.9%. Samples of the static dispersant additive, the biocide additive and ethylene glycol monoethylether were provided by the Ministry of Defence.

Oxygen (99.6% pure), 'white spot' nitrogen (at least 99.98% pure) and 'air' - a special gas mixture of 20% oxygen: 80% nitrogen (± 0.05%) - were obtained from cylinders supplied by the British Oxygen Company. The gases were dried before use by passage through a column containing Linde 5A molecular sieve. Hydrogen bromide (99.8% pure) was obtained from B.D.H. and was used without further purification.

1-decyl hydroperoxide was prepared as follows, from decan-1-ol via the methyl sulphonate using the method of Williams and Mosher[85]. 22.9 g (0.20 mole) methyl sulphonyl chloride and 31.6 g (0.20 mole) decan-1-ol were stirred in an ice-bath, while 31.6 g (0.40 mole) of dry pyridine was added at a temperature of 0.5° C over a period of 3½ hr. The stirring was continued for a further 15 min; the reaction mixture was then poured into 125 cm^3 of ice-cold 10% hydrochloric acid and the product was extracted with 75 cm^3 ether. The resulting solution was washed with two 20 cm^3 portions of water followed by one 30 cm^3 portion of saturated sodium bicarbonate solution. The ether solution was dried over anhydrous potassium carbonate and filtered and the ether was removed with a rotary evaporator. The mixture was distilled under reduced pressure to give 1-decyl methane sulphonate. Yield 60%, b.p. 146-148°C at 2.0 mm Hg (reported[85]

yield 68%, b.p. 120-122 °C at 0.5 mm Hg).

$$CH_3SO_2Cl + C_{10}H_{21}OH \xrightarrow[C_5H_5N]{} CH_3SO_3C_{10}H_{21} + HCl$$

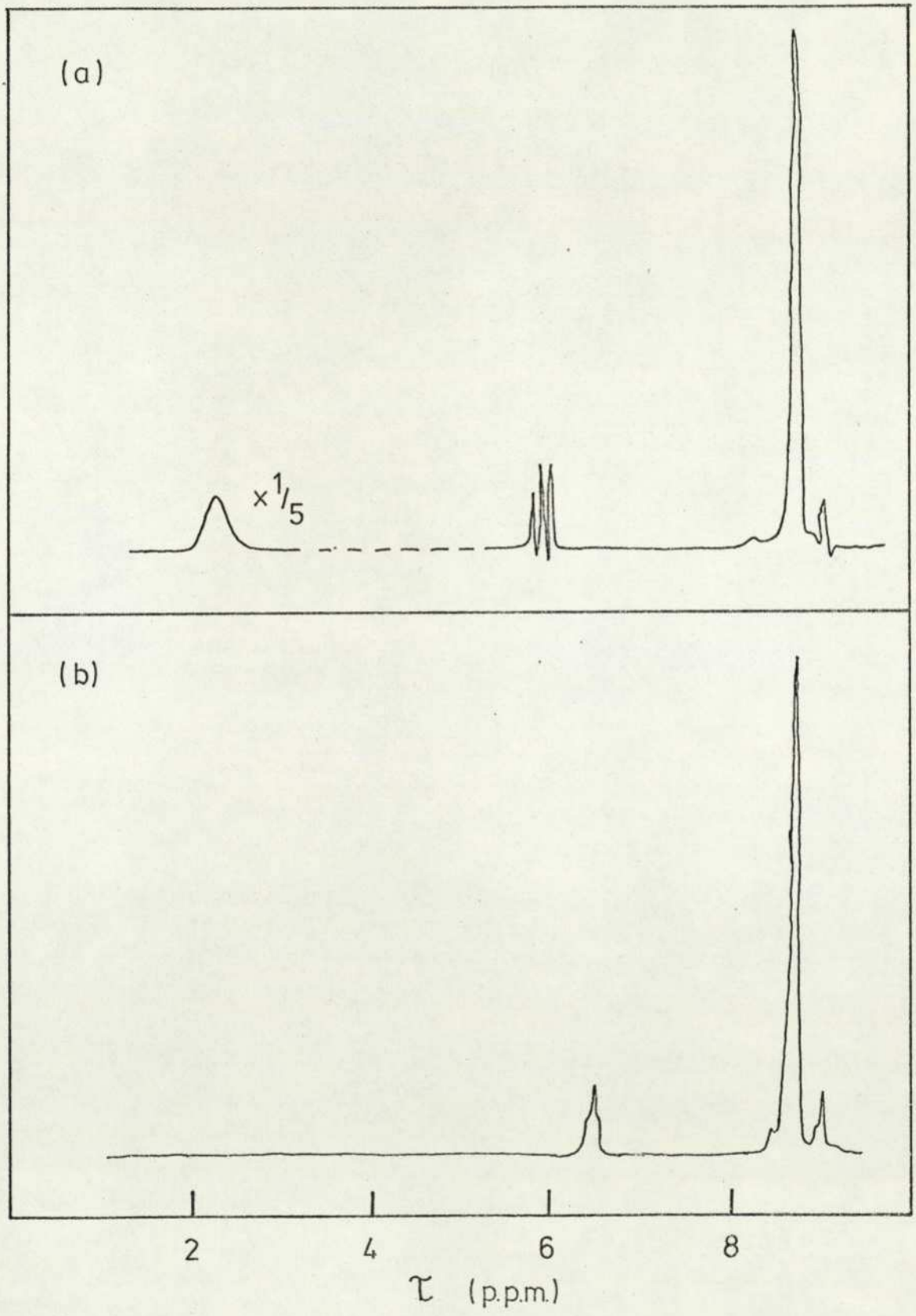
9.45 g (0.040 mole) of the decyl methanesulphonate so prepared was dissolved in 125 cm^3 methanol and 10 cm^3 water. This solution was cooled in an ice bath, while 20.0 g (0.16 mole) of cold 30% hydrogen peroxide, followed by 5 g (0.045 mole) of cold aqueous potassium hydroxide, was added. The mixture was then left, with continuous stirring, in a water bath at 20-25 °C for 44 hr. The reaction mixture was cooled in an ice bath and 15 g of 50% aqueous potassium hydroxide was added; the basic solution was then extracted with three 15 cm^3 portions of hexane. The aqueous layer was cooled in an ice bath and brought to a pH of 7 by addition of concentrated hydrochloric acid. The 1-decyl hydroperoxide was then extracted with three 10 cm^3 portions of benzene. The resulting solution was washed with water, dried over sodium sulphate and the benzene was removed in a rotery evaporator. 1-decyl hydroperoxide was carefully distilled under vacuum in a Kugeluhr apparatus. B.p. 92-94 °C at 1 mm Hg (reported[85] b.p. 61-63 °C at 0.3 mm Hg).

$$CH_3SO_3C_{10}H_{21} + HOOH \xrightarrow[CH_3OH]{KOH} CH_3SO_3H + C_{10}H_{21}OOH$$

In order to check the purity of the hydroperoxide, the nuclear magnetic resonance spectra of both 1-decyl hydroperoxide and decan-1-ol were recorded for a 10% solution in d-chloroform, with tetramethylsilane as internal reference, on a Jeol MH-100 n.m.r. spectrometer operating at 100 MHz. The

Figure 2.1

N.M.R. spectra of (a) 1-decyl hydroperoxide (a) 1-decanol



spectra are shown in figure 2.1 and it can be seen that the hydrogen atoms on the α carbon atom of the hydroperoxide, whose chemical shift, $\tau = 5.92$, were deshielded by ca 0.48 ppm with respect to the same protons of the alcohol ($\tau = 6.40$). Spectra of 5% and 25% solutions of decan-1-ol in d-chloroform were also recorded and these showed that the shift due to the concentration/solvent effect was only 0.08 ppm. The signal due to the -OOH of the hydroperoxide was very broad and was found at low field strengths ($\tau = 2.28$) which reflects the stronger acid character and hydrogen-bonding power of the hydroperoxide. The position of this signal was highly dependent on the concentration of the hydroperoxide. These results agree with those recorded by Burgess et al[86], who found that the protons of the α-carbon atom were deshielded by 0.45 - 0.52 ppm for n-pentyl to n-heptyl hydroperoxides, with respect to the same protons of the corresponding alcohols.

Several attempts were also made to prepare 2-decyl hydroperoxide from decan-2-ol using the method of Williams and Mosher[87]. However, it was found that the 2-decyl methanesulphonate was very unstable and attempts at distillation resulted in its violent decomposition. Hence the mixture of reaction products containing the 2-decyl methanesulphonate was used without prior purification in the second stage of the preparation. After extraction of the reaction products from the second stage, the benzene layer gave a positive result for peroxides using the starch/iodide test and an n.m.r. spectrum showed the presence of a hydroperoxide. The quantity formed was, however, too small for this compound to be successfully isolated.

Other compounds employed in the identification and

calibration of the gas chromatograph were obtained commercially and were used without further purification.

2.2 Apparatus for gas-phase oxidation

2.2.1 The premix system

A standard static vacuum apparatus, in which the fuel and oxidant were premixed, was constructed using Pyrex glass and is shown schematically in figure 2.2. Greaseless PTFE Rotaflo taps were used in the section of the line involved in handling the reactants and products.

Oxygen and nitrogen, introduced into the apparatus through I, were dried by passage through a column of Linde 5A molecular sieve and then condensed and fractionated, using liquid nitrogen cooled traps, TR1 and TR2, before being stored in 5 l globes S1 and S2. These pressures were measured by the mercury manometer M1. Liquid decane was stored under nitrogen in 50 cm^3 flasks, F and F, which were attached to the line using cylindrical joints sealed with Viton rubber O-rings. The flasks could be heated using Isomantles, controlled by Sunvic voltage regulators.

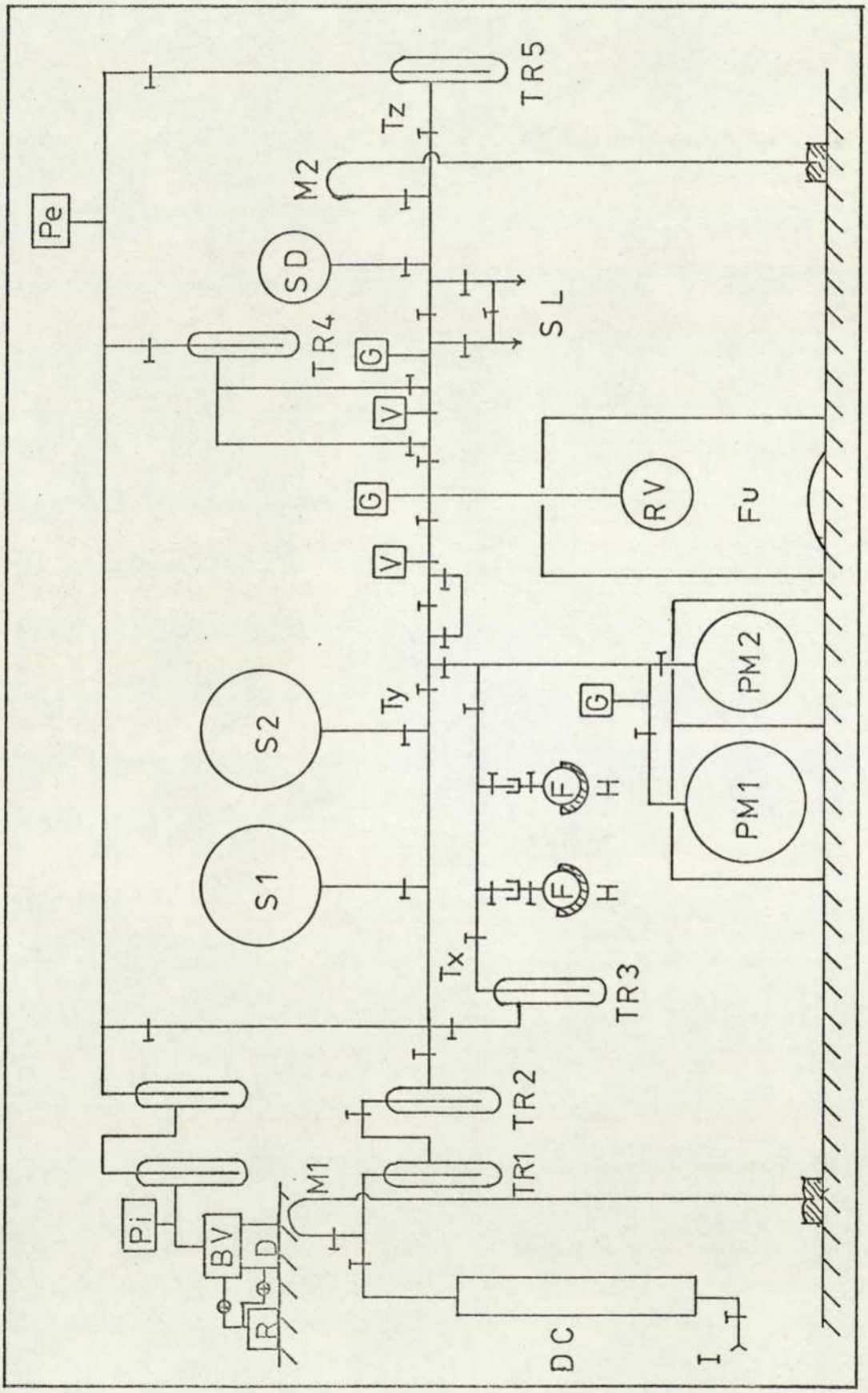
The section of the line between T_x, T_y and T_z, including the premix vessels PM1 and PM2, which were of 5 l and 3 l capacity respectively, was maintained at a temperature of ca 390 K by means of Electrothermal heating tape controlled by Variac voltage regulators. Chromel-alumal thermocouples were used to measure the temperature and to ensure that its distribution was uniform. The premix vessels were covered with glass fibre lagging and then encased in metal boxes as a protection against

Key to figure 2.2

R	Rotary pump
D	Diffusion pump
BV	Baffle valve
I	Gas inlet
DC	Drying column
M1,M2	Mercury manometers
TR1-5	Cold traps
Pi	Pirani guage
Pe	Penning guage
S1,S2	Gas storage globes
F	Fuel storage vessel
H	Heating mantle
PM1,PM2	Premix vessels
RV	Reaction vessel
Fu	Furnace
SD	Sample dump
SL	Sample loop
—T—	'Rotaflo' taps
—⊖—	Edwards high vacuum valves

Figure 2.2

Line diagram of 'premix' system



possible explosion resulting from a 'flash-back' from the reaction vessel. The risk of such a 'flash-back' was reduced by incorporating a flame trap, FT, filled with 2 mm diam. glass beads between the premix vessels and the reaction vessel.

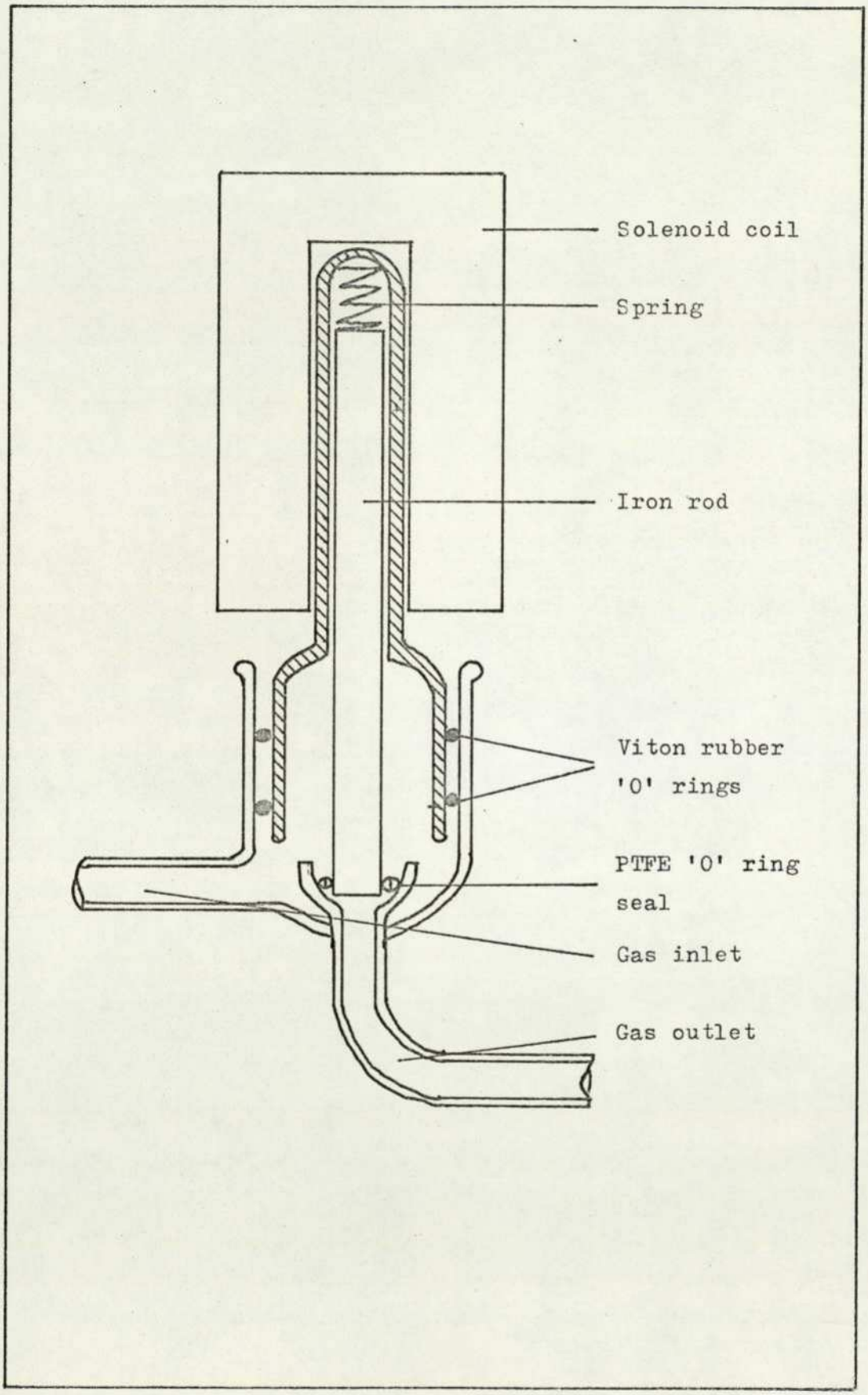
Gas pressures in the premix vessels and in the sample loop were measured using Bell and Howell (type 4-366) 0 - 15 psi pressure transducers. The millivolt output of the transducers was measured using a Croyden type P3 precision potentiometer and was calibrated using M1 and M2.

Reactants were admitted to the reaction vessel through a solenoid-operated valve shown diagrammatically in figure 2.3, and a similar valve was used to sample the reaction products, which were expanded into an evacuated sample loop connected to the gas chromatograph. The opening time of the solenoid valves and the residence time of the reacting mixture in the reaction vessel was controlled electronically using the circuit shown in figure 2.4. This used a Radiospares 555 integrated circuit timer to control a relay which operated the reactant valve and a Radiospares 556 timer which determined the residence time and controlled the relay operating the product valve. An auxiliary resistor-capacitor network RS-CS was needed for each timer, which varied the opening time of the solenoid valves from 0.025 s to 125 s and the residence time from 0.025 s to 40 min. Each timer could be started separately but they were usually interconnected to provide automatic reactant entry, reaction timing and product sampling, the state of each timer being shown by indicator bulbs.

Reactions were performed in a 500 cm^3 spherical Pyrex reaction vessel, RV, which was washed with fuming nitric

Figure 2.3

Diagram of solenoid-operated valve

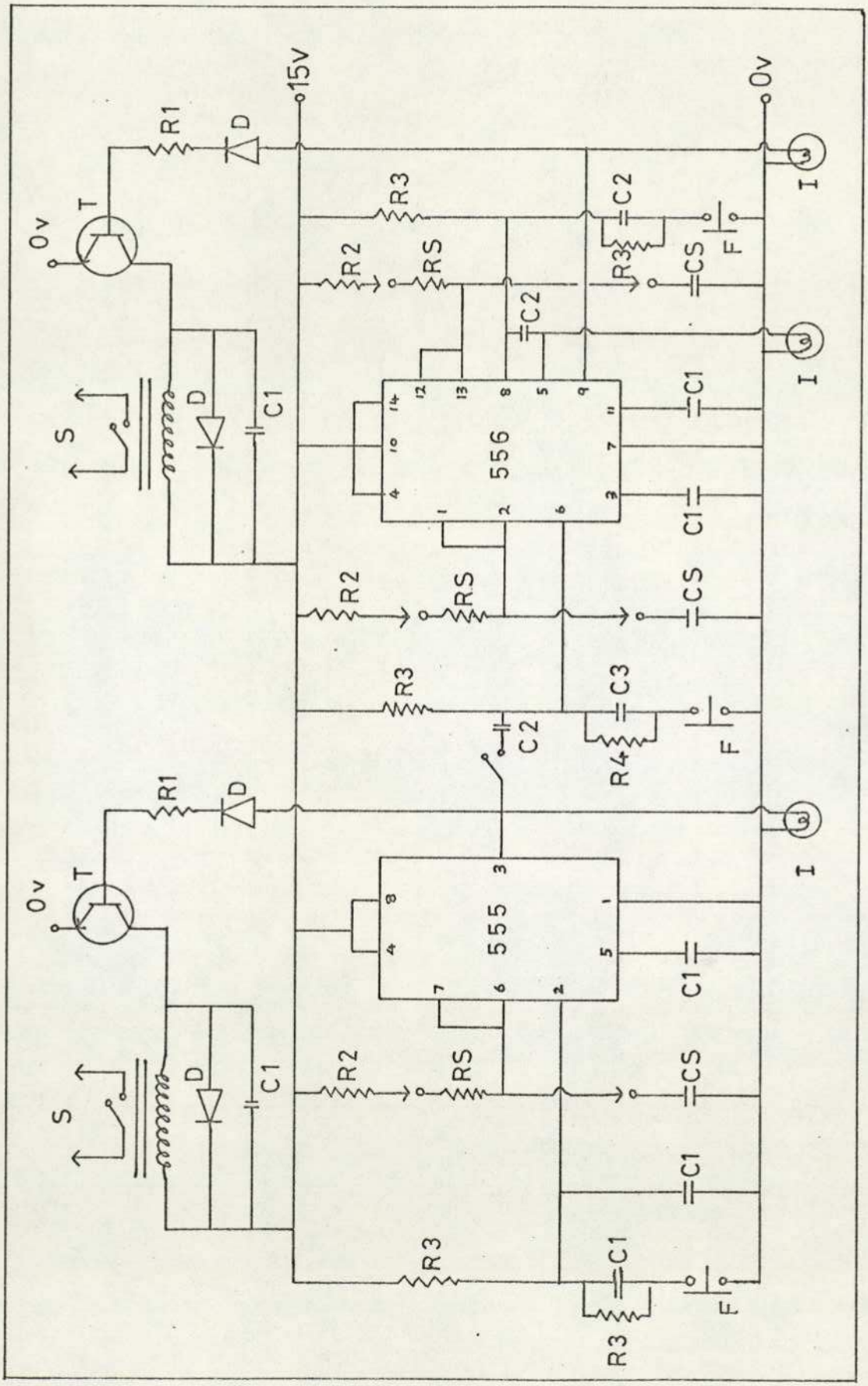


Key to figure 2.4

555	'RS' single timer chip
556	'RS' dual timer chip
S	To solenoid valve
T	BFY 50 transistor
D	IN4002 diode
C1	0.01 MFD capacitor
C2	0.001 MFD capacitor
C3	0.022 MFD capacitor
R1	100Ω resistor
R2	300 kΩ resistor
R3	10 kΩ resistor
R4	15 kΩ resistor
CS	Selected capacitors
RS	Selected resistors
F	Firing switch
I	Indicator bulb

Figure 2.4

Circuit diagram of electronic timer



acid and then with distilled water before use. It was maintained at the required temperature in the uniform temperature region of a vertical tube furnace which was controlled to within $\pm 1^{\circ}$ using an A.E.I. type RT3/R Mk 2 proportional temperature controller and power regulator with temperature feed-back from a 10-ohm platinum resistance thermometer placed next to the reaction vessel.

The system was evacuated by means of an Edwards (type F203 A) oil diffusion-pump, backed by an Edwards Speedivac (type ED50) rotary oil pump; a vacuum of 10^{-4} torr was easily obtained.

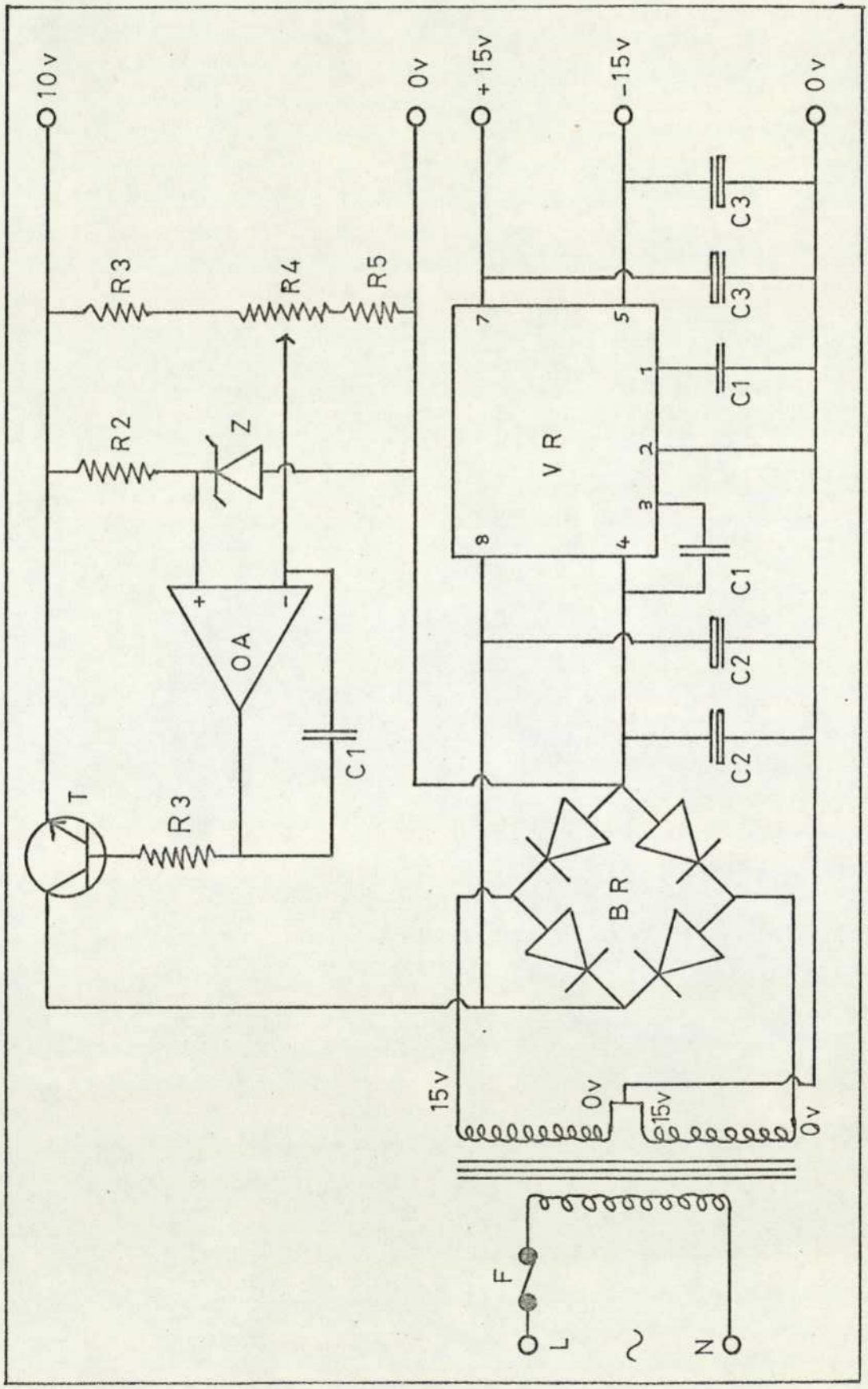
The course of the reaction was followed using a Bell and Howell (type 4-366) transducer, which gave a 0-40 mV output over a 0-50 psi pressure range. The stabilised 10 V d.c. potential required for the excitation of the transducer bridge was provided by the power supply shown in figure 2.5. This power supply also provided the ± 15 V required for the amplifier and was housed in the same cabinet to eliminate noise. Output signals from the pressure transducer were amplified by means of the differential amplifier shown in figure 2.6. This used three Radiospares 741 operational amplifiers with a non-inverting input configuration which gave the desired high-input impedance. This circuit also provided high stability, low noise and the necessary large gain required to drive the matching network. The gain of the amplifier could be altered using the ganged resistors, R_g, and a zero-offset control was provided by the variable resistor, Z. The amplified signal was suitably damped using resistors, R_d, and was subsequently recorded using a Honeywell BB 130A subminiature galvanometer in an ultraviolet oscillograph (Honeywell type 1706 Visicorder).

Key to figure 2.5

T	2N 3053 transistor
OA	'RS' 741 op. amp.
Z	IN 827 zener diode
R1	2.2 kΩ resistor
R2	560Ω resistor
R3	3.3 kΩ resistor
R4	1 kΩ resistor
R5	5.1 kΩ resistor
F	500 mA fuse
BR	'RS' 261-328 silicon bridge rectifier
VR	'RS' 305-636 voltage regulator
C1	0.1 MFD capacitor
C2	1000 MFD 25 v capacitor
C3	10 MFD 25 v capacitor

Figure 2.5

Circuit diagram of power supply

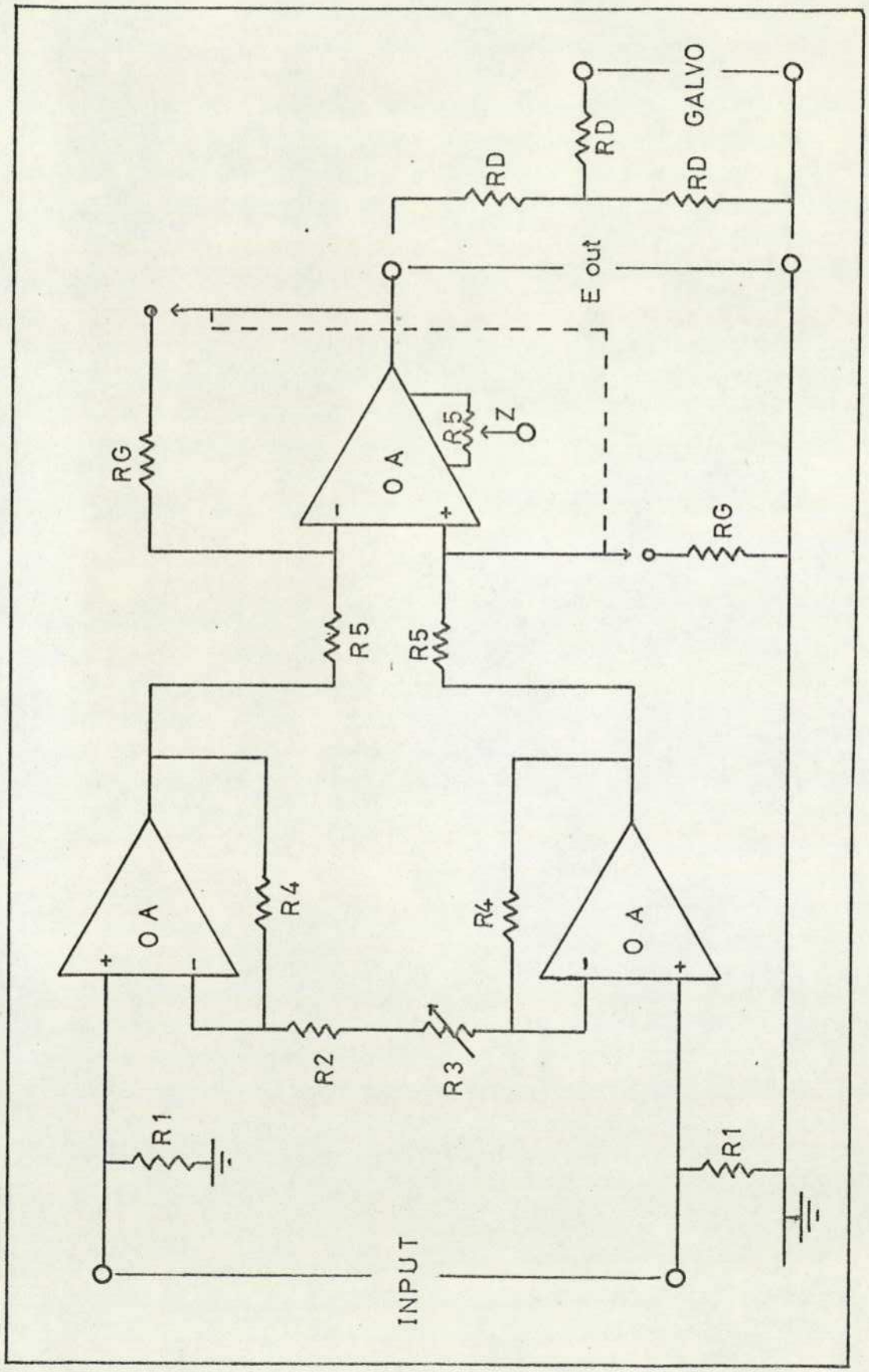


Key to figure 2.6

OA	'RS' 741 op. amp.
R1	1 MΩ resistor
R2	8 kΩ resistor
R3	4 kΩ resistor
R4	47 kΩ resistor
R5	10 kΩ resistor
RG	Selected gain resistor
RD	Damping resistor
Z	Zero offset control

Figure 2.6

Circuit diagram of amplifier



2.2.2 The injection system

An injection apparatus, in which liquid fuel was injected directly into the reaction vessel, was constructed from Pyrex glass and is shown schematically in figure 2.7. Greaseless PTFE Rotaflo taps were used throughout. Air or nitrogen, introduced into the system through I, was dried by passage through a column of Linde 5 A molecular sieve; hydrogen bromide, introduced through I 1, was stored in a 1 l globe. The pressure of these gases was measured by the mercury manometer, M. The section of line between tap T_3 and the cold trap, CT, was maintained at ca 390 K using Electrothermal heating tape, controlled by a Variac voltage regulator.

Reactions were performed in a 500 cm^3 Pyrex vessel, RV, shown in figure 2.8, which was fitted with two side arms; one connected the reaction vessel to the vacuum system with a ball-and-socket joint and the second was fitted with a specially constructed injector which is shown in cross-section in figure 2.9. The body of the injector was machined from stainless steel and was welded to a $\frac{1}{4}$" stainless steel Swagelok fitting; a PTFE ferrule was used and this provided a vacuum-tight seal with the reaction vessel arm. The PTFE-backed silicon rubber injection system was held in place with an aluminium cap, which was provided with fins to aid cooling. Liquid fuel was introduced into the reaction vessel using S.G.E. syringes fitted with 7 cm needles.

The volume of the reaction vessel, side arms and the section of line between T3 and T4 was determined by weighing the amount of Analar acetone required to fill the space at 293 K.

The design of the reaction vessel necessitated the use of a forced-air recirculatory furnace, specially constructed

Key to figure 2.7

VAC	Vacuum pumps
G	Hydrogen bromide storage globe
I	Gas inlet
I1	Hydrogen bromide inlet
M	Mercury manometer
D	Drying column
T	Pressure transducer
RV	Reaction vessel
F	Furnace
CT	Cold trap
RP	Rotary pump
P	Penning guage
Pi	Pirani guage
—<	'Rotaflo' tap

Figure 2.7

Line diagram of injection system

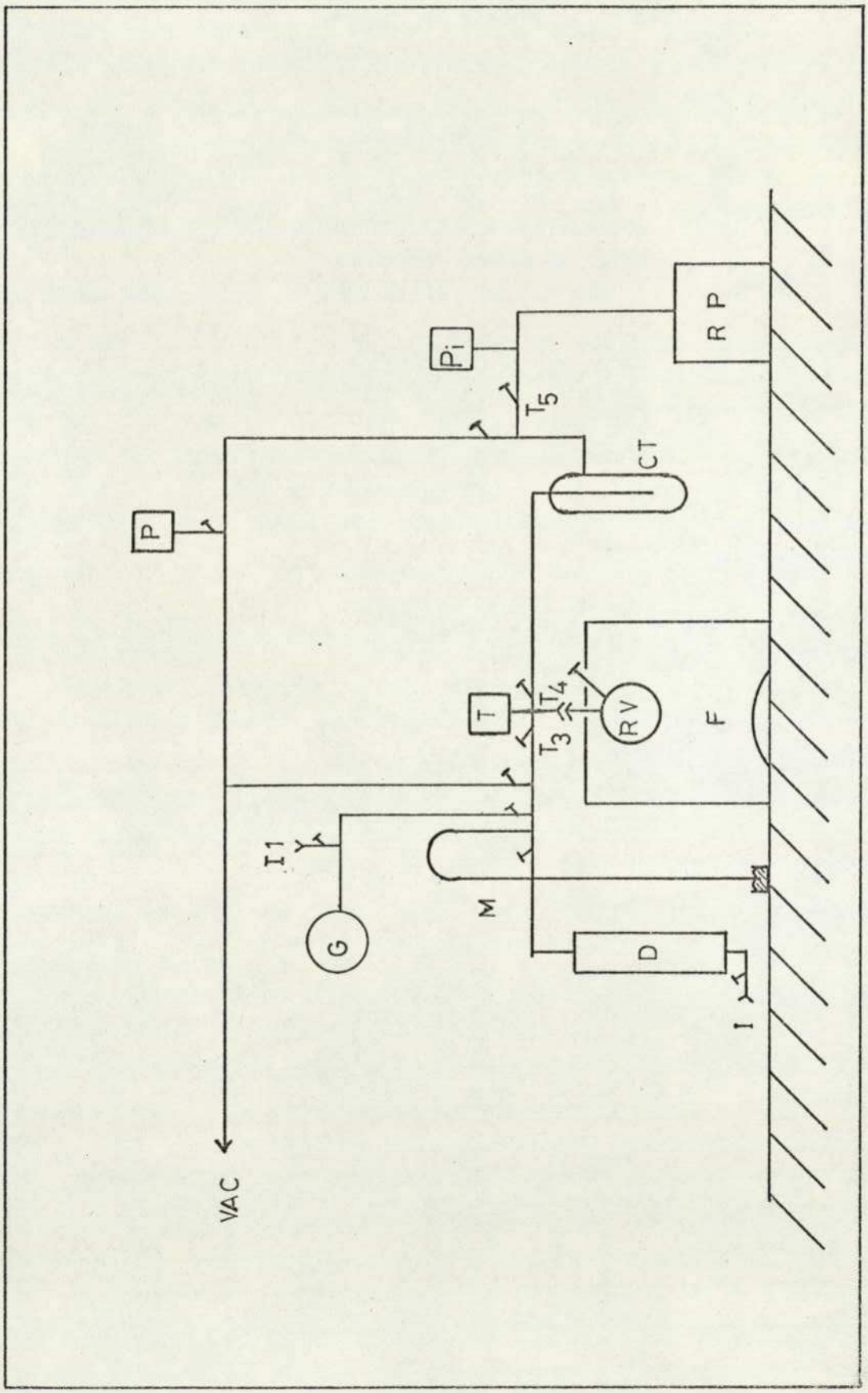


Figure 2.8

Diagram of injection reaction vessel

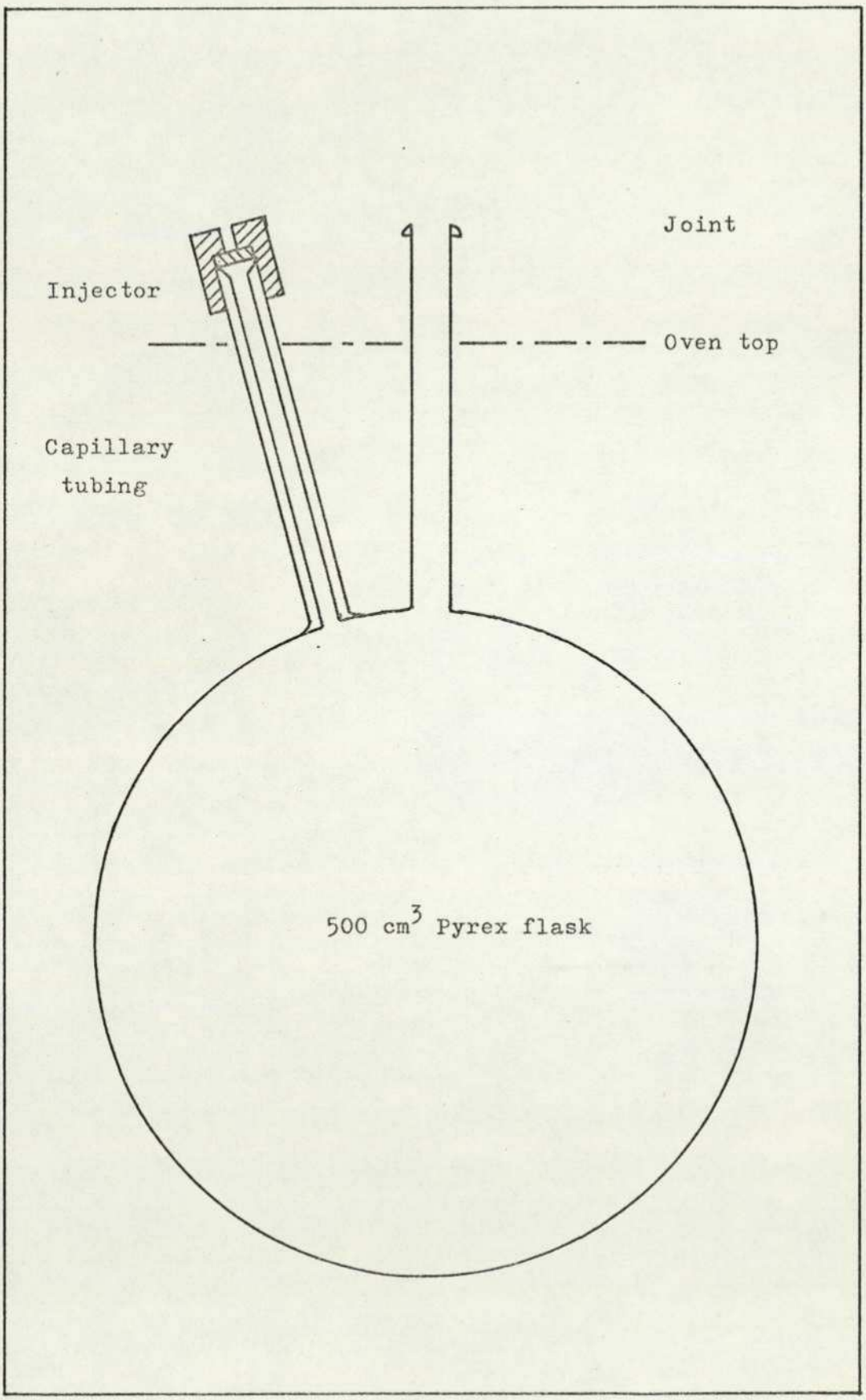
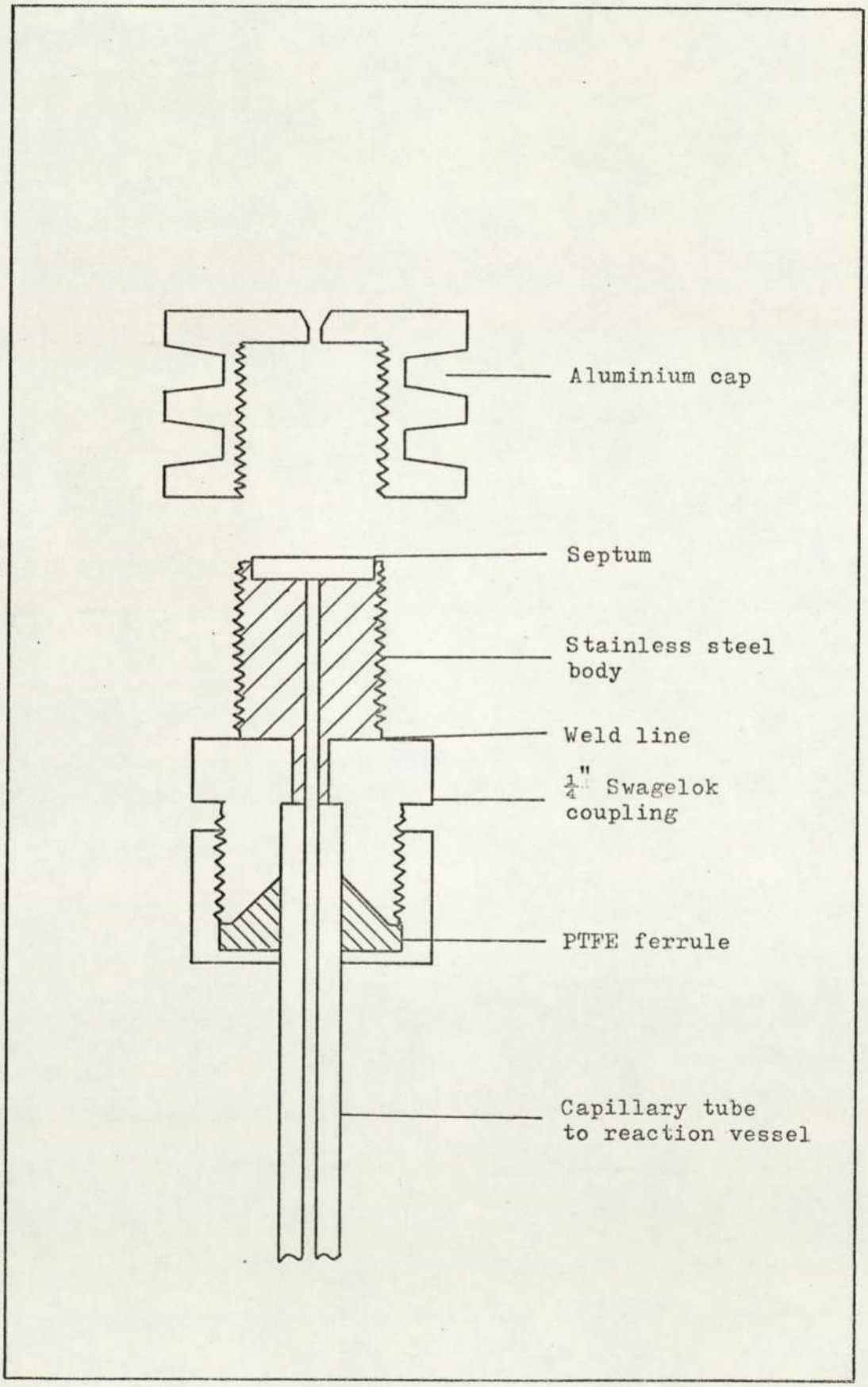


Figure 2.9

Diagram of injector



by R.M. Catterson Smith Ltd. A constant temperature was maintained near the top of the furnace, where the reaction vessel was situated, by hot air circulated by an electric fan. The temperature of the furnace was controlled to within $\pm 2^{\circ}$ using the same apparatus as in the premix system.

A vacuum of 10^{-4} torr was easily obtained in the apparatus using the same pumps as in the premix system but, to prevent contamination of the diffusion pump oil, the reaction vessel was first evacuated to 10^{-1} torr via CT and T5 using an Edwards (type EDM2) rotary oil pump.

The pressure transducer and amplification system used to follow the course of reactions was the same as that used in the premix system.

2.2.3 The metal-free system

In order to determine whether hydroperoxides are present in the low temperature oxidation products of decane, the apparatus shown schematically in figure 2.10 was constructed. In this system the presence of metal, which would catalytically decompose any hydroperoxide formed, has been eliminated.

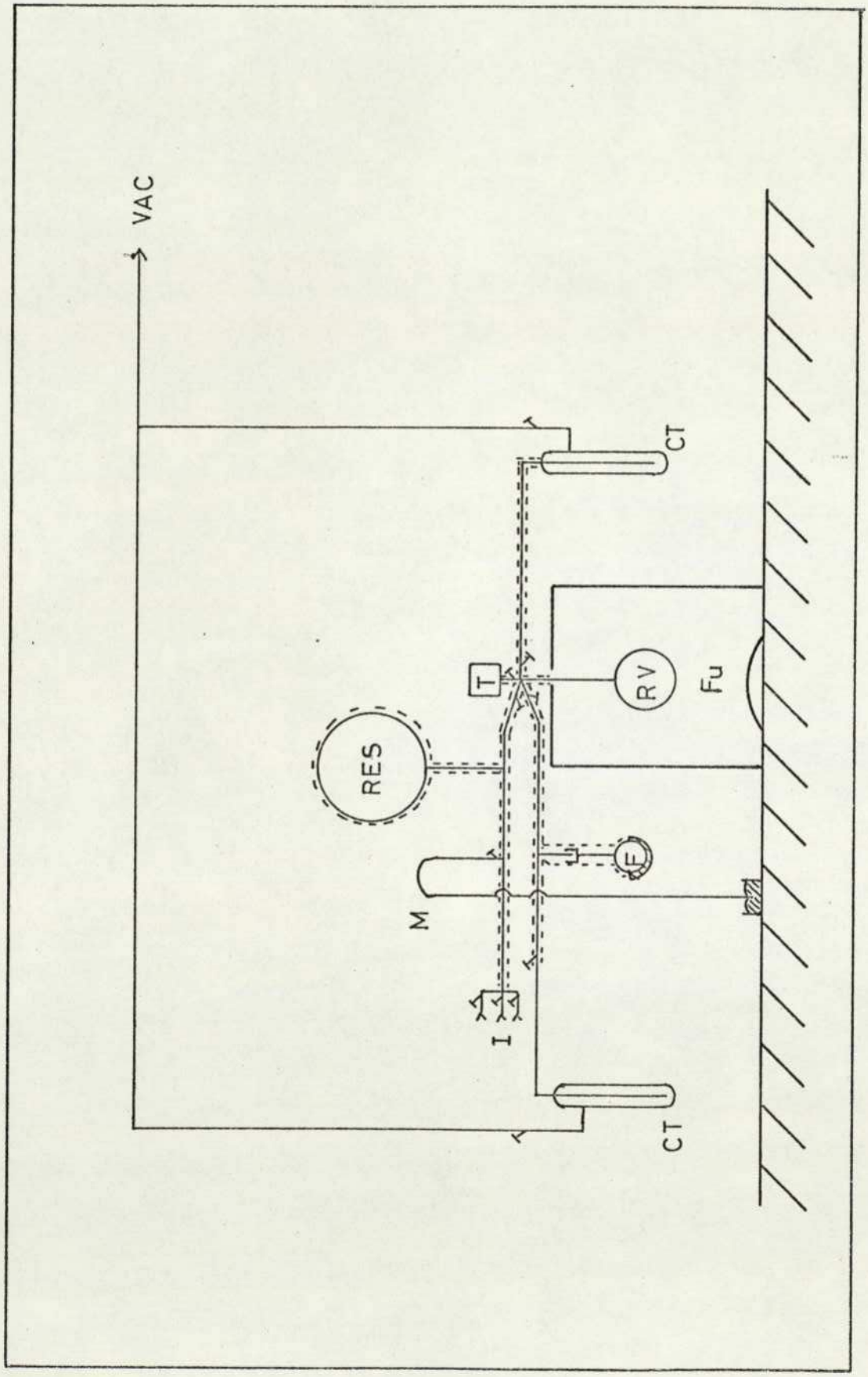
The apparatus was constructed using Pyrex glass and PTFE Rotaflo taps. Liquid decane was stored in a 50 cm^3 flask which could be heated with an Isomantle. Oxygen and nitrogen, admitted to the system via I, were dried by passage through a column of Linde 5A molecular sieve. Mixtures of these gases, prepared using the mercury manometer, M, were subsequently stored in a 3 l gas reservoir which, with the section of line involved in handling the reactants and products, was maintained at 390 K. Reaction mixtures were prepared directly in the 500 cm^3

Key to figure 2.10

VAC	Vacuum system
CT	Cold trap
I	Gas inlet
RES	Gas reservoir
M	Mercury manometer
F	Fuel storage vessel
T	Pressure transducer
RV	Reaction vessel
Fu	Furnace
—›—	'Rotaflo' tap
≠≠≠≠	Heated line

Figure 2.10

Line diagram of 'metal-free' system



Pyrex reaction vessel using a Bell and Howell (type 4-366) 0-25 psi pressure transducer.

The vertical tube furnace and pumping apparatus were the same as used in the premix system and a vacuum of 10^{-4} torr was readily attained.

2.3 Apparatus for liquid-phase oxidation

A line diagram of the apparatus used for liquid-phase oxidations is shown in figure 2.11.

Oxygen, dried by molecular sieve, was regulated using a Glass Precision Engineering (type R51) flowmeter. The flow of oxygen passed into the reactor, which was constructed from a Pyrex tube of length 11 cm, plugged at the bottom by a Youngs (grade 4 porosity) sintered disc. The total internal volume of the reactor was 9 cm^3. The reactor was maintained at the required temperature in a paraffin oil-bath, which was heated and controlled to within $\pm 1^{\circ}$ using a Gallenkamp heating mantle and stirrer.

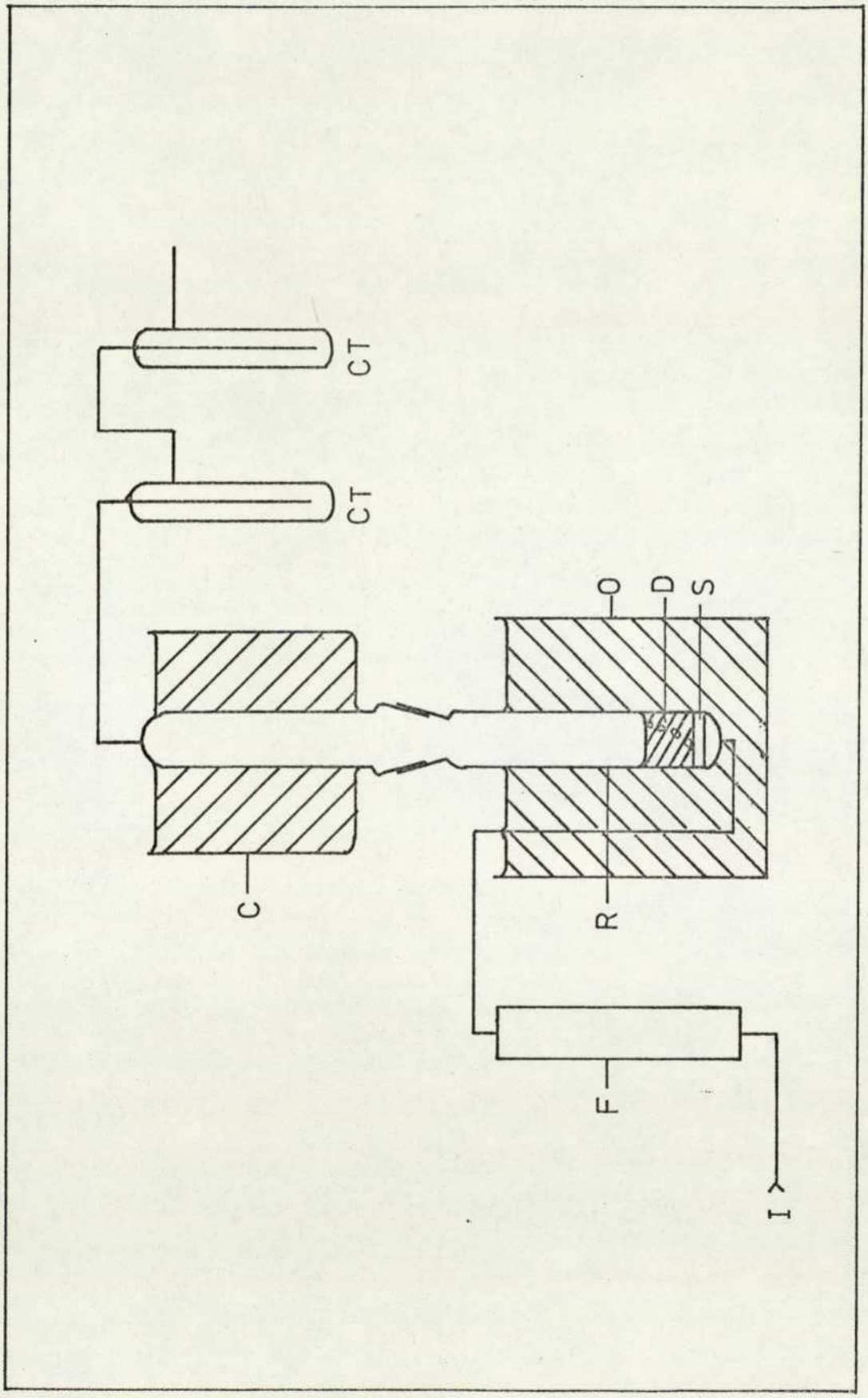
To prevent excessive loss of heat from the reactor, a special condenser was constucted from Pyrex glass which was maintained at ca 235 K by adding solid CO_2 to the acetone surrounding the condenser. This was connected to the top of the reactor with a B10/19 joint using a 'Fi-sleeve' seal. Two cold traps, one cooled by solid CO_2/acetone, the second by liquid nitrogen, were used to trap out any products which were carried through the condenser.

Key to figure 2.11

I	Oxygen inlet
F	Flow meter
R	Reactor
D	Decane
S	Sintered disc
O	Heated oil bath
C	Solid CO_2/acetone condenser
CT	Cold trap

Figure 2.11

Line diagram of apparatus used for liquid-phase oxidation



2.4 General and analytical procedures

2.4.1 Experimental techniques

The output signal from the pressure transducer and ancillary electronic equipment used in the premix and injection systems was calibrated against a mercury manometer using dry nitrogen. Various pressures of nitrogen were admitted to the reaction vessel and the deflection of the Visicorder galvanometer was recorded. This was repeated for each amplification and it was found that the transducer had a linear response from 0 to 100 kPa.

Gaseous reactant mixtures were prepared in the premix vessels and the reaction vessel of the metal-free system on a partial pressure basis. Pressure measurements were made using the 0-25 psi A Bell and Howell (type 4-366) pressure transducers, which were calibrated using dry nitrogen and shown to have a linear response. The output from the transducer was measured with a Croydon (type P3) precision potentiometer, which was accurate to 0.0025 mV corresponding to a pressure of 0.01 kPa. Decane, previously degassed by successive freeze-thaw operations, was first admitted to the vessel from the fuel storage flask. The required pressure of oxygen and nitrogen was then added from the gas storage globes. In the metal-free system, the required ratio of oxygen to nitrogen was first prepared and stored in the heated gas reservoir before being added to the decane. Preparation of the reaction mixture was therefore accomplished within 10 s after which the tap to the pressure transducer was closed.

In the injection system, reactant mixtures were prepared by admitting the desired pressure of 'air', measured by

the manometer, into the reaction vessel. T3 and T4 were then closed and the required volume of fuel was rapidly injected into the reaction vessel with a microsyringe, whose needle tip just protruded into the reaction vessel.

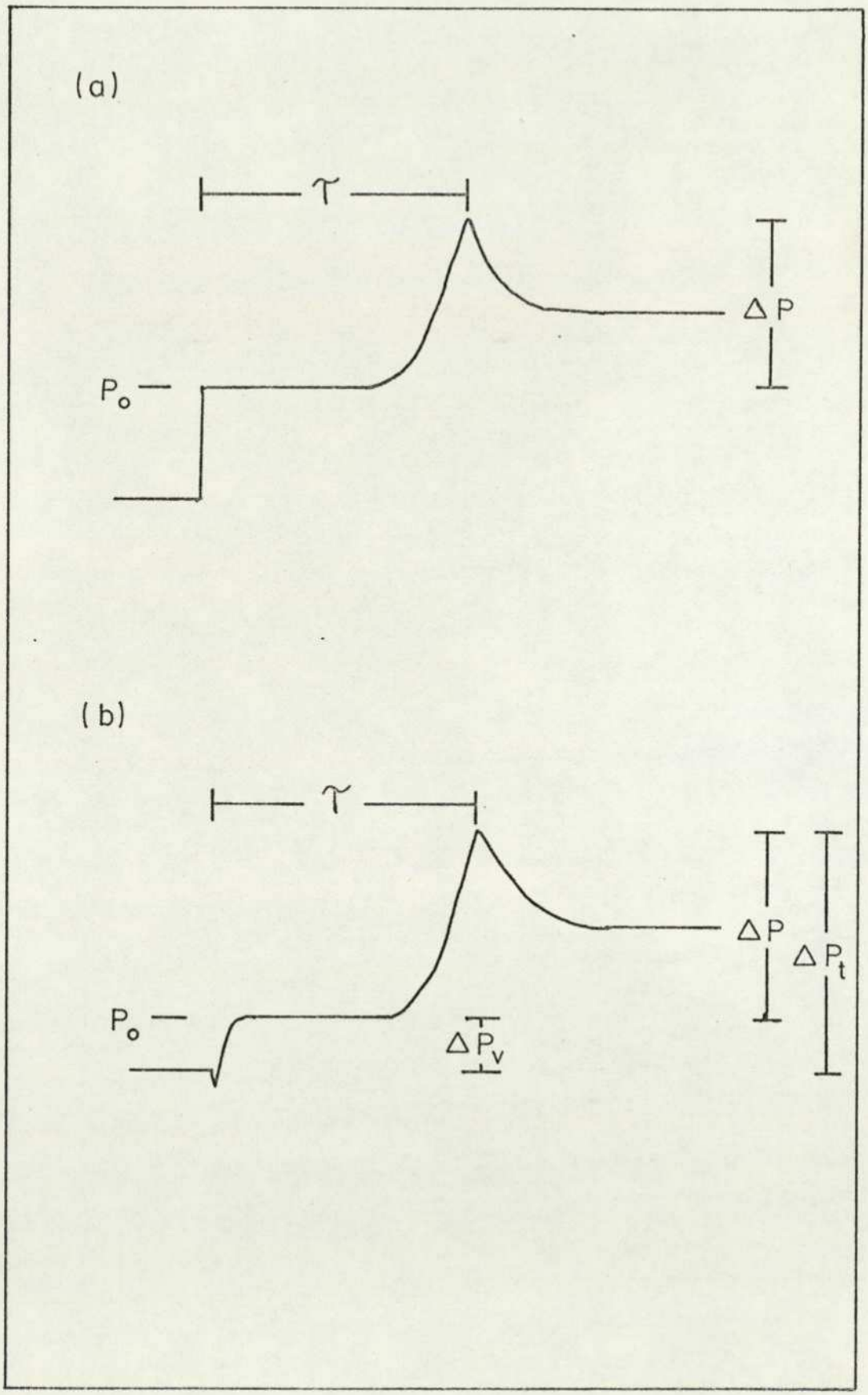
The reaction vessels used in the premix and injection systems were conditioned by performing ca 50 cool-flame and two-stage ignition reactions, using decane as the fuel, to produce a reproducible surface. After this conditioning, the induction period preceding a cool flame varied by less than 5% for consecutive reactions performed under the same initial conditions of temperature, pressure and fuel-air ratio. In order to obtain reproducible results, it was found necessary to pump out the reaction vessel for at least eight minutes between runs.

Typical pressure-time traces, obtained from the Visicorder for cool-flame reactions in both the premix and ignition systems, are shown in figure 2.12. The induction period, τ, of the cool flame was taken as the time elapsing between either the introduction of reactants into the reaction vessel or injection of the fuel into the reaction vessel and the attainment of the maximum pressure rise, ΔP. In the premix system, the initial pressure, P_o, was measured from the zero line which was taken as the transducer output with an evacuated reaction vessel. However, in the injection system, the initial pressure was previously known and, when cool flames with short induction periods occurred, the pressure rise, ΔP, could be calculated from ΔP_t minus ΔP_v, where ΔP_v was the pressure rise due to fuel vaporisation.

In the premix system, the reacting gases were sampled using the solenoid valves and timer previously described.

Figure 2.12

Kinetic measurements from pressure-time traces
(a) premix system (b) injection system



The reaction products passed into the sample dump and sample loop, of known volume, which was directly coupled to the gas chromatograph. The pressure of reaction products in the sample loop was measured by the mercury manometer.

The whole of the reacting mixture in the metal-free system was withdrawn and condensed in a cold trap, which was cooled with liquid nitrogen. The trap was then allowed to reach room temperature and samples of the condensate were used for analysis.

In the apparatus for liquid-phase oxidation an oxygen flow rate of 60 cm^3 min^{-1} was passed through the reactor. 5 cm^3 of decane, which was passed through a column of activated silica immediately before being used to remove any polar impurities, was measured into the reactor using a bulb pipette. The condenser and cold traps were fitted and the reactor was placed in the heated paraffin bath. The reaction was arrested, after the required time, by quickly removing the reactor from the oil bath and stopping the flow of oxygen.

2.4.2 Gas chromatography

A Perkin Elmer F.30 gas chromatograph, fitted with dual flame-ionisation detectors, was employed in all the analyses. The output signal from the chromatograph was integrated using a Smiths Industries Venture Mk II integrator coupled with a Servoscribe 1s recorder. One column in the chromatograph was coupled directly to the sample loop of the premix system via a four-port gas-sampling valve. The second column was fitted with a standard injector, which allowed liquid samples to be analysed. After several experiments using different columns it was found

that the best separation of the complex product mixture arising from decane oxidation could be obtained using a 12 m x 3 mm column packed with 15% Carbowax 20M on Chromosorb W. A nitrogen carrier gas flow rate of 10 cm^3 min^{-1} was used with a temperature programme of 5 min at 70 °C followed by a temperature rise of 2 °C min^{-1} to 200 °C. Figure 2.13 shows a typical chromatogram of the gas-phase combustion products, while figure 2.14 shows the effect of the addition of hydrogen bromide on the product distribution. A typical chromatogram of the products of the liquid-phase oxidation of decane is shown in figure 2.15. The products were identified by comparison of their retention times with those of known compounds and where possible their identity was confirmed by mass spectrometry.

2.4.3 Mass spectrometry

The system consisted of a Pye 104 gas chromatograph fitted with a 6 m x ⅛" Carbowax 20M column connected via a membrane separator to a Kratos MS 30 mass spectrometer. The mass spectrometer was coupled to a DS 50L data handling system and was used to confirm the identity of the products. The presence of C_{10} O-heterocyclic compounds was indicated by mass spectra containing a molecular ion of 156 and a correct fragmentation pattern[88,89]. However, in the absence of reference spectra, it was not possible to identify individual C_{10} O-heterocyclic compounds.

The chromatograms of all reaction products contained four significant peaks with retention times greater than 60 min. These were shown, by mass spectroscopy, to contain more than ten carbon atoms and have been listed as termination products.

Key to figures 2.13 and 2.14

a) Pentane

b) Pent-1-ene

c) Hexane

d) Hex-1-ene

e) Acetaldehyde

f) Heptane

g) Hept-1-ene

h) Propanal

i) Propan-2-one

j) Octane

k) Oct-1-ene

l) Butanal

m) Butan-2-one

n) Non-1-ene

o) Pentan-2-one + pentanal

p) Decane

q) Decenes

r) Hexan-2-one + hexanal

s) Heptan-2-one + heptanal

t) C_{10} O-heterocycles

u) Octan-2-one + octanal

v) Nonan-2-one

w) Decan-5-one + decan-4-one

x) Decan-3-one + decan-3-ol

y) Decan-2-one

z) Decanal

1) Decan-4-ol

2) Decan-5-ol

3) Decan-2-ol

Figure 2.13

Typical chromatogram of the products of the gas-phase combustion of decane

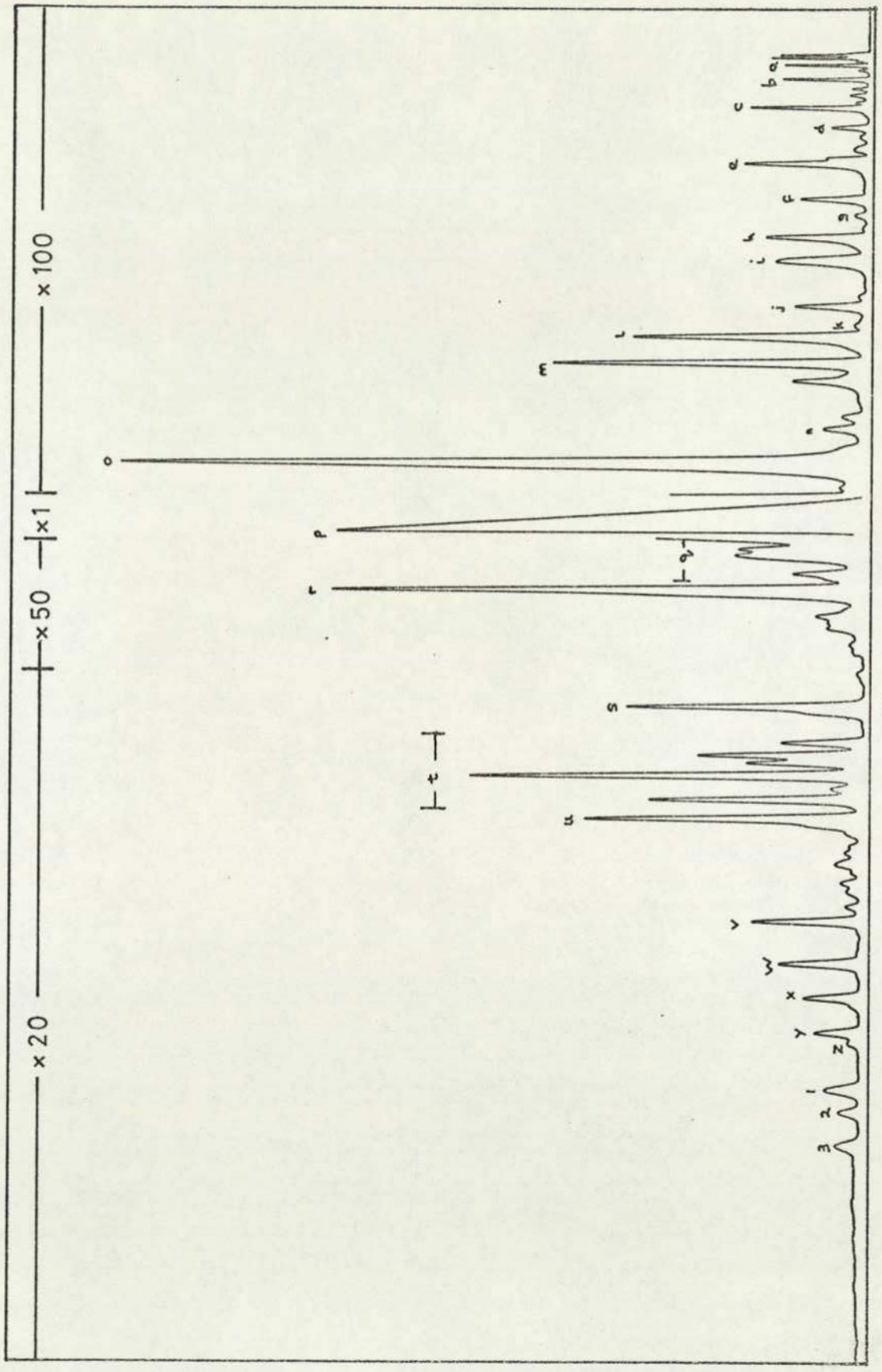
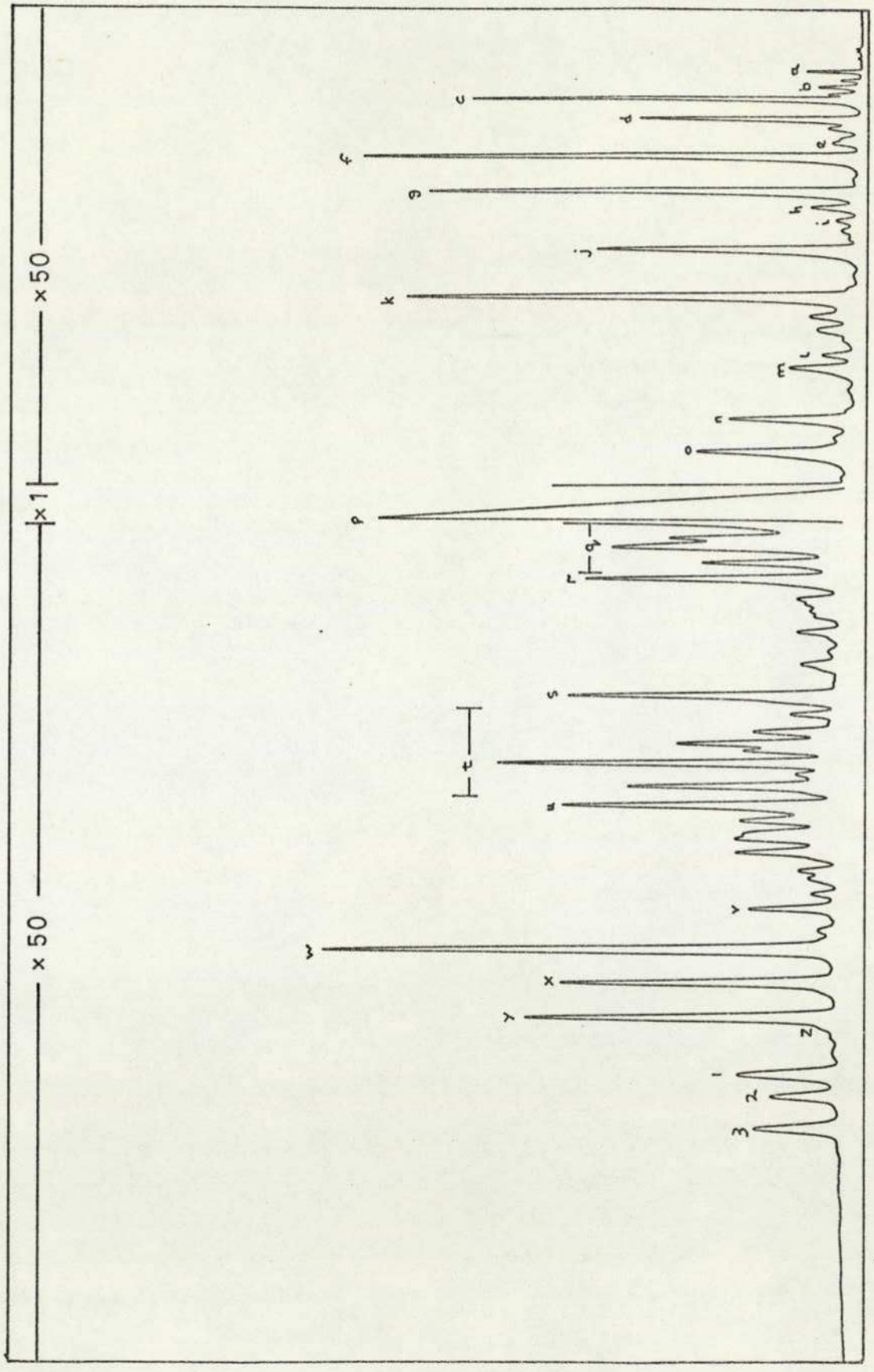


Figure 2.14

Typical chromatogram of the products of the combustion of decane in the presence of hydrogen bromide



Key to figure 2.15

a) Acetaldehyde

b) Propanal

c) Propan-2-one

d) Butanal

e) Butan-2-one

f) Ethanol

g) Pentan-2-one + pentanal

h) Decane

i) Hexan-2-one + hexanal

j) Butan-1-ol

k) Heptan-2-one

l) Heptanal

m) Pentan-1-ol

n) Octan-2-one

o) Octanal

p) Hexan-1-ol

q) Nonan-2-one

r) Nonanal

s) Heptan-1-ol

t) Decan-5-one + decan-4-one

u) Decan-3-one + decan-3-ol

v) Decan-2-one

w) Decanal

x) Octan-1-ol

y) Decan-4-ol

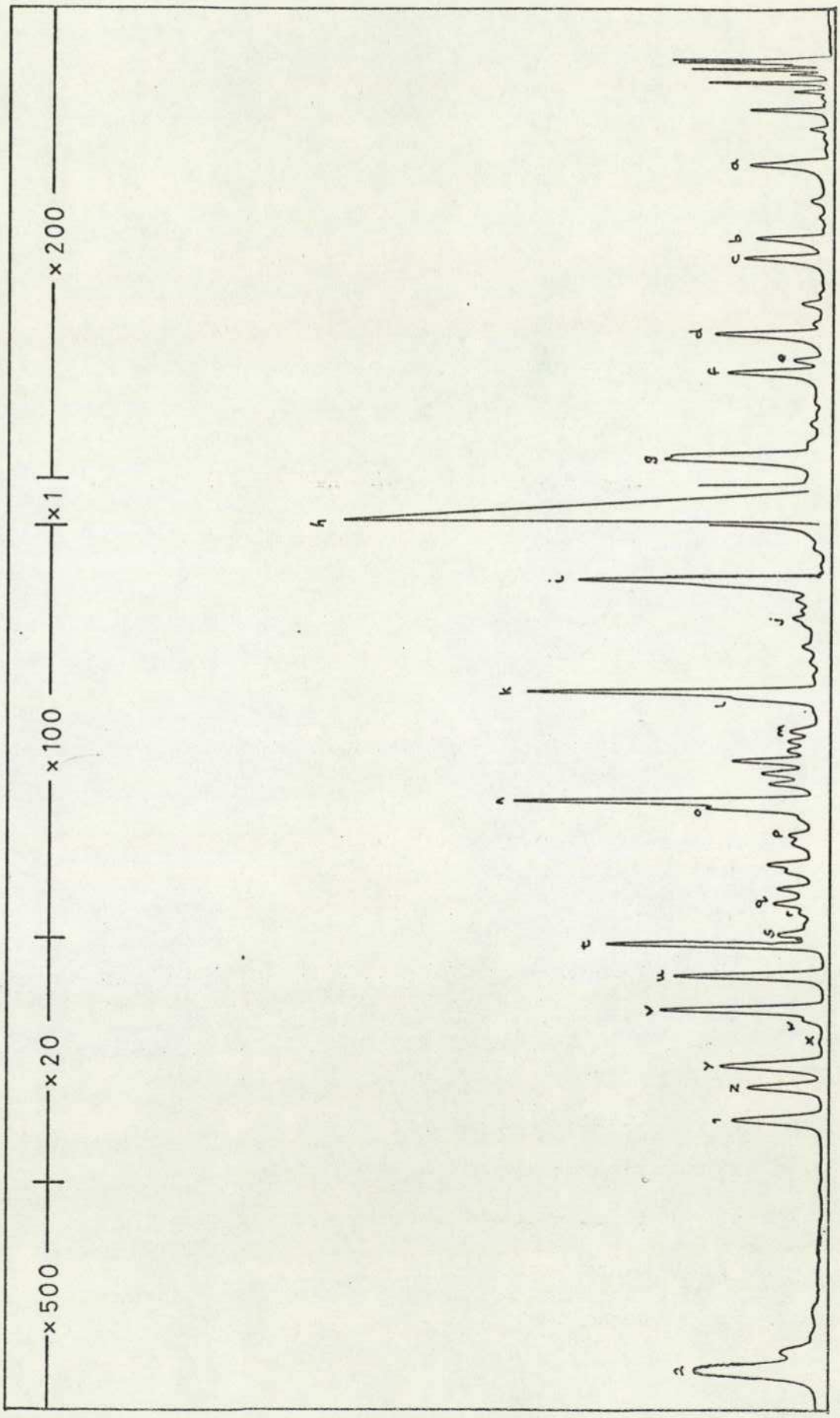
z) Decan-5-ol

1) Decan-2-ol

2) Decan-1-ol

Figure 2.15

Typical chromatogram of the products of the liquid-phase oxidation of decane



2.4.4 Analysis of hydroperoxides

Peroxides were initially identified and determined by the paper chromatographic technique of Cartlidge and Tipper[58]. Whatman No. 3 paper was treated with 20 vol % ethylene glycol in acetone and dried in an air stream. A known quantity of the sample was transferred to the paper with a microsyringe. A descending moving phase of 5 vol % ether in 80-100 ^{o} petroleum ether was used in a tank containing a beaker of the moving phase to saturate the atmosphere. After the front had moved a suitable distance, the paper was removed, dried in a stream of air for one minute and sprayed with ferrous thiocyanate developer which gave blood-red spots immediately where alkyl hydroperoxides were present. The developer was prepared just before use by dissolving ferrous ammonium sulphate (0.7 g) in 10 cm^3 of a solution of ammonium thiocyanate (5 g) and concentrated sulphuric acid (1 cm^3) in water (100 cm^3). An indication of the quantity of decyl hydroperoxides present in samples of the products of decane oxidation was obtained by chromatographic separation of progressively smaller quantities and determination of the stage at which a spot could no longer be detected. It was found in this way that this method could detect 10 μg of 1-decyl hydroperoxide which had a Rf value of 0.85.

On account of the poor accuracy in the quantitative determination of hydroperoxides by the above method, it was decided to investigate the possibility of using high pressure liquid chromatography. Van Tilborg[90] reported the separation of mixtures of C_4 - C_6 alkyl hydroperoxides and also mixtures of alkyl aryl hydroperoxides by reverse-phase gradient elution using acetonitrile and water as solvents with a column of

silanised 10 μm-diam. Merkosorb ST60. Deedler et al[91] used high-pressure liquid chromatography to determine the hydroperoxides formed during the oxidation of cyclohexane. Stainless steel columns (30 cm x 4 mm), filled with 5 μm silica gel powder, were used with a 50% water-saturated mixture of 2,2,4 trimethyl pentane and ethanol (95:5) as the solvent. The column eluent was passed into an on-line packed reactor where the hydroperoxide was allowed to react with sodium iodide in acid solution liberating iodine. The absorbance of the reacting mixture was measured at 362 nm.

Reaction products from the oxidation of decane were therefore analysed using a stainless steel column (45 cm x 4 mm i.d.) filled with 10 μm silica gel powder (Merkosorb SI-60) by a slurry-packing procedure. A Milton-Roy (model 1K) chromatography pump, which was set to deliver solvent at 1 cm^3 min^{-1}, was used with a Cecil Instruments 212 variable wavelength U.V. detector fitted with an 8 μl flow cell. Hexane, ethanol, 2-propanol and terahydrofuran (Fison H.P.L.C. grade) were used as solvents.

The U.V. spectrum of 1-decyl hydroperoxide was measured on a Pye-Unicam SP.800 U.V. spectrophotometer and is shown in figure 2.16. It can be seen that the hydroperoxide has a maximum absorbance at 202 nm. The Cecil U.V. detector was set at 210 nm, it could not be used at lower wavelengths on account of the high background solvent absorbance.

Hexane was used as the base solvent and its polarity was modified by the addition of varying amounts (1 to 5%) of ethanol, 2-propanaol and tetrahydrofuran. It was found that there was no improvement in separation when 50% water-saturated hexane was used as the base solvent. The optimum resolution was

Figure 2.16

U.V. spectrum of 1-decyl hydroperoxide

Concentration: 1 %vol in decane; Reference: decane; Path length 2 mm

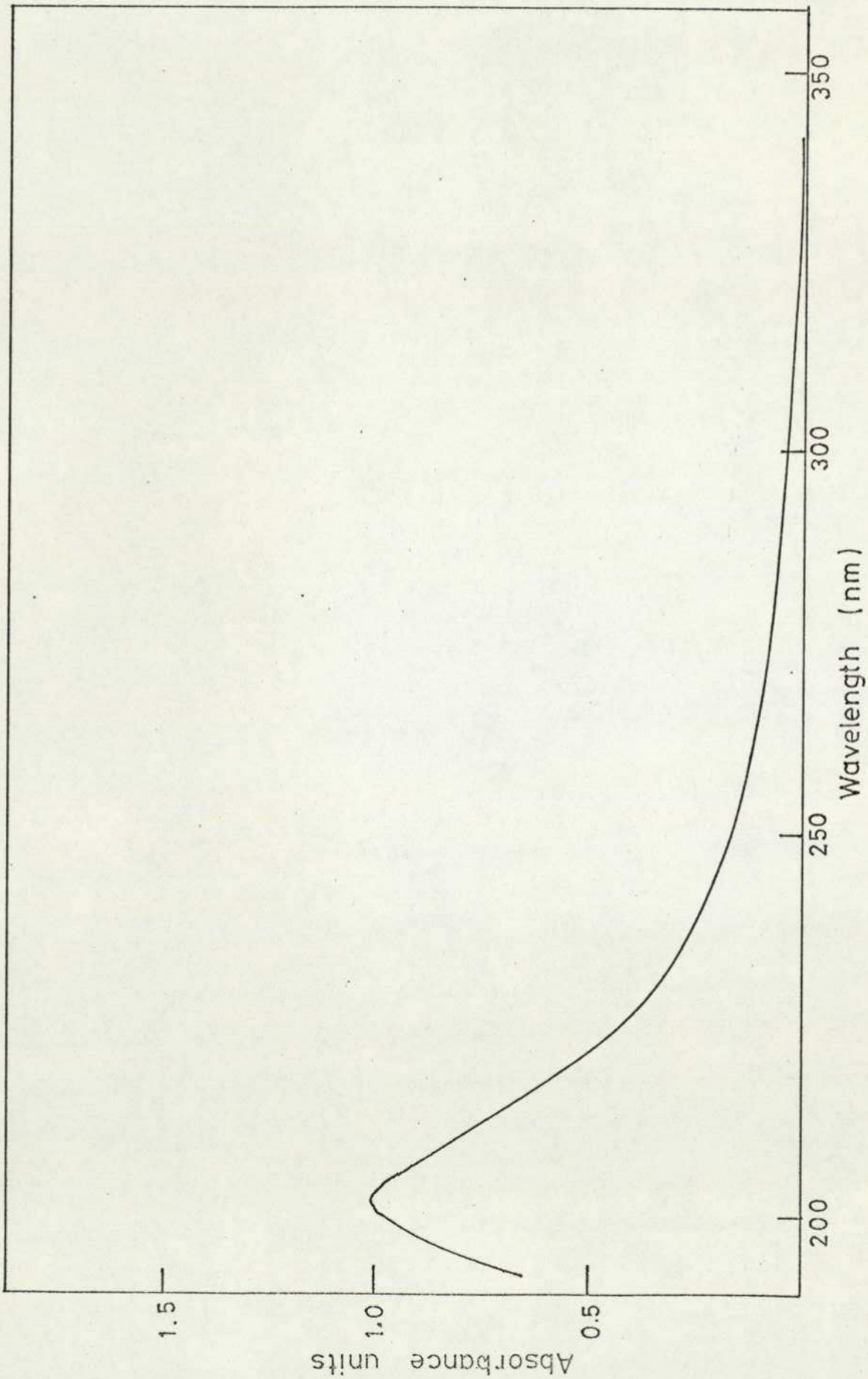
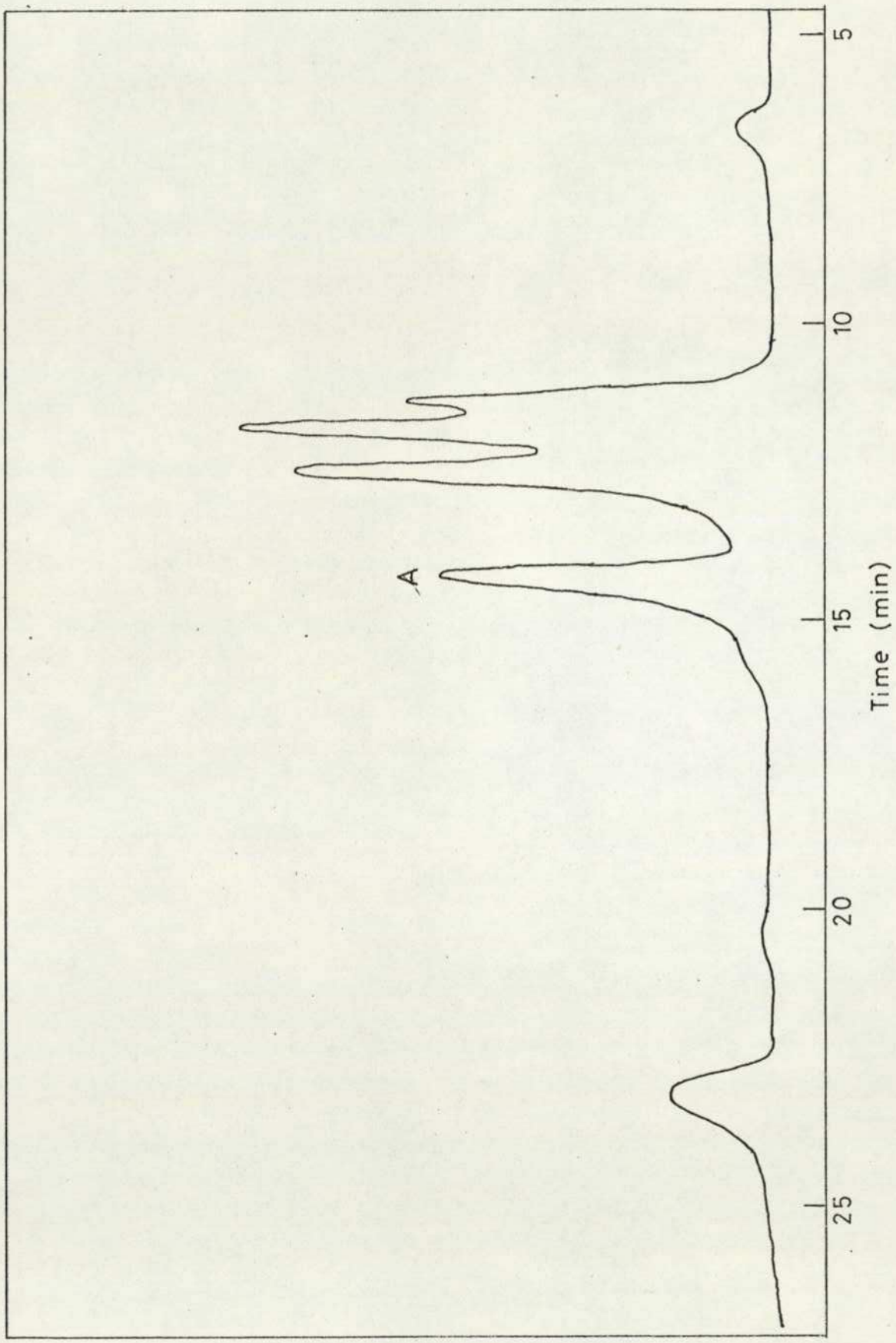


Figure 2.17

High pressure liquid chromatogram of reaction products using detection at 210 nm



obtained with a mixed hexane-ethanol (98:2) solvent. A typical chromatogram of the reaction products is shown in figure 2.17. An injection of a 10% solution of 1-decyl hydroperoxide showed th that its retention time is similar to that of peak A in figure 2.17. The detector eluent was also analysed with the ferrous thiocyanate developer and it was shown that only this peak corresponded to a peroxide.

It was found however that this method of analysis would only detect ca. 100 μg of hydroperoxide. The system was therefore modified to include a post-column reactor as used by Deedler et al[91]. Due to a maximum pressure limitation of 1,000 psi of the Milton Roy pump, a post-column reactor of stainless steel tube (40 cm x 5 mm i.d.) filled with ca. 30 μm glass beads (Phase-sep), was used. Two Waters 600A chromatographic pumps were used to deliver streams of equal flow rate (0.2 cm^3 min^{-1}) of a solution of sodium iodide in 2-propanol (12.5 g l^{-1}) and a mixture of acetic acid and 2-propanol (10:90). These reagent streams were mixed immediately before the post-column reactor on account of the instability of the reagent used for the colorimetric detection of hydroperoxides. The reagent was added to the chromatographic column effluent through 0.1 mm i.d. stainless steel capillary tube and the reactor column was thermostatted at 70 °C. A mixture of 2,2,4 trimethyl pentane and ethanol (95:5), was used as the eluent at a flow rate of 1 cm^3 min^{-1}. The hold-up time in the reactor column was calculated by injection of a solution of nitrobenzene and measurement of its retention time in the system both with and without the reactor present, and was found to be 80 s. The absorbance of the reaction mixture due to the presence of I_3^- ions was continuously

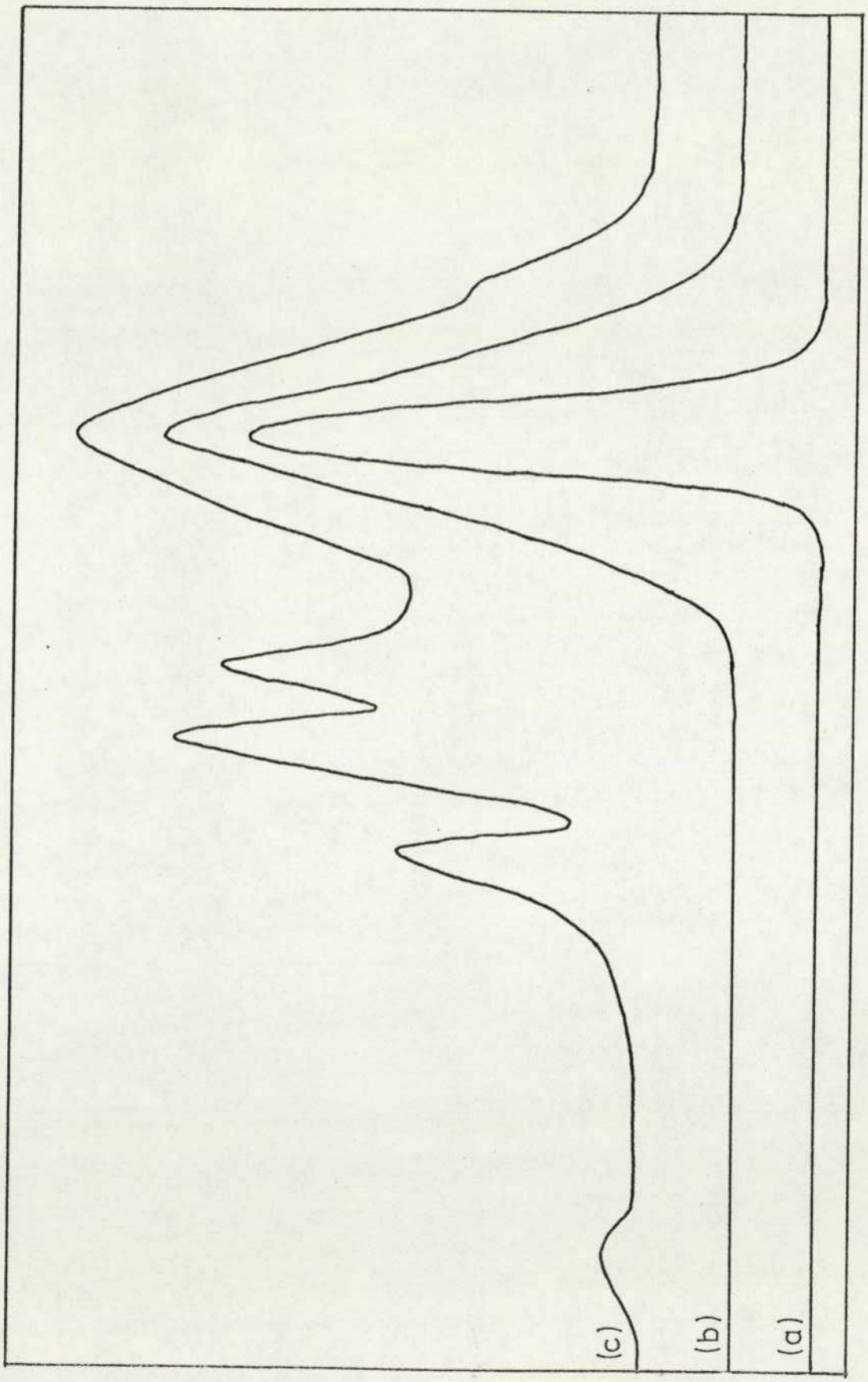
measured at 362 nm using the Cecil U.V. detector.

It was found that this system could detect hydroperoxide concentrations down to 0.1 $\mu g \cdot l^{-1}$ and gave a linear response over the range 0.1 μg to 100 μg. Figure 2.18 shows chromatograms, obtained with this system, of (a) pure 1-decyl monohydroperoxide, (b) liquid-phase reaction products and (c) gas-phase reaction products. It can be seen that only one peak is produced from the liquid-phase reaction products and this has a retention time identical to the standard. In the case of the gas-phase reaction products several partially resolved peaks occur after that corresponding to decyl monohydroperoxide. As this post-column reactor system will only detect peroxides and The separation is produced by a polar column (silica gel), it is reasonable to assume that these peaks represent decane dihydroperoxides. Dihydroperoxides have been shown to be more polar than monohydroperoxides[58,91] and will therefore have a longer retention time.

Figure 2.18

High pressure liquid chromatogram using post-column reactor

a) 1-decyl hydroperoxide b) liquid-phase products c) gas-phase products



SECTION 3

RESULTS

SECTION 3 RESULTS

3.1 Kinetics of the combustion of decane

3.1.1 Premix apparatus results

Reactions were performed in the premix apparatus using a 1:10 decane:air mixture at 523, 533, 573 and 613 K.

Values of the initial pressure, P_o, the pressure rise accompanying the first cool flame, ΔP, and the induction period preceding the first cool flame, τ, were measured from the pressure-time traces.

The variation of the maximum pressure rise accompanying the cool flame has been shown to obey the relationship:[5]

$$\Delta P = A P_o^{\,m} \qquad (3.1)$$

A graph of $\ln \Delta P$ against $\ln P_o$ is shown in figure 3.1 and the value of m, in equation (3.1), was found to vary from 1.3 to 1.7.

Figure 3.2 shows the effect of the initial pressure on the induction period in the temperature range 523 to 573 K. At 613 K the induction period preceding the first cool flame varied between 0.2 and 0,9 s for initial pressures ranging from 16 to 3.5 kPa.

Further studies of the kinetics of the combustion of decane were made using the direct-injection apparatus, which was designed and constructed in order to determine the effect of high molecular weight additives on the ignition characteristics of decane.

3.1.2 Injection apparatus results

The theoretical volumes of decane required to produce the desired fuel:air ratios in the reaction vessel at different temperatures and pressures were calculated from the gas laws

Figure 3.1

Variation of ln ΔP with ln P_o for a 1:10 decane:air mixture

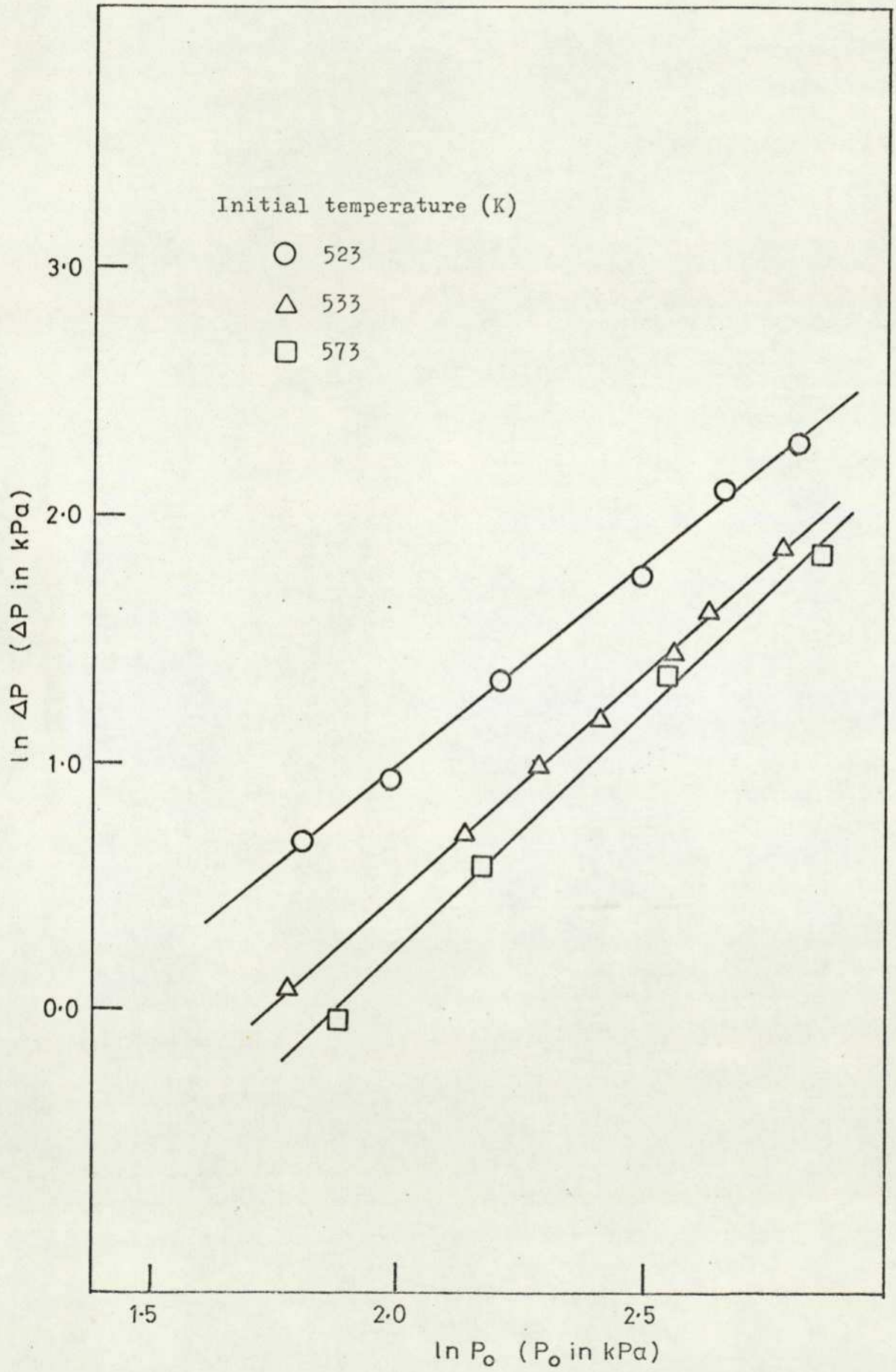
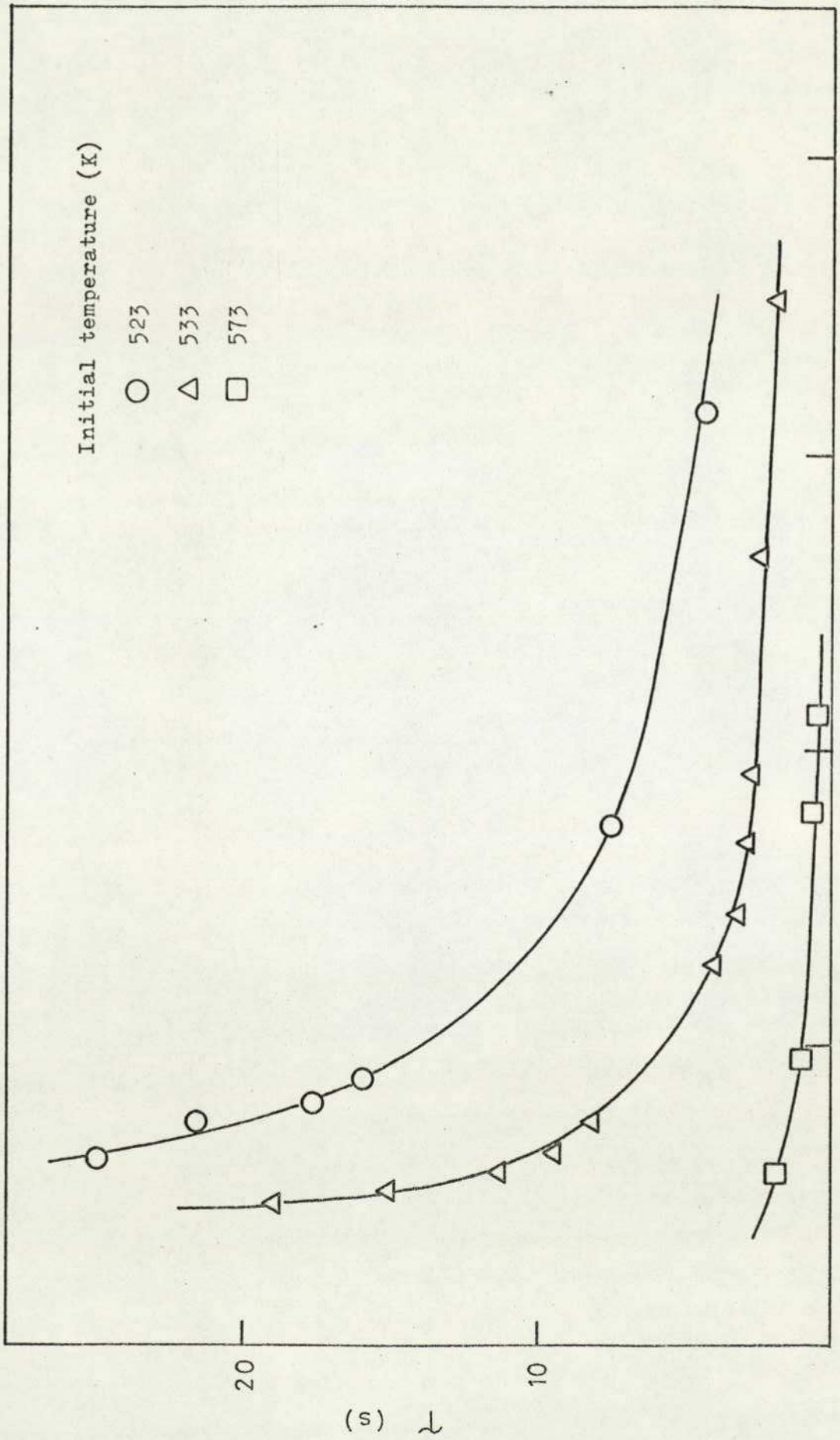


Figure 3.2

Variation of τ with P_o and T_o for a 1:10 decane:air mixture



using a computer program. The calculation was verified and an indication of the vaporisation time was obtained by performing experiments with nitrogen instead of air. These experiments confirmed that the injection of the theoretical volume of liquid decane into an atmosphere of nitrogen produced the expected vapour pressure of decane; they also showed that the time for 95% vaporisation was less than 1 s. It can therefore be assumed that fuel vaporisation is not the rate-determining step, except possibly at the highest temperatures and pressures studied, where the induction period becomes less than 1 s.

Figure 3.3 shows some recorded pressure-time traces obtained at 523 K. Trace (a) shows the injection of fuel into an atmosphere of nitrogen, where the pressure rise is due simply to the vapour pressure of fuel injected. The traces obtained for a typical cool flame and for two-stage ignition are shown in figures 3.3(b) and (c) respectively.

The pressure-time traces shown in figure 3.4 are typical of those obtained at temperatures above 600 K. Trace (a) shows the cool flame observed at low pressures, while traces (b) and (c) represent respectively a cool flame at higher pressures and two-stage ignition. It can be seen that, at these temperatures and at the higher pressures used, the onset of a cool flame or of two-stage ignition may occur before vaporisation of the fuel is complete.

Figure 3.3

Pressure - time traces obtained at 523 K

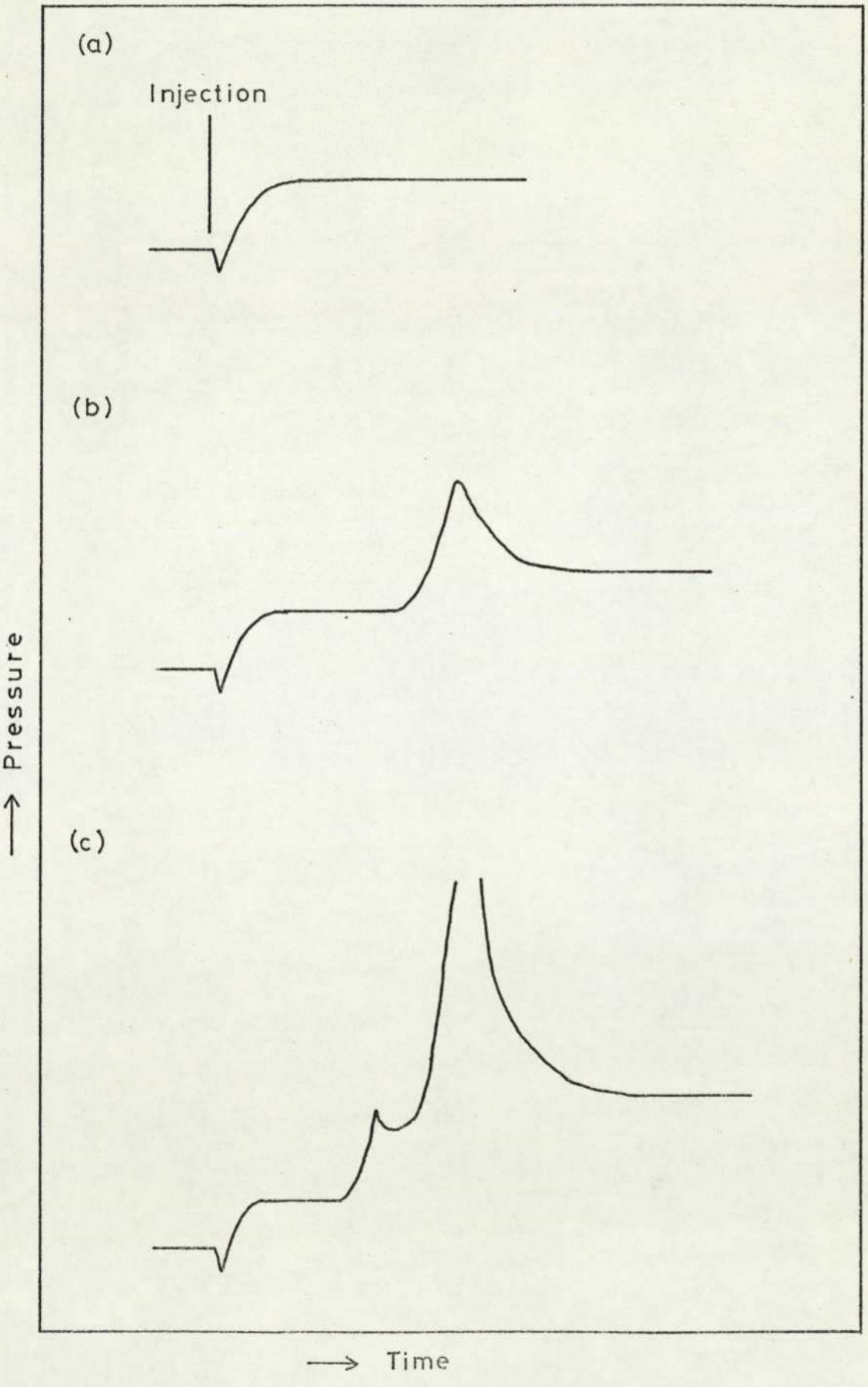
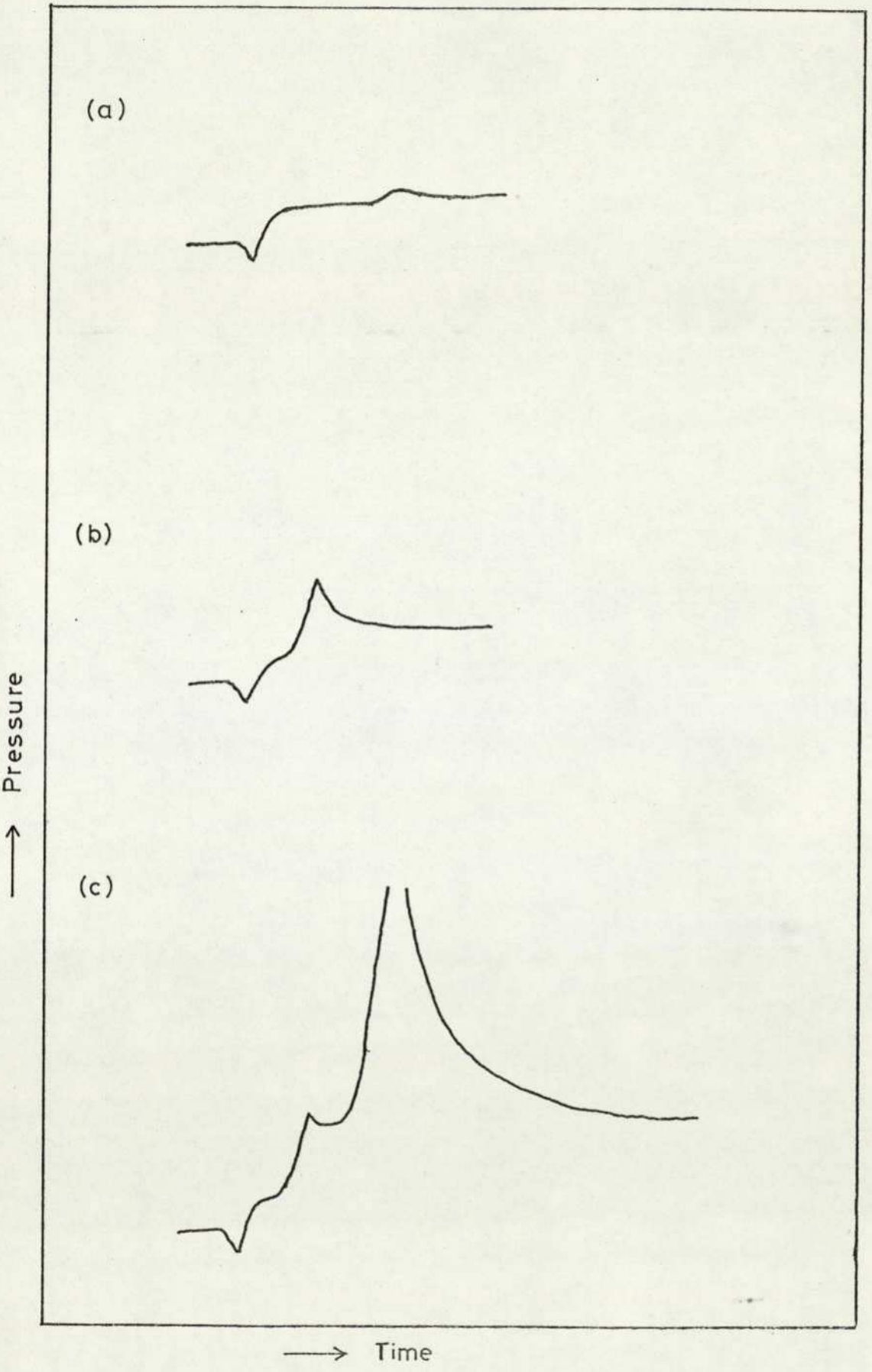


Figure 3.4

Pressure - time traces obtained at temperatures above 600 K



3.1.2.1 Ignition profiles of decane:air mixtures

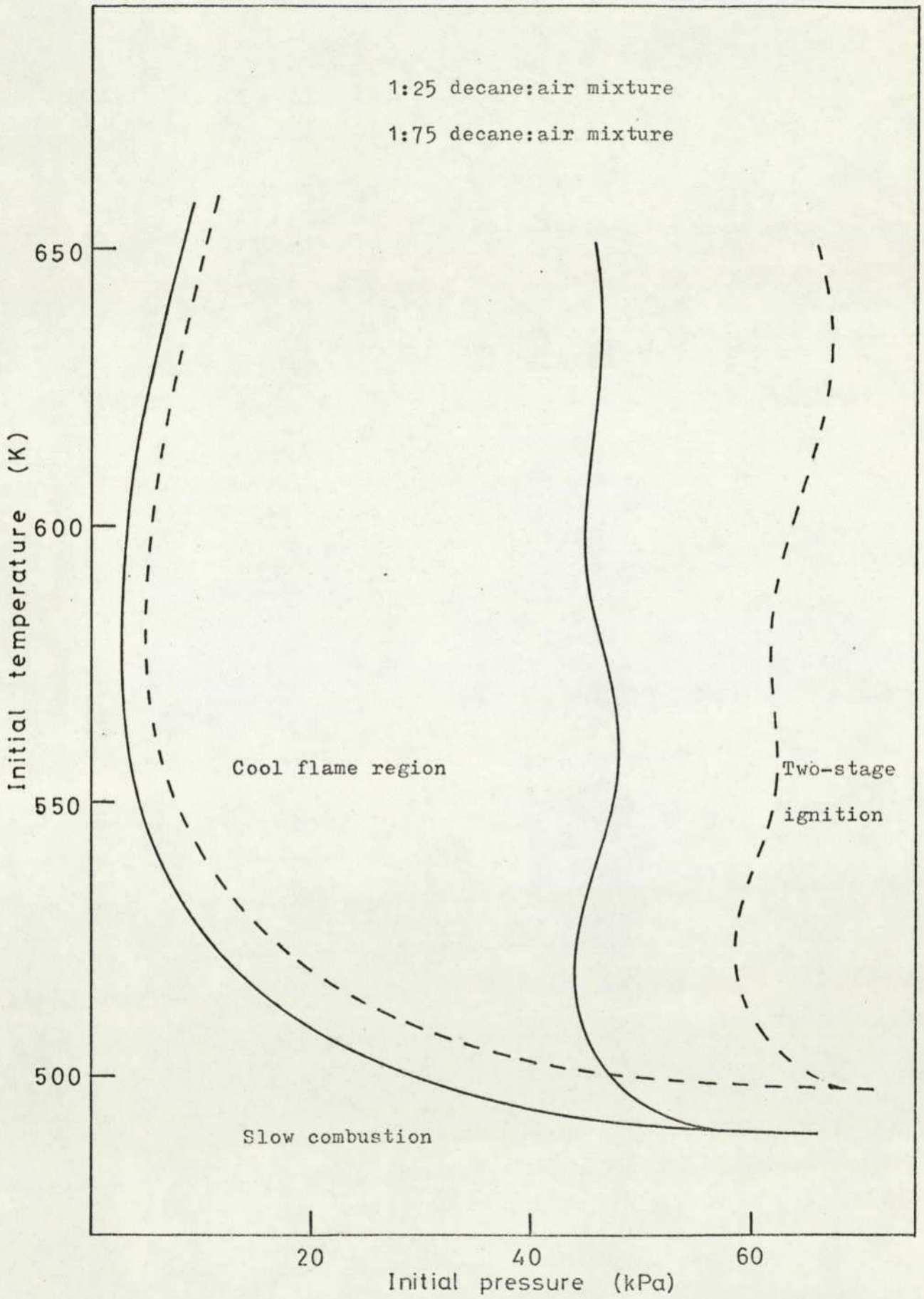
Figure 3.5 shows the ignition profiles for 1:25 and 1:75 decane:air mixtures in the temperature range 480-650 K with initial pressures up to 70 kPa. Reactions were not performed at temperatures above 650 K, because the induction period preceding a cool flame or two-stage ignition was shorter than the time needed for vaporisation of the fuel. It can be seen (figure 3.5) that the ignition diagrams for both mixtures studied have a distinct single cool-flame region, with two-stage ignition occurring at pressures greater than 44 kPa for a 1:25 mixture and greater than 60 kPa for a 1:75 mixture.

The two-stage ignition profile exhibits two lobes which occur at temperatures of ca. 515 and 575 K; these have been called A and B respectively.

No multiple cool-flame region was observed with the 1:75 mixture, while with a decane:air ratio of 1:25 the second pressure pulse was very small and the single cool-flame/multiple cool-flame ignition boundary was ill-defined. The minimum spontaneous ignition temperature for a 1:25 mixture was found to be 490 K, while that for a 1:75 mixture was 498 K; spontaneous ignition occurred at these temperatures when the initial pressures were greater than 60 kPa and 70 kPa respectively. It can be seen that, as the ratio of decane:air is increased, the minimum pressure required for the propagation of a cool flame or for two-stage ignition is also increased.

Figure 3.5

Ignition profiles for 1:25 and 1:75 decane:air mixtures



3.1.2.2 Kinetics of cool-flame reactions

The variation with initial pressure, P_o, of the maximum pressure rise accompanying the cool flame, ΔP, has been shown to obey the relationship:[5]

$$\Delta P = AP_o^{\,m} \qquad (3.1)$$

Figure 3.6 shows the variation of $\ln \Delta P$ with $\ln P_o$ for a 1:25 decane:air mixture at temperatures from 523 to 598 K. In this temperature range the value of the constant, A, in equation 3.1 varies with temperature, whereas m is more or less independent of temperature and varies from 1.2 to 1.7.

The effect of the initial pressure, P_o, on the induction period preceding the cool flame, τ, is shown in figures 3.7 and 3.8 for 1:25 and 1:75 decane:air mixtures. It is apparent that the relationship:

$$\tau = kP_o^{-n} + c \qquad (3.2)$$

holds for the mixtures studied, as it does for many other hydrocarbon-oxygen systems[14]. A plot of $\ln\tau$ against $1/T_o$ has been constructed for the 1:25 mixture at several different initial pressures and this is shown in figure 3.9. It can be seen that the plot exhibits a single discontinuity which is found at an average initial temperature of 540 K.

3.1.2.3 Effect of additives

Studies have been made of the effect of three fuel additives, a biocide, a static dispersant agent and a fuel system icing inhibitor (ethylene glycol monoethyl ether), on the ignition profiles of 1:25 and 1:75 decane: air mixtures in the temperature range 480-650 K and at initial pressures up to 70 kPa. 0.1% by volume solutions of the biocide and the static dispersant

Figure 3.6

Variation of ln ΔP with ln P_o for a 1:25 decane:air mixture

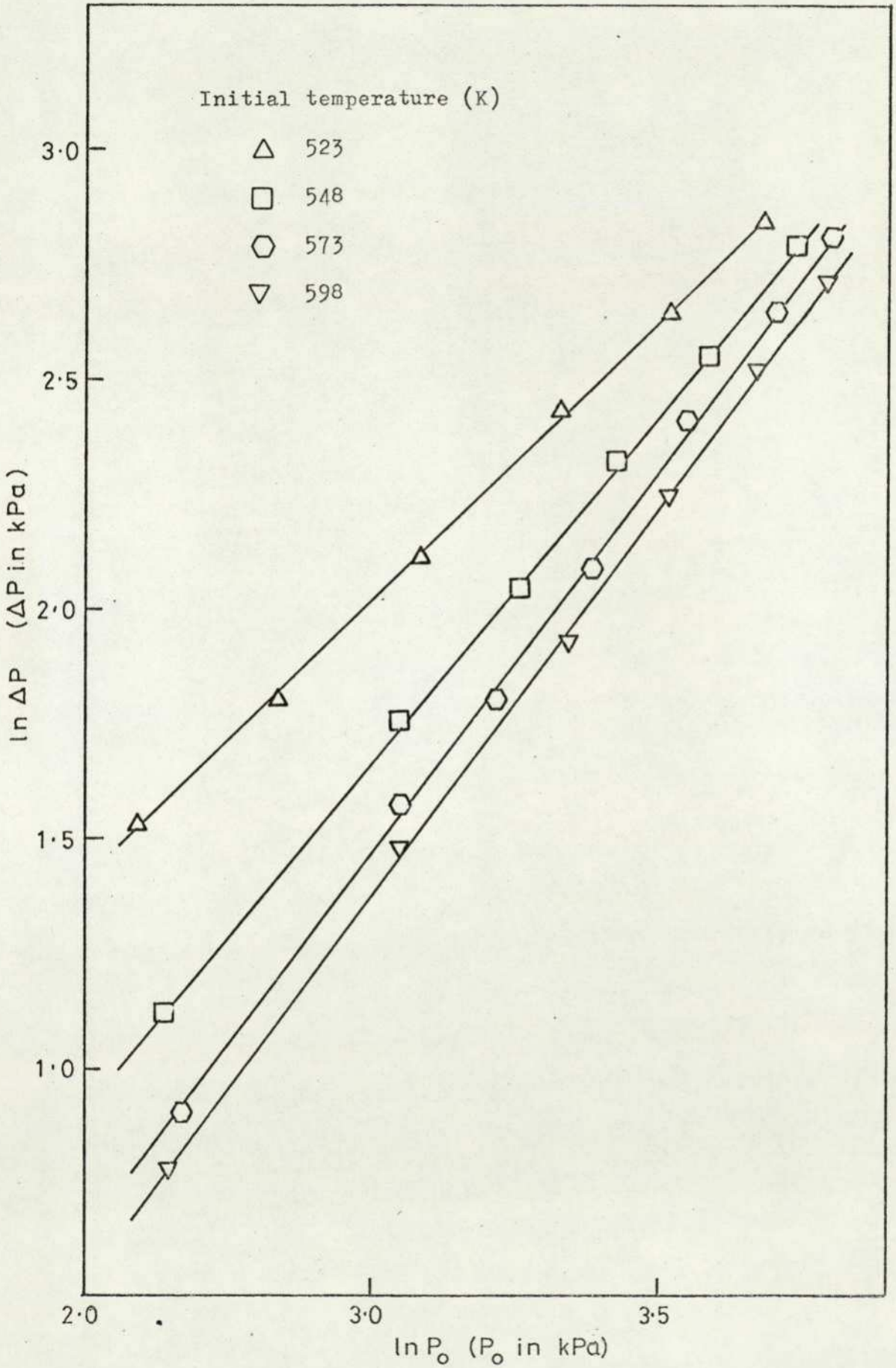


Figure 3.7

Variation of τ with P_o and T_o for a 1:25 decane:air mixture

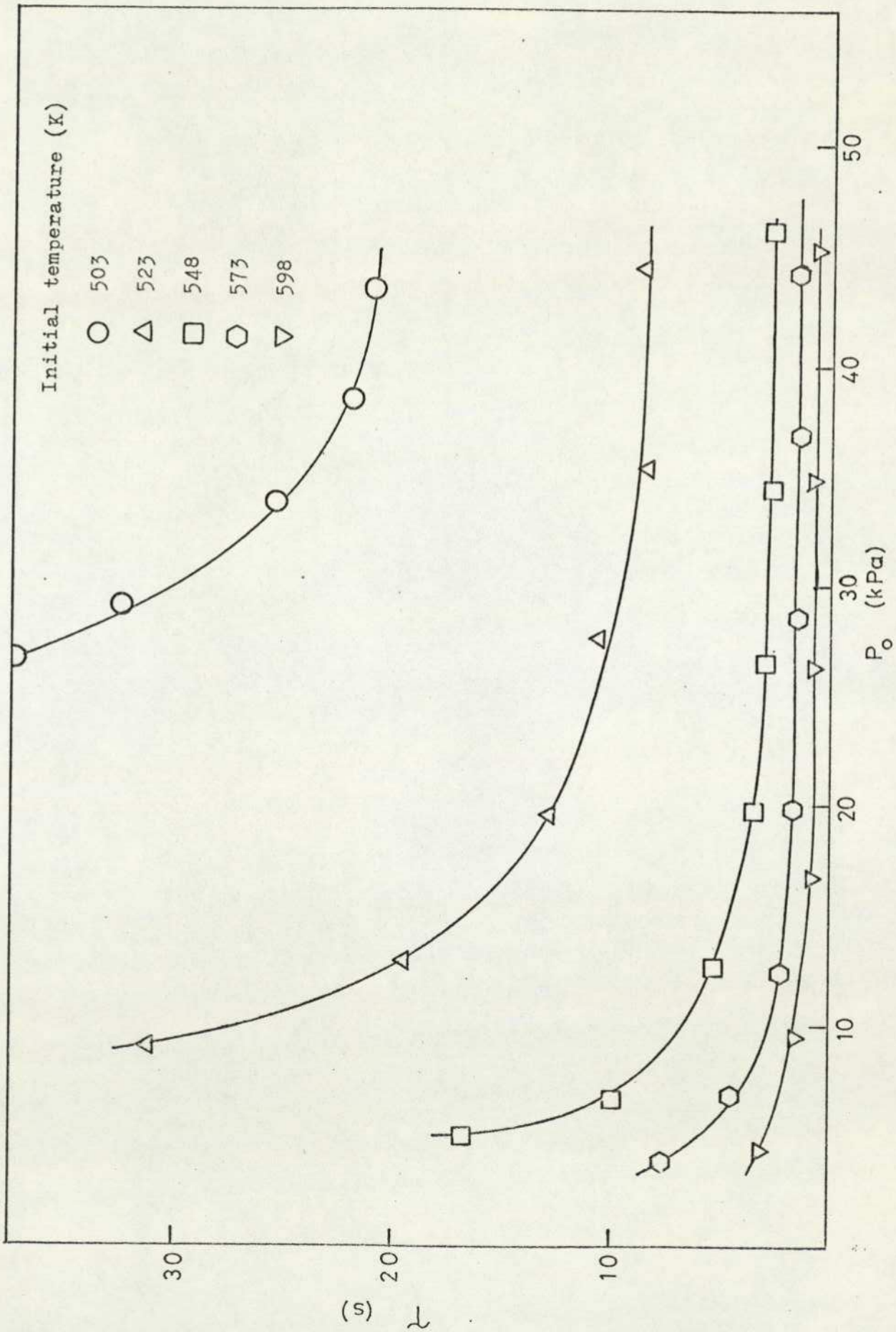


Figure 3.8

Variation of τ with P_o and T_o for a 1:75 decane:air mixture

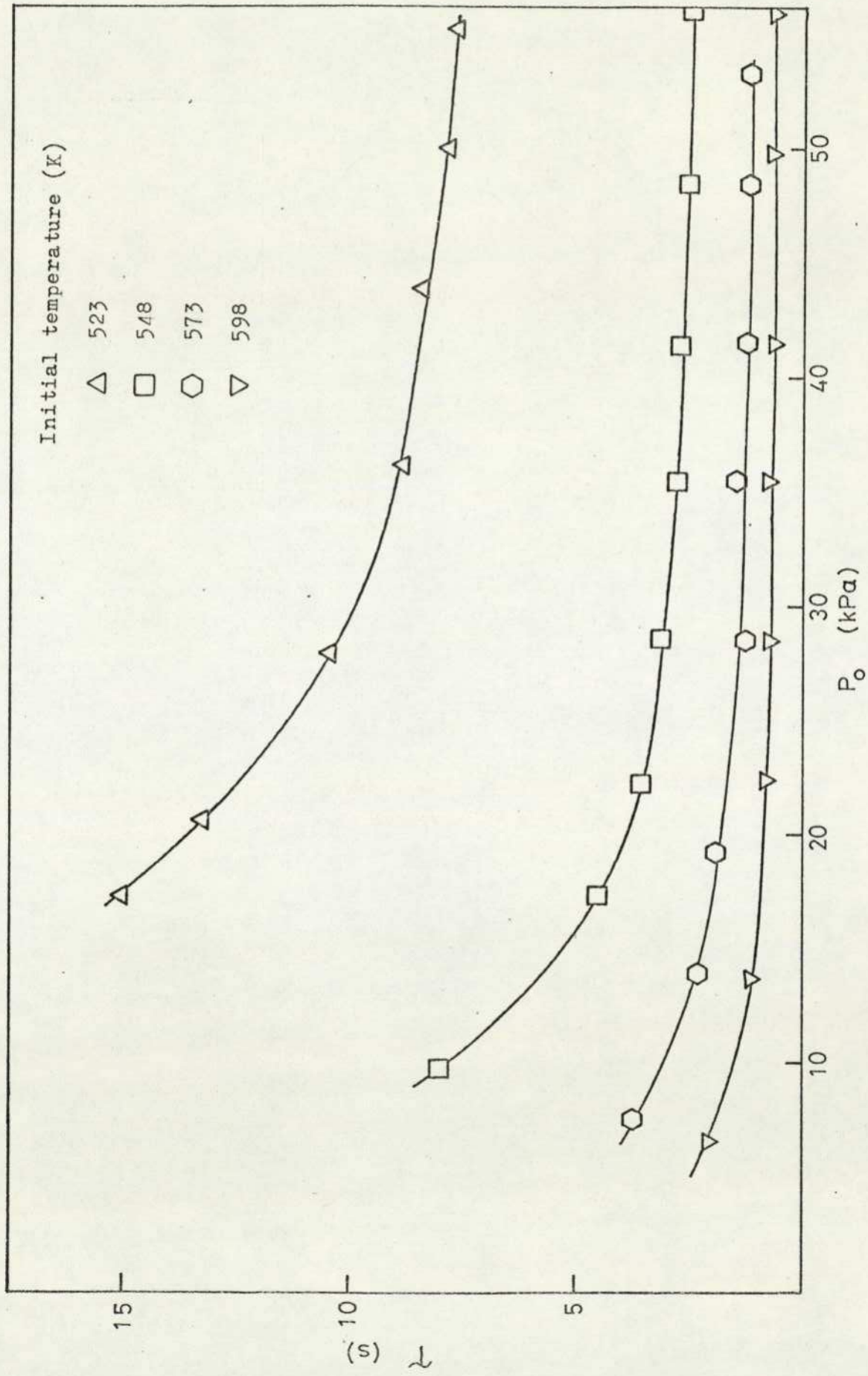


Figure 3.9

Variation of $\ln\tau$ with $1/T_o$ for a 1:25 decane:air mixture at several initial pressures

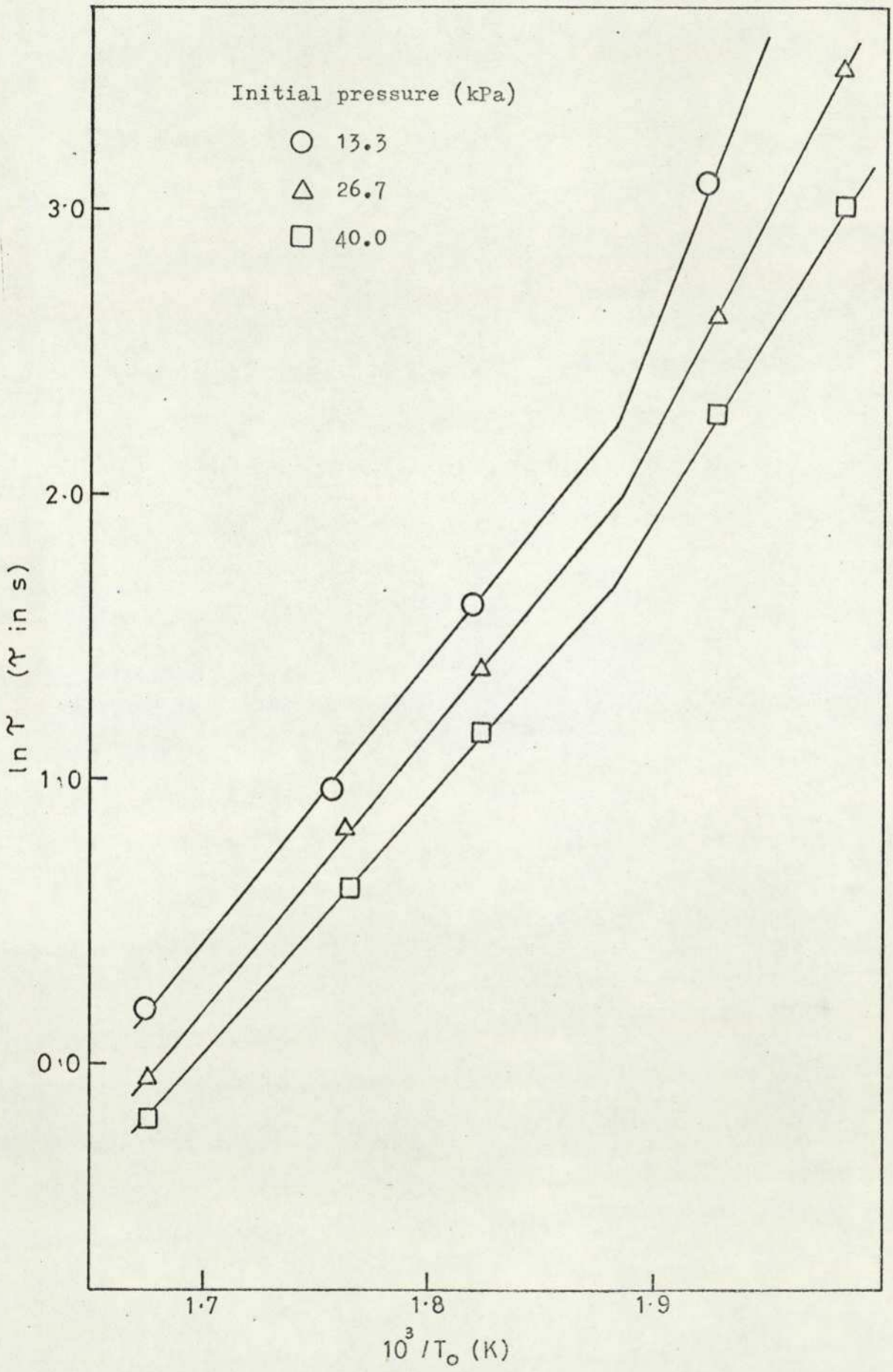
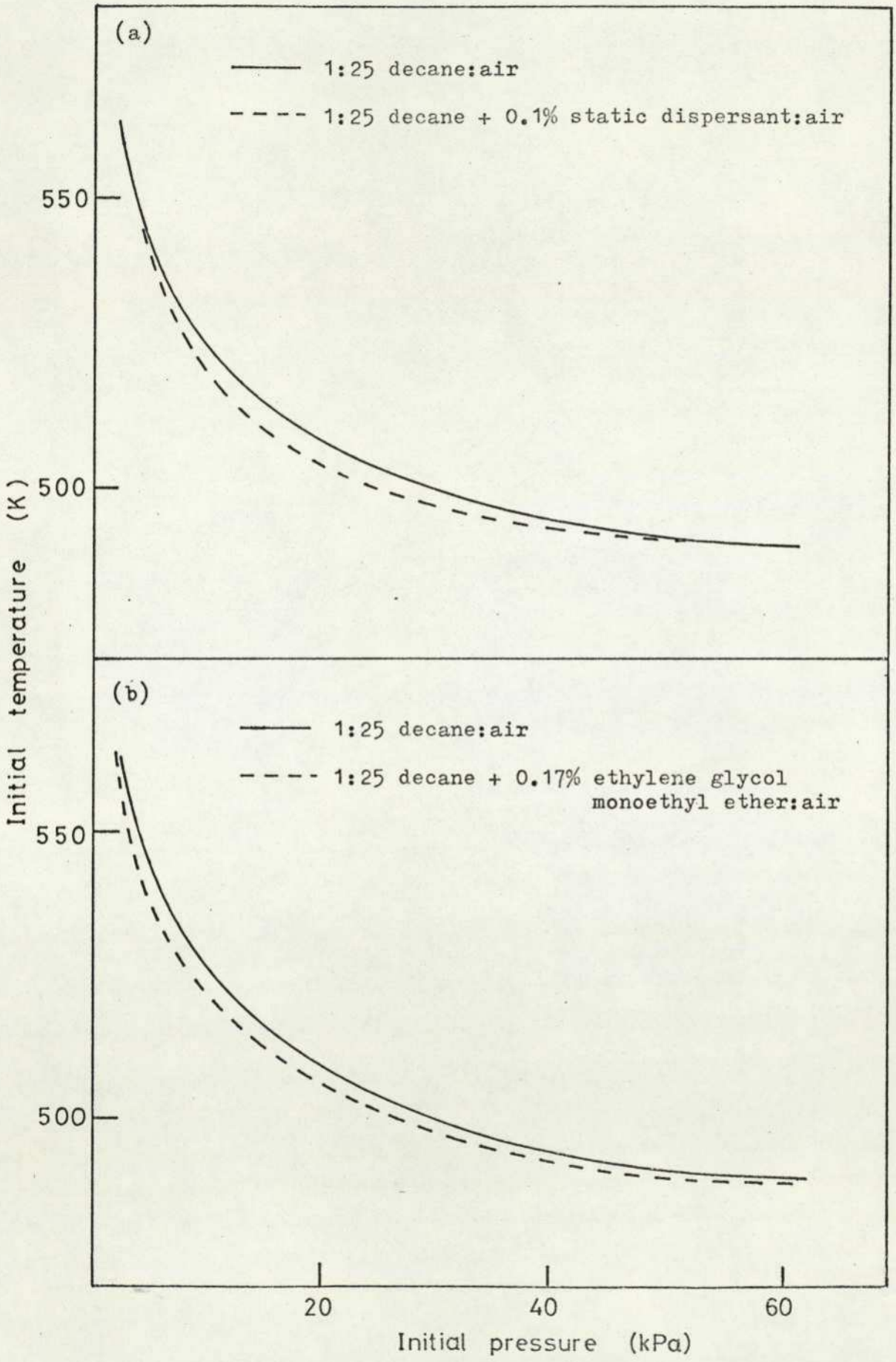


Figure 3.10

Effect of additives on the slow combustion/cool-flame boundary of a 1:25 decane:air mixture



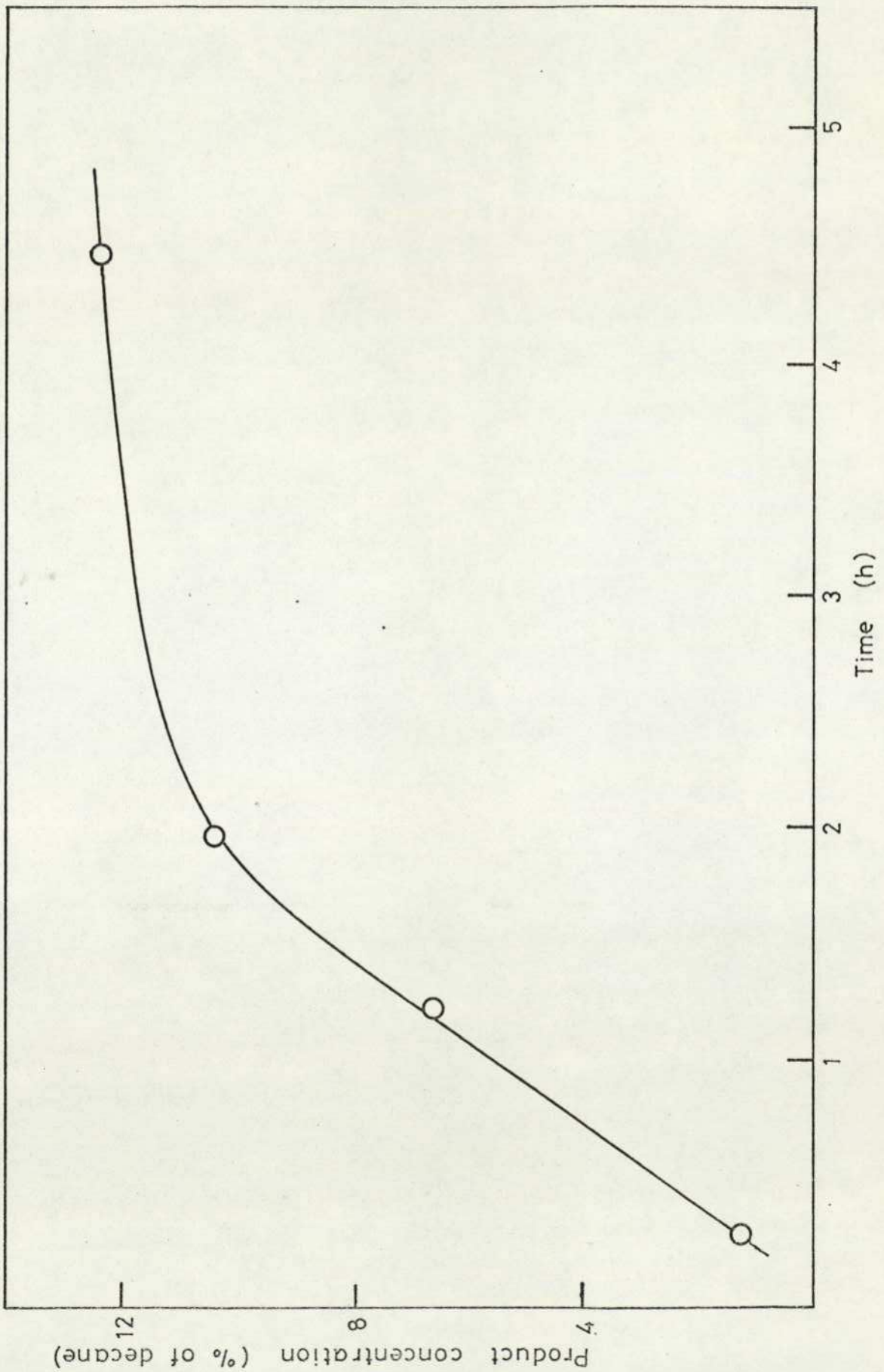
and a 0.17% by volume solution of ethylene glycol monoethyl ether decane were used. None of the additives had any effect on the ignition profile of a 1:75 decane:air mixture; nor did the biocide additive have any measurable effect when used in a 1:25 decane:air mixture. However with a 1:25 decane:air mixture the static dispersant facilitated the passage of cool flames at lower initial pressures in the temperature region 500-550 K (figure 3.10a). The effect of ethylene glycol monoethyl ether on the ignition profile of a 1:25 decane:air mixture is shown in figure 3.10b. This additive also shifted the slow combustion/cool flame boundary to slightly lower temperatures and pressures, facilitating the passage of cool flames.

3.2 Analytical results

Reactions were initially performed in the premix apparatus using a 1:10 decane:air mixture. However, owing to the very short induction periods, it was not possible to sample the reaction products before the first cool flame at temperatures above 573 K. Reactions were sampled before the first cool flame at 533 K and analysis of the products by gas chromatography showed that there were over seventy well-defined peaks, many of which represented as yet unresolved mixtures of pure chemical compounds. When the reaction was sampled using the shortest residence time possible with this apparatus i.e. ca. 1 s, there were still more than thirty products in the reaction mixture. Subsequent analysis of decane:air mixtures taken from the premix vessel showed that appreciable reaction had occurred. The concentration and distribution of the products found after the decane:air mixture had been in the premix vessel for 30 min were

Figure 3.11

Variation of total product concentration with time for a 1:10 decane:air mixture in the premix vessel at 393 K



found to be similar to those obtained during the initial stages of reaction at 533 K. Figure 3.11 shows the variation with time of the concentrations of the products formed in the premix vessel.

Since the reaction of decane in the premix vessel prevented the analysis of the initial products of decane combustion, further analytical studies were performed on reactions of decane in the metal-free apparatus. The injection apparatus, initially constructed to study the effect of fuel additives on decane combustion, was also later used for an analytical study of the effect of temperature and of hydrogen bromide on decane combustion.

3.2.1 Slow combustion of decane

Reactions were performed initially at 443 K in the metal-free apparatus, but it was impossible to obtain consistent results at low pressures (14.67 or 10.67 kPa), where the concentration and distribution of products formed depended on the initial pressure of the previous reaction mixture irrespective of the time for which the reaction vessel had been pumped out. Even after the reaction vessel had been washed with fuming nitric acid and baked for 24 h at 723 K in an oxygen atmosphere, no appreciable reaction occurred at low pressures until a reaction had been performed at a high pressure (73.33 kPa). Subsequent reactions at low pressures showed a gradual decrease in product concentration. All reactions were therefore performed at an initial total pressure of 73.33 kPa with an initial partial pressure of decane of 6.67 kPa; the results obtained under these conditions were found to be repeatable.

The variation with time of the product concentrations was determined using a 1:2:8 decane:oxygen:nitrogen mixture, which

was sampled after reaction times of between 5 and 30 min. These reactions were performed at initial temperatures of 445, 453, 462 and 473 K. It was found that at the highest temperature used (473 K), the condensed reaction products contained a separate aqueous layer and in these cases the analysis was performed on the hydrocarbon layer of the products.

The main products obtained from the gas-phase oxidation of decane may be divided into six types. These are decyl monohydroperoxides, dihydroperoxides, C_{10} alcohols and carbonyl compounds, aldehydes and methyl ketones containing less than ten carbon atoms, C_{10} O-heterocyclic compounds and products containing more than ten carbon atoms which may be called termination products. Minor amounts of C_1- C_6 primary alcohols were also detected in the later stages of reaction at all temperatures.

The variation with time of the yields of these main product types is shown in figures 3.12 to 3.14, while the concentrations of the individual products is shown in tables 3.1, 3.2 and 3.3. It should be noted that no decenes, and only a trace of 1-alkenes with less than ten carbon atoms, were found in this temperature range; decan-1-ol and nonanal were also not detected.

Figure 3.15 shows the variation with temperature of the percentage product concentration after 5 min. reaction time. At the lowest temperature used (445 K), decyl monohydroperoxides are the principal products, but their yields decrease rapidly as the temperature is raised to 473 K. The yield of the other peroxides increases from 445 to 453 K and reaches a maximum between 453 and 462 K; a similar, though less pronounced, trend

Key to figures 3.12 to 3.15

Decyl monohydroperoxides

Decane dihydroperoxides

C_{10} O-heterocycles

C_{10} carbonyls and alcohols

$< C_{10}$ aldehydes and ketones

Figure 3.12

Variation of the yields of products with time at 445 K

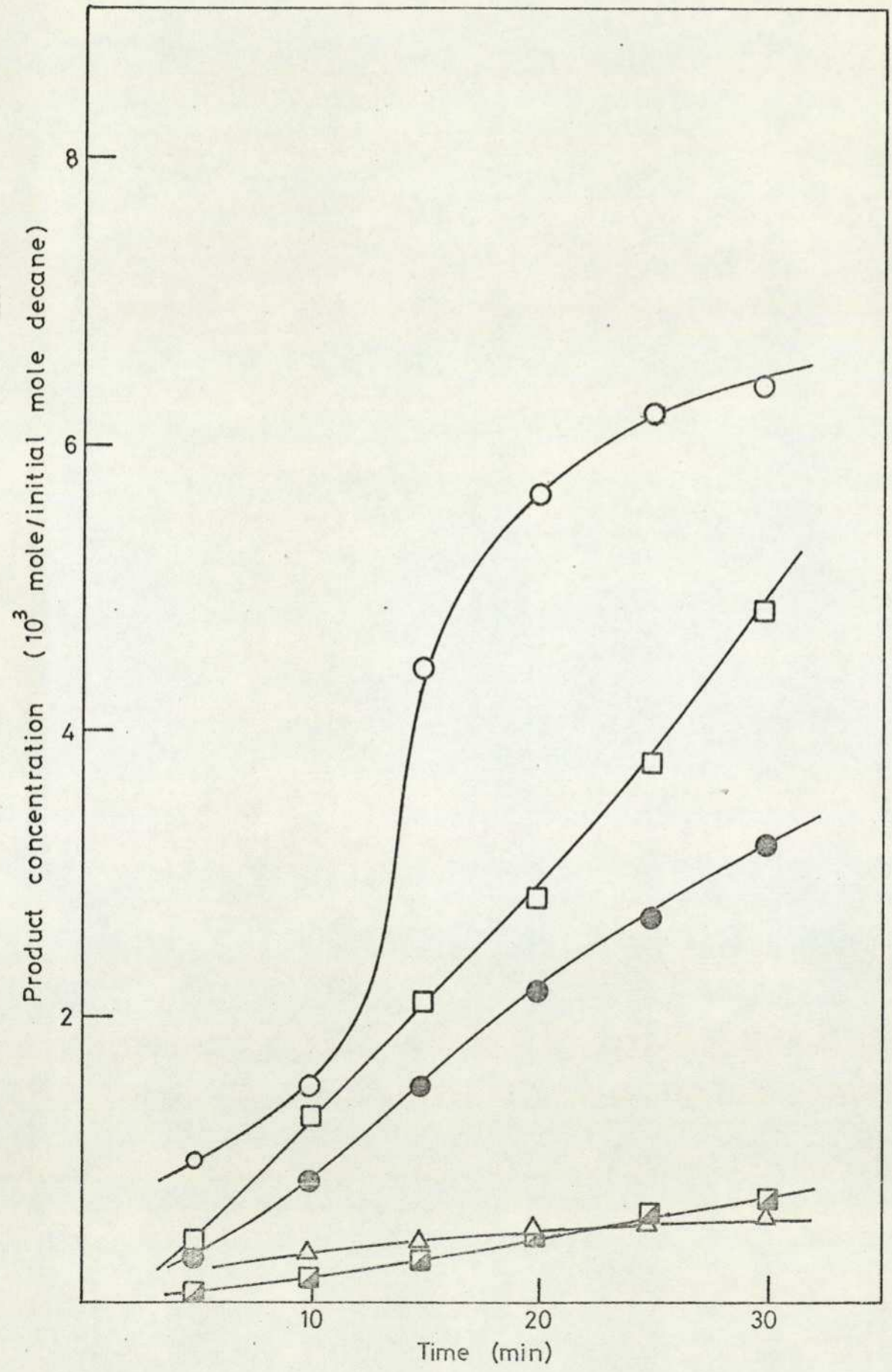


Figure 3.13

Variation of the yields of products with time at 453 K

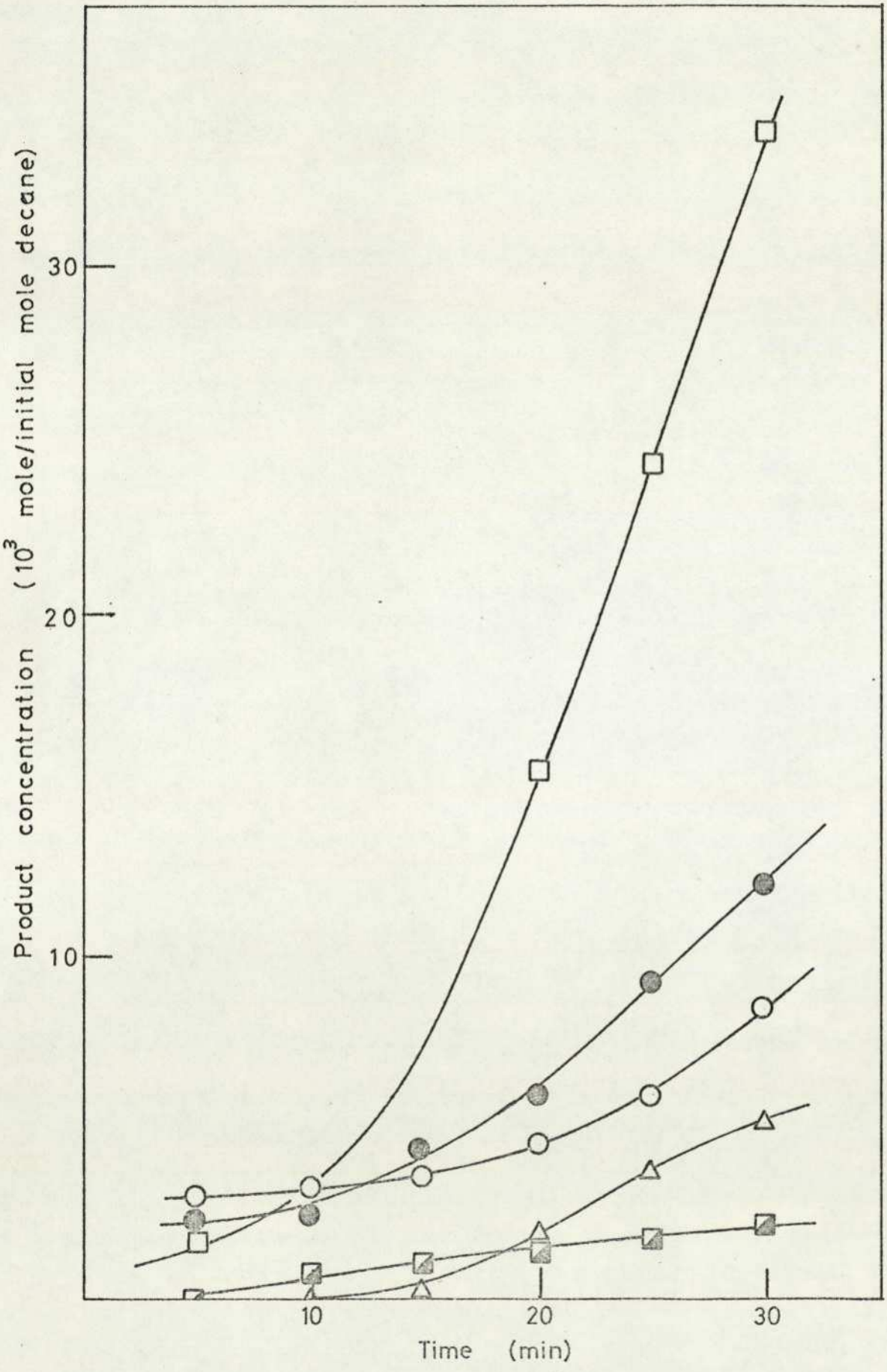


Figure 3.14

Variation of the yields of products with time at 462 K

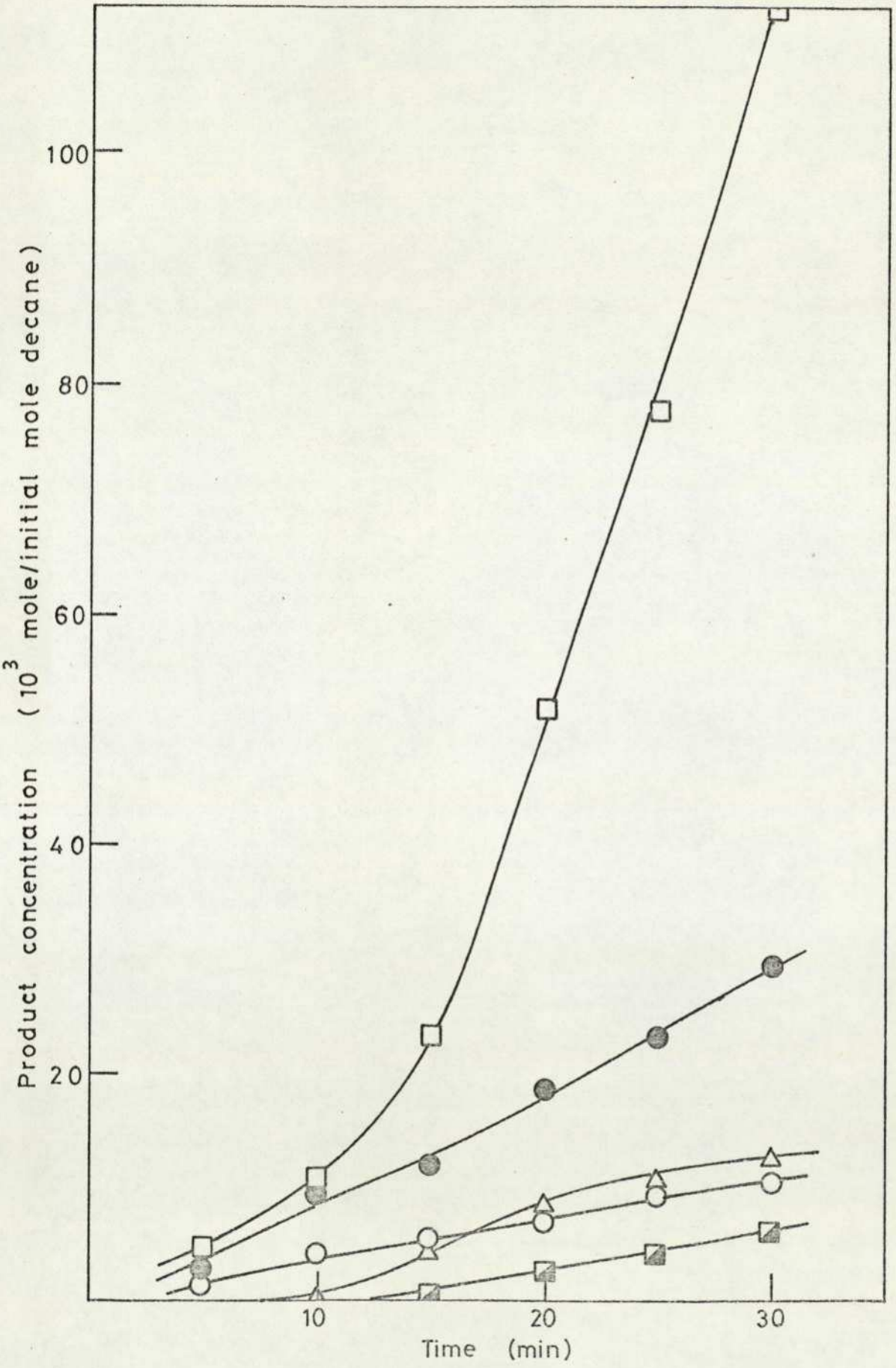


Table 3.1

Variation with time of the products of decane combustion at 445 K

Concentration of products expressed as 10^4 moles per initial mole of decane. Decane pressure, 6.7 kPa; oxygen pressure, 13.3 kPa; nitrogen pressure, 53.3 kPa.

Reaction time (min)	5	10	15	20	25	30
Decyl monohydroperoxides	9.9	14.6	44.0	56.0	61.9	62.2
Decane dihydroperoxides	1.0	8.2	15.6	21.9	26.1	31.7
O-heterocycles	0.2	1.6	3.1	4.4	5.1	6.1
Decan-5-one } Decan-4-one }	-	0.8	0.8	0.9	1.1	1.2
Decan-3-one } Decan-3-ol }	-	0.6	0.6	0.7	0.7	0.9
Decan-2-one	-	0.5	0.6	0.6	0.7	0.8
Decan-2-ol	-	0.3	0.4	0.5	0.6	0.7
Decan-4-ol	-	0.5	0.7	0.8	1.0	1.2
Decan-5-ol	-	0.1	0.2	0.3	0.5	0.5
Decanal	-	0.1	0.2	0.3	0.3	0.4
Total C_{10} alcohols & ketones	-	3.2	3.7	4.1	5.1	5.7
Nonan-2-one	-	0.7	0.9	1.4	1.7	1.9
Octan-2-one	0.1	1.6	2.1	2.5	3.0	3.5
Octanal	0.3	0.6	0.9	1.3	1.8	2.3
Heptan-2-one	-	1.2	2.1	2.8	3.8	5.3
Heptanal	-	0.7	1.0	1.1	1.6	1.9
Hexan-2-one } Hexanal }	0.8	2.4	3.6	4.5	6.4	8.8
Pentan-2-one } Pentanal }	0.9	3.0	4.9	6.0	8.2	10.6
Butan-2-one	-	0.5	0.8	1.0	1.9	2.4
Butanal	0.7	2.0	3.5	4.3	5.2	6.7
Propan-2-one	-	0.6	0.9	1.4	1.5	1.7
Propanal	-	0.5	0.7	1.0	1.6	1.8
Acetaldehyde	-	-	0.6	0.7	0.8	1.1
Total carbonyls ΣC_{10}	2.8	13.8	21.1	28.0	37.5	48.0
Termination products	0.1	2.6	3.4	4.3	5.3	6.5

Table 3.2

Variation with time of the products of decane combustion at 453 K

Concentration of products expressed as 10^4 moles per initial mole of decane. Decane pressure, 6.7 kPa; oxygen pressure, 13.3 kPa; nitrogen pressure, 53.3 kPa.

Reaction time (min)	5	10	15	20	25	30
Decyl monohydroperoxides	25.7	30.2	35.4	45.6	56.3	84.3
Decane dihydroperoxides	21.2	25.7	39.1	61.3	91.2	122.4
O-heterocycles	2.5	4.5	5.7	12.8	16.1	21.9
Decan-5-one } Decan-4-one }	0.4	0.7	0.9	5.3	8.7	9.1
Decan-3-one } Decan-3-ol }	0.2	0.5	0.8	3.7	6.7	7.7
Decan-2-one	0.2	0.5	0.7	2.6	4.8	6.4
Decan-2-ol	0.2	0.4	0.5	3.1	7.6	10.4
Decan-4-ol	0.3	0.5	0.6	3.6	7.4	10.7
Decan-5-ol	0.1	0.2	0.3	2.1	5.0	7.9
Decanal	0.1	0.2	0.3	1.6	3.0	5.6
Total C_{10} alcohols & ketones	1.5	3.0	4.1	22.0	43.2	57.1
Nonan-2-one	0.6	0.9	1.4	5.9	8.0	10.8
Octan-2-one	1.2	1.8	3.3	14.7	21.5	26.6
Octanal	1.1	1.5	1.5	1.6	3.3	4.8
Heptan-2-one	2.3	3.1	4.6	19.5	30.8	36.6
Heptanal	0.9	1.1	1.6	2.2	5.1	7.3
Hexan-2-one } Hexanal }	3.5	4.6	6.7	25.7	39.2	58.7
Pentan-2-one } Pentanal }	5.4	7.4	8.0	27.9	39.1	58.3
Butan-2-one	0.9	1.3	2.3	10.7	20.0	25.9
Butanal	1.3	2.7	5.9	22.6	35.1	54.0
Propan-2-one	0.5	0.7	1.6	5.8	6.2	11.3
Propanal	1.2	1.9	2.6	9.2	18.8	23.1
Acetaldehyde	-	-	1.5	8.1	19.5	22.9
Total carbonyls $< C_{10}$	18.9	27.0	41.0	153.9	246.6	340.2
Termination products	2.8	4.1	6.1	12.5	13.9	16.6

Table 3.3

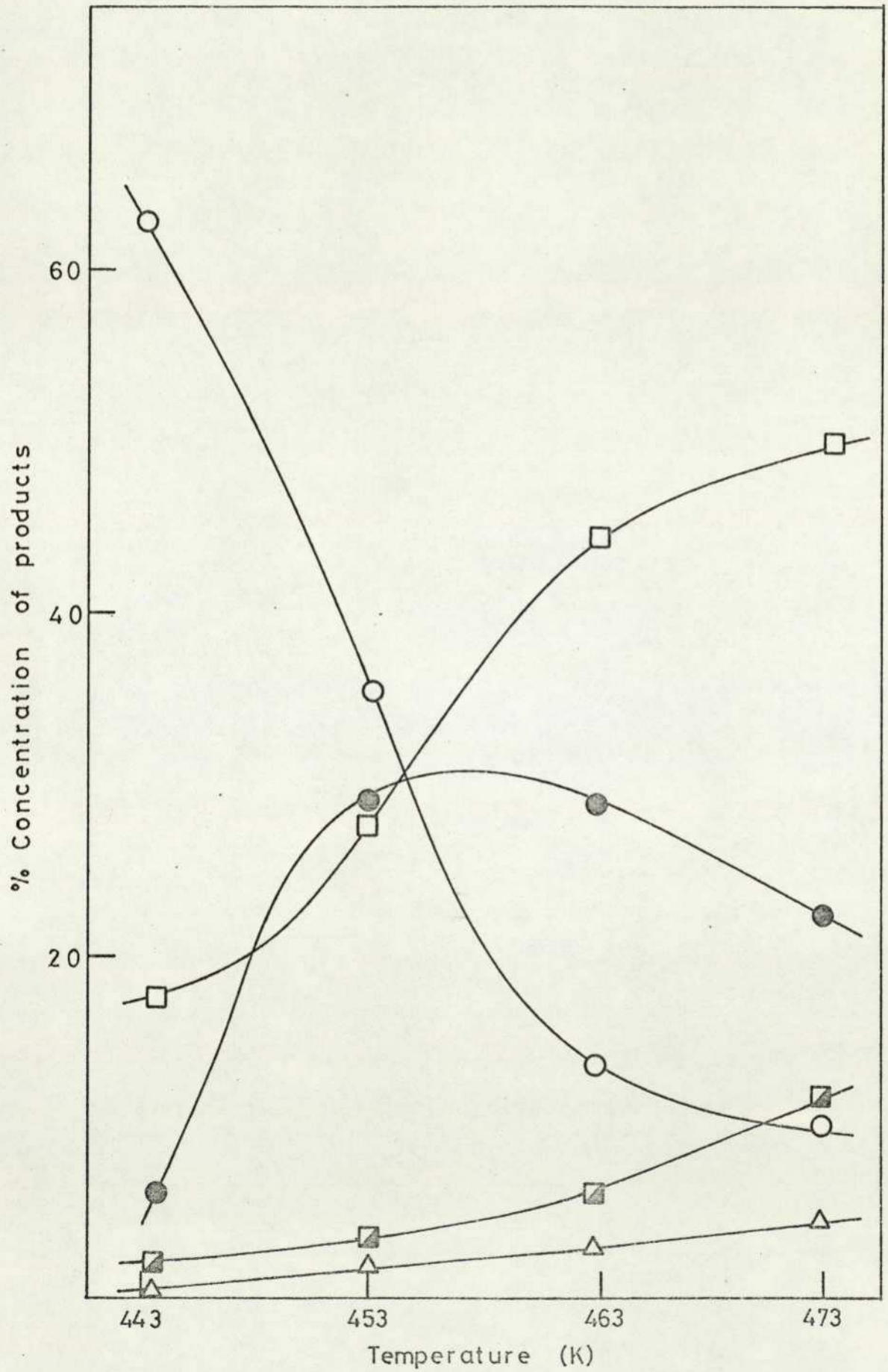
Variation with time of the products of decane combustion at 462 K

Concentration of products expressed as 10^4 moles per initial mole of decane. Decane pressure, 6.7 kPa; oxygen pressure, 13.3 kPa; nitrogen pressure, 53.3 kPa.

Reaction time (min)	5	10	15	20	25	30
Decyl monohydroperoxides	15.5	38.7	49.8	90.0	96.7	108.2
Decane dihydroperoxides	33.4	89.3	120.3	180.2	212.9	290.0
O-heterocycles	6.7	7.4	20.1	32.1	43.3	58.0
Decan-5-one } Decan-4-one }	0.8	1.6	9.4	16.7	19.7	23.0
Decan-3-one } Decan-3-ol }	0.5	1.3	7.0	16.2	18.8	20.5
Decan-2-one	0.6	1.0	3.9	9.9	11.6	14.9
Decan-2-ol	0.5	0.9	3.4	11.6	20.2	23.5
Decan-4-ol	0.6	1.1	3.8	12.5	19.7	23.5
Decan-5-ol	0.2	0.5	2.6	10.3	12.3	16.9
Decanal	0.6	0.7	4.7	10.2	11.7	12.3
Total C_{10} aldehydes & ketones	3.8	7.1	34.8	87.4	114.0	134.6
Nonan-2-one	0.9	2.9	10.8	17.3	23.7	26.9
Octan-2-one	3.0	5.9	18.8	23.5	30.5	57.8
Octanal	2.1	2.8	4.9	8.3	9.6	11.7
Heptan-2-one	3.4	8.0	24.8	38.9	46.2	83.9
Heptanal	1.8	2.7	4.7	11.5	15.6	17.1
Hexan-2-one } Hexanal }	5.6	12.5	45.3	84.2	120.4	157.9
Pentan-2-one } Pentanal }	7.1	13.9	41.6	105.3	157.5	189.1
Butan-2-one	1.5	3.9	14.3	46.3	69.1	86.6
Butanal	4.0	7.3	28.7	64.5	93.7	160.2
Propan-2-one	3.1	5.0	9.1	21.9	38.4	66.7
Propanal	4.7	11.9	14.5	45.6	62.5	98.2
Acetaldehyde	6.2	11.7	16.2	53.7	105.8	140.7
Total carbonyls $< C_{10}$	43.4	98.5	233.7	521.0	773.0	1236.8
Termination products	3.6	8.5	12.0	25.3	50.2	96.9

Figure 3.15

Variation of the yields of products with temperature



is shown by the termination products.

Aldehydes and ketones with less than ten carbon atoms become the major products at temperatures above 453 K but tend towards a maximum value at 473 K. C_{10} O-heterocyclic compounds are relatively minor products at 445 K and increase slowly with temperature to 462 K; above this temperature their yields increase more rapidly. The concentrations of C_{10} carbonyl compounds and alcohols show little change with temperature between 445 and 473 K, their percentage yield increasing very slightly.

3.2.1.1 Effect of oxygen and decane concentrations

The effect of oxygen concentration on the slow combustion of decane was determined in the metal-free apparatus, using decane:oxygen ratios ranging from 1:0.5 to 1:4. These reactions were performed at initial temperatures of 445, 453 and 462 K and were sampled after 10 min. reaction time.

The nature and amounts of the individual products found are shown in tables 3.4 - 3.6 and the variation with oxygen partial pressure of the quantities of the main product types is shown in figures 3.16 - 3.18. As the concentration of oxygen in the reaction mixture is increased, the overall rate of reaction, shown by the total product concentration formed after a given time, also increases. Similarly, there is a marked decrease in the yield of decyl monohydroperoxides and of decanols and decanones and a smaller decrease in that of C_{10} O-heterocyclic compounds, while the amounts of decane dihydroperoxides and of the carbonyl compounds containing less than ten carbon atoms showed corresponding increases.

The effect of oxygen concentration was also studied

Table 3.4

Effect of oxygen concentration on the products of decane combustion at 445 K

Concentration of products expressed as moles percent of total products. Total pressure, 73.3 kPa; decane pressure, 6.7 kPa; balance nitrogen.

Oxygen pressure (kPa)	3.3	6.7	13.3	20.0	26.7
Decyl monohydroperoxides	44.9	39.0	35.7	30.2	27.7
Decane dihydroperoxides	17.3	19.1	23.5	25.4	27.9
O-heterocycles	3.8	3.4	3.0	2.8	2.4
Decan-5-one } Decan-4-one }	1.9	1.7	1.6	1.5	1.3
Decan-3-one } Decan-3-ol }	0.6	1.0	1.1	0.9	0.7
Decan-2-one	0.6	1.0	1.0	1.0	0.6
Decan-2-ol	-	0.3	0.4	0.3	0.3
Decan-4-ol	0.6	1.0	0.9	0.8	0.7
Decan-5-ol	-	0.3	0.3	0.3	0.2
Decanal	-	0.3	0.3	0.2	0.2
Total C_{10} aldehydes & ketones	3.8	5.8	5.8	5.2	4.4
Nonan-2-one	1.3	1.7	1.8	1.8	1.7
Octan-2-one	1.9	2.7	1.7	1.8	2.0
Octanal	1.9	1.7	1.2	0.9	0.8
Heptan-2-one	-	1.8	1.8	2.0	2.2
Heptanal	-	0.7	0.7	0.7	0.9
Hexan-2-one } Hexanal }	7.7	8.2	8.4	8.5	9.0
Pentan-2-one } Pentanal }	10.9	7.2	9.2	10.1	11.4
Butan-2-one	1.3	1.4	1.4	1.5	1.6
Butanal	5.8	5.9	5.9	4.9	4.0
Propan-2-one	-	0.7	0.8	0.9	1.0
Propanal	1.3	1.4	1.4	1.3	1.4
Acetaldehyde	-	-	-	-	-
Total carbonyls $<C_{10}$	31.4	33.4	34.6	35.3	36.0
Termination products	2.6	2.1	5.4	4.8	3.7
Total product concentration (10^3 moles/initial mole decane)	1.56	2.90	4.21	4.95	6.14

Table 3.5

Effect of oxygen concentration on the products of decane combustion at 453 K

Concentration of products expressed as moles percent of total products. Total pressure, 73.3 kPa; decane pressure, 6.7 kPa; balance nitrogen.

Oxygen pressure (kPa)	3.3	6.7	13.3	20.0	26.7
Decyl monohydroperoxides	39.4	36.4	30.9	27.9	24.7
Decane dihydroperoxides	16.4	18.1	25.2	29.2	33.2
O-heterocycles	8.2	5.4	4.8	3.3	2.8
Decan-5-one } Decan-4-one }	0.6	0.6	0.5	0.4	0.3
Decan-3-one } Decan-3-ol }	0.6	0.5	0.4	0.4	0.3
Decan-2-one	0.5	0.5	0.4	0.3	0.3
Decan-2-ol	0.4	0.3	0.2	0.3	0.2
Decan-4-ol	0.4	0.4	0.2	0.2	0.2
Decan-5-ol	-	0.2	0.1	0.1	0.1
Decanal	-	0.2	0.1	0.1	0.1
Total C_{10} aldehydes & ketones	2.5	2.9	2.2	1.8	1.5
Nonan-2-one	0.9	1.2	1.4	1.5	1.7
Octan-2-one	2.2	2.7	2.9	3.0	3.3
Octanal	3.1	2.0	2.1	2.2	2.1
Heptan-2-one	3.7	4.3	4.3	4.4	4.6
Heptanal	1.6	1.4	1.2	1.2	1.4
Hexan-2-one } Hexanal }	3.4	4.6	4.9	5.3	5.0
Pentan-2-one } Pentanal }	4.4	4.5	7.8	8.2	8.4
Butan-2-one	0.6	1.4	1.4	1.4	1.6
Butanal	2.5	3.6	3.8	3.9	4.0
Propan-2-one	0.9	0.8	0.7	0.9	1.0
Propanal	1.9	2.5	2.0	1.6	1.4
Acetaldehyde	2.8	2.4	1.0	1.0	1.2
Total carbonyls $<C_{10}$	28.4	30.7	32.5	33.2	34.2
Termination products	5.0	6.3	4.3	4.0	2.9
Total product concentration (10^3 moles/initial mole decane)	3.17	5.85	9.45	14.50	18.07

Table 3.6

Effect of oxygen concentration on the products of decane combustion at 462 K

Concentration of products expressed as moles percent of total products. Total pressure, 73.3 kPa; decane pressure, 6.7 kPa; balance nitrogen.

Oxygen pressure (kPa)	3.3	6.7	13.3	20.0	26.7
Decyl monohydroperoxides	26.9	20.9	15.5	14.4	12.4
Decane dihydroperoxides	28.9	33.2	35.8	36.7	39.4
O-heterocycles	1.0	2.7	2.9	2.9	2.9
Decan-5-one } Decan-4-one }	0.9	0.7	0.6	0.5	0.4
Decan-3-one } Decan-3-ol }	0.8	0.6	0.5	0.5	0.3
Decan-2-one	0.6	0.4	0.4	0.3	0.2
Decan-2-ol	0.6	0.4	0.4	0.3	0.2
Decan-4-ol	0.7	0.5	0.4	0.3	0.1
Decan-5-ol	0.3	0.3	0.2	0.2	0.2
Decanal	0.3	0.4	0.3	0.2	0.1
Total C_{10} aldehydes & ketones	4.3	3.2	2.8	2.2	1.7
Nonan-2-one	1.1	1.1	1.2	1.7	1.8
Octan-2-one	1.5	2.3	2.4	3.7	3.7
Octanal	0.9	0.8	1.1	0.9	1.0
Heptan-2-one	2.7	3.0	3.2	4.7	4.8
Heptanal	1.2	1.1	1.1	1.2	1.2
Hexan-2-one } Hexanal }	8.5	8.7	9.0	10.0	11.0
Pentan-2-one } Pentanal }	5.3	5.4	5.6	6.7	7.1
Butan-2-one	1.5	1.5	1.6	2.0	2.0
Butanal	2.9	2.8	2.9	2.7	2.8
Propan-2-one	1.1	1.0	2.0	1.6	1.6
Propanal	3.9	4.0	4.8	3.8	3.9
Acetaldehyde	3.5	3.9	4.7	4.0	3.8
Total carbonyls $<C_{10}$	34.3	36.2	39.2	43.0	44.8
Termination products	4.5	3.8	3.4	2.8	2.7
Total product concentration (10^3 moles/initial mole decane)	12.33	19.17	24.95	32.68	39.51

Key to figures 3.16 to 3.19


Decyl monohydroperoxides


Decane dihydroperoxides


C_{10} carbonyls and alcohols


C_{10} O-heterocycles


$< C_{10}$ aldehydes and ketones

Figure 3.16

Variation of the yields of products with oxygen concentration at 445 K

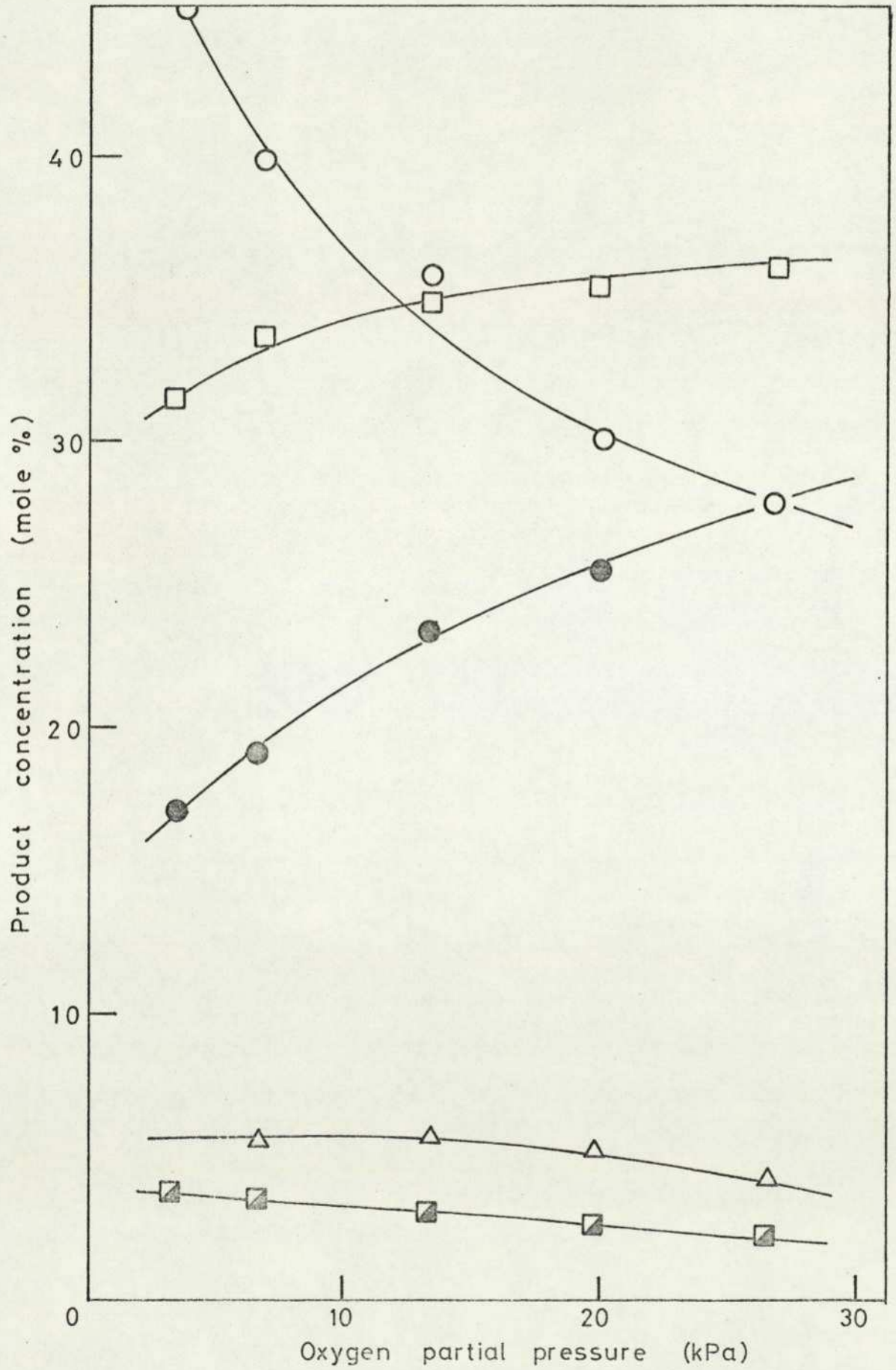


Figure 3.17

Variation of the yields of products with oxygen concentration at 453 K

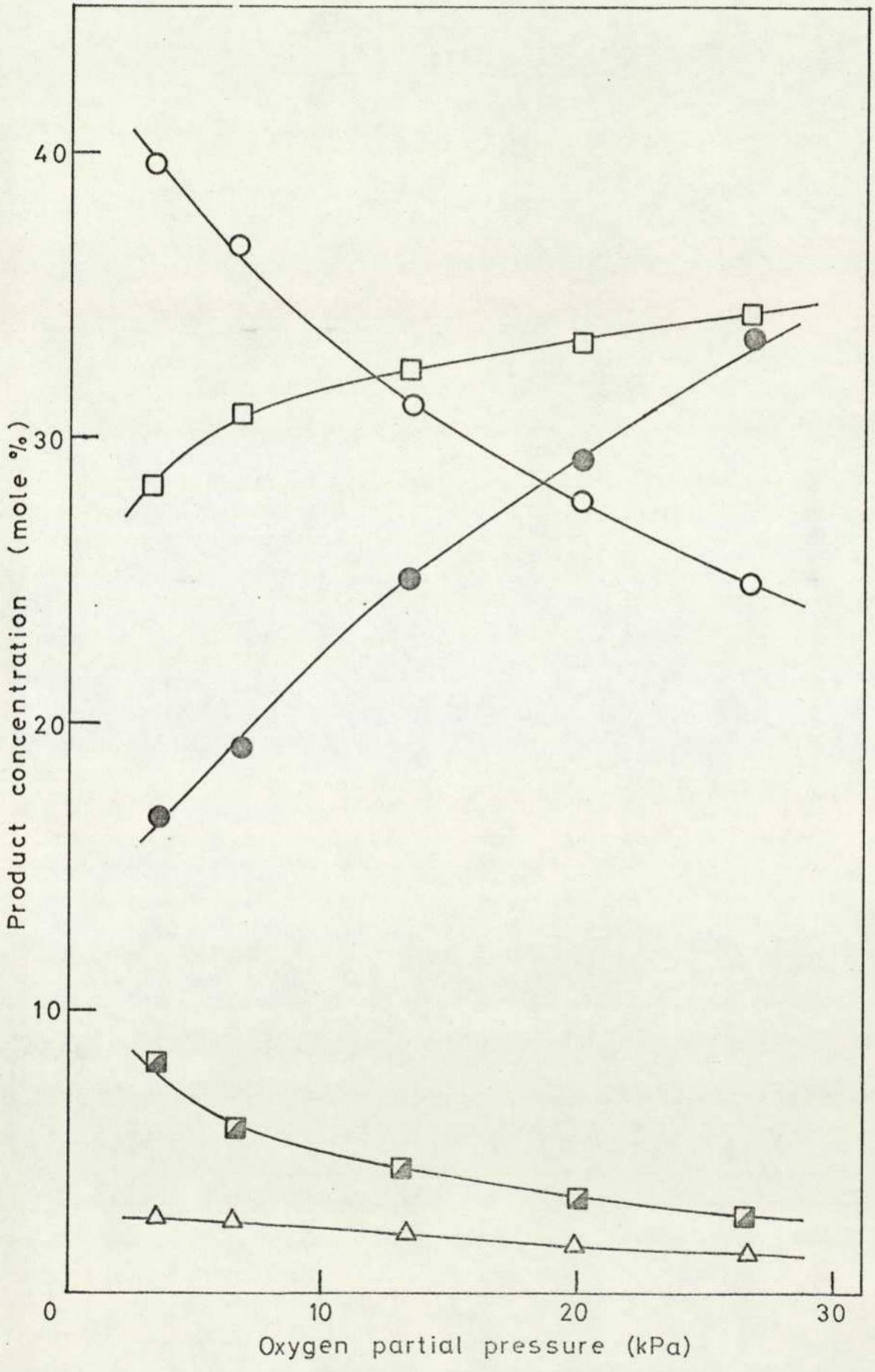


Figure 3.18

Variation of the yields of products with oxygen concentration at 462 K

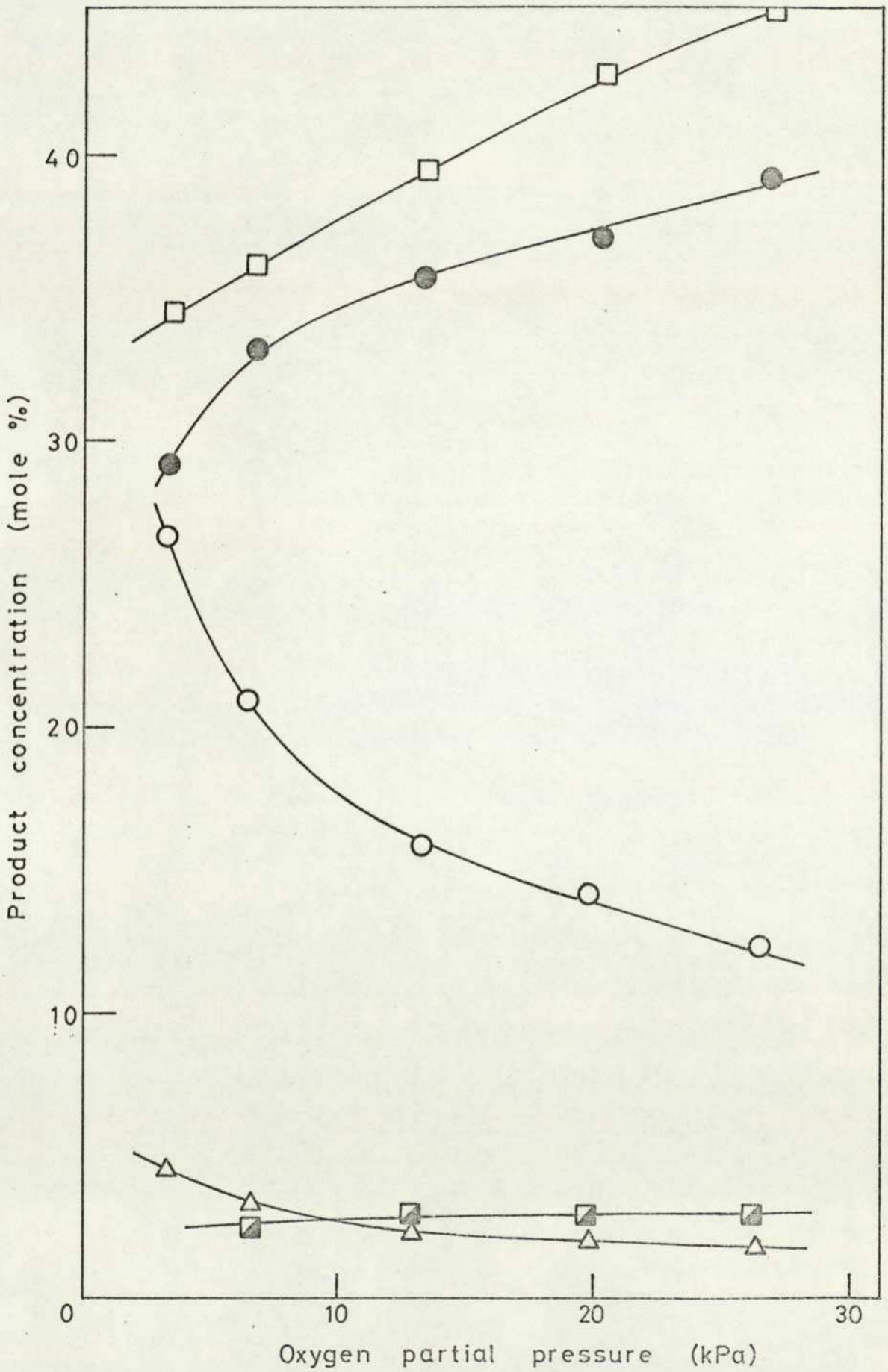


Table 3.7

Effect of oxygen concentration on the products of decane combustion at 458 K

Concentration of products expressed as moles percent of total products. Total pressure, 73.3 kPa; decane pressure, 6.7 kPa; balance nitrogen.

Oxygen pressure (kPa)	1.3	3.3	6.7	13.3
Decyl monohydroperoxides	24.9	21.5	15.4	15.0
Decane dihydroperoxides	41.6	43.4	45.3	49.3
O-heterocycles	13.3	10.3	7.3	5.1
Decan-5-one } Decan-4-one }	0.4	0.6	0.6	0.1
Decan-3-one } Decan-3-ol }	0.4	0.7	0.5	0.1
Decan-2-one	0.3	0.5	0.4	0.3
Decan-2-ol	-	0.2	0.2	0.3
Decan-4-ol	-	0.3	0.3	0.3
Decan-5-ol	-	0.4	0.1	0.2
Decanal	-	0.9	0.2	0.2
Total C_{10} aldehydes & ketones	1.0	2.5	2.3	1.3
Nonan-2-one	1.3	1.6	1.6	1.7
Octan-2-one	1.8	1.9	2.7	4.5
Octanal	2.4	1.1	1.9	0.6
Heptan-2-one	1.9	1.8	2.8	3.6
Heptanal	1.0	0.9	0.9	1.1
Hexan-2-one } Hexanal }	2.5	2.9	4.3	4.5
Pentan-2-one } Pentanal }	1.8	1.4	2.9	4.2
Butan-2-one	0.4	0.6	0.5	0.9
Butanal	2.0	2.3	2.4	1.3
Propan-2-one	0.5	0.4	0.3	0.2
Propanal	0.6	0.9	0.6	0.8
Acetaldehyde	1.2	1.1	1.2	1.2
Total carbonyls $< C_{10}$	41.5	116.8	244.9	469.2
Termination products	2.2	4.6	4.4	4.4
Total product concentration (10^3 moles/initial mole decane)	2.40	6.59	10.99	18.83

Figure 3.19

Variation of the yields of products with oxygen concentration at 458 K

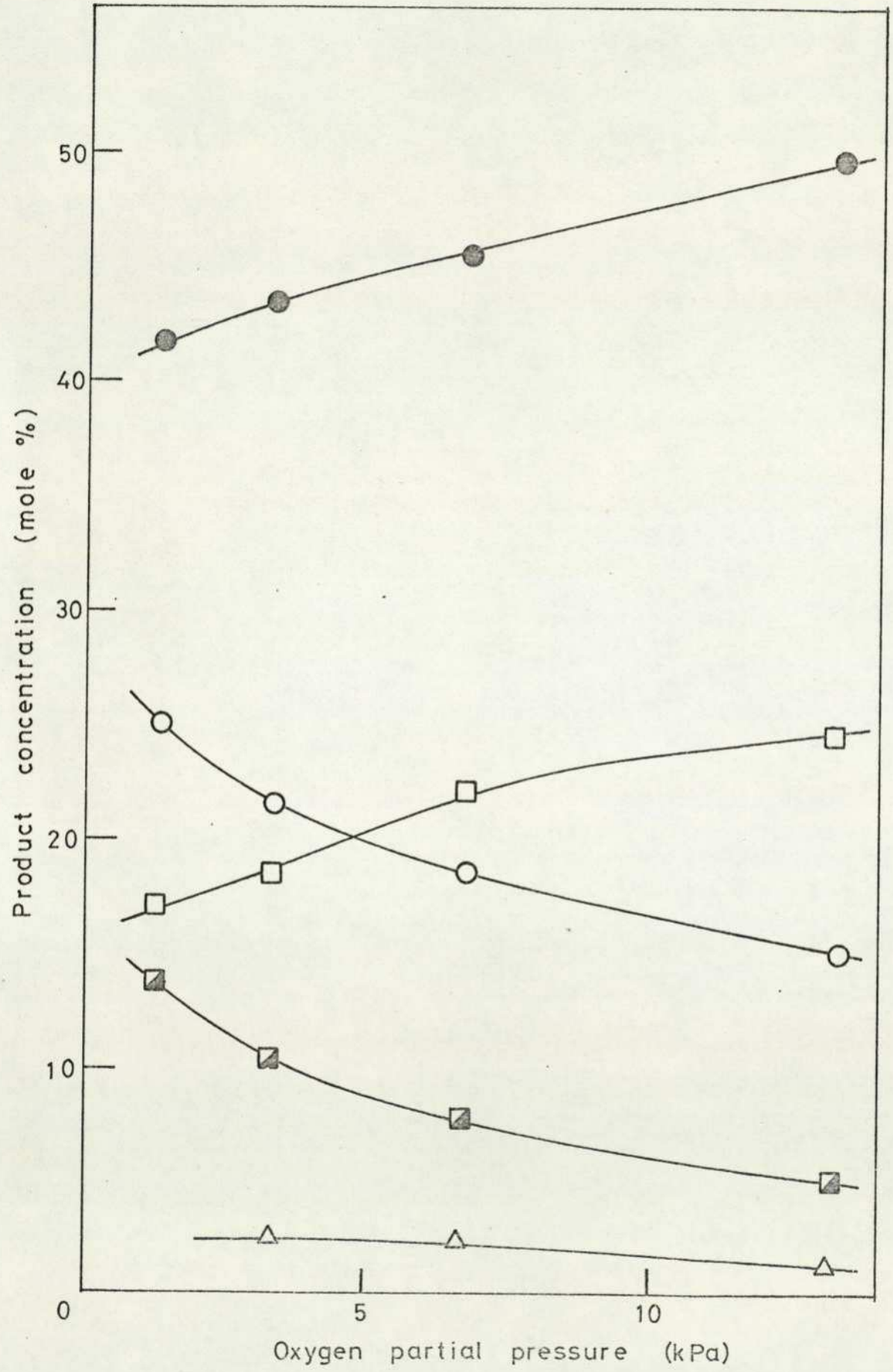


Table 3.8

Effect of decane concentration on the products of decane combustion

Concentration of products expressed as moles percent of total products. Temperature, 458 K; total pressure, 73.3 kPa; oxygen pressure, 3.3 kPa; balance nitrogen.

Decane pressure (kPa)	1.3	3.3	6.7	10.0	13.3
Decyl monohydroperoxides	21.1	21.6	20.2	26.6	32.1
Decane dihydroperoxides	43.1	39.0	41.7	40.7	36.5
O-heterocycles	7.9	9.0	7.3	6.1	5.7
C_{10} alcohols & ketones	1.4	2.1	2.7	2.7	2.9
$< C_{10}$ aldehydes & ketones	24.4	23.6	22.8	20.5	19.0
Termination products	2.1	4.6	5.3	3.4	3.7

Table 3.9

Effect of decane concentration on the products of decane combustion

Concentration of products expressed as moles percent of total products. Temperature, 458 K; total pressure, 73.3 kPa; oxygen pressure, 33.3 kPa; balance nitrogen.

Decane pressure (kPa)	3.3	6.7	10.0	13.3
Decyl monohydroperoxides	19.8	20.1	23.4	23.5
Decane dihydroperoxides	46.0	45.9	44.1	44.7
O-heterocycles	3.0	4.8	3.5	3.4
C_{10} alcohols & ketones	2.2	2.1	2.6	2.9
$< C_{10}$ alcohols & ketones	24.8	23.1	22.3	22.7
Termination products	4.2	4.0	4.0	3.7

in the injection apparatus at 458 K. The reactions were sampled after 5 minutes and the results are shown in table 3.7 and figure 3.19. The products of the combustion of decane in this apparatus showed a similar variation with oxygen concentration.

The effect of the initial concentration of decane was studied in the injection apparatus at 458 K. Two sets of experiments were performed; in the first, an initial oxygen pressure of 3.3 kPa was used with the initial partial pressure of decane varying from 1.3 to 13.3 kPa, while in the second set the initial oxygen pressure was kept at 33.3 kPa with the decane pressure varying from 3.3 to 13.3 kPa.

The results of these experiments are shown in tables 3.8 and 3.9. An increase in decane concentration had only a very small effect on the relative concentrations of the product classes and no significant trends were observed.

3.2.2 Effect of temperature

The effect of increasing temperature from 483 to 673 K on the yields of products formed in the injection apparatus is shown in table 3.10 and figure 3.20. The reaction was sampled after two min, and it was found that between 25 and 33% of the decane had reacted except at the lowest temperature (483 K), where only about 10% of it had been consumed. At 503 K and above, a single cool flame occurred before the reaction was sampled.

As the temperature is increased from 483 to 503 K, the yields of aldehydes and methyl-ketones with less than ten carbon atoms decrease rapidly from being the major product. Table 3.10 shows that the concentration of the lower carbonyls

Table 3.10

Effect of temperature on the products of decane combustion

Concentration of products expressed as 10^3 moles per mole decane

Temperature (K)	483	503	533	563	593	623	673
Decyl monohydroperoxides	33.1	15.4	-	-	-	-	-
Decane dihydroperoxides	95.3	33.6	-	-	-	-	-
O-heterocycles	140.0	175.5	368.6	380.7	381.3	402.9	341.0
Decan-5-one } Decan-4-one }	15.3	12.3	21.8	20.9	21.5	21.9	18.8
Decan-3-one } Decan-3-ol }	11.2	8.7	13.6	12.8	13.2	13.4	11.3
Decan-2-one	8.1	7.6	13.7	13.3	14.1	14.4	13.1
Decan-2-ol	7.3	4.0	3.3	2.9	2.6	1.8	1.8
Decan-4-ol	6.9	4.1	2.6	2.4	2.1	2.1	1.7
Decan-5-ol	7.1	4.2	3.1	2.9	2.6	1.8	1.6
Decanal	3.8	2.3	3.0	2.9	2.7	2.8	1.9
Total C_{10} alcohols & ketones	52.6	43.2	61.0	58.1	58.8	58.2	31.6
Decenes	-	76.7	106.0	130.3	149.7	164.9	153.1
Non-1-ene	-	1.3	14.3	14.9	15.3	18.1	33.2
Oct-1-ene	-	26.6	47.8	50.9	52.7	63.3	121.2
Hept-1-ene	-	27.4	43.0	47.0	48.5	59.7	117.5
Hex-1-ene	-	22.3	25.3	23.4	30.6	38.0	117.5
Pent-1-ene	-	11.5	7.7	11.0	13.6	16.6	22.8
Total alkenes $< C_{10}$	-	89.1	138.1	147.2	160.7	195.7	412.2
Termination products	8.6	6.5	3.0	2.2	1.9	1.9	1.2

Table 3.10 (continued)

Effect of temperature on the products of decane combustion

Concentration of products expressed as 10^3 moles per mole decane.

Temperature (K)	483	503	533	563	593	623	673
Nonan-2-one	17.6	6.3	-	-	-	-	-
Octan-2-one Octanal	61.5	11.8	-	-	-	-	-
Heptan-2-one Heptanal	58.2	10.1	-	-	-	-	-
Hexan-2-one Hexanal	67.3	16.0	7.0	2.1	1.6	1.7	1.4
Pentan-2-one Pentanal	87.4	28.7	7.7	3.6	2.8	2.9	2.7
Butan-2-one	43.0	7.3	3.1	5.1	2.4	3.9	4.1
Butanal	51.3	6.8	10.8	8.0	7.0	8.5	8.4
Propan-2-one	32.0	9.7	2.7	5.7	4.2	4.9	8.6
Propanal	10.0	12.8	6.7	12.0	7.0	8.2	11.3
Total carbonyls $< C_{10}$	428.3	109.5	38.0	36.5	25.0	30.1	36.5

Key to figure 3.20

△ Alkyl peroxides

◪ O-heterocyclic compounds

● C_{10} alcohols and ketones

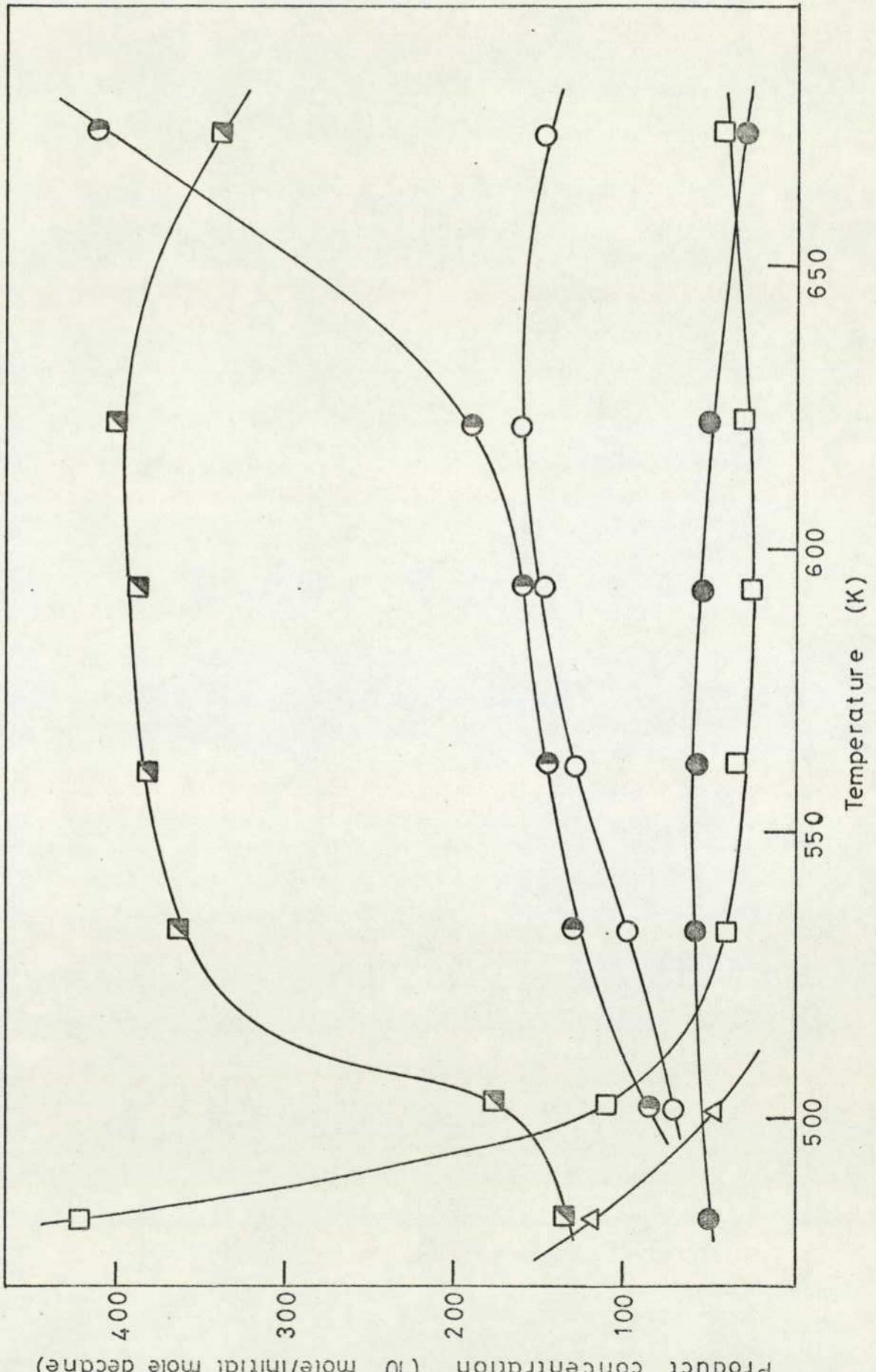
□ $<C_{10}$ aldehydes and methyl ketones

○ Decenes

◐ $<C_{10}$ 1-alkenes

Figure 3.20

Variation of the yields of products with temperature



increases slowly as the temperature is raised above 623 K.

Simultaneously there is a marked increase with temperature of O-heterocyclic compounds and of decenes. Between 503 and 523 K, the concentration of these compounds continues to gradually increase until the temperature reaches 623 K when their yield starts to decrease. Above 623 K, the concentration of 1-alkenes with less than ten carbon atoms increases rapidly and at 673 K these are the major products of decane combustion.

3.2.3 The effect of hydrogen bromide

The effect of 5 vol. % of hydrogen bromide (calculated as a percentage of the total initial pressure of decane and oxygen) on the initial products of decane combustion was determined using the injection apparatus at 458, 483 and 503 K and with reaction times of 10, 5 and 2 min. The nature and amounts of the initial products of decane combustion in the absence and presence of hydrogen bromide is shown in table 3.11. The hydrogen halide has a dramatic effect at all temperatures studied. Its presence decreases the amount of both decyl monohydroperoxides and other peroxides almost to zero and concurrently strikingly increases the quantity of C_{10} ketones. A decrease in the concentrations of C_{10} O-heterocyclic compounds, decenes and, to a lesser extent, aldehydes, methyl ketones and 1-alkenes with less than ten carbon atoms occurs simultaneously with a large rise in the concentration of lower alkanes. Small quantities of primary alcohols containing up to eight carbon atoms were also detected in the reaction products when hydrogen bromide was present.

Table 3.11

Effect of HBr on the initial products of decane combustion

Concentration of products expressed as 10^3 moles per mole decane.

Temperature (K)	Absence of HBr			Presence of 5% HBr		
	458	483	503	458	483	503
Decyl monohydroperoxides	78.3	21.3	15.4	8.4	-	-
Decane dihydroperoxides	186.0	74.2	36.1	-	-	-
O-heterocycles	11.0	152.2	260.1	-	67.7	95.2
Decan-5-one } Decan-4-one }	3.3	14.4	17.9	253.2	101.7	38.8
Decan-3-one } Decan-3-ol }	2.3	10.7	10.8	109.4	45.9	18.5
Decan-2-one	1.8	7.1	11.6	120.4	52.3	20.4
Decan-2-ol	1.8	6.7	3.1	27.1	22.6	7.2
Decan-4-ol	2.1	8.4	2.9	45.4	36.8	8.9
Decan-5-ol	1.2	5.4	2.8	24.0	19.8	6.0
Decanal	1.8	3.8	3.2	-	-	-
Total C_{10} alcohols & ketones	14.3	58.5	52.3	579.5	179.1	99.8

Table 3.11 (continued)

Effect of HBr on the initial products of decane combustion

Concentration of products expressed as 10^3 moles per mole decane.

Temperature (K)	Absence of HBr			Presence of 5% HBr		
	458	483	503	458	483	503
Nonan-2-one	4.5	17.5	14.3	3.4	10.2	8.2
Octan-2-one Octanal	16.5	60.0	28.0	7.1	38.9	25.8
Heptan-2-one Heptanal	23.1	58.9	40.0	12.6	39.1	32.8
Hexan-2-one Hexanal	24.1	66.8	44.0	19.7	48.4	39.5
Pentan-2-one Pentanal	44.0	91.8	56.2	36.0	86.1	50.9
Butan-2-one	9.6	37.0	11.8	7.6	10.6	15.1
Butanal	12.7	72.9	30.5	18.1	59.8	25.8
Propan-2-one	5.1	25.5	12.2	11.8	19.6	10.5
Propanal	7.4	19.4	-	7.1	21.1	-
Total carbonyls $< C_{10}$	143.0	449.3	237.2	123.4	333.9	208.6

Table 3.11 (continued)

Effect of HBr on the initial products of decane combustion

Concentration of products expressed as 10^3 moles per mole decane.

Temperature (K)	Absence of HBr			Presence of 5% HBr		
	458	483	503	458	483	503
Decenes	-	26.2	125.6	-	16.0	58.1
Non-1-ene	-	1.4	24.2	-	1.6	17.1
Oct-1-ene	-	0.9	81.0	-	0.7	55.5
Hept-1-ene	-	1.2	74.9	-	1.0	56.6
Hex-1-ene	-	0.8	52.2	-	0.7	35.7
Pent-1-ene	-	0.6	25.1	-	1.2	11.6
Total alkenes $< C_{10}$	-	4.9	267.4	-	5.2	176.5
Octane	-	-	33.1	-	-	34.4
Heptane	-	3.6	3.4	-	10.2	59.4
Hexane	-	2.7	6.6	-	5.5	40.8
Pentane	-	2.1	2.6	-	6.5	17.1
Total alkanes $< C_{10}$	-	8.4	12.6	-	22.2	117.3
Termination products	7.6	8.6	3.1	4.3	8.2	7.1

3.3 The liquid-phase oxidation of decane

Reactions were performed at 423 K using 5 cm^3 of decane in the reactor, a flow of oxygen of 60 cm^3 min^{-1} and reaction times of 0.5 to 4 h. No appreciable quantities of products were collected in the cold traps situated after the reactor. The yields of the principal products based on the same classification as in Section 3.2 is shown in figure 3.21. The only peroxidic products detected were decyl monohydroperoxides, which were major products under all conditions studied. The yields of non-peroxidic products containing ten carbon atoms were much greater than those of aldehydes and methyl ketones with less than ten carbon atoms. No O-heterocyclic compounds or decenes were detected in the reaction products.

Table 3.12 lists the individual product concentrations. It is apparent that, in the liquid phase, decan -1-ol is formed only in the later stages of reaction and its yield is much smaller than that of the other decanols. Primary alcohols with two to eight carbon atoms are detected in the liquid phase but there is a long delay before they are formed and even then their concentrations were small.

Figure 3.21

Variation of the yields of the major products of liquid-phase oxidation

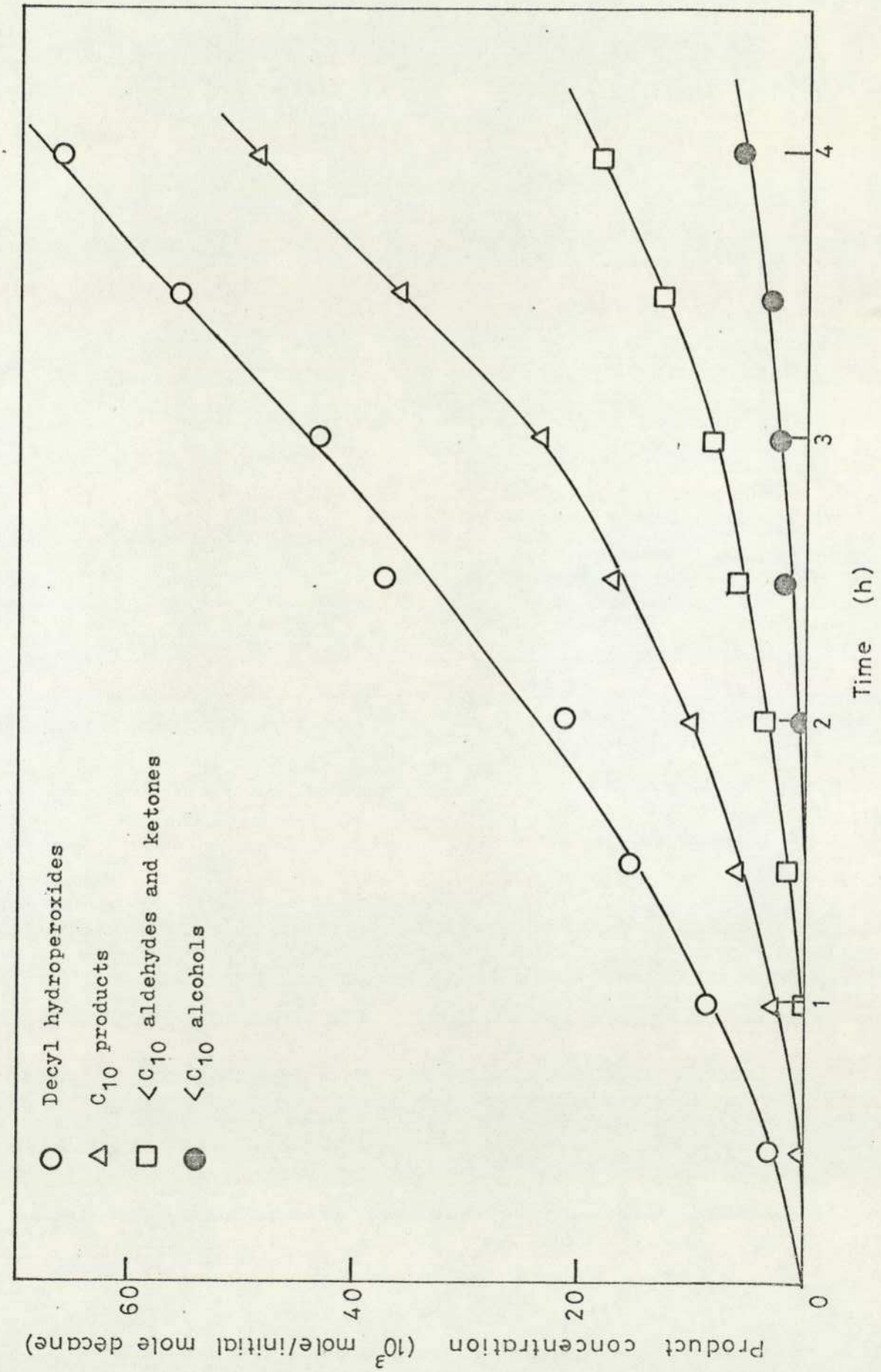


Table 3.12

Product yield from liquid-phase oxidation

Product concentration expressed as 10^4 moles per initial mole decane.

Time (h)	0.5	1	1.5	2	2.5	3	3.5	4
Decyl monohydroperoxides	25.4	75.8	155.8	211.6	386.4	431.0	563.2	662.8
Decan-5-one } Decan-4-one }	2.4	5.6	15.0	26.4	47.2	57.2	83.4	111.0
Decan-3-one } Decan-3-ol }	1.2	3.1	8.1	14.4	26.7	36.9	55.3	63.5
Decan-2-one	0.5	2.0	6.8	13.0	30.2	39.8	43.0	74.5
Decan-2-ol	0.1	2.1	8.5	13.3	30.4	35.1	50.2	73.2
Decan-4-ol	1.0	3.1	9.0	14.5	29.1	37.6	58.4	83.0
Decan-5-ol	0.5	2.2	5.6	9.5	20.5	25.3	42.4	34.9
Decan-1-ol	-	-	1.2	2.4	5.2	6.0	10.4	17.3
Decanal	0.5	2.3	5.9	6.9	7.8	8.7	9.6	10.8
Total C_{10} alcohols & ketones	6.2	20.4	60.1	100.4	197.1	246.6	352.7	488.2
Termination products	-	0.1	1.8	2.9	8.9	12.4	18.6	26.0

Table 3.12 (continued)

Product yield from liquid-phase oxidation

Product concentration expressed as 10^4 moles per initial mole decane.

Time (h)	0.5	1	1.5	2	2.5	3	3.5	4
Nonan-2-one	-	-	0.8	1.0	2.9	3.2	6.2	8.0
Nonanal	-	-	0.3	0.5	0.8	1.2	1.8	2.1
Octan-2-one	0.1	0.6	3.7	5.4	11.2	14.9	33.0	34.3
Octanal	-	0.5	2.7	3.4	6.0	8.6	9.2	10.6
Heptan-2-one	-	0.9	2.1	3.9	8.8	13.8	25.3	28.7
Heptanal	-	0.1	1.0	2.1	4.2	6.0	11.7	12.5
Hexan-2-one } Hexanal }	0.1	2.3	4.5	6.2	11.3	14.6	23.8	39.9
Pentan-2-one } Pentanal }	0.3	0.7	2.2	3.3	8.9	15.5	20.4	24.3
Butan-2-one	0.1	0.2	0.3	0.6	1.2	1.7	2.8	3.4
Butanal	0.5	1.3	1.8	2.6	3.8	4.6	5.2	6.3
Propan-2-one	-	0.1	0.2	0.3	1.6	2.6	2.7	4.5
Propanal	0.2	0.4	0.6	0.8	3.3	5.3	8.2	9.8
Acetaldehyde	0.2	0.5	0.7	1.1	5.7	7.4	9.9	14.1
Total carbonyls $< C_{10}$	1.5	7.6	20.9	31.2	59.7	99.4	150.2	198.5

Table 3.12 (continued)

Product yield from liquid-phase oxidation

Product concentration expressed as 10^4 moles per initial mole decane.

Time (h)	0.5	1	1.5	2.0	2.5	3	3.5	4
Octanol	-	-	-	-	1.5	2.2	6.4	7.9
Heptanol	-	-	0.2	0.4	2.5	1.9	3.9	5.6
Hexanol	-	-	1.2	2.1	2.8	3.5	4.9	5.6
Pentanol	0.3	0.5	1.5	2.3	3.2	4.4	5.5	6.3
Butanol	0.2	0.5	1.2	1.8	2.8	3.1	4.9	6.4
Ethanol	-	0.2	0.5	1.1	2.0	3.1	3.3	3.7
Total alcohols $<C_{10}$	0.5	1.2	4.6	7.7	14.8	18.2	28.9	35.5

SECTION 4

DISCUSSION

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4.1 General features of decane combustion

4.1.1 Ignition profiles

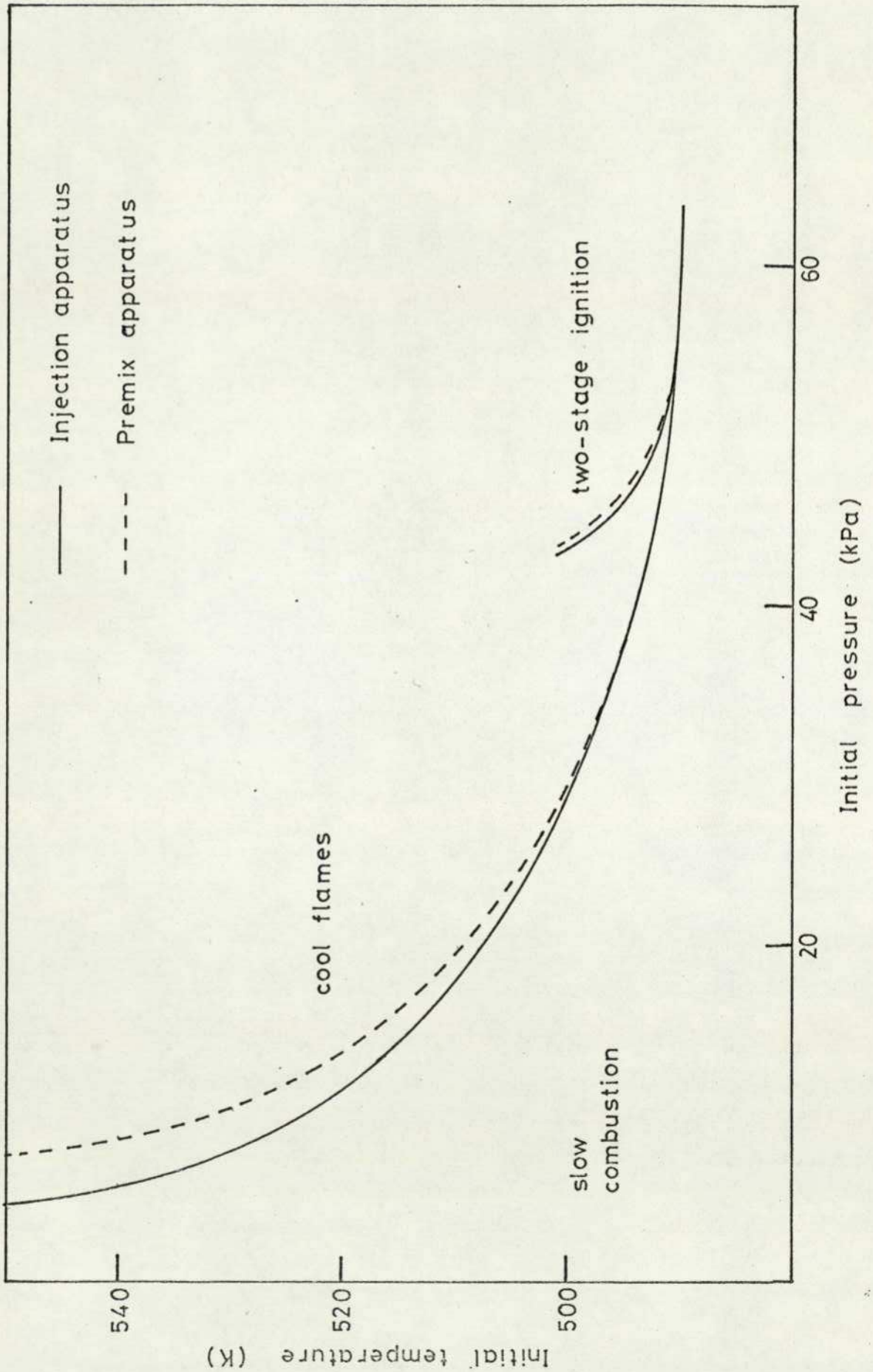
The ignition profiles obtained for 1:25 and 1:75 mixtures of decane and air using the injection apparatus have a structure similar to those previously reported for 1:10 and 1:17.5 decane:air mixtures in a premix apparatus[82]. The minimum spontaneous ignition temperatures measured, 490 K and 498 K for decane:air mixtures of 1:25 and 1:75 respectively, are also in good agreement. Figure 4.1 shows a comparison of the slow combustion/cool flame boundary for the 1:25 decane:air mixture, using the injection apparatus, with that previously obtained in a premix apparatus. It can be seen that there is a good correlation between the results obtained from the two sets of apparatus. The occurrence of a cool flame at pressures slightly lower than those needed in the premix apparatus may be explained by the initiation and propagation of the flame in a fuel-rich area of the reaction vessel before the fuel and air are thoroughly mixed.

The complete absence of secondary cool flames in a 1:75 decane:air mixture and the undefined multiple cool flame/single cool flame boundary in the 1:25 decane:air mixture may be explained by the use of air-rich mixtures in this study. Gray and Felton[92] have shown that an indefinite number of cool flames may be produced in a stirred flow reactor, where there is continual replenishment of the fuel and oxidant.

The existence of lobes on the two-stage ignition profile is associated with changes in the mechanism of oxidation with temperature. Antonik and Lucquin[24,93] have proposed that these lobes are due to changes in the nature of the chain-

Figure 4.1

Comparison of the slow combustion/cool flame boundary for a 1:25 decane:air mixture in a premix system and an injection system



branching agent. Thus lobe A (figure 3.5) has previously been assigned[82] to the L_1 mechanism in which the degenerate chain-branching agents are decyl monohydroperoxides formed by the reaction of decylperoxy radicals:

$$C_{10}H_{21}O_2^{\bullet} \rightarrow AH + {}^{\bullet}OH$$

$$C_{10}H_{21}O_2^{\bullet} + AH \rightarrow C_{10}H_{21}OOH + A^{\bullet}$$

$$C_{10}H_{21}OOH \rightarrow C_{10}H_{21}O^{\bullet} + {}^{\bullet}OH$$

Here AH is a compound such as an aldehyde which contains a hydrogen atom more readily abstracted than those in decane. However the presence of dihydroperoxides in the reaction products indicates that the mechanism is not so simple. Degenerate chain-branching at these temperatures may also be due, therefore, to the decomposition of dihydroperoxides:

$$HOOC_{10}H_{20}OOH \rightarrow \text{carbonyl compounds} + 2{}^{\bullet}OH$$

Similarly lobe B has been assigned to an L_2 mechanism in which aldehydes are further oxidised to peracids, which then act as the degenerate chain-branching agent:

$$RCHO + X^{\bullet} \rightarrow RCO^{\bullet} + XH$$

$$RCO^{\bullet} + O_2 \rightarrow RCOOO^{\bullet}$$

$$RCOOO^{\bullet} + AX \rightarrow RCOOH + A^{\bullet}$$

$$RCOOOH \rightarrow RCOO^{\bullet} + {}^{\bullet}OH$$

Here, the abstracting radical, $X^{\bullet}$, may be either a hydroperoxy or a hydroxy radical and the hydrogen donor is assumed to be another aldehyde molecule.

The occurrence of a change in mechanism between lobes A and B is supported by the kinetic parameters measured for the combustion reaction. Thus a plot of the variation of the induction period of the cool flame with reciprocal temperature (figure 3.9) shows a marked change of slope at 540 K.

4.1.2 Cool flame kinetics

In a reaction vessel of constant volume, the maximum pressure rise accompanying a cool flame, ΔP, results from both a temperature rise due to the exothermicity of the reaction and a concurrent increase in the number of molecules present. Since these changes are to a large extent interdependent, the usefulness of the parameter, ΔP, is rather limited. It does, however, allow a further comparison to be made between the results obtained in different investigations. In this study the value of m in the equation

$$\Delta P = AP_o^{m}$$

varied between 1.3 and 1.7 in the premix apparatus and between 1.2 and 1.7 in the injection apparatus, compared with values of m from 1.2 to 1.7 previously reported for decane combustion[82].

It has been shown (figures 3.2, 3.7, and 3.9) that, at constant temperature, the length of the induction period

preceding the cool flame, τ, decreases as the pressure or concentration of reactants increases. This supports previous suggestions[9,16] that the induction period may be related to the reaction rate and may be expressed in the form of an Arrhenius equation:

$$\text{Rate} \quad \tau = A\exp(E_{eff}/RT_o)$$

where A is a constant, R is the gas constant, T_o is the initial temperature and E_{eff} is the effective overall activation energy of the initial reactions. Thus

$$\ln\tau = \ln A + E_{eff}/RT_o$$

and a plot of $\ln\tau$ against $1/T_o$ should be a straight line. Figure 3.9 shows that this is indeed the case; and the value of the overall activation energy for a 1:25 decane:air mixture, calculated from figure 3.9, was found to be 184 kJ $mole^{-1}$ below 540 K and showed little variation with pressure. At higher temperatures E_{eff} varied with pressure between 113 and 142 kJ $mole^{-1}$. These values compare with values of E_{eff} of 178 kJ $mole^{-1}$ at higher temperatures previously reported for a 1:15 decane:air mixture[82]. This effective activation energy refers to all the processes leading to the cool flame and is therefore of little use in elucidating the mechanism of individual cool-flame reactions; the sharp discontinuity in the plot does, however, provide an indication of an overall change in mechanism at 540 K.

4.1.3 Effect of additives

The previous sections have shown that an injection apparatus may be used to study gas-phase oxidation and that the results obtained are directly comparable with those previously reported for premix systems. It was possible, therefore, to study the effect of certain high molecular weight fuel additives

on the ignition profiles of decane:air mixtures and the results have been presented in Section 3.1.2.3.

The effect of adding 0.17% v/v of ethylene glycol monoethyl ether to decane was to depress the slow combustion/cool-flame boundary of a 1:25 fuel:air mixture to lower temperatures and pressures. This result is not suprising, as it has been reported previously[94] that ethylene glycol monoethyl ether as a 0.15% v/v solution in decane decreases the flash point of decane by 4^{o}.

The static dispersant agent is a complex mixture of organometallic compounds containing chromium and sodium ions. The propagation of cool flames in a 1:25 fuel:air mixture containing a solution of 0.1% v/v of this additive in decane occurred at slightly lower pressures than with pure decane and could be explained by the catalytic effect of these metal ions on the oxidation reactions. It is well known[81] that metal ions promote the decomposition of peroxidic species:

$$ROOH + M \rightarrow RO^{\bullet} + {}^{\bullet}OH + M$$

Thus, if peroxidic compounds are responsible for chain-branching leading to cool-flame propagation, then this reaction could provide an explanation, although in the absence of detailed analytical results for this system this suggestion is inconclusive.

4.2 Mechanism of the oxidation and combustion of decane

4.2.1 Liquid-phase oxidation

The main products of the liquid-phase oxidation of decane at 423 K were decyl monohydroperoxides. This, and the formation of smaller quantities of decanones and decanols, agrees with previous studies of decane oxidation[95,96].

The following hydroperoxide chain mechanism has been shown to account for the oxidation of a wide variety of organic compounds in the liquid phase at temperatures below 473 K:[68]

initiation — production of $R^\bullet$ radicals (4.1)

propagation

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \quad (4.2)$$

$$RO_2^\bullet + RH \rightarrow ROOH + R^\bullet \quad (4.3)$$

termination

$$R^\bullet + R^\bullet \rightarrow \left.\right\} \quad (4.4)$$

$$R^\bullet + RO_2^\bullet \rightarrow \left.\right\} \text{non-radical products} \quad (4.5)$$

$$RO_2^\bullet + RO_2^\bullet \rightarrow \left.\right\} \quad (4.6)$$

The extent to which each of these steps may be used to describe the oxidation of decane will be considered in the following sections.

4.2.1.1 Initial attack

In the absence of a radical initiator, light or ionising radiation, the first radicals in liquid-phase hydrocarbon oxidation are formed by reaction (4.7)[71]

$$C_{10}H_{22} + O_2 \rightarrow C_{10}H_{21}^{\bullet} + HO_2^{\bullet} \qquad (4.7)$$

However, even in the very early stages of the oxidation, this reaction is superseded by secondary initiation involving the abstraction of a hydrogen atom by a radical.

$$C_{10}H_{22} + X^{\bullet} \rightarrow C_{10}H_{21}^{\bullet} + XH \qquad (4.8)$$

Except with very reactive radicals which lead to unselective attack of the hydrocarbon, the activation energy of reaction (4.8) is dependent on the strength of the C-H bond broken. Since the primary C-H bond strength[97] is 410 kJ mole^{-1} compared with 396 kJ mole^{-1} for secondary C-H bonds[98], secondary decyl radicals will be formed preferentially. Although it was not possible to resolve the decyl monohydroperoxides into individual isomers, there was complete absence of both decan-1-ol and decanal in the reaction products during the initial stages of the reaction. As these products could be formed only from primary decyl radicals, this indicates that the initial attack on the decane molecule involves predominantly removal of secondary hydrogen atoms. The formation of secondary decyl alcohols and ketones in approximately equal amounts at the 2 - 5 positions shows that the attack is distributed almost equally between the methylene groups of the decane chain; this is in agreement with the results of previous studies of the liquid-phase oxidation of this hydrocarbon[99].

4.2.1.2 Propagation

Reaction (4.2), the addition of oxygen to a decyl radical, has zero activation energy and is therefore unlikely to be the rate-determining step[73,74]. However it has been shown that the rate of dodecane oxidation in the liquid phase at 473 K is limited by the rate of oxygen diffusion from the gas phase[80]. As it was not possible to use high oxygen flow rates in the present study, diffusion controlled kinetics are expected.

The chain cycle is completed by decylperoxy radicals, formed in reaction (4.2), abstracting a hydrogen atom from an initial fuel molecule to form decyl monohydroperoxides

$$C_{10}H_{21}OO^{\bullet} + C_{10}H_{22} \rightarrow C_{10}H_{21}OOH + C_{10}H_{21}^{\bullet} \qquad (4.3)$$

4.2.1.3 Decomposition of hydroperoxides

The thermal decomposition of a hydroperoxide is generally a complex process, since at least three different reactions can occur simultaneously.

$$C_{10}H_{21}OOH \rightarrow C_{10}H_{21}O^{\bullet} + {}^{\bullet}OH \qquad (4.9)$$

$$C_{10}H_{22} + C_{10}H_{21}OOH \rightarrow C_{10}H_{21}O^{\bullet} + C_{10}H_{21}^{\bullet} + H_2O \qquad (4.10)$$

$$2C_{10}H_{21}OOH \rightleftharpoons (C_{10}H_{21}O\overset{H}{\overset{|}{C}}- - - HOOC_{10}H_{21})$$
$$\rightarrow C_{10}H_{21}O^{\bullet} + H_2O + C_{10}H_{21}OO^{\bullet} \qquad (4.11)$$

The simplest type of decomposition (reaction 4.9) involves the unimolecular fission of the peroxide link. Reaction (4.10) has been proposed to explain the dependence of the unimolecular

decay of the hydroperoxide on the nature of the solvent[100]. A hydrogen-bonded complex has been postulated in order to explain the observed bimolecular decomposition of the hydroperoxide at higher concentrations (reaction 4.11)[101]. These reactions produce decyl, decyloxy and decylperoxy radicals and it is not possible to determine which is the main process occurring under the conditions used in the present study. However the activation energy of reaction (4.11) is believed to be lower than that of reaction (4.9)[76]; consequently, bimolecular decomposition will probably predominate at low temperatures.

4.2.1.4 Reactions of decyloxy radicals

Alkoxy radicals, which are produced by the decomposition of hydroperoxides may decompose by the elimination of a radical fragment. Thus a 2-decyloxy radical may decompose to yield acetaldehyde and an octyl radical[102]

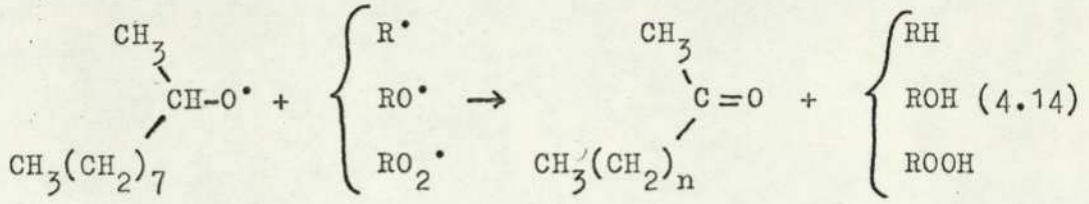
$$CH_3(CH_2)_6CH_2\overset{O^\bullet}{\overset{|}{C}}HCH_3 \rightarrow CH_3(CH_2)_6CH_2^\bullet + CH_3CHO \qquad (4.12)$$

Reaction (4.12) may therefore account for the small yields of carbonyl compounds with less than ten carbon atoms formed.

Decyloxy radicals may also be reduced by the substrate or some oxidation product to form decanols.

$$C_{10}H_{21}O^\bullet + \begin{cases} RH \\ ROOH \\ RCHO \end{cases} \text{ -- } C_{10}H_{21}OH + \begin{cases} R^\bullet \\ RO_2^\bullet \\ RC^\bullet O \end{cases} \qquad (4.13)$$

The oxidation of decyloxy radicals by another radical may likewise occur to give decanones.

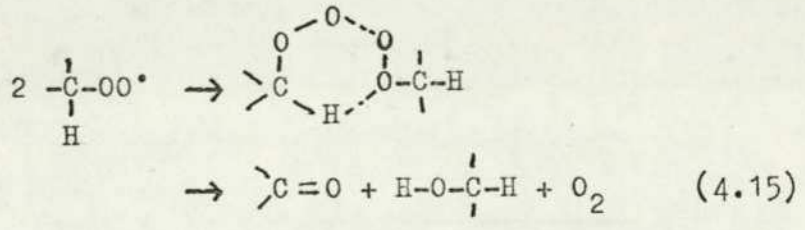


(4.14)

It has previously been shown[76] that reaction (4.13), the formation of an alcohol, occurs more readily than reaction (4.14) in liquid-phase oxidation. However table 3.12 shows that in the present study, decanones and decanols are formed in roughly equal amounts; this indicates that these products are probably formed by other reactions.

4.2.1.5 Termination

As shown in the general scheme for liquid-phase hydrocarbon oxidation (Section 2.1), termination occurs when two radicals react to yield non-radical products. Since reaction (4.2), the addition of oxygen to a decyl radical, is fast, termination reactions are likely to involve the mutual reaction of decylperoxy radicals. It has been suggested[103] that the self-reaction of secondary peroxy radicals involves the decomposition of a tetroxide by way of a cyclic transition state in which one of the α-hydrogen atoms is transferred to give a ketone, alcohol and oxygen.



(4.15)

This reaction would give rise to the observed formation of equal quantities of decanones and decanols.

The formation of small quantities of compounds containing more than ten carbon atoms indicates that other termination processes involving the recombination of radicals are also occurring. However further discussion concerning the mechanism of formation of these products is precluded due to the difficulties associated with analysing the very small amounts of these high molecular weight compounds.

4.2.2 Low-temperature combustion

Reactions performed in the metal-free apparatus at temperatures between 445 and 473 K showed that the main products of decane combustion were decyl monohydroperoxides and aldehydes and ketones containing less than ten carbon atoms. Smaller quantities of O-heterocyclic compounds containing ten carbon atoms and C_{10} alcohols and ketones were also formed. As the temperature was increased from 445 to 473 K, the yield of monohydroperoxides decreased relative to that of dihydroperoxides. However, the total percentage yield of peroxides decreased and there was a concurrent increase in yields of other products, especially O-heterocyclic compounds. No decenes were detected in this temperature range.

An increase in the concentration of oxygen present in the reaction mixture increased the yields of decane dihydroperoxides and carbonyl compounds with less than ten carbon atoms, while the yields of the decyl monohydroperoxides, O-heterocyclic compounds, decanols and decanones decreased.

Although there was little effect on increasing the

concentration of decane in the reaction mixture during slow combustion, an overall trend may be observed in tables 3.8 and 3.9. Thus the yields of decyl monohydroperoxides and decanones and decanols increased slightly with increasing decane concentration and there was a concurrent decrease in the yields of the decane dihydroperoxides, O-heterocycles and carbonyl compounds with less than ten carbon atoms.

4.2.2.1 Initial attack

The initial attack on the decane molecule involves the abstraction of a hydrogen atom to yield a decyl radical. Such abstraction may, in principle, occur at either of the two end carbon atoms of the C_{10} chain to yield a primary decyl radical (reaction 4.8a) or at any of the other eight intermediate carbon atoms to yield a secondary decyl radical (reaction 4.8b):

$$CH_3(CH_2)_8CH_3 + X^{\bullet} \rightarrow CH_3(CH_2)_8\dot{C}H_2 + XH \qquad (4.8a)$$

$$CH_3(CH_2)_7CH_2CH_3 + X^{\bullet} \rightarrow CH_3(CH_2)_7\dot{C}HCH_3 + XH \qquad (4.8b)$$

The abstracting species, $X^{\bullet}$, may be an oxygen molecule, a hydroperoxy radical or a hydroxyl radical. Oxygen and hydroperoxy radicals are well known to be selective in the position they attack[104] and, since the primary C-H bond strength[97] is 410 kJ $mole^{-1}$ compared with 396 kJ $mole^{-1}$ for secondary C-H bonds[98], secondary decyl radicals will be preferentially formed in this case. However, although decan-1-ol was not detected in the reaction products, an appreciable quantity of decanal was

present in the initial stages of the reaction. As this product can be formed only from primary decyl radicals, hydroxyl radicals, which are relatively unselective in their attack, must also act as the abstracting species in the low temperature region.

This suggestion is confirmed by the results obtained when hydrogen bromide is added to the reaction mixture. Table 3.11 shows that the yield of decanal decreased in the presence of hydrogen bromide. This indicates that hydroxyl radicals are being removed by reaction with hydrogen bromide (reaction 4.16) which occurs with virtually zero activation energy.

$$HBr + {}^{\bullet}OH \rightarrow Br^{\bullet} + H_2O \qquad (4.16)$$

The addition of hydrogen bromide is known to promote the low temperature oxidation of hydrocarbons by enhancing the chain initiation, propagation and branching processes[34]. This is due to the lower H-Br bond strength of 365 kJ mole^{-1} compared with that of 396 kJ mole^{-1} for secondary C-H bonds. During the initial stages of the reaction, chain initiation and propagation will therefore take place by reactions involving bromine atoms

$$C_{10}H_{22} + Br^{\bullet} \rightarrow HBr + C_{10}H_{21}^{\bullet} \qquad (4.17)$$

The rates of attack by bromine atoms on primary and secondary hydrogen atoms may be calculated from the rate parameters for this reaction[97,105] and at 458 K, the ratio of the rates of formation of primary decyl radicals to secondary radicals will be 0.05:1. Thus, if bromine atoms are responsible for chain initiation and propagation, the rate of production of primary decyl radicals

will be extremely low, which explains the very small yields of decanal observed when hydrogen bromide is present.

4.2.2.2 Reactions of decyl radicals with oxygen

The production of five different decyl radicals gives rise to the very complex product distribution which was found in decane oxidation even at low temperatures. To simplify the reaction scheme, only the 2-decyl radical will be considered, although it should be noted that, unless otherwise stated, the reactions shown will occur for all five decyl radicals.

The decyl radicals so formed may react with oxygen in basically two ways. Their reaction can be either additive (reaction 4.2), the decyl radical combining with an oxygen molecule to form a decylperoxy radical, or abstractive (reaction 4.18), the oxygen molecule removing a further hydrogen atom from the decyl radical to yield a hydroperoxy radical and the conjugate alkene.

$$CH_3(CH_2)_6CH_2\dot{C}HCH_3 + O_2 \rightarrow CH_3(CH_2)_6CH_2\underset{\displaystyle OO^{\bullet}}{\underset{|}{C}}HCH_3 \qquad (4.2)$$

$$CH_3(CH_2)_6CH_2\dot{C}HCH_3 + O_2 \rightarrow CH_3(CH_2)_6CH{=}CHCH_3 + HO_2^{\bullet} \qquad (4.18)$$

At temperatures below 473 K the main reaction of decyl radicals with oxygen must be additive (reaction 4.2), as no decenes were detected in the reaction products. Reaction (4.2) has an activation energy close to zero, so that the rate constant will be approximately equal to the pre-exponential factor. Various theoretical estimates and experimental determinations have been made, and the accepted mean value appears to be 10^9 l mole^{-1} s^{-1} [40,53].

4.2.2.3 Reactions of decylperoxy radicals

It has often been postulated that, at low temperatures, the predominant fate of alkylperoxy radicals is their abstraction of a hydrogen atom from an original fuel molecule to form the alkyl hydroperoxide, although there is relatively little support for this reaction in most systems studied. However, in the present case, this reaction is likely to be the source of the relatively large amounts of decyl monohydroperoxides positively identified.

$$CH_3(CH_2)_6CH_2\overset{\overset{OO^\bullet}{|}}{C}HCH_3 + C_{10}H_{22} \rightarrow CH_3(CH_2)_6CH_2\overset{\overset{OOH}{|}}{C}HCH_3 + C_{10}H_{21}^\bullet \quad (4.3)$$

At present there appears to be no reliable value reported for the rate constant for alkylperoxy radical abstraction reactions in the gas phase. However, if $D(RO_2 - H)$ equals $D(HO_2 - H)$, as has been suggested by Benson[106], then $E(RO_2^\bullet + RH)$ will be approximately equal to $E(HO_2^\bullet + RH)$. This led Walker[40] to recommend a value of 1×10^9 l mole^{-1} s^{-1} for the pre-exponential factor of reaction (4.3) and activation energies of 81.0, 71.3 and 60.3 kJ mole^{-1} respectively when primary, secondary or tertiary bonds are broken. Hence at 453 K, the rate constant for the formation of decyl monohydroperoxides, involving abstraction of a secondary hydrogen atom by decylperoxy radicals, will be 6.0 l mole^{-1} s^{-1}.

As the overall reaction proceeds, decylperoxy radicals will tend to abstract hydrogen atoms preferentially from further reaction products such as aldehydes rather than from a fuel molecule, as the C-H bond dissociation energy in an aldehyde is 364 kJ mole^{-1} compared with 395 kJ mole^{-1} for a secondary C-H bond in decane[40]. This explains the smaller effect of increasing decane concentration compared with that which occurred for a

corresponding increase in oxygen concentration in the reaction mixture.

An increase in the rate of formation of decyl monohydroperoxides due to reaction (4.19) would also be expected in the presence of hydrogen bromide

$$C_{10}H_{21}OO^{\bullet} + HBr \rightarrow C_{10}H_{21}OOH + Br^{\bullet} \qquad (4.19)$$

Work by Poroikova et al[48] has indicated that for propylperoxy radicals the rate of reaction (4.19) is given by $k = 10^{10}\exp(-28000/RT)$ l mole^{-1} s^{-1}. Thus, if the rate constant for abstraction of hydrogen by decylperoxy radicals is similar, reaction (4.19) will have a rate constant of 6.4×10^{6} l mole^{-1} s^{-1} at 453 K.

Previous studies[67] of the slow oxidation of $C_6 - C_8$ hydrocarbons in the presence of hydrogen bromide, between 423 and 463 K, showed that the main products were indeed alkyl monohydroperoxides. However, Table 3.11 shows that in this study the presence of hydrogen bromide did not increase the net yield of decyl monohydroperoxides presumably due to simultaneous catalysis by the halogen compound of decomposition of the peroxide (see Section 4.2.2.4).

Decylperoxy radicals may also react to give decyloxy radicals

$$2CH_3(CH_2)_6CH_2\underset{\displaystyle OO^{\bullet}}{\underset{|}{C}}HCH_3 \rightarrow 2CH_3(CH_2)_6CH_2\underset{\displaystyle O^{\bullet}}{\underset{|}{C}}HCH_3 + O_2 \qquad (4.20)$$

However, as in the liquid phase, the self-reaction of decylperoxy radicals may also result in direct termination

$$2CH_3(CH_2)_6CH_2\underset{\displaystyle OO^{\bullet}}{\underset{|}{C}}HCH_3 \rightarrow CH_3(CH_2)_6CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 + CH_3(CH_2)_6CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_3 + O_2 \qquad (4.21)$$

Although both decanols and decanones were found in the combustion products of decane, reaction (4.21) is unlikely to be the only route for their formation as their yields were dissimilar. Parkes[108] has shown that for methylperoxy radicals the ratio $k_{4.20}/k_{4.21} = 0.5$ at 298 K, but at about 475 K reaction (4.20) is dominant. In a later paper[109], the ratio $k_{4.20}/k_{4.21}$ is given as 0.72 for isopropylperoxy radicals at 303 K and it is also reported that for all self-reactions of isopropylperoxy radicals the pre-exponential factor is 1.43×10^9 l mole^{-1} s^{-1} and the activation energy is 18.6 kJ mole^{-1}. Use of values of $A = 10^9$ l mole^{-1} s^{-1} and $E = 18.6$ kJ mole^{-1} gives a rate constant for the self-reactions of decylperoxy radicals at 453 K of 7×10^6 l mole^{-1} s^{-1}. Since reaction (4.20) is dominant at this temperature, the disproportionation of decylperoxy radicals will therefore be an important step in the formation of decyloxy radicals, provided that there is a sufficient concentration of decylperoxy radicals present.

4.2.2.4 Reactions of decyl monohydroperoxides

Decyl monohydroperoxides will decompose by scission of the peroxidic O-O bond, D(O-O) = 180 kJ mole^{-1}, to yield decyloxy radicals

$$CH_3(CH_2)_6\overset{\overset{OOH}{|}}{CH_2}CHCH_3 \rightarrow CH_3(CH_2)_6\overset{\overset{O^{\bullet}}{|}}{CH_2}CHCH_3 + {}^{\bullet}OH \qquad (4.9)$$

Reaction (4.9) has a high activation energy of the order of 158 to 162 kJ mole^{-1} [52,110], with a pre-exponential factor of approximately 10^{14} s^{-1}. Thus, at 453 K, the decomposition of decyl monohydroperoxide will have a rate constant of 3×10^{-5} s^{-1}.

The decane dihydroperoxides found in large amounts in

the reaction products could possibly be formed by the further reaction of decyl monohydroperoxides since at 453 K the dihydroperoxides are initially formed in smaller quantities than the monohydroperoxides (see figure 3.15). Such a reaction would involve the abstraction of a hydrogen atom from the decyl monohydroperoxide. The hydrogen atom on the same carbon atom as the -OOH group in the secondary decyl monohydroperoxides will be preferentially abstracted since it is in a sense equivalent to a tertiary hydrogen atom

$$CH_3(CH_2)_6CH_2\overset{\overset{OOH}{|}}{C}HCH_3 + X^{\bullet} \rightarrow CH_3(CH_2)_6CH_2\overset{\overset{OOH}{|}}{\underset{\bullet}{C}}CH_3 + XH \qquad (4.22)$$

Subsequent addition of oxygen will form a hydroperoxydecylperoxy radical (reaction 4.23) which may then abstract a hydrogen atom from a fuel molecule to form the dihydroperoxide (reaction 4.24)

$$CH_3(CH_2)_6CH_2\overset{\overset{OOH}{|}}{\underset{\bullet}{C}}CH_3 + O_2 \rightarrow CH_3(CH_2)_6CH_2\overset{\overset{OOH}{|}}{\underset{\underset{OO^{\bullet}}{|}}{C}}CH_3 \qquad (4.23)$$

$$CH_3(CH_2)_6CH_2\overset{\overset{OOH}{|}}{\underset{\underset{OO^{\bullet}}{|}}{C}}CH_3 + C_{10}H_{22} \rightarrow CH_3(CH_2)_6CH_2\overset{\overset{OOH}{|}}{\underset{\underset{OOH}{|}}{C}}CH_3 + C_{10}H_{21}^{\bullet} \qquad (4.24)$$

However, as no products containing two functional groups on the same carbon atom were detected, it is unlikely that reactions (4.23) and (4.24) are occurring. This is probably due to the steric hindrance of the -OOH group preventing the addition of oxygen to the hydroperoxydecyl radicals formed in reaction (4.22); these radicals, if formed, are therefore more likely to decompose to give decanones

$$CH_3(CH_2)_6CH_2\overset{\overset{OOH}{|}}{\underset{\bullet}{C}}CH_3 \rightarrow CH_3(CH_2)_6CH_2\overset{\overset{O}{\|}}{C}CH_3 + {}^{\bullet}OH \qquad (4.25)$$

the high RO-OH dissociation energy being reduced by the large heat of formation of the C=O bond.

As the reaction products can be satisfactorily explained only by the decomposition of α-, β- or γ-dihydroperoxides (Section 4.2.2.9) it is unlikely that any other hydrogen atom is being abstracted in reaction (4.22), since this would necessarily lead to the formation of ethyl and propyl ketones which were not detected. Thus it is unlikely that decyl monohydroperoxides are the precursors to dihydroperoxide formation.

The most striking effect of adding hydrogen bromide to the reaction mixture was the almost complete elimination of all hydroperoxides, only a very small quantity of decyl monohydroperoxide being formed at 458 K. This rather unexpected result may be explained by the hydrogen bromide catalysed decomposition of the decyl monohydroperoxides to yield decanones which were found as the major product.

Previous studies of the decomposition of tertiary butyl hydroperoxide[111] and 2-pentyl hydroperoxide[60] have shown that in the presence of hydrogen bromide the main product is the corresponding ketone, which is believed to be formed by reaction (4.26)

$$CH_3(CH_2)_6CH_2\underset{\underset{O\text{-}OH}{|}}{\overset{\overset{H}{|}}{C}}\text{-}CH + Br^{\bullet} \rightarrow CH_3(CH_2)_6CH_2\underset{\underset{O\text{-}OH}{|}}{\overset{\overset{\bullet}{|}}{C}}\text{-}CH_3 + HBr$$

$$\rightarrow CH_3(CH_2)_6CH_2\underset{\underset{O}{\|}}{C}\text{-}CH_3 + {}^{\bullet}OH \qquad (4.26)$$

The hydrogen atom on the same carbon atom as the -OOH group in decyl hydroperoxide is probably equivalent to a tertiary hydrogen atom and as such will be very susceptible to attack by bromine atoms.

The decomposition of the radical so formed will take place rapidly after minor rearrangement to give a decanone and a hydroxyl radical.

The activation energy for such reactions is expected to be similar to that for removal of tertiary hydrogen atoms from hydrocarbons[97], and $k_{4.26}$ will therefore be of the order of 5.5×10^6 l mole^{-1} s^{-1} at 453 K. If it is assumed that the concentration of bromine atoms is equivalent to that of hydrogen bromide initially added to the reaction mixture, then at 453 K, $k_{4.26}[Br^{\bullet}] = 1.5 \times 10^3$ s^{-1}. Therefore, even if only one per cent of the hydrogen bromide is dissociated at any one time, reaction (4.26) will be much faster than the uncatalysed thermal decomposition of decyl monohydroperoxide, for which $k_{4.9} = 3 \times 10^{-5}$ s^{-1} at 453 K.

4.2.2.5 Reactions of decyloxy radicals

Decyloxy radicals, which are formed either by the self-reaction of decylperoxy radicals or from the unimolecular decomposition of monohydroperoxides, are relatively reactive and they may be removed either by reaction with a molecular species or by decomposition[102]. Thus the 2-decyloxy radical may abstract a hydrogen atom from a fuel molecule to yield decan-2-ol:

$$CH_3(CH_2)CH_6\overset{O^{\bullet}}{\overset{|}{C}}HCH_3 + C_{10}H_{22} \rightarrow CH_3(CH_2)_6CH_2\overset{OH}{\overset{|}{C}}HCH_3 + C_{10}H_{21}^{\bullet} \quad (4.13)$$

or may react with oxygen to form decan-2-one:

$$CH_3(CH_2)_6CH_2\overset{O^{\bullet}}{\overset{|}{C}}HCH_3 + O_2 \rightarrow CH_3(CH_2)_6CH_2\overset{O}{\overset{\|}{C}}CH_3 + HO_2^{\bullet} \quad (4.14)$$

Reactions (4.13) and (4.14) probably account, therefore, for the formation of the small quantities of decanols and decanones in the reaction products.

A review of the decomposition of alkoxy radicals[102] shows that these radicals tend to decompose by the scission of the C-C bond to yield an aldehyde and an alkyl radical. Thus the 3-decyloxy radical could decompose to yield either propanal and a heptyl radical

$$CH_3(CH_2)_5CH_2\overset{O^\bullet}{\overset{|}{C}}HCH_2CH_3 \rightarrow CH_3CH_2CH_2O + CH_3(CH_2)_5CH^\bullet \qquad (4.27)$$

or octanal and an ethyl radical

$$CH_3(CH_2)_5CH_2\overset{O^\bullet}{\overset{|}{C}}HCH_2CH_3 \rightarrow CH_3(CH_2)_5CH_2CHO + CH_3CH_2^\bullet \qquad (4.28)$$

However, a study of the decomposition products of secondary hexyloxy radicals[112] showed that the decomposition occurred almost exclusively to yield the lower molecular weight aldehyde i.e. for the 3-decyloxy radical reaction (4.27) would occur. It is apparent, therefore, that reaction (4.20), the self-reaction of decylperoxy radicals to yield decyloxy radicals, followed by reaction (4.28), cannot explain the formation of the appreciable quantities of long-chain carbonyl compounds formed in the initial stages of the reaction at these temperatures.

4.2.2.6 Isomerisation of decylperoxy radicals

An alternative reaction of decylperoxy radicals involves their isomerisation by internal hydrogen abstraction to form hydroperoxydecyl radicals. It has previously been shown[9] that

the most important mode of isomerisation is a 1-5 hydrogen transfer, since this involves the smallest ring strain energy, although 1-4 and 1-6 hydrogen transfer will also occur

$$CH_3(CH_2)_4CH_2CH_2\overset{\cdot O-O}{\underset{|}{C}}HCH_3 \;\text{--}\; CH_3(CH_2)_4CH_2\overset{\cdot}{C}HCH_2\overset{HOO}{\underset{|}{C}}HCH_3 \qquad (4.29)$$

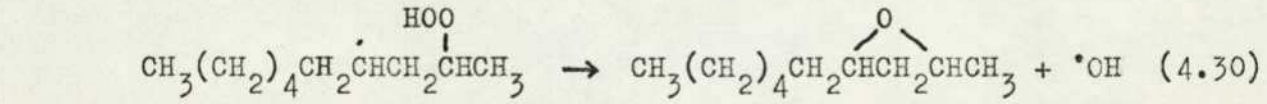
There has been much discussion and disagreement about the rate of the alkylperoxy radical isomerisation, with different workers producing exquisite arguments for a particular value in order to explain the rate and mode of formation of the products produced in individual studies[46,53,113,114]. The Arrhenius parameters for the isomerisation reactions have not been measured directly, but their activation energies have been estimated from the sum of the relevant strain energy involved in the formation of the transition state and the activation energy of the corresponding intermolecular abstraction reaction, $RO_2^{\cdot}$ + RH. Recent studies of the addition of alkanes to slowly reacting mixtures of hydrogen and oxygen has led Walker[40,115] to suggest an activation energy of 98 kJ mole^{-1} and a pre-exponential factor of $10^{12.1}$ s^{-1} for the most favourable 1-5 isomerisation reaction involving a secondary hydrogen atom compared with values of E = 44 kJ mole^{-1} and A = 10^{11} s^{-1} previously suggested by Fish[46]. These give values for the rate constant of the decylperoxy radical isomerisation reaction (4.29), at 453 K, of 6.3 s^{-1} and 8.4 x 10^5 s^{-1} respectively, compared with a rate of $k_{4.3}[C_{10}H_{22}] = 10^{-2}$ s^{-1} for intermolecular hydrogen abstraction when the initial decane pressure is 6.7 kPa. It is apparent, therefore, that the isomerisation reaction (4.29) would occur almost exclusively if the kinetic parameters suggested by Fish[46] are correct. However,

as relatively large yields of decyl monohydroperoxides are detected, which can be formed only by reaction (4.3), the present study shows that the values for the activation energy and Arrhenius factor deduced by Walker[40,115] provide a more accurate explanation of the experimental results.

It has already been show that the addition of hydrogen bromide increases the rate of formation of decyl monohydroperoxides, due to reaction (4.19), although the presence of bromine atoms also catalyses their decomposition. The rate, at 453 K, of reaction (4.19) when 5% hydrogen bromide is added to the reaction mixture will be $k_{4.19}[HBr] = 1.7 \times 10^3\ s^{-1}$. Therefore the addition of hydrogen bromide should reduce the rate of decylperoxy radical isomerisation and this is shown by the large decrease in the yields of O-heterocycles which are formed only from the isomerised decylperoxy radicals.

4.2.2.7 Reactions of hydroperoxydecyl radicals

The formation of C_{10} O-heterocyclic compounds confirms that decylperoxy radicals do indeed isomerise even at these low temperatures as these oxygen compounds can be formed only by the decomposition of isomerised decylperoxy radicals.



$$CH_3(CH_2)_4\dot{C}HCH_2CH(OOH)CH_3 \rightarrow CH_3(CH_2)_4CH_2\overset{O}{\diagup\diagdown}CHCH_2CHCH_3 + {}^{\bullet}OH \quad (4.30)$$

The isomerised decylperoxy radicals may also decompose as shown in Section 1.2.2b. The analytical results show, however, that, in this temperature range, the hydroperoxydecyl radicals do not decompose to give the conjugate alkene

$$CH_3(CH_2)_5\dot{C}H_2\overset{HOO}{\underset{|}{C}}HCHCH_3 \rightarrow CH_3(CH_2)_5CH_2CH{=}CHCH_3 + HO_2^{\bullet} \qquad (4.31)$$

Similarly the hydroperoxydecyl radicals apparently do not decompose by C-C bond scission and O-O homolysis to produce alkenes and carbonyl compounds as virtually no alkenes were detected.

$$CH_3(CH_2)_4\dot{C}H_2CHCH_2\overset{HOO}{\underset{|}{C}}HCH_3 \rightarrow CH_3(CH_2)_4CH_2CH{=}CH_2 + CH_3CHO + {}^{\bullet}OH \qquad (4.32)$$

The presence of decanones in the reaction products indicates that the isomerised decylperoxy radicals could be decomposing by O-O homolysis and hydrogen transfer

$$CH_3(CH_2)_4CH_2CH_2\overset{HOO}{\underset{|}{\dot{C}}}HCHCH_3 \rightarrow CH_3(CH_2)_4CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 + {}^{\bullet}OH \qquad (4.33)$$

However, as this reaction involves a 1:4 hydrogen transfer to form the α-hydroperoxydecyl radical which is energetically unfavourable, it is more likely that the decanones are produced from decyloxy radicals as explained earlier (Section 4.2.2.5).

The above decomposition reactions of hydroperoxydecyl radicals have a relatively high activation energy[46] and at low temperatures an alternative reaction involves the addition of oxygen to the isomerised decylperoxy radical.

$$CH_3(CH_2)_4\dot{C}H_2CHCH_2\overset{OOH}{\underset{|}{C}}HCH_3 + O_2 \rightarrow CH_3(CH_2)_4CH_2\overset{{}^{\bullet}OO}{\underset{|}{C}}HCH_2\overset{OOH}{\underset{|}{C}}HCH_3 \qquad (4.34)$$

This reaction is analagous to reaction (4.2), the addition of oxygen to an alkyl radical, and would therefore also be expected

to proceed with zero activation energy. The larger hydroperoxydecyl radical will, however, reduce the value of the pre-exponential factor and it has therefore been suggested[98] that a reasonable value for the rate constant of reaction (4.34) would be $10^{8.8}$ l mole^{-1} s^{-1}. This reaction will therefore be fast and effectively non-reversible at low temperatures.

Thus at temperatures below 473 K the main fate of the isomerised decylperoxy radicals is either their reaction with oxygen, or, to a lesser extent, their decomposition to give C_{10} O-heterocycles.

An increase in oxygen concentration will increase the rate of formation of the hydroperoxydecylperoxy radicals (reaction 4.34); these radicals will then react further to form greater yields of the decyl dihydroperoxides and their decomposition products. This change in the rate of reaction (4.34) will also affect the equilibrium of the isomerisation reaction (reaction 4.29) thus decreasing the concentration of the decylperoxy radicals. This will therefore reduce the yields of the decyl monohydroperoxides (reaction 4.3) and also decrease the yields of the decanols and decanones. The smaller concentration of isomerised decylperoxy radicals should also result in lower yields of O-heterocyclic compounds (reaction 4.30) as was indeed found to be the case.

4.2.2.8 Reactions of hydroperoxydecylperoxy radicals

The large yields of decane dihydroperoxides indicate that the main reaction of hydroperoxydecylperoxy radicals involves the abstraction of a hydrogen atom, either from an initial fuel molecule or from an oxidation product, e.g.

$$CH_3(CH_2)_4\overset{\cdot OO}{\underset{|}{C}}H_2CHCH_2\overset{OOH}{\underset{|}{C}}HCH_3 + C_{10}H_{22} \rightarrow CH_3(CH_2)_4\overset{HOO}{\underset{|}{C}}H_2CHCH_2\overset{OOH}{\underset{|}{C}}HCH_3 + C_{10}H_{21}^{\cdot} \quad (4.35)$$

The $^{\cdot}OOC_{10}H_{20}OOH$ radical could possibly isomerise by further internal hydrogen abstraction and then react to form a decane trihydroperoxide. The two functional groups already present on the decyl chain will however tend to hinder this isomerisation sterically and hence reduce its rate, while the reaction products also indicate that this reaction is not occurring to any appreciable extent. Thus the formation of the dihydroperoxides via reaction (4.35) would appear to be the main fate of the hydroperoxydecylperoxy radicals.

4.2.2.9 Reactions of decane dihydroperoxides

The preceding discussion has considered the possible reactions of the decylperoxy radicals and has shown that below 473 K these react almost exclusively to form mono- and dihydroperoxides. The other products must therefore be formed by decomposition of these hydroperoxides. The mode of formation of the non-peroxidic products containing ten carbon atoms has already been shown to involve decyloxy radicals produced by the decomposition of the decyl monohydroperoxides.

The formation of large yields of aldehydes and ketones with less than ten carbon atoms may be satisfactorily explained, therefore, only by the decomposition of decyl dihydroperoxides. Alkane dihydroperoxides have previously been detected in the oxidation products of heptane[59,117] and their presence has been

suggested to explain some features of the combustion of pentane[60] and isobutane[118,119].

It is believed that dihydroperoxides decompose by homolysis of the peroxidic O-O bonds and simultaneous C-C bond scission to yield two hydroxyl radicals and two carbonyl compounds; the nature of the carbonyl compounds depends on the relative positions of the two hydroperoxide groups. Thus α-dihydroperoxides will decompose to give two aldehydes; e.g. 2,3-decane dihydroperoxide will give octanal and acetaldehyde.

$$CH_3(CH_2)_5\overset{HOO}{\underset{|}{C}}H_2\overset{OOH}{\underset{|}{C}}HCHCH_3 \longrightarrow CH_3(CH_2)_5CH_2CHO + CH_3CHO + 2^{\bullet}OH \quad (4.36)$$

β-dihydroperoxides will decompose to yield an aldehyde and a methyl ketone e.g. 2,4-decyl dihydroperoxides will give either acetaldehyde and octan-2-one or heptanal and propan-2-one.

$$CH_3(CH_2)_4\overset{HOO}{\underset{|}{C}}H_2CHCH_2\overset{OOH}{\underset{|}{C}}HCH_3 \begin{cases} \nearrow CH_3(CH_2)_4CH_2\overset{O}{\overset{\|}{C}}CH_3 + CH_3CHO + 2^{\bullet}OH & (4.37) \\ \searrow CH_3(CH_2)_4CH_2CHO + CH_3\overset{O}{\overset{\|}{C}}CH_3 + 2^{\bullet}OH & (4.38) \end{cases}$$

The γ-dihydroperoxides can decompose to yield either two methyl ketones or an aldehyde and an ethyl ketone. However, the absence of ethyl ketones in the products indicates that β-C-C bond scission must occur almost exclusively, yielding two methyl ketones. Thus the 2,5 decyl dihydroperoxide will decompose to give heptan-2-one and propan-2-one.

$$CH_3(CH_2)_3\overset{HOO}{\underset{|}{C}}H_2CHCH_2CH_2\overset{OOH}{\underset{|}{C}}HCH_3 \longrightarrow CH_3(CH_2)_3CH_2\overset{O}{\overset{\|}{C}}CH_3 + CH_3\overset{O}{\overset{\|}{C}}CH_3 + 2^{\bullet}OH \quad (4.39)$$

Table 4.1 lists the possible decyl dihydroperoxide precursors for the formation of the carbonyl compounds. Figure 4.2 shows the predicted percentage frequency of formation of the carbonyl compounds, calculated assuming that the rates of formation of all the decyl dihydroperoxides are equal. The predicted values are shown together with those measured after 5 minutes reaction at 462 K. It has already been shown that, if the decyl dihydroperoxides are formed from decylperoxy radicals, then, due to the ring strain energy involved in the isomerisation, α-, β- and γ- dihydroperoxides will be formed in different amounts. α-decyldihydroperoxides, the formation of which involves a 1-4 hydrogen transfer, will be formed in much smaller amounts than either β- or γ-dihydroperoxides. Thus the yields of aldehydes formed by the decomposition of α-dihydroperoxides will be smaller than expected as indeed was found for nonanal, octanal and heptanal. Similarly, as the bond strength of a secondary C-H bond is lower than that for a primary C-H bond, the yields of 1,2, 1,3, and 1,4 decyl dihydroperoxides will be smaller than predicted. This explains why the measured yields of nonanal and nonan-2-one are lower than expected.

The formation of larger yields of carbonyl compounds with four or less carbon atoms may be explained either by secondary reactions or possibly by their formation from the decomposition of decane trihydroperoxides.

4.2.3 High-temperature combustion

It was shown in the previous sections that the products of the slow combustion of decane at low temperatures may be satisfactorily explained by addition of oxygen to decyl radicals to yield decylperoxy radicals. These then may either abstract a hydrogen atom

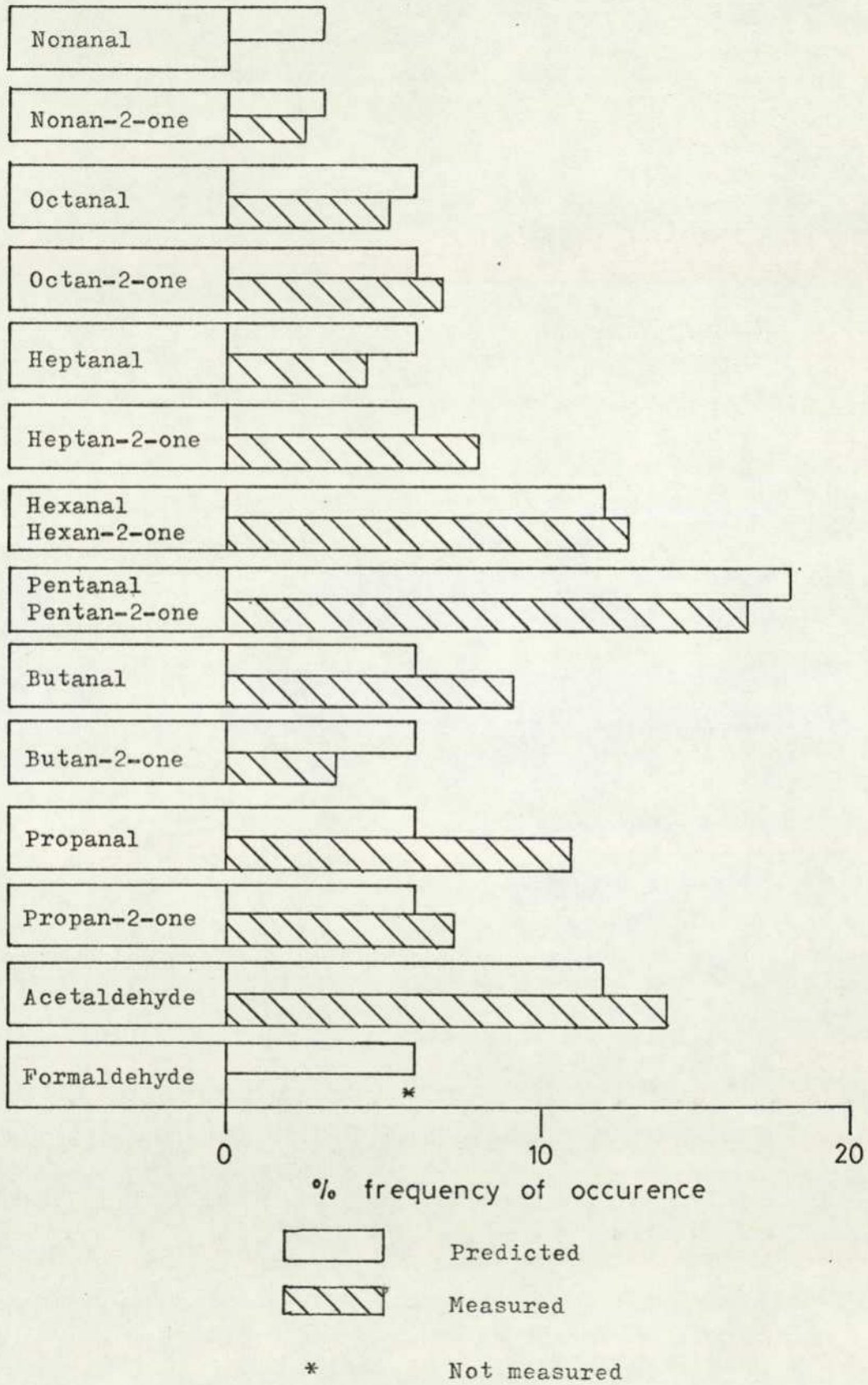
Table 4.1

Possible decyl dihydroperoxide precursors for the formation of carbonyl compounds.

Type of dihydroperoxide	Position of hydroperoxide groups		
	α	β	γ
Nonanal	1,2		
Nonan-2-one		1,3	
Octanal	2,3	1,3	
Octan-2-one		2,4	1,4
Heptanal	3,4	2,4	
Heptan-2-one		3,5	2,4
Hexanal	4,5	3,5	
Hexan-2-one		4,6	3,6
Pentanal	5,6;6,5	4,6	
Pentan-2-one		4,6	4,7;7,4
Butanal	4,5	4,6	
Butan-2-one		3,5	3,6
Propanal	3,4	3,5	
Propan-2-one		2,4	2,5
Acetaldehyde	2,3	1,3;2,4	1,4
Formaldehyde	1,2	1,3	

Figure 4.2

Comparison of predicted and measured yields of carbonyl compounds



to form the decyl monohydroperoxide or isomerise and react further to give decane dihydroperoxides. Decomposition of the mono-hydroperoxides produces decanols and decanones, while the aldehydes and ketones with less than ten carbon atoms are formed by the decomposition of the decane dihydroperoxides.

As the temperature is increased from the slow combustion area into the cool flame region of the ignition profile, the yields of both mono and dihydroperoxides and of the carbonyls containing less than ten carbon atoms decrease. Figure 3.19 shows that this is accompanied by a rapid increase in the yield of C_{10} O-hetero-cycles while decenes and 1-alkenes are also detected in measurable quantities.

4.2.3.1 Initial attack

Previous studies of hydrocarbon combustion have shown that, as the temperature is increased, the initial attack on the hydrocarbon fuel molecule becomes more unselective[48]. This is due to an increase in the rate of attack by hydroxyl radicals which leads to greater quantities of primary alkyl radicals. It was shown in Section 4.2.2.1 that during decane combustion hydroxyl radicals must be involved in the initial attack as decanal was formed even at low temperatures. Examination of the product distribution in table 3.10 shows that the concentration of decanal does not change as the temperature is increased. It would appear, therefore, that the randomness of initial attack on the decane molecule does not appreciably alter as the temperature is increased.

4.2.3.2 Reactions of decylperoxy and hydroperoxydecyl radicals

The rate of isomerisation of the decylperoxy radicals (reaction 4.29) will increase with temperature. However, as the addition of oxygen to these isomerised radicals is reversible with the reverse reaction having a high activation energy, the rate of formation of the hydroperoxydecylperoxy radicals will decrease with increasing temperature as is shown by the decreased yield of decane dihydroperoxides and their decomposition products. It is expected, therefore, that the decomposition products of the hydroperoxydecyl radicals will become more important. This is indeed the case, as the yield of O-heterocyclic compounds increases rapidly between 503 and 523 K. There is a similar increase in the yield of the 1-alkenes which are probably formed by O-O homolysis and scission of a C-C bond in the isomerised decylperoxy radical (reaction 4.32).

The addition of hydrogen bromide to the reaction mixture at higher temperatures has a similar effect to that observed at 458 K. The presence of labile hydrogen atoms increases the rate of formation of decyl monohydroperoxides (reaction 4.19). These are then rapidly decomposed by bromine atoms (reaction 4.26) to give the large observed yields of decanones. The increased rate of removal of decylperoxy radicals will reduce the rate of formation of hydroperoxydecyl radicals. This is shown by the lower yield of C_{10} O-heterocycles when hydrogen bromide is present.

Table 3.10 shows that the yield of decanones relative to decanols also increases as the temperature is raised which indicates that 1:4 isomerisation becomes more important, the decomposition of α-hydroperoxydecyl radicals providing an alternative route for the formation of the decanones,

via reaction (4.33), but not of the decanols.

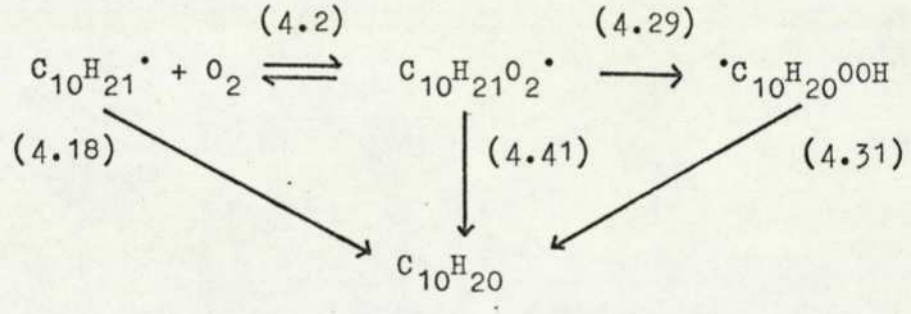
The concentration of radicals in the reaction system will also increase with increasing temperature, and radical-radical reactions such as reaction (4.20) will then become more important. The decomposition of alkoxy radicals produced by this and other similar reactions occurs by C-C bond scission to yield a carbonyl compound and an alkyl radical (reaction 4.27). The larger relative yield of C_1-C_4 carbonyl compounds compared with those containing more than four carbon atoms, which was found as the temperature increased, may therefore be explained by these reactions.

It is interesting to note that while the yield of carbonyl compounds with less than ten carbon atoms is decreased in the presence of hydrogen bromide at the lower temperature studied, this decrease, especially for those compounds containing up to five carbons is not so great at 503 K. This difference confirms that there must be a change in the mechanism involved in their formation. At low temperatures, the carbonyl compounds are produced by the decomposition of decane dihydroperoxides, whose formation is decreased when hydrogen bromide is present. However at higher temperatures, radical-radical reactions play an increasing role in propagation[54] and these will lead to the formation of decyloxy radicals which decompose to yield a carbonyl compound and an alkyl radical (reaction 4.27). The alkyl radicals so formed will then react with the labile hydrogen in hydrogen bromide to produce alkanes with less than ten carbon atoms which were found in large quantities when hydrogen bromide was added

$$C_7H_{15}^{\bullet} + HBr \rightarrow C_7H_{16} + Br^{\bullet} \qquad (4.40)$$

4.2.3.3 Alternative reactions of decyl radicals with oxygen

As the reaction temperature is raised, the rate of the abstractive reaction of oxygen with decyl radicals (reaction 4.18) increases and begins to compete with the additive reaction forming decylperoxy radicals (reaction 4.2). The direct bimolecular abstractive reaction could account for the formation of decenes found in the products of decane oxidation above 483 K. However, the conjugate alkene could also be formed by the decomposition of the decylperoxy radical (reaction 4.41) or via an ∝-hydroperoxydecyl radical (reaction 4.31) which is formed by a 1:4 intramolecular hydrogen transfer step.



It has been shown[47] that, in butane oxidation, the isomerised alkylperoxy radicals are not a major source of the conjugate alkene. As decyl and decylperoxy radicals will be effectively equilibrated at higher temperatures, reactions (4.18) and (4.41) cannot be easily distinguished. However, Baldwin and Walker[120] have argued that the overall reaction to the conjugate alkene is best considered a bimolecular process (reaction 4.18). The formation of decenes by this reaction will also give rise to hydroperoxy radicals. These radicals may react either by abstraction of a hydrogen atom from the original fuel molecule (reaction 4.42) or by a mutual recombination process (reaction 4.43)

$$C_{10}H_{22} + HO_2^{\bullet} \rightarrow C_{10}H_{21}^{\bullet} + H_2O_2 \qquad (4.42)$$

$$2HO_2^{\bullet} + M \rightarrow H_2O_2 + O_2 + M \qquad (4.43)$$

Since decenes are major products at these higher temperatures the concentration of hydrogen peroxide will therefore also be quite large. It is well known that the onset of cool flames is accompanied by temperature rises of up to a hundred degrees or more; thus it is likely that hydrogen peroxide will decompose to give hydroxyl radicals according to reaction (4.44)

$$H_2O_2 + M \rightarrow 2^{\bullet}OH + M \qquad (4.44)$$

4.2.3.4 Decomposition of decyl radicals

Figure (3.19) shows that, above 625 K, the yield of 1-alkenes with less than ten carbon atoms increases rapidly, while that of the decenes decreases. This may be explained by cracking of the decyl radicals via C-C bond fission competing with conjugate olefin formation by reaction with oxygen. Thus reactions such as (4.45), the decomposition of the 2-decyl radical to yield oct-1-ene and an ethyl radical, will occur.

$$CH_3(CH_2)_5CH_2CH_2\dot{C}HCH_3 \rightarrow CH_3(CH_2)_5CH{=}CH_2 + C_2H_5^{\bullet} \qquad (4.45)$$

4.3 Comparison of liquid-phase oxidation and combustion of decane

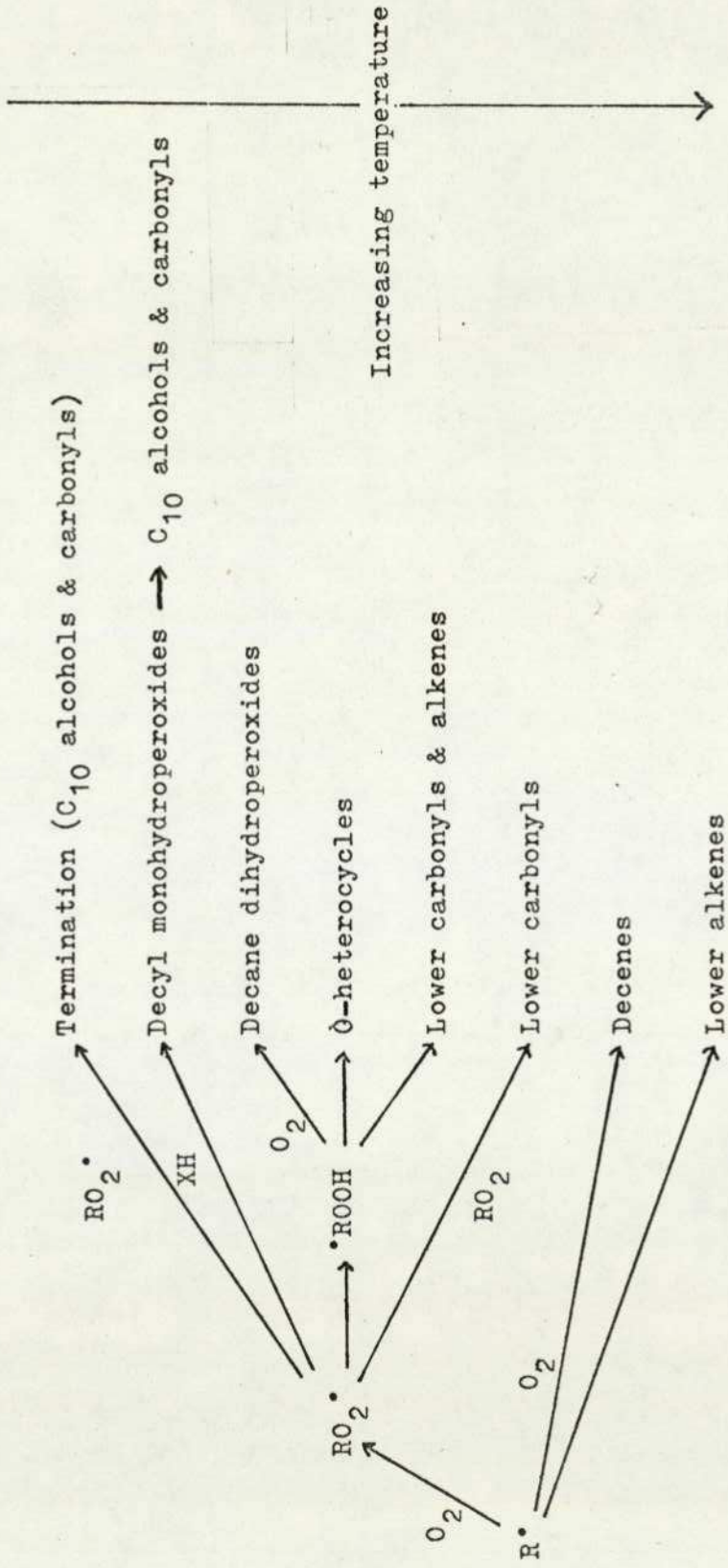
Figure 4.3 shows a general reaction scheme for the mechanism of both liquid-phase and gas-phase oxidation of decane. In both phases, initiation involves the production of decyl radicals. However, an important difference between the mechanisms of liquid-phase and gas-phase oxidation of decane is the nature of the propagating radical. In liquid-phase oxidation decylperoxy radicals are the main chain propagating species while, even at low temperatures, hydroxyl radicals play an important role in the combustion of decane. This is shown by the unselective attack on the initial decane molecule in the gas phase which leads to an appreciable yield of products formed from primary decyl radicals.

Decyl monohydroperoxides are formed as the main product in both phases at temperatures around 440 K and these decompose to give decyloxy radicals which lead to decanones and decanols.

Perhaps the most striking difference between the mechanisms in the two phases is the ability of the decylperoxy radicals to isomerise in the gas phase. The large yields of decane dihydroperoxides and, to a lesser extent, the C_{10} O-heterocycles which are formed indicate that the rate of the isomerisation reaction is quite fast even at low temperatures. In the liquid phase intramolecular hydrogen abstraction by decylperoxy radicals was negligible and it has only previously been found when the fuel molecule contains a conveniently situated tertiary hydrogen atom as occurs in dimethylalkanes. 2,4 and 2,5 dihydroperoxides were detected in the liquid-phase oxidation of 2,4-dimethylpentane and 2,5-dimethylhexane

Figure 4.3

General mechanism for liquid-phase oxidation and combustion of decane



respectively [75] ; this is attributed to the abstraction by tertiary alkylperoxy radicals of the other tertiary hydrogen atom in those radicals, followed by oxidation of the hydroperoxyalkylradicals so formed.

Radical-radical reactions involving decylperoxy radicals occur in both phases. In the liquid phase such reactions are usually termination steps leading to the production of decanones and decanols via the Russell mechanism[103]. However, in the gas phase, the self-reaction of alkylperoxy radicals are often important propagating processes[54] especially as the temperature is increased.

The remaining class of compound which was found in the products of decane combustion is the decenes. It is not surprising that these compounds are not found either in the liquid-phase oxidation or low-temperature combustion of decane as the reactions involved in their formation require a high activation energy; they will therefore only become important at higher temperatures.

4.4 Comparison of combustion of decane and lower alkanes

The combustion of decane takes place, to a measurable extent, at lower temperatures when compared with alkanes containing fewer carbon atoms. This ease of oxidation, coupled with its long chain length gives rise to the highly complex product distribution which was observed in this study. The analytical problems involved in elucidating the mechanism of high molecular weight hydrocarbon combustion have previously deterred its investigation. In fact the only recent study of decane combustion products was performed at a single temperature

and high conversion rates[121]. The results obtained showed that the products included a complex mixture of O-heterocyclic compounds, olefins and carbonyls and no detailed mechanism was proposed.

This study has shown that the combustion of decane involves the production of decyl radicals which, in the low-temperature slow-combustion region, react exclusively by addition of oxygen to form decylperoxy radicals. Alkyl radicals from lower molecular weight fuels such as butane and pentane produce large quantities of the conjugate alkene in this temperature region. This abstractive reaction of decyl radicals with oxygen to produce decenes does not appear to occur until the temperature is raised into the cool-flame region of decane combustion.

In the gas-phase oxidation of lower alkanes, initiation and propagation at low temperatures is believed to involve hydroperoxy or alkylperoxy radicals which are selective in the position they attack. The formation of appreciable yields of products from primary decyl radicals in the present study indicates that even at low temperatures hydroxyl radicals play an important role in the combustion of decane.

The decylperoxy radicals abstract a hydrogen atom at low temperatures to form decyl monohydroperoxides. Alkyl monohydroperoxides have often been postulated as intermediates in hydrocarbon combustion but there has previously been little conclusive proof of their participation. The stabilising effect of the long hydrocarbon chain on the peroxide bond and the occurrence of reaction at low temperatures has allowed the identification of decyl hydroperoxides in this study.

The isomerisation of decylperoxy radicals appears to take place more readily than that for lower alkylperoxy radicals. At low temperatures decane dihydroperoxides are formed by the subsequent oxidation of hydroperoxydecyl radicals. Dihydroperoxides have previously only been detected in the combustion of heptane[59], although their presence has been postulated to explain the products formed during the slow combustion of pentane[60].

4.5 Conclusions and suggestions for further work

The present study has shown that the combustion of high molecular weight hydrocarbons can be satisfactorily examined by using an injection apparatus. The ignition profile and kinetic parameters obtained show good correlation with those from studies using a premix apparatus. The injection apparatus may be readily used to study the effect of fuel additives on the combustion of hydrocarbons. The spontaneous ignition temperature of decane in oxygen-rich mixtures was slightly lowered by the addition of ASA-3, a static dispersant agent, and also by ethylene glycol monoethyl ether, a fuel system icing inhibitor. This indicates that the effect of these additives might be greater in fuel-rich mixtures.

Decane is readily oxidised at low temperatures and it is therefore possible to study its oxidation in both liquid and gas phases at similar temperatures. The mechanism of liquid-phase oxidation of decane was found to agree with the 'hydroperoxide-chain mechanism' previously proposed. The most striking difference between the liquid-phase oxidation and combustion of decane is the complete absence of isomerisation reactions of decylperoxy radicals in the liquid phase even though they readily occurred in the gas phase at a similar temperature.

The mechanism of decane combustion has been shown to change gradually as the temperature is increased. Thus at low temperatures decylmono- and decylhydroperoxides are the major products but as the temperature is raised, decomposition reactions of hydroperoxydecyl radicals and radical-radical reactions play an increasing role. Decenes were only detected in the cool-flame

region while at the highest temperature studied (673 K) the oxygen catalysed decomposition of decyl radicals was the most important reaction.

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