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ORGANOSILICON COMPOUNDS AS ANTIKNOCK ADDITIVES

by

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ABSTRACT

Organosilicon Compounds as Antiknock Additives

Studies have been made of the effects of a varied selection of organosilicon compounds on the combustion of a pure hydrocarbon fuel, viz. 2-methylpentane, in the laboratory. Engine experiments have also been carried out, involving other hydrocarbons.

The Introduction outlines the various combustion phenomena associated with engine knock, and discusses different methods by which knock can be suppressed. An account is given of the environmental problems associated with the continued use, as antiknocks, of lead alkyls, which are believed to constitute a danger to health and mental development, particularly in children. Efforts to find alternative antiknock additives are described. In particular, many organic compounds which exhibit antiknock activity can be used only as blending agents which is not, at present, economical in view of the large quantities required. There is thus still a great need for research into systems with good antiknock potential and no adverse environmental or other problems. The last section in the Introduction consists of a general review of the chemistry of organosilicon compounds with emphasis on thermal and thermoxidative reactions, especially those occurring in the gas phase; this discusses in particular the rôle of the various transient species involved.

The Experimental Section deals with the synthetic methods used for the preparation of many of the compounds tested. It also discusses the apparatus used in this work, which was an injection system. Liquid fuel mixtures could be injected into a reaction vessel containing oxidant gases and the pressure history of the reaction was then measured by means of a pressure transducer. A CFR engine was used to determine the Research Octane Number of various systems.

The Results Section shows, in tabular form, the two-stage ignition limits found in this work as well as various associated kinetic parameters. These limits were found to constitute a good measure of the antiknock effectiveness of these additives. Solid formation and deposition within the cylinder during experiments in a CFR engine in the presence of silicon-based additives caused unreliability in the RON results obtained. Various experiments were subsequently designed to show the validity of the assumption that ignition limit shifts were a good measure of antiknock activity.

The Discussion Section shows, by means of experiments involving the use of organic additives of known antiknock properties, in both the laboratory injection system and the CFR engine, that similar and proportional effects are obtained on the combustion of the base fuel. This indicates the validity of the use of the laboratory experimental set-up. The antiknock activity of the organosilicon compounds investigated is explained in terms of their structure and the different electron densities resulting from the presence of silicon. Whenever possible, comparisons have been made of the behaviour and structure of the silicon-based additives with those of the analogous purely organic compounds.

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INTRODUCTION

1.1 GENERAL BACKGROUND

The phenomenon of "knock" has been known to the practical engineer since at least 1882 (Clerk, 1926). However, the importance of knock among the factors limiting the power output and economy of spark-ignition engines was not immediately realised. Only the problems encountered during the development of such engines - particularly for flying - during the 1914-18 war, led to that realisation. In the years following 1918, much work was done to combat knock by improvement in engine design and by the careful choice of fuels. However, little progress was made in the elucidation of the nature of the reactions leading to knock until the 1930's (Townend, 1937). This was due largely to the lack of understanding of the basic mechanisms operative during hydrocarbon combustion before that time. However, preceding these initial studies came the discovery that knock could be suppressed efficiently by the addition to the fuel of tetraethyllead (Midgley and Boyd, 1922). Subsequent research has been unable to discover satisfactory alternatives to the lead alkyls which have even comparable inhibiting effects on hydrocarbon combustion, although much of the research in this field has been concerned with the chemistry of knock and the development of alternative antiknock compounds. Opposition to the continuing use of lead alkyls on the present scale has stemmed from the lingering doubts over the effects of lead on health, particularly in children, and the contribution of motor vehicle emissions to environmental lead levels. However, experience in the United States, where lead-free petrol has been available since 1975, has suggested that the total removal of lead from petrol would result in a decrease in performance and fuel economy of motor vehicles unless a suitable alternative antiknock additive were available. In

Germany, the lead content of fuel has been limited by law to 0.15 g ℓ^{-1} since January 1976. The octane quality of the fuel has been maintained at its pre-existing level with the result that refineries have been unable to satisfy fully their home-market fuel requirements. This resulted in price increases totalling over 40% between 1975 and 1979. The British Government has now elected to reduce the level of lead in petrol to 0.15 g ℓ^{-1} and to maintain the existing octane quality of the fuel. This step will not affect the performance of motor vehicles, and will not, therefore, require any drastic changes to engine design. However, the burden will be thrown entirely on the refineries, with the result that energy consumption and, therefore, cost will be increased (Working Party on Lead, 1981). Economically, the most satisfactory solution to the problem would therefore be to discover an antiknock compound with an effect approaching that of the lead alkyls, but without any associated environmental problems.

There thus follows an account of the different types of phenomenon involved in the combustion of hydrocarbons, accompanied by a discussion of the underlying chain mechanisms. A description is then given of hydrocarbon combustion in spark-ignition engines and of some of the compounds which have been used as antiknocks. Particular attention is paid to lead alkyls and the environmental implications of their use. Finally, a brief review is given of the principal types of organosilicon compounds and of their preparation, reactions and properties.

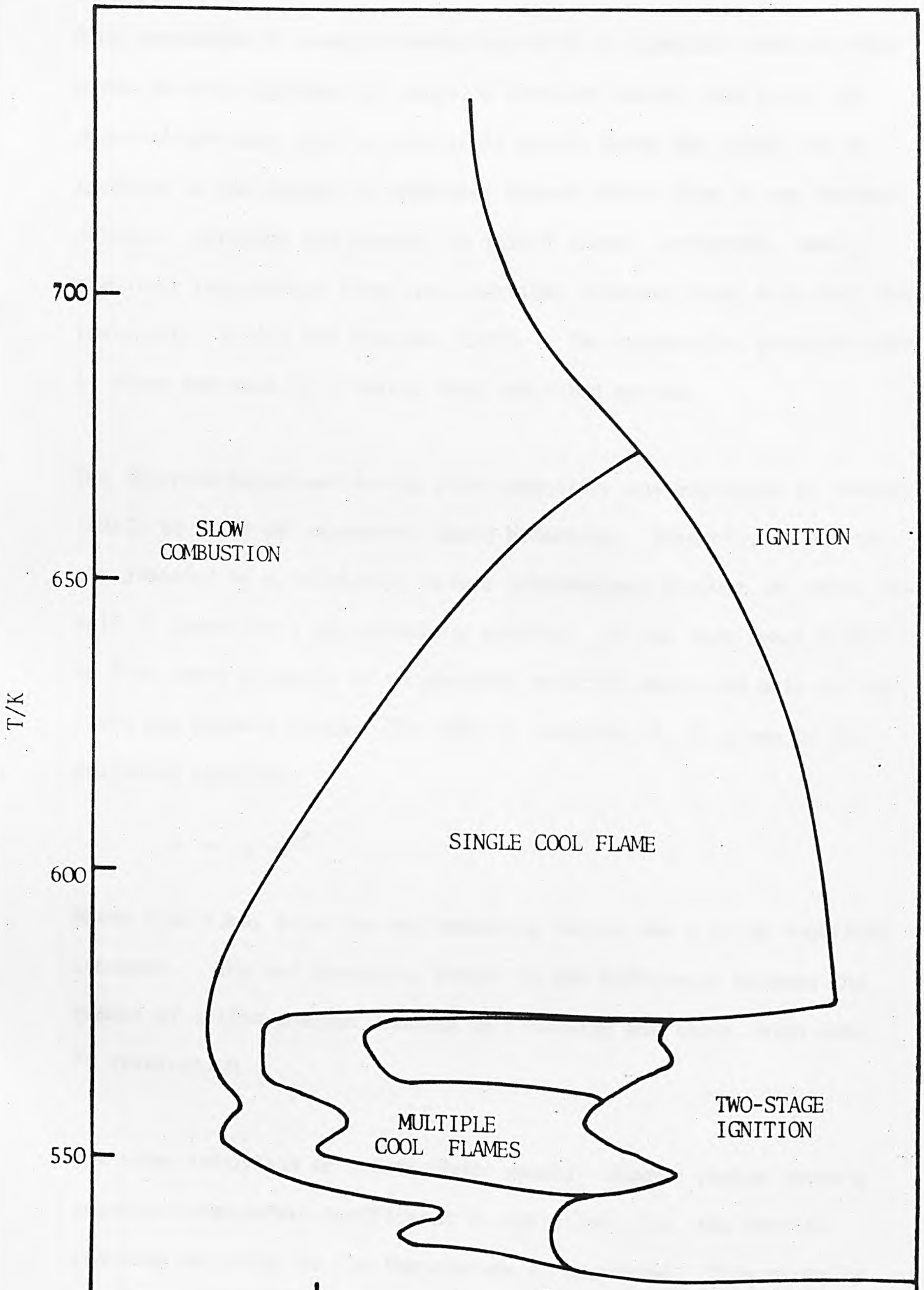
1.2 THE CHEMISTRY OF HYDROCARBON COMBUSTION

1.2.1. General features

The reaction between hydrocarbons and oxygen in the gas-phase may exhibit one of four types of behaviour: slow combustion, cool flames, two-stage ignition and single-stage (or hot) ignition (Barnard and Watts, 1972), dependent on the initial conditions of temperature and pressure of the reactants. The relationship between temperature and pressure and the four phenomena is normally described by means of a pressure-temperature ignition profile, a typical example being shown schematically in Fig. 1.1. The phenomena are identified by the pressure changes observed within the reaction zone as the reaction proceeds. The mode of combustion observed under given conditions of temperature and pressure is also dependent on the nature of the fuel, the oxidants, the fuel:oxidant ratio (Johnson, Crellin and Carhart, 1954; Cullis, Hinshelwood, Mulcahy and Partington, 1947), and to a lesser degree on the size, shape and surface characteristics of the reaction vessel (Thomas, 1961; Cullis, Fish and Gibson, 1966). However, ignition diagrams for hydrocarbon-oxidant mixtures show various common features. The ignition diagram shown exhibits well-defined "high temperature" and "low temperature" regions, the boundary being around 670K. The "high temperature" region is characterised by a sharp transition with increasing initial pressure from slow combustion to a single-stage hot ignition. In the low-temperature region, an intermediate region is observed where slow combustion develops into cool flames as pressure is increased, before the transition into a two-stage ignition region, where the hot ignition pressure pulse is preceded by a cool flame.

FIGURE 1.1

A typical pressure-temperature ignition profile for an alkane-oxygen mixture



1.2.2. Slow combustion

Slow combustion is usually characterised by a sigmoidal pressure-time curve in which the rate of reaction develops slowly, and hence the observed pressure rise is relatively small, being due simply to an increase in the number of molecules formed rather than to any thermal effect. Although the process is indeed almost isothermal, small transient temperature rises are sometimes observed along with very faint luminosity (Newitt and Thornes, 1937). The exponential pressure rise is often preceded by a fairly long induction period.

The observed behaviour during slow combustion was explained by Semenov (1935) in terms of degenerate chain branching. Branching is due to the presence of a relatively stable intermediate product, M, which itself is formed by a non-branching process. It can then react either to form inert products or to generate radicals which are able to initiate the primary chain. The rate of reaction, W, is given by the following equation:

$$W = a \; e^{\phi t}$$

Where t is time, ϕ is the net branching factor and a is an empirical constant. The net branching factor is the difference between the number of active centres leading to branching and those which lead to termination.

The slow combustion of hydrocarbons usually shows a region where a negative-temperature coefficient is operative, i.e. the rate of reaction decreases as the temperature is increased. This normally occurs between 550 and 700K. It is generally accepted (Dechaux, 1973), that the occurrence of such a region is due to a decrease in the rate of chain-branching, although there is some disagreement as to the nature of the branching agent.

1.2.3. Cool flames

The propagation of a cool flame during the low temperature reaction between a hydrocarbon and an oxidant is considered a non-isothermal phenomenon superimposed on an otherwise isothermal reaction. The passage of a cool flame is accompanied by substantial transient increases in pressure (up to 9 kPa) and temperature (up to 200K) due to a large sudden increase in the rate of reaction. A further characteristic of cool flame combustion is the emission of a pale blue light (Newitt and Thornes, 1937; Emeleus, 1926), due to the presence of excited formaldehyde (Ubbelohde, 1935; Gaydon and Moore, 1955), which is formed in radical recombination reactions.

Following the passage of the first cool flame, the reaction may proceed by a slow combustion mechanism until completion, or further cool flames may be generated or it may culminate in ignition. Multiple cool flames have been reported for many hydrocarbons, as many as eleven successive cool flames having been recorded during the combustion of propane (Ben-Aim and Lucquin, 1965; Gray, 1981). Various theories have been proposed to account for the periodicity and self-quenching nature of cool flames, although a clear explanation has yet to be propounded. It is generally believed to be associated with the accumulation of a critical concentration of a branching agent. During the passage of the cool flame, this intermediate would be rapidly consumed, resulting in a lowering of the reaction rate. Following the cool flame, the concentration of branching agent may again rise to a critical level in order to propagate further cool flames and thus exhibit periodicity. This type of behaviour has been demonstrated for aldehydes (Bonner and Tipper 1965; Fish, 1967), and peroxides (Knox and Norrish, 1954; Szabó and Gal, 1958). One of the first theories suggested was by Lotka (1920) and further developed by Frank-Kamenetskii (1955). This is a kinetic "two-product" theory which is dependent on the attainment of critical concentrations of two different intermediates. When the critical concentration of each intermediate is attained, branching reactions lead respectively to odd- and even-numbered cool flames. This sequence may be represented by the following steps:

$$A + X \longrightarrow B + 2X$$
$$X + Y \longrightarrow B + 2Y$$
$$A + Y \longrightarrow B$$

Where A is the reactant, B is an inert final product and X and Y are the intermediates formed autocatalytically from A and X respectively. An alternative theory, proposed by Salnikov (1949) attributes the oscillations to the effect of the temperature rise resulting from the propagation of the flame on the rates of formation and destruction of a single intermediate, X, in the following scheme.

$$A \longrightarrow X \longrightarrow B$$

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

1.2.4. The kinetics of cool flames

It has been shown for a number of alkanes (Fish, 1966; Sokolik, 1963) that, at a given temperature, the relationship between ΔP_{cf}, the pressure rise associated with the cool flame, and P_o, the initial pressure of reactants, approximates to the following equation :

$$\Delta P_{cf} = KP_o^{\,m}$$

where K is a constant and m has values between 1 and 3 for many hydrocarbon-oxidant mixtures (Cullis and Foster, 1974; Fish and Wilson, 1971). ΔP_{cf} is a measure of the cool flame intensity.

A cool flame is preceded by an induction period, τ_{cf}, which is the time between the admission of the gaseous mixture into the reaction vessel, and the passage of the cool flame. During this period, there is no significant rise in pressure. The length of the period is a function of the initial temperature and pressure, and for the first cool flame, it is related to the initial reactant pressure, P_o, by the expression :

$$\tau_{cf} = kP_o^{-n} + c$$

where k, n and c are constants. This relationship has been shown to hold for a large number of hydrocarbons (Fish, 1966; Luckett and Pollard, 1973; Yantovskii, 1966; Cullis, Fish, Saeed and Trimm, 1966). At a constant temperature, the value of c is the shortest possible induction period preceding the cool flame, while the value of n is the effective order of reaction. At constant pressure, the logarithm of the induction period increases exponentially with initial temperature, T_o, and from the variation of log τ_{cf} with $1/T_o$, values have been calculated for the effective activation energy for the cool flame process, E_{eff} (Cullis and Foster, 1974; Fish and Wilson, 1971). Perhaps the most important kinetic parameter associated with the passage of a cool flame is the maximum rate of pressure rise, $(dp/dt)_{max}$, which is a measure of the rate of overall reaction during the cool flame. The variation of $(dp/dt)_{max}$ with initial temperature and pressure has been shown for 2-methylpentane (Fish,1968), as indeed for many other hydrocarbons (Fish and Wilson, 1971) to exhibit a series of lobes which correspond to those observed at the two-stage ignition limits. On this basis it is suggested that the mechanisms operative under given conditions in the low-temperature combustion region should relate to $(dp/dt)_{max}$(Fish, 1968).

1.2.5. Two-stage ignition

Two-stage ignition was reported by Townend et al. (1933); in the systems studied true ignition was preceded by a milder pulse of light. Subsequently, the phenomenon was observed both at low pressures (Townend and Mandlekar, 1933a, b) and under engine conditions (Townend and Chamberlain, 1936).

During the two-stage ignition process there is a rapid consumption of reactants. The large pressure increase and the high transient temperature rise associated with the explosive hot ignition is preceded by a cool flame. It has been suggested (Lewis and von Elbe, 1951) that, following the passage of the cool flame, the mixture contains high concentrations of radicals and of molecular intermediates which can act as branching agents. The temperature rise accompanying the cool flame may heat the mixture sufficiently to increase the rate of the branching reactions, causing further self-heating and leading to the subsequent explosion. The two-stage ignition temperature-pressure limit for hydrocarbon-oxidant mixtures is often complex, with the existence of pressure maxima and minima as the temperature is increased. The "lobes" thus formed in the ignition diagram are designated L_o, L_1, L_2 and L_3 in order of increasing temperature (Walsh, 1963; Antonik and Lucquin, 1968). The number and position of these lobes may be related to the molecular structure of the hydrocarbon. Each lobe may also be related to the various mechanisms operating in the cool-flame region over a given range of temperatures (Fish, 1968; Antonik and Lucquin, 1968).

1.2.6. Products of hydrocarbon combustion

The combustion of hydrocarbon-oxygen mixtures gives rise to a wide variety of products. For 2-methylpentane, at least 65 products have been identified unambiguously (Fish, 1967). The nature and abundance of these products is dependent on the initial conditions of temperature, pressure and fuel:oxidant ratio.

During slow combustion, the yield of organic peroxides is high. However, as conditions are altered and cool flames are propagated, the yield of organic peroxides is greatly reduced as these compounds are rapidly consumed during the passage of a cool flame. Thus, the distribution of products varies greatly between the slow combustion and cool flame regions. The products of cool flame combustion include alkenes, alcohols, ketones, aldehydes, O-heterocycles, various peroxides, oxides of carbon and water (Fish, 1967). Even within the cool flame region, considerable variation in product distribution occurs with changes in temperature. These variations provide evidence for the mechanistic changes in the reactions which occur during cool flame combustion and efforts have been made to relate them to the fine structure of the ignition diagram (Fish, 1967; Fish and Wilson, 1971). In the high temperature region, and with hydrocarbons of low molecular weight ($< C_4$), oxygenated products are less abundant, while the yields of alkenes and hydrogen peroxide are greatly increased.

Two-stage ignition is a highly exothermic process, and the products formed during ignition are quite different from those of cool flame and slow combustion. In this region, the reaction tends towards completion and a large proportion of the hydrocarbon is converted to carbon oxides and water. Substantial amounts of low molecular weight hydrocarbons may also be formed, mainly as a result of cracking of excess fuel.

1.2.7. Mechanisms of hydrocarbon combustion

1.2.7.1. Background

One of the earliest theories of hydrocarbon oxidation, the hydroxylation theory, was proposed by Bone (Bone and Wheeler, 1904), as a result of studies of the slow combustion of methane, ethane and ethene. This theory attempted to explain the formation of intermediates on the basis of successive replacements of C-H groups by C-OH groups. Although this was able to account qualitatively for the formation of aldehydes and acids, it was not possible to explain a large number of the other principal products observed, and was, therefore, abandoned.

Semenov (1935) explained hydrocarbon combustion in terms of free-radical chain reactions with degenerate branching. A branched chain reaction is normally accompanied by a dramatic acceleration in reaction rate due to the formation of more than one new carrier from each branching agent, thus rapidly increasing the number of chain carriers. It was proposed that a moderately stable intermediate is formed with an average lifetime greater than that of the primary chain-carriers and that this intermediate reacts slowly to generate further reactive chain carriers. Such reactions are characterized by initiation, propagation, degenerate branching and termination steps. The detailed mechanisms of these reactions are not fully resolved, but the main features can be explained in terms of the alkylperoxy radical isomerization theory of Fish (1968). The elementary reaction steps which occur in alkane combustion may be represented by the radical chain mechanisms in the following scheme.

1.2.7.2. Initiation

The initiation step of the chain reaction involves the abstraction of a hydrogen atom from the alkane by an oxygen atom to yield an alkyl radical and a hydroperoxy radical (Cullis and Hinshelwood, 1947):

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot \qquad (1.1)$$

The activation energy for this reaction is high (ca. 185-210 kJ mole^{-1}) and therefore the process will be slow and selective. On the basis of the different C-H bond strengths, the ease of hydrogen abstraction decreases in the order tertiary > secondary > primary.

1.2.7.3. Chain propagation

Further reactions of the alkyl radicals could, in principle, include decomposition, recombination, disproportionation, isomerisation or reaction with further fuel molecules. However, in the low temperature region of hydrocarbon combustion (i.e. < 670K) the alkyl radical is found to react almost exclusively with an oxygen molecule to form an alkylperoxy radical:

$$R\cdot + O_2 \rightleftharpoons RO_2\cdot \qquad (1.2)$$

At higher temperatures (i.e. > 670K) however, the alkylperoxy radical is believed to be unstable and to break down almost immediately to form the conjugate alkene and a further hydroperoxy radical (Fish, 1970). At high temperatures, therefore, reaction (1.3):

$$R\cdot + O_2 \longrightarrow \text{alkene} + HO_2\cdot \qquad (1.3)$$

may become more important than reaction (1.2)(Knox, 1965). The alkylperoxy radical may then react with further fuel molecules to complete the primary chain propagation:

$$RO_2\cdot + RH \longrightarrow R\cdot + ROOH \qquad (1.4)$$

However, the most important reaction of alkylperoxy radicals is the intramolecular hydrocarbon abstraction to form hydroperoxyalkyl radicals (Fish, Haskell and Read, 1969):

$$ROO\cdot \longrightarrow \cdot ROOH \qquad (1.5)$$

which may then decompose in various ways to yield products such as O-heterocycles and carbonyl compounds:

$$\cdot\mathrm{ROOH} \longrightarrow \text{products} + \cdot\mathrm{OH} \qquad (1.6)$$

or combine with oxygen to form a hydroperoxyalkylperoxy radical :

$$\cdot\mathrm{ROOH} + \mathrm{O_2} \longrightarrow \cdot\mathrm{OOROOH} \qquad (1.7)$$

The hydroxyl radical produced in reaction (1.6) can abstract a hydrogen atom from a fuel molecule to continue the propagation of the primary chain:

$$\mathrm{RH} + \cdot\mathrm{OH} \longrightarrow \mathrm{R}\cdot + \mathrm{H_2O} \qquad (1.8)$$

1.2.7.4. Degenerate chain branching

There is still some uncertainty as to the identity of the intermediates responsible for chain branching in hydrocarbon combustion. It is thought that peroxides and aldehydes are the most likely agents to perform this rôle, although several intermediate products have been shown to be capable of acting as degenerate branching agents.

Peroxides decompose thermally to yield an alkoxy and a hydroxyl radical:

$$\mathrm{ROOH} \longrightarrow \mathrm{RO}\cdot + \cdot\mathrm{OH} \qquad (1.9)$$

Likewise, at sufficiently high temperatures and in the presence of a third body, hydrogen peroxide will dissociate into hydroxyl radicals:

$$\mathrm{H_2O_2} + \mathrm{M} \longrightarrow 2\cdot\mathrm{OH} + \mathrm{M} \qquad (1.10)$$

Aldehydes are able to act as branching agents as a result of the presence of a weak C—H bond at the carbonyl group. This hydrogen atom may be abstracted by an oxygen molecule or another radical with greater ease than the hydrogen from an alkane:

$$RCHO + O_2 \longrightarrow R\dot{C}{=}O + HO_2\cdot \qquad (1.11)$$

$$RCHO + R'O_2\cdot \longrightarrow R\dot{C}{=}O + R'O\cdot + \cdot OH \qquad (1.12)$$

1.2.7.5. Chain termination

Termination processes may be either homogeneous or heterogeneous. Homogeneous termination may occur by radical recombination to yield stable species or by disproportionation of radicals. Examples of reactions which may be important in chain termination are :-

$$2RO_2\cdot \longrightarrow ROOH + \text{alkene} + O_2 \qquad (1.13)$$

$$2HO_2^{\cdot} \longrightarrow H_2O_2 + O_2 \qquad (1.14)$$

$$RO_2\cdot + HO_2\cdot \longrightarrow ROOH + O_2 \qquad (1.15)$$

$$2RO\cdot \longrightarrow ROOR \qquad (1.16)$$

Heterogeneous termination occurs as a result of the diffusion of chain carriers and branching agents to the walls of the reaction vessel, where they are destroyed.

1.3 HYDROCARBON COMBUSTION IN SPARK-IGNITION ENGINES

1.3.1. Gasoline and the spark-ignition engine

Gasoline contains representatives of all the main groups of hydrocarbons - namely alkanes and cycloalkanes, alkenes and cycloalkenes and aromatics. Straight-run gasoline represents the fraction obtained from the direct distillation of petroleum boiling between 300-480K, generally containing compounds in the range C_5-C_{12} (Owen, 1973). A finished gasoline will vary in composition depending on the refinery processes available, the demand for other products from the refinery and the desired quality of the gasoline. The gasoline quality is generally improved by the following refinery processes: catalytic cracking, catalytic reforming and alkylation, thereby increasing the amounts of alkenes, aromatics and branched-chain alkanes obtainable from the crude petroleum. Further improvements in gasoline quality are obtained by the use of additives.

In the spark-ignition engine (Lichty, 1967) a charge of fuel and air is drawn into the cylinder via the intake valve. The mixture is then compressed by the movement of a piston, before ignition is induced by the passage of a spark. Combustion, under ideal conditions, will then proceed by means of a flame front moving through the mixture until completion. The hot expanding gases force the return of the piston during the power stroke. In an ideal situation, the hydrocarbon fuel should undergo complete oxidation to carbon dioxide and water. However, in practice this is never the case, and the exhaust mixture contains a large number of intermediate products and unburnt hydrocarbons, along with small amounts of oxides of nitrogen and sulphur arising from the presence of compounds containing nitrogen and sulphur in the fuel and partly by fixation of nitrogen at the high temperatures generated during the process. A large number of these combustion products, including carbon dioxide, are undesirable constituents of exhaust gases, due to their contribution to atmospheric pollution (Cullis and Hirschler, 1980).

The power output and thermal efficiency of an engine is dependent on the compression ratio permissible (Lichty, 1967; Ricardo and Hempson, 1968). Besides fuel quality, other factors such as fuel-air ratio, size and speed of engine, combustion chamber design and spark advance determine the limits of compression ratio. The exact stoichiometric amount of air required for the complete combustion of a given fuel depends on the precise composition of the hydrocarbon mixture, but for most gasolines the air:fuel ratio is generally around 15:1. The stoichiometric mixture, however, does not generally develop the maximum power output and thermal efficiency: leaner mixtures (ca. 16:1) are obtained by means of a carburettor to optimise these parameters, and also reduce the levels of hydrocarbon in exhaust emissions.

1.3.2. The occurrence of knock during hydrocarbon combustion

The importance of "knock" in the spark ignition engine lies in the limit it imposes on the usable compression ratio, which, in turn, controls efficiency and, to some extent, power output (Lichty, 1967; Ricardo and Hempson, 1968). During the normal combustion process, the last part of the charge to burn is heated by the compression of the expanding gases and by radiation from the advancing flame front. The flame front will move across to the further wall of the chamber, burning the mixture as it goes. If, however, the temperature and pressure to which the "end-gas" is subjected are sufficiently high, auto-ignition will occur before the flame front reaches it. This results in a severe pressure wave which causes vibration in the cylinder walls, leading to the characteristic metallic "pinking" sound associated with knock. Knock is accompanied by an increase in the rate of heat transfer to the cylinder walls and thus by a marked decrease in the power output of the engine. In severe cases, knock can result in mechanical damage to the engine.

It has been shown that under knocking conditions (Ricardo and Hempson, 1968; Miller, 1947; Male, 1949), combustion of the mixture proceeds normally, but the end-gas, as a result of compression and heating to a critical level by the advancing flame front, undergoes spontaneous ignition. The tendency of a hydrocarbon fuel to knock in an engine has been shown to be related to its low-temperature ignition profile (Walsh, 1963; Fish, Read and Affleck, 1969). Indeed phenomena such as cool flames and two-stage ignition have been observed under engine conditions (Downs, Walsh and Wheeler, 1951; Affleck and Fish, 1967; King et al., 1952). Thus, any condition which raises the temperature and pressure of the charge, such as an increase in compression ratio or air intake temperature, will encourage knock.

The chemical reactions preceding knock are very complex and the mechanisms involved are not fully established. Prior to the passage of the flame front through the charge, the temperature and pressure of the mixture are such that a series of pre-flame reactions will have already commenced. The extent of these reactions will determine whether smooth burning of the whole charge occurs, allowing maximum power to be obtained from the engine. The resistance to knock of a given hydrocarbon is related to the extent of its preflame reactions and, since different hydrocarbons show marked variations in their preflame and ignition characteristics, they differ in their knocking tendency in an engine. In previous studies on preflame reactions (Retailliau, Ricardo and Jone, 1950; Salooja, 1960) it has been found that, in general, those hydrocarbons whose preflame reactions are extensive are also more susceptible to spontaneous ignition and have, therefore, a greater tendency to knock. This tendency to undergo preflame reactions has also been correlated with the octane numbers of various hydrocarbons (Salooja, 1960).

The correlation observed between the low temperature ignition characteristics and the tendency of hydrocarbons to knock indicates that the mechanisms of the chemical reactions involved must be similar (Downs, Walsh and Wheeler, 1951; Affleck and Fish, 1967). Further evidence can be obtained by analysis of the constituents of the end gases present at various stages of an engine cycle during which knock occurs. It is found that formaldehyde, higher aldehydes and peroxides are present immediately before the onset of knock (Lewis and von Elbe, 1951). The intensity of knocking has, indeed, been correlated with the amount of formaldehyde present in end-gas. Knock is never observed under conditions where formaldehyde is not detectable, although the presence of formaldehyde does not lead to knock under all conditions. Further analysis showed that organic peroxides were present in the end gas at concentrations of the order required to induce knocking by the addition of peroxides (Egerton, Smith and Ubbelohde, 1935). This indicates that the operative chain-branching reactions are in some way connected with the presence of these intermediates during knock. The products of cool flame oxidation at low pressures in glass apparatus and at high pressures in a rapid-compression engine have been shown to be identical (Affleck and Fish, 1967).

During the combustion of 2-methylpentane in a rapid compression engine (Affleck and Fish, 1967) and of isooctane in both a motored engine (Maynard, Legate and Graiff, 1967) and a spark ignition engine (Alperstein and Bradow, 1966) the products are found to contain large amounts of O-heterocycles which may have arisen from alkylperoxy radical isomerization. Indeed, the knocking tendency of hydrocarbons has been correlated to the ease of formation of mono- and di-hydroperoxides (Cartlidge and Tipper, 1961).

1.3.3. Knock rating of fuels

1.3.3.1. Measurement of antiknock quality

The resistance of a fuel to knock is expressed in terms of its octane number. This number is based on an arbitrary scale in which isooctane has been given, by definition, a value of 100, while heptane has a value of 0 (Edgar and Hinegarder, 1925). The scale can be extended above 100 by the addition of tetraethyllead to isooctane. The octane numbers of fuels are determined in a CFR (Co-operative Fuel Research) engine (ASTM, 1977) which consists of a variable compression ratio, single-cylinder unit. This is done by matching the knock produced by the fuel concerned with that obtained by the use of blends of isooctane and heptane, or isooctane plus tetraethyllead. These blends are known as primary reference fuels. The octane number is given as the percentage of isooctane in an isooctane-heptane blend.

The general procedure followed for the measurement of octane numbers in the CFR engine is to adjust the fuel-air ratio of the mixture to that necessary for maximum knock. For most hydrocarbons, this mixture is slightly on the fuel-rich side of stoichiometric. The compression ratio is then adjusted until a standard intensity of knock is obtained on an electronically controlled knockmeter. When this knockmeter reading is bracketed by two reference fuels (isooctane-heptane mixtures) which differ by no more than two octane units, the rating of the sample is calculated by interpolation. The antiknock quality given by a gasoline in an average car engine is rated by two laboratory tests involving the CFR engine: the Research Method and the Motor Method, yielding research octane numbers (RON) and motor octane numbers (MON) respectively. The Research Method is less severe than the Motor Method, which results in nearly all motor fuels having a higher RON than MON. The difference between these parameters is referred to as the 'sensitivity' of the fuel to the changes in operating conditions between the two methods (Table 1.1).

1.3.3.2. Gasoline parameters affecting knock

Low-speed knock occurs in a multi-cylinder engine when the throttle is opened at low crankshaft speed. There is a tendency for the highest-boiling fraction of the gasoline to condense on the walls of the induction system, and the charge entering the cylinders therefore consists of the more volatile fractions. The susceptibility to knock will then be determined by the antiknock quality of the lower-boiling fractions of the fuel entering the combustion chambers. The difference between the Research octane number of the complete gasoline and that of the fraction distilled to 373K is known as Delta $100^{o}C$ and is used

TABLE 1.1

Test conditions of CFR Knock Rating Method

	Research	Motor
Engine speed, rev/min	600 + 6	900 + 9
Intake air temp. K	specified but depends on prevailing barometric pressure	310
Intake mixture temp. K	Not specified	420
Coolant, K	373	373
Compression ratio	variable	variable
Ignition advance	13° btdc	variable (14°-26° btdc)
Air intake humidity, grain water/lb. dry air	25-50	25-50

as an indication of the tendency of a fuel to knock under low-speed acceleration. A gasoline with a Delta 100°C above 14 is considered to have poor 'front-end' octane quality.

High-speed knock occurs when a fully warmed-up engine is running with the throttle wide open. Under these conditions, temperatures and pressures within the combustion chamber are likely to be high, and knock is therefore likely to occur. The resistance of a fuel to knock, in a multi-cylinder engine, at medium and high speeds can be correlated with the Motor octane number, the sensitivity and/or the concentration of alkenes in the fuel (BP Petroleum Division, 1972).

1.3.4. The inhibition of knock using antiknock additives

1.3.4.1 Background

The occurrence of knock in internal combustion engines imposes strict limitations on the efficiency and fuel economy of the engine. Knock may be minimised by engine design and operating conditions, or by the use of high-octane gasoline. The required levels of antiknock quality in motor gasoline are obtained at the present time by the modification of refinery processing and blending of gasolines and by the use of antiknock additives. An antiknock additive is a compound which, when added to fuel in small quantities, will severely decrease the tendency of that fuel to knock. By far the most widely used antiknock additives have been the lead alkyls (Midgely and Boyd, 1922; Richardson et al., 1963; van Gulik, 1975), particularly tetraethyllead (TEL) and tetramethyllead (TML), although other organolead compounds have been used and are commercially available e.g. cyclopentadienyllead, dimethyldiethyllead etc. The antiknock effectiveness of tetraethyllead was first discovered, apparently by accident, in the early 1920's by Kettering, Midgely and Boyd (Walsh 1961).

Lead antiknocks are used in conjunction with scavenging agents, such as 1,2-dibromoethane and 1,2-dichloroethane, which react with solid lead oxide particles formed during the combustion process to form volatile lead halides. Thus it is possible to remove lead compounds with ease from the cylinder in the exhaust gases, and hence avoid problems caused by solid deposits. In most cases, blends of tetraethyllead and tetramethyllead are used.

Generally, a greater improvement in antiknock quality is obtained with TEL than with TML, but the advantage gained by the use of blends of these additives lies in their differences in volatility. Some gasoline components, such as catalytic reformate, have a poor front-end octane number, despite having excellent antiknock properties under arduous conditions of high but constant engine speed. Incorporation of TML, which has a boiling point of 383K, improves the front-end octane rating of the component and therefore enhances the low-speed antiknock quality of the finished gasoline. TEL is less volatile, boiling at 473K, and is therefore liable to condense in the fuel induction system under conditions of low-speed acceleration.

The response of gasoline to lead additives depends on the octane quality of the individual components in the blend and, in general, a greater response is observed in those fuels of lower antiknock quality. Studies of the effect of tetraethyllead on the antiknock properties of various hydrocarbons have shown that alkanes have a higher response to TEL than do alkenes and aromatic hydrocarbons (Lovell, 1948; Lovell and Zang, 1951; Defer et al., 1958). Indeed, highly branched alkenes and aromatics with branched or unsaturated side chains have been shown to exhibit poor, and in some cases negative, responses to the presence of TEL.

1.3.4.2. Mechanism of action of lead-based antiknocks

Despite the fact that lead alkyls have found widespread application as antiknock additives since the early twenties, very little fundamental research on the mode of action of these compounds was published for many years, and even now there is some doubt as to the nature of the species responsible for the considerable inhibition effected by TEL. This was due, in part, to the difficulties involved in the handling of lead alkyls and to the irreproducibility of results obtained in laboratory experiments, as a result of the low vapour pressure and the toxicity of TEL, and the strong inhibiting effects of solid lead oxide deposits (Chamberlain et al., 1953; Chamberlain and Walsh, 1952). Subsequent studies in PbO-coated vessels enabled some elucidation of the operative mechanisms (Chamberlain and Walsh, 1952). Early experiments showed, however, that TEL could have an acute inhibiting effect on hydrocarbon combustion in various temperature-pressure regions of the ignition profile. The compound was shown to inhibit high and low-temperature slow combustion, low-temperature two-stage ignition, and high-temperature hot ignition; it had, however, no effect on the induction period preceding the appearance of a cool flame, although ΔP_{cf} was reduced somewhat, and the cool flame pressure limit was increased. The results obtained in experiments involving PbO-coated vessels were shown to parallel those found with TEL. However, at the lowest temperatures of the cool flame region studies in PbO-coated vessels, it was found that for various hydrocarbons the induction period, τ, and the cool flame limits were increased. The effects became less pronounced as the temperature was increased i.e. when chain termination due to diffusion of chain carriers and branching agents to the walls became less important, and as the time interval preceding the cool flame, τ, decreased (Friedlander and Grunberg, 1948; Ouellet et al., 1949; Chamberlain and Walsh, 1949; Malherbe and Walsh, 1950). In addition to these findings, several early studies had demonstrated the necessity of tetraethyllead being oxidised before it showed an inhibiting effect; at temperatures below 473K the compound had little or no effect upon oxidation reactions (Pope et al., 1929; Jost and Rögener, 1941). Indeed, additions of TEL to a reacting mixture of pentane and oxygen in a flow system showed a promoting effect, unless the TEL was allowed to undergo some oxidation beforehand, in which case the reaction was strongly retarded (Pidgeon and Egerton, 1932).

It is widely believed, therefore, that the lead alkyls decompose or are oxidised to form a fine mist of lead monoxide which terminates chains in the preflame reactions and hence suppresses autoignition (Downs et al., 1961). It is established that with hydrocarbon fuels engine knock takes place via a two-stage process, and that tetraethyllead has little effect on the first stage, but a profound effect on the second stage. There is evidence to suggest that the tetraethyllead is oxidized rapidly during the passage of the cool flame and exerts its effect as oxides of lead (Downs et al., 1961). Early experiments (Ross and Rifkin, 1956; Egerton and Gates, 1927) showed that vapours from an arc struck between lead electrodes in the air intake of an engine also exhibited an antiknock effect, thus demonstrating that the presence of tetraethyllead itself is not essential for the inhibition of knock.

The lead monoxide formed as a result of the oxidation of tetraethyllead in both engine (Rifkin, 1952) and laboratory experiments (Salooja, 1965), has been shown to consist mainly of the orthorhombic and tetragonal polymorphs, the relative proportions depending on the temperature and nature of the base fuels. Both forms have been shown to exert an inhibiting effect on the combustion of various hydrocarbons in experiments with PbO-coated vessels (Chamberlain and Walsh, 1952; Salooja, 1965; Bardwell, 1961; Warren, 1952; Cheaney et al., 1959), the tetragonal form exhibiting a more pronounced effect. Results obtained from these experiments led Walsh and co-workers (Chamberlain, Hoare and Walsh, 1953; Hoare and Walsh, 1952), to propose a mechanism whereby the antiknock action of TEL was attributed to the destruction of free radicals such as $\cdot OH$ and $HO_2^{\cdot}$ at the surface of lead monoxide particles formed in the cylinder. Tyndall beam experiments (Downs et al., 1961) indicated the formation of a "fog" of solid PbO particles during the passage of a cool flame in an engine cylinder and thus lent support to this theory.

Norrish (1959), however, argued that in an engine cycle there is insufficient time for tetraethyllead to form a "fog" of lead monoxide particles and that the high pressures of engine gases attained in the cylinder would greatly impede the growth of such particles. Alternatively it was suggested that the observed inhibition is due to homogeneous mechanisms involving gaseous lead and lead oxide species (Norrish, 1965) according to the following scheme :

$$Pb + \cdot OH \longrightarrow PbOH$$

$$PbOH + \cdot OH \longrightarrow PbO + H_2O$$

followed by the conversion of PbO molecules back to Pb atoms :

$$PbO + R^{\cdot} \longrightarrow PbO + RO\cdot$$

This was later revised to include the inhibiting effect of PbO molecules (Erhard and Norrish, 1960) :

$$\begin{array}{rcll}
\mathrm{PbO} & + \cdot\mathrm{OH} & \longrightarrow \mathrm{PbO(OH)} & \\
\mathrm{PbO(OH)} & + \cdot\mathrm{OH} & \longrightarrow \mathrm{PbO_2^{\bullet}} & + \ \mathrm{H_2O} \\
\mathrm{PbO_2} & + \ \mathrm{R}\cdot & \longrightarrow \mathrm{PbO} & + \ \mathrm{RO}\cdot
\end{array}$$

The arguments against such a scheme lie in the fact that the deductions were made on the basis of flash photolysis experiments involving temperatures higher than those likely to be experienced in an engine cycle (>1000K), much lower pressures (∿ 4 kPa) and over a shorter time scale (Callear and Norrish, 1960). No account is taken for the "fog" of particles observed in the engine experiments of Downs, Griffiths and Wheeler (1961). It seems likely, therefore, that the antiknock action of tetraethyllead lies at least partly in the formation, during the passage of the cool flame, of solid PbO particles, which are capable of destroying, heterogeneously, peroxides and $^{\bullet}OH$ and $HO_2^{\bullet}$ radicals (Salooja, 1968) which are responsible for the onset of knock (see Section 1.3.2.).

1.3.4.3. Mechanisms of knock suppression by organic compounds

In contrast to the action of lead alkyls and other organometallic antiknock additives, organic compounds do not in general need to be converted to another species before exerting this effect (Walsh, 1961). The organic compounds which have received attention have been mainly derivatives of benzene, particularly aromatic amines.

A large number of the simple derivatives of benzene have exhibited varying degrees of antiknock effectiveness, correlating with the expected effects of the side chains on the electronic density in the benzene ring (Chamberlain and Walsh, 1949; Walsh, 1961), and suggesting that the ring is the likely seat of the action. In general, side chains which tend to increase the electron density on the benzene ring have a greater antiknock effect than benzene, while those which are electron withdrawing tend to be less effective, and in some cases are proknocks. Thus toluene, phenol and aniline all have a greater effect than benzene, increasing in that order; whereas benzyl alcohol, benzaldehyde and nitrobenzene are less effective.

An advantage of the addition of aromatic compounds to gasoline is that they burn to yield purely gaseous products ("ashless" antiknocks). This, however, also limits their usefulness in that the active species is the unchanged molecule, and there is a correlation between their ease of pyrolysis and oxidation and decreased effectiveness. In some cases this can lead to a proknock action, particularly with derivatives containing large side groups.

The mode of action of simple aromatic compounds involves the formation of a temporary complex between a radical chain carrier and the π electron cloud of the benzene nucleus. If during the lifetime of this radical complex a collision occurs with a further radical, a radical recombination reaction may occur with consequent chain termination. The lifetime of the radical complex would be expected to be dependent on the binding energy of the π electrons on the benzene nucleus; both the lifetime of the radicals and the resulting antiknock effect increase as the binding energy decreases.

The antiknock activity of aromatic amines has been recognised since 1919. The mode of action of derivatives of aniline differs from that of other aromatic compounds in that the active species is a radical of the type $C_6H_5.\dot{N}.R$, which is formed by the abstraction by a free radical of hydrogen attached to nitrogen in the parent molecule (Brown et al. 1955; Salooja, 1963). This theory is in accord with early experiments on the effects of aromatic amines on engine combustion by Boyd (1924), who found that secondary amines were more effective than primary amines and tertiary amines in the suppression of knock. The relative effectiveness of the aromatic amines correlates with the ease of hydrogen abstraction and the stability of the resulting radical, which, if sufficiently inert, is unable to propagate further chains (Salooja, 1963). Brown et al. (1955) found that N,N-dimethylaniline and other anilines where both hydrogens are replaced by alkyl groups have no antiknock effect under engine conditions, although Boyd (1924) found a small inhibiting effect in non-engine experiments. Accordingly, N-methylaniline is found to be a more powerful antiknock additive than aniline, and the effects of ring substitution substantiate this theory.

Aliphatic amines are also known to be inhibitors of knock (Cullis and Waddington, 1957; Cullis and Khokhar, 1959, 1960; Waddington, 1959). In laboratory studies (Walsh, 1961) the following orders of inhibiting power have been established:

methylamine < ethylamine < 1-propylamine < 1-butylamine

and even more pronounced :

primary amines < tertiary amines < secondary amines

This suggests that the seat of action of the aliphatic amines is the nitrogen atom and this would be consistent with a mechanism whereby a complex was formed between a radical and the lone pair electrons on the nitrogen atom. The inhibition would then be due to the ready recombination of radicals, as in the case of aromatic antiknocks. Aliphatic amines are, however, only relatively weak engine antiknocks.

The fact that the organic antiknocks considered so far act as unchanged molecules and not as their oxidation products places a restriction on their usefulness as fuel additives. The present trend in engine design is towards higher compression ratios and operating speeds and thus higher temperatures. The effectiveness of these compounds is minimized since they are gradually destroyed by oxidation or pyrolysis before they can exert their inhibiting effect.

Much interest has been shown over the past few years in the possible use of methyl tert-butyl ether (MTBE) as a constituent of gasoline. MTBE is not an antiknock compound in the same sense as other organic or organometallic antiknocks, inasmuch as small concentrations of the ether do not show a profound inhibiting effect on the combustion of a fuel. Compounds of this type are referred to as octane range extenders or blending agents and include tert-butyl alcohol and several other alcohols and ethers. The combustion products derived from such compounds are purely gaseous and non-toxic, allowing large proportions of the compound to be blended into the base fuel. Concentrations of up to 20% have been tested for MTBE, but until now, blends containing only up to 7% have been approved. The activity of these compounds lies in the superior octane quality displayed when they are used as fuels in their own right (MTBE has a research octane number of 115). Blending with gasoline in substantial amounts results in a composite "gasohol" or "gasether" of greater antiknock quality than the base fuel.

Before the recent price increases in petroleum, it had not been considered economical to produce MTBE in quantities necessary for a significant improvement in the octane quality of gasoline. MTBE is currently produced from methanol and isobutene in the presence of an ion-exchange resin catalyst. The major limit on the growth of MTBE is the availability of isobutene, which is currently used in the production of motor alkylate. Studies have shown that at present it would be economically viable to use the existing isobutene feedstocks in the production of MTBE, since comparisons have shown that the octane improvement obtained with MTBE is 15 octane numbers above that obtained with motor alkylate. A further source of isobutene is the catalytic conversion of n-butane, which is likely to become increasingly available worldwide from liquified petroleum gas and in this country from natural gas. Thus, the role of MTBE as an octane booster is likely to become more important in the future.

Methanol and ethanol have also been considered as large scale blending agents in gasoline. Despite the favourable antiknock properties of these fuels, other problems exist, e.g. the alcohols have lower calorific values than hydrocarbon fuels, thereby increasing fuel consumption. The high vapour pressure of the alcohols can cause vapour-lock problems in hot weather. Their solubility in water can also cause phase separation of a gasoline-alcohol blend. At the present time, the widespread use of low molecular weight alcohols as blending agents is not considered to be feasible, particularly in this country where climatic and agricultural conditions would not favour the large scale production of crops such as sugar beet for fermentation to ethanol, and large scale conversion of natural gas or coal to methanol is not, at present, considered to be economical.

1.3.4.4. Alternative organometallic antiknock agents

The search for a compound showing more powerful antiknock properties than tetraethyllead, coupled with recent legislation concerning atmospheric pollution due to lead emissions and the deleterious effect of lead on exhaust catalysts, has led to the testing of thousands of compounds as alternative antiknocks. The most successful compounds in this respect have been those organometallic compounds which are capable of being oxidised under engine conditions to form "fogs" of oxide particles analogous to those formed by the lead alkyls. The requirement of the metal to form oxide particles and to be able to exist in various oxidation states was realised as early as 1927 (Egerton and Gates, 1927; Egerton, Smith and Ubbelohde, 1935).

Of the many organometallic compounds tested, the strongest antiknock effects have been found with compounds of iron, such as pentacarbonyliron and dicyclopentadienyliron, and tetracarbonylnickel. Methylcyclopentadienylmanganese tricarbonyl (Brown and Lovell, 1958) was found to have antiknock properties comparable with those of tetraethyllead and was marketed for some time in the United States. The material was considered to be too expensive as a total replacement for the lead alkyls, but it was shown to have a synergistic effect when blended with leaded gasolines. However, in the quantities required to maintain existing fuel octane quality, it is thought that the compound is 8-10 times more toxic than lead. In common with the majority of alternative organometallic antiknocks, difficulties are experienced in the scavenging of the metal oxide particles formed during combustion, and these can lead to catastrophic engine wear. The presence of these compounds can also lead to increases in hydrocarbon emissions and have an adverse effect on the life of exhaust catalysts. Indeed, methylcyclopentadienylmanganese tricarbonyl was banned in the United States in 1978 when it failed to meet new exhaust emission controls. The German Government has indeed specifically prohibited the use of other metallic additives in place of lead.

Recent studies have included work on complexes of rare earth metals, such as p-diketonate chelates of cerium, which have been shown to exhibit effects comparable with that of TEL in engine tests (Tischer et al. 1974). Organic titanates (Haskell and Kiovsky, 1981) have been reported to show up to half the activity of lead alkyls, but simple members of the series have been shown to undergo hydrolysis on addition to undried gasoline. The stability towards hydrolysis is improved by chelation, although half the activity is lost after three days' storage in undried gasoline. A concentration of 0.1 g ℓ^{-1} titanium yielded an octane improvement of 0.5 RON.

Other studies have shown the considerable favourable effect on octane numbers of organometallic compounds containing mixed metals. Tributyltin-, trimethylsilyl- and trimethyllead derivatives of cyclopentadienylmanganese tricarbonyl were tested, but found to be inferior to the parent compound (Chernyshev et al. 1979).

Table 1.2 shows the effects obtained with some of the organic and organometallic additives studied in engine experiments, compared with that obtained with aniline.

TABLE 1.2

Relative effectiveness of antiknock compounds and some antiknock fuels (based on aniline = 1) (Calingaert, 1938).

Benzene	0.085
Isooctane	0.085
Triphenylamine	0.090
Ethanol	0.104
Xylene	0.142
N,N-dimethylaniline	0.21
Diethylamine	0.495
Aniline	(1.00)
Ethyl iodide	1.09
Toluidine	1.22
Dimethylcadmium	1.24
M-xylidine	1.40
Triphenylarsine	1.60
Titanium tetrachloride	3.20
Tetraethyltin	4.0
Stannic chloride	4.1
Diethylselenide	6.9
Triethylbismuth	23.8
Diethyltelluride	26.6
Tetracarbonylnickel	35
Pentacarbonyliron	50
Tetraethyllead	118

1.4. LEAD IN THE ENVIRONMENT

1.4.1. Sources of lead in the environment

There is no doubt as to the toxicity of lead, and in particular the adverse effects of lead poisoning on the development of young children. Lead enters the body by three main routes: in food, in drinking water and by inhalation. The relative contributions from the various sources to the body burden of lead have been reviewed by a working party under the Chairmanship of Professor P.J. Lawther (1980). Although there is a wide variation in lead uptake between different individuals, in general the major source is food, the contribution from which is about an order of magnitude greater than that of either water or air. On the basis of these studies, it was suggested that most of the long-term average dietary intakes of lead by individual adults fall within the range of 70-150 mg per day. Of this ingested lead, it was estimated that about 10% was absorbed into the body. The principal sources of lead in food were assumed to arise from the existing levels of lead occurring naturally in soils, from deposition of lead from the atmosphere, from water used in cooking and, in the case of tinned food, from the solders used in the canning process. Information from a study of lead in tap water in the U.K. suggests that this is a negligible source in 60-70% of the population. However, where lead pipes are used, and the water is acidic, the level of uptake may be comparable with that ingested from food. The proportion of lead inhaled from the atmosphere varies considerably and is dependent on the levels to which an individual is exposed. A recent study (Chamberlain et al., 1978) estimated that an individual exposed to an average air lead level of 1 $\mu g\ m^{-3}$ (which corresponds to the upper limit of the annual mean levels recorded from the central areas of major British cities) would breathe in about 15 µg of lead per day of which approximately 50% is deposited in the lungs and then absorbed into the body. An uptake of this magnitude would account for about 16% of the daily intake of lead, although at the levels to which most individuals are exposed, less than 10% of the daily intake is assumed to arise from atmospheric sources. Poisoning from "adventitious" sources, such as lead in paint, is also regarded as a serious problem as far as children are concerned because of their habit of chewing painted articles.

1.4.2. Lead from motor vehicles

Exhaust from motor vehicles accounts for approximately 90% of lead in the atmosphere, except in specific locations where industrial emissions may add a significant contribution. These industrial sources include emissions into the atmosphere from the smelting and refining of lead; it is estimated that these processes release about 200 to 250 tonnes of lead per year. However, these emissions are very localised and levels of lead in air and dust tend to be elevated only in the immediate vicinity of the smelters. Small amounts of lead also enter the atmosphere from the combustion of fossil fuels (60-70 tonnes) and from the processing and weathering of lead products.

Two kinds of particulates are generally emitted from vehicle exhausts, coarse and fine. The coarse particles originate from deposits on the exhaust system walls which are removed by thermal and mechanical shock, and have diameters in the range 200-5000 µm. These consist of lead halide-based salts, lead sulphate and carbonaceous materials. The fine particles are consistent with materials formed during the combustion process or from the volatilisation of previously deposited lead halide salts in the exhaust tract. In general, these also consist of lead halide salts coated with carbon and carbonaceous materials, but are thought to constitute a greater danger to health as a result of their physical state (particle size less than 1 µm) and their solubility in the body.

The contribution from motor vehicles has been the subject of several studies (Chamberlain et al., 1975; 1978; Sinn, 1981; Lynam, Ter Haar and Hall, 1981). The incorporation into the fuel of a short-lived radio-isotope of lead, ^{203}Pb, gave an indication of the levels of lead retained in the lungs, the amount absorbed into the bloodstream, and the half-life of lead in blood. Initial results indicated that an airborne concentration of lead of 1 µg m^{-3} produced an increment of 1 µg/ 100 cm^3 in blood. This was shown to depend largely on the particle size of the airborne lead, and a revised average figure of 2 µg/100 cm^3 was obtained for the same airborne concentration, as an increment to be added to existing average levels of lead in blood of 15-20 µg/ 100 cm^3.

Various studies have been undertaken to determine the influence of traffic density and airborne lead concentrations on lead absorption (Johnson et al., 1978; Sinn, 1981). In one such study, the blood lead levels of residents of Dallas, Texas living near traffic densities varying between 1000 and 30,000 cars per day were compared. No correlation between traffic density and blood lead levels was found. A study conducted in Frankfurt showed that between 1976 (the year in which the West German government reduced the permissible level of lead in petrol from 0.4g ℓ^{-1} to 1.5g ℓ^{-1}) and 1978, the blood lead levels of residents did not change significantly, despite a drop in airborne lead concentration from a maximum level of 3.2 $\mu g\ m^{-3}$ to 0.6 $\mu g\ m^{-3}$ in areas of high traffic density. Similarly, studies of the effect of lead fallout from the atmosphere on the levels found in crops and soil showed that lead from petrol made an insignificant difference, inasmuch as at distances of 32 metres from the roadside in areas of heavy traffic, the lead levels in soils can drop by as much as 75% from that found at 8 metres.

However, in the light of more recent evidence, the case against lead in petrol has gained momentum (McGinty, 1982). In an Italian study, lead from the Broken Hill mine in Australia was added to petrol sold in the Piedmont and Turin areas from 1977 to 1979. The lead from this mine contains a characteristic ratio of the isotopes ^{206}Pb and ^{207}Pb, different to that found from other sources. From the measurements of isotopic ratios in blood lead after this period, it was found that the ratio characteristic of the Broken Hill mine had dropped by 30% for residents of Turin, suggesting that lead from petrol constitutes a similar proportion to the total body burden. Similarly, a survey in the United States over a four year period following the initiative taken to encourage the use of unleaded gasoline in 1975 showed that blood lead levels dropped significantly, and almost exactly in step with the decline in the amount of lead consumed by motor vehicles.

1.4.3. Effects of lead on health

Recent studies have been concerned with the relationship between lead levels, IQ and behaviour in children. Lead levels were found to be inversely related to performance in reading and spelling tests, and behavioural assessments from teachers were also found to correlate in terms of concentration, impulsiveness and distractibility. Past surveys have also shown that elevated lead levels can result in a deficit of IQ of 5 to 7 points, although these take no account of social and genetic factors and are thus open to question.

The effects of various blood lead levels on health are shown in Table 1.3 (Turner, 1980).

TABLE 1.3
Blood lead levels and effects on health

Blood lead level (µg/100 cm)	Health effect
10	Delta-ALAD* inhibition
15-20	Erythrocyte protoporphyrin elevation
40	Increased urinary Delta ALA excretion
	Anaemia
	Coproporphyrin elevation in urine
50-60	Cognitive (CNS) deficits. Peripheral neuropathies
80-100	Encephalopathic symptoms

*Delta-ALAD - delta aminolaevulinic acid dehydratase, an enzyme involved in haem biosynthesis.

1.4.4. The removal of lead from petrol

In 1975, the United States introduced stringent controls on the gaseous emissions from motor vehicles. This legislation required the removal of hydrocarbons, carbon monoxide and 90% of the oxides of nitrogen from exhaust gases. This was achieved by the fitting of exhaust systems containing a noble metal (eg platinum) catalyst. As a result, it was necessary to remove lead totally from gasoline for use in these vehicles, due to the poisoning effect of lead on such catalysts. However, refinery costs and the unavailability of sufficient amounts of crude oil precluded the large-scale production of high octane lead-free fuel to meet the demands of the American market (Dartnell, 1980). As a result, the compression ratios of cars were reduced to enable the use of fuel of a lower octane quality (91 RON). However, this resulted in a 6% rise in fuel consumption due to a loss of efficiency in engines of lower compression ratio. Coupled with this are the common occurrence of knock and an increase in the wear of engine components. Subsequently, it was estimated that 10-15% of American owners used leaded petrol in cars designed to run on lead-free petrol as a result of dissatisfaction with performance (Dartnell, 1980).

A Working Party on Lead in Petrol, consisting of Government officials and representatives of the Petroleum Industry, was set up in the U.K. to consider the feasibility and costs of further action to reduce lead emissions from motor vehicles, in view of the detrimental effects of lead on health. The four options considered were as follows (Dept. of Transport, 1979) :

1. Maintain current lead level (0.4 gl^{-1}) and RON (98).
2. Use lead filters in exhaust systems.
3. (a) Reduce lead to 0.15 gl^{-1} and RON to 95.
    (b) Reduce lead to 0.15 gl^{-1} and leave RON at 98.
4. Eliminate lead, and reduce RON to 92.

In the light of the overwhelming medical evidence on the effects of lead on health, the costs involved in the total removal of lead and the loss of efficiency on reduction of RON, the Working Party concluded that the best course of action was to reduce the level of lead to $1.5\ gl^{-1}$ and maintain RON at 98, although the cost of this action has been estimated at £66 million per year.

1.5 ORGANOSILICON COMPOUNDS

1.5.1. General organosilicon chemistry

1.5.1.1 Introduction

The congeneric relationship of silicon to carbon has stimulated a considerable volume of scientific effort in the exploration of reactions in silicon chemistry analogous to those previously demonstrated in organic chemistry. The preparation of tetraethylsilane by the reaction of silicon tetrachloride with diethylzinc, reported over a century ago by Friedel and Crafts (1863) (reported in Urry, 1970) served as a precursor to the productive investigations which have culminated in the healthy growth of the industrial field of silicone chemistry (Rochow, 1951) mainly pioneered by Kipping and co-workers.

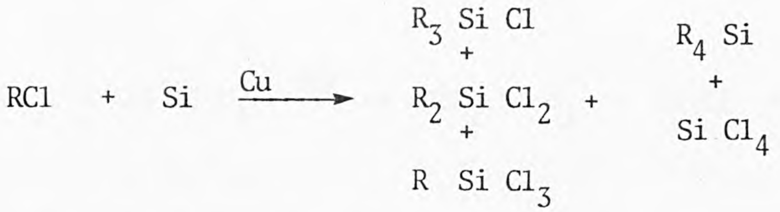
Many organosilicon compounds are distinguished by high thermal stability and chemical inertness. In addition, they are good electrical insulators and can be converted into polymers. In their chemical properties, compounds containing silicon-carbon linkages occupy a position intermediate between organic and organometallic compounds.

1.5.1.2. Formation of organosilicon compounds

The vast number of the organosilicon compounds currently available are derived initially from elemental silicon. Silicon is obtained by the reduction of silica or quartz in the presence of carbon:

$$SiO_2 + C \xrightarrow{\Delta} Si + CO_2$$

The majority of the organosilicon compounds of commercial interest contain methyl or phenyl groups bound to silicon. The principal industrial source of these is the "Direct" process, developed by Rochow (1945), in which elemental silicon is mixed with copper powder in a 1:3 ratio and allowed to react with an alkyl or aryl halide at ca. 570K. A complex mixture of products is obtained consisting largely of alkyl chlorosilanes which are starting materials in the production of silicones:



$$RCl + Si \xrightarrow{Cu} \begin{matrix} R_3\,Si\,Cl \\ + \\ R_2\,Si\,Cl_2 \\ + \\ R\,Si\,Cl_3 \end{matrix} + \begin{matrix} R_4\,Si \\ + \\ Si\,Cl_4 \end{matrix}$$

A typical crude product composition from the process might contain, 80 wt% of the dialkyldichlorosilane and varying amounts of the other constituents. Chlorosilanes may also be obtained from the reaction between elemental silicon and chlorine or hydrogen chloride.

$$Si + 2Cl_2 \xrightarrow{\Delta} Si\,Cl_4$$

$$Si + 3HCl \xrightarrow{\Delta} H\,Si\,Cl_3 + H_2$$

Chlorosilanes may then react with Grignard reagents or with other organometallic compounds to form silicon-carbon bonds:

$$RMg\,Cl + H\,Si\,Cl_3 \longrightarrow RH\,Si\,Cl_2 + MgCl_2$$

$$RLi + Si\,Cl_4 \longrightarrow RSi\,Cl_3 + Li\,Cl$$

A more efficient route to alkylsilanes is through the hydrosilylation of alkenes, which may be catalysed by compounds such as chloroplatinic acid, di-tert-butyl peroxide or amine complexes, to yield, in general, anti-Markovnikov addition products:

$$RCH=CH_2 + HSiCl_3 \xrightarrow[catalyst]{} RCH_2CH_2SiCl_3$$

1.5.1.3. Reactions of organosilicon compounds

Chlorosilanes undergo several important reactions. Firstly, the chlorine atoms may be replaced by hydrogen either by reductive hydrogenation or by treatment with hydride reducing agents:

$$2Ph_2SiCl_2 + LiAlH_4 \xrightarrow{THF} 2Ph_2SiH_2 + LiCl + AlCl_3$$

Secondly, they react with protic materials such as alcohols, primary and secondary amines and phenols to form the silylated derivatives in high yield:

$$RSiCl_3 + 3R'OH \longrightarrow RSi(OR')_3 + 3HCl$$

$$2R_2NH + R'_3SiCl \longrightarrow R_2NSiR'_3 + R_2\overset{+}{N}H_2\,Cl^-$$

The reaction with water is rapid, the bond dissociation energy of Si-O (ca. 450 kJ mole^{-1}) considerably exceeding that of Si-Cl (ca. 380 kJ mole^{-1}); the reaction thus proceeds to completion. The formation of silanols depends, however, on their tendency to lose water and form siloxanes. The range of stability of silanols is :

mono > di > tri-ols

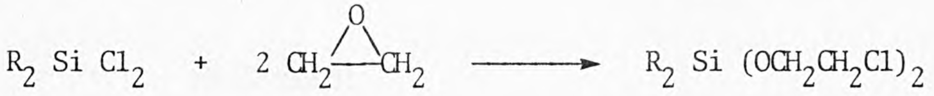
and

phenylsilanols > methylsilanols.

Thus methylsilanols tend to condense to form various polymers and oligomers. This is the basis for silicone manufacture. Dimethyldichlorosilane reacts with water to form a mixture of cyclic and straight-chain oligomers (Chain length ≈ 9 units). Further polymerisation of this mixture can be induced using an acid or alkaline catalyst to form methylsilicone oils.

Other conspicuous reactions of chlorosilanes include:

$$2R_3\,Si\,Cl \quad + \quad H_2S \quad \xrightarrow{Et_3N} \quad R_3\,Si\,S\,Si\,R_3$$



$$R_2\,Si\,Cl_2 \quad + \quad 2\,\overset{O}{CH_2\!-\!CH_2} \quad \longrightarrow \quad R_2\,Si\,(OCH_2CH_2Cl)_2$$

$$RSi\,Cl_3 \quad + \quad (CH_3CO)_2O \quad \longrightarrow \quad R\,Si\,(O\,CO\,CH_3)_3 + 3CH_3COCl$$

$$R_2\,Si\,Cl_2 \quad + \quad Na_2\,Si\,F_6 \quad \longrightarrow \quad R_2\,Si\,F_2 + 2NaCl + Si\,F_4$$

$$2R_3\,Si\,Cl \quad + \quad 2Li \quad \longrightarrow \quad R_3\,Si\,Si\,R_3 + 2Li\,Cl$$

Alkoxysilanes undergo most of the reactions of chlorosilanes and are generally more convenient reagents in that they have a greater resistance to hydrolysis. The reactivity of alkoxysilanes decreases with increasing size of the alkoxy group. The reaction of these compounds with water yields siloxane and alcohol. The alkoxysilanes undergo exchange reactions with hydroxyl-containing materials under conditions similar to those under which carboxylate esters react:

$$MeSi(OEt)_3 \quad + \quad 3Bu^nOH \rightleftharpoons MeSi(OBu^n)_3 \quad + 3EtOH$$

Alkoxysilanes undergo displacement of OR groups on reaction with Grignard reagents, and reduction on treatment with metal hydrides.

Compounds containing Si—H bonds can behave as reducing agents. Triethylsilane and diphenylsilane are employed in the reduction of ketones and esters:

$$R_2C{=}O + Et_3SiH + R'OH \longrightarrow R_2CHOR' + Et_3SiOH$$

Silanes are susceptible to oxidation. Silane itself (SiH_4) is pyrophoric. Hydrogens may be replaced by Cl atoms in silanes on reaction with chlorine. Silanes also react with alkenes and alkynes in the hydrosilylation reaction, to form carbon-silicon bonds.

1.5.1.4 Silylation

The silylation of organic compounds - the ready replacement of protons bound to oxygen, nitrogen, sulphur or other heteroatoms by triorganosilyl groups - has become a very important and popular technique in that the properties of the silylated derivative can differ considerably from those of the parent compound (Klebe, 1970). The general effect of silylation is to reduce the degree of hydrogen bonding between molecules, and thus to increase volatility and solubility in non-polar solvents, e.g. hydrocarbons (Burkoffer and Ritter, 1965). In particular, the presence of a silyl group can alter profoundly the effect of biologically important molecules, or for example, can change the physical properties of organic molecules to facilitate chromatographic analysis. The chromatography of materials such as carbohydrates, amino acids and steroids are examples of this (Sweeley et al., 1963). Derivatization by silylation is also used in the conferment of characterizable mass spectral fragmentation upon organic compounds.

In synthetic applications, the presence of a silyl group may increase the reactivity of a site towards attacking reagents, or may indeed increase the reactivity of adjacent sites to direct the course of reaction. Alternatively, the silyl group may serve as protection for sensitive functional groups during a synthesis. The main advantages afforded by silylation during synthesis lie in the ease of silylation of groups bearing labile protons, and the ease of removal of the silyl group at the end of the synthetic pathway.

Two general methods are available for silylation: reactions with chlorosilanes in the presence of an acid acceptor such as a tertiary amine, and exchange reactions with silicon-nitrogen compounds functioning as silyl donors. The two most common reagents in this respect are trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDS) respectively. The classical chlorosilane method employs a very powerful reagent mixture; the removal of the hydrogen chloride as its amine salt provides sufficient driving force to displace any labile hydrogen bound to heteroatoms by silyl groups. Typically, pyridine or triethylamine are employed as acid acceptors, and the reactions are performed in ether or acetonitrile at ambient temperatures. Separation problems stemming from the formation of amine salts and the corrosive nature of the reagents are the drawbacks of this method.

Silylamines have long been used as alternatives to chlorosilanes. This silylation method is based on the relatively slow silyl-proton exchange between the silyl derivative of a low-boiling amine or of ammonia, and labile protons of the substrate. The reaction equilibria are shifted towards the products by the distillation of ammonia or amine from the reaction mixture:

$$2ROH + Me_3\,Si\,NH\,Si\,Me_3 \rightleftharpoons 2\,Me_3\,Si\,OR + NH_3\uparrow$$

The exchange rate is enhanced by the addition of catalytic amounts of ammonium salts or of chlorosilanes. However, for an adequate conversion, several hours of reflux are required. The advantage of this method is that the final reaction mixture contains only the desired product with an excess of silylating agent.

A more powerful method of silylation involves the use of silylamides or silylureas (Klebe, Finkbeiner and White, 1966). These have the advantage of much higher exchange rates and equilibrium positions which for many substrates are shifted so far towards the product side that the removal of one of the reaction products from the system during the reaction is unnecessary:

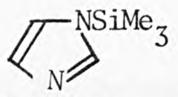
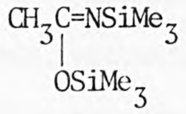
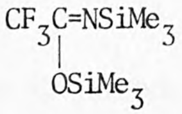
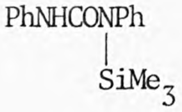
$$\mathrm{RYH} + \mathrm{R'CONHSiMe_3} \rightleftharpoons \mathrm{RYSiMe_3} + \mathrm{R'CONH_2}$$

The greater activity of these silylating agents is due to the activation of the Si—N bond by carbonyl (Klebe, 1970), caused, at least in part, by the ability of the amide group to accommodate a negative charge in the transition state of a displacement reaction, making them good leaving groups. The products of silylation with silylamides are, in general, readily separated by distillation, or, in the case of silylureas, by filtration.

Table 1.4 shows a list of some common trimethylsilylating agents, and the substrates for which they are commonly employed.

TABLE 1.4

Some common trimethylsilylating agents

Agent	Formula	Substrates	Conditions
Trimethylchlorosilane TMCS	Me_3SiCl	most protic compounds	TMCS + BASE 20% molar XS (Et_3N or pyridine) Room temperature.
Hexamethyldisilazane HMDS	$(Me_3Si)_2NH$	Alcohols, phenols, amines, carboxylic acids.	0.6 molar equivalent HMDS 8 hr reflux.
Dimethylaminotrimethylsilane TMSDMA	Me_3SiNMe_2	Alcohols, amines, amino acids, amides, ureas	0.1M excess reagent in solvent (acetonitrile), 60-70°C
Trimethylsilylimidazole TMSI		As above	As above
Bis(trimethylsilyl)acetamide BSA	 $CH_3\underset{\substack{\vert\\OSiMe_3}}{C}{=}NSiMe_3$	General, can convert ketones to silyl ethers.	Reactions at 70°C generally complete within 5 min.
Bis(trimethylsilyl)-trifluoroacetamide BSTFA	 $CF_3\underset{\substack{\vert\\OSiMe_3}}{C}{=}NSiMe_3$	As above	As above
Bis(trimethylsilyl)urea BSU	$Me_3SiNHCONHSiMe_3$	"	Solvent e.g. CH_3CN
Trimethylsilyldiphenylurea TDPU	 $PhNHCO\underset{\substack{\vert\\SiMe_3}}{N}Ph$	"	"

1.5.2. The effect of the presence of silicon on the chemistry of organic compounds

1.5.2.1. Electronegativities and the ionic character of bonds

Silicon (Pauling electronegativity 1.8) is markedly more electropositive than carbon (Pauling electronegativity 2.5)(Colvin, 1978); the Si—C bond has 12% ionic character, and is thus more polar than the C—Cl bond (6% ionic character). It is therefore to be expected that Si—C bonds break in the direction $Si^{+}\ C^{-}$, under electrophilic attack at carbon, or nucleophilic attack at silicon.

The ionic character of Si—halogen bonds is greater than that of carbon-halogen bonds, accounting, at least in part, for the greater reactivity of silicon halides towards nucleophilic reagents.

As a result of the difference in electronegativity between carbon and silicon, it is generally found that their bonds to hydrogen break in opposite directions; C—H generally to $C^{-}\ H^{+}$, and Si—H to $Si^{+}\ H^{-}$ (Eaborn, 1960).

1.5.2.2. Bond energies

Apart from Si—H and Si—C bonds, bonds to silicon are stronger than the corresponding bonds to carbon (Cottrell, 1958). The Si—O bond is particularly strong, and provides the driving force for many important reactions involving silicon, such as the hydrolysis of silicon halides. The strength of the Si—O bond also accounts, in part, for the high thermal stability of silicones (Eaborn, 1960). Table 1.5 lists some energies of bonds involving silicon and compares them with the corresponding values for carbon.

TABLE 1.5

Bond dissociation energies in some bonds involving silicon

	kJ mole^{-1}		kJ mole^{-1}
Si—Si	222	C—Si	230-320
Si—C	230-320	C—C	347
Si—H	290-320	C—H	414
Si—O	370-450	C—O	350-360
Si—N	322	C—N	304
Si—F	540-570	C—F	440-465
Si—Cl	380	C—Cl	339
Si—Br	309	C—Br	284
Si—I	234	C—I	213

Table 1.6 shows the effects of increasing the size of the alkyl group attached to silicon on the Si—C bond strength in alkylsilanes. The fact that the Si—C bond energy changes with the nature of the attached alkyl group accounts for many of the properties observed in organosilicon chemistry.

TABLE 1.6

Bond dissociation energies in alkylsilanes (Waring, 1940)

Bond	Bond energy kJ mole^{-1}	Bond	Bond energy kJ mole^{-1}
Si—Me	313.5	Si—Bu	217
Si—Et	259	Si—Bu^{i}	217
Si—Pr	238	Si—CH=CH$_2$	297

1.5.2.3. Availability of d-orbitals in silicon

The obvious differences observed between analogous silicon and carbon compounds can also be explained by the effect of the availability of d-orbitals in silicon (Eaborn, 1960). This availability manifests itself in four important ways:

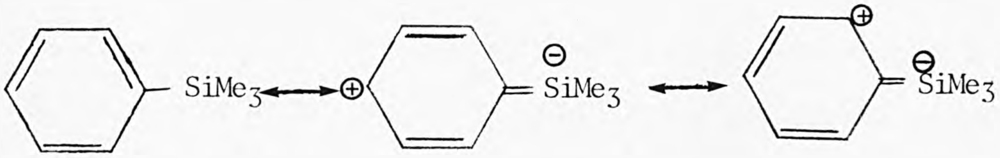
(a) The ability of silicon to expand its valency to form complexes with a coordination number greater than four, as in the $(Si\ F_6)^{2-}$ ion.

(b) The existence of some double-bond character in certain bonds such as Si—O, as a result of $d_\Pi - p_\Pi$ back-bonding; the 3p orbitals in silicon are of too high an energy to give adequate Π overlap with the 2p orbitals of carbon, and so silaethenes, e.g. $Me_2Si{=}CHMe$, are very unstable, and stable compounds containing silicon-oxygen double-bonds are unknown (Colvin, 1978).

(c) The mechanism of substitution at silicon centres differs from that at analogous carbon centres as a result of the ability of silicon to expand its co-ordination number; this is illustrated by the very high reactivity of halides of silicon compared with alkyl halides towards nucleophilic reagents, where, by the involvement of d-orbitals, the attack may be facilitated by a lowering of the energy of transition states, the possible formation of pentacovalent intermediates and by the fact that the nucleophile, Y, may

> approach R_3SiX either from the back of the silicon atom (analogous to an S_N2 mechanism) or from the flank to give a Y—Si—X angle of rather less than 90^o (Eaborn, 1960).
>
> (d) The electrical effect of the Me_3Si- group is such that, relative to the proton, there will be electron release by an inductive (+ I) effect (Eaborn, 1960). The magnitude of this effect is greater than that due to the presence of the Me_3C- moiety in an organic molecule; this manifests itself in the base-strengthening and acid-weakening effects of the Me_3Si- group on aliphatic amines (Sommer and Rockett, 1951) and carboxylic acids (Sommer et al., 1949) respectively.

However, the Me_3Si- group only weakly increases the electron density on aromatic nuclei resulting from contributions from the following resonance (– R) structures:-



due to d_π - p_π bonding between the ring and the d-orbitals of silicon (Chatt and Williams, 1954). Thus when the Me_3Si- group is introduced in the ortho or para positions, the base strength of aniline and dimethylaniline are reduced, and the acid-strength of phenol is increased. Conversely, meta-substitution results in weak base-strengthening and acid-weakening (Benkeser and Krysiac, 1953). The overall effect of trimethylsilyl-substitution in an aromatic nucleus is, therefore, a weak activation of the benzene ring towards electrophilic reagents, compared, for example, with that of the methyl group. In contrast, the Ph_3Si- group is quite strongly electron withdrawing (Benkeser et al., 1956), and the Me_3SiCH_2- group activates the para position much more strongly than does the methyl group (Eaborn and Parker, 1955).

1.5.3. Gas-phase reactions of organosilicon compounds in the absence of oxygen

1.5.3.1. Introduction

Many accounts have recently appeared of the pyrolysis and photolysis of organosilicon compounds in which the nature of the products may be explained by the involvement of silicon-containing reactive intermediates (Davidson, 1970, 1976; Gusel'nikov, Nametkin and Vdovin, 1975; Flowers and Gusel'nikov, 1968; Davidson and Thompson, 1975; Davidson and Matthews, 1976).

Several schemes have been proposed whereby the thermal degradation of an organosilicon compound proceeds through unsaturated intermediates with structures analogous to those found in organic chemistry (e.g. alkenes and ketones). Such species are transient in nature, and, until recently, were thought not to be capable of independent existence owing to the relatively high energy of the silicon 3p orbitals involved in the formation of $p_{\Pi} - p_{\Pi}$ bonds with carbon 2p orbitals (Dasent, 1965). However, good evidence for the existence of many of these species has been obtained from kinetic and trapping experiments (Flowers and Gusel'nikov, 1968) and subsequent spectroscopic analysis (Barton and McIntosh, 1972). Mechanisms of the thermal decomposition of other organosilicon compounds have been shown to proceed via the formation of radical species such as silyl radicals, $R_3Si\cdot$ (Davidson and Howard, 1975) or silylenes, $R_2Si:$ (Davidson and Matthews, 1976). The mechanisms operative during the thermal decomposition and photolysis of organosilicon compounds have been found to be largely dependent on the nature of the substituents bound to silicon (Davidson, 1970; Jackson, 1969).

1.5.3.2. Silyl radicals

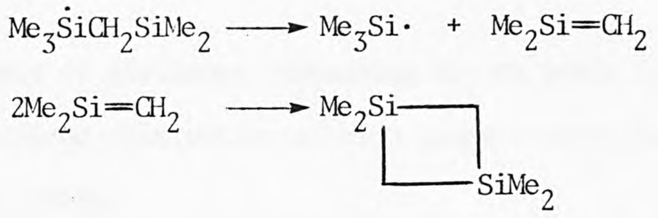
The chemistry of silyl radicals is well developed; many of the reactions that have been observed are parallel to those found with alkyl radicals, with the exception of disproportionation and degradation to silenes. Silyl radicals can be produced by pyrolysis, photolysis or electron transfer processes involving a variety of organosilicon compounds.

In contrast to its carbon analogue, hexaphenyldisilane does not undergo pyrolysis to $Ph_3Si\cdot$ radicals, and is stable enough to be heated for a long time above its melting point (625K) without thermal decomposition. This may be a consequence of the long Si—Si bond in hexaphenyldisilane, resulting in a lowering of steric compression compared with that experienced in the carbon analogue, hexaphenylethane (Sakurai, 1973). However, hexamethyldisilane was found to undergo homolysis in the gas phase to yield silyl radicals (Davidson and Howard, 1973).

The products of pyrolysis of hexamethyldisilane contain mainly the isomeric compound $Me_3SiCH_2SiMe_2H$ as well as trimethylsilane (Shiina and Kumada, 1958). The mechanism of this reaction is believed to be as follows:

$$\begin{aligned}
Me_3Si{-}SiMe_3 &\longrightarrow 2\ Me_3Si\cdot \\
Me_3Si\cdot + Me_3Si{-}SiMe_3 &\longrightarrow Me_3SiH + \cdot CH_2SiMe_2{-}SiMe_3 \\
\cdot CH_2SiMe_2SiMe_3 &\longrightarrow Me_3SiCH_2\dot{S}iMe_2 \\
Me_3SiCH_2\dot{S}iMe_2 + Me_3SiSiMe_3 &\longrightarrow Me_3SiCH_2SiMe_2H + \dot{C}H_2SiMe_2SiMe_3
\end{aligned}$$

At lower pressures, a competing reaction becomes important :



propagating a chain reaction producing a 1,1,3,3-tetramethyl-1,3-disilacyclobutane and increased quantities of trimethylsilane (Davidson and Howard, 1975).

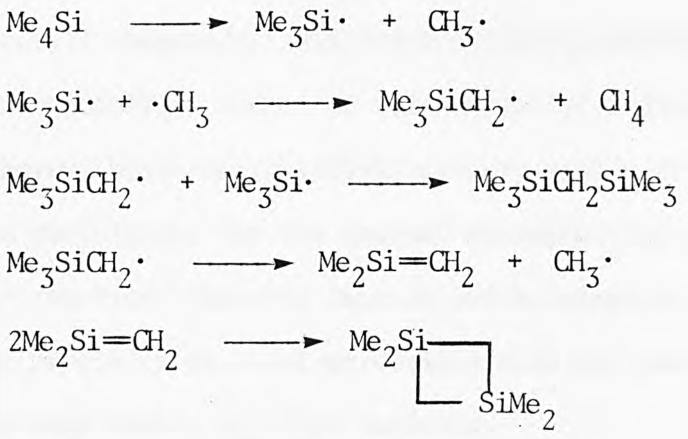
This method of silyl radical generation is limited by the tendency of disilanes to undergo α-elimination to produce silylenes instead of homolytic degradation when an electronegative substituent is attached to silicon. Thus we have competition between the following processes:

$$R_3Si{-}SiR_3 \longrightarrow 2R_3Si\cdot$$

$$R_3Si{-}SiR_3 \longrightarrow R_4Si + R_2Si{:}$$

A very fine balance appears to exist between the two modes of decomposition; for example, hexamethyldisilane decomposes to form silyl radicals (Davidson and Stephenson, 1968), while 1,2-dimethoxytetramethyldisilane eliminates $Me_2Si{:}$ (Atwell et al., 1969). In general, silylene elimination tends to occur in preference to silyl radical formation when R_4Si contains a bond into which $R_2Si{:}$ can readily insert (Davidson, 1970). Such bonds are silicon-hydrogen, silicon-halogen, silicon-oxygen and silicon-nitrogen but not silicon-carbon, carbon-carbon or carbon-hydrogen. This rationalization is supported by considerable experimental evidence (Davidson, 1975). In addition, the pyrolysis of disilanes containing Si—Ph bonds is found to proceed via silylene elimination at high temperatures (Sakurai, Hosomi and Kumada, 1969).

Many alkyl derivatives decompose at high temperatures to yield complicated mixtures of products, the nature of which may be explained by the involvement of free radicals. For example, the pyrolysis of tetramethylsilane at 923K was found to yield a mixture containing more than 40 products (Fritz, 1967), arising from the involvement of some of the following reactions:



$$Me_4Si \longrightarrow Me_3Si\cdot + CH_3\cdot$$

$$Me_3Si\cdot + \cdot CH_3 \longrightarrow Me_3SiCH_2\cdot + CH_4$$

$$Me_3SiCH_2\cdot + Me_3Si\cdot \longrightarrow Me_3SiCH_2SiMe_3$$

$$Me_3SiCH_2\cdot \longrightarrow Me_2Si{=}CH_2 + CH_3\cdot$$

$$2Me_2Si{=}CH_2 \longrightarrow Me_2Si \quad SiMe_2$$

Alkylsilanes containing ethyl and higher alkyl groups break down more readily and this decomposition probably involves β-elimination (Waring, 1940). The thermal decomposition of allyltrimethylsilane has also been shown to undergo silicon-allyl bond rupture in the initial stages to yield trimethylsilyl radicals (Davidson and Wood, 1980).

Although recent values of bond-dissociation energies (Table 1.4) suggest a stronger Si—H bond than the Si—C bond, trialkylsilanes appear to decompose thermally more readily than do tetraalkylsilanes. Evidence suggests that trialkylsilyl radicals are involved in this decomposition (Davidson and Lambert, 1971; Gagneja, Gowenlock and Johnson, 1973), although it is possible that for some alkylhydrosilanes, silylenes are formed in the initial stages (Mares and Chvalovsky, 1966). Silyl radicals may be generated most conveniently from alkylhydrosilanes by treatment with an initiator such as di-tert-butyl peroxide (Sakurai, Hosomi and Kumada, 1967).

A further thermal souce of silyl radicals is the decomposition of silyl mecurial compounds. Bis(triphenylsilyl)-mercury is a convenient thermal or photolytic source of triphenylsilyl radicals (Jackson, 1966), whereas bis(trimethylsilyl)-mercury yields trimethylsilyl radicals upon photolysis, but the thermal decomposition is complicated by molecular reactions (Eaborn, Jackson and Walsingham, 1967; 1973). Thus, the pyrolysis of silyl mercurials does not constitute a clean route, in many cases, to silyl radicals.

Other than coupling to produce disilanes, the most common reaction of silyl radicals is halogen abstraction from alkyl chlorides (Cadman, Tilsley and Trotman-Dickenson, 1973). Trimethylsilyl radicals have also been found to abstract chlorine from Si—Cl bonds (Davidson and Matthews, 1980).

The addition of organosilicon hydrides to alkenes and alkynes (hydrosilylation) was first reported in 1947 (Burkhard and Krieble, 1947;

Barry et al., 1947; Sommer et al., 1947) and is known to proceed via silyl radical intermediates. The ease of hydrosilylation is increased by the presence of electronegative groups bound to silicon. Trialkylsilanes, in general, react very slowly with alkenes in the presence of radical initiators (Seyferth and Rochow, 1955). However, rapid addition reactions of triethylsilyl radicals to the carbonyl oxygen of ketones and esters have been observed (Bowles, Hudson and Jackson, 1971).

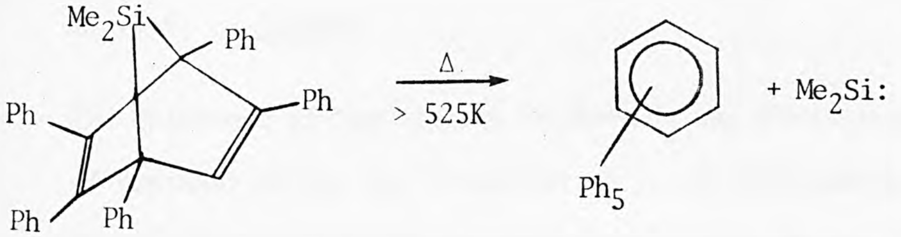
1.5.3.3. Silylenes

The chemistry of silylenes, $R_2Si:$, the silicon analogues of carbenes, has been the subject of a considerable amount of interest since the discovery that the readily available methoxydisilanes undergo thermally-induced α-elimination to yield organosilylenes (Atwell and Weyenberg, 1969). However, as a method of silylene production, the pyrolysis of methoxydisilanes constitutes a poor route, as a result of the high tendency of silylenes to insert into Si—O bonds. The general criteria for the elimination of silylenes from disilanes were discussed in the previous section (Section 1.5.3.2.).

Similar considerations apply to the pyrolysis of monosilanes (Davidson, 1970). Evidence suggests that methylsilane and silane form silylenes on pyrolysis (Kohanek, Estacio and Ring, 1969; Purnell and Walsh, 1966), although the thermal decomposition of tetrahalosilanes gives only low yields of halosilylenes despite the general tendency of silylenes to readily insert into silicon-halogen bonds. This is due to the relatively low bond dissociation energy of the halogen-halogen bond (Atwell and Weyenberg, 1969). This thermodynamic obstacle may be overcome in practice by pyrolysing the halosilanes in the presence of silicon:

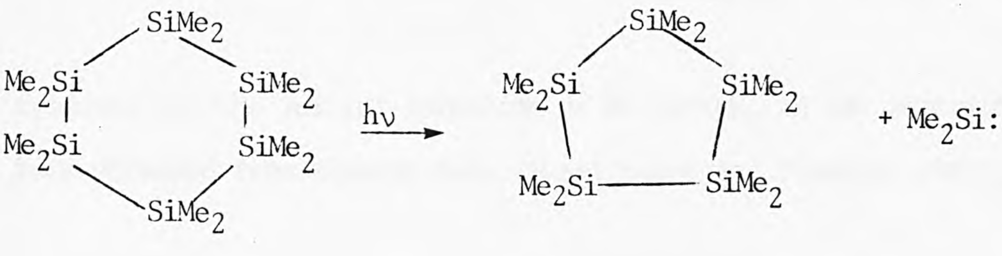
$$SiX_4 + Si \rightleftharpoons 2{:}SiX_2$$

Other methods of silylene generation include the pyrolysis of 7-silanorbornadienes:

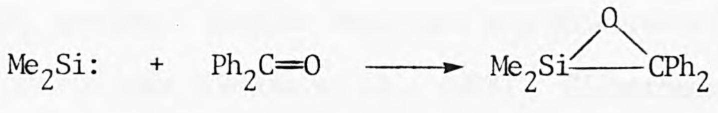


the pyrolysis of silacyclopropanes:

and the photolysis of polysilanes



In their general chemical behaviour, it appears that silylenes and carbenes are very similar. Silylenes can insert into the π-bonds of alkenes and alkynes, and also into C—H, Si—H and various bonds involving silicon bound to electronegative atoms (Davidson and Matthews, 1976; Davidson, Lawrence and Ostah, 1980). Recent evidence strongly suggests that silylenes can insert into the π-bond of a carbonyl group to form an unstable oxasilacyclopropane intermediate :



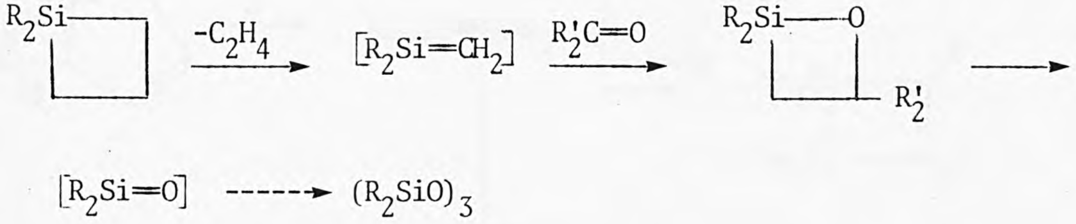
1.5.3.4. Silenes

The existence of the species $Me_2Si=CH_2$ was first proposed as a means of explanation for the formation of 1,1,3,3-tetramethyl-1,3-silacyclobutane in the pyrolysis of tetramethylsilane (Fritz, Grobe and Kummer, 1965). Subsequently, with the acceptance that P_π - P_π bonding to silicon was possible, similar unsaturated species have been proposed as intermediates in many reactions. The most common method of silaethene generation is the pyrolysis of silacyclobutanes. The stable products resulting from this pyrolysis are the corresponding 1,3-disilacyclobutane and ethene (Flowers and Gusel'nikov, 1968):

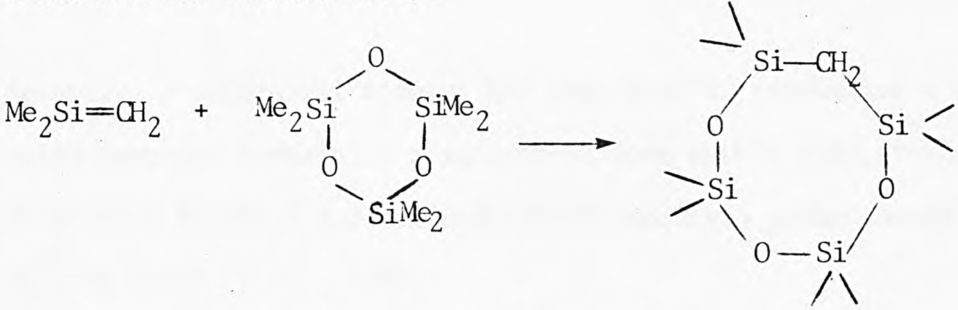
Evidence for the initial formation of $Me_2Si=CH_2$ in the reaction has been obtained from kinetic data (Gusel'nikov and Flowers, 1967), trapping experiments and co-pyrolyses in the presence of substituted silacyclobutanes or higher alkenes (Flowers and Gusel-nikov, 1968).

In the condensed phase, the $Me_2Si{=}CH_2$ units undergo polymerization (Nametkin, Vdovin and Zav'yalov, 1965). In the gas phase, adducts are formed when silacyclobutanes are pyrolysed in the presence of water vapour, ammonia and alcohols, confirming the existence of the $Me_2Si{=}CH_2$ species. Similar reactions are observed with acetonitrile and its derivatives (Golino et al., 1974). Silaethenes undergo cycloaddition to alkenes, and Diels-Alder reactions with dienes. The rate of cycloaddition to alkenes is negligible compared with cyclodimerisation of the silaethenes at the temperature of pyrolysis of the monosilacyclobutanes, and will only become important when a large concentration of an alkene is added (Gusel'nikov, Nametkin and Vdovin, 1975). Highly carbon-substituted silaethenes have been found to undergo head-to-head dimerisation, followed by internal hydrogen-abstraction, rather than cyclisation (Barton, 1978).

Silaethenes react readily with compounds containing carbonyl double bonds, forming mainly trimeric cyclosiloxanes, and the corresponding alkenes (Barton and Kline, 1972):



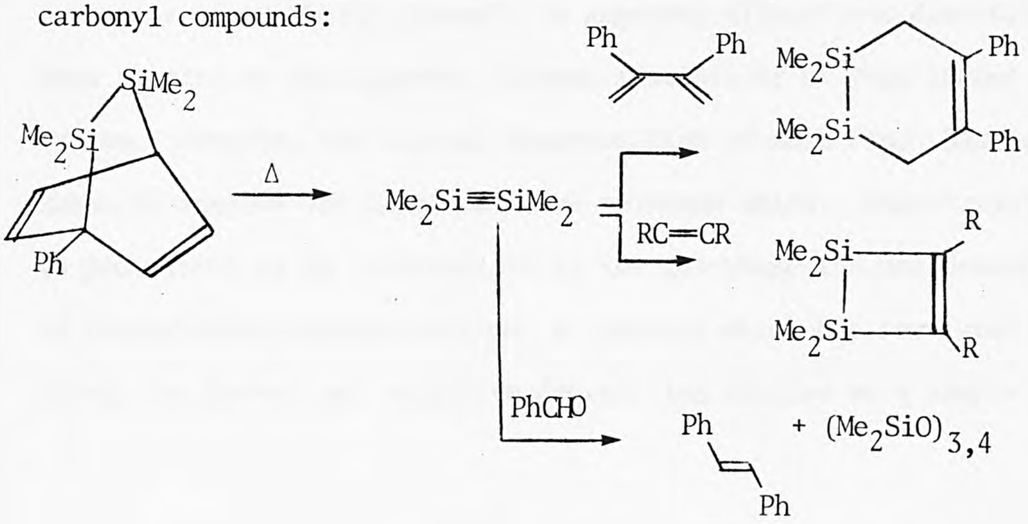
Silaethenes also undergo insertion reactions into Si═O bonds (John, Gowenlock and Groome, 1981):



Recently, a solid silaethene, 2-adamantyl-2-trimethylsiloxy-1,1-bis-(trimethylsilyl)-1-silaethene has been synthesized and isolated, and found to be stable at room temperature, in the absence of air or other reagents (Brook et al., 1981).

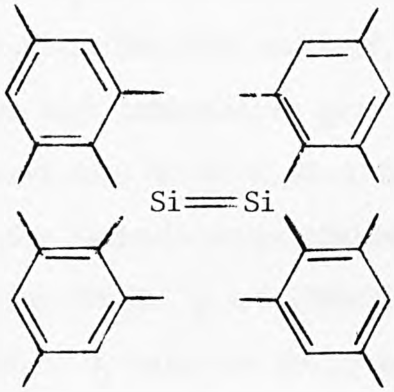
1.5.3.5. Disilenes

Evidence for compounds containing silicon-silicon double bonds first appeared in 1969, when it was found that disilabicyclo [2,2,2]-octadienes thermally extrude tetramethyldisilene, $Me_2Si{=}SiMe_2$, as implied from various reaction products (Peddle et al., 1969; Peddle and Roark, 1972; Barton, 1978). The reactions of disilenes include Diels-Alder reactions with 1,3-dienes, addition to alkynes and reactions with carbonyl compounds:



There is evidence that disilenes may be formed from the dimerization of silylenes under appropriate conditions.

Recently, a successful attempt has been made to synthesize a stable, solid compound containing a silicon-silicon double bond, sterically stabilized by two 2,4,6-trimethylphenyl(mesityl) groups bound to each silicon (West et al., 1981):

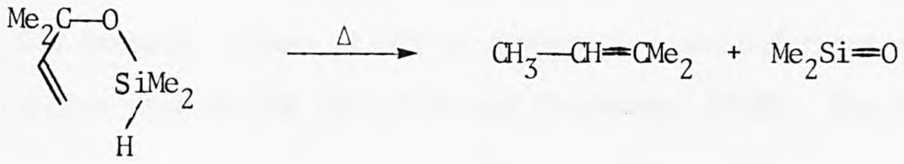


which was synthesised from 2,2-bis(mesityl)hexamethyltrisilane by photolysis in a hydrocarbon solvent. The compound is found to undergo addition reactions with hydrogen halides, oxygen and ethanol.

1.5.3.6. Silanones

A variety of synthetic attempts to generate siloxetanes directly has been stymied by the apparent thermal instability of this tender ring system. However, the thermal decomposition of such rings has been shown to involve the elimination of silanone units. Dimethylsilanone is postulated as an intermediate in the gas-phase thermal decomposition of octamethylcyclotetrasiloxane, a compound which has been used extensively in thermal and oxidative degradation studies as a simple model for methylsiloxane polymers (Davidson and Thompson, 1971; 1975). In the pyrolysis of $(Me_2SiO)_4$, D_4, at conversions of up to 25%, the only products observed are $(Me_2SiO)_3$, D_3, and $(Me_2SiO)_5$, D_5, as a result of the extrusion of $Me_2Si{=}O$, D_1, units and subsequent insertion of D_1 into Si—O bonds. The addition of ethene to the system was found to suppress the formation of D_5, but not D_3, and further studies demonstrated the insertion of D_1 into Si—Cl bonds when D_4 was pyrolysed in the presence of Me_3SiCl (Davidson and Delf, 1982). Experiments with Me_3SiH and Me_4Si at high temperatures gave products that suggest that $Me_2Si{=}O$ cannot insert into Si—H or Si—C bonds, but that addition reactions with $Me_3Si\cdot$ radicals occur (Baldwin, Davidson and Howard, 1975). Copyrolysis involving $(Me_2SiO)_4$ and $(PhMeSiO)_3$ gave further evidence for the involvement of D_1 units in the pyrolysis of siloxanes. Silanones are also formed as a result of the condensation of silicon monoxide with organic compounds. However, unlike the above, they undergo uncontrolled polymerization (Schashel, Gray and Timms, 1972). Silyenes are also found to abstract oxygen from DMSO to form silanones (Weber, 1978).

A convenient, facile source for the generation of dimethylsilanone units has recently been discovered (Lane and Frye, 1979). Dimethylsilanone is generated thermally under relatively mild conditions from vinyldimethylcarbinoxydimethylsilane by an intramolecular mechanism:



Evidence for this elimination was obtained by pyrolysis of $CH_2{=}CHCMe_2$-$OSiMe_2H$ in the presence of trapping agents.

1.5.3.7. Other reactive intermediates

There is some evidence that the nitrogen-containing analogues of cyclic siloxanes undergo pyrolysis via the extrusion of $Me_2Si{=}NH$ units, since the major product of the pyrolysis of $(Me_2SiNH)_4$ is the trimer $(Me_2SiNH)_3$ (Zhinkin, 1963).

Some reactions of gaseous SiO, formed by heating silicon monoxide to ca. 1500K, have been reported (Schashel et al., 1972). Complex product mixtures were obtained, but there was some evidence for addition of SiO across multiple carbon-carbon bonds, and insertion of SiO into C—H, C— halogen, O—H and N—H bonds. SiO is more reactive and less selective than other silylenes.

1.5.4. The gas-phase oxidation of organosilicon compounds

Early studies involving the reactions of organosilicon compounds with oxygen were concerned mainly with organosilicon polymers containing Si—O and Si—C bonds. More recently, however, reports of several studies have been published which give an insight into the mechanisms operative during the oxidation of monomeric organosilicon compounds.

The extreme sensitivity of the silanes to oxygen is well established. For example, silane itself is pyrophoric, and undergoes explosive oxidation even at 80K (Brilkina and Shushunov, 1969). The substitution of alkyl groups into silane decreases the reactivity; indeed, methylsilane no longer ignites spontaneously in air (Finholt et al., 1947) and in oxygen can only be exploded by an electric spark (Stock and Somieski, 1919). Monoalkyl- and dialkylsilanes having a more complex structure exhibit a higher reactivity towards oxygen (Petrov and Ponomarenko, 1953). The liquid-phase oxidation of incompletely-substituted aryl silanes, e.g. Ph_3SiH, was found to proceed at 368K in benzene only in the presence of a chain initiator, e.g. benzoyl peroxide (Curtice et al., 1957).

Silicon-silicon bonds in hexaalkyldisilanes are found to be very stable to oxygen. Hexamethyldisilane can be distilled in air without appreciable oxidation (Brown and Fowles, 1958). Tetraalkyl- and tetraarylsilanes, with the exception of compounds containing unsaturated substituents, exhibit similar passivity. The aerobic oxidation of a series of methylphenylsilanes and their organic analogues in the temperature range 653-738K has revealed that the rates of oxidation of the silanes and their organic analogues are very similar, giving some insight into the mechanisms prevalent during the reaction. The products of oxidation were found to contain involatile siloxane polymers, but no volatile silicon-containing species (Benes, Chvalovsky and Bazant, 1961a). In addition, methyltriphenylsilane was found to be,by far, the most resistant to oxidation of those compounds used. A comparable study involving methylphenylsiloxanes demonstrated that the mechanisms involved in the oxidation of disiloxanes differed considerably from those observed with cyclotetrasiloxanes (Benes, Chvalovsky and Bazant, 1961b), where catalysis at the walls of the reaction vessel had a profound effect on the rate of oxidation of the disiloxanes. In both cases, the rate of oxidation was independent of the nature of the groups (methyl or phenyl) bound to silicon. A further kinetic study of the oxidation of D_4 by an excess of oxygen at 663-743K, revealed that the mode of oxidation of D_4 resembles that of methane and differs significantly from the oxidation of hydrocarbons (Davidson and Thompson, 1976). Oxidation of D_4 by traces of oxygen gave D_3 (Davidson and Thompson, 1975), but in excess oxygen, no volatile silicon compounds were observed. This implies the formation of siloxane polymers and possibly the complete oxidation of siloxanes to SiO_2, without the involvement of species such as $Me_2Si{=}O$ or $Me_2Si{=}CH_2$.

1.6 THE PRESENT WORK

The preceding discussion has indicated the continued need for the addition of antiknock additives to gasoline, and the disadvantages associated with the use of lead alkyls. The present work has been designed to test the effects of a series of compounds on the combustion of a pure hydrocarbon (2-methylpentane) under laboratory conditions, and, in some cases, in a CFR engine. The effects of additives on the ignition limits or other kinetic parameters of hydrocarbon combustion have been demonstrated as a good measure of the antiknock or proknock activity of a given compound. The laboratory study therefore constitutes a quick, reliable screening method for potential antiknock additives.

The versatility of organosilicon compounds lends itself to this study, in that many organic groups can be attached to silicon to yield stable compounds. Thus, the organosilicon compounds used in this study are expected to show a variety of effects on the combustion process. The generation of the various radicals and transient species from organosilicon compounds in the gas-phase and the affinity of silicon for oxygen suggest that these species may have some inhibiting effect on the combustion of hydrocarbons acting, in some senses, analogously to some other known antiknock additives.

EXPERIMENTAL

2.1 MATERIALS

2.1.1. Organosilicon compounds

Most of the organosilicon compounds used during this work were provided by Dow Corning Ltd. Gas chromatography showed that the majority of these compounds were of a purity in excess of 95%, and these were used without further purification. Compounds of a lower purity were fractionally distilled in a semi-micro apparatus, under nitrogen.

Tetramethylsilane (99.9%), tetraethylsilane (98%), hexamethyldisilane (99%) and phenyltrimethylsilane (99%) were obtained from Lancaster Synthesis Ltd. Triphenylsilane (purum grade, > 99%) was obtained from Fluka A.G. Benzyldimethylsilane, 1,4-bis(dimethylsilyl)benzene, bis-(dimethylamino)dimethylsilane, hexamethylcyclotrisilazane, hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane were obtained from the Silar range, supplied by Field Instruments Co. Ltd. The purities of these compounds were verified by gas chromatography, and further purification was not, therefore, necessary.

1,1-dimethylsilacyclobutane and vinyldimethylcarbinoxydimethylsilane were kindly provided by [redacted] of the University of Leicester.

Bis(triphenylsilyl) mercury was synthesized from dibenzylmercury (Lancaster Synthesis Ltd.) in the presence of an excess of triphenylsilane (Jackson, 1966; Eaborn et al., 1972). The reactants were recrystallized, and a mixture was prepared containing dibenzylmercury (2.0g, 5.2 mmol) and triphenylsilane (5.35g, 20 mmol) in a Schlenk tube. The mixture was degassed by successive freezing and thawing in vacuo, and was then heated (in the absence of light) for 8 hours at 413K. The mixture was set aside for 3 days, by which time lemon-yellow crystals of bis(triphenylsilyl)mercury had separated. Dry, degassed cyclohexane (10 cm^3) was added to complete precipitation. The supernatant liquid was removed, and the crystals were washed with cold cyclohexane (2 x 10 cm^3) before being transferred to a vacuum sublimator. Volatile products (cyclohexane and toluene) were pumped off, after which the cold finger of the sublimator was filled with acetone-solid CO_2, and the mixture was heated to 423K to remove the impurities (mercury, dibenzyl and unchanged triphenylsilane) by vacuum sublimation. The pure, dry crystals were left as a residue, m.p. 483K; the yield was 1.32g, 35%. The product was characterized by its UV and mass spectra.

The remaining organosilicon compounds tested in the laboratory were prepared by the silylation of organic compounds bearing labile hydrogen atoms. These syntheses fell into two broad groups: the silylation of alcohols and phenols, and the silylation of primary and secondary amines. Although both alcohol and amine derivatives may be synthesized using the same general methods, variations in the ease of silylation, the stability and the ease of separation of the products made the use of a variety of silylating agents necessary. Some examples of the silylation procedures used are given below.

Trimethylmethoxysilane (Me_3SiOMe)

(a) Trimethylchlorosilane (10.87g, 0.1 mol) in toluene (50 cm^3) was added dropwise, with stirring, to methanol (B.D.H. AnalaR grade) (3.2g, 0.1 mol) in the presence of pyridine (7.9g, 0.1 mol)(Sauer, 1944). The mixture was stirred at room temperature overnight. Pyridinium chloride was filtered off and washed with cold toluene (2 x 25 cm^3). Distillation of the filtrate yielded an azeotropic mixture (b.p. = 329K) containing the desired product, Me_3SiOMe, and methanol. Gas chromatographic analysis showed that these two constituents were present in a ratio of approximately 10:1. Further purification was not attempted.

(b) Another method (Langer, Connell and Wender, 1958) was also employed for the preparation of Me_3SiOMe, in view of the difficulties experienced in the filtration step of the previous procedure. A mixture containing methanol (16.02g, 0.5 mol), excess hexamethyldisilazane (48g, 0.3 mol) and a catalytic amount of ammonium sulphate ($\simeq$ 0.1g) was refluxed at 333K under a stream of dry nitrogen, the product (b.p. 328K) distilling from the mixture as the reaction progressed. Trimethylmethoxysilane (yield 46g, 90%) was shown by gas chromatography to have a purity better than 98.5%.

Trimethyl tert-butoxysilane (Me_3SiO^tBu)

Trimethylchlorosilane (10.87g, 0.1 mol) in ether (40 cm^3) was added dropwise, with stirring, to a mixture containing 2-methylpropan-2-ol (tert-butanol) (B.D.H. AnalaR grade) (7.4g, 0.1 mol) and pyridine

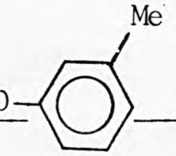
(7.91g, 0.1 mol) in ether (300 cm^3 (Gerrard and Kilburn, 1956). The mixture was stirred overnight under dry nitrogen. Pyridinium chloride was filtered off and washed with ether (2 x 25 cm^3), and the filtrate was distilled to yield a fraction (b.p. = 375-376K) which was shown by gas chromatography to contain the product, Me_3SiO^tBu, contaminated with pyridine (b.p. = 391K).

The pure compound was later obtained by the hexamethyldisilazane method, to give the product, Me_3SiO^tBu (b.p. 375-376K) in 78% yield.

N-tert-butyltrimethylsilylamine (Me_3SiNH^tBu)

N-tert-butyltrimethylsilylamine was prepared from tert-butylamine (Aldrich Gold Label, 99+%), by the chlorosilane method in ether in the presence of triethylamine (Ashby et al., 1978). The product (b.p. = 394-396K; yield = 53%) obtained following filtration and distillation was shown by gas chromatography to have a purity in excess of 95%.

An alternative method was also used to synthesize this compound, involving the more powerful silylating agent, bis(trimethylsilyl)urea (BSU). An ethereal solution was prepared containing BSU (21g, 0.1 mol). This was added, dropwise, to tert-butylamine (14.6g, 0.2 mol) in ether (25 cm^3). The mixture was warmed slightly and stirred overnight. Urea was filtered off, and the product, Me_3SiNH^tBu, was separated by distillation (b.p. 397K: yield = 18g, 56%).

O-trimethylsilyl-meta-cresol (Me$_3$SiO)

A mixture containing meta-cresol (10.8g, 0.1 mol) and hexamethyldisilazane (10g, 0.06 mol) in the presence of a catalytic amount of ammonium sulphate (≃ 0.1g), was refluxed under dry nitrogen (Freedman and Charlin, 1964). The reaction was followed by the detection of the liberation of ammonia as the reaction progressed. Distillation of the resulting mixture yielded O-trimethylsilyl-meta-cresol (b.p. 470-472K; yield 12.2g, 68%, which was shown by gas chromatography to have a purity in excess of 95%.

N-trimethylsilylaniline (Me$_3$SiNHPh)

N-trimethylsilylaniline was synthesized by the addition of trimethylchlorosilane to two equivalents of aniline (B.D.H. AnalaR grade) in ether (Anderson, 1951). The sensitivity of the product to water and the partial solubility of anilinium chloride in ether reduced the value of this method. A better conversion was obtained when aniline (18.63g, 0.2 mol) was mixed with hexamethyldisilazane (20g, 0.12 mol) in the presence of a small amount of ammonium sulphate, and refluxed under dry nitrogen until no further ammonia was liberated from the vessel. The mixture was distilled under vacuum and the fraction collected between 388-390K/6.7 kPa was found by gas chromatography to contain 92% Me$_3$Si-NHPh (yield = 12g, 75%), the major impurity being the di-substituted aniline, (Me$_3$Si)$_2$NPh. The product was characterised by its IR and mass spectra.

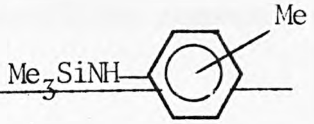
N-trimethylsilyl-N-methylaniline ($Me_3SiNMePh$)

A mixture containing N-methylaniline (Koch-Light Ltd.) (5.35g, 0.05 mol) and bis(trimethylsilyl)trifluoroacetamide (BSTFA)(9.63g, 0.0375 mol) in acetonitrile (50 cm^3) was refluxed for 20 h, the progress of the reaction being followed by gas chromatography. The solvent was removed by distillation at atmospheric pressure. The pressure was reduced and the fraction collected between 332 and 334K/0.25 kPa was found to contain the product, $Me_3SiNMePh$ (yield = 5.6g, 64%) which was shown by gas chromatography to have a purity greater than 95%.

Bis(N-aminophenyl)dimethylsilane ($Me_2Si(NHPh)_2$)

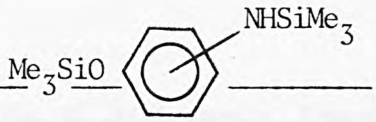
Dimethyldichlorosilane (10g, 0.0775 mol) in benzene (50 cm^3) was added dropwise, with stirring, to an excess of aniline (35g, 0.37 mol) in benzene (25 cm^3)(Larsson and Smith, 1949). The mixture was refluxed for 30 min and then cooled overnight. Anilinium chloride was filtered off and washed with cold benzene (2 x 25 cm^3). The filtrate was distilled at atmospheric pressure to remove solvent and low-boiling impurities before the pressure was reduced to 0.6 kPa, the brown liquid distilling at 447K being collected. On being cooled, the liquid solidified, and was purified by recrystallization from petroleum ether to give solid $Me_2Si(NHPh)_2$ (15g, 80% yield), which was characterized by its IR spectrum and melting point (327K).

Silylated toluidines



Ortho-, meta- and para- toluidines were silylated by an excess of hexamethyldisilazane in the presence of ammonium sulphate as previously described for aniline. The products obtained were of a purity in excess of 90%, gas chromatographic- mass spectrometric analysis indicating the presence of unsubstituted and di-N-substituted toluidines in the product fractions.

Silylated aminophenols



4-Aminophenol (Lancaster Synthesis Ltd.) (10.9g, 0.1 mol) was dissolved in pyridine (100 cm^3) and trimethylchlorosilane (21.74g, 0.2 mol) was added dropwise with stirring (Kojyukov et al., 1974). No precipitation of pyridinium chloride was observed. Excess pyridine was removed under vacuum and a brown solid remained. A small amount of the desired product, $Me_3SiO—C_6H_4—NHSiMe_3$ was obtained by solvent extraction in heptane (3 x 100 cm^2) followed by distillation. However, a more efficient method for the silylation of aminophenols was found to be the hexamethyldisilazane method, in the presence of a few drops of sulphuric acid (Kojyukov et al., 1980). The products were obtained in high yield, with a purity in excess of 85%, by vacuum distillation. Gas chromatographic- mass spectrometric analysis has shown that in all cases, impurities have consisted of mono-O-silylated- and trisilylated derivatives of the parent aminophenol. Thus, further purification was deemed to be unnecessary.

Table 2.1 shows a list of the organosilicon compounds used in the study, and their origins.

2.1.2. Other materials

2-Methylpentane (Aldrich Chemical Co.) was used as the base fuel in the laboratory studies. The purity was shown by gas chromatography to be better than 99.9%, and further purification was not, therefore, considered necessary. Commercial samples of other hydrocarbons were used.

Oxygen (99.6% pure), obtained from the British Oxygen Company, was used in the initial combustion studies. A mixture containing pure nitrogen and oxygen in the ratio 4:1 (B.O.C. Special Gases) was used in subsequent experiments. The oxidant gases were dried before use by passage through a 30 cm column packed with Linde 5A molecular sieve and silica gel.

Tetraethyllead, in the form of a 10% solution in 2-methylpentane, was kindly provided by Associated Octel Ltd. Powdered lead monoxide (> 98% pure) was obtained from B.D.H. Chemicals Ltd. Methyl-tert-butylether (MTBE) was kindly supplied by the Esso Petroleum Company.

TABLE 2.1 Sources of organosilicon compounds used in study

Compound	Source
Me_4Si	Lancaster Synthesis Ltd.
Et_4Si	Lancaster Synthesis Ltd.
Et_3SiH	Lancaster Synthesis Ltd.
Ph_3SiH	Fluka A.G.
$PhCH_2SiMe_2H$	Field Instruments Co. Ltd.
$PhSiMe_3$	Lancaster Synthesis Ltd.
$Me_3SiSiMe_3$	Lancaster Synthesis Ltd.
$p\text{-}(HMe_2Si)_2C_6H_4$	Field Instruments Co. Ltd
$Me_2Si(CH_2)_3$	[redacted] (Leicester).
$(Me_3Si)_2O$	Dow Corning
$(HMe_2Si)_2O$	" "
$(Me_2SiO)_n$	" "
$(Me_2SiO)_3$	" "
$(Me_2SiO)_4$	" "
$(Me_2SiO)_5$	" "
$Me_3SiO(HMeSiO)_{30}SiMe_3$	" "
$(MeO)_3\ SiMe$	" "
$(MeO)_3SiPh$	" "
$(MeO)_3SiCHCH_2$	" "
$(EtO)_4Si$	" "
Me_3SiOMe	S
Me_3SiO^tBu	S
$Me(MeO)Si(O(CH_2)_2Ph)_2$	" "
$(Ph_2SiO)_3$	Field Instruments
$(Ph_2SiO)_4$	Field Instruments
$Me(MeO)Si(OR)_2$	Dow Corning

Continued.....

TABLE 2.1 (Continued...)

Compound	Source
$HMe_2SiOCMe_2CHCH_2$	[redacted]
Me_3SiOPh	S
o-$Me_3SiOC_6H_4Me$	Dow Corning
m-$Me_3SiOC_6H_4Me$	S
p-$Me_3SiOC_6H_4Me$	Dow Corning
$Me_3SiOC_6H_2$2,6-di-Me-4-Cl	Dow Corning
$(Me_3Si)_2NH$	Dow Corning
Me_3SiNH^tBu	Dow Corning
$Me_3SiCH_2NMe_2$	Dow Corning
$Me_2Si(NMe_2)_2$	Field Instruments
$(Me_2SiNH)_3$	Field Instruments
Me_3SiNEt_2	Dow Corning
$(Me_3SiNHCH_2)_2$	Dow Corning
N-Me_3Si-Imidazole	Dow Corning
$(Me_3SiNH)_2CO$	Dow Corning
$(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$	Dow Corning
$Me_3SiNHPh$	S
o-$Me_3SiNHC_6H_4Me$	S
m-$Me_3SiNHC_6H_4Me$	S
p-$Me_3SiNHC_6H_4Me$	S
$Me_3SiNMePh$	S
$PhMe_2SiCH_2NHPh$	Dow Corning
$Me_3SiCH_2NPh_2$	Dow Corning
$Me_2Si(NHPh)_2$	S
o-$Me_3SiO.C_6H_4NHSiMe_3$	S
m-$Me_3SiO.C_6H_4.NHSIMe_3$	S

Continued....

TABLE 2.1 (Continued...)

Compound	Source
p-$Me_3SiO.C_6H_4.NHSiMe_3$	S
Me_3SiCl	Dow Corning
Me_3SiCH_2Cl	" "
$Me_3SiCHCl_2$	" "
$Me(MeO)_2Si(CH_2)_3Cl$	" "
$(MeO)_3Si(CH_2)_3$ Cl	" "
Me_2SiCl_2	" "
Ph_2SiCl_2	" "
Me_3SiI	" "
$(MeO)_3Si(CH_2)_3$ SH	" "
$CF_3CON(SiMe_3)_2$	" "
$(Ph_3Si)_2Hg$	S

S = Synthesized at The City Universty.

2.2 APPARATUS

2.2.1 The Vacuum System

A static Pyrex vacuum apparatus, shown schematically in Fig. 2.1, enabled mixtures of fuel and additive to be injected into a reaction vessel containing oxygen or air. Greaseless PTFE Rotaflo taps were used throughout to avoid the use of high vacuum silicone grease.

Oxygen or air was introduced into the system through a 30cm drying column, DC, containing Linde 5A molecular sieve and silica gel before being stored in a 5dm^3 globe, G, on the vacuum line. The pressure of the oxidant gas was measured by the mercury manometer, M.

Reactions were performed in a 500 cm^3 spherical Pyrex-glass vessel, RV, shown in Fig. 2.2 which was fitted with two side-arms; one connected the reaction vessel to the vacuum system via a cylindrical joint sealed with a Viton 'A' rubber 'O' ring. The other was fitted with an injection port, shown in Fig. 2.3. A vacuum-tight seal was obtained by using a $^1/_4$ in. (0.625cm) Swagelok fitting with PTFE ferrules. The PTFE-backed silicone rubber septa were held in place by an aluminium cap, which was provided with fins to aid cooling. Liquid fuel and additive mixtures were introduced through the port and into the reaction vessel using 250$\mu\ell$ SGE syringes fitted with 11.5cm needles and a needle guide.

The vacuum line was adapted for gas sampling by the addition of a 14.5cm^3 sample loop, SL, and a 500cm^3 Pyrex glass bulb, G$_2$. Involatile products were collected in a liquid nitrogen-cooled trap, CT. The gas pressure in the reaction vessel was measured by means of a Kistler piezoresistive pressure transducer.

Key to Fig. 2.1

VAC	Vacuum system
Pi	Pirani gauge
Pe	Penning gauge
G_1	Gas storage bulb
G_2	Product gas storage bulb
I	Gas inlet
D	Drying tube
M	Mercury manometer
T	Pressure transducer
RV	Reaction vessel
F	Furnace
SL	Gas sampling loop
CT	Cold trap

FIGURE 2.1

The injection apparatus

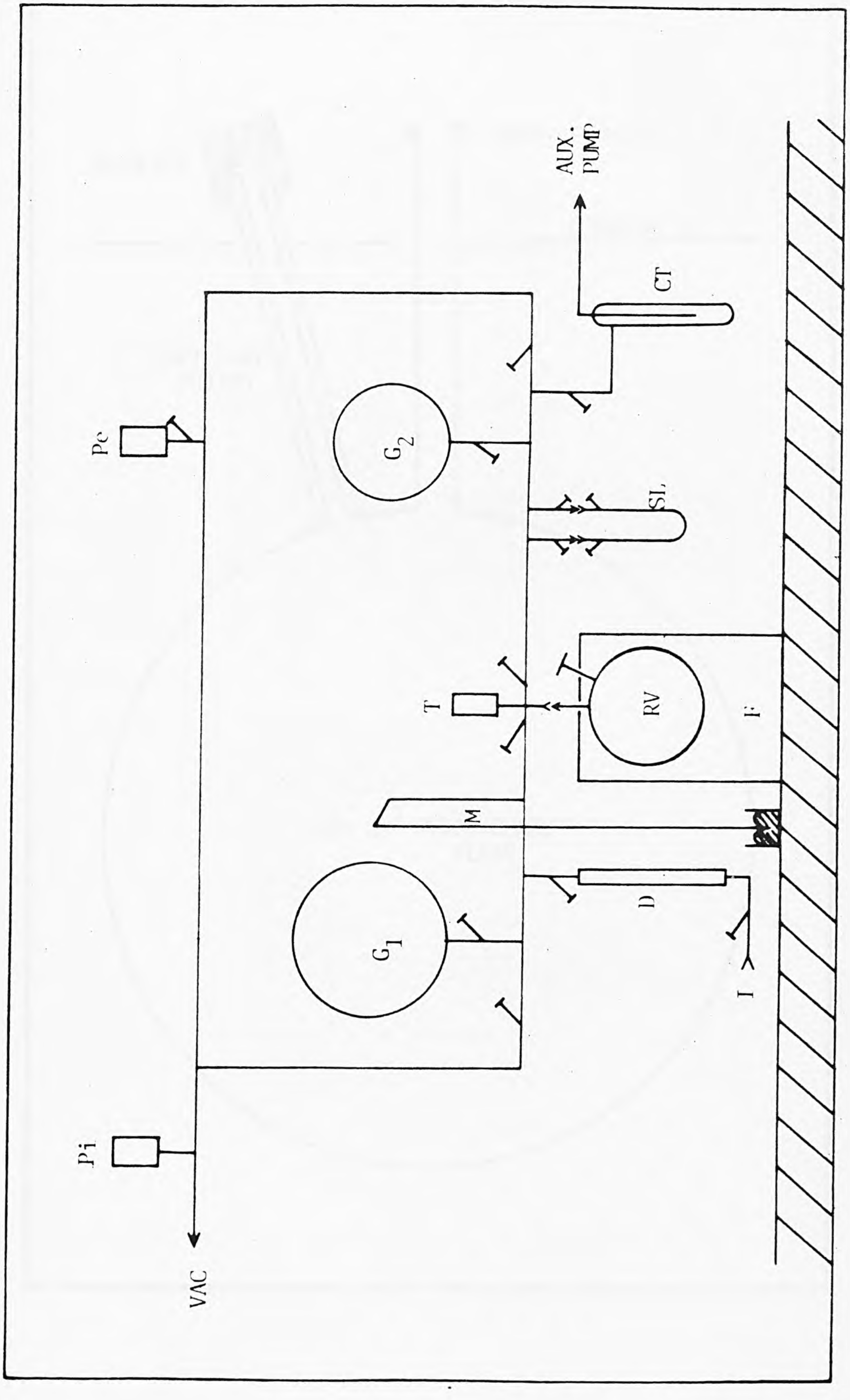


FIGURE 2.2

The reaction vessel

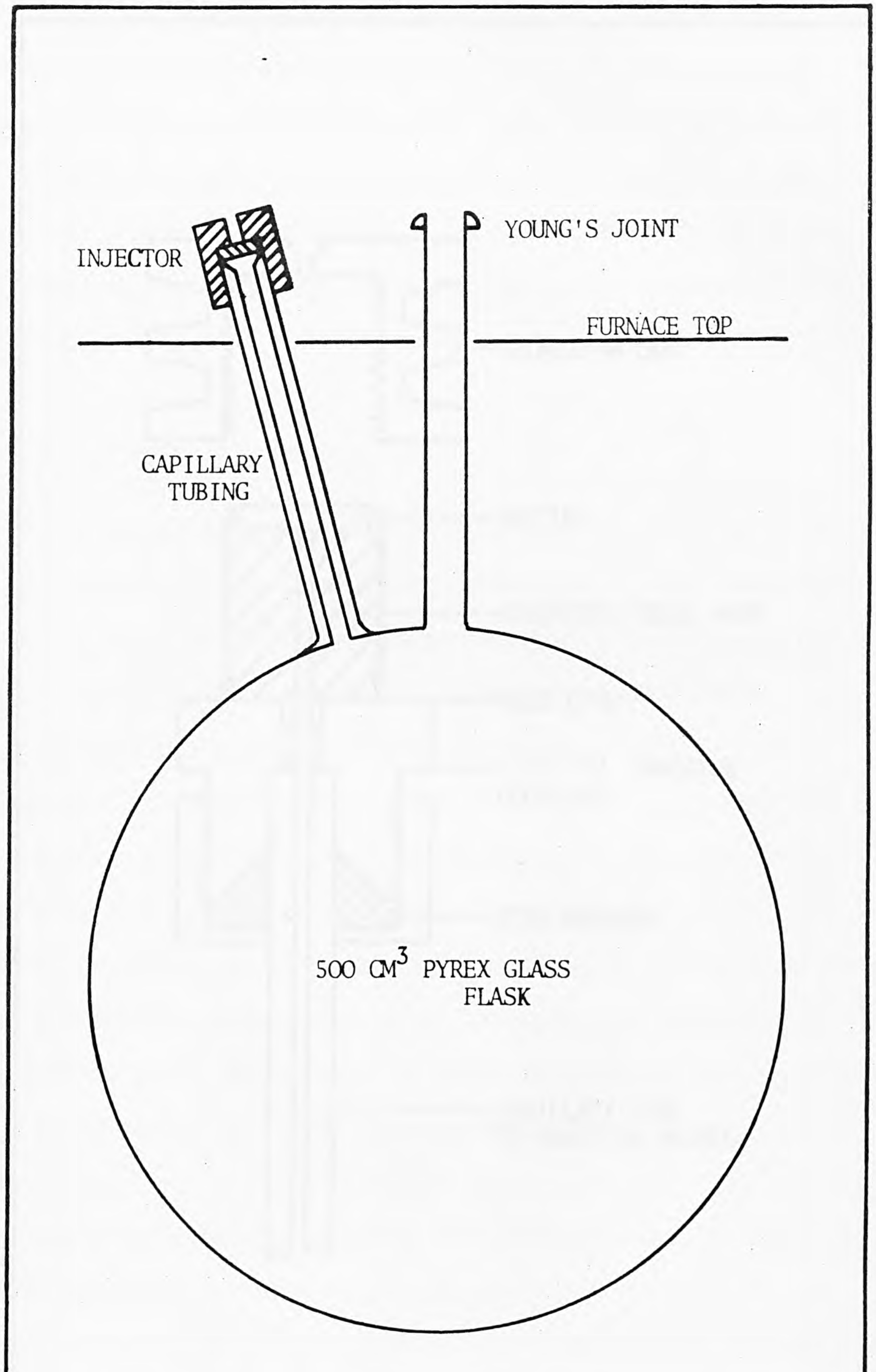
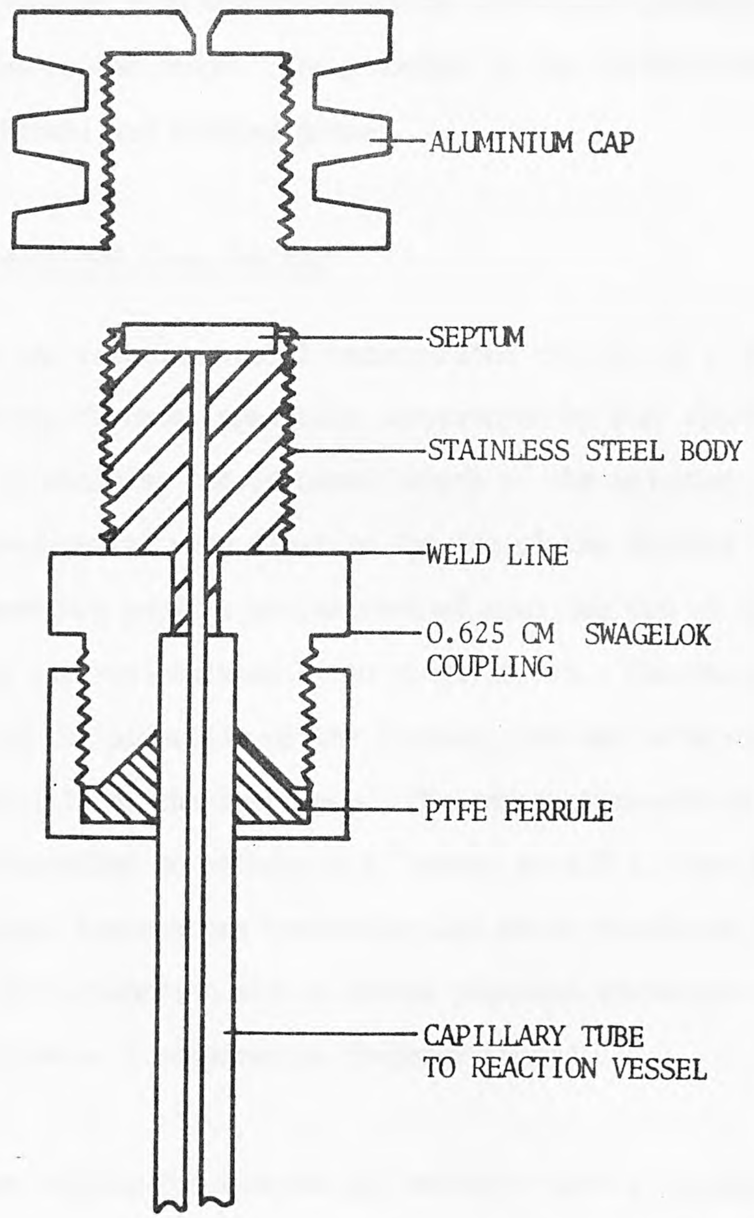


FIGURE 2.3

The injection port



A vacuum of ca. 10^{-2} Pa was easily obtained in the system by the use of an Edwards' (type F 203 A) oil diffusion pump, backed by an Edwards' (type ED50) rotary oil pump. The reactions vessel was pumped out initially using an Edwards' (type EDM2) rotary oil pump which was able to achieve pressures of 10 Pa in the system. The pumps were protected from contamination by combustion products with liquid nitrogen-cooled traps. The pressure in the vacuum system was monitored by Pirani and Penning gauges.

2.2.2. Furnace and Line Heating

The design of the reaction vessel necessitated the use of a forced-air recirculatory furnace, specially constructed by R.M. Catterson-Smith Ltd. To minimise the required length of the injector, the vessel must be situated very close to the top of the furnace. A constant temperature profile was maintained near the top of the furnace by hot air recirculated by an electric fan. The fan motor was situated on the underside of the furnace, and was water-cooled to prolong the life of the bearings. The temperature within the furnace was controlled to within ± 1 $^{\circ}$ using an A.E.I. type RT3/R mk.2 proportional temperature controller and power regulator (A.E.I. type RS4XVT) in conjunction with a 10-ohm platinum resistance thermometer which acted as a temperature feedback sensor.

The temperature within the furnace was measured with a chromel-alumel thermocouple, which was placed adjacent to the wall of the reaction vessel. In later experiments, the thermocouple was replaced by a Beckman temperature probe which gave direct temperature measurements displayed on a digital voltmeter (1mV per $^{\circ}$C).

The section of the line between A and B, including the tubing connecting the pressure transducer and the reaction vessel, was maintained at a temperature of ca. 393K, by means of Electrothermal heating tape controlled by a Variac voltage regulator. The sample bulb, G_2, was heated in the same way. The temperature along the line was monitored using chromel-alumel thermocouples. The heating prevented the condensation of reaction products along the vacuum line.

2.2.3 Pressure measurements and signal amplification

Pressure changes occurring during the course of a reaction were measured by means of a piezo-resistive pressure transducer. This was a Kistler type 4045 A2 transducer with an output of 0-500mV over a pressure range of 0-200 kPa. The linearity of the output signal from the transducer was tested in the range 0-100 kPa by admitting known pressures of dry nitrogen into the reaction vessel. The pressure of nitrogen was measured on the mercury manometer, M, and the corresponding signal was taken from a digital voltmeter. The transducer measures static and transient pressures by means of a silicon measuring cell which is welded onto a thin steel diaphragm on which the pressure acts. The measuring cell consists of diffused piezoresistive resistors connected into a Wheatstone bridge. Through the effect of pressure, the bridge is unbalanced, and an output signal results. The bridge is excited by a constant current, in this case 4.106 mA, which is determined as that current at which the transducer displays the specified value for sensitivity (0-500 mV). The advantage gained by supplying constant current rather than constant voltage to the measuring bridge is that the bridge signal is proportional to the absolute resistance change value rather than to the relative change in bridge resistance. This manifests itself in an improved signal-temperature relationship i.e. the output is less temperature dependent.

The constant current was provided by a Kistler type 4611 piezoresistive amplifier. The amplifier was powered by a ± 15V stabilized d.c. source. The signal from the transducer was amplified using the fixed gain amplifier and measured on a John Fluke model 8050A digital multimeter. Pressure changes during the course of a reaction were measured on a Rikadenki type R10 chart recorder, which had a pen speed of higher than 1000 mm s^{-1}. Thus, the system was easily capable of recording transient pressure pulses accompanying combustion. The recorder also had the facility of 700% zero suppression. It was calibrated at various sensitivities using known pressures of dry nitrogen inside the reaction vessel.

2.2.4 The gas chromatograph

A Hewlett-Packard 5840A gas chromatograph, fitted with duel flame-ionization detectors, was used throughout the work. The gas chromatograph is a digital processor-based instrument incorporating an integrator and a heat-sensitive printer. A gas sampling valve, housed in a heated compartment, enabled the direct analysis of gaseous samples via the sample loop, SL. Several columns were employed in the analysis of a large variety of compounds and samples. The best results were obtained using a 50 m fused silica capillary column (internal diameter, 0.2 mm), the walls of which were coated with SE 54. A 15m stainless steel support-coated capillary column (Carbowax 20M) of 0.5mm i.d. was also used. Stainless steel columns of 3mm i.d. containing various stationary phases were also employed. The chromatograph was able to be used isothermally or with multi-step temperature programming depending on the nature of the analysis.

2.3 PROCEDURES

2.3.1 Calibration of pressure-measuring system

The Kistler pressure transducer was calibrated against a mercury manometer, M, using dry nitrogen. Known pressures of dry nitrogen, in the range 0-100 kPa, were admitted into the reaction vessel, and the corresponding amplified signal from the transducer was displayed on the digital multimeter. The resulting plot, shown in Fig. 2.4. showed that the output from the transducer increased linearly with pressure, and that an output of ca. 50 mV per kPa was obtained.

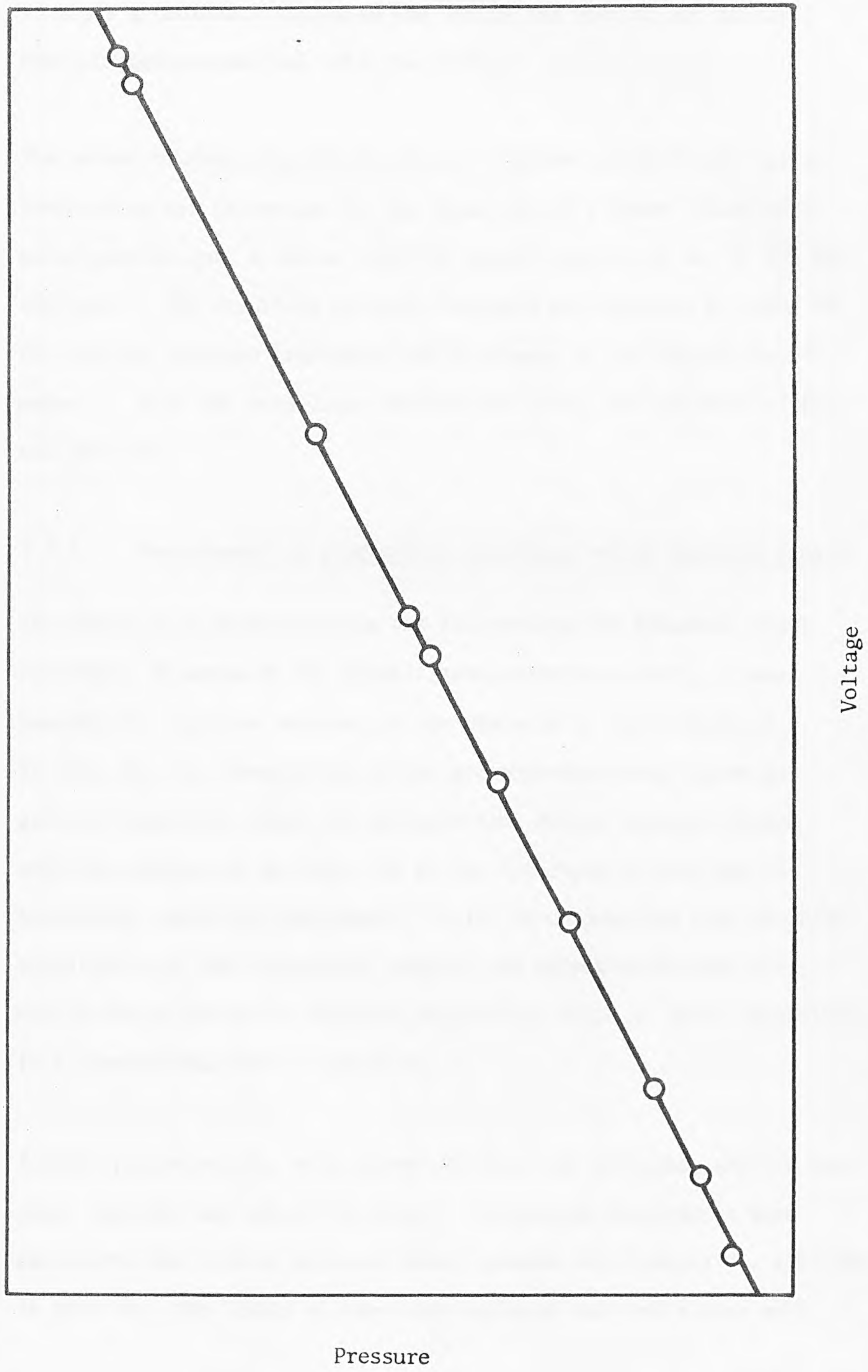
The Rikadenki R10 series chart recorder was also calibrated against a mercury manometer, M, using dry nitrogen, as above, over various ranges of sensitivity. On scales typical of those used in the combustion experiments, i.e. 2V and 5V, responses were found of ca. 6.5 mm kPa^{-1} and 2.6 mm kPa^{-1} respectively.

2.3.2 Preparation and injection of fuel mixtures

Fuel mixtures were prepared by the addition of organosilicon compounds to known volumes of 2-methylpentane using microlitre syringes. For the large majority of organosilicon compounds, laboratory tests were made on 5 and 10 vol% mixtures. Dry air or oxygen was admitted into the evacuated reaction vessel, RV, from the storage bulb, G_1, to a known pressure, P_{ox}, which was measured on the mercury manometer, M. The greaseless PTFE taps, T_1 and T_2 were then closed, sealing the reaction vessel from the rest of the line. Fuel mixtures were then injected rapidly into the vessel using a microlitre syringe, the tip of the needle of which protruded just into the reaction zone. In

FIGURE 2.4

Calibration curve for piezoresistive pressure transducer



experiments where oxygen was used, the fuel:oxygen ratio was 1:3. In later experiments involving the use of the special air mixture, the nitrogen:oxygen:fuel ratio was 8:2:1.

The volume of fuel required to attain a desired pressure at a given temperature was determined by the injection of a known volume of 2-methylpentane into a sealed reaction vessel containing ca. 67 kPa dry nitrogen. The resulting pressure increase was measured by means of the Kistler pressure transducer and displayed on the digital multimeter. From the transducer calibration curve, the pressure of fuel was obtained.

2.3.3 Measurement of progress of reactions and of ignition limits

The course of a given reaction was followed on the Rikadenki chart recorder. By means of the inbuilt zero suppression unit, it was possible to zero the recorder at the pressure of the oxidant, P_{ox}. In this way, the sensitivity of the pressure-measuring system was greatly increased, since the pressure-time curves obtained showed only the changes of pressure due to the injection of fuel and to subsequent combustion phenomena. This, in conjunction with the high sensitivity of the transducer, enabled the detection of even very weak pressure pulses as reaction progressed, which is often impossible in a conventional static apparatus.

Initial pressures, P_0, were chosen for fuel-air mixtures, whereby two-stage ignition was likely to occur. Subsequent experiments were performed, the initial pressure being reduced each time by ca. 1.83 kPa. In this way, the limits of two-stage ignition and cool flames were obtained. The injection system allowed a greater selectivity of initial pressure, and thus provided a fast screening test of the effects of additives on the ignition limits of hydrocarbon fuels.

2.3.4 Conditioning of reaction vessels

The Pyrex glass reaction vessels used in the laboratory study were washed with concentrated nitric acid, rinsed well with distilled water and finally acetone. The vessels were then dried in an oven at 400K, before being attached to the vacuum lines by means of the ball and cup joints. The vessel was evacuated, and heated to the desired reaction temperature (ca. 600K). Repeated injections of the pure hydrocarbon were made into the oxidant-filled vessel at a pressure at which two-stage ignition was expected to take place. After ca. 50 injections, a uniform carbon coating was obtained. Subsequent injections showed that the position of the ignition limits was stable, and that the induction period preceding a cool flame showed very little variation (less than 5%) for successive reactions under the same initial conditions. Further conditioning reactions were necessary when the reaction vessel was exposed to the atmosphere eg. on replacing the septum in the injection port. Deposition of large amounts of siliceous material within the vessel caused changes in the combustion characteristics of the pure fuel. This problem was countered by the injection of pure fuel after experiments involving organosilicon compounds. In this way, it was possible to remain certain that the effects measured in the system were caused by the additive injected, and not by changes in the nature of the walls. Between successive reactions, the vessel was pumped down to ca 10^{-1} Pa in order to ensure reproducible conditions.

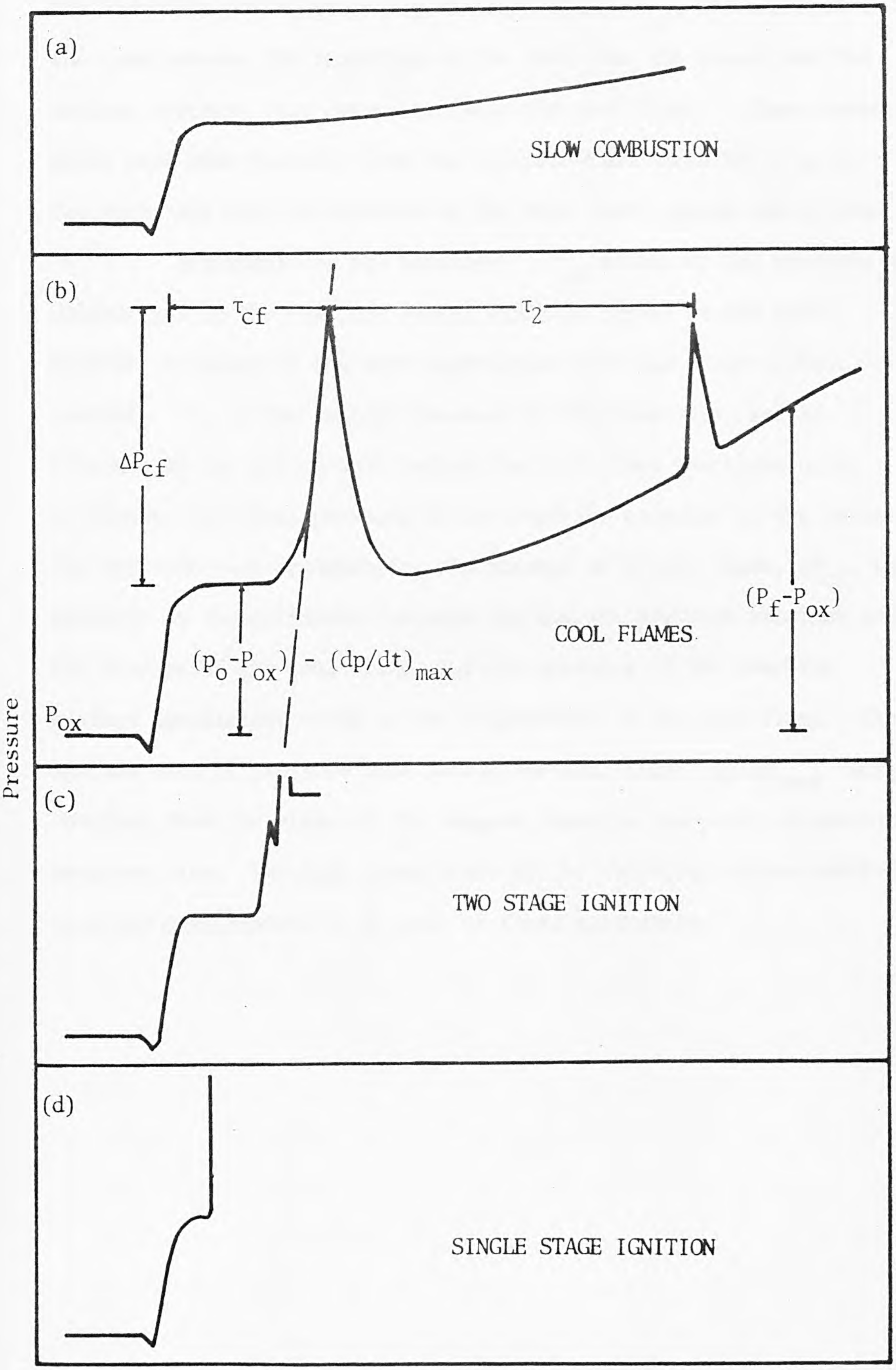
A lead oxide-coated vessel was prepared according to the procedure described by Walsh (1961). Powdered lead monoxide (ca. 2g) was suspended in ca. 20 cm^3 of water, and poured into a Pyrex glass reaction vessel, the surface of which had been prepared in the normal way. The side-arm of the vessel was sealed, and the outlet was connected to a rotary evaporator. The water bath was maintained at ca. 370K, and the vessel was turned slowly. The evaporation of the water left a uniform deposit of lead monoxide on the inner surface of the vessel. Excess powder was removed by swilling with distilled water. The vessel was dried, attached to the vacuum line, and heated under vacuum at ca. 600K for 12 hr. prior to use. The vessel coated by this method required little further conditioning before reproducible results were obtained.

2.3.5 Measurement of kinetic parameters

Kinetic measurements were made from the pressure-time traces recorded from the output of the pressure transducer attached to the reaction vessel. The limits of two-stage ignition, with which there was primary concern, were plotted by the reduction of the initial pressure of the reactants, P_0, between successive reactions by 1.83 kPa. Changes in the two-stage ignition limits in the presence of additives were correlated directly with their "anti-knock" effectiveness. The validity of this assumption was tested by the injection into the system of pure hydrocarbons (other than 2-methylpentane) and of mixtures of hydrocarbons. The ignition limits found for these compounds and mixtures were found to correlate with their stated research octane numbers (RON). Figure 2.5 shows typical pressure-time curves obtained for the combustion of 2-methylpentane.

FIGURE 2.5

Typical pressure-time traces observed during the combustion of 2-methylpentane



Time

The induction period preceding the cool flame, τ_{cf}, was measured as the time between the injection of the fuel into the vessel and the maximum pressure rise associated with the cool flame. These measurements were made directly from the pressure-time trace for a given reaction, and were facilitated by the fast chart speeds (up to 10cm s^{-1}) attainable by the recorder. P_{ox} refers to the pressure of oxidant gas in the reaction vessel which is zeroed on the chart recorder by means of the zero suppression unit and a zero offset control. P_o is the initial pressure of the reactants, and is attained in the system well before the cool flame reactions occur. P_f denotes the final pressure of the reaction products in the vessel. The pressure rise accompanying the passage of a cool flame, ΔP_{cf}, was measured as the difference between the maximum pressure attained and the passage of the cool flame, and the pressure of the reaction mixture immediately prior to the propagation of the cool flame. The maximum rate of pressure rise during the cool flame $(dp/dt)_{max}$ was obtained from the slope of the tangent drawn to the point of maximum pressure rise. The high sensitivity of the recording system enabled accurate measurements to be made of these parameters.

2.4 ENGINE COMBUSTION

2.4.1. The Cooperative Fuel Research engine

Studies of the effects of low concentrations of organosilicon compounds on hydrocarbon combustion in an engine were carried out using a Cooperative Fuel Research (CFR) engine. The CFR engine is a spark ignition engine approved by the American Society for Testing and Materials (ASTM) and used extensively for the evaluation of the knock characteristics of motor fuels. The engine, which is illustrated in Fig. 2.6 consists of a single cylinder with a continuously variable compression ratio. The unit is also provided with a pressure-sensitive knock pick-up, a knock meter, and detonation meter. Four fuel containers, for the storage of reference and test fuels, are linked to the engine via a carburettor. The air-fuel ratio is controlled by a needle valve situated beneath each fuel storage bowl.

2.4.2. Engine tests

Solutions were prepared containing low concentrations (0.1-0.5 vol %) of various organosilicon compounds in a 90:10 2,2,4-trimethylpentane (isooctane):heptane mixture. This fuel mixture has, by definition, a research octane number (RON) of 90. The effects of the organosilicon compounds on the RON of the straight fuel were evaluated by the following procedure: The engine was started and run on the standard 90 RON fuel. The fuel-air ratio was then adjusted to a value at which maximum knock occurred. The compression ratio was then varied until a standard knock intensity (50 ± 5) was observed on the knockmeter. Two further reference fuels (isooctane-heptane mixtures) with RON values of 87.5 and 92.5 respectively were then introduced. The knockmeter readings

Fig. 2.6 The Cooperative Fuel Research Engine (p.112) has been removed for copyright reasons

were recorded, and subsequently the knockmeter was calibrated over a range of 5 octane numbers. The test fuels containing additives were then admitted to the engine, and their RON values were calculated from the knockmeter readings by interpolation. The knockmeter was recalibrated on several occasions during the tests as a precaution against the effects of solid deposits formed in the engine cylinder and on the spark plug, which might contribute to changes in the knockmeter readings.

Further engine tests were carried out on the effects of some organic antiknock compounds on hydrocarbon combustion. The reference fuel used for these tests consisted of isooctane (64.4 vol %), heptane (22.0 vol %) and toluene (13.6 vol %), and had an RON value of 87.4. The RON values for various low concentrations of aniline, MTBE and N-methylaniline were obtained by the above procedure.

RESULTS

3.1 THE COMBUSTION OF HYDROCARBONS IN THE INJECTION APPARATUS

3.1.1 The ignition profile of 2-methylpentane/oxidant mixtures

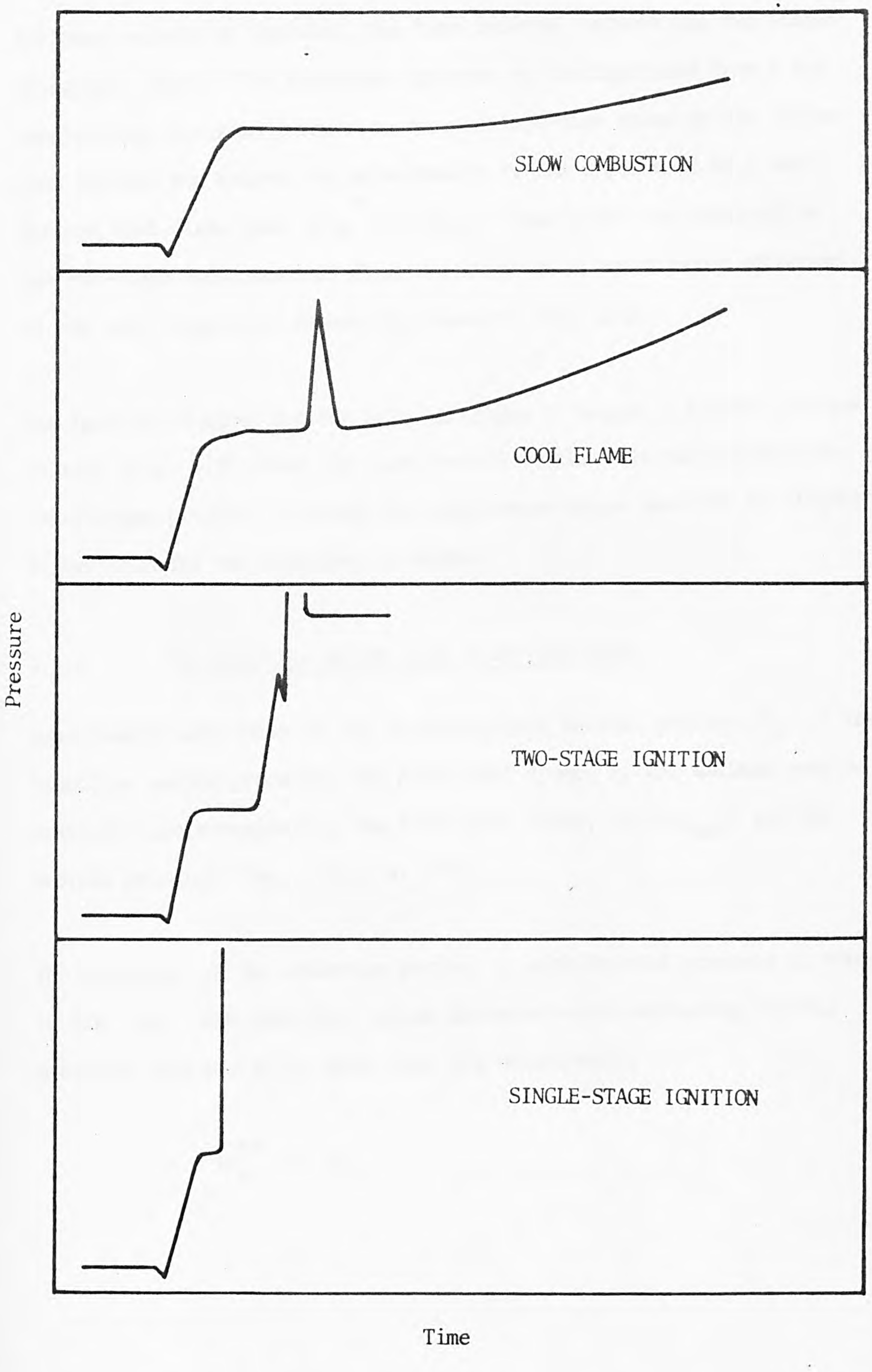
The combustion of 2-methylpentane was studied in the injection system with both oxygen and air as the oxidant. 3:1 mixtures of oxygen and 2-methylpentane and 10:1 mixtures of air and the hydrocarbon were found to undergo combustion accompanied by isothermal and non-isothermal phenomena as shown in Fig. 3.1. The phenomena observed in the reacting mixtures are dependent on the initial conditions of temperature and pressure of the reactants. The influence of these parameters on the type of behaviour observed can be seen in the ignition diagrams shown in Figs. 3.2 and 3.3.

For the 3:1 oxygen-fuel mixture, the reaction below 557K was seen to be of the slow combustion type and is accompanied by a very small pressure rise and preceded by an induction period (Fig. 3.1(a)). Above this temperature, an initial slow reaction is followed by a fairly sudden transition to a cool flame (Fig. 3.1(b)), and subsequently at higher pressures to two-stage ignition (Figs. 3.1(c)). The region at which this type of behaviour is observed lies between 557K and 713K and at pressures greater than 5.3 kPa. At temperatures above 713K, a sharp transition from slow combustion to single-stage ignition occurs, and no cool flames are observed (Fig. 3.1(d)).

In the cool flame region, it was possible to detect up to five successive cool flames. At pressures above 25 kPa, the first cool flame was

FIGURE 3.1

Pressure-time curves obtained with 2-methylpentane-oxidant mixtures



followed rapidly by ignition, the time interval between the two stages being very short. The two-stage ignition is distinguished from a hot single-stage ignition process on the pressure-time trace by the inflection between the stages, or occasionally by the appearance of a well-defined cool flame peak (Fig. 3.1.(c)). Four lobes are observed on the two-stage ignition/cool flame boundary which are clearly reflected on the cool flame/slow combustion boundary (Fig. 3.2).

The ignition diagram for the 8:2:1 nitrogen : oxygen : 2-methylpentane mixture (Fig. 3.3) shows the same overall features as the 2-methylpentane/oxygen profile, although the temperature range involved is slightly higher than for the reaction in oxygen.

3.1.2. The kinetics of the cool flame reactions

Measurements were made of the variation with initial pressure P_o, of the induction period preceding the first cool flame, τ, the maximum rate of pressure rise accompanying the first cool flame, $(dp/dt)_{max}$, and the overall pressure rise, ΔP_{cf}, at 573K.

The variation of the induction period, τ, with initial pressure is shown in Fig. 3.4. The induction period decreases with increasing initial pressure, and it can be shown that the relationship :

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

FIGURE 3.2

Pressure-temperature ignition profile for a 3:1 2-methylpentane-oxygen mixture

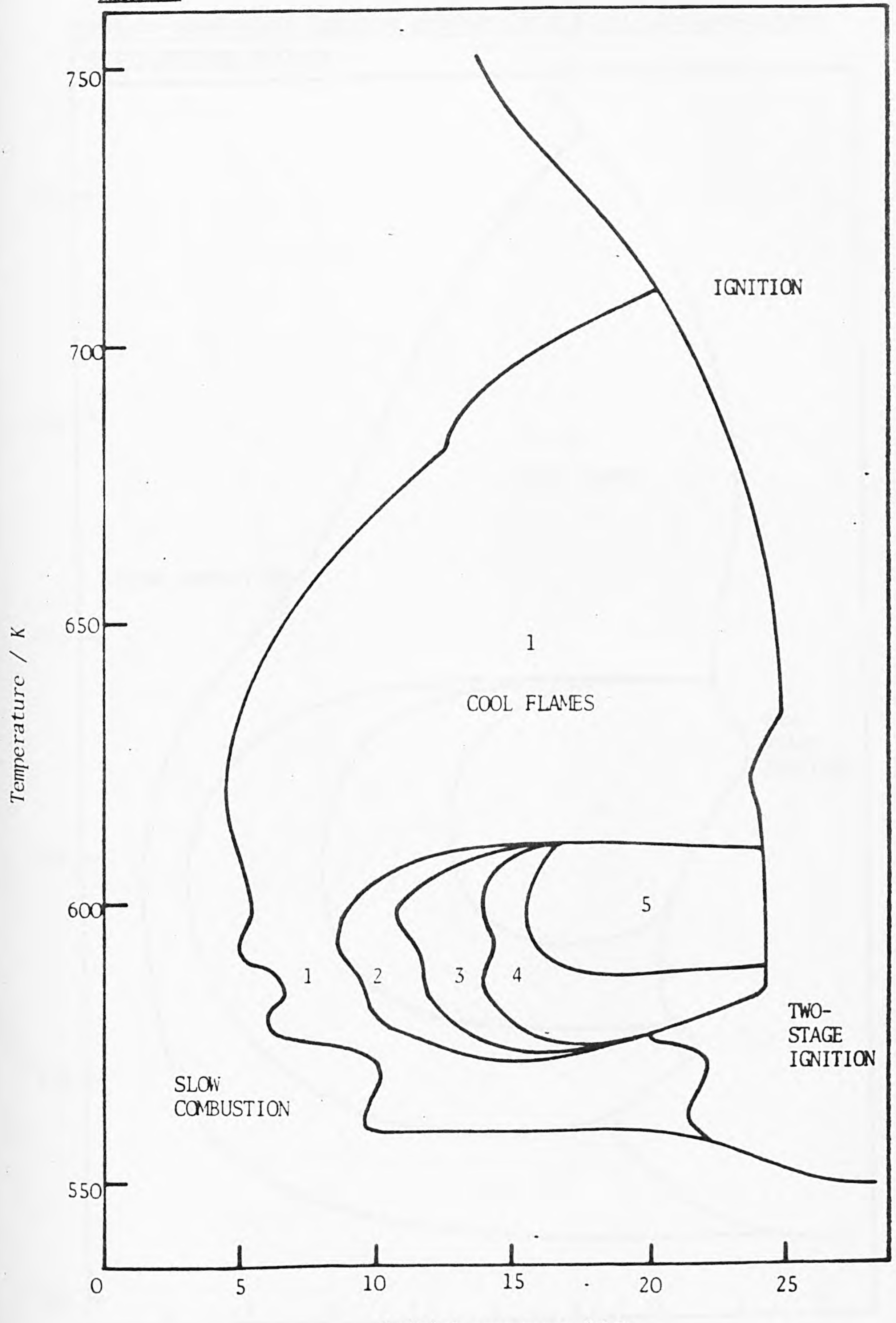


FIGURE 3.3

Pressure-temperature ignition profile for a 8:2:1 nitrogen-oxygen-2-methylpentane mixture

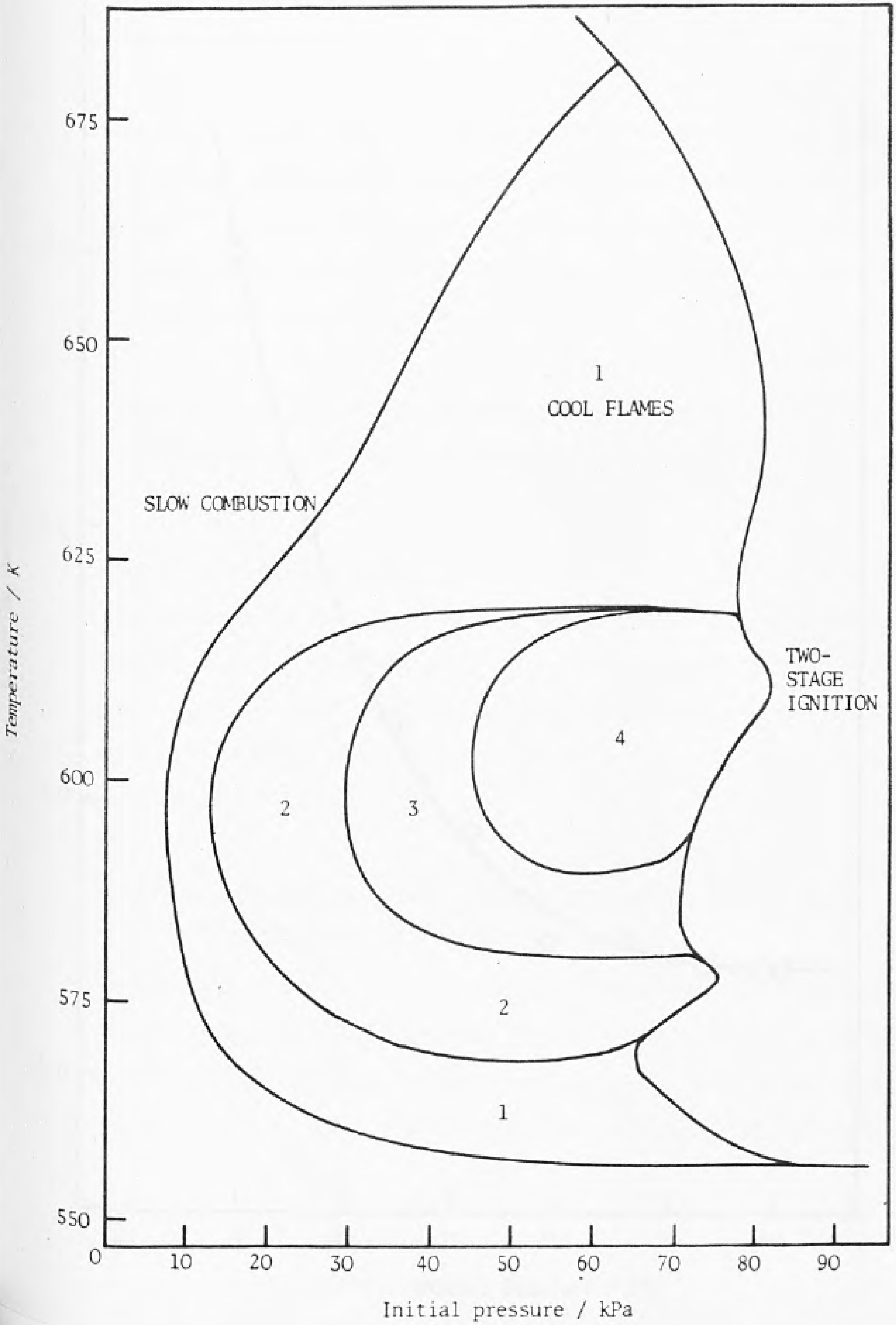
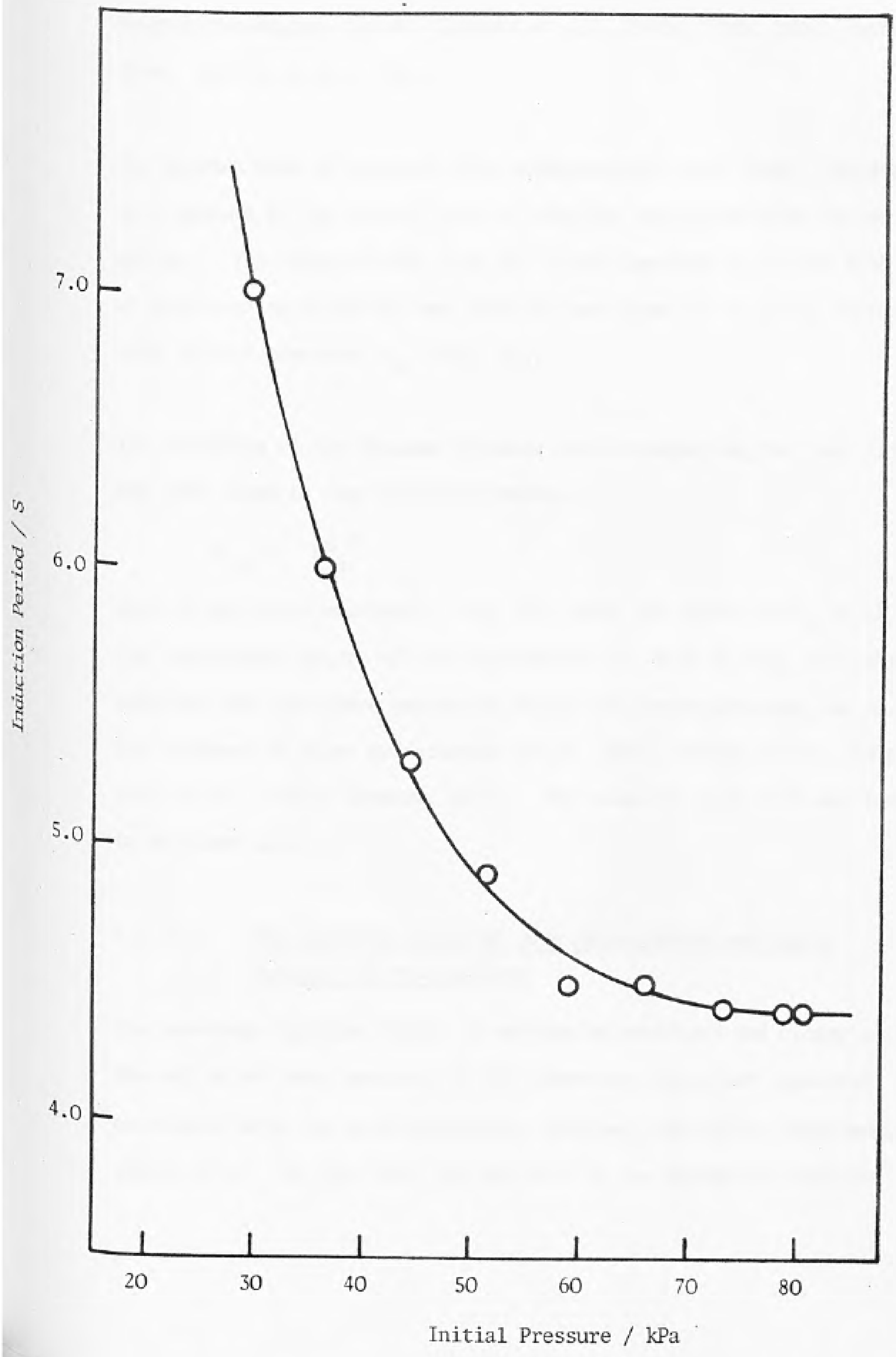


FIGURE 3.4

The variation of the induction period, τ_{cf}, with initial pressure, P_o



holds for 2-methylpentane- oxidant mixtures as it does for many other hydrocarbon-oxygen systems (Luckett et al., 1973; Fish, 1966; Yantovskii, 1966; Cullis et al., 1966).

The maximum rate of pressure rise accompanying a cool flame, $(dp/dt)_{max}$, is a measure of the overall rate of reaction associated with its propagation. The value of this rate for 2-methylpentane in air at 573K and at pressures up to 80 kPa was found to vary from 1.0 to 24.0, increasing with initial pressure, p_o, (Fig. 3.5).

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

$$\Delta P_{cf} = kP_o^{\,m}$$

where k and m are constants. Fig. 3.6 shows the effect of P_o on ΔP_{cf}. The logarithmic nature of the relationship is shown in Fig. 3.7, which confirms that the above expression holds for 2-methylpentane, as it does for a number of other hydrocarbons (Fish, 1966; Cullis et al., 1974; Fish et al., 1971; Semenov, 1935). The value for m at 573K was found to be about 2.0.

3.1.3 The ignition limits of pure hydrocarbons and binary mixtures of hydrocarbons

The two-stage ignition limits of various hydrocarbons and binary mixtures thereof in air were measured in the laboratory injection apparatus, and correlated with the known RON values obtained from engine experiments (Table 3.1). In this way, the validity of the assumption that the

FIGURE 3.5

The variation of $(dp/dt)_{max}$ with initial pressure, P_o

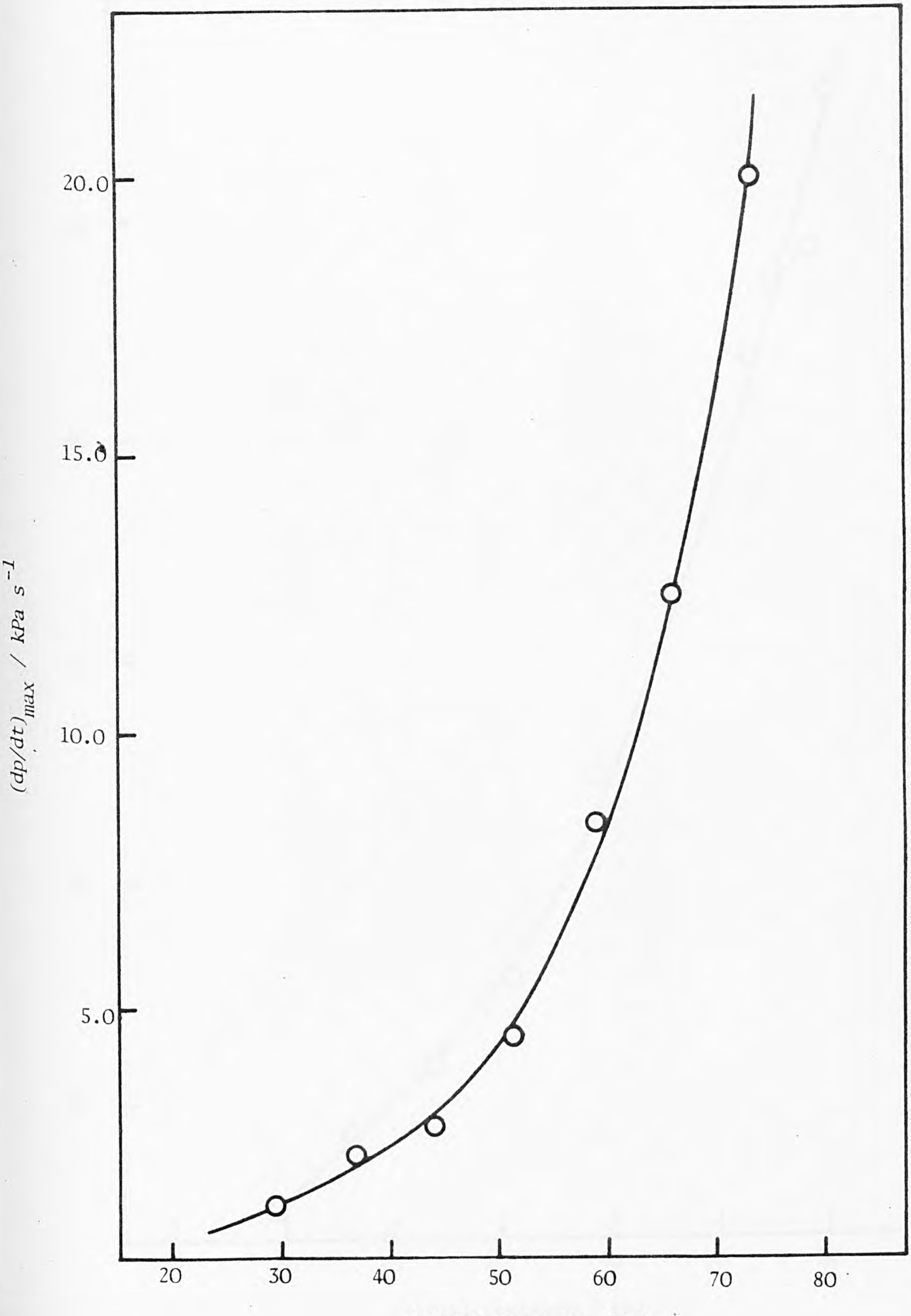


FIGURE 3.6

The variation of ΔP_{cf} with initial pressure, P_o

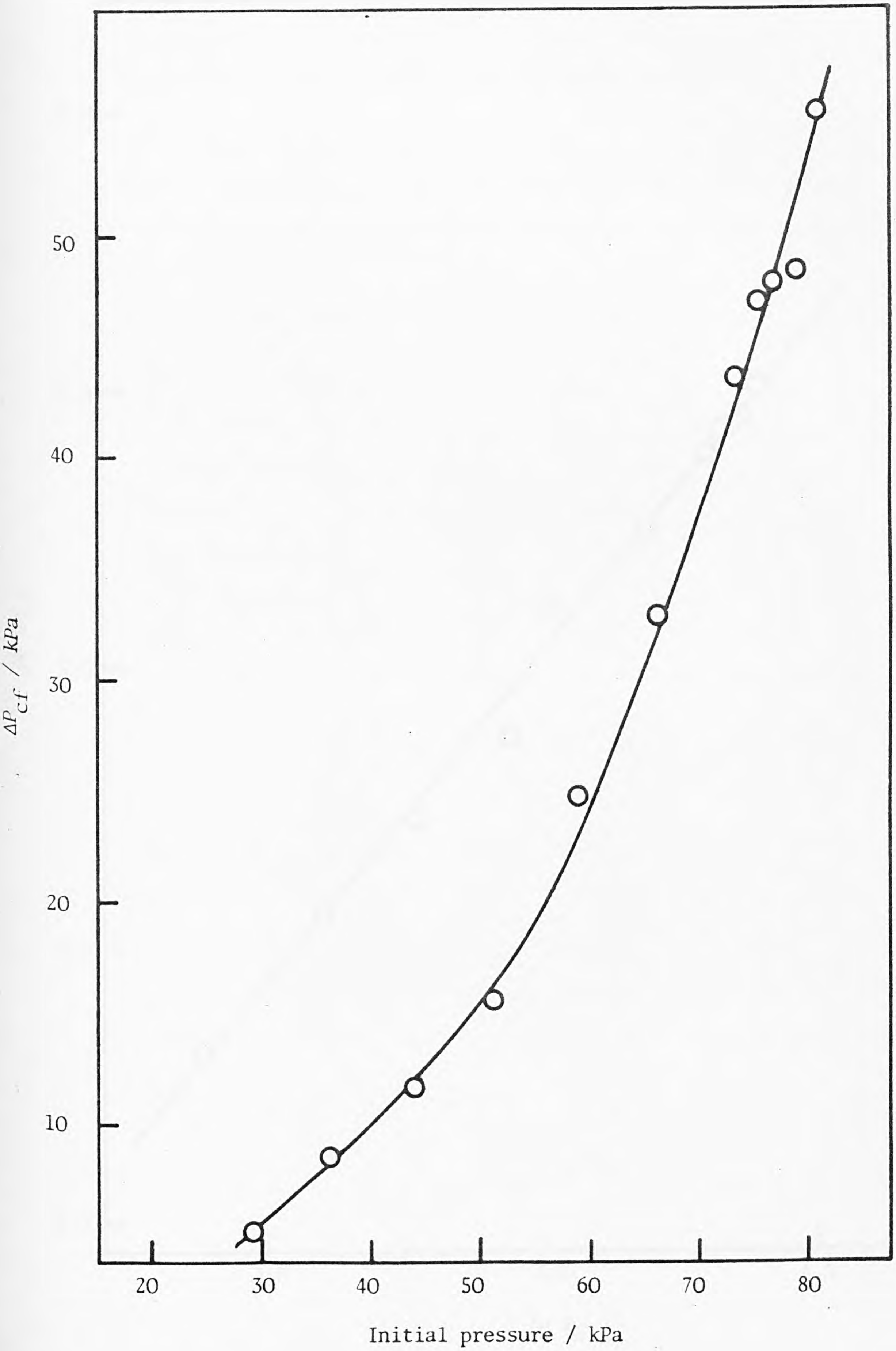


FIGURE 3.7

The variation of ln (ΔP_{cf}) with ln P_o —

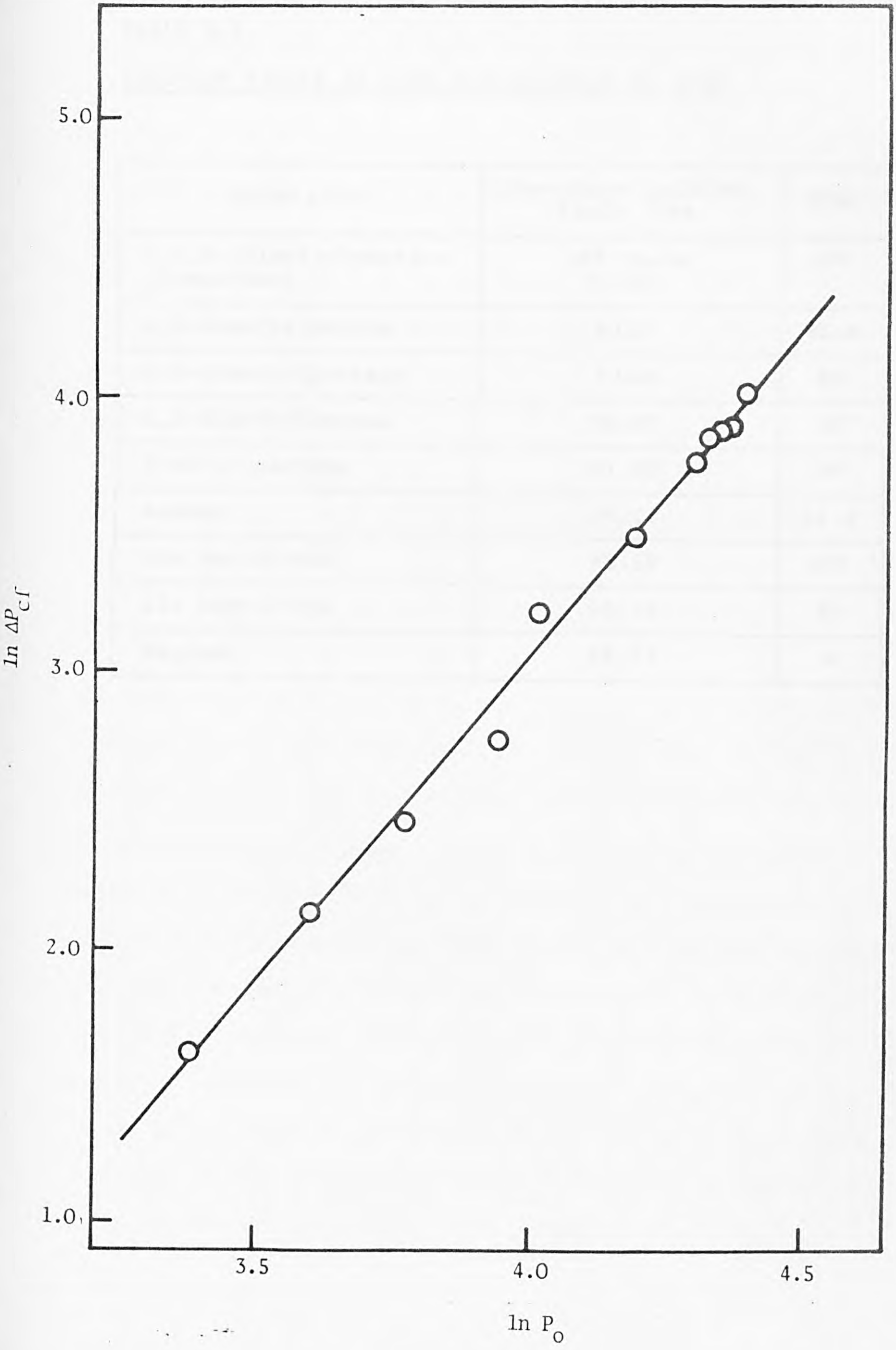


TABLE 3.1

Ignition limits of pure hydrocarbons at 600K

Hydrocarbon	Two-stage ignition limit /kPa	RON
2,2,4-trimethylpentane (isooctane)	Off scale (>110)	100
2,2-dimethylbutane	>110	91.8
2,4-dimethylpentane	>110	80
2,5-dimethylhexane	82.67	69
2-methylpentane	81.60	69
hexane	54.13	24.8
cis pent-2-ene	48.53	107
cis hept-2-ene	48.53	80
heptane	48.53	0

effectiveness of antiknock additives can be measured by changes in ignition limits, could be verified. The correlation between two-stage ignition limits and RON values is of particular importance in the case of binary mixtures of isooctane and heptane, as these mixtures are used as standards in the calibration of CFR engines from which RON data are obtained. The results, shown in Table 3.2, show that there is a definite correlation between the two parameters, although the relationship is seen to break down when comparisons are made of the values obtained by the two methods for compounds of dissimilar nature, e.g. an alkane and an alkene.

3.2 THE EFFECTS OF ORGANOSILICON COMPOUNDS ON THE COMBUSTION OF 2-METHYLPENTANE

3.2.1 The effects of low concentrations of organosilicon compounds on combustion in oxygen

The initial laboratory experiments examining the effects of low concentrations of a selection of organosilicon compounds were performed in the injection apparatus over a temperature range 555-595K, using pure oxygen as the oxidant gas. The fuel : oxygen ratio was maintained at 1:3. Mixtures containing 5 and 10 vol% of organosilicon compounds were used, and the effect of these on the combustion of 2-methylpentane was recorded. The limits of cool flame and two-stage ignition, and the induction period preceding the appearance of the first cool flame were among the parameters measured. Subsequent experiments were performed using lower concentrations of the organosilicon compounds, (0.5 and 1.0 vol%) since engine tests had been undertaken in which concentrations of organosilicon compounds of this order had been used (<0.1 vol%) and been shown to exert a significant

TABLE 3.2

Ignition limits of hydrocarbon mixtures at 600K

Mixture	Two-stage ignition limit /kPa	RON
80/20 isooctane-heptane	>110	80
70/30 isooctane-heptane	92.53	70
60/40 isooctane-heptane	81.60	60
50/50 isooctane-heptane	76.00	50
40/60 isooctane-heptane	65.33	40

effect on RON. Furthermore, in previous laboratory experiments, tetraethyllead had been shown to exert a promoting effect on the combustion of 2-methylpentane when added in concentrations greater than 5 vol%, whereas this compound exerts its antiknock effect in the engine (and indeed in the laboratory) at much lower concentrations.

The effect of low concentrations of several organosilicon compounds on the cool flame and two-stage ignition limits, the induction period and the cool flame intensity were measured. The results obtained are shown in Table 3.3. In general, none of the additives have any significant or systematic effect on the various combustion parameters measured.

3.2.2 The effects of low concentrations of organosilicon compounds on combustion in air

3.2.2.1 Introduction

Further experiments on the effects of organosilicon compounds were performed with a 4:1 nitrogen-oxygen mixture and a fuel:air ratio of 1:10. The reactions were generally carried out at 597K.

The choice of air as oxidant was made in the light of the small effects observed with pure oxygen. It was thought that the absence of sizeable effects might be attributable to the rapid and complete oxidation of the organosilicon compounds immediately they were injected into a relatively high concentration of oxygen.

TABLE 3.3

The effects of organosilicon compounds on the combustion of 2-methylpentane in oxygen

Additive	Vol.%	Temp/K	Cool flame /kPa	Change /kPa	2-stage ign /kPa	Change /kPa	Induction period /S	Change /S	ΔPcf /kPa	Change /kPa
None		555	12.67	-	19.33	-	43.0	-		-
		570	10.0	-	23.33	-	18.0	-	9.60	-
		595	4.67	-	24.67	-	3.7	-	8.93	-
$(HMe_2Si)_2O$	0.5	570	10.00	0	23.33	0	16.5	- 1.5	9.33	+0.27
		595	4.67	0	23.33	-1.33	4.2	+ 0.5	9.60	-0.67
	1.0	570	10.00	0	23.33	0	17.5	- 0.5	9.60	0
		595	4.67	0	24.00	-0.33	4.2	+ 0.5	9.33	-0.4
	5.0	555	6.0	-6.67	16.67	-2.67	32.0	-11.0		
		595	3.33	-1.33	23.33	-1.33	4.9	+ 1.2		
	10.0	555	7.33	-5.33	14.0	-5.33	64.0	+21.0		
		595	3.33	-1.33	22.0	-2.67	4.1	+ 0.4		
$(Me_3Si)_2O$	0.5	570	10.00	0	23.33	0	16.8	- 1.2	9.60	0
		595	4.67	0	24.67	0	3.7	0	8.93	0
	1.0	576	10.00	0	23.33	0	17.0	- 1.0	9.60	0
		595	4.67	0	24.67	0	3.5	- 0.2	9.33	-0.4
	5.0	555	6.0	-6.67	18.0	-1.33	25.0	-18.0		
		595	4.67	0	24.67	0	3.7	0		
	10.0	555	6.0	-6.67	18.0	-1.33	18.0	-25.0		
		595	4.67	0	26.0	+1.33	3.7	0		
$(Me_2SiO)_n$	0.5	570	10.0	0	23.33	0	15.4	- 2.6	9.60	0
		595	4.67	0	23.33	-1.33	3.8	+ 0.1	9.07	-0.13
$n = 3,4,5$	1.0	570	10.0	0	23.33	0	16.2	- 1.8	9.33	+0.27
		595	4.67	0	23.33	-1.33	3.6	- 0.1	8.93	0
	5.0	555	8.67	-4.0	19.33	0	44.0	+ 1.0		
		595	3.33	-1.33	24.67	0	3.5	- 0.2		
	10.0	555	8.67	-4.0	18.0	-1.33	28.0	-15.0		
		595	4.67	0	26.0	+1.33	3.7	0		

cont/....

TABLE 3.3 (cont.)

Additive	Vol.%	Temp/K	Cool flame /kPa	Change /kPa	2-stage ign /kPa	Change /kPa	Induction period /S	Change /S	ΔPcf /kPa	Change /kPa
None		555	12.67	-	19.33	-	43.0	-		-
		570	10.0	-	23.33	-	18.0	-	9.60	-
		595	4.67	-	24.67	-	3.7	-	8.93	-
$MeSi(OMe)_3$	0.5	570	10.0	0	23.33	0	17.8	- 0.2	9.60	0
		595	4.67	0	24.67	0	3.8	+ 0.1	9.06	-0.13
	1.0	570	10.0	0	23.33	0	17.6	- 0.4	9.33	+0.27
		595	4.67	0	23.33	-1.33	3.7	0	8.80	+0.13
	5.0	555	8.67	-4.0	18.0	-1.33	22.0	-21.0		
		595	3.33	-1.33	24.67	0	3.2	- 0.5		
	10.0	555	7.33	-5.33	18.0	-1.33	17.0	-26.0		
		595	4.67	0	24.67	0	1.6	- 0.4		
Me_3SiNH^tBu	0.5	570	8.67	-1.33	23.33	0	14.2	- 3.8	8.0	+1.6
		595	4.67	0	24.67	0	3.2	- 0.5	8.8	+0.13
	1.0	570	7.33	-2.67	22.0	-1.33	14.0	- 4.0	8.27	+1.33
		595	4.67	0	23.33	-1.33	3.6	- 0.1	9.6	-0.67
	5.0	555	6.0	-6.67	18.0	-1.33	24.0	-19.0		
		595	4.67	0	24.67	0	3.3	- 0.4		
	10.0	555	10.0	-2.67	16.67	-2.67	28.0	-15.0		
		595	4.67	0	24.67	0	3.2	- 0.5		
Me_3SiCH_2Cl	0.5	570	10.0	0	23.33	0	18.0	0	9.6	0
		595	4.67	0	23.33	-1.33	3.5	- 0.2	9.06	-0.13
	1.0	570	10.0	0	23.33	0	16.8	- 1.2	9.6	0
		595	4.67	0	23.33	-1.33	3.5	- 0.2	9.6	-0.67
	5.0	555	8.67	-4.0	18.0	-1.33	31.0	-12.0		
		595	3.33	-1.33	23.33	-1.33	3.7	0		
	10.0	555	3.67	-4.0	18.0	-1.33	44.0	+ 1.0		
		595	3.33	-1.33	23.33	-1.33	4.2	+ 0.5		

cont/....

TABLE 3.3 (cont.)

Additive	Vol.%	Temp/K	Cool flame /kPa	Change /kPa	2-stage ign /kPa	Change /kPa	Induction period /S	Change /S	ΔPcf /kPa	Change /kPa
None		555	12.67	-	19.33	-	43.0	-		-
		570	10.0	-	23.33	-	18.0	-	9.60	-
		595	4.67	-	24.67	-	3.7	-	8.93	-
PhSi(OMe)$_3$	0.5	570	10.0	0	23.33	0	18.0	0	9.87	-0.27
		595	4.67	0	23.33	-1.33	3.8	+ 0.1	9.6	-0.67
	1.0	570	10.0	0	23.33	0	17.6	- 0.4	9.6	0
		595	4.67	0	24.0	-0.67	3.6	- 0.1	9.33	-0.4
(Me$_3$Si)$_2$NH	0.5	570	10.0	0	23.33	0	17.6	- 0.4	9.6	0
		595	4.67	0	24.0	-0.67	4.2	+ 0.5	8.93	0
	1.0	570	10.0	0	23.33	0	18.0	0	9.47	+0.13
		595	4.67	0	24.0	-0.67	4.1	+ 0.4	8.93	0
Me$_3$SiCL$_2$	0.5	570	10.0	0	23.33	0	16.7	- 1.3	9.6	0
		595	4.67	0	24.67	0	4.2	+ 0.5	8.93	0
	1.0	570	10.0	0	23.33	0	17.0	- 1.0	9.6	0
		595	4.67	0	24.67	0	4.2	+ 0.5	9.06	-0.13
Ph$_2$SiCl$_2$	0.5	570	10.0	0	23.33	0	16.6	- 1.4	9.60	0
		595	4.67	0	24.67	0	3.4	- 0.3	9.20	-0.27
	1.0	570	10.0	0	23.33	0	16.8	- 1.2	9.6	0
		595	4.67	0	24.67	0	3.6	- 0.1	9.06	-0.13
Me$_4$Si	0.5	570	10.0	0	23.33	0	17.8	- 0.2	9.33	+0.27
		595	4.67	0	24.67	0	3.8	+ 0.1	9.06	-0.13
	1.0	570	10.0	0	23.33	0	18.2	+ 0.2	9.33	+0.27
		595	4.67	0	24.67	0	3.8	+ 0.1	8.80	+0.13

cont/....

TABLE 3.3 (cont.)

Additive	Vol.%	Temp/K	Cool flame /kPa	Change /kPa	2-stage ign /kPa	Change /kPa	Induction period /S	Change /S	ΔPcf /kPa	Change /kPa
None		555	12.67	-	19.33	-	43.0	-		-
		570	10.0	-	23.33	-	18.0	-	9.60	-
		595	4.67	-	24.67	-	3.7	-	8.93	-
Ph_3SiH	0.05 wt.%	570	10.0	0	23.33	0	17.2	- 0.8	9.60	0
		595	4.67	0	24.67	0	3.7	0	8.93	0
	0.1 wt.%	570	10.0	0	23.33	0	17.0	- 1.0	9.60	0
		595	4.67	0	24.67	0	3.6	- 0.1	8.93	0
	0.5 wt.%	570	10.0	0	23.33	0	17.0	- 1.0	9.60	0
		595	4.67	0	24.67	0	3.6	- 0.1	8.93	0
	1.0 wt.%	570	10.0	0	23.33	0	16.6	- 1.4	9.60	0
		595	4.67	0	24.67	0	3.4	- 0.3	8.93	0
	2.0 wt.%	570	10.0	0	23.33	0	16.0	- 2.0	9.60	0
		595	4.67	0	24.67	0	3.2	- 0.5	8.93	0
$(Ph_3Si)_2Hg$	1.0 wt.%	570	4.67	0	23.33	0	16.7	- 1.3	4.60	0
		595	10.0	0	24.67	0	3.6	- 0.1	8.93	0
	2.0 wt.%	570	4.67	0	23.33	0	17.0	- 1.0	9.60	0
		595	10.0	0	24.67	0	3.7	0	8.93	0

Measurements were made of the two-stage ignition limits, the induction period preceding the appearance of the first cool flame, the cool flame intensity and $(dp/dt)_{max}$ for 2-methylpentane in the presence of 5 or 10 vol% of various organosilicon compounds. The position of the boundary between the slow combustion and cool flame regions was unaffected by the incorporation of additives. The data obtained from the measurement of the various kinetic parameters associated with combustion are not usually tabulated since, in most cases, the effect of the presence of additives is insignificant.

3.2.2.2. The effects of silanes

The effects of some alkylsilanes and arylsilanes on the two-stage ignition limit of a 1:10 mixture of 2-methylpentane and air at 573K are shown in Table 3.4. It can be seen that, among the compounds studied, the most effective combustion inhibitors are triphenylsilane and phenyltrimethylsilane, which at a concentration of 10 vol% both raise the ignition limit by about 10%. In contrast, 1,1-dimethyl-1-silacyclobutane is quite an effective promoter of combustion. Very few of the other compounds have significant effects on the limit.

Measurements were also made of the various kinetic parameters accompanying combustion. The cool flame intensities and values of $(dp/dt)_{max}$ were found to be very similar to those measured for the pure fuel at 573K. Compounds containing Si—H bonds increased the induction period preceding the first cool flame. Mixtures containing 10 vol% of these additives were found approximately to double this parameter. Conversely, 1,1-dimethyl-1-silacyclobutane was found to decrease the induction period by about 50%.

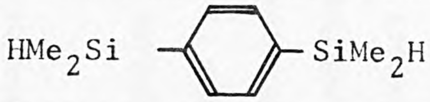
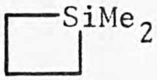
TABLE 3.4

The effects of alkyl and aryl silanes on the two-stage ignition limit of 2-methylpentane in air at 573K

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
None	-	74.27	-
Me_4Si	5	74.27	0
	10	78.00	+ 3.73
Et_4Si	5	74.27	0
	10	74.27	0
Et_3SiH	5	74.27	0
	10	74.27	0
Ph_3SiH	5 wt.%	74.27	0
	10 wt.%	81.60	+ 7.33
$PhCH_2SiMe_2H$	5	76.13	+ 1.86
	10	76.13	+ 1.86

cont/...

TABLE 3.4 (cont.)

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
$PhSiMe_3$	5	76.13	+ 1.86
	10	85.20	+10.93
$Me_3SiSiMe_3$	5	72.41	- 1.86
	10	70.55	- 3.72
	5	74.27	0
	10	76.13	+ 1.86
	5	66.94	- 7.33
	10	65.20	- 9.07

3.2.2.3 The effects of siloxanes

The effects of some siloxanes on the two-stage ignition limit of 2-methylpentane in air at 597K are shown in Table 3.5. It can be seen that the linear siloxanes have little or no effect on the ignition limit, whereas cyclic methylsiloxanes exhibit a marked inhibiting effect. The mixture of cyclosiloxanes originally provided by Dow Corning was found by gas chromatography to contain the three oligomers, D_3, D_4 and D_5 in the ratio 1:8:1 (approx.). During the initial study, this mixture had been found to exhibit one of the largest effects on the ignition limits. Pure samples of D_3, D_4 and D_5 were subsequently obtained to investigate the effects of the minor components of the mixture. A 10 vol% mixture of D_5 in 2-methylpentane was found to increase the ignition limit by about 10%. Measurements of the influence of these compounds on the kinetic parameters accompanying combustion again did not demonstrate any significant effects of the linear siloxanes, whereas the cyclic oligomers D_3, D_4 and D_5 were found markedly to reduce the cool flame intensity, ΔP_{cf}, by as much as 90% when mixtures containing 10 vol% additive in fuel were tested. The values calculated for $(dp/dt)_{max}$ were also considerably reduced; 10 vol% mixtures of each compound were found to reduce the value of $(dp/dt)_{max}$ by about 50% at an initial pressure of 73.33 kPa. In addition, a 10 vol% mixture containing D_4 increased the induction period by a factor of two.

Further experiments were performed to examine the effects of the phenylcyclosiloxanes. Hexaphenylcyclotrisiloxane and octaphenylcyclotetrasiloxane were found to be insoluble in 2-methylpentane and other hydrocarbons.

TABLE 3.5

The effects of siloxanes on the two-stage ignition limit of 2-methylpentane in air at 597K

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
None	-	81.60	-
$(Me_3Si)_2O$	5	81.60	0
	10	81.60	0
$(HMe_2Si)_2O$	5	79.73	- 1.87
	10	77.87	- 3.73
$(Me_2SiO)_n$ n=3,4,5 (D_3, D_4, D_5 mixture)	5	86.00	+ 4.40
	10	86.00	+ 4.40
D_3	5 wt.%	81.60	0
	10 wt.%	85.33	+ 3.73
D_4	5	85.33	+ 3.73
	10	85.33	+ 3.73
D_5	5	87.20	+ 5.6
	10	90.93	+ 9.33
$Me_3SiO(HMeSiO)_nSiMe_3$	10	81.60	0

Suspensions of the two compounds in 2-methylpentane were tested in the injection apparatus. Neither compound was shown to inhibit the combustion of 2-methylpentane. Mixtures containing 2 vol% of these compounds in diethyl ether were tested in the injection apparatus at 450K. The ignition limits and the various other kinetic parameters associated with combustion were found to be unaffected by the presence of either additive, although it was thought that this might be due to the low volatilities of these two compounds (b.p. = 573K and 603K respectively, both at 0.13 kPa).

3.2.2.4 The effects of alkoxysilanes

The effects of some alkoxysilanes on the two-stage ignition limits of a 2-methylpentane-air mixture are shown in Table 3.6. The effects of compounds bearing three methoxy groups vary according to the nature of the alkyl or aryl groups bound to silicon. Phenyltrimethoxysilane appears to have the strongest inhibiting effect, but this is small compared with that observed with the closely related phenyltrimethylsilane, as shown in Table 3.4.

The compounds, trimethylmethoxysilane and trimethyl-tert-butoxysilane, were of special interest since an analogous organic compound, methyl-tert-butylether, is known to have a high resistance to knock and much attention has been paid to its use as a possible replacement for lead alkyls as an octane range extender. The results obtained were not, however, encouraging. Similarly, vinyldimethylcarbinoxydimethylsilane, a possible thermal source of the D_1 unit, dimethylsilanone, was shown to

TABLE 3.6

The effects of alkoxysilanes on the two-stage ignition limit of 2-methylpentane in air at 597K

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
None	-	81.60	-
$(MeO)_3SiMe$	5	84.00	+ 2.4
	10	85.32	+ 3.72
$(MeO)_3SiPh$	5	85.32	+ 3.72
	10	86.00	+ 4.40
$(MeO)_3Si\text{-}CH{=}CH_2$	5	79.73	- 1.87
	10	77.87	- 3.73
$(EtO)_4Si$	5	79.73	- 1.87
	10	79.73	- 1.87
Me_3SiOMe	5	83.47	+ 1.87
	10	83.47	+ 1.87

cont/....

TABLE 3.6 (cont.)

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
Me_3SiO^tBu	5	81.60	0
	10	85.33	+ 3.73
$Me(MeO)Si(O(CH_2)_2Ph)_2$	5	81.60	0
$Me(MeO)Si(OR)_2$*	5	77.87	- 3.73
$HMe_2SiOCMe_2CH=CH_2$	5	79.73	- 1.87
	10	83.47	+ 1.87

*R = $-CH_2-CH=CMe(CH_2)_2CH=CMe_2$

have a negligible effect on the limit at 597K, although the cool flame intensity was reduced by about 50% when the compound was present at a concentration of 10%. The remaining compounds were found to have no significant effect on any of the kinetic parameters accompanying the combustion of 2-methylpentane.

3.2.2.5 The effects of aryloxysilanes

The effects of various derivatives of phenoxytrimethylsilane on the ignition limits of a 2-methylpentane-air mixture are shown in Table 3.7. It can be seen that, although the parent compound displays only a minor inhibiting effect, the ring-substituted derivatives are quite potent inhibitors of combustion. Indeed, a 5% concentration of 3-methylphenoxytrimethylsilane increases the 2-methylpentane ignition limit by more than 10%. These compounds were not, however, found to affect significantly the kinetic parameters measured, although small increases in induction period and decreases in ΔP_{cf} were observed. Values of $(dp/dt)_{max}$ were found to be comparable with those of the pure fuel.

3.2.2.6 The effects of aliphatic nitrogen-containing organosilicon compounds

The effect of some nitrogen-containing organosilicon compounds on the ignition limits of 2-methylpentane are shown in Table 3.8. A variety of effects was observed. N,N'-bis(trimethylsilyl)-1,2-diaminoethane was found to increase the limits by 12.8 kPa (about 15%), whereas N-(trimethylsilylmethyl)dimethylamine decreases the limits by 14.93 kPa (about 18%). Measurements of induction periods revealed that many of

TABLE 3.7

The effects of aryloxysilanes on the two-stage ignition limit of 2-methylpentane in air at 597K

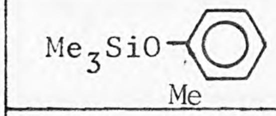
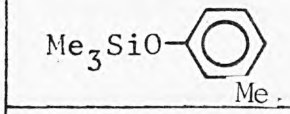
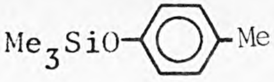
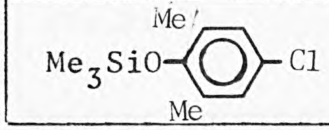
Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
None	-	81.60	-
Me_3SiOPh	5	83.47	+ 1.87
	10	85.33	+ 3.73
	5	85.33	+ 3.73
	10	88.93	+ 7.33
	5	90.93	+ 9.33
	10	92.93	+11.33
	5	89.07	+ 7.47
	10	92.67	+11.07
	5	87.20	+ 5.6
	10	92.93	+11.33

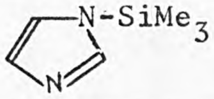
TABLE 3.8

The effects of nitrogen-containing organosilicon compounds on the two-stage ignition limit of 2-methylpentane in air at 597K

Additive	Concentration /vol. %	Two-stage ignition Limit /kPa	Change /kPa
None	-	81.60	-
$(Me_3Si)_2NH$	5	83.47	+ 1.87
	10	85.33	+ 3.73
Me_3SiNH^tBu	5	79.73	- 1.87
	10	79.73	- 1.87
$Me_3SiCH_2NMe_2$	5	70.67	-10.93
	10	66.67	-14.93
$Me_2Si(NMe_2)_2$	5	81.60	0
	10	81.60	0
$(Me_2SiNH)_3$	5	83.47	+ 1.87
	10	87.20	+ 5.60
Me_3SiNEt_2	5	76.00	- 5.60
	10	71.07	-10.53

cont/....

TABLE 3.8 (cont.)

Additive	Concentration /vol. %	Two-stage ignition Limit / Pa	Change / Pa
Me_3SiNH $(CH_2)_2$ Me_3SiNH	5	89.07	+ 7.47
	10	94.40	+12.80
	5	85.33	+ 3.73
	10	88.93	+ 7.33
$Me_3SiNHCONHSiMe_3$	5 wt.%	81.60	0
$(MeO)_3Si(CH_2)_3NH(CH_2)_2NH_2$	5	81.60	0

the compounds increase this parameter. N,N'-bis(trimethylsilyl)-1,2-diaminoethane lengthened the induction period by a factor of 3. This compound also decreased ΔP_{cf} by 30% and $(dp/dt)_{max}$ by 10% when present at a concentration of 10%. The remaining compounds also showed slight decreases in the cool flame intensity and in $(dp/dt)_{max}$.

3.2.2.7 The effects of silylated derivatives of aniline

The effects of various N-silylated derivatives of aniline are shown in Table 3.9. The parent compound, N-trimethylsilylaniline, was found to be the most powerful inhibitor of combustion tested during initial experiments, increasing the limits by about 50% when present at a concentration of 10% at 621K. Derivatives of toluidines were subsequently found to exhibit a greater effect, a 5% concentration increasing the limits by about 30% at 597K. The bis-(anilino)- compound exhibits an effect approximately twice as large as the parent compound. The remaining compounds in the study did not, however, have a strong influence on the combustion of 2-methylpentane.

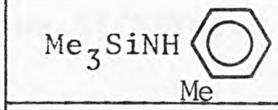
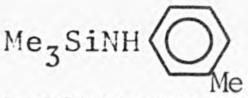
These compounds were found in general to increase the induction periods by up to 60% (observed with $Me_2Si(NHPh)_2$) and to decrease ΔP_{cf} by about 20%, and (dp/dt_{max}) by about 30%.

3.2.2.8 The effects of silylated aminophenols

The effects of silylated aminophenols on the two-stage ignition limits of 2-methylpentane in air are shown in Table 3.10. The di-silylated derivative of 4-aminophenol exhibits the largest inhibiting effect of

TABLE 3.9

The effects of silyl-derivatives of aniline on the two-stage ignition limit of 2-methylpentane in air

Additive	Temperature /K	Concentration /vol. %	Two-stage ignition Limit /kPa	Change /kPa
None	597	-	81.60	-
	621	-	72.40	-
$Me_3SiNHPh$	597	5	98.13	+16.53
		10	>110	>28.4
	621	5	99.87	+27.47
		10	>110	>37.6
	597	5	101.87	+20.27
		10	>110	>28.4
	597	5	101.87	+20.27
		10	>110	>28.4
	597	5	107.33	+25.73
		10	>110	>28.4

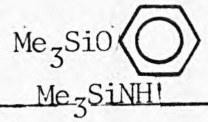
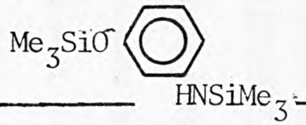
cont/....

TABLE 3.9 (cont.)

Additive	Temperature /K	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
$Me_3SiNMePh$	597	2	83.47	+ 1.87
		5	87.20	+ 5.6
		10	88.93	+ 7.33
$PhMe_2SiCH_2NHPh$	597	5	81.60	0
		10	83.47	+ 1.87
$Me_3SiCH_2NPh_2$	597	5	79.73	- 1.87
		10	79.73	- 1.87
$Me_2Si(NHPh)_2$	597	2	96.27	+14.67
		5	>110	>28.4
	621	2	88.93	+16.53
		5	>110	>37.6

TABLE 3.10

<u>The effects of silylated aminophenols on the two-stage ignition limit of 2-methylpentane in air at 597K</u>

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
None	-	81.60	-
	2	94.40	+12.80
	5	107.33	+25.73
	2	92.67	+11.07
	5	103.33	+21.73
	2	102.00	+20.4
	5	>110	>28.4

the compounds studied; a 2 vol% addition increases the two-stage ignition limit by 25%. The derivative of 2-aminophenol (present at a concentration of 5 vol%) doubles the induction period, reduces the cool flame intensity by about 25% and approximately halves $(dp/dt)_{max}$. The other derivatives have slightly more pronounced effects on the kinetic parameters accompanying combustion (Table 3.11).

3.2.2.9 Effects of other organosilicon compounds

Various other organosilicon compounds were tested in this study, and their effects on the two-stage ignition limit of 2-methylpentane are shown in Table 3.12. This table shows that, among the compounds used, only two exhibit a significant effect. BSTFA increases the ignition limits by about 9% when added at a concentration of 10 vol%. In contrast, the sulphur-containing compound, $(MeO)_3\,Si(CH_2)_3SH$ appears to promote combustion to a similar extent when present at 5 vol%. No significant or systematic variation in the other kinetic parameters was observed on addition of any of the compounds listed in Table 3.12.

3.2.2.10 The effects of some organosilicon compounds on the combustion of 2-methylpentane at 678K

Table 3.13 shows the results obtained when a selection of organosilicon compounds were added to 2-methylpentane and oxidised at 678K in air. These results show that the increase in temperature does not markedly affect the reactivity of this selection of compounds. Similarly, measurements of the kinetic parameters did not reveal significant changes from those of the pure fuel. This study was undertaken in the

TABLE 3.11

The effects of silylated aminophenols on the kinetic parameters accompanying the combustion of 2-methylpentane in air at 573K (kPa = 73kPa).

ADDITIVE	CONC. /vol %	TWO-STAGE IGNITION LIMIT /kPa	CHANGE /kPa	INDUCTION PERIOD, τ /S	ΔP_{cf} /kPa	$(dp/dt)_{max}$ /kPa s^{-1}
NONE	—	74.3	—	3.0	50.3	19.9
o-$Me_3SiNHC_6H_4OSiMe_3$	5	100.0	+25.7	6.0	37.6	10.5
m-$Me_3SiNHC_6H_4OSiMe_3$	5	96.0	+21.7	5.2	39.0	12.2
p-$Me_3SiNHC_6H_4OSiMe_3$	2	94.7	+20.4	5.6	38.0	12.6
	5	>110	>35.7	7.7	32.0	7.7

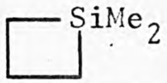
TABLE 3.12

The effects of some other organosilicon compounds on the two-stage ignition limit of 2-methylpentane in air at 597K

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
None	-	81.60	-
Me_3SiCl	5	83.47	+ 1.87
Me_3SiCH_2Cl	5	79.73	- 1.87
$Me_3SiCHCl_2$	5	79.73	- 1.87
$Me(MeO)_2Si(CH_2)_3Cl$	5	81.60	0
$(MeO)_3Si(CH_2)_3Cl$	5	79.73	- 1.87
Me_2SiCl_2	5	81.60	0
Ph_2SiCl_2	5	81.60	0
Me_3SiI	5	83.47	+ 1.87
$(MeO)_3Si(CH_2)_3SH$	5	74.27	- 7.33
$CF_3CON(SiMe_3)_2$ BSTFA	5	86.00	+ 4.40
	10	88.93	+ 7.33
$(Ph_3Si)_2$ Hg	1.0	81.60	0
	2.0	83.47	+ 1.87

TABLE 3.13

The effects of some organosilicon compounds on the two-stage ignition limit of 2-methylpentane in air at 678K

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
None	-	68.67	-
	5	66.80	- 1.87
	10	64.94	- 3.73
$Me_3SiSiMe_3$	5	68.67	0
	10	68.67	0
$HMe_2SiOCMe_2CH=CH_2$	5	68.67	0
	10	68.67	0
$(Me_2SiO)_3$ D_3	5	70.54	+ 1.87
	10	73.34	+ 4.67
$(Me_2SiO)_4$ D_4	5	70.54	+ 1.87
	10	72.40	+ 3.73

cont/....

TABLE 3.13 (cont.)

Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
$(Me_2SiO)_5$	5	70.54	+ 1.87
	10	72.40	+ 3.73
$Me_3SiO(HMeSiO)_nSiMe_3$	5	68.67	0
	10	70.54	+ 1.87

hope that, at higher temperatures, various transient species might be generated from the organosilicon compounds. These species are known to be generated pyrolytically at temperatures greater than 670K.

3.3 THE EFFECTS OF NON-SILICON-CONTAINING ADDITIVES ON THE COMBUSTION OF 2-METHYLPENTANE

3.3.1 Introduction

The effects of a selection of non- silicon-containing compounds on the combustion of 2-methylpentane were measured in the injection apparatus, in an effort to correlate the measurement of ignition limits in the laboratory, with the antiknock properties of additives, and to quantify the effects observed with organosilicon compounds.

3.3.2 The effects of tetraethyllead and the use of lead monoxide-coated vessels

Studies were made of the combustion of 5 vol% and 10 vol% mixtures of tetraethyllead in 2-methylpentane in oxygen at 580K. In both cases, irreproducible effects were observed. The initial injection of a 10 vol% TEL mixture showed a marked inhibiting effect. Slow combustion was observed at pressures normally associated with two-stage ignition for the pure fuel. Repeated injections led to rapid single-stage ignition. Reproducible results were unobtainable at either concentration. Although the 5 vol% mixture consistently inhibited combustion, the 10 vol% mixture appeared usually to promote the reaction. Furthermore, subsequent injections of pure fuel led to slow combustion, as a result of the deposition of PbO on the vessel walls. Mixtures containing lower concentrations of tetraethyllead were injected into the apparatus, following the washing of the vessel with nitric acid. A 0.1 vol% mixture did not affect the ignition limits of 2-methylpentane, but was found to double the induction period and decrease the number of cool flames at an initial pressure of 26.67 kPa from three to two. 0.5 and 1.0 vol% mixtures were found, however, to inhibit the combustion of 2-methylpentane to the extent that neither ignition nor cool flames were observed, even at pressures above those used previously. Injections of pure fuel during these experiments showed that the two-stage ignition limit had remained constant, and, that deposition of PbO on the vessel walls had therefore not occurred to any significant extent.

Subsequent experiments were performed in PbO-coated vessels to investigate the possibility that there might be some synergistic effect between lead and silicon in the inhibition of combustion. The wall-coating increased the two-stage ignition limit of 2-methylpentane by about 10 kPa, the induction period was approximately trebled, and the cool flame intensity was greatly reduced, although this was variable at a given initial pressure so that $(dp/dt)_{max}$ was not measured.

Initial experiments with organosilicon compounds in concentrations of 1.0 vol% showed an elimination of the effect of the PbO surface, although the coating still raised the limits for the pure fuel. Subsequent results suggested that the compounds Me_3SiNH^tBu and Ph_3SiH did, in fact, show indications of synergism, but these effects were not sufficiently reproducible to confirm this conclusion.

3.3.3 The effects of some organic additives

The two-stage ignition limit of 2-methylpentane was measured in the presence of low concentrations of some organic compounds, the antiknock properties of which are well established. The changes in ignition limits are listed in Table 3.14. The results obtained correlate well with the expected antiknock behaviour of the compounds used, and it was possible to distinguish between the large effects of true antiknock compounds, such as aromatic amines, and the smaller effects of blending agents and octane range extenders, such as toluene and methyl tert-butyl ether. The proknock effect due to the addition of a small concentration of heptane to 2-methylpentane was also demonstrated.

TABLE 3.14

The effects of some organic compounds on the two-stage ignition limit of 2-methylpentane at 597K

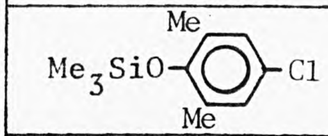
Additive	Concentration /vol. %	Two-stage ignition limit /kPa	Change /kPa
None	-	81.60	-
Heptane	5	76.00	- 5.60
	10	73.33	- 8.27
Toluene	5	85.33	+ 3.73
	10	87.20	+ 5.60
Methyl-tert-butyl ether	5	85.33	+ 3.73
	10	92.80	+11.20
Aniline	~10	>110	>28.4
N-methylaniline	2	98.13	+16.53
	5	>110	>28.4
o-toluidine	2	98.13	+16.53
m-toluidine	2	101.60	+20.00
p-toluidine	2 wt.%	100.67	+19.07

3.4 ENGINE COMBUSTION

Initial engine tests were undertaken on a selection of organosilicon compounds in low concentrations (up to 0.1 vol%) in isooctane. The levels of knock recorded were found to vary with time, but, in general, most of the compounds exerted proknock effects. Subsequent engine experiments were performed with slightly higher concentrations of additive (up to 0.75 vol%) in a 9:1 mixture of isooctane and heptane. The RON values measured are shown in Table 3.15 and were found, in some cases, to be comparable with the shifts in ignition limits observed in the laboratory, the largest antiknock effects being obtained with N-trimethylsilylaniline and the ring-substituted phenoxytrimethylsilane. The RON values measured for some of the organosilicon compounds did not, however, correlate with the laboratory results. In particular, the compounds, $(MeO)_3Si(CH_2)_3SH$ and $Me_3SiCH_2NMe_2$, which markedly decreased the ignition limits of 2-methylpentane in the injection apparatus, were shown to exert an antiknock effect in the engine experiments. Measurements of knockmeter reading made with the base fuel throughout the engine tests showed large variations, and consequently, the knockmeter required frequent recalibration. In these experiments, the knockmeter values varied with time. Inspection of the spark-plug showed extensive deposition of a white solid which was presumably silica. In a previous study, the extent of silica deposition was such that the engine had stopped igniting altogether. Thus, engine tests, involving organosilicon compounds on their own, cannot be taken as a true measure of their tendency to inhibit spontaneous ignition.

TABLE 3.15

The effects of organosilicon compounds on RON

Additive	Concentration /vol. %	Knockmeter Reading	RON	ΔRON
None (initial calibration)	-	55	90.0	-
Me_3SiCH_2Cl	0.5	69	89.2	- 0.8
$(Me_3Si)_2NH$	0.5	71	88.8	- 1.2
Me_3SiNH^tBu	0.5	62	90.2	+ 0.2
$PhSi(OMe)_3$	0.25	72	90.75	+ 0.75
	0.5	60	90.5	+ 0.5
	0.75	73	90.7	+ 0.7
$(MeO)_3Si(CH_2)_3SH$	0.5	61	90.2	+ 0.2
$Me_3SiCH_2NMe_2$	0.5	57	90.6	+ 0.6
$Me_3SiNHPh$	0.1	75	90.4	+ 0.4
	0.2	54	90.8	+ 0.8
	0.1	78	90.1	+ 0.1
	0.3	53	90.9	+ 0.9
Me_3SiCl	0.5	76	90.3	+ 0.3
$Me_3SiCHCl_2$	0.5	80	89.9	- 0.1

Base fuel : isooctane 90%
heptane 10%

Further engine measurements were made on fuel mixtures containing the organic additives, methyl-tert-butyl ether, aniline and N-methylaniline. The RON values obtained are shown in Table 3.16, and these were found to correlate adequately with the shifts in ignition limits determined in the laboratory (Table 3.14). Both engine and laboratory experiments showed that N-methylaniline has about ten times the effect of methyl-tert-butyl ether.

TABLE 3.16

Engine tests on MTBE, aniline and N-methylaniline

Additive	Concentration /vol. %	RON	ΔRON
None	-	87.4	-
Methyl-tert-butyl ether	0.84	88.0	0.6
	4.20	89.1	1.7
	8.40	91.6	4.2
Aniline	0.84	91.1	3.7
	4.20	100	12.6
	8.40	101.5 (approx)	~14.1
N-methylaniline	0.84	92.0	4.6

Base fuel : Isooctane 64.4%
Heptane 22.0%
Toluene 13.6%

DISCUSSION

4.1 INTRODUCTION

The results obtained from the laboratory study of the influence of a wide range of organosilicon compounds on the combustion of 2-methylpentane show a variety of effects. These effects have been shown to be a good measure of the antiknock properties of these compounds by the experiments performed with purely organic additives both in the laboratory and in a CFR engine. Furthermore, the results found in the injection apparatus have been shown to be in good agreement with those obtained in the more conventional premix systems used in previous combustion experiments (Cullis, Hirschler and Rogers, 1981). An apparatus of this type facilitates the study of the combustion of fuels of high reactivity and low volatility and was thus particularly suited to the current investigation. The ignition profile and kinetic parameters obtained for 2-methylpentane show good correlations with those derived from previous studies (Fish, 1968).

The study of the combustion of 2-methylpentane/oxygen mixtures in the presence of additives in the injection apparatus demonstrated only very small effects on the ignition limits and other kinetic parameters. It was thought that this might be due to the rapid and complete oxidation of the organosilicon compounds on injection into an oxygen atmosphere, preventing their involvement, in their original state, in the overall combustion of the hydrocarbon. Thus, in order to dilute this oxygen, air was used as the oxidant in all subsequent experiments. The ignition profile for 2-methylpentane in air showed the same characteristics as the profile obtained when oxygen was used, although the temperature range was found to be slightly higher. It was thought that the replacement of oxygen by air might make the conditions of the laboratory experiments somewhat more representative of those experienced in an engine and that the behaviour of the organosilicon compounds under these conditions might be a better indication of their antiknock properties.

The testing of organosilicon compounds in a C.F.R. engine was found not to provide an accurate measure of their potential antiknock effectiveness (Table 3.15). Although the results obtained from initial engine tests encouraged the further investigation of these compounds in engine and laboratory studies, the initial laboratory experiments yielded results which did not reproduce those found in the engine. Further engine tests were able to demonstrate some of the general trends in the antiknock properties of a group of the compounds, but in some cases, compounds that were expected to be proknock from the laboratory studies actually behaved as antiknocks in the engine. Knock-meter readings were found to vary dramatically as time progressed during the testing of these compounds, and frequent recalibration was required. Subsequent examination of spark-plugs and engine-cylinder showed that extensive deposition of a white solid,probably silica,had occurred during the runs to the extent that sparking of the fuel-air mixture may have been prevented. Subsequent testing of organic antiknock additives in a CFR engine and in the laboratory apparatus demonstrated a definite correlation between shift in ignition limits and RON (Tables 4.1 and 4.2). Thus, further engine experiments with organosilicon compounds were not

TABLE 4.1

Correlation between ignition limits and RON for isooctane-heptane mixtures

MIXTURE	IGNITION LIMITS/kPa	RON
80/20 Isooctane-heptane	> 110	80
70/30 Isooctane-heptane	92.53	70
60/40 Isooctane-heptane	81.60	60
50/50 Isooctane-heptane	76.00	50
40/60 Isooctane-heptane	65.33	40
Heptane	48.53	0

TABLE 4.2 Correlation between ignition limits and RON for some organic additives

ADDITIVE	CONC. / vol %	ΔRON	Δ IGNITION LIMITS / kPa
Methyl-tert-butyl ether	1	0.71	0
	5	2.02	3.73
	10	5.00	11.20
Aniline	1	4.40	–
	5	15.00	–
	10	∿ 16.80	> 28.4
N-methylaniline	1	5.48	+ 5.6
	2	—	16.53
	5	—	> 28.4

undertaken, and the antiknock properties of these compounds were gauged from the results obtained in the injection system. A programme of research into the possibility of the scavenging of silica deposits to facilitate further engine tests, was not undertaken in view of the relatively small inhibiting effects observed with the majority of the organosilicon compounds tested in this study.

The following sections discuss the effects observed in the laboratory experiments with the organosilicon compounds. An attempt is made to correlate the antiknock or proknock activity with molecular structure and other properties arising from the presence of silicon atoms. Where possible, analogies are also drawn with organic compounds of similar structure.

4.2 THE EFFECTS OF SILANES AND DERIVATIVES THEREOF

Simple alkylsilanes were found, in general, to exert little or no effect on the two-stage ignition limits of 2-methylpentane in air (Table 3.4). Tetraethylsilane did not alter the limits at all, and tetramethylsilane was found to have a small inhibiting effect on combustion when present in a concentration of 10 vol% triethylsilane, Et_3SiH, showed no effect on the ignition limits but lengthened the induction period preceding the cool flame by a factor of two. This doubling of the induction period was also observed with other silanes containing hydrogen. The largest shifts in limits were observed with silanes containing aromatic groups, although these effects could be detected only when the silane was present in a concentration of 10 vol%. Hexamethyldisilane, and the cyclic compound, 1,1-dimethyl-1-silacyclobutane promoted the reaction.

The small favourable effect exhibited by tetramethylsilane can be explained by its molecular structure which is analogous to that of 2, 2-dimethylpropane (neopentane) in that both compounds contain only primary hydrogen atoms and are, therefore, relatively resistant to oxidation. Thus, tetramethylsilane exerts an effect which is not anti-knock in the same way as its lead analogue, TML. In contrast, this tetraalkylsilane exerts a rather similar influence to that of organic additives, such as methyltert-butyl ether, which function as extenders and are fuels of high octane quality when used in isolation.

An increase in the size of the alkyl substituents would be expected to counteract this effect as the molecule becomes more "hydrocarbon-like" in character. This is indeed found to be the case with tetraethylsilane, which contains both primary and secondary hydrogen atoms, and thus does not affect either the two-stage ignition limits or the other kinetic parameters associated with the combustion of 2-methylpentane.

The lengthening of induction periods observed with the (Si—H)-containing silanes may be due to the generation of the relatively stable silyl radicals by hydrogen abstraction, although these are probably not present in sufficient concentration to inhibit the overall reaction to the extent of causing a measurable change in the ignition limits. Thus, triethylsilane is found to retard the reaction, to decrease ΔP_{cf} by about 1 kPa, but to have no effect on the ignition limits of 2-methylpentane. This, in itself, may be a useful antiknock property. Triphenylsilane, when present at a concentration of 10 wt%, exerts the same effect on the induction period as Et_3SiH, but, in addition, raises the ignition limits by about 10%. This is thought to be due to the added stability of the triphenylsilyl radical compared with that of the triethylsilyl radical. In addition, the hydrogen atom is more easily abstracted from Ph_3SiH than from Et_3SiH as a result either of the slight resonance stabilization of the $Ph_3Si^{\cdot}$ radical, or of the different inductive influences of the ethyl and phenyl groups which will alter the relative strengths of the Si—H bonds (Curtice et al., 1957). Experiments with the silyl mercurial compound, $(Ph_3Si)_2Hg$, were undertaken to confirm the effect of the triphenylsilyl radical.

Bis(triphenylsilyl)mercury is a convenient source of triphenylsilyl radicals in pyrolysis experiments (Jackson, 1966). Furthermore, the by-product of the pyrolysis of $(Ph_3Si)_2Hg$ is elemental mercury, which does not exert any well-defined effect on combustion either in its own right, or as the oxide (Cramer and Campbell, 1949). The lack of solubility in 2-methylpentane, however, limited the study of this compound to low concentrations. A small raising of the ignition limit viz. by 1.87 kPa, was observed with a 2% addition of $(Ph_3Si)_2Hg$, suggesting that triphenylsilyl radicals may, indeed, exert an antiknock effect. There is some doubt, however, as to the likelihood that triphenylsilyl radicals are formed at all from $(Ph_3Si)_2Hg$ under the oxidising conditions of the combustion process.

In common with other (Si-H)-containing silanes, benzyldimethylsilane and bis 1,4-(dimethylsilyl)benzene increase the induction preceding the cool flame, but neither compound exerts a large effect on the ignition limits. The radicals formed by the abstraction of hydrogen would be stable compared with the triethylsilyl radical, but not with the triphenylsilyl radical, accounting for the small effects observed.

Hexamethyldisilane, which decomposes thermally to yield trimethylsilyl radicals (Davidson and Howard, 1975), shows a marked proknock effect under the experimental conditions normally used in this work (<600 K), but no effect at higher temperatures (Table 3.13). The ability of these compounds to inhibit the combustion of 2-methylpentane thus seems to correlate with the stability of the triorganosilyl radicals formed during the reaction.

The largest proknock effect observed within this group of compounds was that due to the addition of 10 vol% of 1,1-dimethyl-1-silacyclobutane to 2-methylpentane (a shift of 9.07 kPa). This organosilicon compound is known to eliminate ethene at high temperatures with the formation of the transient species 1,1-dimethylsilaethene, $Me_2Si{=}CH_2$. Previous experiments on the pyrolysis of 1,1-dimethyl-1-silacyclobutane at low pressures have shown that $Me_2Si{=}CH_2$ is formed at temperatures above 670K. The combustion experiments performed at 573K in an oxidising environment may not, therefore, involve 1,1-dimethylsilaethene and the proknock effect may be due solely to the instability of the silacyclobutane ring system. At higher temperatures (678K), the proknock effect of this compound was reduced considerably. This may be due to the involvement of the unstable unsaturated silicon moiety. It is more likely, however, that under the more stringent conditions involved in the high-temperature study, additives become less important since the reaction occurs over a much shorter period. The decreased influence of additives seems to be of general occurrence in all the experiments performed in this work at 678K.

The large antiknock effect exerted by phenyltrimethylsilane can be attributed to the presence of the aromatic ring and the inductive (+I) effect of the trimethylsilyl group (relative to that of the hydrogen) attached to the benzene ring, which increases the electron density on the ring. The compound exerts almost twice the effect of toluene on the ignition limits of 2-methylpentane, since the inductive effect of the methyl group is smaller than that of trimethylsilyl. The replacement of the methyl groups on silicon by the more electronegative methoxy groups reduces the inductive effect of the silyl group and thus phenyltrimethoxysilane has a smaller effect on the ignition limits of 2-methylpentane. Similarly, the weaker activating groups HMe_2Si- in the compounds, 1,4-bis(dimethylsilyl)benzene and benzyldimethylsilane, exert only a very small effect on the overall combustion process. Halogenated silane derivatives exhibited only minor effects on the combustion of 2-methylpentane (Table 3.12). Compounds containing Si—Cl bonds, viz. Me_3SiCl, Me_2SiCl_2 and Ph_2SiCl_2, showed negligible effects on the parameters measured apart from a shift in ignition limits of 1.87 kPa due to Me_3SiCl. The same effect was observed with Me_3SiI. This last result is somewhat surprising in view of the anti-knock properties of iodine itself, the inhibiting effect of which may be somewhat counteracted by the promotion due to the presence of trimethylsilyl radicals. The absence of any effect of the dichlorosilanes lies in the lability of chlorine in the Si—Cl bonds and their reactivity towards oxygen-containing species with the ready formation of inert, involatile polymeric materials.

Alkyl-substituted silanes promote the reaction to a very small extent. Neither the length of the alkyl chain nor the number of chlorine atoms bound to the carbon seem to effect the magnitude of the promoting influence.

4.3 THE EFFECTS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

During the present work, studies were made of the effects of a wide variety of compounds containing Si—O bonds on the combustion of 2-methylpentane. The simple siloxane, hexamethyldisiloxane, exerted no effect on the combustion process (Table 3.5). This is consistent with the general chemical inertness of this compound and of the larger members of the siloxane series, which are, in general, quite resistant to oxidation. Tetramethyldisiloxane, on the other hand, exhibits a small promoting effect. This is due to the presence of Si—H bonds in the compound, these hydrogen atoms being abstracted more readily than those of the primary C—H bonds present in $(Me_3Si)_2O$. The resulting radicals may then participate in the propagation steps involved in the combustion of the hydrocarbon. The corresponding siloxane oligomer - $Me_3SiO(HMeSiO)_nSiMe_3$ (when $n < 30$) did not show any effect, but this was probably due to lack of volatility rather than to any latent chemical inertness. The cyclic siloxane oligomers containing up to six units are of greatest interest, since the pyrolysis, and to some extent the oxidation, of some of the members of the series has received much attention (Davidson et al., 1971, 1975, 1976). These compounds are used as convenient models in the study of the oxidation and thermal degradation of silicone polymers.

During the early stages of the present study, a mixture containing hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5) in the ratio of 1:8:1, was found to be one of the more effective additives tested up to that time.

Technical-grade samples of each oligomer were obtained in order to investigate the effects of each compound in isolation, in the hope that the inhibition caused by the mixture might be due to one of the minor components, D_3 or D_5. The results show that the most effective combustion inhibitor was the pentamer, D_5, and that the major component, D_4, exerted a slightly smaller effect than the original mixture. The cyclic siloxanes are known to undergo thermal degradation via the elimination of the D_1 unit, dimethylsilanone ($Me_2Si{=}O$). Studies of the pyrolysis of octamethylcyclotetrasiloxane (D_4) have demonstrated that this species is, indeed, eliminated at temperatures above 700K, and the products include D_3, D_5 and small amounts of the larger oligomer D_6, which itself undergoes thermal decomposition to yield two D_3 molecules. This shows the ability of the D_1 unit to insert into Si—O bonds, the most conspicuous reaction of this species. Evidence has also been found for the cycloaddition of D_1 to alkenes, although neither the resulting silaoxetan nor other adducts have been identified. It was thought that this species, if generated, might react with and destroy chain-propagating species, such as $\cdot OH$ and $HO_2\cdot$ radicals, and thus inhibit combustion. The increased effect observed with D_5 compared with that of D_4 seems to support this hypothesis, in that the D_5 molecule undergoes thermal degradation to yield a possible two D_1 units and a D_3 molecule, while D_4 can only yield one. In addition, it is unlikely that the D_3 molecule eliminates D_1 units due to the instability of the four-membered ring system (D_2) formed in doing so. In keeping with this, D_3 exerts only a small favourable effect on the ignition limits at a concentration of 10 vol%, which is probably due to its resistance to oxidation rather than to the involvement of chain-terminating species in the combustion of 2-methylpentane. Experiments were also performed with these compounds at a higher temperature viz. 678K, in an attempt to facilitate the generation of dimethylsilanone. In this study, D_3 appeared to exert the largest effect on the ignition limits (Table 3.13). Again, this is probably due to an inherent resistance to oxidation, since the generation and involvement of transient species over the time-scale of the hydrocarbon-oxygen reaction at this temperature seems unlikely.

Another, more facile, source of dimethylsilanone is vinyldimethylcarbinoxydimethylsilane (Lane and Frye, 1979). The influence of this compound on the combustion of 2-methylpentane was studied at 597 and 678K but no significant effects on the ignition limits were observed (Tables 3.6 and 3.13). The cool-flame intensity (ΔP_{cf}) was, however, reduced by about 50% when 10 vol% of the additive was present. This was also the case with the cyclic siloxanes, D_3, D_4 and D_5. This suggests that dimethylsilanone, if generated under the experimental conditions used, exerts its inhibiting effect during the early stages of the combustion process, and may be destroyed during the passage of the cool flame. In contrast to this, the extent of the influence of tetraethyllead on the cool flame is only small. During the passage of the cool flame, however, TEL decomposes to form a fog of PbO particles; this fog suppresses the subsequent reactions which would otherwise culminate in ignition. Many organic antiknock additives exert their effect as unchanged molecules and thus also inhibit the reactions leading to, and occurring within, the cool flame. It is thought that the dimethylsilanone species may be formed prior to the cool flame, and this would account for the decrease in ΔP_{cf} and the lengthening of the induction periods. This species may then undergo decomposition during the passage of the cool flame to yield inactive products, reflected in the small shifts in ignition limits observed.

The results obtained from the study of the effects of alkoxysilanes on hydrocarbon combustion (Table 3.6) again show only small shifts in ignition limits and exert no significant effect on the associated kinetic parameters. The replacement of methyl groups by methoxy groups in simple organosilicon compounds does not appear to have a profound effect on the antiknock activity. Methyltrimethoxysilane exerted a slightly larger effect on the ignition limits than tetramethylsilane. This may again be due to an inherent resistance to oxidation by virtue of the presence of only primary hydrogen atoms, and to the decrease in the affinity of silicon for oxygen resulting from the presence of the three methoxy groups. The reactivity of other compounds bearing three such groups, varied according to the nature of the fourth substitutent bound to silicon (Table 3.6). Phenyltrimethoxysilane exhibited the most pronounced positive effect on the ignition limits. However, as previously discussed, this effect was small compared with that of phenyltrimethylsilane as a result of the smaller inductive (+I) effect of $(MeO)_3Si$- compared with that of the Me_3Si- group. Vinyltrimethoxysilane,on the other hand, promoted combustion. This compound is, indeed, very susceptible to oxidation as exemplified by its low flashpoint (296K). 3-Chloropropyltrimethoxysilane exhibited a small proknock effect (Table 3.12) but this was not observed with a similar compound in which one methoxy group was replaced by a methyl group. This suggests that, in general, trimethoxysilanes exert less favourable effects on combustion than the corresponding alkylsilanes. Indeed, tetraethoxysilane was found to promote combustion to a small extent, whereas tetraethylsilane showed no effect. A large proknock effect was observed with the sulphur-containing compound, $(MeO)_3Si(CH_2)_3SH$, but the significance of the presence of silicon in contributing to this effect is doubtful in view of the well-documented promoting behaviour of organosulphur compounds on hydrocarbon combustion (Cullis, Hirschler and Okorodudu, 1982).

The compounds, methoxytrimethylsilane and tert-butoxy-trimethylsilane, were of special interest in that they have a close structural similarity to methyl-tert-butyl ether (MTBE). MTBE has recently received much attention because it has been proposed as a possible substitute for lead alkyls. The octane-extending properties of MTBE lie in its resistance to oxidation (Baronnet et al., 1981). Initial attack by oxygen involves abstraction of a primary hydrogen atom to yield the radical $^{t}Bu{-}O{-}CH_2^{\cdot}$, hydrogen atoms in the O-methyl group being activated by their proximity to oxygen relative to their counterparts in the tert-butyl group. Although oxygen addition to form the peroxy species $^{t}Bu{-}O{-}CH_2O{-}O\cdot$, probably occurs, further reactions (i.e. isomerization) would not be energetically favourable since they would involve the formation of a seven-membered ring transition state and the intramolecular abstraction of a primary hydrogen atom. Far more likely is the breakdown of the $^{t}BuOCH_2\cdot$ radical to form formaldehyde and the tert-butyl radical. Further reactions of the tert-butyl radical produce only relatively unreactive products such as isobutene and $HO_2\cdot$ radicals.

The co-generation of these species from MTBE during the combustion of a hydrocarbon fuel would be expected to decrease the overall rate of reaction. Thus, the antiknock property of MTBE lies in its low overall oxidizability rather than to any destruction of chain-propagating species.

The effects of the silicon analogues of MTBE on the combustion of 2-methylpentane (Table 3.6) were found to be less pronounced than that of the ether itself (Table (3.14), although both compounds raised the ignition limits to a small extent. This suggests that a change in the oxidation mechanism may occur due to the presence of silicon in the compound. The initial point of attack during the oxidation of MTBE is the methyl group bound to oxygen, since the C—H bonds in this group are weakened by the inductive effect of the oxygen atom. However, the enhanced induction due to the presence of a trimethylsilyl group, compared with a tert-butyl group adjacent to the oxygen atom, may counteract this activation to the extent that oxygen attack occurs at the methyl groups bound to silicon; this can be attributed either to an inductive weakening of the C—H bonds in these groups by silicon or simply to statistical considerations. This in itself will increase the susceptibility of these compounds to oxidation. The possibility also now exists that the initially formed radicals may peroxidise and undergo isomerization reactions via energetically-favoured six-membered ring transition states. The small effects observed with these compounds thus arise from the difficulty of the initial abstraction of a primary hydrogen atom from the parent molecule. Further reaction of the resultant species is thus facilitated, relative to the case of MTBE, by the presence of the silicon atom.

The effects observed with the remaining alkoxysilanes in this study can be explained in terms of the degree of susceptibility towards oxidation of the larger side-chains bound to silicon. In the case of the long-chain diolefinic compound, this manifests itself as a small proknock effect, whereas the compound containing aromatic side-chains does not affect the ignition limits.

Among the oxygen-containing organosilicon compounds studied in the laboratory, the largest effects were observed with derivatives of phenoxytrimethylsilane (Table 3.7). The parent compound did not, however, raise the ignition limits to a great extent. Replacement of hydrogen atoms attached to the benzene ring by electron-donating substituents, such as methyl, improved the inhibiting properties of these compounds. The shifts in ignition limits were particularly pronounced with the 3-(meta) and 4-(para) methyl derivatives, and with 2,6-dimethyl-4-chlorophenoxytrimethylsilane. These effects can be explained in terms of the influence of induction and resonance on the electron density of the aromatic nucleus as a result of the presence of the substituents on the ring.

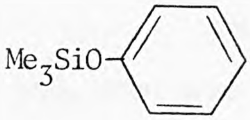
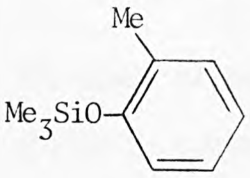
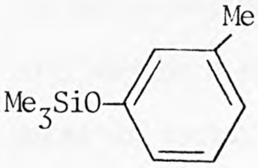
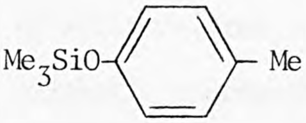
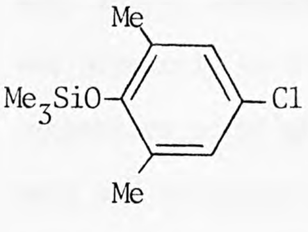
The small effect of the parent compound, phenoxytrimethylsilane, compared with phenyltrimethylsilane, arises from an increased electron density on the benzene ring due to a positive (+R) resonance effect, which is counteracted, to some extent, by a negative (-I) inductive effect (Table 4.3). The substitution of a methyl group for a ring hydrogen atom increases the electron density on the ring by an inductive (+I) effect. In the meta position, this is also increased by a resonance

(+R) effect, which increases the electron density on the 2,4 and 6 positions. In the para and ortho positions, however, the methyl group donates electrons by a (+R) resonance effect to the 1,3, and 5 positions, i.e. to the carbon atom adjacent to the $OSiMe_3$ group. This correlates well with the order of antiknock activity observed in the laboratory with these compounds, the ortho- derivative exerting a smaller effect than the para- compound due to the involvement of steric factors. The highly substituted derivative influences combustion to the same extent as meta-methylphenoxytrimethylsilane as a result of a combination of inductive and resonance effects. The methyl groups exert (+I) inductive and (-R) resonance effects in the ortho positions, whereas the para- chlorine atom has a negative (-I) inductive effect counteracted by a positive (+R) resonance effect. The relative magnitudes of these effects are such that the resulting electron density on the ring is increased (Table 4.3).

The antiknock properties thus seem to depend largely on the electron density on the benzene nucleus, which is in accord with previous theories of the action of other aromatic combustion inhibitors (Chamberlain and Walsh, 1949).

TABLE 4.3

The effect of the presence and position of ring-substituents on the inhibiting effects of derivatives of phenoxytrimethylsilane[a]

	INDUCTIVE (I)	RESONANCE (R)	Δ IGNITION LIMIT/KPa
	(-I)	(+R)	+ 2
	(-I) + I	(+R) - R	+ 4
	(-I) + I	(+R) + R	+ 9
	(+I) + I	(+R) - R	+ 7
	(-I) +I,+I,-I	(+R) +R,+R,+R	+ 9

[a] T: 597K; conc. additive: 5 vol%

4.4 THE EFFECTS OF NITROGEN-CONTAINING ORGANOSILICON COMPOUNDS

Nitrogen-containing organosilicon compounds gave rise to the most pronounced inhibiting and promoting effects on hydrocarbon combustion that were observed during this study. The trends in the ability of these compounds to inhibit combustion were found, in general, to parallel those reported for purely organic amines (Cullis and Khokar, 1960; Tipper and Titchard, 1971), i.e.

secondary > tertiary > primary

and, even more pronounced :

aromatic > aliphatic

The study of the combustion of 2-methylpentane in the presence of aliphatic N- containing organosilicon compounds was confined to simple, low molecular weight compounds (Table 3.8). Thus, the observed activity may be a result of the presence of either the silicon or nitrogen atoms in isolation, or due to some combined effect of the two. With purely organic amines, the inhibiting efficiency is believed to be directly related to the presence of the nitrogen atom, since other aliphatic compounds do not show similar properties (Cullis and Waddington, 1957), whereas purely organic aromatic amines exert their effects due primarily to the presence of the aromatic ring. The antiknock properties of aliphatic amines depend, therefore, in the case of primary and secondary amines, on the ease of hydrogen abstraction from nitrogen and on the stability of the resulting radical, $R_2N\cdot$; with tertiary amines, the antiknock activity is related to the ability to form radical complexes with chain-propagating species such as $\cdot OH$ radicals by the involvement of the lone pair of electrons on nitrogen. The presence of silicon in an amine may thus have a strong influence on these factors.

Studies of the effect of silicon-containing primary amines were restricted to the compound $(MeO)_3Si(CH_2)_3\,NH(CH_2)_2NH_2$, as a result of the tendency of compounds such as Me_3SiNH_2 to condense to form disilazanes. This is an analogous reaction to that found with silanols, which condense to form siloxanes. The stability of aminosilanes appears to be even lower than that of silanols, and therefore, the tendency to condense appears to be greater for N-containing than for O-containing silanes. The compound tested exhibited no significant effect on the ignition limits. This may be due to its low volatility or to competing promoting and inhibiting effects exerted by the primary and secondary amine groups within the structure respectively. The silicon atom in this compound is too distant from the amine groups to influence their antiknock properties.

A variety of effects was observed with organosilicon compounds containing secondary amine groups. Hexamethyldisilazane, HMDS, exerted only a small favourable effect on the ignition limits, whereas the closely related compound, Me_3SiNH^tBu, appeared to promote combustion. These compounds are analogues of the oxygen-containing compounds, $(Me_3Si)_2O$ and $Me_3Si\,O^tBu$, neither of which was found to have a strong influence on hydrocarbon combustion, as a consequence of the absence of secondary and tertiary hydrogen atoms. However, radicals resulting from the abstraction of hydrogen from nitrogen in these amino compounds would be relatively stable, particularly $(Me_3Si)_2N\cdot$. The relative activities of these compounds can be attributed to the higher resonance stability of the $(Me_3Si)_2N\cdot$ radical compared with $Me_3Si{-}\dot{N}{-}CMe_3$.

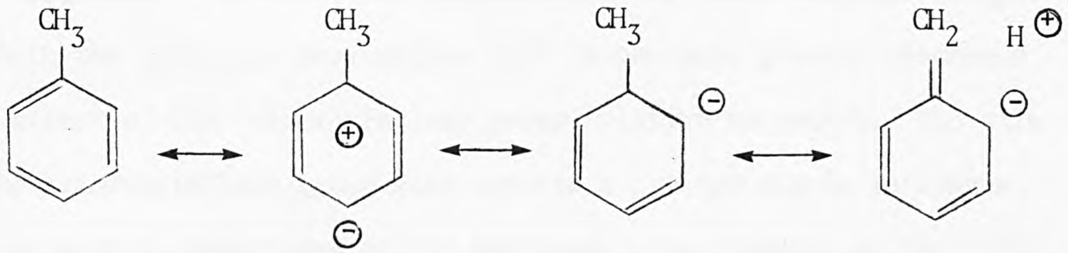
Hexamethylcyclotrisilazane, is an analogue of D_3, the cyclic siloxane. The activity of this compound under the experimental conditions used was,however, greater than that of the oxygen-containing compound. This is a result of the inhibiting power of the secondary amine compared with the ether, this particular compound having three such groups. Cyclic silazanes are of general interest since there is the possibility that, as with the cyclosiloxanes, the former compounds undergo thermal degradation by the elimination of $Me_2Si{=}NH$ units (which are the nitrogen containing equivalents of D_1). These silanimine units may exert a sizeable antiknock effect if generated during hydrocarbon combustion. It is unlikely, however, that under the experimental conditions used in the laboratory studies, these species would be generated from hexamethylcyclotrisilazane. It is probable that silanimine units would have been generated from higher cyclosilazanes which could not, however, be obtained satisfactorily. The effect observed with this compound is, therefore, purely a result of the presence of secondary amine groups.

A considerable inhibiting effect was observed with the disilylated derivative of 1,2-diaminoethane, while bis(trimethylsilyl)urea exerted no effect on the ignition limits. 1,2-Bis(trimethylsilyl)1,2-diaminoethane contains two secondary amine groups adjacent to two trimethylsilyl groups. Thus, radicals resulting from hydrogen abstraction will be relatively stable and the compound should exhibit a pronounced antiknock effect. On the other hand, the lack of effect observed with N,N-bis(trimethylsilyl) urea is probably due to its very low volatility since the compound is a high-melting solid (m.p. = 495K); its involvement in gas-phase reactions will be negligible.

The raising of ignition limits observed with the tertiary amine, N-trimethylsilylimidazole is due to the aromaticity of the ring system which, in the unsilylated compound, confers resistance to oxidation and reduction. The inductive (+I) effect of the trimethylsilyl group increases the electron density on the aromatic nucleus, and therefore improves the antiknock properties of the compound. In this case, the negative resonance contribution of trimethylsilyl groups which affects non-heterocyclic aromatic systems, is virtually absent so that the positive inductive effect will not be counteracted by resonance. Large proknock effects were observed with the tertiary amines $Me_3SiCH_2NMe_2$ and Me_3SiNEt_2, although $Me_2Si(NMe_2)_2$ had no effect whatsoever on the ignition limits. These are, indeed, in accord with results obtained in previous studies which suggest that tertiary amines have a detrimental effect on RON in engine experiments (Standard Oil Dev. Co., 1944; Shell Dev. Co., 1947). The improvement in the antiknock properties of secondary amines when two such groups are present is again reflected here; however the presence of two nitrogen atoms in the diamine counteracts the proknock effect that would be expected with a tertiary amine, resulting in virtually no net effect.

Large shifts in ignition limits were observed with the silylated derivatives of aniline (Table 3.9). In addition, these compounds were found to increase the induction periods, and to decrease ΔP_{cf} and $(dp/dt)_{max}$. Furthermore, silylation of aniline itself not only resulted in an increased inhibiting effect, but also improved the miscibility of the additive in hydrocarbon solvents. The activity of N-trimethylsilylaniline may be due to the increased electron density on the aromatic nucleus arising from the strong resonance (+R) effect due to the $NHSiMe_3$ group, although the inductive effect of this group is only small. Silylation of the amino group of aniline, to form the secondary amine, also stabilizes the radical formed as a result of the abstraction of hydrogen from nitrogen. This additional effect explains the enhanced antiknock properties of the aniline derivatives as compared with the derivatives of phenol (Table 3.7). Indeed, the magnitude of such an effect may be so great that both the resonance and inductive contributions become insignificant. This is exemplified by the result obtained with the compound, $Me_2Si(NHPh)_2$, which contains, essentially, two molecules of aniline (and thus, two secondary amino groups) and raises the ignition limit by approximately twice as much as the mono-aniline derivative. Further evidence for the importance of the presence of the secondary amine group is demonstrated by the results obtained with tertiary aromatic amines. The silylated derivative of N-methylaniline, $Me_3Si\ NMePh$, exerted a markedly smaller effect than N-trimethylsilylaniline (Table 3.9). The difference in the changes in ignition limits is even larger in comparison with N-methylaniline itself (Table 3.14). Indeed, the tertiary amine, $Me_3SiCH_2NPh_2$ actually appears to promote combustion, lowering the ignition limits by ca. 2 kPa. The variation in activity between these two compounds may either be a result of the electronic effects of the substituents on the benzene ring, or be due to steric factors; for the formation of radical complexes with the nitrogen lone pair is hindered by the presence of large substituents such as phenyl groups.

The secondary amine, $PhMe_2SiCH_2NHPh$, which would be expected to form a particularly stable radical, exhibits only a small inhibiting effect on the combustion of 2-methylpentane. This is probably due, however, to its low volatility. Ring-substitution alters significantly the antiknock activity of these derivatives. Both methyl groups and trimethylsiloxy groups (Table 3.10) enhance the antiknock properties of the N-silylated aniline compounds since the combined inductive and resonance effects increase the electron density on the ring and stabilize the $R_2N\cdot$ radicals formed by hydrogen abstraction during combustion. The introduction of methyl groups into the benzene ring increases the electron density on the aromatic nucleus by a weak positive inductive (+I) effect, and a resonance (+R) effect. The additional resonance stabilization of the conjugate radical depends on the position of the substituent on the ring. The methyl group, when attached to the benzene ring, imparts a partial negative charge on the ortho and para positions by resonance :



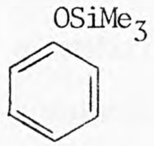
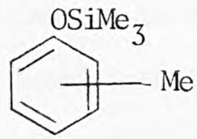
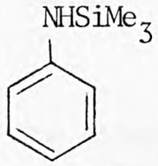
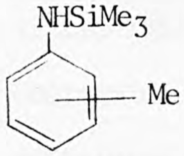
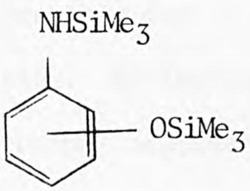
An increase in electron density at the carbon atom attached to nitrogen in the above series of compounds will enhance the stability of the radical formed by hydrogen abstraction from the nitrogen atom. Thus, the order of antiknock effectiveness should increase in the order :

meta $<$ ortho $<$ para

the difference between ortho and para being purely steric in origin. With the silylated toluidines, therefore, it is found that the para-derivative is the most effective, whereas the ortho- and meta- compounds raise the ignition limits by an equal amount.

The most powerful inhibitors of combustion tested in this study were the silylated aminophenol derivatives (Table 3.10). The effects due to the parent aminophenols could not be investigated due to their insolubility in 2-methylpentane and other hydrocarbon solvents. The silylated compounds were, however, completely miscible with 2-methylpentane. The magnitude of this inhibition can be explained in terms of the resonance stability conferred on the radical derived from the compound by hydrogen abstraction from the nitrogen atom. Thus, the mechanism of action of the silylated aminophenols is analogous to that of the silylated aniline derivatives rather than to that of the phenoxy compounds. The increased effectiveness of these compounds compared with the toluidine derivatives lies in the much greater resonance (+R) effect of the trimethylsiloxy group relative to methyl. The size of the trimethylsiloxy group also imparts a greater steric influence on the relative magnitudes of the antiknock effectiveness of the ortho and para derivatives and the difference between ortho and para is therefore much larger. The relative activities of the silylated derivatives of phenols, anilines and aminophenols are shown in Table 4.4 .

TABLE 4.4

ADDITIVE	RELATIVE CHANGE IN IGNITION LIMITS/kPa	EFFECT OF SUBSTITUENT	
		I	R
	2	(-I	+R)
	Ortho 4	+I	+R, 1,3,5
	Meta 9	+I	+R, 2,4,6
	Para 7	+I	+R, 1,3,5
	17	(——	+R)
	Ortho 20	+I	+R, 1,3,5
	Meta 20	+I	+R, 2,4,6
	Para 20	+I	+R, 2,4,6
	Ortho 32	-I	+R, 1,3,5
	Meta 28	-I	+R, 2,4,6
	Para 50	-I	+R, 1,3,5

4.5 CONCLUSIONS

The present work has shown that an injection apparatus constitutes, in many cases, a suitable means by which a study can be made of the effects of additives of low volatility and high reactivity on the combustion of a volatile fuel, viz. 2-methylpentane. Shifts in ignition limits and changes in other kinetic parameters observed when additives are introduced into the fuel have been shown to form the basis of a quick, reliable method for the assessment of the antiknock activity of the additives concerned, thus avoiding the expense as well as practical difficulties (e.g. deposition of solids) associated with systematic engine experimentation.

The silanes and their simple derivatives appear, in general, to have little inhibiting effect on hydrocarbon combustion, although compounds containing aromatic groups do show some promise. As regards oxygen-containing organosilicon compounds, only small effects were again observed with linear siloxanes and alkoxysilanes. Structural analogues of MTBE viz. methoxytrimethylsilane and tert-butyoxytrimethylsilane have less pronounced effects than the organic ether itself although both compounds raise the ignition limits to a small extent, this is probably due to the difficulty of abstraction of a primary hydrogen atom. Cyclosiloxanes are of interest inasmuch as they eliminate on thermal degradation dimethylsilanone units. It has been found that their antiknock activity can be correlated with the ease of elimination of such units. The largest effects observed with oxygen-containing organosilicon compounds were found with derivatives of phenoxytrimethylsilane. Although the parent compound did not raise the ignition limits to a great extent, the increased electron density resulting from replacement of hydrogen atoms attached to the benzene ring by electron-donating substituents produces a significant increase in antiknock activity. The effects found with nitrogen-containing organosilicon compounds, in general, parallel those for purely organic amines. It is not clear, therefore, whether these are due simply to the presence of the nitrogen or to some combined effect of nitrogen or silicon. Large shifts in ignition limits were observed with silylated derivatives of aniline which, in addition, are much more soluble in hydrocarbons than the parent compounds. Calculation of the electron density at the different positions of the aromatic nucleus arising from resonance and inductive effects have shown that the predicted order of antiknock activity correlates well with that found in the laboratory. A full study was carried out of the effects of methyl substitution on the antiknock properties of silylated derivatives of phenol and aniline. All three di-silylated aminophenols were also synthesized and their effects studied. The results show that although there was very little antiknock activity due to phenoxytrimethylsilane, its methylated derivatives are much more effective particularly when the methyl group is in the meta position; this can be attributed to the increased electron density in the ring position between the trimethylsiloxy and methyl groups in the parent compound. The silylated aniline is a much more effective antiknock than phenol. Again, methyl substitution enhances antiknock activity. The presence of a hydrogen atom attached to nitrogen ensures that the best improvement will be found when the electron density is increased at the position to which nitrogen is attached, thus stabilizing the radical formed after hydrogen abstraction. In this case, therefore, it is the para- methyl compound which is most effective. Of all the compounds studied, those exhibiting the greatest antiknock activity were the di-silylated aminophenols. The order of effectiveness of which parallels that of the silylated toluidines.

Although this work has not yet led to the discovery of industrially viable organosilicon additives, it has enabled some interesting deductions to be drawn regarding the effects of molecular structure on antiknock activity, and to uncover some new facts regarding the thermal and thermo-oxidative reactions of organosilicon compounds in the gas phase.

FUTURE WORK

Although the present study did not reveal an organosilicon compound which could be considered as a viable alternative to lead-based antiknock additives, some of the results obtained showed considerable promise. Further experiments should be made on the effects of larger cyclic siloxanes, i.e. D_6 or higher homologues, in view of the improvement in antiknock effectiveness observed with D_5 compared with D_4, and of the possible correlation of antiknock properties with the ease of elimination of the D_1 unit. In conjunction with this study, larger cyclosilazanes, nitrogen-containing analogues of the methylcyclosiloxanes, should be tested, since, during the present work, homologues with rings larger than $(Me_3SiNH)_3$ were not conveniently available.

Further attention might also be paid to the methods by which various silicon-containing transient species might be generated concurrently during hydrocarbon combustion, in view of the rather stringent reaction conditions experienced, particularly in an engine, which would influence, to a large extent, the lifetime of such species and hence, their involvement in the underlying combustion reactions.

Particular attention might additionally be given to methods by which the solid siliceous deposits formed during the combustion of these additives might be scavenged in a similar manner to that by which lead monoxide deposits are removed at present, viz. by reaction with 1,2-dibromoethane to form volatile products. If this was to be achieved, emphasis could then be placed upon the testing of organosilicon compounds in a

CFR engine in conjunction with the laboratory apparatus. Although so far engine testing has not proved to be a reliable measure of the inhibiting power of organosilicon compounds, it is, nevertheless, the only true measure of antiknock effectiveness. Thus, by removing the problems associated with the deposition of solid silica, the correlations between laboratory results and antiknock properties can be more satisfactorily verified.

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