To my Mother, Suharto

and Adrian

EVALUATION AND MECHANISM OF SULPHUR-BOUND ANTIOXIDANTS IN RUBBERS

by

ROSEDIANA SUHARTO

Submitted for the Degree of

DOCTOR OF PHILOSOPHY

of

THE UNIVERSITY OF ASTON IN BIRMINGHAM

November 1982

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SUMMARY

A quantitative study of the extent of the reaction between the hindered phenolic antioxidant 3,5-di-tert-butyl-4-hydroxyphenyl methane thiol (BHBM) and natural rubber latex, showed that this was low, due to naturally occurring non-rubber constituents. In SBR latex, much higher levels of binding were achieved. The concentration of bound antioxidant was estimated using infra-red spectroscopy after exhaustive extraction.

Evaluation of the ageing characteristics of bound BHBM in a conventional CBS vulcanisate showed that the rubber had exceptionally good antifatigue and antioxidant performance before and after solvent extraction.

The mechanism of the binding reaction with BHBM was studied using the related model compound, cyclohexene. It was shown that the molar ratio of peroxide and the temperature of the reaction were critical for high yields of adduct formation.

MADA was mechanochemically bound into synthetic and natural solid rubber using the RAPRA torque rheometer and the Buss Ko Kneader. Efficient binding was attained only for rubbers extracted prior to the processing operation. In all cases, the rubbers containing the bound MADA showed effective thermal oxidative and fatigue resistance after extraction.

The curing characteristics of the modified rubbers in conventional CBS vulcanisates showed that except for some reduction in scorch time, the vulcanisation characteristics were not affected significantly.

The bound antioxidant concentrates have been shown to be suitable for use as conventional additives for unmodified rubbers.

KEY WORDS: Polymer bound antioxidants, mechanochemistry, fatigue, oxidation, masterbatches

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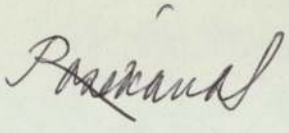
Finally, I owe a deep debt of gratitude to my Mother, Suharto and Adrian for many hours of encouragement, support and contribution throughout the years.

DECLARATION

The work described in this thesis was carried out between January 1979 and June 1982. It has been done independently and submitted for no other degree.



R Suharto November 1982

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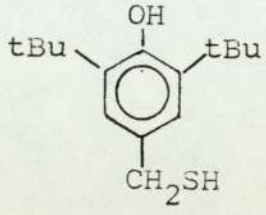
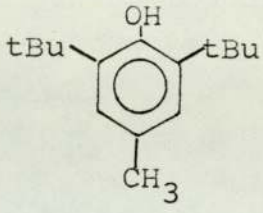
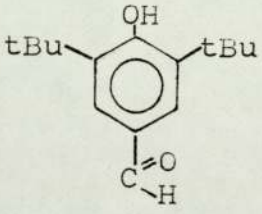
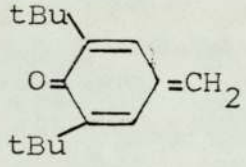
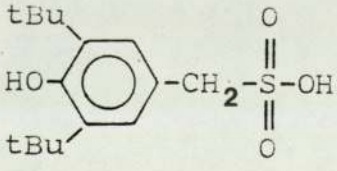
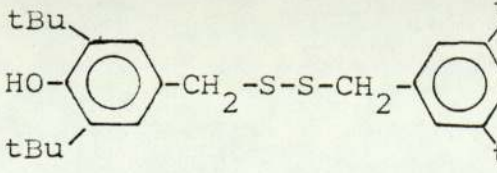
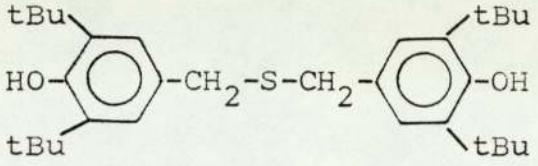
CHEMICAL STRUCTURE	NAME	CODE
	3,5-di-tert-butyl 4-hydroxybenzyl mercaptan	BHBM
	2,6-di-tert-butyl 4-methyl phenol	BHT
	3,5-di-tert-butyl 4-hydroxyphenol carbaldehyde	ALD
	2,6-di-tert-butyl -4-methylene-2,5-cyclohexadien-1-one	QM
	3,5-di-tert-butyl 4-hydroxyphenyl methyl sulphonic acid	BSA
	Bis(3,5-di-tert-butyl-4-hydroxybenzyl)disulphide	Di-S



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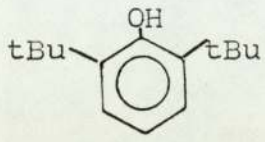
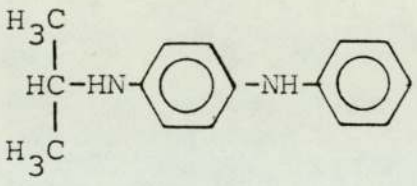
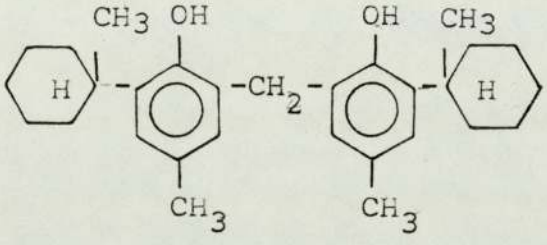


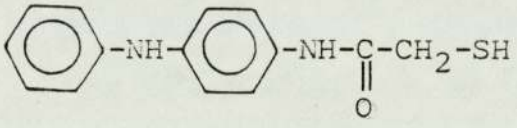
2,6-di-tert-butyl-phenol — Ph



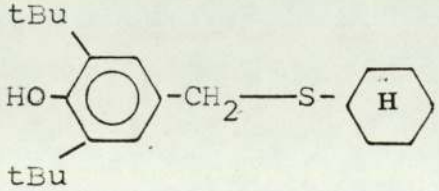
N-isopropyl-N'-phenyl-p-phenylene-diamine — IPPD



2,2'-di-hydroxy-3,3-di/alpha-methyl cyclohexyl)-5,5'-dimethyl-diphenyl methane — **WSP**



4-mercaptoacetamido-diphenylamine — **MADA**



3,5-di-tert-butyl-4-hydroxyphenylmethyl cyclohexylsulphide — Adduct

CHAPTER ONE

AN INTRODUCTION TO THE DETERIORATION OF RUBBERS

1.1 INTRODUCTION

Natural and synthetic polymers lose their useful properties when they are subjected to heat, light or mechanical action, for example during fatiguing[1-3].

Although there are many factors that may be responsible for the deterioration of rubbers, oxygen is the most important. Oxygen attacks the rubber hydrocarbon and the reaction is activated by such factors as light, heat and certain metallic impurities.[4]

Deterioration may result in considerable changes in physical and chemical properties, eg tensile strength, hardness, resilience, elongation at break. In synthetic rubber, especially styrene-butadiene, ageing can increase hardness and tensile strength due to the cross-linking following the initial rupture of the polymer chain.

Compounds known as antidegradants are used widely to retard these deteriorating effects. However, during the service life of the rubber components, these anti-degradants are often lost from the polymer due to

volatilisation effects, leaching effects and migration effects. If these antidegradants are chemically bound to the polymer, the loss of antidegradants can be minimised, and hence the service life of the rubber article lengthened considerably.

1.2 AUTOXIDATION

Autoxidation can be initiated by radical generating reactions involving the substrate, reaction products or impurities. Free radicals are produced from the substrate either by a bimolecular reaction[5] with oxygen (1-1) or from mechanomechanical chain scission or by photolysis of the substrate or of a complex between the substrate and oxygen.

$$RH + O_2 \longrightarrow R + \cdot OOH \qquad (1\text{-}1)$$

$$R\text{-}R' \longrightarrow R^{\cdot} + R'^{\cdot} \qquad (1\text{-}2)$$

The decomposition of hydroperoxide is accelerated by heat (1-3), light (1-4) and metal ions (1-5) capable of undergoing one-electron transfer reaction.

$$2ROOH \xrightarrow{heat} RO + ROO^{\cdot} + H_2O \qquad (1\text{-}3)$$

$$ROOH \xrightarrow{h\nu} RO^{\cdot} + \cdot OH \qquad (1\text{-}4)$$

$$2ROOH \xrightarrow{M^{+}/M^{+2}} RO\cdot + ROO\cdot + H_2O \quad (1\text{-}5)$$

The oxidative degradation process proceeds by a radical chain autoxidation mechanism, originally proposed by Bolland and co-workers[6-10].

Studies at NRPRA on the autoxidation of pure hydrocarbons structurally related to the rubber showed that in the absence of added initiators or inhibitors, the following reaction sequences occurred[11,12]:

Initiation

$$ROOH \longrightarrow RO\cdot + \cdot OH \quad (1\text{-}6)$$

$$2ROOH \xrightarrow{k_1} RO\cdot + RO_2\cdot + H_2O \quad (1\text{-}7)$$

Propagation

$$RO_2\cdot + RH \xrightarrow{kp} ROOH + R\cdot \quad (1\text{-}8)$$

$$R\cdot + O_2 \xrightarrow{fast} RO_2\cdot \quad (1\text{-}9)$$

Termination

$$2R\cdot \longrightarrow R\text{-}R \quad (1\text{-}10)$$

$$R\cdot + RO_2\cdot \longrightarrow RO_2R \qquad (1\text{-}11)$$

$$2RO_2\cdot \longrightarrow \text{Non-radical product} + O_2 \qquad (1\text{-}12)$$

where RH represents a hydrocarbon, R· is alkyl radical produced by hydrogen abstraction from RH and ROO· is the peroxy radical formed by reaction of R· with molecular oxygen. At normal oxygen pressures, the radical present in highest concentration in the system is alkylperoxyl, ROO·. Consequently, termination normally occurs by reaction (1-12).

1.3 ANTIOXIDANTS

There are two basic classes of antioxidants functioning by different mechanisms.

1.3.1 CHAIN BREAKING ANTIOXIDANTS

This type of compound competes with the hydrocarbon in the reaction with the hydroperoxy radicals and alkyl radicals in a chain propagating step.

1.3.1.1 CHAIN BREAKING DONOR ANTIOXIDANTS (CB-D)

Compounds which donate a labile hydrogen or an electron

give rise to a stable (non-propagating) radical. This includes compounds such as phenol and arylamines, which have the ability to transfer labile hydrogens to the propagating radicals, $RO_2\cdot$[14].

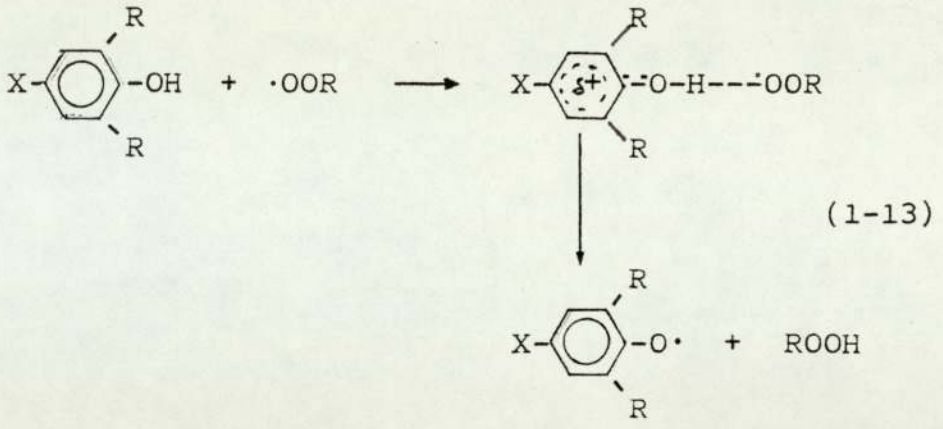
$$ROO\cdot + AH \longrightarrow ROOH + A\cdot \qquad (1\text{-}12)$$

The resulting phenoxy radical has a tendency to react with oxygen or polymer and the rate of the reaction depends on the steric environment of the aryloxy radical. The ease of hydrogen abstraction by the alkylperoxy radical is increased by electron releasing groups in phenols, or in amines, but the same electronic characteristic favours the direct attack of oxygen on the phenolic hydrogen, which is potentially a chain-initiating reaction.

$$AH + O_2 \longrightarrow A\cdot + \cdot OOH$$

The effectiveness of the reaction of a phenolic compound with a peroxy radical lies in the stability of the phenolic radical formed.

The structure of the transition state describes the effect of substituents on activity[14].



(1-13)

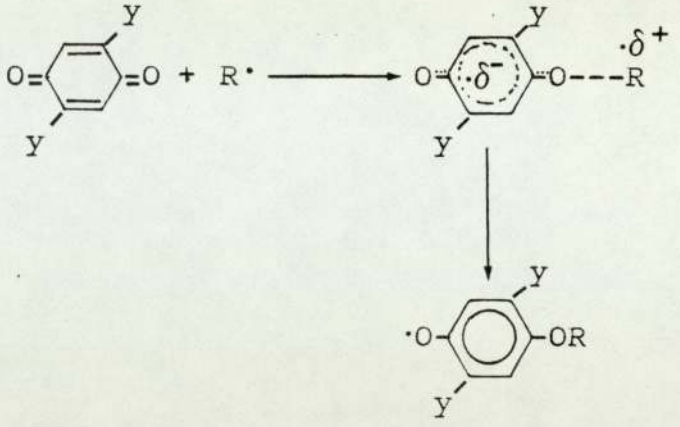
Electron releasing and electron delocalising substituents (X,R) reduce the energy of the transition state and increase antioxidant activity[1].

1.3.1.2 CHAIN BREAKING ACCEPTOR ANTIOXIDANTS (CB-A)

Any compound which can remove alkyl radicals from an autoxidation system is a CB-A antioxidant.

This includes quinones, nitrocompounds, nitrones and a variety of 'stable' radicals, of which the phenoxyls and nitroxyl radicals have been studied. All of these compounds are oxidising agents.

The molecular requirements for an effective CB-A antioxidant can be shown in this transition state of a reaction of an alkyl radical with a quinone[1].

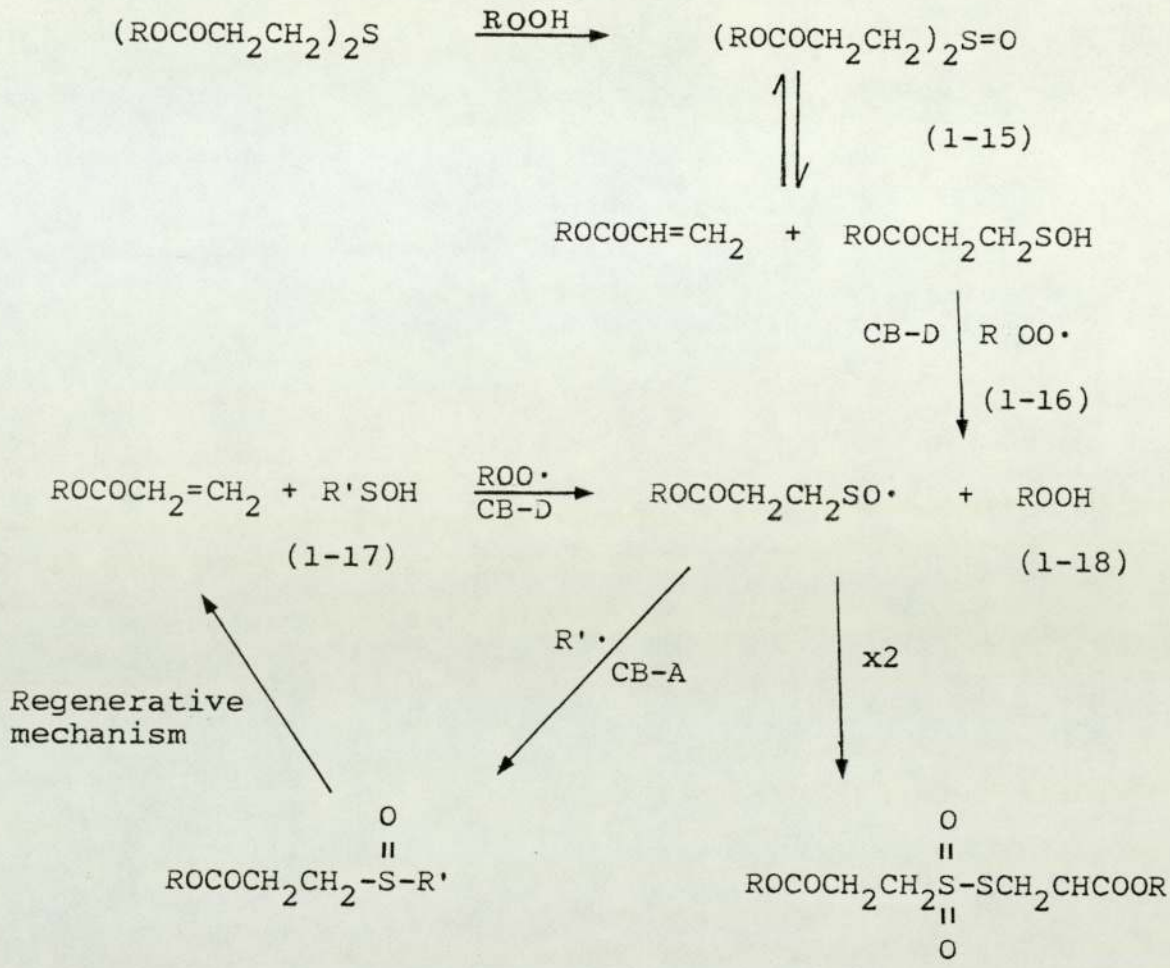


(1-14)

The transition state involves partial transfer of an electron to the aromatic bond and therefore electron attracting and delocalising substitutents (y) will both increase the activity.

1.3.1.3 REGENERATIVE CHAIN BREAKING ANTIOXIDANTS

Some chain breaking antioxidants have the ability to alternate between the oxidised and the reduced state and hence exhibit regenerative behaviour under conditions where both alkyl and alkylperoxyl radicals are important. Dilauryl sulphinyl dipropionate is known to form a sulphoxide and follow the regenerative cycle as follows[15-17]:



Scheme 1-1

However, the sulphinyl radical can be readily removed by dimerisation and this may limit the extent to which the above process occurs.

1.3.2 PREVENTIVE ANTIOXIDANTS

Preventive antioxidants inhibit or retard the formation of free radicals in the initiation step of autoxidation. Hydroperoxides are formed during initiation to produce

active initiating free radicals.

$$nROOH \longrightarrow RO\cdot\ ,\ \cdot OH\ ,\ RO_2^{\cdot}\ ,\ H_2O \qquad (1\text{-}19)$$

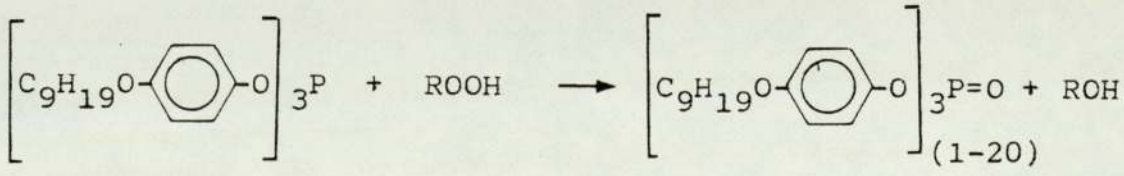
Therefore, this class of preventive antioxidants reacts with hydroperoxides to form a stable non-radical product.

Peroxide decomposers fall into mechanistic classes; stoichiometric reducing agents (PD-S)[18] and catalytic peroxide decomposers (PD-C).

1.3.2.1 STOICHIOMETRIC PEROXIDE DECOMPOSERS (PD-S)

Compounds falling into this category should be capable of substantially reducing hydroperoxide to alcohol without the substantial formation of free radicals.

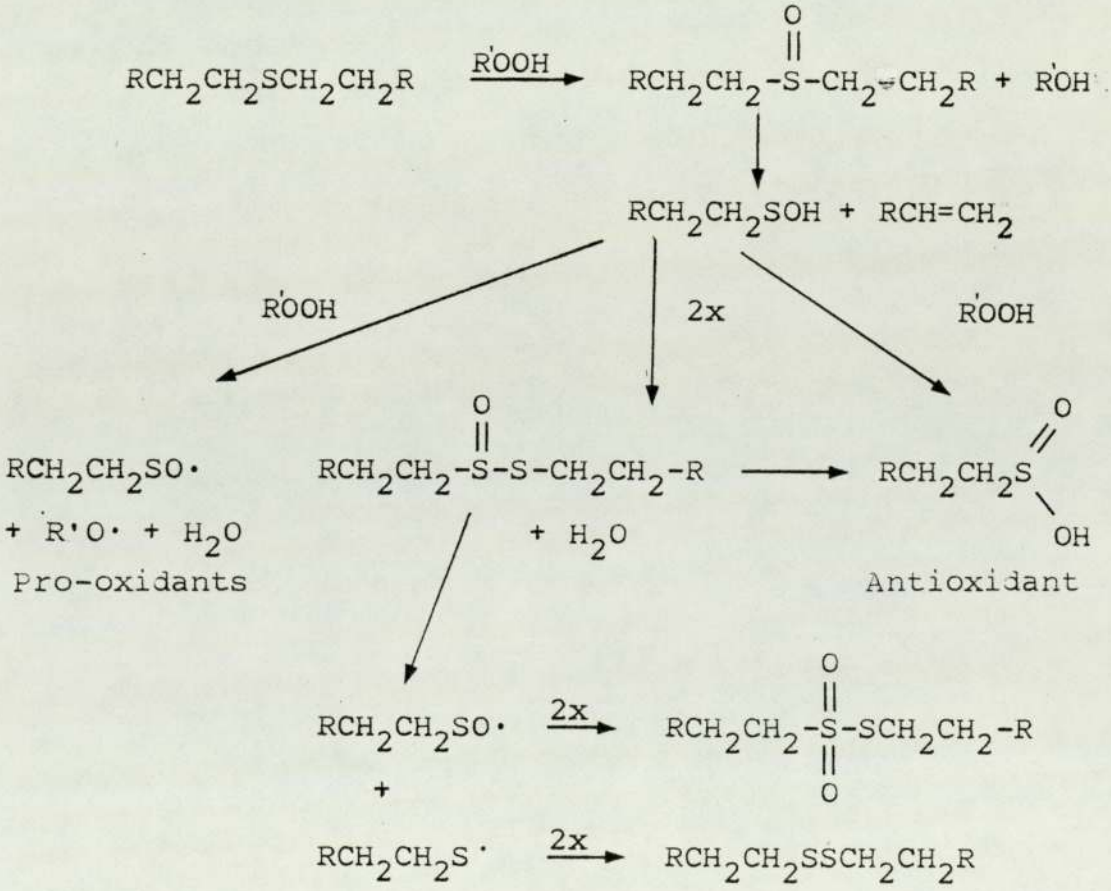
In rubbers, the most widely used PD-S antioxidant, the phosphite esters, such as trinonylphenylphosphate, are known as raw rubber stabilisers.[18]



(1-20)

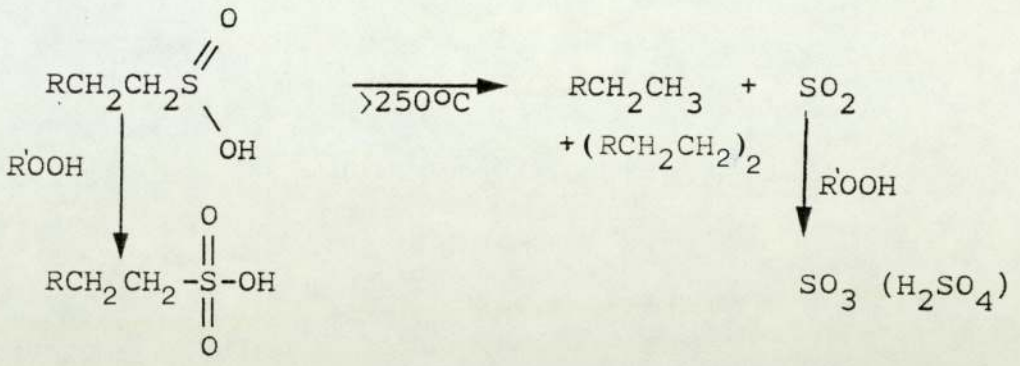
1.3.2.2 CATALYTIC PEROXIDE DECOMPOSERS (PD-C)

Compounds falling into this class have the ability to decompose hydroperoxides through the formation of an acidic product (sulphur oxide or acid). Most sulphur antioxidants fall into this class, however, the antioxidant function is normally preceded by pro-oxidant stage. The antioxidant and pro-oxidant involved in the mechanism of action of monosulphidesbehaviour can be described as follows: [15-19]



Scheme 1-2

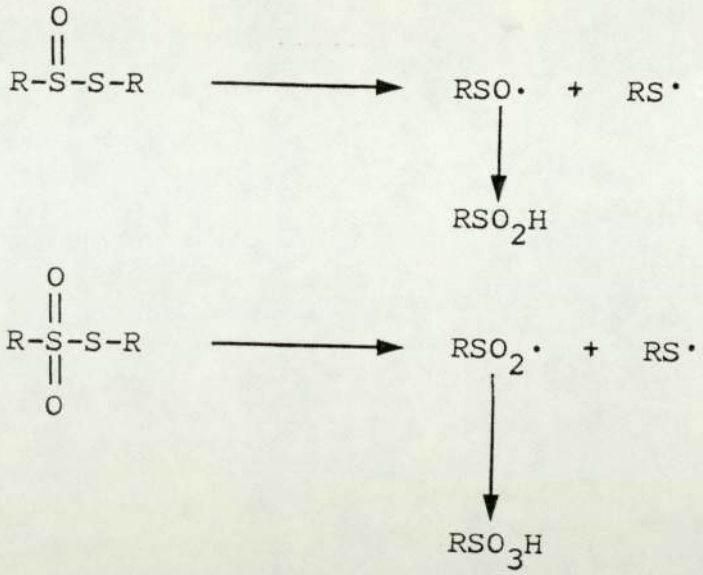
The mechanism below accounts for the formation of organosulphur and their conversion to sulphonic acid[19].



Scheme 1-3

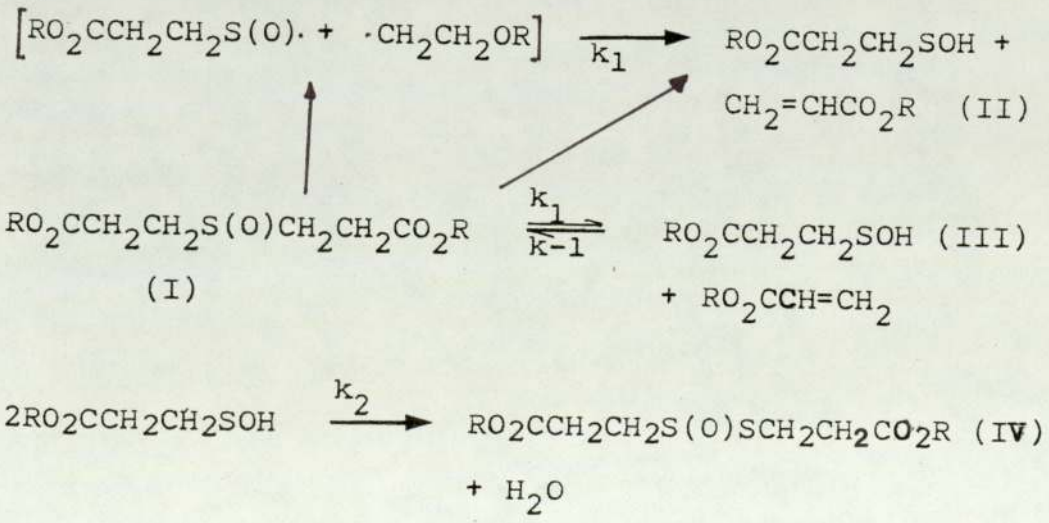
1.3.2.2.1 THE MECHANISMS OF SULPHUR CONTAINING ANTIOXIDANTS

Many sulphur compounds are effective antioxidants when they are incorporated in polymers[1,20]. The effectiveness of alkyl sulphides and disulphides as preventive antioxidants involves initial oxidation by hydroperoxide to form sulphoxide[1,22,23] and thiol sulphinate[24,25]. Sulphonic acid was found to be formed on thermal decomposition of sulphoxide[26-28]. Hawkins and Sautter[29] suggested that sulphinic and sulphonic acids are produced by thermal dissociation of a thiolsulphonate and sulphonate.



Scheme 1-4

Armstrong[15] studied the thermal decomposition of sulphoxide dimethylsulphinyl diproprionate and found that the decomposition at 75°C did not show first order kinetics. Retardation of the reaction by addition of methyl acrylate (II) which in the first elimination process suggested that the reaction was reversible. The following series of reactions was postulated.



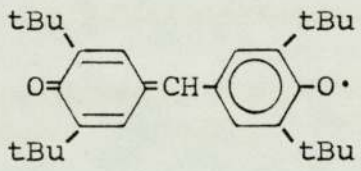
$$2RO_2CCH_2CH_2S(O)SCH_2CH_2CO_2R \longrightarrow RO_2CCH_2CH_2S(O)_2SCH_2CH_2CO_2R \text{ (V)} + RO_2CCH_2CH_2SSCH_2CH_2CO_2R \text{ (VI)}$$

$$RO_2CCH_2CH_2S(O)SCH_2CH_2CO_2R \longrightarrow RO_2CCH_2CH_2SSOH + RO_2CCH{=}CH_2$$

$$RO_2CCH_2CH_2SSOH \longrightarrow \text{Other products}$$

Scheme 1-5

Armstrong[15] also carried out the above reaction (scheme 1-5) in the presence of galvinoxyl, a stable free radical (G·). He showed that the reaction was first



(G·)

order and suggested the dimerisation of sulphonic acid to thiosulphinate. The following scheme was postulated.

$$RO_2CCH_2CH_2S(O)CH_2CH_2CO_2R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RO_2CCH_2CH_2SOH + RO_2CCH{=}CH_2$$

$$RO_2CCH_2CH_2SOH + G\cdot \xrightarrow[\text{fast}]{k_1} RO_2CCH_2CH_2SO\cdot + GH$$

$$2RO_2CCH_2CH_2SO\cdot \longrightarrow RO_2CCH_2CH_2S(O)_2S\text{-}CH_2CH_2CO_2R$$

Scheme 1-6

The thermal decomposition of dimethylsulphinyl dipropionate in the presence of cumene hydroperoxide was found to be first order and it was suggested[16] that rapid reaction was taking place between sulphenic acid and hydroperoxide to give sulphinic acid which could be oxidised to sulphonic acid.

$$CH_3OCOCH_2CH_2SOCH_2CH_2OCOCH_3 \longrightarrow CH_3OCOCH_2CH_2SOH \quad (VII) + CH_3OCOCH{=}CH_2$$

$$CH_3OCOCH_2CH_2SOH + ROOH \longrightarrow CH_3OCOCH_2CH_2SO_2H$$

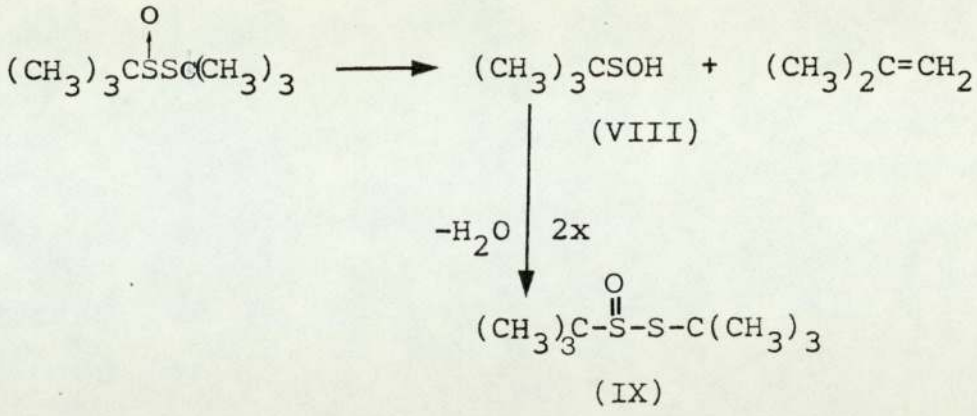
$$CH_3OCOCH_2CH_2SO_2H + ROOH \longrightarrow CH_3OCOCH_2CH_2SO_3H$$

Scheme 1-7

The reaction between sulphenic (VII) acid and hydroperoxide is believed to be the major cause of the pro-oxidant effect observed in cumene[15,16].

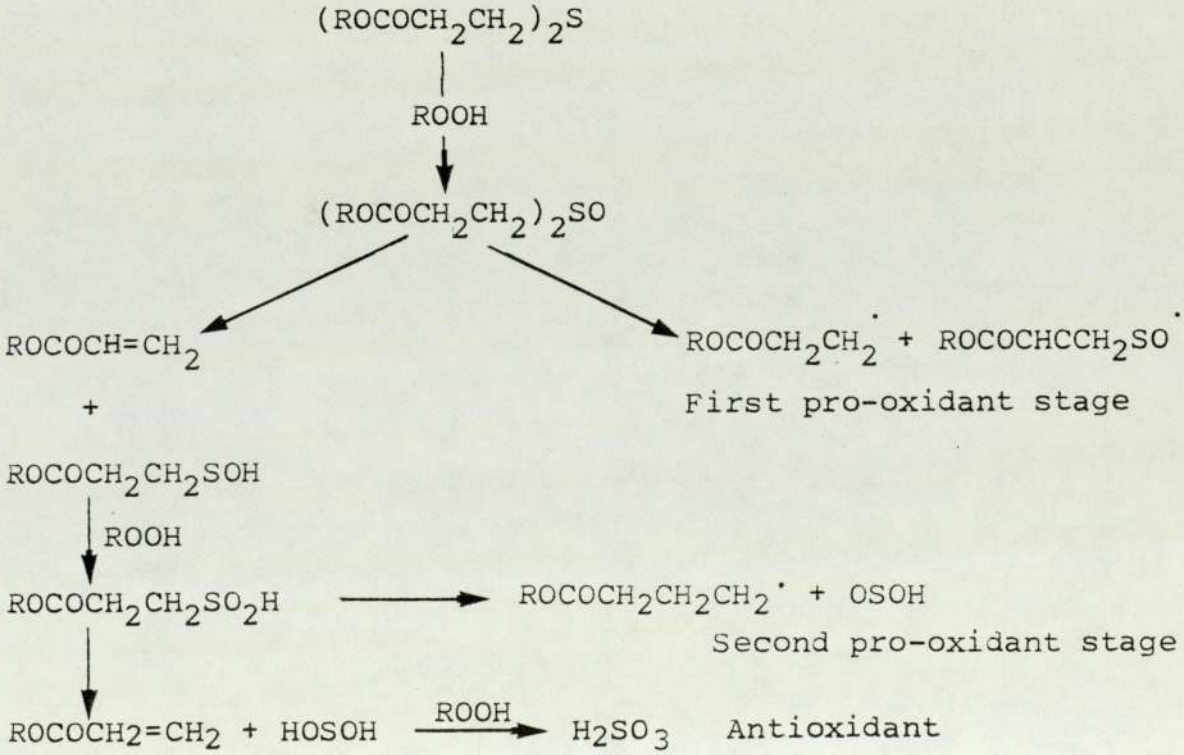
$$RO_2CCH_2CH_2SOH + R'OOH \longrightarrow R'O\cdot + H_2O + RO_2CCH_2CH_2SO\cdot \quad (1\text{-}21)$$

Shelton et al[30] showed that sulphenic acid (VII) is also formed in the following reaction and dimerises to form disulphide (IX):



Scheme 1-8

Scott[31] reported that there are two distinct pro-oxidant effects at low hydroperoxide to antioxidant ratios. The observed pro-oxidant and antioxidant reactions were proposed as follows:

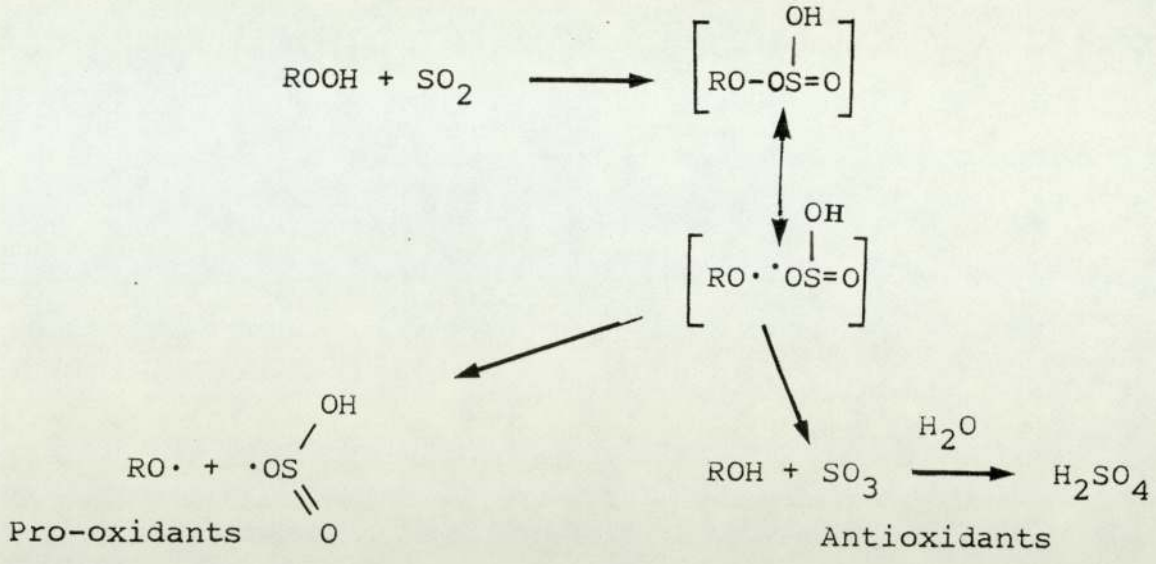


Scheme 1-9

Husbands and Scott[32] studied the behaviour of sulphur dioxide in autoxidising systems in cumene initiated by cumene hydroperoxide and observed the oxidation of cumene is inhibited by the addition of SO_2. They suggested that the sulphinyl and sulphonyl radicals are the main precursors to sulphur trioxide.

Husbands[32] also reported that the product distribution varied according to the molar ratio of CHP to SO_2. At molar ratio $[CHP]/[SO_2] < 1$, radical products predominate, but at molar ratio $[CHP]/[SO_2] > 1$, ionic products are the most important. This clearly explains that the pro-oxidant effect which is observed at lower molar ratios but is not observed at higher molar ratios. The addition of TBH in excess of SO_2 showed that initially TBH was destroyed by SO_2 in a stoichiometric reaction[32]. However beyond 2 mole the catalytic decomposition competes with the stoichiometric reduction.

The reaction between ROOH and SO_2 is shown below:



Scheme 1-10

Similar results have also been reported by Cooray and Scott[33]. They have shown that the reaction between CHP and BHBM are free radical if molar ratio $[CHP]/[BHBM] < 1$ and ionic products predominate if molar ratio $[CHP]/[BHBM] > 1$.

1.4 DEGRADATION OF RUBBERS

The unsaturation in rubber is susceptible to reaction with oxygen leading chain scission. Cross-linking and degradation may result in considerable changes in chemical and physical properties such as hardness, elongation at break, tensile strength, colour, Mooney viscosity.

Therefore the protection of rubber is very important

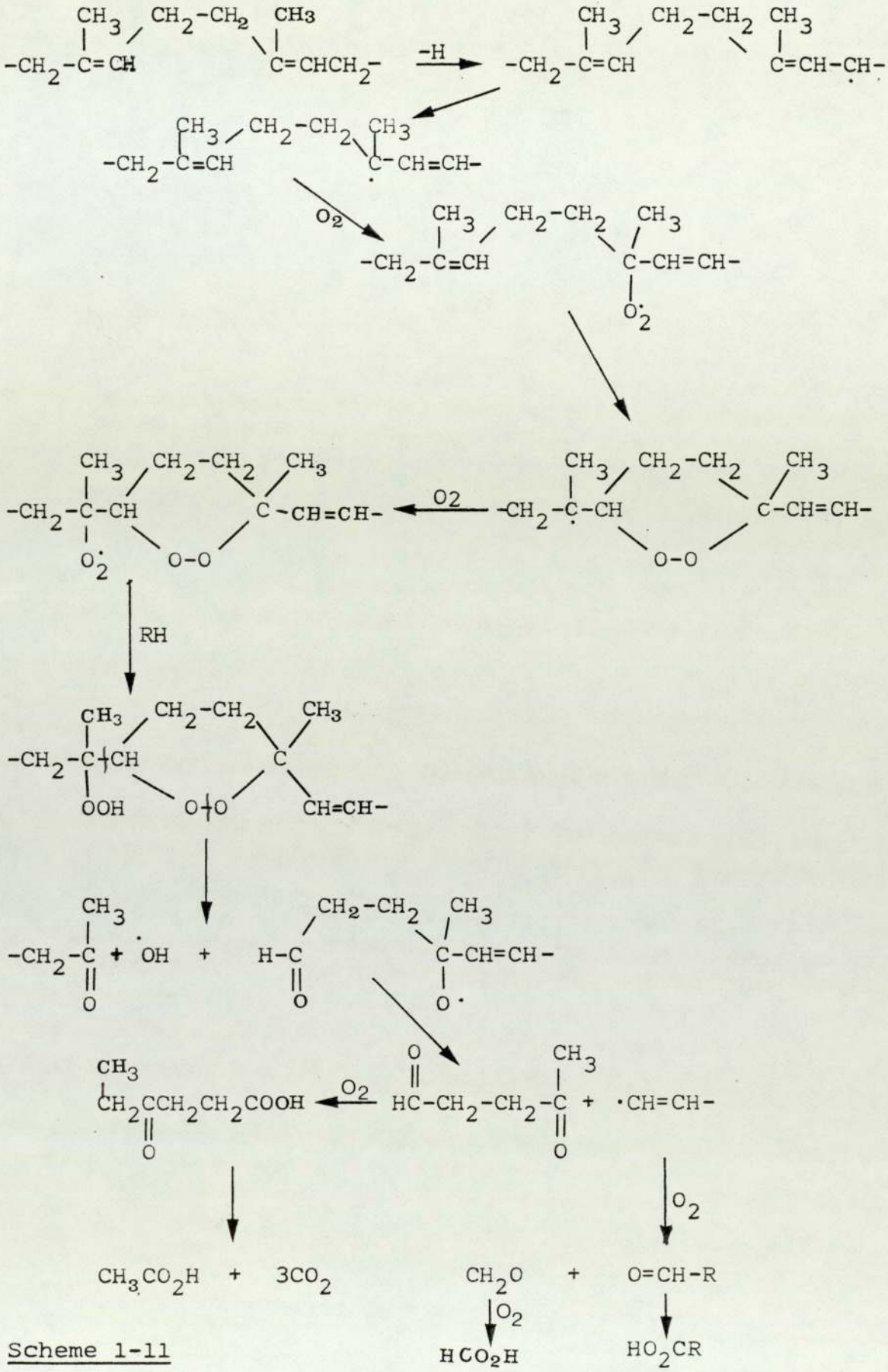
since it is attacked by oxygen even at room temperatures and the reaction is accelerated by heat, light and certain metallic impurities.

1.4.1 OXIDATION OF RAW RUBBERS

Rubber is oxidised even at the very first stage in the latex form. Sekhar[35] reported that excessive contact of latex with air leads to peroxidation of the hydrocarbon. Such peroxidation, leading to scission of the rubber molecule, has been shown by Bevilacqua[36-38] to take place in latex on heating in the presence of air. Morris and Sekhar[37] showed that even at room temperature, absorption of oxygen by latex leads to the formation of an equilibrium concentration of hydroperoxidised polyisoprene, leading to either scission or cross-linking of the rubber molecule.

Synthetic rubber is much purer than natural rubber and is readily attacked by oxygen. Synthetic antioxidants, eg aromatic amines, are normally added to stabilise SBR[39].

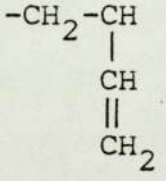
A number of mechanisms have been proposed to account for oxidation of cis-polyisoprene, but the most widely accepted is that proposed by Bevilacqua[40], the essential steps of which are as follows:



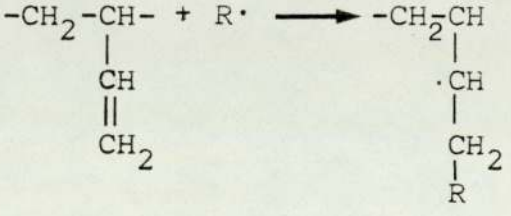
Scheme 1-11

Oxidation of styrene butadiene rubber can cause gel formation[41] and hardening[42,43]. Degradation of SBR leads to change in intrinsic viscosity, molecular weight distribution and mechanical properties[44]. During oxidation, SBR undergoes cross-linking and becomes sharply brittle, while in the case of natural rubber, softening occurs under these conditions[44].

It is well known that in SBR after polymerisation there are about 20% pendant vinyl groups in the polymer[45]



It is thought that the hardening of the SBR upon oxidation is due to cross-linking reactions occurring across these pendant double bonds by addition of macro-alkyl radicals across the vinyl group[45].



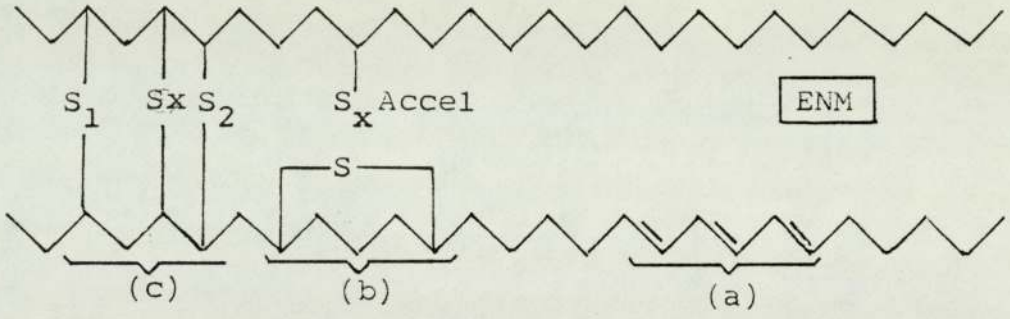
In the case of natural rubber, however, there are no pendant vinyl groups and a methyl group is not susceptible

to cross-linking reactions, chain scission predominates during autoxidation cycle[45].

1.4.2 OXIDATION OF VULCANISED RUBBERS

The strength of a rubber vulcanisate is dependent on the type of rubber used and type of curing system applied[20].

The scheme of sulphur cross-links is shown below:



ENM = extra network material

(a) = unmodified polymer

(b) = pendant and cyclic groups

(c) = cross-link

Structural modification of the main chain occurring during vulcanisation include:

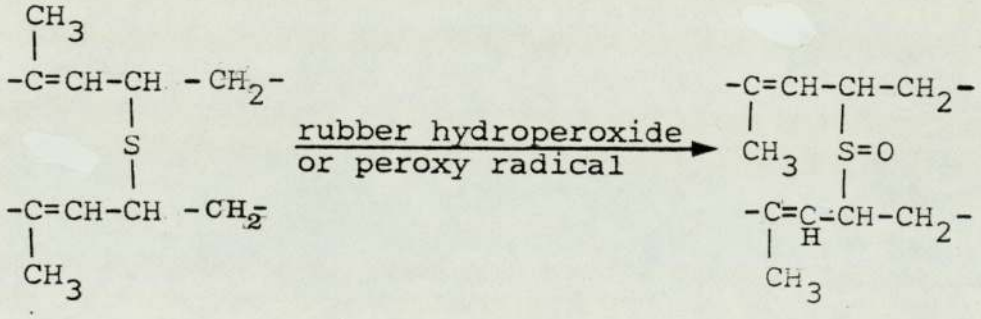
(a) formation of pendant cyclic sulphide,

(b) changes in the olefinic pattern in original rubber, and

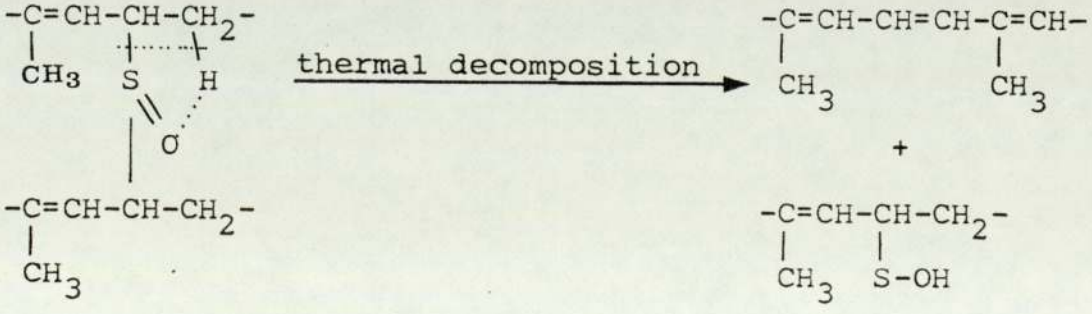
(c) scission of the main chain.

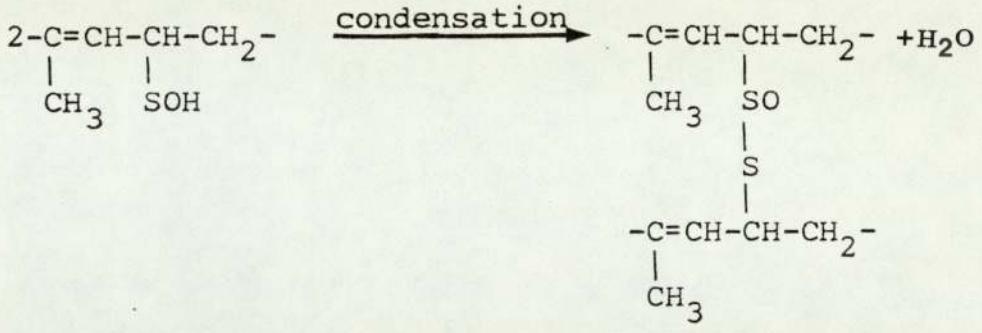
Oxidation of vulcanised rubber leads to deterioration of physical properties of vulcanised rubber, due to cleavage of the vulcanisate network. This can occur via main chain scission or cross-link scission[46]. Oxygen may react with rubber to form peroxide leading to a variety of oxidised sulphur compounds.

The oxidation process will be expected to exhibit similar antioxidant and pro-oxidant behaviour to simple sulphur compounds. The following scheme shows the oxidation of dialkenyl monosulphidic cross-links present in NR vulcanisates prepared from a sulphurless or accelerated sulphur system[47]:



Dialkenyl cross-link

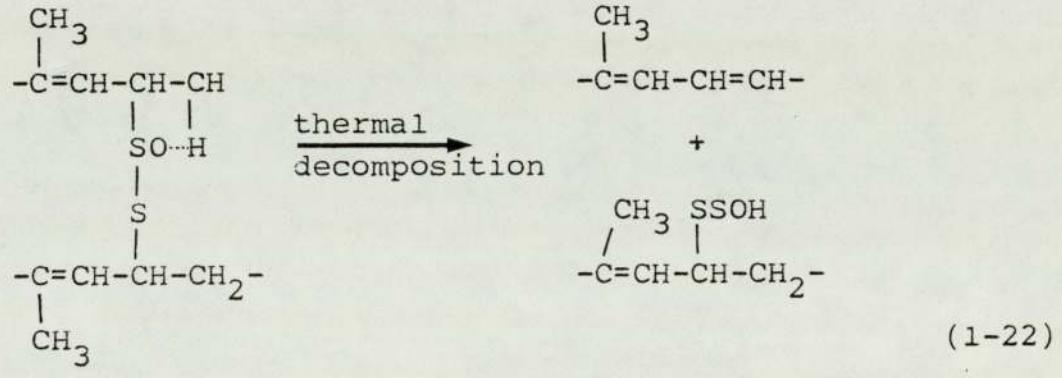




Scheme 1-12

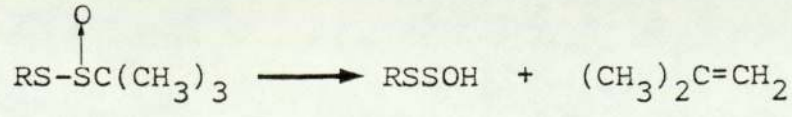
In the above reaction, oxygen as hydroperoxidised or peroxide, oxidised, the sulphur to form sulphoxide, subsequent cleavage of the S=O bond forming S-S bonds sulphenic acid, a conjugated triene and a thiosulphinate cross-link.

This thiosulphinate cross-link can undergo scission as follows:



(1-22)

This mechanism has been suggested by Shelton et al[49,50] for the case of alkyl tertiary butyl thiolsulphinate.



(1-23)

In the case of oxidation of disulphide cross-links, the thiosulphinate group is thermolabile and this will lead to interchange of cross-links resulting in creep and permanent set of the network when strain is applied[46].

$$RSSR \longrightarrow RSOSR \longrightarrow \tfrac{1}{2}RSO_2SR + \tfrac{1}{2}RSSR$$

Little is known about oxidation of polysulphide cross-links but it is believed that they will behave in a similar manner.

1.5 FATIGUE FAILURE

Fatigue is defined as the changes in physical structure and properties of the mass of a rubber component when subjected to repeated deformation[51]. When the rubber is subjected to this type of deformation, cracks are formed which grow and lead to complete failure[52]. In general there are three causes for the failure of rubber upon cyclic deformation. They are:

mechanical scission of rubber chains,
oxidation, and
scission of the chain by ozone.

Oxidation leads to surface crazing, which is a random development of shallow cracks, where as ozonisation

leads to the formation of deep cracks in rubbers under stress. In contrast to oxidation, the ozone cracks always occur perpendicular to the direction of the applied strain or deformation. However, the effects of oxygen and ozone may be synergistic.

1.5.1 THE MECHANISMS OF CRACK PROPAGATION

Studies of crack growth and propagation in rubber by a deliberately produced cut of measurable size under static or dynamic strain has shown that fatigue is primarily a physical phenomenon where the most important feature is tearing at the tip of a crack which is growing.

In the presence of nitrogen, the crack growth was delayed, therefore oxygen is responsible for accelerating crack growth[51]. Oxygen combined with alkyl radicals during mechanical flexture of the rubber component cause failure to the rubber. Other factors which may increase crack formation include microdefects on the surface of the rubber vulcanisate which upon application of stress give rise to cracks which subsequently propagate, ultimately leading to failure. Local inhomogeniety small hard particles, small region of abnormal cross-linking and ozone, can give rise to formation of cracks and lead to failure.

1.5.1.1 TEARING OF RUBBERS

One of the most important concepts used to explain crack growth and propagation is tearing energy[58]. In natural rubber, the static cut growth is governed by a structure developed in the crystalline rubber around the tip as the cut grows. If the test piece is relaxed to zero stress, this structure will dissappear and further cut growth will occur on the next cycle.

It has been found by Thomas[56] that under static conditions cut growth at the tip of a razor cut test piece is given approximately by equation:

$$T^2 = Gs\,\Delta C \qquad (1\text{-}I)$$

ΔC = amount of cut growth/cycle

Gs = static cut growth constant which is between 1 and 3×10^{16} cgsunits

Tearing energy in dynamic strain is analogous with equation (1-I) which is

$$T^2 = Gd\,\Delta C$$

where Gd is dynamic growth constant which has a value of 2×10^{17} cgs units.

In contrast to a strain cystallising natural rubber, tearing in a vulcanisate of non-crystallising SBR occurs at constant deformation. The tearing energy for SBR has been studied by Lake and Lindley[57] based on the equation proposed by Thomas[56]:

$$T^4 = Gd \Delta C$$

Gd = dynamic cut growth constant which is 0.8×10^{28} cgs units

Temperature variation is known to have a considerable effect on SBR gum vulcanisates. The very large reduction of fatigue life correlates well with the increase in static cut growth rate measured over the same temperature[58].

1.5.3 FACTORS INVOLVED IN FATIGUE

The source of failure during fatigue was reported to arise from small flaws in the surface of the rubber and local inhomogenieties, caused by hard particles, or small abnormal cross-linking density within the vulcanisate.

Cracks formed by chemical attack, notably by ozone and oxygen also lead to failure.

1.5.2.1 EFFECT OF COMPOUNDING

Variations in compounding may alter fatigue life of a rubber specimen by affecting the molecular weight of the polymer and dispersion of the compounding ingredients[59]. The dispersibility of the compounding system will affect the uniformity of the cross-linking sites, thus the magnitude of local inhomogeneity will cause variations in strain within the specimen.

1.5.2.2 EFFECT OF THE VULCANISING SYSTEM

The effect of the vulcanising system is important since it is known that a high proportion of polysulphides to monosulphides cross-link provide a high fatigue resistance[60]. This is due to the polysulphide cross-links, as shown by the following mechanism[61]:

1 A network bond by polysulphide cross-links is more flexible than a mono- or disulphide cross-linked rubber. Therefore in the polysulphide network there is a better distribution of the applied stress, more than in the latter case.

2 Furthermore, polysulphide cross-links are known to break and reform during the fatiguing of the rubber, thus enhancing effect of the stress

distribution.

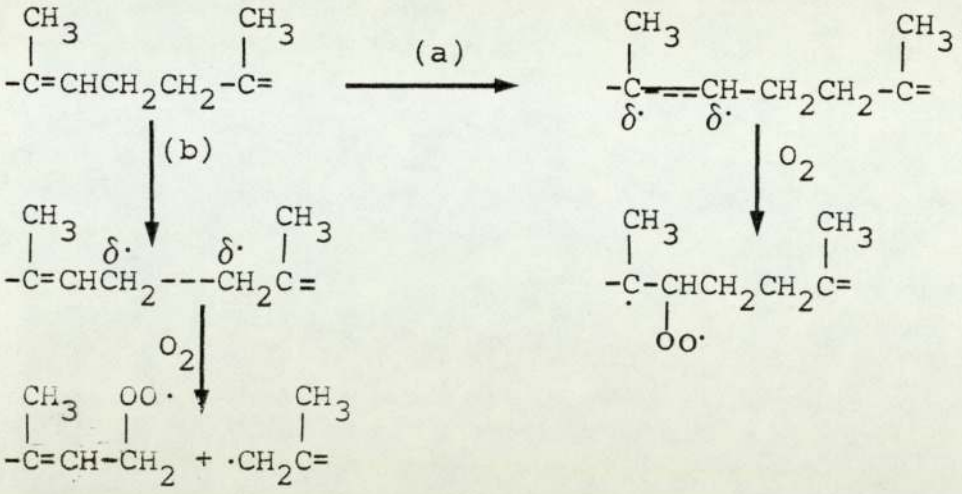
Thus polysulphide cross-linked rubbers have high fatigue lives compared to peroxide or radiation cured rubbers which are cross-linked by carbon-carbon bonds. TMTD sulphurless and EV systems, such as ZMBT/S cure, which have predominantly S_1 and S_2 cross-links are in between.

1.5.2.3 EFFECT OF ATMOSPHERE

The atmosphere surrounding the specimen which is being subjected to repeated deformation can affect the time, for example to failure to occur.

In vacuo, purely mechanical crack growth occurs and the time to fatigue failure is delayed. At atmospheric pressures and in the presence of oxygen, the rate of crack growth and fatigue failure is much faster[51].

The mechanism of the oxygen acceleration of fatigue failure is not yet known. However, it is thought that the strain at the tip of the growing crack activates the rubber molecule towards oxygen. It can be explained either by partially unpairing the electron of the C=C double bonds, or by giving the methylenic bonds, a free radical character[1]. These two processes are shown schematically below:



Scheme 1-12

Ozone can lead to the formation of macro cracks on the surface of the specimen and this will reduce the induction period before fatigue cracking begins. Ozone rupture polymeric chains, thus accelerated crack growth and shortening fatigue life[57].

The initiation of mechanical growth caused by oxygen is much lower than that caused by ozone, this growth in general is mechano-oxidative in nature[51].

1.6 ANTIFATIGUE AGENTS

Most effective antifatigue and antiflex cracking agents are compounds of the diarylamine or a mixture of diarylamine[1]. Diphenylamine itself has antiflex cracking activity but it is not technologically used due to its volatility. Some of its derivatives and in particular

the 4-alkoxy and 4-alkylaminodiphenyl amines are more effective, they are often used in combination with phenyl-ß-naphthylamine which itself gives a useful protective mixture. Most of the effective antiflex cracking agents either contain two functional groups, such as derivatives of aminodiphenyl amine, di-tert-butyl-hydroquinone have been reported to be capable of being oxidised to bifunctional materials.[1]

In contrast to thermal antioxidants, the most effective antiflex cracking agents are readily oxidisable compounds. The mechanism of the antifatigue activity of arylamine was not known until recently. It is now known that they are converted into nitroxyl radicals which are effective radical traps[65].

1.7 OZONE CRACKING

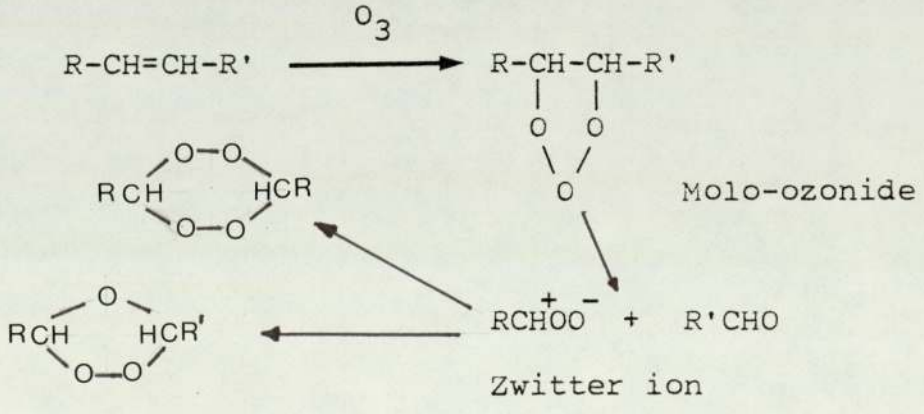
The very small concentrations of ozone within the atmosphere, at ground level, normally a few parts per hundred million, causes cracking of rubber components[20]. The cracks form on the surface of the rubber by direct chemical attack of ozone on the double bond. The by-products of ozone attack include dimeric peroxides, lactones, etc, which could cause further deterioration of the rubber by secondary reactions.

Ozone cracks occur perpendicular to the direction of the applied strain, in contrast to random crazing caused by oxygen attack.

1.7.1 THE MECHANISMS OF OZONE CRACKING

When a strained surface is exposed to ozone, cracks formation does not occur unless the strain exceeds a certain critical value. As the extension is increased above the critical strain, the number of cracks formed increases rapidly and the rate of cut growth becomes a function of strain.[1]

The reaction of ozone with the double bond is ionic and can be explained as outlined below[20]. Ozone attacks the double bonds of the polymer to give unstable molo-ozonide which rapidly rearranges to give one iso-ozonide[1,20].



In unstrained rubber, recombination of the Zwitter ion

and carbonyl compound can take place and the effect is to produce a protective skin on the surface of the rubber. This is the reason for the need for the critical strain. In strained rubber, this recombination is not possible and crack development occurs.

Chain scission could also take place by a series of secondary reactions involving the decomposition of the iso-ozonide and dimeric peroxide (formed from dimerisation of the Zwitter ion) giving rise to a variety of hydroperoxide acids and ketones[1]. It has been reported that ozone regeneration could also occur by reaction of the Zwitter ion with oxygen[63].

1.7.2 OTHER FACTORS AFFECTING OZONE CRACKING

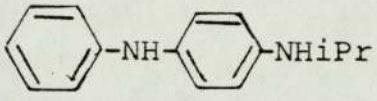
Some of the important factors which affect the rate of ozone cracking are:

Ozone concentration
Strain on the specimen
Chemical nature of the polymer
State of cure
Carbon black
Plasticiser content

1.8 ANTIZONANTS

The most effective antiozonants are the N,N'-disubstituted -p-phenylenediamines[72]. Comparison of the various -p-phenyldiamines have shown that N,N'-di-sec-alkyl derivatives are generally the best antiozonants[73-75]. The order of effectiveness of the dialkylphenylene diamines is para > ortho > meta. Secondary alkyl substituted-p-phenylene diamines are considerably more effective than the primary[1].

On the other hand,-4-isopropylaminodiphenylamine (4010 NA, Nonox ZA) is commercially important antiozonant.



4-Alkoxyaniline is also known to possess antiozonant activity, although of a lower order than the p-phenylene diamine[1].

1.8.1 THE MECHANISMS OF ANTIOZONANT ACTIVITY

The precise mode of activity of the diarylamines as antiozants is not yet clear. However, it is generally accepted that they could act by three modes.

1 The antiozonant scavenges the ozone, before the

ozone can attack the double bond - scavenging mechanism[66].

2 The antiozonants relink broken chains[68].

3 The antiozonants form a protective film on the surface of the rubber[67].

Waxes are known to protect the rubber component from ozone attack by forming a protective layer on the surface of the rubber[1]. This is good for static application, but for dynamic application, the wax layer cracks and the ozone crack is then very severe[69]. Combinations of chemical antiozonants and waxes are used commercially, these too are very effective only f static application. Arylamines are known to react with ozone giving amongst other products nitroso and nitro compounds. And ries et al[70] has reported these products to be present in extracted and exposed rubbers.

All the mechanisms discussed above could contribute towards the antiozonant activity. However, the scavenging mechanism might play a dominant role in the above process.

Recently, MRPRA[71] has reported that selenium containing arylamines are very effective antiozonants.

More effective than the commercial material being used at the moment. However, this work is still in the research stage.

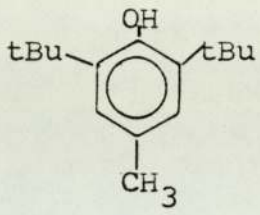
1.9 LOSS OF ANTIOXIDANTS BY VOLATILISATION AND BY LEACHING

Loss of antioxidants and antiozonants by volatilisation and leaching is one of the major problems in the rubber industry. The intrinsic activity of an antioxidant is mainly dependent on its chemical structure. However, in order to achieve maximum activity, the antioxidant has to remain in the polymer. If it is lost by simple volatilisation, leaching or migrating to the surface, the activity of the antioxidant will be very much reduced. Physical loss by volatilisation can be minimised either by increasing the molecular weight[76] or chemically binding to the polymer matrix (this will be discussed later). An increase in molecular weight of antioxidants reduces loss due to volatilisation[77-80]. Spacht et al[81] showed that increased sample thickness reduced the loss of the antioxidant due to volatilisation.

Increasing molecular weight however sometimes increases incompatibility of antioxidants with polymer and reduces its rate of migration to the surface[82,83]. In addition to increasing molecular weight, Plant and Scott[77] have

also shown that intra and inter molecular hydrogen bonding effects the compatibility and volatility of antioxidants in the polymer.

James and Widmer[83] have also studied the effects of volatility on a variety of phenolic and amine antioxidants. They have shown that certain phenolic antioxidants such as



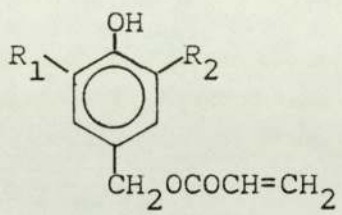
2,6-di-tert-butyl-4-methyl phenol (BHT), Mw = 220, were highly effective when assessed in a closed system but had quite poor performances in a circulating air oven as compared with higher molecular weight phenols. They also showed that N,N'-diphenyl-p-phenylene diamine (DPPD) has approximately the same molecular weight (260) as BHT, the former is 3100 less volatile than the latter. This was suggested to be due to the formation of intermolecular hydrogen bonds in DPPD resulting in lower volatility.

1.10 CHEMICAL BINDING OF ANTIOXIDANTS TO RUBBER LATICES

A potential solution to the problem of antioxidant loss from rubber and plastic is to bind the antioxidant to the polymeric network. This approach can be achieved by attaching the antioxidant to the rubber at a reactive

position at the latex stage or during compounding.

Amarapathy[85] has shown that vinyl antioxidants, as shown below, may be bound into natural rubber latex and that they behaved similarly to antioxidants added conventionally.

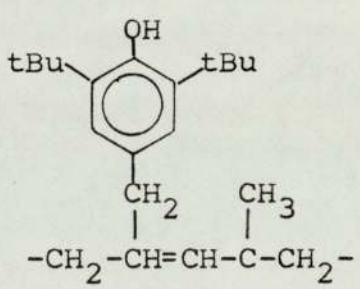


(a) $R_1=R_2=tBu$ (DBBA)

(b) $R_1=tBu$, $R_2=Me$

(c) $R_1=R_2=Me$

Amarapathy and Scott[85-87] demonstrated that phenols containing 4-methylene groups can also react with NR latex to produce a bound antioxidant:



However, the extent of binding of antioxidants of the above type was not high enough to produce latex masterbatches suitable for commercial use. In a subsequent investigation, Fernando[88] has shown that thiol containing antioxidants, such as 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan (BHBM) can also react with natural rubber latex using AZBN as initiator. The main

disadvantage of this technique is that AZBN and BHBM had to be dissolved in chlorobenzene prior to the binding reaction, due to the difficulty of forming an aqueous emulsion.

Kularatne et al[89] using the same antioxidant has shown that 70% of BHBM can be bound to natural rubber latex, as compared to a maximum of 20% in the case of the 2,6-di-tert-butyl-4-methyl phenol (TBC)[90].

Katbab and Scott[65,91,92] reported that 4-(mercapto acetamido)diphenylamine (MADA) reacted with natural rubber latex, leading to a substantial concentration of bound antioxidant and this rubber was shown to have superior ageing properties, compared to commercial antioxidants.

Scott and Tavakoli[92] successfully bound 3,5-di-tert-butyl-4-hydroxybenzyl carboxy ethyl sulphide (BTPA) and 3,5-di-tert-butyl-4-hydroxybenzyl carbomethyl sulphide (BTGA) into natural rubber latex.

The chemistry of the free radical chain reaction of olefin-mercaptan yield products of anti-Markovnikov configuration, first studied by Kharasch et al[92-94]. The reaction involves three essential steps[94]:

(1) Mercaptyl radicals can be generated from mercaptan by a variety of oxidising agents such as hydroperoxides and mild oxidising agents, eg iodine solution by an oxidant upon mercaptan.

(2) Addition of mercaptyl free radical to olefin molecule.

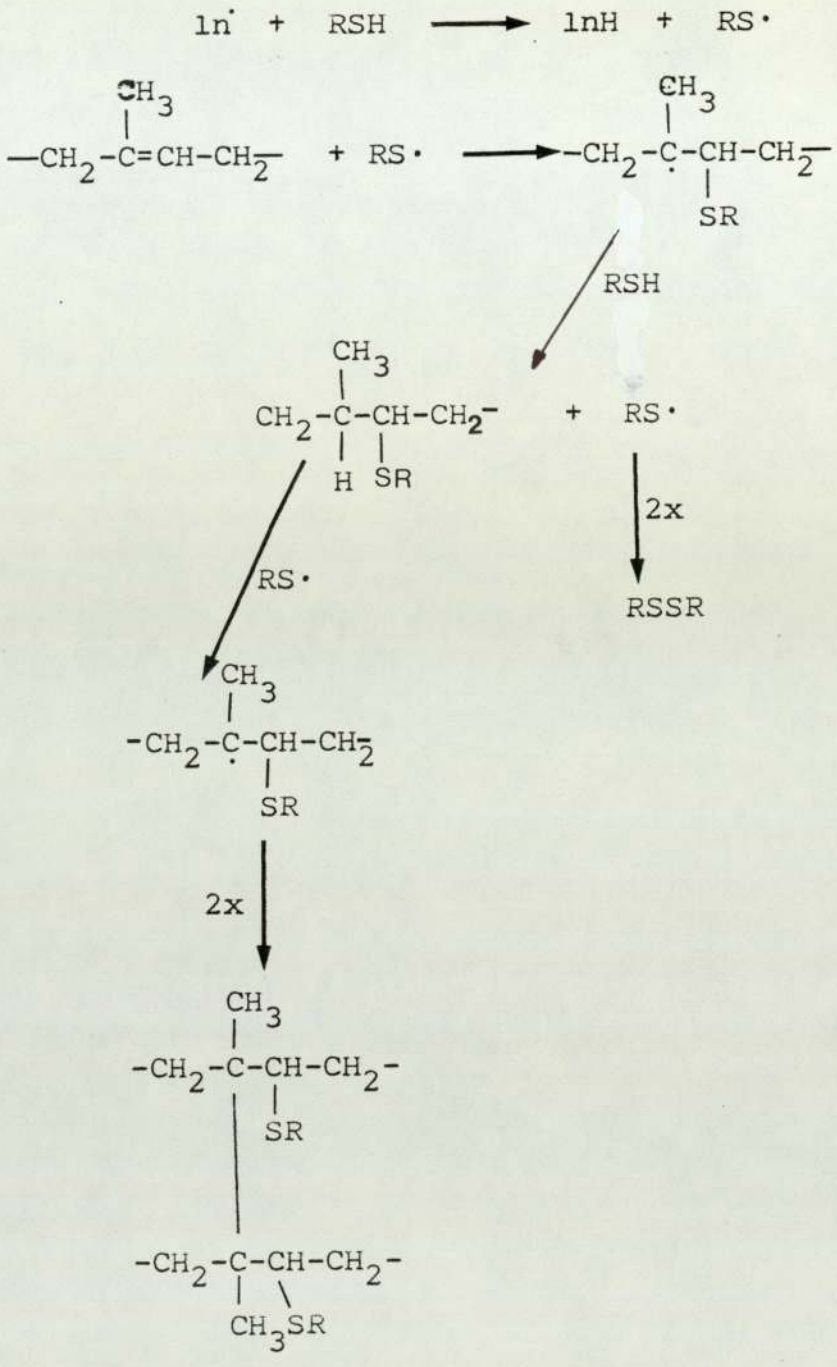
(3) Interaction of the derived free radical formed in the second step and the molecule of mercaptan completes the cycle, at the same time regenerating the chain initiating mercaptyl free radical.

$$RSH + OX \longrightarrow OXH + RS\cdot$$

$$R'CH{=}CH_2 + RS\cdot \longrightarrow R'(RSCH_2)CH\cdot$$

$$R'(RSCH_2)CH\cdot + RSH \longrightarrow R'CH_2CH_2SR + RS\cdot$$

Their reaction is of great importance in both rubber and rubber modified plastics because the grafting of antioxidants to the rubber backbone is achieved by a free radical process involving addition of thiyl radicals to the double bonds. The reaction below shows the steps involved in the reaction between natural rubber and a mercaptan.



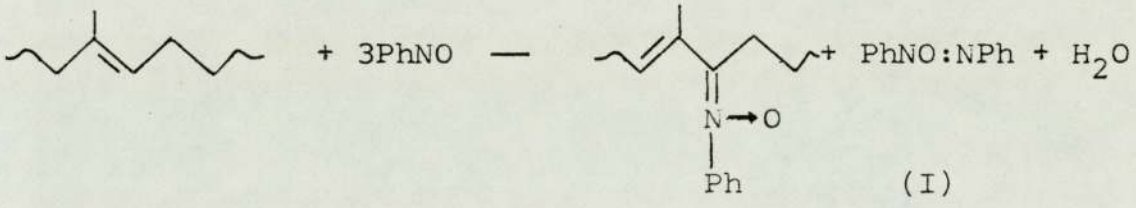
Scheme 1-14

Ajiboye et al[95] reported that 4-mercaptoacetamido diphenylamine (MADA) can be reacted with nitrile rubber to produce a substantial yield of bound antioxidant.

It was also shown that rubber containing bound antioxidants such as TBC, BHBM, BTGA, BTPA and MADA all gave superior stability after solvent and detergent washing compared with those containing a conventional antioxidant[85,89,91,95].

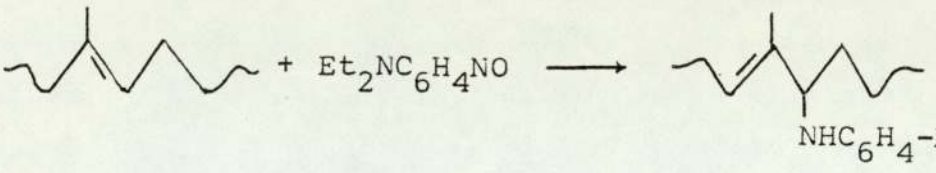
1.11 REACTION OF RUBBER WITH ANTIOXIDANTS DURING COMPOUNDING AND VULCANISATION

Studies at NRPRA[96,97] have shown that by reacting antioxidants containing a nitroso group with rubber during vulcanisation a rubber bound antioxidant results. Previous studies[98,99] had shown that reaction of nitrosobenzene with rubber in benzene solution would produce an iso-rubber nitrone as follows:



(I)

Cain and co-workers[96] have used N,N-dialkyl-p-nitroso-anilines, showing that the latter can be bound to rubber containing α-methylene hydrogen. In model compounds, 2-methyl-2-pentene was found to react with N,N-di-ethyl-p-nitrosoaniline. It also reacts with natural rubber in a similar manner during vulcanisation.



(II)

In a subsequent investigation[100] they showed that 4-nitrosoaniline and 4-nitrosophenol can also react with rubber during vulcanisation to produce rubber bound antioxidants. Nitrosoamine when reacted with rubber gave bound antioxidants which have the same structure as sec-alkyl aminodiphenylamine.

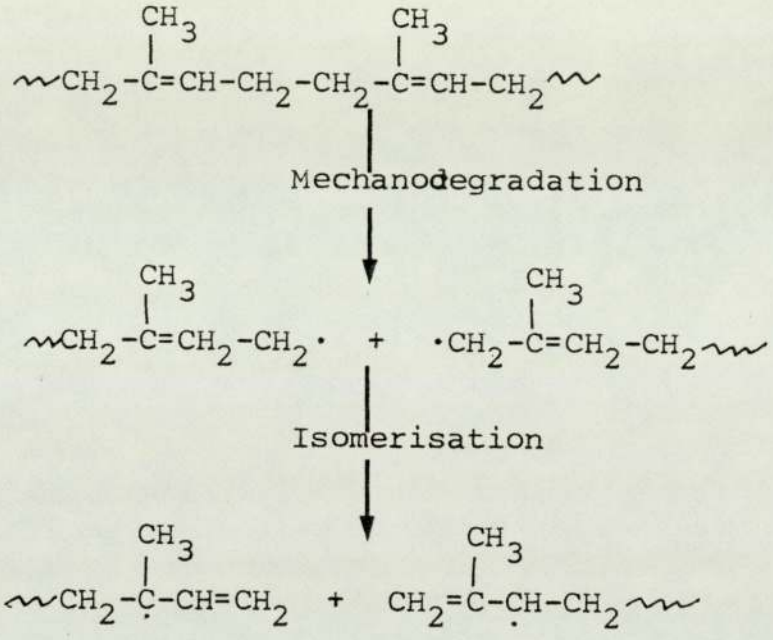
The rubber bound antioxidants obtained were compared with N-isopropyl-N'-phenyl-p-phenylene diamine (IPPD) using an oxygen absorption technique. The activity of the conventional antioxidant is essentially removed after solvent extraction, while the activity of the rubber bound antioxidant is almost unaffected.

1.12 MECHANOCHEMICAL REACTION OF ANTIOXIDANTS DURING PROCESSING

Mechanochemistry involves reactions for which the energy for initial radical formation is supplied mechanically. Mechanical forces acting on polymers are concentrated on separate positions of the chains as a result of non-uniform distribution of the internal stresses. Critical stresses therefore may develop which rupture chemical covalent bonds. This process leads to

the formation of active terminal free radicals, which are very reactive towards the oxygen.

In the case of NR, the bond which is most likely to be ruptured is $-CH_2-CH_2-$ bond since its dissociation is lowered by resonance energy of the alkenyl radical produced in the process.



Scheme 1-15

The primary radicals may undergo isomerisation. This has been observed for polyethylene[102], polystyrene[103] and natural rubber[103].

Mechanochemical free radicals were used to produce rubber bound antioxidants during premixing and vulcanisation stages with the rubbers.

$$R\cdot + nM \longrightarrow R\text{-}M_{n-1}M$$

Scott et al[104-108] reported that three thiols (BHBM, MADA and MPDA) became chemically bound to the polymer during mixing in the absence of oxygen. The reaction occurs in two stages, an initial mechanoradical process and secondary hydroperoxide initiated reaction. The antioxidant can be bound chemically to the polymer in high concentration, which is in the region of 10-20% from the original concentration of 10, 20 and 30%. The rubber bound antioxidants show superior ageing properties after extraction, compared to conventional antioxidants.

1.13 OBJECT AND SCOPE OF THE PRESENT WORK

In order to retard oxidation and improve performance antioxidants are normally incorporated into rubbers, by physical blending together with other additives prior to vulcanisation.

A deficiency of rubber made in this way when they are subjected to high temperatures is the leaching of antioxidants which leads to rapid deterioration of the depleted rubber.

This is a major problem in applications such as rubber threads, gloves, hot water bottles, apperel interlinnings and rubber used for medical goods which are frequently subjected to washing and/or sterilisation. One possible way of overcoming this problem is to chemically attach the antioxidant to the rubber.

The present work is a continuation of earlier studies by Fernando[88] and Kularatne[90] using a masterbatch technique which concentrates of bound antioxidants are added to rubber at low concentrations. This technique is economical since only a small amount of latex is required in the reaction, to produce a substantial amount of bound antioxidant. The antioxidants used for these experiments were phenols and amines,

containing thiol functional groups.

The project is also concerned with an investigation of the problem of the non rubber materials which have been shown to cause a low yield of adduct during the reaction of BHBM. The alternative use of styrene butadiene rubber will also be examined.

The last part of the project is concerned with the study of the mechanism of the BHBM binding reaction in order to elucidate the observations from the latex reaction.

CHAPTER TWO

THE SYNTHESIS AND THE TECHNOLOGICAL EXPERIMENTS

2.1 MATERIALS

2.1.1 NATURAL RUBBER LATEX

Centrifuged natural rubber latex preserved with a high concentration of ammonia was supplied by H W Symington (Qualitex A).

2.1.2 DEPROTEINISED NATURAL RUBBER LATEX

The deproteinised natural rubber latex preserved with ammonia, used in this experiment, was obtained from MRPRA. The latex was stabilised with a non-ionic surfactant, texofor FN30 (alkyl phenol ethoxylate), the latex had a total solid content of 56.6%. The nitrogen content was about 0.02%.

2.1.3 STYRENE BUTADIENE LATEX

The styrene butadiene latex was obtained from International Synthetic Rubber Company (ISR), having the following specifications:

	%
Total solid content	40%
pH	9-10
Particle size	650-750 A^{o}
Soap coverage	40%
Styrene-butadiene	25/75
Soap type	Potassium aleate
Residual styrene	0.1%
Antioxidant	None
Sodium diethyl dithiocarbamate	Trace
Sodium polysulphide	Trace

2.1.4 NATURAL RUBBER SMR-5L

SMR-5L was obtained from Dunlop.

2.1.5 CIS-POLYISOPRENE

Cis-polyisoprene (Nat-Syn 2200) was supplied by Goodyear.

2.1.6 COMPOUNDING INGREDIENTS AND ANTIOXIDANTS

Chemical	Supplier
Permanax WSP	Imperial Chemical Industries
Permanax IPPD	"

N-(cyclohexyl-2-benzothiazyl)-sulphenamide	Monsanto Chemicals
Zinc oxide	Amalgamated Oxides Ltd
Sulphur	Anchor Chemicals
Stearic Acid	
Potassium oleate	Fisons Chemicals
Texofor FN-30	IBM Chemicals
Superase	Pfizer Ltd

2.1.7 OTHER CHEMICALS

Chemical	Supplier
Tertiarybutyl hydroperoxide (70%)	BDH
Tetraethylene pentamine	Aldrich Chemicals
3,5-Ditertiarybutyl phenol	"
Paraformaldehyde	"
Potassium tertiary butoxide	"
Hydrochloric acid	BDH
Paraformaldehyde solution (37% v/v)	"
p-Amino diphenyl amine	Aldrich Chemicals
Thioglycollic acid	"
p-Xylene	Fisons Chemicals

2.1.8 STRIPPING AND COAGULATION OF STYRENE-BUTADIENE LATEX

The SBR latex was stripped, coagulated and extracted as follows in order to remove residual styrene.

2.1.8.1 STRIPPING OF SBR LATEX

The SBR latex was stripped to remove the residual styrene monomer and other non-rubber materials which are known to interfere with the grafting reaction[109].

SBR latex (600 ml) was poured into a one neck, two litre flask connected to a vacuum pump, via 2 sets of liquid nitrogen traps.

The flask was placed in a water bath and the temperature was raised slowly to reach around 60°C, and kept constant for 4-8 hours. The latex was magnetically stirred throughout the whole period of stripping.

After the above period, the flask was allowed to cool and SBR stripped latex was removed and kept in a bottle until required.

2.1.8.2 COAGULATION OF SBR

SBR latex was coagulated with 10% sulphuric acid. The coagulated rubber was soaked and washed several times with water. The coagulum was sheeted on to a 12" laboratory two roll mill, washed several times with water to remove excess acid trapped in the coagulum. The sheet was then dried in a vacuum oven at 40°C. The rubber obtained was extracted with acetone for 48 hours in a soxhlet extraction apparatus under nitrogen, dried in a vacuum oven and then stored in a vacuum desiccator until required.

2.1.9 EXTRACTION OF RUBBER

2.1.9.1 EXTRACTION OF RUBBER BEFORE VULCANISATION

The grafted and ungrafted rubber latex was coagulated with 1% formic acid and the coagulum was sheeted into a thin sheet and washed several times to remove the excess of acid. The rubber was dried in a vacuum oven (40°C), the dried sheet was wrapped in aluminium foil and continuously extracted with acetone for 48 hours, to remove the unreacted antioxidants, non-rubber materials and also other organic by products, which were either present in the latex or formed during grafting reaction. The rubber obtained was kept in a vacuum desiccator to be used in the following work.

2.1.9.2 EXTRACTION OF RUBBER AFTER VULCANISATION

In the case of the assessment of bound antioxidant after vulcanisation, the vulcanisate (prepared according to section 2.2.1) was extracted with azeotrope mixture for at least 90 hours. The solvent used in extraction was azeotrope mixture which has the composition as shown in Table 2.1.

Table 2.1 Composition of the azeotropic mixture

Solvent	Amount in ml
Methanol	42
Acetone	110
1,1,1-trichloroethane	60

Samples after extraction were removed from the soxhlet, dried in a vacuum oven and stored in a desiccator until required.

2.2 COMPOUNDING

Graft extracted or graft unextracted rubbers were mixed with the compounding ingredients on a 12"

laboratory two roll mill. The friction ratio employed during compounding was 1:1. Compounding of natural rubber and polyisoprene samples was carried out using the following formulation:

Natural rubber	100 g
Zinc oxide	5 g
Stearic acid	3 g
Sulphur	2.5 g
CBS	0.6 g

The compounding ingredients for SBR are as follows:

SBR	100 g
Zinc oxide	5 g
Stearic acid	3 g
Sulphur	2.0 g
CBS	1.0 g

Sulphur was the last item to be added in to the rubber after all the ingredients had been incorporated. The total compounding time, usually five minutes, for natural rubber, and eight minutes, for SBR.

2.2.1 VULCANISATION OF RUBBER

The vulcanisation of the compounded samples was carried

out in a stainless steel mould of cavity dimension 13.5 x 13.5 x 0.018 cm in order to produce a vulcanised film of 0.018-0.023 cm thickness. The compounded rubber was first passed through a tight nip on a 12" laboratory two roll mill to make a thin sheet and about 5 g was placed in a clean cavity of preheated mould. The mould was placed between two plates of a steam heated press. The press was momentarily closed and opened to release any entrapped air. A pressure of 50 tons on an eight inch ram was applied and the temperature of the press was maintained at 140^{o}C for 30 minutes for natural rubber and 45 minutes for SBR. The mould was taken out from the press and the samples were removed and cooled down. The samples were wrapped in aluminium paper and stored in a vacuum desiccator until required. The samples used for infra-red and oxygen absorption were cut from the centre of the vulcanised film to eliminate edge effect.

2.3 ESTIMATION OF CONCENTRATION OF BOUND ANTIOXIDANTS

2.3.1 ESTIMATION OF CONCENTRATION OF ANTIOXIDANT REACTED WITH NR LATEX AND POLYISOPRENE RUBBER

Infra-red spectroscopy was used to determine the amount of antioxidant bound to the rubbers. This technique has been used previously[110-112] by several

workers for the estimation of the amount of bound antioxidant containing hydroxyl or carbonyl groups, and other groups. The infra-red spectra of the transparent vulcanised films with thickness of 0.18-0.23 mm were obtained and the following procedure was used to determine the amount of bound antioxidant.

2.3.1.1 CALIBRATION CURVE FOR BHBM

The dried extracted rubber (100 g) was mixed with a known amount of BHBM (ie 0.25, 0.5, 0.75, 1 and 2%) and also with other vulcanising ingredients on a 12" laboratory two roll mill. The samples were vulcanised into a thin film (section 2.2.1) and their infra-red spectra were obtained. The intensity phenolic OH peak was proportional to the amount of added BHBM and was measured as a function of the peak height. To overcome the errors due to the sample thickness, an invariant peak at 2720 cm^{-1} which is a characteristic for NR and polyisoprene was selected. For SBR the reference peak is at 1490 cm^{-1}. The absorbance due to the functional group and absorbance due to invariant group (peak at 2720 cm^{-1}) was calculated using the base line technique[111,113]. Thus the hydroxyl index for a given concentration of BHBM is the ratio of absorbance of the OH group (at 3610 cm^{-1}) to that of the reference peak (at 2710 cm^{-1}).

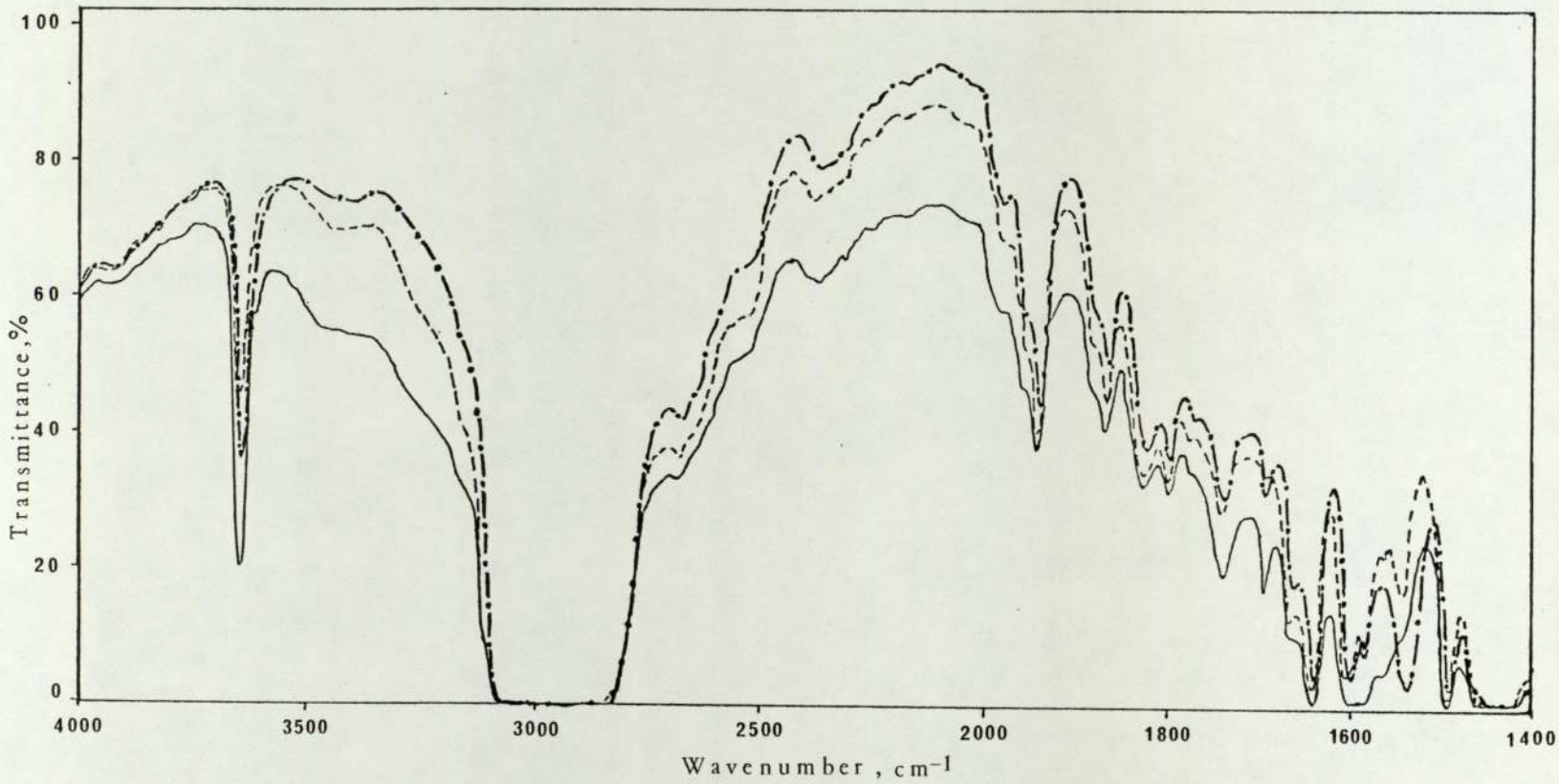


Fig 2.1 Infra red spectra of boundBHBM in SBR

— 1% BHBM added; -·- bound unextracted, --- bound extracted

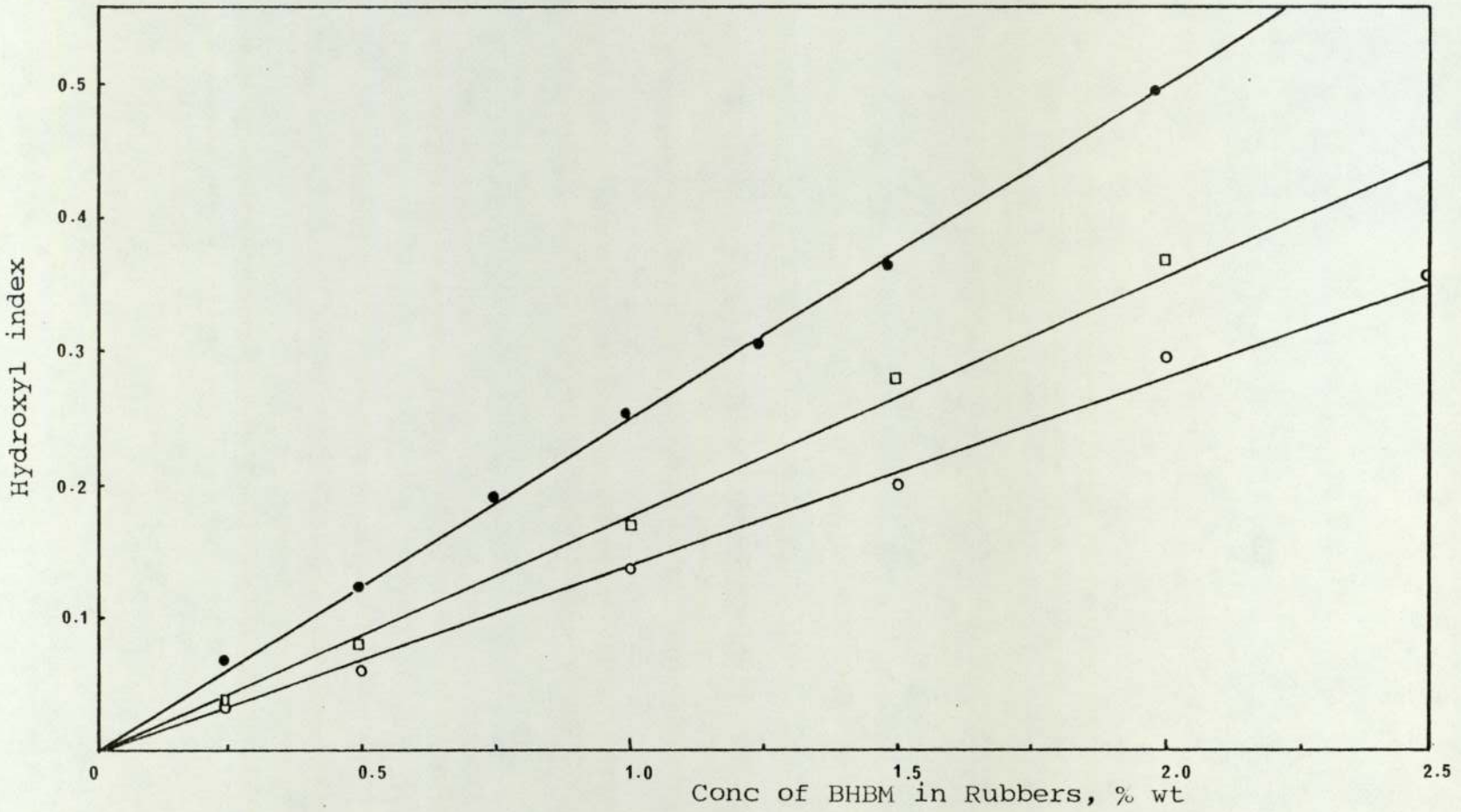


Fig 2.2 Infra-red calibration curve for BHBM in rubbers

● NR, □ DPNR, O SBR

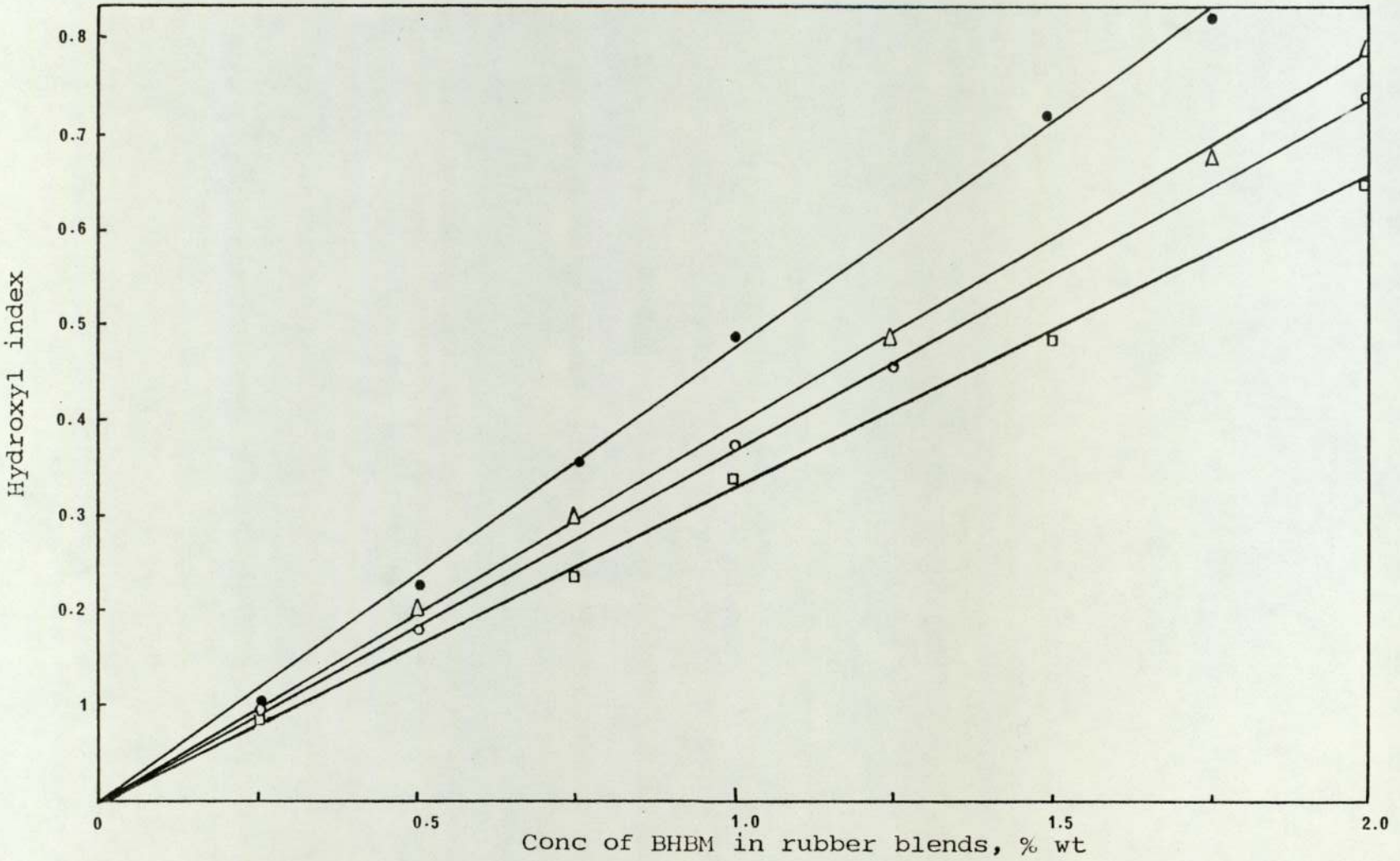


Fig 2.3 Infra red calibration curves for BHBM in various ratios of blends of SBR to NR

● 3:2 △ 1:1 ○ 2:3 □ 1:3

$$\text{Hydroxyl group index} = \frac{\text{Absorbance of the OH peak}}{\text{Absorbance of the reference peak}}$$

The hydroxyl index obtained could then be plotted as a function of concentration of antioxidant added. Typical infra-red spectrum of bound BHBM into SBR is shown in Fig 2.1.

The calibration curve for BHBM in NR, DPNR and SBR are shown in Fig 2.2. The calibration curve for BHBM in the blends of SBR and NR is shown in Fig 2.3.

2.3.1.2 CALIBRATION CURVE FOR MADA

100 g of rubber with a known quantity of MADA (ie 0.25, 0.5, 0.75 and 1%) was mixed for 10 minutes in the torque rheometer. The processed rubber was then passed through a 12" laboratory two roll mill to make a thin sheet.

The preparation of film for infra red measurement and oxygen absorption is described in section 2.2.1.

In the case of 4-mercaptoacetamido diphenyl amine (MADA) the ratio of the intensities of secondary amide at 3280 cm^{-1} due to the antioxidant to that of the

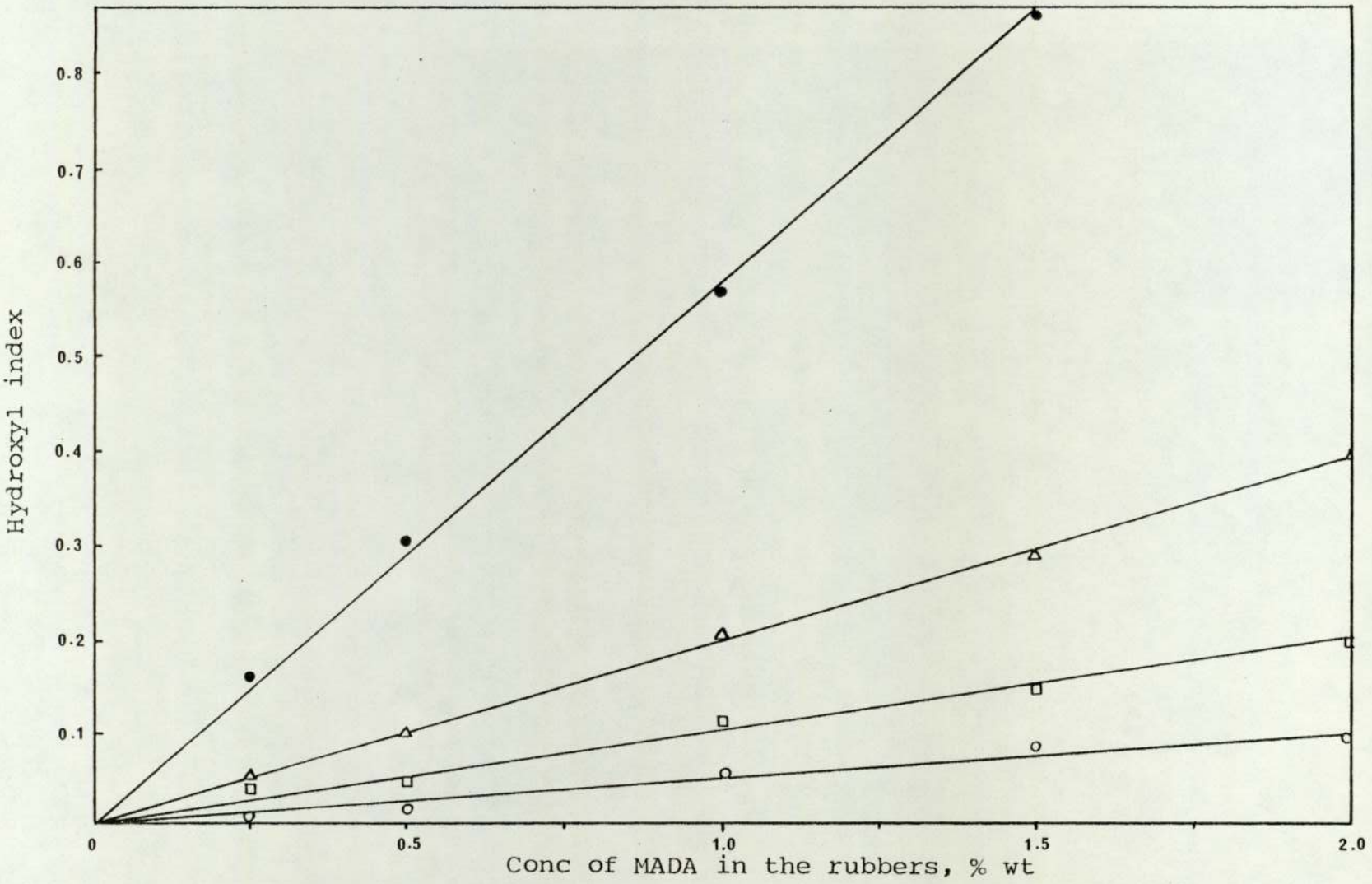


Fig 2.4 Infra red calibration curves for MADA in the rubbers

● SBR △ NR □ DPNR ○ PI

reference peak at 2720 cm^{-1} due to NR and DPNR were measured using the base line technique:

$$\text{Secondary amide index} = \frac{\text{Absorbance of the secondary amide peak}}{\text{Absorbance of the reference peak}}$$

In the case of SBR, the intensities of secondary amide peak at 3280 cm^{-1} and peak at 2720 cm^{-1} was used as a reference peak. The amount of bound MADA in polyisoprene was determined using the peak at 1595 cm^{-1} due to the aromatic ring of antioxidant and a peak at 2720 cm^{-1} were measured.

The calibration curve was obtained by plotting secondary amide index for NR, DPNR, SBR and PI versus concentration of MADA (Fig 2.4).

2.3.1.3 DETERMINATION OF THE PERCENTAGE OF BOUND ANTIOXIDANT AFTER VULCANISATION

Percentage of antioxidant bound after vulcanisation was determined by infra-red spectroscopy on films 0.18-0.23mm thickness. The infra-red spectra of the vulcanisates both before and after extraction with azeotropic acid mixture described in section 2.1.10.2 were run on the same chart paper using the same

instrument setting each time. The absorbances of the appropriate functional group, such as hydroxyl for phenolic antioxidants and secondary amine or aromatic groups for MADA, to that of the reference peak at 2720 cm^{-1} for NR, DPNR, PI and 1490 cm^{-1} for SBR were measured.

2.4 MONSANTO OSCILLATING DISC RHEOMETER

The Monsanto rheometer was used to assess the curing behaviour of NR, DPNR, SBR and PI gum stocks containing different proportion of antioxidants. This instrument consists of an oscillating disc surrounded by rubber at vulcanisation temperature and the change in applied torque with time is measured.

Typical Monsanto rheograph for the vulcanisation of rubber is shown in Fig 2.5.

As shown typically in Fig 2.5, there is an initial drop in torque due to the decrease in the viscosity of the rubber as its temperature rises. This drop then flattens out until the start of cross-linking giving an induction period. This is then followed by an increase in viscosity, indicating that cross-linking is taking place. After a certain period of time, the viscosity reaches a maximum and this may further

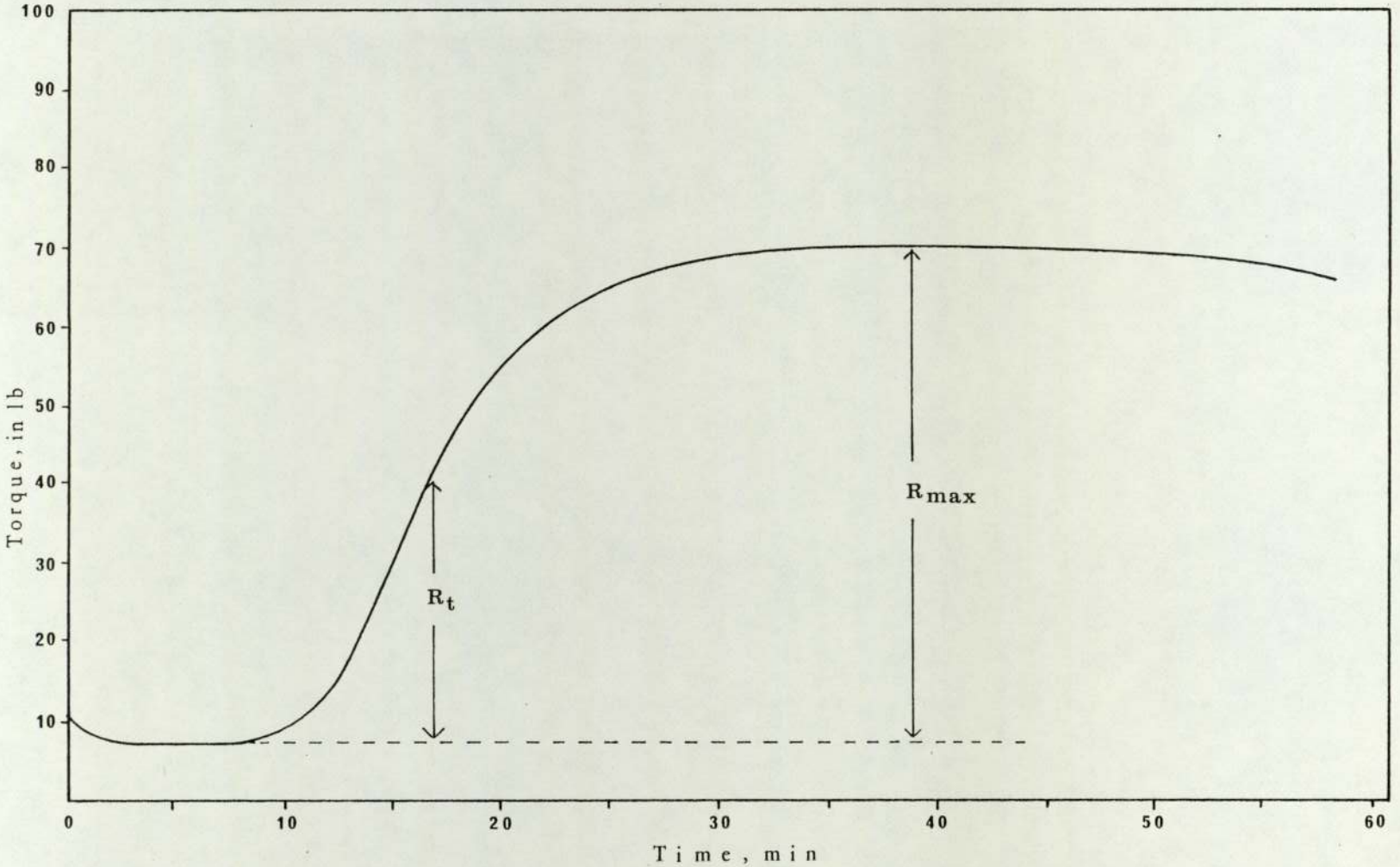


Fig 2.5 Monsanto rheograph for the vulcanisation of rubbers

increase or decrease indicating secondary vulcanisation or reversion respectively at longer times. Reversion is due to the breakdown of the cross-links. The scorch time is normally quoted at an arbitrary number of units of torque above the minimum viscosity (see Fig 2.5).

2.5 TECHNOLOGICAL AGEING TESTS

2.5.1 OXYGEN ABSORPTION

The assessment of antioxidant activity of bound and unbound antioxidants (before and after extraction) were carried out in an oxygen absorption test. This provides very useful data on inhibition as measured by induction period (IP) and oxidisability at the end of the IP.

The rate of oxygen absorption depends on the rate of oxygen diffusion into the rubber and the rate of reaction of oxygen with the rubber. To eliminate the oxygen diffusion variable, the sample used should have the same weight and thickness[114-119] throughout the experiment.

The results were affected by factors such as the amount of oxygen absorbed, the curing system, the temperature of the test, the pressure and concentration

of oxygen.

Oxygen absorption tests were carried out in a pyrex test tube of approximate total volume of 100 ml with a B24 quickfit socket and a cone attachment. The apparatus has been described by previous workers.

The reaction tube containing the samples was flushed with oxygen for several minutes and immersed in a thermostated oil bath. As oxygen was absorbed by the sample, a pressure difference set up between the tubes. The pressure variation was directly recorded as the oxidation curves on a Leeds and Northrup spectrometer recorder.

The pressure oxidation was measured through a transducer Pye Ether model up 3, $\pm$ 5 psi range. The experiments were carried out in a manner that 1 ml of oxygen absorbed by the sample was equivalent to 20 division of chart.

2.5.1.1 PROCEDURE

An accurately weighed specimen (0.3 g) of thickness 0.18-0.23 mm was placed on glass support, so that oxygen was able to diffuse to both sides freely. The glass support with the sample was inserted in the absorption

tube and was purged with oxygen. The apparatus was assembled in the thermostated bath at 70°C and was then connected to the transducer. The ballast tube was already positioned and the system was allowed to equilibrate for 5 minutes so as to reach the temperature of 70°C. The samples were then left to absorb oxygen and the maximum value of oxygen that could be absorbed at this voltage, was, five mls. Hence the required oxygen was added through a Luer needle until the desired pressures were established. The duration of the oxygen absorption of the sample. At the end of the experiment, the samples were removed.

2.5.2 STRESS RELAXATION

Stress relaxation may be carried out either intermittently or continuously. In intermittent stress relaxation the sample is stretched for a short period to measure stress and maintained in the unstretched state during most of the ageing. In the unstretched condition, both cross-linking and chain scission occur which contribute to the stress when the sample is stretched again.

In continuous stress relaxation, the sample is stretched continuously at a given extension. The method of stress relaxation is based upon the kinetic

theory of the rubber elasticity. According to this theory the stress of an extended sample is given by the following equation:

$$f = N K T Ao (\lambda - \lambda^{-2})$$

where

$l/lo = \lambda$

f = force exerted by an extended rubber specimen

N = number of stress supporting network chains per unit volume

K = Boltzmann's constant

T = absolute temperature

Ao = unstretched cross sectional area

= ratio of stretched and unstretched length of the specimen

If parameters such as T, Ao and are kept constant, then the stress is proportional to the N and if during degradation a number (NO-N) of the original NO chains present are broken, the ratio of the final tension f to initiation tension fo is

$$\frac{f}{fo} = \frac{N}{NO}$$

Therefore, during thermal degradation of vulcanised rubber, as the chain reaction occurs, the decay in

stress is a direct measure of the degradation of the vulcanisate network.

2.5.2.1 PROCEDURE

The continuous stress relaxation of vulanisates was followed using the Wallace Shawbury self recording age tester. This equipment consists of six cells in an ageing oven. The cell temperature is adjusted at 100 $\pm$ 2^{o}C due to 1 cu ft per hour of air flow.

Samples were cut from vulcanised sheets using the MR100 apparatus test cutter.

The samples were fixed between two fixed grips. The apparatus was then placed in a thermostatically controlled ageing oven at 100 $\pm$ 2^{o}C with 1 cu ft/hr air flow. The samples were extended and zero time marked on the chart. The change in force applied by the spring is recorded on the paper which is wrapped around a vertically mounted drum. The specimen was then allowed to relax under stress.

The samples used in this experiment have a thickness of 0.7-0.8 mm.

2.5.3 FATIGUE RESISTANCE OF VULCANISATES

2.5.3.1 APPARATUS

The Monsanto Fatigue to Failure Tester has been developed to provide a simple reproducible method of determining the fatigue life or cut growth properties of cured stocks. Dumbell samples are subjected to a repeated rapid strain cycle.

The fatigue cycle consists of a single extension and a single relaxation of rubber specimen. The rubber being extended for the first quarter of the cycle, relaxed over the next quarter and held at zero strain for the remaining half of the cycle. The number of cycles is recorded automatically. The maximum applied strain may be varied by changing the drive cams.

2.5.3.2 PROCEDURE

(a) Curing of the sample

Compounds are moulded as rectangular sheets (2.2 x 7.6 x 0.15 cm) with a beaded edge. Each sheet required about 55-60 g of rubber. Samples were first sheeted out on a laboratory two roll mill and were placed in the cavity of the mould. The mould was

assembled and placed between the platens of a steam heated press, which already reached the required temperature. The pressure applied was 50 tons on an 8" ram, used to give the required thickness. At the end of cure time, the mould was removed and the vulcanisates were placed in a bath of cold water.

(b) Sample mounting

Individual dumbell samples are cut at right angles to the grain using a BS type 'E' dumbell cutter. Samples were mounted at zero strain. At 200% strain, the major axis of the drive cams had to be horizontal and coincided with the horizontal line on the lower carriage. Each sample holder was adjusted so that zero strain was obtained when samples were mounted. The adjustment of each of the sample holders was done by inserting the 6 cm long calibration rod between the upper and lower shackles and adjusting the dumbell until a snug fit was obtained. After the machine had been run for 1000 cycles, the power was turned off and the drive cams were set for zero extension by adjusting each upper shackle with the thumb nut so that when the lower shackle was raised, a slight bow appeared in the sample. Then the machine was run and fatigue life was recorded as the number of cycles to failure. Where single comparisons are made, and the moduli of the stocks are nearly equal, test can be conducted at a

single extension (normally 100%, cam 14).

2.5.3.3 PRESENTATION OF RESULTS

The fatigue to failure results for NR were expressed in terms of the Japanese Industrial Standard (JIS) average[135]. This average is obtained from the highest four readings for the samples tested using the formula:

$$\text{JIS average} = 0.5A + 0.3B + 0.1C + 0.1D$$

where A,B,C,D are the fatigue lives which $A > B > C > D$.

The JIS average is biased towards the high readings however this standard is used because any small defect on the surface of the rubber test piece will drastically reduce the fatigue life and give an erroneous result.

The results for SBR were expressed as the median value. This is due to the greater scattering of results from SBR vulcanisates.

2.5.4 OZONE RESISTANCE OF RUBBER VULCANISATES

2.5.4.1 APPARATUS

Ozone resistance was carried out by the use of a Hampden Shawbury Ozone test cabinet. The cabinet consists of a closed dark test chamber, with thermostatically

controlled temperature. Purified and filtered air is ozonised at a constant temperature by exposure to ultraviolet light. Ozonised air then led into the chamber and recirculating into the cabinet through a lower unit. The test samples in the form of strips are stretched to the required degree in test piece holders and hung from a mobile test piece carrier inside the chamber which is moving at a constant speed to ensure that all test pieces are subjected to identical conditions of exposure. The concentration of ozone (0-140 pphm) is measured by the ozometer which is connected to the chamber. Ozonate Model OZT-2 was used for this purpose. The principle of operation of the Ozonate is that of bubbling air containing ozone through a buffered solution of potassium iodide (KI), made up according to the following formulation:

Potassium iodide	1.500 $\pm$ 0.025 g/l
Sodium monohydrogen phosphite (anhydrous)	1.500 $\pm$ 0.025 g/l
Phosphite di-hydrogen phosphate (anhydrous)	1.400 $\pm$ 0.025 g/l

The ozone oxidises the KI to I_2 according to the following reaction:

$$2KI + O_3 + H_2O \longrightarrow 2KOH + I_2 + H_2O$$

The I_2 effectively conducts the current through the solution by being reduced to I^-, at the cathode and reoxidised back to I_2 at the anode.

$$I_2 + 2e \longrightarrow 2I^-$$

at the cathode:

$$2I^- - 2e \longrightarrow I_2$$

To prevent the iodine reduced at the anode, being recirculated and giving erroneous results, the iodine is conveniently trapped at the anode by making the latter a mercury electrode.

2.5.4.2 PROCEDURE OF OZONE TESTING

The samples are rectangular, size 1-1.2 cm 0.025 cm thickness and 7 cm long, cut from vulcanisate sheets.

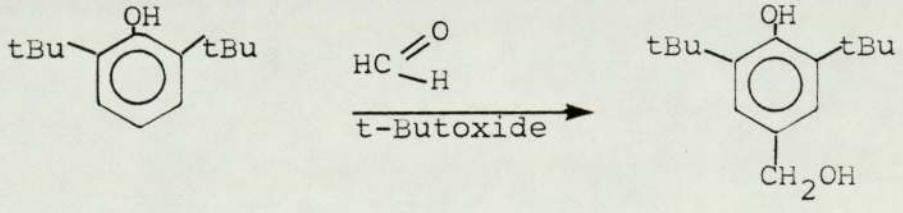
Test pieces were stretched to the required length (5 cm) and clamped tightly. The upper clamp was suspended from a hook in the test chamber roof and the cabinet was closed. The test pieces were exposed to ozone at 25 pphm and 25°C for different periods of time. After exposure, the surface appearance of the

test pieces was studied, under a magnifying glass (5x) according to BS903 [137]. The samples were graded as follows:

Grading	Surface Appearance of the Samples
1	No cracks
2	Cracks just seen when magnified five times
3	Cracks seen under the naked eye
4	Severe cracks more than 1 mm in length
5	Sample broken

2.6 SYNTHESIS AND CHARACTERISTICS OF ANTIOXIDANTS

2.6.1 PREPARATION OF 3,5-DI-TERTIARY-4-HYDROXYBENZYL ALCOHOL[119,139,140]



Scheme 2.1

53.3 ml (0.140 moles) of 7.5% solution of formaldehyde in tertiary butyl alcohol, 50 ml of a 500 g/l solution of 2,6-di-tertiary-butylphenol in anhydrous tertiary-

and 14m of tBuOK in soln(50g in 1000ml tBuOH)
butyl alcohol were mixed at 15-20°C and stirred with a mechanical stirrer under a continuous stream of N_2 for about 30 minutes until the solution changed colour to reddish colour. The reaction mixture was poured into a mixture of excess ice water and allowed to be left in the refrigerator overnight. The two layers were formed the upper layer solidified. The solid was filtered and washed several times with water. The solidformed was washed many times with hexane until yellow crystals formed. The crystals were recrystallised with chloroform and hexane. The white crystal was determined. The melting point of the white crystalline product was 135-137°C (lit 137°C).

IR DATA

Free phenolic OH	3560 cm^{-1}
Hydrogen bond OH	3500 cm^{-1}

NMR DATA

Aromatic proton	2.9 singlet
Phenolic proton	4.9 singlet
Methylenic proton	5.5 singlet
Tertiary proton	8.6 singlet

ANAL DATA

for $C_{15}H_{24}O$, C = 81.8%, H = 10.9%

found, C = 82.1%, H = 10.4%

MASS SPEC

Highest m/e = 236 for the fragmentation pattern (see section 4.3.1.4.

2.6.2 PREPARATION OF 2,6-DI-TERTIARY-BUTYL-4-HYDROXY-BENZYL CHLORIDE

2,6-Di-tertiary-butyl-4-hydroxybenzyl alcohol (2 mol) was stirred at room temperature in 500 g of toluene (slurry). 30% hydrochloric acid (600 ml) was added and the mixture was stirred at 25°C for 3 hours. During this time, the phenol went into the solution.

The solution was heated at 45°C until two layers separated (about 1 hour). The organic layer was washed with water about five times and dried with $MgSO_4$ anhydrous. The solution was evaporated. The syrup so formed was free from solvent and tested.

IR DATA

OH	3500 cm^{-1}
CH_2Cl	1300 cm^{-1}
1,2,3,5 substitution	1800-1700 cm^{-1}

NMR DATA

Methylenic proton	5.5 singlet
Aromatic proton	2.8 singlet
Proton closed to Cl	7-8 multiplet
OH proton	4.8 singlet
t-Butyl proton	8.6 singlet

2.6.3 PREPARATION OF 2,6-DI-TERTIARY-BUTYL-4-HYDROXY-BENZYL MERCAPTAN[121]

In a 500 ml round bottomed flask was added magnesium hydroxide (5.8 g) and N,N-dimethyl formamide (200 ml). Hydrogen sulphide gas was passed into the mixture for 30 minutes while stirring. 3,5-Di-tertiary-butyl-hydroxybenzyl chloride was added drop by drop. The rate of addition should be controlled to prevent yellow colour of sulphides. The mixture was allowed to stand for 90 minutes, then poured into ice water. The organic layer was separated by ether extraction (3 or 4 times). The ether solution being washed several

times with water, dried with magnesium sulphate. The solution was evaporated and distilled under vacuum at 0.3 mm pressure with boiling point of 130-140°C when collected. The distillate crystallised when stored in the fridge. Mp 27-28°C (lit 25°C).

IR DATA

Phenolic OH	3640 cm^{-1}
SH group	2550 cm^{-1}
1,2,3,5 substitution	1760 cm^{-1}
1,2,3,5 substitution	880 cm^{-1}

NMR DATA

Tertiary butyl proton	8.6 singlet
$-CH_2-$ proton	6.3 doublet
	(JCH_2-SH = 7 Hz)
Aromatic proton	2.75 singlet
Phenolic proton	4.75 singlet

MASS SPEC

Highest m/e = 252

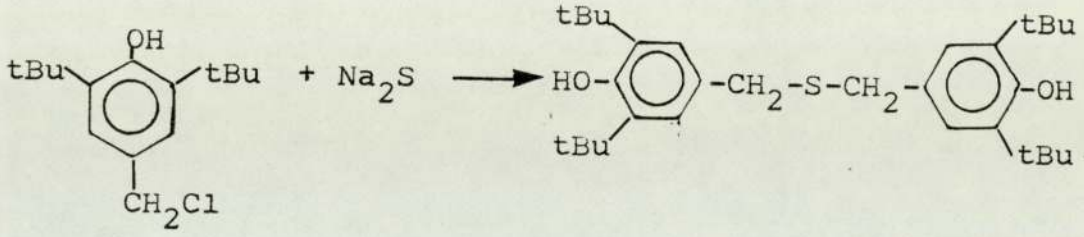
Fragmention described in section 4.3.1.5

ANAL

Calc for $C_{15}H_{24}OS$; C = 71.4%, H = 9.5%, S = 12.7%

found; C = 71.7%, H = 9.8%, S = 13.4%

2.6.4 PREPARATION OF BIS-3,5-DI-TERTIARY-BUTYL-4-HYDROXYBENZYL MONOSULPHIDE(138)



Scheme 2.2

In a 50 ml round bottomed flask equipped with a heater, thermometer, water cooled condenser and a stirrer, was added a mixture of 3.84 g (0.05 moles) of sodium sulphide in 3 ml of water, 24 ml of isopropyl alcohol and 10 g (0.04 moles) of di-tertiary-butyl-4-hydroxy benzyl chloride was refluxed for a period of two hours. The mixture was allowed to cool and left for two days and filtered. The precipitate was washed with distilled water and dried under vacuum. The yellow solid was recrystallised with a micture of isooctane and methanol. The product melted at 141-143°C (lit 143°C).

IR DATA

Phenolic proton	3640 cm^{-1}
C-S closed proton	700 cm^{-1}
Tetra substituted benzene ring proton	880 cm^{-1}
Tertiary-butyl group proton	1370 cm^{-1} and 1360 cm^{-1}

NMR DATA

Tertiary butyl proton	8.6
Methylenic proton	6.4
Aromatic proton	2.9

MASS SPEC

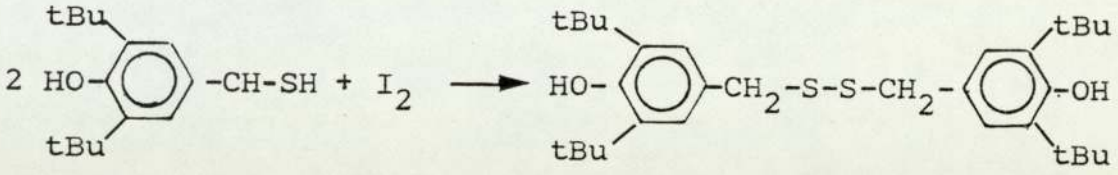
Highest m/e 250 .

ANAL

Calculated for $C_{30}H_{46}SO_2$; C = 76.6%, H = 9.7%

found; C = 77.1%, H = 9.9%

2.6.5 PREPARATION OF BIS-(3,5-DI-TERTIARY-BUTYL-4-HYDROXYBENZYL) DISULPHIDE[121]



Scheme 2.3

To a vigorously stirred mixture containing 2 g (0.008 moles) of 3,5-di-tertiarybutyl-4-hydroxybenzyl mercaptan 30 ml of benzene and 7.5 ml of water, a solution of 2.18 g of iodine in 10 ml of benzene and 2.5 ml of ethanol was slowly added through a dropping funnel. When the thiol solution showed a trace of iodine colour the stirring and addition of iodine were ceased.

The organic layer was separated dried over magnesium sulphate and the benzene was removed on a rotary evaporator. The disulphide was recrystallised from a solution of petroleum: ether benzene. The white crystals obtained had a melting point of 165-166°C (lit 167-168°C).

IR DATA

Phenolic	3610 cm^{-1}
Tertiary butyl group	1310 & 1360 cm^{-1}
-S-S-	525 cm^{-1}

NMR DATA

Tertiary butyl	8.5 singlet
Phenolic	4.9 singlet
Methylenic	6.1 singlet
Benzene ring	2.9 singlet

MASS SPEC

Highest m/e 256 for the fragmentation pattern (see section 4.3.1.6)

ANAL

Calc for $C_{30}H_{46}S_2O_2$: C = 71.7%, S = 12.7%, H = 9.1%

found: C = 69.3%, S = 12.7%, H = 9.2%

2.6.6 PREPARATION OF 4-METHYLENE-2,6-DI-TERTIARY-BUTYL CYCLOHEXA-2,5-DIENONE (QUINONE METHIDE)[122]

A solution of triethylamine (5, 15 g, 0.057 mole) in petroleum ether (25 ml), was added with swirling to a solution of chloromethylated phenol (see section 2.6.2) (13.0 g, 0.057 mole) in petroluem ether (175 ml) while crude cooling was carried out in a -15°C bath and nitrogen was blown into the flask. The mixture was let stand for 2-3 minutes, with occasional swirling, with crude nitrogen blanketing, was filtered through a coarse filter disk funnel under vacuum.

The precipitate was washed two or three times with petroleum ether (total of 150 ml). In a typical experiment, the white precipitate was found after drying in vacuo. The solution of quinone methide very rapidly darkened in colour, so it is necessary to use it immediately.

IR DATA

$\underset{\underset{O}{\|}}{C}$	1750 cm^{-1}
$C{=}CH_2$	3100 cm^{-1}

NMR DATA

Quinone nucleus	2.8 singlet
Methylenic hydrogen	4.0 doublet
Tert-butyl group	8.45-8.6 singlet

MASS SPEC

Highest m/e 218 for the fragmentation pattern, see section 4.3.1.3.

2.6.7 PREPARATION OF BIS-(3,5-DITERTIARY-BUTYL-4-HYDROXYBENZYL) MONOSULPHOXIDE

The procedure used in this preparation was the method applied by Barnard and co-workers[133] and Armstrong[134]. 5.6 g (0.012 mole) of 3,5-ditertiary butyl-4-hydroxybenzyl monosulphide was dissolved in 20 ml of distilled acetone (15.6 g) and poured into a 50 ml round bottom flask. The flask was placed in an ice bath and cooled to 0°C. 3 ml of 30% hydrogen peroxide was then added dropwise over a period of four hours while stirring. The mixture was then left at room temperature for 12 hours. Acetone was removed by rotary evaporation. The white solid obtained was recrystallised from benzene and dried under vacuum. The product had a melting point of 132-134°C.

IR DATA

Phenol	3640 cm^{-1}
Tetra substituted benzene ring	880 cm^{-1}
Tert-butyl group	1320 & 1360 cm^{-1}
$R-CH_2-S-R$	1220 & 1270 cm^{-1}
$R-S-R$	1030 cm^{-1}

NMR DATA

Tert-butyl	8.6 s
Methylenic	6.4 d
Phenol	4.8 s
Aromatic	2.9 s

MASS SPEC

Highest m/e 486, and M^+ 250 due to R-C=S.

2.6.8 PREPARATION OF BIS(3,5-DI-TERT-BUTYL-4-HYDROXY BENZYL) THIOSULPHINATE

BHBM disulphide was oxidised with 80% of the theoretical amount of 30% H_2O_2 by the same procedure as for sulphoxide (section 2.6.7). It was found that the product was unstable to distillation and it was necessary therefore to expose the product to a high

vacuum to remove all volatile impurities.

IR DATA

Phenolic	3610 cm^{-1}
Tert-butyl	1310 cm^{-1}
S-S (=O)	690 cm^{-1}

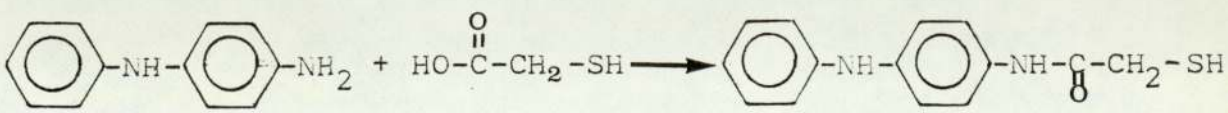
NMR DATA

Tert-butyl	8.6 s
Phenolic	4.9 s
Methylenic proton	6.1 s
Aromatic	2.9 s

MASS SPEC

Highest m/e = 250

2.6.9 PREPARATION OF 4-MERCAPTO ACETAMIDO DIPHENYL AMINE (MADA)[178]



Scheme 2.5

18.4 g (0.10 mole) of 4-aminodiphenylamine was poured into a 500 ml round bottom flask and 300 ml of xylene was added. The mixture was vigorously shaken until all the amine was dissolved. 13.8 g (0.15 mole) of thioglycollic acid was then added to this solution. The excess of thioglycollic acid was used in order to shift the reaction to the right in the above scheme (2.4).

The flask was then fitted with a Dean and Stark apparatus and a water cooled condenser. A stream of nitrogen was bubbled through during the reaction. The mixture was then refluxed for 15 hours. After the reaction was finished the flask was allowed to cool and the mixture was diluted with n-hexane and left to crystallise in an ice bath. The product obtained was filtered and recrystallised with isopropanol and hexane. Mp 135-137^{o}C (lit 135.5-136.5^{o}C).

IR DATA

Secondary NH	3360 cm^{-1}
Secondary NH	3560 cm^{-1}
C-SH	2525 cm^{-1}
Secondary amide	1650 cm^{-1}

NMR DATA

Secondary amine	q1.5 singlet
Aromatic protons	6.5-7.5 doublet
	= 8-10 Hz
Secondary amine	3.3 singlet
Methylenic	6.7 doublet
Thiol	7.4 triplet

MASS SPEC

Highest m/e = 258. Fragmentation at 225 (loss of HS) and 183 (loss of C_2H_2O).

2.6.10 PREPARATION OF 3,5-DI-TERT-BUTYL-4-HYDROXY SULPHONIC ACID[156]

Mercaptan (0.05 mol) was dissolved in methylene dichloride (10 ml) and cooled to -30°C in a deep freeze. Similarly m-chloroperbenzoic acid (MCPBA) (0.2 mol) was dissolved in methylene dichloride (200 ml) and cooled to -30°C. At 0.5 hour interval, MCPBA slurry (10 ml) was pipetted slowly with vigorous stirring (exothermic) into the mercaptan solution and the flasks were returned to the deep freeze. After addition of all the oxidation solution the reaction flask was allowed to stand overnight at -30°C before filtration. To remove the traces of

MCPBA the solution was cooled down to -80°C and filtered. After removal of the MCPBA the procedure consisted solely of evaporating the solvent in rapid nitrogen stream.. The sulphonicacids remained as pale yellow oils. A short period (30 minutes) in an vacuum desiccator (P_2O_5) removed the last traces of moisture.

IR DATA

OH	2340-2790
S=O	100
SO	850

MASS SPEC

Highest m/e = 300, for the fragmentation pattern see Section 4.1.1.6.

NOTE: Sulphinic acid prepared using the above procedure (2.6.10) except that MCPBA was used at 0.1 mol.

2.7 PURIFICATION OF HYDROPEROXIDE[49]

2.7.1 TERT-BUTYL HYDROPEROXIDE

70% t-butyl hydroperoxide were purified by the following procedure. The peroxide was stored over molecular sieve for 24 hours, dried with Na_2SO_4, fractionally distilled under vacuum and the fraction boiling at 24-26^{o}C at 1.75 torr was collected. The distillate usually analysed 97% t-butyl hydroperoxide.

CHAPTER THREE

REACTION OF ANTIOXIDANT WITH RUBBER LATEX

3.1 INTRODUCTION

Natural rubber latex has a composition varying between wide limits. The typical composition of latex is as follows[123]:

	%
Total solid content	36
Dry rubber content	33
Proteins	1-15
Resinous substance	1-2.5
Ash	up to 1
Sugar	1
Water	to 100

The non-rubber constituent in the latex is distributed between three phases. These are the rubber, the aqueous and the lutoid phases. Above 35% of the rubber consists of the rubber particles, the aqueous phase is about 55% and the rest is the lutoid phase. The non-rubber constituents comprise only about 5-8% of the total latex, the most important of these are the naturally occurring antioxidants and proteins.

Scott and co-workers[85-91,95] have extensively studied the grafting of antioxidants to natural rubber latex and to rubber in the melt.

It has been reported that certain thiol-based antioxidants can be reacted with natural rubber latex using tertiary-butyl hydroperoxide (TBH) as the initiator and tetraethylene pentamine (TEPA) as the activator[89-91,101,124].

These have been found to be the only systems that give a good yield of bound antioxidant when the natural rubber latex contamining ammonia was used.

3.1.1 PREPARATION OF THE EMULSION FOR REACTION WITH NATURAL RUBBER LATEX

2.5 g of BHBM in 5 ml of chloroform was poured into a 500 ml conical flask. Texofor FN30 (200 mg) dissolved in 40 ml of water was added. The air was removed from the flask by flushing with nitrogen. The flask was then stoppered tightly and was shaken for 18-24 hours.

3.2 DETERMINATION OF THE OPTIMUM CONDITIONS FOR THE PREPARATION OF 3,5-DITERTIARY-BUTYL-4-HYDROXYBENZYL MERCAPTAN WITH NATURAL RUBBER LATEX

The degree of binding is affected by swelling time,

concentration of initiator and activator, pH, temperature and swelling time. The effect of these variables were studied as follows.

3.2.1 REACTION CONDITIONS FOR BINDING BHBM INTO NR LATEX

The reactions were carried out in a 500 ml five-necked flask fitted with a stirrer and a thermometer, and was immersed in an oil bath which was heated at 60-65^{o}C.

Natural rubber latex (60%) was diluted to 30% and was purged with nitrogen until it reached pH 8-8.5. The partially deammoniated latex was poured into the flask while stirring. The emulsion of BHBM (section 3.2.1) and the initiator were pre-mixed and divided in three aliquots, which then were added to the latex at 1 hour intervals. The activator was added after 10 minutes, after each addition of the initiator. After the addition of the last aliquot, the reaction was allowed to continue for a further six hours.

Typical reaction conditions for the reaction of BHBM with NR latex is summarised in Table 3.1.

After the reaction was completed, the flask was allowed to cool and the rubber was coagulated with 1% formic acid. The coagulum was washed with tap water, sheeted,

Table 3.1 Typical reaction conditions for the reaction of BHBM with NR latex

Additives & Conditions	Quantity & Reaction Conditions
NR latex	100 g (30% DRC)
Swelling time	30 mins
pH	8 - 8.5
BHBM	10 g = 0.04 moles
TBH (70% in water)	5.1 ml = 0.04 moles
TEPA (10% in water)	5.1 ml = 0.003 moles
Molar ratio of BHBM to TBH	1 : 1
Molar ratio of TBH to TEPA	1 : 0.075
Reaction time (inc swelling time)	9 hours
Reaction temperature	60 - 65^{o}C

washed several times and dried in vacuum oven at 40^{o}C. The dried rubber was extracted with acetone and the amount of bound antioxidant was determined according to the method described in section 2.3 and section 2.3.1.1

3.2.1.1 EFFECT OF TEMPERATURE

The conditions used in this reaction were as described in Table 3.1, except that the temperature was varied

(see Table 3.2).

Table 3.2 Effect of temperature on reaction of NR latex with BHBM

Temperature ^{o}C	BHBM Bound (%) ebv
50-60	None
60-65	25
65-70	Coagulated

ebv = extracted before compounding and then vulcanised.

3.2.1.2 EFFECT OF SWELLING TIME

All conditions in this experiment were kept constant as in the typical conditions given in Table 3.1, except the swelling time which was varied from 15 minutes to 60 minutes.

It can be seen that the maximum yield of binding occurs when the swelling time is about 15-30 minutes.

Table 3.3 Effect of swelling time (notation as Table 3.2)

Swelling time	% of BHBM bound (ebv)
15	19
30	35
45	32
60	30

3.2.1.3 EFFECT OF pH

The effect of pH was studied, other conditions applied being constant. The assessment was carried out extracting the rubber sheet and vulcanised (see Table 3.4).

Table 3.4 Effect of pH (notation as in Table 3.2)

pH	BHBM Bound (%) ebv
9-10	36
8-8.5	38
7-7.5	coagulated

Subsequent reactions were carried out at pH 8-8.5.

3.2.1.4 EFFECT OF INITIATOR CONCENTRATION

Conditions in this experiment were as described in Table 3.1, except that the concentration of TBH was varied. The results are given in Table 3.5.

Table 3.5 Effect of initiator (notation as in Table 3.2)

Molar Ratio BHBM / TBH	BHBM Bound % ebv	BHBM Bound % eav*
1 : ½	16	49
1 : 1	25	57
1 : 1½	34	64
1 : 2	38	55
1 : 2½	36	46
1 : 3	35	48

* eav = unextracted before compounding, then vulcanised and extracted

It was noticed that at high molar ratios of TBH / BHBM particularly above the molar ratio 2 : 1, the rubber became markedly soft and tacky due to oxidation.

3.2.1.5 EFFECT OF ACTIVATOR CONCENTRATION

This experiment was carried out using the conditions described in Table 3.1, except that the concentration of TEPA was varied (molar ratio). The results are given in Table 3.6.

Table 3.6 Effect of activator on bound BHBM (notations as in Tables 3.2 and 3.5)

Molar ratio TBH : TEPA	BHBM Bound (%) ebv	BHBM Bound (%) eav
1 : 0.225	17	31
1 : 0.150	17	28
1 : 0.075	18	31
1 : 0.0375	13	27
1 : 0.0128	9	23
1 : 0.0075	8	19

3.2.1.6 EFFECT OF NON ADDITION OF TEPA

The conditions used in this experiment were the same as mentioned in Table 3.1, except that no TEPA was used. The results are given in Table 3.7.

Table 3.7 Effect of non addition of TEPA on bound BHBM (notations as in Tables 3.2 and 3.5)

Molar ratio BHBM : TBH	BHBM Bound (%) ebv	BHBM Bound (%) eav
1 : ½	6	27
1 : 1	11	32
1 : 1½	9	29
1 : 2	8	27
1 : 2½	5	21
1 : 3	3	16

The above results show that BHBM cannot be bound to the natural rubber latex in yields greater than 38% (extracted before vulcanisation) to natural rubber.

This low yield of binding is not technologically acceptable for use in masterbatch concentrations.

3.3 REACTION OF BHBM WITH DEPROTEINISED NATURAL RUBBER LATEX (DPNRL)

It was suspected that the protein in natural rubber was responsible for the low yields in grafting reaction of BHBM. In an attempt to obtain a higher yield of bound BHBM in natural rubber latex, deproteinised

natural rubber latex was used. The latex was prepared according to the method described by MRPRA[84] as follows.

To a concentrated ammoniacal latex (60% DRC) (100 g) was added 10% solution of enzyme trypsin 'Superase' and anionic soap 25% solution of Texofor FN30. The additives were thoroughly mixed and then stored at 30°C for 5 days. After this period, the compound was diluted with 0.5% Texofor FN30 to a total solid content of 20% and creamed using 0.2% of ammonium alginate (based on the total weight of the compound) until the required total solid content (of the cream) was reached.

Tests carried out by MRPRA have shown the protein content of the treated rubber to be about 0.02%.

The results of the reaction of DPNRL with BHBM is shown in Table 3.8 using the conditions described in Table 3.1.

The other conditions of the reaction were kept constant as shown in section 3.2.2.1.

It is clear from the above results that protein is not in itself responsible for the inhibition of BHBM binding reaction. However, there are resinous aromatic amines which are not hydrolysable which could inhibit the

grafting reaction.

Table 3.8 Reaction of DPNRL with BHBM (notation as in Table 3.2)

Molar ratio BHBM : TBH	BHBM Bound (%) ebv	BHBM Bound (%) eav
1 : ½	28	55
1 : 1	32	59
1 : 1½	34	64
1 : 2	36	66
1 : 3	26	49

3.4 DISCUSSION

The results obtained above show a much lower level of binding than has been described earlier[89,90]. The conditions used in the present experiments were different from those used by Kularatne[90]. Tables 3.1 - 3.6 summarise the percentage binding of the thiol to natural rubber. From these tables it is apparent that changing the conditions of the process does not improve the yield of binding significantly. The tackiness of the rubber at high concentrations of initiator to BHBM could be due to oxidation of the rubber by the TBH. It appears then that a small portion

of non-rubber material is responsible for the interference of this binding reaction.

Bloomfield et al[124] have reported similar results during the grafting of methyl methacrylate to natural rubber latex using TBH or CHP as initiator and TEPA or tetraethylene tetraamine (TETA) as activator. It was suggested[124] that the addition of substantially higher proportions of initiator to monomer was necessary to offset the retarding effect of an unknown compound in natural rubber.

Porter[125] and Campbell[126] have reported similar results for the grafting reaction of polystyrene with dry natural rubber. When synthetic polyisoprene was used the percentage of grafting is very high (76%). When acetone extracted natural rubber (SMR 5L) was used the percentage of grafted polystyrene was equally high (73%). However, when natural rubber without prior acetone extraction was used, the percentages of grafted polystyrene dropped to about 30-40%. When DPNR was used without prior acetone extraction the percentage of grafting was even lower (10%). Acetone extracted DPNR yielded a higher level of grafting[127]. The authors have suggested therefore that some material in the rubber is a 'poison' for the grafting reaction; this inhibitor is not the protein but some acetone

extractable material. The acetone soluble fraction of rubber contains rubber carbohydrates, steroids, proteins and resin acids. It is believed that it is the latter of these which cause the retardation of the grafting reaction in unextracted natural rubber.

The use of 2-3% calcium oxide in the unextracted natural rubber[125] has been shown to give an improvement in the percentage of grafting, but still lower than for synthetic polyisoprene. The calcium oxide is thought to function by neutralising some of the resin acids in the unextracted rubber.

These same acids must be interfering with the binding reaction of BHBM in the natural rubber latex in the present study. It is not possible to remove these inhibitors as Porter and Campbell have done for coagulated natural rubber, because there is no known technique for selective extraction of these materials from rubber latex. Acetone is miscible with water and most solvents even though immiscible causes the latex to coagulate.

It will be seen in a later chapter, however, that the level of binding of BHBM and other thiols is substantially increased when synthetic latex is used. Furthermore, acetone extracted natural rubber can be made to react with thiols in the melt in the torque rheometer and

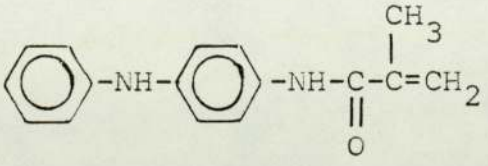
the Buss Ko Kneader gives even higher levels of binding. The level of mechanochemical binding in unextracted natural rubber coagulum is much lower. This confirms that the 'poison' in NR latex and dry rubber must be an acetone soluble extractable material. No further work was done on this aspect since it was not considered to be within the scope of the project.

In view of the difficulties experienced with natural rubber, it was decided to examine the binding of thiol antioxidants to SBR which does not contain the interfering natural products. This is discussed in the following section.

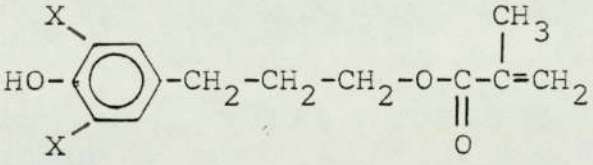
3.5 REACTION OF 3,5-DI-TERTIARY-BUTYL-4-HYDROXYBENZYL MERCAPTAN WITH STYRENE-BUTADIENE RUBBER (SBR) LATEX

It is well known that there are two types of SBR, these are called hot and cold SBR. Hot SBR is manufactured at about 50°C whereas cold SBR is manufactured at 5°C using a redox initiating system[128]. Cold SBR contains much less microgel and the polymer chains are much longer[129]. This difference in microstructure of the polymer chain affects the mechanical properties of the two types: hot SBR being much inferior to cold SBR.

Previous attempts to bind antioxidants into SBR have been carried out by Kline et al[130,131]. This author copolymerised monomers containing antioxidant functions with styrene and butadiene to give styrene based polymer containing bound antioxidants. The antioxidants containing monomer used were of the type I and II:



(I)



(II)

and the polymerisation was carried out in the usual manner using emulsion polymerisation technique.

High levels of bound antioxidant in the polymer can be achieved in this way. Although this method of incorporating antioxidants into the polymer backbone is very effective it suffers from a number of disadvantages of which the following are the most important:

(1) The cost of monomer may be prohibitive.

(2) The antioxidant may not distribute randomly.

(3) Block copolymers will not be as effective as random copolymers since it will be more difficult statistically for a block copolymer to protect all the polymer chains.

(4) The block copolymer may be in separate phases, this causes the antioxidant to be ineffective.

3.5.2 REACTION OF BHBM WITH SBR LATEX

To achieve a high concentration of bound BHBM, various variables were examined. The method applied was the same as shown in Table 3.1 except the latex was SBR which was purified according to section 2.1.8.1.The binding of BHBM to SBR was in this case carried out at 70-75^{o}C. The percentage of bound BHBM was determined by using the calibration curve shown in Figure 2.1. All the assessments of bound antioxidant were extracted before vulcanisation (ebv).

3.5.2.1 SWELLING TIME

The swelling time was determined using the conditions described in Table 3.1. The results are given in Table 3.9.

Table 3.9 Effect of swelling time to reaction of BHBM with TBH in SBR latex

Swelling time (mins)	BHBM Bound (%) ebv*
15	42
30	59
45	67
60	62

* Notation as in Table 3.2

3.5.2.2 EFFECT OF TEMPERATURE

The reaction was carried out using the same conditions as mentioned in Section 3.2.2.1. Only the temperature was varied and the results are shown in Table 3.10.

Table 3.10 Effect of temperature (notation as in Table 3.2)

Temperature (^{o}C)	BHBM bound (%) ebv
50-60	32-40
60-70	75-88
70-80	Coagulated

3.5.2.3 EFFECT OF INITIATOR CONCENTRATION

In this experiment the initiator concentration was varied, keeping other factors described in Table 3.1 constant. The results are summarised in Table 3.11.

Table 3.11 Effect of initiator (notation as in Table 3.2)

Molar Ratio (BHBM : TBH)	BHBM Bound (%) ebv
1 : ¼	25
1 : ½	45
1 : 1	87.5
1 : 1½	72
1 : 2	65
1 : 2½	60
1 : 3	53

3.5.2.4 EFFECT OF ACTIVATOR CONCENTRATION

In this experiment the concentration of the activator (TEPA) was varied, keeping the other variables constant. The results are described in Table 3.12.

Table 3.12 Effect of activator concentration on the reaction of BHBM with TBH in SBR latex (notation as in Table 3.2)

Molar Ratio TBH : TEPA	BHBM Bound (%) ebv
1 : 0.225	50
1 : 0.150	60
1 : 0.075	80
1 : 0.0375	75
1 : 0.0128	72

3.6 DISCUSSION

It is clear that high efficiency of binding can be obtained using SBR latex with BHBM. This must be due to the absence of the naturally occurring materials which inhibit the same reaction in natural rubber latex (see section 3.4).

The optimum conditions for the highest level of binding are summarised below in Table 3.12.

Table 3.12 Typical reaction conditions for the reaction of BHBM with SBR latex

Additives & Conditions	Quantity & Reaction Conditions
SBR latex	100 g (30% DRC)
Swelling time	30 minutes
pH	9-10
BHBM	10 g = 0.04 moles
TBH (70% in water)	5.1 ml = 0.04 moles
TEPA (10% in water)	5.1 ml = 0.003 moles
Molar ratio of BHBM to TBH	1:1
Molar ratio of TBH to TEPA	1:0.075
Reaction time (inc swelling time)	9 hours
Reaction temperature	70-75^{o}C

The yield of binding under these conditions was 80-87%. Changing any of these conditions reduced the optimum level of binding. The reasons for this will be discussed in Chapter Five after the model compound studies.

3.7 REACTION OF BHBM WITH SBR LATEX AT ROOM TEMPERATURE

It was interesting to study the binding of BHBM to SBR latex at room temperature. The method used was as

described in Table 3.13, except for the following modification.

Initiator used	H_2O_2 (30% solution)
Conc activator used	Na_2WO_4, 0.2 phr
Temperature used	25°C

Table 3.14 Percentage of bound BHBM into SBR at room temperature (notation as in Table 3.2)

Molar Ratio (BHBM : H_2O_2)	BHBM bound (%) ebv
1 : ½	40
1 : 1	53
1 : 2	45

3.8 REACTION OF BHBM WITH A BLEND OF SBR AND NR LATEX

Attempts were made to bind BHBM to a blend of differing ratios of SBR and NR latex. The reaction conditions used were those obtained for the optimum binding of SBR described in Table 3.13. The results are summarised in Table 3.15.

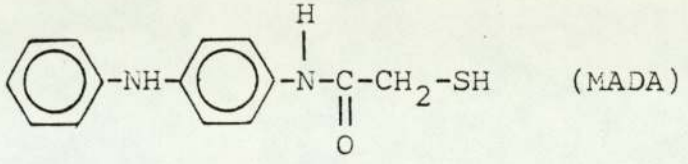
Table 3.15 Percentage of bound BHBM into the blend (notation as in Table 3.2)

Molar Ratio BHBM : TBH	Weight Ratio (dried rubber) SBR:NR			
	1:1	3:2	2:3	1:3
	Bound BHBM (%) ebv			
1 : ½	15	14	11	10
1 : 1	27	22	24	20
1 : 2	40	46	30	38

The low percentage of binding may be due to the presence of the naturally occurring resin acids in the NR latex which inhibit the binding reaction. This has been discussed thoroughly in section 3.4. Another reason could be the incompatibility of the SBR and NR latex particles[132].

3.9 THE REACTION OF 4-MERCAPTOACETAMIDO DIPHENYL AMINE (MADA) WITH SBR LATEX

In view of the high efficiency of binding BHBM to SBR latex, it was interesting to see whether a similar efficiency of binding could be achieved using the amine containing antioxidant, MADA.



(MADA)

The binding reaction was carried out using the same procedure as described in Table 3.1. The reaction was carried out using different emulsion/dispersion agents, unfortunately, the MADA coagulated the latex during the swelling time, (see Table 3.16).

Table 3.16 List of emulsion and dispersion agents used in the MADA reaction with SBR

Emulsion Agents	Dispersion Agents
Potassium oleate	Dispersol LN
Vulcastab LN	Vulcastab LR
Texofor FN30	

3.10 OVERALL CONCLUSIONS

It appears that the binding of BHBM into natural rubber latex is significantly retarded due to the presence of naturally occurring constituents. In contrast the efficiency of binding is substantially higher in SBR latex, as this does not contain any of these naturally

occurring 'inhibitors'. The binding of BHBM into blends of NR and SBR latex was also inefficient for the same reason.

The reaction of an amine containing thiol (MADA) with SBR latex was not successful because of coagulation of the latex during the process.

CHAPTER FOUR

ELUCIDATION OF THE MECHANISM OF THE BINDING REACTION FROM MODEL COMPOUND STUDIES

4.1 INTRODUCTION

In view of the evident dependence of the extent of binding of BHBM into SBR upon the conditions of the reaction, it was considered prudent to study the mechanism of this reaction using model compounds. Cyclohexene was used for this purpose, other model systems that could have been equally well used are squalene and 2-methyl-2-pentene. It is well known that organic sulphides decompose hydroperoxides to give a variety of oxygenated sulphur species, these include

$$-S{=}O,\ -SOH,\ -\overset{\overset{O}{\|}}{S}-OH,\ -\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH,\ SO_2 \text{ and } SO_3\ .$$

The contributory role of these species in the overall binding reaction was studied both in the model systems and in the latex. This was done by identifying and following the formation and decay of intermediates during the process and of cyclohexene adducts during the model compound studies.

4.2 REACTION OF BHBM WITH TERT-BUTYL HYDROPEROXIDE (TBH) IN CYCLOHEXENE

The reaction was carried out in a stirred 100 ml, 3-necked flask fitted with a condenser, thermometer and nitrogen purge. Chromatographic grade cyclohexene (40 g) was poured into the flask and BHBM (2.5 g) was added.

The oil bath was heated to 70-75^{o}C and distilled TBH (0.81 g, molar ratio BHBM / TBH = 1:1) and 10% TEPA solution in chlorobenzene (1.3 ml) were added. The flask was immersed in the oil bath and samples were withdrawn initially at 15 minutes, 30 minutes, 60 minutes and then at one hourly intervals.

4.2.1 GAS LIQUID CHROMATOGRAPHY (GLC)

4.2.1.1 APPARATUS

The instrument used for all GLC analyses was Pye Unicam Model GCD, which had a high accuracy temperature programmer. The detection facility used was flame ionisation. The instrument was equipped with the Servoscribe recorder, RE 511.20.

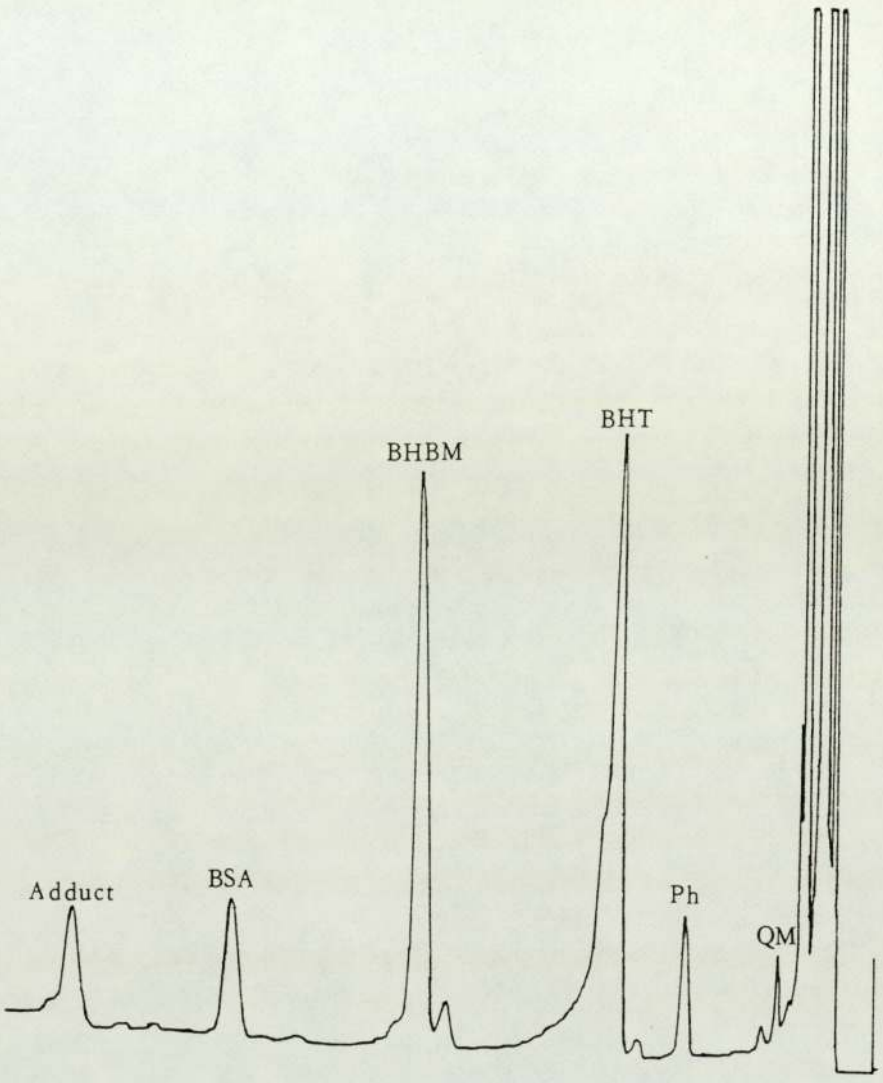


Fig 4.1 Typical GLC chromatogram (Pye Unicam GCD) of products from reaction of BHBM with TBH (Molar Ratio 1:½) in cyclohexene (taken out at 1 hour time) at 70°C

4.2.1.2 QUALITATIVE DETERMINATION OF THE REACTION PRODUCTS OF BHBM WITH TBH

The column used for this analysis was a 5 ft 4 inch glass column packed with 3% SE 30 on chromasorb W HP.

Separation was achieved using an initial temperature of 140°C which was held for one minute after which the temperature was programmed at 80°C per minute until a temperature of 250°C was reached.

The flame ionisation detector was used with nitrogen carrier gas at a flow rate of 30 ml/minute. Nine products were detected as shown in Fig 4.1.

To study the relative concentration of each peak shown in the GLC chromatogram, the peak height ratio method was used.

A study of a fixed amount of the reaction mixture containing a fixed amount of internal standard was made up in cyclohexene. The mixture was injected into the GLC under specified conditions. The peak height ratio, defined as the peak height of the substance to the peak height of the internal standard, was obtained from the chromatograph.

4.2.2 INTEGRATED GAS CHROMATOGRAPHY MASS SPECTROMETRY (GC - MS)

GC - MS was used to analyse the lower mass species. In this experiment a Pye Unicam 304 GC was fitted with a 36 m capillary glass coated with OV-1. Helium was used as the carrier gas. Conditions used to operate the machine were: temperature, 140 - 250^{o}C (at a programmed temperature increase rate of 8 degrees per minute) after a one minute initial hold on injection. After injection the mixture was separated in the GLC column and each component was identified automatically by the integrated mass spectrometer.

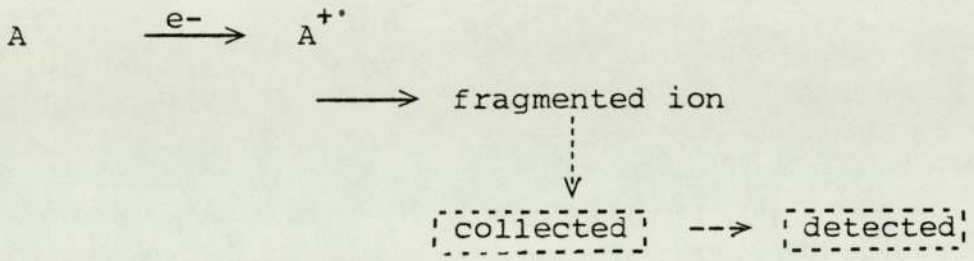
The VG MM 1200 Quadropole mass spectrometer was scanned every two seconds from 20 to 420 mass units, and the information data recorded on a dedicated mini computer data system. The mass scale of the spectrometer was calibrated using heptacosa fluorotributyl amine.

4.2.3 THEORY OF MASS SPECTROMETER

4.2.3.1 PRINCIPLE OF MASS SPECTROSCOPY

Mass spectroscopy consists of bombarding the molecule(s) with a beam of electrons (50 - 70 ev) which excites the molecules and causes fragmentation[152]. The

fragmentation ion (usually positively charged) are deflected in a magnetic field, collected in an ion collector. The signals resulting from the collection of these ions are amplified and recorded on a photographic plate or a magnetic tape to give the mass spectrum of the ionised molecule[153]. The essential process is:



By analysis of the fragmentation pattern, the molecular structure of compound A can be determined (for details see the next section, 4.3.1). Generally mass spectral reactions are unimolecular because the high vacuum used in the ionisation chamber minimises bimolecular reaction.

4.3 RESULTS

4.3.1 QUALITATIVE ANALYSIS OF THE MASS SPECTRA OF THE REFERENCE COMPOUNDS

Compounds either prepared or obtained commercially were used for standard reference. The following compounds were obtained commercially and recrystallised to ensure

purity:

2,6-di-tertiary-butyl phenol - Aldrich
2,6-di-tertiary-butyl-4-methyl phenol - ICI
2,6- di-tertiary-butyl-4-hydroxybenzyl alcohol - Shell Chemicals

The next group of compounds were prepared as described in Chapter Two.

3,5-di-tertiary-butyl-4-hydroxybenzyl mercaptan (section 2.6.3)
2,6-di-tertiary-butyl-4-methylene-2,5-cyclohexadiene-1-one (section 2.6.6)
bis-(3,5-di-tertiary-butyl-4-hydroxybenzyl) disulphide (section 2.6.5)

The mass spectra for these compounds are shown in Figs 4.2 - 4.8 and are interpreted below.

4.3.1.1 THE MASS SPECTRUM AND ITS INTERPRETATION FOR 2,6-DI-TERTIARY-BUTYL PHENOL

The mass spectrum of 2,6-ditertiary-butyl phenol (4-I) is shown in Fig 4.2.

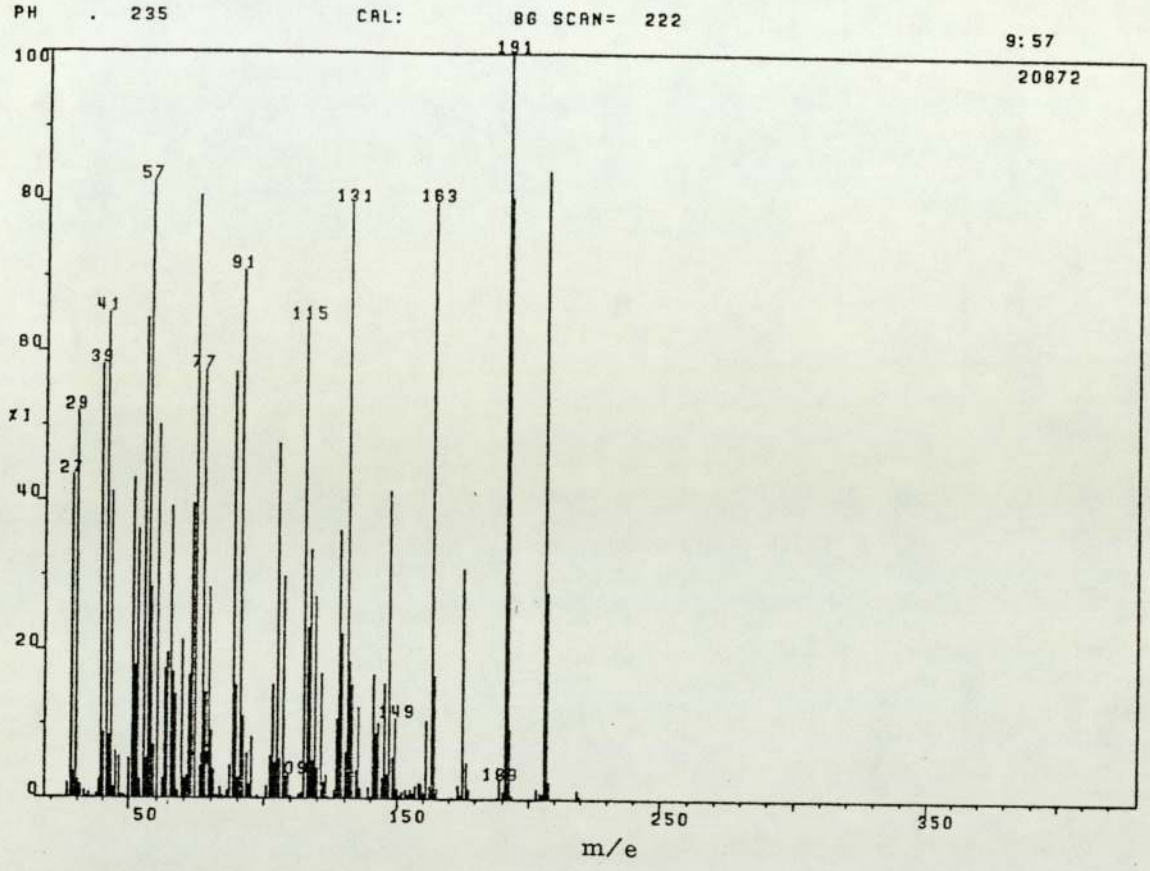
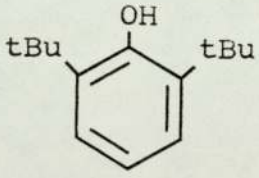


Fig 4.2 Mass spectrum of compound 4-I.

Aczel and Lumpkin[143] studied the mass spectra of aromatic oxygenated compounds and concluded that the (M-1) peak is an important peak for phenols containing alkyl substituents. This peak is derived from , cleavage of the H, of one of the alkyl groups, relative abundance of this peak, however, decreases rapidly with increasing molecular weight of the homologous series.

Generally the peak (M-15) absent from phenols and cresols is due to the elimination of a methyl radical and it grows in abundance for the higher homologous compounds. Thus for 2,6-di-tert-butyl-4-methyl phenol, the base peak corresponds to (M-15). The peak at (M-28) arising from loss of CO is a very important and characteristic peak for phenols. Beymon[144] too has confirmed this interpretation.

In the present study, the spectrum of 2,6-di-tertiary-butyl phenol was studied. Analysis of the spectrum



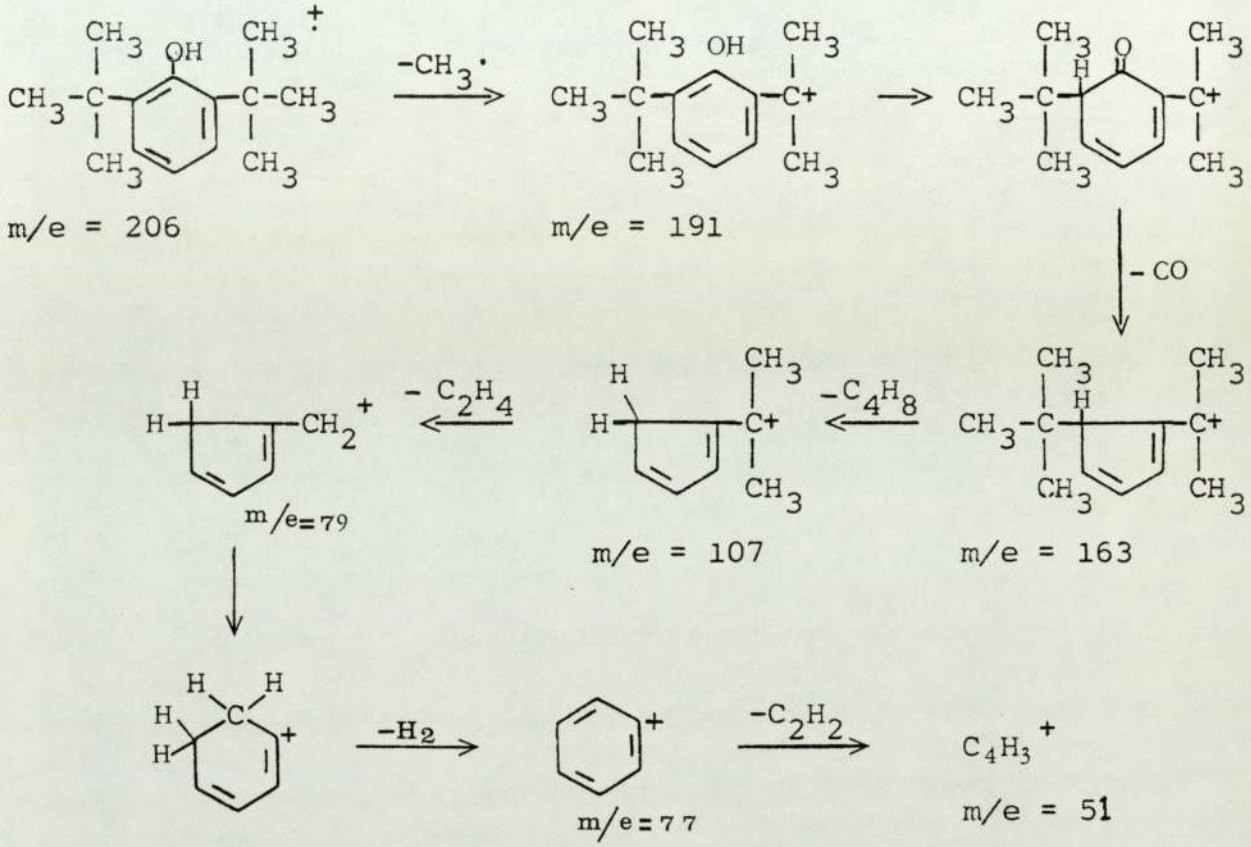
(4-I)

revealed that the mechanism of ion fragmentation (scheme 4.1) for 4-I occurs by two major pathways, as illustrated in Scheme 4.1.

The mass to charge ratio (m/e values) of the fragmentation ions and their relative abundance for compound 4-I are summarised in Table 4.1.

Scheme 4.1

Pathway I



Pathway II

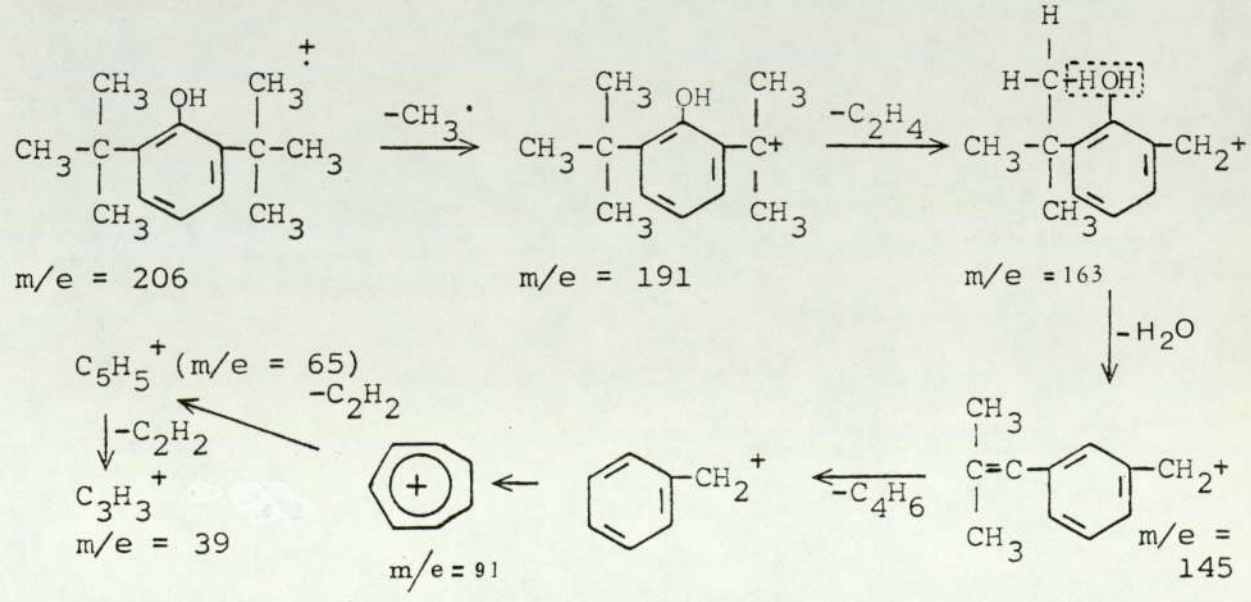
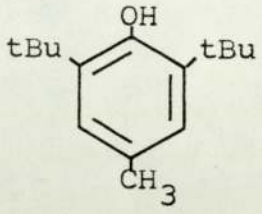


Table 4.1 Fragment loss of 2,6-di-tert-butyl phenol (4-I). Empirical formula $C_{14}H_{22}O$, highest m/e 206 (82°C). Scan range 0-400.

Pathway I		Relative	Pathway II		Relative	GC retention time (minutes)
Fragment loss	m/e residue	Abundance (%)	Fragment loss	m/e residue	Abundance (%)	
$CH_3\cdot$	191	100	$CH_3\cdot$	191	100	9' 57"
CO	163	80	C_2H_4	163	80	
C_4H_8	107	48	H_2O	145	41	
H_2	105	30	C_4H_8	91	90	
C_2H_2	77	58	C_2H_2	65	40	
C_2H_2	51	43	C_2H_2	39	58	

4.3.1.2 THE MASS SPECTRUM AND INTERPRETATION FOR 2,6-DI-TERTIARY-BUTYL-4-METHYL PHENOL (4-II)

The mass spectra of 2,6-di-tert-butyl-4-methyl phenol (4-II) is shown in Fig 4.3. The mechanism for its



(4-II)

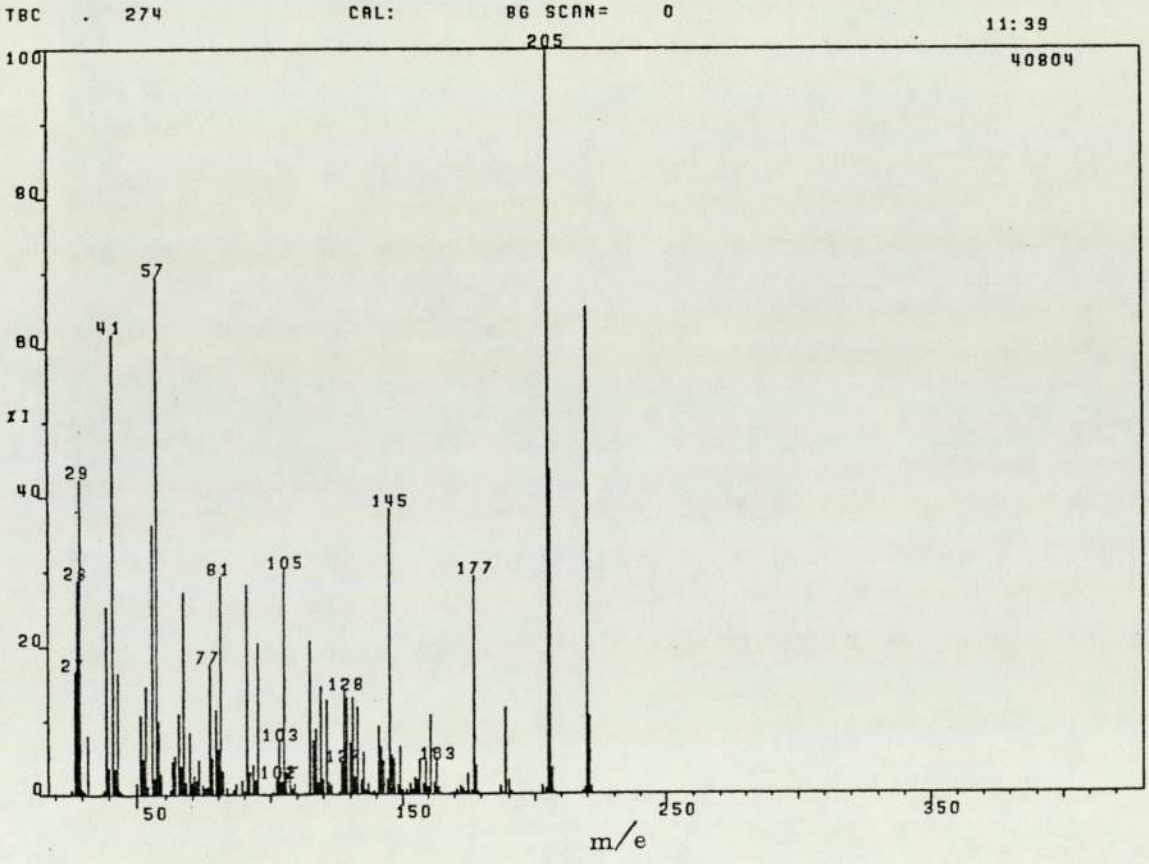
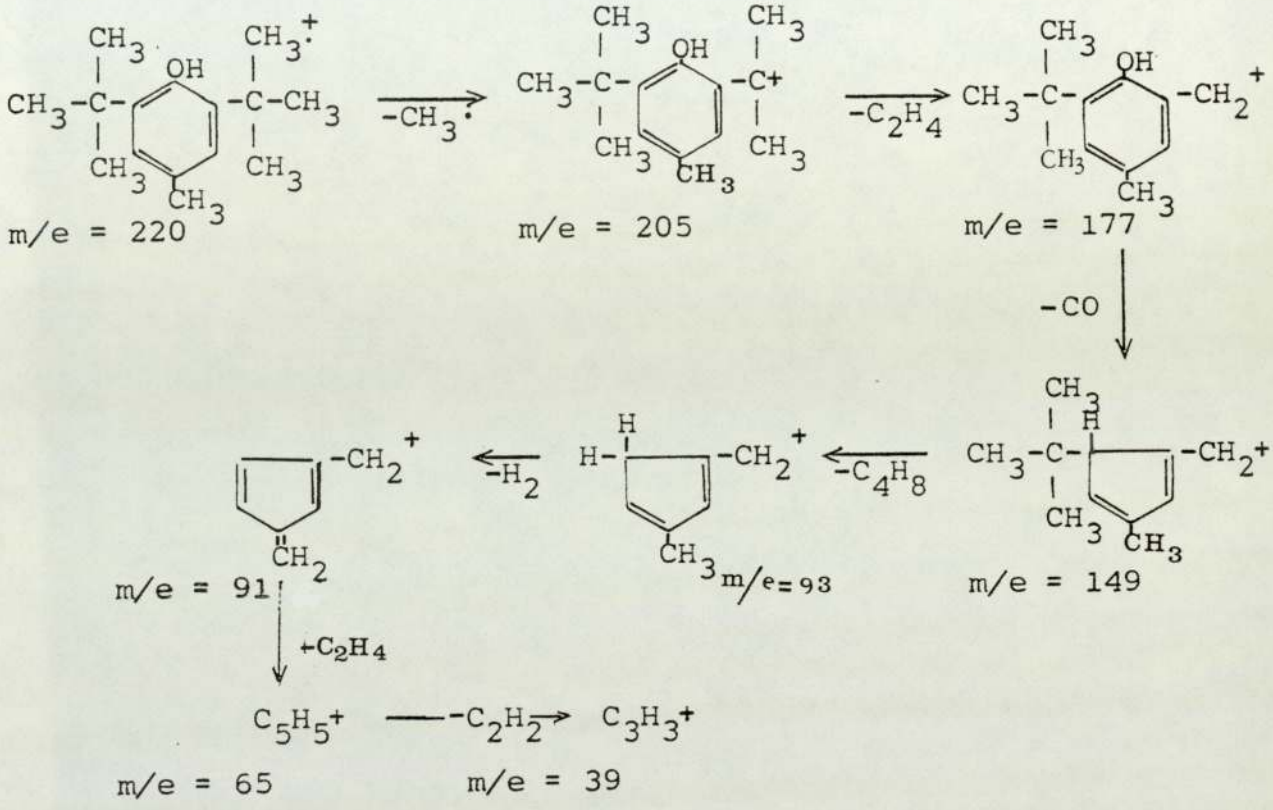


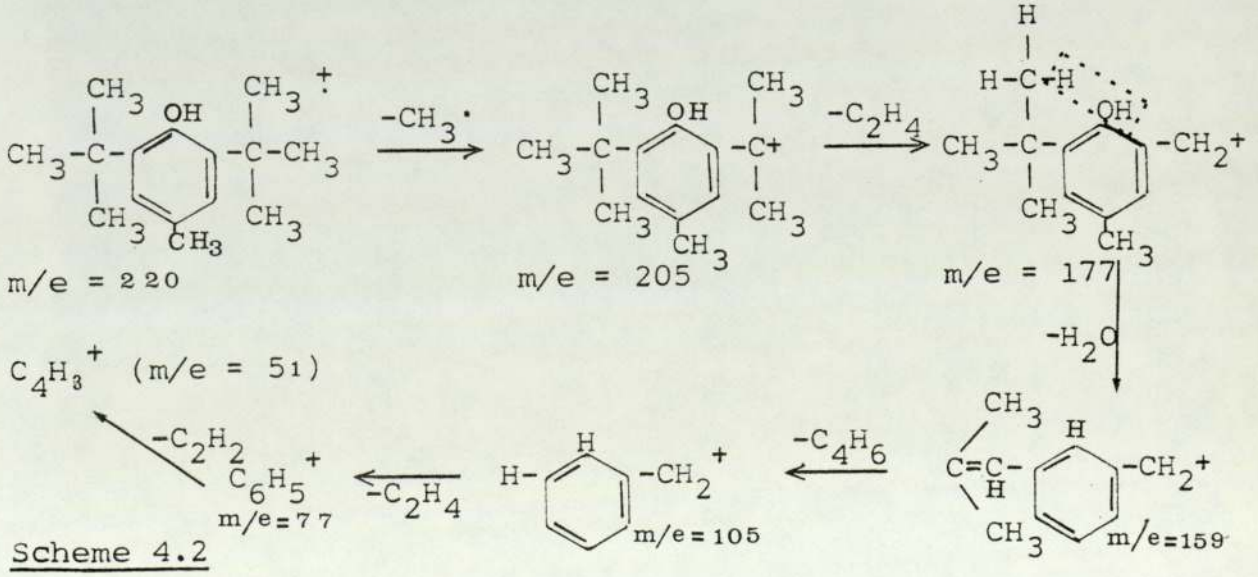
Fig 4.3 Mass spectrum of 2,6-di-tert-butyl phenol

fragmentation is shown in Scheme 4.2.

Pathway I



Pathway II



Scheme 4.2

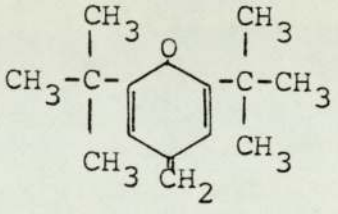
Table 4.2 Fragment loss of compound 4-II . Empirical formula $C_{15}H_{24}O$, highest m/e = 220 (70%), scan range = 0-400.

Pathway I		Relative	Pathway II		Relative	
Fragment loss	m/e residue	Abundance (%)	Fragment loss	m/e residue	Abundance (%)	GC retention time (minutes)
CH_3	205	100	$CH_3\cdot$	205	100	11'39"
C_2H_4	177	29	C_2H_4	177	29	
CO	147	5	H_2O	159	45	
C_4H_8	91	28	C_4H_6	105	30	
C_2H_2	65	28	C_2H_4	77	27	
C_2H_2	39	23	C_4H_3	51	12	

The m/e values of the peak and the relative abundance are summarised in Table 4.2.

4.3.1.3 THE MASS SPECTRUM AND ITS INTERPRETATION FOR 2,6-DI-TERT-BUTYL-4-METHYLENE-2,5-CYCLOHEXADIENE-1-ONE

The mass spectrum of 2,6-di-tert-butyl-4-methylene-2,5-cyclohexadien-1-one (4-III) is illustrated in Fig 4.4



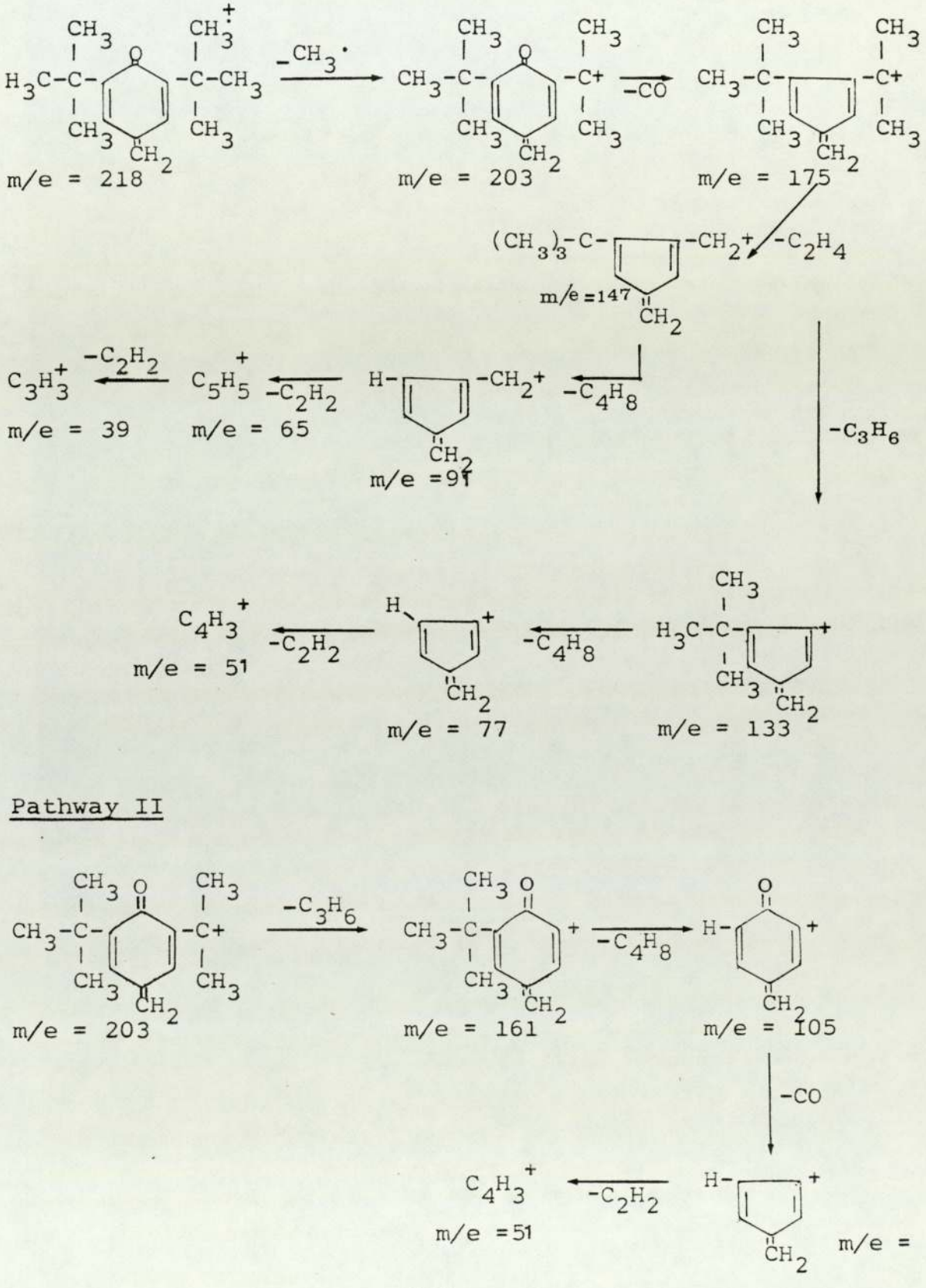
(4-III)

Heiss and co-workers[145] studied the mass spectra of quinonoid compounds and concluded that the characteristics peak arose from the loss of CO (M-28) peak.

The fragmentation of compound 4-III occurs by two pathways as shown in Scheme 4.3. The results of this fragmentation are summarised in Table 4.3.

Scheme 4.3

Pathway I



Pathway II

Table 4.3 Fragment loss of compound 4-III. Empirical formula $C_{15}H_{22}O$, highest m/e = 218 (37%), scan range 0-450.

Pathway I		Relative	Pathway II		Relative	GC retention time (minutes)
Fragment loss	m/e residue	Abundance (%)	Fragment loss	m/e residue	Abundance (%)	
$CH_3\cdot$	203	58	$CH_3\cdot$	203	58	11' 4"
CO	175	41	C_3H_6	161	100	
C_3H_6	133	17.5	C_4H_8	105	27	
C_4H_8	77	23	CO	77	23	
C_2H_2	57	15	C_2H_2	51	15	
*						
C_2H_4	147	18				
C_4H_8	91	36				
C_2H_2	65	22				

* Different route

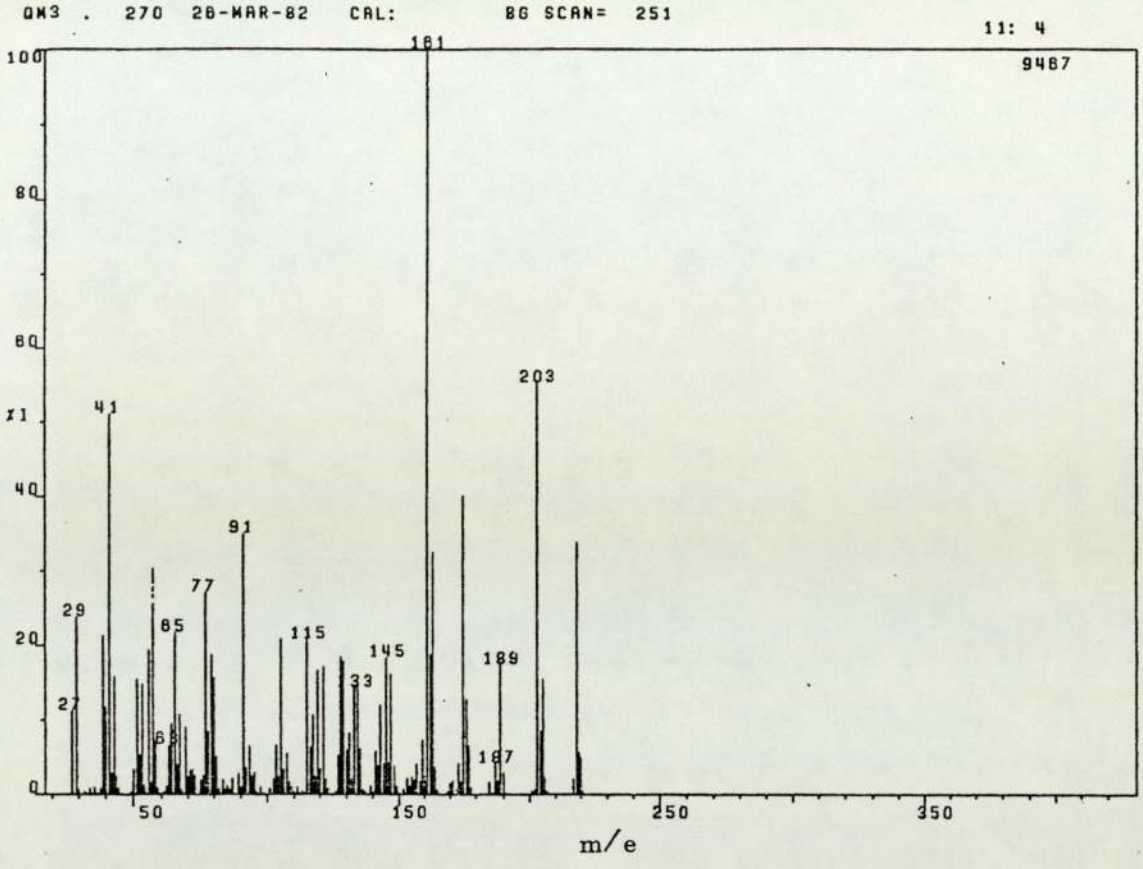


Fig 4.4 The mass spectrum of compound 4-III

4.3.1.4 THE MASS SPECTRUM AND ITS INTERPRETATION FOR 3,5-DI-TERT-BUTYL-4-HYDROXYPHENOL METHANOL[151]

The mass spectrum of 3,5-di-tert-butyl-4-hydroxyphenyl methanol (4-IV) is shown in Fig 4.5.

Aczel and Lumpkin[143] have shown that the mass spectra for benzylalcohols showed very strong abundance for molecular ion. In contrast, the corresponding aliphatic

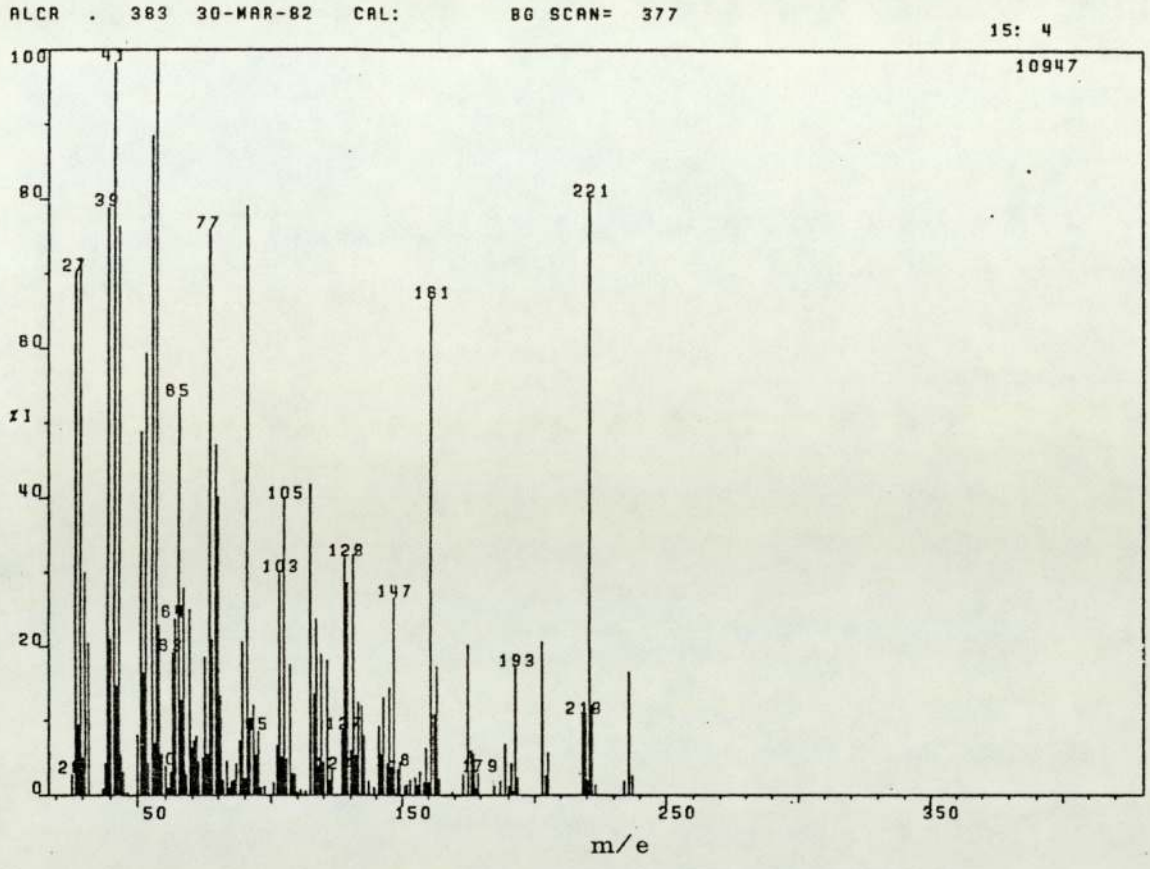


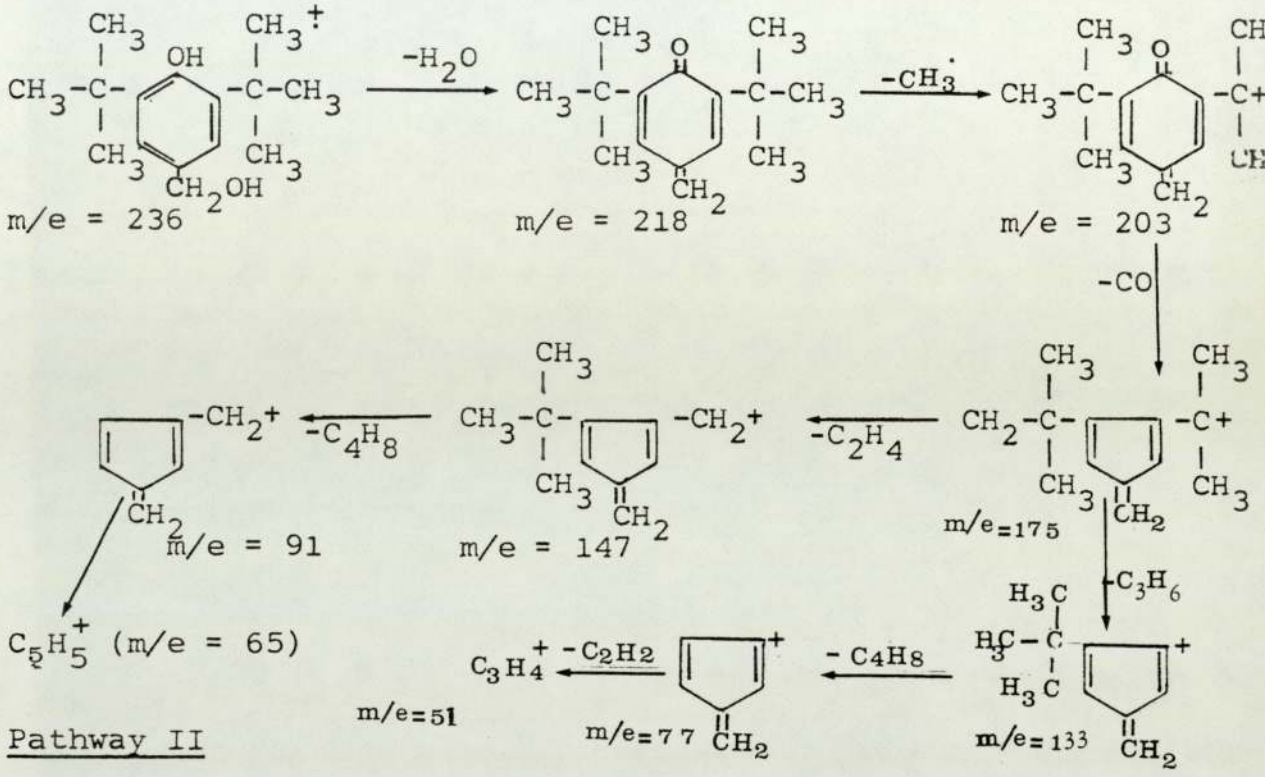
Fig 4.5 The mass spectrum of compound 4-IV

compounds do not have a significant M^+ ion. The difference between the two classes is attributed to the stability of the benzene ring. However, for the former compounds, an increase in molecular weight decreases the intensity of the molecular ion peak. M-15 is also very abundant when a number of methyl substituents are present on the ring.

The mechanism of ion fragmentation of compound 4-IV is is shown in Scheme 4.4 and results of fragmentation in Table 4.4

Scheme 4.4

Pathway I



Pathway II

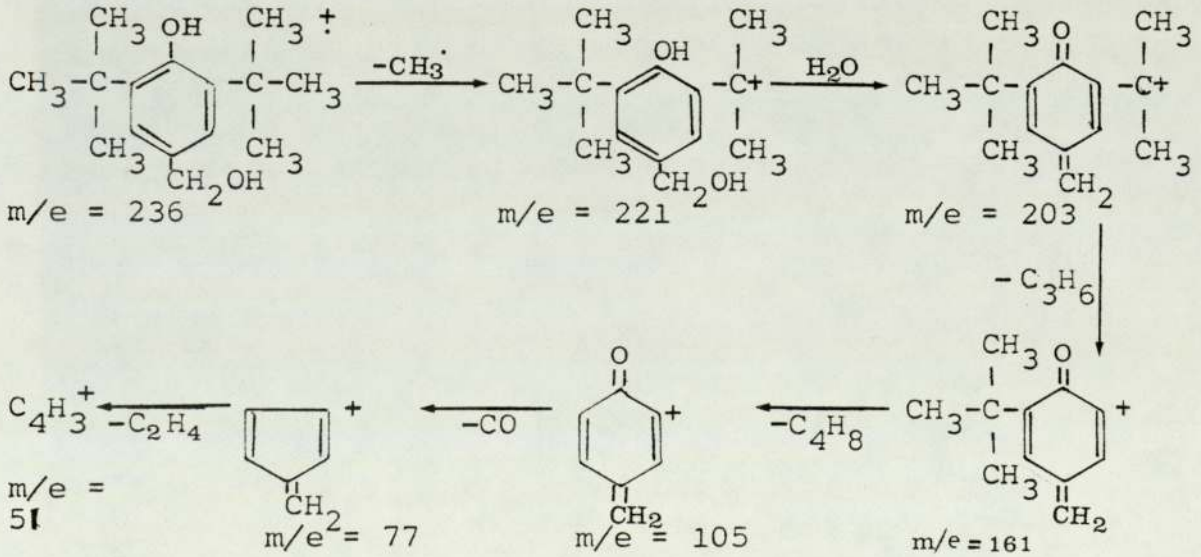


Table 4.4 Fragment loss of compound 4-IV. Empirical formula $C_{15}H_{24}O$, highest m/e = 236 (18%), scan range 0-450.

Pathway I		Relative	Pathway II		Relative	
Fragment loss	m/e residue	Abundance (%)	Fragment loss	m/e residue	Abundance (%)	GC retention time (minutes)
H_2O	218	12	$CH_3\cdot$	221	80	13' 4"
CH_3	203	23	H_2O	203	21	
CO	175	23	C_3H_6	161	74	
C_2H_4	147	28	C_4H_8	105	40	
C_4H_8	91	80	CO	77	77	
C_2H_2 *	65	77	C_2H_2	51	50	
C_3H_6	133	16				
C_4H_8	77	77				
C_2H_4	57					

* Different route

4.3.1.5 THE MASS SPECTRUM AND ITS INTERPRETATION FOR 3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL MERCAPTAN

The mass spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan is shown in Fig 4.6 and fragmentation pattern

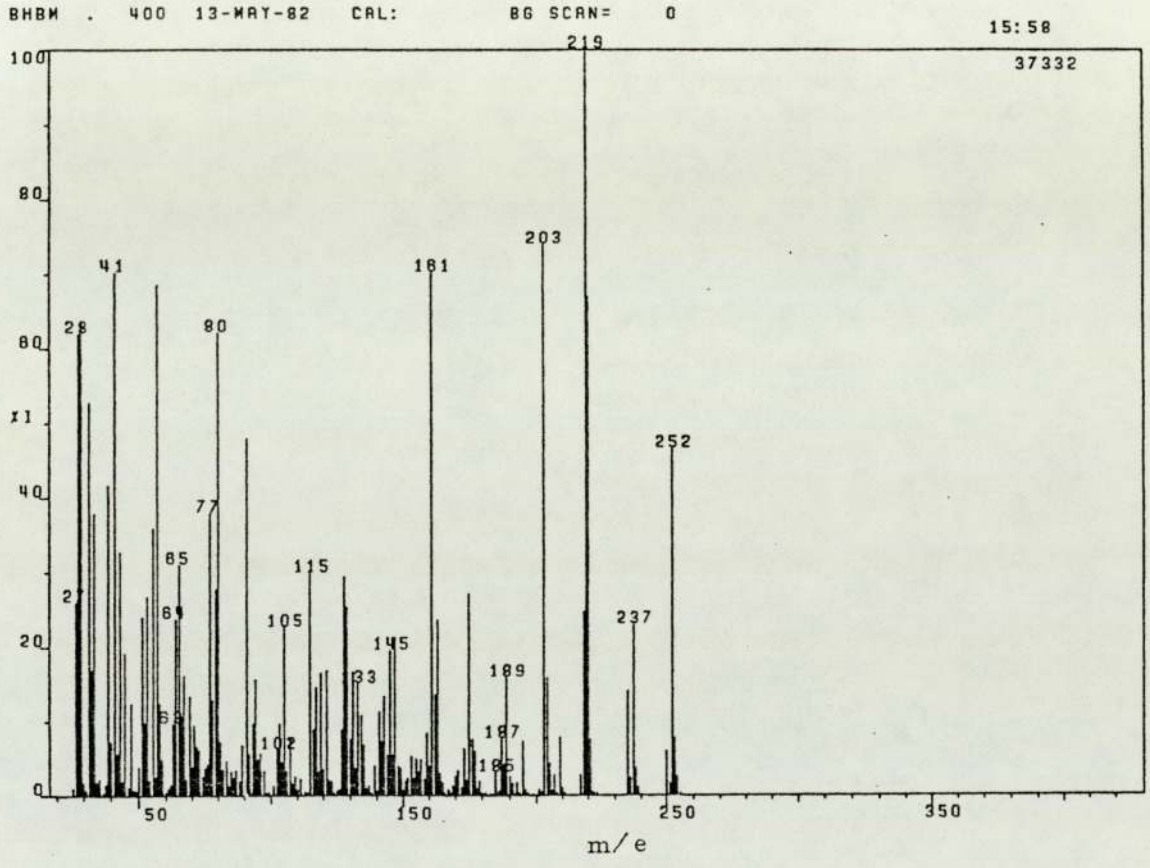
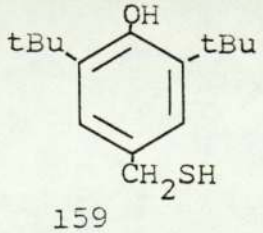


Fig 4.6 The mass spectrum of 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan

is shown in Scheme 4.5.



(4-V)

Scheme 4.5

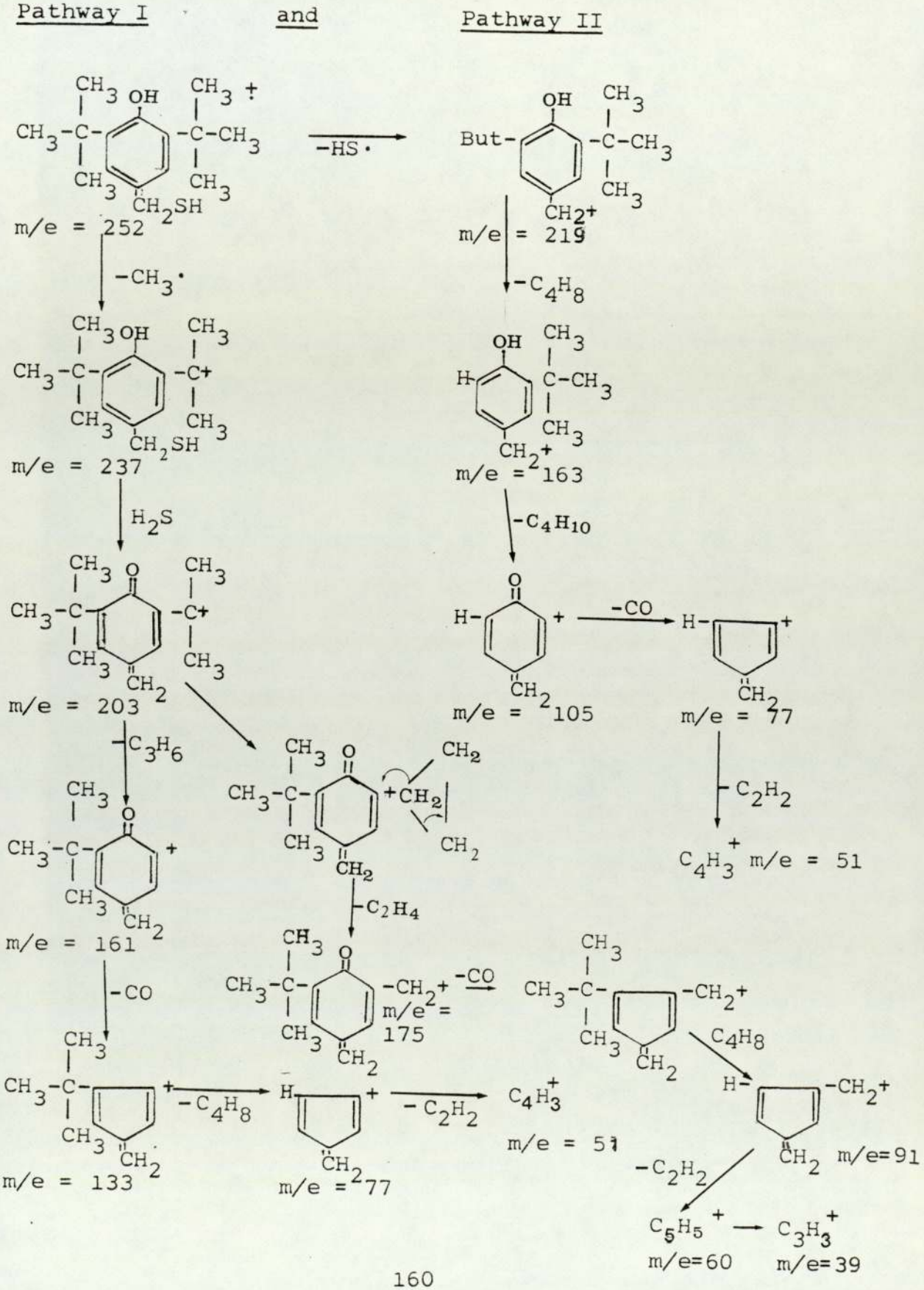

Pathway I
and
Pathway II
m/e = 252
-HS·
m/e = 219
-CH3·
-C4H8
m/e = 237
m/e = 163
H2S
-C4H10
m/e = 203
-CO
m/e = 105
m/e = 77
-C3H6
-C2H2
C4H3+ m/e = 51
m/e = 161
-C2H4
m/e = 175
-CO
-CO
-C4H8
-C2H2
C4H3+
m/e = 51
m/e = 133
m/e = 77
C4H8
m/e=91
-C2H2
C5H5+ → C3H3+
m/e=60
m/e=39

Table 4.5 Fragment loss of compound 4-V. Empirical formula = $C_{15}H_{24}OS$, highest m/e = 252 (.58%), scan range = 0-400.

Pathway I		Relative	Pathway II		Relative	
Fragment loss	m/e residue	Abundance (%)	Fragment loss	m/e residue	Abundance (%)	GC retention time (minutes)
$CH_3\cdot$	237	24	HS·	219	100	15' 58"
H_2S	203	75	C_4H_8	163	20	
C_3H_6	161	70	C_4H_{10}	105	23	
CO	133	18	CO	77	38	
C_4H_8	77	38	C_2H_2	5	22	
* C_2H_4	5	22				
C_2H_4	175	23				
CO	147	22				
C_4H_8	91	48				
C_2H_2	65	31				
C_2H_2	39	42				

* Different route

Lawesson and co-workers[147] have studied the mass spectra of thiophenol and showed that the most abundant peak is (M-HS·). According to Beynon[146] too, the base peak of thiols rarely contains an SH group. The fragmentation of thiol compounds lose HS· or H_2S readily which gives a base peak of high abundance. This is particularly true for aromatic thiols. Furthermore, for aromatic oxygenated compounds, such as phenols, CO or HCO is lost readily giving a peak of high intensity.

The mechanism of the ion fragmentation for compound 4-V is shown in Scheme 4. . The fragmentation loss during the breakdown of the compound (4-V) is summarised in Table 4.5.

It can be clearly seen that the loss of small S-containing particles gives a high fragment residue (m/e = 219, m/e = 203).

4.3.1.6 THE MASS SPECTRUM AND ITS INTERPRETATION FOR BIS(3,5-DI-TERT-BUTYL-4-HYDROXYBENZYL) DISULPHIDE

The mass spectrum of bis(3,5-di-tert-butyl-4-hydroxy-benzyl) disulphide (4-VI) is shown in Fig 4.7 and the ion fragmentation described in Scheme 4.6.

Beynon and co-workers[147] studied the mass spectra of

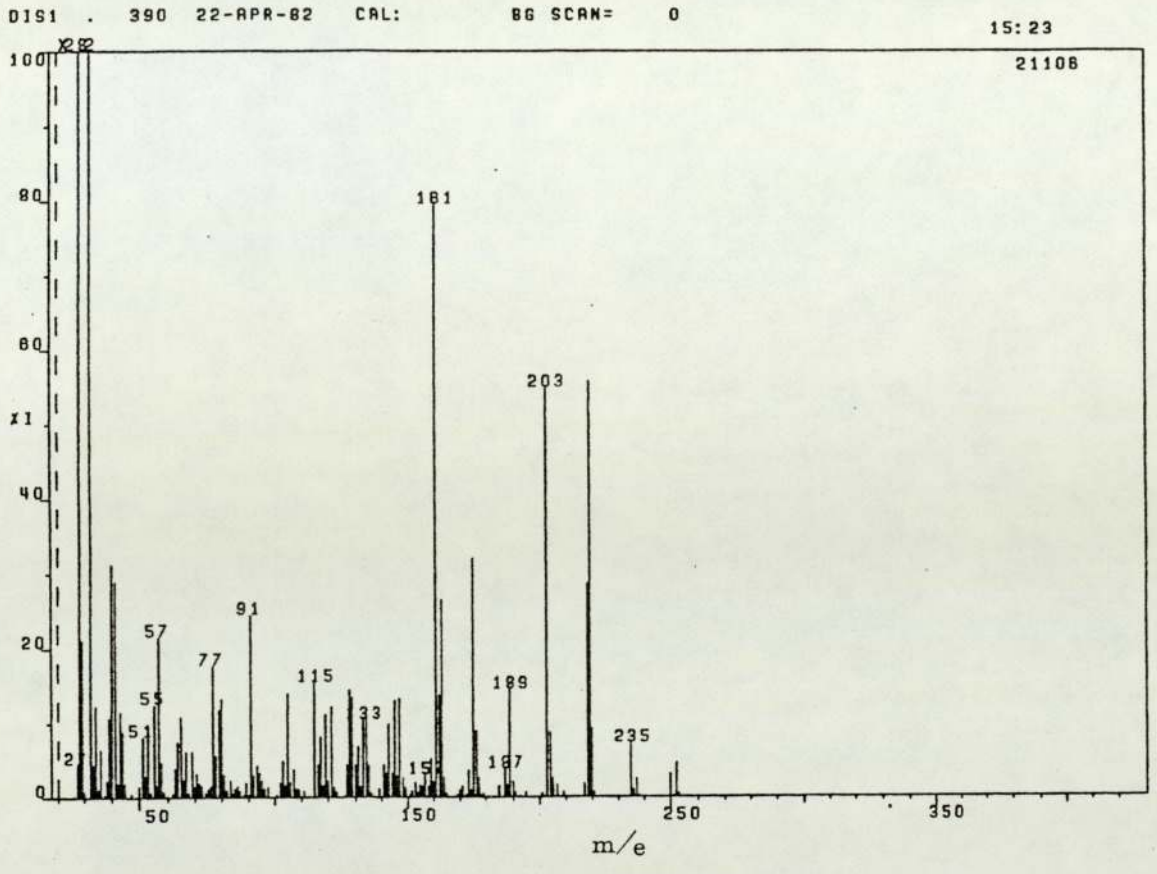
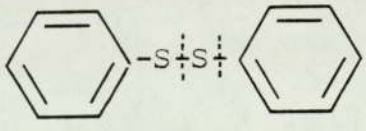


Fig 4.7 Mass spectrum of compound 4-VI

aromatic disulphides and showed that phenyl disulphide fragmented as follows:



It loses sulphur and gave the equivalent diphenyl ion, but the main cleavage proceeded by the scission between two sulphur atoms.

Scheme 4.6

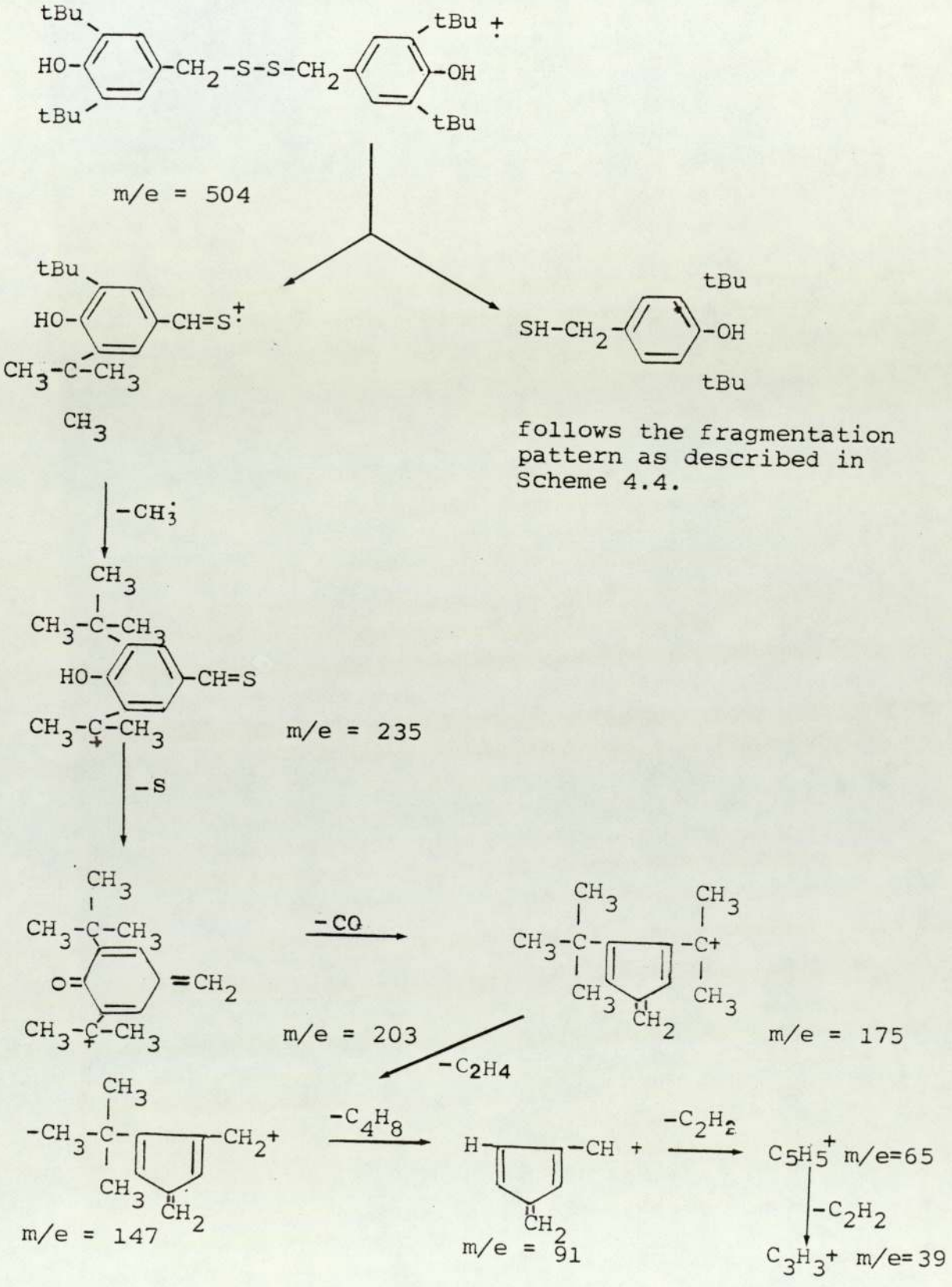
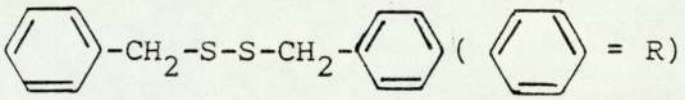

m/e = 504
follows the fragmentation pattern as described in Scheme 4.4.
m/e = 235
m/e = 203
m/e = 175
m/e = 147
m/e = 91
m/e=65
m/e=39

Table 4.6 Fragment loss of compound 4-VI. Empirical formula $C_{30}H_{46}S_2O_2$, highest m/e = 504, scan range 0-500

Pathway I		Relative	Pathway II		Relative	
Fragment loss	m/e residue	Abundance (%)	Fragment loss	m/e residue	Abundance (%)	GC retention time (minutes)
$CH_3^{\cdot}$	235	10				15' 23"
S	263	58				
CO	175	33	AS DESCRIBED IN			
C_2H_4	147	14	SCHEME 4.4			
C_4H_8	91	26				
C_2H_2	65	12				

Bowie and co-workers[150] showed that dibenzyl disulphide



gave (M-S) and (M-2S). Scission at S-S gave RCH_2SH and $RCHS^{+}$ or RCH_2S^{+} and $RCH_2S^{\cdot}$.

In the present case, scission followed the same pattern to give an m/e = 250 and m/e = 252. The fragmentation may be described by the scheme showed in Scheme 4.6.

The m/e values of the peak and the relative abundance are summarised in Table 4.6.

4.4 THE REACTION OF BHBM WITH TBH IN CYCLOHEXENE AT 70°C

4.4.1 REACTION OF BHBM WITH TBH (MOLAR RATIO, 1:½)

The conditions used for this experiment were as described in Section 4.2, except that the molar ratio of BHBM (0.01 mol) to TBH (0.005 mol) was 2:1.

The GC-MS chromatogram showed 14 peaks (Fig 4.8). Fig 4.8 shows the GC-MS chromatogram peak containing M or M^{+} of 218. The mass spectra of each peak are shown in Figs 4.9 - 4.19.

Table 4.7 shows the highest value for m/e of each peak together with scan number and retention time.

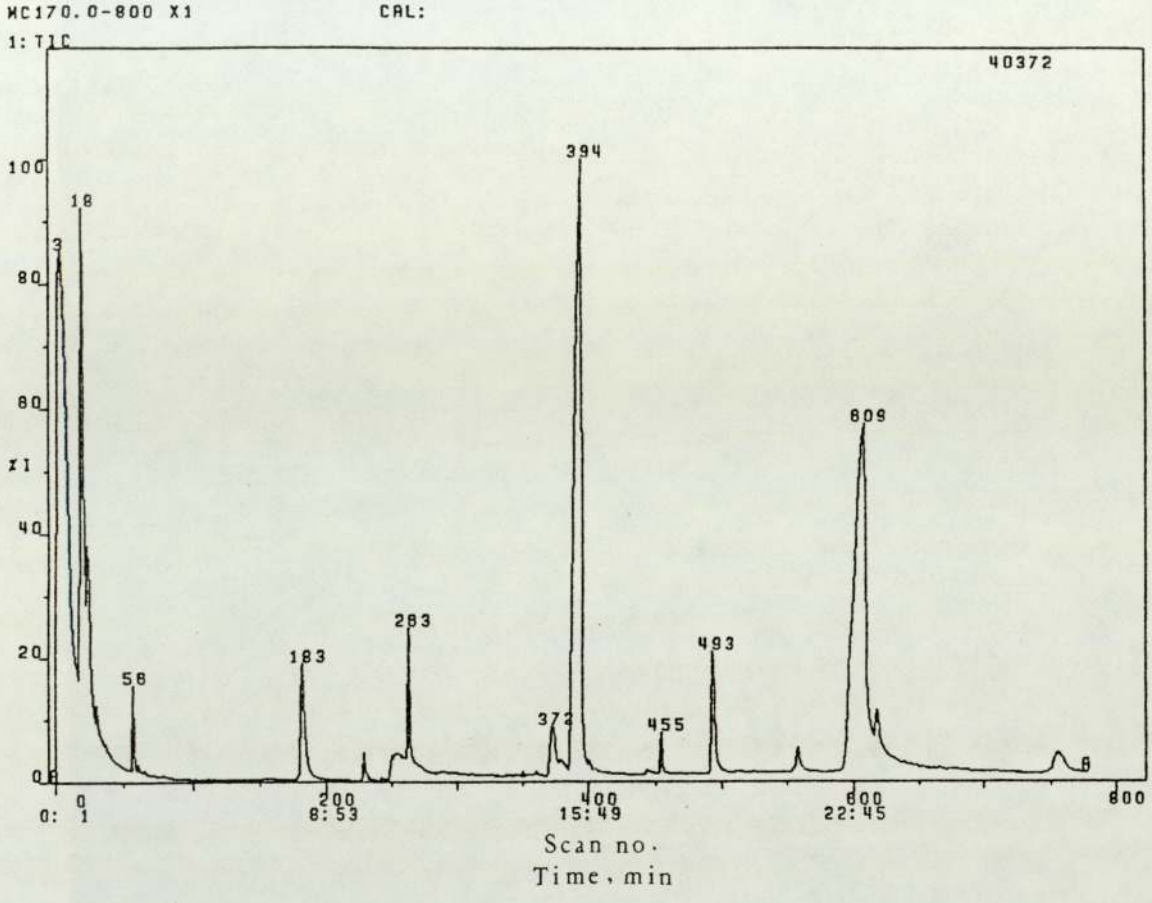


Fig 4.8 GC-MS chromatogram of reaction of BHBM with TBH (molar ratio 1:½)

Table 4.7 Highest m/e values for peaks in reaction of BHBM with TBH (molar ratio 1:½), scan range 0-800

Peak at scan number	Highest m/e	Retention time (minutes)
229	206	9' 53"
258	218	10' 49"
263	220	11' 04"
394	252	15' 36"
493	300	19' 02"
608	334	23' 02"
618	250	23' 22"
750	293/294	27' 57"
371	234	15' 19"

4.4.1.1 A QUALITATIVE ANALYSIS OF THE MASS SPECTRA OF THE REACTION PRODUCTS

4.4.1.1.1 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 229 AND ITS INTERPRETATION

The mass spectrum of peak number 229 is shown in Fig 4.9. The mass spectrum of this peak is identical to the mass spectrum of 2,6-di-tert-butyl phenol, described in Section 4.3.1.1. It is concluded, therefore, that this peak corresponds with compound

4-I, which is 2,6-di-tert-butyl phenol.

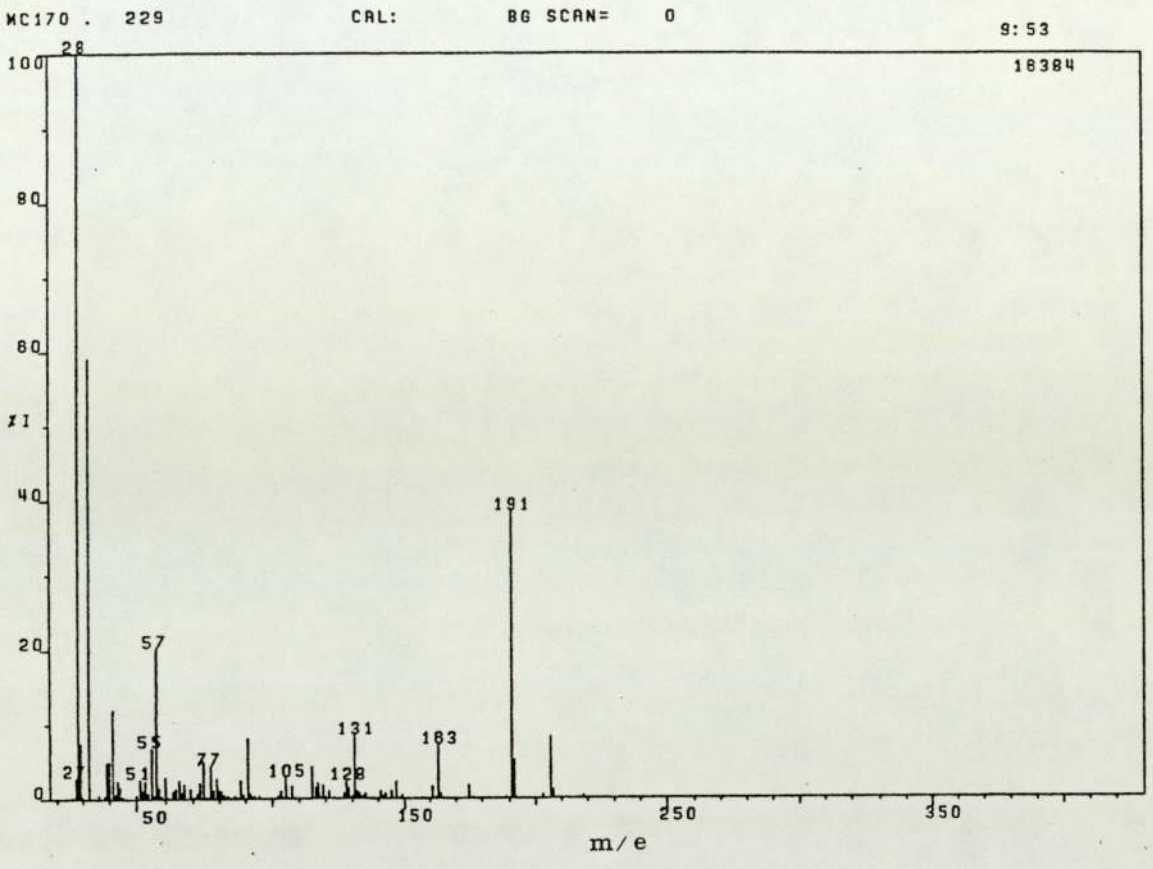


Fig 4.9 The mass spectrum of peak at scan number 229

4.4.1.1.2 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 258 AND ITS INTERPRETATION

The mass spectrum of peak no 258 is shown in Fig 4.10.

The peak at scan number 258 gives a mass spectrum which is identical to that of the reference spectrum of 2,6-di-tert-butyl-4-methylene-2,5-cyclohexadien-1-one

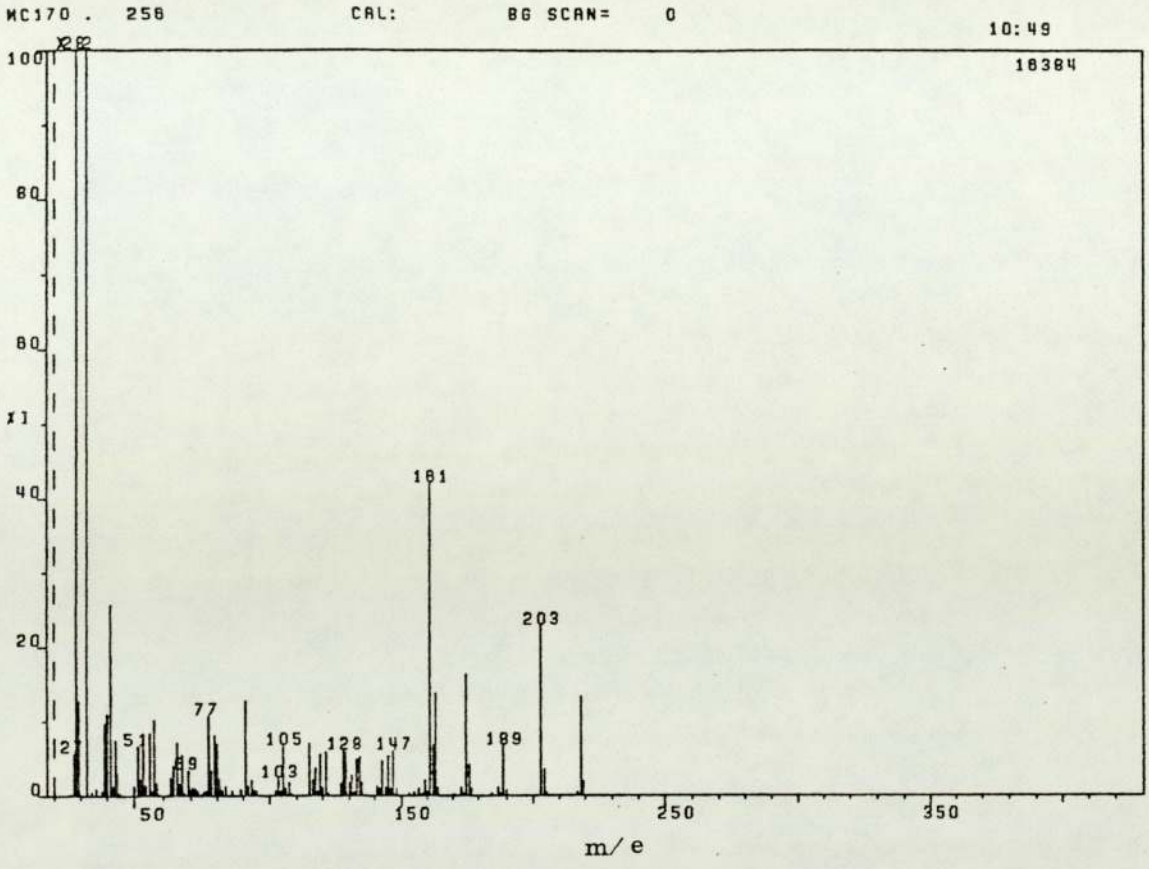


Fig 4.10 The mass spectrum of peak at scan number 258

(compound 4-III) described in Section 4.3.1.3. It is thus concluded that the peak at 258 is identical to that of compound 4-III.

4.4.1.1.3 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 263 AND ITS INTERPRETATION

The mass spectrum of peak number 263 is shown in Fig 4.11.

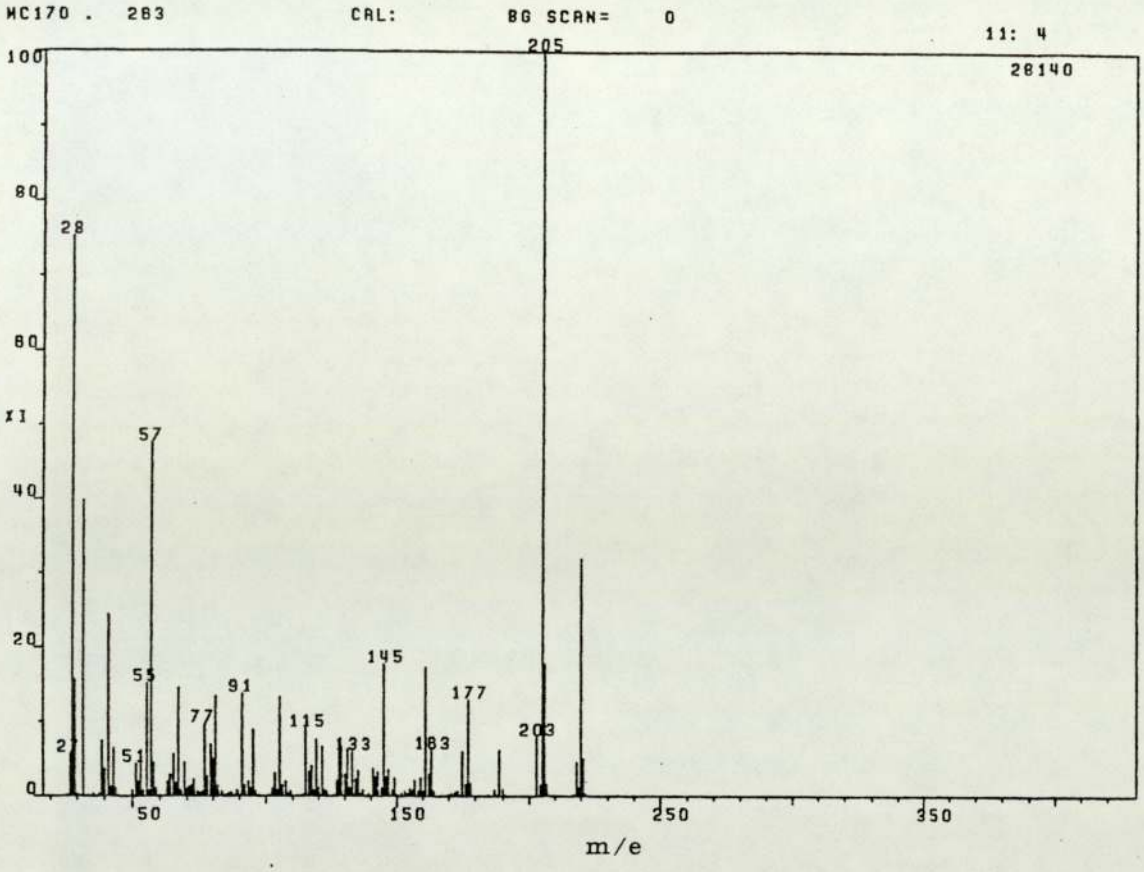


Fig 4.11 The mass spectrum of peak at scan number 263

4.4.1.1.4 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 371 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 371 is shown in Fig 4.12.

The fragmentation of this compound, described later in Section 4.4.2.2, which is3,5-di-tert-butyl-4-hydroxy-phenyl carbaldehyde.

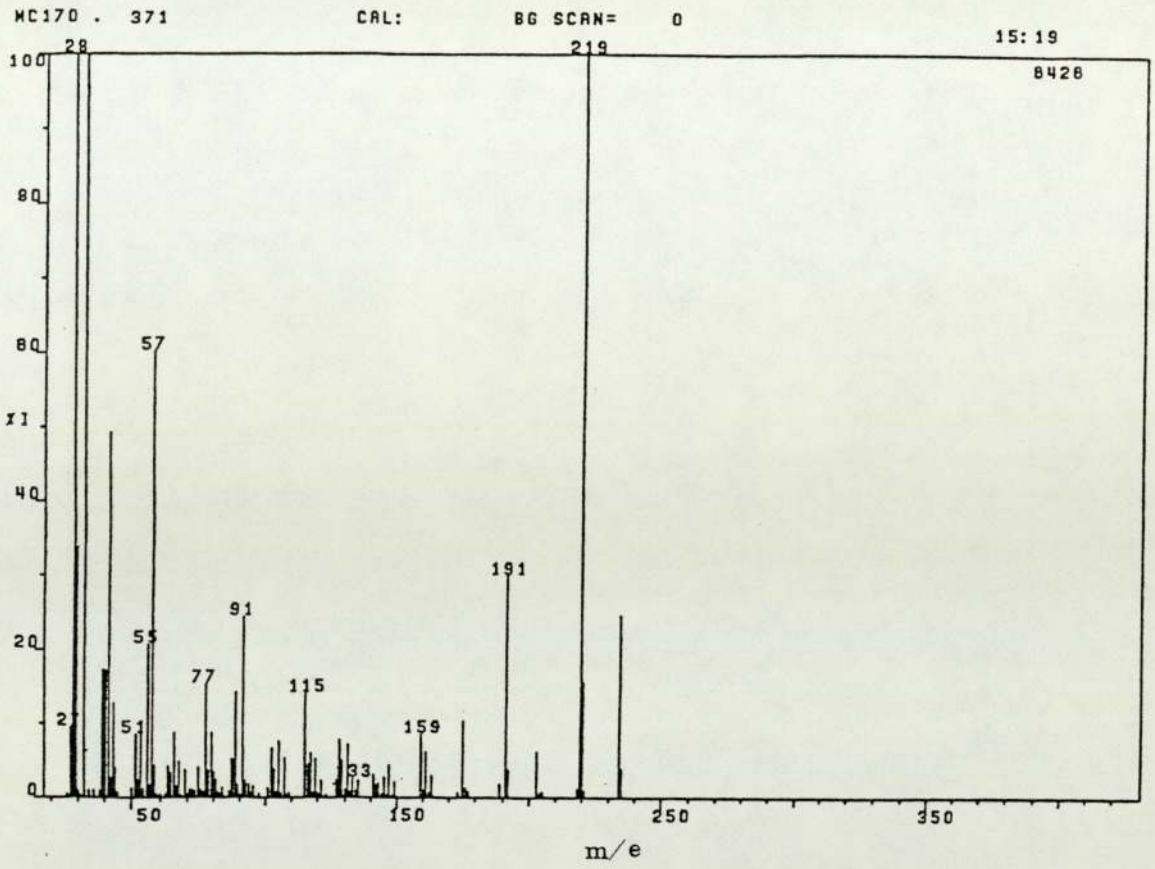


Fig 4.12 The mass spectrum of peak at scan number 371

The mass spectra of peak number 263 corresponds to that shown in Section 4.3.1.2. Hence this compound is 2,6-di-tert-4-methyl phenol.

4.4.1.1.5 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 394 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 394 is shown in Fig 4.13.

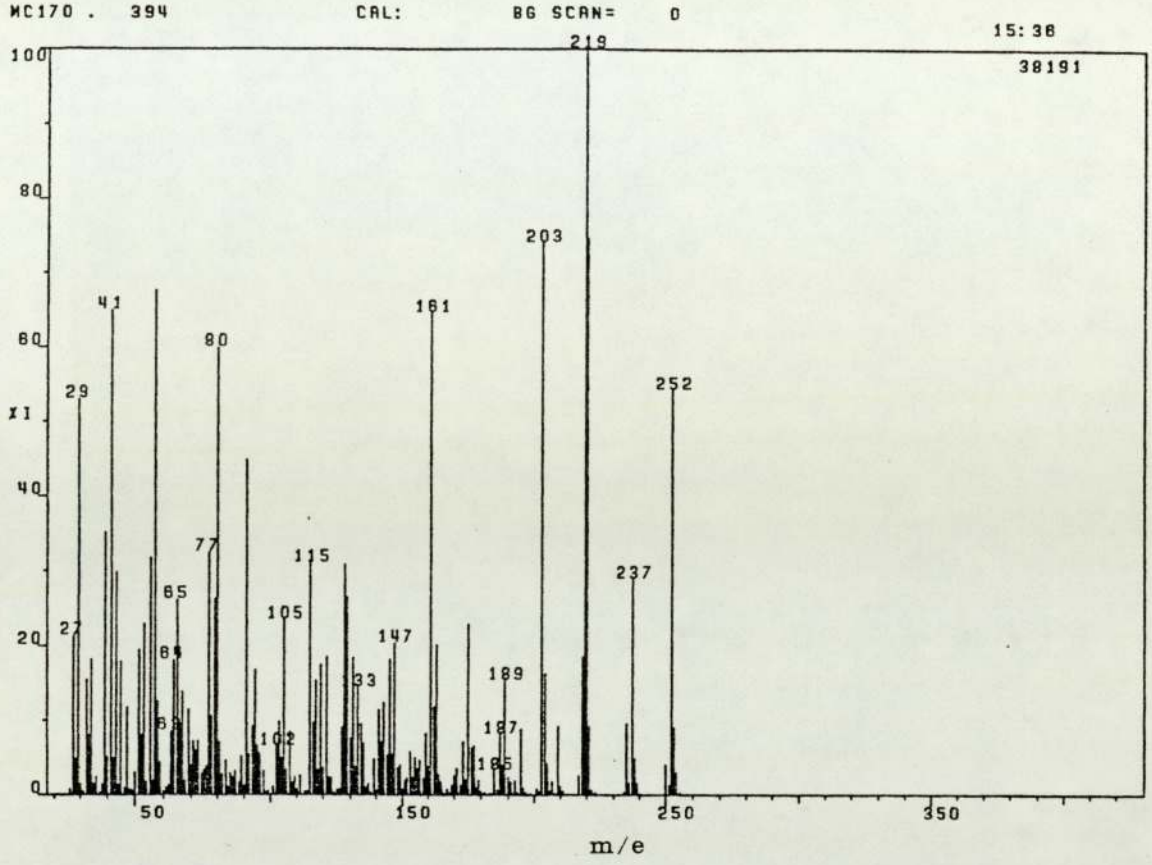


Fig 4.13 The mass spectrum of peak at scan number 394

The mass spectrum of peak at scan number 394 is identical to the reference peak described in section 4.3.1.5 which is 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan (compound 4-V). Thus, the peak at scan number 394 is identical with compound 4-V.

4.4.1.1.6 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 493 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 493 is shown in Fig 4.14.

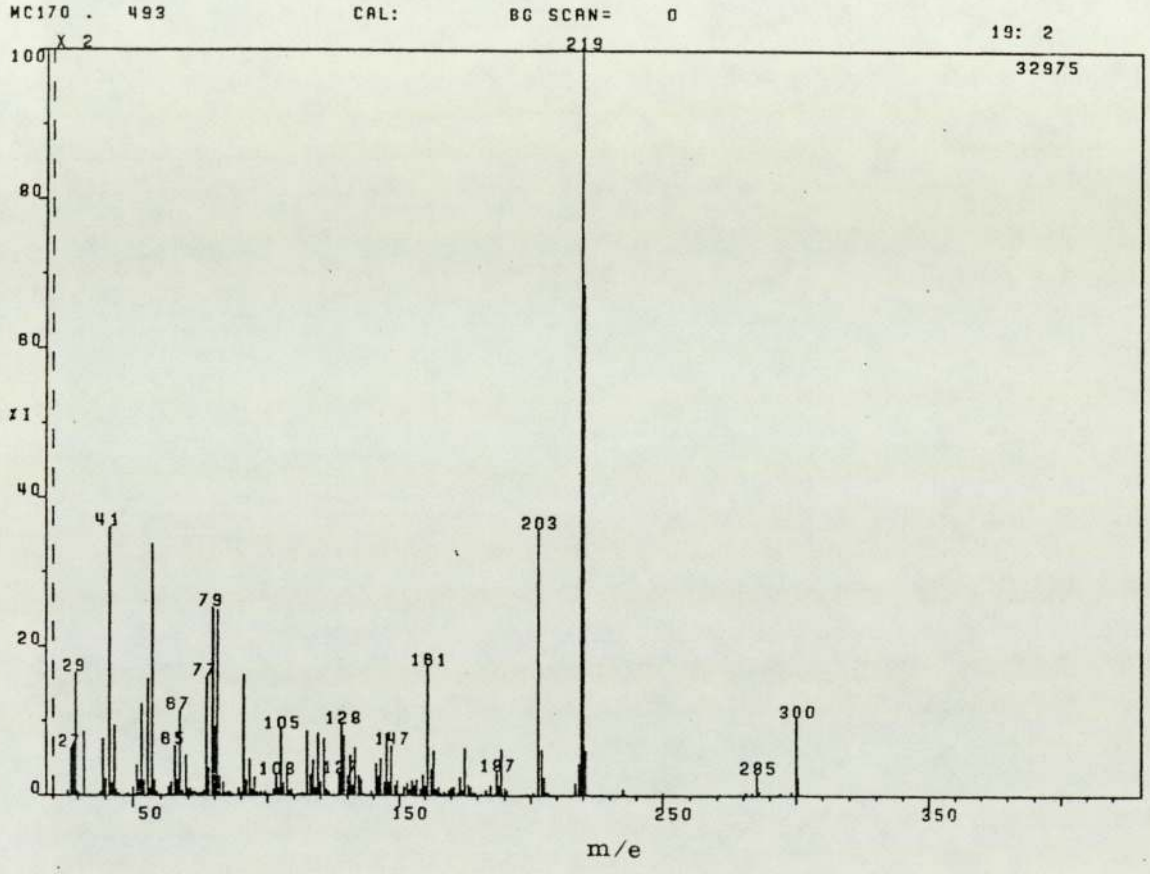
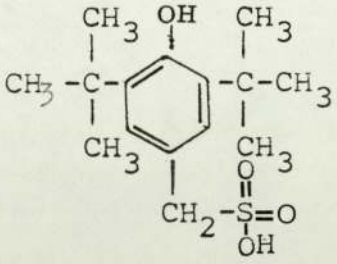


Fig 4.14 The mass spectrum of peak at scan number 493

The mass spectrum of peak number 493 showed highest m/e value of 300. The main fragmentation peaks occur at m/e values of 285, 219, 203, 175, 161, 147, 105, 133, 91, 77, 51, 65 and 39. Analysis of the spectrum by calculating

the isotope abundance showed the empirical formula to be $C_{15}H_{24}SO_4H$. Fitting this empirical formula into the known possible reaction products of the model compound work, the structural formula must be:



3,5-di-tert-butyl-4-hydroxy-phenyl methyl sulphonic acid (4-VII)

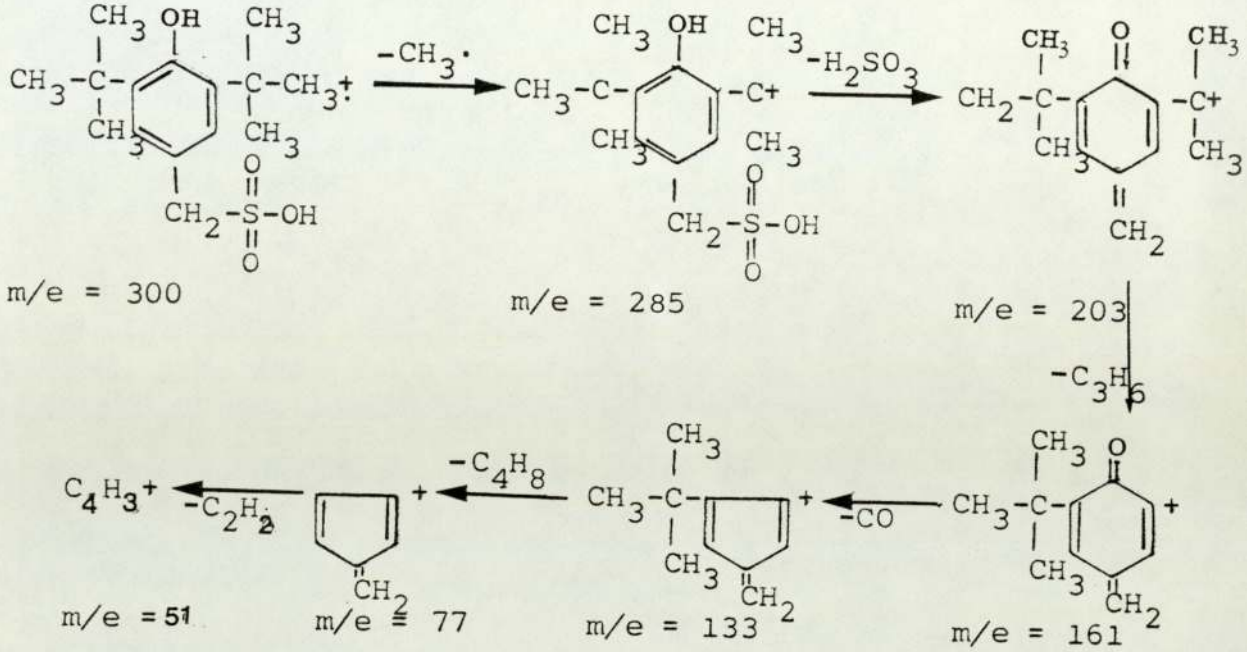
According to the theory[147-150] the fragmentation of this compound should occur as shown in Scheme 4.7.

Examination of the mass spectrum for peak at scan number 493 shows that all these fragment ions occur in the spectrum. Therefore the spectrum corresponds to $C_{15}H_{24}SO_4H$.

The results of the above fragmentation and its relative abundance is summarised in Table 4.8.

Scheme 4.7

Pathway I



Pathway II

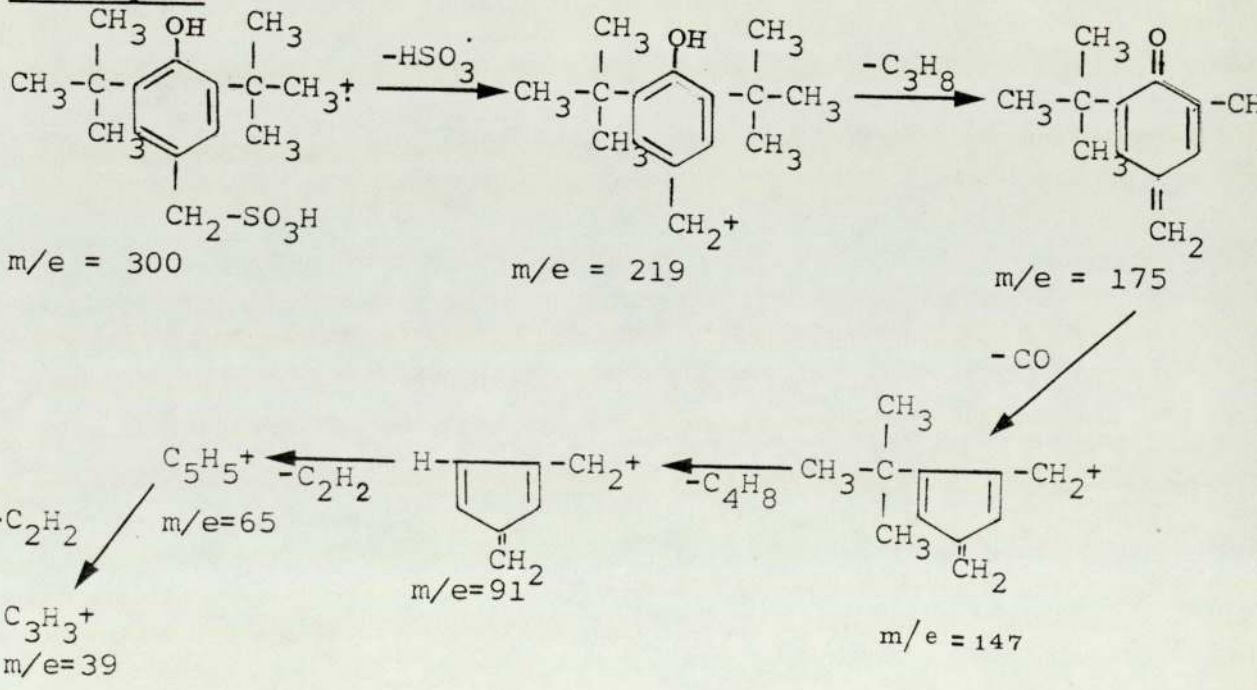
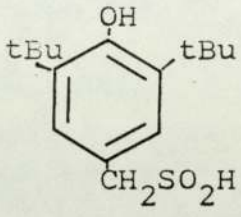


Table 4.8 Fragment loss of peak at scan number 493. Empirical formula $C_{15}H_{24}SO_4H$

Highest m/e = 300, Retention time = 19' 2"

Pathway I			Pathway II		
Fragment loss	Highest m/e	Relative abundance %	Fragment loss	Highest m/e	Relative abundance %
CH_3	285	5	HSO_3	219	100
H_2SO_3	203	40	C_3H_8	175	10
C_3H_6	161	22	CO	147	100
CO	133	10	C_4H_8	91	18
C_4H_8	77	18	C_2H_2	65	13
C_2H_2	5	5	C_2H_2	39	16

Furthermore, 4-VII was synthesised by a literature method[152] and gave an identical mass spectrum as shown in Fig 4.14. Attempts to make the following compound were not successful as the mixture exploded during the isolation procedure.



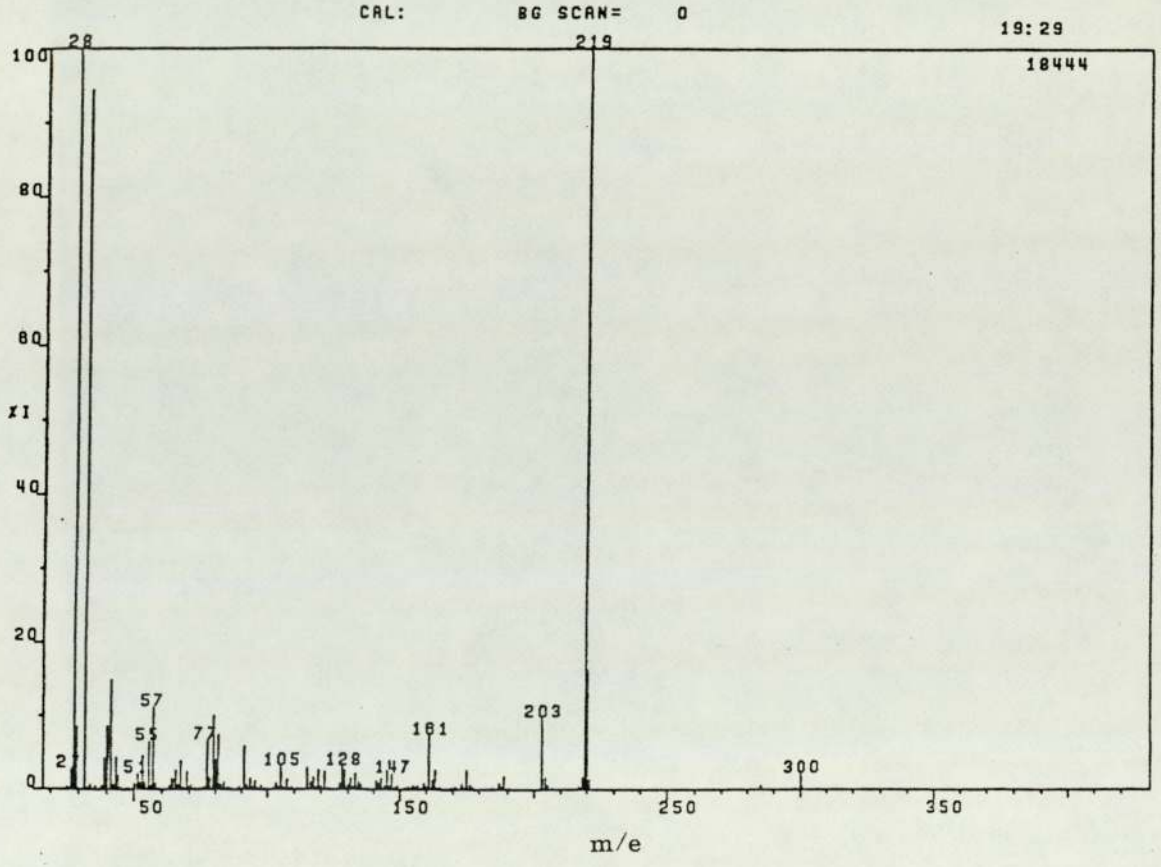
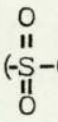


Fig 4.15 The mass spectrum of 3,5-di-tert-butyl-4-hydroxyphenyl methyl sulphonic acid according to a known method[156]

Furthermore, a study of the sulphonic acid group () in the peak at scan number 493 was shown by the computer in GC-MS since no other oxygenated sulphur products were detected. This explained that sulphonic acid is the most stable product compared to sulphenic and sulphinic acid. The GC-MS chromatogram of sulphonic acid (4-VII) is shown in Fig 4.16.

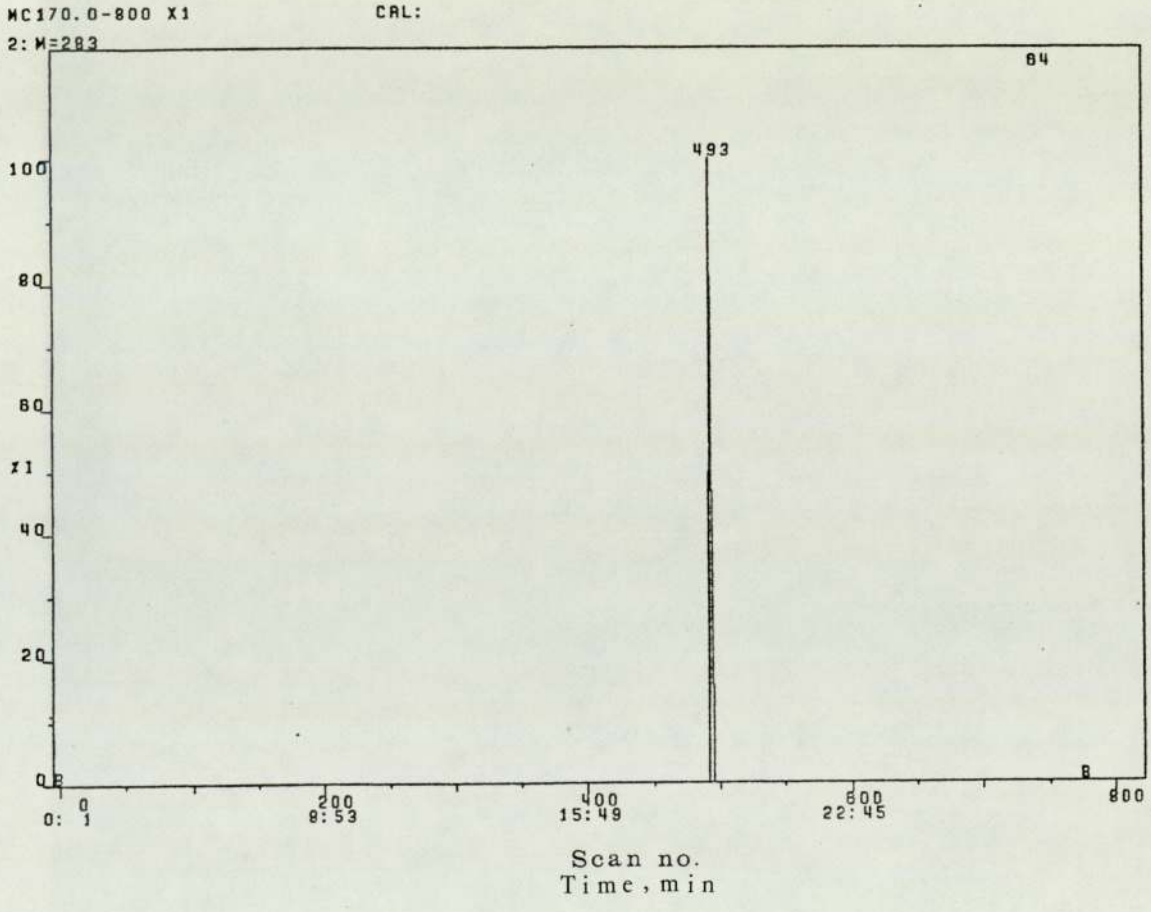


Fig 4.16 GC-MS chromatogram of compound 4-VII

4.4.1.1.7 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 608 AND ITS INTERPRETATION

The main fragmentation peaks occurred at 319, 252, 235, 219, 203, 189, 161, 145,105, 91, 77 as shown in Fig 4.17.

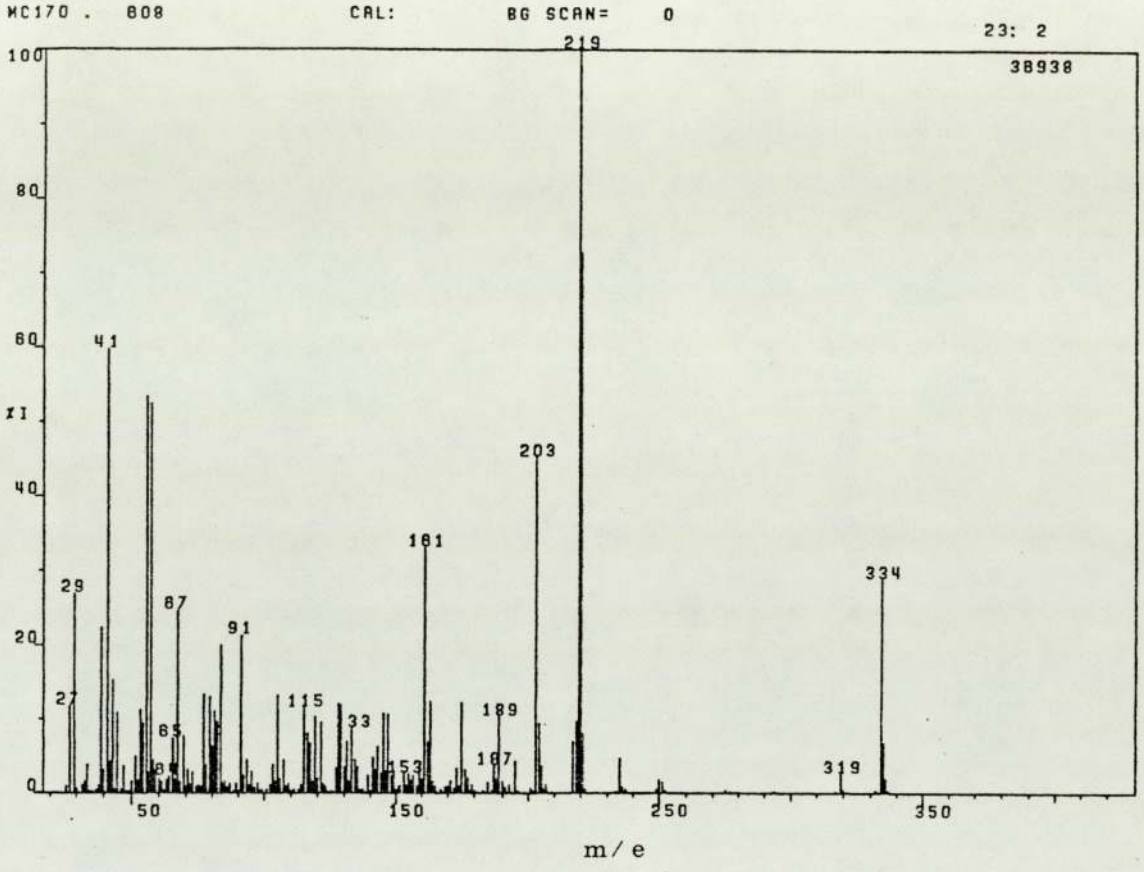
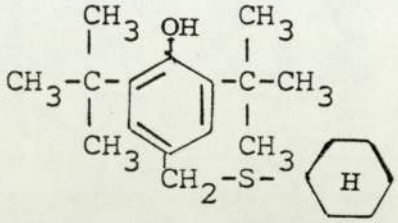


Fig 4.17 The mass spectrum of peak at scan number 608

Analysis of the empirical formula from relative abundance of the M, M+1 and M+2 peaks for the highest m/e = 334 peak revealed the compound of scan number 608 had an empirical formula of $C_{21}H_{34}SO$. Fitting this empirical

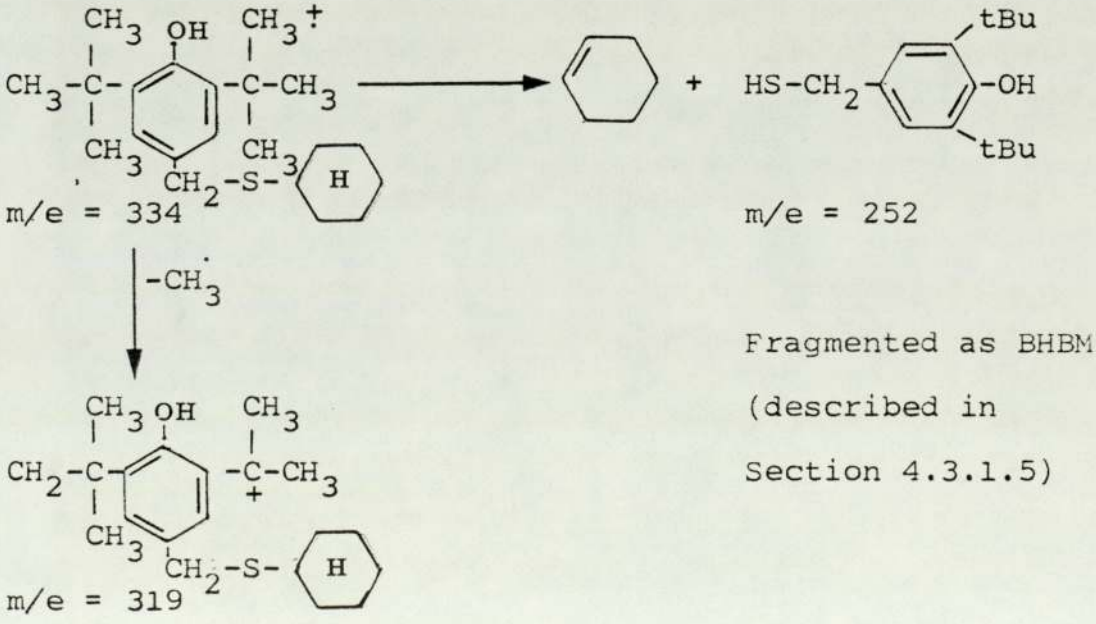
formula into the known possible products of the reaction the compound at scan number 608 must have the following structure:

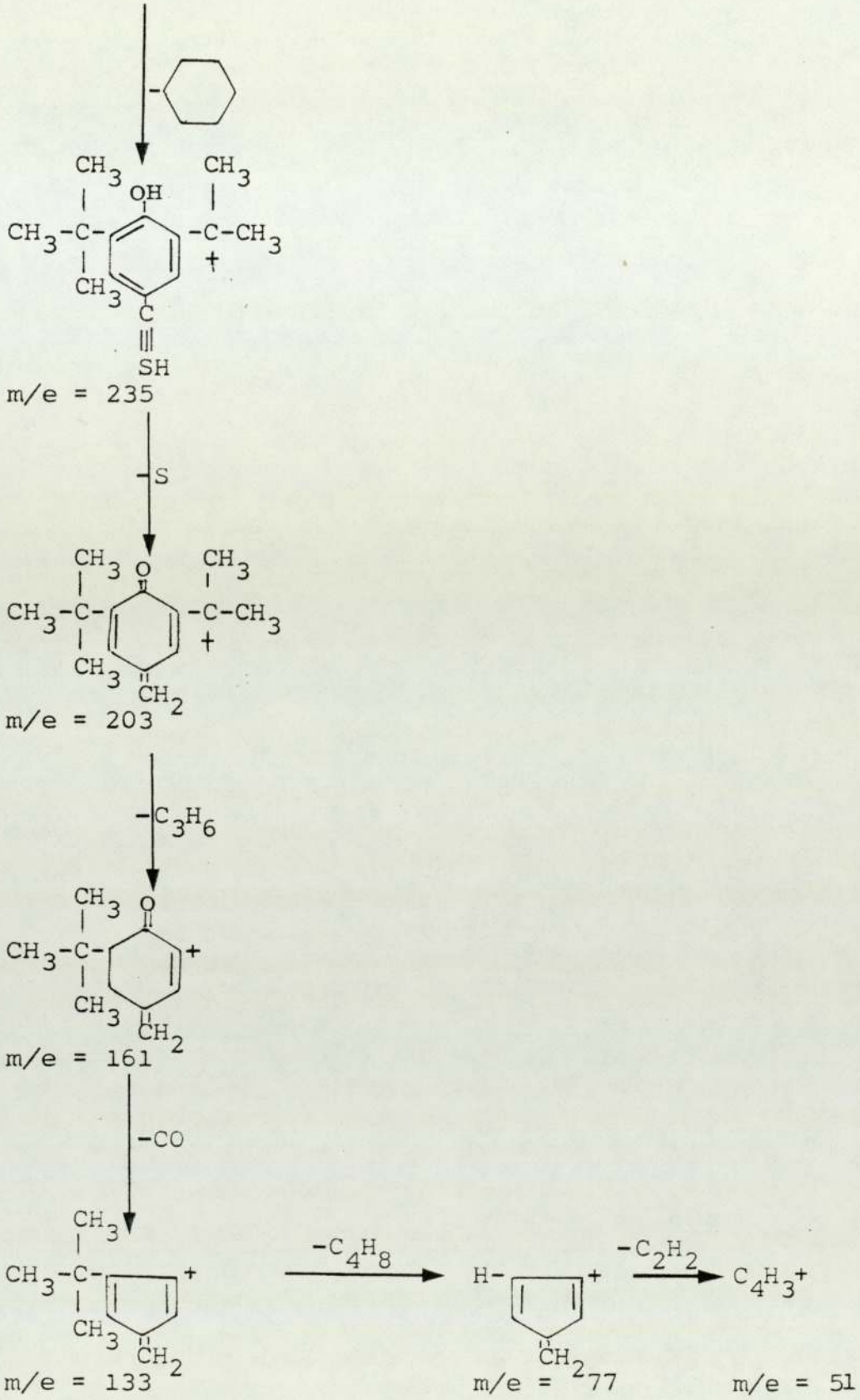


3,5-di-tert-butyl-4-hydroxyphenyl methyl cyclohexyl sulphide (4-VIII)

According to the theory, this compound should fragment to give the following fragmentation ions:

Pathway I and Pathway II





Scheme 4.8

This is summarised in Table 4.9.

Table 4.9 Fragment loss of peak at scan number 608. Empirical formula $C_{21}H_{34}SO$

Highest m/e = 334 (29 %) Retention time = 23' 2"

Pathway I			Pathway II		
Fragment loss	m/e residue	Relative abundance %	Fragment loss	m/e residue	Relative abundance %
$CH_3\cdot$	319	3			
	235	5			
S	203	48			
C_3H_6	161	34	AS DESCRIBED IN SECTION 4.3.1.5		
CO	133	9			
C_4H_8	77	20			
C_2H_2	51	5			

It is concluded that peak at scan 608 is compound 4-VII.

4.4.1.1.8 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 618 AND ITS INTERPRETATION

The main fragmentation peaks occurred at 250, 252; the mass spectrum is shown in Fig 4.18.

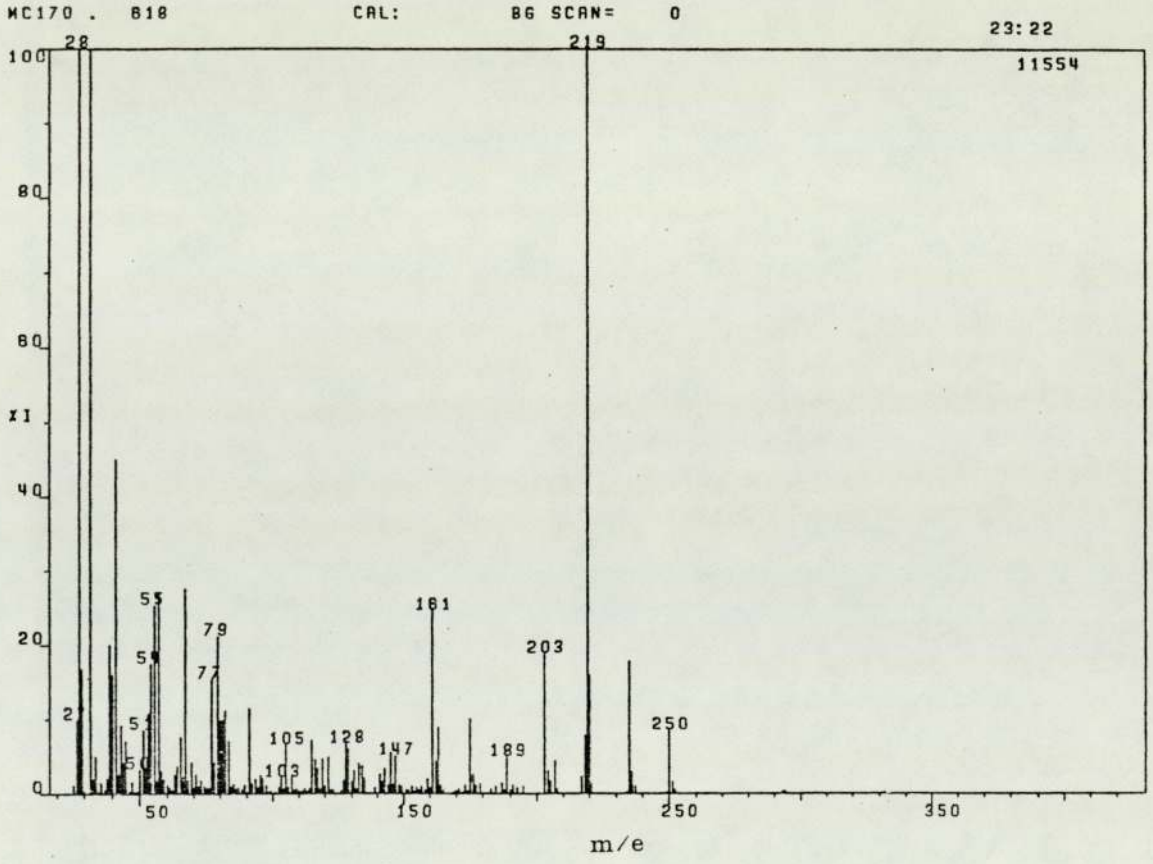


Fig 4.18 The mass spectrum of peak at scan number 618

The retention time of compound shown by the GC-MS was

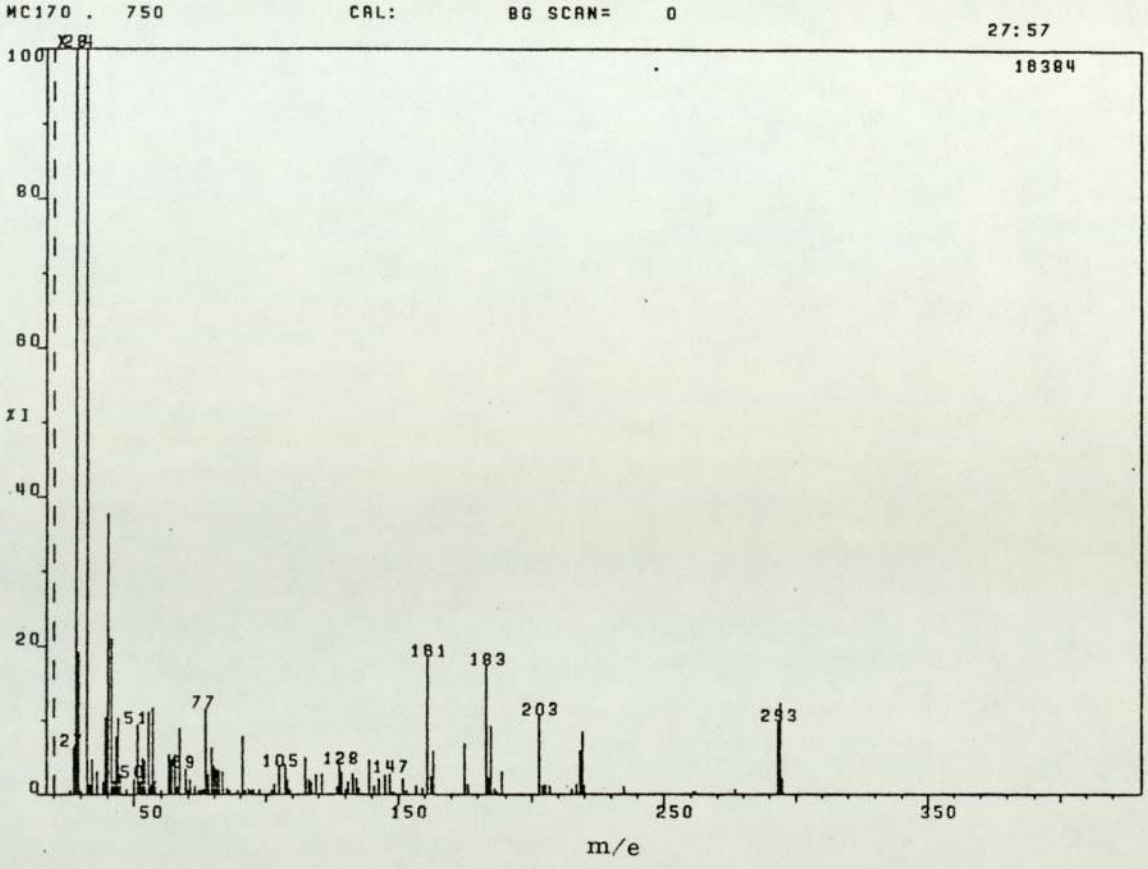


Fig 4.19 The mass spectrum of peak at scan number 759 (which has not yet been identified)

22 minutes and 22 seconds. BHBM has a m/e at 252 and an RT value of 15 minutes and 36 seconds. Since RT is dependant on the molecular weight of the compound, the peak at scan number 618 has a molecular weight greater than 252 and the mass ion recorded for this peak is identical to the mass spectrum of compound 4-VI, described in Section 4.3.1.6. This suggested that the peak at scan number 618 is identical to that of compound 4-VI.

4.4.1.1.9 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 750

The mass spectrum of peak at scan number 750 is shown in Fig 4.19. This peak has not yet been identified.

4.4.2 THE REACTION OF BHBM WITH TBH (MOLAR RATIO 1:1)

The conditions used for this experiment were as described in Section 4.2 (BHBM = 2.5 g, TBH = 0.81 g), (BHBM : TBH = molar ratio 1:1). The chromatogram of the GC-MS showed fourteen peaks as can be seen in Fig 4.19, of these peaks, eight correspond to the reaction products. The mass spectrum of each peak is shown in Figs 4.20-4.27.

Table 4.10 shows the highest m/e value of each peak which scan number, with the retention time.

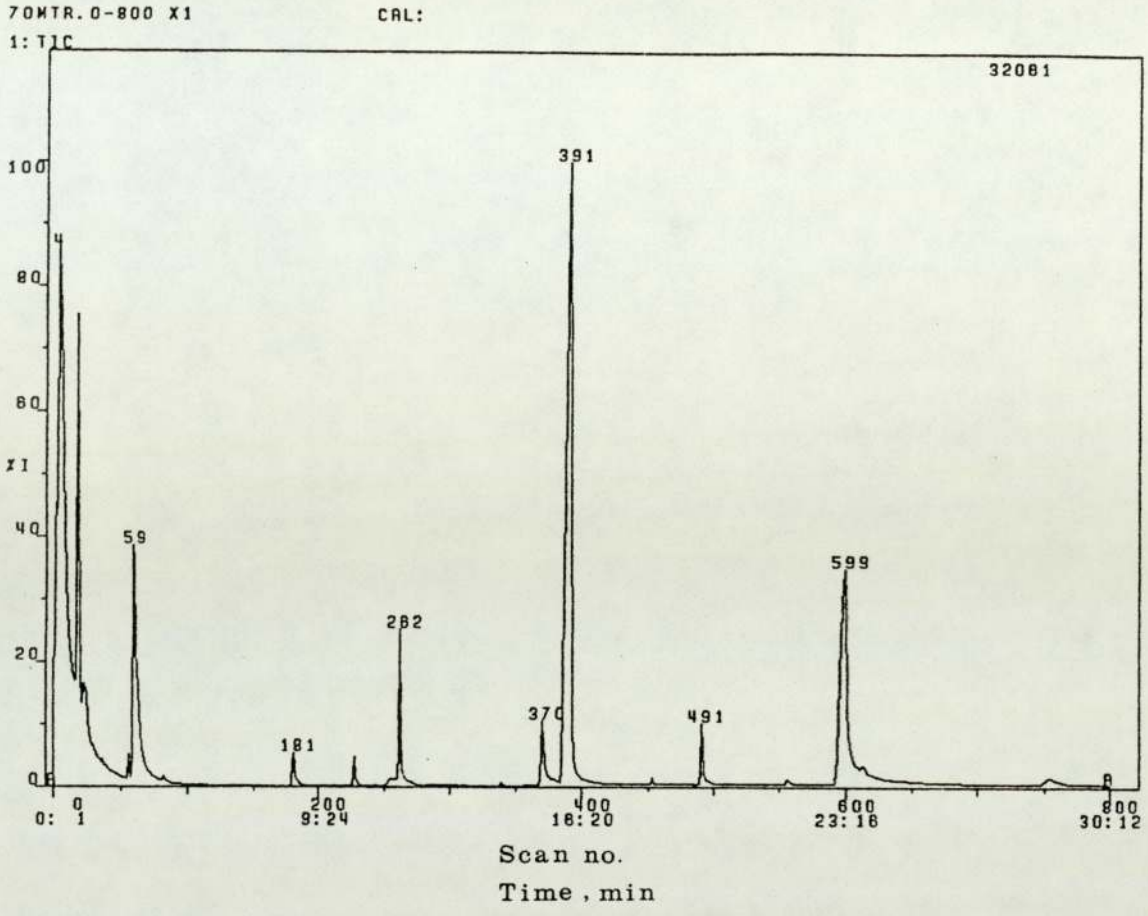


Fig 4.20 GC-MS chromatogram of reaction of BHBM with TBH (molar ratio 1:1)

The mass spectrum of each peak was studied and compared with the reference mass spectra described in Section 4.3.1.1 to Section 4.3.1.6 and also the mass spectra studied in Section 4.4.1.5 and Section 4.4.1.1.6.

Table 4.10 Highest m/e value for peak in reaction of BHBM with TBH (molar ratio 1:1). Scan range 0-800

Peak at scan no	Highest m/e	Retention time
228	206	9' 18"
258	218	10' 22"
262	220	11' 4"
371	234	15' 19"
391	252	16' 1"
491	300	19' 29"
599	334	23' 14"
606	250	23' 2"
755	294	28' 38"

4.4.2.1 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 228 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 228 is shown in Fig 4.21.

The mass spectrum of peak at scan number 228 is identical to that of the mass spectrum of 2,6-di-tert-butyl-phenol, described in Section 4.3.1.1. Therefore, this peak at scan number 228 corresponds

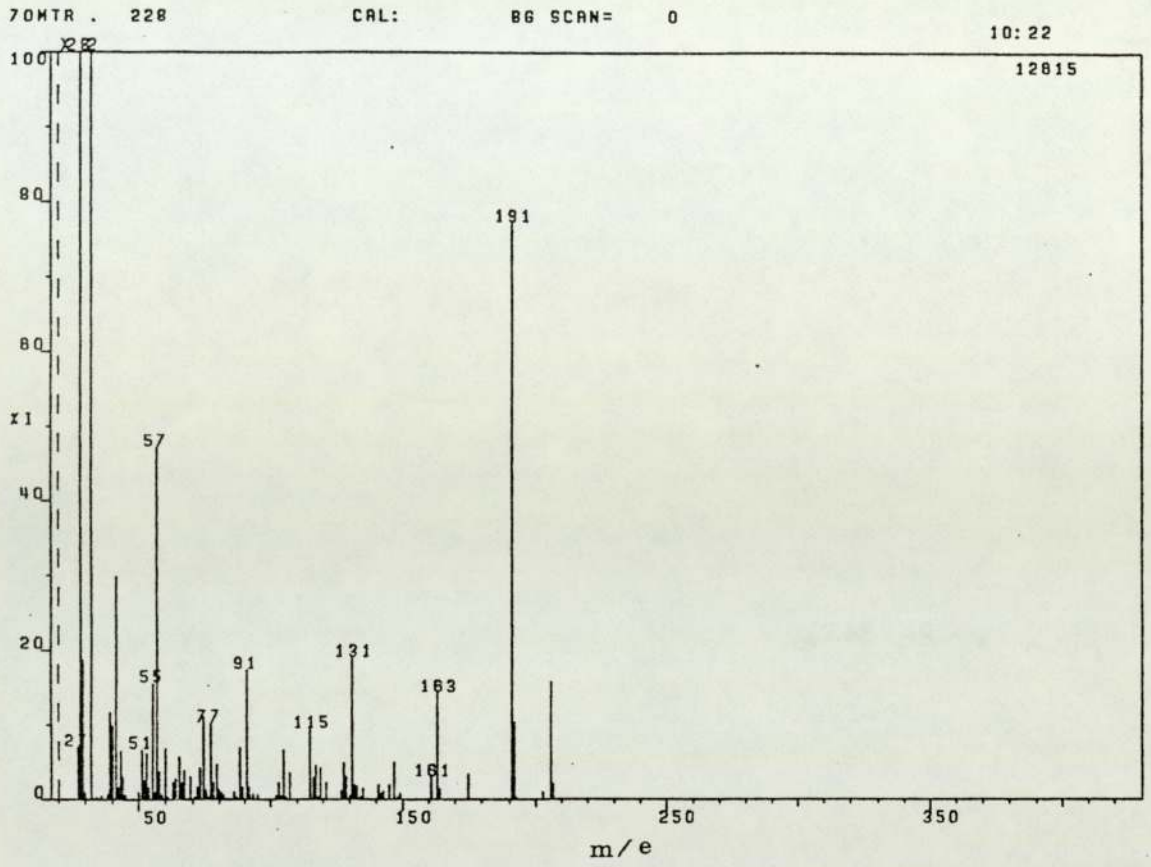


Fig 4.21 The mass spectrum of peak at scan number 228 with compound 4-I.

4.4.2.2 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 258 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 258 is shown in Fig 4.21.

The peak at scan number 258 is identical with the

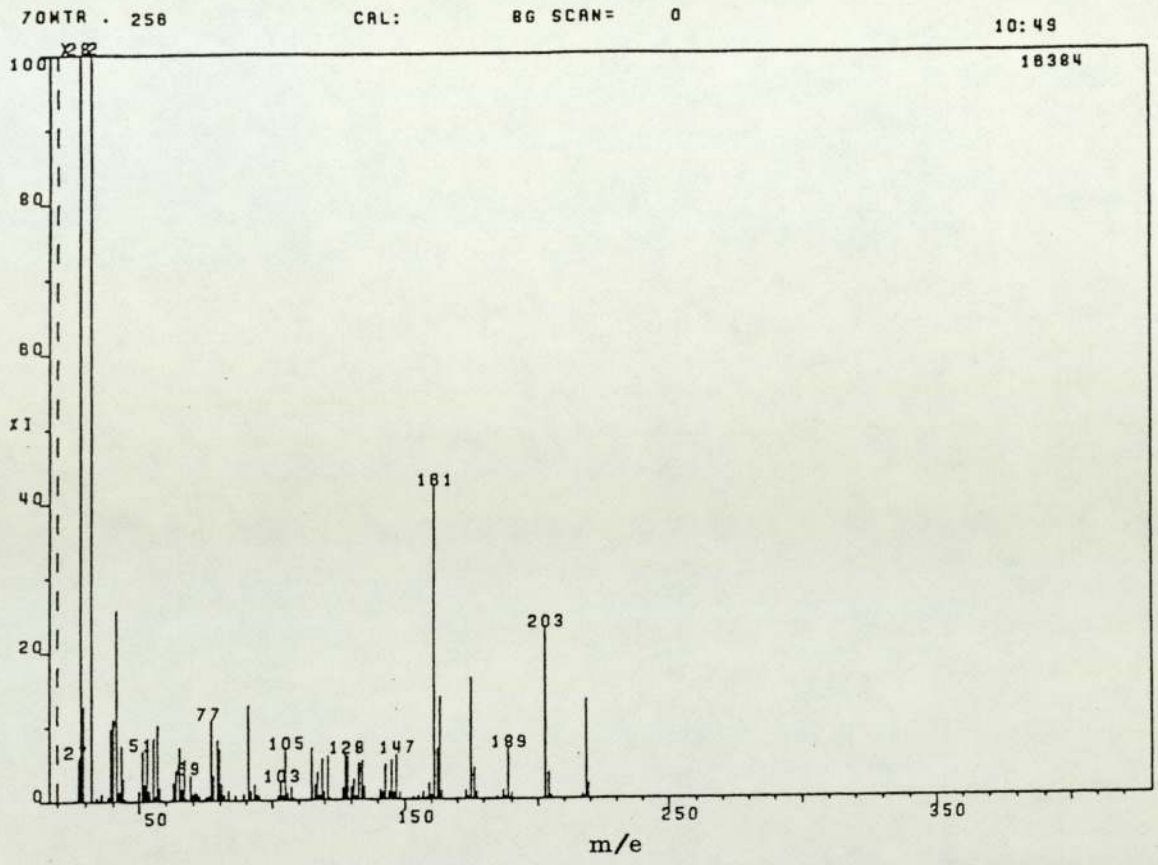


Fig 4.22 The mass spectrum of peak at scan number 258

reference mass spectrum as described in Section 4.4.1.1.2 which is 2,6-di-tert-butyl-4-methylene-2,5-cyclohexadien-1-one (4-III). It is concluded that the peak at scan number 258, is identical to compound 4-III.

4.4.2.3 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 262/3 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 262/3 is

shown in Fig 4.2.3.

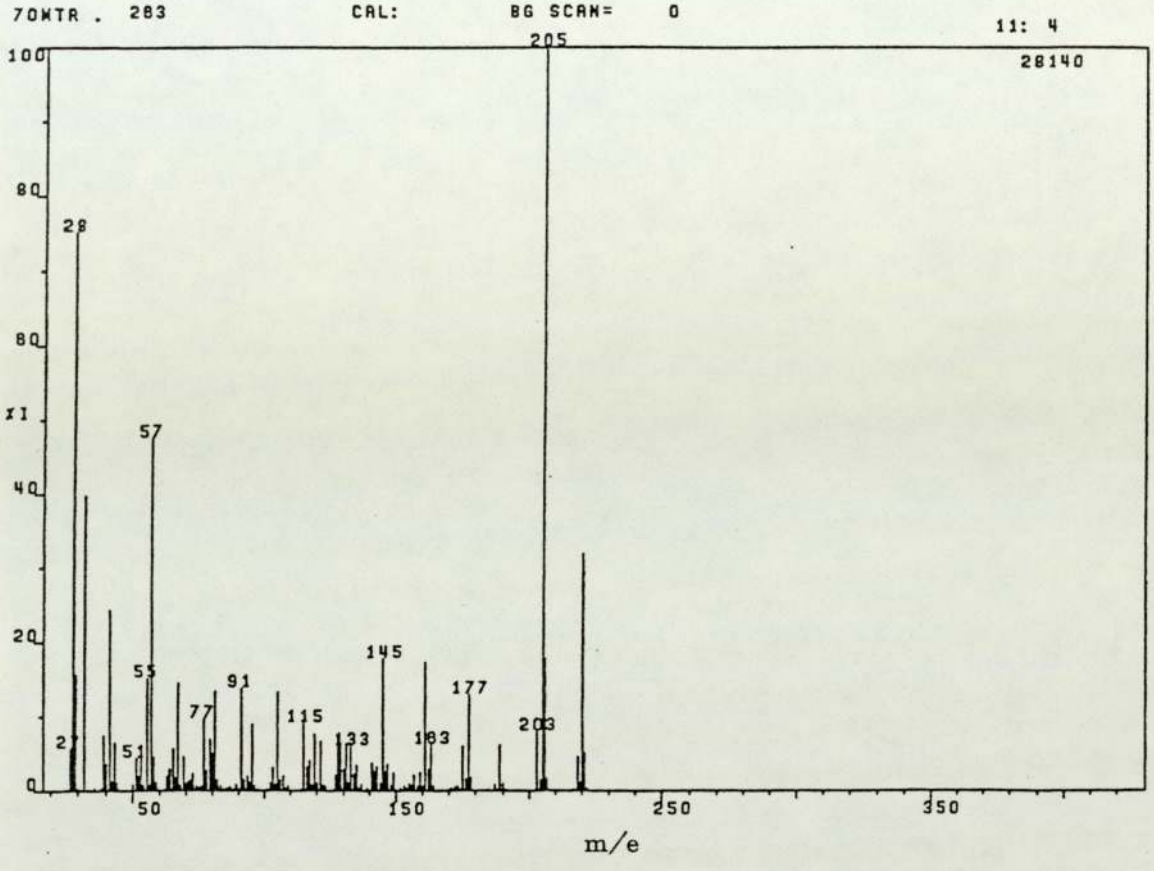


Fig 4.23 The mass spectrum of peak at scan number 262/3

The mass spectrum of peak at scan number 262/3 is shown to correspond to that shown in Fig 4.11, described in Section 4.4.1.1.3, which is 2,6-di-tert-4-methyl phenol (4-II). Therefore the peak at scan number 262/3, is identical to compound 4-II.

4.4.2.4 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 370/1 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 370/1 is shown in Fig 4.24.

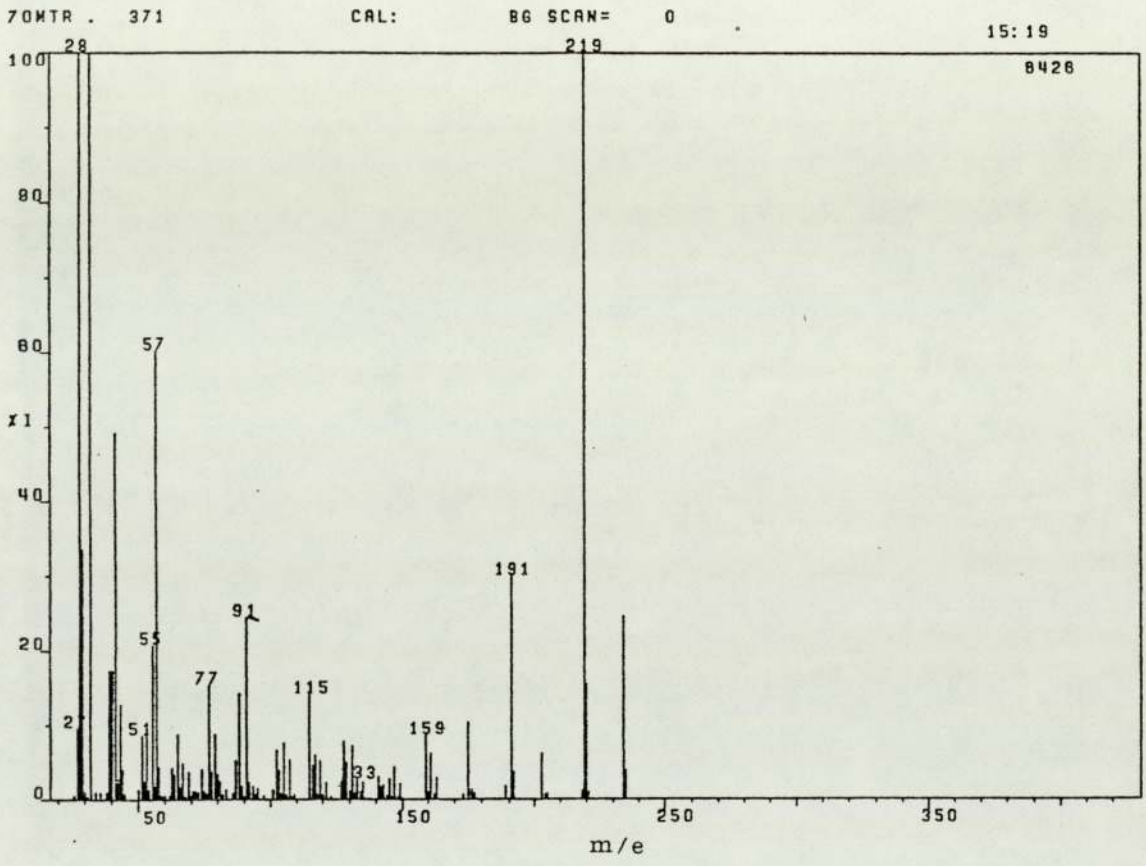


Fig 4.24 The mass spectrum of peak at scan number 370/1

The mass spectrum shown in Fig 4.24 were compared to the mass spectra of the reference materials. Peak at scan number 370/1 which has a higher m/e of 234 (see Table 4.11 and Scheme 4.8) was detected (very weak)

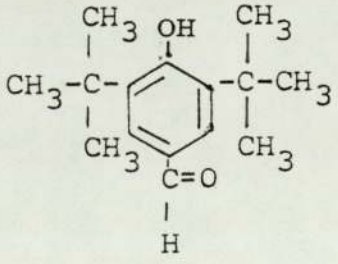
when the reaction was done. At a molar ratio of BHBM to TBH of 2:1.

Therefore, the compound to this peak must be related to the availability of more TBH in the system.

The mass spectrum differs from that of 2,5-di-tert-butyl-4-hydroxybenzyl alcohol (4-IV) described in Section 4.3.1.4 by an m/e of 2 for all fragmentation ions above M$\pm$147. Below this mass, the fragmentation pattern is identical to that of compound 4-IV.

Analysis of the spectrum by calculating M, M+1 and M+2 showed that the empirical formula of $C_{15}H_{22}O_2$.

Fitting this empirical formula into the known possible reaction product[136] of the model compound work, the structural formula must be:



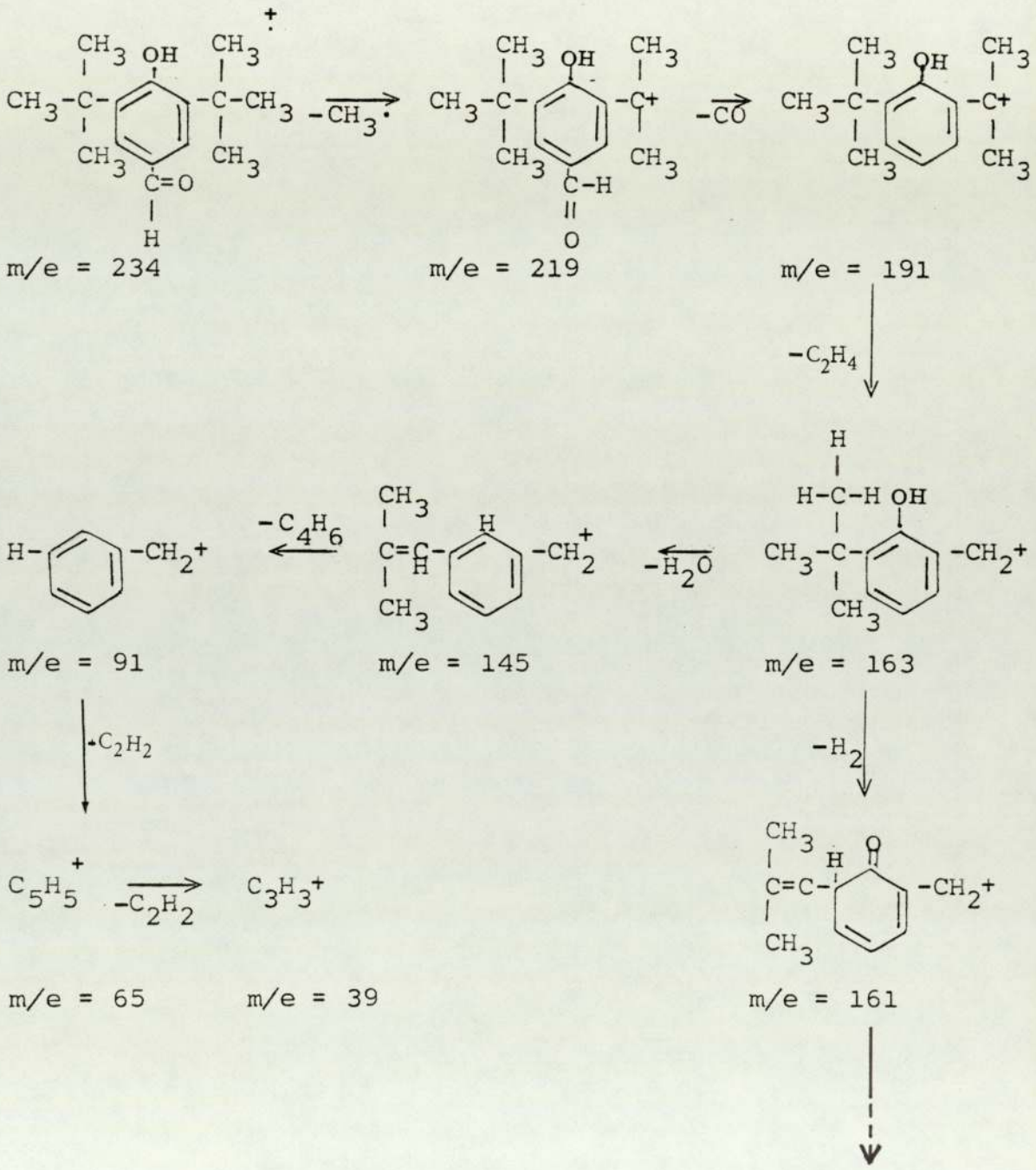
3,5-di-tert-butyl-4-hydroxy-phenylene-carbaldehyde (4-IX)

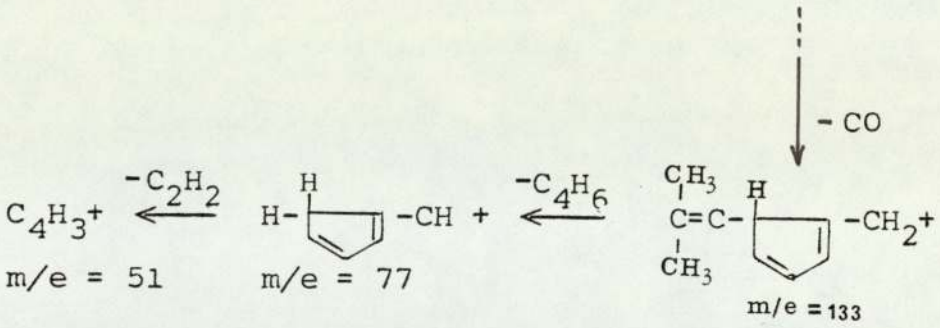
The ion fragmentation of this compound (4-IX) is shown

in Scheme 4.9.

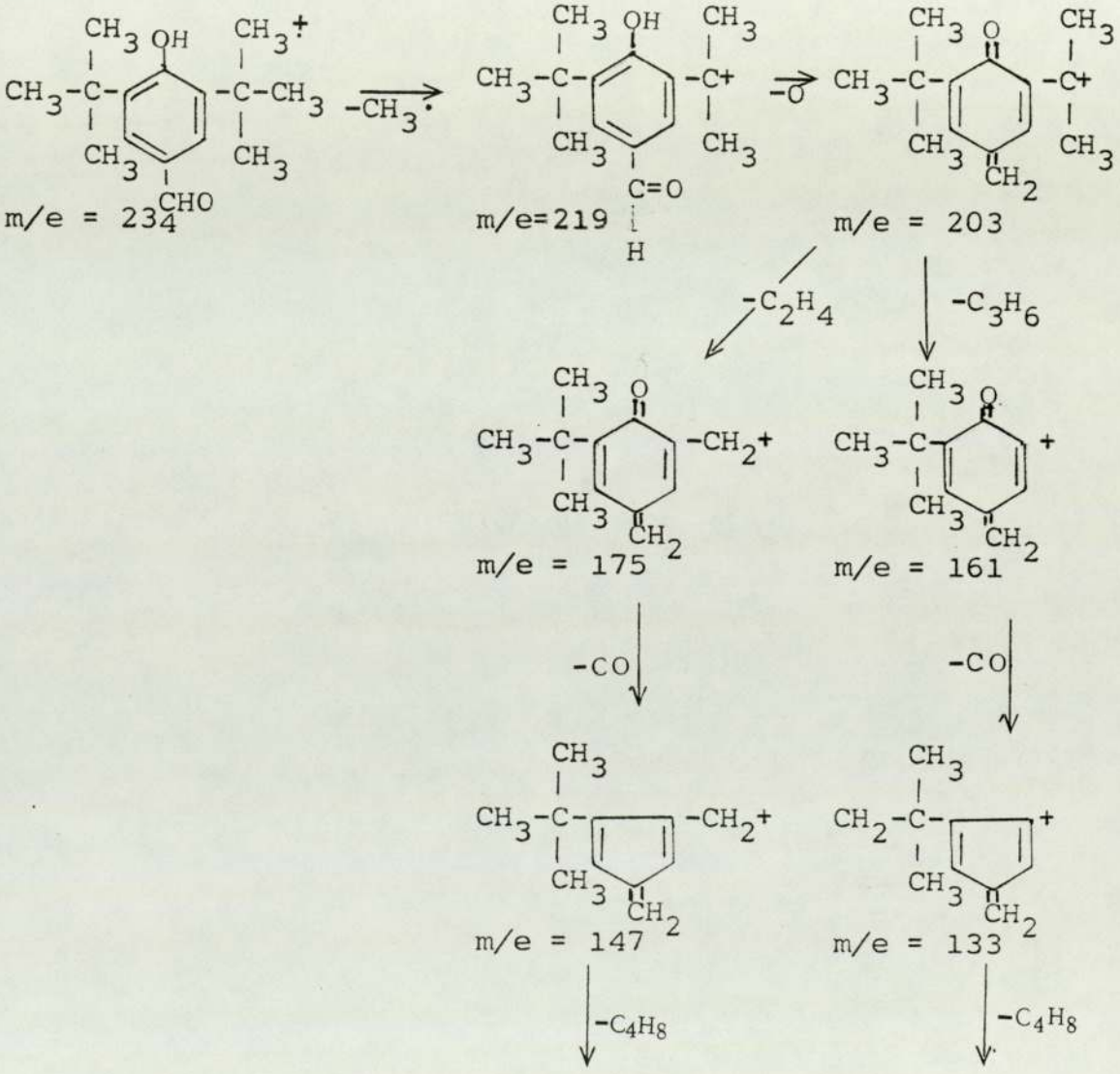
Scheme 4.9

Pathway I




- CO
$C_4H_3^+$
$-C_2H_2$
m/e = 51
H-
-CH +
$-C_4H_6$
m/e = 77
CH_3
C=C-
CH_3
H
$-CH_2^+$
m/e = 133

Pathway II


CH_3 OH CH_3
CH_3-C- -C-CH_3
CH_3 CH_3
CHO
m/e = 234
$-CH_3^{\cdot}$
CH_3 OH CH_3
CH_3-C- -C+
CH_3 CH_3
C=O
H
m/e=219
-O
CH_3 O CH_3
CH_3-C- -C+
CH_3 CH_2 CH_3
m/e = 203
$-C_2H_4$
$-C_3H_6$
CH_3 O
CH_3-C- $-CH_2^+$
CH_3 CH_2
m/e = 175
CH_3 O
CH_3-C- +
CH_3 CH_2
m/e = 161
-CO
-CO
CH_3
CH_3-C- $-CH_2^+$
CH_3 CH_2
m/e = 147
CH_3
CH_2-C- +
CH_3 CH_2
m/e = 133
$-C_4H_8$
$-C_4H_8$
$C_3H_3^+$
m/e=39
$-C_2H_2$
$C_5H_5^+$
m/e=65
$-C_2H_2$
H- -CH_2
CH_2
m/e=91
H- +
CH_2
m/e=77
$-C_2H_2$
$C_4H_3^+$ m/e=51

The fragment loss in scheme 4.8 and its relative abundance is shown in Table 4.11.

Table 4.11 Fragment loss of compound 4-IX. Empirical formula $C_{15}H_{22}O_2$, highest m/e = 234 (23%), peak scan number 371

Pathway I			Pathway II		
Fragment loss	m/e residue	Rel Ab %	Fragment loss	m/e residue	Rel Ab %
$CH_3\cdot$	219	100	$CH_3\cdot$	219	100
−CO	191	31	−O	203	8
C_2H_4	163	3	C_2H_4	175	12
H_2	161	3	CO	147	3
CO	133	3	C_4H_8	91	27
* C_4H_6	77	18	*C_2H_2	65	10
C_2H_2	51	10	C_2H_2	39	18
→H_2O	145	5	→C_3H_6	161	3
C_4H_6	91	27	CO	133	3
C_2H_2	65	10	C_4H_8	77	18
C_2H_2	39	18	C_2H_2	51	10

* Different pathway

Examination of the mass spectrum for the peak at 371 shows that this fragmentation pattern is consistent with the structure $C_{15}H_{22}O_2$.

4.4.2.5 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 391 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 391 is shown in Fig 4.2.5.

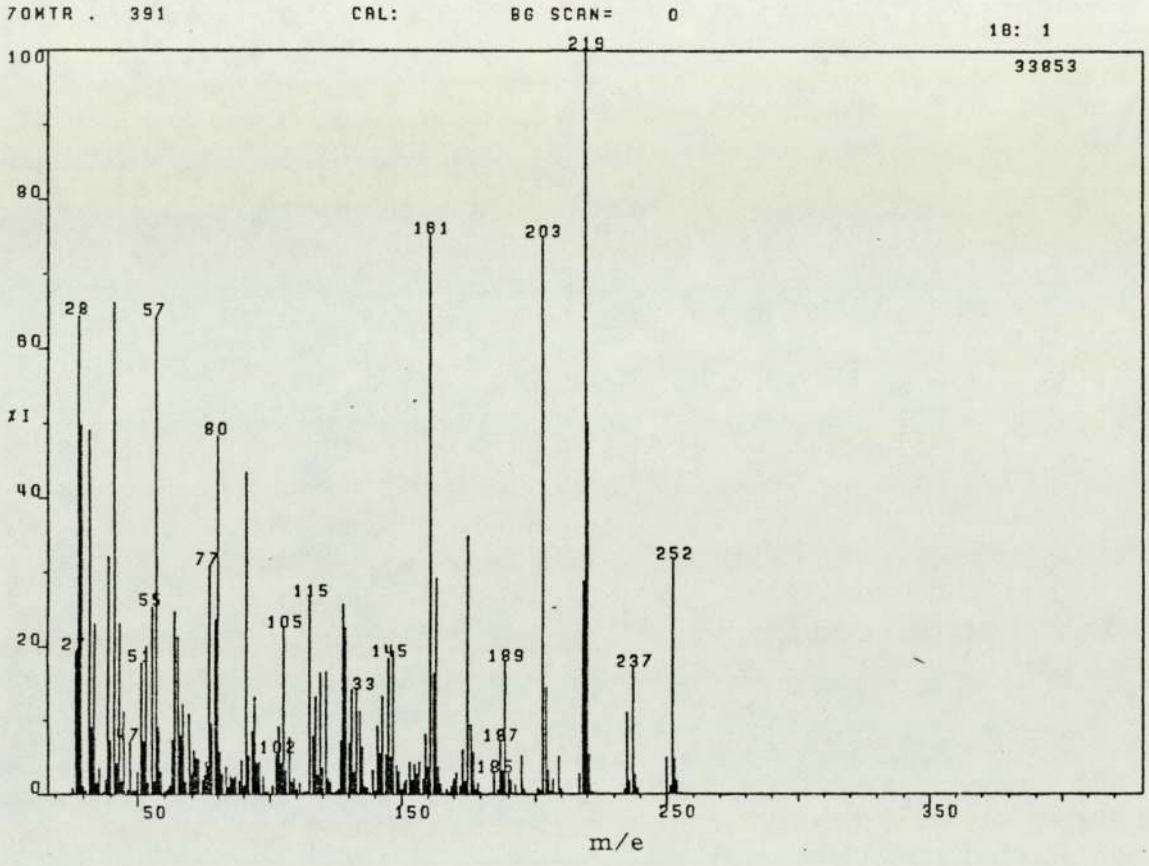


Fig 4.25 The mass spectrum of peak at scan number 391

The mass spectrum is identical with mass spectrum in Fig 4.6 (Section 4.3.1.5). Therefore the peak at scan number 391 corresponds to compound 4-V.

4.4.2.6 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 491 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 491 is shown in Fig. 4.26.

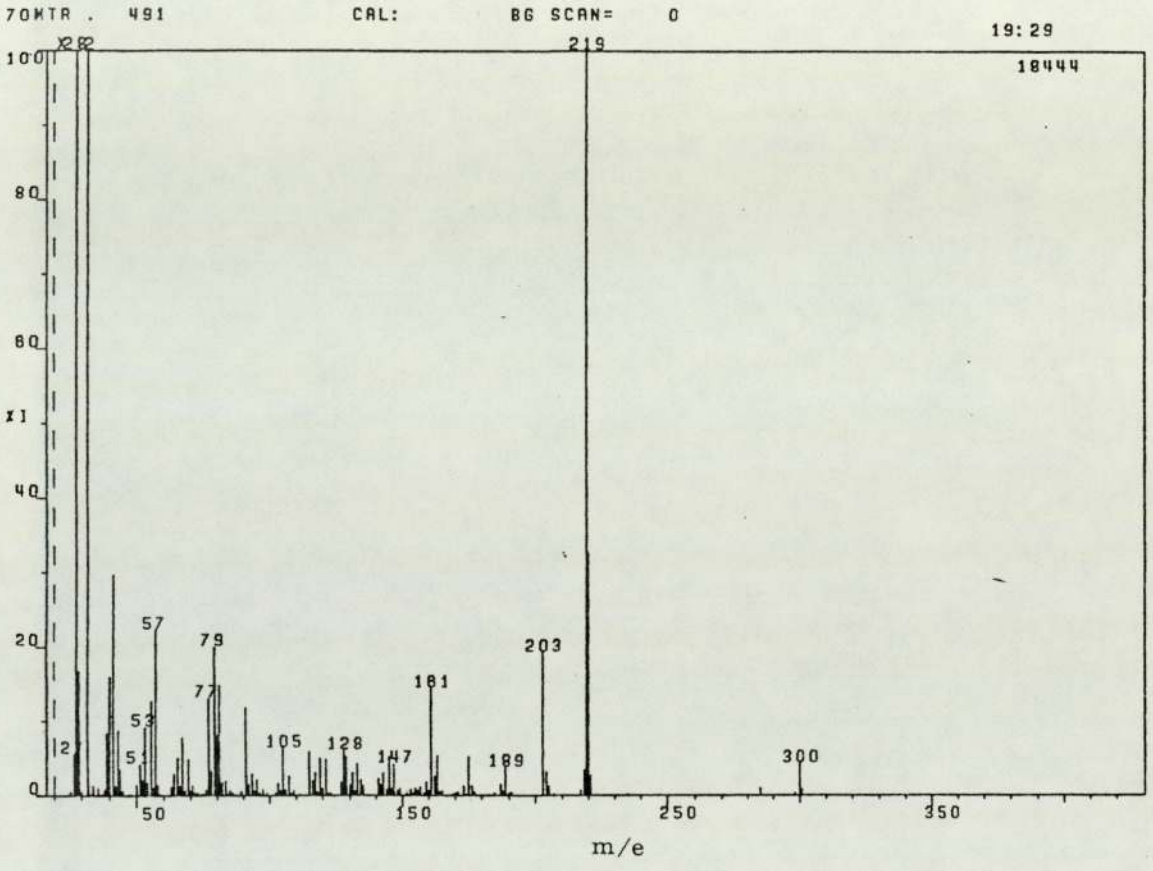


Fig 4.26 The mass spectrum of peak at scan number 491

This is identical with the mass spectrum in Fig 4.13 and the fragment loss is identical to scheme 4.6. Therefore, the peak at scan number 491 is identical to compound 4-VII.

4.4.2.7 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 599 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 599 is shown in Fig 4.27.

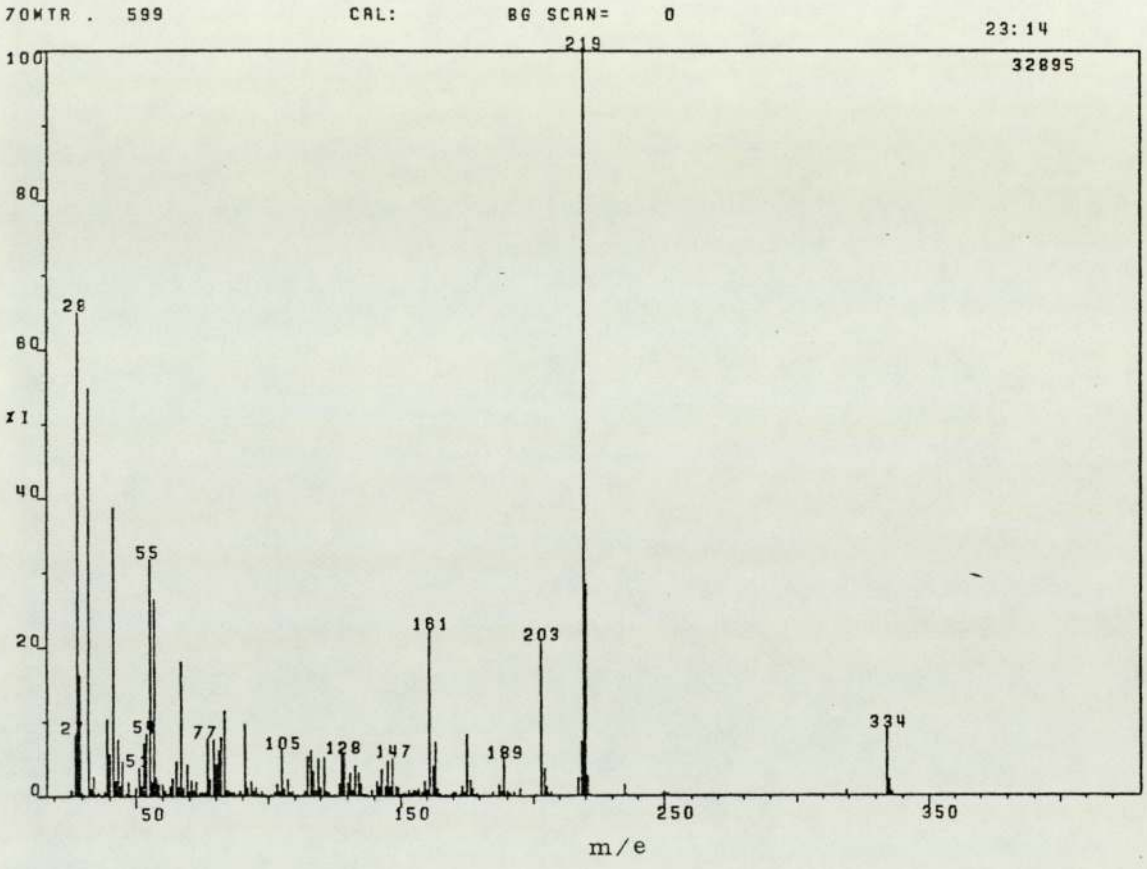


Fig 4.27 The mass spectrum of peak at scan number 599

This is identical with the mass spectrum shown in Fig 4.17. Therefore the peak at scan number 599 is due to compound 4-VIII.

4.4.2.8 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 606 AND ITS INTERPRETATION

The mass spectrum of peak at scan number 606 is shown in Fig 4.28.

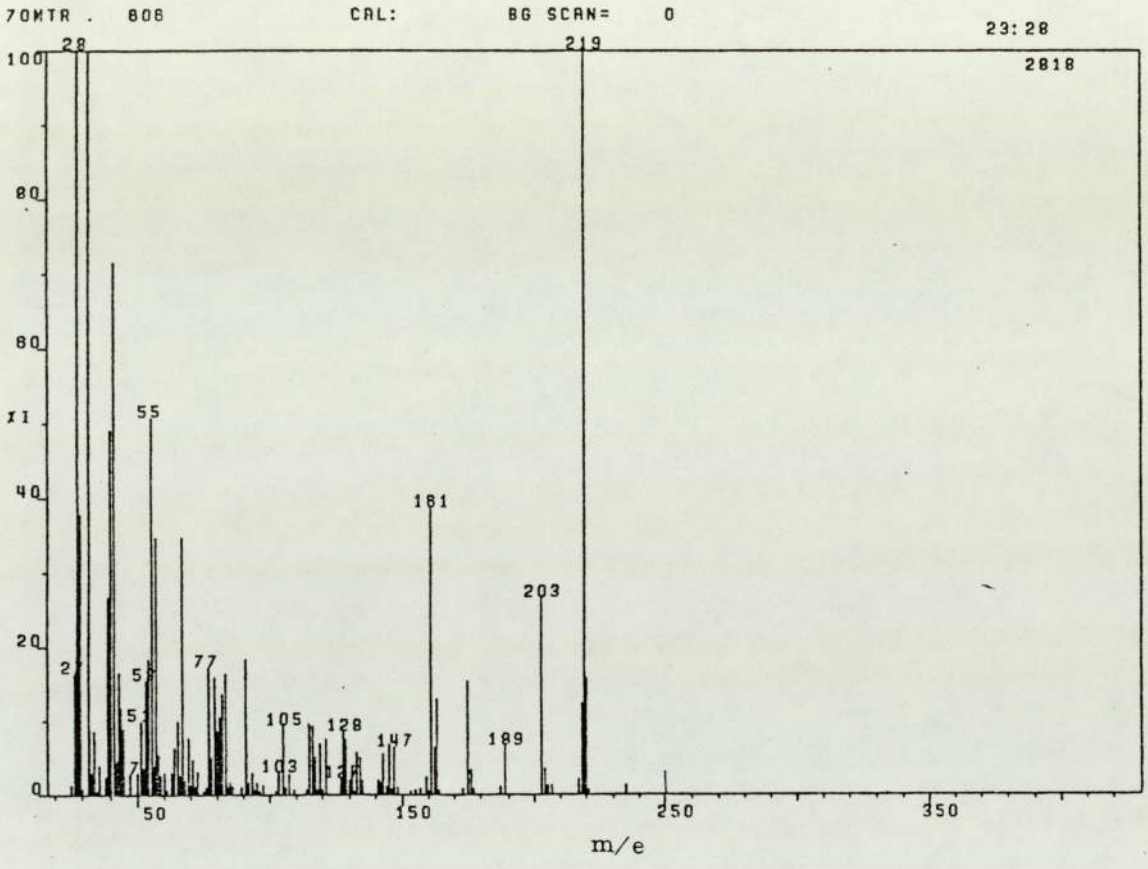


Fig 4.28 The mass spectrum of peak at scan number 606

This is identical to that in Fig 4.7 and described in Section 4.3.1.6. Therefore the peak at scan number 606 corresponds to compound 4-VI.

4.4.2.9 THE MASS SPECTRUM OF PEAK AT SCAN NUMBER 755

This spectrum is shown in Fig 4.29.

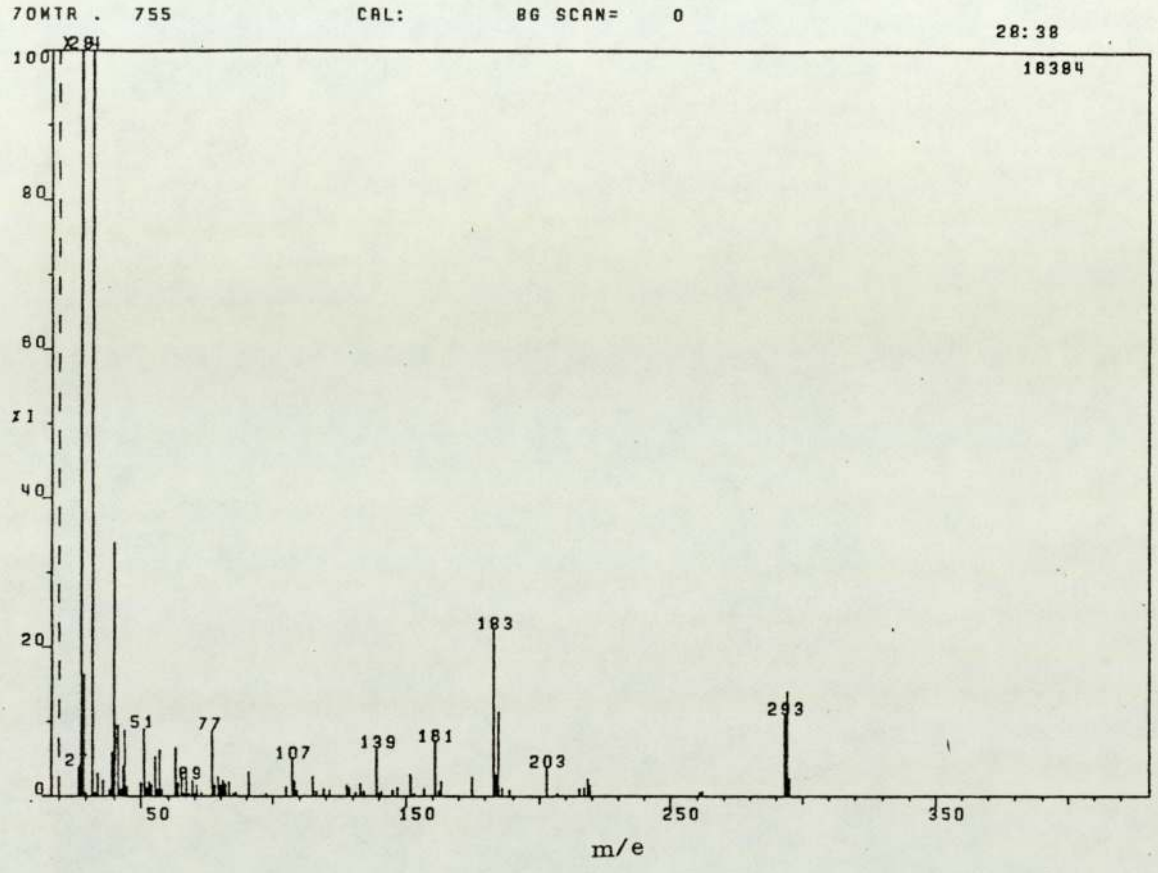


Fig 4.29 The mass spectrum of peak at scan number 755

This compound has not so far been identified.

4.5.1 REACTION OF BHBM WITH TBH (MOLAR RATIO 1:2)

The reaction was carried out using the conditions described in Section 4.2, except that the molar ratio of BHBM (0.01 mol) to TBH (0.02 mol) was 1:2. The GC-MS chromatogram shown in Figs 4.30 and 4.31, showed fourteen peaks of which eight correspond to the reaction products.

4.5.1.1 THE STUDY OF MASS SPECTRA OF PEAKS AT SCAN NUMBERS 232, 257, 268, 375, 403, 498, 600 AND 756 AND THEIR INTERPRETATION

The mass spectra of peaks at scan numbers 232, 257, 268, 375, 403, 498, 600 and 756 are shown in Figs 4.32 - 4.40.

The mass spectra of these peaks were compared to the reference spectra described in Section 4.3.1.1 and mass spectra described in section 4.4.1.1.5, section 4.4.1.1.6 and section 4.4.2.4. The structures and retention times are summarised in Table 4.12.

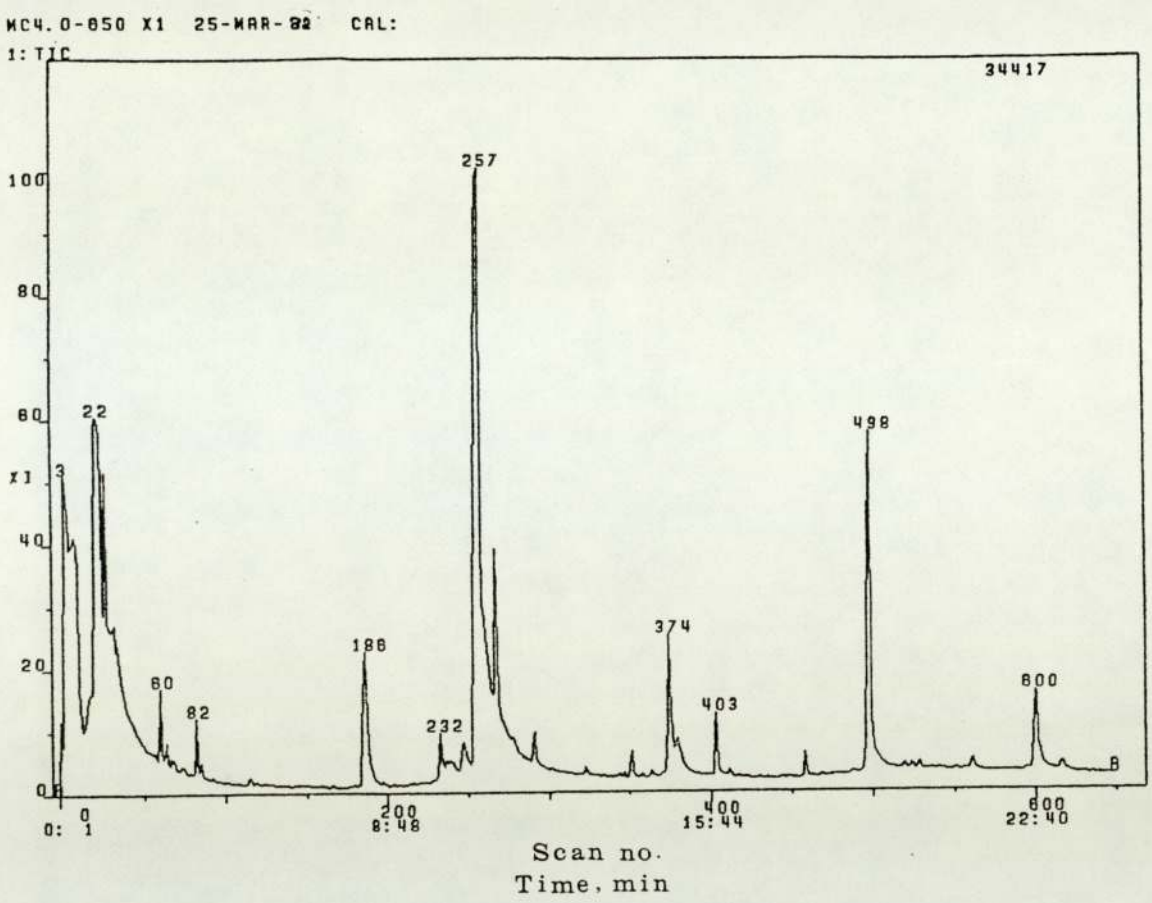


Fig 4.30 GC-MS chromatogram for reaction of BHBM with TBH (molar ratio 1:2) Scan range 0-650

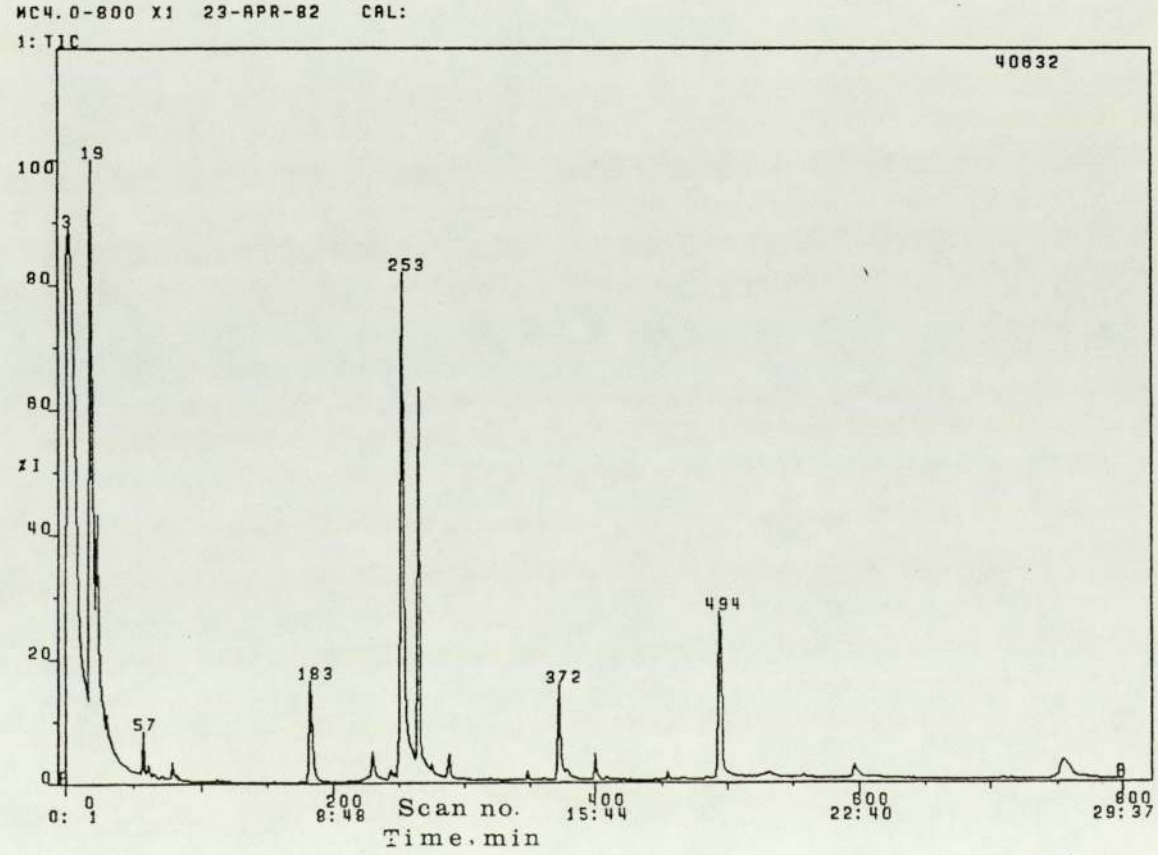


Fig 4.31 GC-MS chromatogram for reaction of BHBM with TBH (molar ratio 1:2) Scan range 0-800

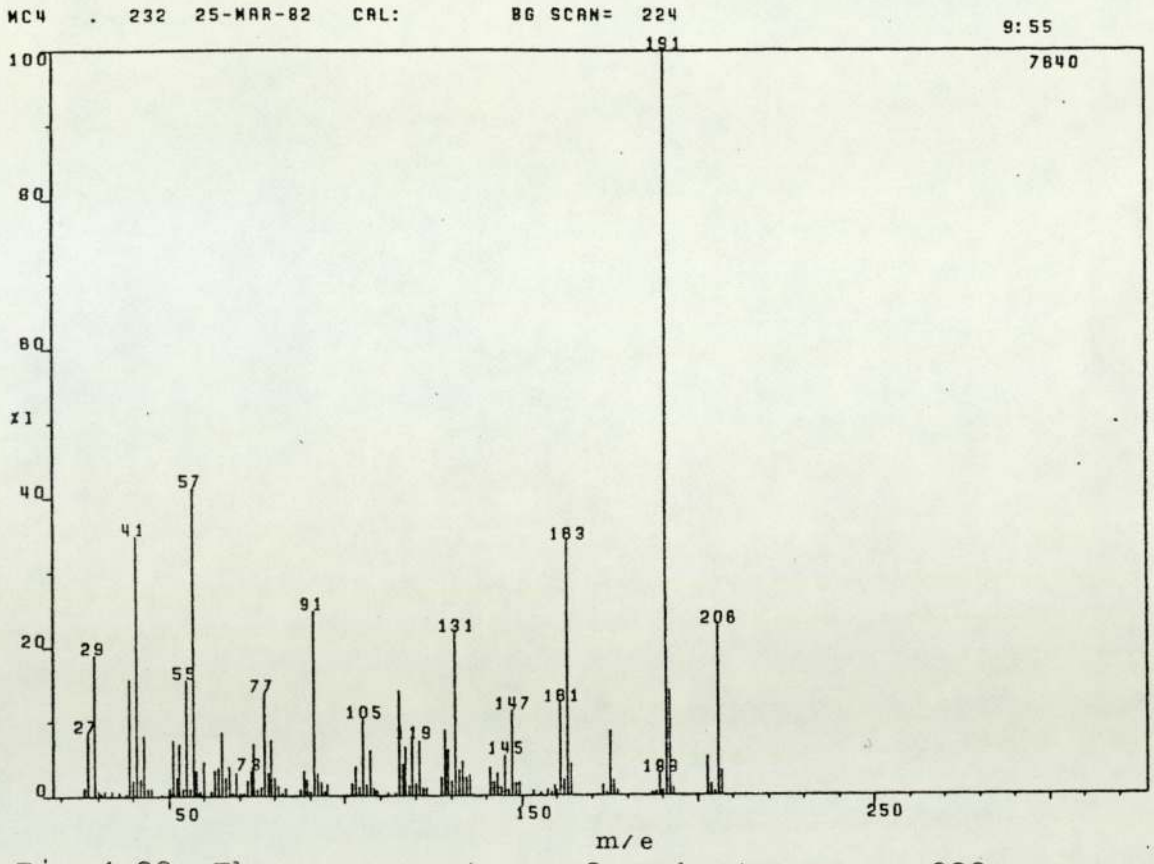


Fig 4.32 The mass spectrum of peak at scan no 232

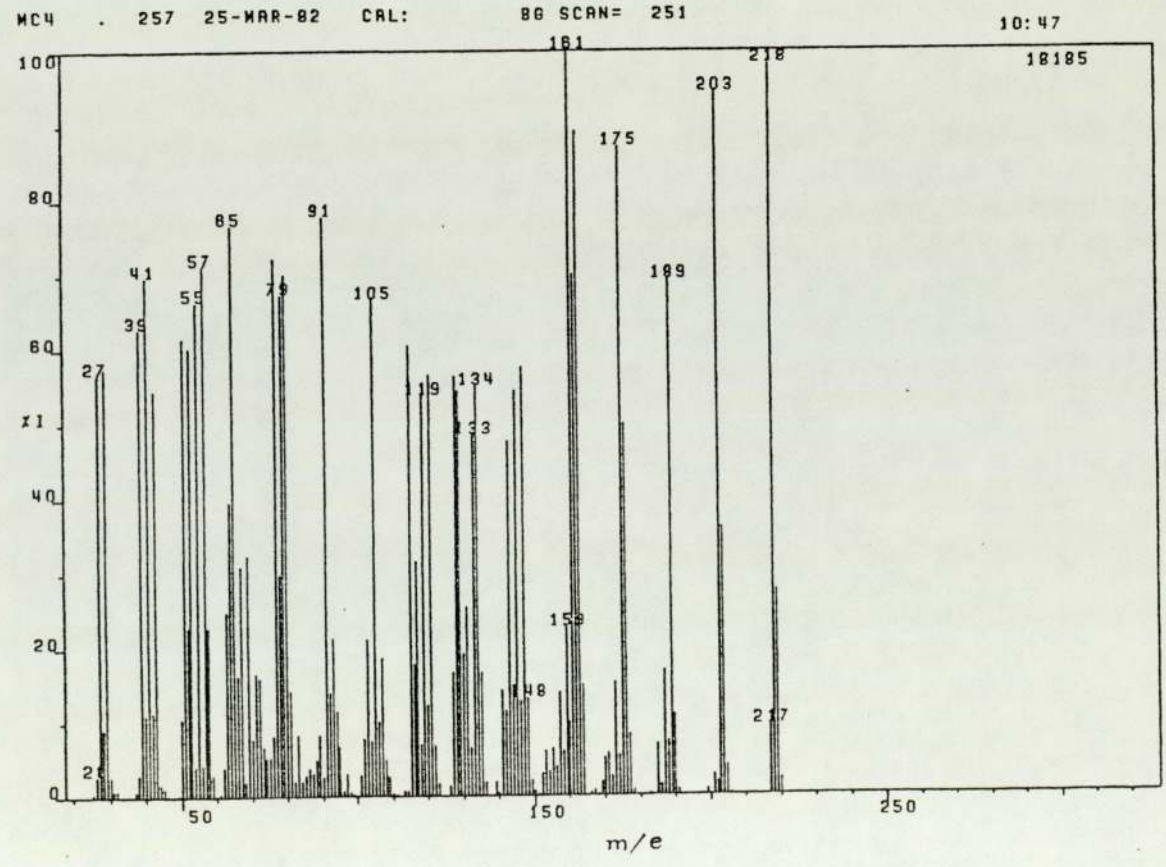


Fig 4.33 The mass spectrum of peak at scan no 257

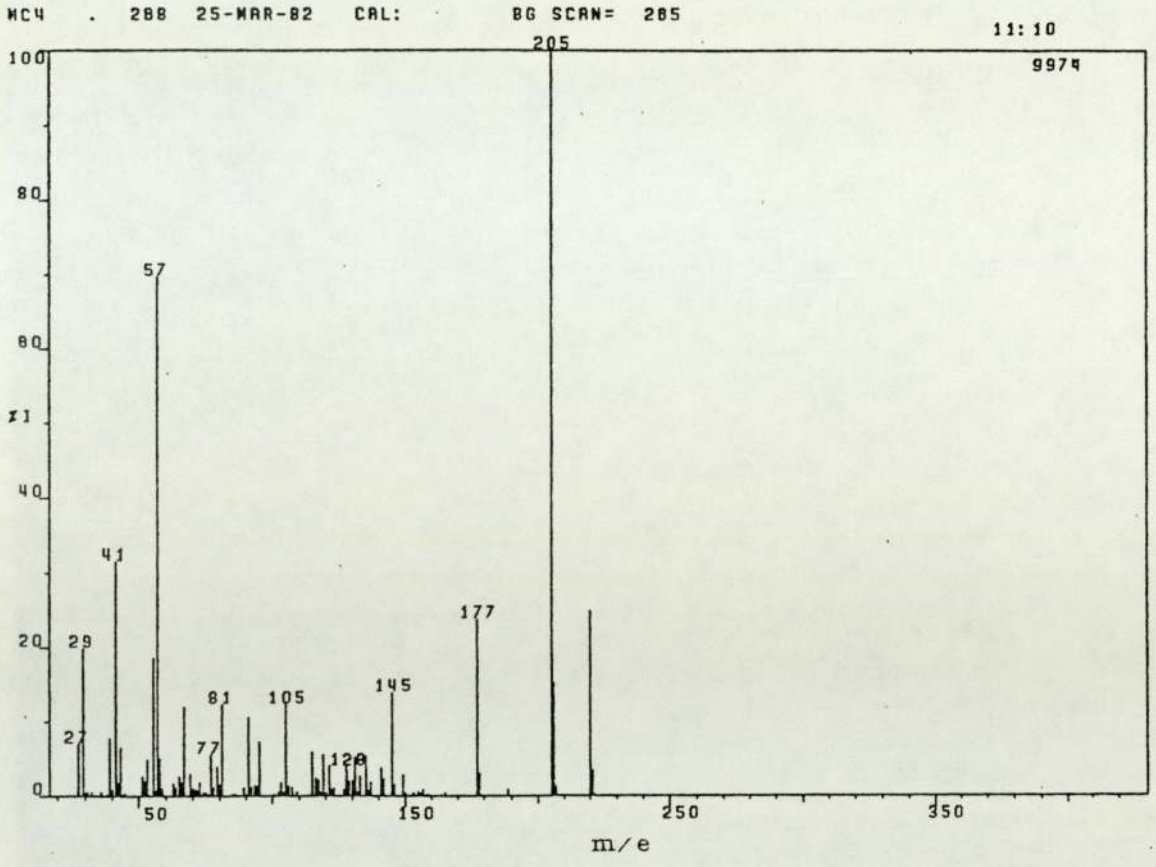


Fig 4.34 The mass spectrum of peak at scan no 268

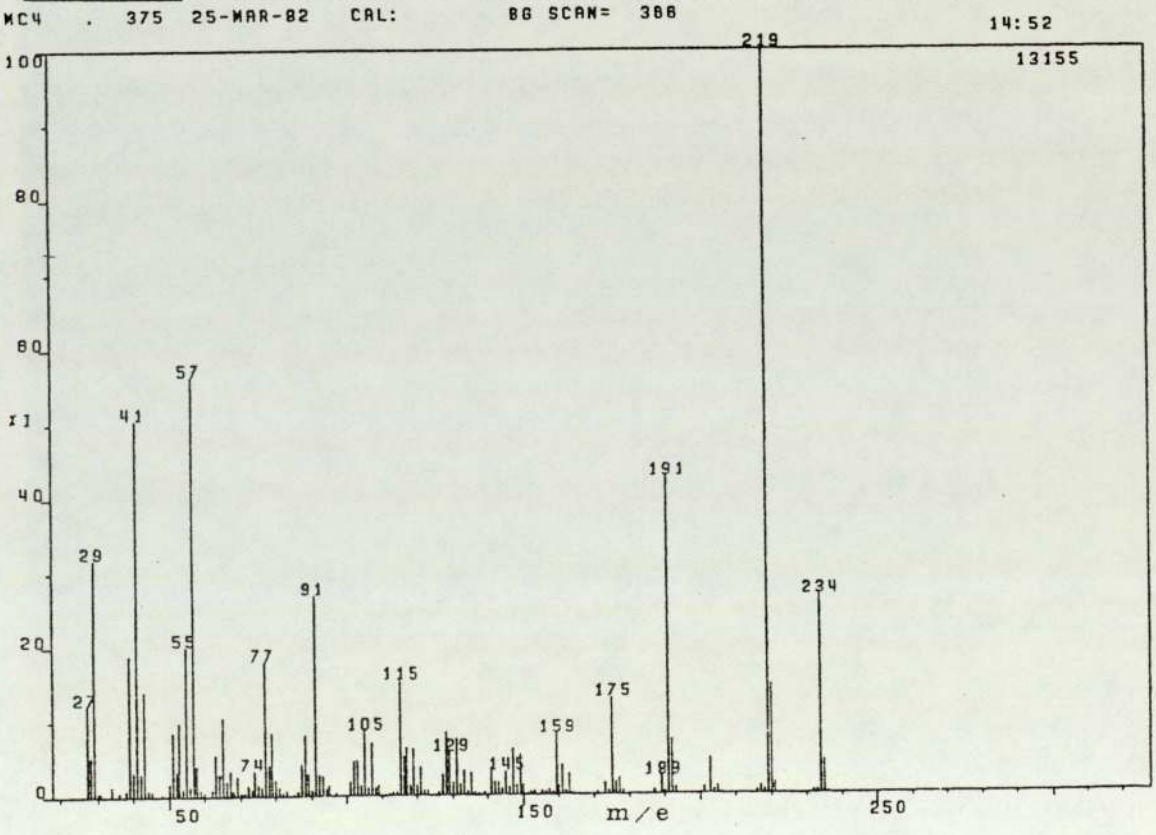


Fig 4.35 The mass spectrum of peak at scan no 375

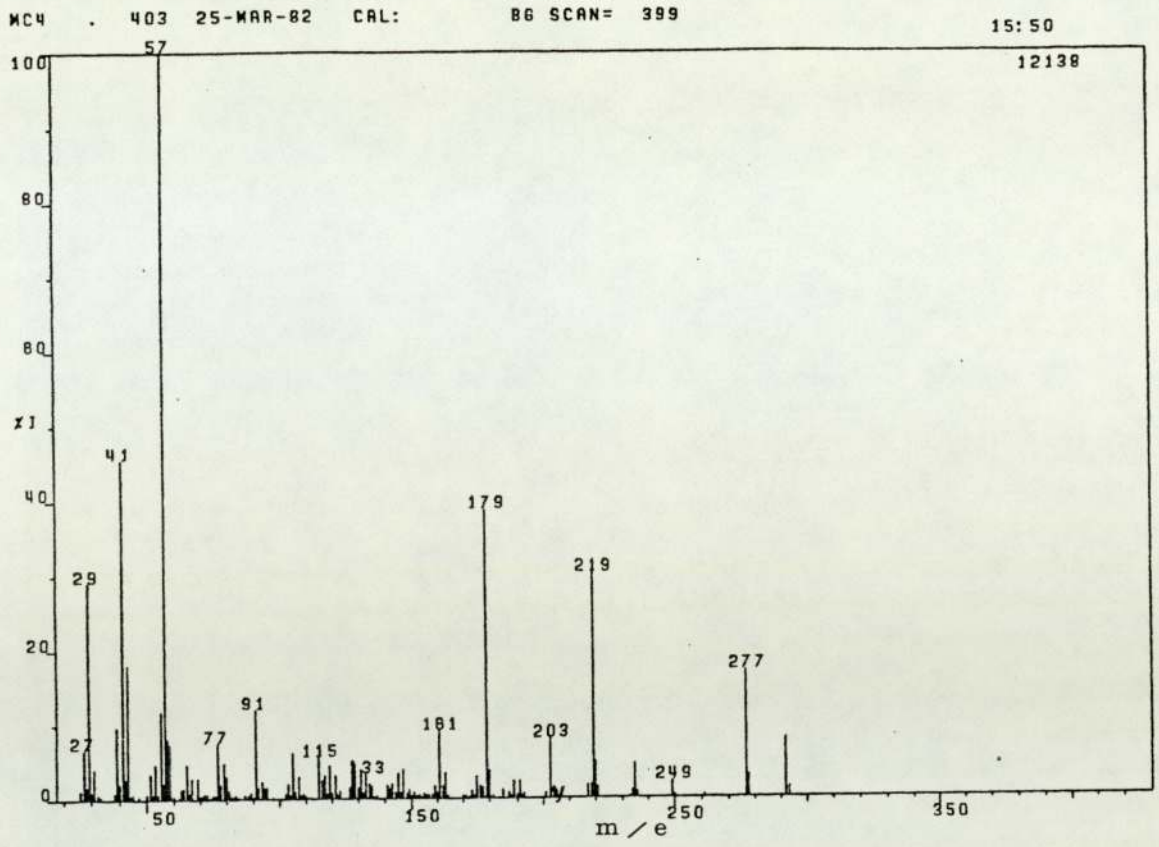


Fig 4.36 The mass spectrum of peak at scan no 403

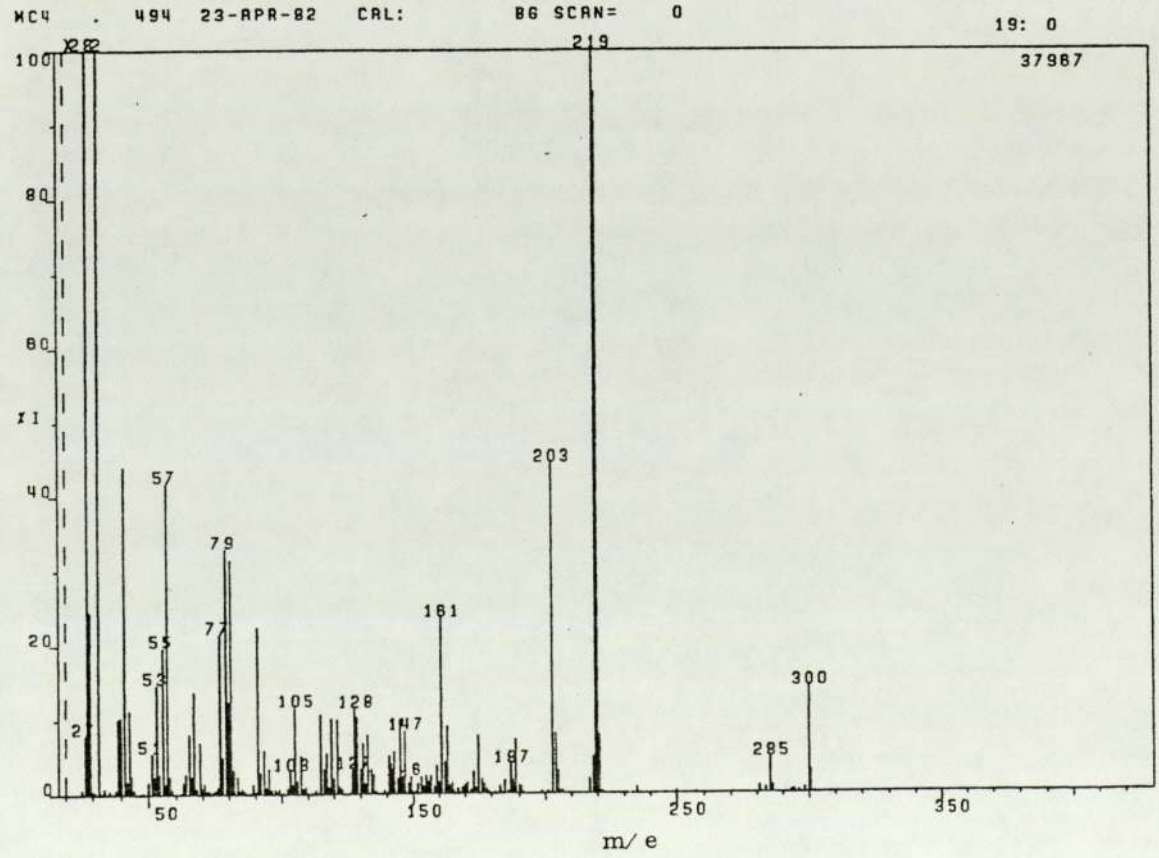


Fig 4.37 The mass spectrum of peak at scan no 494

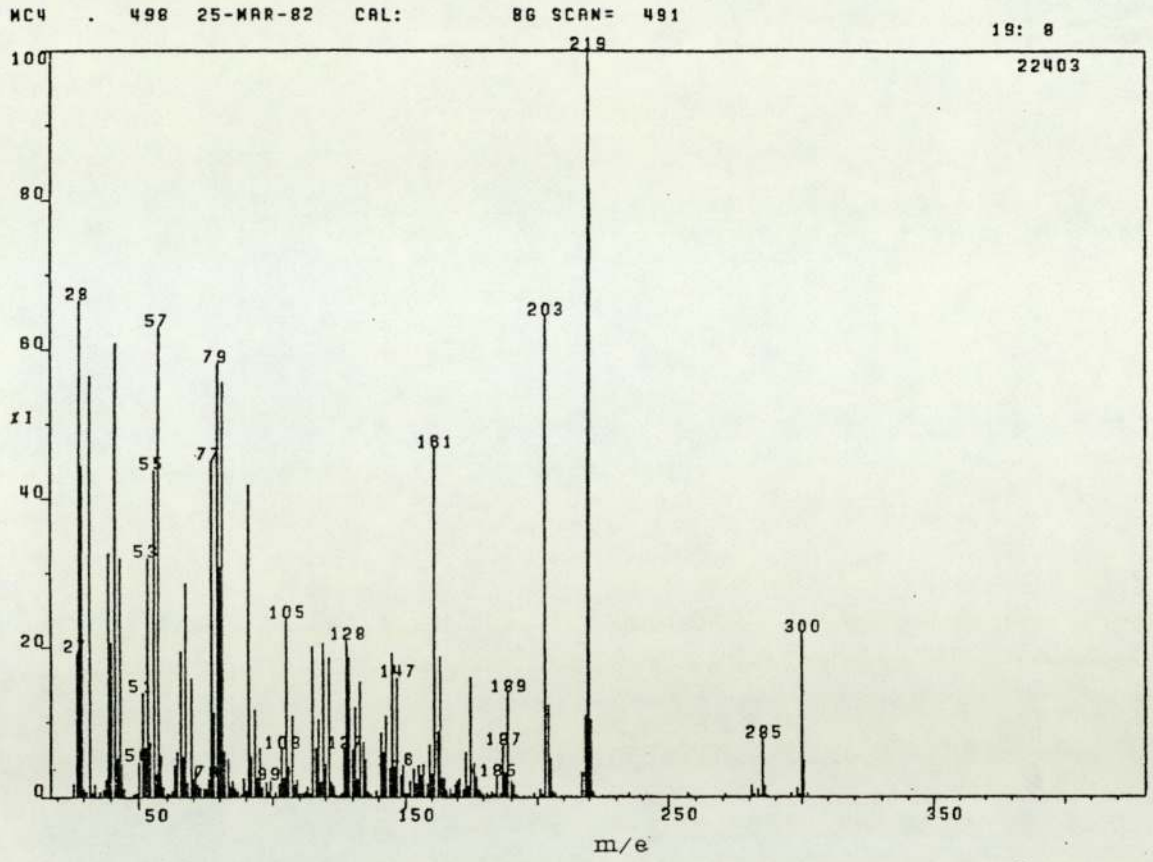


Fig 4.38 The mass spectrum of peak at scan no 498

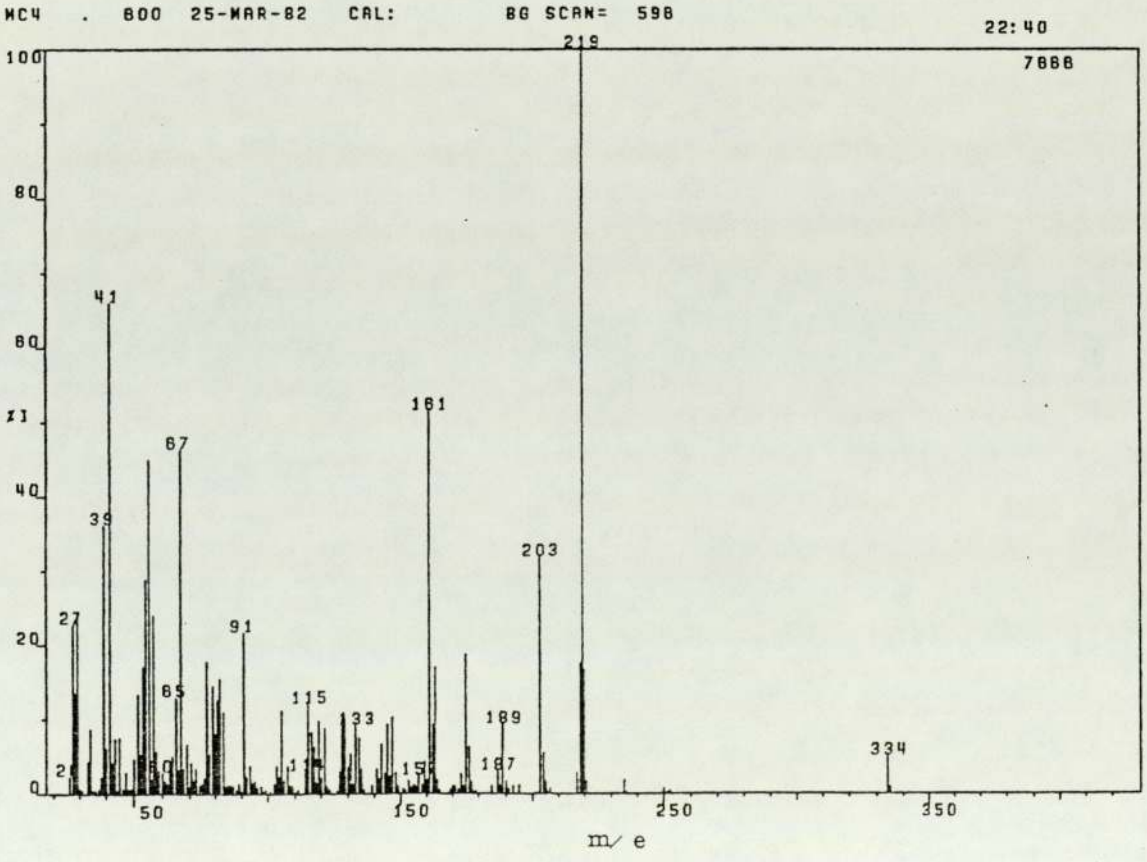


Fig 4.39 The mass spectrum of peak at scan no 600

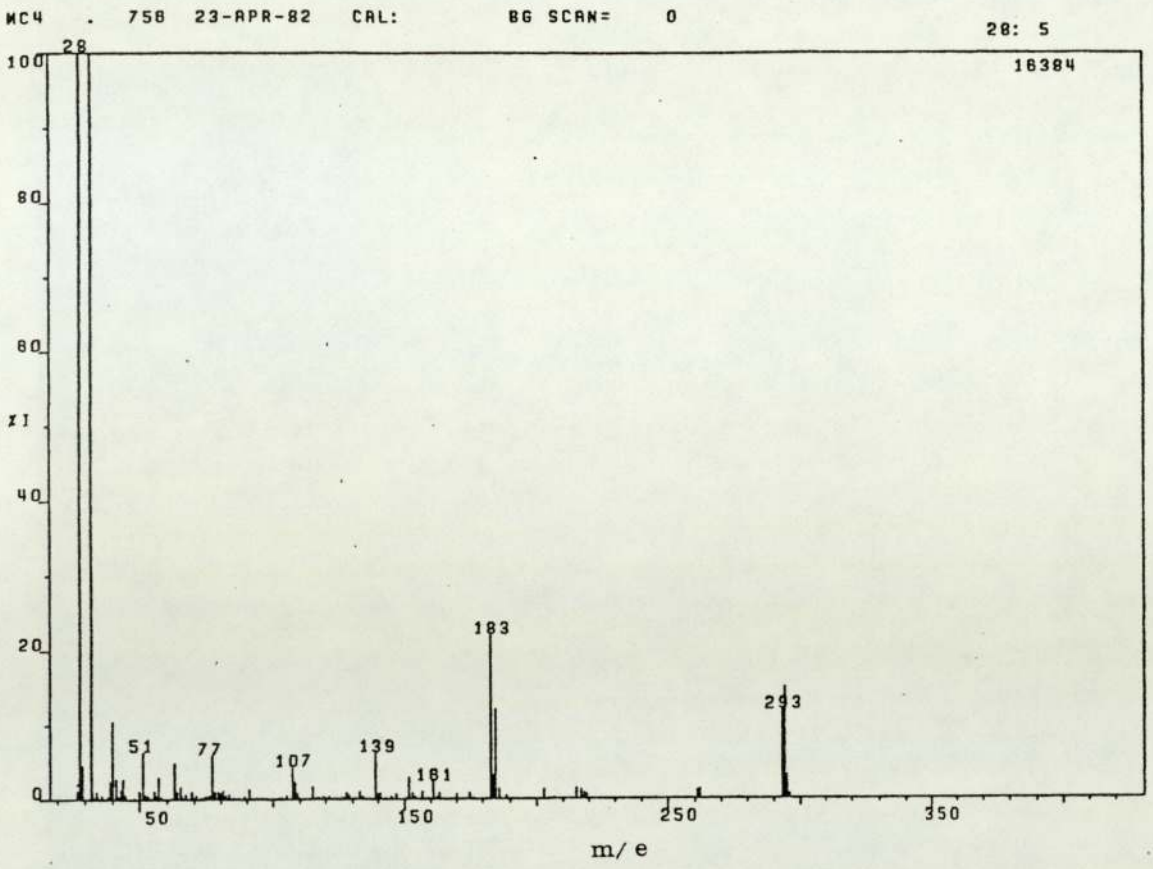


Fig 4.40 The mass spectrum of peak at scan no756

Table 4.12 The highest m/e and corresponding structure of reaction of BHBM with TBH (molar ratio 1:2) scan range 0-650 and scan range 0-800

Peak at scan no	Highest m/e	Corresponding structure	Retention time
232	206	4-I	9' 55"
257	218	4-III	10' 47"
268	220	4-II	11' 10"
375	234	4-IX	14' 52"
403	292	4-X	15' 50"
494/498	300	4-VI	19' & 19'11"
600	334	4-VIII	22' 40"
756	294	-	28' 5"

4.5.1.2 THE MASS SPECTRUM OF PEAK AT SCAN NO 403 AND ITS INTERPRETATION

This peak which appeared at retention time 15 minutes and 20 seconds has the highest m/e = 292 as shown in Fig 4.36.

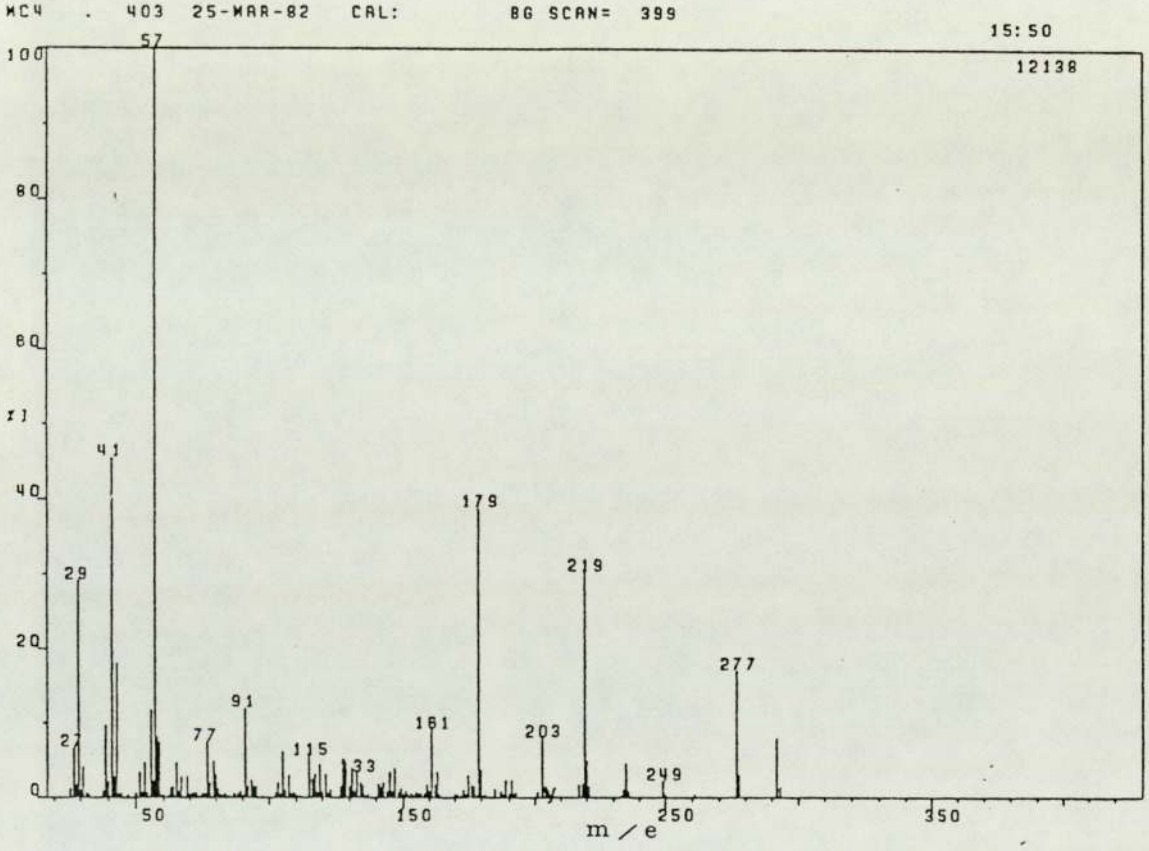
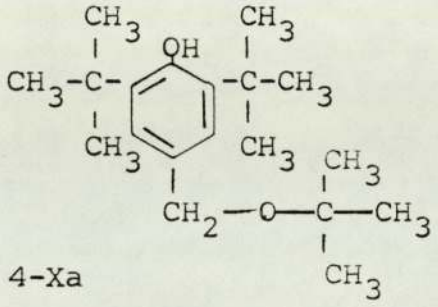


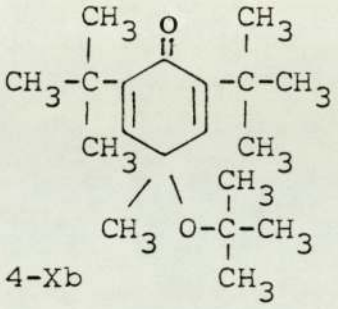
Fig 4.36 The mass spectrum of peak at scan number 403

The main m/e peak for this compound are formed at m/e = 292, 277, 219, 203, 161, 147, 133, 105, 91, 77, 65, 51 and 39. A study of empirical formula of this

spectrum and the fragmentation pattern revealed that this compound was $C_{19}H_{32}O_2$ (4-X). Fitting the empirical formula into the known possible reaction products of the model compound, suggests that there are two possible structure formula which are shown below.



4-Xa



4-Xb

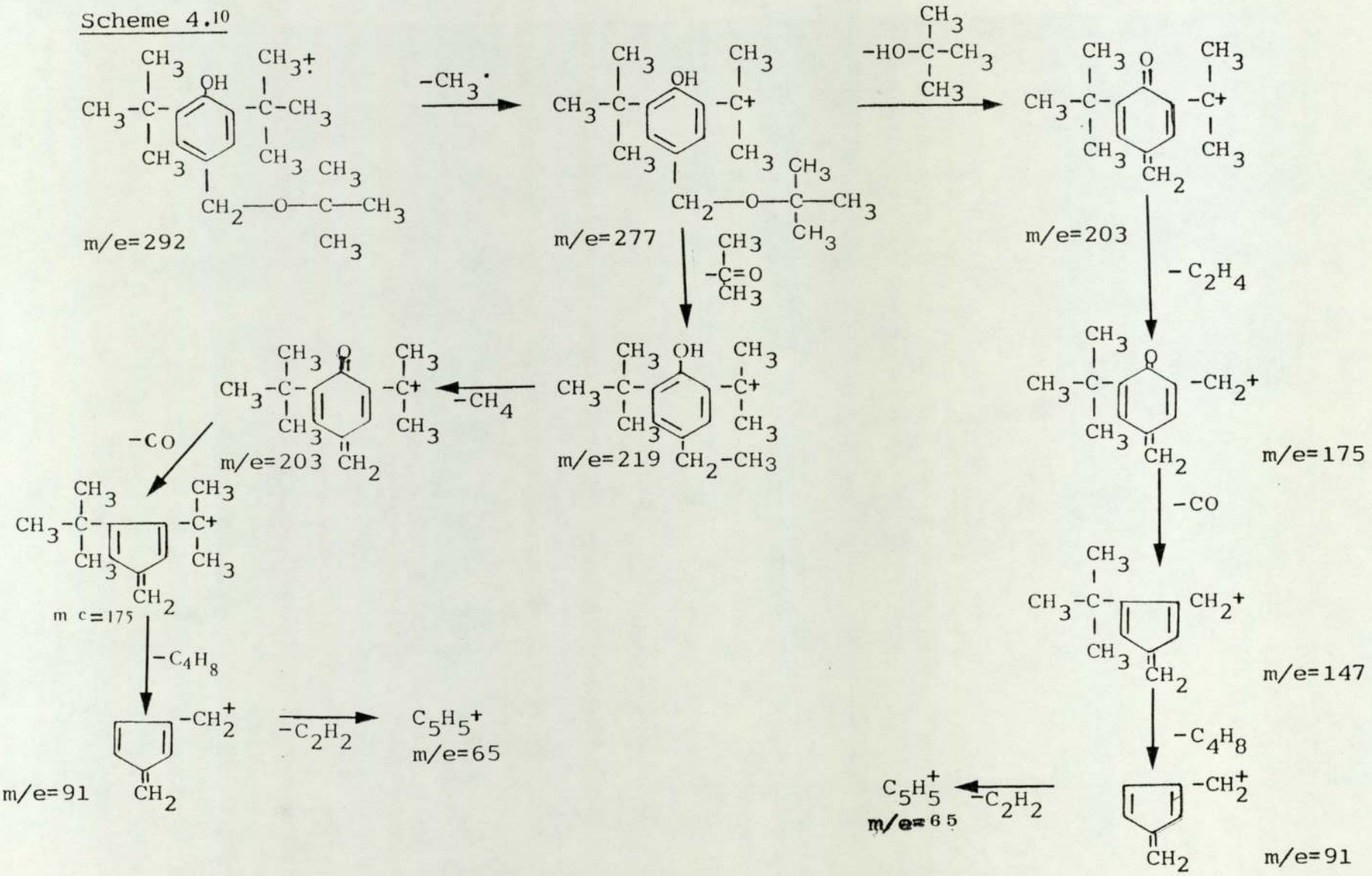
According to the theory[146,152,153] the two compounds follow the fragmentation ion pattern as illustrated in Scheme 4. 10 and 4.11.

The fragment lossof compound 4-Xa is shown in Table 4.13.

The fragment loss for compound 4-Xb is shown in Table 4.14.

It can be concluded that peak at scan number 403 is a mixture of compounds 4-Xa and 4-Xb.

Scheme 4.[10]


m/e=292
m/e=277
m/e=203
m/e=175
m/e=147
m/e=91
m/e=65
m/e=219
m/e=203
m/e=175
m/e=91
m/e=65
-CH3·
-HO-C-CH3
-C2H4
-CO
-C4H8
-C2H2
-CH4
-CO
-C4H8
-C2H2
C5H5+

Pathway II

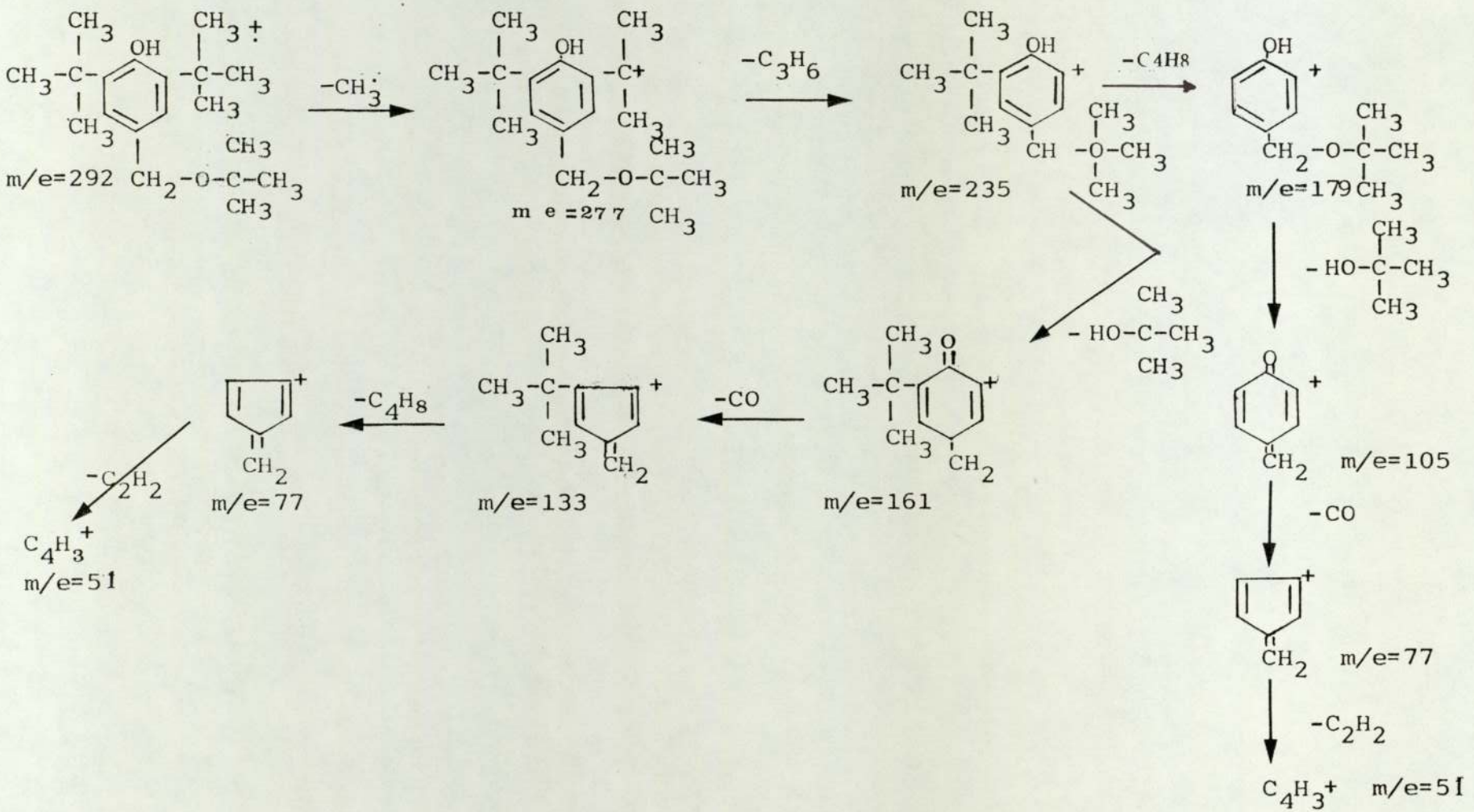
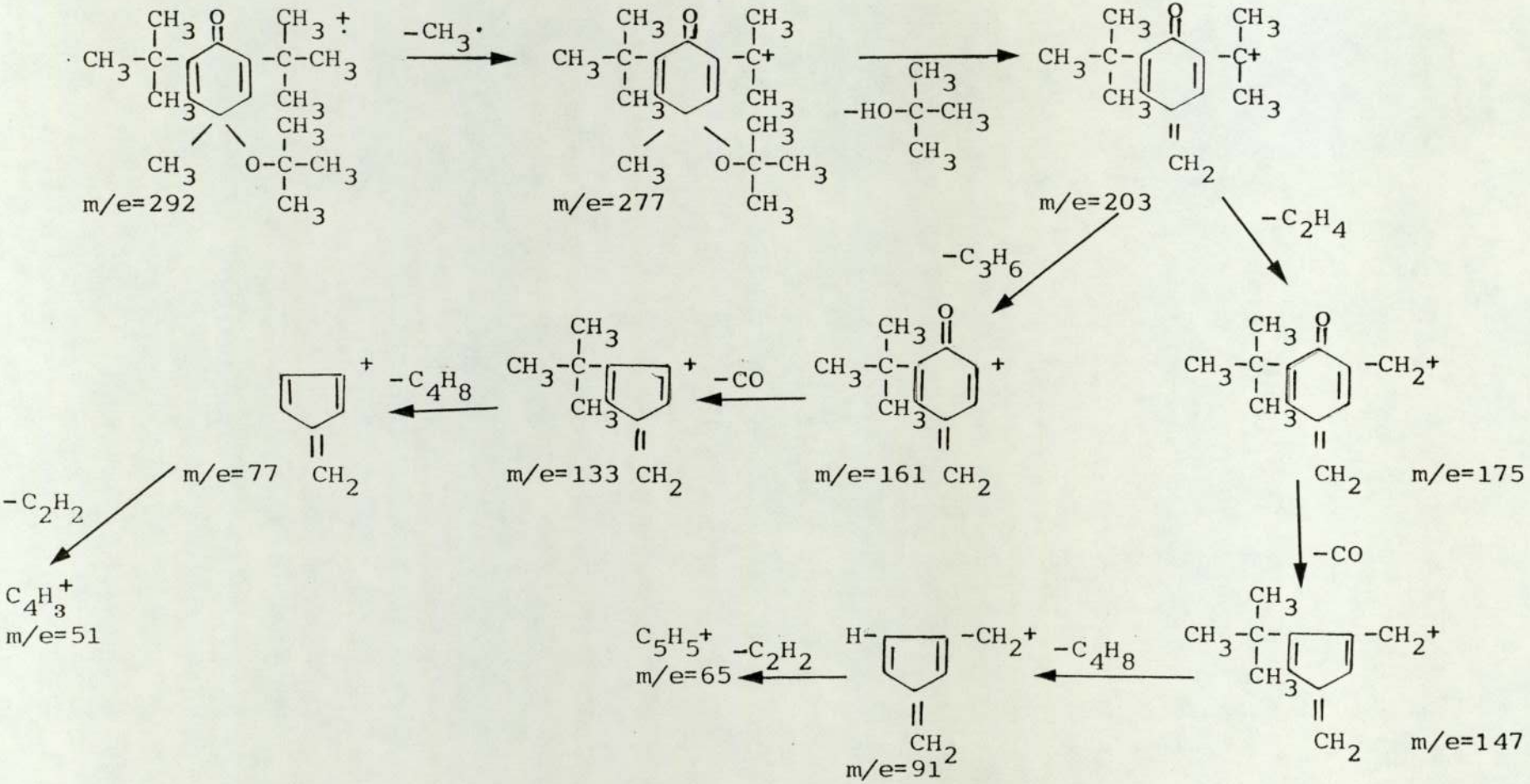

m/e=292
-CH3
m e =277
-C3H6
m/e=235
-C4H8
m/e=179
- HO-C-CH3
m/e=105
-CO
m/e=77
-C2H2
C4H3+ m/e=51
m/e=161
-CO
m/e=133
-C4H8
m/e=77
-C2H2
C4H3+
m/e=51

Table 4.13 Fragment loss of compound 4-Xa. Highest m/e = 292 (10%), empirical formula $C_{19}H_{32}O_2$ peak scan no 403

Pathway I			Pathway II		
Fragment loss	m/e residue	Rel Ab %	Fragment loss	m/e residue	Rel Ab %
$CH_3\cdot$	277	20	$CH_3\cdot$	277	20
$C_4H_{10}O$	203	8	C_3H_6	235	6
C_2H_4	175	4	C_4H_8	179	42
CO	147	5	$C_4H_{10}O$	105	7
C_4H_8	91	12	CO	77	10
C_2H_2	65	5	* C_2H_2	51	11
* C_3H_6O	219	32	$C_4H_{10}O$	161	10
CH_4	203	8	CO	133	5
CO	175	4	C_4H_8	71	10
C_2H_2	91	12	C_2H_2	51	11
C_5H_5	65	5			

* Different route

Scheme 4.11 Pathway I



Pathway II

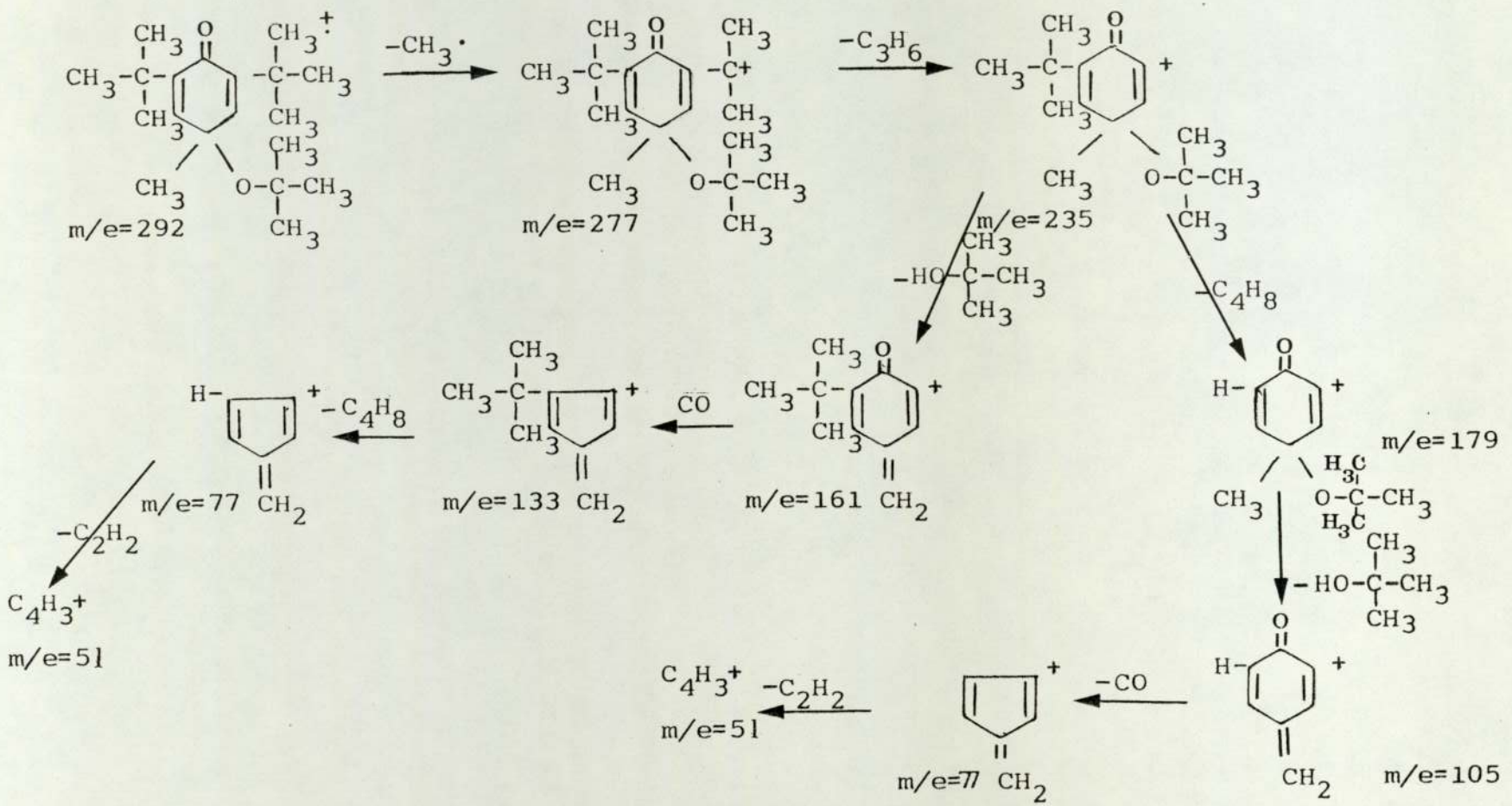

m/e=292
-CH3·
m/e=277
-C3H6
m/e=235
-HO-C(CH3)3
-C4H8
m/e=161
CO
m/e=133
-C4H8
m/e=77
-C2H2
C4H3+
m/e=51
m/e=179
-HO-C(CH3)3
m/e=105
-CO
m/e=77
C4H3+ -C2H2
m/e=51

Table 4.14 Fragment loss of compound 4-Xb. Highest m/e =,292, (10%), empirical formula $C_{19}H_{32}O_2$ peak at scan no 403

Pathway I			Pathway II		
Fragment loss	m/e residue	Rel Ab %	Fragment loss	m/e residue	Rel Ab %
CH_3	277	20	CH_3	277	20
$C_4H_{10}O$	203	8	C_3H_6	233	6
C_2H_4	175	4	C_4H_8	179	40
CO	147	5	$C_4H_{10}O$	105	7
C_4H_8	91	12	CO	77	10
C_2H_2	65	6	C_2H_2	51	11
C_2H_2	39	17			
*			*		
C_3H_6	161	10	$C_4H_{10}O$	161	10
CO	133	5	CO	133	5
C_4H_8	77	10	C_4H_8	77	10
C_2H_2	51	11	C_2H_2	51	54

* Different route

4.6.1 REACTION OF BHBM WITH TBH (MOLAR RATIO 1:1) AT 110°C

It was of interest to study the product of the reaction of BHBM with TBH (molar ratio 1:1) at 110°C, instead of 70°C since this is closer to the use conditions of antioxidants and some sulphonic acids are known to be unstable about this temperature.

The reactions were carried out using the conditions mentioned in Section 4.2, ~~except that~~ no TEPA was used and the temperature was 110°C. The GC-MS chromatogram in Fig 4.40 has twelve peaks.

4.6.1.2 THE MASS SPECTRA OF PEAKS AT SCAN NUMBERS 228, 242, 250, 263, 364, 372, 299, 494, 590 and 759 AND THEIR INTERPRETATION

The mass spectra of peaks at scan numbers 228, 242, 250, 263, 364, 372, 299, 494, 590 and 759 are shown in Figs 4.41 - 4.51.

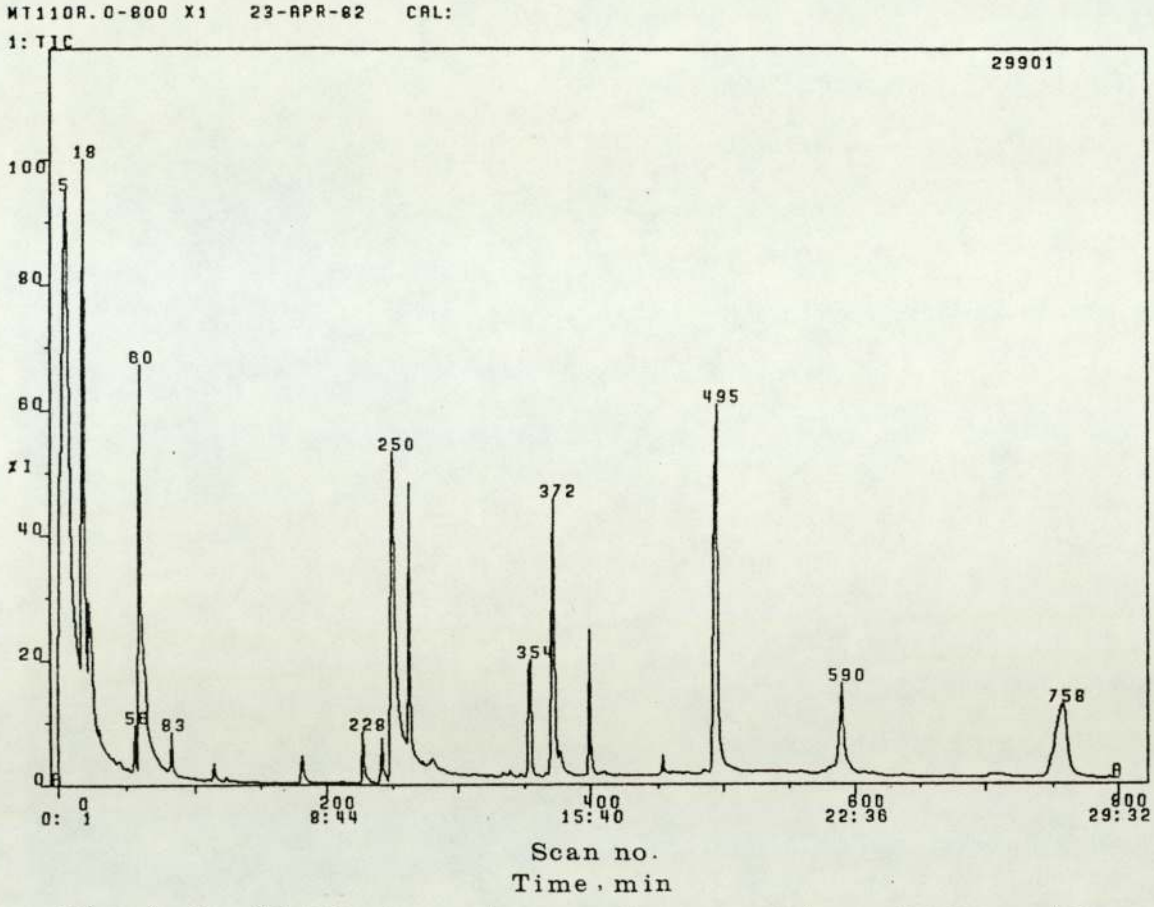


Fig 4.41 GC-MS chromatogram for reaction of BHBM with TBH (molar 1:1) in cyclohexene at 110°C

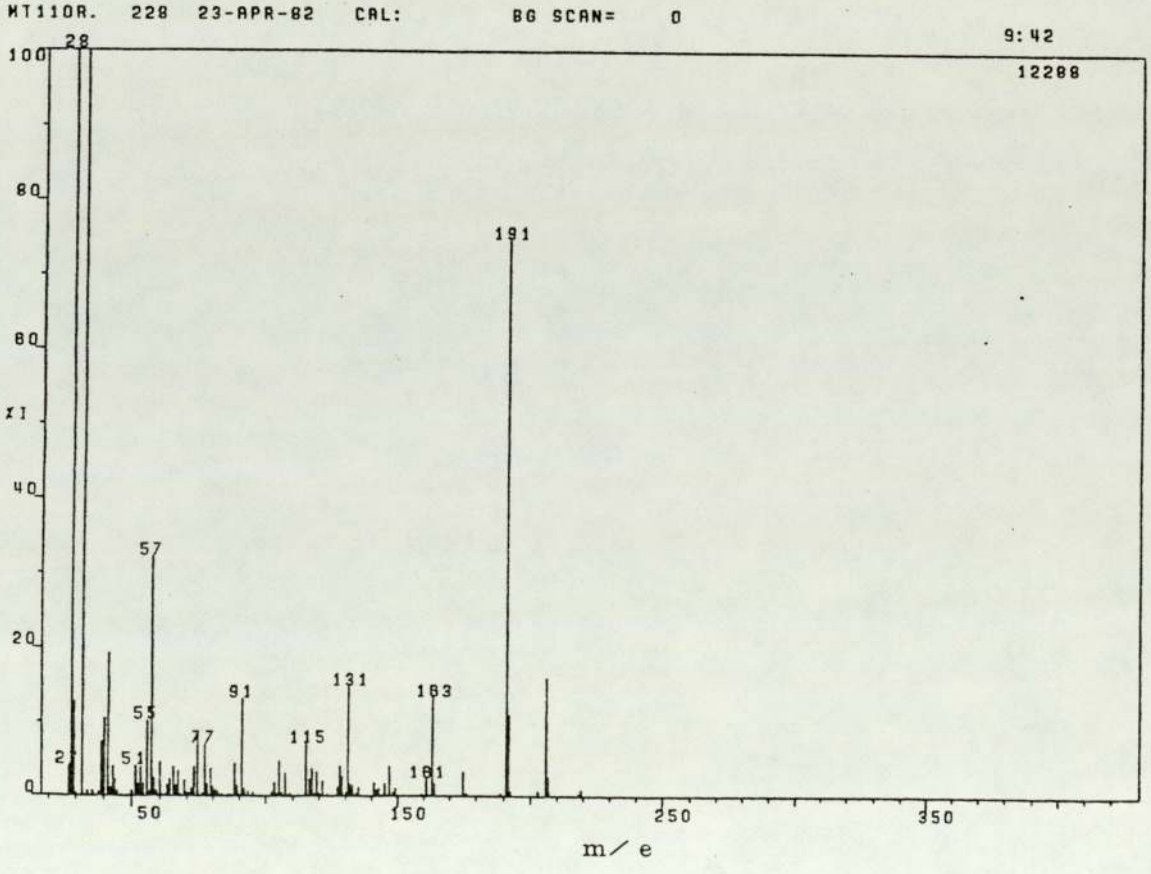


Fig 4.42 The mass spectrum of peak at scan no 228

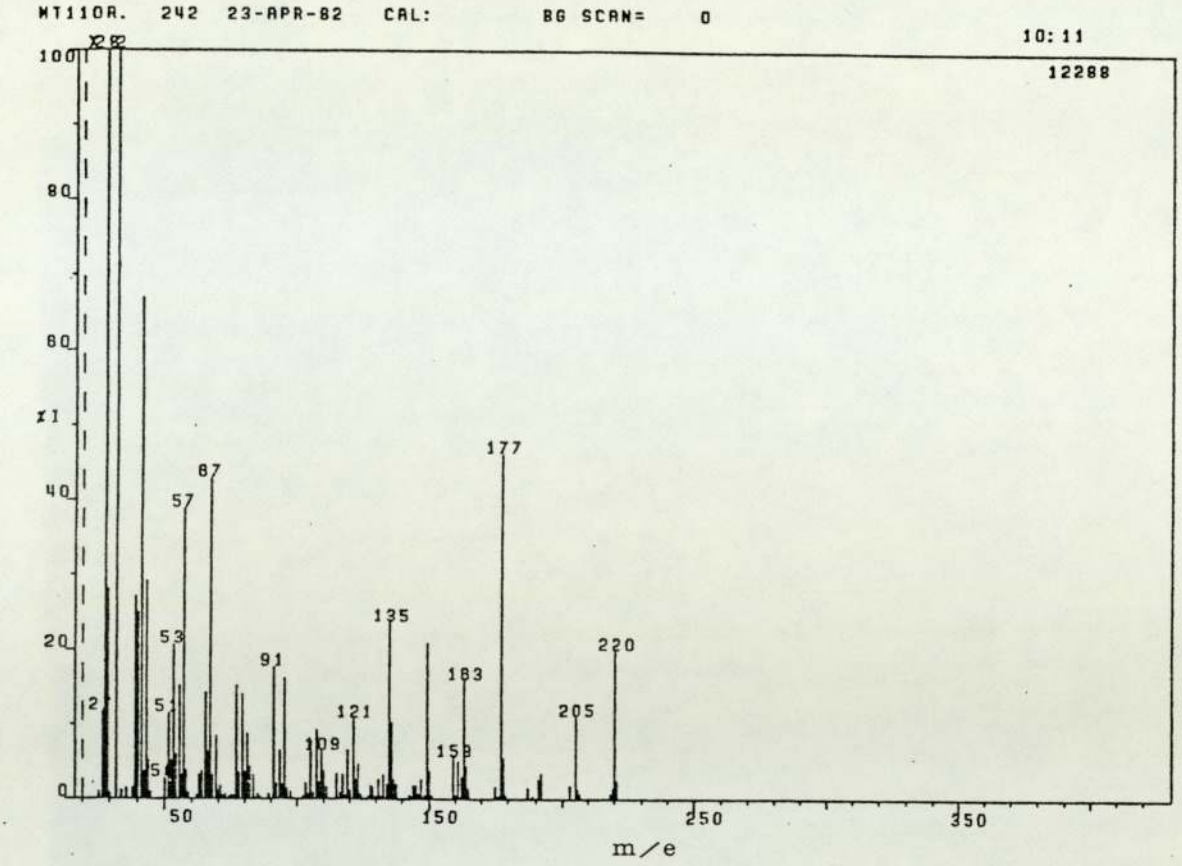


Fig 4.4.3 The mass spectrum of peak at scan no 242

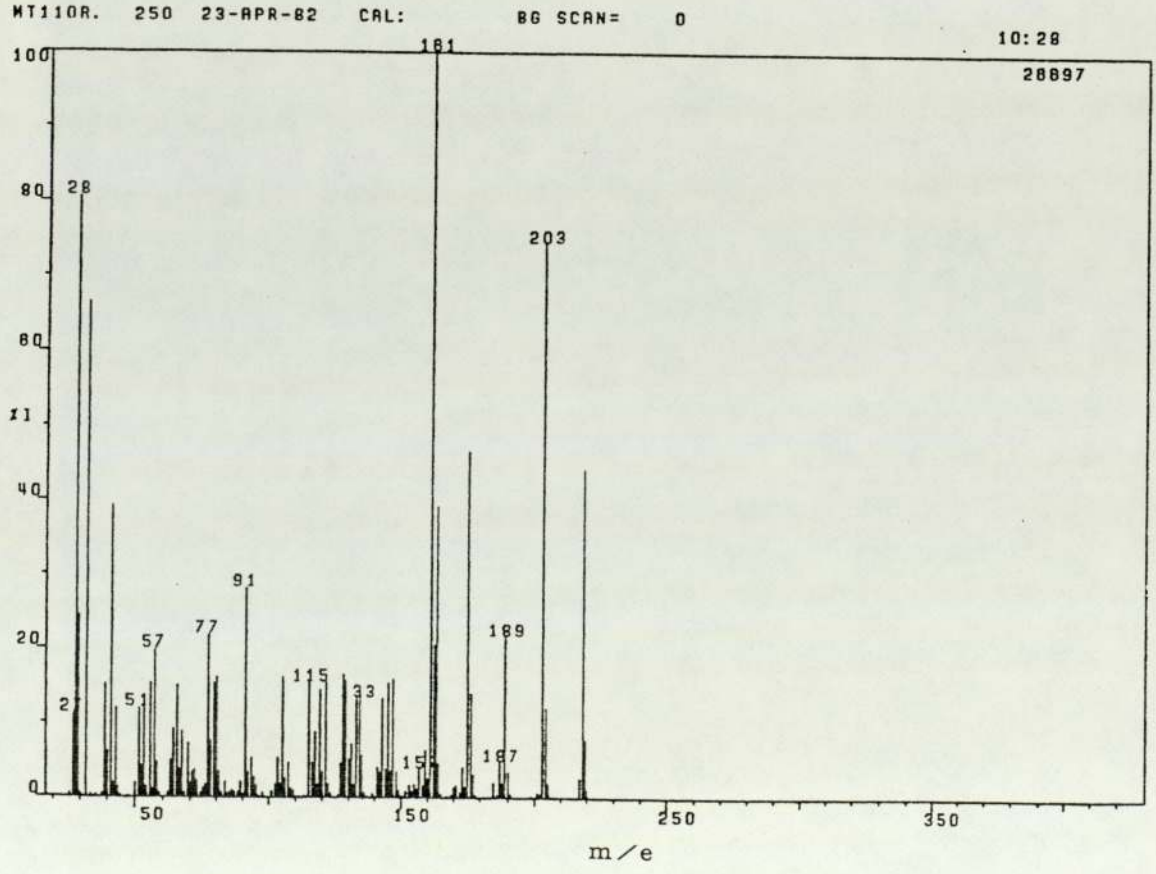


Fig 4.44 The mass spectrum of peak at scan no 250

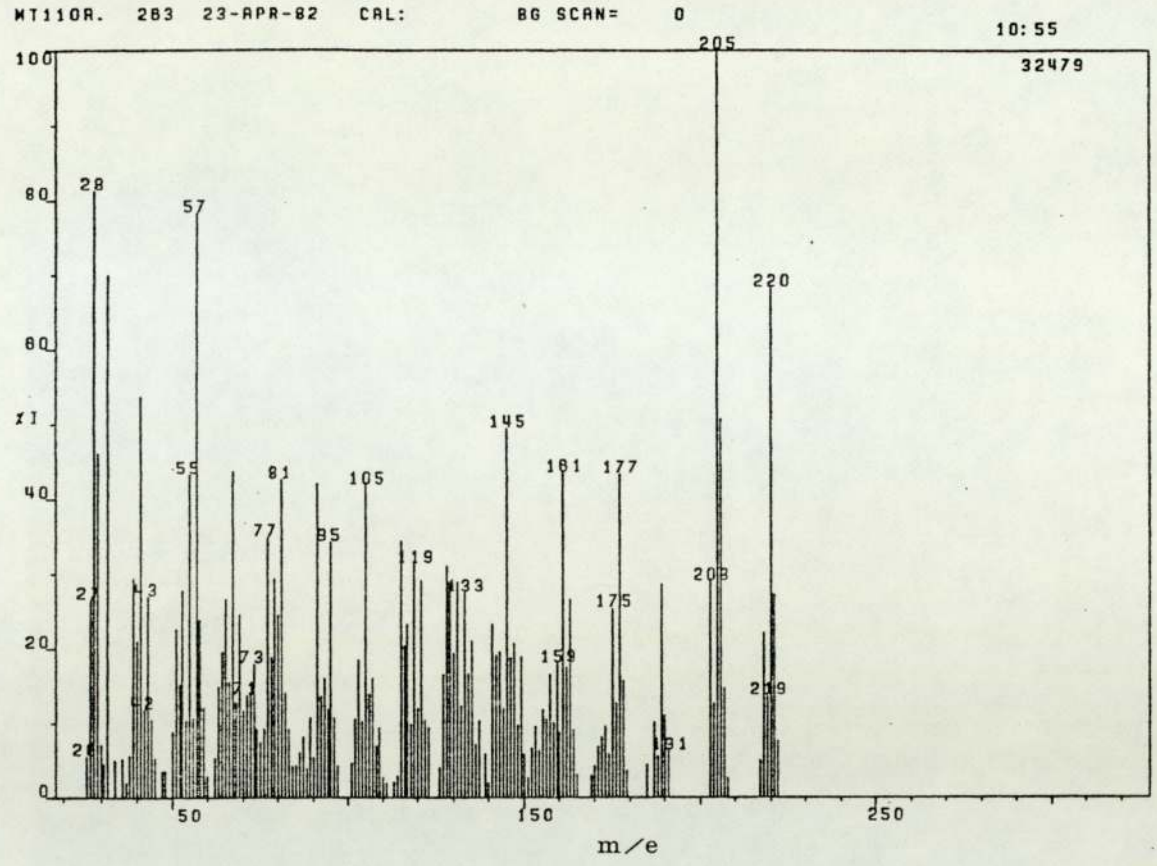


Fig 4.45 The mass spectrum of peak at scan no 263

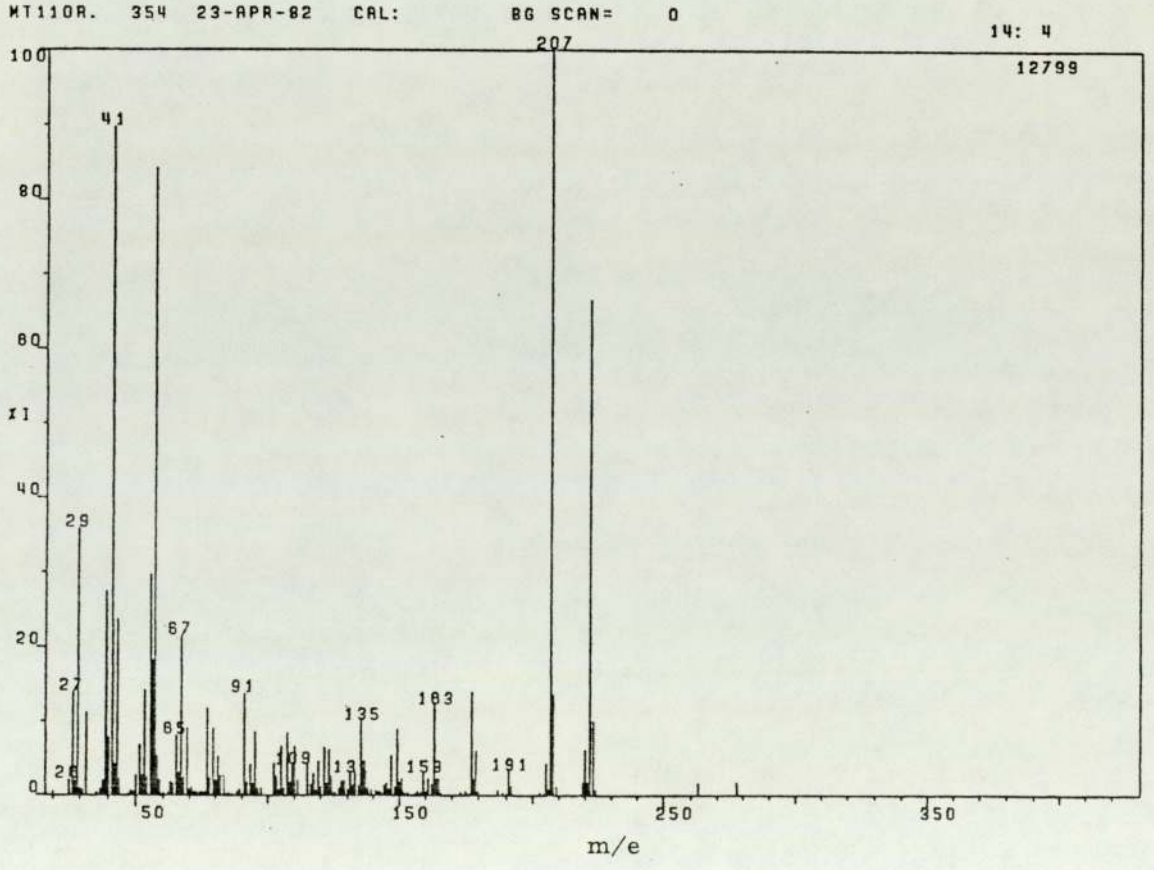


Fig 4.46 The mass spectrum of peak at scan no 354

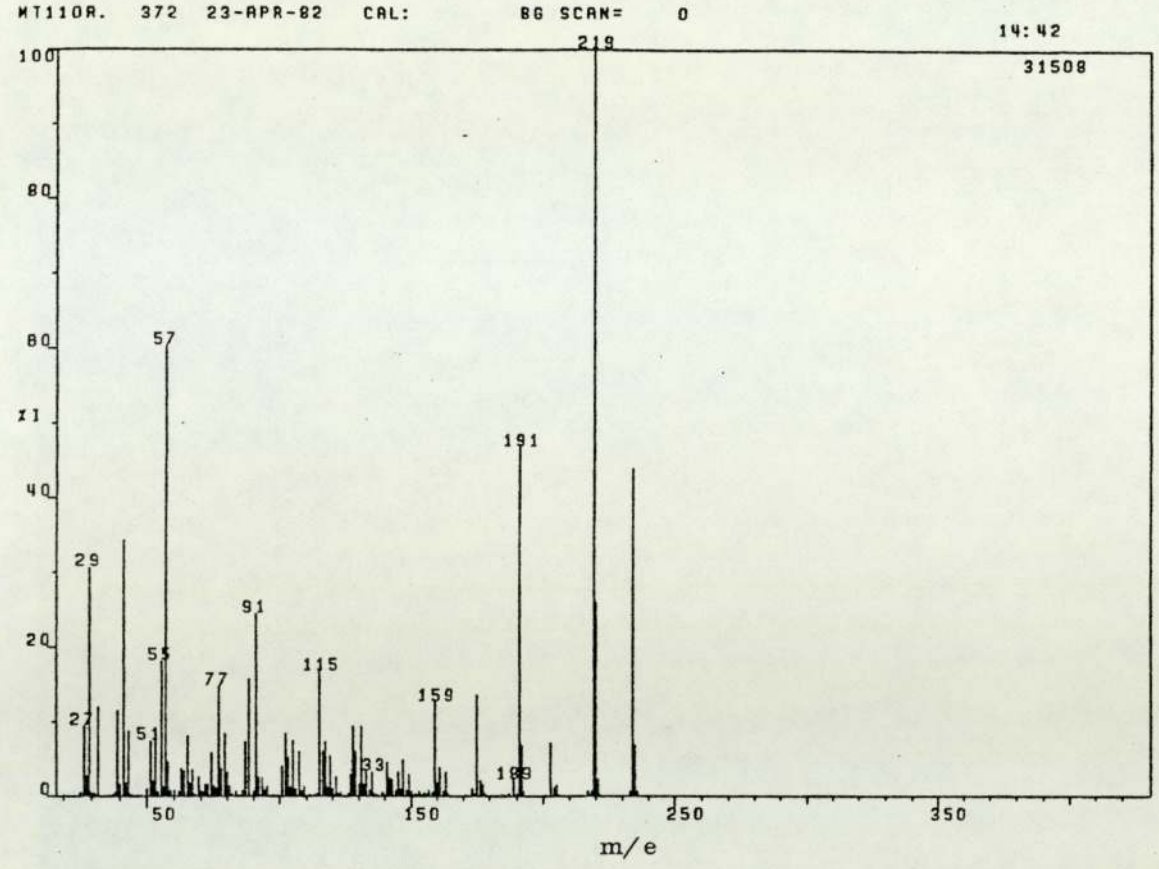


Fig 4.47 The mass spectrum of peak at scan no 372

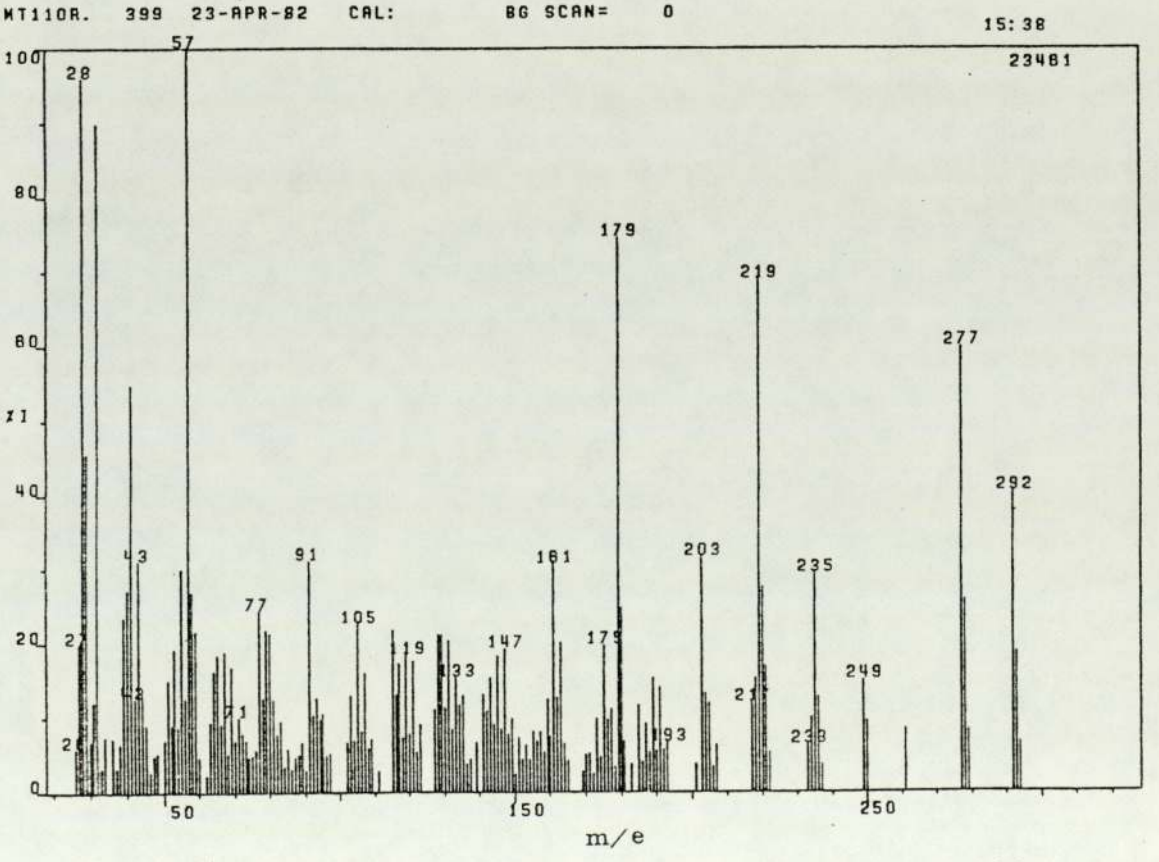


Fig 4.48 The mass spectrum of peak at scan no 399

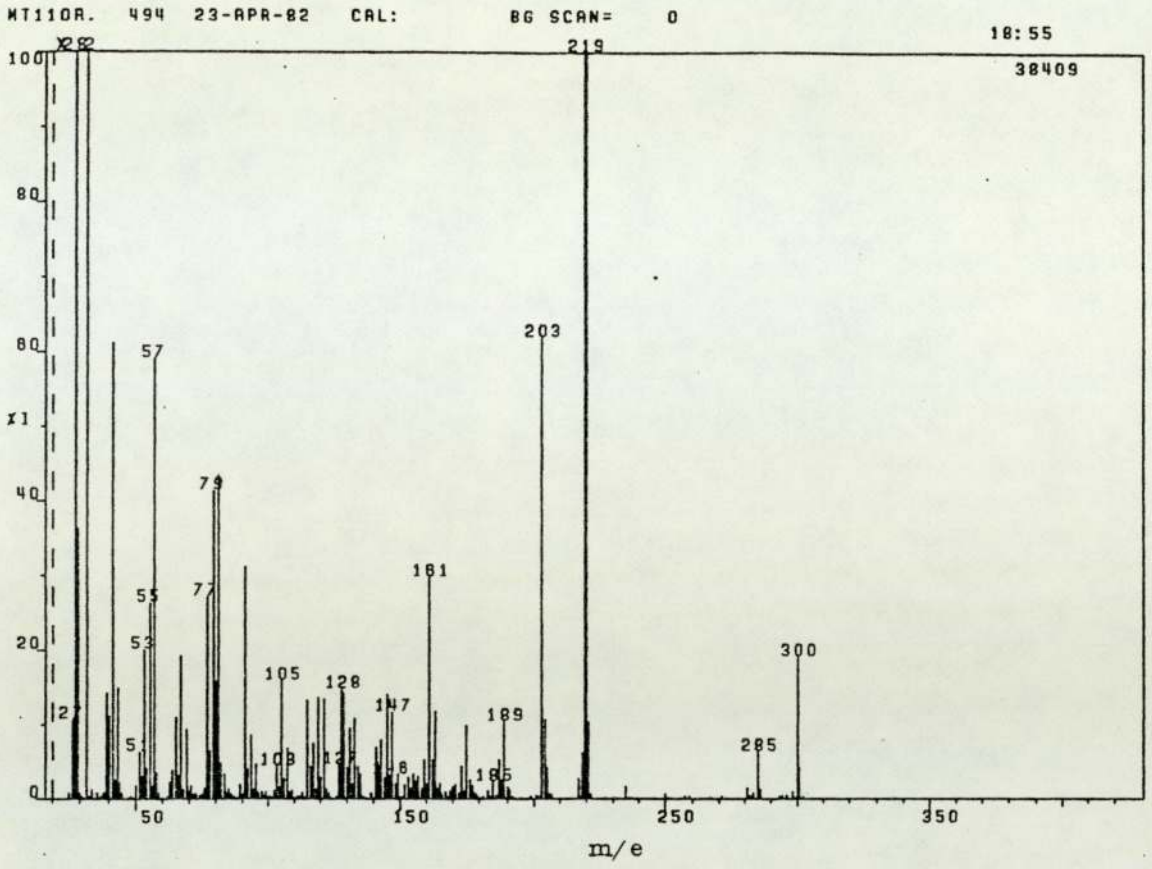


Fig 4.49 The mass spectrum of peak at scan no 494

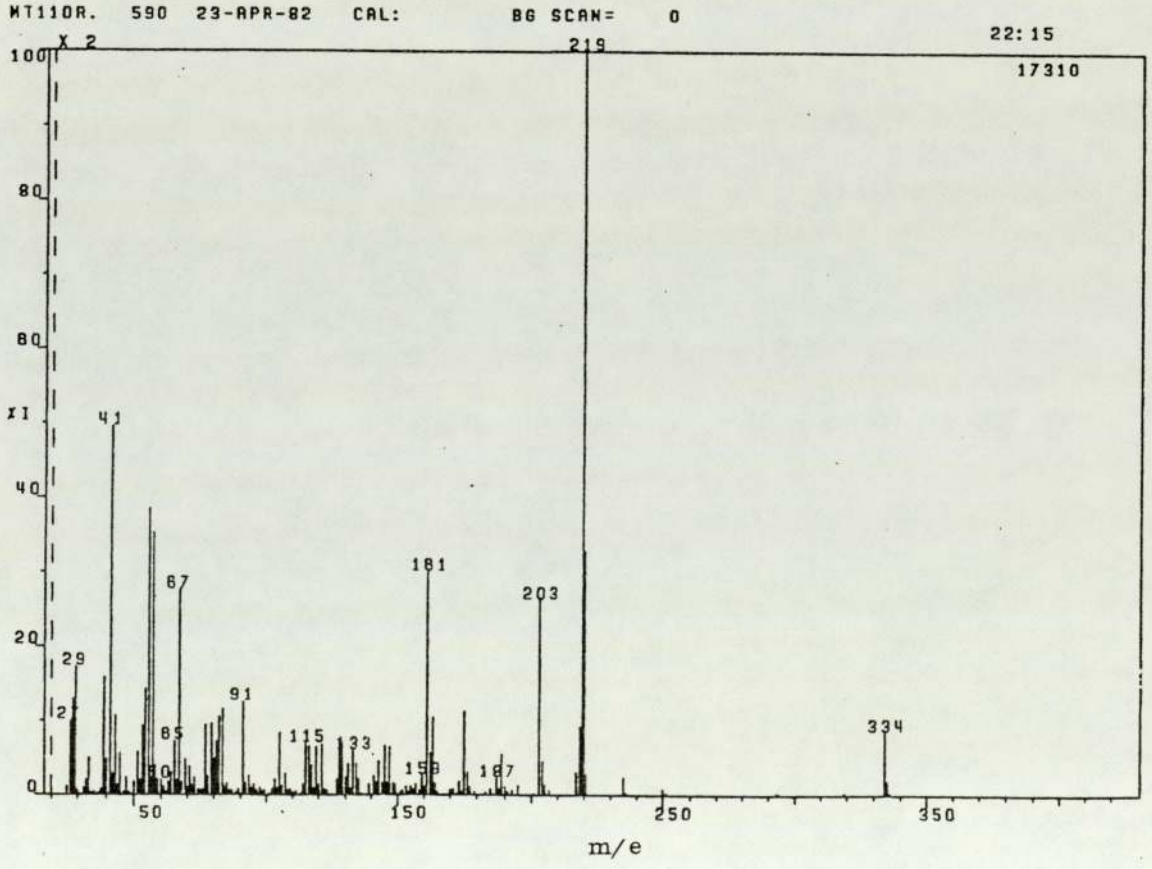


Fig 4.50 The mass spectrum of peak at scan no 590

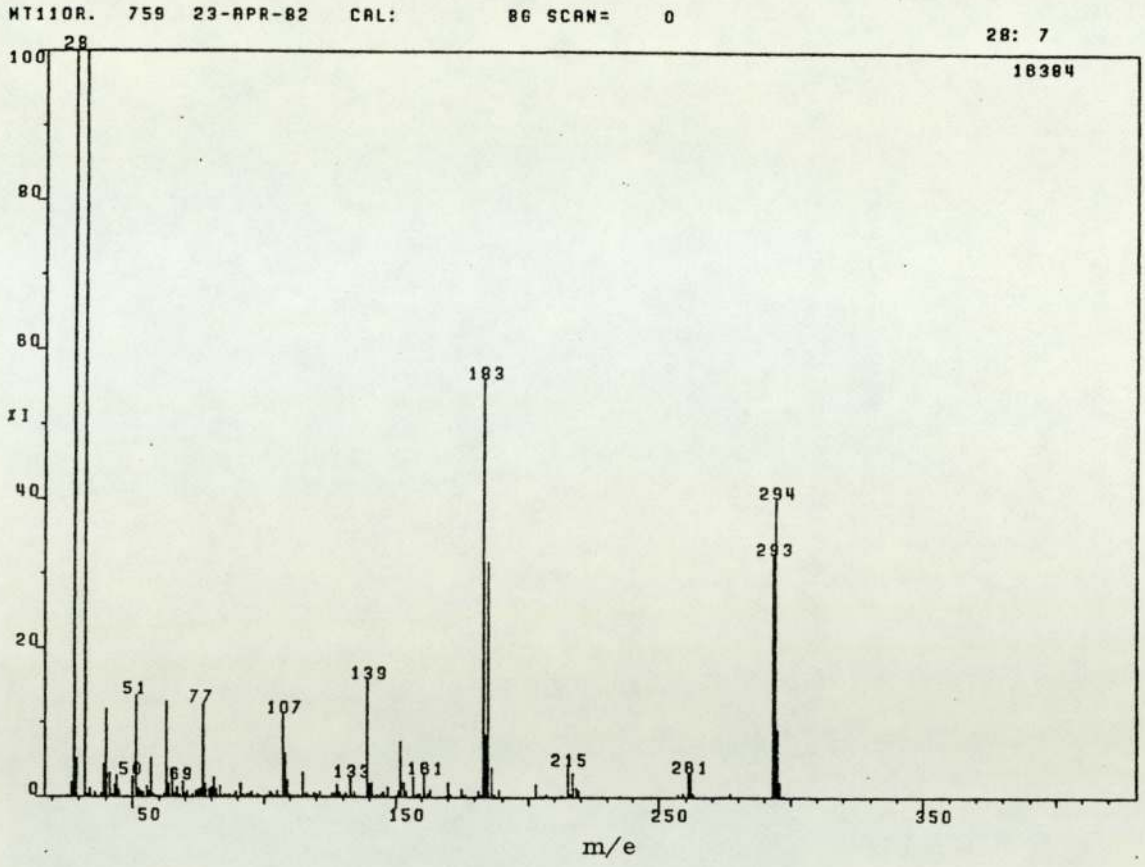


Fig 4.51 The mass spectrum of peak at scan no 759

The main spectra of these reaction products were compared with those of the reference mass spectra, described in Section 4.3.1.1 and mass spectra studied in Sections 4.4.1.1.6 and 4.4.2.4.

The highest m/e corresponding to the peaks mentioned above are summarised in Table 4.15 together with their retention times. Table 4.18 shows the related structures of the peaks.

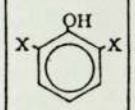
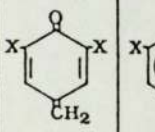
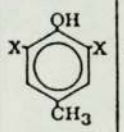
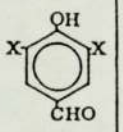
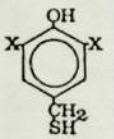
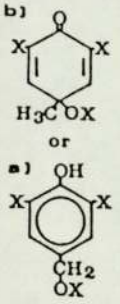
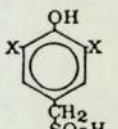
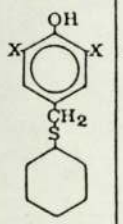
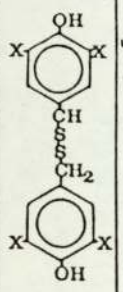
Table 4.15 Highest m/e for reaction of BHBM with TBH (molar ratio 1:1) at 110°C, scan range 0-800

Peak at scan no	Highest m/e	Retention time, mins
228	206	9' 42"
242	220	10' 11"
250	218	10' 28"
263	220	10' 55"
354	292	14' 4"
372	234	14' 42"
399	292	15' 38"
495	300	18' 55"
590	334	22' 15"
759	294	28' 7"

Table 4.16 The highest m/e and corresponding structure of reaction BHBM with TBH (molar ratio 1:1) scan range 0-650

Peak at scan no	Highest m/e	Corresponding structure
228	266	4-I
242-243	220	4-II
250	218	4-III
372	234	4-IX
399/400	292	4-X
494/493	300	4-VI
590	334	4-III
759	294	unidentified

Table 4.17 GC-MS data of products formed in the reaction of BHBM with TBH in cyclohexene

Molar ratio of BHBM to TBH	t (°C)	Compounds number and their highest m/e									
		4-I	4-III	4-II	4-IX	4-V	4-X[a,b]	4-VII	4-VIII	4-VI	—
		206	218	220	234	252	292	300	334	250	293/294
2 : 1	70	VW	W	M	—	S	—	M	S	VW	VW
1 : 1	70	W	W	M	M	S	—	W	M	VW	VW
1 : 2	70	W	S	M	M	W	W	M	W	VW	VW
1 : 1	110	W	M	M	M	—	M	M	W	VW	W
Identity											unidentified

Where; W = weak VW = very weak X = tert-butyl M = medium S = sharp

Table 4.18

Compound No	MW	Trivial Name	IUPAC
4-I	206		2,6-di-tert-butyl phenol
4-III	218		3,6-di-tert-butyl-4-methylene 2,5-cyclohexadien-1-one
4-II	220		3,5-di-tert-butyl-4-hydroxy-phenol
4-IX	234		3,5-di-tert-butyl-4-hydroxy-phenyl carbaldehyde
4-IV	236	3,5-di-tert-butyl-4-hydroxy-benzyl alcohol	3,5-di-tert-butyl-4-hydroxy-phenylmethanol
4-V	252	3,5-di-tert-butyl-4-hydroxy-benzyl mercaptan (BHBM)	3,5-di-tert-butyl-4-hydroxy-phenylmethanethiol
4-X	292		3,5-di-tert-butyl-4-hydroxy-phenyl methyl tert butyl ether
4-VII	300		3,5-di-tert-butyl-4-hydroxy-phenyl methyl sulphonic acid
4-VIII	334		3,5-di-tert-butyl-4-hydroxy-cyclohexyl sulphide
4-VI	504		bis(3,5-di-tert-butyl-4-hydroxybenzyl) disulphide

4.7 OVERALL CONCLUSION

The GC-MS data of products formed during the reaction of BHBM with TBH in the presence of cyclohexene at 70 and 110°C is summarised in Table 4.17.

4.8 NOMENCLATURE

Nomenclature used in this work were trivial and IUPAC. Table 4.18 shows trivial names and IUPAC of each compound.

4.9.1 REACTION OF BHBM WITH TBH (MOLAR RATIO 1:1) IN SBR LATEX

The reaction was carried out as described in Section 3.2.2.1. The latex was coagulated, sheeted, dried and soaked in acetone for 24 hours.

The extract was injected through a GC-MS using conditions described in Section 4.2.2. The GC-MS chromatogram is shown in Fig 4.51. The highest m/e of each peak and its retention time is shown in Table 4.19.

Table 4.19 Reaction product of BHBM with SBR (molar ratio 1:1) with highest m/e and its retention time, scan range 0-450

Peak at scan no	Highest m/e	Retention time, mins
65	218	3' 3"
71	220	3' 16"
123	250/252	5' 4"
144	234	5' 48"
226	256	8' 39"*
262	264	9' 54"*
290	264	16' 52"*

* These peaks are not related to the reaction product

After scan number 200, big peaks appeared of which three were not related to the reaction product. The four peaks which were related to the reaction product, were studied and are summarised in the above Table.

The mass spectra of the latex binding reaction (Figs 4.52 to 4.58) were compared to the reference compound (Section 4.3.1.1) and mass spectra studied in Section 4.4.1.1.6 and Section 4.4.2.4. The results are summarised in Table 4.20.

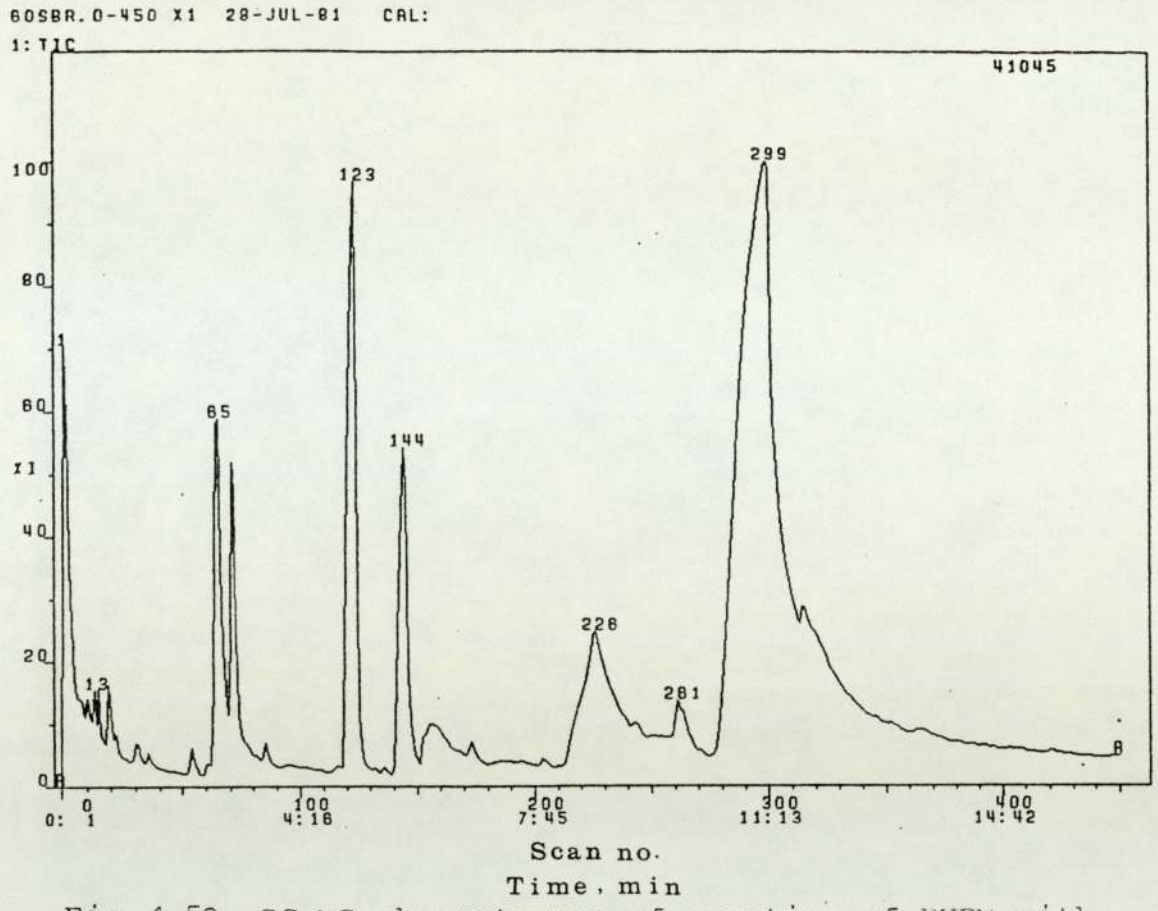


Fig 4.52 GC-MS chromatogram of reaction of BHBM with TBH (molar ratio 1:1) in SBR latex

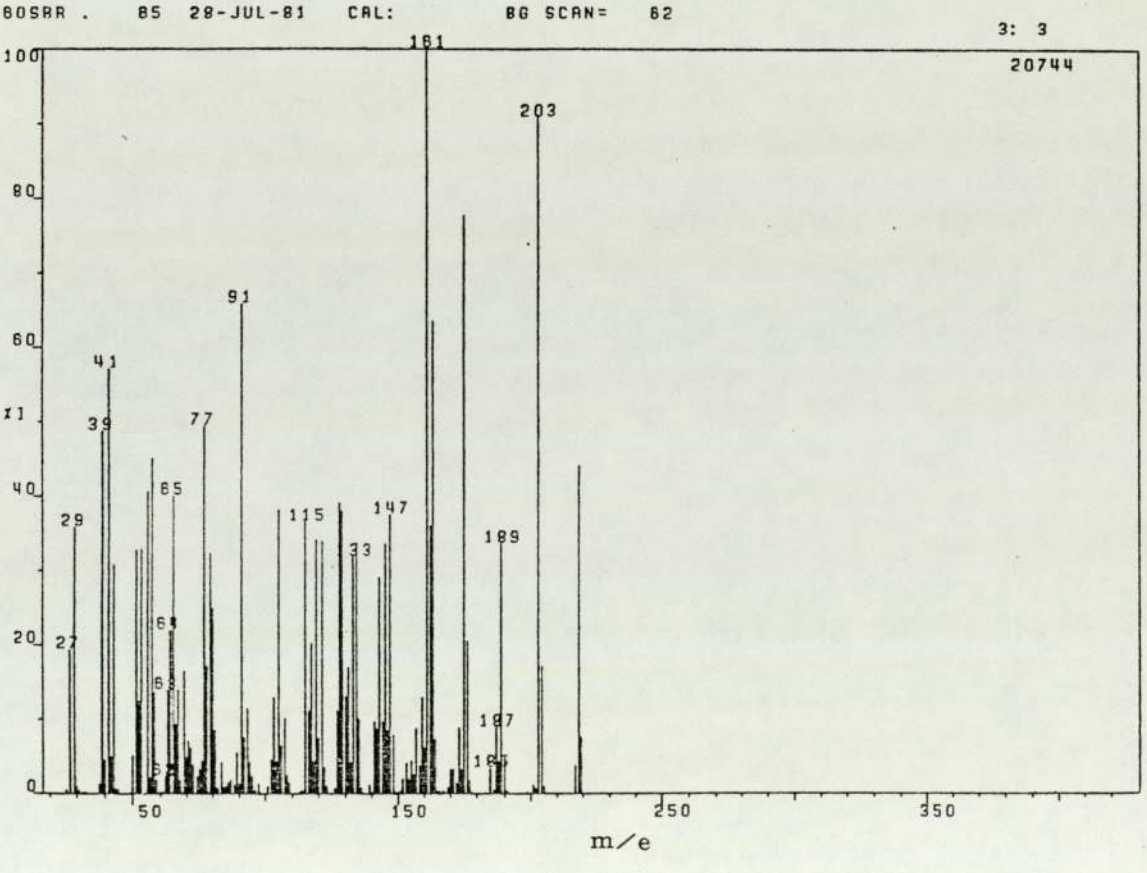


Fig 4.53 The mass spectrum of peak at scan no 65

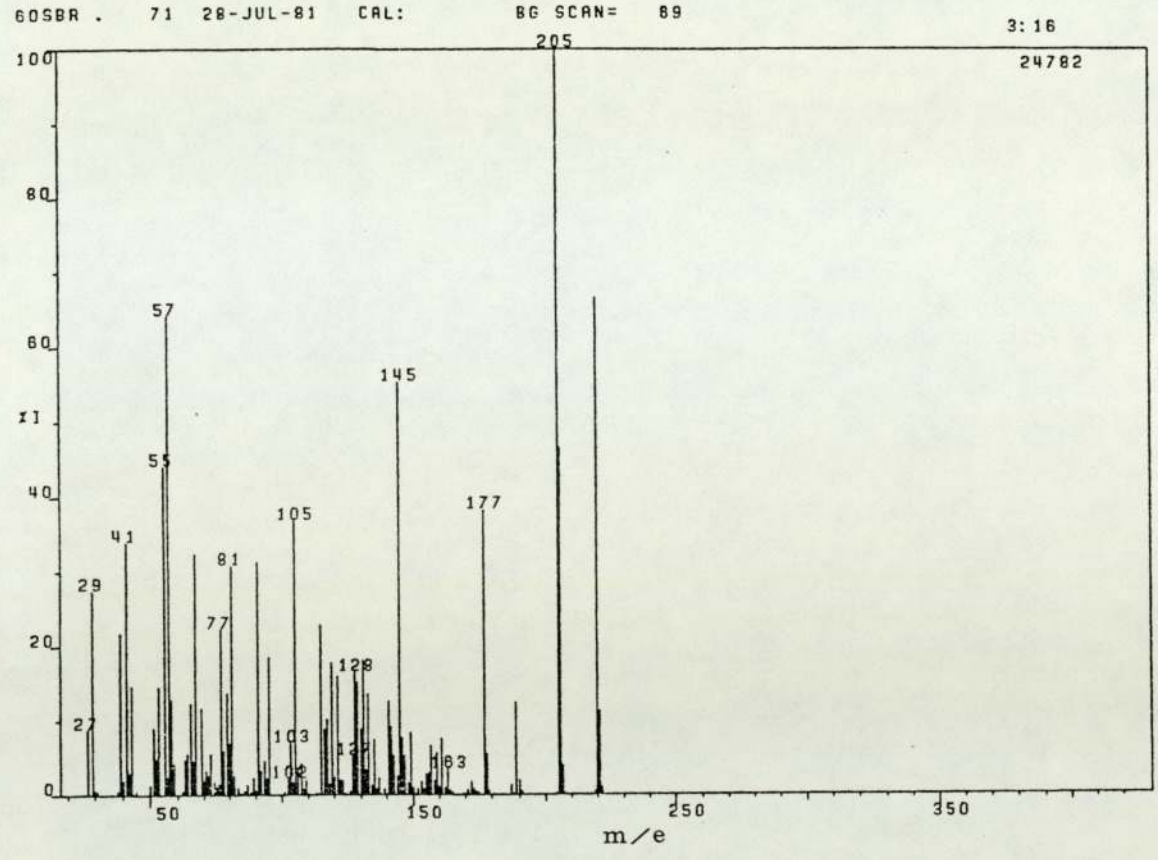


Fig 4.54 The mass spectrum of peak at scan no 71

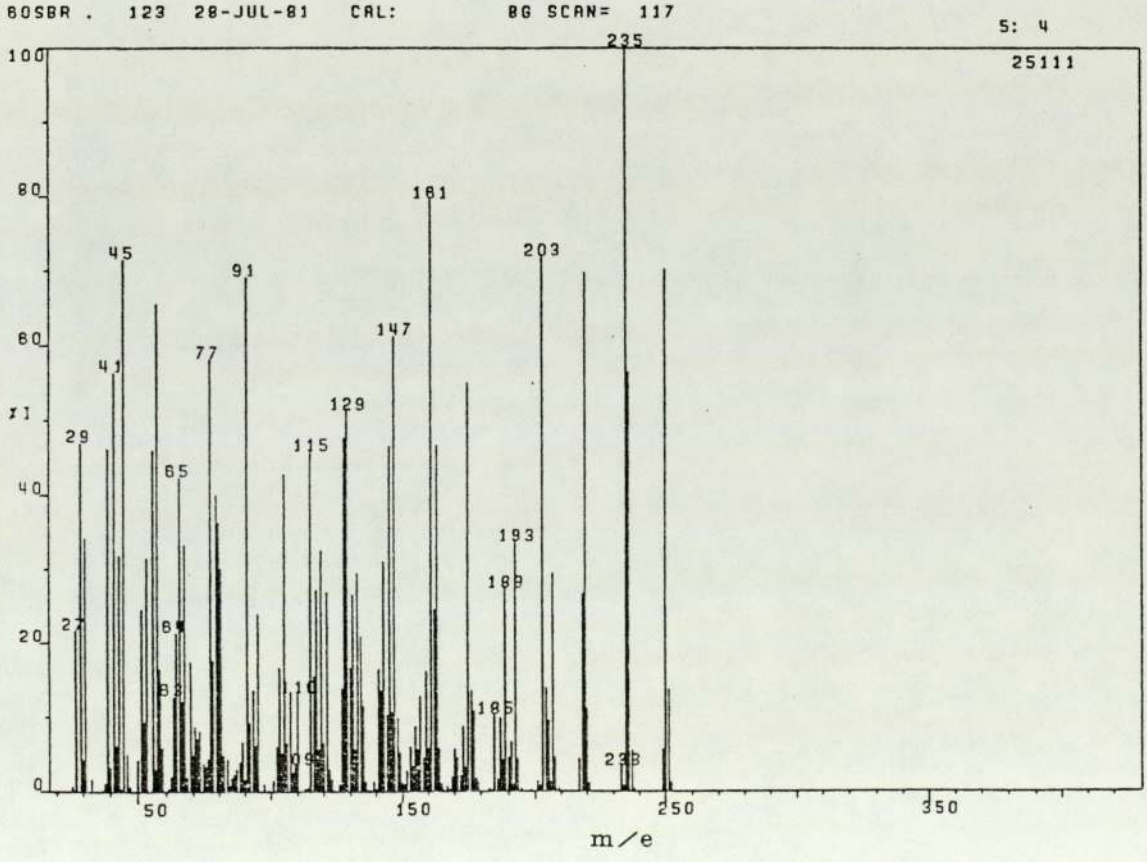


Fig 4.55 The mass spectrum of peak at scan no 123

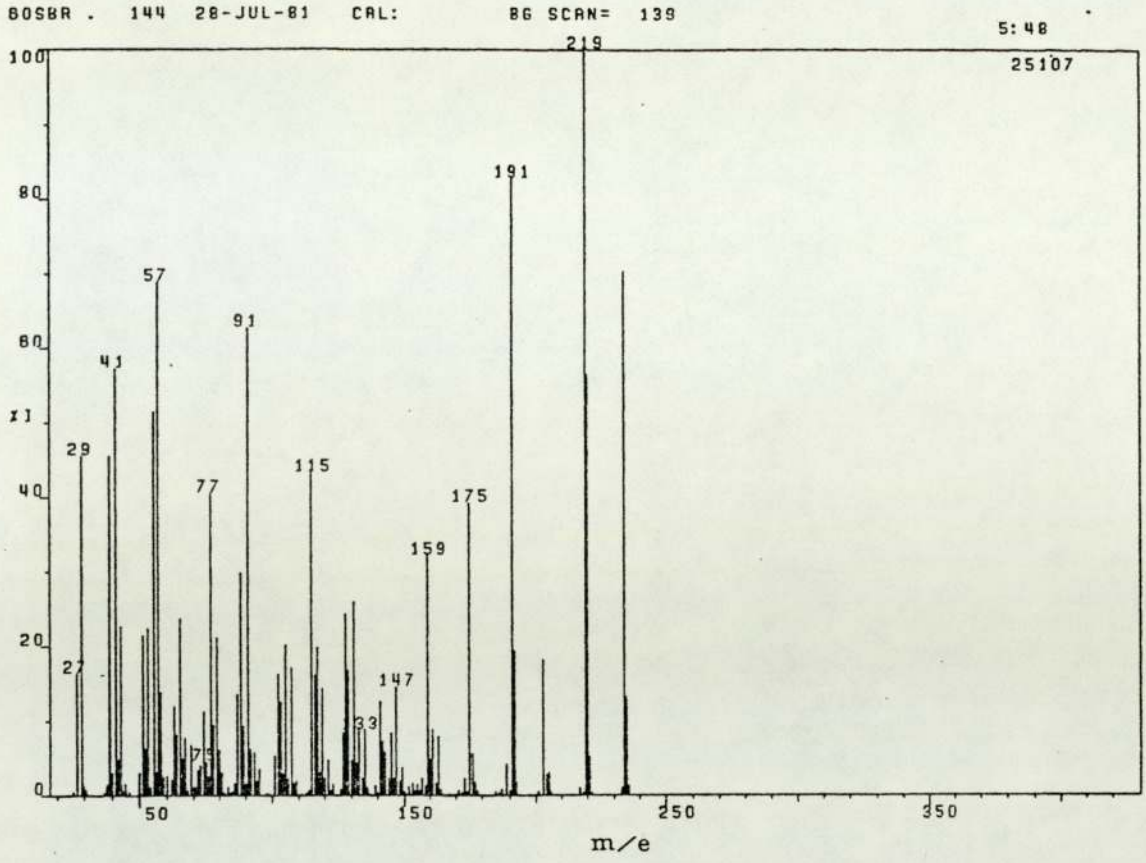


Fig 4.56 The mass spectrum of peak at scan no 144

Table 4.20 Fragment loss, highest m/e, scan number 0-450

Peak at scan no	Molecular weight	Corresponding Compound
65	218	4-III
71	220	4-II
123	252	4-VI
144	234	4-X

Peak numbers 226, 262 and 290 did not show any fragments related to the reaction product of BHBM with TBH.

Fragments at 77 and 91 were not observed. These peaks and their mass spectra can be seen in Figs 4.57 to 4.59. Thus the above three peaks may be related to non-rubber compounds added to the SBR emulsion during manufacture.

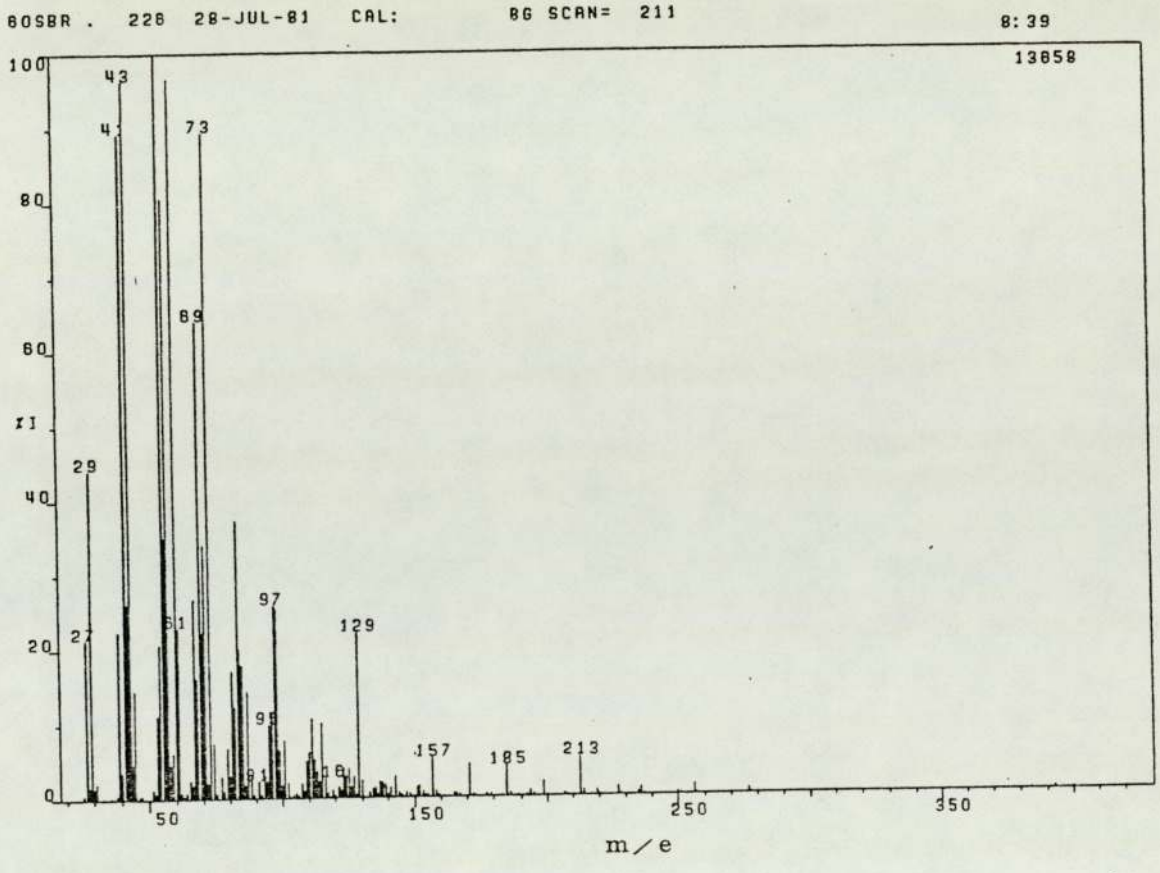


Fig 4.57 The mass spectrum of peak at scan no 226

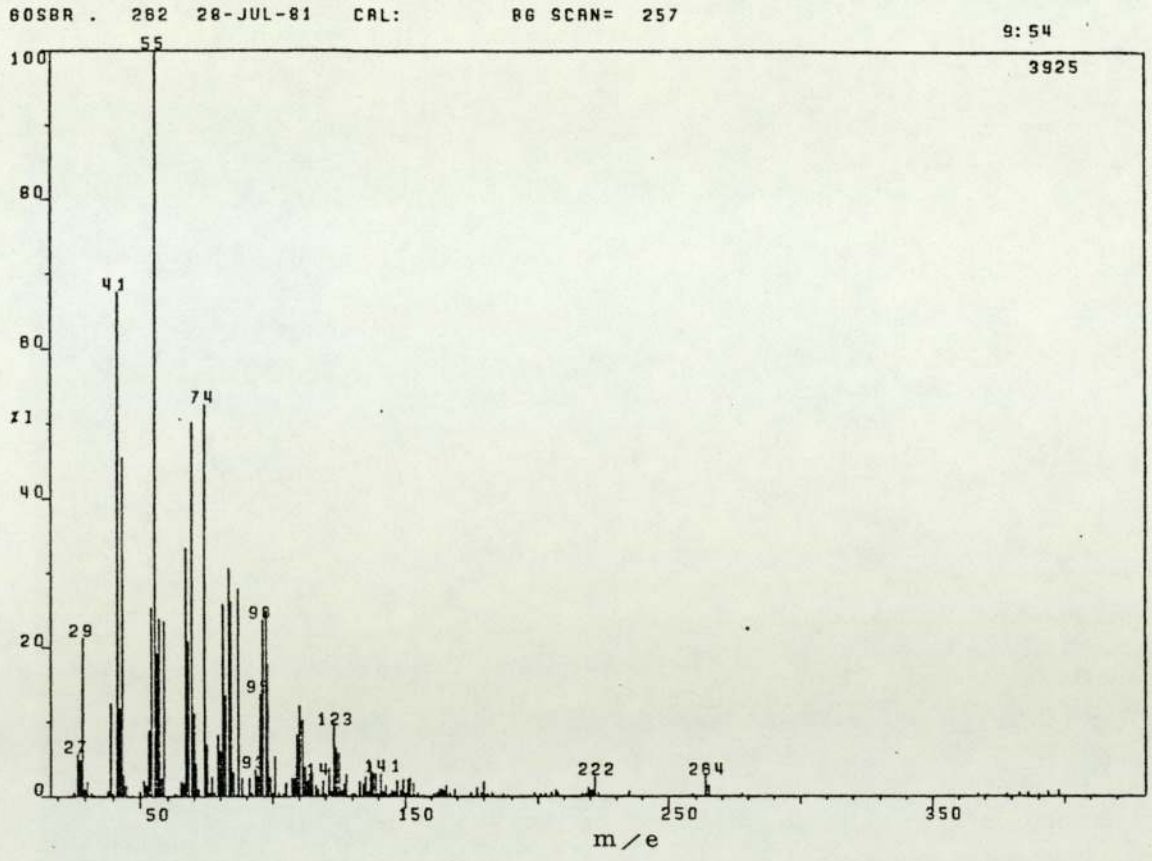


Fig 4.58 The mass spectrum of peak at scan no 262

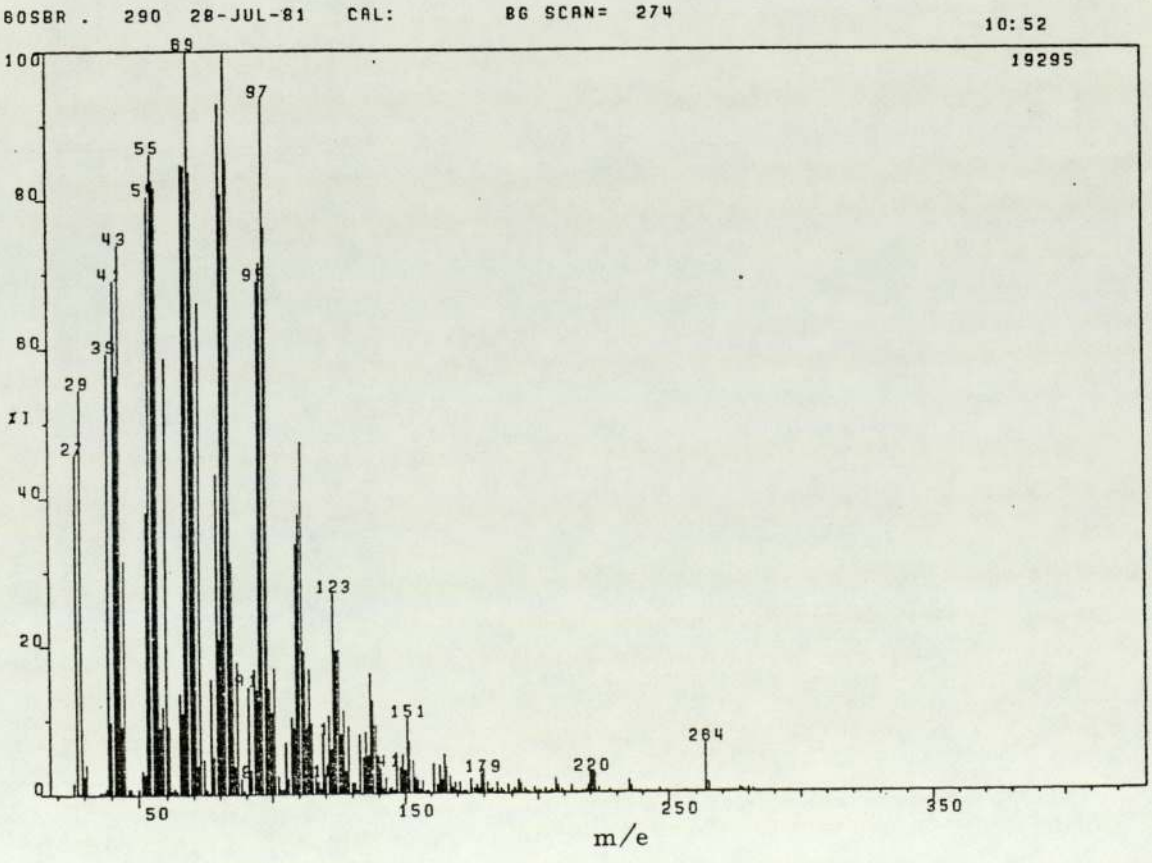


Fig 4.59 The mass spectrum of peak at scan no 290

4.10 QUALITATIVE DETERMINATION OF THE RELATIVE RATES OF FORMATION AND DECOMPOSITION OF INTERMEDIATES DURING THE BINDING PROCESS

In view of the changes occurring at different BHBM / TBH ratios, it was considered to be relevant to also study the relative rates of product formation in the model compound studies, described in Section 4.4.1-4.4.4 and to correlate these results with those from the GC-MS studies.

The experiements were carried out using the Pye Unicam GLC described in Section 4.2.1.2. The results were also treated as described in that section.

4.10.1 REACTION OF BHBM WITH TBH (MOLAR RATIO 1:1½)

Six major peaks were recorded when the samples were injected into columns. A typical chromatogram is shown in Fig 4.1.

The relative rates of formation and decay of the peaks is shown in Fig 4.60.

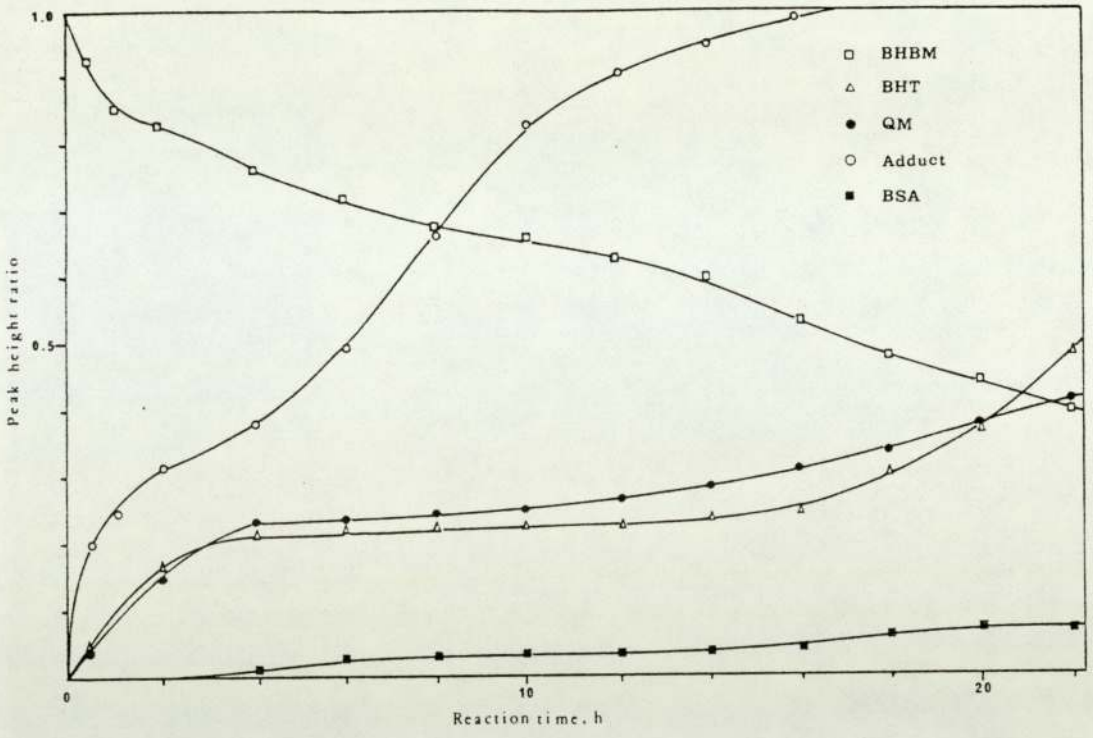
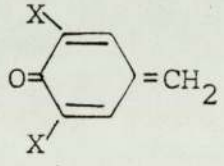
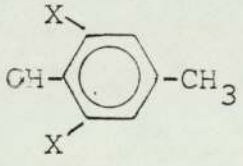
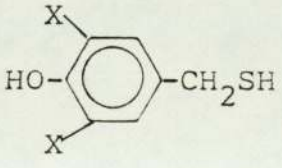
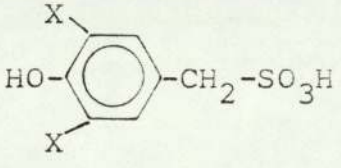
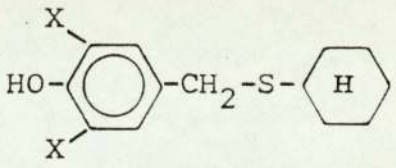


Fig 4.60 Relative rates of formation of products during the reaction of BHBM with TBH (molar ratio 1:½) in cyclohexene at 70°C

4.10.1.1 RESULTS

From Fig 4.60 it can be seen that BHBM reacted with TBH to form the products shown below.

	MW	Initial/Number		Structure
1	218	QM	4-III	
2	220	BHT	4-II	
3	252	BHBM	4-V	
4	300	BSA	4-VI	

5 334 Adduct 4-VIII 

The consumption of BHBM was very rapid during the first three hours of reaction and thereafter was consumed at a lower rate.

The initial formation of adduct was very rapid during the first three hours and thereafter increased steadily but more slowly as the reaction progressed.

The relative initial rates of formation of QM and BHT also was very rapid and this was followed by a slower but steady increase in relative concentration therafter.

The BSA was also formed in low concentration after an induction period of about three hours and this built up to a limiting concentration as shown. It is interesting to note that the initial growth of the adduct QM and BHT mirrors the decrease in concentration of BHBM during the first three to four hours.

Fig 4.60 also shows that the relative concentration of adduct formed during the reaction is high compared to the other products.

4.10.2 REACTION OF BHBM WITH TBH (MOLAR RATIO 1:1)

It is shown in the GC-MS chromatogram that there are 9 peaks, of which only the five strongest appeared on the GLC Pye Unicam (Section 4.4.2). The rates of formation of the products relative to decomposition of BHBM are shown in Fig 4.61.

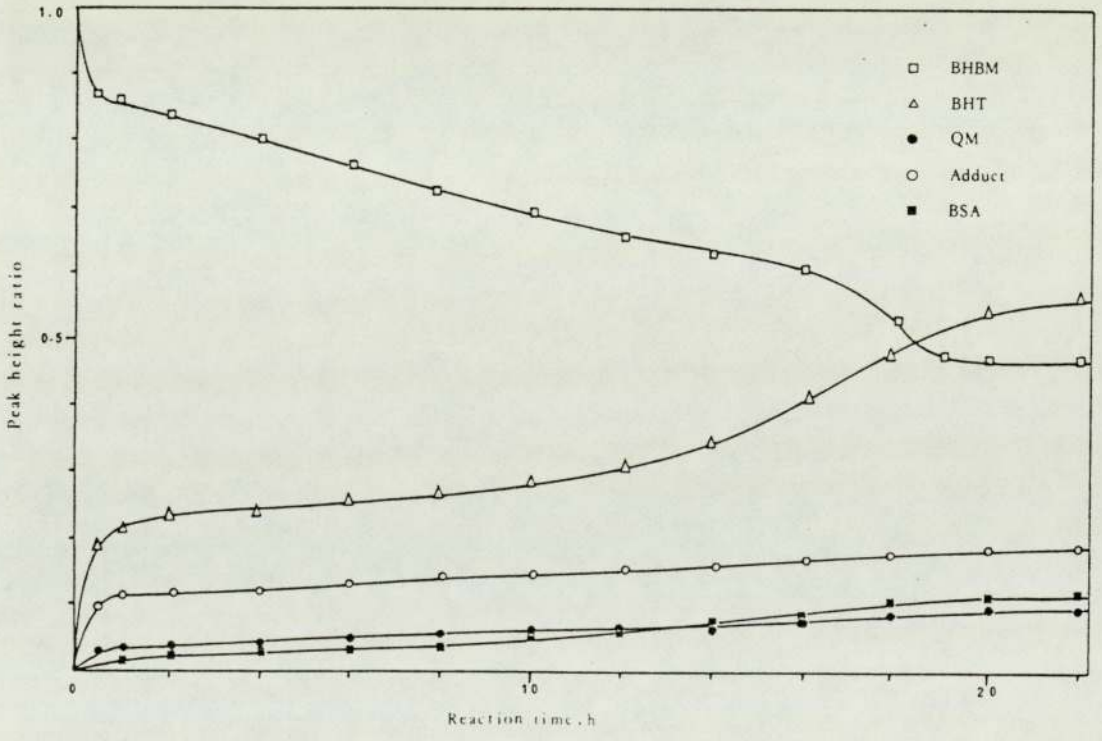


Fig 4.61 Relative rates of formation of product during the reaction of BHBM with TBH (molar ratio 1:1)

4.10.2.1 RESULTS

BHBM reacted with TBH in cyclohexene to give the QM, BHT, BSA. Part of the starting material of BHBM is again remained unreacted. It is seen that the formation of BHT is relatively high, on the other hand, the formation of the adduct is much lower compared to the reaction of BHBM with TBH at higher molar ratio of 1:½. There is a slower but steady increase in both adduct (Add) and quinone methide (QM).

4.10.3 REACTION OF BHBM WITH TBH (MOLAR RATIO 1:2)

The reaction of BHBM with BHT molar ratio 1:2 in cyclohexene at 70°C was described in Section 4.4.3. The chromatogram of GC-MS showed nine peaks, the Pye Unicam showed five peaks. The relative rates of formation of these peaks can be seen in Fig 4.62.

4.10.3.1 RESULTS

At the low molar ratio of BHBM to TBH (1:2), the BHBM peak in the GC-MS chromatogram was weak even after only 15 mins, showing that most of the BHBM had been consumed.

It can be seen from Fig 4.62 that over 90% of BHBM was

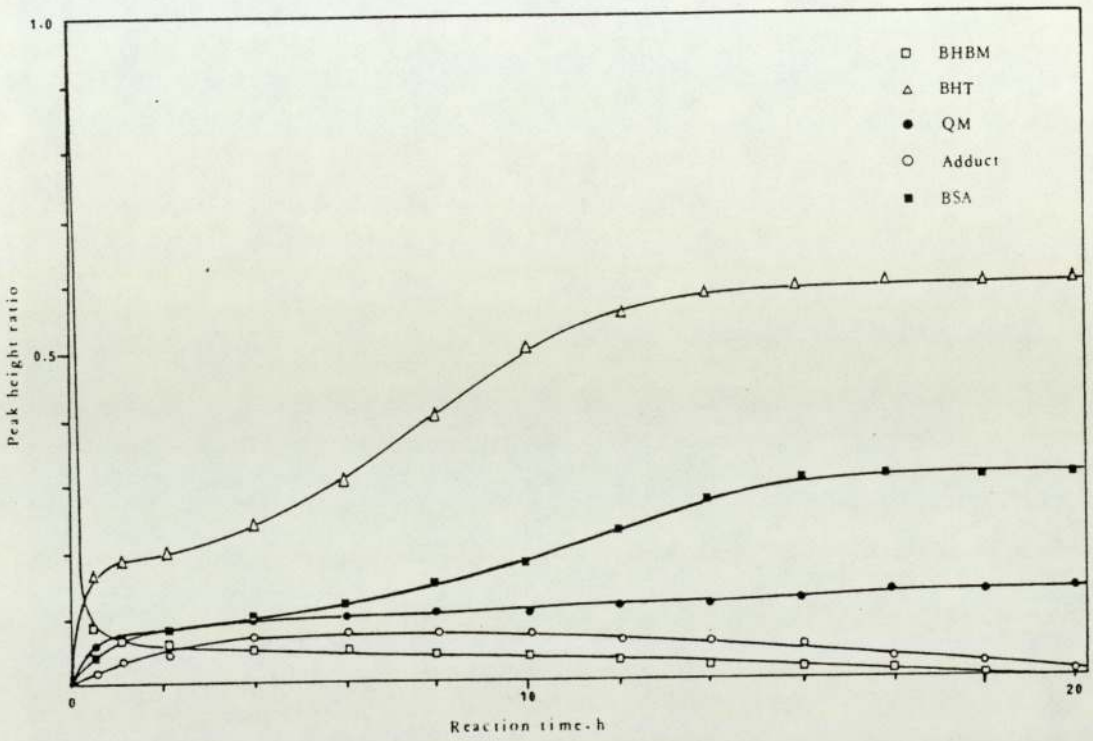


Fig 4.62 Relative rates of formation of products during the reaction of BHBM and TBH (molar ratio 1:2)

consumed during the first hour of reaction. However, the amount of adduct formed is very low at all stages. The formation of BSA and BHT are the predominant reactions in the presence of excess of hydroperoxides.

4.10.4 REACTION OF BHBM WITH TBH (MOLAR RATIO 1:1) AT 110°C

At 110°C a different picture was observed, it was shown in the GC-MS chromatogram that there were ten peaks present, only seven of which were observed in the Pye Unicam GLC (Fig 4.63).

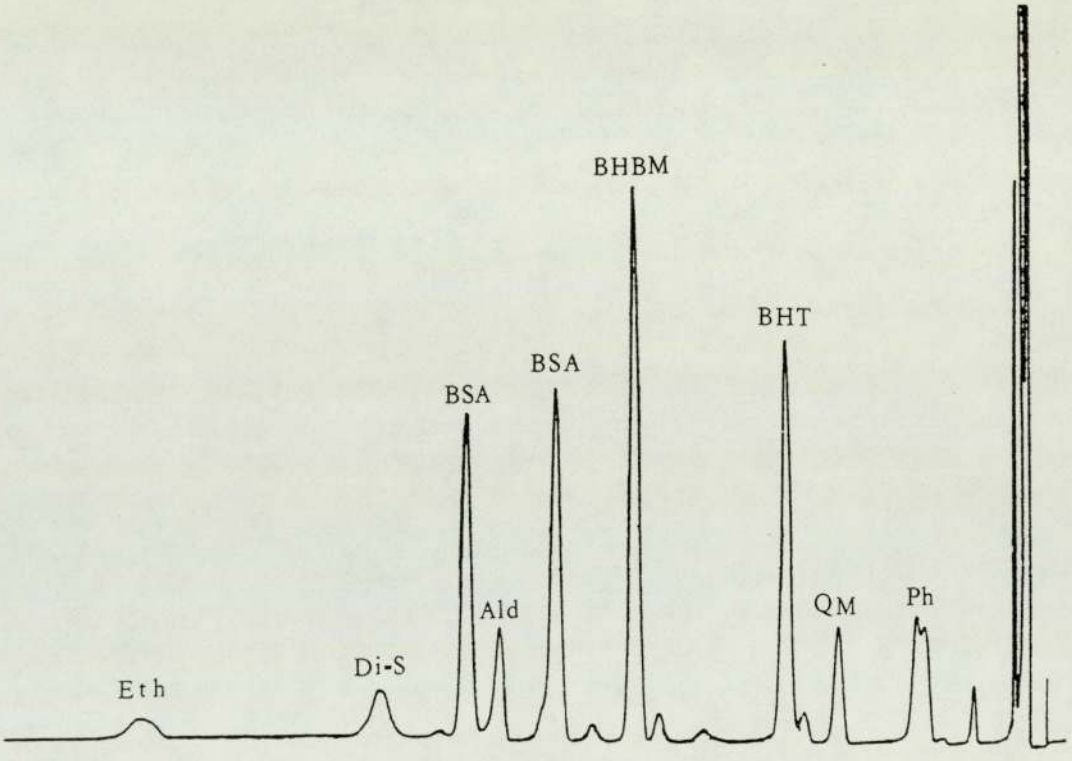


Fig 4.63 Chromatogram of GLC (Pye Unicam GCD) for products from reaction of BHBM with TBH at 110°C (molar ratio 1:1) in cyclohexene

4.10.4.1 RESULTS

There were two additional peaks present in this reaction which code as follows:

MW	COMPOUND NUMBER	CODE
234	4-IX	ALD
292	4-X	ETH
250	4-VII	DiS

The relative rates of formation of products during reaction at 110°C is shown in Fig 4.64 .

The BHBM concentration rapidly decreased over the first hour then decreased at a slower rate followed by a second stage of fast decomposition which reduced the concentration to zero after ten hours.

No adduct was detected.

The QM growth occurred very rapidly over the first hour then tended towards a stationary concentration followed by a more rapid increase towards the end of the reaction.

The BSA behaves similarly but the rate of increase during the second stage was slower. The BHT increased

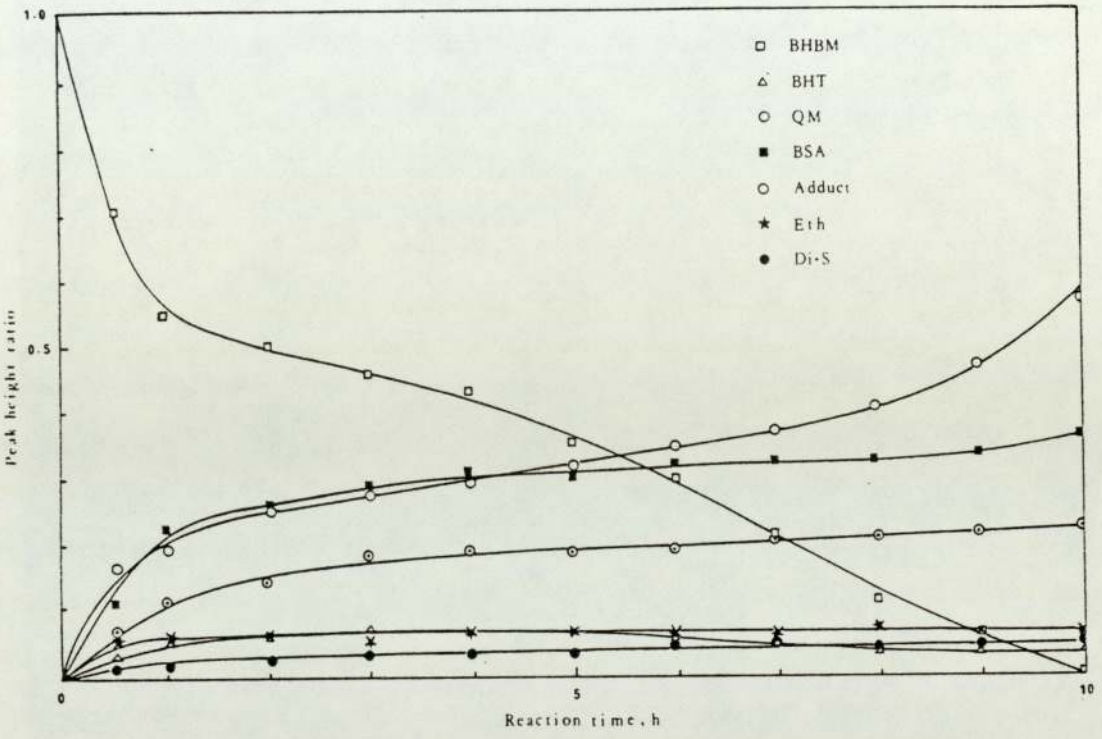


Fig 4.64 The relative rate of formation of products during reaction of BHBM with TBH (molar ratio 1:1) at 110°C in cyclohexene

to a maximum followed by a decrease as the reaction progressed. The decrease of BHT mirrors the increase of QM.

4.11 STUDIES OF HYDROPEROXIDE DECOMPOSITION DURING THE REACTION BETWEEN BHBM AND TBH AT 70°C

In order to correlate the decomposition of hydroperoxide with the formation of the intermediates during the reaction and to get a clearer understanding of the mechanism of the reaction at the various molar concentrations, the rate of decomposition of hydroperoxide was studied using infra red spectroscopy.

4.11.1 EXPERIMENTAL

The Perkin Elmer Grated Infra-red Spectrometer Model IR-599 was used for this purpose. The reaction solution was placed in a sodium chloride cell. The light path length of the cell was 0.5 mm. The volume of solution contained in the cell was 0.2 ml.

At various time intervals samples of the reaction mixture was drawn using a 1 ml syringe equipped with a long needle and the spectra were recorded.

The decay in concentration of the hydroxyl band at 3620 cm^{-1} was followed with time. The absorbance was calculated using a base line technique[111] and expressed as an index relative to the absorbance at 2720 cm^{-1} (reference peak).

Calibration curves were made using various concentrations of TBH in order to calculate the concentration of TBH at the various reactive times.

4.11.2 RESULTS

The decomposition of TBH was shown in Fig 4.65.

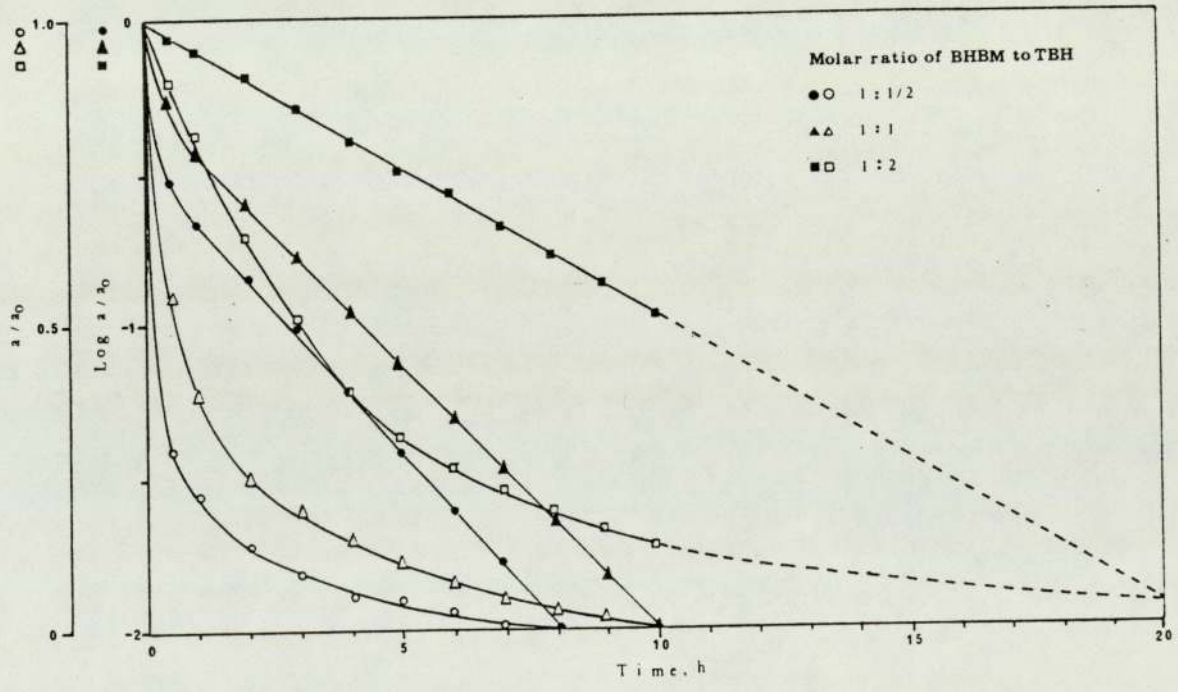


Fig 4.65 The decomposition of TBH in the reaction of TBH with BHBM in cyclohexene

Fig 4.65 shows the zero order and first order plot of

the decomposition of the TBH concentration during the reaction of BHBM to TBH using molar ratio of 1:½, 1:1 and 1:2 respectively.

It can be seen that none of the reactions obey zero order kinetics. However, the first order plot shows that for the molar ratio of 1:1 and 2:1 it was observed that the TBH changes rapidly initially and is followed by a first order catalytic reaction which reduces the hydroperoxide concentration to zero. For molar ratio 1:2 the first order catalytic decomposition occurs from the very start of the reaction.

4.11.3 DISCUSSION

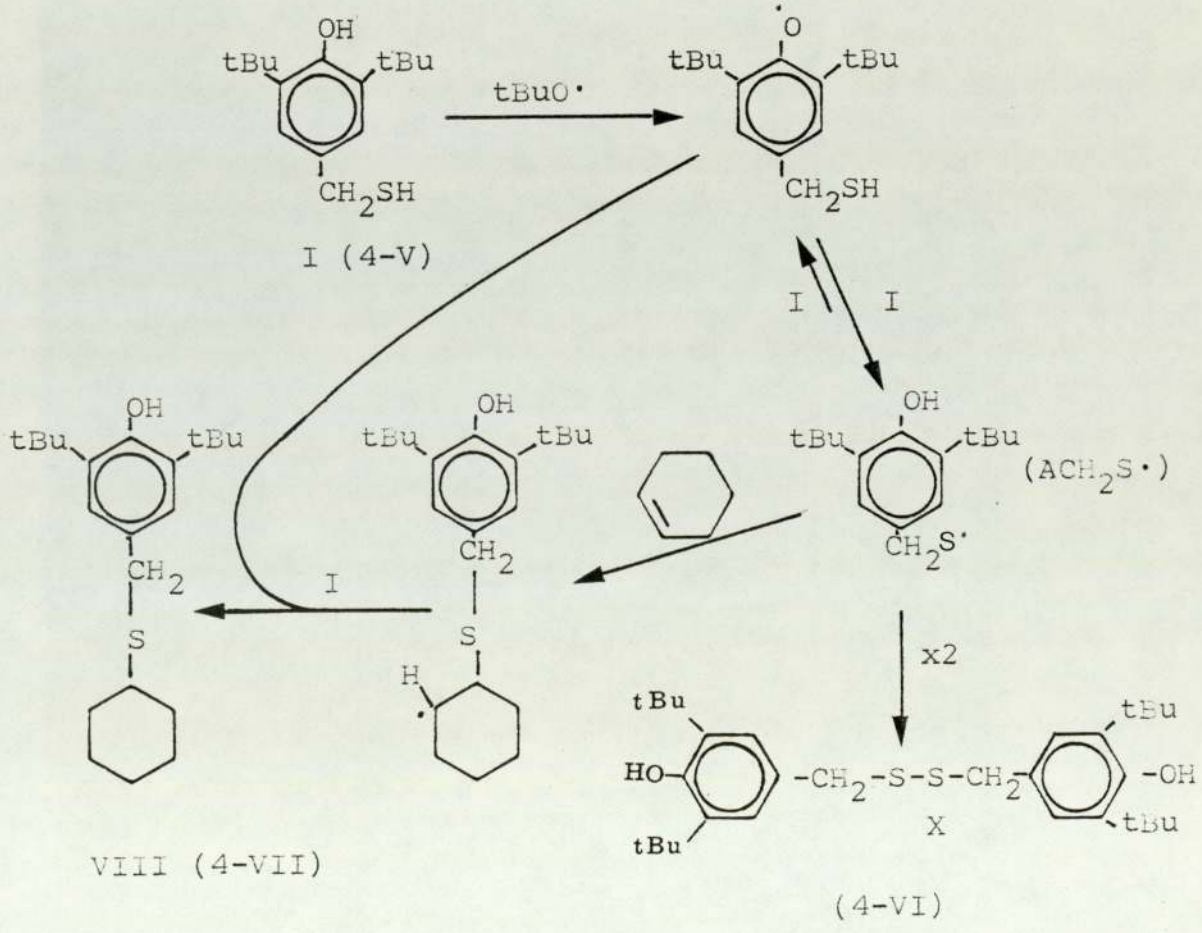
Correlating these results with the antioxidant product studies, it is clear that at molar ratio [BHBM]/[TBH] = 1:½ and 1:1 the reaction is initially a free radical process and this is followed by a slower ionic process. However, if the molar ratio of TBH to BHBM is 2:1, the ionic mechanism operates from the beginning. In the latter case, the free radical decomposition is not seen due to the oxidation of BHBM to sulphur acids by the excess of TBH.

4.12 DISCUSSION

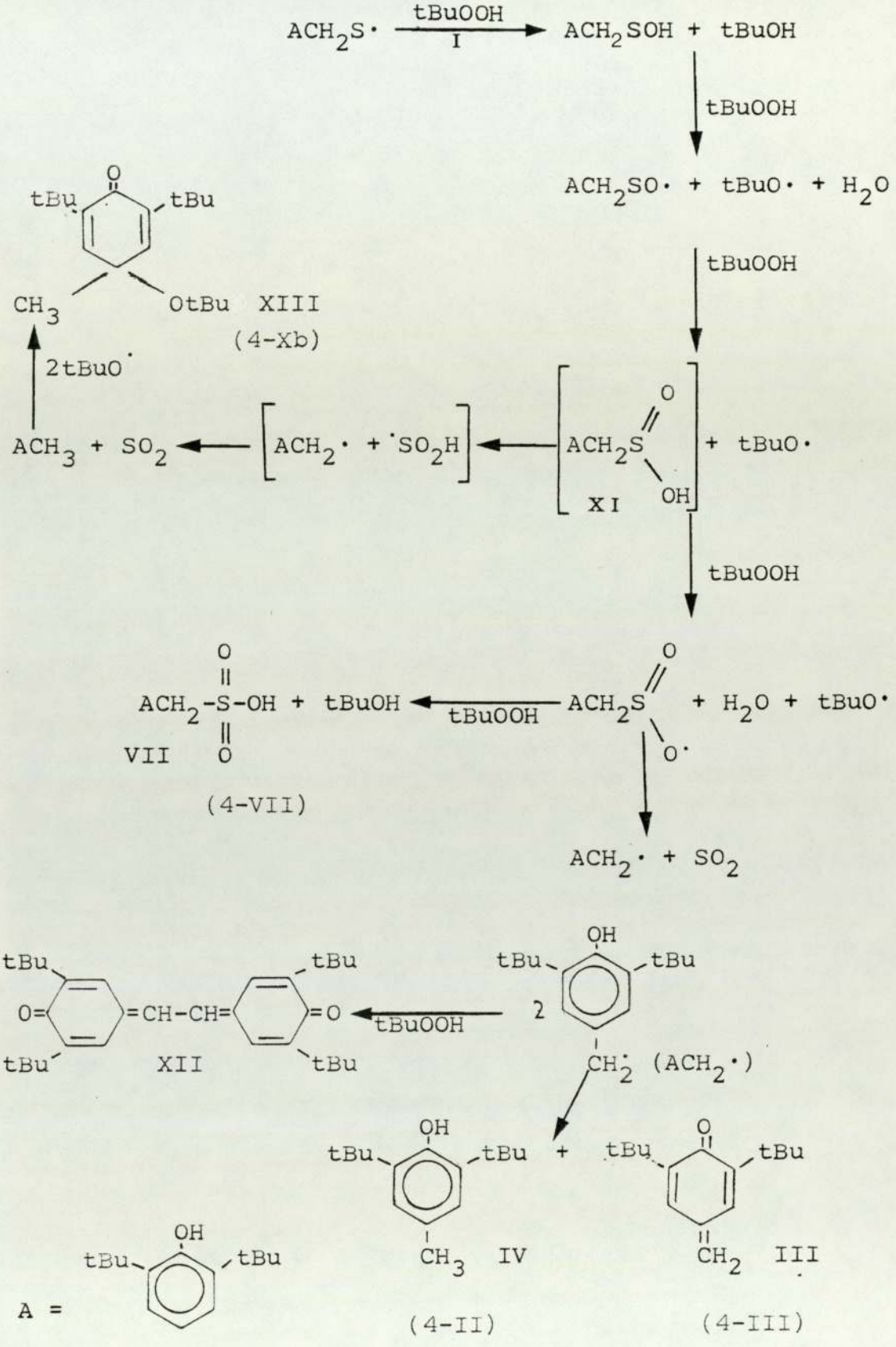
The results from the model compound studies carried out in the GC-MS and the relative rate of formation of the products can be interpreted in the light of the reaction mechanisms reported in the literature[15-20, ,30,32,34,48,135].

The following mechanistic scheme (4.12) is proposed for the reaction of BHBM with TBH in cyclohexene at high BHBM / TBH ratios.

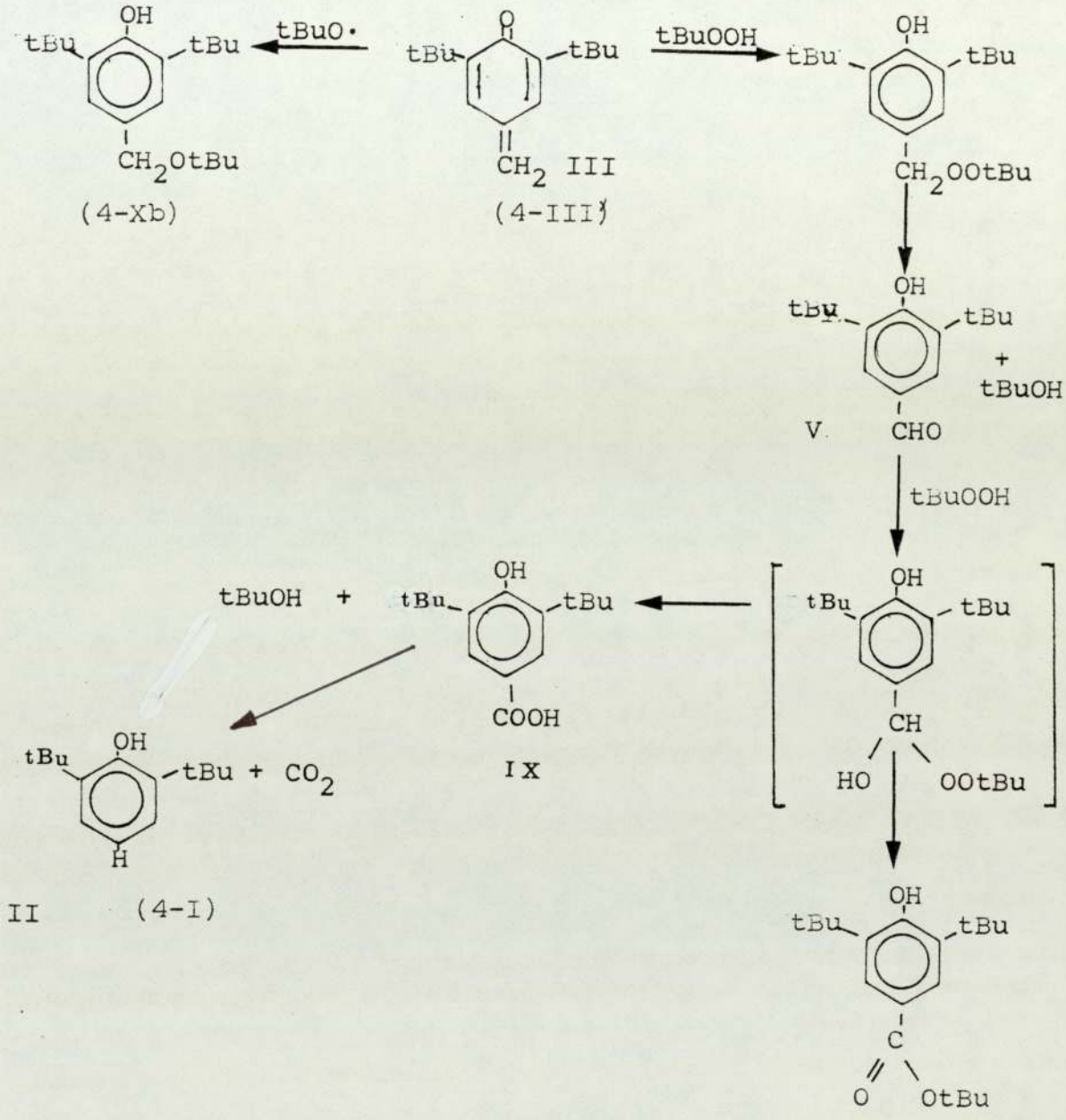
Scheme 4.12



Scheme 4.13 Conversion of BHBM (I) to sulphur acid by a molar excess of TBH



Scheme 4.14



At 70°C and molar ratio 1:½, the formation of adduct was found to be the highest (section 4.9.1.1). This suggests that under these conditions, the probable mechanism is Scheme 4.12, this reaction path is primarily free

radical process.

At 70°C and molar ratio 1:1, however, the production of the adduct is much lower (section 4.9.2.1). This suggests that because of the excess of TBH Scheme 4.13 occurs. Schemes 4.13 and 4.14 involve predominantly ionic processes.

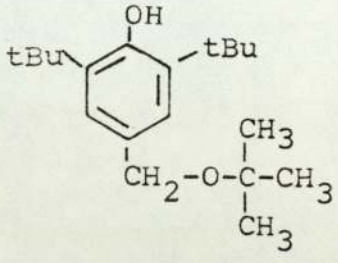
Furthermore, evidence for scheme 4.13 and 4.14 is ionic in nature are exemplified by the study of the hydroperoxide decomposition (section 4.9.1) where the reaction pathways were shown to be mainly ionic.

The free radical mechanism of the reaction at molar ratio 1:½ (section 4.9.1) is supported by the detection of the disulphide of BHBM (section 4.4.1). In the other two cases, the disulphide formation is insignificant.

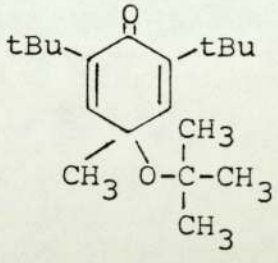
In scheme 4.13 although stilbene and stilbene quinone were not detected, they have been included in the present scheme, since the formation of these compounds have been reported in the literature[18,136].

At 70°C and BHBM to TBH molar ratio 1:2 the concentration of adduct formed is very small and this completely disappeared after twenty hours (see section 4.9.3). The formation of alcohol is predominant here

as the formation of sulphonic acid. The formation of 3,5-di-tert-butyl-4-hydroxyphenyl methyl-tert-butyl ether, was also observed.



and



Furthermore, the concentration of BHBM is drastically decreased to a low value compared to the other molar ratios. These results suggest that due to the high excess of the TBH, scheme 4.12 does not occur significantly and the main pathway must be schemes 4.13 and 4.14.

At 110°C and a molar ratio of 1:1, only traces of adduct formation were observed. Presumably, this fact is due to the decomposition of the adduct at the high reaction temperature.

The reaction of BHBM with TBH in latex must follow the same mechanisms as in the model system because the same reaction products were detected in the GC-MS mass spectra (section 4.10).

During the binding reaction of BHBM into SBR the highest adduct formation (binding yield) was found to

be at a molar ratio of 1:1 (see Section 3.2.2.1). This contrast with the model compound system, where the high adduct formation was at molar ratio [BHBM] / [TBH] 2:1.

The reason for this difference must be the relative insolubility of TBH into the aqueous phase of the latex, thus reducing the overall concentration in the rubber, there making the conditions more like the 1:½ ratio for the model compound.

The decrease in yield of binding (adduct) (see Section 3.5.2.3) at higher molar ratios of TBH to BHBM must be due to Schemes 4.13 and 4.14, competing with Scheme 4.12 therefore, decreasing the degree of adduct formation.

At lower ratios of TBH to BHBM the yield of adduct formation is low because under these conditions, the reaction is predominantly ionic due to the presence of the sulphur acid.

As a consequence the hydroperoxides are destroyed rapidly and since radicals are no longer present there is no other source of free radical.

This is of course why sulphur containing compounds (BHBM) are effective antioxidants, because they destroy hydroperoxides without forming free radicals, particularly

at low [BHBM]/[ROOH] ratios at long reaction times. During the initial stages of the antioxidant action of sulphur containing antioxidants, they are known to function as proxidants because of the low initial ROOH content in the system[32]. This will be discussed further in Chapter Six.

At room temperature, the binding does not proceed significantly (Section 3.6) due to the low rate of radical generation processes at these temperatures.

In the reaction of BHBM with excess TBH (Scheme 4.1[3]) it has been suggested that one of the intermediates is the sulphinic acid. Although this intermediate was proposed and clearly plays a central role in theformation of the other sulphur oxygenated acid, it was not detected by the GC-MS studies. The reason for this is probably due to the lack of stability of this compound.

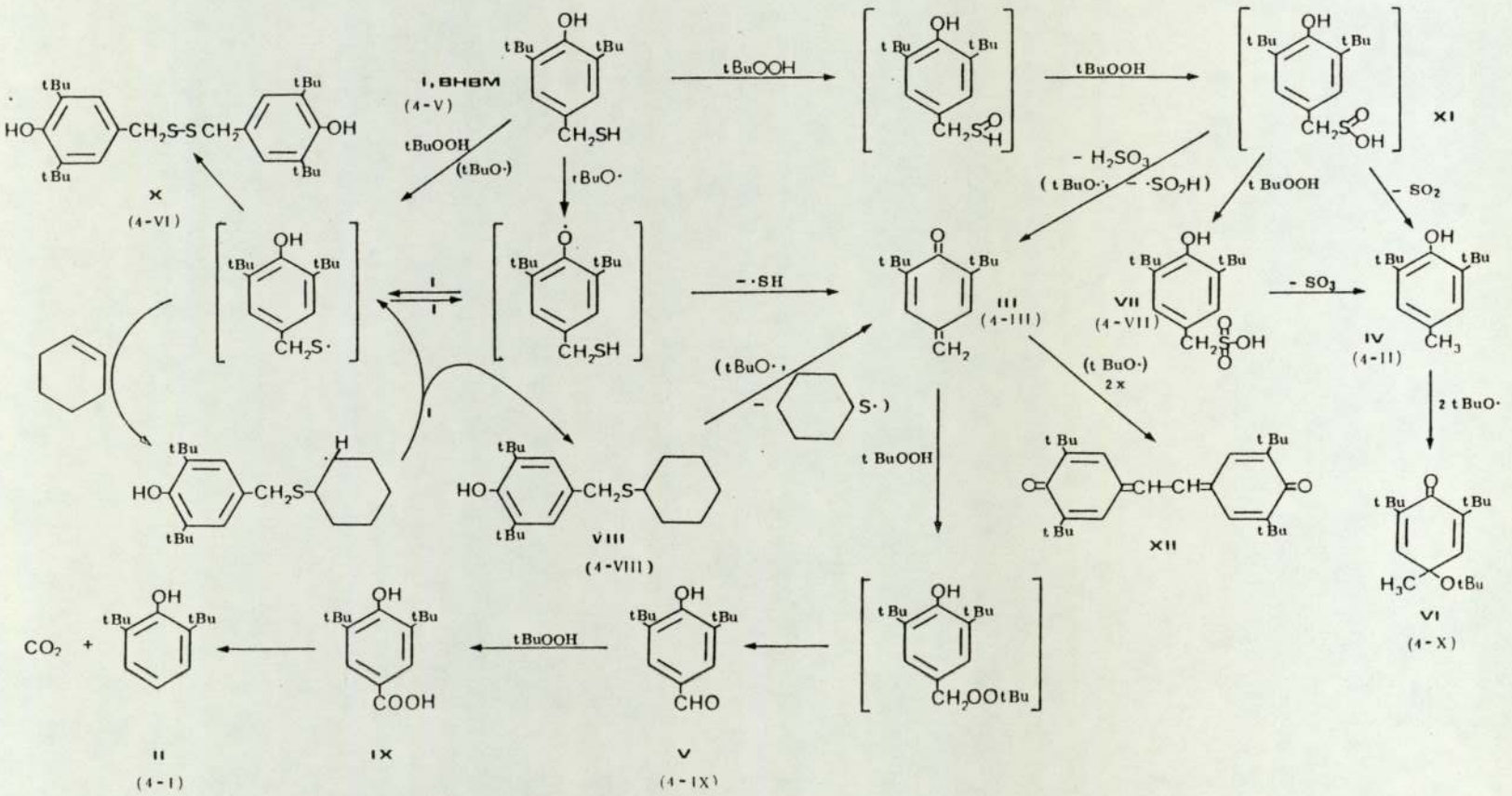
Indeed, when attempts were made to prepare and isolate this compound, it exploded, at room temperature (see Section 4.1.1.6).

Therefore, any sulphenic acid formed during the reaction of TBH with BHBM probably had decomposed before injection into the GC-MS. However, the fact that the BHT, sulphonic acid and quinone were detected indicates

that the reaction must have proceeded through the sulphur acid.

It should be pointed out that the sulphinic acid too (Scheme 4.13) was also not detected. This is probably due to its instability.

Scheme 4.15 Overall mechanism of the reaction of BHBM with TBH in cyclohexene



CHAPTER FIVE

MECHANOCHEMICAL REACTION OF 4-MERCAPTOACETAMIDO DIPHENYLAMINE DURING PROCESSING AND VULCANISATION WITH NATURAL AND SYNTHETIC RUBBERS

5.1 INTRODUCTION

In this study, mechanically induced free radicals were used to produce rubber bound antioxidants during premixing and vulcanisation stage with natural and synthetic rubbers.

Rubber bound antioxidants produced by chemical reaction with latex require adherence to rigid formulation and conditions (see Section 3.2) which makes the whole process longwinded. Therefore it would be of great practical advantage if the binding reaction could be carried out in situ during mixing prior to the compounding and vulcanisation operation of the solid rubber. During the shearing of the solid rubber, mechanically produced free radicals are formed in high concentrations[154].

These free radicals may be used to initiate the binding reaction of the antioxidant to the rubber[108].

In the present work, the degree of adduct formation of MADA with a variety of solid rubbers was studied using the RAPRA torque rheometer[144] and the Buss Ko Kneader. The RAPRA torque rheometer is a small mixing chamber containing two shaped screws which contra rotate to each other. The speed of rotation can be set to either high or low.

During the mixing of the polymer in the chamber, the torque experienced by the screw can be recorded automatically on a separate recorder. The temperature inside the chamber is controlled thermostatically and good temperature control can be achieved. The mixing may be done with the chamber either open or closed to the atmosphere. The latter conditions are achieved by the use of a pneumatic air operated ram.

The chamber has a maximum capacity of 35 g, therefore 27 g of rubber and 3 g of antioxidant was used for the mechanochemical binding reaction. Shearing produced by the RAPRA torque rheometer is limited and only a small quantity of the rubber can be introduced because of the chamber size.

The Buss Ko Kneader[155] is a machine similar to an extruder which produces very high shear and very efficient mixing of the polymer with the additive.

The efficient mixing is much greater than that of a normal extruder.

The mixing efficiency and high shear in the Buss Ko Kneader is due to a combination of the screw and the pins (kneading teeth) inside the mixing barrel of the machine. Because of the presence of the 'kneading teeth' unlike a normal extruder in which the screw rotates in only one direction (Fig 5.1).

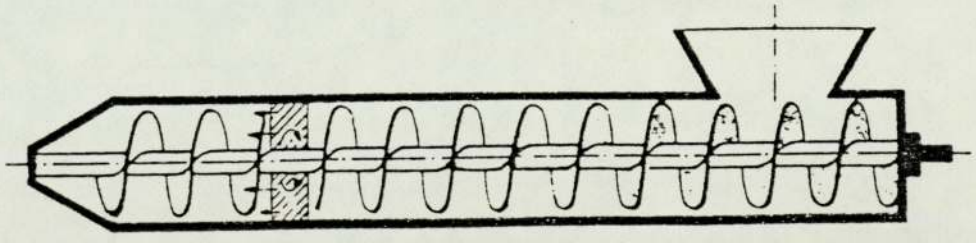


Fig 5.1 Extruder - single or twin screw

The Buss Ko Kneader also has an axially reciprocating motion in addition to the rotary motion (Fig 5.2).

Because of these dual motions of the screw in the Buss Ko Kneader, the shear on the polymer and the efficiency of mixing is very high.

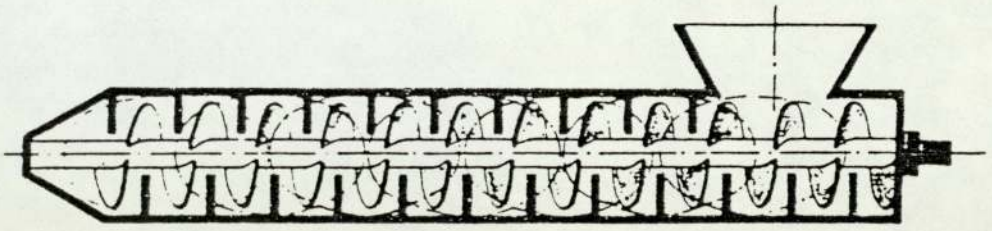


Fig 5.2 Buss Ko Kneader

5.1.1 THE MECHANOCHEMICAL REACTION OF 4-MERCAPTO ACETAMIDO DIPHENYLAMINE (MADA) WITH NR, DPNR AND SYNTHETIC RUBBER

The mechanochemical reaction between MADA with NR, DPNR, SBR and cis-polyisoprene were carried out after sheeting the rubber approximately 1-2 mm thickness on a 12" water cooled laboratory two roll mill. MADA was spread over the sheet which was then folded into an envelope and cut into small pieces. The rubber, plus MADA, was fed into the torque rheometer chamber and processed at 70°C[108]. The level of MADA used was 10, 20 and 30 phr respectively. The processing was done in a closed chamber using 'high' shear for 10 minutes.

Infra-red samples were prepared as described in Sections 2.2.2 and 2.3.1.

The degree of binding before and after vulcanisation was studied by infra red spectroscopy.

The infra-red were recorded for rubber vulcanisates which had been extracted prior to the compounding operation and for the samples which had no prior extraction before compounding but were extracted after vulcanisation.

Typical conditions for binding of MADA with SMR-5L in the RAPRA torque rheometer are shown in Table 5.1

Table 5.1 Typical reaction conditions for MADA with SMR-5L in the RAPRA torque rheometer

Speed & Conditions	Quantity & Reaction Conditions
SMR-5L	27 g
MADA	3 g
Temperature	70^{o}C
Speed of the rotor	68 rpm
Time	10 minutes
Chamber	Closed

5.1.2 THE MECHANOCHEMICAL REACTION OF MADA WITH NR IN THE RAPRA TORQUE RHEOMETER

Mechanochemical reaction of MADA in NR gave the percentage of binding shown in Table 5.2.

Table 5.2 Percent bound MADA in NR processed in the RAPRA torque rheometer

NR / SMR-5L	Original Conc MADA g/100 g	MADA bound %	
		c	d
Unextracted[a]	10	11	15
Extracted[b]	10	31	75

Notation in Table 5.2 is as follows:

a = SMR-5L unextracted before mechanochemical reaction with MADA

b = SMR-5L extracted with hot acetone for 48 hours (see Section 2.1.9.1)

c = Extracted after mechanochemical reaction and before compounding, then vulcanised

d = Unextracted after mechanochemical reaction and before compounding then vulcanised and extracted

5.1.3 MECHANOCHEMICAL REACTION OF MADA WITH DPNR IN THE RAPRA TORQUE RHEOMETER

The experiments were carried out as described in Table 5.1, except that the rubber used was DPNR. The results are shown in Table 5.3.

Table 5.3 Percent bound MADA in DPNR processed in RAPRA torque rheometer

Natural Rubber DPNR	Original Conc MADA g/100 g	MADA Bound % c	d
Unextracted[a]	10	11	33.5
Extracted[b]	10	35	58

Notation as in Table 5.2

5.1.4 THE MECHANOCHEMICAL REACTION OF MADA WITH SBR IN THE RAPRA TORQUE RHEOMETER

All conditions in this experiment were kept constant as described in Table 5.1, except that SBR was used in place of NR. The percentage of bound MADA during processing and vulcanising is shown in Table 5.4.

Table 5.4 Percent bound MADA in SBR processed in RAPRA torque rheometer

SBR	Original Conc MADA g/100 g	MADA bound % c	d
Unextracted[a]	10	10	32
Extracted[b]	10	35	79

Notation as in Table 5.2

5.1.5 THE MECHANOCHEMICAL REACTION OF MADA WITH CIS POLYISOPRENE IN THE RAPRA TORQUE RHEOMETER

Extracted cis-polyisoprene was used in this experiment. The conditions used as described in Table 5.1. The percentage of MADA bound to cis-polyisoprene is shown in Table 5.5.

Table 5.5 Percent bound MADA in cis-polyisoprene in RAPRA torque rheometer

cis-polyisoprene	Original Conc MADA g/100 g	MADA bound % d
Unextracted[a]	10	50
Extracted[b]	10	78

Notation as in Table 5.2

5.2 THE MECHANOCHEMICAL REACTION OF MADA WITH NR AND SYNTHETIC RUBBERS IN THE BUSS KO KNEADER

500 g of rubber was used for this purpose. The rubber was treated with the MADA before loading into the Buss Ko Kneader in the manner described in Section 5.5.1. The rubber and the MADA were loaded into the Buss Ko Kneader and two passes were made at a temperature of 70°C. The MADA was used at a level of 10%, 20% and 30% respectively. The screw speed was set at speed 3 which gives 39 rpm.

Typical processing conditions for mechanochemical reaction of MADA with NR processed in the Buss Ko Kneader are shown in Table 5.6.

Table 5.6 Typical processing conditions for mechanochemical reaction for NR with MADA in the Buss Ko Kneader

Additives & Conditions	Quantity & Reaction Conditions
SMR-5L	450 g
MADA	50 g
Temperature	70°C
Rotor speed	39 rpm
Passes	2

5.2.1 THE MECHANOCHEMICAL REACTION OF MADA WITH NR IN THE BUSS KO KNEADER

The process was carried out as described in Table 5.6, except that the concentrations of MADA used were 10, 20 and 30% respectively. The result of the binding reaction of MADA into NR is shown in Table 5.7.

Table 5.7 Percent bound MADA in SMR-5L processed in Buss Ko Kneader

NR / SMR-5L	Original Conc MADA g/100 g	MADA bound % d
Unextraced[a]	10	15
Extracted[b]	10	87.5
Extracted[b]	20	71
Extracted[b]	30	61

Notation as in Table 5.2

5.2.2 THE MECHANOCHEMICAL REACTION OF MADA WITH DEPROTEINISED NATURAL RUBBER IN THE BUSS KO KNEADER

Deproteinised natural rubber (supplied by MRPRA, having a maximum concentration of protein of 0.02%), was processed as described in Table 5.6. The results are shown in Table 5.8.

Table 5.8 Percent bound MADA into DPNR processed in Buss Ko Kneader

NR / DPNR	Original Conc MADA g/100 g	MADA Bound % d
Unextracted[a]	10	23.5
Extracted[b]	10	58
Unextracted[a]	20	23
Extracted[b]	20	50
Unextracted[a]	30	12
Extracted[b]	30	45

Notation as in Table 5.2

5.2.3 MECHANOCHEMICAL REACTION OF MADA WITH CIS POLYISOPRENE IN BUSS KO KNEADER

In order to circumvent the presence of undesirable non-rubber constituents of NR the binding of MADA into polyisoprene was studied. The method used was described in Table 5.5 and the results are shown in Table 5.9.

Table 5.9 Percentage of bound MADA in cispolyisoprene in the Buss Ko Kneader

Cispolyisoprene	Original Conc MADA g/100 g	MADA bound % d
Extracted[b]	10	80
Extracted[b]	20	67
Extracted[b]	30	42

Notation as in Table 5.2

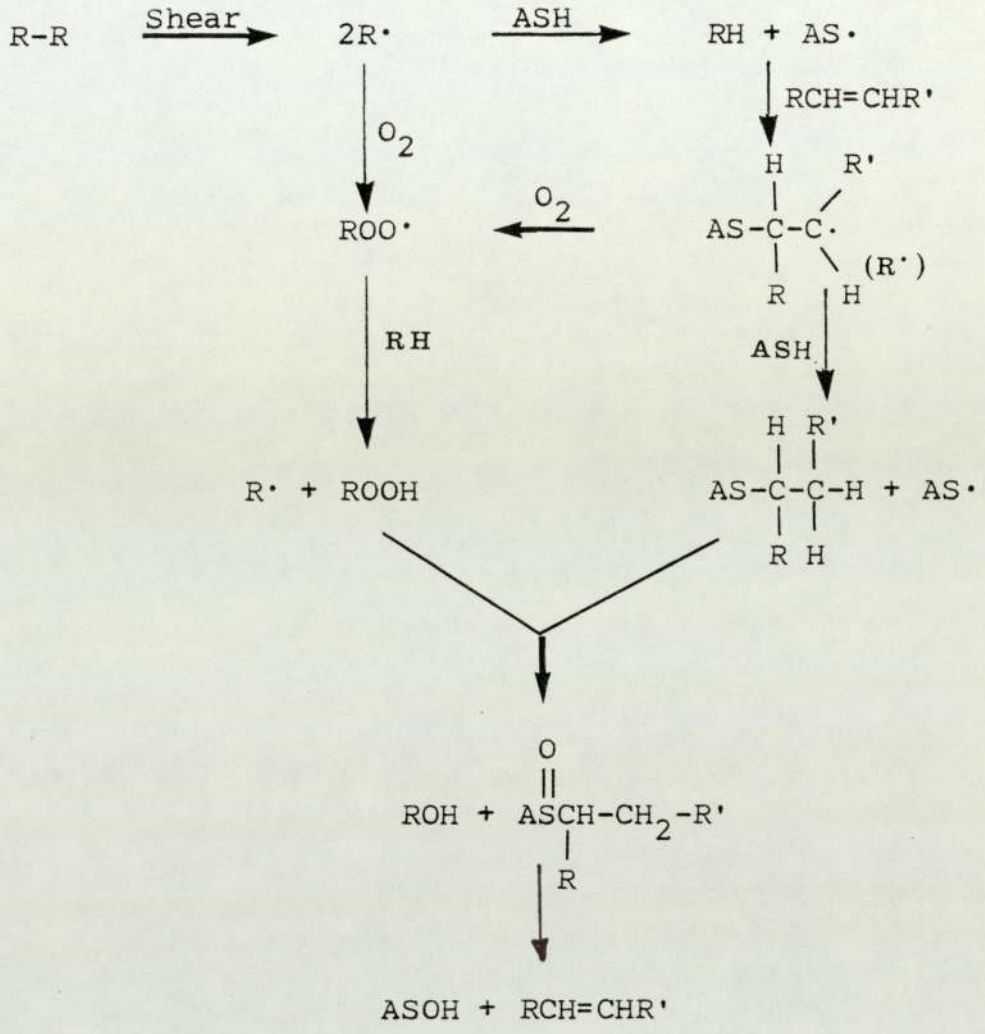
5.3 DISCUSSION

During the processing of rubbers in the RAPRA torque rheometer (closed chamber) or the Buss Ko Kneader, the high shear gives rise to mechanically formed macroradical (alkenyl) radicals. Because the rate of initiation is high and the oxygen availability is low (limited to that 'dissolved' in the rubber) the ratio of alkyl to alkyl peroxyl radicals is high. The main termination reaction in the adduct chain reaction shown in Scheme 5.1[(108)] will be governed by the fate of the alkyl radicals. Under these conditions, part of the binding of the MADA could occur by the following reactions:

$$R\text{-}R \xrightarrow{\text{Shear}} R\cdot \xrightarrow{ASH} RH + AS\cdot$$

$$AS\cdot + R\cdot \longrightarrow AS\text{-}R$$

Scheme 5.1



Traces of hydroperoxides in the system may also initiate the production of thiyl radicals from the thiol (MADA)[1].

$$ASH \xrightarrow{ROOH} AS\cdot + RO\cdot + H_2O$$

These thiyl radicals will then feed into Scheme 5.1. The results shown in Table 5.2 to Table 5.4 and

Tables 5.6 to 5.9 show clearly that high binding of MADA into NR, SBR and cispolyisoprene can be achieved by mechanochemical reaction on the extracted rubbers. In all cases, the unextracted rubbers gave a significantly lower yield of binding. This effect may be rationalised in terms of the presence of non rubber constituents and the presence of monomers in the case of styrene and cispolyisoprene which act as 'poison' for the binding reaction[109].

Prior extraction of the rubber with acetone removed all the inhibitors, hence the overall binding is substantially higher. The Buss Ko Kneader gives higher binding than the RAPRA torque rheometer because the more efficient shear and the mixing in the case of the former. DPNR on the other hand gave a lower yield of binding than SMR-5L after extraction probably because the latter is superior grade rubber made from fresh latex.

Furthermore, traces of ammonium alginate (the creaming agent) left after the deproteinisation of the rubber could 'poison' the binding of the thiol into the DPNR.

Extraction after vulcanisation showed an increase in the percentage of bound antioxidant. This must be due

to some MADA becoming bound to the rubber during the compounding and vulcanisation stages. Previous work[96,97,166] also shown that antioxidant can be bound during compounding and vulcanisation stages.

CHAPTER SIX

EVALUATION OF THE AGEING AND CURING PROPERTIES OF BHBM BOUND TO STYRENE BUTADIENE RUBBER LATEX

6.1 OXYGEN ABSORPTION STUDIES OF BHBM BOUND TO SBR LATEX

6.1.1 INTRODUCTION

Attack by oxygen on the rubber molecules is one of the main factors responsible for the ageing or degradation of rubber compounds. For these reasons the oxygen absorption test method is used as a convenient method to evaluate the ageing characteristics of rubber compounds.

The technique of oxygen absorption has been used for a long time[157,158] since it provides a quick and reproducible test for antioxidant activity.

One of the most important factors affecting the activity of the antioxidants appears to be their compatibility with the polymer[1,157].

It has also been shown[157] that there is a relationship between the physical properties (eg tensile strength) of antioxidants, particularly in the rubber, and their

relative effectiveness in an oxygen absorption test. In general, oxygen absorption will give information about the intrinsic antioxidant activity[158].

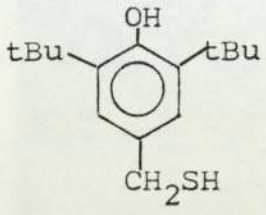
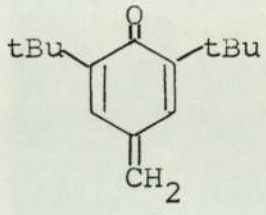
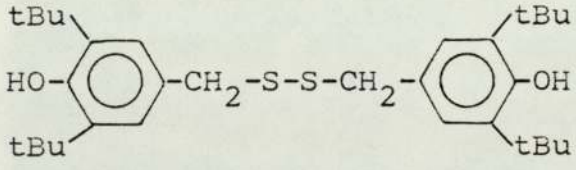
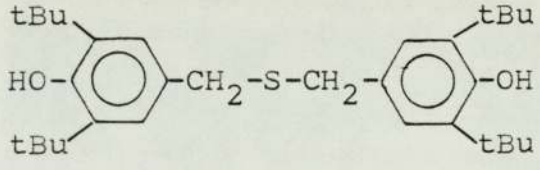
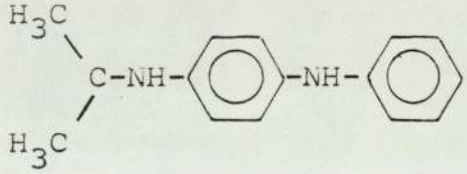
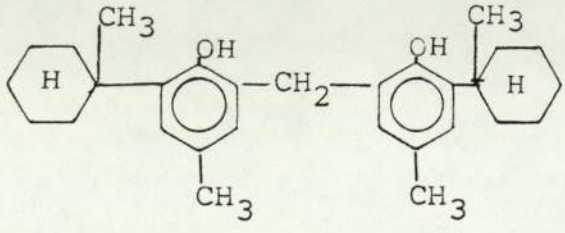
The chemical reaction between rubber and oxygen increases with temperature much more rapidly than does the physical process of diffusion of oxygen through rubber[157] since diffusion of oxygen into the sample is a limiting factor, it is necessary to use sample of rubber which are sufficiently thin, so that diffusion control will not be a problem and to avoid erroneous results. Typical samples of thickness that can be used for reliable results are between 0.006 and 0.008 inches.

6.1.2 RESULTS

In the present work the rubber vulcanisates were protected by antioxidants (prepared in Chapter Five) and were used by extracting the unbound antioxidant from the grafted uncured SBR dried sheet by acetone. The test was carried out on the following samples:

(a) Bound unextracted (unextracted, then vulcanised)
(b) Bound extracted (extracted before compounding and then vulcanised)
(c) Antioxidant as normal additive without binding
(d) Compound in (c) extracted (extraction was done by

Table 6.1 Antioxidant incorporated during compounding stage.

Structure	Code
	BHBM
	QM
	Di-S
	Mono-S
	IPPD
	WSP

azeotropic mixture as described in Section 2.1.9.2)

The antioxidant which was incorporated during compounding were coded as shown in Table 6.1.

Fig 6.1 shows the oxygen absorption curve for the 1% bound BHBM in SBR made up for the 10% masterbatch together with Di-S and Mono-S at the same concentration. Fig 6.2 shows the value for the extracted samples. WSP incorporated as an additive during the compound stage was also tested to compare the activity of bound BHBM with a commercial antioxidant.

It is clear from Fig 6.1 that after the initial induction period, the oxygen uptake is initially slow which is autoretardation and then autoaccelerated stage.

For the extracted samples, however, all showed rapid autoacceleration after the initial induction period, except bound BHBM.

Induction periods and time of 1% oxygen absorption are summarised in Table 6.2.

In Table 6.2 the time to 1, 2 and 3% oxygen absorption is shown. The Table reflects the very good antioxidant activity of the bound BHBM (extracted) because even at

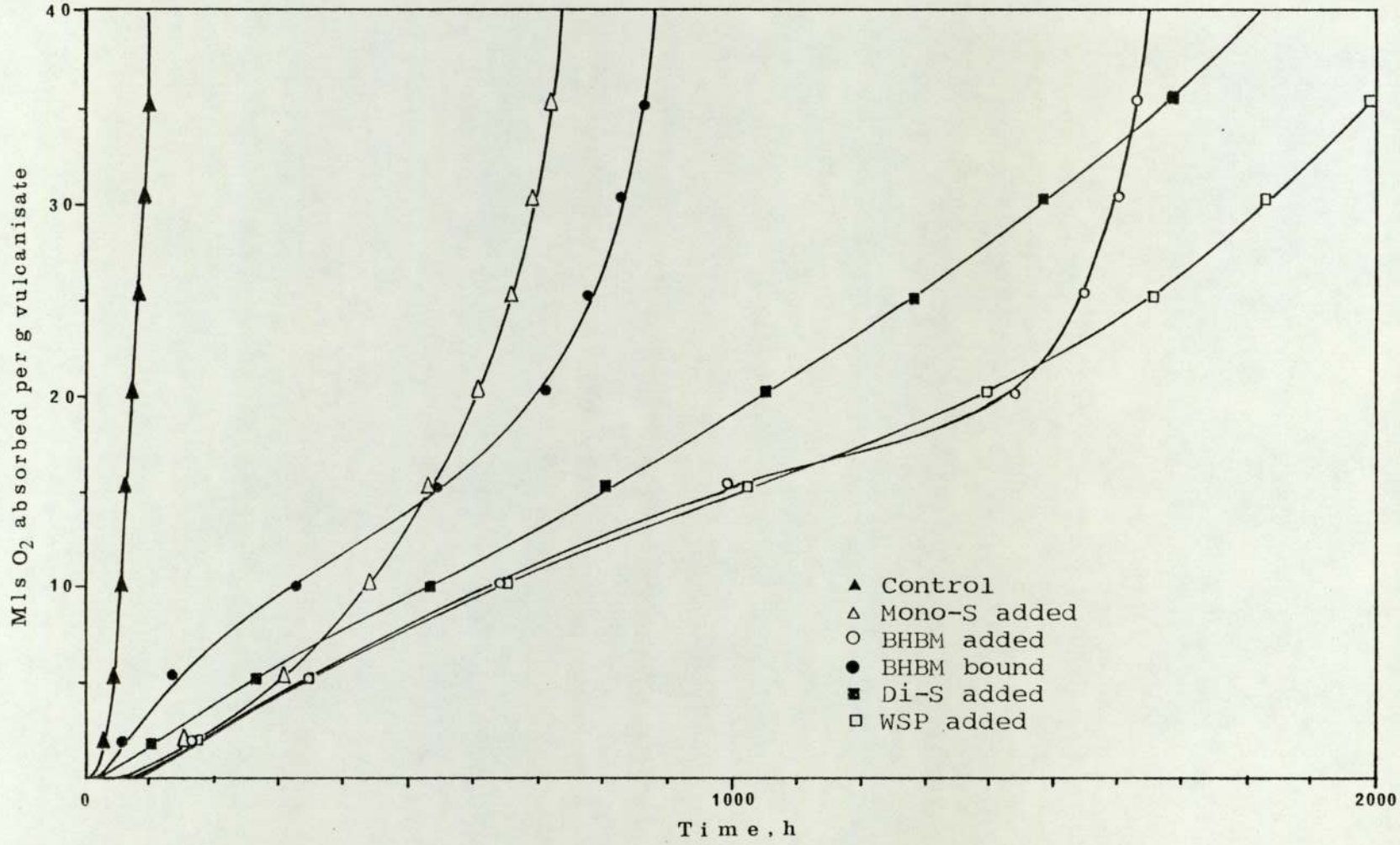


Fig 6.1 Oxygen absorption of unextracted SBR vulcanisates containing 1% BHBM and its derivatives at 70oC

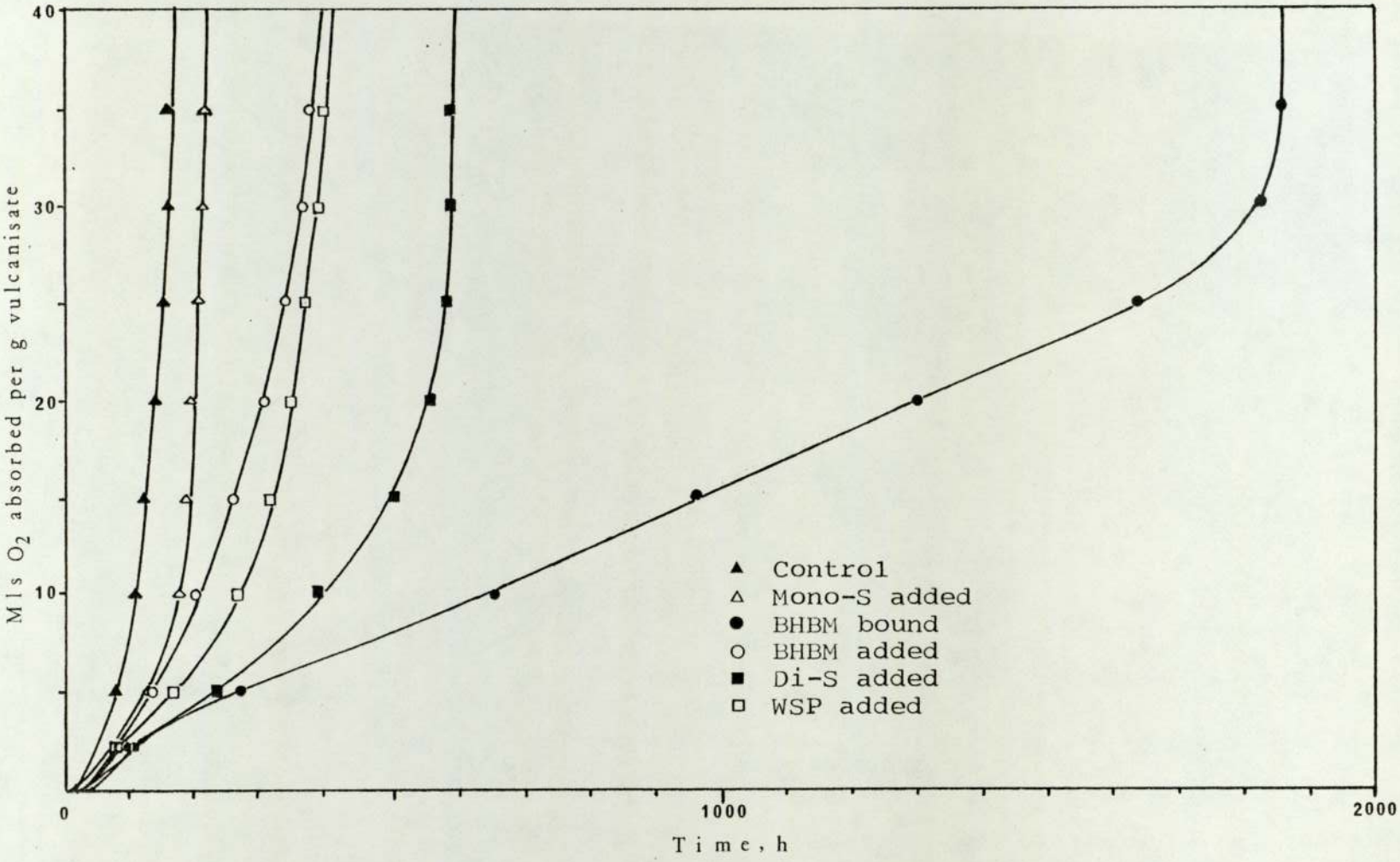


Fig 6.2 Oxygen absorption of SBR vulcanisates containing 1% BHBM and its derivatives at 70°C

Table 6.2 Antioxidant activity of vulcanisates containing bound BHBM, its derivatives and WSP (all at 1% level)

Stock	Bound %	Ind'n Period h		Time to absorb 1% O_2 h		Time to absorb 2% O_2 h		Time to absorb 3% O_2 h	
		Unext	Ext	Unext	Ext	Unext	Ext	Unext	Ext
BHBM	87.5	28	18	186	431	437	1004	748	1277
Di-S	added	45	25	456	274	813	455	1046	563
Mono-S	added	57	15	362	151.5	493	184	670	196
BHBM	added	60	28.5	469	157	916	165	1472	261
WSP	added	66	18	385	175	924	278	1430	331
Control	-	13.5	18	44	75	55	94	72	115

3% O_2 absorption the cure is still autoretarding, whilst all the others showed autoaccelerating behaviour well before the 1% O_2 absorption level.

The Table also shows that in all cases the initial induction period after extraction is considerably less than without extraction. After extraction the time to 1% oxygen uptake is reduced. The 1% bound, however, showed an increase in the time to O_2 uptake relative to the unextracted sample.

6.1.3 DISCUSSION

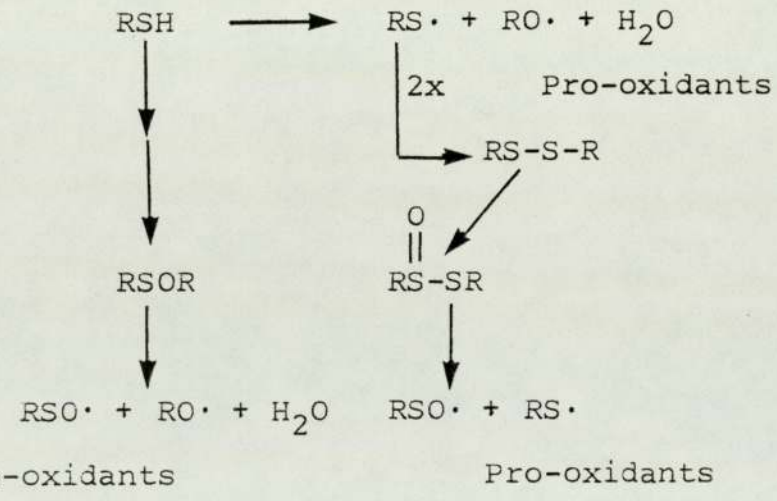
It can be concluded that all antioxidants added during the compounding stage are not efficient after extraction compared to bound material. Furthermore the bound extracted was shown to have a superior antioxidant activity relative to bound unextracted.

The behaviour of all antioxidants incorporated during the compounding stages except Di-S are similar to the control after extraction. The slight differences may be due to the traces of antioxidant left in the rubber possibly bound to the rubber during compounding and vulcanisation stages[160,161], viz:

$$RSSR \longrightarrow RS\cdot \xrightarrow{P\cdot} RSP \qquad (P = \text{polymer})$$

In all cases the unextracted samples behaved similarly having an initial rapid uptake of oxygen followed by autoretardation and then autoacceleration. This behaviour confirms to the known behaviour of sulphur containing compounds[1,18].

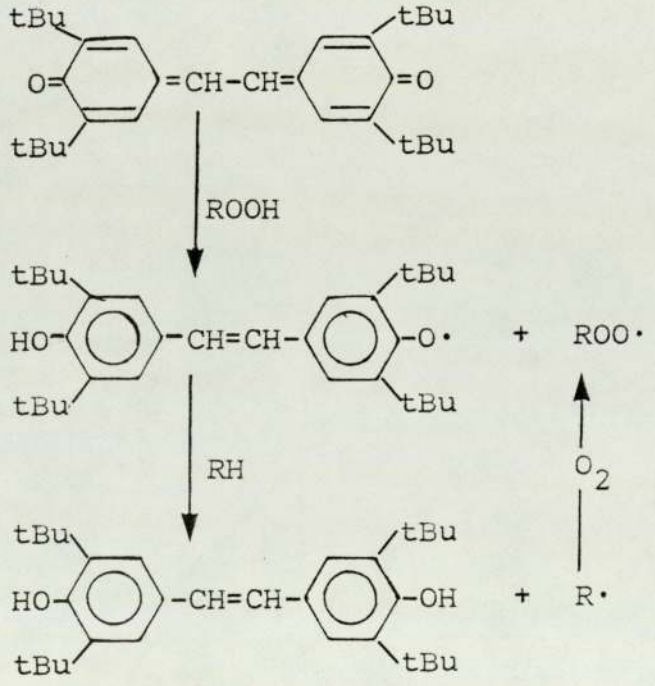
The initial (rapid O_2 uptake) pro-oxidant stage is associated with the interaction of the thiols and its derivatives (and sulphides and derived sulphenic acid) with the limited hydroperoxides formed during the early stages of the oxidative ageing[18].



The autoacceleration stage is due to the catalytic decomposition of hydroperoxides by the SO_3 and SO_2 found from the thiol oxygenated species[18]. The final autoacceleration stage occurs when all the stabiliser is consumed.

The reason for the better activity of 1% BHBM bound after extraction relative to before extraction must be due to some reaction products of the binding reaction which can act as pro-oxidants. The mechanistic studies in Chapter Four have shown that quinonoid species could be formed during the binding reaction in small concentration. This was particularly pronounced for the reaction at 140°C.

Quinonoid species are known to be pro-oxidant due to the oxidation of polymer[1,18]. They act as pro-oxidants by taking part in hydrogen abstraction reaction as shown in Scheme 6.1.



Scheme 6.1

Although during the binding stage, the concentration of quinonoid species formed was small (Section 4.8.1 and Scheme 4.12) during the subsequent vulcanisation at 140°C it is possible that more quinones could be formed from the side products of the binding reaction.

The difference between BHBM bound and BHBM added (Fig 6.1) highlights this effect, since the latter cannot form as much quinone during processing. In the former case, the rubber already contains species (side products of the binding reaction) which could generate the formation of quinonoid species under the vulcanising conditions (temperature, 140°C, vulcanisation time, 45 minutes). Extraction removes the quinonoid species and other side products.

Alternatively, the unreacted hydroperoxide left in the rubber during the binding reaction were trapped in side the rubber on the subsequent coagulation stages. These hydroperoxides could interact with the sulphur oxidised moieties giving pro-oxidant species, especially during the early stages of oxygen absorption. Extraction of the rubber prior to testing removes these sulphur oxidised species and the unreacted hydroperoxide. Therefore subsequent ageing will not give rise to as many pro-oxidant species as before extraction, than give better ageing characteristic to the rubber.

6.2 STRESS RELAXATION STUDIES OF VULCANISATES

Stress relaxation developed by Tobolksy and coworkers[161] gives very useful information about network degradation of rubber. Recently this technique has been widely used to assess antioxidant activities of various stabilisers, providing the same vulcanisation formulation is used in all cases.

They are two types of stress relaxation, continuous and intermittent. Intermittent stress relaxation is normally used to indicate whether cross-linking occurs during ageing.

In the present study, continuous stress relaxation was used since only the stabilising effect of the antioxidants in the rubber was being assessed.

6.2.1 RESULTS

The continuous stress relaxation curves of grafted extracted and grafted unextracted vulcanisates containing 1% BHBM are shown in Fig 6.3. This Figure also shows the stress relaxation curves for the vulcanisate containing BHBM derivatives. Table 6.3 shows the f50 values for the vulcanisates before and after extraction.

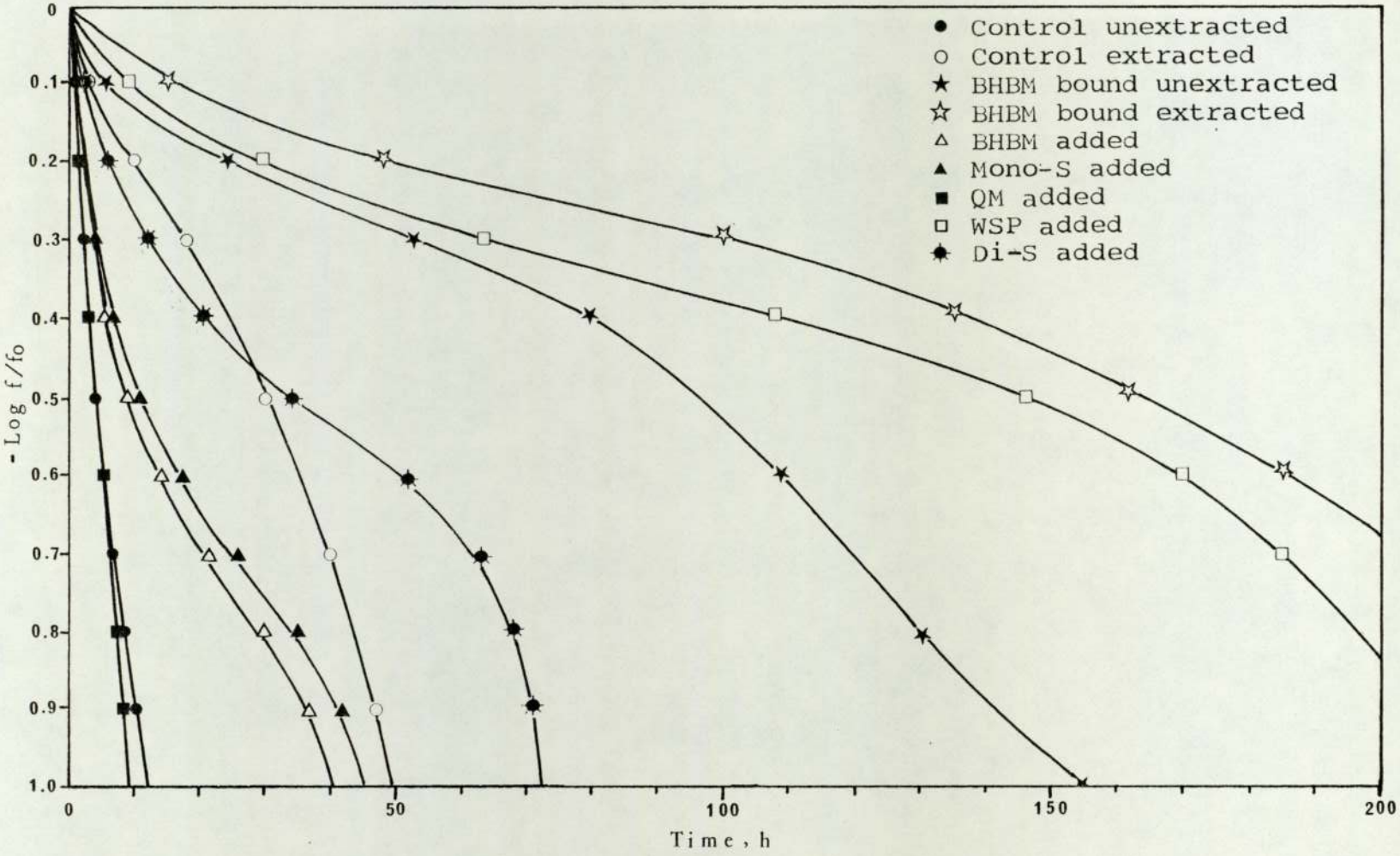


Fig 6.3 Continuous stress relaxation of SBR vulcanisates containing 1% BHBM and its derivatives at 100°C

Table 6.3 f50 of SBR vulcanisates containing 1% antioxidants

Samples	Bound %	f50 h, unext	f50 h, ext
Control	-	2	8
BHBM	75	57	116
Di-S	added	13	2*
BHBM	added	3	1*
QM	added	2	**
Mono-S	added	8	**
WSP	added	62	1,5

* Samples broken after the time indicated

** Samples broken

Fig 6.3 and Table 6.3 show that most of the vulcanisates other than QM show resistance towards oxidative stress relaxation, relative to the control. BHBM grafted has better antioxidant activity when compared with BHBM (additive).

As in the case of oxygen absorption, grafted extracted rubber shows superior antioxidant activity to grafted unextracted.

The conventional (WSP) has good activity before extraction but after extraction this is essentially lost.

6.2.2 DISCUSSION

These results agree well with the results of oxygen absorption studies. The enhanced antioxidant activity of the BHBM grafted extracted over the BHBM grafted unextracted may be rationalised in the same terms as that discussed for the oxygen absorption results (see Section 6.1.3).

The loss of activity for the conventional antioxidant WSP after extraction highlights the problem of leaching of additives when they are bound into the rubber.

However, the difference between extracted and unextracted is much less, suggesting that the pro-oxidant impurity is volatile.

6.3 FATIGUE RESISTANCE OF VULCANISATES

The Monsanto Fatigue to Failure tester provided a useful means of assessing the degree to which a vulcanisate can resist the repeated mechanical stresses during service, and the ability of an antifatigue agent to protect a rubber vulcanisate against degradation.

In the present studies, the antifatigue activity of BHBM grafted into SBR (1 g/100 g rubber) was evaluated. This

activity was compared to a commercially used antifatigue agent (IPPD) and to BHBM added as a normal additive during the compounding stage. To study the contributory roles of the by products of the binding reaction on the fatigue life of rubber of the SBR various derivatives of BHBM were also assessed.

6.3.1 RESULTS

Table 6.4 shows the fatigue lives of the grafted extracted and grafted unextracted vulcanisates having 1 g of BHBM bound into 100 g SBR from 10% masterbatches.

The fatigue life of the commercial antifatigue agent (IPPD), BHBM and its derivatives added as normal additive during compounding stage are shown in Table 6.4.

This improvement was not seen for added BHBM. The conventional antifatigue agent, IPPD, has also good activity, however, it was lower than the grafted BHBM and also lower than that vulcanisate containing added BHBM at the same molar concentration.

Upon extraction of the grafted BHBM, some activity was retained, although the activity is about one fifth of that before extraction. On extraction of the other vulcanisates before testing, in all cases the activity

Table 6.4 Improvement of fatigue lives of bound BHBM to SBR (from 10% masterbatches), BHBM derivatives and WSP (all at concentration 1%) at 100% extension

Stock	Bound %	Fatigue life h		Improvement over control %	
		Unext	Ext	Unext	Ext
Control	-	0.78	0.16	-	-
BHBM	75	90.65	38	11522	2275
BHBM	added	3.1	0.4	297	150
Mono-S	added	2	0.3	162	56
Di-S	added	4.8	0.4	515	138
IPPD	added	3.8	0.4	387	150
QM	added	4.2	0.2	439	38

was lost.

Table 6.5 shows the improvement of fatigue life of grafted extracted BHBM and grafted unextracted BHBM but at a lower percentage of binding (40%).

This Table shows that when the percentage of bound BHBM is low the fatigue life is very much inferior to the 75% BHBM binding.

The fatigue life improvement of BHBM bound to the SBR and NR blend (ratio 2:3) are shown in Table 6.6.

In order to check whether phase separation existed in the vulcanisates of the rubber blend, viscoelastic studies were done using the Rheovibron (model no DDV-IIB). The results (not shown) suggested that indeed phase separation did exist within the vulcanisate. Dudley and co-worker [16.2] have similar phase separation to SBR/NR blends.

6.3.2 DISCUSSION

Fatigue processes in vulcanised rubber are known to involve the activation of the polymer to oxygen as a result of the mechanochemically formed alkyl radicals (see Section 1.5). Under these conditions and because of the limited availability of oxygen (diffusing in and that soluble in

Table 6.5 Improvement of fatigue life of BHBM bound in SBR (from 10% masterbatch) at 100% extension

Stock	Bound %	Fatigue life h		Improvement over control %	
		Unextracted	Extracted	Unextracted	Extracted
Control	-	0.78	0.16	-	-
BHBM	40	3.2	0.43	403	169

Table 6.6 Improvement of fatigue life of bound BHBM to the blend of SBR:NR (2:3) from 10% masterbatch, concentration 1% at 100% extension

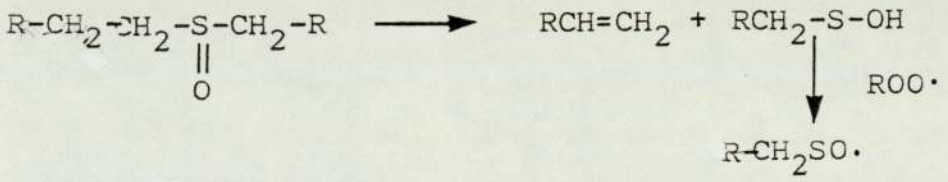
Stock	Bound %	Fatigue life h		Improvement over control %	
		Unextracted	Extracted	Unextracted	Extracted
Control	-	10	6	-	-
BHBM	30	15	8	50	33.3

Table 6.7 Improvement of fatigue of BHBM bound to SBR (10% masterbatch diluted with NR latex in ratio 2:3) at 100% extension

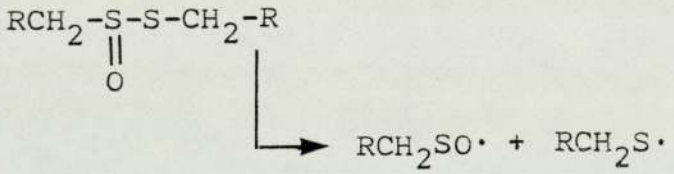
Stock	Bound %	Fatigue life h		Improvement over control %	
		Unextracted	Extracted	Unextracted	Extracted
Control	-	10	6	-	-
BHBM (bound in SBR)	87.5	12	6	20	-

the rubber) the ratio of alkyl radicals to alkylperoxy radicals is higher than it is in normal conditions.

Recently, it has been shown[163] that sulphur containing compounds have some limited antioxidant activity. The mechanism has been explained in terms of the formation either by elimination of the sulphoxide (Scheme 6.1) in the availability of O_2 or by the mechano-activated degradation of the thiosulphinate (Scheme 6.2).

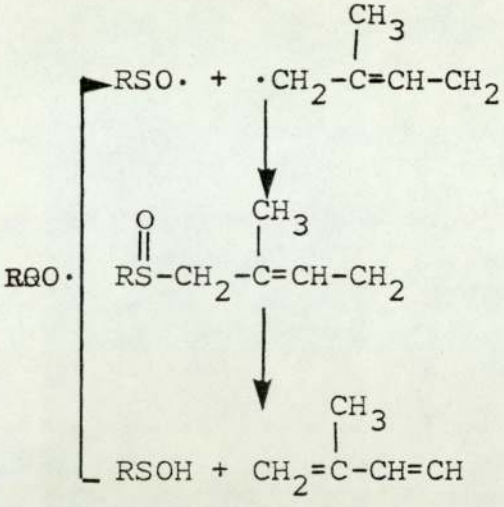


Scheme 6.2



The sulphenyl radical may be regenerated by the mechanism outlined in Scheme 6.3.

The limited activity of oxygenated sulphur derivatives of BHBM as additives may be accounted for by this scheme of reactions.

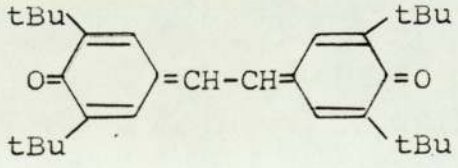


Scheme 6.3

The enhanced activity of the bound BHBM must be due to the contribution of some side products formed during the binding and the vulcanisation stages (Section 6.1.3).

These compounds by themselves show a little activity but still in relation to the control they do possess some activity. The enhanced antifatigue activity of the bound BHBM must be due to the formation of hydroquinone, which is known to be a good antifatigue agent[165].

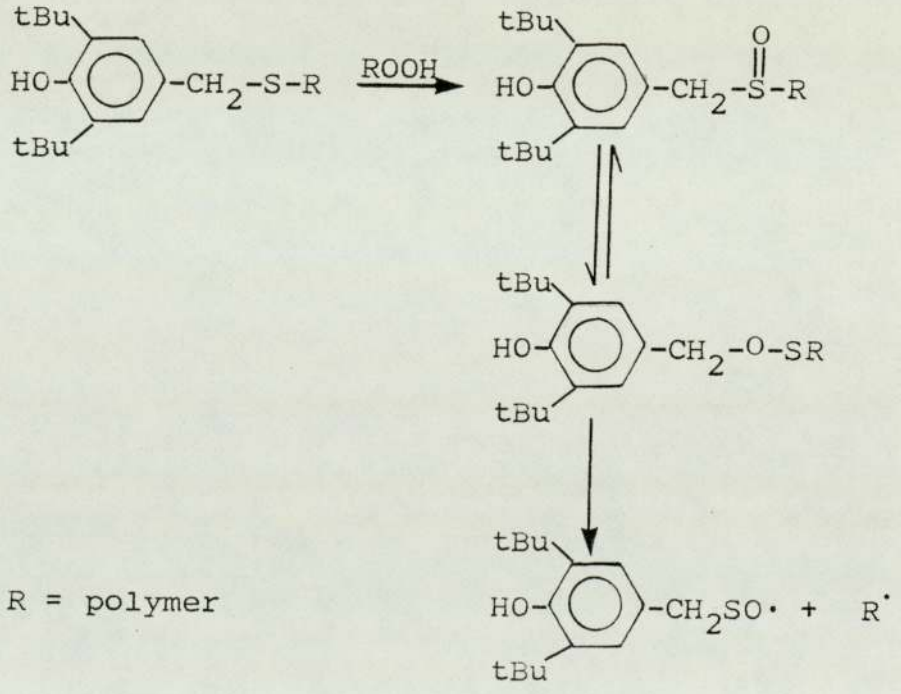
In the model compound studies (Scheme 4.13) it is shown that



could be present in the reaction, this compound has high fatigue resistance[165].

This effect and a synergistic effect of all these additives operated together simultaneously.

The bound BHBM too is capable of releasing a sulphenyl radical by the following reaction:[166]



Scheme 6.4

The sulphenyl radical formed in this way is capable of regeneration by Scheme 6.3.

Extraction leaves only the bound BHBM and traces of the other side products (which are acetone soluble). These

traces could still synergise with the sulphenyl radical. This must be why the activity is still high after extraction but considerably lower than before extraction.

6.4 OZONE RESISTANCE OF VULCANISATES

It is important in rubber technology to predict service performance of manufactured articles from laboratory data. Ozone attack is one of the causes of rubber degradation. The deteriorant is effect of ozone on rubber can be conveniently studied in the laboratory using an ozone chamber (Section 2.5.4).

All antiozonants which are physically mixed with the rubber will diffuse to the surface of the rubber where they scavenge ozone due to their greater reactivity towards ozone than that of the rubber double bond[167].

Scott and co-workers[174] showed that MADA is more reactive as antiozonant when pretreated with rubber than if added conventionally during compounding stage.

6.4.1 RESULTS

In this study, the bound extracted and bound unextracted of BHBM was evaluated for ozone resistance using Hampden Shawbury ozone test cabinet and samples

were extended at 20%. The test results are shown in Table 6.8.

Table 6.8 Ozone resistance of bound BHBM and its derivatives, concentration 1% in SBR and blend of SBR/NR (3:2)

Stock	Blend %	Complete failure h	
		Unextracted	Extracted
SBR			
Control	-	15	16
BHBM	75	15	9
IPPD (1%)	added	28	12
SBR/NR Blend (3:2)			
Control	-	52	24
BHBM	30	57	23

6.4.2 DISCUSSION

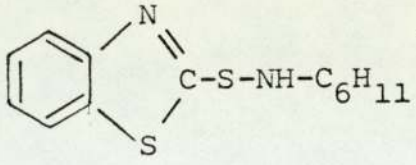
S-containing compounds are known not normally to possess antiozonant activity. On the other hand, IPPD is used as commercial antiozonant in the rubber industry. It is therefore not surprising that none of the rubbers containing BHBM were found to have any activity relative to the control and IPPD.

6.5 ASSESSMENT OF VULCANISATION CHARACTERISTICS

Vulcanisation is the process which makes the rubber useful for service applications. During vulcanisation the rubber molecule becomes cross-linked. The cross-linking can be achieved conveniently by the use of sulphur and an accelerator system. The cross-links formed by this system mainly polysulphide links. Other vulcanisation systems include TMTD sulphur cures, peroxide cure and radiation cross linking of rubber. After vulcanisation the rubber loses the tackiness, becomes insoluble in solvent and is more resistant to deterioration.

For economical reasons, there should be minimal cross-linking before vulcanisation, fast curing during vulcanisation and minimum reversion. The vulcanisation process can therefore be characterised by the time for cross-linking to start (scorch time), the rate of cure, optimum cure time, optimum modulus and resistance to reversion.

All these parameters will be affected by the curing system. In industry, the most popular curing formulation for rubber articles is the conventional CBS (N-cyclohexyl-2-benzothiozole sulphenamide).



(CBS)

Other additives too, especially antioxidants, can affect the curing characteristics by increasing or decreasing the vulcanisation parameters described above. Therefore it was necessary to evaluate the effect of the bound antioxidant. It is widely accepted that the vulcanisation process for the CBS accelerated curing system proceeds through a polar mechanism by the steps outlined below: (168,169)

(1) Formation of a zinc accelerator complex.

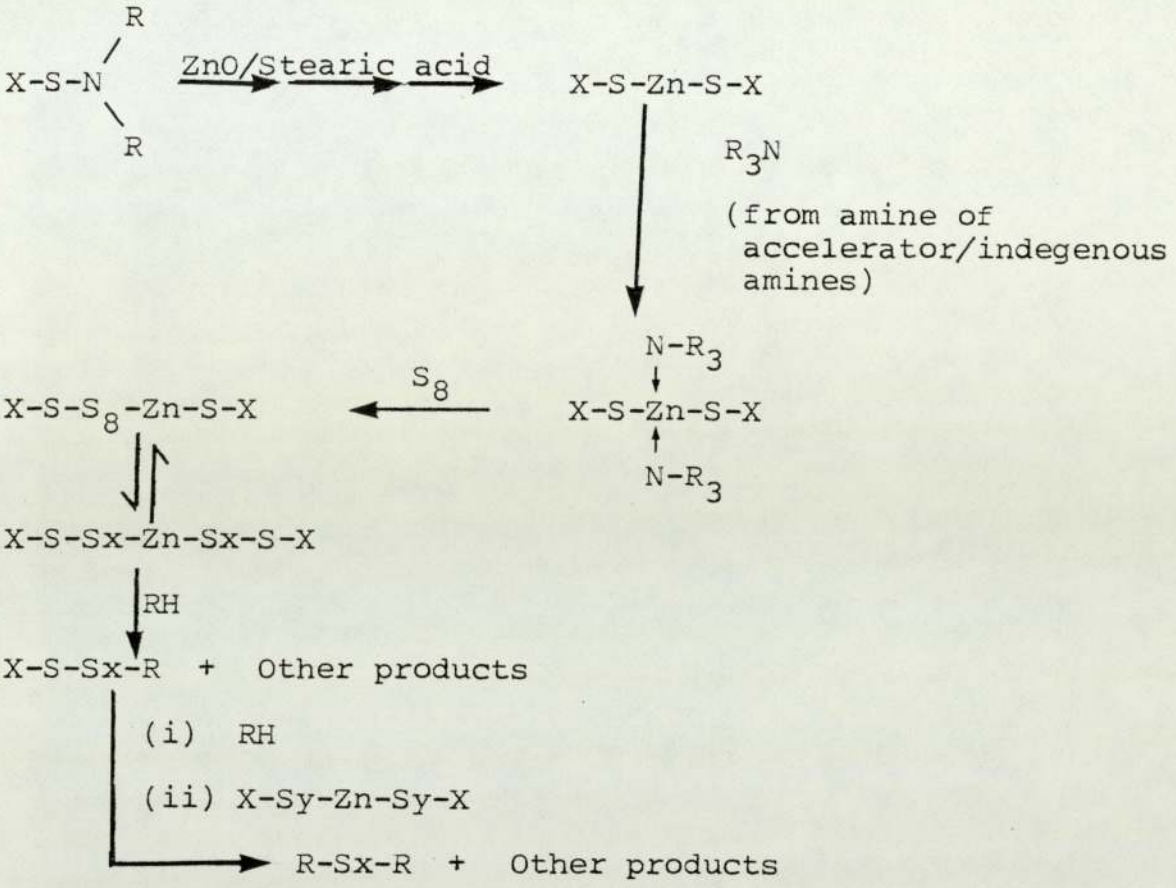
(2) Reaction of the sulphur with the zinc accelerator complex. This is normally activated by amine co-ordination on to the zinc complex.

(3) Incorporation of the sulphur into the zinc accelerator complex to form perthio-mercaptide.

(4) Reaction of this perthiomercaptide with rubber at α-methylenic or α-methylic position.

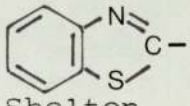
(5) Formation of the cross-link catalysed by the zinc accelerator complex.

These reactions are summarised in Scheme 6.5.



Scheme 6.5

x/y = any no. between 1-8

X = $R_2N-\overset{S}{\overset{\|}{C}}-$ or 

A radical mechanism has also been suggested by Shelton and McDonel[170] and later Manik and Banarjee[171] has suggested that both free radical and polar mechanisms may operate together.

The curing characteristics of BHBM were studied using the Monsanto Rheometer (Section 2.4). A typical rheograph curve is shown in Fig 2.5.

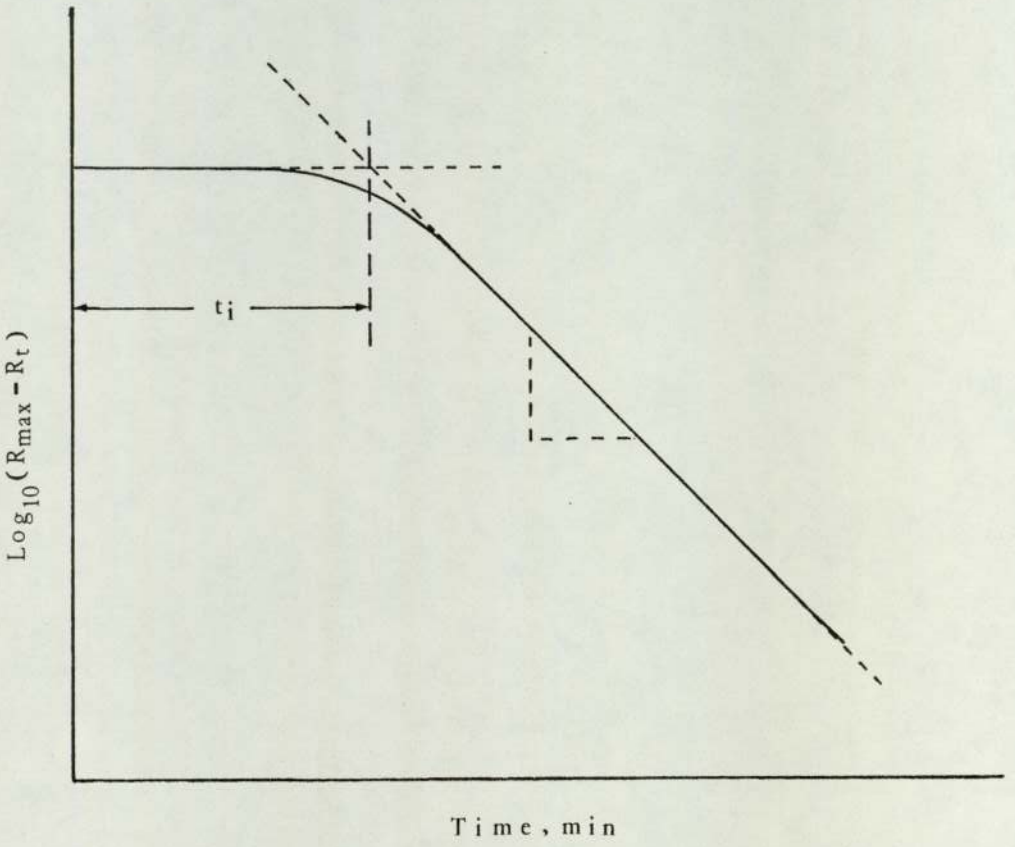


Fig 6.4 Typical first order kinetic plot for the vulcanisation of rubber[173,174]

Rough estimates of the scorch time may be obtained directly from the rheograph by taking the time for the cure to increase 3 or 5 units above the minimum torque.[172] However, more accurate values of the scorch time and the rate of cure may be obtained by assuming the vulcanisation rate to be first order and using the following equation developed by Coran[173,174].

$$\log (R_{max} - R_t) = \log R_{max} + \frac{k}{2.303} (t-ti)$$

where R = maximum torque

k = rate of first order cross link

t = time of cure

ti = scorch time

A plot of log $(R_{max} - R_t)$ against time gives a straight line with slope k/2.303 after the induction t_i (Fig 6.4)

6.5.2 RESULTS

The cross-linking characteristic of bound extracted and bound unextracted BHBM and its derivatives were studied using the Monsanto Rheometer. The vulcanisation parameters derived from the plot (shown in Fig 6.4) together with the control are shown in Table 6.9.

Table 6.9 Cure parameters of the bound unextracted and extracted BHBM and its derivatives at 140°C

Stock	Conc of Antioxidant	Modulus max m-kg x 0.06	t_i	k, min^{-1} x 10^{-1}
Control Unext	-	55	10	1.02
Control Ext	-	66	10.5	2.3
Bound BHBM Unext	1	67	26.5	2.0
Bound BHBM Ext	0.75	72	19	1.9
BHBM 'added' Unext	1	59	17	1.4
Di-S 'added' Unext	1	57	19.5	1.3
Mono-S 'added' Unext	1	58	16	1.5
IPPD 'added' Unext	1	65	19	1.2

6.5.3 DISCUSSION

It can be seen that the torque for the extracted control was slightly higher than that for the unextracted. Furthermore the first order rate constant for the latter was lower than the former.

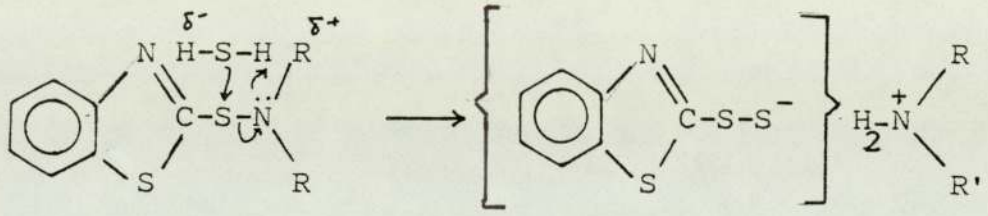
The scorch time of the controls were not affected. This suggests that the unextracted control contained some material which retarded the curing process. This material was extracted by acetone and it is most likely that some stabilisers had been incorporated into the latex at the manufacturing stage.

The rubber containing the bound BHBM made from the 10% masterbatch relative to the corresponding unextracted control gave a higher modulus at 45 minutes, a faster rate of cure but a longer scorch time.

The longer scorch time must be due to the retardation of the initial cross linking by the interaction with the activated complex and/or the amines which are formed from the CBS which are necessary for the activation of the ZMBT complex. Once the cross linking has started the faster rate of cure, and the higher optimum modulus at 45 minutes may be explained by the known capacity for sulphur containing compounds and thiols to accelerate

the rate of cross linking.

It is known[169] that hydrogen sulphide formed by reaction of sulphur compound with amine moiety of the sulphenamide can act as important reducing agent leading to the formation of amine salt by MBT.



I II

The salt (II) will then react rapidly with zinc soap to give persulphenyl MBT which will be the active acceleration leading to activating of elemental sulphur.

The bound extracted BHBM showed a slower rate of cure, and a shorter scorch time compared to the bound unextracted. Extraction of the rubber removed the side product of the binding reaction extraction could not remove the traces of the side products. This shown by the rate of the reaction which showed that some of the sulphur products were still present.

CHAPTER SEVEN

EVALUATION OF THE AGEING AND CURING PROPERTIES OF MADA BOUND TO NR, DPNR, SBR AND CIS POLYISOPRENE

In view of the efficient binding of MADA into the extracted rubber (synthetic and natural rubber as described in Chapter Five) the ageing characteristics of their conventional CBS vulcanisates were assessed. In all cases, the original masterbatches were diluted to 1% bound MADA by appropriate distribution with fresh rubber on the 2-roll open mill.

The vulcanisation for the O_2 absorption, stress relaxation, fatigue and resistance to ozone crack was done as described in Section 2.2.

The subsequent compounding and vulcanisation were done as described in Section 2.5.

7.1 OXYGEN ABSORPTION STUDIES OF VULCANISATES CONTAINING BOUND MADA IN NR, DPNR, SBR AND CIS POLYISOPRENE

The technique of O_2 absorption has been described in Section 2.5.1.1 and Section 6.1. The same procedure was adopted here. The O_2 absorption were done on both unextracted and extracted vulcanisates in order

to assess the effect of extraction.

7.1.2 RESULTS

Fig 7.1 shows that the oxygen absorption curve for the bound MADA (87.5% bound), MADA as additive and WSP in natural rubber (SMR-5L) vulcanisates. It is clear that after the initial induction period the unextracted samples shows retardation relative to the control. After extraction, bound MADA shows a pronounced retardation effect relative to before extraction. However, MADA added during the compounding stage and WSP rapidly lost their effects after extraction. The induction periods and times 1% oxygen absorption are summarised in Table 7.1.

Fig 7.2 shows that O_2 absorption curve for MADA bound (58%), MADA and WSP in DPNR vulcanisates. The binding was done in the Buss Ko Kneader.

This figure shows that after the initial induction period the bound MADA (unextracted) and MADA as additive (unextracted) shows autoretardation. All other samples show autoacceleration except bound MADA (extracted) which shows autoretardation in the early stages of oxidation.

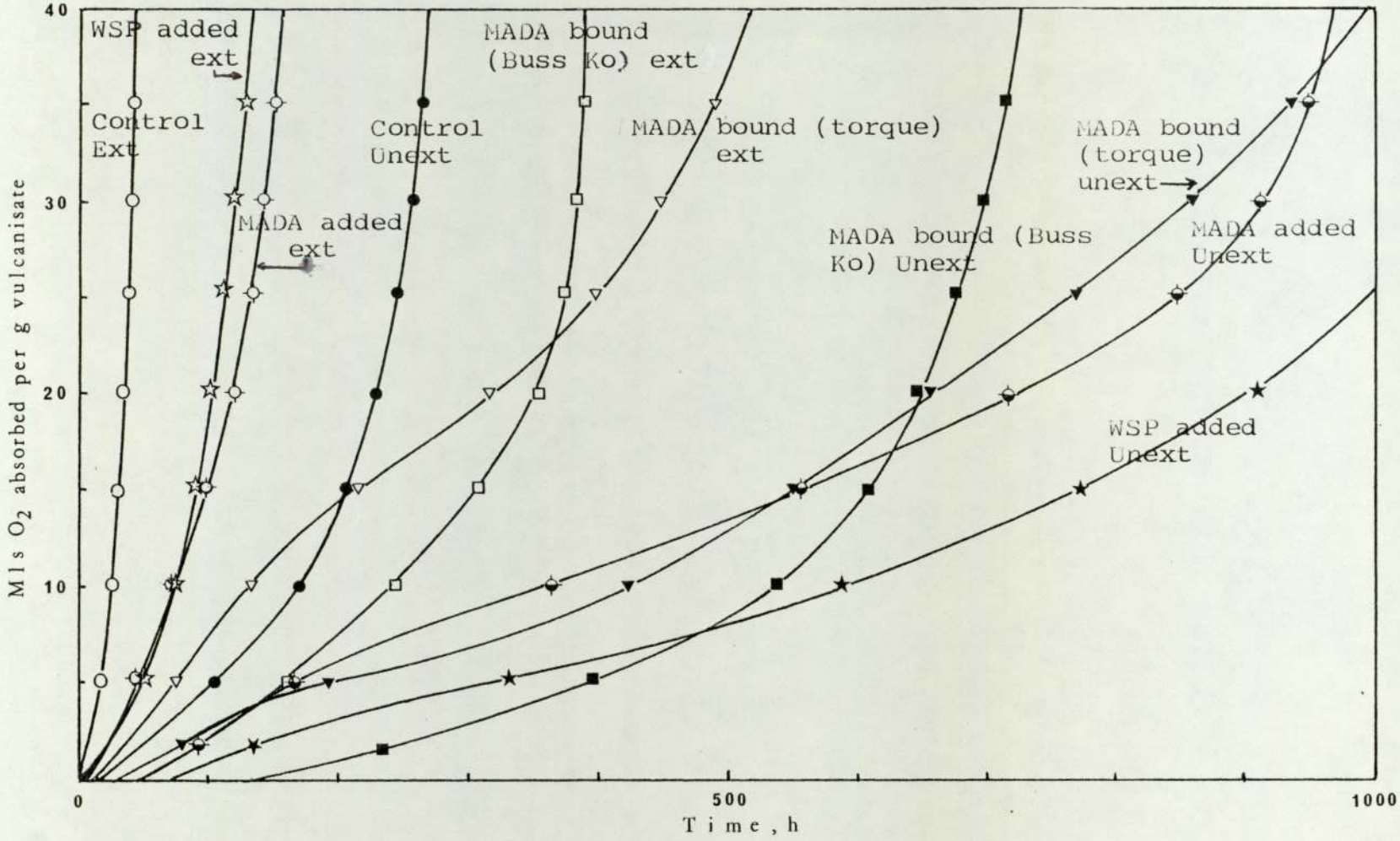


Fig 7.1 Oxygen absorption of SMR-5L vulcanisates containing 1% antioxidant at 70°C

Table 7.1 Antioxidant activities of vulcanisates containing bound MADA at concentration 1% in NR

Stock	Bound %	Induction period, h		Time to absorb 1% O_2, h	
		unextracted[e]	extracted[f]	unextracted[e]	extracted[f]
Control	-	15	0	129	30
MADA (torque)	75	25	45	475	99
MADA (Ko Kneader)	87.5	121	42	395	10
MADA	added	48	15	270	60
WSP	added	75	12	450	60

Notation

e - SMR-5L extracted before mechanochemical reaction with MADA and vulcanised

f - extracted before mechanochemical reaction with MADA vulcanised and extracted

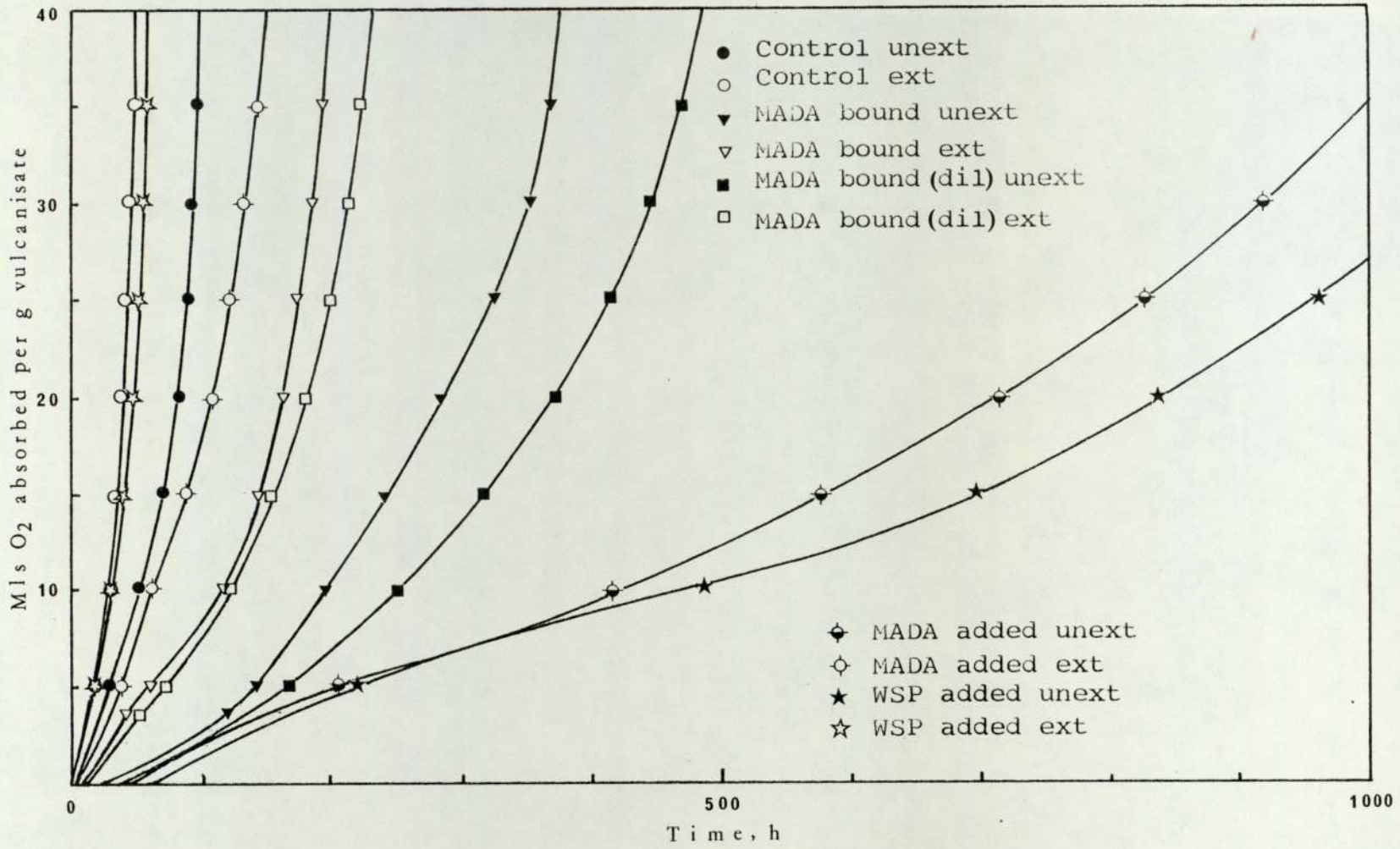


Fig 7.2 Oxygen absorption of DPNR vulcanisates containing 1% antioxidant at 70°C

Table 7.2 Antioxidant activity of vulcanisates containing bound MADA (from 10% masterbatch diluted with DPNR and NR) at 1% concentration (notation as in Table 7.1)

Stock	Bound %	Induction period, h		Time to absorb 1% O2, h	
		unextracted[e]	extracted[f]	unextracted[e]	extracted[f]
Control	-	0	3	45	25
MADA (+ DPNR)	58	33	12	165	90
MADA (+ NR)	58	45	21	205	102
MADA	added	42	11	325	45
WSP	added	45	3	415	25

It can be seen that MADA bound to DPNR diluted with NR show a little improvement activity both before and after extraction. The induction period and times to absorb 1% oxygen is shown in Table 7.2.

Fig 7.3 shows the oxygen absorption curves for MADA bound to SBR (79% bound), MADA as additive and WSP in SBR vulcanisate. The binding was done in the torque rheometer. It is seen that MADA bound unextracted shows a pronounced autoretardation after the initial induction period.

After extraction the MADA bound (extracted) shows superior resistance to O_2 absorption than either MADA additives or WSP.

Table 7.3 shows the induction periods and times to 1% oxygen absorption for MADA bound to SBR.

Fig 7.4 shows the oxygen absorption curve for MADA bound in cis polyisoprene. The figure also compares the effect of masterbatches containing 10%, 20% and 30% MADA process in Buss Ko Kneader (80% bound, 60% bound and 30% bound respectively) after appropriate dilution to 1%.

It is clear from the figure that for the unextracted vulcanisates the MADA added and WSP are superior to

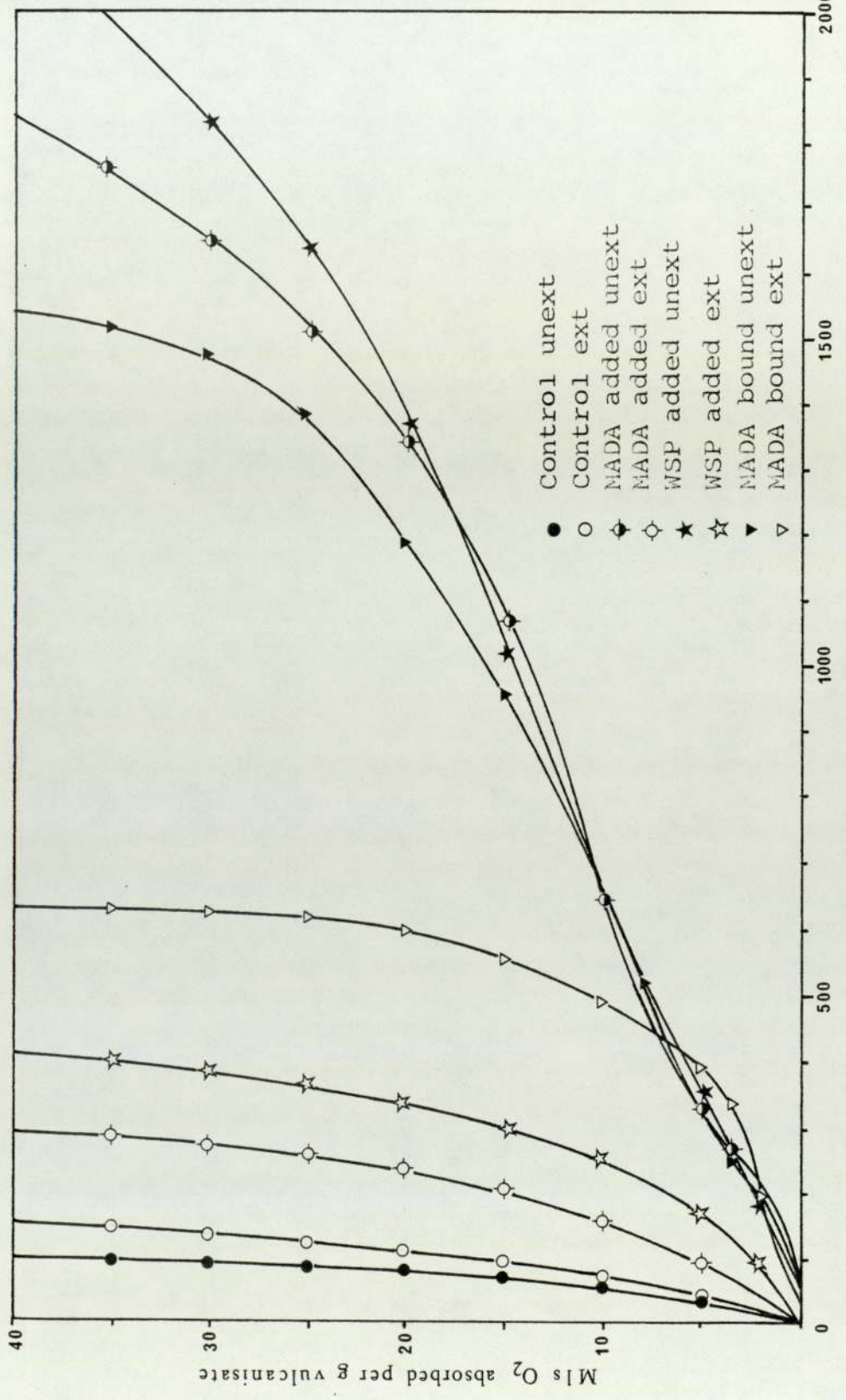


Fig 7.3 Oxygen absorption index of SBR vulcanisates containing 1% of antioxidant at 70°C

Table 7.3 Antioxidant activity of vulcanisates containing bound MADA (from 10% masterbatch) in SBR at 1% concentration (notation as in Table 7.1

Stock	Bound %	Induction period, h		Time to absorb 1% O_2, h	
		unextracted[e]	extracted[f]	unextracted[e]	extracted[f]
Control	-	13.5	18	50	75
MADA (10% MB)	79	84	48	590	425
MADA	added	70	20	600	150
WSP	added	66	18	610	240

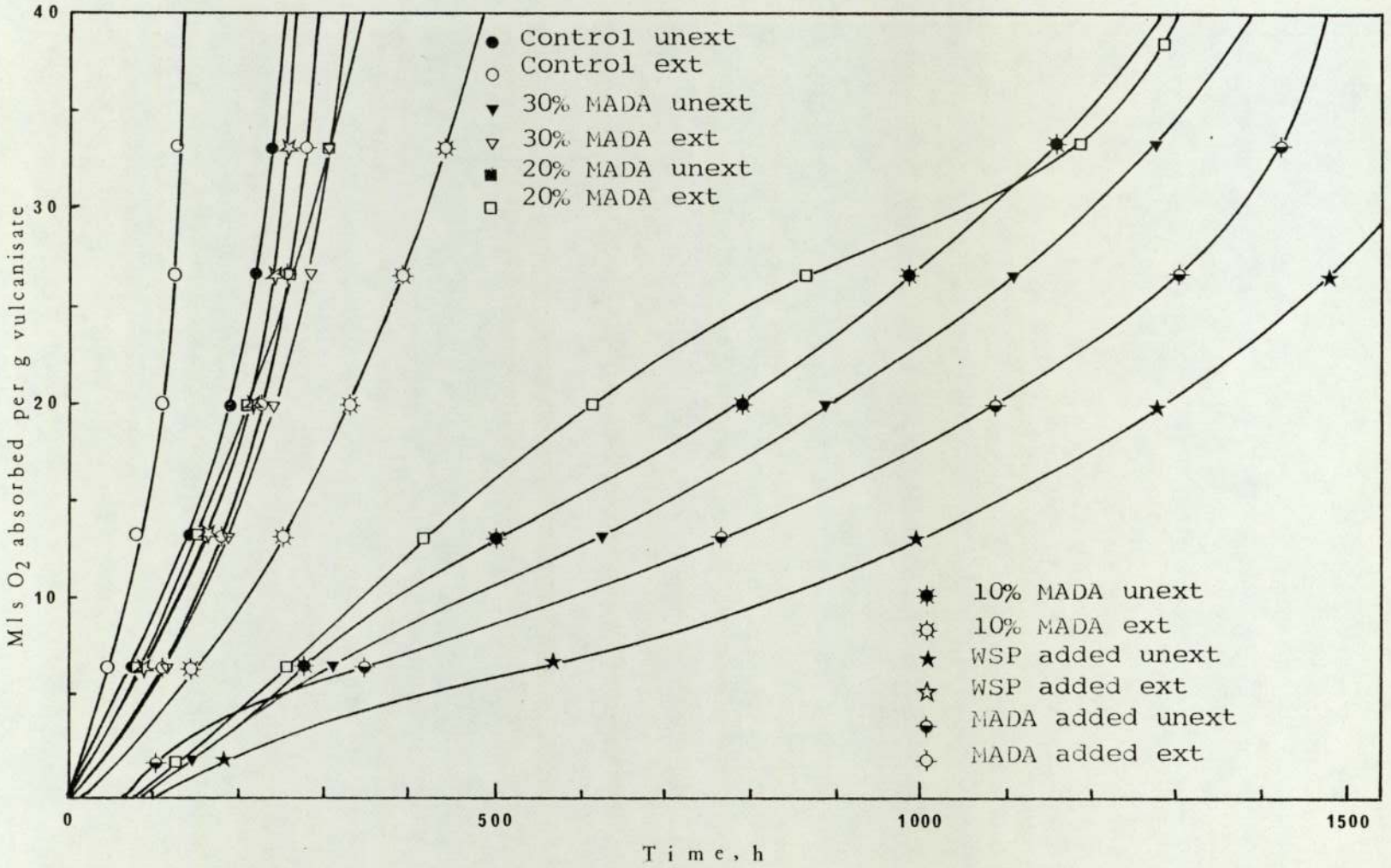


Fig 7.4 Oxygen absorption of cis-polyisoprene containing 1% antioxidant at 70°C

Table 7.4 Antioxidant activity of bound MADA (from 10%, 20% and 30% masterbatches) at concentration 1% in cis-polyisoprene (notation as in Table 7.1)

Stock	Bound %	Induction period, h		Time to absorb 1% O_2, h	
		unextracted[e]	extracted[f]	unextracted[e]	extracted[f]
Control	-	3	0	54	40
MADA (10% MB)	80	78	22	294	134
MADA (20% MB)	67	69	13	251	112
MADA (30% MB)	42	64	12	318	92
MADA	added	21	9	406	86
WSP	added	80	10	648	70

the MADA bound. However, after extraction, they are inferior to the bound.

Before extraction there is no difference for the vulcanisates made from the various masterbatches. After extraction however they do differ, the 10% masterbatch has the highest activity and the 30% masterbatch has the lowest.

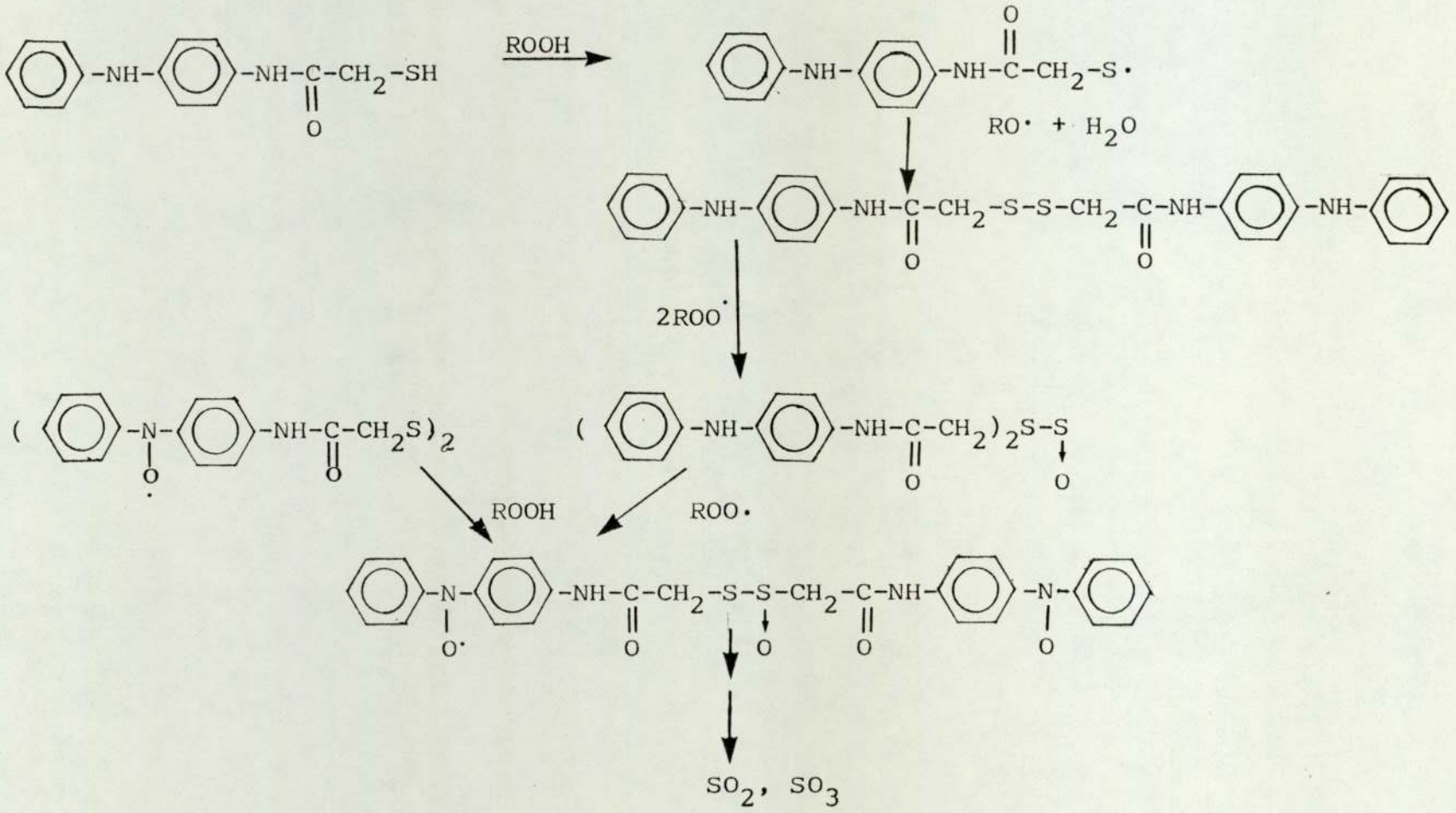
The induction period and time to absorb 1% oxygen are listed in Table 7.4.

7.1.3 DISCUSSION

It is known that MADA is an effective antioxidant in NR[65,107,108]. The efficiency of NR, DPNR, SBR and cis-polyisoprene in bound form after extraction is higher than commercial antioxidant.

This is due to retention of the antioxidant in the rubber due to it being attached to the rubber backbone. MADA functions as a powerful hydroperoxide decomposer due to the presence of sulphur in the molecule. Scott and co-workers[91,108] have proposed that MADA may react with alkylperoxy radical to form thiyl radicals which subsequently dimerised to form the corresponding disulphide. The mechanism is outlined in Scheme 7.2.

Scheme 7.2



(see Section 4.1.5)

The initial pro-oxidant effect that was observed during the oxygen absorption studies, is due to the radical species generated during the early stages of the reaction as shown in Scheme 7.2. The subsequent autoretardation and autoacceleration stages is due to formation and consumption of the catalytic sulphur oxidised species formed (see Chapter Four).

7.2 STRESS RELAXATION OF RUBBER VULCANISATES CONTAINING BOUND MADA

The continuous stress relaxation of MADA bound to SMR-5L DPNR, SBR were studied by the technique shown in Sections 2.5.2.1 and 6.2.

Grafted MADA in SBR (extracted) was not determined due to the brittleness of the sample. However, f50 for MADA bound (unextracted) is 35 hours, whilst MADA added has f50 = 22 hours.

7.2.1 RESULTS

The effect of bound MADA (from 10% masterbatches) and MADA as an additive on the stress relaxation of SMR-5L and DPNR at 100^{o}C are shown in Figs 7.5 and 7.6.

Table 7.5 and Table 7.6 show f50 for NR and DPNR

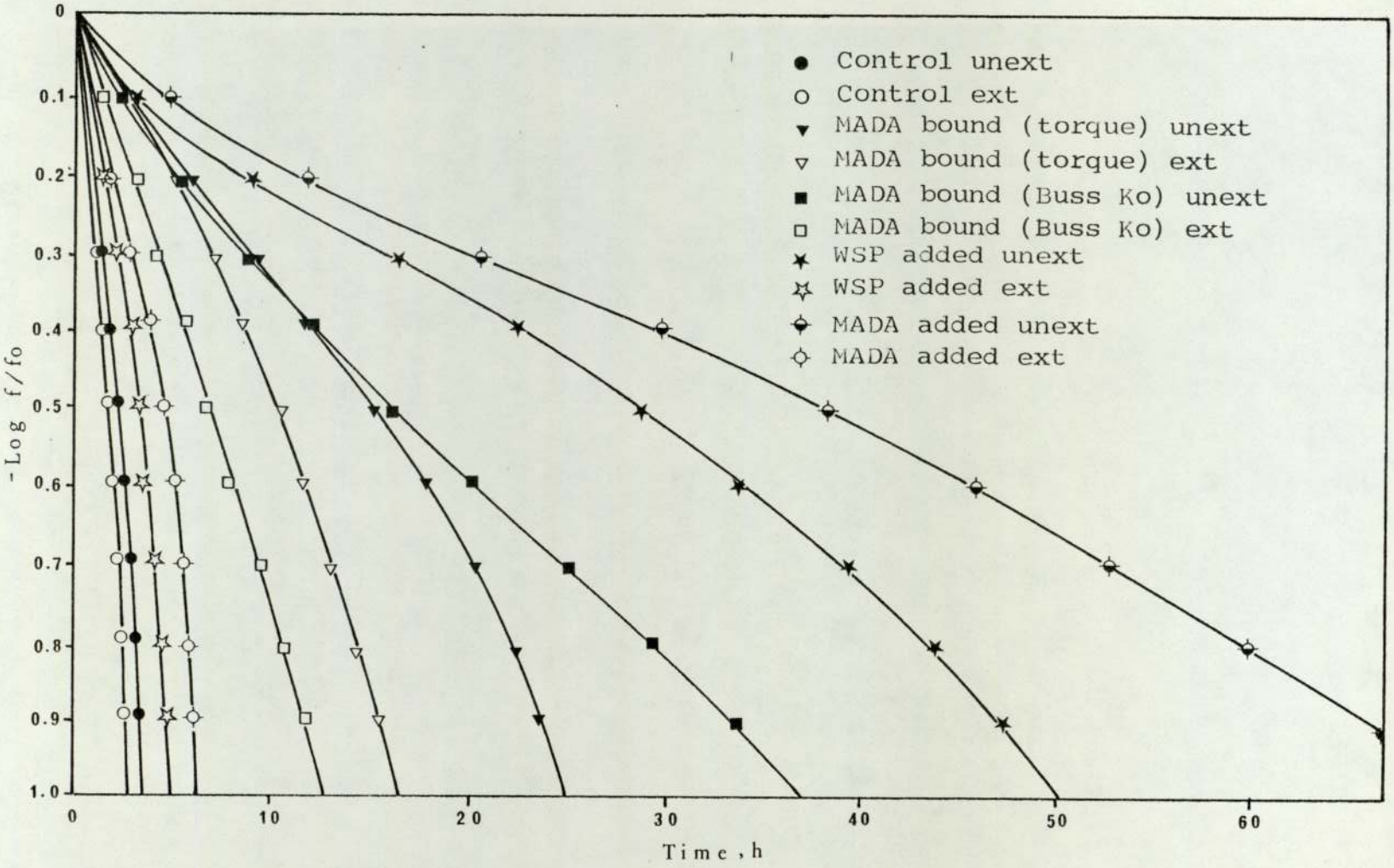


Fig 7.5 Continuous stress relaxation of NR (SMR-5L) vulcanisates containing 1% antioxidant at 100°C

vulcanisates.

Table 7.5 f50 of SMR-5L (10% masterbatch) vulcanisates containing 1% antioxidants (notation as in Table 7.1)

Stock	Bound %	f50	
		unextracted[e]	extracted[f]
Control	-	1.5	2
MADA (torque)	79	14.5	5
MADA (Ko Kneader)	87.5	14.5	9
MADA	added	17.5	2
WSP	added	16	1,5

Table 7.6 shows that f50 for DPNR vulcanisates is lower than that for the bound MADA in SMR-5L it is also shown that f50 of DPNR 10% masterbatch diluted with SMR-5L.

Figs 7.5 and 7.6 and Tables 7.5 and 7.6 show most the vulcanisates after extraction lost its resistance towards stress relaxation, hence oxidation relative to control. It is also shown that MADA grafted has better antioxidant activity.

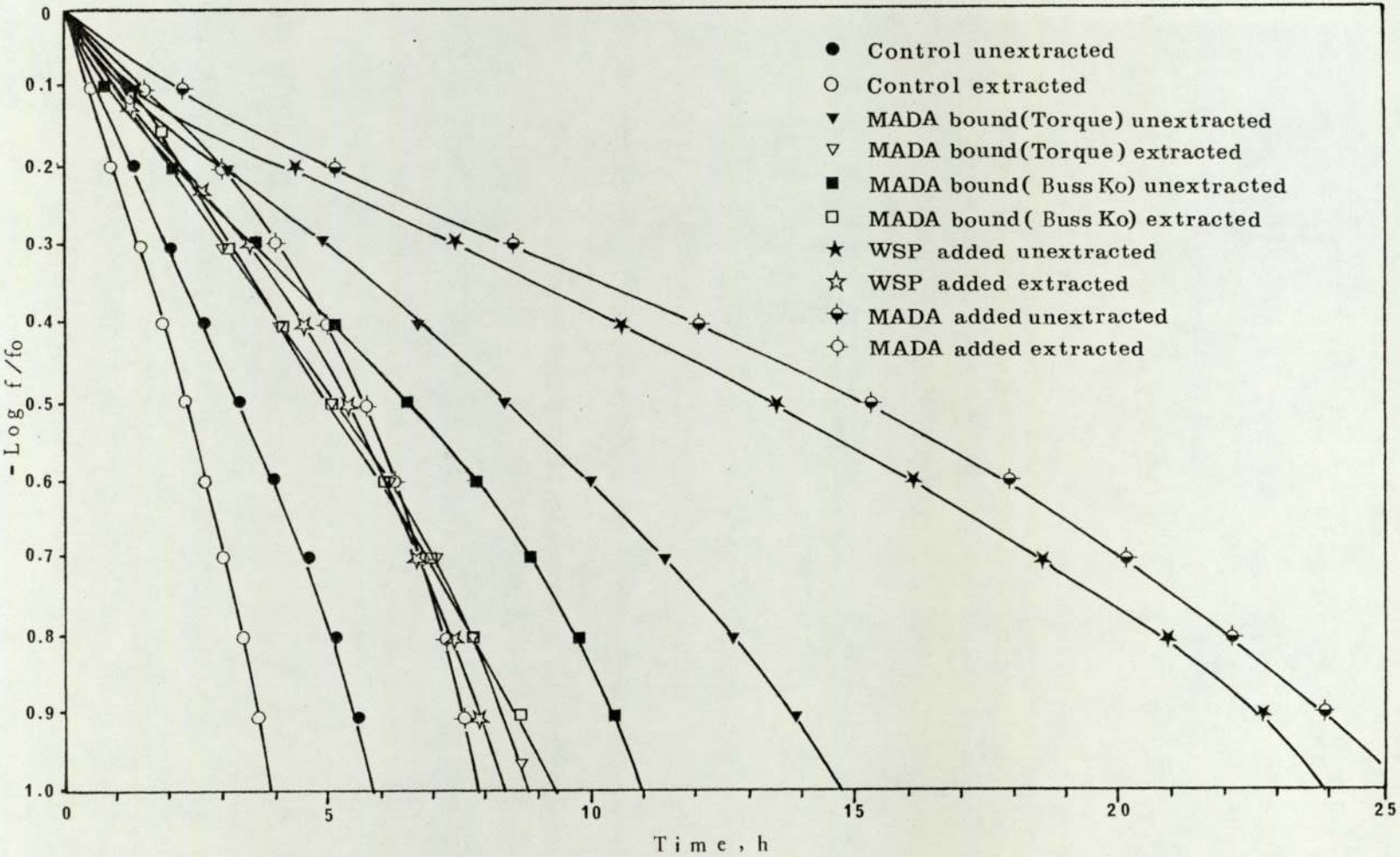


Fig 7.6 Continuous stress relaxation of DPNR vulcanisate containing 1% antioxidant at 100°C

Table 7.6 f50 of DPNR (10% masterbatch) vulcanised diluted with DPNR and SMR-5L at 1% concentration (notation as in Table 7.1)

Stock	Bound %	f50	
		unext[e]	ext[f]
Control	-	2	1.5
MADA (torque+DPNR)	58	5.5	4
MADA (Ko Kneader+ SMR-5L)	58	4.5	4
MADA	added	8	3
WSP	added	7.5	2.5

7.2.2 DISCUSSION

The results of stress relaxation are consistent with the results of oxygen absorption studies. The antioxidant activity of MADA bound extracted are good compared to control and extracted commercial WSP. This may be rationalised in the same terms as discussed for the oxygen absorption results (Section 7.1.3).

The loss of activity for the commercial WSP as described earlier (Section 7.1.3) is due to leaching of the unbound additive.

MADA added during compounding after extraction shows a lower level of activity but somewhat better than the control. This must be due to a small amount of binding to the rubber during compounding stages (section 5.3).

7.3 FATIGUE RESISTANCE OF VULCANISATES

The antifatigue activity of MADA bound into SMR-5L, DPNR and SBR was studied and compared to IPPD and to MADA as a normal additive.

7.3.1 RESULTS

Table 7.7 shows the fatigue lives of the bound extracted and bound unextracted vulcanisates of NR. Tables 7.8-7.11 show fatigue lives of NR,DPNR,SBR processed differently.

7.3.2 DISCUSSION

It is clearly shown from Tables 7.7 - 7.11 that the fatigue life of bound MADA in three different rubbers shows improvement relative to the control. However, the improvement is not as high as that for IPPD before extraction.

It is known that N-alkyl-N'-aryl-p-phenylene diamine have antifatigue activity when incorporated into the rubber.

Table 7.7 Improvement of fatigue lives of MADA bound in SMR-5L (10% masterbatches) processed in RAPRA torque rheometer at 1% concentration at 100% extension

Stock	Bound %	Fatigue lives h		Improvement % *	
		unextracted	extracted	unextracted	extracted
Control	-	8	6	-	-
MADA	75	24	12	200	100
IPPD	added	27	7.5	237.5	25
MADA	added	16	8	100	33.3

* Relative to control

Table 7.8 Improvement of fatigue lives of MADA bound in SMR-5L (from 10% masterbatches) processed in Ko Kneader at 1% concentration, 100% extension

Stock	Bound %	Fatigue lives h		Improvement* %	
		unextracted	extracted	unextracted	extracted
Control	-	8	6	-	-
MADA	87.5	22	9	175	50
IPPD	added	27	7.5	237.5	25

* relative to control

Table 7.9 Improvement of fatigue lives of MADA bound to DPNR, processed in torque rheometer at 1% concentration at 100% extension

Stock	Bound %	Fatigue lives h		Improvement* %	
		unextracted	extracted	unextracted	extracted
Control	-	6	4	-	-
MADA	58	22	7	267	75
IPPD	added	36	6	500	50
MADA	added	22	7	267	75

* relative to control

Table 7.10 Improvement of fatigue lives of MADA bound to DPNR processed in Buss Ko Kneader, MADA and IPPD as additives, concentration 1%, at 100% extension

Stock	Bound %	Fatigue lives h		Improvement* %	
		unextracted	extracted	unextracted	extracted
Control	-	6	4	-	-
MADA (+DPNR)	58	19	8	217	100
MADA (+NR)	58	24	15	300	275
MADA	added	22	7	267	75
IPPD	added	36	6	500	50

* relative to control

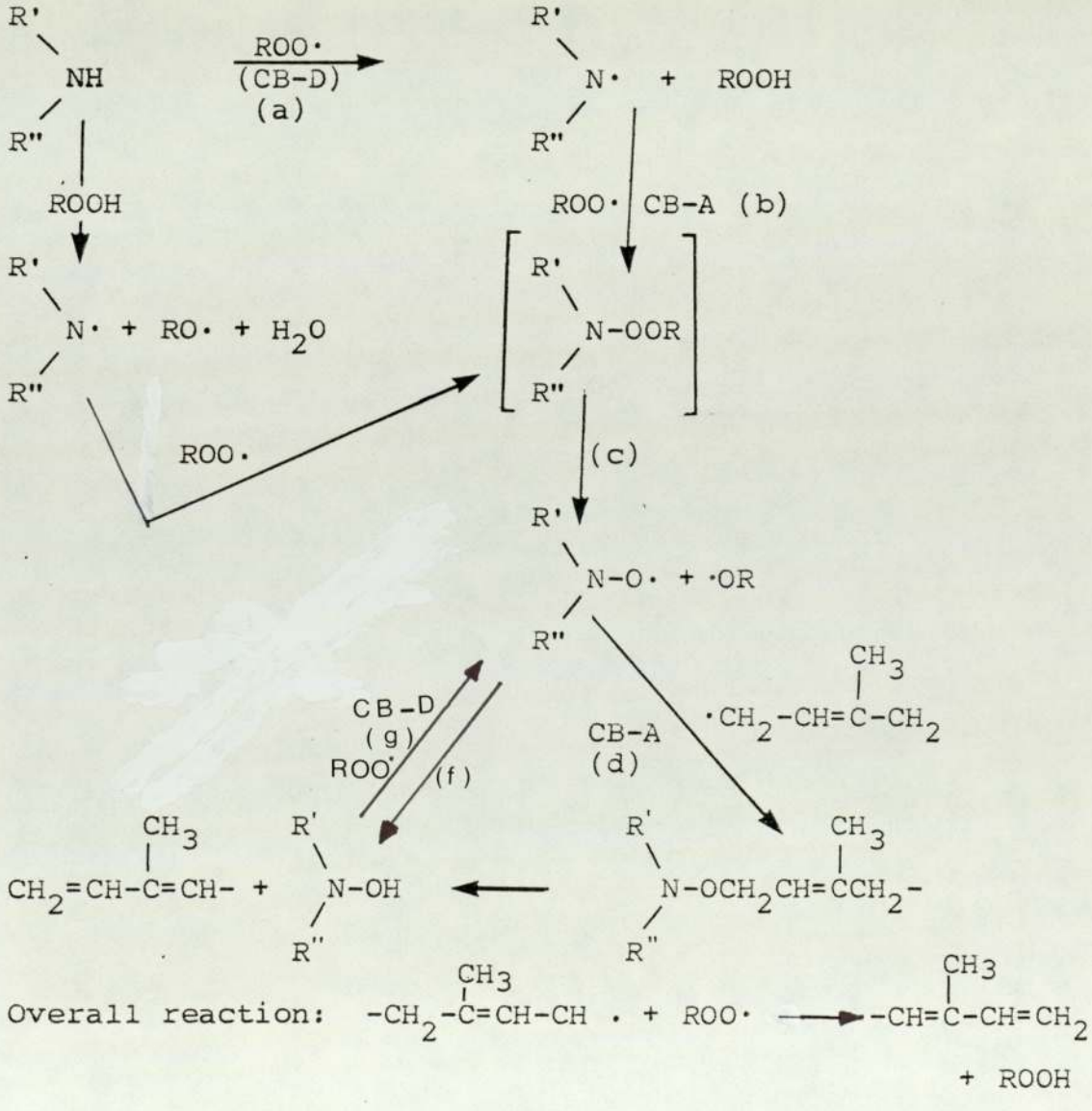
Table 7.11 Improvement of fatigue lives of MADA bound to SBR processed in RAPRA torque rheometer, MADA additive, concentration 1%, at 100% extension

Stock	Bound %	Fatigue lives h		Improvement* %	
		unextracted	extracted	unextracted	extracted
Control	-	3	2.7	-	-
MADA	79	10	6	233	122
MADA	added	8	4	167	48
IPPD	added	14	3.7	366	37

* relative to control

Scott and co-worker [65] have shown that nitroxyl radical is formed during fatiguing of the rubber. Nitroxyl radicals are known to be efficient free radical traps and during the fatiguing of the rubber they continuously regenerated in a cyclical process involving the corresponding hydroxylamine. This is shown in Scheme 7.3.

Scheme 7.3



The improvement of bound MADA as an additive could also be explained on the basis of the same mechanism (Scheme 7.3).

7.4 OZONE RESISTANCE OF VULCANISATES

In this study the bound extracted and unextracted MADA in SMR-5L, DPNR and SBR were tested for ozone as described in Section 6.4.

7.4.1 RESULTS

The test results are shown in Table 7.12.

7.4.2 DISCUSSION

The result is unusual since Katbab and Scott[175] have recently reported good antiozonant activity for MADA bound into natural rubber. However, Dweik[176] too has found a lack of activity for MADA in natural rubber and this must be due to the different processing methods. Katbab and Scott[177] incorporated the MADA into the rubber through a chemical binding reaction in the latex In the present study, the MADA was incorporated into the rubbers by mechanochemical binding into solid rubber in the torque rheometer and Ko Kneader. In the two cases therefore the extent of oxidation of the sulphur compounds

Table 7.12 Ozone resistance of bound MADA and its derivatives, concentration 1%

Stock	Bound %	Complete failure h	
		unextracted	extracted
SMR-5L			
Control	-	33	21.5
MADA (torque)	75	21	12
IPPD	added	44	23
MADA (Ko Kneader)	87.5	21	16
MADA	added	23	21
IPPD	added	44	23
DPNR			
Control	-	25	20
MADA (torque)	58	25	16
MADA (Ko Kneader)	58	25	18
IPPD	added	40	21
SBR			
Control	-	15	16
MADA (torque)	79	25	15
IPPD	added	28	12

may be different.

7.5 ASSESSMENT OF VULCANISATION CHARACTERISTICS

The vulcanisation characteristics of MADA bound to SMR-5L DPNR, SBR and cis-polyisoprene were studied using the method described in Section 6.5

7.5.1 RESULTS

Table 7.13 shows the curing characteristic of SMR-5L processed in torque and Ko Kneader.

7.5.2 DISCUSSION

The results described in Tables 7.13 to 7.16 show that vulcanisation of rubbers by a conventional CBS curing system in which MADA was bound into the rubber chains or added during the vulcanisation stages, the scorch time is reduced. After extraction, the bound MADA still shows a reduction in scorch time.

The acceleration of vulcanisation and the reduction in the scorch time in the presence of MADA must be due to its interaction with the curing system. This effect may be rationalised in terms of basicity of MADA since amines are known to accelerate cure. Furthermore any retardation effect due to the thiol would be offset by the presence of the amine in the MADA.

Table 7.13 Curing characteristics for MADA bound to SMR-5L (1%) processed in Torque and Buss Ko Kneader

Stock	Bound %	Modulus max mkg x 0.056		t_i		k min^{-1} x 10^{-1}	
		Unex	Ext	Unext	Ext	Unext	Ext
Control	-	54	56	11	10	19	1.5
MADA (torque)	75	60	59	6.5	7.0	0.99	1.2
MADA (Ko Kneader) MB10%	87.5	68	59	6	7.5	0.86	1.4
MADA (Ko Kneader) MB20%	71	65	54	4	6	1.02	1.1
MADA (Ko Kneader) MB30%	61	63	52	4.8	5.5	1.08	1
MADA	added	56	-	5	-	0.92	-
IPPD	added	57	-	10	-	1.7	-

Table 7.14 Curing characteristics of bound MADA in DPNR concentration 1%, processed in torque rheometer and Buss Ko Kneader

Stock	Bound %	Modulus max mkg x 0.056		t_i		$k\,min^{-1} \times 10^{-1}$	
		Unext	Ext	Unext	Ext	Unext	Ext
Control	-	57	56	21.5	21	1.9	1.7
MADA (torque)	58	49	57	4	13.6	1.2	2.1
MADA (Ko Kneader)	58	47	56	3.5	11.5	1.4	1.9
MADA	added	49	-	3.6	-	1.4	-
IPPD	added	53	-	17	-	1.1	-
WSP	added	52	-	19	-	1.7	-

Table 7.15 Curing characteristics of bound MADA in SBR, concentration 1%, processed in torque rheometer

Stock	Bound %	Modulus max mkg x 0.056		t_i		k min^{-1} x 10^{-1}	
		Unext	Ext	Unext	Ext	Unext	Ext
Control	-	58	65	10	12	1.9	2.1
MADA	7.9	59	57	8	9	1.2	1.3

Table 7.16 Curing characteristics of bound MADA in cispolyisoprene, concentration 1%, processed in Ko Kneader

Stock	Bound %	Modulus max mkg x 0.056		t_i		k min^{-1} x 10^{-1}	
		Unext	Ext	Unext	Ext	Unext	Ext
Control	-	68	60	20	15	3.1	1.6
MADA (10% MB)	80	69.5	85	3	9.5	2.7	1.4
MADA (20% MB)	67	70.5	88	3	8.5	5.5	1.4
MADA (30% MB)	42	60	82	4	9.5	2.9	1.4

CHAPTER EIGHT

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1 CONCLUSIONS

This thesis has described the study of the chemical attachment by adduct formation of thiol antioxidants to the rubber backbone. Two antioxidants which are at present being developed commercially were used, namely BHBM and MADA. Adduct formation was carried out by grafting the thiol into natural rubber latex, SBR latex and by mechanochemical reaction in solid rubbers.

The work has demonstrated that BHBM cannot be bound into NR latex in technologically acceptable yields (ie 60%). The reasons for the inefficient binding of the BHBM into the NR latex is attributed to the presence of naturally occurring non-rubber constituents which poison the binding reaction.

When SBR latex was used however yields of up to 75% were obtained for a masterbatch of formulation of 10% BHBM. The high binding in SBR latex was rationalised in terms of the absence of the natural products that are present in the NR latex and which poison the reaction in the latter.

Dilution of the masterbatch to 1% and subsequent studies of the technological ageing properties in conventional CBS vulcanisates showed that the antioxidant conferred high fatigue resistance and very good thermo-oxidative protection, even after extraction of the vulcanisates. Extraction actually improved the thermal antioxidant performance. Before extraction the antifatigue activity of the bound BHBM was very much higher than after extraction. The activity of the bound BHBM was rationalised in terms of synergism between combination of the sulphenyl radical, the sulphur oxidised by products including quinonoid species which are formed during and after the binding and vulcanisation stages. The improved antioxidant performance after extraction was rationalised in terms of extraction of these by products. No antiozonant activity was observed but this was not unexpected.

The mechanisms of binding were studied in related model compound reactions using cyclohexene and BHBM initiated by TBH. These studies showed that oxidised sulphur acids and quinonoid species are by products of the addition reaction. Furthermore it was shown that the molar ratio of TBH to BHBM and the temperature of the reaction were critical for high yield of adduct formation.

Attempts to bind MADA into SBR latex were not successful as the latex coagulated during reaction. Therefore MADA was bound into the rubber using a mechanochemical reaction. The mechanochemical binding reactions were done using the RAPRA torque rheometer and Buss Ko Kneader. Using these techniques MADA was bound into SBR, NR, DPNR and cis polyisoprene. In all cases, good binding was only achieved when the rubber was extracted prior to the processing operation. Without extraction, the binding was very low and was attributed to the presence of non-rubber constitutents.

A study of the technological performance of the rubber containing the bound MADA (in rubber extracted prior to the binding) showed good antifatigue and antioxidant protection even after extraction of the vulcanisates. No antiozonant behaviour was observed for the MADA bound to the rubber in this manner.

In all cases, BHBM and MADA reduced the scorch time of the vulcanisation process considerably. However, the other vulcanisation characteristics were more or less unaffected. The reduction in the scorch time was attributed to interaction of the thiol with the acceleration system.

The results in this thesis suggest that the loss of the

protective effectiveness of the antidegradant due to the leaching effect during the service life of rubber compounds can be overcome by chemically attaching the stabilisers to the backbone.

8.2 SUGGESTIONS FOR FURTHER WORK

It has been demonstrated that the level of binding of BHBM into NR was low. The reason for this was attributed to the presence of non rubber constituents in the latex, which poison the binding reaction. The nature of this 'poison' must be identified and if possible 'neutralised' so that good binding can be effected.

Very good antifatigue activity for BHBM bound into SBR latex (optimum yield) was found in this study. Although suggestions have been proposed to account for this antifatigue effect, work needs to be done to establish the precise nature of the activity. The contribution of the by products formed from BHBM during binding and vulcanisation should also be studied. The role of the sulphenyl radical in the antifatigue activity of BHBM (bound and unbound) must be established and proved mechanistically by electron spin resonance spectrometry.

Mechanochemically bound MADA was found to have good ageing protection in synthetic and natural rubber. Therefore its action in model compound should be studied, especially since it differs from BHBM in that it contains an amine group together with the thiol function.

In view of the efficient binding of the BHBM and MADA and their good antioxidant and antifatigue properties, a large scale trial of these materials would be useful in order to optimise conditions for a possible industrial use.

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