A MECHANISTIC STUDY OF ESTERS OF THIODIPROPIONIC ACID AS ANTIOXIDANTS

by

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SUMMARY

The mechanism of the thermal decomposition of the dialkyl sulphinyldipropionates alone and in the presence of 2,6-di-tert-butyl-1-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyloxy (Galvinoxyl) has been investigated. Results show that radical intermediates capable of initiating oxidations are not produced under the conditions of study. This result is also substantiated by studying the effect of dimethyl sulphinyldipropionate on the thermal and $\alpha\alpha'$-azoisobutyronitrile (AZBN) initiated polymerisation of styrene which in fact shows that the sulphoxide has free-radical chain interrupting activity. The effect of the sulphoxide on the polymerisation of styrene initiated by cumene hydroperoxide has, however, shown that free radicals are produced by a reaction between the hydroperoxide and the sulphoxide. This reaction is probably responsible for the pro-oxidant effect which can occur when using dialkyl thiodipropionates as antioxidants and certain possible reactions have been postulated.

The means by which dialkyl sulphinyldipropionates function as antioxidants has been studied by oxygen absorption techniques. Results show that these sulphoxides are capable of both interrupting the free radical chain mechanism of autoxidation and deactivating the hydroperoxide. The free-radical interrupting activity is consistent with the effect of the sulphoxide on the polymerisation of styrene and a common mechanism has been postulated to explain these effects. The deactivation is not due to complex formation between hydroperoxide and sulphoxide. In order to study the effect of the sulphoxide on the hydroperoxide the kinetics and products of the reaction of dimethyl sulphinyldipropionate with cumene hydroperoxide have been studied. Results indicate that a species capable of catalytically decomposing the hydroperoxide is produced. A series of reactions which may explain these results has been proposed but an unambiguous identification of the peroxide decomposing species has not been made.

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Chapter 1

INTRODUCTION

1.1. Autoxidation and Antioxidants

Oxidations which involve oxygen and are catalysed by their products, hydroperoxides, is known as autoxidation. A basic reaction scheme for the autoxidation of simple olefins such as ethyl linoleate was first developed. This scheme can explain many of the kinetic features[1] of autoxidation and has since been applied to saturated hydrocarbons and polymer oxidations[2].

Initiation

$$RH + O_2 \longrightarrow R\cdot \qquad (1)$$

$$RO_2H \longrightarrow RO\cdot + \cdot OH \qquad (2)$$

$$2RO_2H \longrightarrow RO_2\cdot + H_2O + RO\cdot \qquad (3)$$

Propagation

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (4)$$

$$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot \qquad (5)$$

Termination

$$2RO_2\cdot \longrightarrow \text{non-propagating species} \qquad (6)$$

Basic Autoxidation Scheme (BAS)

Some industrial processes are dependent upon oxidation to develop the desirable properties. Amongst these are the setting of surface coatings and the compounding of raw rubber. However in the majority of cases the properties of oxidizable materials deteriorate. It is therefore necessary to stabilise foodstuffs, oils and polymers against atmospheric oxidation[3].

Compounds which carry out this function are known as antioxidants.

There are two fundamental types of antioxidants. The type which intereferes with the propagating species is known as chain-terminating antioxidants. Examples of these are aromatic amines and hindered phenols[4]. The second class interfere with the initiation. The basic autoxidation scheme (p.1) shows that the primary product is the hydroperoxide and that this gives rise to the main source of initiating radicals. Removal of the hydroperoxide by a non-radical reaction will, therefore, result in a suppression of autoxidation. Organic phosphites and sulphides function as antioxidants by this mechanism.

This thesis is concerned with the mechanisms of the sulphide antioxidants and more specifically with the esters of thiodipropionic acid (I). These, and in particular the dodecyl ester

$$RO\cdot CO\cdot CH_2CH_2SCH_2CH_2\cdot CO\cdot OR$$

(I)

($R=C_{12}H_{25}$), are by far the most widely used dialkyl sulphide antioxidants. They function outstandingly compared to other dialkyl sulphides[5] and are used in foodstuffs[6] and polyolefins[7,8].

1.2. Sulphur Compounds in Autoxidation

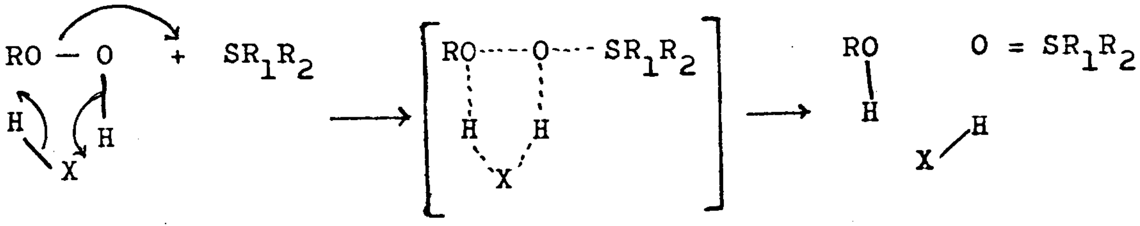
Denison and Condit[9,10] were the earliest workers to investigate the behaviour of sulphur compounds in an autoxidising media. It was concluded that the hydroperoxide reacted with dialkyl sulphides stoichiometrically to produce the sulphoxide (reaction 7). A further reaction of the sulphoxide with another molecule of hydroperoxide could give the sulphone (reaction 8). Sulphides

$$ROOH + R_2'S \longrightarrow ROH + R_2'S = O \qquad (7)$$

$$R_2'S = O + ROOH \longrightarrow ROH + R_2'SO_2 \qquad (8)$$

which contain at least one aliphatic or cycloaliphatic group attached to the sulphur atom were most effective[10]. Diaryl sulphides were ineffective. Oxygen absorption experiments were used to compare the inhibitary power of dicetyl sulphide with dicetyl sulphoxide and dicetyl sulphone. The sulphone was ineffective while the sulphoxide showed an inhibitary action appreciably less than that of the sulphide.

A detailed mechanistic study of the reaction of organic sulphides with hydroperoxides was undertaken by The Natural Rubber Producers' Research Association[11,12,13]. To explain the kinetics and solvent effects the reaction was postulated to proceed via a ring complex (reaction 9).



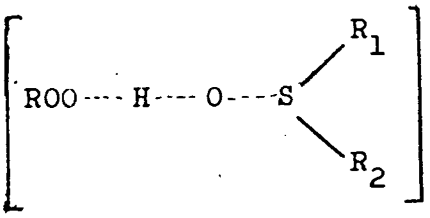
(9)

H — X is a hydroxylic solvent or a second molecule of hydroperoxide. This explains why the reaction in hydroxylic solvents is first order in both reactants while it is first order in sulphide and second order in hydroperoxide in non-hydroxylic solvents.

Barnard[14] has studied the reaction of organic hydroperoxides with alk-2-enyl sulphides and has found that the yield of sulphoxide is always less than the theoretical amount. The yield was found to decrease with an increase in temperature and C — S bond scission occurred with the formation of disulphide.
The importance of this step was found to depend on the sulphide. Reactions (10) and (11) were advanced for the reaction of unsaturated

sulphides with hydroperoxides[13,14]. It was concluded that the inhibitary effect of the sulphides in olefin autoxidations was due to (i) their interaction

$$ROOH' + AOH'' + R_1SR_2 \longrightarrow ROH'' + AOH' + R_1SOR_2 \qquad (10)$$



$$+ R_1SR_2 \longrightarrow R_1SSR_1,\ H_2O \text{ etc.} \qquad (11)$$

with the hydroperoxides and (ii) the independent action by the disulphide produced.

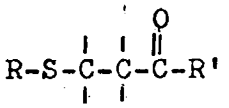
More recently Pobedimskii[15] has examined the reactions of didodecylthiodipropionate and dibenzylsulphide with tert-butyl hydroperoxide in an attempt to elucidate the mechanism of their antioxidant action. They suggest that the reaction occurs by a caged free-radical mechanism and has a 1:1 stoichiometry. The cyclic complex (reaction 9) is argued against in favour of the mechanism (12) below. They reach their conclusions by comparing the rate of decomposition of ~~hydroxide~~ hydroperoxide with the rate of disappearance of an added free radical scavenger 2,2',6,6'-tetramethyl-piperidine-1-oxyl.

$$ROOH + R_1R_2S \longrightarrow \underbrace{\left\{ RO\bar{O}H{-}{-}{-}{}^{+}SR_1R_2 \longrightarrow R\ddot{O}S(OH)R_1R_2 \right\}}_{\text{cage}} \longrightarrow$$

$$\begin{cases} \longrightarrow ROH + O = SR_1R_2 \\ \longrightarrow RO^{\bullet} + \dot{S}(OH)R_1R_2 \end{cases} \qquad (12)$$

Pobedimskii[15] has not appeared to have examined the reaction of the free radical scavenger with the sulphoxide produced by the reaction. This information is essential before any of his conclusions can be made. Marshall[16] has also shown that at least twenty-five moles of hydroperoxide are decomposed by 1 mole of dilauryl thiodipropionate.

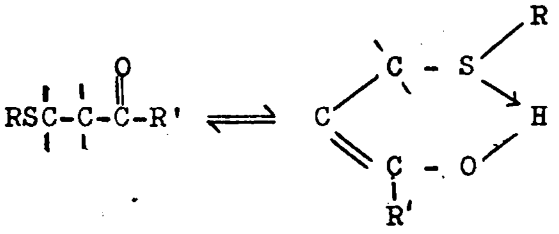
The dependence of the effectiveness of monosulphides as antioxidants on the structure of the attached group has been studied by several workers. Thompson[17] found that β-alkylmercaptoketones (II) were potent antioxidants and the most effective were those which allowed close approximation of the ketone oxygen and the sulphur atom



$R{-}S{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}R'$

(II)

Two reasons[18] for the potency of this structure were suggested. Firstly the β-carbonyl activates the sulphur atom to oxidation by the hydroperoxide. This gives the sulphoxide which was consequently found to be an extremely potent antioxidant. Secondly an available hydrogen atom can be produced by an enolization of the keto group. The enol being capable of stabilisation by hydrogen bonding (13).



(13)

No evidence to support this second reason comes from a spectroscopic study of keto sulphides[19]. Other groups, such as nitro, cyanide αpyridyl attached β to the mercapto group give ineffective antioxidants[20]. The sulphone and the sulphoxide groups attached to the β carbon atom gave antioxidants similar in efficiency to the carbonyl compounds[20].

Barnard et al[21] examined the effect of numerous mono and disulphides on the autoxidation of squalene. They found that both di-tert-butyl sulphide and di-n-butyl disulphide strongly retard the autoxidation of squalene only after a small quantity of oxygen had been absorbed. The inhibition of oxidation was therefore attributed to the derived sulphoxide and thiolsulphinate respectively. The antioxidant activity of the sulphoxide, RSOR', was found to depend greatly on the nature of R and R'. "Bulky" alkyl substituents confer high activity; di-n-alkyl and diaryl sulphoxides are almost inactive. Thiolsulphinates, RSS(O)R', were found to be less dependent on R and R'.

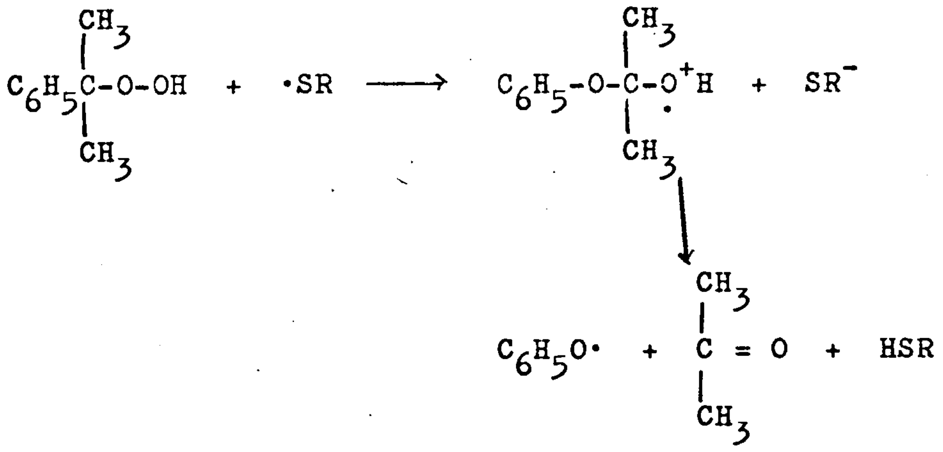
Colclough and Cunneen[22] observed that sulphoxides which were efficient antioxidants were also thermally unstable. Barnard et al[23] also reported that the longest induction period occurred when the most thermally unstable sulphoxide was used as the antioxidant. The sulphinic acid, sulphonic acid, sulphone, thiolsulphonate and thiolsulphinate which are capable of being produced from the sulphide were not as active as the sulphoxide. It was claimed that the sulphoxide was the true retarder. It was found[23] that after an initial uptake of oxygen, oxygen uptake is depressed to a value determined by (i) the efficiency of the sulphoxide as inhibitor (ii) the ease with which the sulphoxide is formed from the monosulphide under the oxidation conditions, and (iii) the readiness with which the sulphoxide undergoes thermal decomposition.

Cain and Cunneen[24] extended the work on monosulphides by studying a series of aliphatic keto-sulphides, $R{\cdot}CO{\cdot}(CH_2)_nSR'$ where n = 0 to 4. Only the homologues having n = 2 inhibit the thermal oxidation of squalene at 75°C. Initial absorption of small amounts of oxygen by squalene - γketosulphide mixtures before inhibition occurs indicates that the effective antioxidant is formed from the γ-ketosulphide. The inhibitory action was associated with the sulphoxide. The differences in activity of different γ-ketosulphides were explained by differences in the thermal stability of the γ-ketosulphoxides.

From their study of the antioxidant action of sulphoxides Bateman et al[25] deduced that their action of the sulphoxides was not due to a rapid reaction with the hydroperoxide. It was found that on addition of di-tert-butyl sulphoxide to autoxidizing squalene the rate of oxygen absorption immediately reduced to zero, whereas the fall in hydroperoxide content occurred much more slowly[25]. They concluded that the primary source of inhibition lies not in removal of hydroperoxide but in some form of molecular association between the sulphoxide and the hydroperoxide. This is consistent with the fact that the addition of stearic acid, which bonds strongly with sulphoxides, can disrupt their complex formation with hydroperoxide and hence counteract their inhibitory action. It was also reported[25] that any given sulphoxide inhibits more efficiently the earlier it is added during autoxidation, its concentration relative to hydroperoxide is then greater. This ratio should be unity for substantial inhibition to result. Di-tert-butyl sulphoxide and 4,4,dimethyl-1-t-butylsulphinylpentan-3-one which are both effective when this ratio is 0.1 is a significant anomaly..

Apart from the above anomaly this 'complexing out mechanism' does not explain why the activities of the antioxidant depend so greatly on the substituents R and R'. It also leaves unexplained the facts that the most effective antioxidant (i) promotes the decomposition of the hydroperoxide most readily and (ii) the most effective are the most thermally unstable.

Kennerly and Patterson[26] also studied various sulphides as antioxidants and also concluded that they were only the precursor of the active antioxidant whose function was to decompose hydroperoxides by a non-radical mechanism. With cumene hydroperoxide the sulphide gave phenol as a product. This is the acid catalysed decomposition products[27] and suggests an ionic mechanism. As there is no obvious route for the conversion of the phenol sulphides, which were used, to a sulphonic acid Kennerly suggested that a thiyl radical intermediate was responsible for the decomposition (reaction 14).



$$C_6H_5\overset{CH_3}{\underset{CH_3}{C}}\text{-O-OH} + \cdot SR \longrightarrow C_6H_5\text{-O-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}\dot{O}^{+}H + SR^{-}$$

$$\downarrow$$

$$C_6H_5O\cdot + \overset{CH_3}{\underset{CH_3}{C}} = O + HSR \qquad (14)$$

$$HSR + C_6H_5O\cdot \longrightarrow C_6H_5OH + \cdot SR$$

However in view of work on the decomposition of peroxides by substituted phenols this mechanism seems unlikely[28,29].

Hawkins and Sautter[30] considered the stabilising effects of elemental sulphur, disulphides and sulphur dioxide. It was again shown that the disulphide was the precursor of the active antioxidant. An extension of these studies[5] showed that in general

monosulphides were less effective than disulphides in peroxide decomposition. However didodecylthiodipropionate is a notable exception. Results showed that the oxidation of disulphides to thiolsulphinates is only the first of a series of reactions which leads eventually to the formation of active stabilisers.
In addition to other products sulphur dioxide was detected and tested as a decomposer of cumene hydroperoxide. The decomposition was rapid and did not take place by a stoichiometric reaction. Hawkins and Sautter[5] therefore suggest that sulphur dioxide, formed directly and rapidly from thiolsulphinates, may be an important active stabiliser functioning through peroxide decomposition. It would be formed only as oxidation is taking place and only as required to inhibit oxidation.

Hawkins and Sautter[5,31] also envisage formation of active peroxide decomposers by thermal dissociation of thiolsulphinates and thiolsulphonates. The intermediate sulphinyl and sulphonyl radicals (15 and 16) can react with the hydroperoxide to produce sulphinic and sulphonic acids respectively which can then catalytically decompose hydroperoxides by an ionic mechanism[27].

$$RS(O)SR \longrightarrow RSO\cdot + RS\cdot \qquad (15)$$

$$RSO_2SR \longrightarrow RSO_2\cdot + RS\cdot \qquad (16)$$

No pro-oxidant effects were reported.

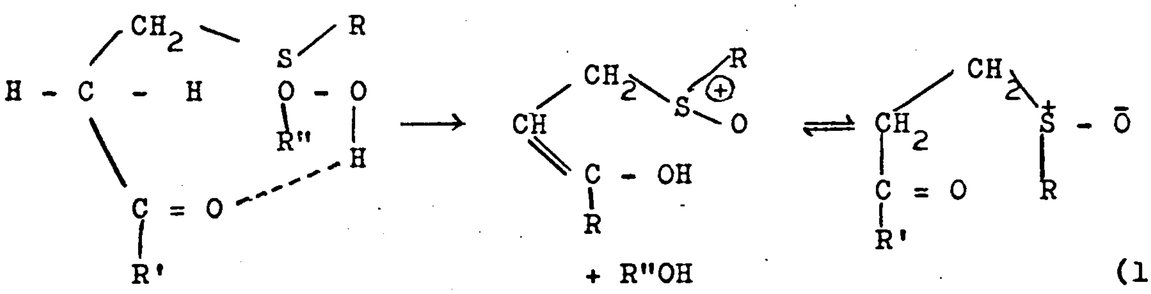
Cain and Cunneen[32] were able to show that dialkenyl and alkenyl alkyldisulphides showed different antioxidant behaviour to that of dialkenyl monosulphides, alkenyl alkyl monosulphides and dialkyl disulphides, and ~~therefore~~ γ-ketosulphides. Thermal oxidation of squalene with the former antioxidants added proceeded autocatalytically but at a much reduced rate. The latter antioxidants produce oxidation curves which provide evidence of secondary antioxidant formation. It was shown that the former type of disulphides had the ability to chaim terminate. The actual process of chain termination was not clarified.

More recently Rahman and Williams[33] studied the effect of disulphides (dialkyl, dibenzyl and diaryl), aryl and alkyl thiols, and phenyl and benzyl sulphoxides on autoxidizing n-decane. The mechanism of inhibition of the disulphides is postulated to be due to interaction with the chain propagating radicals (R· and RO_2·). Eventual products are sulphur dioxide and sulphonic acids which will decompose the hydroperoxide. From the series of radical reactions envisaged it seems surprising that they did not find acceleration of oxidation before final complete inhibition of oxidation. The mode of inhibition by the sulphoxides remains unexplained[33]. No sulphur dioxide was isolated and results would perhaps suggest that inhibition was due to complex formation.

1.3. Dialkyl Thiodipropionates as Antioxidants

The previous section has reviewed the chemistry of sulphides as antioxidants. Reference has already been made to didodecyl thiodipropionate and it is recorded that it is a very effective and widely used antioxidant. The γ-keto structure appears to be one of the important factors involved. Nothing has been reported that indicates that the esters of thiodipropionic acid function in a unique way. Indications are that its effectiveness is due to (a) its oxidation to form the sulphoxide and (b) the effectiveness of the sulphoxide as an antioxidant and that this is linked with its thermal instability. The aim of this section is to provide further information from the literature which is particularly relevant to the thiodipropionates and also forms the basis for the objectives of this project.

Marshall[16] has found the kinetics of the initial stages of the oxidation of didodecyl thiodipropionate to be first order with respect to both hydroperoxide and sulphide. This contrasts with the behaviour of simple dialkyl sulphides which give kinetics that are second order with respect to hydroperoxide in non-hydroxylic solvents ~~(17)~~ and accords with the view that the β carbonyl is involved in the conversion of the sulphide to sulphoxide as suggested by Scott[34] (17). This complex formation therefore facilitates the conversion of the γ-ketosulphide to the sulphoxide which results in the sulphide being a more effective antioxidant.

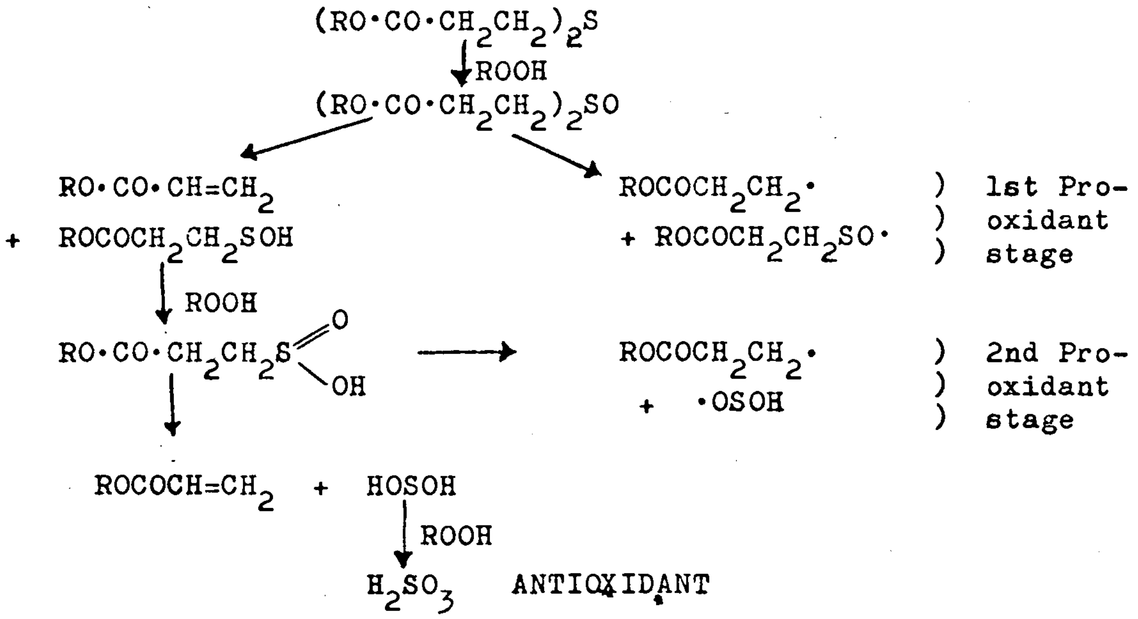


(17)

Holdsworth et al[35] studied the effect of typical peroxide-decomposing antioxidants. With autoxidizing tetralin, didodceyl thiodipropionate was observed to have an initial pro-oxidant effect (rate of oxidation accelerated) before becoming auto-inhibiting. In the later stages liberation of a gas was observed. The pro-oxidant effect was found to be more pronounced the larger the amount of peroxide decomposer added. The products formed by antioxidant-catalysed decomposition of cumene hydroperoxide were consistent with the cationic decomposition, namely phenol and acetone. The hypothesis that sulphur dioxide might itself be the active peroxide decomposer was supported by further experiments in which catalytic amounts of sulphur dioxide caused an immediate and rapid decomposition of cumene hydroperoxide. Phenol and acetone were again the major products.

The pro-oxidant effect of dilauryl thiodipropionate was further studied by Scott[36] and was shown to depend upon the ratio of hydroperoxide to antioxidant. At lower hydroperoxide concentrations two distinct phases of pro-oxidant activity are evident. This was interpreted as arising because of two free radical generating steps occurring before gas evolution. Dilauryl sulphinyl-dipropionate, which is the first product formed in the reaction of dilauryl thiodipropionate with hydroperoxide, was shown to give a larger pro-oxidant effect. In both cases addition of a small amount of phenolic antioxidant removes the initial radical generating reaction. These facts are not consistent with the assumption that sulphoxides may themselves be the effective antioxidants formed from the sulphide[23] Scheme 1 is the series of reactions postulated by Scott[36] to explain both the pro-oxidant and antioxidant effects of the thiodipropionates.

Scheme 1



(Decomposition of ROOH catalytic[27])

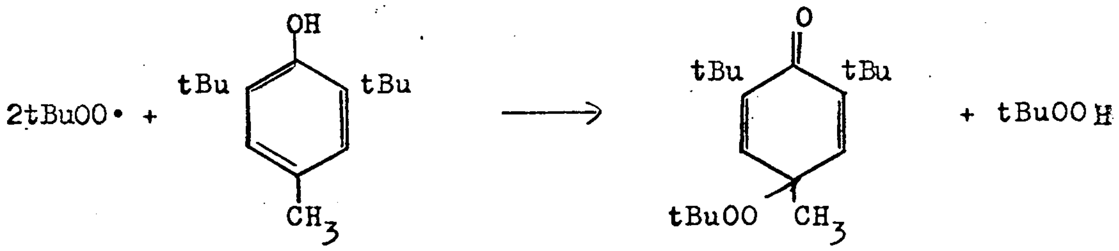
Didodecyl thiodipropionate is marketed by I.C.I. under the trade name of Neganox DLTP. In their technical information leaflet R42 [37] potential users are informed that "in polymers containing relatively high proportions of Neganox DLTP the melt viscosity at high process temperatures tends to decrease". Scott and Shearn[38] have systematically investigated the effect of dilauryl thiodipropionate on the melt stability of polypropylene and have shown that in their early stages of oxidation the stabilising effect of dilauryl thiodipropionate decreases with an increase in the quantities used. However the overall antioxidant activity is increased. When the sulphoxide was used instead of the sulphide, antioxidant activity was never observed. This is consistent with the mechanism of action proposed by Scott[36] and shown in Scheme 1. At high temperatures the dissociation of the sulphoxide is rapid and the pro-oxidant effect becomes controlling.

Neureiter and Bown[8] have shown that the activity of dialkyl thiodipropionates is independent of the alkyl group. Plant and Scott[39] have reached similar conclusions from studies in a sealed system. It was also shown that sulphur dioxide in a sealed autoxidizing system of decalin at the same molar concentrations was as effective as the thiodipropionates[39], giving further support for Scott's mechanism[36]. (Scheme 1).

1.4. Technological Aspects

The end use and the manner of processing of a stabilised product is important in determining the stabiliser system, (i.e. extrusion of polypropylene can require temperatures up to 200°C). To obtain a satisfactory antioxidant system the sulphur compounds are generally used synergistically with phenols. That is, by use of two or more different types of antioxidants the resistance to oxidation of the organic substrate is improved by a greater extent than would be predicted on the basis of strict additivity. For a discussion of synergism see Scott[2] and Reich and Stivala[1].

Scott[36] has suggested that synergism is due to the phenols suppressing the pro-oxidant activity of the thiodipropionates. Neureiter and Bown[8] showed that didodecyl thiodipropionate reacted with the peroxydienone, which is a product of a phenolic antioxidant in action, regenerating the phenol and also giving the sulphoxide (18 and 19)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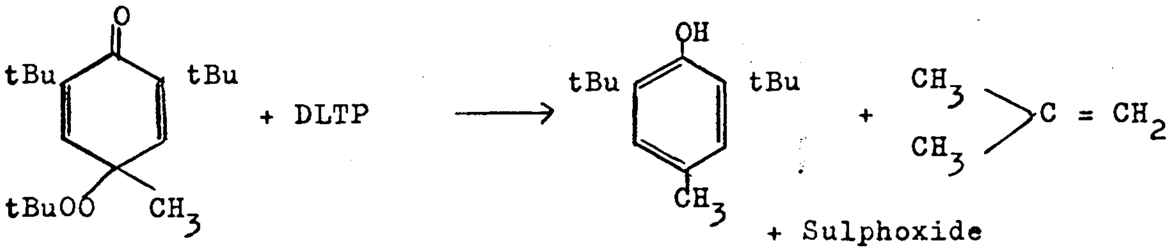
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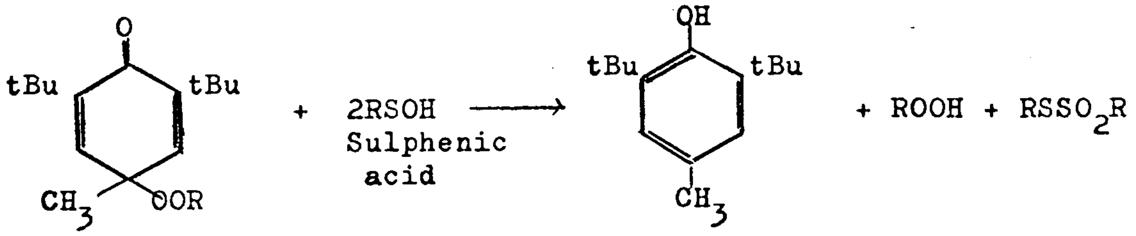
De Paolo and H.P.Smith[42] also suggest that the phenol can be regenerated by the sulphenic acid which is a primary product of the thermal decomposition of dilauryl sulphinyldipropionate[8] (reaction 20)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Polackova [43] believes that the phenolic antioxidant accelerates the reaction of the hydroperoxide with the thioether to give the active species, the sulphoxides.

Mobility, volatility and compatibility of the antioxidant in a technological system are other factors which may determine the effectiveness of an antioxidant[39,44]. The intrinsic antioxidant activity of the alkylthiodipropionates is independent of the alkyl group[8,39], but their effectiveness in technological media is dependent on the alkyl group because of these factors.

From the studies on monosulphide antioxidants it has been established that the sulphoxide is the precursor to the actual antioxidant. However in a stabilising system it is still beneficial to use the sulphide as the antioxidant. This is probably because of the instability of sulphoxides and is illustrated by the work of Scott and Shearn[38]. They found that under processing conditions the sulphoxides were ineffective stabilisers while the sulphides resulted in protection, By using the sulphide the sulphoxide is only produced as required and so acts as a reservoir for the sulphoxide.

A comprehensive review of the patent literature has been published by Voigt[45].

1.5. Scope and Objectives of the Project

Monosulphides, and especially the dialkylthiodipropionates, are an important class of antioxidants. The antioxidant activity is associated with the sulphoxide[8,18,21,22,23,24,25,36], and two explanations for the antioxidant activities of the sulphoxides have been proposed. Firstly, it has been suggested that the sulphoxides merely associate with the hydroperoxide[25] and so deactivates it towards initiation. This mechanism is supported by a number of findings but is unable to explain why the effectiveness of the sulphoxide as an antioxidant depends upon its thermal instability or why di-tert-butyl sulphoxide is effective in immediately stopping the oxidation of squalene when the ratio of hydroperoxide present to the sulphoxide added is 10. The second explanation proposed is that the sulphoxide is a precursor to some active species which decomposes hydroperoxides via a polar mechanism[16,35,36]. The scheme proposed by Scott (page 12) is able to explain why the effectiveness of the sulphoxide depends upon its thermal instability but cannot explain the findings that, under certain conditions, on addition of the sulphoxide to a oxidising substrate oxidation stops immediately. It has also been established that the sulphoxide, under certain conditions, is a pro-oxidant. Dissociation of sulphoxides has been suggested by Cram[46] to account for some of the features of the inversion of optically active sulphoxides and by Stirling[47] to account for the formation of free radical coupled by-products in the rearrangement of 1-naphthylmethyl-p-tolyl sulphoxide to the corresponding sulphenate ester. Miller et al[48] also postulates that racemisation of benzyl-p-tolyl sulphoxide occurs via homolytic scission. Scott[36] therefore suggested that the pro-oxidant effect was a result of the dissociation of the sulphoxide into free radicals which were capable of initiating oxidations.

At high processing temperatures thermal dissociation of the sulphoxide may occur and could account for the pro-oxidant effect under these conditions[38]. The pro-oxidant effect has, however, been established to occur at more moderate temperatures[36]. It was therefore the first aim of this project to investigate the thermal decomposition of dialkyl sulphinyldipropionates under the moderate conditions and establish whether or not the pro-oxidant effect is associated with thermal dissociation. A better understanding of the pro-oxidant effect would allow estimates of the technological importance to be made and perhaps result in improved antioxidant systems. Chapters 3, 4 and 5 are concerned with the pro-oxidant effect.

The second aim of the project was to throw light on how the dialkyl thiodipropionates actually function as antioxidants and in particular to explain why their effectiveness depended upon the thermal instability of the sulphoxide. As it was well established that the thiodipropionates function via their sulphoxide it was decided to study the dialkyl sulphinyldipropionates directly. The methyl ester (to be known as DMSD) was chosen for the study so that kinetic and product analysis would be simplified. The emphasis on this part of the project has been on the attempt to elucidate the true peroxide decomposer. Chapters 3, 6 and 7 are concerned with the antioxidant stage.

Chapter 2

EXPERIMENTAL METHODS

2.1. Apparatus and Techniques

2.1.1. Spectroscopy

Infrared spectra were recorded using Perkin-Elmer spectrophotometers. Unless otherwise stated the model 237 was used for general purpose while the models 457 and 225 were employed for studies requiring better resolution and ordinate expansion.

Visible Spectroscopy. The Perkin-Elmer model 137 spectrophotometer was used in the colourmetric determination of hydroperoxides.

Near-infrared spectroscopy. The region of concern was 5,000 cm^{-1} to 4,500 cm^{-1} and this is covered by the Perkin-Elmer model 225 instrument. This was used in conjunction with the "225 additional recording system".

Nuclear Magnetic Resonance was carried out on Perkin-Elmer R10 (60 Mc/s) and R14 (100 Mc/s) spectrometers. These were equipped with facilities to integrate and use was made of them. Tetramethyl silane was used as the internal standard.

Electron Spin Resonance studies were carried out on a Hilger and Watts Microspin ESR3 spectrometer with 100 KHz modulation and an X-band klystron in conjunction with a Hilger and Watts W937 double-sample cavity.

Mass spectra were obtained using an AEI MS9 mass spectrometer. For exact mass determinations heptacosafluorotri-n-butylamine was employed as the standard.

2.1.2. Gas Liquid Chromatography. Analysis was carried out on a Pye series 104 model 64 instrument. A flame ionisation detector was used unless stated and in the other circumstances a Katharometer was employed. In the former case nitrogen was always employed as the carrier gas at a flow rate of 40 mls per minute. Helium was used for the carrier gas when the Katharometer detector was used. The columns which were employed during the project were 5 feet glass, ¼ inch diameter packed with (a) 15% squalene on 60/80 celite (b) 10% silicone gum on 60/80 celite (c) 10% PegA on 60/80 celite and (d) a 5 foot stainless steel column packed with Parapak S.

Peak areas were measured with a fixed arm planimeter.

2.1.3. Dry Box

The preparation and manipulation of methyl-β-sulphopropionate were carried out using a two compartment dry box manufactured by SLEE (London). The box was purged with dry nitrogen and a beaker of concentrated sulphuric acid and a dish of phosphorous pentoxide were kept in both compartments.

2.1.4. Distillation Techniques

Fractional Distillation. For quantities in excess of 100 mls the materials were distilled through a 2 foot column packed with Dixon Gauze rings. For smaller quantities a 9 inch column was usually employed.

2.1.5. Oxygen Absorption

2.1.5.1. The apparatus

The oxygen absorption of the solutions studied were followed continuously and automatically using the apparatus[49] shown diagramatically in Figure 2.1. The reaction vessel is a 50 ml three-necked quick-fit round bottom flask fitted with a tap which has a luer needle cemented in at the opening. This allows the flask to be vented to the atmosphere and for calibration of the equipment. To the second neck the bucket dropping device (Figure 2.1, A) or a tube crushing device (Figure 2.1, B) is fixed. These allow the additive to be added at will to an autoxidizing solution. The choice of the device used depends upon the nature of the compound to be added. The reaction vessel is charged with the oxidizing solution, purged with oxygen, placed in a thermostatted bath and then connected by capillary glass tubing to the wet side of a pressure transducer. The dry side of the pressure transducer is connected to a ballast flask, which has the same volume as the reaction vessel, and is placed alongside the reaction vessel in the bath. Capillary tubing is used for connections outside the bath and the distance is kept small so that the volume of the apparatus not thermostatted is negligible to the total volume of the apparatus. Any pressure difference between the reaction vessel and the ballast flask is proportional to the voltage output of the pressure transducer, and this is recorded using a Servoscribe (Smiths Ltd.) millivolt recorder. Hence as oxygen is absorbed by the contents of the reaction vessel the pressure difference becomes greater and the voltage becomes correspondingly greater.

The transducer used was a strain gauge type manufactured by Pye Ether Ltd. and is model UP1 (± 10" WG). The size of the output voltage is proportional to the input voltage so by varying the input voltage the sensitivity of the transducer to pressure fluctuations can be varied.

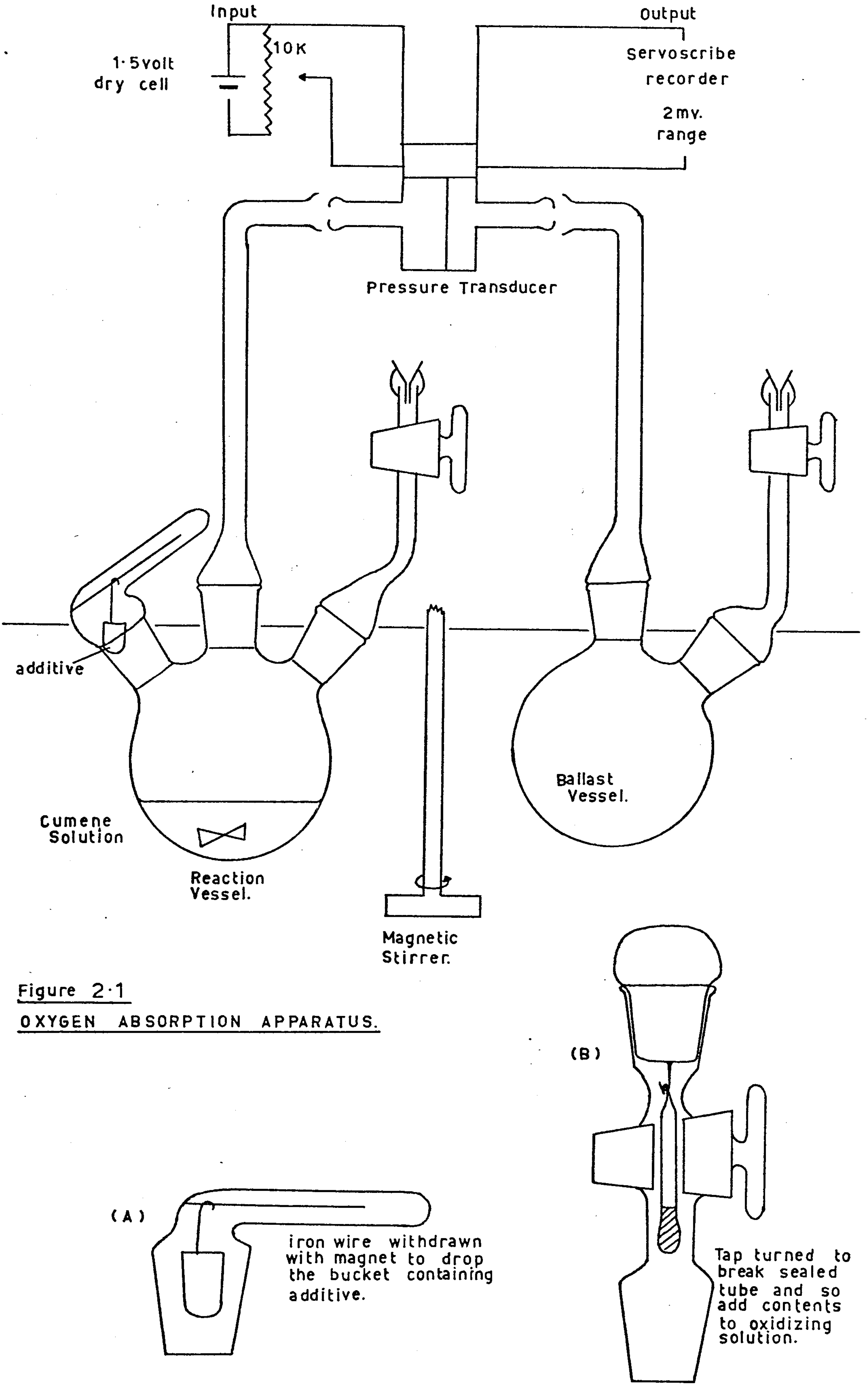


Figure 2·1

OXYGEN ABSORPTION APPARATUS.

To determine the amount of gas that is absorbed or evolved a syringe is fitted to the luer needle attached to the tap. Volumes of air are added or withdrawn and the corresponding deflection on the recorder recorded. In practice a calibration check was made at the end of each run by simply syringing out a number of different volumes of gas and marking the corresponding deflections alongside the recording of the oxygen absorption of the experiment.

The maximum pressure change which was allowed to occur was 8%. If oxygen was still being absorbed oxygen was simply added by carefully opening the tap to a atmosphere of oxygen. The reaction is therefore carried out, to all intents and purposes, at constant pressure. Also the rate of oxygen absorption above 100 mm pressure is independent of oxygen pressure[50].

2.1.5.2. Reproducibility

Pyrex glass reaction vessels were used and it was found that an ageing period was required before reproducible results were obtained. A solution of cumene hydroperoxide in cumene oxidized faster in a virgin vessel than in an aged one. On ageing the rate of oxidation of a stock solution of cumene hydroperoxide in cumene was reproducible within ± 8%. However if a solution of $\alpha\alpha$-azoisobutyronitrile (AZBN) in cumene was studied then the rate was reproducible within ± 3%. To age the vessels the flasks, complete with glass stirrer and bucket, were filled with a solution of hydroperoxide in cumene and left open to the atmosphere, immersed in a bath at 75°C and left for a few days. Once aged the vessels were merely washed with acetone and water between runs.

2.1.5.3. Procedure

The solution of pure cumene and initiator (AZBN or cumene hydroperoxide) was pipetted (5 mls) into the reaction vessel. In the case of dimethyl thiodipropionate and dimethyl sulphinyldipropionate the additive was weighed into the small glass bucket and suspended by the iron wire sheathed in glass in the dropping device (Figure 2.1, A). This was attached to the vessel along with the tap, via which the flask was purged with oxygen while the solution was stirred by the magnetic follower, also sheathed in glass. After ten minutes the apparatus was transferred to the bath (± 0.05°C) and connected to the transducer. The ballast flask was already attached and after about 5 minutes the taps on both vessels were opened to the atmosphere and then both closed so that the vessels were now at atmospheric pressure. The cumene solution was stirred fairly fast and the oxygen absorption was recorded. When a constant rate of oxygen absorption was apparent the additive was added using a magnet to withdraw the iron wire and so dropping the bucket. The effect of the additive was then recorded.

2.1.5.4. The Addition of Methyl-β- Sulphopropionate.

Methyl-β-Sulphopropionate is very hygroscopic and had to be manipulated in a dry box. A preweighed drawn-out tube was therefore filled with the sulphonic acid, stoppered, reweighed and finally sealed placing a hook on the end. This small glass ampoule was then suspended as shown in Figure 2.1, B and when the acid was required to be added the ~~t~~ap was turned, crushing the glass ampoule and dropping the contents into the vessel.

2.1.5.5. Recording of Results

The results given in Chapter 3 have all been recorded in the above manner. On multi-result curves the rate of oxygen absorption before addition (the control) is a mean of the individuals recorded. In the case of Figure 3.2 the results were traced off the recorded curves, superimposed and photographically reduced. Other results have been taken off the actual traces by measurement, applying a suitable scaling factor where needed.

2.1.6. Gas Evolution Measurement

The apparatus described above was also used to follow the gas evolution occurring during the decomposition of dimethyl sulphinyldipropionate and the reaction of methyl-β-sulphopropionate with cumene hydroperoxide. The pressure of the ballast flask was initially greater than the pressure of the reaction vessel. As gas was evolved the voltage output of the transducer was reduced.

2.1.7. Kinetics of Methyl Acrylate Formation

Solutions of dimethyl sulphinyldipropionate (DMSD) were made up in the appropriate solvent and n-octane was added to it as an internal standard for g.l.c. measurements. The solutions were portioned into Carius tubes and thoroughly degassed by freezing, evacuating and warming and repeating the procedure until no more dissolved gases were apparent. The tubes were finally sealed under vacuum and immersed in a thermostatted bath (± 0.05°C) and then removed periodically, opened, and the contents analysed for methyl acrylate by g.l.c. For carbon tetrachloride, dioxan and chlorobenzene, the squalene column was used at 75°C while the silicone gum column was used at 75°C for the styrene solutions. A fixed arm planimeter was used to determine the peak areas of the methyl acrylate and n-octane peaks. Calibrations were made with solutions of freshly fractionated methyl acrylate and n-octane. Linear plots of concentration of methyl acrylate against the peak area of methyl acrylate over the peak area of the constant amount of n-octane used were obtained. The reproducibility was within ± 2% (Figure 2.2).

When determinations were carried out in the presence of Galvinoxyl, a solution of dimethyl sulphinyldipropionate and n-octane was added to a weighed amount of Galvinoxyl and the above procedure repeated.

2.1.8. Disappearance of Galvinoxyl

Quartz tubes were filled, using an Agla syringe, with equal volumes of a solution in carbon tetrachloride containing the dimethyl sulphinyldipropionate and Galvinoxyl (0.0015 moles ℓ^{-1}). The solutions were thoroughly degassed, as in section 2.1.7., and sealed. For a standard solution a thoroughly degassed solution of Galvinoxyl (0.0015 mole ℓ^{-1}) in carbon tetrachloride was used and this was found to give a constant e.s.r. signal over many weeks. This solution was kept in one of the cavities. The solutions to be examined were immersed in a thermostatted bath for various intervals of time and then transferred to the remaining e.s.r. cavity and the e.s.r. signal recorded. Immediately afterwards the signal of the standard Galvinoxyl solution was recorded and the signals compared. Calibrations using solutions of known concentration of Galvinoxyl were made and a linear plot of concentration of solution against the ratio of the amplitudes of the signals of the sample and standard was obtained. The signals were not fully resolved because a two minute sweep over 50 gauss was employed. However the method proved very satisfactory for following the disappearance of Galvinoxyl. The spectrum of the Galvinoxyl solution was fully resolved from time to time so as to establish whether or not Galvinoxyl was the only species present. In all cases a well resolved spectrum identical to that reported for Galvinoxyl was obtained[51].

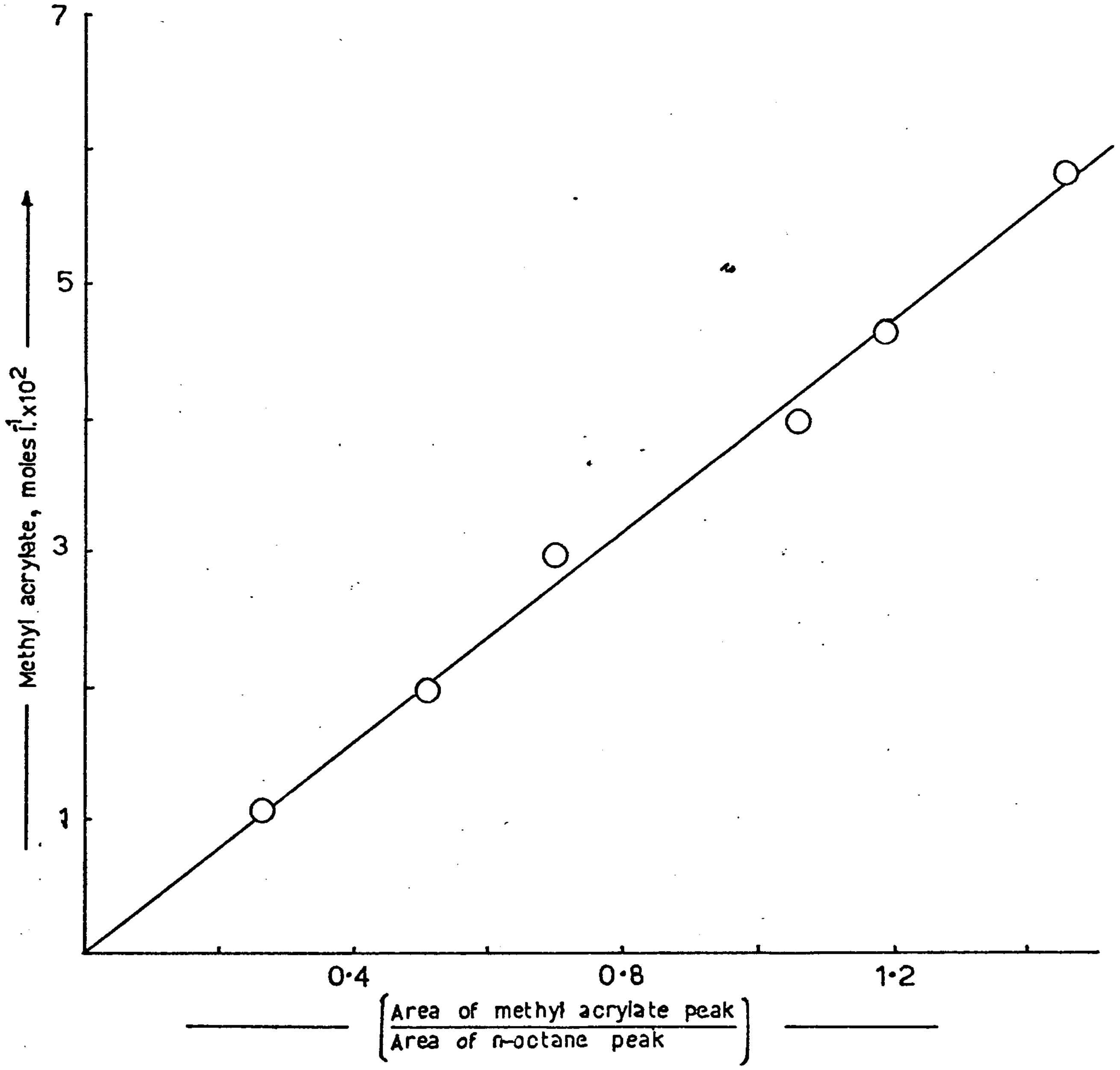


Figure 2·2

Calibration graph used for the quantitive determination of methyl acrylate by g.l.c.

Column - Squalene on Celite
Temperature - 75° C
n-Octane - 0·015 M

2.1.9. Measurement of the Rates of Polymerisation

2.1.9.9. Theory

Tha rates of the polymerisation of styrene were followed and calculated by dilatometry. It has been shown that the densities of polymer and monomer bear a linear relationship to composition[52] and that the apparent specific volume of polystyrene in solution does not vary with the degree of polymerisation, if the latter is sufficiently high[53]. Hence if the density of the monomer and polymer are d_m and d_p respectively, for a 100% conversion of monomer into polymer the percentage contraction in volume occurring $= \dfrac{({}^{1}/dm - {}^{1}/dp)100}{1/dm}$. If the contraction in volume of a known volume of styrene can be measured the percentage contraction can be expressed as the percentage conversion

$$\text{i.e. Percentage Conversion} = \frac{\text{percentage contraction}}{\left(\dfrac{{}^{1}/dm - {}^{1}/dp}{{}^{1}/dm}\right)}$$

By means of dilatometry the rate of polymerisation is followed by determining the rate of contraction, and by knowing the volume of styrene this is expressed as the percentage rate of contraction which can then be converted, using the above, to the percentage rate of conversion. Hence the rate of polymerisation can be expressed as x% conversion per minute or in moles litre^{-1} sec^{-1} according to:

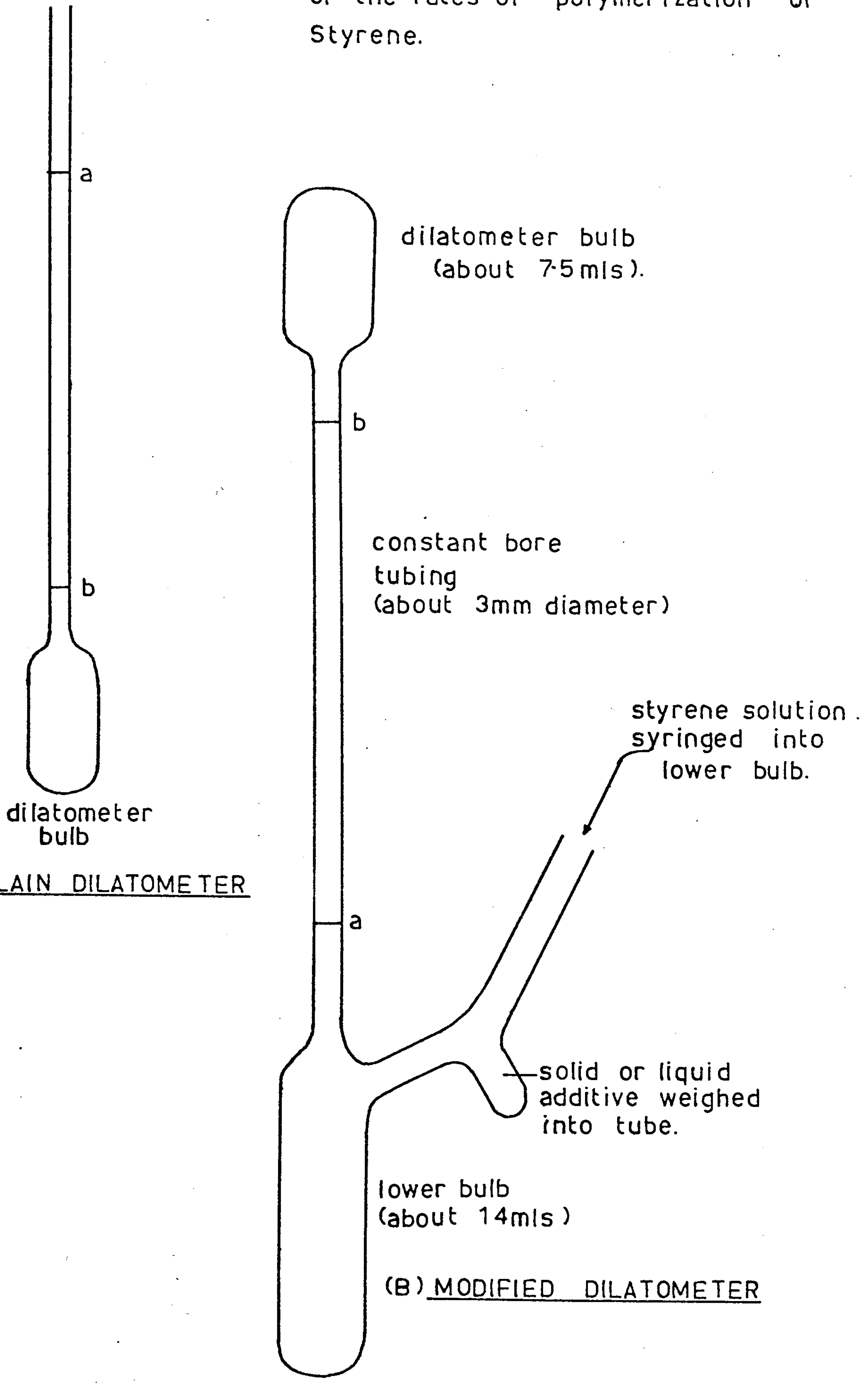
$$\text{Rate of Polymerisation (moles } \ell^{-1} \text{ sec}^{-1}) = \frac{x \times dm \times 10}{\text{Mol.wt.of monomer} \times 60}$$

2.1.9.2. Apparatus

For the experiments dilatometers shown in Figure 2.3 were calibrated accurately,at room temperature, using mercury. The volumes of the bulbs up to b and the volumes of the tube between

Figure 2·3

Dilatometers used in the measurement of the rates of polymerization of Styrene.



(A) PLAIN DILATOMETER

(B) MODIFIED DILATOMETER

a and b were measured by weighing the dilatometers full of mercury to a and b. The distance between a and b was measured accurately using a cathetometer and hence the volume per cm length of dilatometer tubing was also calculated. The calibration data for each dilatometer were not corrected to the temperature of the measurements and Table 2.1 shows that errors in determinations at 75°C could only be small. A comparison with the rates of AZBN and thermal initiated polymerisation of styrene that we have obtained show good agreement with results obtained by other workers.

Table 2.1

Comparison of results obtained for the polymerisation of styrene with the results of other workers

	Our results	Other workers
Rate of bulk polymerisation of styrene at 75°C 10^6 x moles ℓ^{-1} sec^{-1}	9.7	9.25 [54]
Rate of polymerisation of styrene initiated by AZBN (0.01M) at 75°C 10^4 x moles ℓ^{-1} sec^{-1}	3.1	3.4 [55]

2.1.9.3. Procedure for thermal and AZBN initiated polymerisation studies

Styrene freed of inhibitor was redistilled under reduced pressure immediately before use and then outgassed with nitrogen before making up the styrene solutions. The solutions were then transferred to the pre-calibrated plain dilatometers (Figure 2.3, A) reflushed with nitrogen and sealed. The dilatometers were then immersed in a thermostatted oil bath (± 0.05°C) using viscometer holders. After allowing for thermal equilibrium to be attained the height of the meniscus was followed using a cathetometer. During the course of the readings the level of the mark b was recorded, enabling the total volume of styrene in the dilatometer to be calculated. The rate of contraction was then calculated from a plot of meniscus height against time. This was then converted to the rate of polymerisation using the procedure outlined in section 2.1.9.1. The values of d_m and d_p used were obtained from the tabulation by Patnode and Scheiber[56].

During the course of polymerisation the concentration of monomer and catalyst decrease while there is an increase in the viscosity of the system. Such changes affect the polymerisation processes (termination especially). In the experiments carried out the rates of polymerisation were constant during the period of study which corresponded to between 5 and 10% conversion. The results are therefore not affected by these complicating factors. The rates were reproducible within 5%.

2.1.9.4. Procedure for the cumene hydroperoxide (CHP) initiated studies.

The above method did not give reproducible results for the polymerisation of styrene initiated by CHP in the presence of dimethyl sulphinyldipropionate (DMSD). The dilatometer shown in Figure 2.3, B was therefore designed. The DMSD was weighed into the small tube shown and then the styrene containing the CHP was syringed into the larger "lower bulbs". The solution was then rigorously degassed by freezing, evacuating, warming and repeating the process several times. The dilatometer was finally sealed under vacuum. Just before measurement, the styrene was warmed in the thermostatted bath, mixed with the DMSD, and then transferred to the smaller "dilatometer bulb". The dilatometer was then immersed in the thermostatted bath and the rate of polymerisation measured as in 2.1.9.3. This technique was used for determining the rates of polymerisation shown in Figures 5.3 curves A and B. Reproducibility was within 6%.

2.1.9.5. Measurements in Oxygen

The styrene was out-gassed with oxygen for fifteen minutes before making up the solutions. The plain dilatometers were used with the ends left open to the atmosphere.

2.1.9.6. The effect of dimethyl thiodipropionate on the polymerisation of styrene

The procedure given in section 2.1.9.3. was used.

2.1.10. Near infra-red and infra-red study of the sulphoxide - hydroperoxide association

2.1.10.1. Demonstration of complex formation

Two, 2 cm spectrosil cells were placed alongside each other in the sample path of the 225 spectrophotometer. One of the cells contained a 0.04M solution of dimethyl sulphinyldipropionate in carbon tetrachloride while the other contained a 0.04M solution of cumene hydroperoxide (CHP) also in CCl_4. The matched cells full of carbon tetrachloride were placed in the reference beam and the spectrum in the region 4,500 to 5,000 cm^{-1} was recorded. Without touching the cells the contents of the cells containing the DMSD and CHP were intermixed by use of two glass syringes. The spectrum was rerecorded. Figure 6.1 shows the result of mixing the two solutions together. No other changes were observed in the region studied.

2.1.10.2. Estimation of the equilibrium constant, K, for complex formation

A 5 cm (22 mm diameter) spectrosil cell was filled with CHP in carbon tetrachloride and the band at 4,830 cm^{-1} recorded using the model 225 spectrophotometer with the model 225 additional recorder attached. This allowed the spectrum to be expanded and facilitated more accurate measurements. A plot of the band height, "h", as shown in Figure 6.1 against the concentration of CHP gave a smooth curve. The process was repeated under identical conditions using a solution of CHP in carbon tetrachloride with added dimethyl sulphinyldipropionate (0.04M). At the concentrations of CHP studied "h" was always reduced when DMSD was present. It was therefore assumed that this reduced value of "h" was due to unassociated cumene hydroperoxide and the amount present (CHP) free could be read directly off the calibration graph. The temperature of the cells was allowed to come to equilibrium before the spectra were recorded. The temperature of the cell was determined by use of a iron-constantine thermocouple.

The equilibrium constant of formation of the molecular complex was determined by a method similar to Augdahl et al[57]. The basic assumption is that it is a 1:1 complex and therefore for

$$a + b \rightleftharpoons x$$

$$K = \frac{x}{(a-x)(b-x)}$$

$$= \frac{[\mathrm{CHP}]_{\mathrm{initial}} - [\mathrm{CHP}]_{\mathrm{free}}}{[\mathrm{CHP}]_{\mathrm{free}} \times \left([\mathrm{DMSD}] - ([\mathrm{CHP}]_{\mathrm{initial}} - [\mathrm{CHP}]_{\mathrm{free}})\right)}$$

where $[\mathrm{CHP}]_{\mathrm{initial}}$ = concentration of CHP made up in solution

$[\mathrm{CHP}]_{\mathrm{free}}$ = concentration of [CHP] that is apparently in solution according to calibration graph.

$[\mathrm{DMSD}]_{\mathrm{initial}}$ = concentration of dimethyl sulphinyldipropionate in the original solution.

A study of the sulphur oxygen stretch at 1052 cm^{-1} using the Perkin-Elmer 457 spectrophotometer fitted with 2½ x expansion facilities gave similar results. Figure 6.2 shows the reduction of the intensity of the band caused by the presence of CHP. Spectra were recorded using KBr plates with a 1 mm spacer. A plot of the percentage transmittance of the bond at 1057 cm^{-1} against the concentration of a pure DMSD solution in carbon tetrachloride gave a smooth curve. A stock solution of DMSD in carbon tetrachloride (0.02M) was then used to make up solutions containing various amounts of CHP. The spectra of these solutions were then recorded immediately after the calibration and it was observed that while the transmittance of other bands in the spectra were unaltered the transmittance of the sulphur oxygen stretch was reduced. It was thus assumed that the band at 1057 cm^{-1} was due to unassociated sulphoxide and so the concentration of associated sulphoxide and hence the concentration of the molecular complex could be estimated from use of the calibration graph. K was then calculated according to

$$K = \frac{[DMSD]_{initial} - [DMSD]_{free}}{[DMSD]_{free} \times \left([CHP]_{initial} - ([DMSD]_{initial} - [DMSD]_{free})\right)}$$

2.1.11. The Kinetics of the DecompositionofCumene hydroperoxide (CHP)

2.1.11.1. Quantitative analysis of CHP in the presence of DMSD was carried out according to the method developed by Bocek[58]. DMSD and its decomposition products do not interfere.

A volume of the solution containing about 6 x 10^{-7} moles of hydroperoxide was added to a 25 ml volumetric flask and about 10 ml of Analar benzene then added followed by 0.5 ml of a 0.004M solution of phosphoric acid in methanol. 5 ml of the standard 0.0005M solution of ferrous ammonium sulphate in methanol was then added and washed down with benzene. The flask was allowed to stand for fifteen minutes before adding 1 ml of 0.5% solution of σ-phenanthraline in benzene and finally made up to the mark with benzene. The sample was allowed to stand for half an hour and then analysed in the Perkin-Elmer 137 spectrophotometer between 490 and 520 mμ. A blank sample was prepared in the same way, with pure benzene in place of the specimen.

The difference between the absorbance of the blank sample and the analytical sample then gives the quantity of divalent iron that has been oxidised by the hydroperoxide. Using a fixed volume of solution and varying the concentration of hydroperoxide a calibration of the difference in absorbance against hydroperoxide concentration was constructed.

The standard ferrous solution was made up by dissolving 1.9608 g of ferrous ammonium sulphate in a 100 ml volumetric flask with 1.38 mls of concentration sulphuric acid in methanol (Analar grade). 10 mls of this solution was diluted to 1ℓ using methanol. The solution was kept well stoppered. Blank measurements were made very frequently (at least one per experiment).

2.1.11.2. Determination of the Rate of Decomposition of CHP by DMSD

The reaction vessel employed is shown in Figure 2.4. A solution of the CHP in the appropriate solvent was pipetted (2 mls) into one arm of the vessel while the solution of DMSD was pipetted into the other. The vessel being made so that pipettes (2 ml) could be placed in the arms of the vessel when the taps were removed. The vacuum taps were replaced and the rubber septum secured over the sampling end. If the run was to be carried out in the absence of oxygen the solution was then degassed by freezing, evacuating the vessel and then warming. This procedure being repeated several times before filling the tube with white spot nitrogen, which had previously been passed over red-hot copper turnings. The vessel was then transferred to a thermostatted oil bath (± 0.05°C) and the solution allowed to equilibrate for ten minutes. At time $t = 0$ the solutions were mixed by tipping the solutions from one arm to the other. Samples of the solution were then withdrawn via the rubber septum with a syringe fitted with a six inch needle which was capable of reaching the bottom of the vessel. The analytical sample was then added to a 25 ml volumetric flask and the amount of hydroperoxide determined by the method given in 2.1.11.1.

For the majority of the experiments a solution containing 0.15 moles litre^{-1} of CHP was used. In these circumstances a

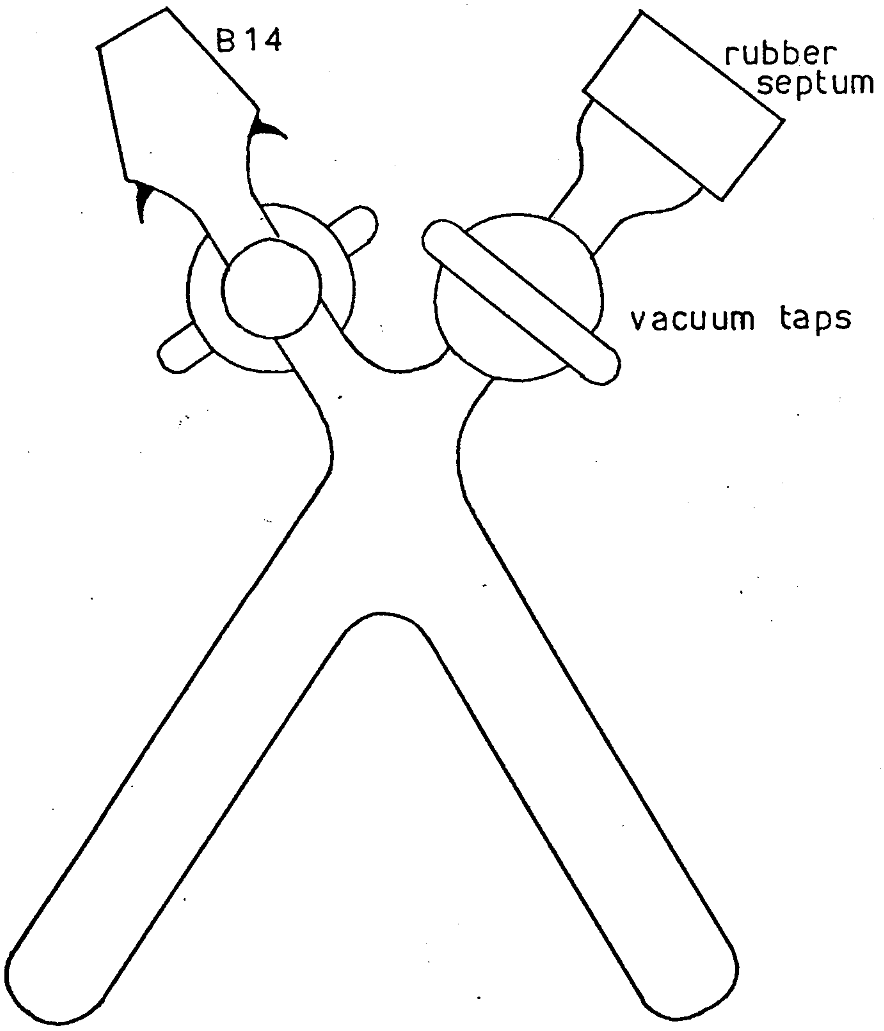


Figure 2·4
Reaction vessel employed in the study of the decomposition of cumene hydroperoxide.

5µl SGE syringe was used to withdraw 4µl of solution. This meant that initially 6.0 x 10^{-7} moles of hydroperoxide were analysed. The volume of the sample was always adjusted so this was the initial amount of hydroperoxide for analysis (i.e. at time t = 0).

The results of hydroperoxide decomposition were then plotted according to a first-order rate expression, i.e. the log of $[CHP]_0/[CHP]_t$ against the time t, where $[CHP]_0$ is the concentration of hydroperoxide at the beginning of the reaction and $[CHP]_t$ is the concentration at time t. Results were reproducible within 5%

2.1.11.3. The Decomposition of CHP by U1.

U1 is the solid product obtained from the reaction of DMSD with CHP (Section 6.3.3.). The solid was weighed into a quick-fit test tube and the cumene hydroperoxide solution (0.15M) pipetted on to it. The test tube was then fitted with a tap adaptor which had a rubber septum fitted and immersed in the thermostatted bath. The tube was continuously shaken and 4µl samples removed for hydroperoxide analysis, by means of a syringe, through the rubber septum and bore of the tap. The solution (4µl) was added to a 25 ml volumetric flask and the concentration of hydroperoxide determined by the procedure of 2.1.11.1.

2.1.11.4. The Decomposition of CHP by methyl-β-sulphopropionate

Methyl-β-sulphopropionate was placed into a preweighed well stoppered, volumetric flask in a dry box. The flask was then reweighed and chlorobenzene quickly added. With agitation the small amount of solid required dissolved. The solution was then pipetted into one arm of the reaction vessel (Figure 2.4). CHP in chlorobenzene was pipetted into the other arm, the taps replaced and the rubber septum placed into position. The reaction vessel was then thermostatted at 75°C ± 0.05°C for ten minutes before mixing the solutions. The final concentration of CHP was 0.15 molesℓ^{-1} and therefore $4\mu\ell$ samples were removed periodically and the solution analysed for hydroperoxide as previous (2.1.11.1.).

In the case of the most concentrated solution of methyl-β-sulphopropionate the solution was added to neat CHP previously weighed into the other arm.

2.1.11.5. Decomposition of CHP by sulphur dioxide

2.1.11.5.1. Sulphur dioxide solution

Sulphur dioxide was fractionated from a lecture bottle into chlorobenzene and a stock solution of approximately 0.75M made by weighing. The concentration of the solution was then accurately determined by volumetric analysis.

Sulphur doxide reacts with iodine according to

$$SO_2 + 2H_2O + I_2 \longrightarrow H_2SO_4 + 2HI$$

1 ml of the solution was therefore added to 25 mls of a 0.1N iodine solution and the excess iodine titrated with a 0.05M sodium thiosulphate solution previously standardised using potassium iodate. The sulphur dioxide solution was determined as 0.75M.

Portions of the above sulphur dioxide solution were diluted and added to CHP and the time required for complete decomposition of the CHP by the SO_2 estimated. It was found that a solution of sulphur dioxide (7.5×10^{-4} moles litre^{-1}) completely decomposed CHP (0.15M) in about the same time that DMSD (0.01M) decomposed CHP (0.15M)

2.1.11.5.2. Kinetics of Decomposition of CHP by sulphur dioxide

Pure CHP was weighed into one arm of the reaction vessel (Figure 2.4) and 2 mls of the sulphur dioxide solution (7.5×10^{-4}M) were pipetted into the other arm. The taps of the vessel were replaced along with a rubber septum. The vessel was then thermostatted at 75°C and after ten minutes the chlorobenzene solution added to the CHP to make a 0.15M CHP solution. Samples of the solution were then syringed out periodically and the amount of hydroperoxide determined (2.1.11.1.).

2.1.12. The rate of formation of acetone and α-methylstyrene from the reaction of CHP with DMSD.

Two mls of a solution containing CHP (0.15 moles ℓ^{-1}) and DMSD (0.01 moles ℓ^{-1}) in chlorobenzene were pipetted into quick-fit tubes fitted with tap adaptors. The solutions were then degassed by freezing, evacuating, warming and repeating the procedure several times. The tubes were then thermostatted at 75°C ± 0.05°C and removed periodically. One ml of a solution of dioxan in chlorobenzene was then added to the solutions and the amount of acetone and α-methylstyrene present determined by g.l.c. Dioxan is the internal standard and the method is given in section 2.2.5. A solution of CHP in chlorobenzene gave negligible quantities of acetone and α-methylstyrene when chromatogrammed under the same conditions.

2.2. Product Analysis

2.2.1. Methyl Acrylate was identified by g.l.c. using peak enrichment with authentic samples of methyl acrylate. The procedure for quantitative analysis is given in section 2.1.7.

2.2.2. Dimethyl dithiodipropionate

The product solution of DMSD in carbon tetrachloride decomposition was chromatographed on the silicone gum column at 193°C. The presence of dimethyl dithiodipropionate was established by peak enrichment using an authentic sample of dimethyl dithiodipropionate. In the case of the CHP-DMSD product solution the disulphide analysis was made at 170°C and the disulphide was just detectable.

2.2.3. Methyl-β-mercaptopropionate was not detected as a product of the thermal decomposition of DMSD. The carbon tetrachloride solution of the products was chromatogrammed at 95°C on a silicone gum column. No peaks occurred with the same retention time as an authentic sample of methyl-β-mercaptopropionate. For the CHP-DMSD solution the analysis was made at 70°C and results showed that the thiol was not a product.

2.2.4. Quantitative Analysis of Water

(a) Karl-Fischer Method. The potentiometric apparatus, for the determination of water using Karl-Fischer reagent, manufactured by Baird & Tatlock (London) Ltd., was modified by fitting 5 ml burettes and using drying tubes fitted with phosphorous pentoxide on cotton wool. The Karl-Fischer reagent was made up using Cellosolve[59] (2 methoxylethanol) and standardised according to Vogel[60]. The recipe used was 33.25g of iodine, 106.25 mls of pyridine, 425 mls of Cellosolve and 17.25 mls of sulphur dioxide. Standardisation showed that 1 ml of this reagent was equivalent to 0.00255 g of water. Standard water solutions were made up using A.R. methanol distilled from calcium turnings.

For the determination DMSD in carbon tetrachloride (0.04M) was decomposed at 75°C for seven half lives and while still hot 20 mls syringed into the apparatus. The amount of water was determined. This was repeated using 20 mls of carbon tetrachloride solvent and so the amount of water produced by the decomposition of DMSD was calculated. Two determinations gave values of 0.0191 and 0.0194 moles litre^{-1}. The procedure used for calculating the values is well explained in Vogel[60].

When the procedure was repeated using a solution of DMSD decomposed in the presence of excess Galvinoxyl the galvinometer registered excess Karl-Fischer reagent immediately the solution was added to the flask. As the addition of some of the standard water solution did not cause the galvinometer to return, it was concluded that the Galvinoxyl interfered with the method.

(b) Determination by use of g.l.c. Dioxan was freshly fractionated from sodium and solutions of DMSD (0.04M) with and without Galvinoxyl made up. Dry nitrogen was used to flush out these solutions before stoppering. Sealing in the normal way using a torch proved impracticable because on opening the ampoules with the torch,moisture was produced which gave large errors.

The solutions were then decomposed at 75°C. The same dioxan as used to prepare the solutions was used to prepare standard solutions of dioxan and water. These were chromatogrammed on Parapak S at 170°C with helium as carrier gas and a Katharometer detector. 10μl samples of the solutions were injected and the peak area corresponding to water was measured using a fixed arm planimeter. An internal standard was not used but a minimum of three injections of each solution were made and the peak area found to vary ± 5%. A calibration graph of peak area against concentration of water gave a straight line with a small positive intercept (Figure 2.5). This corresponds to the small amount of water present in the dioxan solvent. The product solutions were then analysed under exactly the same conditions and the calibration then rechecked. The amount of water produced by the decomposition was determined by measurement of the peak area of the water peak and reading the corresponding water concentration off the calibration graph. Without Galvinoxyl present 0.019 ± 5% moles ℓ^{-1} of water was produced. With Galvinoxyl no water was produced.

2.2.5. Quantitative determination of acetone, phenol, α methylstyrene αα dimethylbenzyl alcohol and acetophenone

The above products of the decomposition of cumene hydroperoxide were quantitatively analysed using g.l.c. The method required only the PegA column at two operating temperatures and the use of two internal standards. Calibration graphs for the individual products were first constructed. Solutions containing various amounts of α methylstyrene and acetone but a fixed and known amount of dioxan as an internal standard were chromatogrammed at 67°C. The peak heights of the peaks corresponding to acetone, dioxone and α-methyl styrene (retention times 0.5, 1.3 and 5.9 minutes respectively) were measured and plots made of the ratio of the peak height of acetone to dioxane, and α methyl styrene to dioxane against the concentration of the product (Figure 2.6). This procedure was repeated at 145°C using solutions of acetophenone, αα dimethylbenzyl alcohol, 2,6-di-tert-

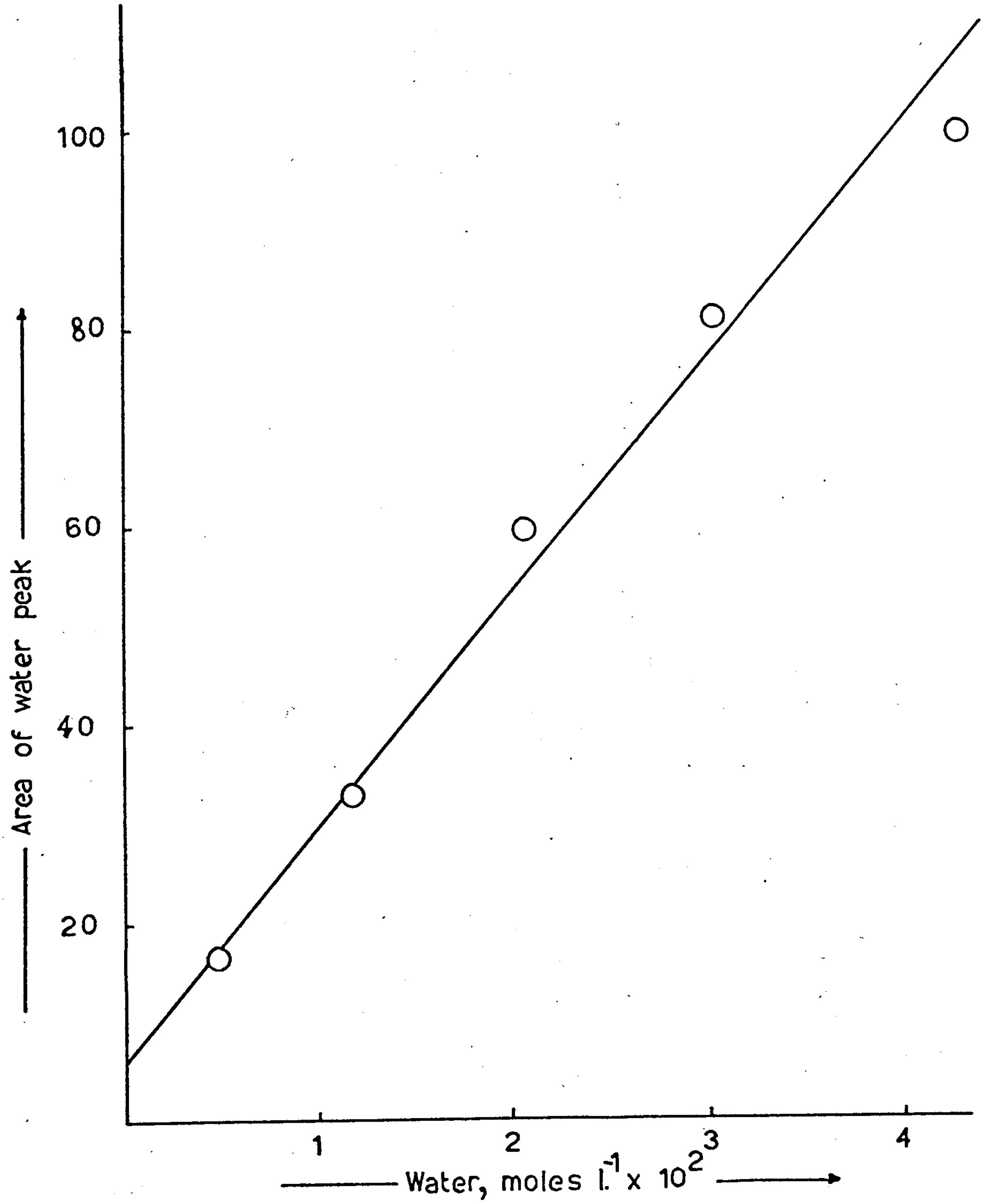


Figure 2·5
Calibration graph used for the quantitive determination of water. Solutions of water in dioxan chromatogrammed on Porapak S at 170°C.

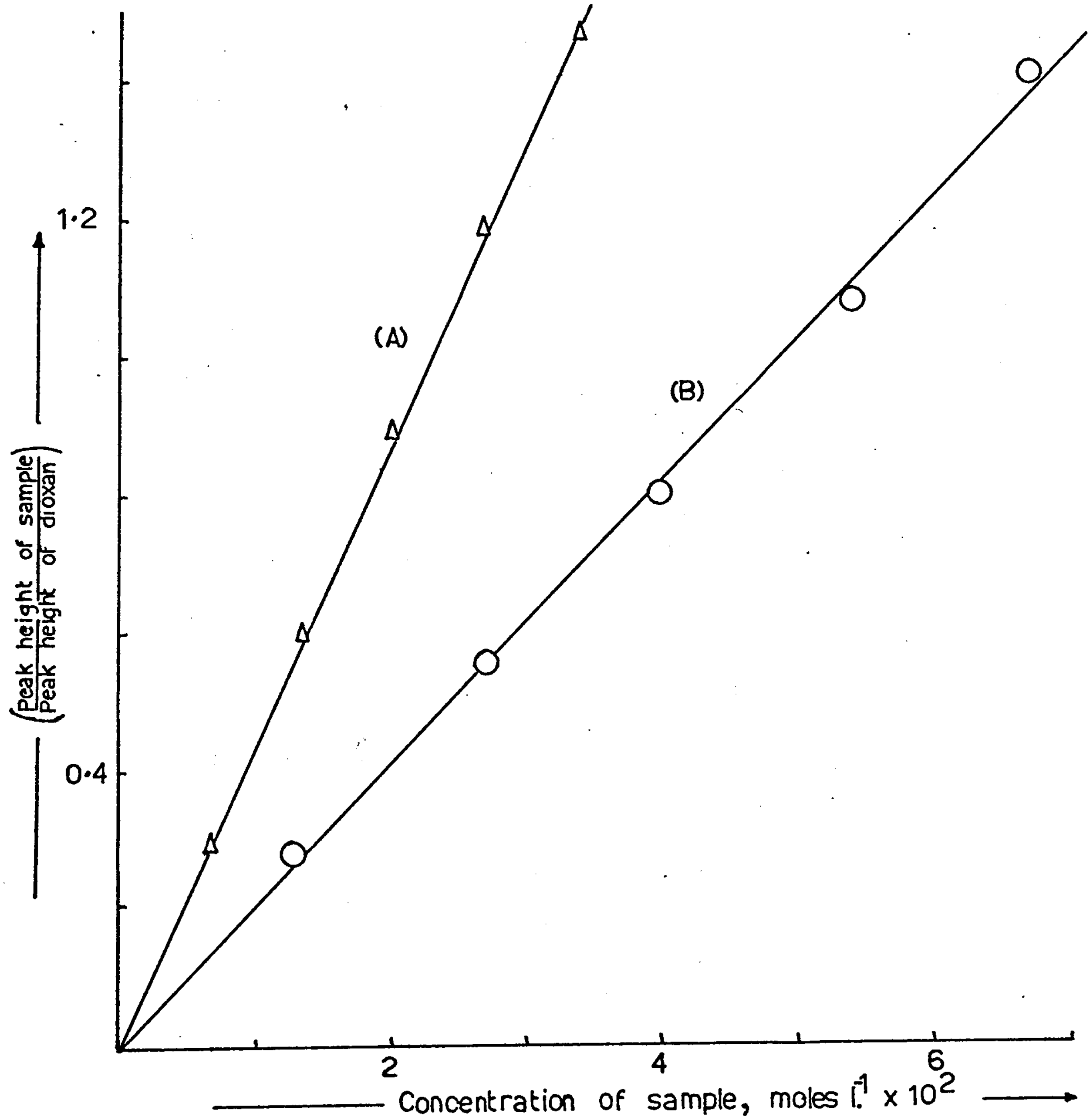


Figure 2·6
Calibration graphs used for the quantitive determination of acetone and αmethyl styrene by g.l.c.

(A)—△— methyl styrene.
(B)—○— acetone.

Column — Peg A
Temperature — 67° C
Dioxan — 0·0022g / 1ml of solution containing sample.

butyl-4-methylphenol (Nonox TBC) as the internal standard, and phenol (retention times 1.5, 2.0, 3.6 and 4.8 minutes respectively). The heights of product to the height of Nonox TBC being plotted against the concentration of product. In the case of phenol the peak area was measured and ratioed with the peak height of the internal standard. In all cases the calibration plots were linear (Figure 2.7).

For the analysis a solution of the internal standards, dioxan and Nonox TBC, was added to a known volume of the solution of the cumene hydroperoxide decomposition products so that the final concentrations of the internal standards were the same as those used for the calibrations. The resulting solution was then chromatogrammed on the PegA column at 67°C and also at 145°C and the peaks corresponding to the products and the internal standards measured. The amount of products in the solution was then determined from the calibration graphs and this quantity was multiplied by a factor which took into account the dilution caused by the addition of the solution of internal standards. This was then the concentration of the product produced by the decomposition of cumene hydroperoxide.

2.2.6. Dimethyl sulphonyldipropionate

The product solution was spotted on to a silica gel t.l.c. plate (pre-heated at 70°C for thirty minutes) alongside an authentic sample of dimethyl sulphonyldipropionate. The plate was developed using chloroform and the compounds located by leaving the plate in an atmosphere of iodine vapour. The sulphone was found to have an R_F value of 0.35 but no dimethyl sulphonyldipropionate was apparent in the product solution.

2.2.7. Sulphur dioxide detection

Attempts to detect the presence of sulphur dioxide as a product of the CHP-DMSD reaction were made using mass spectroscopy. CHP and DMSD in chlorobenzene (300 mls of 0.15M and 0.02M respectively) were reacted in a sealed flask fitted with a tap adaptor for four hours at 75°C. The flask was then attached to an evacuated flask and the taps opened allowing the atmosphere of the CHP-DMSD system to expand into the evacuated flask.. This flask was then attached to the gas sampling valve of the MS9 spectrometer and the mass spectra of the gas recorded. No peak with an m/e value of 64 was apparent.

The product solution was also examined by injecting some into the liquid sample intake of the spectrometer. A small peak at m/e = 64 was apparent. The spectrometer was then adjusted so that only ions of m/e = 64 were monitored. Authentic sulphur dioxide was then introduced into the spectrometer and it was observed that it had a higher m/e value than the ion produced from the solution. Therefore no evidence for the presence of sulphur dioxide was produced.

A solution of the methyl -β- sulphopropionate was similarly studied and again no evidence for sulphur dioxide was established.

2.2.8. Isobutyronitrile was analysed for in the investigation of the chain transfer reaction postulated to occur (3.2). The solutions in chlorobenzene containing (i) AZBN (0.05M), (ii) AZBN (0.05M) + DMSD (0.05M), (iii) AZBN (0.05M) + CHP (0.05M) and (iv) AZBN + CHP + DMSD (all at 0.05M) were degassed and heated at 75°C. After three hours the contents were chromatogrammed on PegA at 65°C. In all cases a small amount of isobutyronitrile was detected by peak enrichment using an authentic sample of isobutyronitrile.

2.2.9. Acid Equivalent Weight determination of U1 and $\beta\beta$'sulphonyldipropionic acid.

A 0.01N sodium hydroxide solution was standardised using sulphamic acid. The acid compound was weighed accurately into a conical flask, distilled water added and the solution boiled. Phenolphthalien was then added as indicator and the solution titrated against the standardised sodium hydroxide. This was repeated using bromothymol blue as indicator.

$$\text{Equiv.wt.} = \frac{1000 \times \text{wt. of acid}}{\text{Vol.of NaOH} \times \text{Normality}}$$

2.3. Purification of Solvents and Reagents

Solvents and reagents were purified by modifications of the methods given in Weissberger[61]. Literature values are quoted from the Hand Book of Chemistry and Physics[62], Weissberger[61], or the Dictionary of Organic Compounds[63].

Carbon tetrachloride. - Analar grade was kept over calcium chloride and fractionated before use. The first 10% was discarded and the fraction boiling at 77°C used.

Dioxan. - Technical grade dioxan was refluxed with sodium for 24 hours, distilled, fractionated and kept over sodium lead-alloy. It was fractionated before use and the fraction boiling at 101°C used. η_D^{21} 1.4212 (η_D^{20} 1.4224)[61].

Chlorobenzene was fractionated from phosphorous pentoxide and the fraction boiling at 132°C collected. η_D^{19} 1.5228 (η_D^{15} 1.52748)[61].

Styrene was washed with aqueous sodium hydroxide, dried over magnesium sulphate, and then fractionated under reduced pressure. It was then stored at -20°C and a final distillation under reduced pressure carried out immediately before use. The fraction boiling at 37°C/11 mm was collected. η_D^{21} 1.5452. (b.pt. 145°C/760 mm, η_D^{20} 1.5469) [61].

Nitrobenzene was fractionated from phosphorous pentoxide and the fraction boiling at 210°C collected. η_D^{21} = 1.5515 (b.pt. 210.8/760 mm; η_D^{20} 1.5528) [61].

Cumene. - Technical grade cumene was washed with concentrated sulphuric acid, water, sodium bicarbonate and finally water and then dried before fractionally distilling under nitrogen. The fraction boiling at 152°C was collected and stored at -20°C in a well stoppered flask, and refractionated regularly. η_D^{21} 1.4910 (b.pt. 152.39/760 mm, η_D^{20} = 1.4915) [61].

Cumene hydroperoxide was purified via the sodium salt according to the method of Kharash[64]. It was vacuum distilled and the fraction boiling at 52 - 55°C/0.01 - 0.1 mm Hg collected. Iodiometric titration[65] gave values of purity within 98 - 100% . η_D^{20} = 1.5250. (B.pt. 60°C/0.2 mm) [66].

$\alpha\alpha$-Azoisobutyronitrile (AZBN) (ex-Koch-Light) recrystallised from ether. m.pt. 104°C (106°C) [62].

Karl-Fischer Reagent. - This was made up according to the recipe given in 2.2.4. The pyridine and 2-methoxyethanol being previously distilled.

Methylacrylate was fractionated immediately before use and the fraction boiling at 80°C collected. η_D^{20} 1.3975 (b.pt. 80.5°C/760, η_D^{20} 1.3984) [62].

n-Octane (ex-BDH) was fractionated and the fraction boiling at 125.5°C collected. (125.7°C).[61]

Phenol was distilled and the fraction boiling at 182°C collected. m.pt. 40 - 41°C. (m.pt. 43°C) [63].

αα dimethyl benzyl alcohol was distilled and the fraction boiling at 202°C collected. This was then recrystallised from pet-ether (60-80) m.pt. 33°C. (m.pt. 35-37°C) [63].

Acetone. - Analar grade was used without further purification.

Acetophenone was fractionally distilled and the fraction boiling at 202°C collected. η_D^{21} 1.5313. (b.pt. 202°C/760 mm, η_D^{25} 1.5322) [61].

α methylstyrene was distilled and the fraction boiling at 165°C used. η_D^{21} 1.5362. (b.pt. 167-70°C, $\eta_D^{17.4}$ 1.5384) [63].

Isobutyronitrile (pure - ex Koch-Light) was used without further purification.

2,6-di-tert-butyl-4-methylphenol (Nonox TBC) was recrystallised three times from ethanol/water. m.pt. 71°C. (m.pt. 69°C) [63].

Reagents for hydroperoxide determination. Analar grade benzene, methanol and ferrous ammonium sulphate were used. 1,10 phenanthroline hydrate (ex-BDH - indicators) was used for the indicator.

2.4. Preparation of Compounds

2.4.1. Preparation of Dimethyl thiodipropionate.

Thiodipropionic acid (ex-Robinsons Ltd.) was esterified by its reaction with methanol. The procedure given in Vogel[67] for the esterification of dibasic acids was followed. After removing the benzene and excess methanol on a rotary evaporator the ester was vacuum distilled and the fraction boiling at 131 - 132°C/1 mm of Hg collected. Yield 75% on thiodipropionic acid.

η_D^{21} 1.4745. (b.pt. 162-164/18 mm of Hg, η_D^{25} 1.4713)[68]. N.m.r. analysis gave a singlet at 6.35τ and a multiplet at 7.35τ in the ratio of 3:4. This is consistent with the structure of dimethyl thiodipropionate. (No other absorptions were present.) Infra-red analysis was consistent with the ester grouping, $\nu_{C=O}$ = 1740 cm^{-1}.

2.4.2. Preparation of Dimethyl sulphinyldipropionate (DMSD)

This was prepared according to the method of Barnard[69]. Dimethyl thiodipropionate (28g) was dissolved in A.R. acetone (112 g) and cooled to 0°C. Hydrogen peroxide (28%) was then added slowly (18.5 mls) over a period of four hours. The solution was then left at room temperature for two days before removing the acetone on a rotary evaporator. The acetone was then replaced with an equal volume of A.R. chloroform and the solution dried over magnesium sulphate. After removing the chloroform a white solid remained (28.4g - 88% yield). This was recrystallised several times, first with pet-ether and chloroform and then with A.R. carbon tetrachloride to give white crystals m.pt. 64 - 65°C. Overall yield 60%. Found: C, 43.4; H, 6.35, S, 14.4, $C_8H_{14}O_5S$ requires C, 43.2; H, 6.3; S, 14.4%.

Infra-red analysis of a 0.04M solution in carbon tetrachloride with a 1mm spacer gave bands at 1740 cm^{-1} and 1052 cm^{-1}. These have been assigned to the ester carboxyl[70] and the sulphur oxygen stretch of the sulphoxide[69,71] respectively.

Nuclear magnetic resonance analysis gave only two absorptions. A singlet at 6.25τ and a multiplet at 7.05τ. The ratio of the integrated spectrum was 3:4 respectively. These are therefore assigned to the methyl group and methylene protons.

2.4.3. Dimethyl sulphonyldipropionate $(CH_3OCOCH_2CH_2)_2SO_2$.

Attempts to prepare the above from dimethyl thiodipropionate and hydrogen peroxide were not successful. Dimethyl thiodipropionate was oxidised to the sulphone using acid potassium permanganate. The method used is a modification of Barnard et al[69].

Dimethyl thiodipropionate (10.15 g) was dissolved in chloroform (100cc). 3N sulphuric acid was added (250 cc) and the solution stirred vigorously as crushed potassium permanganate (8 g) was added slowly. After the addition, sodium bisulphite was used to decolourize the solution. Distilled water was then added along with sodium hydroxide pellets until the solution was alkaline. The chloroform was separated from the aqueous layer which was further extracted with more chloroform. The extracts were bulked, dried over magnesium sulphate and finally the chloroform was removed on a rotary evaporator to yield 5.5 g of solid. (47.5% yield.)

m.pt. 112 - 113°C (recrystallised twice from ethanol).

Found: S = 13.2, $C_8H_{14}O_6S$ requires 13.4%

N.m.r.:- Three absorptions occur, a singlet at 6.2τ and two distorted triplets at 6.7τ and 7.05τ in the ratios of 3:2:2. Infra-red spectra contains bonds at 1130 and 1307 cm^{-1} which can be assigned to the sulphur oxygen stretch (sym.and asym. respectively) of a dialkyl sulphone[70].

Mass spectral analysis gave no molecular ion ~~occurs~~ corresponding to the sulphone. The peak with the largest m/e value occurs at 207. Exact peak matching gives m/e = 207.03246.

$C_7H_{11}O_5S$ requires m/e = 207.032715 and therefore corresponds to the fragment $(CH_3O\cdot CO\cdot CH_2CH_2SO_2CH_2CH_2\cdot CO\cdot)^+$

2.4.4. Preparation of Methyl-β-mercaptopropionic acid

($CH_3O \cdot CO \cdot CH_2CH_2SH$). By esterification of β-mercaptopropionic acid according to the method used by Baker[72].

A mixture of β-mercaptopropionic acid (101.4g), concentrated sulphuric acid (3 cc), chloroform (300 cc) and methanol (200cc) was refluxed for sixteen hours under a soxhbet apparatus containing anhydrous magnesium sulphate in the thimble. The solution was then washed with water (800 mls - total) and the resulting solution dried over magnesium sulphate. The chloroform was then removed on a rotary evaporator and the resulting liquid vacuum distilled. The fraction boiling at 58-59°C/12 mm was collected, (80 g). Yield 70% on β-mercaptopropionic acid η_D^{20} 1.4633. (b.pt.64-65/13mm [72] and η_D^{19} 1.4625 [73]). Found: S = 27.0, $C_4H_8O_2S$ requires 26.6%. Infra-red spectra contain band at 2570 cm^{-1}, assigned to S-H stretch[70].

N.m.r. Three absorptions occur at 6.25τ, 7.3τ and 8.15τ and the integrated spectrum gives the intensities as 3:4:1 respectively. This is consistent with the compound being methyl-β-mercaptopropionate.

2.4.5. Preparation of Dimethyl dithiodipropionate

Methyl-β-mercaptopropionate (28 g) was dissolved in benzene (200 ml) Water (125 ml) was added and the solution vigorously stirred while iodine (27g) was added in small portions. The benzene layer was separated from the aqueous layer which was further extracted with benzene. The combined organic layer was dried ($MgSO_4$) and the benzene removed. Vacuum distillation gave a middle fraction at 124-125°C/0.3 mm and corresponded to a yield of 71.5%

Found: M, 238.033, $C_8H_{14}O_4S_2$ requires M^+, 238.033.

Found: S = 27.1, $C_8H_{14}O_4S_2$ requires S = 26.9%

η_D^{21} 1.5060

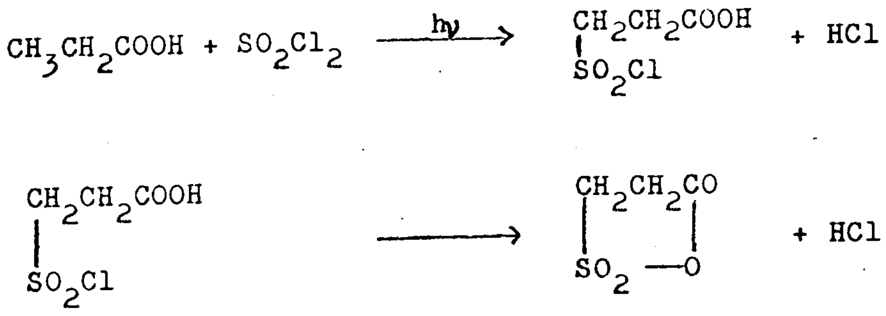
$\nu_{c=o}$ = 1740 cm^{-1}

2.4.6. Preparation of methyl-β-sulphopropionate

Methyl-β-sulphopropionate was prepared by the method due to Kharash[74].

(a) Preparation of β-sulphopropionic acid anhydride

Anhydrous propionic acid (74g) and sulphuryl chloride (185.6 g) were placed in a flask and irradiated with a 300 watt tungsten filament bulb for eight hours. The excess sulphuryl chloride and propionic acid were then removed by distillation under reduced pressure. On addition of dry benzene to the remaining oil a white crystalline solid was obtained. This was filtered and recrystallised from thionyl chloride in a dry box. White fluffy crystals were obtained. M.pt. 78-79°C (m.pt.76-77°C)[74]



$$CH_3CH_2COOH + SO_2Cl_2 \xrightarrow{h\nu} \underset{SO_2Cl}{CH_2}CH_2COOH + HCl$$

$$\underset{SO_2Cl}{CH_2}CH_2COOH \longrightarrow \underset{SO_2\text{—}O}{CH_2CH_2CO} + HCl$$

(b) Preparation of the sulphonic acid from the anhydride

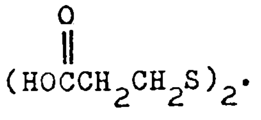
"Super pure methanol" was first prepared according to the method of Vogel[67]. Methanol (A.R.) was reacted with magnesium (with iodine), refluxed for half an hour, fractionated and collected under dry conditions.

All procedures were then carried out in the dry box. β-sulphopropionic acid anhydride (0.055 moles) was added to the pure methanol (0.059 moles) in a small weighing bottle. At the end of the addition, which took half an hour, a white solid crystallised out. The bottle was then transferred to a desiccator which was then evacuated to remove excess methanol from the solid. The melting point of the solid was taken by filling the m.pt. tube in the dry box and stoppering it with grease. m.pt. = 76-77.5°C (previously reported 73-74°C)[74] No further purifications were carried out. Immediately the compound was exposed to the atmosphere it became liquid due to its very hygroscopic nature[74].

Infra-red spectra were recorded as mulls using fluorocarbon and nujol. The mulls were prepared in the dry box. The band at 1735 cm^{-1} was assigned to the carbonyl stretch of the ester function and a small shoulder at 1700 cm^{-1} suggested that a small amount of the ester had in fact been hydrolysed. The band at 1155 cm^{-1} was assigned to the sulphonic acid function[75].

Mass spectral analysis was carried out by quickly transferring a small amount on to the probe of the MS9 spectrometer. No molecular ion was produced but the largest fragment ion had a m/e value of 151. Peak matching gave an accurate mass number of 151.0064. $C_4H_7O_4S$ requires 151.0065 (½ ppm error). The likely structure of this fragment ion is $CH_3OCOCH_2CH_2SO_2^+$ which is consistent with its source being methyl-β-sulphopropionate.

2.4.7. Preparation of ββ'dithiodipropionic acid



$(HO\overset{\overset{O}{\|}}{C}CH_2CH_2S)_2$.

The disulphide was prepared by a method similar to that used by Stoner and Dougherty[76].

$$ClCH_2CH_2COONa + Na_2S_2O_3 \longrightarrow NaOSO_2SCH_2CH_2CO_2Na$$

Bunte salt

$$2NaOSO_2SCH_2CH_2CO_2Na + I_2 + 2H_2O \longrightarrow$$

$$(SCH_2CH_2CO_2H)_2 + 2NaHSO_4 + 2NaI$$

3-Chloropropionic acid (10.9g) was dissolved in water (45 cc), neutralised with sodium carbonate and heated for one hour at 100°C with a solution of sodium thiosulphate (25 g) in water (30 cc). While still hot iodine (12.7 g) was added in small portions during a period of ten minutes. After the addition the acid was precipitated immediately. On cooling the acid was filtered off and desiccated by using a Dean and Starks apparatus and distilling benzene from it. 7.6 g of the disulphide was obtained. (71.5% of theoretical yield). The solid was recrystallised using an ethyl acetate and benzene mixture. M.pt. 153-154°C (m.pt. 155°C) [76].

M^+ = 210.0021 $C_6H_{10}O_4S_2$ requires 210.0021

(Error $<$ 1 ppm)

Infra-red spectrum. Broad H-bonding typical of carboxylic acid. $\nu_{c=o} = 1700\ cm^{-1}$.

2.4.8. Preparation of $\beta\beta'$sulphonyldipropionic acid.

$(HO\cdot CO\cdot CH_2CH_2)_2SO_2$.

This was prepared by a modification of the method of Barnard et al[69].

Thiodipropionic acid (ex-Robinsons Ltd) (9 g) was added to 3N sulphuric acid (250 mls). Crushed potassium permanganate was then added over 15 minutes with vigorous stirring. The reaction is exothermic and the solution was allowed to warm up quite considerably. At the end of the addition the solution was decolourized using sodium bisulphite. A solid was already crystallising out and when the solution was cold it was filtered to obtain 8 g of a white solid (75.5% Yield).

3g of the solid was recrystallised using 50 ml of distilled water. 2.7g of white crystals (90%), m.pt. 218-219°C were obtained.

Percentage S = 14.9, $C_6H_{10}O_6S$ requires 15.25%

Mass spectral analysis gave no molecular ion. The largest mass fragment was at m/e = 137. Exact mass number determined as 136.990658. $C_3H_5O_4S$ is given to be 136.9907 (Error 1.8 ppm). Therefore the fragment corresponds to $HO\cdot CO\cdot CH_2CH_2SO_2^+$.

Infra-red spectrum is consistent with a carboxylic acid function: H-bonding, $\nu_{C=O}$ = 1700 cm^{-1} and also sulphone $\nu_{S{=O \atop =O}}$ 1120 and 1320 cm^{-1} [70].

Acid equivalent weight determined to be 105. (Required 105).

2.4.9. Galvinoxyl (2,6-di-tert-butyl-α-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolyloxy) was prepared by the procedure of Bartlett[73]. 4,4'-dihydroxy-3,5,3',5'-tetra-tert-butyldiphenylmethane (22g) was dissolved in anhydrous ether (270 mls) and stirred with 55g of lead dioxide for three hours. The solution was filtered and the filtrate stirred with another 37g of lead dioxide for three more hours. The solution was filtered and the ether removed on a rotary evaporator. Dark blue crystals (21g) were obtained. These were rapidly recrystallised several times from ethanol. (m.pt. 156-157°C). Overall yield 58%. (Reported m.pt. = 153°C) [77]. Iodiometric titration[77] gave the purity as 99% and from the measurement of the extinction coefficient at 780mμ [77] the purity was estimated to be 96%.

2.4.10. The attempt to prepare methyl-β-sulphinopropionate.

(a) Preparation of methyl-β-sulphinylchloropropionate.

The sulphinylchloride was prepared according to the method of Douglas et al[78]. Methyl-β-mercaptopripionate (30g) and glacial acetic acid (15g) were placed in a three necked flask, cooled in a bath of ice and salt and stirred as chlorine (35.5g) was allowed to vapourize into the flask. The latent heat of vaporization was sufficient to control the rate of addition of the chlorine. The flask was fitted to a cold trap (CO_2 and acetone), the outlet of which was attached to a system for absorbing HCl in water. After all of the chlorine had been reacted the flask was heated to 35°C under reduced pressure to remove the acetyl chloride. The residue was then vacuum distilled and 36g of a fraction boiling at 80-82°C/ 0.45mm collected. (84% yield). The liquid was very pale yellow.

Percentage S = 18.5%, $C_4H_7O_3SCl$ requires 18.8%

Infra-red spectrum. A sharp band occurs at 1180 cm^{-1} and this has been assigned to the S=O stretch[79]. No additional band occurs around 1360 cm^{-1} as required if the sulphonylchloride was present ($\nu_{S=O}$ Asym)[80]. Other bands were consistent with the propionate structure. (1740 cm^{-1}, $\nu_{C=O}$)

$$RSH + Cl_2 \longrightarrow RSSR + HCl$$

$$RSSR + 2CH_3COOH + 3Cl_2 \longrightarrow 2RS(O)Cl + 2CH_3COCl + 2HCl$$

(b) Methyl-β-sulphinopropionate

18.5g of the sulphinylchloride was added to 100ml of distilled water at room temperature. Excess water was then removed under reduced pressure to leave a pale yellow oil

Percentage S = 20.6, $C_4H_8O_4S$ requires 21.0%

Infra-red spectrum. Bands at 2510, 1075 and 830 cm^{-1} were present. These are consistently present in sulphinic acids[80]. The band at 1740 cm^{-1} was assigned to the carbonyl of the propionate structure. Further characterisation was not undertaken (See 7.4.).

Chapter 3

OXYGEN ABSORPTION STUDIES

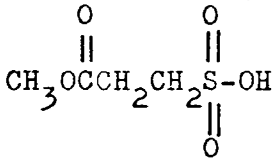
3.1. Introduction

Oxygen absorption studies provide a very useful means of classifying the mechanisms by which an antioxidant functions. This is achieved by studying the effect of the antioxidant on the oxygen absorption of a substrate whose mode of initiation is controlled. If a chain terminating antioxidant is added to a substrate whose oxidation has been initiated by added hydroperoxide or a free radical initiator such as $\alpha\alpha'$-azodi-isobutyronitrile (AZBN) then the rate of oxidation in both cases will be reduced to a value determined by the effectiveness with which the antioxidant scavenges the propagating radicals. However, if a peroxide decomposing antioxidant is added to an oxidising substrate whose autocatalysis by hydroperoxide initiation is rendered trivial by addition of a free radical initiator the rate of oxidation is unaltered. In the case where the peroxide decomposer is added to the hydroperoxide initiated oxidation the oxidation becomes autoinhibiting[10].

Scott et al[35] used the above technique to show that zinc diethyl dithiodicarbamate and zinc dinonyl dithiophosphate function mainly as peroxide decomposers. Bateman et al[25] investigated the antioxidant action of sulphoxides by changing the mode of initiation. Their results indicated that tert-butyl sulphoxide, which is an effective antioxidant, did not have any chain terminating activity.

The studies in this chapter, using the above technique, provide information relevant to both the pro-oxidant effect and the antioxidant mechanism of dialkylthiodipropionates. The effect of methyl-β-

sulphopropionate (II) on autoxidizing systems have been studied in order to help reach conclusions relating to the possibility of it being the actual antioxidant derived from the sulphoxide in the autoxidizing system.



$CH_3O\overset{\overset{O}{\|}}{C}CH_2CH_2\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}OH$

(II)

3.2. The Effect of Dimethyl thiodipropionate and Dimethyl sulphinyldipropionate on Oxidizing Cumene - Results and Discussion

The pro-oxidant effects of dimethyl thiodipropionate and dimethyl sulphinyldipropionate on the oxidation of cumene initiated by cumene hydroperoxide (Figures 3.1 and 3.2) are similar to those reported[36] for the effects of didodecyl thiodipropionate and didodecyl sulphinyldipropionate on the oxidation of tetralin initiated by tetralin hydroperoxide. The pro-oxidant effect is more pronounced when using the sulphoxide and occurs in two stages. This study shows that when using the sulphoxide at high hydroperoxide to sulphoxide ratios a strong inhibition occurs immediately. This can only be due to a combination of hydroperoxide decomposition and a chain interrupting process . Inactivation of the hydroperoxide towards initiation by complex formation, as suggested by Bateman[25] for the action of sulphoxides, cannot explain the immediate cessation of oxidation when there is eighteen times as much hydroperoxide as sulphoxide present, (Figure 3.2). The addition of dimethyl thiodipropionate does not show immediate inhibition of oxidation (Figure 3.1) and therefore the chain interrupting mechanism involves the sulphoxide and not the sulphide.

This was substantiated by showing that dimethyl thiodipropionate has no effect on the oxidation of cumene initiated by A.Z.B.N.

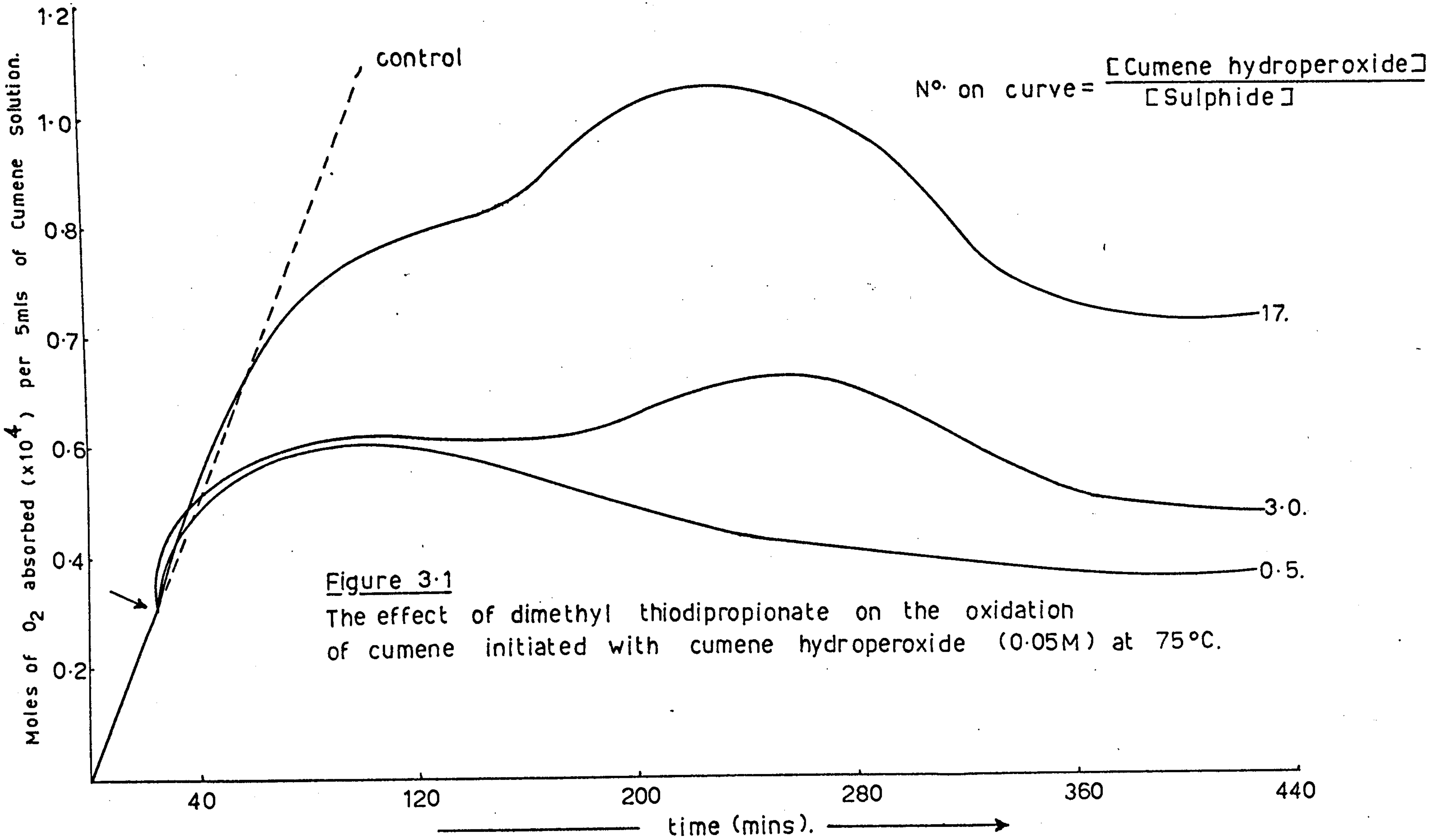


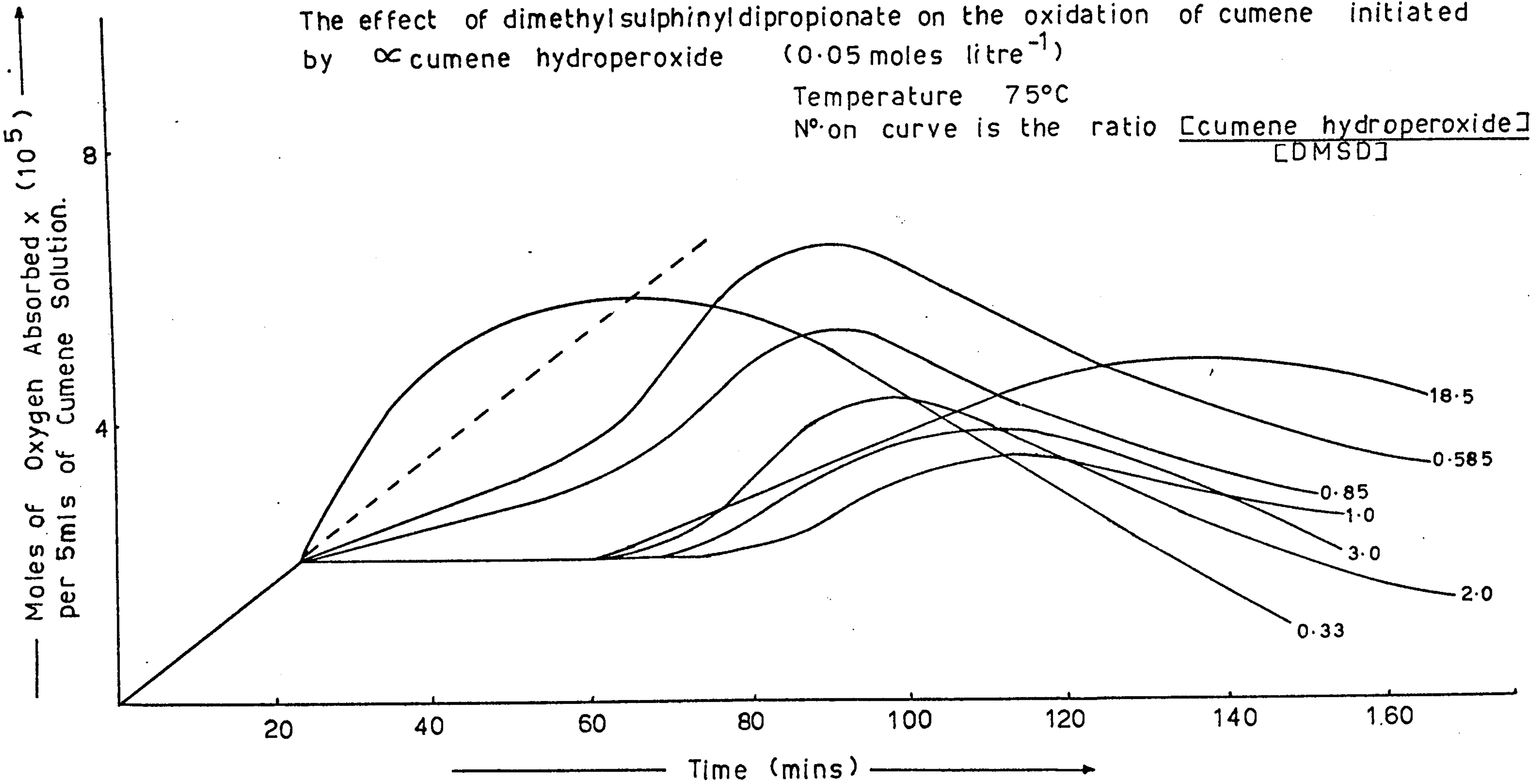
Figure 3·1
The effect of dimethyl thiodipropionate on the oxidation of cumene initiated with cumene hydroperoxide (0·05M) at 75°C.

Figure 3·2

The effect of dimethylsulphinyldipropionate on the oxidation of cumene initiated by ∝ cumene hydroperoxide (0·05 moles litre^{-1})

Temperature 75°C

N°·on curve is the ratio $\frac{[\text{cumene hydroperoxide}]}{[\text{DMSD}]}$



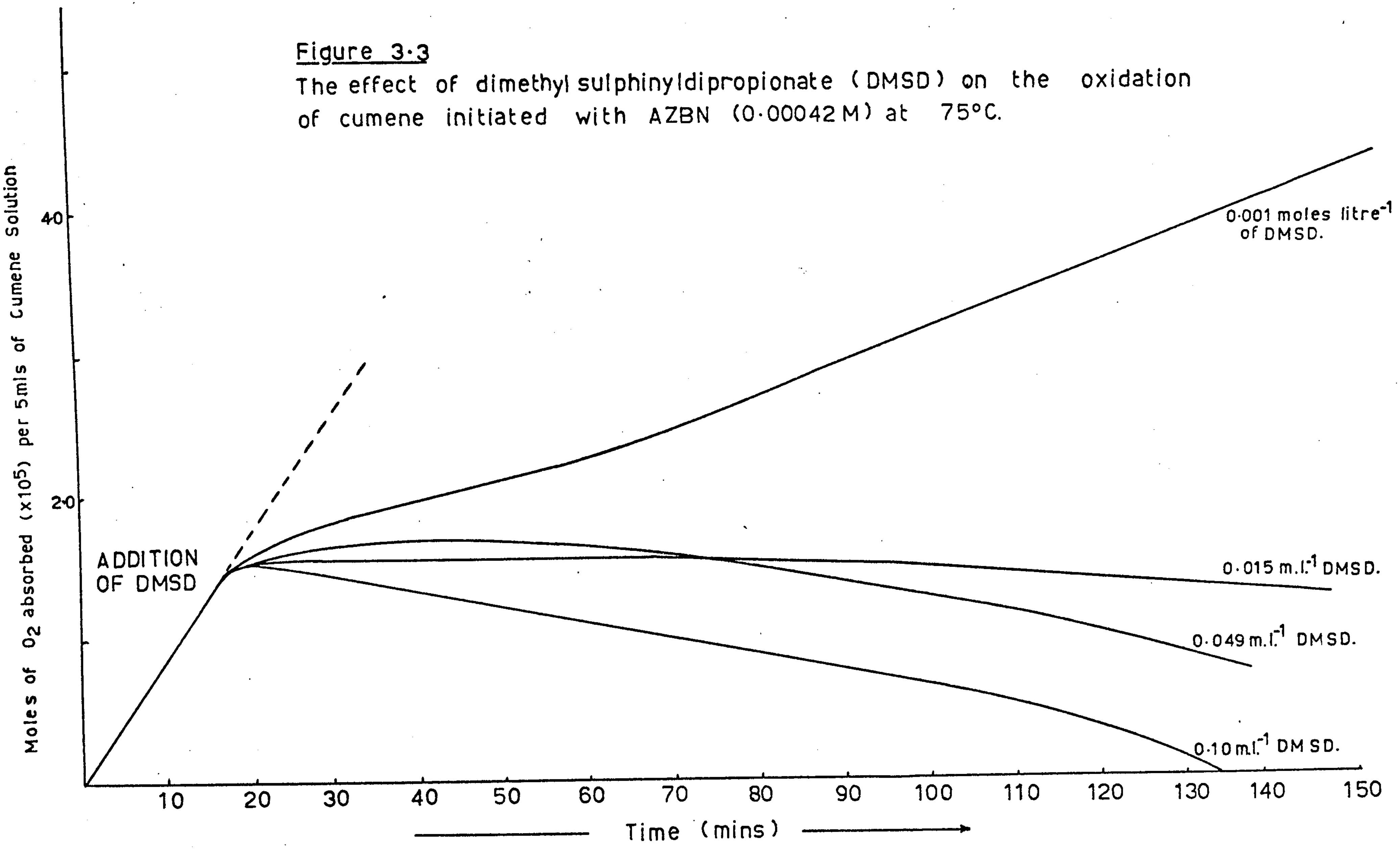
The effect of varying the concentration of dimethyl sulphinyldipropionate while keeping the concentration of initiating hydroperoxide constant shows that at least two free-radical generating reactions occur. The initial pro-oxidant effect, indicating a radical generating process, occurs effectively at ratios of hydroperoxide to sulphoxide less than one. This is consistent with the results obtained from a study of the initiation of polymerisation of styrene using hydroperoxide/sulphoxide (Chapter 5). Product analysis of hydroperoxide decomposition by dimethyl sulphinyldipropionate also shows that the largest amounts of products corresponding to a free-radical induced decomposition occur when this ratio is small (Figure 6.7).

The second pro-oxidant stage occurs after oxidation has been inhibited for a period which appears to be independent of the amount of sulphoxide added (Figure 3.2).

Gas evolution follows the oxidation and then no further oxidation occurs during the forty-eight hours for which the systems were examined. The second stage must be involved with antioxidant formation. A similar effect has been reported for dialkenyl monosulphides[32], which are, however, not very potent antioxidants.

Competing with the free-radical generating reactions is a reaction which interrupts the chain propagating process. Further evidence for this is provided by Figure 3.3. The oxidation of cumene ~~is~~ was initiated by an amount of AZBN which gives a rate similar to that for the cumene hydroperoxide initiated oxidation. Addition of similar amounts of dimethyl sulphinyldipropionate to that used in the cumene hydroperoxide initiated experiments (Figure 3.2) stops the oxidation immediately. This is in contrast to the result obtained

Figure 3·3
The effect of dimethyl sulphinyldipropionate (DMSD) on the oxidation of cumene initiated with AZBN (0·00042 M) at 75°C.



by Bateman[25] for ditert-butylsulphoxide. No pro-oxidant stages were observed and this is again consistent with the polymerisation results (Chapter 5), which show that while dimethyl sulphinyldipropionate does not initiate the polymerisation of styrene it can accelerate the hydroperoxide initiated polymerisations.

The curves of Figure 3.3. show pressure increases corresponding to gas evolution at higher sulphoxide concentrations. Examination of a pure solution of dimethyl sulphinyldipropionate in nitrogen at 75°C showed that this is due to products of the sulphoxide decomposition. The products were not identified completely. The mass-spectrum and infra-red indicated only the presence of solvent and methylacrylate. Methylacrylate was shown to be responsible for part of the increase in pressure of the system.

In order to obtain further information about the chain interruptive process the effect of dimethyl sulphinyldipropionate on the oxidation of cumene initiated with larger amounts of AZBN was studied, (Figure 3.4). The effect of the sulphoxide differs from normal chain-terminating antioxidants in that the effectiveness with which it interrupts the free-radical chain depends upon the concentration added. The oxidation also becomes autoinhibiting.

Reactions (I) to (4) are part of the basic autoxidation scheme previously described (Chapter 1 (1.1))

$$RH \longrightarrow R\cdot \qquad (1)$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \qquad (2)$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot \qquad (3)$$

$$ROO\cdot + XH \longrightarrow ROOH + X\cdot \qquad (4)$$

Chain terminating antioxidants, XH, function by competing with reaction (3). For the antioxidant to be effective X· does not

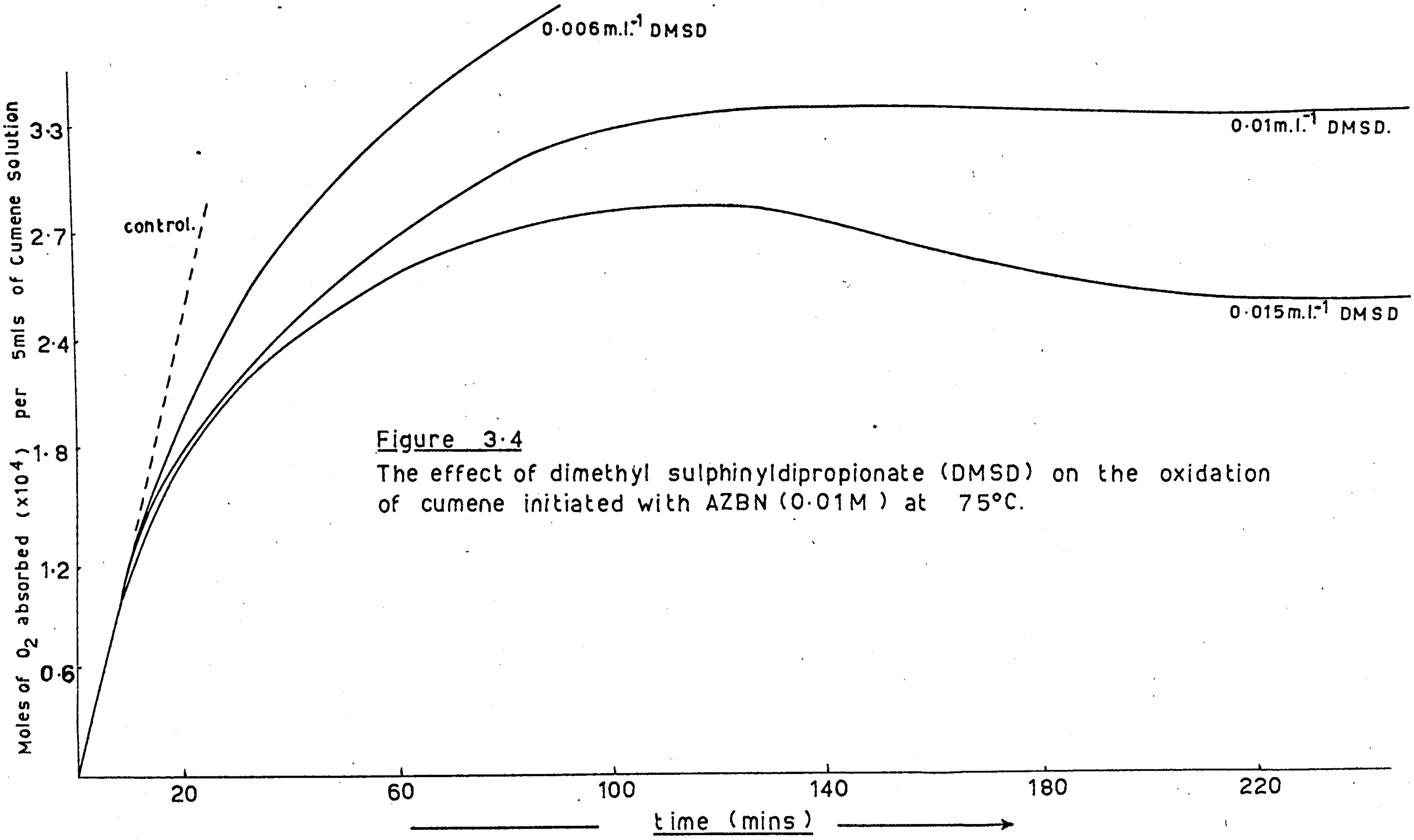
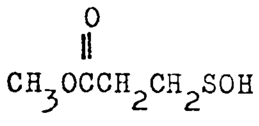


Figure 3·4
The effect of dimethyl sulphinyldipropionate (DMSD) on the oxidation of cumene initiated with AZBN (0·01M) at 75°C.

initiate new oxidation chains and the rate of reaction $4 \gg 3$. If the sulphoxide interrupts the chain propagating process of oxidation by this mechanism then a molecule containing a labile hydrogen atom would have to be generated from it in some way. The sulphenic acid (III) is the primary product of the thermal decomposition of dimethyl sulphinyldipropionate (Chapter 4).



$$CH_3O\overset{\overset{O}{\|}}{C}CH_2CH_2SOH$$

(III)

A chain transfer reaction of the sulphenic acid with polystyrl radicals has been postulated to account for the retardation of the free-radical polymerisation of styrene by dimethyl sulphinyldipropionate (Chapter 5). A similar mechanism can be envisaged for the chain interrupting effect which is obtained when the sulphoxide is added to autoxidizing cumene (5)

$$ROO\cdot \ + \ R'SOH \longrightarrow ROOH \ + \ R'SO\cdot \qquad (5)$$

An attempt to obtain direct evidence for a hydrogen transfer reaction occurring with dimethyl sulphinyldipropionate was made. 2-Cyano-2-propyl radicals are generated by the thermal decomposition of AZBN and it has been shown that these radicals abstract hydrogen atoms from thiols to produce isobutyronitrile[81]. A similar reaction was envisaged for the sulphenic acid (III). Dimethyl sulphinyldipropionate was decomposed in the presence of AZBN in an inert solvent and atmosphere. Control experiments involving AZBN in the solvent; solvent and cumene hydroperoxide; solvent, cumene hydroperoxide and sulphoxide were also studied. The solutions were thermostatted at 75°C for three hours and then analysed for isobutyronitrile. In all cases small and similar amounts of isobutyronitrile were detected.

The quantity obtained corresponds to that produced by disproportionation of 2-cyano-2-propyl radicals[82]. As no difference was obtained in the amount of isobutyronitrile produced by the controls and dimethyl sulphinyldipropionate and AZBN alone, no evidence can be put forward for the hypothesis that the sulphenic acid is responsible for the chain interrupting process.

The evidence, however, cannot be used negatively. A brief study of the energetics of the sysyem shows why. For a rapid hydrogen-abstraction reaction the bond which is formed should be at least as strong as the bond that is broken. The carbon-hydrogen bond strength of isobutyronitrile has been estimated to be a few kilocals/mole less than 86 Kcals/mole[81]. The sulphur-hydrogen bond strengths of thiols are about 89 Kcals/mole[83,84]. The bond strength, O-H, of hydroperoxides has been estimated to be 90 Kcals/mole[85]. It is therefore energetically more favourable for a reaction between a peroxy radical and a thiol, than for a reaction between the 2-cyano-2-propyl radical and a thiol. Both the 2-cyano-2-propyl radical and the peroxy radical are good accepter radicals[86]. That is, they can stabilise a negative charge. It is therefore doubtful ~~that~~ if polar effects in the transition state could explain any difference between abstraction from the sulphenic acid by the 2-cyano-2-propyl radical and abstraction by the peroxy radical. It may therefore be that in an autoxidising system at partial oxygen pressures above 100mm of Hg when the rate controlling propagation step of the autoxidation chain involves the attack by the peroxy radical on the substrate, chain transfer with the sulphenic acid or another species derived from the sulphoxide does ~~not~~ occur.

The dependence of the effectiveness of the chain interrupting process on the amount of sulphoxide added (Figure 3.4) is further evidence which suggests that there is a fine energetic balance. This indicates that the rate of reaction (4) is comparable to the rate of reaction (3). That is we are dealing with a poor chain interrupting species.

A feature of the chain interrupting process is the auto-inhibiting effect. This is consistent with a build up of the chain interrupting species from the decomposition of the sulphoxide, but is not consistent with the species being the sulphenic acid. Sulphenic acids are very reactive and it seems likely that a steady state concentration would be soon attained, (Chapter 4). An alternative suggestion is that as well as a chain interrupting process occurring the AZBN is being removed from the system. It is possible that the sulphenic acid can add across the azo group and therefore compete with the thermal decomposition of AZBN to give free-radicals. This explanation has been postulated to account for the fact that AZBN is very effective in suppressing the decomposition of cumene hydroperoxide by DMSD (Chapter 6).

3.3. The Effect of Methyl-β-sulphopropionate on Oxidising Cumene - Results and Discussion

Strong acids have been detected as products when sulphur compounds are used as antioxidants[10,16,87]. It has been suggested that sulphonic acids are the species involved and that they are in fact the actual antioxidants[87]. No suggestions other than Scott's[36] have been made with respect to the production of the acid from the sulphoxides. Kinetic results on the decomposition of dimethyl sulphinyldipropionate are consistent with a reaction between the sulphenic acid, produced from the decomposition, and a hydroperoxide (Figure 4.5). Reactions (6) and (7) are therefore postulated to represent a possible pathway to the sulphonic acid from a sulphoxide

$$\mathrm{RS(O)R} \longrightarrow \mathrm{RSOH} + \text{Alkene} \qquad (6)$$

$$\mathrm{2R'OOH} + \mathrm{RSOH} \longrightarrow \mathrm{RSO_3H} + \mathrm{2R'OH} \qquad (7)$$

The sulphonic acid (II) which would be derived from dimethyl sulphinyldipropionate according to reactions (6) and (7) was therefore synthesised and its effect on autoxidising cumene initiated by hydroperoxide and AZBN was studied.

On addition of the sulphonic acid to the hydroperoxide initiated oxidation at 75°C an immediate gas evolution occurred after which oxidation ceased. No further oxidation occurred over the next twenty-four hours (Figure 3.5.). The period for which gas evolution occurred corresponded closely to the time that would have been required for complete decomposition of the hydroperoxide (Section 7.2), e.g. when the acid was added to cumene hydroperoxide in chlorobenzene (0.15M) at 75°C, so that the resulting solution contained 0.02 $m.l.^{-1}$ of the sulphonic acid no cumene hydroperoxide remained after five minutes. Methyl-β-sulphopropionate was also very effective in inhibiting the AZBN initiated oxidation of cumene (Figure 3.6) and therefore has chain interrupting activity as well as peroxide decomposing ability.

The results therefore suggest that the sulphonic acid which can be envisaged to be derived from dimethyl sulphinyldipropionate is a very effective antioxidant. (In terms of intrinsic activity). The oxygen absorption results provide no evidence to suggest that the acid could not be the active species. However further studies (Section 7.2) indicate that the acid cannot be the main species responsible for the antioxidant activity of dialkyl thiodipropionate.

The action of the sulphonic acid remains interesting. However, as an antioxidant it cannot have any commercial use. It is extremely hygroscopic and is rapidly hydrolysed in air to β-sulphopropionic acid which is itself hygroscopic[74].

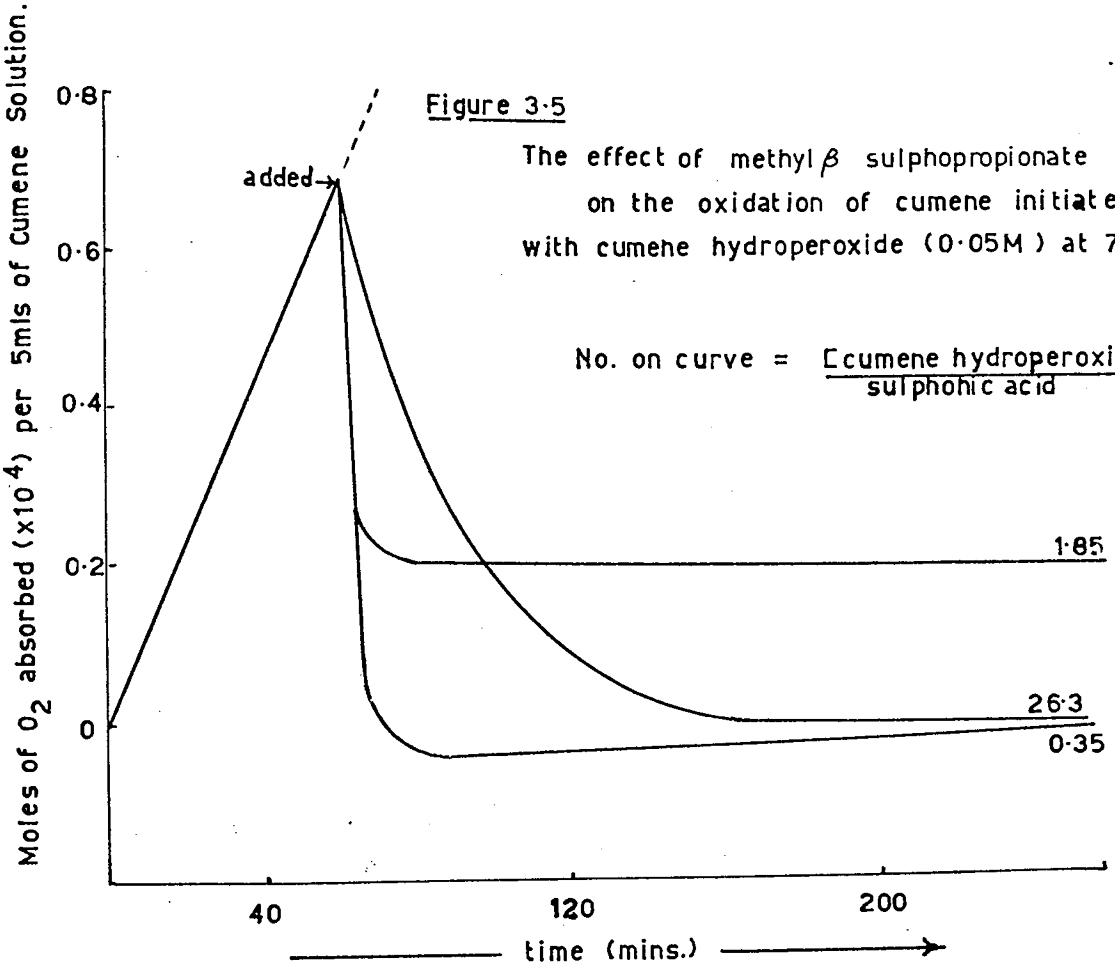


Figure 3·5

The effect of methyl β sulphopropionate on the oxidation of cumene initiated with cumene hydroperoxide (0·05M) at 75°C.

No. on curve = $\frac{[\text{cumene hydroperoxide}]}{\text{sulphonic acid}}$

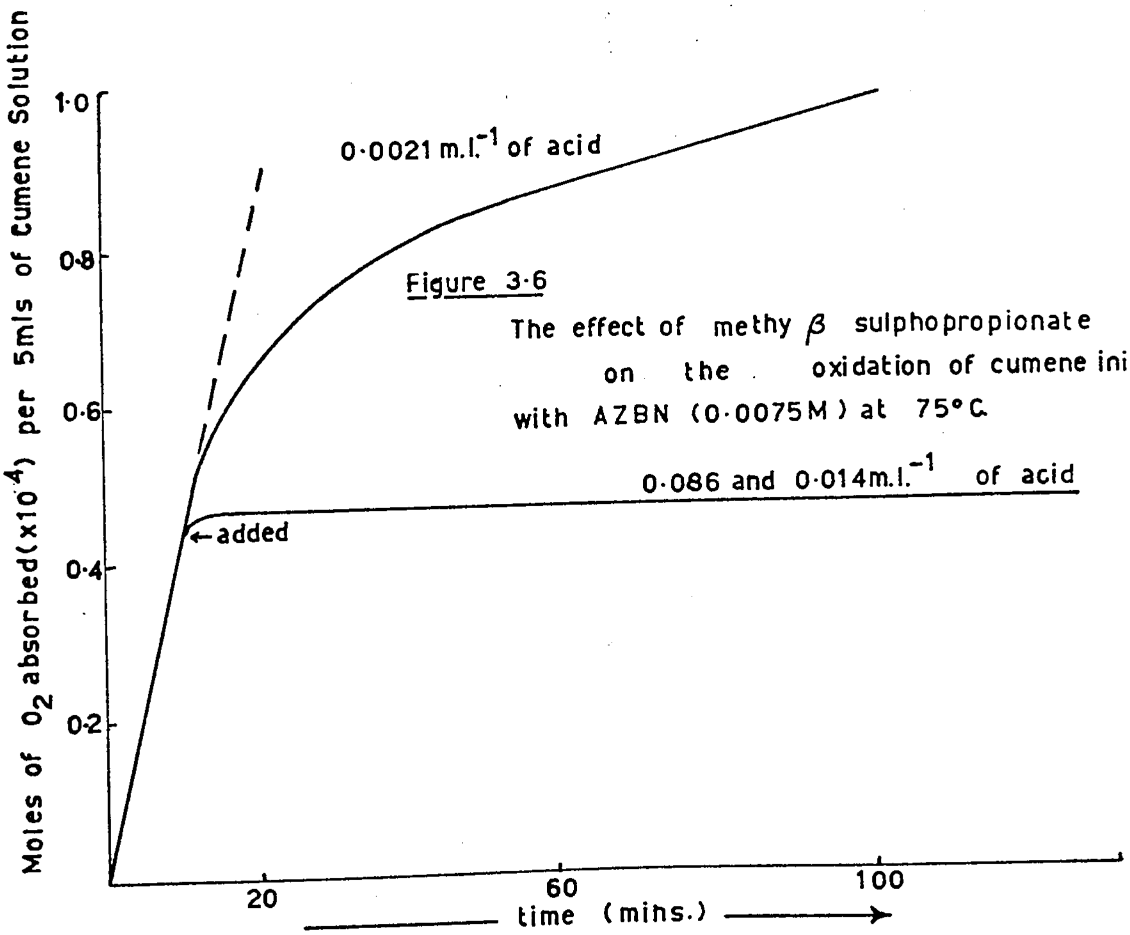


Figure 3·6

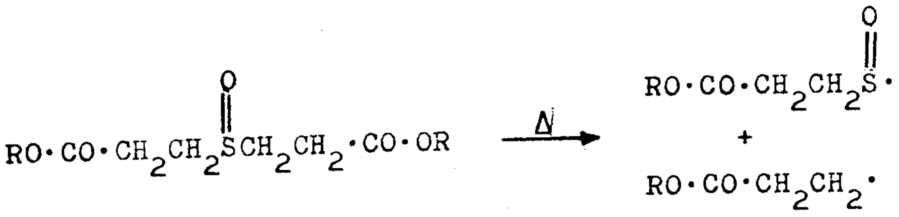
The effect of methy β sulphopropionate on the oxidation of cumene initiated with AZBN (0·0075M) at 75°C.

Chapter 4

AN INVESTIGATION OF THE PRO-OXIDANT STAGE. THE THERMAL DECOMPOSITION OF DIMETHYL SULPHINYLDIPROPIONATE (DMSD)

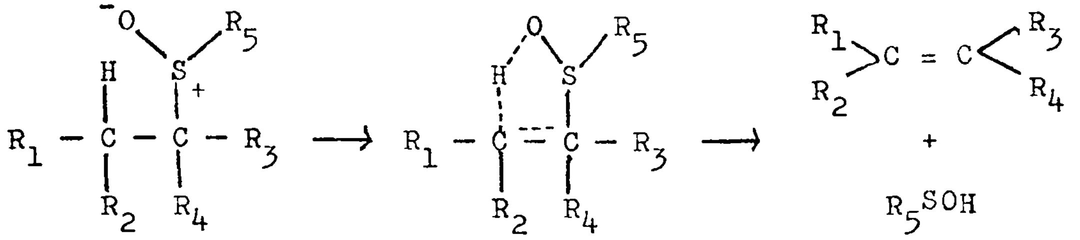
4.1. Introduction

The oxygen absorption studies reported in Chapter 3 illustrate the pro-oxidant effects that are encountered when using dimethyl thiodipropionate and dimethyl sulphinyldipropionate as antioxidants, (Figures 3.1 and 3.2). For a pro-oxidant effect to occur, either free-radicals capable of initiating oxidative chains must be produced by the additive or the mode of termination of the free-radical autoxidation chain must be less efficient. The former explanation is most likely and as thermal dissociation of sulphoxides by a radical pair mechanism had previously been reported[46,47] Scott[36] proposed by analogy that the thiodipropionates function as pro-oxidants via the corresponding sulphinyldipropionate. He suggested that these sulphoxides thermally dissociated producing radicals that are capable of initiating oxidative chains (1)



$$\mathrm{RO\cdot CO\cdot CH_2CH_2\overset{O}{\overset{\|}{S}}CH_2CH_2\cdot CO\cdot OR} \xrightarrow{\Delta} \mathrm{RO\cdot CO\cdot CH_2CH_2\overset{O}{\overset{\|}{S}}\cdot} + \mathrm{RO\cdot CO\cdot CH_2CH_2\cdot} \qquad (1)$$

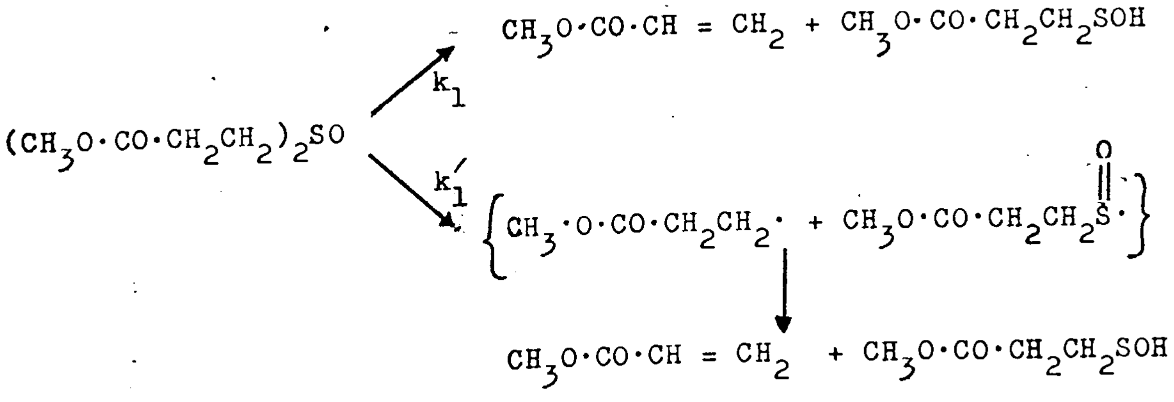
Investigations[22,88-94] of the mechanism of the thermal decomposition of a variety of dialkyl sulphoxides provides evidence which suggests that when the sulphoxide contains a labile β-hydrogen the more important mechanism involved is the five-centred elimination, first suggested by Kingsoury and Cram[46]. (2)



(2)

Alkenes and sulphenic acids are the primary products of the decomposition. Yields of the alkene are usually high and the thermal decomposition of sulphoxides may be used for the synthesis of alkenes[95-97]. In the case of the thermal decomposition of didodecyl sulphinyldipropionate the dodecyl ester of acrylic acid has been identified as one of the products[8]. Even in the decomposition of a sulphoxide by a radical pair mechanism alkene results as a primary product[46].

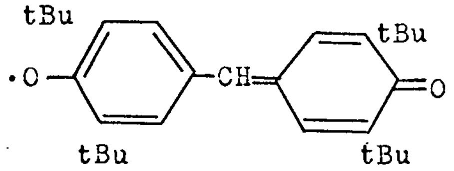
To establish whether or not thermal dissociation of dialkyl sulphinyldipropionate occurred giving rise to radicals which are capable of initiating oxidative chains the thermal decomposition of dimethyl sulphinyldipropionate was investigated. It was envisaged that methyl acrylate, which could be readily quantitatively analysed would be produced both by the five-centred elimination mechanism (2) and by dissociation into free-radicals followed by an inter-cage reaction (3).



(3)

If the radicals produced by the dissociation are responsible for the pro-oxidant effect then it should be possible to scavenge them.

The rate of formation of methyl acrylate in the presence and absence of Galvinoxyl (IV)[77] was therefore measured. Galvinoxyl is a very effective scavenger of alkyl and alkoxy radicals[77,98]. The effect of the Galvinoxyl was further studied by measuring its rate of disappearance in the presence of dimethyl sulphinyldipropionate.



(IV)

4.2. The rate of formation of methyl acrylate and the effect of added Galvinoxyl

DMSD decomposes thermally to produce methyl acrylate (M) and by use of g.l.c. the rates of formation of methyl acrylate were measured at several temperatures and in several solvents. If we assume that (3) describes the production of methylacrylate (M) from DMSD then the amount of DMSD decomposed will be proportional to the amount of methyl acrylate produced. Therefore after complete reaction

$$[\mathrm{DMSD}] \propto [\mathrm{M}]_{\infty}$$

and the concentration of DMSD, at any time t, in solution is

$$[\mathrm{DMSD}]_t \propto [\mathrm{M}]_{\infty} - [\mathrm{M}]_t$$

and therefore if the decomposition is first-order

$$\log_e\left(\frac{[\mathrm{M}]_{\infty}}{[\mathrm{M}]_{\infty} - [\mathrm{M}]_t}\right) = kt \qquad [1].$$

and

$$k = (k_1 + k_1') \qquad [2]$$

In carbon tetrachloride the decomposition of DMSD, as monitored by methyl acrylate formation, showed first-order behaviour for a period corresponding to two half lives (Figure 4.1, Curve A). The half life being determined from the apparent first-order rate constant. Changes in the initial concentration of DMSD did not significantly alter the apparent first order rate constants (Table 4.1)

Table 4.1

The apparent first-order rate constant (k) for the decomposition of dimethyl sulphinyl-dipropionate (DMSD) in carbon tetrachloride at 75°C.

DMSD (10^2M)	6.08	4.0	1.0	0.608
10^5k(sec^{-1})	5.4	5.8	6.0	7.1

Figure 4.2 is a plot of the log of the initial rate against the log of the initial concentration of DMSD. A good straight line is obtained which has a slope of one. Therefore DMSD decomposes thermally according to equation [3] in the initial stages

$$-\frac{d[\mathrm{DMSD}]}{dt} = k\ [\mathrm{DMSD}] \qquad [3]$$

Figure 4.1A indicates that deviation occurs after about two half lives. The value of k obtained from the initial rate plot (Figure 4.2) is 8.7 x 10^{-5} sec^{-1}.

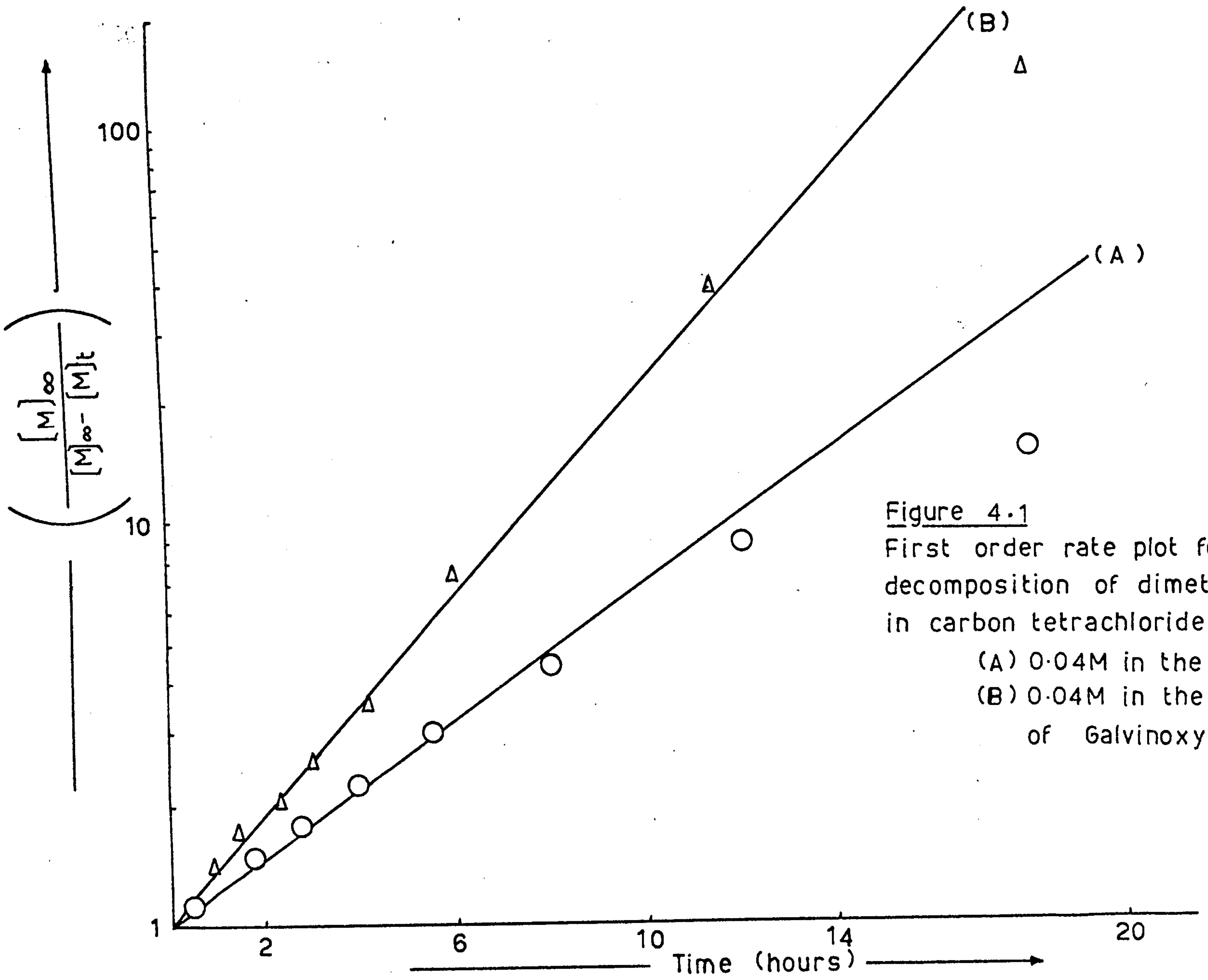


Figure 4.1
First order rate plot for the thermal decomposition of dimethyl sulphinyldipropionate in carbon tetrachloride at 75°C.

(A) 0·04M in the absence of Galvinoxyl.
(B) 0·04M in the presence of 0·194 mole litres^{-1} of Galvinoxyl.

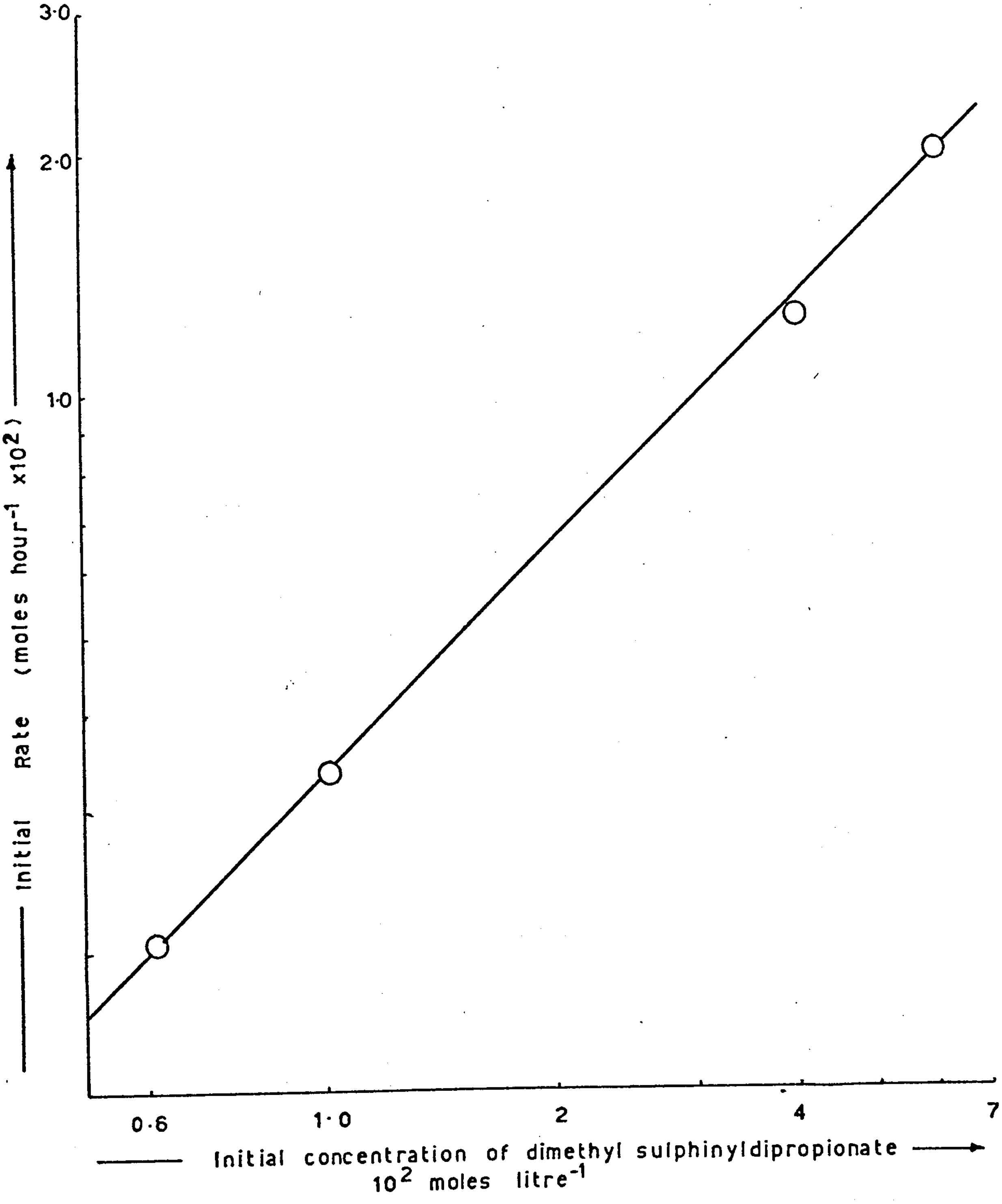


Figure 4·2

Plot of log. of the initial rate of decomposition of dimethyl sulphinyldipropionate in carbon tetrachloride at 75 °C against log initial concentration.

Table 4.2 lists the values of k determined at various temperatures together with the Arrhenius parameters and Figure 4.3 curve A shows the fit that is obtained when these rate constants are plotted according to the Arrhenius equation.

Table 4.2

The apparent first-order rate constant $(k)_i$, activation energy (E_A), frequency factor (A), the entropy of activation ($\Delta S^{\ddagger}$) for the thermal decomposition of DMSD in carbon tetrachloride.

$T^{o}C$	75	70	65	55	50
$10^5 k(\text{sec}^{-1})$	5.8	3.58	2.54	0.73	0.54

E_A (Kcals mole^{-1})	22.2
A (sec^{-1})	4.6×10^9
$\Delta S^{\ddagger}$ cal deg^{-1} mole^{-1}	-14.6

Figure 4.1 curve B shows that in the presence of an excess of Galvinoxyl the decomposition of DMSD obeys a first-order rate equation for over 95% of the reaction (5 half lives). In all cases when the decomposition of DMSD in carbon tetrachloride was carried out in the presence of Galvinoxyl the final yield of methyl acrylate was reduced. Figure 4.4. shows that the initial rate of methyl acrylate formation is not affected by Galvinoxyl and it is only after one and a half half lives that it becomes apparent that the amount of methyl acrylate being produced is reduced. There is no reaction between Galvinoxyl and methyl acrylate.

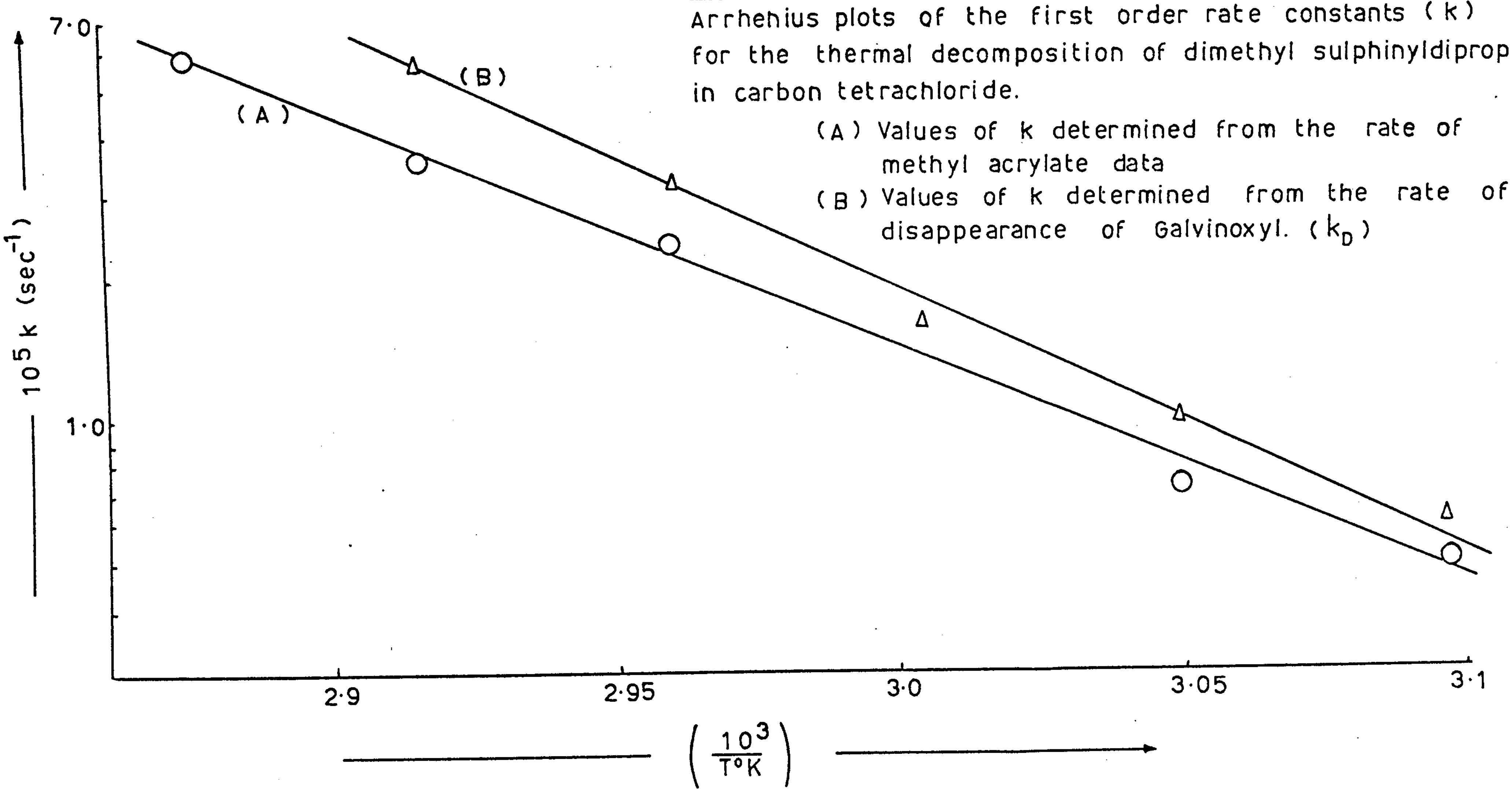


Figure 4·3
Arrhenius plots of the first order rate constants (k) for the thermal decomposition of dimethyl sulphinyldipropionate in carbon tetrachloride.

(A) Values of k determined from the rate of methyl acrylate data

(B) Values of k determined from the rate of disappearance of Galvinoxyl. (k_D)

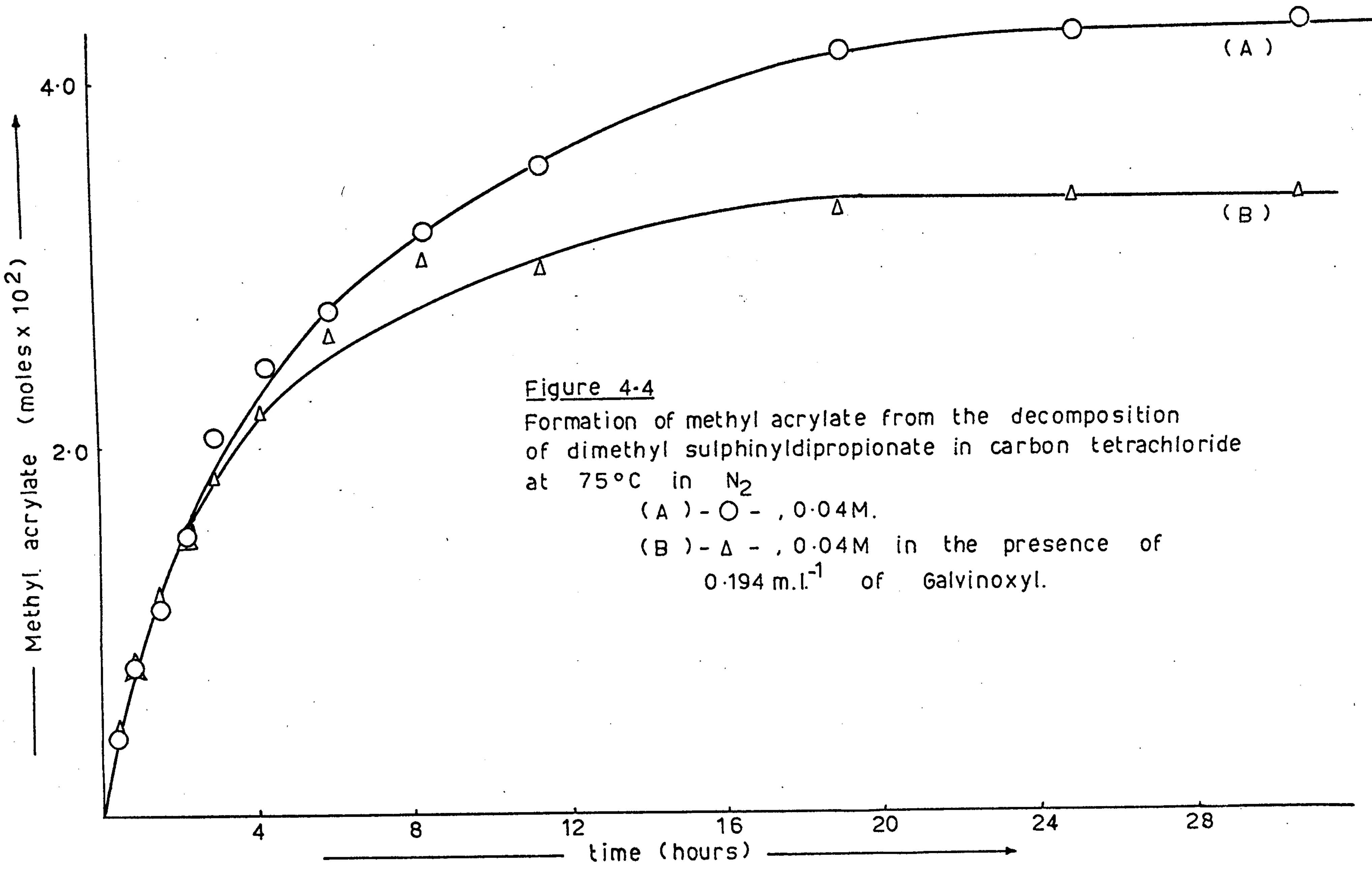


Figure 4·4

Formation of methyl acrylate from the decomposition of dimethyl sulphinyldipropionate in carbon tetrachloride at 75°C in N_2

(A) - ○ - , 0·04M.

(B) - Δ - , 0·04M in the presence of 0·194 m.l.$^{-1}$ of Galvinoxyl.

Figure 4.1 curves A and B appears to show that the DMSD decomposes at a faster rate in the presence of Galvinoxyl and yet Figure 4.4 indicates that initially the decomposition occurs at the same rate. The two graphs are compatible, however, as for any one determination

$$\left(\frac{[M]_\infty}{[M]_\infty - [M]_t} \right)_{\text{Galvinoxyl}} > \left(\frac{[M]_\infty}{[M]_\infty - [M]_t} \right)_{\text{No Galvinoxyl}}$$

because in the case of the Galvinoxyl $[M]_\infty < [M]_{\infty\,\text{no Galvinoxyl}}$ (Figure 4.4). If the amount of Galvinoxyl used in the experiments giving Figure 4.1 and Figure 4.4 is increased no further decrease in the yield of methyl acrylate occurs.

In all the experiments the solutions were rigorously degassed. The effect of oxygen is similar to that of Galvinoxyl. For the first two half lives of the reaction oxygen has no apparent effect and then the yield of methyl acrylate is reduced slightly compared to a run in an inert atmosphere. However, the overall effect is very small compared to the effect of Galvinoxyl.

The rate constants, k, determined from the integrated first-order rate plots, of which Figure 4.1, curve A is typical, are only pseudo-first-order rate constants. The plot of the log of the initial rate against the log of the initial concentration is one and therefore the initial decomposition of DMSD corresponds to a true first-order reaction and the corresponding rate constants (k_{in}) can be derived from the initial slopes. Table 4.3 gives the various values of k_{in} at different temperatures together with the first-order rate constants (k_G) determined from the integrated first order rate plots for the decomposition of DMSD in the presence of Galvinoxyl of which Figure 4.1 curve B is typical.

Table 4.3

The first-order rate constants k_{in} and k_G as determined for the rate of decomposition of DMSD in carbon tetrachloride (0.04M)

T^oC	75	70	65	55	50
$10^5k_{in}(sec^{-1})$	7.8	4.5	3.2	0.96	0.57
$10^5k_G\ (sec^{-1})$	8.4	-	2.6	0.9	0.59

The activation energies were computed for k_{in} and k_G and found to be 23.6 and 23.8 Kcals $mole^{-1}$ respectively.

The thermal decomposition of DMSD in dioxan and chlorobenzene did not show any first-order behaviour. When an excess of Galvinoxyl was added to the solutions first-order behaviour was obtained (Figure 4.5, curves A and B). The values of the rate constants obtained are given in Table 4.4.

Table 4.4.

First-order rate constants for the decomposition of DMSD (0.04M) in the presence of Galvinoxyl (0.815M) at 75°C in N_2 and in the presence of cumene hydroperoxide (k_{CHP}) -(0.09M)

Solvent	Dioxan	Chlorobenzene
$10^5k_G(sec^{-1})$	5.3	6.2
$10^5k_{CHP}(sec^{-1})$	5.0	4.9

The decomposition of dimethyl sulphinyldipropionate in styrene, without added Glavinoxyl, was first-order with respect to sulphoxide

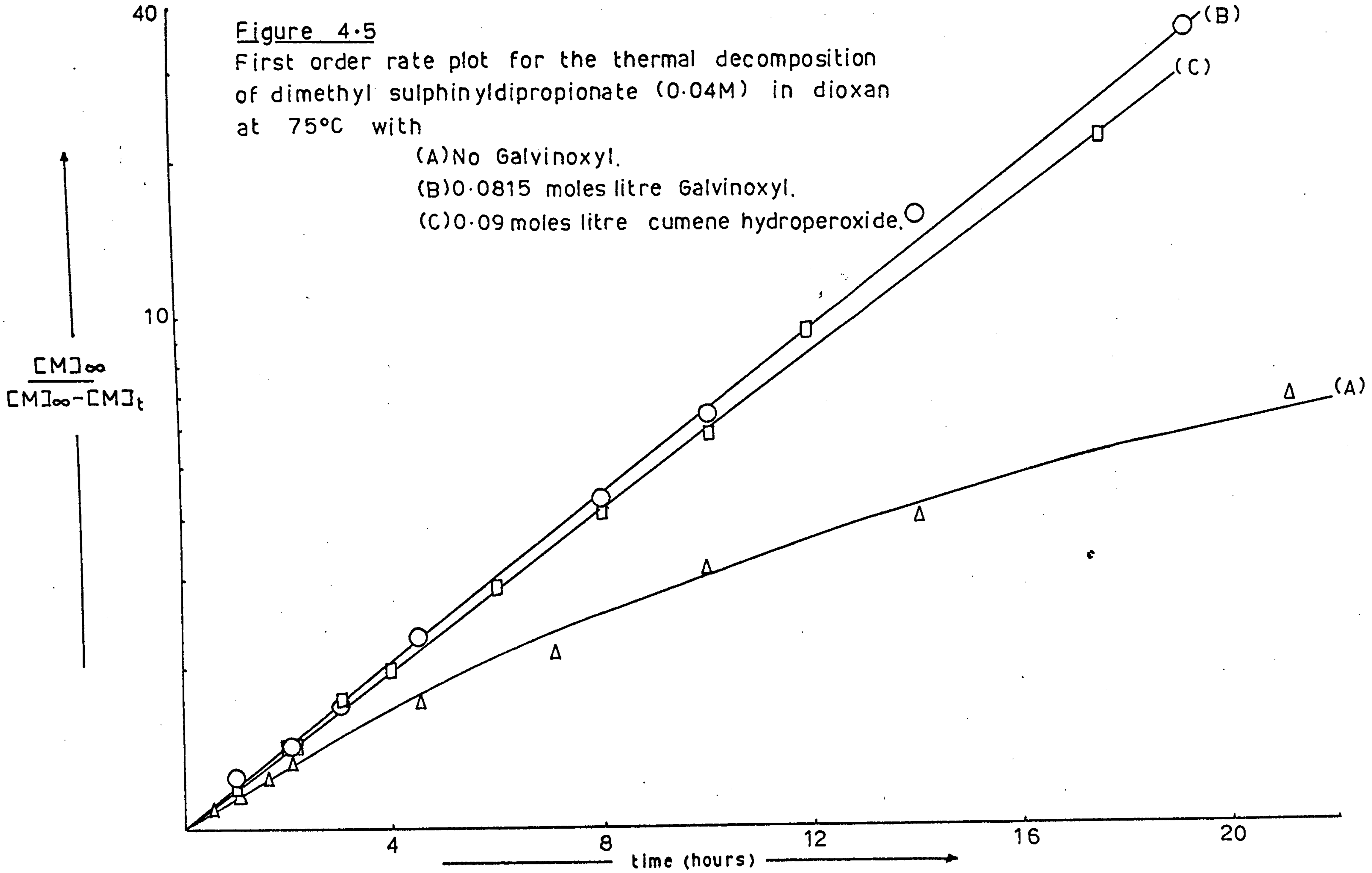


Figure 4·5
First order rate plot for the thermal decomposition of dimethyl sulphinyldipropionate (0·04M) in dioxan at 75°C with
(A) No Galvinoxyl.
(B) 0·0815 moles litre Galvinoxyl.
(C) 0·09 moles litre cumene hydroperoxide.

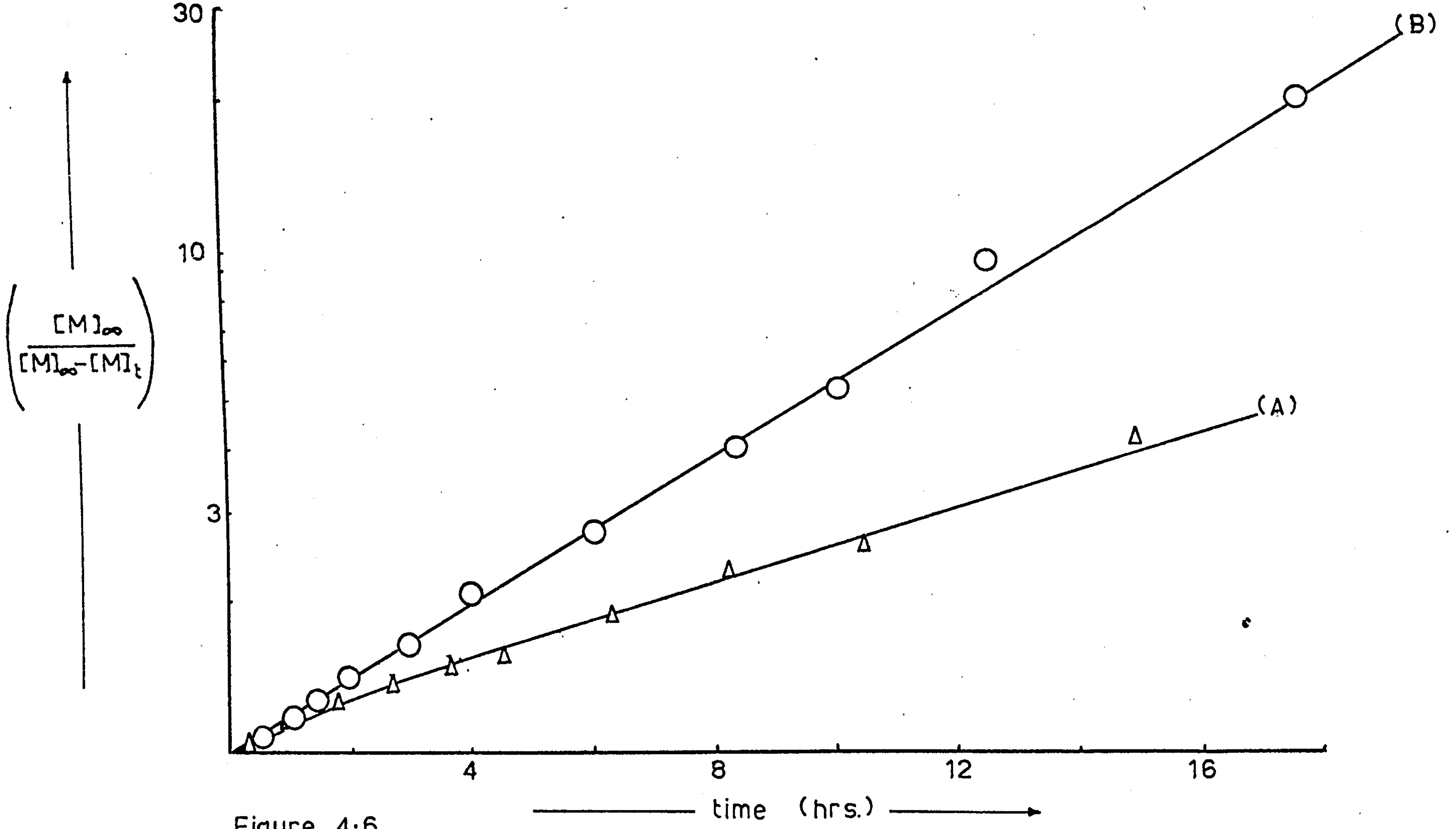


Figure 4·6

First order rate plot for the thermal decomposition of dimethyl sulphinyldipropionate (0·04M) in chlorobenzene at 75°C in nitrogen.

(A) without hydroperoxide. (B) 0·09 moles l.$^{-1}$ cumene hydroperoxide.

for over 90% of the reaction. The first-order rate constant for the decomposition of DMSD in styrene (0.04M) at 75°C is 5.10×10^{-5} $\sec^{-1}$ (Figure 4.7).

The deviation of linearity of the first-order rate plots in the absence of Galvinoxyl suggests that the decomposition may be reversible. Table 4.5 shows the effect of added methyl acrylate on the yield of methyl acrylate from the decomposition of DMSD and establishes the inhibiting effect of methyl acrylate.

Table 4.5

Yield of methyl acrylate from the decomposition of DMSD (0.04M) with and without added methyl acrylate (0.04M) at 75°C.

	Solvent		
	carbon tetrachloride	dioxan	chlorobenzene
Yield ($m.\ell.^{-1}$) in the presence of added methyl-acrylate	0.0375	0	0
Yield ($m.\ell.^{-1}$) without added methylacrylate	0.045	0.038	0.038

The rate of formation of methyl acrylate from the decomposition of DMSD in the presence of cumene hydroperoxide was also studied. With dioxan and chlorobenzene as solvents and a two times molar excess of cumene hydroperoxide to DMSD first-order rate plots were obtained. Figure 4.5, curve C and Figure 4.6 show that there is no deviation from first-order behaviour. The values of the first-order rate constants were equivalent to those obtained when the decomposition

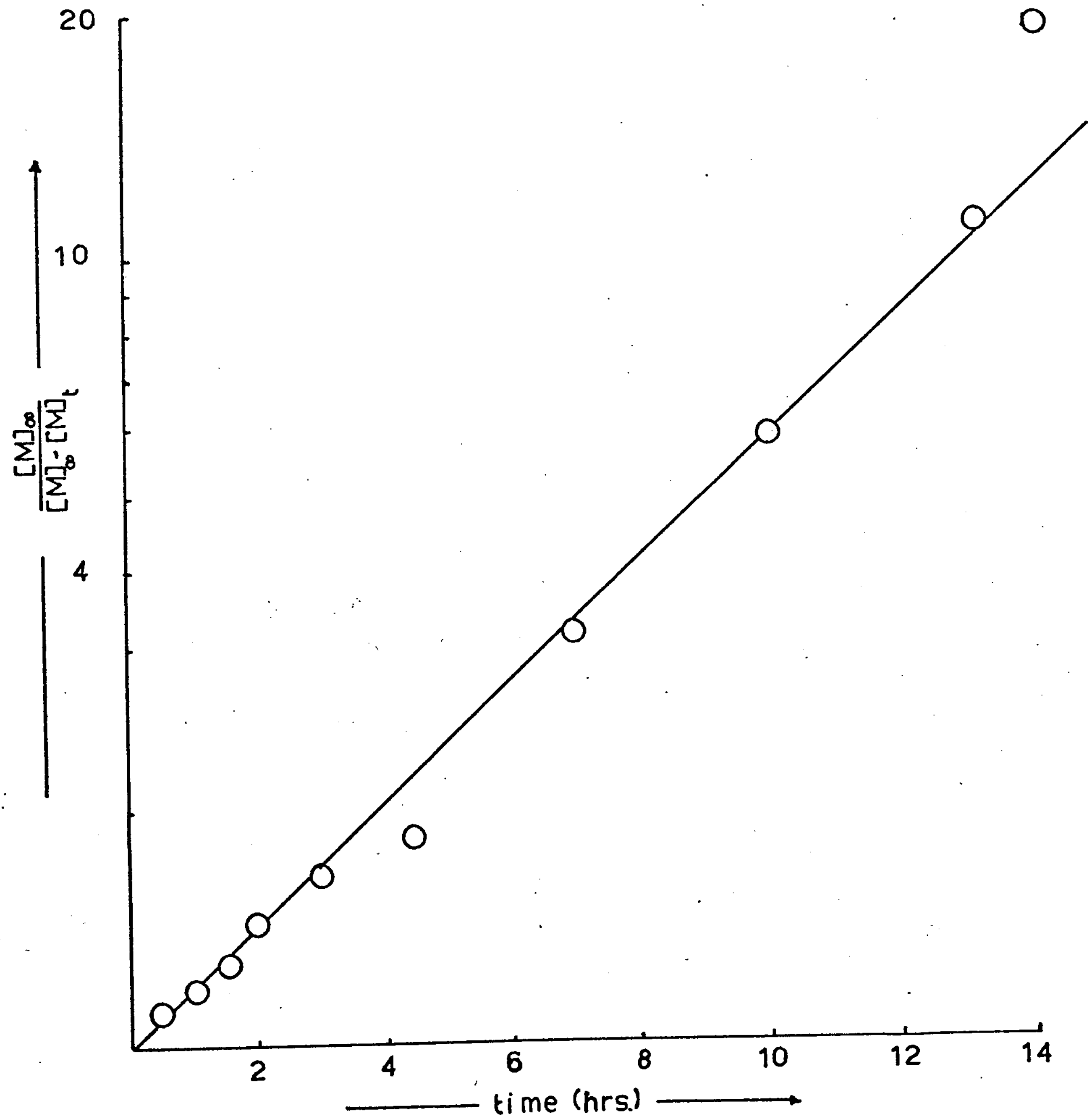


Figure 4·7

First order rate plot for the thermal decomposition of dimethyl sulphinyldipropionate (0·4M) in styrene at at 75°C in nitrogen.

of DMSD is carried out in the presence of excess Galvinoxyl.(Table 4.4) The yield of methylacrylate from the decomposition of DMSD (0.04M) in the presence of the cumene hydroperoxide corresponded to 75% of DMSD decomposing to give methyl acrylate. (Yields of 0.032 and 0.0295 m.$\ell.^{-1}$ were recorded.)

4.3. The rate of disappearance of Galvinoxyl in the presence of decomposing DMSD

It was observed that Galvinoxyl had no effect on the quantities of methyl acrylate produced during the initial stages of the decomposition of DMSD in carbon tetrachloride. The colour of the solution, however, faded indicating that the Galvinoxyl was involved in the reaction. The disappearance of Galvinoxyl was therefore followed in order to obtain information relative to its function.

When a large excess of DMSD in carbon tetrachloride was decomposed in the presence of Galvinoxyl the rate of its disappearance was constant throughout its life time. Figure 4.8 is typical of the plots that were obtained using e.s.r. to follow the Galvinoxyl concentration. From these plots the rate of disappearance of Galvinoxyl was determined at various concentrations of DMSD. The rate was plotted against the concentration of DMSD and a straight line obtained (Figure 4.9). All the plots at the temperatures studied gave the same result. The rate of disappearance of Galvinoxyl is therefore given by equation [4].

$$-\frac{dG}{dt} = k_D\left[\text{DMSD}\right] \qquad [4]$$

To confirm the zero-order dependence of the rate of disappearance of Galvinoxyl on the concentration of Galvinoxyl solutions containing the same amount of DMSD, but different amounts of Galvinoxyl were studied. Over a six fold increase in the concentration of Galvinoxyl its rate of disappearance remained the same.

The first-order rate constants, k_D, were determined at various temperatures (Table 4.6) and the activation energy of the reaction involved computed to be 24.3 Kcals mole^{-1}. Figure 4.3, curve B shows the fit obtained when k_D is plotted according to the Arrhenius equation.

Figure 4·8

The disappearance of Galvinoxyl in a solution containing 0·016m.l.$^{-1}$ dimethyl sulphinyldipropionate and 0·0015m.l^{-1} of Galvinoxyl in carbon tetrachloride in N_2 at 60°C.

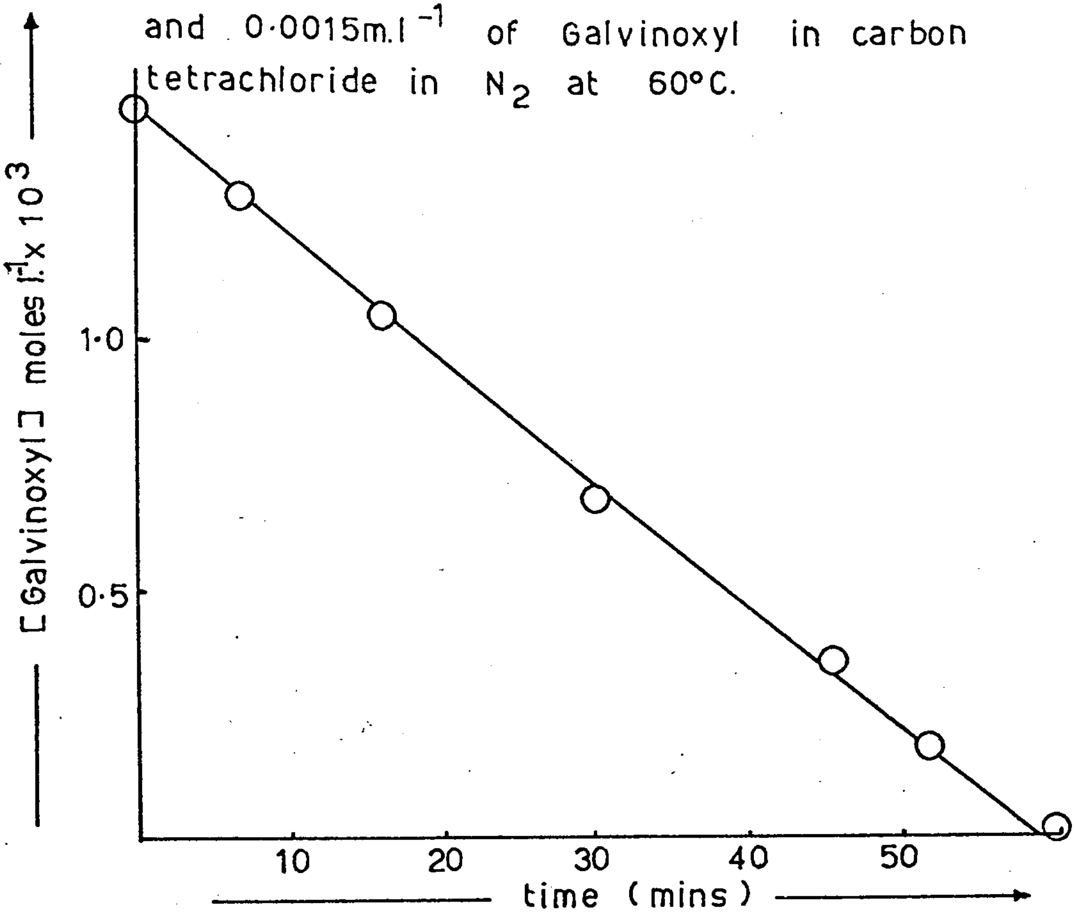


Figure 4·9

The rate of disappearance of Galvinoxyl in carbon tetrachloride (0·0015 m.l.$^{-1}$) at 60°C in the presence of various concentrations of dimethyl sulphinyldipropionate.

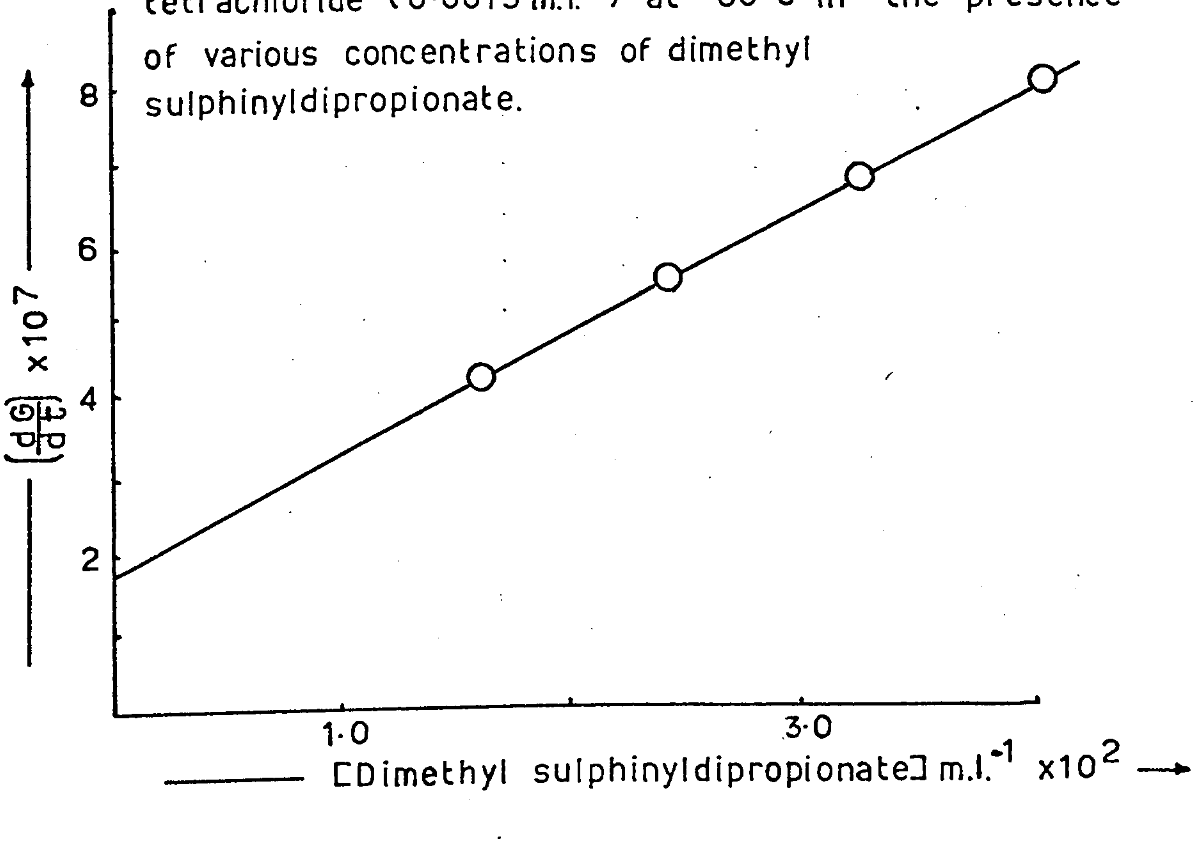


Table 4.6

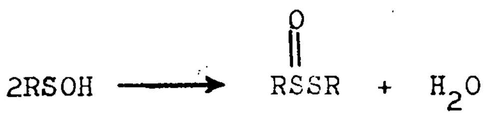
The rate constant (k_D) derived from the rate of disappearance of Galvinoxyl versus dimethyl sulphinyldipropionate concentration.

T°C	70	65	60	55	50
$10^5 k_D (sec^{-1})$	5.4	34	1.6	0.99	0.65

4.4. Product Analysis

The yields of methyl acrylate were measured in the various solvents by use of g.l.c. 0.04 m.ℓ^{-1} of DMSD in carbon tetrachloride produced 0.045 m.ℓ^{-1} of methyl acrylate. In dioxan and chlorobenzene 0.038 m.ℓ^{-1} were obtained. The primary products are therefore methyl acrylate and the sulphenic acid.

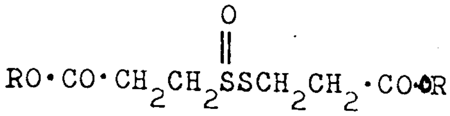
Sulphenic acids[99,100] have been postulated as intermediates in various reactions but only four are actually known and these are mono and diacids of anthraquinone[101-103]. Sulphenic acids disproportionate, giving the thiolsulphinate and water (4)



$$2RSOH \longrightarrow R\overset{O}{\overset{\|}{S}}SR + H_2O \qquad (4)$$

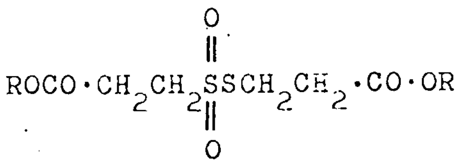
The extent to which the reaction occurs in the decomposition of DMSD was estimated by the determination of water. A 0.04M solution of DMSD in carbon tetrachloride gave 0.019 moles ℓ^{-1} of water as determined by the Karl Fischer method. This represents 95% of the theoretical amount if all of the sulphenic acid disproportionates. Galvinoxyl interferred with the Karl Fischer reagent and therefore the determination was repeated using g.l.c. with dioxan as the solvent. In the absence of Galvinoxyl 95% of the theoretical amount of water was produced and with excess Galvinoxyl no water was produced.

Changes in the infra-red spectrum of DMSD at 75°C were consistent with the formation of the thiolsulphinate[104] (V) ($\nu_{s=o}$ 1068 cm^{-1}) and the thiosulphonate[80] (VI) ($\nu_{s=o}$ 1335 cm^{-1}, 1130 cm^{-1}).



$$RO\cdot CO\cdot CH_2CH_2\overset{\overset{O}{\|}}{S}SCH_2CH_2\cdot CO\cdot OR$$

(V)



$$ROCO\cdot CH_2CH_2\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}SCH_2CH_2\cdot CO\cdot OR$$

(VI)

Evidence for the presence of dimethyl dithiodipropionate (VII) in the product solution was obtained by using g.l.c. and employing peak enrichment using an authentic sample.

$$CH_3O\cdot CO\cdot\ CH_2CH_2SSCH_2CH_2\cdot CO\cdot O\ CH_3$$

(VII)

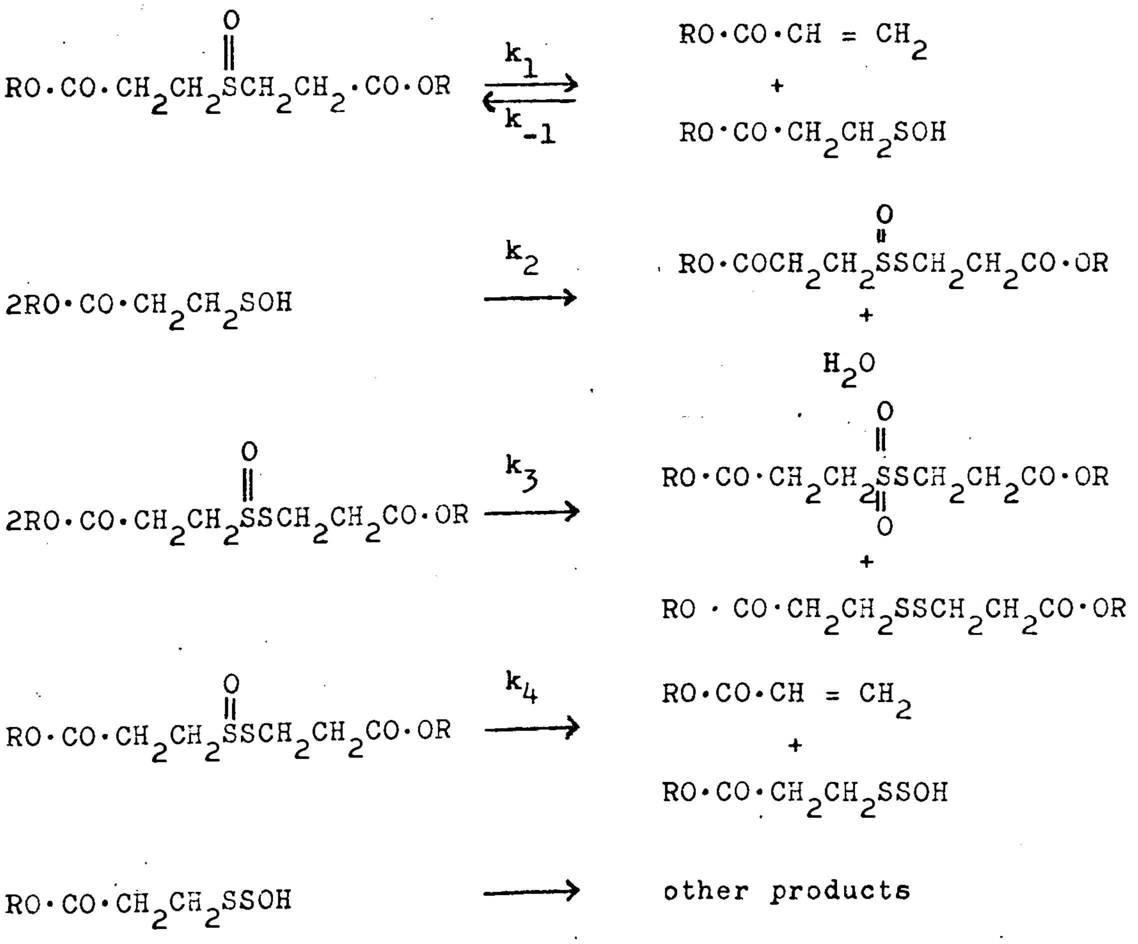
4.5. Discussion

The kinetics of the decomposition of DMSD are not simply first-order as have been found for other sulphoxides[46,91,92,93,94]. A reaction scheme for the thermal decomposition of dialkyl sulphinyldipropionate has to take into account the inhibitary effect of methyl acrylate and the stoichiometry of the reaction, which in the case of carbon tetrachloride solutions is not 1:1 for the production of methylacrylate (Table 4.5). The effect of Galvinoxyl does not support the proposal[36] that DMSD decomposes thermally, at the temperatures studied, to produce radicals which are capable of initiating oxidations. If DMSD did dissociate to produce free radicals and these were capable of initiating oxidative chains, then it is reasonable to suppose that these radicals would be scavenged by Galvinoxyl and so reduce the yield of methylacrylate. The reduction of the yield of methyl acrylate would be throughout the course of the reaction. Figure 4.4 shows that while the overall yield is reduced there is no difference in the initial stages. The final difference is about 15% but this cannot be due to scavenging of primary radicals since the initial yield is not affected. Any reaction scheme has also to account for the disappearance of Galvinoxyl (Figure 4.8).

The Arrhenius parameters (Table 4.2) for the decomposition of DMSD do not support a free radical reaction. The negative entropy of activation indicates the formation of a highly ordered transition state. This is consistent with the β-elimination mechanism proposed by Kingsbury and Cram[46] for the thermal decomposition of sulphoxides (2). The activation energy is consistent with this conclusion.

A reaction scheme, consistent with the above findings, describing the major reactions involved in the thermal decomposition of dialkyl sulphinyldipropionates is given below (Scheme 2).

Scheme 2



$$RO\cdot CO\cdot CH_2CH_2\overset{O}{\overset{\|}{S}}CH_2CH_2\cdot CO\cdot OR \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RO\cdot CO\cdot CH = CH_2 + RO\cdot CO\cdot CH_2CH_2SOH \tag{5}$$

$$2RO\cdot CO\cdot CH_2CH_2SOH \xrightarrow{k_2} RO\cdot COCH_2CH_2\overset{O}{\overset{\|}{S}}SCH_2CH_2CO\cdot OR + H_2O \tag{6}$$

$$2RO\cdot CO\cdot CH_2CH_2\overset{O}{\overset{\|}{S}}SCH_2CH_2CO\cdot OR \xrightarrow{k_3} RO\cdot CO\cdot CH_2CH_2\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}SCH_2CH_2CO\cdot OR + RO\cdot CO\cdot CH_2CH_2SSCH_2CH_2CO\cdot OR \tag{7}$$

$$RO\cdot CO\cdot CH_2CH_2\overset{O}{\overset{\|}{S}}SCH_2CH_2CO\cdot OR \xrightarrow{k_4} RO\cdot CO\cdot CH = CH_2 + RO\cdot CO\cdot CH_2CH_2SSOH \tag{8}$$

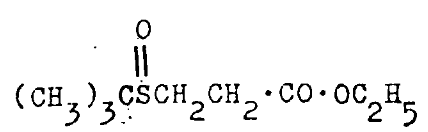
$$RO\cdot CO\cdot CH_2CH_2SSOH \longrightarrow \text{other products} \tag{9}$$

Reaction 5, the thermal decomposition of the sulphoxide, corresponds to a β-elimination to produce the alkene and the sulphenic acid. Sulphenic acids have been postulated as intermediates in various reactions[99,100] and the almost quantitative yield of water in the decomposition of DMSD indicates that disproportionation occurs in this case to give the thiolsulphinate (Reaction 6). Aryl thiolsulphinates are unstable and one of their best known reactions is their disproportionation into thiolsulphonate and disulphide[105-108]. The mechanism of this reaction has been studied and a free radical process is involved[106, 108]. The alkyl thiolsulphinates have not received as much attention as the aryl compounds but they are thermally unstable[109] and also disproportionate to give disulphide[110]. In our study dimethyl dithiodipropionate has been identified as a product and the infra-red of the product solution indicates the presence of thiolsulphonate. This is therefore consistent with the disproportionation of the thiolsulphinate to the disulphide and thiolsulphonate (Reaction 7).

The elimination of methyl acrylate from the thiolsulphinate (Reaction 8) will account for the overall stoichiometry of the decomposition. Bown[8] has reported the same reaction for the thiolsulphinate derived from didodecyl sulphinyldipropionate.
The reversibility of reaction (5) accounts for the inhibition of the decomposition of dimethyl sulphinyldipropionate by added methyl acrylate (Table 4.5). The reaction of t-butyl sulphenic acid with ethyl acrylate[94] to give ethyl β-(2-methylpropyl-2-sulphinyl)propionate (Reaction 10) provides further evidence for the feasibility for the reverse of reaction (5).

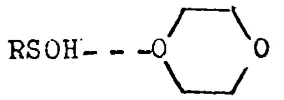
$$(CH_3)_3CSOH + C_2H_5O\cdot CO\cdot CH = CH_2$$

(10)



$$\longrightarrow (CH_3)_3C\overset{\overset{O}{\|}}{S}CH_2CH_2\cdot CO\cdot OC_2H_5$$

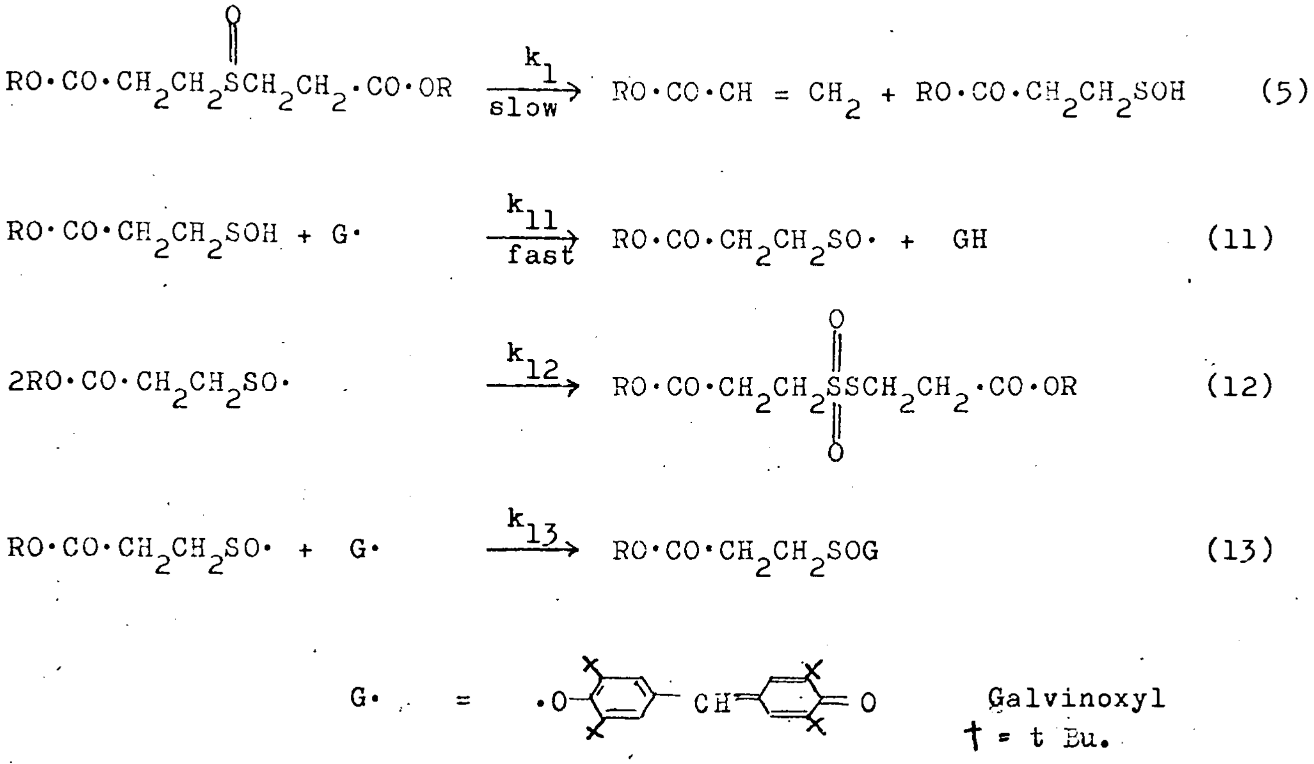
The addition of β(methylpropionyl)sulphenic acid to methyl acrylate (the reverse of reaction (5)) must proceed much slower in carbon tetrachloride than in dioxan and chlorobenzene in order to explain the differences in the kinetics of the decomposition of DMSD in these solvents. There are two possible explanations for this solvent effect. The first is that the addition is favoured by more polar solvents. In the case of dioxan the medium will rapidly become polar due to the miscibility of the solvent with the water produced by the overall reaction. Chlorobenzene is more polar than carbon tetrachloride ($\varepsilon = 5.6$ and 2.2 respectively). The second, and perhaps more feasible, explanation is that the dioxan and chlorobenzene are capable of promoting electron shifts required for the addition. In the case of the dioxan the shift may be brought about by an association shown below and in the case of chlorobenzene by a π complex.



No evidence was obtained to support the possibility that carbon tetrachloride was involved in the reaction. No chloroform was detected by g.l.c. and the high yield of water both suggest that the carbon tetrachloride does not react with the sulphenic acid.

In the presence of Galvinoxyl the decomposition of DMSD can no longer be explained in terms of Scheme 2. The reaction gives good first order rate plots and the yield of methyl acrylate is reduced. Also no water is produced which indicates that reaction 6 no longer occurs. Scheme 3 is postulated to account for these results and also the disappearance of Galvinoxyl according to equation [4].

Scheme 3



$$\mathrm{RO{\cdot}CO{\cdot}CH_2CH_2\overset{O}{\overset{\|}{S}}CH_2CH_2{\cdot}CO{\cdot}OR \xrightarrow[slow]{k_1} RO{\cdot}CO{\cdot}CH = CH_2 + RO{\cdot}CO{\cdot}CH_2CH_2SOH} \tag{5}$$

$$\mathrm{RO{\cdot}CO{\cdot}CH_2CH_2SOH + G{\cdot} \xrightarrow[fast]{k_{11}} RO{\cdot}CO{\cdot}CH_2CH_2SO{\cdot} + GH} \tag{11}$$

$$\mathrm{2RO{\cdot}CO{\cdot}CH_2CH_2SO{\cdot} \xrightarrow{k_{12}} RO{\cdot}CO{\cdot}CH_2CH_2\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}SCH_2CH_2{\cdot}CO{\cdot}OR} \tag{12}$$

$$\mathrm{RO{\cdot}CO{\cdot}CH_2CH_2SO{\cdot} + G{\cdot} \xrightarrow{k_{13}} RO{\cdot}CO{\cdot}CH_2CH_2SOG} \tag{13}$$

The disappearance of Galvinoxyl is not explained by the reaction with intermediate free-radicals produced by dissociation of DMSD. It has already been argued that if this did occur the yield of methyl acrylate in the presence of Galvinoxyl would be reduced and the first-order rate constant (k) would be reduced by k_1' defined in reaction (3). (Assuming maximum efficiency for radical scavenging). Figure 4.1, curves A and B show that this is not the case. It is therefore postulated that the Galvinoxyl reacts directly with the sulphenic acid (Reaction 11). The reaction of phenoxy radicals with thiols has been shown to lead to the formation of disulphides in some cases[111-113] and sulphinic acids also react with Galvinoxyl[114]. This explains why water is no longer a product of the decomposition of DMSD in the presence of Galvinoxyl. The first order rate plots obtained for the decomposition of DMSD should also give the true first-order rate constants corresponding to β-elimination.

We can further explain the rate of disappearance of Galvinoxyl and if we assume that $k_{11} \gg k_{-1}$

$$\therefore \quad -\frac{dG}{dt} = (k_{11}[RSOH] + k_{13}[RSO\cdot])G \qquad [5]$$

and if reaction (5) is very slow compared to reaction (11) the Bodenstien steady-state hypothesis can be applied to the sulphenic acid (RSOH)

$$\therefore \quad k_1[RS(O)R] = k_{11}[RSOH][G]$$

and
$$[RSOH] = \frac{k_1\,[RS(O)R]}{k_{11}\,[G]} \qquad [6]$$

Similarly if $k_{13} \gg k_{12}$

$$[RSO\cdot] = \frac{k_1}{k_{13}}[RS(O)R] \qquad [7]$$

Substituting [7] and [6] into [5]

$$-\frac{dG}{dt} = 2k_1\; RS(O)R \qquad [8]$$

The rate of disappearance of Galvinoxyl $\left(\frac{dG}{dt}\right)$ will therefore be constant so long as the concentration of DMSD can be regarded as constant. The initial concentration of Galvinoxyl used in our studies was much smaller than the initial concentration of sulphoxide and therefore during the consumption of the Galvinoxyl the sulphoxide concentration changes very little and hence a plot of [G] against time is linear (Figure 4.8). This procedure parallels the common procedure used for measuring the rate at which free-radicals are produced in a given system[115,116].

By comparison of Equations [4] and [8]

$$k_D = 2k_1$$

Table 4.7. compares the first-order rate constants for the decomposition of DMSD determined by different means with the values of k_D.

Table 4.7.

Comparison of k_D with k, k_G and k_{in} determined for the decomposition of DMSD in carbon tetrachloride (0.04M) at various temperatures.

First order rate constants $10^5k(\text{sec}^{-1})$ / Temp. T^oC	75	70	65	60	55	50	E_A Kcals mole^{-1}
k_D	-	5.4	3.4	1.6	1.0	0.65	24.3
k_G	8.4	-	2.6.	-	0.9	0.59	23.8
k_{in}	7.8	4.5	3.2	-	0.96	0.57	23.6
k	5.8	3.58	2.54	-	0.73	0.54	22.2

It appears that

$$k_D \hat{=} k_G \hat{=} k_{in} \hat{=} k$$

and that there is a better agreement between k_D and the rate constants k_D and k_{in} than k_D and k. This is consistent because k_D, k_G and k_{in} are only dependent on the initial stages of decomposition while k is the pseudo first-order rate constant for the whole process.

If instead of the assumption that $k_{13} \gg k_{12}$ we assume that $k_{12} \gg k_{13}$ then according to Scheme 3

$$-\frac{dG}{dt} = k_1 \left[RS(O)R\right] \qquad [9]$$

and $k_D = k_1$, which is in agreement with experimental results (Table 4.7)

The Galvinoxyl, therefore, does not react very effectively with the sulphinyl radicals and this is probably due to steric hindrance and preferential dimerization which is a well known reaction of sulphinyl radicals[106, 107,117,118] (reaction 12).

The activation energy for the decomposition of DMSD determined using k, k_{in} and k_G are comparable to the activation energy determined using the values of k_D (Table 4.7). This is required if Schemes 2 and 3 are correct.

The rate of disappearance of Galvinoxyl at zero sulphoxide concentration obtained graphically (Figure 4.9) is a great deal larger than the actual decay of a pure Galvinoxyl solution. Therefore at low sulphoxide concentration $\frac{dG}{dt}$ is no longer independent of Galvinoxyl concentration and equation [4] no longer holds.

The decomposition of dimethyl sulphinyldipropionate in styrene at 75°C produces 98% of the theoretical amount of methyl acrylate required by a 1:1 stoichiometry. If free-radicals were produced during decomposition then it would be unlikely that the yield of methyl acrylate would be so high. One could expect some of the radicals to react with the solvent molecules. This therefore provides additional evidence for the non-radical nature of the decomposition of dialkyl sulphinyldipropionate. The first order kinetics of the decomposition of DMSD in styrene (Figure 4.7) can be explained by a reaction of the sulphenic acid with styrene which is analogous to the reaction of the sulphenic acid with methylacrylate.

The decomposition of DMSD in the presence of cumene hydroperoxide gives good first order kinetics as determined by methylacrylate formation (Figures 4.5 and 4.6). This can be explained by cumene hydroperoxide reacting very rapidly with the sulphenic acid (14).

$$\begin{array}{l} RS(O)R \xrightarrow{\Delta} \text{Alkene} + RSOH \\ RSOH + R'OOH \xrightarrow{\text{fast}} \text{Products} \end{array} \qquad (14)$$

The greater decrease in the yield of methylacrylate that occurs when the reaction is carried out in the presence of cumene hydroperoxide compared to Galvinoxyl is probably due to the removal of the sulphoxide by an alternative reaction.

This deduction, that there is a fast reaction between the sulphenic acid and a hydroperoxide is very important in terms of the antioxidant mechanism (Chapter 6).

Chapter 5

AN INVESTIGATION OF THE PRO-OXIDANT STAGE. THE EFFECT OF DIMETHYLSULPHINYLDIPROPIONATE ON THE POLYMERISATION OF STYRENE

5.1. Introduction

A common procedure which is used to detect radical formation during a reaction is to study the reaction in the presence of a reaction which proceeds by a radical chain process, such as polymerisation[119]. the radical formation is then enormously emphasised as it initiates the chain process producing effects which can be easily studied. The pro-oxidant effect is really the result of such an effect. It was therefore believed that further studies of the reactions of DMSD in styrene would provide information relative to the free radical intermediates which are produced and capable of initiating oxidative chains.

Styrene polymerises readily by a free-radical chain mechanism and has been studied extensively[119-121]. The mechanism is generally discussed in terms of initiation, propagation, termination and transfer reactions. Scheme 4 serves to illustrate the mechanism involved.

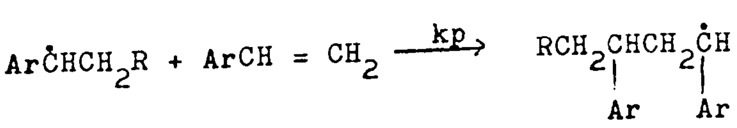
Scheme 4

(1) Initiation

$$\text{Radical source} \longrightarrow R\cdot$$

$$R\cdot + ArCH = CH_2 \xrightarrow{k_i} Ar\dot{C}HCH_2R$$

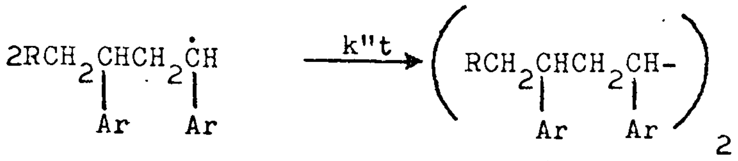
(2) Propagation



$$Ar\dot{C}HCH_2R + ArCH = CH_2 \xrightarrow{kp} RCH_2\underset{Ar}{\underset{|}{C}}HCH_2\underset{Ar}{\underset{|}{\dot{C}}}H$$

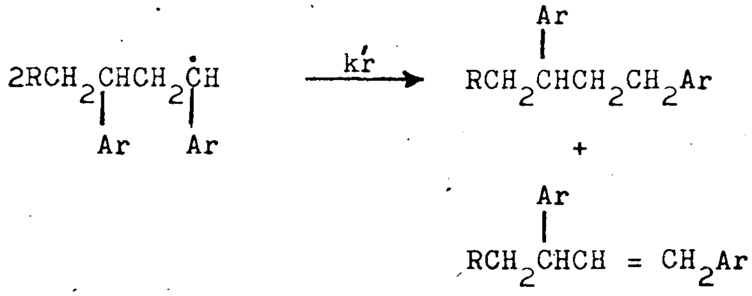
(3) Termination

(a) by combination



$$2RCH_2\underset{Ar}{C}HCH_2\underset{Ar}{\dot{C}}H \xrightarrow{k''t} \left(RCH_2\underset{Ar}{C}HCH_2\underset{Ar}{C}H-\right)_2$$

(b) by disproportionation



$$2RCH_2\underset{Ar}{C}HCH_2\underset{Ar}{\dot{C}}H \xrightarrow{k'r} RCH_2\overset{Ar}{C}HCH_2CH_2Ar + RCH_2\overset{Ar}{C}HCH = CH_2Ar$$

(4) Transfer - Basically, if $R\cdot_M$ is the growing polymer radical it may react with a molecule which has a labile atom, XY, so that

$$R\cdot_M + XY \longrightarrow R_MY + X\cdot$$

The new radical X· may either propagate or react in some other manner. Transfer to monomer, polymer, solvent or any other species present may occur. However, transfer to monomer and polymer does not affect the rate of polymerisation and therefore for the bulk polymerisation of styrene we can derive an expression for the rate of polymerisation. Assuming steady-state conditions exist, that is

rate of initiation = rate of termination

$$k_i[R\cdot][M] = k_t[M\cdot]^2$$

therefore Rate of polymerisation (Rp) = $kp[M][M\cdot]$

$$\therefore \quad Rp = kp\left(\frac{k_i}{k_t}[M][R\cdot]\right)^{1/2}[M]$$

The initiation rate, $k_i[M][R\cdot]$, may be written as $k_d.f.[In]$ where In represents the source of radicals, the initiator; f is the fraction of these radicals which result in initiation of polymerisation and kd is the rate constant for the radical production from this initiator.

$$\therefore \quad Rp = kp\left(\frac{kd}{kt}.f.[In]\right)^{1/2}[M] \qquad [1]$$

Hence by adding different concentrations of a proposed initiator and observing the rate of polymerisation of styrene the radical generating reaction can be studied.

DMSD was added to pure styrene and its effect on the rate of the thermal polymerisation was studied . It was anticipated that if DMSD decomposed thermally to produce radicals then the rate of polymerisation would be greatly accelerated and a plot of log Rp against log [DMSD] would be linear with a slope of 0.5 (according to [1]). However the effects observed when using pure DMSD indicated that free-radicals capable of initiating polymerisation were not produced. It was therefore believed that hydroperoxide must be involved in the pro-oxidant reaction. A study of DMSD and cumene hydroperoxide in styrene was therefore undertaken.

5.2. Results

The rate of the thermal polymerisation of pure styrene in nitrogen is effectively retarded by the addition of DMSD (Figure 5.1). No induction periods were apparent and the rate of polymerisation was constant for the period of study which corresponded in the case of these results to about 4% conversion of monomer into polymer. Rates were reproducible within 5% and the thermal polymerisation of the pure styrene proceeded at 9.7×10^{-6} moles litre^{-1} sec^{-1} at 75°C. A value of 9.25×10^{-6} moles litre^{-1} sec^{-1} has previously been recorded[54].

The effect of DMSD on AZBN initiated polymerisation of styrene was also studied and Figure 5.2 confirms that DMSD retards the free-

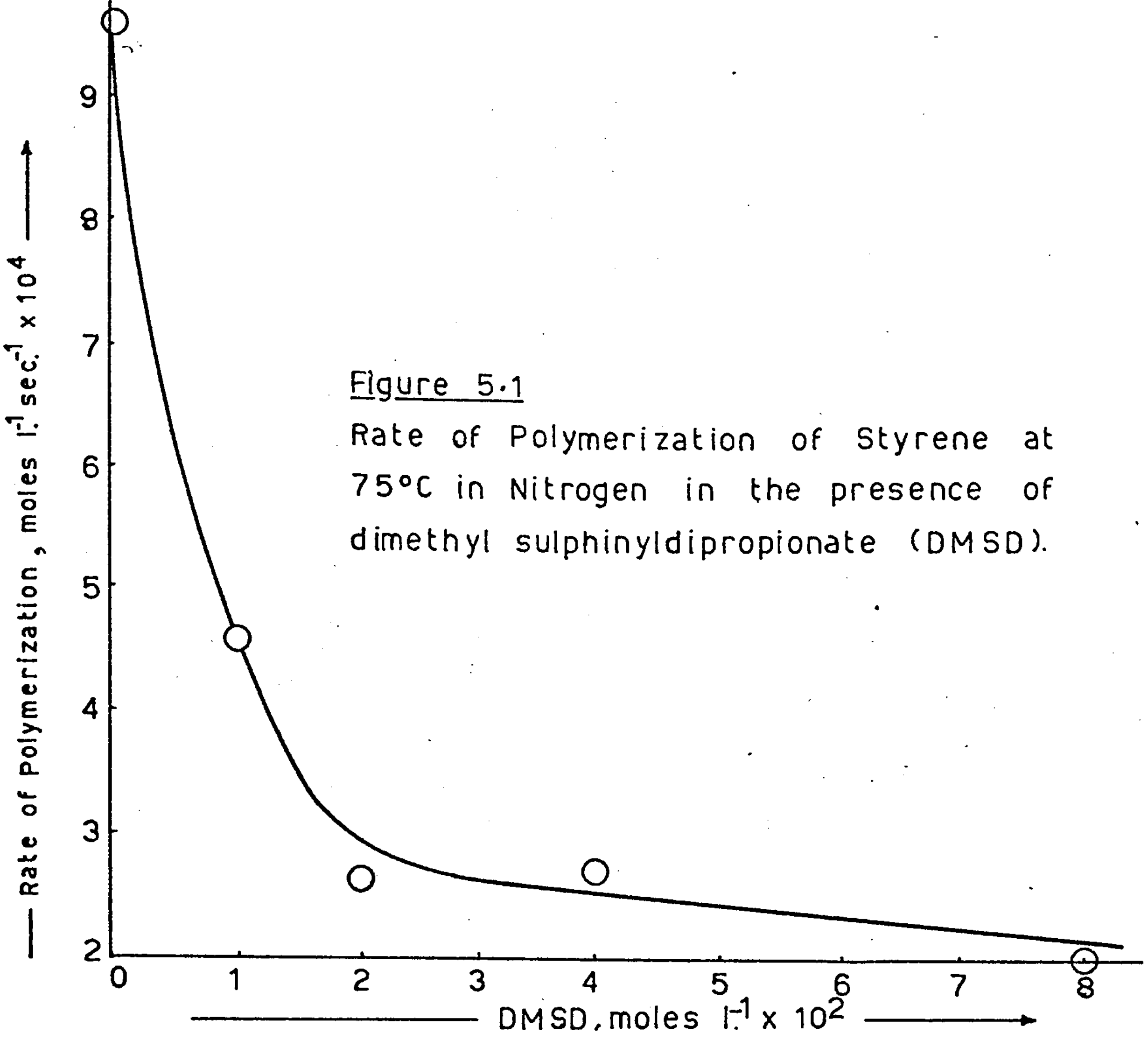


Figure 5·1

Rate of Polymerization of Styrene at 75°C in Nitrogen in the presence of dimethyl sulphinyldipropionate (DMSD).

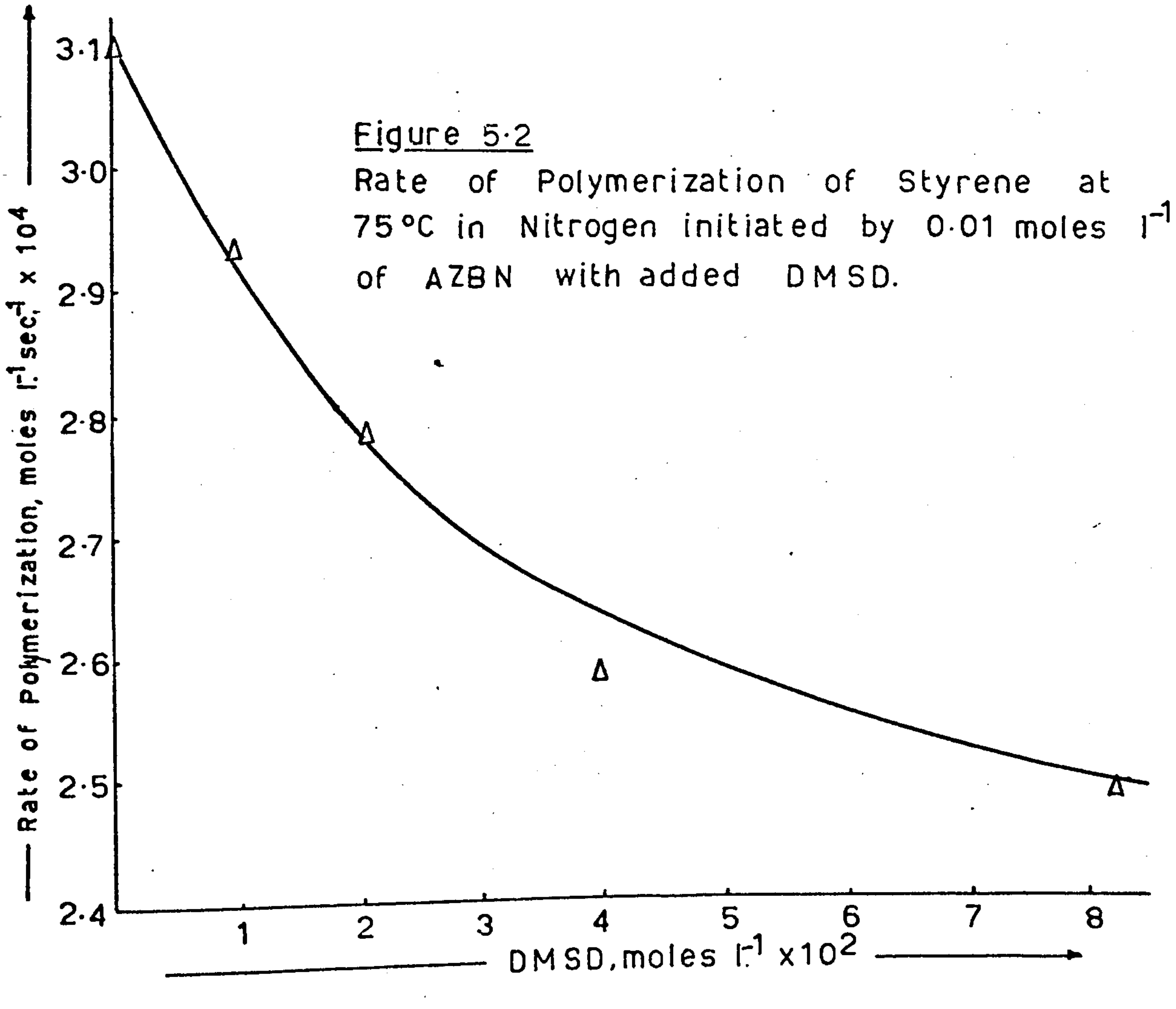


Figure 5·2

Rate of Polymerization of Styrene at 75°C in Nitrogen initiated by 0·01 moles l^{-1} of AZBN with added DMSD.

radical polymerisation of styrene. No induction periods were observed and the rates of polymerisation were constant for at least 10% conversion.

It was therefore apparent that the overall effect of DMSD is to inhibit free-radical polymerisation and no evidence of DMSD acting as an initiator was produced.

The effect of DMSD on the polymerisation of styrene initiated with CHP showed complex behaviour. Depending upon the concentration of DMSD added the rate of polymerisation of styrene was either retarded or initiated (Figure 5.3; A). While the reproducibility of the determination of the rate of polymerisation of CHP initiated polymerisation was satisfactory, difficulty was encountered in reproducing the rates of polymerisation of the CHP-DMSD system. Table 5.1 lists five separate determinations of the rate of polymerisation of a 0.038M solution of CHP in styrene at 75°C. The measurements were made using different batches of styrene and different dilatometers. Excellent reproducibility is recorded.

Table 5.1

Reproducibility of the measurement of the rate of polymerisation of styrene initiated by 0.038m.$^{-1}$ of cumene hydroperoxide (CHP).at 75°C

Determination	1	2	3	4	5
Rp 10^4 moles ℓ^{-1} sec^{-1}	1.18	1.16	1.17	1.16	1.18

The difficulty in obtaining reproducibility with the DMSD-CHP systems was overcome by using the specially designed dilatometer shown in

Figure 5·3

The rate of Polymerization of Styrene at 75°C in vacuo.

(A)-○-; Styrene containing 0·038 m.l.$^{-1}$ of CHP in the presence of DMSD

(B)- Δ -; Styrene containing 0·055 m.l.$^{-1}$ of DMSD in the presence of CHP.

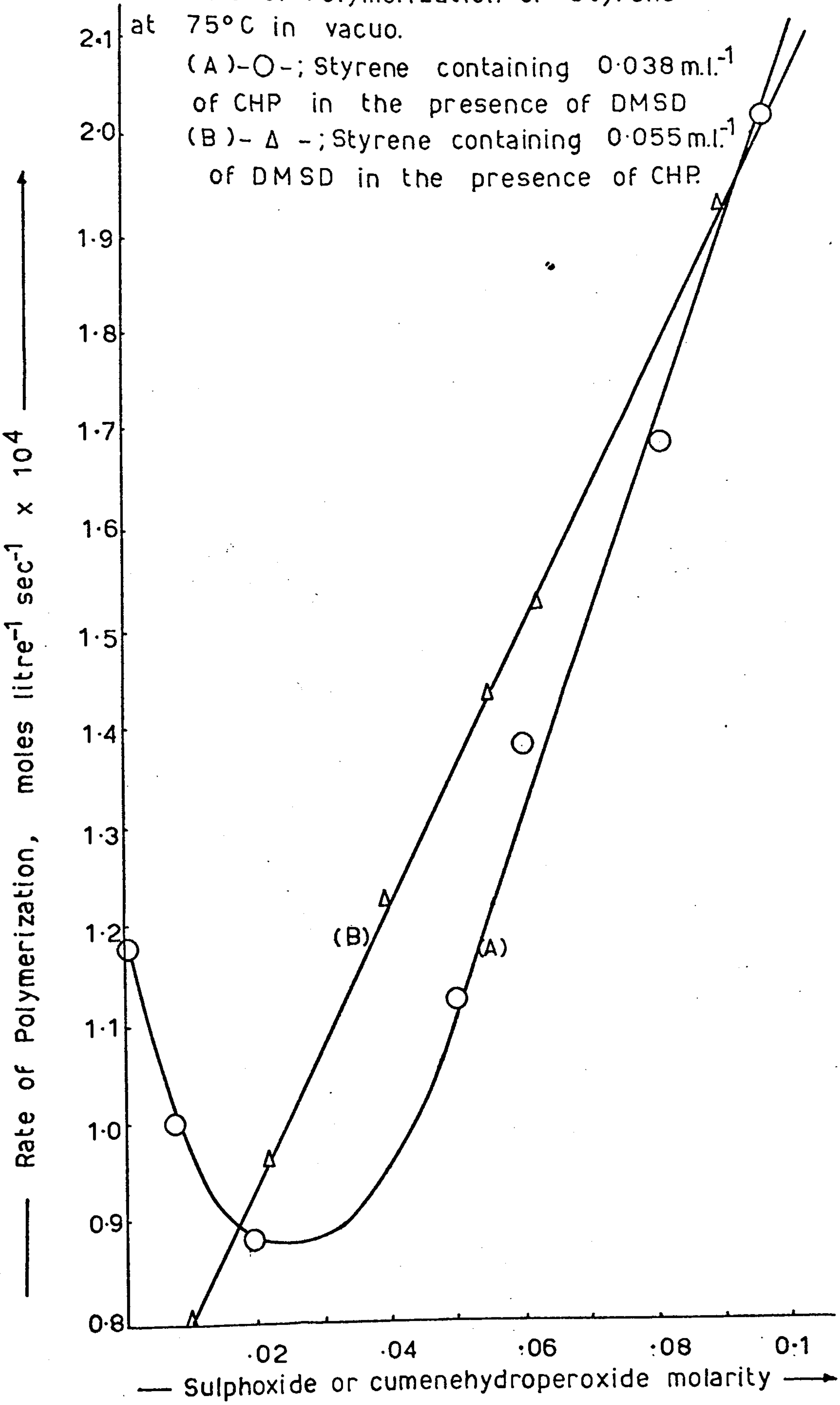


Figure 2.3. This dilatometer allowed the styrene to be degassed more rigorously and also enabled the DMSD to be added to a CHP solution just before the determination was to be made. The rates of polymerisation were then reproducible within 6%.

The effect of oxygen was further studied by using solutions of styrene which had been outgassed with oxygen. In the presence of oxygen induction periods to polymerisation occur. Figure 5.4 shows that there is an optimum value for this induction period and this corresponds to the concentration of DMSD which when added is most effective at retarding the polymerisation (Figure 5.3). After the induction periods the polymerisation is retarded and is only accelerated at a much larger concentration of DMSD (Figure 5.5).

The rates of the polymerisation were followed for periods corresponding to about 5% conversion. During this time rates of polymerisation were fairly constant. A product derived from DMSD decomposes CHP by a cationic mechanism (Chapter 6). However there is an induction period to this reaction and the effects that we were observing occurred during this period.

At 55°C DMSD can also either retard or accelerate the polymerisation of styrene initiated by CHP (Table 5.2).

<u>Table 5.2</u>

Rates of polymerisation of styrene initiated by CHP (0.038M) at 55°C in the presence of DMSD. Measurements made using plain dilatometers (Figure 2.3) and with solutions outgassed with nitrogen.

DMSD (moles $\ell.^{-1}$)	0	0.02	0.04	0.178
Rate of polymerisation (10^5 mole $\ell.^{-1}$sec^{-1}	3.8	2.9	2.9	6.39

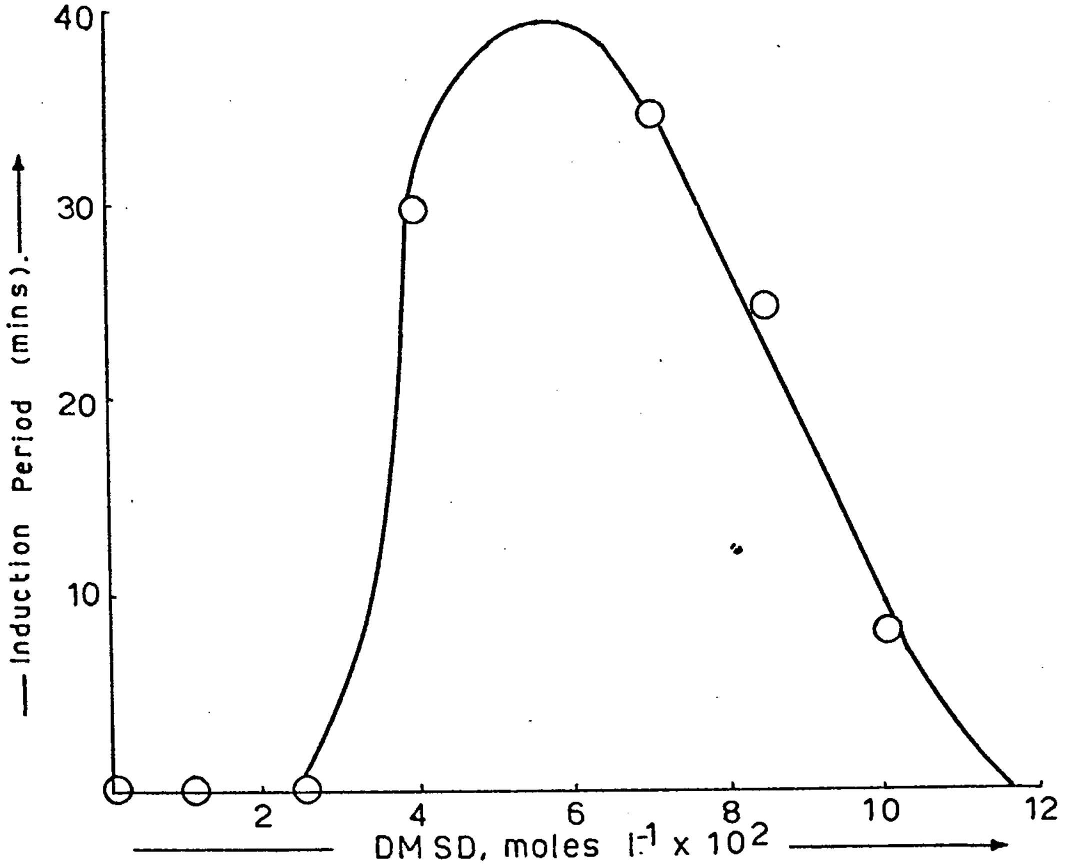


Figure 5·4
Induction Periods which occur before the polymerization of styrene outgassed with oxygen and initiated by CHP (0·038M) at 75°C in the presence of DMSD.

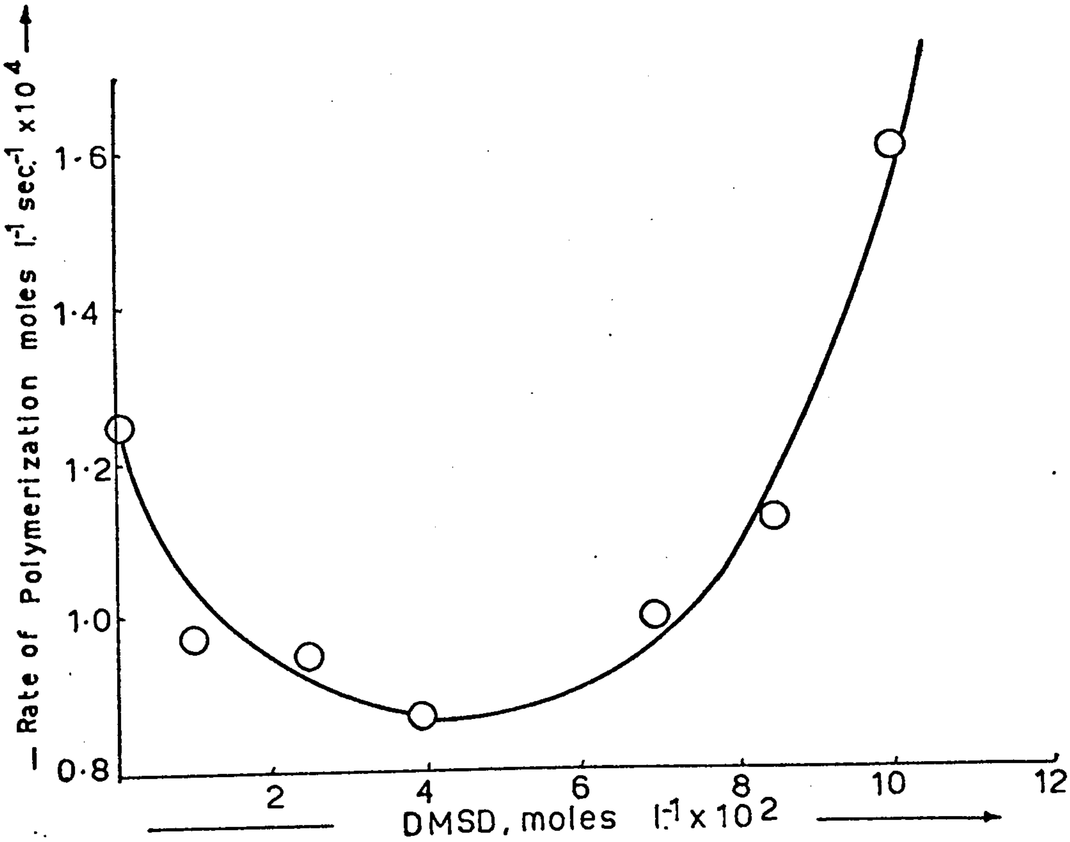


Figure 5·5
Rate of polymerization of styrene at 75°C in oxygen initiated by CHP (0·038M) in the presence of DMSD.

The rates of polymerisation of a stock solution of DMSD-CHP in styrene in N_2 were therefore measured at temperatures between 55 and 75°C. The resulting rates were then plotted according to the Arrhenius equation. When near-equimolar amounts of CHP and DMSD were used the Arrhenius equation was not obeyed (Figure 5.6 - A). However with an excess of sulphoxide the rates of polymerisation varied with temperature according to the Arrhenius equation and the activation energy was calculated to be 14.3 Kcal mole^{-1} (Figure 5.6, B). The values of the rates at different temperatures are given in Table 5.3.

Table .5.3.

The rates of polymerisation of styrene at various temperatures containing CHP (0.038M) and DMSD (0.09M) in nitrogen.

T°C	55	60	65	70	75
Rate (10^5 mole $\ell.^{-1}$ sec^{-1})	5.25	6.9	9.1	13.0	18.4

The effect of varying the concentration of CHP added to the polymerisation of styrene containing DMSD (0.055M) showed that the order with respect to cumene hydroperoxide for the rate of polymerisation of a CHP-DMSD-styrene system was one (Figure 5.3, B).

The effect of dimethyl thiodipropionate on the cumene hydroperoxide initiated polymerisation of styrene was also studied. Table 5.4 shows that even at high concentrations of added sulphide the rate of polymerisation is unchanged. The variation of the rates recorded is ± 5% of the rate obtained for the CHP initiated polymerisation The rates were measured up to 5% conversion and during this period were constant.

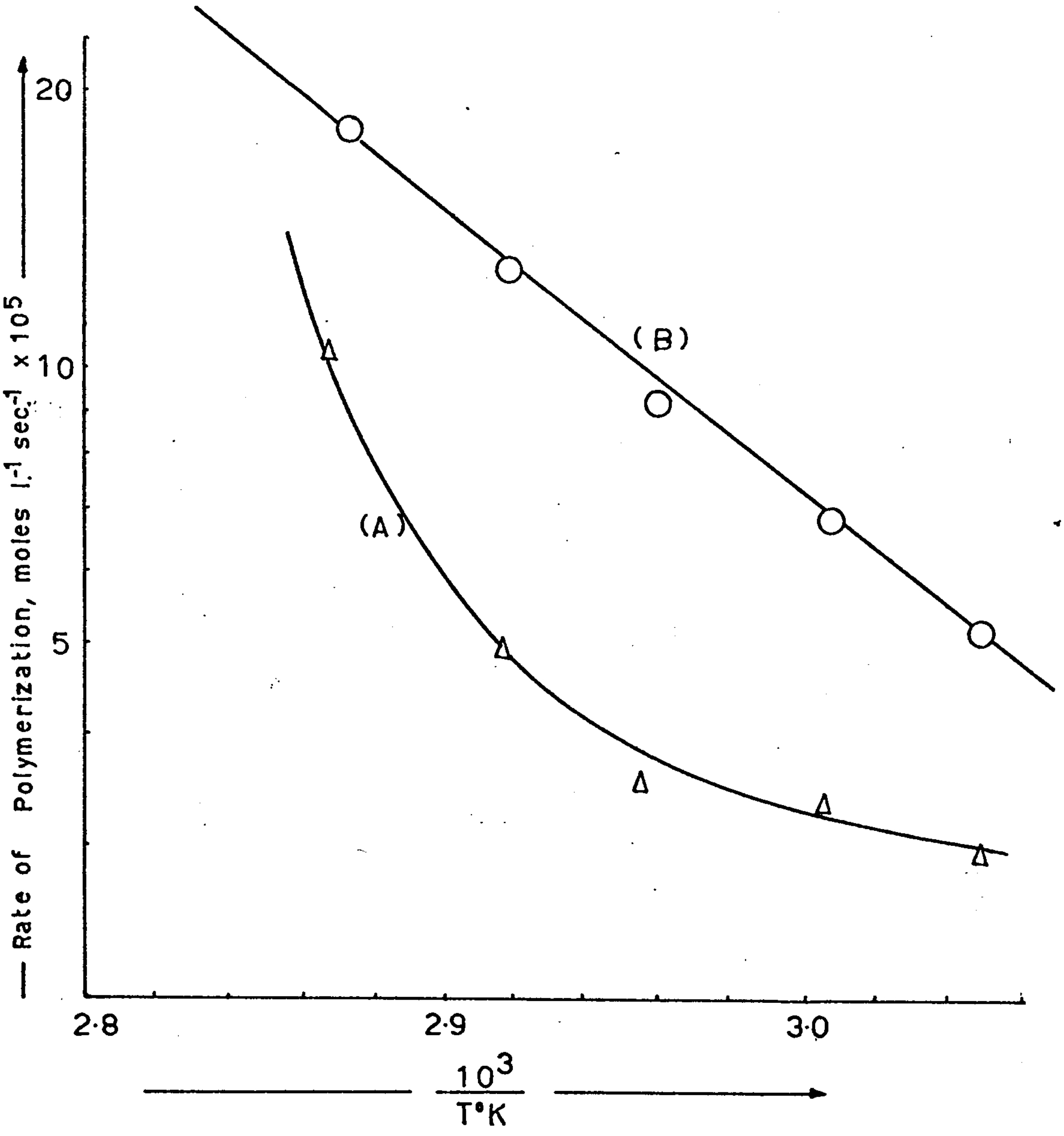


Figure 5·6
The Arrhenius plots for the rate of polymerization of Styrene initiated by CHP (0·038M) at 75°C and containing
(A) 0·04 moles l.$^{-1}$ of DMSD
(B) 0·09 moles l.$^{-1}$ of DMSD

Table 5.4

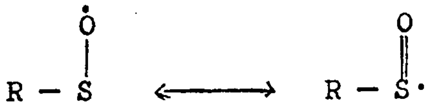
Rate of polymerisation of styrene initiated by CHP (0.037M) at 74.3°C, outgassed with nitrogen, in the presence of dimethyl thiodipropionate.

Dimethyl thiodipropionate 10^2 moles litre^{-1}	0	1.0	2.9	4.9	7.8	11.2	18.4
Rp 10^4 moles ℓ^{-1} sec^{-1}	1.05	1.08	0.915	1.1	1.05	0.96	1.0

5.3. Discussion

The addition of DMSD to styrene does not result in the initiation of polymerisation. In fact polymerisation is retarded and therefore no evidence can be proposed in favour of the postulate[36] that free radicals, capable of initiating oxidations, are produced during the thermal decomposition of DMSD at temperatures up to 75°C.

It has been shown that 98% of the theoretical amount of methyl acrylate is produced when DMSD is thermally decomposed in styrene. This indicates that there is no direct reaction between the styrene or styryl radicals and the DMSD. However a study of the kinetics of methyl acrylate formation in styrene indicate that the sulphenic acid, also produced by the decomposition, does not react with the methyl acrylate (Figure 4.7). This is contrary to the results obtained for the decomposition of DMSD in chlorobenzene, dioxan and, to a lesser extent, in carbon tetrachloride. This would appear to indicate that the sulphenic acid reacts preferentially with the styrene. Thiols are known to react with styrene[119,122,123] and are used as chain transfer agents[119,124]. The hydrogen atom of the sulphenic acid is likely to be more labile than the thiols, due to the resonance of the resulting radical



$$\mathrm{R-S-\dot{O}} \longleftrightarrow \mathrm{R-\overset{O}{\overset{\|}{S}}\cdot}$$

and therefore it is conceivable that the sulphenic acid will react with the polystyryl radicals (1)

$$\mathrm{Ar\dot{C}HCH_2R' + RSOH \longrightarrow ArCH_2CH_2R' + \underset{(i)}{RSO\cdot}} \qquad (1)$$

The sulphinyl radicals (i) can then add to the styrene to initiate polymerisation, terminate by combination with propagating radicals, or dimerise to produce thiolsulphonate. Attempts to add sulphinyl radicals to olefins were unsuccessful[118] and Kock[108] found that aryl sulphinyl radicals did not act as chain carriers. These results are in accord with the findings of Kice[114,125] which suggest that the sulphinyl radical is fairly stable. Our results ~~(Figure 4.3)~~, in agrement with other workers[106,107,117,118], also indicate that dimerisation of the sulphinyl radicals is facile and therefore if reaction (1) occurs it is likely that retardation of polymerisation will result.

No induction periods are apparent and therefore the effectiveness of the sulphenic acid as a retarder cannot be compared to that of the hindered phenols which completely inhibit polymerisation. The shape of Figure 5.1 is also perhaps consistent with the view that while the sulphenic acid is the retarder it is not very efficient. The addition of a small quantity of DMSD results in a substantial reduction in the rate of polymerisation. However as the amount added is increased its effectiveness soon levels off. This can be explained in terms of competitive reactions. The reaction of the polystyryl radicals with the sulphenic acid will be first-order with respect to the sulphenic acid and the disproportionation of the sulphenic acid to thiolsulphinate will be second order. Hence at low concentration chain termination may predominate while at higher concentrations disproportionation becomes more prominant.

With the AZBN initiated polymerisations (Figure 5.2) the addition of DMSD retards the rate but with a reduced effectiveness. This is to be expected because the steady-state concentration of radicals is much higher and therefore the net number of radicals scavenged by the DMSD will be a smaller percentage. AZBN decomposes by a first-order reaction to produce two radicals capable of initiating polymerisation.

The first-order rate constant at 75°Cis 7.3×10^{-5} sec^{-1} [126], and the efficiency of the initiating radicals is about 80%[127]. DMSD decomposes at a similar rate at 75°C to produce one mole of sulphenic acid (Table 4.7). By comparison of the rates of polymerisation of styrene initiated by AZBN at 75°C at different concentrations of DMSD the efficiency of the proposed retarded, the sulphenic acid, can be estimated. If 0.04 $m.\ell^{-1}$ of DMSD is added to AZBN in styrene (0.01M) the effective concentration of AZBN is reduced by 28% to 0.0072M. The efficiency decreases with increasing concentration of DMSD. These results show that DMSD is less efficient at retarding the AZBN initiated polymerisation of styrene than in retarding the oxidation of cumene initiated by the same amount of AZBN (compare Figures 5.2 and 3.3 and 3.4).

The rate of polymerisation of styrene initiated by cumene hydroperoxide obeys equation [1] [128]. The actual mode of initiation is still uncertain but Walling and Chang[129] have proposed that initiation involves hydrogen transfer (2).

$$\mathrm{ROOH} + \mathrm{CH_2} = \mathrm{CHAr} \longrightarrow \mathrm{ROO}^{\bullet} + \mathrm{CH_3} - \mathrm{\dot{C}HAr} \qquad (2)$$

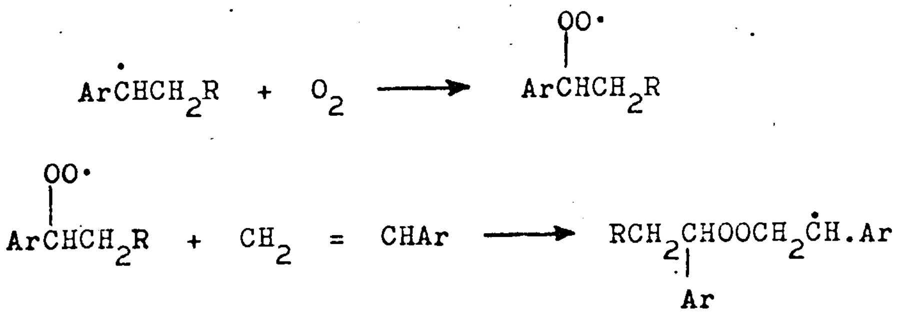
Benson[130] approached the problem of cumene hydroperoxide initiated polymerisation of styrene thermodynamically and concluded that the likely reaction involved was

$$2\mathrm{ArCH} = \mathrm{CH_2} + \mathrm{ROOH} \longrightarrow \mathrm{Ar\dot{C}HCH_2CH_2CH_2Ar} + \mathrm{RO_2}^{\bullet}$$

In both cases a styryl and a peroxy radical are involved.

In the presence of DMSD the initiation of polymerisation by CHP is complex. Retardation and initiation appear to occur simultaneously (Figure 5.3, Table 5.2). The retardation is not due to the concentration of CHP being reduced by decomposition induced by DMSD because measurements were only made on the first 5% conversion and the period involved corresponds to the induction period for the decomposition reaction (Chapter 6). Also during the period of measurement the rate of polymerisation was constant. The retardation is most probably due to a transfer reaction between the sulphenic acid and the polystyryl radicals as in the case discussed above.

When DMSD is added to CHP initiated polymerisation of styrene in oxygen retardation is much more effective and induction periods are recorded (Figures 5.4 and 5.5). In the presence of oxygen the polymerisation of styrene does not follow Scheme 4. This is because the growing polymer radicals react with oxygen 2.5 x 10^5 times faster than they react with a monomer molecule[131], resulting in the formation of a 1:1 copolymer of styrene and oxygen[131] (Reaction 3).



$$\mathrm{Ar\dot{C}HCH_2R + O_2 \longrightarrow Ar\overset{OO\cdot}{\overset{|}{C}}HCH_2R}$$

$$\mathrm{Ar\overset{OO\cdot}{\overset{|}{C}}HCH_2R + CH_2 = CHAr \longrightarrow RCH_2\underset{\underset{Ar}{|}}{C}HOOCH_2\dot{C}H.Ar} \qquad (3)$$

Therefore the effect of oxygen on the CHP-DMSD-styrene system may be explained in terms of a preferential reaction of the inhibitor with the peroxy radical rather than with the polystyryl radical. The O—H bond dissociation energy of hydroperoxides[85] is 90 Kcals mole^{-1} while the benzyl C—H bond dissociation energy is 78 Kcals mole^{-1} [119]. The transfer of a hydrogen atom to the peroxy radical, assuming that the same inhibitor is involved, is therefore 12 Kcal mole^{-1} energetically more favourable. The polar character of the transition state is also important in determining the likelihood of the transfer reactions[86]. The peroxy radical is an acceptor radical in that it can assume anionic character while a benzylic radical is a donor radical in that it can assume cationic character in the transition state. The sulphenic acid is likely to be a donor substrate because the oxygen will be able to stabilise a positive charge. If this is the case the sulphenic acid would favour transfer with an acceptor radical. Therefore transfer with the peroxy radical will be favourable to a transfer with the benzyl radical on purely polar grounds.

At high concentrations of DMSD the rate of polymerisation is accelerated (Figure 5.3). This occurs when the ratio CHP/DMSD is less than one which is consistent with the oxygen absorption studies. These show that the greatest pro-oxidant effect occurs when there is an excess of sulphoxide (Figure 3.2).

The accelerated rate of polymerisation of styrene initiated by CHP at higher sulphoxide concentrations indicates that a free-radical generating process is occurring as well as a retarding reaction. The process must involve hydroperoxide as well as sulphoxide because no accelerated rates are encountered in the absence of cumene hydroperoxide (Figures 5.1 and 5.2). A radical generating reaction that could account for initiation invokes the bimolecular reaction of the sulphenic acid with the hydroperoxide (Reaction 4).

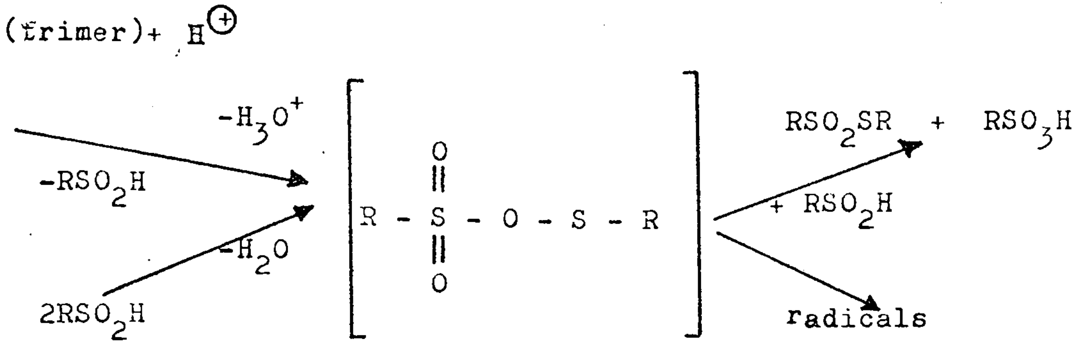
$$\mathrm{ROOH} + \mathrm{R'SOH} \longrightarrow \mathrm{RO}\cdot + \mathrm{R'SO}\cdot + \mathrm{H_2O} \qquad (4)$$

Since the sulphenic acid may be regarded as a thiohydroperoxide this is analogous to the self-induced decomposition of hydroperoxides[132] and also to the reactions of thiols with hydroperoxides to give thiyl and alkoxy radicals[133]. However the reaction of the sulphenic acid with the hydroperoxide can be envisaged to produce the sulphinic acid (Reaction 5) and an alternative suggestion is that sulphinic could be responsible for radical generation within the system.

$$R'SOH + ROOH \longrightarrow R'SO_2H + ROH \qquad (5)$$

Aromatic and isobutyl sulphinic acids have been reported to be initiators for the bulk polymerisation of styrene[134] and a reaction between oxygen and sulphinic acids has also been shown to initiate the copolymerisation of styrene and butadiene[135]. Hydroperoxides are also reported to accelerate the initiation of polymerisation by sulphinic acids[136]. Overberger[137] has studied the rates of polymerisation of methylacrylate initiated by p-methoxybenzene-sulphinic acid and also separately with benzene sulphinic acid in the absence of oxygen. It was believed that the rates determined were due to the rate of the decomposition of the sulphinic acid. Evidence was also provided for the free-radical nature of the reaction by a study of the composition of a resulting copolymer.

Amdur and Shavit[138-140] have investigated the kinetics and mechanism of the initiation of polymerisation by p-toluene sulphinic acid. A mechanism which involved their disproportionation was suggested. It is postulated that two parallel steps, one a bimolecular reaction and the other involving a trimer of the sulphinic acid, yield the corresponding sulphenyl sulphonate. This labile compound then decomposes into free radicals or reacts with another molecule of the sulphinic acid producing the thiolsulphonate and the sulphonic acid (5). This mechanism is able to explain the variety and unusually high orders encountered in polymerisation initiated by sulphinic acid initiators.



(5)

In the case of styrene the order is 0.5 with respect to sulphinic acid, indicating a monomolecular radical formation[191]. Shavit[140] believes that the above scheme takes this into account by the competing non-radical reaction of the sulphinic acid.

The disproportionation of sulphinic acids is believed to proceed via the sulphinyl sulphone[141-144]. These dissociate very rapidly[114,125] and therefore it is more likely that the initiation of polymerisation by sulphinic acids would result from the sulphinyl sulphone. The sulphonyl radical is the likely initiating species and will add to the styrene and possibly abstract a benzyl hydrogen atom to reform sulphinic acid[114]. The sulphinyl radical, which has previously been discussed, is likely to dimerise to produce the thiolsulphonate.

A redox reaction between the sulphinic acid and the hydroperoxide may also be envisaged (6).

$$RSO_2H + R'OOH \longrightarrow RSO_2\cdot + R'O\cdot + H_2O \qquad (6)$$

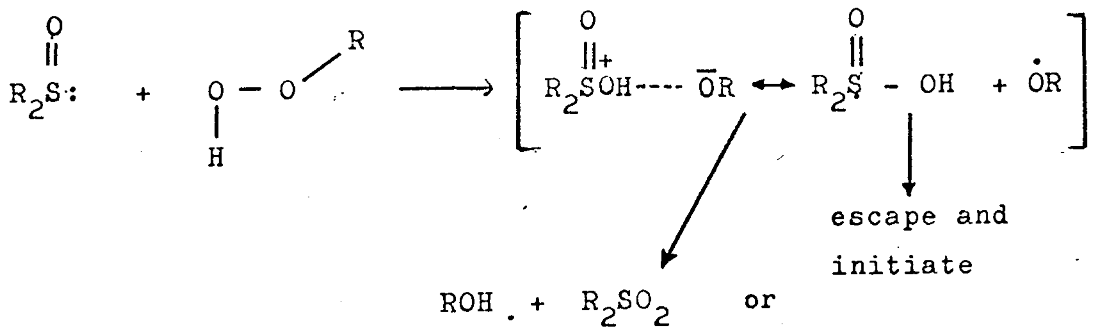
This is analogous to the reaction of the hydroperoxide and sulphenic acid previously proposed (5). This reaction may account for the accelerating effect of hydroperoxide when added to polymerisations initiated by sulphinic acids[136]. Desulphonylation of the sulphonyl radical may also occur (7) and the sulphur dioxide would then

$$RSO_2\cdot \longrightarrow R\cdot + SO_2 \qquad (7)$$

catalytically decompose the hydroperoxide (Chapter 7). This could account for the oxygen absorption results which show that a pro-oxidant effect occurs immediately before final inhibition (Figure 3.2).

The suggestions for the initiating reactions (both the pro-oxidant effect and polymerisation) are attractive in that they explain the need for the presence of hydroperoxide. However an explanation for why the reaction should be favoured by excess sulphoxide is not apparent.

A third possible explanation for the initiating reaction that should be considered involves a nucleophilic attack, by the sulphoxide, on the hydroperoxide (8)



(8)

Minoura[145] has reported that benzyl sulphoxide accelerates the polymerisation of methyl acrylate initiated by cumene hydroperoxide. The rate of polymerisation was proportional to $[\mathrm{CHP}]^{0.5}[\mathrm{Sulphoxide}]^{0.5}$ and he explained the results in terms of a nucleophilic attack. Similar reactions to (8) have been postulated for tertiary amines with peroxides[146]. The reaction of dimethyl aniline with benzoyl peroxide induces the polymerisation of styrene and methyl acrylate[146-148]. Humphris[149] and Pobedimskii[150] also postulate a similar mechanism for the oxidation of a phosphite to a phosphate.

If the above reaction (8) was occurring one would expect that addition of the sulphide to accelerate the rate of the polymerisation of styrene initiated by CHP even more than the addition of the same amount of the sulphoxide. Table 5.4 shows that this is not the case and also provides further evidence in support of the theory that the sulphoxide is the precursor to the pro-oxidant species. Consistent with the above reasoning is that Minoura[145] finds dibenzyl sulphide more effective than the sulphoxide in accelerating the rate of polymerisation of methyl acrylate initiated by CHP. The fact that dimethyl thiodipropionate does not accelerate the rate of the CHP initiated polymerisation of styrene (Table 5.4) implies that the mechanism postulated by Pobedimskii[15] for the reaction of didodecyl thiodipropionate with hydroperoxide is not correct. Acceleration of polymerisation did not occur even though sulphoxide ~~will~~ must be produced. This is consistent with the previous observation that excess sulphoxide is required for this effect to occur.

The rate of polymerisation of styrene in the presence of CHP-DMSD appears to vary according to an equation which is first-order in cumene hydroperoxide (Figure 5.3, B). The order with respect to the DMSD, after the initial retardation effect, also appears to be one as Figure 5.3, A shows that the rate varies linearly with sulphoxide concentration. The first-order dependence of the rate of polymerisation on the initiating species suggests that either the initiating reaction is second order in both components or that the termination reaction no longer involves two polymer radicals.. This latter explanation is more feasible for it is difficult to envisage a reaction which will be second order in both hydroperoxide and sulphoxide.

When nearly equimolar amounts of CHP and DMSD are used to initiate the polymerisation the rates of polymerisation at different temperatures are not related by the Arrhenius equation. This implies that there are at least two different processes involved which have different overall activation energies (Figure 5.6, A).

$$\text{i.e.} \quad Rp = C_1\left[\text{Reactants}\right] \pm C_2\left[\text{Reactants}\right]$$

The activation energy corresponding to C_1 is different to C_2's. However when there is an excess of DMSD present it appears that the rates of polymerisation vary with temperature according to the Arrhenius equation and therefore

$$Rp = C\,[\text{Reactants}]$$

In other words the processes having different activation energies become insignificant (Figure 5.6, B). The activation energy corresponding to C is 14.3 Kcals mole^{-1}. If we accept that the termination involves only one polymer radical the rate of polymerisation will not obey equation [1]. Assuming the steady-state hypothesis still applies and

$$\text{Rate of initiation} = f\,k_c\,[\text{DMSD}]^x\,[\text{CHP}]^y$$

$$\text{Rate of termination} = k_t'\,[M\cdot]\,[Z]$$

$$[M\cdot] = \frac{f\,k_c[\text{DMSD}]^x[\text{CHP}]^y}{k_t'\,[Z]}$$

$$\therefore \quad Rp = \frac{k_p k_c f\,[\text{DMSD}]^x\,[\text{CHP}]^y\,[M]}{k_t'\,[Z]}$$

and therefore

$$C = \frac{k_p k_c}{k_t'}$$

and $\therefore$ Energy of activation $= Ep + Ec - E_t'$

If we assume that the activation energy (Ep) for the propagation reaction is unchanged in the presence of DMSD and the termination reaction (E_t) has an activation energy similar to the bimolecular termination reaction Ec can be calculated. Ep and E_t have been calculated by a number of workers[151] and if we use the values of Matheson[152], whose determinations involved the largest temperature range, E_c is estimated as

$$14.3 = 7.8 + E_c - 2.8$$

$$\therefore \quad E_c = 9.3 \text{ Kcals mole}^{-1}$$

That is the activation energy corresponding to the initiating reaction. If equation [1] is considered to be still applicable the value that is determined is 16.8 Kcals mole^{-1}.

If the initiating reaction is not a direct bimolecular reaction between DMSD and CHP, and it appears unlikely that it is, then the value of E_c estimated must correspond to the sum of a number of reactions which are involved. It cannot be directly related to the thermal decomposition of DMSD which has an activation energy of about 23.5 Kcals mole^{-1} (Table 4.7).

No obvious kinetic interpretations have been produced to explain the CHP-DMSD-styrene system. However the study has served to illustrate that free-radicals are produced in the reactions between CHP and DMSD and that the system is complex. It can also be concluded that it is unlikely that radicals are produced during the thermal decomposition of DMSD at temperatures up to 75°C. Further evidence has also been produced for the chain interrupting activity of the dialkylsulphinyldipropionates.

Chapter 6

AN INVESTIGATION OF THE ANTIOXIDANT STAGE. THE ASSOCIATION OF DIMETHYL SULPHINYLDIPROPIONATE WITH CUMENE HYDROPEROXIDE AND THE DECOMPOSITION OF CUMENE HYDROPEROXIDE BY DIMETHYL SULPHINYLDIPROPIONATE.

6.1. Introduction

The results of the oxygen absorption studies indicate that dialkyl thiodipropionates, functioning through the corresponding sulphoxide, inhibit autoxidations by interrupting the oxidative chain process and by decomposing the main initiating species, the hydroperoxides (Chapter 3). The studies in this chapter are largely concerned with the mechanism by which the dialkyl sulphinyldipropionates decompose the hydroperoxides.

It is known that dialkyl sulphinyldipropionates decompose hydroperoxides catalytically[16] but no detailed kinetic or product studies have been carried out and no mechanism postulated. Cumene hydroperoxide (CHP) was chosen for our study. The modes of its decomposition have been well studied[153,154] and it is thermally stable up to 100°C in inert solvents[64,155,156]. The products of CHP decomposition occurring by an ionic mechanism[27,153,157] are acetone and phenol while α-methylstyrene, $\alpha\alpha$-dimethylbenzyl alcohol and acetophenone are the main products of a free-radical decomposition[64,153]. These products can be easily and rapidly analysed quantitatively and so provide a means of establishing the basic decomposition mechanism involved. Section 6.3. reports the results and discussion of kinetic and product studies of the reaction of dimethyl sulphinyldipropionate (DMSD) with cumene hydroperoxide.

The theory that the sulphoxides function as antioxidants through the inactivation of the hydroperoxide by complex formation receives no support from the oxygen absorption studies. For completeness a more direct approach to the examination of this theory has been made. Section 6.2. reports and discusses results of a study of the complex formation between dimethyl sulphinyldipropionate and cumene hydroperoxide.

6.2. Inhibition and Complex Formation - Results and Discussion

The effect of dimethyl sulphinyldipropionate (DMSD) on the oxidation of cumene initiated by cumene hydroperoxide (CHP) has already shown that molecular interaction cannot account for the inhibition under certain circumstances (Chapter 3). For example, oxygen absorption stopped immediately on the addition of sulphoxide when the ratio of CHP present to the DMSD added was 18.5 (Figure 3.2). However in systems where a ratio of 1 is encountered it may still be argued that inhibition occurs by complex formation. This section is an attempt to discuss the part played by molecular association under such circumstances. No attempt has been made to exhaustively study the association and the experimental methods employed are not rigorous. However the results are consistent and do enable conclusions to be reached.

The inactivation of hydroperoxides by molecular interaction with the sulphoxide has been suggested to involve hydrogen bonding[25]. Several workers have investigated complex formation of sulphoxides with phenols[158-161], carboxylic acids[162] and amides[163]. Barnard et al[164] have studied the association of cyclohexyl methyl sulphoxide with tert-butyl hydroperoxide and CHP at $25^{\circ}C$. The equilibrium constant of formation of the complexes were determined to be 35 and 22 $\ell.mole^{-1}$ respectively.

By definition hydrogen-bond formation involves an equilibrium reaction[165] (1).

$$\begin{array}{ccccc} \mathrm{ROOH} & + & \mathrm{O=SR_1R_2} & \rightleftharpoons & [\mathrm{ROOH}\cdots\mathrm{OSR_1R_2}] \\ [a - x] & & [b - x] & & [x] \end{array} \qquad (1)$$

Whether or not this is effective in inactivating the hydroperoxide will depend upon the extent of the reaction to the right. Any free hydroperoxide present ($[a - x]$) will be still capable of initiating autoxidation and as it is removed by such reactions the equilibrium will be re-established. The data on complex formation between CHP and cyclohexylmethyl sulphoxide[164] indicates that there is a substantial quantity of 'free' hydroperoxide present. The strength of the complex formation between acceptor molecules and sulphoxides can, however, depend upon the groups attached to the sulphoxide[161]. The molecular association between DMSD and CHP was therefore investigated.

Evidence for complex formation occurring between dimethyl sulphinyldipropionate and cumene hydroperoxide was obtained using near-infra-red and infra-red spectroscopy. The hydroxyl group of hydroperoxides absorbs at 4,830 cm^{-1} and 6,900 cm^{-1} [166]. The former is probably a combination band of ν_{OOH} at 1270 cm^{-1} and the fundamental hydroxyl stretch found at 3560 cm^{-1}. This combination band and the sulphur oxygen stretch[69] of dimethyl sulphinyldipropionate at 1057 cm^{-1} were used to study the complex formation.

The actual formation of a complex between dimethyl sulphinyldipropionate and cumene hydroperoxide was first demonstrated by recording the infra-red spectra of solutions of the components in carbon tetrachloride contained in separate cells but side by side in the sample beam. The contents of the cells were then intermixed and the spectra recorded. Figure 6.1 shows that on mixing the two solutions the intensity of the band at 4830 cm^{-1} is reduced while the major part of the spectra remains unchanged. Figure 6.2 shows the effect of hydroperoxide on the sulphur-oxygen stretching band.

The equilibrium constants of formation of the molecular complex were estimated by a method similar to that used by Augdahl et al[57]. The basic assumption for the calculation is that reaction (1) describes the complex. That is, it is a 1:1 complex. The equilibrium constant of formation, K, is then given by equation [1]

$$K = \frac{x}{(a-x)(b-x)} \qquad [1]$$

The initial concentrations of hydroperoxide, $[a]$, and sulphoxide, $[b]$, are known and the concentration of the unassociated hydroperoxide $[a-x]$, or the unassociated sulphoxide, $[b-x]$, is determined from the infra-red of the solution. The concentration $[x]$ can therefore be determined and K calculated.

Table 6.1 gives K determined using the hydroxyl band and Table 6.2 are values determined using the sulphur-oxygen stretch.

Table 6.1

The equilibrium constant of formation of the complex at various concentrations of $[CHP]_{initial}$. ($[DMSD]_{initial}$ = 0.04M)

$[CHP]_{initial}$ (molar)	K litres $mole^{-1}$ (30°C)
0.051	10.7
0.0363	8.65
0.017	11.9
0.0116	9.9

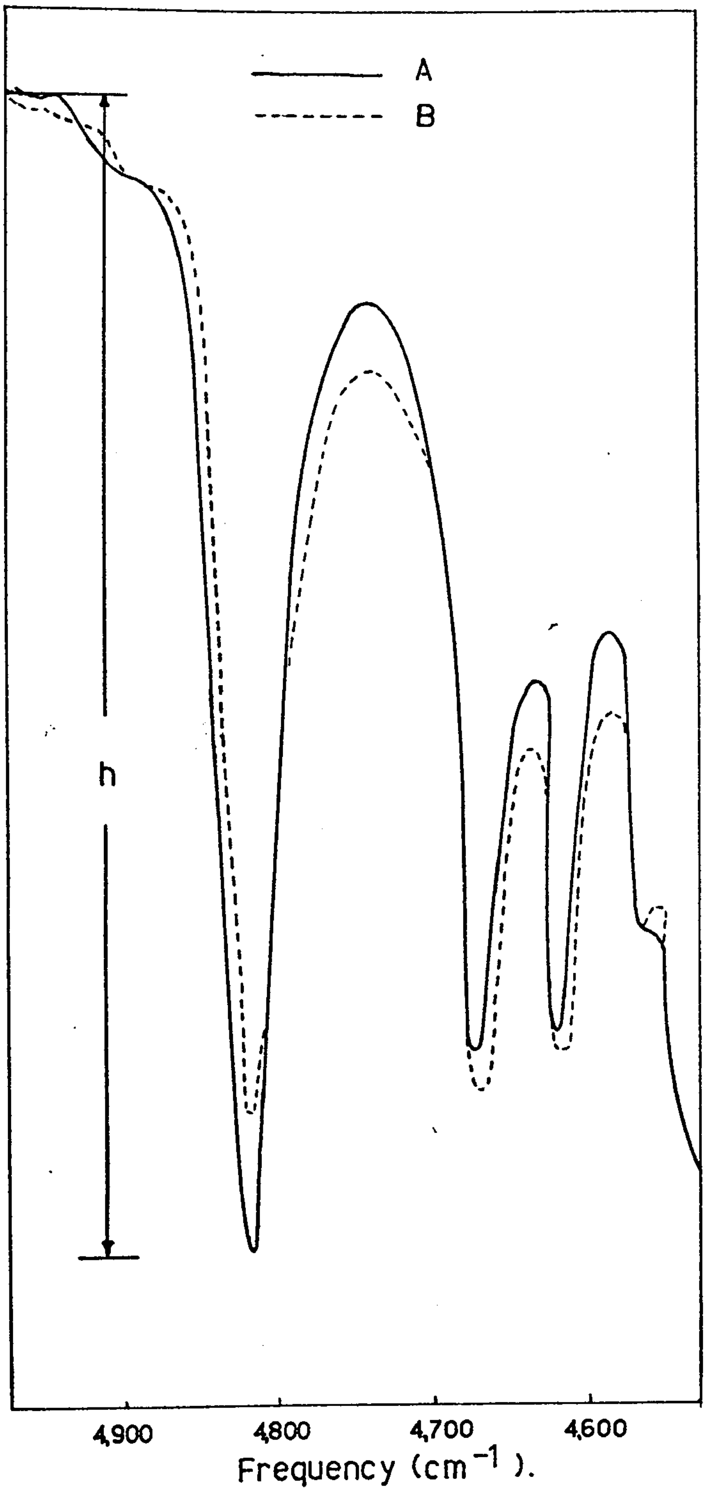


Figure 6·1

The-near infrared spectra of

(A) A solution of cumene hydroperoxide in CCl_4 (0·04M) in a 2cm cell alongside a 2cm cell containing dimethyl sulphinyldipropionate in CCl_4 (0·04M).

(B) The contents of the above cells immediately after intermixing.

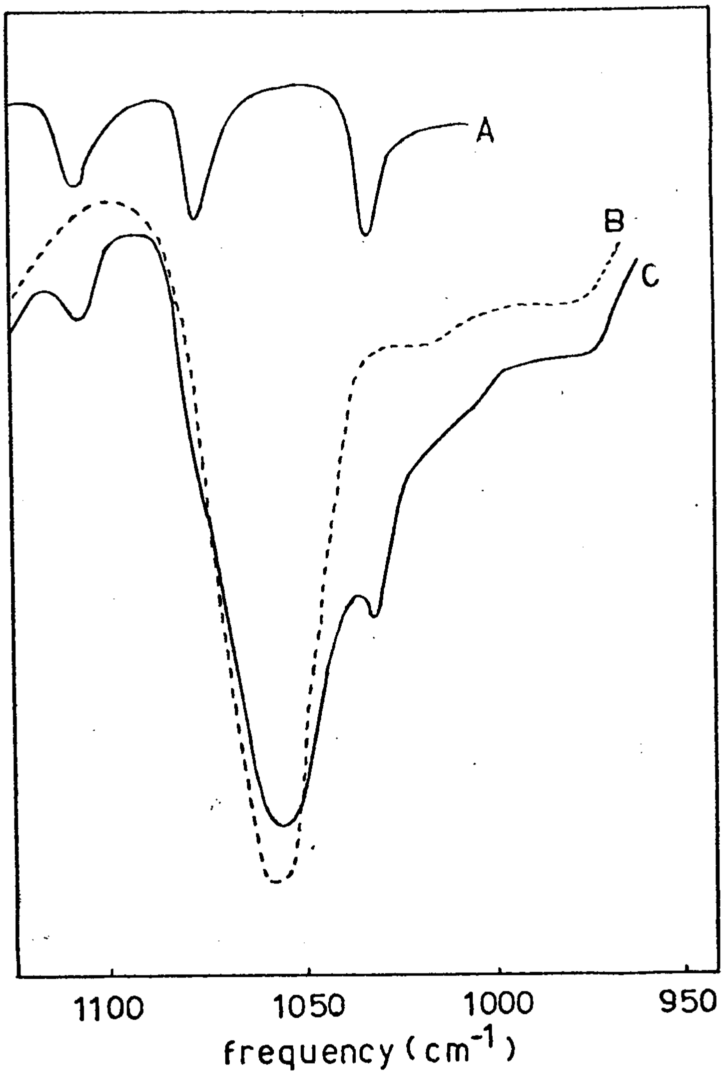


Figure 6·2

The infrared spectra of carbon tetrachloride solutions containing,

(A) Cumene hydroperoxide (0·025M).

(B) Dimethyl sulphinyldipropionate (0·02M).

(C) Cumene hydroperoxide (0·025M) and dimethyl sulphinyldipropionate (0·02M).

Table 6.2

The equilibrium constant of formation of the complex at various concentrations of $[CHP]_{initial}$. $\left((DMSD)_{initial} = 0.02M\right)$

$[CHP]_{initial}$ (M)	K litres $mole^{-1}$ (29°C)
0.0383	7.8
0.025	8.4
0.0036	10.4

The values of K show general agreement over a range of concentrations and this supports the assumption that a 1:1 stoichiometry is involved. The values compare with those obtained by Barnard et al[164] for cyclohexyl methyl sulphoxide. The results indicate that when the hydroperoxide to sulphoxide ratio is one there is sufficient free hydroperoxide present to partake in initiating reactions. Further support for this view was obtained when the infra-red spectra, in the region 4,000 to 800 cm^{-1}, of the complex (a solution containing equimolar amounts of sulphoxide and hydroperoxide) in carbon tetrachloride was compared with the sum of the spectra of the two components. The only marked difference, apart from the intensity changes illustrated (Figures 6.1 and 6.2) was the appearance of a weak broad band at 3280 cm^{-1}. General lack of change in the infra-red spectra on complex formation has been used to distinguish between weak and strong complexes[167].

6.3. The decomposition of cumene hydroperoxide (CHP) by dimethyl sulphinyldipropionate (DMSD)

6.3.1. Kinetics of CHP - DMSD reaction

Several methods for the quantitative determination of CHP in the presence of DMSD were evaluated. The iodometric method of Mair and Graupner[65] is rapid and DMSD does not appear to interfere when added directly to the solution. However a solution of the decomposition products of DMSD was found to interfere and the method was judged unsatisfactory. Marshall[16] had used a iodiometric method for the determination of CHP in the presence of didodecyl sulphinyldipropionate and therefore this method was similarly assessed. The decomposition products of DMSD were again found to interfere. The method of Barnard[168], which employs stannous chloride as a reducing agent, was found to be unaffected by DMSD or its decomposition products. The method of Bocek[58] was similarly unaffected and this method was finally used in favour of Barnard's because of practical advantages and greater reproducibility between determinations.

The rate of disappearance of CHP in the presence of DMSD was followed in various solvents and in the temperature range of 60-80°C. In all of the solvents, excepting cumene, cumene hydroperoxide was thermally stable throughout this temperature range and therefore all of the decomposition can be attributed to the effect of DMSD.

Analysis of the data on the rate of decomposition of CHP showed - that after a slow period, the rate of decomposition is first order with respect to hydroperoxide, (Figure 6.3). The decomposition is catalytic and at least fifty moles of hydroperoxide can be decomposed by one mole of DMSD. The induction period (I.P.) of the reaction was obtained by extrapolation of the first-order rate plots. Table 6.3 shows the dependence of the first-order rate constants (k) and the induction periods (I.P.) for the reaction on the initial concentration of DMSD. The concentration of CHP being kept constant and chlorobenzene used as the solvent. In an inert atmosphere there is some dependence of the first-order rate constant on the concentration of

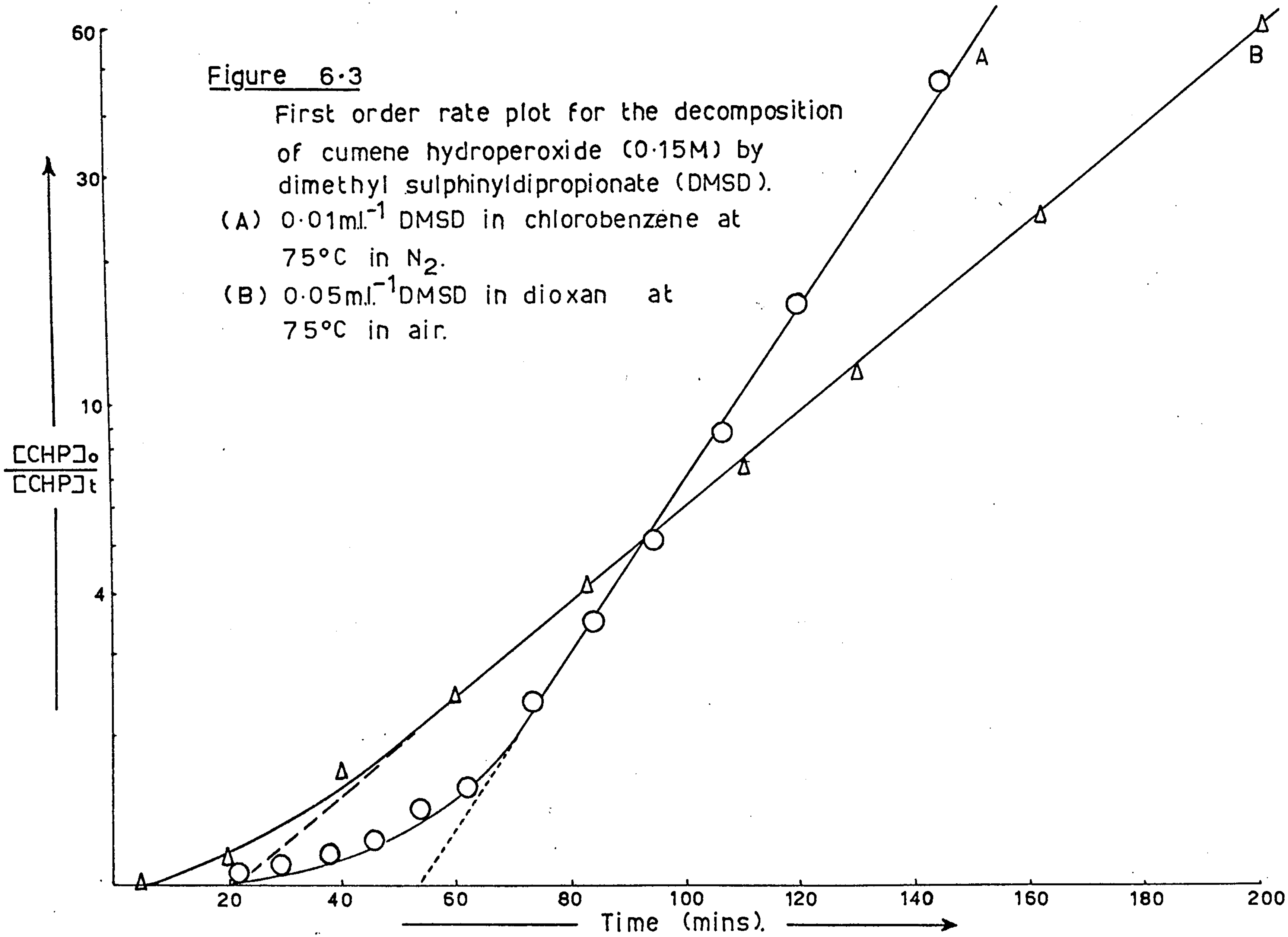


Figure 6·3

First order rate plot for the decomposition of cumene hydroperoxide (0·15M) by dimethyl sulphinyldipropionate (DMSD).

(A) 0·01ml.$^{-1}$ DMSD in chlorobenzene at 75°C in N_2.

(B) 0·05ml.$^{-1}$ DMSD in dioxan at 75°C in air.

DMSD used to bring about the decomposition but there is virtually no dependence on sulphoxide concentration when the reaction is carried out in air. Figure 6.4 describes graphically the results of Table 6.3 together with the variation of the first-order rate constants with hydroperoxide concentration.

Table 6.3

The first-order rate constants (k) and the induction period (I.P) for the reaction of CHP in chlorobenzene (0.15 m.ℓ^{-1}) with DMSD at 75°C

Initial concentration of DMSD (M)	$\frac{[CHP]}{[DMSD]}$	Atmosphere	$10^4 k$ sec^{-1}	I.P. (mins.)
0.2	0.75	N_2	3.1	23
0.1	1.5	N_2	4.5	38
0.06	2.5	N_2	5.2	40
0.038	4.0	N_2	5.6	55
0.027	5.6	N_2	6.4	52.5
0.02	7.5	N_2	6.8	42
0.01	15.0	N_2	6.9	50
0.0072	21.0	N_2	6.8	44
0.005	30.0	N_2	6.5	44
0.15	1.0	Air	6.2	33
0.05	3.0	Air	5.9	28
0.03	5.0	Air	6.2	33
0.02	7.5	Air	6.15	60
0.003	50	Air	4.35	43

The effect of temperature on the reaction was studied using a solution containing 0.15 m.ℓ^{-1} CHP and 0.01 m.ℓ^{-1} DMSD in chloro-

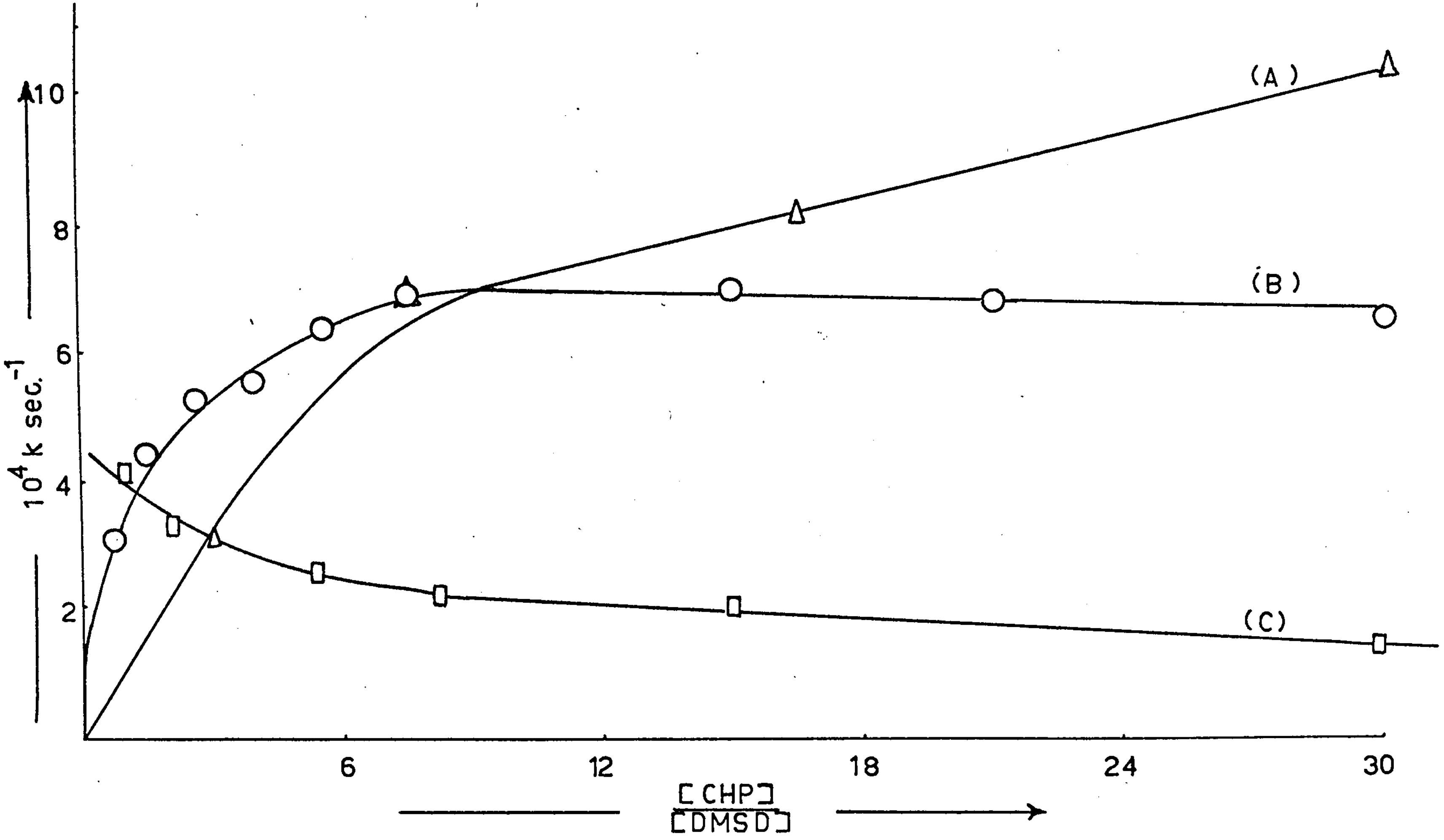


Figure 6·4

The dependance of the 1st order rate constants (k) of the reaction of cumene hydroperoxide (CHP) with dimethyl sulphinyldipropionate (DMSD) at 75°C on the ratio $\frac{[CHP]}{[DMSD]}$.

(A) [DMSD] = 0·02 m.l.$^{-1}$ in chlorobenzene, [CHP] varied.
(B) [CHP] = 0·15 m.l.$^{-1}$ in chlorobenzene, [DMSD] varied.
(C) [CHP] = 0·15 m.l.$^{-1}$ in dioxan in air at 75°C.

benzene. Table 6.4 gives the values of the induction periods and the first-order rate constants at different temperatures.

Table 6.4

The dependence of the induction periods (I.P.) and the first order rate constants (k) on the temperature of the reaction of CHP (0.15M) and DMSD (0.01M) in chlorobenzene in N_2

T^oC	$10^4k\ sec^{-1}$	I.P. (mins)
80	14.2	29
75	6.8	50
68	2.9	98
60	0.82	252

A plot of the log of the reciprocal of the induction period against the reciprocal of the temperature is shown in Figure 6.5 together with the Arrhenius plot of the rate constants. Table 6.5 lists the Arrhenius parameters. The entropy of activation being calculated according to

$$A = \frac{RT}{N_h} e^{\Delta S^{\ddagger}/R}$$

It was apparent that an insoluble product was produced during the reaction of CHP and DMSD in chlorobenzene. In dioxan the reaction mixture remained homogeneous throughout the period of reaction. The reaction was therefore studied in dioxan in an attempt to establish whether or not the non-dependence of the rate of decomposition of CHP on the initial concentration of DMSD was due to the active peroxide decomposer coming out of solution. Figure 6.3, B shows that

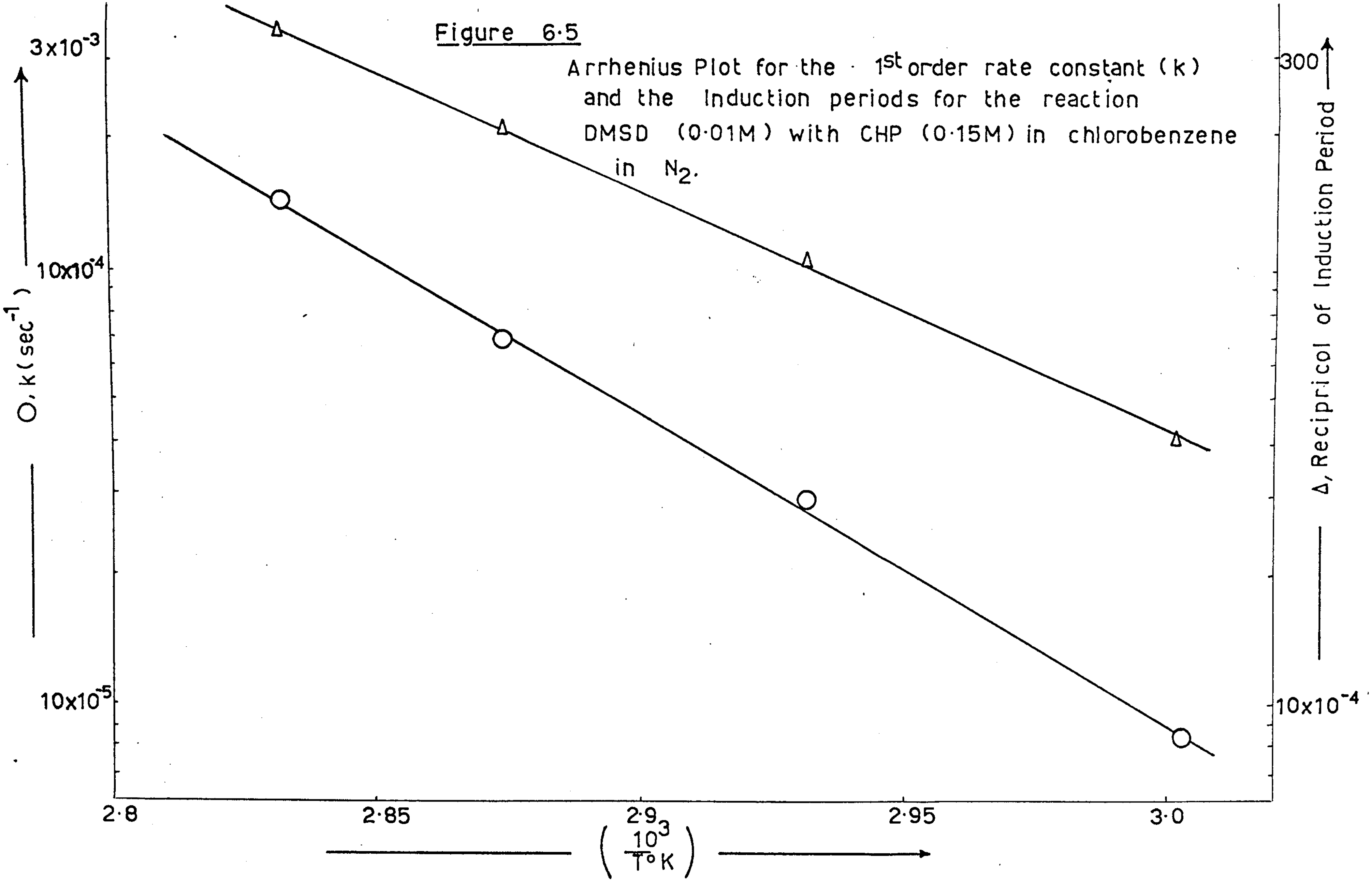


Figure 6·5

Arrhenius Plot for the 1st order rate constant (k) and the Induction periods for the reaction DMSD (0·01M) with CHP (0·15M) in chlorobenzene in N_2.

Table 6.5

Arrhenius parameters for the reaction of CHP (0.15M) and DMSD (0.01M) in chlorobenzene in N_2 Between 60 and 80°C.

Energy of Activation E_A	32.8 Kcals $mole^{-1}$
Entropy of Activation $\Delta S^{\ddagger}$	+ 21.0cal.$deg^{-1}mole^{-1}$
Frequency Factor A	2.8×10^{17} sec^{-1}
Activation Energy corresponding to Induction Period E_{IP}	24.6 Kcal $mole^{-1}$

decomposition of CHP in dioxan by DMSD has the same kinetic features. That is, there is an induction period followed by a first-order reaction. Table 6.6. and Figure 6.4, C show that the first-order rate constants are virtually independent of the initial concentration of DMSD.

Table 6.6.

The first-order rate constants (k) and the induction periods (I.P.) for the reaction of CHP in dioxan (0.15 m.l.$^{-1}$) with DMSD at 75°C.

Initial DMSD concentration (M)	[CHP]/[DMSD]	Atmosphere	$10^4 k(\sec^{-1})$	I.P. (mins)
0.15	1	Air	4.1	18
0.075	2	Air	3.3	17
0.03	5	Air	2.6	13
0.02	7.5	Air	2.18	15
0.01	15.0	Air	2.14	33
0.005	30.0	Air	1.32	29
0.15	1	N_2	3.6	53
0.03	5	N_2	1.5	58

The reaction was studied in nitrobenzene so as to observe the effect of the dielectric of the media and in autoxidising cumene so as to be able to correlate the results with the effect of DMSD on oxygen absorption. In both cases the reaction possessed the same kinetic features previously described for the chlorobenzene solutions (Table 6.7 and Figure 6.6.).

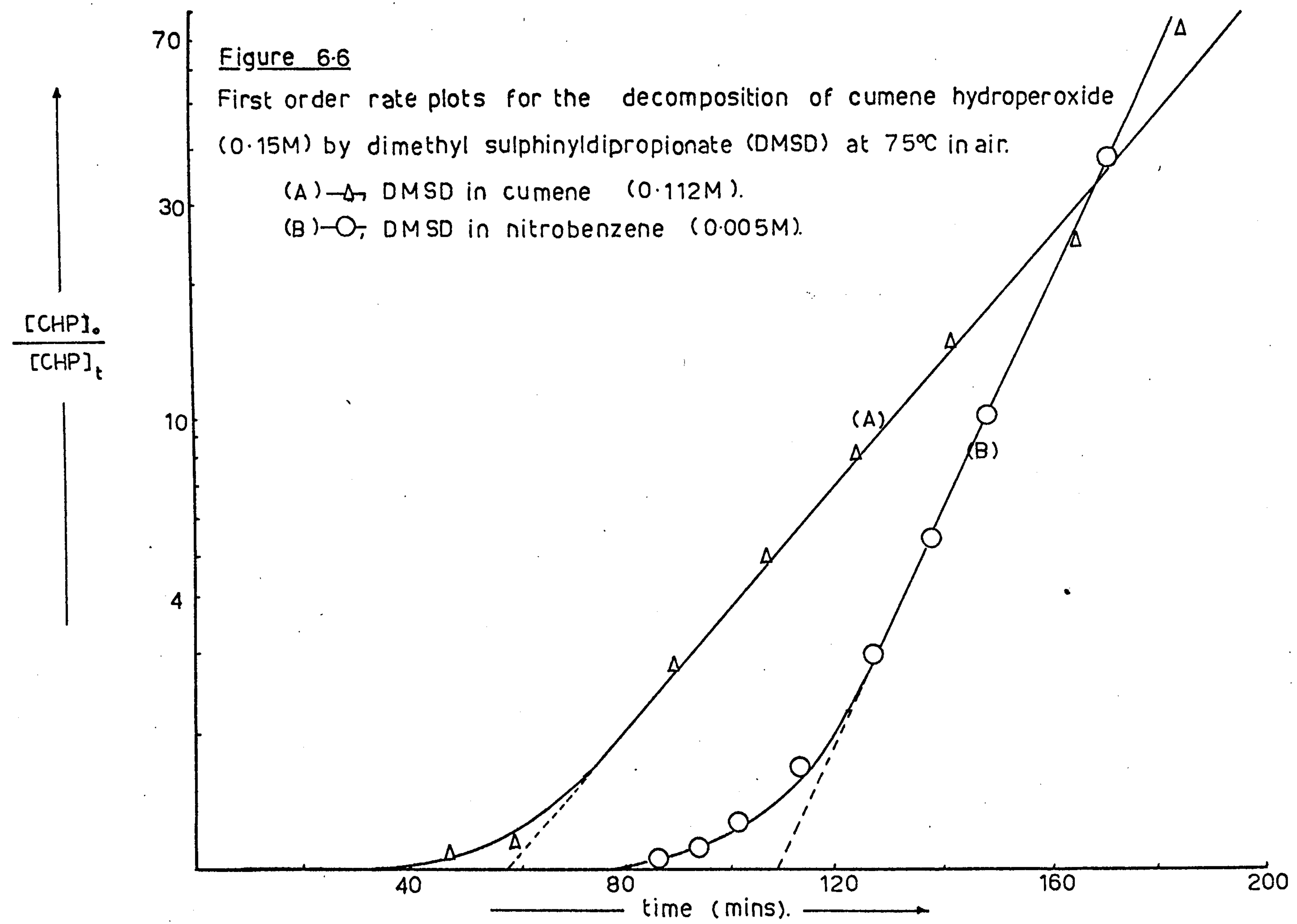


Figure 6.6

First order rate plots for the decomposition of cumene hydroperoxide (0·15M) by dimethyl sulphinyldipropionate (DMSD) at 75°C in air.

(A) —△—, DMSD in cumene (0·112M).

(B) —○—, DMSD in nitrobenzene (0·005M).

Table 6.7

The first-order rate constants (k) and the induction periods (I.P.) for the reaction of CHP (0.15M) with DMSD in air at 75°C.

Solvent	Initial concentration of DMSD (M)	$\frac{[CHP]}{[DMSD]}$	$10^4 k(sec^{-1})$	I.P. (mins)
Nitrobenzene	0.15	1	7.45	49
Nitrobenzene	0.005	30	12.8	109
Cumene	0.112	1.34	6.2	58
Cumene	0.03	5.0	6.1	74
Cumene	0.01	15.0	5.75	90

6.3.2. The effect of various additives on the CHP-DMSD reaction

2,6,Di-t-butyl,4-methyl phenol (TBC) is very effective in terminating free-radical chain reactions which involve peroxy radicals[2]. Table 6.8 shows that TBC has very little effect on the first-order decomposition of CHP in the presence of DMSD in chlorobenzene in air. The effect on the induction period is appreciable however.

Table 6.8

The effect of TBC on the reaction of DMSD ($0.015 m.\ell^{-1}$) and CHP ($0.15 m.\ell^{-1}$) in chlorobenzene in air at 75°C

TBC moles $\ell.^{-1}$	I.P. (mins)	$10^4 k\ (sec^{-1})$
0	51	6.2
0.06	103	5.1

The effect of free radicals on the reaction was studied by carrying out the reaction in the presence of αα'-azoisobutyronitrile (AZBN) in air. The decomposition of CHP was effectively suppressed when AZBN (0.02 moles ℓ^{-1}) was added to a solution containing DMSD (0.01 moles ℓ^{-1}) and CHP (0.15 moles ℓ^{-1}) in chlorobenzene at 75°C. Over six hours only a small amount of hydroperoxide had been decomposed. TBC does not interfere effectively with the reaction leading to this suppression of decomposition (Table 6.9).

Table 6.9.

The effect of AZBN in reducing the ability of DMSD (0.02 m.ℓ^{-1}) to decompose CHP (0.15 m.ℓ^{-1}) in chlorobenzene at 75°C in air

AZBN	0	0.04 m.ℓ^{-1}	0.04 m.ℓ^{-1}	0.04 m.ℓ^{-1}	0.04 m.ℓ^{-1}
TBC	0	0.0	0.04 m.ℓ^{-1}	0.08 m.ℓ^{-1}	0.12 m.ℓ^{-1}
Percentage CHP decomposed after 4 hours	100	20	9	13	17.5

The addition of an equimolar amount of pyridine to DMSD resulted virtually in complete suppression of the decomposition of cumene hydroperoxide. Methyl acrylate added at the beginning of the reaction had no effect.

6.3.3. Product Analysis of the CHP-DMSD reaction

Phenol, acetone, α-methyl styrene, acetophenone and αα-dimethyl benzyl alcohol were detected as products of the decomposition of cumene hydroperoxide by DMSD. Figure 6.7 shows how, in the case of chlorobenzene as solvent, the amounts of the individual products

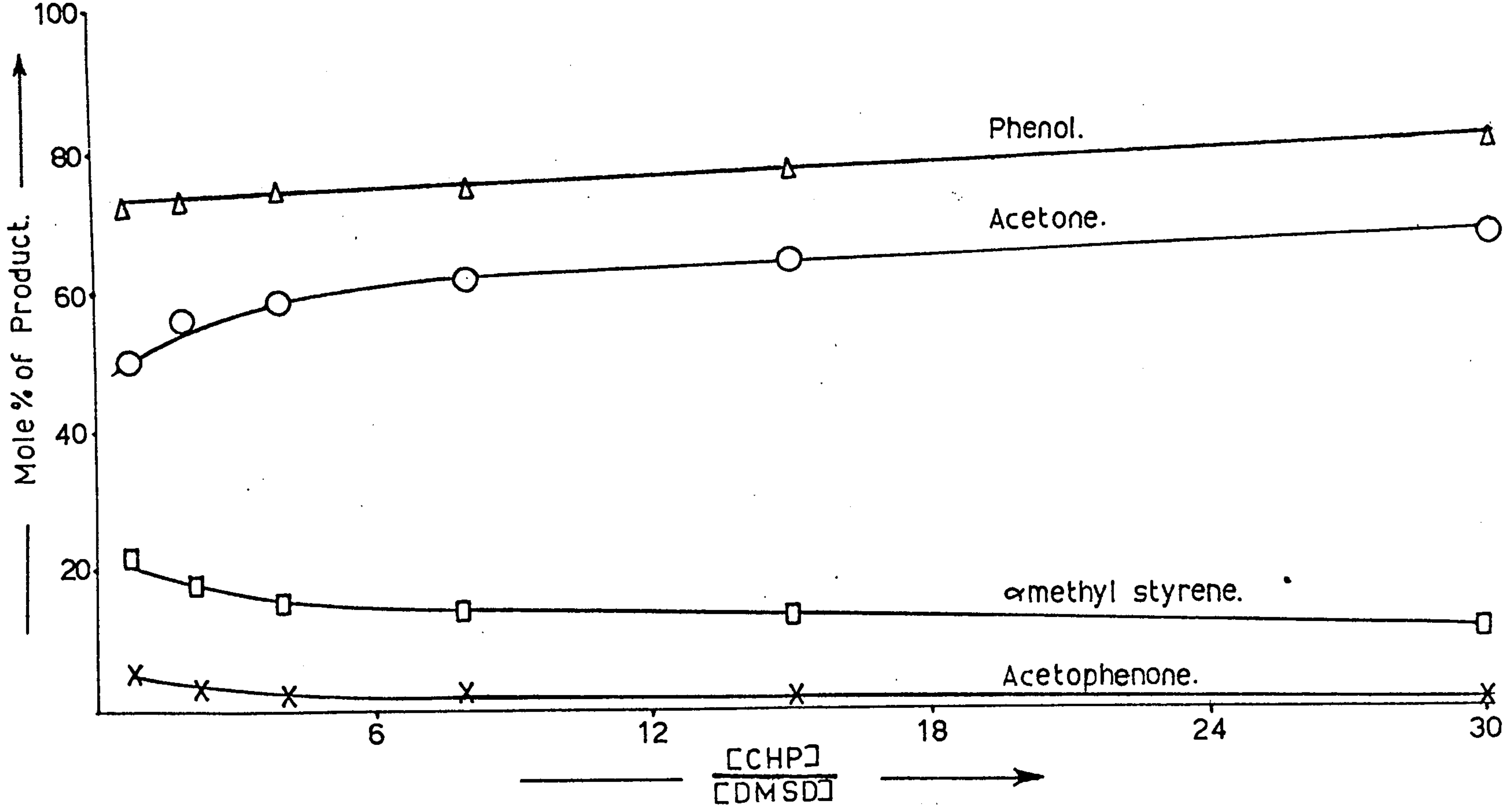


Figure 6·7
Products from the reaction of cumene hydroperoxide (CHP) with dimethyl sulphinyldipropionate (DMSD) in chlorobenzene in N_2 at 75°C (Constant [CHP] = 0·15 m.l.$^{-1}$).

depend upon the ratio of CHP to DMSD in the reaction mixture. The amount of dimethylbenzyl alcohol produced was negligible. On a mass balance 86 ± 3% of the CHP is accounted for by these products and phenol and acetone are shown to be the major products. Similar results were obtained when the decomposition was carried out in nitrobenzene and cumene (Table 6.10).

Table 6.10

Products of the reaction of CHP (0.15M) and DMSD in nitrobenzene and cumene at 75°C.

moles litre^{-1}						
DMSD	Acetone	Phenol	αα-dimethyl benzyl alcohol	Acetophenone	αmethyl styrene	Mass balance %
0.005 in nitrobenzene	0.125	0.14	negligible	negligible	0.0075	88.5
0.03 in cumene	0.068	0.095	2.5×10^{-3}	4.5×10^{-3}	0.051	85.0

The possibility that αmethyl styrene may be produced by dehydration of αα-dimethylbenzyl alcohol was investigated. Table 6.11 shows that if the decomposition of CHP by DMSD is carried out in the presence of added αα-dimethylbenzyl alcohol dehydration of the alcohol occurs. DMSD alone is not responsible for the dehydration.

Table 6.11

The production of α-methyl styrene from αα-dimethylbenzyl alcohol by the reaction of DMSD (0.01 m.ℓ^{-1}) with CHP (0.15 m.ℓ^{-1}) and by DMSD (0.01 m.ℓ^{-1}) alone in chlorobenzene at 75°C.

	Amount of αα dimethylbenzyl added (moles litre^{-1})	Amount of α-methyl styrene produced after 4 hours (moles litre $^{-1}$)
CHP + DMSD	0	0.017
CHP + DMSD	0.05	0.048
DMSD alone	0.05	0.000

The rates of formation of acetone and α-methyl styrene produced from the reaction of DMSD and CHP were studied. Both are produced during the initial slow period of reaction. Acetone is then produced according to a first-order reaction with the first-order rate constant equal to 6.6 x 10^{-4} sec^{-1} (Figure 6.8). The first-order rate constant for the reaction determined by the rate of disappearance of CHP is 6.8 x 10^{-4} sec^{-1}. α-Methyl styrene is not produced according to a first-order reaction and is still being formed after all of the CHP has been decomposed (Figure 6.9). This indicates that the α-methyl styrene is produced by a secondary reaction and this is consistent with the theory that it is produced by dehydration of αα dimethylbenzyl alcohol.

Methyl-β-mercaptopropionate (VIII) and dimethyl sulphonyldipropionate (IX) were not detected as products using g.l.c. and t.l.c. respectively. Dimethyl dithiodipropionate(VII) was just detectable using g.l.c.

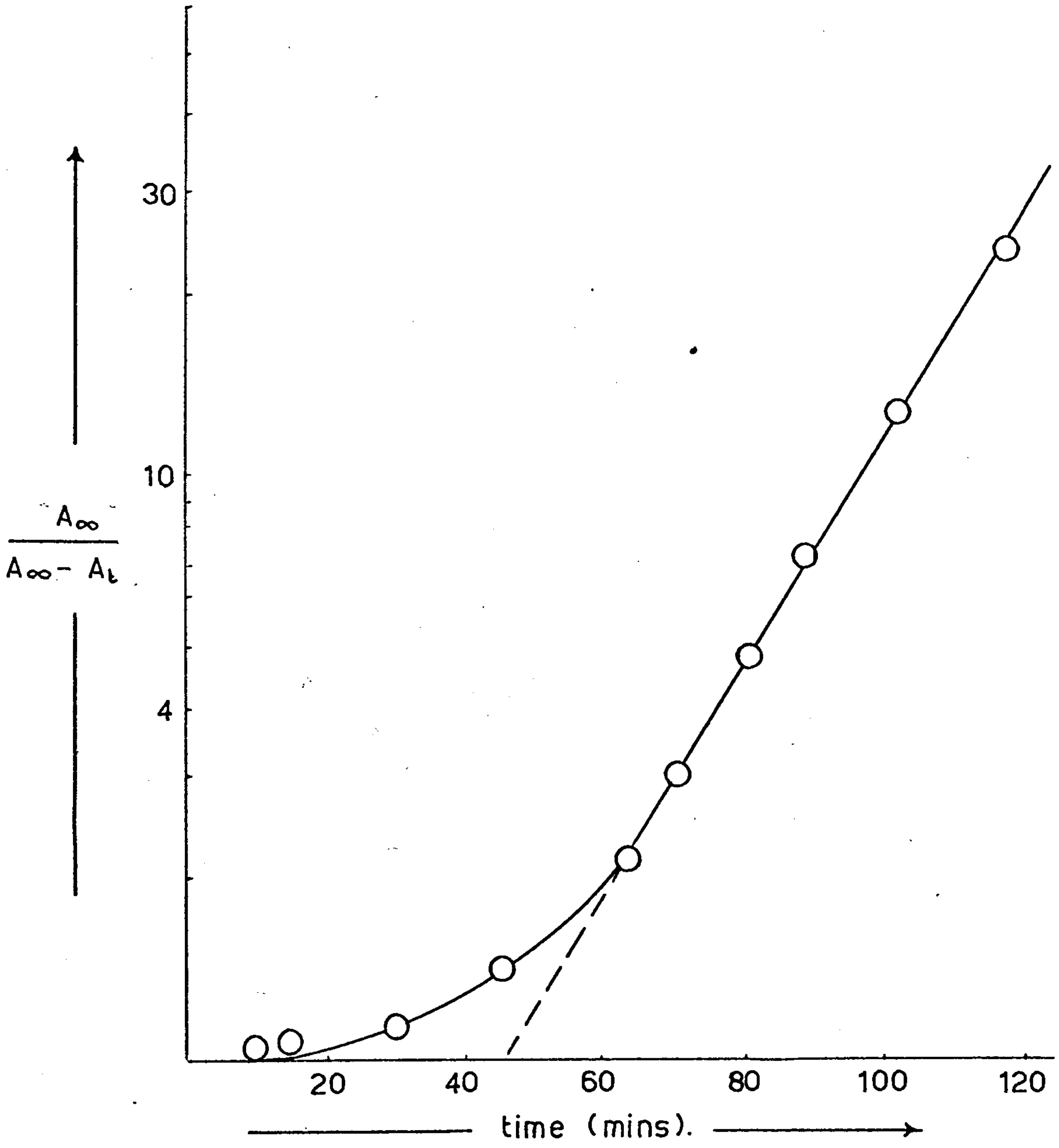


Figure 6-8

First order rate plot for the decomposition of cumene hydroperoxide (0·15 m.l.$^{-1}$) by dimethyl sulphinyldipropionate (0·01M) in chlorobenzene at 75°C in N_2 determined by the rate of formation of acetone.

A_t = [Acetone]$_t$ = amount of acetone at time t.

A_∞ = [Acetone]$_\infty$ = amount of acetone at the end of the reaction.

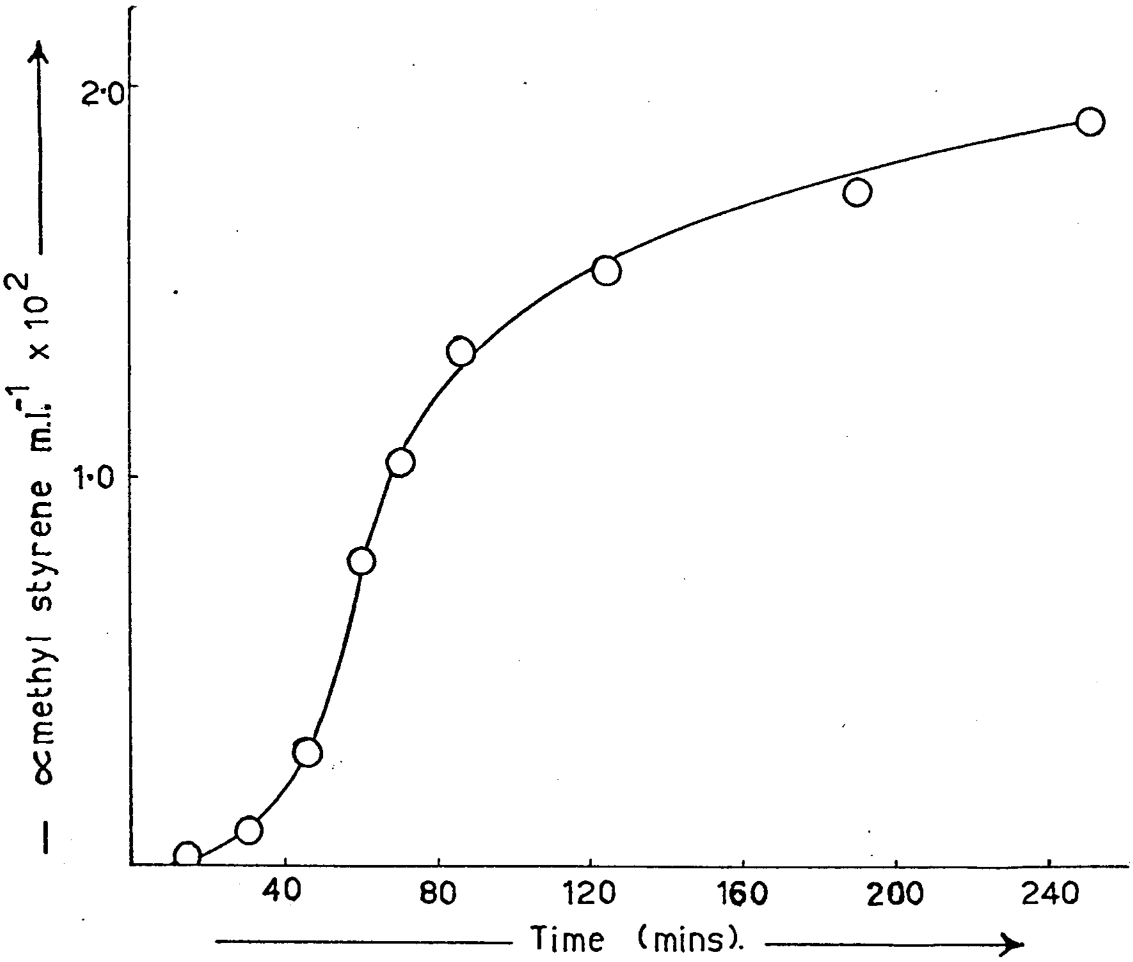
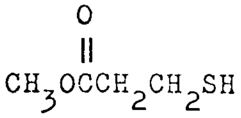
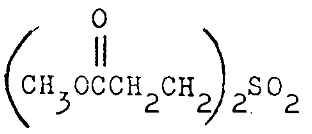


Figure 6·9
The formation of ∝methyl styrene from the decomposition of cumene hydroperoxide (0·15M) by dimethyl sulphinyldipropionate (0·01M) in chlorobenzene at 75 °C in N_2.



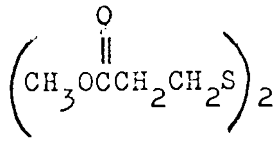
$CH_3O\overset{O}{\overset{\|}{C}}CH_2CH_2SH$

(VIII)



$\left(CH_3O\overset{O}{\overset{\|}{C}}CH_2CH_2\right)_2SO_2$

(IX)

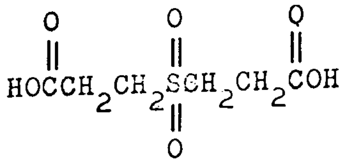


$\left(CH_3O\overset{O}{\overset{\|}{C}}CH_2CH_2S\right)_2$

(VII)

As previously reported, a product comes out of solution when the reaction is carried out in chlorobenzene. A solution of 2g of DMSD and 6.4g of CHP in 300 ml of chlorobenzene was reacted at 75°C to completion (4 hours), and the product solution centrifuged off. The remaining solid was triturated using a very small amount of acetone to give 0.0315g of a white solid. A repeat of the above using 3g DMSD and 9.5g of DMSD in 450mls of chlorobenzene gave 0.05g of the solid. No further purification of the solid was carried out before it was subjected to infra-red, mass spectral and elemental analysis.

Infra-red analysis showed that the solid was a hydrogen-bonding material. Strong sharp bands occuring at 1700, 1120 and 1320 cm^{-1} are consistent with the presence of a carboxylic acid group and the sulphuryl group of an aliphatic sulphone. (For dialkyl sulphone $\nu_{SO} = 1140$ and $1320\ cm^{-1}$)[70]. The acid equivalent weight of the solid was obtained by titrating against standardised sodium hydroxide. Using phenolphthalien and bromothymol blue as indicators the values determined were 111 and 108 respectively. The fact that both indicators gave the same value for the acid equivalent suggested the presence of fairly strong acid groupings. Carbon, hydrogen and sulphur analysis of the solid gives the empirical formula as $C_{5.7}H_{10}O_{5.8}S$. The analytical data therefore suggest that the solid is $\beta\beta'$sulphonyldipropionic acid (X)

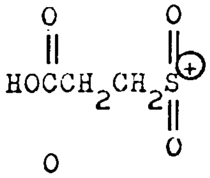
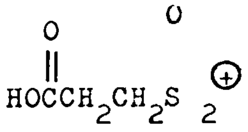
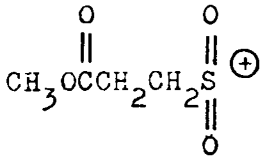
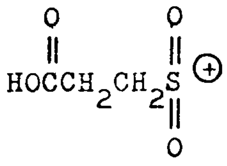


$HO\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}CH_2CH_2\overset{O}{\overset{\|}{C}}OH$

(X) $C_6H_{10}O_6S$, Mol.wt. = 210; Acid equivalent = 105 ββ'sulphonyldipropionic acid was synthesised and the infra-red shown to be identical with the solid. The equivalent weight determination, using the same two indicators, gave values of 105. The melting points differ in that the synthesised material melted at 218-219°C to a clear liquid while the isolated solid darkened from 120°C and at 210°C was black and the sides of the m.pt. tube misted up. Figure 6.10 compares the mass fragmentation pattern of the synthesised ββ'sulphonyldipropionic acid with the solid. Exact mass determinations or mass fragments of both compounds are given in Table 6.12.

Table 6.12

Mass spectral analysis of ββ'sulphonyldipropionic acid and unknown.

Compound	Exact mass of ion	Molecular formula corres-ponding to ion	Error (ppm)	Possible structure of ion
ββ'sulphonyldipropionic acid	136.990658	$C_3H_5O_4S$	1.8	 $HO\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{}^{\oplus}$
unknown	209.998793	$C_6H_{10}O_4S_2$	2	 $HO\overset{\overset{O}{\|}}{C}CH_2CH_2S_2^{\oplus}$
unknown	151.006294	$C_4H_7O_4S$	2	 $CH_3O\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{}^{\oplus}$
unknown	136.990366	$C_3H_5O_4S$	4	 $HO\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{}^{\oplus}$

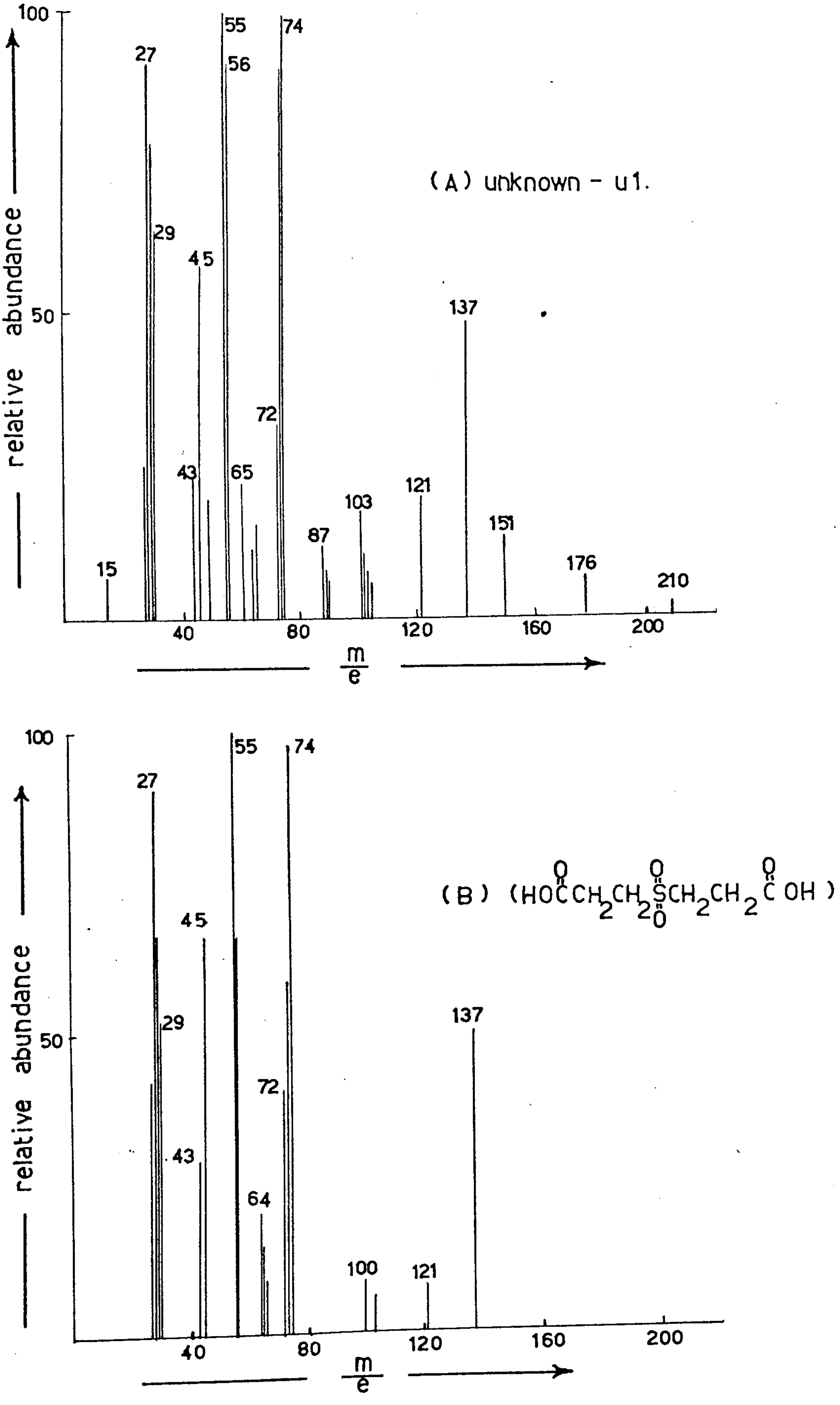
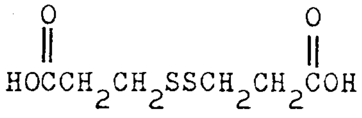


Figure 6·10

Mass fragmentation spectrum obtained under normal operating conditions for

(A) unknown (B) ββ′ sulphonyl dipropionic acid.

ββ'sulphonyldipropionic acid does not give a parent ion. All the major molecular ions may be interpreted in terms of the structure (X). The unknown solid gives a molecular ion with m/e = 210 but this has been shown to correspond to $C_6H_{10}O_4S_2$ and the most likely source of this is ββ'dithiodipropionic acid (XI)



$HO\overset{O}{\overset{\|}{C}}CH_2CH_2SSCH_2CH_2\overset{O}{\overset{\|}{C}}OH$

mol.wt. = 210

(XI)

Mass spectral analysis of synthesised ββ'dithiodipropionic acid shows that this compound does give the parent ion. In the mass spectrum of the unknown m/e = 151 corresponds to $C_4H_7O_4S$ and the most likely source of this is dimethyl sulphonyldipropionate (methyl ester of X).

The solid product, to be known as U1, is therefore probably impure. The analytical data are consistent with the majority of U1 being ββ'sulphonyldipropionic acid (X). Likely impurities are the methyl ester and the disulphide (XI).

No evidence, using i.r., g.l.c. and mass spectrometry, was obtained for the presence of sulphur dioxide either in gas or liquid phase.

6.3.4. The peroxide decomposing ability of products of the CHP-DMSD reaction

Section 6.3.3. reports the isolation and investigation of the solid U1 from the reaction of cumene hydroperoxide with dimethyl sulphinyldipropionate. Figure 6.11 establishes that U1 decomposes

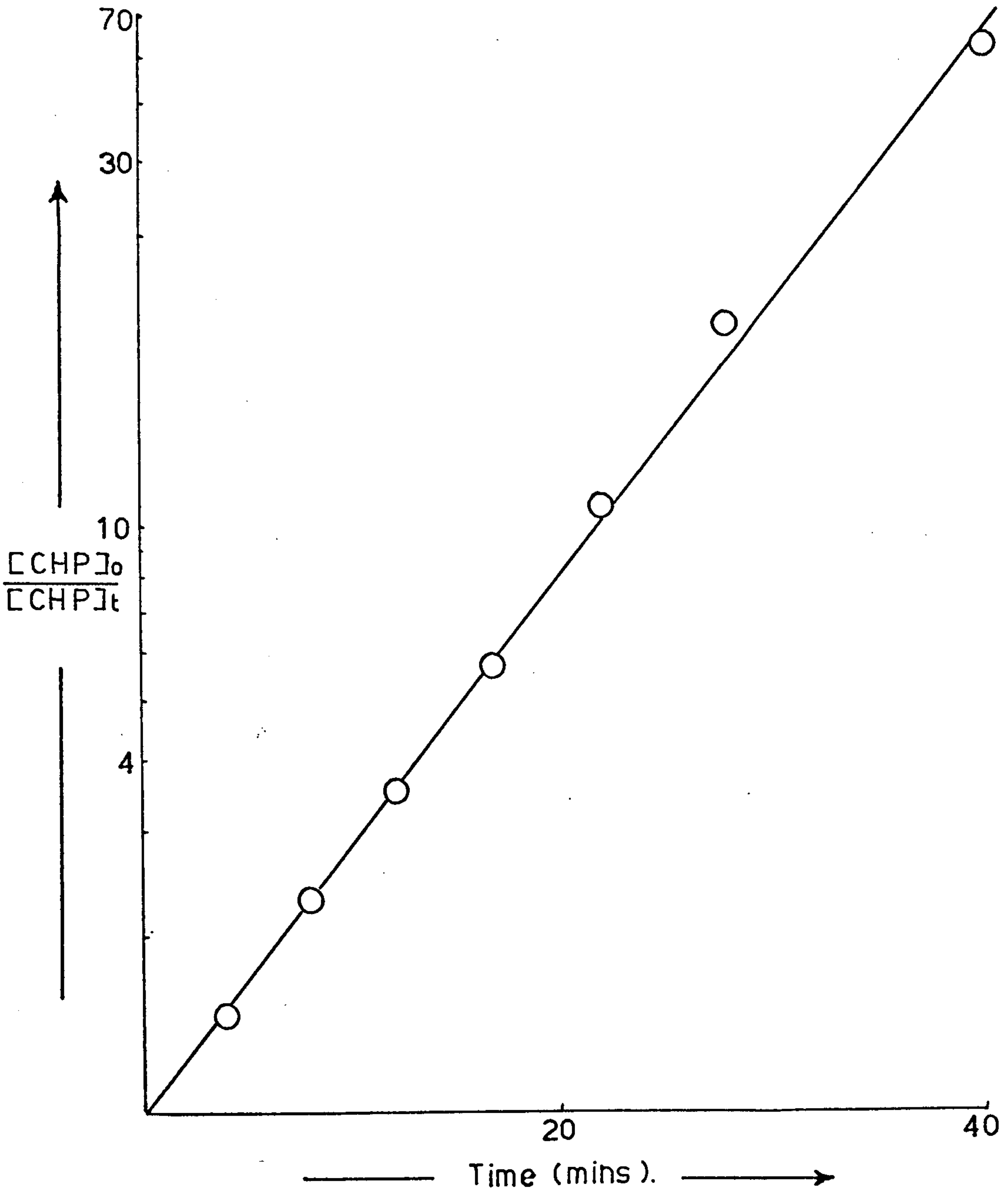


Figure 6·11

First order rate plot for the decomposition of cumene hydroperoxide (CHP) in chlorobenzene (0·15M) at 75°C by 0·0119g of unknown per 1ml. of solution.

CHP in chlorobenzene. The reaction is first-order with respect to hydroperoxide and there is no induction period. The solid does not appear to dissolve in chlorobenzene but Table 6.13 shows that an increase in the weight of U1 results in an increase in the rate of decomposition. The solid is soluble in dioxan but decomposition occurs at a reduced rate compared to the chlorobenzene solutions (Table 6.13).

Table 6.13

The first-order rate constants (k) for the decomposition of CHP (0.15M) by U1 at 75°C.

Solvent	Weight of U1 per ml.	$10^4 k(\text{sec}^{-1})$
Chlorobenzene	0.0119g	19
Chlorobenzene	0.0051g	5.9
Chlorobenzene	0.0019g	0.68
Dioxan	0.0061g	1.1

The reaction is only first-order with respect to time[169] and equation 2 represents the most probable form of the rate equation with respect to concentration

$$-\frac{d[\text{CHP}]}{dt} = k_u[\text{U1}]^x[\text{CHP}] \qquad [2]$$

and therefore

$$k = k_u[\text{U1}]^x$$

$$\text{and } \log k = \log k_u + x \log[\text{U1}].$$

A plot of log of the weight of U1 per ml. of chlorobenzene solution versus the log of the pseudo first-order rate constants for the three determinations does not produce a good straight line. The limiting slopes are 0.9 and 2.1 and therefore no further deductions may be made about the reaction involved. Large errors in k, due to the solutions not being homogeneous, may account for this result.

The products derived from CHP by the reaction with U1 are mainly acetone and phenol (Table 6.14).

Table 6.14.

Products of the CHP (0.15M) and U1 reaction in chlorobenzene at 75°C

	moles litre^{-1}.					
U1 wt.per ml (g)	Acetone	Phenol	αα dimethyl benzyl alcohol	Aceto-phenone	α methyl styrene	Mass balance %
0.0019	0.09	0.12	0.0011	2.3×10^{-3}	0.025	86
0.0051	0.07	0.12	negligible	1.25×10^{-3}	0.0225	79
0.0119	0.072	0.125	negligible	1.4×10^{-3}	0.01	75

All analytical data suggest that U1 is ββ' sulphonyldipropionic acid with traces of the methyl ester and ββ' dithiodipropionic acid present. These compounds were therefore synthesised and their peroxide decomposing ability tested by reacting them with cumene hydroperoxide. Using exactly the same conditions, quantities and procedure, negligible decomposition of cumene hydroperoxide occurred in the period corresponding to complete decomposition of hydroperoxide by U1.

6.3.5. Discussion

The CHP-DMSD reaction has the following features. After a slow period of hydroperoxide decomposition, the rate becomes first-order in hydroperoxide. This result is exactly the same as that previously recorded[16] for the reaction of didodecyl sulphinyldipropionate (1.6×10^{-2}M) with tetralin hydroperoxide (5×10^{-2}M) in chlorobenzene. In the case of the CHP-DMSD reaction a large variation in DMSD concentration does not greatly affect the rate of decomposition of the hydroperoxide and so the empirical rate equation for the reaction with respect to both time and concentration is

$$- \frac{d[\mathrm{CHP}]}{dt} = k' [\mathrm{CHP}] \qquad [3]$$

Figure 6.4 and Tables 6.3 and 6.6. illustrate this for the reaction in chlorobenzene and dioxan. Table 6.7 indicates that this is also true when the reaction is carried out in oxidising cumene.

In chlorobenzene, cumene and nitrobenzene the solutions become non-homogeneous as the reaction proceeds. It is therefore conceivable that equation [3] can be explained by the actual peroxide decomposer reaching a limiting concentration in solution. In dioxan the reaction mixture is homogeneous throughout the decomposition of the hydroperoxide but the decomposition still possesses the kinetic features previously described, (Figures 6.3 and 6.4). It must therefore be concluded that the apparent independence of the rate of hydroperoxide decomposition on the DMSD concentration, over a certain concentration range, is a true kinetic feature of the reaction.

The kinetics of the CHP-DMSD reaction preclude the possibility that DMSD is the actual peroxide decomposing species. If this was the case an increase in DMSD concentration would have to be paralleled by an increase in the rate of peroxide decomposition. The stoichiometry of the reaction requires that a species, X, catalytically decomposes the peroxide (Reaction 2)

$$X + CHP \longrightarrow \text{Acetone} + \text{Phenol} + X \qquad (2)$$

Acetone and phenol are the major products and this suggests that X is an acid species[27,153,157]. This is supported by the fact that pyridine inhibits the peroxide decomposition (6.3.2.). Large quantities of TBC added to the reaction in air has no significant effect on the first-order decomposition (6.3.2.), and therefore no evidence is provided for a free radical chain reaction occurring.

A number of reactions must be involved in the formation of the catalytic decomposer. It may be possible that more than one species is involved but the fact that good first-order rate plots are obtained (Figures 6.3 and 6.7) means that they all would have to reach steady-state concentration. A one step reaction such that

$$DMSD \longrightarrow X \qquad (3)$$

and then $X + CHP \longrightarrow \text{Products} + X$ (4)

and $X + DMSD \longrightarrow \text{Products}$ (5)

could explain the independence of the rate on sulphoxide concentration if a steady-state approach was applied to X. However this scheme is unable to explain Figure 6.4, A, which seems to indicate that the hydroperoxide is involved in the formation of the active species.

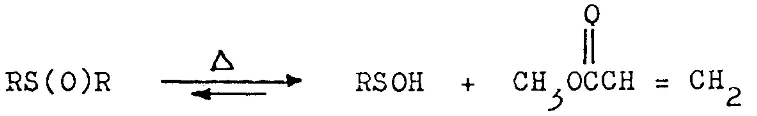
After the induction period the reaction is first-order and this indicates that a steady-state concentration of the catalytic species has been attained. This steady-state concentration is likely to arise by a competitive reaction which involves the removal of X and the sulphoxide, or possibly an intermediate which leads to the production of X. The occurrence of such a reaction (the form of reaction 5) may well account for the apparent independence of the rate of peroxide decomposition on DMSD concentration.

It appears that a series of consecutive and competitive reactions are involved in the overall CHP-DMSD reaction. Sulphoxides can be oxidised by peroxides to the sulphones[170] and therefore the peroxide decomposing ability of dimethyl sulphonyldipropionate was examined, (6.3.4). The sulphone was ineffective compared to the sulphoxide and it is therefore concluded that the sulphone plays no part in the sequence of reactions which leads to the catalytic species.

The potency of sulphoxides as antioxidants correlates with their thermal instability[23]. It has been shown that DMSD decomposes so as to produce the corresponding sulphenic acid and methyl acrylate (Chapter 4). This reaction in chlorobenzene and dioxan is not first-order in sulphoxide. However in the presence of Galvinoxyl it becomes first-order (Figure 4.5). Results are consistent with this being due to a rapid reaction between the Galvinoxyl and the sulphenic acid. A similar result has been obtained when DMSD is decomposed in chlorobenzene in the presence of a two-fold excess of hydroperoxide (Figures 4.5 and 4.6). The reaction becomes first-order in sulphoxide and therefore suggests that the sulphenic acid is reacting rapidly with the hydroperoxide. This cannot be the complete explanation, however, as the decomposition of the sulphoxide proceeds according to a first-order rate equation with a half life of about 3.8 hours. The decomposition of the hydroperoxide would be completed in about four and a half hours. The yield of methyl acrylate from the decomposition of the DMSD in the presence of hydroperoxide is 75% of the theoretical and this suggests that some of the sulphoxide is removed from the system in a manner which does not give methyl acrylate. This may possibly be oxidation to the sulphone.

There is therefore some support for the hypothesis that the thermal decomposition of the sulphoxide is important in explaining its antioxidant activity, and that this is linked with a reaction between the sulphenic acid and the hydroperoxide. Further indications that this may be correct comes from the study of the induction periods of the CHP-DMSD reaction. The induction period must represent a period during which the steady-state concentration of the peroxide decomposer, X, is being attained. The log of the reciprocal of the induction period varies linearly with the reciprocal of the absolute temperature of the reaction, (Figure 6.5.). This implies that the induction period is inversely proportional to the rate constant relating the rate of formation of X to the reactants producing it. If the thermal decomposition of the sulphoxide is the rate determining step in the sequence of reactions leading to X, then at the beginning of the reaction when $[X] = 0$, the rate of production of X will be equal to the rate of decomposition of sulphoxide. This means that the induction period would be inversely proportional to the first-order rate constant for the thermal decomposition of DMSD. The activation energy for the thermal decomposition of DMSD is given in Table 4.7, and has an average value of 23.5 Kcals mole^{-1}. The induction periods of the CHP-DMSD reaction give a value of 24.6 Kcals mole^{-1} (Table 6.5, Figure 6.5). These values are comparable and suggest that the thermal decomposition of the sulphoxide is the rate determining step in the sequence of reactions leading to the production of the active species.

As methyl acrylate does not inhibit the peroxide decomposition (6.3.2.) and the thermal decomposition of DMSD is first-order in the presence of CHP (Figures 4.5 and 4.6) it is unlikely that the sulphenic acid is the peroxide decomposer. Figure 6.4, A, also indicates that hydroperoxide is involved in the formation of the active species. It therefore seems likely that the sulphenic acid is oxidised to the sulphinic acid (Reaction 7). Further reactions, (8-15), some of which have previously been reported, may be important in the decomposition of the hydroperoxide are listed and discussed below.



$$RS(O)R \underset{\longleftarrow}{\xrightarrow{\Delta}} RSOH + CH_3OC(=O)CH = CH_2 \qquad (6)$$

$$RSOH + R'OOH \xrightarrow{fast} RSO_2H + R'OH \qquad (7)$$

$$RSO_2H + R'OOH \longrightarrow RSO_3H + R'OH \qquad (8)$$

$$RSO_2H \longrightarrow RH + SO_2 \qquad (9)$$

$$RSO_2H + R'OOH \longrightarrow RSO_2\cdot + R'O\cdot + H_2O \qquad (10)$$

$$RSO_2\cdot \longrightarrow R\cdot + SO_2 \qquad (11)$$

$$3RSO_2H \longrightarrow RSO_2SR + RSO_3H + H_2O \qquad (12)$$

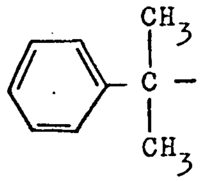
$$RSO_2H + RSOH \longrightarrow RSO_2SR + H_2O \qquad (13)$$

$$2RSOH \longrightarrow RS(O)SR + H_2O \qquad (14)$$

$$SO_2 + R'OOH \longrightarrow SO_3 + R'OH \qquad (15)$$

$R = CH_3O\cdot CO\cdot CH_2CH_2$

R' =



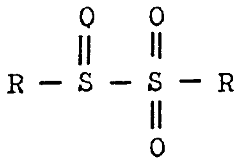
The thermal decomposition of DMSD (Reaction 6) has been investigated (Chapter 4) and results indicate that the normal fate of the sulphenic acid (RSOH) is its disproportionation to thiolsulphinate and water, (Reaction 14). However as the decomposition of DMSD is first-order in the presence of CHP in chlorobenzene and is not in its absence (Figure 4.6) reaction (14) is believed to become insignificant compared to Reaction (7). The sulphinic acid may then be further oxidised to the sulphonic acid (Reaction 8) which can then catalyse the decomposition of the hydroperoxide (7.2).

Wellisch et al[171] have reported that desulphonylation of benzene sulphinic acid, 1,butanesulphinic acid, 1,4-butanedisulphinic acid and 1,dodecyl sulphinic acid occurs above 200°C (Reaction 9). The reaction is believed to involve a free radical chain mechanism and alkenes are produced by a transfer reaction[171]. Diphenylmethanesulphinic acid desulphonylates at room temperature[171] and 2,4-dinitrobenzenesulphinic acid is converted to m-dinitrobenzene and sulphur dioxide by refluxing in benzene[172]. 2-Chloro-5-nitro-p-toluenesulphinic acid loses sulphur dioxide with the production of 2-chloro-5-nitrotoluene when heated in pyridine[173]. It may be that such a reaction is involved in the CHP-DMSD reaction giving rise to sulphur dioxide which catalytically decomposes CHP very effectively (7.3). Unfortunately, due mainly to lack of time, a fully characterised sample of the sulphinic acid (RSO_2H) was not obtained and therefore no conclusions concerning this reaction can be made. Section 7.4. describes the small amount of work carried out towards this end and appears to indicate that the sulphinic acid is not very stable.

Reaction 10 is a redox reaction between the sulphinic acid and the hydroperoxide and is analogous to the reactions of thiols with hydroperoxides[133]. Sulphinic acids can initiate free radical polymerisation[134] and it has been reported that the initiation is accelerated by hydroperoxides[136]. This may be due to the redox reaction. The sulphonyl radical produced (Reaction 10) may then lose sulphur dioxide (Reaction 11) which can then catalytically decompose hydroperoxides. This Reaction (Reactions 10 and 11) is particularly attractive as it may be able to explain the experimental fact that when

DMSD is added to cumene whose oxidation has been initiated with cumene hydroperoxide a pro-oxidant effect occurs immediately before the final inhibition (Figure 3.2).

The disproportionation of sulphinic acids (Reaction 12) is well known; aliphatic sulphinic acids are less stable than aromatic sulphinic acids and short-chain aliphatics are less stable than the longer chain acids[174]. The mechanism of the disproportionation of aromatic sulphinic acids has been studied in anhydrous dioxan[141], water[142] and acetic acid[143,144]. The results suggest the involvement of a sulphinylsulphone (XII), which are known to dissociate readily[114,125]. The actual mechanisms envisaged for the disproportionation are, however, ionic.



$$R-\overset{O}{\overset{\|}{S}}-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-R$$

(XII)

No parallel study of aliphatic sulphinic acids has apparently been made. Marvel and Johnson[174] have reported that 1,dodecyl sulphinic acid disproportionated on standing to give the thiosulphonate but on warming a solution of it in ether this did not occur. Further investigations of aliphatic sulphinic acids are therefore desirable.

Reaction 13, the reaction of the sulphinic acid with the sulphenic acid, has previously been postulated[175]. It may be important in the CHP-DMSD reaction in that it competes with the formation of the peroxide decomposers and so account for the complex kinetics.

In the above reactions discussed (6-15) three species are produced which may catalytically decompose the hydroperoxide by an ionic mechanism. The sulphonic acid produced by Reactions 8 and 12 has been synthesised and examined as a peroxide decomposer (7.2). In chlorobenzene it is an effective catalyst for the decomposition but in dioxan the acid is ineffective. DMSD is effective in both chlorobenzene and dioxan (Figure 6.3, Tables 6.3 and 6.6.) and therefore it must be concluded that the sulphonic acid cannot be entirely responsible for the activity of DMSD. Sulphur dioxide, produced by Reactions 9 and 11, is even more effective than the sulphonic acid in decomposing cumene hydroperoxide (7.3). Sulphur dioxide has not been detected as a product in the CHP-DMSD reaction and this may be because it functions via sulphur trioxide (Reaction 15). The reaction of sulphur dioxide and cumene hydroperoxide has been studied by De Jong[176] and the results are interpretted in terms of sulphur trioxide being the catalytic species. A third possibility is that the sulphinic acid is capable of functioning as a Lewis Acid as sulphur dioxide (7.3) and so catalyse the decomposition of cumene hydroperoxide.

80 mole % of phenol and 67 mole % of acetone are produced from the decomposition of CHP by catalytic quantities of DMSD (Figure 6.7) in chlorobenzene. Similar results are obtained for the reaction in cumene and nitrobenzene (Table 6.10). Other workers[27,177] have similarly found that larger quantities of phenol than acetone are produced in acid catalysed decompositions. One would expect equivalent amounts of acetone and phenol. No evidence was obtained for the removal of acetone from the system by a subsequent reaction. At the completion of the decomposition of CHP the quantity of acetone remained constant. The rate of formation of acetone also followed the rate of peroxide decomposition (Figure 6.8). 15 mole % of α methylstyrene is also produced from the decomposition of CHP by DMSD. Table 6.11 and Figure 6.9 show that the most likely source of this is

dehydration of αα-dimethyl benzyl alcohol. Some of the αα dimethyl benzyl alcohol would be produced by reactions 7, 8 and 15, if they occur. Other quantities would arise by oxidation of the sulphoxide by the hydroperoxide to the sulphone. Analytical data suggest the formation of ββ'sulphonyldipropionic acid. The alcohol, α-methylstyrene and acetophenone are products of a free-radical induced decomposition of cumene hydroperoxide[178]. The presence of free-radical intermediates in the CHP-DMSD reaction may be deduced from the oxygen absorption studies (Chapter 3), the polymerisation studies (Chapter 5) and the presence of acetophenone as a product (Figure 6.7 and Table 6.10).

It seems reasonable to assume that the dehydration of αα-dimethyl benzyl alcohol will be catalysed by the same species which catalytically decomposes the hydroperoxide. Gandini and Plesch[179] have shown that the dehydration of dilute solutions of aromatic carbinols in methylene chloride by catalytic quantities of strong acids is extremely rapid even at room temperature. It has also been reported that catalytic quantities of sulphur dioxide dehydrate αα-dimethyl benzyl alcohol[180]. The sulphonic acid and sulphur dioxide would therefore both dehydrate αα-dimethyl benzyl alcohol under the conditions of our study.

Further product analysis studies have detected the presence of ββ'sulphonyldipropionic acid and ββ'dithiodipropionic acid. Hydrolysis of the ester grouping of DMSD therefore occurs during the course of the reaction. This is consistent with the presence of a strong acid. It is known that methyl-β-sulphopropionate catalyses its own hydrolysis to β-sulphopropionic acid[74] and therefore this may be responsible for the ester hydrolysis occurring in the CHP-DMSD system.

Product analysis has shown that likely products such as dimethyl sulphonyldipropionate and dimethyl dithiodipropionate are not produced in significant amounts. They have also been shown to be ineffective relative to DMSD as peroxide decomposers. The analysis of the solid, U1, is consistent with it being impure $\beta\beta'$sulphonyldipropionic acid. The likely impurities are $\beta\beta'$dithiodipropionic acid and dimethyl sulphonyldipropionate. Investigation of authentic samples of these compounds showed that they were ineffective peroxide decomposers.

An anomalous result concerning U1 is that it decomposes hydroperoxides catalytically to give phenol and acetone (Table 6.14). There is no induction period and the reaction is first-order with respect to hydroperoxide (Figure 6.11). The fact that the effectiveness of the solid in chlorobenzene increases with the quantity added (Table 6.13) while not appearing to dissolve suggests that the active species may only be present in small amounts and is capable of going into solution. Some weight to this argument may be obtained from the result that, while all the solid dissolves in a dioxan solution the rate of the hydroperoxide is no faster but is in fact slower than when the same amount is used in chlorobenzene (Table 6.13).

The identity of the peroxide decomposer, U1, still remains unknown. Whether or not it is the species actually responsible for all the activity of DMSD is uncertain. The quantities of U1 that would be obtained from a CHP-DMSD reaction solution in chlorobenzene are much smaller than the quantities used in studying U1 as a peroxide decomposer and it is not possible to estimate the quantity of U1 still in solution resulting from the CHP-DMSD reaction. It may be that only small amounts of an active product is produced and this does not affect the kinetics of the CHP-DMSD reaction greatly. The "coming-out" of solution would then have to be explained by complexing out with the inactive $\beta\beta'$ sulphonyldipropionic acid.

An alternative theory is that the active species has been isolated in the form of U1. The deduction from the kinetic results that an amount of active species is produced independent of the initial concentration of DMSD must be still valid (Dioxan solution - Table 6.6).

The CHP-DMSD reaction does not show a large solvent dependence. A change in the dielectric constant from 4.9 to 27 (chlorobenzene and nitrobenzene at 75°C respectively) results in only a two-fold increase in the rate of the first-order decomposition (Tables 6.3, 6.6 and 6.7). This suggests that while there is a polar transition state it is unlikely that there is a large separation of charge. In oxidising cumene there is a larger proportion of products corresponding to an induced free radical decomposition of cumene hydroperoxide (Table 6.10). This will be partly due to the instability of the CHP in cumene at 75°C. Free radical decomposition occurs, as shown by the initiation of oxidation of cumene by cumene hydroperoxide under these conditions (Chapter 3).

Oxygen appears to increase the rate of the first-order decomposition only at high sulphoxide concentrations (Table 6.3). This is not understood and does not appear to be explicable in terms of reactions 6-15. AZBN is very effective in suppressing the decomposition of the hydroperoxide (Table 6.9). DMSD inhibits the free-radical decomposition of styrene and it has been postulated that this is due to a transfer reaction between the sulphenic acid and the styryl radicals (Chapter 5). It is therefore possible that part of the inhibition by AZBN is due to the removal of the sulphenic acid by a reaction with the 2-cyano-2-propyl radicals which are produced by thermal decomposition of AZBN. The reaction was carried out in air and therefore the reaction is more likely to involve the peroxy radicals and this reaction is believed to be energetically more favourable (Chapter 3). The degree of the suppression of the CHP-DMSD reaction by added AZBN suggests that an alternative reaction may also be occurring, It is possible that the removal of sulphenic acid from the system occurs by addition to the azo group of AZBN. If this does occur then the autoinhibiting effect recorded when DMSD is added to oxidising cumene initiated by AZBN may be explained (Chapter 3). If the sulphenic acid is removed by the AZBN in preference to the sequence of reactions envisaged (6-15) then the production of the active species is interrupted and will result in the suppression of the decomposition.

TBC in air does not have a large effect on the reaction (Table 6.8). A four-fold excess of TBC to DMSD decreases the first-order rate slightly but increases the induction period two-fold. This suggests that TBC does interfere with intermediates producing the active species. However it seems apparent that if free radical reactions are involved, the radical intermediates are not easily scavengeable.

It is therefore possible to explain many of the experimental results concerning the CHP-DMSD reaction in terms of reactions 6-15. Unfortunately a kinetic analysis of these reactions has proved indeterminable and it appears that an increase in the initial concentration of DMSD would result in an increase in the concentration of sulphur dioxide and the sulphonic acid. A scheme based on reactions 6-15 that may give kinetics shown by the CHP-DMSD system is given below

Scheme

$$R = CH_3OCO\cdot CH_2CH_2$$

$$RS(O)R \xrightarrow[\text{slow}]{k_6} RSOH \qquad (6)$$

$$RSOH + CHP \xrightarrow[\text{fast}]{k_{16}} X \qquad (16)$$

$$X + CHP \xrightarrow{k_2} \text{Acetone and Phenol} + X \qquad (2)$$

$$X + RSOH \xrightarrow{k_{17}} \text{Products} \qquad (17)$$

$$\xrightarrow{k_{18}} \text{inactive products} \qquad (18)$$

if $k_{16} \gg k_6$ and subsequent reactions to the formation of X are also very much faster than the thermal decomposition of DMSD (6) X may be the sulphonic acid, sulphur dioxide or the sulphinic acid.

On assuming this the steady-state hypothesis may be applied to the sulphenic acid

$$\therefore \quad k_6[RSOR] = k_{16}[RSOH][CHP] + k_{17}[X][RSOH]$$

$$\therefore \quad [RSOH] = \frac{k_6[RS(O)R]}{k_{16}[CHP] + k_{17}[X]} \qquad [4]$$

First-order kinetics are obtained for the decomposition of CHP and therefore X is constant during this part of the reaction

$$\therefore \quad k_{16}[RSOH] = k_{17}[X][RSOH] + k_{18}[X][RS(O)R]$$

$$\therefore \quad [RSOH] = \frac{k_{18}[X][RS(O)R]}{k_{16}[CHP] - k_{17}[X]} \qquad [5]$$

Equating [4] and [5]

$$k_{17}k_{18}[X]^2 + (k_{18}k_{16}[CHP] + k_6k_{17}[X] - k_6k_{16}[CHP] = 0.$$

Assuming that $k_{17}k_{18}[X]^2$ is negligible

$$[X] = \frac{k_6k_{16}[CHP]}{k_{18}k_{16}[CHP] + k_6k_{17}} \qquad [6]$$

Hence the concentration of X is independent of the initial concentration of DMSD and if $k_{18}k\,[CHP] > k_6k_{17}$

$$[X] \simeq \frac{k_6}{k_{18}}$$

and therefore

$$-\frac{d[CHP]}{dt} \simeq \left(k_{16}[RSOH] + \frac{k_6k_2}{k_{18}}\right)[CHP] \qquad [7]$$

RSOH is very small and the major decomposition occurs by an acid catalysed mechanism and therefore the rate of decomposition will occur according to a first-order rate equation such as

$$k' \simeq \frac{k_6 k_2}{k_{18}} \qquad [8]$$

The Arrhenius parameters for the first-order reaction of CHP and DMSD have been determined (Table 6.5). As the reaction is complex the parameters may be made up of several individual values. In terms of equation [8] the activation energy for k' will be given by

$$E' = E_6 + E_2 - E_{18}$$

E_6, the activation energy for the thermal decomposition of DMSD, is 23.5 Kcals/mole (Table 4.7). E_2 corresponds to the activation energy for the acid catalysed decomposition of CHP. In benzene the value given is 8.5 Kcals mole^{-1} [177] while in acetic acid as solvent the value is 21 Kcal mole^{-1} [27]. E' is 32.4 Kcals mole^{-1} (Table 6.5) and as this was determined in chlorobenzene a value of E_2 = 8.5 is used to give a value for $E_{18} \simeq$ 8Kcals mole^{-1}.

In order to obtain these kinetics it was found necessary to introduce reaction 18. There appears to be no known reaction between DMSD and sulphur dioxide, the sulphonic acid or the sulphinic acids which would satisfy the requirement that the products are inactive. Acid catalysed decomposition of the DMSD[181] may occur but this would not result in removal of the acid species from the system. Disproportionation of sulphinic acids and sulphoxides has been reported[182] but this results in the sulphide and the sulphonic acid. The sulphonic acid could then catalytically decompose hydroperoxide.

It must therefore be concluded that more information is required before a scheme of reactions can be formally proposed to explain our findings concerning the CHP-DMSD reaction. Evidence consistent with the conclusion that the first step in the reaction is the thermal decomposition of DMSD has been provided. The sulphinic acid, produced from the sulphenic acid, is believed to be an active intermediate. A detailed study of the sulphinic acid should therefore be undertaken in an attempt to arrive at a satisfactory conclusion.

Chapter 7

INVESTIGATION OF THE ANTIOXIDANT STAGE. THE DECOMPOSITION OF CUMENE HYDROPEROXIDE (CHP) BY POSSIBLE PRODUCTS OF THE REACTION OF CUMENE HYDROPEROXIDE WITH DIMETHYL SULPHINYLDIPROPIONATE.

7.1. Introduction

Chapter 6 has provided evidence suggesting that the thermal decomposition of DMSD is the first reaction involved in the decomposition of CHP by catalytic quantities of DMSD. It is believed that the sulphenic acid then reacts rapidly with the CHP to give the sulphinic acid. Further reactions are envisaged which result in the formation of methyl-β-sulphopropionate (SA) and sulphur dioxide (Reactions 6-15, page 123). The feasibility that these compounds were the catalysts for the peroxide decomposition were therefore studied.

Unfortunately, due to lack of time, a technique enabling the preparation of a pure sample of the sulphinic acid was not developed. The attempt undertaken is reported and it appears to show that the sulphinic acid is not very stable.

7.2. The decomposition of cumene hydroperoxide (CHP) by methyl-β-sulphopropionate (SA).

7.2.1. Results

Methyl-β-sulphopropionate (II), to be known as SA, can be envisaged to be derived from dimethyl sulphinyldipropionate (DMSD) Chapter 6, page 104)

$$CH_3O\cdot CO\cdot CH_2CH_2SO_3H$$

II - SA

It has also been previously suggested that sulphonic acids are responsible for the antioxidant activity of the sulphide antioxidants[16,87] and for this reason the above compound was synthesised and investigated as a peroxide decomposer.

CHP is decomposed by SA in chlorobenzene by a reaction which is first-order with respect to hydroperoxide. Figure 7.1 shows the first-order rate plots obtained using different concentrations of SA. There are no induction periods and the greater the concentration used the greater is the rate of decomposition. However a solution of SA in chlorobenzene was found to be unstable and if left overnight before being added to CHP no hydroperoxide decomposition took place. All determinations were made immediately the solutions were made up. SA is fairly insoluble in chlorobenzene but at the very low concentrations required this did not prove too difficult a problem. Oxygen has no apparent effect on the reaction between SA and CHP.

It has been shown that the concentration of SA affects the rate of decomposition and therefore the reaction between SA and CHP can only be first-order with respect to time[169]. Equation [1] represents the most probable rate equation with respect to concentration.

$$-\frac{d[\mathrm{CHP}]}{dt} = k''\,[\mathrm{CHP}]\,[\mathrm{SA}]^{x} \qquad [1]$$

SA will remain effectively constant during the course of any one experiment and therefore the pseudo first-order rate constants that are determined, k, are given by equation [2].

$$k = k''\,[\mathrm{SA}]^{x} \qquad [2]$$

Figure 7.2 is a plot of log k against log [SA]. A straight line is obtained with a slope of 2.1 and therefore the order of reaction with

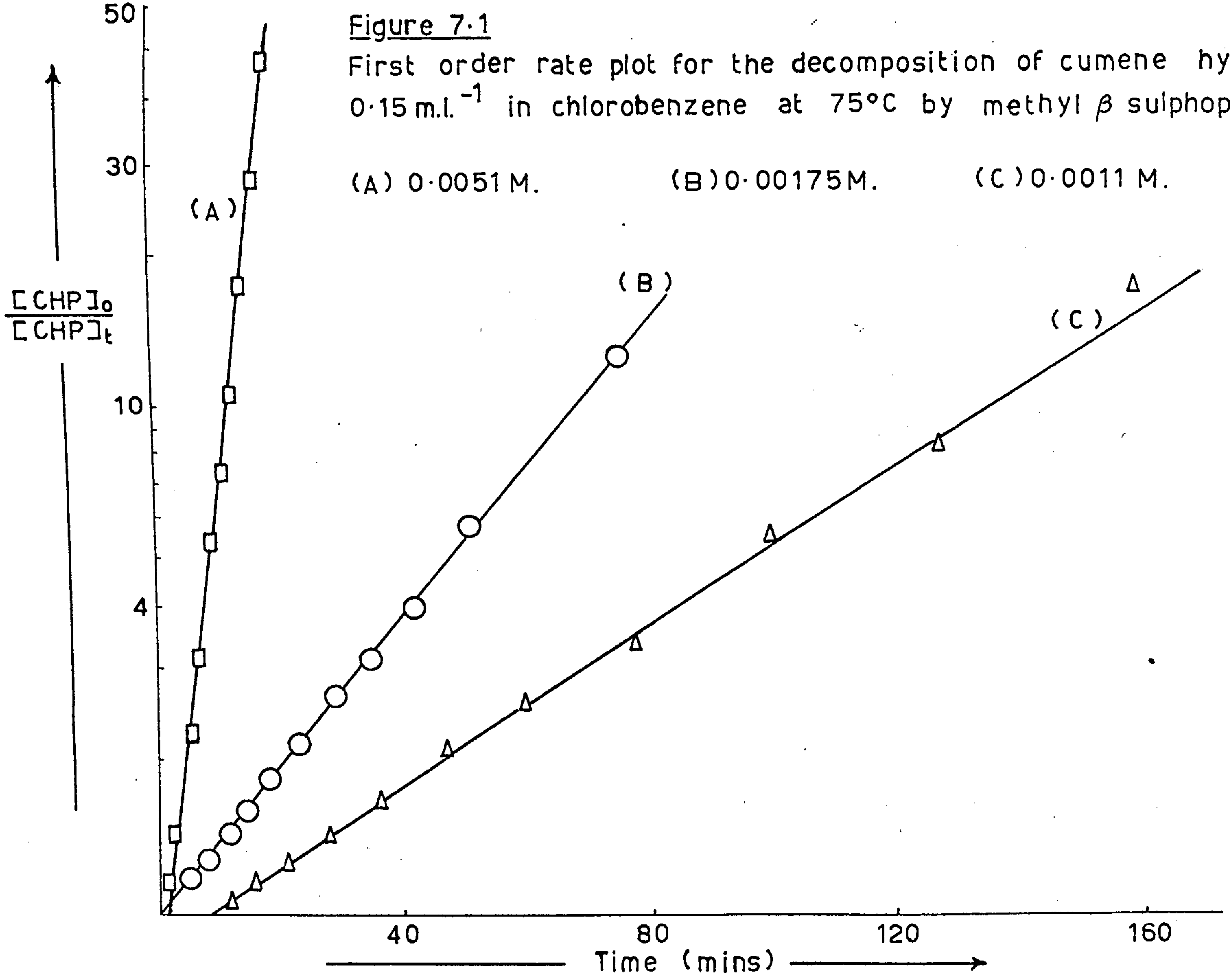


Figure 7·1

First order rate plot for the decomposition of cumene hydroperoxide (CHP), 0·15 m.l.$^{-1}$ in chlorobenzene at 75°C by methyl β sulphopropionate.

(A) 0·0051 M. (B) 0·00175 M. (C) 0·0011 M.

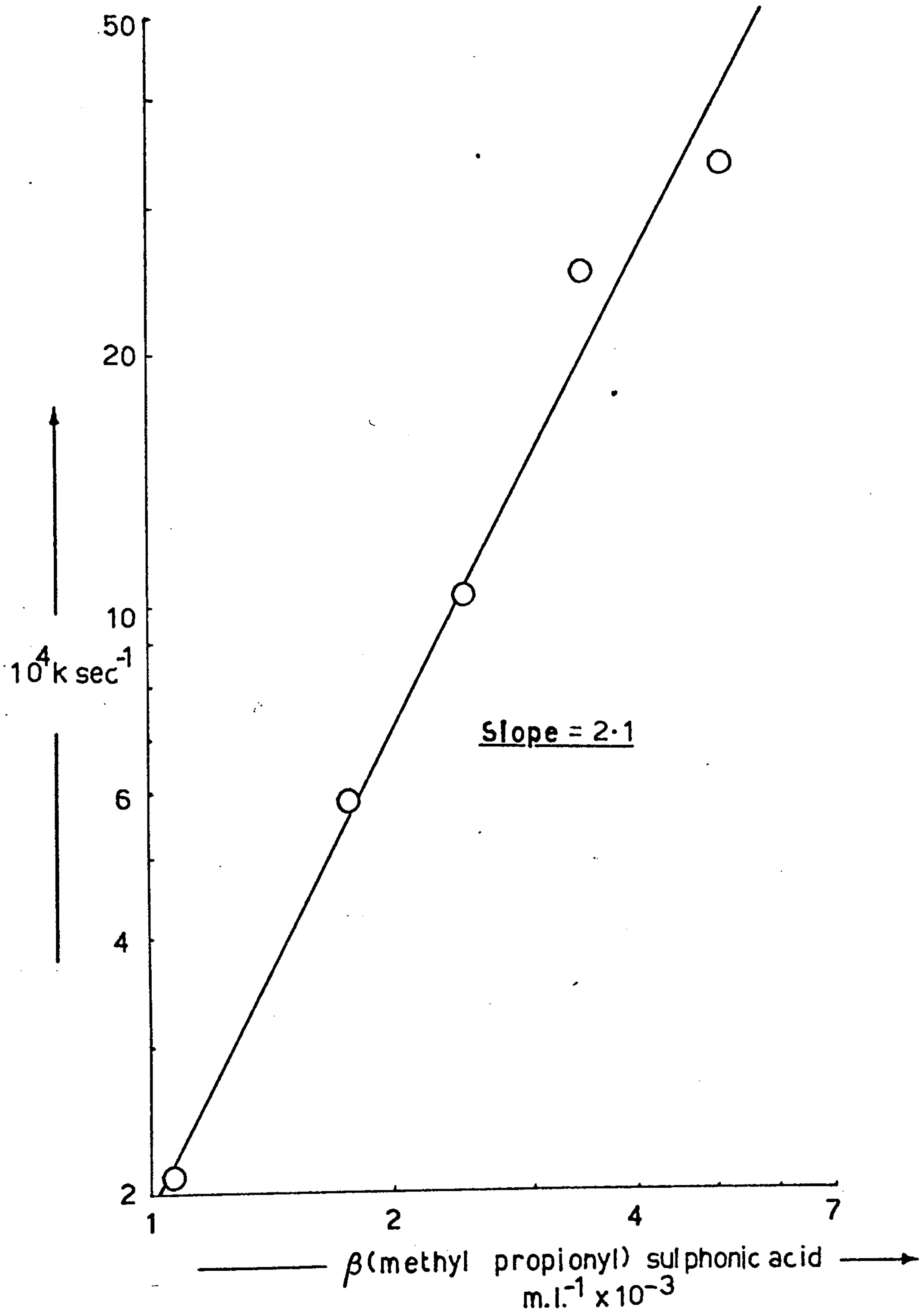


Figure 7·2
Log of the first order rate constants for the decomposition of cumene hydroperoxide (0·15M) in chlorobenzene at 75°C versus the log of methyl β sulphopropionate concentration.

respect to concentration is[3] (Equation [3]).

$$-\frac{d[CHP]}{dt} = k''[CHP][SA]^2 \qquad [3]$$

The products of CHP decomposition were determined and shown to be mainly phenol and acetone (Table 7.1).

Table 7.1

Products of the reaction of CHP (0.15M) and SA in chlorobenzene at 75°C

moles litre^{-1}						
SA	Acetone	Phenol	αα dimethyl benzyl alcohol	Acetophenone	α methyl styrene	Mass balance %
0.001	0.068	0.11	0.005	0.006	0.023	78
0.005	0.11	0.14	Trace	Trace	0.008	89

SA is very soluble in dioxan and it was found that even at high concentrations it was ineffective in decomposing CHP. With a concentration of 0.15 m.ℓ.$^{-1}$ of CHP in dioxan and [CHP]/[SA] = 20 there was negligible decomposition of hydroperoxide after six hours at 75°C. In chlorobenzene with the ratio [CHP]/[SA] = 63 the half life of the reaction is eleven minutes.

It has already been reported that a gas is evolved immediately SA is added to oxidising cumene initiated by cumene hydroperoxide. Using the same experimental procedure it was shown that on the addition of SA to CHP in chlorobenzene in nitrogen a rapid gas evolution also occurred. 1.7 x 10^{-4} moles of SA added to 2.5 x 10^{-4} moles of CHP in 5 mls of chlorobenzene gave a pressure change in the reaction vessel corresponding to 4.0 x 10^{-5} moles of gas. The chlorobenzene solution was then examined for the presence of sulphur dioxide using mass spectrometry. No sulphur dioxide was detected. The same experiment was repeated using dioxan as solvent and no gas evolution occurred.

The possibility of SA thermally eliminating according to Reaction 1 was investigated

$$CH_3O{\cdot}CO{\cdot}CH_2CH_2SO_3H \xrightarrow{\Delta} CH_3O{\cdot}CO{\cdot}CH = CH_2 + H_2SO_3 \qquad (1)$$

No methyl acrylate was produced when a solution of SA in chlorobenzene was decomposed at 75°C.

7.2.2. Discussion

Methyl-β-sulphopropionate catalytically decomposes cumene hydroperoxide in chlorobenzene to give phenol and acetone (Table 7.1). There is no induction period and the reaction is first-order with respect to hydroperoxide. To examine the feasibility of SA being the active species it is necessary to know the concentration that would be required to be produced from the DMSD to decompose the hydroperoxide at the same rate. In the CHP-DMSD reaction the first-order rate constants are virtually independent of the initial concentration of DMSD. At DMSD equal to 5.0×10^{-3} moles litre^{-1} k is beginning to decrease as the initial concentration of DMSD is decreased (Figure 6.4) and at this concentration $k = 6.8 \times 10^{-4}$ sec^{-1}. The amount of SA needed to decompose the hydroperoxide under the same conditions at the same rate is 1.9×10^{-3} moles litre^{-1} (Figure 7.2). It is therefore feasible that this quantity of SA could be produced in the CHP-DMSD reaction.

If SA is the active species it is necessary for this quantity to be produced during the induction period of the reaction. Assuming that

SA is produced only by the reactions which are discussed in Chapter 6 (Reactions 6-15) and that the thermal decomposition of DMSD is the rate determining step it is possible to estimate the time required to produce this concentration of SA (1.9×10^{-3} moles litre^{-1}). Under the conditions of the study the first-order rate constant for the thermal decomposition of DMSD is 5.8×10^{-5} sec^{-1} (Chapter 4). The initial concentration of sulphoxide used is 5.0×10^{-3} moles litre^{-1} and therefore it would require the minimum of 135 minutes to produce 1.9×10^{3} moles litre^{-1}of SA. This calculation has assumed that no competitive reactions are involved. The induction period for the DMSD-CHP reaction under these conditions is 44 minutes and the actual time taken before first-order peroxide decomposition occurs in 55 minutes (Table 6.3). Hence, while it remains feasible for SA to be the active species in chlorobenzene solutions, the mode of production in the DMSD-CHP reaction cannot simply involve the oxidation of the sulphenic acid to the sulphonic acid.

The catalytic nature of the decomposition of CHP by sulphonic acids has been previously studied[27,177]. Vaughan[27] found that with p-toluene sulphonic acid in acetic acid decomposition occurred according to [4]

$$-\frac{d[\mathrm{CHP}]}{dt} = k[\mathrm{CHP}][\text{p-toluene sulphonic acid}] \ldots\ldots [4]$$

Shushunov et al[177] found that when using benzene sulphonic acid in benzene the decomposition occurred according to [5].

$$-\frac{d[\mathrm{CHP}]}{dt} = k[\mathrm{CHP}][\text{Benzene sulphonic acid}]^{2} \ldots\ldots [5]$$

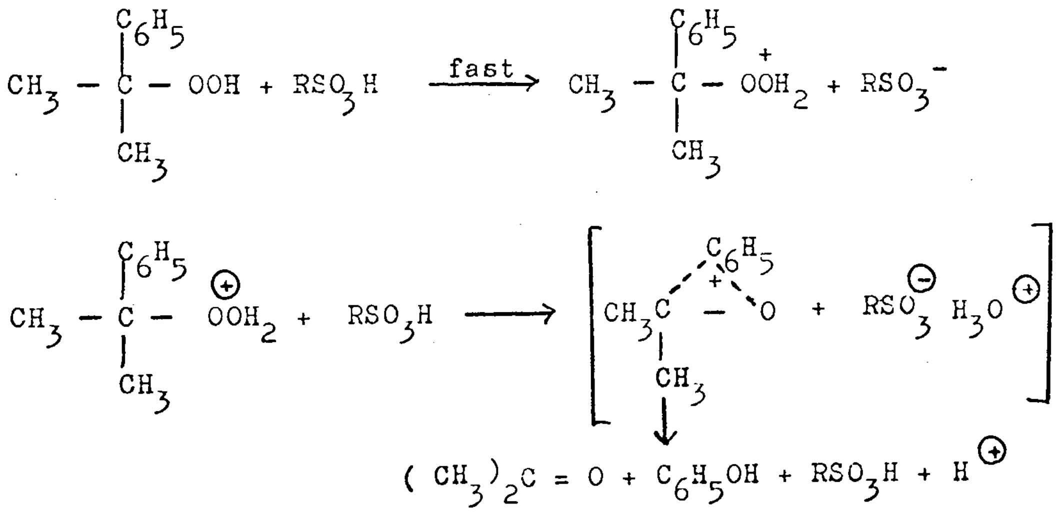
The results for methyl-β-sulphopropionate are consistent with equation [5]. They may be interpreted in terms of a rapid equilibrium followed by a slow reaction (Reactions (2) - (4)), as proposed by Sushunov[177].

$$\mathrm{RR'R''COOH + (RSO_3H)_2 \rightleftharpoons RR'R''COOH\cdot(RSO_3H)_2} \qquad (2)$$

$$\mathrm{RR'R''COOH\cdot(RSO_3H)_2 \longrightarrow R'R''(RO)COH\cdot(RSO_3H)_2} \qquad (3)$$

$$\mathrm{RR''(RO)COH\cdot(RSO_3H)_2 \longrightarrow R'COR'' + ROH + 2RSO_3H} \qquad (4)$$

Alternatively a fast protonation of the hydroperoxide followed by a slow rearrangement to products, (5) would account for the equation [3]



$$\mathrm{CH_3-\overset{C_6H_5}{\underset{CH_3}{C}}-OOH + RSO_3H \xrightarrow{fast} CH_3-\overset{C_6H_5}{\underset{CH_3}{C}}-\overset{+}{O}OH_2 + RSO_3^-}$$

$$\mathrm{CH_3-\overset{C_6H_5}{\underset{CH_3}{C}}-\overset{\oplus}{O}OH_2 + RSO_3H \longrightarrow \left[CH_3\overset{C_6H_5}{\underset{CH_3}{C}}\overset{+}{-}O + RSO_3^{\ominus}\ H_3O^{\oplus}\right] \longrightarrow (CH_3)_2C=O + C_6H_5OH + RSO_3H + H^{\oplus}} \qquad (5)$$

In dioxan SA is inactive as a peroxide decomposer, while DMSD in dioxan decomposes hydroperoxides by a reaction which has the same kinetic features as DMSD in chlorobenzene (Figures 6.3 and 6.4). It is therefore most unlikely that SA is the species responsible for the activity of DMSD. The most probably explanation for the inactivity of SA in dioxan is that a strong oxonium salt is formed[183]. The relative bascities of weak organic bases have been measured by studying their retarding effect on acid catalysed reactions[184]. It is however possible that SA is extremely unstable in dioxan. The activity of SA in chlorobenzene decreases if the solution is allowed to stand at room temperature before being added to the hydroperoxide. It is therefore conceivable that this instability in dioxan is greater and results in the inactivity of SA in decomposing CHP in dioxan. The instability of SA in solution is not understood and requires investigation.

Mass spectral analysis provided no evidence for the production of sulphur dioxide during the reaction between CHP and SA in chlorobenzene. The fact that α-methylstyrene is produced as well as phenol and acetone (Table 7.1) indicates that more than one mechanism for the decomposition of the hydroperoxide is occurring. It is possible that the small amount of gas that is evolved is oxygen[153].

7.3. The decomposition of cumene hydroperoxide by sulphur dioxide

7.3.1. Results

The kinetics of cumene hydroperoxide decomposition by catalytic amounts of sulphur dioxide were studied using exactly the same technique that was used for the CHP-DMSD reactions. All samples for hydroperoxide analysis are removed via a rubber septum and a tap so that the system is effectively sealed and no gas losses to the atmosphere should occur. However, as Figure 7.3 shows, first-order kinetics for the decomposition were not obtained. Sulphur dioxide is, however, extremely effective in decomposing cumene hydroperoxide. 7.5×10^{-4} moles litre^{-1} of sulphur dioxide in chlorobenzene decomposes 0.15 m.ℓ^{-1} of CHP in less time than 5×10^{-3} moles litre^{-1} of DMSD decomposes the same amount of cumene hydroperoxide. The products produced are mainly phenol and acetone (Table 7.2). Sulphur dioxide was also effective in decomposing cumene hydroperoxide in dioxan.

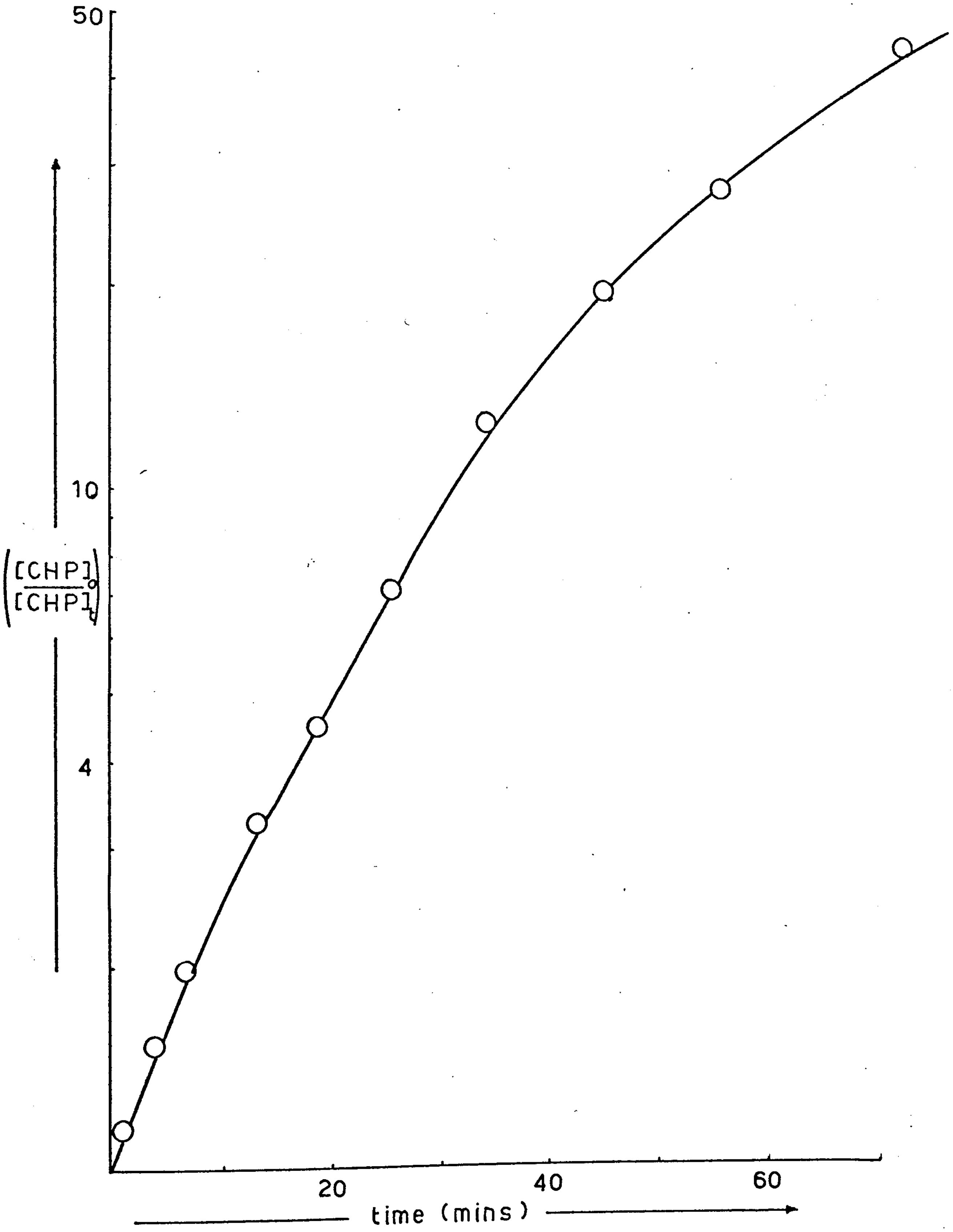


Figure 7·3
First-order rate plot for the decomposition of cumene hydroperoxide (CHP) in chlorobenzene (0·15M) at 75°C by sulphur dioxide ($7{\cdot}5\times10^{-4}$ M).

Table 7.2.

Products of the reaction of CHP (0.15M) and SO_2 (0.00075M) in chlorobenzene at 75°C.

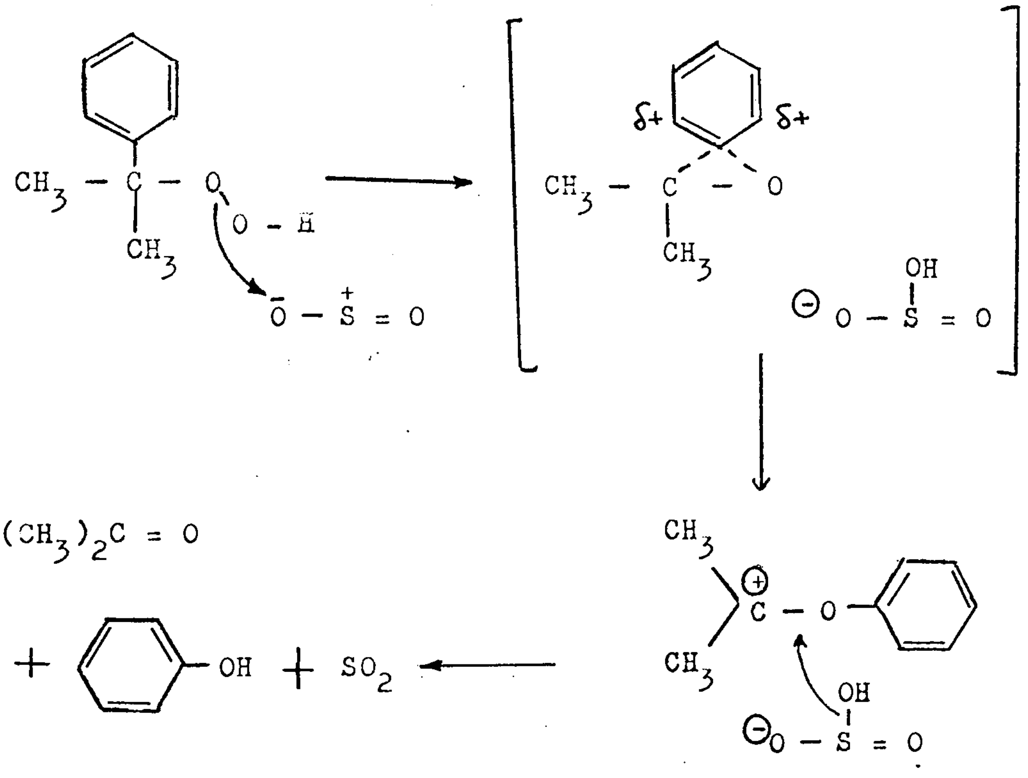
moles litre^{-1}					
Acetone	Phenol	αα dimethyl-benzyl alcohol	Aceto-phenone	α methyl-styrene	Mass balance %
0.12	0.126	1.65×10^{-3}	negligible	0.019	92

7.3.2. Discussion

The kinetic behaviour of the sulphur dioxide is not clear and it may be that a modification of the technique used to study the reaction is required. If the reaction does give a non-first-order rate equation then this does not preclude it from being the active species produced from the DMSD. In the CHP-DMSD system the active species is produced so as to maintain a steady concentration and therefore does not appear as a variable in the rate equation.

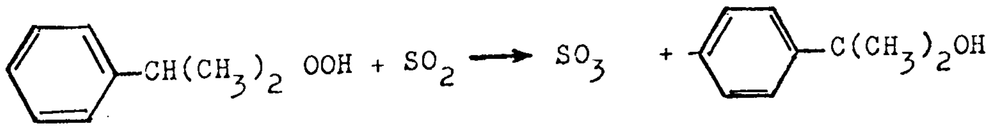
Using the same argument that was applied to methyl-β-sulphopropionate the minimum period that would be required to produce the sulphur dioxide from DMSD can be calculated. If the thermal decomposition of DMSD is the rate determining step then 45 minutes would be required to produce 7.5×10^{-4} moles litre^{-1} of sulphur dioxide. This concentration decomposes 0.15 m.ℓ^{-1} of CHP in a shorter period than 5.0×10^{-3} moles litre^{-1} of DMSD. The induction period for the CHP-DMSD reaction under these conditions is 44 minutes (Table 6.3) and the reaction becomes first-order in hydroperoxide after 55 minutes. It is therefore feasible that sulphur dioxide is responsible for the activity of DMSD and it is produced by a series of reactions which involves the thermal decomposition of DMSD as a relatively slow step.

The products of the reaction are mainly phenol and acetone (Table 7.2). Kharasch[153] was the first person to mention sulphur dioxide as a catalyst for the decomposition of CHP and its activity is explained as being due to functioning as a Lewis Acid (6).

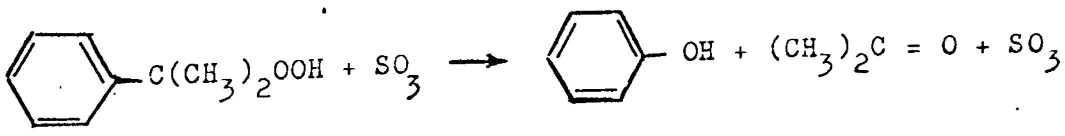


(6)

The commercial production of acetone and phenol from cumene by the reaction of sulphur dioxide with cumene hydroperoxide has been patented[185], and the method is described by Fortuin and Waterman[186]. De Jong[176] appeared to show that by adding acceptors of sulphur trioxide, such as pyridine, the reaction of the hydroperoxide with sulphur dioxide in fact proceeds according to (7) and (8)



(7)



(8)

If equimolar amounts of sulphur dioxide, cumene hydroperoxide and pyridine are reacted then it is possible to obtain near quantitative yields of αα-dimethylbenzyl alcohol[176].

The above reaction of SO_2 and CHP would afford an explanation for the presence of some of the α-methylstyrene in the product mixture (Table 7.2). This would be produced by dehydration of the αα-dimethylbenzyl alcohol which is catalysed by sulphur dioxide[180].

The presence of free radicals in the reaction of hydroperoxides with sulphurdioxide have been demonstrated by the use of e.s.r.[187] and free radical acceptors[188]. The studies involve excess and equimolar amounts of sulphur dioxide to hydroperoxide and were carried out below 20°C. The results were interpreted in terms of reactions (9) and (10)

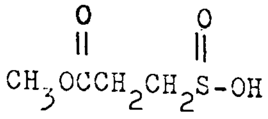
$$RO_2H + SO_2 \longrightarrow RO\cdot + HO\dot{S}O_2 \qquad (9)$$

$$\left.\begin{array}{l} RO_2H + SO_2 \longrightarrow H\dot{O} + RO\dot{S}O_2 \\ H\dot{O} + SO_2 \longrightarrow HO\dot{S}O_2 \end{array}\right. \qquad (10)$$

If free radical intermediates are present in the SO_2 - CHP system then an induced free-radical decomposition of the hydroperoxide will also take place and account for further quantities of α-methylstyrene (Table 7.2).

The brief examination of the SO_2 - CHP reaction therefore suggests that it is feasible that sulphur dioxide is the active species in the CHP-DMSD reaction. The fact that no sulphur dioxide was detected in this reaction may mean that sulphur trioxide is the actual peroxide decomposer.

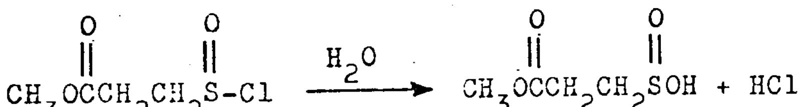
7.4. Methyl-β-sulphinopropionate



$$\mathrm{CH_3O}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\overset{\overset{O}{\|}}{\mathrm{S}}\mathrm{-OH}$$

(XIII)

Methyl-β-sulphinopropionate (XIII) is believed to be involved in the series of reactions which must take place in the reaction of CHP with DMSD (Chapter 6). Low molecular weight sulphinic acids are viscous oils which are subject to rapid decomposition[189]. The higher molecular weight sulphinic acids have been isolated as crystalline solids[174]. The methods of preparation of sulphinic acids have been reviewed by Truce and Murphy[189] and the sulphination of Grignard Reagents has been used successfully for the aliphatic compounds[189,174]. However due to the ester function present in (XIII) this method was not attempted and the method used was hydrolysis of the sulphinyl chloride (11)



$$\mathrm{CH_3O}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\overset{\overset{O}{\|}}{\mathrm{S}}\mathrm{-Cl} \xrightarrow{H_2O} \mathrm{CH_3O}\overset{\overset{O}{\|}}{\mathrm{C}}\mathrm{CH_2CH_2}\overset{\overset{O}{\|}}{\mathrm{S}}\mathrm{OH} + \mathrm{HCl} \qquad (11)$$

The sulphinylchloride, prepared from methyl-β-mercaptopropionate, was added to excess water at room temperature, and the excess water removed under reduced pressure. A pale yellow oil remained. Examination of the infra-red spectrum of the crude oil showed the presence of a large broad band starting at 3,700 cm^{-1}, a broad bond at 2510 cm^{-1} and strong bonds at 1740 cm^{-1}, 1075 cm^{-1}(b) and 830 cm^{-1}(b). These bands are consistent with the structure (XIII), as three bonds which are consistently present in the i.r. of sulphinic acids occur at 2790-2340, 1090-990 and 870-810 cm^{-1} [79]. The band at 1740 cm^{-1} has been assigned to the carbonyl stretch of the ester function and the broad band at 3,700 cm^{-1} to H-bonding.

Attempts were made to purify the oil by forming the lead salt and then regenerating the acid by passing hydrogen sulphide through an ethanol suspension of the salt but these were unsuccessful. Similarly, shaking the salt in dilute hydrochloric acid and extracting with ether gave an oil with a different i.r. spectrum. In the case of the ethanol solution the oil would not reform a lead salt. It was therefore decided to estimate the quantity of the sulphinic acid present in the crude oil by formation of the ferric salt[190]. On addition of ferric chloride to the solution of the oil in water a deep red-brown solution resulted. No precipitate was produced. As a specific property of sulphinic acids is the formation of insoluble, voluminous salts with the formula $(RSOO)_3Fe$ [190], this result implied that the oil was not the sulphinic acid.

Further attempts to prepare the sulphinic acid could not be made due to lack of time. However the infra-red spectra of the oil were consistent with it being the sulphinic acid. Small quantities of the oil decomposed much larger portions of pure CHP at room temperature. The reaction was violent. If DMSD was added to CHP under the same conditions no reaction occurred. However as the oil was not characterised this study could not be taken further. It was observed that the oil changed to a sticky white solid on standing in air. This also occurred when the oil was heated under vacuum at 60°C for three hours. Attempts to identify the solid was unsuccessful but bands in the i.r. indicated the presence of carboxylic acid (1700 cm^{-1}) and perhaps the formation of thiolsulphonate and sulphonic acid (1315, 1120 and 1165 cm^{-1}). This would be consistent with disproportionation of the sulphinic acid followed by hydrolysis of the ester grouping catalysed by the sulphonic acid.

Chapter 8

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1. Conclusions

In agreement with the results of previous work[36] dialkyl thiodipropionates and dialkyl sulphinyldipropionates have been shown to act as pro-oxidants as well as antioxidants. It has been conclusively established that the pro-oxidant effect at moderate temperatures is not due to thermal dissociation of the dialkyl sulphinyldipropionate. The results of oxygen absorption and polymerisation studies indicate that the radical generating reaction involves both the hydroperoxide and the sulphoxide. The mode of production of radicals, which gives rise to the pro-oxidant effect, has not been established but a direct bimolecular reaction between the sulphoxide and the hydroperoxide has been shown to be unlikely. It is therefore suggested that a redox reaction may occur between the sulphenic acid, a product of the thermal decomposition of the sulphoxide, and the hydroperoxide. The sulphinic acid has also been postulated as a possible product of the reaction of cumene hydroperoxide and dimethyl sulphinyldipropionate. It is therefore possible that the sulphinic acid is one of the species which gives rise to the pro-oxidant effect. This may, in fact, account for the second pro-oxidant stage which is encountered.

The dialkyl sulphinyldipropionates inhibit autoxidation by both interrupting the propagating oxidative chains and by decomposing the main initiator of oxidation, the hydroperoxide. Evidence suggests that association between the hydroperoxide and the sulphoxide is not important in explaining the antioxidant activity of the thiodipropionates.

The chain interrupting activity of the sulphoxides has not been previously reported. It is shown that this effect occurs in an autoxidising system and in free-radical polymerisation. As the theoretical yield of methylacrylate from the decomposition of dimethyl sulphinyldipropionate in styrene was obtained it was concluded that the free-radical interrupting species was not the sulphoxide. It has been suggested that the sulphenic acid is the species responsible and functions by a chain transfer reaction with the propagating radicals.

It has previously been observed that the thermal instability of a sulphoxide is important in determining its effectiveness as an antioxidant[22,23]. No mechanistic explanations other than Scott's[36] (Scheme 1, page 12), was provided. The mechanism proposed to explain the chain interrupting activity of the sulphoxides depends upon the thermal instability of the sulphoxide and so provides another explanation for the observation. Evidence is also provided which suggests that the thermal decomposition of the sulphoxide is the first step in a series of reactions leading to the formation of a species which can catalytically decompose hydroperoxides. This is in agreement with Scott's proposal (Scheme 1, page 12).

A rapid reaction between the sulphenic acid and the hydroperoxide to give the sulphinic acid has been proposed to account for kinetic results. This is believed to be the second step in the series of reactions leading to the peroxide decomposer. Further reactions envisage the formation of alkyl-β-sulphopropionates and sulphur dioxide. The feasibility that these may be the peroxide decomposers was investigated. The results suggest that the alkyl-β-sulphopropionate cannot be entirely responsible for the activity of DMSD. However it is possible that sulphur dioxide or sulphur trioxide is the actual peroxide decomposer.

The overall kinetics of the DMSD-CHP reaction are complex and an explanation in terms of a reaction scheme has not been forthcoming.

Further information is required and it is believed that an examination of the chemistry of alkyl-β-sulphinopropionates both alone and in the presence of peroxides would be useful.

8.2. Suggestions for further work

It has been proposed that the sulphinic acid, which is capable of being produced from the sulphoxide, is an important compound involved in the antioxidant action of the sulphoxide. It is therefore suggested that methyl-β-sulphinopropionate be prepared and a study of it alone and in the presence of hydroperoxide be made. The relative importance of the reactions of the sulphinic acid, envisaged to occur in the reaction of dimethylsulphinyldipropionate with cumene hydroperoxide may then be assessed.

The potency of thiodipropionates as antioxidants relative to other dialkyl sulphides has been accounted for in terms of its ease of oxidation to the sulphoxide and by the thermal instability of this sulphoxide. By studying different sulphinic acids it will be possible to determine whether or not any other factors are involved in accounting for the variation of antioxidant activity with structure of the original sulphide.

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