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A THESIS

entitled

AUTOXIDATION OF OLEIC ACID AND OLEYL ALCOHOL
AND ITS INHIBITION

by

MEHRAN DAHESH

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

1975

ABSTRACT

Methods have been developed for the purification of oleic acid, oleyl alcohol and related substrates and for the determination of polyunsaturated impurities and peroxides in these compounds.

The autoxidation of purified oleic acid and oleyl alcohol has been studied in the absence of additives and in the presence of deliberately added impurities. These studies show that impurities, especially polyunsaturated impurities, are of great importance in determining the stability of these substrates.

These studies have been extended to examine the effect of a range of antioxidant types on the oxidation of both pure and deliberately contaminated substrates. The effects of antioxidant type and substrate type are discussed .

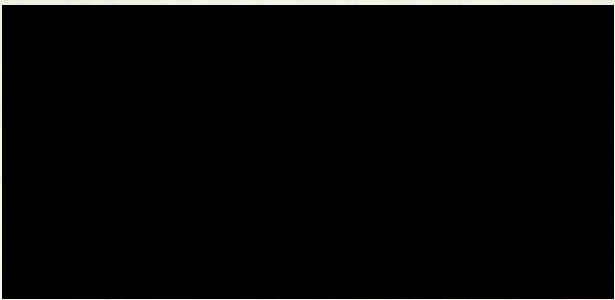
Synergism between different antioxidants has been examined and found to be significant. The implication of these results for the stabilisation of fatty substrates in commercial practice is discussed.

The action of the newly developed nickel complex {bis (stilbene dithiolato) nickel (II)} as an antioxidant has been investigated both by oxygen absorption and by inhibitor consumption measurements on both the original complex and a series of related molecules whose syntheses are described. These complexes are found to be efficient antioxidants for oleyl alcohol but are relatively inefficient in oleic acid. The induction periods in all cases are terminated by the onset of a very rapid oxidation which is beleived to be catalysed by the presence of free nickel ions which are released during the thermal autoxidation of these nickel chelates.

Furthermore, the observed induction period for oxygen uptake is somewhat larger than the time required to consume all of the initial nickel complex. These results simply imply that the initial products of oxidation of the complex are able to act as efficient inhibitors.

A brief investigation of the action of metal catalysts has been made. The indications are that these metal catalysts act as powerful pro-oxidants in the thermal autoxidation reactions of oleic acid and oleyl alcohol, and the phenomenon of catalyst-inhibitor conversion does not occur in these systems.

The work described in this thesis has been carried out in the Chemistry Department of The City University during the period 1971 to 1974. It is, unless otherwise stated, the work of the author, and has not been submitted for any other degree.



ACKNOWLEDGEMENT

I am grateful to Gestetner for their financial support which has made this work possible.

I wish to express my deepest gratitude and appreciation to Professor C. F. Cullis and late Professor N. Uri, joint supervisors of this research, for their guidance and encouragement during the course of this investigation.

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I acknowledge the help provided by all the staff of Chemistry Department, particularly [REDACTED], in the preparation of this thesis.

Finally, I would like to thank my colleagues in the Oxidation and Combustion groups who helped to create a pleasant atmosphere during my research at The City University.

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CHAPTER I

INTRODUCTION

1.1 GENERAL INTRODUCTION.

Atmospheric oxygen is the most universally prevalent as well as economically important oxidising agent for a wide variety of organic compounds including fats and fatty acids. Its action may be beneficial or deleterious depending on the conditions and circumstances under which it occurs. Large quantities of organic chemicals are produced by the controlled oxidation of petroleum hydrocarbons. The process of film hardening in applied protective coatings is essentially an oxidative process. The ultimate failure of these protective coatings, however, is a result of prolonged and excessive oxidation. Rancidification and other forms of oxidative deterioration of many fats and fat-containing materials are likewise due to oxidation by atmospheric oxygen.

Both the favourable and unfavourable consequences of atmospheric oxidation result from the same type of reactions between oxygen and the organic components of the materials in question. Because of the spontaneous nature of the reaction between atmospheric oxygen and many types of organic compounds, the process is frequently referred to as "autoxidation".

Several factors such as light, heat, concentration of oxygen, moisture, and the presence of catalysts or inhibitors affect the autoxidation reactions, often with seemingly very different results. It is sometimes difficult to evaluate the effect of a specific environmental factor in the overall oxidation process because in most cases several of these factors are operating simultaneously. Owing to the complexity of the autoxidation reactions an enormous amount of effort has been, and is still being, expended in attempting to understand the fundamental principles of

autoxidations. Underlying all investigations in this field is a desire not only to learn the nature of the products formed, but also to understand the primary mechanisms involved, since only by control of these mechanisms can the desired products be produced or the undesirable products be avoided.

Because autoxidation is a complex process, the relative importance of the elementary steps may change with temperature so that considerable care is needed in extrapolating the result of accelerated autoxidation experiments, performed at high temperatures, to ambient temperatures.

The studies of the kinetics and mechanisms of the autoxidation of organic substrates have been extensively reviewed^{1,2,3}; the following sections summarize some of the important conclusions which have been reached and the areas of uncertainty which remain.

1.2 KINETICS OF AUTOXIDATION REACTIONS.

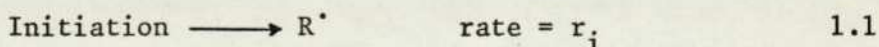
There is ample evidence that the thermal oxidation of organic compounds proceeds by a free-radical chain reaction, since autoxidation is readily inhibited by typical inhibitors of other free-radical processes. Spectroscopic studies have shown that in all cases the primary products of autoxidations are hydroperoxides, although at elevated temperatures and high conversion a wide range of carbonyl-containing products may be formed. In common with other radical chain processes, autoxidation requires a radical-generating initiation step. Initiation can be artificially induced by the homolysis of thermally unstable compounds (initiators), by photochemical processes, or by radical forming oxidation-reduction reactions often catalysed by small amounts of metal salts. However, the detailed mechanism of initiation in individual cases is often uncertain.

The formation of hydroperoxide is the result of a propagation cycle, consisting of two steps: (a) alkyl radical addition to molecular

oxygen, forming a peroxy radical and (b) attack by the peroxy radical upon the substrate molecule, transferring a hydrogen atom, forming a molecule of hydroperoxide and generating another alkyl radical to continue the kinetic chain.

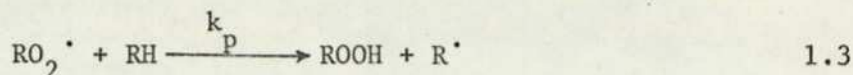
One of the rate-limiting factors in all radical chain reactions is the ease with which free-radicals combine or disproportionate with one another to form non-radical products (termination). Since there are two kinds of radicals involved in simple propagation cycles (ignoring initiator radicals) there are in principle three kinds of radical-radical terminations, i.e. that between two alkyl radicals, between two alkyl peroxy radicals, or between an alkyl radical and a peroxy radical. Actually the situation is much simpler than this. Molecular oxygen behaves as a diradical and hence there is virtually no energy requirement to reach the transition state for the oxygen addition step, i.e. the oxygen addition to alkyl radicals is extremely fast. On the other hand the hydrogen transfer step, which involves C - H bond rupture, requires the investment of some appreciable amount of energy to attain its transition state and is nearly always the slower and rate determining propagation step. At any given instant the free-radical population of an autoxidising system is made up almost entirely of peroxy radicals, provided that there is a sufficient concentration of oxygen to allow all the alkyl radicals to react rapidly. Therefore the most common biradical termination step in simple autoxidation is that which occurs between two peroxy radicals.

To generalise, it can be said that simple free-radical autoxidation will consist of some initiation process whereby the substrate-derived radical $R^\bullet$ is generated:

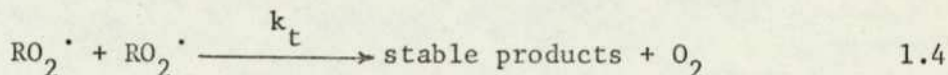


a propagating cycle consisting of alternate oxygen additions and hydrogen

transfer steps:



and a termination reaction which most commonly involves two peroxy radicals:



This simple mechanism was first proposed by Bolland and Gee⁴ and its overall kinetics are readily predicted. Making the steady state assumption with respect to each of the chain carrier free-radicals it follows that:

$$r_i + k_p [RH] [RO_2^{\bullet}] = k_o [O_2] [R^{\bullet}] \quad 1.5$$

$$k_o [O_2] [R^{\bullet}] = k_p [RH] [RO_2^{\bullet}] + 2k_t [RO_2^{\bullet}]^2 \quad 1.6$$

Adding equations 1.5 and 1.6:

$$r_i = 2k_t [RO_2^{\bullet}]^2$$

or:

$$[RO_2^{\bullet}] = (r_i / 2k_t)^{\frac{1}{2}} \quad 1.7$$

The rate of formation of hydroperoxide in reaction 1.3 is simply:

$$d [ROOH] / dt = k_p [RO_2^{\bullet}] [RH] \quad 1.8$$

Substitution of 1.7 by the relationship of equation 1.7 gives the general rate law for the simple autoxidation scheme represented by equations 1.1-1.4:

$$-d [O_2] / dt = d [ROOH] / dt = r_i^{\frac{1}{2}} k_p [RH] / 2k_t^{\frac{1}{2}} \quad 1.9$$

indicating that the rate of autoxidation is expected to be independent of the oxygen concentration, provided that this is sufficiently high to ensure that reaction 1.4 is the only significant termination step.

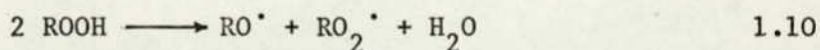
Although this simple scheme has been of considerable value in interpreting the kinetics of autoxidation, it has considerable limitations.

In particular this simple scheme does not predict the autoacceleration which is frequently observed in autoxidations and is discussed further in section 1.3.

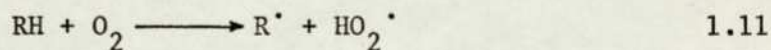
1.3 INDIVIDUAL REACTIONS OCCURRING DURING AUTOXIDATION.

1.3.1 Initiation.

While the propagation and termination steps of autoxidation processes are well understood, there appear to be some major differences of opinion amongst the investigators in the attempt to explain the initiation process in autoxidation reactions. In an attempt to establish the kinetics of the initiation step, Bolland and Gee⁴ obtained a linear relation between the rate of oxidation and the extent of oxidation (i.e. the concentration of the hydroperoxide produced in the course of the reaction) for the aerobic oxidation of ethyl linoleate. It was later confirmed that this relationship is also obeyed in other olefinic autoxidations⁵. Such a relationship is consistent with the occurrence of a chain process involving a bimolecular reaction which Bolland and Gee postulated to be:



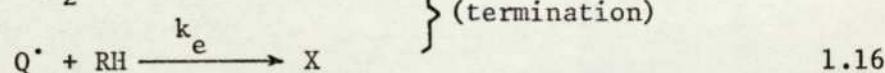
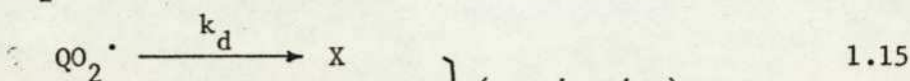
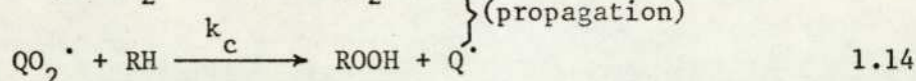
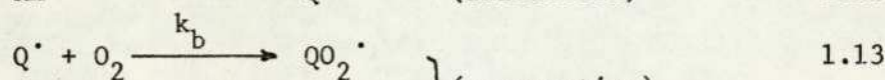
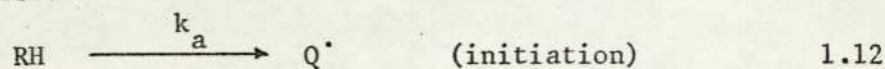
Extrapolation of the above mentioned plot gives a definite intercept which was originally interpreted as being due to the thermal reaction between oxygen and the olefin, i.e.



However, experiments at extremely low hydroperoxide concentrations carried out later by Bateman and his co-workers^{6,7} indicated that the rate of oxidation actually did not follow the extrapolated line, but a curved line falling sharply towards the origin. This behaviour is consistent with

an initiation process which is unimolecular in hydroperoxide at low concentrations. Very similar results have also been obtained with a non-olefinic hydroperoxide by Stannett and Mesrobian⁸.

According to one school of thought, therefore, the initiation of olefin autoxidation can be accounted for by the autocatalysis due to unimolecular and bimolecular decomposition of hydroperoxide. This hydroperoxide initiating mechanism of autoxidation proposed by Bolland and his co-workers, which is now accepted for a large number of saturated and unsaturated hydrocarbons, has been found to fail in the case of aldehydes. Mulcahy and Watt⁹ have found that the oxidation of benzaldehyde is auto-retarding. Perbenzoic acid is not an initiator for the oxidation and its breakdown products (e.g. benzoic acid) retard. They postulated the following reaction steps in which $Q^{\cdot}$ is an unspecified energetic chain carrier and X is an inert product:



Making the usual stationary state assumptions, this leads to the rate equation 1.17:

$$-\frac{d[O_2]}{dt} = \frac{[RH]^2 [O_2]^2}{k_e k_a^{-1} k_b^{-1} [RH]^2 + k_d k_a^{-1} k_c^{-1} [O_2]} \quad 1.17$$

George, Rideal, and Robertson¹⁰ also found a second order dependence on hydrocarbon concentration in the oxidation of tetralin and Mulcahy and Watt⁹ believe that a common mechanism, quite distinct from

the free-radical chain reaction is superimposed upon the latter and is particularly important in the absence of added initiators.

In a recent attempt to review the Hilditch concept¹¹ of direct interaction between olefins and molecular oxygen in a more complex form, Khan proposed that the primary phase of autoxidation does not involve the rupture of α -methylinic C - H bond¹² as had been thought before, but the formation of hydroperoxide via a cyclic transition state by direct addition of oxygen to the olefin. In a later publication¹³ he argues that the exclusive formation of 9- and 13-hydroperoxides and the absence of the 11-isomer in the autoxidation products of methyl linoleate precludes a free-radical mechanism and is a further evidence in support of his direct oxygen-olefin interaction theory. Whilst strong objections have been put forward for this line of reasoning^{14,15}, Khan's concept should be considered as an alternative theory.

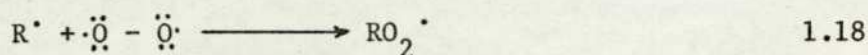
One other important theory which has emerged in recent years is the theory of metal catalysis and the significance of trace metal impurities first put forward by Uri¹⁴, in which the initiation of the autoxidation process has been regarded to be solely due to the catalysis of hydroperoxide decomposition by the trace metals particularly in the case of fats and fat-containing materials. Uri obtained both quantitatively and qualitatively similar relationships between the efficiencies of various antioxidants in pure linoleic acid and in ethyl benzoate solutions of 0.1M linoleic acid in the presence of ferrous phthalocyanine as catalyst at a concentration of 5×10^{-6} M. The close quantitative agreement in the relationship of antioxidant efficiencies for the metal catalysed reaction on the one hand and the autoxidation of linoleic acid on the other has been viewed as proof for the hypothesis that autoxidation in its initial stages is in fact a trace metal catalysed reaction. Uri further claims that free-radical reactions could not be expected to be dependent on the polarity

of the solvent to any significant extent, and the very large differences in the induction periods, rather than in the propagation rate of the chain reaction of the autoxidation can hardly be explained other than by the assumption that initiation is catalysed by metals. A more detailed account of the concept of metal catalysis is presented in a later section of this work (section 1.5).

1.3.2 Propagation.

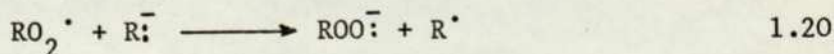
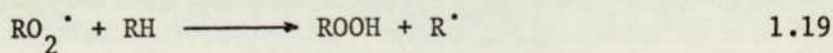
Propagation reactions are the product-controlling reactions of the autoxidation sequence. There appears to be a general agreement amongst the investigators as far as the propagation reactions (1.2 and 1.3) are concerned, and research has been concentrated on the modes by which alkyl radical and peroxy radical reactions occur.

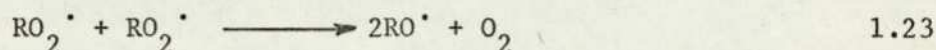
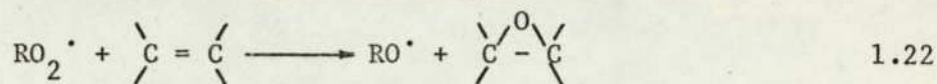
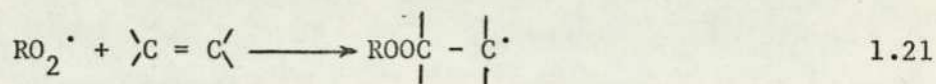
(a) - Reactions of Alkyl Radicals:- Once an alkyl radical has been generated in an initiation reaction it nearly always reacts readily with oxygen. Oxygen behaves as a diradical, and its reaction with an alkyl radical can be viewed as a radical coupling reaction¹⁶.



Reaction 1.18 occurs with ease for most hydrocarbon radicals and hence does not play an important part in determining the rate of the chain propagation and termination except at very low partial pressures of oxygen, or with reactive organic substrates^{6,17}.

(b) - Reactions of Peroxy Radicals:- Depending upon the structure of the materials being oxidised, peroxy radicals can react in one of the following ways (reactions 1.19 - 1.23):





The most common reaction is the abstraction of a hydrogen atom to give a molecule of hydroperoxide and to regenerate an alkyl radical (reaction 1.19). The major factors controlling the reactivity of a C - H bond towards a peroxy radical are the resonance stabilisation of the alkyl radical being formed^{6,17}, and the availability of electrons at the C - H bond which is being ruptured¹⁸⁻²⁰.

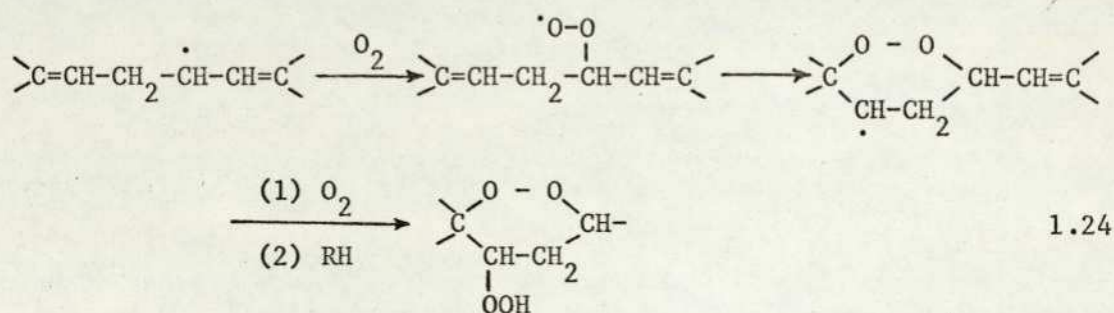
Russell^{21,22}, after examining the autoxidation rates of a number of pure hydrocarbons under uniform condition has found that the relative reactivities of the α -hydrogen atoms of toluene, ethyl benzene, and cumene towards a peroxy radical are 0.08, 0.5, and 1.00 respectively, which indicates the strengths of primary, secondary, and tertiary carbon-hydrogen bonds involved.

Wibaut and Strang²³ pointed out that the attack of a peroxy radical upon a C - H bond can occur either by an intermolecular or an intramolecular reaction, and that an intramolecular reaction is especially favoured in aliphatic systems if two reactive hydrogen atoms are located in 1,4-positions. This phenomenon is particularly important in the oxidation of polyolefins, where it may lead to the formation of long sequences of intramolecular hydrogen bonded hydroperoxide groups²⁴.

Another process by which a peroxy radical can give rise to a molecule of hydroperoxide involves electron transfer with an anion (reaction 1.20). This process has been demonstrated to occur in the oxidation of 2-nitropropane in aqueous basic solutions, where the resulting hydroperoxide

is not stable but gives a quantitative yield of acetone and nitrite ion upon reaction with another 2-nitropropane anion²⁵. Reactions of this kind are not expected to be very important in the oxidation of hydrocarbons.

Although peroxy radicals, react with unactivated double bonds containing α -hydrogen atoms by hydrogen abstraction, activated double bonds of polymerisable olefins, diolefins, and ketones react preferentially by addition²⁶. The ease of the addition of a peroxy radical to a double bond is again determined by the stability of the radical formed, and as in the previous case it can proceed either by an intermolecular or an intramolecular reaction. The intramolecular reaction is often observed in the oxidation of 1,5-diolefins such as squalene²⁷:



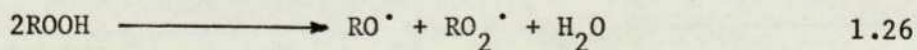
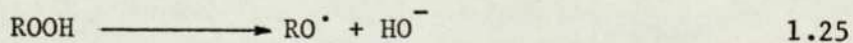
If reaction 1.21 occurs with a polymerisable olefin, the resulting radical may either add another monomer unit or may undergo an addition reaction with oxygen (reaction 1.2). Under favourable conditions a 1:1 copolymeric peroxide of oxygen and monomer may be formed^{26,28}.

Emanuel and his co-workers²⁹ have concluded that, as the oxidation proceeds, the propagating peroxy radicals generally tend to react more with the oxygenated products than with the, as yet, unoxidised molecules, since the former frequently contain more reactive C - H bonds. This effect creates severe problem in the interpretation of kinetic data obtained at high conversions.

1.3.3 Thermal Decomposition of Peroxides.

Peroxides are the main source of chain initiating radicals in autoxidation and as such much effort has been concentrated in order to obtain some knowledge of the factors which determine their rate of decomposition. The O - O bond is the weakest bond in all types of peroxides and its scission gives rise to powerfully oxidising alkoxy or hydroxy radicals leading to branching of the kinetic chain. These reactions are partly responsible for the autocatalysis observed in many autoxidation reactions. Although the rate of branching is a function of the concentration of hydroperoxide³⁰, the overall decomposition is very complex, since at least three different reactions can occur simultaneously. Moreover the solvent generally plays an important role in the decomposition of hydroperoxide³¹, often causing the rate of decomposition to change during an autoxidation reaction as the substrate is progressively oxidised³², and the reaction medium becomes more polar.

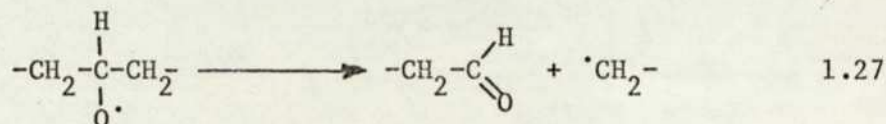
At low concentration of hydroperoxides the initial rate of decomposition is generally first order in hydroperoxide, but at higher concentrations there are substantial deviations³³, and as is shown by Bell et al³⁴, and Fordham and Williams³⁵, the apparant rate constant increases, probably due to the increasing importance of bimolecular and chain reactions. The dependence of rate on concentration can often be expressed as the sum of the rates of a first order and a higher (usually second) order process^{8,35,36}. The thermal decomposition of hydroperoxides can thus be described in terms of the reactions 1.25 and 1.26.



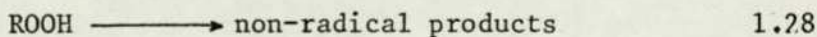
Thomas and Harle³⁷ have shown that the importance of reaction 1.26 relative to reaction 1.25 decreases with increasing temperature and decreasing concentration of hydroperoxide, a result which is consistent with the

suggestion of Bateman and Hughes³⁸ that reaction 1.26 results from a hydroperoxide dimer. The increasing concentration of higher order reactions at higher hydroperoxide concentrations appears to be associated with the formation of hydrogen bonded aggregates of hydroperoxide molecules. These aggregates are readily detected by ir spectroscopy, and it has been shown that they disappear as the concentration of hydroperoxide is reduced^{38,39}.

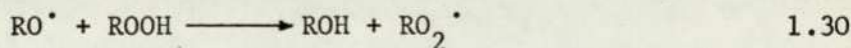
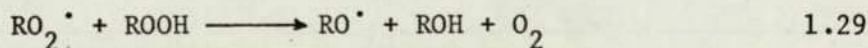
It is important to notice that alkyl-oxy radicals formed by reactions 1.25 and 1.26 may not reinitiate the oxidation in this form. Radicals of this type readily rearrange by reaction of the form 1.27, leading to the production of carbonyl containing products and alkyl radicals. These latter radicals rapidly oxidise to $\text{ROO}^\bullet$ radicals.



Morse⁴⁰ has shown that the thermal decomposition of hydroperoxides at lower temperatures may not involve an initial split into free-radicals, since the rate of the first order decomposition reaction of dodecane hydroperoxide is unaffected by the addition of an inhibitor of free-radicals. Certain other hydroperoxides can also apparently decompose without the production of free-radicals⁴¹. In order to take account of this effect in a kinetic scheme it is necessary to include a reaction of the form 1.28:



In addition to the simple thermal decomposition described above hydroperoxides are susceptible to induced decomposition reactions of the form:

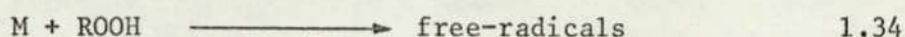
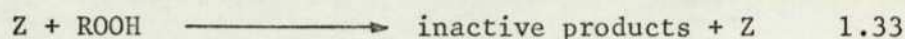
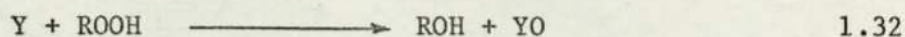


Reactions of this type lead to hydroxyl products and represent the

decomposition of hydroperoxides by chain reaction mechanism leading to additional kinetic complications.

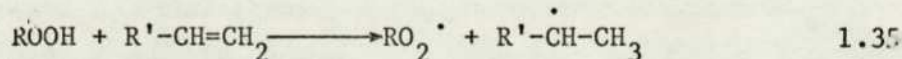
1.3.4 Catalysed Decomposition of Peroxides.

The catalysed decomposition of hydroperoxides can be represented by the reactions 1.31 - 1.34.

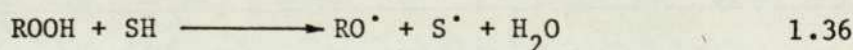


where X, Y, and Z are three different types of decomposers of organic peroxides and M is a metal. Reactions of the type 1.31 and 1.34 lead to radical production resulting in chain branching and an increase in the overall oxidation rate. Reactions of the form 1.32 and 1.33, which do not produce radicals cause the overall oxidation rate to be retarded or inhibited.

Reaction 1.31 involves induced decomposition by substances not containing heavy metal with production of free-radicals. A number of alcohols, ketones, ethers, and fatty acids fall into this class (e.g. reaction 1.35)



Thomas and Harle³⁷ have found that for these reactions the rate of decomposition can be affected by different saturated hydrocarbon solvents and suggested that the influence of such solvents (SH) is due to reactions of the type:



The evidence that this reaction serves as a major source of free-radicals

is rather limited, since conflicting results have been obtained by Knorre, Maizus, and Emanuel³⁰ on the one hand and by Twigg³⁶ and subsequent workers^{42,43} on the other.

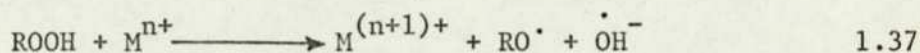
Reaction 1.32 involves a stoichiometric process in which the hydroperoxide is converted to the corresponding alcohol. Denison⁴⁴ was the first to suggest that certain sulphur compounds particularly the monosulphides which contain at least one aliphatic or cycloaliphatic group attached to the sulphur atom, are capable of hydroperoxide decomposition by this type of reaction. Although many sulphides are fairly stable towards oxygen, both sulphides and sulphones are autoxidised rapidly forming strong acids which are able to catalyse decomposition of further peroxides by ionic rearrangement processes⁴⁵.

The presence of a sulphur-containing compound in a system subject to autoxidation, however, is not always advantageous since it may promote the development of resinous compounds and sludges; Denison and Condit⁴⁶ have suggested that some of the disadvantages associated with sulphides can be overcome by the use of selenides which result in fewer deleterious end-products, and which are more effective decomposers of peroxides. However, the value of this suggestion must be limited by the high toxicity of selenium and its compounds.

The mechanism of decomposition of peroxides by sulphides has been discussed in detail by Bateman and Hargrave⁴⁷ who concluded that the reaction can be both unimolecular and bimolecular depending upon the solvent medium. Kennerly and Patterson⁴⁸ have also tested a variety of sulphur-containing compounds as decomposers of peroxides for peroxidised mineral oil and for cumene hydroperoxide in mineral oil. The reaction showed first order dependence on peroxide and high yields of phenol were obtained which suggested the occurrence of an ionic rearrangement process of the type

catalysed by sulphonic acids.

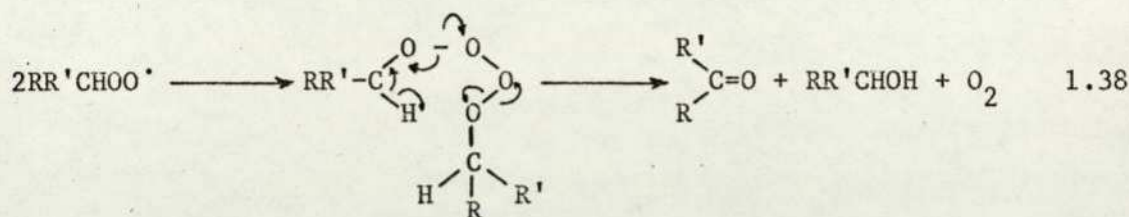
Hydroperoxides are very sensitive to decomposition catalysed by traces of transition metal ions. The first stage of this process is a one-electron transfer reaction of the form:



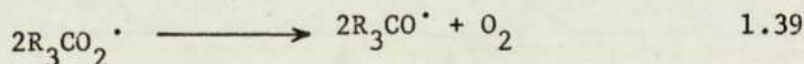
Reactions of this kind are responsible for the role of trace metal impurities as catalysts of autoxidation; they are discussed in more detail together with reactions of the form 1.33 in sections 1.5 and 1.4 respectively.

1.3.5 Termination.

When the sole termination reaction of an initiated oxidation involves the interaction between two peroxy radicals to give non-radical products the overall rate of oxidation will be independent of oxygen pressure. For the interaction of primary and secondary alkylperoxy radicals the following reaction has been postulated by Russell⁴⁹, which portrays more concisely other suggestions^{34,50} advanced to explain the formation of an alcohol and a ketone:



For tertiary alkylperoxy radicals this type of chain termination is not possible due to the lack of hydrogen atom on the α -carbon. It is generally assumed^{34,49,51,52} that these radicals undergo a non-terminating interaction to produce alkoxy radicals and oxygen:



Some of the alkoxy radicals may dimerise while some may enter into further

chain reactions and yield varied products.

At low oxygen pressures the reaction between alkyl radicals and peroxy radicals becomes an important termination reaction of the autoxidation. This process becomes more important with an increase in the stability of alkyl radical since the most stable alkyl radicals react slowly with oxygen.

A third type of termination is the reaction which occurs in the presence of most antioxidant inhibitors and is discussed in the following section.

1.4 MECHANISM OF ANTIOXIDANT ACTION.

1.4.1 Introduction.

By definition and in its briefest sense an antioxidant is a substance capable of slowing the rate of oxidation in autoxidisable materials. Antioxidants occur naturally in many organic compounds of an unsaturated configuration, and both natural and synthetic antioxidants are added to many processed or manufactured products. They are particularly important to aid the longevity of fats, oils, fatty foods, soap, cosmetics, pharmaceuticals, rubber, petroleum products, plastics etc.. In principle several different mechanisms of antioxidant action can be distinguished. The most common antioxidants are compounds such as phenols and aromatic amines, which are capable of interrupting the propagation chain by reaction with alkyl or alkylperoxy radicals; antioxidants of this type are frequently called "chain-breaking antioxidants".

A second class of antioxidants are those, termed "preventive antioxidants", which operate by preventing the action of radical sources in the system. The most important substances of this type are organic sulphides, polyfunctional acids, and organometallic complexes especially

nickel chelates which are able to decompose hydroperoxides without the formation of radicals. Other systems of this type function by complexing of trace metals to prevent their redox reaction with hydroperoxides. Because chain-breaking and preventive antioxidants interfere at different points in the autoxidation process, they may mutually reinforce one another leading to an effect greater than the sum of the effect of each antioxidant alone. This phenomenon is commonly called "synergism" and is discussed in detail in section 1.4.6.

1.4.2 Early Theories of Antioxidant Action.

It was recognised from an early date that most effective antioxidants were readily oxidisable compounds⁵³, and a popular interpretation of their action was that they competed with the substrate for oxygen. A simple refutation of this view was provided by Mourea and Dufraisse⁵⁴ who showed that when benzaldehyde and a phenolic inhibitor were allowed to stand in the presence of oxygen in a closed vessel no oxygen was absorbed. The theory which gradually became preferred, although the name "antioxygen" was retained to describe the phenomenon, was that inhibitors act by destroying active peroxides which are the primary cause of oxidative degradation. Bach⁵⁵ had shown that a wide variety of compounds gave peroxides on oxidation and suggested that these are involved in further reactions leading to the ultimate stable end-products.

Although the peroxide decomposition theory of antioxidant action was generally accepted by a number of investigators, some attention must also be paid to a theory put forward originally by Titoff⁵⁶ which was supported by a considerable amount of experimental evidence, and still remains today, as one explanation of antioxidant action. Titoff observed a marked acceleration by traces of ionic copper, concentrations as low as 10^{-13} M being effective.

This lead him to suggest that inhibitors act by suppressing the action of catalysts, whether added or adventitiously present. Later work by Rogers and Taylor⁵⁷ on the mechanism of antioxidant action in the presence of metal salts showed that this was not a complete explanation, since although the effects of metal ions were reduced by antioxidants they could not be completely suppressed.

Closely related to the two mechanisms of inhibitor action were the two theories put forward to explain the occurrence of an induction period. In the first the peroxides were considered to be the true catalysts for the oxidation, and the increase in their concentration was taken as the reason for the characteristic autoaccelerating oxygen absorption rate curves. Accordingly the induction period was believed to be due to the virtual absence of the peroxide. The alternative theory supposed the presence during the induction period of adventitious antioxidants which were gradually destroyed by the peroxides. Evidence to support this was provided by the experiments carried out by Hilditch and his co-workers^{58,59}, in which natural oils were carefully purified by fractional distillation, when it was found that the fractionated components, or the reconstituted oils in which the purified materials were mixed in the correct proportions, oxidised much more rapidly than the crude materials.

Most of the older theories of antioxidant action, notably that of Mourea and Dufraisse, failed to provide a satisfactory explanation for the extreme effectiveness of small quantities of antioxidants. Backstrom's conclusion^{60,61} that alcohols and phenols inhibited the autoxidation of benzaldehyde by interfering with the chain reaction of the autoxidation was an important step towards understanding the mechanism of antioxidant action, but he was unable to give a chemical interpretation of the effect since it was not clearly understood at that time that the energetic

intermediates involved in the autoxidation were in fact free-radicals.

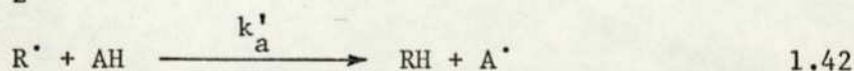
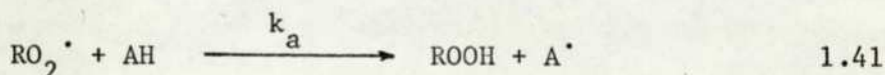
1.4.3 Kinetics of Reactions of Radical Chain-breaking (Phenols & Amines) Antioxidants.

While the general principles of chain termination by free-radical acceptors in autoxidation reactions had been clearly recognised by Backstrom^{60,61}, the first detailed kinetic study was carried out by Bolland and ten Have^{62,63}. Their system consisted of autoxidising ethyl linoleate containing benzoyl peroxide and ethyl linoleate hydroperoxide as initiators and hydroquinone as inhibitor. In the absence of antioxidant the rate of oxidation is given by 1.40 (see section 1.2).

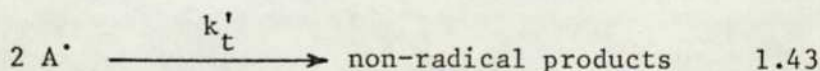
$$-\frac{d[O_2]}{dt} = r_u = k_p k_t^{-\frac{1}{2}} r_i^{\frac{1}{2}} [RH] \quad 1.40$$

where r_i = total rate of chain initiation.

In the presence of the inhibitor AH, Bolland and ten Have considered that both the following chain-ending reactions could occur:



followed by the termination reaction:



There are two limiting equations for the rate of inhibited autoxidation (r_a). The first (1.45) holds when $k_a \gg k'_a$

$$r_a = r_u^2 k_t k_p^{-1} k_a^{-1} [RH]^{-1} [AH]^{-1} \quad 1.44$$

or:

$$k_t k_p^{-1} k_a^{-1} = \frac{r_a}{r_u^2} [RH] [AH] = K \quad 1.45$$

and the second (1.47) when $k'_a \gg k_a$

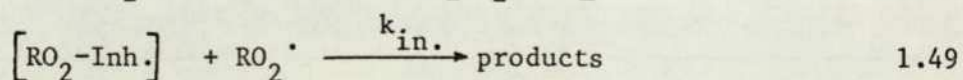
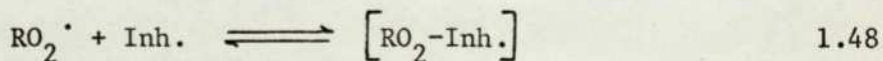
$$r_a = r_u^2 k_t k_p^{-2} k_o^{-1} k'_a^{-1} [O_2] [RH]^{-2} [AH]^{-1} \quad 1.46$$

$$\text{or: } k_t k_p^{-2} k_o^{-1} k_a'^{-1} [O_2]_{100\text{mm}} = \frac{r_a}{r_u} \cdot \frac{100}{pO_2} [RH]^2 [AH] = K' \quad 1.47$$

Equation 1.45 was found to be in agreement with the experimental results whilst equation 1.47 was not. It was, therefore, concluded by Bolland and ten Have that for all practical purposes the free-radical acceptor reacts with $RO_2^{\cdot}$ radicals and not with $R^{\cdot}$ radicals.

From equation 1.45, since k_p and k_t depend (at least on the basis of the underlying assumptions of the above scheme) only on the structure of the olefin, then $1/K$ is a quantitative measure of the chain-breaking efficiency of the antioxidant. Bolland and ten Have compared in this way the efficiency of a number of phenolic antioxidants which were shown to operate by the same mechanism as hydroquinone and, therefore, confirmed their postulated reaction mechanism. This mechanism of antioxidant action which had been recognised, qualitatively, by Backstrom⁶¹ was thus put on a firm kinetic basis. The same basic principles of mechanism and kinetics were used by Davies et al⁶⁴ in a study of relative antioxidant efficiencies in relation to structure. This work is discussed in greater detail in section 1.4.4.

A completely different mechanism, however, has been proposed by Boozer et al⁶⁵ which involves complex formation between $RO_2^{\cdot}$ radicals and the antioxidant (inhibitor), and a reaction of the complex with another $RO_2^{\cdot}$ radical as the rate-determining step of the inhibitor reaction. The scheme is shown by equations 1.48 and 1.49 with the latter being the rate-determining step:

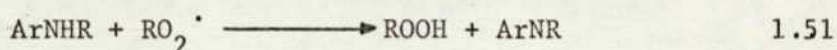


Stationary state kinetics lead to a rate equation which is substantially different from that postulated by Bolland and ten Have, and " r_a ", the rate

of oxygen uptake in the presence of the inhibitor, is evaluated as:

$$r_a = \frac{-d O_2}{dt} = (k_p [RH] (r_i/k_{in.} [Inh.]))^{\frac{1}{2}} \quad 1.50$$

When this rate equation (1.50) was tested for the autoxidation of tetralin in chlorobenzene with azoisobutyronitrile as initiator and phenol and N-methylaniline as respective inhibitors, it was found that the rate of oxygen uptake was inversely proportional to the square root of the inhibitor concentration in contrast to the previous experience whereby it was always reported to be inversely proportional to the first power of the inhibitor concentration. It was also shown that no isotope effect occurred with deuterated aromatic amines; the isotope effect could be expected if the rate-determining step in the inhibition reaction was:



Conflicting evidence appears, therefore, to be present in the literature with regard to the basic mechanism of antioxidant action. It should be pointed out that the mechanism involving complex formation of the inhibitor with the free-radical has been confirmed only for a number of relatively weak antioxidants, which are referred to by Boozer, Hammond and their co-workers as antioxidants of "intermediate activity". It is feasible that this complex formation is of importance only when the hydrogen abstraction reaction (1.41) is not fast enough in the competitive system of reactions which involve the $RO_2^{\cdot}$ radical as is the case with weak antioxidants. Bearing in mind these exceptions, it appears that the above-mentioned hydrogen abstraction reaction is the most important one in antioxidant action.

1.4.4 Relation Between Antioxidant Activity and Structure.

Antioxidant activity is the resultant, firstly, of the ability of

the material to deactivate the alkylperoxy radicals and, secondly, of the tendency of the antioxidant radical to continue the kinetic chain. The distinction between an inhibitor and a retarder is most conveniently made by the fact that, ideally, the inhibitor gives no oxygen absorption indications in the sample during the induction period, implying high chain transfer efficiency (equation 1.41) and negligible reinitiation (reaction 1.42), while the retarder shows a measurable rate of oxygen absorption during the initial stage of oxidation which is a consequence of effective reinitiation or inefficient chain transfer.

As a result of the complexity of the kinetics of inhibited reactions the empirical comparison of antioxidants has largely been carried out for simple organic liquids. Two techniques have been used to measure antioxidant activity. The first, which was developed by Bolland and ten Have⁶², using ethyl linoleate, and has been followed up by Davies et al⁶⁴, and by Bickel and Kooyman⁶⁶, involves the measurement of the rate of reaction of oxygen with the substrate during the induction period, in the presence of a constant source of free-radicals and a chain-breaking antioxidant. From the kinetics obtained which vary with the antioxidant, it is possible to obtain relative values of k_a (equation 1.45) which are a measure of true efficiency of the antioxidant. In the case of highly efficient antioxidants, however, the rate of oxygen absorption is too low to be measured accurately during the induction period, and most other investigators have, therefore, based their measurements of the relative antioxidant efficiency on the evaluation of the induction period. Two recent studies by Rosenwald and his co-workers^{67,68} based on the estimation of the induction periods, contain a comprehensive survey of alkylated phenols and alkylated hydroxyanisoles. In the first study⁶⁷ the relative antioxidant efficiency of alkylated phenols in gasoline oxidation was ascertained by determination of the antioxidant concentration

which permitted a standard amount of oxygen uptake during a fixed time interval. It was shown that under these conditions the efficiency of an antioxidant per unit concentration (molar potency) was frequently dependent on the concentration itself. The induction period is represented by the function:

$$\log y = r + s \log x \quad 1.52$$

where y is the induction period, x is the inhibitor concentration; r and s are constants which can be either positive or negative.

For alkylated hydroxyanisoles Rosenwald and Chenicek⁵⁹ used an inhibitor ratio defined by $(t_a - t_o) / (t_s - t_o)$ where t_o is the length of the induction period in the absence of antioxidant and t_a and t_s are respectively the lengths of the induction periods obtained in the presence of an arbitrary antioxidant at a given concentration and that of a standard antioxidant at the same concentration. In these studies certain empirical rules, albeit without theoretical correlation, were proposed to allow the calculation of the appropriate efficiency for a given structure. Uri¹⁴ considers that the validity of the dependence of antioxidant efficiency on concentration observed by Rosenwald and Chenicek is largely due to the disappearance of the antioxidant by "forbidden route" of a chain reaction.

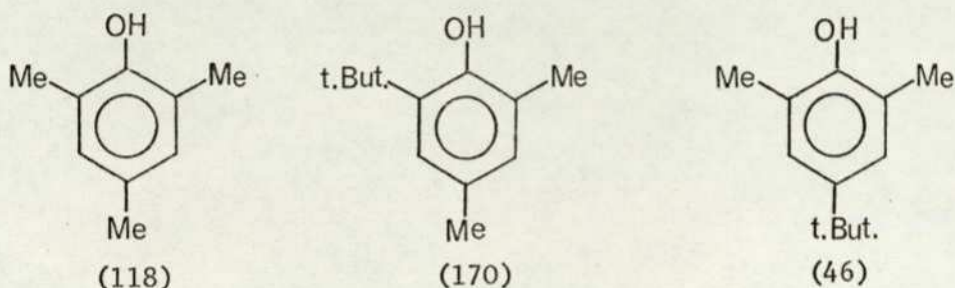
Apart from the two techniques outlined above, any suitable parameter which changes sharply at the end of the inhibition period, such as the rate of oxygen absorption, the development of hydroperoxides or their breakdown products (e.g. carboxylic acids) may also be used. After the accumulation of a vast quantity of literature on 2,4,6-substituted phenols in a variety of substrates, and on the basis of the kinetic measurements of " k_a ", Scott⁶⁹ has stated the following generalisations on the relative efficiencies of phenolic antioxidants:

(a) Electron releasing groups (e.g. methyl, *t*-butyl and methoxy) in the

ortho- and para-positions markedly increase the antioxidant activity. (This is also true of substituents in the meta-position although much less so than in ortho- or para-positions).

(b) Electron attracting groups (e.g. nitro, carboxy, halogen etc.) decrease activity.

(c) α -Branched ortho-alkyl groups considerably increase antioxidant activity whereas such groups in the para-position decrease activity. This is illustrated by comparing the following dimethyl phenols, where the bracketed figures represent an average value for antioxidant activity in petroleum:



Less systematic structure variation has been carried out in the amine antioxidant field, but a sound basis has been laid in the work of Bickel and Kooyman⁷⁰ who determined the antioxidant activity of most of the more common amines. Pedersen⁷¹ has also compared a number of amines in petrol by the induction period method and has found that substitution of amine hydrogen by methyl has a relatively minor effect upon the antioxidant efficiency whereas α -branched N-alkyl groups markedly increase antioxidant activity.

N-Aryl substituents also have a powerful augmenting effect upon the antioxidant activity, and some of the most important industrial antioxidants are diarylamines. Electron releasing groups in the para-position of the benzene ring and particularly dialkylamino and alkoxy have shown pronounced effects and have been studied extensively by Kuzminskii and Angert^{72,73,74}.

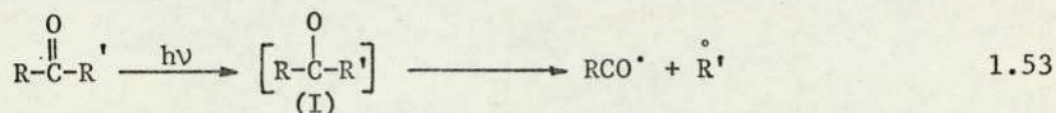
1.4.5 Mechanism of the Action of Preventive (Sulphur Containing and Metal Chelating) Antioxidants.

In conjunction with the breaking of the kinetic chains once they have started an equally important antioxidant mechanism is the prevention of chain initiation. There are several possible processes which may be involved in the introduction of free-radicals into the hydrocarbon system, but the most important source of free-radicals is the hydroperoxide, and both metal ions and uv light are powerful catalysts for their homolytic decomposition. This leads to three main preventive mechanisms viz. the deactivation of metal ions, the absorption or screening of uv light, and the decomposition of hydroperoxides to non-radical products. However any discussion of these three main preventive mechanisms of antioxidant action is complicated by the fact that very often one compound can act in two or more ways (c.f. sec. 1.7.2). Thus many chain-breaking antioxidants are also metal deactivators, and some metal deactivators are also peroxide decomposers or in some cases uv absorbers.

There is now a good deal of evidence to suggest that metal ions exert their pro-oxidant effect by forming unstable co-ordination complexes with alkyl hydroperoxides followed by electron transfer to give free-radicals (see sec. 1.5) . Chalk and Smith have suggested that the inhibition of metal catalysed reactions may be achieved either by strongly complexing the ion to its maximum co-ordination number and thereby inhibiting the further co-ordination of hydroperoxide⁷⁵, or alternatively, and in some cases additively, by stabilising one valency state of the metal at the expense of others⁷⁶.

As far as the photoinitiated autoxidation is concerned some doubt exists in the identity of groups responsible for the photosensitisation of hydrocarbon polymers, but the most likely possibility is that traces of carbonyls may be responsible⁷⁷. Pitts and his co-workers⁷⁸ have shown that

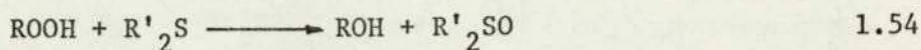
some aromatic ketones (e.g. benzophenone) are particularly effective as photo-activators since the diradical state (I) of the photo-activated ketone is an efficient hydrogen abstracting agent (equation 1.53).



In contrast to benzophenone itself, 2-hydroxybenzophenones which show similar uv absorption characteristics are the most important class of uv deactivators in use. This effect arises because abstraction of the hydroxyl proton by the excited carbonyl would lead to the highly unfavourable loss of the resonance energy of the aromatic ring; compounds of this form, therefore, absorb strongly in uv but reradiate the energy without chemical reaction. The effect of long alkyl chains in improving the effectiveness of the 2-hydroxy-4-alkoxybenzophenone as uv deactivators was investigated by Coleman⁷⁹, who showed that $\text{C}_{17}\text{H}_{35}$ improved the performance of the 2,2'-dihydroxy-4-alkoxybenzophenone by at least six fold.

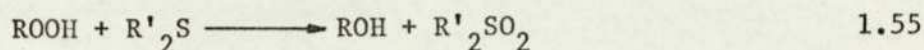
In the case of peroxide decomposing antioxidants, it has been demonstrated by Grant and Tipper⁸⁰ that strong acids inhibit the autoxidation of diphenylmethane. Strong acids are not, however, very practical as antioxidants due to their corrosive action, but Denison and Condit^{81,82}, in an extensive study of the effects of sulphides as antioxidants in purified hydrocarbons, showed that a variety of sulphides have the capacity to decompose hydroperoxides. Bateman and Cunneen⁸³ have carried out a more fundamental study of the antioxidant action of sulphides. They found that many are auto-inhibiting and that sulfoxides and thiosulphinates derived from them are highly effective antioxidants. Hawkins et al⁸⁴ have also found that a wide variety of sulphur containing compounds are effective heat stabilisers. Bateman and others⁸⁵ have shown that sulphur-containing compounds without amino- and phenolic groups inhibit the oxidation process by the decomposition

of hydroperoxides with the formation of stable molecules according to the reaction:



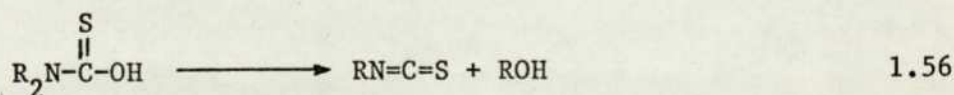
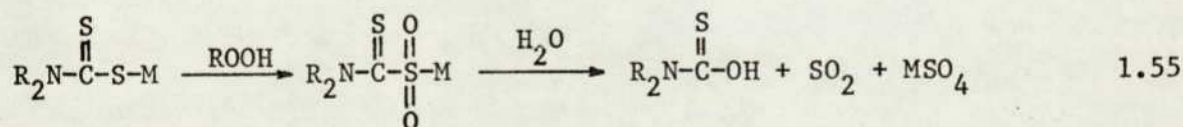
However, this reaction is undoubtedly an oversimplification, since it has been shown that in some systems each molecule of dialkylsulfide may be responsible for the decomposition of many molecules of hydroperoxide.

In a study of the kinetics of the reaction of a hydroperoxide with sulfides it was shown that the reaction was first order with respect to the hydroperoxide⁴⁸, with sulfides being oxidised further to sulfoxes.

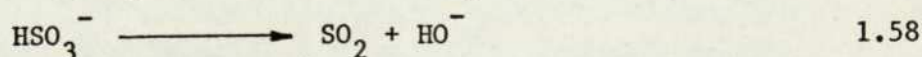
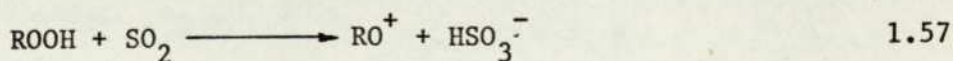


Hagrove⁸⁶ pointed out that apart from the reactions mentioned above sulfides can be oxidised by peroxy radicals without chain termination so that they are consumed and their effectiveness is reduced.

Another important class of sulphur-containing antioxidants is the group of metal chelates derived from α -dithiodiketones, or metal dithiocarbamates. Detailed studies⁸⁷ of the products formed when metal dithiocarbamates were oxidised have indicated the formation of sulphur dioxide and isothiocyanate among the products. It has been suggested⁸⁸ that the reaction sequence for these inhibitors involves the intermediate formation of an unstable sulphonate according to the following scheme:



The liberated sulphur dioxide is an effective catalyst for the decomposition of hydroperoxide by reactions of the form:



which leads to the decomposition of many hydroperoxide groups by each molecule of antioxidant. The metal ion released can also decompose peroxides with radical formation. The antioxidant activity of the nickel chelates of α -dithiodiketones are discussed in detail in section 1.7.2

1.4.6 Fundamental Bases of Synergism in Antioxidant Action.

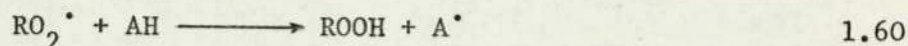
When two or more inhibitors are introduced into the substance undergoing autoxidation, an antioxidant effect in excess of the additive value is frequently observed. Such an effect of the mixture is usually called synergism and is defined by the expression:

$$\tau_{1,2} > \tau_1 + \tau_2 \quad 1.59$$

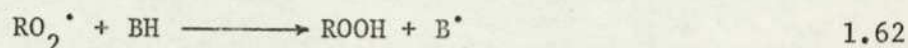
where $\tau_{1,2}$, τ_1 and τ_2 are the induction periods for the mixture and the individual components respectively. Levin and his co-workers^{89,90} have defined the synergistic effect as "one in which the antioxidant efficiency of the induction period for the mixture is higher than for any one component taken separately at a concentration equal to the overall concentration of the mixture".

Two mechanistically distinct types of synergism can be recognised in theory. Firstly homo-synergism involving two compounds one of which is a conventional antioxidant and the other a weak antioxidant which operates by the same mechanism. Secondly hetero-synergism which is the co-operative effect of two antioxidants acting by different mechanisms, such as the combined action of a free-radical acceptor with a metal chelating reagent. The kinetics of the homo-synergism were explained by Uri¹⁴ in the following manner. Consider two antioxidants AH and BH and assume that the bond dissociation energy B - H is smaller than that of A - H, and also assume that the radical derived from the autoxidising substrate ($RO_2^{\cdot}$) reacts slowly with BH

because of low steric factor. The following reaction sequence would then materialise:



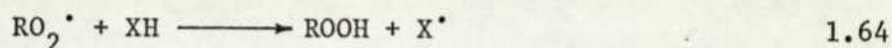
Hence full use is made of the low bond dissociation energy B - H by side-stepping the low steric factor of the "hypothetical" reaction:



with the added result that the tendency of $\text{A}^\bullet$ radical to disappear by the "forbidden route" (reaction 1.63) is substantially reduced.



An excellent example of this type is the combination of a phenolic antioxidant (AH) and ascorbic acid (BH). A mixture of two phenolic antioxidants may also exhibit synergism; the important synergistic condition is that in the inhibition reaction:



one of the two antioxidants (jointly represented by XH) exhibits both a lower activation energy (due to a lower bond dissociation energy) and simultaneously a lower steric factor than the other.

In one form of the hetero-synergism, where a metal complexing reagent is mixed with a free-radical acceptor, the important feature is the partial inactivation of the pro-oxidant impurities by the metal complexing reagent. A free-radical acceptor appears to be essential for achieving protection against all pro-oxidant impurities, but in autoxidising systems it can be supported by a metal complexing reagent which may inactivate part of the trace metal content. This partial inactivation can be so efficient that a substantial gain would be obtained when the synergistic effect is evaluated on the basis of additivity principle. Lundberg and his co-workers⁹¹ have shown that since free-radicals are produced in an electron transfer reaction involving

different valency states of the metal, those metal complexing reagents which reduce the lability with regard to electron transfer could have metal inactivating properties. A classic example of this type of synergist is citric acid which does not appear to be an antioxidant alone, although it is known to form chelates with iron and copper ions^{92,93}. Frankel, Evans, and Cooney⁹⁴ studied its reactivity as a synergist with tocopherol in the presence of iron. As well as increasing the induction period for hydroperoxide formation, citric acid caused a reduction in the rate of destruction of the phenolic antioxidants. The synergistic properties of citric acid have also been investigated in this work (in conjunction with Embanox RHA) and some remarkably favourable results have been obtained especially for oleyl alcohol (see sec. 3.3).

Some remarkable observations concerning the synergistic effect of amines were recently reported by Olcott and Kuta⁹⁵. The theoretical basis of the effect of amines, however, is not yet fully understood, although chelating of heavy metal porphyrines is a possibility which should be taken into consideration

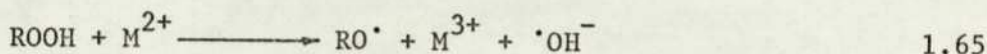
A second and particularly important form of hetero-synergism is exhibited by mixtures of a peroxide decomposing agent with a chain breaking antioxidant. Termination of a propagation reaction by a chain breaking antioxidant inevitably leads to the production of some hydroperoxides; if these are decomposed without radical production then the antioxidant efficiency may be markedly increased. Moreover, many peroxide decomposers are in themselves sensitive to oxidations with peroxy radicals so that their lifetime can be prolonged by the presence of a radical trapping agent⁹⁶⁻⁹⁸.

In the case of synergism with mixtures of three or more antioxidants the mechanism of the reaction kinetics becomes more complex. However much better results may be obtained from combination of three antioxidants as has been shown in this work (see section 3.5).

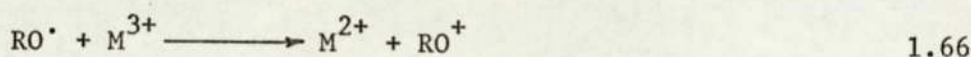
1.5 KINETICS OF METAL-CATALYSED AUTOXIDATION.

1.5.1 Catalysis by Transition Metal Ions.

The thermal decomposition of hydroperoxides, ROOH, can give the radicals $RO_2^\cdot$ and $HO^\cdot$ both of which are active enough to attack the C-H bonds of organic compounds, but the decomposition reaction is slow and kinetically complex³⁸. However, the ions of a number of the transition metals are effective as secondary catalysts of autoxidation. In one scheme, initially they act as one-electron donors to give $RO^\cdot$ radicals by reaction 1.65

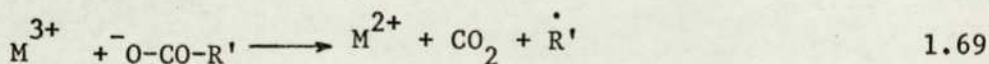
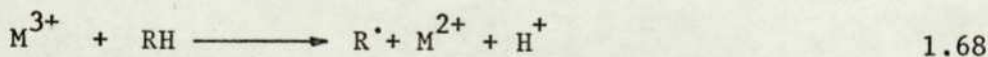
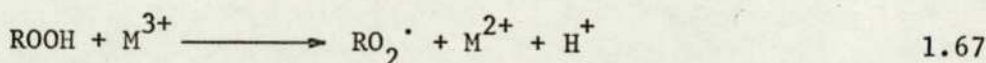


In the absence of any competing reaction the $RO^\cdot$ radicals will react further with the metal ions:



leading to a true catalytic decomposition of the peroxide.

According to Waters⁹⁹, with the effective catalysts this oxidation of M^{2+} to M^{3+} is followed by a second radical producing reaction (1.67, 1.68, and 1.69 are all possibilities) which regenerates M^{2+} so that a second chain sequence is set up.



If 1.65 is the rate determining catalytic reaction then the rate of auto-oxidation (reaction 1.9) becomes:

$$\begin{aligned} \text{Catalysed Autoxidation Rate} &= k_p \{k_{\text{cat}} [ROOH] [M^{2+}] / k_t\}^{\frac{1}{2}} \\ &= K' [RH]^{\frac{3}{2}} [M^{2+}]^{\frac{1}{2}} \end{aligned} \quad 1.70$$

But since 1.65 destroys ROOH molecules a limiting state is soon reached in

which reactions 1.3 and 1.65 balance. Then:

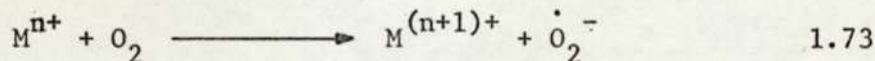
$$[\text{ROOH}]_{\text{lim.}} = k_p^2 [\text{RH}]^2 / (k_{\text{cat.}} K_t [\text{M}^{2+}]) \quad 1.71$$

from which it follows that there is a limiting autoxidation rate (equation 1.72) which is independent of the concentration or the reactivity ($k_{\text{cat.}}$) of the metal catalyst, a conclusion which was first reached by Woodward and Mesrobian⁵⁰ and later verified by Walling¹⁰⁰.

$$-\frac{d[\text{O}_2]}{dt_{\text{lim.}}} \approx \frac{d[\text{RH}]}{dt_{\text{lim.}}} = k_p^2 [\text{RH}]^2 / k_t \quad 1.72$$

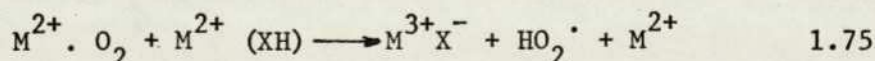
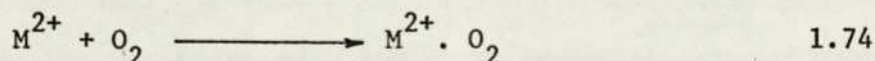
If other reactions such as 1.68 or 1.69 are rate determining then 1.72 is still valid except that k_t then needs a modifying numerical factor (fk_t)¹⁰⁰.

The direct reaction of a metal ion with oxygen has been suggested to occur in some metal catalysed autoxidations studied by Bawn and his co-workers^{101, 102}.



The $\dot{\text{O}}_2^-$ radical ion formed in this reaction would readily react with a proton to form an $\text{HO}_2^\cdot$ radical which could initiate autoxidation. In accordance with the general experience it would be expected that metal activity would be enhanced in organic media.

A third type of metal catalysis based on the kinetic evidence obtained by George¹⁰³ and Weiss¹⁰⁴ is the complex formation of metal compounds with oxygen and subsequent formation of an $\text{HO}_2^\cdot$ radical.



This theory was supported also by Heaton and Uri on the basis of their findings in the case of cobaltous stearate^{105, 106}. Further evidence for

this type of reversible oxygen complex formation (similar to haemoglobin) has been obtained by Martell and Calvin¹⁰⁷ with many cobalt compounds.

1.5.2 Effects of Ligand Groups on Catalytic Reactivity.

It is well known that different compounds of the same transition metal may differ greatly in catalytic activity. This is understandable because free metallic cations do not exist in solution; they are always surrounded by solvent molecules or by other ligand groups so that to oxidise or reduce a transition metal an electron has to be extracted from, or added to, the d-orbitals of the metal by way of a ligand. There are two general routes for this electron transfer viz. outer sphere and inner sphere reaction process. For example in the case of a cobalt (III) complex for which an outer sphere reaction process has been claimed⁹⁹ an unfilled T_{2g} orbital of the cobalt atom can accept one further electron and this can pass in from a p-electron of an organic radical or from a π -electron of an olefin by hybridization.

Inner sphere reactions are two-stage processes in which the attacking reagent first displaces a ligand group. Following this the path for electron movement to or from the metal atom is easy and, therefore, the catalytic activity of the metal is enhanced.

Ligands can also alter catalytic activity by altering the electron density at the metallic centre of a complex ion and so its redox potential. Since in electronic language oxidation is equivalent to electron loss and reduction to electron gain it follows that metallic ions with vacant d-orbitals of low energy level and a high localised positive charge are strong oxidisers.

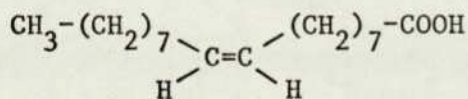
1.6 AUTOXIDATION OF FATTY SUBSTRATES.

1.6.1 Fatty Substrates.

1.6.1.1 Oleic Acid, cis-Octadec-9-enoic Acid $\{\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}\}$.

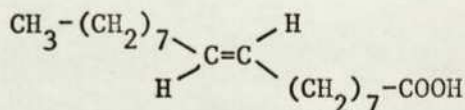
Oleic acid was first recognised as a constituent of several common fats by Chevreul in his "Recherches sur les Corps Gras" in 1815, although it was probably not prepared in the pure condition until much later. Its chemical constitution was subject to intensive investigations in the nineteenth century. For a long time after Varrentrapp¹⁰⁸ had shown in 1840 that palmitic acid was produced in large quantities when oleic acid was fused with caustic potash, it was considered that the acid had the constitution $\text{CH}_3(\text{CH}_2)_{14}\text{CH}=\text{CHCOOH}$, but this reaction undoubtedly involves the migration of a double bond towards the carboxyl group under the influence of molten potash. The structure at present accepted for oleic acid was first proposed by von Meyer and Jacobsen¹⁰⁹ in 1893, and later confirmed by Brauch¹¹⁰.

As it is possible for the mono-ethylinic higher fatty acids to exist in two geometric isomeric forms, octadec-9-enoic acid shows the two isomeric forms (II) and (III) of which the more stable, higher melting form is the trans-isomer (elaidic acid, III).



(II)

Oleic, cis-Octadec-9-enoic Acid



(III)

Elaidic, trans-Octadec-9-enoic Acid

Whilst oleic acid, which is the most widely distributed of all fatty acids occurs naturally, elaidic acid has not been found in any natural fat (except in small proportions in the fats of ruminant animals¹¹¹) but it

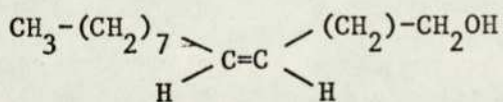
has long been known that on treatment with oxides of nitrogen, or by heating with small quantities of sulphur, oleic acid is partially transformed into its isomeric (elaidic) acid which still has the double bond in the 9-position.

Pure oleic acid crystallises in two forms¹¹², one melting at 13 - 13.2°C and the other at 16 - 16.3°C. It partly decomposes on distillation at atmospheric pressure, but can be distilled at reduced pressures; its boiling point is 285.5 - 286°C/100mm., 232.5°C/15mm., and 153.0°C/1mm.¹¹³.

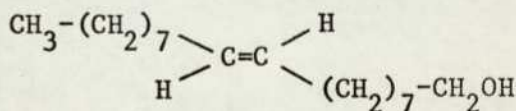
1.6.1.2 Oleyl Alcohol, cis-9-Octadecen-1-ol, $\{\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OH}\}$

This is the most important of the unsaturated aliphatic fatty alcohols. It was discovered independently by Tsujimoto¹¹⁴ and by Toyama¹¹⁵ in certain shark oils and also in sperm oils. Both authors state that the greater part of the alcohols present in the body of the ordinary sperm and Arctic sperm whale consist of oleyl alcohol, while Hilditch and Lovern¹¹⁶ give the percentage of the alcohol in sperm body oil as 66-70 per cent and that in the head oil as about 27-30 per cent of the total higher alcohols present.

As in the case of oleic acid, there are two isomeric forms of the alcohol with the cis-isomer (IV) being oleyl alcohol and the trans-isomer (V) known as elaidyl alcohol.



(IV)



(V)

Oleyl Alcohol, cis-Octadecen-1-ol

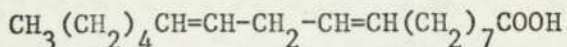
Elaidyl Alcohol, trans-Octadecen-1-ol

Pure oleyl alcohol is a colourless syrupy liquid which solidifies at $\approx 2^\circ\text{C}$ ¹¹³, and boils at 208 - 210°C/15mm., and 150 - 152°C/1mm.

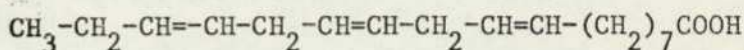
1.6.1.3 Other Fatty Substrates.

Other major fatty substrates used in this work include the following:

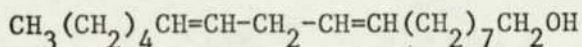
(a) Linoleic Acid, *cis-cis*-Octadeca-9,12-dienoic Acid



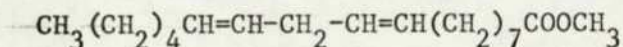
(b) Linolenic Acid, *cis-cis-cis*-Octadeca-9,12,15-trienoic Acid



(c) Linoleyl Alcohol, Octadeca-9,12-dienol



(d) Methyl (all *cis*) Linoleate, Methyl *cis-cis*-Octadeca-9,12-dienoate



1.6.2 Autoxidation of Oleic Acid and Oleyl Alcohol.

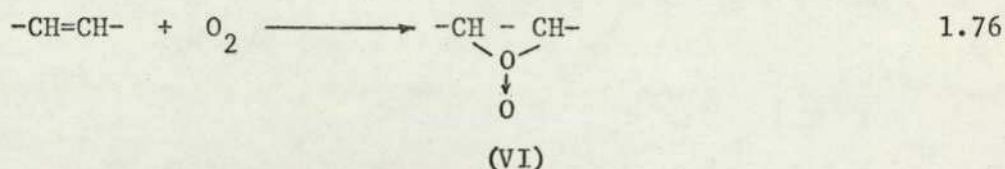
In the past fats and fatty acids have been selected by numerous investigators for autoxidation studies owing to the ease with which they absorb atmospheric oxygen. Natural fats, however, are too complex to permit drawing of far-reaching generalisations concerning the mechanisms involved in autoxidative processes. Consequently much work involving these reactions has been carried out with simple substances such as oleic and linoleic acids, their esters, and oleyl alcohol.

The bulk of the autoxidation studies of oleic acid and oleyl alcohol reported in the literature have been concentrated in the two decades 1930-1950, when speculations about the kinetics of the mechanism of auto-oxidation processes were at their height. The first study of the oxidation of oleic acid appears to be that by Scala¹¹⁷ in 1897. Much later Skellon¹¹⁸

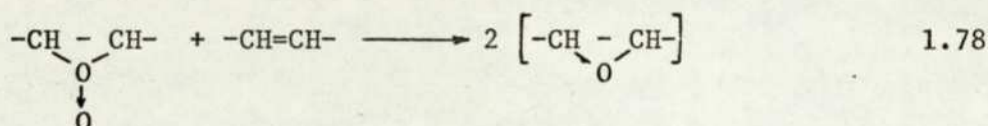
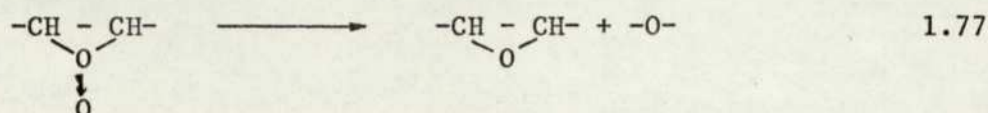
and Ellis¹¹⁹ also investigated the oxidation of oleic acid by the isolation and examination of the end products after prolonged exposure to oxygen. Although some mention of the autoxidation of oleic acid was made in the work of Szent-Gyorgyi¹²⁰, it was Meyer¹²¹ who first investigated the autoxidation of oleic acid in a Warburg apparatus in the presence of chlorophyll, and on the basis of the results obtained suggested that the oxidation occurred with the formation of hydroxyoleic acid. A year later, Hamilton and Olcott¹²²⁻³ followed the course of autoxidation of oleic acid, oleyl alcohol, and methyl oleate in an apparatus specially designed to measure quantitatively the oxygen absorbed and the water and carbon dioxide evolved at constant temperature and pressure. They found that in the initial reactions at the double bond each molecule of methyl oleate and oleic acid absorbed approximately four, and each molecule of oleyl alcohol approximately five atoms of oxygen. Simultaneously, each of the three compounds lost one molecule of water. They also found that the peroxide level in the early stages of autoxidation was higher in oleyl alcohol and methyl oleate than in oleic acid. This difference between oleic acid on the one hand and oleyl alcohol and methyl oleate on the other was attributed to the presence of the carboxyl group of oleic acid which would be capable of reacting with the peroxide to form a hydroxyl group.

Following the findings of Hamilton and Olcott, and using an improved version of the same apparatus, Deatherage and Mattill¹²⁴ also investigated the autoxidation of oleic acid, oleyl alcohol, methyl oleate, and cis-9-octadecene. The last compound was a valuable addition to the substrates which were studied by Hamilton and Olcott since it contains no functional groups other than the autoxidisable double bond. They reported the compounds to autoxidise in a similar manner and to yield the same types of products, amongst which peroxides, peracids, aldehydes, substituted

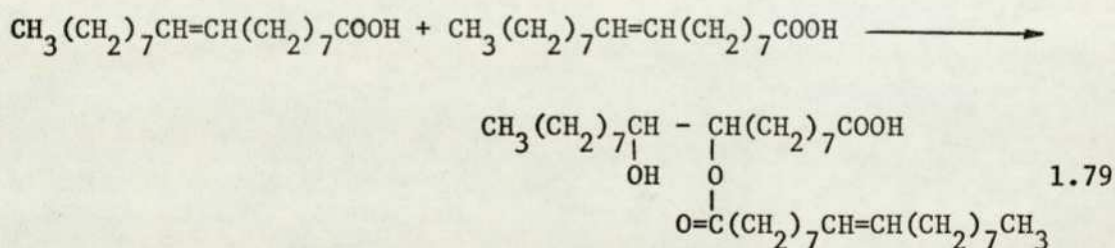
ethylene oxides, acids, alcohols, combination of these and water were detected. On the basis of their findings, these authors suggested that autoxidation occurs through the reaction between gaseous oxygen and the double bond of the ethylenic linkage according to the reaction 1.76.



(VI) is then reduced to the "oxido-oleic acid" either by the loss of an oxygen atom (equation 1.77) or by the oxidation of a second ethylene linkage (equation 1.78)



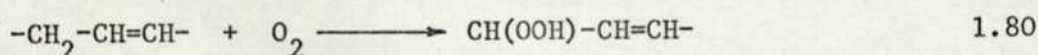
Deatherage¹²⁵ claims that although "oxido-oleic acid" is not found in autoxidised oleic acid in appreciable amounts, it is formed during the course of autoxidation and subsequently esterified to form a half ester of dihydroxystearic acid according to the equation:



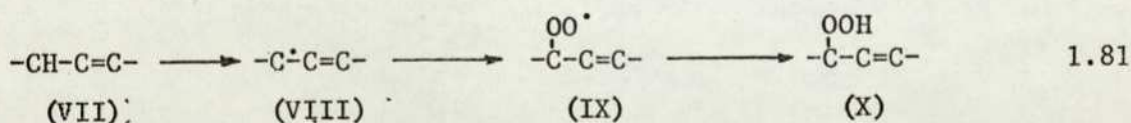
The formation of "oxido" compound as the primary step in the autoxidation of fats and fatty acids was rejected by Franke and Jerchel¹²⁶ on the grounds of the unreliability of the peroxide and iodine values obtained by the investigators at the State University of Iowa Laboratories.

As a result of a series of experiments in which various oxidation products such as dihydroxymaleic acid, oxalacetic acid, acetaldehyde etc. were added to the unoxidised or autoxidised fatty acids, Franke and Jerchel stated that the peroxide and iodine methods gave reliable results in the early stages of oxidation. However, in the late stages, when secondary products of oxidation were present, the methods become increasingly unreliable. Their conclusion was that the primary formation of peroxides affords the only logical explanation of autoxidation of fatty compounds.

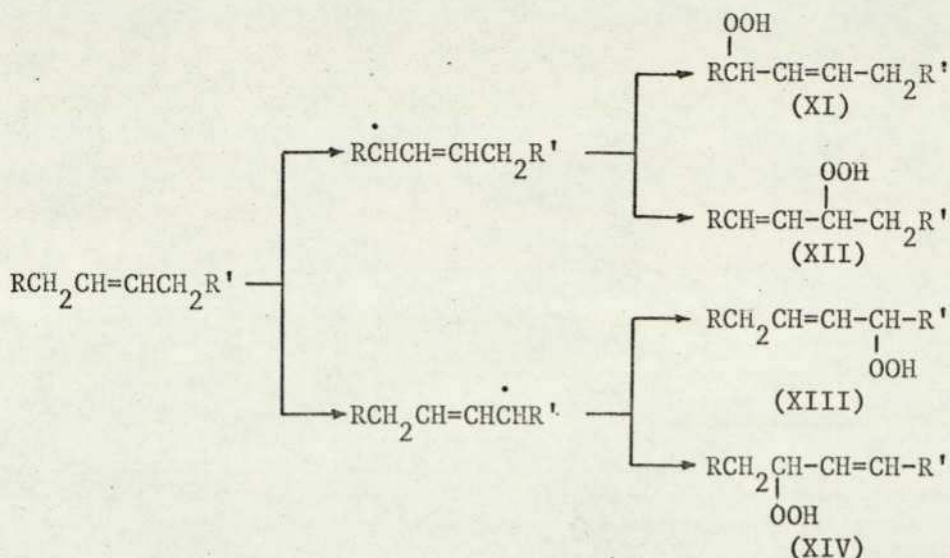
To Farmer and his co-workers¹²⁷⁻²⁹ is due the credit for developing the hydroperoxide hypothesis of autoxidation (see section 1.1) especially in its application to fatty acids. According to Farmer, the autoxidation of practically all unconjugated olefinic compounds proceeds by the addition of a molecule of oxygen to the carbon atom adjacent to the double bond to form a hydroperoxide having an intact double bond thus:



Of the various mechanisms by which hydroperoxide formation may occur, Farmer and Sutton¹³⁰ incline to the view that olefinic peroxidation occurs by way of free-radical mechanism in which the olefin passes through the stages (VII) - (X).



Recently, Ansell¹³¹ has confirmed that the radical intermediate is a mesomeric allylic radical, and in the case of oleic acid (an unsymmetrical olefin) four hydroperoxides (XI - XIV) are possible according to the following scheme:



Ansell claims that although these peroxides have not been individually isolated, good evidence has been obtained for their formation. He points out further that such an allylic rearrangement during formation of the hydroperoxides from oleic acid may be the explanation for the formation of hydroperoxides with trans-double bonds during the autoxidation of oleic acid.

Although several other workers in this field have also supported the theory of the formation of four hydroperoxide isomers^{132,133}, Khan has rejected this in favour of a two-isomer theory¹³⁴. He states that the whole question of confusion about the number of isomers arises for two main reasons: (a) the products of oxidation have been studied for very different extents of reaction and (b) the products are subjected to severely drastic experimental conditions, so changing their original structures during analysis. Khan's findings, from a set of carefully controlled experiments on the autoxidation of methyl oleate, are that two hydroperoxide isomers are formed in approximately equal amounts, and that the hydroperoxide groups reside on the carbon atom adjacent to the double bond.

Peroxide formation in oleic acid and other fatty substrates

has been further studied by Kartha¹³⁵, and it appears that actively autoxidising fats contain two distinct peroxide forms designated I and II. The structures of these peroxides were not identified, but it was suggested that they show different decomposition rates in the presence of antioxidants. Kartha points out that peroxide I is not detectable during the induction period, but after active autoxidation has started its concentration increases gradually to a maximum peroxide value of 40-50. The increase in peroxide I never exceeds 30% of the increase in peroxide value and after the maximum value of 40-50 is reached, further increase is due entirely to an accumulation of peroxide II.

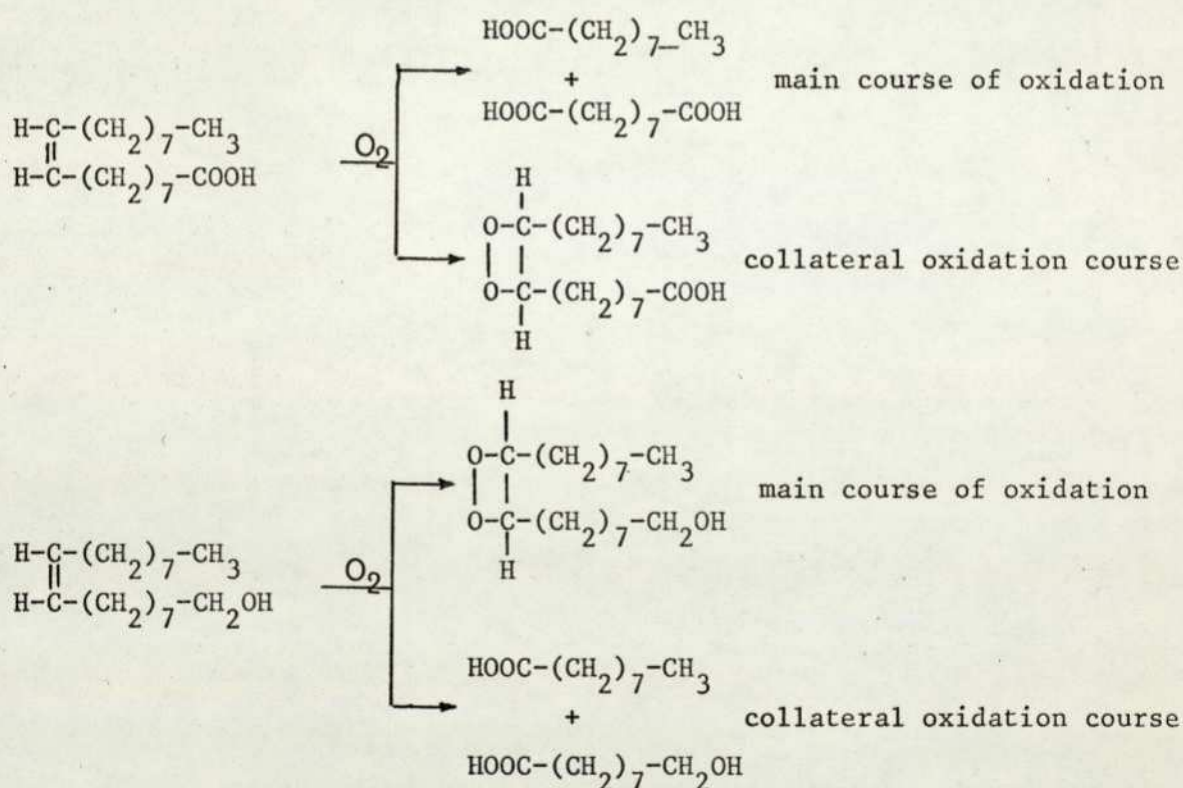
Some work has also been carried out on the role of peroxides in the autoxidation of oleic esters and elaidic acid by King^{136,137}. His investigations which were concentrated on the secondary changes which result from the decomposition of hydroperoxides in the autoxidised substrates lead to the following conclusions:

- (a) - The decomposition of peroxides at 80-90°C appears to give rise invariably to hydroxy compounds, and in the early stages of autoxidation to α - and β -unsaturated ketones, but not to peroxides.
- (b) - Thermal decomposition of peroxide-enriched fractions from oleic esters yields also other carbonyl compounds in which the carbonyl group is not vicinal to the double bond.

The formation of α - and β -unsaturated ketones is also noticed by Mariani and Pochetti¹³⁸ who followed the autoxidation of oleic acid in air/O₂ at 100-170°C by a continuous time study of the ir carbonyl band at 5.7-5.8 μ m and found that the α -carbon next to the unsaturation was particularly active leading to the formation of α - and β -unsaturated ketones¹³⁹.

In a recent study of oxidation process of oleyl alcohol and

oleic acid, Sliwiok and Kowalska¹⁴⁰ followed the reactions by the measurements of the peroxide, iodine and acid numbers, refractive index, the partition and absorption chromatography, and ir and uv spectroscopy. Their results suggest that the oxidation of oleic acid differs from that of oleyl alcohol, largely due to the influence of their characteristic groups. The carboxylic group accelerates the splitting of the molecules of oleic acid during the autoxidation with simultaneous formation of low molecular weight fatty acids. The hydroxyls account for the increase of hydroperoxides in the neighbourhood of a double bond in the molecules of oleyl alcohol. On the basis of these findings, they present the two following schemes for oleic acid and oleyl alcohol oxidation:



Sliwiok and Kowalska point out that temperature is an important factor since it accelerates the course of oxidation of oleyl alcohol towards

cumulation of peroxides, and the course of oleic acid towards a more effective splitting of the molecule.

Recently several papers have been published on the mechanisms of the autoxidation of fatty acids and their methyl esters, both in the presence and absence of inhibitors, by Polish¹⁴¹⁻³, Czech¹⁴⁴, Bulgarian¹⁴⁵ Russian¹⁴⁶⁻⁸, and Japanese¹⁴⁷⁻⁵⁰ workers. Nadin and Mitskevich¹⁴⁶ have found that oleic acid oxidises considerably more than its methyl esters at elevated temperatures, but at 121°C, although the oxidation rate of methyl oleate at the beginning of the experiment is somewhat slower than that of oleic acid, this situation is reversed as the oxidation proceeds. These investigators also point out that cobalt stearate catalyses the oxidation of these fatty compounds substantially, even at lower temperatures such as 60.3°C.

One other aspect of the oxidation of oleic acid and oleyl alcohol is the adverse effect exerted by other unsaturated substrates, mainly dienes and trienes. This effect was originally studied by Gunstone and Hilditch¹⁵¹ who investigated the autoxidation of methyl oleate in the presence of small proportions of methyl linoleate. Their results showed that the autoxidation of methyl oleate was strongly accelerated, and the induction period much reduced, in the presence of 1% of added methyl linoleate at 20°C, or of 0.2% of the latter at 50°C. Figs. 1.1 and 1.2 show the results obtained by these authors for different concentrations of added methyl linoleate to methyl oleate at 20° and 50°C respectively.

In the light of these observations, Hilditch¹⁵² concludes that, at ordinary temperatures, initiation of autoxidation is a function solely of long chain unsaturated compounds which contain the pentadiene system: $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$ with a central reactive methylene group; and that the simple mono-ethenoid system: $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$ is not susceptible

to similar direct attack by oxygen at temperatures below about 50°C.

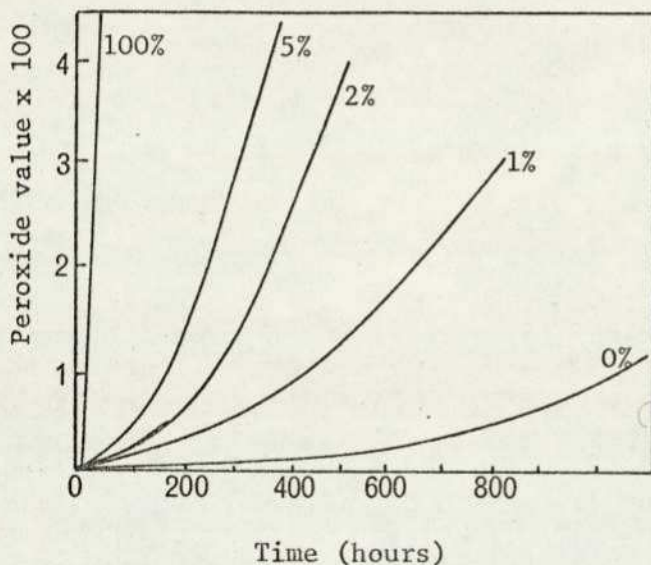


Fig. 3.1

Autoxidation of methyl oleate and methyl linoleate mixtures at 20°C.

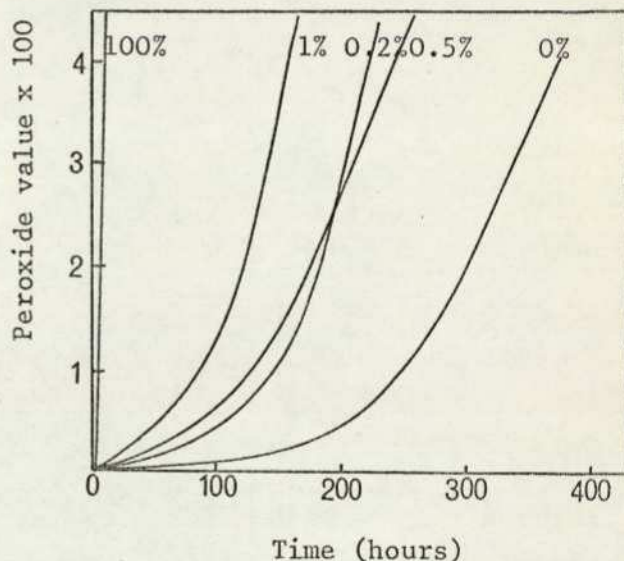


Fig. 3.2

Autoxidation of methyl oleate and methyl linoleate mixtures at 50°C.

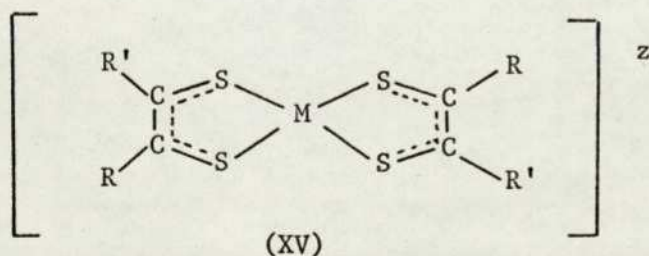
Other workers¹⁵³⁻⁵ have also attributed the reactivity of linoleic acid and its esters to the point of attack by oxygen being between two double bonds. Bolland¹⁷ has pointed out that the resultant decrease in bond strength increases the diene's reactivity by approximately 30 times compared to a corresponding mono-etheneic substrate. Advanced oxidation of linoleic acid and its esters may lead to the formation of cross-linked peroxides due to the $RO_2^{\cdot}$ radical adding to the double bond system of another molecule¹⁵⁶.

In the present work the effect of the deliberate addition of linoleic and linolenic acids to oleic acid and also the effect of the deliberate addition of linoleyl alcohol to oleyl alcohol have been studied at different temperatures in the presence and absence of antioxidants.

1.7 BIS (STILBENEDITHIOLATO) NICKEL (II) COMPOUNDS.

1.7.1 Preparation and Properties.

These nickel chelates are from the general group of bis-dithiolato- α -diketone metal complexes of composition $M(RCSCSR)_n$, where M is a transition metal, n is normally 2 or 3, and R represents an alkyl or an aryl group. They were first discovered by Schrauzer and Mayweg¹⁵⁷. The early preparations of the nickel chelate; the first representative of this new class of compounds, included either the reaction of diphenylacetylene with nickel sulphides^{157,158}, or by the action of H_2S/HCl on benzoin in the presence of nickel chloride¹⁵⁹. Analogous complexes were also reported by the reaction of disubstituted alkynes with metal carbonyls in the presence of sulphur¹⁵⁹. In a later paper Schrauzer and his co-workers^{160,161} claimed that if acyloins were reacted in inert solvent (e.g. xylene) by heating with phosphorous pentasulphide, phosphorothioic esters of the dithioacyloins are obtained, which frequently react directly with metal salt solutions to yield the complex (XV). In this way they prepared the chelates of V, Cr, Mo, W, Re, Fe, Co, Ni, Ru, Os, Pt, and Pd.



Further work has proved that the best results are achieved when the appropriate benzoin is used in place of acyloin¹⁶². The yield is also improved if equimolar quantities of benzoin and phosphorous pentasulphide are reacted in 1,4-dioxan¹⁶³.

Since their discovery the structure of these compounds has been subject to intensive investigation¹⁶⁴. Schrauzer et al^{158,159} formulated these complexes as square planar structures. However, in a subsequent examination¹⁶⁴ they concluded that only certain of these metal chelates possess this type of structure and that the complexes of V, Cr, Mo, W, Re, Ru, and Os are in fact 6-coordinated complexes. The 6-coordinate nature of these complexes was firmly established in several different studies¹⁶⁵⁻⁷.

Davison and others¹⁶⁸ have shown that in (XV), z may have values of 0, -1, and -2 for the same metal and substituents R. This interesting structural property has led to a novel synthetic route for the preparation of complexes of the general type (XV) by electron transfer reactions¹⁶⁹.

In Fig. 1.3 the bond lengths (Å) and the angles obtained by Sartin and Truter¹⁷⁰ for the nickel chelate ring are shown.

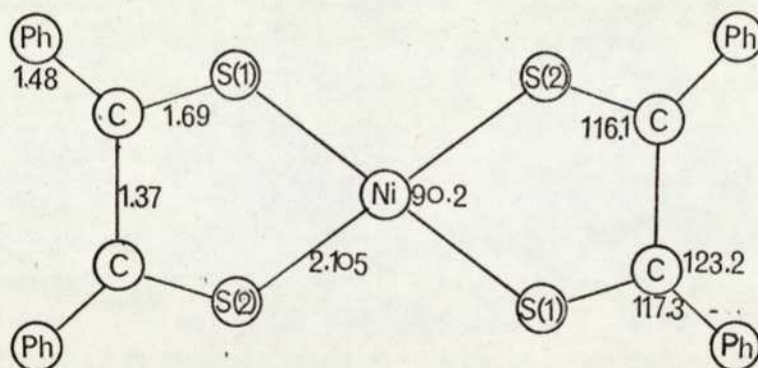
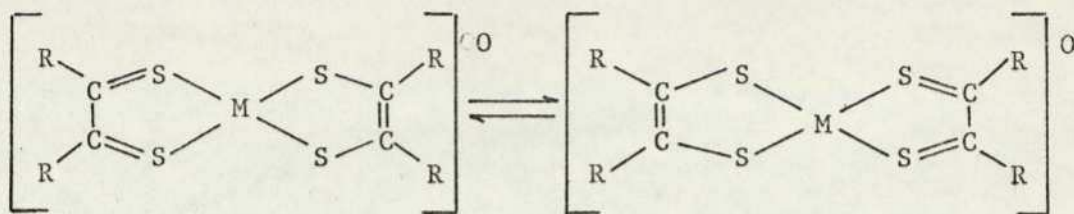
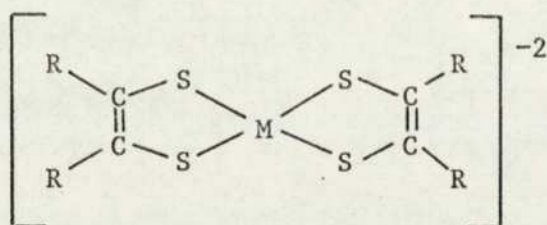


Fig. 1.3

Also Sartin and Truter's findings confirm the theory of Schrauzer and Mayweg^{171,172} that the variations in z do not correspond to changes of oxidation state of the metal but result from extensive ground state delocalisation, or in the valence bond representation:



while the anion with $z=-2$ is simply:



1.7.2 Inhibiting Properties.

The fact that sulphur-containing chelates of heavy metals could be expected to act as peroxide decomposers induced Copping and Uri¹⁷³ to investigate the antioxidant effect of these newly discovered metal chelates derived from stilbene dithiol. The results obtained by these workers from a series of autoxidation experiments suggested that these chelates are not only effective hydroperoxide decomposers, but also efficient free-radical acceptors. Amongst these metal chelates, the one containing palladium was proved to be the most active inhibitor followed by the nickel chelate. This interesting observation was studied in more detail and Uri¹⁷⁴ reported that apart from the above-mentioned properties, these complexes act as very effective uv stabilisers.

Chien and Boss¹⁷⁵ have also investigated the inhibitory effect of these metal chelates, and have put forward some theories for the hydroperoxide decomposition by these metal complexes¹⁷⁶. The recent findings of Copping and Uri regarding the antioxidant behaviour of the nickel and other

heavy metal chelates of this type has been patented¹⁷⁷.

In the present work the antioxidant efficiency of bis (stilbene dithiolato) Ni (II), (NiSDT), and some of its para-substituted compounds in oleic acid and oleyl alcohol has been investigated. Two of these para-substituted complexes, viz. bis (di-p-isopropyl stilbene dithiolato) Ni(II), and bis (di-p-tert.butyl stilbene dithiolato) Ni(II), were new compounds and had to be synthesised from the more common starting materials.

CHAPTER 2

EXPERIMENTAL TECHNIQUE

2.1 APPARATUS.

2.1.1 Warburg Apparatus.

A conventional circular Warburg apparatus was used for the auto-oxidation reactions and related manometric studies up to 80°C (Plate 2.1). The apparatus consisted of a circular bath fitted with a heating coil and a mechanical stirrer. The heating unit was controlled by a contact thermometer and the actual temperature setting was accurately determined using a 50mm immersion "Jena glass" reference thermometer. The shaking motor was situated in the lower part of the apparatus, beneath the manometer support tray, and was controlled by an on/off switch, positioned on the right foot of the stand. The manometer support tray was internally geared to the shaking motor and its shaking speed, together with the amplitude of the shaking stroke, could be adjusted by means of the position of the connecting rubber belt.

The manometers used were of the standard double-capillary type (model 20-205) with a graduated range of 0-300mm, having a calibration of approximately 1.5 ml. These were employed in conjunction with calibrated Warburg reaction flasks (model 30416) of approximately 14 ml. capacity, containing an inner well for absorbants and a side arm, fitted with a vent valve, to permit flushing of the manometric system with gas.

The manometer fluid was Brodies Solution which was a mixture of sodium chloride, a wetting agent, and alcoholic thymol solution, stained dark blue with acilan black. A 10,000mm Brodie column corresponds to 760mm Hg. which gives very high sensitivity.

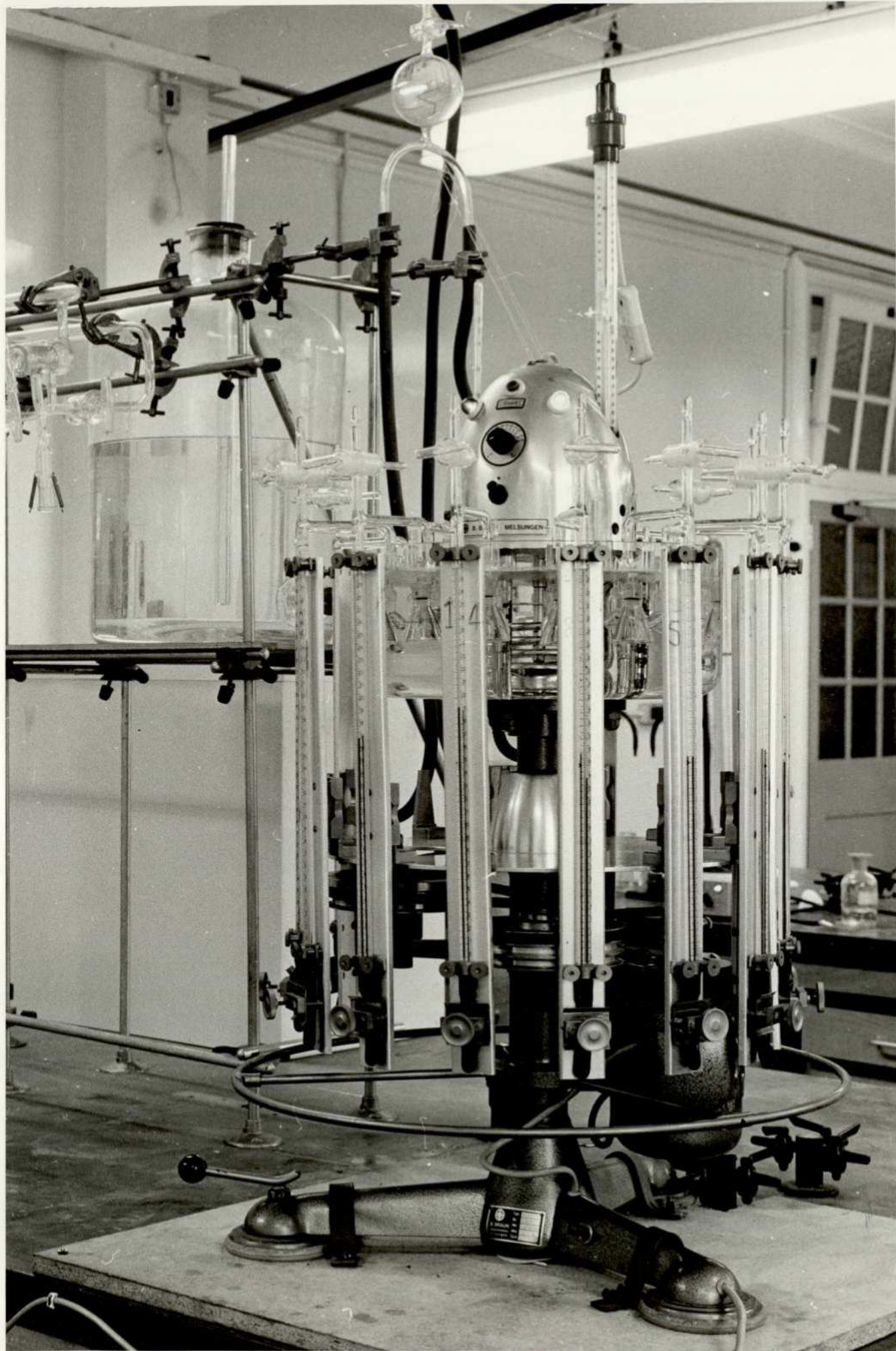


PLATE 2.1

WARBURG APPARATUS

2.1.1.1 Modifications.

Most of the experiments performed in this work took place at temperatures well above 60°C , which was the operating limit of the plexiglass perspex bath originally supplied and, therefore, the latter was replaced by a pyrex glass bath made to specifications by [REDACTED] (of Hemel Hempsted). Also the $0-50^{\circ}\text{C}$ contact and reference thermometers were replaced by the corresponding $0-100^{\circ}\text{C}$ thermometers.

The other important modification was the replacement of the normal manometer-to-flask joints with greaseless ones. This was found to be necessary since experiments of long duration at high temperatures were adversely affected by penetration of Apiezon T grease into the reaction vessels. The manometer cones had grooves cut into them to allow "Viton A" O-rings of the type EP101/80, I.D.=10.5mm, O.D.=13.5mm, thickness=1.5mm (obtained from James Walker & Co. Ltd.) to be used. The corresponding joints on the reaction flasks were also polished to remove all grinding marks, making them of "Clearfit" type (see Plate 2.2).

2.1.2 Automatic Oxygen Absorption Recording Apparatus.

This apparatus, the one most suitable for experiments carried out above 70°C , was a larger modified version of the type originally described by Sylvester¹⁷⁸, later modified by [REDACTED]¹⁷⁹ and ultimately by [REDACTED] and [REDACTED]¹⁸⁰ (Plate 2.3). It was constructed by the Mechanical Engineering Department's workshop under the supervision of [REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED] [REDACTED] to the specifications supplied by the Explosive Research and Development Establishment, [REDACTED].

The apparatus consisted of a stainless steel tank of 15 litres capacity, fitted with a Pyrotenax stainless steel sheathed mineral/insulated heating cable of $\frac{1}{8}$ " diameter (specification 125-HTR), adjusted by means of

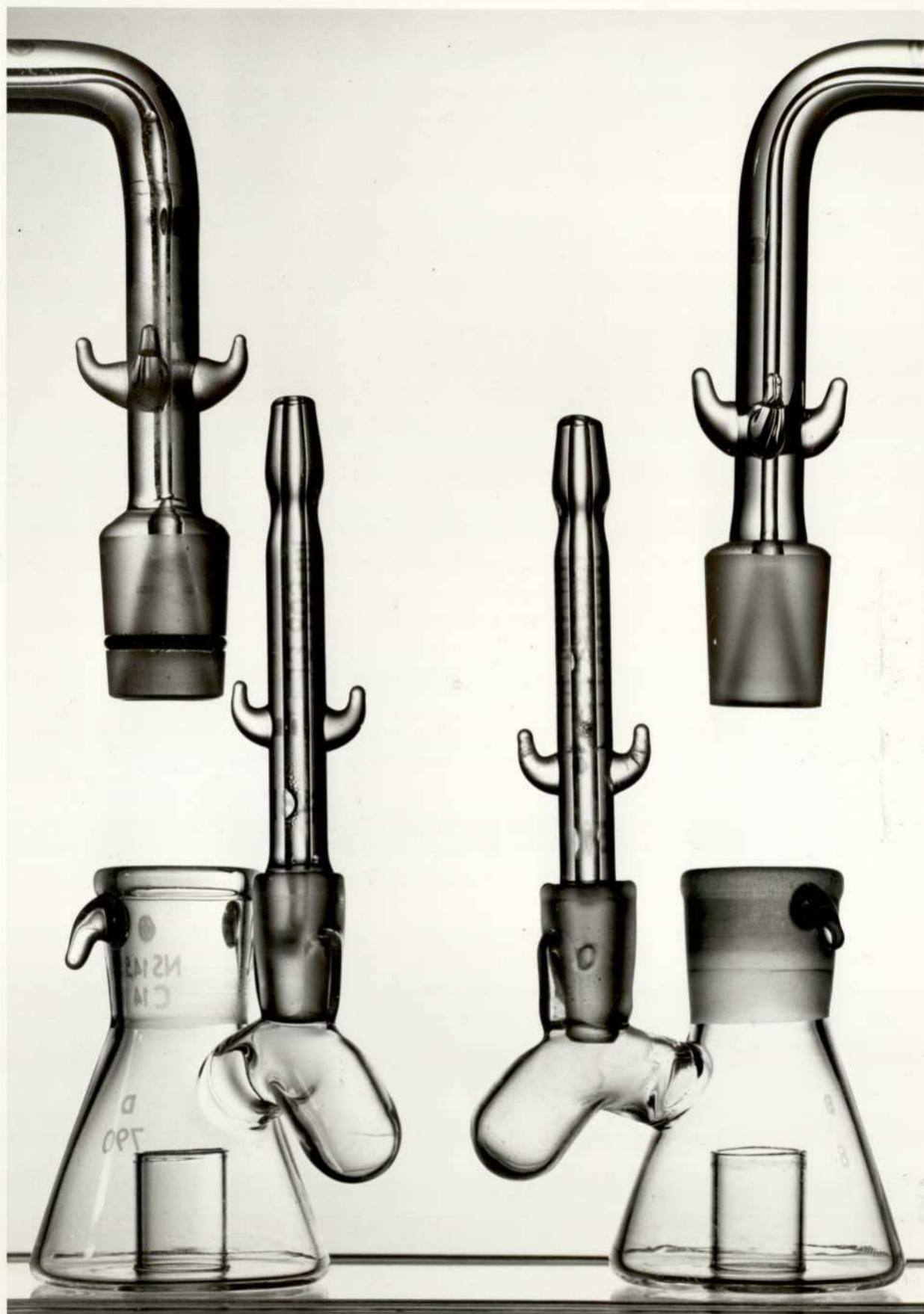


PLATE 2.2

GREASELESS AND CONVENTIONAL
MANOMETER JOINTS

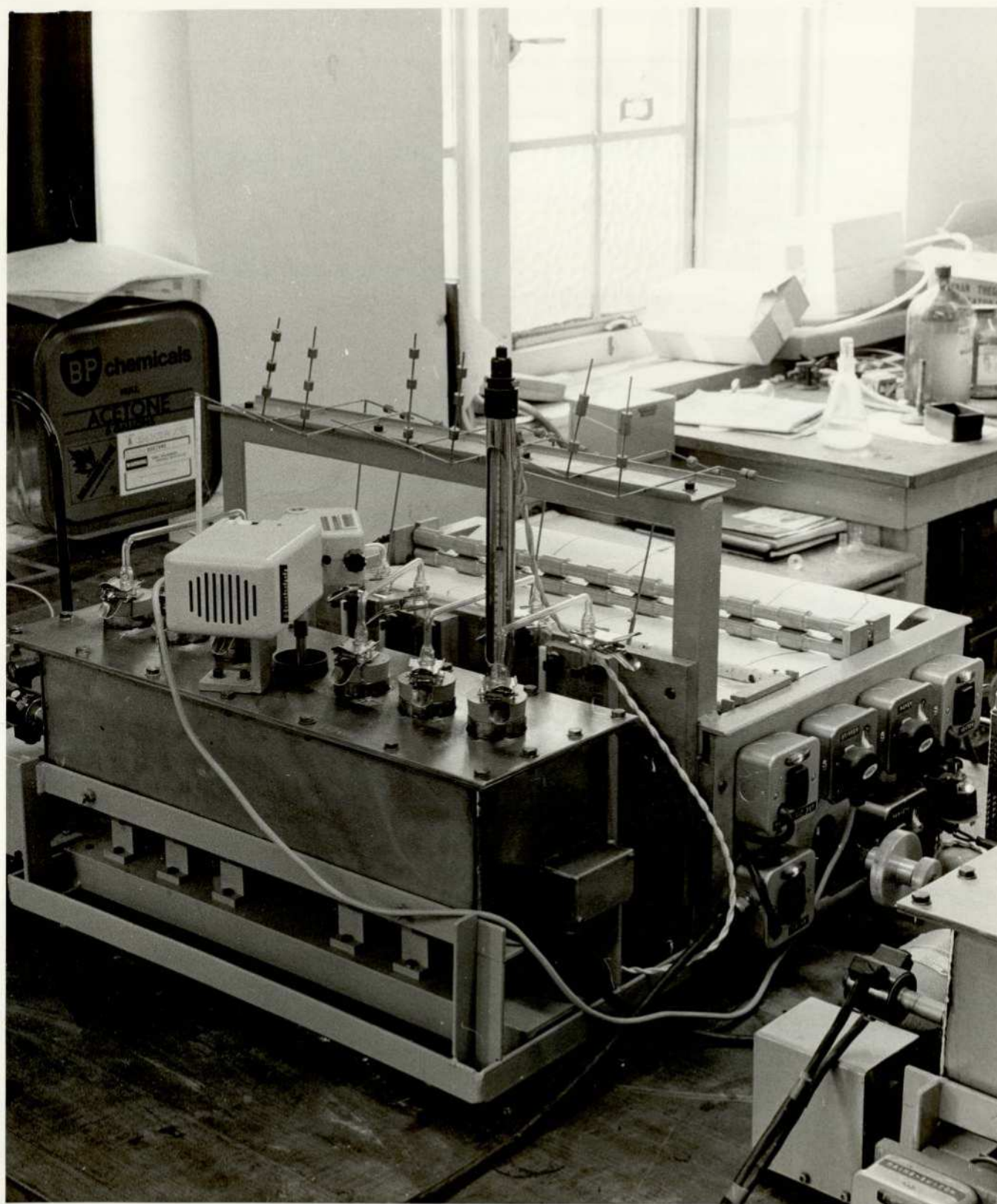


PLATE 2.3
AUTOMATIC OXYGEN ABSORPTION RECORDING APPARATUS

a variac transformer, and thermostatically controlled by a contact thermometer (0-200°C) in conjunction with a mercury relay switch. The heating fluid was high quality silicone oil (MS-550) and was stirred with a mechanical stirrer.

The reaction flasks, each of approximately 25 ml. capacity, usually contained 1 ml. of the sample and were stirred continuously throughout the experiment by means of glass-coated micro-magnetic followers and rotating magnets close to the underside of the tank. Provision was made for each flask to have a glass bucket of freshly baked (300°C for 2-3 hours) calcium oxide (AR grade) inserted in order to absorb any volatile products formed during the course of the reaction. Up to a maximum of six reaction flasks could be used per experiment, usually one being the thermal barometer, thus compensating for any atmospheric pressure changes. Each flask was connected to a U-tube mercury manometer, and changes in the mercury level in the open manometer arm were followed by means of a PTFE float connected to a balanced lever system, coupled to a recorder pen which produced a trace parallel to the direction of the chart movement the speed of which could be varied. The chart paper (obtained from Reed Charts Ltd.) was of the unperforated grade AN-470, and its speed was adjusted to 10.25 mm per hour. The dimensions of the apparatus (see section 2.3.4.2) gave an overall sensitivity of approximately 75 μ l of oxygen absorption per millimeter of the recorder pen deflection.

2.1.2.1 Modifications.

The only modification of the Automatic Oxygen Absorption Recording Apparatus was the substitution of greaseless ball and socket joints (obtained from J. Youngs Ltd.) incorporating "Viton A" O-rings for the original Quickfit joints. The Viton A rings had the same dimensions as those used with the Warburg flasks.

2.1.3 Shaking Reaction Incubator.

For the purposes of studying the kinetics of the inhibition of the autoxidation of the substrates by nickel chelates at high temperatures, a Gallenkamp shaking reaction incubator was used. This consisted of a 15 litre capacity stainless steel waterbath, thermostatically controlled by a direct reading Compensat (solid state) thermostat, which was fitted with a rack carriage. Shaking of the racks was carried out by a Citenco drive motor with a variable speed control.

The design of the thermostat element was such that the use of liquids other than water in the bath was not advisable and for experiments at temperatures higher than 70°C a 3mm layer of olive oil on the surface of the water was used to prevent evaporation. The olive oil used was of high purity and, in order to delay its oxidative degradation, Embanox 4 antioxidant (section 2.2.9) was added at a volume concentration of 2%. It was found that for most practical purposes this method was very effective up to 90°C. At 85°C the olive oil (650 ml.) was changed every two weeks.

2.1.4 Low Temperature Filtration Apparatus.

For the preparation and purification of the fatty acid substrates (sections 2.2.7 and 2.2.8) an improved design of a low temperature filtration apparatus was constructed by the University glassblower (Plates 2.4 and 2.5). The filter funnel contained a glass sinter disc (a range of porosities was available) and had a working capacity in excess of 500 ml. The outer section was a Dewar jacket to minimise unwanted temperature effects. When assembled, the space between the two sections could be filled with an acetone/dry ice mixture in order to obtain the desired temperature which was maintained by the periodic addition of small lumps of solid carbon dioxide. A Quickfit

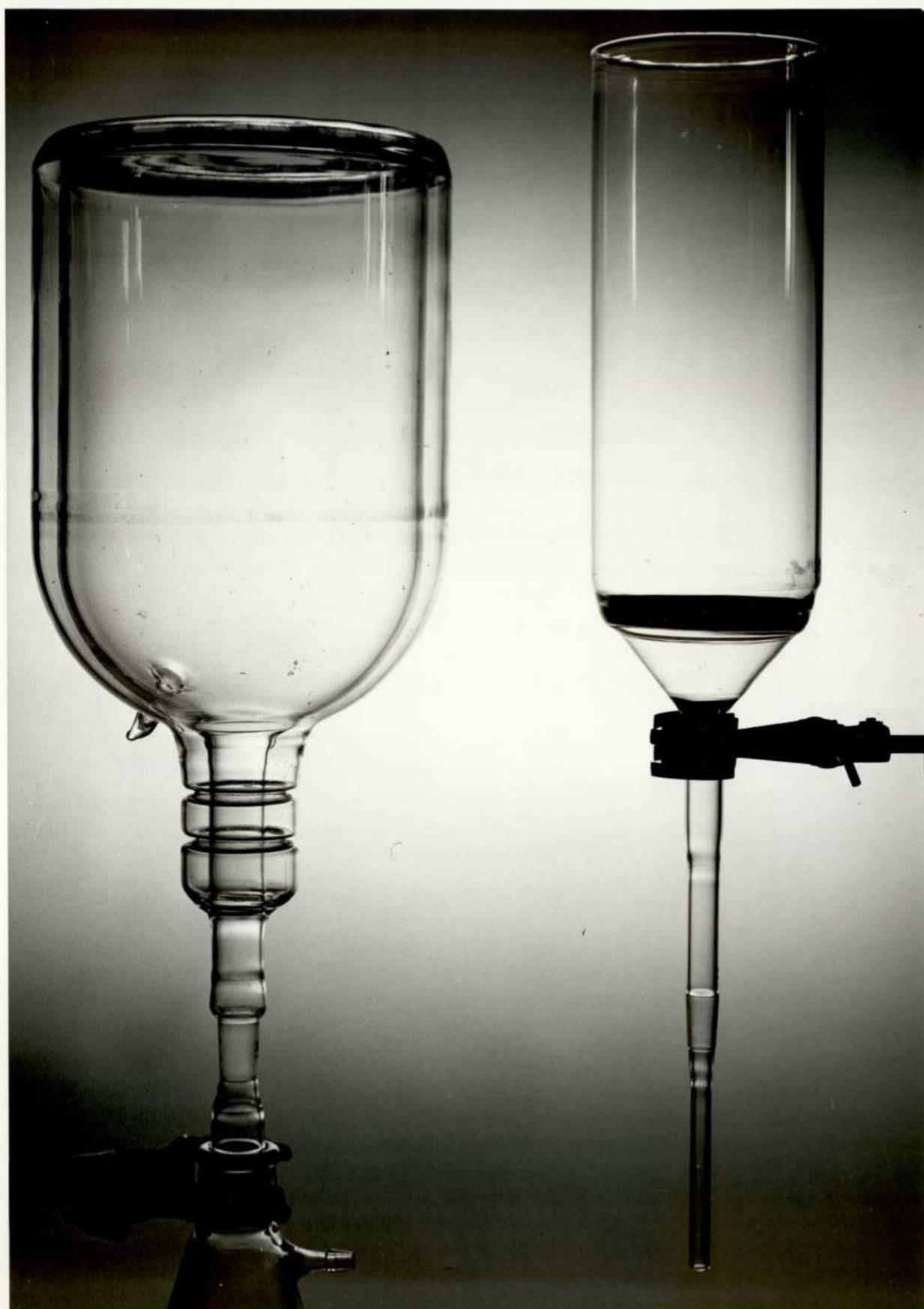


PLATE 2,4
LOW TEMPERATURE FILTRATION APPARATUS
FILTER FUNNEL AND JACKETING



PLATE 2.5
LOW TEMPERATURE FILTRATION APPARATUS
ASSEMBLED

joint at the extended lower section which was slightly greased (with silicone grease) ensured the prevention of any leakage of the jacketing liquid and helped with the easy removal of the filter funnel at lower temperatures.

2.1.5 Distillation Apparatus.

As it was not possible to remove all the trace impurities and hydroperoxides by low temperature filtration, it was found necessary to further purify the fatty substrates by vacuum distillation, with a slow flow of O_2 -free nitrogen prior to distillation, and for this purpose a distillation apparatus was designed (Plate 2.6). The important feature of this unit was the 20 cm. Vigreux column which was surrounded by an evacuated glass jacket, which allowed a higher grade of purity in the distillate to be obtained. Furthermore, the fractional distillation receiver head enabled the first 5% of the distillate to be discarded, thus ensuring maximum purity of the distillate.

2.2 REAGENTS.

2.2.1 Commercially Available Reagents.

Most of the common solvents for this work were obtained from the commercial suppliers in their purest grade available. Acetone and Chloroform, both AR grades, were obtained from Hopkin and Williams. Ethyl benzoate was purchased from Koch-Light laboratories who also supplied the Fe (III)-acetyl-acetate and elaidic acid. Commercial oleic acid (Priolene) together with commercial oleyl alcohol (A 11) were supplied by Prices Chemicals Ltd. (Bromborough, Cheshire) although it is believed that the oleyl alcohol (A 11) was originally manufactured by Henkel in Germany. Linoleic and linolenic acids, linoleyl alcohol, methyl linoleate, and methyl linolenate were

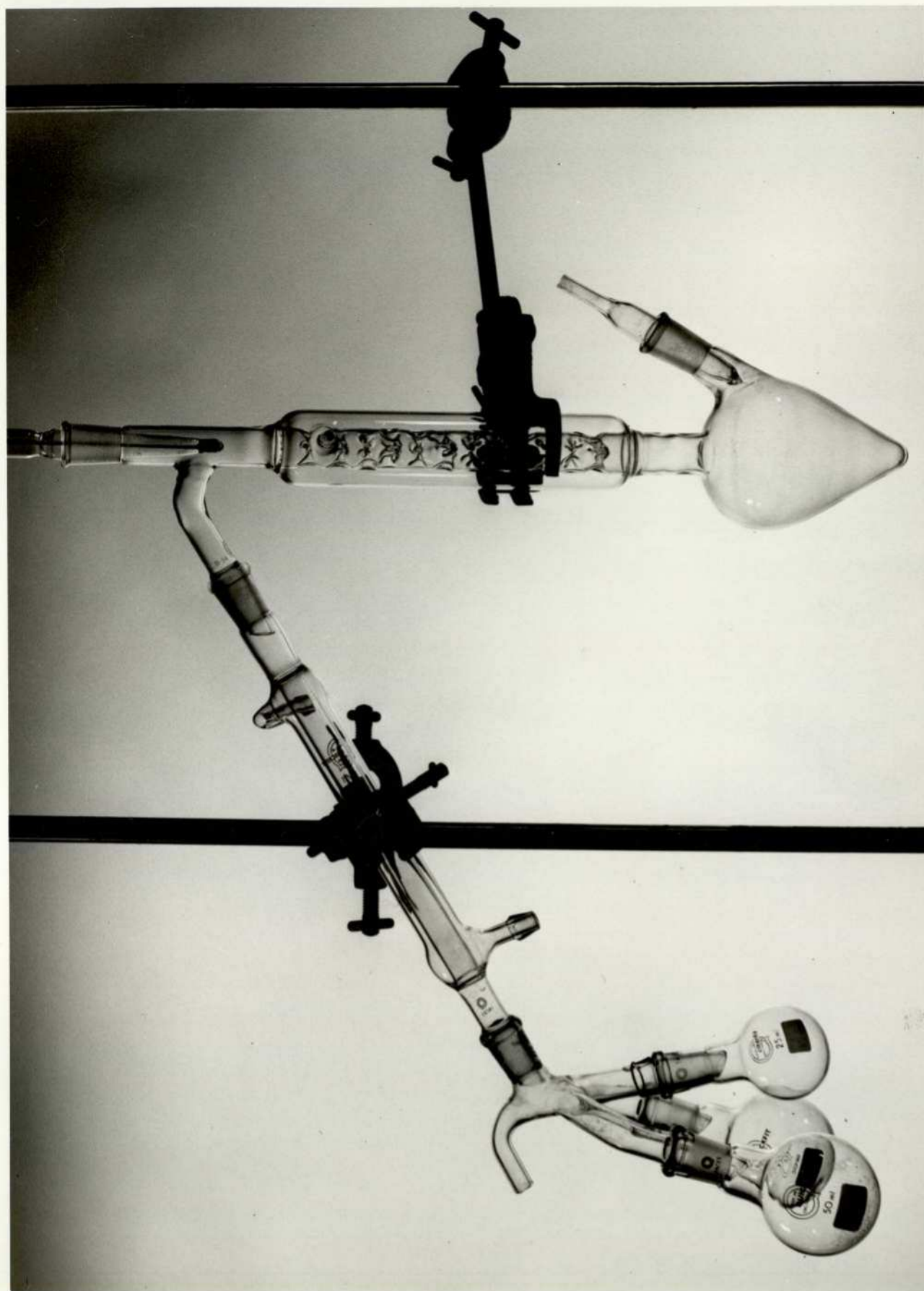


PLATE 2.6
DISTILLATION APPARATUS

obtained from The Lipid Preparation Laboratories of The Hormel Institute (Austin, Minnesota, U.S.A). These laboratories are now closed and no longer supply the fatty substrates.

2.2.2 Oxygen-free Nitrogen.

For the determination of peroxide concentration (section 2.4.2) and for some purification by distillation techniques (section 2.3.1), the use of oxygen-free nitrogen was required. For this purpose commercial O_2 -free nitrogen (99.9%) was further purified by the method of Heaton and Uri¹⁸¹. The gas was passed through three Friedrich gas-washing bottles (without joints) filled with a solution of sodium hydrosulphite (15%) plus sodium hydroxide (10%) containing 0.2% sodium anthraquinone sulphonate as indicator. The purified nitrogen was then bubbled through two further gas-washing bottles containing 10% and 0.1% potassium permanganate solutions respectively, to remove any traces of sulphur dioxide carried over from the previous bottles, and finally passed through distilled water. The dilute potassium permanganate solution acts as an indicator for any reducing impurities in the nitrogen gas.

In the case of peroxide determinations, an extra bottle containing the solvent mixture (acetic acid / chloroform) was used in order to saturate the purified gas with solvent vapour before it entered the sample bottles.

2.2.3 Carbonyl-free Methanol.

For the determination of the carbonyl contents of the samples the use of carbonyl-free methanol was required. This was obtained from AR grade methanol by the method of Lappin and Clark¹⁸².

Approximately 10 grams of 2,4-dinitrophenylhydrazine and a few drops of concentrated hydrochloric acid were added to 1000 ml. of AR-methanol and the resulting mixture was refluxed for 2-3 hours. The reflux apparatus

was then converted to a distillation unit, and the purified methanol was distilled through a 50 cm. Vigreux column, and redistilled until completely colourless. The methanol so obtained could be used up to several months after the purification.

2.2.4 Wijs's Iodine Value Reagent.

For the iodine value determinations (section 2.4.4) Wijs's reagent (iodine monochloride solution) was required. This was prepared by dissolving separately 7.9 grams of pure iodine trichloride and 8.7 grams of pure iodine in glacial acetic acid, by heating each solution separately on a water bath, taking care to prevent the absorption of moisture. The two solutions were then mixed together in a 1000 ml. volumetric flask, cooled and diluted with glacial acetic acid. This reagent (Wijs's solution) was stored in the dark, and since it deteriorated with time, a fresh solution was prepared for every determination. To ensure purity, only solutions having a freezing point above 15.2°C were used.

2.2.5 Alkaline Ethylene Glycol.

For the spectrophotometric determination of linoleic and linolenic acids by the method of Hilditch, Morton, and Riley¹⁸⁴ (section 2.4.5), an alkaline ethylene glycol solution was required. The ethylene glycol was first purified by fractional distillation under vacuum. 7.5 g. of AR grade potassium hydroxide (assaying at least 85% KOH) were dissolved in 100 ml. of the purified ethylene glycol. The solution was then heated to 190°C for two minutes, cooled and stored in a stoppered flask.

2.2.6 Aldehyde-free Ethanol.

This reagent was also required for the spectrophotometric

determination of linoleic and linolenic acids (section 2.4.5). 1000 ml. of 99.9% absolute alcohol was refluxed for one hour with 20 g. of zinc dust and 20 g. of potassium hydroxide, and was then distilled at atmospheric pressure through a 50 cm. Vigreux column and stored in a stoppered container.

2.2.7 Oleic Acid, cis-Octadec-9-enoic Acid.

Crude oleic acid was obtained from Prices Chemicals Ltd. (section 2.2.1) under the trade name of Priolene. Several purity grades of these were commercially available of which Priolenes 64, 95, and 96 were analysed. Priolene 95 had a relatively lower concentration of other polyunsaturated fatty acids present and was, therefore, selected for use throughout this work. Pure oleic acid was prepared from Priolene 95 by the low temperature crystallisation techniques. Originally the method of Gupta and Hilditch¹⁸⁵ was utilised. A 10% solution of Priolene 95 in AR-grade acetone was first cooled to -55°C and filtered. The filtrate, which contained mainly polyunsaturated fatty acids, was discarded. The solid residue was allowed to melt and after the addition of sufficient acetone to restore the concentration of the fatty acid to 10% the solution was cooled and filtered at -50°C , and the filtrate was again discarded. The acetone was then removed from the precipitate on a rotary film evaporator, and the substrate dissolved in diethyl ether at a concentration of 15-20%. This solution was then cooled to -30°C and filtered. The precipitate containing mainly saturated fatty acids was discarded. The excess ether was removed from the filtrate, and the oleic acid thus obtained was distilled at reduced pressures under a slow bleed of nitrogen gas.

Analysis of oleic acid, purified by this method, indicated the presence of small amounts of linoleic and linolenic acids, whose presence was undesirable, since they are relatively sensitive to oxidation. In order

to achieve a higher standard of purity, the purification method used by Swern, Knight, and Findley¹⁸⁶ was tried. In this procedure a 10% solution of Priolene 95 in AR-grade acetone was slowly cooled, in a Dewar flask containing a mixture of acetone and dry ice, to -20°C with continuous stirring. The mixture was maintained at this temperature for one hour with occasional stirring, and then filtered through the low temperature filter funnel which had been pre-cooled to -20°C . The precipitate containing mainly saturated fatty acids was discarded. The filtrate was diluted with acetone to its original volume and cooled to -50°C with stirring. After being maintained at this temperature for about one hour, the mixture was filtered through the filter funnel cooled to -55°C . The filtrate containing mainly polyunsaturated fatty acids was discarded, and the white crystalline cake of oleic acid was sucked and pressed as dry as possible, and washed on the filter funnel with about 500 ml. of acetone cooled to -70°C . It was then allowed to melt at room temperature and the occluded acetone removed on a rotary film evaporator.

The purified oleic acid was distilled under vacuum (3 mmHg) with a very slow flow of O_2 -free nitrogen, and the fraction boiling in the range $174\text{--}186^{\circ}\text{C}$ was collected as a colourless liquid. Analysis showed a peroxide value of zero (see section 3.2) and an extremely low carbonyl value, which could be attributed to a trace of residual acetone and higher ketones. The result of the analysis for linoleic and linolenic acids is given in section 3.2.1.

2.2.8 Oleyl Alcohol.

Commercial oleyl alcohol (A 11) was supplied by Prices Chemicals Ltd. (section 2.2.1). Its purification was carried out by the method of Swern Knight, and Findley¹⁸⁶, which is similar to the method described for the purification of oleic acid. The temperatures for the two crystallisation

stages were -10° and -45°C . After the removal of the excess acetone from the final precipitate on the rotary film evaporator, the purified oleyl alcohol was distilled under vacuum with a slow current of nitrogen bubbling through the solution to prevent any oxidation. The fraction boiling in the range $145-158^{\circ}\text{C}$ (1 mmHg) was collected as a colourless liquid, having zero peroxide and negligible carbonyl values. The result of analysis for other polyunsaturated fatty alcohols is given in section 3.2.1.

2.2.9 Antioxidants.

With the exception of the nickel chelate antioxidants, which were prepared in the laboratory (section 2.2.10), a list of all the other antioxidants, together with their commercial names and chemical structures is given in Table 2.1.

The Topanol antioxidants were obtained from ICI, the Embanox antioxidants were supplied by May and Baker, and Dilaurylthiodipropionate DLTP, was obtained from Robinson Brothers (Ryders Green, West Bournemouth).

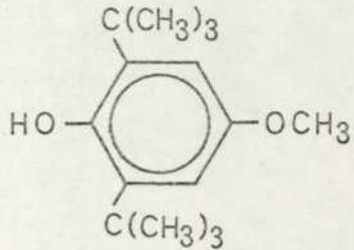
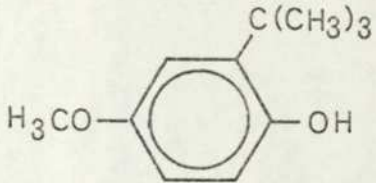
2.2.10 Nickel Chelate Antioxidants.

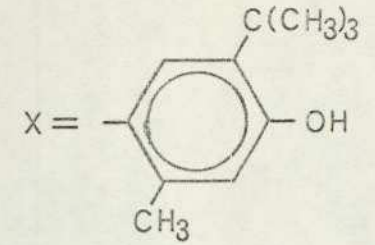
The bis (stilbene dithiolato) nickel (II) and its para-substituted compounds, which were used as antioxidants, were prepared in the laboratory by the method of Schrauzer and Mayweg¹⁵⁸. In the cases where the appropriate benzoin needed for the preparation of a particular substituted compound was not commercially available, this had to be prepared first.

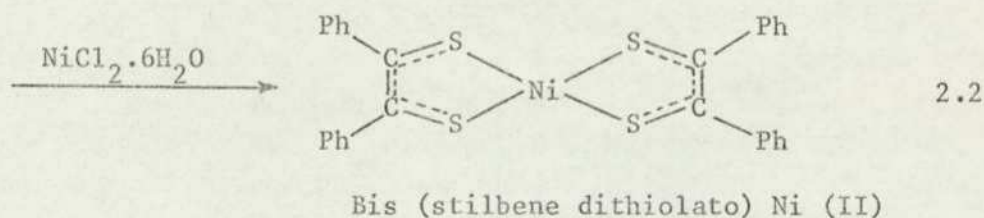
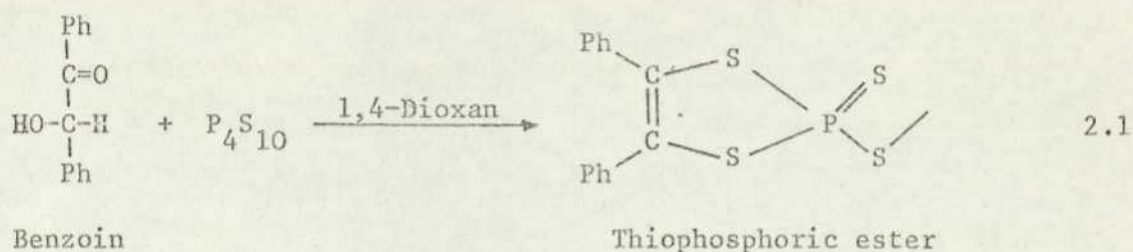
2.2.10.1 Bis (stilbene dithiolato) Nickel (II), NiSDT.

The preparation consisted of two stages which are shown by the equations 2.1 and 2.2:

TABLE 2.1

ANTIOXIDANT	COMMERCIAL NAME	FORMULA
1,1,3-Tris (2-methyl-5-tert.butyl-4-hydroxy phenyl) butane.	Topanol CA	$\text{CHX}_2-\text{CH}_2-\text{CHX}-\text{CH}_3$
3,5-Di(tert.butyl)-4-hydroxyanisole.	Topanol 354	
3-tert. Butyl-4-hydroxyanisole.	Embanox BHA	
20 per cent Embanox. BHA with 20 per cent citric acid in propylene glycol.	Embanox 4	
Dilaurylthiodipropionate.	D.L.T.D.P.	$(\text{C}_{12}\text{H}_{25}\text{OCOCH}_2\text{CH}_2)_2\text{S}$

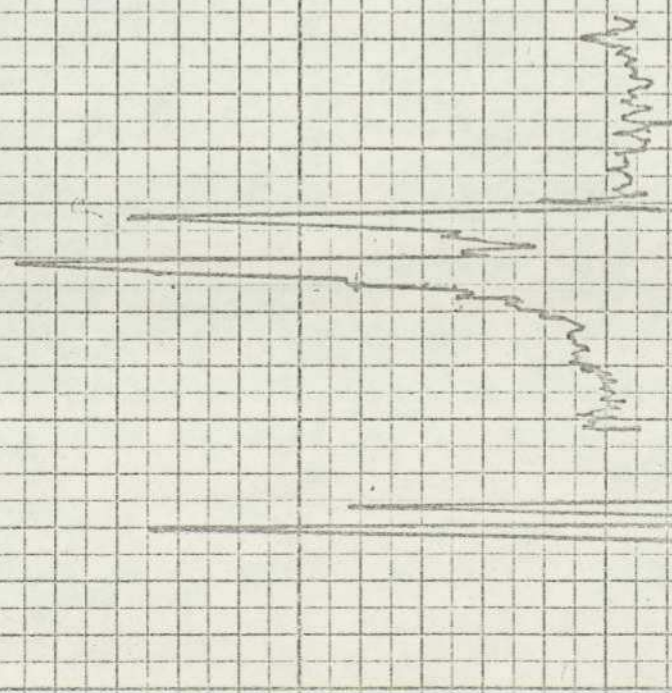


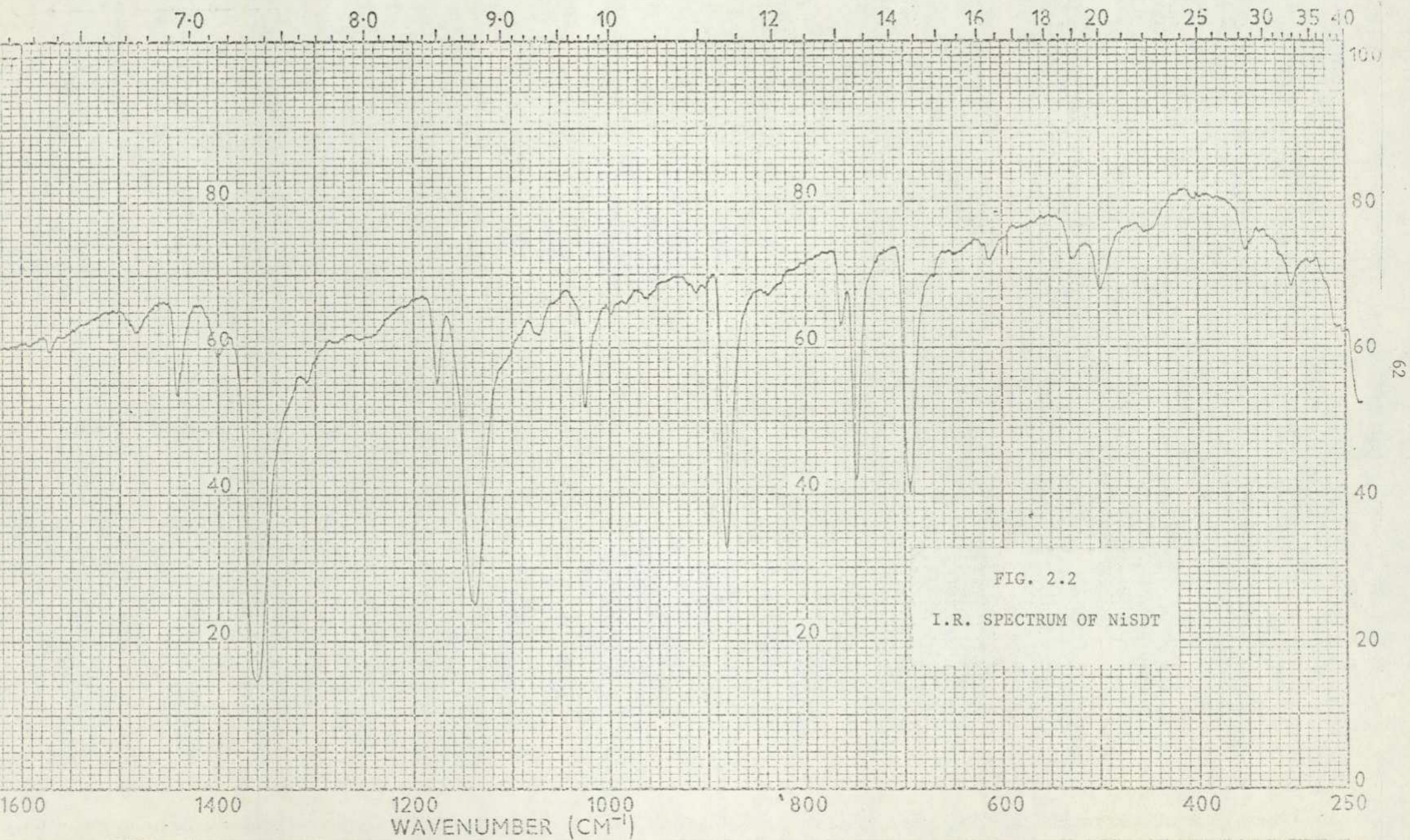


Equal amounts (35 g.) of benzoin and phosphorous pentasulphide together with 250 ml. of 1,4-dioxan as solvent were placed in a 500 ml. round-bottomed flask fitted with a mechanical stirrer. (This ratio of the reactants which corresponded to almost 100% excess of benzoin has been found¹⁷³ to be advantageous). The flask and its contents were heated on an isomantle, and the mixture was refluxed for three hours. During this period a current of nitrogen was passed through the vessel to assist in removing the hydrogen sulphide which was formed during the course of the reaction. At the end of this period (2 hours) the resulting solution was allowed to cool, and filtered through a number 4 porosity glass-sinter filter funnel, to remove the unreacted starting materials. The filtrate was replaced in the reaction flask and a solution of 17.5 g. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 ml. of water was added, with continuous stirring. The mixture was then heated on a steam bath for 2-2½ hours. At the end of the reaction time, the mixture was chilled in an ice bath and the product filtered off on a number 4 porosity glass-sinter filter funnel.

For the purification of the crude products, a hot-cold recrystallisation from chlorobenzene was preferred to the soxhlet extraction with

FIG. 2.1
N.M.R. SPECTRUM OF NiSDT





toluene, since in the latter method, a large proportion of the product is lost in the toluene solvent. The purified dark green crystals of NiSDT were dried for 3 hours at 70°C in a vacuum oven. The final yield was 22.3 g. of pure NiSDT (48% ex benzoin) which melted, with decomposition, at 292.6°C, (literature value = 292°C). The identity of the product was confirmed by a high resolution nmr spectrum obtained by the Physico-Chemical Measurements Unit (PCMU) at Harwell using deuterated chloroform as the solvent (Fig. 2.1) and by the ir spectrum (Fig. 2.2).

The nmr spectrum clearly showed the presence of a phenyl group with the splitting of the ring protons caused by the electron deficient nucleus. The peaks at 2.6τ were due to the protons at the ortho- and meta-positions thus showing two shoulders (c.f. expanded spectrum) while the peak at 2.68τ was assigned to the protons in the para-positions. The ir spectrum showed three characteristic absorptions (ω_1 , ω_2 , & ω_3) in the 3000-600 cm^{-1} range. These which were also observed in all the para-substituted complexes of this type, were assigned as follows: $\omega_1=1360 \text{ cm}^{-1}$ due to perturbed C=C; $\omega_2=1138 \text{ cm}^{-1}$ due to perturbed C=S; $\omega_3=880$ due to stretching vibration of the $\text{R}-\text{C} \begin{smallmatrix} \nearrow \text{S} \\ \searrow \text{C} \end{smallmatrix}$ system. The position of the characteristic absorption bands of the electronic spectrum and their extinction coefficients were obtained with the Hitachi Perkin-Elmer EPS-3T recording spectrophotometer and are given in the results section (section 3.5.3).

2.2.10.2 Bis (di-p-isopropyl stilbene dithiolato) Ni (II), DIP-NiSDT.

The di-p-isopropyl benzoin necessary for the preparation of this metal complex was not commercially available and, therefore, was prepared in the laboratory by the following procedure, derived from a general method for the synthesis of benzoin first used by Ide and Buck¹⁸⁷. A solution of 200 g. of cuminic aldehyde in 700 ml. of 95% ethanol was mixed with a solution

of 50 g. of AR-grade potassium cyanide in 100 ml. of water and placed in a 2000 ml. round-bottomed flask. The mixture was heated on an isomantle and refluxed for three hours. It was then allowed to cool and stand overnight. Yellow crystals of the di-p-isopropyl benzoin were filtered off and washed twice with cold ethanol. A hot-cold recrystallisation from ethanol gave 110 g. of faintly yellow needle-like crystals of di-p-isopropyl benzoin. M. Pt. = 166.5°C (Yield = 55% ex cuminic aldehyde).

The preparation of DIP-NiSDT was effected from the benzoin in much the same way as for NiSDT itself. 108 g. of di-p-isopropyl benzoin with 108 g. of phosphorous pentasulphide dissolved in 500 ml. of 1,4-dioxan were refluxed for $2\frac{1}{2}$ hours, and the cooled solution was filtered. 50 g. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 200 ml. of water was added to the filtrate and the mixture was heated on a steam bath for 3 hours. The crude crystals of DIP-NiSDT, obtained on filtration, were purified from 1,2-dichlorobenzene and dried in a vacuum oven at 70°C for 3 hours. The green crystals of bis (di-p-isopropyl stilbene dithiolato) nickel (II) (34 g.) melted, with decomposition, at 294°C . The structure of this compound was confirmed by ir and nmr analysis and the interpretation of these spectra is described in section 3.

2.2.10.3 Bis (di-p-tert.butyl stilbene dithiolato) Ni (II), DTB-NiSDT.

For the preparation of this metal chelate di-p-tert.butyl benzoin was required. The synthesis of the latter had never been published and, therefore, it was assumed to be a new compound. The p-tert.butyl benzaldehyde intermediate was prepared from p-tert.butyltoluene. The whole synthesis consisted of the five following stages (see also section 3.

(a) p-tert.Butylbenzyl bromide. This was prepared by Verley's method¹⁸⁸.

75 g. of p-tert.butyltoluene were placed in a 500 ml. 3-necked round-bottomed flask and heated to 115°C on an isomantle. 75 g. of bromine were placed in a separating funnel and were added to the toluene drop by drop from the side neck. The solution was stirred continuously with a mechanical stirrer, and the temperature of the solution was maintained at 115°C. The bromination takes place exclusively at the methyl group of the toluene and not at the tert.butyl group as shown by the fact that it is impossible to carry out the same reaction with mono- or di-tert.butylbenzenes¹⁸⁸. The reaction also yielded hydrogen bromide which was absorbed by passage through a dilute solution of potassium hydroxide.

The crude light brown p-tert.butylbenzyl bromide so obtained was purified by fractional distillation under vacuum (0.2 mmHg), and the fraction boiling in the range 64-70°C was collected as 64 g. of colourless liquid with a pungent odour. The nmr and ir spectra analyses confirmed the sample as being p-tert.butylbenzyl bromide. (Found C=58%, H=6.4%, Br= 35.6%; calc. C=58.2%, H=6.6%, Br=35.2%).

(b) p-tert.Butylbenzaldehyde. This was prepared according to the method of Baker, Davis, and Heming¹⁸⁹, by the controlled oxidation of p-tert.butylbenzyl bromide with an equimolecular proportion of hexamethylenetetramine in 60% ethanol.

60 g. of p-tert.butylbenzyl bromide were placed in a 2000 ml. round-bottomed flask and a solution of 38 g. of hexamethylenetetramine in 900 ml. of 60% ethanol was added to it. The mixture was refluxed for 3½ hours with a current of carbon dioxide gas being passed through the solution all the time. After the removal of the ethanol on the rotary film evaporator, the mixture was steam distilled (using a current of oxygen-free nitrogen to prevent further oxidation) and 4000 ml. of the steam distillate were

collected. The aldehyde was extracted with ether and dried. After the evaporation of ether, the aldehyde was first purified through its bisulphite derivative and then by fractional distillation under vacuum, with a slow current of nitrogen gas. The fraction boiling in the range $62-76^{\circ}\text{C}$ was collected (22 g.) as a colourless liquid with a bitter almond odour. The nmr and ir spectra analyses confirmed the compound to be p-tert.butylbenzaldehyde. (Found C=81.3%, H=8.5%; calc. C=81.4%, H=8.7%).

(c) Di-p-tert.butyl benzoin. The benzoin condensation was carried out according to the method described by Ide and Buck¹⁸⁷. 20 g. of p-tert.-butylbenzaldehyde mixed with 130 ml. of 95% ethanol were placed in a round-bottomed flask containing 10 g. of potassium cyanide dissolved in 50 ml. of water. The mixture was refluxed for 3 hours and was then allowed to stand. On cooling a pale yellow precipitate was obtained which was filtered and washed with cold water.

The purification was carried out by recrystallisation from ethanol, and 11 g. of faintly yellow needle-like crystals were collected. M. Pt.= 172.6°C . (Yield = 62% ex p-tert.butylbenzaldehyde). The structure of di-p-tert.butyl benzoin was confirmed by nmr and ir analyses and the interpretation of these spectra is described in section 3.

(d) Bis (di-p-tert.butyl stilbene dithiolato) Ni (II). The preparation was carried out in a similar way to the preparation of NiSDT itself, as described by Schrauzer and Mayweg¹⁵⁸. 10 g. of di-p-tert.butyl benzoin together with 10 g. of phosphorous pentasulphide were dissolved in 80 ml. of 1,4-dioxan in a round-bottomed flask and refluxed for 3 hours. At the end of the reaction period the solution was cooled and filtered to remove any impurities. Then 6 g. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 20 ml. of water were added to the filtrate and the reaction mixture was heated on a steam bath for $2\frac{1}{2}$ hours. During the

reaction the mixture was stirred continuously with a mechanical stirrer. The dark green crystals of the complex which were formed were then filtered from the cooled solution. The purification was effected by dissolving the crude crystals in a solution of hot chlorobenzene and reprecipitating the pure crystals by the addition of excess cold methanol to the mixture. The green crystals of bis (di-p-tert.butyl stilbene dithiolato) nickel (II) (5 g.) were filtered through a number 4 porosity glass sinter filter funnel and dried in a vacuum oven at 70°C for 3 hours. The compound melted, with decomposition, at 328.5°C. The structure was confirmed from the high resolution nmr and the ir spectra. Interpretation of these spectra is described fully in section 3.

2.2.10.4 Bis (di-p-chlorostilbene dithiolato) Ni (II), Cl-NiSDT.

The synthesis of this nickel chelate required the use of the corresponding di-p-chlorobenzoin which was not commercially available, and was, therefore, prepared in the laboratory by the method of Ide and Buck¹⁸⁷, for general syntheses of benzoin.

In a 1000 ml. round-bottomed flask 30 g. of p-chlorobenzaldehyde dissolved in 300 ml. of methanol was mixed with a solution of 20 g. of potassium cyanide in 50 ml. of water and the mixture was refluxed for 3½ hours. Methanol was used in place of ethanol since the p-chlorobenzoin was reported to be excessively soluble in ethanol and its recovery from the latter solvent would have been difficult. The di-p-chlorobenzoin (9 g.) was obtained from the reaction mixture by dilution and refrigeration, in the form of an orange paste. All attempts to purify the latter from several different solvents failed to produce any pure crystals and, therefore, the product was used as the paste in the preparation of the corresponding nickel chelate.

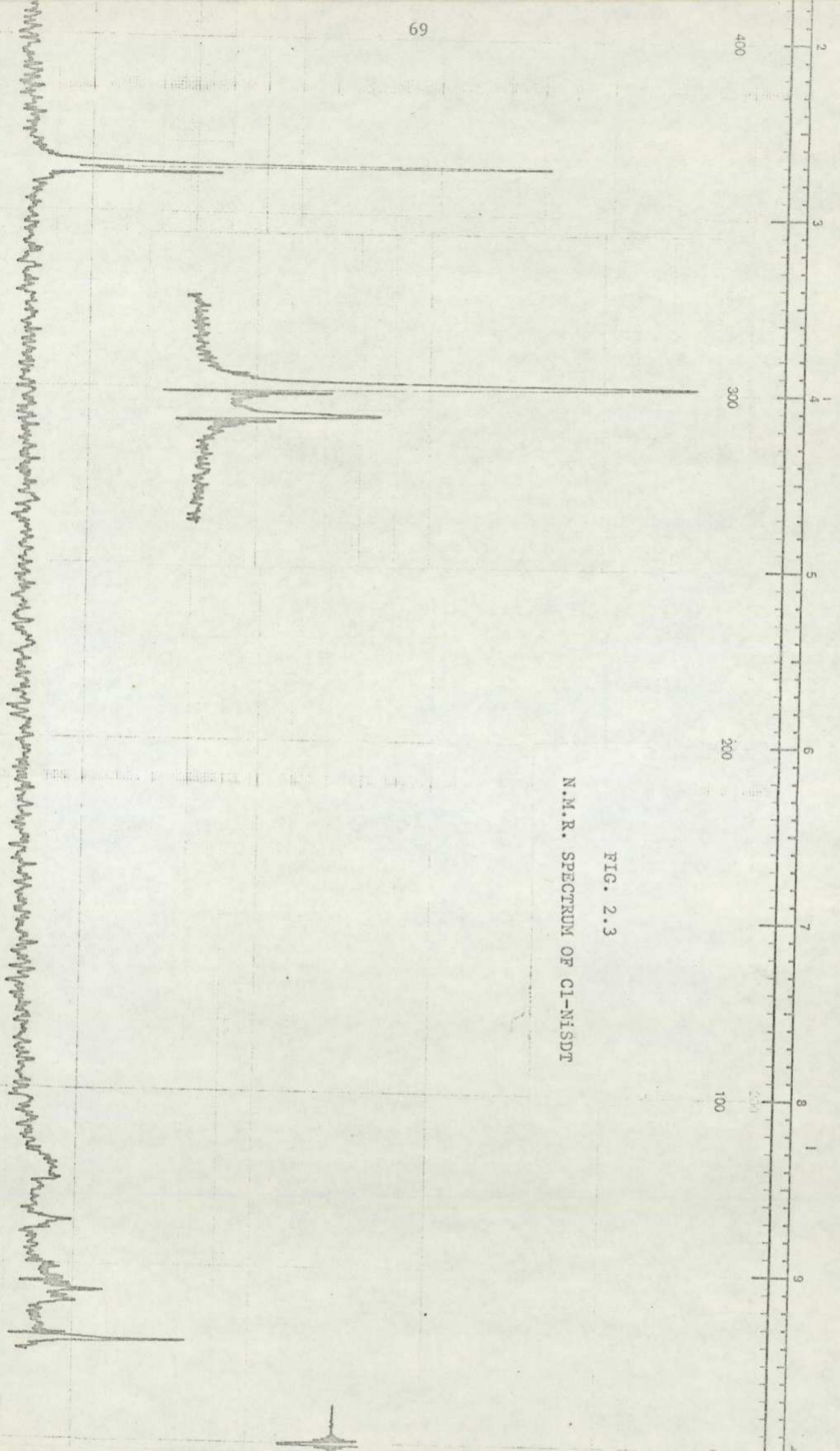
The preparation of the chloro-substituted nickel chelate was

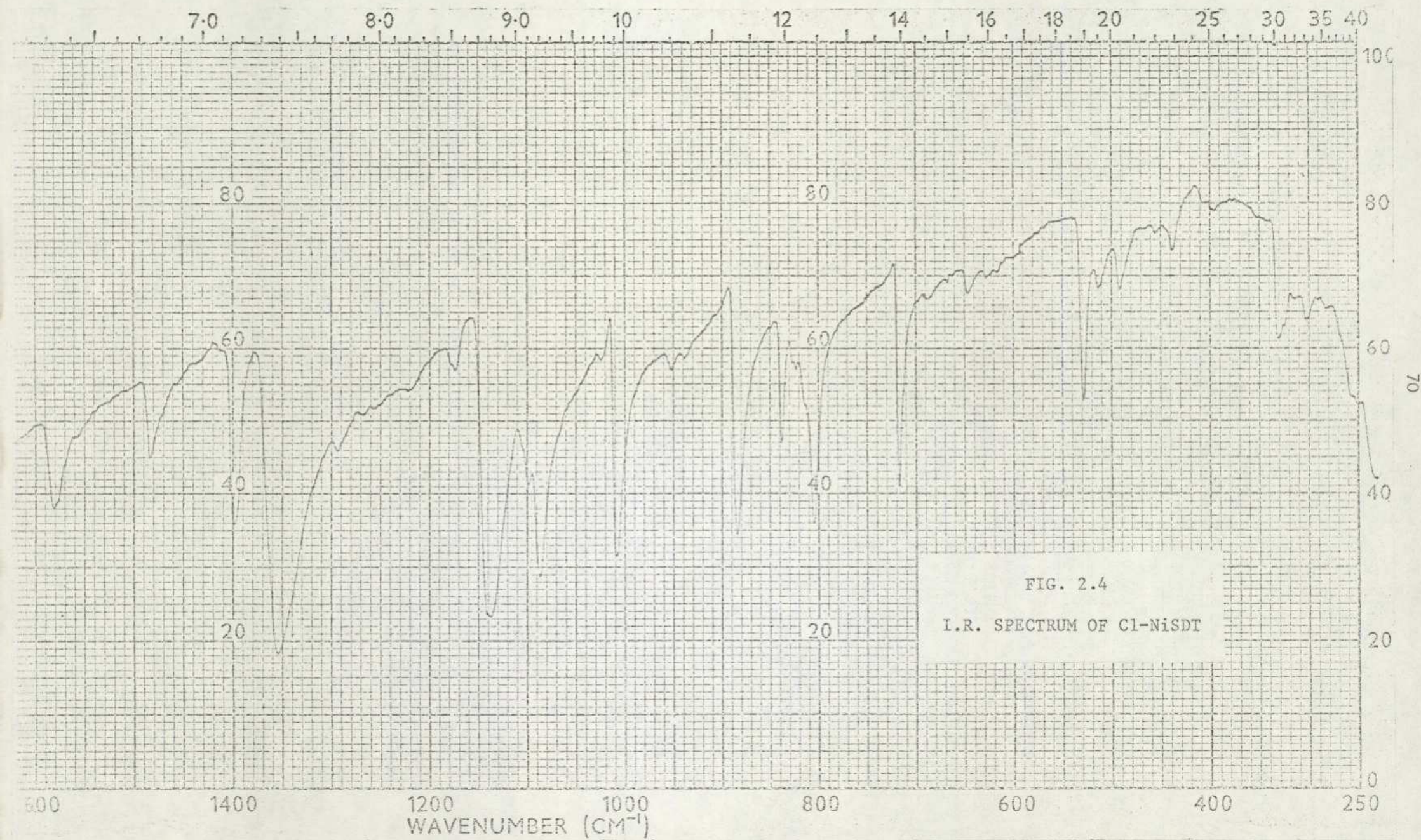
carried out in a similar way to that for NiSDT as described by Schrauzer and Mayweg¹⁵⁸. 8 g. of the p-chlorobenzoin (prepared previously) together with 8 g. of phosphorous pentasulphide were dissolved in 80 ml. of 1,4-dioxan and refluxed for 2 hours. The solution was allowed to cool to room temperature and filtered. 5 g. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 40 ml. of water was added to the filtrate and the mixture was heated on a steam bath for $2\frac{1}{2}$ hours. After cooling, the impure crystals of the product were filtered through a number 4 porosity glass sinter filter funnel.

The purification was effected by dissolving the product in chlorobenzene and reprecipitating the crystals by the addition of excess chilled methanol. The precipitate was filtered and dried in a vacuum oven at 70°C for 3 hours. The dark green crystals (3 g.) of Cl-NiSDT melted, with decomposition, at 335°C (Schrauzer and Mayweg value = 335°C). The high resolution nmr (Fig. 2.3) clearly indicated the presence of the aromatic peak at 2.72τ . It appeared that, since the electron donating power of both carbon and chlorine atoms were the same, an "accidental magnetic equivalence" had occurred whereby no splitting of the peak of the aromatic ring was observed (c.f. expanded peak). The small peak at 2.78τ was due to the chloroform impurity in deuterated chloroform which was used as the solvent. The ir spectrum (Fig. 2.4) showed the characteristic absorption bands (section 2.2.10.1) which occurred at $\omega_1=1355\text{ cm}^{-1}$, $\omega_2=1139\text{ cm}^{-1}$, & $\omega_3=885\text{ cm}^{-1}$. The position of the characteristic absorption bands of the electronic spectrum and their extinction coefficients are given in the result section (section 3.5.3).

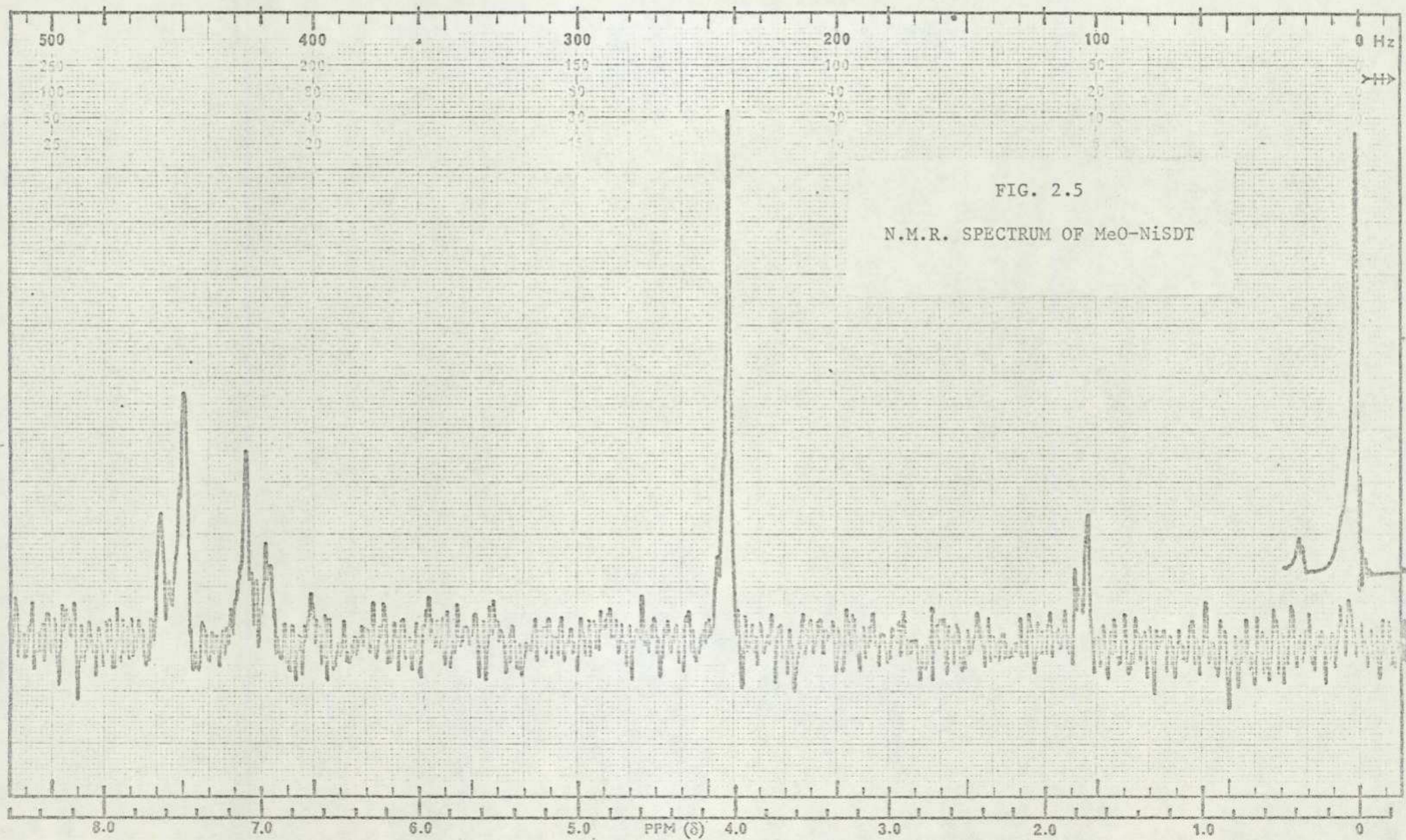
2.2.10.5 Bis (di-p-methoxy stilbene dithiolato) Ni (II), MeO-NiSDT.

The starting material, anisoïn (4,4'-dimethoxy benzoin), for the synthesis of this metal chelate was commercially available. The procedure for this preparation was very similar to that for NiSDT as described by Schrauzer









and Mayweg¹⁵⁸. 17.5 g. of green-black crystals (41% yield ex benzoin) were obtained which melted, with decomposition at 330°C (Schrauzer and Mayweg value=329°C). The structure of the compound was confirmed from its nmr and ir spectra. The nmr (Fig. 2.5) showed the aromatic peak being split with the signal due to the ortho-hydrogens being moved upfield by the oxygen atom. The peak at 6.18 τ was that of the protons in the methyl group which had been moved downfield due to the deshielding effect of the electronegative oxygen atom. In the ir spectrum (Fig 2.6) the positions of the three characteristic absorption bands (section 2.2.10.1) were as follows: $\omega_1=1343\text{ cm}^{-1}$, $\omega_2=1140\text{ cm}^{-1}$ and $\omega_3=884\text{ cm}^{-1}$. The position of the characteristic absorption bands of the electronic spectrum and their extinction coefficients are given in the result section (section 3.5.3).

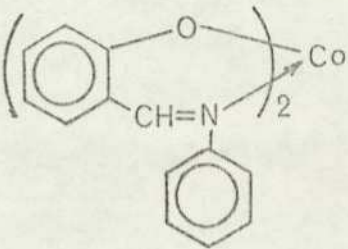
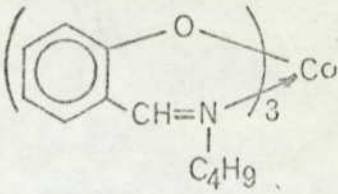
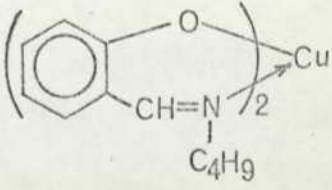
2.2.11 N-(n-alkyl) Salicylaldiamine Chelates.

The cobalt and copper chelates of n-alkyl salicylaldiamine, which were used as catalysts/inhibitors in this work, were prepared at ERDE. Tris-(n-butyl salicylaldiamino) Co (III) was prepared by the method of Nishikawa et al¹⁹⁰ which was based on the interaction of the amine, salicylaldehyde, and cobalt acetate. For the preparation of bis-(phenyl salicylaldiamino) Co (II) and bis-(n-butyl salicylaldiamino) Cu (II) the procedure described by Sacconi et al¹⁹¹ was used which involved the prior preparation of the salicylaldehyde metal complex. A full list of all the metal catalysts used in this work is given in Table 2.2.

2.2.12 Preparation of Gas-Liquid Chromatography Column Packing.

The packing of this column was selected for the fatty substrates according to the specifications given in the Perkin-Elmer Gas Chromatography Supplies hand book. About 0.5 g. of Apiezon L was dissolved in 25 ml. of hexane, and 12 g. of Chromosorb W-AWDMCS (80-100 mesh) was added to the

TABLE 2.2

METAL	LIGAND	FORMULA
Co (II)	Bis (phenyl salicylaldiamino)	
Co (III)	Tris (n-butyl salicylaldiamino)	
Fe (III)	Acetylacetonate	$(\text{CH}_3\text{COCHCOCH}_3)_3 \text{Fe}$
Cu (II)	Bis (n-butyl salicylaldiamino)	
Cu (II)	Acetylacetonate	$(\text{CH}_3\text{COCHCOCH}_3)_2 \text{Cu}$

solution and mixed thoroughly. The hexane solvent was then removed on a rotary film evaporator. The column, made of stainless steel, 3 meters long and 0.5 cm. in diameter was packed in the usual way.

2.3 GENERAL PROCEDURES.

2.3.1 Purification of Substrates.

For all experiments the absence of peroxides and carbonyls in the substrates was checked beforehand by the Heaton and Uri method¹⁸¹ (section 2.4.2) for the peroxide determinations and the Lappin and Clark method¹⁸² (section 2.4.3) for carbonyls. Due to the polarity of oleic acid and oleyl alcohol the removal of hydroperoxides by column Chromatography with Brockman grade 1 alumina was not possible. However, these could be removed by repeated distillations under reduced pressure with a slow current of nitrogen.

2.3.2 Cleaning of the Glassware.

Owing to the sensitivity of the experiments the cleaning of the glassware, especially the Warburg and the Automatic Oxygen Absorption Recording Apparatus flasks, was of utmost importance. The method used was adhered to throughout this work, so as not to adversely affect the reproducibility of the experimental data. Usually, after removing the bulk of the fatty substrates from the flasks with acetone and water, the flasks were immersed in a bath of fuming nitric acid overnight to remove any residual organic products, in particular traces of the antioxidants and metal catalysts. The flasks were then removed and rinsed with tap water and subsequently several times with distilled water and finally dried in a vacuum oven.

2.3.3 Commencement of Experiment.

In order to ensure the purity of solutions, each solution was made up freshly prior to every experiment. The antioxidants were introduced into the substrates by a direct weighing method, using 10 ml. volumetric flasks. Where the quantity of the antioxidants or the catalysts present was very small (e.g. 5×10^{-5} mol. dm.⁻³) a bulk solution of the latter in chloroform was made up and the appropriate amounts were pipetted into each flask. The chloroform solvent was then evaporated off very slowly under reduced pressure, thus leaving the required amount of the catalyst or antioxidant in the flask to which the substrates were then added. For all experiments carried out in either the Warburg or the Automatic oxygen Absorption Recording Apparatus the sample size used was 1 ml., while for the shaking incubator experiments 2.5 ml. samples in each test tube were normally used. Usually after the immersion of the flasks in the baths, they were left open to the atmosphere for a period not exceeding 10 minutes in order to equilibrate. Since a 24-hour monitoring of the reactions on the Warburg Apparatus or the shaking reaction incubator was not possible, in some cases, the flasks were removed and stored at -40°C overnight, where the rate of the reaction was assumed to be negligible.

2.3.4 Calculation of the Results.

2.3.4.1 Automatic Oxygen Absorption Recording Apparatus.

The induction periods and the rates of oxygen absorption were calculated from the trace which was produced on the chart paper. The induction period was usually taken as the time from the start of the experiment up to the point where a sharp break from the straight trace was noticeable. For those reactions, where the rate of oxygen uptake was very slow, the induction

period was defined as the time taken for the absorption of the first 150 μ l of oxygen.

For the calculations of the rates of oxygen absorption the ratio of the volume of oxygen absorbed, at STP, V (ml) to the pen movement, L (cm.) was given by the equation 2.3.

$$\frac{V}{L} = \frac{R}{P_o} \left[V_f T_f + V_m T_m + \frac{1}{2} X_m T_m (P_1 - P_o) \right] \quad 2.3$$

where: R = ratio of the pressure change (cm. Hg) to corresponding pen movement.

V_f = volume of air in the reaction flask (corrected to STP) (ml.)

V_m = volume of air in the manometer (corrected to STP) (ml.)

X_m = cross-sectional area of manometer tube (cm.²)

T_f = temperature of the reaction flask (K)

T_m = temperature of the manometer (K)

P_1 = initial flask pressure (cm. Hg)

P_o = normal pressure (76 cm. Hg)

In a typical system the second order term in L is small enough to be ignored and hence the equation is reduced to equation 2.4.

$$\frac{V}{L} = \frac{R}{P_o} \left[V_f T_f + T_m \left(V_m + \frac{1}{2} X_m P_1 \right) \right] \quad 2.4$$

In our system the parameters were: such that approximately each 75 μ l. of oxygen uptake corresponded to a pen movement of 1 mm.

2.3.4.2 Warburg Apparatus.

In this apparatus the amount of the oxygen absorbed was measured by the pressure change in a constant volume system. This was indicated by the difference in the levels of the double capillary manometer. The total gaseous volume, V_1 (μ l.) at the start was given by equation 2.5 and after a corrected manometric pressure change of h mm. by V_2 (μ l.) in equation 2.6.

$$V_1 = V_g \cdot \frac{273}{T} \cdot \frac{P - R}{P_o} + V_f \cdot \alpha \cdot \frac{P - R}{P_o} \quad 2.5$$

$$V_2 = V_g \cdot \frac{273}{T} \cdot \frac{P - R + h}{P_o} + V_f \cdot \alpha \cdot \frac{P - R + h}{P_o} \quad 2.6$$

where: V_g = volume of the gaseous part of the system (μ l.)
 V_f = volume of the liquid sample (μ l.)
 P = initial pressure of the gaseous part of the system (mm. Brodie)
 R = vapour pressure of the liquid sample (mm. Brodie)
 P_o = normal pressure (760 mm. Hg = 10,000 mm. Brodie)
 T = temperature of the reaction (K)
 α = gas absorption coefficient (ml. gas/ml. liquid) and denotes the extent of the solubility of the gas in the liquid sample. A typical value of 0.1 was used throughout.

The quantity of gas evolved or taken up, $X \mu$ l. is then given by equation 2.7.

$$X = V_1 - V_2 = \left[\frac{V_g \cdot 273/T + V_f \cdot \alpha}{P_o} \right] h = K h \quad 2.7$$

where K was referred to as the reaction flask constant, consisting entirely of parameters which were known and remained constant throughout the experiment. The values of K for our system were within the range 1.0-1.2, and therefore, a full scale deflection of the manometer (150 mm. Brodie) corresponded to 150-180 μ l. of oxygen absorbed at STP. During the reaction when a significant amount of oxygen had been absorbed, readings were taken and the original pressure restored by opening the manometer taps to the atmosphere, resetting the fluid levels to the 150 mark and closing the taps again.

Almost all experiments were confined to the early stages of the oxidation where the amount of oxygen absorbed by the sample rarely exceeded 300 μ l. Since the total volume of air in the system was typically 15 ml. of which one-fifth is oxygen, the volume of oxygen available is about 3 ml. Absorption of 300 μ l. of oxygen thus corresponds to a 10% reduction in the

partial pressure of oxygen in the system. This represent an upper limit in the worst possible case and was considered to be negligible for all practical purposes.

2.3.4.3 Shaking Reaction Incubator.

This apparatus was essentially used for measuring the fall in the concentration of the nickel chelate antioxidants with time at different temperatures. Usually the start of two parallel sets of duplicate experiments was staggered at 12 hours intervals because of the uncertainty of the duration of the induction period, and the need to take frequent readings during the critical period in which the steady reaction becomes autocatalytic. During the experiment, at suitable time intervals, 0.5 ml. samples were taken from each test tube and the concentration of the nickel chelate in the solution was determined spectrophotometrically (section 2.4.1), using 0.1 cm. cells. Since this testing was not destructive, the samples were returned after the measurement of the concentration. Depending upon the nature of the experiment either pure oleic acid/oleyl alcohol or pure ethyl benzoate were used in the reference cell. The optical density and hence, the concentration of the antioxidant, was measured as a function of time and the rate of deterioration of the antioxidant in the sample calculated from a time/concentration graph.

2.3.5 Solubility of Nickel Chelates.

In order to determine the maximum solubility of the nickel chelates in oleic acid and oleyl alcohol, an excess quantity of the chelate was placed in a flask containing about 5 ml. of the substrate. The mixture was gradually heated in a water bath to 75-80°C and kept at this temperature for approximately one hour. At the end of this period the bath was removed and the solution was allowed to cool to room temperature. A strong current of nitrogen

gas was passed through the solution for five minutes before the commencement of the heating and continued throughout the experiment until the contents of the flask had reached the room temperature. The solution was then filtered at the pump using a micro-filter flask and funnel and the filtrate was kept under a nitrogen atmosphere at room temperature for 24 hours. The concentration of the nickel chelate was then measured spectrophotometrically.

2.4 ANALYTICAL PROCEDURES.

2.4.1 Spectroscopy.

Unless otherwise stated all nmr spectra were 60 MHz. spectra obtained at the Physico-Chemical Measurements Unit, PCMU, (Harwell). The ir spectra were run on a Perkin-Elmer 457 grating infrared spectrophotometer, and the electronic absorption spectra were obtained with a Hitachi Perkin-Elmer EPS-3T drum recording spectrophotometer.

2.4.2 Determination of Nickel Chelate Concentration.

The concentration of nickel chelates was measured spectrophotometrically. The peak selected for the concentration determinations was that occurring in the range 850-950 nm. (slight variation in the position of this peak for different substituted nickel chelates existed - see Table 3.) where for all practical purposes the absorption of substrates, solvents or any other ingredients was negligible.

2.4.3 Determination of Peroxide Concentration.

The hydroperoxide concentrations in the samples were determined by the iodometric method due to Heaton and Uri¹⁸¹, which depends upon estimation of the iodine liberated by the reaction of peroxides with KI. For reacted samples containing a higher quantity of peroxides the macro-method

was used, the liberated iodine being determined by titration, while for the determination of the purity of some substrates the more sensitive micro-peroxide determination procedure was adopted, the liberated iodine being determined spectrophotometrically.

2.4.3.1 Macro-peroxide Determination:- The unit of apparatus used in this method was a neckless pear-shaped Pyrex flask of 200 ml. capacity fitted with a B-19 ground glass socket and gas inlet tube with corresponding cone (Plate 2.7). For practical purposes as many as 12 flasks could be connected in series by means of rubber tubing. The solvent mixture consisted of two volumes of glacial acetic acid (AR-grade) and one volume of chloroform. 70 ml. of this mixture was placed in each flask and the samples (usually 0.5 ml.) were introduced into each flask and dissolved. With all samples the dissolution occurred instantaneously. The de-aeration was effected by bubbling oxygen-free nitrogen (section 2.2.2) vigorously through the solution and continued for approximately one hour. A freshly prepared saturated aqueous solution of potassium iodide (0.5 ml.) was added to the last flask in the de-aeration train, by slightly raising the gas inlet tube, while nitrogen continued to pass through the solution. The specially designed elongated jet of the inlet tube remained inside the solvent mixture during this manipulation, thus preventing the sucking in of any atmospheric oxygen. After the addition of the potassium iodide solution the inlet tube was replaced and de-aeration continued for a further 5 minutes before the flask was removed from the system and kept in the dark for one hour with both taps closed. 30 ml. of 5% aqueous solution of KI were then added and the contents rapidly titrated against a solution of 0.002N aqueous sodium thiosulphate, starch being added shortly before the end-point was reached.

2.4.3.2 Micro-peroxide Determination:- The unit of apparatus applied to the

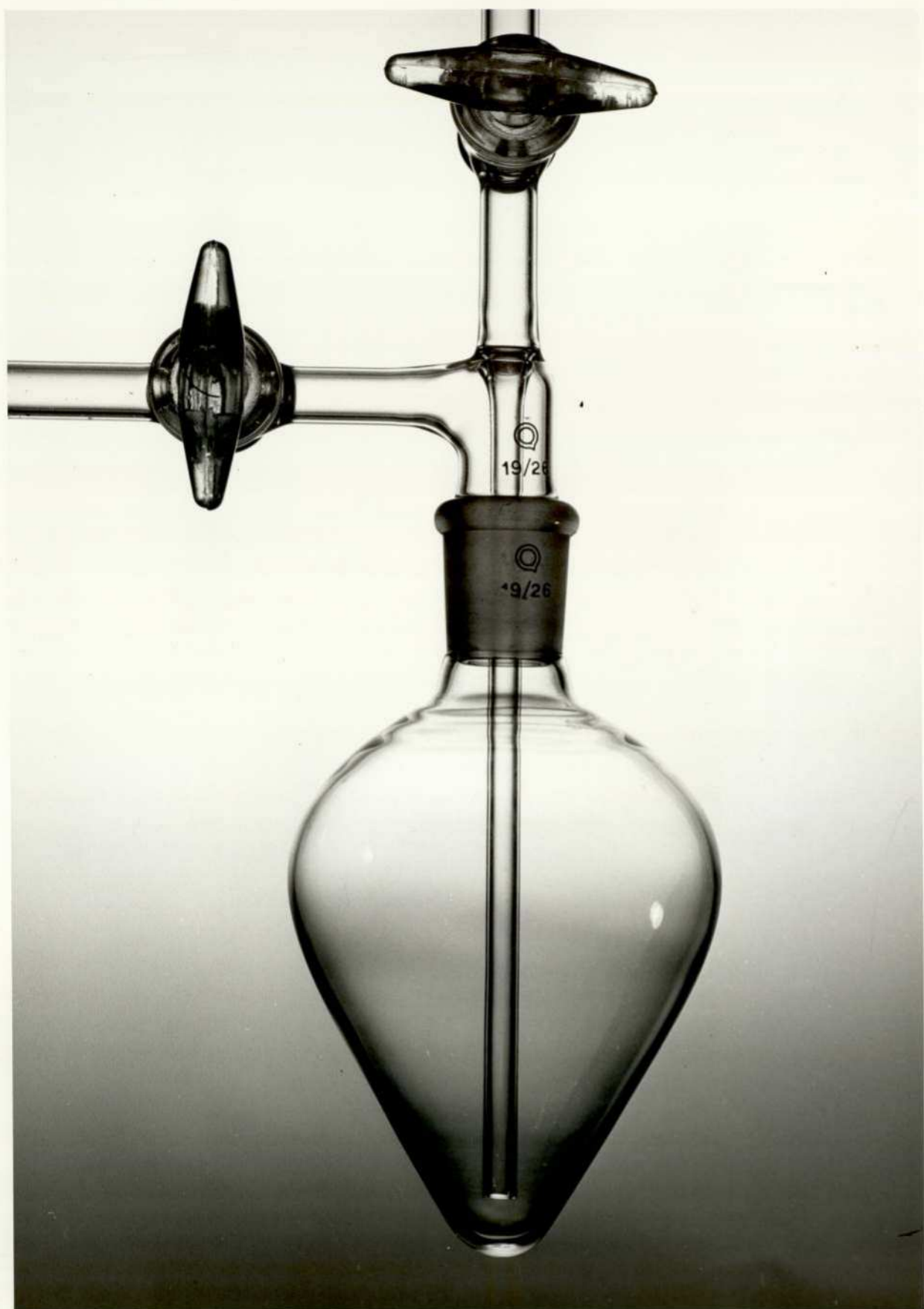


PLATE 2.7
MACRO-PEROXIDE FLASK ARRANGEMENT

micro-peroxide determination (Plate 2.8) was used in conjunction with a Unicam SP 600 spectrophotometer which was fitted with a special lid to accomodate the special cells. The lower part of the test tube was fused to 1 cm. matched spectrophotometric cells. The gas inlet tubes were designed in a similar way to the ones previously described in the macro-determination, except that care was taken to adjust the height of the inlet so that it did not interfere with the optical path. The same solvent mixture as the macro-determination method was used, but since the de-aeration in situ was rather slow, the solvent mixture was deaerated in bulk prior to use. 7.5 ml. of the solvent mixture was used together with 1 ml. samples. The test was carried out exactly as in the macro-method; one additional tube containing the solvent plus potassium iodide being used as the blank in the spectrophotometer.

The measurement of the optical density was carried out in the region 370-500 nm with the Unicam SP 600 spectrophotometer. Variation of the observing wavelength according to the concentration permitted readings to be taken in the optimum range.

2.4.4 Determination of Carbonyl Concentration.

For the determination of the carbonyl contents of the samples, the spectrophotometric method described by Lappin and Clark¹⁸² was used. This method was most suitable for carbonyl concentrations in the range of 10^{-3} to 10^{-6} molar and, therefore, for samples containing higher concentration of carbonyl, a prior dilution was found to be necessary. To 1 ml. of the sample or its solution in carbonyl-free methanol (section 2.2.3) placed in a 10 ml. volumetric flask, 1 ml. of a saturated solution of 2,4-dinitrophenyl hydrazine in CO-free methanol was added, together with two drops of dilute hydrochloric acid. the flask was loosely stoppered and maintained in an oven at 50°C for 2 hours. After cooling 5 ml. of a solution of 10 g. of potassium hydroxide

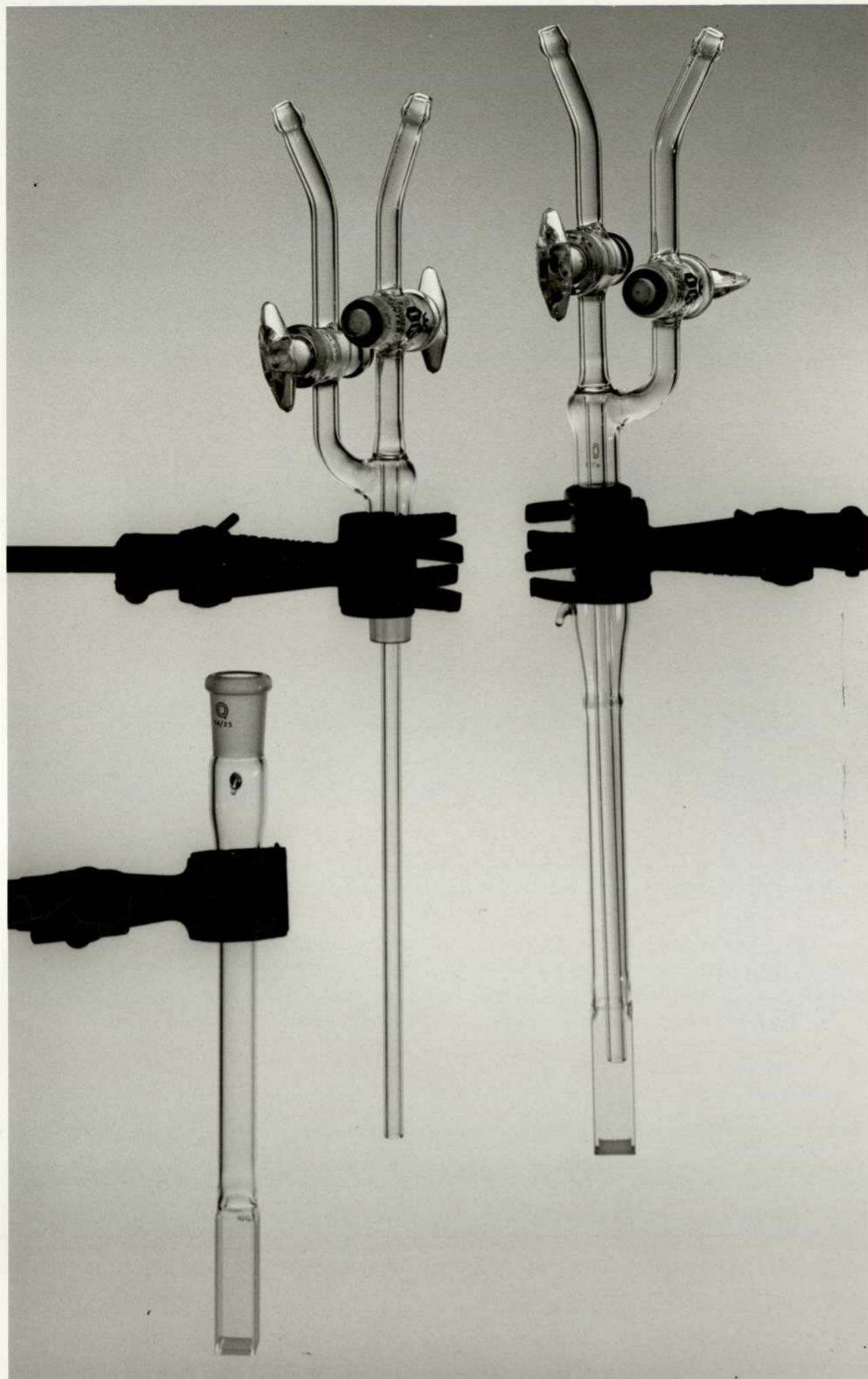


PLATE 2.8
MICRO-PEROXIDE FLASK ARRANGEMENT

dissolved in 20 ml. of water and made up to 100 ml. with CO-free methanol was added. The resulting black solution which rapidly cleared to a characteristic wine-red colour was made up to the 10 ml. mark with CO-free methanol. A blank solution was prepared simultaneously using 1 ml. of CO-free methanol in place of the sample. The optical density of the solution was measured using the Unicam SP 1800 recording spectrophotometer, the measurement being taken at the peak maximum. For the calculation, the average value of the molar extinction coefficient of 2.72×10^{-4} was employed.

2.4.5 Determination of the Iodine Value.

The iodine value is defined as the amount of halogen (expressed as iodine) which reacts with 100 g. of the material under specified conditions.

A determination of the iodine values was carried out in order to measure the purity of oleyl alcohol and oleic acid according to the procedure outlined in Institute of Petroleum Standard Test Methods¹⁸³. Special iodine value determination flasks of 500 ml. capacity were used. About 0.1 g. of the fatty substrate was weighed accurately on a watch-glass and was quantitatively transferred into the iodine value flask with 20 ml. of carbon tetrachloride (AR-grade). 25 ml. of the iodine solution (section 2.2.4) were pipetted into the flask, and the flask with its contents were shaken until a clear solution was obtained. It was then allowed to stand in the dark for 2 hours at room temperature. At the end of the reaction period 20 ml. of an aqueous solution of potassium iodide containing 100 gram per litre were added and mixed well. The neck and the inside walls of the reaction flasks were washed with 200 ml. of water and the excess iodine was titrated with a 0.1N standardised sodium thiosulphate solution using starch as an indicator near the end of the titration. A blank determination was also carried out using

the same quantities of all the reagents but omitting the sample.

The results were calculated by means of the equation 2.8:

$$I = 12.7 N (B - A) / W \quad 2.8$$

where: I = iodine value

N = normality of the thiosulphate solution

B = volume of thiosulphate solution used for blank (ml.)

A = volume of thiosulphate solution used for sample (ml.)

W = weight of the sample (g.)

The iodine values obtained for oleic acid and oleyl alcohol are given in Table 3.3 (section 3.2.2) together with the theoretical values.

2.4.6 Determination of Linoleic and Linolenic Acids and Linoleyl Alcohol.

Amongst the several methods¹⁹²⁻⁶ which were available for the spectrophotometric determination of polyunsaturated fatty acids and alcohols the method of Hilditch, Morton, and Riley¹⁹⁵ was selected. This method had the advantage of utilising simple apparatus and non-toxic reagents, and consisted of two separate determinations. In the first determination, for linolenic acid samples of approximately 0.1 g. were weighed accurately in small glass buckets, dropped into stoppered Pyrex test tubes containing 10 ml. of the alkaline ethylene glycol solution (section 2.2.5), and heated in an oil bath at 170°C for 15 minutes. These were then removed and chilled rapidly in an ice bath and the contents of each test tube were quantitatively transferred into a 250 ml. volumetric flask, and made up to the mark with aldehyde-free ethanol (section 2.2.6). No further dilution was found to be necessary and the flasks were allowed to stand overnight at 0°C. A blank solution, using the alkaline ethylene glycol solution was prepared simultaneously in exactly the same way and was used in the reference cell.

The spectral measurements were carried out using the Unicam SP 1800 recording spectrophotometer. The region between 235-310 was scanned for each sample with 0.5 cm. cells.

For the determination of the percentage of linoleic acid present the above procedure described for the determination of linolenic acid was used in exactly the same way with the exception that the samples were heated at 180°C for 60 minutes in the oil bath.

For the calculation of the results, the extinction coefficients of 1% solutions in 1 cm. cells given by the authors were used according to Table 2.3.

Table 2.3

Values of the extinction coefficients for 1% solutions of linoleic and linolenic acids as given by Hilditch et al¹⁹⁵.

Substrate	Extinction coefficient
Linoleic acid	906 (at 234 nm.)
Linolenic acid	569 (at 234 nm.)
Linolenic acid	532 (at 268 nm.)

While the percentage of linolenic acid was found directly from the optical density measurements, for the determination of the percentage of linoleic acid in the sample the increment of the absorption coefficient due to the observed proportion of linolenic acid had to be deducted from the optical density. The results obtained from these determinations are given in Tables 3.1 and 3.2 (section 3.2.1) for the impurities present in oleic acid and oleyl alcohol respectively.

2.4.7 Gas-Liquid Chromatography Analysis of Fatty Substrates.

According to James and Martin^{197,198} the analysis of the fatty acids

and alcohols by G.L.C. was possible, using a semi-polar column at temperatures in the range of 196-205°C, and with a carrier gas flow rate of 96 ml. per minute. The analysis was carried out using the Perkin-Elmer Model F11 gas-liquid chromatograph with a hydrogen flame ionization detector. The column (section 2.2.12) was set up in the oven and 2 µl. aliquots of sample dissolved in acetone were injected into the column in every case.

A preliminary analysis indicated that while the oven temperature setting of 196°C was adequately high, the nitrogen flow rate of 96 ml. per minute was rather too fast and was, therefore, reduced to 60 ml. per minute.

The chromatogram of the earlier batches of purified oleic acid showed one sharp peak and two smaller peaks which were due to the presence of linoleic and linolenic acid impurities. In the later batches of oleic acid which were purified by Swern, Knight, and Findley method¹⁸⁶ (section 2.2.7) these impurity peaks did not appear at the attenuations as low as 5. In the case of oleyl alcohol only one broad peak belonging to oleyl alcohol was indicated and no other impurities were observed.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 PRELIMINARY TESTS ON COMMERCIAL OLEIC ACID AND OLEYL ALCOHOL.3.1.1 Diene and Triene Contents of Commercial Oleic Acid and Oleyl Alcohol.

The principal impurities in the commercial oleic acid (Priolene) were linoleic and linolenic acids, whilst the impurities of the commercial oleyl alcohol (A 11) included mainly linoleyl and linolenyl alcohols. The analyses for the determination of these impurities were carried out by the method of Hilditch, Morton, and Riley¹⁸⁴ (section 2.4.6). In every case the sample (approximately 0.1 g.) was accurately weighed, in a small glass bucket, and dropped into a loosely stoppered Pyrex test tube containing the alkaline ethylene glycol solution. Heating was carried out in a thermostatically controlled bath containing silicone fluid (MS 550). For the peak measurements Unicam SP 500 spectrophotometer was used and the results were confirmed using a Unicam SP 1800 recording spectrophotometer.

The results of the analyses of the fatty acids and alcohols by this procedure are given in Tables 3.1 and 3.2 (section 3.2.1) respectively, together with the manufacturer's values.

3.1.2 Determination of Iodine Value, Peroxide Value, and Carbonyl Content.

The peroxide values of the commercial samples of oleic acid and oleyl alcohol were determined by the macro-method of Heaton and Uri¹⁸¹. Two 2 ml. samples of each of the fatty substrates were introduced into the flasks and analysed in accordance with the procedure outlined previously (section 2.4.3).

For the determination of the carbonyl contents of the commercial oleic acids and oleyl alcohol by the method of Lappin and Clark¹⁸², 1.0 ml. samples were used according to the procedure described previously (section 2.4.4). The value of the maximum absorbance was measured on Unicam SP 1800 recording spectrophotometer and the average value of the extinction coefficient was taken as 2.72×10^{-4} for calculation of the results.

The iodine value determinations were carried out according to the method described in the experimental section¹⁸³ (section 2.4.5). About 0.2 g. of each substrate was used for the determination.

Table 3.3 (section 3.2.2) shows the results which were obtained for the iodine, peroxide, and carbonyl values of the commercial grades of oleic acid and oleyl alcohol together with the values for the purified substrates.

3.2 PURIFICATION AND TEST OF PURITY OF OLEIC ACID AND OLEYL ALCOHOL.

3.2.1 Diene and Triene Contents of Purified Oleic Acid and Oleyl Alcohol.

Pure oleyl alcohol was obtained from the commercial grade (A 11) by the method of Swern, Knight, and Findley¹⁸⁶, whilst the purification of oleic acid was first effected from Priolene 95 using the method of Gupta and Hilditch¹⁸⁵. However, the results of the diene and triene tests on the purified substrates indicated that although the purification of oleyl alcohol by the method of Swern, Knight, and Findley had been successful in removing most of the linoleyl and linolenyl alcohol impurities, the method of Gupta and Hilditch for the purification of oleic acid had failed to completely remove the linoleic and linolenic acid impurities. For this reason the method of purification of oleic acid was changed to that recommended by Swern, Knight, and Findley (section 2.2.7).

The diene and triene contents of the purified substrates were determined by the method of Hilditch, Morton and Riley (section 2.4.6) using 0.1 ml. samples. Tables 3.1 and 3.2 show the results of these analyses for oleic acid and oleyl alcohol respectively.

TABLE 3.1

Analytical results for determination of polyunsaturated impurities in oleic acid.

Sample	% Linoleic acid		% Linolenic acid	
	Calculated	Theory*	Calculated	Theory*
Purified (Gupta)	3.2	-	0.04	-
Purified (Swern)	0.2	-	0.03	-
Priolene 64A	7.6	6.0	2.1	1.0
Priolene 64B	7.7	6.0	2.2	1.0
Priolene 95	2.4	1.5	0.7	0.5
Priolene 96	4.0	3.0	1.7	1.0

TABLE 3.2

Analytical results for determination of polyunsaturated impurities in oleyl alcohol

Sample	% Linoleyl alcohol		% Linolenyl alcohol	
	Calculated	Theory*	Calculated	Theory*
Purified (Swern)	0.59	-	0.09	-
Oleyl alcohol A 11	4.3	4.0	0.45	0.3

* Values quoted by manufacturer.

3.2.2 Determination of Iodine Value, Peroxide Value, and Carbonyl Content.

These determinations were carried out on the freshly purified oleic acid and oleyl alcohol. The peroxide values were determined by the

method of Heaton and Uri¹⁸¹, using two 4.0 ml. samples of each of the fatty substrates for the macro-determination, and two 0.5 ml. samples for the micro-analysis. The carbonyl contents were measured by the method of Lappin and Clark¹⁸², using duplicate 0.1 ml. samples. For the iodine value determination, approximately 0.2 g. of each substrate was weighed accurately and used as described before¹⁸³ (section 2.4.5). The results of these analyses are shown in Table 3.3.

TABLE 3.3

Analytical results for determination of iodine values, peroxide values, and carbonyl contents of purified and commercial grades of oleic acid and oleyl alcohol.

Substrate	Iodine value	Peroxide value	Carbonyl content
		mol. cm. ⁻³	mol. cm. ⁻³
Oleic acid (pure)	89.82*	0	0.96 [†]
Oleyl alcohol (pure)	94.61*	0	3.2 [†]
Priolene 64A	85.0	2.4	12.9
Priolene 64B	84.0	2.6	13.4
Priolene 95	88.0	2.1	16.0
Priolene 96	87.0	7.1	20.9
Oleyl alcohol A 11	90.6	9.9	17.6

* Theoretical values; Oleic acid = 90.07, Oleyl alcohol = 94.77

† This residual carbonyl content of the purified substrates was attributed to the presence of traces of acetone which was used as the solvent in the purification procedure.

From Tables 3.1, 3.2, and the results obtained from the earlier G.L.C. analyses (section 2.4.7) the indications were that the purification techniques used for oleyl alcohol and oleic acid (S.K.F. method) gave satisfactory results. Attempts to purify these substrates any further would have been uneconomical in terms of time and material wastage. The results shown in Table 3.3 confirmed the high degree of purity achieved for oleic

oleic acid and oleyl alcohol; the close agreement between the theoretical and calculated iodine values indicated the presence of unsaturated impurities in the substrates to be negligible, while the zero peroxide values are in accord with the expected results. Having obtained these materials at a satisfactorily high degree of purity state, we proceeded with the main autoxidation investigations.

3.3 EFFECT OF ANTIOXIDANTS.

3.3.1 Pure Substrates.

3.3.1.1 Oxidation Without Any Additives

All the experiments described in section 3.3 were carried out on the Automatic Oxygen Absorption Recording Apparatus (section 2.1.2), using duplicate 1 ml. samples. An initial study of the autoxidation of pure oleic acid and oleyl alcohol was made; the induction periods together with the maximum rates of oxygen absorption (corrected to STP) are shown in Tables 3.4-3.6 for oleic acid at 75°, 85°, and 95°C respectively, and in Table 3.7 for oleyl alcohol at 85°C.

3.3.1.2 Comparison of the Effect of Antioxidants at Constant Molarity.

In order to be able to make a direct comparison of the effects of various antioxidants on oleic acid and oleyl alcohol, the concentration of the antioxidants in this investigation was set at 2×10^{-4} mol.dm.⁻³. In the case of Embanox 4 (which is a synergistic mixture of 20% Embanox BHA and 20% citric acid in propylene glycol) the molarity was based on its BHA content only. The induction periods and maximum rates of oxygen absorption (corrected to STP) from this series of experiments are shown in Tables 3.4-3.6 for oleic acid at 75°, 85°, and 95°C respectively, and in Table 3.7 for

oleyl alcohol at 85°C.

TABLE 3.4

Induction periods and maximum rates of oxygen absorption for oleic acid at 75°C.

Antioxidant	Induction period		$\frac{IP^*}{IP_o}$	Max. rate O ₂ uptake	
	hr.			$\mu\text{l. (STP) hr.}^{-1} \text{cm.}^{-3}$	
	Sample 1	Sample 2		Sample 1	Sample 2
No antioxidant	4.1	4.0	—	35.3	36.6
D.L.T.D.P.	4.3	4.6	1.1	34.1	33.1
Embanox BHA	45.0	45.2	11.1	32.8	31.2
Embanox 4	51.1	51.1	12.6	36.8	42.8
Topanol 354	21.0	22.8	5.4	26.1	27.0
Topanol CA	43.0	44.1	10.8	56.0	36.4

TABLE 3.5

Induction periods and maximum rates of oxygen absorption for oleic acid at 85°C.

Antioxidant	Induction period		$\frac{IP^*}{IP_o}$	Max. rate O ₂ uptake	
	hr.			$\mu\text{l. (STP) hr.}^{-1} \text{cm.}^{-3}$	
	Sample 1	Sample 2		Sample 1	Sample 2
No antioxidant	1.8	1.8	-	42.1	51.8
D.L.T.D.P.	2.1	2.2	1.2	48.8	39.0
Embanox BHA	39.8	38.6	21.7	43.3	41.8
Embanox 4	33.1	30.9	25.3	45.9	45.4
Topanol 354	15.6	14.6	10.0	39.5	37.4
Topanol CA	35.2	33.8	18.9	58.5	57.0

* Ratio of average induction periods for inhibited and uninhibited samples.

TABLE 3.6

Induction periods and maximum rates of oxygen absorption
for oleic acid at 95°C.

Antioxidant	Induction period		$\frac{IP^*}{IP_o}$	Max. rate O_2 uptake	
	hr.			$\mu l. (STP) hr.^{-1} cm.^{-3}$	
	Sample 1	Sample 2		Sample 1	Sample 2
No antioxidant	1.1	1.2	-	69.0	70.1
D.L.T.D.P.	1.2	1.3	1.1	62.4	61.8
Embanox BHA	5.2	5.3	4.6	54.1	74.0
Embanox 4	12.6	13.0	11.1	50.9	53.0
Topanol 354	6.3	6.6	5.6	61.6	58.6
Topanol CA	10.4	10.8	9.2	74.0	78.7

TABLE 3.7

Induction periods and Maximum rates of oxygen absorption
for oleyl alcohol at 85°C.

Antioxidant	Induction period		$\frac{IP^*}{IP_o}$	Max. rate O_2 uptake	
	hr.			$\mu l. (STP) hr.^{-1} cm.^{-3}$	
	Sample 1	Sample 2		Sample 1	Sample 2
No antioxidant	2.4	2.4	-	31.9	30.1
D.L.T.D.P.	2.5	2.5	1.0	31.1	28.7
Embanox BHA	43.5	44.1	18.3	40.4	42.2
Embanox 4	101.0	98.9	41.6	58.2	59.8
Topanol 354	39.0	42.0	16.9	36.5	34.9
Topanol CA	45.0	45.9	18.9	36.8	36.0

* Ratio of average induction periods for inhibited and uninhibited samples.

At the first glance, it appears from Tables 3.4-3.6 that, according to the expectation, the magnitudes of the induction periods are lowered and

the maximum rates of oxygen absorption increased as the experimental temperature is raised from 75° to 95°C. However, within one temperature, different degrees of inhibition, as indicated by the induction periods, are obtained for various antioxidants. Also, while there is very little change in the magnitudes of the maximum rates of oxygen absorption for the uninhibited samples and those containing D.L.T.D.P. , Embanox BHA, and Embanox 4, the corresponding values for samples with Topanol antioxidants show slight deviations. The lower values obtained for Topanol 354 may be attributed to the fact that the autoxidation products of Topanol 354 may themselves act as retarders in the system.

Figs. 3.1 and 3.2 show the Arrhenius plots of induction periods and maximum rates of oxygen absorption respectively obtained for samples of oleic acid containing various antioxidants at 2×10^{-4} mol. dm.⁻³ concentration. The respective activation energies calculated from these graphs are given in Table 3.8.

TABLE 3.8

Activation energies of induction periods (E_{IP}) and maximum rates of oxygen absorption (E_R) obtained for samples of oleic acid containing 2×10^{-4} mol. dm.⁻³ concentration of antioxidant.

Sample	$E_{IP}/\text{KJ mol}^{-1}$	$E_R/\text{KJ mol}^{-1}$
No antioxidant	159.4	84.1
D.L.T.D.P	156.1	85.2
Embanox BHA	?	72.1
Embanox 4	157.5	43.7
Topanol 354	149.0	99.9
Topanol CA	152.0	73.2

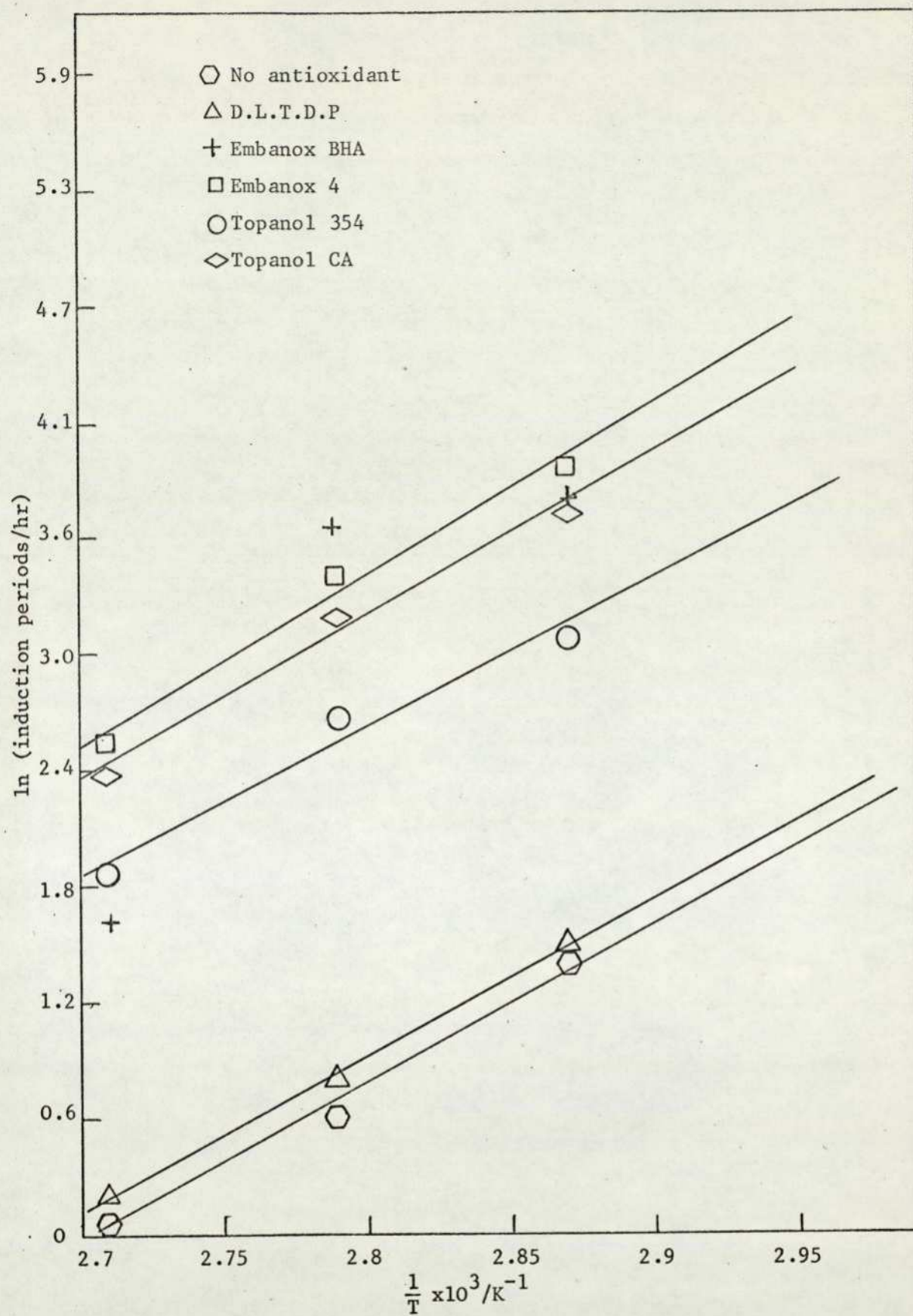


FIGURE 3.1

Arrhenius plots of $\ln$ (induction period) vs. $1/T$ for autoxidation of oleic acid in the presence of antioxidants.

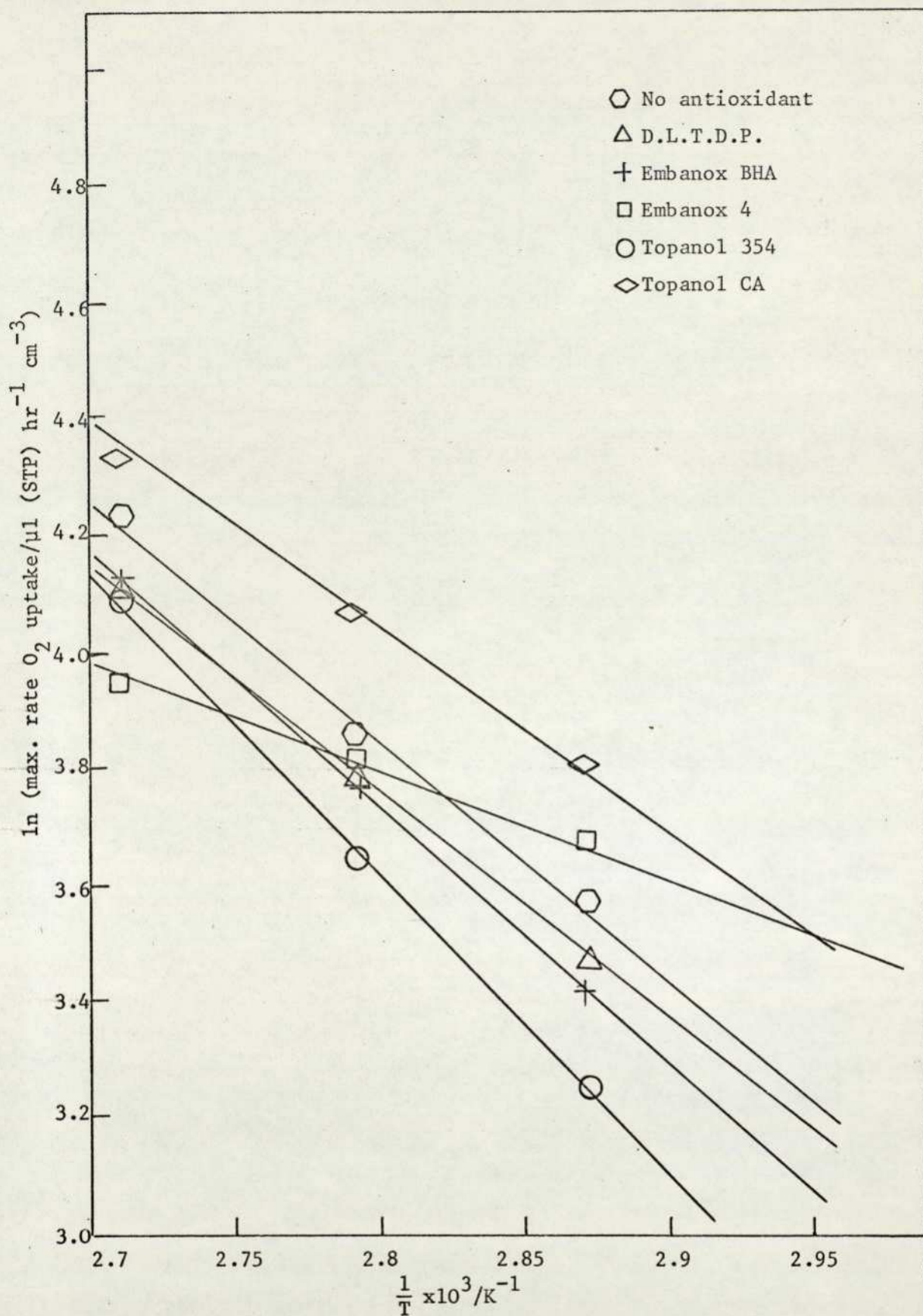


FIGURE 3.2

Arrhenius plots of $\ln$ (maximum rate of oxygen absorption) vs. $1/T$ for autoxidation of oleic acid in the presence of antioxidants.

Within the limits of experimental error the activation energy associated with the induction period appears to be unchanged by the inclusion of antioxidants; a distinctly non-linear Arrhenius plot was obtained for Embanox BHA and is attributed to experimental error. The data for reaction rates is somewhat more scattered but the only major activation energy change occurs with Embanox 4, which shows a very low activation energy arising from the fact that this antioxidant appears to be an efficient retarder at 95°C.

3.3.1.3 Comparison of the Effect of Antioxidants at Constant Weight Percentage.

For many practical applications, antioxidant activities are compared at constant weight concentrations rather than at constant molarities. It was, therefore, thought desirable to supplement the study of the activities of antioxidants for oleic acid and oleyl alcohol by the comparison of their effectiveness at a constant weight concentration of 0.0125% (equivalent molarities are in the range of 6.6×10^{-4} - 2×10^{-4} mol. dm.⁻³). In the case of Embanox 4 the weight concentration was based on the total antioxidant mixture; the equivalent weight concentration of Embanox BHA was then 0.0025%. The results obtained from these experiments, carried out at 85°C only, for oleic acid and oleyl alcohol are represented in Tables 3.9 and 3.10 respectively.

From a direct comparison of the induction periods in Tables 3.5 and 3.9 for oleic acid and Tables 3.6 and 3.10 for oleyl alcohol, all at 85°C, the following conclusions can be drawn:

(i)- The induction periods for samples containing D.L.T.D.P. are longer in experiments involving constant weight of antioxidant. This is due to the fact that D.L.T.D.P., having a large molecular weight, is present in

TABLE 3.9

Comparison of the induction periods and maximum rates of oxygen absorption using antioxidants at constant weight per cent for oleic acid at 85°C.

Antioxidant	Induction period		$\frac{IP^*}{IP_o}$	Max. rate O_2 uptake	
	hr.			$\mu l. (STP) \text{ hr.}^{-1} \text{ cm.}^{-3}$	
	Sample 1	Sample 2		Sample 1	Sample 2
No antioxidant	1.8	1.8	-	42.1	51.8
D.L.T.D.P.	5.0	5.0	2.8	34.2	63.1
Embanox BHA	25.5	26.6	14.5	53.0	53.3
Embanox 4	21.3	20.6	11.6	53.2	53.0
Topanol 354	22.8	21.5	12.3	38.7	54.7
Topanol CA	21.8	21.7	12.1	58.0	55.7

TABLE 3.10

Comparison of the induction periods and maximum rates of oxygen absorption using antioxidants at constant weight per cent for oleyl alcohol at 85°C.

Antioxidant	Induction period		$\frac{IP^*}{IP_o}$	Max. rate O_2 uptake	
	hr.			$\mu l. (STP) hr.^{-1} cm.^{-3}$	
	Sample 1	Sample 2		Sample 1	Sample 2
No antioxidant	2.2	2.4	-	48.3	49.8
D.L.T.D.P.	3.1	3.2	1.4	38.9	41.6
Embanox BHA	62.2	61.6	26.9	37.8	44.2
Embanox 4	31.1	32.3	13.8	57.0	44.5
Topanol 354	58.8	58.9	25.6	36.6	33.7
Topanol CA	23.3	22.8	10.0	34.2	29.0

* Ratio of average induction periods for inhibited and uninhibited samples.

much lower weight concentrations when its molar concentration is 2×10^{-4} mol. dm^{-3} . Its concentration, therefore, in the sample for experiment at constant weight is increased, resulting in its improved inhibiting properties. This improvement is, however, more apparant for oleic acid.

(ii)- There is a dramatic reduction in the induction period of samples of oleyl alcohol containing Embanox 4 at the constant weight experiment. This behaviour is a direct result of the much smaller quantity of Embanox 4 being present at constant weight experiment. For the experiments carried out at constant molarity, since the molarity of Embanox 4 has been based on its BHA content only (which is 20%), its total quantity present was five times that of Embanox BHA.

(iii)- The induction periods of samples containing Topanol 354 have increased in the case of experiments carried out at constant weight per cent. This is again due to the larger quantity of Topanol 354 (8.3×10^{-5} g. /100 g. substrate) being present.

(iv)- There is very little change in the values of the maximum rates of oxygen absorption between the two sets of experiments. Any marginal differences can be attributed to the experimental errors.

3.3.1.4 Molar Concentration of Topanol CA.

Topanol CA, being an outstanding tris-phenolic free-radical acceptor, was selected for a study of the effects of the variation of the starting antioxidant concentration. The experiments were carried out at 85°C and the effect was investigated in the concentration range 2×10^{-3} - 1×10^{-4} mol. dm^{-3} of antioxidant. The most concentrated solution (2×10^{-3} mol. dm^{-3}) was prepared by direct weighing and the other solutions were made up from the stock solution by successive dilution. Figs. 3.3 and 3.4 show graphs of the mean induction periods and the mean maximum rates of oxygen absorption

respectively against concentration of antioxidant for oleic acid and oleyl alcohol.

FIGURE 3.3

Variation of induction period with starting Topanol CA concentration for autoxidation of oleic acid and oleyl alcohol at 85°C.

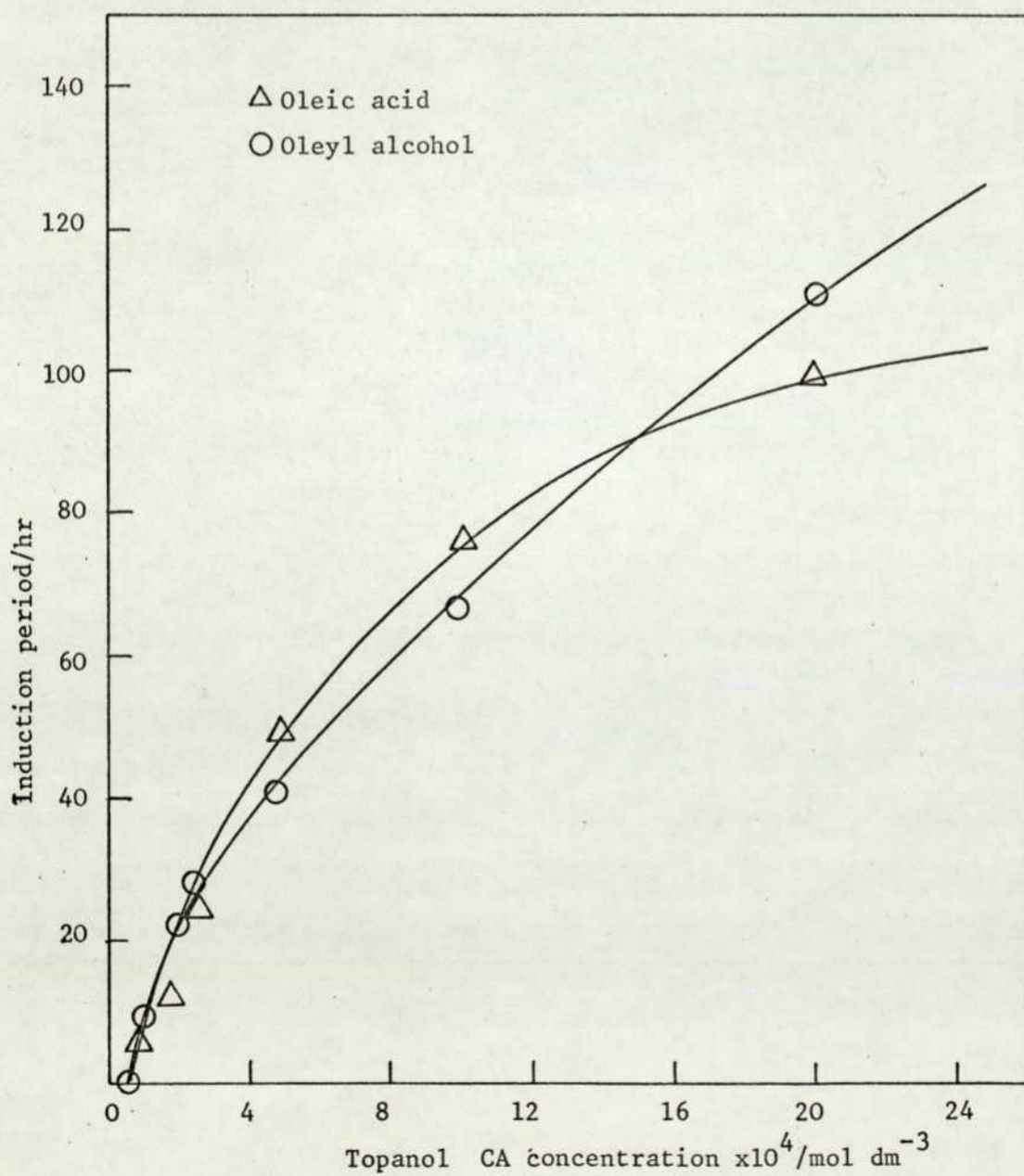


FIGURE 3.4

Variation of maximum rates of oxygen absorption with starting Topanol CA concentration for autoxidation of oleic acid and oleyl alcohol at 85°C.

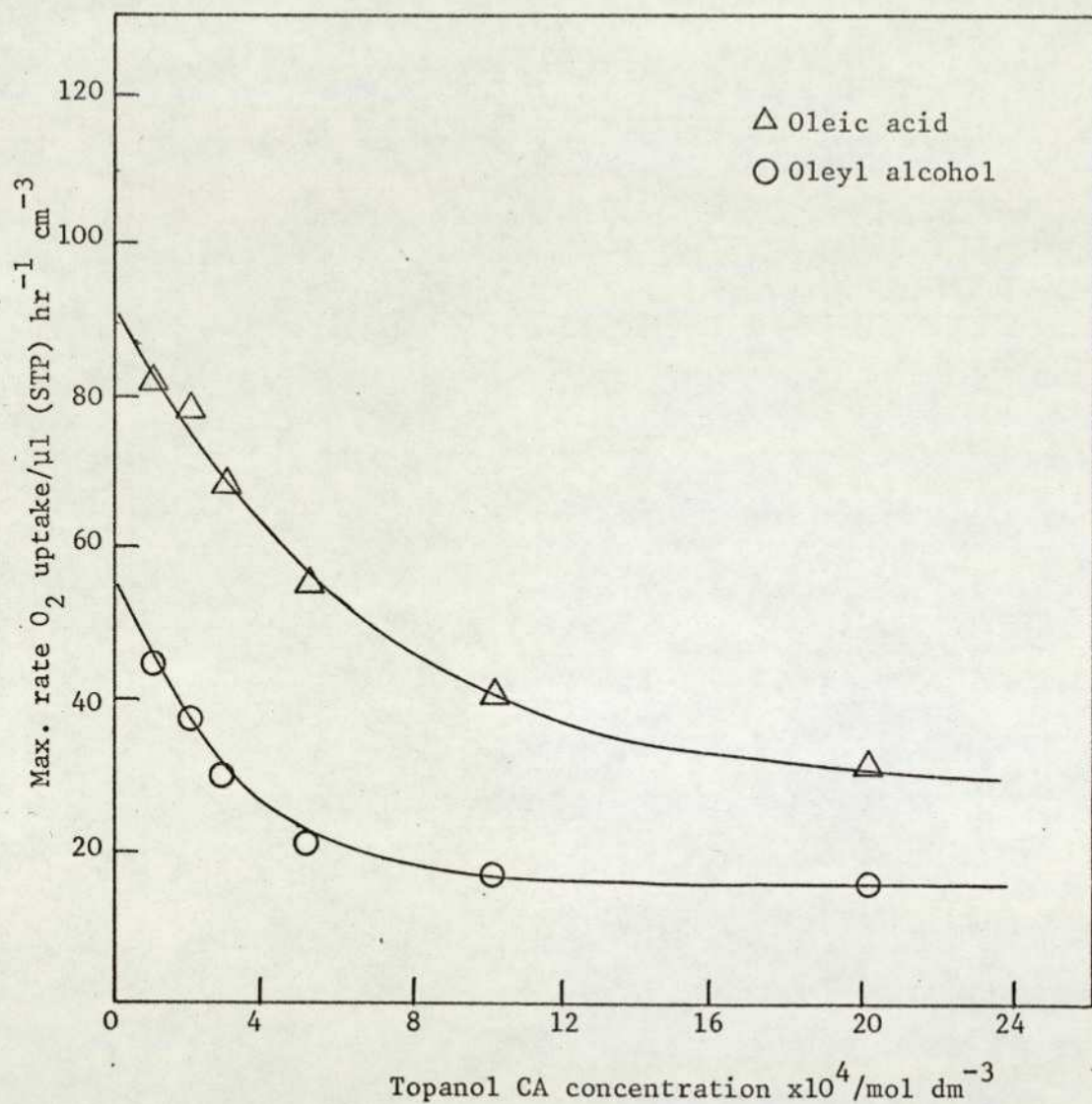
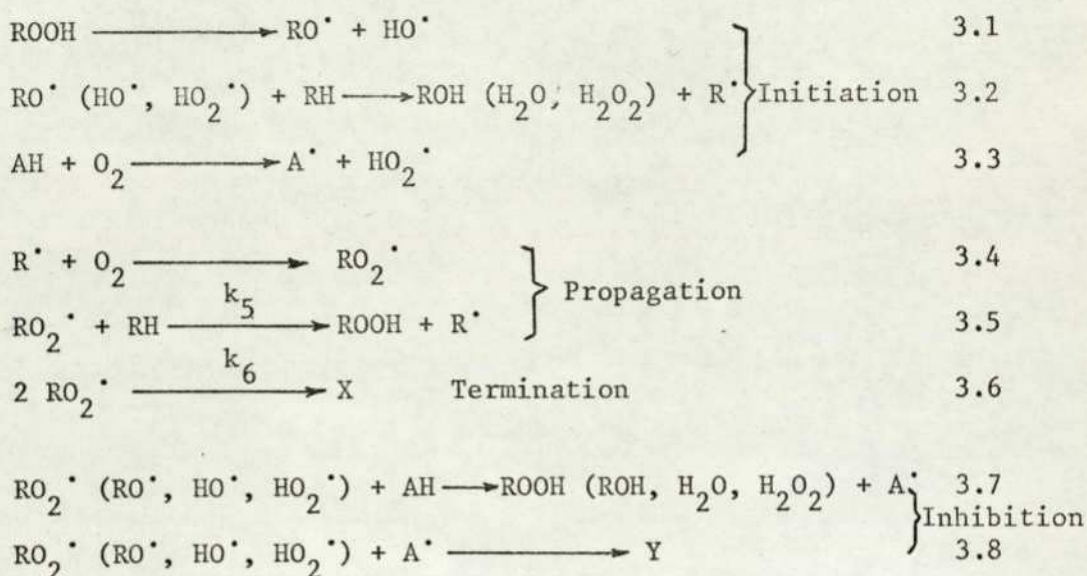


Fig. 3.3 which illustrates the dependence of the induction period on the starting concentration of Topanol CA clearly shows that at the lower concentrations up to $3 \times 10^{-4} \text{ mol. dm}^{-3}$ there is a linear relationship between the induction period and the inhibitor concentration; at higher concentrations

the graph becomes curved indicating some loss of efficiency of the antioxidant. This type of behaviour can be explained in the following way. Consider the typical reactions 3.1 - 3.8 taking place in the system:



As the inhibitor concentration is raised reaction 3.7 proceeds more rapidly and is able to compete more strongly with reaction 3.5 for peroxy radicals. This reduces the amount of hydroperoxide formed by reactions 3.4 and 3.5. By thus lowering the rate of formation of hydroperoxides, the hydroperoxide concentration at any given time is lowered. This lowers the rate of formation of radicals by slowing down reaction 3.1. The radicals formed in reaction 3.1 ultimately consume inhibitor molecules, so that reducing the rate of reaction 3.1 reduces the rate of inhibitor consumption. Therefore, the overall effect of raising the concentration of the antioxidant is to lower the rate of its consumption; thus, for example, doubling the starting concentration of Topanol CA should more than double the induction period if reaction 3.3 could be ignored. However, the rate of reaction 3.3 is directly dependent on inhibitor concentration. As the inhibitor concentration is raised, reaction 3.3 followed by reactions 3.7 and 3.8, will eventually

contribute significantly to the total inhibitor consumption. The overall effect of this process would be that doubling the starting inhibitor concentration would less than double the induction period. By reasoning along the same lines, Ingold¹⁹⁹ explained similar behaviour which he observed for a large number of phenolic antioxidants. He also pointed out that, with the exception of some inhibitors at low concentrations, the induction period is proportional, not to the first power of the inhibitor concentration, but to some fractional power between 0.5 and 1.0. Moreover the order decreases as the inhibitor concentration is increased. In the present work this observation is fully confirmed. A double logarithmic plot of the data in Fig. 3.3 gives a power dependence of 1.0 at low concentrations of inhibitor and 0.5 at higher concentrations.

Fig. 3.4 shows that, as for the induction periods, the rate of oxygen absorption decreases linearly with the starting concentration of Topanol CA at the lower concentration range. However, at the higher Topanol CA concentrations, where the oxygen-inhibitor reaction predominates, the effectiveness of the added Topanol CA for the rates of oxygen absorption falls off rapidly. Since these maximum rates of oxygen absorption were measured at the end of the induction period, i.e. when all the Topanol CA molecules had been consumed, this dependence of the rates on concentration indicates that the products of the reaction of Topanol CA with hydroperoxides are in themselves retarders of the autoxidation reactions of the fatty substrates. The shapes of the graphs, however, suggest that the retarding properties of these products are also subject to the same conditions as Topanol CA itself. In other words, at higher concentrations their reaction with atmospheric oxygen becomes more significant, resulting in a reduction of their efficiency in the system. Antagonism, as a result of their

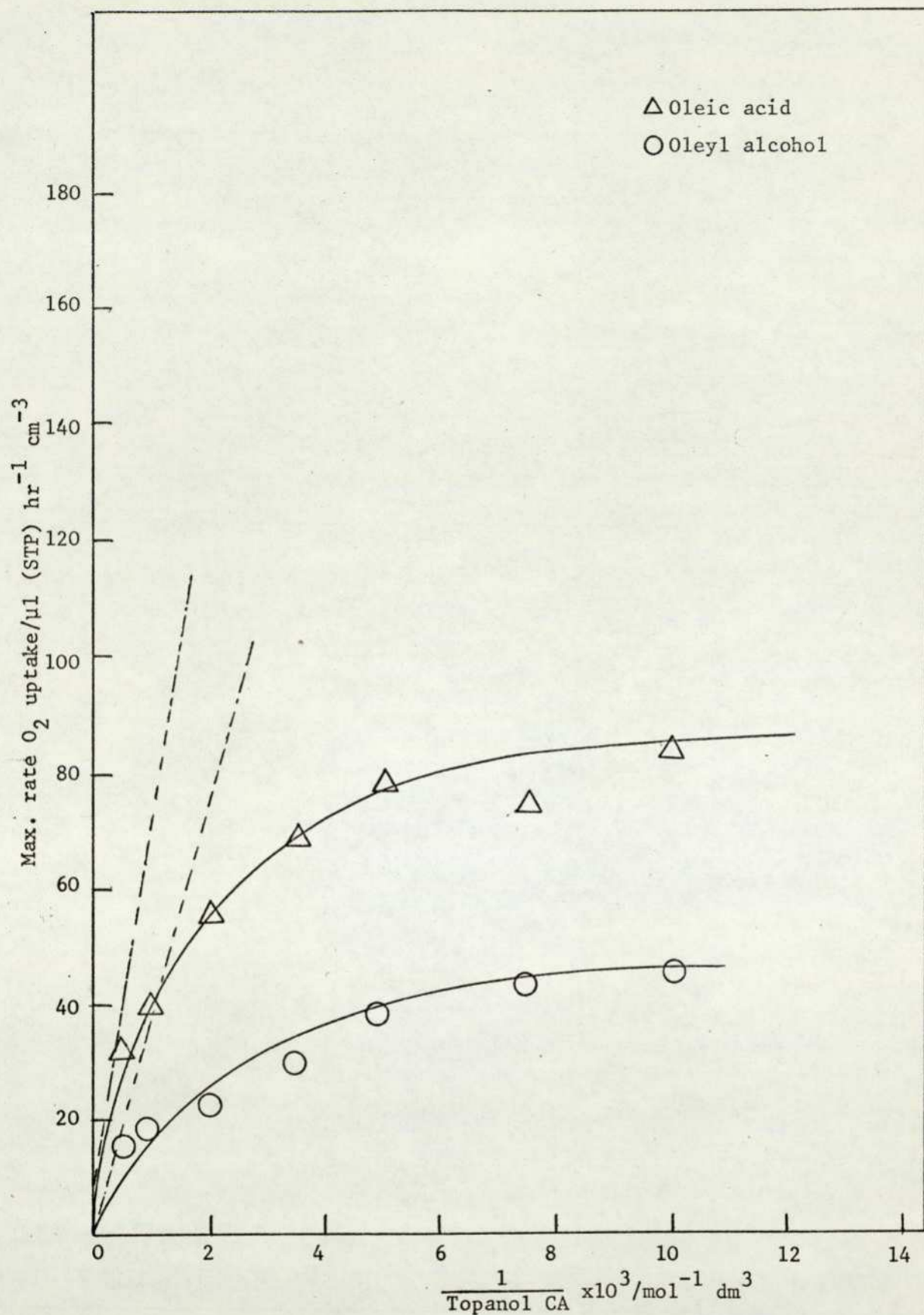


FIGURE 3.5

Variation of maximum rate of oxygen absorption with the reciprocal of of the starting concentration of Topanol CA at 85°C .

interaction at higher concentrations, may also be a possible mechanism affecting their efficiency.

One other point of interest which emerges from the results obtained in this set of experiments is the significance of the termination reaction. By a steady state analysis of reactions 3.1 - 3.8 and assuming that $r_{3.8} > r_{3.6}$ the following expression for the overall rate of oxygen absorption is obtained (see section 1.2).

$$-\frac{d[O_2]}{dt} = \frac{k_5 [RH]}{k_8 [AH]} r_i \quad 3.9$$

Therefore, a graph of the rate of oxygen absorption against the reciprocal of the antioxidant concentration should produce a straight line the slope of which is $k_5 [RH] r_i / k_8$. Such a graph for the above experiment is illustrated in Fig. 3.5 for oleic acid and oleyl alcohol. These graphs approach linearity only at the very early parts of the curves (along the dotted lines), where the concentration of Topanol CA is quite high. This indicates that a substantial rate of termination occurs via reaction 3.6 at low concentrations of Topanol CA, while as its starting concentration is increased, reactions 3.7 and 3.8 become more significant.

3.3.2 Oleic Acid with Added Polyunsaturated Fatty Acid Impurities.

3.3.2.1 Added Linoleic Acid.

In order to establish the effect of linoleic acid on oleic acid solutions containing 10%, 5%, 2.5%, and 1% by weight of linoleic acid in oleic acid were prepared by the direct addition of linoleic acid to oleic acid. Where antioxidant was present its concentration was $2 \times 10^{-4} \text{ mol dm}^{-3}$. The experimental temperatures selected for this study were 75° , 85° , and 95°C .

Tables 3.11-3.13 show the induction periods obtained at 75°, 85°, and 95°C respectively, while the corresponding results of the maximum rates of oxygen absorption (corrected to STP) are given in Tables 3.14-3.16.

TABLE 3.11

Induction periods (hr.) for solutions of oleic acid containing different percentages of linoleic acid at 75°C.

LINOLEIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	1.0	1.0	1.9	1.9	2.4	2.4	3.7	3.5
D.L.T.D.P.	1.0	1.0	1.7	1.6	2.2	2.3	3.7	3.8
Embanox BHA	6.6	6.7	9.4	9.5	18.8	19.3	33.4	34.0
Embanox 4	9.3	9.6	12.7	13.0	22.4	23.1	29.9	29.7
Topanol 354	3.9	4.0	7.9	8.2	10.6	10.5	14.4	14.2
Topanol CA	13.6	13.2	18.0	17.6	23.5	24.1	29.6	29.9

TABLE 3.12

Induction periods (hr.) for solutions of oleic acid containing different percentages of linoleic acid at 85°C.

LINOLEIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	0.6	0.6	1.1	1.1	1.3	1.4	1.7	1.7
D.L.T.D.P.	0.5	0.5	0.9	0.9	1.3	1.3	1.7	1.8
Embanox BHA	4.4	4.2	8.6	8.1	17.1	15.1	28.9	27.3
Embanox 4	7.3	6.9	10.1	10.4	20.2	20.7	23.8	25.5
Topanol 354	2.0	3.1	6.4	6.6	7.0	7.0	10.6	10.1
Topanol CA	10.6	9.6	14.2	14.6	21.2	21.3	24.6	24.9

TABLE 3.13

Induction periods (hr.) for solutions of oleic acid containing different percentages of linoleic acid at 95°C.

LINOLEIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	0.2	0.2	0.5	0.5	0.7	0.7	1.0	1.0
D.L.T.D.P.	0.2	0.2	0.5	0.5	0.9	0.9	1.1	1.1
Embanox BHA	1.8	1.8	2.5	2.3	3.9	3.8	4.4	4.7
Embanox 4	2.7	2.4	4.5	4.7	6.3	5.9	6.8	7.4
Topanol 354	1.0	0.9	1.6	1.6	2.3	2.3	3.8	4.0
Topanol CA	1.4	1.5	2.3	2.4	3.1	3.1	4.5	4.9

TABLE 3.14

Maximum rates of oxygen absorption ($\mu\text{l (STP) hr}^{-1} \text{ cm}^{-3}$) for solutions of oleic acid containing different percentages of linoleic acid at 75°C.

LINOLEIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	61.7	61.2	51.3	49.8	42.5	40.0	39.6	38.0
D.L.T.D.P.	63.0	60.1	49.1	48.6	39.7	39.6	38.6	38.1
Embanox BHA	60.5	61.5	51.0	52.9	39.2	40.0	36.1	35.0
Embanox 4	69.8	70.0	59.3	59.7	47.6	48.8	43.2	41.0
Topanol 354	49.7	50.8	41.9	42.1	33.1	36.5	30.1	30.0
Topanol CA	67.2	64.0	56.1	54.2	45.6	46.2	39.8	39.2

TABLE 3.15

Maximum rates of oxygen absorption ($\mu\text{l (STP) hr}^{-1} \text{ cm}^{-3}$) for solutions of oleic acid containing different percentages of linoleic acid at 85°C .

LINOLEIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	78.5	75.9	69.5	68.8	62.0	61.0	59.3	59.7
D.L.T.D.P.	73.5	77.0	67.5	67.0	59.3	58.8	54.2	55.1
Embanox BHA	70.2	73.8	65.5	63.5	54.8	54.4	48.5	47.6
Embanox 4	78.0	77.0	69.6	68.5	57.4	58.9	50.9	51.0
Topanol 354	69.5	67.4	61.0	59.7	51.4	53.7	43.3	46.9
Topanol CA	81.4	82.6	75.1	75.3	69.8	71.9	63.4	65.0

TABLE 3.16

Maximum rates of oxygen absorption ($\mu\text{l (STP) hr}^{-1} \text{ cm}^{-3}$) for solutions of oleic acid containing different percentages of linoleic acid at 95°C .

LINOLEIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	90.8	90.2	86.4	87.4	81.0	79.9	76.2	75.0
D.L.T.D.P.	83.4	84.5	79.6	78.5	73.7	73.0	68.1	68.7
Embanox BHA	81.9	82.6	75.0	74.6	68.2	69.5	60.5	61.8
Embanox 4	84.2	82.8	74.2	76.5	66.2	66.9	58.8	58.9
Topanol 354	83.1	83.3	76.5	77.4	73.1	72.9	67.7	68.1
Topanol CA	95.8	96.6	95.2	93.1	88.2	86.9	81.1	79.0

3.3.2.2 Added Linolenic Acid.

This series of experiments with linolenic acid was carried out in a similar manner to the experiments with linoleic acid (section 3.3.2.1). The following percentages by weight of linolenic acid in oleic acid were used: 10%, 5%, 2.5%, and 1%. The temperatures selected for these investigations were 75°, 85°, and 95°C. Where antioxidant was present its concentration was $2 \times 10^{-4} \text{ mol dm}^{-3}$. The induction periods obtained from these experiments at 75°, 85°, and 95°C are given in Tables 3.17 - 3.19 respectively, while the corresponding maximum rates of oxygen absorption (corrected to STP) are shown in Tables 3.20 - 3.22.

TABLE 3.17

Induction periods (hr) for solutions of oleic acid containing different percentages of linolenic acid at 75°C.

LINOLENIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	0.5	0.5	0.8	0.9	1.2	1.2	1.7	1.8
D.L.T.D.P.	0.9	0.9	1.2	1.1	1.6	1.4	2.3	2.3
Embanox BHA	7.2	7.2	11.7	10.8	14.4	15.3	18.7	18.9
Embanox 4	4.5	4.9	7.2	7.2	14.4	14.4	16.2	16.3
Topanol 354	6.7	8.1	9.8	10.3	13.3	14.4	17.5	18.0
Topanol CA	5.8	8.1	13.5	13.9	17.2	17.5	19.8	20.9

TABLE 3.18

Induction periods (hr) for solutions of oleic acid containing different percentages of linolenic acid at 85°C.

LINOLENIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	0.2	0.2	0.2	0.2	0.5	0.5	1.0	1.0
D.L.T.D.P.	0.2	0.2	0.2	0.2	0.6	0.6	1.2	1.2
Embanox BHA	2.7	2.7	5.4	5.8	7.2	7.6	9.4	9.9
Embanox 4	3.4	3.4	4.1	4.5	5.2	5.4	8.1	7.7
Topanol 354	3.1	3.6	4.1	4.1	4.9	4.9	5.9	6.1
Topanol CA	2.0	1.8	4.3	4.5	9.0	8.8	14.4	13.9

TABLE 3.19

Induction periods (hr) for solutions of oleic acid containing different percentages of linolenic acid at 95°C.

LINOLENIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	0.2	0.2	0.2	0.2	0.5	0.5	0.5	0.5
D.L.T.D.P.	0.2	0.2	0.2	0.2	0.5	0.5	0.7	0.7
Embanox BHA	0.9	0.9	2.0	2.1	2.3	2.3	2.7	2.7
Embanox 4	0.9	1.2	1.8	1.8	3.2	3.0	4.1	4.1
Topanol 354	1.4	1.6	1.8	1.8	2.0	2.0	2.2	2.2
Topanol CA	1.0	1.0	2.3	2.7	3.1	3.2	4.3	4.7

TABLE 3.20

Maximum rates of oxygen absorption ($\mu\text{l (STP) hr}^{-1} \text{ cm}^{-3}$) for solutions of oleic acid containing different percentages of linolenic acid at 75°C .

LINOLENIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	70.0	70.8	54.1	53.3	46.7	47.7	36.2	39.5
D.L.T.D.P.	63.4	62.5	49.6	50.0	45.3	43.4	39.7	39.2
Embanox BHA	66.9	64.8	59.8	55.2	49.2	48.7	41.8	41.5
Embanox 4	75.0	73.6	61.2	58.5	51.2	51.1	44.0	43.0
Topanol 354	53.8	55.7	44.9	47.5	41.0	40.2	33.7	32.1
Topanol CA	80.1	82.8	68.7	69.1	62.0	60.1	50.8	50.0

TABLE 3.21

Maximum rates of oxygen absorption ($\mu\text{l (STP) hr}^{-1} \text{ cm}^{-3}$) for solutions of oleic acid containing different percentages of linolenic acid at 85°C .

LINOLENIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	82.5	82.0	72.4	72.0	66.3	65.7	59.2	58.1
D.L.T.D.P.	78.8	78.0	66.3	64.5	58.4	59.9	57.6	58.8
Embanox BHA	79.8	79.5	70.4	71.3	63.5	62.5	57.2	60.0
Embanox 4	77.5	75.6	70.9	70.1	59.9	59.7	55.2	51.0
Topanol 354	66.2	65.4	57.6	59.4	52.0	51.0	44.8	43.2
Topanol CA	89.9	89.6	83.5	81.0	75.6	73.2	66.7	66.1

TABLE 3.22

Maximum rates of oxygen absorption ($\mu\text{l (STP) hr}^{-1} \text{ cm}^{-3}$) for solutions of oleic acid containing different percentages of linolenic acid at 95°C .

LINOLENIC ACID %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	94.7	95.6	89.9	90.1	83.4	82.5	78.1	77.5
D.L.T.D.P.	90.1	89.5	79.6	79.5	74.5	73.4	69.7	69.8
Embanox BHA	90.5	90.0	82.5	81.6	75.2	76.8	64.1	65.9
Embanox 4	88.4	88.8	77.2	79.3	65.8	67.7	58.4	58.5
Topanol 354	88.0	88.2	80.4	81.6	73.1	71.4	70.1	70.2
Topanol CA	96.5	97.6	91.2	91.1	87.2	79.0	82.3	81.4

3.3.2.3 Added Methyl Linoleate

In order to establish the function of the carboxylic group of the impurities, such as linoleic and linolenic acids, present in oleic acid, an experiment was carried out at 85°C in which solutions of oleic acid containing 10%, 5%, 2.5%, and 1% concentration by weight of added methyl linoleate were autoxidised. The concentration of antioxidant, where present, was $2 \times 10^{-4} \text{ mol dm}^{-3}$. The results obtained for the induction period and maximum rate of oxygen absorption from this set of experiments are given in Tables 3.23 and 3.24 respectively.

TABLE 3.23

Induction periods (hr) for solutions of oleic acid containing different percentages of added methyl linoleate at 85°C.

ANTIOXIDANT	10%		5%		2.5%		1%	
	METHYL LINOLEATE							
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
No antioxidant	0.6	0.6	0.9	0.9	1.2	1.3	1.5	1.6
D.L.T.D.P.	0.9	0.9	1.3	1.3	1.5	1.5	2.0	2.0
Embanox BHA	6.3	6.7	8.3	8.7	9.3	9.4	10.3	10.3
Embanox 4	2.5	2.4	3.8	3.8	4.9	4.9	5.9	5.6
Topanol 354	2.3	2.1	3.3	3.1	4.1	4.0	5.1	5.0
Topanol CA	3.1	3.4	4.7	5.3	6.7	6.8	7.6	7.6

TABLE 3.24

Maximum rates of oxygen absorption ($\mu\text{l (STP) hr}^{-1} \text{ cm}^{-3}$) for solutions of oleic acid containing different percentages of methyl linoleate at 85°C.

ANTIOXIDANT	10%		5%		2.5%		1%	
	METHYL LINOLEATE							
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
No antioxidant	81.1	79.9	74.0	71.2	64.7	63.5	57.3	56.4
D.L.T.D.P.	81.4	78.6	73.8	71.6	63.2	64.0	54.1	55.2
Embanox BHA	69.8	72.9	66.5	67.2	58.4	59.3	51.7	50.6
Embanox 4	83.1	81.2	70.6	72.8	61.3	59.6	51.4	53.7
Topanol 354	71.6	72.0	62.1	60.0	52.7	52.3	43.5	45.6
Topanol CA	85.6	82.4	79.1	79.6	73.2	71.4	64.2	64.3

3.3.3. Oleyl Alcohol with Added Linoleyl Alcohol.

A series of experiments with oleyl alcohol containing different percentages of deliberately added linoleyl alcohol was performed in a similar manner to those with oleic acid in the presence of linoleic and linolenic acids. Solutions of oleyl alcohol containing 10%, 5%, 2.5%, and 1% concentration by weight of linoleyl alcohol were autoxidised in the usual manner at 85°C. The concentration of antioxidant, where present, was 2×10^{-4} mol dm⁻³. The observed induction periods and maximum rates of oxygen absorption are given in Tables 3.25 and 3.26 respectively.

TABLE 3.25

Induction periods (hr) for solutions of oleyl alcohol containing different percentages of linoleyl alcohol at 85°C.

LINOLEYL ALCOHOL %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	0.8	0.8	1.0	1.1	1.2	1.3	2.1	2.2
D.L.T.D.P.	0.8	0.8	1.1	1.1	1.6	1.5	2.2	2.2
Embanox BHA	5.5	5.0	13.9	15.5	29.1	29.0	37.2	36.7
Embanox 4	26.1	26.6	42.7	41.1	57.7	60.2	88.9	92.2
Topanol 354	9.5	9.8	16.7	16.7	27.2	28.7	34.4	35.5
Topanol CA	5.2	5.8	9.4	10.0	28.9	28.9	35.5	35.8

TABLE 3.26

Maximum rates of oxygen absorption ($\mu\text{I (STP) hr}^{-1} \text{ cm}^{-3}$) for solutions of oleyl alcohol containing different percentages of linoleyl alcohol at 85°C

LINOLEYL ALCOHOL %	10%		5%		2.5%		1%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
ANTIOXIDANT								
No antioxidant	57.5	56.7	49.8	50.1	42.0	39.9	33.2	33.5
D.L.T.D.P.	55.6	52.4	48.3	47.5	37.6	38.4	33.0	32.6
Embanox BHA	62.1	60.4	56.0	52.8	47.0	46.1	43.9	42.6
Embanox 4	84.5	83.8	71.9	77.2	68.6	68.5	63.3	62.4
Topanol 354	58.2	59.1	47.6	48.3	39.1	40.2	36.1	34.0
Topanol CA	63.3	64.5	57.8	55.6	49.1	48.2	39.0	38.4

From a survey of the results given in Tables 3.11 - 3.26 the following conclusions can be drawn:

- (i) - The effect of the impurity on the substrate is to drastically reduce the magnitude of the induction period and increase the corresponding value of the maximum rate of oxygen absorption.
- (ii) - While the number of ethylenic double bonds present in the impurities has an important effect on the autoxidation behaviour of oleic acid, the effect of the functional groups (such as carboxylic group) present in the impurities is almost negligible.
- (iii) - The presence of antioxidants in the system results in an improvement in the induction periods, even at impurity concentrations as high as 10%. There is, however, very little change in the values of the maximum rates

of oxygen absorption between samples containing various antioxidants and those without any antioxidant. This is, of course, due to the fact that the maximum rates of oxygen uptake measurements were taken at the end of the induction period, when the antioxidant in the system had been totally consumed. It is conceivable, however, that the products of the thermal autoxidation of some of the antioxidants used may themselves act as retarders or accelerators in the samples (c.f. section 3.3.1.4) leading to the slight differences in the rates.

(iv) - The temperature range $75^{\circ} - 95^{\circ}\text{C}$ at which the autoxidation of oleic acid in the presence of linoleic and linolenic acids was investigated proves to be an adequate range, with the best results being obtained at 85°C .

(v) - Judging by the induction periods only, it appears that although increasing the percentage of impurity has a worsening effect on the substrates it is the first 1% of the impurity which causes the most significant reduction in the induction period.

Figs. 3.6 and 3.7 show the dependence of the induction periods and maximum rates of oxygen absorption respectively on the weight percentage of linoleic acid in oleic acid at 85°C for samples containing various antioxidants at $2 \times 10^{-4} \text{ mol dm}^{-3}$. Similar graphs are also obtained for linoleic acid and methyl linoleate in oleic acid, and for linoleyl alcohol in oleyl alcohol. Since these plots are all non-linear it is convenient for the purposes of comparing the adverse effects of different impurities, to define two constants K_A and K_B such that K_A is the slope of the tangent drawn at the initial part (zero concentration of impurity) to the curves of induction period against weight per cent at 85°C , and K_B is the corresponding slope of the tangent drawn at the initial part to the curves of maximum

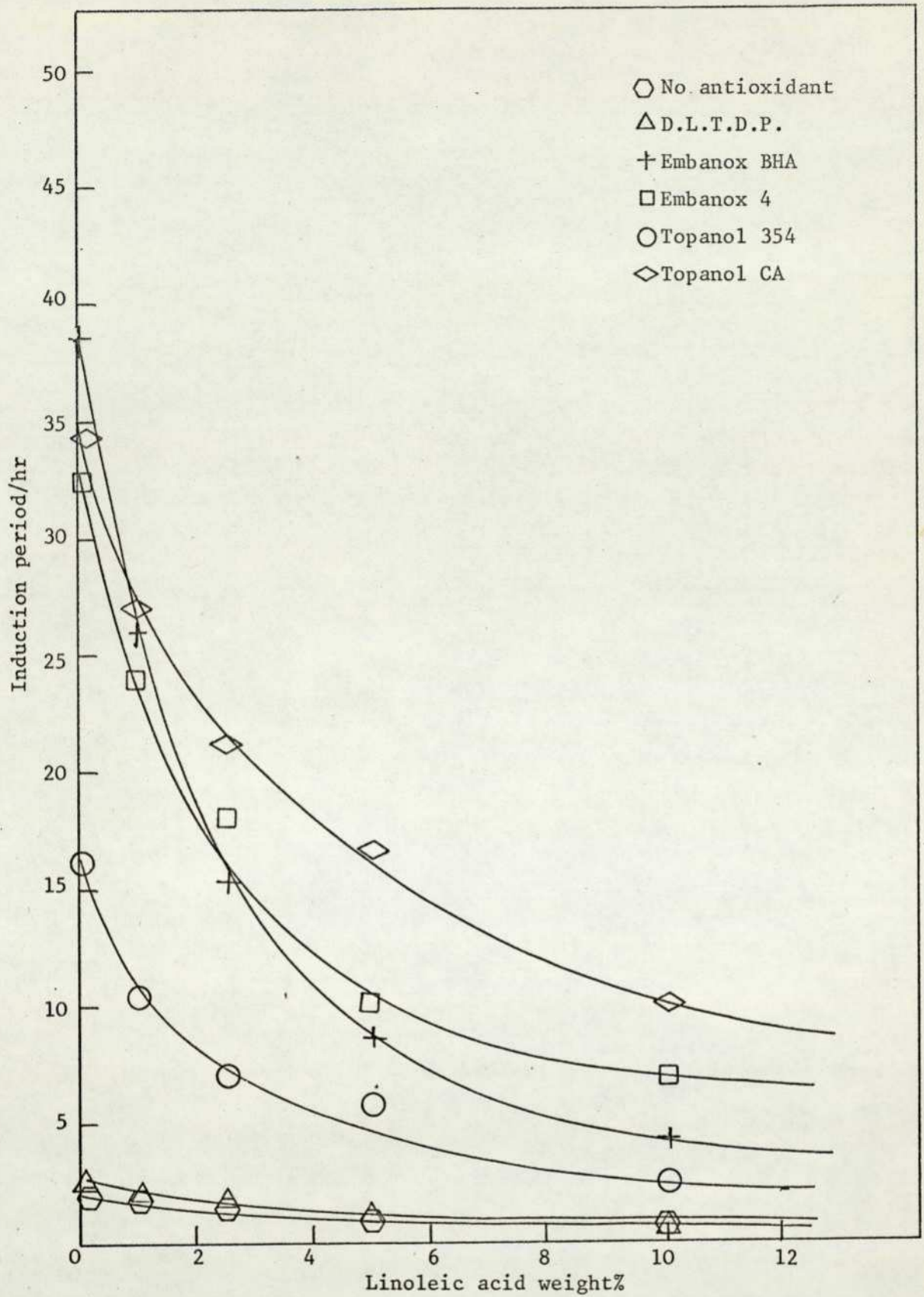


FIGURE 3.6

Graphs of induction periods against percentage of linoleic acid in oleic acid samples containing various antioxidants at 85°C.

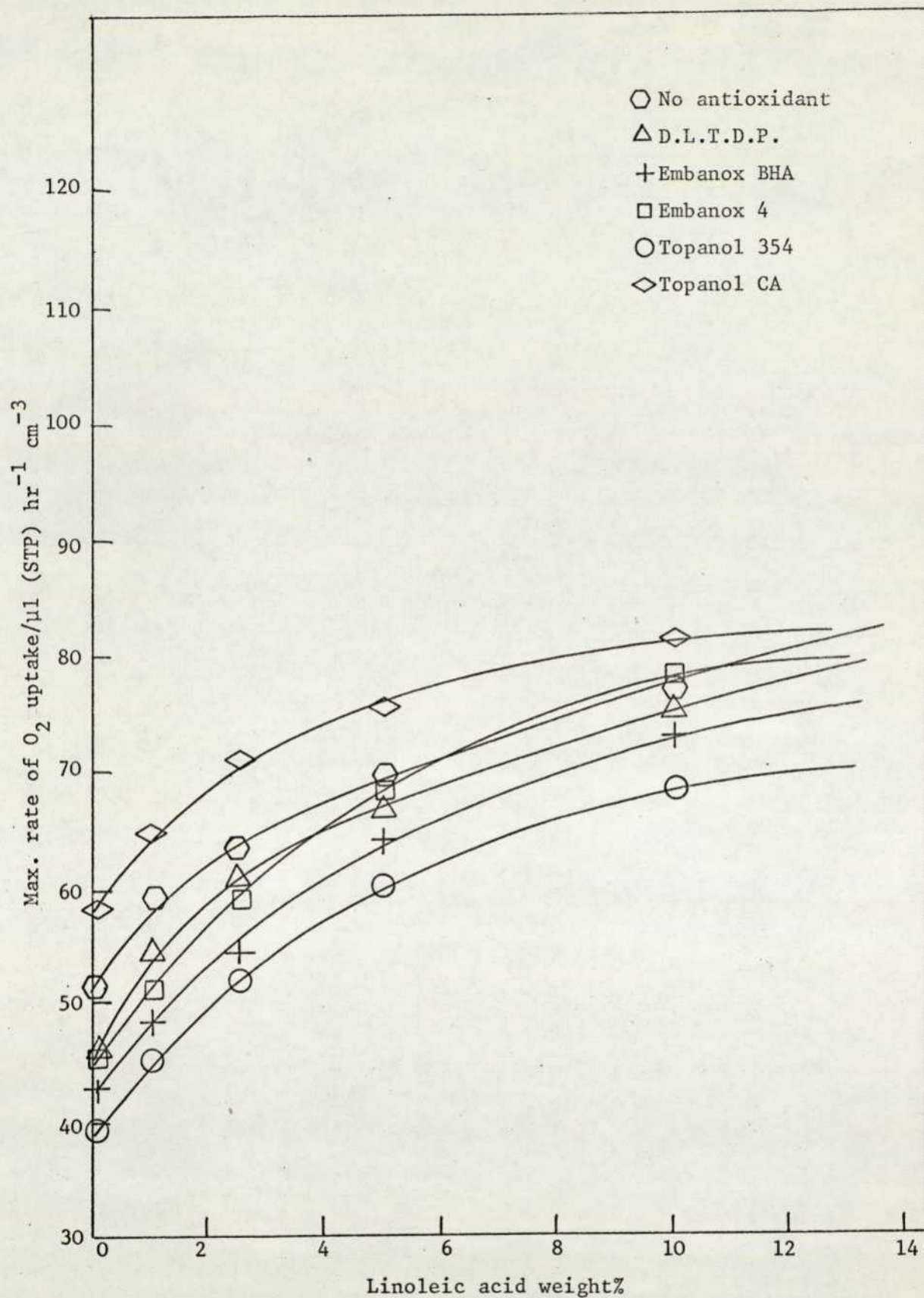


FIGURE 3.7

Graphs of maximum rates of O_2 uptake vs. percentage of linoleic acid in oleic acid samples containing various antioxidants at $85^\circ C$.

rate of oxygen absorption against weight per cent at 85°C. The values of K_A and K_B obtained in this way are indicated in Table 3.27.

TABLE 3.27

Values of K_A and K_B for autoxidation of oleic acid and oleyl alcohol containing added impurities and antioxidants at 85°C.

SUBSTRATE	IMPURITY	ANTIOXIDANT	K_A^*	K_B^*
Oleic acid	Linoleic acid	No antioxidant	0.18	8.5
		D.L.T.D.P.	0.2	8.8
		Embanox BHA	12.5	5.5
		Embanox 4	8.4	6.1
		Topanol 354	5.6	5.5
		Topanol CA	7.7	5.5
Oleic acid	Linolenic acid	No antioxidant	0.45	6.3
		D.L.T.D.P.	0.5	5.7
		Embanox BHA	93.7	9.1
		Embanox 4	64.0	8.5
		Topanol 354	15.1	6.6
		Topanol CA	28.8	8.1
Oleic acid	Methyl linoleate	No antioxidant	0.22	5.4
		D.L.T.D.P.	0.25	9.0
		Embanox BHA	28.8	7.6
		Embanox 4	26.7	9.0
		Topanol 354	10.1	5.7
		Topanol CA	26.5	6.0
Oleyl alcohol	Linoleyl alcohol	No antioxidant	0.3	5.2
		D.L.T.D.P.	0.31	4.3
		Embanox BHA	6.8	3.0
		Embanox 4	12.5	3.8
		Topanol 354	28.9	2.5
		Topanol CA	9.7	5.7

* Units of K_A and K_B are hr wt.^{-1} and $\mu\text{l O}_2(\text{STP}) \text{ hr}^{-1} \text{ cm}^{-3} \text{ wt.}^{-1}$ respectively.

These results show that the presence of polyunsaturated impurities not only affects the stability of the pure substrates, but also the effect of antioxidants. This latter effect is revealed by an examination of the values of K_A in Table 3.27 which vary very widely between antioxidants. From the point of view of commercial utility it is clear that removal of polyunsaturated compounds can have a very dramatic effect on the stability of these fatty substrates.

In the case of experiments carried out with oleic acid containing linoleic and linolenic acids as impurities, since the results were obtained at three different temperatures, it was possible to plot the Arrhenius graphs. Figs. 3.8 and 3.9 illustrate the typical Arrhenius graphs which are obtained when the maximum rates of oxygen absorption are plotted against the reciprocal values of the absolute temperature of the experiment for samples of oleic acid containing 2×10^{-4} mol dm⁻³ of antioxidant and 5% concentration by weight of linoleic acid and linolenic acid respectively. The pattern shown by these graphs are very similar to those which are obtained when the Arrhenius graphs are plotted for other concentrations of the polyunsaturated acid impurities.

The corresponding Arrhenius plots for the induction periods were, however, rather scattered owing to the significant influence of these impurities on the magnitude of the induction period when present at 1% and, therefore, were omitted.

From Figs. 3.8 and 3.9 and the corresponding Arrhenius plots obtained for experiments with 1%, 2.5%, and 10% impurities, it appears that at higher temperatures (95°C and above), antioxidants such as Embanox 4 and Embanox BHA are quite efficient in retarding the rate of autoxidation of oleic acid contaminated with linoleic and linolenic acid impurities. As the temperature is lowered, however, their efficiency is reduced and in fact

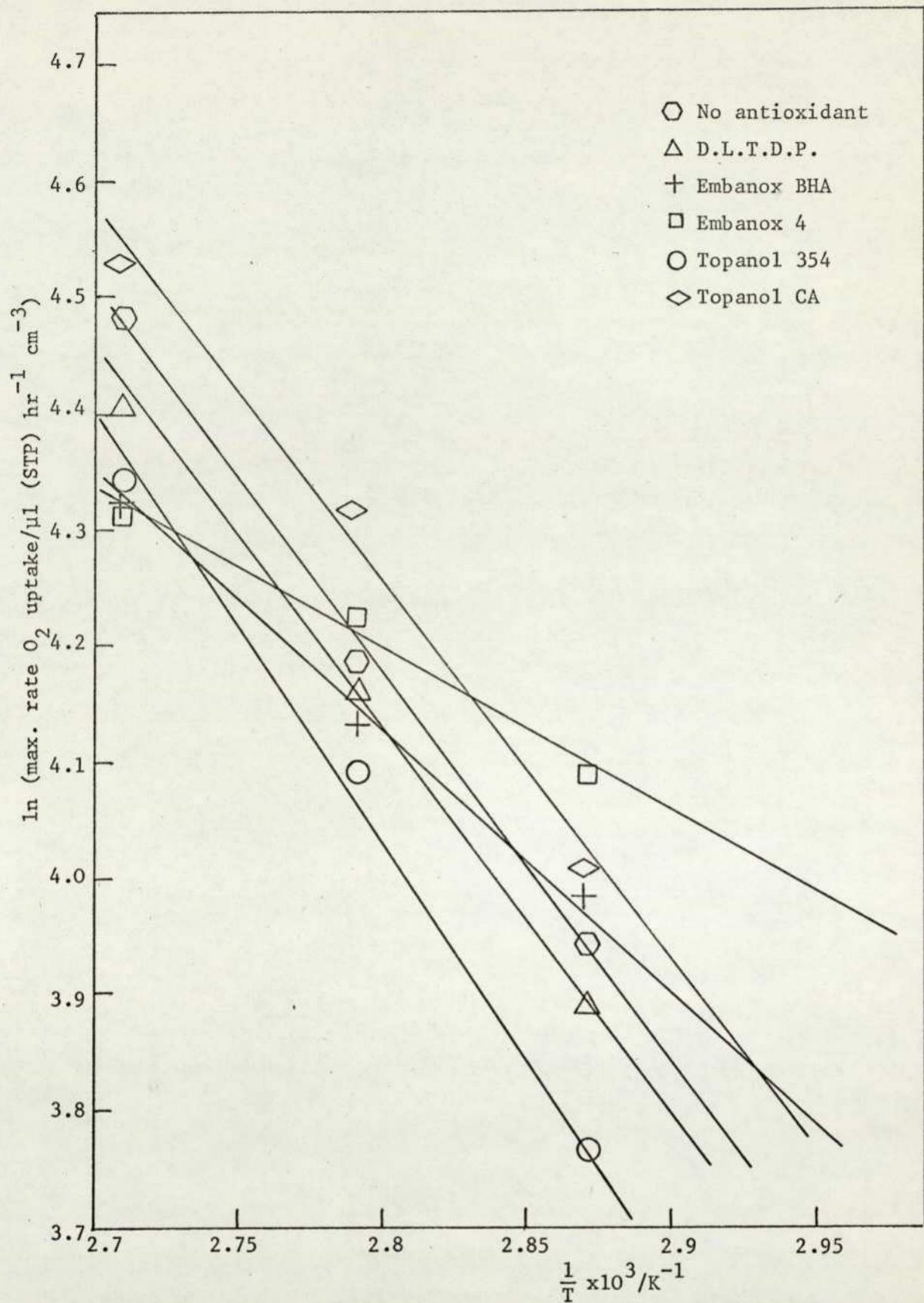


FIGURE 3.8

Arrhenius plots of the maximum rates of oxygen absorption for oleic acid samples containing 5% by weight linoleic acid and various antioxidants at $2 \times 10^{-4} \text{ mol dm}^{-3}$ concentration.

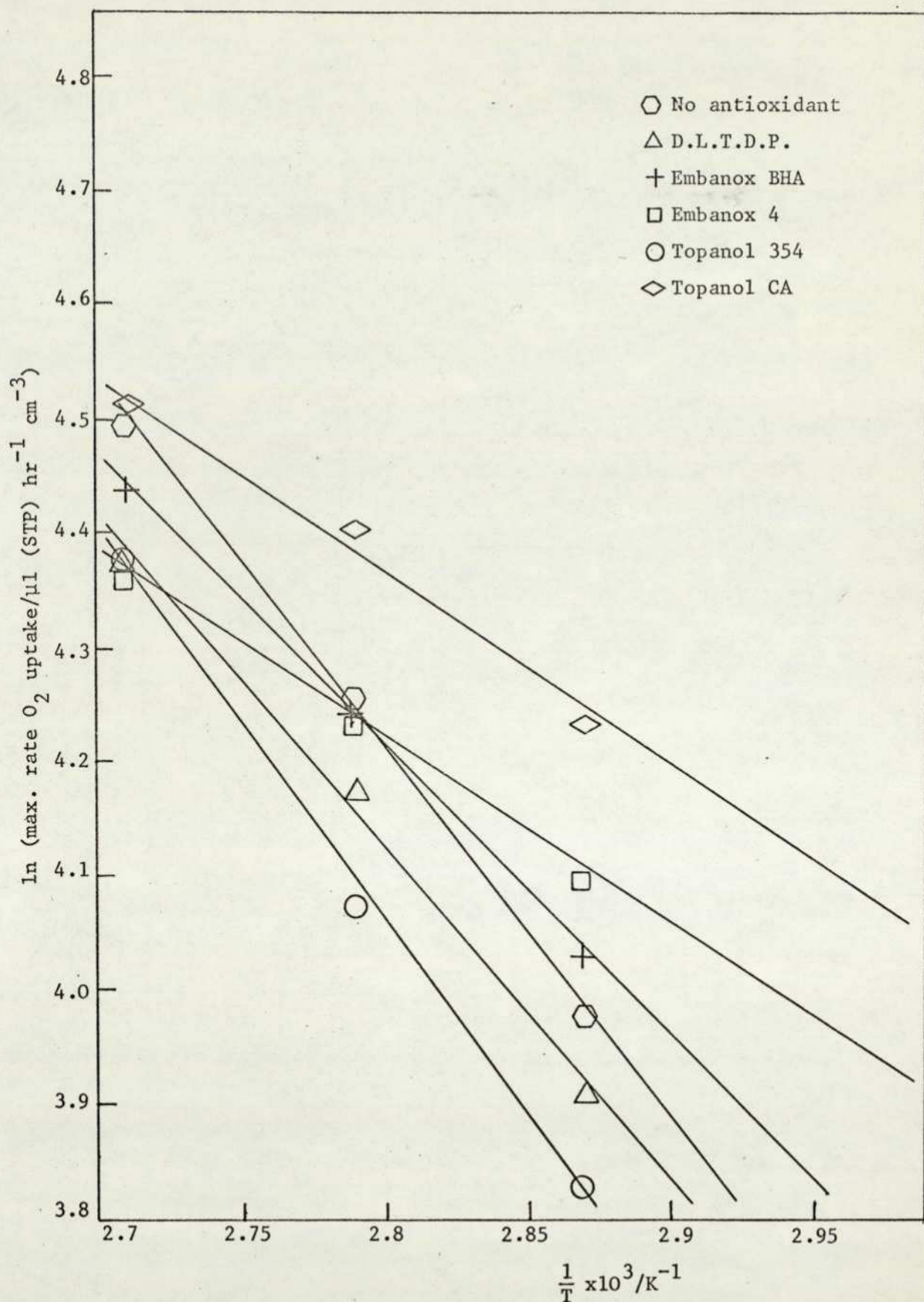


FIGURE 3.9

Arrhenius plots of the maximum rates of oxygen absorption for oleic acid samples containing 5% by weight of linolenic acid and various antioxidants at $2 \times 10^{-4} \text{ mol dm}^{-3}$ concentration.

at temperatures of 75°C and below they markedly increase the rate of oxygen absorption of the substrate. For samples containing Topanol 354 or D.L.T.D.P. as antioxidants, however, the efficiency for the reduction of the rates of oxygen absorption is operative even at lower temperatures.

The activation energies obtained from the Arrhenius plots of the maximum rates of oxygen absorption of oleic acid samples containing different weight percentages of linoleic and linolenic acid impurities are given in Tables 3.28 and 3.29 respectively.

TABLE 3.28

Activation energies (KJ mol^{-1}) for maximum rates of oxygen uptake of oleic acid samples containing different percentages of linoleic acid.

LINOLEIC ACID %	10%	5%	2.5%	1%	Negligible
ANTIOXIDANT					
No antioxidant	45.3	64.2	76.0	79.9	84.1
D.L.T.D.P.	38.0	63.1	75.1	78.5	85.2
Embanox BHA	19.8	43.1	61.7	63.1	72.1
Embanox 4	12.7	26.7	37.5	41.7	43.7
Topanol 354	60.8	79.4	90.9	95.7	99.9
Topanol CA	46.7	61.0	69.1	72.8	73.2

TABLE 3.29

Activation energies (KJ mol^{-1}) for maximum rates of oxygen uptake of oleic acid samples containing different percentages of linolenic acid.

LINOLENIC ACID %	10%	5%	2.5%	1%	Negligible
ANTIOXIDANT					
No antioxidant	37.3	54.6	67.0	83.8	84.1
D.L.T.D.P.	39.8	56.0	61.5	74.4	85.2
Embanox BHA	39.6	49.3	55.7	70.2	72.1
Embanox 4	19.5	31.8	35.7	39.6	43.7
Topanol 354	56.0	66.5	65.2	86.6	99.9
Topanol CA	13.3	35.2	36.8	58.2	73.2

The values given in Tables 3.28 and 3.29 show a sharp drop in the activation energies as the concentration of polyunsaturated impurity is increased. Mostly, activation energies are halved with the presence of 10% impurity, and in some cases (e.g. with linoleic acid in conjunction with Embanox 4) the activation energy is reduced by a factor of 3.

3.4 SYNERGISM IN ANTIOXIDANT ACTION.

3.4.1 Combination of Two Antioxidants.

In these experiments the synergistic effects for the two following systems were investigated at 85°C on the Automatic Oxygen Absorption Recording Apparatus:

- (i) - Dilaurylthiodipropionate (D.L.T.D.P.) plus one of each of the other

antioxidants.

Solutions of oleic acid and oleyl alcohol containing 2×10^{-4} mol dm⁻³ concentration of D.L.T.D.P. were prepared in bulk. Using these solutions the sample solutions were made up containing 2×10^{-4} mol dm⁻³ concentration of one of each of the other antioxidants.

(ii) - Embanox 4 (which itself is already a synergistic combination of monophenolic Embanox BHA (20%) mixed with citric acid (20%) in propylene glycol) with trisphenolic Topanol CA antioxidant.

The solutions of oleic acid and oleyl alcohol with the two antioxidants were prepared in such a way that the concentration of each antioxidant was 2×10^{-4} mol dm⁻³ with respect to the substrate, and 1 cm³ duplicate samples of these solutions were used. The induction periods obtained from these experiments are given in Table 3.30 (section 3.4.2).

3.4.2 Combination of Three Antioxidants.

The effect of synergism for the following combinations of antioxidants were investigated at 85°C:

- (i) - D.L.T.D.P. + Embanox 4 + Topanol CA.
- (ii) - D.L.T.D.P. + Embanox 4 + Topanol 354.
- (iii) - D.L.T.D.P. + Embanox BHA + Topanol CA.
- (iv) - D.L.T.D.P. + Embanox BHA + Topanol 354.

In every case, the concentration of each individual antioxidant was fixed at 2×10^{-4} mol dm⁻³ with respect to the substrate. Since D.L.T.D.P. was the common antioxidant in all these experiments, stock solutions of oleic acid and oleyl alcohol containing 2×10^{-4} mol dm⁻³ concentration of D.L.T.D.P. were prepared in advance. Appropriate quantities of each of the other antioxidants were weighed in volumetric flasks and the final solutions

were made up by the direct addition of the stock solutions of oleic acid or oleyl alcohol to each flask. The flasks were shaken thoroughly using a mechanical shaker to ensure complete dissolution of the antioxidants, and the experiments were then carried out in the usual way. The induction period obtained for each of these systems are given in Table 3.30 together with the induction period for each individual antioxidant at 85°C.

TABLE 3.30

Induction periods (hr) obtained for each antioxidant and the synergistic combination of antioxidants at 85°C.

ANTIOXIDANT	OLEIC ACID			OLEYL ALCOHOL		
	IP_o^*	$IP_e^\dagger$	$\frac{IP_o}{IP_e}$	IP_o^*	$IP_e^\dagger$	$\frac{IP_o}{IP_e}$
No antioxidant	1.8			2.3		
DLTDP	2.1			2.5		
Embanox BHA	39.1			43.5		
Embanox 4	46.3			101.1		
Topanol 354	16.8			40.2		
Topanol CA	34.0			45.1		
DLTDP + Embanox BHA	46.6	41.2	1.13	51.3	46.0	1.11
DLTDP + Embanox 4	53.2	48.4	1.09	118.4	103.6	1.14
DLTDP + Topanol 354	22.4	18.9	1.18	49.5	42.7	1.15
DLTDP + Topanol CA	43.0	36.1	1.19	57.9	47.6	1.21
Embanox 4 + Topanol CA	92.2	80.3	1.14	225.5	146.2	1.54
DLTDP+Embanox BHA+Topanol 354	71.4	58.0	1.23	184.0	86.2	2.13
DLTDP+Embanox BHA+Topanol CA	93.8	75.2	1.24	136.6	91.1	1.49
DLTDP+Embanox 4+Topanol 354	81.7	65.2	1.25	291.9	143.8	2.02
DLTDP+Embanox 4+Topanol CA	97.1	82.4	1.17	277.2	148.7	1.86

* IP_o = Observed induction period.

† IP_e = Expected induction period calculated by summing induction periods for each antioxidant when used alone.

From Table 3.30, it appears that, for all the antioxidant combinations which were investigated some degree of synergism is obtained, and none of the mixtures show antagonistic effects. In the case of the combination of two antioxidants a mild synergistic effect is shown which is fairly comparable in both substrates. For the triple antioxidant combinations while there is no drastic change in the induction periods of oleic acid samples, some significant synergisms (which in some cases are more than 100%) are achieved for samples of oleyl alcohol.

Considering the typical reactions taking place in an autoxidation system (section 3.3.1.4), however efficient a free-radical inhibitor may be at suppressing reaction 3.5, some hydroperoxide is bound to be formed from reaction 3.7 if from no other source. If this hydroperoxide is destroyed by a peroxide decomposer before it can decompose into free-radicals, the effectiveness of the free-radical inhibitor will be increased. Furthermore, since the peroxide decomposer may itself be subject to attack by peroxy radicals^{47,98}, its own effectiveness is also improved by the free-radical inhibitor. It is clear, therefore, that a free-radical inhibitor and a peroxide decomposer play complementary roles in inhibiting autoxidation reactions. The highly hindered phenols such as Topanol CA, Topanol 354, and Embanox BHA are quite strong inhibitors, but are very inactive peroxide decomposers. Their rate of reaction with peroxides is, in fact, sufficiently small that the reaction can be neglected in oil autoxidations²⁰⁰, and they can, therefore, be considered to function solely as free-radical traps. The results given in Table 3.30 show that mixtures containing these antioxidants always exhibit true synergism which suggest that the second inhibitor (D.L.T.D.P. or Embanox 4) is functioning as a peroxide decomposer. This behaviour of D.L.T.D.P. as an active synergist is consistent with the findings of Neureiter and Brown²⁰¹ who discovered that amongst all the sulphur

containing antioxidants which they investigated, D.L.T.D.P. showed the most outstanding synergistic activity.

The anomalously large synergistic effect which is shown for the triple antioxidant combinations in the case of oleyl alcohol may be due to the formation of primary products which are themselves inhibitors in oleyl alcohol. Also the favourable synergistic antioxidant combination of Embanox 4 for oleyl alcohol is a major factor influencing the results obtained for oleyl alcohol.

3.5 SYNTHESES OF NEW NICKEL CHELATES.

In order to investigate the inhibiting effect of bis (stilbene dithiolato) nickel (II), (NiSDT) compounds in more detail, and to examine the effects of changes in structure upon inhibition efficiency, the need arose for the preparation of certain para-substituted NiSDT compounds. For this reason, the syntheses of bis (di-p-isopropyl stilbene dithiolato) Ni(II) (DIP-NiSDT) and bis (di-p-tert.butyl stilbene dithiolato) Ni(II), (DTB-NiSDT) were carried out.

3.5.1 Bis (di-p-isopropyl stilbene dithiolato) Ni (II).

The di-p-isopropyl benzoin intermediate necessary for this synthesis was prepared by the condensation of cuminic aldehyde as described in the previous section (section 2.2.10.2). After purification the benzoin was reacted with phosphorous pentasulphide and the mixture heated with a solution of nickel chloride as described before (section 2.2.10.2). A yield of 34 g. of DIP-NiSDT was obtained which melted with decomposition at 294°C. The structure of the compound was confirmed from its nmr and ir spectra. In the high resolution nmr spectrum (Fig. 3.10), as was expected, the aromatic

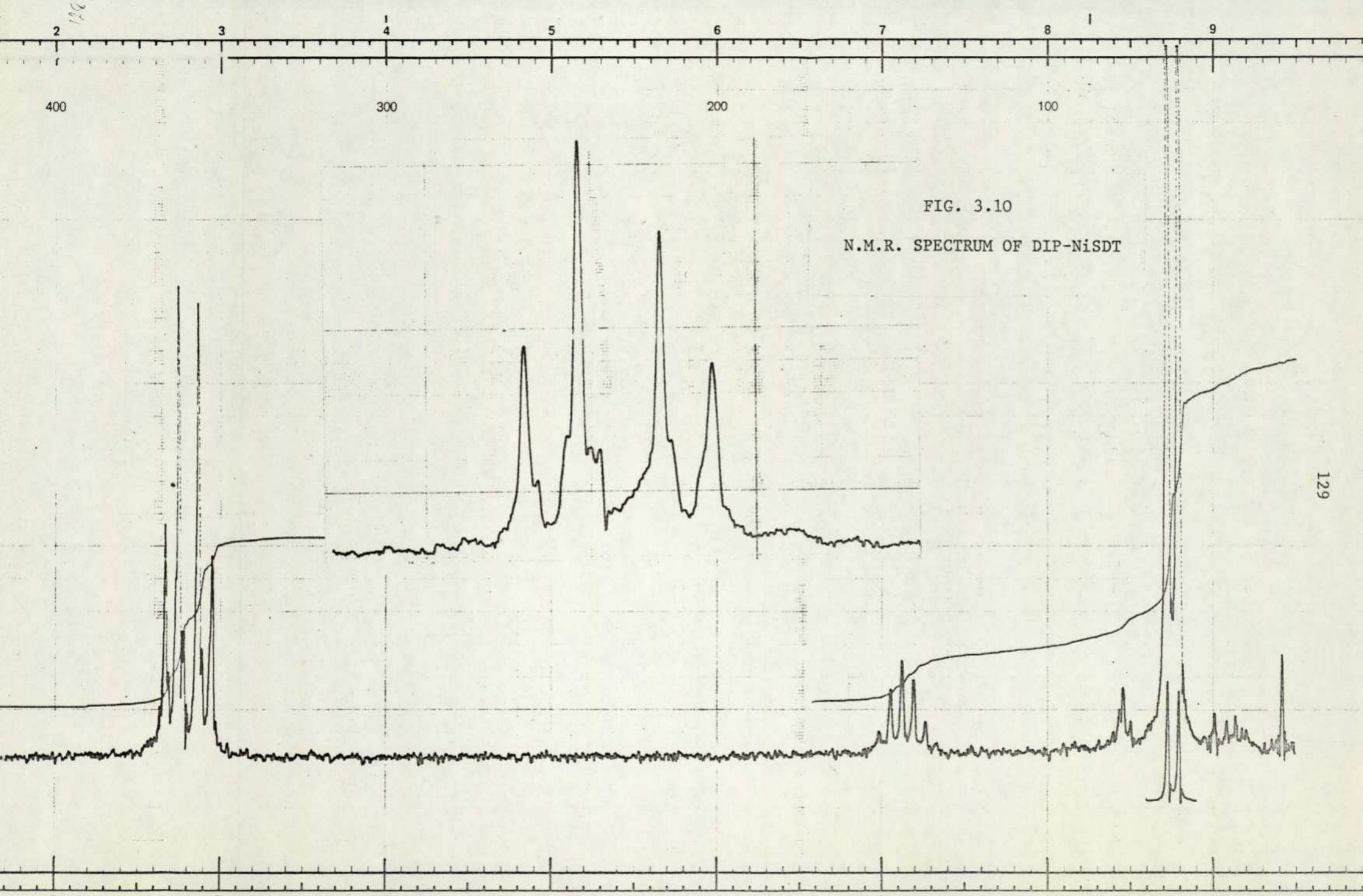
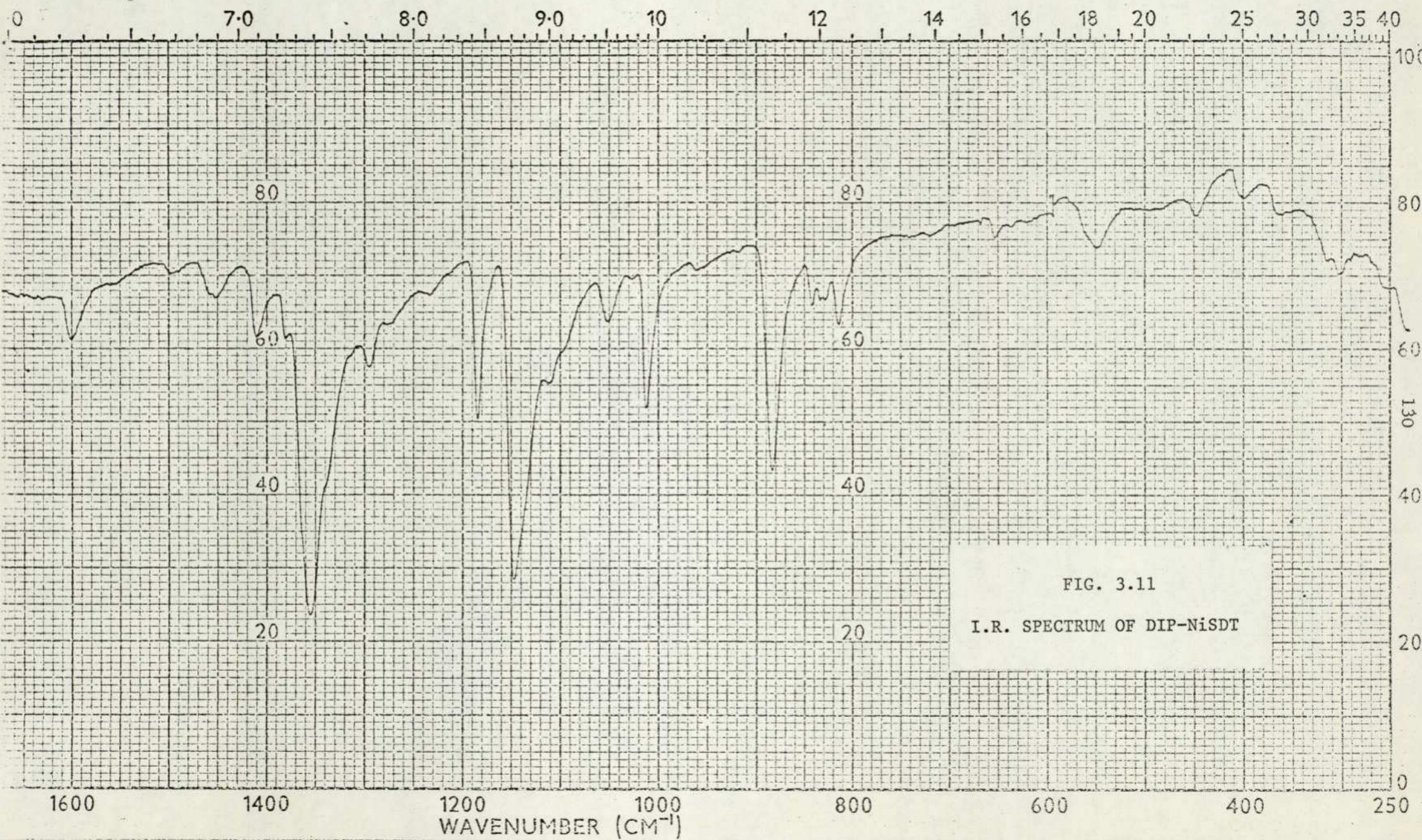


FIG. 3.10
N.M.R. SPECTRUM OF DIP-NiSDT

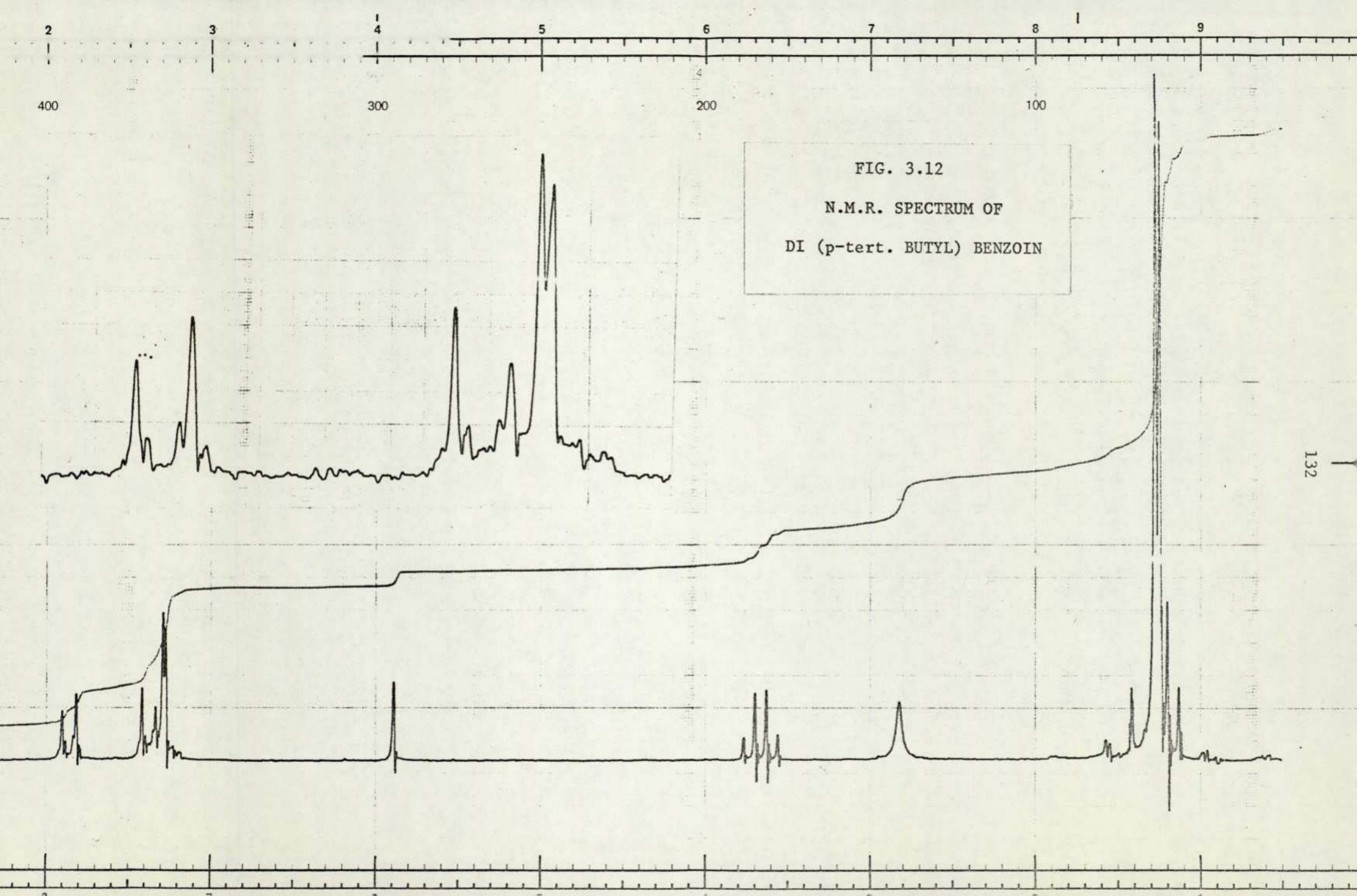


protons were split into doublets with coupling constant, $J_{ab} = 8 \text{ Hz}$ (expected value of J for the para-positions is 6 - 9 Hz). The peak at 7.6τ (heptet) was assigned to the single proton of the isopropyl group while the protons of the methyl groups were shown by the doublet at 8.76τ . In the ir spectrum from a KBr disc (Fig. 3.11) the characteristic peaks (section 2.2.10.1) occurred at $\omega_1 = 1355 \text{ cm}^{-1}$, $\omega_2 = 1148 \text{ cm}^{-1}$, and $\omega_3 = 882 \text{ cm}^{-1}$. The absorption bands and their extinction coefficients obtained from the electronic spectrum of DIP-NiSDT are given in Table 3.31 (section 3.5.3).

3.5.2 Bis (di-p-tert.butyl stilbene dithiolato) Ni (II).

Since none of the intermediate compounds necessary for this synthesis was commercially available, p-tert.butyl toluene was chosen as the starting material (section 2.2.10.3). 75 g. of the toluene were brominated exclusively at the methyl group. The p-tert.butylbenzyl bromide (I) (64 g.) was oxidised to the aldehyde (II) using hexamethylenetetramine (Sommeletts' Reaction). The benzoin condensation of the p-tert.butylbenzaldehyde (22 g.) yielded 11g. of faintly yellow needle-like crystals of di (p-tert.butyl) benzoin (III), melting at 172.6°C . The structure was confirmed from the nmr and ir spectra analysis. In the high resolution nmr (Fig. 3.12) the aromatic protons are split three ways with the peaks at $2.1 - 2.2\tau$ and 2.5τ being due to the protons of the phenyl ring adjacent to the $\text{C} = \text{O}$ group and the doublet at 2.7τ due to the protons of the second phenyl group. The single peak at 4.11τ was assigned to the isolated hydrogen atom and the peak at 7.18τ was that of the OH group. The tertiary butyl protons appear as a doublet at $8.71-3\tau$.

Bis (di-p-tert.butyl stilbene dithiolato) nickel (II) was prepared by first reacting di(p-tert.butyl) benzoin with phosphorous pentasulphide



in 1,4-dioxan, and heating the ester (IV) with an aqueous solution of nickel chloride. Green crystals (5 g.) of DTB-NiSDT (V) were obtained which melted with decomposition at 328.5°C . The structure was confirmed from the high resolution nmr (Fig. 3.13) and ir (Fig. 3.14) spectra analysis. Interpretation of the nmr spectrum was very simple, with the peak at 2.72τ being assigned to the aromatic protons (not affected by the tert.butyl group) and the peak at 8.69τ being due to the protons of the methyl groups of the tert.butyl substituents. (The small peak at 2.79τ was due the chloroform impurity present in the deuterated chloroform which was used as the solvent).

In the ir spectrum the characteristic bands (section 2.2.10.1) occurred at $\omega_1=1350\text{ cm}^{-1}$, $\omega_2=1140\text{ cm}^{-1}$, and $\omega_3=880\text{ cm}^{-1}$. The absorption bands, together with their extinction coefficients, of the electronic spectrum are given in Table 3.31 (section 3.5.3). A reaction scheme for the preparation of bis (di-p-tert.butyl stilbene dithiolato) nickel (II) is presented on the next page.

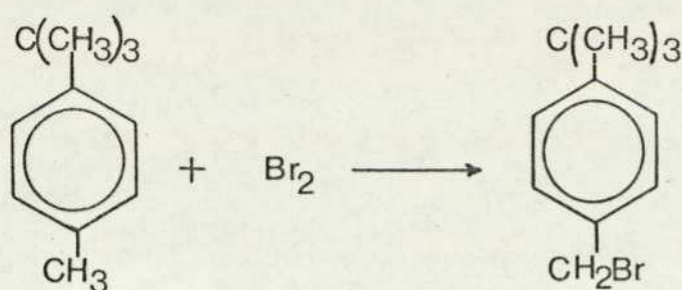
3.5.3 Visible and U.V. Absorption Spectra of the Nickel Chelates.

The positions and the extinction coefficients for the characteristic absorption bands of the nickel chelate and its para-substituted compounds, used in this work, are given in Table 3.31. The visible and uv spectra of these compounds in chloroform were obtained on a Hitachi Perkin-Elmer EPS-3T drum recording spectrophotometer, using 0.1 cm cells.

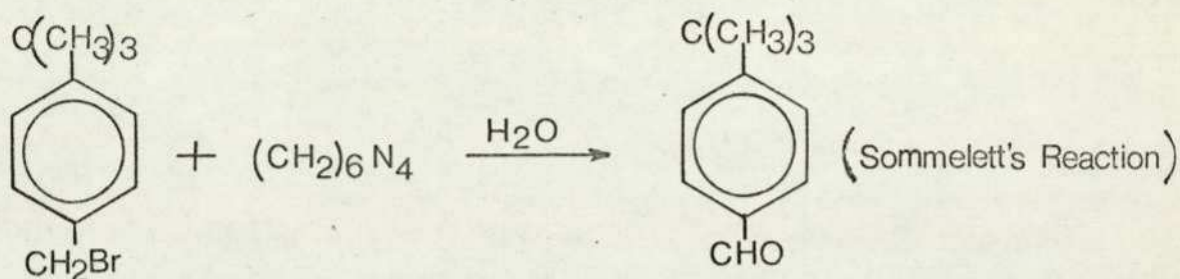
The spectra obtained and the extinction coefficients were in close agreement with literature values wherever the latter were available. The extremely high values of the extinction coefficients for the visible region bands of these compounds implies that even extremely dilute solutions are quite strongly coloured; this factor may be a limitation in practical

REACTION SCHEME FOR THE PREPARATION OF DTB-NiSDT

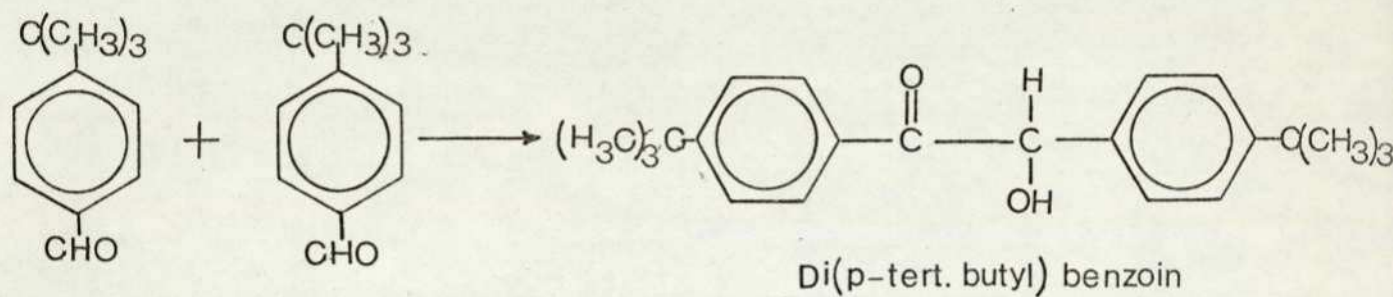
II)



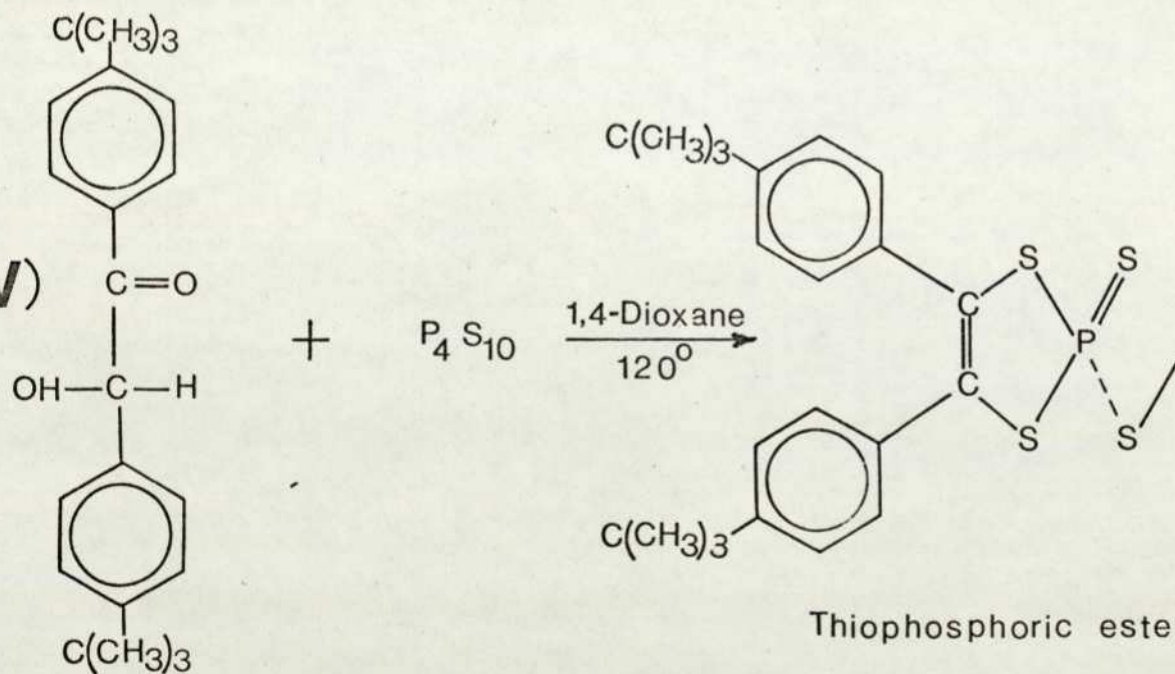
III)



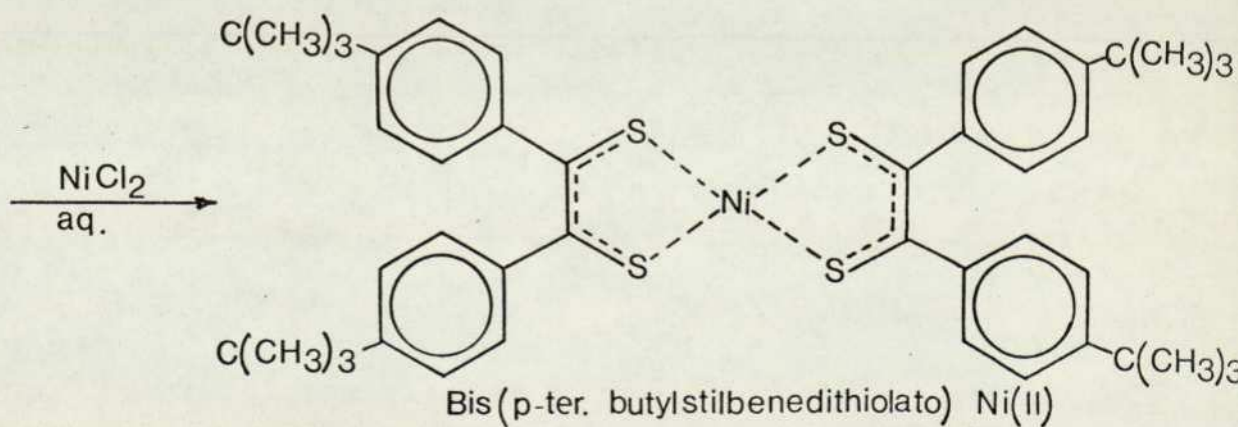
IV)



IV)



(V)



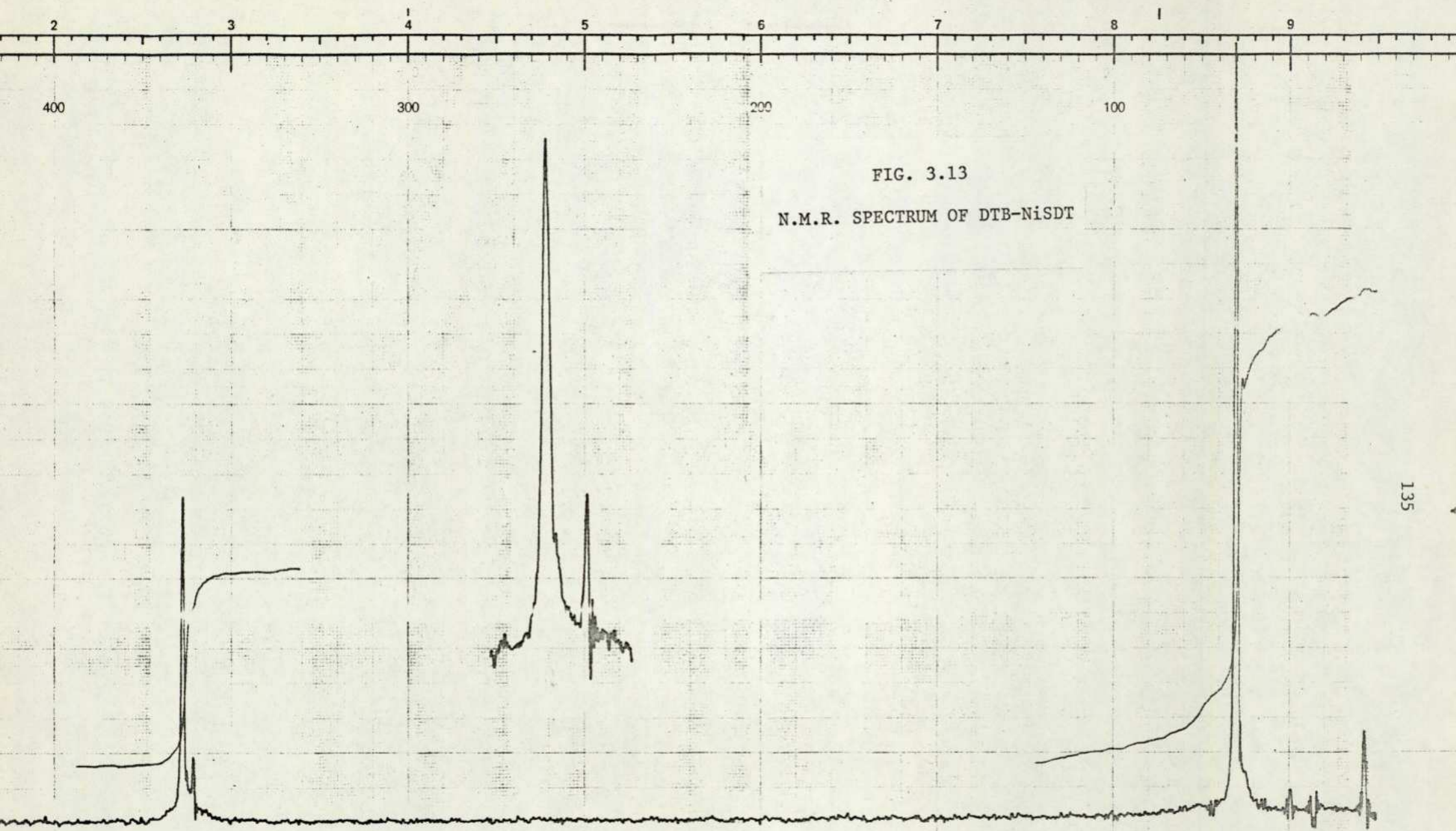
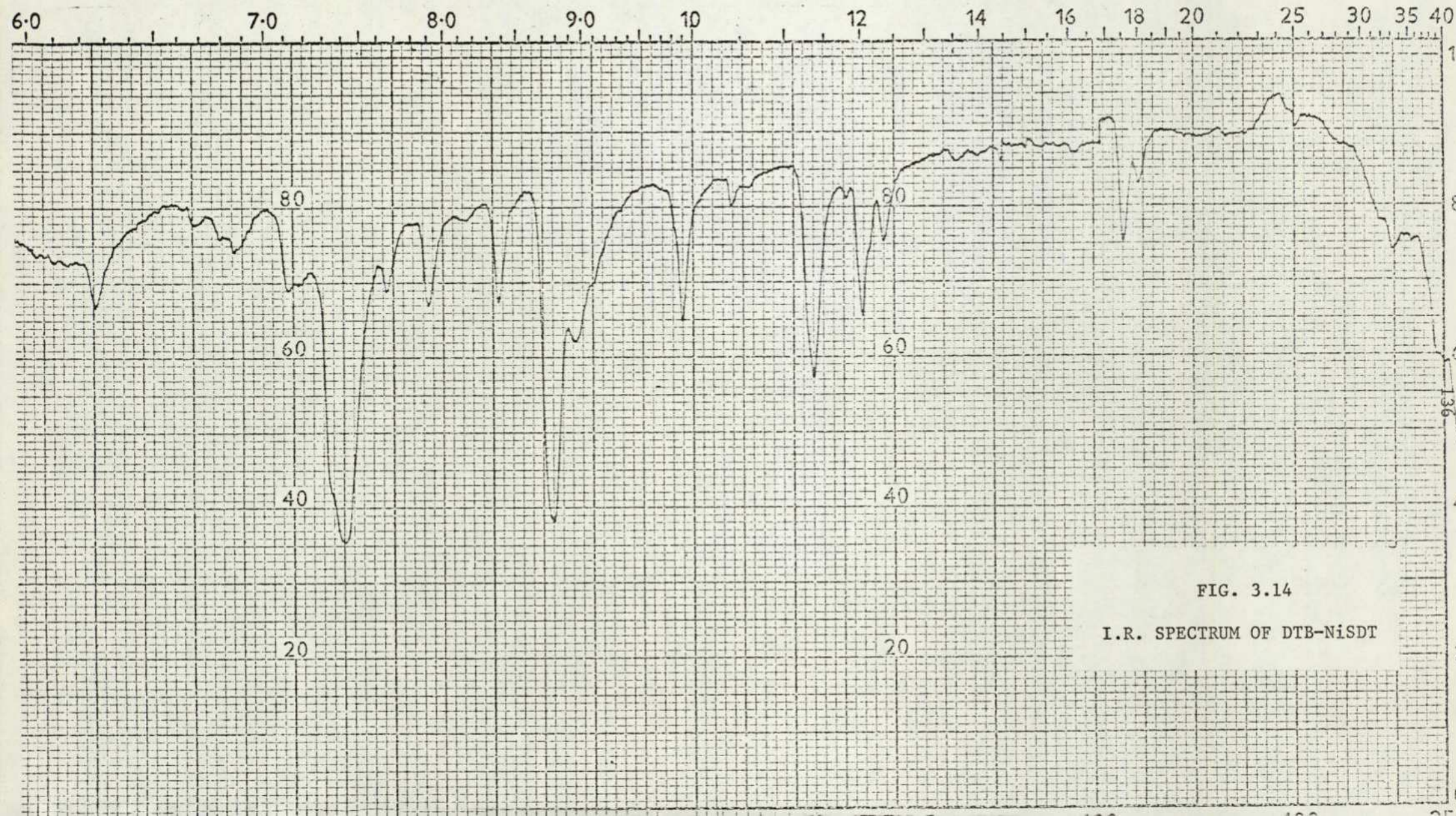


FIG. 3.13
N.M.R. SPECTRUM OF DTB-NiSDT



use of these compounds.

TABLE 3.31

Values of λ_{max} . (nm) for the principal absorption bands of NiSDT and its para-substituted derivatives. Values of $\log \epsilon$ are indicated in parentheses.

NICKEL CHELATE	ν_1	ν_2	ν_3	ν_4	ν_5
NiSDT	865(4.49)	602(3.31)	317(4.71)	271(4.55)	
DIP-NiSDT	895(4.54)	595(3.54)	320(4.72)	278(4.66)	236(4.53)
DTB-NiSDT	896(4.47)	625(3.39)	324(4.64)	277(4.59)	237(4.44)
Cl-NiSDT	870(4.53)	605(3.54)	322(4.72)	278(4.66)	237(4.54)
MeO-NiSDT	930(4.57)	635(3.38)	332(4.56)	303(4.70)	285(4.66)

3.6 SOLUBILITY OF NICKEL CHELATES.

A series of solubility tests was carried out on the nickel chelate inhibitors, using different solvents (see section 2.4.2). The values of the maximum solubility (in molar concentration) for each of the nickel chelates in chloroform, ethyl benzoate, oleic acid, and oleyl alcohol are given in Table 3.32.

Clearly the introduction of hydrocarbon substituents has a beneficial effect on the solubility of the complexes in the fatty substrates, while polar substituents markedly reduce the solubility. From these solubility data it was concluded that, with the exception of MeO-NiSDT, all the other nickel complexes have a greater solubility than $2 \times 10^{-4} \text{ mol dm}^{-3}$ in oleic

acid and oleyl alcohol. These chelates could, therefore, be incorporated in these fatty substrates up to concentrations of 2×10^{-4} mol dm⁻³ without the need for a carrier solvent.

TABLE 3.32

Maximum solubility ($\times 10^{-4}$ mol dm⁻³) for various nickel chelates in chloroform, ethyl benzoate, oleic acid, and oleyl alcohol at room temperature.

COMPOUND	CHLOROFORM	ETHYL BENZOATE	OLEIC ACID	OLEYL ALCOHOL
NiSDT	37	14	5.0	2.7
DIP-NiSDT	48	19	5.4	3.1
DTB-NiSDT	51	20	5.7	3.2
Cl-NiSDT	39	11	4.6	2.2
MeO-NiSDT	17	8.8	1.2	0.7

3.7 KINETIC STUDIES WITH NICKEL CHELATE ANTIOXIDANTS.

3.7.1 Experiments Without Carrier Solvent.

In this series of experiments the inhibiting effect of NiSDT and its para-substituted derivatives on oleic acid and oleyl alcohol was investigated at different temperatures. While the Warburg apparatus was used for the measurement of the induction periods and the rates of oxygen absorption the determination of the kinetics of consumption of these chelates was carried out using Shaking Reaction Incubators.

3.7.1.1 Experiments Using Warburg Apparatus.

Solutions containing 2×10^{-4} mol dm⁻³ concentration of NiSDT and its para-substituted compounds were prepared from the more concentrated bulk solutions. 1 cm³ samples were placed in the reaction flasks and immersed in the Warburg baths, set at temperatures 65°, 75°, and 85°C. The induction periods and the maximum rates of oxygen absorption which were measured for each sample are given in Table 3.33 for oleic acid and oleyl alcohol.

TABLE 3.33

Induction periods and maximum rates of oxygen absorption (corrected to STP) obtained for samples of oleic acid and oleyl alcohol with different nickel chelates at 65°, 75°, and 85°C.

The induction periods (IP) are given in hours and the maximum rates of oxygen absorption (RATE) are given in $\mu\text{l (STP) hr}^{-1} \text{ cm}^{-3}$.

SUBSTRATE	CHELATE	65°C		75°C		85°C	
		IP	RATE	IP	RATE	IP	RATE
Oleic acid	-	-	-	4.1	36.1	1.8	46.8
	NiSDT	21.5	109.1	15.0	117.2	9.0	125.3
	DIP-NiSDT	18.5	113.2	11.4	122.1	6.5	130.6
	DTB-NiSDT	51.0	96.4	27.5	102.0	18.0	107.8
	Cl-NiSDT	41.5	99.2	24.0	106.8	13.5	114.3
Oleyl alcohol	-	-	-	-	-	2.4	31.0
	NiSDT	175.0	62.8	88.0	69.1	56.5	76.3
	DIP-NiSDT	163.2	65.7	77.0	74.3	45.5	83.4
	DTB-NiSDT	214.6	57.3	121.5	63.9	68.1	70.5
	Cl-NiSDT	182.0	62.0	93.0	68.7	52.0	75.6

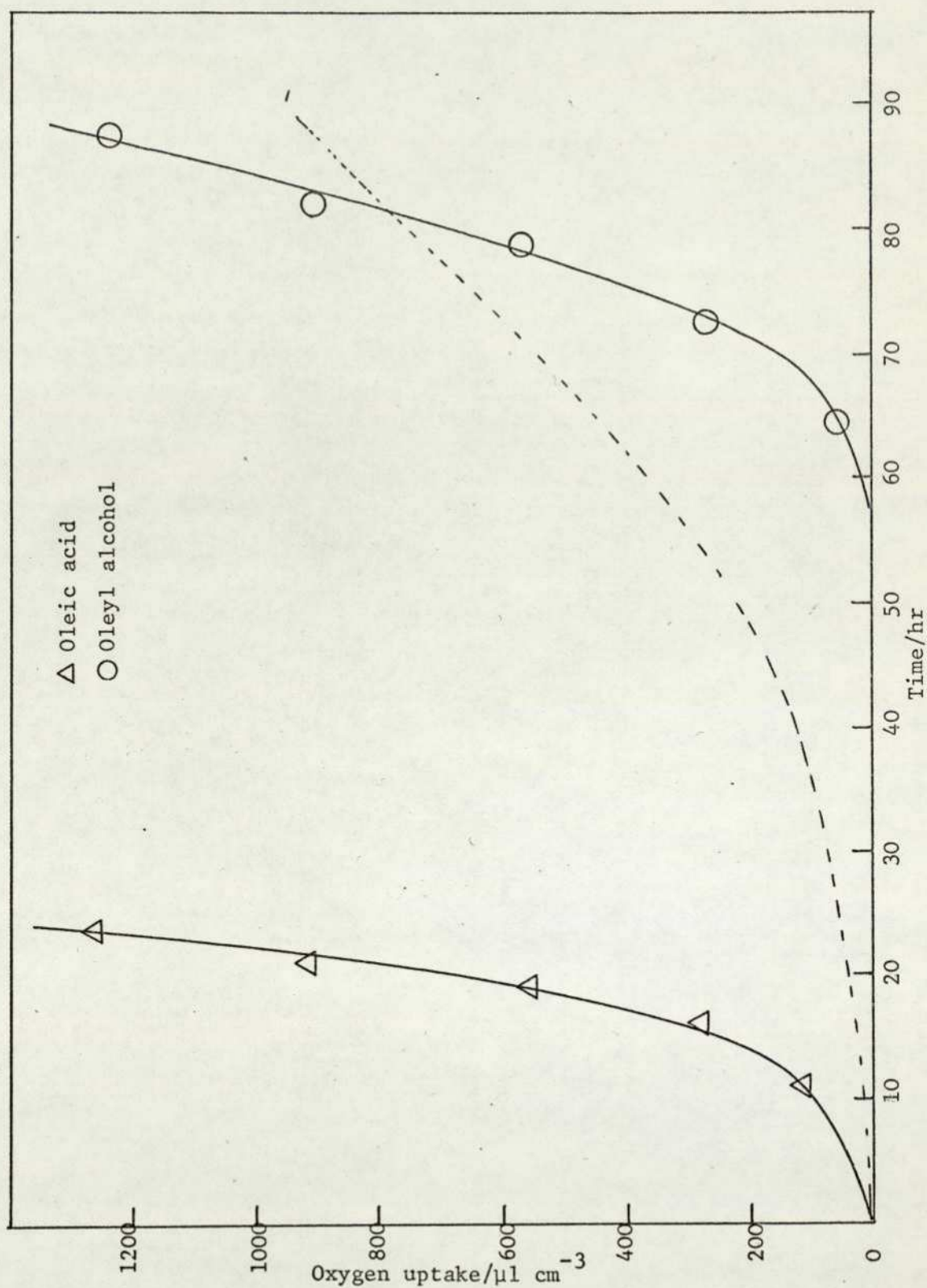


FIGURE 3.15

Typical oxygen uptake graphs for samples of oleic acid and oleyl alcohol containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ DTB-NiSDT at 85°C .

Dotted line represents the O_2 uptake of oleyl alcohol containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Topanol CA at 85°C .

Since the concentration of the nickel chelate antioxidants used in this set of experiments, i.e. $2 \times 10^{-4} \text{ mol dm}^{-3}$, is the same as the concentration of the conventional antioxidants which were used in the parallel set of experiments previously (section 3.3.1.2), it is possible to compare and contrast these results, particularly those obtained at 85°C , directly with those given in Tables 3.5 and 3.7 for oleic acid and oleyl alcohol. It is evident that the antioxidant efficiency of the nickel chelate antioxidants, as indicated by the induction periods is rather poor compared to the conventional phenolic antioxidants for oleic acid solutions. However, the chelates show much better efficiency in solutions of oleyl alcohol and, in fact, in most cases they are better inhibitors than the conventional mono- and tris-phenolic antioxidants.

Fig. 3.15 shows the typical oxygen uptake graphs for oleic acid and oleyl alcohol with DTB-NiSDT from which it can be seen that the ending of the induction period in system containing these nickel chelate antioxidants is extremely sharp compared with other inhibitors. This is consistent with the idea that free metal ions are released during the induction period and are able to catalyse the subsequent degradation. This conclusion is amply confirmed by the high rates of oxygen absorption indicated in these reactions and the comparatively low activation energies which are obtained for the post inhibition rates.

The activation energies for the induction periods and the maximum rates of oxygen absorption which were obtained from the Arrhenius plots for oleic acid and oleyl alcohol containing various nickel chelates are given in Table 3.34.

TABLE 3.34

Activation energies of induction periods (E_i) and maximum rates of oxygen absorption (E_r) for oleic acid and oleyl alcohol samples containing various nickel chelate antioxidants.

NICKEL CHELATE	OLEIC ACID		OLEYL ALCOHOL	
	$\frac{E_i}{\text{KJ mol}^{-1}}$	$\frac{E_r}{\text{KJ mol}^{-1}}$	$\frac{E_i}{\text{KJ mol}^{-1}}$	$\frac{E_r}{\text{KJ mol}^{-1}}$
No additive	159.4	89.1	-	-
NiSDT	95.7	27.4	125.2	28.2
DIP-NiSDT	119.7	30.7	143.6	29.8
DTB-NiSDT	117.0	24.4	126.4	22.1
Cl-NiSDT	126.0	26.6	143.6	25.0

3.7.1.2 Experiments Using Shaking Reaction Incubator.

Solutions containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ concentration of the nickel chelates prepared previously (section 3.7.1.1) were used for these experiments. 2.5 cm^3 samples were placed in stoppered Pyrex test tubes and immersed in the Shaking Reaction Incubator baths set at temperatures 65° , 75° , and 85°C . The fall in the concentration of the nickel chelates with time, which was measured spectrophotometrically, are shown in Figs. 3.16 - 3.18 for oleic acid at 65° , 75° , and 85°C , and in Figs. 3.19 - 3.21 for oleyl alcohol at 65° , 75° , and 85°C respectively.

The shapes of the curves implied that the order of the reactions

Fig. 3.16 - Concentration-time curves for oleic acid containing 2×10^{-4} nickel chelates at 65°C .

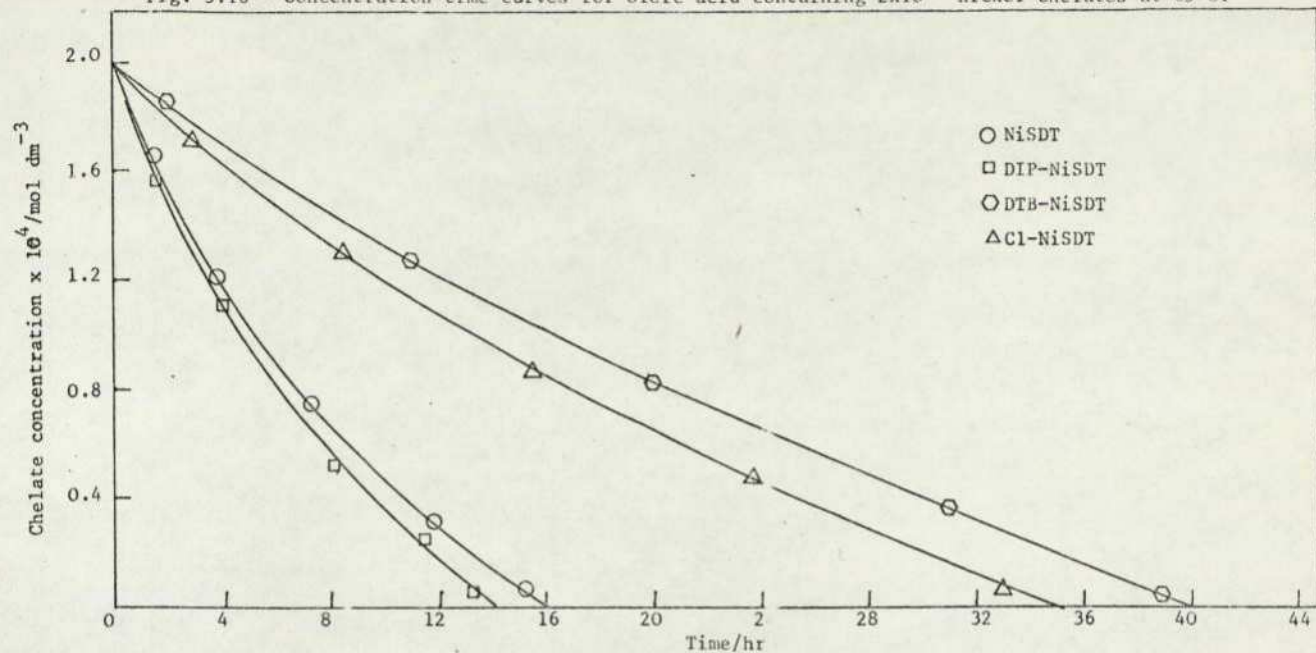


Fig. 3.17 - Concentration-time curves for oleic acid containing 2×10^{-4} nickel chelates at 75°C .

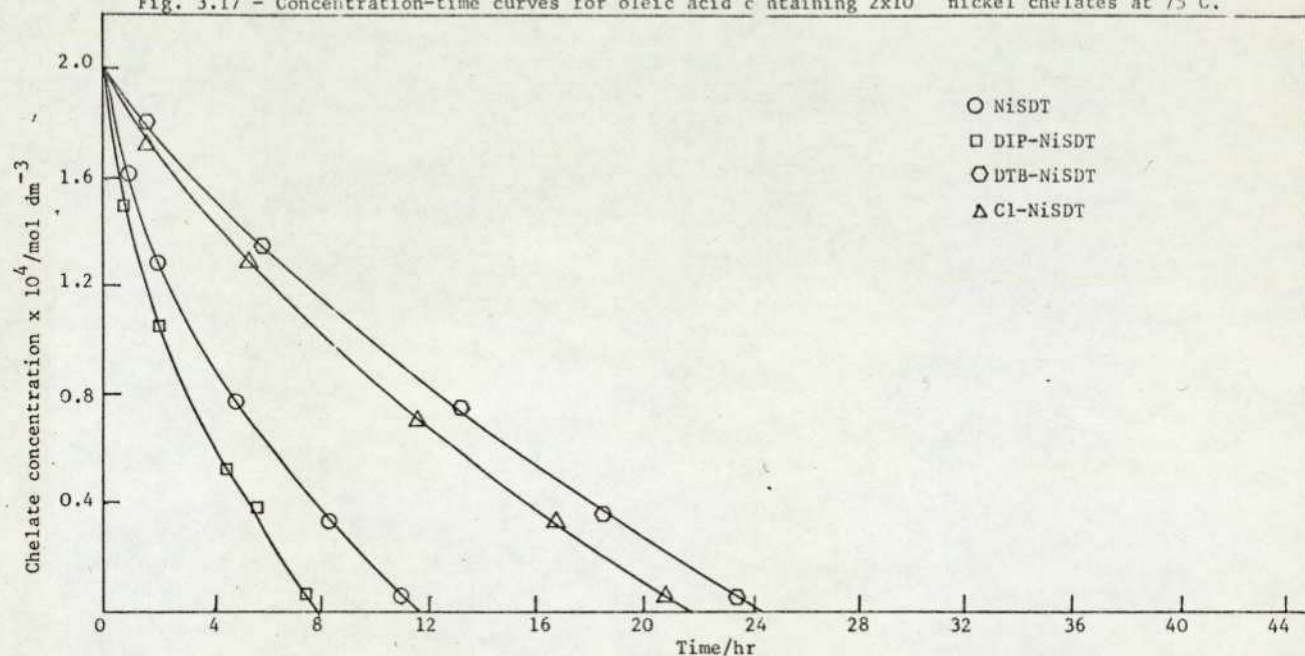


Fig. 3.18 - Concentration-time curves for oleic acid containing 2×10^{-4} nickel chelates at 85°C .

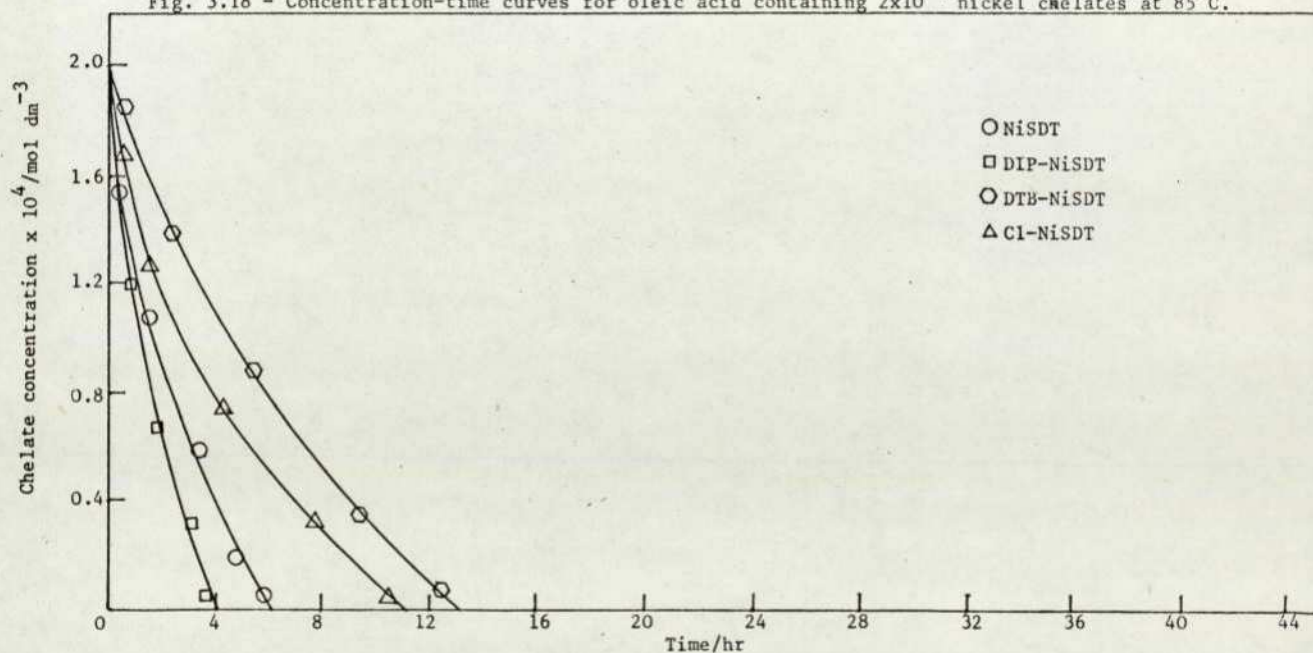


Fig. 3.19 - Concentration-time curves for oleyl alcohol containing 2×10^{-4} nickel chelats at 65°C .

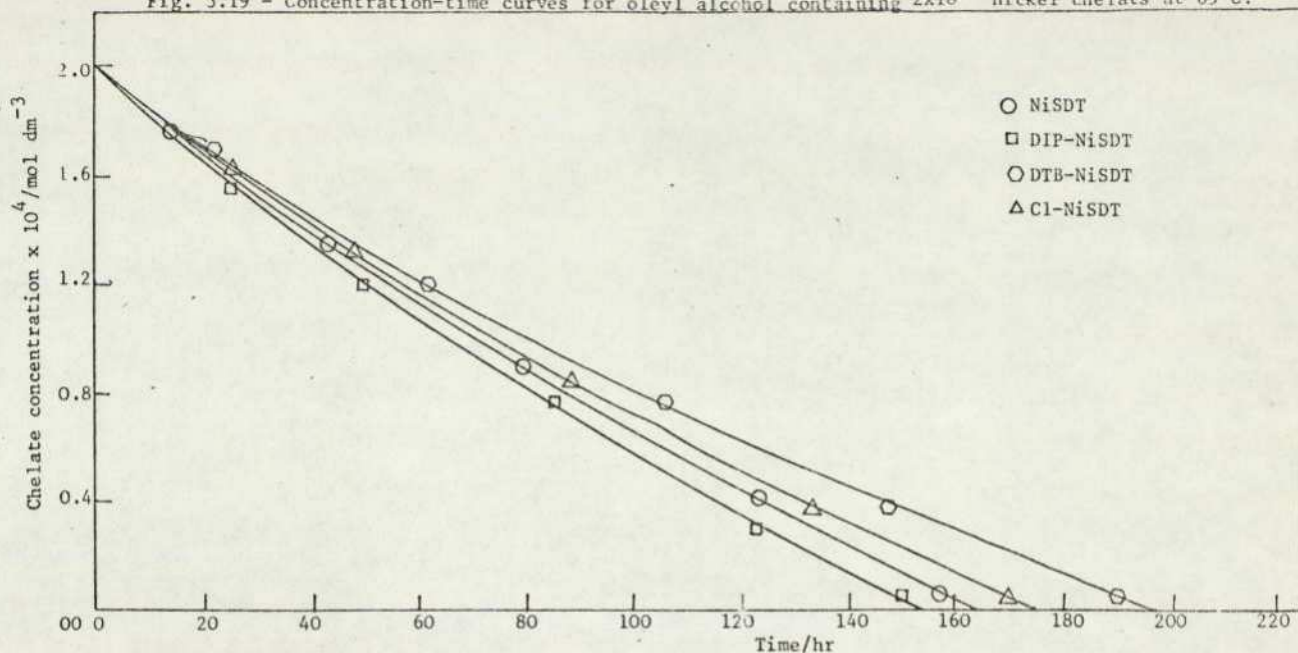


Fig. 3.20 - Concentration-time curves for oleyl alcohol containing 2×10^{-4} nickel chelates at 75°C .

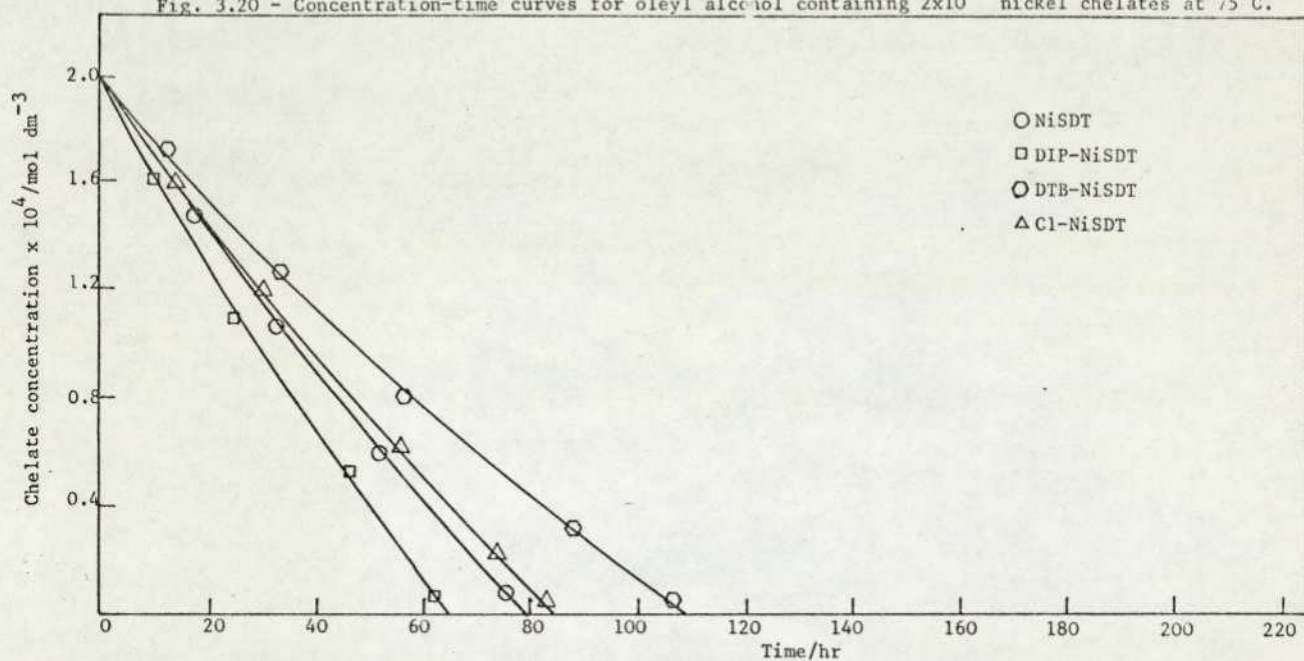
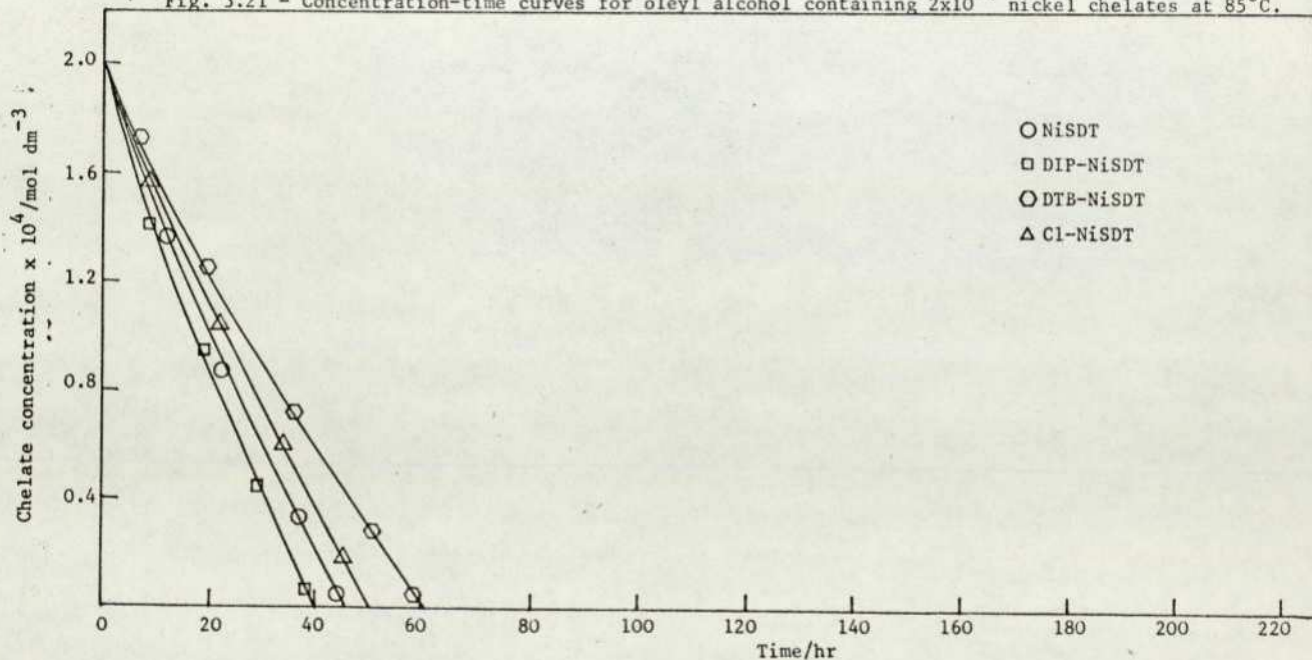


Fig. 3.21 - Concentration-time curves for oleyl alcohol containing 2×10^{-4} nickel chelates at 85°C .



was non-zero. The data for the consumption of the nickel chelates with time were, therefore, checked for 1st.-order, 2nd.-order, and half-order reactions. In the case of graphs plotted as tests for first-order or second-order reactions a linear relationship was observed only for the first 40% consumption after which a sharp deviation from this linearity occurred. In the case of graphs plotted as a test for half-order reactions, however, a straight line was obtained for more than 75% of the chelate consumption, suggesting that the reactions of these nickel chelate antioxidants in pure oleic acid and oleyl alcohol are closer to being half-order than to any other order of the reaction. Some typical plots for half-order reactions are shown in Fig. 3.22. The very steep fall observed in the graphs, after approximately 75% of the chelate has been consumed, can be attributed to the autocatalytic nature of the autoxidation process of the fatty substrates, owing to the significant increase in the number of branching reactions occurring simultaneously, and is almost certainly exaggerated by the catalytic effect of the free metal ions released during the chelate consumption.

The rate constants obtained from the graphs of the square roots of the concentration of the chelate against time are given in Table 3.35 for oleic acid and oleyl alcohol at the three different temperatures at which the experiments were performed.

The pattern shown by the values of the rate constants for the half-order reactions is very similar to that shown by the activation energies given in Table 3.34. It is interesting to note that these K_r values are entirely consistent with the induction periods obtained previously (Table 3.33), which justifies the assumption of a half-order reaction taking place at least for the first 75% of the chelate consumption.

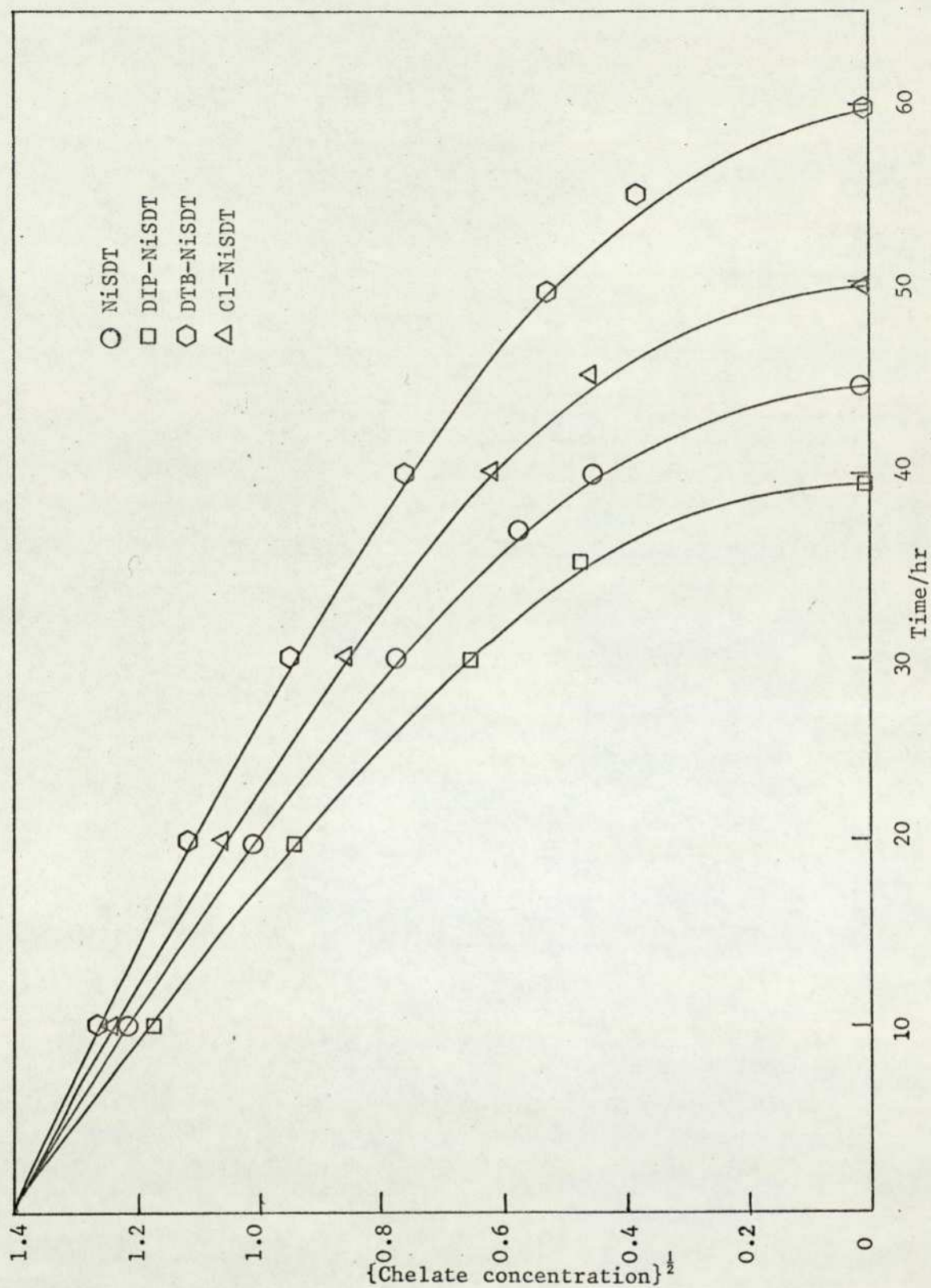


FIGURE 3.22

Typical graphs for half-order reactions of nickel chelate antioxidants in oleyl alcohol solutions tested at 85°C.

TABLE 3.35

Rate constants (K_r) obtained for the half-order reactions of the nickel chelates in oleic acid and oleyl alcohol at 65°, 75° & 85°C.

SUBSTRATE	CHELATE	K_r $10^{-4} \text{ mol}^{\frac{1}{2}} \text{ dm}^{-\frac{3}{2}} \text{ hr}^{-1}$		
		65°C	75°C	85°C
Oleic acid	NiSDT	3.54	4.87	9.50
	DIP-NiSDT	4.12	7.25	14.33
	DTB-NiSDT	1.01	2.20	4.30
	Cl-NiSDT	1.50	2.47	5.37
Oleyl alcohol	NiSDT	0.31	0.57	1.06
	DIP-NiSDT	0.33	0.76	1.25
	DTB-NiSDT	0.26	0.45	0.81
	Cl-NiSDT	0.29	0.54	0.91

It is worth noticing that the time taken for the complete consumption of the nickel chelates in oleic acid and oleyl alcohol appeared to be somewhat shorter than the induction periods which were indicated in the previous experiments (section 3.7.1.1). This time lapse between the total consumption of the nickel chelate antioxidants and the start of oxygen absorption by the samples (i.e. the end of the induction period) is given in Table 3.36 for each individual nickel complex.

Although these time intervals are not very long, nevertheless they are significant enough to suggest that the initial products of the

thermal autoxidation of these chelates in the fatty substrates are acting as inhibitors. Taken in conjunction with the previous arguments, the implication is that an initial oxidation of the chelate produces certain products which have low extinction coefficient values but are still antioxidants; subsequent decomposition, however, produces free metal ions which act catalytically.

TABLE 3.36

Comparison of the time taken for the complete consumption of nickel chelate antioxidants (T_c) and the corresponding induction periods (T_i) in oleic acid and oleyl alcohol at 65°, 75°, and 85°C.

SUBSTRATE	CHELATE	65°C		75°C		85°C	
		T_c /hr	T_i /hr	T_c /hr	T_i /hr	T_c /hr	T_i /hr
Oleic acid	NiSDT	16.0	21.5	11.9	15.0	6.1	9.0
	DIP-NiSDT	13.8	18.5	8.0	11.4	4.2	6.5
	DTB-NiSDT	39.8	51.0	24.0	27.5	13.2	18.0
	Cl-NiSDT	36.0	41.5	22.0	24.0	10.8	13.5
Oleyl alcohol	NiSDT	165.0	175.0	80.0	88.0	46.0	56.5
	DIP-NiSDT	154.5	163.5	66.5	77.0	39.5	45.5
	DTB-NiSDT	198.0	214.6	111.0	121.5	60.0	68.1
	Cl-NiSDT	171.0	182.0	84.0	93.0	49.0	52.0

Because of the limited solubility of NiSDT in the fatty substrates it was considered difficult to study the variation of the rate of its

consumption with the chelate concentration. Accordingly it was decided to use ethyl benzoate as a carrier solvent so that the rate of disappearance of the chelate could be studied as a function of the initial concentration of both substrates and chelate.

3.7.2 Kinetic Studies with Ethyl Benzoate as Carrier Solvent.

In this series of experiments ethyl benzoate was used as carrier solvent for the nickel chelate antioxidants. The use of ethyl benzoate as solvent not only enabled experiments with solutions of higher NiSDT concentrations to be used, but also permitted the investigation of the solutions containing different molarities of oleic acid or oleyl alcohol. Ethyl benzoate was chosen as a convenient solvent for the following reasons: (a) in its pure form it is fairly stable against autoxidation, (b) it is a good solvent for long-chain fatty acids and their derivatives, and also for most antioxidants, (c) it has a low vapour pressure even at elevated temperatures, and would thus allow an easy and accurate measurement of the oxygen uptake of the autoxidation reactions.

In one set of experiments, solutions containing 1 mol dm^{-3} of oleic acid or oleyl alcohol in ethyl benzoate were prepared. NiSDT was then introduced in these solutions at concentrations of 2×10^{-4} , 2.5×10^{-4} , 3.3×10^{-4} , and $5 \times 10^{-4} \text{ mol dm}^{-3}$. 2.5 cm^3 samples of each mixture were studied using the Shaking Reaction Incubator at 85°C in the usual way. Fig. 3.23 represents the results obtained for solutions of oleic acid and oleyl alcohol when the fall in the concentration of NiSDT is plotted against time.

In the second set of experiments, solutions containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ of NiSDT and various concentrations of oleic acid or oleyl alcohol in ethyl benzoate were prepared. The molar concentrations of

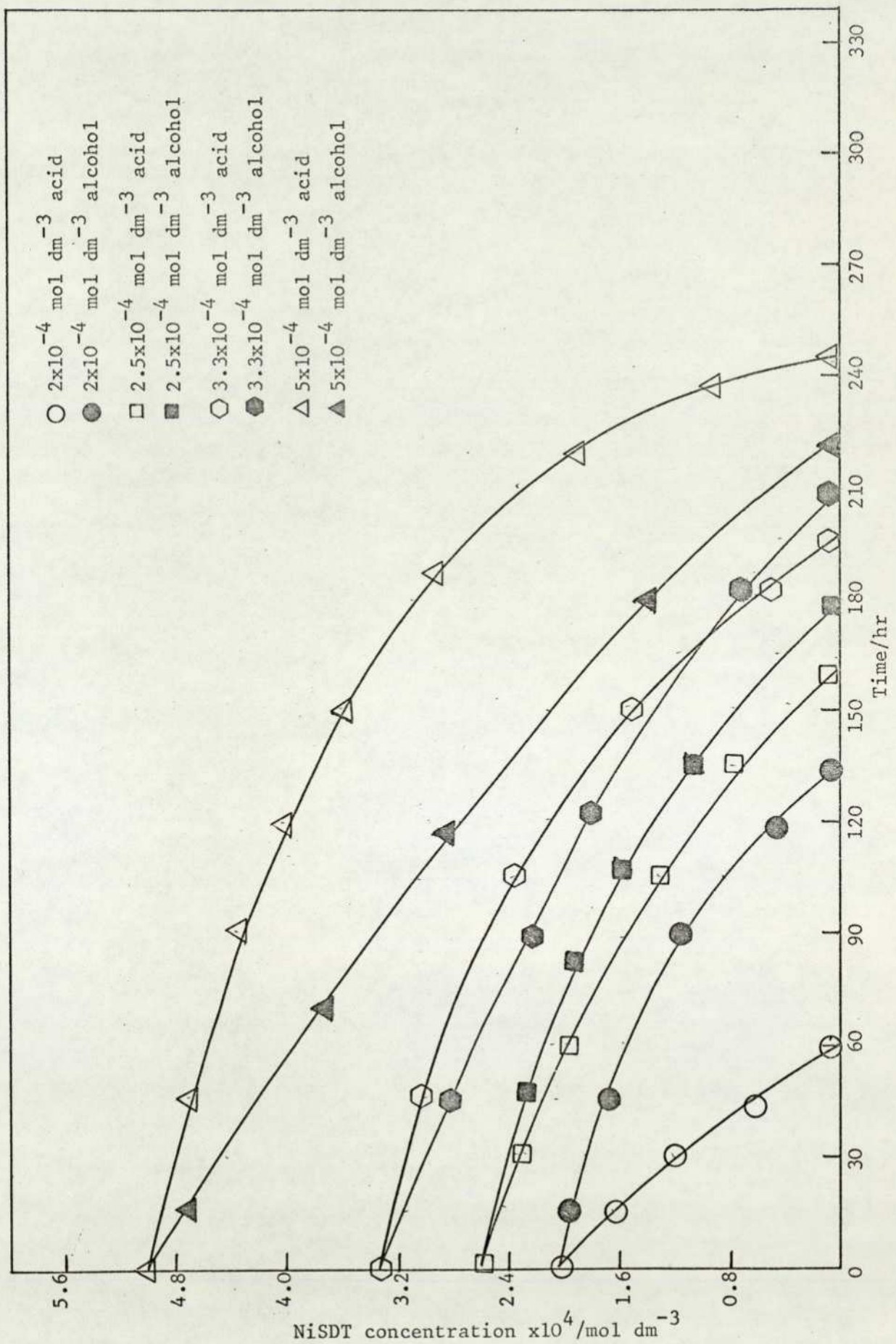


FIGURE 3.23

Effect of variations in starting concentration of NiSDT at 85°C for oleic acid and oleyl alcohol.

the fatty substrates selected for these investigations were 1, 0.75 , 0.5 and 0.25 mol dm^{-3} . In the case of the samples containing 0.25 mol dm^{-3} concentration of the fatty substrates, the time required for the complete consumption of NiSDT was far too long (>600 hours) and, therefore, the experiment for that particular run was not completed. The results obtained for the fall in the concentration of NiSDT with time for solutions containing different molar concentrations of oleic acid and oleyl alcohol in ethyl benzoate at 85°C are shown in Fig. 3.24.

From a comparison of the results presented in Figs. 3.23 and 3.24 with those presented in Figs. 3.16 - 3.21 it is immediately obvious that the introduction of ethyl benzoate has induced a change in the mechanism of inhibition. In the pure substrates the maximum rate of inhibitor consumption occurs at the beginning of the experiment, where the NiSDT concentration is highest. In contrast, when a carrier solvent is used the inhibited consumption is autoaccelerative. In view of this observation it was considered that the results obtained with a carrier solvent could not be correlated directly with those obtained with pure substrates. In view of the already complex reactions involved this approach was therefore abandoned.

3.7.2.3 Antioxidant Efficiency of MeO-NiSDT.

Solubility determination experiments (Table 3.32, section 3.6) indicated that bis (di-p-methoxy stilbene dithiolato) nickel (II) was practically insoluble in both oleic acid and oleyl alcohol at room temperature. In order to investigate the antioxidant efficiency of this nickel chelate, therefore, the use of a carrier solvent such as ethyl benzoate was necessary. Solutions containing 1 mol dm^{-3} concentration of oleic

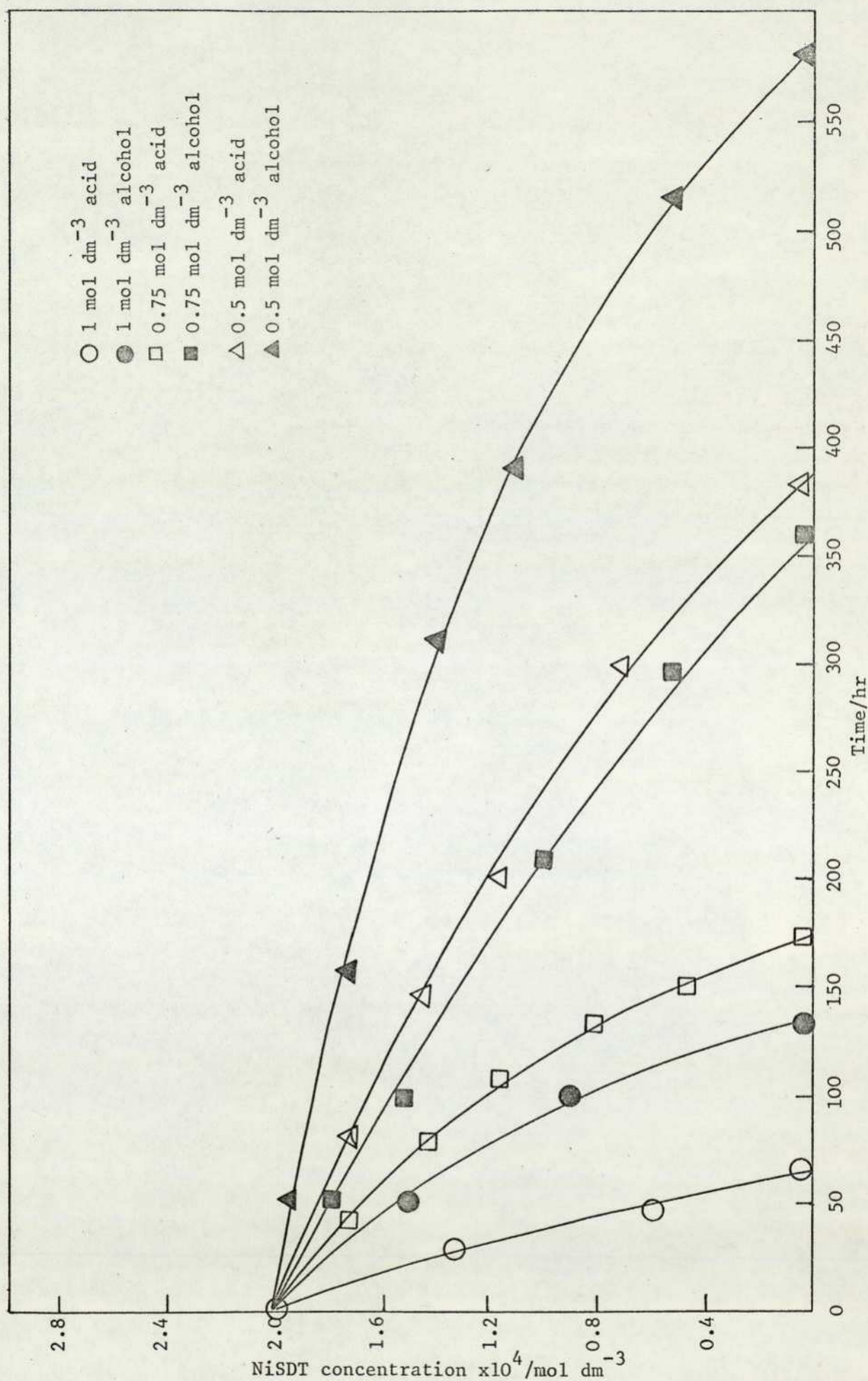


FIGURE 3.24

Effect of variation of oleic acid and oleyl alcohol concentration at 85°C .

acid (or oleyl alcohol) and 2×10^{-4} mol dm⁻³ MeO-NiSDT in ethyl benzoate were prepared. The fall in the concentration of the chelate with time was measured in the usual way, using the Shaking Reaction Incubator at 85°C.

The time taken for the complete consumption of MeO-NiSDT for solutions of oleic acid and oleyl alcohol in ethyl benzoate were 34.5 hr and 119.0 hr respectively, at 85°C. The corresponding periods for the complete consumption of NiSDT in solutions of oleic acid and oleyl alcohol in ethyl benzoate were 60.0 hr and 134.0 hr respectively, at 85°C (section 3.7.2.1). Therefore, although as in the case of previous nickel chelates, it appears that the efficiency of MeO-NiSDT inhibitor for oleyl alcohol is much greater than that for oleic acid, nevertheless it is a much poorer antioxidant compared to the other nickel chelate antioxidants used in this work. This result can also be regarded as a further confirmation of the fact that the mechanism by which these nickel compounds inhibit the autoxidation reactions of hydrocarbons is completely different to that of the conventional phenolic antioxidants, since according to Scott's findings⁶⁹, the effect of the addition of a strong electron releasing group such as methoxy group to the para-position of a phenolic antioxidant is to enhance the inhibiting efficiency of the latter.

Furthermore, the effect of MeO-NiSDT as an antioxidant in oleic acid and oleyl alcohol must be somewhat limited owing to the fact that its solubility is extremely low in these fatty substrates. There is, therefore, no advantage attached to the use of this particular para-substituted nickel complex as an antioxidant for fatty acids and alcohols.

3.8 KINETICS AND MECHANISM OF METAL CATALYSIS.

3.8.1 Experiments in the Absence of Antioxidants.

The metal complexes of Co (II), Co (III), Fe (III), and Cu (II) (section 2.2.11, Table 2.2) were introduced into solutions of oleic acid and oleyl alcohol at the three different concentrations of 2×10^{-4} , 1×10^{-4} , and 5×10^{-5} mol dm⁻³, by the direct addition of the complexes to the substrates. After the complete dissolution of the complexes, 1 cm³ samples were placed in reaction flasks and immersed in the Warburg bath at 50°C. The induction period and the oxygen absorption for each sample were measured and a graph of the latter against time was plotted for each sample.

Fig. 3.25 shows the catalytic effect of tris (n-butyl salicylaldiamino) Co(III) at different concentrations in oleic acid and oleyl alcohol at 50°C. At this temperature the induction period in the absence of catalyst is extremely long and oxygen absorption is indetectable in the time scale of these experiments. Very similar results were also obtained with other metal complexes used. The indications were that the catalytic activity of the metal complexes increased only slightly with their increasing concentration. The effect was much more severe in the case of oleic acid. The order of the catalytic activity for the individual metals was Co (III) > Co (II) > Fe (III). Surprisingly, the two copper chelates which were examined, i.e. Cu (II)-acetylacetonate and bis (n-butyl salicylaldiamino) Cu(II), showed very little catalytic activity.

From their investigations of the catalytic behaviour of certain metal chelates, which were also used in this work, Betts and Uri¹⁸⁰ have reported that while the autoxidation of 2,6,10,14-tetramethylpentadecane

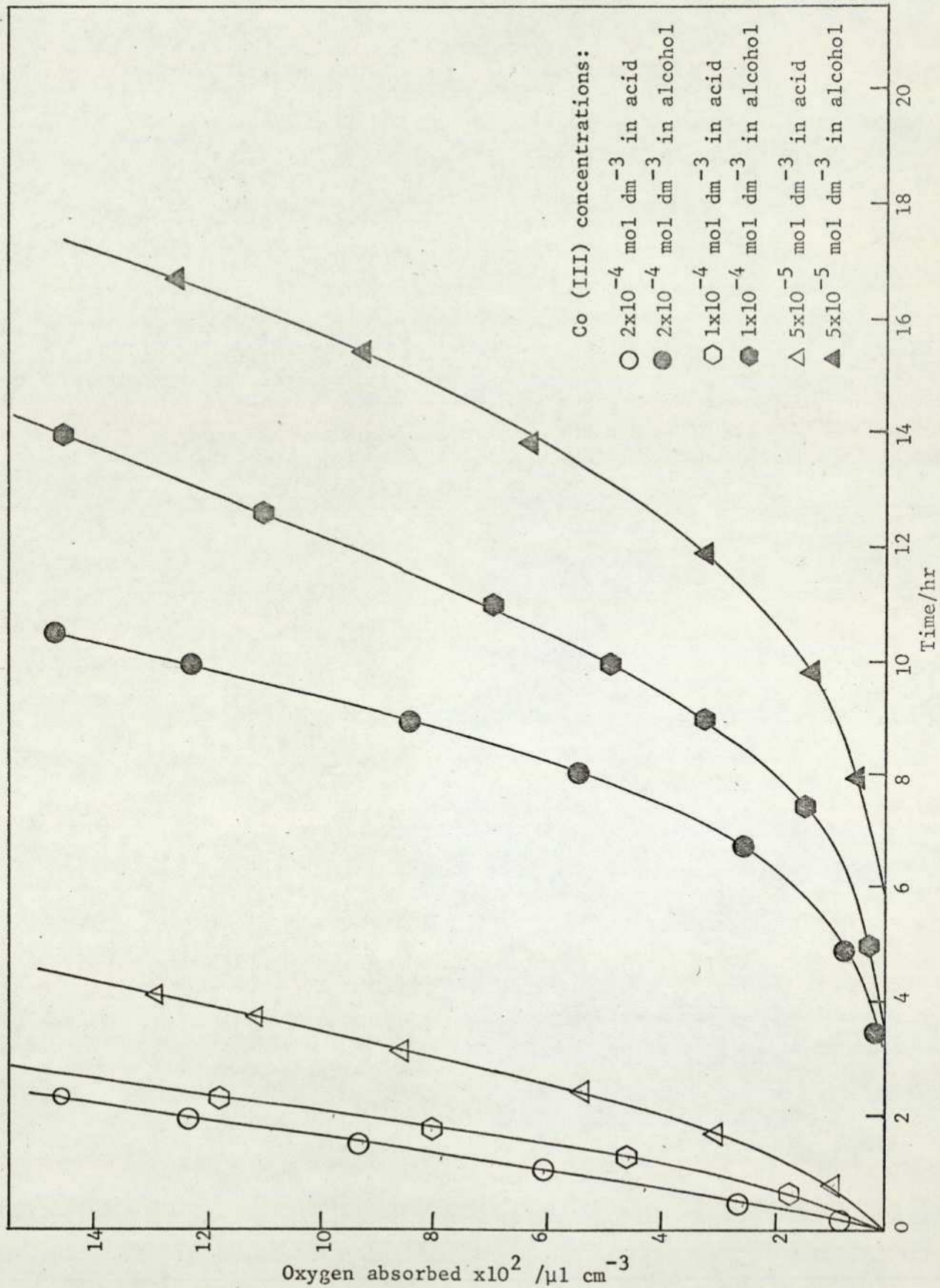
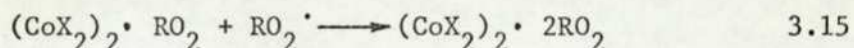
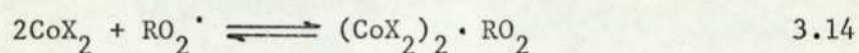
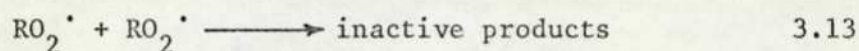
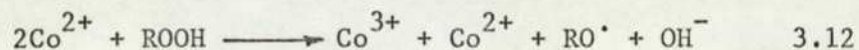
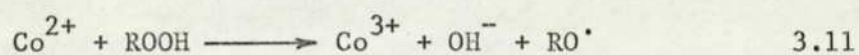
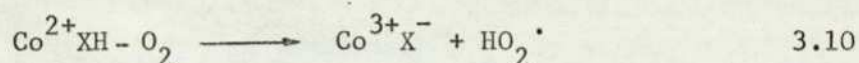


FIGURE 3.25

Catalytic effect of tris (n-butyl salicylaldiamino) Co (III) at different concentrations on oleic acid and oleyl alcohol at 85°C.

(TMPD) was strongly catalysed by bis (n-butyl salicylaldiamino) Co (II) at low concentrations up to $5 \times 10^{-5} \text{ mol dm}^{-3}$, at 1×10^{-4} concentration of the latter the first indications of prolonged induction periods occurred, and this induction period increased to over 700 hours when the cobalt chelate's concentration was increased to $5 \times 10^{-3} \text{ mol dm}^{-3}$, so that it could be regarded as an efficient inhibitor. These authors have argued that in these systems the following reactions are all possible:



As long as the concentration of hydroperoxide is very low, a relatively inefficient initiation reaction of the type 3.10, involving molecular oxygen, which is first order with regard to cobalt, competes with termination reactions 3.13 - 3.15; reactions 3.14 and 3.15 being second order with regard to cobalt. Since initiation reaction 3.11 (a first order reaction with regard to Co) is also possible, at low concentrations of the metal the latter reaction (3.11) produces radicals at a much faster rate than the termination reaction 3.13 destroys them. Hence an overall catalytic action is observed. At higher concentrations of cobalt, however, the significance of the second order termination reactions 3.14 and 3.15 increases rapidly, and the chelate acts as a free-radical scavenger,

showing inhibiting properties in autoxidation reactions.

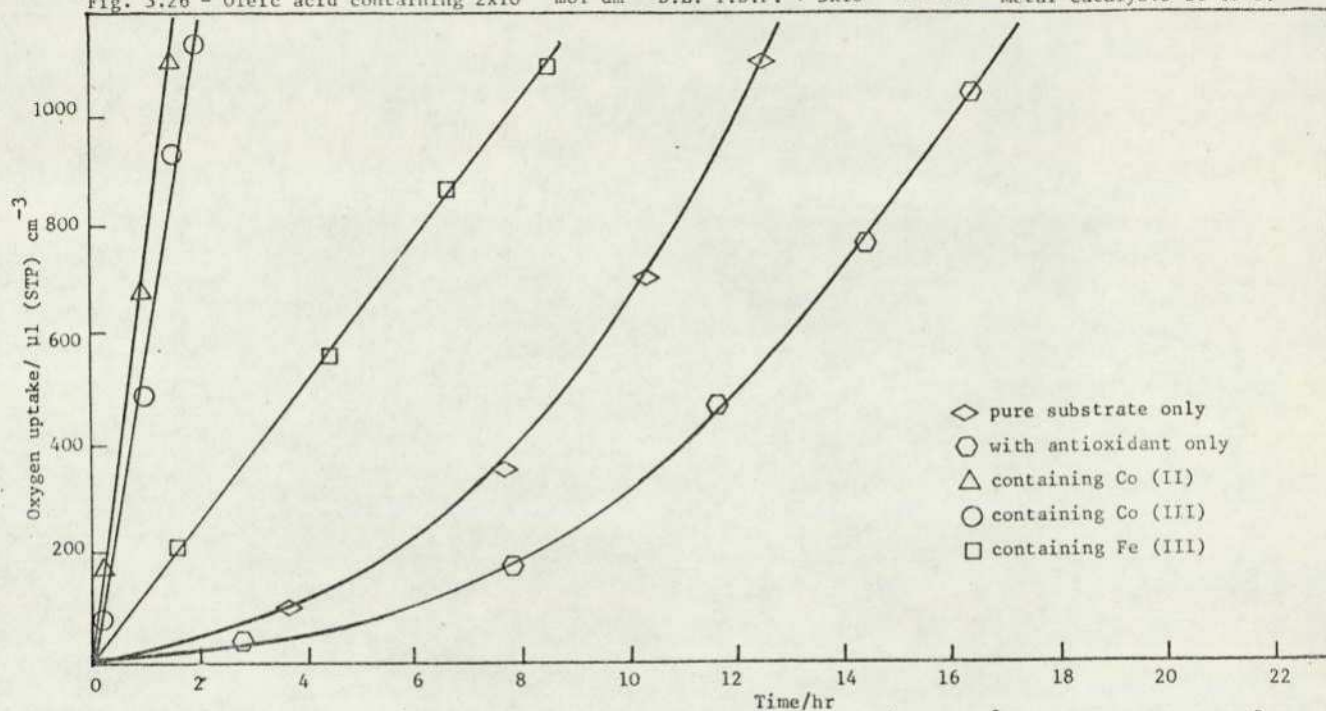
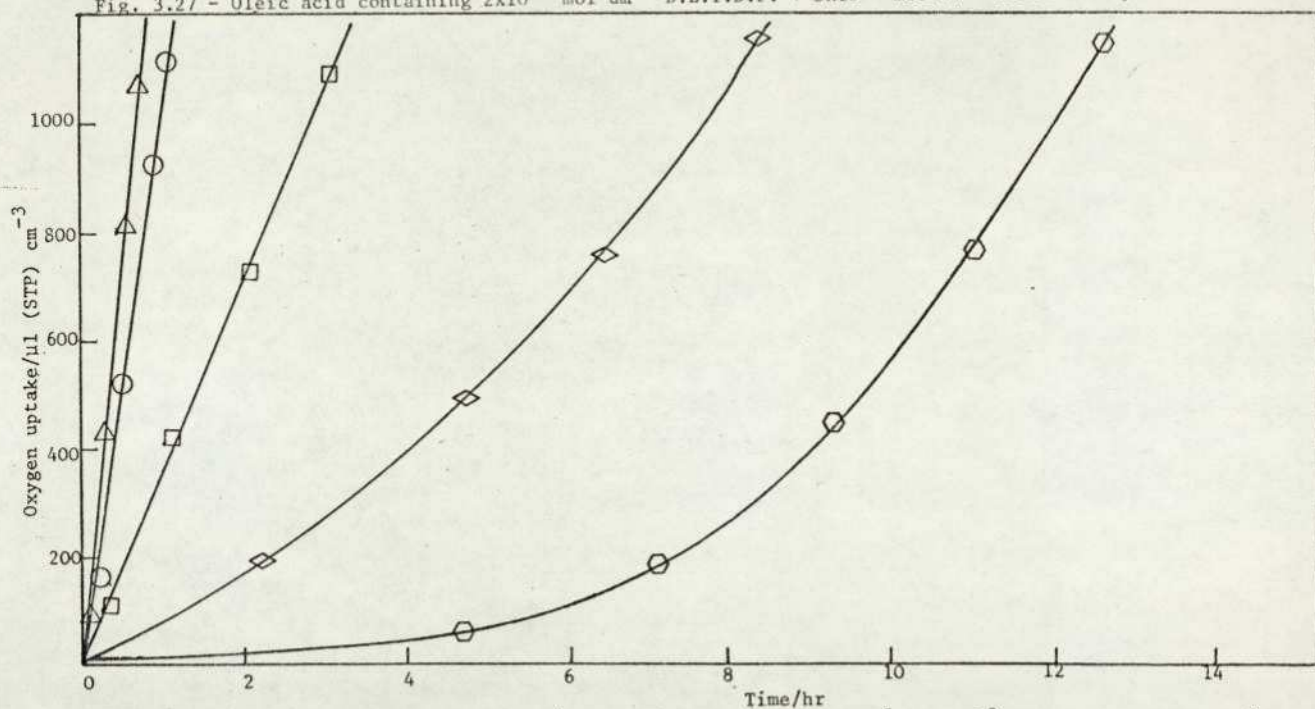
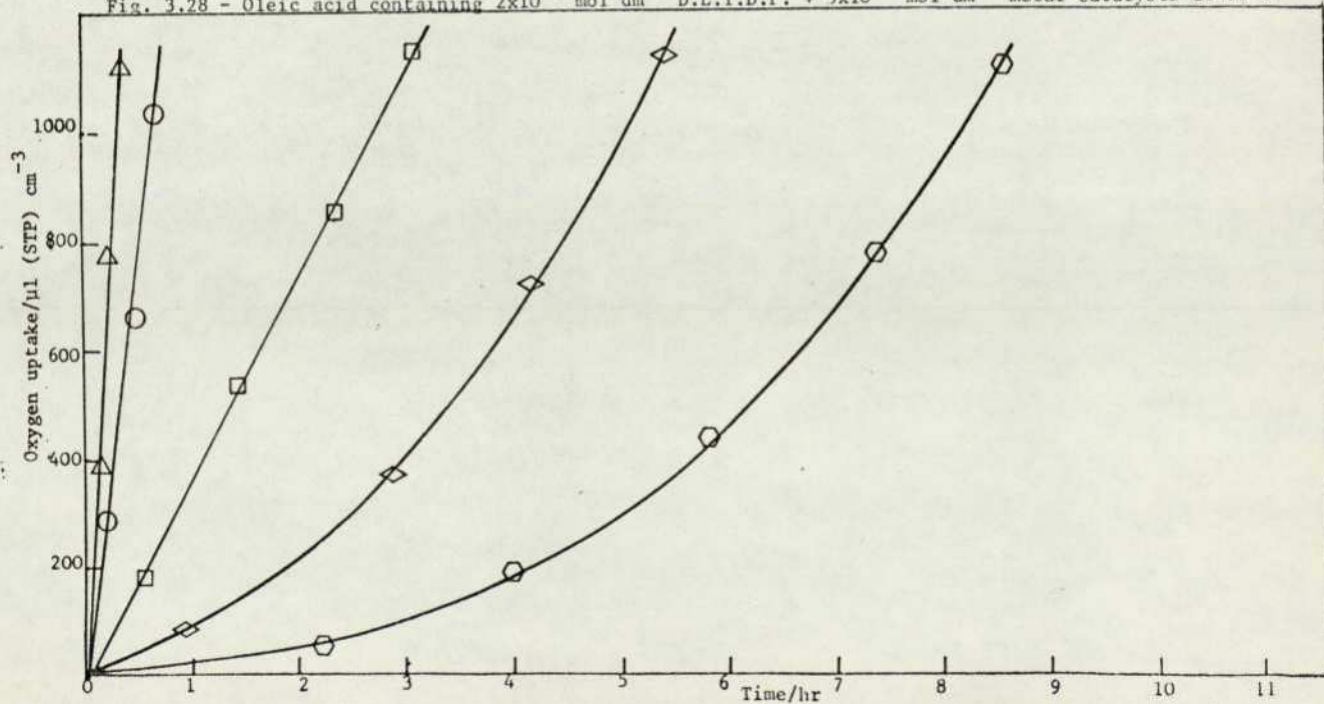
This catalyst-inhibitor conversion phenomenon, however, did not appear to take place in oleic acid or oleyl alcohol at the metal complex concentration of $5 \times 10^{-3} \text{ mol dm}^{-3}$ for any of the catalysts used in this work. Owing to the solubility difficulties experiments at higher concentrations of these metal catalysts were not attempted.

3.8.2 Experiments in the Presence of Antioxidants.

The three antioxidants which were selected for investigation in conjunction with metal catalysts were Embanox 4, Topanol CA, and Dilaurylthiodipropionate (D.L.T.D.P.), each at the concentration of $2 \times 10^{-4} \text{ mol dm}^{-3}$. It was shown by the experiments carried out previously (section 3.8.1) that, with the exception of the two copper chelates, the metal complexes catalyse the autoxidation reactions of oleic acid and oleyl alcohol efficiently at $5 \times 10^{-5} \text{ mol dm}^{-3}$ concentration and, therefore, this concentration of the metal catalysts was chosen for these investigations. As in the previous experiments, Warburg apparatus was used for these studies, which were carried out at 60° , 70° , and 80°C with 1 cm^3 samples.

Figs. 3.26 - 3.34 represent the graphs which were obtained for the experiments with oleic acid solutions, when the amount of oxygen absorbed was plotted against time. Figs. 3.35 - 3.43 show the corresponding graphs of the oxygen uptake against time obtained with samples of oleyl alcohol. Each set of three graphs represents the results obtained in conjunction with each individual antioxidant at the three different experimental temperatures of 60° , 70° , and 80°C .

The shapes of these graphs suggest that the thermal autoxidation

Fig. 3.26 - Oleic acid containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ D.L. T.D.P. + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 60°C .Fig. 3.27 - Oleic acid containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ D.L.T.D.P. + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 70°C .Fig. 3.28 - Oleic acid containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ D.L.T.D.P. + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 80°C .

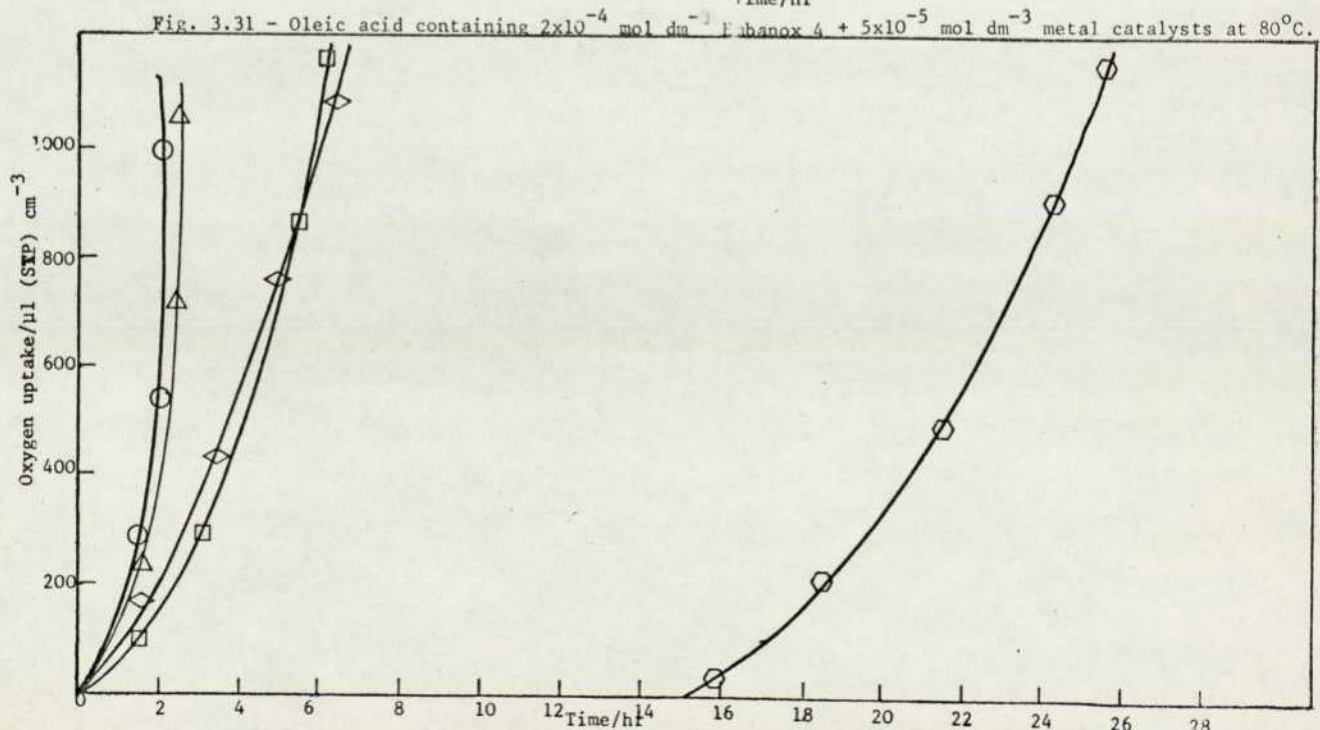
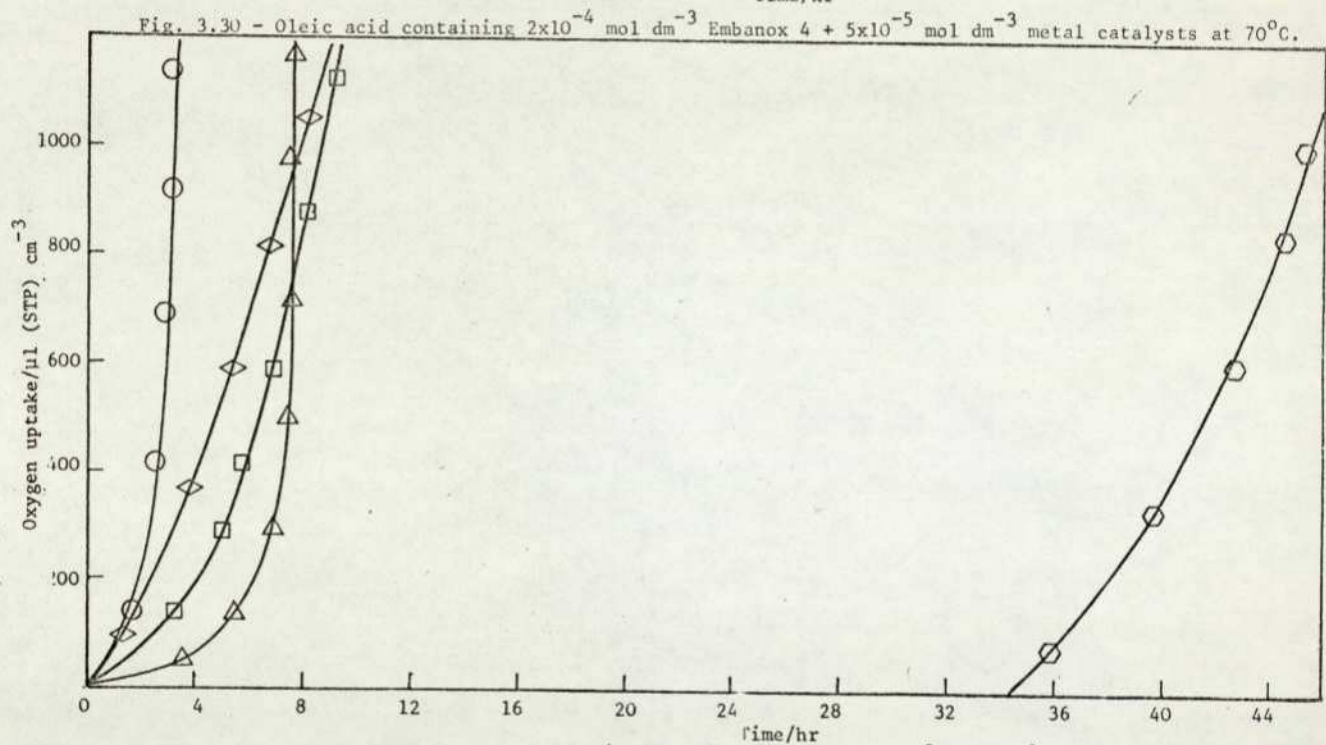
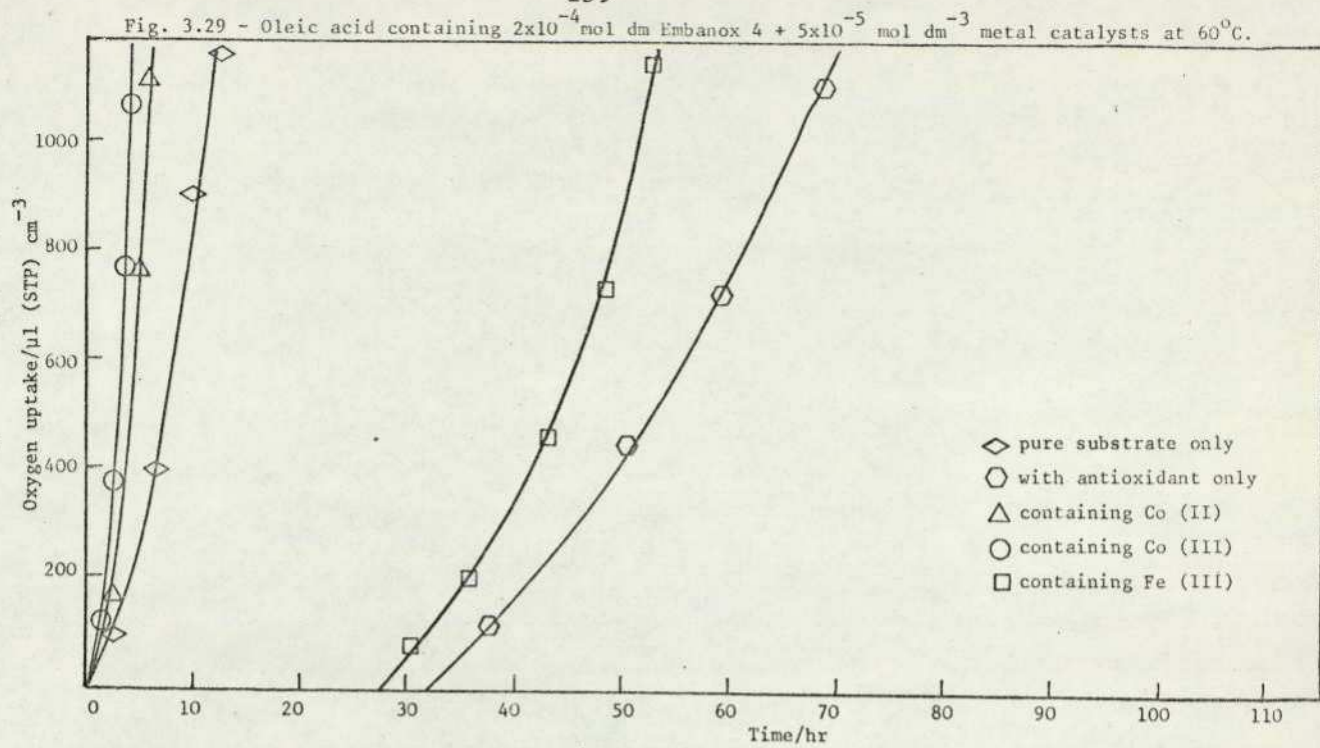


Fig. 3.32 - Oleic acid containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Topanol CA + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 60°C .

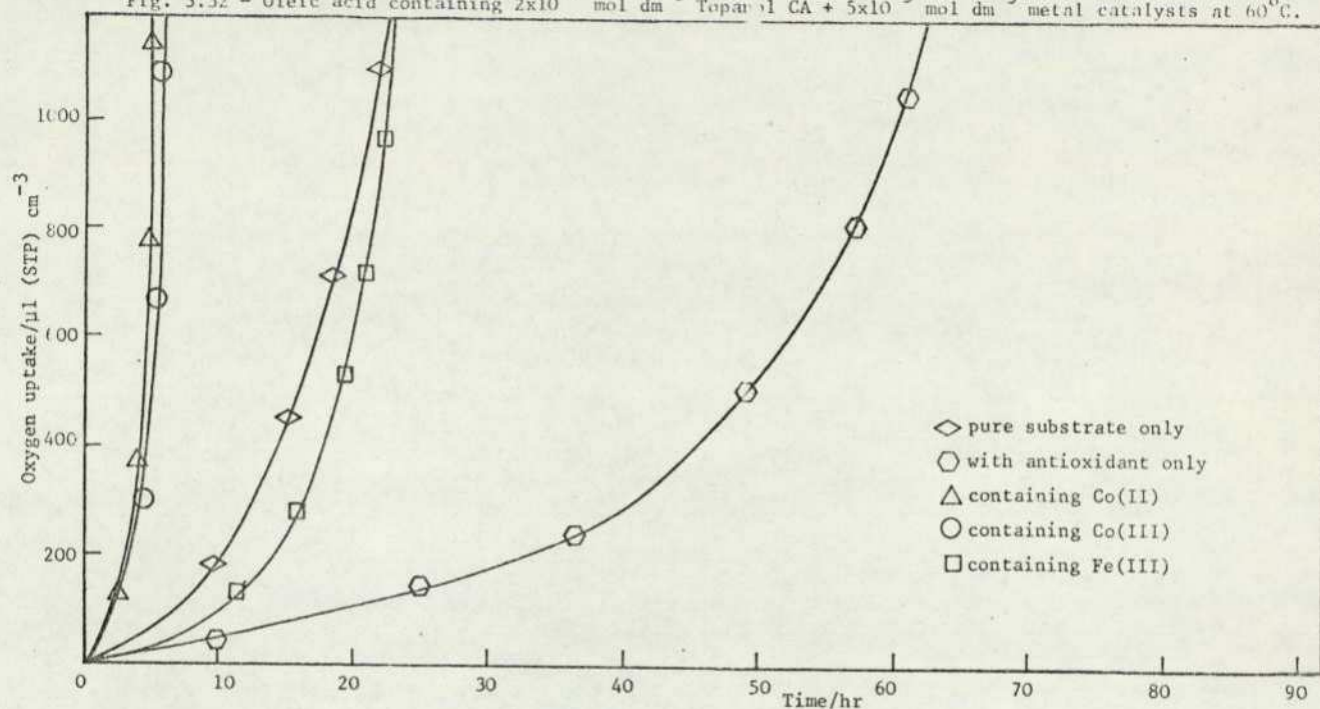


Fig. 3.33 - Oleic acid containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Topanol CA + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 70°C .

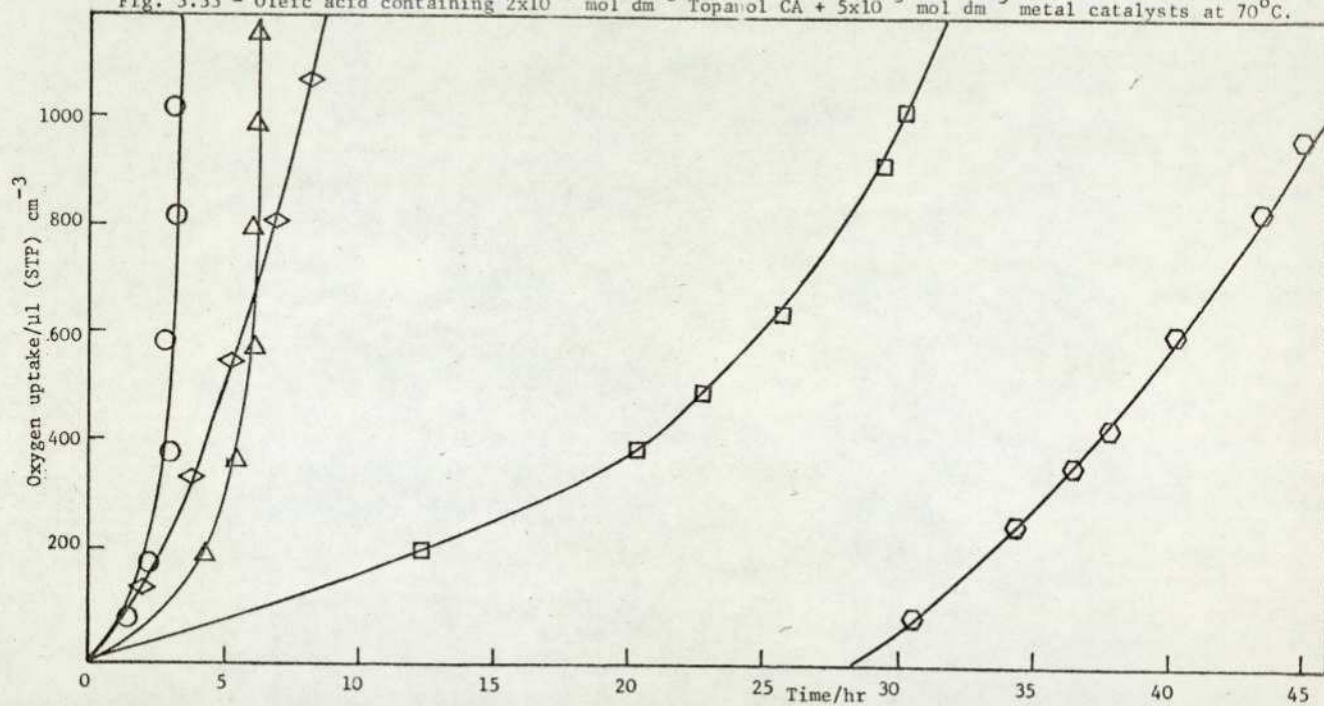


Fig. 3.34 - Oleic acid containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Topanol CA + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 80°C .

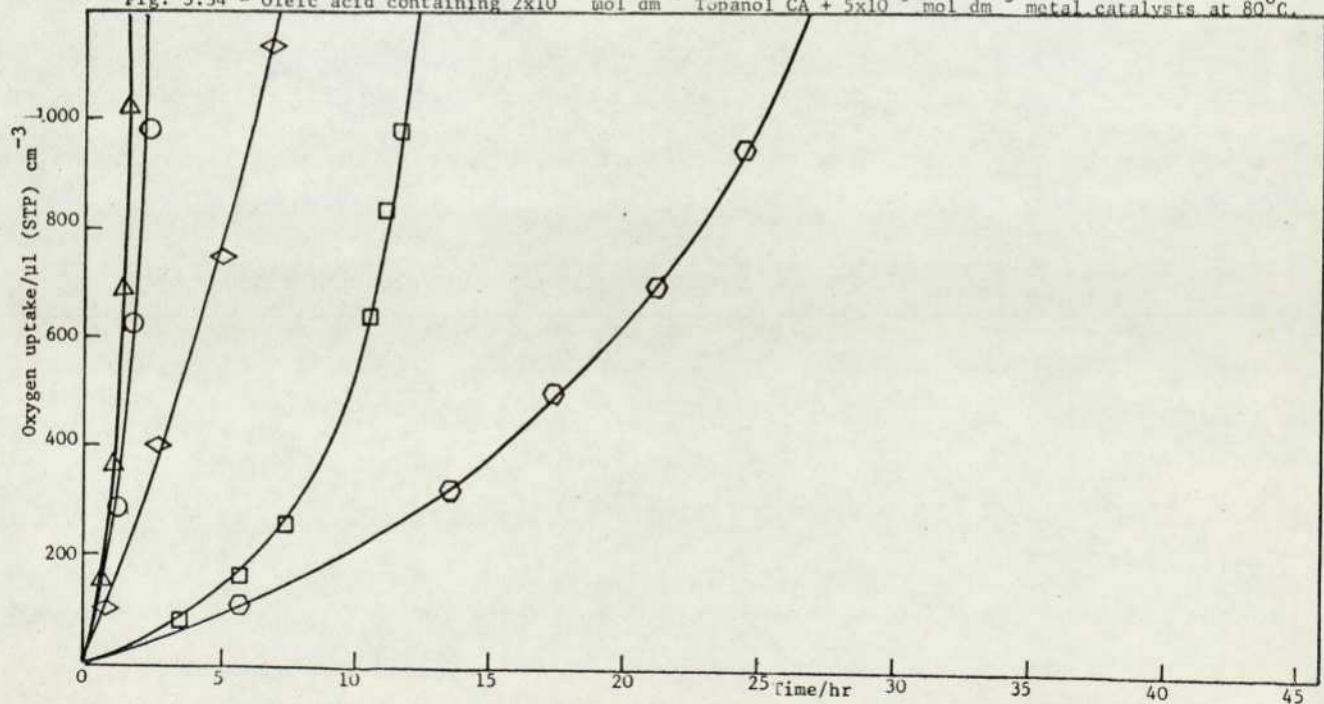


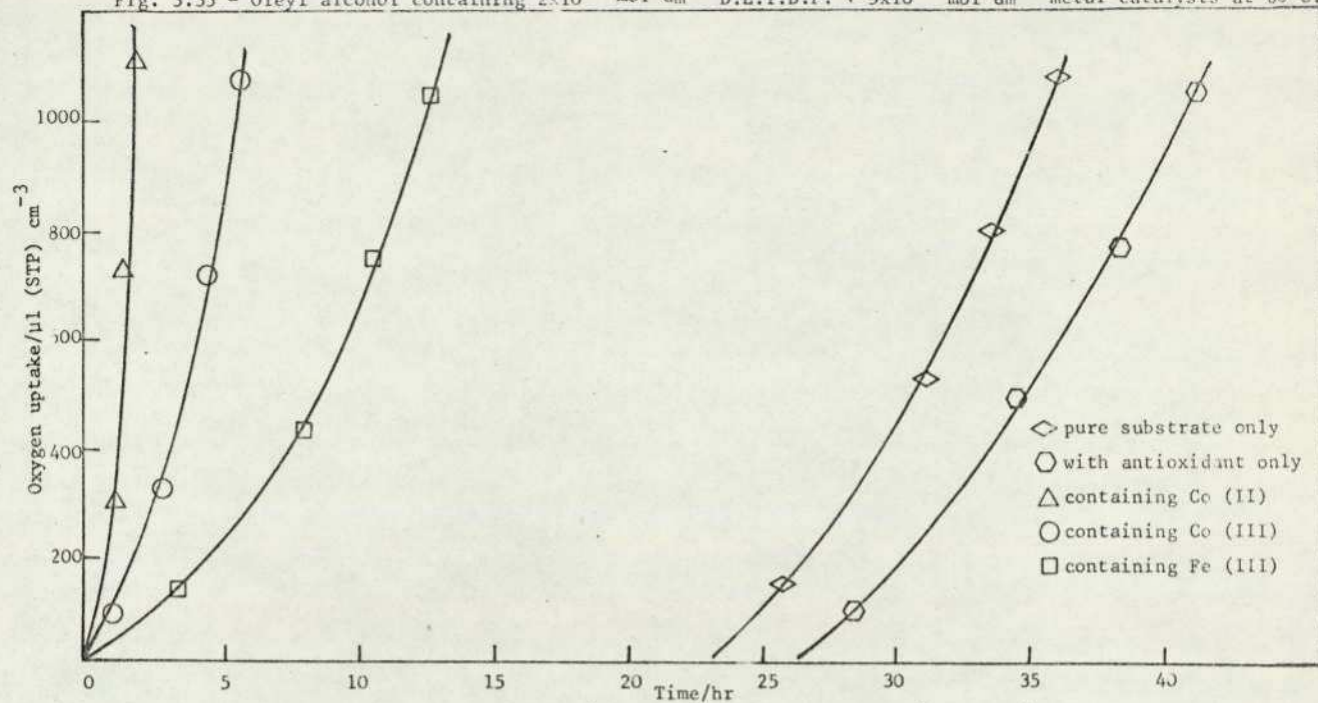
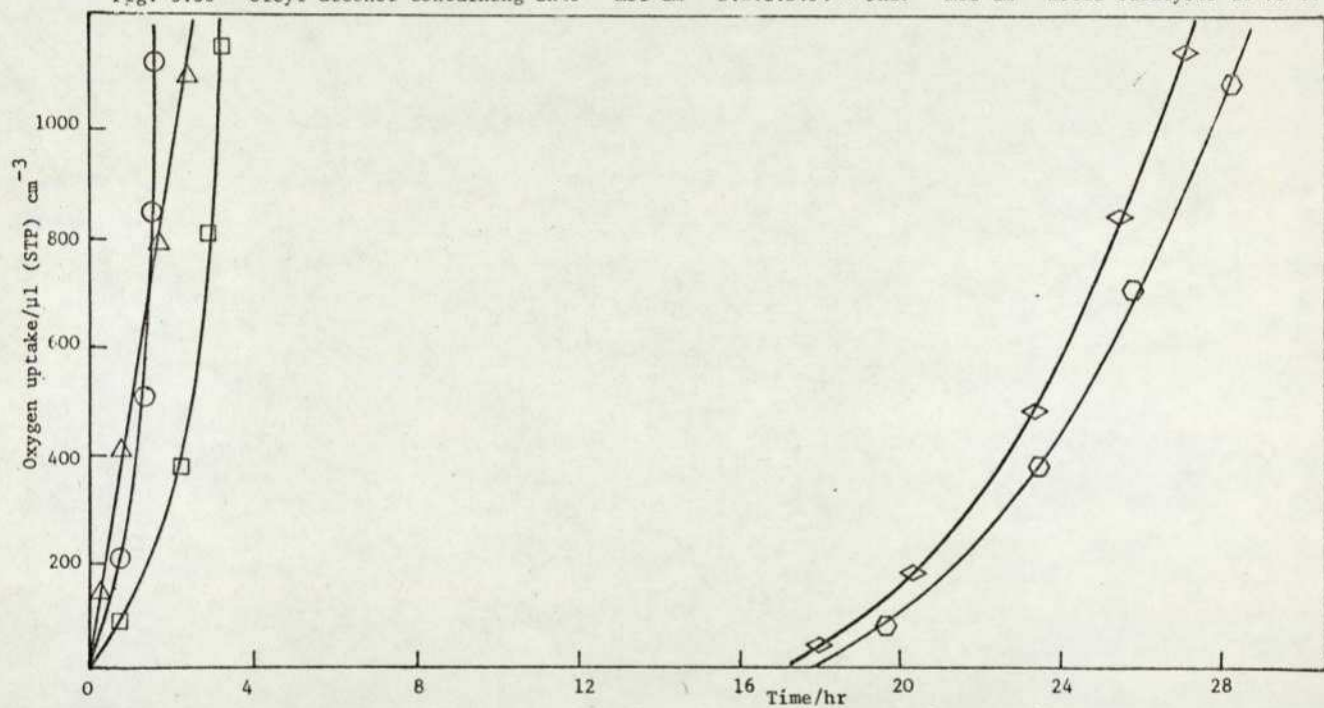
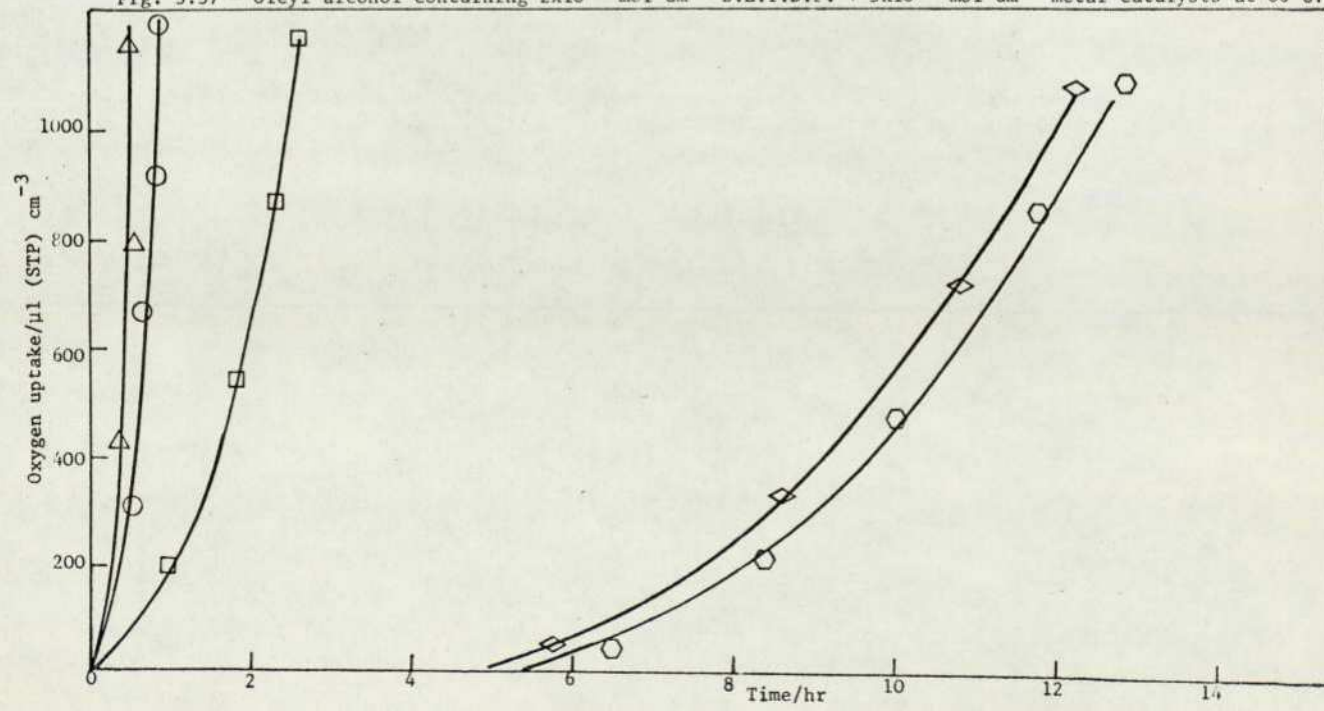
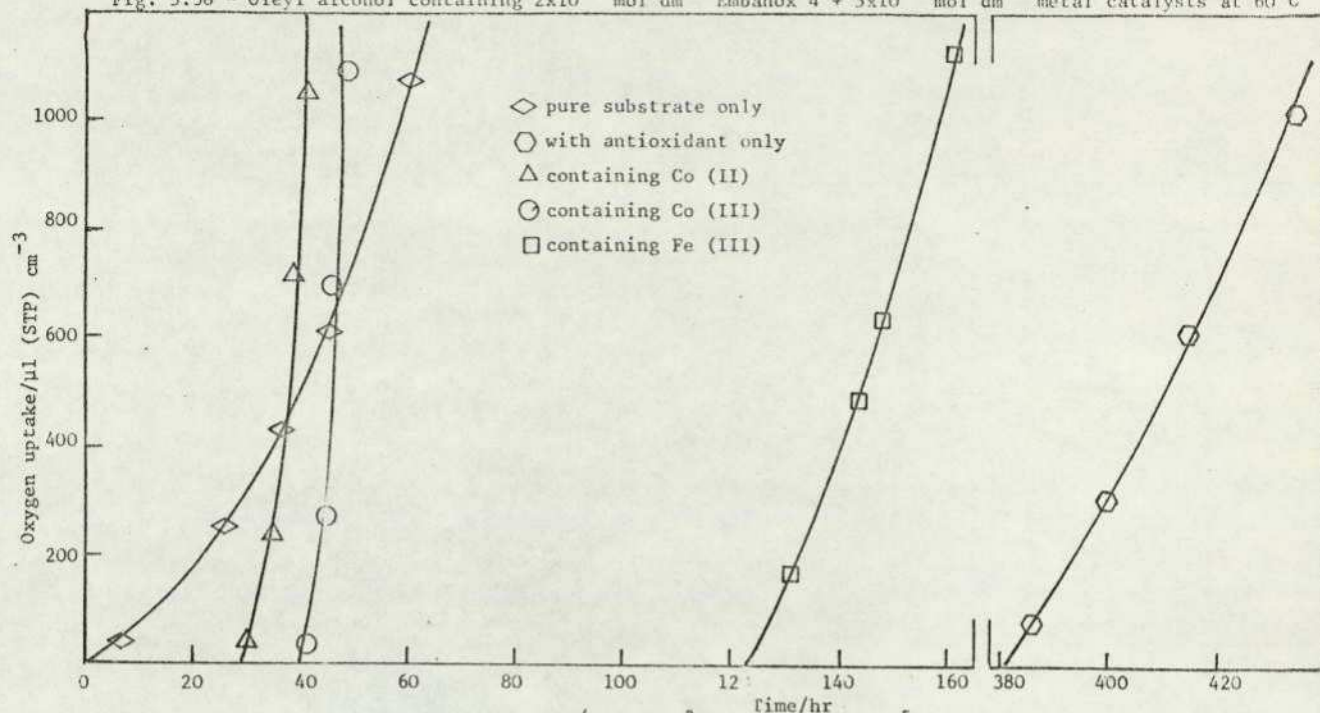
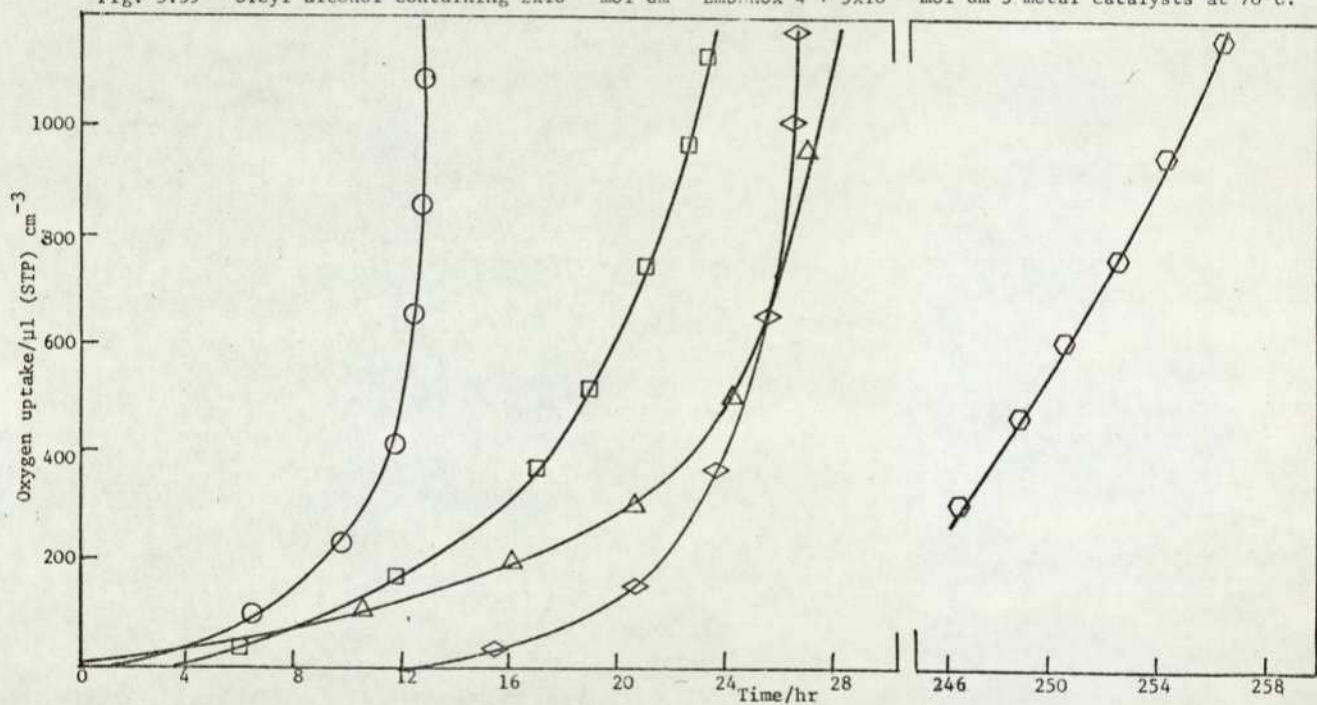
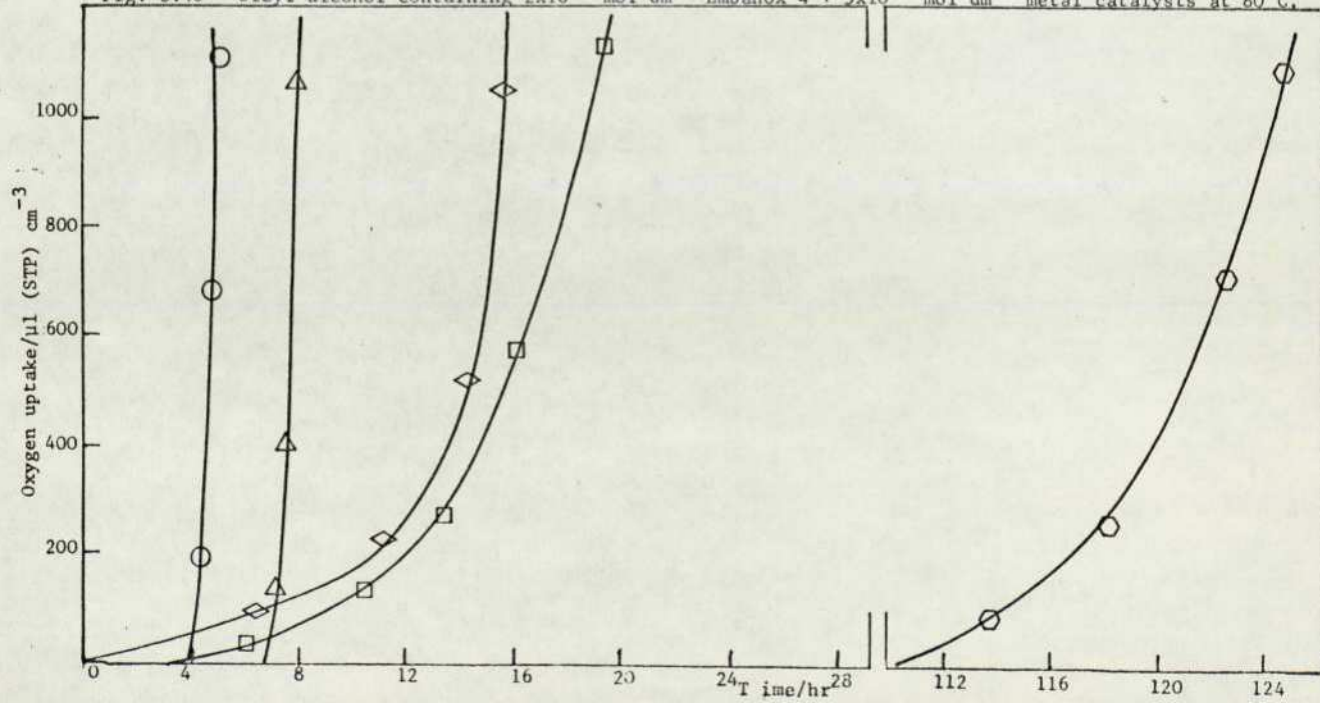
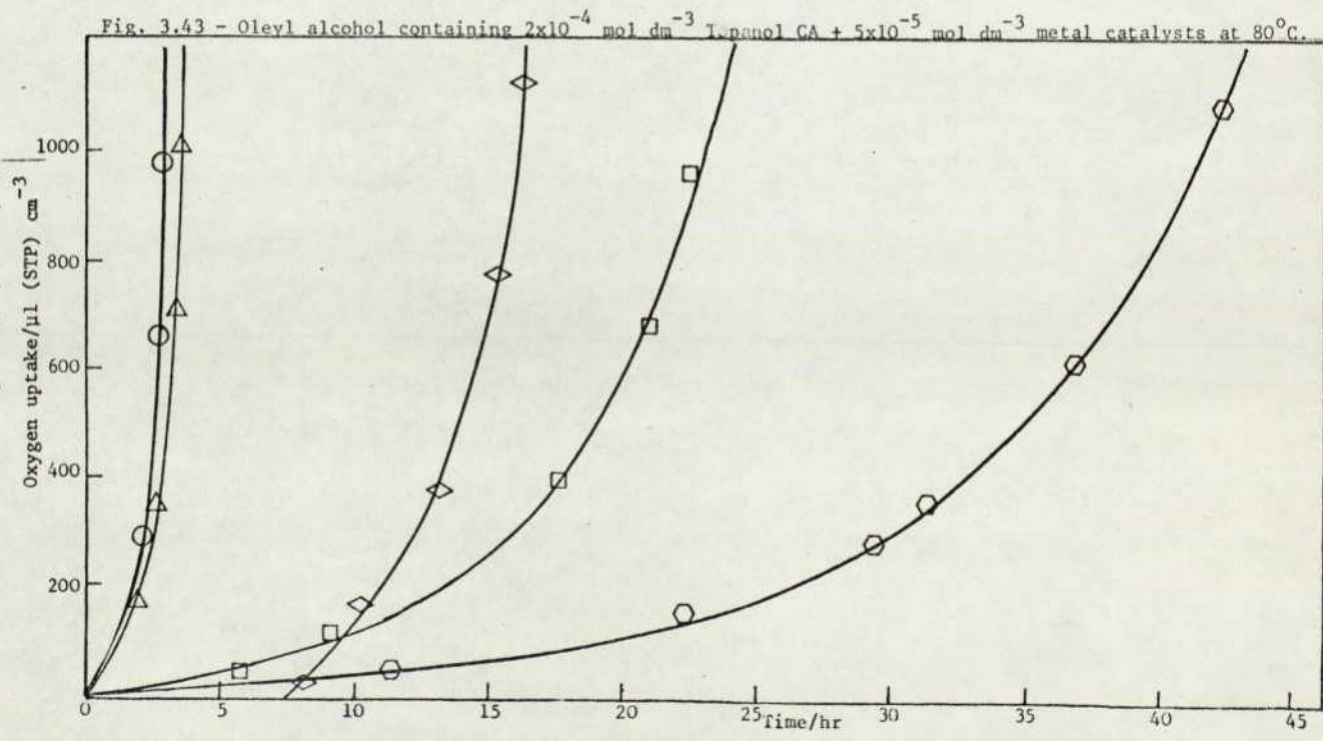
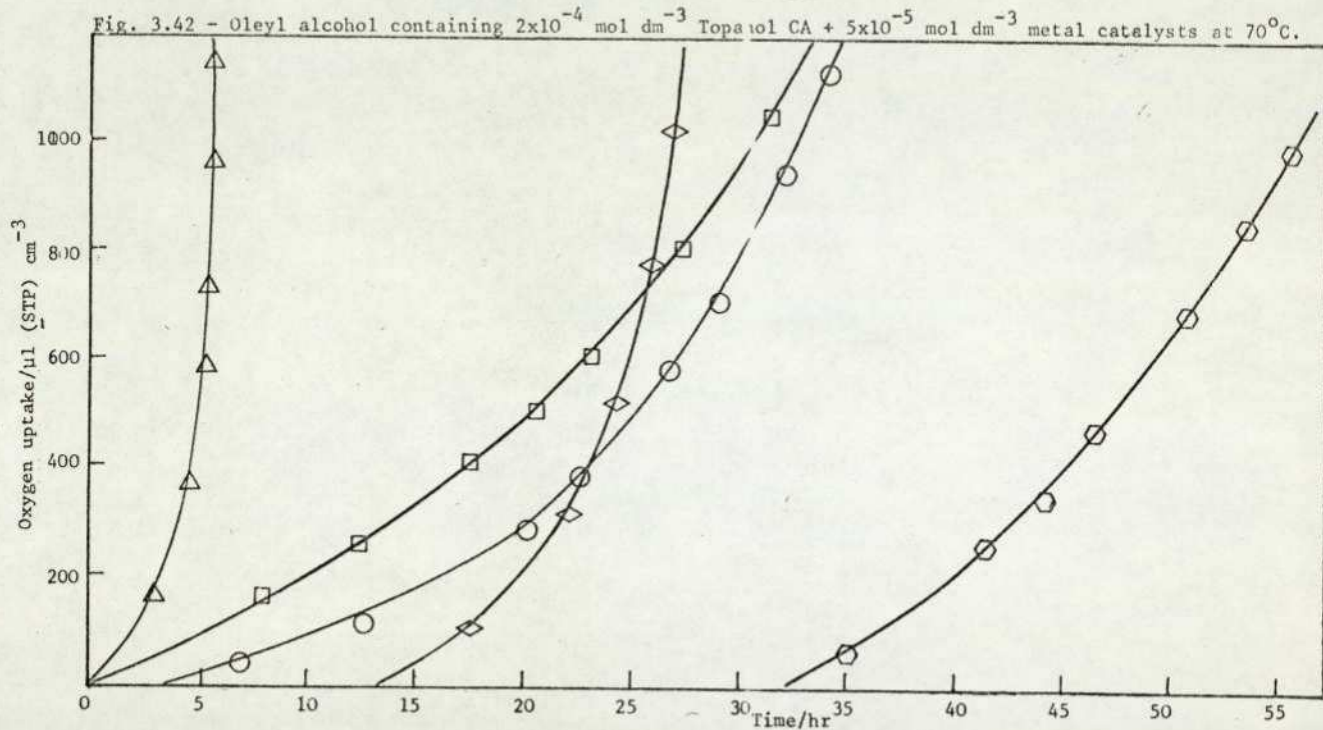
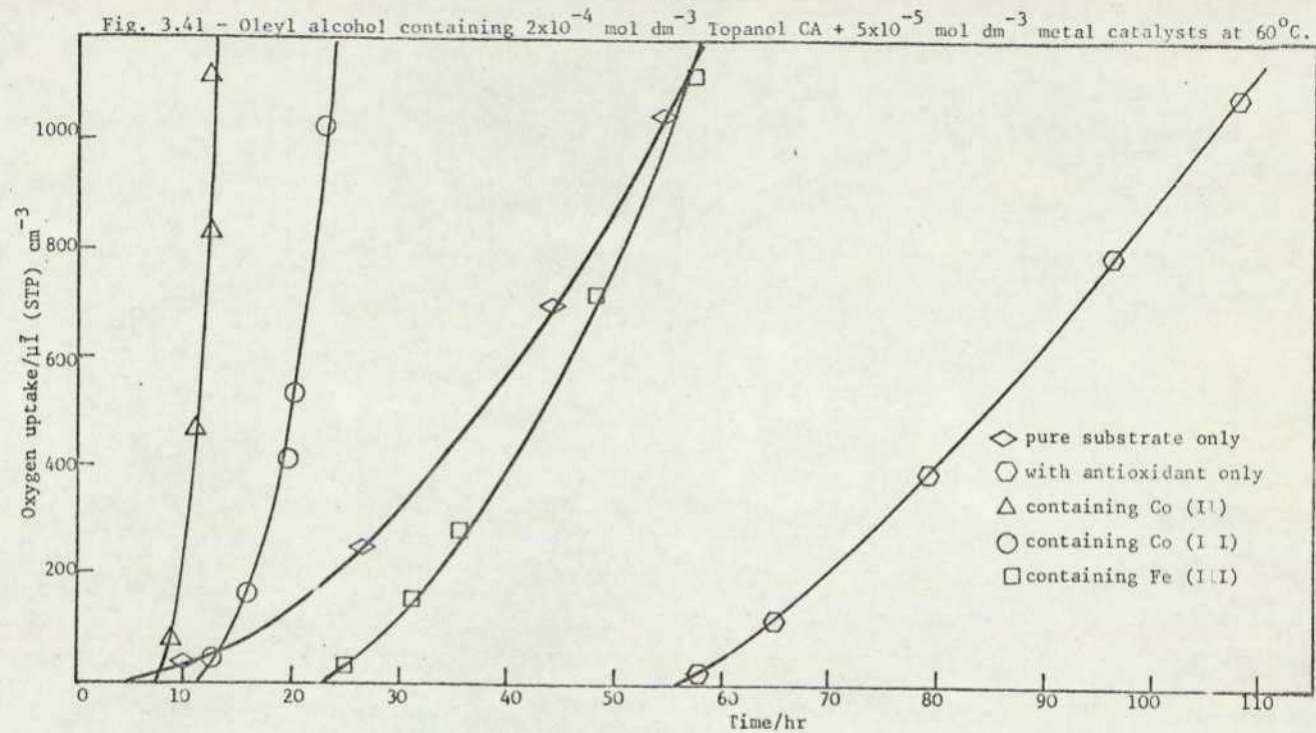
Fig. 3.35 - Oleyl alcohol containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ D.L.T.D.P. + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 60°C .Fig. 3.36 - Oleyl alcohol containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ D.L.T.D.P. + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 70°C .Fig. 3.37 - Oleyl alcohol containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ D.L.T.D.P. + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 80°C .

Fig. 3.38 - Oleyl alcohol containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Embanox 4 + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 60°C Fig. 3.39 - Oleyl alcohol containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Embanox 4 + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 70°C .Fig. 3.40 - Oleyl alcohol containing $2 \times 10^{-4} \text{ mol dm}^{-3}$ Embanox 4 + $5 \times 10^{-5} \text{ mol dm}^{-3}$ metal catalysts at 80°C .



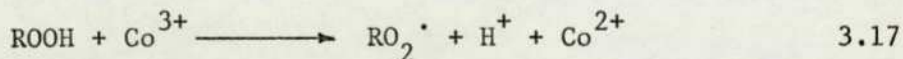
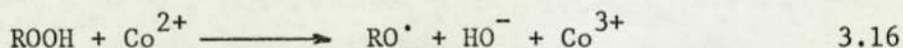
reactions of oleic acid and oleyl alcohol are strongly catalysed by the presence of certain transition metal ions, even when antioxidants are present in the system. The indications are that the catalysis exhibited by the two cobalt compounds is much more pronounced than that shown by the iron complex for oleic acid samples, with the Co (III) complex showing the most significant catalysis. This is in close agreement with the findings of Uri¹⁴, regarding the catalytic activity of some transition metals in fatty substrates. Uri has found that for different metal catalysts in the form of heavy metal stearates, the order of catalytic activity of the metals in the autoxidation reactions of linoleic acid and methyl linoleate were as follows: $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Mn}^{2+}$.

While this is true for the experiments carried out with oleic acid, it appears that the catalytic activity of Fe (III)-acetylacetonate is enhanced for solutions of oleyl alcohol and in some cases, it shows a greater catalytic effect than tris (n-butyl salicyaldiamino) Co(III). The reason for this behaviour may be the influence exerted by the change in the polarity of the medium from oleic acid to oleyl alcohol. It has been well established¹⁴ that most metal compounds which are efficient reducing agents are more readily oxidised in non-polar media. The magnitude of the effect depends on the particular compound, but it has been shown that certain metal catalysts in which the metal is oxidisable by one electron transfer, are less efficient catalysts in polar environments.

No catalytic activity is shown by the two compounds of copper which were used in this work. An explanation for this type of behaviour may be found in the work of Uri regarding the catalytic activity of copper compounds. Uri points out that copper (II) compounds are active catalysts only if peroxide is present in the system (Cu (II) compounds

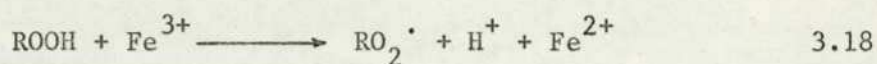
act as catalysts in the decomposition of the peroxide, thus producing free-radicals) or in the presence of reducing agents. In the latter case free-radicals are formed in the course of the reduction of Cu^{2+} ion to Cu^+ ion which is being continuously re-oxidised by the aerobic oxygen. It is, therefore, possible that in some systems Cu^{2+} ion is practically inactive while in different circumstances it might be one of the most powerful catalysts. The lack of catalytic activity of the copper complexes shown in our systems could be attributed to the absence of any peroxides in the purified oleic acid or oleyl alcohol as was shown by the tests carried out previously (section 3.2). Further examples of this remarkable lack of catalytic activity shown by Cu^{2+} ions are given in the work of Lundberg²⁰¹.

It is also apparent from the graphs that in almost all the experiments the rate of oxygen absorption by the samples containing Fe (III)-acetylacetonate is considerably lower than the corresponding samples containing either of the two cobalt compounds. The mechanism which is operating in the case of cobalt ions present in the system can be represented by the equations 3.16 and 3.17:



Both Co^{2+} and Co^{3+} ions are effective catalysts (as has been shown by the work of Uri¹⁴ and Waters⁹⁹) for the autoxidation reactions of fats and fat containing materials, and their speedy interconversion of the form $\text{Co}^{2+} \longrightarrow \text{Co}^{3+} \longrightarrow \text{Co}^{2+}$ etc., which is taking place in the reactions leads

to the rapid formation of free-radicals in the system and is responsible for the phenomenally fast rates of oxygen absorption observed in these reactions. In the case of the Fe^{3+} ions, the reaction occurring is of the form of reaction 3.18:



The reverse reaction involving $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+}$ step, however, does not occur with the same speed as the corresponding reaction for Co^{2+} , since Fe^{2+} ion is a much weaker peroxide decomposer metal ion¹⁴. Hence, as the autoxidation proceeds, the concentration of Fe^{2+} ions increase at the expense of Fe^{3+} ions, resulting in a slower rate of oxygen absorption observed in these samples.

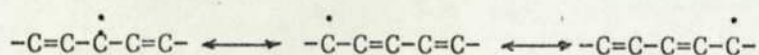
CHAPTER 4

CONCLUSION

4.1 AUTOXIDATION OF UNINHIBITED SUBSTRATES.

Although there are several methods available for the separation and purification of fatty acids and alcohols, amongst which urea complex formation and gas-liquid chromatographic techniques have been extensively reported in the literature, the slightly modified low temperature crystallisation method of Swern, Knight, and Findley used in this work (sections 2.2.7 and 2.2.8) appeared to be successful in removing almost all of the polyunsaturated fatty acids or alcohols and other impurities normally present in commercial oleic acid and oleyl alcohol. Substrates thus purified contained only traces of polyunsaturated impurities which have been regarded as insignificant in studies of autoxidation. However, the results of the present study indicate that the presence of even trace amounts of the polyunsaturated impurities may have a drastic effect upon the oxidative stability of oleic acid and oleyl alcohol. Thus by reference to the results shown in section 3.3.2 and Figs. 3.6 and 3.7, it can be seen that the deliberate addition of linoleic acid, linolenic acid, and methyl linoleate to oleic acid, and the addition of linoleyl alcohol to oleyl alcohol caused an appreciable reduction in the magnitude of the induction periods of both inhibited and uninhibited samples of the fatty substrates. Although the induction periods decreased and the maximum rates of oxygen absorption increased with an increase in the percentage of these polyunsaturated impurities present in the system, the effect is

most pronounced for the first 1% of the impurity addition. Furthermore, the substrates were more adversely affected by linolenic acid than by linoleic acid or methyl linoleate, the effect of the latter two compounds being almost the same. This implies that the autoxidation of oleic acid and oleyl alcohol is accelerated by the presence of polyunsaturated impurities containing ethylenic double bonds, with effect increasing markedly as the number of double bonds in the impurity increases; the role of the functional groups, such as carboxylic or hydroxyl groups, in the autoxidation reactions of the fatty substrates being relatively unimportant. This effect undoubtedly arises from the high reactivity of the α -methylene hydrogen atoms in the polyunsaturated acids. A methylenic hydrogen atom flanked by two double bonds is readily abstracted, since the resulting radical can be stabilised by delocalisation over two double bonds:



An important additional point can be made by reference to Figs. 4.1 and 4.2 which show the Arrhenius plots for the induction period and maximum rate of oxygen absorption of samples of pure oleic acid and of oleic acid containing 1 % by weight of either linoleic acid or linolenic acid, plotted on a scale which allows extrapolation to room temperature. It is apparent that polyunsaturated substrates not only accelerate the rate of oxidation but also lower the activation energies for the degradation (Tables 3.28 and 3.29). Thus as the temperature is lowered, the effects of impurities would be expected to become much more significant. Although extended extrapolations of this kind can be criticised on theoretical grounds, and are subject to experimental error, the present results emphatically seem

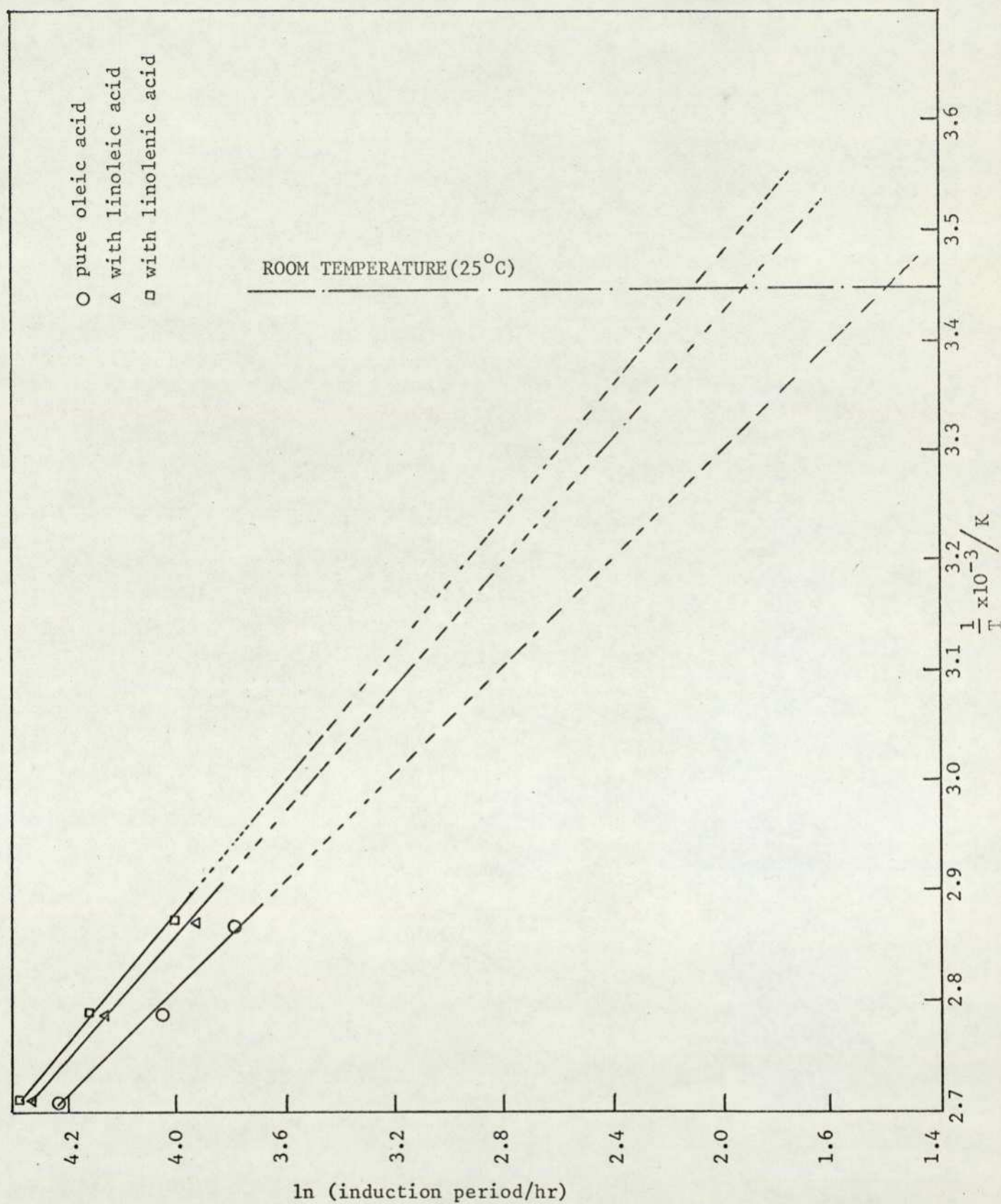


FIGURE 4.1

Arrhenius plots for the induction period for samples of pure oleic acid and oleic acid containing 1% by weight of either linoleic acid or linolenic acid.

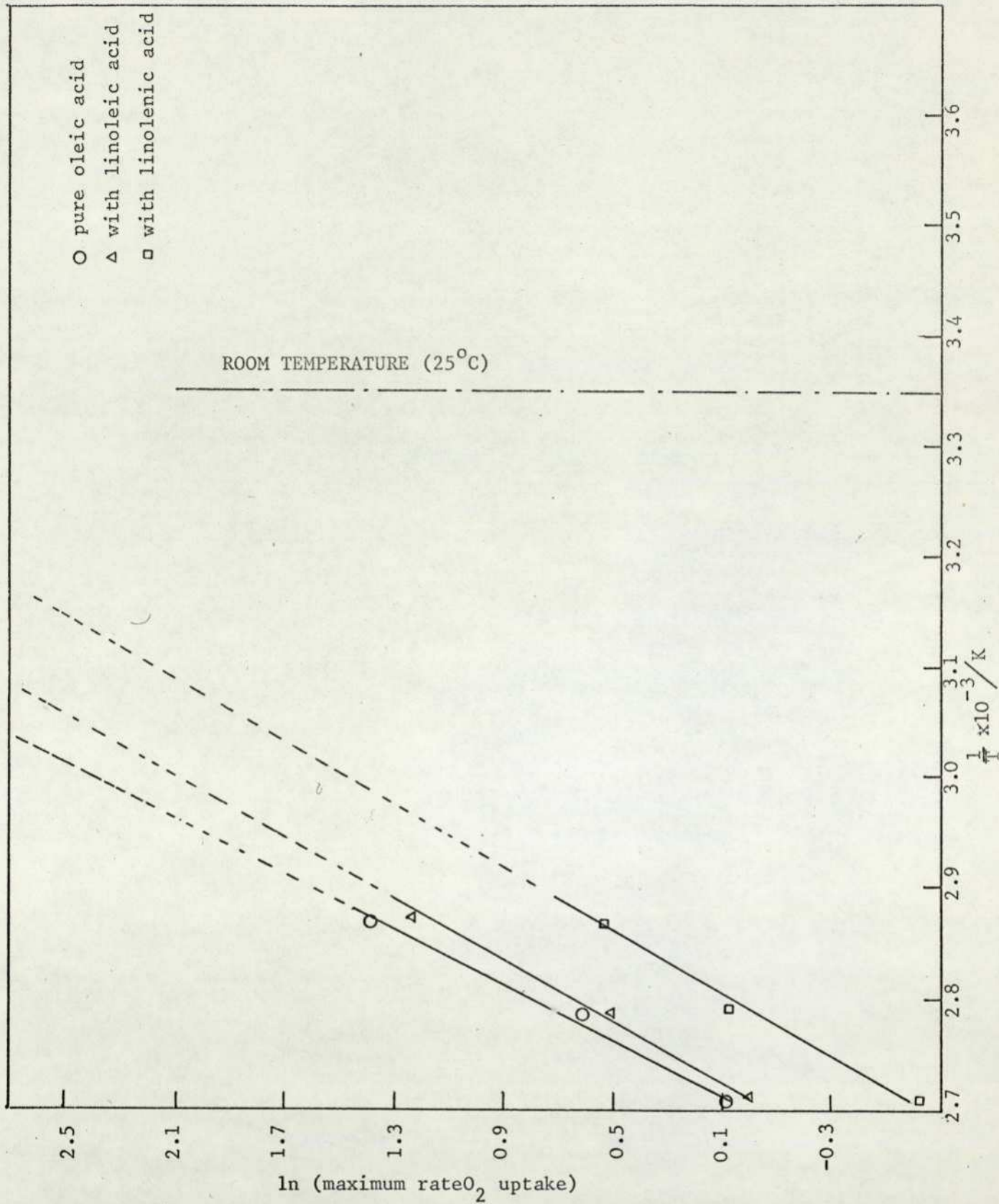


FIGURE 4.2

Arrhenius plots for the maximum rate of oxygen absorption for samples of pure oleic acid and those containing 1% of either linoleic acid or linolenic acid.

to point to the desirability of using highly purified substrates where long shelf-life at room temperature is needed; it is unfortunate that economical considerations make this approach unattractive to commercial users.

In the present work all substrates have been purified to leave only trace amounts of polyunsaturated impurities. Furthermore, induction periods and oxidation rates were generally reproducible. It seems reasonable to conclude that although there may well be some contribution from initiation by oxidation of impurities, this contribution is, at least, reproducible from sample to sample, and will not affect our general conclusions.

From the data in Tables 3.5 and 3.7 it can be seen that at 85°C the induction periods for uninhibited samples of oleic acid and oleyl alcohol are rather similar as are the maximum rates of oxygen absorption. Oleyl alcohol is more stable than oleic acid, but the effect is not large. These results suggest that the effect of changing functional groups from -COOH to $\text{-CH}_2\text{OH}$ is to produce only a moderate change in stability, which is consistent with the view that oxidation occurs mainly at the double bond, where the distant terminal substituent would not be expected to have any effect. However, this conclusion does not extend to experiments involving antioxidants which are discussed in the following section.

4.2 EFFECTS OF CONVENTIONAL ANTIOXIDANTS.

The results of the studies of the autoxidation of purified oleic acid and oleyl alcohol in the presence of a cross-section of typical conventional antioxidants are summarised in Tables 3.4 - 3.7. The antioxidants employed included monophenolic (Embanox BHA), trisphenolic (Topanol CA),

and synergistic (Embanox 4) chain-breaking compounds, and the hydroperoxide decomposing compound dilaurylthiodipropionate (D.L.T.D.P.). From these results the following general conclusions are easily drawn:

- (i) - D.L.T.D.P. alone is a very inefficient antioxidant, although as will be discussed later it is a very efficient synergist.
- (ii) - Considerable improvements in stability are produced by all of the other systems studied, although the newly developed Topanol 354, which is highly effective in pure hydrocarbons, is relatively ineffective in fatty substrates.
- (iii) - No significant change is observed in the values of the maximum rates of oxygen absorption for the inhibited and uninhibited samples; this is due to the fact that the rate measurements are taken after the total consumption of the antioxidant in the system.

From a comparison of Tables 3.5 and 3.7 it is interesting to note that there are some remarkable differences in the efficiencies of some antioxidants in the two substrates. Thus at 85°C the efficiencies of D.L.D.T.P., Topanol CA, and Embanox BHA, as determined by the fractional increase in the induction periods, are similar in both substrates. However, Embanox 4 is a very much more efficient antioxidant in oleyl alcohol than in oleic acid. Since the efficiency of Embanox BHA is comparable in the two substrates, the implication is that the citric acid component of Embanox 4 is very much more efficient as a synergist in oleyl alcohol than in oleic acid. The synergistic effect of citric acid has been attributed to a deactivating effect on metal ions. However, since citric acid alone is not effective as an antioxidant, this view is undoubtedly an oversimplification of the problem, and the mechanism of synergism is not understood. A probable explanation of the results in this case arises from the fact

that citric acid is readily dehydrated under acid conditions; in oleic acid solutions this reaction could lead to rapid consumption of citric acid with a consequent reduction of its synergistic effect. If this conclusion is true, it would be expected that consumption of the synergist might be very much slower at room temperature, so that the efficiency of Embanox 4 may rise rapidly as temperature is lowered, implying a non-linear Arrhenius plot. This possibility is not observed in present results (Fig. 3.1) which were obtained at high temperatures.

From Table 3.8 it can be seen that all antioxidants in oleic acid increase the induction period without major changes in its activation energy. This result implies that (with the reservation for Embanox 4 outlined above) the relative efficiencies of these stabilisers do not change appreciably upon lowering the temperature.

The detailed investigation of the antioxidant efficiency of Topanol CA as a function of its starting concentration (Figs. 3.3 and 3.4) revealed that, while increasing the inhibitor concentration in the samples leads to an increase in the induction periods, the relationship is non-linear at higher starting concentrations of the antioxidant, a doubling of the quantity of the latter in the system may result in only a fractional increase in the induction period; a possible interpretation of these results in terms of destruction of the antioxidant by reaction with oxygen has been discussed in detail in section 3.3.1.4.

Studies of the synergistic effects of antioxidant combinations have been described and discussed in section 3.4. In this connection it is interesting to note that synergistic effects of pairs of antioxidants are similar in oleyl alcohol and oleic acid, but that of some triple antioxidants combinations show marked enhancement of synergism in oleyl

alcohol. In particular the two antioxidants which have higher efficiency in oleyl alcohol (Topanol 354 and Embanox 4) also extend this behaviour to a higher level of synergism in oleyl alcohol. From these results it is clear that D.L.T.D.P. is a relatively inefficient synergist in these fatty materials, its synergistic property being no more marked than that of the citric acid component of Embanox 4. The reason for the relative inefficiency of D.L.T.D.P., compared to its behaviour in hydrocarbons is not clear.

4.3 STUDIES INVOLVING NICKEL CHELATES.

Studies made in connection with the inhibiting property of NiSDT were rather limited owing to the low solubility of the latter in the fatty substrates. It was thought that the addition of alkyl groups to the phenyl rings of the complex would lead to an improvement in the solubility of the chelate in oleic acid and oleyl alcohol. For this purpose, two such para-substituted derivatives, viz. bis (di-p-isopropyl stilbene dithiolato) Ni (II) and bis (di-p-tert.butyl stilbene dithiolato) Ni (II), were synthesised from simple starting materials. Also to investigate the effects of electron donating and withdrawing groups on the antioxidant activity of the chelate, bis (di-p-chlorostilbene dithiolato) Ni (II) and bis (di-p-methoxy stilbene dithiolato) Ni (II) were prepared in the laboratory. All structures were confirmed from nmr and ir analyses, and a list of characteristic absorption bands with their coefficients of absorption of the electronic spectrum of each individual nickel chelate was obtained.

Solubility determinations (Table 3.34) indicated that, with the

exception of MeO-NiSDT, all other nickel chelates were sufficiently soluble in oleic acid and oleyl alcohol to allow solutions of 2×10^{-4} mol dm⁻³ concentration of these nickel chelates to be examined, with DIP-NiSDT and DTB-NiSDT showing the greatest solubilities.

The autoxidation experiments carried out with the nickel chelates endorsed the view that such complexes show some antioxidant activity for the thermal autoxidation of fatty substrates, with the order of their efficiency being DTB-NiSDT > Cl-NiSDT > NiSDT > DIP-NiSDT > MeO-NiSDT (Table 3.33). The induction periods produced in oleic acid samples were rather poor compared to the conventional phenolic antioxidants at the same molar concentration, but there was a marked improvement for samples of oleyl alcohol, particularly with DTB-NiSDT which proved to be a much better inhibitor than all the antioxidants previously tested. However, the ending of the induction period was very sharp and extremely large rates of oxygen absorption were recorded (Table 3.33, Fig. 3.15). This strongly suggests that nickel ions are released by the reactions of NiSDT during the induction period and act as catalysts of the oxidation in the post-inhibition period. Similar effects have been observed with related compounds such as the transition metal salts of thiocarbamic acid¹⁷⁵.

The kinetic measurements for the determination of the rate of consumption of these nickel chelates during the induction period showed that the order of the reactions is nearest to being half-order for the first 75% consumption (Fig. 3.22); however, owing to the autocatalytic nature of these reactions, and the occurrence of several branching reactions near the end of the induction period, the order of the reaction is disturbed during the last 20% or so of the chelate consumption. There is also a

definite time interval between the complete consumption of the chelates and the commencement of absorption of oxygen by the samples (Table 3.36). A likely explanation for this is the formation of secondary inhibitors, which are the thermal oxidation products of the chelates, and act as retarders of the autoxidation of the fatty substrates.

Chien and Boss¹⁷⁶ have studied the decomposition of hydroperoxides by metal sulphur complexes and concluded that much of the activity of these complexes results from the release of sulphur dioxide by the oxidation of the complexes. Sulphur dioxide is a powerful co-catalyst for the decomposition of hydroperoxides by an acid catalysed mechanism. It seems plausible to suggest that a mechanism of this kind is operating in our system resulting in the extended induction period. In view of the observed complexity of these reactions which involve the simultaneous production of a hydroperoxide decomposer (SO_2) and an autoxidation catalyst (free nickel ions), it is doubtful whether the observed half-order consumption of NiSDT and its para-substituted compounds can be explained in terms of a detailed reaction mechanism; indeed this half-order behaviour may be fortuitous.

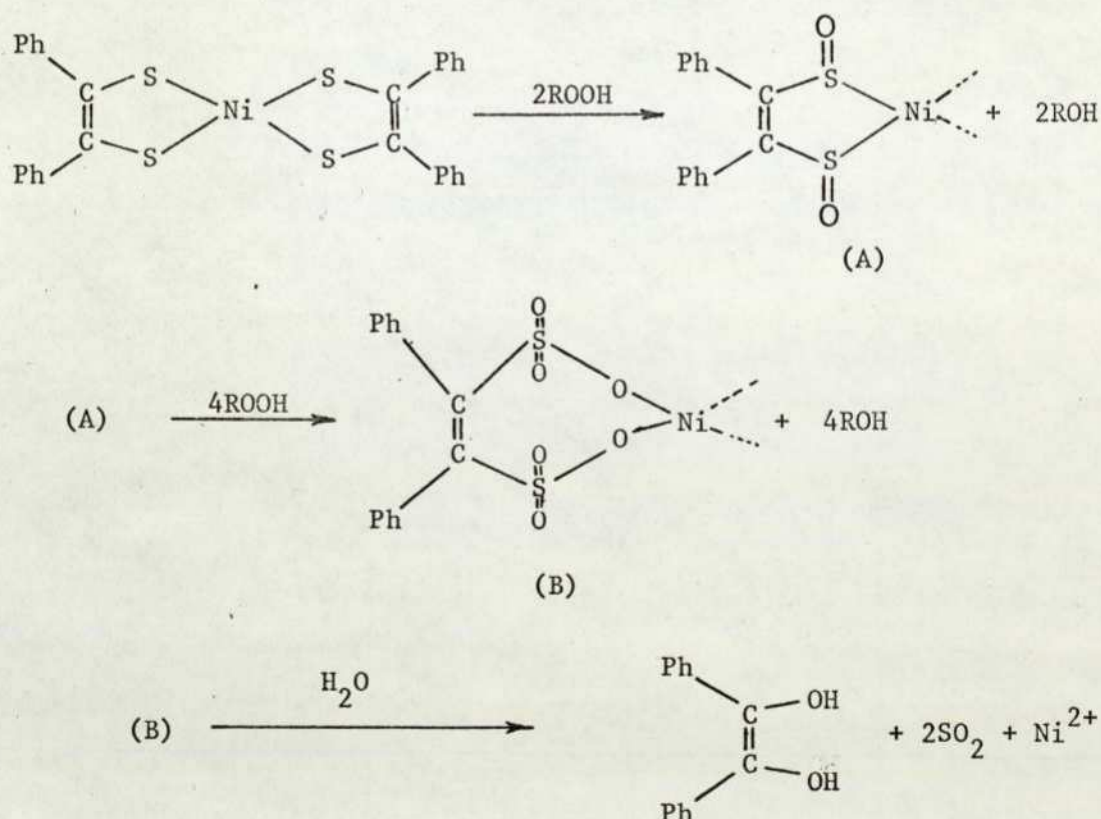
The large difference in induction periods observed with oleic acid and oleyl alcohol might be attributed to one of the following possibilities:

- (i) - Decomposition of NiSDT by reaction with oleic acid
- (ii) - Reduction in the efficiency of NiSDT as a hydroperoxide decomposer or free-radical scavenger in acid medium.
- (iii) - Reduction of the efficiency of sulphur dioxide or other oxidation products of NiSDT as hydroperoxide decomposers in the presence of acids.
- (iv) - Enhancement of the rate of peroxide decomposition to radical

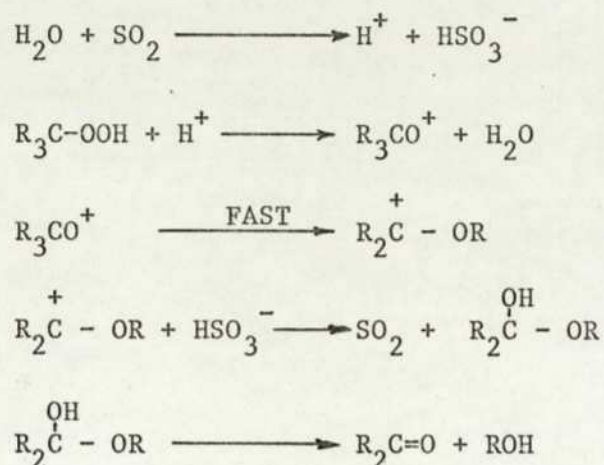
products catalysed by free nickel ions in acid medium.

The first of these possibilities was ruled out by an experiment in which NiSDT was heated with oleic acid at 85°C in an inert atmosphere; after 96 hours no change in the concentration of NiSDT occurred. The present results are insufficient to allow the remaining possibilities to be distinguished although the known ability of organic acids to alter the redox potentials of metal ions by chelation suggests that (iv) may be important.

Schrauzer and his co-workers^{172,202} have suggested that oxidation at one of the sulphur atoms of NiSDT will lead to activation of the second sulphur atom of the same ligand towards further reaction. In the light of this observation the following mechanism can be tentatively proposed to account for hydroperoxide decomposition by NiSDT.



If this reaction sequence can proceed in both ligands then each molecule of NiSDT should be able to decompose 12 molecules of hydroperoxide. However, nickel ions released can catalyse hydroperoxide decomposition by the familiar redox reaction, whilst sulphur dioxide catalytically decomposes hydroperoxides by reactions of the form:



This mechanism follows those postulated by other workers but a considerably more detailed investigation of the inhibiting behaviour of such compounds in fatty substrates is needed before its validity can be proven.

4.4 ACTION OF METAL CATALYSTS.

From the experiments which were carried out with oleic acid and oleyl alcohol samples containing different concentration of various salts of Co (II), Co (III), Fe (III), and Cu (II) metals, it was concluded that the catalytic activity of these metal complexes increases only slightly with their increasing concentration; this catalytic effect being much more

severe for oleic acid. The order of the catalytic activity observed for the individual metals was $\text{Co (III)} > \text{Co (II)} > \text{Fe (III)}$. The two copper chelates did not show any significant catalytic effect; the reasons for this have been discussed fully in section 3.8.2. Also the phenomenon of catalyst-inhibitor conversion, which has been observed by Betts and Uri^{180,203} with certain of these metal complexes was not observed in these fatty substrates, even at catalyst concentrations as high as $5 \times 10^{-3} \text{ mol dm}^{-3}$.

A series of investigations of the catalytic activities of these transition metal salts in conjunction with antioxidants demonstrated the drastic effect of these metal catalysts (Figs. 3.26 - 3.43) on the autoxidation of oleic acid and oleyl alcohol. The appreciable catalytic activity of the two cobalt salts was attributed to the ability of the interconversion reactions of the form $\text{Co}^{2+} \longrightarrow \text{Co}^{3+} \longrightarrow \text{Co}^{2+}$ etc. to proceed rapidly.

4.5 FINAL CONCLUSIONS AND FUTURE WORK.

The studies described in this thesis have provided a basis for understanding the effects of a wide variety of conditions (oxidation temperature, impurities, antioxidants, and pro-oxidants) on the autoxidation of fatty substrates. Whilst the results have clear implications in the choice of substrate and antioxidant in commercial use, it is very clear that the reactions involved in these systems are extremely complex. For future development of this work it would seem reasonable to suggest that many of the systems which have been examined might be worthy of much more detailed kinetic investigation in the hope of clarifying the

underlying reaction mechanisms. It is hoped that this thesis will serve as a useful basis for such studies in the future.

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