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A THESIS

entitled

INHIBITION OF THE AUTOXIDATION OF POLYMER MODEL COMPOUNDS BY A NICKEL CHELATE

by

MICHAEL DAVID LARKINS

Submitted for the

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of

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1975

ABSTRACT

The mechanism by which a relatively new chelate — bis(stilbenedithiolato)nickel — inhibits autoxidation has been investigated. To this end, the literature has been reviewed with particular reference to the known reactions of this complex. The chelate and some related molecules have been synthesised and the effect of alternative solvents on the synthesis has been investigated with a view to making it more suitable for industrial purposes.

Experimental investigation has established that the chelate is an extremely efficient antioxidant — particularly in aromatic substrates for which 'critical' phenomena have been found. Detailed kinetic studies of the inhibition of autoxidation and of the reactions between the chelate and a model hydroperoxide show that the chelate exhibits two modes of inhibition — radical termination and hydroperoxide decomposition. The initial products from the chelate are also efficient inhibitors and the inorganic products from the reaction between the chelate and hydroperoxide have been identified. The radical-trapping function shows indications of steric effects with long-chain hydrocarbons and has been shown to depend on a separate part of the inhibitor molecule to the hydroperoxide-decomposing function.

On the basis of the results obtained and the known chemistry of the complex, mechanisms are proposed for both modes of inhibition.

ACKNOWLEDGEMENTS

The task of compiling a list of names of the large number of people to whom one becomes indebted in the course of over three years' study would be impossible. Nevertheless, I should particularly like to express my appreciation to Professor C.F. Cullis and the late Professor N. Uri for their guidance and encouragement, and to Dr. N.C. Billingham for his assistance with the manuscript after the death of Professor N. Uri in August 1974. I am also obliged to the members of the Combustion and Oxidation Research Laboratory for many stimulating discussions and to my wife, [redacted], for her patience and forebearance whilst typing this thesis.

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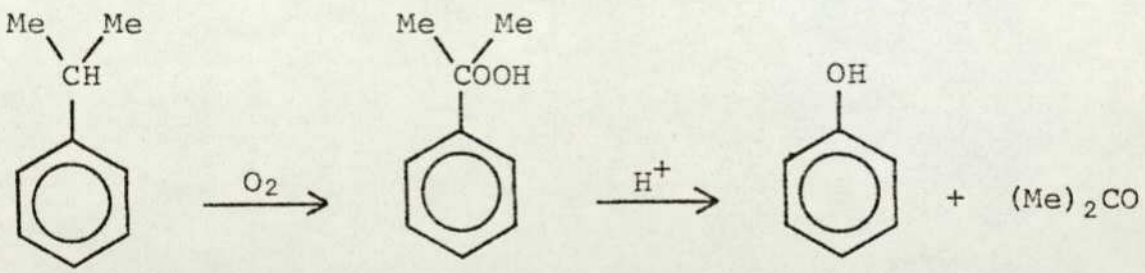
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1 INTRODUCTION

1.1 General Introduction

The phenomenon of autoxidation is an everyday occurrence and has been defined[1] as 'oxidation which can be brought about by oxygen at normal temperatures without the intervention of a visible flame or of an electric spark'. Such reactions are generally autocatalytic in nature and different sectors of industry have made considerable efforts in attempting either to catalyse or to suppress autoxidation. The many beneficial uses of autoxidation include the atmospheric drying of some paints (e.g. linseed oil based) and a large number of industrial syntheses. The growth of the petrochemical industry has greatly increased the number of synthetic applications, since many of the starting materials for the production of man-made fibres, organic solvents etc. may be obtained from controlled oxidation of petroleum hydrocarbons[2,3]. One of the better known synthetic applications is the manufacture of phenol and acetone from cumene (isopropylbenzene) by decomposition of cumene hydroperoxide with strong acids[2].



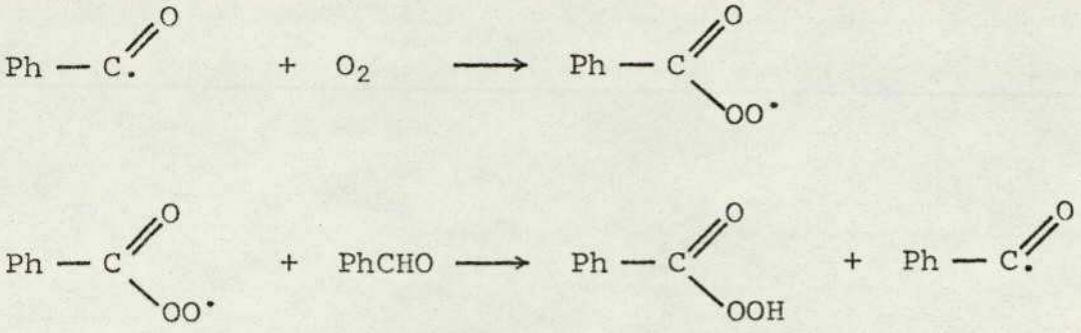
However, autoxidation is also responsible for the deterioration of many materials, e.g. the rancidity of fats and the breakdown of polymers, and much research has been concentrated on discovering suitable additives, known as antioxidants or stabilisers, to prevent or severely restrict this reaction. The industrial approach to this problem in the past was largely empirical, which meant that the understanding of the inhibition

process lagged seriously behind the technology of inhibition. The large volume of research into this aspect over the past 20 years has now clarified the processes involved, although some problems, e.g. the mechanism of the initiation step, are not yet fully solved. A fundamental understanding of the mode of action of all the types of inhibitors is extremely important, as such knowledge would contribute greatly to the synthesis of 'tailor-made' antioxidants for specific applications.

1.2 Historical development of autoxidation

The first scientific record of autoxidation may have been the slow transformation of benzaldehyde to benzoic acid described by Wohler and Liebig[4] in 1832. This was followed by Schönbein's[5] extensive work in the 1860's, although his mechanistic theories tended to be influenced markedly by his earlier discovery of ozone[6]. Towards the end of the nineteenth century, theories were proposed[7-10] which regarded the mechanism of autoxidation as the addition of molecular oxygen to the substance undergoing oxidation, with the subsequent formation of a highly reactive peroxide — thereby laying the basis for our current understanding of autoxidation.

Following Gomberg's discovery of free radicals[11] in 1900, the essential concept of a chain reaction was introduced by Bodenstein[12] in 1913 and was subsequently developed separately by Semenov and Hinshelwood with particular reference to gas-phase kinetics. It was the work of Bäckström[13] shortly after this time, together with the researches by Haber and his school[14,15], that provided the precursor to modern autoxidation mechanisms. Bäckström proposed a radical chain process[16,17] for the autoxidation of benzaldehyde, with the propagation steps:-



Research on the autoxidation of hydrocarbons had been proceeding in much the same manner during the 20's and 30's although considerable effort was being expended on reporting the empirical effects of antioxidants[18]. (The theories concerning the inhibition of autoxidation that were held at that time have been summarised by Butler[19].) However, research of a more fundamental nature was being carried out, and this led to the isolation and identification of the hydroperoxides of cyclohexene[20-23] and tetralin[24]. It was this isolation of purified hydroperoxides from cyclohexene and many other autoxidised olefins that constituted one of the major advances of the 1930's and caused the decline in acceptance of the older autoxidation theories which were prevalent at that time. (Further information regarding these theories may be obtained from two reviews of the period by Moureu[25] and Milas[26].) Following the discovery of the hydroperoxide, Farmer et al[27] carried out extensive work on the autoxidation of fatty acids and proposed that the autoxidation of practically all unconjugated olefinic compounds proceeded by a chain reaction involving the addition of oxygen to the carbon atom adjacent to the double bond to form a hydroperoxide. Farmer's concept was extended by Bolland and Gee[28] into the free radical chain mechanism of hydroperoxide formation. This is now widely accepted as being applicable to a large variety of organic materials and the older theories

of direct oxygen addition across a double bond retain only very minor support[29-32].

1.3 The autoxidation of hydrocarbons

1.3.1 The general mechanism

The general scheme of oxidation proposed by Bolland and Gee[28] comprises the three stages of initiation, propagation and termination.

$$RH \longrightarrow R^{\bullet} \quad (\text{rate} = r_i) \qquad \text{Initiation} \qquad (1)$$

$$R^{\bullet} + O_2 \xrightarrow{k_o} RO_2^{\bullet} \qquad (2)$$

$$RO_2^{\bullet} + RH \xrightarrow{k_p} ROOH + R^{\bullet} \qquad (3)$$

(2) and (3): Propagation

$$2RO_2^{\bullet} \xrightarrow{2k_t} \qquad (4)$$

$$R^{\bullet} + RO_2^{\bullet} \xrightarrow{2k_t'} \qquad (5)$$

$$2R^{\bullet} \xrightarrow{2k_t''} \qquad (6)$$

(4), (5) and (6): Termination to non-radical products

If it is assumed that the steady-state approximation is valid for both $[R^{\bullet}]$ and $[RO_2^{\bullet}]$, then the rate of oxygen uptake for long autoxidation chains can be shown to be:-

$$-\frac{d[O_2]}{dt} = r_i^{\frac{1}{2}} \cdot \frac{k_p[RH]}{(2k_t)^{\frac{1}{2}}} \cdot \frac{k_o k_t^{\frac{1}{2}}[O_2]}{k_p k_t''^{\frac{1}{2}}[RH] + k_o k_t^{\frac{1}{2}}[O_2]} \qquad (7)$$

(The chain length of an autoxidation is the number of molecules of oxygen taken up for each initiation step.) As the rate of reaction (2) is extremely high with respect to reaction (3), the population of alkyl radicals is very low and termination can be assumed to be exclusively by reaction (4) provided that there is sufficient oxygen available[33]. Under these conditions, application of the steady-state approximation allows the overall oxidation rate to be expressed as:-

$$-\frac{d[O_2]}{dt} = \frac{r_i^{\frac{1}{2}} k_p [RH]}{(2k_t)^{\frac{1}{2}}} \qquad (8)$$

Similar considerations allow the kinetic chain length (N) to be derived from:-

$$N = -\frac{d[O_2]}{dt} \Big/ r_i = \frac{k_p [RH]}{(r_i \cdot 2k_t)^{\frac{1}{2}}} \qquad (9)$$

Under mild conditions, it has been found[34-36] with certain substrates that oxygen consumption and hydroperoxide yield agree closely. However, the hydroperoxide may decompose to further radical species, by for example (10),

$$ROOH \xrightarrow{k_{10}} RO^{\bullet} + {}^{\bullet}OH \qquad (10)$$

and these radicals will also take part in the chain reaction. The increasing initiation from this source is responsible for the typical autocatalytic type of autoxidation reaction that is frequently observed, i.e. a slow initial rate which accelerates as the reaction proceeds. For an autoxidation initiated by hydroperoxide in this manner, the rate equation is of the form:-

$$-\frac{d[O_2]}{dt} = \frac{k_{10}k_p[ROOH]^{\frac{1}{2}}[RH]}{(2k_t)^{\frac{1}{2}}} \qquad (11)$$

The true mechanism of any given autoxidation may be considerably more complex, with alternative reactions and decompositions occurring. For example, above certain hydroperoxide concentrations, which are dependent on the particular system, the decomposition of the hydroperoxide becomes bimolecular[37-40].

$$2ROOH \xrightarrow{k_{12}} RO_2^{\bullet} + RO^{\bullet} + H_2O \qquad (12)$$

Infra-red spectroscopic evidence[38] for molecular association between hydroperoxide molecules has been obtained. It has also been found[36,41,42] that the propagation sequence for some hydrocarbons, e.g. styrene, can involve peroxy-radical addition to a double bond (13),

$$RO_2^{\bullet} + CH_2{=}CH.C_6H_5 \longrightarrow RO_2CH_2.\dot{C}H.C_6H_5 \qquad (13)$$

rather than hydrogen abstraction to form the hydroperoxide. Addition polymerisation (14)

$$RO_2CH_2.\dot{C}H.C_6H_5 + CH_2{=}CH.C_6H_5 \longrightarrow RO_2CH_2.CH(C_6H_5)CH_2.\dot{C}H.C_6H_5 \qquad (14)$$

may then follow, or reaction (2) may occur to subsequently give a polyperoxide. Other hydrocarbons, such as indene[42,43], can undergo both reactions (3) and (13), thereby producing hydroperoxide and polyperoxide. Thus,

although the overall reaction scheme is fairly simple, it is only a general picture and considerable research has been carried out on specific aspects. The main divisions of the overall scheme will be considered individually below.

1.3.1.1 Initiation

The production of free radicals at the start of autoxidation can be achieved in various ways:-

(a) by radiation-induced splitting of a molecule into radicals,

(b) by the thermal decomposition into radicals of peroxy compounds,

(c) by the action of metal catalysts,

(d) by direct reaction between the substrate and oxygen.

It is the latter two possibilities with which we are most concerned in the present work. Except in special cases, initiation in a pure RH/O_2 system will proceed by (d):-

$$RH + O_2 \longrightarrow R^{\bullet} + HO_2^{\bullet} \qquad (15)$$

$$2RH + O_2 \longrightarrow 2R^{\bullet} + H_2O_2 \qquad (16)$$

Reaction (16) is energetically more favourable for C—H bond dissociation energies of less than 360 kJ mol^{-1} and Denisov[43] has obtained experimental evidence for termolecular initiation in tetralin, cyclohexanol and cyclohexanone. Carlsson and Robb[44] confirmed this work for tetralin and also established a termolecular initiation for indene, in agreement with the work of Dulog[45]. However, although the pre-exponential factors obtained by Carlsson and Robb agreed with those calculated from bond dissociation considerations by the Denisov[46,47] method, the observed activation energies

were intermediate between the values predicted for either bimolecular or termolecular initiation. An attempt to explain this deviation by the prior formation of an oxygen-hydrocarbon charge-transfer complex was not substantiated by a further series of experiments by Betts and Robb[48-50].

From the viewpoint of practical autoxidation, the effect of external factors may be significant. For example, Carlsson and Robb[44] have noted marked differences in autoxidation rates caused by differing reaction vessel pre-treatments. More important is the presence of trace amounts of heavy metals at levels sometimes requiring neutron activation analysis for their detection. Heavy metals have long been known as catalysts[51-53] of autoxidation. Apart from initiating autoxidation by converting hydroperoxides to radicals[54-56], they have been reported[57,58] to cause initiation by the oxidation of particularly reactive substrates such as linoleic acid.

$$M^{(n+1)^+} + RH \longrightarrow M^{n+} + R^{\bullet} + H^+ \qquad (17)$$

Reaction with molecular oxygen in the absence of hydroperoxide has also been observed[59-61]. For bis(N-butylsalicylaldimino)cobalt(II) and similar compounds, this reaction has been formulated by Uri[59] as:-

$$M^{n+}.O_2(XH) \longrightarrow M^{(n+1)^+} X^- + HO_2^{\bullet} \qquad (18)$$

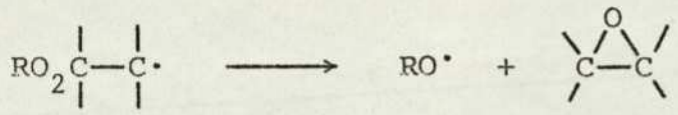
The formation of a complex between oxygen and the chelate precedes the radical-producing step[59-62]. Thus, Uri has postulated[54,58-63] that elimination of all trace metals would result in no significant initiation occurring in an autoxidation system. The elimination of trace metal effects had been claimed by Carlsson and Robb[44] using column chromatography

although Pitkethly[64] considered that this technique seriously risks the introduction of further trace metals (particularly iron) from the adsorbents. Direct experimental evidence in favour of Uri's hypothesis was obtained by Denisov et al[65] from a cobalt(II)-catalysed styrene system. As only polyperoxides are formed in the styrene system, a direct study of the cobalt-oxygen reaction may be undertaken without interference from the reactive hydroperoxide which normally occurs in autoxidation.

It is clear that, although the process of autoxidation is well understood, the elemental reaction of chain initiation is still obscure. The trace metal hypothesis of Uri seems to offer the best explanation of the phenomenon, but the difficulties of investigation of such a theory have hindered its universal acceptance up to the present time. It is considered that the particular theoretical importance of the initiation step warrants further research and the use of more sophisticated techniques, such as electron spin resonance, may throw new light on this problem.

1.3.1.2 Propagation

The two propagation steps (reactions (2) and (3)) form the basis of the chain reaction. The rate determining step of the overall mechanism is reaction (3) as the addition of oxygen to an alkyl radical, reaction (2), is extremely rapid ($k_o = 10^7 - 10^8$ l mol^{-1}s^{-1}). In contrast, values of k_p are typically in the range 0.05 - 13 l mol^{-1}s^{-1} [66-71]. The propagation steps also generally determine the reaction products in the early stages. The most common propagation step is reaction (3), i.e. the formation of hydroperoxide by hydrogen abstraction from the substrate. Other propagation steps include the formation of polyperoxide, mentioned earlier for styrene (reactions (13) and (14)), and the formation of epoxides from certain monoolefins[41,72,73] by decomposition of alkylperoxy radicals formed in reaction (2).



(19)

The present work concentrates on those substrates undergoing the hydrogen abstraction reaction and further information on alternative propagation steps may be found in various review articles[74,75].

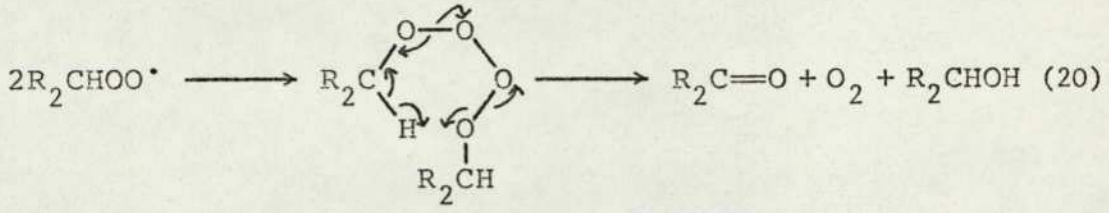
The rate of abstraction will be dependent to a large extent on the molecular structure of the hydrocarbon undergoing oxidation and primarily on the strength of the relevant R—H bond[76]. The activation energy for the reaction can be as low as 20 kJ mol^{-1} for 1,4-dienes[77] and as high as 60 kJ mol^{-1} for paraffins[78], reflecting the differences in bond dissociation energies (ca. 280 and 400 kJ mol^{-1} respectively). Further discussion of the structural effects on autoxidation will be carried out in section 1.3.2.

1.3.1.3 Termination

Chain termination, the destruction of free radicals, may occur by interaction of the radical with the reactor wall or by a bimolecular reaction between two free radicals. However, the density of the medium in liquid phase oxidation and the consequent slow diffusion to the wall ensure that, under normal conditions of reactor volume-to-surface-area ratio, termination occurs bimolecularly as in reactions (4), (5) and (6). These radical recombinations take place with a very low activation energy (ca. 4 - 8 kJ mol^{-1}) and termination rate constants are typically in the range 10^4 - 10^7 l $mol^{-1}s^{-1}$ [66-71].

For primary, secondary and tertiary alkylperoxy radicals, the rate of the termination reaction within each class is mainly dependent on steric factors[74]. Primary and secondary radicals terminate by transfer of

an α-hydrogen atom to give an alcohol and a ketone as products via a cyclic transition state[79,80].



This mechanism is based on the stoichiometry of the reaction and on experimental evidence showing that substitution of an α-deuterium atom in the peroxy radical reduces the rate of the termination reaction by a factor of approximately two[79-82]. Tertiary peroxy radicals, which lack an α-hydrogen atom, generally interact more slowly to give a pair of alkoxy radicals within a solvent cage. Low temperature e.s.r. studies have shown the first stage to be the reversible formation of a tetroxide[82-83], which subsequently decomposes.

$$RO_2^{\bullet} + RO_2^{\bullet} \rightleftharpoons ROO{\cdot}OOR \qquad (21)$$

$$ROO{\cdot}OOR \longrightarrow RO^{\bullet} + O_2 + {}^{\bullet}OR \qquad (22)$$

The alkoxy radicals formed may combine within the cage to form a dialkyl peroxide, ROOR, or, more commonly, diffuse apart. These radicals may initiate further chains or fragment to smaller radicals which terminate efficiently. For example, in the oxidation of cumene[84]:-

$$C_6H_5(CH_3)_2CO^{\bullet} \longrightarrow C_6H_5COCH_3 + CH_3^{\bullet} \quad (23)$$

$$CH_3^{\bullet} + O_2 \longrightarrow CH_3OO^{\bullet} \quad (24)$$

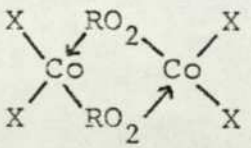
$$CH_3OO^{\bullet} + C_6H_5(CH_3)_2COO^{\bullet} \longrightarrow C_6H_5(CH_3)_2COH + HCHO + O_2 \quad (25)$$

Further experimental evidence for the overall termination reaction may be inferred from the formation of O^{16}- O^{18} oxygen[85] in the autoxidation of cumene with O_2^{16} and O_2^{18}.

Transition metals have also been observed to take part in termination reations[55,56,59-61]. Uri[59,60] has postulated the formation of inactive bidentate chelates with cobalt(II) salicylaldimines, a reaction which is second-order with respect to the metal chelate:-

$$2CoX_2 + RO_2^{\bullet} \rightleftharpoons (CoX_2)_2 \cdot RO_2 \quad (26)$$

$$(CoX_2)_2 \cdot RO_2 + RO_2^{\bullet} \longrightarrow \quad (27)$$



Since initiation by metal chelates is often a first-order process, where the metal acts as both initiator and terminator reactions (26) and (27) become increasingly significant at high concentration of metal. This causes these compounds to exhibit the unusual phenomenon of being autoxidation catalysts at low concentration and antioxidants at higher concentrations.

1.3.1.4 The hydroperoxide

The formation and chemical properties of hydroperoxides have been extensively described[86-88] in the literature and a review of the subject is beyond the scope of this work. The importance of the hydroperoxide in autoxidation is mainly due to its decomposition into radicals which give rise to chain-branching and autocatalysis. This decomposition can be complex. As mentioned previously, the thermal decomposition may be uni- or bimolecular depending on the hydroperoxide concentration[37-40]. The rate and type of decomposition may also be influenced by solvents[89,90], pH of the medium[91,92] and other components of the autoxidising system[93]. The tendency of hydroperoxides, alcohols and acids to form hydrogen bonds will have an effect in any autoxidation system producing these compounds, due to the weakening of O—H and O—O bonds by dimer formation. Ketones, another common component, can have varying effects. Cyclohexanone has been found to catalyse the decomposition of t-butyl hydroperoxide[94] and to catalyse the oxidation of cyclohexane[95,96]. Conversely, α-tetralone appears to inhibit the oxidation of tetralin[97,98], although this may not be directly attributable to the ketone[99].

Transition metal compounds also have a significant effect on hydroperoxide decomposition[54-56]:-

$$M^{n+} + ROOH \xrightarrow{k_{28}} M^{(n+1)+} + RO^{\cdot} + OH^{-} \qquad (28)$$

$$M^{(n+1)+} + ROOH \xrightarrow{k_{29}} M^{n+} + RO_2^{\cdot} + H^{+} \qquad (29)$$

Metals which can alternate between adjacent oxidation states decompose hydroperoxides catalytically in this manner. At the steady-state, the

rate of initiation is given by:-

$$r_i = 2k_{28}k_{29}\left[M\right]\left[ROOH\right] \Big/ (k_{28} + k_{29}) \qquad (30)$$

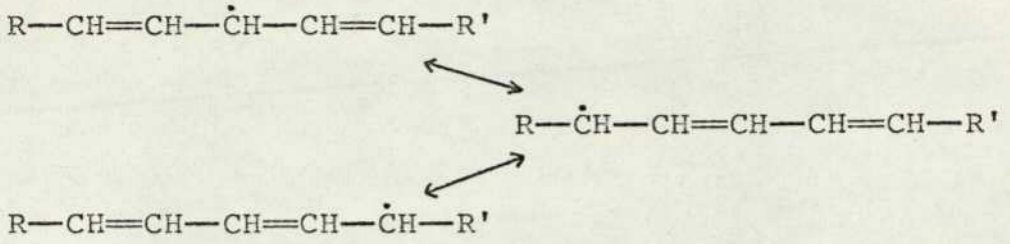
where $\left[M\right] = \left[M^{n+}\right] + \left[M^{(n+1)^+}\right]$.

The rate of autoxidation is thus proportional to the square root of the total metal concentration. However, when the hydroperoxide concentration reaches a maximum value, at which its formation equates exactly with its decomposition, the limiting autoxidation rate may be shown[55,56,100] to be independent of the total metal concentration and given by:-

$$-\frac{d[O_2]}{dt} = \frac{k_p^{\,2}[RH]^2}{2k_t} \qquad (31)$$

1.3.2 Structural effects

The effect of a hydrocarbon's structure upon its rate of autoxidation is primarily related to the strength of the R—H bond undergoing reaction (3). Polar and steric factors also play a part but, in most cases, these are less important. The formation of an alkylperoxy radical by reaction (2) is extremely rapid and has a very low activation energy, with the structure of the alkyl radical only being important in certain compounds in which the radical is extensively stabilised. An example of this kind occurs in the oxidation of 1,4-dienes where delocalisation of the radical over two double bonds leads to considerable resonance stabilisation:-



The structure of the alkylperoxy radical also does not generally affect the reaction rate to any great extent, as the reactive centre is based mainly on the peroxy group[82] which is rather remote from the variable alkyl portion. Exceptions to this are the tertiary alkylperoxy radicals, such as cumylperoxy and t-butylperoxy, which have diminished reactivity due to steric hindrance[101,102] in the reaction with the parent hydrocarbon. Thus, the rate of reaction of a hydrocarbon with any given alkylperoxy radical will depend primarily on the strength of the weakest C—H bond. In all unsaturated compounds, the presence of more than one double bond will decrease the C—H bond strength of a methylene group which is α to both. This is illustrated by the markedly increased reactivity of methyl linoleate compared to methyl oleate and of 9,10 dihydroanthracene compared to tetralin. Similarly, the relative reactivities of the α-hydrogen atoms of toluene, ethylbenzene and cumene towards an alkylperoxy radical[35] reflect the decrease in bond strength on going from a primary to a tertiary carbon-hydrogen bond. The rate of oxidation of these compounds is also significantly affected by polar substituents. The effect of substituents on electron distribution is most marked in aromatic compounds due to the nature of the π-bonding system. It has been found by Russell[35,103] that the oxidation rates of toluenes and cumenes are increased by electron-donating ring substituents and decreased by electron-withdrawing substituents. In illustration of this effect, it was found

that k_p for 4-methoxycumene is approximately twice, and for 4-nitrocumene approximately half the value for cumene itself[103].

The foregoing is, of necessity, a rather brief outline of a wide and involved aspect of autoxidation. The interactions between differing types of hydrocarbons and peroxyradicals (e.g. 1^o hydrocarbon and 3^o radical) and the correlation of the data obtained can be extremely complex, requiring the consideration of many factors. This increases the many difficulties of attempting to forecast the behaviour of hydrocarbon mixtures during oxidation. More extensive information on all the aspects involved may be obtained from references 74, 75 and the references quoted therein.

1.4 The inhibition of autoxidation

The usefulness of autoxidation in many applications has to be balanced with its harmful effects in others. Consequently, an extensive amount of research has been carried out in an attempt to find substances capable of severely restricting this reaction in, for example, edible oils and fats. The identification and study of these substances has been carried out for at least 100 years, but only comparatively recently has any significant understanding of their mechanism of action been achieved. Research in the earlier part of this century was mainly confined to reporting the empirical effects of antioxidants and examples of this, together with the early theories of antioxidant action, may be found in references 18, 19, 25 and 26. The establishment of a free radical chain mechanism for autoxidation by Bolland and Gee[28] contributed greatly to the understanding of the action of antioxidants. From the mechanism of Bolland and Gee (section 1.3.1), it is clear that there are two possible means of interfering with the course of an autoxidation — either by preventing the initiation of a reaction chain or by preventing the reaction chain from

developing. The first case, the preventive mechanism, generally relies on the antioxidant decomposing any hydroperoxides in the system (whether indigenous or formed in situ) to non-radical products. The second case, the chain-breaking mechanism, relies on the antioxidant effectively competing with the substrate in the propagation reaction (3) and, of the two types, the latter has been the most extensively studied.

1.4.1 Chain-breaking antioxidants

The basic mechanism of a chain-breaking antioxidant (AH) is the replacement of propagation reaction (3) with an alternative reaction (32):-

$$RO_2^{\bullet} + RH \xrightarrow{k_p} ROOH + R^{\bullet} \qquad (3)$$

$$RO_2^{\bullet} + AH \xrightarrow{k_a} ROOH + A^{\bullet} \qquad (32)$$

The radical $A^{\bullet}$ produced by (32) is relatively non-reactive compared to the alkyl radical produced by (3). It is apparent that, for an antioxidant to be at all efficient, the rate of reaction (32) must be at least as fast and preferably much faster than the rate of reaction (3). Earlier considerations (section 1.3.2) have shown the rate of reaction (3) to be mainly dependent on the strength of the relevant C—H bond and, similarly, an efficient antioxidant will need at least one labile hydrogen atom[104,105]. However, the hydrogen atom should not be obtained from a weak C—H bond as this would lead to a chain reaction rapidly destroying the antioxidant. These conditions are most commonly met by the use of aromatic amines and phenols which have readily abstractable hydrogen atoms and produce resonance stabilised radicals. Bond strengths of 300 - 340 kJ mol^{-1} have been obtained[106] for such antioxidants.

The first detailed kinetic study of inhibition was carried out by Bolland and ten Have[104] using a peroxide-initiated ethyl linoleate system containing hydroquinone as inhibitor. By application of the stationary-state approximation to the scheme for autoxidation at oxygen saturation, the rate of oxygen uptake for the uninhibited reaction was shown to be:-

$$-\frac{d[O_2]}{dt} = \frac{r_i^{\frac{1}{2}} k_p [RH]}{(2k_t)^{\frac{1}{2}}} \qquad (8)$$

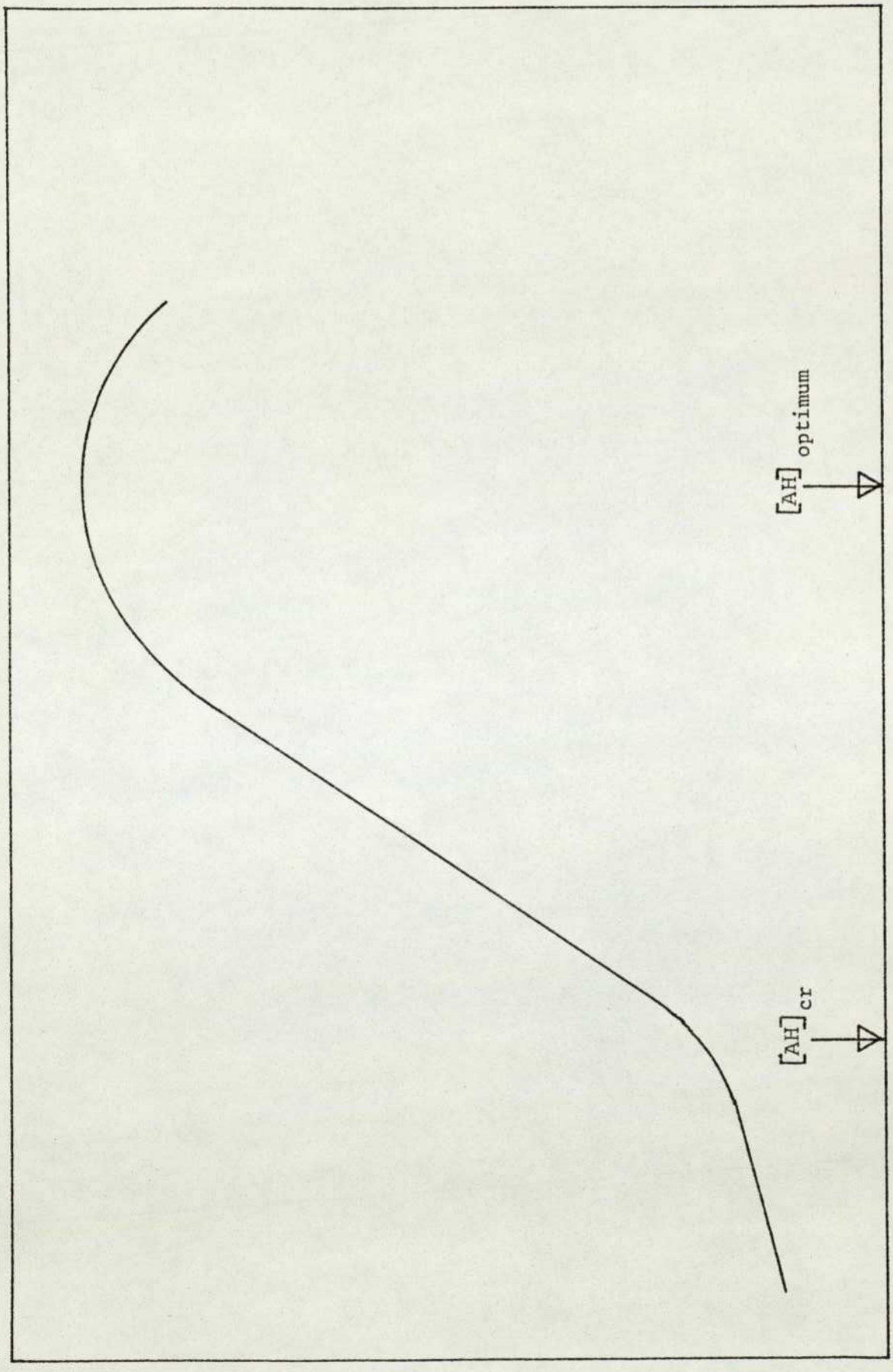
By assuming that all radical termination occurs by reaction (32) in the inhibited system, the rate of oxygen uptake becomes:-

$$-\frac{d[O_2]}{dt} = \frac{r_i \, k_p [RH]}{2k_a [AH]} \qquad (33)$$

More detailed studies, particularly of initiated autoxidations, allow the rate of initiation, the stoichiometry of the radical-inhibitor reaction and the rate constant for reaction (32) to be obtained[104,107-109]. For a wide range of common phenolic and amine antioxidants, k_a is typically in the range $10^2 - 10^5$ l $mol^{-1}s^{-1}$ [110-114] which is considerably higher than the values found for k_p[66-71].

The inclusion of free-radical acceptors in an oxidising system may lead to the occurrence of 'critical' phenomena in the kinetics. The possibility of such phenomena occurring in degenerate-branching reactions was predicted by the Semenov[115,116] theory of chain reactions and experimental investigations have shown the existence of a critical antioxidant concentration[117-120] at which the reaction abruptly changes from an autocatalytic to a slow steady rate. The induction period of the reaction also increases sharply at this critical concentration ($[AH]_{cr}$) as shown in figure 1.1.

Fig. 1.1: Induction period as a function of antioxidant concentration



The majority of the research into this aspect has been carried out by Russian workers with considerable emphasis on the theoretical considerations[119-123], and an expression for the critical concentration, $[AH]_{cr}$, has been derived:-

$$[AH]_{cr} = \frac{n}{1-n} \cdot \frac{k_p [RH]}{k_a} \qquad (34)$$

where n is the number of radicals produced in the degenerate-branching reaction. The value of n is always less than one[124].

An extremely comprehensive mathematical treatment of critical phenomena in chain reactions may be obtained from reference 123.

The foregoing has laid emphasis on the primary antioxidant reation (32) as the basis of inhibition. However, the overall effectiveness of a chain-breaking antioxidant depends not only upon its rate of interaction with alkylperoxy radicals, but also upon the fate of the radical $A^{\bullet}$. This will largely depend upon the structure of the radical and research on the effect of substituents has been carried out by many workers[81,105,107,109,125-128]—mainly with phenolic antioxidants. The possible reactions of $A^{\bullet}$ are[114,129]:-

$$2A^{\bullet} \longrightarrow A—A \text{ (or AH + inactive product)} \qquad (35)$$

$$A^{\bullet} + RO_2^{\bullet} \longrightarrow AOOR \qquad (36)$$

$$A^{\bullet} + O_2 \longrightarrow AO_2^{\bullet} \xrightarrow{RH} AOOH + R^{\bullet} \qquad (37)$$

$$A^{\bullet} + RH \longrightarrow AH + R^{\bullet} \qquad (38)$$

$$A^{\bullet} + ROOH \longrightarrow AH + RO_2^{\bullet} \qquad (39)$$

It is clear that whereas (35) and (36) are terminating reactions in the sense that radicals are removed from the system, the other reactions are chain-transfer steps. These will lead to continuation of the chain, reaction (37) being chain-branching in some cases due to decomposition of the hydroperoxide.

The amino radicals from primary and secondary amine antioxidants (ANH) can also undergo reactions (38) and (39)[111,130] in addition to reacting with further alkylperoxy radicals (40):-

$$RO_2^{\bullet} + ANH \longrightarrow ROOH + AN^{\bullet} \qquad (32')$$

$$RO_2^{\bullet} + AN^{\bullet} \longrightarrow RO^{\bullet} + ANO \qquad (40)$$

The nitroxide formed is itself a weak antioxidant and the alkoxy radical will initiate further chains. Thus, substituents may affect the activity of an antioxidant by either altering the rate of reaction (32) or by changing the ratio of the chain-transfer to termination reactions of the radical $A^{\bullet}$.

From the extensive research into substituent effects on 2,4,6-substituted phenols, the following generalisations may be made:-

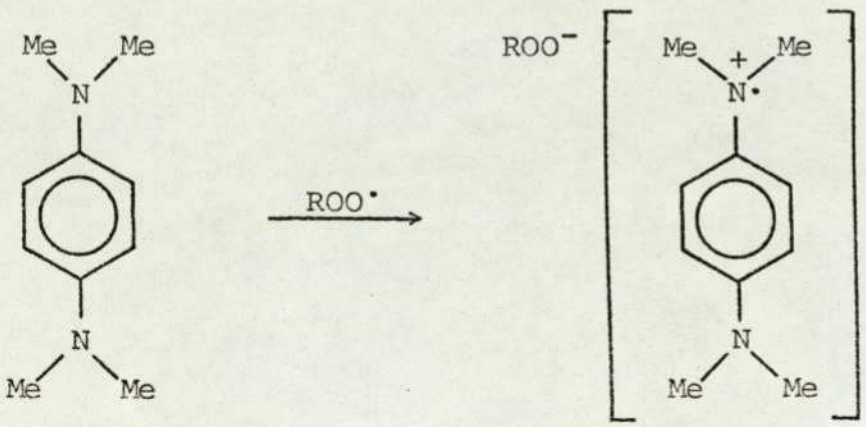
(a) Antioxidant activity is significantly increased by electron-donating groups.

(b) Electron-withdrawing groups decrease the antioxidant activity.

(c) α-Branched alkyl groups, particularly t-butyl, in the *ortho*-positions considerably increase the activity, whereas these groups decrease the activity when in the *para*-position.

The first two cases may be explained in terms of the electrophilic nature of the alkylperoxy radical and the increase or decrease in electron density

at the hydroxyl group caused by the substituents. Similar considerations apply to amine antioxidants[109,128] in which the occurrence of electron-transfer complexes is more important. The completely alkylated amines, for example tetramethyl-p-phenylenediamine(I), are efficient antioxidants and the resultant Würster radical-ion(II) can be identified as a product



(I) (II)

of the oxidation under autoxidation conditions[127]. The increase in anti-oxidant efficiency due to the insertion of bulky substituents in the *ortho*-positions, case (c), is due to steric hindrance of the active centre. The less sterically hindered phenoxy radicals will have a greater tendency to continue the chain reaction. This was shown by Bickel and Kooyman[125] in a comparison between 2,4,6-trimethylphenol and 2,6-di-t-butyl-4-methylphenol. Although the trimethylphenol was more efficient as an antioxidant in terms of its k_a value, it was less effective in practical terms. As before, similar considerations apply to amine antioxidants[125,128].

The application of the above criteria has led to the development of many extremely efficient polyphenolic antioxidants. However, as chain-breaking antioxidants simply reduce the lifetime of chains already present, they may be ineffective in certain instances. The high initiation rate of a hydrocarbon containing large quantities of hydroperoxide would be one

example. For this reason, the investigation and development of antioxidants which suppress the act of initiation (section 1.4.2) has been of importance and this class of compound is being increasingly used in synergistic combinations (section 1.4.4) with the chain-breaking antioxidants.

1.4.2 Preventive antioxidants

The purpose of preventive antioxidants is to suppress the initiation of the radical chain by removing sources of free radicals. The most important source is the hydroperoxide, and both metal ions and ultra-violet light are powerful catalysts for its decomposition into free radicals. Thus, there are three main preventive mechanisms — the deactivation of metal ions, absorption or screening of u.v. light and the decomposition of hydroperoxides to non-radical products. The effect of metal ions on the hydroperoxide[54-56] has been mentioned previously (section 1.3.1.4) and deactivation may be carried out by either strongly complexing the ion to its maximum co-ordination number[131,132] or by stabilising one valency state at the expense of others[133]. The latter case will result in either reaction (28) or (29), or both, becoming negligible. The denticity of the chelating agent will be one of the important factors in determining the stability of metal complexes[134]. However, some care has to be exercised in the selection of metal deactivators as in some cases the formation of a chelate may further increase the activity of the metal. For example, the copper deactivator disalicylidene ethylenediamine has been found to accelerate the iron or cobalt catalysed oxidation of cyclohexene[133]. The stabilisation of substrates to u.v. radiation is of great importance in the polymer industry and screening substances, such as carbon black and 2-hydroxybenzophenones, are widely used. Of the three mechanisms, the hydroperoxide

decomposer is generally useful and this class of preventive antioxidant will be considered in more detail.

1.4.2.1 Hydroperoxide decomposers

The earliest work on hydroperoxide-decomposing antioxidants was carried out by Denison and Condit[135,136] in an extensive study of the effects of naturally occurring inhibitors in the autoxidation of lubricating oils. These authors found that a wide variety of organic sulphides had the capacity to inhibit autoxidation by decomposing hydroperoxides. Some of the more effective inhibitors caused an initial rapid uptake of oxygen followed by autoinhibition. Conversion of the sulphides to sulphoxides and sulphones occurred, and the reaction was assumed to be the stoichiometric formation of sulphoxide based on hydroperoxide destroyed:-

$$ROOH + R'_2S \longrightarrow ROH + R'_2SO \qquad (41)$$

A more fundamental study of the autoxidation of sulphides was carried out by Bateman et al[137,138] who also found that a large number were autoinhibiting. The sulphoxide and thiosulphinate products were found to be effective antioxidants — being generally of a higher activity than the sulphides from which they were derived[139,140]. This would help to explain the initial oxygen uptake prior to autoinhibition in the lubricating oil systems of Denison and Condit[135,136]. The reaction of hydroperoxides with sulphur-containing compounds is often catalytic[141-143] and can be complex. Varying effects have been obtained depending on sulphide and sulphoxide structure[140,144-146], the nature of the solvent[144,145,147], the molar ratio of hydroperoxide to sulphide[139,148] and the reaction temperature[149]. In a large number of cases, the active antioxidant species has been shown

to be sulphur dioxide derived from the oxidation products of the original sulphide[142,143,150-153]. For example, dialkylthiodipropionate inhibitors have been shown to decompose hydroperoxides catalytically, with 1 mole of inhibitor being able to decompose up to 100 moles of hydroperoxide. The following scheme has been postulated to account for this observation[143]:-

$$(ROCOCH_2CH_2)_2S \xrightarrow{ROOH} (ROCOCH_2CH_2)_2SO \longrightarrow$$

$$ROCOCH{=}CH_2 + ROCOCH_2CH_2SOH \xrightarrow{ROOH} ROCOCH_2CH_2SO_2H$$

$$\longrightarrow ROCOCH{=}CH_2 + H_2SO_2 \xrightarrow{ROOH} H_2SO_3$$

$$\longrightarrow SO_2$$

Sulphur dioxide has been found[142,150] to be a powerful Lewis acid catalyst for the ionic decomposition of hydroperoxides:-

$$Ph{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}OOH + SO_2 \longrightarrow Ph{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}O^{+} + SO_3^{-}H$$

$$\longrightarrow PhOH + (CH_3)_2CO + SO_2 \qquad (42)$$

However, due to the complexities mentioned previously, the exact mechanism of many sulphur-containing hydroperoxide decomposers, apart from those producing sulphur dioxide, remains controversial.

Phosphites and phosphines have also been found[154,155] to decompose peroxides and their antioxidant activity arises from stoichiometric

reduction of the hydroperoxide:-

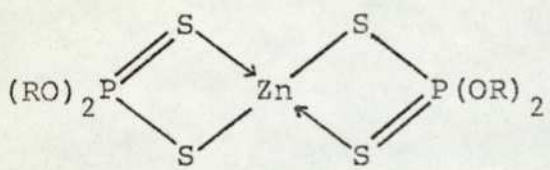
$$ROOH + (R'O)_3P \longrightarrow ROH + (R'O)_3PO \qquad (43)$$

$$ROOH + R'_3P \longrightarrow ROH + R'_3PO \qquad (44)$$

There is no evidence of catalytic decomposition for these compounds and, thus, sulphur compounds are generally more effective.

1.4.3 Multi-functional antioxidants

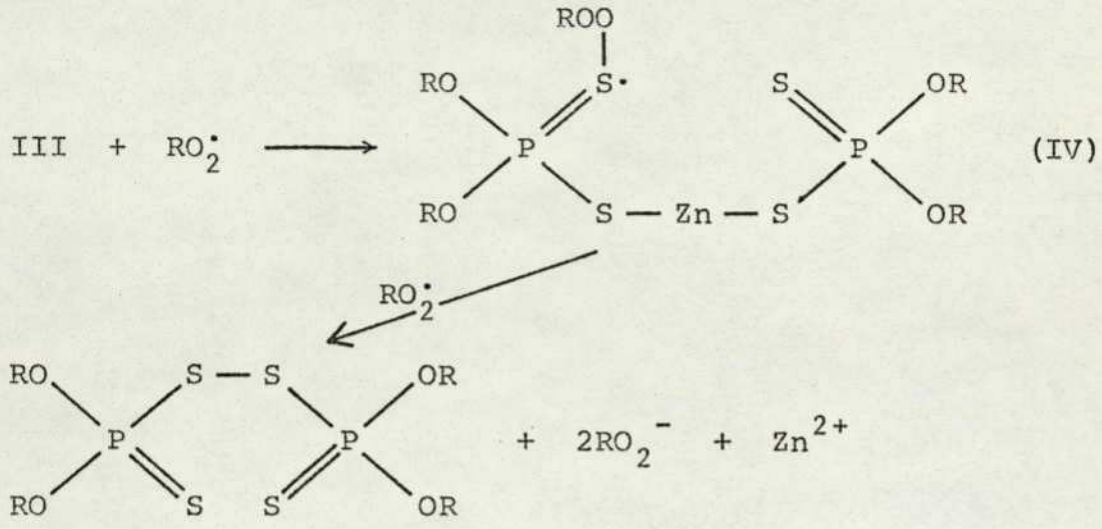
The development of antioxidants in the 1950's produced an important class of powerful inhibitors containing both metal and sulphur atoms — the most important members of this class being the zinc dialkyldithiophosphates(III)[141,156]:-



(III)

These compounds are now extensively used as antioxidants, particularly for lubricating oils. Research into their inhibition mechanism established that they were efficient hydroperoxide decomposers[141,142], giving products suggesting an ionic decomposition[141]. A detailed mechanism was not suggested at this time and it was thought for some years that the zinc dialkyldithiophosphates were merely hydroperoxide decomposers. However, investigations by Colclough and Cunneen[157] and Burn[158] established that these compounds also acted as chain-breaking antioxidants. A mechanism was proposed[158] involving electron transfer from an electron-rich sulphur atom to give a stabilised peroxy intermediate(IV) with the alkylperoxy

radical and this intermediate then reacts with another radical to give inactive products:-



(IV)

Reaction products apparently agreeing with this scheme were identified[159]. The active species responsible for hydroperoxide decomposition was not identified.

Further researches on the radical-trapping properties have disagreed with this scheme, particularly as infra-red studies[160] have indicated that the main reaction centre is the metal-sulphur bond. No experimental evidence for alkylperoxy radicals reacting with the sulphur atom has been obtained[161]. It is considered by Ingold et al[162], on the basis of initial rate and e.s.r. measurements, that the reaction between the inhibitor and alkylperoxy radicals takes place either by an electron-transfer process (45) or by an S_H2 displacement process (46) at the metal atom:-

$$III + R'O_2^{\bullet} \longrightarrow R'O_2^{-} + (RO)_2PS_2Zn^{+} + (RO)_2P(=S)(=S)^{\bullet} \quad (45)$$

$$III + R'O_2^{\bullet} \longrightarrow R'O_2ZnS_2P(RO)_2 + (RO)_2P(=S)(=S)^{\bullet} \quad (46)$$

Rate constants for the interaction were determined and were found to be between 10^3 and 10^4 l $mol^{-1}s^{-1}$ at 50°C. The exact value depends upon the structure of R. The mechanism by which hydroperoxide decomposition occurs was not investigated by these authors and remains obscure despite the large amount of research on the subject. It has been established that the decomposition depends on the molar ratio of inhibitor to hydroperoxide[159] with the ionic decomposition occurring when hydroperoxide is in excess. Various studies also indicate that homolytic decomposition of the hydroperoxide to free radicals occurs[163,164,166-168]. The zinc is precipitated as the sulphate[159,165]. It is considered[167,168] that interaction between the hydroperoxide and the inhibitor leads to an inactive form of the zinc compound which is reactivated by the radicals produced from the homolytic decomposition. This leads to zinc sulphate precipitation and the formation of an unidentified compound which rapidly decomposes hydroperoxides heterolytically into non-radical products. The rate of decomposition of the hydroperoxide to free radicals was found to be approximately 10^{-3} of the rate of decomposition to molecular products[163].

It is clear that further investigation into the action of this

inhibitor is necessary before its mechanism is fully understood. The most interesting aspect of its behaviour is the exhibition of both types of antioxidant behaviour in one molecule. This 'autosynergism' is also exhibited to a larger extent by the inhibitor forming the basis of this work, bis(stilbenedithiolato)nickel, which has certain structural similarities. The chemical and antioxidant properties of bis(stilbenedithiolato)nickel are examined in more detail in section 1.5.

1.4.4 Synergism

It has been frequently observed that when two or more antioxidants are used together to inhibit the autoxidation of an organic substrate, their combined effect is greater than would be expected on a purely additive basis. This effect is termed 'synergism' and the component which is the least active by itself is referred to as the 'synergist' for the second component. (The converse of this effect is 'antagonism'.)

The two antioxidants do not necessarily have to function differently, as the many synergistic combinations reported in the literature include combinations of free-radical acceptors. These are presumed to act by an interplay between activation energies and steric factors[169]. For example, if we have two antioxidants AH and BH and assume that the bond dissociation energy of B—H is smaller than that of A—H and that the reaction of BH with $RO_2^{\bullet}$ is slow due to steric factors, then the following reaction sequence will occur:-

$$RO_2^{\bullet} + AH \longrightarrow ROOH + A^{\bullet} \qquad (32)$$

$$A^{\bullet} + BH \longrightarrow B^{\bullet} + AH \qquad (47)$$

Hence, the full potential of BH's low dissociation energy is realised, with the added result that the tendency of A$^{\bullet}$ to disappear by a chain reaction (37)

$$A^{\bullet} + O_2 \longrightarrow AO_2^{\bullet} \xrightarrow{RH} AOOH + R^{\bullet} \qquad (37)$$

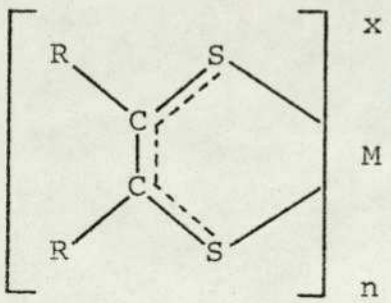
is reduced. However, this type of synergistic combination is not quite so significant as the more common, and the most generally effective, combination — i.e. one containing a free-radical acceptor and a hydroperoxide decomposer. Most antioxidant systems for polymers are of this type, often with the inclusion of a u.v.-screening compound. The reasons for synergism in the radical acceptor/hydroperoxide decomposer system are apparent from previous statements. However efficient a free-radical acceptor may be at suppressing the propagation reaction (3), some hydroperoxide will be formed from the inhibition reaction (32). If this hydroperoxide can be destroyed before it can decompose into free radicals and initiate further chains, the effectiveness of the free-radical acceptor will be enhanced. Additionally, the free-radical acceptor will protect the decomposer from degradation by radical attack. The regeneration of a free-radical acceptor from its phenoxy radical has also been reported[170]. This occurs by hydrogen donation from sulphenic acids formed, via the sulphoxide, from the hydroperoxide decomposer.

The use of synergistic antioxidant combinations is becoming increasingly important due to the severe conditions of operation to which many organic substances are being subjected at present, and theoretical treatments to establish optimum concentrations of both components of a synergistic combination have been attempted[171-173]. Future research into antioxidants would be expected to increasingly concentrate on this area as

it would appear to offer greater scope for development — particularly in the area of autosynergism mentioned previously.

1.5 Bis(stilbenedithiolato)nickel

The bis(stilbenedithiolato)nickel chelate belongs to a relatively recently discovered category of complexes. These are the olefin dithiol or dithio-α-diketone complexes of general structure (V):-



(V)

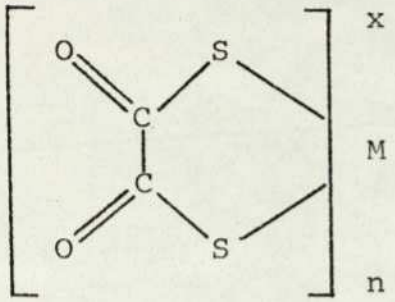
where R = H, alkyl, C_6H_5, CF_3, CN;

for n = 2; x = 0, -1, -2

for n = 3; x = 0, -1, -2, -3.

This type of compound may be obtained for many of the transition metals, but this work is mainly concerned with the complex where M = Ni, R = C_6H_5, n = 2 and x = 0.

The existence of compounds containing a transition metal chelated via four sulphur atoms has long been known. Jones and Tasker[174] reported in 1909 that the dithio-oxalate ion formed anionic bis- and tris-chelates with transition metals. These compounds(VI) were intensely coloured and very stable:-



(VI)

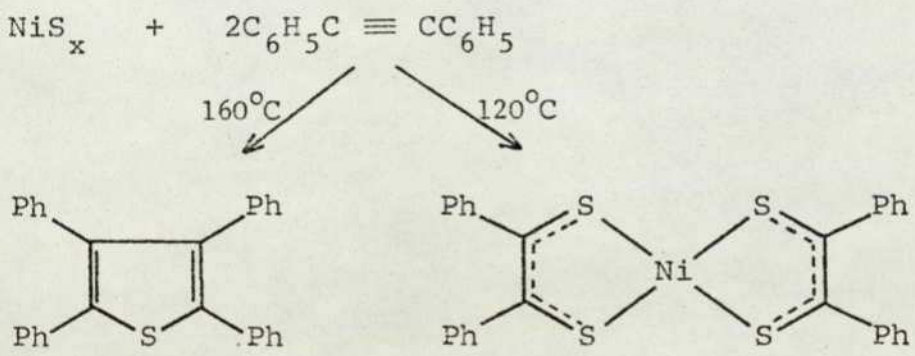
where n = 2; x = -2

n = 3; x = -3

The complexes where n = 2 were later shown[175] to be of square-planar structure. However, the unusual properties and reactivity of the dithio-α-diketone chelates put them into a category of their own.

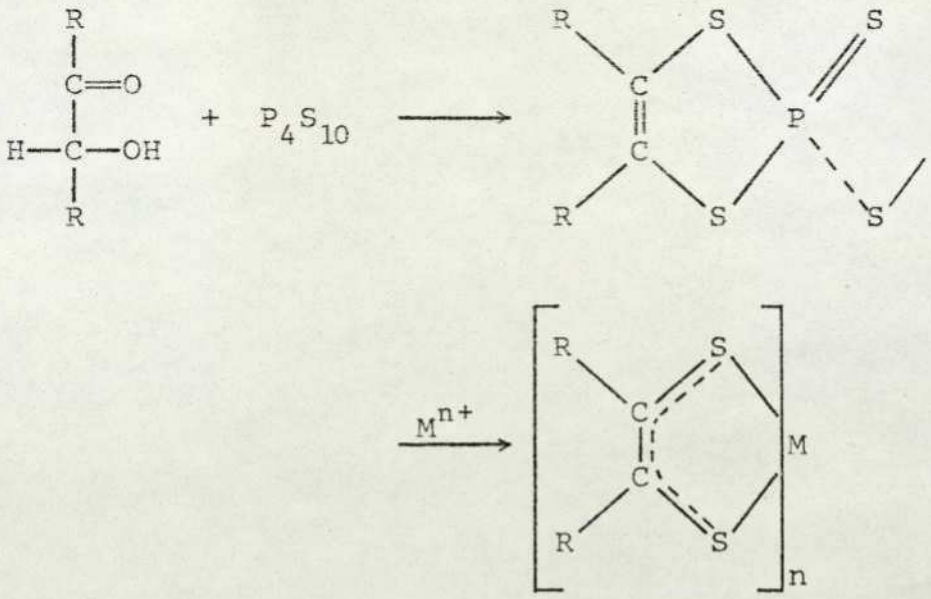
1.5.1 Preparation and structure

Bis(stilbenedithiolato)nickel (NiSDT) was first prepared by Schrauzer and Mayweg[176], who considered that the Steinkopf synthesis of thiophen[177] from acetylene and pyrites might yield organometallic complexes if conducted under milder conditions. By reacting nickel sulphide with diphenylacetylene in toluene at 120°C, a very dark green crystalline complex of composition $NiC_{28}H_{20}S_4$ was deposited:-



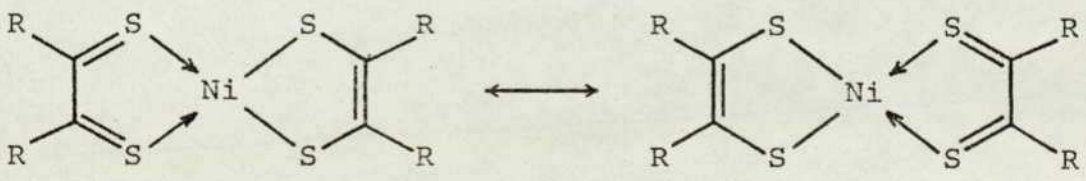
(VII)

From the results of a proton magnetic resonance spectrum and magnetic measurements, Schrauzer assigned the structure (VII) in which the nickel atom is surrounded by two molecules of dithiobenzil in a square-planar arrangement. He assigned a formal charge of +2 to the metal atom. The importance of NiSDT as the first representative of a new class of compounds was recognised by Schrauzer, but the methods of synthesis, i.e. diphenylacetylene and nickel sulphide or by the action of H_2S/HCl on benzoin in the presence of nickel chloride[178], gave only very low yields and were not generally applicable. Consequently, another synthetic route was devised by Schrauzer[179] in which acyloins were reacted with phosphorus pentasulphide in inert solvents to give thiophosphoric esters of the dithioacyloins[180]. These were found to react directly with metal salt solutions to yield the required complexes:-



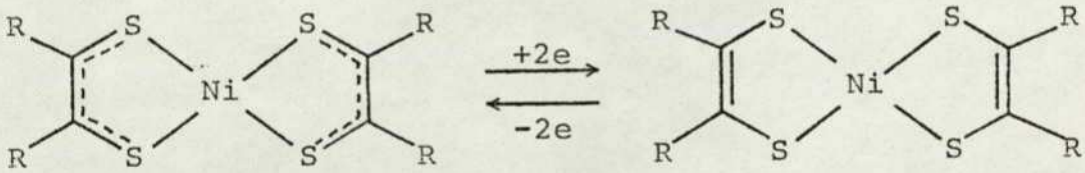
Using this synthesis, Schrauzer was able to synthesise a wide range of dithiodiketone metal complexes in yields of up to 38% based on the acyloin employed[179,181].

Schrauzer's structural assignment regarding the formal charge of the nickel atom is still somewhat controversial. Davison et al[182] considered the neutral complexes to contain two dianions with the metal in the +4 oxidation state. This view was generally discounted by Fackler[183] for a large number of compounds of this type, and these complexes are now generally considered to be ligand-oxidised nickel(II) chelates[181,184]. However, a recent paper by Grim et al[185] has postulated that these compounds are best assigned a formal oxidation state of zero for the nickel atom. This postulate is based on the measurement of the nickel binding-energies by X-ray photoelectron spectroscopy and comparison of the values obtained with those for nickel compounds of known oxidation state. This third possibility had been previously rejected by Schrauzer[184] on the grounds that a zero-valent complex would not be planar and it would only be favoured if the ligands were weakly π-bonding, which is not the case with the dithiodiketones. A zero-valent complex would be tetrahedral[186] and the square-planar structure of NiSDT has now been confirmed by X-ray diffraction measurements[187,188]. Infra-red[189] and mass spectral[190] studies have also been carried out. The square-planar structure is one in which the electrons are extensively delocalised and encompass the whole π-bonding system. A good representation of the ground state may be achieved[181,184] by using Kekulé-type structures, with resonance occurring between the two structures (IX) and (X):-



(IX) (X)

The dianionic complex is generally agreed to contain nickel in the +2 oxidation state co-ordinated with two stilbenedithiolato dianions and it has been established that the extra charges on reduction are taken up by the ligand system[181,184,191-197]:-



It is the tendency of the sulphur atoms to form covalent bonds with metals, combined with the high electron affinity of the ligands, that leads to the unusual chemical and physical properties of this class of compounds.

1.5.2 Properties

The dithiodiketone complexes are all crystalline, air-stable and intensely coloured solids. The bis(stilbenedithiolato)nickel complex is a very dark green crystalline solid, melting at 292-3°C, at which temperature it decomposes to give nickel sulphide, sulphur and 2-phenylthianaphthene as the exclusive organic product[179,181]. It exhibits limited solubility in common organic solvents and is insoluble in water. Although NiSDT is unaffected by moderately concentrated mineral acids, it reacts with a number of nitrogen bases forming salts of the anions. This is a general feature of these complexes and several polarographic studies have been carried out[191-193]. An electrochemically generated trianion has also been reported and characterised[198]. The novel delocalised system of these chelates, together with their ease of reduction, also gives them interesting electrical properties. An investigation by Rosa and Schrauzer[195] found the dithiodiketone complexes to have semi-conducting properties

comparable with large organic aromatic hydrocarbons and charge-transfer complexes, with observed resistivities between 10^3 and 10^{15} ohm cm at 25°C depending on the particular structure of the chelate. The large infra-red absorption of these complexes has also aroused commercial interest[199].

The chemical properties of the dithiodiketone complexes have also been extensively investigated. The reaction of NiSDT with alkynes was found to yield thiophene derivations[176,181], indicating the correctness of Schrauzer's original postulate[176] regarding the Steinkopf thiophen synthesis[177]. (The reaction scheme is shown in figure 1.2 on page 40.) Under mild conditions only one of the ligands reacts, leaving a tetrameric nickel salt as residue. This tetrameric complex can also be formed by reacting NiSDT with metallic nickel or $Ni(CO)_4$.

With certain dienes and other unsaturates, NiSDT tends to form labile 1 : 1 adducts. Investigation of the norbornadiene (bicyclo(2.2.1) hepta-2,5-diene; (XI)) adduct by Schrauzer[200] showed that the type of adduct occurring depends on the method of preparation. (The reaction scheme is shown in figure 1.3 on page 41.) Complex (XIV) was formed preferentially on refluxing with a large excess of norbornadiene, whilst (XIII) occurred at room temperature via the labile adduct intermediate (XII).

Adduct formation is a general property of the dithiodiketones, the palladium and platinum complexes forming a wider range of more stable adducts than does NiSDT[181].

Fig. 1.2 : The reaction of NiSDT with alkynes

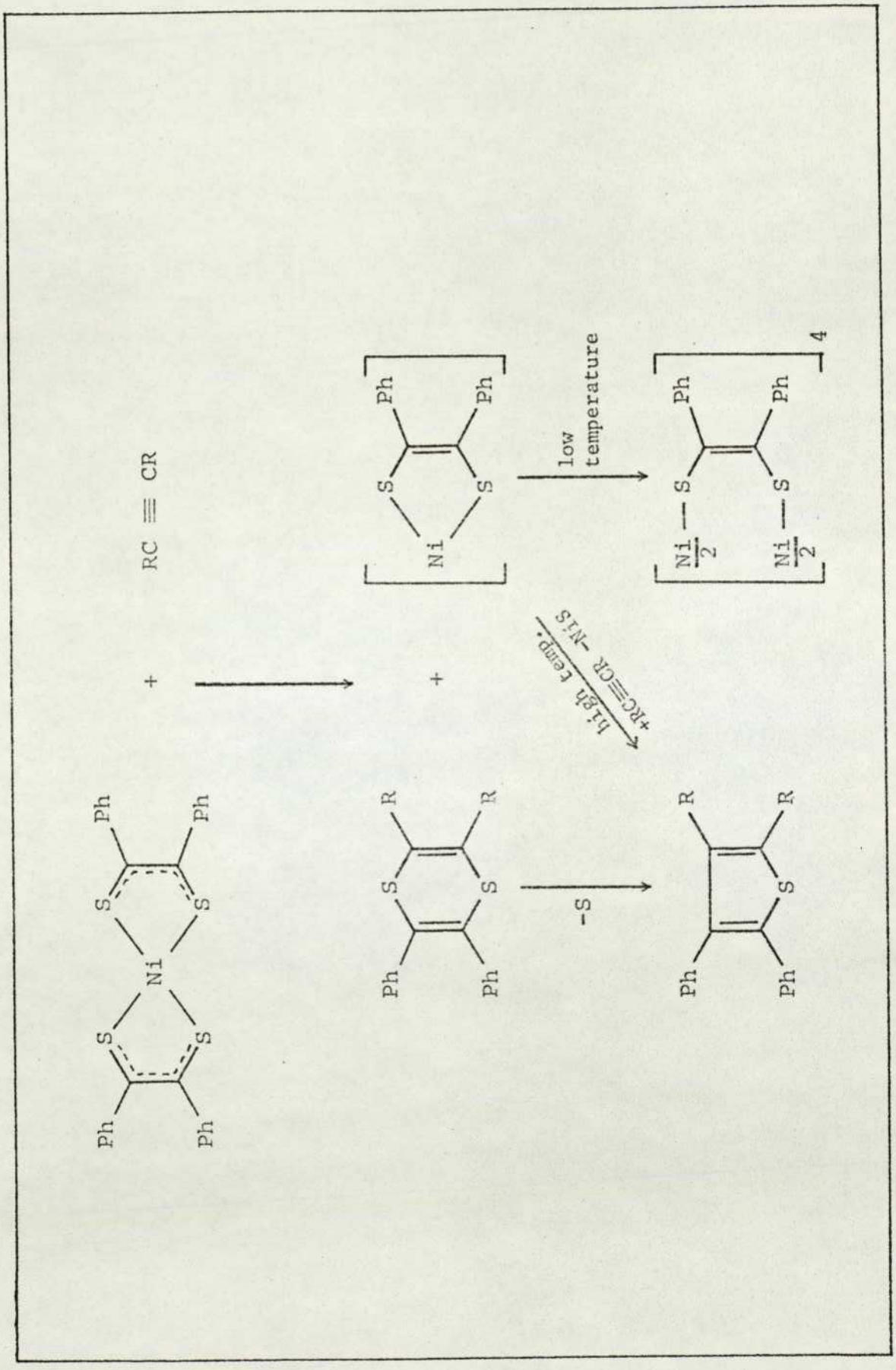
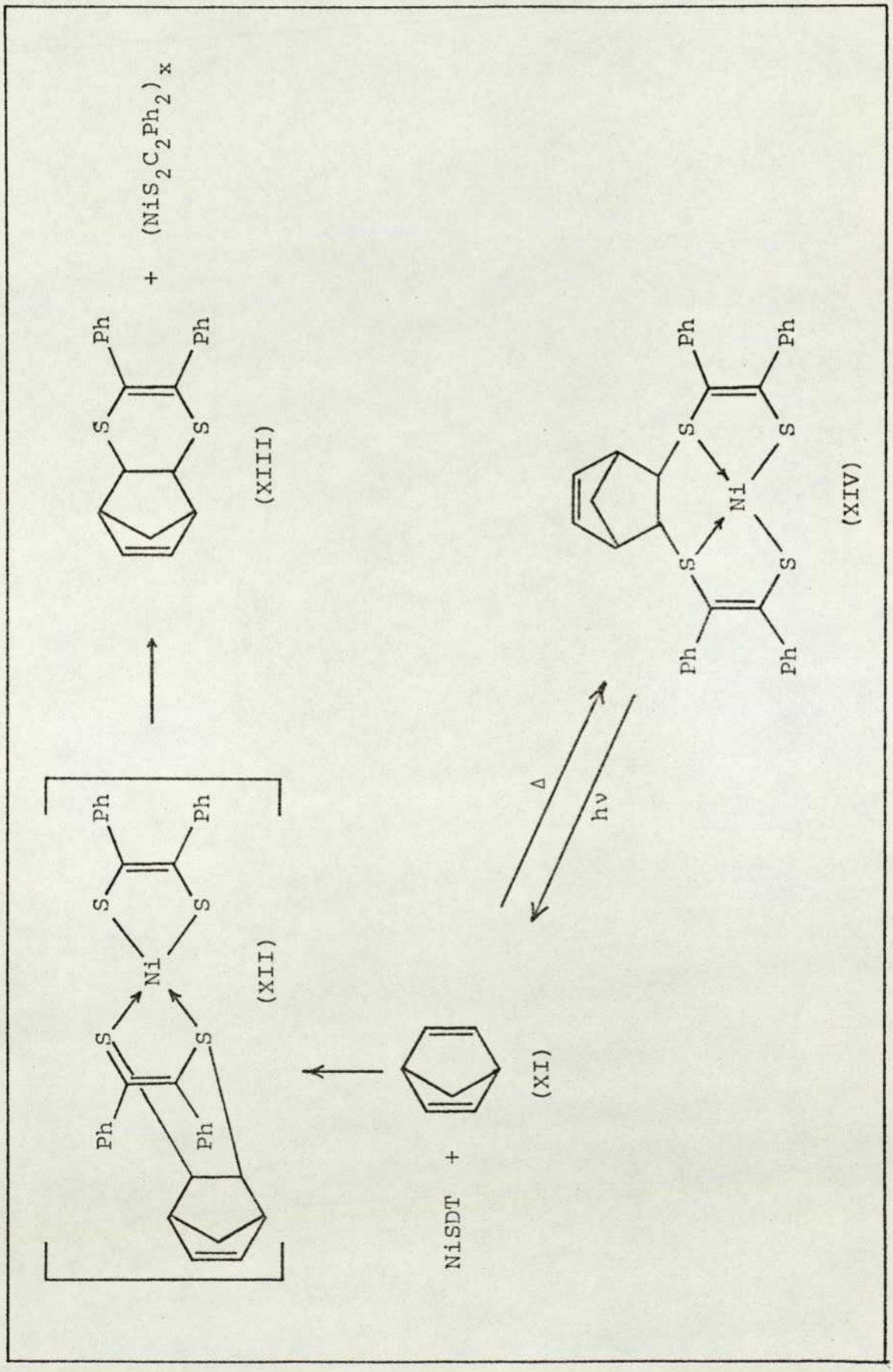
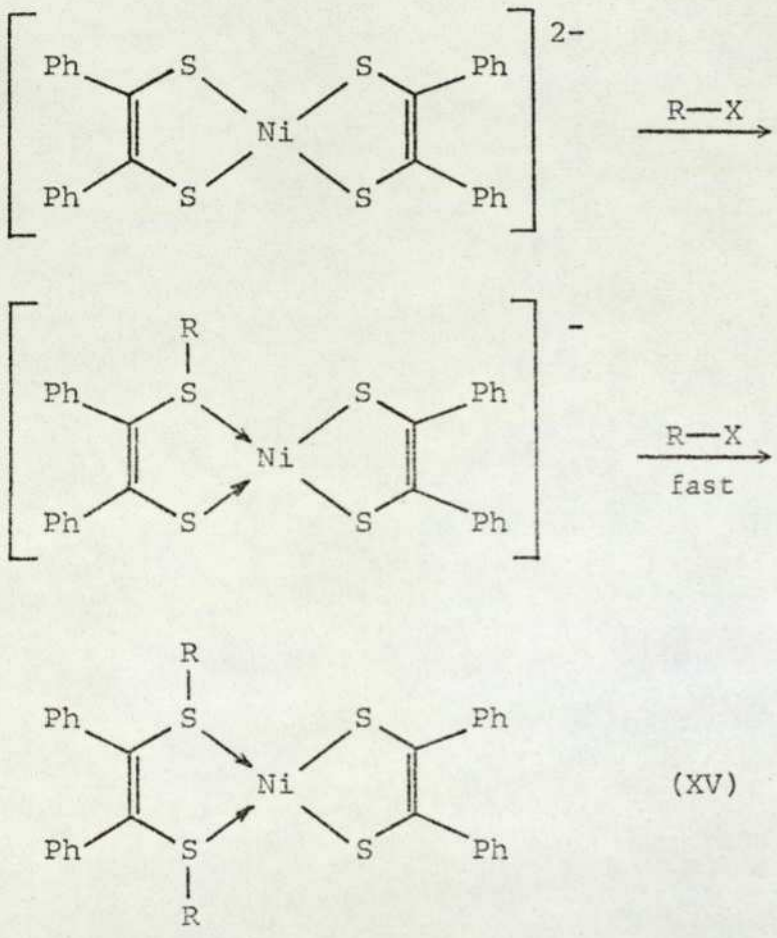


Fig. 1.3 : The reaction of NiSDT with norbornadiene

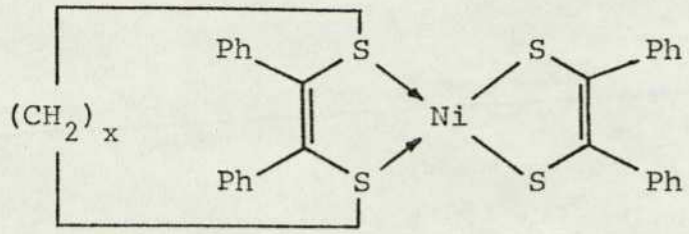


Many of the chemical properties of NiSDT arise from the ease with which this complex may be reduced and the subsequent reactions of the anionic species. Schrauzer found[194] that the sulphur atoms in the dianion possessed sufficient nucleophilic character to yield neutral 1,4-S-bisdialkyl substituted complexes (XV) on reaction with alkylating agents:-



(XV)

These planar alkyl derivatives are a remarkably stable class of compounds, the dimethyl derivative being capable of dissolution in concentrated sulphuric acid without decomposition. Chelates of structure (XVI) for x = 5-12 have also been produced by the above method[200].



(XVI)

Davison[201] has shown that ligand exchange reactions can occur between tetra-alkylammonium salts of the dithiodiketone complexes and salts of several of the mixed-ligand species have been isolated. These complexes have properties intermediate to those of the corresponding symmetrical species.

1.5.3 Antioxidant activity

The use of NiSDT as an antioxidant has not been so extensively investigated. The possibilities of the dithiodiketones as antioxidants were first recognised by Uri[61,202,203] who investigated their catalytic and inhibitory properties in typical autoxidation systems. A survey of the action of various transition-metal bis(stilbenedithiolato) complexes in the autoxidation of methyl cumate showed them all to be efficient autoxidation inhibitors, the palladium chelate being the most active. This was found to apply also to a survey conducted in an AIBN-initiated tetralin system. The results obtained from the initiated system confirmed that the chelates exhibited free-radical acceptor properties, the induction periods produced increasing linearly with the chelate concentration. The catalytic effect of the dithiodiketones on the decomposition of tetralin hydroperoxide was also investigated and found to be of unprecedented magnitude — one mole of metal chelate being found to catalytically decompose at least 1000 moles of hydroperoxide. The palladium chelate was again found to be the most efficient. The reaction was shown to be second-order

with respect to the hydroperoxide and experiments with NiSDT at various temperatures gave an activation energy of 60.5 kJ mol^{-1}, with a pre-exponential factor of $2.6 \cdot 10^9$ l^2 $mol^{-2}s^{-1}$. The overall negative catalysis exhibited by the dithiodiketones was considered to indicate that the decomposition of hydroperoxide proceeded without producing any free radicals and it was thought that adduct formation played a major part in the mechanism of action. The greater activity of the palladium complex in comparison with the platinum and nickel complexes is in agreement with Schrauzer's observations on olefin adduct formation[181]. Additional research by Uri[202,203] showed that the dithiodiketones, particularly the nickel complex, were efficient u.v.-stabilisers and established that NiSDT was a very powerful antioxidant for polypropylene and some other polyolefins. The inhibition exhibited by NiSDT, in both photochemical and thermal oxidations, was considerably greater than the inhibition exhibited by some of the more conventional antioxidants — even when these were present in synergistic combinations.

The radical-acceptor properties of NiSDT were also investigated by Ivanov and Youritsin[204] who made a comparative study of NiSDT and zinc diisopropyldithiophosphate (ZDTP) by chemiluminescence methods using ethylbenzene as a common substrate. The chemiluminescence of the radicals was decreased by the addition of the inhibitors. The rate constant for the interaction between the inhibitor and ethylbenzylperoxy radicals, calculated from the light intensity before and after adding the inhibitor, was $2.6 \cdot 10^5$ l $mol^{-1}s^{-1}$ for NiSDT and $2.3 \cdot 10^4$ l $mol^{-1}s^{-1}$ for ZDTP. These values show that NiSDT is the more effective radical acceptor and its higher activity was confirmed by e.s.r. measurements. Chemiluminescence and e.s.r. measurements during the interaction between tetralin hydroperoxide and NiSDT, however, indicated an accelerated decomposition of the

hydroperoxide with the formation of free radicals, contrary to the view of Uri[61]. The particular technique used by Ivanov — passing air into a high concentration (1.5 mol l^{-1}) of hydroperoxide followed by addition of NiSDT — together with the very low concentrations of NiSDT used ($3 \cdot 10^{-6}$ to $3 \cdot 10^{-4}$ mol l^{-1}), may have significantly influenced this finding, although work carried out by Chien and Boss[173] also produced results indicative of slight radical production in the reaction between NiSDT and hydroperoxide. This conclusion was based on the formation of polystyrene from freshly-distilled styrene present in the reacting system. The reaction was shown to be second-order in hydroperoxide, in agreement with Uri, and it was observed that the initial green colour of the NiSDT quickly disappeared. This was also noted by Ivanov[204]. Chien and Boss also tested NiSDT as a thermal antioxidant for polypropylene and an epichlorohydrin-ethylene oxide co-polymer. Their results indicated that NiSDT was a pro-degradant rather than an antioxidant as reported by Uri. Chien has since indicated[205] that the results of the heat-stability tests for polypropylene were erroneous and that NiSDT is, in fact, an antioxidant for polypropylene and certain other polymers.

A reaction scheme for the interaction between hydroperoxide and NiSDT has been postulated by Chien and Boss, based on the assumption that the neutral species and the ionic complexes, which form a redox couple, are both active hydroperoxide decomposers. The hydroperoxide used was t-butyl hydroperoxide and the main reaction product (90 - 95%) was found to be di-t-butyl peroxide (DTBP):-

$$ML_2 + ROOH \rightleftharpoons [RO_2 \cdot ML_2]^- H^+ \quad (48)$$

$$[RO_2 \cdot ML_2]^- H^+ + ROOH \rightleftharpoons [ML_2]^{2-} 2H^+ + ROOR + O_2 \quad (49)$$

$$[ML_2]^{2-} 2H^+ + ROOH \rightleftharpoons [RO \cdot ML_2]^- H^+ + H_2O \quad (50)$$

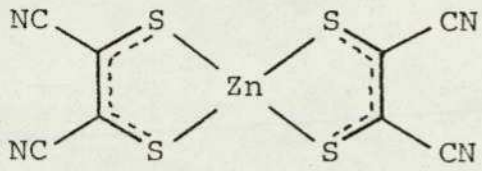
$$[RO \cdot ML_2]^- H^+ + ROOH \rightleftharpoons ML_2 + H_2O + ROOR \quad (51)$$

It is the instability of the radical-ion intermediates

$$[RO_2 \cdot ML_2]^- H^+ \rightleftharpoons [ML_2]^- H^+ + RO_2^{\cdot} \quad (52)$$

to which Chien attributed the radical production during the reaction and, erroneously, the prodegradant properties in polypropylene.

Although this reaction scheme explains the production of DTBP, it does not fully explain other results noted by Chien[173] and Ivanov[204]. The rapid discharge of the original NiSDT colouration in the presence of a large excess of hydroperoxide cannot be correlated with this mechanism. The spectra of the ionic complexes bear no relationship to those of the neutral compounds[181] (e.g. the band responsible for the green colouration is absent) but, if this scheme is solely responsible for the hydroperoxide decomposition, the solution should remain noticeably green for some considerable time. Also, the assumption that the ionic complexes are as efficient hydroperoxide decomposers as the neutral compounds, has not been proved. Chien based this assumption on the fact that similar hydroperoxide decomposition properties were obtained with zinc bis(maleodinitriledithiolate), (XVI), which should in itself be a neutral complex:-



(XVI)

It is apparent that, although the anionic species cannot be completely excluded as intermediates, the mechanism of action of NiSDT as a hydroperoxide decomposer is far from clear.

1.6 The present work

Recent work on the use of NiSDT as an antioxidant has given some indication of the potential of this chelate in the stabilisation of organic materials. The efficient combination of a u.v.-stabiliser, peroxide decomposer and free-radical acceptor in one molecule, a form of 'autosynergism', is possibly unique. The mechanism by which NiSDT carries out these functions is still obscure and the separate assessment of each mode of action is of importance.

In the present work, a study of the action of NiSDT in various substrates, including some of the conventional polymer model compounds, has been carried out, together with a more intensive study of the NiSDT/tetralin and NiSDT/tetralin hydroperoxide systems. The results of these investigations help to reveal the mechanism of some of the functions of this important new antioxidant.

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2 EXPERIMENTAL

The most generally used method for following the course of an autoxidation reaction is by directly measuring oxygen absorption into the reacting solution. Alternative techniques have been developed for following oxygen comsumption in the solution — for example by u.v.-spectroscopy[48-50] or with an oxygen electrode[206,207]. Reaction rates have also been followed by sensitive thermocouples[68,208] and chemiluminescence techniques[209]. By studying the autoxidation under stationary-state conditions, ratios of rate constants may be obtained from the type of equations previously defined. The determination of absolute rate constants requires the study of autoxidation under non-stationary conditions — for example by the rotating-sector method of interrupted illumination[210] or the study of photochemical pre- and after-effects[67,210].

In the present work, rates of autoxidation have been determined by measurement of oxygen absorption from the gas phase using a conventional circular Warburg apparatus and a purpose-built automatic recording apparatus.

2.1 Apparatus

2.1.1 Warburg apparatus

A conventional circular Warburg apparatus (figure 2.1) was used for all autoxidation reactions and related manometric studies up to 80°C. The standard double-bore capillary manometers were employed in conjunction with Warburg flasks of approximately 14 ml capacity containing one centre well for adsorbents. The manometric fluid was Brodies solution which is a mixture of sodium chloride, a wetting agent and alcoholic thymol solution, stained dark-blue with acilan black. A 10,000 mm Brodie column corresponds to 760 mm Hg. The shaking speed and the amplitude of the shaking stroke

Fig. 2.1 : Circular Warburg apparatus



1	Control head	14	Speed reduction pulleys
2	Bath	15	Pin
3	Contact thermometer	16	Hub
4	Foot	17	Rating label
5	Rotating rail	18	Thermometer cable
6	Manometer support	19	Switch for stirrer and heater
7	Brake	20	Yellow lamp (heater)
8	Manometer	21	Red lamp (boost-heater)
9	Switch for shaking motor	22	Start button
10	Heater	23	Power control
11	Stirring propeller	24	Reference thermometer
12	Connecting cable	25	Cooling coil
13	Shaking motor	26	Manometer platform

were both variable to ensure a sufficient supply of dissolved oxygen for the reactions to proceed at a rate which is not determined by oxygen diffusion itself.

2.1.1.1 Modifications

The original Plexiglass bath (No.2 in figure 2.1) was replaced by a pyrex bath made to specification by Jencons. (Plexiglass softens above 60°C.)

The most important modification was the conversion of the manometer-to-flask joints to greaseless operation. It was found that the longer experiments (over 250 hours duration) at 70°C and above were adversely affected by penetration of the reacting solutions with Apiezon 'T' grease leached from this joint. The manometers' cones had grooves cut into them to allow 'Viton A' O-rings to be used. (These rings were not of standard size and were made by James Walker & Co. Ltd.) The corresponding joints on the reaction flasks were polished to remove all grinding marks, making them of the 'Clearfit' type (Plate 1).

2.1.2 Automatic recording apparatus

Experiments at temperatures above 80°C were carried out using an automatic recording apparatus of a type described by Martin[211] (Plate 2). This was constructed by the Department of Mechanical Engineering to specifications supplied by the Explosives Research and Development Establishment, Waltham Abbey. The constant-temperature bath contained approximately 15 litres of MS550 silicone fluid and could accommodate up to six reaction flasks. Each flask, of approximately 30 ml capacity, was stirred continuously by means of a small glass-coated magnetic follower and a rotating magnet close to the underside of the tank.



PLATE 1

MODIFIED AND
CONVENTIONAL
WARBURG GLASSWARE

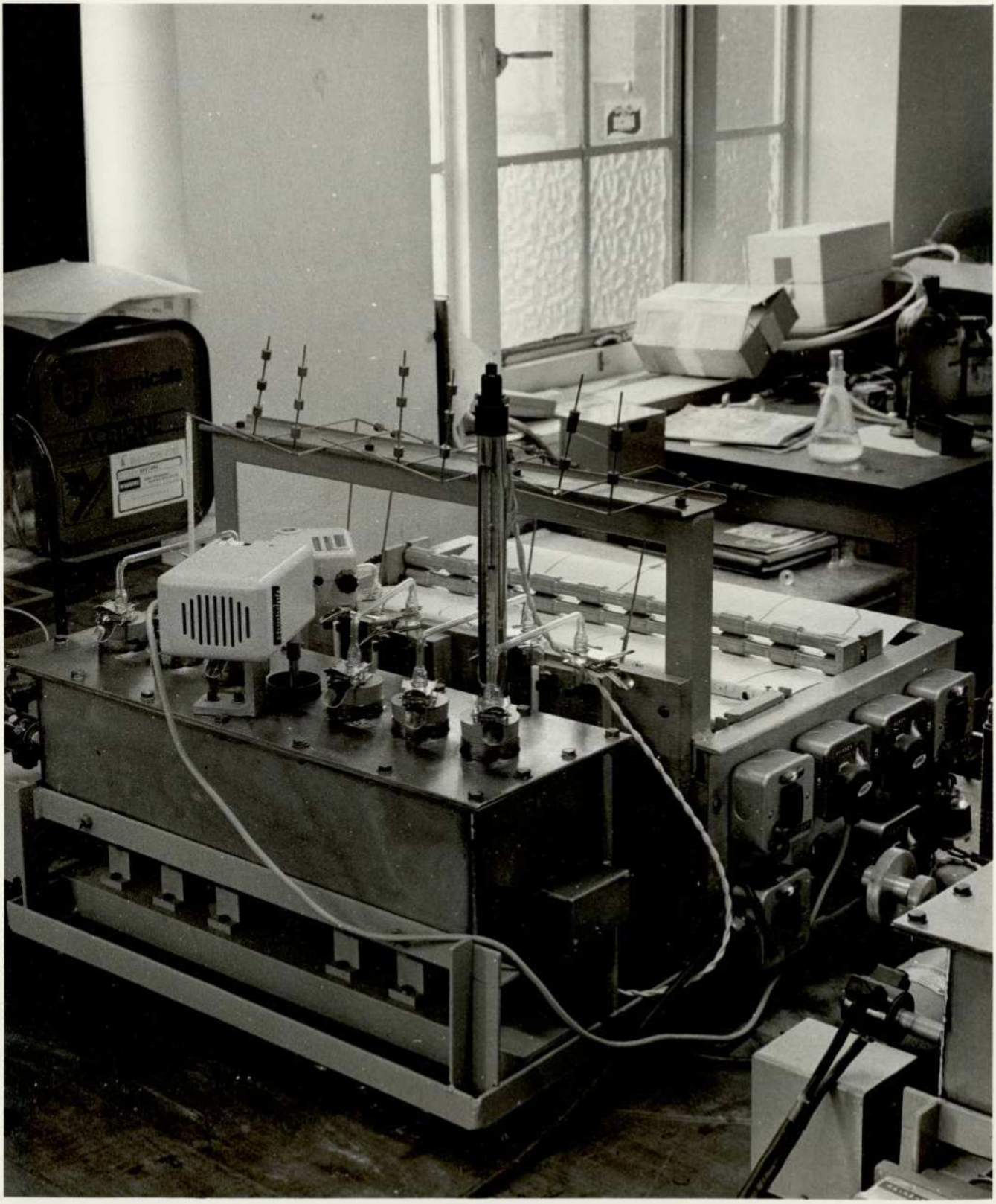


PLATE 2

AUTOMATIC RECORDING APPARATUS

Provision was made for each flask to have a glass bucket of freshly-calcined CaO inserted to absorb any volatiles formed in the course of the reaction. Uptake of oxygen by the reacting substrates was followed by monitoring the decrease in pressure in the reaction flasks with a mercury-filled U-tube manometer. The movement of the mercury was transmitted to the chart paper by a PTFE float attached to the rigid pen linkage. The dimensions of the apparatus (section 2.3.4.2) gave an overall sensitivity of approximately 70 µl of oxygen absorbed per millimetre of pen deflection, and the gearing of the chart-recorder mechanism gave a time scale of 0.92 hours per centimetre of chart paper.

2.1.2.1 Modifications

The only modification to E.R.D.E. specifications was the substitution of a standard 'Viton A' ball and socket joint for the original Quickfit joints. This eliminated any problems of grease penetration.

2.1.3 Low temperature filtration apparatus

The preparation and/or purification of some substrates (sections 2.2 and 2.3) required recrystallisation at temperatures down to -70°C and the apparatus illustrated in Plates 3 and 4 was constructed for this purpose. The central, cylindrical section contained a sintered disc (a range of porosities were available) and had a working capacity in excess of 500 ml. The outer section was a Dewar jacket to minimise ambient temperature effects. When assembled (Plate 4), the space between the two sections was half-filled with acetone and, by regulating the amounts of solid carbon dioxide added, any temperature down to -70°C could be maintained.



PLATE 3

LOW TEMPERATURE
FILTRATION APPARATUS
(COMPONENT PARTS)



PLATE 4

LOW TEMPERATURE
FILTRATION APPARATUS
(ASSEMBLED)

2.2 Reagents

2.2.1 Commercially available reagents

The majority of the substrates used in this work were obtained from commercial suppliers in the purest grade available. This was generally better than 99% pure.

Tetralin(1,2,3,4-tetrahydronaphthalene), TMPD(2,6,10,14-tetramethylpentadecane), Hexadec-1-ene and DHA(9,10-dihydroanthracene) were obtained from Koch-Light, as was the ethyl benzoate which was used as solvent throughout the work.

p-Isopropylbenzoic acid (cumic acid) was obtained from Eastman Kodak.

Topanol CA(1,1,3-tris(2methyl-5-t-butyl-4-hydroxyphenyl)butane), an efficient trisphenolic antioxidant, was obtained from I.C.I. Ltd.

2.2.2 Oxygen-free nitrogen

For the determination of peroxide concentration (section 2.4.2) and for some synthetic procedures (section 2.2.6), a supply of oxygen-free nitrogen was necessary. The method used to purify commercial 'White-spot' nitrogen (B.O.C.) was a slight modification of the method described by Heaton and Uri[212]. The commercial oxygen-free nitrogen was passed through three Friedrich gas-washing bottles, each containing an aqueous solution of 15% sodium hydrosulphite, 10% sodium hydroxide and 0.2% sodium anthraquinonesulphonate as indicator. The purified nitrogen was then passed through two further gas-washing bottles containing potassium permanganate solution to remove any traces of sulphur dioxide carried through from the first three bottles. Finally, the nitrogen was passed through distilled water.

When peroxide determinations were being carried out, an extra

bottle, containing the acetic acid/chloroform solvent mixture used in this procedure, was included in order to saturate the purified nitrogen with solvent vapour.

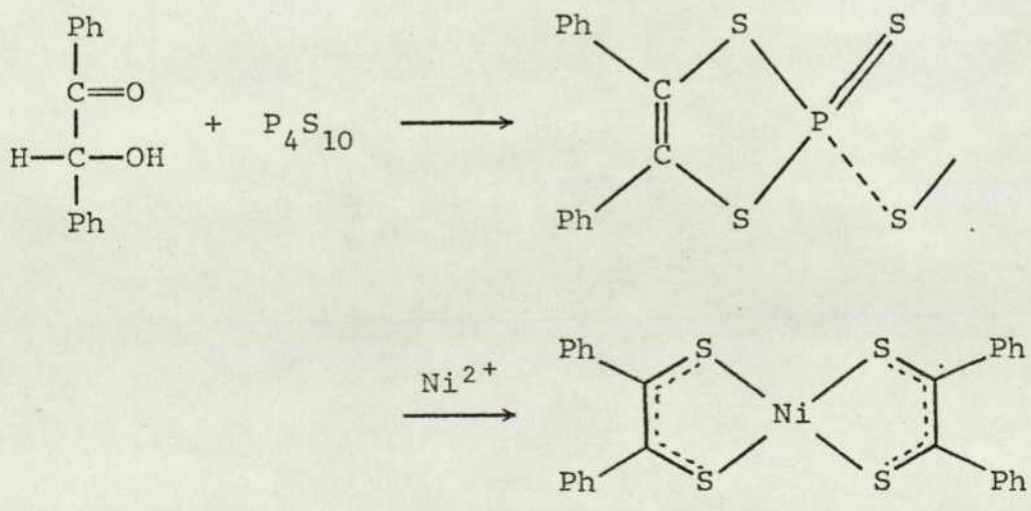
2.2.3 Carbonyl-free methanol

Certain analytical procedures require the use of quantities of carbonyl-free methanol and A.R.-grade methanol was purified for this purpose by the method of Lappin and Clark[213].

Approximately 10 g of 2,4-dinitrophenylhydrazine, with a few drops of concentrated hydrochloric acid, were added to 1000 ml of methanol and the resulting mixture was refluxed for two hours. The purified methanol was then distilled through a Vigreux column and redistilled until colourless. The resulting carbonyl-free methanol was suitable for use up to several months after purification.

2.2.4 Bis(stilbenedithiolato)nickel

Bis(stilbenedithiolato)nickel (NiSDT) was prepared by the method of Schrauzer and Mayweg[181] with only minor modifications. This method, which produces considerably greater yields than the original methods by which this compound was obtained[176,178], is a two-stage process as shown below:-



The starting materials used were benzoin (Koch-Light) and phosphorus pentasulphide (B.D.H.), equal weights (35 g) of which were placed in a stirred vessel with 250 ml of dioxan solvent (Koch-Light). (This ratio of reactants, which corresponds to a nearly 100% molar excess of benzoin, has been found[61] to give the best yield.) The mixture was refluxed for two hours during which time a stream of nitrogen was constantly passed through the vessel to assist in removing and dispersing the hydrogen sulphide evolved in the course of the reaction. After refluxing, the resulting solution was allowed to cool and then filtered to remove any unreacted starting material. (In this particular preparation, the reaction was complete and no solid residue was detected.) A solution of 17.5g of nickel chloride (BDH; A.R.-grade) in 75 ml of water was added to this clear solution whilst stirring. The resulting mixture was heated on a steam bath for two hours. After cooling, the mixture was chilled in ice and the crude NiSDT suspension filtered. The weight of crude product obtained at this stage was 26.4g.

Purification was carried out by a Soxhlet extractive recrystallisation with toluene (BDH) and the resulting dark-green crystals were dried for four hours at 50°C in a vacuum oven. The final yield was 21.1g of pure NiSDT (47% yield ex benzoin) melting and decomposing at 293°C. (Literature values[181] are 35% and 292°C respectively.) Spectrophotometric measurements with the toluene used for the recrystallisation indicate that 3% of the product is lost during the purification procedure.

The NiSDT was characterised by its electronic spectrum, the transition and extinction coefficients being given in table 3.2 together with those obtained by Schrauzer[181]. The identity of the product was confirmed by a high resolution n.m.r.-spectrum obtained by the Physico-Chemical Measurements Unit at Harwell (figure 2.2).

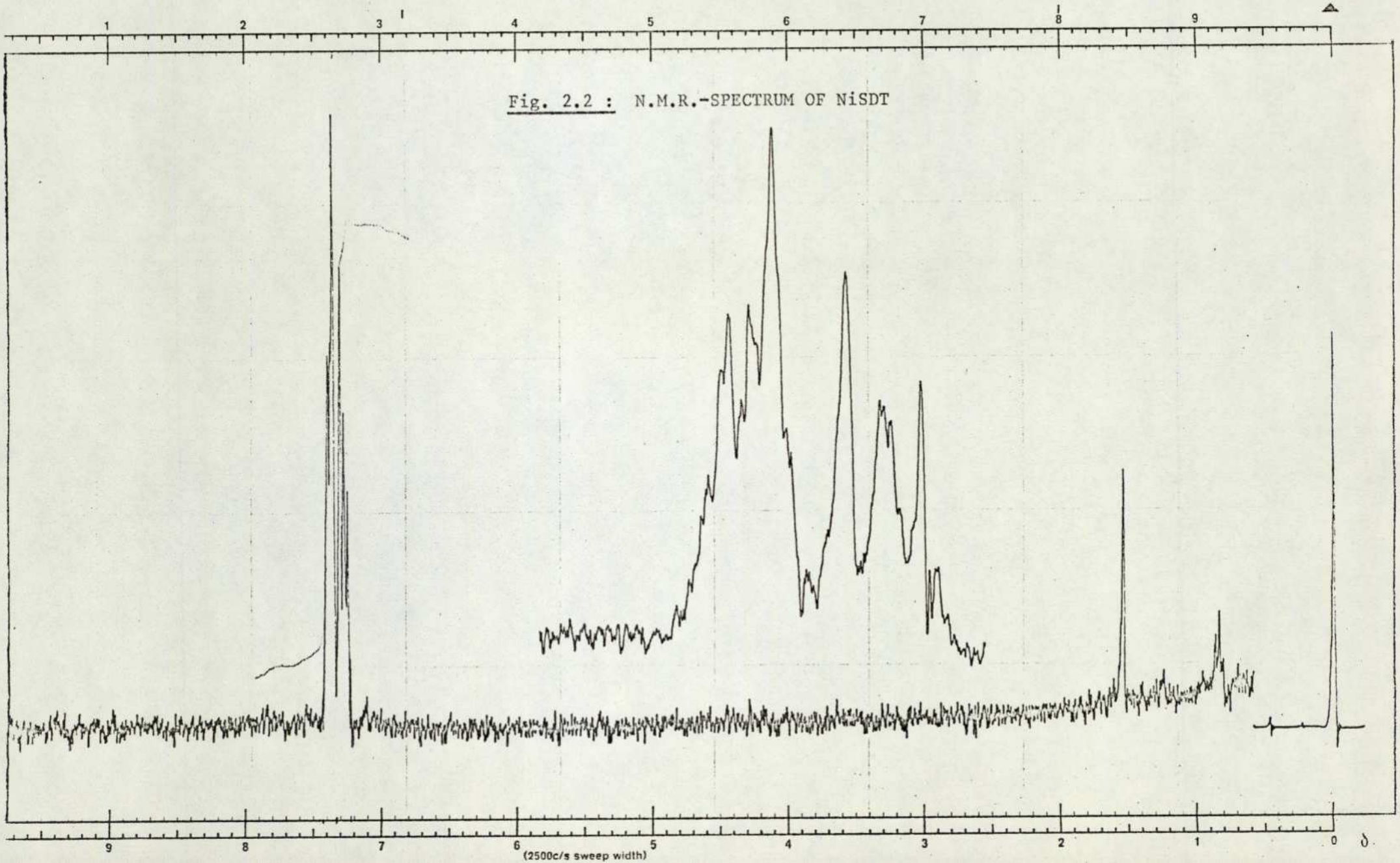


Fig. 2.2 : N.M.R.-SPECTRUM OF NiSDT

This spectrum clearly shows the presence of a phenyl group with splitting of the ring protons caused by the electron-deficient nucleus of the complex. The actual assignment of the two peaks is difficult, as the integrals are unreliable due to a proton signal from residual $CHCl_3$ in the $CDCl_3$ solvent being superimposed. However, the peak at 2.64τ would be expected to be the signal for the two protons nearest the nucleus.

2.2.5 Substituted bis(stilbenedithiolato)nickel complexes

2.2.5.1 p-Substituted derivatives

It was considered advantageous to obtain some nickel complexes substituted in the para-positions of the phenyl rings in an attempt to improve the solubility of the original NiSDT in aliphatic substrates like oleic acid and oleyl alcohol. However, very few of the relevant benzoin reagents required are available commercially and the best route to these compounds is oxidation of the corresponding p-substituted toluene with chromyl chloride or ceric ammonium nitrate, followed by benzoin condensation of the aldehyde so formed. A sample of p-isopropyl substituted NiSDT was prepared in this fashion and donated by Professor N. Uri of E.R.D.E. This compound proved to be at least 5 to 10 times more soluble in the above-mentioned substrates than the original NiSDT[214], but experimental results (section 3.7.1) showed it to be a weaker antioxidant. The electronic spectrum of the compound is presented in table 3.5 and the identity of the compound was confirmed by a high resolution n.m.r.-spectrum (figure 2.3) as previously. This shows again the splitting of the phenyl ring protons (four in this case) and the other peaks show a strong doublet at 8.75τ, attributable to the six methyl protons split by the tertiary hydrogen of the isopropyl group, as well as a septet at 7.13τ due to the tertiary hydrogen signal being split by the six methyl protons.

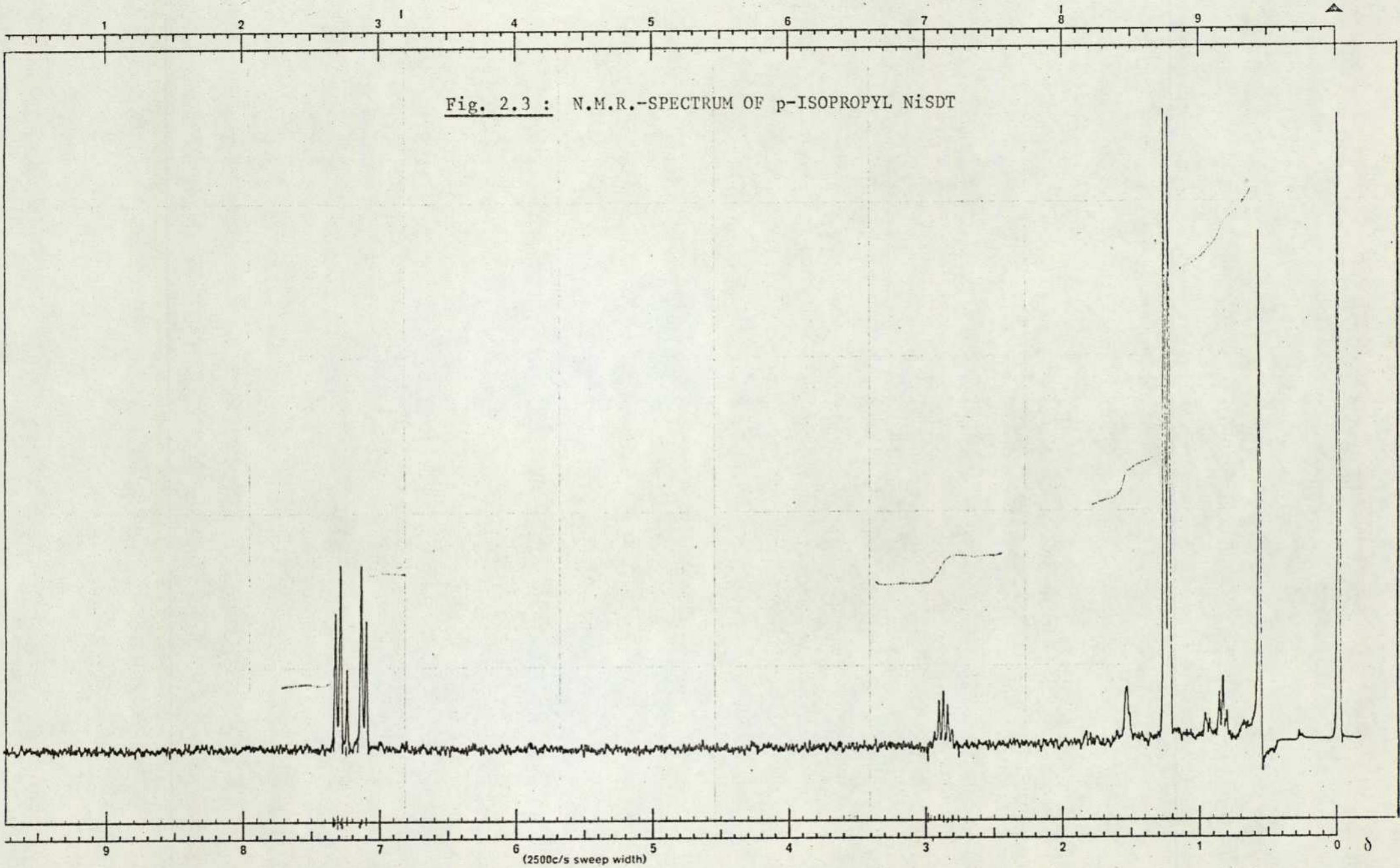


Fig. 2.3 : N.M.R.-SPECTRUM OF p-ISOPROPYL NiSDT

A p-methoxy substituted NiSDT was prepared from a commercially available benzoin according to the method described in section 2.2.4. The starting material used was anisoin (4,4'-dimethoxybenzoin; Emmanuel) and 17.5g of green-black crystals (41% yield ex anisoin) were obtained. These crystals melted and decomposed at 330°C. (Literature values[181] are 34% and 329°C respectively.) The same characterisation procedure was adopted with this complex as for the other nickel chelates. The electronic spectrum is given in table 3.3, together with the data obtained by Schrauzer[181], and the high resolution n.m.r.-spectrum is given in figure 2.4. The n.m.r.-spectrum confirms the p-methoxy substituent, with the major peak, attributable to the three methyl protons, at 6.18τ. This peak has been moved downfield from the normal methyl position (ca. 7.5τ) due to deshielding by the electronegative oxygen atom. It is also noticeable that the splitting between the phenyl ring protons has increased, the signal for the two protons nearest the substituent being moved upfield by the oxygen atom.

The p-methoxy substituted NiSDT was found to be at least as good an antioxidant (section 3.7.1) as the original NiSDT, but was almost totally insoluble in oleic acid and oleyl alcohol[214].

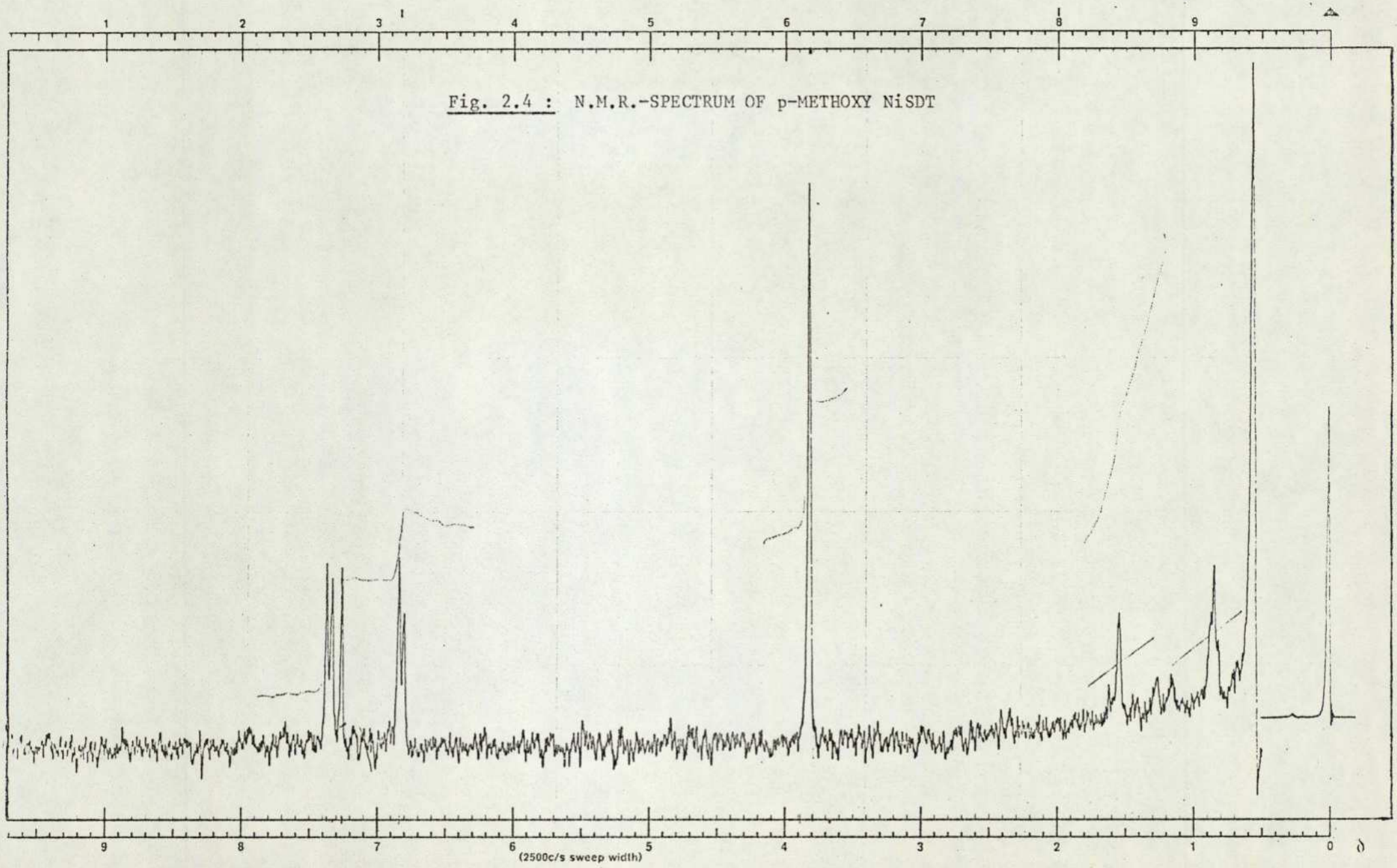


Fig. 2.4 : N.M.R.-SPECTRUM OF p-METHOXY NiSDT

2.2.5.2 1,4-S-dimethyl derivative

As mentioned in section 1.5.2, the sulphur atoms in NiSDT possess sufficient nucleophilic character to form addition-complexes with alkylating agents and the dimethyl derivative was synthesised to determine its effect on hydroperoxide decomposition. The general synthesis of Schrauzer and Rabinowitz[194] was followed (section 1.5.2) with only minor modifications.

The starting material used was the original NiSDT complex, 20g of which were suspended in 300 ml of methanol containing 5g of sodium hydroxide. To reduce the complex to the dianion, 1.5g of sodium borohydride were added and the reaction mixture was heated to 50°C at which temperature it was continuously stirred for one hour. The addition of 12g of methyl iodide completed the procedure and olive-green crystals were precipitated after standing overnight. Purification was carried out by recrystallisation from a methylene chloride/methanol solvent pair. As with the previous complexes, characterisation was by the electronic spectrum of the compound which is presented in table 3.4 together with the values obtained by Schrauzer[194]. Identification of the complex was carried out by a high resolution n.m.r.-spectrum (figure 2.5). This shows two peaks at 2.88τ and 7.63τ, with relative intensities of ten and three respectively, which are assigned to the phenyl ring protons and the methyl group. Although the electronic spectrum differed in some respects to Schrauzer's (section 3.1.2), the n.m.r.-spectra agree almost exactly. Schrauzer reports two peaks of relative intensities of ten and three at 2.81τ and 7.64τ. From the electronic spectrum, the purity of the complex was determined to be 99.1% — the impurity being unreacted NiSDT.

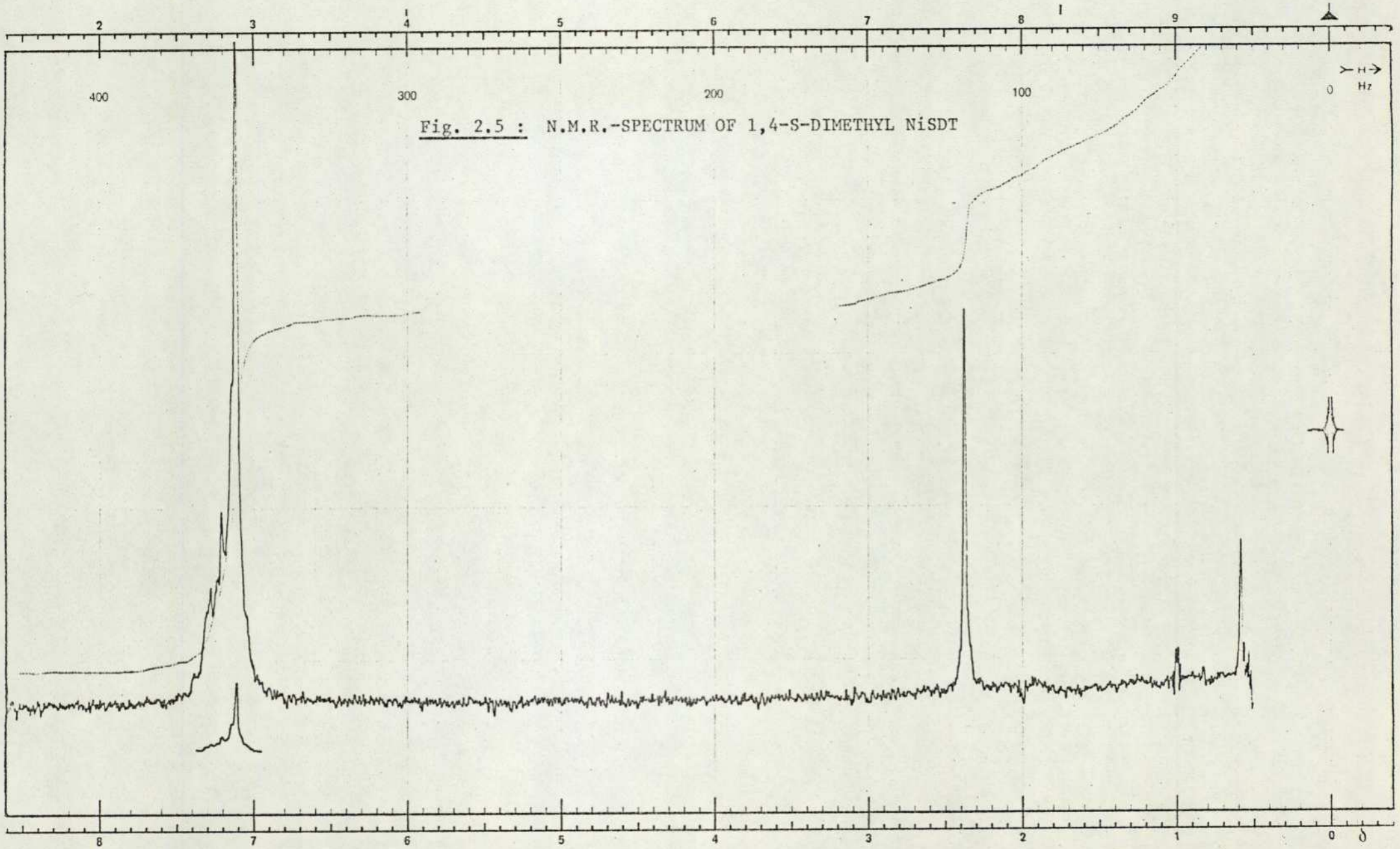


Fig. 2.5 : N.M.R.-SPECTRUM OF 1,4-S-DIMETHYL NiSDT

2.2.6 Linoleic acid

This 1,4-diene was prepared from safflower oil (ca. 55 - 80% linoleic acid; Younghusband, Barnes & Co., London) according to the procedure described by Heaton and Uri[58]. The preparation is a four-stage process. The first two stages are saponification and formation of the stable[63] urea complex. The third stage is a fractional low temperature crystallisation to remove saturated and monoethenoid acids with the final stage being vacuum fractionation.

Preparation of the fatty acids:

A cooled solution of 54g of sodium hydroxide in 200 ml of water was added to 250g of safflower oil dissolved in 250 ml of ethanol. A red-brown homogeneous solution formed, accompanied by a significant increase in temperature. Addition of 250 ml of 20% aqueous sulphuric acid to the cooled solution caused separation of the fatty acids which were removed and washed thoroughly with distilled water.

Formation of the urea complex was accomplished by adding the fatty acids to a solution of 750g of urea in 1500 ml of boiling A.R.-grade methanol. The mixture was allowed to cool and then left to stand overnight at $0^{o}C$. The precipitated urea complexes were filtered off under vacuum and washed four times with methanol. The crude linoleic acid was recovered by adding the urea complex to 1400 ml of 2mol l^{-1} hydrochloric acid at $65^{o}C$.

Throughout these procedures, all the reacting solutions had either oxygen-free nitrogen (section 2.2.2) bubbled through them or were stored under an atmosphere of oxygen-free nitrogen to prevent losses through premature oxidation.

Purification of linoleic acid:

The crude linoleic acid was dissolved in 1000 ml of A.R.-grade

acetone and left to stand for four hours at -35°C. The precipitated saturated acids were removed by filtration at -35°C using the low temperature filtration apparatus (section 2.1.3). The solution was further cooled to -50°C and allowed to stand for two hours. Monoethenoid acids were removed by filtration at the same temperature and the solution was finally cooled to -70°C and left to stand for four hours. The precipitated linoleic acid was filtered at -70°C and washed with 250 ml of acetone cooled to the same temperature.

The residual traces of solvent were removed under vacuum and the pale yellow product was fractionally distilled to yield a colourless liquid. The fraction boiling at 157 - 159°C/0.2 mm Hg was collected and was found to have an acid value of 199. 'Acid value' is defined as the number of milligrams of potassium hydroxide required to neutralise 1g of the sample and the calculated value for linoleic acid is 199.

2.2.7 Methyl linoleate

Methyl linoleate was prepared by esterification of the linoleic acid, obtained by the above procedure, according to the method of Heaton and Uri[58].

Anhydrous hydrogen chloride was passed through a solution of 40 ml of linoleic acid dissolved in 200 ml of A.R.-grade methanol until two layers separated. This required approximately 20 minutes to occur and, after continuing to pass the hydrogen chloride for a further five minutes, the solution was diluted with 400 ml of distilled water and extracted three times with A.R.-grade 30 - 40° petroleum ether. The petroleum ether extracts were thoroughly washed with distilled water until the washings were free from acid and dried with anhydrous sodium sulphate.

After evaporation of the solvent under vacuum, the methyl linoleate

was fractionally distilled. The fraction boiling at 141 - 142°C/0.4 mm Hg was collected and found to have an acid value of zero.

2.2.8 Methyl cumate

The esterification of cumic acid (p-isopropylbenzoic acid) was carried out in an identical manner to the esterification of linoleic acid described above except that, as no separation of layers occurs[61], the hydrogen chloride was passed through the solution for two hours to ensure completion of the reaction. Collection of the fraction boiling at 89 - 91°C/2 mm Hg yielded a colourless product with an acid value of zero.

2.2.9 Tetralin hydroperoxide

Tetralin hydroperoxide was prepared by oxidation of tetralin according to the method of Knight and Swern[215].

A finely dispersed stream of oxygen was passed through 600g of tetralin which was held at 70°C for 48 hours. Unreacted tetralin was removed from the reaction mixture by vacuum distillation at 32 - 36°C/0.2 mm Hg. The distillation was carried out at a pot temperature of no greater than 70°C and the pot residue, a viscous amber oil, was dissolved in 450 ml of A.R.-grade toluene and cooled to -50°C. After standing for one hour, the precipitate was filtered out at -50°C using the low temperature filtration apparatus. Two further recrystallisations, each from 500 ml of toluene at -30°C, yielded 86g of tetralin hydroperoxide as a white solid melting at 54.0 - 54.3°C. (The literature value[215] is 54.0 - 54.5°C.) No decomposition of the hydroperoxide was noted after storage for several months in the dark at 0°C.

Tetralin hydroperoxide was found to be an extreme skin irritant and care should be employed when handling this compound.

2.3 General procedures

2.3.1 Purification of substrates

Most of the substrates used in this work were rigorously purified by the method described by Betts and Uri[59] for the removal of hydroperoxides. After prior redistillation, a 10% solution of the substrate in A.R.-grade petroleum ether (30 - 40°; free from aromatic hydrocarbons) was passed through a column of Brockman Grade 1 alumina, neutral (CAMAG). The petroleum ether solvent was removed under vacuum in a rotary film evaporator and the purified substrate was stored at -40°C under nitrogen. The substrates were re-purified immediately before each experiment and were only used if no hydroperoxide could be detected in a 10 ml sample by the method employed (section 2.4.2) for peroxide determination.

The only exceptions to the above procedure applied to those substrates which were too polar to pass through the column and/or too insoluble in the petroleum ether solvent. These were linoleic acid, cumic acid and 9,10-dihydroanthracene, the latter two being solids at ambient temperatures. Purification of these two substrates was by repeated recrystallisation from A.R.-grade methanol until no hydroperoxide could be detected in a 10g sample. Linoleic acid was purified by recrystallisation from A.R.-grade acetone at -70°C followed by vacuum distillation. The fraction collected at 158°C/0.2 mm Hg was used.

2.3.2 Cleaning of glassware

The reaction flasks from the Warburg apparatus and the automatic recording apparatus, together with all glassware used in the preparation of experimental solutions, were rigorously cleaned before each usage. The method used was adhered to throughout the work so as not to adversely affect the reproducibility of experimental data. Carlsson and Robb[44] have

observed effects on subsequent reaction rates caused by different methods of cleaning the reaction vessels.

After cleaning with acetone and water to remove the bulk of the previous contents, the glassware was immersed in fuming nitric acid to remove any residual organic products or traces of nickel compounds from the NiSDT inhibitor. After at least two hours, the glassware was removed, washed under running water and thoroughly rinsed three times with distilled water before being finally dried in a vacuum oven. The reaction flasks were stored in a dessicator until they were used.

2.3.3 Commencement of experiment

After purification of the substrate (section 2.3.1), solutions of the required composition were made up and immediately introduced into the reaction flasks. In those cases where no ethyl benzoate solvent was used, the inhibitor was introduced into the flask in chloroform solution, which was evaporated under reduced pressure. The required amount of substrate was then added. The sample size used for the Warburg apparatus was 1 ml and for the automatic recording apparatus it was generally 2 ml. The solutions were then placed into the constant-temperature baths and a glass bucket of freshly calcined CaO absorbent was placed in the neck of the automatic apparatus's flasks. The dessicants used for the Warburg flasks, i.e. silica-gel and soda-asbestos, were inserted into the central well or side-arm prior to the introduction of the sample. Each apparatus had two flasks containing only the ethyl benzoate solvent (or empty when no solvent was being used) to act as thermal barometers. After equilibriation for ten minutes, the systems were closed to the atmosphere.

At a convenient time, half of the flasks on the Warburg apparatus were removed and stored for 12 hours at $-40^{\circ}C$ before being replaced. This

procedure was necessary as 24-hour monitoring of the reactions was not possible.

For those reactions between tetralin hydroperoxide and NiSDT on the Warburg apparatus, the above procedure was followed except that the two reactants were introduced into the flasks separately. The tetralin hydroperoxide solution (0.5 ml) was introduced normally and the NiSDT solution (0.5 ml) was placed in the side-arm of the flask. After allowing equilibration for five minutes, the two solutions were mixed at zero time.

2.3.4 Calculation of oxygen uptake

2.3.4.1 Warburg apparatus

The system used in the Warburg apparatus relies on observation of the pressure change in a constant-volume reaction system. The quantity of oxygen taken up or evolved in the course of a reaction can be calculated by considering the change in total gaseous volume of the system, at 760 mm Hg and 25°C, between the commencement and end of the experiment.

The total gaseous volume, V_1 µl, at the start is given by:-

$$V_g \cdot \frac{298}{T} \cdot \frac{P - R}{P_o} + \alpha \cdot V_f \cdot \frac{P - R}{P_o}$$

After a corrected manometric pressure-change of h mm, the total gaseous volume, V_2 µl, is:-

$$V_g \cdot \frac{298}{T} \cdot \frac{P - R + h}{P_o} + \alpha \cdot V_f \cdot \frac{P - R + h}{P_o}$$

where V_g = Volume of the gaseous part of the system in µl

V_f = Volume of the liquid sample in µl

P = Initial pressure of the gaseous part of the system in mm manometric fluid

R = Vapour pressure of the liquid sample in mm manometric fluid

P_o = Standard pressure (760 mm Hg = 10,000 mm Brodie)

T = Temperature of the reacting system, K

α = Gas absorption coefficient in ml gas/ml liquid and denotes the extent of the solubitity 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 µl, is then:-

$$X = V_1 - V_2$$

$$= V_g \cdot \frac{298}{T} \cdot \frac{h}{P_o} + \alpha \cdot V_f \cdot \frac{h}{P_o}$$

$$= \left[\frac{V_g \cdot 298/T + V_f \cdot \alpha}{P_o} \right] \cdot h$$

$$= k \cdot h$$

where k is referred to as the reaction flask constant, consisting entirely of parameters which are known and remain constant throughout the experiment. The constant, k, for the systems used fell within the range 1.0 - 1.2 and thus, a fullscale deflection of the manometer (150 mm Brodie) corresponds to 150 - 180 µl oxygen (STP). As experiments covered significantly larger amounts of oxygen uptake, it was necessary to periodically restore the original pressure to the system. Thus, at any time, t, the total oxygen uptake, X_{TOT}, is obtained from:-

$$X_{TOT} = \sum_{t=0}^{t=t} X$$

It is also necessary with these systems to restore the original atmosphere after a total manometric change of 750 mm Brodie to ensure that the decrease in oxygen partial pressure is sufficiently small not to influence the reaction rate.

2.3.4.2 Automatic recording apparatus

The calculation of the quantity of oxygen absorbed in the course of a reaction using the automatic recording apparatus is very similar to the calculation used for the Warburg apparatus, except that allowance must be made for the decrease in system volume due to the movement of mercury in the U-tube manometer. As before, the majority of the terms in the equation are fixed dimensions or constant parameters.

Thus, for oxygen uptake of V ml with a pen movement of L cm, one obtains:-

$$\frac{V}{L} = \frac{R}{P_o}\left[V_F \cdot T_F + V_M \cdot T_M + \tfrac{1}{2}X_M \cdot T_M (P - RL)\right]$$

where R = Ratio of the change in pressure (cm Hg) to the corresponding pen movement in cm

V_F = Volume of the reaction flask, minus the sample volume, in ml

V_M = Volume of the manometer in ml

X_M = Cross-sectional area of the manometer tube in cm^2

T_F = $298(298 + \text{flask temperature (K)})^{-1}$

T_M = $298(298 + \text{manometer temperature (K)})^{-1}$

P = Initial flask pressure in cm Hg

P_o = Standard pressure (76 cm Hg).

(This formula gives the volume, V ml, corrected to STP.)

In practice, the second-order term is sufficiently small to be ignored and the final equation is:-

$$\frac{V}{L} = \frac{R}{P_o}\left[V_F \cdot T_F + (V_M + \tfrac{1}{2}X_M \cdot P)\, T_M \right]$$

In a typical system used, an absorption of 67 µl O_2(STP) corresponded to a pen movement of 1 mm.

2.4 Analytical prodecures

2.4.1 Determination of inhibitor concentration

The concentration of NiSDT and its p-substituted derivatives was determined spectrophotometrically with a Hitachi-Perkin Elmer EPS-3T recording spectrophotometer. The peak used for these determinations was at 865 nm for NiSDT — the equivalent peak being used for the p-substituted derivatives. The EPS-3T machine was also used for all the spectral measurements presented in tables 3.2 to 3.5.

2.4.2 Determination of peroxide concentration

The concentration of hydroperoxide in the reacted solutions was determined by the iodometric method of Heaton and Uri[212] using the type of flask illustrated in Plate 5. The solvent used was a mixture of two volumes of A.R.-grade acetic acid to one volume of A.R.-grade chloroform. For 9,10-dihydroanthracene, the chloroform concentration was increased to 50% to improve the solubility of this substrate.

The samples were introduced into the 70 ml of solvent mixture previously placed in each flask and vigorously de-aerated with oxygen-free nitrogen (section 2.2.2) for one hour. A blank test accompanied each set of determinations.

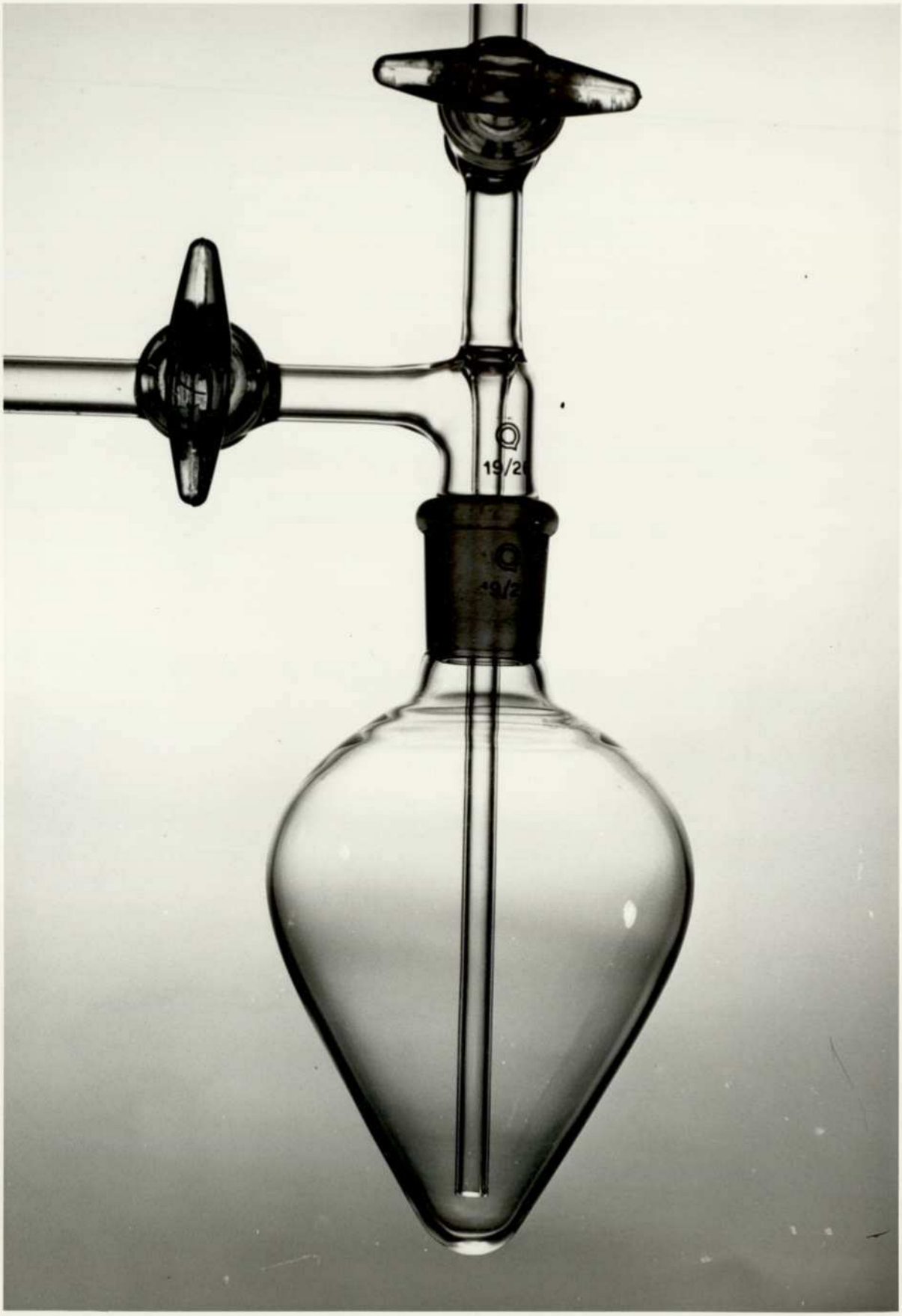


PLATE 5

PEROXIDE FLASK

A 0.5 ml aliquot of a freshly-prepared saturated aqueous solution of potassium iodide was then added to the last flask in the de-aeration train after raising the gas inlet tube, the design of the flasks permitting this to be carried out without removing the tube from the liquid. This ensures that no air is drawn into the flasks by the jet effect of the nitrogen stream.

After passing the nitrogen for a further five minutes, the flask was removed and stored in the dark with the taps closed. The above procedure was then repeated for the remaining flasks. After one hour, the flask was removed and 30 ml of 5% aqueous potassium iodide were added. The contents of the flask were then titrated rapidly with 0.002 N sodium thiosulphate solution to a starch-indicator endpoint:-

1 ml 0.002 N sodium thiosulphate $\equiv$ 1 µmol peroxide.

2.4.3 Determination of carbonyl concentration

Carbonyl compounds were determined as their 2,4-dinitrophenylhydrazones according to the spectrophotometric method of Lappin and Clark[213]. The method is suitable for carbonyl concentrations between 10^{-3} and 10^{-5} mol l^{-1}.

A 1 ml aliquot of a carbonyl-free methanol (section 2.2.3) solution of the sample was placed in a 10 ml volumetric flask and 1 ml of a saturated solution of 2,4-dinitrophenylhydrazine in carbonyl-free methanol was added together with one drop of dilute hydrochloric acid. The flask was loosely stoppered and maintained at 50°C for two hours. After cooling, 5 ml of a potassium hydroxide solution (10g KOH dissolved in 20 ml distilled water, made up to 100 ml with carbonyl-free methanol) was added. The resulting, almost black solution rapidly cleared to the characteristic wine-red colour and was made up to 10 ml with carbonyl-free methanol.

A simultaneous blank solution was prepared using 1 ml of carbonyl-free methanol in place of the sample solution. The optical density of the solution was determined with a Unicam SP600 spectrophotometer, with the blank test being used as the reference solution. All measurements were carried out at the absorbance peak (ca. 460 - 470 nm for the samples used) and an average molar extinction coefficient of $2.72 \cdot 10^4$ was employed in the subsequent calculations.

2.4.4 Mass spectrometry

In the course of investigating the reaction between tetralin hydroperoxide and NiSDT, attempts were made to determine the structure of the breakdown products of the hydroperoxide and inhibitor by using mass spectrometry. Samples were taken from specially prepared reacting solutions at two stages of the reaction — when the solution had changed from green to yellow in colour and when the change from yellow to colourless occurred. Microlitre quantities of these samples were placed in the all-glass heated inlet system (AGHIS) of an A.E.I. MS20 mass spectrometer and their mass spectra were determined. Due to lack of accurate control over the heating oven of the AGHIS, only qualitative indentification of the products could be obtained owing to their widely differing boiling-points under high vacuum.

Further experiments using this technique could not be carried out owing to a prolonged breakdown of the instrument.

RESULTS AND DISCUSSION

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3 RESULTS AND DISCUSSION

3.1 Bis(stilbenedithiolato)nickel

3.1.1 Alternative solvents for the synthesis

The synthesis of bis(stilbenedithiolato)nickel described in section 2.2.4 has a particular disadvantage for potential industrial production. This is centred on the use of dioxan as the reaction solvent. As the addition of water in the second stage is unavoidable, solvent recovery would be extremely difficult owing to the close proximity of the boiling points of dioxan and water (101°C and 100°C respectively). By contrast, sulpholane (tetrahydrothiophen-1,1-dioxide), which is also miscible with water, boils at 285°C and it was thought that dioxan could be advantageously replaced with sulpholane to give similar or possibly improved yields. Other candidate solvents (generally of high polarity and miscible with water), such as tetrahydrofuran and dimethylformamide, were less useful, the yield of NiSDT being very small and difficult to extract from the reaction mixture. Somewhat better results were obtained with p-xylene, where the second stage is heterogeneous. One run under optimum conditions — 2.5 hours refluxing in the first stage — produced a yield of crude material in excess of 30% ex benzoin. However, this yield was extremely difficult to reproduce, the heterogeneous second stage apparently having critical stirring parameters.

The use of sulpholane as the reaction solvent proved very successful. Table 3.1, presented overleaf, shows that the yield obtained with sulpholane was very reproducible under conditions which appeared to be in the optimum range. By carrying out the first stage at 120°C for 2.5 hours, an average yield slightly in excess of 50% was obtained. This is somewhat better that that obtained from dioxan.

Table 3.1 : Conditions in the first stage* and yields (ex benzoin) for the synthesis of NiSDT

Solvent	Temp./^{o}C	Time/hr	Yield
1,4-dioxan	Reflux	2.0	47%
p-xylene	Reflux	2.5	30%†
sulpholane	145	0.3	42%
sulpholane	100	4.0	44%
sulpholane	120	2.5	52%
sulpholane	120	2.5	50%

* The second stage of the reaction in each case was exactly as described in section 2.2.4.

† Unpurified material.

Although the use of p-xylene was not as successful as sulpholane, it is felt that, given efficient mixing, p-xylene offers some advantages for an industrial synthesis. The homogeneous first stage of the reaction, involving benzoin and phosphorus pentasulphide, appeared to be at least as efficient as in any of the other solvents and the crude material obtained at the end of the second stage was far purer than for either dioxan or sulpholane. The crude material from the p-xylene syntheses was well-shaped crystals with no appreciable sulphide odour. It is possible that, by adjusting the quantities used in the synthesis with p-xylene, the need for further purification of the crude material could be avoided or, at least, very much reduced. Alternatively, any purification necessary might be

carried out with p-xylene instead of either toluene or dichloromethane, thereby simplifying any solvent recovery system used. The p-xylene solutions were also found to be easier to handle than the sulpholane solutions, particularly after the second stage of the reaction where the crude, NiSDT-containing, sulpholane solution is extremely viscous. Filtration is, therefore, extremely slow, even when carried out at up to 80°C. Actual solvent recovery should be equally easy with either p-xylene or sulpholane although the power requirements for p-xylene may be smaller due to its lower boiling-point (137°C). Thus, whilst the use of sulpholane would be recommended in place of dioxan on the basis of the results obtained, further investigation of the p-xylene system may be advantageous from the industrial point of view.

3.1.2 Spectra of bis(stilbenedithiolato)nickel and substituted derivatives

The spectra of chloroform solutions of NiSDT and the substituted derivatives described in section 2.2.5 are presented in figures 3.1 to 3.4. Extinction coefficients for the major peaks are given in tables 3.2 to 3.5 together with the corresponding figures obtained by Schrauzer, where available.

Fig. 3.1 : Spectrum of bis(stilbenedithiolato)nickel
Solvent; $CHCl_3$: Path length; 1 cm

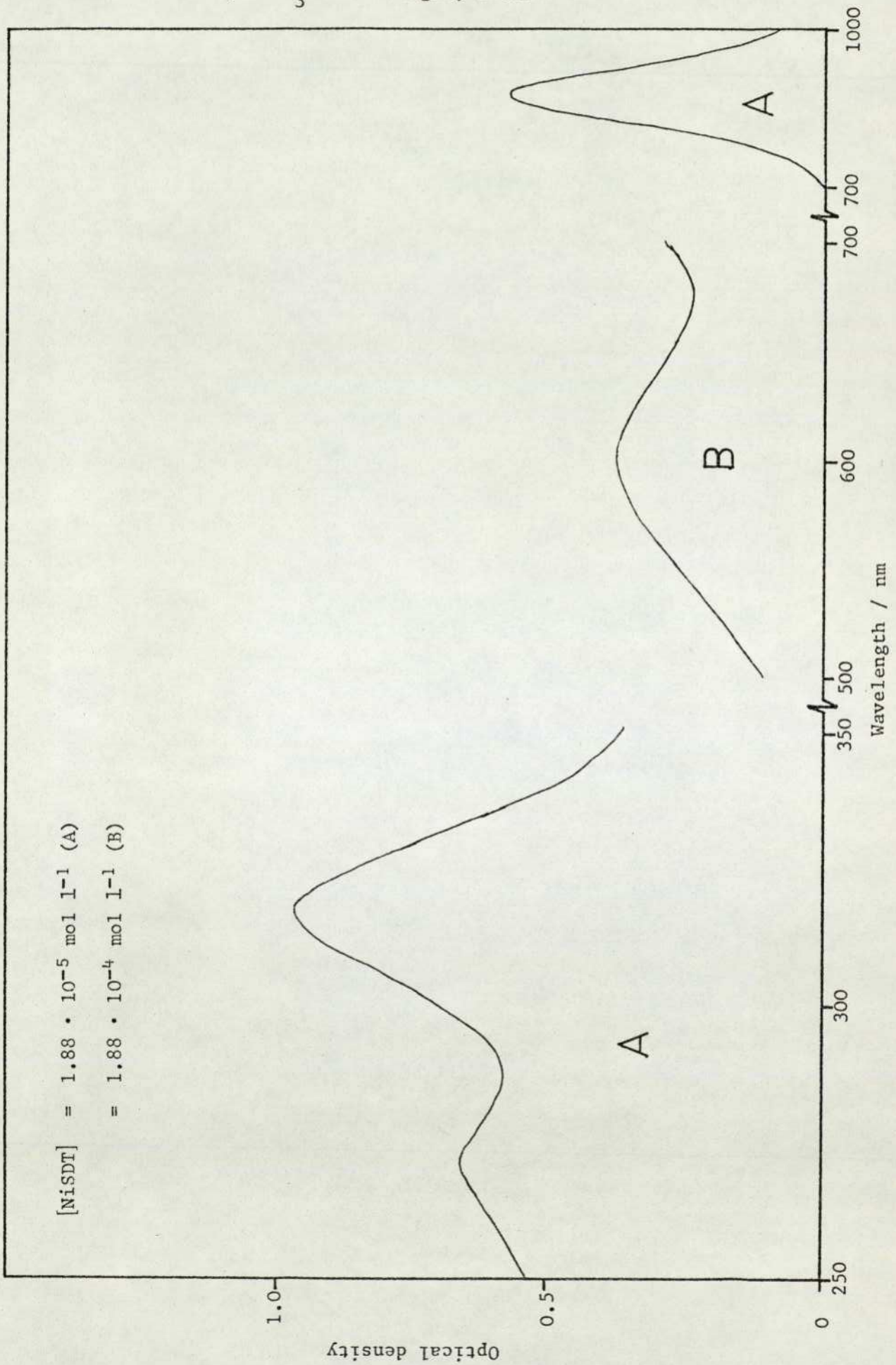


Fig. 3.2 : Spectrum of p-methoxy substituted NiSDT
Solvent; $CHCl_3$: Path length; 1 cm

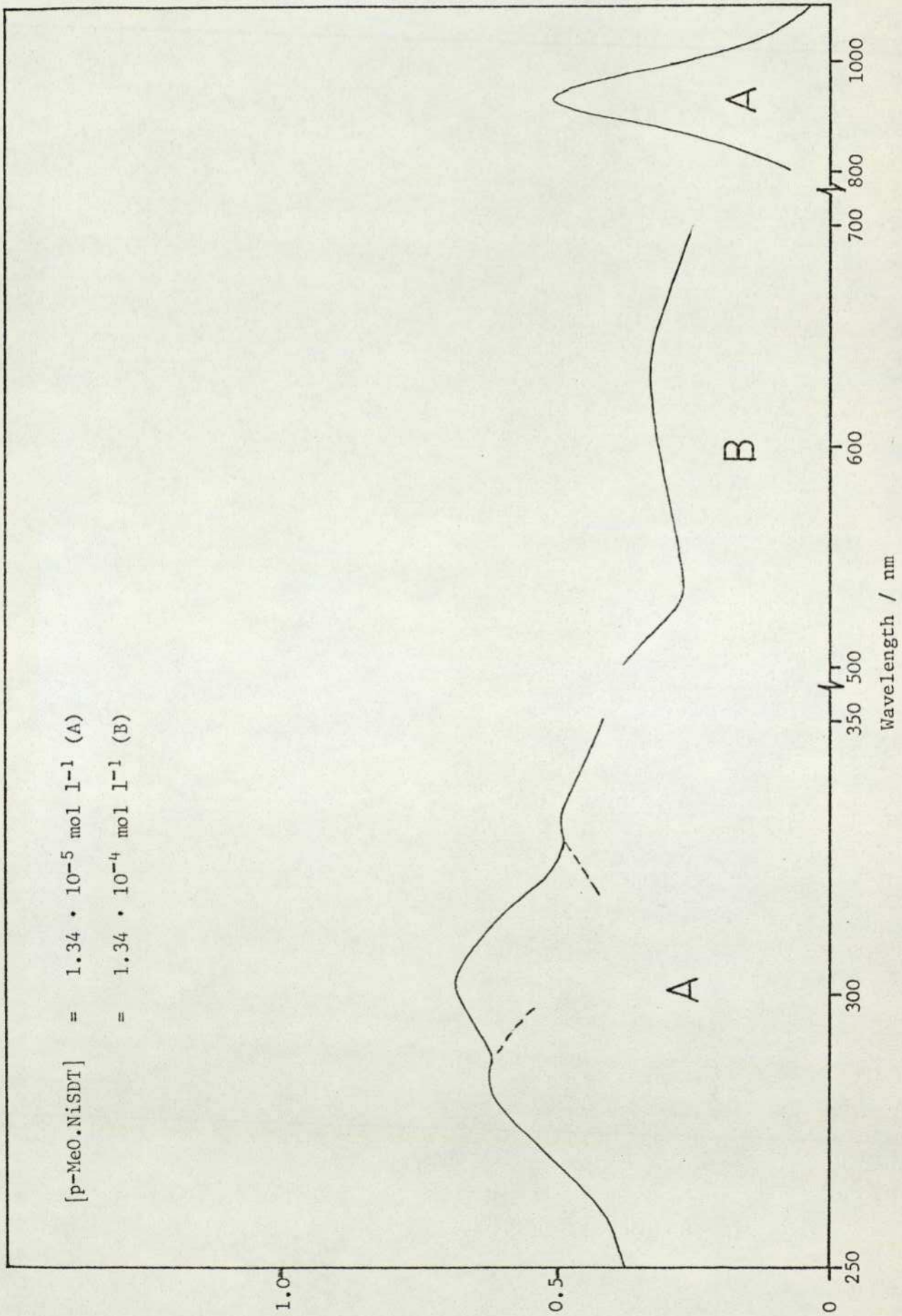


Fig. 3.3 : Spectrum of 1,4-S-dimethyl substituted NiSDT
Solvent; $CHCl_3$: Path length; 1 cm

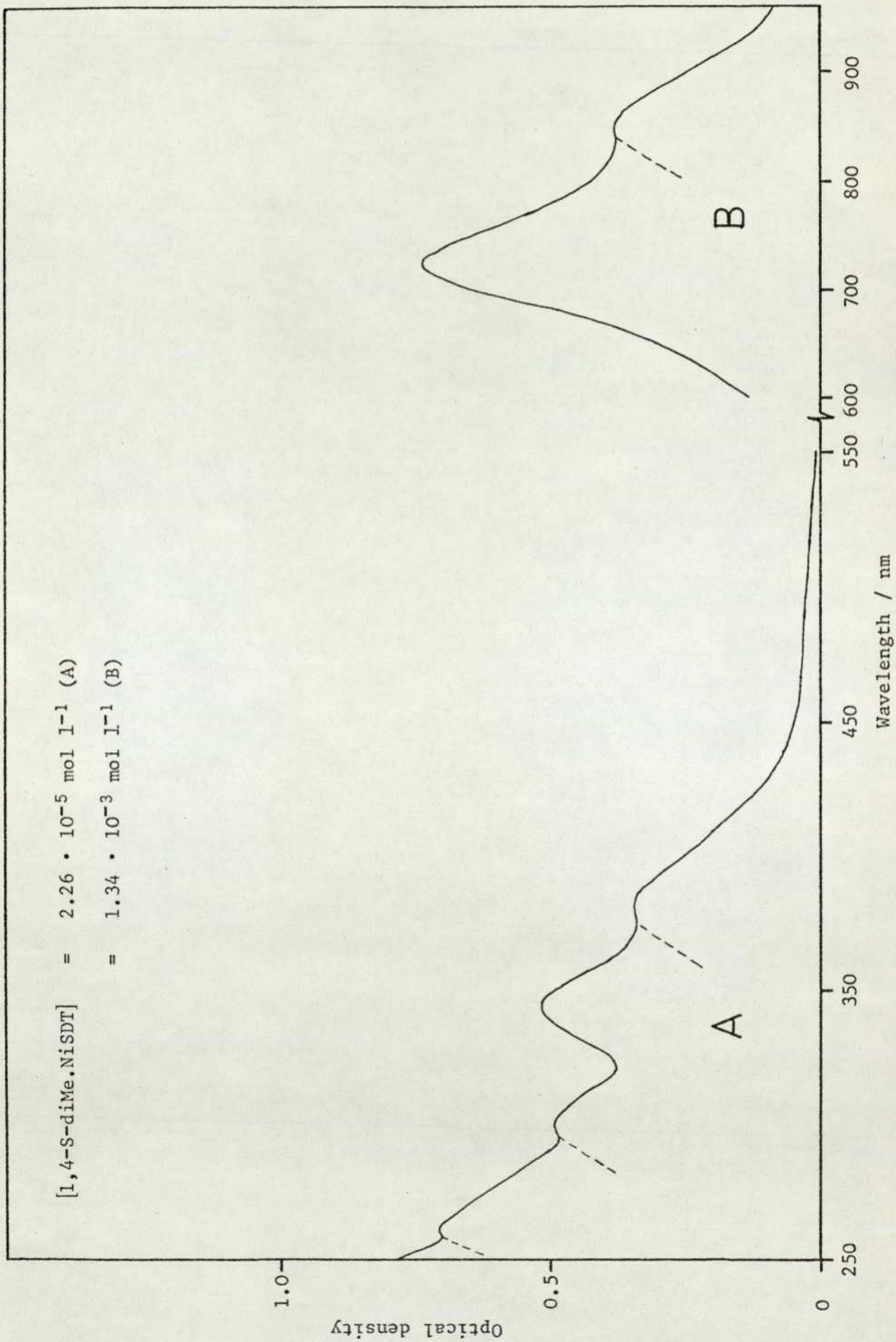


Fig. 3.4 : Spectrum of p-isopropyl substituted NiSDT
Solvent; $CHCl_3$: Path length; 1 cm

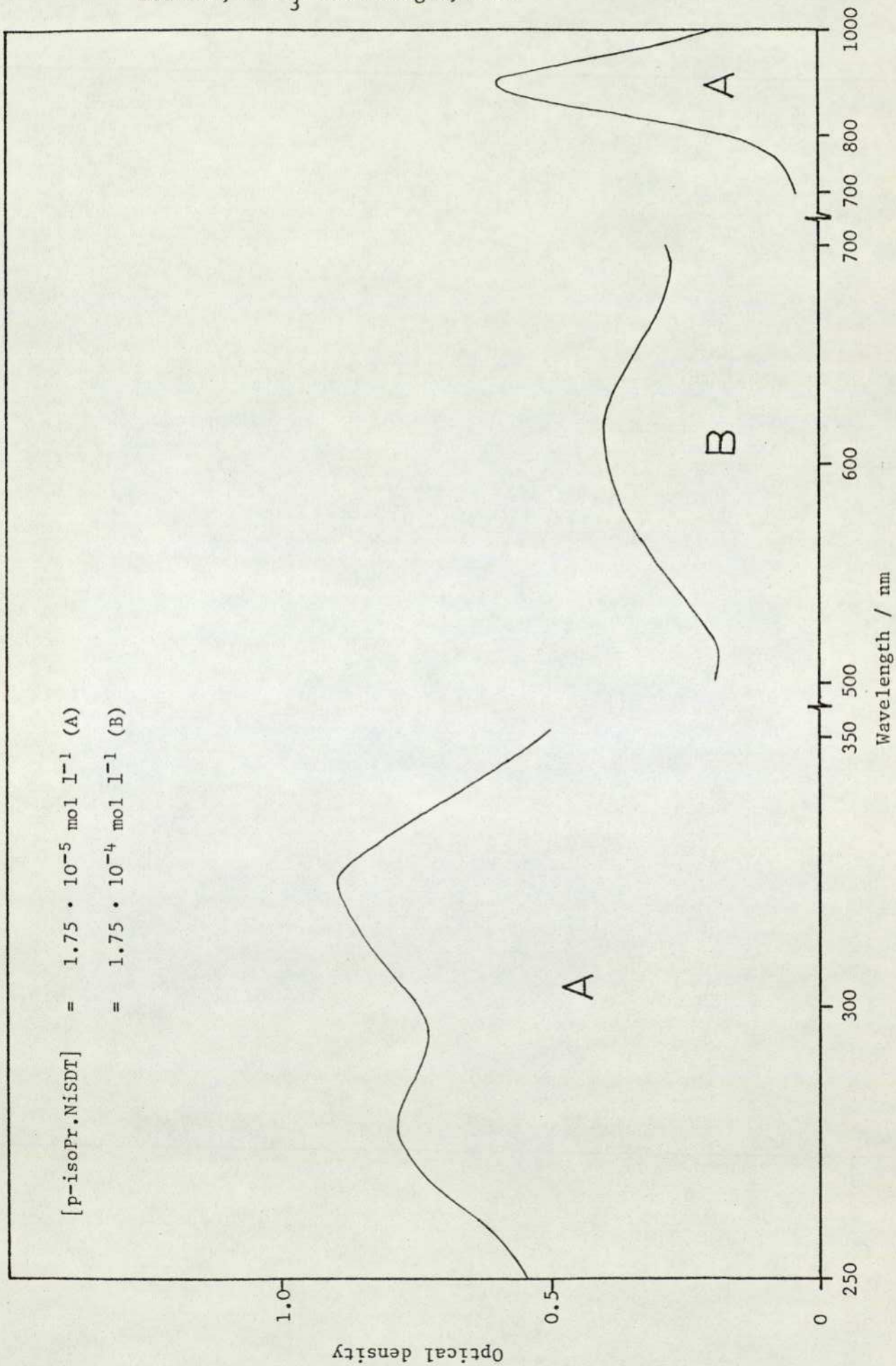


Table 3.2 : Comparison of NiSDT spectrum with that of Schrauzer[181]

NiSDT		NiSDT (Schrauzer)	
$\lambda_{max.}$/nm	log ε	$\lambda_{max.}$/nm	log ε
865	4.49	866	4.49
602	3.31	602	3.34
317	4.71	316	4.71
271	4.55	270	4.57

Table 3.3 : Comparison of p-methoxy NiSDT spectrum with that of Schrauzer[181]

p-MeO.NiSDT		p-MeO.NiSDT (Schrauzer)	
$\lambda_{max.}$/nm	log ε	$\lambda_{max.}$/nm	log ε
930	4.57	925	4.40
635	3.38	640	3.22
332	4.56	330	4.39
303	4.70	302	4.53
285	4.66	285	4.49

Table 3.4 : Comparison of 1,4-S-dimethyl NiSDT spectrum with that of Schrauzer[194]

1,4-S-diMe.NiSDT		1,4-S-diMe.NiSDT (Schrauzer)	
$\lambda_{max.}$/nm	log ε	$\lambda_{max.}$/nm	log ε
720	2.74	708	2.75
-	-	465	3.40
380	4.18	380	4.18
343	4.36	342	4.45
298	4.34	-	-
263	4.49	-	-

Table 3.5 : Spectrum of p-isopropyl NiSDT

$\lambda_{max.}$/nm	log ε
895	4.52
614	3.35
322	4.70
278	4.65

The data obtained for NiSDT are in good agreement with Schrauzer and both p-substituted derivatives exhibit a red-shift of the $\lambda_{max.}$ values which would be expected for electron-donating substituents. The extinction coefficients obtained for the p-methoxy NiSDT do not agree with those found by Schrauzer and there is some discrepancy in the 1,4-S-dimethyl NiSDT values. It is considered that Schrauzer's figures for the p-methoxy NiSDT may be incorrect. Other electron-donating p-substituents examined by Schrauzer appear to increase the extinction coefficient of the intense near infra-red transition (e.g. p-methyl NiSDT; log ε = 4.50), whereas electron-withdrawing groups decrease it (p-chloro NiSDT; log ε = 4.43). The results for p-isopropyl NiSDT (log ε = 4.52) follow this trend. Thus, the extinction coefficient for the near infra-red transition of p-methoxy NiSDT would be expected to be higher than that of NiSDT (log ε = 4.49) as the methoxy group is a powerful electron-donor in aromatic systems. However, the value quoted by Schrauzer (log ε = 4.40) is much lower than the value for the p-chloro substituted chelate. It is believed that these low values are due to practical difficulties. The p-methoxy NiSDT was not easily soluble and the intense colouration of the solutions makes it extremely difficult to determine whether or not the material has completely dissolved. The value of log ε = 4.57 for p-methoxy NiSDT was obtained several times but, on each occasion, the chloroform solutions had to be stirred continuously for 48 hours before total dissolution occurred. With the large extinction coefficients exhibited by these compounds, it does not require much deviation from the calculated concentrations to significantly affect the absolute numerical figures obtained.

Having regard to the figures obtained for the 1,4-S-dimethyl derivative, no explanation for the discrepancies with Schrauzer's figures can be given. However, it is not known how much reliance can be placed on

Schrauzer's figures in this case. In his paper[194], he states that all spectra were determined in methanol solution — 1,4-S-dimethyl NiSDT is totally insoluble in methanol which is used as the solvent in the preparation of this compound (section 2.2.5.2). The spectrum obtained shows evidence of NiSDT impurity, a shoulder at ca. 860 nm, which is calculated to be present at 0.9% $^{w}/_{w}$. The extinction coefficients quoted for the 1,4-S-dimethyl derivative have been corrected to take this into account.

3.2 The efficiency of NiSDT as an antioxidant

3.2.1 Preliminary survey

The initial stage in the investigation of the action of NiSDT was a survey of its inhibiting efficiency in a range of substrates. To aid comparison between the substrates used, each was investigated at 1 mol l^{-1} concentration in a common solvent, ethyl benzoate, to minimise as far as possible any individual solvent effects. The NiSDT concentration was constant at $2 \cdot 10^{-4}$mol l^{-1}. The results in table 3.6 give the data obtained for the first five substrates investigated. In each case, the induction period was defined as the time required for 1 ml of sample to absorb 100 µl(STP) of oxygen. Samples were removed from the oxidation apparatus and analysed for peroxide and carbonyl content when they had absorbed an amount of oxygen corresponding to between 10 and 25 times that absorbed in the induction period. The 'efficiency' of the NiSDT was defined as:-

$$\frac{t_i - t_u}{t_u}$$

where t_i = induction period of the inhibited sample

t_u = induction period of the uninhibited sample.

Table 3.6 : The efficiency of NiSDT in different substrates — [Substrate] = 1 mol l^{-1} in ethyl benzoate

Substrate	*	Temp./ ^{o}C	Induction period/ hr	Max.rate/ $\mu l O_2$(STP) $ml^{-1}hr^{-1}$	Peroxide/ $\mu mol\ ml^{-1}$	Carbonyl/ $\mu mol\ ml^{-1}$	Corresponding O_2 absorption/ $\mu mol\ ml^{-1}$	% O_2 analysing as ROOH	Antioxidant efficiency
Hexadec-1-ene	U	130	12	355	41.0	28.0	64.0	64.1	1.1
	I		25	335	29.5	28.0	51.0	57.8	
2,6,10,14-Tetramethyl-pentadecane	U	140	2.5	760	36.3	15.7	45.7	79.4	2.6
	I		9	365	11.0	18.8	47.6	23.1	
Linoleic acid	U	50	14	155	49.2	NA†	54.4	90.4	1.8
	I		39	155	49.2	NA	54.3	90.6	
Methyl linoleate	U	50	15	105	87.0	NA	87.6	99.3	0.3
	I		20	115	91.5	NA	92.0	99.5	
Tetralin	U	70	8	100	36.5	NA	39.0	93.6	91
	I		740	60	53.0	NA	56.0	94.6	

* U = uninhibited sample; I = inhibited sample ($2 \cdot 10^{-4}$mol l^{-1} NiSDT)

† NA = not analysed

From table 3.6, it can be seen that NiSDT is an efficient antioxidant for most of the substrates, even at 140°C. However, the efficiency in tetralin is an order of magnitude higher than for any other substrate. As this was the only aromatic substrate examined, the survey was extended to include methyl cumate and 9,10-dihydroanthracene (DHA) at the same NiSDT concentration. Figures 3.5 and 3.6 show the results obtained. The results for methyl cumate (figure 3.5) were determined without solvent as a molar methyl cumate solution had not oxidised after 250 hours at 70°C. The inhibitor concentration in an equivalent solution had only been reduced to $1.25 \cdot 10^{-4}$mol l^{-1} after 350 hours. Figure 3.5 includes uninhibited and inhibited ($2 \cdot 10^{-4}$mol l^{-1} NiSDT) tetralin without solvent for comparison.

The experiment with DHA (molar solution in ethyl benzoate with $2 \cdot 10^{-4}$mol l^{-1} NiSDT) was not taken to completion as the total duration would have been in excess of 600 hours. Nevertheless, it illustrates the marked inhibitory properties of NiSDT for this type of system. The uninhibited DHA is not shown in figure 3.6 as, with an induction period of less than ten minutes and an extremely fast rate of oxidation (ca. 3000 $\mu l O_2(STP) ml^{-1} hr^{-1}$), it is practically indistinguishable from the vertical axis.

The DHA system (and, to a lesser extent, the methyl cumate system) differ from previous substrates in that considerable oxygen uptake occurs throughout the period in which the green colour of the inhibitor is still noticeable. This indicates that radical termination is not occurring efficiently and that the propagation reaction is proceeding to some degree. Further experiments with DHA at a higher temperature will be reported in section 3.5.

Fig. 3.5 : Autoxidation of methyl cumate and tetralin in bulk at 70°C

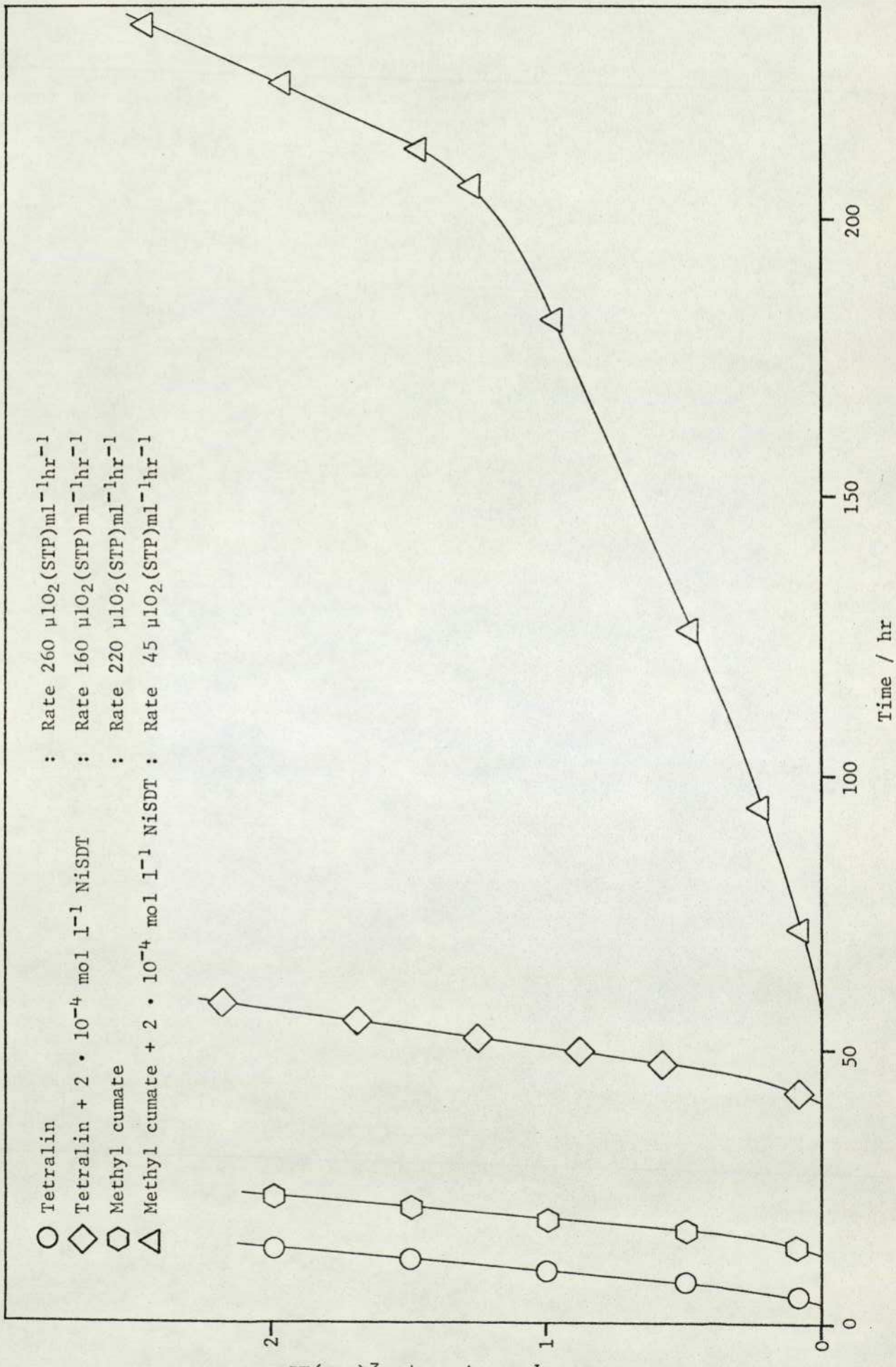
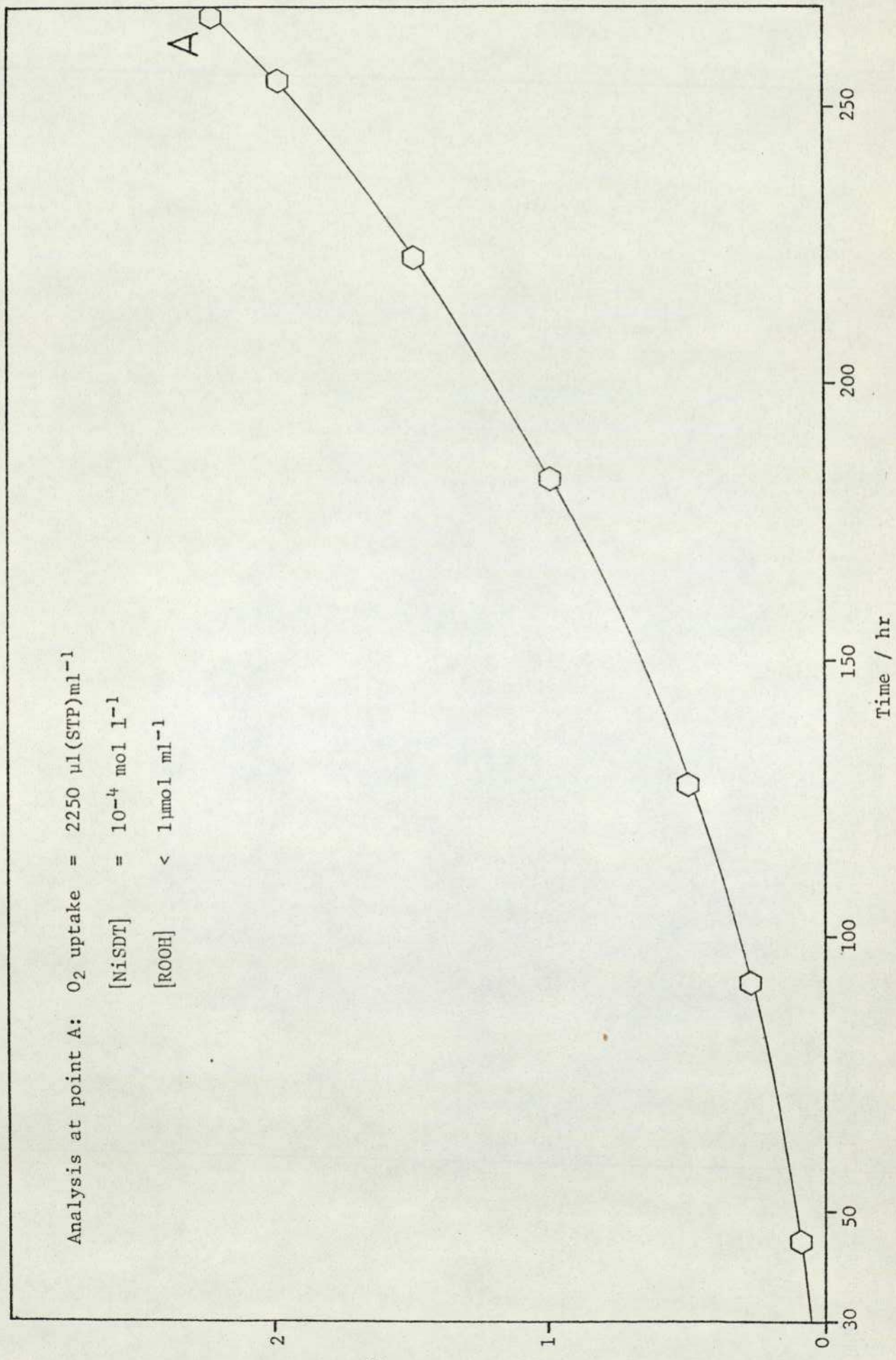


Fig. 3.6 : Autoxidation of 1mol l^{-1} DHA with 2 · 10^{-4}mol l^{-1} NiSDT at 70°C



It is of interest to note from the data in table 3.6 that NiSDT appears to behave as a classical inhibitor in that the final rate of oxidation after the induction period is normally the same for both the inhibited and uninhibited samples. The proportion of absorbed oxygen which is converted to hydroperoxide also does not differ between the two samples. Visual examination of the oxidising solution, where possible, suggested that the NiSDT was totally consumed (as evidenced by the disappearance of its colour) before the end of the induction period. This implies that, as expected, the products of primary reaction of NiSDT are in themselves inhibitors of autoxidation. Since the induction period continued beyond the point where NiSDT is totally consumed, the products of its reaction must normally be equally efficient as inhibitors. This suggests that the end of the induction period corresponds to complete de-activation of the NiSDT. The major exception to this statement is 2,6,10,14-tetramethylpentadecane (TMPD), where there is very marked retardation in the post-inhibition region and a marked reduction in hydroperoxide formation. It seems reasonable to suggest that, in this case, the retardation is due to hydroperoxide decomposition by oxidation products of the inhibitor.

In the case of tetralin, the results seem to suggest that there is some post-inhibition retardation. However, the yield of hydroperoxide remains high. This anomaly can be attributed to the insensitivity of the Warburg apparatus to low oxidation rates combined with the very long duration of the experiment. A very low rate of oxygen uptake (e.g. 2 $\mu l O_2$(STP) $ml^{-1}hr^{-1}$) would not be resolved from the background 'noise' in the apparatus but over a period of 700 hours would correspond to a large undetected oxygen uptake and, hence, a high hydroperoxide figure. It is, therefore, tentatively suggested that tetralin should be ranked with TMPD.

From the overall results obtained for the preliminary survey, it is

clear that, as a class of substrate, the aromatics can be more effectively inhibited by NiSDT. One possibility is that the dissociated π-bonding system of the aromatics is involved in complex formation with the antioxidant at its electron-deficient centres. However, no evidence for such a reaction has been obtained in any of the investigations of the antioxidant's chemistry. A more likely explanation can be obtained from consideration of the actual substrate molecules involved. The aromatic compounds investigated are all rigid molecules with relatively easily accessible reactive sites. These molecules are also relatively small. Conversely, the aliphatic substrates are large molecules with the reactive radical sites hindered to some degree by the rotation available at the carbon-carbon single bonds. Thus, it would seem probable that the increased efficiency of NiSDT in aromatic substrates is due to the influence of steric factors and the use of molecular models was found to support this proposition. Consideration of the figures in table 3.6 for TMPD show that, although the efficiency of the antioxidant is only 2.6 in terms of induction period, there is efficient hydroperoxide decomposition. The percentage of the oxygen forming hydroperoxide falls from 79.4% for the uninhibited sample to 23.1% for the inhibited sample. Thus, it would appear that the radical-trapping ability of NiSDT for these larger, more hindered molecules is limited, although its ability as a hydroperoxide decomposer seems unimpaired. This might also indicate that the two functions of NiSDT are dependent on different parts of the inhibitor molecule.

3.2.2 Comparison with a tris-phenolic antioxidant

A comparison between NiSDT and Topanol CA (1,1,3-tris(2-methyl-5-t-butyl-4-hydroxyphenyl) butane) at the same concentration ($2 \cdot 10^{-4}$ mol l^{-1}) was carried out with four of the substrates (table 3.7).

Table 3.7 : Comparison between NiSDT and Topanol CA antioxidants

[Substrate] = 1 mol l^{-1} in ethyl benzoate

Substrate	Temp./ °C	Uninhibited		$2 \cdot 10^{-4}$ mol l^{-1} NiSDT		$2 \cdot 10^{-4}$ mol l^{-1} Top.CA	
		Induction period/ hr	Max.rate/ $\mu l O_2$(STP) $ml^{-1}hr^{-1}$	Induction period/ hr	Max.rate/ $\mu l O_2$(STP) $ml^{-1}hr^{-1}$	Induction period/ hr	Max.rate/ $\mu l O_2$(STP) $ml^{-1}hr^{-1}$
2,6,10,14-Tetramethylpentadecane	140	2.5	760	9	365	3.0	310
Tetralin	70	8.0	100	740	60	105	50
Methyl cumate	120	3.0	240	>300	—	24	200
9,10-Dihydroanthracene	100	<0.2	—	>110	—	<0.2	—

The results given in table 3.7 support the previous reasoning regarding the increased inhibition of aromatics by NiSDT. It can be seen that a purely radical-trapping antioxidant has little effect on TMPD, but is a fairly efficient antioxidant for tetralin. NiSDT inhibits TMPD but, presumably, mainly by preventing initiation from the hydroperoxide. For tetralin, where NiSDT can function efficiently as a radical trap in addition to decomposing the hydroperoxide, prolonged protection occurs due to synergism between the two functions.

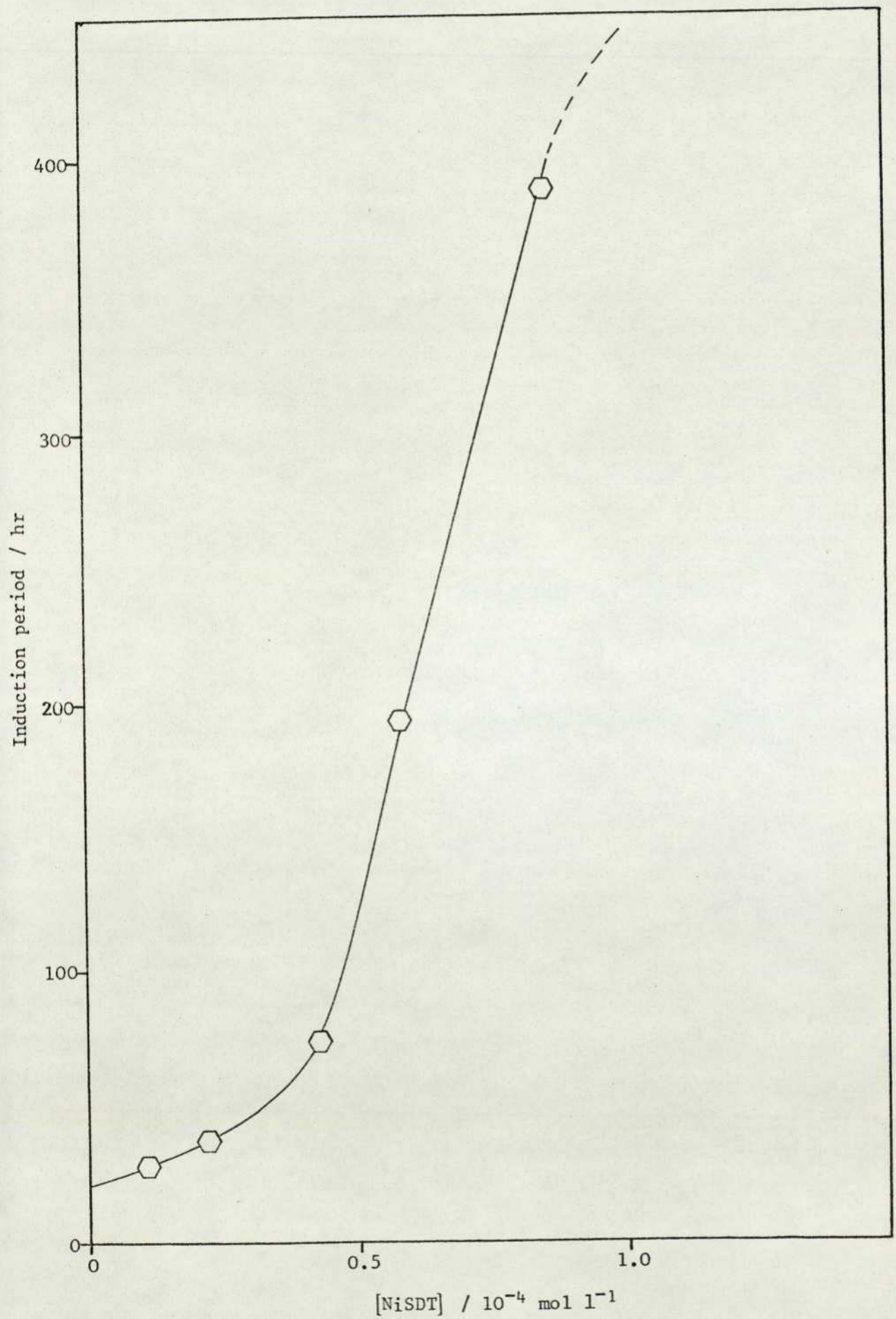
From the results of the initial experiments, it was decided to further investigate one of the aromatic systems. Tetralin was the major substrate chosen for reasons of availibility and solubility in the ethyl benzoate solvent.

3.3 Variation of NiSDT concentration

3.3.1 Tetralin

The dependence of the induction period of a molar tetralin/NiSDT system on the inhibitor concentration (figure 3.7) was found to be of the 'critical concentration' type mentioned in section 1.4.1. A marked increase in the inhibitory effect of NiSDT was observed above a concentration of $4 \cdot 10^{-5}$mol l^{-1}. A double logarithm plot of the data in figure 3.7 showed that the induction period changed from being approximately proportional to $[NiSDT]^{0.75}$ at concentrations below the critical value to being approximately proportional to $[NiSDT]^{2.5}$ at concentrations higher than the critical value. As the NiSDT concentration is increased above 10^{-4}mol l^{-1}, figure 3.7 again becomes non-linear as indicated. Curvature of this type is a well-established feature of many inhibited oxidations and is discussed further in section 4.2.

Fig. 3.7 : Inhibited autoxidation of 1 mol l^{-1} tetralin at 70°C
Induction period vs. inhibitor concentration



The maximum rates of subsequent oxidation were found to lie in the range 40 — 60 $\mu l O_2 (STP) ml^{-1} hr^{-1}$ and did not differ sufficiently to justify graphical interpretation, as the experimental error was too significant. The uninhibited rate under these conditions was 100 $\mu l O_2 (STP) ml^{-1} hr^{-1}$.

The establishment of a critical concentration with NiSDT is of interest, but the kinetics of such phenomena do not seem to be well understood. Equation (34) mentioned in section 1.4.1 has been modified[171] to include the case where a hydroperoxide decomposer is present in addition to the radical-trapping antioxidant but, as each component is treated separately, application to NiSDT, where the two roles are interdependent, would be extremely difficult. Furthermore, there is no evidence for the radical-terminating reaction of NiSDT producing hydroperoxide, as does a conventional phenolic antioxidant (section 3.7.1), and this is an integral part of the mathematical treatment by the Russian workers. However, this treatment contains anomalies and some of the assumptions made are not particularly valid.

The reaction scheme used by these workers[119,123,171] is:-

$$RH \xrightarrow{r_i} R^{\bullet} \qquad (1)$$

$$R^{\bullet} + O_2 \xrightarrow{k_o} RO_2^{\bullet} \qquad (2)$$

$$RO_2^{\bullet} + RH \xrightarrow{k_p} ROOH + R^{\bullet} \qquad (3)$$

$$RO_2^{\bullet} + AH \xrightarrow{k_a} ROOH + A^{\bullet} \qquad (32)$$

$$ROOH + RH \xrightarrow{k_b} nRO_2^{\bullet} \quad (\text{where } n < 1) \qquad (53)$$

$$ROOH + R_2'S \xrightarrow{k_s} \text{inactive products} \qquad (54)$$

The following equations were then derived:-

$$\frac{d[RO_2^{\bullet}]}{dt} = r_i - k_a[AH][RO_2^{\bullet}] + nk_b[RH][ROOH]$$

$$\frac{d[ROOH]}{dt} = k_p[RH][RO_2^{\bullet}] + k_a[AH][RO_2^{\bullet}] - k_s[ROOH][R_2'S] - k_b[ROOH][RH]$$

Investigation of these two equations shows that, whilst allowance is made in the first for hydroperoxide production by the normal propagation reaction (3), the consequent disappearance of alkylperoxy radicals has been neglected in the second. There are valid reasons for either totally including or totally excluding this reaction, but no reason can be found for including it in one equation and neglecting it in the other.

By the application of the steady-state approximation to these two equations, the stationary concentration of $[RO_2^{\bullet}]$ was shown to be:-

$$[RO_2^{\bullet}]_{st} = \frac{r_i}{k_a[AH] - \dfrac{nk_b[RH](k_p[RH] + k_a[AH])}{k_b[RH] + k_s[R_2'S]}} \qquad (55)$$

The assumption is then made that $[RO_2^{\bullet}]_{st}$ is infinite for autocatalytic oxidation which will occur below the critical antioxidant concentration. $[AH]_{cr}$ was thus obtained by equating the denominator of (55) to zero and rearranging:-

$$[AH]_{cr} = \frac{n}{(1-n)} \cdot \frac{k_p k_b [RH]^2}{k_a k_b [RH] + k_a k_s [R_2'S]}$$

The validity of this assumption is clearly open to question and

therefore the value of these equations must be regarded as dubious, although the phenomenon itself is well defined experimentally.

It is a feature of this kind of concentration dependence that the inhibitor disappears at a slow, steady rate until the critical concentration is reached. Below this critical concentration, a rapid increase in the rate of disappearance occurs. This rapid decrease in antioxidant concentration in a NiSDT-inhibited system can be attributed to the appearance of hydroperoxide. Separate experiments with NiSDT and tetralin hydroperoxide (section 3.6) have shown that the hydroperoxide causes rapid decomposition of the NiSDT into other effective hydroperoxide-decomposing species. Thus, it appears that at the critical concentration NiSDT becomes much less effective as a radical trap, thereby allowing the normal autoxidation reactions to proceed at an increasing rate. The maximum rate of subsequent oxidation should therefore be affected only by the hydroperoxide-decomposing action of the species derived from NiSDT. With the tetralin/NiSDT system, certain assumptions can be made. The lack of measurable oxygen uptake before the inhibitor is practically consumed indicates very good efficiency for the radical-trapping stage. As the critical concentration is approached, this efficiency decreases. Therefore, at some point the rate of the radical-trapping reaction will equal the rate of the normal propagation reaction — i.e. $k_p[RH][RO_2^{\bullet}] = xk_a[RO_2^{\bullet}][NiSDT]$ (where x = the number of radicals consumed per inhibitor molecule). If the left-hand side of this equation becomes markedly larger than the right-hand side, then propagation becomes significant. It therefore seems reasonable to associate the critical concentration with the concentration at which the rates of reaction of alkylperoxy radicals with NiSDT and the substrate are equal and we obtain:-

$$\left[NiSDT\right]_{cr} = k_p\left[RH\right]/xk_a$$

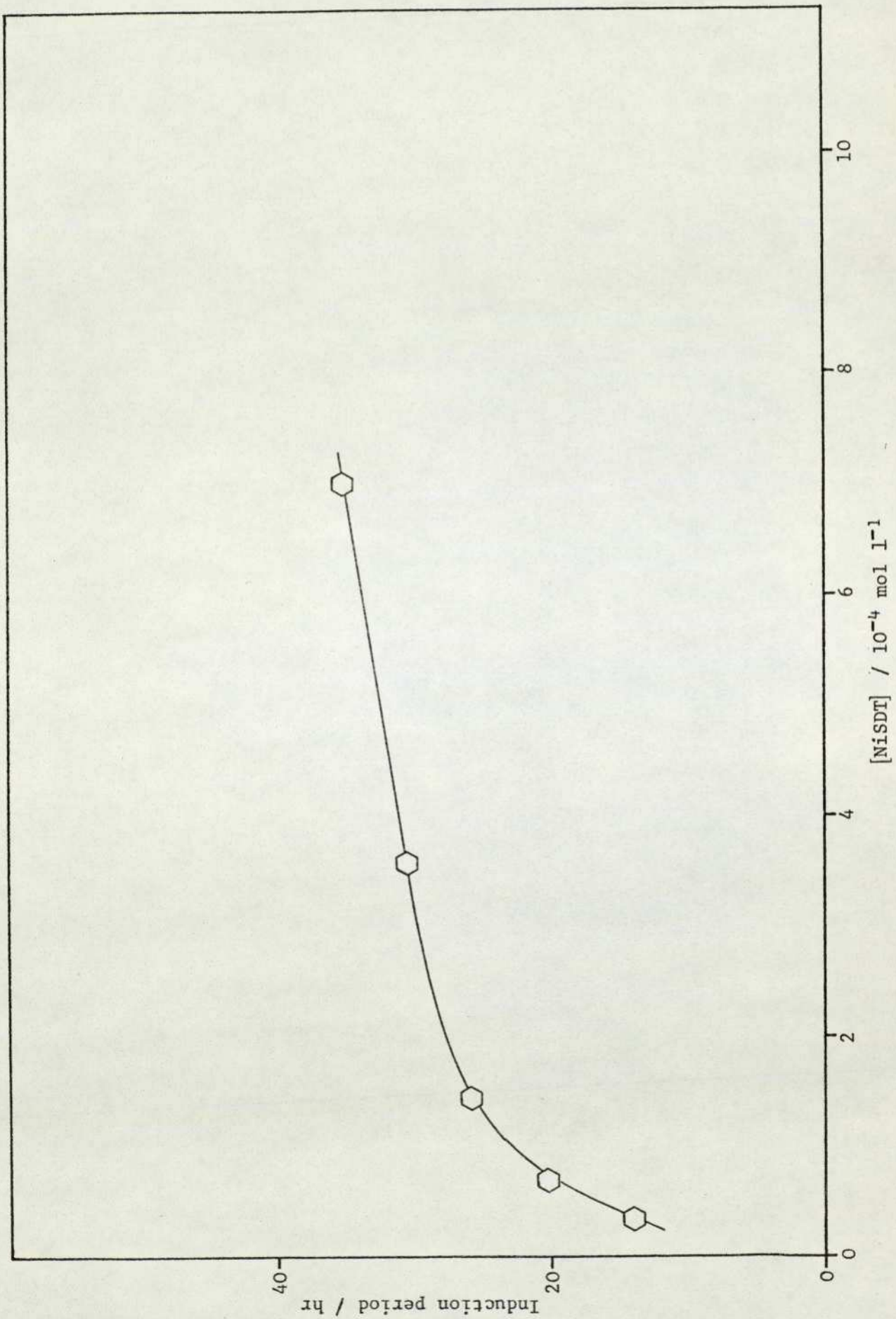
From the known[71] k_p value for the oxidation of tetralin, xk_a is calculated to be equal to $3.3 \cdot 10^5$ l $mol^{-1}s^{-1}$. According to Uri[61], each molecule of NiSDT is able to trap two alkylperoxy radicals, although the trapping of the first radical is rate-determining — i.e. x = 1. If this is taken to be the case, then $k_a = 3.3 \cdot 10^5$ l $mol^{-1}s^{-1}$. This result is in good agreement with the value of $2.6 \cdot 10^5$ l $mol^{-1}s^{-1}$ found by Ivanov and Youritsin[204].

The relationship between induction period and NiSDT concentration above and below the critical concentration ($[NiSDT]^{2.5}$ and $[NiSDT]^{0.75}$ respectively) is more difficult to exlain — indeed, no explanation can be offered for the $[NiSDT]^{0.75}$ dependence. Above the critical concentration, the dependence on $[NiSDT]^{2.5}$ can be explained by assuming that the products of the alkylperoxy radical/NiSDT interaction are themselves hydroperoxide decomposers. Scott[216] has shown that inhibition by hydroperoxide decomposers should give induction periods proportional to the square of the inhibitor concentration and this has been verified experimentally by Kennerley and Patterson[141]. If the hydroperoxide decomposer is formed from a preliminary radical-trapping step of the same inhibitor, then an induction period dependence on $[inhibitor]^{2.5}$ may well result.

3.3.2 Hexadec-1-ene

The establishment of critical phenomena in the tetralin/NiSDT system prompted a similar investigation of the hexadec-1-ene/NiSDT system to determine whether the relatively weaker antioxidant efficiency of NiSDT for this substrate was due to it being present below its critical concentration. The results shown in figure 3.8 indicate that this was not the case and it appears that critical phenomena are not exhibited by this system in the concentration range studied. This may be taken as additional evidence

Fig. 3.8 : Inhibited autoxidation of 1 mol l^{-1} hexadec-1-ene at 130°C
Induction period vs. inhibitor concentration



that the radical-trapping role of NiSDT does not function well for this kind of substrate. The shape of the graph again shows the decreasing efficiency of NiSDT at higher concentrations, which is discussed further in section 4.2.

3.4 The tetralin/NiSDT system

3.4.1 Variation of tetralin concentration

The concentration of tetralin in both the uninhibited and inhibited ($5.9 \cdot 10^{-5}$mol l^{-1} NiSDT) system was varied from 1 to 2 mol l^{-1} at 70°C. Figures 3.9 and 3.10 show the data obtained for the uninhibited and inhibited systems respectively. Taking the reciprocal induction period as a measure of oxidative rate during the induction period, a plot of ln (1/IP) against ln [tetralin] (figure 3.11) gave rather inconclusive results. Only for the inhibited system was the plot sufficiently accurate to justify the postulation of a slope of two. This would indicate that the initiation reaction is dependent on $[RH]^2$. The uninhibited reaction appears to approximate to a slope of two at the higher concentrations. Previous workers[43,44] have indicated that the initiation of tetralin autoxidation takes place by a termolecular reaction with oxygen

$$2RH + O_2 \xrightarrow{k_{16}} 2R^{\cdot} + H_2O_2 \qquad (16)$$

and the rate constant has been quoted by Denisov[43] as:-

$$k_{16} = 3.4 \cdot 10^3 \exp(-20,700/RT)\, l^2 mol^{-2} s^{-1}$$

However, the experimental work on which these authors base their findings was carried out at concentrations above 1 mol l^{-1}.

Fig. 3.9 : Autoxidation of tetralin at 70°C
Variation of tetralin concentration

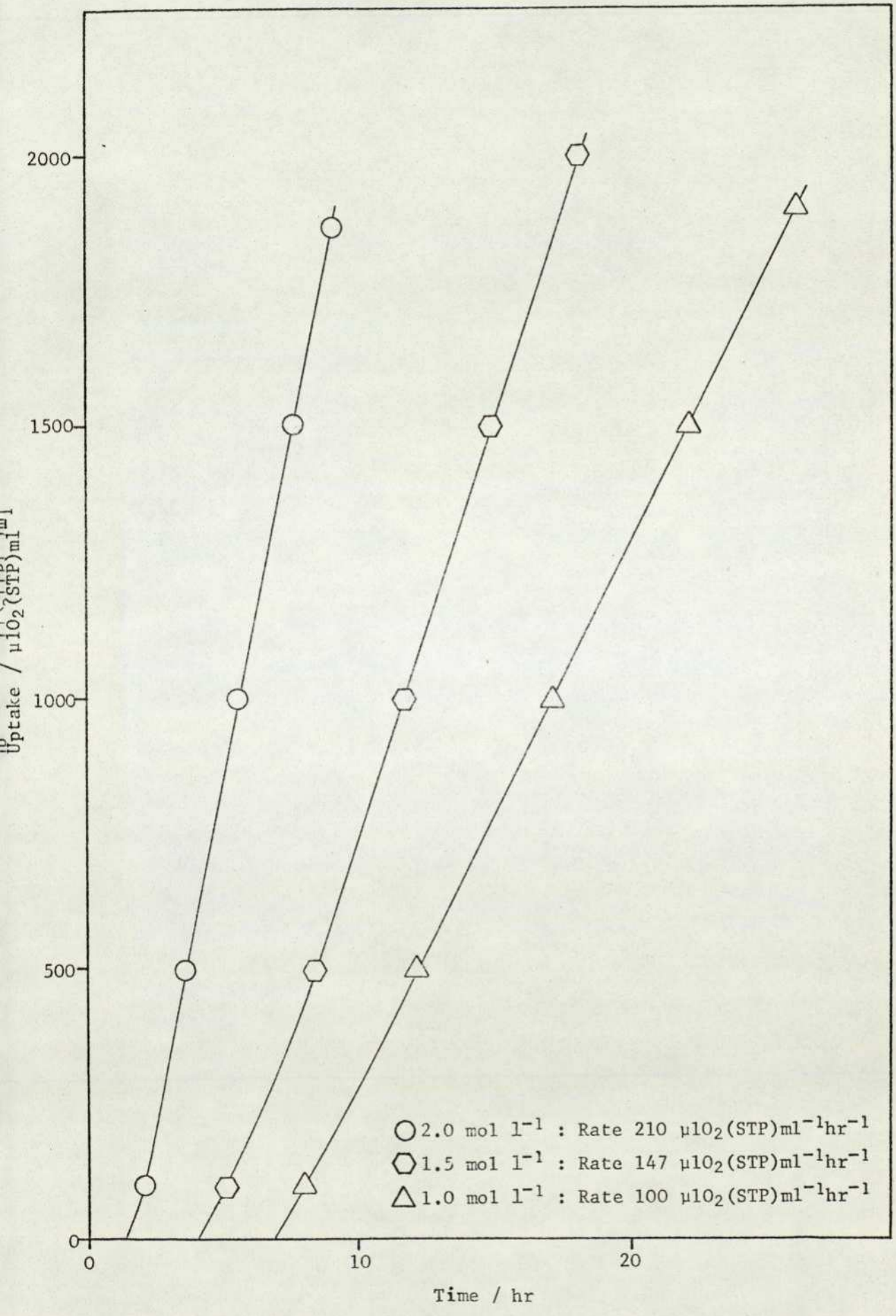


Fig. 3.10 : Autoxidation of tetralin with $5.9 \cdot 10^{-5}$ mol l^{-1} NiSDT at 70°C
Variation of tetralin concentration

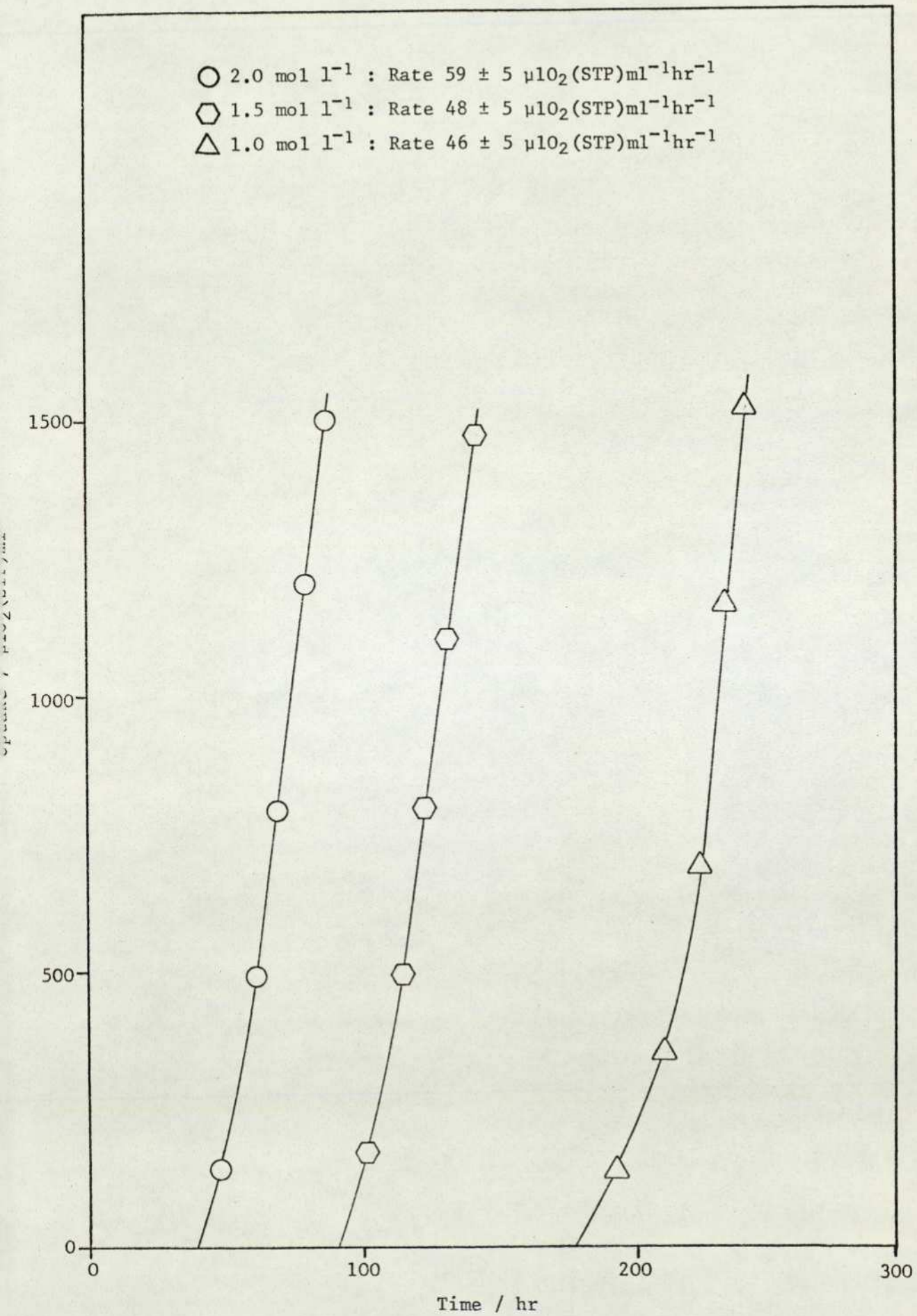
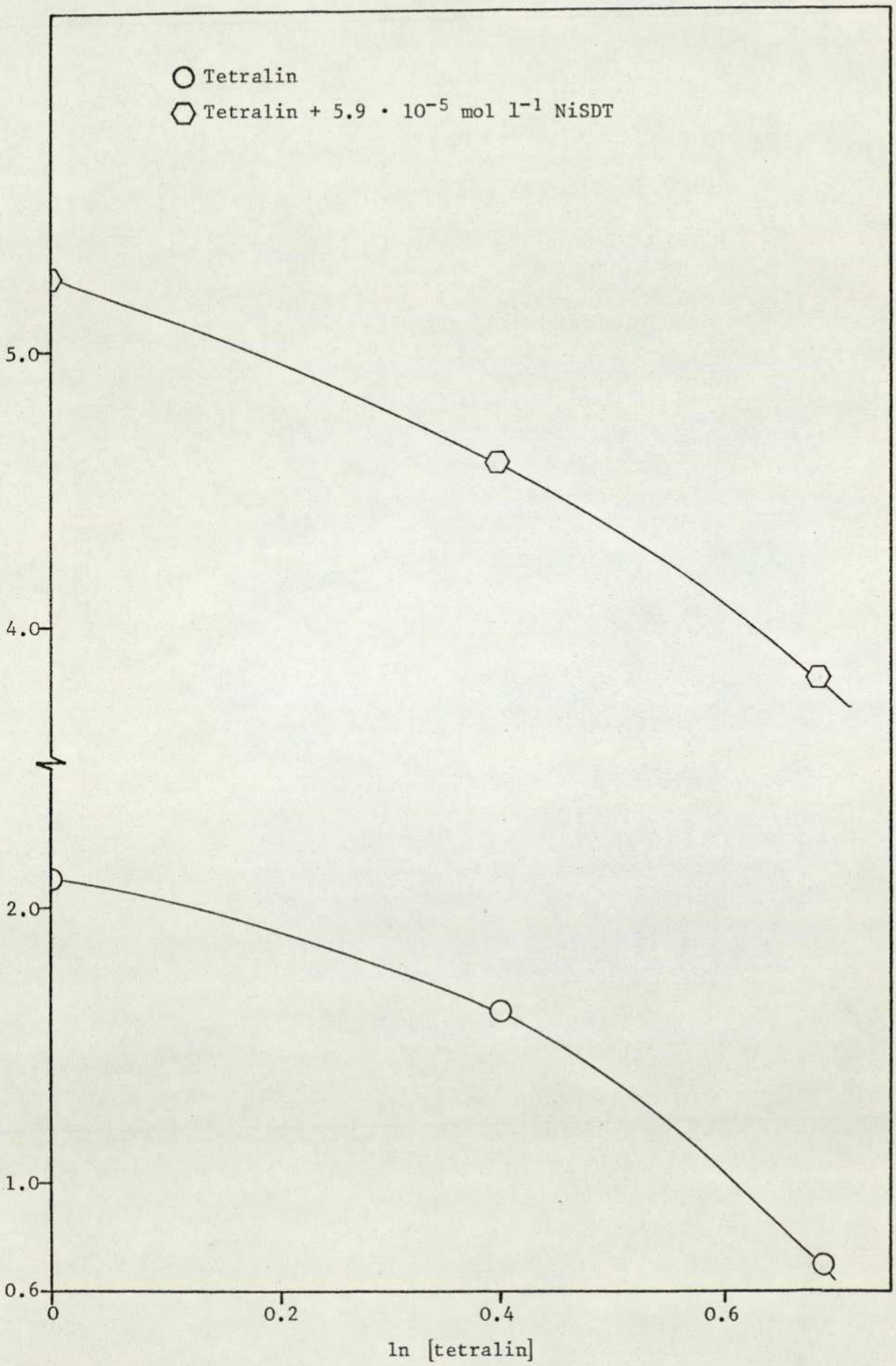


Fig. 3.11 : Autoxidation of tetralin at 70°C
ln (1/IP) vs. ln [tetralin]



It is considered probable that the initiation of tetralin autoxidation may be bimolecular at concentrations of 1 mol l^{-1} and below, and that there is an increasing termolecular contribution above this concentration. Such an occurrence would account for the pronounced curvature of the lines. Differences between the uninhibited and inhibited lines may be attributed to the greater accuracy with which the uninhibited system's induction period can be determined.

3.4.2 Variation of temperature

The temperature of autoxidation of 1 mol l^{-1} tetralin solution was varied from 70°C to 80°C in 5°C increments for both uninhibited and inhibited ($5.9 \cdot 10^{-5}$mol l^{-1} NiSDT) systems. The data obtained are presented in figures 3.12 and 3.13 respectively. The accuracy and small variation of the autoxidation rates do not permit accurate graphical interpretation but suggest in both cases an activation energy of approximately 20 kJ mol^{-1}. As this activation energy is primarily that of the propagation reaction, this is in reasonable agreement with the results of other workers[66,71] for this reaction. The lack of variation between the two systems would indicate that, after the induction period, the compounds derived from NiSDT do not affect the normal propagation sequence. This is in agreement with earlier conclusions. Further induction period determinations were carried out for the inhibited system at 85°C and 90°C using the automatic recording apparatus. The uninhibited system was not investigated at these higher temperatures as the apparatus is unsuitable for induction periods of less than one hour. The resulting graphs (figure 3.14) of ln (1/IP) against $(\text{temperature})^{-1}$ gave activation energies of 139 and 130 ± 12 kJ mol^{-1} for the uninhibited and inhibited systems respectively.

Fig. 3.12 : Autoxidation of 1 mol l^{-1} tetralin
Variation of temperature

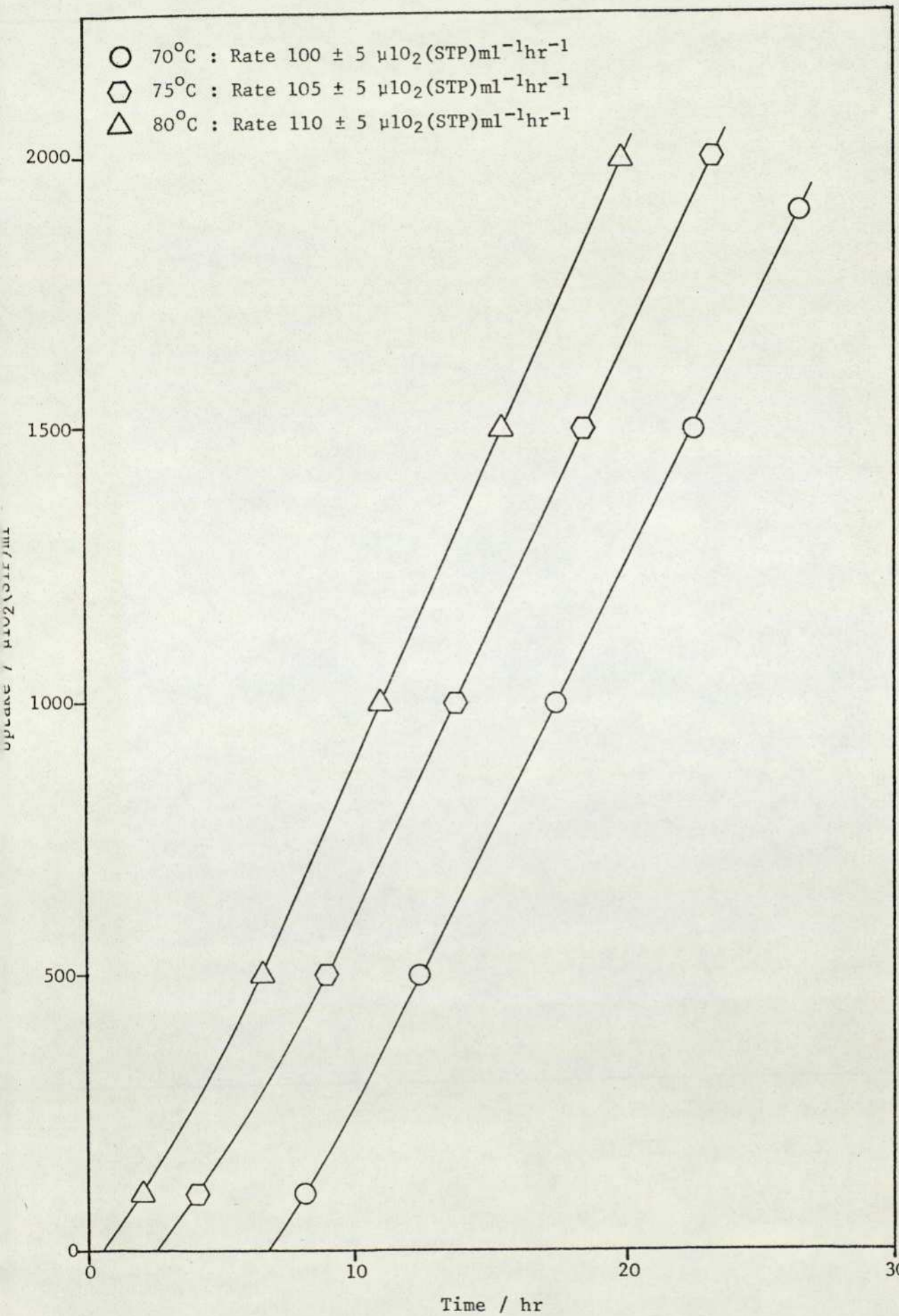


Fig. 3.13 : Autoxidation of 1 mol l^{-1} tetralin with $5.9 \cdot 10^{-5}$mol l^{-1} NiSDT
Variation of temperature

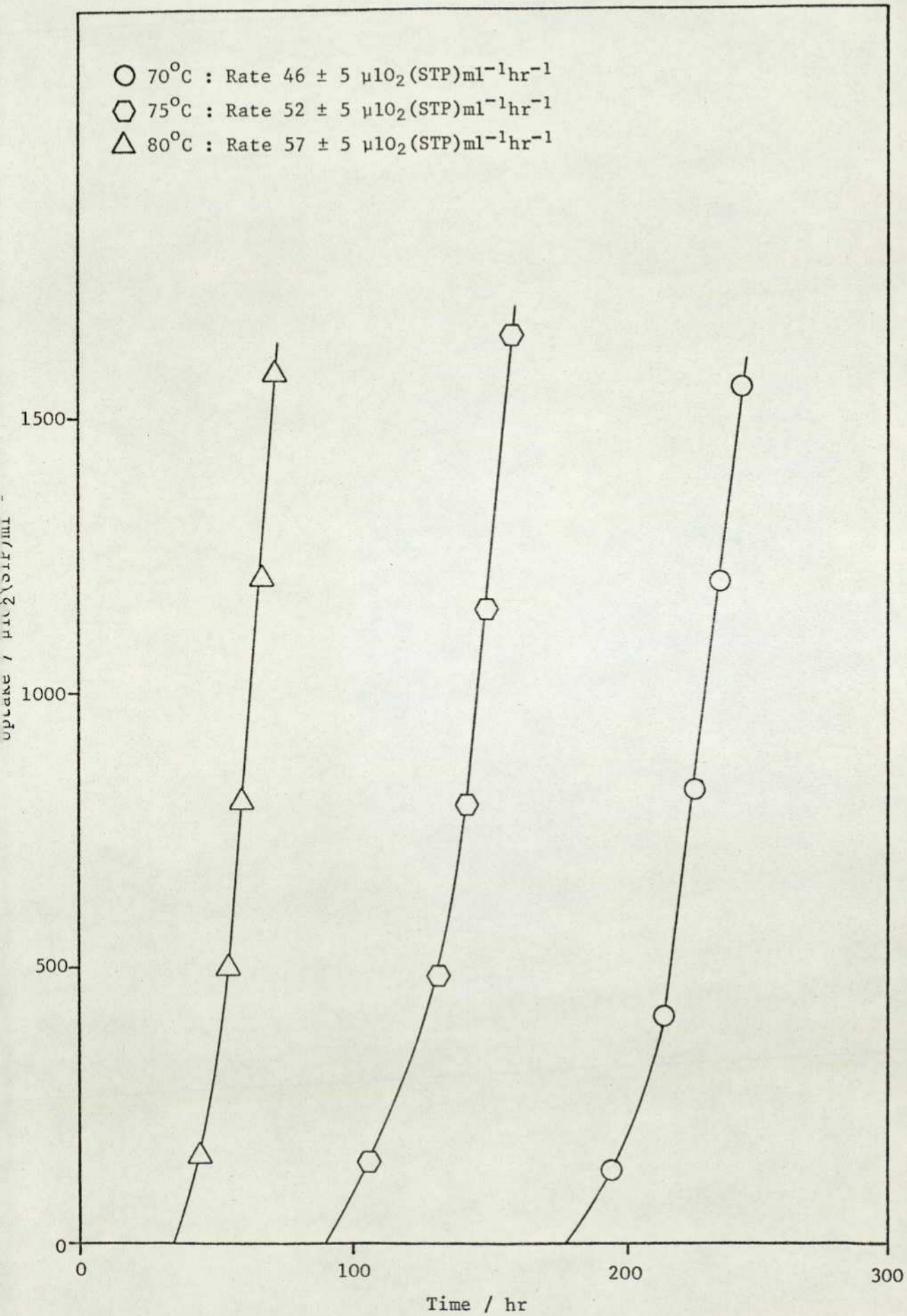
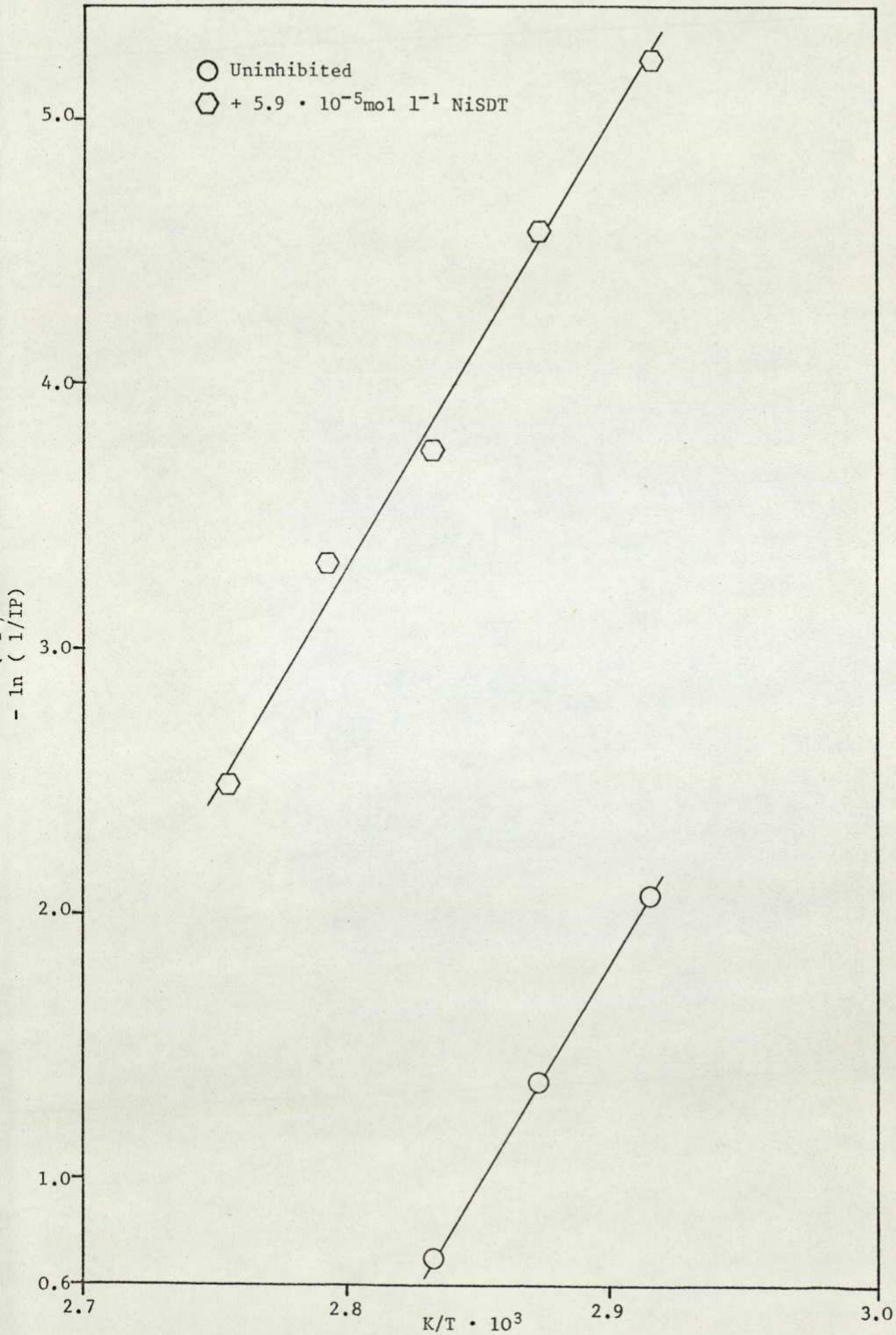


Fig. 3.14 : Autoxidation of 1 mol l^{-1} tetralin
ln (1/IP) vs. K/T



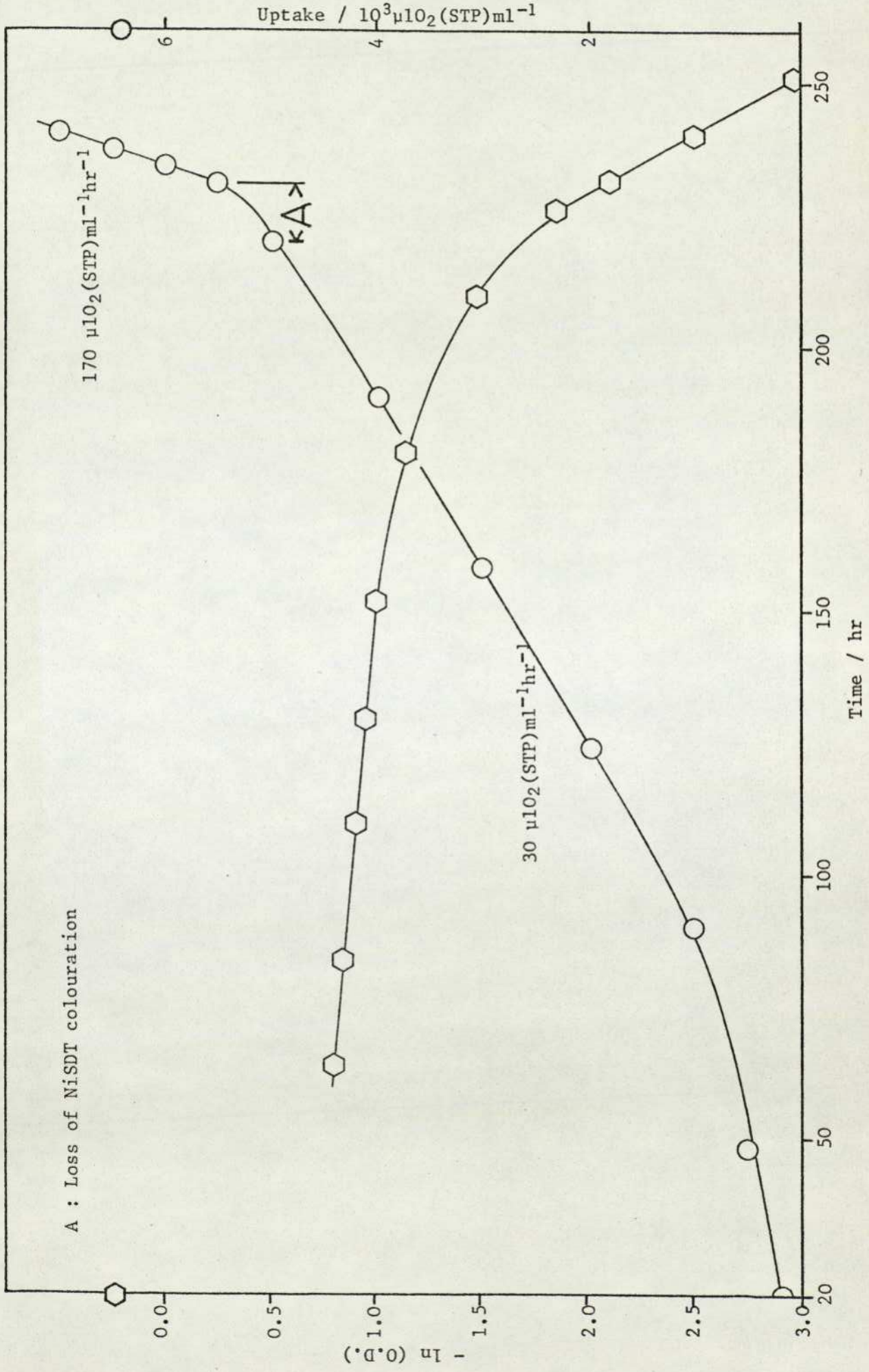
Activation energies determined in this way are primarily the activation energy of the initiation process and calculated values of the activation energies for the bi- and termolecular initiation of tetralin, derived from bond dissociation consideration by the Denisov method[46,47], are quoted by Robb[44] as 117.5 kJ mol^{-1} and 50.5 kJ mol^{-1} respectively. The values obtained indicate that initiation is bimolecular at the concentration used in the present system and they are in reasonable agreement with the literature (100 ± 4 kJ mol^{-1} [44]).

The bimolecular initiation of autoxidation at this concentration agrees with the conclusions reached in section 3.4.1.

3.5 The dihydroanthracene/NiSDT system

As mentioned previously, the NiSDT/DHA system exhibited features different to the majority of the other systems investigated and further experiments were carried out. A 1 mol l^{-1} DHA solution containing $2 \cdot 10^{-4}$ mol l^{-1} NiSDT was reacted at 80°C and a parallel experiment with a shaking incubator was undertaken to monitor the changes in NiSDT concentration over this period. The results are presented in figure 3.15. The oxidation of DHA shows three distinct stages; a slow autocatalytic build-up to a steady oxidation rate followed by an abrupt increase in rate after loss of the inhibitor. Previous substrates have shown no detectable oxygen uptake during the period in which the green colour of the inhibitor was present. The total oxygen uptake cannot be attributable to the termination of all alkylperoxy radicals by the NiSDT. If this were the case, it would indicate that each molecule of NiSDT could terminate some 1500 alkylperoxy radicals. Clearly, this is extremely improbable and, thus, it must be concluded that the normal propagation reaction is occurring to form hydroperoxide, most of which is subsequently destroyed by the inhibitor.

Fig. 3.15 : Autoxidation of 1mol l^{-1} DHA with $2 \cdot 10^{-4}$mol l^{-1} NiSDT at 80°C
Oxygen uptake and [NiSDT] data



The initial autocatalytic build-up to the intermediate steady rate can be attributed to competition occurring between the inhibitor and substrate for the alkylperoxy radicals until a threshold concentration of hydroperoxide has accumulated upon which the NiSDT can act. Previous work[205] has indicated that an excess of ROOH over the NiSDT is necessary for the decomposition mechanism to occur. Thus, we have both mechanisms of inhibitor action occurring throughout the reaction — radical chain-breaking with hydroperoxide decomposition keeping further initiation to a minimum by reducing the hydroperoxide level to a steady, low concentration.

The reactions involved in inhibition of oxidation by simultaneous radical-trapping and hydroperoxide decomposition may be expressed in the form of a simplified kinetic scheme:-

$$RH \longrightarrow R^{\bullet} \qquad (\text{rate} = r_i) \qquad (1)$$

$$R^{\bullet} + O_2 \xrightarrow{k_o} RO_2^{\bullet} \qquad (2)$$

$$RO_2^{\bullet} + RH \xrightarrow{k_p} ROOH + R^{\bullet} \qquad (3)$$

$$ROOH + RH \xrightarrow{k_b} nRO_2^{\bullet} \qquad (53)$$

$$xRO_2^{\bullet} + NiSDT \xrightarrow{k_a} \text{Inactive products} \qquad (56)$$

$$yROOH + NiSDT \xrightarrow{k_c} \text{Inactive products} \qquad (57)$$

For this scheme we may write:-

$$\frac{d[RO_2^{\cdot}]}{dt} = r_i - k_p[RO_2^{\cdot}][RH] - xk_a[RO_2^{\cdot}][NiSDT] + nk_b[ROOH][RH]$$

$$\frac{d[ROOH]}{dt} = k_p[RO_2^{\cdot}][RH] - yk_c[ROOH][NiSDT] - k_b[ROOH][RH]$$

$$-\frac{d[NiSDT]}{dt} = xk_a[RO_2^{\cdot}][NiSDT] + yk_c[ROOH][NiSDT]$$

Using the steady-state approximation:-

$$\frac{d[RO_2^{\cdot}]}{dt} \text{ and } \frac{d[ROOH]}{dt} = 0$$

it follows that:-

$$xk_a[RO_2^{\cdot}][NiSDT] = r_i - k_p[RO_2^{\cdot}][RH] + nk_b[ROOH][RH]$$

$$yk_c[ROOH][NiSDT] = k_p[RO_2^{\cdot}][RH] - k_b[ROOH][RH]$$

and therefore:-

$$-\frac{d[NiSDT]}{dt} = r_i + (n-1)k_b[ROOH][RH] \qquad (58)$$

i.e. the change in NiSDT concentration depends solely on the overall rate of initiation and is independent of the concentration of the inhibitor. Previous experiments have suggested that, when the concentration of NiSDT is reduced to below a critical level, radical-trapping becomes insignificant

by comparison with hydroperoxide decomposition. Under these conditions equation (56) can be neglected and equation (58) becomes:-

$$-\frac{d[\text{NiSDT}]}{dt} = yk_c[\text{ROOH}][\text{NiSDT}] \qquad (59)$$

implying pseudo first-order behaviour if [ROOH] is constant.

To assess the validity of this scheme, the initial and final sections of the NiSDT curve in figure 3.15 were considered separately on an expanded scale. Figure 3.16 shows that for the lower concentrations of NiSDT, the disappearance of the inhibitor follows first-order kinetics in agreement with equation (59). The rate constant is calculated to be 0.046 hr^{-1}. Similar considerations for the higher concentration section (figure 3.17) show that the best fit to a straight line is given by a plot of concentration (as optical density) against time — i.e. the disappearance of NiSDT is zero-order at this point with a rate constant of $2.93 \cdot 10^{-7}$ mol $l^{-1}hr^{-1}$. However, although this result is in agreement with equation (58), the small concentration range over which the disappearance of the inhibitor could be monitored makes the assignment of zero-order kinetics difficult to justify.

If the above mechanism is accepted then, in the course of autoxidation, NiSDT is initially consumed at a rate proportional to the overall rate of initiation until a critical concentration is reached. At this point, the inhibitor disappears by a first-order reaction with the hydroperoxide. Previous work[214] has shown the inhibitor to disappear initially by a half-order reaction in fatty acid substrates. The above scheme will not apply to these types of substrates which have metal-chelating ability, as they will cause some of the nickel products of the inhibitor to be solubilised. These may well act as pro-oxidants to initiate further oxidation.

Fig. 3.16 : NiSDT consumption in the later part of the reaction with DHA (expanded scale)

Time vs. A; - ln (O.D.) and Time vs. B; (O.D.)

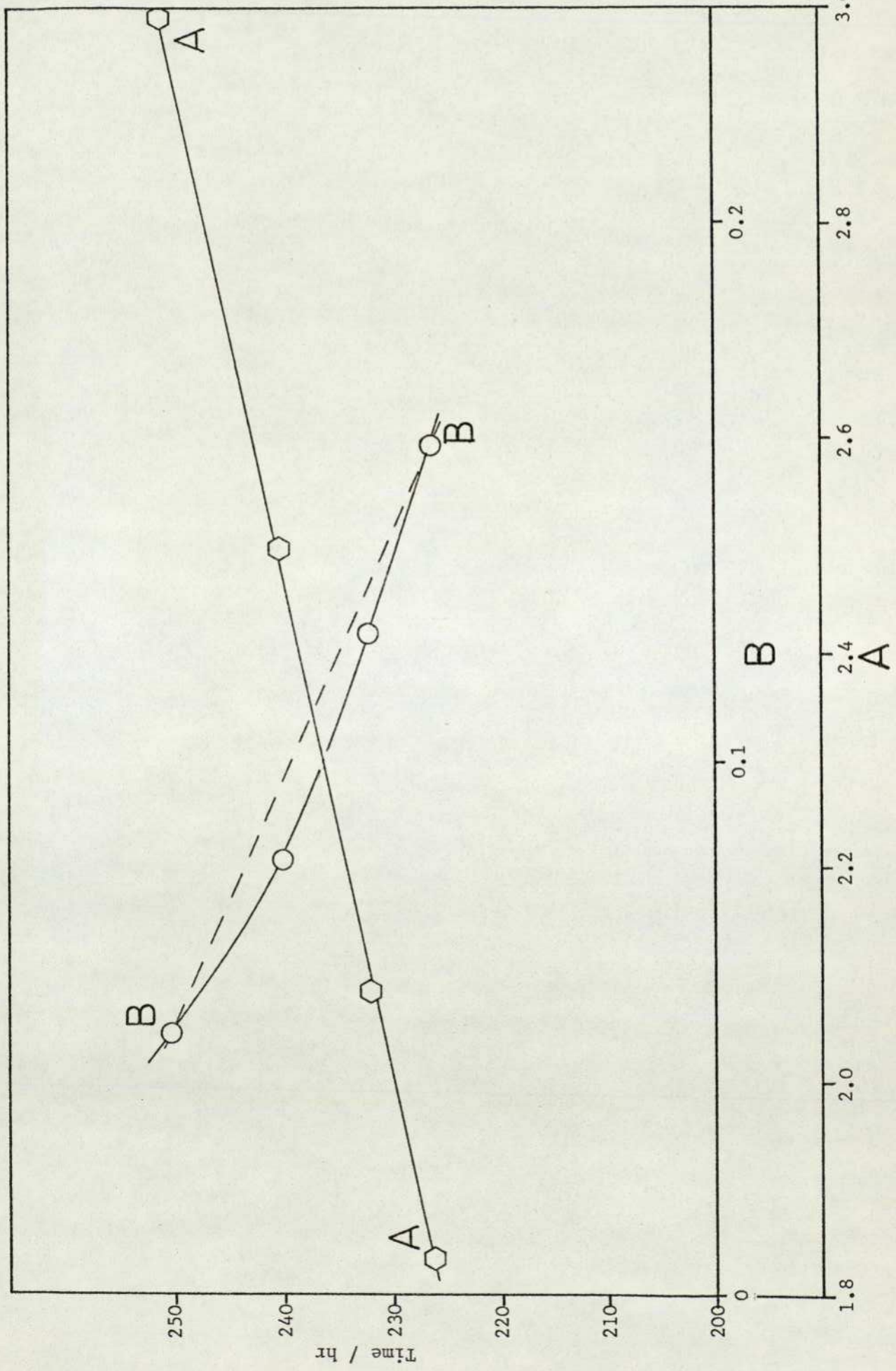
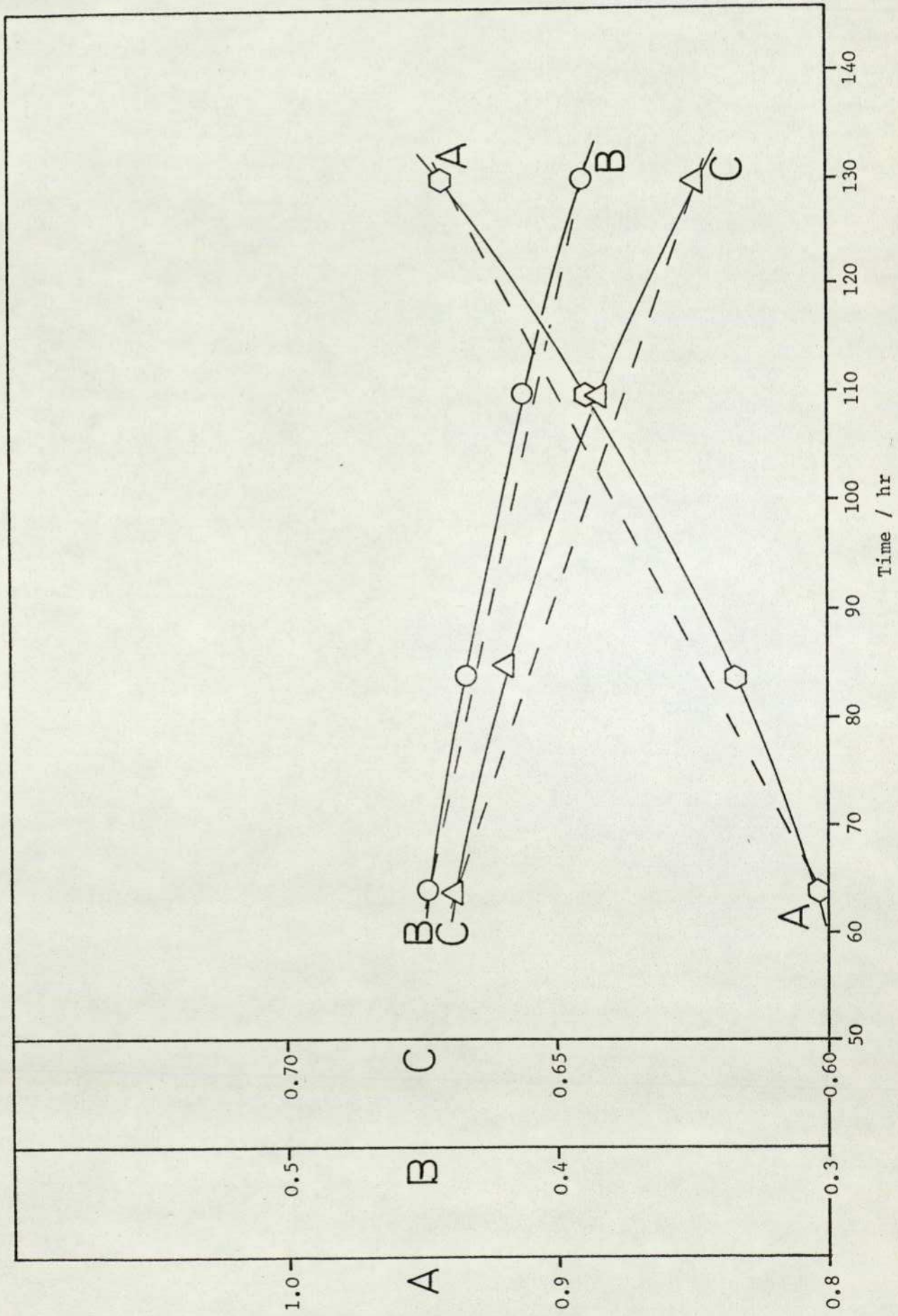


Fig. 3.17 : NiSDT consumption in the early part of the reaction with DHA (expanded scale)

Time vs. A; - ln (O.D.) and Time vs. B; (O.D.) and Time vs. C; $(O.D.)^{\frac{1}{2}}$



It has been shown (section 1.3.1.4) that initiation by metal catalysis is generally first-order in metal concentration but, in this case, with the metal pro-oxidant being formed via a chelate breakdown reaction, it is entirely possible that half-order kinetics might occur. Thus, as in the early stages the NiSDT consumption is proportional to the overall initiation rate, the consumption of the inhibitor in these substrates may become proportional to the square-root of its concentration.

The complexities of the NiSDT reactions in this system do not permit further kinetic information to be easily derived from the results. With a normal phenolic antioxidant, further information could be obtained relating to the initiation rate and number of radicals consumed per inhibitor molecule. However, the necessary assumptions to apply various derived formulae — particularly in this case that of all termination occurring at the inhibitor — are not particularly valid except in the very early part of the reaction. Determination of changes in NiSDT concentration in this range cannot be carried out with any degree of accuracy, since the changes are small and comparable with the experimental error, which is significant at this point. The assumptions previously applied to the tetralin/NiSDT system (section 3.3.1) are similarly not applicable at the same point in this case. With competition occurring between the substrate and inhibitor from very early in the reaction, when the apparently critical concentration of $1.1 \cdot 10^{-4}$ mol l^{-1} is reached, $k_p[RH][RO_2^{\bullet}]$ is greater than $k_a[RO_2^{\bullet}][NiSDT]$ and has been greater for some time as the inhibitory properties have been dependent on the removal of hydroperoxide by the NiSDT as well. The marked increase in rate at this point is dependent on the hydroperoxide produced from the unequal competition between the substrate and inhibitor increasingly rapidly removing the NiSDT and thereby further decreasing its radical-trapping efficiency. However, at the very beginning

of the reaction, the rate of oxygen uptake is extremely slow and gradually exhibits increasingly autocatalytic behaviour until a steady rate of 30 $\mu l O_2 (STP) ml^{-1} hr^{-1}$ is achieved. Up to this point, the NiSDT/hydroperoxide reaction begins to increasingly occur — i.e. the situation at which the tetralin/NiSDT system passes its critical concentration. Thus, at the start of the reaction before this point is reached, the slow rate of oxygen uptake allows the assumption of $k_p [RO_2^\bullet] [RH] = xk_a [RO_2^\bullet] [NiSDT]$ to be made. The subsequent autocatalytic behaviour indicates where this assumption ceases to be valid. By taking the concentration of NiSDT at a point before this autocatalysis becomes apparent and inserting the relevant k_p value[74] as before, the value of xk_a obtained is $1.15 \cdot 10^6$ l $mol^{-1} s^{-1}$. Thus, by taking x = 1, the rate constant for the inhibitor/radical reaction, k_a, is $1.15 \cdot 10^6$ l $mol^{-1} s^{-1}$. Again, this is comparable to the value of $2.6 \cdot 10^5$ l $mol^{-1} s^{-1}$ determined by Ivanov and Youritsin[204].

Attempts to formulate a more complete equation describing the oxidation characteristics of a system in which NiSDT acts in both roles have been unsuccessful.

3.6 Hydroperoxide decomposition

An assessment of the decomposition of tetralin hydroperoxide by NiSDT was carried out manometrically with the Warburg apparatus. Tetralin hydroperoxide was chosen due to its ease of preparation and purification (section 2.2.9).

3.6.1 Variation of NiSDT concentration in air and nitrogen atmospheres

A preliminary experiment to study the effect of NiSDT concentration on the decomposition of a 1 mol l^{-1} ethyl benzoate solution of tetralin hydroperoxide was carried out in both air and nitrogen atmospheres. The results are presented in figures 3.18 and 3.19.

Fig. 3.18 : Decomposition of 1 mol l^{-1} tetralin hydroperoxide in air and nitrogen atmospheres at 70°C
Variation of NiSDT concentration

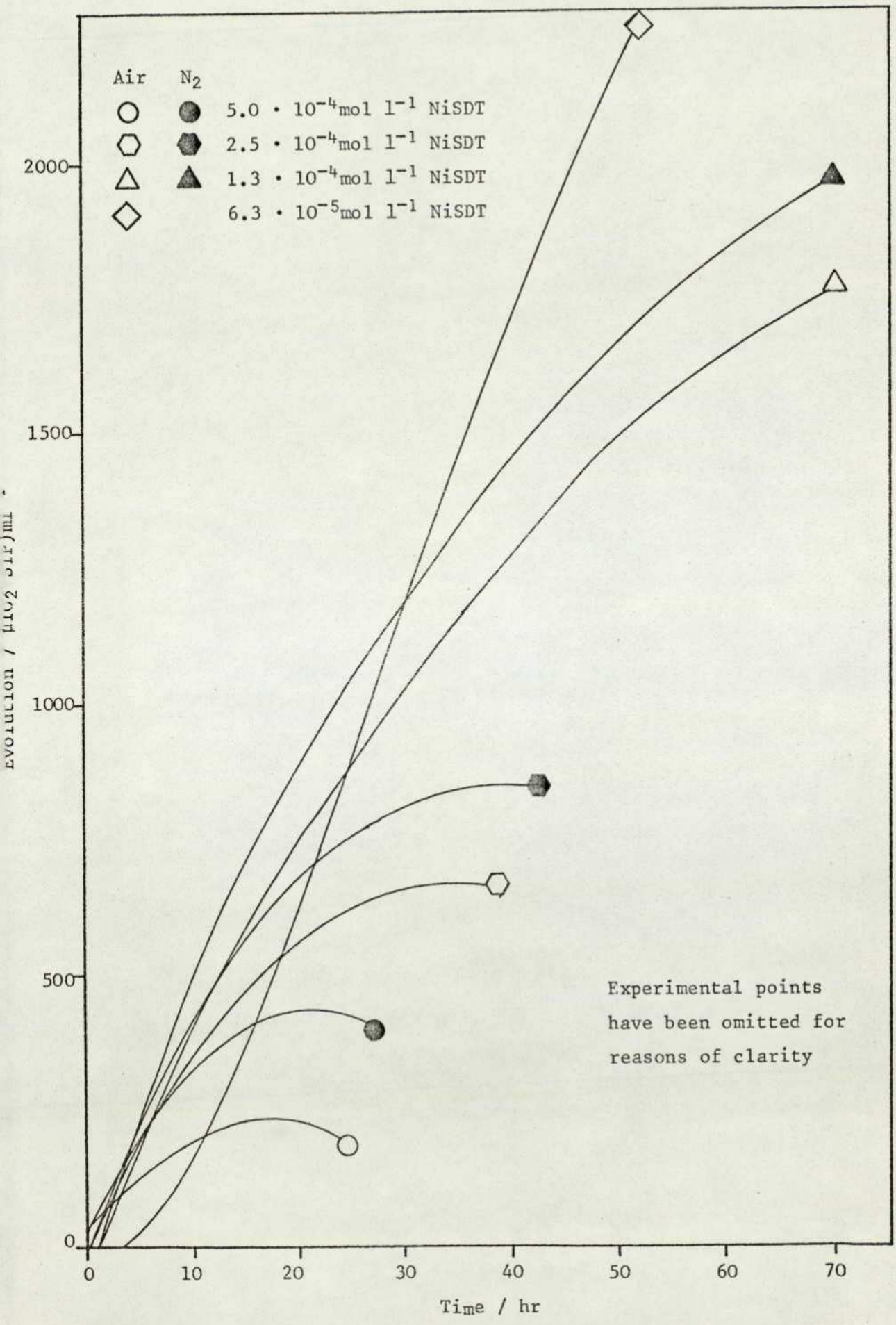
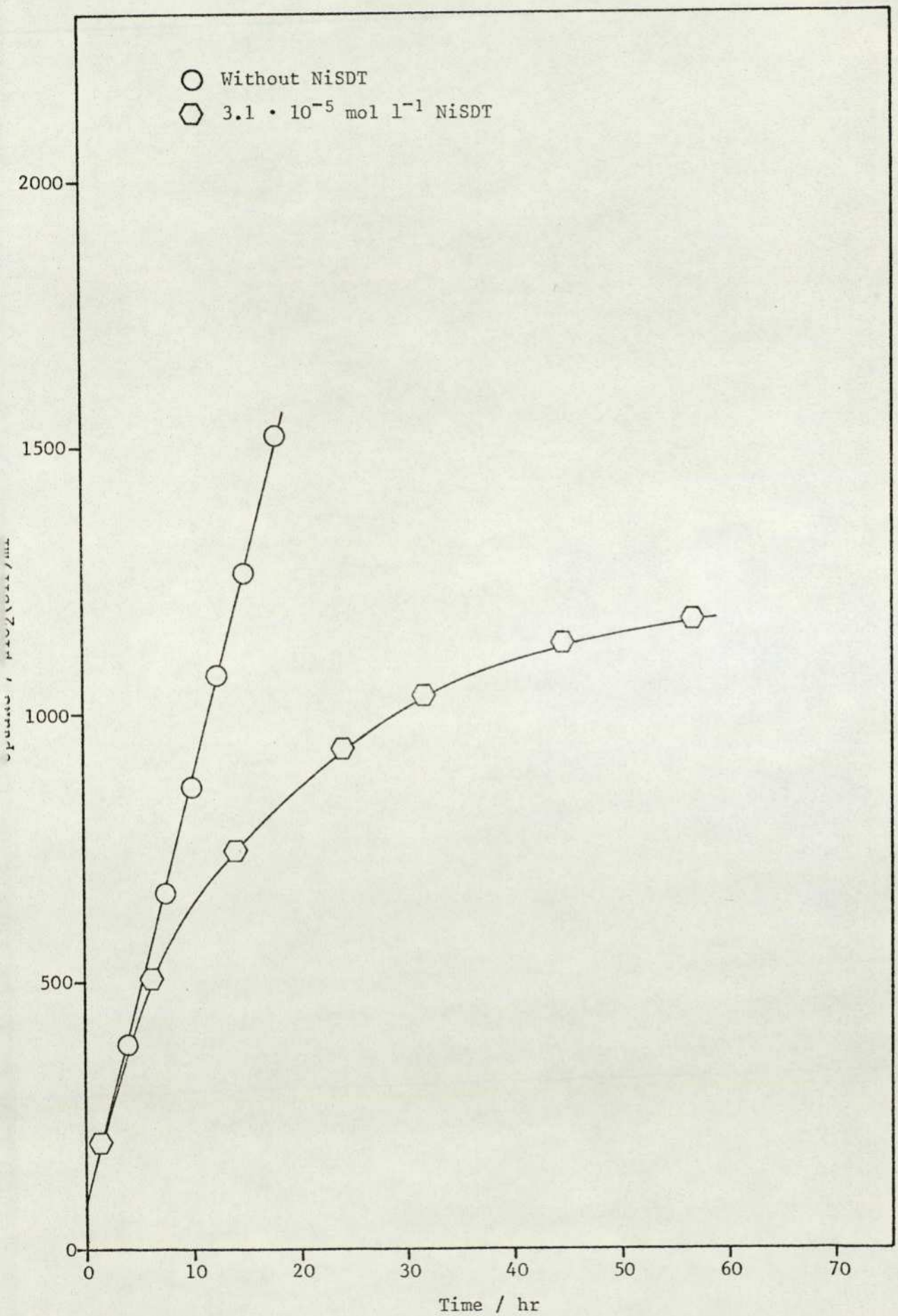


Fig. 3.19 : Decomposition of 1 mol l^{-1} tetralin hydroperoxide in air at 70°C
Oxygen uptake data



All the solutions showed the same characteristics. On mixing the NiSDT and tetralin hydroperoxide reactants, a fast colour change (green — yellow — colourless) was observed. Spectroscopic examination of the yellow colouration produced in an equivalent experiment at ambient temperatures showed the intense near infra-red band at 866 nm, characteristic of the complex, to be entirely absent, whilst a new band had appeared at 420 nm.

For concentrations of NiSDT above the critical value of $4 \cdot 10^{-5}$ mol l^{-1}, oxygen evolution was observed irrespective of whether the ambient atmosphere was oxygen or nitrogen (figure 3.18). This contrasts with oxygen absorption observed in the absence of NiSDT and when NiSDT was present below the critical concentration (figure 3.19). Shortly after the green colour of the inhibitor was discharged, a solid product was deposited in the reaction flask (section 3.6.4.1).

At first sight, the results obtained seem curious. Although oxygen evolution occurs in all experiments at concentrations above the critical concentration of NiSDT, the greatest evolution occurs at *lower* NiSDT concentrations. Also, more oxygen evolution occurs in the experiments conducted in a nitrogen atmosphere than for equivalent experiments in an air atmosphere. Taking the latter point, this is an effect due to oxygen starvation of a radical oxidation. The presence of initiating radicals from the thermal decomposition of the hydroperoxide would be expected in this system and these can attack other hydroperoxide molecules at the reactive 4-position leading to a normal oxidation chain sequence. However, at low oxygen concentrations the rate of an autoxidation becomes dependent on the oxygen partial pressure[33] and thus, in the experiments conducted under nitrogen this rate will be considerably slowed. The measured evolution in all these experiments is, therefore, the difference between a rate

of oxygen uptake and a rate of oxygen evolution and variations between the two atmospheres are caused by the faster oxygen uptake occurring in the air atmosphere.

The oxygen evolution is rather more difficult to explain. The change in the quantities evolved with changing NiSDT concentration is a function of the two competing reactions mentioned above — an uptake of oxygen due to initiation of oxidation by the hydroperoxide and an evolution of oxygen due to a decomposition reaction, presumably bimolecular, of the hydroperoxide. (As the NiSDT is totally destroyed before any evolution occurs, it may be assumed that this phenomenon is not a result of the direct interaction between the two reactants.) The observed effect in the absence of NiSDT is clearly the sum of the effects of these two reactions. The data found when NiSDT is present in the system can be qualitatively explained if it is assumed that the two reactions are not equally affected by the inhibitor. Since oxidation is a chain process, it is reasonable to assume that its effect will be completely eliminated by very low concentrations of the NiSDT. However, the bimolecular decomposition of ROOH will continue to compete with its decomposition by the inhibitor to much higher concentrations of NiSDT. This effect is illustrated schematically in figure 3.20 which reproduces the observed effect — an increasing evolution of oxygen as the NiSDT concentration is decreased, changing to an absorption of oxygen below a certain NiSDT concentration.

Fig. 3.20 : Decomposition of tetralin hydroperoxide in the presence of NiSDT

Fig. 3.20a: The individual reactions

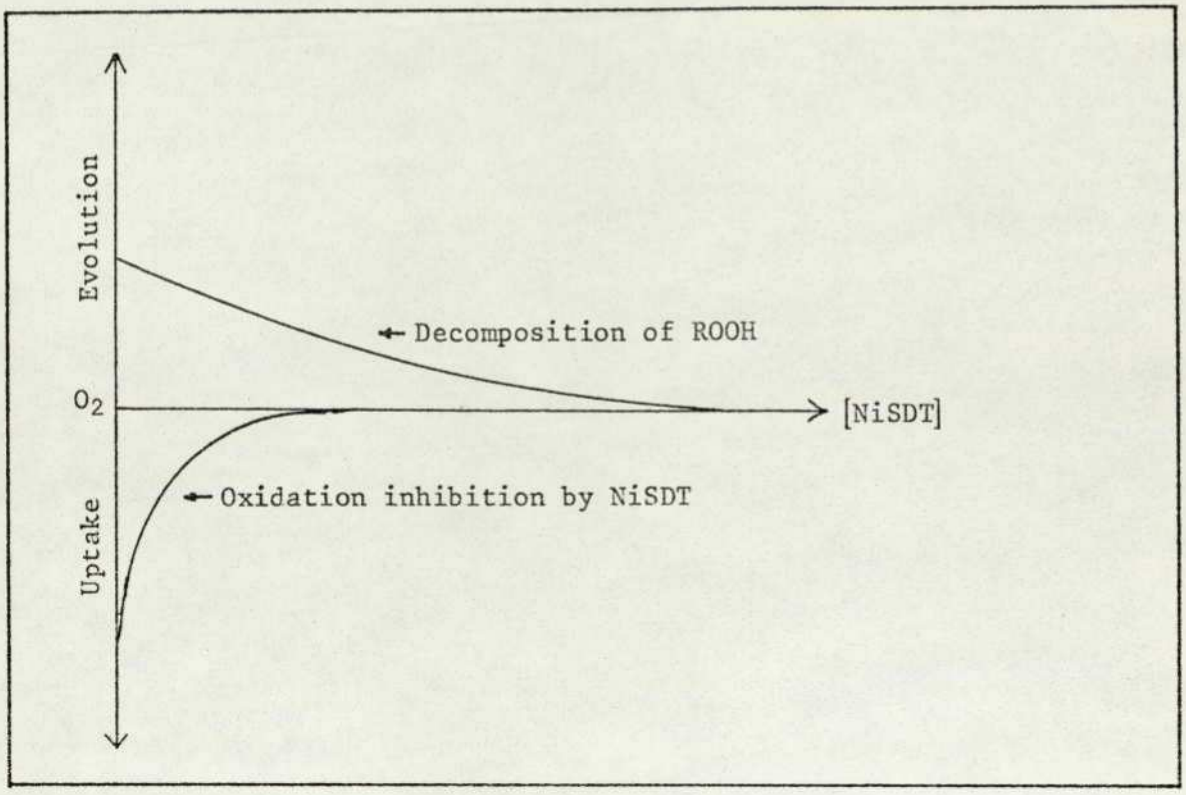
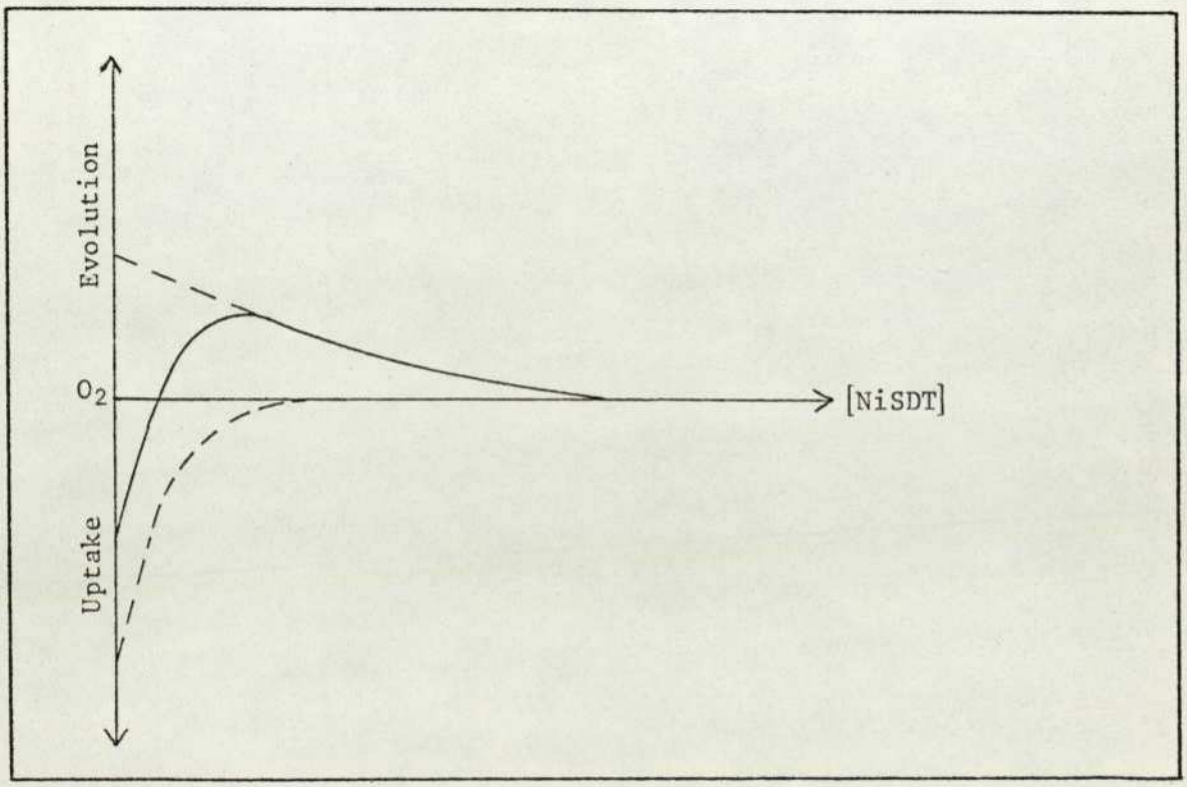


Fig. 3.20b: The overall effect



3.6.2 Variation of hydroperoxide concentration

The concentration of tetralin hydroperoxide was varied from 0.38 mol l^{-1} to 1.25 mol l^{-1} at 70°C with a NiSDT concentration of $1.25 \cdot 10^{-4}$ mol l^{-1}. The oxygen evolution data are presented in figure 3.21. (The corresponding data for oxygen uptake of the hydroperoxide solutions without NiSDT present are shown in figure 3.22.) A graph of ln (initial rate) against ln [tetralin hydroperoxide] for the inhibited system gave a straight line with a gradient of two (figure 3.23) indicating that the reaction is second-order in hydroperoxide concentration. However, the oxygen evolution reaction is being considered and not the decrease in hydroperoxide concentration directly. Thus, although the result confirms the earlier proposition for the oxygen formation, it does not give information regarding the means of decomposition of the NiSDT. Other work[61,205] based on measurements of hydroperoxide and NiSDT concentrations have indicated that this reaction is also second-order in hydroperoxide.

3.6.3 Variation of temperature

The reaction temperature of an 0.75 mol l^{-1} tetralin hydroperoxide solution and an 0.75 mol l^{-1} tetralin hydroperoxide/$1.25 \cdot 10^{-4}$mol l^{-1} NiSDT solution were varied from 60°C to 80°C in 10°C increments (figures 3.24 and 3.25 respectively). A plot of ln (initial rate) against (temperature)$^{-1}$ for both systems is shown in figure 3.26.

Activation energies for the uninhibited and inhibited systems are 84 and 73.5 kJ mol^{-1} respectively. Uri[61] has obtained a value of 60.5 kJ mol^{-1} for the NiSDT/tetralin hydroperoxide system, but this was from measurements of hydroperoxide concentrations and thus, the same reaction is not being considered. The value of 73.5 kJ mol^{-1} is presumably the activation energy of the bimolecular decomposition of the hydroperoxide.

Fig. 3.21 : Decomposition of tetralin hydroperoxide with $1.25 \cdot 10^{-4}$ mol l^{-1} NiSDT at 70°C
Variation of hydroperoxide concentration

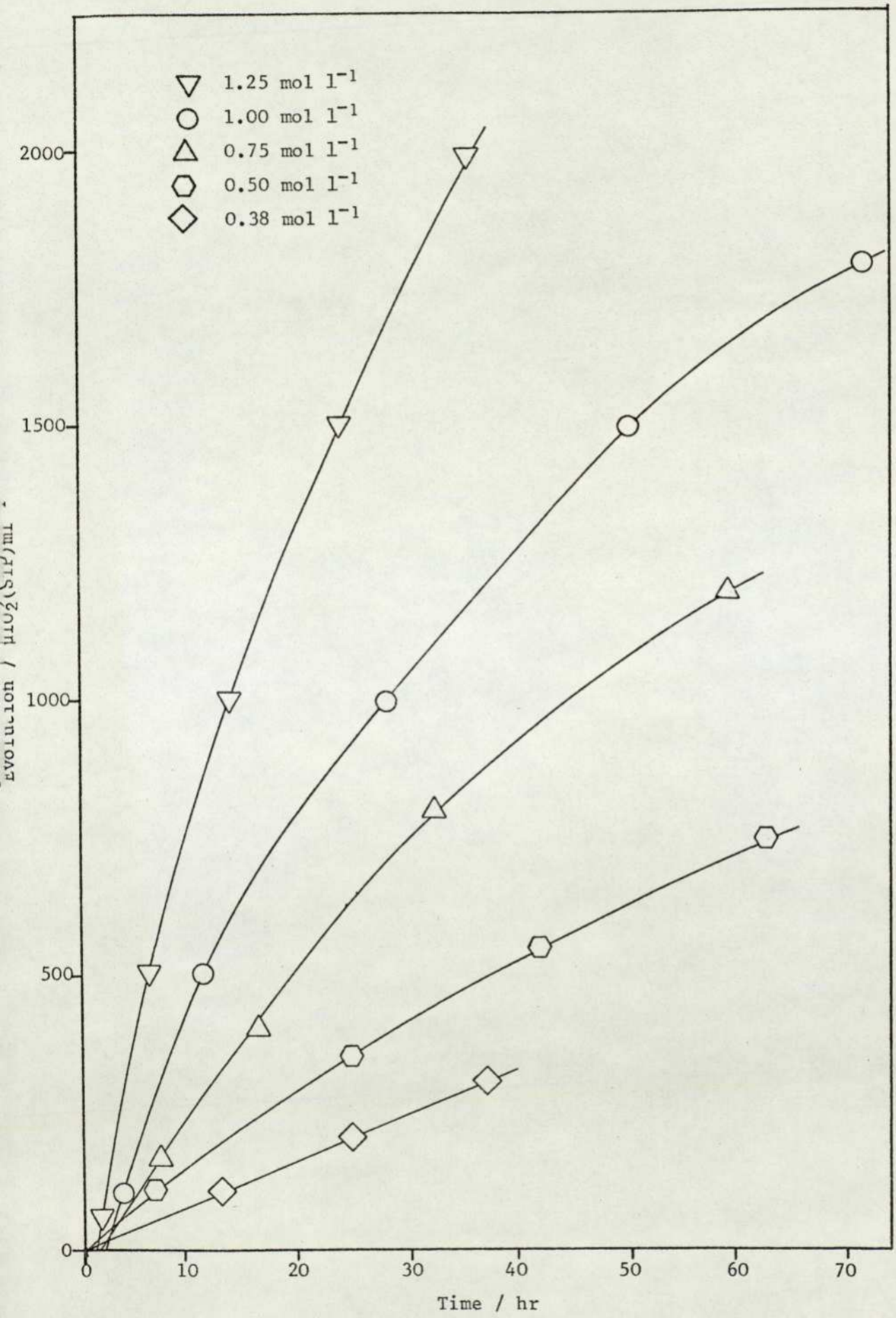


Fig. 3.22 : Decomposition of tetralin hydroperoxide at 70°C
Variation of hydroperoxide concentration

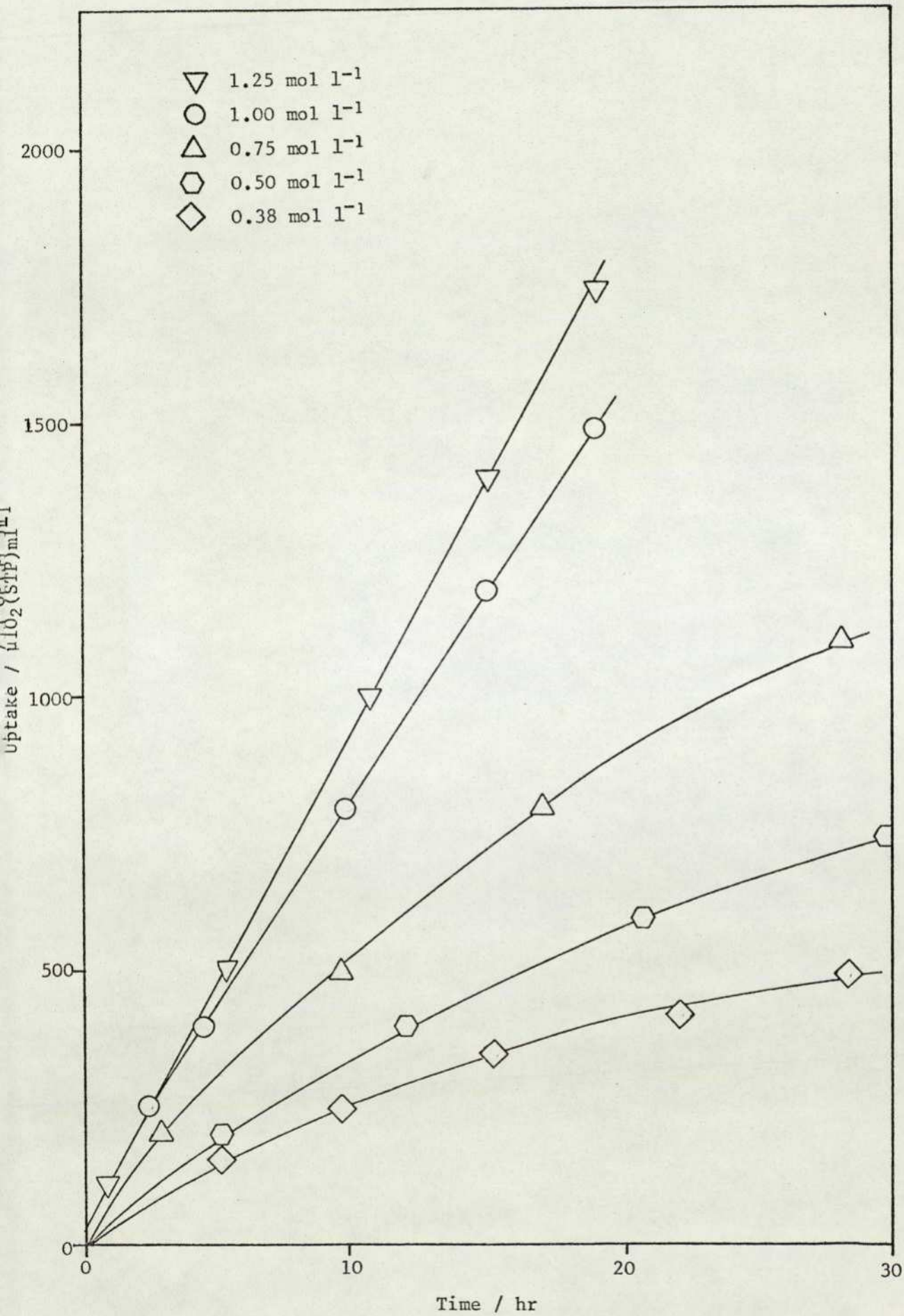


Fig. 3.23 : Decomposition of tetralin hydroperoxide with $1.25 \cdot 10^{-4}$ mol l^{-1} NiSDT at 70°C
ln (initial evolution rate) vs. ln [Tet-OOH]

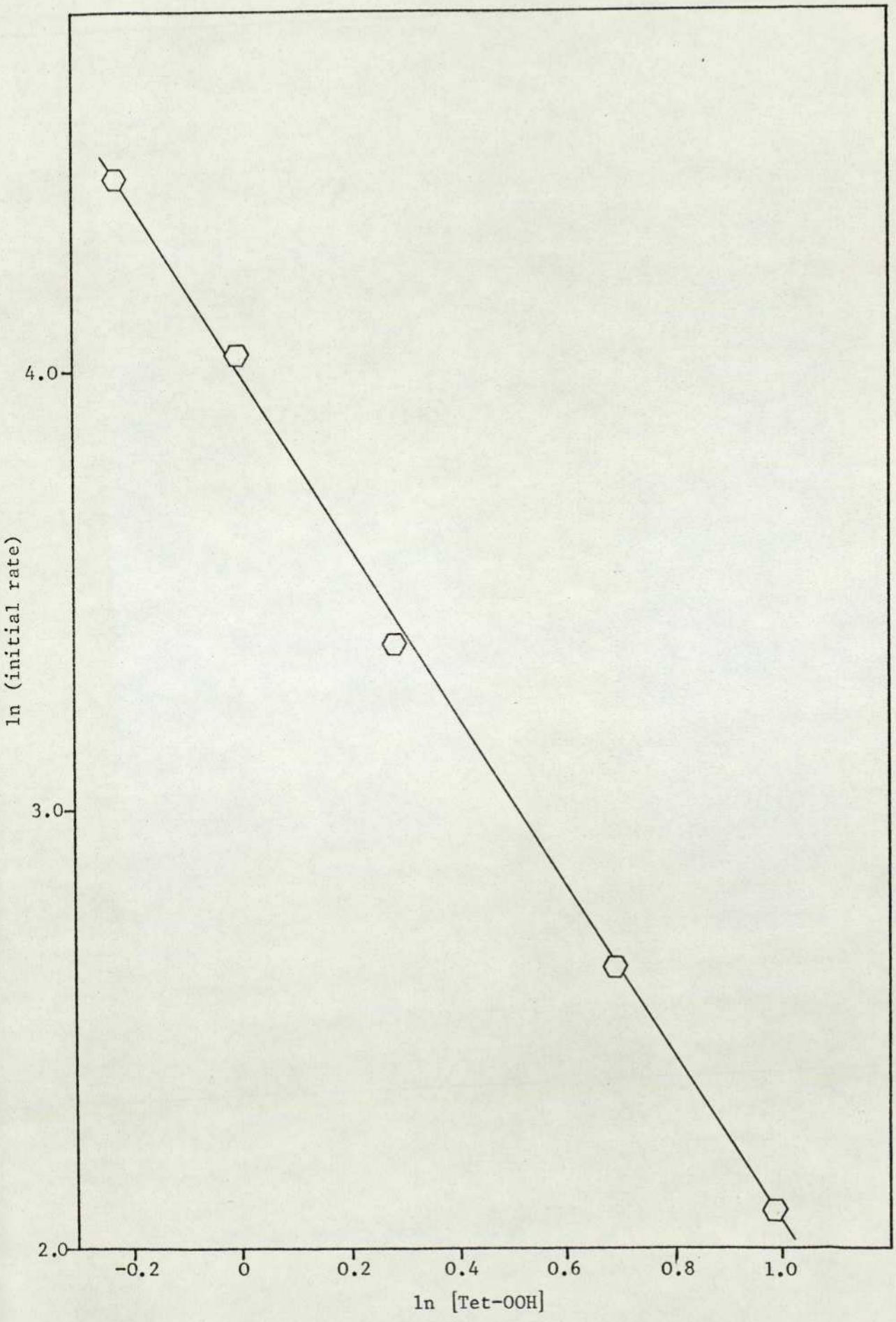


Fig. 3.24 : Decomposition of 0.75 mol l^{-1} tetralin hydroperoxide
Variation of temperature

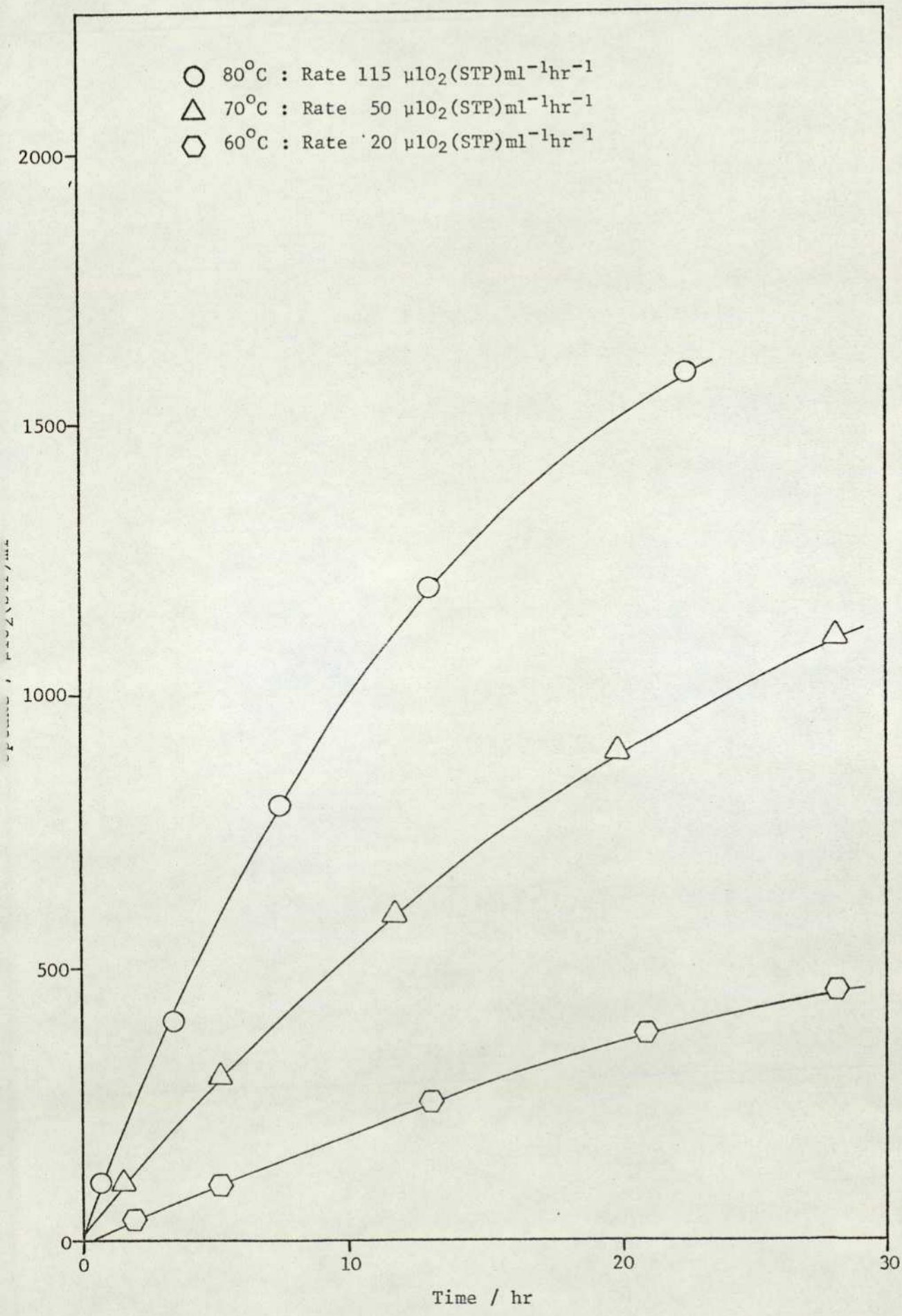


Fig. 3.25 : Decomposition of 0.75 mol l^{-1} tetralin hydroperoxide with 1.25 · 10^{-4}mol l^{-1} NiSDT
Variation of temperature

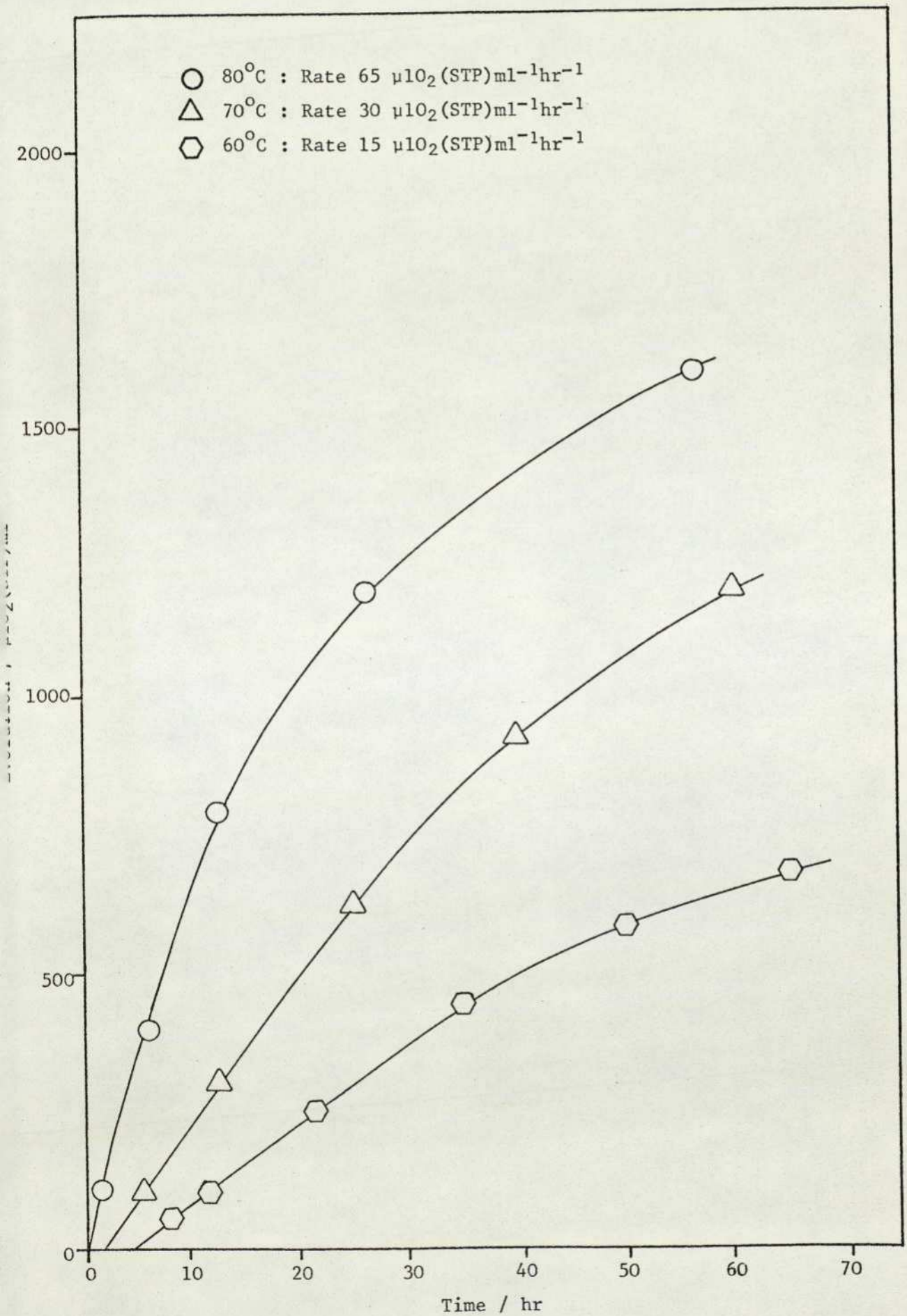
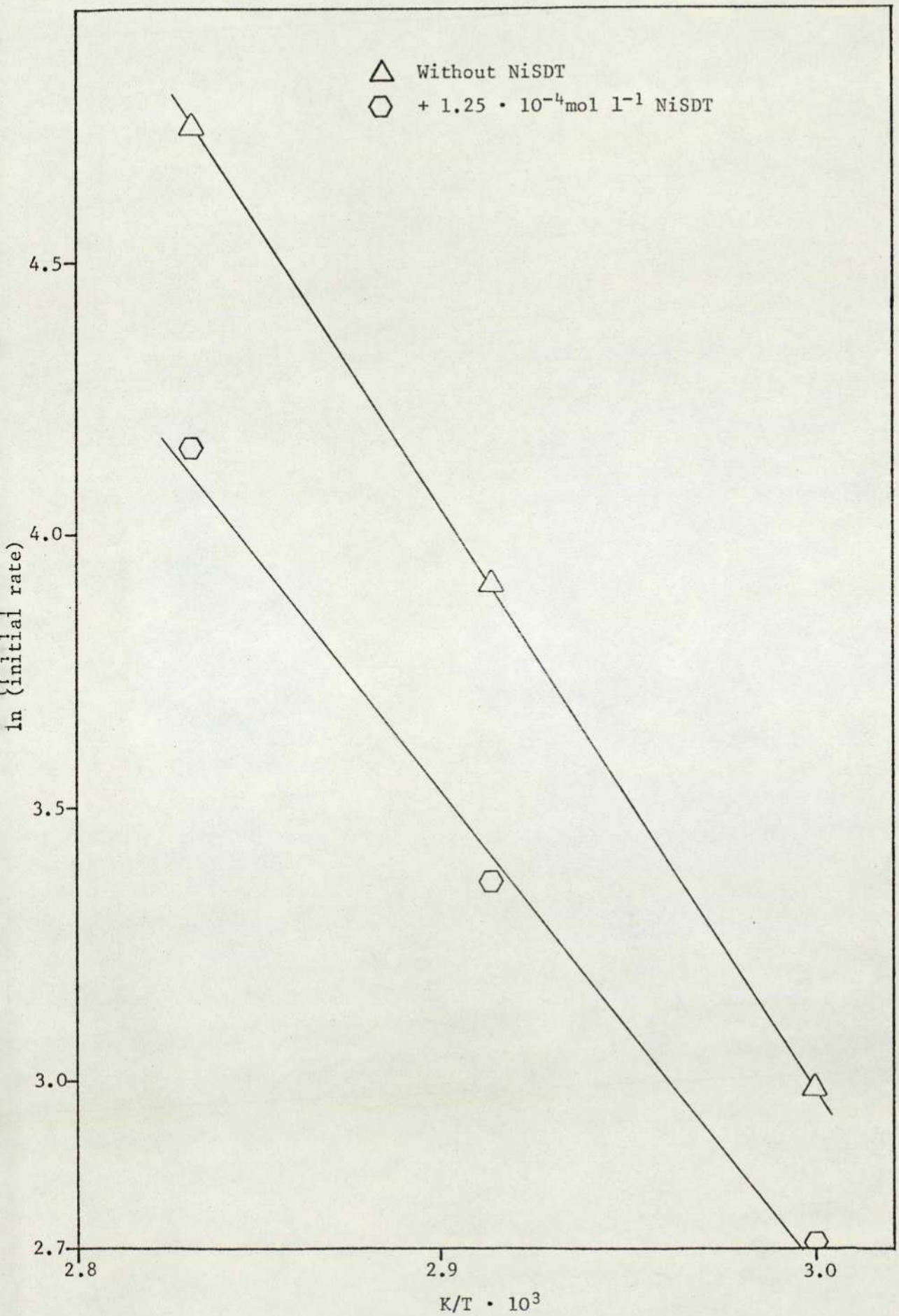


Fig. 3.26 : Decomposition of 0.75 mol l^{-1} tetralin hydroperoxide
ln (initial rate) vs. K/T



Literature values for the bimolecular decomposition of tetralin hydroperoxide have not been found, but values for the monomolecular decomposition have been quoted at 100 to 120 kJ mol^{-1} [71,217]. Hydrogen-bonding in the bimolecular reaction would be expected to lower this figure, so the value obtained is of the correct order.

The continuing decomposition of hydroperoxide after the initial rapid loss of NiSDT indicates that the chelate is only the precursor to an efficient hydroperoxide decomposer derived from the ligands. To assist in determining the active products, an analysis of the breakdown products of the chelate was attempted.

3.6.4 Product analysis

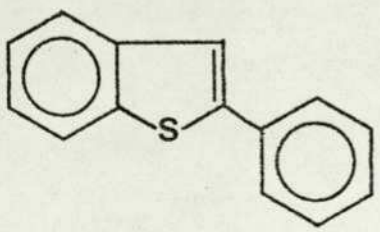
Analysis of the products was carried out in two stages — characterisation of the solid product and an attempt to characterise the organic products from the inhibitor by mass spectrometry.

3.6.4.1 The solid product

As described earlier, the initial stage in the tetralin hydroperoxide/NiSDT reaction is accompanied by the deposition of solid. By considerably increasing the concentrations involved and carrying out the decomposition on a larger scale, a mixed green/white solid was obtained. An investigation of the solid by X-ray microbeam analysis indicated the presence of a quantity of nickel and approximately twice that quantity of sulphur. No other elements were found although the apparatus does not detect elements of a lower atomic weight than fluorine. Standard qualitative examination of the solid showed it to be a mixture of nickel sulphate and sulphur. This would indicate that the active component is an organosulphur compound derived from the ligands. However, the presence of

sulphur is of great interest as elemental sulphur has been reported[150,218] to be an effective hydroperoxide decomposer.

The presence of the above components give an indication of the remaining organic compound. It was found by Schrauzer[179,181] that thermal decomposition of NiSDT gave nickel sulphide, sulphur and only one organic compound which was indentified as 2-phenylthianaphthene (XVII):-



(XVII)

The production of sulphate rather than sulphide in the present case may be attributed to the conditions employed. Schrauzer does not mention whether the decomposition was carried out in air or nitrogen, but nitrogen would be customarily employed if the identity of evolved organic products was required. Therefore, it would appear extremely likely that the organic product decomposing hydroperoxides is 2-phenylthianaphthene. Confirmation of this was attempted by mass spectrometry.

3.6.4.2. Mass spectrometry

In an attempt to confirm the above proposition concerning the active decomposer and to gain some insight into the reaction products, mass spectrometry was carried out on the following samples. Ethyl benzoate was the solvent in each case:-

A : 2mol l^{-1} tetralin + 2 mol l^{-1} tetralin hydroperoxide
+ 10^{-3}mol l^{-1} NiSDT

(Volume ratio 1 : 1 : 1; reaction sampled at the yellow stage)

B : As 'A' (reaction sampled at the colourless stage)

C : Ethyl benzoate

D : 1 mol l^{-1} tetralin

E : 1 mol l^{-1} tetralin hydroperoxide

The mass peaks obtained for both A and B indicated the presence of α-tetralol and α-tetralone, although this may have been a function of the AGHIS system as these peaks were also obtained from E but only after heating for longer periods. Solution A also gave mass peaks at 162/163 mass units (m.u.), 164/165 m.u. and at approximately 180 m.u. These peaks were small and also difficult to assign accurately. The experiments were unsuccessful in the main object, the characterisation of the organic product from NiSDT, and were only intended as a preliminary investigation. A possible peak of 2-phenylthianaphthene is at 133 m.u. (loss of phenyl), but there is a tetralin peak at 132 m.u. (molecular ion). The other small peaks obtained can be explained by products of the further oxidation of tetralin hydroperoxide at the 4-position. The hydroperoxide could give a molecular ion at 164 m.u. and the 180 m.u. peak could correspond to an $HOORO^{+}$ ion. It was also hoped to discover whether any ditetralyl peroxide was produced, as Chien and Boss[173] have stated that NiSDT efficiently converts t-butyl hydroperoxide into di-t-butyl peroxide. The mass spectrum of ditetralyl peroxide is unknown and attempts to synthesise this compound were unsuccessful. Several attempts were made, following the procedure(s) of Triebs and Pellmann[219], without result. This published procedure is confusing and it is believed that these authors may have been mistaken in

their claims. There is no other evidence in the literature for the formation of this compound during tetralin autoxidation and no evidence for its presence could be found in the mass spectra from the above experiments.

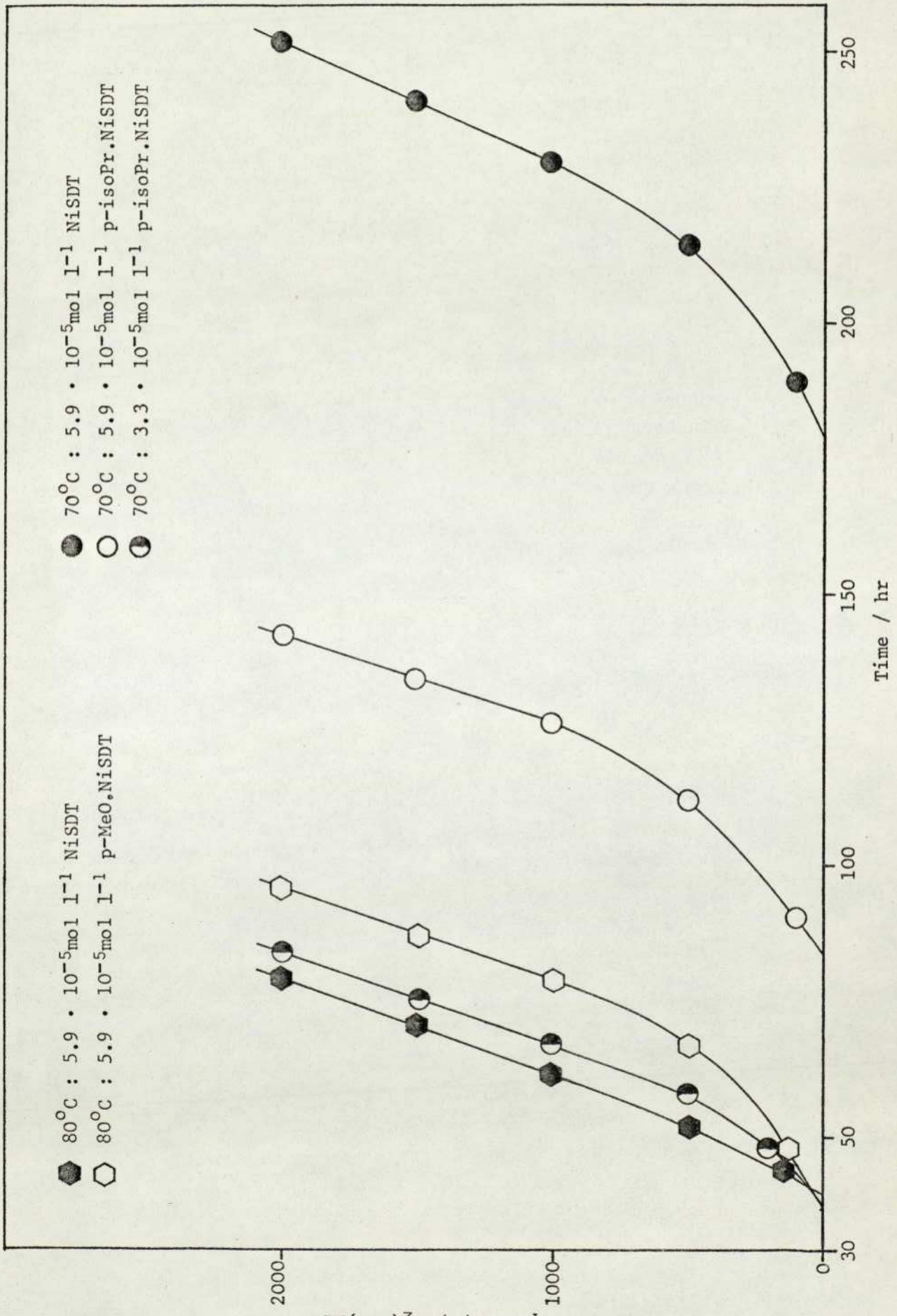
Further experiments were planned at much higher NiSDT concentrations using chloroform as a solvent and omitting the tetralin. It was hoped in this manner to magnify any higher mass peaks and to simplify the interpretation of the spectra obtained. These experiments could not be carried out for the reason given in section 2.2.4.

3.7 Substituted NiSDT derivatives

3.7.1 Effect of p-substitution on tetralin autoxidation

It was originally thought that, as the p-hydrogen atoms in the phenyl rings were the least tightly bound atoms, they could be playing some role in the radical-trapping action of NiSDT. This was investigated by studying the effects of p-isopropyl NiSDT and p-methoxy NiSDT on the autoxidation of 1 mol l^{-1} tetralin. The oxygen uptake data for two concentrations ($5.9 \cdot 10^{-5}$ and $3.3 \cdot 10^{-5}$mol l^{-1}) of p-isopropyl NiSDT and for $5.9 \cdot 10^{-5}$mol l^{-1} p-methoxy NiSDT are presented in figure 3.27 together with the corresponding data for unsubstituted NiSDT, where available. (From figure 3.7, the expected induction period for $3.3 \cdot 10^{-5}$ mol l^{-1} NiSDT at 70°C would be 50 hours.)

Fig. 3.27 : Autoxidation of 1 mol l^{-1} tetralin
Effect of p-substituted NiSDTs



From the data, it can be seen that p-hydrogens play no significant part in the inhibition. p-Methoxy NiSDT is, in fact, a marginally better antioxidant than the unsubstituted inhibitor. As the rates of subsequent oxidation are very similar (57 and 60 $\mu l O_2 (STP) ml^{-1} hr^{-1}$ for the unsubstituted and substituted inhibitors respectively), the improvement appears to be mainly in the radical-trapping properties. The effect of p-methoxy substitution would be to slightly increase the electron-density at the sulphur atoms and thus, it would appear that radical attack occurs at this point.

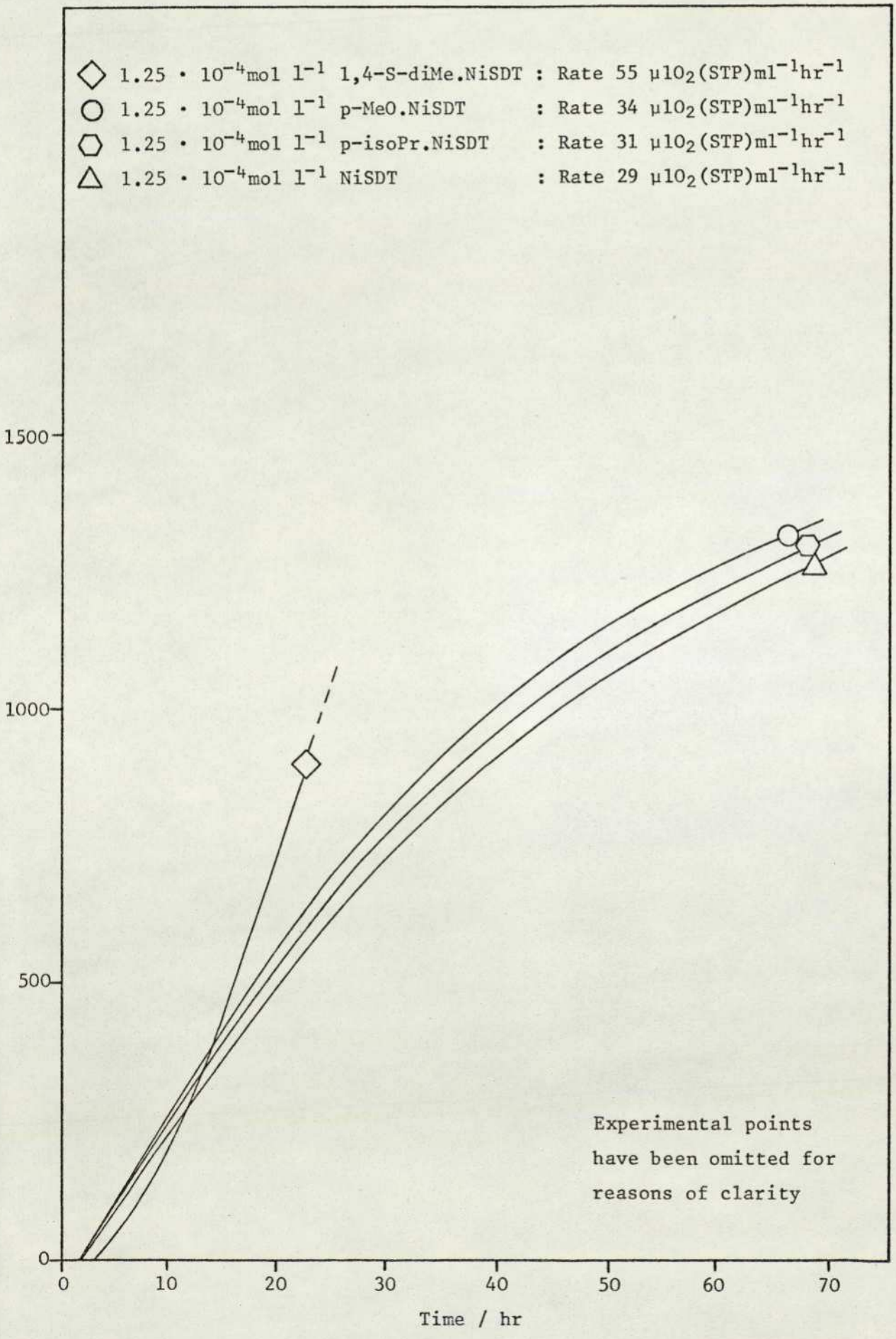
The p-isopropyl derivative was found to be considerably poorer as an antioxidant. This may be attributed to the weak C—H bond in the isopropyl group being attacked by alkylperoxy radicals. The subsequent inhibitor radical formed may well be stable, but the generation of hydroperoxide from this reaction will rapidly remove the remaining inhibitor.

3.7.2 Effect of substituents on hydroperoxide decomposition

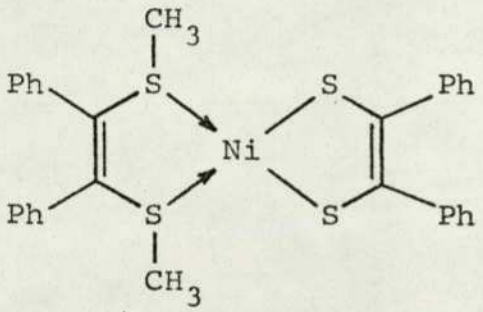
The effect of p-substitution was also investigated for the hydroperoxide-decomposing reaction, together with the effect of adding methyl groups onto two of the sulphur atoms. Each inhibitor was investigated at a concentration of $1.25 \cdot 10^{-4} mol\ l^{-1}$ and the results are presented in figure 3.28 overleaf.

The data obtained show that the features of the reaction with the p-substituted derivatives are virtually identical with the unsubstituted inhibitor. The previous suggestion (section 3.2.1) that the two functions of NiSDT occur at separate parts of the molecule, together with the fact that inclusion of electron-donor groups into the molecule has no apparent effect on the hydroperoxide-decomposing properties, would indicate that the sulphur atoms are not where initial attack of the hydroperoxide occurs.

Fig. 3.28 : Decomposition of 0.75 mol l^{-1} tetralin hydroperoxide at 70°C
Effect of substituted NiSDTs

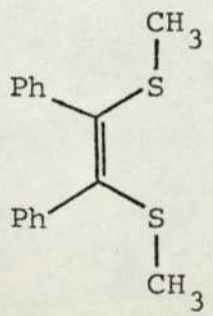


The result obtained with the 1,4-S-dimethyl derivative (XVIII) is of interest in this respect.

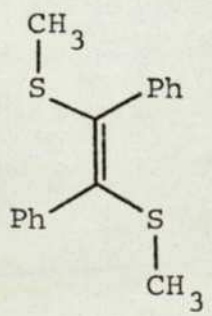


(XVIII)

The initial characteristics of the reaction (rapid loss of colour, solid deposition, etc.) are not markedly different from unsubstituted NiSDT, as would be expected if the initial attack was at the sulphur atoms. However, the initial rate of oxygen evolution is considerably larger than that of the other inhibitors, indicating that the active hydroperoxide decomposer is present at a much *lower* concentration. This would agree with the suggestion (section 3.6.4.1) that 2-phenylthianaphthene is the active species, as the quantity produced from $1.25 \cdot 10^{-4}$mol l^{-1} 1,4-S-dimethyl NiSDT should be approximately equal to that obtained from $6.3 \cdot 10^{-5}$mol l^{-1} NiSDT. The added methyl groups prevent one side of the molecule cyclising to form this compound and Schrauzer[194] has identified the relevant products as a mixture of cis- and trans-α,α'-bismethylthiostilbene ((XIX) and (XX)).



(XIX)



(XX)

CONCLUSIONS

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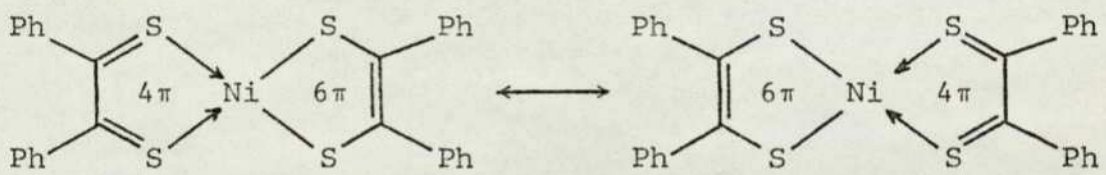
4 CONCLUSIONS

4.1 General conclusions

From the results discussed in the previous section, it is apparent that NiSDT is an extremely efficient antioxidant — particularly for aromatic substrates where steric factors in the radical-trapping stage are not so significant. It has also been established that the radical-trapping and hydroperoxide-decomposing functions of NiSDT are dependent on separate parts of the molecule, with the main hydroperoxide-decomposing properties coming from breakdown products of the chelate. On the basis of the results obtained and the known chemistry of the complex, the following mechanisms are suggested.

4.2 The radical-trapping mechanism

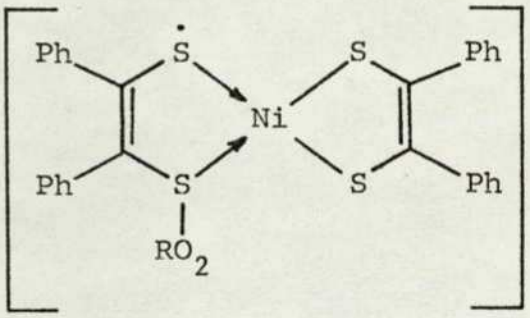
The results obtained for the effect of p-substituted complexes on the autoxidation of tetralin (section 3.7.1) have indicated that radical attack on the NiSDT molecule occurs initially at the sulphur atoms. The electrophilic nature of the alkylperoxy radical would make the presence of a significant negative charge at this point a necessary prerequisite. It is known[181,184,194] that the ground-state structure of NiSDT may be considered as:-



with the ring containing the extra electrons having a significant part of the excess negative charge localised on the sulphur atoms. A comprehensive molecular-orbital treatment by Eisenberg[220] is in agreement with this,

and he states that in the neutral complexes certain π-orbitals are unfilled and "it is possible for these π-functions to therefore serve as 'acceptor orbitals' ". Thus, the prerequisite mentioned above is fulfilled, and the first stage of the reaction may be visualised as:-

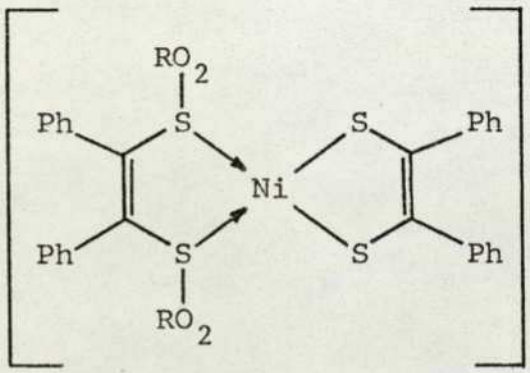
NiSDT + $RO_2^{\bullet}$ ⟶



(XXI)

This is similar to the first, rate-determining stage in the synthesis of the 1,4-S-dialkyl complexes[194] and the addition of the first radical has been stated to increase the nucleophilicity of the sulphur atom in the *same* ring by altering the hybridisation of these two atoms. Hence, the addition of the second alkylperoxy radical will occur very readily at this point:-

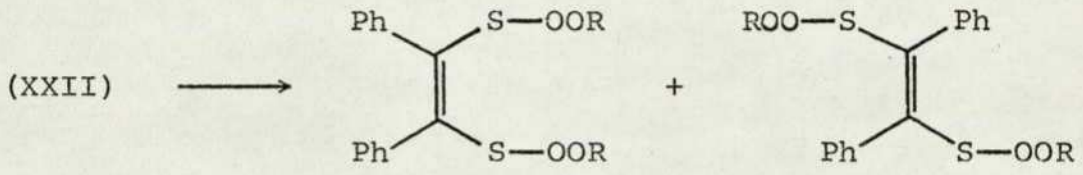
(XXI) + $RO_2^{\bullet}$ $\xrightarrow{\text{fast}}$



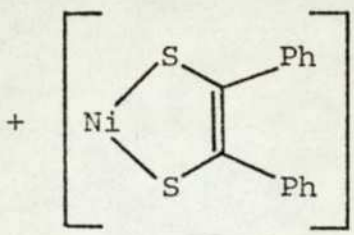
(XXII)

Although the alkyl derivatives produced in a similar way are extremely stable compounds, this is undoubtedly due to electron-donation to the

deficient ligand system. The addition of alkylperoxy radicals will cause an opposite effect due to the electronegativity of the oxygen atoms and this would be expected to break up the complex with the formation of the type of products found by thermally decomposing the 1,4-S-dialkyl derivatives[194]:-

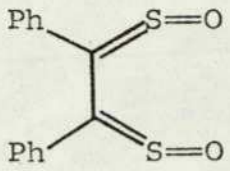


(XXIII) (XXIV)



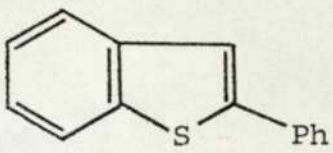
(XXV)

It is believed that hydroperoxide decomposers are formed from (XXII) — section 3.3.1 — and these must be derived from (XXIII) to (XXV). Compounds of the type (XXIII) and (XXIV) would not be expected to be stable, although their mode of decomposition is difficult to envisage. Compound (XXIV) may not occur in this case as the different electronic effects caused by the addition of alkylperoxy radicals, rather than alkyl radicals, may prevent the necessary rearrangement. If it is assumed that only (XXIII) is formed, then a *possible* mechanism of decomposition could be:-

(XXIII) ⟶  + 2RO·

The close proximity of the alkoxy radicals so formed in a solvent cage would lead to recombination to form an alcohol and a ketone for primary or secondary radicals. Tertiary radicals would form a dialkyl peroxide. The sulphoxy compound from the decomposition of (XXIII) may rearrange to a more stable form, which may in itself be a hydroperoxide decomposer.

The decomposition of (XXV) is more clear and, from Schrauzer's[181] work, we have:-

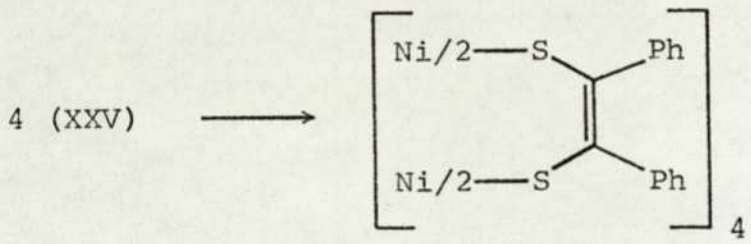
(XXV) ⟶  + NiS

(XXVI)

Compound (XXVI) is 2-phenylthianaphthene and is the compound considered earlier (section 3.6.4.1) to be the active hydroperoxide decomposer produced from NiSDT by the action of hydroperoxide. Thus, it is clear that the radical-trapping reaction of NiSDT can produce at least one hydroperoxide decomposer and bears out the assumption made earlier in section 3.3.1. It is of interest to note that the radical-trapping behaviour of NiSDT is of the type attributed to 'weak' antioxidants — i.e. termination of two radicals via an intermediate complex. The rate of oxidation in the presence of this type of antioxidant was found[109,127] to be proportional to $[AH]^{-0.5}$ — i.e. the reaction's induction period is proportional to

$[AH]^{0.5}$. This fact, together with Scott's view[216] view that the induction period of an autoxidation in the presence of a hydroperoxide decomposer should be proportional to $[\text{inhibitor}]^2$, may well account for the induction period dependence found in section 3.3.1.

The diminishing efficiency of NiSDT at higher concentrations may also be explained by the stated mechanism. As this effect occurs at approximately the same concentration of NiSDT in both the tetralin (figure 3.7) and the hexadec-1-ene (figure 3.8) systems, it is apparent that the decrease in efficiency is related to some alternative higher-order reaction of the inhibitor occurring. The chemistry of the complex contains examples of such reactions and the most relevant is the reaction of (XXV) to form an unreactive[181] tetramer:-

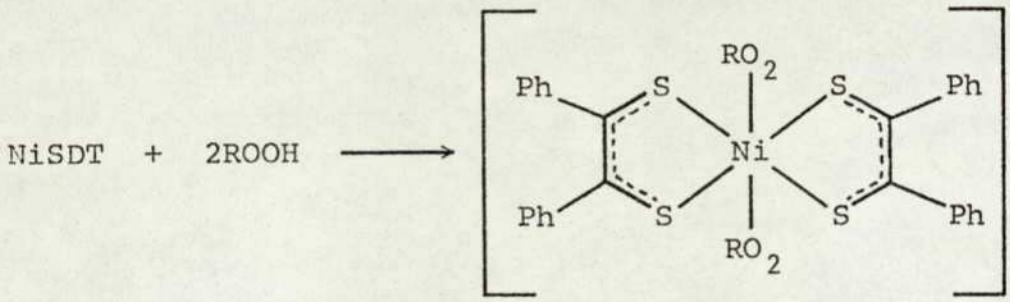


The occurrence of this reaction will prevent the formation of 2-phenylthianaphthene, thereby severely reducing the antioxidant's efficiency.

The above mechanism differs considerably from the radical-trapping mechanism proposed for the dialkyldithiophosphates of similar structure, in which the initial radical/inhibitor interaction is at the metal atom (section 1.4.3). This is to be expected as, although the two types of complex are similar in that each contains a metal atom co-ordinated by four sulphur atoms, the electronic structures differ considerably. In particular, the 'acceptor orbitals', mentioned above for NiSDT, are totally absent from these complexes.

4.3 The hydroperoxide-decomposing mechanism

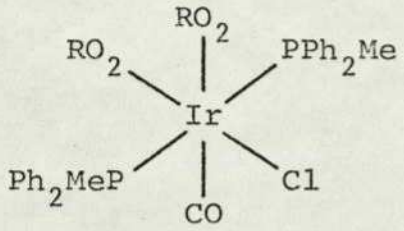
From the results obtained and those of Uri[61,205], the initial reaction between hydroperoxide and NiSDT has been shown to be second-order in hydroperoxide. This reaction then produces an efficient hydroperoxide decomposer together with sulphur and nickel sulphate. Experimental evidence also exists[173,204] indicating that the initial reaction produces a small concentration of alkylperoxy radicals. From the evidence that the hydroperoxide-decomposing mechanism is initially dependent on a separate part of the molecule to the radical-trapping mechanism, it is clear that the initial interaction must occur by the addition of two molecules of hydroperoxide to the metal atom to form an octahedral complex (XXVII):-



(XXVII)

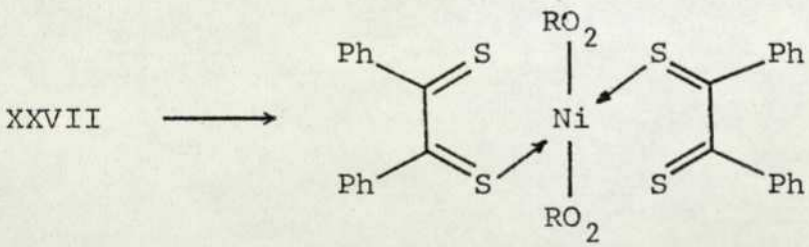
Bonding will be from the peroxy-oxygen after loss of hydrogen rather than by donation of lone pairs of electrons from the alkoxy-oxygen, as this latter case would give rise to a 20-electron complex against the tenets of the 18-electron rule for organometallic compounds[221]. (The subsequent fate of the hydrogen atoms is unknown, but their reactivity is such that they would be quickly absorbed by many of the system's components.) Indirect evidence for this initial reaction can be obtained from two sources. The tendency of square-planar nickel complexes to gain two additional ligands to form octahedral complexes is well known and is extensively documented[222]. Thus, this reaction is in agreement with known properties

of nickel complexes. Of more interest is the recent isolation of compound (XXVIII) from a reaction between a hydroperoxide and a square-planar iridium complex[223] — also a d^8 configuration.



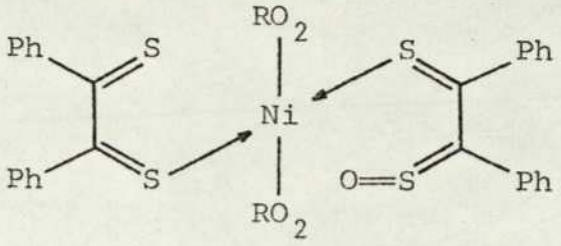
(XXVIII)

The iridium in this complex is raised from a +1 to a stable +3 oxidation state. ((XXVIII) is unstable in the presence of further hydroperoxide, decomposing to give catalysis of autoxidation[224].) Thus, the production of (XXVII) in the initial reaction would seem extremely likely and, presumably, is responsible for the observed yellow colouration. However, (XXVII) is not very stable as the nickel will be in the +4 oxidation state. As this oxidation state generally requires strongly electronegative groups to stabilise it[225], the next stage is presumed to be:-



(XXIX)

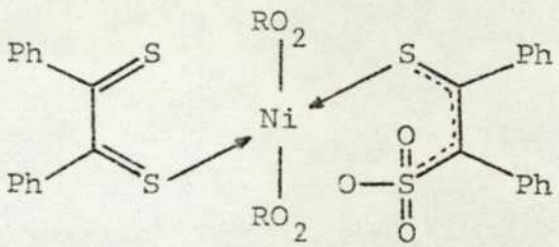
thereby regaining the Ni^{2+} configuration. The resulting free sulphur atoms will be reactive towards hydroperoxide to form, initially, a sulphoxide:-

XXIX $\xrightarrow{ROOH}$  + ROH

(XXX)

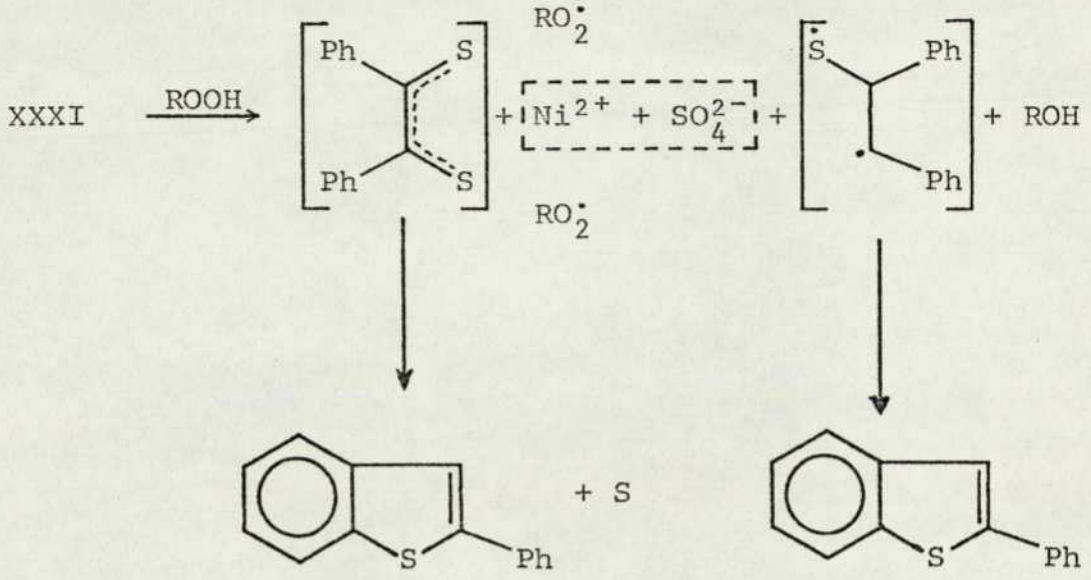
Alternatively, (XXVII) may proceed directly to (XXX) by reaction with hydroperoxide. It is considered that both may occur, the relative predominance of one over the other being dependent on the hydroperoxide concentration.

Formation of (XXX) will tend to deactivate the other free sulphur atom and further hydroperoxide decomposition will occur at the same place:-

XXX $\xrightarrow{2ROOH}$  + 2ROH

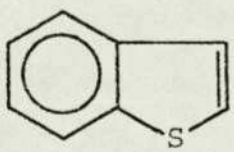
(XXXI)

Continuing reaction with hydroperoxide will cause the complex to break up with the formation of the known products:-



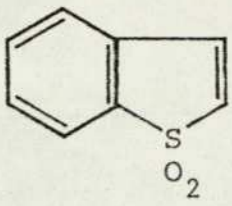
The production of two alkylperoxy radicals at this stage seems unavoidable and this would be in agreement with the work of Chien[173] and Ivanov[204]. The production of nickel sulphate and sulphur is thus explained with the production of two molecules of 2-phenylthianaphthene as the active hydroperoxide decomposer.

The reasons for considering 2-phenylthianaphthene to be the active species are based on the known chemistry of this type of compound. Very little is known about the 2-phenyl derivative, but the following reactions are well documented for thianaphthene (XXXII).

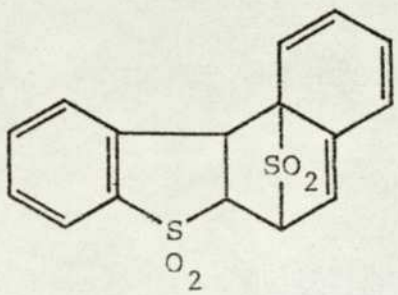


(XXXII)

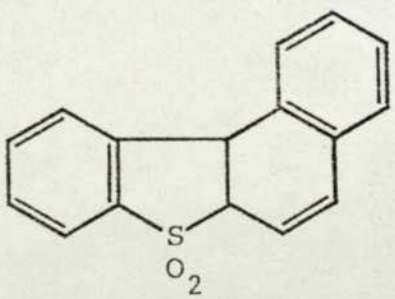
Reaction of (XXXII) with peroxides has been found[226] to give a 1,1-dioxide (XXXIII), which no longer has aromatic character and behaves as a vinyl sulfone[227]. (The insertion of a phenyl group at the 2-position should increase the reactivity of the sulphur toward sulphone formation[228].)

XXXII $\xrightarrow{ROOH}$  (XXXIII)

It is considered that the subsequent reaction of (XXXIII) is responsible for the continued catalytic decomposition of hydroperoxide. These compounds can act as both a diene and a dienophile, and consequently dimerise via a Diels-Alder reaction[229,230] to give the adduct (XXXIV):-

2 XXXIII $\longrightarrow$  (XXXIV)

(XXXIV) then decomposes to give a product (XXXV) and sulphur dioxide:-

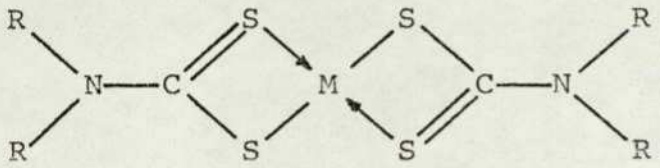
XXXIV $\longrightarrow$  + SO_2

(XXXV)

The subsequent activity of (XXXV) is unknown, but it is possible that further oxidation by hydroperoxide may occur. Sulphur dioxide, however, is known[142,150] to be a powerful and catalytic decomposer of hydroperoxides (section 1.4.2.1). The presence of this compound, together with

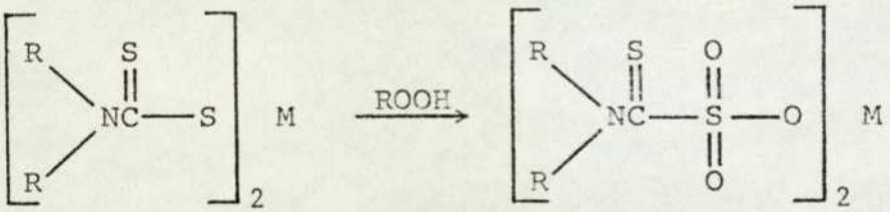
the hydroperoxide decomposition occurring due to compounds of the type (XXXII) and the presence of sulphur — another known hydroperoxide decomposer[150,218] — could well account for the remarkable activity shown by NiSDT.

The initial reaction between the hydroperoxide and NiSDT may have some relevance to the hydroperoxide-decomposing properties of the dithiocarbamates (XXXVI):-

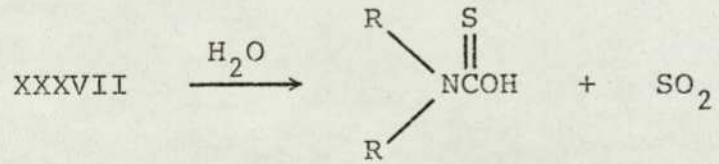


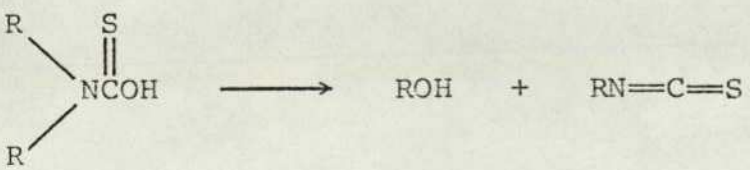
(XXXVI)

Scott[142,148] has proposed the following reaction sequence to explain the formation of isothiocyanate and sulphur dioxide:-



(XXXVII)





It is considered that when M is a transition metal other than zinc, the type of reaction that NiSDT undergoes may provide an easier route to (XXXVII) — i.e. co-ordination of hydroperoxide to the metal, causing two sulphur-metal bonds to break with a consequent increase in reactivity of the two sulphur atoms. In the case of zinc, for which the mechanism was originally proposed, octahedral co-ordination is unlikely and the stated ring-enlargement reaction will occur.

4.4 Final conclusions and future work

Inhibition by NiSDT has been proposed to occur by two mechanisms — radical-trapping by addition of alkylperoxy radicals to the sulphur atoms on one side of the complex and hydroperoxide decomposition by octahedral co-ordination of the nickel to produce an efficient hydroperoxide decomposer which ultimately degrades to sulphur dioxide. Confirmation for these two mechanisms could be obtained by further experiments. The radical-trapping mechanism may be examined by reacting NiSDT under nitrogen with a source of alkyl radicals. If the stated mechanism is correct, stable compounds of the 1,4-S-dialkyl type should be isolated. With regard to the hydroperoxide-decomposing mechanism, a useful experiment would be to determine all the organic products formed, possibly by high-pressure liquid chromatography, and to establish the presence of 2-phenylthianaphthene and sulphur dioxide. Experiments testing the inhibitory properties of 2-phenylthianaphthene could also be carried out, although this compound would have to be synthesised[231,232]. Evidence to confirm the initial interaction between NiSDT and hydroperoxide may be obtained by using the platinum or palladium derivatives. Both of these metals have more stable +4 oxidation states than nickel and, by using the methods employed for the iridium peroxy-complex[223,224], it may be possible to isolate the octahedral intermediate (XXVII).

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