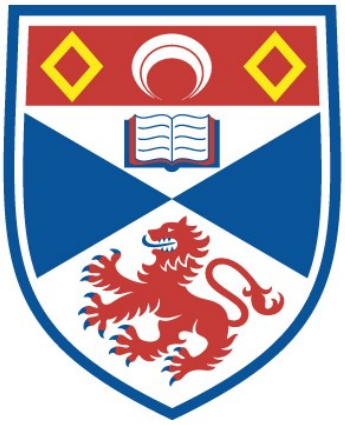
EXPLORATORY TESTING OF CURRENT AND NEW LUBRICANT ANTIOXIDANTS

Alan Burton

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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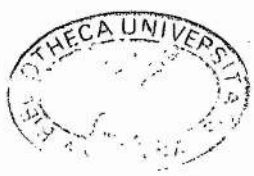
Exploratory Testing of Current and New Lubricant Antioxidants

A thesis presented by Alan Burton, BSc., to the University of St. Andrews, in application for the Degree of Doctor of Philosophy



Declaration

I, Alan Burton, hereby certify that this thesis has been compiled by myself, that it is a record of my work and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Signed____ _____ Date 30/4/95

I was admitted to the Faculty of Science of the University of St. Andrews, under Ordinance General No. 12 on 1st October 1990, and as a candidate for the Degree of Doctor of Philosophy on 1st October 1991.

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I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the Degree of Doctor of Philosophy.

Signature of Supervisor____ _____ Date 30/4/95

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Acknowledgments

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Abstract

Chapter one is a general introduction to lubricant degradation. Subjects discussed include the problems associated with oil degradation, the mechanism of the autoxidation process, products generated by autoxidation, methods used for controlling the autoxidation process, the reasoning for constant lubricant development and the conventional industrial screening tests. The concept of the radical clock, and the rationale for testing an antioxidants ability to trap alkyl radicals, are also introduced.

Chapter two deals with the measurement of the rate constant, k_H, at which the aminyl hydrogen is removed by alkyl radicals from 4,4'-disubstituted diphenylamines. The method used was based on the ability of some radicals to rearrange irreversibly. The radical clocks employed for this study were the 5-hexenyl and the neophyl rearrangements. Results indicated that the 5-hexenyl radical rearrangement was too fast so all the quantitative results were obtained using the neophyl rearrangement. The alkyl radicals were generated by the decomposition of a diacyl peroxide. Problems encountered with this source were radical disproportionation and heterolytic scission, both of which form 2-methyl-2-propenylbenzene. Various methods of overcoming these problems were discussed and, by taking into account the alkene formation, k_H was obtained for a variety of diarylamines at differing temperatures. From these results the Arrhenius pre-exponential factors and activation energies were obtained. Log k_H was found to correlate with σ_P^+ values for the *para* substituents. The experimental results show that diphenylamines with electron releasing substituents in the

para position were the most efficient at trapping alkyl radicals; this was found to correlate with kinetic studies involving peroxyl radicals.

Chapter three describes the measurement of the rate constant, k_H, at which the phenolic hydrogen is removed by alkyl radicals from 2,6-di-t-butyl-4-substituted phenols. For this study the neophyl radical rearrangement was used. Solutions to problems associated with radical disproportionation and heterolytic scission are again suggested. The experimental results show that phenols with electron withdrawing substituents in the *para*- position were the most efficient at trapping alkyl radicals. Kinetic studies with peroxyl radicals give the opposite result in that phenols with electron releasing substituents in the *para* position were the most efficient.

Chapter four deals with the testing of 4,4'-disubstituted diphenylamines with existing industrial screening tests. The results show that in general diphenylamines with electron releasing substituents in the *para* position were the most efficient antioxidants. The effect that the lubricant basestock has on these results was also investigated.

Chapter five deals with slow release antioxidants. These compounds were designed to release a fresh supply of antioxidant as the original materials are consumed. Compounds under consideration were the *N*-amides, *N*-silyl diphenylamines, *N*-oxides and *N*-alkyl diphenylamines. Of these only the *N*-alkyl diphenylamines were further investigated using flash vacuum pyrolysis (FVP) and the industrial screening tests. The FVP results indicated that the *N*-alkyl diphenylamines were decomposing by cleavage of the N-C bond, although other mechanisms were

probably important. The industrial screening tests indicated that the decomposition involved the oxidation of the nitrogen to the *N*-oxide which easily decomposed to the hydroxylamine, an active antioxidant.

Chapter six gives a brief summary of the experimental results and the conclusions derived from them.

Chapter 1

Introduction

1.1 The functioning of a lubricant

One of the most important components of every engine is the lubricant oil. There are a number of functions it performs within an internal combustion engine. First of all it provides a thin film of oil between moving parts thus reducing friction and wear, furthermore it cools some components, keeps parts clean, protects against corrosion, seals the combustion pressures within the piston ring zone and minimises combustion chamber deposits.

All the lubricants used within a car engine are based on hydrocarbon oils of some type, and have to perform all these functions at high temperatures and pressures in the presence of oxygen, dissolved metals and blowby products of the combustion process. Normally under such conditions the basestock would undergo rapid autoxidation.

The problems that arise from lubricant oxidation include increases in viscosity, the formation of various deposits and the generation of acidic compounds which can lead to corrosion. This in turn leads to decreased oil lubrication, blocked oil ways and in extreme cases even to engine seizure.

The mechanism involved in the degradation of a lubricant is a free radical autoxidation[1,2] .

Autoxidation

Autoxidation is the reaction of organic compounds with atmospheric oxygen under mild conditions. The initial products of this process are the hydroperoxides, but through the decomposition of these hydroperoxides, other oxygenated products such as alcohols, ketones and carboxylic acids are formed. These products are formed by a complex sequence of

simple reactions which can be represented by the following free radical chain reaction.

1) Initiation

Production of free radicals

2) Propagation

$RO_2^{\cdot} + RH \rightarrow RO_2H + R^{\cdot}$

$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$

3) Termination

$2RO_2^{\cdot} \rightarrow$ molecular products

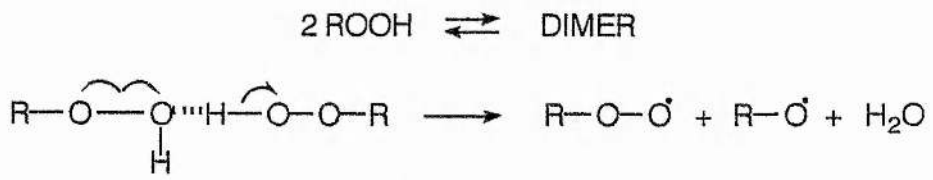
Scheme 1.1
Schematic overview of the
autoxidation process

1.2 The Initiation reactions

There are numerous ways in which autoxidations can be initiated within a fired engine. The combustion process itself releases large numbers of free radicals, some of which escape past the piston rings to eventually end up in the lubricant. However, once the autoxidation has become established, the most important source of radicals is the decomposition of hydroperoxides[3]. This decomposition can either occur by a simple unimolecular process in which the radicals are formed via a unimolecular, homolytic scission of the peroxide bond to give alkoxyl and hydroxyl radicals;

Scheme 1.2
Unimolecular decomposition
of hydroperoxides

or by the energetically favoured bimolecular reaction in which the hydroperoxides first form hydrogen bonded dimers. The decomposition occurs via a concerted reaction in which both molecules decompose at the same time to give an alkoxyl radical, a peroxyl radical and water.



Scheme 1.3
Bimolecular decomposition of
hydroperoxides

The mechanism by which hydroperoxides decompose depends on their concentration and the temperature of their environment. At high peroxide concentrations and temperatures below 100°C the bimolecular process is favoured, whereas at high temperatures or low peroxide concentrations the unimolecular decomposition is prevalent.

Hydroperoxide decomposition is also catalysed by a variety of transition metals[4]. The most important of these is iron as it is always present within an engine. The catalytic decomposition of hydroperoxides is thought to occur via a redox cycle in which the metal ion can undergo both oxidation and reduction reactions with the hydroperoxide. Oxidation of the metal centre gives an alkoxyl radical and a hydroxide anion, whereas reduction of the metal centre gives the hydroperoxyl radical and a proton.

Oxidation of metal centre

$$M^{n+} + ROOH \longrightarrow M^{(n+1)+} + RO^{\bullet} + OH^{-}$$

Reduction of metal centre

$$M^{(n+1)+} + ROOH \longrightarrow M^{n+} + ROO^{\bullet} + H^{+}$$

Scheme 1.4
Metal catalysed decomposition of hydroperoxides

1.3 Propagation reactions

The two most important propagation reactions in any autoxidation at low temperatures, with ample oxygen, is the combination of oxygen with alkyl radicals to form peroxyl radicals;

$$R^{\bullet} + O_2 \rightleftharpoons ROO^{\bullet}$$

Scheme 1.5
Formation of peroxyl radicals

and their subsequent reactions with the basestock giving alkyl radicals and hydroperoxides, which in turn can initiate further radical reactions.

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$

Scheme 1.6
Reaction of peroxyl radicals with hydrocarbons

Peroxyl radical formation

Oxygen is not reactive enough to combine directly with the lubricant but will combine with alkyl radicals at rates close to the diffusion controlled limits, to form the peroxyl radical. The reverse reaction is normally unimportant, but as the temperature

rises, the alkyl radical plays an increasingly important role in the autoxidation processes.

Hydroperoxide and alkyl radical formation

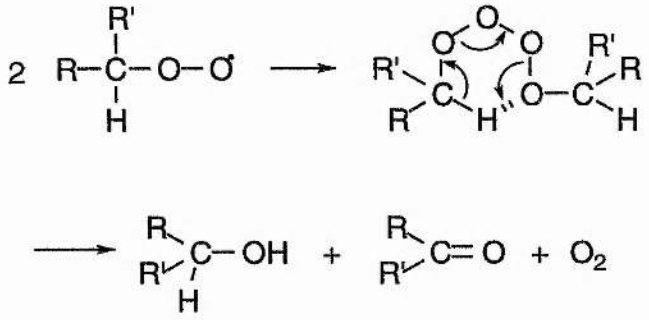
Alkyl radicals are formed rapidly by hydrogen abstractions from the basestock, by hydroxyl and alkoxyl radicals or by β-scission of alkoxyl radicals but both the alkoxyl and hydroxyl radicals are generated from the decomposition of hydroperoxides, consequently the rate at which an autoxidation proceeds is dependant upon the rate at which peroxyl radicals can abstract hydrogen from the basestock to form the hydroperoxide.

The rate at which peroxyl radicals can abstract hydrogen from the basestock is generally dependant upon the strength of the bonds which are broken and those which are formed. The ROO-H bond has been measured at 88 kcal mol^{-1} [5] which is weaker than alkyl C-H bond (95-98 kcal mol^{-1}) but stronger than the allyl or benzyl C-H bond (ca. 76 kcal mol^{-1}), whereas the strength of the RO-H and HO-H bond are about 104 and 110 kcals mol^{-1} [6] respectively. On bond energy considerations alone it would be expected that peroxyl radicals would be much less reactive than the alkoxyl or hydroxyl radicals and more selective in their reactions, as they would have difficulty in abstracting hydrogen from alkanes to form the hydroperoxide, but would instead preferentially attack allyl and benzyl hydrogens.

Experimental observation proves that alkyl aromatics and allylic hydrocarbons do indeed undergo autoxidation more readily than alkanes[7,8].

1.4 Termination reactions

The termination reactions effectively remove radicals from the autoxidation process. Within a fired engine the most important radical termination reactions is the combination of two peroxyl radicals, to form a tetroxide intermediate. The tetroxide then decomposes to form the alcohol, ketone and singlet oxygen.



Scheme 1.7
Termination reaction involving
two peroxyl radicals

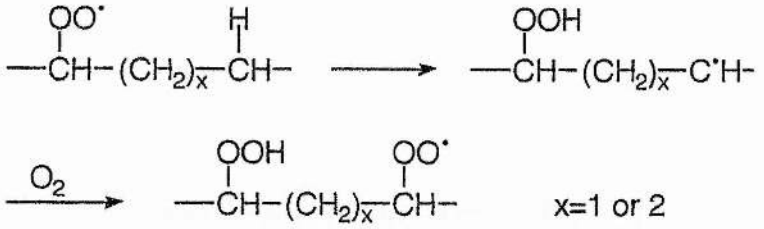
1.5 Products of lubricant autoxidation

Although a wide range of products are formed in the autoxidation of a lubricant, the actual processes involved are relatively simple. The initial products of the autoxidation are the hydroperoxides, these are formed by the hydrogen transfer between the peroxyl radical centre and unreacted basestock (see scheme 1.6), these hydrogen abstractions can be both intermolecular and intramolecular in nature[9,10].

Intermolecular reaction gives simple monofunctional products;

Scheme 1.8
Intermolecular hydrogen abstractions
by peroxyl radicals

whereas the intramolecular reaction gives more complex, multifunctional products.

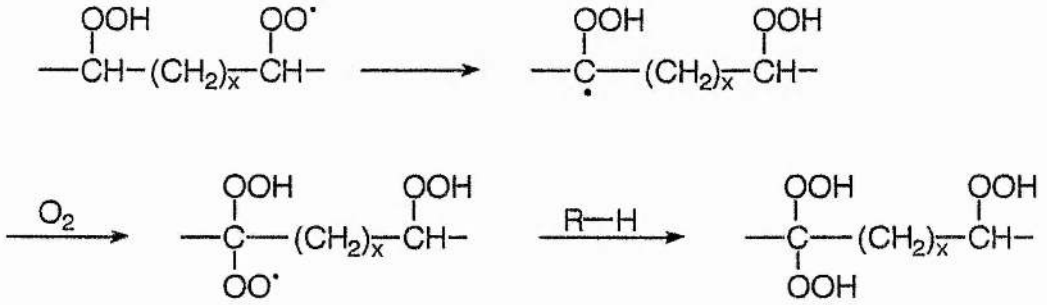


Scheme 1.9
Intramolecular hydrogen abstractions
by peroxyl radicals at a methylene group

The peroxyl radical can again undergo further intramolecular hydrogen abstractions, either abstracting hydrogen from a methylene group:

Scheme 1.10
Further peroxyl radical attack at a
methylene group

or attacking the hydrogen at a hydroperoxide group;

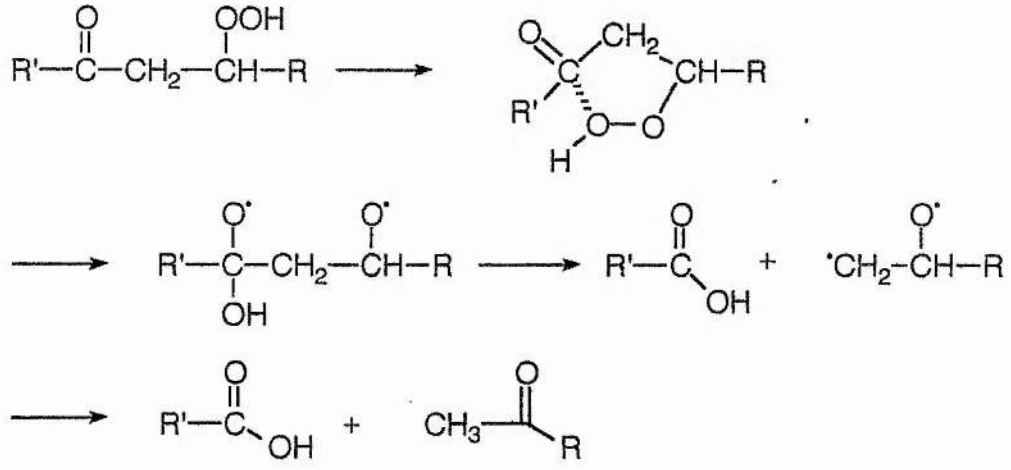


Scheme 1.11
Peroxyl radical attack at the
alpha-hydrogen of a hydroperoxide

If the alkyl hydroperoxide radical does not combine with oxygen then it can decompose to form a hydroxyl radical and a ketone.

Scheme 1.12
Decomposition of an alkyl hydroperoxide radical

The alpha-gamma hydroperoxide ketones formed in reaction 1.11 can undergo cleavage to produce a carboxylic acid and a methylketone.



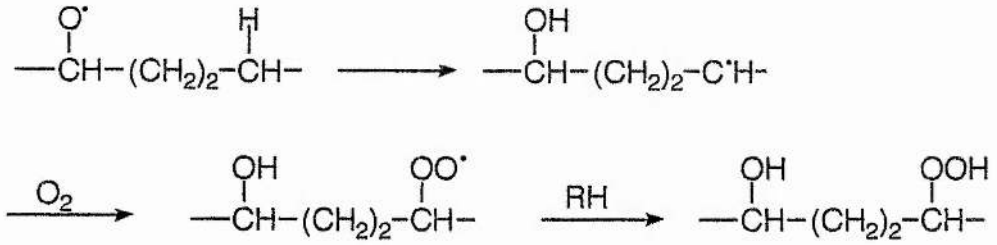
Scheme 1.13
Cleavage of alpha-gamma hydroperoxide ketones

Two peroxyl radicals can also terminate forming a ketone and an alcohol. (see section 1.4)

The decomposition of hydroperoxides generates alkoxyl radicals (see section 1.2), which can also undergo both intermolecular and intramolecular hydrogen abstractions, the intermolecular reaction gives a simple monoalcohol;

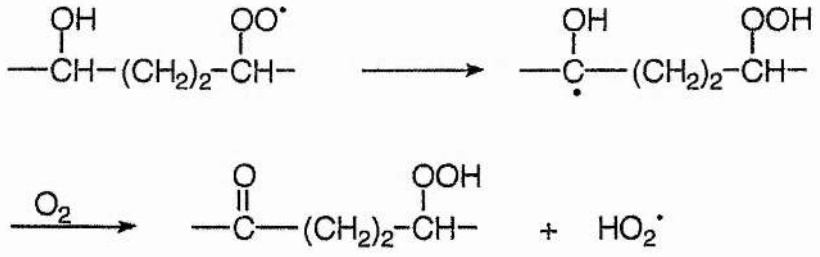
Scheme 1.14
Intermolecular hydrogen abstractions
by the alkoxyl radical

whereas the intramolecular reaction again leads to more complex multifunctional products.



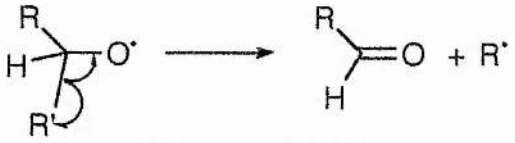
Scheme 1.15
Intramolecular hydrogen abstractions
by the alkoxyl radical

The peroxyl radical formed can abstract the hydrogen from the alcoholic carbon, this can react with oxygen forming a ketone and a hydroperoxyl radical.



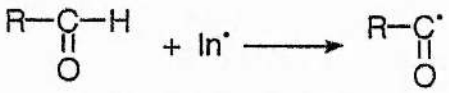
Scheme 1.16
Peroxyl radical attack at the
alpha-hydrogen of an alcohol

An alkoxyl radical only has a limited lifetime, if it does not abstract hydrogen to form the alcohol, it will undergo β-scission to give an aldehyde and an alkyl radical.



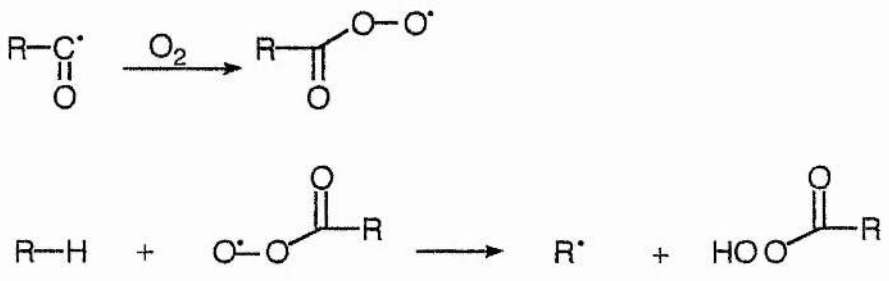
Scheme 1.17
β-Scission of alkoxyl radicals

Aldehydes formed within an engine are more prone to autoxidation than the basestock, so once formed they are rapidly degraded by further oxidation. The oxidation of an aldehyde is a typical autoxidation process. Within a fired engine initiation is by transfer of the acyl hydrogen to any radicals present[11].



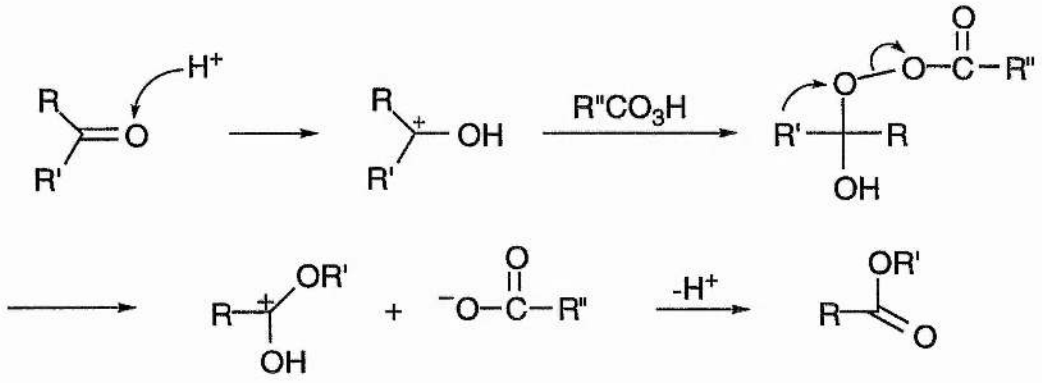
Scheme 1.18
Initiation of aldehyde autoxidation
within a lubricant

The carbonyl radical reacts rapidly with oxygen to form an acylperoxyl radical which can then abstract hydrogen from the basestock to form a peracid.



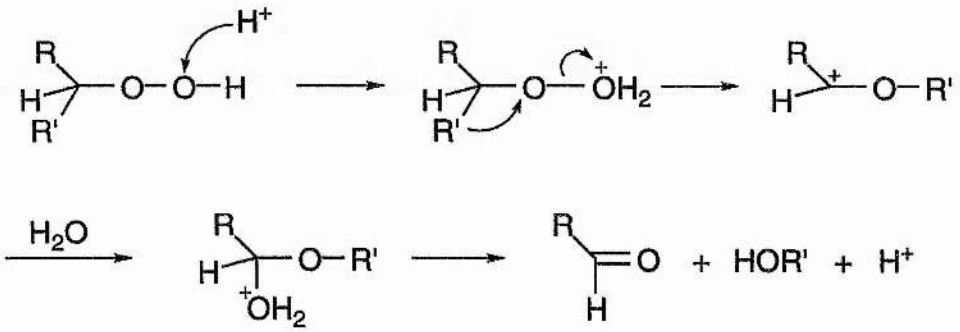
Scheme 1.19
Propagation reactions of aldehyde
autoxidation within a lubricant

These peracids can react with aldehydes and ketones to form carboxylic acids or esters respectively. This reaction is commonly known as the Baeyer Villiger rearrangement[12].



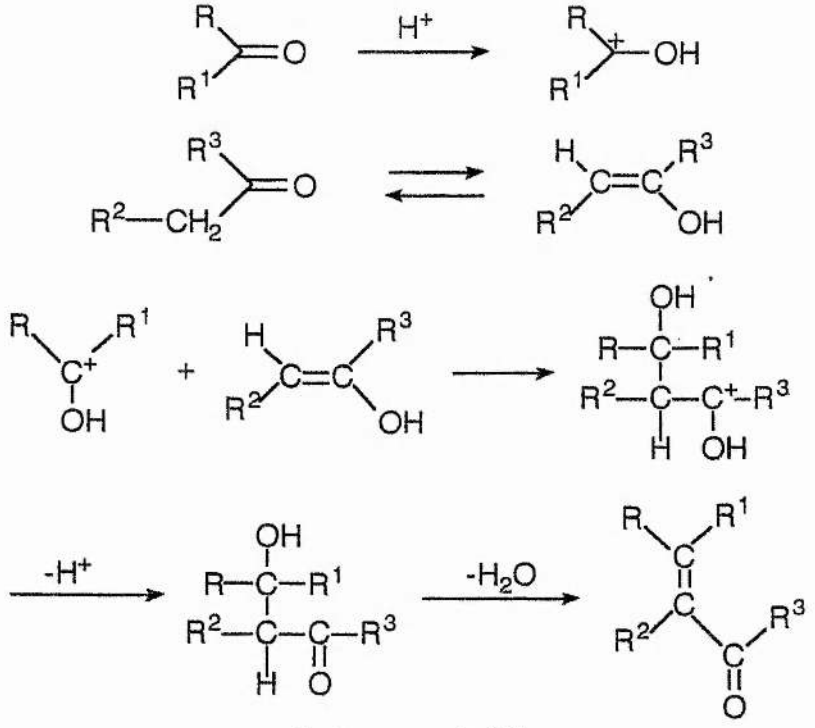
Scheme 1.20
Baeyer Villiger reaction

Acids formed within an engine will decompose hydroperoxides via a non radical pathway. The products of this reaction are an aldehyde and an alcohol[13,14]. The reaction involves protonation of the hydroperoxide followed by the migration of an alkyl functional group. If the hydroperoxide group is centred on a benzylic carbon, the aromatic ring will migrate in preference to any other group to give a phenol instead of the alcohol.



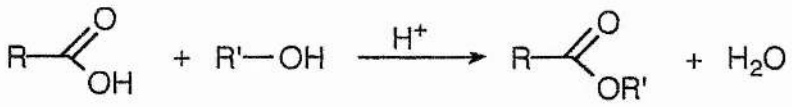
Scheme 1.21
Acid decomposition of hydroperoxides

Ketones are amongst the more common products of the autoxidation of a lubricating oil. Once formed they can undergo an aldol type condensation, the product of which is also a ketone and so is able undergo further condensations. The aldol condensation involves the reaction of the protonated form of the ketone with the enol. This reaction is catalysed by strong acids and accelerated by high temperatures and pressures; the type of conditions found within a fired engine[15].



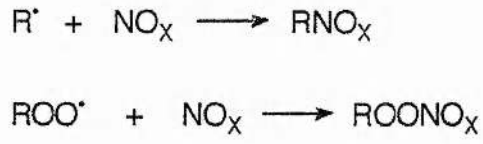
Scheme 1.22
Aldol condensation

Other common products include carboxylic acids and alcohols. These will undergo esterification under acidic conditions, the reaction being driven to completion by the removal of water. Within a fired engine strong acids are formed which will catalyse this reaction, the high temperatures at which an engine operates will drive off the water[16].



Scheme 1.23
Esterification reaction

The blowby gases of the combustion process contain nitrogen oxides, which will readily combine with both alkyl and peroxyl radicals to form nitro and peroxynitro compounds[17].



Scheme 1.24
Combination of nitrogen oxides
with a lubricant intermediates

These products are thermally unstable and soon decompose to form deposits.

The products of autoxidation are all highly polar, their increased interactions lead to the increase in viscosity associated with oil degradation. Many of the products of autoxidation are multifunctional hydroxy-carboxylic and ketocarboxylic acids. These products will readily polymerise within a fired engine forming sludge and other deposits.

1.6 Lubricant composition

A typical motor oil is made up of about 75% basestock and 25% additives. There are a wide range of basestocks available for lubrication purposes. These include fully synthetic basestocks such as polyalkylated olefins and pentaerythritol esters, semi

synthetic basestocks which are natural basestocks that have been chemically treated, and natural basestocks.

The additives are used to prolong the life of the lubricant and to adjust its physical properties. They include antioxidants, dispersants, bases, viscosity improvers and antifoamants. The antioxidants interrupt the autoxidation process; the dispersants prevent products of the autoxidation from coagulating and hence from forming sludge. Bases neutralise any acids which form and consequently slow down corrosion. Through viscosity improvers the negative effects of extreme temperature variations on the oil are reduced by preventing the oil from freezing or thinning at low and high temperatures respectively. As the peak efficiency of the oil pump is compromised by air getting into it, the foaming of the oil which reduces the oil pressure has to be prevented, therefore it is imperative that antifoamants are added to warrant a trouble free performance.

1.7 Antioxidants

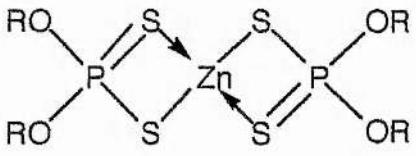
There are three types of antioxidant added to motor lubricants;

1. Peroxide decomposers, which decompose hydroperoxides via a non radical pathway and so prevent initiation.
2. Metal deactivators which prevent the metal catalysed decomposition of hydroperoxides.
3. Chain inhibitors which slow down the rate of radical propagation.

Peroxide decomposers

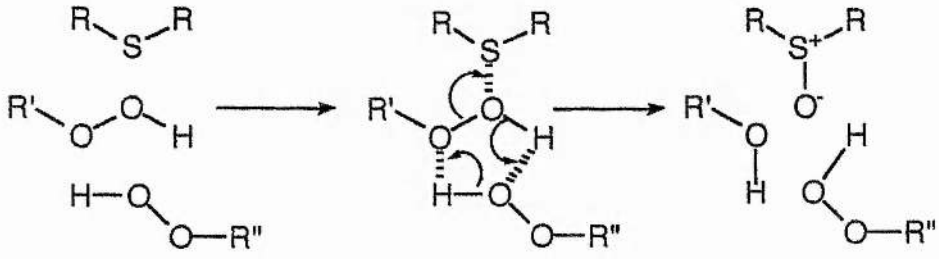
Peroxide decomposers are usually sulphur based. They either reduce the hydroperoxide to the corresponding alcohol or

act as a catalyst in its non radical forming decomposition. The most commonly used additives of this type are the zinc dialkyldithiophosphonates (ZDDP). Naturally occuring organic sulphur compounds which are present in the basestock also act as antioxidants.



Scheme 1.25
Structure of a ZDDP molecule

The reduction process is a first order reaction for the hydroperoxide in a protic solvent, but second order in a neutral solvent. The sulphur compound associates with the peroxyl oxygen, the following reduction process is then thought to go via a hydrogen bonded cyclic transition state with little charge transfer to give the alcohol and an oxidized sulphur product[19].

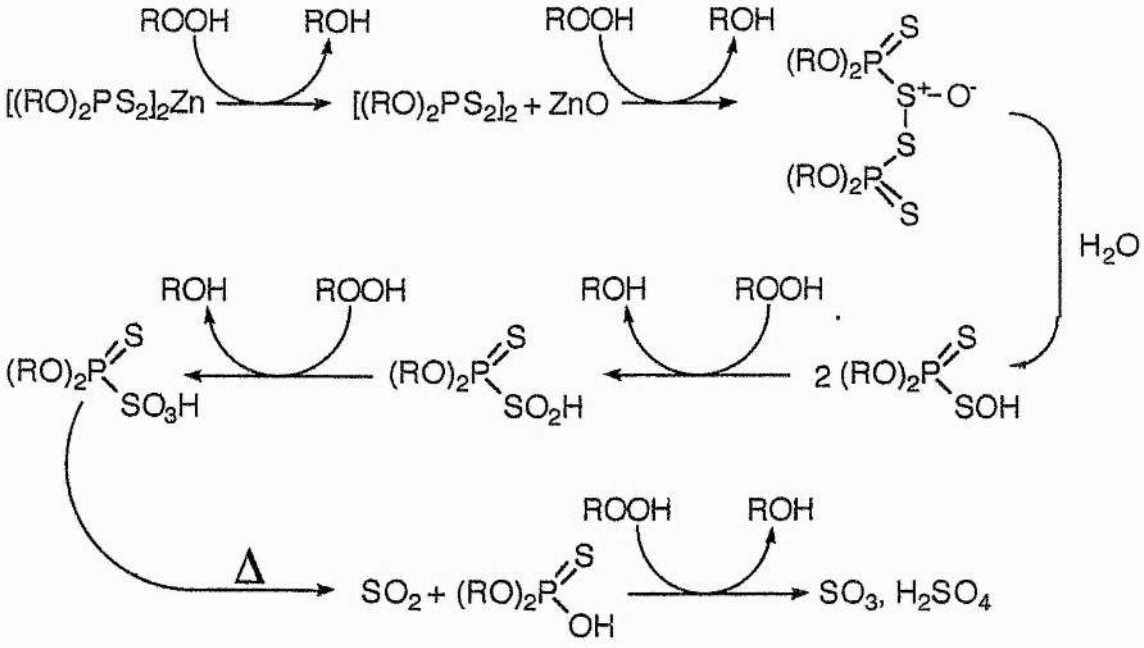


Scheme 1.26
Reduction of hydroperoxides
by sulphur compounds

Experimentally it has been found that 1 mole ZDDP is capable of decomposing up to 10,000 moles of cumene hydroperoxide. The products of this reaction are acetone and

phenol, which are also formed in the acid catalysed decomposition of cumene hydroperoxide.

To account for this it has been proposed that the ZDDP is oxidized stepwise through a variety of PS_xO_yH compounds to eventually give sulphuric acid which acts as the main catalytic antioxidant[20,21]. The phosphorus part of the molecule eventually end up as an inorganic phosphate.



Scheme 1.27
Oxidation of ZDDP's by hydroperoxides
to strong acids

Metal ion deactivators

Metal ion deactivators are generally diamines, amino acids, hydroxy acids or other bifunctional compounds, which are able to form a strong chelate complex with the metal ion and thus can trap it in a single oxidation state by preventing any interactions of the hydroperoxides with the metal centre[22,23].

Chain inhibitors

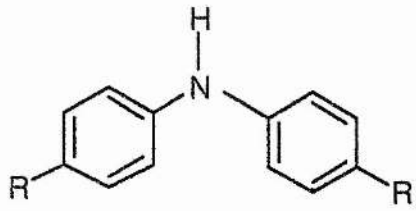
This class of antioxidants prevent oxidation by scavenging free radicals and so inhibit chain propagation. This can be achieved either by hydrogen transfer to the free radical:

$RO_2^{\cdot} + AH \rightarrow RO_2H + A^{\cdot}$

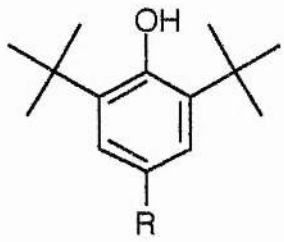
(The resulting radical based on the antioxidant has to be relatively stable and inert so it does not initiate further radical reactions .)
or by radical capture:

$RO_2^{\cdot} + A \rightarrow$ non radical products

Typical antioxidants of this type are 4,4'- disubstituted diarylamines:

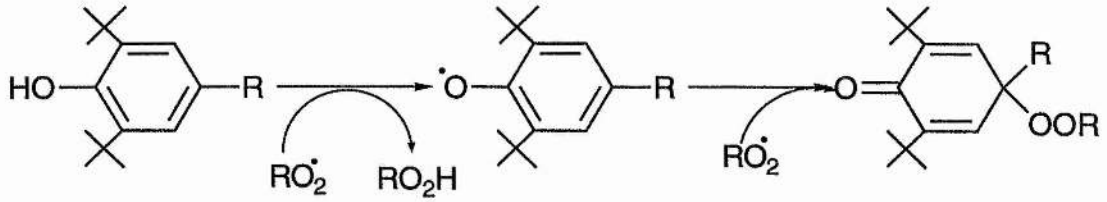


and 2,6-di-*tert*-butyl-4- substituted phenols:



The substituted phenols are able to trap two peroxyl radicals for each molecule of phenol. They first inhibit propagation by hydrogen transfer to the peroxyl radical. The phenoxyl radical can

then combine with a second peroxyl radical to give an inactive peroxycyclohexadieneone derivative[24].

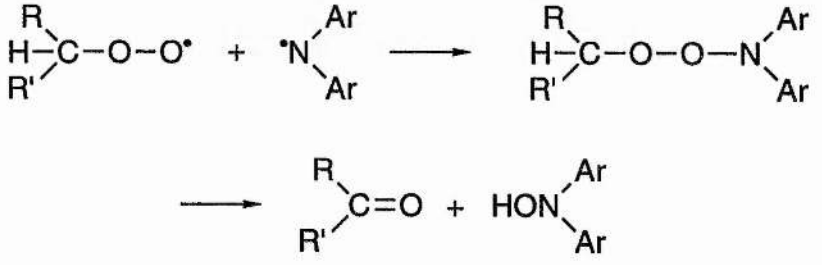


Scheme 1.28
Antioxidant action of
2,6-di-*tert*-butyl-4-substituted
phenols

Diarylamines also prevent propagation by hydrogen transfer to the peroxyl radical.

Scheme 1.29
Abstraction of the aminyl hydrogen
by peroxyl radicals

The resulting aminyl radical is able to react with a further peroxyl radical to give a ketone and a diarylhydroxylamine.

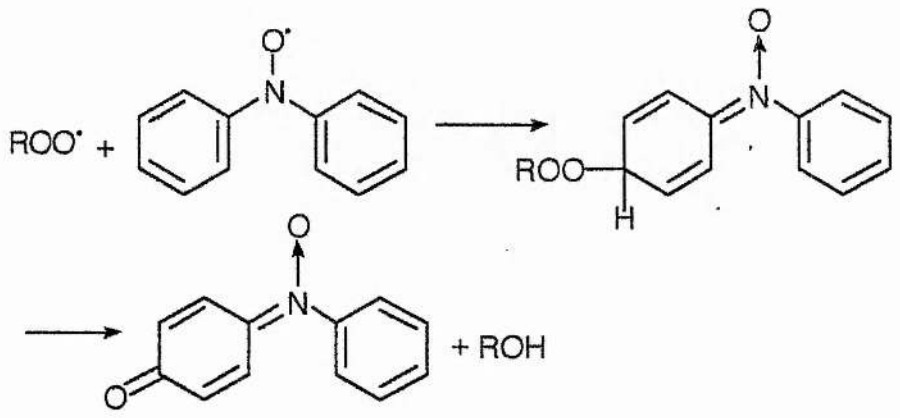


Scheme 1.30
Reaction between an aminyl
and peroxyl radical

The hydroxylamines are also effective antioxidants in that they readily donate hydrogen to free radicals.

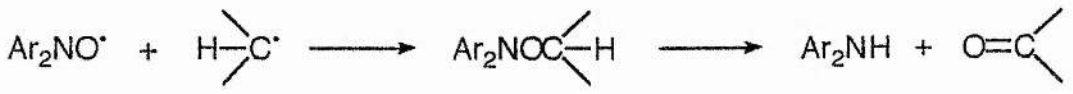
Scheme 1.31
Abstraction of the active hydrogen from
a hydroxylamines by a peroxyl radical

The nitroxide formed in this way can react with both alkyl and peroxyl radicals. With peroxyl radicals the product is an alcohol and *N*-phenyl-*o* or *p*-benzoquinoneimine-*N*-oxide.



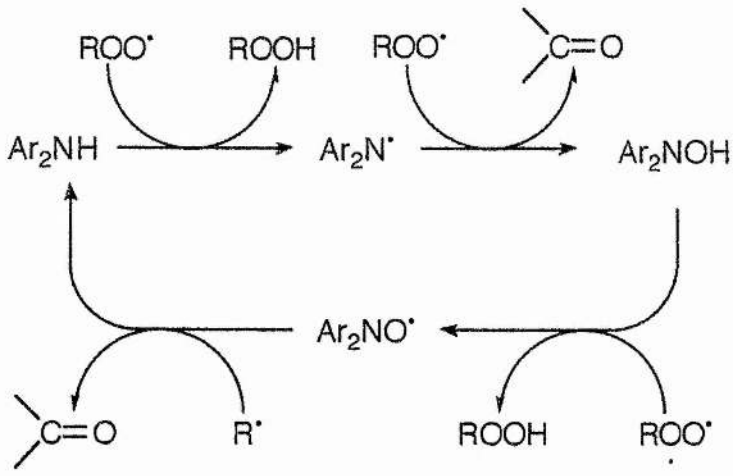
Scheme 1.32
Reaction of the diarylnitroxide
with a peroxyl radical

The nitroxides react with alkyl radicals to give amines and ketones in a disproportionation process[25].



Scheme 1.33
Reaction of a diarylnitroxide
with an alkyl radical

Diarylamines have been known to be able to destroy up to 3000 peroxyl radicals per molecule of amine. To account for the catalytic inhibitory activity of these amines a cyclic set of reactions can be set up which involves scavenging of both alkyl and peroxyl radicals[26].



Scheme 1.34
Reaction scheme for the catalytic action
of diarylamine antioxidants

Synergism

Within a lubricating oil all three types of antioxidants are used together. By preventing both the initiation and propagation reactions together, the overall effect of the antioxidants is greater than the sum of the protection afforded by each of the antioxidants singly.

1.8 Basestocks

As already discussed in section 1.3 the rate at which an autoxidation proceeds is dependant upon the strengths of the C-H bonds within the basestock.

The strongest C-H bonds are those of aromatic hydrocarbons which are therefore the most resistant to autoxidation. Their major drawback is that the high boiling point basestocks required for automotive use are solid at room temperature. However they do find limited use in jet engine lubrication.

The most resistant lubricants used in car engines are based on saturated hydrocarbons and pentaerythritol esters. Their only drawback is that in comparison to the more commonly used natural basestocks they are rather expensive, thus they are generally used in the highest quality lubricating oils.

For the large majority of lubricants though, natural basestocks are employed. They are mostly paraffinic in nature but they also contain a high proportion of alkyl aromatics, aromatic, organic sulphur and nitrogen compounds. As some of the components of these natural basestocks readily undergo autoxidation, it needs a careful choice of additives to turn them into suitable lubricants.

1.9 Engine development

The necessity for car manufacturers to remain competitive in the large automotive market, has continuously led to the development of more powerful, more economical and more environmentally friendly cars.

The maximum efficiency of any heat engine is limited by Carnot's equation[27]. It states that the maximum efficiency obtainable is equal to $1-T_C/T_H$, T_C being the temperature of the cold reservoir and T_H the temperature of the hot reservoir. For the internal combustion engine this translates to T_C being the temperature at the end of the power stroke and T_H the

temperature at its peak. To achieve greater efficiency either T_H can be raised or T_C decreased. T_H can be raised by increasing the compression ratio and by making the engine run at higher temperatures, or T_C can be decreased by making the power stroke longer than the compression stroke, thus achieving a greater volumetric efficiency.

Other developments in car manufacturing involve the re-emergence of the two-stroke engine. The advantages of a two stroke over the conventional four-stroke is the fact that every cylinder produces power at each engine revolution, whereas a conventional engine produces power every other revolution, hence a two-stroke will be more powerful than the same sized four-stroke engine. The major drawback of a two-stroke engine is that they generally produce more exhaust emissions.

Motor manufacturers are investigating all these possibilities, but the current trend is for hotter engines. The use of hotter engines means that greater oxidative stress is placed upon the lubricant. To keep servicing down to a reasonable level, lubricants have had to develop along with engine technology.

1.10 Lubricant development

Almost every new chemical produced is seen as a potential oil additive. To screen out the useful ones the new compound is dissolved in a series of standard test oils and subjected to a range of bench tests, these are used to evaluate the lubricant's ability to prevent wear, resist oxidation and retain it properties as a lubricant over a wide temperature range. Any useful compounds are given a code and tested with combinations of other oil additives to find a potentially marketable product.

If a lubricant formulation passes all the bench tests then it will be tried within an engine. The engine tests are used to simulate various types of driving, which range from 'start stop' driving normally associated with travelling short distances in a town to 'hard' motorway driving. To shorten test times the engines are run over an extreme temperature range and to speed up wear and tear, components are tightened up more firmly. After the tests the engines are completely stripped and the various components weighed and measured to determine wear and corrosion.

The ultimate tests for any lubricant are the field trials in which they are used within a road going car. The lubricant is regularly checked to ensure a proper performance. After it has passed this test, it is sent for independent trials.

The best known organisation for this is the American Petroleum Institute (A.P.I.), this organisation sets the standards for potential lubricants which are tested and then graded according to this quality. The current A.P.I. grading for petrol engine lubricants is 'SG' which will be superseded by 'SH'. For diesel engines the lubricants are presently given the grade 'CE' to again be superseded by 'CF'.

1.11 Oxidation bench tests

The Ercot

This test is designed to simulate conditions within an engine sump. The lubricant under test is heated to about 160°C and air is bubbled through it. To speed up the autoxidation process an iron catalyst is added. Samples are then removed at specified times and their viscosity is measured at a standard temperature. To

pass this test its viscosity must not increase by more than 25% after 96 hours.

Panel coker test

The panel coke test is designed to simulate conditions within the cylinders. The test involves heating an aluminium panel to 320°C onto which the test oil is then splashed for about an hour. The panel is then cooled, washed to remove any unreacted oil and weighed to determine the amount of material deposited. The panel is also visually rated, this involves dividing the panel into small sections and estimating the colour of deposits in each region. Thick, black deposits are given the worst rating and no deposit the best, the plate is then given an overall average rating.

Differential scanning calorimetry

In this test the lubricant is heated in a thin film on a metal plate in an oxygen atmosphere. Eventually the lubricant will start to oxidize uncontrollably which will be noticed as a sudden rise in temperature. The temperature at which this occurs can be used to evaluate the oil.

High temperature autoxidation

At temperatures of over 100°C the antioxidant's effectiveness begins to wane. There are a number of reasons for this. At higher temperatures the decomposition of the hydroperoxides occurs via a unimolecular process (see figure 1.2). Thus even if the peroxyl radical is trapped the resulting hydroperoxide decomposes rapidly to give radicals. The rapid decomposition of the hydroperoxides also means that peroxide decomposers will not have a lot of time to act. The formation of

radicals by the direct action of oxygen on the lubricant also becomes an important source of radical initiation.

At temperatures of over 180°C it has been observed that chain terminations involved alkyl rather than the peroxyl radicals indicating that the alkyl radicals were important as chain propagating spieces[81]. This could be explained by a combination of a low solubility of oxygen in the oil at these high temperatures, hence a low rate of oxygen transfer from the gas phase into the oil, and the reversibility of the reaction that forms the peroxyl radicals.

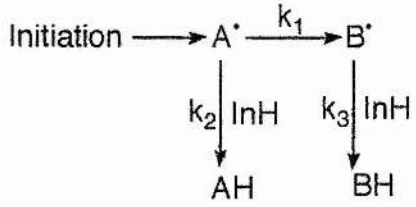
The autoxidation process can therefore be controlled if it was possible to find chain breaking antioxidants which efficiently trapped alkyl radicals, i.e. the reaction:

$$R^{\bullet} + AH \longrightarrow RH + A^{\bullet}$$

must be fast and if possible catalytic.

A new bench test for antioxidants?

To measure how effectively an alkyl radical can be trapped by an antioxidant we proposed to use a 'radical clock' rearrangement[31,32,33]. The basis of these radical clocks is the ability of some radicals to rearrange irreversibly. Once the alkyl radical has been formed, it can either react with the inhibitor, InH, or rearrange to form a second radical, which can also react with the inhibitor. The rate at which the alkyl radicals are trapped can be calculated from the ratio of unrearranged product to rearranged products, which can be conveniently determined using gas chromatography.



Scheme 1.35
Reaction of a radical clock
with an inhibitor

A major aim of this research was to develop a suitable radical clock and use it to measure the rate of hydrogen abstraction from a range of inhibitors based on diarylamine and hindered phenols. The information obtained can then be compared with existing information on these antioxidants and used to find the optimum high temperature lubricants.

1.12 Slow release antioxidants.

As a motor oil ages it uses up its reserves of antioxidants. One idea to extend its lifetime is to add various compounds in which the antioxidants are initially bound as inactive components which decompose during the lifetime of the lubricant releasing fresh antioxidants into the oil.

The antioxidants could be released from their bound state by acid hydrolysis, since acids are formed in the engine during its operation. The antioxidants might also be released by the thermolysis of suitable precursor molecules in the hot regions of the engine, this may have the added bonus of releasing antioxidants in the harshest environment within an engine.

A major aim of this research was to investigate potential slow release antioxidants. Compounds under consideration are

amides, diaryl-alkyl-amine oxides , *N*-alkylated diarylamines and *N*-diarylsiloxamines.

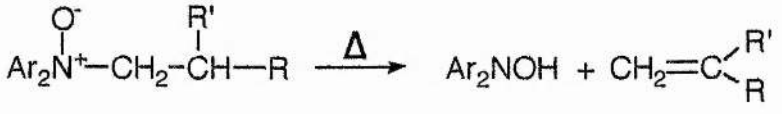
The amides and siloxamines are expected to be hydrolysed by acids which are formed while the the engine is running. The amides are expected to give the free diarylamine antioxidant and a carboxylic acid.[28]

Scheme 1.36
Hydrolysis of the amide

The siloxamine hydrolyses to again generate the free diarylamine and a silicone oil. The silicone oil has the added benefit of acting as an antifoamant.

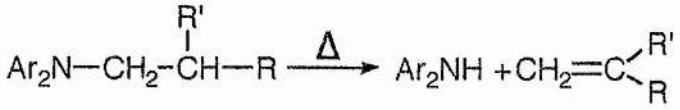
Scheme 1.37
Hydrolysis of the siloxamine

The diaryl-alkylamineoxides and the *N*-alkylated diarylamines are expected to release active antioxidants on thermal decomposition. The *N*-oxide decomposes to give an alkene and a hydroxylamine[29].



Scheme 1.38
Thermolysis of the *N*-oxides

The *N*-alkylated diarylamine will be expected to give an amine antioxidant.



Scheme 1.39
Thermolysis of *N*-alkyl diarylamines

Chapter 2

Measurement of the rate constants (k_H) for hydrogen abstractions from diarylamines by carbon centred radicals

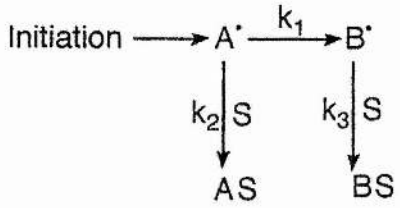
2.1 Aims

1. Measurement of the rate of hydrogen transfer from a 4,4'-disubstituted diphenylamine to an alkyl radical using a radical clock rearrangement.
2. To determine what effects differing functional groups have on the rate of hydrogen transfer.
3. If there are differences due to functionality, is there any correlation to σ values in a Hammett relationship?
4. To find if there is any correlation to the rate of hydrogen transfer from diarylamines to peroxyl radicals.

2.2 Kinetic measurements of radical molecule reactions

The rates of radical reactions can be measured using a variety of techniques. The general procedure for measuring these reactions is to fire a pulse of energy into the experimental mixture to generate the free radicals and then to follow the decay of these free radicals spectroscopically. Radical-molecule reactions are usually fast, which means that special equipment is required to measure them[30].

A cheap method for measuring the rate of some radical reactions is to use a 'radical clock'. The basis of these radical clocks is the ability of some radicals to rearrange irreversibly. If the rate of the rearrangement is known then the rate of a radical reaction can be calculated from the ratio of the rearranged to unrearranged products and the rate of the radical rearrangement.[31,32,33] The ratio of products can be determined using conventional techniques such as gas chromatography(GC).



Scheme 2.1
Ideal radical clock reaction

For example an initial radical A• can either react with a substrate S or rearrange to form a second radical B• which then reacts with S; the rate of the reaction between A and S can then be calculated from the ratio of unrearranged products, AS against rearranged products, BS assuming the rate of rearrangement is known (see appendix 1 for derivation).

For these experiments, the 5-hexenyl radical was initially chosen as the basis of the "clock". However this eventually proved to be unsatisfactory (see below) and the neophyl radical which rearranges by a 1,2-phenyl migration was selected. The activation energy and the Arrhenius pre-exponential factors have been documented for both reactions.

The 5-hexenyl radical rearrangement was to be used to study the hydrogen transfers between alkyl radicals and the antioxidants for temperatures ranging from 60 to 120°C and the neophyl radical rearrangement was to be used for temperatures above 150°C.

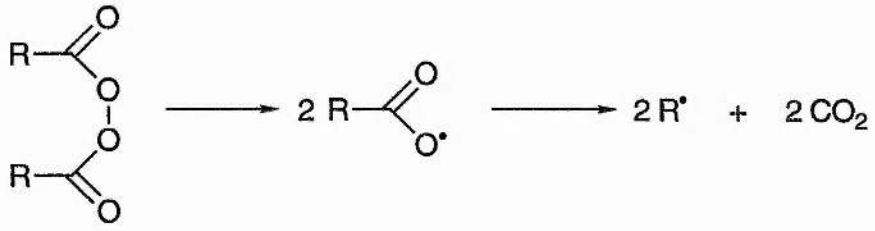
The kinetic experiments were to be run over a range of antioxidant concentrations, the rate of alkyl radical capture could then be calculated by plotting the antioxidant concentration against the radical clock ratio. By running these experiments over

a wide range of temperatures the Arrhenius A-factor and activation energy could be calculated.

2.3 Methods of thermally generating alkyl radicals

For the radical clock experiments the alkyl radicals were to be generated thermally. At temperatures above 150°C initiation was to be by halogen abstraction by tin centred radicals[34].

Initiation at lower temperatures was by the decomposition of the diacyl peroxide[35];



The latter decomposes to form acyloxyl radicals, which rapidly decarboxylate to form alkyl radicals and carbon dioxide.

2.4 Synthesis of diarylamines as test antioxidants

The test compounds for the experiments using the radical clock rearrangement were 4,4'-disubstituted diphenylamines. To test the effects of the *para*- substituents on the rate of hydrogen transfer from a diarylamine antioxidant to an alkyl radical, it was necessary to use functional groups with differing electronic properties. Differences in the efficiency of these antioxidants could be assessed and the results used for prediction purposes. For

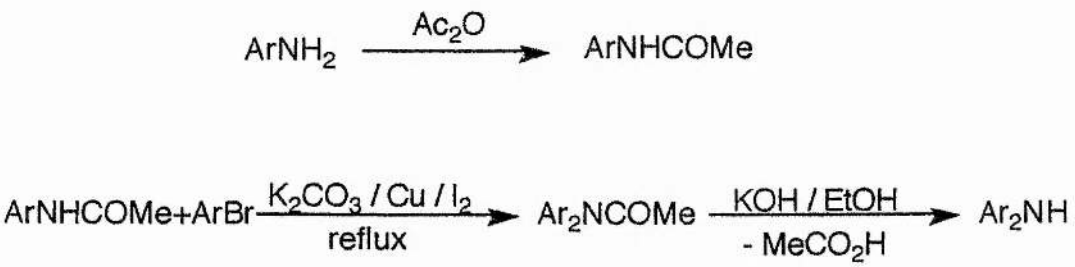
comparison purposes Naugalube 438L was also tested, which is a commercial antioxidant, consisting mostly of 4,4'-dinonyldiphenylamine.

The diarylamine test compounds were synthesized using two general methods;

1. The coupling of *para*- substituted anilines with other *para*-substituted aromatic compounds.
2. Aromatic electrophilic substitution on diphenylamine.

1. Coupling reactions

Coupling reactions were used to produce the 4,4'-dimethyl and the 4,4'-dimethoxy derivatives of diphenylamine. Both of these were conveniently prepared by the Goldberg reaction[36]. The synthesis firstly involved the conversion of the *para*- substituted aniline into its *N*- acetyl derivative, which was then refluxed with a *para*-substituted bromobenzene over potassium carbonate in the presence of a copper catalyst, which was activated with a few crystals of iodine. The diarylamine was then obtained by hydrolysis of the amide formed in this way. The amines were purified by distillation and recrystallization.



Scheme 2.2
Overall scheme for the Goldberg reaction

2. Electrophilic substitution

Aromatic electrophilic substitution was used to synthesize diarylamines with electron withdrawing substituents. Both dibromo- and dinitro-diphenylamines were prepared this way[37]. Due to the activating nature of the amine functional group, the electrophilic substitutions were carried out on the *N*-benzoyl derivative.

The dibromo compound was prepared by the action of bromine upon the amide in methylene chloride, this was then hydrolysed to give the amine.

$$Ph_2NCOPh \xrightarrow[CH_2Cl_2]{Br_2} (p\text{-}BrC_6H_4)_2NCOPh$$

$$\xrightarrow[-\ PhCO_2H]{KOH\ /\ EtOH} (p\text{-}BrC_6H_4)_2NH$$

Scheme 2.3
Overall scheme for bromination
of diphenylamine

Nitration of the amide was carried out in acetic acid using concentrated nitric acid as the nitrating agent. The amine was obtained by hydrolysis of the amide.

$$Ph_2NCOPh \xrightarrow[AcOH]{HNO_3} (p\text{-}O_2NC_6H_4)_2NCOPh$$

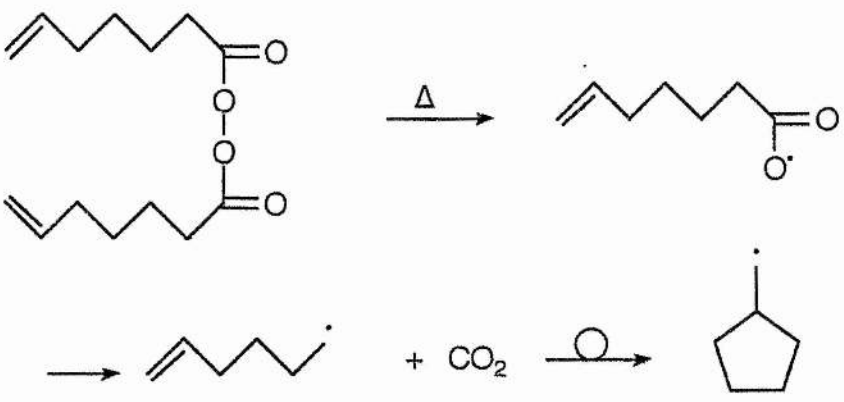
$$\xrightarrow[-\ PhCO_2H]{KOH\ /\ EtOH} (p\text{-}O_2NC_6H_4)_2NH$$

Scheme 2.4
Overall scheme for nitration
of diphenylamine

2.5 The 5-hexenyl radical clock rearrangement

At low temperatures the rate of hydrogen abstraction from the test compounds was to be measured using the 5-hexenyl radical rearrangement. When the 5-hexenyl radical is formed it can rearrange irreversibly to predominantly give the cyclopentylmethyl radical, a side reaction generates the cyclohexenyl radical in a yield of about 5%. This rearrangement has been extensively studied[31], to the effect that the activation energy and the Arrhenius pre-exponential factor are known. The activation energy for this reaction is 6.1kcal/mole and the log of the Arrhenius factor (s^{-1}) is 9.5.

For these experiments the 5-hexenyl radicals were generated by the decomposition of di-hept-6-enoyl peroxide.

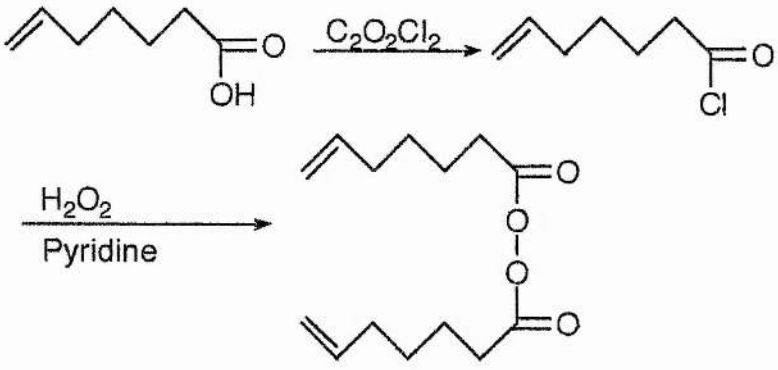


Scheme 2.6
Formation of 5-hexenyl radical
and its rearrangement

2.6 Synthesis of di-hept-6-enoyl peroxide

The di-hept-6-enoyl peroxide was synthesized from hept-6-enoic acid. The acid was converted to the acid chloride by treatment with oxalyl chloride in the usual way. The second stage

of this synthesis was the treatment of the acid chloride with hydrogen peroxide in pyridine to yield the diacylperoxide[55].

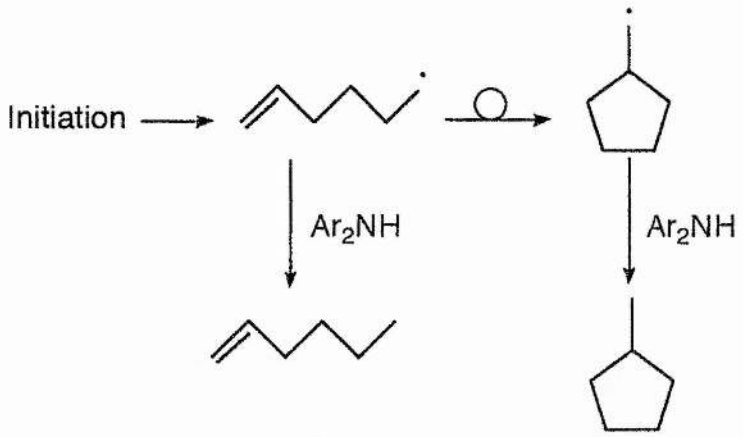


Scheme 2.7
Overall scheme for synthesis of
dihept-6-enoyl peroxide

2.7 Kinetic Measurements using the hexenyl clock

The kinetic measurements simply involved generating the 5-hexenyl radicals in the presence of the amine antioxidant. Once formed the 5-hexenyl radical could either abstract hydrogen from the antioxidant forming hex-1-ene or rearrange irreversibly to give the cyclopentylmethyl radical, which could also abstract hydrogen to form methylcyclopentane.

The rate of the radical rearrangement could be calculated from activation energy, the Arrhenius factor and the temperature of the experiment, hence the ratio of hex-1-ene to methylcyclopentane could be used to determine the rate of hydrogen abstraction from the antioxidants.



Scheme 2.8
Reaction scheme for the
kinetic experiments

Kinetic experiments

The initial experiments were carried out at 80°C using diphenylamine as the antioxidant. The concentration of the antioxidant was varied from 0 to 2.44 mol dm^{-3}. Analysis of the mixture was by GC and by GC with a mass spectrometric analysis (GC-MS)

2.8 Results using the hexenyl clock

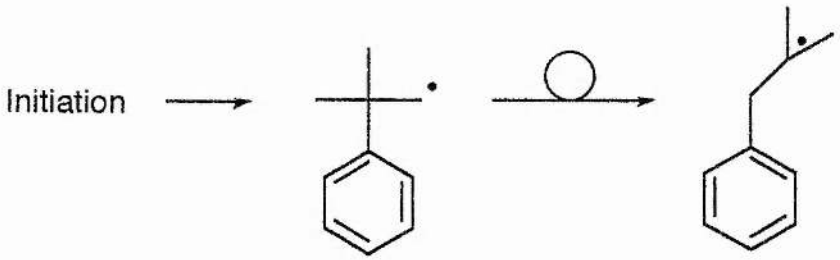
Analysis by GC gave four peaks with the approximate retention time expected for the products of the radical clock. GC-MS identification of the products was achieved by comparing the retention times and the mass spectra obtained from the reaction mixture with those of authentic samples. Using this method, only methylcyclopentane could be positively identified. The other peaks were diethylether, methylene chloride and hex-2-ene. Even at 2.44 mol dm^{-3} diphenylamine, hex-1-ene was formed in too small quantity for positive identification. Methylcyclopentane was by far the major product.

2.9 Conclusion from using the hexenyl clock

From the results obtained with the hexenyl clock, it appears that the hexenyl cyclisation was too rapid to enable the rate of hydrogen abstraction from diphenylamine to be measured.

2.10 Neophyl radical clock rearrangement

The neophyl radical once formed can rearrange irreversibly by means of a 1,2-phenyl shift to form a tertiary radical based on isobutylbenzene;



Scheme 2.9

Rearrangement of the neophyl radical

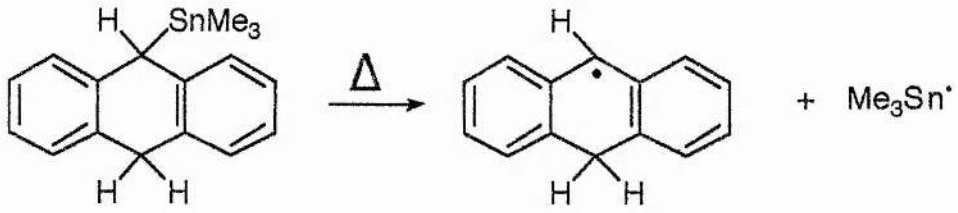
The rate of rearrangement can be calculated from the activation energy and the Arrhenius factor[38]. The most recent evaluation of the neophyl radical rearrangement gives log (A/s^{-1})= 10.98 and an activation energy of 10.83kcal mol^{-1}.

2.11 Initiation by tin centred radicals

Originally the neophyl radical rearrangement was to be used to measure the rate of hydrogen transfer between alkyl radicals and the antioxidants at temperatures above 150°C. These

reactions were to be initiated by the abstraction of a chlorine from 1-chloro-2-methyl-2-phenylpropane by a tin centred radical[34].

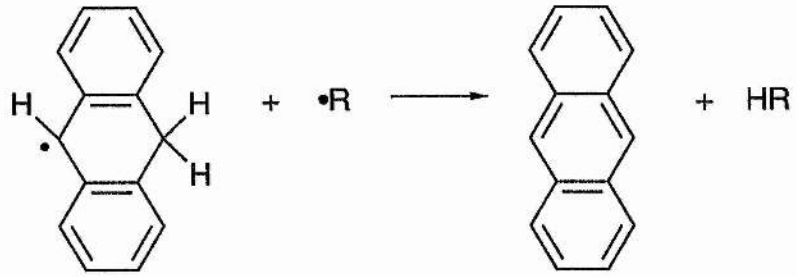
The initial source of tin radicals was the thermal decomposition of 9-trimethylstannyl - 9 , 10 - dihydroanthracene [34], its decomposition gives the trimethylstannyl radical and an alkyl radical based on 9,10-dihydroanthracene. The tin centred radical can then abstract the chlorine from 1-chloro-2-methyl-2-phenylpropane to give the neophyl radical.



Scheme 2.10
Generation of trimethylstannyl radicals from
9-trimethylstannyl-9,10-dihydroanthracene

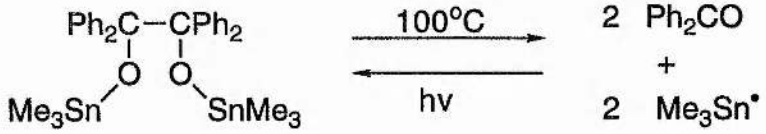
When a mixture of neophyl chloride and 9-trimethylstannyl - 9 , 10 - dihydroanthracene were heated together a 1:1 mixture of both rearranged and unrearranged products was obtained.

The unrearranged product should not form unless there is a source of abstractable hydrogen. A potential source is the the radical derived from the hydro-anthracene, this will readily donate a hydrogen to the neophyl radical to form anthracene and *tert*- butylbenzene.



Scheme 2.11
Disproportionation between the alkyl radical
based on 9,10-dihydroanthracene
and an alkyl radical

To overcome this problem another source of tin radicals was required, which did not interfere with the radical clock reactions. The most hopeful candidate was bis-trimethylstanylbenzpinacol. This was prepared by the photolysis of benzophenone with hexamethylditin. At temperatures above 100°C it decomposes to generate tin radicals and benzophenone. The benzophenone, however, takes no further part in any radical reactions[39].

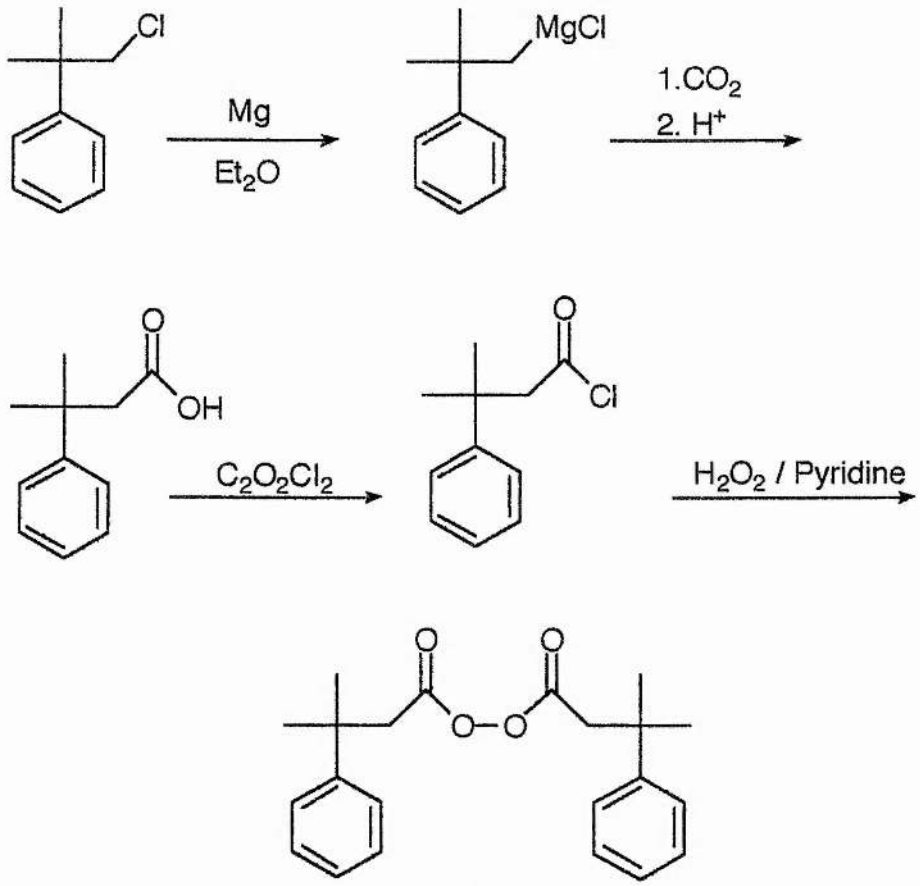


Scheme 2.11
Bis-trimethylstanylbenzpinacol as
a possible source of tin radicals

Only one attempt was made to synthesize this compound. When this proved unsuccessful we decided to test out the diacyl peroxide as the neophyl radical source. For these experiments radical initiation was by the decomposition of 3-methyl-3-phenylbutanoyl peroxide.

2.12 Synthesis of 3-methyl-3-phenylbutanoyl peroxide

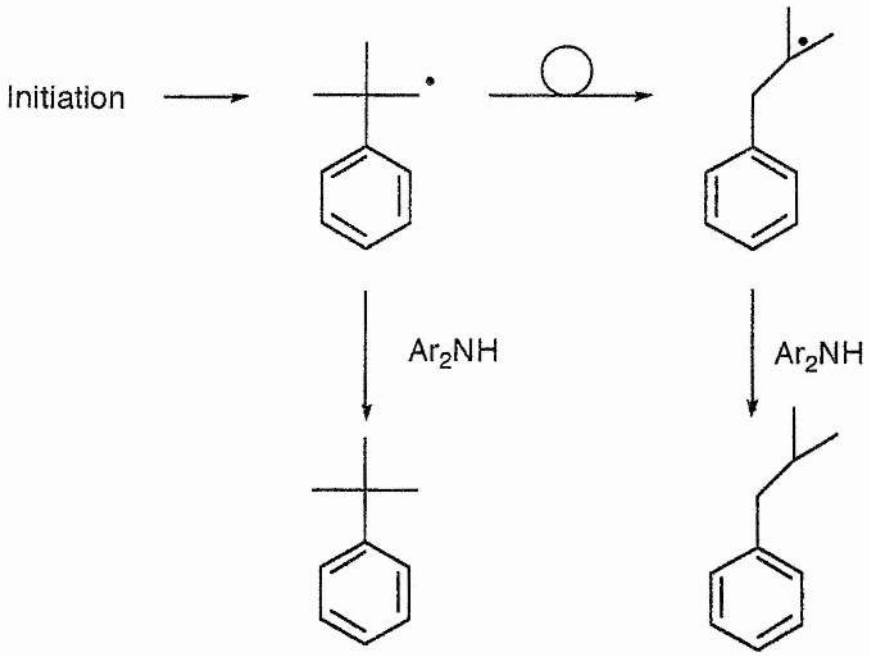
The starting material for this synthesis was 1-chloro-2-methyl-2-phenylpropane, more commonly known as neophyl chloride. The neophyl chloride was converted to the Grignard reagent by the action of magnesium[56]. Bubbling carbon dioxide gas through the Grignard reagent, followed by acidification, gave the corresponding carboxylic acid. Treatment of the acid with oxalyl chloride afforded the acid chloride, which was converted to the diacyl peroxide by the action of hydrogen peroxide in the presence of pyridine[55].



Scheme 2.12
Overall scheme for the synthesis of
3-methyl-3-phenylbutanoyl peroxide

2.13 Measurements of k_H using the neophyl radical clock

The kinetic measurements involved generating the neophyl radicals in the presence of the amine antioxidant. Once formed the neophyl radical could either abstract hydrogen from the antioxidant forming *tert* -butylbenzene or rearrange irreversibly to form the 2-phenyl-*t*- butyl radical, which could also abstract hydrogen to form *isobutylbenzene*.



Scheme 2.8
Neophyl radical
clock products

The rate of the radical rearrangement could be calculated from the known activation energy, Arrhenius factor and the temperature of the experiment, and hence the ratio of *tert* - butylbenzene to isobutylbenzene could be used to determine the rate of hydrogen abstraction from the antioxidants.

Analysis was again by GC and GC-MS, the products could be identified by comparison of GC retention times with those of the

authentic compounds and by GC-MS. Product identification was by the comparison of the mass spectra with those of the authentic standards.

2.14 Results of product analysis

Analysis of the radical clock reactions showed that along with the isomeric butylbenzenes expected from the neophyl rearrangement, significant amounts of 2-methyl-2-propenylbenzene were also being formed. The ratios of all three products were affected by changes in antioxidant concentration. The products of possible termination reactions between the alkyl radicals were sought but none were identified, this was possibly due to their signals being hidden by the solvent peak.

2.15 Effects of radical termination reactions upon k_H

Alkyl radical termination reactions are second order processes and so are dependant upon [Alkyl radicals]^2. For the sake of simplicity, a high concentration of antioxidant was used, in comparison to the concentration of radical initiator. Under these conditions the radical clock measurement is forced into a pseudo first order behaviour, dependant only on the concentration of the antioxidant. At high antioxidant concentrations the alkyl radicals are rapidly mopped up, hence the radical termination reactions should be of little importance.

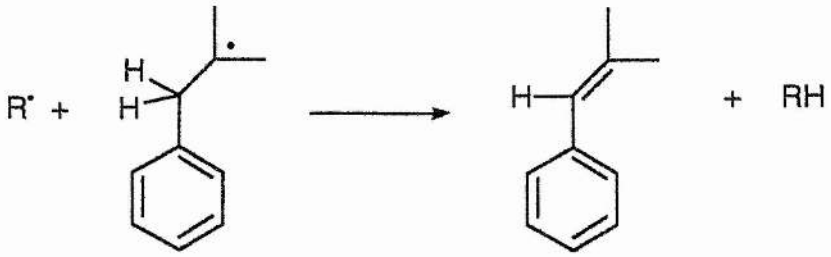
However during the initiation process, radical termination reactions are very likely. This is because the initiator molecule in solution is surrounded by solvent molecules, which in effect creates a 'solvent cage'. On decomposition the initiator produces a

pair of radicals close to each other within this solvent cage increasing the chances of termination reactions.

Although coupling reactions may be occuring within a solvent cage, they have no effect on the measurement of k_H since no isomeric butylbenzenes are formed. The termination reactions within the solvent cage do remove alkyl radicals from the reaction system, decreasing the amount of potentially available isomeric butylbenzenes.

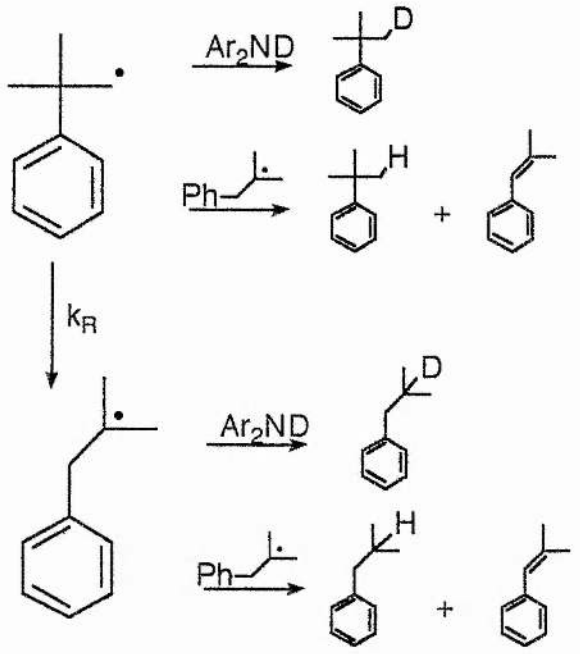
2.16 Alkene formation and its effects on the measurement of k_H

A possible mechanism for the formation of the alkene involves radical disproportionation, in which a benzylic proton is abstracted from the tertiary radical[40,41,42]. This is possible because the benzylic hydrogens are readily abstracted.



Scheme 2.9
The radical disproportionation reaction

Evidence for the disproportionation reaction was provided by running the neophyl radical clock experiments in the presence a deuteriated diphenylamine, which acted as the antioxidant.



Scheme 2.10
Radical 'clock' reactions
involving Ar_2ND

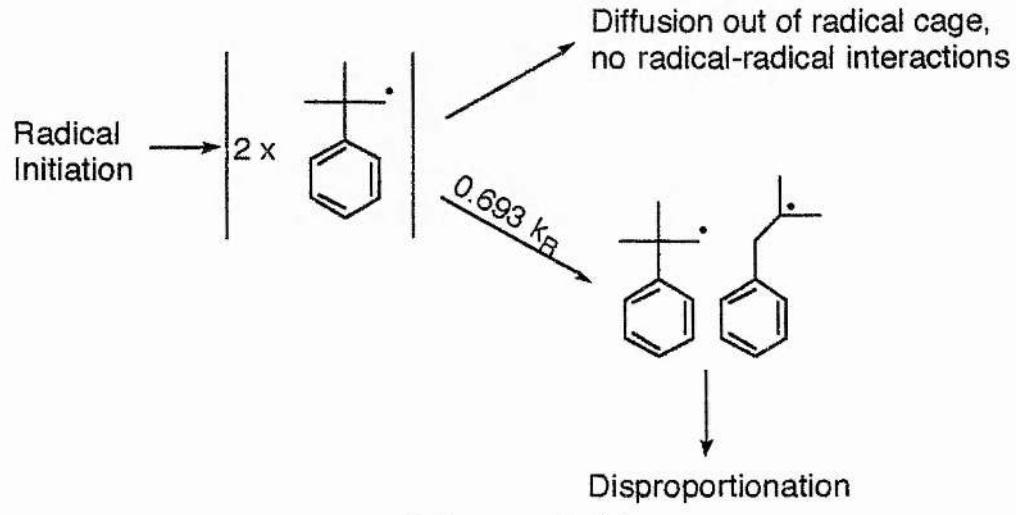
The scheme 2.10 shows that the abstraction of deuterium from the deuterodiphenylamine by the neophyl radical or the 2-phenyl-*t*- butyl radical derived from its rearrangement, will lead to products which contain 1 deuterium atom per molecule; the isomeric butylbenzenes thus obtained will have a mass of 135. The disproportionation reaction on the other hand, introduces hydrogen into the products of the neophyl radical clock rearrangement rather than deuterium, hence the derived isomeric butylbenzenes will have a mass of 134.

Product analysis by GC-MS showed two peaks for the *tert*-butylbenzene, one at Mr=134 and one at 135, this indicates that some of the *tert*- butylbenzene was formed by disproportionation and some was formed by abstraction of deuterium from the *N*-deuterodiphenylamine. The isobutylbenzene gave a peak at

Mr=135, this result showed that all the isobutylbenzene was formed by the abstraction of deuterium from the deuterodiphenylamine.

The disproportionation reaction generates extra *tert*-butylbenzene and converts the radical derived from the rearrangement of the neophyl radical into the alkene, this leads to a high estimate of the rate of hydrogen abstraction from the amine antioxidants. To compensate for the disproportionation reaction a new formula was derived for calculating k_H (appendix 2).

Although the concentration of alkyl radicals in these reactions was low, disproportionation may be favoured if the local concentration was high. The process of initiation generates a pair of radicals in close proximity to each other, increasing their chance of interaction, this would be exacerbated if the initiator molecule inhabited a solvent cage[43]. Upon initiation the radicals would occupy this cage increasing their chance of interaction.



Scheme 2.11
Possible routes the radicals may take

It may be possible to get an estimate of the cage lifetime from the radical clock products at zero antioxidant concentration. The radical initiation generated two neophyl radicals, while the two neophyl radicals co-exist within the radical cage no radical disproportionation can occur. After a period of time, one of these neophyl radicals rearranges to form the *tert*-radical based on isobutylbenzene. The rate at which the neophyl radical rearrangement k_R has been calculated at 43808 s^{-1} at 373K, hence:

$$\frac{d[\text{neophyl radical}]}{dt} = [\text{neophyl radical}]43808,$$

therefore;

$$\frac{d[\text{neophyl radical}]}{[\text{neophyl radical}]} = 43808\ dt$$

Upon integration this gives the relationship:

$$\{\ln[\text{neophyl radical}]\}_b^a = 43808t,$$

hence the average time taken for one of the pair of neophyl radicals to rearrange is

$$\ln 2 - \ln 1 = 43808t,$$

which gives a time of $1.6*10^{-5}$ s. Assuming that the disproportionation reaction is rapid compared to the lifetime of the solvent cage, and that all the *tert*-butylbenzene is formed by disproportionation within the solvent cage then an estimate of the rate at which these cages break up can be obtained. After $1.6*10^{-5}$ s the *tert*-butylbenzene made up 51.2% of the product, 48.8% of the radicals produced escaped from the cage to give other products. Assuming the breakup of the cage (k_b) was a first order reaction, the cage break up occurs at a rate of:

$$\frac{d[\text{solvent cage}]}{dt} = k_b[\text{solvent cage}],$$

therefore;

$$\frac{d[\text{solvent cage}]}{[\text{solvent cage}]} = k_b\, dt$$

Upon integration this gives the relationship:

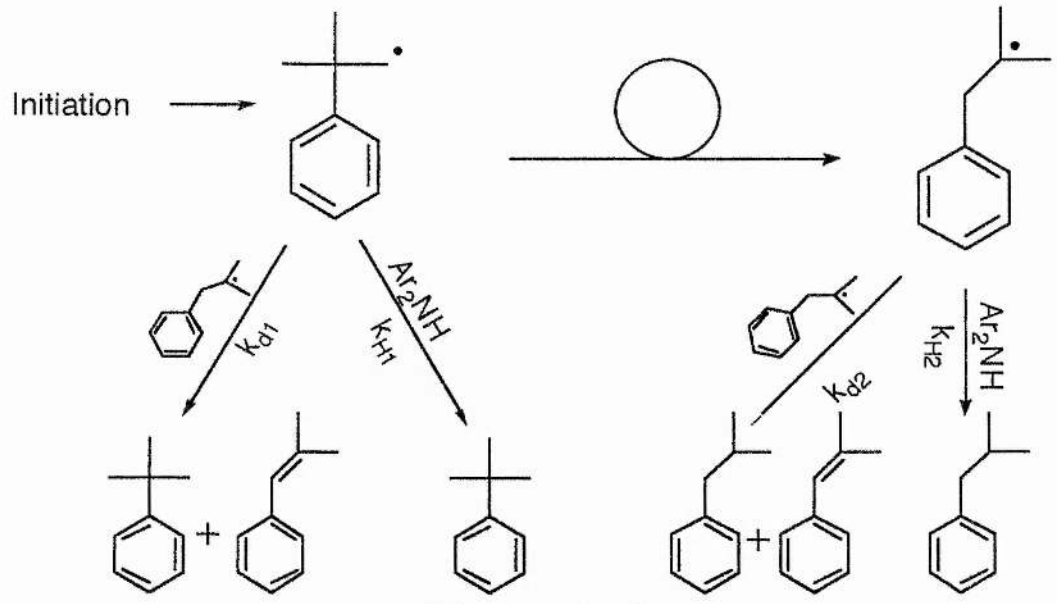
$$\{\ln[\text{solvent cage}]\}_b^a = \{k_b\, t\}_t^0,$$

$$\ln 100 - \ln 51.2 = k_b * 1.6 * 10^{-5}$$

which gives $k_b = 4.2 * 10^{4}\ s^{-1}$.

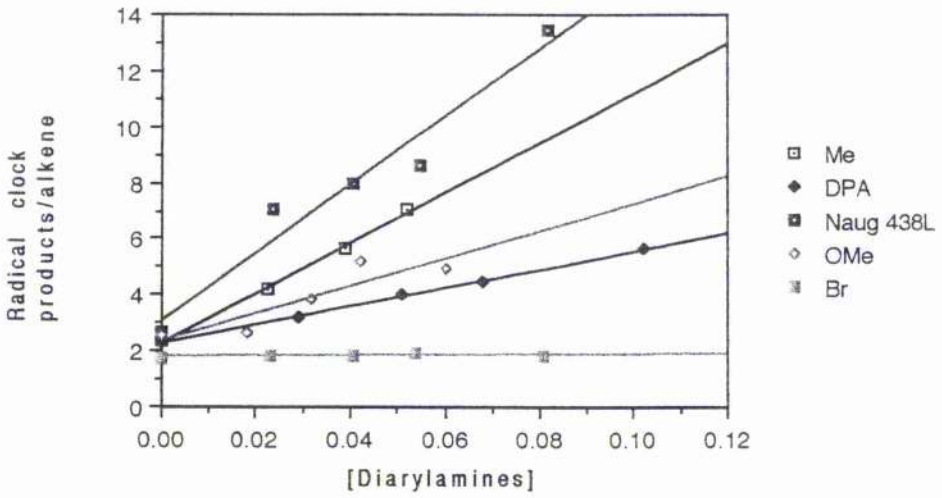
Although this method only works if radical termination reactions are unimportant in the solvent cage. For an accurate estimate of cage lifetime all the termination products need to be identified.

In the presence of a diarylamine antioxidant the alkyl radicals involved in the neophyl radical rearrangement can either undergo disproportionation or abstract the aminyl hydrogen from the diarylamines.



Scheme 2.12
Scheme of possible reactions in the radical clock experiments

The disproportionation reaction is competitive with the abstraction of the aminyl hydrogen from the diarylamines, so increasing the rate of hydrogen abstraction will be at the expense of alkene formation. The rate of hydrogen abstraction can be enhanced by increasing the concentration of the diarylamine. The graph below shows the effect of amine concentration upon the proportion of alkene in the radical clock products.

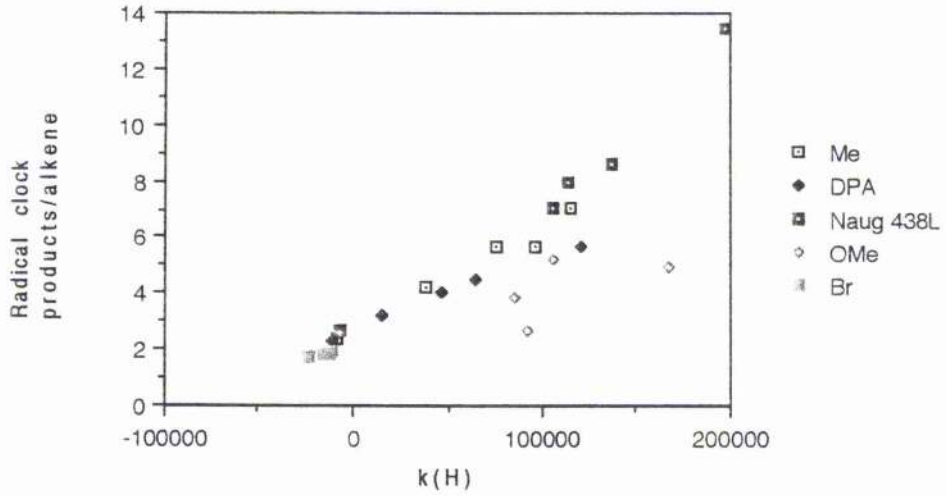


Graph 2.1
Relationship between alkene formation and [Diarylamine] at 373K

The graph 2.1 proves that by increasing the concentration of the diarylamines, the proportion of alkene in the radical clock products decreases. One obvious exception to this trend occured when 4,4'-dibromodiphenylamine was used as the antioxidant. As its concentration was increased so the proportion of alkene formed also increased slightly; indicating that a different mechanism may be operating in tandem with disproportionation.

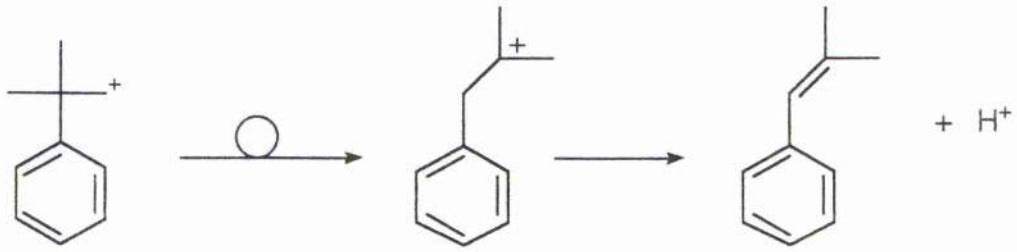
The graph 2.2 shows that the actual formation of the alkene was dependant upon the rate of hydrogen transfer, which is a

function of the concentration of the diarylamine antioxidant and its efficiency at trapping the alkyl radicals derived from the neophyl radical rearrangement.



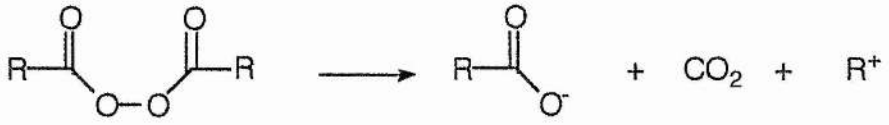
Graph 2.2
Relationship between k_H
and alkene formation

The results obtained from graph 2.1 showed that the 4,4'-dibromodiphenylamine was producing a large excess of the alkene. The most plausible explanation is that the alkene was also being formed via a cationic route. If the neophyl cation can form, it is able to rearrange to give a tertiary cation. Elimination of a benzylic proton gives the alkene.



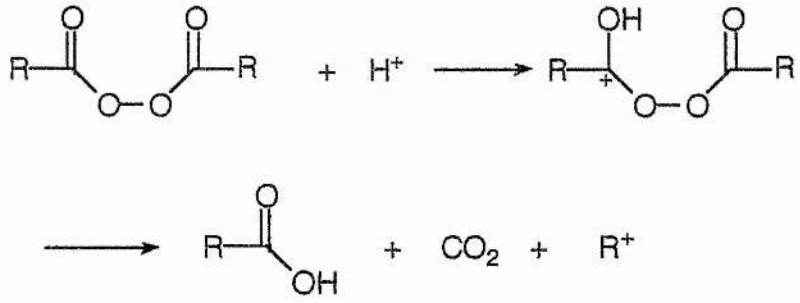
Scheme 2.10
Alkene formation via the
carbocation

A possible mechanisms for carbocation formation involves the heterolytic decomposition of the diacylperoxide[45,46,47].



Scheme 2.11
Heterolytic decomposition of
the diacylperoxide

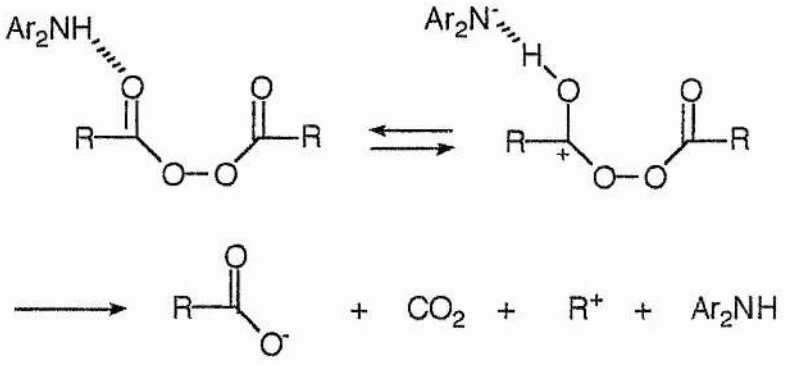
This reaction is known to be catalysed by acids[13,14].



Scheme 2.12
Acid catalysed decomposition of
diacylperoxides

Experimentally it was found that amines with electron withdrawing substituents in the *para* position i.e the 4,4'-dibromodiphenylamine formed a higher proportion of the alkene. A possible reason for this is that these amines are more capable of catalysing the heterolytic decomposition of the diacylperoxides, with the amines developing some negative charge which is stabilised by electron withdrawing substituents. Although not as potent as strong acids, the particular amine antioxidants may be

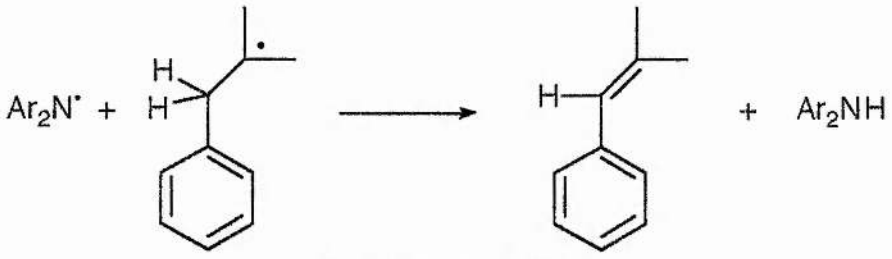
capable of catalysing the heterolytic decomposition of the diacylperoxides via the same general mechanism.



Scheme 2.13
A possible mechanism by which amine antioxidants can induce the heterolytic scission of the peroxide bond

Alkene that was formed via a non radical pathway, will not affect the radical clock calculations.

The alkene may also be formed if the aminyl radical is able to remove the benzylic proton from the *tert* - radical.



Scheme 2.14
Radical disproportionation between the aminyl and tert radical

This reaction is more likely with the less effective amine antioxidants. This reaction was assumed to be unimportant since the aminyl radical was only present in small amounts when

compared to the diarylamine concentration. The amount of alkene formed by disproportionation and via the carbocation cannot be distinguished. For most of the amines this was unimportant, but for the 4,4'-dibromodiphenylamine it was necessary to be able estimate the amount of alkene formed by disproportionation.

The results from the experiments run with the deuterodiphenylamine showed that all the isobutylbenzene was formed by the abstraction of deuterium. Since none was formed by disproportionation it served as a useful basis for estimating the amount of disproportionation. A series of graphs were prepared in which the ratio of (*tert*- butylbenzene / isobutylbenzene) was plotted against (alkene / isobutylbenzene). From these plots the following results were obtained. At 100°C $y=1.25 + 5.1*10^{-2}x$, at 80°C $y=1.33 +1.25*10^{-2}x$ and at 60°C $y= 1.75 + 7.16*10^{-2}x$, where x=(*tert*- butylbenzene / isobutylbenzene) and y = (alkene / isobutylbenzene). Since x had a maximum value of around 3 and the correlation was poor, the ratio of alkene to isobutylbenzene was assumed to be the constant obtained from the graphs. The amount of alkene formed by disproportionation was then calculated by multiplying the amount of the isobutylbenzene by this constant.

2.17 Neophyl radical clock results

The rate at which alkyl radicals could abstract the aminyl hydrogen from diarylamine antioxidants was calculated using an equation which accounted for the radical disproportionation. #(see appendix 2 at the end of this chapter for derivation and assumptions). For the 4,4'-dibromodiphenylamine compound the amount of alkene formed by disproportionation at each

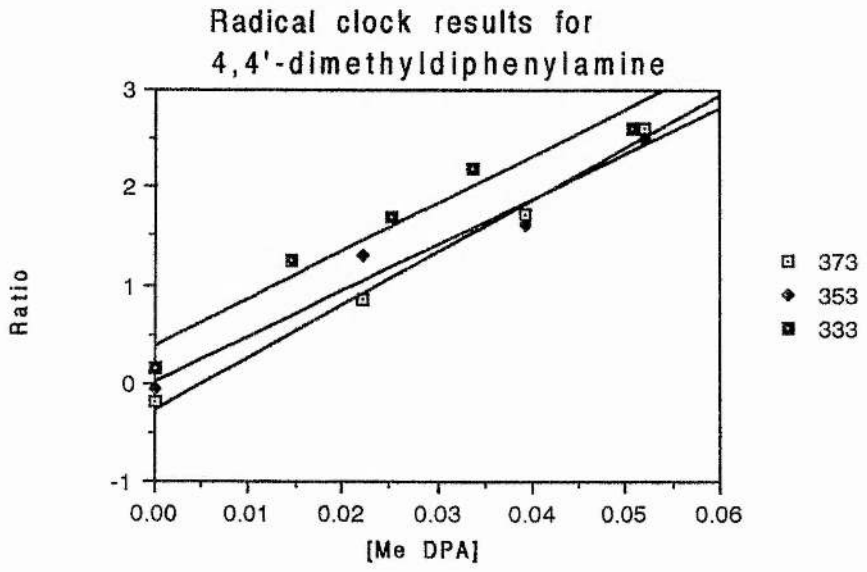
temperature was estimated by multiplying the amount of isobutylbenzene by the constants derived at the end of the previous section.

The major source of error was that it was impossible to know how much of the alkene product was formed by disproportionation and how much by other mechanisms. For the Arrhenius plots, an upper limit was obtained by assuming that all the alkene was formed via the carbocation. The lower limit assumes that all the alkene was formed by disproportionation between the neophyl and tertiary radicals. The results for $\log(A/s^{-1})$ and the activation energy were obtained from the lower limits only, except for the 4,4'-dibromodiphenylamine for which the extent of the disproportionation reaction was estimated.

Other sources of error include the temperature of the experiment. It was found that the oven temperature in which the experiments took place was accurate to within + or- 5°C or around 1%.

The analysis also suffered. The main problem was that the peaks for the isomeric butylbenzenes and the alkene overlapped to some extent, especially if one of the peaks was large in comparison to the others. Errors in the estimates of k_H from the GC results were about 1 or 2%.

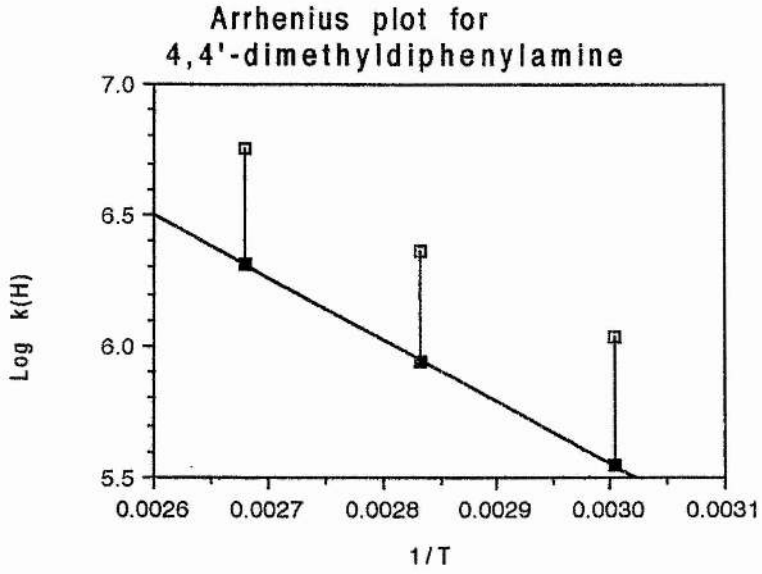
The errors shown in the results were derived from errors in the temperature and in the calculation of k_H.



373K $k_H = 2.3*10^6\ M^{-1}\ s^{-1}$

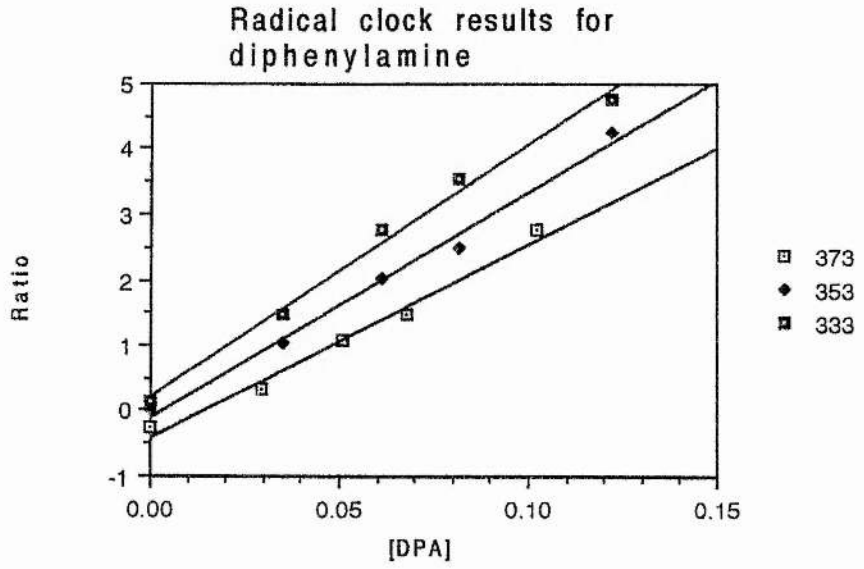
353K $k_H = 8.7*10^5\ M^{-1}\ s^{-1}$

333K $k_H = 3.6*10^5\ M^{-1}\ s^{-1}$



$\log(A/M^{-1}s^{-1}) = 12.8 +/- 2.2$

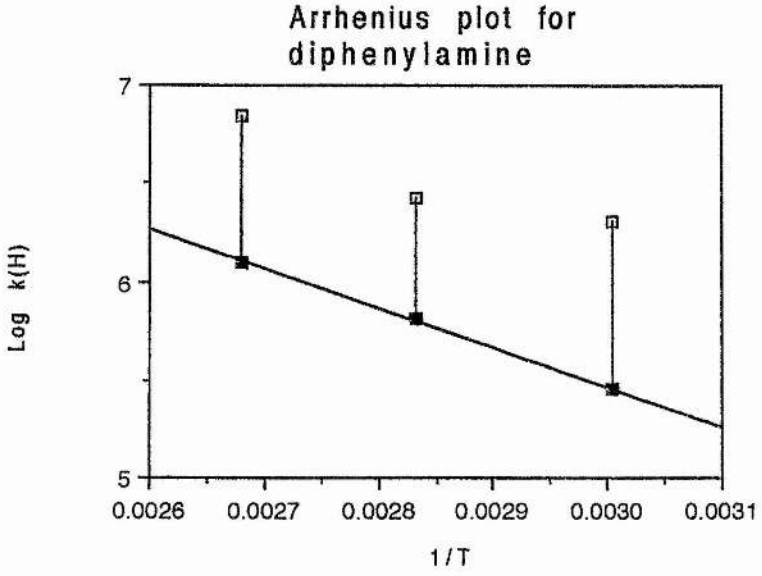
$Ea = 11.0 +/-3.6$ kcal mol^{-1}



373K $k_H = 1.3*10^6\ M^{-1}\ s^{-1}$

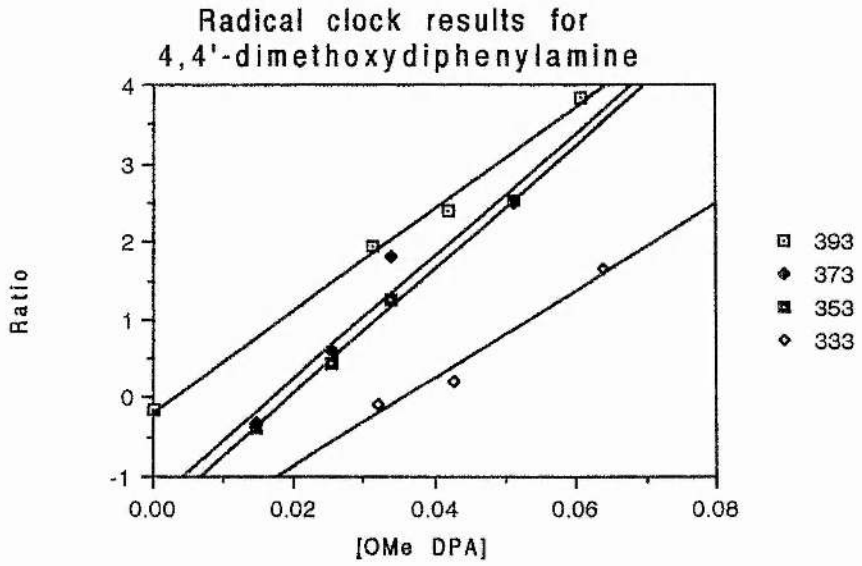
353K $k_H = 6.5*10^5\ M^{-1}\ s^{-1}$

333K $k_H = 2.9*10^5\ M^{-1}\ s^{-1}$



$\log(A/M^{-1}s^{-1}) = 11.5 +/- 1.9$

$E_a = 9.2 +/- 3.1$ kcal mol^{-1}

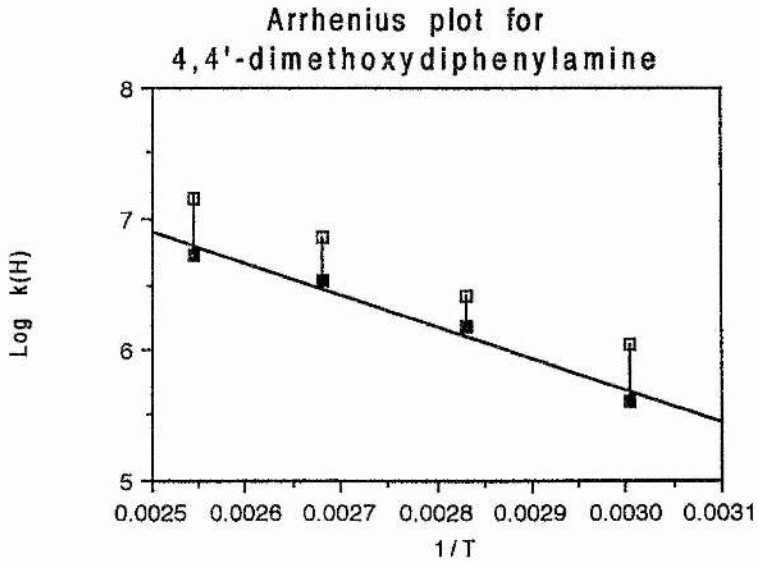


393K $k_H = 5.8*10^6\ M^{-1}\ s^{-1}$

373K $k_H = 3.4*10^6\ M^{-1}\ s^{-1}$

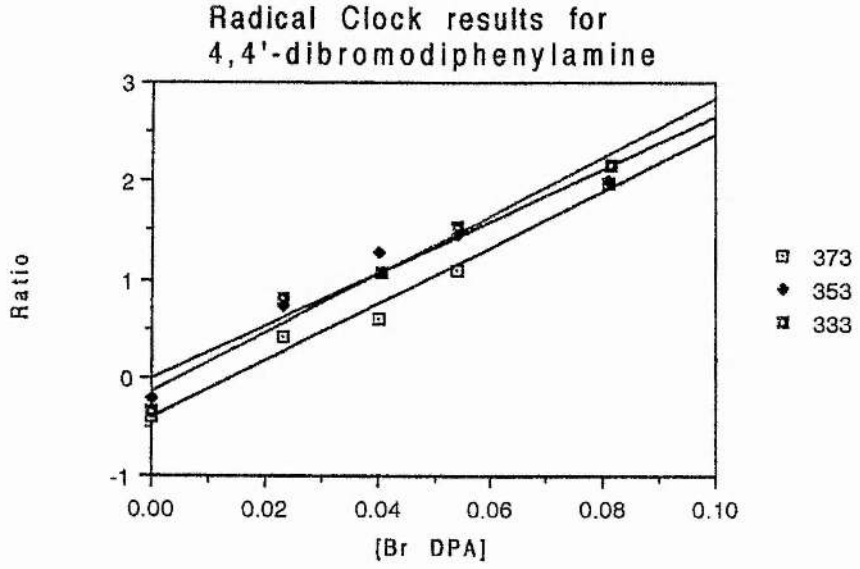
353K $k_H = 1.5*10^6\ M^{-1}\ s^{-1}$

333K $k_H = 4.1*10^5\ M^{-1}\ s^{-1}$



$\log (A/M^{-1}s^{-1}) = 13.2 +/- 1.5$

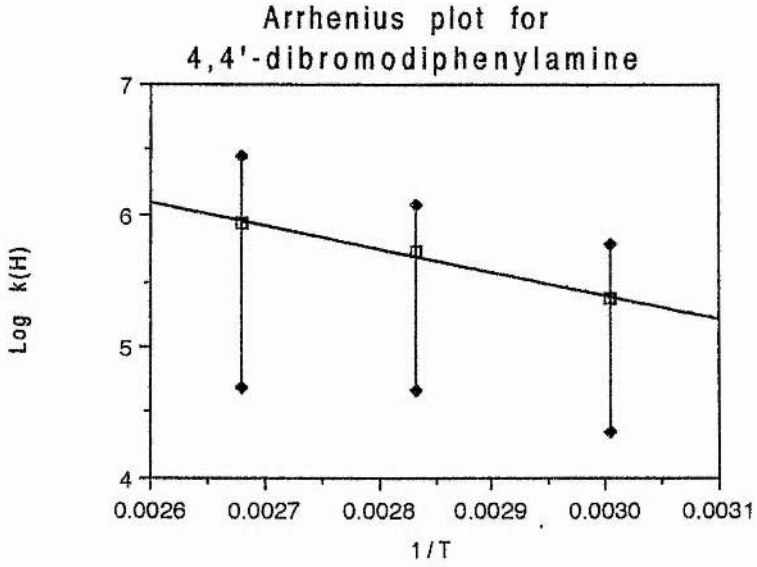
$Ea = 11.5 +/- 1.8$ kcal mol^{-1}



373K $k_H = 8.8*10^5\ M^{-1}\ s^{-1}$

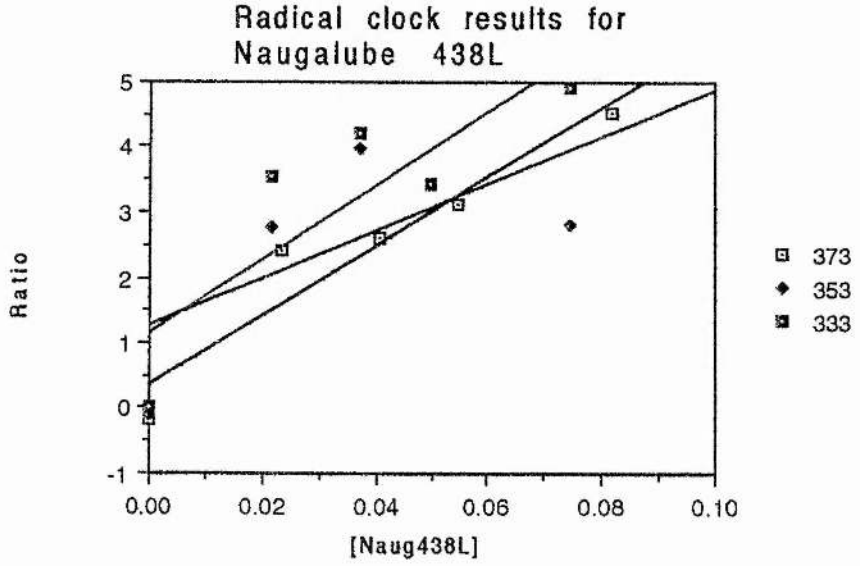
353K $k_H = 5.3*10^5\ M^{-1}\ s^{-1}$

333K $k_H = 2.4*10^5\ M^{-1}\ s^{-1}$



$\log(A/M^{-1}s^{-1}) = 10.8 +/- 2.2$

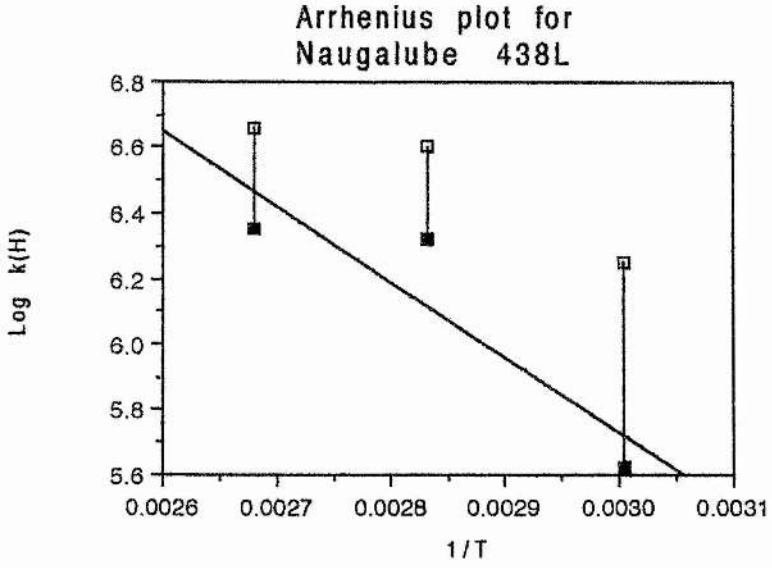
$Ea = 8.2 +/- 3.4$ kcal mol^{-1}



373K $k_H = 2.3*10^6\ M^{-1}\ s^{-1}$

353K $k_H = 6.8*10^5\ M^{-1}\ s^{-1}$

333K $k_H = 4.2*10^5\ M^{-1}\ s^{-1}$

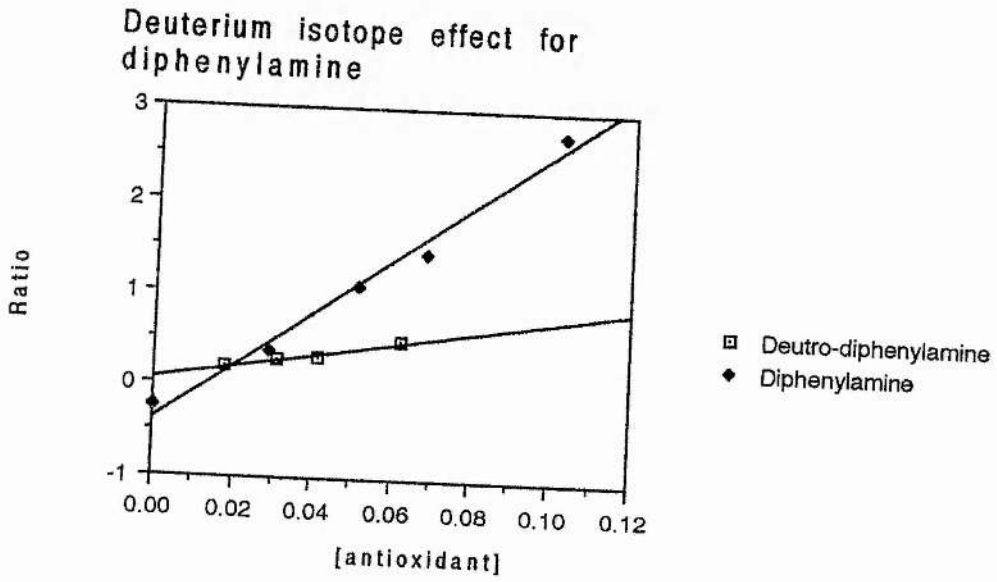


$\log (A/M^{-1}s^{-1}) = 12.3 +/- 2.5$

$Ea = 10.3 +/- 4.3$ kcal mol^{-1}

Deuterium isotope effect

The *N*-deuterodiphenylamine was prepared from triply recrystallized diphenylamine. This was dissolved in dodecane and the resulting solution shaken and then stored over 99.8% deuterium oxide. The experiments involved taking 1ml of this solution and diluting it down to the required concentration, 1ml of the peroxide solution was added, the whole reaction was carried out in the presence of a drop of deuterium oxide. The isotope effect was determined from the ratio of the rate of hydrogen abstraction from diphenylamine k_H to the rate of deuterium abstraction from deuterodiphenylamine k_D.



Deuterium isotope effect k_H/k_D= 4.4 for diphenylamine at 373K

2.18 Summary of the results and discussion

$k_H * 10^{-5}$ $M^{-1}s^{-1}$

Amine	k_H 373K	k_H 353K	k_H 333K	Log(A/ $M^{-1}s^{-1}$)	Ea Kcal mol^{-1}	k_H/k_D
OMe	34	23	4.1	13.2 +/-1.5	11.5 +/- 1.8	-
Me	23	8.7	3.6	12.8 +/-2.2	11 +/-3.6	-
H	13	6.8	4.2	11.5 +/-1.9	9.2 +/-3.1	4.4
Br	8.8	5.3	2.4	10.8 +/-2.2	8.2 +/-3.4	-
Naug 438L	23	6.8	4.2	12.3 +/-2.5	12.3 +/-4.3	-

From the table above, amine antioxidants with electron releasing substituents in the para positions were the most efficient at trapping alkyl radicals.

What was unusual about these results was that the reaction which had the lowest, experimentally measured activation energy also had the lowest A factor.

The rate of a chemical reaction $k= Ae^{-Ea/RT}$. The A factor is a measure of how often the reactants interact. Of these only the interactions with an energy higher than the activation energy will react. The proportion of molecules with this amount of energy is dependant upon the temperature.

The experimental results gave log A factors ranging from 10.8 for the 4,4'-dibromodiphenylamine to 13.2 for the para methoxy derivative which indicates that the aminyl hydrogen of

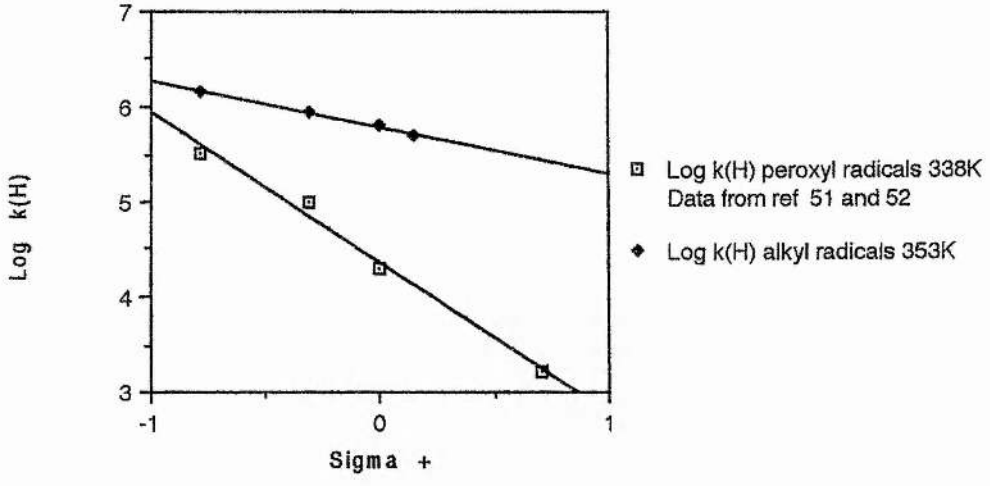
the methoxy derivative interacts more effectively with neophyl radical in comparison to the similar interactions with 4,4'-dibromodiphenylamine.

In the reaction mixture the amount of steric hindrance about the aminyl group is approximately the same for all the amine antioxidants tested, therefore the A factors would be approximately the same if this was the only factor. The unusual results could be simply due to experimental error in extrapolation, which in turn is due to the experiments being carried out over such a narrow temperature range.

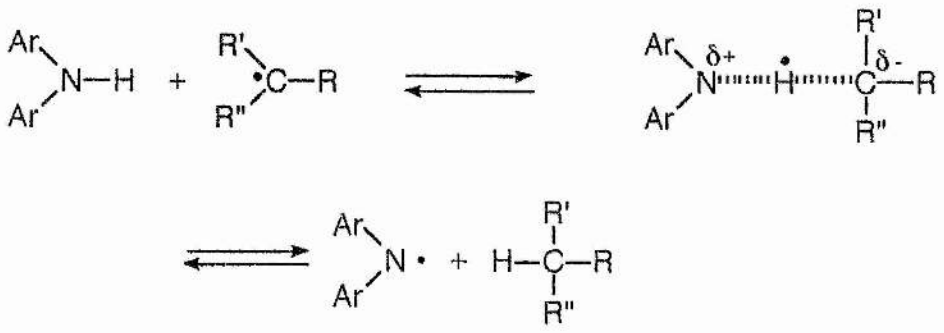
If the A factors are about right then electronic effects must be responsible for the differences in the A factors. Alkyl radicals are slightly nucleophilic and so are naturally attracted to areas of low electron density. The N-H bond in diarylamine antioxidants is polar, with the hydrogen taking on a partial positive charge, i.e it is a region of low electron density. Electron density can be removed from the N-H bond by placing electron withdrawing substituents in the *para* position. This should make the aminyl hydrogen more attractive to alkyl radicals. However the nitrogen is attached directly to the aromatic rings and so will be more strongly influenced by the electronic effects of substituents in the aromatic ring, therefore the presence of electron withdrawing substituents in the *para* position will preferentially remove electron density away from the nitrogen. The decrease of electron density on the nitrogen in comparison to the aminyl hydrogen will decrease the dipole moment of the N-H bond making the aminyl hydrogen less attractive to alkyl radicals.

2.19 Hammett relationship

The Hammett relation links the rate of a chemical reaction to the electronic effects of the functional groups. The equation states that log $k/k_0 = \sigma\rho$ where k is the rate of the reaction with a functional group present, k_0 is the rate of the reaction with no functionality, σ is a value assigned to the effect of the functional group present and ρ the susceptibility of the reaction to these effects.



A correlation was found between the rate of hydrogen abstraction by alkyl radicals and H.C.Brown's σ^+ values[77]. The susceptibility ρ was measured at -0.49 at 353K. The relationship between σ^+ and k_H may be used to predict the rate at which alkyl radicals will be trapped by 4,4'-disubstituted diphenylamines assuming the σ^+ value is known for the substituents. The correlation with σ^+ also indicates that there is some charge separation within the transition state, with a partial positive charge developing on the nitrogen, which would be stabilised by electron donating groups.



Scheme 2.15
Abstraction of an aminyl hydrogen
by alkyl radicals

2.20 Comparison with literature results
for peroxyl radicals

The rate at which peroxyl radicals abstract hydrogen from diarylamines was found to be dependant upon the nature of the attacking radical. At 323K the rate of hydrogen abstraction from 4,4'-dimethoxydiphenylamine varies from $1.5*10^6$ M^{-1} s^{-1} for a peroxy radical based on N,N-dimethylcyclohexylamine[48] to $1.2*10^4$ $M^{-1}s^{-1}$ for one based on dimethylaminoethylmethacrylate [49]. At the same temperature the abstraction of hydrogen by the neophyl radical was calculated to be $1.8*10^5$ M^{-1} s^{-1}. The benzylic peroxyl radical based on ethylbenzene abstracts hydrogen from diphenylamine at a rate of $4.4*10^4$ $M^{-1}s^{-1}$ at 333K [50], for the neophyl radical at the same temperature this rate was measured at $2.9*10^5$ $M^{-1}s^{-1}$.

A series of 4,4'-disubstituted diphenylamine inhibitors were tested in the oxidation of styrene at 338K[51,52] from which a Hammett plot was made; again there was a good correlation with σ^+ values for the functional groups. The deuterium isotope effect was found to be 3 for diphenylamine and 1.32 for the *para*

dimethoxy derivative. The rates of hydrogen abstraction by peroxyl radicals derived from styrene, were found to be more susceptible to polar effects with $\rho = -1.6$, indicating that more charge separation occurs in the transition state than with the alkyl radicals. This may be due to the electronegative nature of the oxygen in the peroxyl radical in comparison to the carbon in the alkyl radical. The nitrogen develops a positive charge which is stabilised by electron donating substituents.

The best high temperature diarylamine antioxidant ?

The results from the radical clock experiments show that 4,4'-dimethoxydiphenylamine was the most efficient, of the amines tested at trapping alkyl radicals. The efficiency of the antioxidant at trapping alkyl radicals was found to correlate with the σ^+ values of the substituents in the 4-position. The susceptibility was found to be negative. The similar correlation was found when 4,4'-disubstituted diarylamines were used for trapping peroxyl radicals, therefore the best high temperature antioxidant would be expected to be the diarylamines in which the *para* substituents had low σ^+ values.

2.21 Synthesis and experimental

Measurement of k_H

The kinetic experiments were carried out in resealable glass tubes which could be attached to a gas line. The solvent used for these reactions was n-dodecane which had any polar impurities removed by passing it through an aluminium oxide column.

The procedure involved taking 1ml of a standard solution of the radical source and 1ml of a standard solution of the antioxidant and diluting the solution with known amounts of solvent. The mixture was degassed by a freeze, pump, thaw cycle. The experiments were carried out under nitrogen at a few Torr of pressure.

The reactions were carried out five at a time, within the same heating environment at a preset temperature. The samples were heated for three to five days to ensure complete peroxide conversion. The oven used for these experiments was a Pye-Unicam GC oven.

Analysis was generally by GC, using a 5 metre column. The stationary phase was OV 101 at 10% loading, the mobile phase was nitrogen at a pressure of 11p.s.i.. GC analysis was carried out at 95°C using flame ionisation detection. The chart speed was set at 2mm min^{-1}, retention times were generally in the region of 1 hour. After each reading the column needed to be purged for about an hour at a temperature of 250°C.

N-Benzoyl diphenylamine. Diphenylamine (34g, 0.2 mol) was heated to 150°C, benzoyl chloride (29g, 0.206 mol) was added dropwise while the mixture was continuously stirred. The addition was stopped if the evolution of hydrogen chloride became too excessive; HCl was absorbed onto moist sodalime. After the

addition the mixture was heated until the emission of HCl ceased. The crude product was dissolved in methylene chloride and stirred with a solution of sodium bicarbonate overnight. The methylene chloride was removed and the product was washed with hot 40-60 petroleum ether (2*70 ml). The product was filtered and dried in an oven. Yld 46.9g, 86%, mp 178°C, lit. mp 180°C[83]

4,4'-Dibromodiphenylamine[37]. *N*-benzoyldiphenylamine (6.83g, 0.025 mol) was dissolved in methylene chloride (100ml). To this bromine (8g, 0.1 mol) dissolved in methylene chloride (50ml) was added dropwise. After the addition the mixture was refluxed until HBr evolution ceased, the solvent was then removed. The crude amide was then dissolved in ethanol (200ml) to which sodium hydroxide (3g, 0.075 mol) had been added. The mixture was then refluxed for 8 hours. The crude amine was recrystallized from 60-80 petroleum. Yld 5.88g, 72%, mp 104-6°C, lit mp 105.5-7°C[37].
H^1 NMR (60 MHz, $CDCl_3$,) δ_H 5.6 (1H, s), 6.8 (4H, d, J10 Hz), 7.3 (4H, d, J10 Hz)

4,4'-Dinitrodiphenylamine[37]. *N*-Benzoyldiphenylamine (6.83g, 0.025mol) was dissolved in acetic acid (37.5 ml). The mixture was heated to between 90 and 95°C and HNO_3 (6.75 ml, d1.52) was added dropwise with stirring. After the addition the mixture was stirred for a further hour after which it was poured onto ice. The crude amide was extracted with methylene chloride, which was removed and replaced with ethanol (200ml) into which potassium hydroxide (2g, 0.036mol) had been added. The mixture was refluxed for an hour after which it was acidified with dilute HCl. The product was filtered and washed with water.

The product was only slightly soluble in 40-60 petroleum ether and was found to be insoluble in the radical clock media, hence it was of no use for the radical clock reactions. Yld 0.98g, 16%, mp 210-215°C, lit mp 217-8°C[37], H^1 NMR (60MHz, $CDCl_3$) δ_H 6.7 (s, 1H), 7.25 (m, 8H)

4,4'-Dimethoxydiphenylamine[36]. To *para*- methoxyaniline (6.16g, 0.05mol) was added acetic anhydride (5g, 0.05mol), after a brief exothermic reaction the mixture was refluxed for 20 minutes and excess acetic acid was distilled off to leave crude *para*-methoxyacetanilide. The crude anilide was added to *para*-bromoanisole (8g, 0.043mol), potassium carbonate (5g, 0.036mol) and 0.3g of copper powder activated with a few crystals of iodine. The mixture was then refluxed for 8 hours. The crude 4,4'-dimethoxydiphenylamide was extracted with boiling toluene (5*30ml) which was later removed. The crude amide was dissolved in 100ml of ethanol to which 4g of potassium hydroxide had been added, this was then refluxed for 4 hours. The crude amine was precipitated by the addition of water which was then extracted with methylene chloride. The solvent was removed and the 4,4'-dimethoxydiphenylamine was distilled under reduced pressure. Further purification was by recrytallization from 100-120 petroleum ether. Yld 1.5g, 13%, mp=99-100°C, lit. mp = 103°C[36], H^1 (60MHz, $CDCl_3$) δ_H 3.9 (s, 6H), 7.0 (8H), lit. H^1 δ_H 4 (s, 1H), 3.8 (s, 6H), 7.0 (8H)[36].

4,4'-Dimethyldiphenylamine[36]. To *para*-methylaniline (21.4g, 0.2mol) was added acetic anhydride (30g, 0.3mol), after a brief exothermic reaction the mixture was refluxed for 20 minutes and excess acetic acid was distilled off to leave crude *para*-methylacetanilide. The crude anilide was added to *para*-

bromotoluene (43g, 0.25mol), 42g of potassium carbonate and 6g of cupric iodide. The mixture was then refluxed for 21 hours. The crude 4,4'dimethyldiphenylamide was extracted with boiling toluene (5*100ml) which was later removed. The crude amide was dissolved in 200ml of ethanol to which 15g of potassium hydroxide had been added, this was refluxed for 4 hours. The crude 4,4'-dimethyldiphenylamine was precipitated by the addition of water which was then extracted with methylene chloride. The solvent was removed and the crude amine was distilled under reduced pressure. Further purification was by recrytallization from 40-60 petroleum ether. Yld 17.4g, 44%. mp 75-76°C, bp 140°C at 3.5 Torr, 102-6°C at 0.15 Torr, lit mp 79°C[36], lit. bp = 330°C at 760 Torr[36], ^{1}H NMR (200MHz, $CDCl_3$) δ_H 6.2 (s, 1H), 3.0 (s, 6H), 7.7 (8H).

N-Deuterodiphenylamine. 0.2104g of triply recrystallized diphenylamine (0.2104g, 0.001243mol) was dissolved in dodecane (10ml), to this was added 5ml of 99.8% D_2O, the resulting mixture was stirred for 1 hour. For the kinetic runs involving deuterodiphenylamine, samples were removed and diluted accordingly, care was taken to include some D_2O to avoid back substitution from the glass reaction vessel.

Attempted synthesis of diphenylamine sulphonic acid. To *N*-acetyldiphenylamine (6.1g, 0.029mol) was added to 10ml of conc sulphuric acid. The mixture was heated to 150°C for two hours with continuous stirring, after this period only one layer remained. Attempts to isolate the free acid were unsuccessful.

Attempted preparation of disulphonyldiphenylamine dihexyl ester. *N*-Acetyldiphenylamine (5g, 0.024mol) was dissolved in 20ml of methylene chloride. The resulting solution was added

dropwise to chlorosulphonic acid (8g, 0.07mol), with continuous stirring. The whole apparatus being cooled in an ice bath. The mixture was stirred for 12 hours. To this mixture was added n-hexanol (8g, 0.08mol) with pyridine (5.4g, 0.07mol) over an hour. After the addition, water (100ml) was carefully added along with sodium carbonate. When the release of carbon dioxide had ceased the mixture was extracted with methylene chloride (2*50ml). When the solvent was removed no product was isolated.

Attempted synthesis of dibutoxycarbonyldiphenylamine. The method tried was a Friedel-Crafts acylation using chloroformylbutyl ester. To *N*-acetyldiphenylamine (2g, 0.0095mol) was added 3.3 molar equivalents of resublimed aluminium chloride (3.8g, 0.0285mol). To this mixture was added chloroformylbutylester (3g, 0.022mol), the mixture was heated in a water bath for an hour after which water was added dropwise. The water was poured away to leave a brown tar insoluble in most solvents.

Heptenoyl peroxide from 1,2,6-trihydroxy hexane[53,54,55]

1,2,6-Tribromohexane. Phosphorous tribromide (162g, 0.6mol) was added dropwise to 1,2,6-trihydroxyhexane (50g, 0.373mol). When the addition was complete the mixture was refluxed for an hour, after which it was poured into water and filtered. The filtered liquid was extracted with diethylether (3*50ml) and the extracts were combined and washed with dilute sodium hydroxide solution and water, after which they were dried over sodium sulphate. The product was purified by distillation. Yld 31.61g, 42.76%; Bp 104°C at 1.2 Torr, ^{1}H NMR (200MHz, $CDCl_3$) δ_H 4.15(1H), 3.85 (2H), 3.4 (2H), 2.2-1.8 (6H), ^{13}C NMR δ_C 52.6, 36.5, 35.5, 33.7, 32.4, 26.0.

6-Heptenoic acid. 1,2,6-Tribromohexane (31.6g, 0.098mol) was dissolved in dry ether (50ml), to which magnesium turnings (6.6, 0.25mol) was added. After a vigorous reaction had occured, carbon dioxide gas was bubbled through the resulting Grignard solution for 3 hours. Dilute HCl was added and the resulting mixture was extracted with 40-60 petroleum ether (3*50ml). The combined extracts were shaken with sodium hydroxide solution (3*100ml of 4 M), these were combined and acidified. The acid solution was extracted with pentane (3*150ml), this was dried over anhydrous sodium sulphate. The solvent was removed to yield the free acid. Yld 5.8g, 46%; IR 3000cm^{-1} strong hydroxyl absorption, 1730cm^{-1} strong carbonyl absorption in region expected for carboxylic acids, NMR ^{1}H (200MHz, $CDCl_3$) δ_H 11.7 (1H, s), 5.8 (1H, m), 5.0 (2H, m), 2.35 (2H, t), 2.05 (2H, quintet), 1.65 (2H, quintet), 1.4 (2H, quintet); ^{13}C δ_C 24.5, 28.75, 33.8, 34.2, 115.3, 138.7, 181.1.

Dihept-6-enyl peroxide. 6-Heptenioc acid (1g, 0.0077mol) was dissolved in dry ether (10ml) and cooled in an ice bath. To this was added oxalyl chloride (2g, 0.016mol), after the addition the mixture was stirred for about an hour, the excess oxalyl chloride was then removed by distillation at reduced pressure, the yield of the acid chloride was 0.89g, 0.006M. The acid chloride was redissolved in dry ether and again cooled in an ice bath. To 5ml of ether was added hydrogen peroxide (0.4g of a 27.5% solution, 0.003mol H_2O_2) along with pyridine (0.5g, 0.0063mol). This solution was added dropwise to the acid chloride. After the addition the mixture was stirred for a further hour, it was then washed with sodium hydroxide (3*20ml of 1M) and dried over anhydrous sodium sulphate. The product was never concentrated

for a yield to be recorded. A small portion was evaporated and spectra run on the unpurified residue. NMR; ^{1}H essentially the same as for the acid; the acidic hydrogen had disappeared and the hydrogens at δ= 2.35 had moved up to 2.45; $^{13}C\,\delta_C$ 24.5, 28.5, 30.0, 33.5, 115.4, 138.5, 169.6.

Attempted preparation of bis-trimethylstanylbenzpinacol[39]. This experiment was carried out in preparative photolysis equipment. Benzene (200ml) was degassed by bubbling nitrogen gas through it for 20 minutes, into this was added the hexamethylditin (1g, 0.0031mol) and benzophenone (1.11g, 0.0061mol). The solution was photolysed, using a high pressure mercury lamp, for 7 hours, the whole experiment being carried out under an inert atmosphere. A sample was taken and the solvent was removed at room temperature under reduced pressure.

Studies of the product by NMR showed only the presence of starting material.

<u>3-Methyl-3-phenylbutanoyl peroxide from neophyl chloride</u>

3-Methyl-3-phenylbutanoic acid[56]. Neophyl chloride (21g, 0.125mol) was dissolved in dry ether (100ml). To this was added magnesium turnings (3.2g, 0.13mol) the mixture was then refluxed for 10 hours under a dry nitrogen atmosphere. Dry carbon dioxide was bubbled through the resulting Grignard for 5 hours. The mixture was acidified with dilute HCl and extracted with ether (3*100ml), the resulting extracts were combined and concentrated. This was then treated with sodium hydroxide (200ml, 5M) and the resulting solution was washed with ether (3*70ml) to remove any starting material. The free acid was released by acidification and extracted with ether (2*100ml). Yld 11.37g, 50%; mp 55°C, NMR $^{13}C\,\delta_C$ 178.5, 149.0, 128.7, 126.5, 125.9,

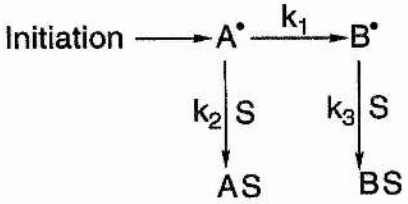
48.5, 36.0, 28.9; ^1H (200MHz) δ_H 7.2-7.5 (m, 5H), 2.65 (s, 2H), 1.5 (s, 6H)

Bis-3-methyl-3-phenylbutanoyl peroxide. 3-Methyl-3-phenylbutanoic acid (1.78g, 0.01mol) was dissolved in 20ml of dry ether, to this oxalyl chloride (3g, 0.024mol) was added. The whole procedure being carried out under anhydrous conditions cooled in an ice bath. When the addition was complete the mixture was refluxed for two hours. The solvent and excess oxalyl chloride were removed under vacuum to leave a clear liquid. This was redissolved in 20ml of ether and cooled in an ice bath. To this was added hydrogen peroxide (0.62g of a 27.5% solution, 0.005mol H_2O_2) followed by pyridine (1g, 0.013mol), the mixture was stirred for 2 hours at temperatures below 2°C. The product was first washed with dilute HCl and then with saturated sodium carbonate solution, the solution was then dried over anhydrous sodium sulphate. No attempt was made to concentrate all the product to record a yield, but a portion was evaporated to record spectra on the unpurified residue. NMR ^{13}C δ_c167.2, 149.0, 128.7, 126.5, 125.9, 44.4, 36.0, 28.9; ^1H (200MHz, $CDCl_3$) δ_H 7.2-7.5 (c, 5H), 2.7 (s, 2H), 1.5 (s, 6H)

Naugalube 438L. This is a commercial antioxidant commonly used in lubricant oils. The main component is 4,4'-n-dinonyldiphenylamine, but it also contains various mono and branched chain derivatives. No attempt was made at purification because it would normally be used in a lubricant in this form.

Appendix 1

Determination of the rate of a radical reaction using an ideal radical clock



$$\frac{dAS}{dt} = k_2[A^\bullet][S]$$

$$\frac{dBS}{dt} = k_3[B^\bullet][S]$$

Assume the rate of formation of $B^\bullet$ is equal to the loss of $B^\bullet$

$$\frac{dB^\bullet}{dt} = 0 = k_1[A^\bullet] - k_3[B^\bullet][S]$$

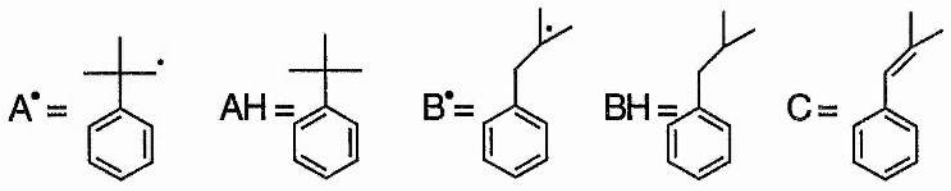
$$\Rightarrow k_1[A^\bullet] = k_3[B^\bullet][S]$$

$$\text{Ratio of products } \frac{A}{B} = \frac{(dAS/dt)}{(dBS/dt)} = \frac{k_2[A^\bullet][S]}{k_1[A^\bullet]}$$

$$= \frac{k_2[S]}{k_1}$$

Appendix 2

Determination of the rate of radical reaction incorporating radical disproportionation



1. $A^\bullet$ -> $B^\bullet$
2. $A^\bullet$ + RH -> AH + $R^\bullet$
3. $B^\bullet$ + RH -> BH + $R^\bullet$
4. $A^\bullet$ + $B^\bullet$ -> AH + C
5. $B^\bullet$ + $B^\bullet$ -> BH + C

$dAH/dt = k_2[A^\bullet]\,[RH] + k_4[A^\bullet]\,[B^\bullet]$

$dBH/dt = k_3[B^\bullet]\,[RH] + k_5[B^\bullet]\,[B^\bullet]$

$dC/dt = k_4[A^\bullet]\,[B^\bullet] + k_5[B^\bullet]\,[B^\bullet]$

Assuming the rate of formation of $B^\bullet$ = rate of consumption of $B^\bullet$ then;

$$\frac{dB^\bullet}{dt} = 0 = k_1[A^\bullet] - k_3[B^\bullet]\,[RH] - k_4[A^\bullet]\,[B^\bullet] - k_5[B^\bullet]\,[B^\bullet]$$

$$\Rightarrow k_1[A^\bullet] = k_3[B^\bullet]\,[RH] + k_4[A^\bullet]\,[B^\bullet] + k_5[B^\bullet]\,[B^\bullet]$$

$$\frac{AH\text{-}C}{BH\text{+}C} = \frac{k_2[A^\bullet]\,[RH] + k_4[A^\bullet]\,[B^\bullet] - k_4[A^\bullet]\,[B^\bullet] - k_5[B^\bullet]\,[B^\bullet]}{k_3[B^\bullet]\,[RH] + k_5[B^\bullet]\,[B^\bullet] + k_4[A^\bullet]\,[B^\bullet] + k_5[B^\bullet]\,[B^\bullet]}$$

$$= \frac{k_2[A^\bullet]\,[RH] - k_5[B^\bullet]\,[B^\bullet]}{k_1[A^\bullet] + k_5[B^\bullet]\,[B^\bullet]}$$

If $k_5[B\bullet]\,[B\bullet]$ is small then it can be ignored in this equation to give the result

$$\frac{k_2\,[RH]}{k_1}$$

Chapter 3
Measurement of the rate constants (k_H) for hydrogen abstraction from 2,6-di-t-butyl-4-substituted phenols by alkyl radicals

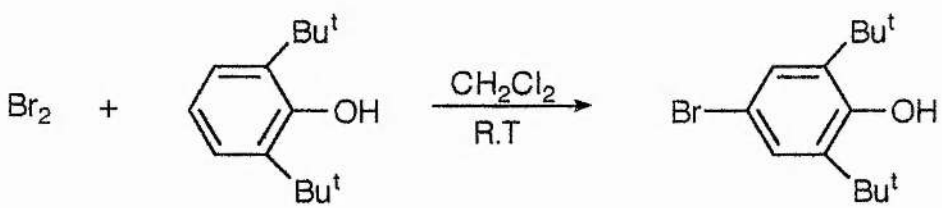
3.1 Aims

1. Measurement of the rate of hydrogen abstraction from 2,6-di-t-butyl-4-substituted phenols by alkyl radicals.
2. To determine what effects the differing functional groups have on this rate.
3. To find if it is possible to construct a Hammett type plot for prediction purposes.
4. Is there any correlation to the rate of hydrogen abstraction by peroxyl radicals in the literature.

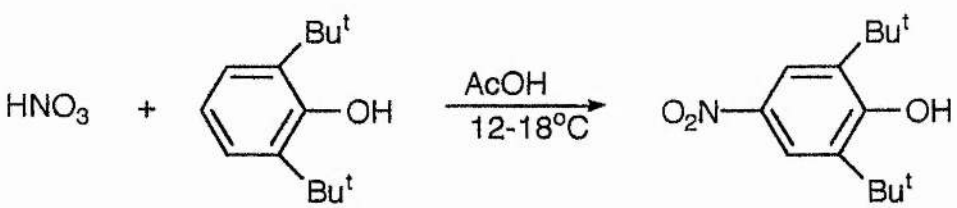
3.2 Synthesis of the phenols

Most of the phenols used for these experiments were commercially available, the only ones which required synthesis were the *para*- nitro and -bromo derivatives. These were conveniently prepared by electrophilic substitution carried out on 2,6-di-t-butyl phenol (DBPh).

The bromo derivative was prepared by the action of bromine on DBPh in methylene chloride, at room temperature.

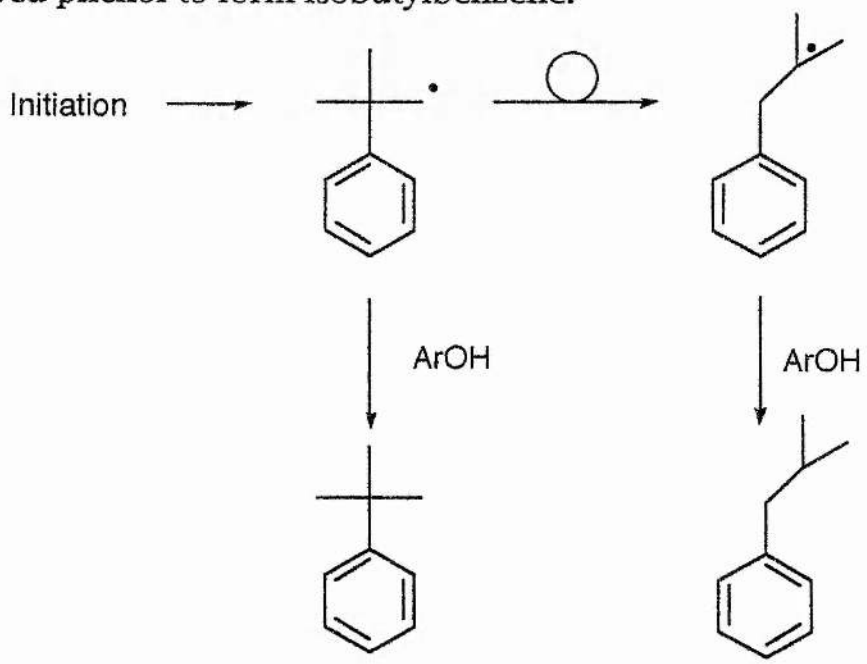


The nitro compound was prepared by the treatment of DBPh with concentrated nitric acid in acetic acid, this reaction was carried out at temperatures ranging from 12-18°C[56,57].



3.3 Kinetic measurements

The measurement of k_H from phenolic antioxidants was attempted using the neophyl radical rearrangement[32,33,34]. The method used was the same as that employed in measurement of k_H for the amine antioxidants. This involved generating the neophyl radicals in the presence of the phenolic antioxidant, the radicals being generated by the decomposition of a diacylperoxide. Once the neophyl radicals had been generated, they could either abstract hydrogen from the hindered phenol forming *tert* - butylbenzene or rearrange irreversibly to give the 2-phenyl-*tert* - butyl radical, which could also abstract hydrogen from the hindered phenol to form isobutylbenzene.



Scheme 3.1
Reaction scheme for the
kinetic experiments

The rate of the radical rearrangement could be calculated from the known activation energy, the Arrhenius A-factor[38] and the temperature of the experiment, hence the ratio of *tert* -

butylbenzene to isobutylbenzene could be used to determine the rate of hydrogen abstraction from the phenols.

Analysis was by GC and GC-MS. The products were identified by comparison of GC retention times with those of authentic materials and by GC-MS where the products previously separated by GC are ionised in a mass spectrometer. Products can then be identified by the comparison of the mass spectra obtained by GC-MS with those of the authentic standards.

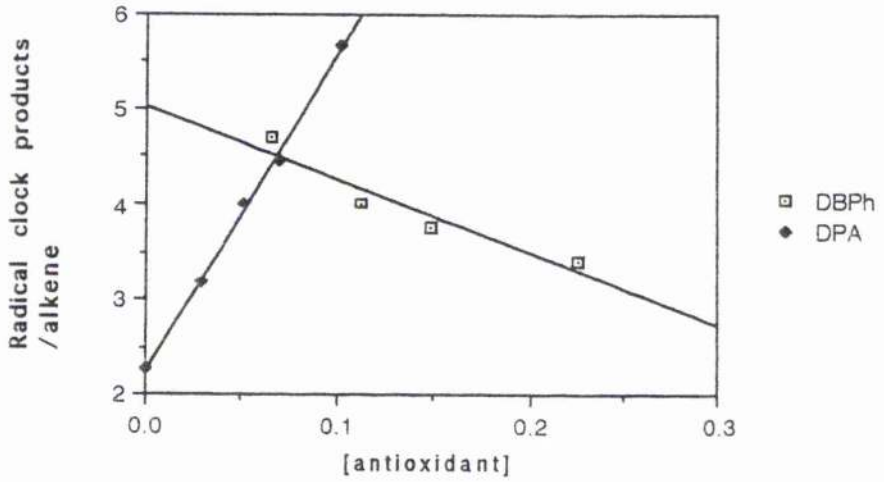
3.4 Results of product analyses

Analysis at the end of radical clock reactions showed that along with the products expected from the neophyl rearrangement, significant amounts of 2-methyl-2-propenylbenzene were also being formed. The proportions of all three products were affected by changes in antioxidant concentration.

3.5 Alkene formation and its effect on the measurement of k_H

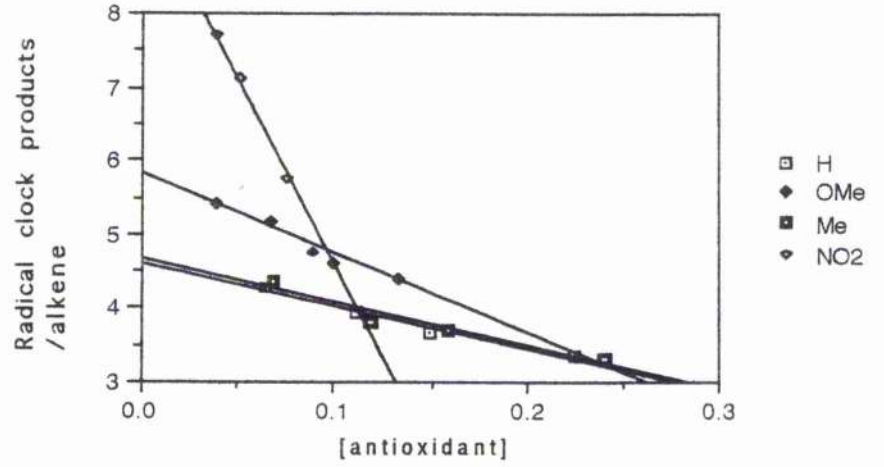
As discussed in section 2.15 the alkene can be formed by both radical disproportionation and via the carbocation. With radical disproportionation, increasing the concentration of the phenol decreases the amount of alkene formed via this route. If however the antioxidant is able to induce the heterolytic scission of the diacyl peroxide, then increasing its concentration will increase the proportion of alkene found in the radical clock products.

Graph 3.1 shows how the proportion of the alkene varies with antioxidant concentration. The alkene formation for both diphenylamine (DPA) and DBPh at 373K are compared.



Graph 3.1
Comparison of alkene formation
for DPA and DBPh at 373K

The most obvious difference between the two plots is that for diphenylamine the proportion of alkene decreases with increasing amine concentration, whereas increasing the concentration of phenol, increases the proportion of alkene. Graph 3.2 shows that all the phenolic antioxidants behave in this manner.



Graph 3.2
Alkene formation for phenolic
antioxidants at 393K

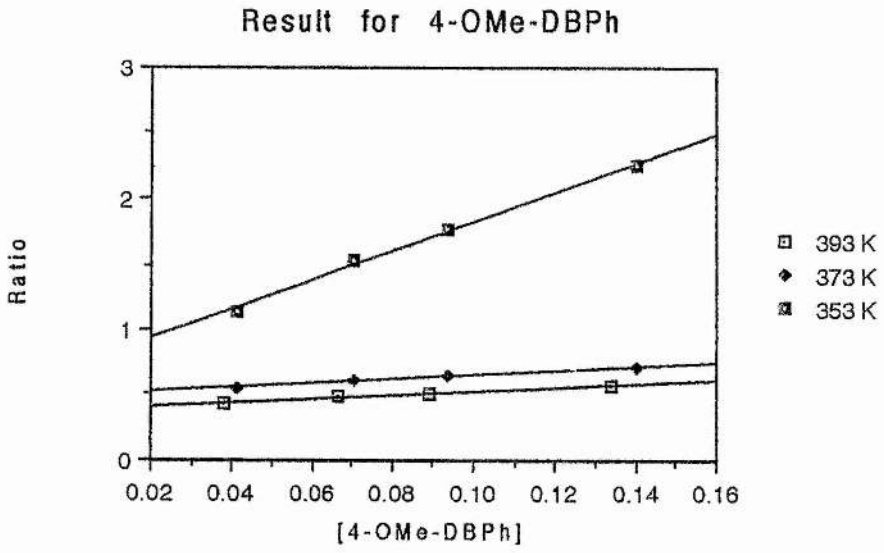
Although some of the alkene was formed via the carbocation, radical disproportionation will still occur. It was therefore important to be able to estimate the amount of alkene formed via disproportionation, this was necessary for the calculation of k_H for the phenolic antioxidants.(See section 2.15)

3.6 Estimation of the disproportionation reaction

The total amount of alkene formed is a sum of what is formed via the carbocation and via disproportionation. A similar problem was encountered with the amine antioxidants. It was assumed that all the isobutylbenzene was formed by the abstraction of the phenolic hydrogen by the 2-phenyl-*tert*- butyl radical. The proportion of alkene was then estimated by multiplying the amount of the isobutylbenzene by the constants derived at the end of section 2.15. At 120°C this constant had to be estimated due to a lack of data.

3.7 Radical clock results

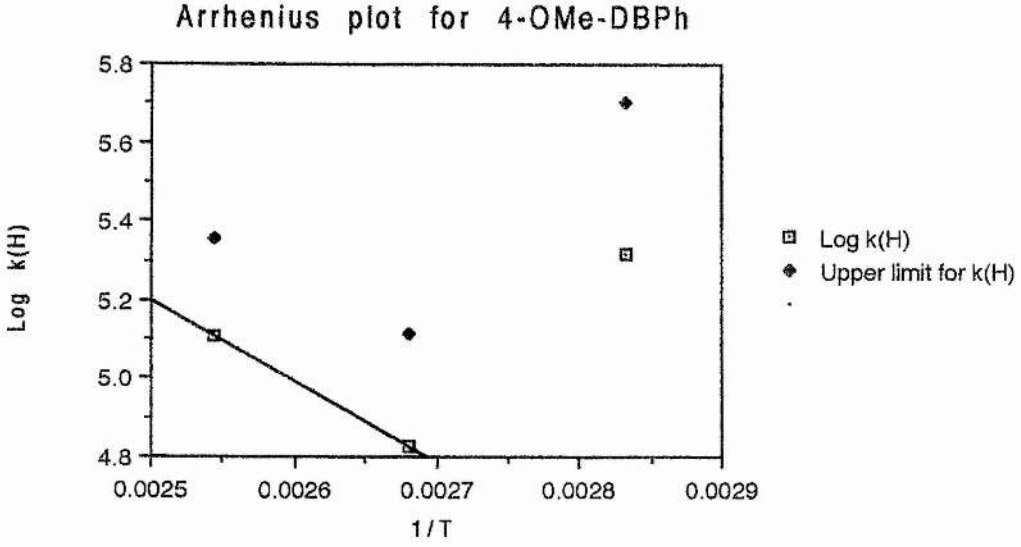
These results were obtained using an estimate for the alkene formed by disproportionation. The upper limits in the Arrhenius plots assumed that all the alkene was formed via the carbocation. A lower limit would be obtained if all the alkene was produced by disproportionation. However for the majority of these results, this required the log of negative numbers.



k_H 393K = $13*10^{-4}$ $M^{-1}s^{-1}$

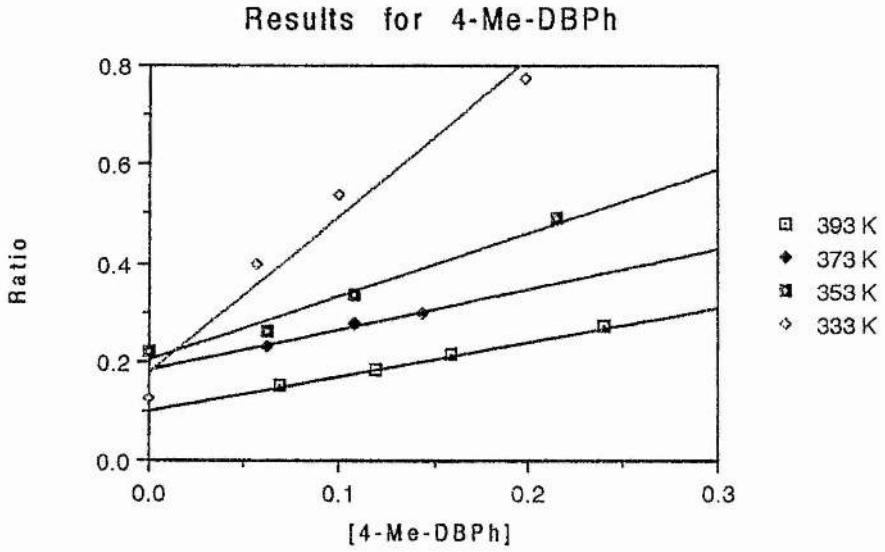
k_H 373K = $6.7*10^{-4}$ $M^{-1}s^{-1}$

k_H 353K = $21*10^{-4}$ $M^{-1}s^{-1}$



Log ($A/M^{-1}s^{-1}$) = 10.36 s^{-1}

Ea = 9.4 kcal mol^{-1}

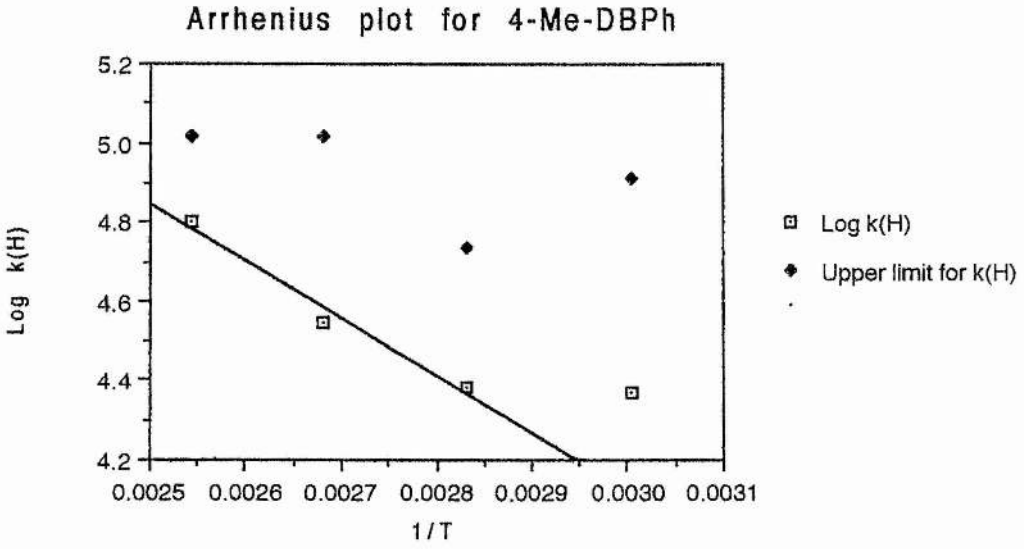


k_H 393K = $6.3*10^{-4}$ $M^{-1}s^{-1}$

373K = $3.5*10^{-4}$ $M^{-1}s^{-1}$

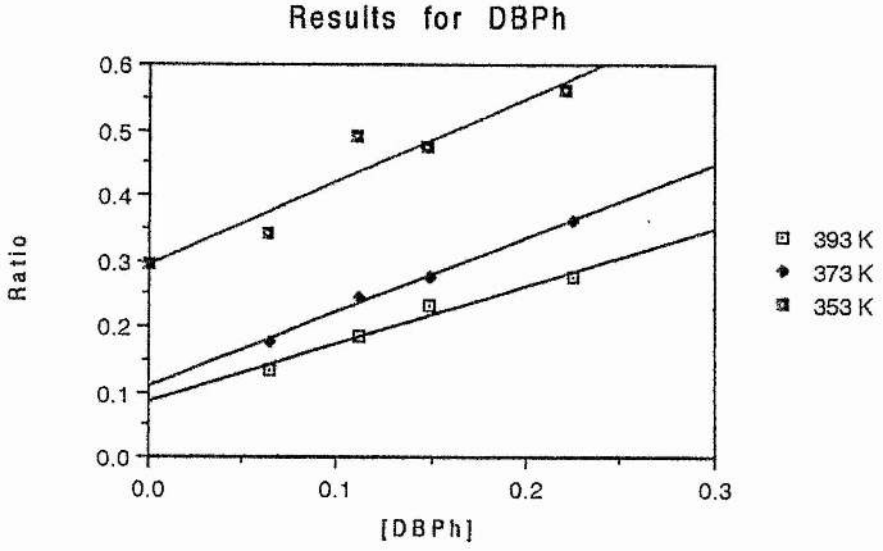
353K = $2.4*10^{-4}$ $M^{-1}s^{-1}$

333K = $2.3*10^{-4}$ $M^{-1}s^{-1}$



Log ($A/M^{-1}s^{-1}$) =8.45

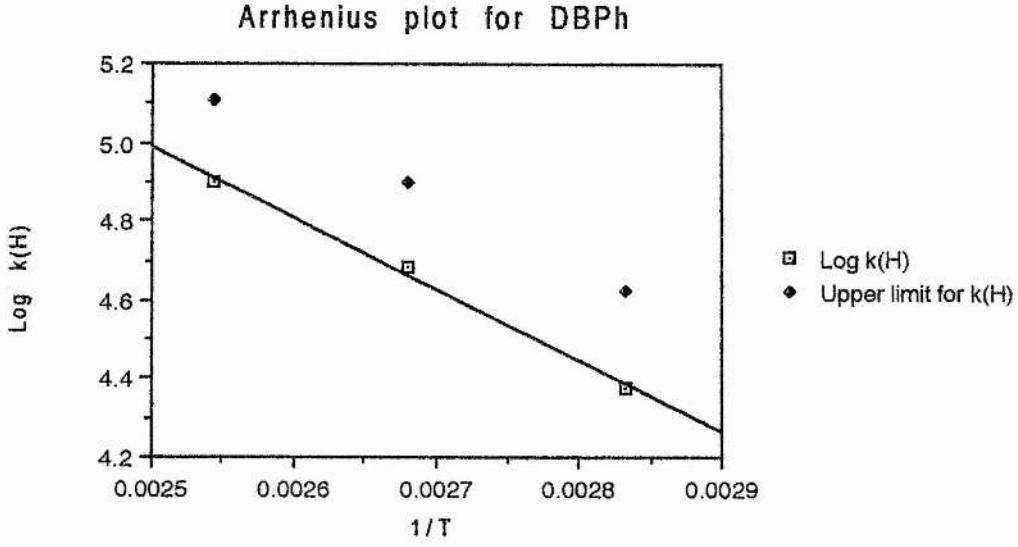
Ea = 6.6 kcal mol^{-1}



k_H 393K = $7.9*10^4\ M^{-1}s^{-1}$

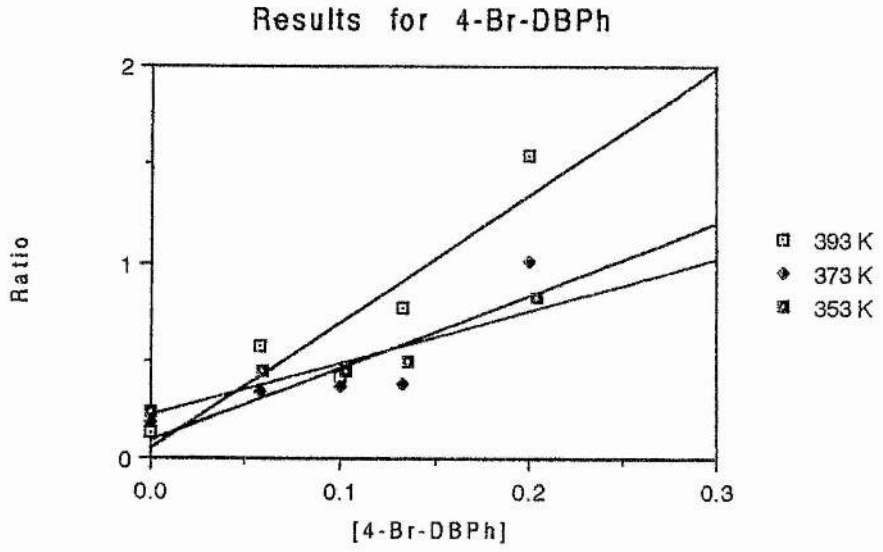
373K = $4.8*10^4\ M^{-1}s^{-1}$

353K = $2.4*10^4\ M^{-1}s^{-1}$



Log $(A/M^{-1}s^{-1})$ = 9.54

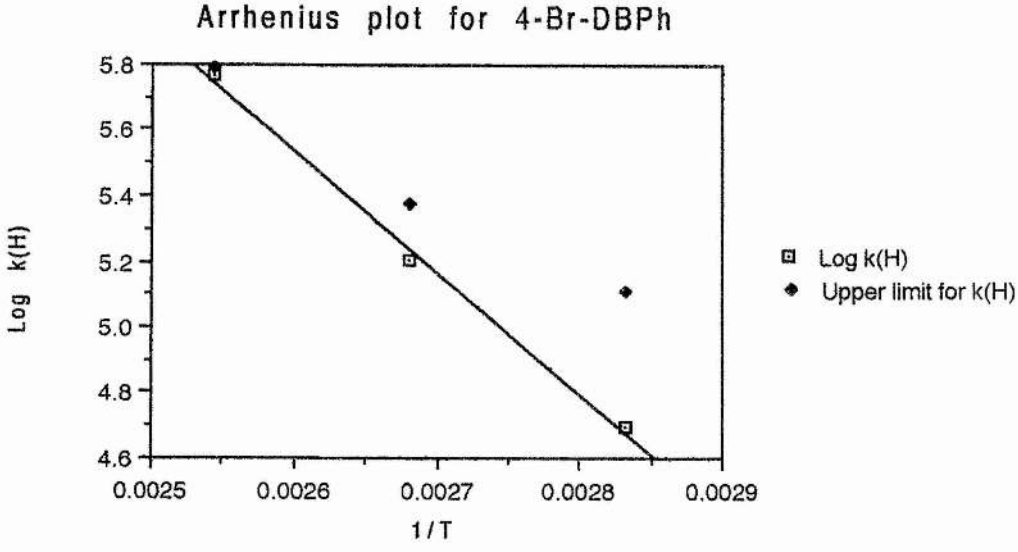
Ea = 8.3 kcal mol^{-1}



k_H 393K = $58*10^4 M^{-1}s^{-1}$

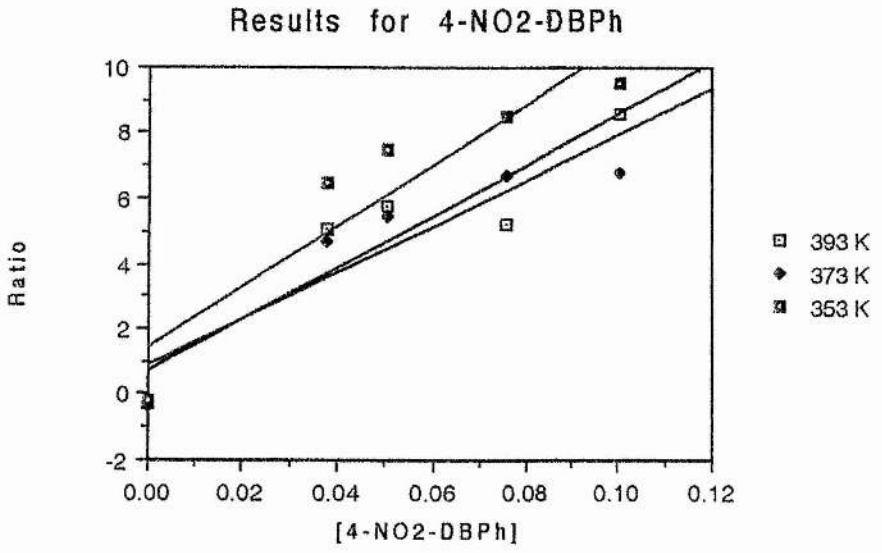
373K = $16*10^4 M^{-1}s^{-1}$

353K = $4.9*10^4 M^{-1}s^{-1}$



Log $(A/M^{-1}s^{-1})$ = 15.2 s^{-1}

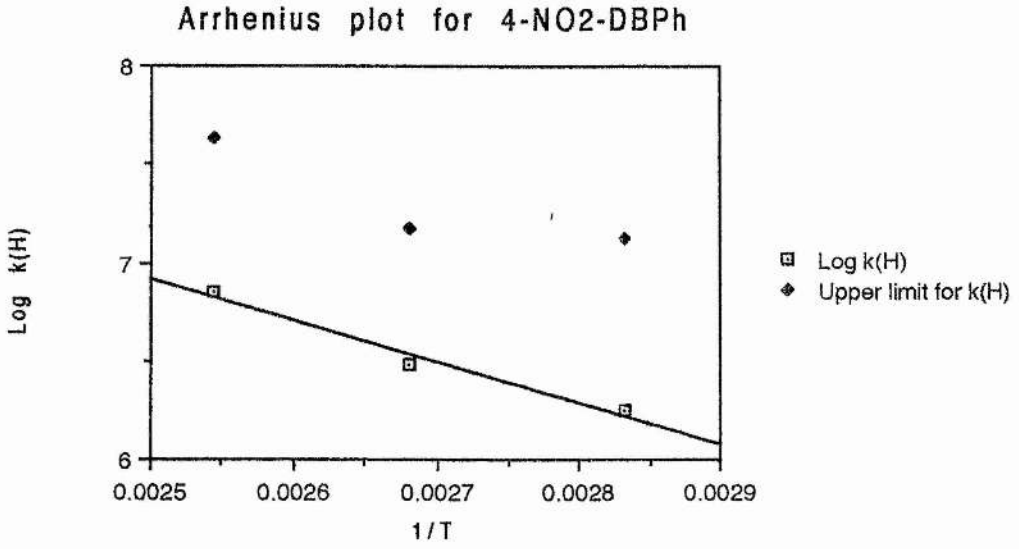
Ea = 17 kcal mol^{-1}



k_H 393K = $700*10^4 M^{-1}s^{-1}$

373K = $300*10^4 M^{-1}s^{-1}$

353K = $170*10^4 M^{-1}s^{-1}$



Log $(A/M^{-1}s^{-1})$ = 12.14

Ea = 9.6 kcal mol^{-1}

3.8 Summary of the results and discussion

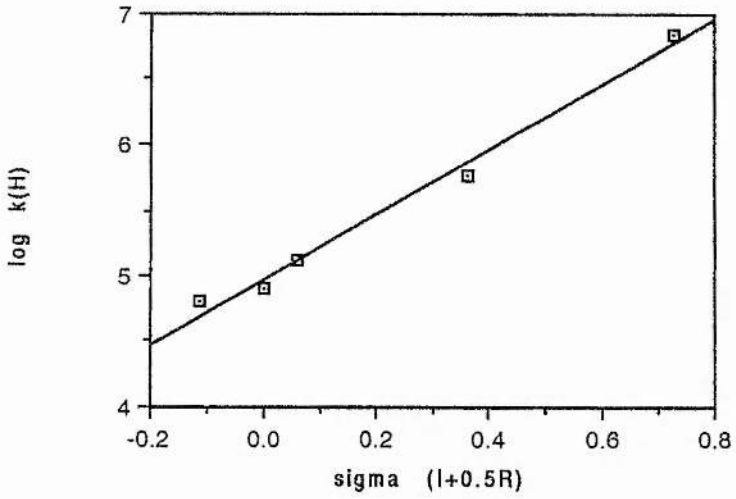
	$k_H * 10^{-4}$ $M^{-1}s^{-1}$				
Phenol	393K	373K	353K	log (A/ $M^{-1}s^{-1}$)	Ea kcal mol^{-1}
OMe	13	6.7	21	10.4	9.4
Me	6.3	3.5	2.4	8.5	6.6
H	7.9	4.8	2.4	9.5	8.3
Br	58	16	4.9	15.2	17
NO_2	700	300	170	12.1	9.6

From the above results phenols with electron withdrawing substituents in the *para* position were the most effective at donating hydrogen to the neophyl radical.

As discussed already in the section on amine antioxidants, alkyl radicals are nucleophilic in nature and so are attracted to areas of low electron density. With the hindered phenols the 2,6 - *t*- butyl groups are areas of high electron density. The phenolic hydrogen sits between the two *t*- butyl groups. As this is attached to an electronegative oxygen, it is an area of low electron density and so is attractive to alkyl radicals. Placing electron withdrawing substituents in the para position will further remove electron density away from the phenolic hydrogen in comparison to the *t*-butyl groups making it more attractive to alkyl radicals.

3.9 Hammett relationship

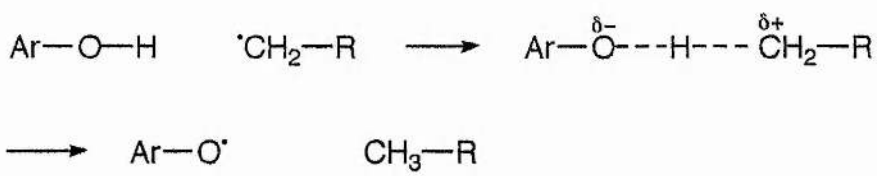
The Hammett relationship links the electronic effects of the functional groups with the log of the rate constants of the reaction. Since a variety of functional groups had been used a Hammett plot could be made.(see section 2.17).



Graph 3.3
Hammett type plot for k_H at 393K

Although there was not a particularly good correlation with Hammetts σ_P values, when these were split into their respective field and resonance contributions[58], σ_I and σ_R, a good correlation was obtained using σ' values which were equal to $(\sigma_I + 0.5*\sigma_R)$ from which $\rho' = 2.5$ was obtained.

For the abstraction of hydrogen from antioxidants based on DBPh by the neophyl radical, electric field effects played a more important role than resonance stabilisation. The positive gradient and the high value of ρ also imply that in the transition state there is substantial charge separation with the phenolic oxygen taking on a partial negative charge, which will be stabilised by electron withdrawing groups.



Scheme 3.2
The abstraction of the phenolic
hydrogen by alkyl radicals

3.10 Comparison with literature results for the trapping of alkyl radicals

There are very few results available for the abstraction of hydrogen from phenolic antioxidants by alkyl radicals. The rate of hydrogen abstraction from vitamin E was measured at $1.7*10^6$ $M^{-1}s^{-1}$ at 343K using the hexenyl radical rearrangement[59]. A similar reaction was measured using pulse radiolysis at room temperature, this time the alkyl radical was one based on cyclohexane from which k_H was assumed to be less than or equal to $1*10^5$ $M^{-1}s^{-1}$ [60]. For the attack of the $HOCH_2^{\bullet}$ and the *tert* -butyl radicals upon DBPh at room temperature these rates were measured at 702 and 93 $M^{-1}s^{-1}$ respectively[61].

The most surprising result was that 4-nitro-DBPh is so effective at trapping alkyl radicals with a k_H of about $1*10^6$ $M^{-1}s^{-1}$ at 343K, which is only half that obtained for vitamin E, which is known to be one of the most effective antioxidants.

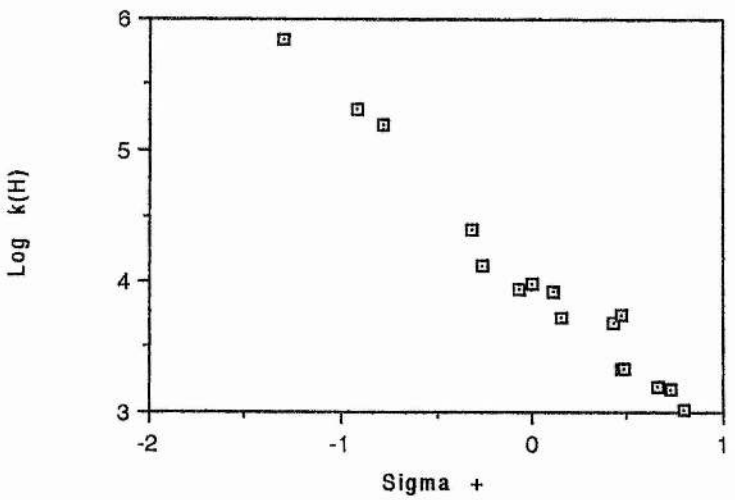
3.11 Comparison with literature results for the trapping of peroxyl radicals.

For hydrogen donation to peroxyl radicals, DBPh based antioxidants with electron releasing substituents were the most effective. A comprehensive set of results has been obtained using *para*-substituted DBPh antioxidants to trap peroxyl radicals derived from the autoxidation of ethylbenzene[62]. The rate constant at which the *para*-methyl-DBPh donates hydrogen to these peroxyl radicals, was measured at $2.5*10^4$ $M^{-1}s^{-1}$ at 333K, for the neophyl radical our rate constant was calculated to be $2.3*10^4$ $M^{-1}s^{-1}$ at the same temperature. For the 4-nitro-DBPh the peroxyl radical was trapped at a rate of only $1.1*10^3$ $M^{-1}s^{-1}$, at

the same temperature the neophyl radical was calculated to be trapped at a rate of $7.7*10^5$ $M^{-1}s^{-1}$, which is about 700 times faster.

A Hammett plot has been made from these results (graph 3.4). They clearly show the effects that the functional groups have on k_H. A good correlation was found between the rate at which these radicals were trapped and the σ_P^+ values for the electrical effects of the functional groups, the susceptibility ρ was measured at -1.3.

A similar correlation was found with the *tert* -butylperoxyl radical at 237K[63], k_H was measured at $2.5*10^3$ for the unsubstituted DBPh, a correlation was found with σ_P^+ constants[77] with ρ= -0.85.



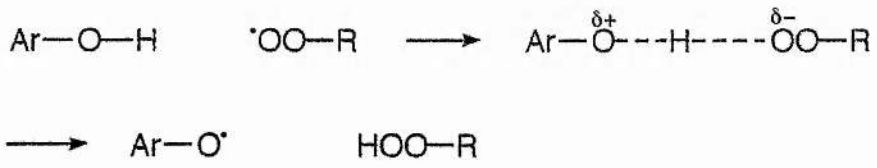
Graph 3.4

Hammett plot for the trapping of peroxyl radicals based on ethylbenzene by para substituted DBPh at 333K[62]

Discussion of results obtained with alkyl and peroxyl radicals

The most obvious difference between the two sets of results was the fact that the phenol derivatives with electron withdrawing substituents were the most effective at trapping alkyl radicals, whereas for the trapping of peroxyl radicals they were the least effective.

The most likely cause for these differences lies in the nature of the abstracting radicals and the transition state they form with the phenols. Peroxyl radicals are electrophilic in nature and so are attracted to regions of high electron density. This behaviour can be attributed to the electronegativity of the oxygen on which the peroxyl radical is centred. Increasing the electron density of the phenolic hydrogen will make it more attractive to peroxyl radicals. This can be achieved with electron releasing substituents in the *para* position. This behaviour is shown in the transition state; the peroxyl oxygen attracts electron density away from the phenolic oxygen and so takes on some negative charge. The phenolic oxygen in being depleted of electron density takes on a positive charge which will be stabilised by electron donating groups.



Scheme 3.3

Abstraction of the phenolic hydrogen

by peroxyl radicals

For the attack of the neophyl radical on a phenol the opposite is true, in this case the alkyl radical is attracted to regions of low electron density. Electron withdrawing substituents in the *para* position remove electron density away from the phenolic hydrogen making it more attractive to the neophyl radical. In the transition state the phenolic oxygen takes on a negative charge, which is stabilised by electron withdrawing substituents, and the carbon a positive charge.

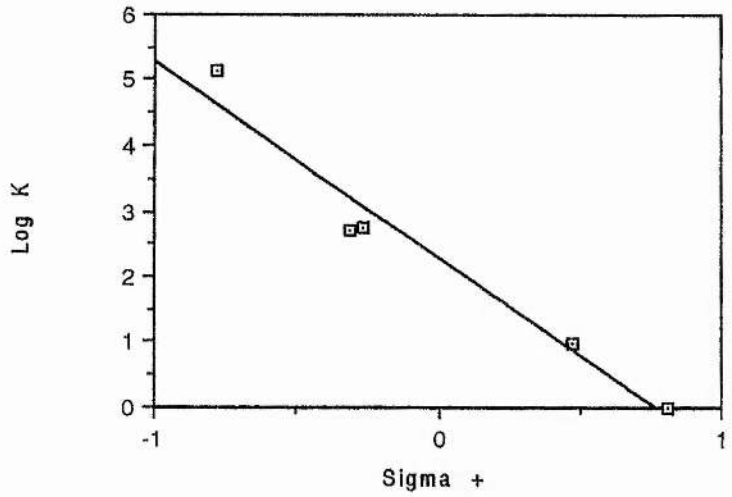
A similar effect has been recorded in the abstraction of benzylic hydrogens from *para* substituted toluenes. Silicon centred radicals are attracted to regions of high electron density. For the triethylsilyl radical a correlation was found with σ^* values for which the susceptibility, ρ^* was measured at +0.3[64] but for radicals centred on more electronegative elements a correlation was found with σ_p^+ for which ρ was negative[65].

3.12 Comparison with equilibrium studies[66]

The abstraction of hydrogen from phenolic antioxidants is subject to both kinetic and thermodynamic effects. The thermodynamic effects have been isolated by the study of the equilibrium obtained between a mixture of phenols and their corresponding phenoxyl radicals.

$$Ar{-}O^{\bullet} + H{-}O{-}Ar' \rightleftharpoons Ar{-}O{-}H + {}^{\bullet}O{-}Ar'$$

Results from these studies show that phenols with electron donating substituents form the most stable phenoxyl radical. A Hammett plot of these results is shown in graph 3.5.



Graph 3.5
Hammett plot derived from the equilibrium studies[66]

A good correlation was obtained with σ_p^+ with $\rho = -3$. From these results it would be expected that phenols which form the most stable free radicals would also be the best antioxidants and for the trapping peroxyl radicals this is indeed the case. For the trapping of the neophyl radical, kinetic factors may be of greater importance than thermodynamic considerations.

3.13 Comparison with amine antioxidants

Alkyl radicals

The most obvious difference is that amine antioxidants with electron donating substituents are the most effective at trapping alkyl radicals, whereas phenols with electron withdrawing substituents are the more effective. The phenols having $\rho = 2.5$, are more susceptible to the electric effects of the functional groups than the amine antioxidants, for which $\rho = -0.49$. At 373K the actual rate constants vary from $3.4*10^6$ $M^{-1}s^{-1}$ for the 4,4'-dimethoxy derivative to $8.8*10^5$ $M^{-1}s^{-1}$ for 4,4'-

dibromodiphenylamine. Rate constants for the phenolic antioxidants ranged from $3*10^6$ $M^{-1}s^{-1}$ for the 4-nitro derivative to $3.5*10^4$ $M^{-1}s^{-1}$ for 4-methyl-DBPh.

Peroxyl radicals

Both types of antioxidant behave similarly when the attacking species is a peroxyl radical. The rate at which DPA traps a peroxyl radical derived from the autoxidation of ethylbenzene was measured at $4.4*10^4$ $M^{-1}s^{-1}$ [51]. For DBPh this rate was measured at $1.32*10^4$ $M^{-1}s^{-1}$ [62], both measurements being made at 333K. The electrical susceptibility was measured at ρ =-1.6 for the amine antioxidants[51,52] and -1.3 for the phenols. The fact that DPA is able to trap peroxyl radicals more effectively than DBPh combined with the higher value of ρ means that amine antioxidants with electron donating substituents will be the more effective at trapping peroxyl radicals.

For trapping both peroxyl and alkyl radicals together, the diarylamine based antioxidants with electron donating substituents were the more effective.

Best high temperature 2,6-di-t-butyl-4-substituted phenolic antioxidants ?

For trapping alkyl radicals, antioxidants based on 2,6-di-t-butyl-4-substituted phenols with electron withdrawing substituents were found to be the most effective. For trapping the neophyl radical a correlation was found with σ' values which were equal to $(\sigma_I + 0.5*\sigma_R)$. The susceptibility ρ' was found to be 2.5. For trapping peroxyl radicals a correlation was found with σ^+ values, the susceptibility was found to be negative. For high

temperature applications the best solution may be to use a pair of phenolic antioxidants, one which has substituents in the *para* position with low σ^+ values for trapping peroxyl radicals and a second with high σ' values for trapping alkyl radicals.

3.14 Experimental

4-Bromo-2,6-di-t-butylphenol. To a stirred solution of 10.32g of DBPh, in 100ml of methylene chloride were added 8g of bromine dissolved in 50ml of methylene chloride, the addition taking place over an hour. The mixture was then left stirring for 10 hours. The solvent was then removed along with any excess bromine to leave the crude product. Purification was by recrystallization from a mixture containing 80% ethanol and 20% water. Yld 8.4g, 59%; NMR ^1H (200MHz, $CDCl_3$) δ_H 1.3 (18H, s, 2 Bu^t), 5.1 (1H, s, OH), 7.2, (2H, s, ArH)

4-Nitro-2,6-di-t-butylphenol[56]. To a stirred solution of DBPh (10.32g, 0.05mol), in 100ml of cyclohexane were added 8ml of a 1:1(V/V) mixture of nitric acid (d.1.42) and acetic acid in 50ml of cyclohexane, the addition taking 10 minutes with the reaction temperature never exceeding 18°C. The solid product was dissolved in methylene chloride and this solution was washed with water. Evaporation of the methylene chloride yielded the crude product. Purification was by recrystallization from 40-60 petroleum ether which gave pale yellow crystals.

Yld 5.3g, 42%; mp 152-153°C, lit. mp154-155°C, NMR H^1 (200MHz, $CDCl_3$) δ_H 8.1 (2H, s, ArH) 5.9 (1H, s, OH), 1.4 (18H, s, Bu^t).

Chapter 4

Performance of the amine antioxidants in the industrial screening tests.

4.1 Aims

1. Is it possible to compare amine antioxidants directly using the industrial screening methods?
2. To determine what effect if any the oil basestock has on these results.
3. To compare the results obtained from the industrial screening tests with the kinetic results for the trapping alkyl and peroxyl radicals.

4.2 Description of the ERCOT

The ERCOT was designed to simulate conditions within the engine sump, in which bulk lubricant autoxidation occurs. The basic ERCOT essentially involves placing a 300g sample of a lubricant into a large tube of about 75cm in length and 5cm in diameter and heating it to temperatures of around 150°C. Into this was placed a "bubbler" which, as its name suggests, was used for bubbling air through the sample[69]. To shorten test times, an oxidation catalyst consisting of an oil soluble iron complex was added. The performance of the sample was then rated by removing a small amount and measuring the increase in viscosity[70]. The smaller the increase in viscosity the better the sample had performed. Variations on this basic test include bubbling a mixture of air and engine exhaust gasses through the sample and placing a condenser at the neck of the tube to reflux any volatile compounds.

Another effect of lubricant degradation which can be observed using the ERCOT is the formation of sludge. The amount of sludge formation can be estimated by filtering a known volume of the well mixed sample. Any sludge which is obtained can be

subdivided into separate classes, products which are soluble in pentane, chloroform and the insolubles.

ERCOT tests with amine antioxidants

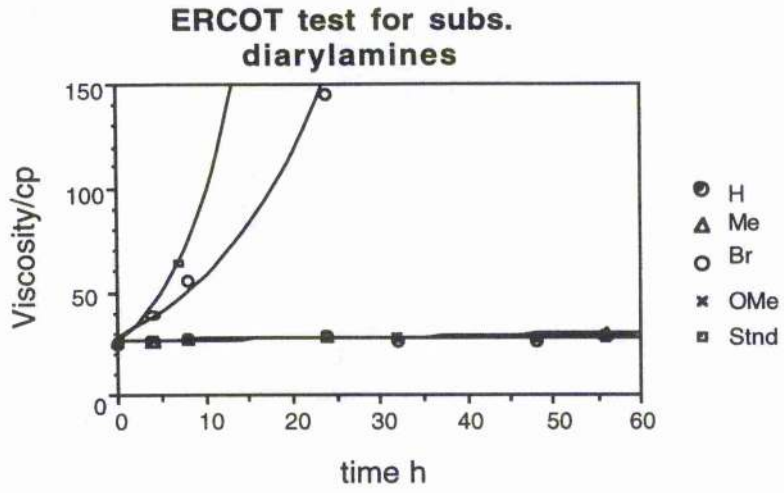
The main objective behind the ERCOT experiments was to determine if it could be used to differentiate between the various amine antioxidants and if so, what effects do the functional groups have? Can the ERCOT results be compared with those obtained for the trapping of alkyl and peroxyl radicals? What effects do changes in antioxidant concentration, temperature and basestock composition have on these results?

4.3 ERCOT's using NS150 as a basestock

NS150 was the most plentiful basestock available. It is a mineral oil derived from North Sea crude and consists of a complex mixture containing paraffinic, alkyl aromatic, aromatic, organic sulphur and nitrogen compounds.

The samples prepared for the ERCOT were simply the antioxidant dissolved in the basestock. The oxidizing agent was air and to speed up the test times an oxidation catalyst consisting of an oil soluble iron complex was included. All the following tests were run at 165°C.

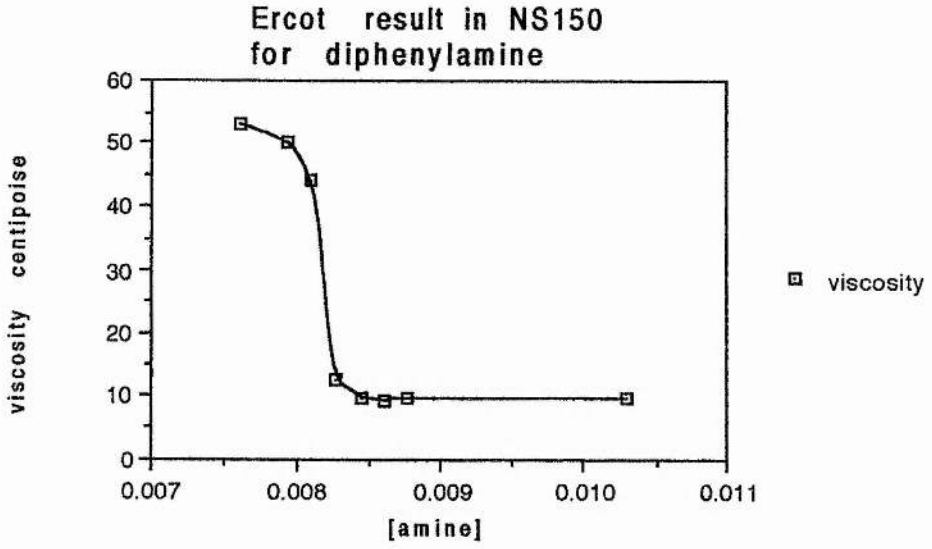
The first experiment with this basestock was to test all the antioxidants at the same concentration, the results of which are plotted over the page.



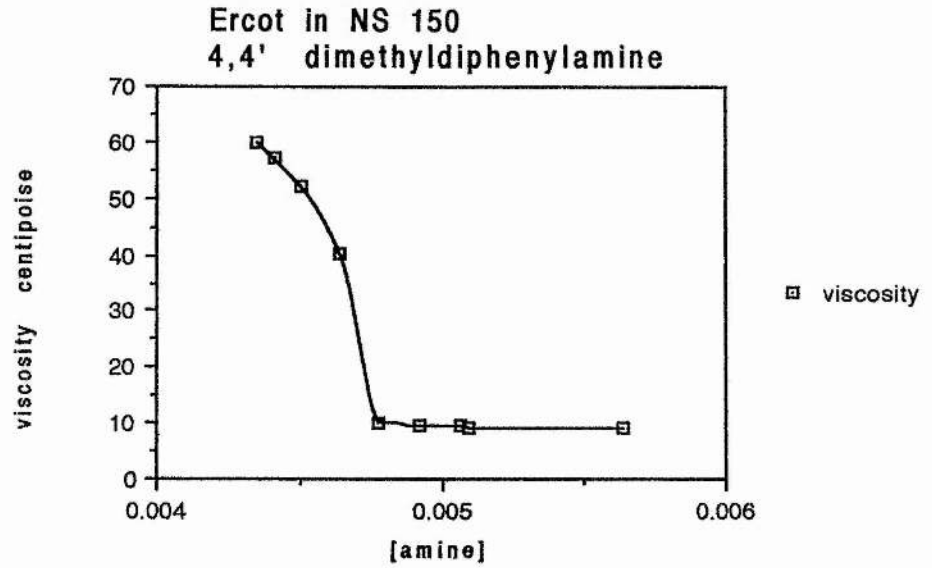
As can be seen from the graph above, diphenylamine, 4,4' dimethyl and 4,4'dimethoxy derivatives of diphenylamine were able to protect the oil against viscosity changes. These were allowed to run for 150 hours, but even after this time the best antioxidant could not be identified. The 4,4'-dibromodiphenylamine offered some protection when compared to a standard which contained no added antioxidants.

To try and differentiate between the various amine antioxidants the concentration was varied. The initial experiments were carried out over a wide range of concentrations. After each experiment, the concentrations at which the antioxidant went from being ineffective to effective were located and subsequent tests were then carried out between these concentrations values.

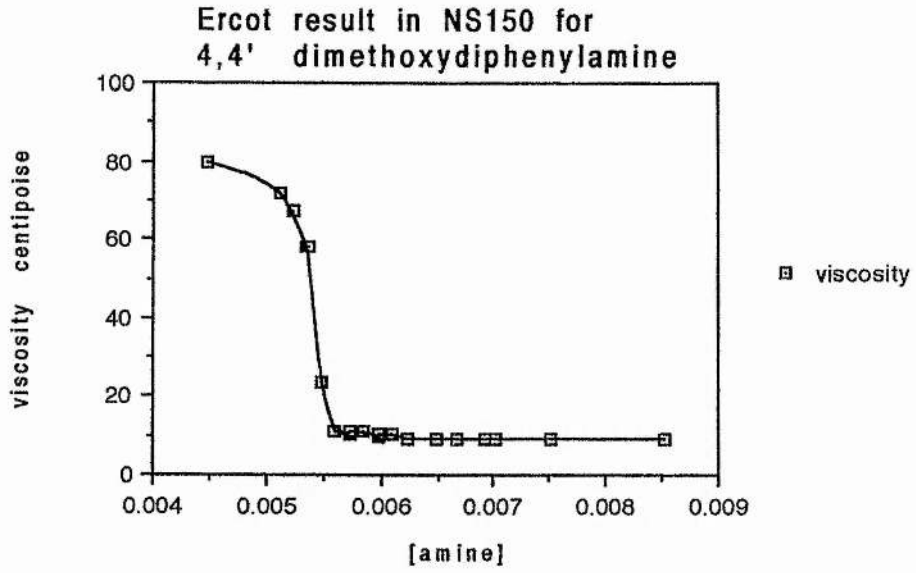
With this procedure it was found that the ERCOT was indeed very sensitive to small changes in amine concentration and that each antioxidant had its own concentration range over which it became active. Using this property it was now possible to differentiate between the various amine antioxidants. The results of these experiments are plotted over the page.



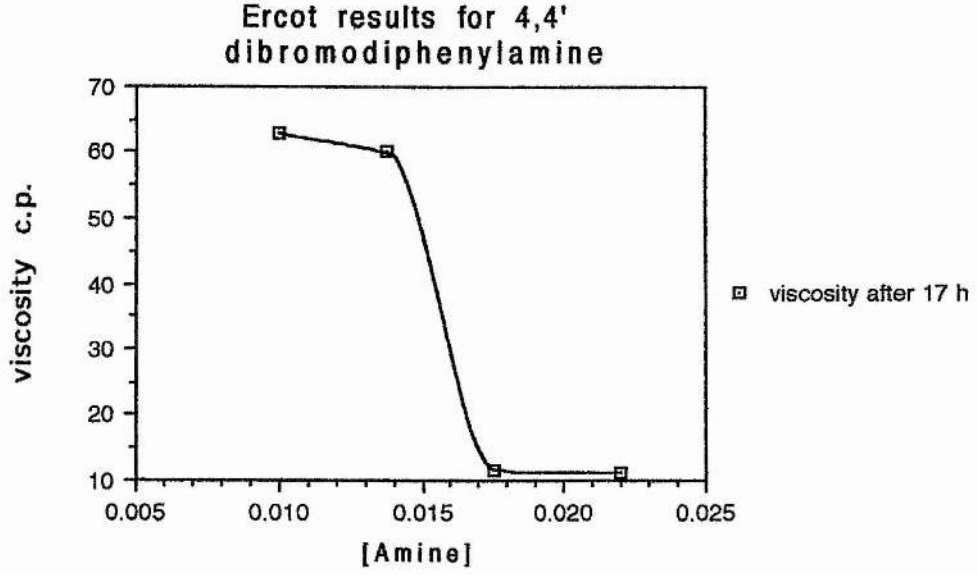
Diphenylamine became effective as an antioxidant at concentrations above 0.008273 molal.



4,4'-Dimethyldiphenylamine was found to be effective as an antioxidant above 0.004642 molal.



4,4'-Dimethoxydiphenylamine was found to be effective as an antioxidant above 0.005608 molal.



4,4'-Dibromodiphenylamine was found to be effective as an antioxidant above 0.01749 molal.

Summary of ERCOT results in NS150

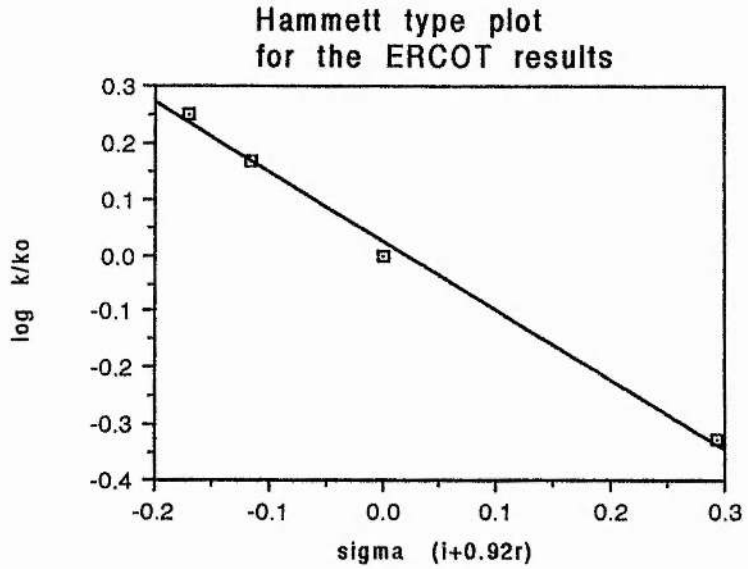
Diarylamine	Min. effective concentration
Ph_2NH	0.008273
4,4'-diMe	0.004642
4,4'-diOMe	0.005608
4,4'-diBr	0.0175
4,4'-diNO_2	insoluble

Using the criteria that the most active antioxidant was the one which performed at the lowest concentration, 4,4'-dimethyldiphenylamine was the found to be the most effective. The activity of the antioxidant was found to decrease in the following order, Me > OMe > H > Br. The 4,4'-dinitrodiphenylamine was insoluble in the oil basestock. The results obtained from the ERCOT's in NS150 did not correlate well with the kinetic results obtained using alkyl and peroxyl radicals [51,52].

Hammett relationship

The rate at which the amine antioxidants are able to mop up any free radicals is dependant upon a rate constant k, which in turn is dependant upon the antioxidant and its concentration. For a system in which the rate of initiation was constant, then if k[Amine] ≥ the rate of radical generation, then the sample will not undergo rapid autoxidation. For ERCOT's run in NS150 such a situation appeared to have existed. The rate k, at which radicals were trapped is proportional to 1/[amine], when the [amine] was just high enough to prevent the oxidation process. Diphenylamine

was chosen as the standard amine antioxidant, to which all the other amine antioxidants were compared, from this, k_0, was assumed to be proportional to [diphenylamine]$^{-1}$. Therefore k/k_0 = [diphenylamine]/[amine], from this k could be expressed in terms of k_0. The log k/k_0 was used to construct a Hammett plot. A correlation was found with σ' values = $(\sigma_I + 0.92*\sigma_R)$[58], the susceptibility ρ' = -1.2, where σ_I and σ_R are the contributions made by the field and resonance effects respectively.



For trapping alkyl and peroxyl[51,52] radicals a correlation was found when the log k_H was plotted against σ^+[77], the susceptibility ρ = -0.49 and -1.6 respectively.

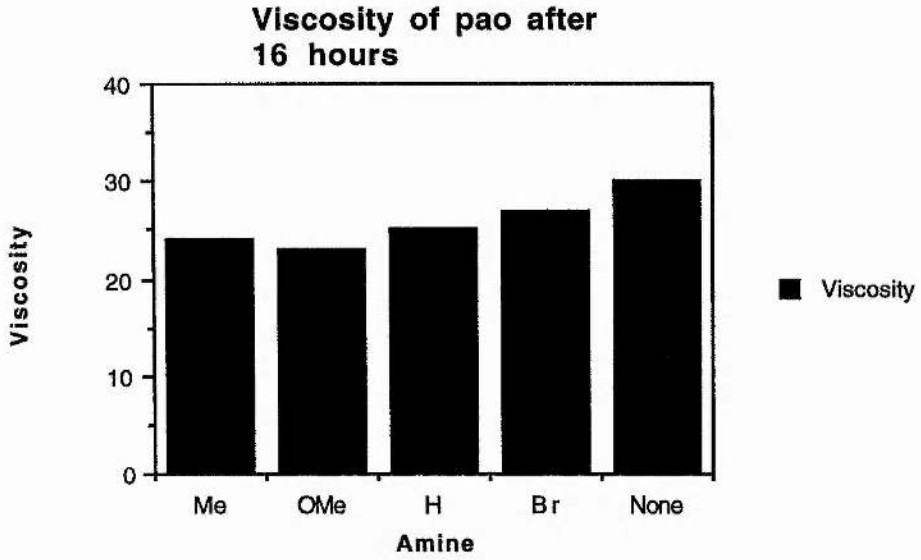
4.4 ERCOT's using other basestocks

Paraffinic basestocks

The basestocks used for these experiments were either the technical white oil, which is a highly refined oil, consisting of only the paraffinic components of the original mineral oil or the poly alkylated olefins, (PAO) which is a fully synthetic paraffinic

basestock. Samples prepared for the ERCOT's simply involved dissolving the amine into the basestock.

The first set of ERCOT's was a direct comparison of all the amine antioxidants. These were dissolved in PAO at a concentration of 0.0169 molal. To speed up test times an oxidation catalyst of iron was included. The viscosity of the samples at the start of these tests was 8.75 centipoise. The viscosity was observed after 16 hours, the results are shown below.



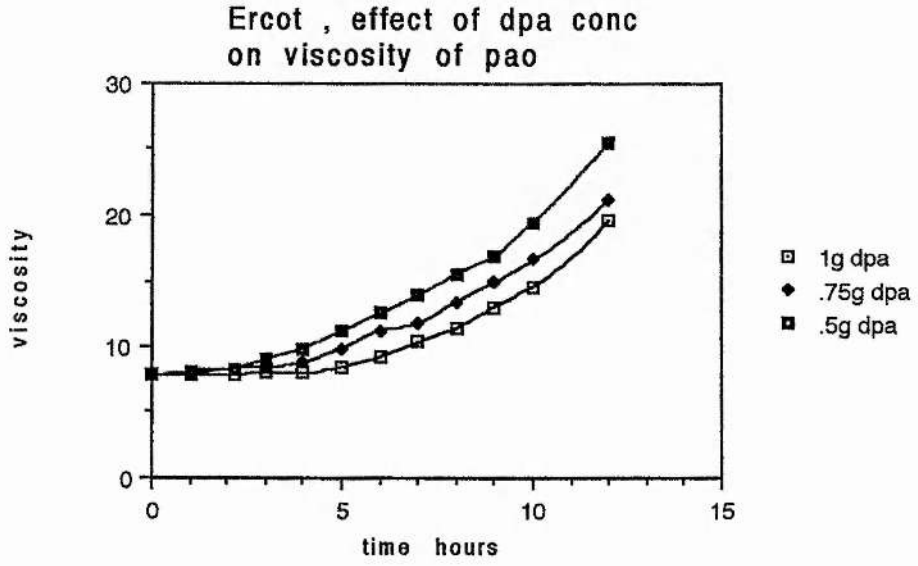
The graph above shows that after only 16 hours all the samples have substantially increased in viscosity. The samples showing the smallest increases in viscosity were assumed to contain the best antioxidant. In this basestock amines with electron donating substituents were the most effective, with the 4,4'-dimethoxy-diphenylamine proving to be the best antioxidant.

The effect of changes in amine concentration

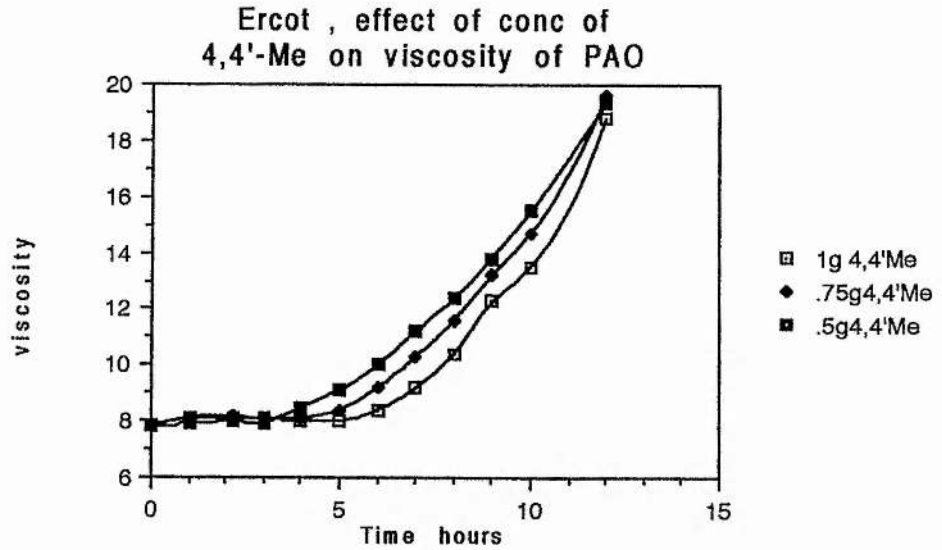
The next set of experiments were designed to establish whether the oxidation process was slowed down by the presence of the antioxidant, or was there an induction period during which

time the autoxidation was inhibited until all the antioxidant was consumed after which the sample rapidly oxidized.

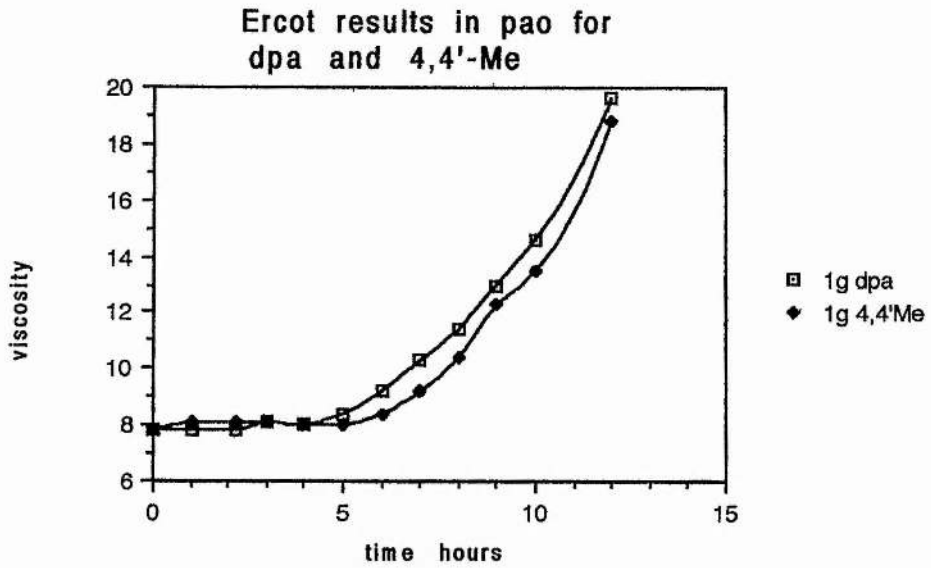
For these ERCOT's both diphenylamine and 4,4'-dimethyl diphenylamine were used as the antioxidants. The samples consisted of the antioxidant dissolved in the basestock. The measurements used for these experiments were grams of antioxidant in 350g of the basestock. Samples were removed every hour for a viscosity reading. The results are shown below.



The first graph shows the effect that diphenylamine concentration has on the viscosity of the samples. The induction period increases by about 1.5 hours for every 0.25g added to the sample.(This corresponds to an increase in amine concentration of $1.48*10^{-3}$ molal)



The results obtained for 4,4'-dimethyldiphenylamine are similar to the ones obtained for diphenylamine, in that the addition of an extra 0.25g of amine increased the induction period by about 1.5 hours. (This corresponds to an increase in concentration of $1.25*10^{-3}$ molal)

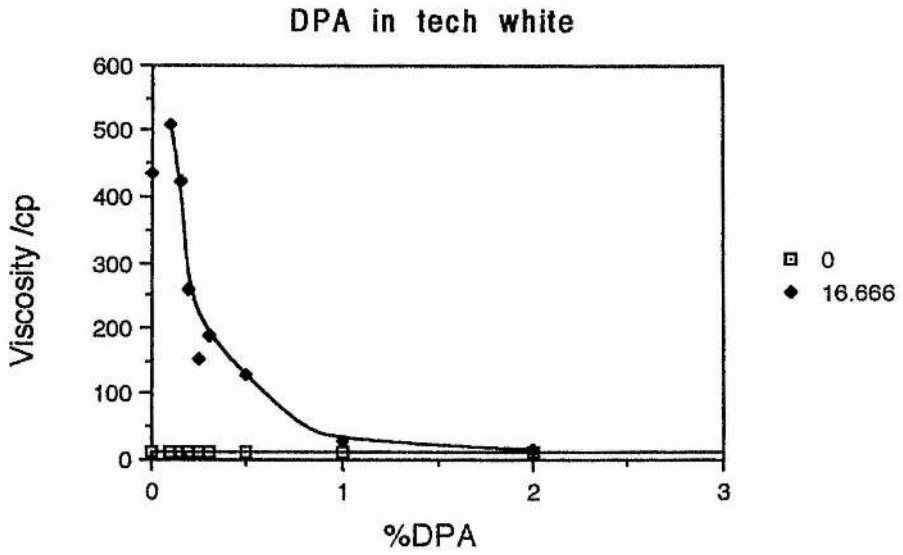


The final graph is a direct comparison of the two antioxidants, it shows that 1g of the dimethyl derivative has a longer induction period than 1g of diphenylamine. Gram for gram

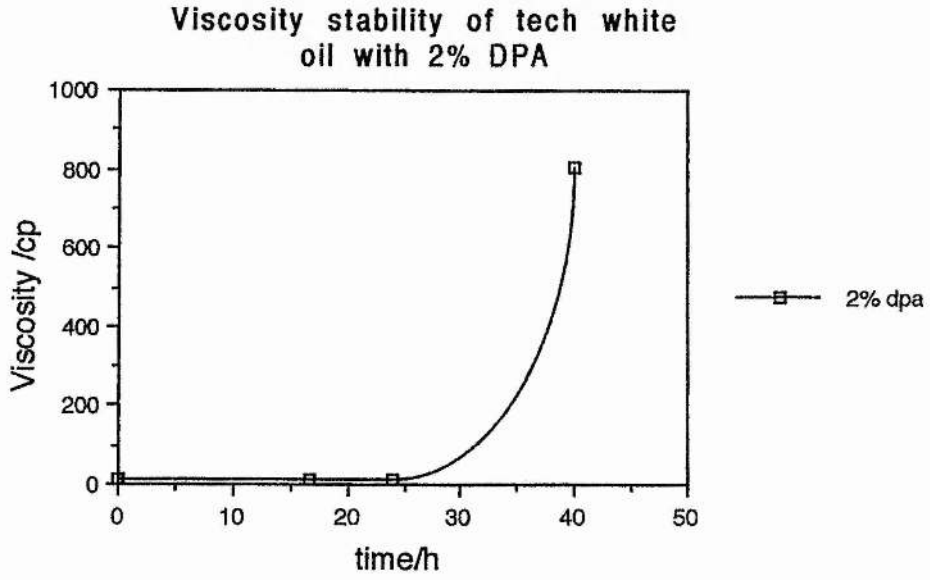
the dimethyl derivative was a better antioxidant than diphenylamine despite its higher molecular weight.

The results show that there was an induction period during which the autoxidation was a slow process. After this induction period the autoxidation proceeded rapidly. The best antioxidant would therefore be the amine which had the longest induction period with all other criteria being equal.

The final set of ERCOT's were run to find out if there was an amine concentration above which the sample behaved like the ERCOT's run in NS150. The basestock used was technical white oil. The experiments were run at 165°C in the presence of an iron based oxidation catalyst. Diphenylamine was used as the antioxidant. The amount of diphenylamine in the sample was varied between 0 and 2% by weight (0 and 0.118 molal). The results of this experiments are shown below.



The sample containing 2% DPA, showed no increase in viscosity after 16.7h. This sample was allowed to run for a longer period, but it lasted less than 40 hours.



These experiments confirmed that the amine antioxidants were able to control the autoxidation for a certain induction period which was dependant upon their concentration. Once all the antioxidant had been consumed the autoxidation process could proceed uninhibited.

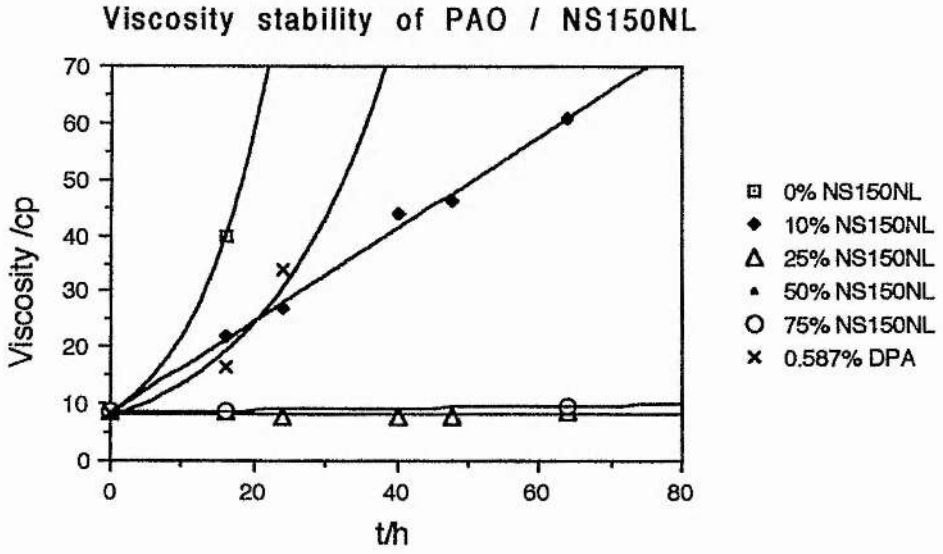
Summary of ERCOT results in paraffinic basestocks

ERCOT's run in PAO and technical white oil, using diarylamines as the only antioxidants, had a limited lifetime before they would start to increase in viscosity. The lifetime of the sample was found to be proportional to amine concentration. The most effective antioxidant was found to be the 4,4'-dimethoxy derivative. The order of effectiveness was OMe > Me > H > Br. This

agrees with kinetic studies using peroxyl radicals[51,52] as well as the radical clock results.

A mixture of NS150 and PAO

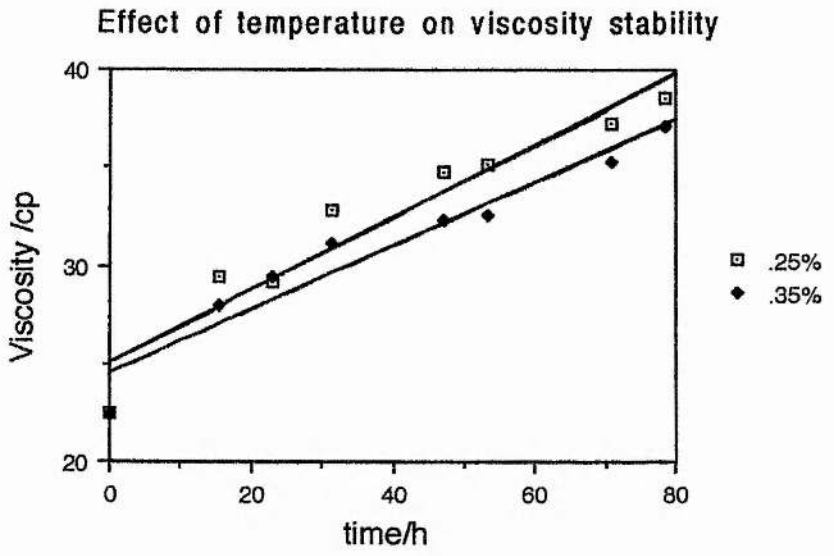
A mixture of polyalkylated olefin and NS150 was used as the basestock. The proportion of NS150 was varied between 0 and 75% by weight. Diphenylamine was used as the antioxidant at 0.286% by weight except for one test which was run in pure PAO with 0.587% diphenylamine by weight. This was used for comparisons. The results are plotted below.



The results above show that PAO with 10% NS150 and 0.286% diphenylamine was more resistant to autoxidation than PAO with 0.587% diphenylamine. This shows that something in the NS150 was acting as an antioxidant. At 10% NS150 the lifetime is improved dramatically and with 25% NS150 present the viscosity stability was comparable to that of 100% NS150. It was also noticed that sludge formation only occured in samples containing NS150.

4.5 Effect of temperature on amount of diphenylamine required for viscosity stability in NS 150

The amount of diphenylamine was varied between 0.15 and 0.35% by weight, the basestock used was NS150; to speed up the oxidation process an oxidation catalyst was included. The test was run at 185°C. The results of this experiment are plotted below.



At 0.15% DPA the viscosity increase at 185°C was too rapid for measurement, 0.14% by weight was required at 165°C to give good viscosity stability, hence increasing the temperature increases the amount of diphenylamine required to give good oxidation control. For the other tests, the increases recorded were higher than for a similar sample at 165°C.

The fact that a higher concentration of diphenylamine was required at the higher temperature may be due to a greater increase in the rate of radical initiation and propagation reactions when compared to the inhibition reactions.

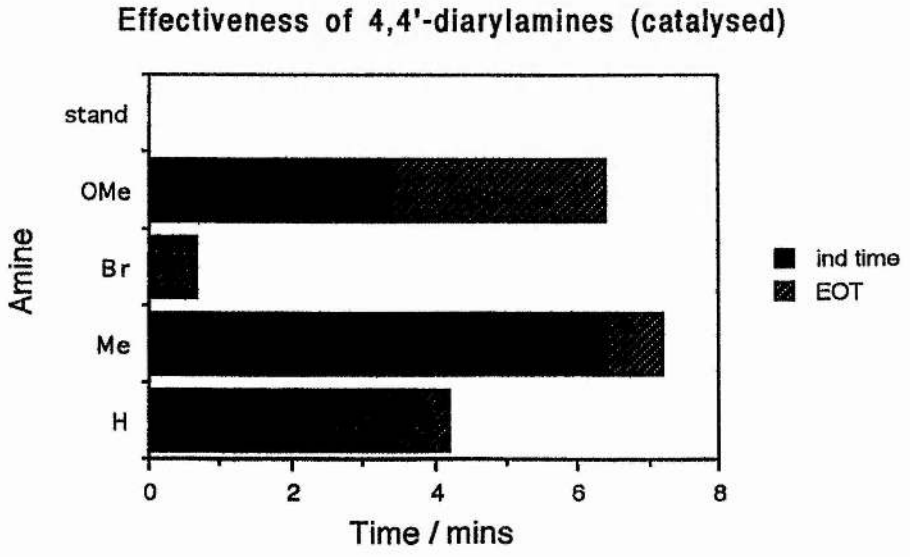
4.6 Differential scanning calorimetry (DSC)

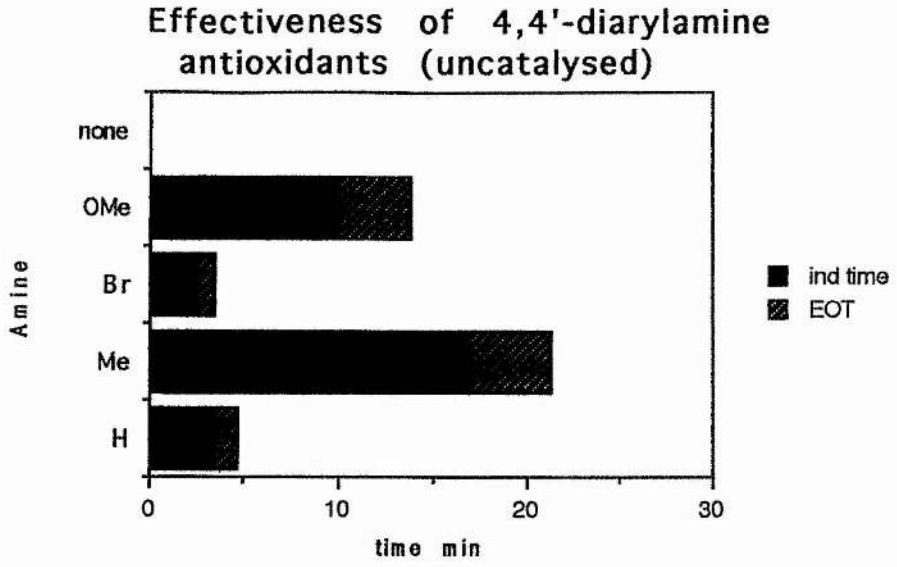
The DSC was used to assess a lubricant's resistance to oxidation. The technique involves heating a small sample of the lubricant to a high temperatures under an atmosphere of pure oxygen at 200p.s.i. The temperature of the sample is then monitored. In general there is a period during which the sample is able to control autoxidation, a so called 'induction period' after which there is a second period where the oxidation of the oil occurs rapidly. The DSC's can be either catalysed or uncatalysed. Catalysed DSC's are run at 190°C. The oxidation catalyst consists of oil soluble lead and iron compounds. Uncatalysed DSC's are run at 210°C.

Effectiveness of various antioxidants

The antioxidants were all 4,4'-diarylamines dissolved in NS150 basestock at 0.0144 molal concentration. The catalysed tests contained 500ppm of iron and 2000ppm of lead.

Results

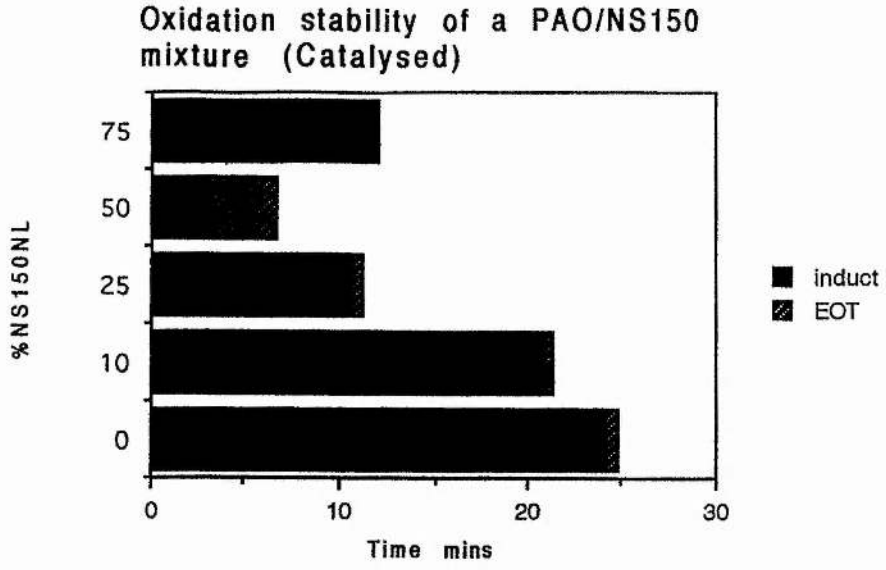




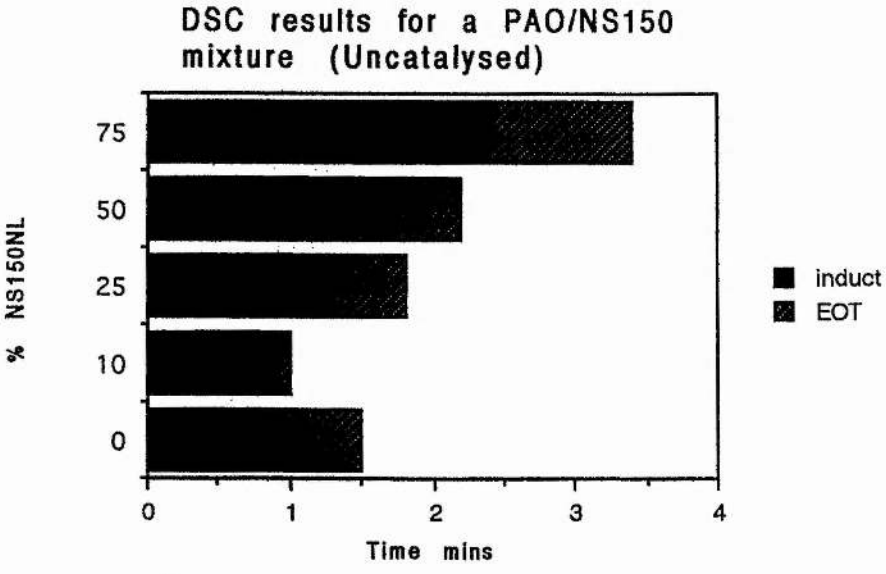
With all the DSC's carried out in NS150 4,4'-dimethyldiphenylamine was the most effective antioxidant. The order of effectiveness was Me > OMe > H > Br. These results correlate well with the ERCOT's run in NS150 but not so well with kinetic studies using alkyl and peroxyl [51,52] radicals. In general, amines with electron releasing substituents in the para positions were the most effective antioxidants.

Effect of basestock on the DSC's

The basestock used for these experiments contained a mixture of NS150 and PAO, the percentage of NS150 is shown in the results. With all these DSC's diphenylamine was used as the only antioxidant. This was present at a concentration of 0.01696 molal. The results are shown over the page.



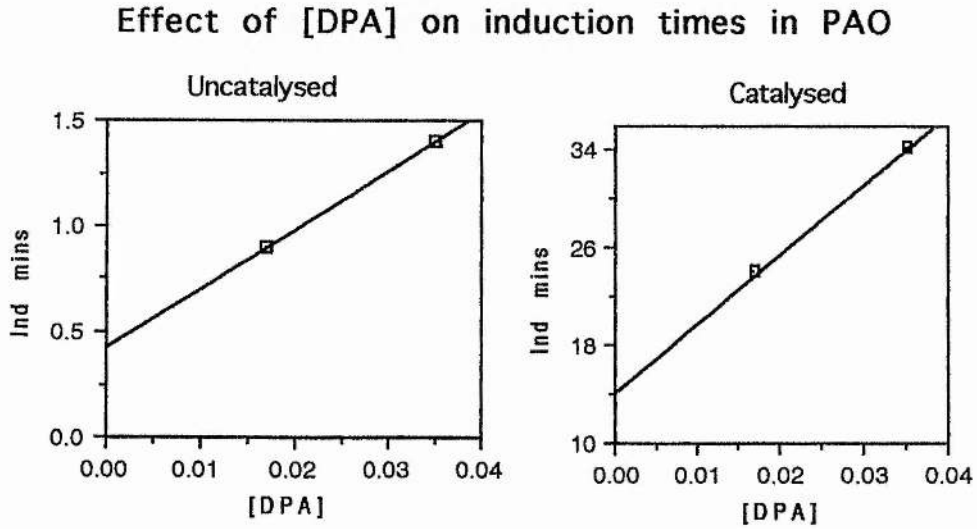
The results show that for the catalysed system the straight basestocks have the longest induction period, the mixture containing 50% NS150 had the shortest lifetime. The addition of NS150 appeared to shorten the lifetime of the PAO sample.



With no oxidation catalyst present the sample with the highest proportion of NS150 had the longest life span.

Effect of amine concentration on induction times

For these experiments the amine was present at 0.01696 or 0.03487 molal. The DSC's were carried out in a pure PAO basestock. The results are shown below.



The results show that for both the catalysed and uncatalysed systems increasing the concentration of amine increased the induction period.

4.7 Discussion of the results

The industrial screening tests carried out in the NS150 basestock found the best antioxidant was the 4,4'-dimethyl-diphenylamine. A Hammett plot derived from the ERCOT results gave a good correlation when $\sigma' = (\sigma_I + 0.92*\sigma_R)$, with the susceptibility $\rho' = -1.2$. However in PAO the 4-methoxy derivative was the most effective antioxidant.

Another observation was that ERCOT's run in NS150 appeared to have an almost indefinite lifetime when the antioxidant was present above a certain 'critical concentration'

whereas in PAO the sample lifetime was proportional to the amine concentration.

The DSC's run with PAO/NS150 mixtures in the presence of the oxidation catalyst gave the result that the samples with the highest proportion of PAO was the most stable whereas without the catalyst the samples with the highest proportion of NS150 were the more resistant.

The most likely explanation involves the oxidation products of the basestocks. The NS150 contains organic sulphur compounds which on oxidation give strong sulphur based acids which can act as powerful peroxide decomposers so preventing radical initiation.

The DSC's run with PAO/NS150 mixtures will form these strong acids. The metal catalyst may react with the acids effectively removing them from the experiment. The PAO is inherently resistant to oxidation due to the high strength of the C-H bonds. NS150 contains alkyl aromatic compounds which readily undergo autoxidation, hence in the absence of the strong acids the PAO/NS150 mixtures would more readily undergo autoxidation. At higher proportions of NS150, so much acid may be formed that it may be able to react with all the catalyst leaving some to act as an antioxidant. This type of behaviour would explain why when the sample which contained 50% PAO/50% NS150 had the shortest induction time but as the proportion of NS150 was further increased so the induction time also increased. DSC's run with PAO/NS150 mixtures without the catalyst would be able to form the acid, hence increasing the proportion of NS150 increased the induction period.

The formation of a strong acid would also affect the chemistry of the ERCOT's. The presence of sludge in samples

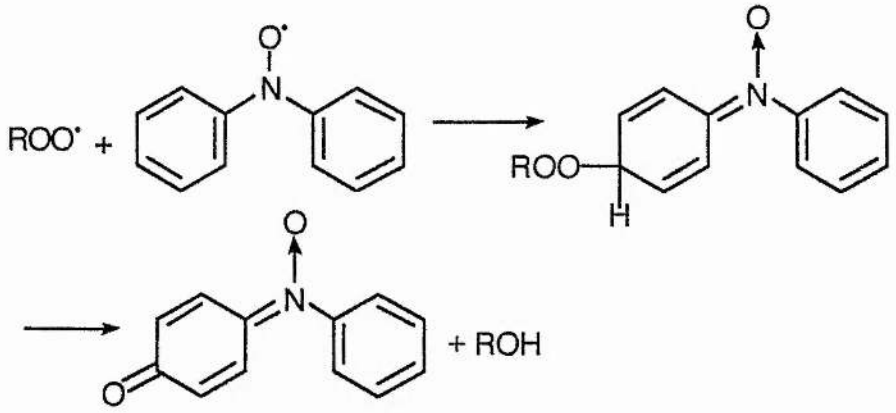
containing NS150 indicated that strong acids were being generated. The acids are able to decompose hydroperoxides via a non-radical pathway. Eventually an equilibrium situation would exist when the rate of formation of the hydroperoxides = the rate of their destruction, this in turn would lead to a constant peroxide concentration and hence a constant rate of radical initiation. If the amines are able to keep the average number of propagation steps below one then the autoxidation would be a slow process. This leads to the 'critical concentration' which is the minimum concentration of antioxidant required to achieve this[107].

Even under these conditions it would be expected that there would still be some consumption of the antioxidants. When the concentration falls below the critical value then the autoxidation process would be expected to proceed at a rapid rate. ERCOT's run with amine concentrations just above the critical concentration showed no significant increases in viscosity, even when the experiments were run for 70 hours. The fact that the autoxidation hadn't taken hold could be due to secondary chain stopping antioxidants being generated from the basestock.

This though does not seem to be the case. If secondary antioxidants were being formed then the rate of autoxidation would be expected to slow down. When experiments were run with the concentration of amine just below the critical value the rate of degradation of the sample appeared to accelerate indicating that the formation of secondary antioxidants was not important. The alternative is that the amines were not being consumed.

As discussed in section 1.7 of chapter one, amine antioxidants are converted through a series of stages to the inert

N-phenyl-*o* or *p*-benzoquinoneimine-*N*-oxide. The final step of this process is the reaction of the diaryl-nitroxide with peroxyl radicals. To inhibit the consumption of the amine antioxidant the pathway which eventually forms the nitroxide must become unfavourable. The presence of the strong acid opens up the possibility of a catalytic cycle which prevents the formation of the nitroxide and hence prevents the consumption of the amines.



Scheme 4.1
Destruction of diarylamine antioxidants

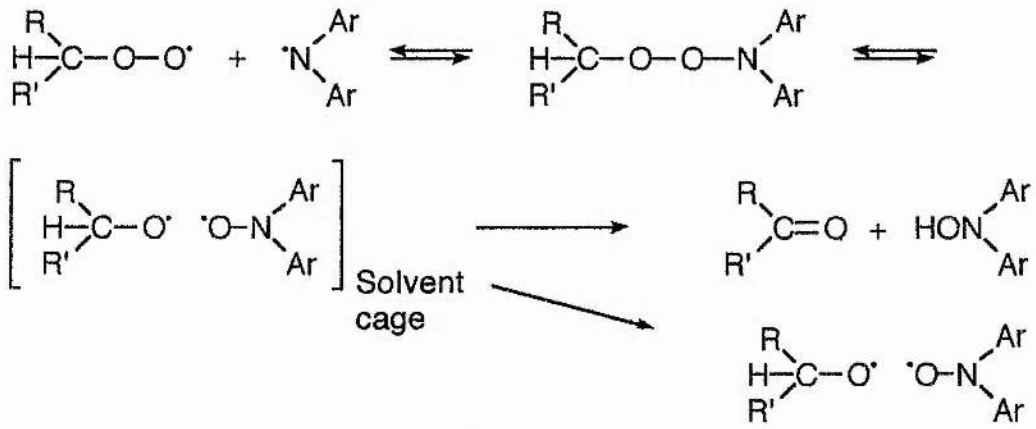
The first step of the proposed catalytic cycle is the abstraction of the aminyl hydrogen by an alkyl or peroxyl radical.

$$ROO^{\bullet} + Ar_2NH \longrightarrow ROOH + Ar_2N^{\bullet}$$

Scheme 4.2
Abstraction of the aminyl hydrogen by a peroxyl radical

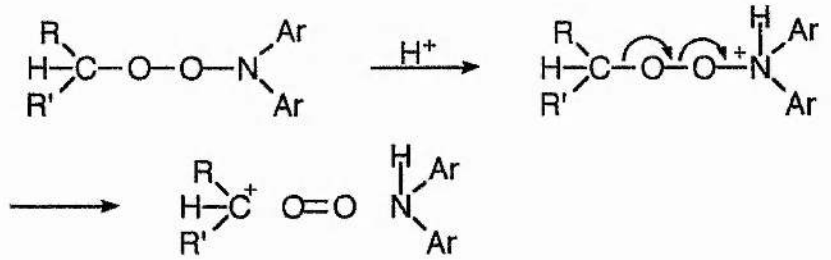
The resulting amino radical is able to combine with a peroxyl radical. The resulting intermediate can decompose to give a ketone and a diarylhydroxylamine which in turn leads to the formation of

nitroxide. The mechanism of this reaction involves the cleavage of the O-O bond to form alkoxyl and nitroxide radicals, these two radicals then disproportionate to give the hydroxylamine and ketone[1].



Scheme 4.3
Thermal interactions of the
aminyl and peroxyl radicals

In the presence of a strong acid the nitrogen can be protonated, the resulting intermediate may then be able to decompose giving a carbocation, diphenylamine and oxygen. The carbocation can either react with any nucleophiles or eliminate a proton to give an alkene.



Scheme 4.4
The possible mechanism for acid catalysed
decomposition of a *N*-peroxyalkane

If scheme 4.4 is more rapid than 4.3 then the amines will only be consumed at a slow rate, however if scheme 4.3 is the more important then the amines will be rapidly consumed.

In the presence of a strong acid the most active antioxidant would be the one which is able to go through the proposed catalytic inhibitory cycle the most rapidly. This could explain why 4,4'-dimethyldiphenylamine was a more active antioxidant in NS150.

A possible alternative to the activity problem is that the protonated amines have different activities to the unprotonated forms so the overall activity would be dependant upon the amount of protonation and the activities of the protonated and unprotonated forms of the amines. This again could lead to the 4,4'-dimethyldiphenylamine being more active than the corresponding methoxy derivative. However the activities of the methoxy and methyl derivatives were similar, so experimental errors could also make the methyl derivative appear more active.

4.9 Experimental

ERCOT's

A 350g ERCOT sample was prepared by dissolving the required amount of antioxidant into 200g of the basestock. The sample was then made up to 350g by the further addition of the basestock. From this 300g was placed into the ERCOT tube. To this was added an oil soluble iron catalyst. The iron was present in the sample at 40ppm. The samples were then placed into the oven at the desired temperature and air was blown through them.

Small samples of approximately 10ml were periodically removed and their viscosity was measured at 40°C on a Haake PK 100 viscometer.

DSC samples

The DSC sample weighed 30g. The sample was prepared by dissolving the required amount of antioxidant in 20g of oil, to this was added 0.05g of ferrocene and 0.25g of a standard lead solution comprising 24% by weight of lead. The sample was then made up to 30g.

Chapter 5

Slow release antioxidants

5.1 Aims

1. Synthesis of a number of diphenylamine derivatives as possible candidates for slow release antioxidants.
2. To subject these compounds to a series of lab. tests to determine which, if any, are potential slow release antioxidants
3. To try any potential candidates in the industrial bench oxidation tests.

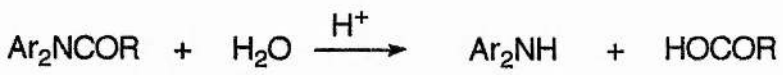
5.2 Slow release antioxidants

As an automotive oil ages it consumes its supply of antioxidants. Delayed release compounds are intended to introduce fresh antioxidants as the older ones are depleted. The ideal slow release agent should introduce fresh antioxidant over the entire lifetime of the lubricant. On average a motor oil is changed every 6-10,000 miles which corresponds to around 100-200 hours driving, therefore these compounds should decompose over a similar time period in a fired engine.

The types of compounds seen as potential candidates were the *N*-amides, *N*-silyl amines, *N*-oxides and *N*-alkyl derivatives of diphenylamine.

The amides

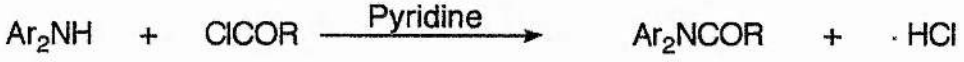
The amides were designed to be hydrolysed by any acids which form while the engine is running. The products are the free amine and a carboxylic acid.



Scheme 5.1
Hydrolysis of the amides

The main drawback in using amides is that the liberated carboxylic acid could cause lead corrosion problems. (Lead is used for many of the plain bearing surfaces of an engine.) Possible ways of overcoming this problem are to use amides prepared from dicarboxylic acids such as terephthalic acid, the free acid is known to be able to inhibit lead corrosion by the formation of a protective film[72]. Or to use amides in which the free carboxylic acid would rapidly decarboxylate under the conditions within a fired engine.

Although the amides can be easily prepared by the treatment of diarylamines with carbonyl chlorides, they were never seriously investigated.

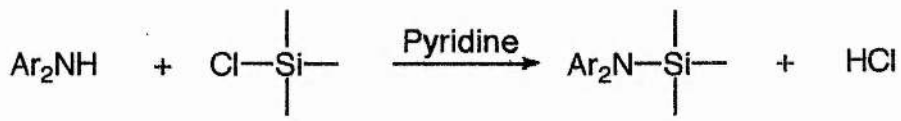


Scheme 5.2
Synthesis of amides

N-Silyl compounds

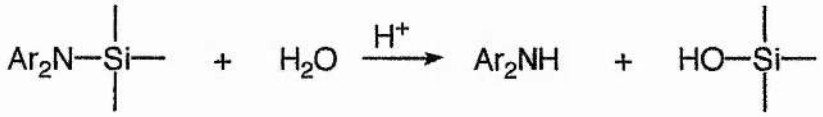
These compounds upon hydrolysis give the free amine and a silicone oil. The *N*-silyl derivative has the added advantage of generating a silicone oil, which acts as an antifoamant within the lubricant.

The attempted synthesis of this class of compound was by the treatment of the amine with a silyl chloride[73].



Scheme 5.3
Attempted synthesis of
N-silyl compounds

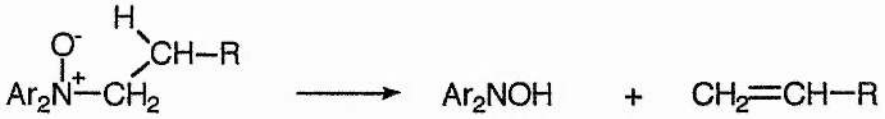
The *N*-silyl compound was never isolated after an aqueous work up, hence it was concluded that this class of compound was too easily hydrolysed to warrant further investigation.



Scheme 5.4
Hydrolysis of the *N*-silyl compounds

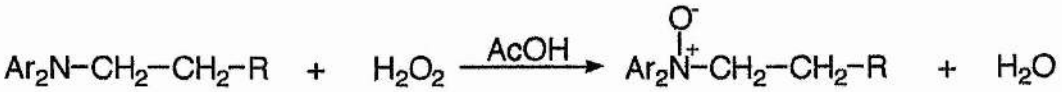
N-Oxides

These compounds were designed to decompose upon thermolysis in the high temperature regions of the engine, giving an alkene and a diarylhydroxylamine.



Scheme 5.5
Thermolysis of tertiary amine *N*-oxides

The attempted synthesis of these compounds was by the action of hydrogen peroxides upon a tertiary diphenyl, alkyl amine[74].



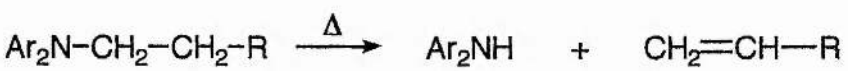
Scheme 5.6
Synthesis of the tertiary amine *N*-oxides

Several attempts were made to synthesize these compounds. In all cases a deep red oil was produced upon working up, which on examination by electron spin resonance, turned out to be the diaryl nitroxide radical.

These compounds are known to decompose by a process of β-hydrogen elimination[75]. If derivatives were prepared without any β-hydrogens, for example the *N*-methyl derivative, then the elimination reaction could not occur. Such compounds may be of some use as slow release antioxidants. However, in general these compounds were thermally too unstable to warrant further investigation.

N-Alkylated diarylamines

Of all the compounds investigated the *N*-alkylated diarylamines were the most promising. At the elevated temperatures found in some regions of car engines, these compounds were expected to decompose by β-hydrogen elimination, to give a diarylamine and an alkene.



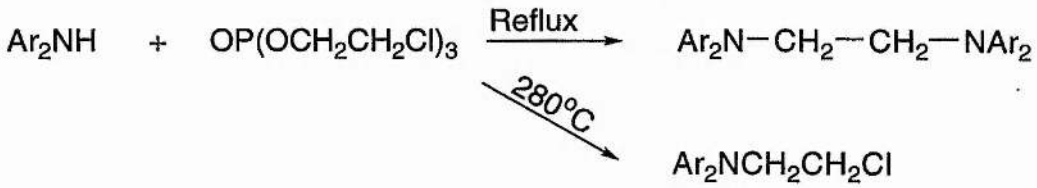
Scheme 5.7
Thermolysis of *N*-alkyl diphenylamine

5.3 Synthesis

Due to the poor nucleophilic nature of diphenylamine many of the methods tried gave poor yields. Good yields of the n-alkyl derivatives were eventually obtained by refluxing the amine with a trialkylphosphate[76].

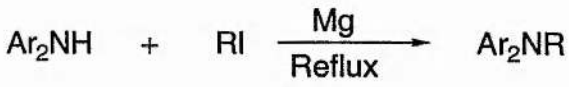
Scheme 5.8
Synthesis of *N*-alkyl DPA , using a trialkylphosphate

The *N,N,N',N'*-tetraphenylethane-1,2-diamine was synthesized by heating diphenylamine in the presence of tri(2-chloroethyl) phosphate. Attempts to synthesize the 2-chloroethyl derivative were by refluxing the mixture in the presence a high boiling inert solvent.



Scheme 5.9
Reaction of DPA with $OP(OCH_2CH_2Cl)_3$ under differing conditions

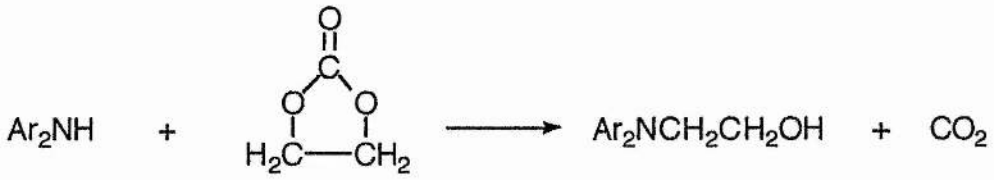
For branched alkyl derivatives this method proved ineffective. These were finally synthesized in good yields by refluxing the amine with the appropriate alkyl iodide over magnesium turnings[77].



Scheme 5.10
Synthesis of secondary *N*-alkyl derivatives

For *N*-ethyl derivatives with functional groups present on the β-carbon, the best method found was to reflux the amine with ethylene carbonate, this gave *N*-(2-hydroxyethyl)

diphenylamine[78]. The alcoholic function could then be manipulated to give other functional groups.



Scheme 5.11
Synthesis of the *N*-(2-hydroxyethyl) diphenylamine

The bromo compound was synthesized by the treatment of the alcohol with phosphorus tribromide[79].

Scheme 5.12
Bromination of *N*-(2-hydroxyethyl) diphenylamine

Other methods tried included alkylation via the *N*-alkali metal diphenylamide. The amide anions were formed by a variety of methods. These included the treatment with butyl lithium[80,81], liquid sodium in toluene, sodamide and sodium hydride. The alkylating agents tried were alkyl halides, tosylates[82] and phosphate esters. In all cases the percentage of *N*-alkylation was low.

5.4 Thermal decomposition

The aim of these experiments was to evaluate the effects that the differing alkyl groups have on the thermal stability of the *N*-alkylated diphenylamines and to identify the major products

from their pyrolysis. To compare the thermal stabilities of these compounds the amount of decomposition was measured at a constant temperature. The most stable amine would be the one with the highest proportion of starting material remaining after the thermolysis. The techniques employed for this study were flash vacuum pyrolysis (FVP) and conventional pyrolysis. (For more details on pyrolysis techniques see ref. 83)

FVP involves vaporising the test sample and passing it through a hot tube under high vacuum conditions. The products are then condensed within a liquid nitrogen trap. The temperatures involved with FVP can be up to 1000°C, but the reactants are only in contact with the hot region for a few milliseconds.

Conventional pyrolysis is carried out at much lower temperatures but the contact times are only limited by the experimental requirements.

To determine which of the compounds were the most stable the products of the pyrolyses needed to be analysed. The techniques employed were NMR, GC-MS, GC and thin layer chromatography (TLC).

5.5 Conventional pyrolysis

The conventional pyrolyses were carried out in a heated fluidized sand bath. The samples were prepared by placing a few drops of the *N*-alkylated amine into 2ml ampoules, these were then degassed and sealed under a few Torr of nitrogen.

The pyrolysis involved placing the samples under the surface of the sand and removing them after a known time. The temperatures of the experiments were monitored using a

thermocouple. The experiments were started at a temperature of 250°C and increased by 25°C for each experimental run. A normal run used 6 samples, one of which was removed each hour.

The percentage of decomposition was estimated by using ^1H NMR. This was possible because the aromatic rings were unaffected by the thermolysis, so changes in the ratio of the aromatic to alkyl hydrogens could be used to measure the percentage decomposition.

Problems experienced with this set-up were that the samples kept coming lose and floating up to the surface, where the temperature was cooler by as much as 100°C. Also, within the samples, there was no pressure release mechanism so occasionally they exploded. At 350°C the procedure was abandoned due to the samples exploding. For all the experiments *N*-ethyldiphenylamine was used.

Results

250°C no appreciable decomposition after 6 hours

275°C no decomposition

300°C no decomposition

325°C 6 hours, 5 % of decomposition, $k_d = 2.4*10^{-6}\ s^{-1}$.

350°C 1 hour, 7% decomposition, $k_d=2*10^{-5}\ s^{-1}$.

2 hours, 38% decomposition, $k_d=6.6*10^{-5}\ s^{-1}$.

Average $k_d = 4.3*10^{-5}\ s^{-1}$.

Other samples cracked or broke free.

Product analysis

The products of these reactions were analysed by NMR and TLC. Apart from the starting material, the only product detected was diphenylamine.

5.6 FVP experiments

The amount of decomposition the *N*-alkylated amines undergo during pyrolysis will be dependant upon the rate of decomposition and the time the molecules are in contact with the hot zone.

The experiments were run at a pressure of $5*10^{-3}$ Torr, measured with a Pirani gauge between the cold trap and the oil pump. Under these conditions it was assumed that molecular interactions were minimal, hence the flow through the hot zone was molecular. The contact time was estimated from the velocity of the molecule and the length of the hot zone.

The velocity of the molecule through the hot zone was estimated from the kinetic energy the molecule would have at the thermolysis temperature. The kinetic energy of a free molecule is 3/2 RT, 1/2 RT for movement in each dimension, where R is the gas constant and T is the absolute temperature. Molecules passing through a hot zone of temperature T will have a velocity along the tube averaging $(RT/M_r)^{1/2}$ ms^{-1}, where M_r is the molecular weight of the molecule in kilograms. The length of the hot zone was also known, hence the rate of decomposition at each temperature could be estimated. From this the pre-exponential factor and the activation energy were obtained, although these would be very crude estimates. The products of the FVP were captured using a trap cooled by liquid nitrogen.

The percentage decomposition was estimated from the ^1H NMR integral ratio's and by GC. Product identification was by GC-MS, isolation of any products was by TLC after which ^1H NMR and MS were applied. After the FVP, the aromatic hydrogens were left

relatively intact and so could be used as a reference to monitor disappearance of the alkyl groups.

The samples used for these experiments were the *N*-methyl (Ph_2N-Me), *N*-ethyl (Ph_2N-Et), *N*-n-butyl (Ph_2N-Bu^n), *N*-n-hexyl (Ph_2N-Hex^n), *N*-isopropyl (Ph_2N-Pr^i), *N*-(2-bromoethyl) (Ph_2N-CH_2CH_2Br), 2-hydroxyethyl (Ph_2N-CH_2CH_2OH) diphenylamines, *N,N,N',N'*-tetraphenylethane-1,2-diamine (Ph_2N-CH_2CH_2-NPh_2) and a mixture of 2- and 4-methyl-*N*-methyldiphenylamine (2- and 4-Me-$C_6H_4N(Ph)Me$).

5.7 FVP of *N*-methyldiphenylamine, results and discussion

The major products isolated from the FVP of Ph_2N-Me were 2- and 4-methyldiphenylamines, diphenylamine and tetraphenylhydrazine. Other products detected in smaller amounts were Ph_2N-Et, 2- and 4-methyl-*N*-methyldiphenylamines, bis(diphenylamino)methane and carbazole. The table below shows the major products and their proportions.

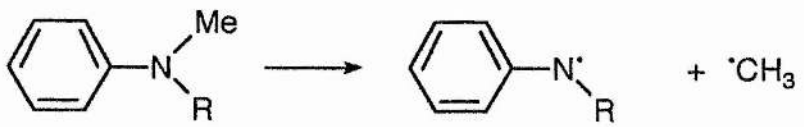
Temp °C	%Ph_2N-Me*	%Ar-Me	% DPA	Other
700	73	7	8	12
750	32	11	26	31
800	2	10	34	54

*Unreacted Ph_2N-Me

For the decomposition of Ph_2N-Me, log (A/s^{-1})=13.8 and Ea= 53.3kcal mol^{-1}.

Ph_2N-Me would be expected to decompose by homolytic cleavage of the N-C bond to give a methyl and an aminyl radical. A similar reaction is known to occur in the thermal decomposition of

N-methylated anilines [84]. In this reaction the products are again the methyl and aminyl radicals.



R = H, Me

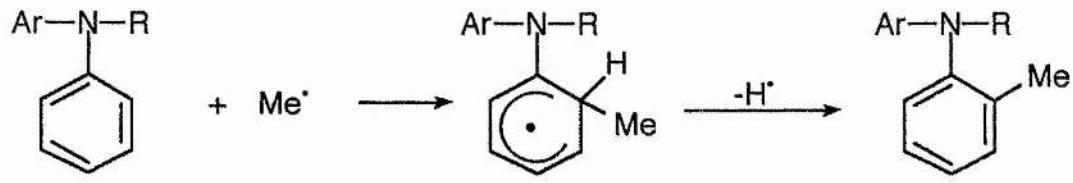
Scheme 5.13
Decomposition of *N*-methylated anilines

The pre-exponential factor and activation energy have been determined for scheme 5.13, when R=H, $\log(A/s^{-1})=13.4$ and Ea=60kcal[84], and when R=Me, $\log(A/s^{-1})=12.9$ and Ea=57kcal[84]. For the decomposition of Ph_2N-Me a lower energy of activation and a higher overall rate of decomposition would be expected due to the extra stabilisation of the aminyl radical by the second aromatic ring. The experimental result was in accord with this (see above).

Aryl methylation

A substantial proportion of the FVP product contained methyl groups in the 2- or 4- position. Theoretically these derivatives can be produced by three different mechanisms.

The first mechanism involves the addition of a methyl radical to an aromatic ring of diphenylamine (or the starting material). The resulting radical is stabilised by delocalisation of the unpaired electron in the aromatic rings. The loss of the tertiary hydrogen, either by abstraction or elimination gives the aryl methyl derivative[85].



Scheme 5.14
Possible mechanism for the formation of
aryl methyl derivatives

The addition of a methyl radical to the starting material should give 2- and 4- methyl-*N*-methyl diphenylamine, especially at temperatures where the amount of decomposition was low. However these products were only found in minute quantities indicating that attack on the starting material was unimportant. Also some 3-methyl product would be expected whereas none was found. The presence of a methyl group on the nitrogen should not significantly affect the reactivity of the aromatic rings towards the methyl radical, therefore this mechanism cannot be important.

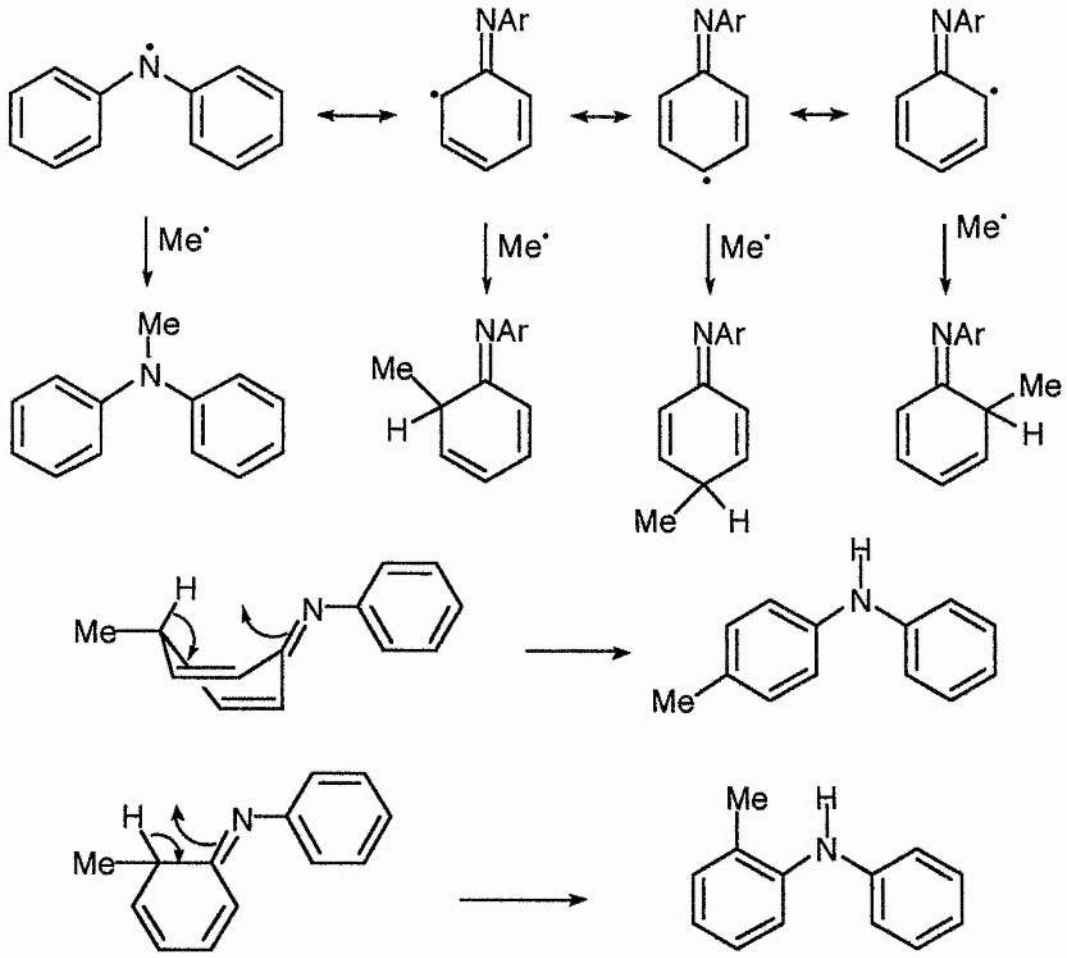
This can be explained by looking at the thermodynamics of a simple model system based on scheme 5.14. For the model, the addition of a methyl radical to benzene was examined. The energy released by the addition of a hydrogen atom to benzene has been calculated to be 28 kcal mol^{-1} [86]. The average C-C bond is about 16 kcal mol^{-1} weaker than the average C-H bond, hence the energy released by the addition of a methyl radical to benzene was estimated to be 12 kcal mol^{-1}. The change in entropy associated with this process was estimated to be -34.3 cal mol^{-1} deg^{-1}. ΔG for the addition would be positive above about 80°C, i.e. the decomposition of the radical intermediate would be favoured over its formation. The equilibrium constant K is related to ΔG by the formula $\Delta G=-RTlnK$. At 700°C the rate constant for the

decomposition was estimated to be $7.5*10^{4}$ times the rate constant for the formation of the intermediate radical. The addition reaction is further disfavoured by the low pressures associated with FVP. This is because the combination reaction is a bimolecular process and so is dependant upon the concentration of both the methyl radical and the diarylamine, whereas the decomposition is a unimolecular process. Both factors therefore make scheme 5.14 highly unfavourable.

Although scheme 5.14 is highly implausible, methyl radicals can add onto the aromatic rings of the diphenylaminyl radical. Resonance stabilisation of the aminyl radical leaves the *ortho* and *para* positions prone to attack. The imine derivatives thus derived can undergo an intramolecular hydrogen shift to give the methylated diarylamine. A similar mechanism is known to operate when a methyl radical reacts with a phenoxyl radical[86].

Thermodynamically this process is favourable. The energy released by the addition of the methyl radical to the aromatic system of the diphenylaminyl radical is approximately 37kcal (See end of chapter for assumptions and derivation). The change in entropy associated with the addition of a methyl radical to the aromatic ring was assumed to be the same as the addition of a methyl radical to a phenyl radical. The equilibrium constant for the addition reaction at 1000K is approximately 4, i.e the rate constant for the combination reaction is 4 times more rapid than the decomposition. However at the low pressures associated with FVP the decomposition would be greatly favoured. However the rearrangement is also favourable due to the release of a large amount of energy when the aromatic system is regenerated. This is further enhanced by the ease with which the transition states

for these processes are attained and that the change in entropy associated with these processes is minimal.



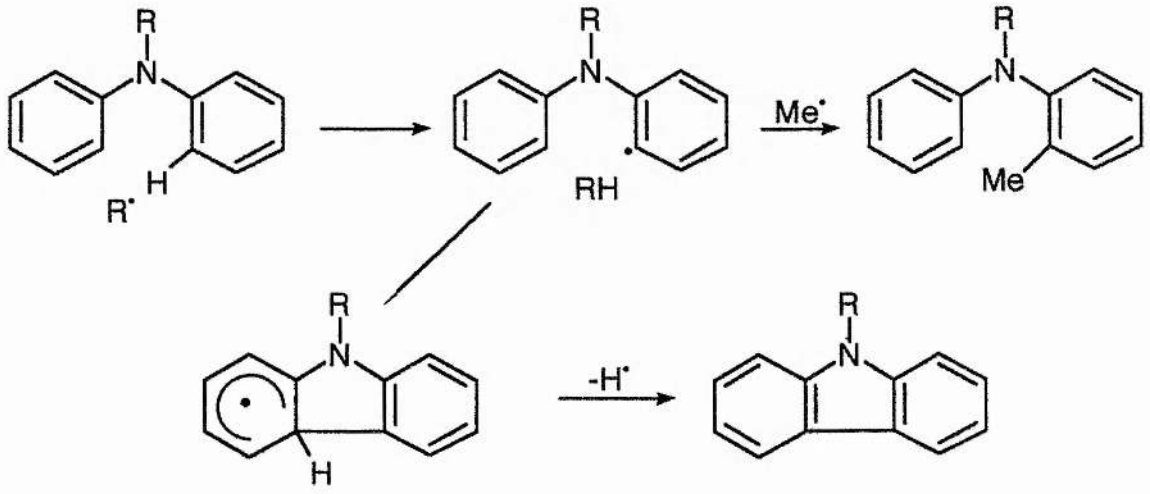
Scheme 5.15
Reaction of methyl radicals with the diphenylaminyl radical

As shown in scheme 5.15, there are three possible products. These are Ph_2N-Me, 2- and 4- methyldiphenylamine. The thermodynamically more favourable products are the 2- and 4-methyldiphenylamines. Estimates of the equilibrium constant ranged from 41 to 1400 in favour of the aryl-methyl derivative at 1000K. The addition of methyl radicals to the diphenylaminyl

radical should be similar in character to the addition of methyl radicals to the phenoxyl radical. In this reaction only 8% of the methoxy derivative is formed, the 2- and 4-methyl derivatives make up the other 92% [86], showing that for this reaction the thermodynamic considerations were the more important. It would be expected that the addition of methyl radicals to the diphenylaminyl radical will behave similarly.

Scheme 5.15 explains why two of the major products were the 2- and 4-methyl diphenylamines but it doesn't explain how the 2- and 4-methyl-*N*-methyl diphenylamines were formed.

The third possibility is that the methyl radical undergoes a termination reaction with an aryl radical. The presence of carbazole in the reaction products indicated that the 2-aryl radical was being created during the thermolysis. If the aryl radical isn't destroyed then it can go on to attack the second aromatic ring. Loss of the tertiary hydrogen from the intermediate radical, either by elimination or abstraction, gives carbazole[85].



Scheme 5.16
The formation of methyl derivatives
and carbazole

Generation of the aryl radical is by abstraction of one of the aryl hydrogens. Possible abstracting agents are the methyl radical or the hydrogen atom. The abstraction by the methyl radical is endothermic to the extent of 5.9 kcal mol^{-1}, the change in entropy was estimated to be -2.9 cal deg^{-1} mol^{-1}. At 1000K the equilibrium constant for the abstraction of hydrogen from the aromatic ring by a methyl radical is 0.22 i.e. the abstraction of hydrogen from methane by an aryl radical is about 4.5 times more rapid than the abstraction of hydrogen from benzene.

The same calculations carried out for the hydrogen atom give ΔH= +6.6 kcal mol^{-1}. ΔS for this process however was found to be -8.6 cal deg^{-1} mol^{-1}. The equilibrium constant is 2.7 at 1000K, i.e. the abstraction of hydrogen, by a hydrogen atom, from the aromatic ring is about 3 times quicker than abstraction of hydrogen from a hydrogen molecule by an aryl radical. (See end of chapter for assumptions and calculations.) Therefore the more active abstracting agent in the pyrolysis system is likely to be the hydrogen atom.

At lower temperatures, when the amount of decomposition of the starting material was low, scheme 5.16 should produce a large proportion of dimethylated products since statistically there was a good chance of attack on the starting material. However the reaction depicted in scheme 5.15 would only give monomethyl derivatives. In the product mixture at 700 and 750°C almost all of the aryl methylated product had no aminyl methyl group indicating that methyl radical attack on the aminyl radical was the most important of the aryl methylating reactions.

Formation of diphenylamine

Experimentally it was found that diphenylamine was the major product in the thermolysis of the Ph_2N-Et. The Ph_2N-Me can be converted to Ph_2N-Et by the abstraction of one of the methyl hydrogens from the starting material to give a diphenylaminomethyl radical. This can combine with a second methyl radical to give the Ph_2N-Et derivative, which on thermolysis gives diphenylamine. (See FVP of *N*-ethyldiphenylamine derivative, results and discussion)

$$Ar_2N{-}Me \longrightarrow Ar_2N^{\bullet} + Me^{\bullet}$$

$$Ar_2N{-}Me + Me^{\bullet} \longrightarrow Ar_2N{-}\dot{C}H_2 + MeH$$

$$Ar_2N{-}\dot{C}H_2 + Me^{\bullet} \longrightarrow Ar_2N{-}CH_2{-}CH_3$$

$$Ar_2N{-}CH_2{-}CH_3 \longrightarrow Ar_2NH + H_2C{=}CH_2$$

Scheme 5.17
Possible formation of the Ph_2N-Et

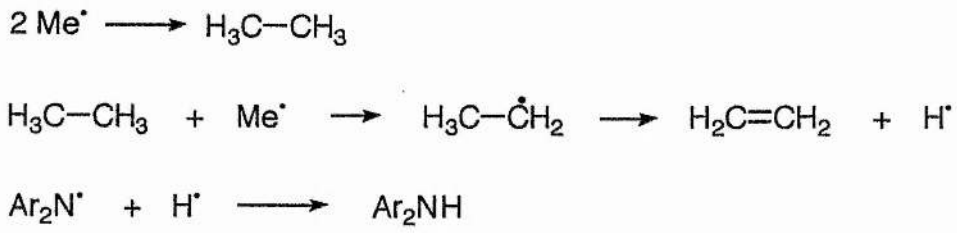
The diphenylaminomethyl radical can also combine with an aminyl radical to generate the bis(diphenylamino)methane.

$$Ar_2N{-}\dot{C}H_2 + {}^{\bullet}NAr_2 \longrightarrow Ar_2N{-}CH_2{-}NAr_2$$

Scheme 5.18
Formation of
bis(diphenylamino)methane

Diphenylamine can also be formed by the combination of a hydrogen atom with the aminyl radical. The hydrogen atoms can be generated by the combination of two methyl radicals to give

ethane, hydrogen abstraction from the ethane gives an ethyl radical which can decompose to form ethylene and a hydrogen atom.



Scheme 5.19
Formation of hydrogen atoms

The tetraphenylhydrazine was formed by the combination of two aminyl radicals.

Scheme 5.20
Formation of tetraphenylhydrazine

The major drawbacks with schemes 5.17 and 5.19 is that they require a number of intermediate steps. Under FVP conditions reactive interactions are normally rare. Another possibility is that the aminyl radicals are able to abstract hydrogen from the walls of the pyrolysis tubes.

5.8 FVP of *N*-ethyl diphenylamine, results and discussion

The major products formed in the pyrolysis of Ph_2N-Et were DPA, 2- and 4-methyldiphenylamines, Ph_2N-Me and tetraphenylhydrazine. Other products detected and identified in smaller amounts were bis(diphenylamino)methane, carbazole and 2- and 4-ethyldiphenylamines. The table below shows the major products and their proportions.

Temp °C	%Ph_2NEt^*	%Ph_2NMe	%Ar-Me	%DPA	Other
650°C	100	0	0	0	0
700°C	66	3	2.7	29	0
750°C	20	7	5.7	66	4
800°C	0	3	8.7	79	11

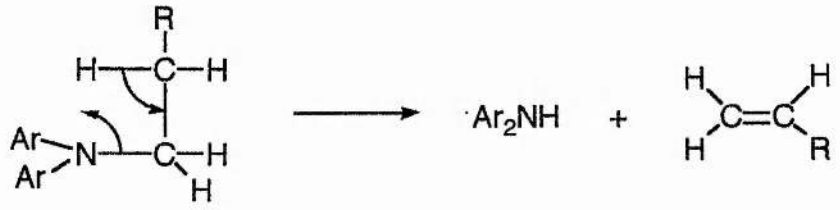
* Unreacted starting material

For the decomposition of Ph_2N-Et the Log (A/s^{-1})=13.4 and Ea= 49.4kcal mol^{-1}.

Formation of diphenylamine

The major product found in the decomposition of Ph_2N-Et derivative was Ph_2N-H. This can be formed by an intramolecular β–hydrogen elimination or by a free radical mechanism.

At 1000K the thermodynamically most favoured process is the β-hydrogen elimination. The products of this are ethylene and diphenylamine. Although the energy released in this process is small, the main driving force would be the increase in entropy associated with the formation of two molecules from the original starting material. ΔG was estimated to be -29.5 kcal mol^{-1} at 1000K (see end of chapter for calculations).



Scheme 5.21

Formation of DPA by β-hydrogen elimination

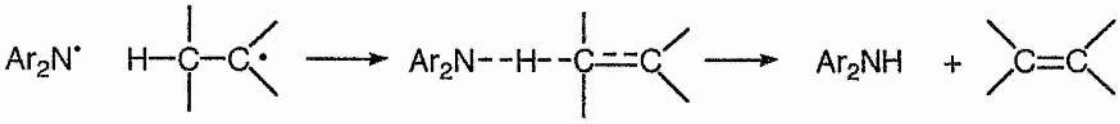
The free radical processes would be initiated by cleavage of the N-C bond to give the aminyl and ethyl radicals. Thermodynamically this process is unfavourable compared to the

β-hydrogen elimination. At 1000K ΔG was estimated to be +13 kcal mol^{-1}. For the decomposition, K= $1.4*10^{-3}$, i.e. the rate constant for the recombination is 700 times larger than the rate constant for the decomposition. The recombination is a bimolecular process, so at the pressures associated with FVP, i.e. 0.1-0.001 Torr, the rate of decomposition was calculated to be 1800 to $1.8*10^5$ times more rapid than the recombination. (For assumptions and calculations see the end of this chapter.)

It would be expected that if the *N*-Et derivative was decomposing by cleavage of the N-C bond then the activation energy for its decomposition should be close to that found for the *N*-Me derivative. Experimentally there was only a few kcal mol^{-1} difference between the two activation energies. The presence of tetraphenylhydrazine in the reaction products indicated that cleavage of the N-C bond was occuring during the pyrolysis.

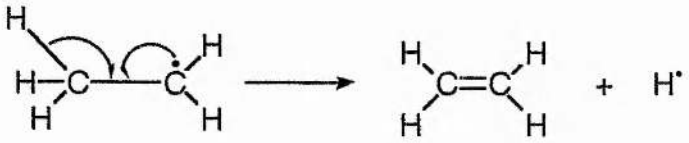
The final products derived from the thermolysis would depend upon the behaviour of the radicals. Thermodynamically the most favourable process during pyrolysis is the disproportionation between two ethyl radicals. Disproportionation between the ethyl and aminyl radicals is also highly favourable, but the ethyl radical is also able to abstract the aminyl hydrogen from any diphenylamine which may form. If the free radical reactions were limited to disproportionation and hydrogen abstraction then the major product would be tetraphenylhydrazine. In cooler regions of the apparatus the most favourable process is the termination reaction between two ethyl radicals. The fact that diphenylamine was the major product indicates that both ethyl radical disproportionation and the

abstraction of the aminyl hydrogen were comparatively unimportant.



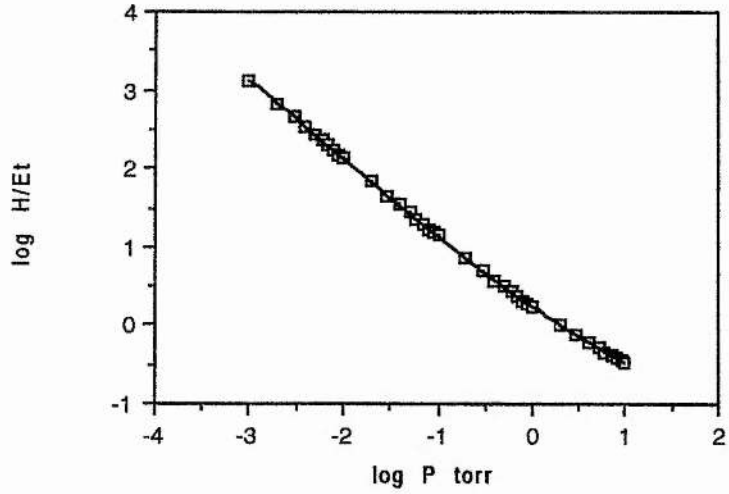
Scheme 5.22
Formation of DPA by
radical disproportionation

In the hot zone the ethyl radical can also decompose to give a hydrogen atom and ethylene. Diphenylamine can then be formed by the combination of a hydrogen atom with the aminyl radical.



Scheme 5.23
Decomposition of the ethyl radical

To determine what type of reactions were occuring the kinetics of ethyl radical reactions were estimated. At 1000K the rate of decomposition of the ethyl radical = $[Et^{\cdot}]*2.9*10^{5}$ [87], the decomposition is reversible, the rate of its formation = $[H][C_2H_4]*2.7*10^{10}$ [87]. Decreasing the pressure of the system decreases the probability of the hydrogen atom combining with the ethylene, which in turn favours the decomposition.



Graph 5.1
Variation of [H]/[Et] with pressure
for a model system

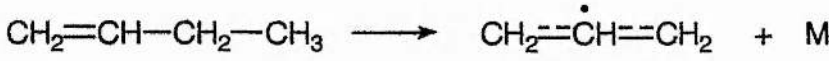
At the pressures associated with flash vacuum pyrolysis, i.e 0.1-0.001 Torr the ratio of hydrogen to ethyl radicals ranges from approximately 10 to 1 to 1000 to 1 in favour of hydrogen. At the higher pressures diphenylamine can be generated by the combination of a hydrogen atom with the aminyl radical, or by a disproportionation reaction between an ethyl and an aminyl radical. On statistical grounds the disproportionation between two ethyl radicals is unfavourable. As the pressure is decreased so the addition of the hydrogen atom to the aminyl radical becomes more important due to the increasing scarcity of the ethyl radical.

Once the diphenylamine is formed then the aminyl hydrogen can be abstracted by hydrogen atoms. For diphenylamine to be the major product this reaction could not have been important. Diphenylamine can be formed by a head to head termination reaction between the aminyl radical nitrogen and the hydrogen atom. But once the diphenylamine has been formed then

statistically it is just as probable that a hydrogen atom will come along a similar path and remove the aminyl hydrogen. However if a scheme like 5.15 was important, with the methyl radical being replaced by a hydrogen atom, then the interaction of the hydrogen atom with almost any part of the diphenylaminyl radical will form diphenylamine, whereas abstraction of the aminyl hydrogen would still involve the interaction of the aminyl hydrogen with a hydrogen atom, which is only a small part of the molecule. Statistically the addition reaction would then be more favourable.

Formation of the methyl derivatives

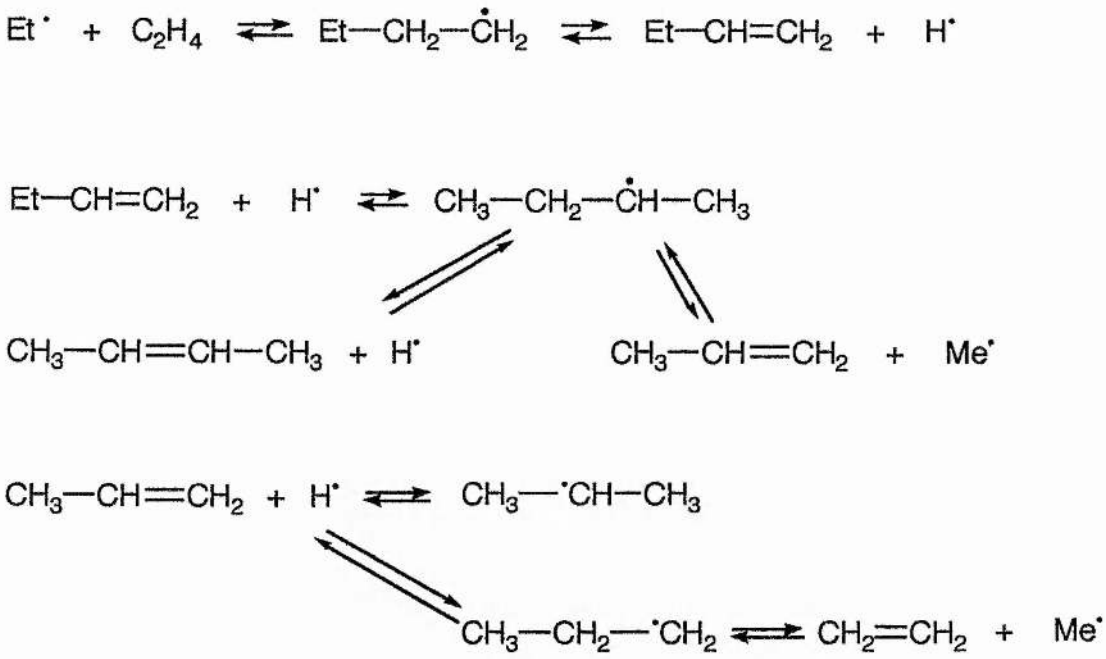
Problems are still encountered when radical reactions are used to describe the formation of the methyl derivatives. The ethyl radical cannot decompose to give a methyl radical as this also requires the formation of methylene, but an ethyl radical can combine with ethylene to give a butyl radical. On decomposition this can either give the starting compounds or decompose to give a hydrogen atom and butene. But-1-ene is able to decompose to give a methyl radical and a resonance stabilised allyl radical.



Scheme 5.24
Decomposition of but-1-ene

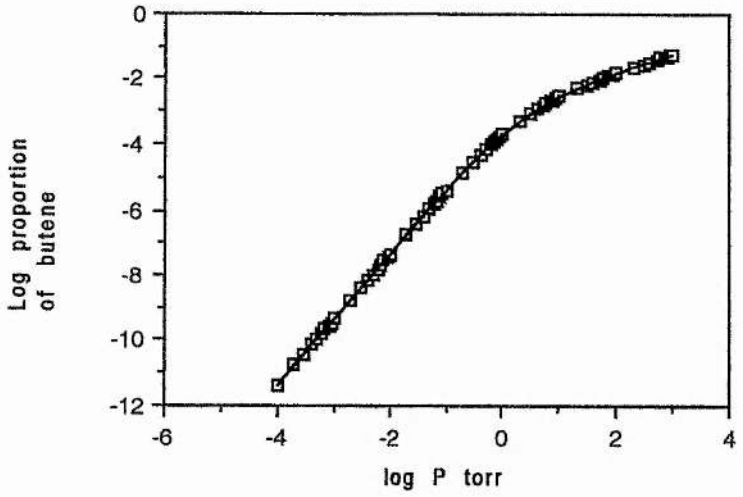
Reported rate constants for this decomposition range from 8.25 s^{-1} [88] to 0.112 s^{-1} [89] at 1023K, i.e for a contact time of about 2ms the amount of decomposition of a sample of but-1-ene will range from 1.6% to 0.02% depending upon which rate constant is used. Methylated derivatives made up 19% of the thermolysis products at 1023K.

A possible alternative is that a hydrogen atom is adding to the butene to give the secondary radical which on decomposition gives both methyl radicals and hydrogen. Once 2-butene or propylene have formed then further interactions with hydrogen atoms lead to the generation of methyl radicals.



Scheme 5.25
The formation of methyl radicals

Looking at the kinetics of a simple model system, the rate of formation of butene = [n-Bu•]*1*10^{6} [87], the rate of formation of the n-butyl radical = [Et•][C_2H_4]*1.56*10^{6} [87], and the rate of the reverse reaction = [Bu•]*2.12*10^{7} [87]. The following graph shows the approximate proportion of butene formed at the end of the pyrolysis assuming that the contact time is approximately 2ms for a system derived from the decomposition of the ethyl radical, i.e. [H] = [C_2H_4] and termination reactions are unimportant.



Graph 5.2
Proportion of butene formed
in a model system

The graph shows that at the pressures associated with flash vacuum pyrolysis, i.e. 0.1 to 0.001 Torr the proportion of butene ranges from one molecule in $2.5*10^5$ to $2.8*10^9$. Even at one Torr this ratio is 1 in 4900. The amount of butene is low, therefore it cannot act as a useful intermediate in the generation of methyl radicals.(See end of chapter for further details of the model system.)

In the real pyrolysis radicals would be lost from the system by termination reactions, which further decreases the likelihood of butene formation. If this mechanism was important then it would be expected that Ph_2N-Bu^n would readily form methyl radicals on FVP and therefore a higher proportion of methylated derivatives. Experimentally however it was found that a lower proportion of methyl derivatives were obtained than from Ph_2N-Et.

The alternative is that the methyl radicals were being generated directly from the starting material or a derivative

obtained by the interaction of radicals with the starting material. Cleavage of the C-C bond would be feasible as a source of methyl radicals if the resulting diphenylaminomethyl radical was highly stabilised.

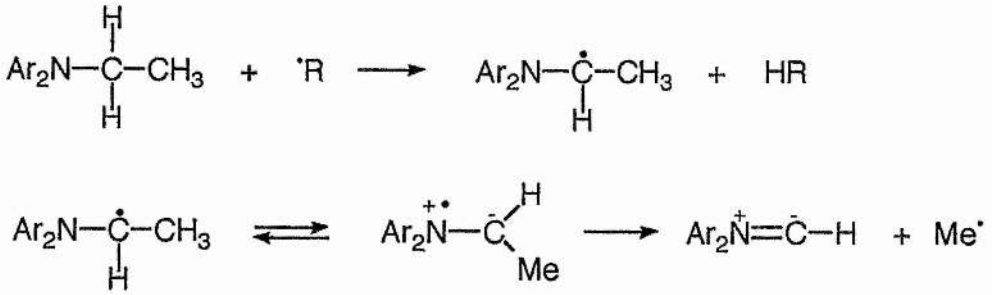
$$Ph_2NCH_2CH_3 \longrightarrow Ph_2NCH_2^{\bullet} + {}^{\bullet}CH_3$$

Scheme 5.26

The decomposition of N-ethyldiphenylamine by C-C cleavage

The amount of *N*-methylation should increase if the second fragment was stabilised relative to the methyl radical. It would be expected that both the Ph_2N-Bu^n and Ph_2N-CH_2CH_2OH derivative should both generate a higher proportion of Ph_2N-Me, since both the n-propyl and hydroxymethyl radicals are stabilised relative to the methyl radical[90], however this argument would only be valid if these amines decomposed by the same route. Experimentally it was found that Ph_2N-Bu^n formed a lower proportion of methylated products and Ph_2N-CH_2CH_2OH formed only minute amounts. (See FVP of *N*-n-butyl diphenylamine and *N*-(2-hydroxyethyl) diphenylamine, results and discussion.)

Another possibility was that an α-hydrogen was being abstracted from the starting material to give an alkyl radical which is able to delocalise its radical centre onto the nitrogen. Loss of the methyl radical gives a nitrogen ylid, which can react with hydrogen to give the *N*-methyl derivatives.



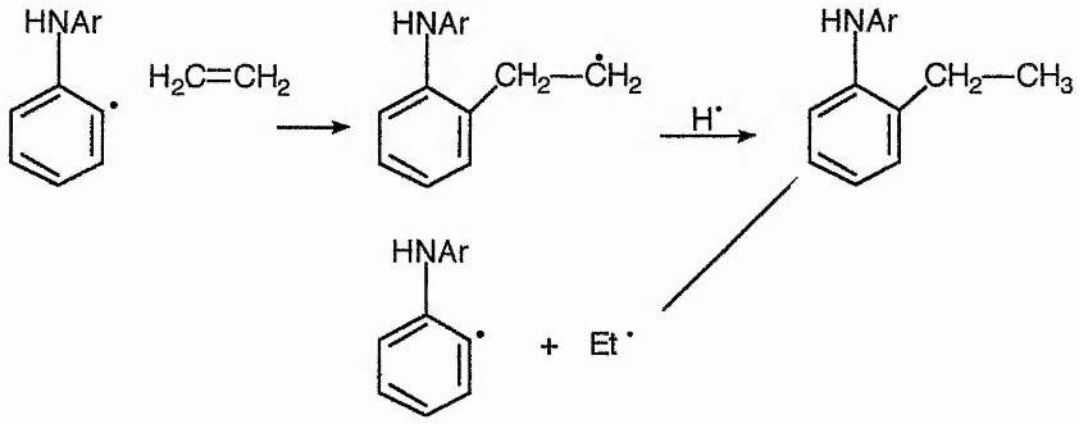
Scheme 5.27
Possible mechanism for the
formation of methyl radicals

The Ph_2N-Me derivative can also be formed by termination reactions between the aminyl and methyl radicals. Schemes like 5.26 and 5.27 should produce a high ratio of *N* to aryl methylation when compared to the combination of a methyl with the diphenylaminyl radical (scheme 5.15). The best example of the latter mechanism involves the decomposition of the Ph_2N-Pr^i derivative. Cleavage of the N-C bond readily occurs generating the aminyl and isopropyl radical. The isopropyl radical can, through various processes, give methyl radicals. (see FVP of *N*-isopropyldiphenylamine, results and discussion) Once formed the methyl radicals can combine with the aminyl radicals to form the methylated derivatives. For Ph_2N-Pr^i the proportion of the *N*-Me product was the lowest for any of the alkylated amines but the amount of aryl methylation was, at 650 and 700°C, the highest. (see FVP of *N*-isopropyldiphenylamine results and discussion)

Arylethyl derivatives

The aryl ethyl derivatives can be formed by three possible mechanisms. The radical termination reaction between an aryl and ethyl radical, the addition of an aryl radical to ethylene, the resulting radical would then have to combine with a hydrogen

atom to form the aryl-ethyl derivative and the addition of an ethyl radical with the aromatic ring of the diphenylaminyl radical (see scheme 5.15). The aryl-ethyl derivatives once formed can decompose to give a methyl and a benzyl radical. If this was formed in appreciable amounts then it would be expected to decompose at a rate similar to ethyl benzene. Ethyl benzene decomposes at a rate of about 0.4 s^{-1} at 1000K [91]. This gives it a half life of about 2 seconds which is approximately 1000 times longer than the contact time, hence the aryl ethyl derivative will not act as a useful source of methyl radicals.



Scheme 5.28
Formation of the aryl ethyl derivatives

It can be concluded that although the formation of diphenylamine can be explained by β-hydrogen elimination, other products detected in the reaction mixture can only be explained if free radicals were being formed. It is possible that both of these processes are occuring during the thermolysis, with the free radical route becoming more important at higher temperatures.

5.9 FVP of *N*-isopropyldiphenylamine, results and discussion

The products formed from the pyrolysis of Ph_2N-Pr^i were essentially the same as those formed from the decomposition of Ph_2N-Et. New products identified in small amounts were *N*-isopropyl-2-methyldiphenylamine and *N*-isopropyl-4-methyldiphenylamine. The table below gives the major products and their proportions.

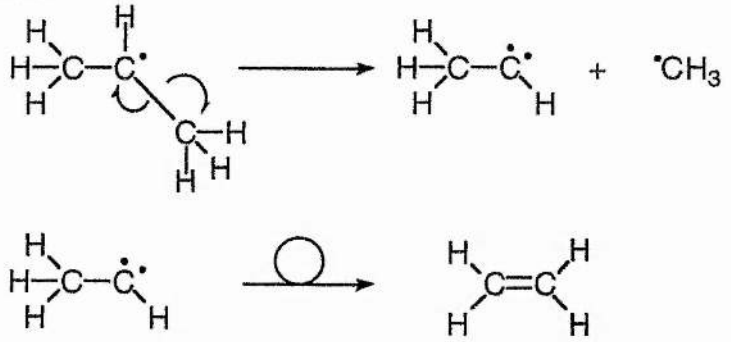
Temp °C	%Ph_2NPr^i	%Ph_2NMe	%Ar-Me	%DPA	Other
600	100	0	0	0	0
650	54	1	15	30	0
700	11	2.5	10	76	1
750	3.5	1	5.7	82	8
800	0	0	4	88	8

Ph_2NPr^i was unreacted starting material.

For the decomposition of Ph_2N-Pr^i Log (A/s^{-1})=10.0, Ea=33 kcal mol^{-1}.

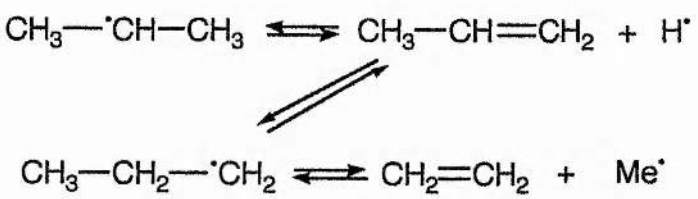
Experimentally it was found that of all the unsubstituted *N*-alkyl diphenylamines, Ph_2N-Pr^i decomposed the most readily. Possible reasons for this are that the molecule in having six β-hydrogens, (Ph_2N-Me has zero, Ph_2N-Et has three, and all the others have two) would undergo β-hydrogen elimination more readily on statistical grounds than the other derivatives. A second possibility is that the isopropyl radical is stabilised by the presence of two methyl groups, hence Ph_2N-Pr^i would be expected to undergo radical reactions more readily because cleavage of the N-C bond is also more favourable.

For the isopropyl radical to directly generate methyl radicals it also has to form a carbene intermediate, which can rearrange to give ethylene.



Scheme 5.29
Direct formation of methyl radicals
from the isopropyl radical

The alternative is that the isopropyl radical decomposes to give propene and a hydrogen atom. The hydrogen atom can add on to both ends of the unsaturated carbon-carbon bond forming both the n- and isopropyl radical. The n-propyl radical readily decomposes to give ethylene and a methyl radical.



Scheme 5.30
Formation of methyl radicals
via propene

If the isopropyl radical was decomposing by the mechanism depicted in scheme 5.29, the amount of decomposition will only be dependant upon temperature, therefore the proportion of methylated product will only depend upon the temperature of the

pyrolysis. If scheme 5.30 was the more important process then the amount of methylated product would depend upon the formation of the n-propyl radical. This is formed by a bimolecular process, therefore the amount of methylated product will depend upon both pressure and temperature. Unfortunatly the exact mechanism was never seriously investigated, but it should be possible to determine the mechanism by varying the pyrolysis conditions at a contant temperature.

At 923K, the experimental ratio of methylated product to diphenylamine was 2 to 1 in favour of diphenylamine, and at 1023K the experimental ratio of methylated products to diphenylamine was 14 to 1 in favour of diphenylamine.

5.10 FVP of *N*-n-butyldiphenylamine, results and discussion

The products formed from the pyrolysis of Ph_2N-Bu^n were essentially the same as those formed from the decomposition of the Ph_2N-Et. The table below gives the major products and their proportions.

Temp °C	%Ph_2Bu^n	%Ph_2NMe	%Ar-Me	%DPA	Other
650	90	0	0	10	0
700	64	2.2	2.2	34	0
750	4.7	5.5	3.6	77	9

Ph_2N-Bu^n is unconverted starting material

For the decomposition of Ph_2N-Bu^n diphenylamine log $(A/s^{-1})=16.4$, $Ea=63.9$kcal mol^{-1}.

At 973K the n-butyl radical is able to decompose via two different pathways, neither of which generates methyl radicals. One reaction produces a hydrogen atom and butene while the

second produces an ethyl radical and ethylene; the ethyl radical can then go on to generate a hydrogen atom and ethylene. The favoured route is for the formation of the ethyl radical, which is formed at approximately 23 times the rate of formation of the hydrogen[87].

For the methyl derivatives to form, the methyl radicals have to first be generated. One possibility is the decomposition of the secondary butyl radical which could be generated by addition of hydrogen to but-1-ene. (See FVP of *N*-ethyldiphenylamine results and discussion). The methyl radical could also be obtained from the decomposition of an alkyl radical derived by abstraction of hydrogen from the alkyl chain of the starting material. Breakup of the resulting alkyl radical inevitably leads to the formation of methyl, aminyl and methylaminyl radicals.

Experimentally the ratio of diphenylamine to methylated products was about 8 to 1 at 973K, which was the highest in favour of DPA for any of the alkylated amines.

5.11 FVP of *N*-n-hexyldiphenylamine, results and discussion.

The products formed from the pyrolysis of the Ph_2N-Hex^n derivatives were essentially the same as those formed from the decomposition of Ph_2N-Et , except that Ph_2N-Pr^n and hexene were also identified. The table below gives the major products and their proportions.

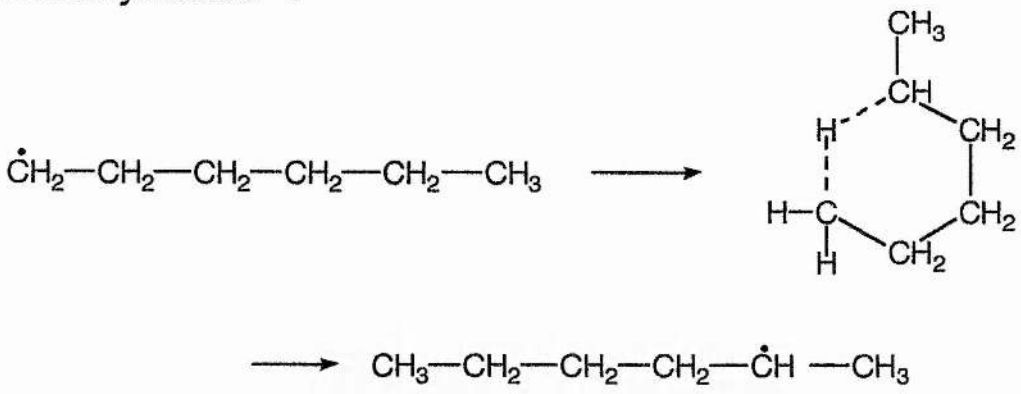
Temp °C	Ph_2N-Hex^n *	%Ph_2NMe	%Ar-Me	%DPA	Other
600	100	0	0	0	0
650	92	0	0	8	0

700	33.4	11.6	9	42	3
750	17.4	17.7	12.6	43	9
800	9.9	16	13	45	16

*Starting material

For the decomposition of Ph_2N-Hex^n log (A/s^{-1})=11.6, Ea=42.9 kcal mol^{-1}

The n-hexyl radical is able to undergo an intramolecular 1,5 hydrogen shift via a six membered cyclic transition state, to give a secondary radical[92].



Scheme 5.31
Formation of the secondary hex-2-yl radical
by an intramolecular 1,5 hydrogen shift

This can decompose by a number of pathways eventually giving both methyl radicals and hydrogen atoms. The experimental ratio of methylated product to diphenylamine at 973K was 2 to 1 in favour of diphenylamine.

Other radical reactions would also be initiated by hydrogen abstraction from the alkyl chain of the starting material. The alkyl radicals generated could also decompose via a number of different mechanisms giving products which have previously been described.

5.12 FVP of *N,N,N',N'*,-tetraphenyldiaminoethane, results and discussion

The only product identified in the pyrolysis of this compound was tetraphenylhydrazine. The table below gives the major product and its proportions relative to minor components.

	%		
Temp °C	$Ph_2NC_2H_4NPh_2$	$\%Ph_2N\text{-}NPh_2$	Other
600	100	0	0
650	67	33	0
700	0	99	1
750	0	98	2

There was not enough information for an Arrhenius plot but the rate of decomposition was calculated to be $193s^{-1}$ at 650°C.

The tetraphenylhydrazine was probably formed by the initial cleavage of one of the N-C bonds to give an aminyl and an aminoethyl radical. The aminoethyl radical eliminates ethylene to give a second aminyl radical. The aminyl radicals pair up to give tetraphenylhydrazine[79].

$$Ar_2N{-}CH_2{-}CH_2{-}NAr_2 \longrightarrow Ar_2N^{\bullet} + {}^{\bullet}CH_2{-}CH_2{-}NAr_2$$

$$\longrightarrow Ar_2N^{\bullet} + CH_2{=}CH_2 + {}^{\bullet}NAr_2 \longrightarrow Ar_2N{-}NAr_2$$

Scheme 5.32
Decomposition of *N,N,N',N'*,-tetraphenyldiaminoethane

5.13 FVP of *N*-(2-hydroxyethyl)diphenylamine, results and discussion

The major products were tetraphenylhydrazine, diphenylamine and carbazole. Minor amounts of Ph_2N-Me, 2- and 4-methyldiphenylamine and bis(diphenylamino)methane were also identified. The table below shows the major products and their proportions.

Temp °C	%Ph_2N-CH_2CH_2OH*	Ph_2N-NPh_2	DPA	Other
650	100	0	0	
700	73	22	2	3
750	46	43	6	5
800	24	52	10	14

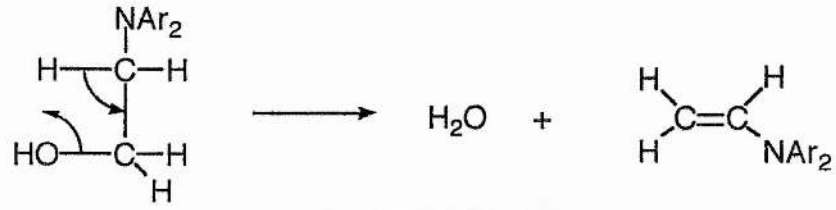
*Unreacted starting material

For the decomposition of Ph_2N-CH_2CH_2OH log (A/s^{-1})=9.6, Ea=32.4kcal mol^{-1}.

The low proportion of diphenylamine seems to indicate that β–hydrogen elimination was of little importance. During pyrolysis alcohols have been known to decompose by cleavage of the carbon chain between the α– and β-carbon atoms to generate free radicals[93]. However if cleavage of the carbon chain was occuring in the starting material then one of the products would be the diphenylaminomethyl radical. Products readily derived from this are bis(diphenylamino)methane and Ph_2N-Me. Since these were only detected in small amounts, cleavage of the carbon chain was considered to be of little importance.

The low energy of activation could indicate that the starting material was decomposing via another mechanism, possibly a β–

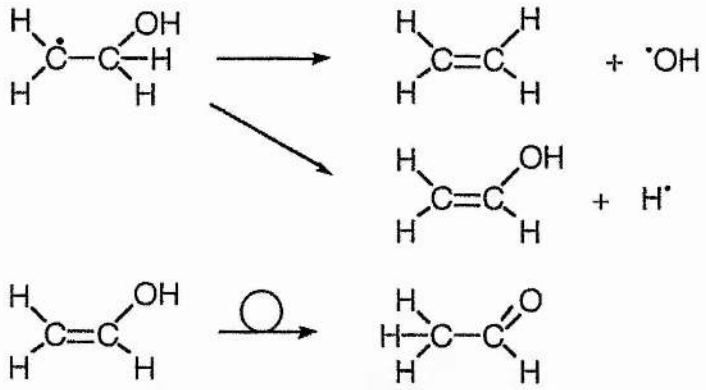
hydrogen elimination, with a water molecule being eliminated rather than diphenylamine[94].



Scheme 5.33
Elimination of water by
β-hydrogen elimination

The other product would be *N*-vinyldiphenylamine. In general groups attached to an alkene functional group are more strongly held than groups attached to alkanes. If this general rule applies to the *N*-vinyldiphenylamine then N-C cleavage will be disfavoured in comparison to when the aminyl group is attached to an alkyl chain. Hence some would be expected to survive the thermolysis. Since this was not detected, elimination of water was considered to be unimportant.

The decomposition of the Ph_2N-CH_2CH_2OH was probably initiated by the cleavage of the N-C bond to give a β-hydroxyethyl and an aminyl radical. Once formed the β-hydroxyethyl radical can undergo disproportionation reactions either with itself to give ethanol and ethanal or with the aminyl radical to form diphenylamine and ethanal. It can also decompose, eliminating either a hydrogen atom or a hydroxyl radical. Diphenylamine can then be formed by the addition of the hydrogen atom to the aminyl radical.



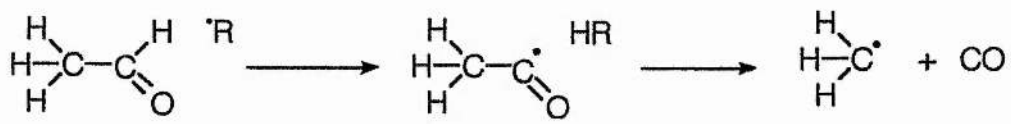
Scheme 5.34
Possible routes for the decomposition
of the hydroxyethyl radical

The C-H and C-O bonds are approximately 6 kcal mol^{-1} weaker in the β-hydroxyethyl radical than the C-H bonds of the ethyl radical, therefore it would be expected that the β-hydroxyethyl radical would decompose more rapidly than the ethyl radical. (See end of chapter.) The decomposition can follow two pathways, one produces the hydroxyl radical and ethylene, while the second gives vinyl alcohol and a hydrogen atom. The vinyl alcohol is the enol form of ethanal, to which it largely rearranges.

Thermodynamically the pyrolytic elimination of the hydroxyl radical is slightly favoured, but statistically the hydrogen elimination is more favourable, due to there being two hydrogens compared to the one hydroxyl group. The hydroxyl radical is highly reactive and can abstract hydrogen from almost any organic compound to give water and a carbon centred radical. Hydroxyl radicals are known to be able to add onto aromatic rings to give a phenol derivative[96], but any phenol derivatives which may have formed were not positively identified.

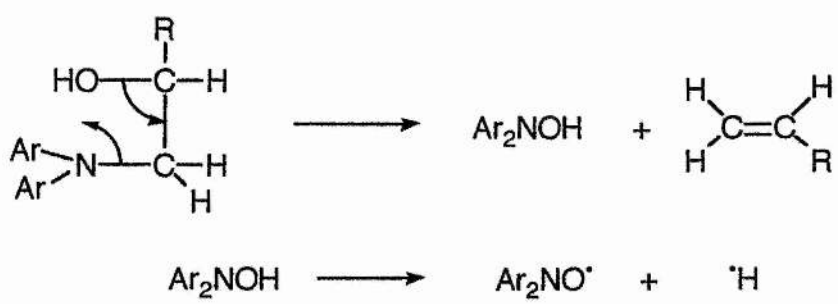
The hydrogen atoms can undergo termination reactions with the carbon centred radicals generated from the attack of the hydroxyl radical, combine directly with the hydroxyl radicals or combine with the aminyl radicals to form diphenylamine which in turn can donate its aminyl hydrogen to most radicals. Any excess hydrogen goes on to form diphenylamine.

The formation of ethanal during the pyrolysis should lead to the formation of methyl radicals. The C-H bond on the aldehyde function has been measured at 86 kcal mol^{-1} [95]. This is a relatively weak bond and as a result hydrogen can be abstracted by almost any radical present to form the acyl radical. The elimination of carbon monoxide then gives a methyl radical. The low amount of arylmethylated product indicated that this reaction was unimportant.



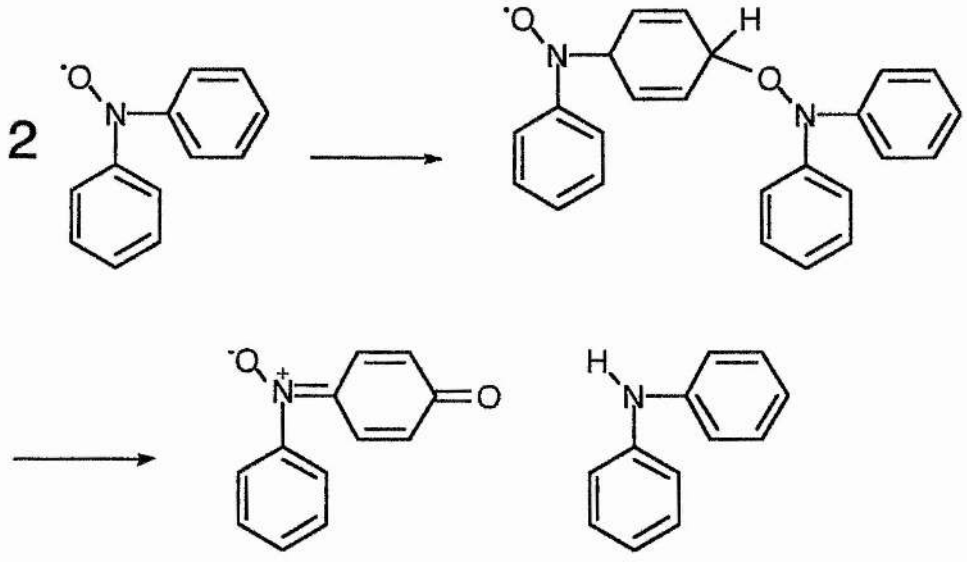
Scheme 5.35
Formation of methyl radicals

Another possibility is that the molecule may undergo β-hydroxyl elimination to generate the hydroxylamine and ethylene.



Scheme 5.36
β-Hydroxy elimination

The N-O bond for hydroxylamine was calculated to be 79 kcal mol^{-1}. Using this value for the N-O bond the β-hydroxy elimination was found to be exothermic to the extent of 3kcal mol^{-1}. The change in entropy was assumed to be around 30cal mol deg^{-1}. At the temperatures of thermolysis this process is very favourable. If the N-O bond is approximately 70 to 80 kcal mol^{-1} for diphenylhydroxylamine then it would be expected that the N-O bond would survive the pyrolyses. However the nitroxide could react with alkyl radicals, this gives diphenylamine and a ketone (scheme 1.33). Diphenylnitroxides also self react, the mechanism is thought to involve the *para* coupling of the nitroxide oxygen with an aromatic ring of the second diphenylnitroxide. This intermediate decomposes to give diphenylamine and *N*- phenyl-p-benzoquinoneimine-*N*- oxide.



Scheme 5.37

The reaction between two diphenylnitroxides

The hydroxylamine, nitroxide and *N*- phenyl-p-benzoquinoneimine-*N*- oxide were never positively identified among the reaction products, indicating that β–hydroxy elimination was not an important process.

5.14 FVP of *N*-(2-bromoethyl)diphenylamine, results and discussion

The major product indentified form the pyrolysis of *N*-(2-bromoethyl)diphenylamine was tetraphenylhydrazine. No other products could be identified.

Temp °C	$\%Ph_2N\text{-}CH_2CH_2Br$	$\%Ph_2N\text{-}NPh_2$
550	100	0
600	32	68
650	11	89

For the decomposition of the $Ph_2N\text{-}CH_2CH_2Br$ derivative, log $(A/s^{-1})=8.3$, $Ea=22.1$ kcal mol^{-1}.

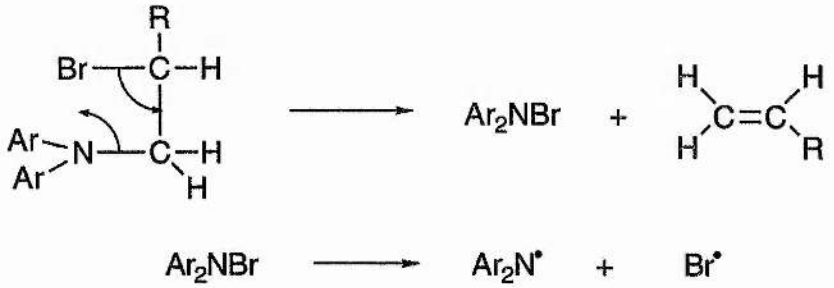
The absence of diphenylamine or *N*-vinyldiphenylamine in the product mixture indicated that the bromo derivative was not decomposing via β-hydrogen elimination, with either HBr or diphenylamine being eliminated.

The alternatives are that the N-C bond was undergoing cleavage to give the bromoethyl radical. This can decompose by two mechanisms, either a C-H bond undergoes cleavage or the C-Br bond. The average C-H bond energy is 99kcal mol^{-1} whereas the average C-Br bond is only 68kcal mol^{-1} [97] hence the elimination of the bromine atom is strongly favoured over that of hydrogen. This conclusion is confirmed when looking at the rate at which the β-bromoethyl radical decomposes. At 600°C the

bromoethyl radical decomposes at a rate of $1.4*10^{10}$ s^{-1} [87] to give ethylene and a bromine atom. Assuming that the elimination of hydrogen occurs at a similar rate to the other alkyl radicals then the elimination of bromine is approximately $2*10^5$ times quicker.

The rate constant at which a bromine atom combines with ethylene is $5.9*10^{11}$ mol dm^{-3} s^{-1} [87] which is only 42 times the rate constant for the decomposition. The recombination of a bromine atom with ethylene is bimolecular, hence the low pressure in the apparatus strongly favours the decomposition, which in turn leads to a very low concentration of the bromoethyl radicals. At the pressures associated with FVP (0.1 to 0.001 Torr) the ratio of bromine atoms to the bromoethyl radical is approximately $2.6*10^4$ to $2.6*10^6$ at 600°C. The low concentration of the bromoethyl radical also means that disproportionation with the aminyl radical would not be important.

A possible alternative is that the molecule decomposes by a process of β–bromo elimination. The *N*-bromodiphenylamine which is formed can then decompose to give the aminyl radical and a bromine atom.



Scheme 5.38
β–Bromo elimination

At 600°C ΔG was estimated to be around -8.6 kcal mol^{-1}. For the β–hydrogen elimination ΔG was estimated at about -26 kcal mol^{-1} at the same temperature. At the same temperature a concerted decomposition giving the aminyl radical, ethylene and a bromine atom was found to have a ΔG value of around -5 kcal mol^{-1}.

Scheme 5.39
Concerted decomposition of
N-(2-bromoethyl)diphenylamine

Another problem with a β–bromo elimination is that the diphenylaminyl and the bromo groups are both large, so the lowest energy configuration for this molecule would have these functional groups as far apart as possible. This also forces the β–hydrogens into a more favourable position for the β–hydrogen elimination.

All the mechanisms suggested above will give the same products. The actual mechanism involved could not be determined from the results of the FVP.

5.15 FVP of 2- and 4-methyl-*N*-methyldiphenylamine, results and discussion.

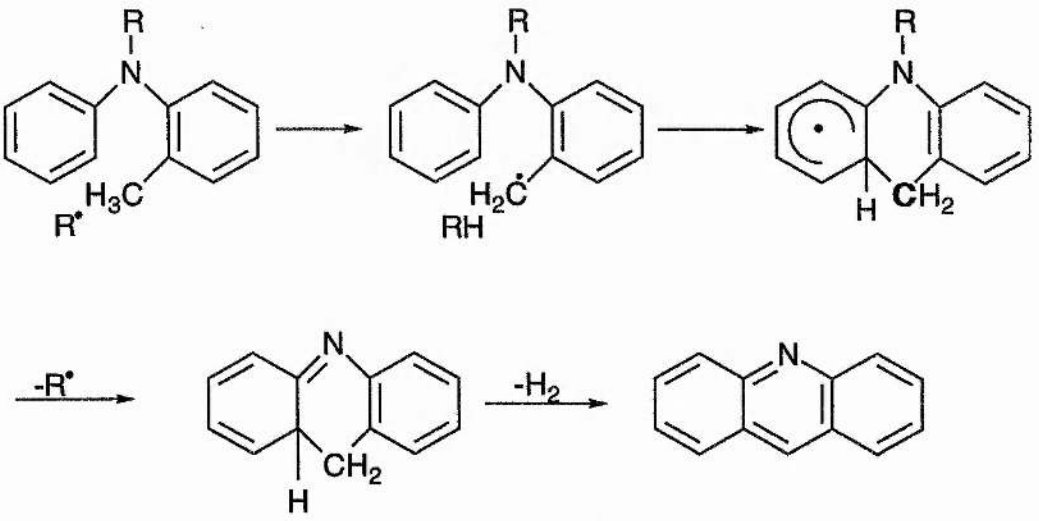
The major products identified were, 4-methyl-carbazole, 2- or 4-Me-C_6H_4(Ph)N-N(Ph)-2-or-4-Me-C_6H_4 and acridine. Smaller amounts of 2- or 4-Me-C_6H_4(Ph)N-CH_2-N(Ph)-2-or-4-Me-C_6H_4 and a wide range of products which involved the addition of aminyl radicals to the 2-or 4-aminobenzyl radical were also implicated.

The table below shows the proportions of the major products at each thermolysis temperature.

Temp °C	%N-Me	%Ar-Me	% N-N	Carbazole	Other
650	100	100	0	0	
700	100	96	0	0	
750	34	56	12	36	18
800	3	44	17	44	36

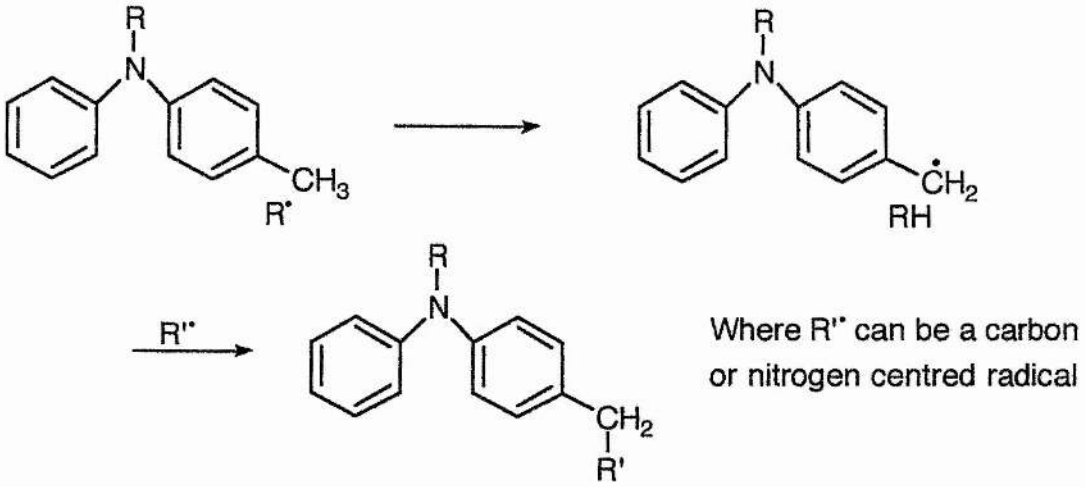
This experiment was designed to find out if the methyl groups could be lost from the aromatic rings. The results from the thermolysis indicated that the aminyl methyl group was first lost to leave a nitrogen centred radical and a methyl radical.

The acridine can be formed from attack of the 2-aminobenzyl radical upon the second aromatic ring, loss of the *N*-alkyl group produces the dihydroacridine derivative. Loss of a hydrogen molecule, either by elimination or abstraction gives acridine.



Scheme 5.40
Formation of acridine

The generation of the benzylic radical in the 4- position leads to the formation of 4- substituted combination products.



Scheme 5.41
Formation of 2- or 4- substituted dimer products

In general the methyl groups were not eliminated from the aromatic rings but used as the bridging group in the formation of 2- and 4- substituted dimer products.

5.16 Summary of FVP results and discussion

The table below gives the activation energy and the pre-exponential factor for the decomposition of the alkylated amines.

R	Log (A/s^{-1})	Ea kcal mol^{-1}	Max Ph_2NH
Me	13.8	53.3	34
Et	14.7	54.6	79
Bu^n	16.4	63.9	77
Hex^n	11.6	42.9	45
CH_2CH_2OH	10.1	36.6	10
N-Pr^i	10.0	33	88
CH_2CH_2Br	8.3	22.1	0
$Ph_2NCH_2\}_2$	-	-	0

For the $Ph_2NCH_2CH_2NPh_2$ not enough points were available for such a calculation, however, the rate of decomposition was calculated to be $193s^{-1}$ at 650°C.

The diphenylamine can be formed by both a free radical mechanism or by β-hydrogen elimination. If a free radical mechanism was operating then the activation energy for the decomposition of these compounds will be about the same as Ph_2N-Me. Experimentally it was found that the activation energies ranged from 63.9 kcal mol^{-1} for Ph_2N-Bu^n to 22.1 kcal mol^{-1} for Ph_2N-CH_2CH_2Br indicating that there were differences in the way these compounds decomposed. However the experimental errors were probably large since the temperature of the furnace could not be measured accurately. However apart from Ph_2N-CH_2CH_2Br all the Ph_2N-R derivatives started to decompose at around 650°C and were almost fully decomposed at around 750°C, indicating that they were all decomposing via the same general mechanism.

Further evidence for a free radical mechanism was provided by some of the other products detected in the decomposition. The tetraphenylhydrazine could only form by the combination of two aminyl radicals, which in turn could only be generated by cleavage of the N-C bond. The methylated products could only be formed if free radicals were present. As discussed in section 5.5 the 2- and 4-methyl diphenylamine was formed mainly by the addition of methyl radicals to the aryl rings of the diphenylaminyl radical (Scheme 5.15), with only a small contribution from scheme 5.16. As discussed in section 5.6 the methyl radicals were probably formed by cleavage of the bond between the α and β carbon atoms. Thermodynamically the addition to the aromatic ring is the favoured reaction and this is shown in 5.7 when almost

all the methylation is on the aromatic ring. Therefore the ratio of *N* to aryl methylation should be around 1 to 1 for Ph_2N-Et. Allowing for the loss of some methyl radicals this ratio will be altered in favour of the *N*-methyl derivative. However if the major mode of decomposition was the β-hydrogen elimination then there would be a high concentration of diphenylamine in the pyrolysis equipment. Methyl radicals would be trapped by the abstraction of the aminyl hydrogen from the newly formed diphenylamine. As already shown the methyl radicals would have to find an aminyl radical to form the 2- or 4-methyldiphenylamine, these would not be present if the *N*-alkylated amines decomposed only by β–hydrogen elimination.

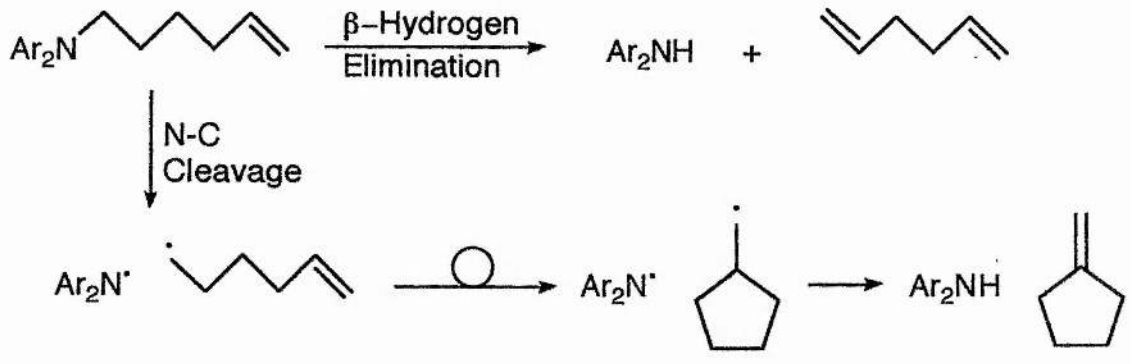
The final evidence for a free radical mechanism comes from The absence of diphenylamine from the pyrolysis of the *N*-(2-bromoethyl)diphenylamine and Ph_2N-C_2H_4-NPh_2. Both these compounds have large functional groups in the β–positions. The favoured configuration of both these compounds would have the β-hydrogens in a favourable position for elimination. The β-hydrogens for these derivatives are also slightly activated[109], in spite of this diphenylamine was not detected.

If a free radical mechanism was operating then the thermal stability of the *N*-alkyl diphenylamines should be dependant upon the stabilisation energy of the free radicals derived from the decomposition of the starting material. The more stable the radical products the more readily the corresponding amine derivative decomposes. The exception to this is the Ph_2N-CH_2CH_2Br, which may decompose by a concerted type mechanism.

During the FVP, the mechanism by which these compounds decompose is probably the free radical mechanism. These would

mainly be initiated by the cleavage of the N-C bond. At lower temperatures the β-hydrogen elimination is probably more important but may still make an important contribution to diphenylamine formation during the FVP experiments. Unfortunatly there was no direct evidence for the β-hydrogen elimination.

Evidence for β-hydrogen elimination could possibly be obtained from the thermolysis of Ph_2N-$(CH_2)_4CHCH_2$ at around 350°C. If β-hydrogen elimination was occuring then the major product would be hexa-1,5-diene. If N-C cleavage was occuring then the resulting 5-hexenyl radical would rearrange to give the cyclopentylmethyl radical. Abstraction of the tertiary hydrogen then gives methylenecyclopentane.



Scheme 5.42
Experimental scheme to determine
the mechanism by which *N*-alkylated
diphenylamines decompose

A second experiment involves the thermolysis of the *N*-n-propyldiphenylamine. If N-C cleavage was a major mode of decomposition then the resulting n-propyl radical would rapidly decompose to give mostly methyl radicals. The major products would therefore be the methylated derivatives of diphenylamine.

If β–hydrogen elimination was the major route of decomposition then diphenylamine will be the major product.

From the thermolysis experiments it was not possible to say which would be the most effective as a slow release antioxidant since the lifetime within a fired engine cannot be estimated. However the highest yield of diphenylamine was obtained from *N*-isopropyldiphenylamine. (see *N*- isopropyldiphenylamine, results and discussion.)

5.17 The Panel coker test

Introduction

This test was designed to simulate conditions in the region of the piston rings of an engine. In this region the oil is subjected to high temperatures and comes into contact with air and the combustion process which power the engine.

The test involves splashing a formulated oil onto a hot metal plate in a controlled manner. On contact with the plate the oil oxidises rapidly eventually forming a deposit of coke. The performance of the oil is then rated by weighing the amount of material deposited.

A visual rating is also performed, in which the plates are divided into a number of smaller regions and for each region the severity of the deposited material is compared to a set of standards. These range from black which is given a rating 10 to a very light amber which has a rating of 1. A region with no deposits is given zero rating. The calculation of the results involves averaging the ratings from all the regions and subtracting this value from 10, so the better the sample's performance the higher the rating.

The antioxidants under test were all *N*-alkylated diphenylamines. On contact with the hot metal plate, these were designed to decompose, giving diphenylamine and an alkene. The freed diphenylamine can then act as an antioxidant. The rate at which the antioxidant is generated will depend on how easily the *N*-alkyl group is lost, hence the alkylated amine which decomposes the most readily, should be the most effective as an antioxidant.

Panel coker experiments

The amines tested were diphenylamine, *N*-Et, *N*-Bu^n, *N*-Hex^n and *N*-Pr^i DPA. The samples were prepared by dissolving the amines into 200g of the basestock and then making up the samples to 250g.

For these experiments the temperature of the oil reservoir was 100°C and the metal plate 320°C. The oil was mechanically splashed onto the metal plate in a controlled fashion for 15 seconds every minute. The plate was held at an angle of 30° to the horizontal, this allowed the oil to run off. The duration of the test was 1 hour.

In the first experiment the amines were dissolved into NS150 basestock. The concentration of amines in all the samples was 0.0148 molal. A standard was used in which no antioxidants were present. The results of this experiment are shown over the page.

Amine	weight of deposit g	average merit
Ph_2N-H	0.0241	2.07
Ph_2N-Et	0.0368	0.47
Ph_2N-Bu^n	0.0203	4.12
Ph_2N-Hex^n	0.0144	3.25

Ph_2N-Pr^i	0.0228	5.18
None	0.0224	2.92

From these results Ph_2N-Hex^n was the most effective at controlling the formation of deposits on the plate. All the samples had performed poorly.

The next experiment was to try the amines in a formulated basestock. The amines were dissolved in a basestock at a concentration of 0.0148 molal. The basestock consisted of :-

5.25% dispersant ECA12819

1.5% ZDDP PX14

0.5% Magnesium sulphonate ECA11190

2.3% Calcium sulphonate ECA11785

0.5%Sulphurised phenol ECA9946

89.95% NS150

The results of these experiments are shown in the table below.

Amine	weight of deposit g	average merit
Ph_2N-H	0.0017	4.87
Ph_2N-Et	0.0063	5.52
Ph_2N-Bu^n	0.0092	7.03
Ph_2N-Hex^n	0.0082	7.81
Ph_2N-Pr^i	0.0092	7.08
None	0.013	6.92

The panel with the least deposits was as expected the free diphenylamine, the worst was the standard sample. Of the *N*-alkylated amines the Ph_2N-Et derivative performed the best. The visual ratings did not correlate well with the amount of material deposited.

5.18 Comparison of the FVP and panel coker results.

The FVP results showed that the Ph_2N-Et derivative was thermally, one of the most stable of the alkylated amine, whereas in panel coker tests the opposite was true. The Ph_2N-Pr^i was the least stable of the amines in the thermolysis reactions but in the panel coker it appeared to be the most stable.

These differences could be explained if the decomposition of the *N*-alkylated diphenylamines was initiated by chemical attack upon the aminyl nitrogen. The most likely agents of attack are the hydroperoxides which can oxidize the aminyl nitrogen to the *N*-oxide, this readily decomposes to give the hydroxylamine which is known to be an active antioxidant. The increased steric hindrance offered by the larger alkyl groups, particularly by the isopropyl group, slow down the rate of this reaction, therefore in these tests the *N*- isopropyl derivative was more stable.

5.19 ERCOTs with slow release agents

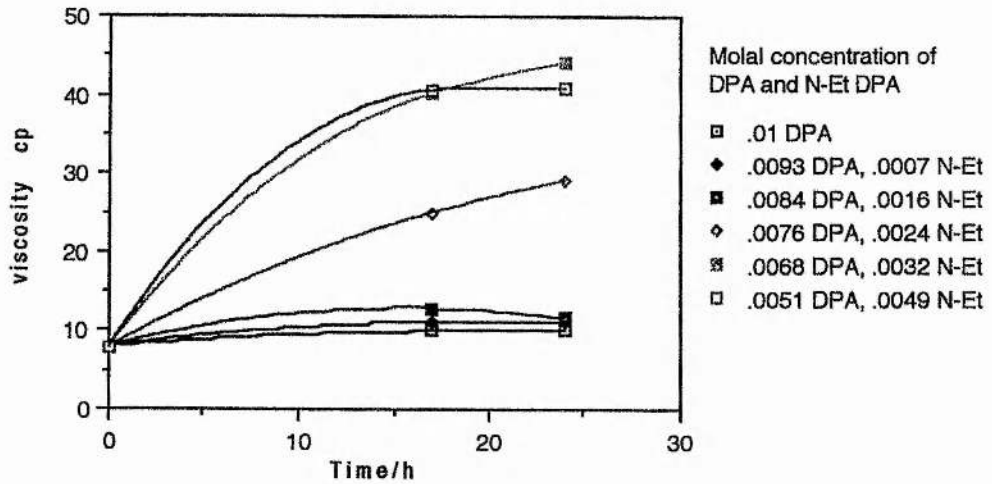
This test was designed to find the approximate lifetime of the alkylated amines in the ERCOT. From previous ERCOT's it was found that diphenylamine could protect a sample of NS150 almost indefinitely when it was present above a certain critical concentration.

These experiments were run in NS150. The antioxidant was a mixture of diphenylamine and *N*-ethyldiphenylamine. The total amount of free antioxidant was below the critical concentration but the amount of potentially available antioxidant was above.

During the ERCOT, the slow release agent was expected to release its antioxidant. The rate of release would ultimately affect the results. If the bound antioxidant was released rapidly then the

samples would not significantly increase in viscosity. If the release was very slow then the sample would behave as if there was no slow release agent present.

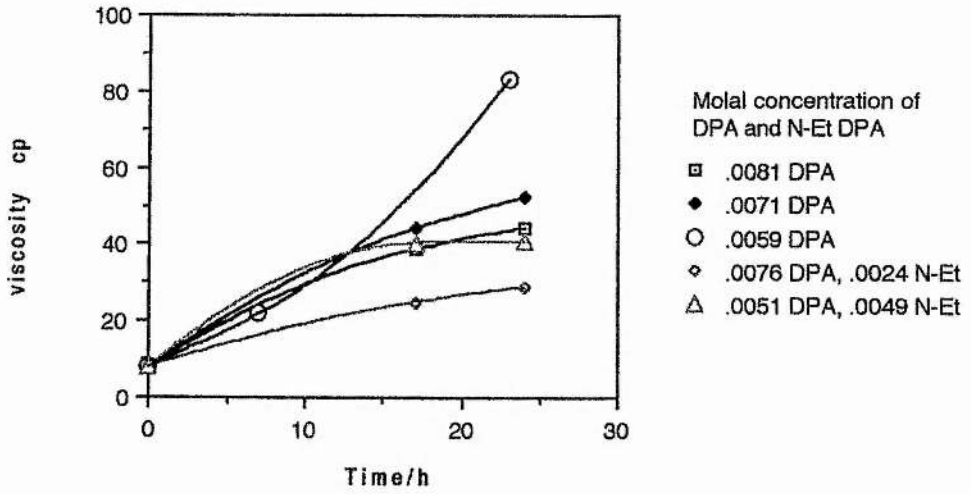
For these experiments an NS150 basestock was used. The amount of DPA was varied from 0.01- 0.0051 molal. The critical concentration had already been determined at 0.0083 molal. To this Ph_2N-Et was added so the amount of diphenylamine potentially available was 0.010 molal. The results obtained from these experiments are shown in the graphs below.



Graph 5.3
ERCOT results for samples containing a mixture of diphenylamine and *N*-Et diphenylamine

Graph 5.3 shows that for three of the ERCOT's run with the slow release antioxidant the viscosity had increased significantly, but the rate of increase appears to be slowing down indicating that the slow release agent was releasing significant amounts of diphenylamine over the duration of the experiment.

Graph 5.4 compares samples which contain both diphenylamine and the slow release agent with samples which contain just the diphenylamine component.



Graph 5.4
Comparison of ERCOT results obtained with
DPA and a mixture of DPA/N-Et DPA

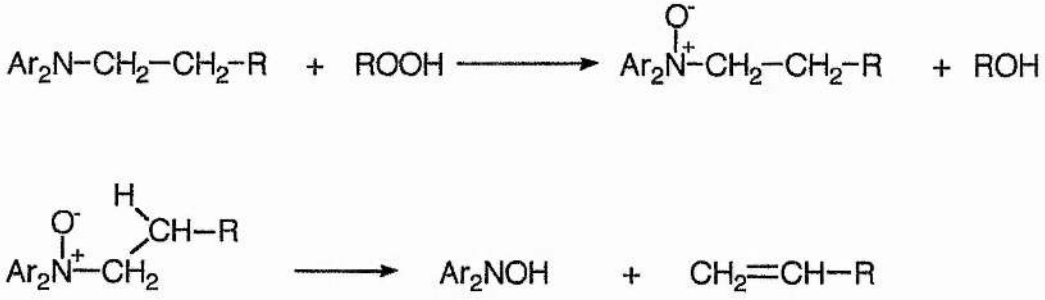
Graph 5.4 shows that a mixture containing 0.0051 molal DPA and 0.0049 molal *N*-Et DPA performed better than samples containing only DPA at concentrations of 0.0071 and 0.0081 molal. These ERCOT are further evidence that a significant portion of the slow release agent had decomposed.

5.20 Discussion of Results

The Ph_2N-Et DPA showed signs of appreciable decomposition in the ERCOT's, which were run at 165°C, whereas in the conventional pyrolysis there was no evidence of decomposition at 250°C.

Tert-amines can decompose at lower temperatures if the *N*-oxides are first formed. The latter can be generated by the reaction of the *tert*- amine with hydroperoxides. Once formed the

N-oxide readily decomposes via β-hydrogen elimination to give the hydroxylamine and an alkene[74,75]. The hydroxylamine can then trap chain propagating radicals and augment the antioxidant activity.



Scheme 5.43
Low temperature decomposition
of *tert*- amines

In the panel coker test it was found that large alkyl groups were able to slow down the rate at which *N*-alkylated diphenylamines decomposed. This was probably due to steric hindrance, which slowed down the rate at which the hydroperoxides were able to oxidise the aminyl nitrogen.

The major problems with the slow release agents tested so far was their relatively short lifetimes. As already discussed in the introduction, a motor oil is changed after around 150 hours of normal driving. The alkylated amines were showing signs of considerable decomposition after around 20 hours.

Possible ways of extending the lifetime of the slow release antioxidants is to use larger alkyl groups to increase steric hindrance around the nitrogen, to use β-substituents which will deactivate the β-hydrogens or to use substituents without β-hydrogens.

5.21 Experimental

FVP experimental

The sample size for the analytical FVP experiments was generally 0.2g. For preparative FVP the sample size was 1g. The samples were placed in a kinked inlet tube which could hold a liquid sample. The sample was heated externally in a controlled fashion. The time taken to vaporise the sample was half an hour.

The pressure for the FVP experiments was in the range of $1*10^{-2}$ to $5*10^{-3}$ Torr, and the temperature of the furnace was set at 700°C for the first experimental run with a sample, this was then changed by plus or minus 50°C depending upon the amount of decomposition. The products were then condensed in a trap cooled by liquid nitrogen.

Product analysis

The product was removed from the trap by dissolving in methylene chloride, which was then evaporated and the product dissolved in deuterochloroform. The amount of decomposition was estimated from the ratio of alkyl to aryl hydrogen. This method was only effective if the aryl hydrogens were relatively unaffected by the FVP.

Determination of the products was achieved by a combination of GC, GC-MS, TLC, and ^{1}H NMR. The GC-MS separates the mixture into its component parts and then carries out a mass spectrum on each component. A library search facility was used to identify many of the components from their mass spectra.

The TLC was used to separate the product mixture into its component parts after which ^{1}H NMR and MS were used. The stationary phase was silica and the mobile phase was 40-60 petroleum ether with 5% diethylether.

The GC was used to separate the products and measure the relative amounts. The column used was of 1mm radius and 1m length. The stationary phase was OV 101 at 3% loading, the mobile phase was nitrogen at 15 psi, the oven temperature was set at 220°C, the injector and detector were also at this temperature. Detection was by flame ionisation. Chart speed was set at 0.5mm min^{-1}. Identification of any products was by comparison of retention times with those of known standard samples.

Volatile products were examined by addition of deuterochloroform to the product mixture and analysis of this by ^1H NMR.

Conventional pyrolysis

The amines (0.2g) were placed in 2ml ampoules. These were degassed by freeze, pump, thaw cycles and then flame sealed under vacuum. For each run six samples were prepared. The pyrolyses were carried out in a fluidized sand bath. The pyrolysis experiments were started at 250°C, after each experimental run the temperature was increased by 25°C. The temperature was monitored using a thermocouple. The samples were tied to a glass rod and held under the surface of the sand and a sample was then removed each hour. Analysis was by ^1H NMR. The amount of decomposition was estimated from the ratio of alkyl to aromatic hydrogens.

Panel coker test

This test essentially involved splashing an oil sample onto a hot metal plate and weighing the amount of deposit. The samples for the panel coker were prepared by dissolving the amines into the required basestock and making up the sample to 250g. The

metal plates for the experiments were made from aluminium, and these were cleaned and weighed.

The sample was heated up to a temperature of 100°C and the metal plate to 320°C, the metal plate was at an angle of 30° to the horizontal, this allowed the sample to run off. The oil was splashed onto the metal plate using a splined spindle which was rotated by an electric motor. The splashing occured for 15 seconds every minute. The duration of the test was one hour.

The plate was then removed and washed twice in hexane to remove any unreacted oil and dried in an oven. This was then weighed for the amount of deposits.

A visual rating was also done. For this the plate was divided into small sections and each section was assessed for the severity of the deposit. The severity was estimated from its colour. The colour was compared to a standard set of 10 colours ranging from pale amber to black. Black was given a rating of 10 and pale amber 1. The average merit was then calculated from all the regions and this value was subtracted from 10 to give a rating. The higher the rating the better the performance of the sample.

Syntheses

Attempted synthesis of N-trimethylsilyldiphenylamine. Diphenylamine (1.7g, 0.01mol) was dissolved in methylene chloride (20ml). The resulting solution was added dropwise to trimethylsilylchloride (1.3g, 0.012 mol). The mixture was then refluxed for half an hour. Water (0.24g, 0.013mol) and pyridine (0.95g, 0.012mol) were dissolved in dry tetrahydrofuran which was added dropwise to the reaction mixture. The solvent was then removed and water added to the mixture which was extracted with diethyl ether (3*25ml), the combined extracts were dried

over magnesium sulphate. Product analysis indicated that a dimeric trimethyl silicone and diphenylamine were the only components.

Synthesis of the *N*-oxides

Attempted preparation of N-ethyldiphenylamine-N-oxide [74]. A mixture of acetic anhydride (30ml) and hydrogen peroxide (30ml of a 30% solution in water, 0.3mol H_2O_2) was prepared. This was cooled in a salt/ice bath and stirred. To this was added *N*-ethyldiphenylamine (10g, 0.058mol) over a period of an hour. The mixture was stirred for a further two hours. This was then treated with potassium hydroxide solution (50ml, 1M) and extracted with ether (3*50ml). The extracts were combined and dried over anhydrous sodium sulphate. On removal of the solvent a dark red liquid was obtained. Yld of *N*- oxide 0g, 0.0%; ^1H NMR($CDCl_3$, 200MHz) δ_H 6.9-7.5 (10H, m); IR no N-oxide present; ESR a(N)=9.3G indicating that $Ph_2N\text{-}O^{\bullet}$ was the only paramagnetic product.

Attempted preparation of N-n-butyldiphenylamine-N-oxide [74]. *N*-n-butyldiphenylamine (11.26, 0.05mol) was used, all other conditions being the same as those used in the preparation of the *N*-ethyl, *N*-oxide. Product analysis indicated that $Ph_2N\text{-}O^{\bullet}$ was again produced.

Attempted preparation of N-n-hexyldiphenylamine-N-oxide [74]. *N*-n-hexyldiphenylamine (12.66g, 0.05mol) was used, all other conditions being the same as those used in the preparation of the *N*-ethyl, *N*-oxide. Product analysis indicated that the product was again $Ph_2N\text{-}O^{\bullet}$.

Tri-n-hexylphosphate. Trichlorophosphate (7.5g, 0.05mol) was dissolved in 40-60 petroleum ether (100ml). A mixture containing

hexanol (15.4g, 0.15mol) and pyridine (11.9g, 0.15mol) was prepared and this was added dropwise to the trichlorophosphate solution. After the addition was completed the mixture was refluxed for half an hour cooled and filtered. The solvent was then removed to leave the product. Yield 16.8g, 96%; ^1H ($CDCl_3$, 60MHz) δ_H 4.05 (q, 2H), 1.7 (quintet, 2H), 1.3 (m, 6H), 0.9 (t, 3H).

Tri-isopropylphosphate. The tri-isopropylphosphate was prepared by the same method used for the synthesis of the tri-n-hexylphosphate. The reactants used were trichlorophosphate (7.5g, 0.053mol), isopropyl alcohol (9g, 0.15mol) and pyridine (11.85g, 0.15mol). Yield 11g, 98%; ^1H NMR(60MHz, $CDCl_3$) δ_H 4.4 (octet, 1H), 1.0 (doublet, 6H)

Attempted preparation of tri-tert-butylphosphate. Trichlorophosphate (7.6g, 0.05mol), *tert*-butyl alcohol (11.1g, 0.15mol) and pyridine (11.9g, 0.15mol) were used in the preparation. The phosphate ester was prepared by the same method used to synthesize the tri-n-hexylphosphate. Preparation of the ester was unsuccessful.

Tri-isobutylphosphate. Trichlorophosphate (7.5g, 0.05mol), isobutyl alcohol (11.1g, 0.15mol) and pyridine (11.85, 0.15) were used in the preparation. The phosphate ester was prepared by the same method used to synthesize the tri-n-hexylphosphate. Yield 12g, 90%; ^1H NMR (60MHz, $CDCl_3$) δ_H 3.9 (t, 2H), 2.0 (m, 1H) 1.0 (d, 6H).

Tri-methoxyethylphosphate. The phosphate ester was prepared by the same method used to synthesize the tri-n-hexylphosphate. Trichlorophosphate (7.5g, 0.05mol), methoxyethanol (11.42, 0.15mol) and pyridine (11.85g, 0.15mol) were used. Yield 12.4g,

91%; ^{1}H NMR (60MHz, $CDCl_3$) δ_H 4.25 (quartet, 2H), 3.6 (t, 2H), 3.4 (s, 3H).

Tri-dodecylphosphate. The method used to produce the tridodecylphosphate was the same as that employed in the synthesis of the tri-hexylphosphate. Trichlorophosphate (7.6g, 0.05mol), pyridine (11.9g, 0.15mol) and dodecylalcohol (27.9g, 0.15mol) were used for the synthesis. Product analysis showed that the ester had not formed.

N-alkylation of diphenylamine with trialkylphosphates

Methods for working up

For all the alkylation reactions with trialkylphosphates, working up involved firstly the removal of unreacted trialkyl phosphate then the removal of unreacted diphenylamine.

Removal of unreacted trialkylphosphates.

The unrefined amine was dissolved in ethanol (100ml) to which sodium hydroxide (5g, 0.125mol) had been added. The mixture was then refluxed for two hours. After this the mixture was poured into water (200ml) and extracted with 40-60 petroleum ether (3*50ml). The extracts were combined and the pet ether removed to give the crude amine.

Removal of unreacted diphenylamine

Method one

Acetic anhydride (10ml) was added to the crude amide and the mixture refluxed for half an hour. The mixture was poured into water (100ml) and stirred for 10 hours, the aqueous mixture was then extracted with 40-60 petroleum ether (3*50ml), the combined extracts were combined and evaporated to a third of its original volume. This was cooled in an ice/salt bath to -5^{o}C and filtered. The filtered liquid was then dried over magnesium

sulphate, filtered and the remaining pet ether removed to yield the amine. The amine was then distilled under reduced pressure.

Method two

The unreacted diphenylamine was removed by refluxing the crude amine with benzoyl chloride (7g, 0.05mol) for half an hour. The excess benzoyl chloride was removed by distillation under reduced pressure. The remaining material was dissolved in 50ml of boiling 40-60 petroleum ether. The resulting solution was filtered, cooled to -5°C and filtered again. The remaining liquid was then stirred with 100ml of saturated sodium carbonate for 10 hours. The organic layer was then separated and dried over anhydrous sodium sulphate. This was filtered and the solvent removed to yield the amine. This was then distilled under reduced pressure.

N-Methyldiphenylamine [76]. Diphenylamine (6.9g, 0.04mol) was added to trimethylphosphate (10g, 0.07mol). The mixture was heated until a vigorous reaction occured, after which the reaction mixture separated into two layers. The heat source was removed and the mixture allowed to cool. The top layer was dissolved away with 40-60 petroleum ether after which the bottom layer was discarded. The solvent was removed and the crude amine was dissolved in ethanol (100ml) to which sodium hydroxide (5g, 0.125mol) had been added. The alcoholic solution was then refluxed for two hours after which it was poured onto 200ml of water. The amine was extracted with 40-60 petroleum ether (3*50ml). The combined extracts were dried over magnesium sulphate. Yield 6.8g, 91%; % *N*-Methylation 94%; ^{1}H NMR (60MHz, $CDCl_3$) δ_H 3.25 (s, 3H), 6.9-7.5 (m, 10H)

N-Ethyldiphenylamine [76]. Diphenylamine (8.45g, 0.05mol) was added to triethyl-phosphate (5g, 0.027mol). The mixture was heated until a vigorous reaction occured after which the reaction mixture separated into two layers. A sample was taken from the top layer and analysed by ^{1}H NMR. If the aminyl hydrogen was still prominent at δ_H 5.5 then more triethylphosphate (5g, 0.027mol) was added and the procedure repeated. The top layer was then decanted off and any remaining product was removed with 40-60 petroleum ether, which was combined with the decanted liquid and the solvent was removed. Removal of unreacted diphenylamine was by method one (see above).Yield 4.72g, 48%; bp 114°C at 0.4 Torr, lit. bp 152-153°C 12 Torr[98]; % alkylation in the product, 100%; ^{1}H NMR (200MHz, $CDCl_3$) δ_H 1.1(t, 3H), 3.6 (q, 2H), 6.85 (m, 6H) 7.15 (m, 4H); ^{13}C NMR δ_C 148.4, 129.9, 121.7, 121.6, 47.1, 13.3.

N-n-Butyldiphenylamine [76]. Diphenylamine (8.45g, 0.05mol) was added to tri-n-butyl-phosphate (7.4g, 0.028mol). The mixture was heated until a vigorous reaction occured after which the reaction mixture separated into two layers. A sample was taken from the top layer and analysed by ^{1}H NMR. If the aminyl hydrogen was still prominent at δ_H 5.5 then more tri-n-butylphosphate (5g, 0.027mol) was added and the procedure repeated. The top layer was then decanted off and any remaining product was removed with 40-60 petroleum ether, this was combined with the decanted liquid and the solvent was removed. Removal of unreacted diphenylamine was by method one (see above). Yield 6.63g, 59%; bp 124-131°C at 1 Torr; ^{1}H NMR (200MHz, $CDCl_3$) δ_H 0.9 (t, 3H), 1.3 (sextet, 2H), 1.65 (quintet, 2H), 3.65 (t, 2H), 6.9 (m, 6H), 7.25 (m, 4H); ^{13}C δ_C 14.7, 21.0, 30.3, 52.8, 121.6, 121.8, 129.9, 148.9.

N-n-Hexyldiphenylamine [76]. Diphenylamine (8.45g, 0.05mol) was added to tri-n-hexyl-phosphate (6.76g, 0.019mol). The apparatus was set up to allow for the distillation of any volatile products. The reaction was heated until a vigorous reaction occured. (The reaction also produced a volatile liquid which was collected, analysed and found to be hex-1-ene.) The heat source was then removed. After the reaction had subsided the mixture formed two layers. The reaction was allowed to cool to room temperature and the top layer decanted off. Any remnants of the top layer were extracted with 40-60 petroleum ether and combined with the previously decanted top layer. The bottom layer was then discarded. The pet. ether was removed on a Buchi to leave the crude product. Removal of unreacted diphenylamine was by method 2(see above). Yield 10.3g, 34%; bp 128°C at 0.27 Torr; % alkylation in product 100%; ^{1}H NMR (200MHz) δ_H 0.85 (t, 3H), 1.25 (m, 6H), 1.65 (quintet, 2H), 3.65 (t, 2H), 6.85-7.0 (m, 6H) 7.1-7.2 (m, 4H); ^{13}C NMR δ_C148.8, 129.9, 121.7, 121.6, 53, 32.4, 28.4, 27.5, 23.4, 14.8.

Attempted preparation of N-isobutyldiphenylamine [76]. The method used was the same as that used for the preparation of the *N*-ethyldiphenylamine, diphenylamine (8.45g, 0.05mol) was refluxed with tri-isobutylphosphate (8g, 0.03mol). % Alkylation in crude product 0%.

N-(2-Methoxyethyl)diphenylamine [76]. This derivative was prepared by the same method used for the synthesis of the *N*-n-hexyldiphenylamine. Diphenylamine (8.5g, 0.05mol) was refluxed with tri-methoxyethylphosphate (12g, 0.044mol). The crude product contained 51% *N*-alkylated product.

To remove the unreacted tri-methoxyethylphosphate the crude amine was dissolved in 40-60 petroleum ether (100ml) and the resulting solution was washed with water (4*100). This was dried over anhydrous sodium sulphate. The product was filtered and the solvent removed to yield the crude amine. Removal of unreacted diphenylamine was by method 2(see above)

Yield 1.2g, 10.1%. % alkylation in product 85%; ^{1}H NMR (60MHz, $CDCl_3$) δ_H 3.3 (s, 3H), 3.7 (t, 2H), 4.0 (t, 2H), 6.7-7.3 (m, 10H).

N,N,N',N'-Tetraphenyl-1,2-diaminoethane [76]. Diphenylamine (8.5g, 0.05mol) was refluxed with 6g of tri-(2-chloroethyl)phosphate (6g, 0.021mol). A vigorous reaction occured after which the reaction separated into two layers. The top layer was extracted with boiling toluene (4*50ml). The volume of toluene was reduced to 50ml and the resulting solution cooled to -5°C and filtered. The solid material was recrystallized from 40-60 petroleum ether. Yield 6.7g, 74%; mp 167-169°C, lit. mp 168-169.5°C[99]; % alkylation in final product 100%; ^{1}H NMR (200MHz, $CDCl_3$) δ_H 4.0 (s, 4H), 7.0 (m, 12H), 7.3 (m, 8H); ^{13}C NMR δ_C 50.1, 121.3, 122.0, 129.9, 148.2.

Attempted synthesis of N-chloroethyldiphenylamine [76]. Diphenylamine (1.69g, 0.01mol) was refluxed with trichloroethylphosphate (2.85g, 0.01mol) and diethylene glycol dimethoxyether (2ml) for half an hour. The mixture was allowed to cool and was then dissolved in 40-60 petroleum ether (20ml) and washed with water (5*100ml). The organic layer was then dried over magnesium sulphate and the solvent removed to give the crude amine. Product analysis showed that alkylation was by the displacement of the chlorine as well as the phosphorus.

Attempted synthesis of N-hydroxyethyldiphenylamine. The crude product obtained in the attempted synthesis of *N*-(2-cloroethyl)diphenylamine was dissolved in methanol (100ml) to which water (10ml) and sodium hydroxide (3g) had been added. The mixture was refluxed for 2hours. The reaction was diluted with water (200ml) and the aqueous mixture was extracted with methylene chloride (3*70ml). The extracts were combined and dried over magnesium sulphate. Yield of hydroxyethyl derivative; 0%

N-Isopropyldiphenylamine [76]. The *N*-isopropyldiphenylamine was prepared by the same method used for the synthesis of *N*-hexyldiphenylamine. The reactants used were diphenylamine (8.5g, 0.05mol) and tri-isopropyl-phosphate (11.2g, 0.058mol). The crude amine contained only 17% of the *N*-alkylated product.

N-Isopropyldiphenylamine via the N-alkali metal amide [80]. Diphenylamine (5g, 0.03mol) was dissolved in dry ether (50ml), under a dry nitrogen atmosphere. To this was added n-butyl lithium (22ml of 1.6M solution of n-butyl lithium, 0.0352mol). The mixture was then stirred for 1 hour. Dry 2-bromopropane (4.4g, 0.036mol) was added dropwise and the mixture stirred for 10 hours. The reaction was treated with water (50ml) and extracted with ether (3*30ml), the combined extracts were dried over magnesium sulphate.

Product analysis showed that there was only 8% *N*-alkylation in the crude amine. The use of dry toluene as the reaction solvent increased the percentage of alkylated product to 60%. In THF the % alkylation was only 26%.

N-Isopropyldiphenylamine from 2-iodopropane, reaction over potassium carbonate [36]. Diphenylamine (16.9g, 0.1mol) was

refluxed with 25.5g of iodopropane (25.5g, 0.15mol) over potassium carbonate (25g, 0.45mol) and copper powder (0.25g). The mixture was refluxed for 10 hours. The reaction mixture was allowed to cool and was diluted with diethylether (100ml) and filtered. The mixture was then distilled under reduced pressure to leave the crude amine. Analysis of this showed that there was only 7% *N*-alkylation in the crude amine.

N-Isopropyldiphenylamine from 2-iodopropane, reaction over magnesium [75]. Diphenylamine (8.45, 0.05mol) was refluxed with 18.7g of iodopropane (18.7g, 0.11mol) over magnesium turnings (1.5g, 0.062). The mixture was refluxed for 6 hours producing a green solid. The reaction was allowed to cool after which toluene (50ml) was added. Hydrochloric acid (1M) was then added dropwise until all the green solid had disappeared. The mixture was extracted with diethylether (3*50ml) and the combined extracts were washed with aqueous sodium hydroxide (25ml, 1M) and water (25ml). The ether solution was then dried over anhydrous sodium sulphate.

Product analysis showed 75% alkylation in the crude amine. The use of 2-bromopropane gave no alkylation. The use of toluene as a reaction solvent gave 32% alkylation. Removal of unreacted diphenylamine was by method 2 (see above). Yield 4.9g, 46%; bp 108°C at 0.2 Torr, 116°C at 0.3 Torr, lit. bp 160-165°C at 15 Torr[98]; % alkylation in the product 100%. ^{1}H, (60 MHz, $CDCl_3$) δ_H 1.0 (d, 6H), 4.2 (heptet, 1H), 6.7-7.3 (m, 10H).

N-Isobutyldiphenylamine via 1-iodo-2-methylpropane over magnesium [75]. The method used was the same as that employed in the synthesis of the *N*-isopropyldiphenylamine. The crude product contained 45% *N*-alkylated material when diphenylamine

(8.5g, 0.05mol) and 1-iodo-2-methylpropane (18.4g, 0.1mol) were refluxed over magnesium (1.22g, 0.05mol). Removal of unreacted diphenylamine was by method 2 (see above). Yield 1.4g, 12%; % alkylation in final product 80%; ^{1}H NMR δ_H 0.8 (d, 6H), 1.8 (m, 1H), 3.4 (d, 2H), 6.8-7.4 (m, 10H).

N-Tert-butyldiphenylamine from 2-iodo-2-methylpropane, reaction over magnesium [75]. Diphenylamine (8.45g, 0.05mol) and 2-iodo-2-methylpropane (18.4g, 0.1mol) were dissolved in dry 40-60 petroleum ether (50ml). This solution was refluxed over magnesium turnings (1.22g, 0.8mol) for 48 hours. The mixture was filtered and any volatile components distilled off under reduced pressure to leave the crude amine. NMR analysis of the crude amine showed that it contained 34% alkylated product. Removal of unreacted diphenylamine was by method 2 (see above). Yield 0.13g, 1.1%; % alkylation in the product 75%; ^{1}H NMR (60MHz, $CDCl_3$) δ_H 1.1 (s, 9H), 6.75-7.3 (m, 10H).

Attempted alkylations with the tosylate ester

2-Methoxyethyl-p-toluenesulphonate [82]. Methoxyethanol (7.6g, 0.1mol) and pyridine (7.9g, 0.1mol) were dissolved in methylene chloride (50ml), the solution was then cooled in an ice bath. Toluenesulphonyl chloride (19g, 0.1mol) was dissolved in methylene chloride (50ml) and this was added dropwise to the first solution. The reaction was continuously stirred and the addition was at a rate which kept the temperature below 10°C. After the addition was completed the mixture was stirred for a further 3 hours. The reaction was then washed with HCl (2*100ml of 1M) and sodium hydroxide (2*100ml of 1M). The organic solution was then dried over magnesium sulphate. Yield 20.1g,

87%; ^{1}H NMR δ_H 2.2 (s, 3H), 3.05 (3H, s), 3.3 (t, 2H), 3.9 (t, 2H), 7.1 (d, 2H), 7.6 (d, 2H).

Reaction of the 2-methoxyethyl-p-toluenesulphonate with lithium diphenylamide. Diphenylamine (1g, 0.06mol) was dissolved in toluene (30ml). To this was added n-butyl lithium (4ml of 1.6M, 0.0064mol). The mixture was stirred for 1 hour. 2-Methoxyethyl-p-toluenesulphonate (1.5g, 0.0065mol) was dissolved in toluene (20ml), this solution was added dropwise to the reaction mixture. After the addition was complete, the mixture was stirred for a further hour, after which 1ml of water was added. The organic layer was then washed with water and the solvent removed. The remaining product was then dissolved in methanol (50ml) to which sodium hydroxide (1g) had been added. The mixture was refluxed for half an hour. Water (100ml) was then added and the resulting mixture extracted with 40-60 petroleum ether (3*30ml), the extracts were combined and dried over magnesium sulphate. Product analysis showed that no alkylated product was formed.

Reaction with diphenylamine. Diphenylamine (1g, 0.06mol) was heated with methoxyethyl-tosylate (1.36g, 0.06mol). Reaction formed a black solid, no *N*-alkylation recorded.

N-Hydroxyethyldiphenylamine [78]. Diphenylamine (3.38g, 0.02mol) was refluxed with ethylene carbonate (1.94g, 0.022mol) in the presence of zinc chloride (0.5g). The reaction was allowed to cool and methylene chloride (50ml) was added. The solution was filtered and the solvent removed to yield the crude amine. To remove unreacted ethylene carbonate the crude amine was treated with 100ml of boiling water, the water was allowed to cool and the crude amine was filtered and dried in a desiccator. The remaining product was dissolved into 20ml of 40-60 pet ether and

cooled to -5°C and filtered. The solvent was then removed to yield the amine. Yield 1.8g, 42%; ^{1}H NMR (60MHz, $CDCl_3$) δ_H 3.6 (t, 4H), 6.7-7.3 (m, 10H); lit. δ_H = 2.85 (s, 1H), 3.65 (t, 4H), 6.98 (m, 10H)[78].

N-(2-Bromoethyl)diphenylamine [79]. *N*-(2-Hydroxyethyl)-diphenylamine (1g, 0.047mol) was dissolved in dry toluene (20ml) and cooled to 0°C. To this was added phosphorus tribromide (1.3g, 0.048mol) over a period of an hour. After the addition the mixture was stirred for a further 4 hours. Water (40ml) was added and the resulting mixture stirred for 30 minutes. This was then extracted with methylene chloride (2*30ml), the extracts were combined and dried over magnesium sulphate. The product was purified by recrystallization from methanol. Yield 0.9g, 69%; mp 32°C, lit. mp 32-33°C[79]; ^{1}H NMR (200MHz, $CDCl_3$) δ_H 3.6 (t, 2H), 3.7 (t, 2H), 6.9-7.1 (m, 6H), 7.3-7.4, (m, 4H). ^{13}C NMR δ_C 40.1, 54.1, 121.4, 122.5, 129.9, 148.0.

2- And 4-methyl-N-methyldiphenylamine [76]. Diphenylamine (3.3g, 0.0195mol) was added to trimethyl phosphate (10g, 0.071). The mixture was heated until a vigorous reaction occured. After this the reaction was refluxed. Every 10 minutes a sample was removed to determine the extent of alkylation. The reaction was stopped when the ratio of aromatic methyl to aminyl methyl was 1 to 1.

The top layer was rinsed away with 40-60 pet. ether. The solvent was removed and the crude amine was boiled with 200ml of water. This was allowed to cool, the amine was redissolved into pet. ether and the resulting solution dried over magnesium sulphate. Yield 3.5g, 91%; ^{1}H NMR (60MHz, $CDCl_3$) δ_H 1.7-2.1 (3H), 2.7-3 (3H), 6.7-7.2 (9H).

A second mixture was prepared with the same amount of diphenylamine and trimethylphosphate. This was refluxed for 3 hours to yield a product with 2 aromatic methyl groups for every aromatic hydrogen. As there are 10 available positions on the ring systems the composition is approximately that of *N*-methyl, hexamethyl diphenylamine.

5.22 Calculations, derivations and assumptions

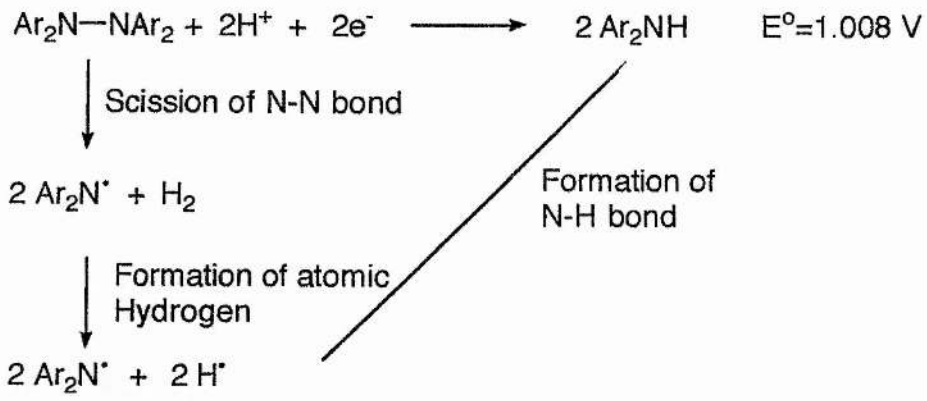
Thermodynamic calculations

General assumptions made in these calculations were that the entropy and the enthalpy of the reaction did not vary with temperature. The entropies of many compounds are known to increase with temperature. These increases can mainly be attributed to the increased importance of bond vibrations. Assuming that the increases in entropy on the reactant and product side are the same then the entropy changes with temperature will approximately cancel.

N-H bond energy

From the oxidation potential of diphenylamine

ΔH for the addition of a hydrogen atom to an aminyl radical was estimated from the redox potential of diphenylamine which has been measured at 1.008V[100]. Assuming that the oxidized form of diphenylamine was tetraphenylhydrazine then the following N-H bond energy was calculated.



As the overall reaction is a two electron process, ΔH for the overall reaction = 1.008V * eV * N * 2 = 46.5 kcal mol^{-1}

The reduction of a pair of protons to a molecule of hydrogen is 0 kcal mol^{-1} by definition.

The scission of the N-N bond in tetraphenylhydrazine has been measured at 29.2 kcal mol^{-1} [101].

The formation of 2 moles of atomic hydrogen from molecular hydrogen = 2*52.1 kcal mol^{-1}.

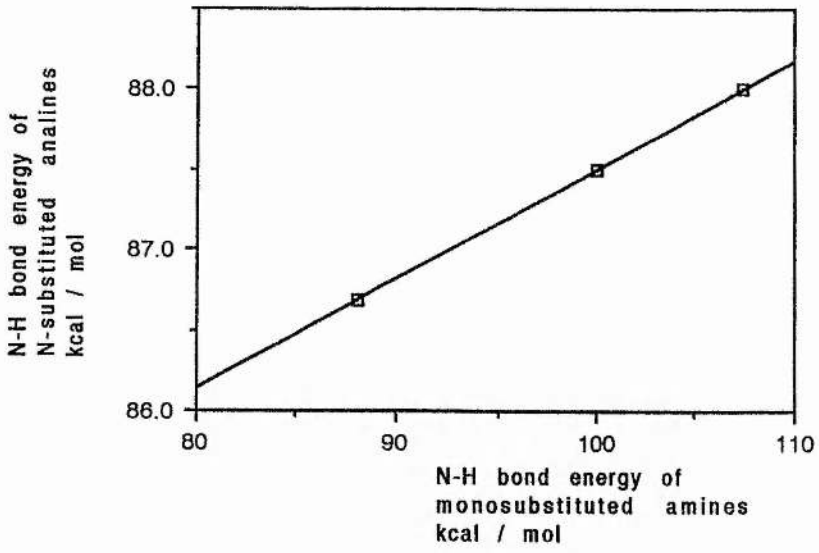
The strength of the N-H bond in diphenylamine is therefore;

(29.2 + 2*52.1 + 46.5) / 2 = 89.95 kcal mol^{-1}.

From bond energies of similar compounds

Compound	N-H/kcal mol^{-1}	Compound	N-H/kcal mol^{-1}
H_2N-H	107.4	(Ph)HN-H	88
(Me)HN-H	100	(Ph)(Me)N-H	87.5
(Ph)HN-H	88	$(Ph)_2N$-H	?

Plot N-H bond energies for the monosubstituted amines against bond energies for *N*-substituted anilines and extrapolate for diphenylamine. (N-H bond energies from ref. 102)



Graph 5.5
Plot of N-H bond energy for monosubstituted amines against the N-H bond energy for *N*-substituted anilines .

From graph 5.3 the N-H bond energy for diphenylamine was estimated to be 86.7 kcal mol^{-1}.

Thermodynamics of the addition of a methyl radical to benzene

Benzene, ΔH_f = 19.8 kcal mol^{-1}, S^0= 64.3 cal mol^{-1} deg^{-1} [102]

Methyl radical ΔH_f = 34.9 kcal mol^{-1} [107], S^0= 46.43 cal mol^{-1} deg^{-1} [83]

Addition of a hydrogen atom to benzene releases 28 kcal mol^{-1} [85], the average C-C bond is approximately 16 kcal mol^{-1} weaker than the average C-H bond[103]. Therefore the energy released by the addition of a methyl radical to the aromatic ring is approximately 12 kcal mol^{-1}.

Assuming that the intermediate radical has the same entropy as toluene then S^o for the intermediate = 76.4 cal mol^{-1} deg^{-1} [103].

ΔS for the overall process is -34.73 cal mol^{-1} deg^{-1}.

Energy released by the addition of a methyl radical to an aminyl radical

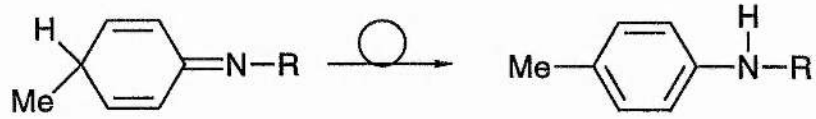
All bond energies are from ref. 103

Bonds formed		Bonds broken	
5* C-C	5*83	Aromatic sys	6*124
C-N -> C=N	147-73		
2* C=C	2*146		
total	781		744

Energy released by this process is approximately = 781-744 = 37 kcal mol^{-1}

Energy released for the rearrangement of the imine

All bond energies are from ref. 103 unless otherwise stated.



Bonds formed		Bonds broken	
N-H	88	C-H	75.75 [104]
Ar system	6*124	4* C-C	4*83
		2* C=C	2*146
		C=N -> C-N	147-73
Total	832 kcal		774 kcal

C-H was assumed to be the same as the $(C=C)_2CH$-H

For the rearrangement the energy released was estimated to be around 832-774 = 58 kcal mol^{-1}

Thermodynamics of the abstraction of an aromatic hydrogen by a hydrogen atom

$C_6H_6 + H \leftrightarrow C_6H_5^{\bullet} + H_2$

The aromatic system used for these calculations was benzene.

Benzene, ΔH_f = 19.8 kcal mol^{-1}, S^0= 64.3 cal mol^{-1} deg^{-1} [102]

H, ΔH_f = 52.1 kcal mol^{-1}, S^0= 27.4 cal mol^{-1} deg^{-1} [105]

Phenyl radical, ΔH_f = 78.5 kcal mol^{-1}, S^0= 69.1 cal mol^{-1} deg^{-1} [83]

H_2, ΔH_f = 0 kcal mol^{-1}, S^0= 31.2 cal mol^{-1} deg^{-1} [105]

For the overall process, ΔH = 6.6 kcal mol^{-1}, ΔS= -8.6 cal mol^{-1} deg^{-1}

The forward and reverse reaction are bimolecular therefore changes in pressure will effect both processes equally. At 1000K ΔG = -2 kcal =-RTlnK, therefore K= 2.7, i.e the rate of the forward reaction is 2.7* more rapid than the reverse.

Thermodynamics of the abstraction of an aromatic hydrogen by a Methyl radical

$C_6H_6 + Me^{\bullet} \leftrightarrow C_6H_5^{\bullet} + MeH$

The aromatic system used for these calculations was benzene.

Benzene, ΔH_f = 19.8 kcal mol^{-1}, S^0= 64.3 cal mol^{-1} deg^{-1} [102]

Methyl radical ΔH_f = 34.9 kcal mol^{-1} [107], S^0= 46.43 cal mol^{-1} deg^{-1} [83]

Phenyl radical, ΔH_f = 78.5 kcal mol^{-1}, S^0= 69.1 cal mol^{-1} deg^{-1} [83]

Methane, ΔH_f = -17.9 kcal mol^{-1}, S^0= 44.5 cal mol^{-1} deg^{-1} [102]

For the overall process, ΔH = 5.9 kcal mol^{-1}, ΔS= -2.87 cal mol^{-1} deg^{-1}

The forward and reverse reaction are bimolecular therefore changes in pressure will effect both processes equally. At 1000K

ΔG = 3.0 kcal mol^{-1} =-RTlnK, therefore K= 0.22, i.e the rate of the reverse reaction is 4.6* more rapid than the forward.

Thermodynamic calculations for the *N*-ethyl system at 1000K

The combination of aminyl radical with ethyl radicals

$$Ar_2N^{\bullet} + {}^{\bullet}CH_2{-}CH_3 \longrightarrow Ar_2N{-}CH_2{-}CH_3$$

Heat of formation of the N-C bond was assumed to be the same as the activation energy for N-C cleavage. From FVP results ΔH= 55kcal mol^{-1}.

The value of ΔS for the recombination was assumed to be the same as the change in entropy for the recombination of a phenyl radical with an ethyl radical to form ethylbenzene.

S^o for the phenyl radical was 69.1 cal mol^{-1} deg^{-1} at 298K[83].

S^o for the ethyl radical was 59.0 cal mol^{-1} deg^{-1} at 298K[83].

S^o for ethylbenzene was 86.2 cal mol^{-1} deg^{-1} at 298K[102].

ΔS for the reaction was 42 cal mol^{-1} deg^{-1}.

ΔG at 1000K, = ΔH-$T\Delta S$

= $-55*10^3 + 42*1000 = -13$ kcal mol^{-1}.

Disproportionation between the aminyl radical and the ethyl radical

$$Ar_2N^{\bullet} + {}^{\bullet}CH_2{-}CH_3 \longrightarrow Ar_2NH + CH_2{=}CH_2$$

Treatment of this problem was in two stages. Stage one was the decomposition of an ethyl radical to ethylene and a hydrogen atom. This reaction has been studied.

$$^{\cdot}CH_2—CH_3 \longrightarrow CH_2=CH_2 + H^{\cdot}$$

ΔH for this reaction was measured at 38.6 kcal mol^{-1} [86].

The second process is the combination of a hydrogen atom with the aminyl radical. The energy released will be the same as the N-H bond energy in diphenylamine.

$$Ar_2N^{\cdot} + H^{\cdot} \longrightarrow Ar_2NH$$

Entropy effects due to N-H bond rotations are zero, the change in the overall mass is small and changes in the moment of inertia are also negligible, therefore the change in entropy on going from the aminyl radical to diphenylamine were assumed to be zero.

For the ethyl radical, ΔH_f = +25.3 kcal mol^{-1} [83], S^o= 59.0 cal mol^{-1} deg^{-1} at 298K[83].

For ethylene, ΔH_f = +12.5 kcal mol^{-1}, S^o= 52.4 cal mol^{-1} deg^{-1} at 298K.

ΔS for the disproportionation reaction was calculated to be - 6.6 cal mol^{-1} deg^{-1}.

Assuming that the N-H bond = 88 kcal then at 1000K, $\Delta G = \Delta H - T\Delta S$

$= -49.4*10^3 + 6.6*1000 = -42.8$ kcal mol^{-1}.

<u>Combination of two ethyl radicals</u>

$$2\ ^{\cdot}CH_2—CH_3 \longrightarrow CH_3—CH_2—CH_2—CH_3$$

For the ethyl radical, ΔH_f = +28.3 kcal mol^{-1} [107], S^o= 59.0 cal mol^{-1} deg^{-1} at 298K[83].

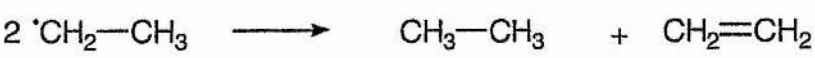
For butane, ΔH_f = -29.8 kcal mol^{-1}, S^o= 74.1 cal mol^{-1} deg^{-1} at 298K [102].

ΔH for the overall process = -86.4 kcal.

ΔS for the overall process = -43.9 cal.

At a 1000K, $\Delta G = \Delta H - T\Delta S$ = -86.4 + 43.9*1000 = -42.5 kcal mol^{-1}.

Disproportionation between two ethyl radicals



For the ethyl radical, ΔH_f = +28.3 kcal mol^{-1} [110], S^o= 59.0 cal mol^{-1} deg^{-1} at 298K[83].

For the ethane, ΔH_f = -20.2 kcal mol^{-1}, S^o= 54.8 cal mol^{-1} deg^{-1} at 298K[102].

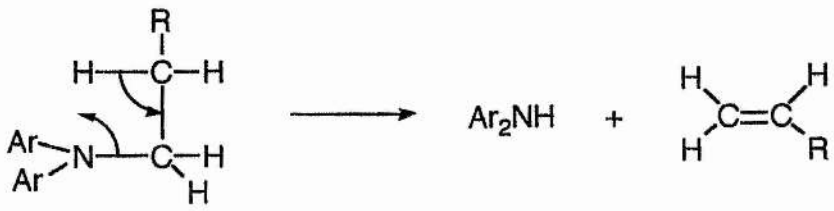
For the ethylene, ΔH_f = +12.5 kcal mol^{-1}, S^o= 52.4 cal mol^{-1} deg^{-1} at 298K[102].

ΔH for the overall process = -61.3 kcal.

ΔS for the overall process = -10.8 cal.

ΔG for the overall process at 1000K = $\Delta H - T\Delta S$ = -61.3 + 10.8*1000 = -50.5 kcal.

β-Hydrogen elimination



ΔH was estimated from the bonds which were broken and those which were formed.

Bonds broken

N-C, ΔH = + 53kcal mol^{-1} (From FVP results)

C-H, ΔH = +99kcal mol^{-1} [103]

Bonds formed

C=C, ΔH = -63kcal mol^{-1} [103]

N-H, ΔH= -88kcal mol^{-1} (mean of both methods)

ΔH for the overall reaction is approximately +1kcal mol^{-1}

ΔS was assumed to be the same as the decomposition of ethylbenzene to ethylene and benzene, ΔS for this reaction is 30.5 cal mol^{-1} deg^{-1}.

For the overall reaction at 1000K $\Delta G = +1*10^3 - 30.5*1000 = -29.5$ kcal mol^{-1}.

Kinetics of a model ethyl radical system

$$\cdot CH_2—CH_3 \longleftrightarrows H + CH_2=CH_2$$

The ethyl radical decomposes to give ethylene and a hydrogen atom, it was therefore assumed that $[H] = [C_2H_4]$.

The rate of the decomposition at 1000K = $[Et\cdot] * 2.9*10^5$ [87]

Rate of formation at 1000K= $[H] * [C_2H_4] * 2.7*10^{10}$ [87]

$= [H]^2 * 2.7*10^{10}$.

The $[gas] = [H] + [C_2H_4] + [Et\cdot] = 2[H] + [Et\cdot] \Rightarrow [gas] - 2[H] = [Et\cdot]$

At 760 Torr and 273K,1 mole of gas occupies 22.4 dm^3.

At 1 Torr and 1000K, 1 mole gas occupies $6.24*10^4$ dm^3, hence concentration of gas = 1/vol $=1.6*10^{-5}$ mol dm^{-3}.

$[gas] = P * 1.6*10^{-5}$.

At equilibrium, $[Et\cdot] * 2.9*10^5 = [H] * [C_2H_4] * 2.7*10^{10}$

$\Rightarrow [Et\cdot] = [H] * [C_2H_4] * 9.3*10^4$

therefore $[Gas] - 2[H] = [H]^2\ 9.3*10^4$

$\Rightarrow [H]^2\ 9.3*10^4 + 2[H] - [Gas] = 0$

$$[H] = \frac{-2 + \sqrt{4-4*9.3*10^{4}*-[Gas]}}{2*9.3*10^4}$$

From this the [H] could be calculated at any pressure and therefore the [Et·]. The concentration of butyl radicals was calculated from [Et·] and the $[C_2H_4]$, at equilibrium [Bu·] * $2.12*10^7$ is approximately = $[Et\cdot]*[C_2H_4]*1.56*10^6$. Rate of formation of butene [Bu·]*$1*10^6$. If the contact time is approximately 2 ms then the amount of butene formed = [Bu·]*$1*10^6*2*10^{-3}$.

N-CH_2CH_2OH bond energies

C_2H_5-OH 94 kcal mol^{-1} [95]

$C_2H_5OH \rightarrow CH_3CH\bullet OH + H$

ΔH_f kcal mol^{-1} $-56.2^{[102]} \rightarrow -15.2^{[95]} + 52.1^{[105]} \Rightarrow \Delta H = 93.1$

$C_2H_6 \rightarrow C_2H_5\bullet + H$

ΔH_f kcal mol^{-1} $-20.2^{[102]} \rightarrow 28^{[106]} + 52.1^{[105]} \Rightarrow \Delta H = 100.3$

$C_2H_5\bullet \rightarrow C_2H_4 + H$

ΔH_f kcal mol^{-1} $28^{[106]} \rightarrow 12.5^{[102]} + 52.1^{[105]} \Rightarrow \Delta H = 36.6$

36.6 kcal = Energy required to cleave C-H bond + energy given out in the formation of C=C bond => C-H bond = $36.6 + 63^{[103]} = 99.6$

For the decomposition of the ethyl radical the C-H bond energy is approximately the same as the C-H bond energy of ethane. Assuming that the bond energies are approximately the same in the radicals as they are in the compounds from which they are derived then the C-H and the C-O bonds are approximately 6kcal mol weaker than the C-H bond in the ethyl radical.

Kinetics of a model bromoethyl radical system

Temperature of model system was 600°C. At 1 Torr the concentration of gas is $1.837*10^{-5}$ mol dm^{-3}. [gas] = P * $1.837*10^{-5}$.

The 2-bromoethyl radical decomposes to give ethylene and a bromine atom, therefore assumed that [Br] = [C_2H_4].

The rate of the decomposition at 873K = [Br-CH_2CH_2•] * $1.4*10^{10}$ 87

Rate of formation at 873K= [Br] * [C_2H_4] * $5.9*10^{11}$ 87

= $[Br]^2 * 2.7*10^{11}$.

The [gas]= [Br] + [C_2H_4] + [Br-CH_2CH_2•] => 2[H] + [Br-CH_2CH_2•] => [gas] - 2[H] = [Br-CH_2CH_2•]

At equilibrium, [Br-CH_2CH_2•] * $1.4*10^{10}$ = [H] * [C_2H_4] * $5.9*10^{11}$

=> [Et•] = [H] * [C_2H_4] * 42

therefore [Gas] - 2[H] = $[H]^2$ 42

=> $[H]^2 *42 + 2[H] - [Gas] = 0$

$$[H] = \frac{-2 + \sqrt{4-4*42*-[Gas]}}{2*42}$$

From this the [Br] could be calculated at any pressure and therefore the [Br-CH_2CH_2•].

Thermodynamics of β-bromine elimination

ΔS for the process was assumed to be the same as for the β-hydrogen elimination = 30.5 cal mol^{-1} deg^{-1}.

For ΔH the N-Br bond energy is required. Nitrogen and bromine have approximately the same electronegativity, therefore the electron cloud in the N-Br bond will be relatively undistorted. This leads to the N-Br bond energy having the average energy of the N-N bond and the Br-Br bond. The N-N bond in tetraphenylhydrazine is 29.2 kcal mol^{-1} [101], the Br-Br bond

energy is 46.2 kcal mol^{-1}, therefore the strength of the N-Br bond in *N*-bromodiphenylamine is approximately 38 kcal mol^{-1}.

The energy released during the β-bromine elimination will be the sum of the bonds broken and the bonds formed.

Bonds formed		Bonds broken	
N-Br	38*	C-N	53**
C=C	63[103]	C-Br	66[103]
Total	101 kcal		119 kcal

* Estimated bond energy

** Experimentally determined

For the overall process ΔH= 18 kcal mol^{-1}.

Chapter 6
Conclusions

6.1 Effects of para substituents upon k_{II} values for diarylamine antioxidants

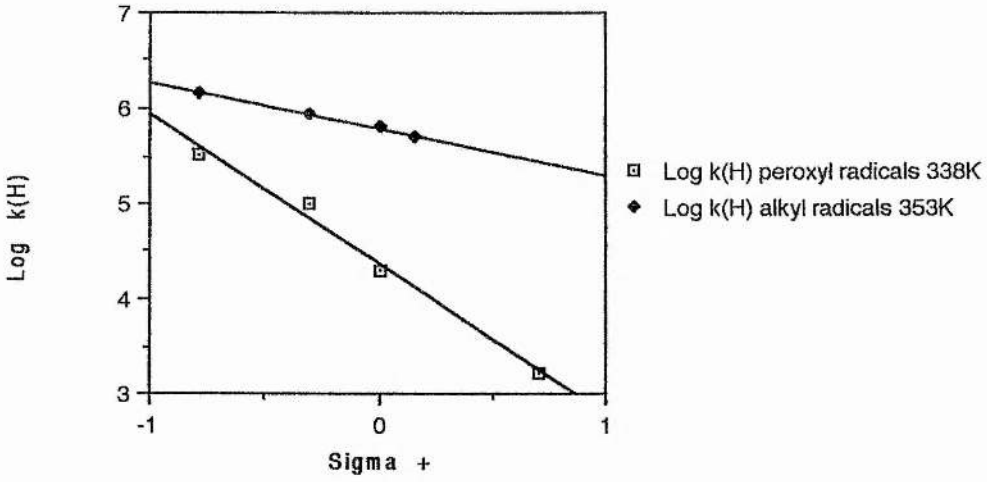
The rate constants, k_{II}, at which alkyl radicals abstract the aminyl hydrogen from 4,4'-disubstituted diphenylamines were measured using the neophyl radical rearrangement. k_{II} was measured at three different temperatures to give the activation energy and the pre-exponential factor. The results of these experiments are shown in the table below.

	$k_H * 10^{-5}$ M^{-1} s^{-1}					
Amine	k_H 373K	k_H 353K	k_H 333K	Log(A/ M^{-1} s^{-1})	Ea Kcal mol^{-1}	k_H/k_D
OMe	34	23	4.1	13.2 +/-1.5	11.5 +/- 1.8	-
Me	23	8.7	3.6	12.8 +/-2.2	11 +/-3.6	-
H	13	6.8	4.2	11.5 +/-1.9	9.2 +/-3.1	4.4
Br	8.8	5.0	2.2	12.3 +/-2.2	10.8 +/-3.4	-
Naug 438L	23	6.8	4.2	12.3 +/-2.5	12.3 +/-4.3	-

Table 6.1
Radical clock results for
diarylamine antioxidants

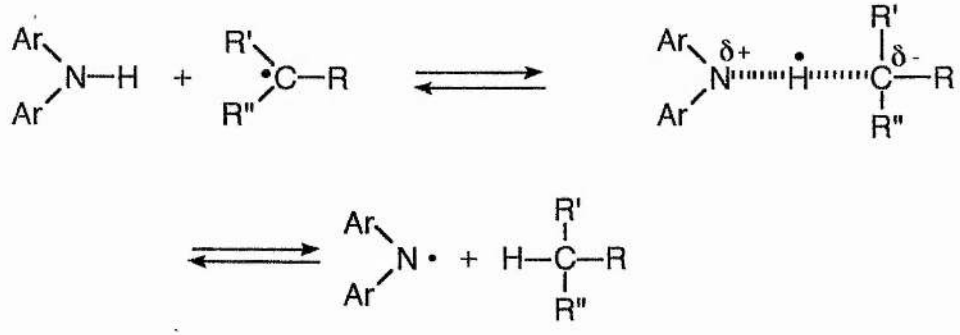
At 353K, log (k_H/k^o_H) was found to correlate well with σ_P^+ values[77] (k^o_H is the rate at which the neophyl radical abstracts hydrogen from diphenylamine). The susceptibility ρ was found to

be -0.49. Increasing the temperature had the effect of increasing the magnitude of ρ, when k_H was calculated from the results shown in table 6.1.



Graph 6.1
Hammett plot comparing the trapping of alkyl and peroxyl radicals with amine antioxidants

The correlation with σ_P^+ indicated that in the transition state there was some charge separation with the nitrogen developing a partial positive charge which was stabilised by electron releasing substituents.



Scheme 6.1
Abstraction of the aminyl hydrogen by an alkyl radical

Attempts were made to find a correlation with $\sigma^{\bullet}$ values for the substituents[110,111]. This would link the rate constant k_{II} with radical stability. However no correlation was found indicating that polar effects were far more important.

The neophyl radical was expected to be slightly nucleophilic in nature and would therefore be attracted to regions of low electron density. The experimental results indicated that the neophyl radical was being attracted to aminyl hydrogens with a high electron density, but the results obtained with phenolic antioxidants gave the opposite result, in that the neophyl radical was being attracted to a phenolic hydrogen with a low electron density.

A possible explanation for this observation involves the strength of the N-H dipole. In diarylamines the N-H bond naturally forms a dipole. The nitrogen is an electronegative atom and so is able to attract electron density away from the hydrogen leaving the nitrogen with a partial negative charge and the hydrogen with a partial positive charge. The hydrogen would then be naturally attractive to nucleophilic radicals. The presence of functional groups on the aromatic rings of diphenylamine would affect the electron distribution. This effect decreases with distance from the functional group, therefore the nitrogen, being directly attached to the aromatic rings, will be more affected by the functional groups than the aminyl hydrogen. The presence of electron withdrawing groups such as the bromine atom will preferentially remove electron density away from the nitrogen. This has the effect of decreasing the strength N-H dipole, making the aminyl hydrogen less attractive to the neophyl radical.

The results obtained for the abstraction of the aminyl hydrogen by peroxyl radicals also gives a correlation with σ_P^+, the susceptibility ρ = -1.6. The peroxyl radical is known to be electrophilic in nature and so is attracted to regions of high electron density. The increase in the magnitude of the susceptibility can be attributed to the electronegativity of the element on which the radical is centred. The oxygen is more electronegative than carbon, hence in the transition state it is able to induce a large amount amount of charge separation with the oxygen taking on a partial negative charge.

The correlation with σ_P^+ means that the rate constants, k_H, can be predicted for other para-substituted diarylamines, assuming σ_P^+ is known.

6.2 Comparison of k_H with the industrial screening test results for diarylamine antioxidants.

Using the results obtained from the kinetic studies, amines with para substituents with low σ_P^+ were expected to be the best antioxidants. For ERCOT's run in PAO this appeared to be true. In this basestock 4,4'-dimethoxydiphenylamine was the best antioxidant. However in NS150, 4,4'-dimethyldiphenylamine was found to be more effective. The results of the DSC's run in NS150 gave similar results, in that the 4,4'-dimethyldiphenylamine was a more effective antioxidant in NS150 than the 4,4'-dimethoxy derivative. However, the difference between the two was not large.

A Hammett plot derived from the results of the ERCOT's run in NS150 gave a good correlation with $\sigma' = (\sigma_I + 0.92*\sigma_R)$[58], with the susceptibility ρ' = -1.2. This result can be used for predictive

purposes, assuming that σ_I and σ_R are known for the *para* substituents. This result would be limited to ERCOT's run in NS150, since, as already determined, the 4,4'-dimethoxydiphenylamine was a more effective antioxidant in PAO.

6.3 Deductions about optimum high temperature diarylamine antioxidants

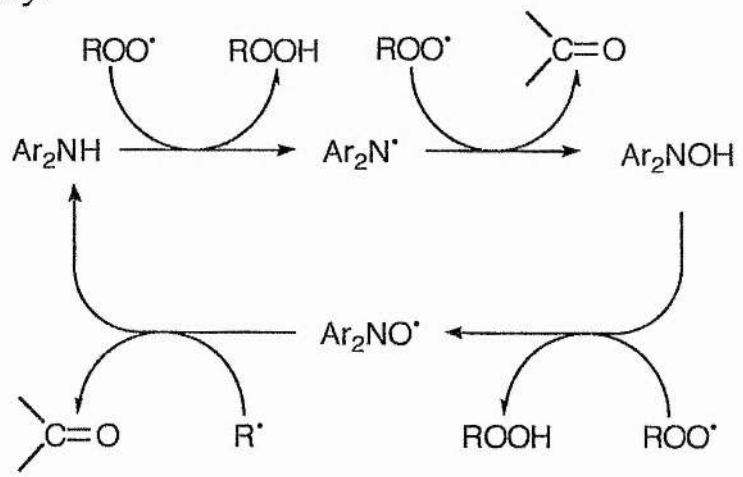
At high temperatures radical propagation involving alkyl radicals becomes more important and therefore a high temperature antioxidant package should be able to inhibit radical propagation by both alkyl and peroxyl radicals.

The rates at which 4,4'-disubstituted diarylamines trap both the neophyl and peroxyl radical[51,52] were found to correlate with σ_P^+ values for the para substituents. The susceptibility was negative for both the neophyl and peroxyl radicals, therefore the most efficient high temperature antioxidant would presumably be the ones with low σ_P^+ values for the *para* substituents. Industrial screening tests carried out in paraffinic basestocks agreed with this result, the best antioxidant was found to be the one with the lowest σ_P^+ value.

However ERCOT and DSC results from experiments run in the NS150 basestock did not correlate with the kinetic studies. From these experiments the most effective 4,4'-disubstituted diarylamine antioxidant was the 4,4'-dimethyl derivative.

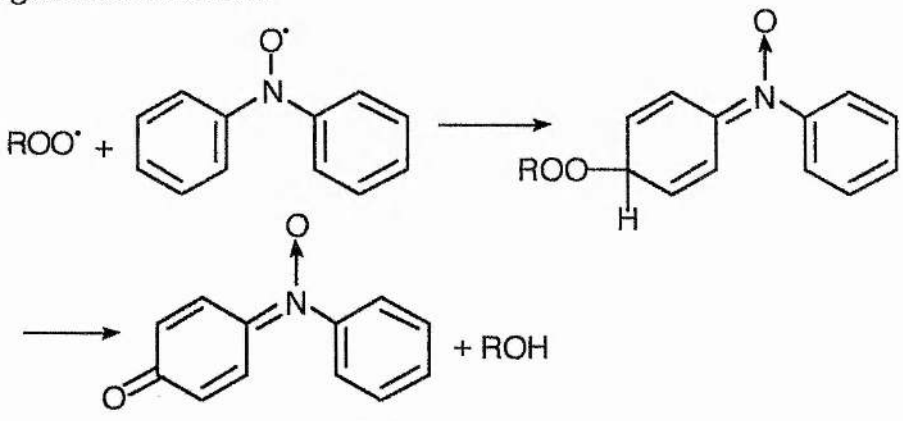
A possible reason for these differences is that the diarylamine antioxidants are able to inhibit autoxidation by a catalytic inhibitory cycle. The cycle depicted in scheme 6.2 was constructed from reactions that the amines or their derivatives are known to undergo. Under these conditions the most effective

amine antioxidant would be the one which is able to go through the catalytic inhibitory cycle the quickest, which is not necessarily the diarylamine which is able to donate its aminyl hydrogen the most rapidly.



Scheme 6.2
Catalytic inhibitory cycle
of amine antioxidants

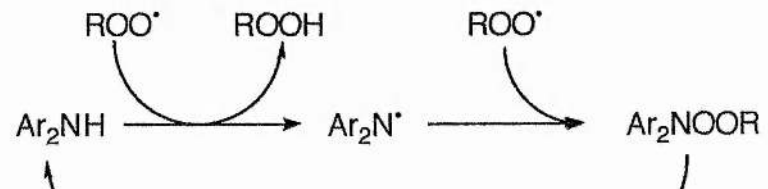
However the amines can be converted to inert compounds if the diaryl-nitroxide reacts with a peroxyl radical. The product of this reaction are an alcohol and *N*-phenyl-o or *p*-benzoquinoneimine-*N*-oxide, which is unable to inhibit radical propagation reactions.



Scheme 6.3
Reaction of a peroxyl radical
with a nitroxide

For effective long lasting protection against radical propagation the amine should be protected against conversion to the *N*-phenyl-o or *p*-benzoquinoneimine-*N*-oxide. This is possible by placing bulky groups in the *meta* positions, sterically hindering attack at the *ortho* and *para* positions, placing inert functional groups in the *ortho* and *para* positions or using *N*-alkylamines without any β-hydrogens. Any loss of activity can be made up for by increasing the concentration of the antioxidant.

The presence of a strong acid opens up the possibility of other catalytic cycles involving acid hydrolysis of the various intermediates formed by combinations of the aminyl with peroxyl radicals. Such a situation probably existed with the ERCOT's and DSC's run in the NS150 basestock.



Scheme 6.4
Catalytic inhibitory cycle of amine antioxidants in presence of acid

If the catalytic cycle depicted in scheme 6.4 is occuring, then the presence of the strong acid inhibits the reaction which forms the hydroxylamine and hence the nitroxide. Again the best amine antioxidant will be the one which goes through the catalytic inhibitory cycle the most rapidly, which in NS150 was found to be the 4,4'-dimethyl derivative.

The most effective high temperature amine antioxidant should be the one which is able to go through the various catalytic inhibitory cycles the quickest without being consumed.

6.4 Effects of *para*- substituents upon k_H for 2,6-di-t-butyl-phenols.

The rate constants, k_H, at which alkyl radicals abstract the phenolic hydrogen from 2,6-di-t-butyl-4-substituted phenols were measured using the neophyl radical rearrangement. k_H was measured at three different temperatures to give the activation energy and the pre-exponential factor. The results of these experiments are shown in the table 6.2.

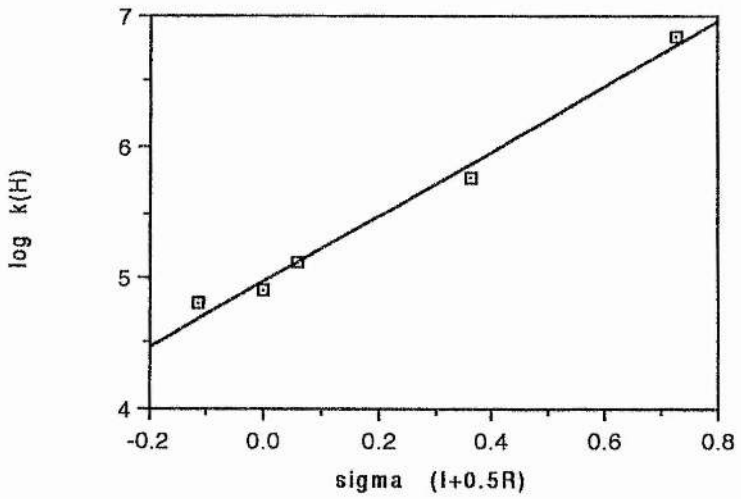
	k_H*10^{-4} M^{-1} s^{-1}				
	k_H 393K	k_H 373K	k_H 353K	Log(A/M^{-1} s^{-1})	Ea Kcal mol^{-1}
OMe	13	6.7	21	10.4	9.4
Me	6.3	3.5	2.4	8.5	6.6
H	7.9	4.8	2.4	9.5	8.3
Br	58	16	4.9	15.2	17
NO_2	700	300	170	12.1	9.6

Table 6.2
Radical clock results for
phenolic antioxidants

From the results shown in table 6.2, phenols with electron withdrawing substituents in the *para* position were the most effective at trapping the neophyl radical.

At 393K, log (k_H/k^o_H) was found to correlate with a σ' values[82] which were equal to ($\sigma_I + 0.5*\sigma_R$) from which $\rho' = 2.5$ was

obtained. Increasing the temperature appeared to have little effect upon the susceptibility.



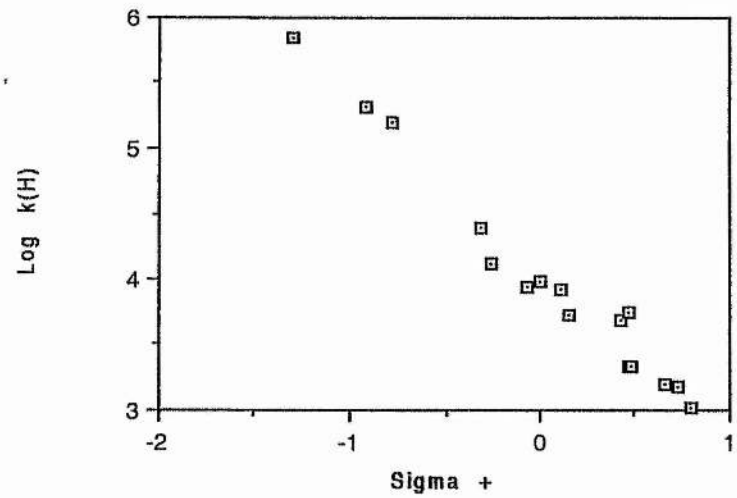
Graph 6.3
Hammett type plot for k_H at 393K[62]

Attempts were made to find a correlation with $\sigma^{\cdot}$ values for the substituents[110,111]. This would link the rate constant k_H with radical stability. However no correlation was found indicating that polar effects were far more important.

For the abstraction of hydrogen from antioxidants based on 2,6-di-t-butyl-4-substituted phenols by the neophyl radical, electric field effects appeared to play a more important role than resonance stabilisation. The positive gradient and the high value of the susceptibility also imply that in the transition state there is substantial charge separation with the phenolic oxygen taking on a partial negative charge, which was stabilised by electron withdrawing groups. This is further enhanced if the neophyl radical is slightly nucleophilic in nature. The phenol naturally forms a dipole with the hydrogen having a partial positive charge, i.e. it is a region of low electron density and therefore attractive to

alkyl radicals. The phenolic hydrogen also sits between two t-butyl groups, which are regions of high electron density. The placement of electron withdrawing substituents in the para position will preferentially remove electron density away from the phenolic hydrogen, in comparison to the t-butyl groups, making it even more attractive to the neophyl radical.

For trapping peroxyl radicals, 2,6-di-t-butyl-4-substituted phenols with electron releasing substituents in the *para* position were found to be the most effective. Hammett plots derived from the attack of a peroxyl radical derived from ethylbenzene at 333K give a good correlation with σ_p^+ values for the electrical effects of the functional groups, the susceptibility ρ was measured at -1.3. A similar correlation was found with the *tert* -butylperoxyl radical at 237K[63], with ρ= -0.85.



Graph 6.4
Hammett plot for the trapping of peroxyl radicals based on ethylbenzene by para substituted DBPh at 333K

The differences in the susceptibility can be attributed to the electronegativity of the element on which the radical is centred. The oxygen is more electronegative than carbon, hence in the transition state it is able to induce a partial positive charge onto the phenolic oxygen, whereas in the case of the abstraction by alkyl radicals the phenolic oxygen takes on a partial negative charge.

6.5 Deductions about optimum high temperature phenolic antioxidants

In high temperature autoxidations the propagation by alkyl radicals becomes more important. At these high temperatures a chain inhibiting antioxidant system must be able to trap alkyl radicals. It is unlikely that an efficient agent for trapping alkyl radicals will be able to trap every one, the remainder are likely to react with oxygen to give peroxyl radicals. Hence it is probably necessary to include an efficient peroxyl radical trap as well. The best phenolic antioxidants for trapping peroxyl radicals were those with electron releasing substituents in the para position whereas for trapping alkyl radicals electron withdrawing substituents in this position were more effective.

For high temperature applications a pair of phenolic antioxidants would probably be the most effective. One with an electron releasing substituent for trapping peroxyl radicals and the other with electron withdrawing substituents for the trapping of alkyl radicals.

6.6 Deductions about the radical clock rearrangement as a potential screening test

The radical clock experiments identified that the hindered phenolic antioxidants with electron withdrawing substituents in the *para* position were the most efficient at trapping alkyl radicals. Although this needs confirming by further experimentation, this result would have been missed by the conventional screening tests. Therefore the radical clock rearrangement would make a useful contribution to the identification of potentially useful antioxidants.

The major problem experienced with the neophyl radical rearrangement was the disproportionation reaction. This can be attributed to the way in which the neophyl radical was generated. The radicals were formed in pairs in close proximity to each other therefore disproportionation was likely especially if the radical pair occupy a solvent cage.

To overcome this problem the alkyl radicals need to be formed individually. This can be achieved by the abstraction of a halogen by a tin centred radical. An alternative would be to use an alkyl radical which will not undergo the disproportionation reaction, but which rearranges at about the same rate as the neophyl radical. A possible candidate is the cyclobutylcarbinyl rearrangement. Because there are no benzyl hydrogens in this system radical disproportionation should be less important.

Scheme 6.5
cyclobutylcarbinyl rearrangement

6.7 Slow release antioxidants

Of the original slow release agents discussed in section 5.2 only the *N*-alkylated amines warranted serious investigation. The results of these experiments are shown in table 6.3.

R	Log (A s^{-1})	Ea kcal	Max Ph_2NH
Me	13.8	53.3	34
Et	14.7	54.6	79
Bu^n	16.4	63.9	77
Hex^n	11.6	42.9	45
CH_2CH_2OH	10.1	36.6	10
N-Pr^i	10.0	33	88
CH_2CH_2Br	8.3	22.1	0
$Ph_2NCH_2\}_2$	-	-	0

Table 6.3
FVP results

The major product formed when most of the *N*-alkylated amines were thermally decomposed was diphenylamine. This can be formed by both β-hydrogen elimination and a free radical process. There was evidence that they decomposed by homolytic scission of the N-C bond to give an aminyl and alkyl radical. The products derived were then determined by how these radicals behaved. The thermal stability would depend on the strength of the N-C bond, which in turn is generally dependant upon the stability of the radicals produced. The higher the stability of the radical products, the more readily the starting material decomposed.

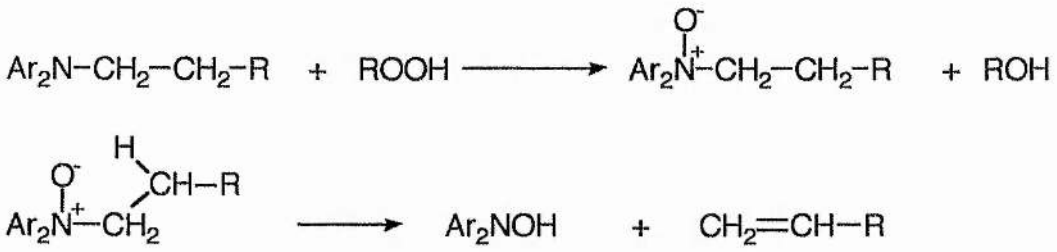
The β-hydrogen elimination would only form diphenylamine and an alkene. However if radical reaction were occuring along

side then radicals can add onto the alkene which will then rapidly fragment forming ethylene, methyl radicals and hydrogen atoms. Therefore in the FVP evidence for β-hydrogen elimination would be easily erased.

In the panel coker test the stability of the compounds was found to be dependant upon how much steric hindrance could be offered by the *N*-alkyl group, indicating that the decomposition of the *N*-alkylated diphenylamines was initiated by a reaction with the basestock or with products derived from the oxidation of the basestock.

ERCOT's run with the slow release agents in NS150 at 165°C showed signs of appreciable decomposition after around 20 hours, but in thermolysis experiments were showing no sign of decomposition at 250°C. This again indicates that the decomposition was occuring by a different mechanism to the thermolysis experiments.

It is known that tertiary amines react with hydrogen peroxide to form *N*-oxides. *N*-Oxides readily decompose via β hydrogen elimination to give hydroxylamines and an alkene[74,75]. This reaction has been used for producing alkenes under mild conditions and is commonly known as the Cope reaction.



Scheme 6.6
Low temperature decomposition
of *tert*- amines

A similar reaction may be occuring in the ERCOT and panel coker test. Although direct evidence was lacking, the fact that large *N*-alkyl groups on the nitrogen slowed down the rate of decomposition indicated that attack on the nitrogen was important in initiating the decomposition.

The active antioxidant derived from this reaction would be the hydroxylamine, which can readily donate its hydroxyl hydrogen to both alkyl and peroxyl radicals. This gives the nitroxide, which as already shown in scheme 6.3, can be converted to inert compounds by the action of the peroxyl radicals on the aromatic rings.

To inhibit this the peroxyl radicals need to be prevented from interacting with the aromatic system. This can be achieved by steric hindrance or by placing inert groups in the *ortho* and *para* positions.

The useful lifetime of an oil is between 5000 and 10000 miles, this corresponds to around 100 to 200 hours of driving. For a slow release agent to be of any use it should release its antioxidants over a similar time period. In the ERCOT test these compounds were showing evidence of appreciable decomposition after 20 hours. Possible ways of slowing down the decomposition are to use alkyl groups with no β-hydrogens or to use very large alkyl groups which will hinder the attack upon the nitrogen.

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