A STUDY OF ~~RADICALS FORMED DURING~~ THE
AUTOXIDATION OF HYDROQUINONES AND
QUINONES BY ELECTRON SPIN RESONANCE
SPECTROSCOPY

By

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ABSTRACT

The work reported in this thesis started from an
investigation of the types of reactions occuring during the
autoxidations of hydroquinones and quinones in alkaline solution.
The free radical intermediates were identified by means of their
E.S.R.spectra.

In dilute alkali the primary radicals were observed, but
in stronger alkali the spectra obtained corresponded to hydroxylated
'secondary radicals' which were characterised by producing identical
spectra in the alkaline autoxidation of 1,2,4- Triacetoxybenzene
derivatives. In some cases different isomeric radicals were
obtained in different solvents.

Added hydrogen peroxide had no apparent effect on the
course of the reaction and the ease of formation of the secondary
radicals seemed to depend on the concentration of the alkali and
the presence of a fairly sterically unhindered site in the
quinonoid ring. The adduct I is suggested as the intermediate
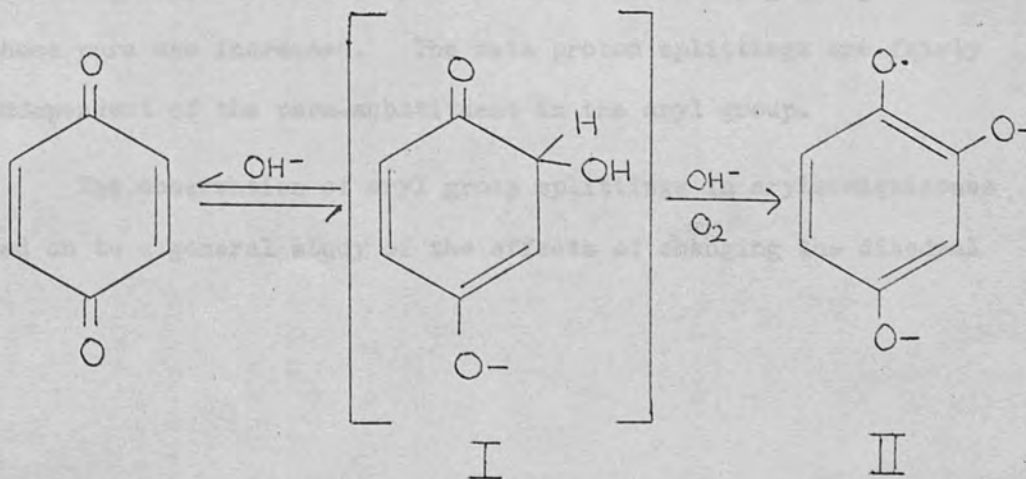
in the formation of the secondary radical II, which is shown
to be capable of reducing excess quinone back to the primary
radical.

When the quinonoid ring is free of bulky substituents,
'tertiary radicals' are often observed under certain conditions,
and these appear to arise from coupling through carbon at some
stage of the reaction sequence.

The coupling constants of the primary radicals containing
a wide range of substituents (X= alkyl, OMe, Cl etc.) show
that the semiquinone ring splittings appear to depend on the
electron-releasing ability of X and on its steric bulk. The
electron-releasing effect influences the spin densities ortho
and para to the substituent, while spin densities meta to X
are affected mainly by the steric interaction between X and
the adjacent carbonyl group. The splittings in the secondary
radicals also show these trends.

The study of the hyperfine splittings in a wide range of
Para-substituted Arylsemiquinones appears to show the effects of
varying the electron-donating ability of the substituent exclus-
ively. The splittings of semiquinone ring protons ortho to the
substituent are decreased by more electron-releasing groups while
those para are increased. The meta proton splittings are fairly
independent of the para-substituent in the aryl group.

The observation of aryl group splittings in arylsemiquinones
led on to a general study of the effects of changing the dihedral

angle between the two rings. The aryl group splittings are found to vary in different ways for ortho, meta and para protons on increasing the dihedral angle by the addition of bulky ortho substituents. The variation of the splittings can be rationalised by considering the two possible mechanisms by which spin density can be transferred from the semiquinone ring to the aryl ring. The π-delocalisation mechanism(important at low values of the dihedral angle) and σ-spin delocalisation (important as θ approaches 90°), treated seperately, account quite well for the variation of the splittings for protons and other groups (Me, F,) at the various positions in the aryl ring.

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PART I

INTRODUCTION

1. HISTORICAL

Early interest in the autoxidation reactions of hydro-
quinones arose from their use, along with other hydroxy-
benzenes, as photographic developing agents[1,2]. More
recently, attention has been drawn to many biologically
important chemicals belonging to the quinonoid class of
compounds[3], notably the vitamins E and K, and there is
evidence to suggest that their role in the body arises from
participation in oxidation processes[4].

The hydroquinone-quinone redox system has received a
great deal of attention[1,2,5-7], and it has been established
that the autoxidation of hydroquinone in alkaline media
involves the dianion of hydroquinone I[5] and produces quinone
III and hydrogen peroxide[6]. The semiquinone intermediate
radical-ion II was first postulated by Michaelis[7] and has
since been observed by Electron Spin Resonance Spectroscopy[8].

$$I \qquad II \qquad III$$
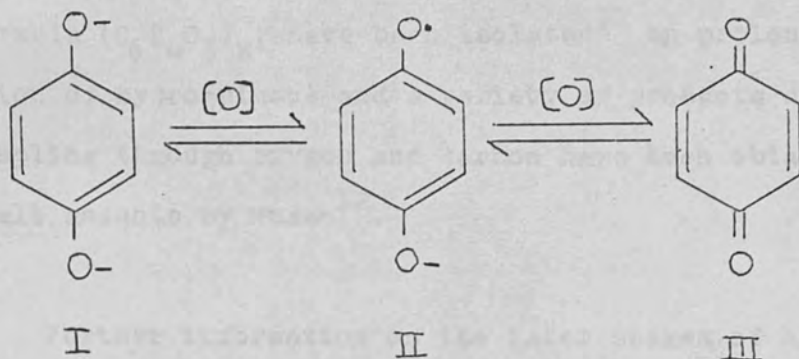
It was obvious, however, to the early workers, that the complete autoxidation process was highly complex, involving many secondary reactions, and the kinetics were far from simple. The quinone ring was shown to be susceptible to attack by nucleophiles present in the solution[1] and notably, hydroxylation products have been isolated[2,9]. It was suggested[9] that hydroxyl ion attack on the quinone occured producing the semiquinone of trihydroxybenzene IV which was then susceptible to further oxidation to the hydroxyquinone V.

$$IV \qquad \qquad V$$
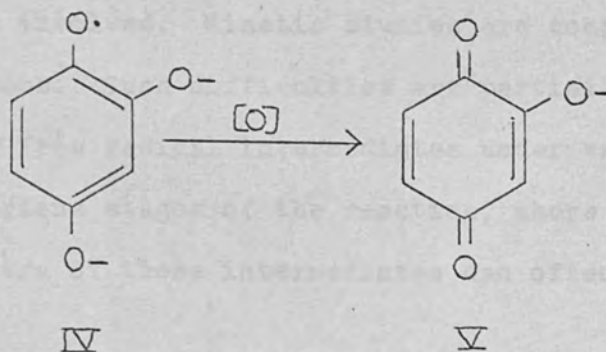
The autoxidation is further complicated by coupling reactions[10], to which phenolic compounds are particularly susceptible. Humic acids, polymeric products of general

formula $(C_6H_4O_3)_x$, have been isolated[11] on prolonged oxid-
ation of hydroquinone and a variety of products due to
coupling through oxygen and carbon have been obtained in
small amounts by Musso[12].

Further information on the later stages of hydroquinone
autoxidation have been afforded by studies on trihydroxy-
benzenes[13,14]. Hydroxylation and coupling reactions were
observed, as well as the formation of cyclopentane deriv-
atives by reaction of the hydroxyquinones with hydrogen
peroxide formed in the early stages of the reaction.

The work reported in this thesis stems from an attempt
to use the technique of electron spin resonance spectroscopy
to investigate the autoxidations of hydroquinones and
quinones. Methods which rely on identifying reaction
products, meet some difficulty due to the very large number
of species formed and the 'consecutive' nature of the
reactions involved. Kinetic studies are complicated for the
same reasons. Such difficulties are partially overcome by
observing free radical intermediates under varying conditions,
and at various stages of the reaction, where more or less
pure spectra of these intermediates can often be obtained.

The technique of E.S.R. spectroscopy has been of some
use in following the course of certain autoxidations of
this kind, but before these are discussed it was thought
necessary to give a brief outline of the relevant theory

and background of the technique, especially with regard to the aromatic-type radicals involved in this study.

2. GENERAL THEORY OF E.S.R. SPECTROSCOPY

If the electron is considered as a spinning charged body it has an associated magnetic moment, and since the spin quantum number can take values of $\pm\frac{1}{2}$, the magnetic moment may be aligned either parallel or antiparallel to an applied field. These two orientations are associated with different energies, the energy difference being prop- ortional to the strength of the applied field.

The energy difference E is given by:

$$E = g B_e H$$

where:

H = magnetic field strength

B_e = Bohr Magneton

g = gyromagnetic ratio, dependent on the coupling
between the spin and orbital moments of the
electron.

In the case of organic radicals 'g' is close to the value for a free electron, i.e. g_o = 2.0023.

The c.g.s. unit of magnetic field (Gauss) is used

throughout this thesis but a much used unit now in the S.I. system is the 'tesla' or millitesla, where lmT = 10 Gauss.

The frequency of radiation required to induce transitions between the two energy levels is given by the quantum relation:

$$hv = gB_eH.$$

The population of the two energy levels is given by the Boltzmann distribution i.e.

$$n_1 = n_2 \cdot \exp\left(\frac{gB_eH}{KT}\right)$$

where n_1 and n_2 refer to the numbers in the lower and upper levels respectively. The probability of an absorption increases with the number of electrons in the lower level and hence the intensity of absorption is favoured by high fields and frequencies. Practical difficulties of handling high frequencies have limited sensitivity and led to the general use of fields of about 3000 Gauss and microwave radiation of about 3cm wavelength. The resulting absorption under these conditions is called Electron Spin Resonance (E.S.R.).

Interaction of the electron with nuclei in the radical which have non-zero spin leads to the phenomenon of 'hyperfine structure'. The single absorption line is replaced by a number of lines depending on the nuclear spin. In an

applied field the nuclear magnetic moment can be aligned in
a variety of ways, the number being 2n+1, where n is the
nuclear spin. The field experienced by the electron is
therefore modified and the electron energy levels are each
split into 2n+1 components. The nuclear spin remains
unchanged during emission and absorption with the result
that the single absorption line is replaced by 2n+1 lines.
For the hydrogen atom a doublet is obtained, the separation
of the lines being known as the 'hyperfine splitting'. The
splitting is normally measured in units of magnetic field,
in Gauss, since the magnetic field is scanned at a fixed
frequency in most instruments.

Just as the coupling of an odd electron with a proton
gives rise to two energy levels, one associated with α -
and the other with β - spin of the proton, so with two
protons there are four energy levels corresponding to spins
$\alpha\alpha$; $\beta\beta$, $\alpha\beta$ and $\beta\alpha$. If the protons couple equally,
then the energy levels for $\alpha\beta$ and $\beta\alpha$ will be degenerate.
Under the conditions of observation α - and β - spins
have virtually equal probabilities and so the absorption
pattern is three equally spaced lines of intensities 1:2:1.
If $\alpha\beta$ and $\beta\alpha$ are not degenerate (i.e. unequal coupling
of the two protons) then four lines of equal intensity are
obtained.

In general coupling with n_1 protons of type 1, n_2
protons of type 2 .... gives rise to (n_1+1)(n_2+1)..:..

lines, some of which may overlap.

There are two mechanisms which give rise to hyperfine structure in organic radicals, an isotropic and an anisotropic mechanism. Isotropic splitting arises when there is a finite probability of the electron being found at the nucleus in question. This is only true when the orbital occupied by the electron has some s-character. The isotropic hyperfine interaction is independent of the orientation of the radical; on the other hand the anisotropic coupling is critically dependent on the positions of the electron and the nucleus relative to the applied field. Anisotropic coupling is important when that part of the radical containing the magnetic nucleus is fixed in a particular orientation, for example in the solid state, but in solution the rapid tumbling and rotation of the radicals averages the anisotropic part to zero and the observed splitting is due to the isotropic interaction.

Hyperfine coupling occurs not only with nuclei around which the electron is delocalised but also with neighbouring nuclei. For example aromatic protons in the semiquinone radical[8] lie in the nodal plane of the π- orbitals embracing the carbon and oxygen atoms in which the odd elctron is delocalised.
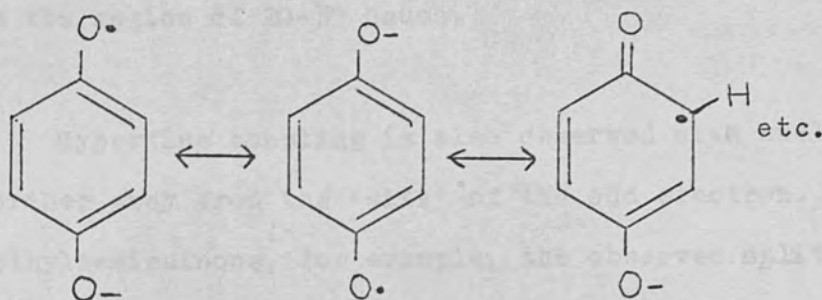
Out of plane C-H vibrations are too small to account for the observed splitting of ca. 2.4 Gauss[8]. A solution to the problem came from a consideration of 'configurational interaction'[16-20], or a mixing of the π - and σ - systems.
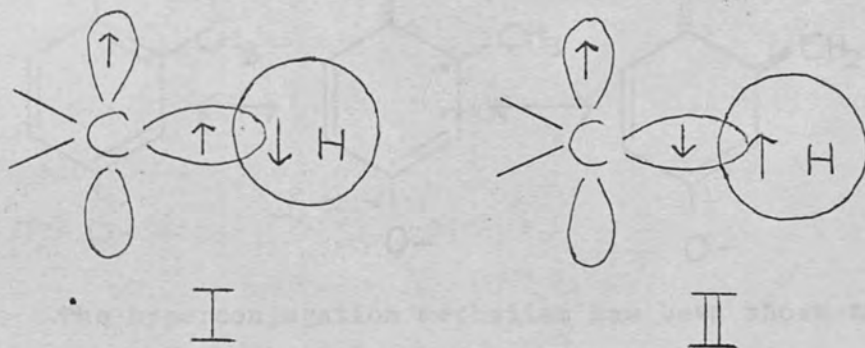
Considering the example of a $>\overset{\bullet}{C}-H$ fragment of an aromatic radical, the spin states I and II normally have equal weightings. However if interaction between the π - and σ - systems is allowed then I has a slightly greater probability than II (a modification of Hund's rule) and there is a net unpaired negative spin density in the s-orbital of the proton. The C-H bond is said to be 'spin polarised'. The observed hyperfine splitting is given approximately by ρQ[19,20] where ' ρ ' is the odd-electron

density on the carbon atom and 'Q' is a negative constant in the region of 20-30 Gauss.

Hyperfine coupling is also observed with nuclei even further away from the 'site' of the odd electron. In methylsemiquinone, for example, the observed splitting from the methyl group is about the same as those of the aromatic protons[21]. This has been attributed to hyperconjugation[17], and a valence bond picture of this is given below.
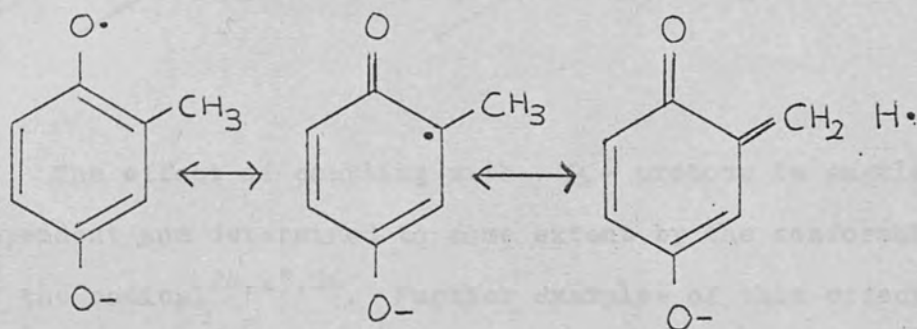
The hyperconjugation mechanism has been shown to account for the large β - proton splittings in alkyl radicals[22,23]. The observed splitting is again given by ρQ[22], where 'ρ' is the odd electron density on the α - carbon, and Q is a 'positive' constant in the region of 28 Gauss, since the spin associated with the protons is the same as the total spin of the radical.

The E.S.R. spectra of radicals such as I and II

I   II
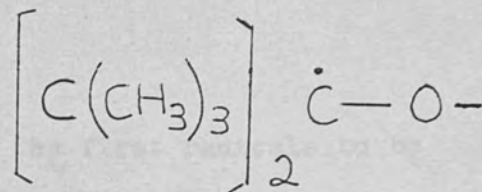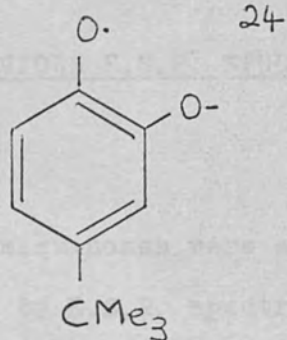
imply that hyperconjugation can occur with groups other than hydrogen[26]: i.e.
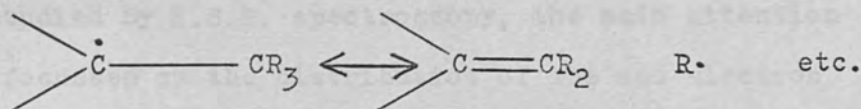
The effect of coupling with β - protons is angular dependent and determined to some extent by the conformation of the radical[24,25,26]. Further examples of this effect will be described and discussed later in this thesis.

Other magnetic nuclei frequently met in organic radicals are the halogens and nitrogen. Of the halogens fluorine (spin 1/2) and chlorine (spin 3/2) are the most common. Chlorine splits the electron resonance line into four lines of equal intensity and nitrogen three lines. In general, for a nucleus of spin I, $2I+I$ lines are obtained.

3. PREVIOUS E.S.R. STUDIES OF SOME AUTOXIDATION REACTIONS

Semiquinones were among the first radicals to be studied by E.S.R. spectroscopy because they are easily produced and can generally be obtained in relatively high concentrations. The observation of hyperfine splitting from the four equivalent protons of the semiquinone radical[8] led to a great deal of interest in these types of radicals. A wide range of para-semiquinones[21,24,27-34] have since been studied by E.S.R. spectroscopy, the main attention being focussed on the distribution of the odd electron around the aromatic ring. Alkylated semiquinones have provided data for testing theories of hyperconjugation and spin polarisation and molecular orbital calculations have been performed, with some success, on the system[24,27,35]. The variation of the splitting constants of aromatic hydrogens with methyl and chlorine substituents was shown to obey a nearly additive relation[27], but this does not seem to hold for all substituents, e.g. tert. butyl.

As well as the para-semiquinones, a host of similar radicals have been investigated by E.S.R. The closely related ortho-semiquinones I[24,28,29,36] and the semiquinones of 1,2,4-trihydroxybenzene II[37], and pyrogallol III[29,36] have been studied in some detail.

I   II   III
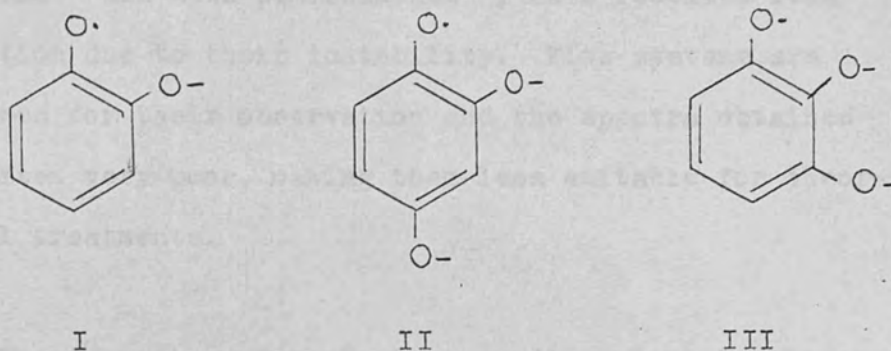
The equilibrium between the semiquinone anion and
protonated forms has been studied by Carrington et al[33]
and the effects of solvent[31,34] and ion-association[32] have
been investigated for these types of radicals. In anhydrous
solvents, for example tertiary butanol, the spectra of
simple semiquinones are very dependent on any cations
present[32]. The spectra have been interpreted in terms of
an equilibrium between the tightly bound ion-pair I and the
free, or at most weakly associated, radical anion II. In

I   II
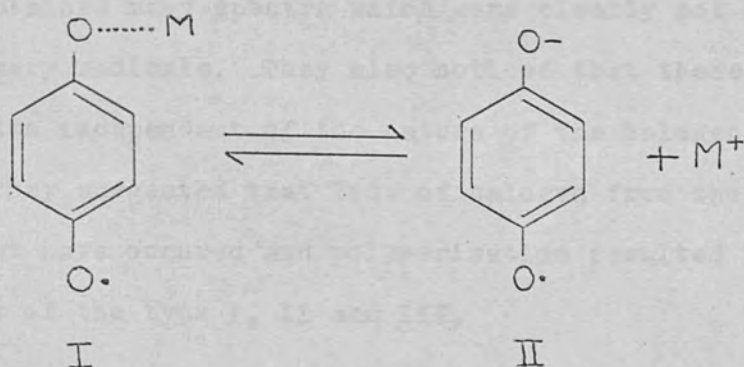
aqueous sovents, the variation of the coupling constants
with ions present in the solution is small due to the pres-
ence of a solvent sheath around the ions.

Certain radicals related to the semiquinones, aryloxy radicals[38] and meta-semiquinones[39], have received less attention due to their instability. Flow systems are required for their observation and the spectra obtained are often very poor, making them less suitable for theoretical treatments.

The formation of semiquinone radical-ions is, however, only the initial step in the autoxidation of dihydric phenols and during the first observation of para-semiquinone[8] certain additional lines were observed as well as the expected five-line spectrum. This observation could only be explained by the formation of secondary radicals involved in a later stage of the autoxidation process. It was suggested that the secondary radicals may be intermediates in the formation of the hydroxyquinones.

During a study of halogenated semiquinones[30], Anderson et al obtained many spectra which were clearly not due to the primary radicals. They also noticed that these spectra were often independent of the nature of the halogen substituent. They suggested that loss of halogen from the quinone ring must have occured and polymerisation resulted in products of the type I, II and III.

OH OH

OH OH OH O O OH

OH OH OH OH OH

I   II   III
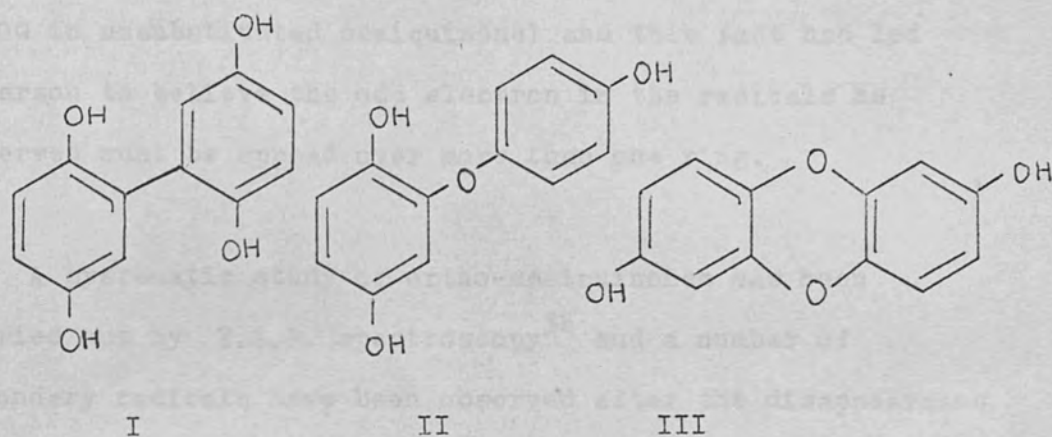
This suggestion was, however, purely speculative, and no attempt was made to reproduce the spectra they obtained by preparing the polymeric products.

It was later shown[40], in fact, that many of the spectra obtained by Anderson were not due to polymeric radicals but were formed by attack of alkoxyl ions present in the alcoholic solutions they had used. Wertz et al prepared 2,5 dialkoxy - quinones IV which on reduction gave the semiquinones V,

O   O·

OR   OR

OR   OR

O   O-   R = Me, Et.

IV   V
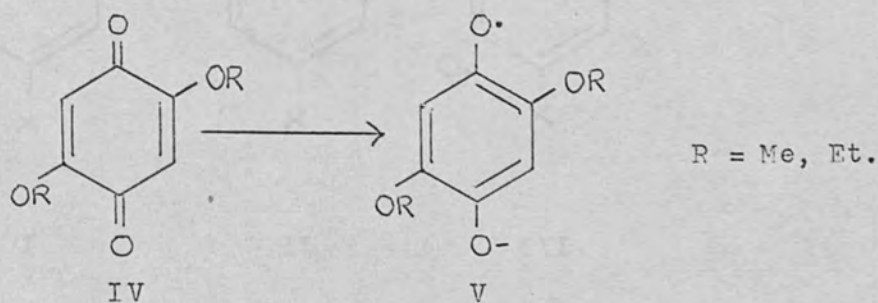
and the spectra were identical to some of those ascribed to

the dimers I, II and III. The aromatic proton splittings were considerably reduced by the presence of the alkoxyl groups in the semiquinone ring (ca. 0.3G as compared to ca. 2.40G in unsubstituted semiquinone) and this fact had led Anderson to believe the odd electron in the radicals he observed must be spread over more than one ring.

A systematic study of ortho-semiquinones has been carried out by E.S.R. spectroscopy[36] and a number of secondary radicals have been observed after the disappearance of the primary spectrum. Catechol and substituted catechols were autoxidised in alkaline dimethylformamide and hydroxlated radicals were observed as well as the primary ortho-semiquinones. It was suggested that attack by hydroxyl ions on the quinone I resulted in either the formation of pyrogallol semiquinones II (X=CHO, COMe) or semiquinones III of 1,2,4-trihydroxybenzene (X=Alkyl).

I   II   III
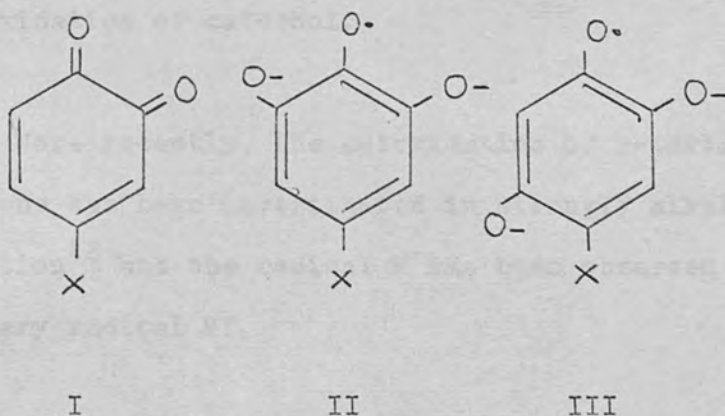
Their mechanism for the formation of the trihydroxy-

benzene derivatives was esentially similar to that given by Eigen and Matthies[9].

Stone and Waters obtained no hydroxylated radical from catechol itself, however, but obtained instead a spectrum which they showed to be due to the dimeric radical IV.
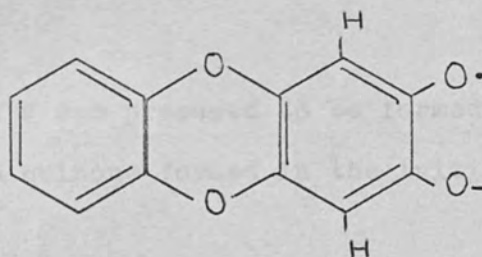
IV

The quinone of IV was prepared by an unambiguous method and on reduction gave a simple triplet spectrum (1:2:1, 0.64G) identical to that observed during the alkaline autoxidation of catechol.

More recently, the autoxidation of 2-tert. butylhydroquinone has been investigated in strongly alkaline alcoholic solution[42] and the radical V has been observed along with the primary radical VI.
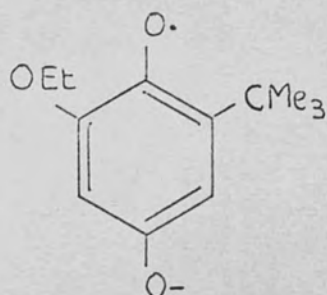
V   VI

Radical V was presumed to be formed by alkoxyl ion attack on the quinone formed in the initial oxidation steps.

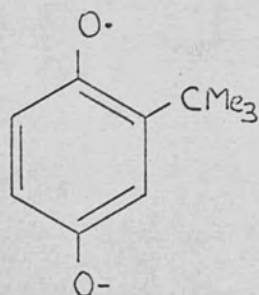A systematic study of the autoxidation reactions of hydroquinones has not however, as yet, been undertaken or accomplished by means of E.S.R. spectroscopy; although in the light of previous work the technique appears highly suitable. The work reported in this thesis began as an attempt to elucidate the apparent variety of reactions occuring in these systems. The investigation led on to a more general study of the radicals observed, interesting both from the point of view of the mechanism of their formation and from the trends in their coupling constants.
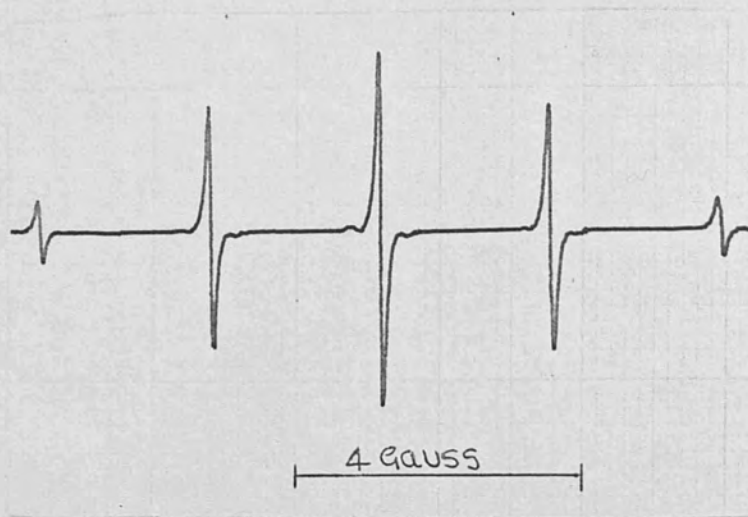
4 Gauss

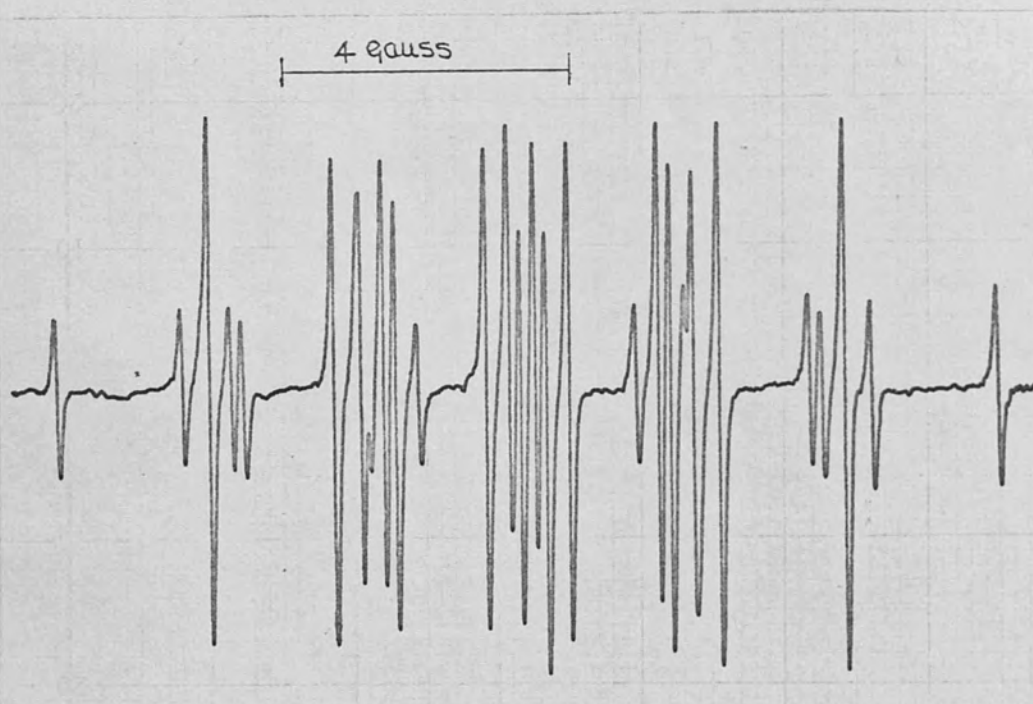Figure 1. Primary radical from Hydroquinone.

4 Gauss

Figure 2. Primary radical from Methylhydroquinone.

4. INITIAL STUDY OF THE AUTOXIDATION OF SOME SIMPLE HYDROQUINONES.

The first experiments were carried out using hydro-
quinone and methylhydroquinone under varying conditions of
autoxidation. It was found that by changing the alkalinity
and the nature of the solvent, different radicals could be
observed corresponding to various stages of the autoxidation.

HYDROQUINONE:

When a dilute aqueous solution of hydroquinone (ca.
0.01M) was made slightly alkaline by addition of a little 1%
sodium hydroxide solution a deep yellow colour was obtained,
and the solution gave rise to a strong E.S.R. absorption.
The five line spectrum (fig.1) was that of the unsubstituted
semiquinone radical-anion and the coupling constant of the
four equivalent protons, 2.37G, is consistent with its
previous observation[8]. That it is the primary oxidation
product was confirmed by its observation in fast flow
systems, ca.0.01 sec. after mixing solutions of hydroquinone
and alkali. The best spectra of this primary radical were
obtained with 50% ethanol as solvent, alcohol stabilising the
radical, and it can be observed for up to a few hours under
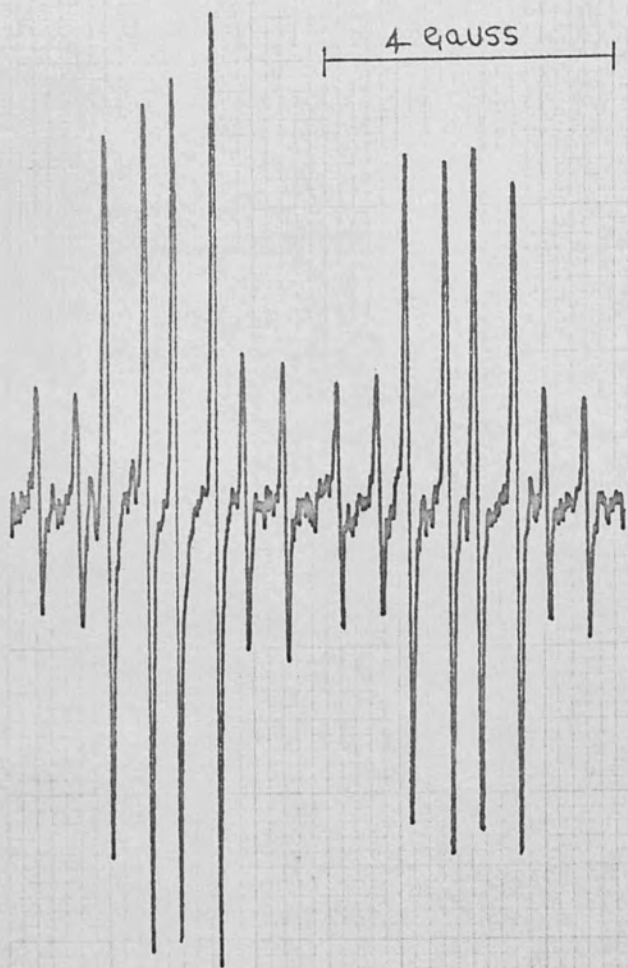these conditions in a static system.

4 Gauss

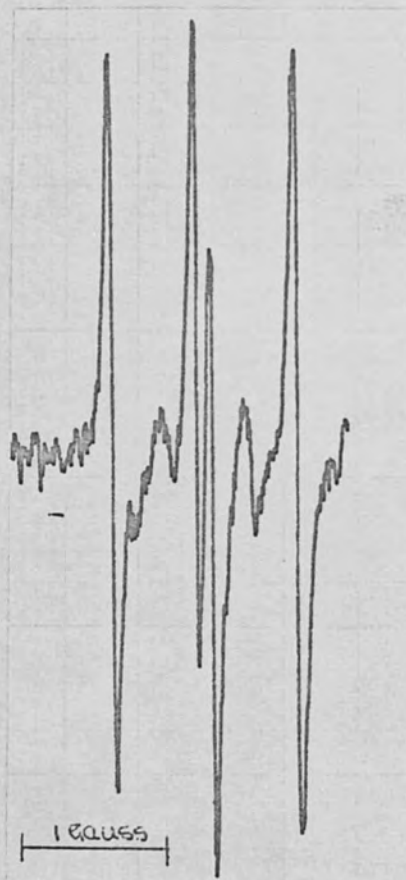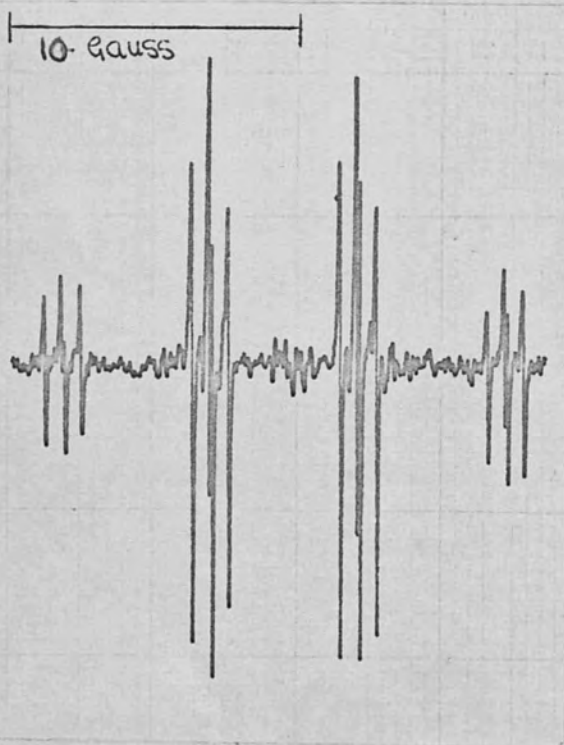Figure 3. Secondary radical B from Methylhydroquinone.

10- Gauss

1 Gauss

Figure 4. Secondary radical A from Methylhydroquinone in 50% aq. EtOH.

In aqueous solutions of hydroquinone containing more
sodium hydroxide the primary radical was less stable, the
solutions eventually showing no signs of any definite
radical species. In solutions containing 10% alkali some
fairly simple spectra were obtained, but no definite conc-
lusions as to their interpretation were possible at this
stage, except to suggest that they were probably due to
radicals formed by polymerisation. The formation and nature
of these radicals is treated in more detail later in this
thesis.

METHYLHYDROQUINONE

The 28-line spectrum obtained from methylhydroquinone
in dilute alkaline solution (50% aqueous ethanol) is shown in
fig. 2. It is clearly due to the methylsemiquinone radical
ion; the coupling constants, 2.61G, 2.41G, 2.12G (Me
quartet) and 1.76G agree closely with those of previous
observations[21,27]. In aqueous solutions of methylhydro-
quinone containing up to about 2% NaOH, the E.S.R. spectrum
obtained was due solely to the primary radical. Increasing
the alkalinity even further produced fairly complex spectra
due to the primary radical and other radical species, and
these spectra changed fairly rapidly with time. However,
in 5% NaOH the spectrum obtained (fig. 3) was clearly due to
a single radical with one less ring proton than the primary
radical. The coupling constants 4.98G, 1.34G (Me quartet)
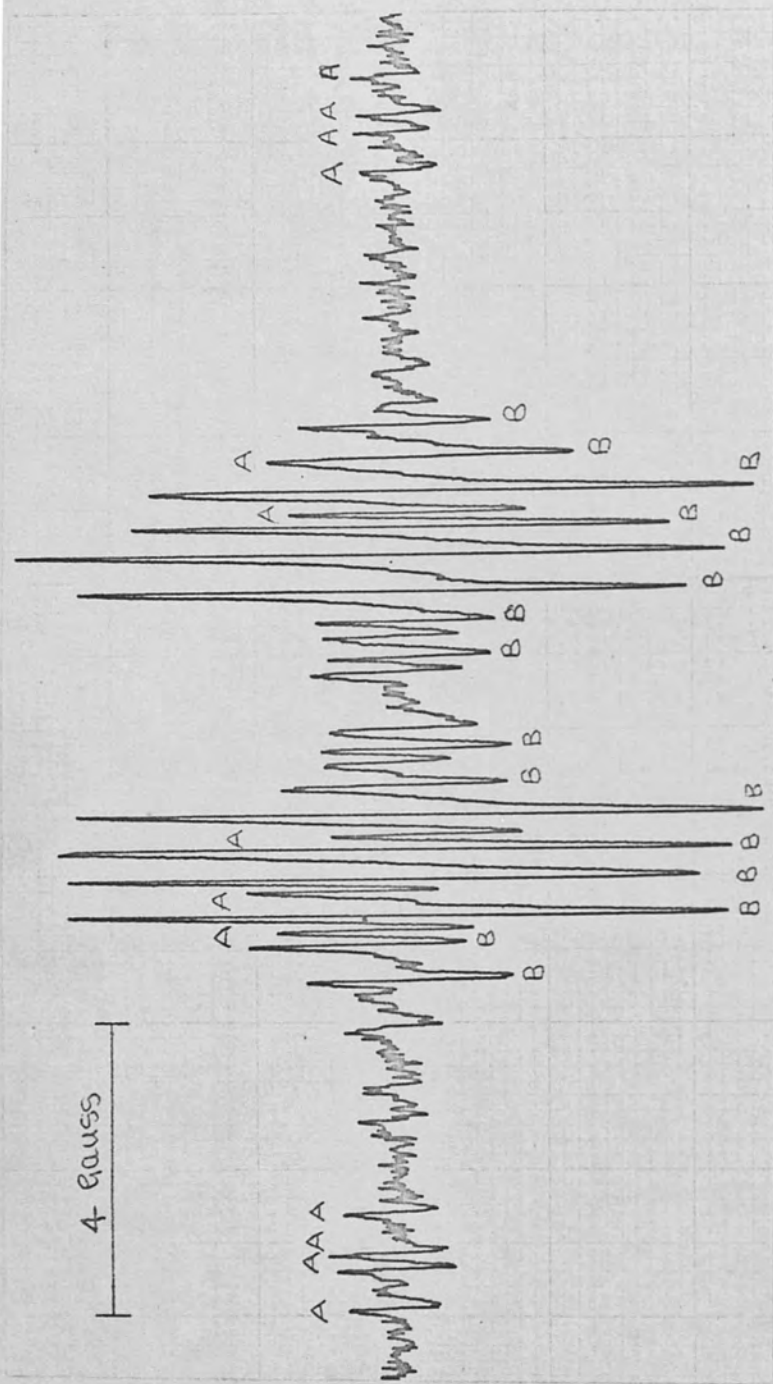
Fig. 5 : Mixture of Secondary radicals from Methylhydroquinone in aq. D.M.F.

and 0.60G are very different from those in methylsemiquinone,
and are consistent with the semiquinone I[37] of 6-methyl,
1,2,4-trihydroxybenzene.
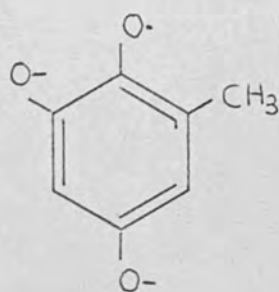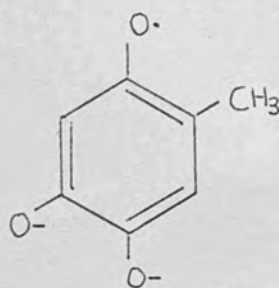
        I   II

In strongly alkaline solutions of methylhydroquinone
containing 50% ethanol a different secondary radical was
observed (fig.4). The coupling constants, 5.12G (Me quartet),
0.69G and 0.58G are those of the semiquinone of 5-methyl,
1,2,4-trihydroxybenzene previously observed in other
reactions[36,37]. In aqueous dimethylformamide a mixture of
radicals I and II was observed (fig.5) illustrating the
influence of the solvent on the formation and stabilities
of the two secondary radicals.

These preliminary experiments led on to a more general
study of the radicals obtained in solutions of hydroquinone
and simply substituted hydroquinones. The first group
studied contained mainly alkyl substituents and these are
described in part II of this thesis. Quinones have been
included in the study since they form a separate starting

point in the autoxidation process, and in certain cases gave
spectra which were not obtainable from the corresponding
hydroquinone.

PART II

5. RADICALS FORMED IN THE AUTOXIDATION OF ALKYL-
SUBSTITUTED HYDROQUINONES AND QUINONES.

The second part of this thesis deals mainly with
hydroquinones and quinones containing one or more alkyl
substituents. The initial experiments with hydroquinone
and methylhydroquinone have been discussed previously in
Part I, and the technique of observing the free radical
intermediates formed under varying conditions of autoxidation
has been applied to further members of the series. Primary,
secondary and, in some cases, tertiary radicals have been
identified by E.S.R. Spectroscopy and these intermediates
appear to correspond to successive stages of the autoxidation
process.

Primary radicals

These radicals are the initial oxidation products of
hydroquinones and are observed in mildly alkaline solutions.
They may be obtained by flow methods or in a static system,
the latter generally producing the most well-resolved
spectra. It was found that the best way of obtaining good
spectra of the primary radicals was as follows:

To a ca. 0.01M solution of the hydroquinone in 50%
aqueous ethanol, a few drops of 1% NaOH were added. The
resulting solution was transferred to an aqueous cell and
the spectrum recorded immediately.

Under these conditions a steady concentration of the
primary radical was normally maintained for a considerable
time, often several hours, the solution being stabilised by
the presence of alcohol. Primary radicals were also observed
in mildly alkaline solutions of the corresponding quinones[9],
a rather curious result, since the formation of semiquinones
in this case involves a reduction of the quinone. The spectra
were not so stable, however, and the primary radical was
often contaminated with other radical species; generally
the method was not satisfactory for obtaining good spectra.

Secondary radicals

In general secondary radicals were observed during a more vigourous oxidation of the hydroquinone or quinone than was necessary to produce primary radicals. In Part I it was established that during autoxidation of methylhydroquinone in strong alkali, radicals were formed which had an additional oxygen bonded to the aromatic ring i.e. derived from the 1,2,4-trihydroxybenzene system. The term 'secondary radical' is reserved here for these derivatives and generally their observation was favoured by high alkalinity of the solution.

Characterisation of the secondary radicals

It was felt that the E.S.R. spectra alone did not enable it to be deduced with certainty the exact nature of all the secondary radicals. A definite characterisation is only possible by producing the secondary radicals in a different, unambiguous way and obtaining identical E.S.R. spectra.

The most obvious method was to syntheise the 1,2,4-trihydroxybenzene derivatives, which on autoxidation give semiquinones[37], and these should correspond to the secondary

radicals obtained from hydroquinones. However, since the composition of the solvent and the degree of alkalinity have an effect on the coupling constants of these types of radicals[31,32], it was important that the conditions used be similar to those in the particular hydroquinone autoxidation. This was found to be not always possible since the tri-hydroxybenzenes often gave complex mixtures of radicals under comparable conditions.

Good spectra were obtained, however, from the tri-acetoxy derivatives under any degree of alkalinity up to 30% NaOH. The triacetoxy compound II was prepared by a Thiele acetylation[43] of the corresponding quinone I. In alkaline

I   II   III   IV
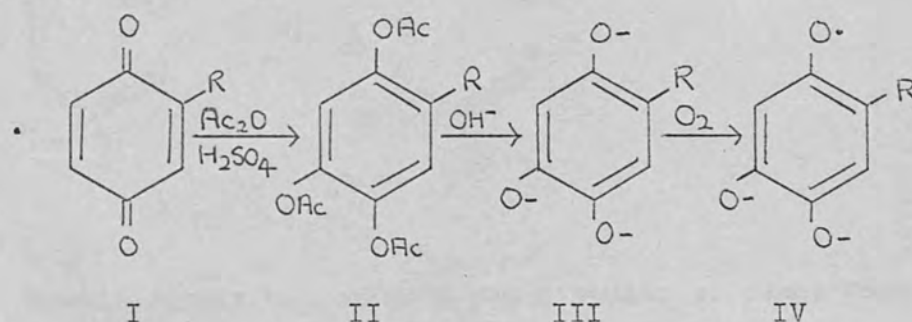
solution the triacetoxy compound is hydrolysed to give the anion III which on autoxidation produces the semiquinone IV of the trihydroxybenzene derivative. It appears that the relatively slow hydrolysis of II inhibits the formation of other radicals and only radical IV is observed even in strong alkali.

A limitation of this method is that the Thiele acetyl-
ation of mono-substituted alkylquinones leads to only one
of the possible isomers[43], acetylation occuring para to the
alkyl group. Where two isomeric secondary radicals were
obtained in the autoxidation of the hydroquinone, only one
could be definitely characterised in this way.

A second route to these radicals has already been
refered to in Part I (see page 15), the autoxidation of
catechols[36]. This reaction was carried out for a number
of substituted catechols to provide further support for the
characterisation.
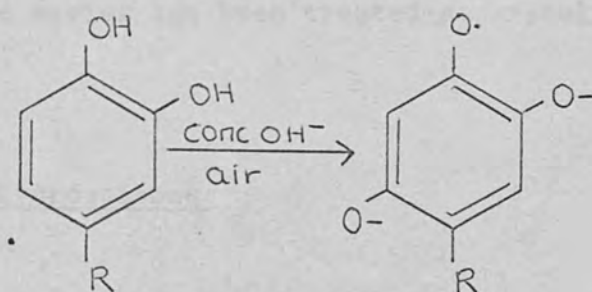
Having firmly established for a number of cases that
the secondary radicals are the semiquinones of 1,2,4-tri-
hydroxybenzene derivatives, it seems reasonable to identify
further members of the series on the basis of their E.S.R.
spectra alone. For alkyl-substituted semiquinones, the
splittings are not expected to vary considerably by changing
the alkyl group, and so it is viable to identify a secondary
radical by comparison of its E.S.R. spectra with that of a

similar secondary radical whose structure has been estab-
lished in some other manner.

The conditions required to obtain good spectra of the
secondary radicals were found to be very dependent on the
amount of substitution on the quinone ring and on the size
of the substituents. In some cases, where structurally
possible, different isomeric radicals were obtained depend-
ing on the solvent employed. Since the observation of each
secondary radical was favoured by certain conditions depend-
ing on the particular hydroquinone or quinone, each member
of the series has been treated separately here.

Hydroquinone

It proved difficult at first to observe the secondary
radical II from unsubstituted hydroquinone or quinone. The
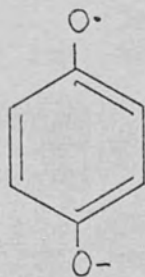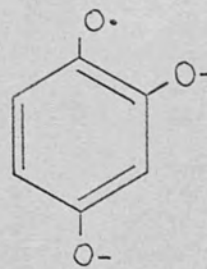
I   II

Figure 6a. Secondary radical from Hydroquinone (lines A).

Figure 6b. Radical obtained from 1,2,4-Triacetoxybenzene in 5% NaOH.

primary radical I (fig 1, page 18) was observed in alkaline

solutions containing up to ca. 2% NaOH, but disappeared

fairly rapidly leaving a solution containing no definite

radical species. On increasing the alkalinity, complex

mixtures of radicals were generally observed none of which

corresponded to II[36,37]. These 'tertiary radicals' are
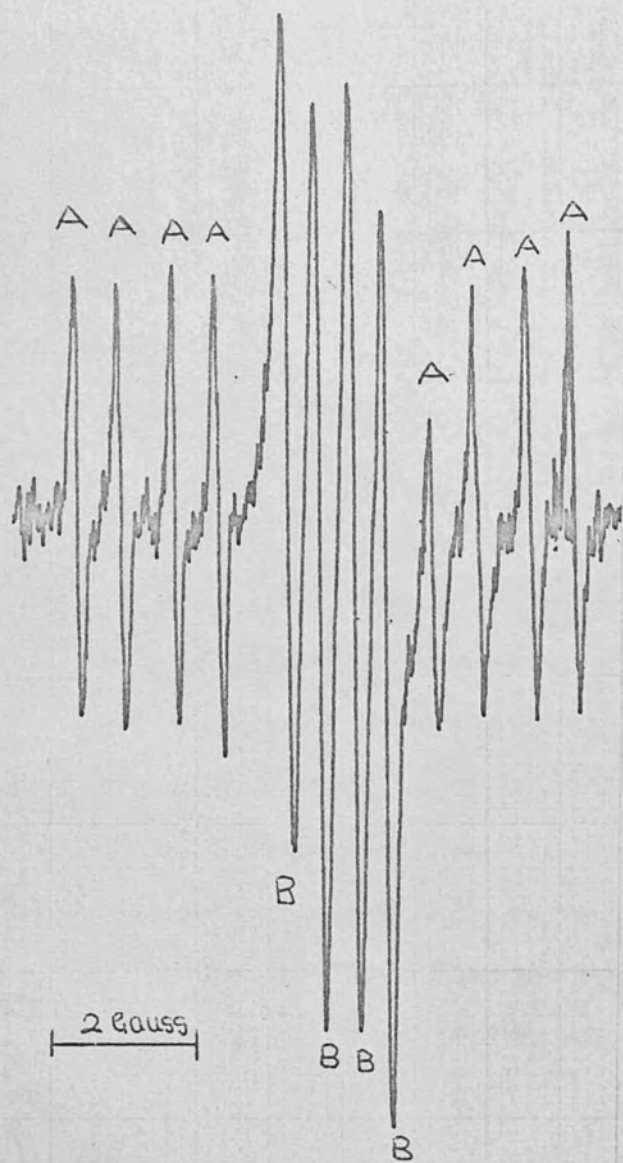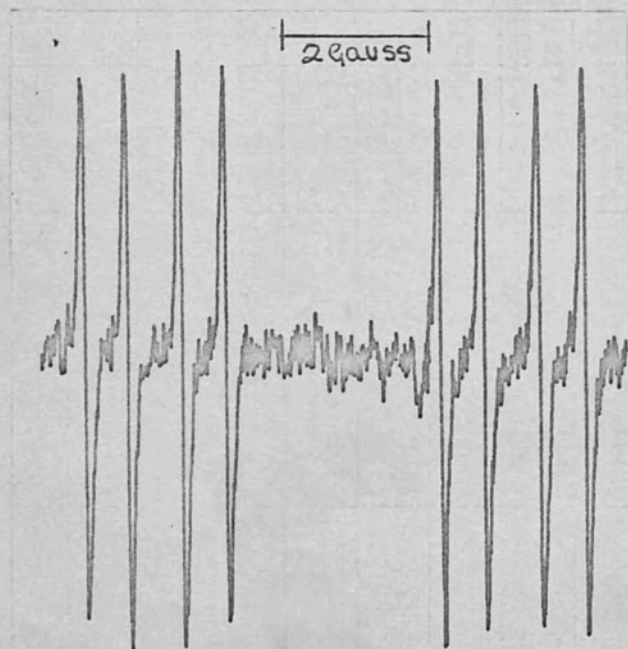
discussed in a separate section later in Part II.

The secondary radical was eventually observed (fig 6a),

along with a tertiary radical, in a solution prepared by

adding hydroquinone or quinone (ca. 0.01M in water) dropwise

to 5% NaOH and recording the spectrum immediately. The

coupling constants were 4.98G, 1.34G and 0.60G (compare

4.80G, 1.35G and 0.62G[37]). Under the cond itions of drop-

wise addition the tendancy for coupling reactions to occur

was apparently reduced and a good spectrum of the hydroxyl-

ated product was obtained.

Fig. 6b shows the E.S.R. spectrum obtained from 1,2,4-

triacetoxybenzene in 5% NaOH, clearly identical to that of

fig.6a (lines A).

The same radical has also been observed in a solution

made by adding catechol (0.01M in water) dropwise to 5% NaOH

(fig. 6c). Previous work[41] on the autoxidation of catechol

has shown that the primary radical I and the dimer II are

formed. As with hydroquinone, the dropwise addition employed

here apparently favours the formation of III by hydroxlation
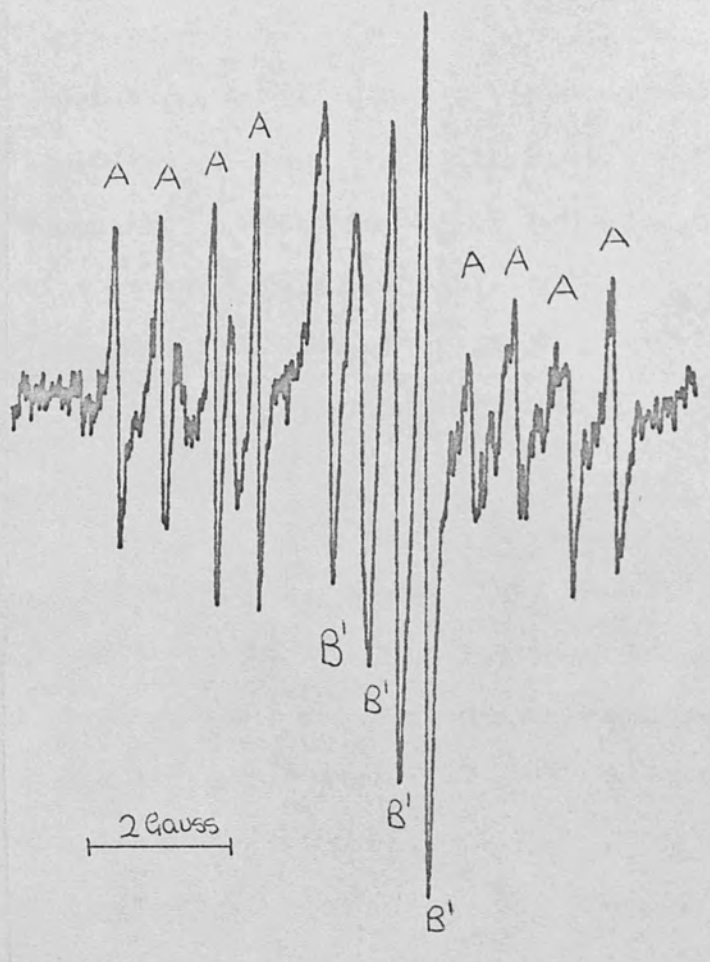
Fig. 6c.. Spectrum from Catechol in 5% NaOH.

Lines A: Secondary radical
Lines B' :   Tertiary radical

I   II   III

rather than the dimer. The four additional lines in fig. 6c. appear to be the same as those in fig. 6a. from hydroquinone and are probably due to intermediates in coupling reactions.

Methylhydroquinone

The primary and secondary radicals from methylhydro- quinone (figs. 2-5) have been already discussed on page 19 . There are three possible isomeric secondary radicals from such a mono-substituted hydroquinone, A,B and C; in fact only A and B have been observed here. All three isomeric radicals have been obtained[37] by preparation of the tri-

hydroxybenzenes and subsequent oxidation, but it is clear
that hydroxylation at the 3-position of the ring is much
less likely to occur, in the system studied here, for steric
reasons. Attack at the 5 and 6 positions is clearly free

from steric interaction with the
methyl group and we observe only
the radicals formed by substitution
in these positions. No doubt some
attack does occur at the 3-position,
but the observation of radical C
is made impossible by the presence
of A and B in much larger concen-
trations.
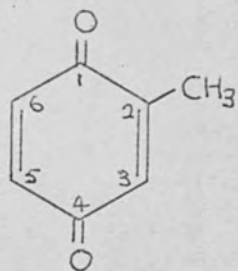
Where two isomeric secondary radicals are observed, the
convention adopted here is that the radicals formed by
attack at the 5- and 6-positions be called radicals A and B
respectively.

4 gauss
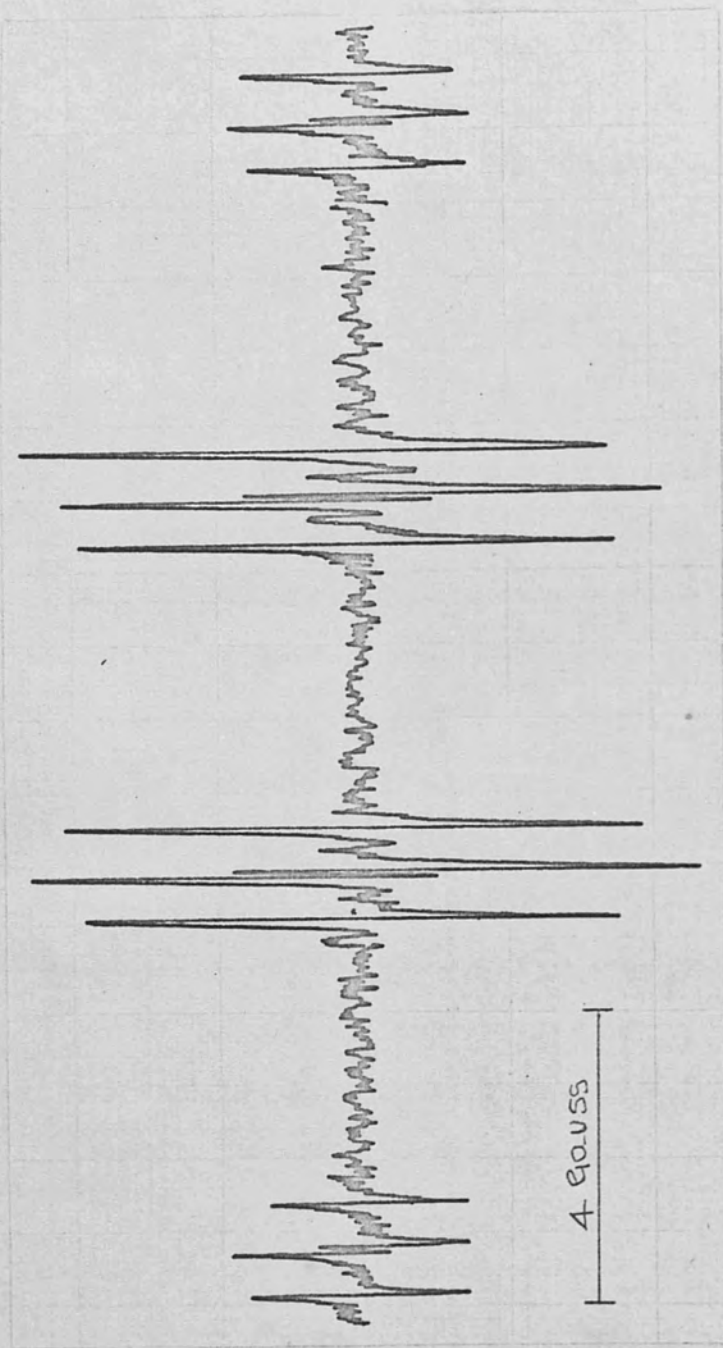
Fig. 7a: Radical from 5-Methyl;1,2,4-triacetoxybenzene in 5% NaOH.

4 gauss
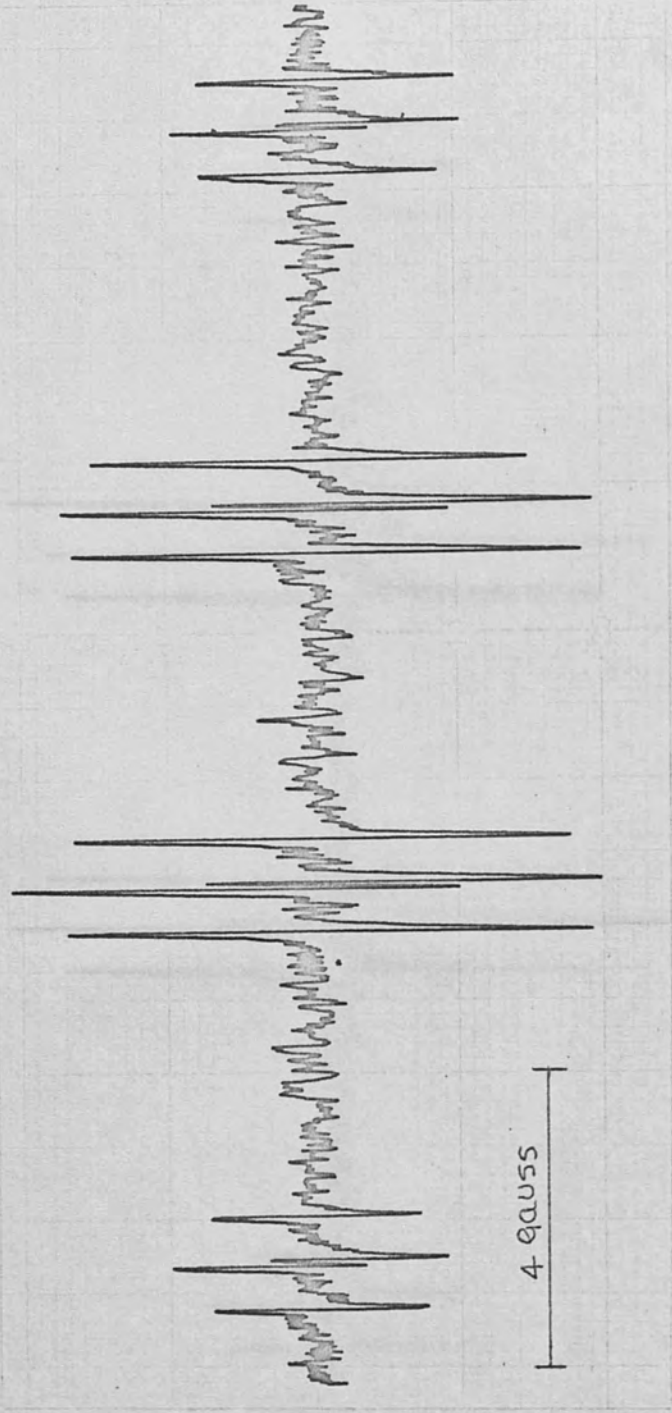
Fig. 7b : Radical from 4-Methylcatechol in 5% NaOH.

Fig. 7a shows the E.S.R. spectrum of the radical
obtained from 5-methyl,1,2,4-triacetoxybenzene in 5% sodium
hydroxide. The coupling constants are very nearly identical
to those of the secondary radical A from methylhydroquinone
and clearly the two radicals are the same.

Fig. 7b shows the same radical produced by autoxidation
of 4-methylcatechol in 5% NaOH.

Ethylhydroquinone

Ethylhydroquinone behaved in a similar way to the
methyl compound, a primary and two isomeric secondary
radicals being observed under varying conditions. The
E.S.R. spectrum of the primary radical I is shown in Fig. 8.

I   A   B
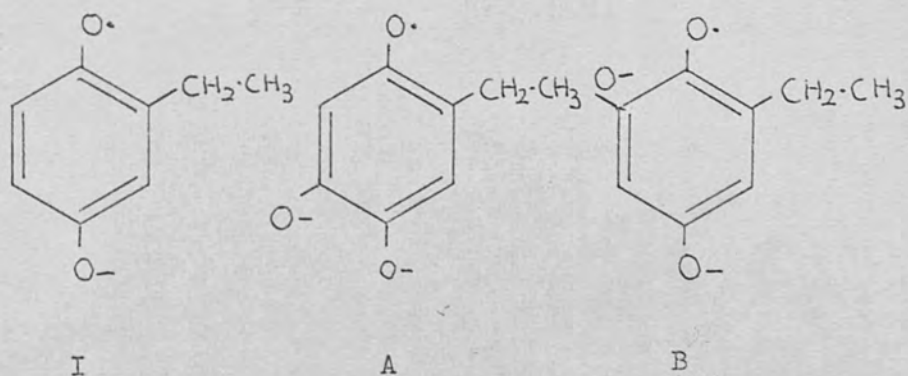
The secondary radicals were observed separately in different

Figure 8. Primary radical from Ethylhydroquinone.
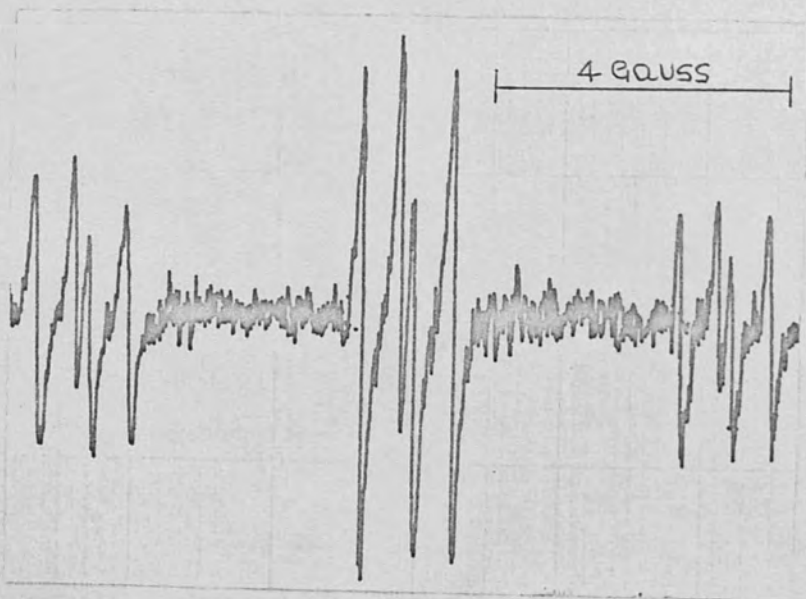
Figure 9. Secondary radical A from Ethylhydroquinone.
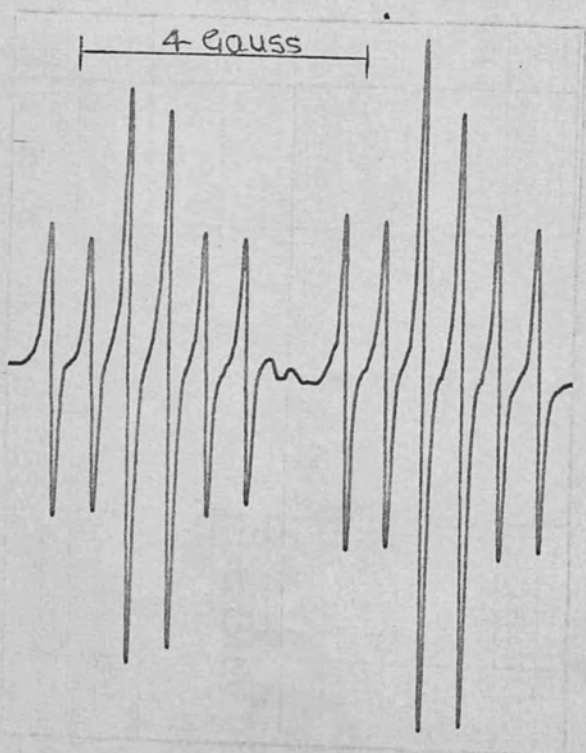
Figure 10. Secondary radical B from Ethylhydroquinone.

solvents containing 5-10% NaOH, radical A in 50% aqueous
ethanol (fig. 9) and radical B in totally aqueous solution
(fig. 10). This solvent effect was identical to that
observed for methylhydroquinone.

As might be expected no great change in the coupling
constants of the three radicals occurs in going from methyl
to ethyl and the spectra are similar in appearance except
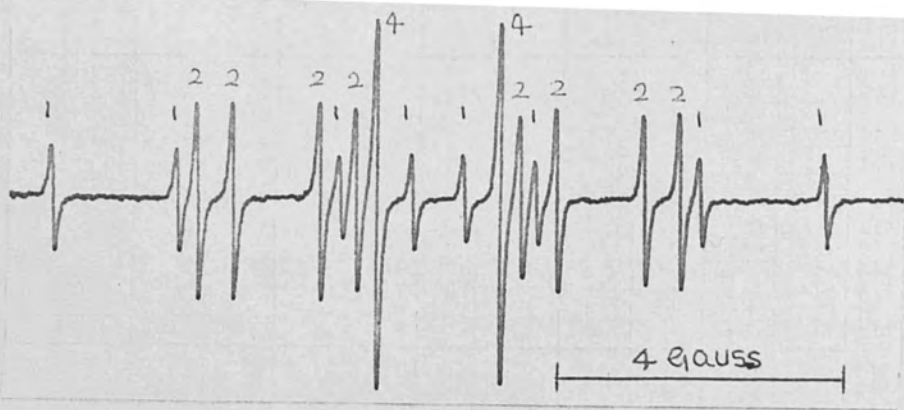for the methyl quartet splitting being replaced by a triplet
due to coupling with the α-hydrogens of the ethyl group.
No splitting was observed for the β-protons, although the
lines were noticably broader than in the methyl-substituted
radicals. This was particularly evident in secondary
radical A where the splittings for the ethyl group are the
largest.

Experiments were carried out with ethylquinone as well
as the hydroquinone, the spectra normally showing complex
mixtures of radicals present. The primary radical could be
identified in the mixtures especially at low concentrations
of alkali in ethanolic solution, and at higher concentrat-
ions (ca. 5-10% NaOH) the two secondary radicals were
clearly present. The quinone, however, proved to be a poor
starting point for obtaining pure spectra.
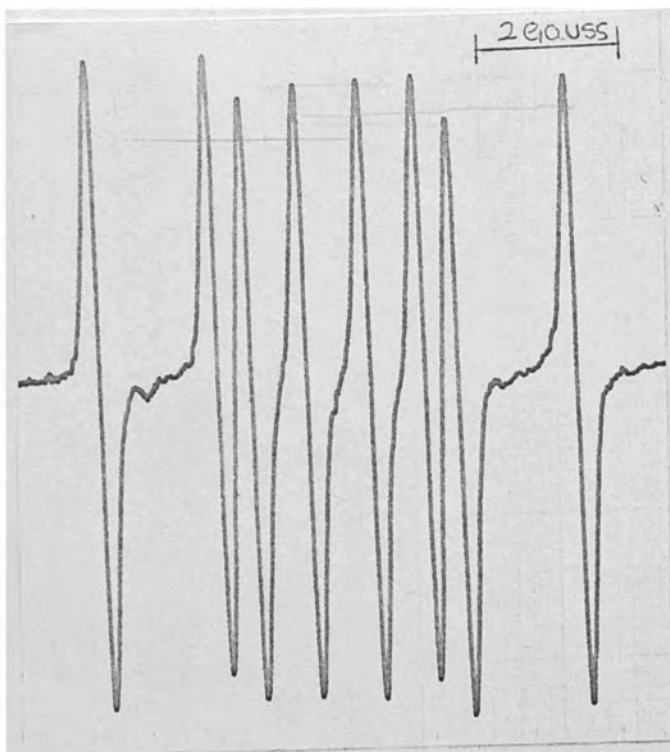
Figure 11. Primary radical from tert.Butylhydroquinone.
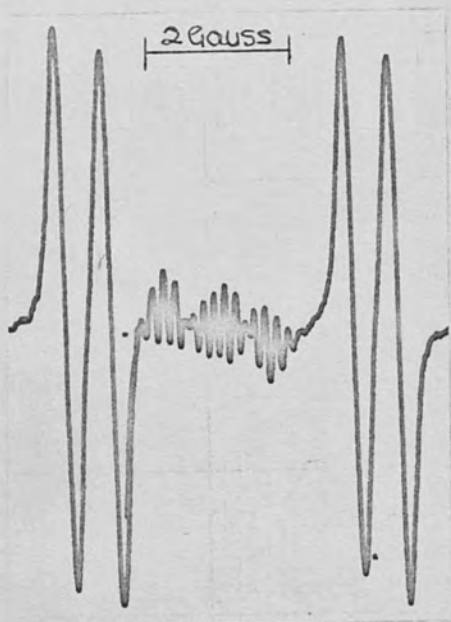
Figure 12a. Mixture of Secondary radicals from tert. Butylhydroquinone.
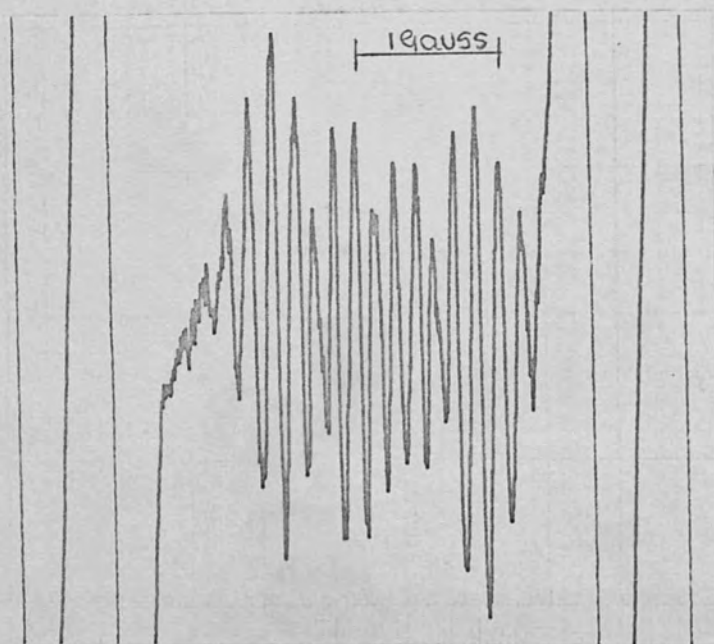
Figure 12b. Same spectrum as fig. 12a. at higher receiver gain showing Secondary A.

Tert. butylhydroquinone

The primary radical from the tert. butyl compound (fig. 11) was obtained in the normal way. No splitting was observed from the tert. butyl group, but the 8 lines obtained were very broad compared to those in, for example, methyl-semiquinone. Tert. butyl splitting has been observed in this radical by other workers[24] (ca. 0.06G), in 50% aqueous methanol. The primary radical was much more stable than the methyl- and ethylsemiquinones and could be observed pure even in 5% NaOH.

As the alkalinity was increased, four additional broad lines began to appear in the primary spectrum. In 20% NaOH, no primary radical could be detected and the spectrum corresponded to a mixture of two secondary radicals (fig. 12a), one of which clearly had splitting from the tert. butyl group. Fig. 12b is the same spectrum at higher receiver gain, showing the slight overlap of the spectra of the two individual radicals.

The four broad lines are attributed to radical B and the remainder to the isomeric radical A. Fig. 13a shows the radical obtained from 5-tert. butyl-1,2,4-triacetoxybenzene in 20% NaOH, the spectrum being identical to that of second-ary radical A in fig. 12b. The same spectrum was obtained
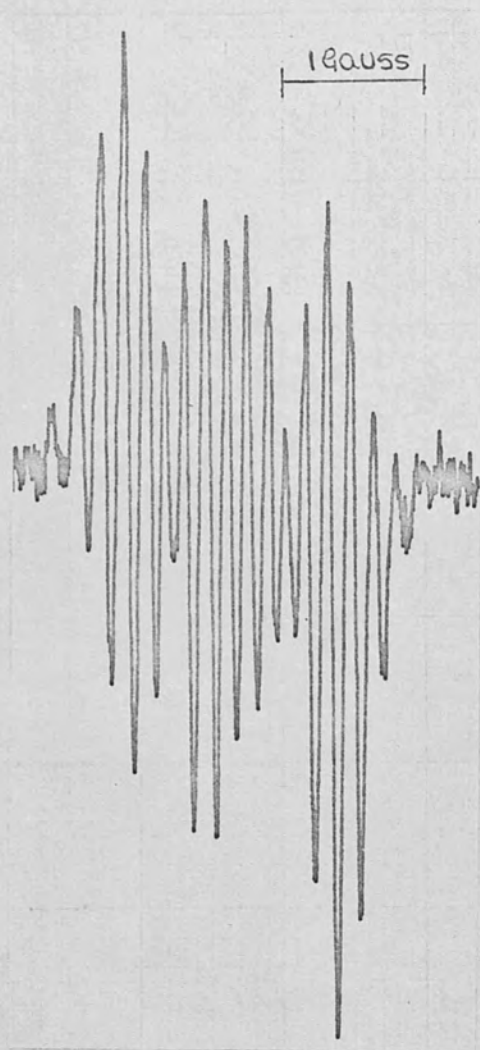
Figure 13a. Radical obtained from 5-tert.Butyl-1,2,4-triacetoxybenzene in 20% NaOH.
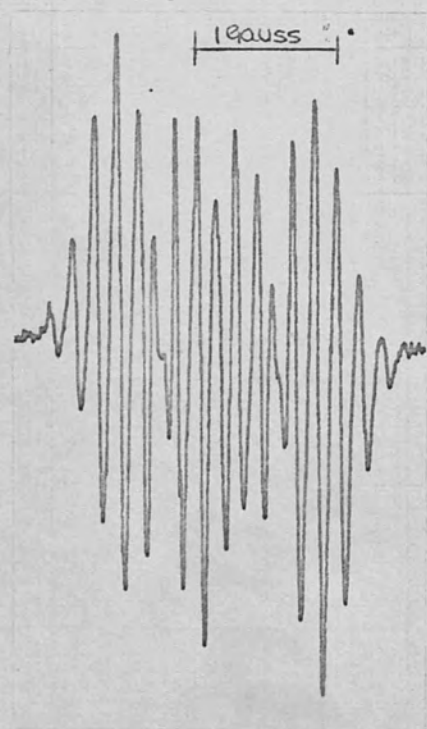
Figure 13b. Secondary radical from 4-Tert.Butylcatechol in 20% NaOH.
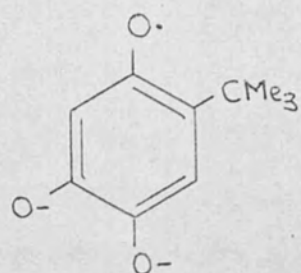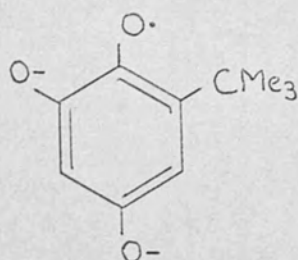
A   B

from 4-tert.butylcatechol in 20% NaOH (fig. 13b). On analysis this spectrum shows:

<div align="center">

a doublet splitting : o.86G

a doublet splitting : 0.54G

a septet splitting : 0.16G

</div>

Septet splitting from tert. butyl groups has been observed previously[24] in cases where the group is adjacent to an oxygen on an aromatic ring, as in secondary radical
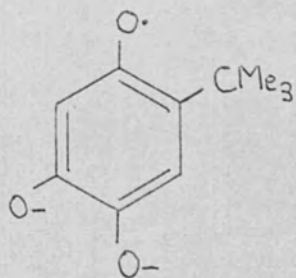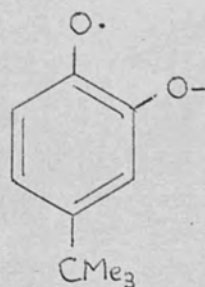
I   II

Figure 14: Primary radical from 2,3-Dimethylhydroquinone.
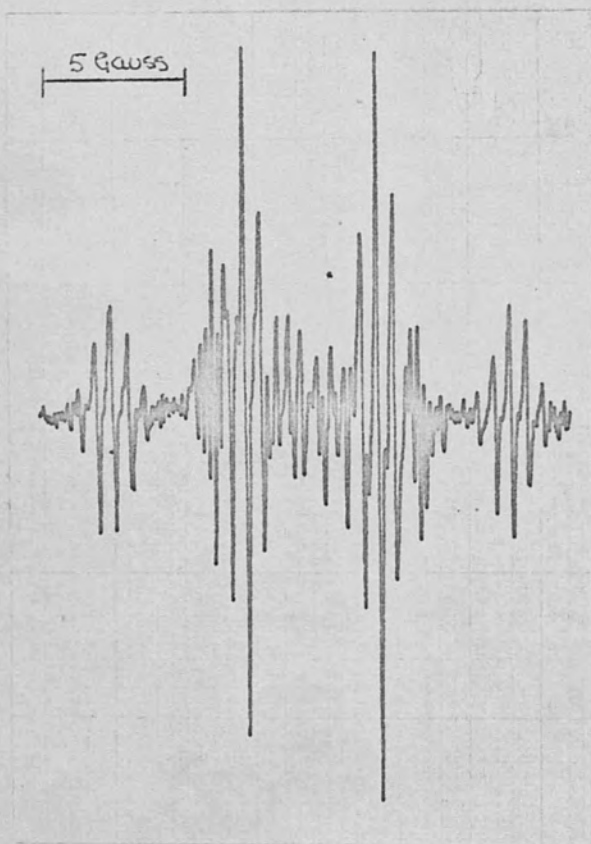
Figure 15 : Secondary radical from 2,3-Dimethylhydroquinone.

A(I). Splitting from the expected nine protons was obtained[24]
in radicals such as II, where the group is flanked by
two aromatic hydrogens. In radical I the rotation of the
group about the bond to the aromatic ring is restricted by
the adjacent oxygen atom, and this may be sufficient to
force an inequivalence of the three methyl groups, only
two of them giving rise to a detectable hyperfine splitting.

2,3-Dimethylhydroquinone

The spectrum of the primary radical I is shown in fig.14,
splitting from the two aromatic protons (2.62G) and from
the six methyl protons (1.74G).

The secondary radical was observed in solutions of the
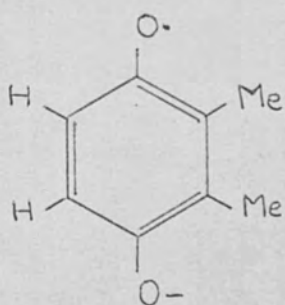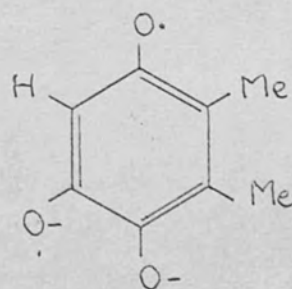
I   II
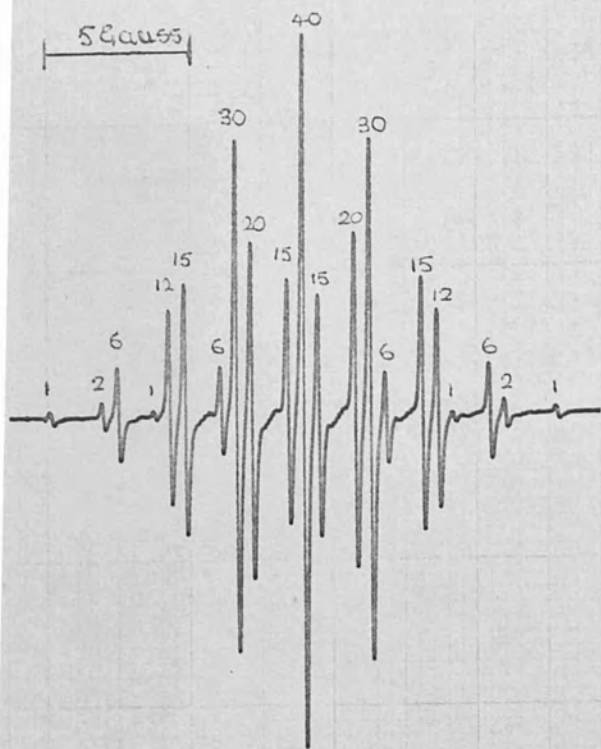
Figure 16. Primary radical from 2,5-Dimethylhydroquinone.
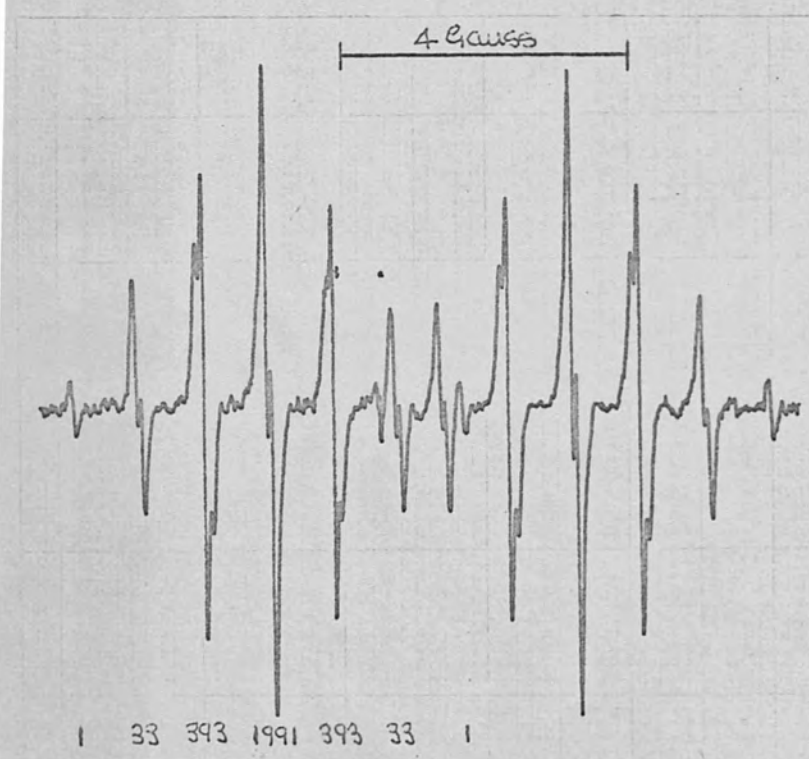
Figure 17. Secondary radical from 2,5-DimethylQuinone showing splitting pattern from 2 methyl groups with slightly different hyperfine splittings.

hydroquinone containing ca. 10% NaOH (fig. 15). The large quartet splitting (4.70G) is evident from the spectrum, with further splittings of 0.60G (Me quartet) and 0.50G. The secondary radical was always accompanied by another radical (doublet splitting: 7.25G; septet splitting: 0.21G). The septet is possibly due to splitting from the two methyl groups, but the doublet splitting of 7.25G is larger than observed in any radicals of the semiquinone type. The identity of this radical has not been established.

2,5-Dimethylhydroquinone

Good spectra of the primary radical (fig. 16) were obtained from either the hydroquinone or quinone under the normal conditions for observing primary radicals. It was found impossible to obtain a spectrum of any definite secondary radical from the hydroquinone, complex mixtures always being obtained in strong alkali.

Starting from the quinone however a good spectrum of the secondary radical (fig. 17) was obtained using 50% dimethylformamide as solvent and 5% NaOH. A doublet split-

ting (4.20G) in the spectrum shows definitely that the large splitting observed in all these secondary radicals is from the 5-position of the 1,2,4-tri-
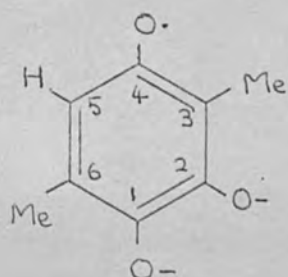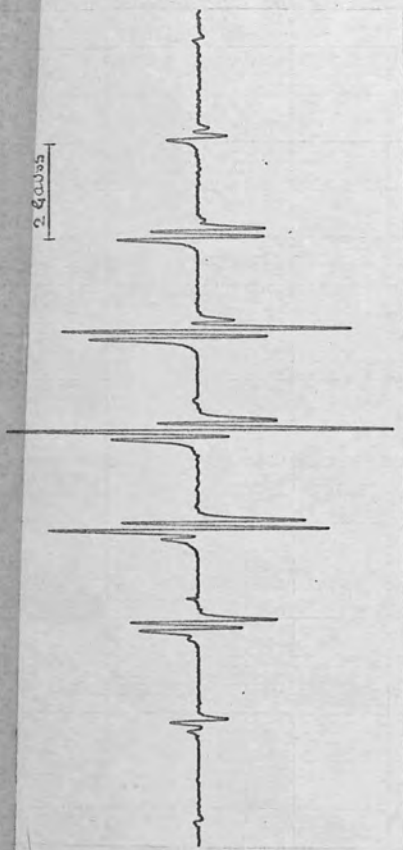
Figure 18 : Primary radical from 2,6-Dimethylhydroquinone.

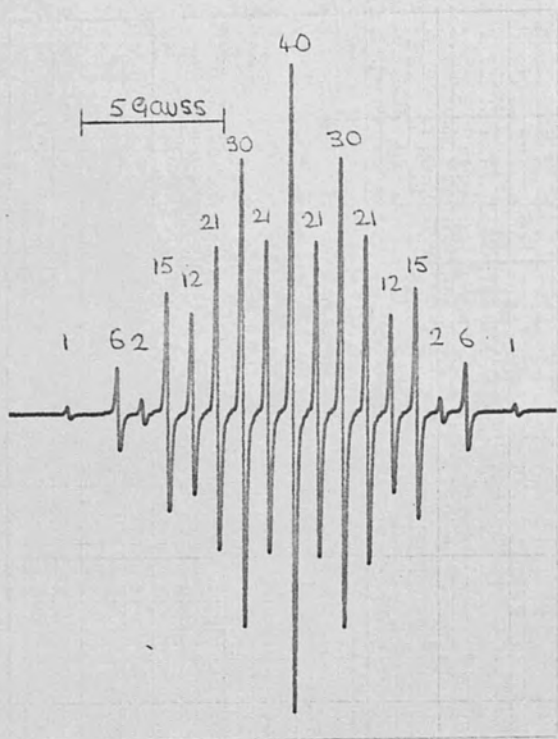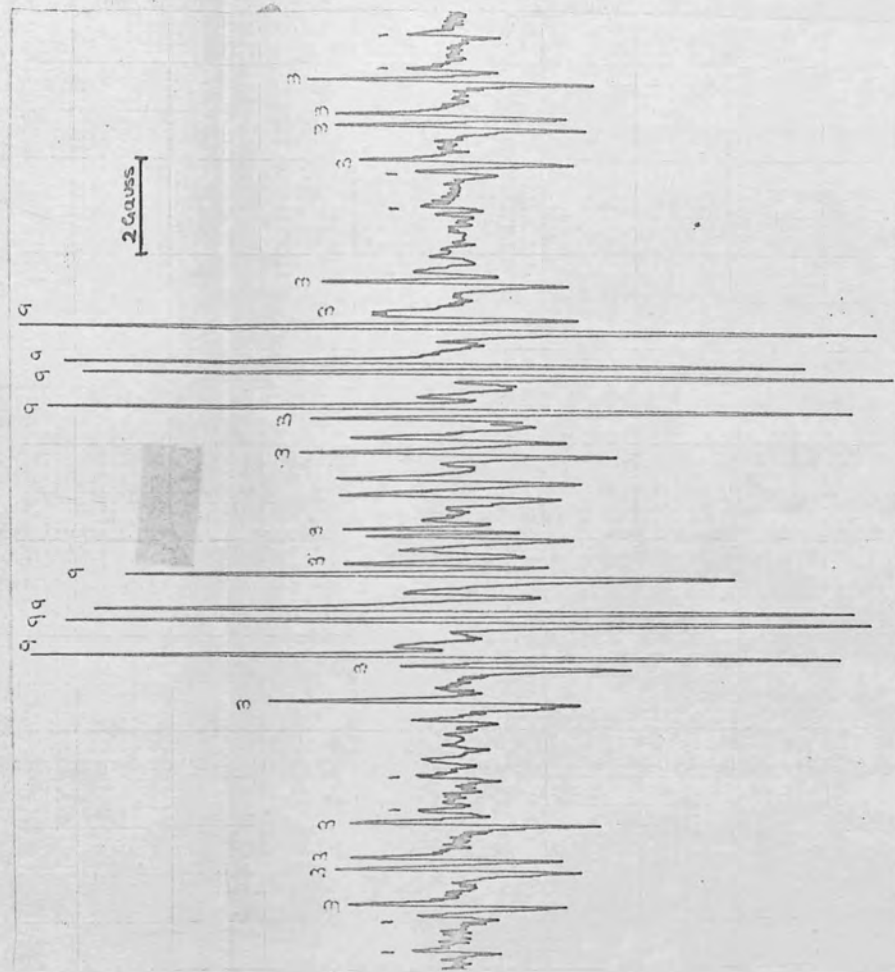Figure 19 : Secondary radical from 2,6-Dimethylhydroquinone.

hydroxybenzene system. Further splittings from the methyl groups (0.98G, 0.88G) were found.

2,6-Dimethylhydroquinone

The 2,6-dimethyl compound was similar in reactivity to the 2,5-dimethyl. The primary radical spectrum is shown in fig. 18.

Again the hydroquinone gave rise to very complex spectra in strong alkali and only the quinone was able to give a good spectrum of the secondary radical (fig. 19). The conditions were as for the 2,5-dimethyl compound, 5% NaOH and 50% aqueous D.M.F. as solvent. The large quartet splitting (5.20G) is assigned to the methyl group para to the oxygen introduced into the aromatic ring (i.e. the 5-position), and the remaining splittings are 0.97G (Me quartet) and 0.72G (compare 5.02G (Me), 0.95G (Me) and 0.70G)[37].
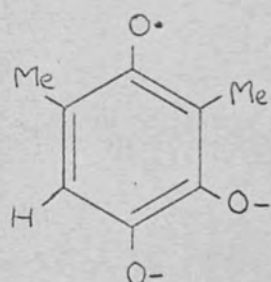
Thymohydroquinone

The 2-methyl,5-isopropyl compound gave a primary
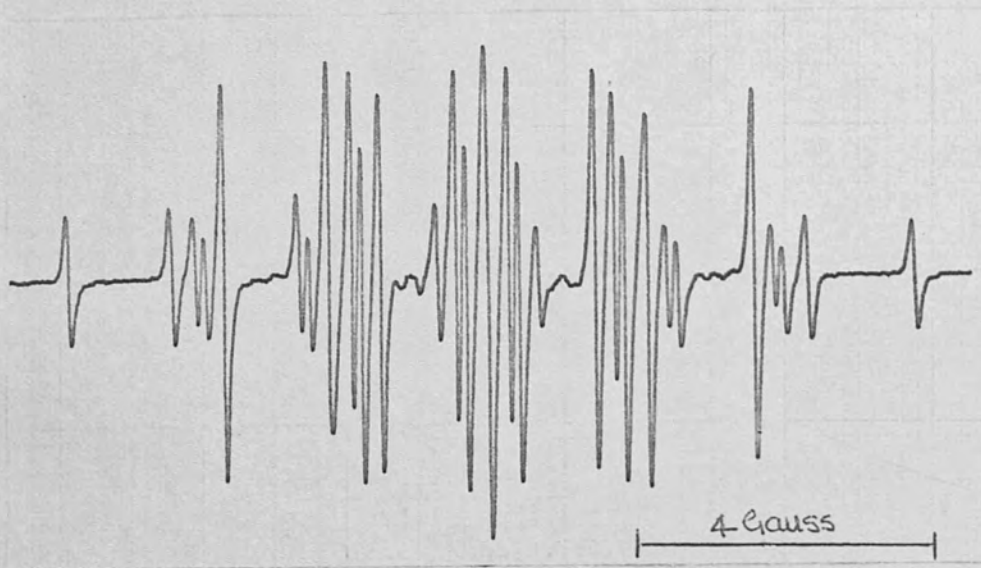
Figure 20. Primary radical from Thymohydroquinone.
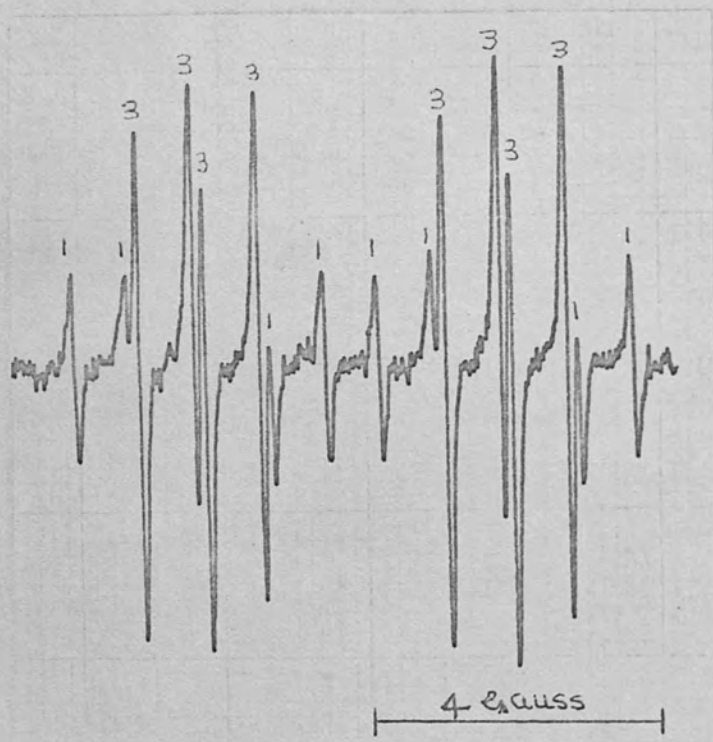
Figure 21. Secondary radical from Thymohydroquinone.

radical (fig. 20) in mild alkali and a good secondary
spectrum (fig. 21) in 15% NaOH. The initial spectrum
showed a mixture of radicals but on exposure to air for
ca. 30 minutes, a pure spectrum of a secondary radical was
obtained.

Two possible secondary radicals can be formed here,
but from steric considerations alone, it is clear that I
is more likely than II. Attack at the position adjacent to

I   II
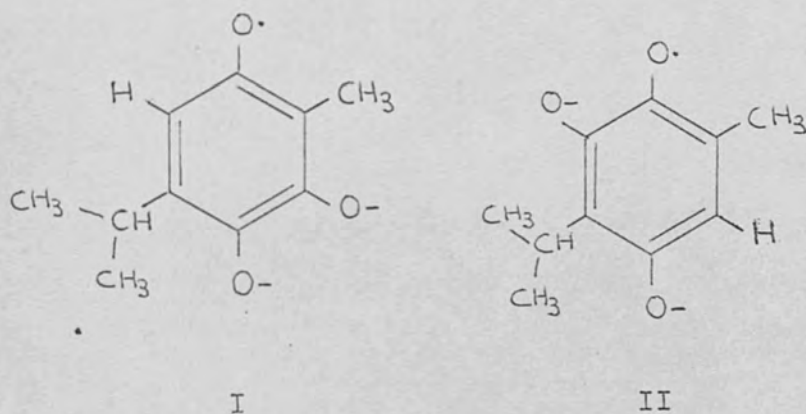
the methyl group is subject to much less steric interference
than attack at the ring position adjacent to the much
larger isopropyl group. The secondary radical is there-
fore assumed to correspond to structure I.

2 Gauss
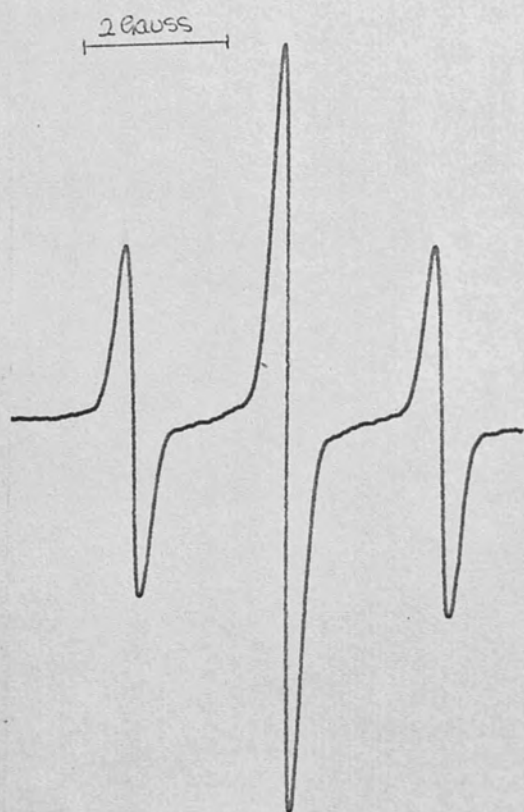
Fig. 22:   Primary radical from

2,5-Ditert.butylhydroquinone.

2,5-Ditert.butylhydroquinone

The E.S.R. spectrum of the primary radical (fig. 22) shows a simple triplet splitting from the two aromatic protons of 2.09G. No splitting was observed from the tert. butyl groups although the lines were very broad.

No secondary spectra could be obtained from the hydroquinone or quinone, even in hot concentrated alkali. The steric bulk of the tert.butyl groups would be expected to make hydroxylation of the ring very difficult and a sufficient concentration of the secondary radical for observation is never obtained. The fact that the primary radical is observed in alkaline solutions of the quinone does suggest that some hydroxylation occurs, but a discussion of this point will be left until later in part II, where the mechanism of the reactions involved is considered.

The effect of added hydrogen peroxide in the reaction mixture

During the autoxidation of hydroquinones in alkali, hydrogen peroxide is one of the products formed[6]. Experiments were carried out to establish whether the hydrogen peroxide played any part in the formation of the hydroxylated

secondary radicals observed. No evidence for this was found.

Varying amounts of hydrogen peroxide were added to solutions of hydroquinones and quinones over a wide range of alkalinities. The radicals observed were the same as those in identical solutions containing no added peroxide. If, indeed, the peroxide was the hydroxylating agent, we would have expected to observe the secondary radicals more easily in solutions to which it had been added. As it was, the observation of the secondary radicals appeared to depend solely on the alkalinity of the solutions.

The primary and secondary radicals from alkylhydroquinones, with their E.S.R. coupling constants, are shown in tables I and II. A discussion of the coupling constants is reserved until later in part II of this thesis.

Table I : Coupling Constants of Primary Radicals
from Alkylhydroquinones and Quinones.

Parent hydroquinone	Coupling Constants (Gauss).			
	a_2	a_3	a_5	a_6
Hydroquinone	$\longleftarrow$	2.37	$\longrightarrow$	
2- Methyl	2.12(Me)	1.76	2.61	2.41
2- Ethyl	2.02(CH_2)	1.74	2.53	2.53
2-tert.Butyl	—	1.65	2.12	2.89
2,3-Dimethyl	1.74(Me)	1.74(Me)	2.62	2.62
2,5-Dimethyl	2.34(Me)	1.80	2.34(Me)	1.80
2,6-Dimethyl	2.09(Me)	1.93	1.93	2.09(Me)
2,5-Ditert.Butyl	—	2.09	—	2.09
2-Methyl,5-isoPr.	2.18(Me)	1.92	1.46(Pr^i)	1.76

Table II : Coupling Constants of Secondary Radicals
from Alkylhydroquinones and Quinones.

Parent hydroquinone		Coupling Constants (Gauss)		
		a_3	a_5	a_6
Hydroquinone		0.60	4.98	1.34
2-Methyl	A	0.58	5.12(Me)	0.69
	B	0.55	4.15	0.95(Me)
2-Ethyl	A	0.54	4.56(CH_2)	0.71
	B	0.56	4.15	1.08(CH_2)
2-tert.Butyl	A	0.54	0.16(Bu^t)	0.86
	B	0.66	4.02	—
2,3-Dimethyl		0.50	4.70(Me)	0.60(Me)
2,5-Dimethyl		0.98(Me)	4.20	0.88(Me)
2,6-Dimethyl		0.97(Me)	5.20(Me)	0.72
2-Methyl,5-isopropyl		0.92(Me)	4.20	0.75(Pr^i)
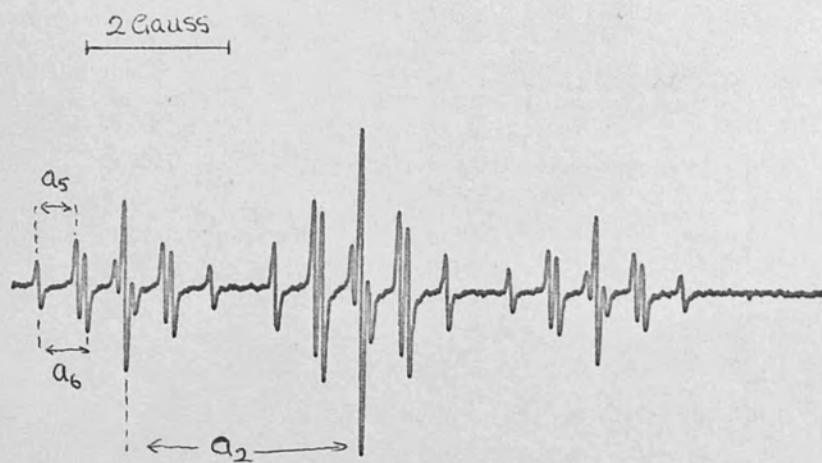
Figure 23: Primary radical from 1,4- Naphthohydroquinone.
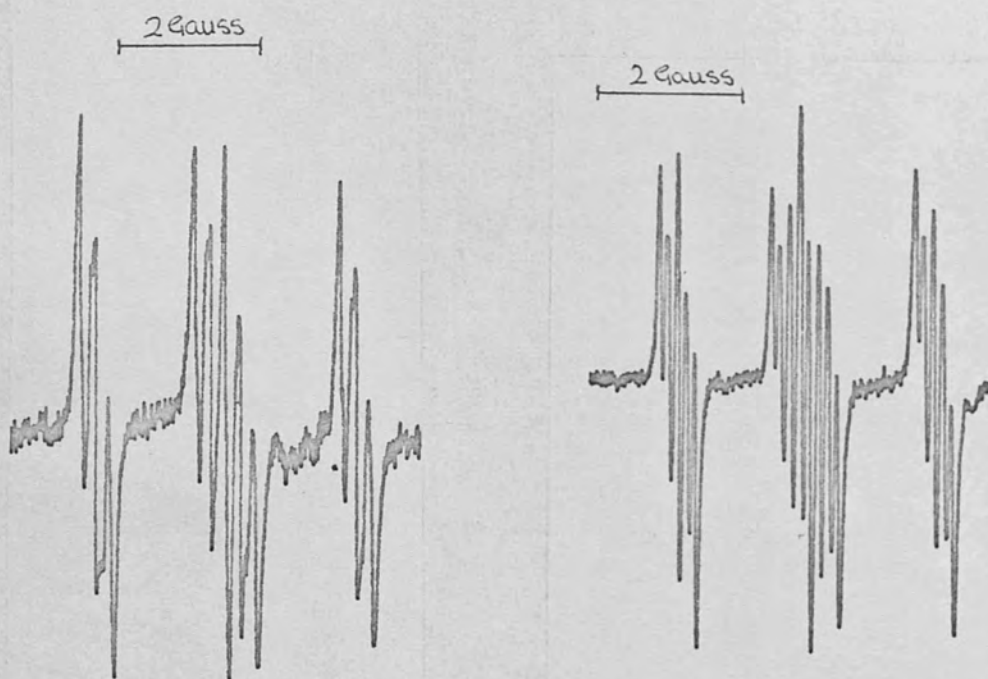
Figure 24: Secondary radical from
1,4- Naphthohydroquinone.

Figure 25: Radical obtained
from 1,2,4- Triacetoxy-
naphthalene in 10% NaOH.

6. RADICALS FORMED IN THE AUTOXIDATION OF HYDROQUINONES CONTAINING OTHER SUBSTITUENTS

1,4-Naphthohydroquinone

This compound is expected to behave in a similar way to a 2,3-dialkylhydroquinone and this was found to be the case. The primary radical was obtained in dilute alkali, using 50% aqueous D.M.F. as solvent (fig. 23) and a secondary radical (fig. 24) was observed in 10% NaOH. The same spectrum was obtained (fig. 25) from 1,2,4-triacetoxynaphthalene, showing that the secondary radical was the expected hydroxylation product.

The coupling constants of the primary radical have been previously assigned[44] in the light of M.O. calculations and this assignment is adopted here. The assignments for the secondary radical are rather tentative.

3 Gauss
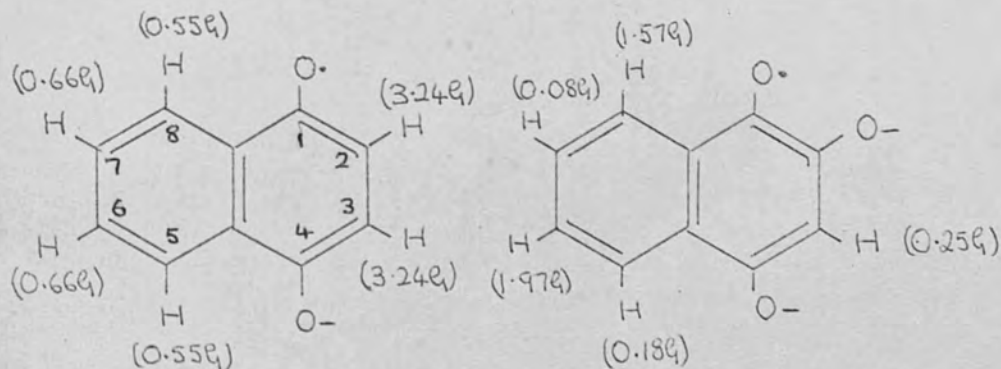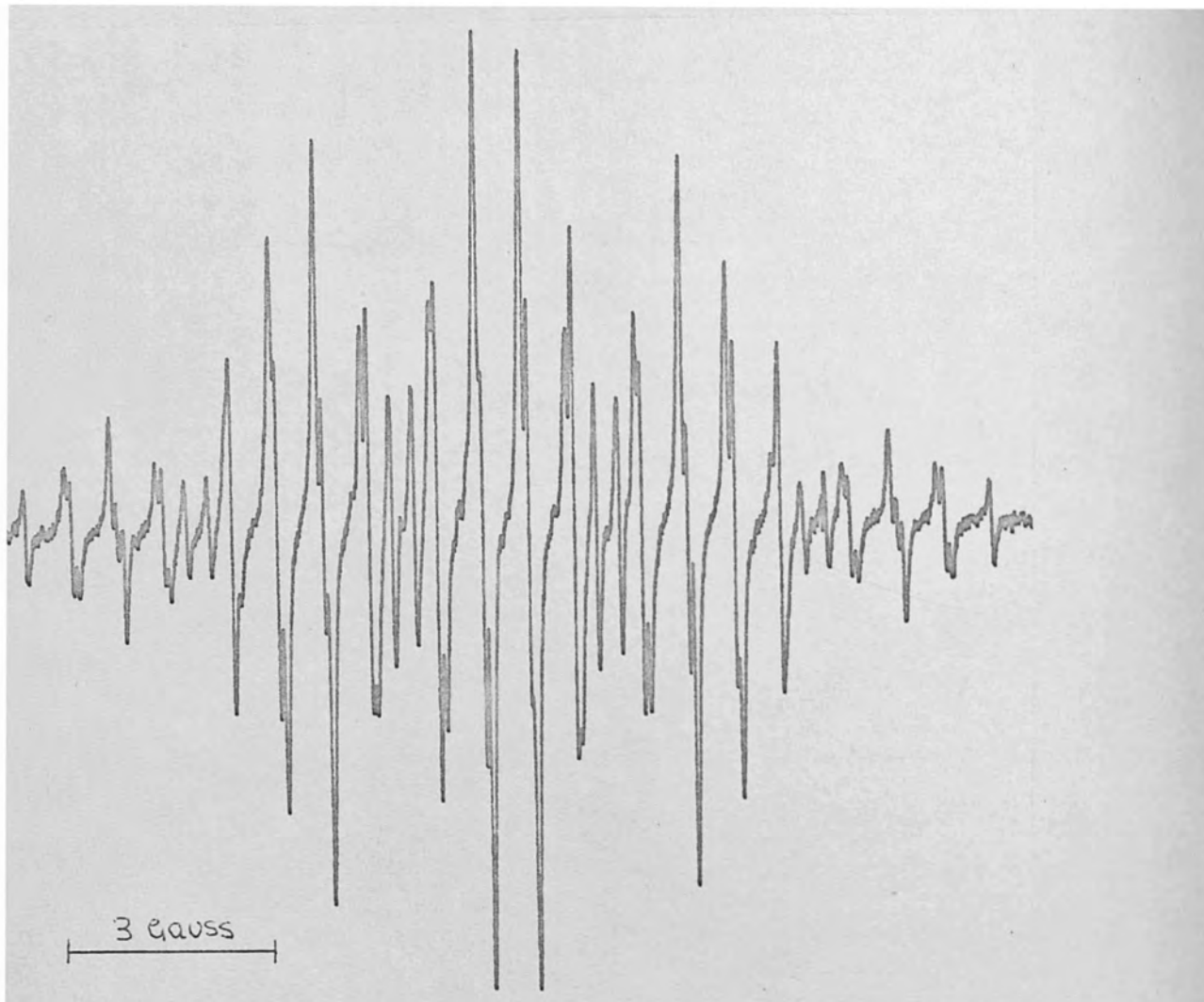
Figure 26 : Primary radical from 2-Methylnaphthohydroquinone.

2 Gauss
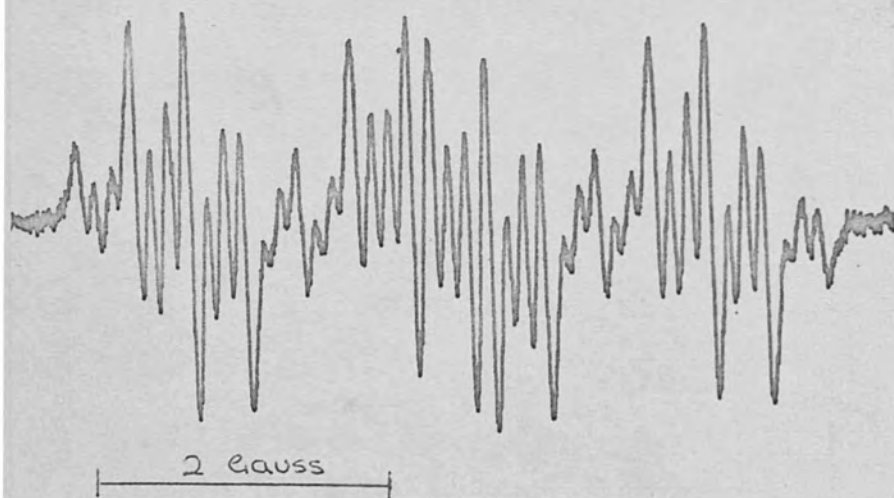
Figure 27 : Secondary radical from 2-Methylnaphthohydroquinone.

2-Methylnaphthohydroquinone

The primary radical from the quinol of vitamin K_3 is shown in fig. 26. The coupling constants given below are in line with previous assignments[44].

The secondary radical (fig. 27) was more difficult to obtain than that from the unsubstituted compound due to the steric bulk of the methyl group. It was observed however in a solution of the hydroquinone containing 20% NaOH. The spectrum is almost identical to that previously obtained from a sample of 2-hydroxy,3-methyl,1,4-naphthoquinone[45].

Primary radical   Secondary radical
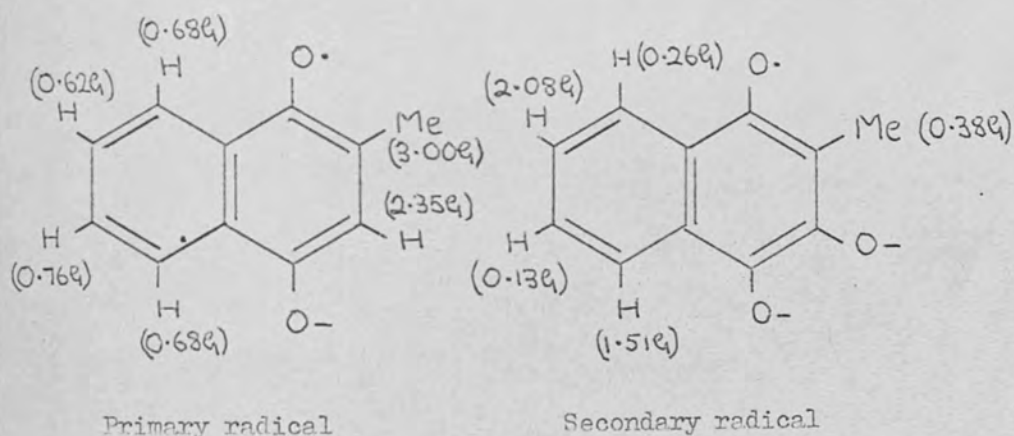
Chlorohydroquinone

The primary radical spectrum is shown in fig. 28. The coupling constants of the aromatic protons are consistent with previous observations[27] and no chlorine splitting was

2 Gauss
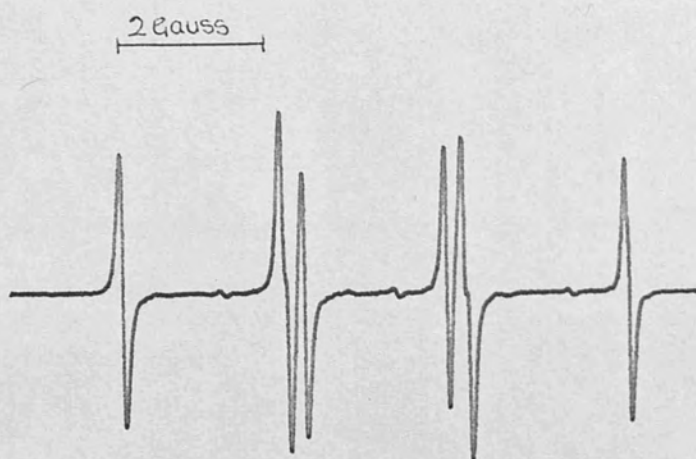
Figure 28: Primary radical from Chlorohydroquinone.

observed, although the lines were quite broad.
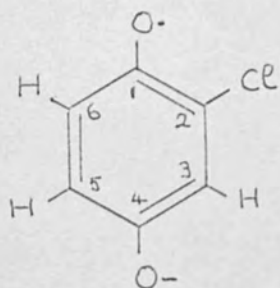
a_3 : 2.16G   2.21G [27]

a_5 : 2.44G compare 2.45G

a_6 : 2.24G   2.21G

In stronger alkali, no definite secondary radicals were observed, a single broad line always being obtained.

5-Methyl,2-Chlorohydroquinone

The E.S.R. spectrum of the primary radical is shown in fig. 29. Again no chlorine splitting was observed. The assignment given here for the aromatic protons
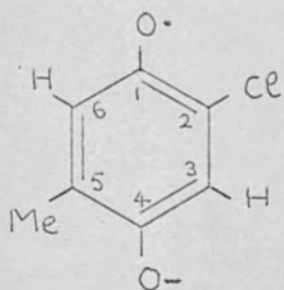
a_3 : 2.26G

a_5 : 2.24G (Me quartet)

a_6 : 1.54G

allots the smaller coupling constant to the proton adjacent to the methyl group. This is justified later in part II where the coupling constants of the radicals are discussed.
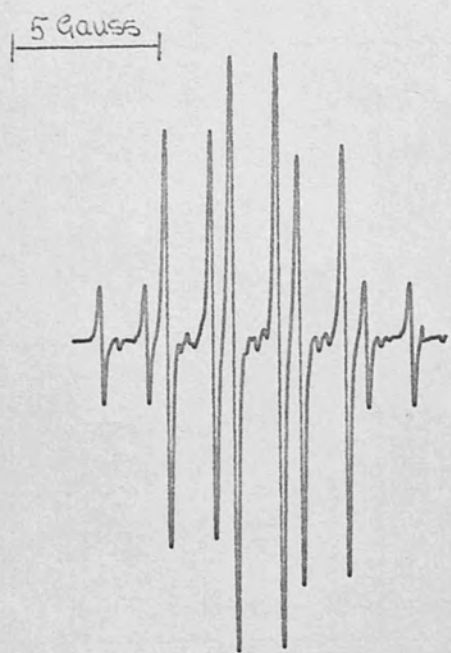
Figure 29. Primary radical from 5-Methyl,2-Chlorohydroquinone.
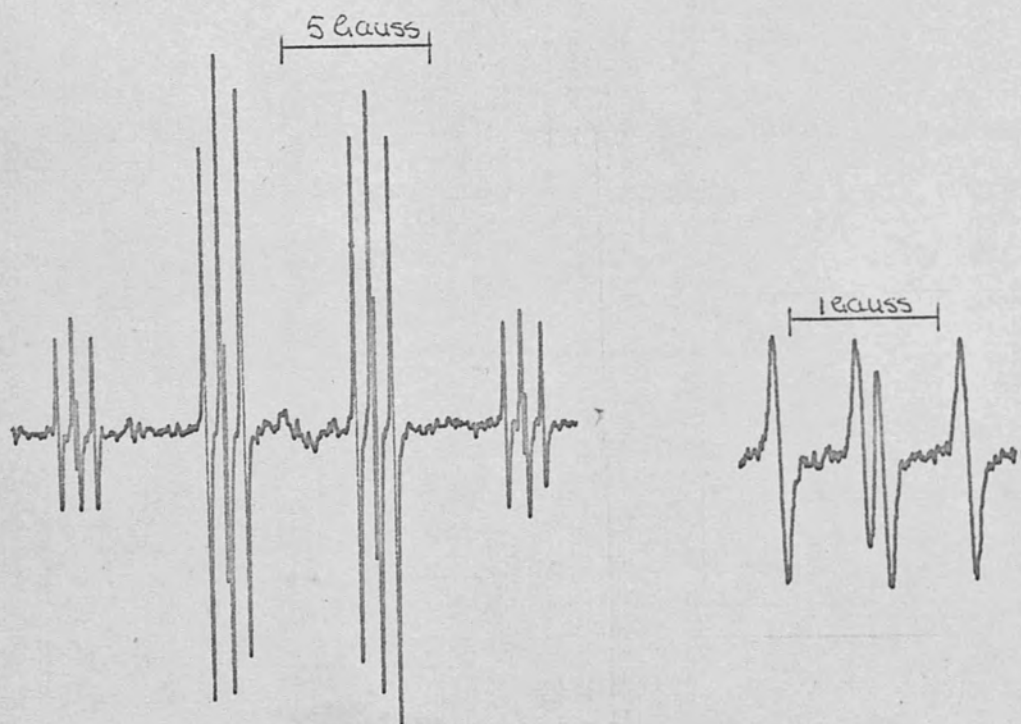
Figure 30. Secondary radical from 5-Methyl,2-Chlorohydroquinone.

In aqueous solutions of the hydroquinone to which
strong alkali was added, complex mixtures of radicals were
observed and any identification was not possible. However,
when 50% ethanol was used as the solvent, a single secondary
radical (fig. 30) was observed in solutions containing ca.
5% NaOH. The spectrum is identical to that obtained from
5-methyl,1,2,4-triacetoxybenzene (fig. 7a) and corresponds
to a radical formed by replacement of the halogen by an
oxygen atom. The replacement of halogen by hydroxyl ions
is to be expected in solutions of such high alkalinity and
no secondary radical in which the chlorine is retained has
been observed here.

Methoxyhydroquinone

The methoxy group might be expected to be fairly
labile in strongly alkaline solutions of methoxyhydroquinone
and experiments were carried out to see whether the group
was replaced instead of hydrogen.

The primary radical I was obtained in dilute alkali
(fig. 31) and a splitting from the methoxy group of 0.81G
was found.

In stronger alkali secondary radical B, in which
replacement of a ring hydrogen had occured, was observed
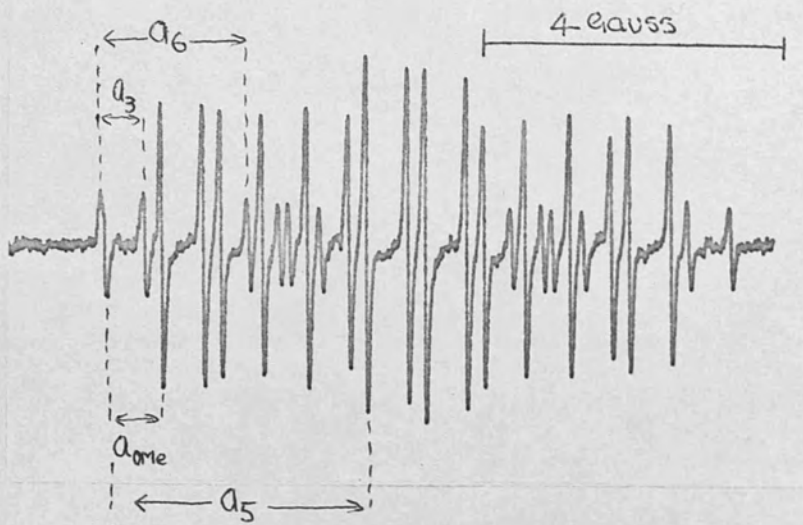
Figure 31. Primary radical from Methoxyhydroquinone.
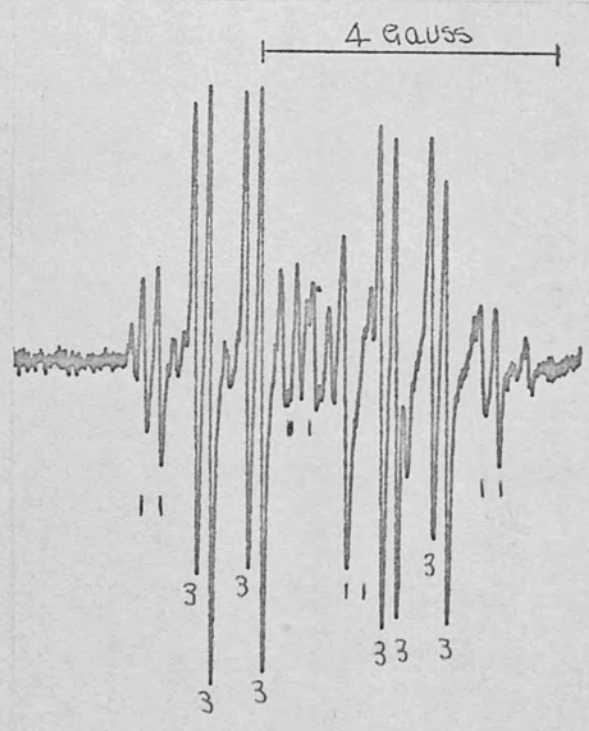
Figure 32. Secondary spectrum from Methoxyhydroquinone
in 5% NaOH.
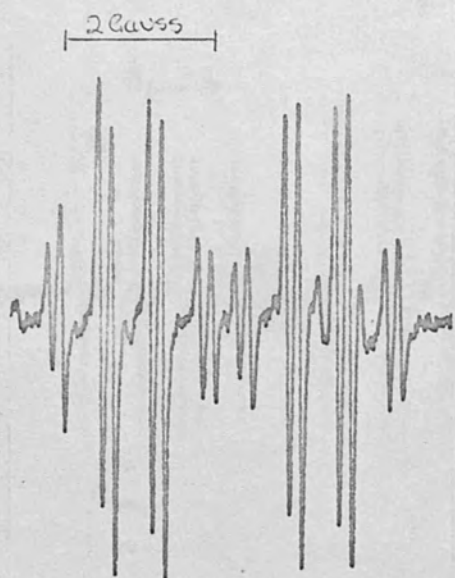
Figure 33. Radical obtained from 6-Methoxy, 1,2,4-Triacetoxybenzene in 5% NaOH.(Secondary B).
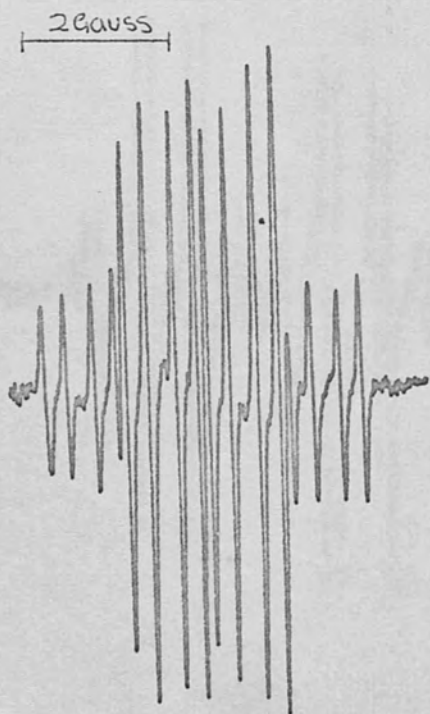
Figure 34. Radical obtained from 5-Methoxy, 1,2,4-Triacetoxybenzene in 5% NaOH. (Secondary A).

among a mixture of radicals. The spectrum (fig.32) clearly shows a large doublet splitting of 2.56G and a quartet splitting of 0.66G, so the methoxy group appears to have been retained. No evidence for the formation of secondary radical A was found under any conditions.

I   A   B

However, acetylation of methoxyquinone in the usual way produced a mixture of two triacetoxy compounds which were successfully separated by crystallization. The spectra obtained are shown in figs. 33 and 34. Fig. 33 is clearly due to radical B of fig. 32, while fig. 34 must be due to the isomeric radical A in which the methoxy group is para to the additional oxygen, and has a larger splitting than in the primary radical I.

It appears, then, that replacement of hydrogen is more favourable than replacement of methoxy from this compound. Attack of hydroxyl at the carbon bearing the methoxy group will be less likely for steric reasons and possibly the non-

lability of the methoxy group is due mainly to this.

7. MECHANISM OF FORMATION OF SECONDARY RADICALS

Several observations form a useful starting point for a proper understanding of the mechanism of the autoxidation of hydroquinones and quinones.

1. Primary radicals are observed from hydroquinones in dilute alkaline solution, and in more concentrated alkali secondary radicals having an extra oxygen on the aromatic ring are seen to be formed.

2. Para-quinones containing at least one hydrogen atom in the quinonoid ring (Group 1 quinones) are susceptible to attack by nucleophiles[1,2], particularly hydroxyl ions[5,9], in which case the hydroxyquinones are formed.

3. Para-quinones having a fully alkylated ring (Group 2 quinones) do not form hydroxyquinones in alkaline solution[46].

4. Para-quinones of group 1 are capable of being
reduced to their corresponding semiquinones in
alkaline solution without the presence of an
added reducing agent[9], whereas those of group 2
are not[47].

5. The presence of hydrogen peroxide in the
solution has apparently no effect on the course
of the reaction.

The initial steps in the autoxidation of hydroquinone
I are well known, and lead to the quinone III via the
intermediate primary radical II.

I   II   III
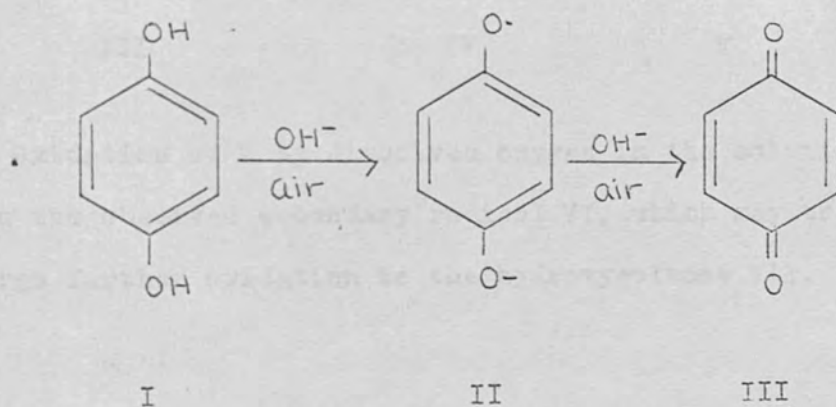
The next steps introduce an additional oxygen into
the aromatic ring if a free quinonoid position is available,
and the result is the formation of the hydroxyquinone.

The secondary radicals observed here appear to be the

intermediates in this process and are obtained from both the
hydroquinone or the quinone. Since the observation of the
secondary radicals is favoured by high alkalinity of the
solutions it seems reasonable to suggest that their formation
arises from hydroxyl ion attack on the quinone III. The
adduct IV, is then able to lose the aromatic proton in the
alkaline medium to give the anion of trihydroxybenzene V.

III   IV   V
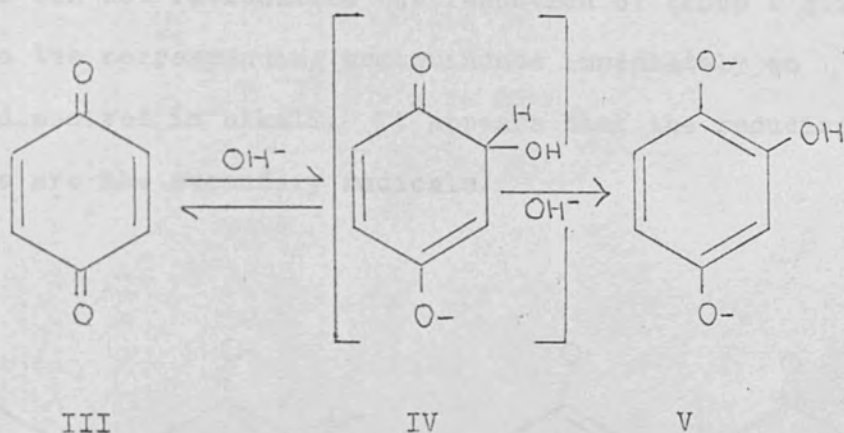
Oxidation of V by dissolved oxygen in the solution
gives the observed secondary radical VI, which may then
undergo further oxidation to the hydroxyquinone VII.

V   VI   VII
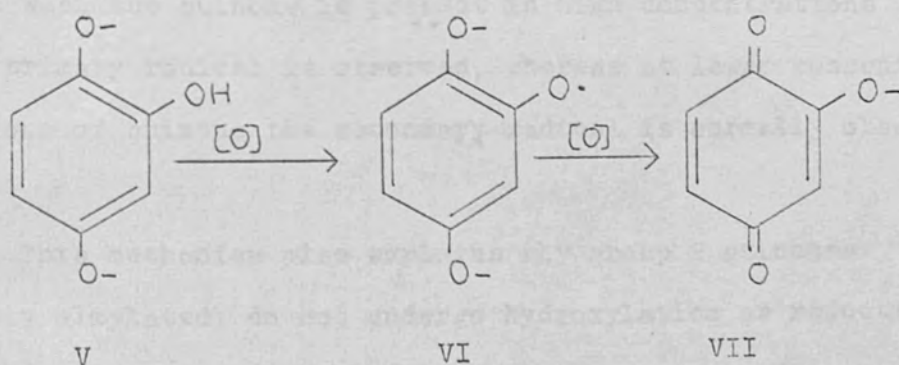
In mildly alkaline solutions of hydroquinones the initial step leading to the primary radical is the one observed by E.S.R., but as the alkalinity is increased the hydroxylation process becomes more important and the secondary radical is observed. At intermediate degrees of alkalinity a mixture of primary and secondary radicals is often observed.

We can now rationalise the reduction of group 1 quinones to the corresponding semiquinones immediately on being dissolved in alkali. It appears that the reducing species are the secondary radicals.
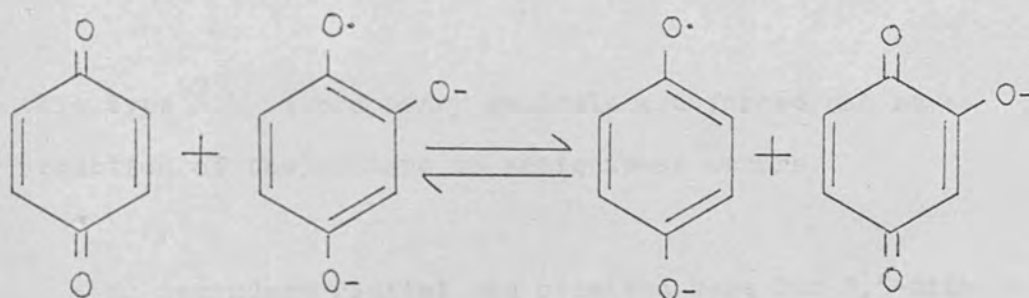
This possibility is strengthened by the observation that when the quinone is present in high concentrations the primary radical is observed, whereas at lower concentrations of quinone the secondary radical is normally observed.

This mechanism also explains why group 2 quinones (fully alkylated) do not undergo hydroxylation or reduction to the semiquinones in alkaline solution.

Secondary radicals cannot be formed from these quinones as there is no replaceable hydrogen in the quinonoid ring. The adduct VIII, formed by hydroxyl ion attack, is unable to regain the aromatic-type structure, since this would involve loss of an alkyl group, and so no hydroxylation occurs. Tetramethylquinone and anthraquinone are among quinones of

VIII
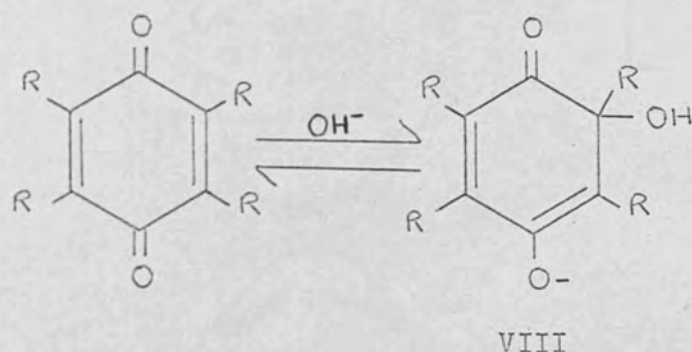
this type[47]. No secondary radicals are formed and so no reduction of the quinone to semiquinone occurs.

No secondary radical was observed here for 2,5-ditert. butylhydroquinone (see page 38), but the fact that the primary semiquinone was observed in alkaline solutions of the quinone suggests that some secondary radical must have been formed. We would expect this since there are two free quinonoid positions, but presumably hydroxylation is slow due to the steric effect of the large tert.butyl groups, and the concentration of secondary radical is never suffic-ient for observation.

The complete mechanistic scheme for hydroquinones having a free quinonoid position is given below.

Presumably further hydroxylation of the hydroxyquinone formed can occur, but no radicals corresponding to this process have been observed here. Also no account has been taken, in the scheme shown above, of possible coupling reactions or dimerisation of the radicals. There is evidence for reactions of this sort in some of the spectra and these tertiary radicals are discussed a little later.

The observation of different isomeric secondary radicals
in different solvents (methyl- and ethylhydroquinones) is an
odd effect, and no explanation has yet been found. Of the
two secondary radicals observed, B would be expected to be
more susceptible to further attack because the ring position
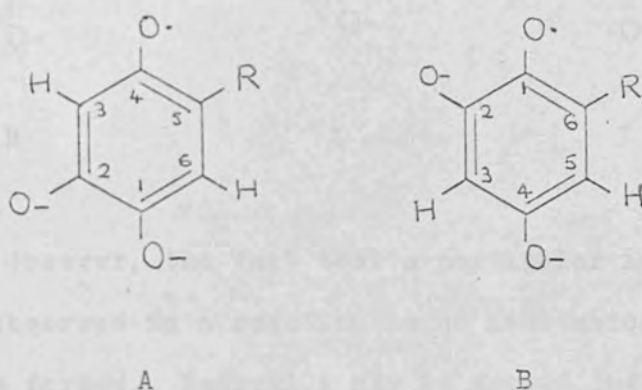
of highest spin density (the 5-position) bears a replaceable
hydrogen. However, it was generally easier to obtain radical
B than radical A and the spectra were normally more stable.

For the methoxy compound the formation of secondary
radicals presumably occurs by the same mechanism as for the
alkyl-substituted hydroquinones, replacement of a quinonoid
hydrogen being the process observed by E.S.R. The fact that
only secondary radical B is observed in strong alkali was
rather unexpected since the reaction of p-benzoquinone with
alkoxyl ions (OMe^-, OEt^-) has been shown[40] to give the
2,5-dialkoxylquinone I.

B   A   I
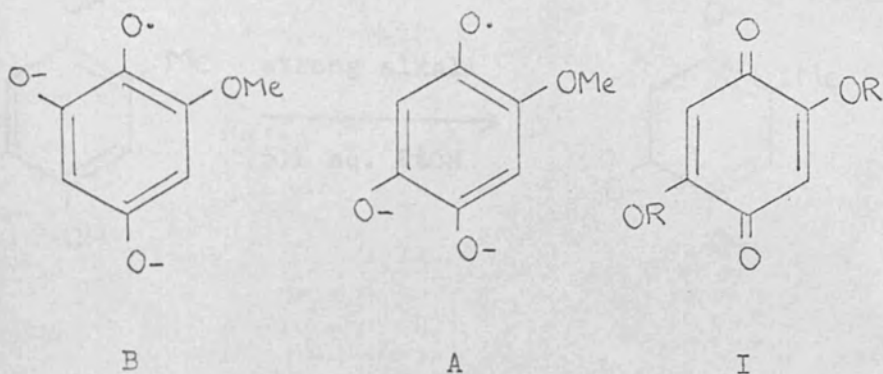
However, the fact that a particular intermediate is not observed in a reaction is no indication that it is not being formed. Radical A may be formed just as readily as B, but its relative instability may preclude observation. The possibility exists that radical A is much more readily oxidised to the quinone, than is radical B, and so is never present in comparable concentrations.

The chlorinated hydroquinone II (see page 44) was shown to favour loss of halogen in strongly alkaline solutions.

II   III
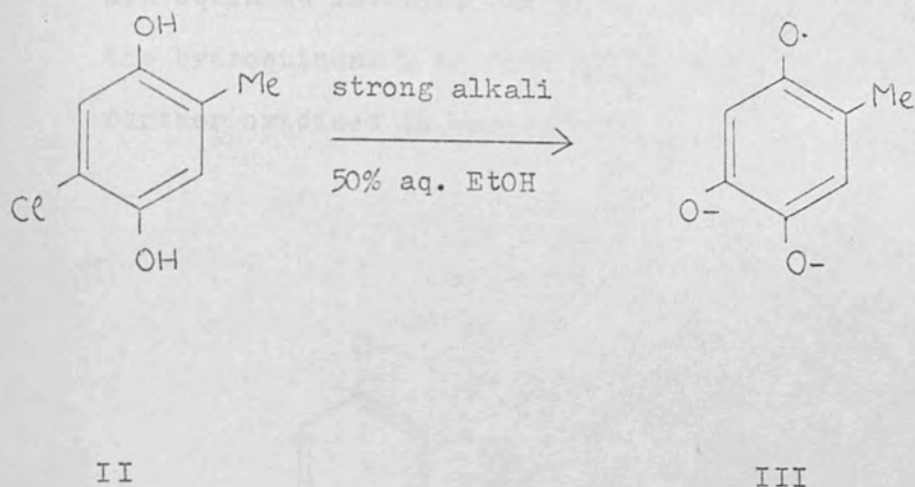
The formation of radical III probably involves a
simple nucleophilic displacement of halogen by hydroxyl
ions, either prior to any oxidation of the hydroquinone or
after the formation of the halogenated quinone in the
initial oxidation step.

The possibility of hydrogen peroxide being the hydrox-
ylating agent in the form of O_2H^-, as suggested by James[1,2],
appears unlikely in the light of this work. Not only does
added peroxide appear to have no effect on the reactions
producing the secondary radicals, but hydroxylation is
observed starting from the quinone in which case no hydrogen
peroxide is produced in the reaction. Hydrogen peroxide is
only formed in the initial steps of the reaction, i.e. the
oxidation of hydroquinone to quinone.

In a recent paper by Pederson[48], it is suggested that the mechanism of formation of secondary radicals from the hydroquinone involves attack by oxygen on the dianion of the hydroquinone I to give the adduct II, which is then further oxidised to radical III. How the observed secondary
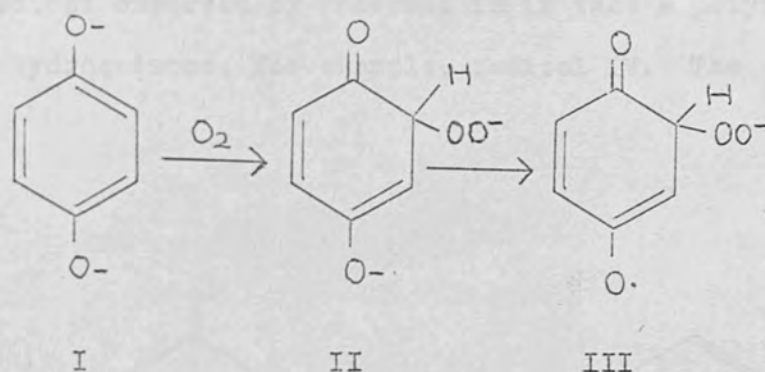
radical is formed from III was not specified in his paper.

The existance of III is claimed because of the observation in small concentrations, of another radical (doublet splittings 2.85G, 2.08G and 1.66G) in the primary spectrum of hydroquinone. The three doublet splittings were attributed to the aromatic protons of III, with no methylene proton splitting.

Radical III has the cyclohexadienyl structure, very different to that of semiquinone, and it was not made clear why the aromatic proton splittings should be similar to those of a semiquinone radical. Also the absence of a

methylene proton splitting is in contrast to the observation of
large coupling constants from such protons in hydroxycyclo-
hexadienyl radicals[49,50].

The coupling constants are very similar, however, to
those of the quinonoid ring protons in arylsemiquinones
discussed in part III of this thesis, and it appears likely
that the radical observed by Pederson is in fact a polymeric
product of hydroquinone, for example, radical IV. The
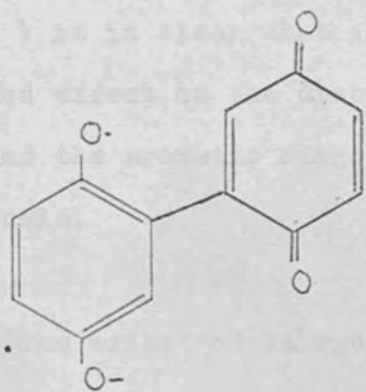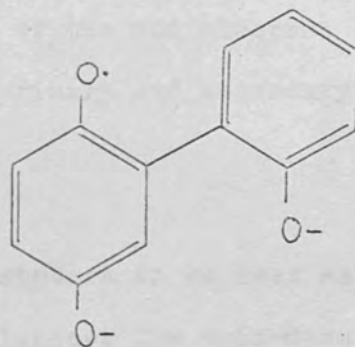
IV   V

closely related radical V has semiquinone ring splittings
of 2.65G, 2.28G and 1.82G, of the same order as those in the
radical obtained by Pederson.

The suggestion that oxygen is the hydroxylating agent
for hydroquinones[48] is based solely on the assumption that
the E.S.R. spectrum obtained corresponds to the peroxy-

adduct III. Since this is unlikely, for the reasons just
given, it follows that the evidence for attack by oxygen
is at present very scant, and it seems more likely that the
mechanism of formation of secondary radicals involves the
quinone only and hydroxyl ions.

8. DISCUSSION OF THE COUPLING CONSTANTS OF PRIMARY AND SECONDARY RADICALS.

From an examination of tables I and II (pages 40 and
41) it is clear that alkyl substituents have a fairly
marked effect on the distribution of the odd electron
around the aromatic rings of the primary and secondary
radicals.

'The effect of halogen atoms appears to be less marked,
but the methoxy group clearly influences the spin-density
distribution much more than do alkyl groups.

The assignments of coupling constants given in tables
I and II are based on previous data for semiquinones, and
on certain rules adopted here with the aid of primary and
secondary radicals having unambiguous splitting constants.

Primary Radicals

In the radicals I and II, it is clear that the aromatic
proton splittings are highly dependent on their position
on the ring relative to the methyl groups. In radical I

I   II
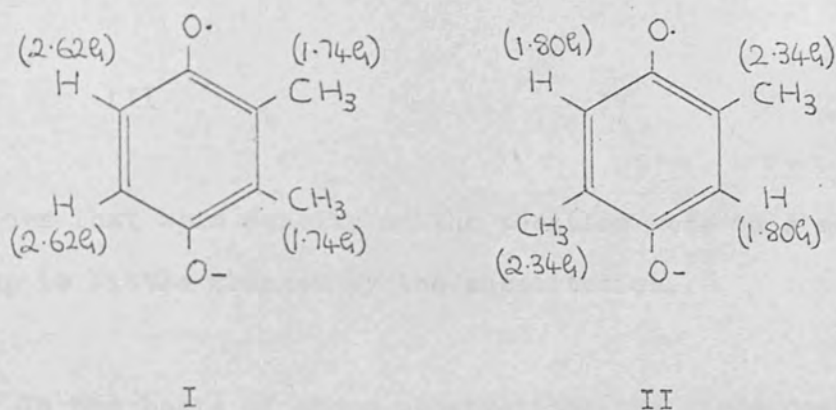
each ring proton is meta to one methyl group and para to
the other; whereas in II they are meta and ortho to the
methyl groups. It appears then, that spin densities are
increased relative to the unsubstituted case (2.37G) by a
para methyl group, but are decreased by an ortho methyl
group.

Applying this to radical III, the aromatic proton
splittings are lower (1.93G) than in the unsubstituted semi-
quinone (2.37G); since they are both ortho and para to
methyl groups, it appears that the ortho effect is the
larger. The methyl proton splittings in II (2.09G) are very
close to those in the mono-methyl radical IV (2.12G) and it
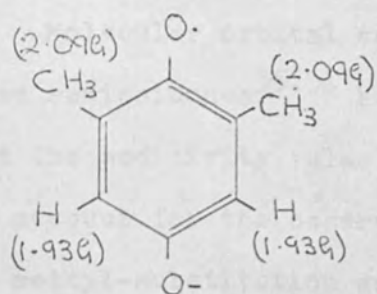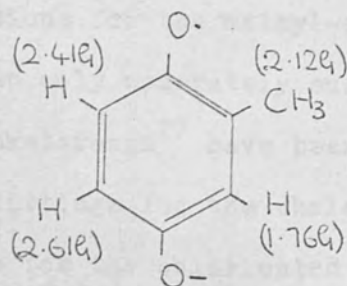
III   IV

follows that spin density on the position meta to a methyl
group is little changed by the substitution.

On the basis of these observations the three doublet
splittings in **IV** can be assigned as shown.

It is also apparent from radicals I-IV that aromatic
proton splittings are generally slightly greater than the
corresponding methyl splittings.

We can summarise the rules relating to the splittings
in methyl-substituted semiquinones thus:

1. Spin densities on ring positions para to a methyl
    group are increased by the substitution, while
    those ortho to a methyl group are decreased, the
    effect at the ortho position being the larger.

2. Spin densities on ring positions meta to a methyl
    group are little changed.

3. Aromatic proton splittings are generally slightly

greater than corresponding methyl proton splittings.

Molecular orbital calculations for the methyl-substit-uted semiquinones[35,51] have been only moderately successful, but the additivity rules of Venkataraman[27] have been shown to account for the observed splittings for the whole range of methyl-substitution and also for the chlorinated semi-quinones.

The parameters 'ortho', 'meta' and 'para' were used[27] to represent the changes in spin density at the ring positions relative to the methyl or chlorine substituent. In the poly-substituted semiquinones, the effects produced by each substituent were shown to be very nearly additive.

Previous assignments of the splittings in tert.butyl-semiquinone I[24,51] have put the largest splitting to the

		a_3:	1.55G[24]
1.65G			
2.89G	compare	a_5:	2.82G
2.12G		a_6:	2.07G

I
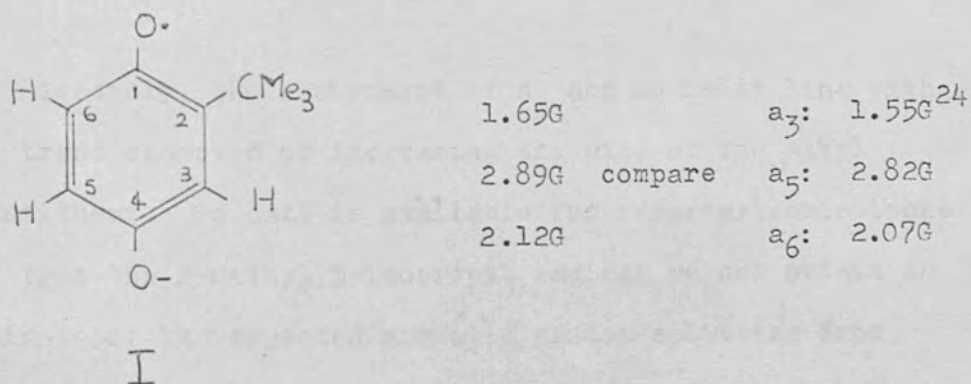
proton on the 5-position (para to the tert.butyl group), and it has been stated[24,51] that the ditert.butylsemiquinones

do not fall in line with the additivity rules of Venkataraman.

However, there appears to be a good case for reversing the splittings previously assigned to a_5 and a_6 and the assignment adopted here is shown below. Firstly the observed splitting of 2.09G for the ring protons of 2,5-ditert.butylsemiquinone can now be rationalised by considering each tert. butyl group as producing the same effect as observed in the mono-substituted radical I. The small aromatic proton splitting of 1.17G[24] in 2,6-ditert.butyl semiquinone can also be explained in this way by assuming that spin densities are decreased on the ring position para to the tert. butyl group introduced.
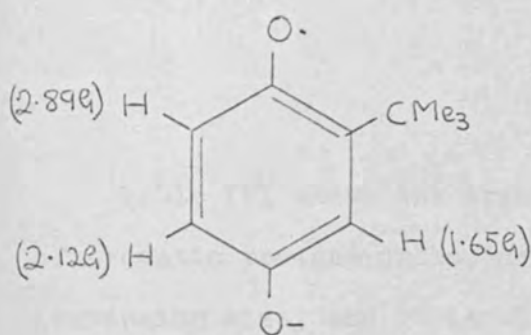
Secondly, the assignment of a_5 and a_6 is in line with the trend observed on increasing the size of the alkyl substituent. No data is available for isopropylsemiquinone but from the 2-methyl,5-isopropyl radical we can obtain an estimate of the expected aromatic proton splitting from the position para to the isopropyl group. The methyl proton splitting (2.18G) is slightly higher than that in methyl-semiquinone, so it appears that the isopropyl group is
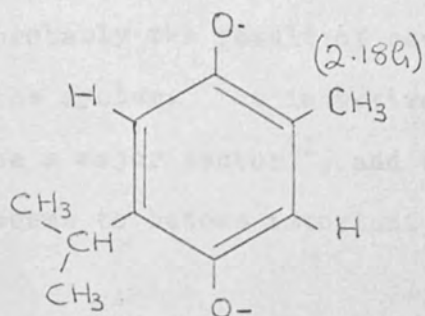
increasing the spin density in the para position but only by a small fraction ($\approx \frac{1}{35}$). This gives an estimated aromatic proton splitting of 2.45G when para to an isopropyl group.

Table III shows the trends observed in the splittings of aromatic protons ortho, meta and para to alkyl groups of increasing size, and it is clear that the new assignment for tert.butylsemiquinone fits into the series.

Table III: Aromatic Proton Splittings in Alkylsemi-
                    quinones.

Alkyl Group	Aromatic Proton Splittings (Gauss)		
	Ortho	Meta	Para
Methyl	1.76	2.41	2.61
Ethyl	1.74	2.53	2.53
Isopropyl	1.73	2.57	2.45
Tert.butyl	1.65	2.89	2.12

The effect on the spin density distribution by the

introduction of an alkyl group into the semiquinone ring is
probably the result of several separate perturbations of
the system. The inductive effect of the group appears to
be a major factor[51], and the steric effect of the group
seems to become important in the case of tert.butyl.

The substitution of chlorine has little effect on the
semiquinone ring splittings, whereas the much more electron-
releasing methoxy group has a large effect, much greater
than for alkyl groups.
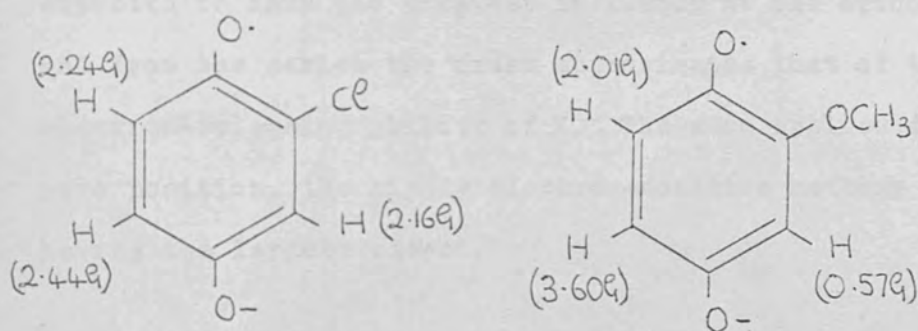
Considering the position ortho to the group introduced,
the aromatic proton splitting is always decreased by the
substitution and the influence of the group X decreases
along the series:-

$X = OMe \gg t.butyl > Et \approx Me \gg Cl > H$
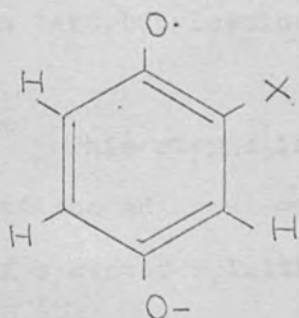
At the meta position the ability of the group X to increase the splitting decreases along the series:-

X= t.butyl ≫ Et > Me > H > Cl > OMe
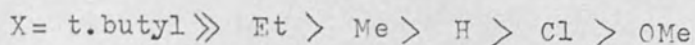
For the proton at the para position the ability of X to increase the splitting decreases along the series:-

X= OMe ≫ Me > Et > Cl > H > t.butyl
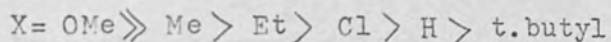
The inductive effect of the substituent might be expected to have the greatest influence at the ortho position and from the series the order approximates that of the electron-releasing ability of X. The same applies for the para position, the highly electron-donating methoxy group having the largest effect.

The spin density at the meta position, however, appears to be much more dependent on the size of the substituent. It might be expected that any steric interaction with the adjacent carbonyl group would effect spin density at the meta position more than any other and it appears that this interaction is responsible for the large splitting observed in tert.butylsemiquinone.

This steric interaction between the tert.butyl group and the adjacent oxygen is apparent from the observation of a septet splitting from the tert.butyl group. This seems

to indicate that the group is not freely-rotating, two
methyl groups apparently being in a different environment
from the third.

Secondary radicals

From the observed splittings in I, the only possible
secondary radical from 2,5-dimethylhydroquinone, the presence

$$\text{I} \qquad\qquad \text{II} \qquad\qquad \text{III}$$
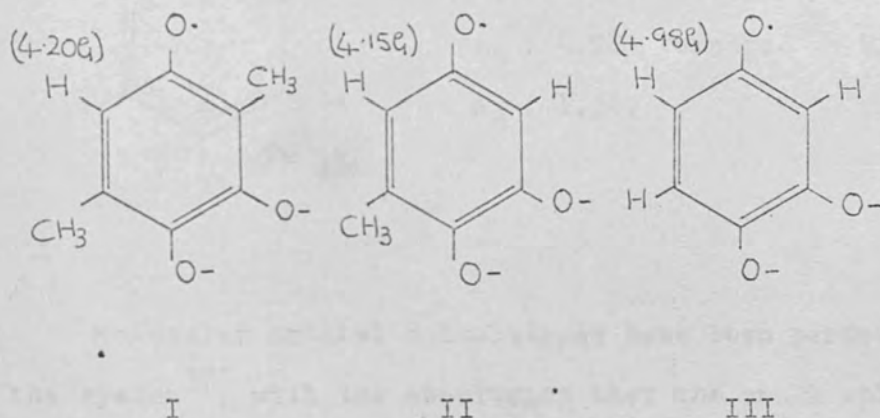
of a large doublet (4.20G) suggests that the largest split-
ting in all the observed secondary radicals (generally 4-5G)
arises from coupling with protons on the 5-position, para
to the introduced oxygen atom. The splittings of 4.20G
and 4.15G in radicals I and II are considerably lower than
in III, the unsubstituted compound (4.98G) and it appears
that the methyl group is having the same effect as that
observed in the primary radicals, i.e. decreasing spin

density on the adjacent carbon atom.

The whole range of methyl-substituted semiquinones of 1,2,4-trihydroxybenzene[37] have peviously been studied by E.S.R., and these studies led to the assignment of the three doublet splittings for the unsubstituted radicals as shown below, together with the splittings observed in this work.

$$a_3 : 0.60G \qquad 0.62G^{37}$$
$$a_5 : 4.98G \text{ compare} \qquad 4.80G$$
$$a_6 : 1.34G \qquad 1.35G$$
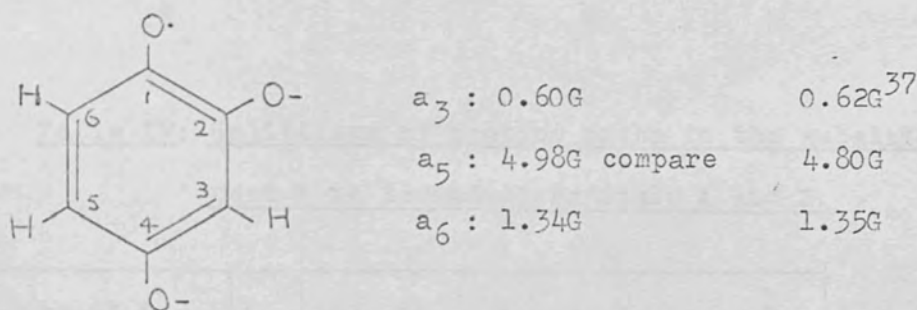
Molecular orbital calculations have been performed on the system[37], with the conclusion that the small spin density at the 3-position is negative.

The assignments given in table II (page 41) for the secondary radicals obtained here agree with the previous data, and the splittings can be fairly well accounted for on the basis of various trends in the spin density distribution with substitution.

Table IV shows the effects of the group X on the hyper-

fine splittings of the aromatic protons on the position
ortho with respect to X in the secondary radicals A and B.
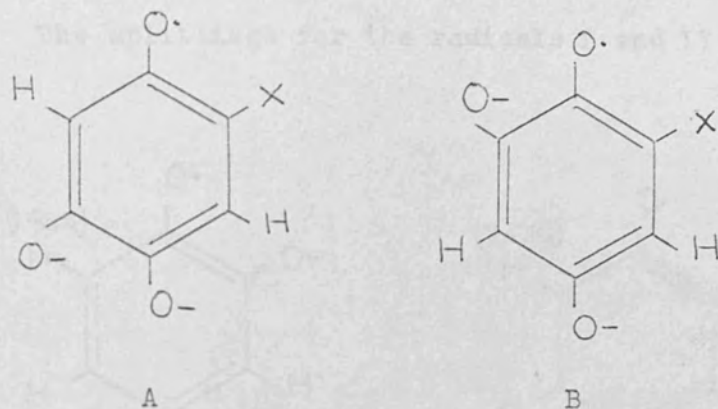
Table IV: Splittings of protons ortho to the substit-
uent X in secondary radicals A and B.

Substituent X	Coupling Constants (Gauss)	
	A	B
H	1.34	4.98
Me	0.69	4.15
Et	0.71	4.14
t.Butyl	0.54	4.02
OMe	0.29	2.56

Clearly the ability of the group X to decrease spin
density at the ortho position follows the same order as that
observed for primary radicals:

OMe $\gg$ t.butyl $>$ Et $\approx$ Me $\gg$ H
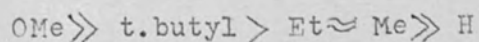
The trends in the hyperfine splittings for protons meta and para to the substituent X are small and indefinite, but the effect of the methoxy group is worth consideration.

The splittings for the radicals I and II at first

I   II
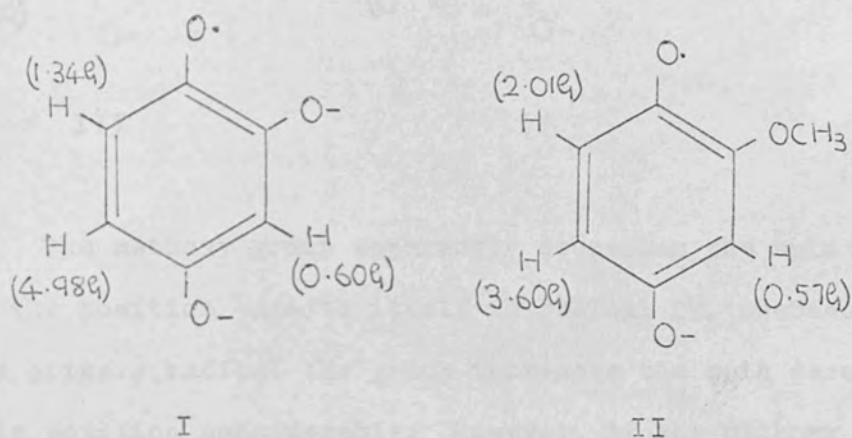
appear to indicate that the effect of the methoxy group is as great at the ortho position as that of $-O^-$, whereas the effects at the para and meta positions are considerably less.

However, if the spin density at the 3-position is negative in I, as suggested[37], but positive in II, then the methoxy group is clearly less effective in decreasing the spin density at this position. There is some evidence for this possibility in the secondary radical B from methoxy-hydroquinone IV.

III   IV
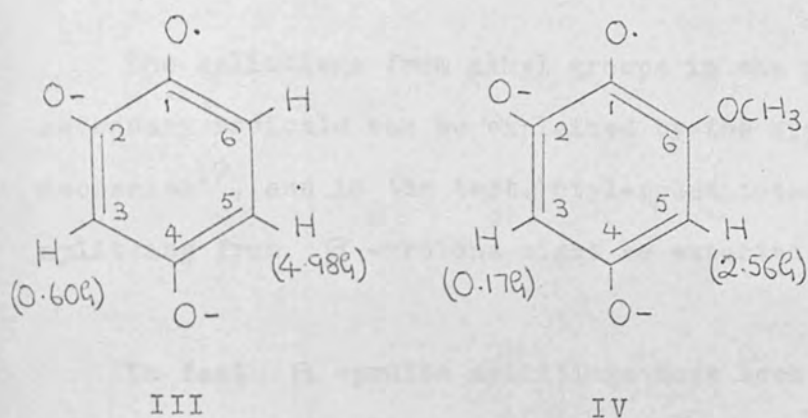
The methoxy group apparently decreases the spin density
in the position para to itself in radical IV, whereas in
the primary radical the group increases the spin density in
this position considerably. However, if the methoxy group
is in fact enhancing 'positive' spin density, then the
effect would be to lower the coupling constant at the 3-
position (since this position appears to have 'negative'
spin density). This may explain the unexpectedly small
hyperfine splitting of 0.17G.

The secondary radical III can, in fact, be envisaged
as a primary radical containing the substituent - O⁻, and
clearly this substituent has the largest effect on the spin
density distribution of all the substituents so far consid-
ered. The effect of the oxygen is similar to that of methoxy,
but much stronger, and since the sizes of the two groups are
comparable, the electron-donating ability of - O⁻ must be
the main factor in producing the large changes in hyperfine

splittings relative to the unsubstituted semiquinone.

The splittings from alkyl groups in the primary and secondary radicals can be explained by the hyperconjugation mechanism[17], and in the tert.butyl-substituted radicals splitting from β -protons might be expected.

In fact β -proton splittings have been observed only in secondary radical A from tert.butylhydroquinone (0.16G),
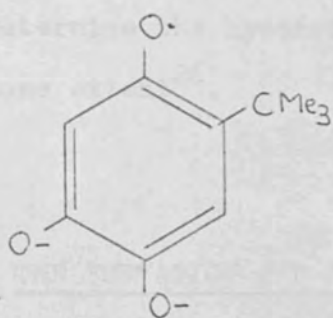
and it is clear that even if alkyl—hyperconjugation was as effective as that for hydrogen the resultant splitting is expected to be small.
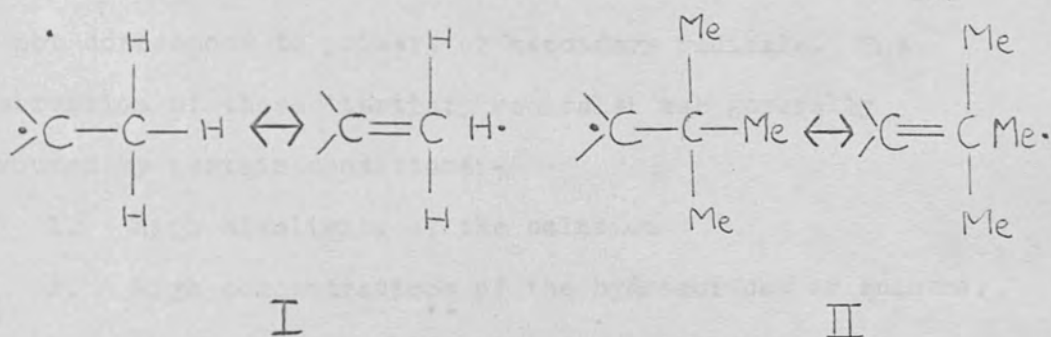
If structures I and II are equally effective in transferring spin density, then:

ratio of splittings in I and II ≈ ratio of splittings in hydrogen atom and methyl radical = $\dfrac{506}{23}$

The observed splitting in secondary radical A from methylhydroquinone is 5.12G, so we expect a splitting from the tert.butyl group in the corresponding radical of :-

$$a_{t.butyl} \approx 5.12G \times \frac{23}{506} \approx 0.23G$$

This value is fairly close to the hyperfine splitting observed (0.16G), but clearly no account has been taken of the conformation of the radical, which has been shown to determine the hyperconjugative coupling with β -protons to some extent[26].

9. THE FORMATION AND CHARACTERISATION OF TERTIARY RADICALS

A number of spectra have been obtained which clearly do not correspond to primary or secondary radicals. The observation of these 'tertiary radicals' was generally favoured by certain conditions:-

1. High alkalinity of the solution

2. High concentrations of the hydroquinone or quinone.

3. A relatively unsubstituted quinonoid ring.

In most cases the spectra were very poor, and often highly complex, but some were well-defined and appeared to be due to coupled products of the reaction.
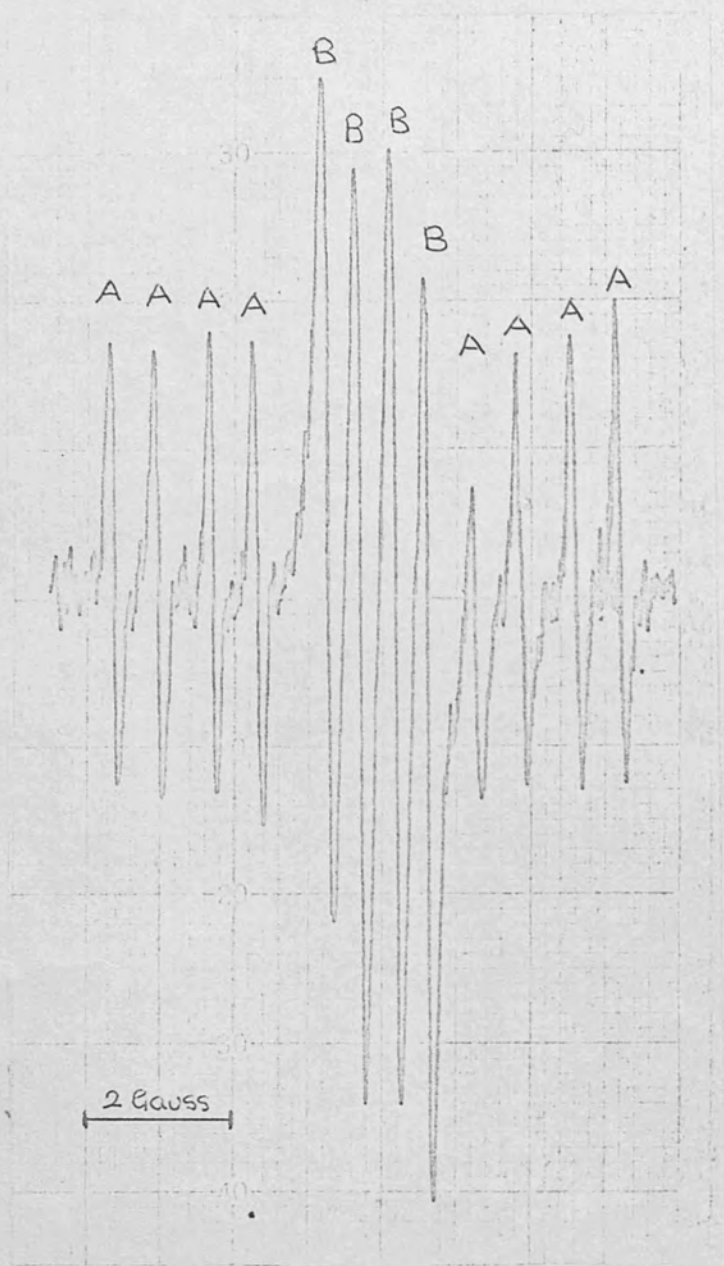
Figure 35: Mixture of secondary and tertiary radicals from Hydroquinone.

Lines A: Secondary radical

Lines B: Tertiary radical

Hydroquinone
_____

The unsubstituted compound gave rise to a variety of
tertiary radicals, the spectra normally being very simple
with coupling from two or three protons.

The four lines appearing in the secondary spectrum
of hydroquinone (fig. 6a) were clearly due to coupling with
two equivalent protons (0.90G, 0.45G). The spectrum is
included again here as fig. 35. The four-line spectrum
(lines B) appears to arise from radical I in which there is
no observed coupling with the second ring. The coupling

I   II   III

constants are similar to those observed by Reitz et al[40] from
the reduction of quinone II by glucose in 10% NaOH. Their

splittings were 0.92G, 0.45G and they apparantly saw a further splitting of 0.10G.

It is unlikely that these splittings are due to radical III, as they suggested, for two reasons. Firstly, it is unlikely that a primary product would be obtained in 10% NaOH, and secondly the splittings observed are not those expected for radical III. If there is no delocalisation of the odd electron around the second ring then we would expect the semiquinone ring splittings to be close to those normally observed for primary radicals. In phenylsemi-quinone, for example, these splittings are 1.99G, 2.12G and 2.56G.

The coupling constants do, however, agree well with those expected for radical I. In part III of this thesis radicals from aryl semiquinones are discussed, but it is useful here to give the splittings for radical IV, the secondary radical A from ortho-hydroxyphenylhydroquinone.
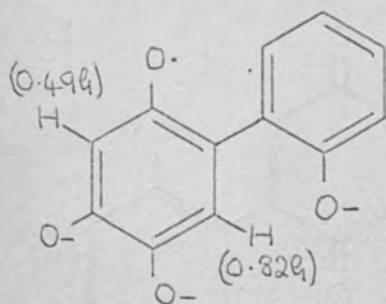
The semiquinone ring splittings of 0.82G and 0.49G are of the same order as those of the tertiary radical I (0.90G, 0.45G).

IV

Radical I is possibly formed by coupling of the second-
ary radical with a molecule of quinone, attack occuring at
the position of highest spin density in the secondary
radical (the 5-position).
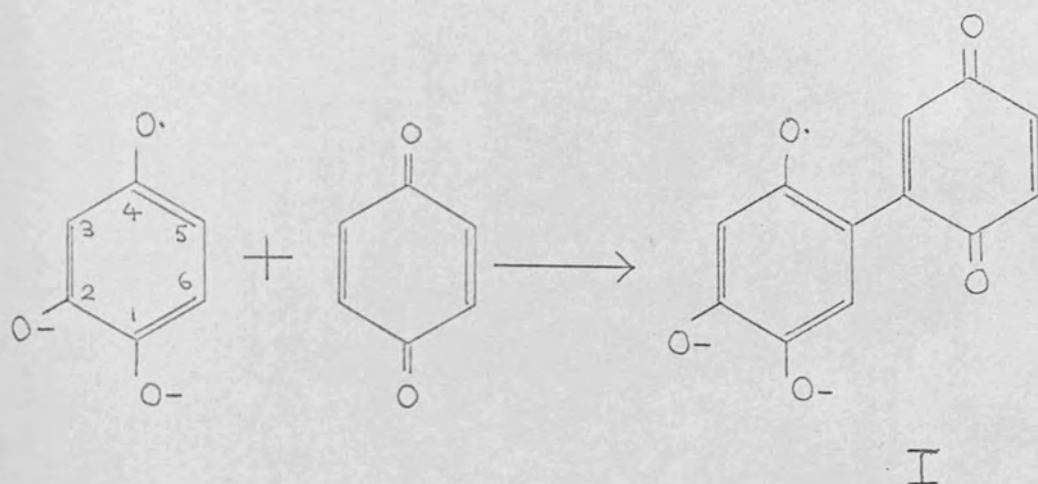
Another possibility is that coupling occurs prior to
any hydroxylation of the quinone ring, by dimerisation of
the primary radicals, for example. If this was the case,
then hydroxylation of the dimer V could lead to two possible
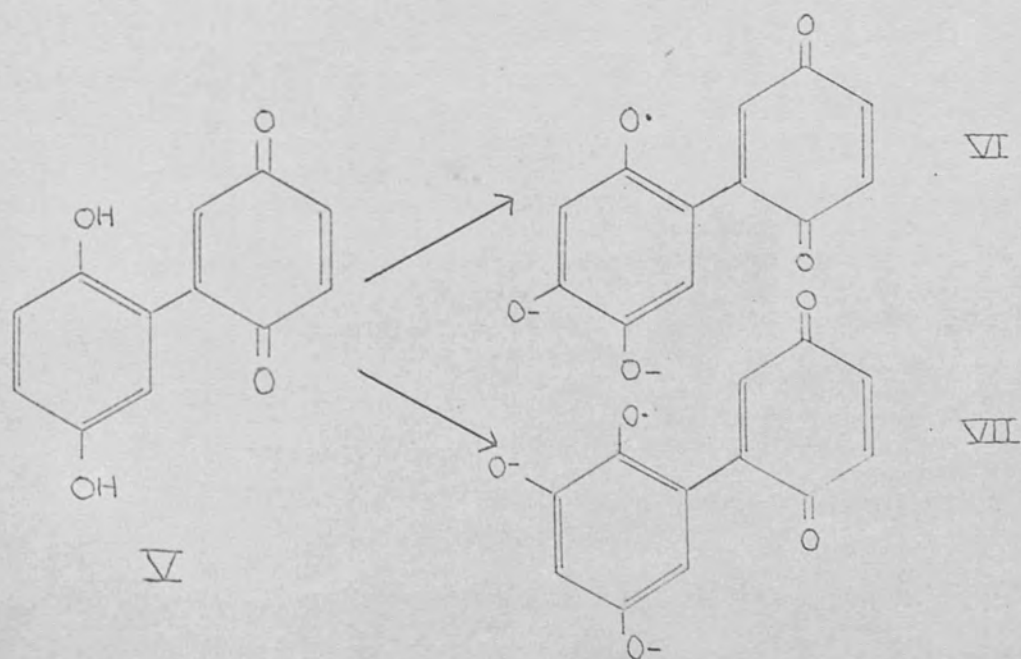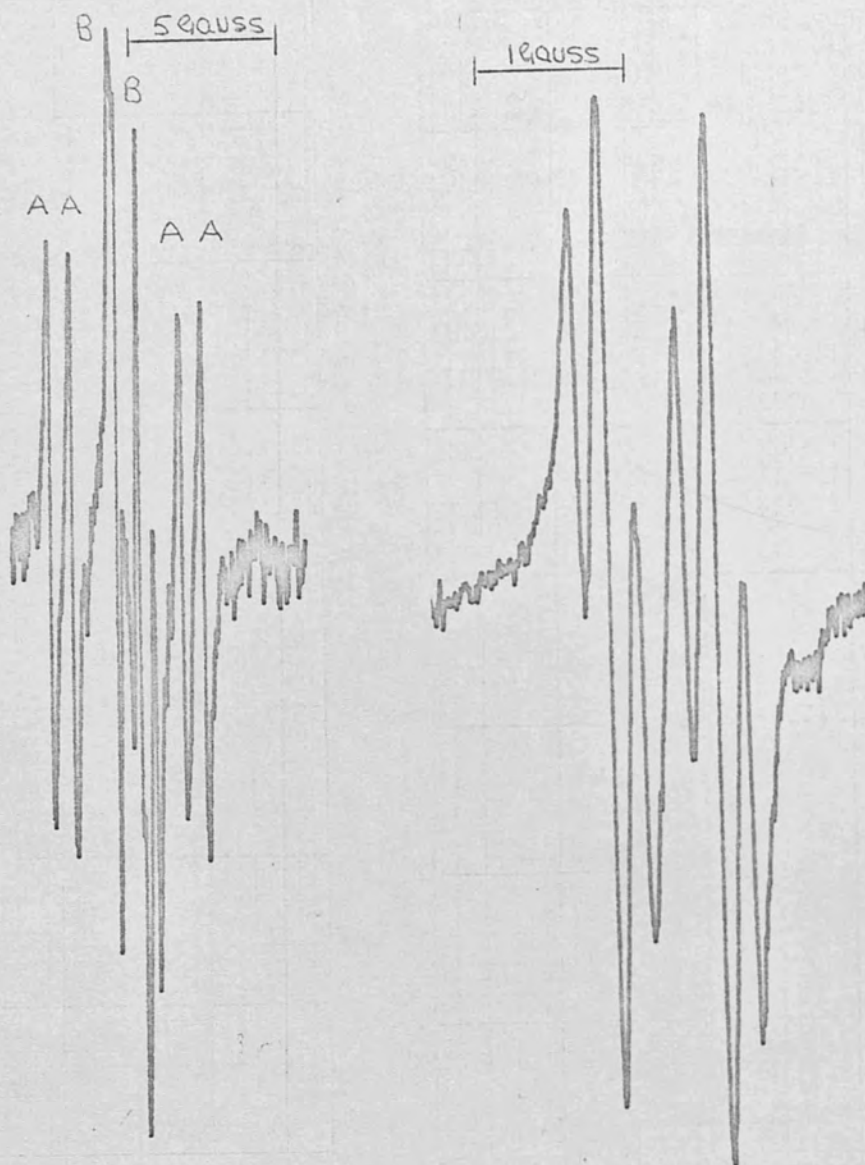
Figure 36: Mixture of tertiary radicals from p-benzoquinone
in 50% D.M.F.

    (a) Mixture of radicals.

    (b) Lines B only , on expanded scale, showing
         doublet of triplets.

tertiary products, VI, just discussed, and radical VII, which is expected to have a large doublet splitting and a small doublet splitting. A spectrum corresponding to radical VII has been observed in strongly alkaline solutions of benzoquinone in 50% aqueous D.M.F. (fig. 36 lines A). The observed splittings (4.52G, 0.70G) are consistent with the expected values for radical VII.

The other radical observed in fig. 36 (lines B) has a doublet splitting (0.70G) and a small triplet splitting (0.20G). It is observed in solutions of benzoquinone in a variety of solvents in the presence of strong alkali, but its identity has not been established.

Catechol

In the secondary spectrum from catechol (fig. 37) as well as the hydroxylated radical (lines A), four additional lines were obtained (lines B), with splittings the same as those of the tertiary radical from hydroquinone (fig. 35). The radical can clearly not be the same as that from hydro-quinone, identified as I, but the radical II, formed by hydroxylation and dimerisation of the ortho-quinonoid nucleus would be expected to have very similar splittings, since apparantly little delocalisation of the odd electron
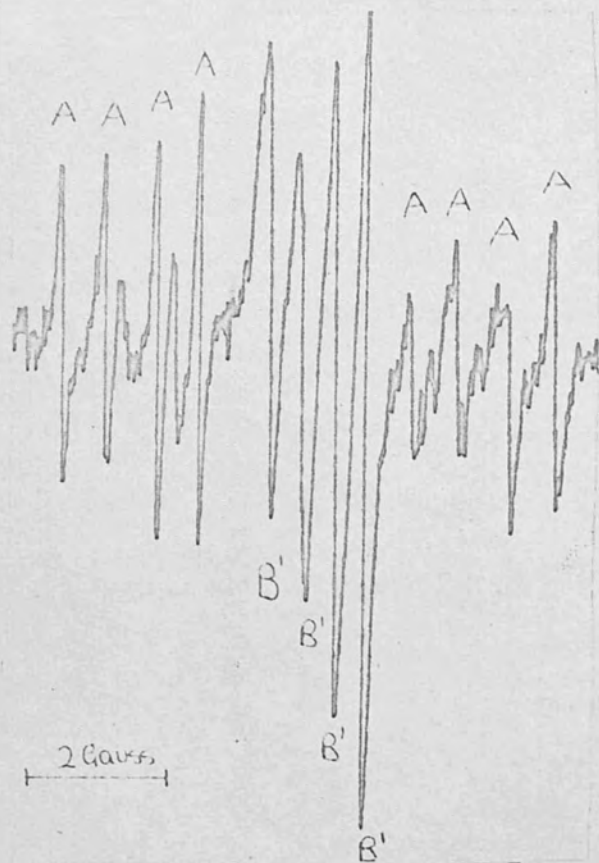
Fig. 37: Secondary spectrum
from Catechol.
Lines A. Secondary radical.
Lines B. Tertiary radical.
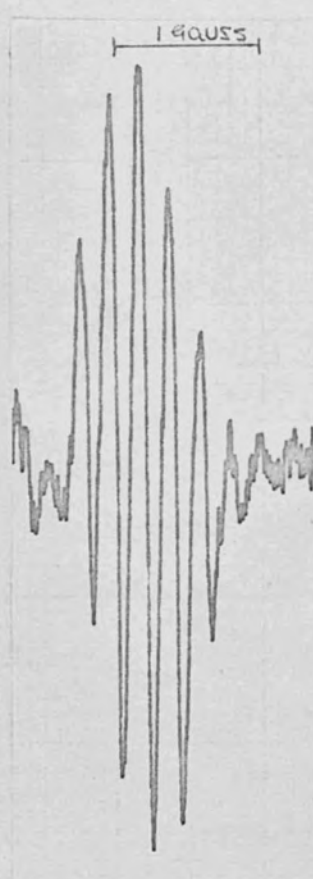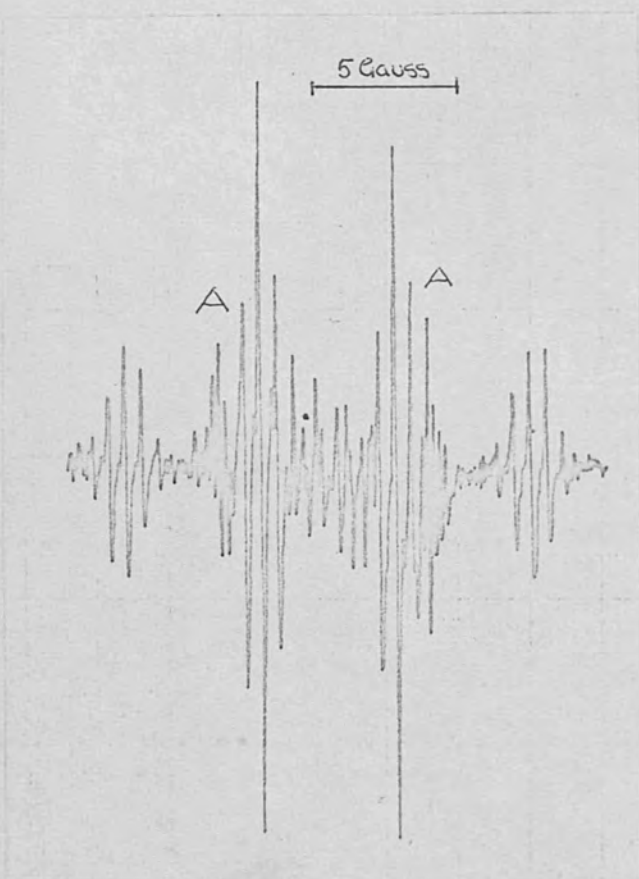
Figure 38: Spectrum showing tertiary radical from
2,3-Dimethylhydroquinone(lines A), with expanded septet.
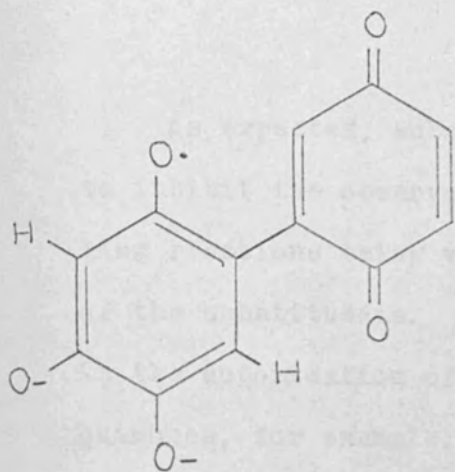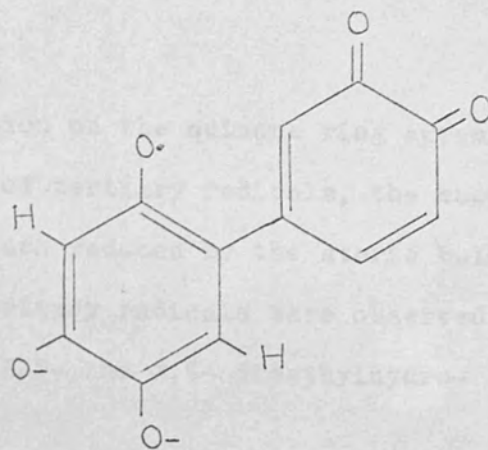
I   II

occurs into the secondary ring. The four lines of fig. 37
are thus ascribed to the tertiary radical II.

2,3-Dimethylhydroquinone

This was the only other hydroquinone which gave a well-
defined tertiary radical, shown previously in fig. 15 and
reproduced here as fig. 38. The splittings are a doublet,
7.25G and a septet of 0.21G. The large doublet splitting
is much larger than any encountered in radicals of the
semiquinone-type and the identity of this radical has not
been established.

As expected, substitution on the quinone ring appears to inhibit the observation of tertiary radicals, the coupling reactions being very much reduced by the steric bulk of the substituents. No tertiary radicals were observed in the autoxidation of the 2,5- and 2,6- dimethylhydroquinones, for example.

PART III

10. PRIMARY AND SECONDARY RADICALS FORMED IN THE
     AUTOXIDATION OF META- AND PARA- SUBSTITUTED
     ARYLHYDROQUINONES.

In part II of this thesis radicals formed during the
autoxidation of hydroquinones containing alkyl and other
simple substituents were discussed. In addition to the
primary semiquinones, secondary radicals derived from
1,2,4-trihydroxybenzenes were observed by E.S.R. spectro-
scopy.

A parallel series of radicals were formed during the
autoxidation of arylhydroquinones and these radicals have
proved interesting from the point of view of the delocal-
isation of the odd electron around the semiquinone and the
aryl rings.

In order that the electronic effects of substituents
on the aryl ring could be studied, substitution was confined
to the meta and para positions. Ortho substitution would
be expected to considerably affect the conformation of the

radicals with respect to twisting of the two rings of the
biphenyl-type system. The steric effects in ortho substit-
uted arylsemiquinones are discussed separately in part IV.

Preparation of the Arylhydroquinones

The arylquinones were prepared by direct arylation
of p-benzoquinone[52] via the diazonium salts (see experimen-
tal section), and reduction of the quinones with zinc and
25% hydrochloric acid yielded the corresponding hydroquinone.

Formation of Primary and Secondary Radicals

The primary radicals were generated in the normal
way in mildly alkaline solutions of the arylhydroquinone
(ca. 0.01M) in 50% aqueous ethanol. The spectra were stable
under these conditions, often remaining unchanged for
several hours.

Secondary radicals were observed in more concentrated
alkali in aqueous solutions, the normal procedure being to
add a solution of the hydroquinone (ca. 0.01M) to an equal
volume of 15% NaOH. The secondary radicals were always
obtained initially as a mixture of the two isomeric radicals
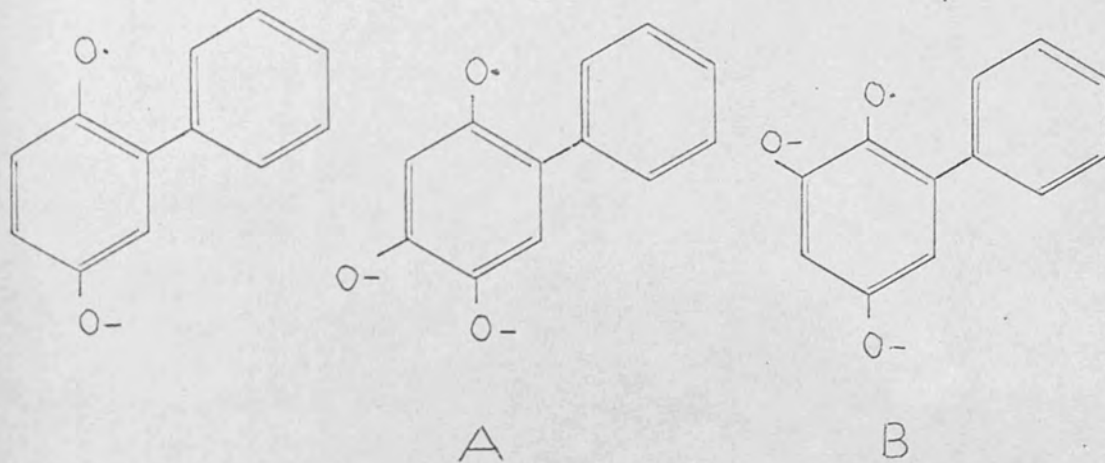
PRIMARY RADICAL   SECONDARY RADICALS

A and B. This contrasts with the behaviour of alkylhydro-
quinones which could be made to yield one or other isomer
depending on the conditions. When the solutions were left,
however, radical B decayed, often leaving a pure spectrum
of radical A. Improved spectra of the secondary radicals
could often be obtained by acetylation of the arylquinones[43]
followed by alkaline hydrolysis, again a mixture of the two
isomeric radicals being obtained.
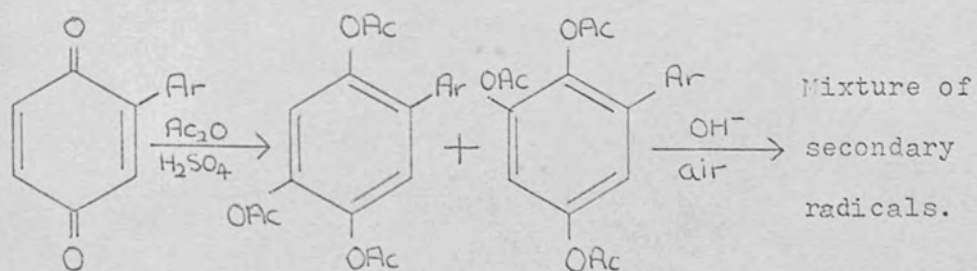
The E.S.R. spectra were generally well-resolved and
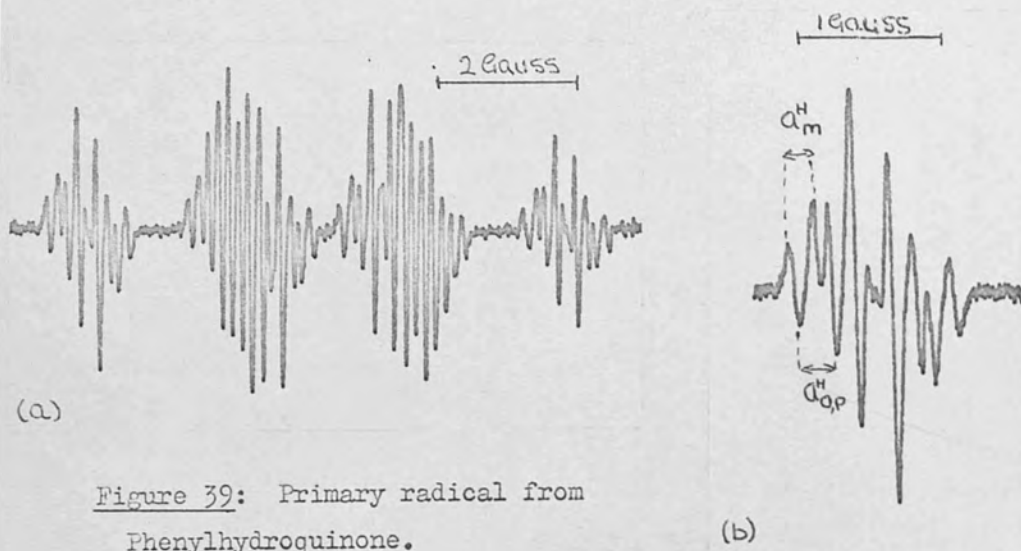
Figure 39: Primary radical from Phenylhydroquinone.

(a) Complete spectrum.
(b) Wings of spectrum.
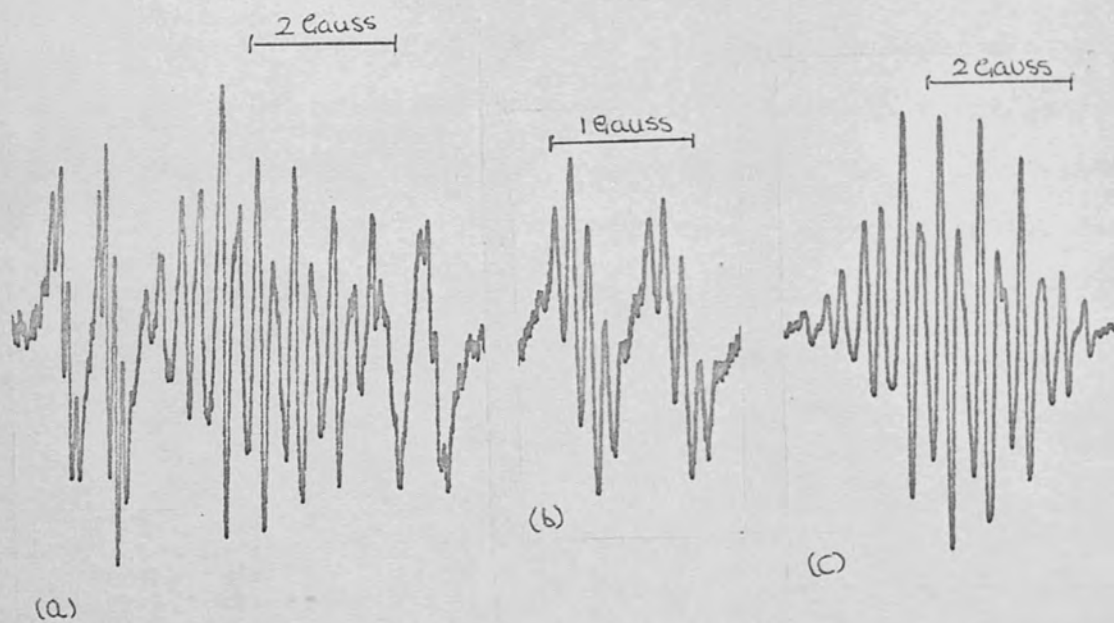
Figure 40: Secondary radicals from Phenylhydroquinone.

(a) Mixture of A and B.
(b) Wings of spectrum.
(c) Secondary radical A (after 30 minutes).

2 Gauss
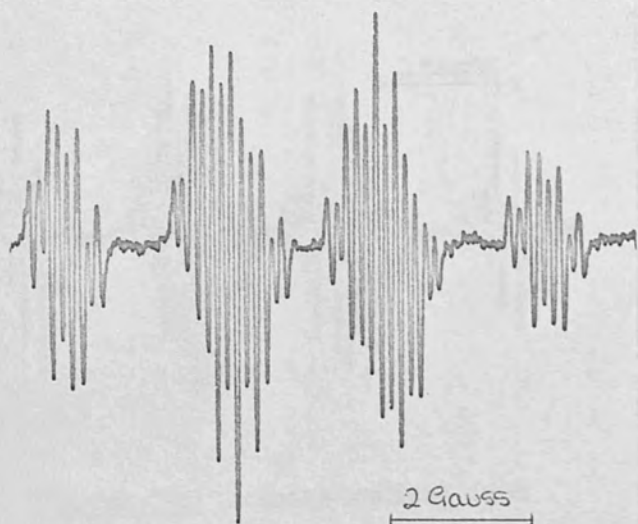
Figure 41: Primary radical from m-Chlorophenylhydroquinone.

2 Gauss
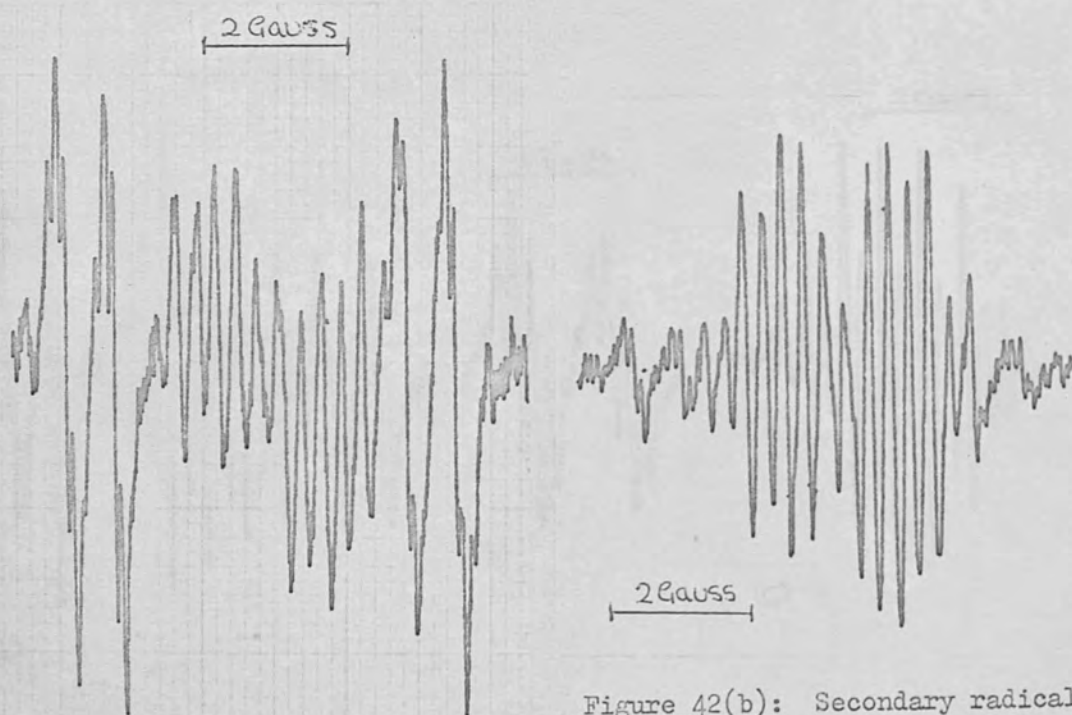
Figure 42(a): Mixture of
secondary radicals from
m-Chlorophenylhydroquinone.

2 Gauss

Figure 42(b): Secondary radical A
alone, after solution was left for
ca. 10 minutes.

although mixtures of secondary radicals were obtained, both
spectra could be analysed because the overlap between them
was minimal.

The E.S.R. spectra of the primary and secondary radic-
als from phenylhydroquinone are shown in figs. 39 and 40.
The primary radical clearly shows an approximate quartet
splitting (1:3:3:1) of ca. 2 Gauss, ascribed to the three
semiquinone ring protons.

Analysis of each side-group of lines (fig. 39b) reveals
the following hyperfine splittings:

    quartet splitting : 0.27G (1:3:3:1)

    triplet splitting : 0.16G (1:2:1)

These splittings are apparently due to coupling with the
aromatic protons in the phenyl group and show that the odd
electron is delocalised onto the second ring to some extent.

Figures 41 and 42 show the E.S.R. spectra of the
primary and secondary radicals from the meta-chloro comp-
ound. The aryl group coupling constants in the primary
radical,

    Quartet : 0.27G

    Doublet : 0.15G

show that the smaller splitting is due to coupling with
protons at the meta position, and that the larger ortho
and para splittings are equal.

The primary and secondary radicals from the para-
chloro compound are shown in figs. 43 and 44. The absence
of one of the larger splittings from the aryl group is
observed, as expected. In the primary radical the aryl
group shows:

> triplet splitting : 0.28G
>
> triplet splitting : 0.16G

Difficulties arose in the interpretation of several
of the spectra because the smallest splittings were occas-
ionally of the same order as the line widths, and since we
observe the first derivative of the absorption spectrum,
overlapping of adjacent maxima and minima can lead to
reductions of apparent intensity or even total annihilation
of some lines. This leads in certain cases to some uncert-
ainty in the smaller coupling constants.

Fig. 45, for example, shows the E.S.R. spectrum of the
primary radical from para-nitrophenylhydroquinone. The
three doublet splittings from the semiquinone ring protons
are easily obtained from the spectrum, but the coupling
with the four aryl ring hydrogens and the nitrogen gave a
splitting pattern consisting of eight equally spaced lines,
the separation of the lines being 0.15G (fig. 45b).

Some indication of the splittings in the primary
radical can be gained from the corresponding secondary
radical A (fig. 46), in which the coupling with the aryl

2 Gauss

½ Gauss
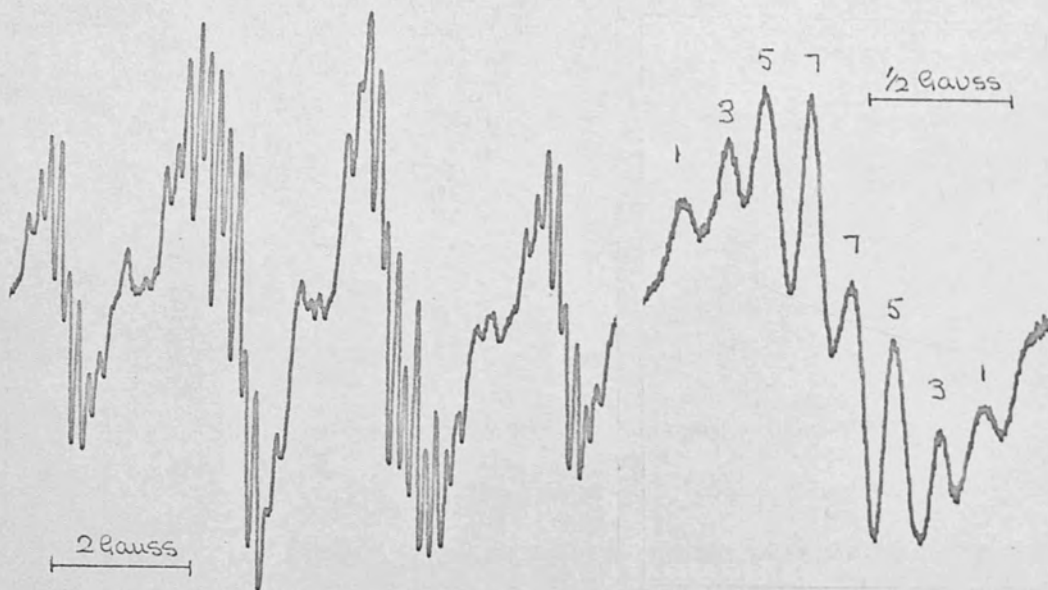
Figure 45: Primary radical from the Para-nitro compound.
    (a) Complete spectrum .
    (b) Wings, showing splitting from aryl group.

1 Gauss
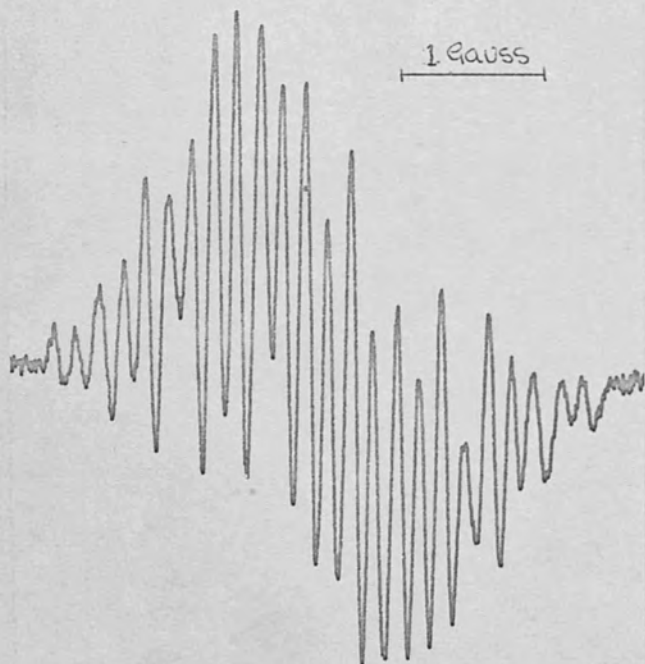
Figure 46: Secondary radical A from
    p-Nitrophenylhydroquinone.

group is generally about twice as large. In secondary
radical A:

$$a_{ortho(H)} \quad : \quad 0.60G \ (1:2:1)$$

$$a_{meta(H)} \quad : \quad 0.30G \ (1:2:1)$$

$$a_{N} \quad : \quad 0.15G \ (1:1:1)$$

In fact the 8-line pattern in the E.S.R. spectrum of
the primary radical from the para-nitro compound can be
rationalised using the coupling constants:

$$a_{ortho(H)} \quad : \quad 0.30G \ (1:2:1)$$

$$a_{meta(H)} \quad : \quad 0.15G \ (1:2:1)$$

$$a_{N} \quad : \quad 0.075G \ (1:1:1)$$

This gives a splitting pattern of 1:1:3:2:5:3:7:4:7:3:5:2:
3:1:1, but if alternate lines are missing due to overlapping
of adjacent maxima and minima, then this reduces to an
8-line spectrum (1:3:5:7:7:5:3:1), consistent with that of
fig. 45b.

11.   DISCUSSION OF THE COUPLING CONSTANTS OF RADICALS

DERIVED FROM ARYLHYDROQUINONES

The primary and secondary radicals from meta- and
para- substituted arylhydroquinones, with their E.S.R.
coupling constants are given in tables V, VI and VII.

Table V : Coupling Constants of Primary Radicals
from Meta- and Para-Substituted Arylhydroquinones.

Aryl Group	Coupling Constants (Gauss)						
	a_3	a_5	a_6	Aryl Group Splittings			
				$a_{o(H)}$	$a_{m(H)}$	$a_{p(H)}$	$a_{substituent}$
Ph	1.99	2.12	2.56	0.27	0.16	0.27	
Para-F	2.01	2.12	2.54	0.28	0.15		$a_F = 0.57$
Para-Cl	2.10	2.10	2.54	0.28	0.16		
Meta-Cl	2.00	2.13	2.52	0.27	0.15	0.27	
Para-Br	2.04	2.04	2.48	0.28	0.16		
Para-Me	1.88	2.13	2.55	0.28	0.16		$a_{Me} = 0.28$
Para-OMe	1.85	2.16	2.56	0.30	0.15		
Meta-OMe	2.02	2.05	2.54	0.26	0.15	0.26	
Para-OH	1.38	2.33	2.53	0.32	0.14		
Meta-OH	1.81	2.17	2.57	0.26	0.15	0.26	
Para-NO_2	2.38	1.92	2.50	0.30	0.15		$a_{NO_2} = 0.07*$
Meta-NO_2	2.26	1.94	2.44	0.27	0.17	0.27	$a_{NO_2} = 0.04*$
Para-CO_2H	2.10	2.10	2.56	0.27	0.17		
Para-CO_2Me	2.26	1.95	2.56	0.29	0.18		
Para-Ph	1.98	2.10	2.58	0.28	0.20		

*: Unresolved splitting, estimated from observed splitting
in Secondary Radical A.

Table VI : Coupling Constants of Secondary Radicals A from Meta- and Para-Substituted Arylhydroquinones.

| Aryl Group | Coupling Constants (Gauss) | | | | | |
| | a_3 | a_6 | Aryl Group Splittings | | | |
			$a_{o(H)}$	$a_{m(H)}$	$a_{p(H)}$	$a_{substituent}$
Ph	0.50	1.08	0.54	0.31	0.54	
Para-F	0.51	1.09	0.58	0.30	—	$a_F = 1.09$
Para-Cl	0.48	1.16	0.59	0.31	—	
Meta-Cl	0.52	1.19	0.54	0.29	0.54	
Para-Br	0.49	1.13	0.59	0.31	—	
Para-Me	0.50	0.90	0.58	0.31	—	$a_{Me} = 0.58$
Para-OMe	0.53	0.90	0.59	0.29	—	
Meta-OMe	0.54	1.08	0.54	0.29	0.54	
Para-OH	0.53	0.53	0.65	0.27	—	
Meta-OH	0.51	0.96	0.51	0.27	0.51	
Para-NO_2	0.45	1.48	0.60	0.30	—	$a_N = 0.15$
Meta-NO_2	0.43	1.42	0.60	0.30	0.60	$a_N = 0.09$
Para-CO_2H	0.48	1.17	0.58	0.32	—	
Para-Ph	0.50	1.12	0.58	0.33	—	

Table VII: Coupling Constants of Secondary Radicals B
from Meta- and Para-Substituted Arylhydroquinones.

Aryl Group	Coupling Constants (Gauss)					
	a_3	a_5	Aryl Group Splittings			
			$a_{o(H)}$	$a_{m(H)}$	$a_{p(H)}$	$a_{substituent}$
Ph	0.67	4.52	0.12	0.12	0.12	
Para-F	0.66	4.48	0.12	0.12	—	$a_F = 0.24$
Para-Cl	0.68	4.58	0.12	0.12	—	
Meta-Cl	0.67	4.62	0.12	0.12	0.12	
Para-Br	0.67	4.56	0.12	0.12	—	
Para-Me	0.67	4.42	0.13	0.13	—	$a_{Me} = 0.13$
Para-OMe	0.65	4.40	0.12	0.12	—	
Meta-OMe	0.68	4.56	0.12	0.12	0.12	
Para-OH	0.63	4.00	0.14	0.10	—	
Meta-OH	0.66	4.36	0.12	0.12	0.12	
Para-NO$_2$	0.70	4.86	0.12	0.12	—	
Meta-NO$_2$	*					
Para-CO$_2$H	0.67	4.66	0.12	0.12	—	
Para-Ph	0.66	4.52	0.12	0.12	—	

* :   Spectrum not obtained.

The assignments of aryl group splittings were made
with reference to unambiguous cases (e.g. meta-chloro-
phenyl), and it was found that the couplings with ortho and
para protons were equal, and of the order of twice those
for meta protons.

The semiquinone ring splittings were more difficult
to assign, but the trends observed on changing the aryl
group were consistent with the rules applied to alkylsemi-
quinones in part II. The assignments given in tables V-VII
are based on these rules, which are shown to consistently
account for the observed splittings in the primary and
secondary radicals.

Aryl group splittings

The splittings from aryl protons were found to be
fairly independent of the nature of the substituent on the
aryl ring, and the total splitting from ortho and meta
protons in the case of a para substituent X was found to
be reasonably constant (see table VIII).

Table VIII. Coupling constants of ortho and meta protons
of the aryl group with a para-substituent X.

| Substituent X | Coupling constants (Gauss) | | | | | |
| | Primary | | | Secondary A | | |
	a_{ortho}	a_{meta}	total	a_{ortho}	a_{meta}	total
H	0.27	0.16	0.86	0.54	0.31	1.70
F	0.28	0.15	0.86	0.58	0.30	1.76
Cl	0.28	0.16	0.88	0.59	0.31	1.80
Me	0.28	0.16	0.88	0.58	0.31	1.78
OMe	0.30	0.15	0.90	0.59	0.29	1.76
OH	0.32	0.14	0.92	0.65	0.27	1.84
NO_2	0.30	0.15	0.90	0.60	0.30	1.80
Ph	0.28	0.20	0.96	0.58	0.33	1.82

From table VIII it appears that any substituent on
the aryl ring is capable of increasing the total spin
density on ring protons, but the effect is small. The
largest increase occurs with OH as substituent, the ortho
splitting being increased by ca. 20% relative to the unsub-
stituted phenyl group.

The effect on aryl proton splittings of a meta-
substituent is even smaller than that for a para-substituent,
as might be expected, and shows no definite trend.

2 Gauss

Figure 47:   Primary radical from p- Fluorophenylhydroquinone.

2 Gauss

1 Gauss
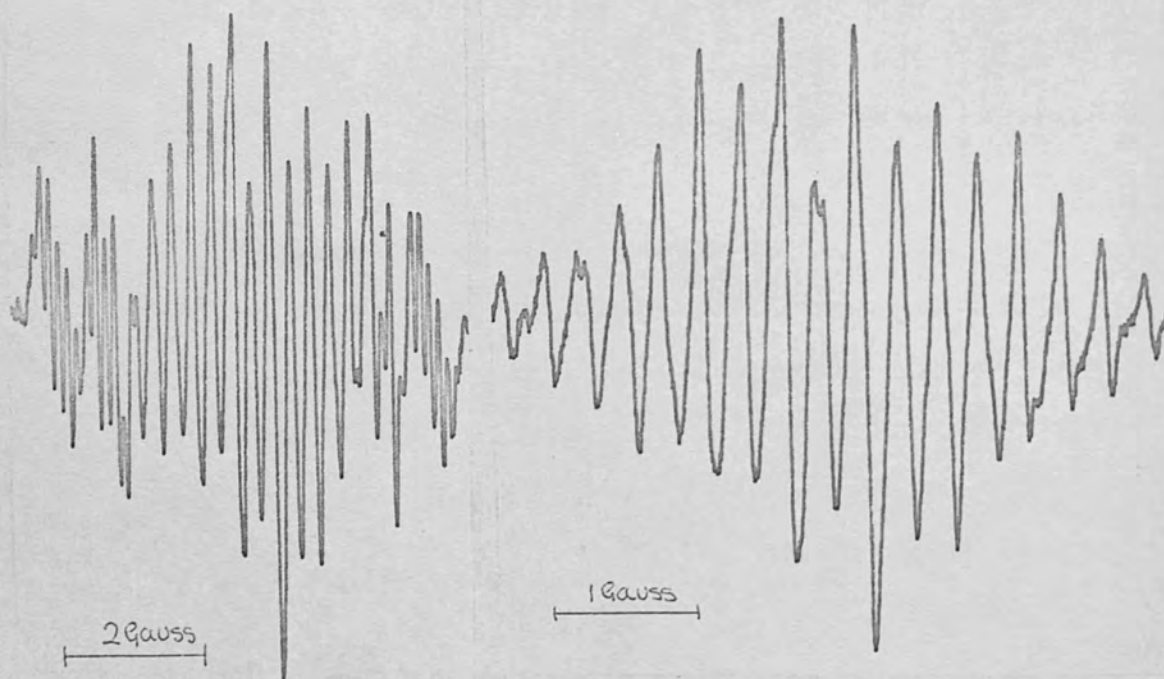
Figure 48:   (a)   Mixture of secondary radicals from p-fluoro compound.

(b)   Secondary radical A alone.

When the overall spin density in the aryl ring is large, as in secondary radical A, the ortho and para proton coupling constants are of the order of twice those of the meta protons, but as the overall coupling decreases the splittings become more equal (table IX).

Table IX. Splittings from ortho and meta protons in the primary and secondary radicals with a para-substituent X.

| Substituent X | Coupling Constants (Gauss) | | | | | |
| | A | | Primary | | B | |
	a_{ortho}	a_{meta}	a_{ortho}	a_{meta}	a_{ortho}	a_{meta}
H	0.54	0.31	0.27	0.16	0.12	0.12
Cl	0.59	0.31	0.28	0.16	0.12	0.12
OH	0.65	0.27	0.32	0.14	0.14	0.10
NO_2	0.60	0.30	0.30	0.15	0.12	0.12

As well as coupling with the aromatic protons of the aryl group, splitting from the substituent X was observed in certain cases:

      1. In the three radicals from para-fluorophenylhydroquinone, (figures 47 and 48), fluorine splittings were observed which were about twice as large as those for aromatic protons in the same position.

2 Gauss

(a)

½ Gauss

$\leftarrow a_m^H \rightarrow$

$\leftarrow a_p^{CH_3} \rightarrow$
$= a_o^H$

(b)
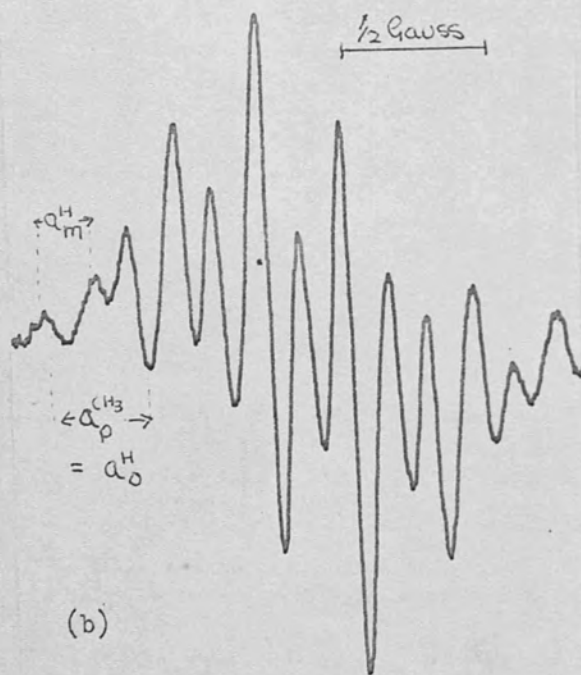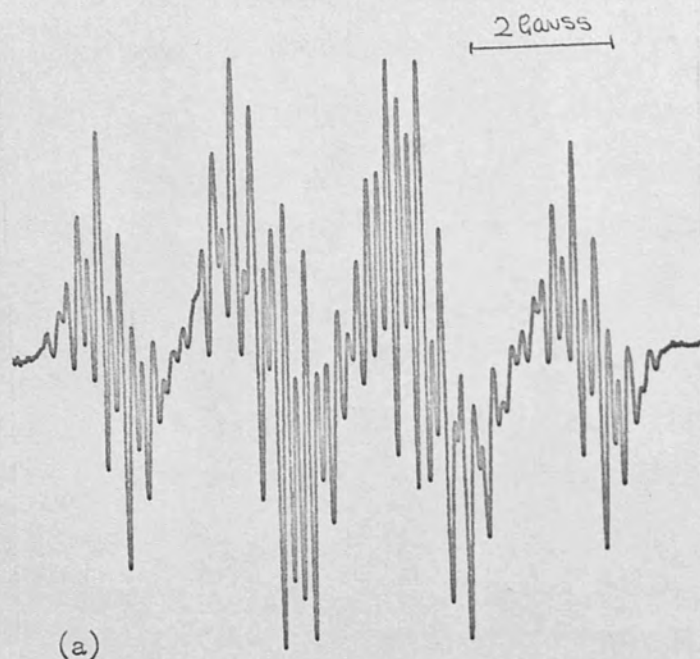
Figure 49 : Primary radical from p- Methylphenylhydroquinone.

    (a) Complete spectrum.

    (b) Wings, showing aryl group splittings.

	Primary	Secondary A	Secondary B
Ortho (H)	0.28G	0.58G	0.12G
Para (F)	0.57G	1.09G	0.24G

Previous observations of aromatic fluorine splittings in aryloxy radicals[39] and semiquinones[30] also show a ratio of a_F : a_H of approximately 2:1.

2.   Methyl proton splittings in the para-methyl radicals are the same as expected for an aromatic proton in the para position. In the primary radical from the para-methylphenyl compound, for example (fig. 49) a sextet splitting of 0.28G was observed, due to equal coupling with the two ortho protons and the para methyl group.

Methyl proton splittings in aryloxy radicals[39] and in methylsemiquinones[27] are generally of the same order as the corresponding aromatic proton splittings, although the spin densities are of the opposite sign in the two cases[17].

3.   Splitting from nitrogen in the meta and para-nitro substituted radicals is apparent, but is only large enough to be measured in the secondary radicals A, where the aryl group coupling is increased by the additional oxygen on the semiquinone ring. The para-nitro radical (fig. 46), has a nitrogen splitting of 0.15G compared to that of the ortho protons splitting of 0.60G. This ratio of 1:4 is similar to that observed in the para-nitro-
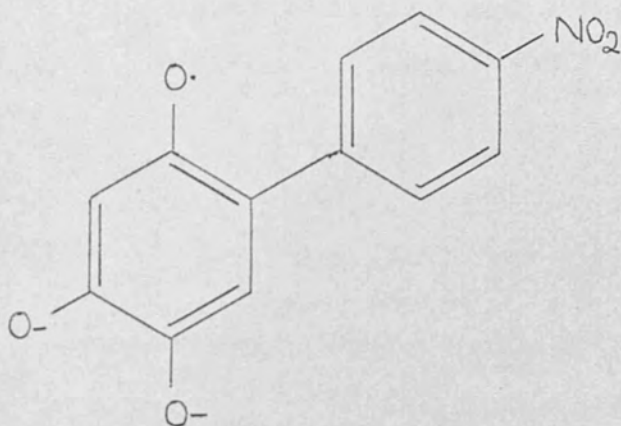
I

phenoxy radical[39].

The fact that splittings from flourine, nitrogen and methyl in the para position are of the order expected from the values obtained in phenoxy radicals, implies the mechanism for the transfer of spin density is similar in both cases (for para substituents), i.e. through π-type interactions.

Semiquinone ring splittings.

The assignments for the semiquinone ring coupling

2 Gauss

Fig. 50: Primary Radical from Para-Bromophenylhydroquinone.

1 Gauss

2 Gauss

a_o^H

a_m^H

(a)

(b)
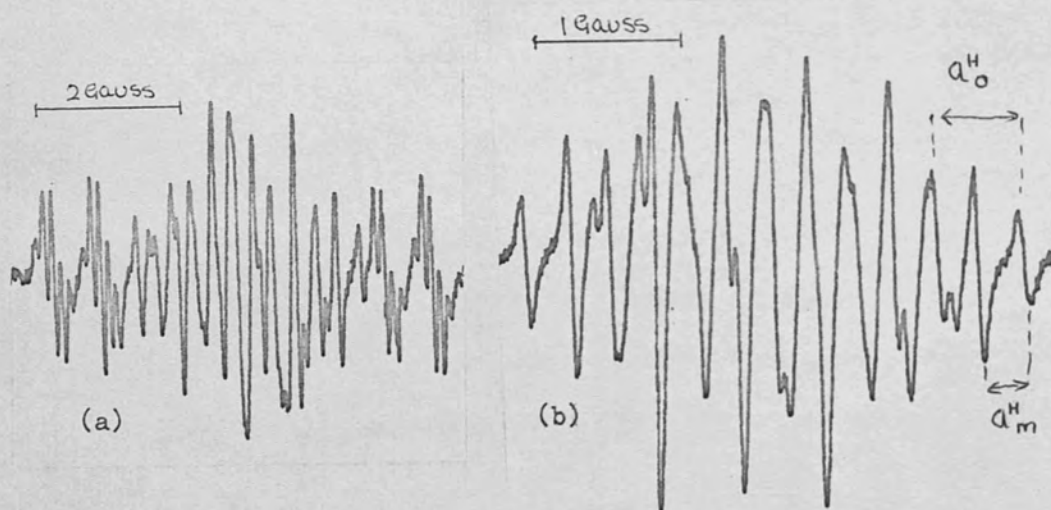
Fig. 51: Secondary Spectra from p-Bromo Compound.
(a) : Mixture of Secondary Radicals.
(b) : Secondary Radical A only.

constants given in tables V-VII are based on obvious trends in the splittings with the change of substituent in the aryl group. The rules adopted in part II to account for the splittings in alkylsemiquinones are found to apply equally well to arylsemiquinones.

Protons ortho to the aryl group

In the secondary radicals B, the two semiquinone ring splittings, a_3 and a_5, are totally unambiguous, a_5 being

much the larger of the two due to the additional oxygen atom para with respect to position-5. In these radicals we can follow the effects of groups X on the two semiquinone ring splittings.
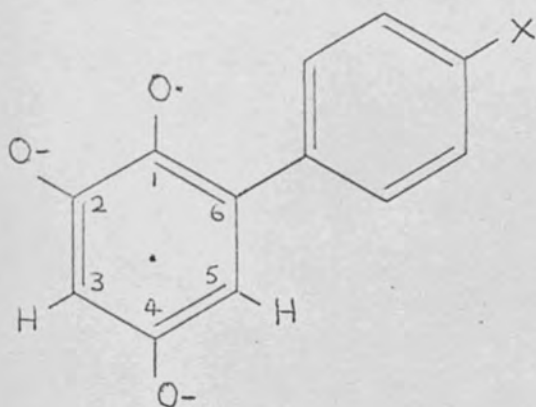
Table X shows the trend observed for the large splitting a_5 in secondary radicals B on changing the substituent X. The effect is seen to be quite large, a change in the magnitude of the splitting of almost 1 Gauss on going from OH to NO_2 as the para substituent X in the aryl group.
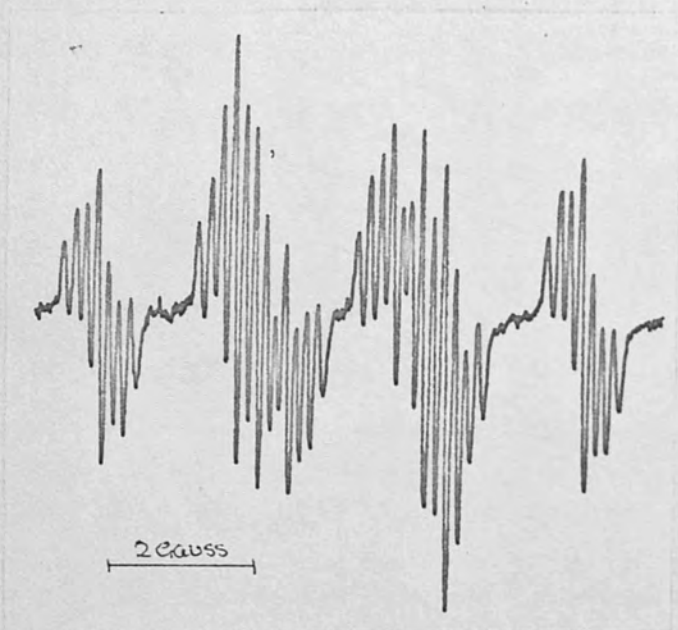
Fig. 52 : Primary Radical from Para- Methoxy Compound.

(a)

(b)

Fig. 53 : Secondary Spectra from Para - Methoxy Compound.

    (a)   Mixture of Secondary Radicals.
    (b)   Secondary Radical A alone.

Table X

Substituent X	OH	OMe	Me	H	Cl	CO_2H	NO_2
Coupling Constant (Gauss)	4.00	4.40	4.42	4.52	4.58	4.66	4.86

It is clear that electron-donating substituents in the aryl group decrease spin density at the 5-position, ortho to the aryl group, the order of the splittings directly following the expected order of electron-releasing ability of the group X. The fact that the hydroxyl group has a much greater effect than methoxy seems to imply that the hydroxyl proton has been lost to the alkaline medium, and the group producing the effect is, in fact, $-O^-$.

The assignments of the splittings for this position in the primary radicals and secondary radicals A are based on the observations of similar trends in one of the splittings in these radicals. It was shown in part II that the effect at the ortho position was similar in all the three types of radicals from alkylhydroquinones.

Table XI shows the splittings assigned to protons ortho to the aryl group in the primary radicals and secondary radicals A. The largest changes are again recorded for the hydroxyl and the nitro groups, as might be expected since they are by far the strongest groups electronically.

Fig.54: Primary Radical from Meta-Methoxy Compound.

Fig. 55: Secondary Radicals from Meta-Methoxy Compound.

    (a) Mixture of secondary radicals.

    (b) Secondary radical A.

Table XI

Substituent X	OH	OMe	Me	H	Cl	CO_2H	NO_2
Primary	1.38	1.85	1.88	1.99	2.10	2.10	2.38
Secondary A	0.53	0.90	0.90	1.08	1.16	1.17	1.48

It is significant that the changes in the coupling constants of the protons ortho to the aryl group are comparable in the three types of radicals. On going from OH to NO_2, for example, the splittings increase by ca. 1 Gauss, and this shows that the effect is fairly independent of the actual spin density at the carbon bearing the substituent.

Protons meta and para to the aryl group.

In the secondary radicals only two semiquinone ring splittings are present and since one has been assigned to

A   B

4 Gauss
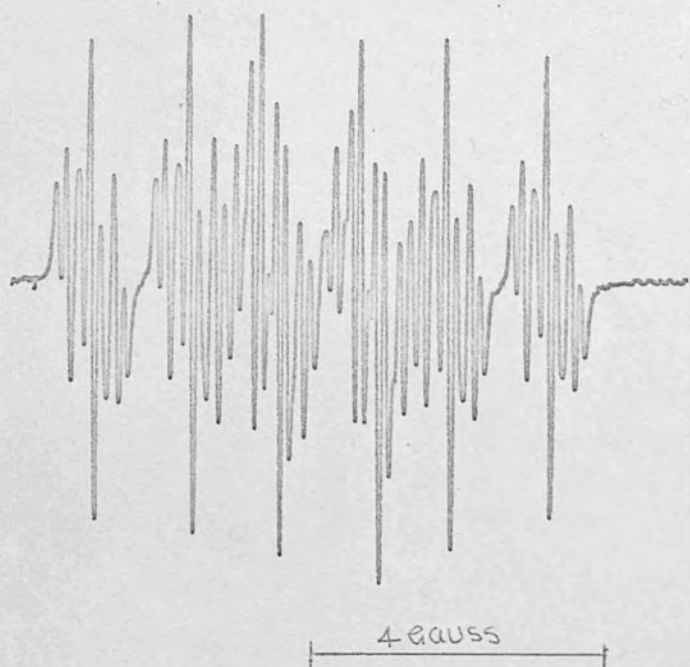
Fig. 56: Primary Radical from Para-Hydroxyphenylhydroquinone.

4 Gauss

(a)

(b)

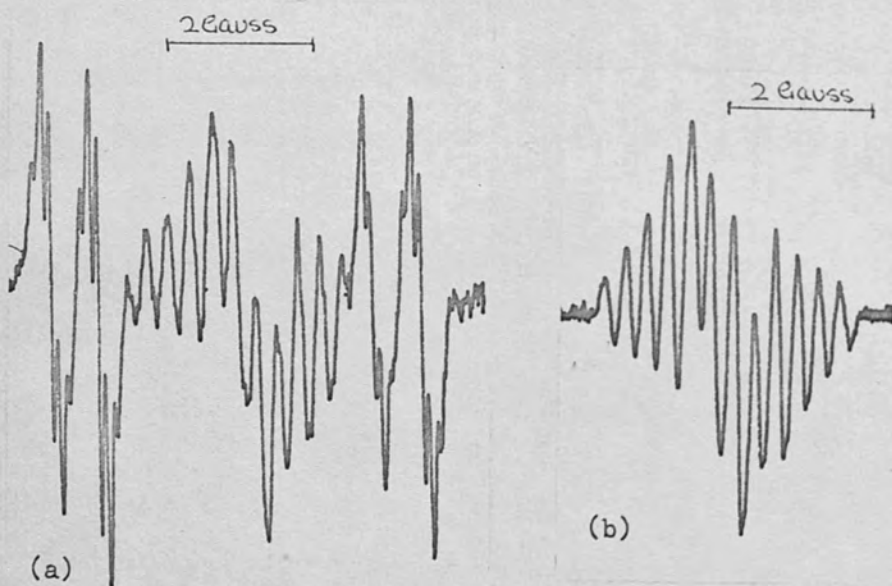1 Gauss

Fig. 57: Secondary Spectra from Para-Hydroxy Compound.

(a) Mixture of secondary radicals.

(b) Secondary radical A.

the position ortho to the aryl group, the other is determ-
ined as that due to coupling with the proton at the 3-
position, flanked by two oxygens on the semiquinone ring.
By following changes in a_3 in the two secondary radicals,
the effect of the aryl group at the meta position (secondary
A) and the para position (secondary B) can be investigated.

In part II it was shown that
the effects of a group Y in the
primary radicals (Y= Alkyl, OMe)
on the splittings a_5 and a_6 were
reversed in the secondary
radicals.A and B where those
positions were flanked by two
oxygens. It was suggested that
this was due to the primary radicals having a positive spin
density on the ring carbons, while carbon-3 in the second-
ary radicals had a negative spin density. Molecular orbital
calculations on the system have implied that this is in
fact the case[37].

On this basis we would expect the splittings a_3 in the
secondary radicals from arylhydroquinones to show the
opposite trends to the splittings a_5 and a_6 in the primary
radicals. Table XII shows the effects of substitution in
the para position of the aryl ring on the splittings a_3 in
the secondary radicals A and B.

<u>Table XII</u>

Substituent in aryl ring	Coupling Constants a_3 (Gauss)	
	Secondary A	Secondary B
OH	0.53	0.63
OMe	0.53	0.65
Me	0.50	0.67
H	0.50	0.67
Cl	0.48	0.68
CO_2H	0.48	0.67
NO_2	0.45	0.70

A   B
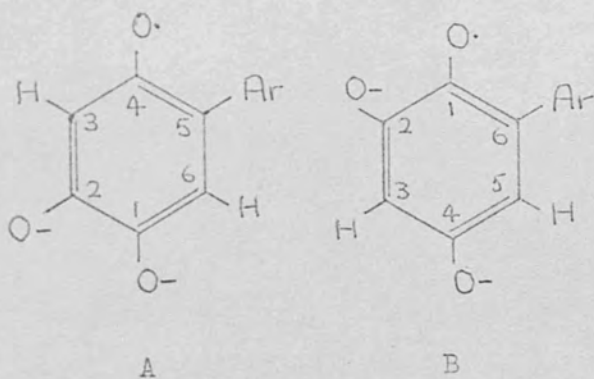
The following rules seem to apply for the splitting a_3 in the secondary radicals A and B from arylhydroquinones.

    1.   The splitting a_3 is greater when para to the aryl group than when meta to the aryl group.

    2.   The effect of electron-releasing substituents in the aryl ring is to increase a_3 when
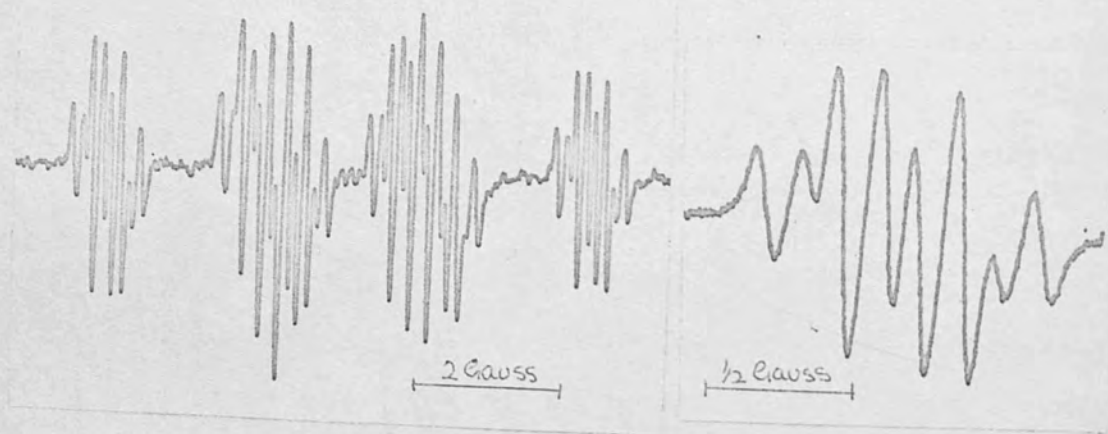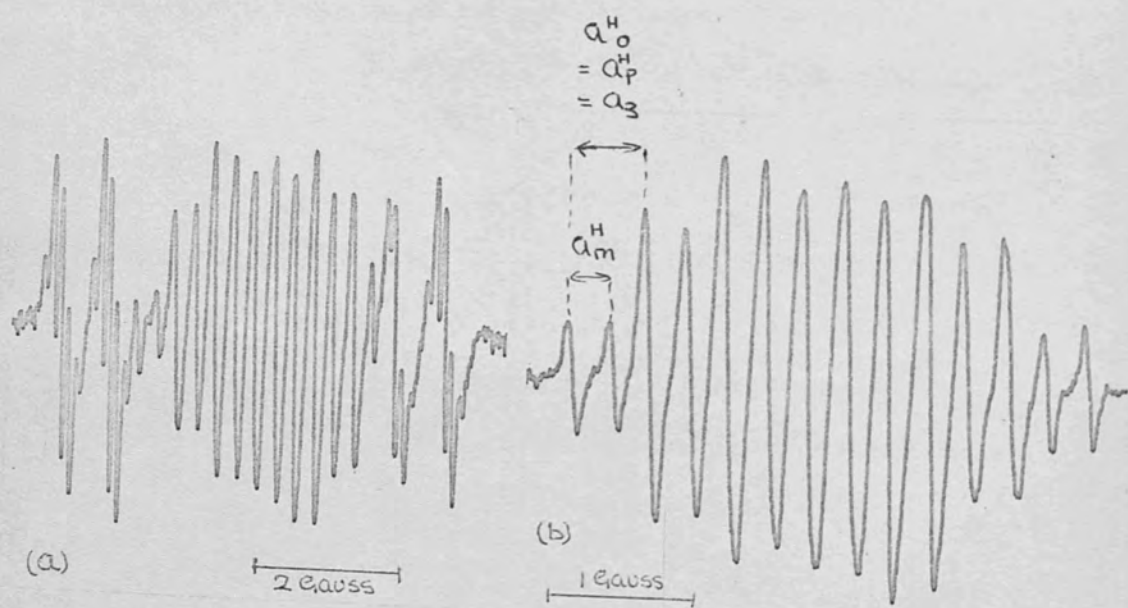
Fig.58: Primary Radical from Meta-Hydroxy Compound.

(a)

(b)
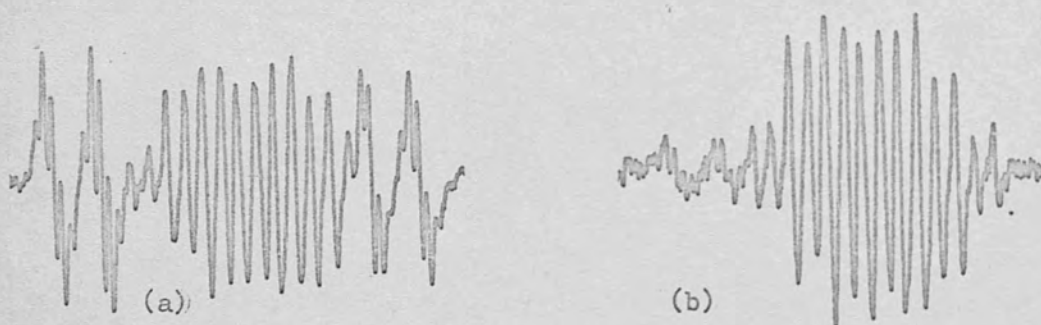
Fig.59: Secondary Radicals from Meta-Hydroxy Compound.

    (a) Mixture of secondary radicals.
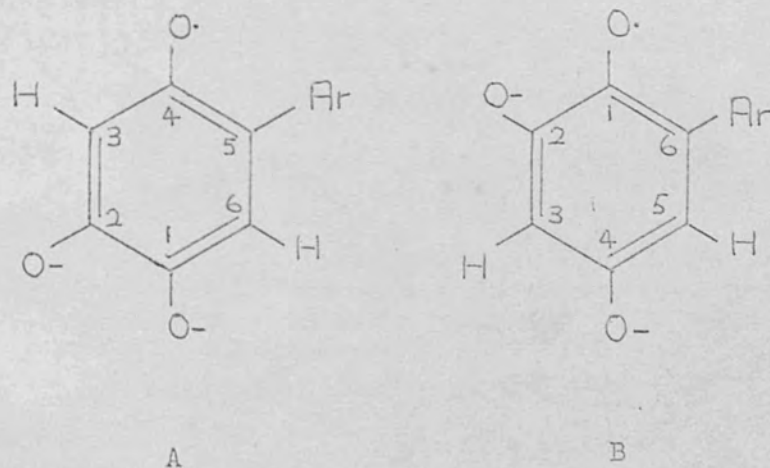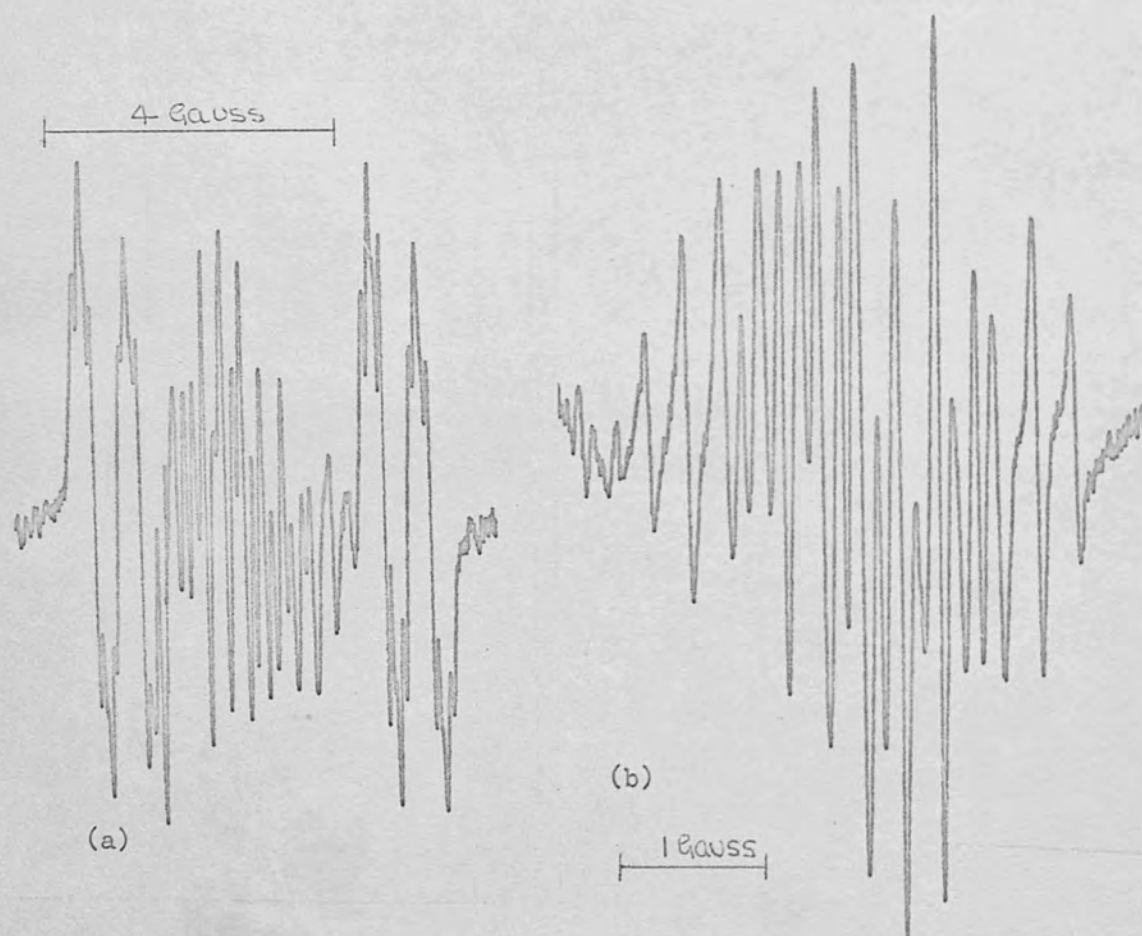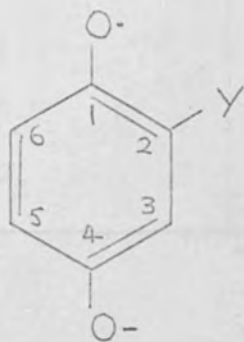
    (b) Secondary radical A.

meta to the aryl group and decrease a_3 when para to the aryl group.

In the primary radicals the splittings from a_5 and a_6 show that one is increased by electron-donating substituents, while the other remains fairly constant and is always the larger of the two. The former smaller splitting has therefore been assigned to the position para to the aryl group (a_5) since the trend at that position in the primary radical is then opposite to that in secondary radical B, as is observed for alkylsemiquinones. The larger, and fairly constant splitting has been assigned to the position meta to the aryl group (a_6).

With this assignment of a_5 and a_6, the trends in the coupling constants are directly in line with those observed for the semiquinones discussed in part II containing alkyl and other substituents (O^-, OMe, Cl). The splitting a_6, meta to the substituent, was shown to be fairly independent of the electron-donating ability of the group, but more dependent on the size. For arylsemiquinones containing only meta and para-substituents, the steric interaction between the aryl ring and the adjacent oxygen is expected to be reasonably unchanged throughout the series, and in fact the splittings assigned to this position are found to be fairly constant.

The coupling constants assigned to a_5 in the primary radicals follow the usual trend of being increased by electron-donating substituents, the effect being smaller than the accompanying decrease at the ortho position.

A set of rules can now be drawn up to cover the complete range of primary and secondary radicals discussed in this thesis. These rules consistently account for the observed hyperfine splittings in almost all cases.

Rules governing hyperfine splittings in primary and secondary radicals.

1. In the primary and secondary radicals the semiquinone ring carbons carry a positive spin density with the exception of carbon-3 in the secondary radicals, which is flanked by two oxygens, and carries a negative spin density.

2. Spin densities on ring positions ortho to a substituent Y become less positive as the electron-donating ability of the group increases. The following order of influence of Y is observed.

$$Y = O^- \gg OMe \gg p\text{-}OH\phi > t.butyl > Et \approx Me > p\text{-}OMe\phi \approx p\text{-}Me\phi >$$
$$\phi > Cl > H \approx p\text{-}NO_2\phi$$
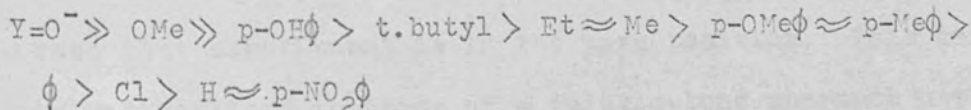
3. Spin densities on ring positions meta to a

substituent become less positive with the electron-donating
ability of Y, but the effect is much smaller than that at
the ortho position. Spin densities become more positive
as the steric bulk of the group increases.

4.   Spin densities on ring positions para to a
substituent become more positive with the electron-donating
ability of the group Y. The order of influence of Y is the
same as that at the ortho position. The spin densities
appear to become less positive as the steric bulk of the
substituent is increased.

These rules consistently account for the observed
trends in the splittings in all three types of radicals
studies. In alkylsemiquinones the steric and electronic
effects are unable to be considered separately, but it
appears that in the arylsemiquinones discussed here the
steric influence of the group can be considered constant
throughout the series, and only the electronic effects of
the substituent are involved.

The effects produced by substituents in the meta
position of the aryl group are, as expected, less than
when that substituent is in the para position. This can
be rationalised in terms of a valence-bond approach to these
radicals in which the odd electron is largely associated

with the oxygens. The only canonical structures which have reasonably low energies and can lead to delocalisation of the odd elctron are those having a double bond to, or a negative charge on, the oxygen. The delocalisation of the odd electron onto the aryl group must occur largely through structures of the type I-III and explains why the

I   II   III
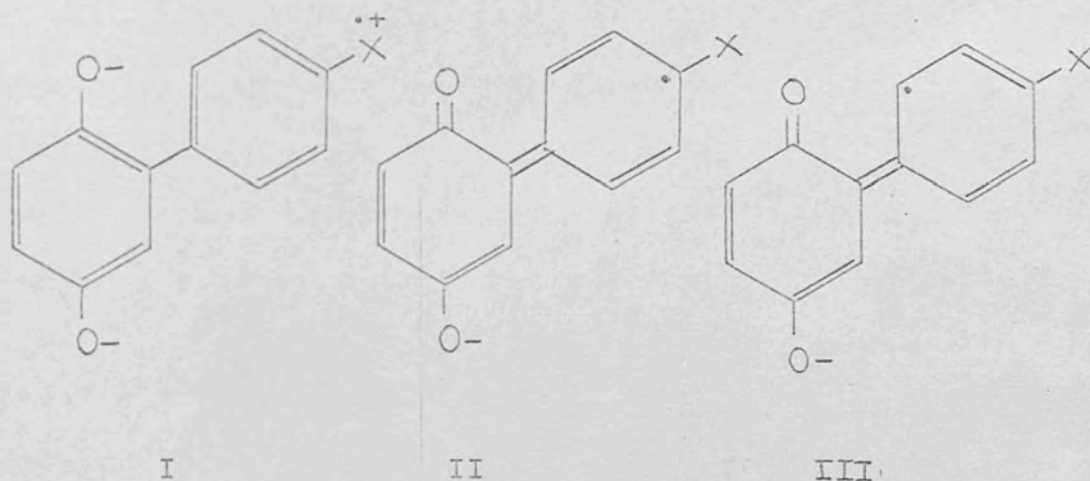
ortho and para positions have greater spin density than the meta positions. A substituent in the meta position will clearly have less effect than a para substituent on the spin density distribution since it cannot be involved in structures of the type I.

Electron releasing substituents decrease the total spin density on proton-bearing carbons in the three types of radical. The aryl group, then, attracts spin density

more when the substituent X releases electrons easily.

Structures of type I suggest an explanation for this observation, and for O⁻ as substituent, the structure IV is likely to be of some importance in reducing the total spin density associated with the semiquinone ring.
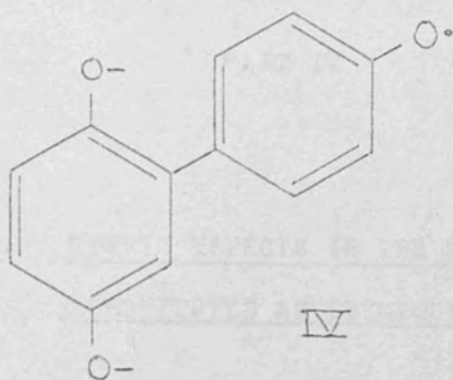
O—

O•

O—

IV

PART IV

12. STERIC EFFECTS IN THE E.S.R. SPECTRA OF ORTHO-
SUBSTITUTED ARYLSEMIQUINONES

In part III the E.S.R. spectra of radicals derived
from arylhydroquinones containing meta- and para-substit-
uents in the aryl group were discussed. The electronic
effects of these substituents on the hyperfine splittings
of protons attached to the semiquinone ring and the aryl
fragment were examined. The results indicated that the
distribution of spin density within the semiquinone ring
was highly dependent on the electron-releasing ability of
the substituent, and aided in the isolation of the various
factors which determine the hyperfine splittings of semi-
quinones in general.

When ortho-substituents are introduced into the aryl
ring, it would be expected that the conformations of the
radicals, with respect to the dihedral angle between the
two rings, would be highly dependent on the amount of
ortho substitution and on the sizes of the substituents.

To investigate the steric effects in this system a
wide range of arylhydroquinones have been prepared contain-
ing one or two ortho substituents in the aryl ring and the
E.S.R. spectra of the primary and secondary radicals obtain-
ed.

Production of the primary and secondary radicals.

The arylquinones were prepared by the same method as
that described for the meta- and para-substituted compounds,
by direct arylation of ρ-benzoquinone via the diazonium
salts[52]. The extra steric strain in the ortho-substituted
compounds was evident from the fact that they were initially
obtained as oils. They were, however, eventually obtained
in pure crystalline state (see experimental section).
Reduction of the arylquinones with zinc and 25% hydrochloric
acid yielded the corresponding hydroquinone.

Primary radicals were generated in the usual way from
the corresponding hydroquinones in mildly alkaline solutions
with 50% aqueous ethanol as solvent.

Secondary radicals were obtained from the hydroquinones
in $7\frac{1}{2}$% NaOH solution. As for the meta- and para-substituted
compounds, a mixture of the two isomeric secondary radicals
was initially obtained, but secondary radical B decayed more
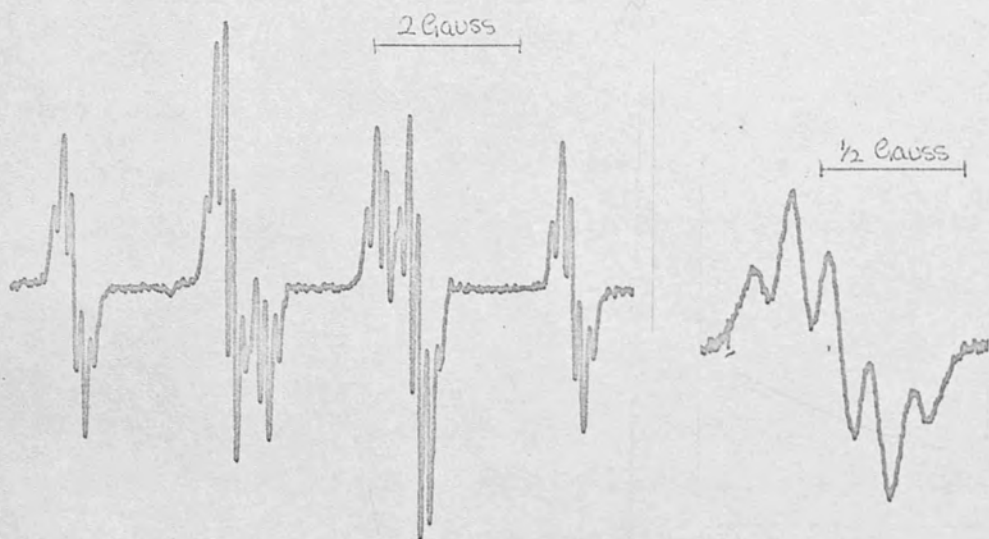
Fig. 60:   Primary radical from Ortho- Methyl Compound.
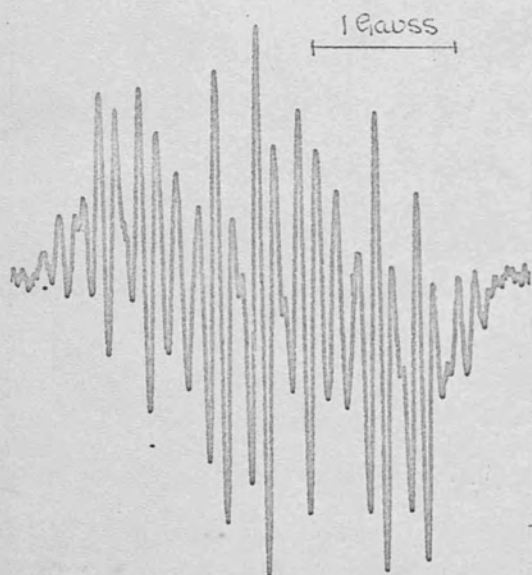
Fig. 61:   Secondary radical A from Ortho-Methyl Compound.

quickly when the solutions were left and a pure spectrum
of A could be recorded. The overlap between the spectra of
A and B was at the most very small, and both spectra could
be analysed.

Discussion of the E.S.R. Spectra of Ortho-substituted Arylsemiquinones.

The radicals obtained from ortho-substituted aryl-
hydroquinones and their E.S.R. coupling constants are given
in tables XIII - XV. The corresponding meta- and para-
substituted radicals have been included in these tables for
easy comparison of the effects of substitution at the
different aryl ring positions.

A number of the E.S.R. spectra obtained are reproduced
along with the discussion of the hyperfine splittings.

Semiquinone ring splittings

The effects produced by ortho substituents on the
semiquinone ring splittings are much smaller than when
those substituents are in the para position, and are comp-
arable to those in the corresponding meta derivatives.

TableXIII: Coupling Constants of Primary Radicals from Mono-Substituted Arylhydroquinones.

Aryl Group	Coupling Constants (Gauss)						
	a_3	a_5	a_6	Aryl Group Splittings			
				$a_{o(H)}$	$a_{m(H)}$	$a_{p(H)}$	$a_{substituent}$
Ph	1.99	2.12	2.56	0.27	0.16	0.27	
Ortho-F	2.07	2.21	2.52	0.16	0.16	0.16	$a_F = 0.56$
Meta-F	2.02	2.13	2.56	0.28	0.15	0.28	$a_F \approx 0.04$*
Para-F	2.01	2.12	2.54	0.28	0.15	---	$a_F = 0.57$
Ortho-Cl	2.12	2.22	2.52	⊕			
Meta-Cl	2.00	2.13	2.52	0.27	0.15	0.27	
Para-Cl	2.10	2.10	2.54	0.28	0.16	---	
Ortho-Br	2.10	2.20	2.50	0.10	0.10	0.10	
Para-Br	2.04	2.04	2.48	0.28	0.16	---	
Ortho-Me	2.09	2.20	2.51	0.13	0.13	0.13	$a_{Me} \approx 0.05$*
Meta-Me	1.96	2.14	2.58	0.27	0.18	0.27	$a_{Me} = 0.09$
Para-Me	1.88	2.13	2.55	0.28	0.16	---	$a_{Me} = 0.28$
Ortho-OMe	2.05	2.17	2.63	0.15	0.15	0.15	
Meta-OMe	2.02	2.05	2.54	0.26	0.15	0.26	
Para-Ome	1.85	2.16	2.56	0.30	0.15	---	
Ortho-OH	1.82	2.28	2.65	0.14	0.14	0.14	
Meta-OH	1.81	2.17	2.57	0.26	0.15	0.26	
Para-OH	1.38	2.33	2.53	0.32	0.14	---	
Ortho-NO_2	2.10	2.10	2.56	0.16	0.16	0.16	$a_{NO_2} \approx 0.06$ *
Meta-NO_2	2.26	1.94	2.44	0.27	0.17	0.27	$a_{NO_2} \approx 0.04$*
Para-NO_2	2.38	1.92	2.50	0.30	0.15	---	$a_{NO_2} \approx 0.07$*
Ortho-Ph	2.06	2.06	2.60	⊕			
Para-Ph	1.98	2.10	2.58	0.28	0.20	---	

* : Unresolved splitting, estimated from Secondary A.

⊕ : Aryl group splittings not resolved.

Table XIV :   Coupling Constants of Secondary Radicals A
from Mono-Substituted Arylhydroquinones.

Aryl Group	Coupling Constants (Gauss)					
	a_3	a_6	Aryl Group Splittings			
			$a_{o(H)}$	$a_{m(H)}$	$a_{p(H)}$	$a_{substituent}$
Ph	0.50	1.08	0.54	0.31	0.54	
Ortho-F	*					
Meta-F	0.53	1.15	0.53	0.28	0.53	$a_F = 0.08$
Para-F	0.51	1.09	0.58	0.30	----	$a_F = 1.09$
Ortho-Cl	0.50	1.27	0.25	0.25	0.20	
Meta-Cl	0.52	1.19	0.54	0.29	0.54	
Para-Cl	0.48	1.16	0.59	0.31	----	
Ortho-Br	0.48	1.23	0.24	0.24	0.17	
Para-Br	0.49	1.13	0.59	0.31	----	
Ortho-Me	0.51	0.96	0.28	0.28	0.28	$a_{Me} = 0.11$
Meta-Me	0.52	1.06	0.52	0.32	0.52	$a_{Me} = 0.16$
Para-Me	0.50	0.90	0.58	0.31	----	$a_{Me} = 0.58$
Ortho-OMe	0.52	1.12	0.26	0.26	0.26	
Meta-OMe	0.54	1.08	0.54	0.29	0.54	
Para-OMe	0.53	0.90	0.59	0.29	----	
Ortho-OH	0.49	0.82	0.24	0.24	0.30	
Meta-OH	0.51	0.96	0.51	0.27	0.51	
Para-OH	0.53	0.53	0.65	0.27	----	
Ortho-NO$_2$	*					$a_N = 0.13$
Meta-NO$_2$	0.43	1.42	0.60	0.30	0.60	$a_N = 0.09$
Para-NO$_2$	0.45	1.48	0.60	0.30	----	$a_N = 0.15$
Ortho-Ph	0.48	1.04	0.30	0.30	0.20	0.10(2 protons)
Para-Ph	0.50	1.12	0.58	0.33	----	

* :   Spectra not analysed.

Table XV : Coupling Constants of Secondary Radicals B
from Mono-Substituted Arylhydroquinones.

| Aryl Group | Coupling Constants (Gauss) | | | | | |
	a_3	a_5	$a_{o(H)}$	$a_{m(H)}$	$a_{p(H)}$	$a_{substituent}$
Ph	0.67	4.52	0.12	0.12	0.12	
Ortho-F	0.68	4.72	⊕			$a_F = 0.40$
Meta-F	0.66	4.64	0.12	0.12	0.12	$a_F \approx 0.00$
Para-F	0.66	4.48	0.12	0.12	—	$a_F = 0.24$
Ortho-Cl	0.65	4.72	⊕			
Meta-Cl	0.67	4.62	0.12	0.12	0.12	
Para-Cl	0.68	4.58	0.12	0.12	—	
Ortho-Br	0.64	4.74	⊕			
Para-Br	0.67	4.56	0.12	0.12	—	
Ortho-Me	0.64	4.56	⊕			
Meta-Me	0.65	4.45	0.12	0.12	0.12	
Para-Me	0.67	4.42	0.13	0.13	—	$a_{Me} = 0.13$
Ortho-OMe	0.67	4.65	⊕			
Meta-OMe	0.68	4.56	0.12	0.12	0.12	
Para-OMe	0.65	4.40	0.12	0.12	—	
Ortho-OH	0.64	4.16	⊕			
Meta-OH	0.66	4.36	0.12	0.12	0.12	
Para-OH	0.63	4.00	0.14	0.10	—	
Ortho-NO$_2$	†					
Meta-NO$_2$	†					
Para-NO$_2$	0.70	4.86	0.12	0.12	—	$a_N \approx 0.00$
Ortho-Ph	0.64	4.44	⊕			
Para-Ph	0.66	4.52	0.12	0.12	—	

⊕ : Aryl group splittings not resolved.

† : Spectra not obtained.

Fig.62: Primary radical from Ortho-Methoxy Compound.

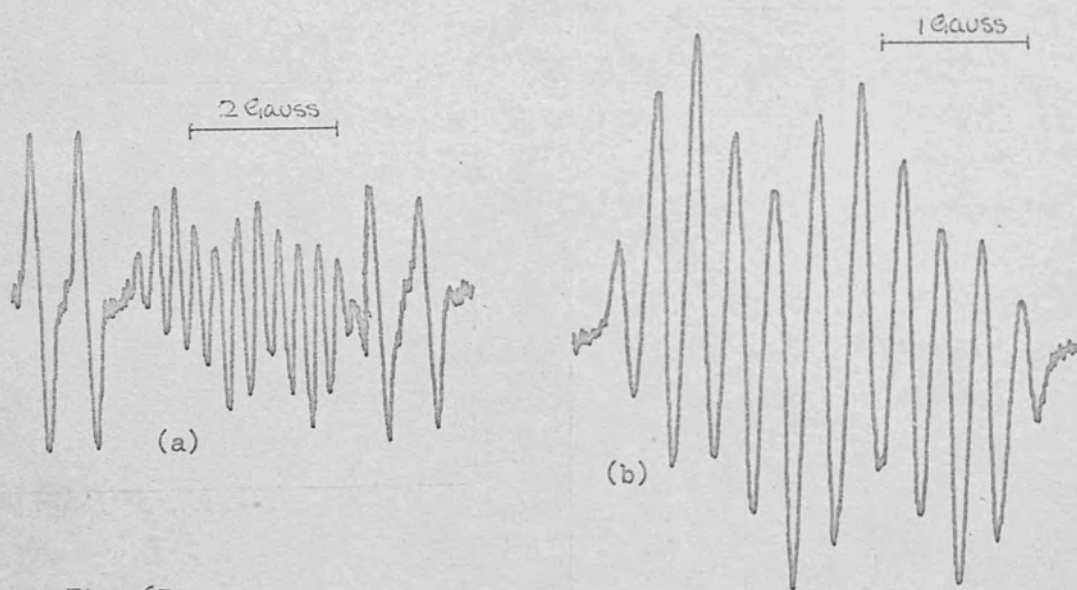

Fig. 63:

Secondary Spectra from Meta-Methoxy Compound.

    (a) Mixture of Secondary radicals.

    (b) Secondary radical A.

Table XVI shows the primary radical semiquinone ring splittings, hydroxyl and nitro as substituent in the ortho, meta and para positions of the aryl ring.

Table XVI

Substituent	Semiquinone ring splittings (Gauss)		
	a_3	a_5	a_6
H	1.99	2.12	2.56
ortho-OH	1.82	2.28	2.65
meta-OH	1.81	2.17	2.57
para-OH	1.38	2.33	2.53
ortho-NO_2	2.10	2.10	2.56
meta-NO_2	2.26	1.94	2.44
para-NO_2	2.38	1.92	2.50

The results in table XVI indicate that it is the π-system which is mainly responsible for the transmission of the electronic effects of substituents in the aryl ring. Firstly, meta-substituents have a much smaller effect than para-substituents where the dihedral angle between the two rings should be about the same. Secondly, it would be expected that the effects of ortho and para substituents would be comparable if the dihedral angle was the same. Clearly, the dihedral angle is increased substantially by the introduction of an ortho nitro group, for example, and the conjugation between the π-systems of the two rings is
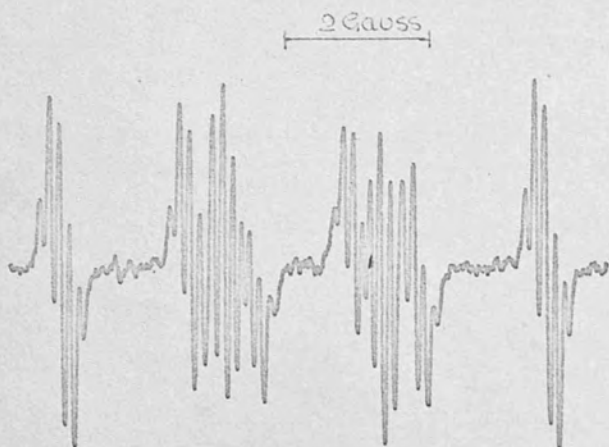
Fig. 64: Primary radical from Ortho-Hydroxy Compound.
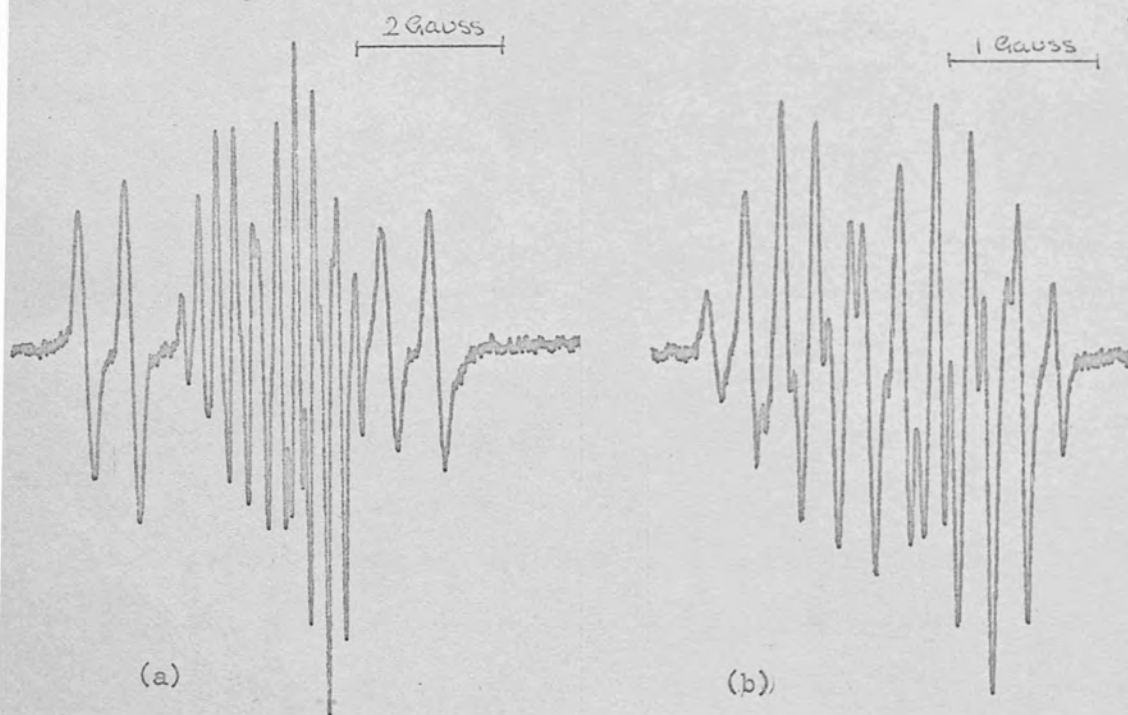

(a)

(b)

Fig. 65: Secondary spectra from Ortho-Hydroxy Compound.

(a) Mixture of secondary radicals.

(b) Secondary radical A.

reduced.

The trends in the semiquinone ring coupling constants
with changes of the ortho-substituent are less definite than
those for a meta- or para-substituent. This might be
expected since the electronic effect of the ortho-substituent
X, transmitted through the π-system, is presumably accomp-
anied by some steric interaction between X and the adjacent
carbonyl oxygen, and also the adjacent semiquinone ring
proton.

This interaction will depend not only on the size of
the group X but also on its electronic nature[53]. The
hydroxyl substituent for example, in the form of $-O^-$, would
be expected to repel the adjacent carbonyl oxygen more
strongly than the methyl group, even if the sizes of the
two are comparable.

The assignments given in tables XIII - XV for the
ortho-substituted radicals generally follow the rules
adopted and developed in parts II and III of this thesis,
but clearly additional factors are involved in determining
the semiquinone ring splittings by the introduction of
groups into the ortho position of the aryl ring.

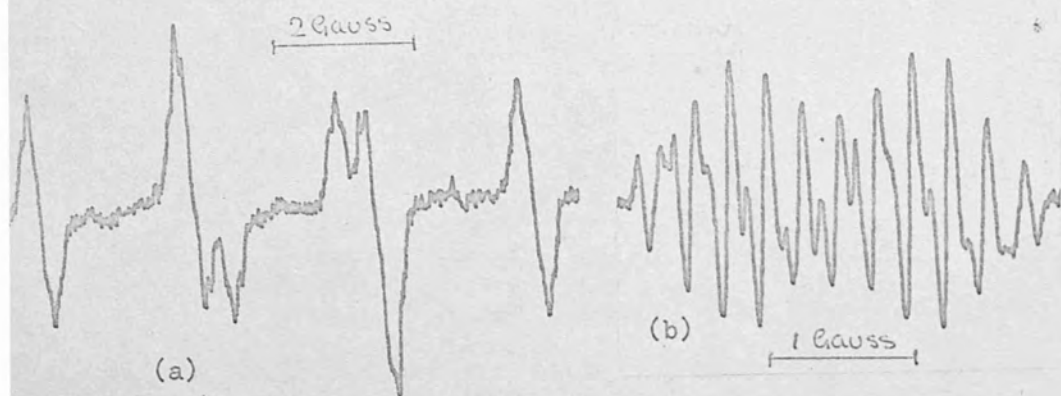Fig. 66: Spectra from - O-Bromophenylhydroquinone.
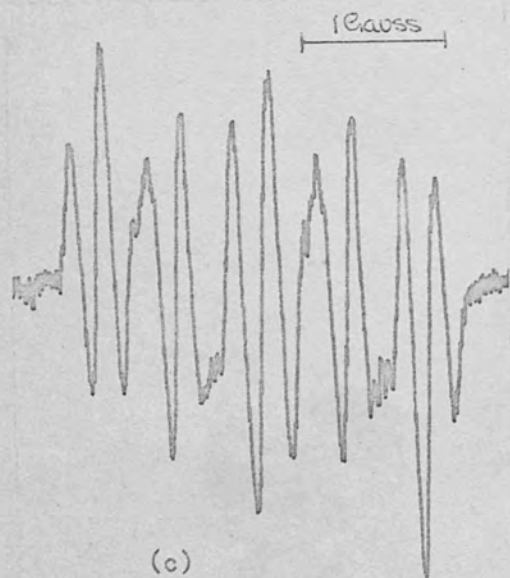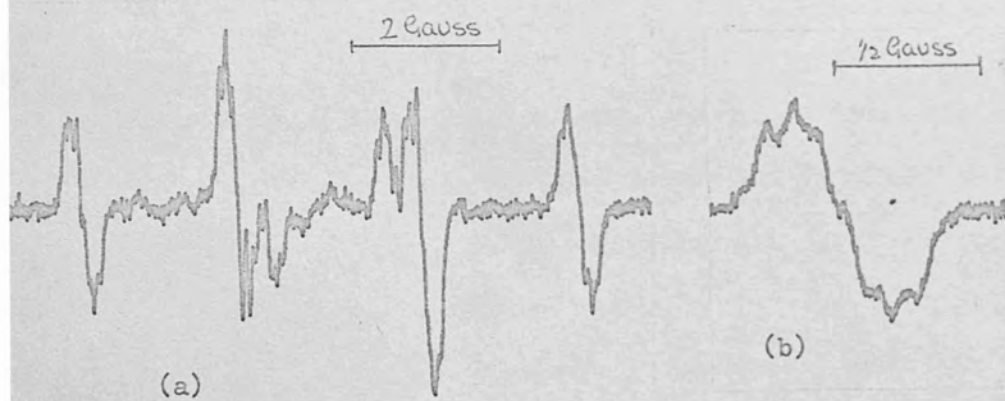(a) Primary radical.
(b) Secondary radical A.

Fig. 67: Spectra from
α-Naphthylhydroquinone.
(a) Primary radical.
(b) Wings of (a) showing splitting
from α-naphthyl group.
(c) Secondary radical A.

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Table XVII: Coupling Constants of Primary Radicals
from Polysubstituted Arylhydroquinones.

Aryl Group	Coupling Constants (Gauss)						
	a_3	a_5	a_6	Aryl Group Splittings			
				$a_{o(H)}$	$a_{m(H)}$	$a_{p(H)}$	$a_{substituent}$
α-naphthyl	2.16	2.16	2.52	0.10 (2 protons) 0.16 (1 proton)			
2,Me,3-Cl	2.20	2.20	2.52	⊕			
2,3-DiMe	2.05	2.18	2.52	0.12	0.12	0.12	
2,4-DiMe	2.05	2.18	2.55	0.13	0.13	—	$a_{Me(p)}=0.13$
2,5-DiMe	2.05	2.17	2.55	0.12	0.12	0.12	
2,6-DiMe	2.10	2.26	2.50	—	0.15	—	$a_{Me(o)}=0.05*$
2-Me,6-Cl	2.14	2.18	2.50	—	0.13	—	
2,6-DiCl	2.10	2.42	2.50	—	0.10	—	
2,6-DiMe,4-Cl	2.20	2.20	2.48	—	0.15	—	$a_{Me(o)}=0.05*$
2,6-DiMe,4-Br	2.20	2.20	2.49	—	0.14	—	$a_{Me(o)}=0.05*$
2,4,6-TriMe	2.11	2.26	2.54	—	0.16	—	$a_{Me(o)}=0.04*$ $a_{Me(p)}=0.00$
2,4,6-TriMe, 3-Br	2.16	2.16	2.50	—	0.11	—	

⊕ : Aryl group splittings not resolved.

* : Unresolved splitting, estimated from splitting in
Secondary A.

Table XVIII: Coupling Constants of Secondary Radicals A from Polysubstituted Arylhydroquinones.

Aryl Group	Coupling Constants (Gauss)					
	a_3	a_6	Aryl Group Splittings			
			$a_{o(H)}$	$a_{m(H)}$	$a_{p(H)}$	$a_{substituent}$
α-naphthyl	0.53	1.16	0.23(2 protons) 0.34(1 proton)			
2-Me,3-Cl	*					
2,3-DiMe	0.48	1.10	0.24	0.24	0.24	
2,4-DiMe	*					$a_{Me(o)}= 0.10$
2,5-DiMe	*					
2,6-DiMe	0.51	1.08	—	0.31	—	$a_{Me(o)}=0.09$
2-Me,6-Cl	0.54	1.18	—	0.30	—	
2,6-DiCl	0.54	1.38	—	0.27	—	
2,6-DiMe,4-Cl	0.51	1.08	—	0.30	—	$a_{Me(o)}=0.08$
2,6-DiMe,4-Br	0.50	1.09	—	0.30	—	$a_{Me(o)}=0.09$
2,4,6-TriMe	0.49	1.00	—	0.32	—	$a_{Me(o)}=0.08$ $a_{Me(o)}=0.00$
2,4,6-TriMe, 3-Br	*					

* = Spectra not resolved or fully analysed.

Table XIX : Coupling Constants of Secondary Radicals B
from Polysubstituted Arylhydroquinones.

Aryl Group	Coupling Constants (Gauss)		Aryl Group Splittings
	a_3	a_5	
α-naphthyl	0.64	4.60	*
2-Me,3-Cl	0.64	4.64	*
2,3-DiMe	0.64	4.48	*
2,4-DiMe	0.64	4.52	*
2,5-DiMe	0.64	4.52	*
2,6-DiMe	0.62	4.52	$a_{meta(H)} = 0.08$
2-Me,6-Cl	0.56	5.86	*
2,6-DiCl	1.20	5.16	*
2,6-DiMe,4-Cl	0.63	4.62	*
2,6-DiMe,4-Br	0.64	4.62	*
2,4,6-TriMe	0.65	4.52	$a_{meta(H)} = 0.08$
2,4,6-TriMe 3-Br	0.64	4.60	*

* : Aryl Group Splittings not resolved.

Aryl group splittings.

From tables XIII - XV it is clear that the aryl ring proton splittings are about twice as large when the substituent occupies the meta or para positions, than when it is ortho with respect to the bond joining the two rings.

Tables XVII - XIX give the primary and secondary radicals from polysubstituted arylhydroquinones with their E.S.R. coupling constants, many containing two ortho substituents. Examination of the hyperfine splittings for all arylsemiquinone radicals reveal the following main points:-

1.   Whereas the meta proton coupling constants seem to remain reasonably constant with increasing ortho-substitution on the aryl group, the ortho and para splittings decrease sharply. No splitting is observed for para protons in the radicals containing two ortho-substituents in the aryl ring.

2.   For methyl substituents on the aryl group:-

(a) Para methyl proton splittings are about the same as those of para hydrogens.

(b) Ortho methyl proton splittings are less than those of ortho hydrogens.

(c) Meta methyl proton splittings are about half those of meta hydrogens.
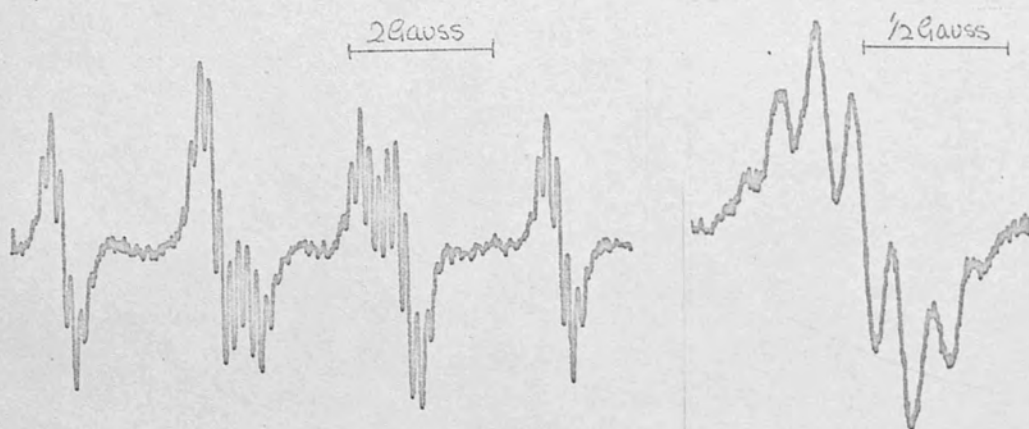
Fig. 68: Primary radical from 2,4-dimethylphenyl compound.

Fig. 69: Secondary radical A from 2,4-dimethylphenyl compound

3. When the aryl group has two ortho methyl groups, a
    para-chloro or a para-methyl group does not affect
    the resolution of the E.S.R. spectra. On the other
    hand in the ortho-chlorophenylsemiquinone, the aryl
    proton splittings are not resolved (due probably to
    broadening of the lines by hyperfine coupling with
    ^{35}Cl and ^{37}Cl nuclei).

4. For ^{19}F as a substituent on the aryl ring:-

    (a) The ortho fluorine splitting is about 4 times as
        large as that of the ortho hydrogen in the same
        radical.

    (b) The meta fluorine splitting is much less than
        that of the meta hydrogen.

    (c) The para fluorine splitting is twice that of a
   hydrogen in the same position.

    These, and other points, can be explained in terms of
the increase in the dihedral angle between the semiquinone
and the aryl rings when the ortho hydrogens are replaced by
larger groups.

Theoretical model of the system.

    A theoretical model to explain the observed aryl group
splittings in a simple but satisfactory way is not difficult
to develop. Firstly the aryl group splittings in the three

types of radicals appear to bear a definite relationship
to each other, i.e. the coupling constants of methyl or
aryl protons in the ring vary in the same way for all three
types of radical. These splittings in secondary radicals B
are about half those in the corresponding primary radicals,
which in turn are about half those in secondary radicals A.

This suggests firstly that the dihedral angle is
probably the same in all three types of radical and secondly,
that the splittings in the aryl group are proportional to the
spin density on the carbon atom to which it is attached.
Support for this second possibility comes from the coupling
constants in semiquinone itself and the radical from tri-
hydroxybenzene.
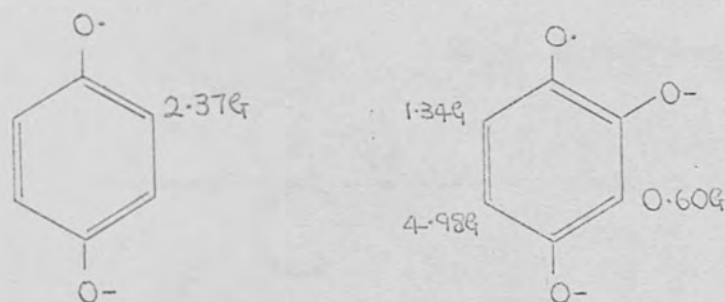
expected ratio of aryl proton splittings is:-

Secondary B : Primary : Secondary A

   1.34   :   2.37 :   4.98

i.e. approximately 1:2:4, as observed.

Molecular orbital model: The delocalisation of the odd
electron onto the aryl ring can be considered as being

similar to that in the benzyl radical; the aryl fragment and the carbon atom on the semiquinone ring to which it is attached are involved.

This problem, together with the variation of spin densities with the angle of twist about the carbon-aryl bond has been discussed at various levels of sophistication for benzyl radicals[54,55] and aromatic nitroxide radicals[56].

Some understanding can be gained, however, using simple molecular orbital theory. If the dihedral angle between the two rings is θ (see fig. 70.a), then the $2p\pi$ orbital of the adjacent carbon atom in the semiquinone ring can be resolved into two parts, one, $\phi_0 \cos\theta$, which has the
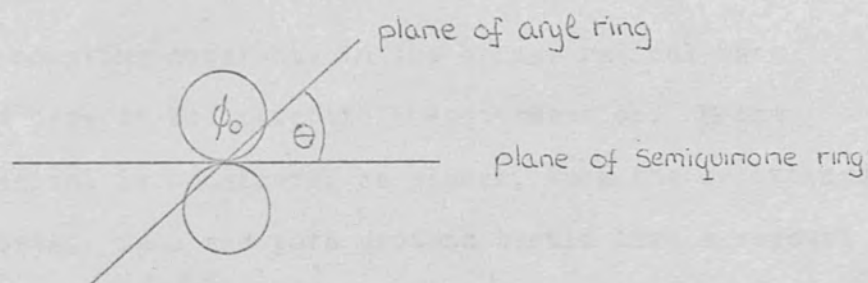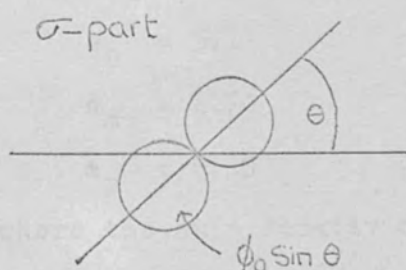

plane of aryl ring

plane of semiquinone ring

Fig. 70(a)

σ-part

$\phi_0 \sin\theta$

Fig. 70(b)

π-part

$\phi_0 \cos\theta$
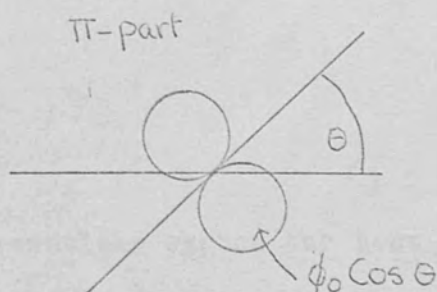
Fig. 70(c)

same symmetry as the π-orbitals of the aryl substituent, and the other, $\phi_0 \sin\theta$, which has interactions only with the σ-orbitals of the aryl group (see figs. 70 b and 70 c). Spin density if therefore transmitted effectively via two distinct routes, and the hyperfine splittings can be written as a simple sum of two terms:-

$$a(\theta) = a_\pi(\theta) + a_\sigma(\theta)$$
$$= a_\pi(0^\circ)\cos^2\theta + a_\sigma(90^\circ)\sin^2\theta$$

The values of $a_\pi(0^\circ)$ and $a_\sigma(90^\circ)$ can be estimated empirically or theoretically.

π-part.

The coupling constants in the benzyl radical have been used here to estimate the π-contribution. If the benzyl radical is considered as planar, then the splittings for the ortho, meta and para protons should give a measure of the effective delocalisation, through the π-system, of the odd electron. The splittings observed for the benzyl radical are,

$$a_o = 5.1G$$
$$a_m = 1.7G$$
$$a_p = 6.1G$$

where the spin density on the extranuclear carbon has been calculated as 0.57[57]. This leads to the following

expressions for the splittings (due to the π-part) at the ring positions in arylsemiquinones:-

ortho : $a_o^\pi(H) = \dfrac{-5.1}{0.57} . \rho . \cos^2\theta \approx - a_o^\pi(CH_3)$

meta : $a_m^\pi(H) = \dfrac{+1.7}{0.57} . \rho . \cos^2\theta \approx - a_m^\pi(CH_3)$

para : $a_p^\pi(H) = \dfrac{-6.1}{0.57} . \rho . \cos^2\theta \approx - a_p^\pi(CH_3)$

which gives :-

$$a_o^\pi(H) = -8.7 \, \rho \cos^2\theta \approx -a_o^\pi(CH_3)$$

$$a_m^\pi(H) = +2.6 \, \rho \cos^2\theta \approx -a_m^\pi(CH_3)$$

$$a_p^\pi(H) = -10.5 \, \rho \cos^2\theta \approx -a_p^\pi(CH_3)$$

σ-part.

For the σ-part it is again π-interactions which are responsible for the spin delocalisation, but in this case it is π-type interactions involving the carbon hybrid orbitals of the aryl ring, each of which has $2/3 \, \rho$ character. These orbitals can be resolved into part along the adjacent c-c bond and part perpendicular to it. The π-interactions between carbon sp^2 hybrid orbitals in ethylene are half the magnitude of the resonance integral assigned to the π-bond so they are by no means negligable.
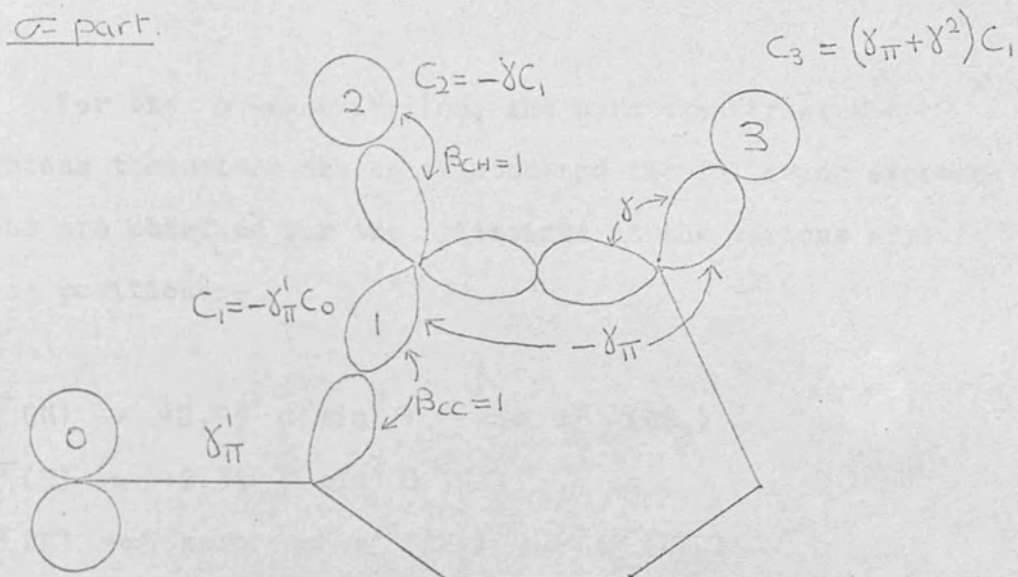
$\sigma-$ part.

Fig. 71.

The parameters shown in fig. 71 have been shown to account for a variety of coupling constants in N.M.R. spectra[58] and for certain effects in elimination reactions[59]. It has been found that

$$\gamma_{\pi} \approx 1/4 , \qquad \gamma \approx 1/4\sqrt{2}$$

roughly reproduce the coupling constants in the vinyl radical[60], and the formula for the splitting,

$$a_H(\sigma) = 508 \, \rho_H$$

where ρ_H = spin density in the hydrogen 1S orbital

has been used. This corresponds to an effective atomic

number of hydrogen of unity.

For the σ-contribution, the spin density at the protons themselves are calculated and the following expressions are obtained for the splittings at the various aryl ring positions:-

$$a_o^\sigma(H) = +0.95 \, \rho \, \sin^2\theta \approx a_o^\sigma(CH_3)$$
$$a_m^\sigma(H) = +2.54 \, \rho \, \sin^2\theta$$
$$a_p^\sigma(H) \approx zero \approx a_m^\sigma(CH_3) \approx a_p^\sigma(CH_3)$$

For the three types of radicals observed, only the value of ρ, the spin density on the extranuclear carbon, is different. To estimate ρ the splittings in the radicals obtained from methylhydroquinone can be used, with the assumption that the spin density at the semiquinone ring is the same whether it holds a methyl or an aryl substituent.

For secondary radicals A, where the splittings from the aryl group are largest,

$$a_{CH_3} = 5.12G$$
using $Q_{CH_3} \approx 30G$:
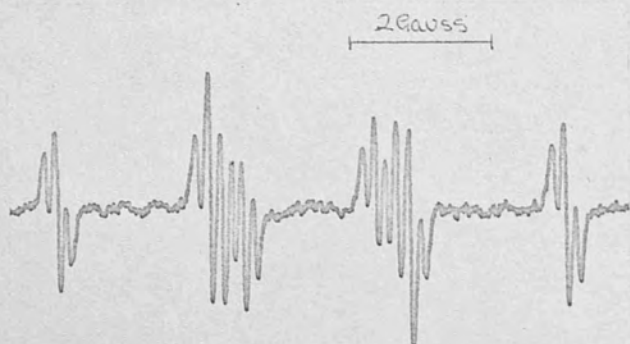$$\rho_{secA} \approx 1/6$$

2 Gauss

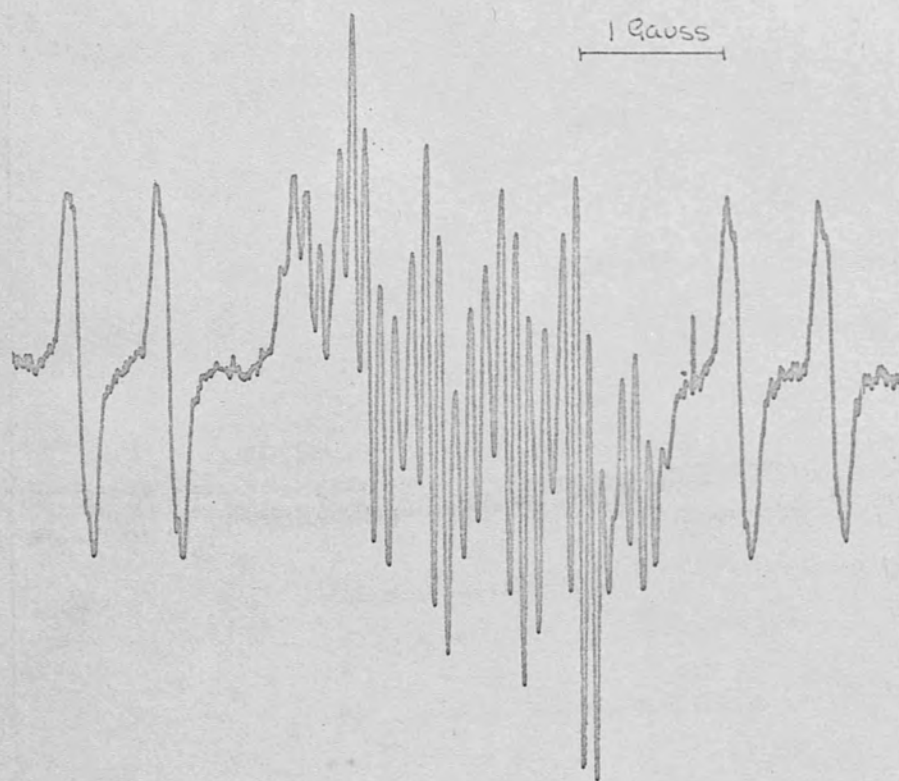Fig. 72: Primary radical from 2,6-Dimethylphenylhydroquinone.

1 Gauss

Fig. 73: Mixture of secondary radicals from
2,6-Dimethylphenylhydroquinone.

Table xx: Comparison of Calculated Coupling Constants of
Aryl Group Protons with some of those observed in
Secondary Radicals Type A.

$\theta = 45°$

Type of Proton	Calculated	Observed Ar= p-MeC$_6$H$_4$	Ar= m-MeC$_6$H$_4$
a_o(H)	(−) 0.62	0.58	0.52
a_o(CH$_3$)	(+) 0.78	----	----
a_m(H)	(+) 0.43	0.31	0.32
a_m(CH$_3$)	(−) 0.22	----	0.16
a_p(H)	(−) 0.87	----	0.52
a_p(CH$_3$)	(+) 0.87	0.58	----

$\theta = 60°$

Type of Proton	Calculated	Observed Ar = o-MeC$_6$H$_4$
a_o(H)	(−) 0.23	0.28
a_o(CH$_3$)	(+) 0.47	0.11
a_m(H)	(+) 0.42	0.28
a_m(CH$_3$)	(−) 0.11	----
a_p(H)	(−) 0.45	0.28
a_p(CH$_3$)	(+) 0.45	----

$\theta = 90°$

Type of Proton	Calculated	Observed Ar=2,6-DiMeC$_6$H$_3$	Ar=2,4,6-TriMeC$_6$H$_4$
a_o(H)	(+) 0.16	----	----
a_o(CH$_3$)	(+) 0.16	0.09	0.08
a_m(H)	(+) 0.42	0.31	0.32
a_m(CH$_3$)	zero	----	----
a_p(H)	zero	zero	----
a_p(CH$_3$)	zero	----	zero

Table XX compares the calculated and observed aryl group splittings for methyl-substituted arylsemiquinones (secondary radicals A) with varying amounts of substitution in the ortho position. The theory is shown to account quite well for the variation of the coupling constants, the greatest deviation from the predicted values being for ortho-methyl group splittings. This might be expected since distortion is most likely to occur at the ortho position[61]; by bending of the $C-CH_3$ bond the methyl group is forced out of the plane of the ring with a resulting decrease in the hyperfine coupling.

From the theoretical point of view this simple approach gives much the same variations with dihedral angle as do the more sophisticated theories[54-56]. The effect of σ-spin delocalisation, responsible for aryl group coupling when the angle Θ approaches 90°, arises mainly from π-type interactions involving the carbon hybrid orbitals, each of which has 2/3 p character.

Meta proton splittings.

Out of the theory, and also from the experimental results comes the fact that the meta proton splittings are remarkably constant throughout the series of aryl substituents studied. This shows that the coupling constant has
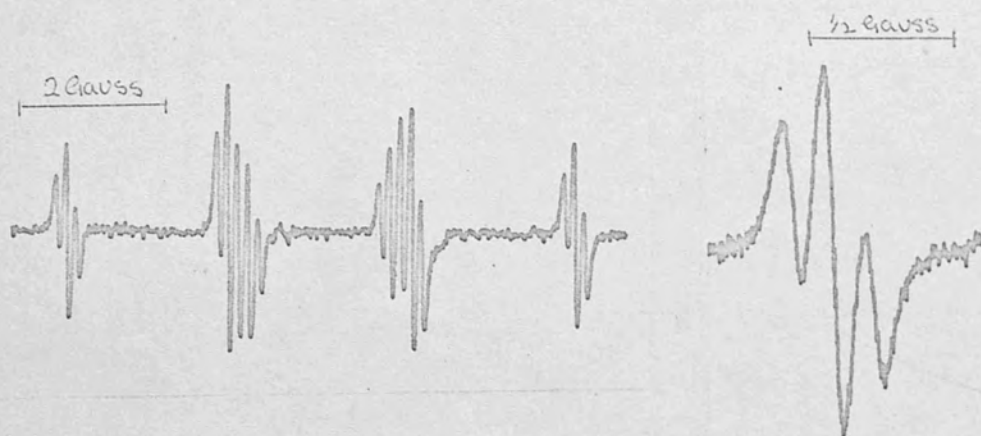
2 Gauss

½ Gauss

Fig. 74: Primary radical from
2,6-Dimethyl,4-Br phenyl compound.

1 Gauss

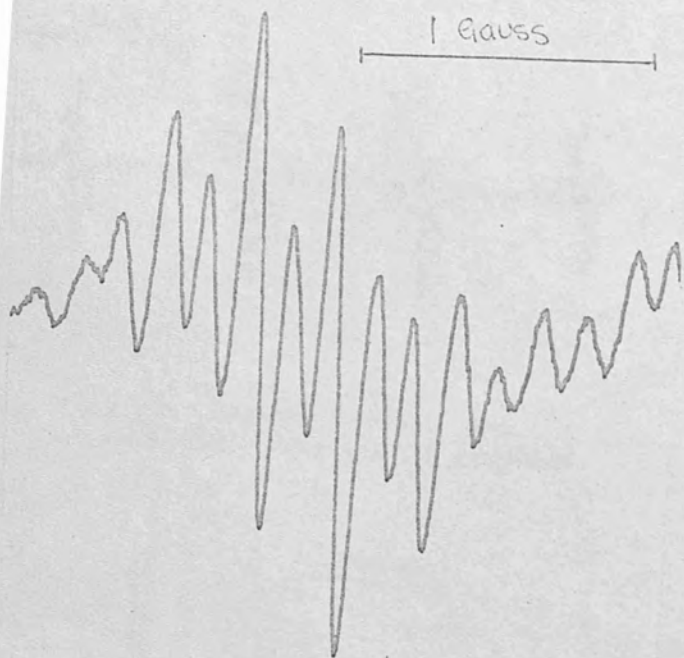Fig. 75: Secondary radical from the 2,6-DiMe, 4-Br phenyl compound.

1 Gauss

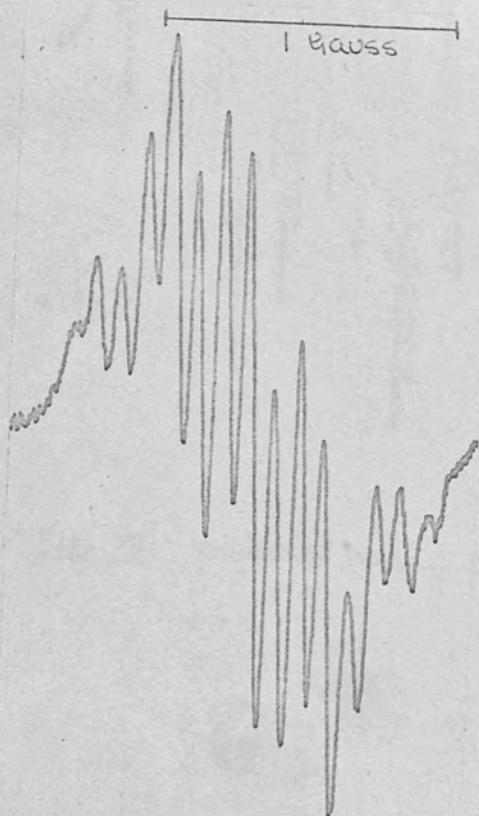Fig.76: Aryl Group splittings from p-Me compound.

1 Gauss

Fig.77: Aryl Group splittings from m-Me compound.

the same sign at all dihedral angles. Since in the near
perpendicular conformations (2 ortho substituents) these
splittings arise effectively from hyperconjugation i.e.
direct transmission of spin density, the sign should be
POSITIVE. This means that if the spin-polarisation mech-
anism in π-type radicals is accepted, the spin density in
in the meta-carbon $2p\pi$ orbital must be NEGATIVE.

Dihedral angles

The absence of hyperfine splitting from the para
protons in the di-ortho substituted radicals, confirms that
the dihedral angle in these cases is close to 90°. Similarly
when there is no ortho substituent, the angle, by comparison
with theory, is apparently of the order of 45°. With a
single ortho substituent the situation is intermediate
between the two ($\approx 60^\circ$).

Methyl group splittings

The theory is seen to account quite well for the
splittings from methyl group protons in the meta and para
positions of the aryl group. The ortho methyl splittings
are much lower than the predicted values and this may be
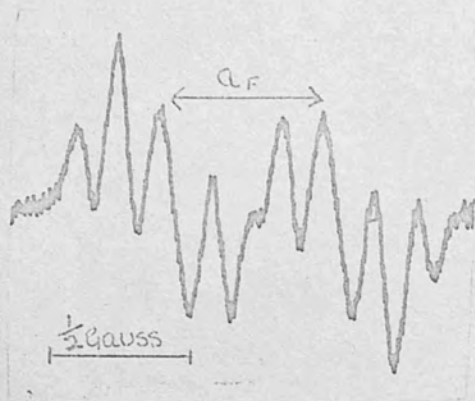
(a) Ortho-Fluorophenyl.
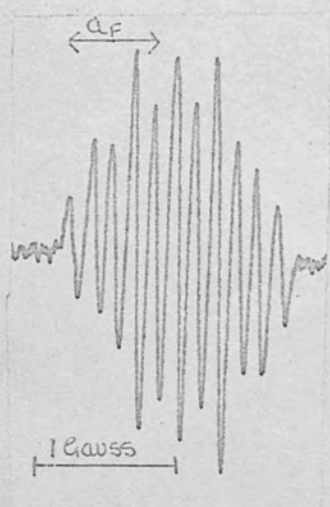
(b) Para-Fluorophenyl.   (c) Meta-Fluorophenyl.

Fig. 78: Aryl Group splitting patterns for Primary radicals from Fluorophenylhydroquinones.

(a) Ortho-F. $a_o^F = 4a_o^H$

(b) Para-F. $a_p^F = 2a_p^H$

(c) Meta-F. a_m^F : Too small to be resolved.

due to bending of the $C-CH_3$ bond out of the plane of the aryl ring due to steric interaction with the semiquinone ring. This bond-bending would be accompanied by a decrease in the hyperfine coupling with the methyl group.

^{19}F Splittings

From table XXI , it is clear that the ortho-fluorine splitting is unexpectedly large compared to the ortho-proton splitting, whereas the ^{19}F splitting at the meta position is unexpectedly small.

Table XXI : ^{19}F splittings in primary radicals from fluorophenylhydroquinones.

Aryl group	Coupling constants (Gauss)	
	a_H	a_F
o-Fluoro	0.16(o)	0.56
m-Fluoro	0.15(m)	0.04
p-Fluoro	0.28(p)*	0.57

*: Estimated proton splitting for that position.

In π-type radicals fluorine splittings are of the order of twice the corresponding proton splittings[30,39], and this is seen to be the case for the para-position. The

ortho and meta ^{19}F splittings can be explained by the fact
that when fluorine is attached to a π-system, the ^{19}F
coupling constants are thought to be of opposite sign to
corresponding proton splittings because spin density can
get directly onto the fluorine atom via the F(2pπ) orbital.
Similarly, in the case of β-fluorine coupling constants,
spin density is transmitted onto a F(2pσ) orbital, presum-
ably also giving rise to a positive contribution to the
hyperfine splitting.

The result of these two effects is that $a_\pi(^{19}F)$ and
$a_\sigma(^{19}F)$ have the same sign for ortho-fluorine, but have
opposite signs for meta-fluorine nuclei, because the π-part
is derived from negative spin density on the meta carbon
2pπ orbital. From the calculations a_π^m and a_σ^m are approx-
imately equal for hydrogen nuclei with a dihedral angle of
45°. For a fluorine nucleus in the meta position these two
contributions would also be expected to have almost the same
magnitude, but of opposite sign, so they appear to very
nearly cancel to give a small resultant splitting.

For the ortho-fluorine, the two contributions are of
the same sign and a comparatively large splitting is observed.

13. EXPERIMENTAL

Autoxidation experiments and E.S.R. spectra.

All the E.S.R. spectra were recorded using a Varian
E-4 instrument employing 100KHz modulation. For the flow
experiments a Varian mixing-cell was used, the observation of
the radicals occuring ca. 0.1 sec after mixing of the two
solutions. The experiments in a static system were carried
out using a Varian aqueous-cell.

In the flow experiments a solution of the hydroquinone
or quinone (ca. 0.001M in the chosen solvent) was flowed
against aqueous sodium hydroxide solution, the radicals
being observed ca. 0.1 sec. after mixing. It was found
difficult to flow solutions of alkali greater than ca. 5%,
due to the viscosity of the solution, and the primary spectrum
was invariably observed by this method.

The most useful experiments were performed in a static
system and in this case a solution of the hydroquione or
quinone was made alkaline by the addition of sodium hydrox-
ide solution, shaken in air, and the E.S.R. spectrum recorded

at regular intervals. The spectra were analysed for definite radical species.

The concentrations of hydroquinone or quinone and of the alkali were varied, and the effects of changing the solvent were studied. The amount of oxygen present in the solutions could be increased by shaking vigorously in air. The particular conditions required to observe definite radicals varied considerably with the hydroquinone or quinone, and for this reason the experimental conditions in each case have been described earlier along with the discussion of the spectra. Well-resolved spectra of the primary and secondary radicals could, however, normally be obtained by the general methods described below.

Primary radicals

To a solution of the hydroquinone (ca. 0.01M) in 50% aqueous ethanol, a few drops of 1% NaOH were added. The resulting solution was transferred to an aqueous-cell in the cavity of the E.S.R. spectrometer and the spectrum recorded immediately.

Secondary radicals

Good spectra of the secondary radicals were normally obtained by making a solution of the hydroquinone or quinone (ca. 0.01 M) strongly alkaline and shaking the

resultant solution in air. A 'pure' spectrum was often
obtained immediately, but occasionally only developed after
a period of time.

The strength of the alkali required depended to a great
extent on the particular hydroquinone or quinone, and the
conditions in each case have been described along with the
discussion of the spectra. The effects of varying the
solvent have also been described for the individual hydro-
quinones earlier in this thesis.

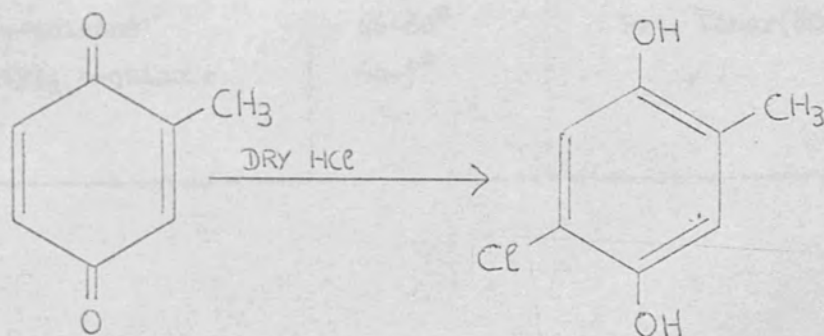## Preparation of Hydroquinones and Quinones

Alkylquinones

When neither the quinone nor the hydroquinone was
commercially available, the alkylquinone was prepared by
oxidation of the corresponding phenol with Fremy's salt
according to the method of Teuber and Rau[62].

The phenol (1 Mole), in a suitable solvent (methanol,
acetone), was reacted at room temperature with a solution of
2 Moles of Fremy's salt (Potassium nitrosodisulphonate) in
water. The quinone formed was extracted with ether after
ca. 1 hour and the solid obtained recrystallized from a
suitable solvent. The yields obtained were generally of the
order of 50%.

e.g.
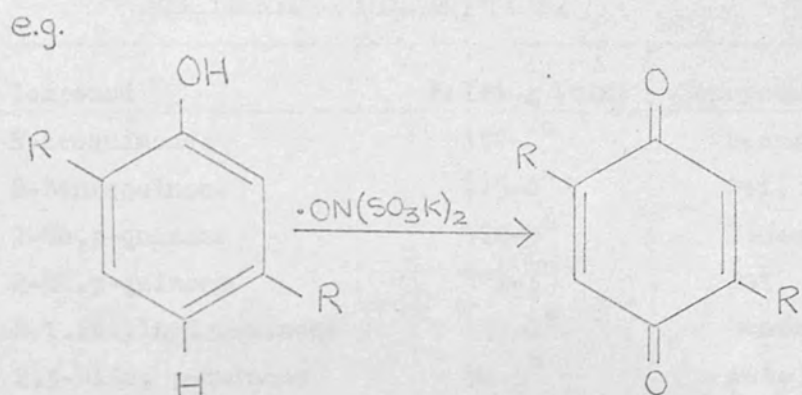
The chlorinated compounds were prepared in good yield by passing dry hydrogen chloride into a solution of the corresponding quinone in chloroform[63]. The chlorinated hydroquinone was deposited and recrystallized from chloroform.

The hydroquinones and quinones described in part II, containing mainly alkyl substituents, are set out in table XXII , with their melting points and recrystallizing solvents.

The hydroquinones in table XXII were converted to the corresponding quinones, where required, by oxidation with

Table XXII: Hydroquinones and Quinones Containing Alkyl
and Other Simple Substituents with their Melting Points
and Recrystalling Solvents.

Compound	Melting Point	Recrystalling Solvent
Hydroquinone	170-2°	Benzene
P-Benzoquinone	115-6°	Pet, Ether(60-80°)
2-Me,p-quinone	124-5°	Benzene
2-Et,p-quinone	112-3°	Pet. Ether(60-80°)
2-t.Butylhydroquinone	127-9°	Benzene
2,3-DiMe, p-quinone	54-5°	Pet. Ether(60-80°)
2,5-DiMe, p-quinone	125-6°	,,
2,6-DiMe, p-quinone	72-3°	,,
2,5-Dit.Butylhydroquinone	217-8°	Benzene
Thymoquinone	106-7°	Pet.Ether(60-80°)
1,4-Naphthoquinone	124-5°	,,
2-Me, 1,4-Naphthoquinone	104-5°	,,
2-Chlorohydroquinone	106-7°	Chloroform
5-Me,2-Cl,hydroquinone	172-3°	Chloroform
2-Methoxy, p-quinone	139-40°	Pet. Ether(60-80°)
Cathecol	105-6°	Benzene
4-Me, o-quinone	66-68°	Pet, Ether(60-80°)
4-t.Butyl, o-quinone	66-7°	,,

chromic anhydride at 0°C in aqueous acetic acid solution[64].

The quinones given in the table were reduced to the corresponding hydroquinones with zinc dust and 25% hydrochloric acid. Extraction with ether and recrystallization of the product yielded the pure hydroquinone; this method was very convenient for small amounts of compound.

The triacetoxy compounds were prepared by the Thiele acetylation reaction[43], previously mentioned in part II.

A mixture of the quinone (1 Mole), acetic anhydride (5 Moles) and a few drops of conc. H_2SO_4 were heated to about 80°C until reaction occured. After ca. $\frac{1}{2}$ hr. the mixture was poured into a large volume of cold water and the triacetoxy compound recrystallized from ethanol.

Arylquinones

The arylquinones were prepared by direct arylation of p-benzoquinone via the diazonium salts, according to the method of Brassard and L'Ecuyer[52].

To a suspension of p-benzoquinone (0.1 mole) in 750 ml. of water at 15°C was added 0.1 Mole of the diazonium salt prepared in the usual manner. The pH of the solution was kept at ca. 5 by the addition of solid sodium acetate. After ca. 1 hr. at 15°C the solid was filtered off and

was recrystallized from a suitable solvent, normally
petroleum ether (60°-80°).

In the case of ortho substituents in the aryl group,
the arylquinones were obtained initially as black oils.
Repeated crystallization from petroleum ether (60°-80°) at
ca. -50°C eventually yielded the pure product.

The arylquinones and their melting points are given
in tables XXIII and XXIV . The corresponding hydroquinones
were obtained by reduction with zinc and 25% HCl as previously
described for arylquinones.

The direct arylation method did not succeed for the
ortho-hydroxyphenyl compound and this quinone was prepared
by oxidation of 2,2' -dihydroxybiphenyl with Fremy's salt[62].
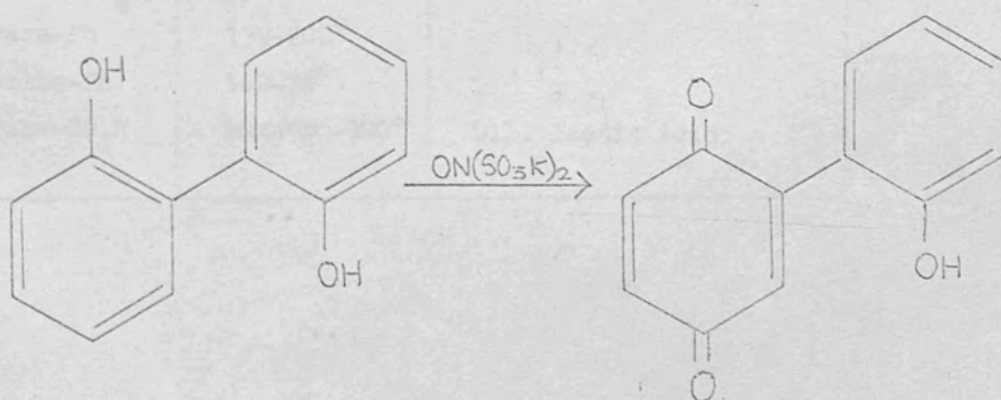
The arylation was successful in all other cases attempted.

Table xxⅢ   Mono-Substituted Arylquinones with their

Melting Points and Recrystalling Solvents.

Aryl Group	Melting Point	Recrystalling Solvent
Ph	112-3°	Pet. Ether (60° 80°)
Para-F	116-7°	,, ,,
Meta-F	88-9°	,, ,,
Ortho-F	69-70°	,, ,,
Para-Cl	129-30°	,, ,,
Meta-Cl	142-3°	,, ,,
Ortho-Cl	83-4°	,, ,,
Para-Br	143-4°	,, ,,
Ortho-Br	98-100°	,, ,,
Para-Me	126-7°	,, ,,
Meta-Me	86-7°	,, ,,
Ortho-Me	58-60°	,, ,,
Para-OMe	118-20°	,, ,,
Meta-OMe	104-5°	,, ,,
Ortho-OMe	58-9°	,, ,,
Para-OH	176-8°	Aq. Ethanol
Meta-OH	152-3°	Aq. Ethanol
Ortho-OH	193-5°	Benzene
Para-NO_2	136-7°	Pet.Ether(60°-80°)
Meta-NO_2	126-8°	Pet.Ether(60°-80°)
Ortho-NO_2	99-100°	,, ,,
Para-Ph	199-200°	,, ,,
Ortho-Ph	168-70°	,, ,,
Para-CO_2H	Decomp.~200°	Dil. Acetic Acid

Table xxiv: Poly-Substituted Arylquinones with their
Melting Points and Recrystalling Solvents.

Aryl Group	Melting Point	Recrystalling Solvent
α-naphthyl	76-8°	Pet, Ether (60-80°)
2-Me, 3-Cl	81-2°	,,
2,3- DiMe	66-8°	,,
2,4- DiMe	73-4°	,,
2,5- DiMe	70-1°	,,
2,6- DiMe	63-4°	,,
2-Me,6-Cl	81-3°	,,
2,6-DiCl	104-5°	,,
2,6-DiMe,4-Cl	76-7°	,,
2,6-DiMe,4-Br	82-83°	,,
2,4,6-TriMe	91-2°	,,
2,4,6-TriMe, 3-Br	101-3°	,,

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Secondary Radicals in the Autoxidation of Hydroquinones

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Secondary Radicals in the Autoxidation of Hydroquinones

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Summary Strongly alkaline solutions of hydroquinones, shaken in air, may give e.s.r. spectra corresponding to radicals other than the expected semiquinones; secondary or even tertiary stages of the autoxidation may thus be observed.

THE autoxidation of hydroquinones in alkaline solution is well known to be a radical process involving initial formation of p-semiquinone radicals,[1] which are short-lived in aqueous solution, but can be kept for much longer periods in strongly alcoholic media. The relative stability of these 'primary' radicals in alcoholic solution[2] has, to a certain extent, precluded further investigation of what appears to be a complex autoxidation process.

The autoxidation of 4-methylcatechol in aqueous alkali has been found to give a secondary radical, in which an

additional oxygen is bonded to the aromatic ring.[3] . This extends our knowledge of the autoxidation process in that particular case, and now, using e.s.r. spectroscopy, we have found rather similar results for some substituted hydroquinones and p-quinones.

In contrast to the situation in ethanolic solutions, more than one type of radical may be observed in largely aqueous solutions of certain hydroquinones or p-quinones, depending on the conditions. For example, in 1% sodium hydroxide solution, simple p-semiquinone radicals are usually observed, but after a relatively short time, their e.s.r. spectra disappear. In more concentrated alkali (5—20% NaOH), totally different e.s.r. spectra are obtained (apart from cases where we might expect strong steric hindrance), corresponding to 'secondary' radicals. These arise from substitution of an aromatic hydrogen, probably by hydroxyl, to give radicals derived from the 1,2,4-trihydroxybenzene system.
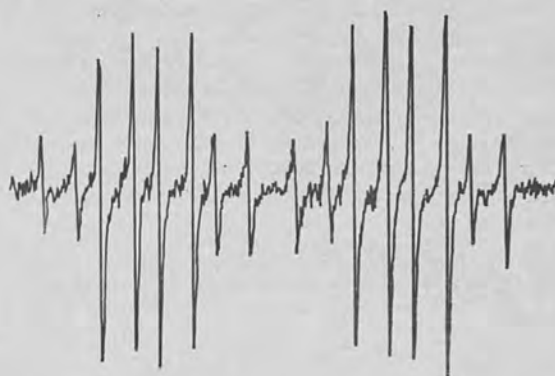
FIGURE. *E.s.r. spectrum of secondary radical from methylhydroquinone.*

Coupling constants in the e.s.r. spectra of the observed radicals

| Hydroquinone or p-quinone	Proton	Primary (weak alkali)	Secondary (strong alkali)				
			A		B	C	
Unsubstituted	2	2·38 [a]					
	3	2·38					
	5	2·38					
	6	2·38					
2-Methyl-	2	2·12 [b]		a			a
	3	1·75	0·55 (H)		0·95 (Me)	0·56 (H).	0·66 (H)
	5	2·54		4·15 (H)		5·18 (Me)	
	6	2·45	0·95 (Me)		0·55 (H)	0·66 (H)	0·56 (H)
2,5-Dimethyl-	2	2·32 [c]		d			
	3	1·84	0·98 (Me)		0·88 (Me)		
	5	2·32		4·31 (H)			
	6	1·84	0·88 (Me)		0·98 (Me)		
2,6-Dimethyl-	2	2·15c					
	3	1·98		0·97 (Me)			
	5	1·98		5·20 (Me)			
	6	2·15		0·72 (H)			
2,5-Di-t-butyl	2	b					
	3	2·09					
	5						
	6	2·09					

[a] Aqueous solution. [b] 1:1 H_2O–EtOH. [c] 1:1 H_2O–DMF. [d] 3:1 H_2O–DMF.

One characteristic of the ensuing radical is that the coupling constants of methyl or aromatic protons *para* to an oxygen atom (*i.e.* on C-5), are much larger than in the original p-semiquinone radical (Table).

A   B   C
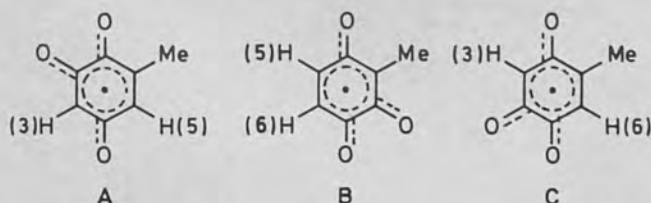
It is clear that competing reactions in these solutions are finely balanced, for changes of solvent have a marked effect on the ease of formation and lifetimes of the observed radicals and also, in one case, that of methylhydroquinone, at least two secondary radicals can be observed depending on the conditions (A—C).

(a) In cold sodium hydroxide (5—20%) radical A (or radical B, which would be expected to have similar coupling

D   E
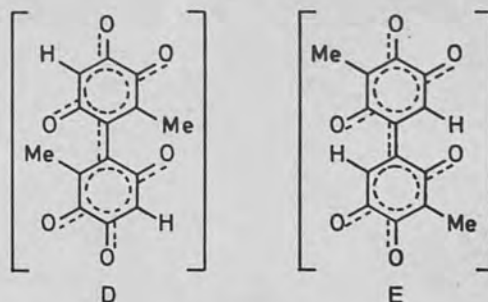
constants) was observed (Figure); (b) in hot, strong alkali radical C, the same as that observed by Stone and Waters from 4-methylcatechol, was obtained; and (c) in mildly

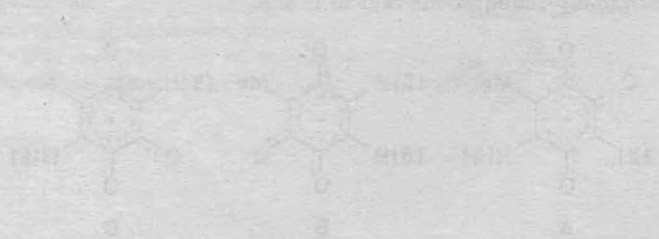alkaline aqueous DMF a spectrum corresponded to a mixture of both radicals was obtained.

In the case of methylhydroquinone a 'tertiary' radical was obtained in very strong, cold alkali (30% NaOH). The resulting spectrum appears to correspond to a biphenyl derivative, D or E, where there is conjugation between the two rings, the coupling constants being approximately half those in the secondary radical (A or B) from which it would be formed.

The formation of this dimer is apparently favoured by the high spin-density on the position *para* to an oxygen (*i.e.* on C-5), and the presence of a replaceable hydrogen at that position.

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Electron Spin Resonance Spectra of Radicals derived from Arylhydroquinones

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Electron Spin Resonance Spectra of Radicals derived from Arylhydroquinones

By **P. Ashworth** and **W. T. Dixon**,* Bedford College, Regents Park, London N.W.1

The e.s.r. spectra of radicals formed in the autoxidation of arylhydroquinones show hyperfine splitting from protons attached to the aryl group, showing that the odd electron is delocalised over both rings. Substituents on the phenyl group influence the various proton coupling constants in a way which is related to their electron-donating or electron-withdrawing properties.

WE have reported how several different types of radical intermediate can be observed during the autoxidation of alkylhydroquinones and quinones.[1,2] In addition to semiquinones, radicals derived from 1,2,4-trihydroxybenzenes can be seen by means of e.s.r. spectroscopy. A parallel series of radicals are formed during the autoxidation of arylhydroquinones, showing that the aryl groups have little effect on the reactivity of the quinone nucleus, although the hyperfine splittings of aryl protons indicate that the odd electron is delocalised on to the second ring to some extent. Substituents on the aryl group have only a small effect on the coupling constants although the trends are reasonably definite.

The parent quinones were made by direct arylation of *p*-benzoquinone *via* the diazonium salts,[3] and the ease with which this reaction could be made to yield the arylquinone varied somewhat from one case to another. The primary radicals were generated easily in dilute alkaline solutions and the secondary radicals from more concentrated alkali. The latter were always obtained initially as a mixture of two isomeric radicals, (A) and (B). This contrasts with the behaviour of alkylhydroquinones which could be made to yield one or other isomer depending on the conditions. However, when the solutions were left the (B)-type radical decayed, often leaving a pure

spectrum from type (A). Improved spectra of the secondary radicals could be obtained by acetylating the

Primary radical   Secondary radicals
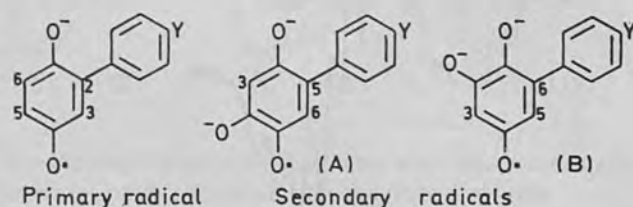
arylquinones followed by alkaline hydrolysis (Scheme 1). The e.s.r. spectra were in general well resolved and

SCHEME 1
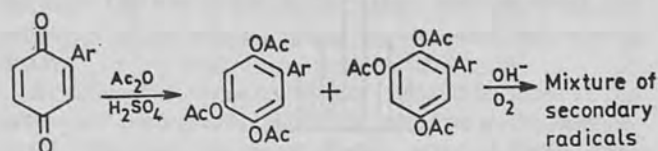
although there was a mixture of secondary radicals both spectra could be analysed because the overlap between them was minimal (see Figure 1). Difficulties arise in a few cases because the smaller splittings are of the same

[1] P. Ashworth and W. T. Dixon, *Chem. Comm.*, 1971, 1150.
[2] P. Ashworth and W. T. Dixon, *J.C.S. Perkin II*, 1972, 1130.

[3] P. Brassard and P. L. Écuyer, *Canad. J. Chem.*, 1958, **36**, 700.

order as the line-widths, and since we observe the first derivative of the absorption spectrum, overlapping of maxima and minima can lead to reductions of apparent
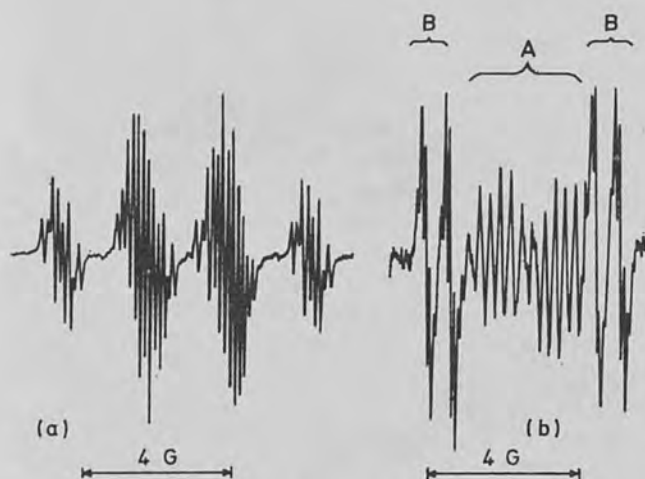
previous workers.[4-6] These rules may be summarised thus: (1) coupling constants of protons *para* to a substituent on the semiquinone nucleus are large; (2) coupling constants of protons *ortho* to an electron-donating

FIGURE 1 E.s.r. spectra of radicals from *m*-chlorophenylhydroquinone, (a) primary radical (in 50% aqueous ethanol, 0·5% sodium hydroxide); (b) secondary radicals (in 7·5% sodium hydroxide)

TABLE 1

Coupling constants of primary radicals

| | Coupling constants/G | | | | | |
| | a_2 | | | | | |
Aryl group	a_{ortho}	a_{para}	a_{meta}	a_3	a_5	a_6
Ph	0·27		0·16	1·99	2·56	2·12
p-OH	0·32		0·14	1·38	2·53	2·33
p-OMe	0·30		0·15	1·85	2·56	2·16
p-Me	0·28		0·16	1·88	2·55	2·13
p-Ph	0·28		0·20	1·98	2·58	2·10
m-Cl	0·27		0·15	2·00	2·52	2·13
p-Cl	0·28		0·16	2·10	2·54	2·10
p-CO$_2$H	0·27		0·17	2·10	2·56	2·10
p-CO$_2$Me	0·29		0·18	2·26	2·56	1·95
p-NO$_2$	0·30		0·15	2·38	2·50	1·92
	$a_N = 0·75$					
2,5-Diphenyl	0·25		0·14	2·20		2·20
2,5-Di-*p*-Cl	0·31		0·16	1·78		1·78

intensity or even total annihilation of some lines. This leads, in the case of *p*-nitrophenylsemiquinone to some uncertainty in the smaller coupling constants (see Figure 2).

TABLE 2

Coupling constants/G of secondary radicals

| | Secondary radical (A) | | | | | Secondary radical (B) | | | | |
| | | a_5 | | | | | | a_6 | | |
Aryl group	a_3	a_{ortho}	a_{para}	a_{meta}	a_6	a_3	a_5	a_{ortho}	a_{para}	a_{meta}
Ph	0·50	0·54		0·31	1·08	0·67	4·52	0·12		0·12
p-OH	0·53	0·65		0·27	0·53	0·63	4·00	0·14		0·10
p-OMe	0·53	0·59		0·29	0·90	0·65	4·40	0·12		0·12
p-Me	0·50	0·58		0·31	0·90	0·67	4·42	0·13		0·13
p-Ph	0·50	0·58		0·33	1·12	0·66	4·52	0·12		0·12
m-Cl	0·52	0·54		0·29	1·19	0·67	4·62	0·12		0·12
p-Cl	0·48	0·59		0·31	1·16	0·68	4·58	0·12		0·12
p-CO$_2$H	0·48	0·58		0·32	1·17	0·67	4·66	0·12		0·12
p-NO$_2$	0·45	a_{ortho} = 0·60	a_{para} a_N = 0·15	0·30	1·48	0·70	4·86	0·12		0·12

FIGURE 2 One of the side bands of the e.s.r. spectrum of *p*-nitrophenylsemiquinone, with the reconstructed 'stick' spectrum (alternate lines are 'missing')

The assignments given in Tables 1 and 2 are based on the rules adopted in our previous paper [2] on alkyl semiquinones and which are in agreement with the results of

substituent are small. As an example, consider structure (I). Position 5 is *para* to X; positions 5 and 6 are *ortho* to O⁻; position 3 is *ortho* to O⁻ and to X. Hence $a_3 < a_6 < a_5$; (3) the influence of the group X decreases along the series O⁻ ≫ Bu^t > Me > Ph > Cl > H.

(I)
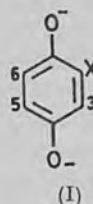
In the case of primary radicals we expect substitution into the phenyl ring to affect H-3 more than H-5, and we

[4] B. Venkataraman, B. G. Segal, and G. K. Fraenkel, *J. Chem. Phys.*, 1959, **30**, 1006.

[5] A. Fairbourn and E. A. A. Lucken, *J. Chem. Soc.*, 1963, 258.
[6] K. A. K. Lott, E. L. Short, and D. N. Waters, *J. Chem. Soc.* (B), 1969, 1232.

assign the larger splitting to H-3 in two cases: (a) $Y = NO_2$ and (b) $Y = CO_2Me$ (see Table 1).

The coupling constants of protons on the phenyl ring were assigned by reference to unambiguous cases (e.g., m-chlorophenyl) and in the primary radicals and the secondary radicals of type (A) the ortho- and para-proton splittings were of the order of twice the meta-proton coupling constants.

Trends in the Coupling Constants.—There seems to be a small but definite relationship between the electron-donating power of the substituent on the phenyl ring and the coupling constants of the various protons. For example, the rules applying to the protons attached to the original quinone nucleus are as follows. For protons ortho to the aryl group, the coupling constants decrease with increasing electron-donating power of Y, as shown in Table 3. Protons meta to the aryl group have coupling

TABLE 3

Y	O⁻	OMe	Me	H	Cl	CO₂Me	NO₂
a_{ortho}							
Primary	1·38	1·85	1·88	1·99	2·10	2·26	2·38
Secondary (A)	0·53	0·90	0·90	1·08	1·16		1·48
Secondary (B)	4·00	4·40	4·42	4·52	4·58		4·86

constants which increase with increasing electron-donating power of Y, as shown in Table 4. Protons para to the

TABLE 4

Y	O⁻	OMe	Me	H	Cl	CO₂Me	NO₂
a_{meta}							
Primary	2·33	2·16	2·13	2·12	2·10	1·95	1·92
Secondary (A)	0·53	0·53	0·50	0·50	0·48		0·45

aryl group are little affected by the substituent Y, if anything the trend is similar to that for ortho-substituents, as shown in Table 5. When the overall spin density in

TABLE 5

| Y	O⁻	OMe	Me	H	Cl	CO₂Me	NO₂
a_{para}							
Primary	2·53	2·56	2·55	2·56	2·54	2·56	2·50
Secondary (B)	0·63	0·65	0·67	0·67	0·68		0·70

the aryl ring is large the ortho- and para-proton coupling constants are of the order of twice those of the meta-protons, but as this overall coupling decreases the splittings become more equal. The difference between the coupling constants of the ortho- and meta-protons is

TABLE 6

Y	Primary		(A)		(B)	
	O⁻	Cl	O⁻	Cl	O⁻	Cl
a_{ortho}	0·32	0·28	0·65	0·59	0·14	0·12
a_{meta}	0·14	0·16	0·27	0·31	0·10	0·12

apparently increased somewhat by electron-donating substituents in the para-position, as shown in Table 6. Addition of the proton coupling constants gives us a

measure of the amount of spin associated with carbon atoms attached to hydrogen, provided that the splittings all have the same sign. If this is the case, then it appears that electron-donating substituents on the phenyl ring tend to decrease the probability of the odd electron being on carbon atoms attached to hydrogen. It, therefore, appears to be probable that the >C–Y group tends to 'attract' spin density more when Y releases electrons more easily. We can rationalise this in terms of valence-bond approach to radicals in which the odd electron is largely associated with oxygen. The only canonical structures which have reasonably low energies and can lead to delocalisation of the odd electron are those having a double bond to, or a negative change on, the oxygen, i.e., for phenoxyl or semiquinone radicals the main canonical structures are of types (i), (ii), and (iii). The
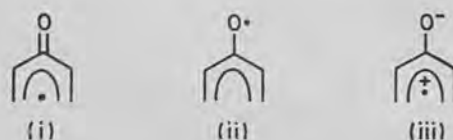
odd electron density will be greater on positions which yield electrons more easily, for the canonical structures in which the odd electron is associated with these positions will have higher probabilities owing to contributions of canonical structures of type (II). The delocalisation of the odd electron to the phenyl group must occur largely through structures such as (II)—(IV) and that explains
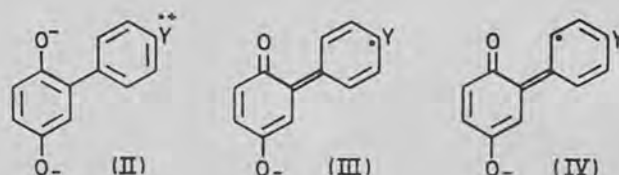
why the spin density on the ortho- and para-positions is generally greater than that on the meta-positions.

Similarly on the hydroquinone nucleus, the trends of the coupling constants of protons meta to phenyl substituents probably arises from the lack of conjugation between the two positions and also, perhaps, from the influence of the phenyl group on the adjacent oxygen atom.

By difference, these trends are opposite to those at the ortho- and para-positions, which, from the usual valence-bond viewpoint, are more directly affected by the substituents, although the observed changes at the para-position are very small.

Finally the extra stability of the radicals of type (A) compared with corresponding radicals (B) is probably due not so much to the fact that there is greater delocalisation of the odd electron in type (A), but more to the availability of a position of high spin density for further attack in the type (B) radicals.

EXPERIMENTAL

E.s.r. spectra were recorded on a Varian E4 instrument. To obtain the primary radicals a solution of the arylhydroquinone (0·01M) in ethanol was mixed with an equal volume of 1% sodium hydroxide solution, both flow and static methods being used. The secondary radicals were obtained by adding an aqueous solution of the hydroquinone (0·05M) to an equal volume of 15% sodium hydroxide solution.

Materials.—The arylquinones were obtained by direct arylation of *p*-benzoquinone *via* the diazonium salts according to the method of Brassard and L'Écuyer.[3] In certain cases, where appreciable amounts of the diarylquinone tended to be formed, it was convenient to use a large excess of the *p*-benzoquinone. The arylquinone was much easier to separate from the excess of starting material than from the diaryl compound. Reaction of the arylquinone in aqueous acetone with further diazonium salt produced the 2,5-diaryl compound in moderate yield.[3]

The triacetoxy-derivatives were prepared by heating the quinone with acetic anhydride and a little concentrated sulphuric acid at 80 °C.
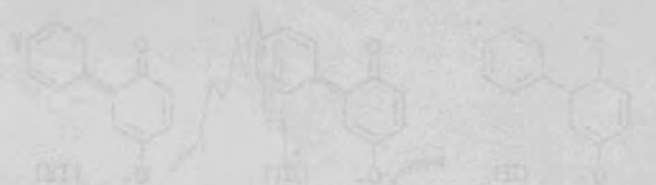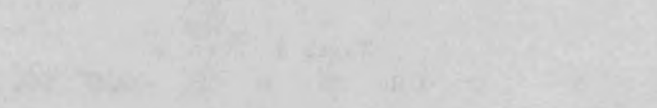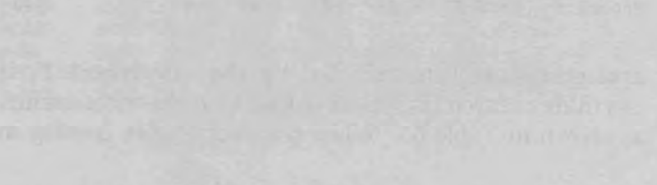
Secondary Radicals in the Autoxidation of Hydroquinones and Quinones

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Secondary Radicals in the Autoxidation of Hydroquinones and Quinones

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The autoxidation of hydroquinones and quinones in strongly alkaline solution gives rise to radical intermediates other than the expected semiquinones. These ' secondary ' radicals, which are derived from 1,2,4-trihydroxybenzene, can be characterised by means of e.s.r. spectroscopy. Different isomeric radicals may be formed, depending on the solvent, and apparently these may reduce any excess of quinone present to the corresponding semiquinone.

SEMIQUINONES were among the first radicals to be investigated by means of e.s.r. spectroscopy because they are easily produced and can generally be obtained in relatively high concentrations. A wide range of *ortho-*, *meta-*, and *para*-semiquinones have been studied.[1-4] However, the formation of semiquinones is only the first stage in the autoxidation of dihydric phenols in alkaline solution. Further stages can profitably be followed by changes in the e.s.r. spectra of the solutions. For example, Stone and Waters [4] have observed semiquinones of trihydroxybenzenes in the autoxidation of some substituted catechols. It is surprising that this

has not been reported before, in any detail, in relation to the autoxidation of hydroquinones, since slight variations in alkalinity, concentration, and in the composition of the solvent lead to radicals derived from 1,2,4-trihydroxybenzenes rather than the expected *p*-semiquinones.[5] These ' secondary ' radicals can be characterised from their e.s.r. spectra which are frequently well defined and easily resolved.

High concentrations of semiquinones can be obtained just as easily from quinones as from the corresponding hydroquinones,[5,6] in spite of the fact that in the latter

[1] G. K. Fraenkel and B. Venkataraman, *J. Amer. Chem. Soc.*, 1955, **77**, 2707.
[2] R. Hoskins, *J. Chem. Phys.*, 1955, **23**, 1975.
[3] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1964, 4302.
[4] T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 1965, 1488.
[5] P. Ashworth and W. T. Dixon, *Chem. Comm.*, 1971, 1150.
[6] D. C. Reitz, J. R. Hollahan, F. Dravnieks, and J. E. Wertz, *J. Chem. Phys.*, 1961, **34**, 1457.

case there is aerial oxidation, and in the former an overall reduction. This apparent paradox can be resolved by postulating intermediates capable of reducing quinones and it seems that these may well be the secondary radicals which we have been investigating. Under certain conditions we observed spectra which appear to arise from products of coupling reactions and we will refer to these as ' tertiary ' radicals.

The radicals we obtained and their e.s.r. coupling constants are shown in the Table. In practice the

stituted and the 2,3-dimethylhydroquinones. (b) The hydroquinone or quinone (ca. 0·005M) was left in 1% sodium hydroxide solution for ca. 1 h and then an equal volume of 10% sodium hydroxide was added. This was effective for the disubstituted compounds where method (a) gave only primary radicals. (c) A solution of the quinone (ca. 0·01M) was added dropwise to an excess of alkali (5% NaOH).

The solutions were immediately transferred to an aqueous cell in the cavity of an e.s.r. spectrometer. The

Coupling constants of primary (as I) and secondary (as II) radicals

	Coupling constants/G									
	Primary radical (in 50% aq. EtOH)					Secondary radical				
Parent hydroquinone:	a_2	a_3	a_5	a_6		a_3	a_5	a_6	Solvent	
Hydroquinone		←―――2·37――――→				0·60	4·98	1·34	Water	
Methyl	2·12 (Me) (quartet)	1·76	2·61	2·41	A	0·58	5·12 (Me)	0·69	50% aq. EtOH	
					B	0·55	4·15 (Me)	0·95	Water	
Ethyl	2·02 (Et) (triplet)	1·74	2·53	2·53	A	0·54	4·56 (Et)	0·71	50% aq. EtOH	
					B	0·56	4·14 (Et)	1·08	Water	
t-Butyl		1·65	2·89	2·12	A	0·52	0·16 * (Bu^t) (septet)	0·84	Water	
					B	0·66	4·02		Water	
2,3-Dimethyl	1·74 (Me)	1·74 (Me)	2·62	2·62		0·55	4·70 (Me)	0·55 (Me)	Water	
2,6-Dimethyl	2·09 (Me)	1·93	1·93	2·09 (Me)		0·97 (Me)	5·20 (Me)	0·72	50% aq. DMF †	
2,5-Dimethyl	2·34 (Me)	1·80	2·34 (Me)	1·80		0·88 (Me)	4·20	0·98 (Me)	50% aq. DMF †	
5-Isopropyl-2-methyl	2·18 (Me)	1·76	1·92 (Pr^i) (doublet)	1·46		0·92 (Me)	4·20	0·75 (Pr^i) (doublet)	Water	

* Splitting from 6 equivalent protons showing that the t-butyl group is not freely-rotating (C. Trapp, C. A. Tyson, and G. Giacometti, J. Amer. Chem. Soc., 1968, 90, 1394). † Dimethylformamide.

observation of each secondary radical was favoured by certain conditions. A working guide for producing the radicals is as follows.

Primary Radicals.—These are produced in even faintly alkaline solutions of hydroquinones and quinones and are more stable in alcoholic media. The spectra are best observed by use of a flow system and in this case a solution of the hydroquinone (0·005M) in ethanol was allowed to flow against 1% sodium hydroxide solution.

Secondary Radicals.—Although these are formed in dilute alkali, more concentrated alkali is usually required to obtain good e.s.r. spectra. Different isomeric radicals may be obtained depending on the solvent (see Table) and sometimes mixtures of these radicals are observed. The techniques used for obtaining e.s.r. spectra of the secondary radicals were as follows. (a) A solution of the hydroquinone (ca. 0·01M) in the appropriate solvent was added to 10% sodium hydroxide solution. This technique was particularly effective for the monosub-

spectra observed were then normally uncontaminated by the presence of other radicals and subsequent interpretation was made easier. The exact values of the coupling constants of the secondary radicals were found to depend on the nature of the solvent, as observed for primary radicals.[7]

Characterisation of the Radicals.—We felt that the e.s.r. spectra alone did not enable us to deduce with certainty the nature of the secondary radicals, so we tried to gather supporting evidence. The most obvious method was to synthesise the 1,2,4-trihydroxybenzene derivatives which on autoxidation should give semiquinones which correspond to the secondary radicals. We did this for three hydroquinones by means of the sequence[8] (1). When R = H we observed the same eight-line spectrum (from three doublet splittings) as that ascribed to the secondary radical of hydroquinone

[7] E. W. Stone and A. H. Maki, J. Chem. Phys., 1962, 36, 1944.
[8] E. B. Vliet, Org. Synth., Coll. Vol. I, 317.

R R

(see Figure 2). When R = Me we observed the same spectrum as that of radical A from 2,5-dihydroxytoluene. When R = Bu^t we observed the same spectrum as that

(a)

(b)

(c)

FIGURE 1 The e.s.r. spectra obtained from alkaline solutions of ethylhydroquinone: (a) primary radical in 50% ethanol, 1% NaOH; (b) secondary radical A in 50% ethanol, 10% NaOH; (c) secondary radical B in 10% NaOH
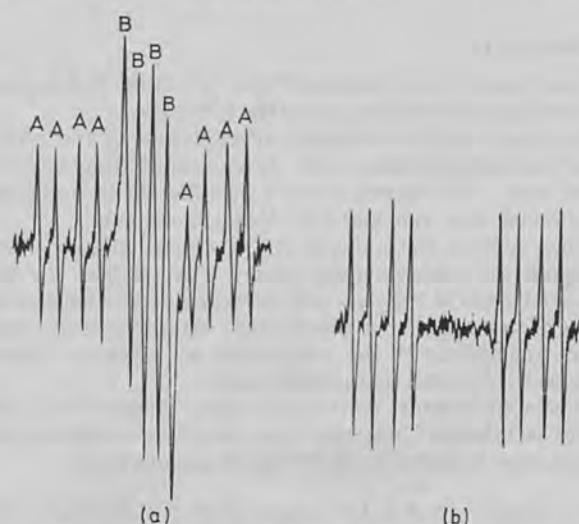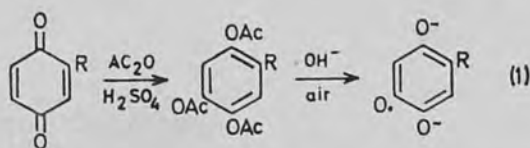

(a)

(b)

FIGURE 2 (a) Spectrum from hydroquinone (0·001M) in 5% NaOH; lines A due to secondary radical; lines B due to tertiary radical. (b) spectrum from 1,2,4-triacetoxybenzene in 5% NaOH

of radical A from 1,4-dihydroxy-2-t-butylbenzene. The three radicals just discussed were also reproduced by

(1)

adding solutions of catechol and the 4-substituted catechols (0·01M) dropwise to 5% sodium hydroxide. If 5% alkali is added to a more concentrated solution of

catechol (0·05M) a different type of radical is observed along with the o-semiquinone, i.e., the dimer observed by Stone and Waters.[9]

Having thus proved the identity of these three radicals we reasonably infer the structure of other secondary radicals on the basis of their e.s.r. spectra and a knowledge of the starting material. The following rules seem to apply: (i) Spin densities para with respect to oxygen atoms are high (proton coupling constants ca. 4—5 G); (ii) methyl proton coupling constants tend to be slightly higher than corresponding aromatic proton splittings; (iii) spin densities on ring carbon atoms between those attached to two oxygen atoms are apparently lower than those on carbon atoms adjacent to only one carbon–oxygen linkage.

On the basis of these empirical rules we could consistently account for the observed hyperfine splittings. Our assignments imply that hydroxyl is introduced into the ring at the least hindered position, as expected.

DISCUSSION

Since our secondary radicals are derived from 1,2,4-trihydroxybenzenes, we now ask how they arise. It is of interest that both hydroquinones and quinones can be used as starting materials.

It is not difficult to arrive at a feasible reaction scheme. The first steps (2) in the autoxidation of hydroquinone lead to benzoquinone. We are not concerned here with coupling products so the next stage is the introduction of a further oxygen atom into the ring. Here we are

(2)

(3)

(4)
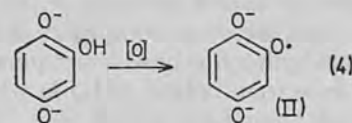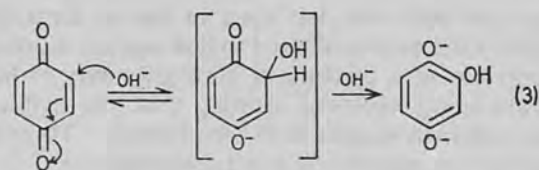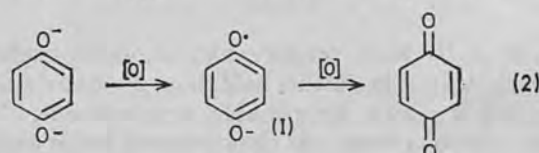
helped by two well-established reactions in which no overall oxidation of the quinone takes place. First, there is addition of HCl to give chloroquinol,[10] and secondly there is the Thiele acetylation[8,11] discussed above. We might, therefore, expect a base-catalysed addition (3) of the elements of water. If this is so there

[9] T. J. Stone and W. A. Waters, J. Chem. Soc., 1964, 408.
[10] J. B. Conant and L. F. Fieser, J. Amer. Chem. Soc., 1923, 45, 2194.
[11] J. Thiele and E. Winter, Annalen, 1900, 311, 341.

must then be further attack by oxygen (4) to give the semiquinone of trihydroxybenzene.

We can now rationalise the observed reduction of quinones when their alkaline solutions are shaken in air. It appears that they are reduced by the corresponding secondary radicals. This possibility is strengthened by our experiments on quinones. When the quinone is always present in high concentration (e.g., 0·01M), the primary radical is observed in alkaline solution, whereas if the concentration of the quinone is kept low (i.e., by adding a 0·01M solution dropwise to alkali) a secondary radical is observed.

Similarly when an alkaline solution of benzoquinone (ca. 0·01M) is left, the signal due to the semiquinone decays. After ca. 1 h, addition of fresh alkali leads to the secondary radical, showing that the trihydroxy-benzene derivative must have replaced the quinone.

Therefore, we suggest the Scheme for the cycle of reactions leading to the formation of primary and second-

SCHEME
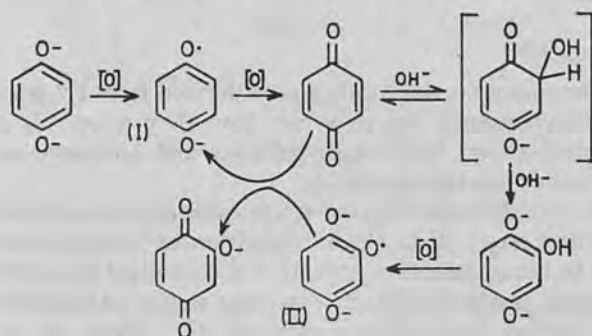
ary radicals.[12] Both primary and secondary radicals may be destroyed by further oxidation, by dimerisation, or by coupling with, for example, benzoquinone. The further oxidation stage was demonstrated by an experiment in which a solution of t-butylhydroquinone in 5% sodium hydroxide was left open to the air for a day. When the mixture was allowed to flow against dithionite the spectrum of a mixture of both secondary radicals (see Table) was observed showing that the hydroxy-quinone derivatives must have been formed. There was no trace of the spectrum of t-butylsemiquinone.

We have obtained a number of well defined spectra which are probably due to coupled products of the reaction. For example the quartet which appears in the secondary spectrum from hydroquinone or benzoquinone (Figure 2) appears to arise from radical (IIIa) in which there is no delocalisation around the second ring. The

coupling constants, 0·90 and 0·45 G, are similar to those obtained by Reitz et al.[6] starting from the quinol (IV) but they apparently saw a further splitting of 0·1 G. We did not observe this small splitting but we feel justified in our assignment because, first, the magnitudes of the coupling constants are just those expected for a trihydroxy-compound and not for a substituted semi-quinone (cf. radical A from t-butylhydroquinone in the Table). Secondly, under the conditions of their experiment (10% NaOH), we would expect a secondary-type radical.
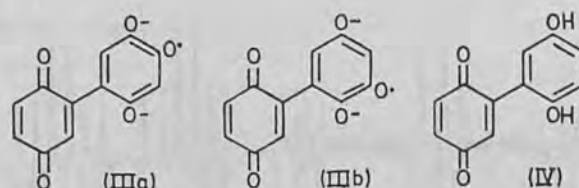
If we add 10% sodium hydroxide to a solution of benzoquinone in 50% dimethylformamide we observe a different quartet (splittings 4·52 G, 0·70 G) which we ascribe to the isomeric radical (IIIb). However, the situation with regard to these tertiary radicals is still not clear and further study is required.

EXPERIMENTAL

E.s.r. spectra were obtained with a Varian E-4 instrument by use of both flow and static methods.

Quinones could be obtained by oxidation of the corresponding hydroquinones with chromic anhydride in 60% acetic acid. The reverse process was effected by reducing the quinone with zinc and 25% hydrochloric acid.

When neither the quinone nor the hydroquinone were available the corresponding phenol was oxidised to the quinone by use of Frémy's salt, according to the method of Tauber and Rau.[13] 4-Substituted catechols were prepared analogously,[14] the o-quinones so produced being reduced by zinc and hydrochloric acid.

Triacetoxybenzene derivatives were prepared by the Thiele acetylation[8] and were used directly since the acetyl groups were hydrolysed off by the alkaline medium.

[12] M. Eigen and P. Matthies, Chem. Ber., 1961, 94, 3309.
[13] H.-J. Teuber and W. Rau, Chem. Ber., 1953, 86, 1036.
[14] H.-J. Teuber and G. Staiger, Chem. Ber., 1955, 88, 802.