

AN ELECTRON SPIN RESONANCE STUDY OF
REACTIONS OF AROMATIC HYDROCARBONS WITH SULPHURIC ACID

by

The author wishes to express his thanks to
Professor G.H. Williams and Dr. A. Horsfield for their
friendly advice, encouragement and many helpful discussions.

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The author is indebted to Dr. S. J. D. Jones for
running the ESR spectra of some samples.

A THESIS

Thanks are accorded to various institutions for
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The author is indebted to his wife, Ursula, for
her patience and encouragement and for typing this thesis.

UNIVERSITY OF LONDON

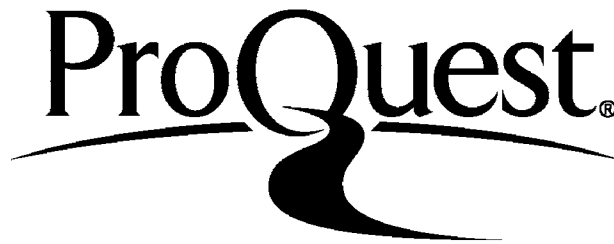
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Abstract

The object of this research was to investigate the utility of the e.p.r. technique itself, and where necessary, in conjunction with other spectroscopic techniques, in studying the complex reactions of polyalkylated aromatic hydrocarbons which have low first ionisation potentials, with sulphuric acid.

The formation of immediate electron paramagnetic resonance (e.p.r.) signals from hexamethylbenzene (H.M.B.), pentamethylbenzene (P.M.B.) and durene on admixture with sulphuric acid has been investigated in the presence and absence of ultra-violet light. The kinetics of the H.M.B. system have been studied, and the activation energy measured.

The prolonged reaction of hexamethylbenzene with 98% sulphuric acid has been investigated and leads to the formation of the 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene radical cation, as a result of Jacobsen rearrangement of hexamethylbenzene. This radical cation is also formed rapidly by exposure of a solution of 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene in 98% sulphuric acid to ultra-violet light.

Finally, a mechanism is postulated for the reactions of hexamethylbenzene with 98% sulphuric acid.

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Electron Paramagnetic Resonance Spectroscopy

The following brief account of electron paramagnetic resonance spectroscopy (e.p.r.) and associated phenomena is essentially a qualitative one, and mathematical principles are introduced only when necessary.

1A. Basic Theory.

Since the primary requirement of e.p.r. is that the system

SECTION I

Electron Paramagnetic Resonance Spectroscopy

under investigation must have an unpaired electron, it is first necessary to discuss some of the basic properties of fundamental particles such as electrons and protons.

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Fig. 1

Electron Paramagnetic Resonance Spectroscopy.

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1A. Basic Theory.

Since the primary requirement of e.p.r. is that the system under investigation must have an unpaired electron, it is first necessary to discuss some of the basic properties of fundamental particles such as electrons and protons.

Consider a modified Stern-Gerlach experiment in which a stream of electrons (in place of alkali metal atoms) is passed through an inhomogeneous magnetic field and any effect is observed on a photographic plate perpendicular to the beam. Development of the photographic plate would then reveal the pattern shown in the following diagram.

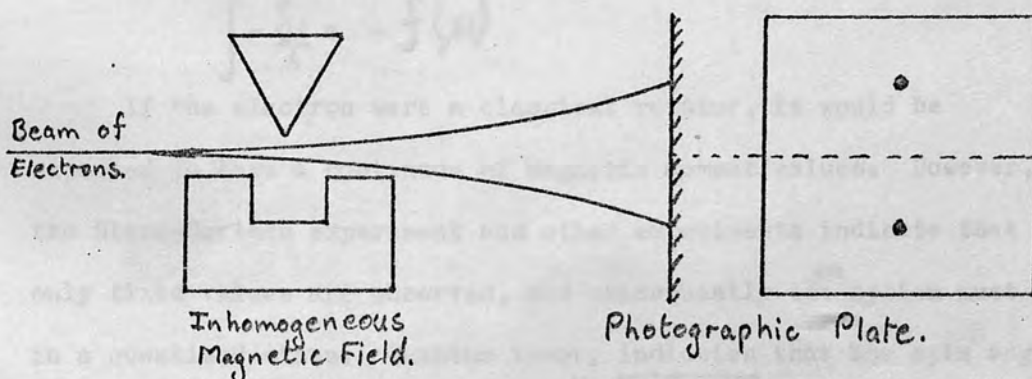


Fig. 1.

This resultant pattern of two discrete spots allows two conclusions to be drawn :

- (a) the electron has a magnetic moment.
- (b) there are two sorts of electrons whose magnetic moments are opposite in sign and equal in magnitude.

Accepting that two other fundamental properties of an electron are its mass m and charge e , and further assuming that the charge is spinning, a magnetic moment μ arises as follows :

If the electron is considered to be a sphere with its charge concentrated on the surface, then an elemental strip of area δA is equivalent to a current of magnitude $-e \frac{\delta A}{A}$ flowing in a wire, and by analogy with classical electricity a magnetic field is produced perpendicular to the plane of the wire.

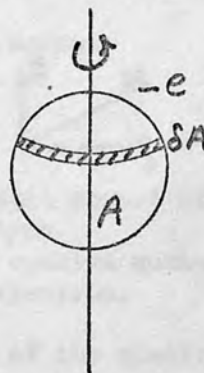


Fig. 2.

Thus
$$-\frac{\delta A}{A} e = \delta \mu$$

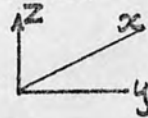
and summing these elemental strips over the whole sphere, the resultant magnetic moment μ is given by

$$\int -\frac{\delta A}{A} e = f(\mu)$$

If the electron were a classical rotator, it would be expected to have a continuum of magnetic moment values. However, the Stern-Gerlach experiment and other experiments indicate that only fixed values are observed, and consequently the system must be in a quantized state. Quantum theory indicates that the spin angular momentum is quantized in units of $\hbar \sqrt{S(S+1)}$ where S is the total spin angular momentum. Thus the resultant magnetic moment

must also be quantized such that $\mu = -g\beta\sqrt{S(S+1)}$ in units of \hbar . In these equations, \hbar is Planck's constant divided by 2π , β is the Bohr magneton for the electron, which has the value 9.2732×10^{-21} erg gauss⁻¹, g is the Lande splitting factor, which has the value 2.0023 for a free electron and may be thought of as a correction factor allowing for an admixture of orbital and spin momentum contributions.

As a result of space quantization, the maximum observable value of the spin angular momentum differs from its actual magnitude, and hence the measureable component of the magnetic moment (in the S_z direction of a cartesian axis system



has the value

$$\mu_e = -g\beta M_s$$

μ_e represents the magnetic moment of an electron
 M_s represents the spin quantum number for the electron.

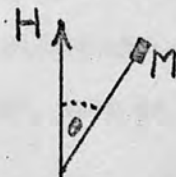
Since the quantum laws permit only two orientations of the electron with $M_s = \pm \frac{1}{2}$,

$$\mu_e = -\frac{1}{2}g\beta \text{ or } +\frac{1}{2}g\beta$$

If a bar magnet is placed in a magnetic field energy must be supplied in order to hold a magnet with a magnetic moment M at some angle θ to the direction of a field of magnitude H . The energy required is given by the equation

$$E = -MH \cos \theta$$

i.e. vectorically $E = -\vec{M} \cdot \vec{H}$



By analogy with the bar magnet the energy of an electron with its resultant magnetic moment in an external field of strength H may be expressed as

$$E = -\vec{\mu}_e \cdot \vec{H}$$

Thus $E = -g\beta M_s H$

However in the presence of a magnetic field, the energy levels of an electron are no longer degenerate, but split into two levels whose energies are given by $E = \pm \frac{1}{2}g\beta H$. This splitting of energy levels is approximately linear in H for the electron

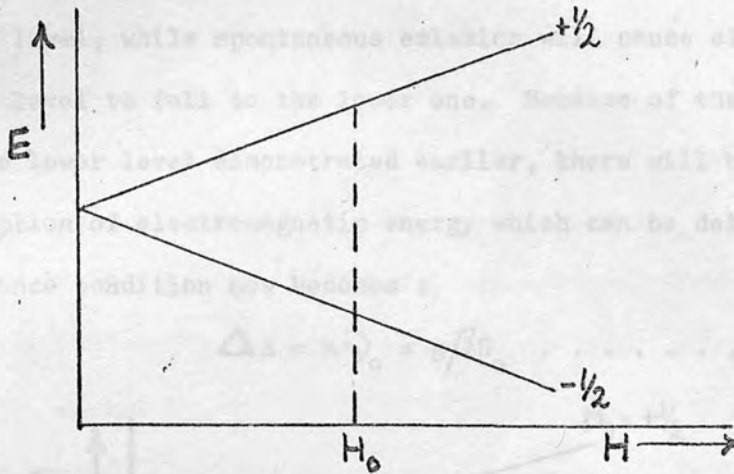


Fig. 3.

and at a particular field H_0 this energy difference is given by

$$\underline{\Delta E = g\beta H_0.}$$

Now in a statistical sample of weakly interacting free electrons which are in equilibrium in a magnetic field, some will have their magnetic moments aligned parallel and others anti-parallel to the field. A Boltzmann distribution will govern the number of electrons in each level ($N_{+1/2}$ and $N_{-1/2}$ respectively), with an excess in the lower level, given by :

$$\frac{N_{+1/2}}{N_{-1/2}} = e^{-\frac{\Delta E}{RT}} \sim 0.998 \text{ at } 25^\circ\text{C}$$

and the electron paramagnetic resonance experiment relies on the existence of this population difference. The greater the population difference, the greater the sensitivity of the technique.

If this equilibrium distribution is now perturbed by applying electromagnetic radiation of frequency ν to the sample containing the unpaired electrons, such that the energy quanta are equivalent to the energy difference ΔE between the two levels at a field H_0 , then electrons in the lower level will be promoted to the upper level, while spontaneous emission will cause electrons in the upper level to fall to the lower one. Because of the excess population in the lower level demonstrated earlier, there will be a net absorption of electromagnetic energy which can be detected. Thus the resonance condition now becomes :

$$\Delta E = h\nu_0 = g\beta H_0 \dots \dots \dots \text{equation 1.}$$

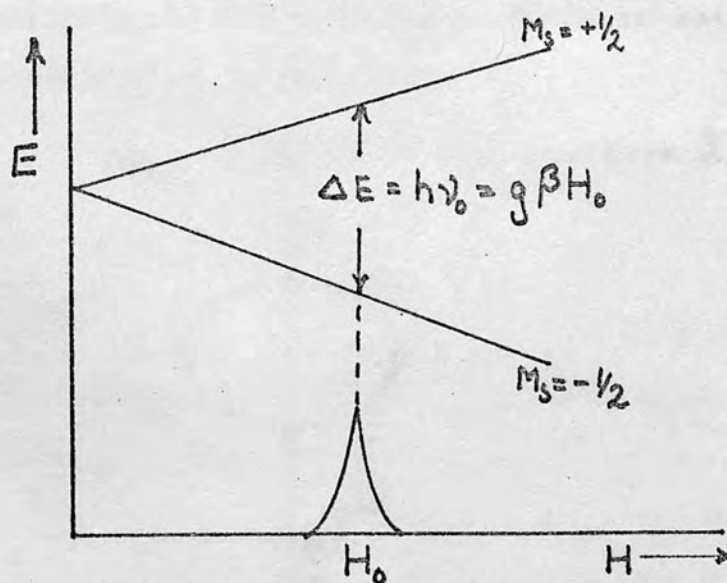
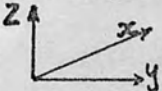


Fig. 4.

The $+1/2$ state is the high energy state, because in this state the resolved component of the angular momentum in the z direction in a cartesian axis system, , is in the field direction, and the z component of the resultant magnetic moment is opposed to the field direction.

As was stated earlier, the transitions between these levels can be induced by the interaction of the electromagnetic radiation frequency ν_0 as indicated in equation (1). The interaction which causes these transitions is between the magnetic dipole of the electron and the oscillating magnetic field associated with the exciting electromagnetic radiation, and this interaction may be envisaged in the following way.

As a result of space quantization the magnetic moment vector never exactly aligns itself along the applied field direction, instead it executes a precessional motion about the axis of the field, such that the angle θ remains constant. The angular frequency of this precession ω_0 is termed the "Larmor frequency" and is related to the applied field H_0 by the equation

$$\omega_0 = \gamma H_0 \text{ --- --- equation 2.}$$

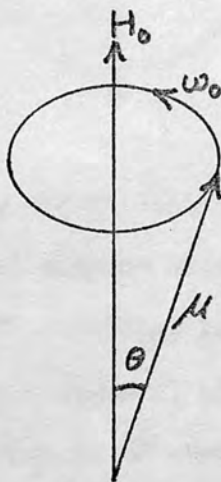


Fig. 5.

where γ is the magnetogyric ratio of the dipole i.e. the ratio of the magnetic moment to the angular momentum. Now the energy of such a dipole in the field H_0 may be expressed as : $E_m = -\mu H_0 \cos \theta$ where E_m is quantized corresponding to discrete values of θ .

If a field H_1 is now applied perpendicular to the plane containing μ and H_0 , the dipole will experience a second couple $\mu H_1 \cos \theta$ tending to cause precession about H_1 .

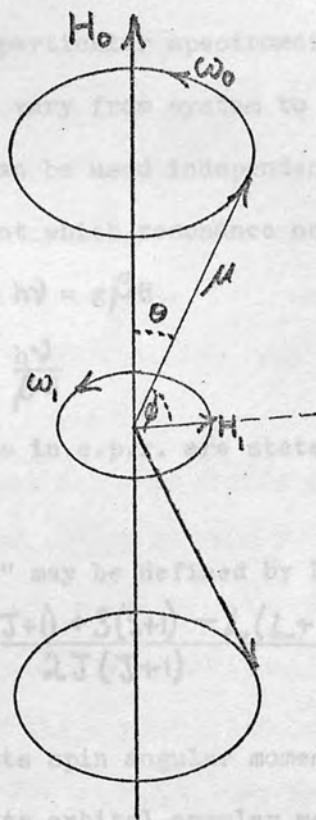


Fig. 6.

If H_1 is now caused to rotate about H_0 at a frequency ω_1 , the combination of the two precessional moments when $\omega_1 \neq \omega_0$ will cause disturbance in the direction of μ resulting in phase changes between μ and H_1 , but θ will not change. However, if $\omega_1 = \omega_0$ the dipole μ will oscillate, since a change in θ corresponds to a change in energy of the system. This change is quantized, thus inducing transitions between the magnetic energy levels when this applied field rotates at the Larmor precession frequency. The resonance condition arises this way.

1B. g-Factors.

In order to measure the position of an e.p.r. line in a manner that is of use to other workers, the measurement should be independent of the particular spectrometer used. Since both the field and frequency vary from system to system for a given sample, neither parameter can be used independently and hence the ratio of frequency to field at which resonance occurs is employed, i.e. from the basic equation $h\nu = g\beta H$

$$\text{we obtain } g = \frac{h\nu}{\beta H}$$

hence line positions in e.p.r. are stated in terms of "g-values" or "g-factors".

The "g-factor" may be defined by Lande's formula :

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

where: S represents spin angular momentum

L represents orbital angular momentum

J represents total angular momentum

and allows for contributions arising from angular momenta other than spin angular momentum which may affect the resultant magnetic moment of the spin system. For a free electron, $S = \frac{1}{2}$, $L = 0$ and thus $J = S$. Substitution in Lande's expression would lead to a g-value of 2.0000; however, as was stated earlier, the g-factor for the free electron has the value 2.0023. This value differs from 2.0000 because it is necessary to apply a relativistic correction, which is discussed in more detail later.

Further consideration of real systems indicates that an electron may also possess orbital angular momentum with an associated magnetic moment. For atoms, linear molecules with unpaired electrons

and other systems with orbitally degenerate ground states in the gas phase; the spin and orbital moments must combine and transitions are then observed between the various combined states. However, systems with lower symmetry, not having orbitally degenerate ground states, or species in which the orbital degeneracy has been removed by the environment so that the ground state is effectively an orbital singlet, are of more relevance to the work reported in this dissertation. In these cases the deviation is small and may be thought of as stemming from small perturbing fields arising from a very small induced orbital motion. This adds to or subtracts from the external field, giving a negative ($-\Delta g$) or positive ($+\Delta g$) shift.

Consider these g -shifts with respect to the molecule NO_2 . Since none of the orbitals of this bent molecule can be degenerate, the ground state of the molecule cannot possess electron orbital angular momentum. Now consider what happens as the molecule bends, and the energies of the two in-plane and out-of-plane orbitals diverge. (Fig. 7)

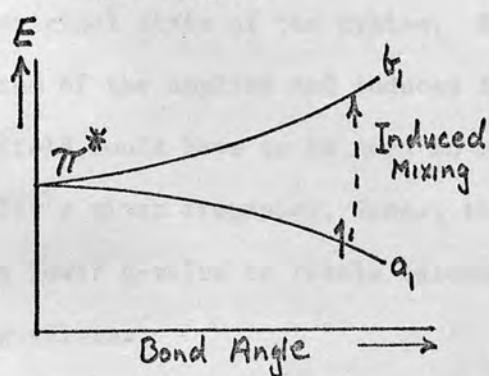


Fig. 7.

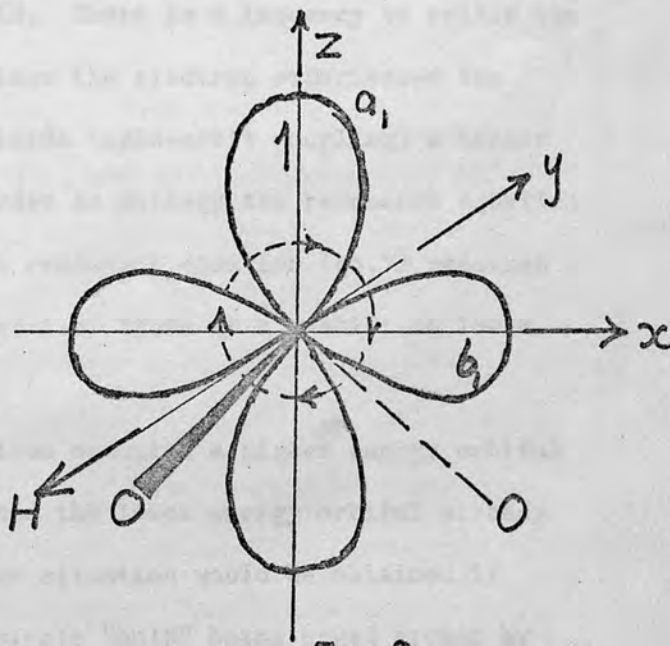


Fig. 8.

In the linear state the p_x and p_y atomic orbitals contribute to a doubly degenerate orbital and the unpaired electron therefore has unit angular momentum about the internuclear axis. When the molecule bends, the degeneracy of the orbitals is removed and the electron occupies the lower a_1 orbital. Since the unpaired electron can only circulate the molecular framework about the y -axis by excitation through the b_1 orbital, the ground state of the molecule has no orbital angular momentum. If the molecule experiences an external field, as it does in the e.p.r. experiment, then this field will provide the energy required to overcome energy barrier between the a_1 and b_1 orbitals and will tend to 'drive' the orbital angular momentum to an extent governed by the energy difference between the two orbitals. Hence the presence of an applied field induces mixing of the a_1 and b_1 orbitals, resulting in an effective orbital motion of the electron in the plane perpendicular to the applied field. This motion gives rise to an induced magnetic field that opposes the external applied field. There is a tendency to retain the original state of the system. Since the electron experiences the sum of the applied and induced fields (spin-orbit coupling) a higher field would have to be used in order to satisfy the resonance equation for a given frequency. Hence, the resonance equation (eq.1) requires a lower g -value to retain balance; i.e. there is a g -shift to lower g -values.

Conversely if the unpaired electron occupied a higher energy orbital in the scheme depicted earlier, and the lower energy orbital already contained electrons, then the same situation would be obtained if the system were considered as a single "hole" being urged around by the applied field. Since this "hole" is positive with respect to

the electron, the induced field experienced by the electron is increased and consequently the resonant condition is met for a lower value of the external applied field, giving a shift of the g-value to higher values.

Further by applying the field perpendicularly to the yz plane, orbital motion may be induced about the x-axis. By an analogous argument application of the field perpendicularly to the xy plane would lead to induced orbital motion about the z-axis. It is unlikely that any of these pairs of orbitals would be degenerate and thus one would expect to observe a g-value which was different from that in the other two directions. This leads to the result that the field at which resonance occurs depends upon the degree of spin orbital coupling in the molecular system and also, the orientation with respect to the external field, hence the term anisotropy (direction dependence) of the g-value.

In solution, this anisotropy is averaged to a median value as a result of the random Brownian motion of the molecules - termed the isotropic value;

$$\text{i.e. } g_{\text{iso}} = \frac{1}{3} (g_{\text{xx}} + g_{\text{yy}} + g_{\text{zz}})$$

This averaging leads to a rather more simple system for initial interpretation.

1C. Hyperfine Structure.

1C.1 Origin - So far, only the interaction of the unpaired electron with the externally applied field has been considered. However, any real system may well contain other nuclei with resultant magnetic moments that will influence the energy levels of the unpaired electron. The most commonly occurring such nucleus in organic systems

with a magnetic moment is the proton with a nuclear spin of $+\frac{1}{2}$, and as with the electron this may align itself with its resultant magnetic moment 'parallel' or 'anti-parallel' to the externally applied field and thus, modifies the energy levels of the unpaired electron. Consider a free radical containing a proton such as $\text{OH}\cdot$ or $\text{CH}(\text{SO}_3)_2^-$. The oxygen or the carbon and sulphur atoms may be ignored as their naturally abundant isotopes have no resultant magnetic moment ($I=0$). This coupling between the magnetic moments of the proton and the electron leads to four possible combinations of the orientations of the magnetic moments i.e.

M_S	M_I
$+\frac{1}{2}$	$+\frac{1}{2}$
$+\frac{1}{2}$	$-\frac{1}{2}$
$-\frac{1}{2}$	$-\frac{1}{2}$
$-\frac{1}{2}$	$+\frac{1}{2}$

which leads to the following energy level diagram (Fig.9)

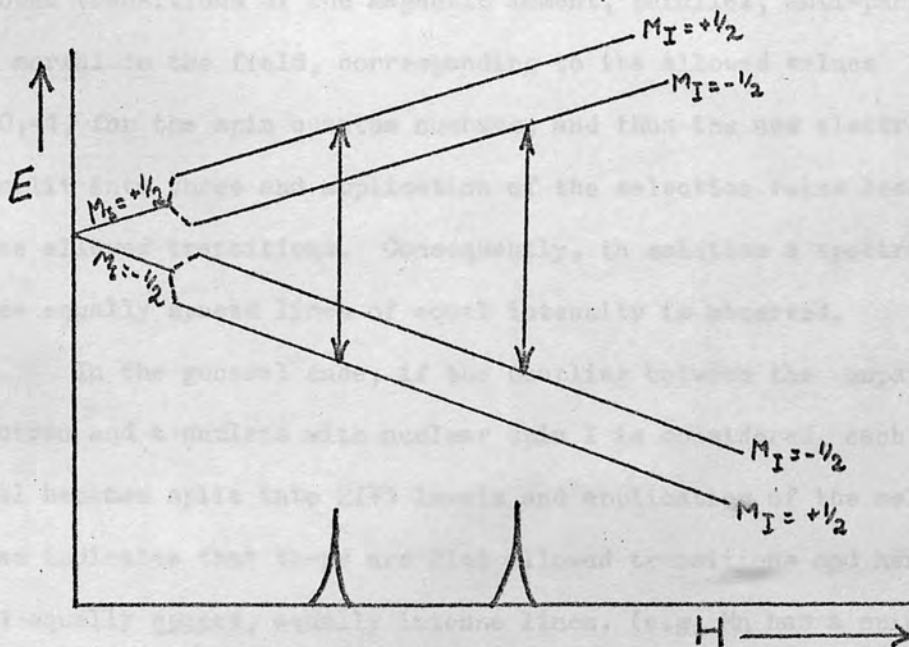


Fig. 9.

Hence, the additional coupling from a proton further splits the basic electron energy levels to give a total of four energy levels. Calculations show that a finite probability only exists for transitions satisfying certain selection rules. By applying these selection rules governing the transitions, namely :

$$\Delta M_S = \pm 1$$

$$\Delta M_I = 0$$

it can be seen that two energy transitions are allowed and hence a spectrum with two lines is observed as the external magnetic field is swept, as indicated in fig. 9. The spectrum may be said to exhibit "hyperfine structure" and the separation between the lines (generally measured in gauss or MHz where 1 gauss = 2.80MHz) is termed the "hyperfine splitting".

This treatment may be extended to nuclei with spins greater than $\frac{1}{2}$, e.g. ^{14}N which has a spin $I=1$. In this case there are three allowed transitions of the magnetic moment, parallel, anti-parallel, and normal to the field, corresponding to the allowed values +1,0,-1, for the spin quantum numbers, and thus the new electron level is split into three and application of the selection rules leads to three allowed transitions. Consequently, in solution a spectrum of three equally spaced lines of equal intensity is observed.

In the general case, if the coupling between the unpaired electron and a nucleus with nuclear spin I is considered, each electron level becomes split into $2I+1$ levels and application of the selection rules indicates that there are $2I+1$ allowed transitions and hence $2I+1$ equally spaced, equally intense lines. (e.g. Mn has a spin of $\frac{5}{2}$ hence a solution of MnSO_4 in water gives a spectrum of six lines)

1C.2 Coupling with equivalent protons - So far consideration

has been given only to interaction of the unpaired electron with one other magnetic nucleus, the effect of two or more additional, equivalent nuclei, such as two protons in $\text{>}\dot{\text{C}}\text{H}_2$ is as follows :

For the $M_S = +\frac{1}{2}$ electron spin state the following set of proton spin states exist :

$M_I =$	Proton 1	Proton 2
	$+\frac{1}{2}$	$+\frac{1}{2}$
	($+\frac{1}{2}$	$-\frac{1}{2}$)
	($-\frac{1}{2}$	$+\frac{1}{2}$)
	$-\frac{1}{2}$	$-\frac{1}{2}$

Fig.10

As these two protons are equivalent there is no difference in energy between the two spin states bracketed together in figure 10, as far as the electron is concerned. These two combinations therefore form a doubly degenerate level. An exactly similar set of sub-levels also exist for the $M_S = -\frac{1}{2}$ electron level. Thus, application of the selection rules, leads to three allowed transitions as indicated in figure 11.

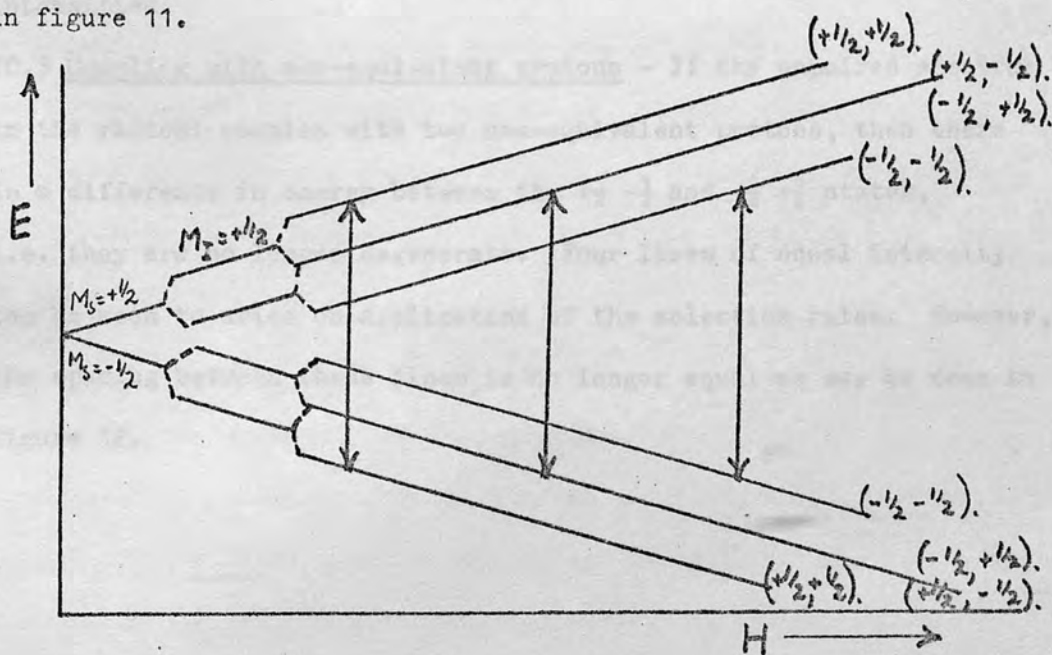
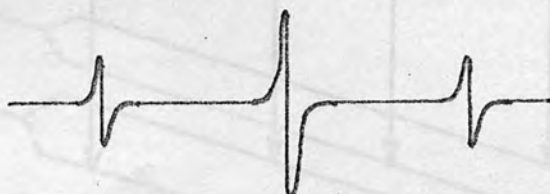


Fig. 11.

These transitions give rise to three equally spaced lines with double the intensity for the transition between the doubly degenerate levels. The spectrum therefore appears as follows :



Intensities: 1 : 2 : 1

Extending this argument to three equivalent protons as in the methyl radical, the spectrum contains four equally spaced lines with the intensity distribution 1:3:3:1, since the inner levels of each group are three-fold degenerate. Thus 'n' equivalent protons lead to (n + 1) equally spaced lines with a binomial distribution of intensities.

10.3 Coupling with non-equivalent protons - If the unpaired electron in the radical couples with two non-equivalent protons, then there is a difference in energy between the $+\frac{1}{2} -\frac{1}{2}$ and $-\frac{1}{2} +\frac{1}{2}$ states, i.e. they are no longer degenerate. Four lines of equal intensity can be seen to arise on application of the selection rules. However, the spacing between these lines is no longer equal as may be seen in figure 12.

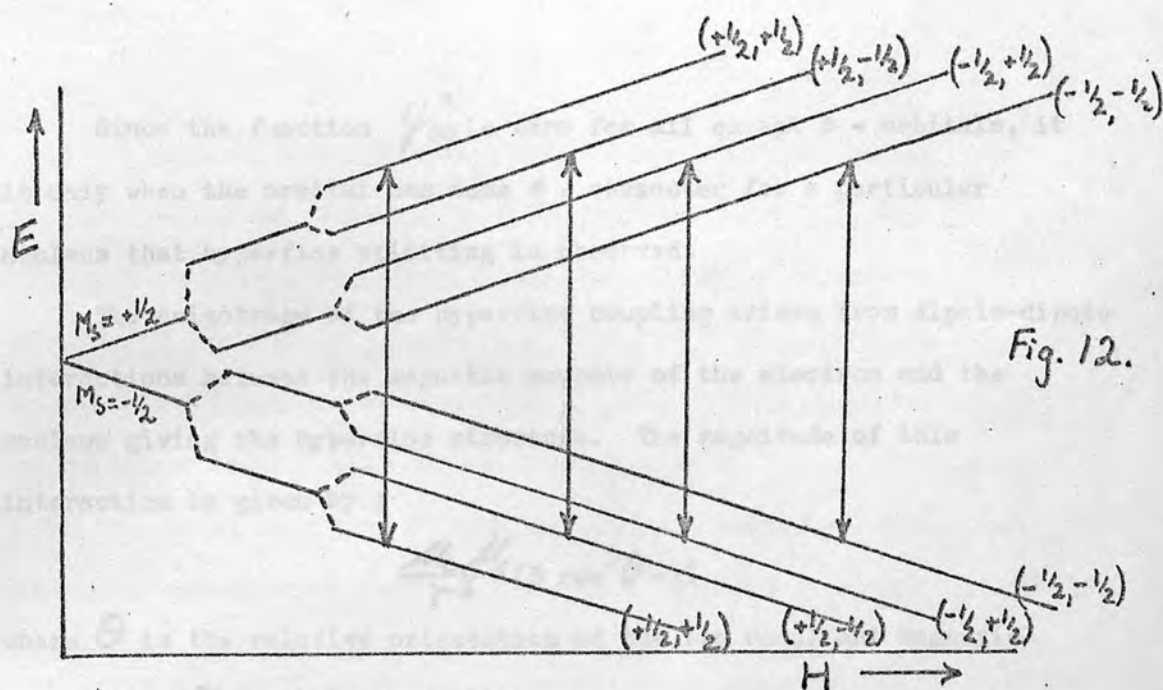


Fig. 12.

In general n non-equivalent protons give rise to 2^n lines of equal intensity, with n distinct hyperfine splittings. (n.b. n nuclei of spin I give $(2I+1)^n$ lines).

1D. Information about the odd-electron orbital.

Hyperfine structure provides information about the orbital of the unpaired electron. The hyperfine splitting is a result of the coupling between the magnetic moment of the electron and the nucleus in question, and this coupling may be separated into two components, the isotropic and anisotropic components. Fermi¹ showed that the isotropic splitting was proportional to the probability of finding the electron at the nucleus, and the hyperfine splitting A is given by the relation :

$$A = \frac{8\pi}{3} g_e g_I \beta_e \beta_I \psi(0)^2$$

where g_e is the g -factor for the electron

g_I is the g -factor for the nucleus in question

β_e is the Bohr magneton for the electron

β_I is the Bohr magneton for the nucleus in question

$\psi(0)^2$ is the probability of the electron existing at the nucleus

Since the function $\psi_{(0)}^2$ is zero for all except s - orbitals, it is only when the orbital has some s - character for a particular nucleus that hyperfine splitting is observed.

The anisotropy of the hyperfine coupling arises from dipole-dipole interactions between the magnetic moments of the electron and the nucleus giving the hyperfine structure. The magnitude of this interaction is given by :

$$\frac{\mu_B \mu_N}{r^3} (3 \cos^2 \theta - 1)$$

where θ is the relative orientation of the two resultant magnetic moments, and r is their separation.

If the radical is in solution, then its orientation with respect to the external field changes rapidly and randomly as a result of Brownian motion, under these conditions the dipolar interaction is averaged to zero, as was the case with the g-value anisotropy. This leaves the Fermi contact interaction as the source of the hyperfine splitting.

1E. Linewidths and Intensities.

In this discussion it has been implied that e.p.r. absorption occur at precise values of the applied magnetic field and at no others i.e. the lines are infinitely narrow, whereas in fact they have a finite width. The main reason for this is that the electrons not only interact with the external applied field, but also with their environment in the sample, in a more or less random way. Consequently the resultant magnetic field experienced by a population of electron spins is not the same throughout the population for a given value of the applied field. Thus the resonance absorption line obtained for a given value of the resultant field is obtained for a

range of values of the applied field. Hence, environmental information may be obtained by observing linewidth changes.

Now consider the basic e.p.r. experiment a little more closely. It was shown earlier that there is a preponderance of spins in the lower state, but still a considerable proportion in the upper state. Thus at the beginning of an e.p.r. experiment there exists an imbalance of populations, and therefore absorption processes outweigh emissions. There is a tendency to equalise the populations and the absorption signal might be expected to disappear gradually. This is not the case, and hence there must be some mechanism which transfers spins from the upper level to the lower level, enabling the system to tend to a condition of thermal population equilibrium. Such mechanisms are referred to as relaxation processes.

1E.1 Spin-Lattice Relaxation T_1 - This is the process which restores the equilibrium ratio of the Boltzman distribution, and involves the thermal equilibrium of the spin system with the lattice or environment of the spin system. This radiationless decay process may be envisaged as a result of oscillating local electrically charged particles producing fluctuating magnetic fields which can couple with the magnetic moment of the electron and hence induce transitions. The energy from the spin system is dissipated as lattice photons, resulting eventually in increased vibrational and translational motion in the environmental molecules. This type of relaxation process has a fairly long relaxation time, T_1 , and is highly temperature dependent.

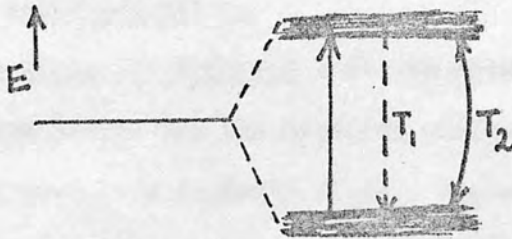


Fig. 13.

1E.1 Spin-Spin Relaxation (T_2) - This process does not affect the population of electron spins, but merely the time that the electrons exist in the upper state. Assume the electron to be in the upper state for a time δt . Heisenberg's Uncertainty principle may be written as

$$\delta E \cdot \delta t = h/2\pi \quad \text{equation 2.}$$

where δE represents a small change in E .

Further, relating energy to frequency ν

$$E = h\nu \quad \text{equation 3.}$$

Now if E becomes $E + \delta E$ eq. 4.

and ν becomes $\nu + \delta\nu$ eq. 5.

where $\delta\nu$ represents a small change in frequency ν

Then substituting equations 4 & 5 in equation 3 gives

$$\delta E = h\delta\nu \quad \text{equation 6}$$

Further, substitution of equation 6 in equation 2 gives

$$\begin{aligned} \delta\nu \cdot \delta t &= 1/2\pi \\ \therefore \delta\nu &= \frac{1}{2\pi\delta t} = \frac{1}{2\pi T_2} \end{aligned}$$

Since T_2 is equivalent to δt by initial definition. If $\delta\nu$ is the spectral linewidth, then T_2 governs the linewidth.

1F. Instrumentation.

1F.1 Basic Spectrometer - It was shown earlier that there are two energy levels for the unpaired electron when a paramagnetic sample is placed in a magnetic field. The energy difference between those levels is denoted by the relationship expressed in equation 1.

For the greatest sensitivity in the spectrometer, the largest difference in population between the energy levels is required, which means having ΔE and hence H as large as possible. For a free electron having a g-value of 2.0023, the radio-frequency required for transitions in a magnetic field of 3,000 gauss, is about 9,000 MHz which is in the microwave region of the electromagnetic spectrum. This is convenient experimentally because microwave components for the frequency range 8,500 - 10,000MHz, called X-band, are commercially available. Other microwave frequencies such as 24GHz, 35GHz etc. have been used, but the following description refers to 9.5GHz systems.

1F.2 Construction - Microwave energy is supplied by a klystron oscillator and is transmitted along a waveguide. It is then directed to a sample chamber, which is a microwave resonant cavity and is coupled via an iris coupling screw to a circulator which has the property that all the power incident on the input port of the circulator is directed to the cavity, and all of the reflected signal at resonance from the cavity is directed through the circulator to the "Backdiode" detector.

The microwave resonant cavity may be thought of as a small piece of waveguide, an integral number of half wavelengths long (i.e. $n\lambda/2$ where $\lambda \sim 3$ cms for the X-Band) with one end closed

and a small coupling hole with an iris coupling screw at the other end. It allows a standing wave pattern of the electric (E_1) and magnetic field (H_1) vectors to be set up. In this work a rectangular mode microwave cavity is employed in which the standing wave pattern shown in the diagram below (fig.14) obtains. This mode pattern is technically known as the TE_{102} mode³⁰. The cavity has a plane of zero E_1 - vector permitting observation of samples in media with high dielectric constants without degrading the efficiency of the system.

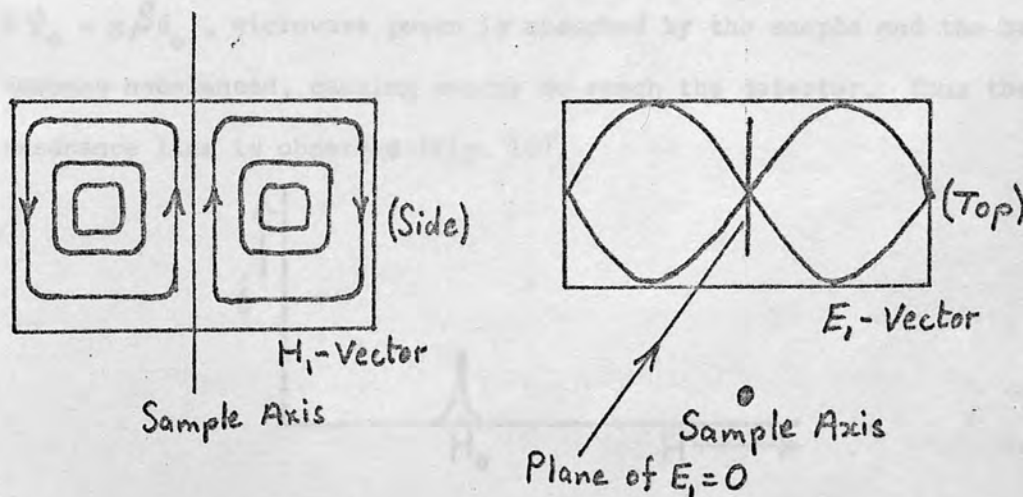


Fig. 14.

This microwave resonant cavity is placed between the pole pieces of a large electromagnet. The iris coupling screw is adjusted so that the 'bridge' formed by the circulator between the klystron and the cavity, and the cavity and the detector is perfectly balanced, consequently no current appears at the detector output.

If the magnetic field is now scanned linearly with respect to time as indicated in fig. 15.

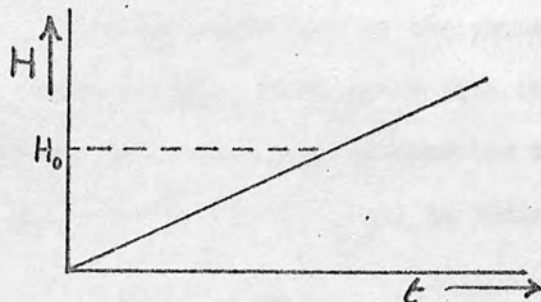


Fig. 15.

When the field reaches the value H_0 satisfying the resonance condition $h\nu_0 = g\beta H_0$, microwave power is absorbed by the sample and the bridge becomes unbalanced, causing energy to reach the detector. Thus the resonance line is observed (fig. 16).

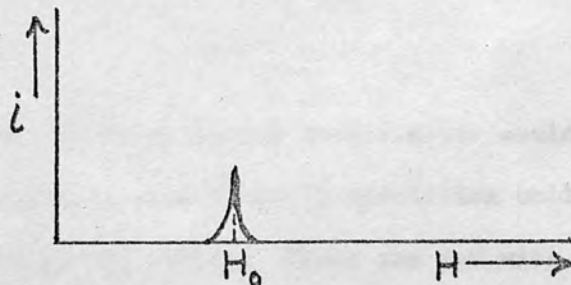


Fig. 16.

In reality the crystal detector works more efficiently if it is biased. This is achieved by mismatching the bridge with the iris coupling screw so that power is reflected from the cavity, thus providing a bias current for the crystal detector.

In some experiments the lines were narrow and easily saturated with microwave power, necessitating an attenuator to reduce the incident microwave power to an acceptably low level. Under these

conditions crystal biasing is attained by the use of a reference back arm in the bridge. This takes power from the source before attenuation, and after adjustment of the phase, applies a current to bias the detector which is in phase with that coming from the cavity. Consequently when power is absorbed by the sample at resonance, the detector current falls as indicated in Fig. 17.

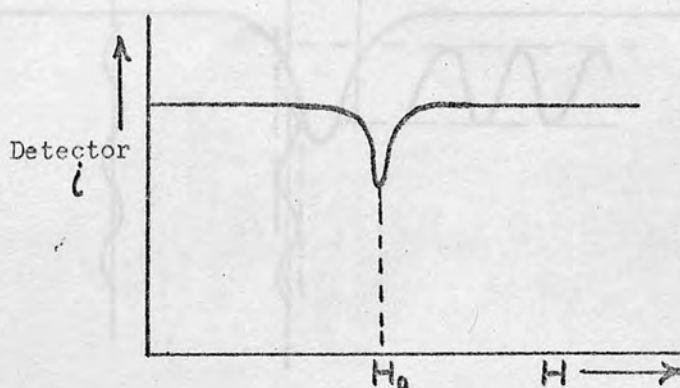


Fig. 17.

The sensitivity of such a spectrometer would be very poor, and to improve this, a pair of small modulation coils are added, one on each side of the cavity. These are fed with an alternating current, and produce a small alternating magnetic field with a variable amplitude of up to about 40 gauss peak to peak (p.p.). Thus as the magnetic field is swept, the modulation field is superimposed as indicated in fig. 18.

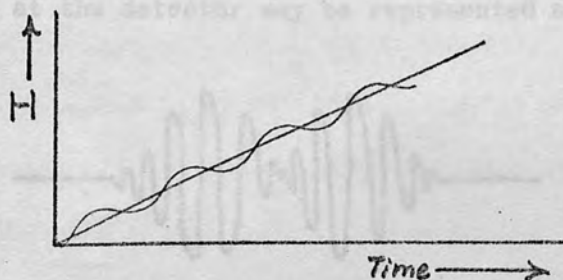


Fig. 18.

Consequently as the field passes through the resonance condition an A.C. component is picked up at the crystal detector. Referring to fig. 19, at 'A', the A.C. component picked up at the crystal detector is zero, because the microwave power is not changing with magnetic field.

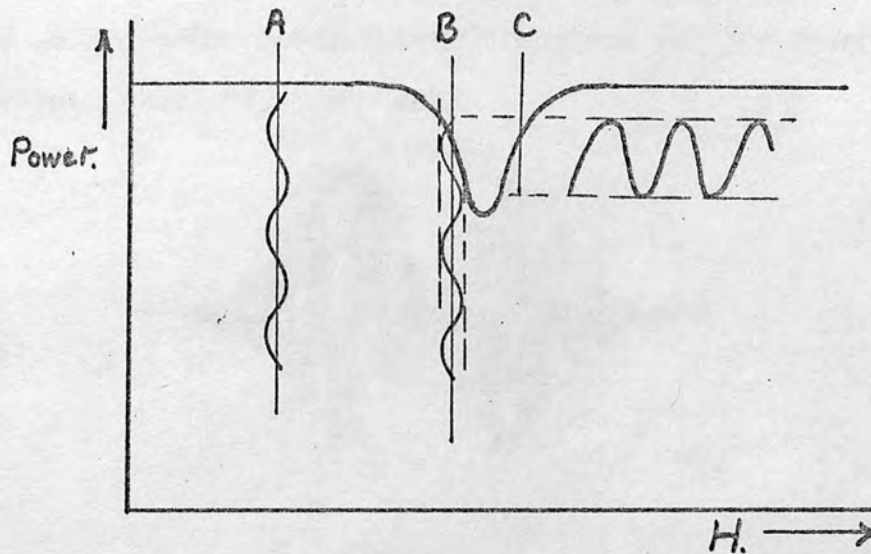


Fig. 19.

At 'B' the modulation of the field causes the reflected microwave power to be modulated at the same frequency, the amplitude of the modulation depending on the slope of the absorption line at B. At 'C', the modulation has the opposite phase from B, because the slope of the line is now positive instead of negative. Thus the signal at the detector may be represented as in fig. 20.

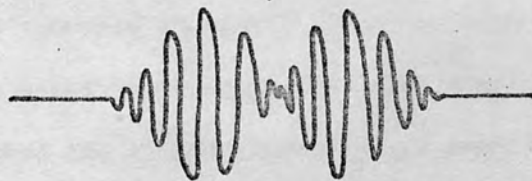


Fig. 20.

This signal is amplified by an amplifier tuned to the modulation frequency, and the amplified signal is then fed into a phase sensitive detector which is essentially a switch opening and closing at the modulation frequency. If the phasing is correctly adjusted, only positive half cycles will be detected, and as the system passes through resonance, only the shaded portion of fig. 21 is detected.

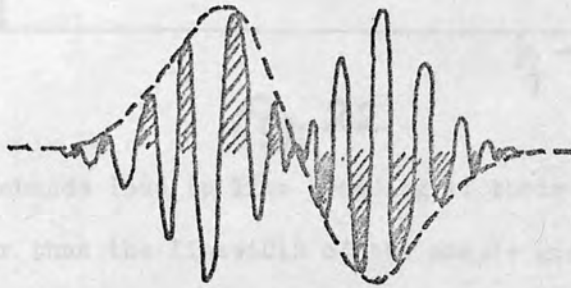


Fig. 21.

If a suitable filter is inserted, the detected signal is a slowly varying D.C. signal as indicated by the dotted line in figure 21, this output being the first derivative of the absorption line with respect to the field.

The question of modulation frequency arises since crystal detectors produce random noise, the average noise level varying inversely with frequency. Thus an increase in modulation frequency leads to an increase in signal to noise ratio for the system. However, an upper limit must be imposed since information theory indicates that the signal passed by the amplifier consists of a fundamental frequency together with sidebands, whose separation depends on the frequency.

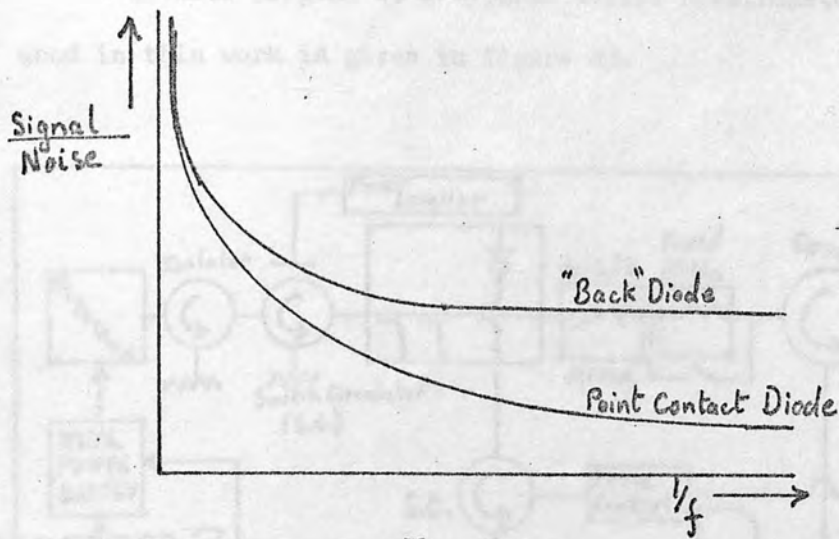


Fig. 22.

These sidebands lead to line broadening if their separation is greater than the linewidth of the sample under investigation. Most spectrometers employ 100KHz modulation frequency with a sideband separation of 70 milligauss (mg.) thus striking a compromise between resolution and sensitivity which is adequate for a large number of applications. However, when a Phillco "back-diode" is used in place of the more usual point contact diode for detection, the signal to noise ratio dependence on frequency is different as indicated in figure 22. The spectrometer can therefore be operated at 10KHz modulation frequency with the same sensitivity as at 100KHz, with the sideband separation reduced to approximately 7mg. Thus magnetic field homogeneity, rather than modulation frequency, is the limiting factor in resolution.

A block diagram of a typical e.p.r. spectrometer as used in this work is given in figure 23.

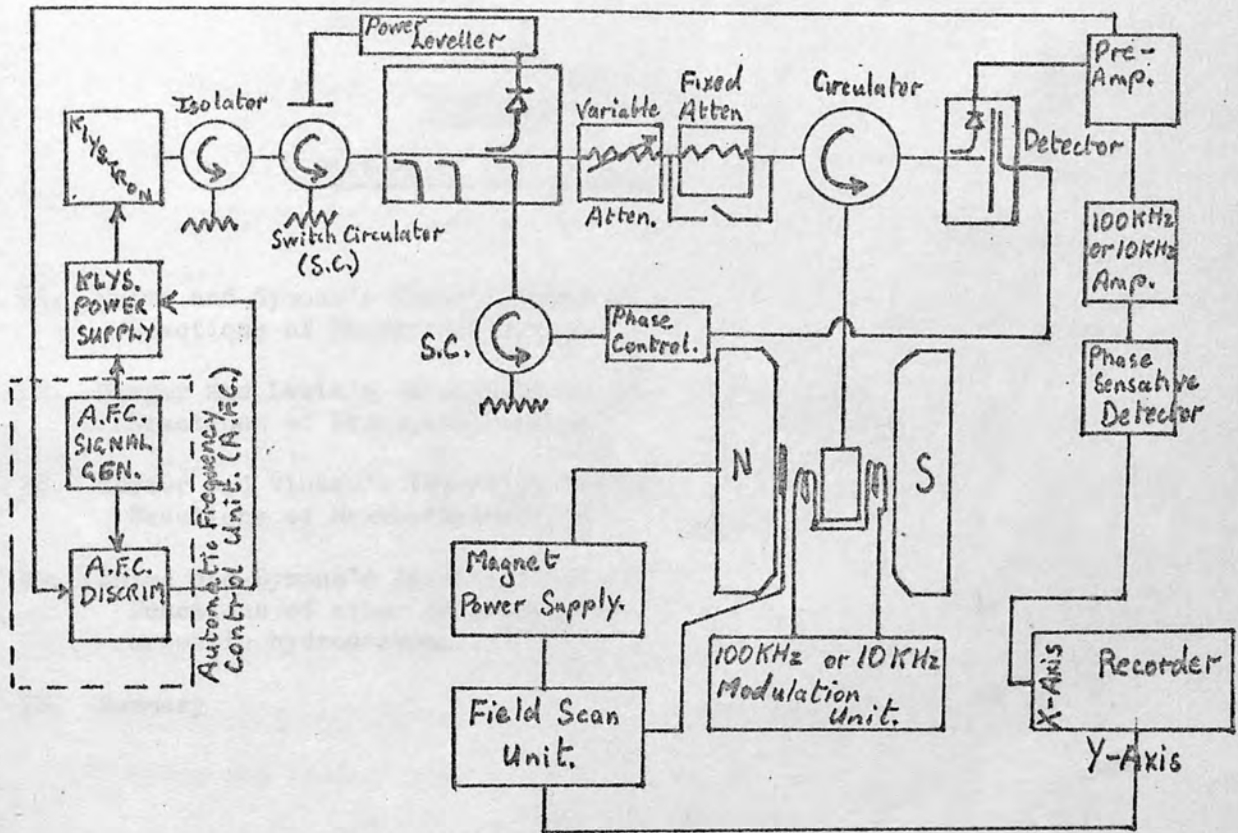


Fig. 23.

Historical and General.

The study by experiment of chemical-cations and chemical anions of polynuclear aromatic hydrocarbons and the theoretical interpretation of the resultant spectra are being fairly well documented. The study of polyalkylated aromatic hydrocarbons and their reactions in sulphuric acid is an interesting question concerning both the reaction products and the large number of end products

SECTION 2

Historical and General.

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Hulme and Symons showed that hexamethylbenzene (H.M.B.) dissolved slowly in 90% sulphuric acid (H₂SO₄) and yielded a yellowish red solution with an absorption maximum at 4.5 μ. Exposure of this solution to ultraviolet light yielded an e.p.s. spectrum with a pattern of 2.00269 ± .0001. This spectrum consisted of a single, well-resolved set of equally spaced lines separated by 0.45 ± .05 gauss. Identification of the species as the H.M.B. radical cation was based on the following arguments:

- (1) The spectrum is remarkably simple, showing only one doublet with a hyperfine coupling constant.
- (2) Only thirteen of the expected sixteen lines were detected, but the relative intensities were totally different from thirteen

Historical and General.

The study by e.p.r. of radical-cations and radical-anions of polynuclear aromatic hydrocarbons and the theoretical interpretation of the resultant spectra has been fairly well documented.^{2,3,4} The study of polyalkylated aromatic hydrocarbons and their reactions in sulphuric acid has posed a number of interesting questions concerning both the reaction pathway and the large number of end products that may be formed.

An investigation of the formation of radical-cations of substituted aromatic hydrocarbons with low first ionisation potentials such as hexamethylbenzene (H.M.B.) pentamethylbenzene (P.M.B.) and 2,3,5,6 - tetramethylbenzene (durene) was carried out initially by Hulme and Symons^{5,6,7} and later by Singer and Lewis⁸ and from a more theoretical standpoint by Carter and Vincow⁹ between 1960 and 1970.

2A. Hulme and Symons's Investigation of Reactions of Hexamethylbenzene.

Hulme and Symons observed that hexamethylbenzene (H.M.B.) dissolved slowly in 98% sulphuric acid (H_2SO_4) and yielded a yellowish red solution with no e.p.r. signal. Exposure of this solution to ultraviolet light yielded an e.p.r. spectrum with a g-factor of $2.00267 \pm .0001$. This spectrum consisted of a single, odd-numbered set of equally spaced lines separated by $6.45 \pm .05$ gauss. Identification of the species as the H.M.B. radical cation was based on the following arguments.

- (1) The spectrum is remarkably simple, showing only one proton hyperfine coupling constant.
- (2) Only thirteen of the expected nineteen lines were detected, but the relative intensities totally eliminate either fourteen

or sixteen equivalent protons, and give a better fit with eighteen protons rather than twenty.

- (3) Only two different types of carbon atom could be seen from the ^{13}C hyperfine satellite lines. Their intensities for the outermost pairs of lines are correct for molecules having six equivalent carbon atoms, one being ^{13}C .
- (4) The linewidth could not be reduced below 0.25 gauss, and lines did not broaden under the maximum available microwave power.
- (5) The proton hyperfine splitting of 6.45 gauss is acceptable for the H.M.B. radical cation and also the g -factor is close to those obtained for other aromatic hydrocarbon cations, and differs substantially from those generally observed for oxidised species such as protonated semiquinones.

The authors indicate that these results are qualitatively similar to those for the anion of benzene ¹⁰ and the cation and anion of coronene ^{11,12} which, like the H.M.B. cation, have orbitally degenerate ground states.

Hulme and Symons ⁵ further observed that on prolonged standing the H.M.B. reacted slowly to give a stable radical-cation, characterised by an e.p.r. spectrum at $g = 2.0027 \pm .0003$. This spectrum exhibited an asymmetric triplet with an approximately 1:2:1 intensity ratio. The group at the low - field side was somewhat broader than that at the high - field. Under high amplification, 25 lines were detected in each group. Under superheterodyne detection conditions, further lines were resolved under the central lines of the central group. In deuteriosulphuric acid the major triplet was lost, and was replaced

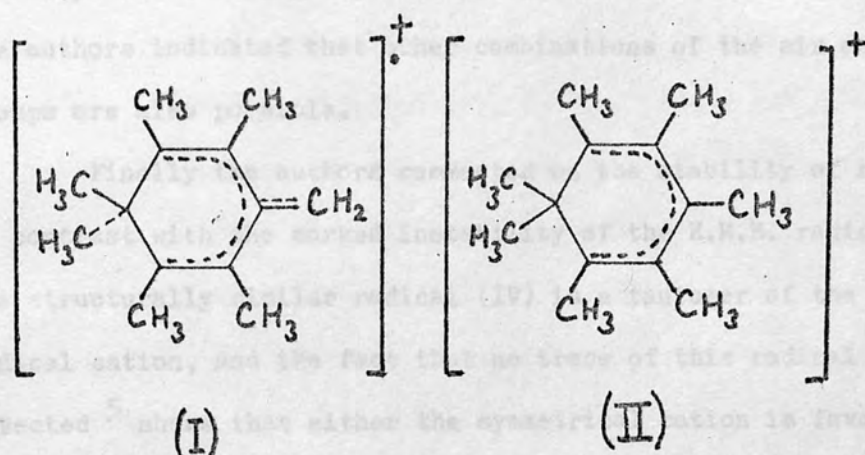
by a quintuplet with relative intensities approximately 1:2:3:2:1, with a hyperfine splitting about one sixth that of the original. The remainder of the spectrum was unchanged, thus establishing that only two strongly interacting protons are readily exchanged with solvent protons.

The authors interpreted the spectrum in the following manner.

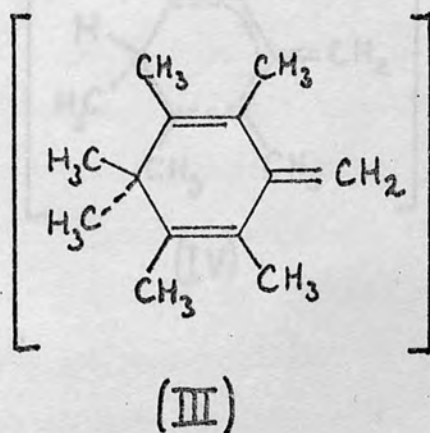
- (1) The major triplet splitting of 5.4 gauss is unambiguously assigned to two equivalent protons.
- (2) Since these are the only protons which readily exchange with the solvent they cannot be two protons of a methyl group sterically constrained to a fixed orientation with respect to the ring.

Hulme and Symons therefore suggested that the radical is of the form $\text{R}\dot{\text{C}}\text{H}_2$. The fact that the residual splitting of 1.7 gauss is composite is implied by the partial resolution of the central lines. If one hyperfine coupling is set equal to 1.7 gauss and the other is approximately twice this value then the central lines of each group should consist of alternating sets of three and four lines. Further, at least 25 main lines have been detected in each of the three groups. This eliminates the possibility that the 1.7 and 3.4 gauss splittings stem from two pairs of two equivalent methyl groups, since this could give only 19 lines. The authors suggest that the most likely alternative is that there is one set of six equivalent protons from two equivalent methyl groups, and one set of twelve from four equivalent methyl groups. This would give 31 lines with about the correct ratio of intensities. The outer lines would be extremely weak relative to the centre and probably lost in the background noise.

Hulme and Symons postulated that the most probable radical is the hexamethylbenzyl radical cation (I). This postulate was based on the spectroscopic evidence presented in the preceding paragraph, and on the fact established by other works¹³, that protonated hexamethylbenzene in sulphuric acid can readily transfer a methyl group to give the heptamethylbenzene ion (II).

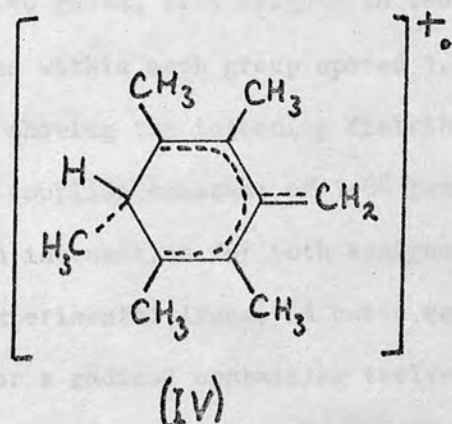


Ion (II) can then lose a proton to give (III).



Oxidation of (II) or (III) could give (I), whilst an equilibrium between (II) and (III) could provide a route to exchange with deuteriosulphuric acid (D_2SO_4) at the methylene group only, provided oxidation is rapid compared with the rate of migration of the methyl group in (II). Consequently a reasonable assignment of the two small coupling constants would then be 1.7 gauss to the two aliphatic methyl groups and 3.4 gauss to the ring methyls. The authors indicated that other combinations of the six methyl groups are also possible.

Finally the authors commented on the stability of radical (I) in contrast with the marked instability of the H.M.B. radical cation. The structurally similar radical (IV) is a tautomer of the H.M.B. radical cation, and the fact that no trace of this radical was detected⁵ shows that either the symmetrical cation is favoured, or that the process of decay of the H.M.B. cation involves this ion as an intermediate.



2B. Singer and Lewis's Investigation of Reactions and Hexamethylbenzene.

A similar investigation by Singer and Lewis⁸ was published in 1965.

2B.1 Singer and Lewis confirmed that although H.M.B. does not react immediately with 98% sulphuric acid it does undergo a slow rearrangement to form a stable radical which is not the simple H.M.B. cation.

The ultra-violet - visible absorption spectra obtained from H.M.B. in concentrated sulphuric acid showed initial bands at 393m μ and 280m μ which were attributed to the protonated H.M.B. radical cation (IV).

As time progressed the solution of H.M.B. in 98% sulphuric acid turned red and developed new bands at 520m μ and 334m μ . These bands increased in intensity with time and indicated the formation of a second species, which was presumed to be a free radical in the sulphuric acid solution.

The same e.p.r. spectrum observed by Hulme and Symons, was also obtained by Singer and Lewis, comprising the three groups of lines separated by 5.40 gauss, with heights in the ratio 1:2:1 and the individual lines within each group spaced 1.68 gauss apart. Singer and Lewis plotted curves showing the intensity distribution for 18 and 36 equivalent protons with a coupling constant of 1.68 gauss. It is apparent that the decrease in intensities for both assignments is much more rapid than for the experimental lines. A curve representing the intensity distribution for a radical containing twelve protons with a hyperfine coupling of 3.36 gauss and six protons with a hyperfine coupling of 1.68 gauss gives good agreement with the experimental distribution. This assignment predicts 31 lines in each group, although the authors observed only 21 lines.

The deviation of the three major groups of lines from the expected 1:2:1 ratio was accounted for in terms of the variation in linewidths between the outer groups which are approximately 10 - 20% wider than the central groups. Further, these linewidths variations suggest that there may be restricted rotation involving the two protons which give rise to the large splitting ¹⁴. Such an effect would be expected to exhibit a temperature dependence. At 54°C the ratio of the amplitudes for the three groups of lines were within 15% of the expected 1:2:1 distribution. Further, a decrease in the viscosity of the solution brought about by addition of trifluoroacetic acid led to a decrease in the widths of the outer groups of lines. Singer and Lewis then used the coupling constants 12H, $a_1 = 3.36$, 6H, $a_2 = 1.68$ and 2H, $a_3 = 5.40$ gauss in a simulation of the spectrum with a computer and confirmed this assignment by comparison with the experimental curves obtained at 25°C. Assignment of coupling constants to groups of 12, 6 and 2 equivalent protons shows that the observed radical contains two more protons than the original H.M.B.

The prolonged reaction of H.M.B. was carried out using D_2SO_4 in place of sulphuric acid, in order to determine whether the additional protons came from the solvent. The resultant e.p.r. spectrum was the same as that observed by Hulme and Symons in which the 5.40 gauss triplet was no longer visible. Singer and Lewis observed 37 equally spaced lines with a separation of 0.84 gauss. The spectrum became consistent with the earlier assignment only if the two protons which give rise to the 5.40 gauss splitting are replaced by deuterons. This assignment was also confirmed by comparing a computer simulation of the spectrum with the experimental trace.

Singer and Lewis indicated that the most likely explanation of the spectral results is that the two additional protons in the H.M.B. radical arose directly from the sulphuric acid solvent. In view of the known ease of rearrangement of methylbenzenes in sulphuric acid ¹⁵, they also suggested the possibility that these two protons resulted from intermolecular methyl addition reactions. In order to distinguish between these alternatives, Singer and Lewis attempted to prepare the H.M.B. radical species in media which do not contain exchangeable protons.

Two aprotic reagents which have been employed as electron acceptors for the preparation of aromatic radical cations are iodine ¹⁶ and antimony pentachloride ¹⁷. The spectrum resulting from a 3×10^{-3} M. solution of H.M.B. in iodine at 125°C consisted of at least 23 equally spaced lines with a separation of about 1.7 gauss and a linewidth of approximately 1.0 gauss. The spectrum was incompletely resolved but, nevertheless, it was compared with two computer-simulated spectra, with and without the 5.40 gauss splitting from the two methylene protons. The authors concluded that a better fit was obtained in terms of 12-6-2 proton assignment as before. Further, when a dilute solution of H.M.B. in CD_2Cl_2 was treated with antimony pentachloride, the sample exhibited an e.p.r. signal identical with that for H.M.B. in sulphuric acid. As a result of these experiments Singer and Lewis concluded that all 20 protons in the H.M.B. radical arise from H.M.B. molecules, and, since only two of the protons exchange with deuterium in D_2SO_4 , that two protons must be bound differently from the remaining 18 protons.

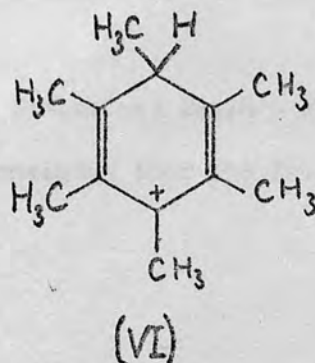
The g-factor for the radical formed from H.M.B. in 98% sulphuric acid was $2.0024 \pm .0001$ and this value eliminated the possibility that the H.M.B. radical is a quinone cation similar to that formed by

oxidation of p-xylene in sulphuric acid potassium persulphate solution, since oxygen-containing free radicals generally have considerably higher *g*-values in the range between 2.0034 to 2.0047. The *g*-value obtained for the H.M.B. radical in molten iodine had a high value of 2.0057 and was consistent with other observations made by the authors in solvent systems of molten iodine, and it was suggested that the large spin-orbit coupling constant of iodine ¹⁸ may be responsible for the large positive *g*-shifts when molten iodine is used as a solvent.

2B.2 Nuclear Magnetic Resonance (n.m.r.) Study. - Rearrangement reactions of methylbenzenes in strong acids, called the Jacobsen reaction, are known ^{19,15} and the mechanism has been postulated as involving free-radical intermediates ²⁰. N.M.R. studies have also demonstrated chemical exchange and rearrangement reactions of H.M.B. in the presence of strong acids ^{21,22,13}.

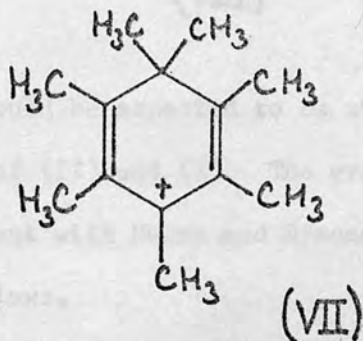
In order to obtain more evidence for rearrangement reactions of H.M.B. in oxidizing media, Singer and Lewis studied the n.m.r. spectra of H.M.B. in sulphuric acid and in antimony pentachloride/methylene chloride systems. This work confirmed that rearrangement and exchange reactions of H.M.B. occur.

In 98% sulphuric acid at 25°C, only a single broad line at 2.35 p.p.m. was observed, and was attributed to ion (VI), which undergoes rapid



proton exchange with the solvent. In 98% deuteriosulphuric acid no methyl resonance was detected, although a peak attributed to the presence of sulphuric acid was observed to grow as the H.M.B. went into solution, thus demonstrating the presence of solvent - H.M.B. exchange reactions which involve either the radical or the protonated ion (VI).

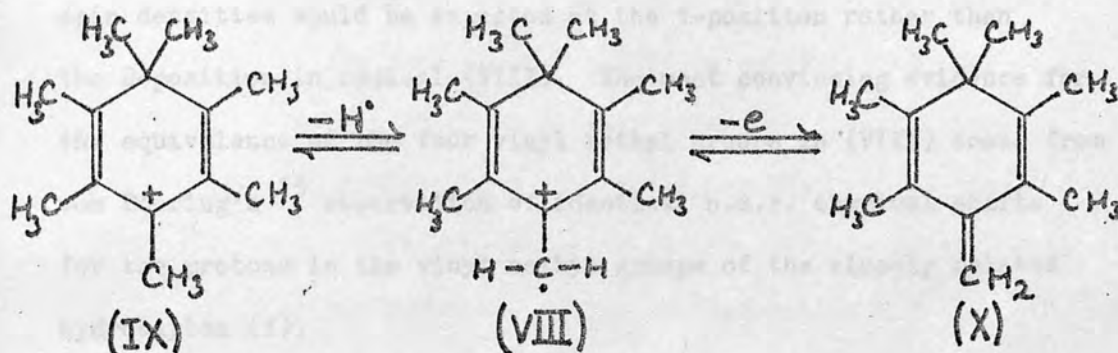
Treatment of H.M.B. with $\text{SbCl}_5/\text{CH}_2\text{Cl}_2$ at room temperature, after filtration, yielded a solution whose n.m.r. spectrum contained five proton peaks with chemical shifts between 1.9 and 3.1 p.p.m. These peaks are very similar to those reported for the methyl groups in the H.M.B. cation (VI) ^{21,22} and ion (VII) ¹³.



The resonance at 1.9 p.p.m. is attributed to an ~~aliphatic~~ out-of-plane methyl group and the remaining peaks to aromatic methyl groups. The large downfield shifts observed for these groups show that the H.M.B. species in $\text{SbCl}_5/\text{CH}_2\text{Cl}_2$ are positive ions.²¹ Finally the presence of an aromatic proton peak and the chemical shifts for the methyl protons show the occurrence of demethylation and methyl rearrangement reaction.

2B.3 Conclusions drawn by Singer and Lewis - From their extensive experiments the authors concluded that the free radical formed from

H.M.B. in 98% sulphuric acid has the structure (VIII). This structure could readily result from the loss of a hydrogen atom from the heptamethylbenzonium ion (IX), or from one electron oxidation of the conjugate base (X)



Further, (VIII) would be expected to be stable in solution in view of the stability of (IX) and (X). The evidence for structure (VIII) (which is coincident with Hulme and Symons's structure (I)) may be summarized as follows.

- (1) The large splitting of 5.40 gauss can be assigned to the two methylene protons since a large spin density would be expected at the adjacent carbon. This is further supported by the D_2SO_4 selective exchange results, and the temperature dependence of the spectrum associated with hindered rotation of a methylene group about a bond with considerable double bond character.
- (2) The small splitting of 1.68 gauss attributable to the six equivalent protons in the aliphatic methyl groups is consistent with that observed for methyl substituents in related aliphatic free radicals²³.

- (3) The twelve proton splitting of 3.36 gauss would thus be assigned to the four vinyl methyl groups.

Singer and Lewis stated that it is not obvious that all four methyl groups should give rise to the same splitting, especially since molecular orbital calculations indicate that much higher spin densities would be expected at the 1-position rather than the 2-position in radical (VIII). The most convincing evidence for the equivalence of the four vinyl methyl groups in (VIII) comes from von Doering's ¹³ observation of identical n.m.r. chemical shifts for the protons in the vinyl methyl groups of the closely related hydrocarbon (X).

2C. Carter and Vincow's Investigation of Reactions of Hexamethylbenzene.

Carter and Vincow ⁹ dissolved hexamethylbenzene in 20% oleum in sufficient quantity to obtain a blood-red solution. After heating this solution until bubbles of gas appeared, and then quickly cooling to room temperature, an e.p.r. spectrum consisting of 13 evenly spaced lines was observed. This spectrum was centered at $g=2.00266 \pm .00002$ with a splitting between the hyperfine lines of $6.53 \pm .01$ gauss. This is in good agreement with the value of $6.45 \pm .05$ gauss reported for the 13 line spectrum arising from ultra-violet radiation of hexamethylbenzene in concentrated sulphuric acid by Hulme and Symons ⁵. Carter and Vincow also attributed this spectrum to the H.M.B. cation, on the basis of the following evidence.

- (1) The spectrum consists of an odd number (13) of evenly spaced lines with relative intensities matching those expected for a group of 18 equivalent protons.

- (2) The magnitude of the hyperfine splitting and the g-value is in agreement with those reported by Hulme and Symons⁵ for the H.M.B.cation.
- (3) A sample of ultra-violet irradiated H.M.B. in a rigid boric acid glass possess a very similar e.p.r. spectrum to that observed in solution. The g-value is the same and the hyperfine splitting of 6.67 gauss is only about 2% larger. Previous investigations by the authors lead them to expect that illumination of an aromatic hydrocarbon in a boric acid matrix leads to the formation of the radical cation^{24,25}.

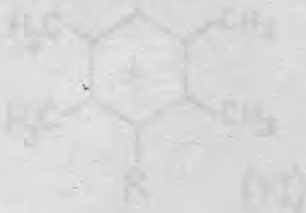
Carter and Vincow also discussed a similar series of results for the e.p.r. spectrum attributed to the radical cation of hexaethylbenzene.

2D. Hulme and Symons Investigation of Reactions of other polyalkylated aromatic Hydrocarbons.

Hulme and Symons studied the reactions of pentamethylbenzene⁶ (P.M.B.) and ~~2,3,5,6~~^{1,2,4,5-} - tetramethylbenzene⁵ (durene) with sulphuric acid since they have low first ionisation potentials.

2D.1 Pentamethylbenzene - Attempts to produce the radical cation of P.M.B. in 98% sulphuric acid in a similar way to hexamethylbenzene were unsuccessful.

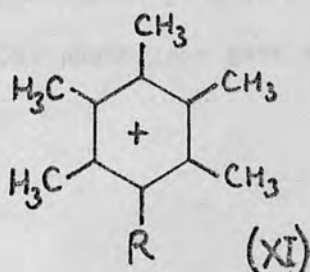
Photolysis of a solution of P.M.B. in 98% sulphuric acid immediately yielded an e.p.r. spectrum with an odd numbered set of lines separated by 6.5 gauss. This spectrum was short lived and exactly analagous to the cation of H.M.B. The assignment of the spectrum to the P.M.B. cation would require that the splitting between



symmetric and antisymmetric orbitals was very small, and that both orbitals were equally populated. These conditions would lead to equality of all five methyl groups. This would give rise to 16 lines and the odd number of lines observed could be accounted for only if the proton splitting was identical with that of the methyl protons. This would give rise to 17 lines. Exact equality is unlikely and the authors suggested that the spectrum arose from a trace impurity of H.M.B. formed by rearrangement of a small quantity of P.M.B.

Prolonged photolysis (2 - 3 minutes) led to the observation of an e.p.r. spectrum which was attributed to the diprotonated duroquinone cation formed by slow disproportionation of P.M.B.

A radical having an e.p.r. spectrum in accordance with that expected for the cation of pentamethylbenzene was obtained by dissolution of hexamethylbenzene in concentrated olea. The spectrum was analysed in terms of two sets of equivalent methyl groups which gave rise to two nearly equal septets with hyperfine coupling constants of 10.3 and 10.85 gauss. A further weakly interacting methyl group gave rise to a quartet with a splitting of 0.56 gauss, but no splitting from the ring proton could be detected. The authors found difficulty in understanding the very small interaction with the ring proton in view of the clearly resolved quartet from the fifth methyl group, as well as the fact that the ion is readily obtainable from H.M.B. They suggested that the radical is not (XI) ($R = H$) but (XI) ($R = COOH$ or SO_3H) since in all cases R is predicted to lie at a node in the orbital of the unpaired electron



The lack of equivalence of the two sets of methyl groups is quite comparable with that found for the 2,6 and 3,5 ring protons of the toluene anion²⁶.

If P.M.B. was left to stand in 98% sulphuric acid, the resultant solution became dark red and yielded the same e.p.r. spectrum as was obtained from H.M.B. and described earlier. This was explained in terms of intermolecular methyl group migration²⁷, but no mechanism was proposed.

2D.2 Durene - Sulphuric acid slowly dissolved durene to yield a pale straw-yellow solution which did not give rise to a detectable e.p.r. spectrum. Exposure to ultra-violet light gave the diprotonated duroquinone cation in high yield. This same spectrum was obtained by the addition of potassium persulphate to the initial solution. The spectrum exhibits a linewidth alternation and a complete interpretation has been given by Bolton and Carrington²⁸. The essential feature of Bolton and Carrington's interpretation is that the total splitting from all alkyl groups is constant. If the rate of cis-trans interconversion is slow, the e.p.r. spectrum must be a simple superposition of the two corresponding spectra. At high rates of interconversion (i.e. when τ (average lifetime) $< \frac{1}{\Delta\omega}$ where $\Delta\omega$ is the hyperfine splitting in c.p.s.) an average spectrum should be seen. However, when $\tau \sim \frac{1}{\Delta\omega}$ transitions from the two isomers lead to alternative sharp and narrow lines in the time-averaged spectrum.

In dilute olea photolysis gave no radicals. For more concentrated olea (>30%) photolysis gave a spectrum consisting of

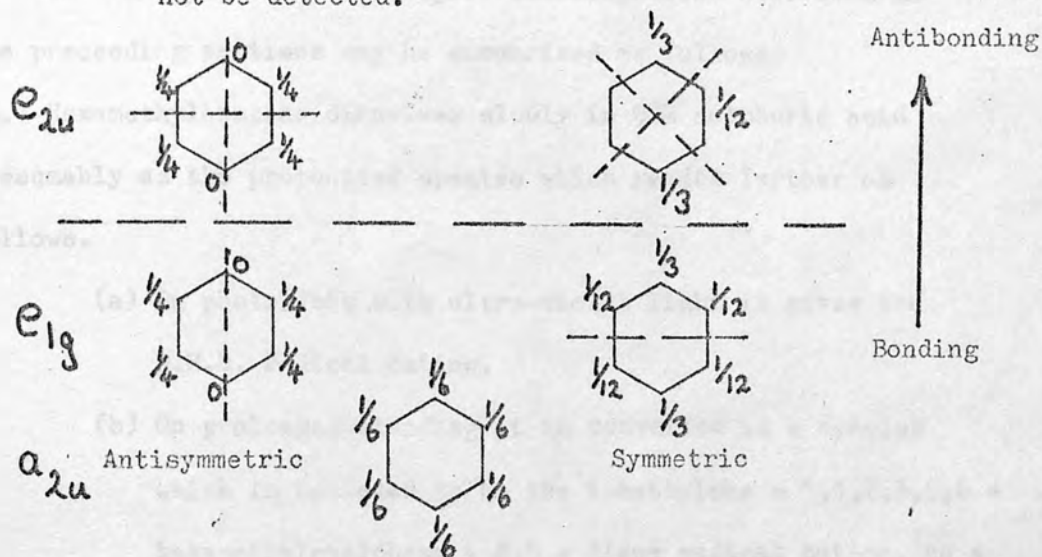
a single odd numbered set of lines, with a hyperfine splitting of 11.0 ± 0.2 gauss, centered at $g = 2.0027 \pm .0001$. Hulme and Symons detected only eleven lines with certainty, but the intensities of these lines compared favourably with the expected 13 line spectrum, exhibiting a binomial intensity distribution. As with the spectrum attributed to the H.M.B. cation, the lines were broad and could not be resolved into further components. The spectrum also showed additional features due to the duroquinone cation.

Identification of the species which gave rise to the e.p.r. spectrum as the radical cation of durene was based on the following evidence.

- (1) The spectrum was simple, consisting of just one proton hyperfine splitting. The eleven observed hyperfine lines had their relative intensities close to those expected for 13 lines. The durene radical cation should have twelve equivalent protons coupling strongly with the unpaired electron, provided that the degeneracy of the symmetric and antisymmetric orbitals is sufficiently lifted by the asymmetry of the ion, in such a manner that the antisymmetric level is uppermost.

Since by hyperconjugation, methyl groups can help fill the 'hole' in the π -system, it may be expected that the antisymmetric level would be half filled and have a node passing through the two ring protons, provided the orbital splitting is sufficiently large,

hyperfine coupling to these two protons would not be detected.



Spin densities associated with bonding and antibonding orbitals for hexamethylbenzene and durene.

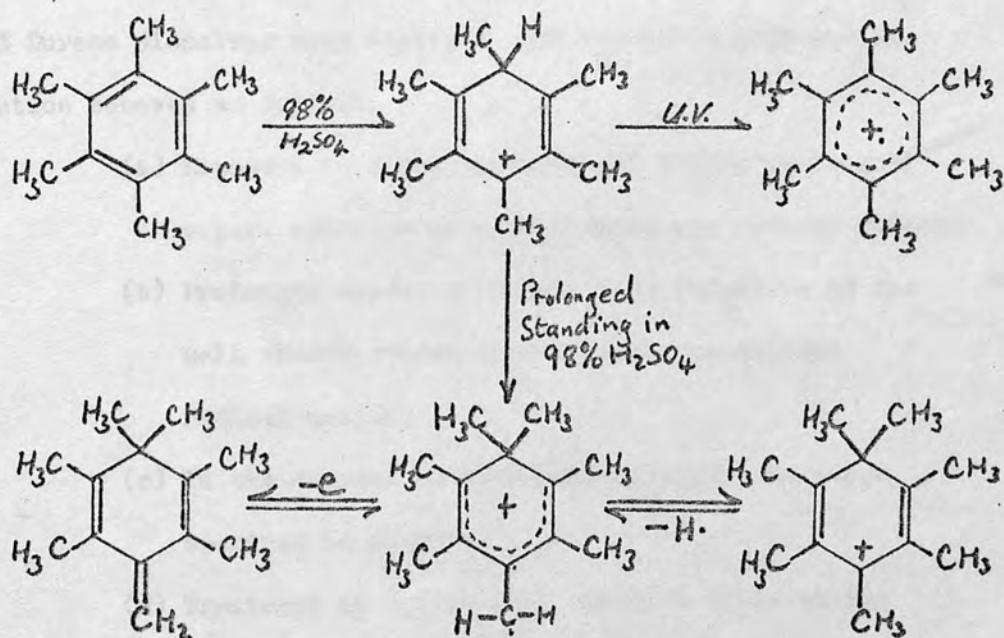
- (2) The hyperfine coupling constant of 11.0 gauss is in accordance with expectation. The very small value (< 0.2 gauss) for the hyperfine splitting of the two ring protons is unexpected. It has been suggested that this may be the result of a fortuitous cancellation of two effects, one giving rise to a small negative spin density, and the other a small positive spin density. The former would result from configuration interaction with excited states and the latter could be the result of a vibronic coupling.
- (3) The g -value is that expected for the simple cation of an aromatic hydrocarbon and is clearly different from that for an oxidised species.

2E. Summary.

The results of all the e.p.r. investigations described in the preceding sections may be summarised as follows.

2E.1 Hexamethylbenzene dissolves slowly in 98% sulphuric acid presumably as the protonated species which reacts further as follows.

- (a) On photolysis with ultra-violet light it gives the H.M.B. radical cation.
- (b) On prolonged standing it is converted to a species which is believed to be the 4-methylene - 1,1,2,3,5,6 - hexamethylcyclohexa - 2,5 - diene radical cation, as a result of intermolecular methyl group migrations.



- (c) Treatment of H.M.B. with 60% oleum appears to lead to the formation of the P.M.B. radical cation.

Further consideration of the conditions and observations:
2E.2 Pentamethylbenzene in 98% sulphuric acid behaves as follows.

- (a) Exposure to ultra-violet light does not yield the expected P.M.B. radical cation, but a weak spectrum attributed to the H.M.B. radical cation resulting from intermolecular methyl exchange is observed.
- (b) Prolonged exposure to ultra-violet light leads to the formation of the diprotonated duroquinone radical cation via a disproportionation reaction.
- (c) Prolonged standing in the absence of ultra-violet light leads to the same species as was reported for H.M.B.

2E.3 Durene dissolves very slowly in 98% sulphuric acid and the solution behaves as follows.

- (a) Exposure to ultra-violet light yields no initial e.p.r. spectrum attributable to the radical cation.
- (b) Prolonged exposure leads to the formation of the well characterised diprotonated duroquinone radical cation.
- (c) In the absence of ultra-violet light, no e.p.r. spectrum is observed.
- (d) Treatment of durene with 60% olea leads to the formation of the radical cation of durene, whereas dilute olea give no free radicals detectable by e.p.r.

Further consideration of the experiments and observations described in section 2, leads to the following postulates.

- (1) Since H.M.B., P.M.B., and durene all have low first ionisation potentials and dissolve slowly in 98% sulphuric acid, it appears reasonable to expect that in the absence of oxygen all should form radical cations with similar rates of formation.
- (2) In olea these aromatic hydrocarbons are under ideal sulphonating conditions and in consequence it would be reasonable to expect electrophilic attack, preferentially at an unsubstituted ring position leading to the formation of sulphonated radical cations of the relevant aromatic hydrocarbons
- (3) If the postulated structure (I) is accepted (section 2A) then two interesting questions arise, the first concerning the large hyperfine coupling to the six aliphatic methyl protons and the second the equivalence of the four remaining methyl groups. These effects may be accounted for to some extent in terms of a strong hyperconjugative interaction.
- (4) Previous investigations of the Jacobsen rearrangement which is thought to be involved in the formation of the 4-methylene - 1,1,2,3,5,6 - hexamethylcyclohexa-2,5-diene radical cation, indicate that it is the presence

of an $-SO_3H$ group which promotes the rearrangement. If this is correct, then considering the degeneracies involved in the interpretation of the spectrum attributed to the cation (VIII), and the difficulty in accounting for the values of the hyperfine splitting involved, it would be possible to propose other models which fit the observed e.p.r. spectrum.

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Results and Discussion

The polyalkylated aromatic hydrocarbons which have been investigated in this work have low first ionization potentials and very similar chemical properties. In the absence of oxygen it is to be expected that these compounds would

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Results and Discussion.

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Results and Discussion

The polyalkylated aromatic hydrocarbons which have been investigated in this work have low first ionisation potentials and very similar chemical properties; consequently in the absence of oxygen it is to be expected that all three compounds would undergo very similar reactions with 98% sulphuric acid in both the presence and absence of ultra-violet radiation. The previous work carried out in this field and reviewed earlier would indicate that this expectation is not necessarily correct.

As a result of technological advances in instrumentation and cavity design and development, a reinvestigation of some of these reactions has led to some new observations as well as to the confirmation of earlier postulates.

3A. Immediate Reaction of Hexamethylbenzene with 98% sulphuric acid and dideuteriosulphuric acid.

Initial dissolution of hexamethylbenzene (H.M.B.) in 98% sulphuric acid promptly yielded a very weak e.p.r. signal. This spectrum (i) was centered at $g = 2.0026 \pm .0001$. Only five lines with a hyperfine splitting of 6.36 gauss were visible above the noise level. Irradiation of this sample with ultra-violet light led to a dramatic increase in the intensity of these lines (spectrum (ii)) so that thirteen lines were now visible with the same g -value and hyperfine splitting constant. The relative intensities of these lines did not fit the expected binomial distribution of intensities for twelve equivalent protons but gave a best fit to eighteen equivalent protons. (Table 1)

Table 1

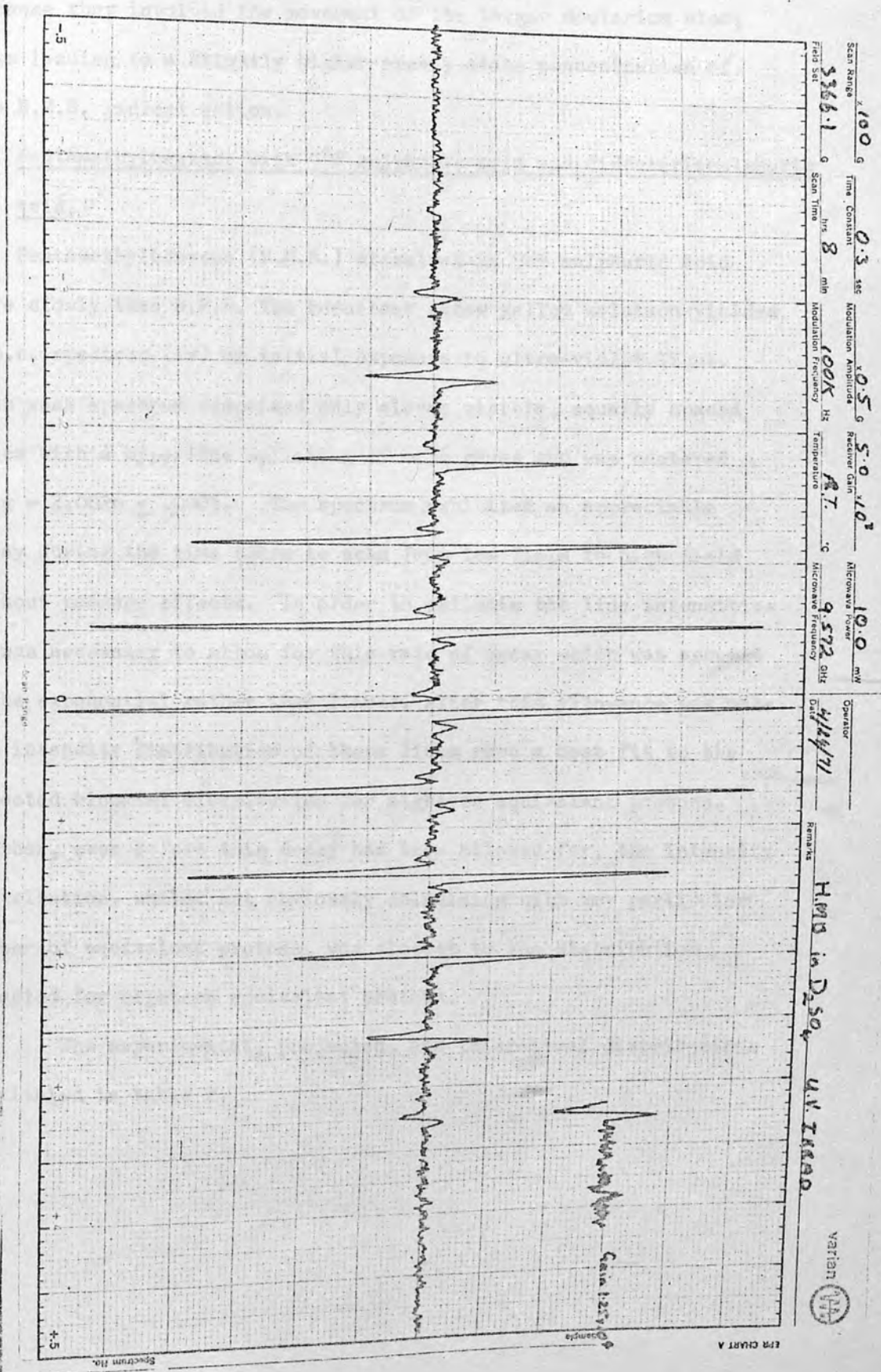
Comparison of relative intensities of spectral lines with those calculated for a binomial distribution for 18 lines.

Line	0 (centre)	1	2	3	4	5	6
Exptl. Ratio	58.5	52.8	38.2	22	10	3.5	1
Theoretical Ratio	60.0	53.9	39.2	22.8	10.7	3.75	1

This would arise if the methyl groups of the hexamethylbenzene were all equivalent and consequently the most likely species formed under these conditions would be the radical cation of hexamethylbenzene. This result is in concordance with the observations and conclusions drawn by Hulme and Symons as discussed earlier.

The experiment was repeated using dideuteriosulphuric acid, primarily as part of a more important reaction to be discussed later, but also to serve as an indication that this initial reaction was a simple process involving no movement of the methyl groups during which proton/deuteron exchange with the solvent could take place. This was confirmed since the resultant e.p.r. spectrum (iii) was identical in all aspects to spectrum (ii) obtained earlier. However the spectral intensity appeared to be higher, either because hexamethylbenzene was more readily soluble in dideuteriosulphuric acid than sulphuric acid under the same physical conditions, or because

Spectrum (iii)



secondary reactions of the hexamethylbenzene radical were slower because they involved the movement of the larger deuterium atom, thus leading to a slightly higher steady state concentration of the H.M.B. radical cation.

3B. Pentamethylbenzene with 98% sulphuric acid and dideuteriosulphuric acid.

Pentamethylbenzene (P.M.B.) dissolved in 98% sulphuric acid more slowly than H.M.B. The resultant straw yellow solution yielded e.p.r. spectrum (iv) on initial exposure to ultra-violet light. This weak spectrum comprised only eleven visible, equally spaced lines with a hyperfine splitting of 6.36 gauss and was centered at $g = 2.0026 \pm .0001$. The spectrum exhibited an appreciable decay during the time taken to scan from low field to high field without passage effects. In order to estimate the line intensities it was necessary to allow for this rate of decay which was assumed to be exponential rather than linear. After this allowance was made the intensity distribution of these lines gave a best fit to the expected binomial distribution for eighteen equivalent protons. Further, even before this decay had been allowed for, the intensity distribution, whilst not obviously coinciding with any particular number of equivalent protons, was closest to the distribution expected for eighteen equivalent protons.

The experimental, projected, and theoretical distributions are listed in table 2.

Table 2

Comparison of relative intensities of spectral lines with those calculated for a binomial distribution for 18 lines.

Line No.	0 (centre)	1	2	3	4	5
Exptl. Intensity Ratio	13.2	12.00	9.5	5.75	2.75	1
Projected Intensity Ratio	15.4	13.9	10.26	6.02	2.78	1
Theoretical Intensity Ratio	16.0	14.3	10.4	6.05	2.8	1

This spectrum was short lived and exactly analogous to that obtained from H.M.B. and attributed to the radical cation of H.M.B. The spectrum could only be assigned to the P.M.B. radical cation if the splitting between the symmetric and antisymmetric orbitals was very small, and both orbitals equally populated, thus leading to equality of all five methyl groups. This would only give rise to sixteen lines, and the odd number observed could only be accounted for if the remaining proton splitting was identical to the methyl protons, which would then give rise to seventeen lines. Exact equality would be unlikely, as was suggested by Hulme and Symons⁵. Further the observed and projected intensity distribution does not agree with that expected for seventeen lines, but better fits nineteen lines.

The attribution of spectrum (iv) as arising from H.M.B. is consistent with the mass spectrum obtained from the purified P.M.B. since there is a very small parent ion peak at mass 168 which

corresponds to H.M.B. Consequently the initial spectrum is attributed to a trace impurity of H.M.B. in the recrystallized P.M.B. rather than the H.M.B. arising as a result of a rearrangement of the protonated pentamethylbenzene in 98% sulphuric acid solution as proposed by Hulme²⁶. Rearrangement of P.M.B. to give H.M.B. on the time scale of the experiment leading to these results is unlikely in the light of results obtained from the experiments described in section 4D.

Prolonged photolysis of pentamethylbenzene in 98% sulphuric acid leads to the formation of spectrum (v). This spectrum, centered at $g = 2.0034 \pm .0001$ exhibits a hyperfine structure consisting of thirteen groups of triplets with a hyperfine splitting of 2.06 gauss and 2.70 gauss respectively with a marked linewidth effect at room temperature. This spectrum is identical with the spectrum obtained by photolysis of duroquinone in 98% sulphuric acid which consists of thirteen main lines with a separation of 2.06 gauss, arising from the twelve equivalent methyl protons. Each of these lines is further split into a triplet with a splitting of 2.70 gauss by the hydroxyl protons. Consequently spectrum (v) formed by prolonged photolysis of pentamethylbenzene is attributed to the radical cation of diprotonated duroquinone formed by the slow disproportionation of the P.M.B. This result is in concordance with that obtained by Hulme²⁶.

Pentamethylbenzene dissolved in 98% dideuteriosulphuric acid as is described in section 4C, gave rise to an e.p.r. spectrum which was identical in all respects to that obtained when P.M.B. was

dissolved in 98% sulphuric acid and as is to be expected, confirmed that there was no observable proton/deuteron exchange.

Prolonged photolysis of the P.M.B./dideuteriosulphuric acid system led to the formation of spectrum (vi), which exhibited a marked alternating linewidth effect ²⁷. This spectrum is the same as spectrum (v), except that the triplet structure of the -OH protons is replaced by a much smaller quintet structure, with a hyperfine splitting of 0.4 gauss. This quintet structure arises from the two -OD groups, which result from exchange with the dideuteriosulphuric acid solvent.

3C. Durene (2,3,5,6 - tetramethylbenzene) with 98% sulphuric acid and dideuteriosulphuric acid.

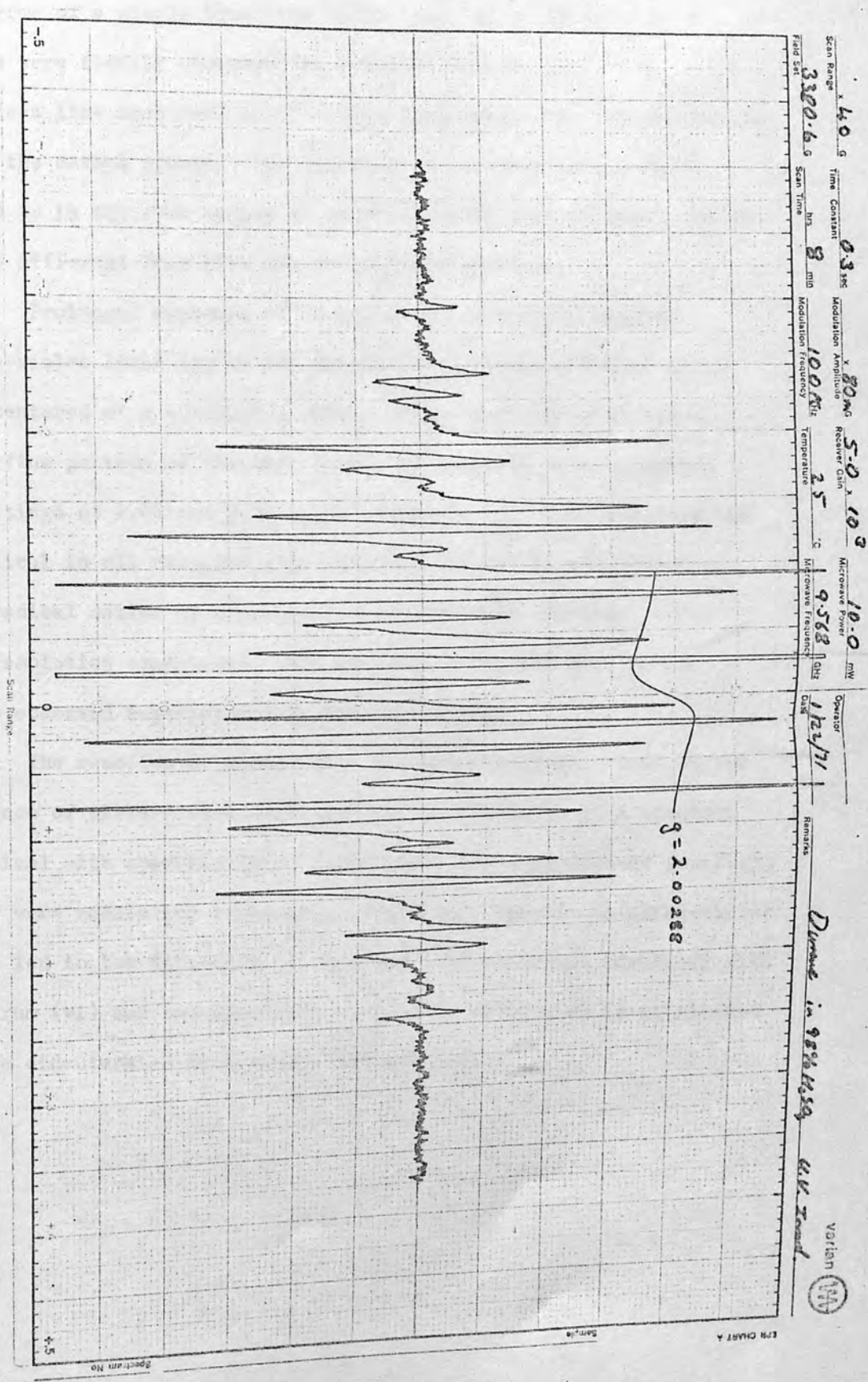
Durene dissolved in 98% sulphuric acid much more slowly than either H.M.B. or P.M.B. The resulting solution was a pale straw-yellow colour and on initial exposure to ultra-violet light gave rise to spectrum (vii). This e.p.r. spectrum was very weak and only nine times were observed with a hyperfine splitting of 10.2 gauss. The spectrum was centered at $g = 2.0028 \pm .0001$. Superimposed on this spectrum were a series of lines where intensities steadily increased with time. These lines were centered downfield from the prompt signal. The intensity distribution of the central seven lines from the prompt signal gave a best fit to the expected binomial distribution of thirteen lines as shown in table 3.

Table 3
Comparison of relative intensities
of spectral lines observed with those
calculated for a binomial distribution
for 13 lines.

Line No.	0 (centre)	1	2	3
Exptl. Intensity Ratio	4	3.4	2.0	1
Theoretical Intensity Ratio	4.2	3.6	2.2	1

The e.p.r. spectrum is attributed to the formation of the radical cation of 2,3,5,6 - tetramethylbenzene, in which the protons in the 1,4-positions show no resolvable hyperfine splitting. This is feasible provided that the degeneracy of the symmetric and antisymmetric orbitals is sufficiently lifted by the symmetry of the ion, in such a way that the antisymmetric level is uppermost. (Fig.24). Since by hyperconjugation, methyl groups can help compensate for the electron deficiency in the π -system, it may be expected that the antisymmetric level would be half filled and to have a node passing through the two ring protons. Provided the orbital splitting is sufficiently large, hyperfine coupling to the 1,4-protons would not be detected. An alternative explanation for apparent lack of spin density at the 1,4 positions involves the fortuitous cancellation of two effects, one giving rise to a small negative spin density, and the other a small positive spin density⁵. (see section 2D.2).

Spectrum (viii)

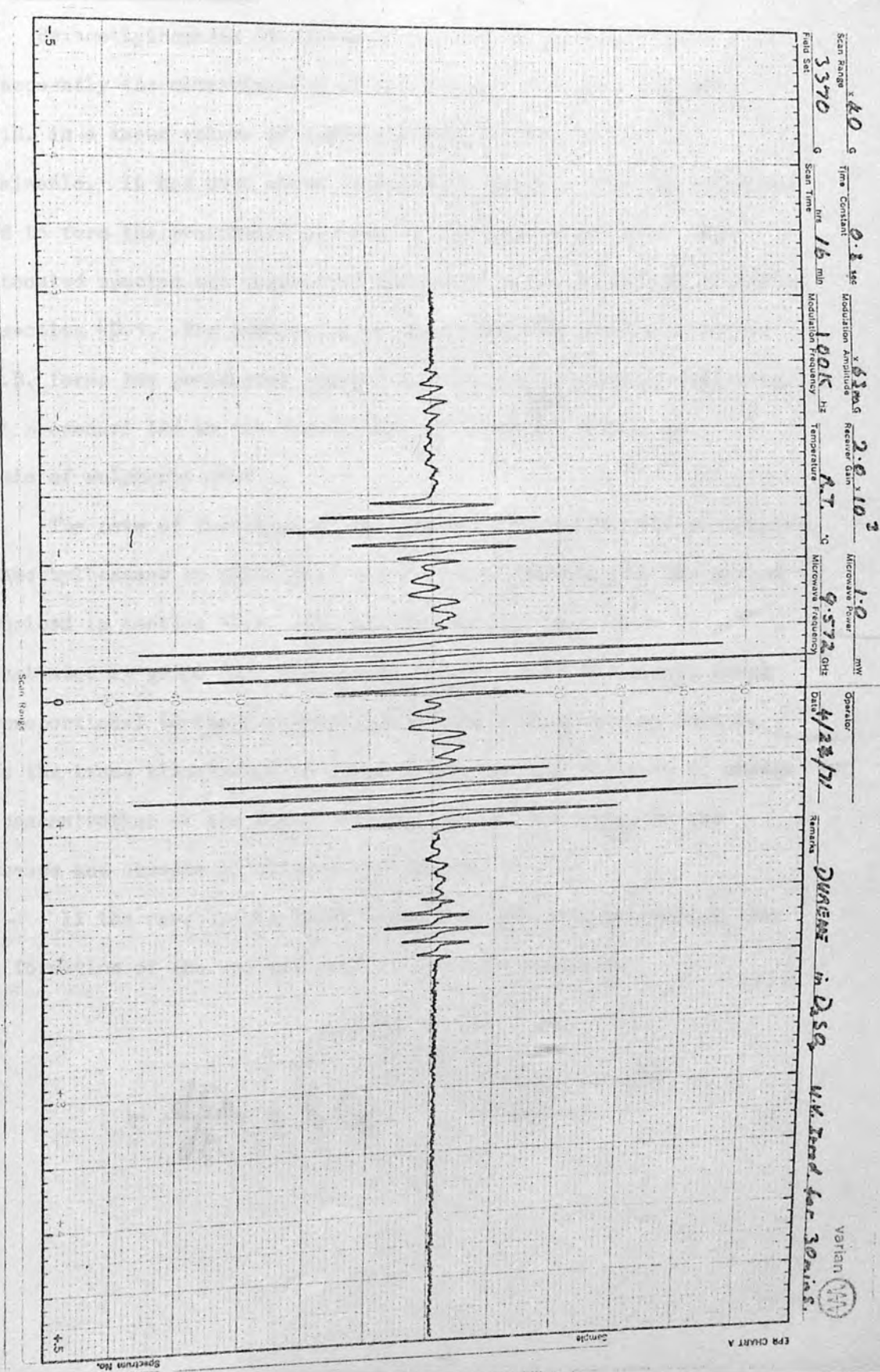


Further evidence in support of the durene radical cation is the simplicity of the prompt spectrum and its accountability in terms of a single hyperfine splitting. Although only seven lines were clearly observed the relative intensities fit a thirteen line spectrum, which arises from twelve equivalent protons from the methyl groups. The spectrum is centered at $g = 2.0028$ which is in the same region as other aromatic hydrocarbons, and is quite different from that for an oxidized species.

Prolonged exposure of durene in 98% sulphuric acid to ultra-violet light led to the formation of spectrum (viii) which was centered at $g = 2.0034 \pm .0001$. This spectrum exhibited a hyperfine pattern of thirteen groups of triplets with hyperfine splittings of 2.06 and 2.70 gauss respectively. This spectrum was identical in all respects with spectrum (v) and is attributed to the radical cation of diprotonated duroquinone. Further, under low resolution conditions, this spectrum coincided with those lines observed superimposed on spectrum (vii).

The reaction of durene with dideuteriosulphuric acid in the presence of ultra-violet light led to the formation of a spectrum identical with spectrum (vii) except that the superimposed downfield lines were modulation broadened. Continued exposure to ultra-violet light led to the formation of spectrum (ix) which was identical with spectrum (vi) and was discussed earlier in section 3B is attributed to the dideuterated duroquinone radical cation.

Spectrum (ix)



3D. Kinetic study of the rate of formation of the radical cation of Hexamethylbenzene.

Hexamethylbenzene dissolves slowly in 98% sulphuric acid consequently the determination of the initial concentration of H.M.B. in a known volume of sulphuric acid is not readily attainable. It has been shown that H.M.B. dissolves in 98% sulphuric acid to form the protonated species ⁷. The concentration of this protonated species was calculated according to the procedure described in section 4D.1. The assumption is made that 100% of the dissolved H.M.B. forms the protonated species H.M.B.⁺ The result of following that procedure led to the dissolution of 0.0035^{gms} of H.M.B. in 4.8mls of sulphuric acid.

The rate of formation of the radical cation from the protonated hexamethylbenzene by photolysis was followed according to the method described in section 4D.2. The general form of this trace is illustrated in graph (i). The intensity change in the signal level is proportional to the concentration of the radical cation formed, thus the trace illustrated in graph (i) represents the rate of change in concentration of the H.M.B. radical cation with time, in the presence and absence of ultra-violet light.

If the reaction is first order then the rate constant k_1 for the formation of the radical cation may be expressed as

$$-\frac{dC_A}{dt} = k_1 C_A$$

equation 7

where C_A is the concentration of protonated hexamethylbenzene (H.M.B.⁺) at a time t .

Integration of equation 7 gives equation 8 where a is the initial concentration of H.M.B.⁺ and x is the decrease in concentration of H.M.B.⁺ due to reaction up to a time t .

$$\ln \frac{a}{(a-x)} = -k_1 t \quad \text{equation 8}$$

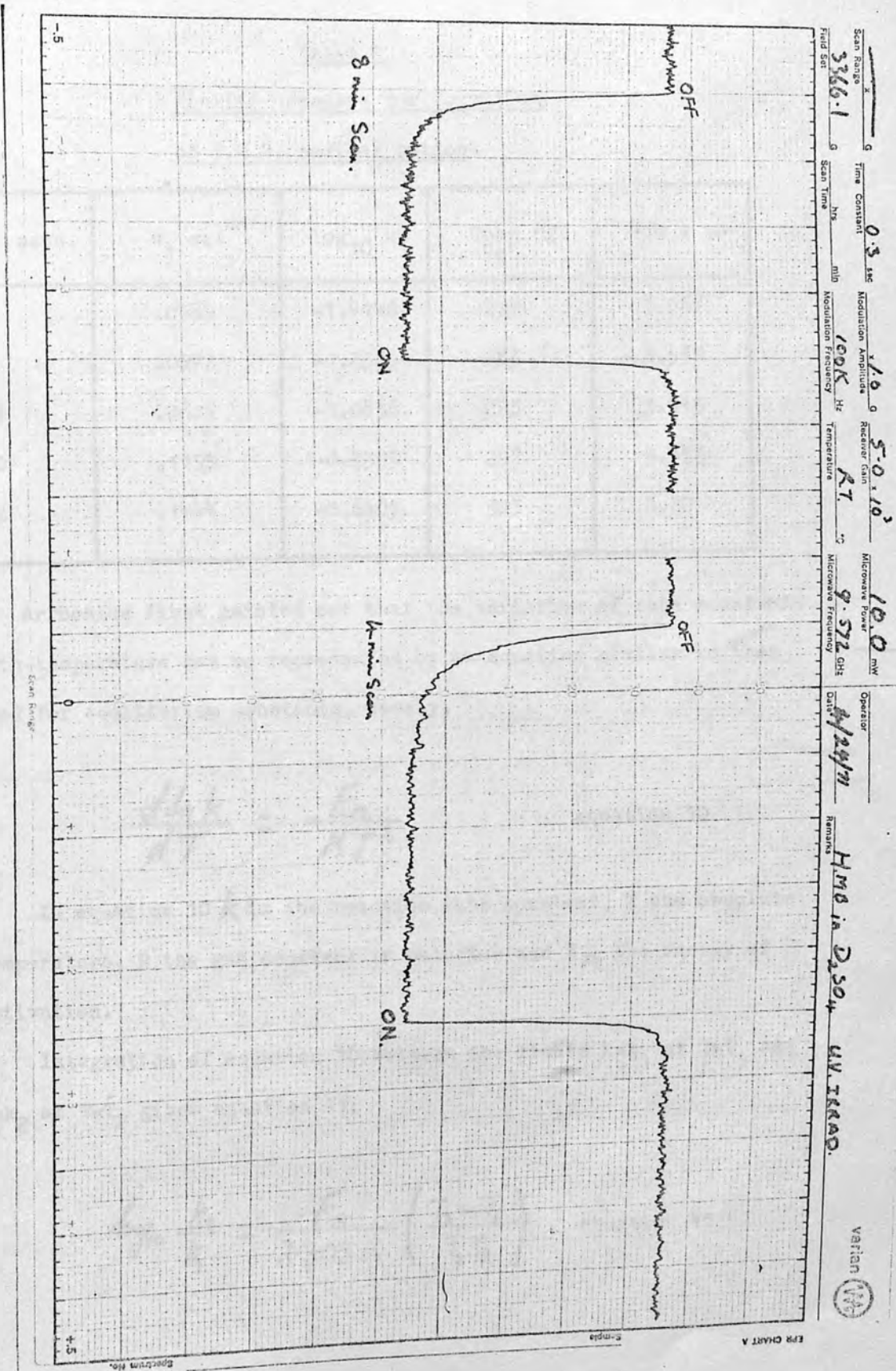
When half of the H.M.B.⁺ has undergone reaction, $a-x = a/2$ and the time, $t_{1/2}$ required for this to occur follows from equation 9.

$$t_{1/2} = \frac{\ln 2}{k_1} \quad \text{equation 9}$$

The time taken for the initial concentration to change by one half was measured from the upward curve of the trace obtained at 25°C (similar to graph i). It is found that the time taken for the change in concentration a , to $a/2$, is equal to the time for the change in concentration $a/2$ to $a/4$ and $a/4$ to $a/8$. Thus the formation of the radical cation of hexamethylbenzene from the protonated hexamethylbenzene in sulphuric acid by photolysis, proceeds by a first order reaction. The value obtained for $t_{1/2}$ at 25°C was 6 secs, and substitution of this value in equation 9 gives a specific rate constant for the reaction of 0.116 sec^{-1} .

The photolysis experiment was repeated under variable temperature conditions according to the procedure outlined in section 4D.2, 4D.3.

Graph (i)



The results of the variable temperature study are summarized in table 4.

Table 4

Kinetic results for formation
of H.M.B. radical cation.

secs.	$k_1 \text{ sec}^{-1}$	$\log_{10} k_1$	Temp. (T) °K	$1/T \times 10^3$
18	.0385	-1.4146	273	3.664
12	.0577	-1.2385	283	3.535
8.4	.0825	-1.0836	293	3.415
6.0	.1155	-0.9375	298	3.355
4.8	.1444	-0.8405	303	3.30

Arrhenius first pointed out that the variation of rate constants with temperature can be represented by an equation similar to that used for equilibrium constants, namely,

$$\frac{d \ln k}{dT} = \frac{E_A}{RT^2} \quad \text{equation 10}$$

In equation 10 k is the reaction rate constant, T the absolute temperature, R the gas constant in calories and E_A the energy of activation.

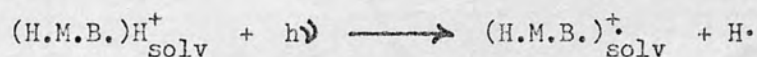
Integration of equation 10 between the limits $k=k_1$ at $T=T_1$ and $k=k_2$ at $T=T_2$ gives equation 11.

$$\log_{10} \frac{k_2}{k_1} = \frac{E_A}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad \text{equation 11}$$

If a graph is plotted of $\log_{10} k$ against $1/T$ this should be straight line if the Arrhenius equation, equation 10 is correct. Further the slope of the line yields to the activation energy E for the reaction as denoted in equation 12.

$$\text{slope} = -\frac{E_A}{2.303R} = -\frac{E_A}{4.576} \quad \text{equation 12}$$

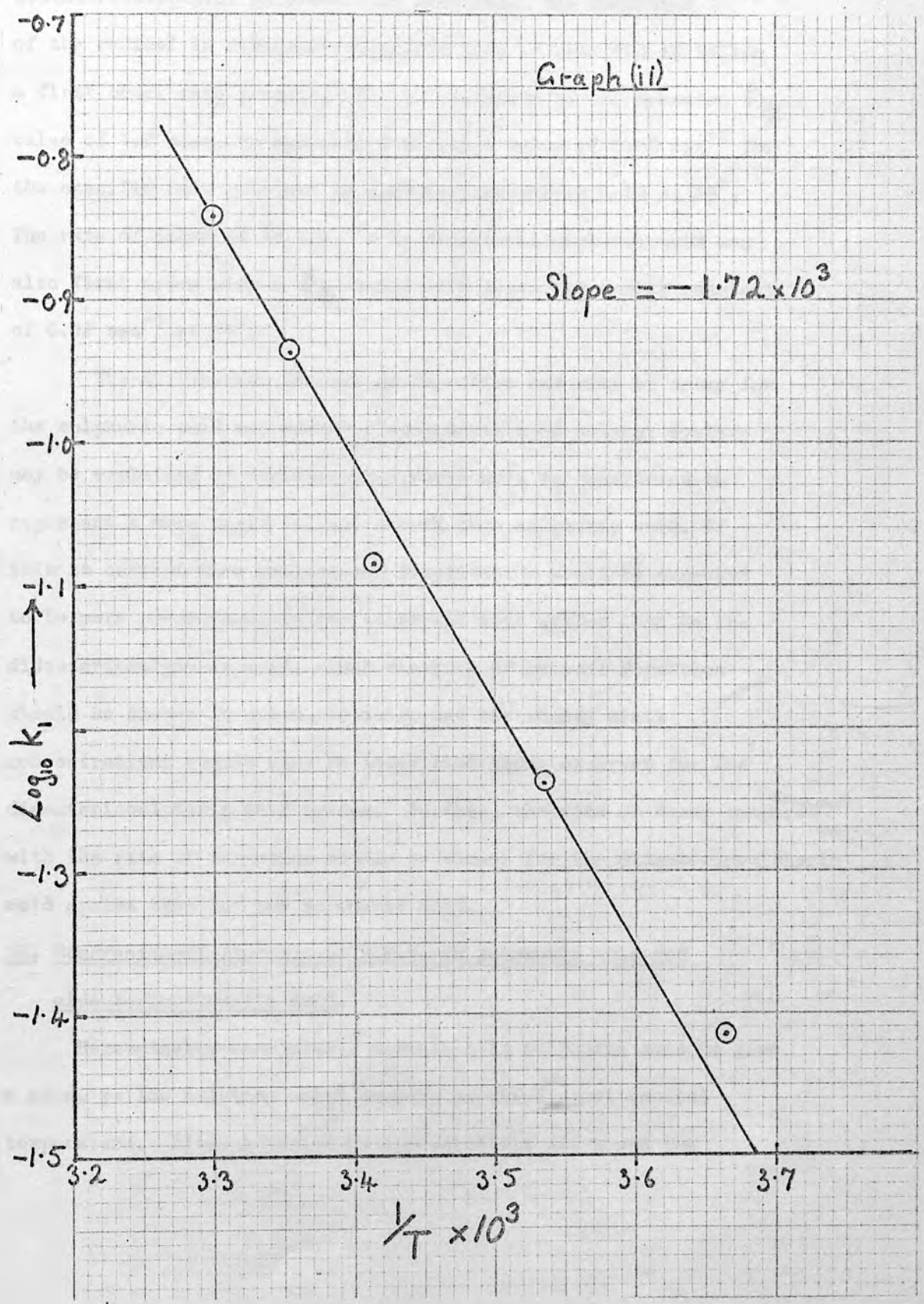
The results presented in table 4 were used to plot graph (ii) of $\log_{10} k_1$ against $1/T \times 10^3$. The activation energy (E_A) for the formation of the radical cation of hexamethylbenzene (H.M.B.)⁺ is calculated from the slope of graph (ii) by substitution in equation 12. The value of E_A obtained in this way for the reaction.



is 7.9 ± 0.8 kcal. mole⁻¹. The accuracy with which the temperature was controlled during the experiment ($\pm 1^\circ\text{C}$) and the accuracy in measuring the $t_{1/2}$ values, represent areas of experimental error in this kinetic study.

The rate of decay of the (H.M.B.)⁺ to the protonated ion after irradiation is stopped also follows a first order rate process with a $t_{1/2}$ value of 11.4 secs.

In view of the increase in intensity of the radical cation formed by photolysis of H.M.B. in dideuteriosulphuric acid compared with sulphuric acid, the rate constant for the reaction at 25°C in



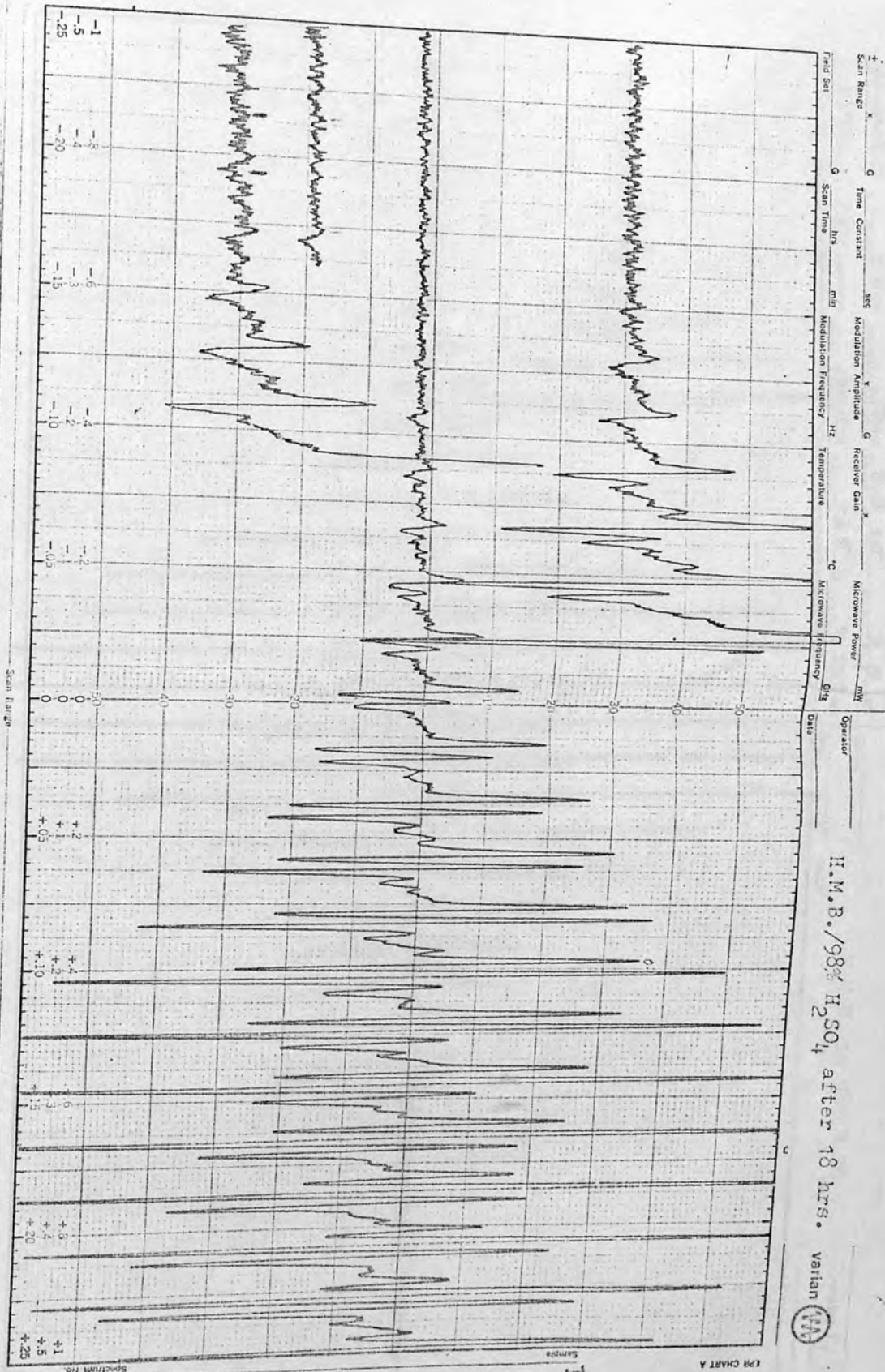
dideuteriosulphuric acid was also measured. The formation of the radical in dideuteriosulphuric acid is observed to follow a first order rate process. The substitution of the measured $t_{1/2}$ value of 1.2 secs. in equation 9 yields a value of 0.58 sec^{-1} for the specific rate constant in dideuteriosulphuric acid at 25° . The rate of decay of $(\text{H.M.B.})^+$ in dideuteriosulphuric acid was also first order with a $t_{1/2}$ value of 6 secs. and a rate constant of 0.12 sec^{-1} at 25° .

The differences in rate of formation and rate of decay for the sulphuric acid and dideuteriosulphuric acid solvent systems may be explained if dideuteriosulphuric acid is considered to represent a more rigid solvent matrix than sulphuric acid. If this is correct then collisional deactivation would be expected to be more predominant in the sulphuric acid system than in the dideuteriosulphuric acid. Thus the rate of radical formation should be slower in sulphuric acid, and the steady state concentrations should also be lower than those observed for the dideuteriosulphuric acid system. Further, the rate of decay compared with the rate of formation should be slower for the dideuteriosulphuric acid system than for the sulphuric acid.

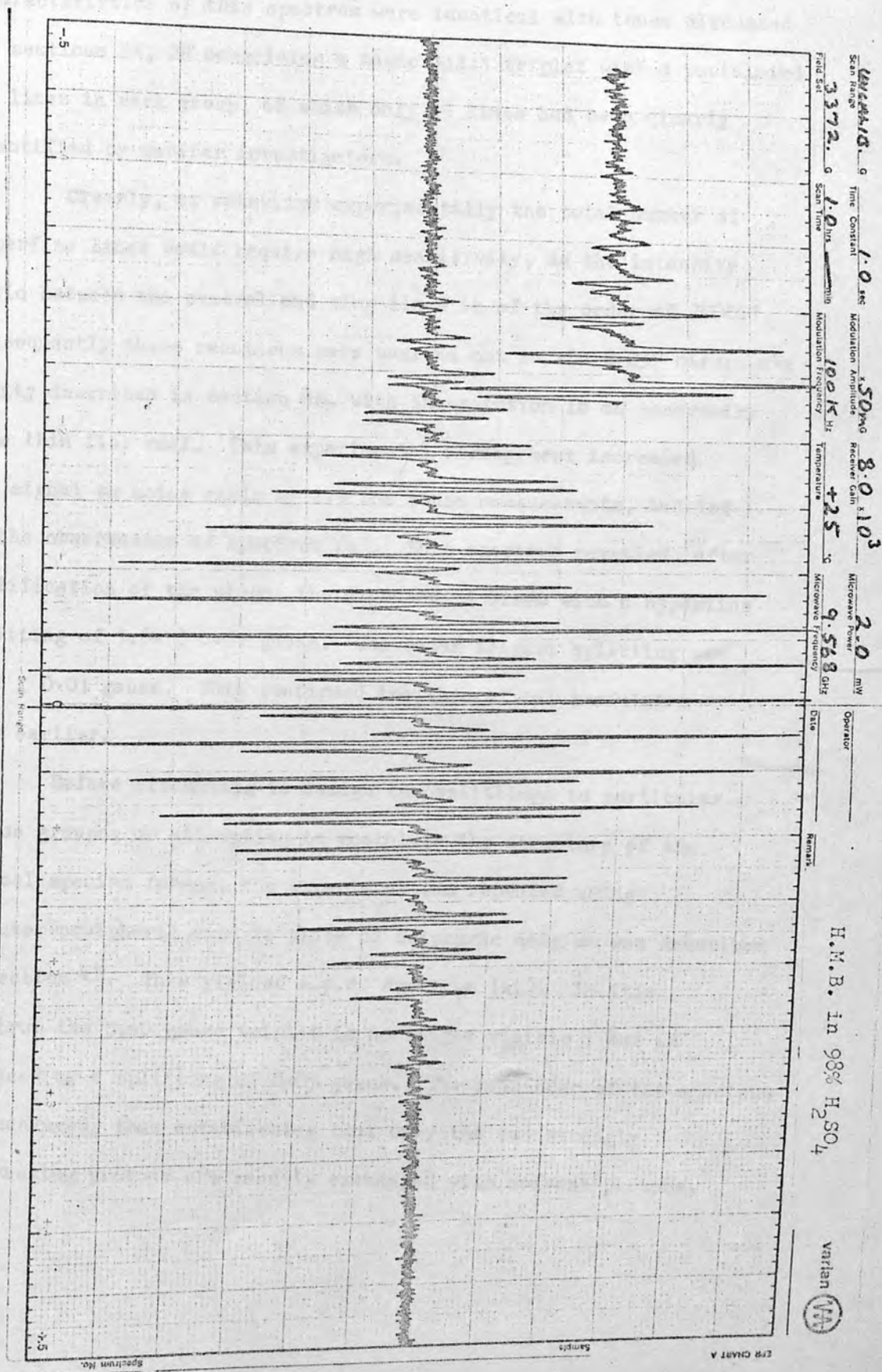
3E. Rearrangement reaction of H.M.B. in sulphuric acid and dideuteriosulphuric acid.

Hexamethylbenzene slowly dissolves in sulphuric acid to give a straw yellow solution which darkens on standing at ambient temperature. After a period of approximately six hours the

Spectrum (x)



Spectrum (x(a))

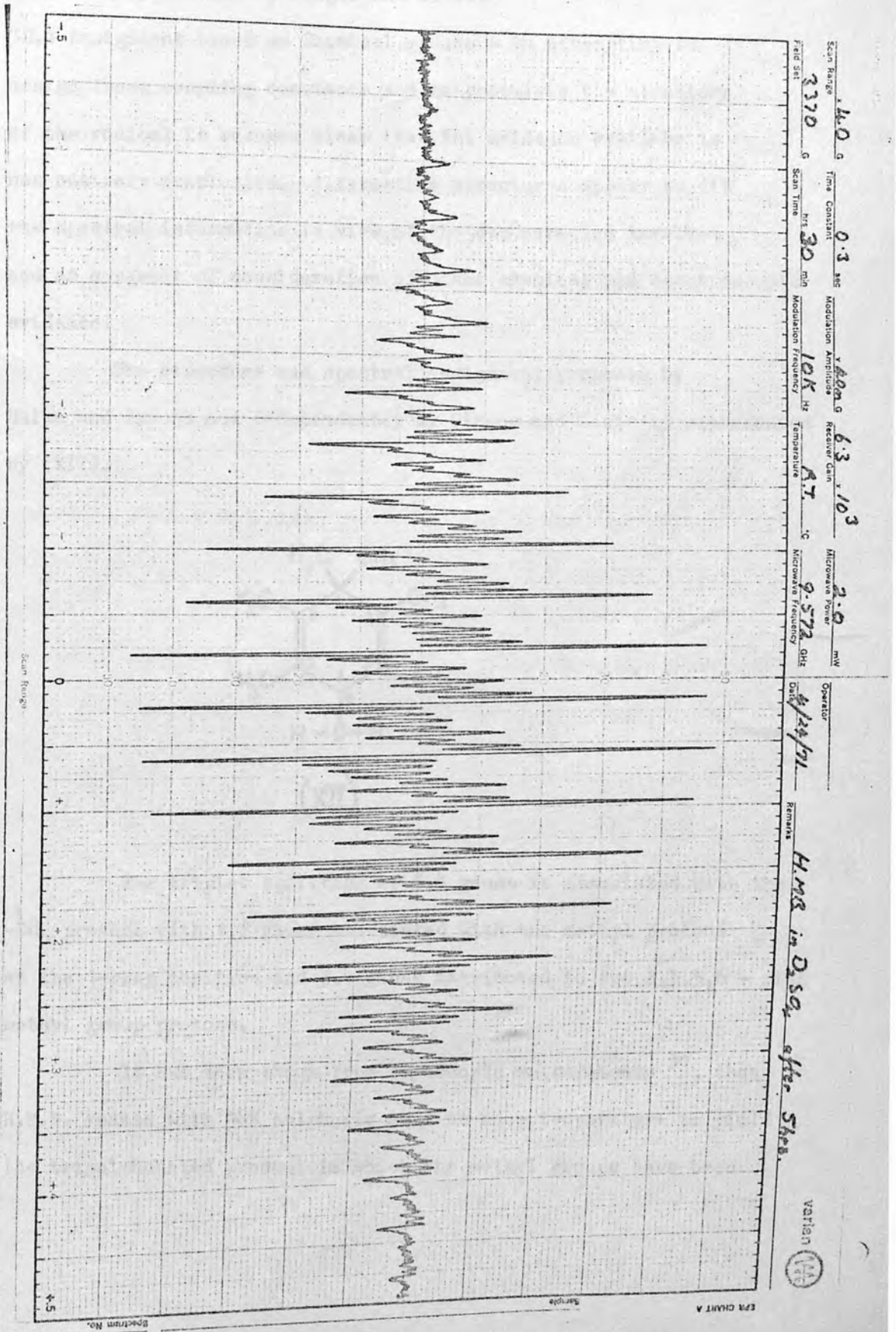


resulting dark red solution exhibits an e.p.r. spectrum. The characteristics of this spectrum were identical with those discussed in sections 2A, 2B comprising a basic 1:2:1 triplet with a postulated 31 lines in each group, of which only 25 lines had been clearly identified by earlier investigators.

Clearly, to establish experimentally the total number of hyperfine lines would require high sensitivity, as the intensity ratio between the central and wing lines is of the order of 2000:1. Consequently these reactions were carried out in the E-237 microwave cavity described in section 4M. with the solution in an abnormally wide thin flat cell. This experimental arrangement increased the signal to noise ratio by 1.9 for these measurements, and led to the observation of spectrum (x). This spectrum revealed, after amplification of the wings, the expected 31 lines with a hyperfine splitting of 1.64 ± 0.01 gauss. The major triplet splitting was 5.40 ± 0.01 gauss. This confirmed the theoretical postulates made earlier.

Before attempting to assign the splittings to particular proton groups, or attempting to postulate the structure of the radical species formed, the experiment was repeated using dideuteriosulphuric acid in place of sulphuric acid as was described in section 4E. This yielded e.p.r. spectrum (xi). In this spectrum the 5.40 gauss triplet is no longer visible, but is replaced by a splitting of 0.85 gauss. The remainder of the spectrum is unchanged, thus establishing that only the two strongly interacting protons are readily exchanged with solvent protons.

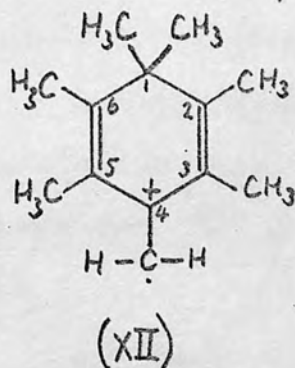
Spectrum (xi)



These results are perfectly consistent with those obtained by Hulme and Symons and by Singer and Lewis.

3E.1 Assignment based on Chemical groups - In attempting to assign these coupling constants and to postulate the structure of the radical it becomes clear that the evidence available is not entirely conclusive. Alternative structures appear to fit the spectral information in view of the degeneracies involved and as a result of consideration of other chemical and spectroscopic evidence.

The structure and spectral assignment proposed by Hulme and Symons and independently by Singer and Lewis is represented by (XII).

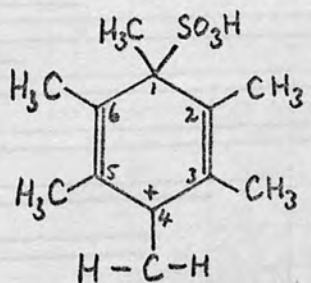


The triplet splitting of 5.4 gauss is associated with the $\dot{\text{C}}\text{H}_2$ protons with 1.7 gauss associated with the methyl protons at the 1-ring position and 3.4 gauss attributed to the 2,3,5,6 - ring methyl group protons.

It has been shown from cryoscopic measurements³¹, that H.M.B. reacts with 98% sulphuric acid at room temperature to yield the trisulphonated product in which the methyl groups have been

replaced by sulphonic acid groups. This reaction is successful under the conditions for cryoscopy because the concentration of reacting hexamethylbenzene is small compared with the quantity of sulphuric acid. Consequently dilution of the acid by the water produced during the reaction has little effect on the overall acid concentration, and therefore sulphonation can proceed beyond monosulphonation. Whilst the concentration of H.M.B. in sulphuric acid is higher in the e.p.r. investigations, it is not as high as in a normal preparative sulphonation reaction. Consequently it is reasonable to expect at least monosubstitution by the sulphonic acid group in the reaction under investigation.

Singer and Lewis postulated a Jacobsen rearrangement for the reaction of H.M.B. under investigation⁸. The Jacobsen rearrangement is initiated by the presence of a sulphonic acid group¹⁵. Thus from a chemical standpoint the presence of a sulphonic acid group in the intermediate under investigation appears to be feasible, and structure (XVI) is therefore proposed.



(XVI)

This structure would have the following spectral assignments if it were to account for the e.p.r. spectrum

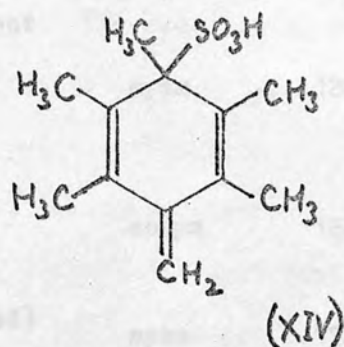
observed.

- (1) The triplet splitting of 5.4 gauss must be associated with the two methylene protons.
- (2) The methyl groups in the 2,3,5,6-ring positions can no longer be equivalent because of the presence of the $-\text{SO}_3\text{H}$ group.
- (3) Applying the non-equivalence postulated in (2) above leads seven lines from the 3,5-methyl groups split four lines from the 2-methyl group, further split by four lines from the 6-methyl group further split by four lines from the 1-methyl group. If the splittings between these lines are related in the order $1:1/3:1/3:2/3$ respectively with a smallest splitting of 1.7 gauss, then that relationship leads to a superposition of lines giving a total of 31 lines.

Application of the above relative splittings and intensities leads to the histogram illustrated in graph (iii). The line intensities compare well with those observed experimentally. This is to be expected in view of the high degeneracy involved in this assignments.

If the intermediate is a sulphonated species then it should

be possible to isolate it as structure (XIV)



This isolation and identification was carried out as indicated in section 4F. The isolated end product was believed to be the correct species since it yielded a very weak, prompt, e.p.r. signal when dissolved in 98% sulphuric acid. This spectrum is identical to that obtained after prolonged reaction of H.M.B. with 98% sulphuric acid. The presence of a sulphonyl group was investigated by the following methods.

(a) Lassaigne's sodium fusion test for sulphur with sodium nitroprusside according to the procedure described in section 4E indicated that there was no sulphur present in the product isolated. The test worked successfully on a sample of prehnitene sulphonyl acid yielding a positive result.

(b) It has been shown by infra-red spectroscopy that sulphonyl acids give the following bands in the infra-red region ³².

S = O in sulphonic acids; denotes frequency in cm^{-1}

Covalent	assym	1352	1340 cm^{-1}) Strong,))
	symm	1200	1100 cm^{-1}	

Ionic (hydrated)	assym	1220	1150 cm^{-1}
	symm	1120	1030 cm^{-1}

Traces of water induce almost complete ionisation ^{28.}



O-H in sulphonic acids;

Covalent	2900 cm^{-1}	strong and broad
(Anhydrous)	2400 cm^{-1}	weaker and broad
Ionic	2600 cm^{-1}) very broad)))
	2250 cm^{-1}	
	1680 cm^{-1}	

Although maxima of the S=O bands are at about the same frequencies in hydrated acids as in salts of the species, they may be distinguished since the two S=O bands from a broad absorption block in acids with two maxima.

Salts show two separate bands. The O-H structure in hydrated acids appear as a very broad band.

The information above was used in interpreting the infra red spectra obtained from the isolated product. The spectra showed no band that was consistently attributable to the presence of a sulphonic acid group.

As a result of this investigation there is no evidence for the presence of a sulphonic acid group in the intermediate isolated according to the procedure outlined in section 4F.

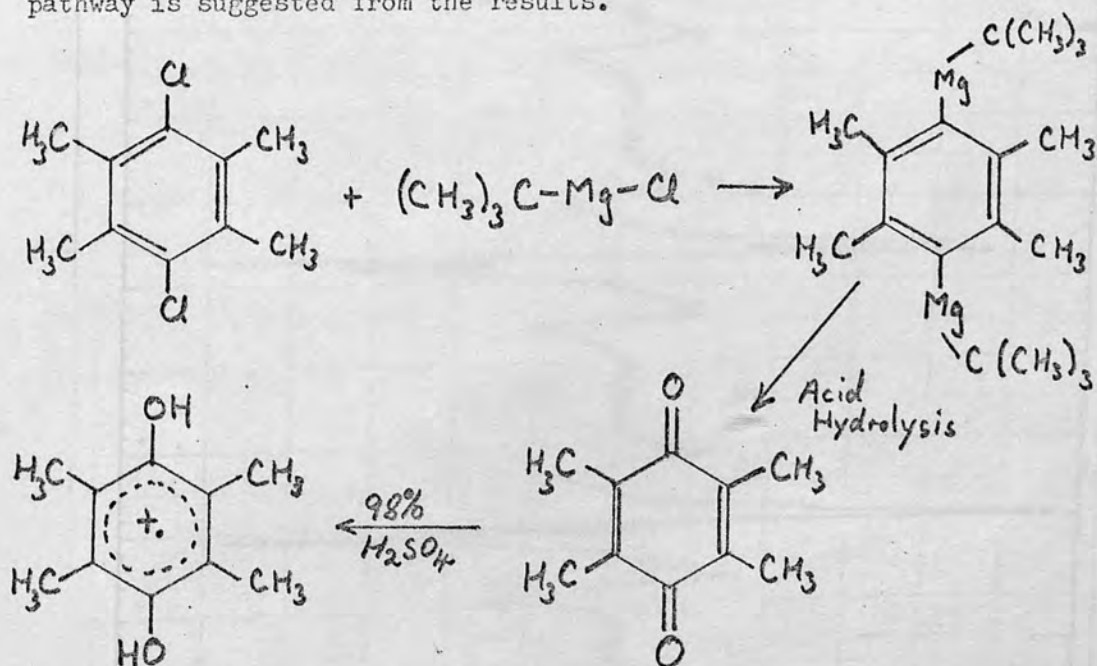
If the e.p.r. spectrum resulting from the prolonged reaction of H.M.B. with 98% sulphuric acid could be simplified then the resultant interpretation would be less open to question. One way to achieve this simplification, assuming a similar rearrangement reaction occurs, is to synthesise a molecule in which some of the methyl groups are substituted by groups that could not give rise to any hyperfine splitting. Such a substituent would have to have approximately the same inductive and electromeric effects as the methyl group, and not alter the reactivity of the aromatic system. A substituent that fits the requirements is the t-butyl group in which the interaction with the unpaired electron in the π -system is extremely small. Clearly the probability of observing any hyperfine splitting from the protons of the t-butyl group is almost zero. Consequently the synthesis of 1,4-di-t-butyl-2,3,5,6-tetramethylbenzene was attempted according to the method described in section 4F.

The product of the reactions described in section 4J was taken and its n.m.r. spectrum showed a single peak at 2.35 p.p.m.

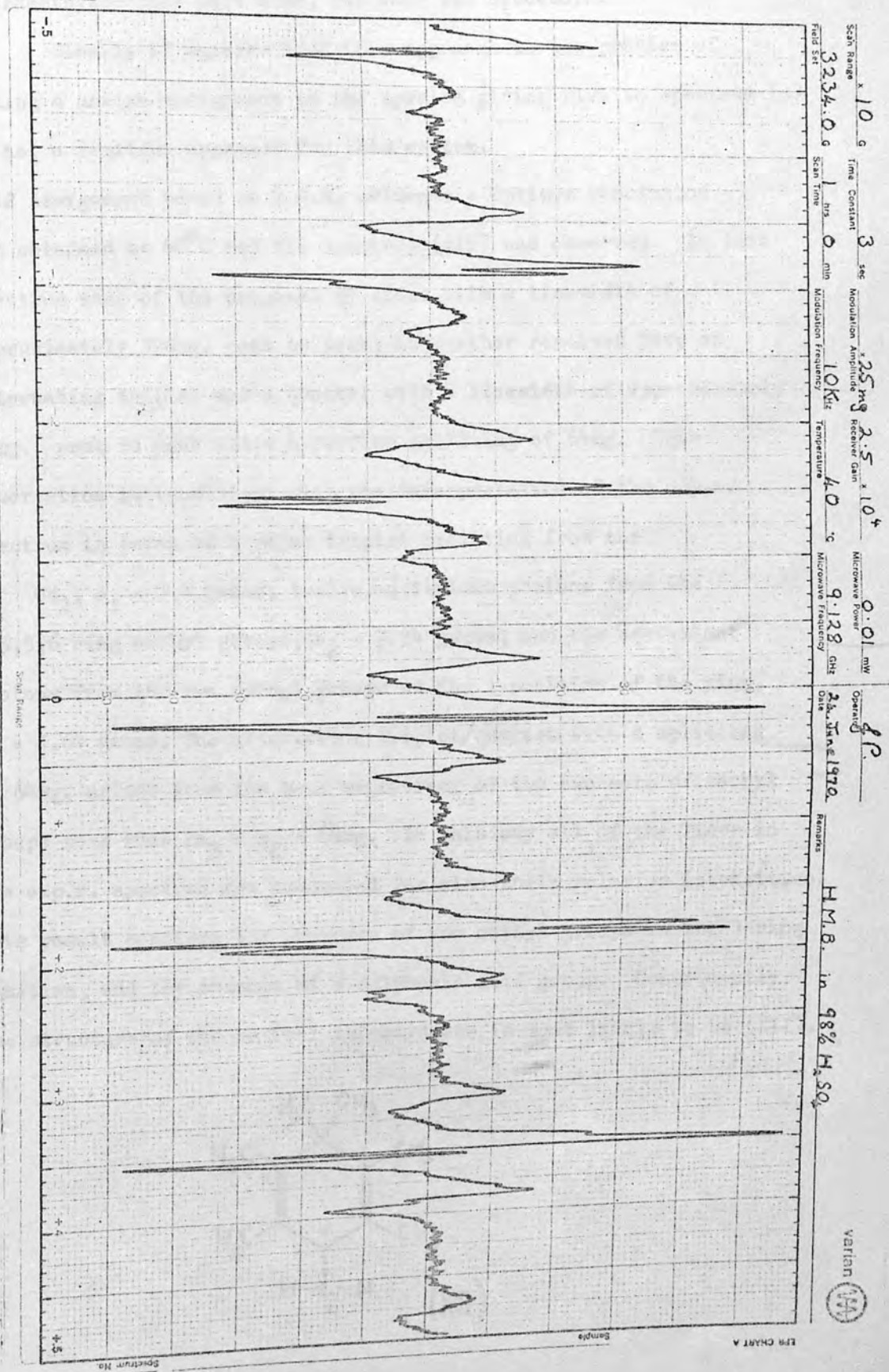
Thus it appears that all of the methyl groups are equivalent, and this is not what would be expected if the dichlorodurene had been t-butylated at the 1,4-positions. The n.m.r. peak corresponded very closely to the starting material, despite the different physical and chemical properties. Further, the product reacted with 98% sulphuric acid to yield an e.p.r. spectrum of thirteen groups of triplets, with splitting constants 2.06 gauss and 2.70 gauss respectively. Clearly the e.p.r. spectrum is identical with spectrum (viii) and is attributed to the diprotonated duroquinone radical cation.

The infra red spectrum of a nujol mull of the product showed little difference between this product and the starting material, with the exception of a small band at 1720 cm^{-1} attributable to $\text{C}=\text{O}$.

It appears from these results, that the t-butylation via a Grignard reagent had not proceeded as expected. The following pathway is suggested from the results.



Spectrum (xii)

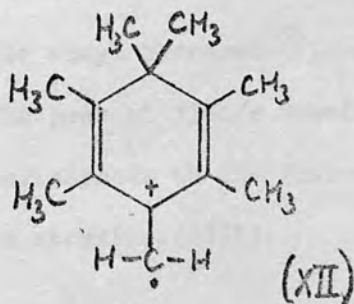


Further attempts to synthesise the 1,4-substituted tetramethylbenzene were made, but none was successful.

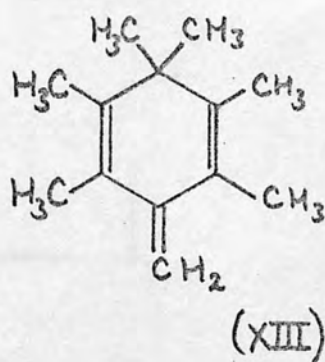
Clearly it appears that this approach to the problem of making a unique assignment to the species giving rise to spectrum (x) is not a fruitful approach for this system.

3E.2 Assignment based on E.P.R. evidence - Optimum resolution was obtained at 40°C and the spectrum (xii) was observed. In this spectrum each of the original 93 lines with a linewidth of approximately 120mg. peak to peak, is further resolved into an alternating triplet and a quartet with a linewidth of approximately 25mg. peak to peak and a hyperfine splitting of 64mg. This observation is consistent with the interpretation of the e.p.r. spectrum in terms of a major triplet splitting from the

CH_2 , $a_1 = 5.4$ gauss, twelve equivalent protons from the 2,3,5,6 ring methyl groups, $a_2 = 3.34$ gauss, and six equivalent protons from the two methyl groups at the 1-position of the ring, $a_3 = 1.64$ gauss. The alternating triplet/quartet with a splitting of 64mg. arises from the near degeneracy of the two sets of methyl groups such that $2a_3 = a_2 - 64\text{mg}$. In this way all of the lines in the e.p.r. spectrum are accounted for also their relative intensities. This result confirms the presence of two methyl groups in the 1-ring position, and the absence of a sulphonic acid group. Consequently the structure of the radical intermediate is most likely to be (XII).



This intermediate by removal of an electron, gives structure (XIII).

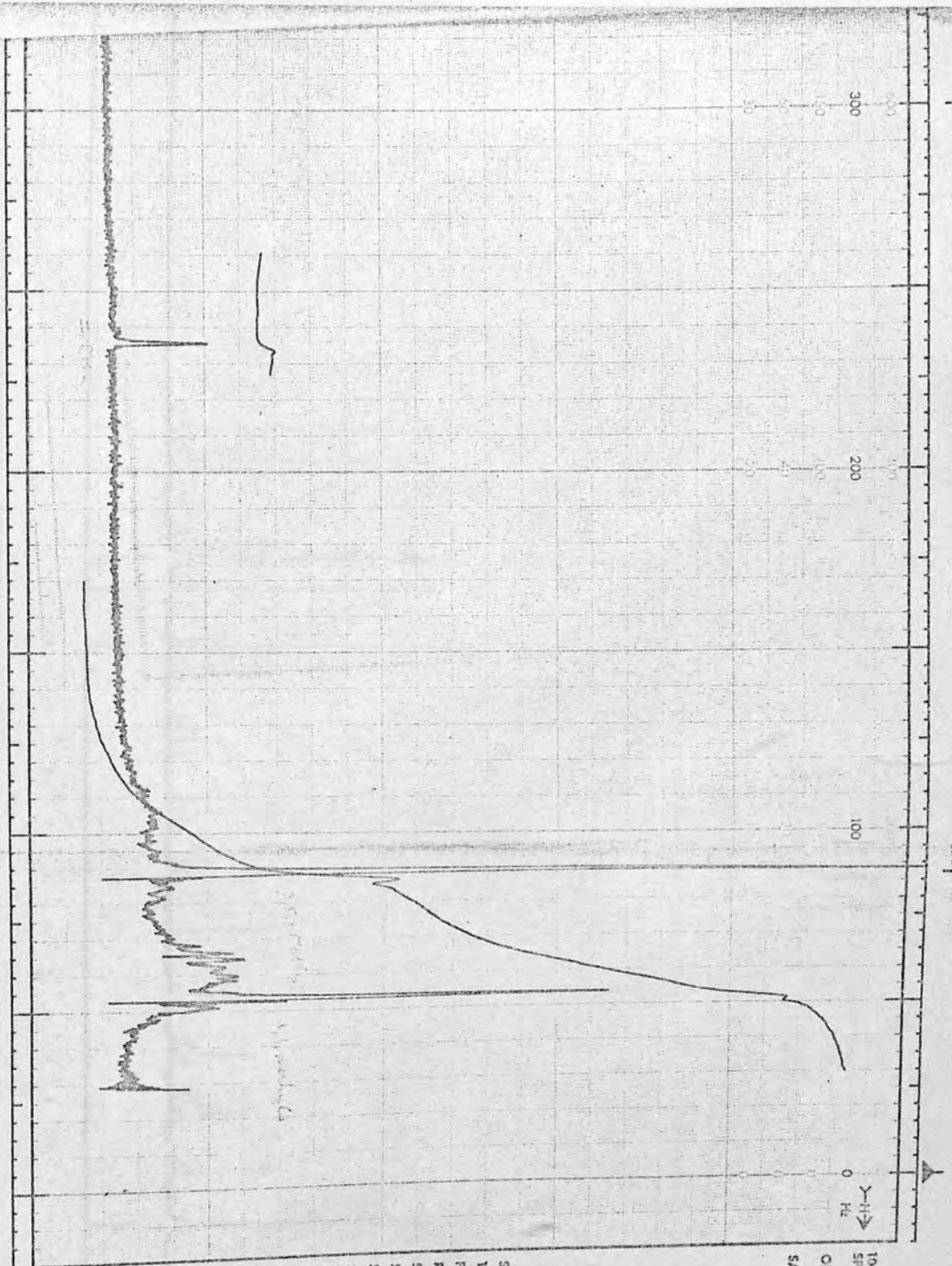


These structures are identical to those proposed by Hulme and Symons, and Singer and Lewis.

If the 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene structure (XIII) represents the stable product by loss of an electron from the radical (XII), it should be possible to reform the radical by dissolving (XIII) in 98% sulphuric acid. A prompt e.p.r. signal which has the same characteristics as the spectrum obtained after prolonged reaction of H.M.B. with 98% sulphuric acid should be obtained. 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene was therefore synthesised (section 4J), and was identified by its n.m.r. spectrum in carbon tetrachloride, (spectrum xiii). The following assignments of the n.m.r. absorptions were made.

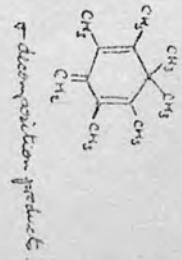
- (1) The peak at 471c/s downfield from tetramethylsilane (T.M.S.) corresponds in position to that indicated for vinyl hydrogen ³⁴.
- (2) The peak at 178c/s downfield from T.M.S. corresponds to the four vinyl methyl groups in structure (XIII).

Spectrum (xiii)



HA-100 SPECTRUM

100 MHz NMR
SPECTRUM NO.
OPERATOR: *S. K. Nigam* DATE: *17.11.62*
SAMPLE: *233 John Borden*

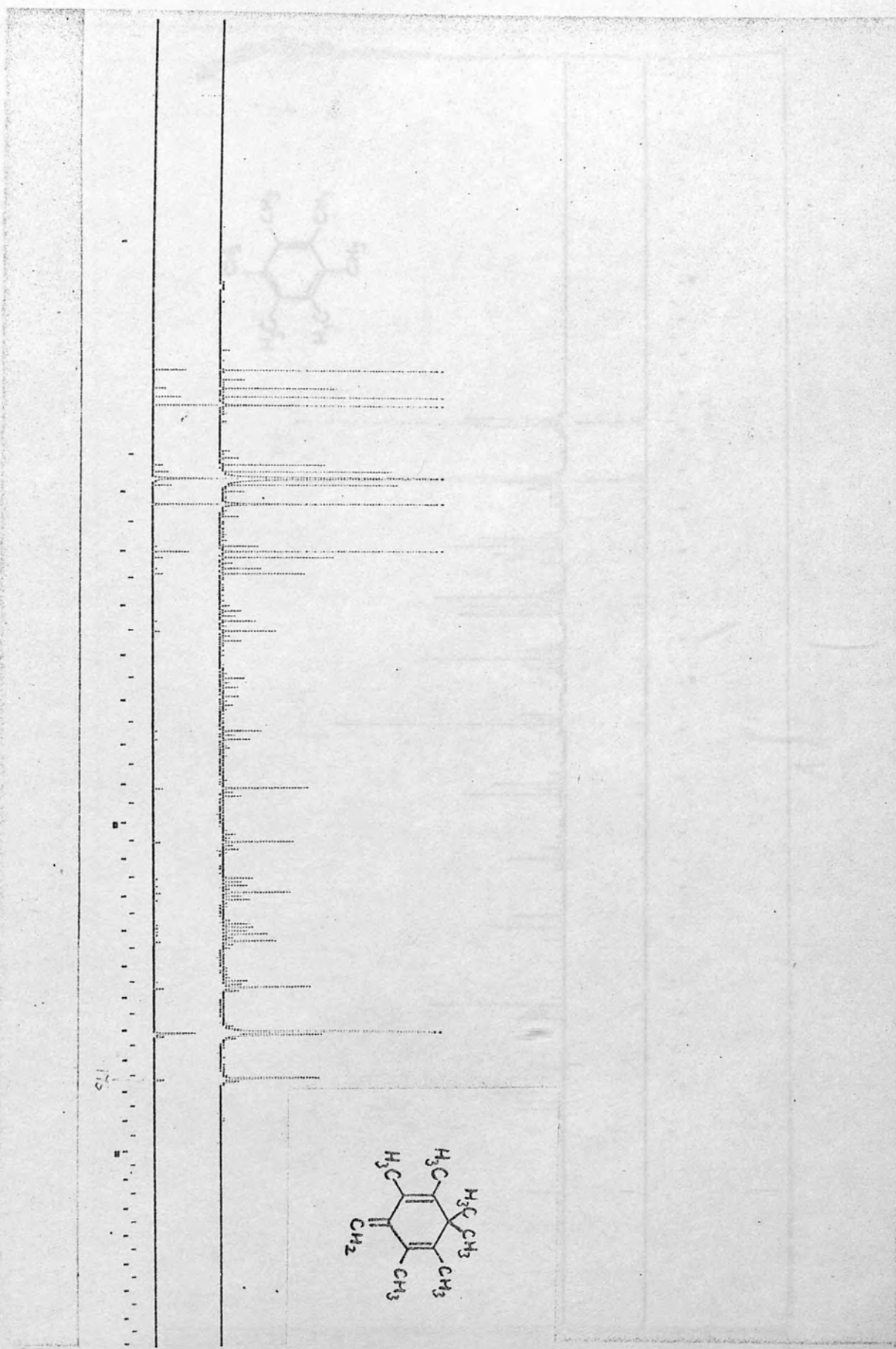


SOLVENT	—	—
TEMPERATURE	—	—
FREQ. RESPONSE	—	—
R.F. ATTENUATOR	—	—
SWEEP TIME	—	—
SWEEP WIDTH	—	—
SWEEP OFFSET	—	—
SPECTRUM AMP.	—	—
LOCK SIGNAL	—	—
FIELD MILLICAUSS (MAIN OSC. FREQ.)	—	—
FIELD MILLICAUSS (SWEEP FREQ.)	—	—
FIELD SWEEP	—	—

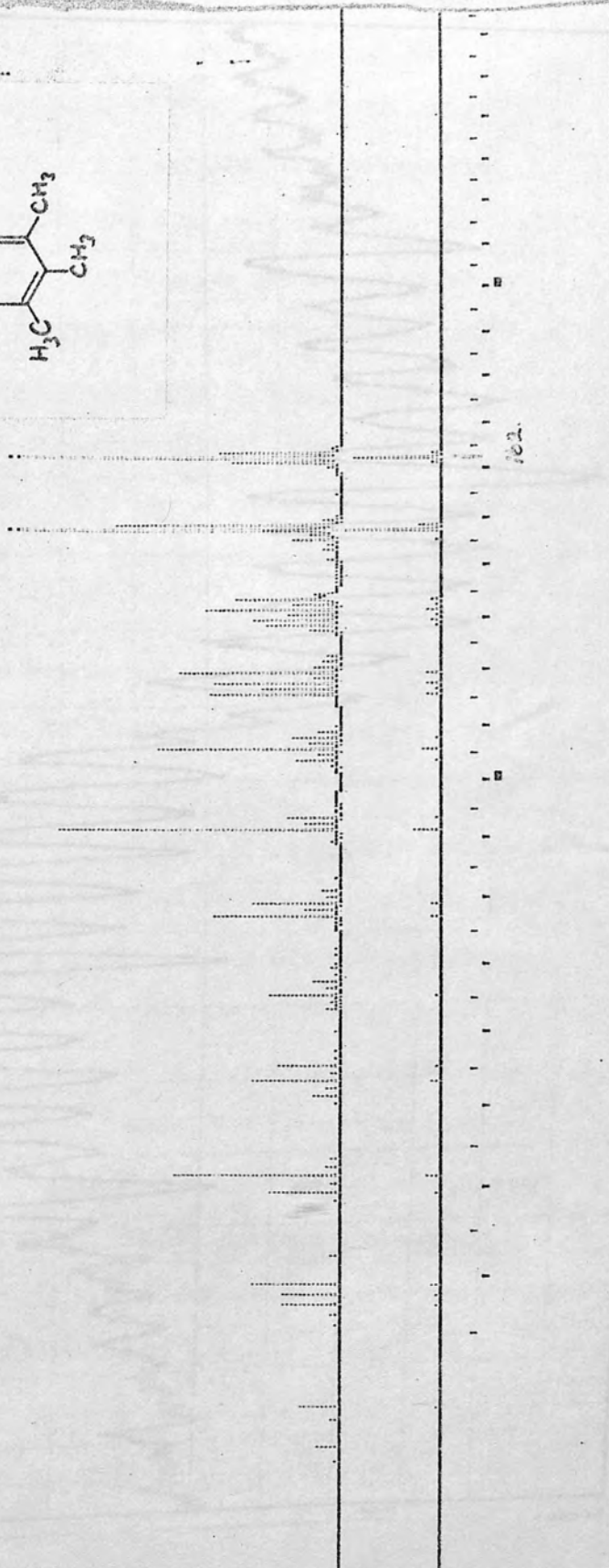
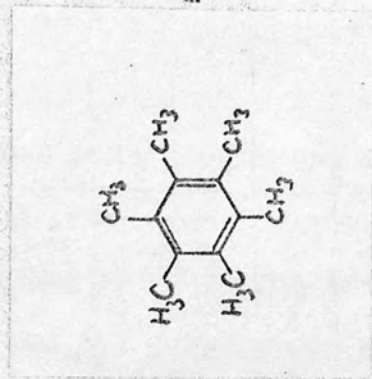


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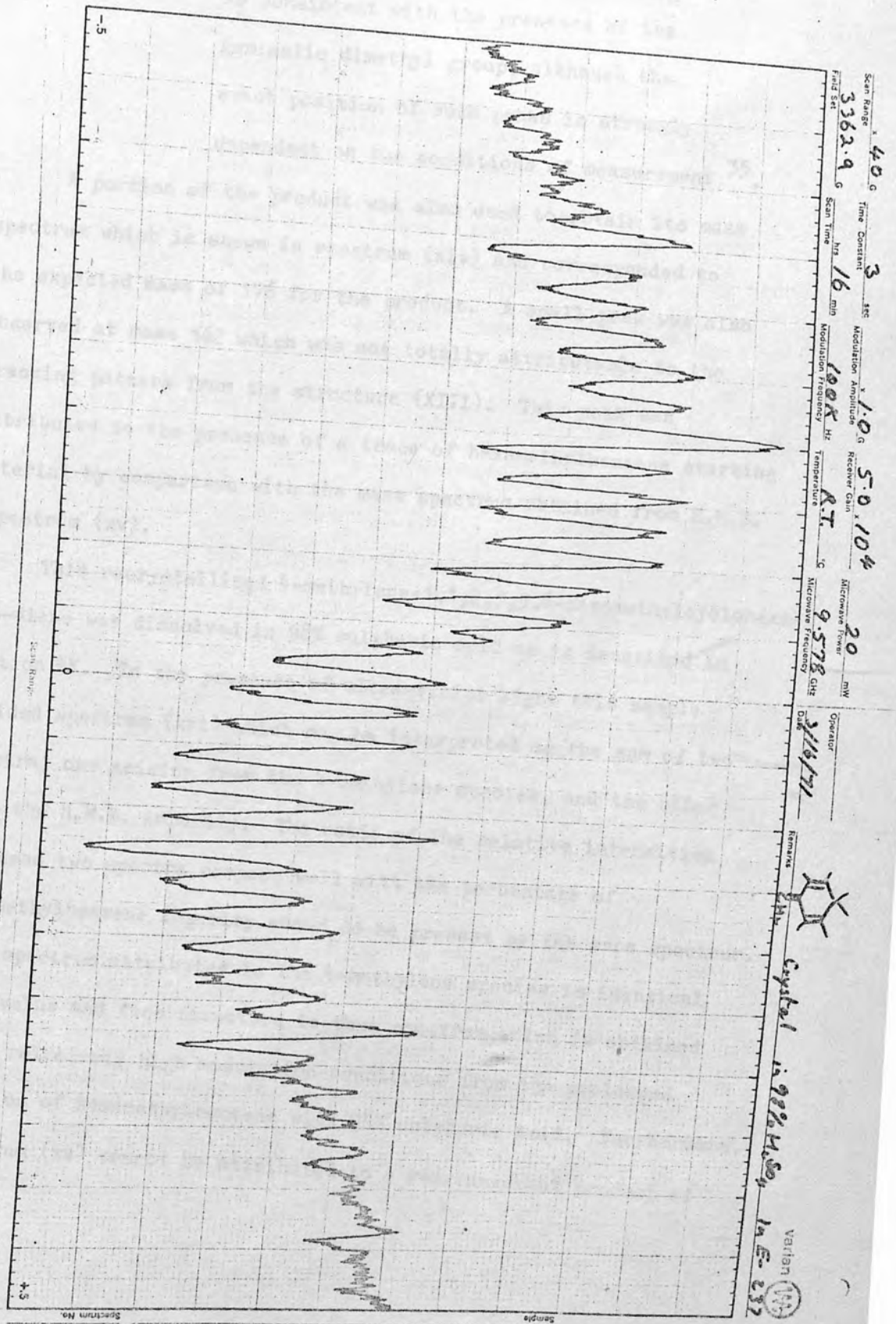
Spectrum (xiv)



Spectrum (xv)



Spectrum (xvi)



(3) The peak at 108c/s downfield from T.M.S. is consistent with the presence of the geminatic dimethyl group, although the exact position of such peaks is strongly dependent on the conditions of measurement³⁵.

A portion of the product was also used to obtain its mass spectrum which is shown in spectrum (xiv) and corresponded to the expected mass of 176 for the product. A small peak was also observed at mass 162 which was not totally attributable to the cracking pattern from the structure (XIII). This peak was attributed to the presence of a trace of hexamethylbenzene starting material by comparison with the mass spectrum obtained from H.M.B. (spectrum (xv)).

This recrystallized 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene was dissolved in 98% sulphuric acid as is described in section 4K. In the presence of ultra-violet light this sample yielded spectrum (xvi) which may be interpreted as the sum of two spectra; one arising from the 4-methylene species, and the other from the H.M.B. impurity. The ratio of the relative intensities of these two spectra compare well with the percentage of hexamethylbenzene impurity shown to be present by the mass spectrum. This spectrum attributed to the 4-methylene species is identical in *g*-value and fine structure to that spectrum which is obtained under relatively high modulation conditions from the prolonged reaction of hexamethylbenzene with 98% sulphuric acid. Furthermore, spectrum (xv) cannot be attributed to a rearrangement product of

the hexamethylbenzene impurity for the following reasons:

(1) The e.p.r. signal observed was a prompt signal formed within a maximum of five minutes from the time of initial solvation in 98% sulphuric acid. During this time hexamethylbenzene showed no rearranged product detectable by e.p.r. and in the presence of ultra-violet light formed only the H.M.B. radical cation.

(2) The hexamethylbenzene spectrum followed the same first order reaction with respect to the formation of H.M.B. radical cation in the presence and absence of ultra-violet light, with no detectable intensity change during the time of the experiment. If the spectrum attributed to the 4-methylene species resulted from rearranged H.M.B., the signal intensity from the H.M.B. cation would be expected to decrease with time as a result of that rearrangement.

3E.3 Conclusion - As a result of the experiments leading to the information discussed in section 3E, the species that is most likely to give rise to spectra (x), (xii), and (xvi), is (XII). This structure is stabilized in the manner indicated in section 2E.1.

3F. Summary.

As a result of the investigations discussed in this work the following statements may be made.

- (1) Hexamethylbenzene and durene dissolved in 98% sulphuric acid to form the protonated species which on exposure to ultra-violet light forms by a first order reaction the related radical cation. In the case of durene this species is short lived and readily undergoes oxidation to form the stable diprotonated duroquinone radical cation.
- (2) Pentamethylbenzene dissolved in 98% sulphuric acid, presumably as the protonated species. This undergoes a disproportionation reaction to yield to the diprotonated duroquinone radical cation when exposed to ultra-violet light.
- (3) Prolonged reaction of hexamethylbenzene with 98% sulphuric acid leads to the formation of the species to which structure (XII) is attributed. This species is believed to be formed as a result of Jacobsen rearrangement of hexamethylbenzene.
- (4) The radical cation (XII) is also formed rapidly by exposure of a solution of 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene in 98% sulphuric acid to ultra-violet light.

SECTION 4

Experimental

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Experimental.

4A. Materials.

Hexamethylbenzene (H.M.B.) Koch Light) m.p. 165°C) was shown to be pure by gas chromatography and nuclear magnetic resonance spectroscopy (n.m.r.)

Pentamethylbenzene (P.M.B.) (Koch Light) and durene (2,3,5,6-tetramethylbenzene) (B.D.H.) were recrystallized from glacial acetic acid. The pentamethylbenzene (P.M.B.) yielded colourless crystals, m.p. 54°C . Durene yielded colourless plates, m.p. 79°C . Both samples were shown to be pure by gas chromatography, although there may have been an impurity (0.6%) obscured by the 'tail' of the solvent peak. The n.m.r. spectra were in accord with those expected for pure P.M.B. and durene.

"Analar" grade 98% sulphuric acid (B.D.H.) and 20% oleum were used without purification. The specific gravity of the sulphuric acid was checked before the kinetic measurements.

4B. E.P.R. Measurements.

Electron paramagnetic resonance measurements were made in a Varian E-12 spectrometer operating at about 9,500MHz with either 10KHz or 100KHz modulation frequencies. Two types of microwave resonant cavities were used, E-231, and E-237, both are resonant in the TE_{102} mode³⁰ and have a plane of zero electric field vector to facilitate measurements in high dielectric solvents. Samples with a high dielectric loss require the use of a thin flat quartz cell which is inserted into the microwave cavity such that the plane of the sample is coincident with the plane of zero electric field

vector of the microwave cavity. In this position the sample plane is parallel to the external magnetic field direction.

The E-231 and E-237 cavities both allow the passage of visible and ultra-violet light to irradiate the sample through a 50% transmission grid on the front face of the cavity.

The sample temperature was varied by use of the Varian E-257 variable temperature accessory. The temperature is varied by passing a stream of nitrogen gas over the sample tube. The gas is cooled by passage through a coil immersed in liquid nitrogen and warmed to the desired temperature by passing over a heating element. The temperature of the gas is measured just below the sample with a platinum resistance thermometer and is regulated to within $\pm 1^\circ$ in the range 0° to 100° . The sample is thermally isolated from the microwave cavity by a quartz dewar insert which fits through the access ports of the microwave cavity.

High sensitivity e.p.r. measurements were made utilizing the E-237 cavity. This cavity is described in detail in section 4M.

High resolution measurements were made in the standard E-231 cavity using 10KHz modulation frequency with very low amplitude (20 to 32mg) to avoid modulation broadening. These measurements also require the use of low microwave power levels, 50 to 60dB. attenuation on a 200mw source, to avoid saturation of the spin system.

4C. E.P.R. Measurements on H.M.B., P.M.B., Durene on initial dissolution in 98% sulphuric acid and dideuteriosulphuric acid.

Hexamethylbenzene (0.006 - 0.007gms) was shaken with 98% sulphuric acid (5mls) for about 1 minute, and was then left to stand for a further 4 minutes. The golden yellow solution was then decanted off and about 1ml. was pipetted into a thin flat quartz e.p.r. cell which had been previously checked for background e.p.r. signals when filled with 98% sulphuric acid both in the absence and presence of ultra-violet light. This gave rise to a very weak e.p.r. spectrum (spectrum (i)). Photolysis of this sample gave rise to a dramatic enhancement in signal intensity - spectrum (ii). This effect was completely reversible with respect to the alternate presence and absence of the ultra-violet light.

Hexamethylbenzene (0.003gms) was then added to 99% atomic purity 98% dideuteriosulphuric acid (2mls) under the same conditions as were previously described and on irradiation with ultra-violet light yielded e.p.r. spectrum (iii).

Pentamethylbenzene (0.006gms) was added to 98% sulphuric acid (5mls) under the conditions described earlier and on exposure to ultra-violet light yielded e.p.r. spectrum (iv) initially and spectrum (v) after prolonged exposure. The mass spectrum of P.M.B. was taken to check its purity.

Pentamethylbenzene (0.003gms) was added to 99% atomic purity 98% dideuteriosulphuric acid (2mls) under the same conditions as were previously described and on irradiation with ultra-violet light yielded spectrum (vi). Durene (0.006 was added to 98%

sulphuric acid (5mls) under the conditions described earlier and on exposure to ultra-violet light yielded e.p.r. spectrum (vii) initially and spectrum (viii) after prolonged exposure.

Durene (0.003gms) was added to 99% atomic purity 98% dideuteriosulphuric acid (2mls) under the conditions previously described and on irradiation with ultra-violet light yield spectrum (iv).

4D. Determination of Initial concentration of H.M.B. in 98% sulphuric acid and kinetics of the reaction $\text{H.M.B.}^+ \longrightarrow \text{H.M.B.}^\ddagger$

4D.1 A known weight (W_1) of hexamethylbenzene was placed in a sintered glass Buchner funnel which had previously been dried to constant weight, (W_2). To this was added 98% sulphuric acid (5mls). This was then left to react with the H.M.B. at room temperature for 4 minutes, and during this time a certain amount of the H.M.B. went into solution. The resulting straw yellow mixture was then filtered at the pump, initially in air, and later under an inert atmosphere of argon. The liquor was collected in a previously weighed Buchner flask (W_3) and the weight of the flask containing H.M.B. dissolved in 98% sulphuric acid was recorded (W_4). The funnel containing the undissolved H.M.B. and a certain amount of residual 98% sulphuric acid was then carefully washed with distilled water, and dried to constant weight (W_5). Thus:-

$$W_5 - W_2 = \text{Weight of undissolved H.M.B. } (W_6)$$

$$W_1 - W_6 = \text{Weight of H.M.B. dissolved in sulphuric acid } (W_7)$$

$$W_4 - W_3 = \text{Weight of sulphuric acid and dissolved in H.M.B. } (W_8)$$

$$W_8 - W_7 = \text{Weight of sulphuric acid used as solvent } (W_9)$$

Consequently since the specific gravity (Sp.Gr.) of the sulphuric acid was measured earlier, $W_9 / \text{Sp.Gr.}$ gave the volume of sulphuric acid actually used. In conjunction with W_7 , this yielded the concentration of hexamethylbenzene as the protonated species in 98% sulphuric acid.

4D.2 This solution was placed in the thin flat quartz cell and was inserted in the E-237 cavity. The sample was then irradiated with ultra-violet light and the magnetic field was adjusted such that the recorder pen sat on top of the central line of the resultant e.p.r. spectrum. The field sweep of the instrument was then switched off and when the radiation was subsequently removed the recorder plotted the decrease in intensity of the transition with time. The sample was re-exposed to the ultra-violet light and the intensity increase was plotted with time, as was shown in graph (i). These measurements were carried out at ambient temperature ($\sim 25^\circ\text{C}$).

4D.3 This experiment was repeated at various temperatures in the range 0°C to 40°C as described in section 4B. The results are presented in table 4, from which the activation energy for the reaction was calculated.

4E. Prolonged reaction of H.M.B. with sulphuric acid and didenteriosulphuric acid.

A solution of hexamethylbenzene in 98% sulphuric acid ($\sim 10^{-3}\text{M}$) was prepared as indicated in section 4C, and was allowed to stand at ambient temperature (approx. 25°C) for about 6 hrs. This solution was then placed in a thin flat cell in the E-237 cavity to attain the maximum sensitivity, and the resultant

e.p.r. spectrum was recorded (spectrum (x)).

This experiment was repeated using a solution of hexamethylbenzene in 99% atomic purity dideuteriosulphuric acid and after standing for a period of 6 hours the resultant e.p.r. spectrum was recorded (spectrum (xi)).

As an alternative to leaving the solution to stand for a period of 6 to 18 hrs., it was found that if the freshly prepared solution was heated on a water bath at about 80°C for approximately four minutes and then cooled to room temperature the deep red solution yielded the same e.p.r. spectrum as spectrum (x).

4F. Isolation and identification of the stable intermediate of the H.M.B. Rearrangement.

To establish whether or not the e.p.r. spectrum resulting from prolonged reaction of H.M.B. with sulphuric acid involved sulphonation the following attempt was made at isolating and identifying this stable intermediate as a species containing an $-SO_3H$ group.

Hexamethylbenzene (0.95gms) was dissolved in 98% sulphuric acid (20mls). The resultant partial solution was heated on a water bath at 80°C for 8 minutes, poured on ice (50gms) and stirred for a few minutes. This yielded a greenish-brown precipitate which was separated by filtration. The resultant orange-yellow aqueous filtrate was believed to be a solution of prehnitene sulphonic acid. The precipitate was washed with isopentane ; and shaken with acetone, giving a dark green solution and a residue

which yielded no e.p.r. spectrum either itself or on treatment with 98% sulphuric acid. After evaporation of the acetone the resultant dark green precipitate yielded a prompt e.p.r. signal in 98% sulphuric acid. This precipitate could still contain a trace of H.M.B. Consequently the green precipitate was taken up in concentrated hydrochloric acid (10mls) and filtered through a sintered glass funnel. The residue after drying had m.p. 162°C . This melting point was not sharp ($160^{\circ} - 165^{\circ}\text{C}$) and was probably due to impure H.M.B. The acid fraction was then extracted with isopentane and the solvent evaporated to yield an almost colourless residue. This residue gave an orange-red solution on treatment with 98% sulphuric acid and yielded a very weak e.p.r. spectrum which appeared to be identical with that obtained under modulation broadened conditions after prolonged standing of H.M.B. in 98% sulphuric acid.

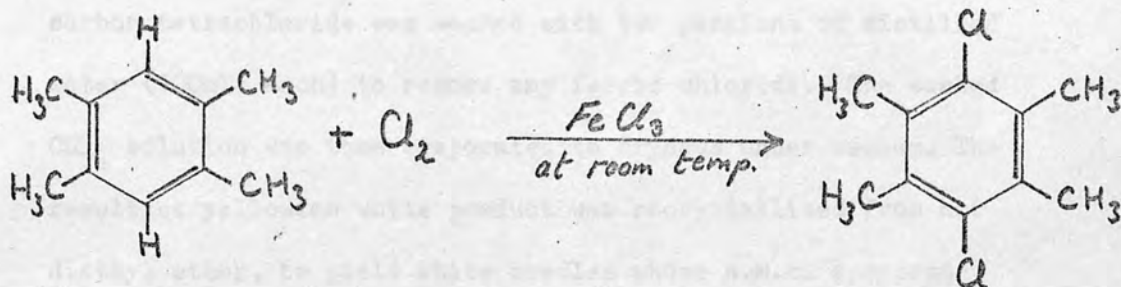
In order to identify the presence of an $-\text{SO}_3\text{H}$ group in the product isolated previously the following experiments were carried out:-

- (a) Lassaigne sodium fusion test for sulphur. This test yielded a consistent negative result, whilst a blank on prehnitene sulphonic acid yielded a positive result.
- (b) Infra-red spectroscopy of sulphonic acids. Infra-red spectra were taken on a nujol mull and on solutions in carbon tetrachloride and chloroform. The resultant spectra were compared with solvent blanks and showed no evidence of bands consistently attributable to a sulphonic acid group.

4G. Attempted sunthesis of 1,4-di-t-butyl-2,3,5,6-tetramethylbenzene.

To aid the interpretation of the e.p.r. spectrum (x) the synthesis of 1,4-di-t-butyl-2,3,5,6-tetramethylbenzene from durene was attempted.

(a) Preparation of dichlorodurene.



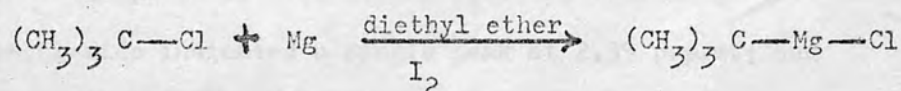
Durene (2.7gms) was dissolved in carbon tetrachloride (50mls) and was poured into a threeneck flask. To this was added some ferric chloride (5.5gms) as a catalyst. Chlorine gas was then bubbled through this stirred solution at room temperature, and samples were taken after 1 hour, and 2 $\frac{1}{4}$ hours; the reaction being stopped after 2 $\frac{1}{2}$ hours.

N.M.R. spectra taken during the course of the reaction showed that after 1 hours there was no aromatic peak and just a single methyl peak. The gain was increased by a factor of 100 and as a result a small aromatic proton peak was distinguished along with a doublet at 4.5 p.p.m. After 2 $\frac{1}{4}$ hours, one of the peaks at the 4.5 p.p.m. region had increased whilst the other decreased. Thus it appears that the chlorination of the 1,4 ring

positions was complete after about $\frac{3}{4}$ hours. After this time, despite the low temperature and a halogen carrier as a catalyst, chlorination of the methyl group substituents on the ring occurs to give $-\text{CH}_2\text{Cl}$. However, this side reaction occurred only to the extent of approximately 5% of the total reaction after 2 hours.

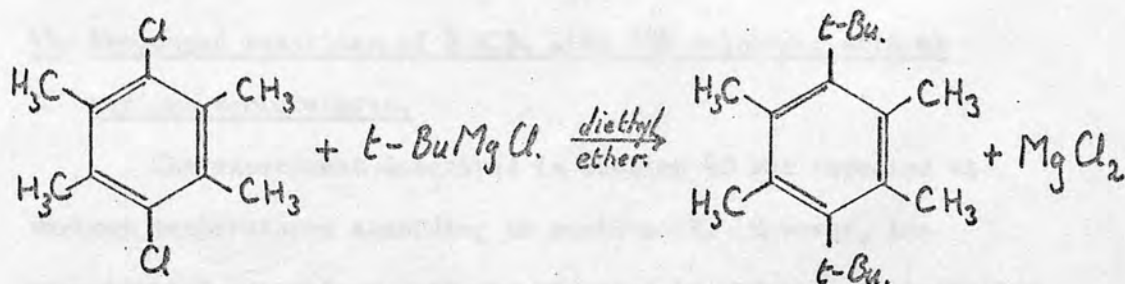
The flow of chlorine was stopped and the solution in carbon tetrachloride was washed with two portions of distilled water (100mls each) to remove any ferric chloride. The washed CCl_4 solution was then evaporated to dryness under vacuum. The resultant yellowish white product was recrystallized from hot diethyl ether, to yield white needles whose n.m.r. spectrum corresponded to that expected from 1,4-dichlorodurene. The needles gave a melting point of 188° (lit.³⁶ m.p. 189°).

(b) Preparation of t-butylmagnesium chloride.



t-Butyl chloride (15mls) was added to some dry diethyl ether (25mls) and this resultant mixture was added to clean magnesium (1.0gms) at such a rate that the solution refluxed gently. When all of the t-butyl chloride/diethyl ether solution had been added a small iodine crystal was added and the reactants heated very gently in order to maintain reflux until the reaction ceased.

(c) Preparation of 1,4-di-t-butyl-2,3,5,6-tetramethylbenzene.



To the freshly prepared Grignard reagent was added an ethereal solution of dichlorodurene. (0.40 gms in 25 mls diethyl ether). The resultant solution was then refluxed for $\frac{1}{2}$ hour, allowed to cool, hydrolysed with dilute hydrochloric acid and extracted with carbontetrachloride. Evaporation of the solvent at room temperature gave yellow plates (m.p. 111°). The n.m.r. spectrum of this product in carbontetrachloride indicated a single peak at 2.35 p.p.m.; and consequently it appeared that all of the methyl groups were equivalent. This is not what would be expected if *t*-butylation had occurred at the 1,4-positions. This n.m.r. peak corresponded very closely to the starting material, but the product had different physical and chemical properties. Further the yellow plates on standing in 98% sulphuric acid yielded an e.p.r. spectrum of thirteen groups of triplets; the splitting constants being 2.06 gauss and 2.70 gauss respectively. This infra red spectrum of a **nujol**-mull of the product showed very little difference between the starting material and final product except for a small C=O band at 1720cm⁻¹. Thus it would appear that the *t*-butylation had not proceeded as expected.

Further attempts were made to synthesise the 1,4-substituted tetramethylbenzene by Wurtz-Fittig reactions, but none of these attempts were successful.

4H. Prolonged reactions of H.M.B. with 98% sulphuric acid at various temperatures.

The experiment described in section 4D was repeated at various temperatures according to section 4B. However, the experimental parameters were now adjusted in order to optimize the resolution. This led to e.p.r. spectrum (xii) which was obtained at 40°C, after careful adjustment of the instrumental parameters.

4J. Preparation and Purification of 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene.

Hexamethylbenzene (1.20gms) was dissolved in toluene (30mls) and was poured into a three necked flask fitted with a stirrer, reflux condenser with an HCl gas trap, and an inlet pipe for bubbling methyl chloride gas below the toluene surface. To this solution was added some finely ground anhydrous aluminium trichloride (2.0gms). This solution was heated on a water bath at a solution temperature of 85°C for 2½ hours, while methyl chloride gas was bubbled through the vigorously stirred solution, with the evolution of hydrogen chloride. The resultant solution which contained a dark red oil was allowed to cool and the red oil was separated off, and crystallized after a few moments. This material was then shaken with isopentane and the pentance fraction was discarded. The remaining fraction was hydrolysed with ice cold

water and then extracted with isopentane. The combined isopentane solutions were then extracted with a total of 10-15mls of concentrated hydrochloric acid. The acid extracts were then poured on ice water and neutralized with sodium carbonate. This neutralized solution was extracted with isopentane and dried (Na_2SO_4). This dried pentane solution was then distilled gently under vacuum to remove the greater portion of isopentane and was then left to stand to crystallize slowly under nitrogen. This yielded colourless crystalline plates with a m.p. of 46°C and an n.m.r. spectrum (spectrum (xiii)) which corresponds to that expected for the pure product, 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene.

The mass spectrum of a portion of the product was taken on a Varian - M.A.T. CH7 mass spectrometer and compared with that of hexamethylbenzene. This comparative analysis indicated that the product of the above reaction contained approximately 5.5% of unchanged hexamethylbenzene.

4K. E.P.R. investigation of the reaction of 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene with 98% sulphuric acid.

The product of the reaction described in section 4J was dissolved immediately in 98% sulphuric acid to give a dark red solution. A portion of this solution was placed in thin flat quartz cell and was positioned in an E-237 microwave resonant cavity. This sample yielded prompt e.p.r. spectra (spectra (xiv) and (xv)) which represented a superposition of two species.

The intensities of the lines associated with each of these species were summed and the ratio was compared with ratio of the hexamethylbenzene impurity shown to be present in the 4-methylene-1,1,2,3,5,6-hexamethylcyclohexa-2,5-diene preparation by the mass spectrum.

4L. Ultra-violet Irradiation System design and development.

In order to provide a convenient general purpose source of ultra-violet light, with optics suitable for use with an c.p.r. spectrometer, it was decided to design and produce such a system which could be readily manufactured.

The concept of the system was to use a newly developed compact mercury arc lamp. This type of lamp behaves optically as a point source, and was readily available from Engelhard Hanovia Ltd. This light source was then made the centre of an optical system designed to trap as much light as possible, and project an evenly illuminated disc of light to the cavity. The area of the disc covering the active sample region. Thus a surface aluminised silicon oxide coated spherical mirror was placed behind the source such that light travelling away from the sample direction was reflected back to a focus at the point source. This light and the radiation from the source were then collected by a high quality synthetic fused quartz lens which had aberrations introduced into it in order to produce a reasonably evenly illuminated disc of light at the centre of the microwave resonant cavity. The quartz used had a high water content in order to absorb a large percentage of the infra-red radiation emitted by the source thus minimising the thermal drift of the microwave frequency by heating.

A constant current power supply was subsequently developed to drive the lamp and complete the system.

4M. E-237 Cavity Design and Function.

The E-237 microwave resonant cavity which was employed in a number of measurements is a large access rectangular cavity resonant in the TE_{102} mode³⁰.

Microwave theory indicates that there is no limitation to the width of a rectangular mode microwave resonant cavity; only its length and height govern the resonant mode and frequency assuming a constant load. Thus by increasing the width of the cavity the size of the access stacks may also be increased. Furthermore, because the surface to volume ratio has increased the Q factor of the cavity has increased to approximately 8,000. However, the disadvantages lie in the fact that there is now appreciable 'bulge' of the microwave field at the stacks and a loss of microwave power up the stacks. However despite these disadvantages it was possible to increase the sample size for high dielectric samples thus increasing the sensitivity of the e.p.r. system by a factor of 1.90 at room temperature for a large number of samples.

There was, however, a decrease in the maximum value of the modulation amplitude and also in the maximum value of the H_1 microwave field attainable at the sample. Nevertheless these factors did not present any limitations to the experiments described in this work.

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