

ELECTRON SPIN RESONANCE STUDIES OF
ORGANOMETALLIC RADICALS.

by
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A Thesis submitted for the degree of Doctor of Philosophy
in the Faculty of Science at the University of Leicester.

June 1974.

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Statement

Except for the work on transition metal carbonyl radicals, which was carried out in conjunction with Dr. S.A.Fieldhouse and Dr. G.W.Neilson, the work described in this thesis was carried out by the author in the Department of Chemistry at the University of Leicester during the period January 1972 - May 1974. This work has not been presented and is not being concurrently presented for any other degree.


B.W.Fullam

June 1974

To my Wife.

ACKNOWLEDGEMENTS

Firstly, I would like to thank Professor M.C.R.Symons for the constant help, guidance and assistance he has given me during the course of these studies.

I would also like to thank Drs. G.W.Neilson and S.A.Fieldhouse for the valuable discussion and practical assistance they gave throughout my stay at Leicester.

I would like to thank all the members of the Physical Chemistry group, who have made my period of research so enjoyable, and in particular Mrs. V.Thompson who has been a constant provider of apparatus and Mrs. S.Kent for her unfailing helpfulness.

ABSTRACT

A brief account of the principles and experimental techniques of electron spin resonance is given in Chapters 1 and 2.

In Chapter 3, the γ -radiolysis of alkyl mercuric halides and dimethyl mercury is discussed. In the spectra of the first group of compounds two radicals were identified, these being $R_2\dot{C}HgX$ and $Et\dot{H}g$ (or $X\dot{H}g$) species. The negative ion $MeHgMe^-$ was trapped in irradiated Me_2Hg , at 77K.

The mechanisms to be found in the solid state radiolysis of trivalent phosphorus compounds are discussed in Chapter 4. The hyperfine couplings for the radicals generated are tabulated and trends in the ^{31}P couplings discussed with respect to the ligand electronegativities. U.v. photolysis of the phosphites $(MeO)_3P$ and $(MeS)_3P$ is shown to produce two phosphorus centred species, identified as $\dot{P}L_2$ and $Me\dot{P}L_2$ radicals. Production of radicals of the type $H_2\dot{C}SP(SMe)_2$ occurred both on photolysis and γ -irradiation. These radicals did not exhibit the large hyperfine coupling to phosphorus found with $H_2\dot{C}CH_2PR_2$ radicals.

In Chapter 5 a range of previously unknown $\dot{P}L_2$ radicals, produced by γ -radiolysis of PL_3 compounds, is considered. The ^{31}P hyperfine couplings for these radicals are remarkably constant when compared to a similar group of nitrogen-centred radicals, this being taken to show a very small degree of spin-delocalisation onto the ligands.

The radiolytic decomposition of a number of organo-silyl compounds is considered in Chapter 6. The trimethylsilyl radical $Me_3\dot{S}i$ is found to behave normally in a range of solvents,

contrary to previously reported results.

Chapter 7 covers firstly the matrix isolation of cobalt and manganese carbonyl peroxo-species, and secondly the u.v. photolysis of transition-metal carbonyls, in the presence of t-butyl peroxide. In this latter section the photolysis of MeCpMn(CO)_4 , $\text{Co(CO)}_3\text{NO}$ and CpV(CO)_4 is discussed. Photolysis of $\text{Mn}_2(\text{CO})_{10}$ in MeTHF is not found to give the $\dot{\text{Mn}}(\text{CO})_5$ radical as reported previously.

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CHAPTER 1

Principles of Electron Spin Resonance.

1.1 Introduction.

There have been many books written on the subject of e.s.r., covering both theoretical and experimental aspects of the subject. With this in mind the following chapter will only give a very brief outline of the basic principles underlying magnetic resonance. A far more detailed coverage can be found in the texts referenced at the end of the chapter.

1.2 Principles.

In 1926, Uhlenbeck and Goudsmit⁹, in explaining a doublet splitting found in some optical spectra, suggested that the electron possesses an intrinsic angular momentum. Quantum theory requires that the magnitude of this angular momentum, or spin as it is more commonly known, for a single electron, is given by $\frac{1}{2}h/2\pi$, where h is Plank's constant. For systems possessing n unpaired electrons the total spin takes the value $S = n/2, n/2 - 1, n/2 - 2, \dots, \frac{1}{2}$ or 0, and the magnitude of the resulting spin vector being given by $S(S + 1).h/2\pi$. It is upon the property of electron spin that e.s.r. spectroscopy is based.

Under normal circumstances electrons in molecules are spin paired such that their spin angular momenta sum to zero. Wherever possible the orbital angular momentum is also reduced to zero by the formation of closed shells of electrons. The possession of an unpaired electron in the outer valence shell is usually a sign of instability, such entities reacting readily in order to gain a second pairing electron. Molecules or fragments possessing such unpaired electrons need therefore to be studied under conditions that increase their stability, i.e. by reducing the temperature. Paramagnetic

transition metal ions, in which the unpaired electron is to be found in an incomplete inner orbital are, in many cases, quite stable, many of the characteristic properties of these species being due to the electrons' presence.

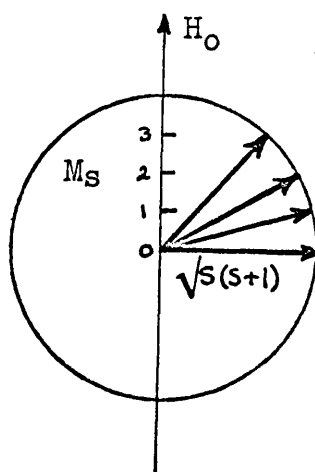
1.3 Interaction of an electron with a magnetic field.

A bar magnet placed in a magnetic field experiences a torque which tends to align it in the direction of the applied field. The electron, by virtue of its spin, exhibits a dipolar magnetic field, similar to a bar magnet, and therefore undergoes similar behaviour when placed in a magnetic field. Classically, the energy of a magnetic dipole of moment μ in a field H_0 is given by

$$E = -\mu \cdot H_0 \cdot \cos \theta \quad (1.1)$$

where θ is the angle between the axis of the dipole and the field direction. Different orientations of the magnet to the field therefore correspond to different energies. The quantum restrictions, previously mentioned, on the magnitude of the spin angular momentum of the electron also restrict the possible orientations with respect to the applied field. Thus, for an atom possessing a total angular momentum of $Sh/2\pi$ assuming all orbital angular momentum is quenched, there are $2S + 1$ possible orientations.

Figure 1.



The further consideration that only the resolved component of the momentum vector along the direction of the field has any physical significance, means that the vector is never aligned exactly along the field direction. Instead, it precesses around the applied field, with θ remaining constant, in a similar manner to the precession of a gyroscope.

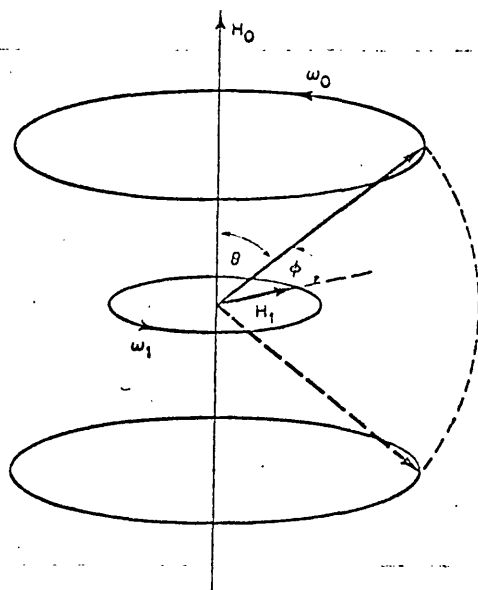
The application of a magnetic field to an electron has the further effect of lifting the degeneracy of the energy levels assigned to the two possible directions of spin. The energy levels are then raised to the values

$$E = E_0 \pm \frac{1}{2}g\beta H_0 \quad (1.2)$$

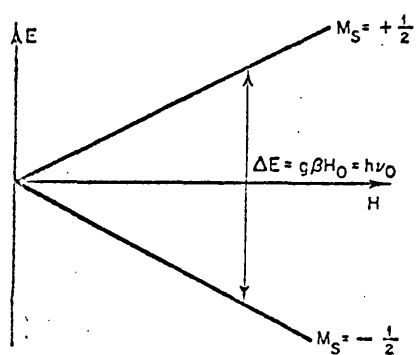
By applying a second field H_1 perpendicular to the plane containing μ and H_0 the electron dipole can be made to experience an additional couple $\mu H_1 \cos \phi$, which leads to a second precession, around H_1 . When the frequencies of precession around both H_0 and H_1 are equal the dipole will undergo a nutatory motion. (Fig. 2) Such a motion corresponds to an energy change in the system and can therefore be considered as a transition between magnetic energy levels. This is the resonance condition.

The field H_1 is the magnetic field associated with the electromagnetic energy which is applied to induce the transition between the two electron spin-energy levels. In the case of e.s.r. the energy requirements are such that the applied radiation is in the microwave region of the electromagnetic spectrum. The difference in energy between the two spin levels as given by (1.2) is

$$\Delta E = g.\beta.H_0 \quad (1.3)$$

Figure 2.

Vector diagram for the precession of a magnetic dipole under the influence of a static magnetic field H_0 and a rotating magnetic field H .

Figure 3.

Zeeman energy levels for a single unpaired electron as a function of magnetic field.

The energy of the applied radiation is directly related to the magnetic field by the equation

$$h\nu = g\beta H_0 \quad (1.4)$$

This is shown diagrammatically in figure 3.

For various, mainly historical, reasons only a limited number of microwave frequencies have been utilised in e.s.r. spectrometers. The two most commonly used frequencies are 9GHz (X-band) and 34GHz (Q-band), the magnetic fields associated with them being 3000 and 12000 gauss respectively. Since it is difficult to accurately vary the microwave frequency over any appreciable range of values, it is usual to use a fixed frequency microwave generator (klystron) and vary the applied field. (Chapter 2).

1.4 Interaction of an electron with its environment.

The g - factor, given in equation 1.4, has been shown to take the value 2.00232 for a non interacting electron. (The small deviation from the classical value of $g = 2$ is due to a relativistic correction.) This free spin value for g is for an electron which possesses only spin angular momentum and is normally a good approximation for most free radicals where the orbital angular momentum is wholly quenched. For paramagnetic ions the magnetic dipole of the electron is tied, to a greater or lesser extent, to that corresponding to the orbital angular momentum. Changes in g , therefore, give a measure of the admixture of orbital momentum with that of the electron spin, though there is no simple correspondance between the two.

The environmental interaction that is of greatest

interest to the chemist is that of the free spin with surrounding nuclei possessing a spin similar to that of the electron. Such nuclei interact with the electron spin-energy levels producing multiple transitions. The extent of these interactions provides information on the structure and electronic distribution of the radical under study.

1.5 General Hamiltonian.

The total interaction of a paramagnetic species can be described by writing the Hamiltonian operator. This it will be recalled is a quantum mechanical operator whose eigen values are the energies of the states of the system. In the absence of a magnetic field the complete hamiltonian operator is given by

$$\mathcal{H} = T + V_c + V_{so} + V_{ss} + V_{si} + V_x \quad (1.5)$$

where T is the total kinetic energy of the electron k of momentum p_k and mass m_0 , and the V -terms are potential energy terms.

V_c is the coulombic term and consists of two parts, one describing the coulombic attraction between nucleus and electrons, the second representing the coulombic repulsion.

The term V_{so} describes the potential energy due to spin-orbit coupling. For most free radicals the assumption is made that this interaction is decoupled, the term then equalling zero.

The fourth term, V_{ss} , represents the magnetic dipole-dipole interaction between electrons. It is normal to sum this interaction over all pairs of electrons.

The fifth term describes the interaction between unpaired electrons and nuclear magnetic moments. This term

which is of primary interest to e.s.r. spectroscopy, consists of two parts, one which is isotropic in nature and depends upon the electron density at the nucleus, and a second which is essentially anisotropic.

The final term, V_x , represents the interaction of paramagnetic species with the crystal field and is essentially electrostatic in nature.

1.6 Spin Hamiltonian.

The general hamiltonian, described above, is very difficult to handle. By applying perturbation theory it is possible to obtain a much simpler expression.

$$\mathcal{H} = \beta S \cdot g \cdot H + S \cdot A \cdot I + S \cdot \Phi \cdot S - g_n \beta_n I \cdot H \quad (1.6)$$

This is the so called "effective spin hamiltonian" or spin hamiltonian for simplicity. In the most complete analysis g , A and Φ are second rank tensors and S is the effective electron spin operator. No attempt will be made here to provide such a detailed analysis, since a qualitative feel for the quantities involved is all that is needed to understand the results of this study.

The first term of the spin hamiltonian effectively combines the spin-orbit coupling and crystal-field terms of the general case. The g -tensor now consists of the free electron g -value and an anisotropic correction due to the spin-orbit coupling. It is therefore possible for the three principle g -values to take differing values, depending upon the symmetry of the radical and its environment, so giving a number of different spectra. (see section 1.8) For a radical tumbling in a solution the g -values average out to a scalar quantity g_{av} .

The second term, $S \cdot A \cdot I$, is the hyperfine term and describes the interaction between the electron and neighbouring nuclear spins. The hyperfine coupling tensor A is made up of two contributions, an isotropic and an anisotropic part. The isotropic interaction was first postulated by Fermi, who showed that it was related to $\psi^2(0)$ the unpaired spin density at the nucleus. Since only s or σ orbitals have $\psi^2(0)$ non-zero this contribution to the hyperfine coupling provides a measure of the s -character of the unpaired spin orbital. The admixture of s -character in the unpaired spin orbital can be calculated using the equation

$$a = A_0 \cdot c_{ns}^2 \quad (1.7)$$

where a is the experimental isotropic hyperfine coupling, A_0 is the calculated isotropic coupling assuming the unpaired electron is wholly in the ns -orbital, and c_{ns}^2 is the coefficient of ψ_{ns} in the wavefunction for the atom or molecule. It has been suggested that inner-orbital polarisation¹⁰ can also contribute to the isotropic coupling, since the unpaired electron, by attracting one electron in an inner s -orbital and repelling the other, will cause a change in $\psi^2(0)$. The error produced by neglecting this effect, which is difficult to quantify, is normally small enough not to invalidate calculations on free radicals, but must be taken into account in studies of transition metal ions.

The anisotropic term contributing to A is a classical dipole-dipole interaction. In liquid-phase spectra this averages to zero.

For the study of free radicals, the last two terms of the spin hamiltonian can be neglected, the third term

containing a contribution from spin-orbit coupling and spin-spin interaction and the fourth term describing the interaction of magnetic nuclei and the applied field.

1.7 Spin - Polarisation.

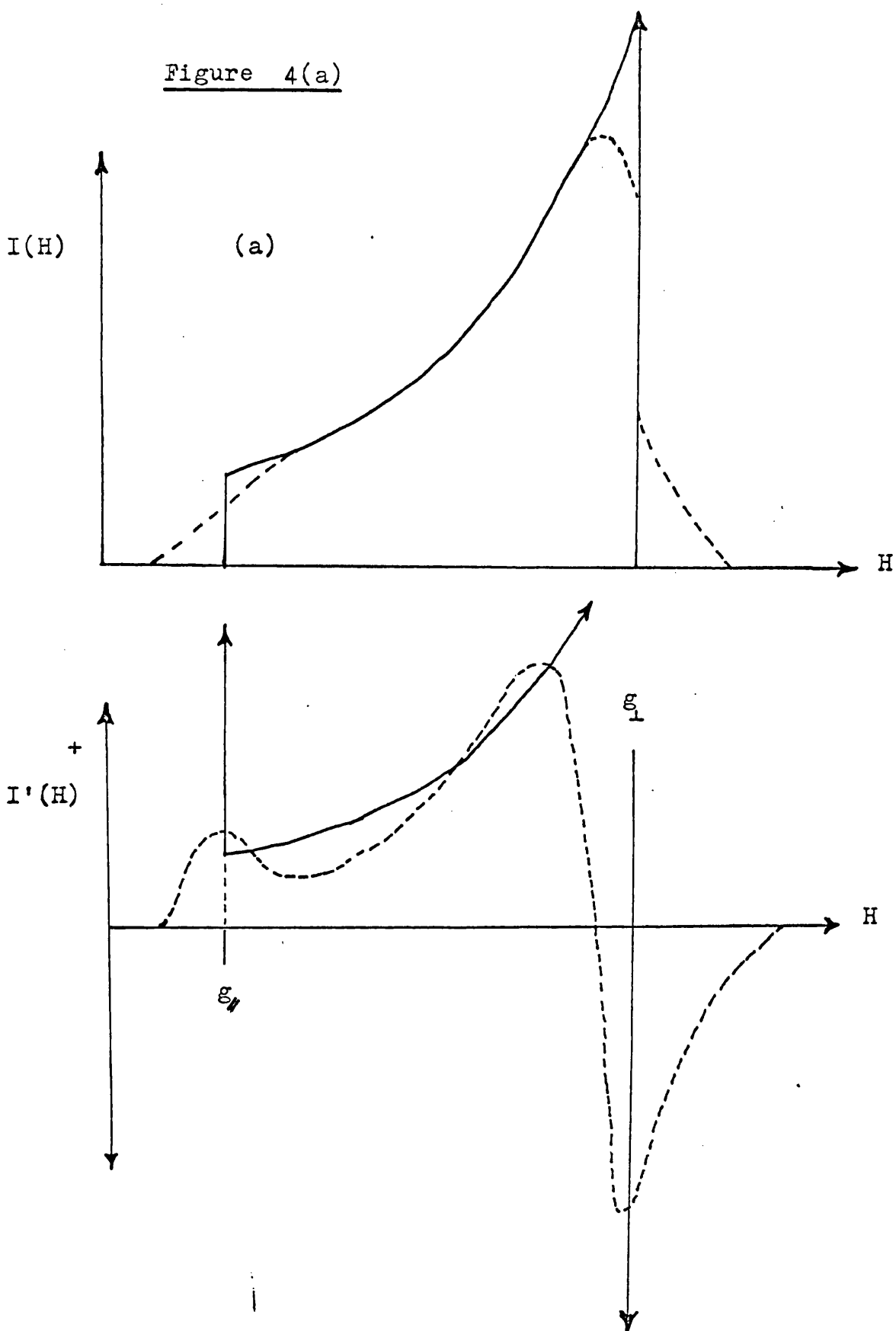
Isotropic hyperfine coupling can also occur when the unpaired electron is in a p-orbital, which has a node at the nucleus, and cannot therefore interact directly via the Fermi contact interaction. The simplest example of this is the methyl radical which, even though the free spin is in a $2p_z$ -orbital, shows a quartet of lines due to the three protons, and when ^{13}C enriched a coupling to the carbon atom. This interaction occurs because in the presence of the unpaired electron, the electrons in the C-H σ -bonds become slightly spin-decoupled, leading to a negative spin-density at the protons, and a positive one at the carbon. (For further details see chapter 4.)

Spin-polarisation reduces in intensity very quickly the further from the unpaired electron the atom under consideration is, yet coupling to β -protons has been found to be greater than that due to α -coupling. This β -coupling has been attributed to a hyperconjugative mechanism, which occurs by a direct overlap of the unpaired electron orbital and the sp^3 hybrid orbital of the β C-H bond. The magnitude of this interaction is dependant upon the dihedral angle between the C-H bond and the p_z -orbital. (see chapter 4)

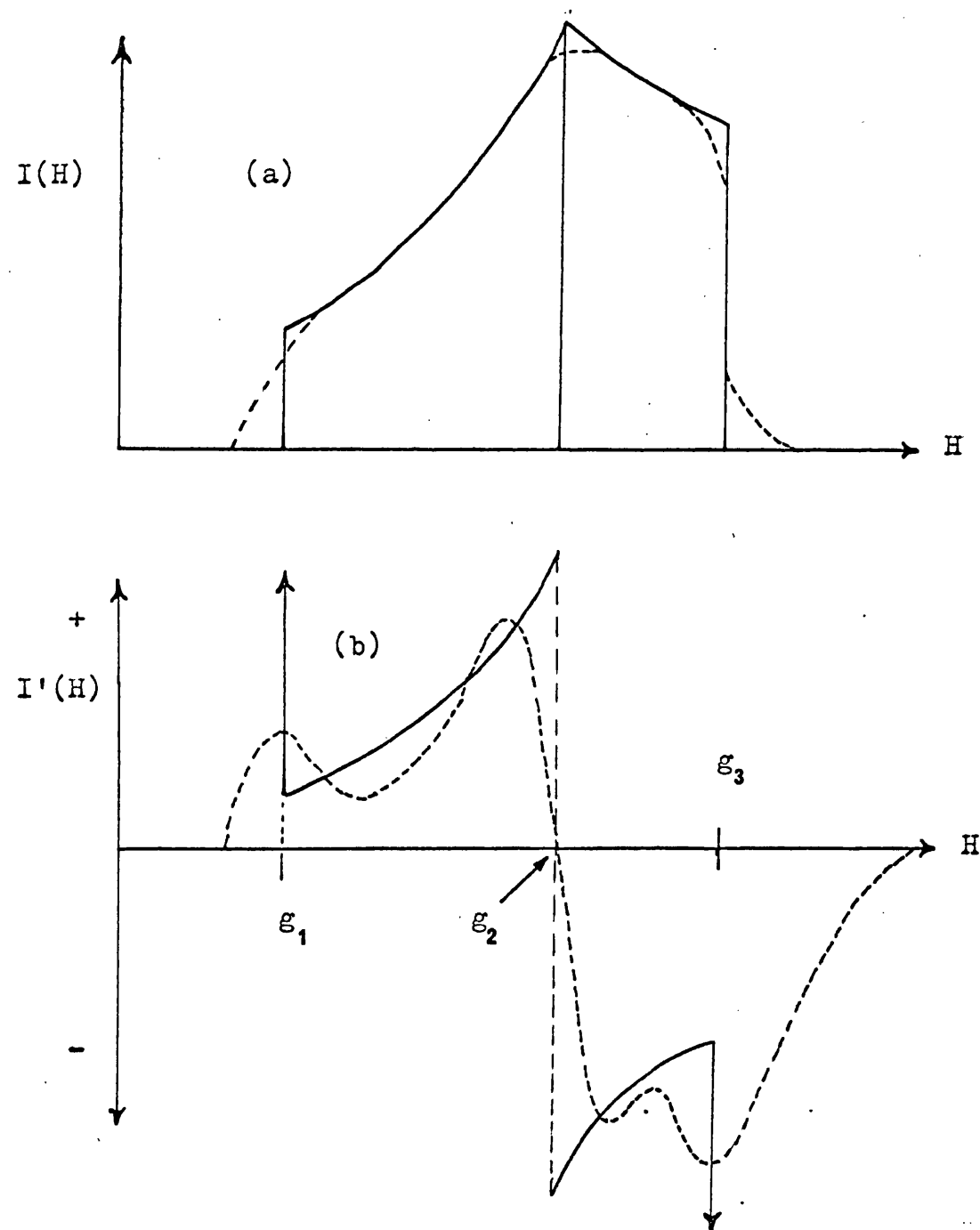
1.8 Spectra Interpretation.

Single crystal studies of solid-state radicals provide the largest amount of information for any given system, but are at best tedious and in many cases difficult to carry out.

Because of this, it is usual to use glassy or polycrystalline matrices wherever possible, using single crystal studies only when necessary. Within such matrices the radicals will be randomly orientated, such that only the overall absorption envelope is seen. Theoretical studies of such line shapes have shown that much valuable information can be obtained from radicals in amorphous matrices, especially where identification of the radicals present rather than a complete analysis of their structure, is of primary importance. The figures given below are examples of the different spectral shapes seen in powders and glasses, with the associated g and A assignments.

Figure 4(a)

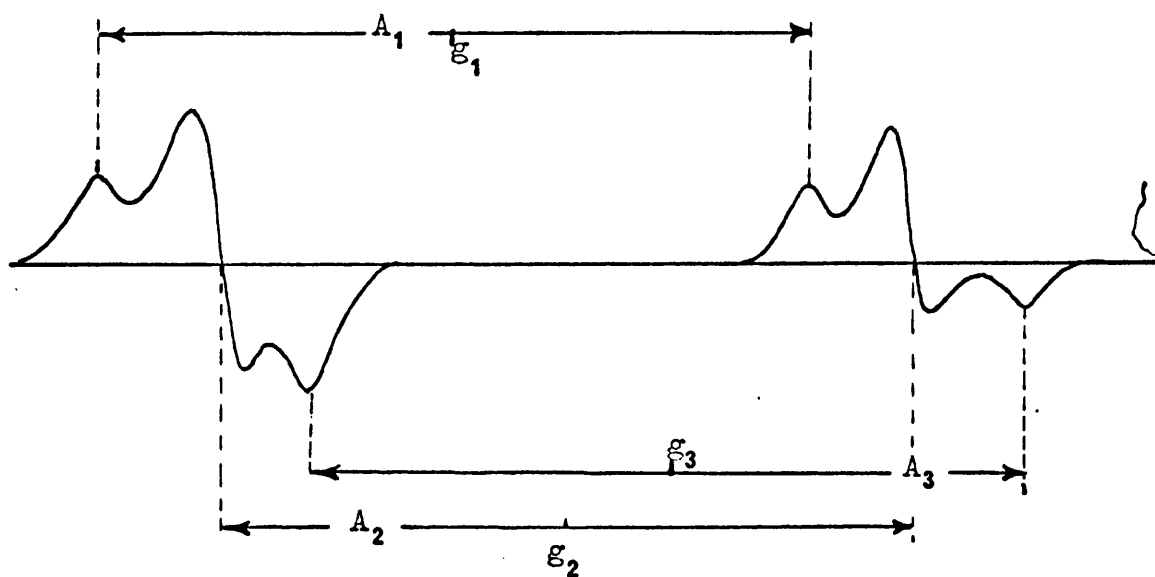
The absorption (a) and first derivative curve (b) for a radical with a g -tensor that is axially symmetric.

Figure 4(b).

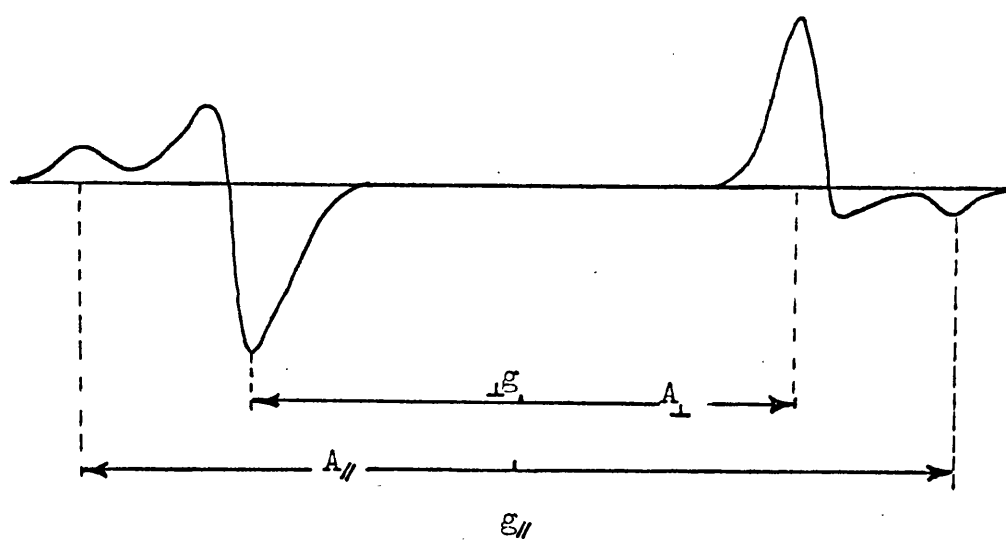
The absorption (a) and first derivative curve (b) for a radical with a g -tensor that is anisotropic

Figure 4(c).

(a)



(b)



Typical powder spectra for radicals with one spin- $\frac{1}{2}$ nucleus.

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CHAPTER 2

Experimental Techniques.

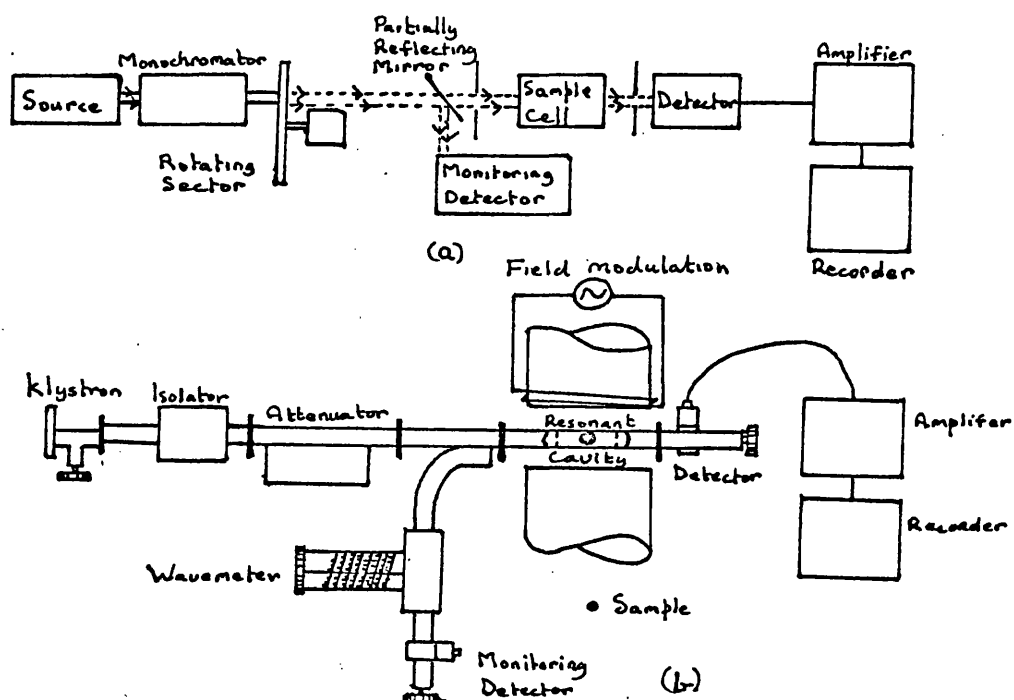
2.1 Introduction.

All reasonably comprehensive texts¹⁻⁵ on e.s.r. contain some information on instrumentation and experimental methods, and a few specialized works^{6,7} are available that provide a very full description of the components of a spectrometer. With this in mind the following description of instrumentation will be very brief.

2.2 Instrumentation.

The general function of the components of an e.s.r. spectrometer are directly comparable to those of an optical absorption spectrometer.

Figure 1.



(a) Block diagram of an optical spectrometer (b) Block diagram of an analogous e.s.r. microwave spectrometer.

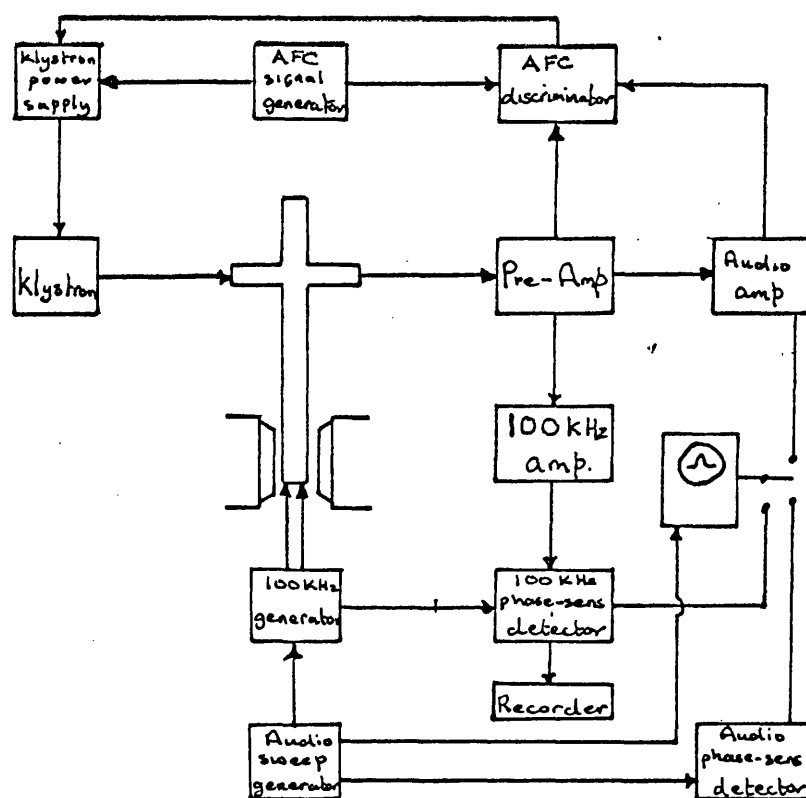
The klystron energy source provides electromagnetic radiation over only a small range of frequencies so no monochromator is necessary. The radiation is guided to the sample through rectangular metal tubing (waveguide) whose dimensions are related to the wavelength of radiation used. The structure of the sample cell is more complex than that required for an

optical spectrometer since, in order to increase the energy available to the sample, a resonance cavity is used. Absorption of energy by the sample is detected by a silicon diode.

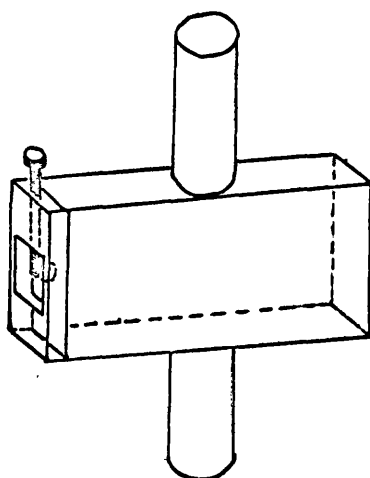
The spectrometer shown in figure 1 suffers from a number of defects, all of which reduce the sensitivity and resolution to a point where such a machine is of no practical use. Modern commercial spectrometers are considerably more sophisticated, a generalised line diagram for one being given in figure 2.

The Klystron, whilst providing effectively mono - chromatic radiation, must do so for considerable periods of time. It is therefore usual to employ some sort of frequency locking device, enabling the klystron to be locked to the resonance frequency of the cavity. Of the wide range of klystron frequencies available, for mainly historical reasons, only a small number are in general use. X-band (9GHz) is probably the most commonly used frequency for e.s.r. spectrometers though the advent of commercial K (23GHz) and Q-band (34GHz) machines is slowly changing this. Both the higher frequency machines suffer from disadvantages with sample handling.

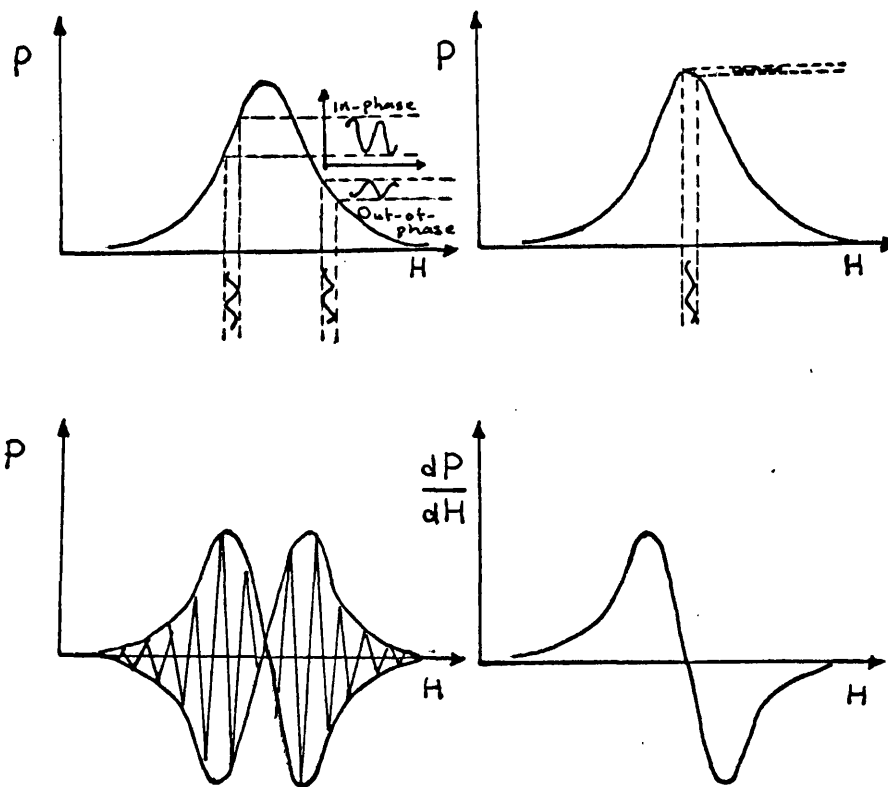
The microwaves, guided down metal tubing, are made to form a standing-wave pattern in the sample cavity. By using such a cavity the small energy density associated with a travelling wave can be stored and considerably increased at the point of sample insertion (Fig. 3). The construction of the cavity both establishes the spectrometer frequency and contributes substantially to the sensitivity, so care of the cavity is of paramount importance. Cavity body construction is usually of brass, though a large number of other materials have been used. By thinly coating the inside of the cavity

Figure 2.

Block diagram of a typical X-band ESR spectrometer employing 100-KHz phase-sensitive detection.

Figure 3.

A rectangular parallelepiped TE microwave cavity. Cylindrical extensions above and below the cavity prevent excessive leakage of microwave radiation and act as positioning guides for a sample.

Figure 4.

Phase-sensitive detection.

with a metal of low resistance (e.g. copper, silver, gold) dissipative power losses are considerably reduced so increasing the overall sensitivity of the machine.

Since the microwave frequency is effectively fixed, the magnetic field must be variable over a considerable range of field values. It must also be stable to within at least 0.1G and uniform over the whole area of the cavity. This is achieved by using a highly regulated power supply system and a feedback loop to detect and correct any field instabilities.

Detection of the reflected microwave radiation from the cavity is greatly enhanced by the use of field modulation. This involves the superposition of a small sinusoidal magnetic field upon the applied field such that the rectified signal at the detector is amplitude modulated. The improvement in sensitivity brought about by this modulation occurs by the operation of a number of different processes. By using a radio-frequency modulation, commonly 100KHz, the inherent noise of the silicon crystal detector is reduced below that of other components. Phase sensitive detection of the modulated signal permits better signal-to-noise discrimination through the reduction of the noise contributing component to frequencies close to the modulation frequency. Finally, phase sensitive detection provides, as an output, not the absorption signal but its first derivative (Fig. 4) thereby improving the detection of very broad signals and the resolution of absorptions very close together.

Both spectrometers used in this study, the Varian E-3 and V4502/03, were X-band instruments using 100KHz field modulation.

2.3 Sample Preparation.

Beads. - Samples that were reasonably stable liquids or solutions could be most readily irradiated as small frozen beads. The bead making process involved dropping liquid from a pasteur pipette into an insulated petri dish of liquid nitrogen. The beads, so formed, were transferred, using small plastic tweezers, to screw-top glass sample bottles cooled in liquid nitrogen. For irradiation, these bottles were lowered into the irradiation dewars attached to short pieces of wire.

Sealed tubes. - Sealed silica tubes were used to handle samples that readily decomposed when in contact with air or moisture. The tubes (4m.m. O.D.), closed at one end, were attached to the vacuum line by a B19 quickfit socket, for evacuation and sealing. Samples in tubes, having been cooled to 77K, were evacuated, degassed using repeated freeze-pump-thaw cycles, and then sealed under vacuum ($< 10^{-3}$ torr).

Chlorosilanes. - All of the chlorosilanes readily undergo hydrolysis, necessitating the use of sealed samples. The silanes were stored in a nitrogen filled dry-box and when needed, small quantities were transferred to stoppered 50ml round-bottomed flasks, frozen, and removed to the vacuum line. Here they were degassed and vacuum distilled into the sample tubes. When required, solvents were added at this stage. The sample tubes, sealed under vacuum ($< 10^{-3}$ torr), were transferred to the irradiation dewar and irradiated at 77K.

Phosphorus compounds. - Most of the compounds studied reacted, to a greater or lesser extent, with oxygen. This meant handling the samples either in a nitrogen atmosphere or on the vacuum line. Since most of these compounds did not readily distil under vacuum the samples were transferred to

stoppered sample tubes in a nitrogen filled dry box or bag, frozen and removed to the vacuum line. Except for the samples photolysed at 77K, all were then degassed and sealed.

Whilst it was possible to make beads of some of the samples within the dry box, it was found to be more convenient to handle the samples in sealed tubes. This had the added advantage of minimising the extremely obnoxious smell of these compounds.

Powders. - These were finely ground, using an agate mortar and pestle, before being transferred to screw-topped sample bottles for irradiation.

2.4 γ -Source.

Samples were irradiated, either at room temperature or 77K, in a top loading Vickrad ^{60}Co γ -source (dose rate $\sim 3\text{M rad h}^{-1}$). For low temperature irradiation samples were transferred, in small glass bottles or sealed tubes, to a metal cased glass dewar containing liquid nitrogen. This was lowered into the source for the required period of irradiation. γ -irradiation of sealed silica tubes was found to induce an e.s.r. signal in the silica which could be partially photo-bleached using a tungsten-filament light source.

After irradiation samples were transferred to a storage dewar containing liquid nitrogen, and when needed for study removed to the finger dewar or variable temperature unit.

2.5 Sample Handling in the Microwave Cavity.

Beads, powders or sealed tubes that were to be studied at 77K were transferred to an unsilvered dewar that narrowed at the bottom to form a long finger, which fitted into the cavity. This finger portion was constructed of fused silica, the upper portion being made of borosilicate glass.

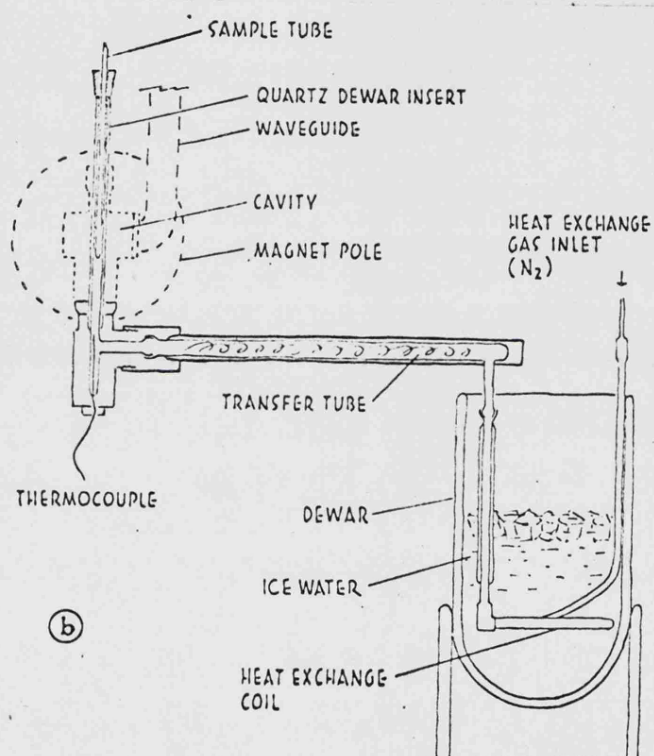
Two methods were available for annealing samples so as to cause a preferential loss of some radicals. The first consisted of pouring the liquid nitrogen from the finger dewar, replacing it into the cavity, and scanning through the spectrum whilst the sample warmed. This had the advantage of permitting the anneal to be controlled to a certain extent, the sample being refrozen at the required point. The second method involved removing the sample, usually beads or a tube, from the finger dewar and permitting it to warm for a fixed period of time before quenching in liquid nitrogen again. This process could only be followed when the progress and time of anneal were already known by the prior use of method 1.

The variable-temperature unit, in which the sample temperature could be controlled accurately between 77 and 270K, was used specifically when controlled annealing was needed. It consists of a vacuum-jacketed tube, which passes through the cavity (Fig. 4), and has in the bottom half a platinum resistance thermometer and heating coil. Gaseous nitrogen, cooled by passage through a heat exchanger immersed in liquid nitrogen, is heated to the required temperature by the heating coil and passed through the tube. The flow of nitrogen gas through the unit was adjusted until the temperature, indicated on the control unit, was reached. This variable-temperature unit was also used for "in situ" photolysis experiments since the tubular portion was made of fused silica.

2.6 Sublimation Apparatus.

The apparatus, used in the sublimation experiments of the first half of Chapter 6, was essentially that described by Keller et al^{8,9} (Fig. 5). The major part of the unit consisted of a finger dewar which could be evacuated, and to the bottom

Figure 4(b).



Variable-temperature unit for controlling the sample temperature between 77 and 270K.

of which could be attached the samples under study. The sublimation surface, centred in the cavity, was cooled by filling the dewar with liquid nitrogen.

Samples of metal carbonyl, cooled in liquid nitrogen, were transferred to the apparatus in 50ml round-bottomed flasks and evacuated for varying periods of time. (5 minutes to 2 hours) After evacuation the samples were warmed slowly to room temperature, the amount of sublimation being controlled by tap T_1 .

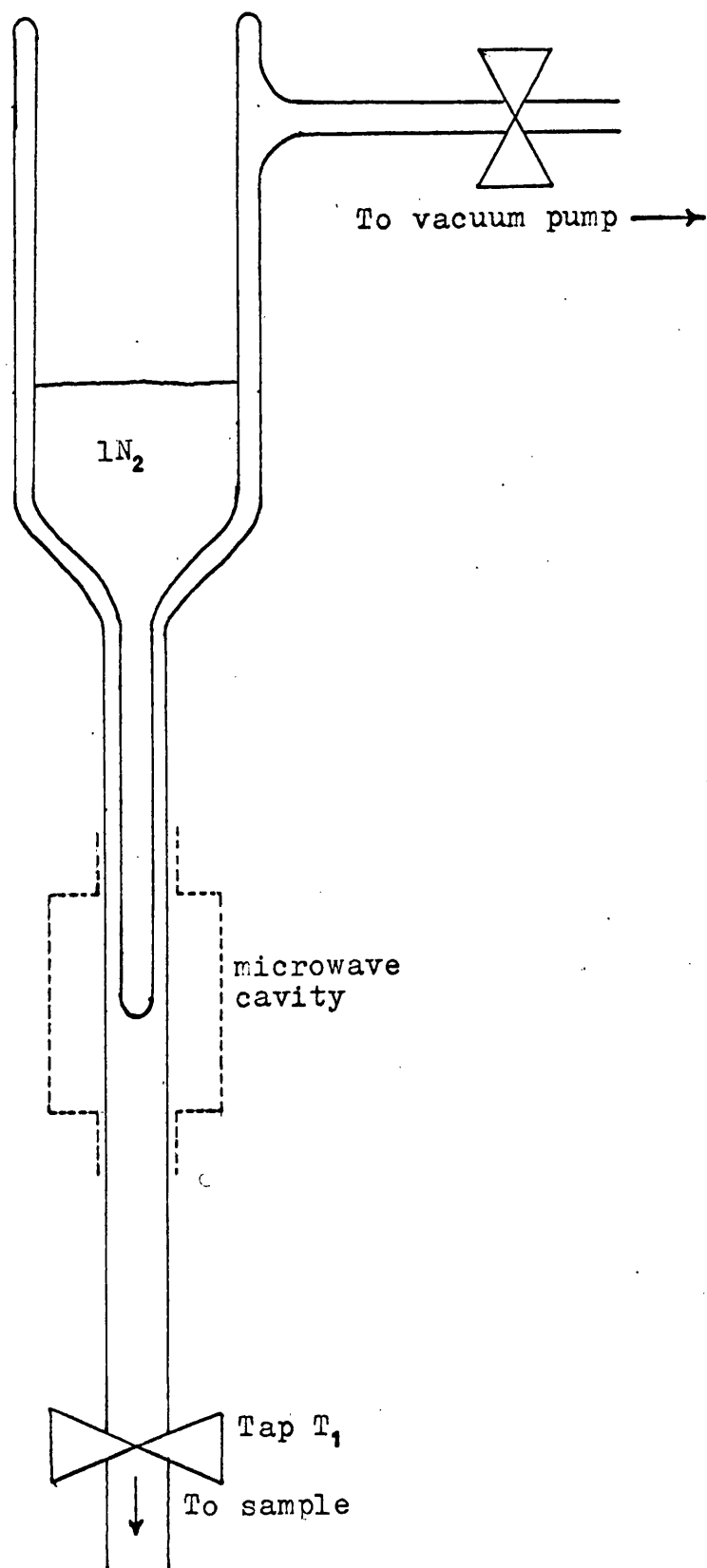
2.7 Photolysis Experiments.

Sample to be photolysed were sealed, under vacuum, in silica tubes, either alone or in a suitable solvent, with t-butyl peroxide. Unless the samples were solids or high boiling point liquids, all were vacuum distilled into a quantity of degassed peroxide, in the sample tube. The solvent was introduced last. Where the substance under study was a liquid the proportion of compound to peroxide to solvent in the solution was 1:1:10.

Photolysis at 77K took place in a large finger dewar, the finger portion of which was composed of fused silica. Samples to be photolysed at varying temperatures were transferred to the v.t.-unit in the cavity of the spectrometer. For "in situ" photolysis, a Wooten 200W super-high-pressure mercury lamp, in a Bosche and Lombe 250W lamp housing, was used, the light being focussed into the cavity with a four inch silica lens. A 2KW Xenon lamp (Carl Zeiss, Jena) was used for both in situ and external photolysis. A Rayonet model RPR-100 photochemical reactor was also used for both room temperature and liquid nitrogen photolysis, using lamps of fixed wavelength output.

Figure 5.

Sublimation Apparatus.



2.8 Preparation of Trimethyl and Tri-n-propyl thiophosphite.

The method, as published by C. Wu¹⁰, was used for the preparation of both compounds. The preparation of trimethyl thiophosphite only will be detailed here.

Dimethyl disulphide (9.4g) was added to powdered white phosphorus (6.4g) in a 100ml round-bottomed flask, which was flushed continuously with nitrogen. Acetone (50ml) and 2-3 drops of 15N KOH solution were added and the reactants stirred at room temperature until all of the phosphorus had disappeared.

At the end of the reaction the acetone was distilled off and the resulting thiophosphite transferred, in a nitrogen filled dry bag, to a storage flask. Further purification of the thiophosphite was not needed since ³¹P n.m.r. spectra showed the presence of only one phosphorus compound. The white phosphorus used in the reaction was powdered by cryogenic grinding.

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CHAPTER 3

Alkyl Mercury Compounds.

3.1. Introduction.

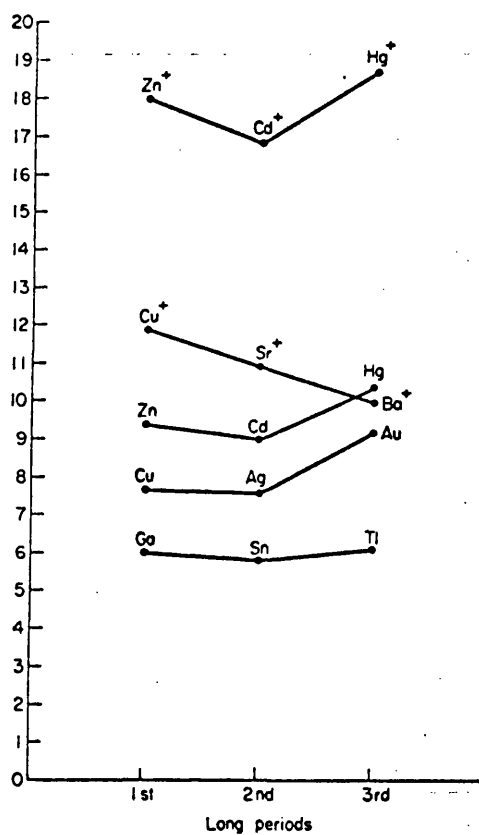
Mercury metal has probably been known since the bronze age, the extraction process being so simple. It was certainly known to the Romans and its compounds have had medicinal uses through until the present day. A combination of its apparently unusual state of being a liquid at room temperature, and its medicinal properties has produced a considerable body of work on the element and its compounds.

The work in this chapter considers the behaviour of organo - mercury compounds when subjected to γ - radiation and the free radicals so produced. The mercury atom has the electronic ground state (Xe Core) $4f^{14} 5d^{10} 6s^2$ and as such can be compared with Barium (Xe Core) $6s^2$ and the other two Group IIB elements Zinc and Cadmium, whose electronic ground states are (Ar Core) $3d^{10} 4s^2$ and (Kr Core) $4d^{10} 5s^2$ respectively. In contrast to the IIA elements, whose Ionisation Potentials show a steady decrease from Calcium to Strontium, the Group IIB elements show a minimum at Cadmium, and in general, have higher values to the A subgroup. Figure 1 gives the Ionisation Potentials of the Group IB, IIA and IIB elements¹, Table 1 the Ionisation Potentials of the IIB metals.

Table 1

Ionisation Potentials and Valence State Promotion Energies of Group IIB metals.

	<u>Zn</u>	<u>Cd</u>	<u>Hg</u>
I.P. of $M \rightarrow M^+$ (ev)	9.4	9.0	10.4
I.P. of $M^+ \rightarrow M^{++}$ (ev)	18.0	16.9	18.7
$ns^2 \rightarrow ns^{11}$ (Kcal)	103.2	97.4	125.3

Figure 1.

Ionization potentials of Group IB, IIA, and IIB elements.

(C.E.Moore, Atomic Energy Levels, N.B.S., Washington, 1958).

Mercury, because of its much higher Atomic Number and the lower "shielding" effect of the 4f and 5d electrons on the two outer 6s - electrons, has a considerably higher ionisation potential than Barium, the first ionisation potential of Mercury being greater than the second ionisation potential of Barium.

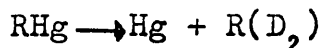
Table 1 also gives the Valence State Promotion Energies for Zinc, Cadmium and Mercury, the most noticeable feature being the promotion energy of Mercury. The effect of this is that Mercury readily forms two covalent bonds, using sp^1 hybrid orbitals, and will only accept further ligands with great reluctance.

3.2. Bond Energies of Mercury Halides and Alkyls.

The bond dissociation energies of the Dialkyl mercury and Alkyl mercuric halides show for the reaction



normal behaviour. It is only when the second dissociation reaction



is considered that apparent anomolous behaviour is seen.

(See Table 2)

Table 2

Bond Dissociation Energies for Some Dialkyl Mercury and Alkyl Mercuric Halide Compounds.²

<u>Compound</u>	<u>$D_1 + D_2$</u>	<u>D_1</u>	<u>D_2 (K cals)</u>
$(CH_3)_2 Hg$	58.4	51.5	6.9
$(C_2H_5)_2 Hg$	48.4	42.5	5.9
$HgCl_2$	106	81	24
$HgBr_2$	89	72	17

Table 2 (cont.)

<u>Compound</u>	<u>D₁ + D₂</u>	<u>D₁</u>	<u>D₂ (K cal/s)</u>
CH ₃ HgCl	88	64.3	24.0
CH ₃ HgBr	78.8	61.8	17.0
CH ₃ HgI	69.0	59.0	8.0
C ₂ H ₅ HgCl	84.3	60.3	24.0

As can be seen, there is a considerable difference between D_1 , the first dissociation energy, and D_2 , the second. The reason for this becomes clear on considering the valence state promotion energies³ previously mentioned. In forming the first bond $R - Hg$ it is necessary to promote one of the 6s electrons into a 6p orbital, such that the energy evolved on forming the bond only just cancels out the energy required for this process. The second bond is formed without much further reorganisation of the Mercury orbitals. This effect is also to be found with Zinc and Cadmium compounds, though not to such a great extent.

Numerous studies have been made on the structure of compounds of the type $R - Hg - R$, where R is either Alkyl or Aryl, and $R - Hg - X$, where X is a halide group. These studies indicate that the basic skeleton is linear, and include electron diffraction work on Dimethyl mercury⁴, X-ray studies of Diphenyl⁵ and di-p-tolyl⁶ mercury, X-ray and neutron diffraction studies of Methyl mercuric cyanide⁷, microwave⁸ and vibrational spectra of the methyl mercuric halides and vibrational-rotational studies of the alkyl mercuric halides in the solid and gaseous states.

The only studies that question the linearity of the $X-Hg-X$ skeleton, are those where the dipole moments have been

measured. Such measurements on the diaryl derivatives give a small , non - zero result which indicates some deviation from the linear structure. It is thought that these results are an indication of the easy deformability of the CHgC angle.

Vibrational spectra confirm that low-lying bending modes are easily excited.¹²

3.3 Dialkyl Mercury Compounds.

The Dialkyl mercury compounds are mostly monomeric, volatile liquids. Their stability varies considerably, but as a general rule it decreases with increases in the alkyl chain length. Dimethyl mercury is the most stable, undergoing no perceptible decomposition at room temperature. Diallyl mercury is one of the more unstable compounds, decomposing readily to Diallyl and Mercury. All of these compounds are susceptible to photodecomposition and as such should be stored in the dark. All of the Dialkyl compounds are extremely toxic, and should therefore be handled with the utmost care.

Infra-red and Raman studies¹³ of Dimethyl Mercury have shown that the methyls are freely rotating, pure rotational Raman spectra having been used to give accurate bond lengths of the methyl derivatives of Zinc, Cadmium, and Mercury.¹⁴

Table 3.

Zn -C, $1.929 \pm 0.004\text{\AA}$

Cd -C, $2.112 \pm 0.004\text{\AA}$

Hg -C, $2.094 \pm 0.005\text{\AA}$

The value measured for Dimethyl Mercury is only 0.02 - 0.03A greater than those of Methyl Mercuric Chloride and Bromide.

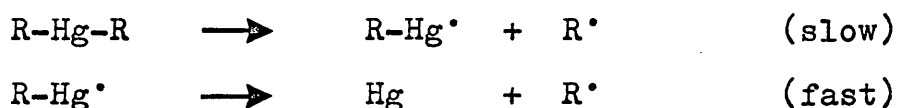
The alkyl derivatives of Mercury are frequently

used as free radical sources, the use of dimethyl mercury being especially common, since it is not readily attacked by water or oxygen but is easily split into methyl radicals and mercury, a relatively innocuous pollutant.

3.4. Dimethyl Mercury.

The photolysis and thermal decomposition of dimethyl mercury has been thoroughly studied,¹⁵⁻³⁰ the majority of studies being concerned with the gas - phase kinetics of the decomposition.

The thermal breakdown of the alkyl and aryl compounds has been found to fall into two main categories. In the first, the activation energy of the primary step is equal to D_1 , the energy required to detach an alkyl radical $R^\cdot$ from the parent compound. This leads to a two step decomposition



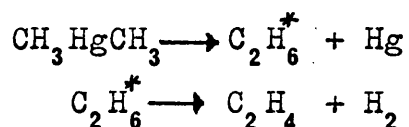
and is undergone by dimethyl mercury, diethyl mercury, and some of the alkyl halides.

The second class of decomposition takes place via a one step process



and in this the activation energy equals $(D_1 + D_2)$. Belonging to class II are di-n-propyl and di-isopropyl mercury, dibutyl mercury and diphenyl mercury.

The γ -radiolysis of solid and liquid dimethyl mercury has been extensively studied by Wolf and Walker,²⁹ the yields of the major products, CH_4 , Hg , C_2H_6 and $\text{CH}_3\text{HgC}_2\text{H}_5$ and the minor products H_2 , C_2H_4 , C_3H_8 and C_3H_6 , varying considerably both between the liquid and solid phases and the different temperatures studied (- 196 and - 78°C as a solid, - 21, 0 and 28°C as a liquid). In the liquid phase the presence of a radical scavenger such as oxygen was found to considerably reduce the yield of methane and ethyl mercury. This would point to these two products being formed by diffusion-controlled free radical reactions. The other product yields, that are not affected to anywhere near the same extent, are probably produced by one of two categories of reaction. Either straight forward molecular reactions or by radical recombination reactions within a radiolysis spur, prior to the onset of diffusion. An example of the sort of molecular reaction postulated is that needed to explain the production of both ethylene and hydrogen using a non-radical mechanism.



This mechanism is consistent with the finding that the yields of the ethylene and hydrogen are independent of temperature, radiolysis phase and the presence of oxygen. Most of the radical reactions postulated follow upon the reaction involving the scission of a Me-Hg bond or a C-H bond forming $\cdot\text{HgMe} + \text{Me}\cdot$ and $\cdot\text{CH}_2\text{HgMe} + \text{H}\cdot$ respectively. Little was said about the reaction mechanisms to be found in the solid at - 196°C, though it was noted that the production of ethane probably occurred via a radical recombination reaction within a

radiation spur.

3.5. Alkyl Mercuric Halides.

Both the alkyl and the aryl compounds are crystalline solids, ethyl mercuric halide forming silvery iridescent leaf-like crystals from hot alcohol. Many of the alkyl mercuric halides are sufficiently volatile to sublime under reduced pressure, though the vapour pressures have been found³⁰ not to depend greatly on the halogen, e.g. at 0°C, the vapour pressure of MeHgCl is 0.0040 mm., -Br, 0.0048mm., -I, 0.0049mm. The bond lengths of the methyl halides have been measured by microwave spectroscopy⁸

Me - Hg - Cl

2.061 2.282Å

Me - Hg - Br

2.074 2.406Å

the C - Hg bond lengthening with the decrease in the electronegativity of the halide.

The properties of these compounds depend strongly on the covalent character of the Hg - X bond. If X is highly electronegative, e.g. F⁻, NO₃⁻, SO₄⁼, then the compounds behave as salts and are more soluble in water than organic solvents. The Hg - X bond for Cl, Br and I, is virtually wholly covalent in character as is shown by the non-solubility of these compounds in water. The alkyl mercuric halides are known to dissociate in liquid ammonia -33°C.³¹ Electrolysis of the resulting solution forms an intriguing "organic metal" at the cathode.³² This probably consists of a metallic lattice of R.Hg⁺ ions, together with the equivalent number of free electrons.

3.6 E.S.R. Studies of Mercury Centred Radicals.

Previous electron spin resonance studies of γ irradiated mercury compounds³³⁻³⁶ have involved the use of mercurous or mercuric salts in mainly aqueous acidic media. Mercuric salts were found to give the electron capture product Hg^+ and HgH^{2+} ions in fairly high yield, dimeric mercury radical ions being identified in the spectra of mercurous salts. Mixed solutions of silver and mercury (II) salts gave the ion AgHg^{2+} ³⁷. The only mercury centred radicals with organic ligands that were identified in this series of studies were those originating in aqueous ethanol solution. These alkoxides HgOR^{2+} (see table 4) are probably formed by reaction with RO radicals .



The results in Table 4 show that mercury centred radicals can be characterised by the presence of high field lines in the (4-6000 G) region. These lines are due to the two isotopes of mercury having a nuclear spin ^{199}Hg ($I=\frac{1}{2}$) and ^{201}Hg ($I = \frac{3}{2}$). The presence of these lines, and the resulting very large hyperfine coupling constants, is due to the unpaired electron being centred on the mercury atom in an orbital with a high s character. Hg^+ should have, in a non perturbing environment, 100% s character. Isoya and Fujiwara³⁸ have identified Hg^+ ions in irradiated potassium tetra - cyanomercurate $\text{K}_2(\text{Hg}(\text{CN})_4)$, the K - band spectrum showing the complete number of lines due to ^{199}Hg and ^{201}Hg .

The radicals HgH and HgCN have been isolated in inert gas matrices by Knight et al^{39,40}, the other group IIB analogues CdH , ZnH also being studied. The bonding in the

hydrides shows an increase in the $p\sigma$ character between CdH and HgH as is typical of mercury chemistry, whilst the cyanide is mainly ionic in character with an $A_{1so}(Hg)$ value approaching that of Hg^+ .

3.7 Experimental.

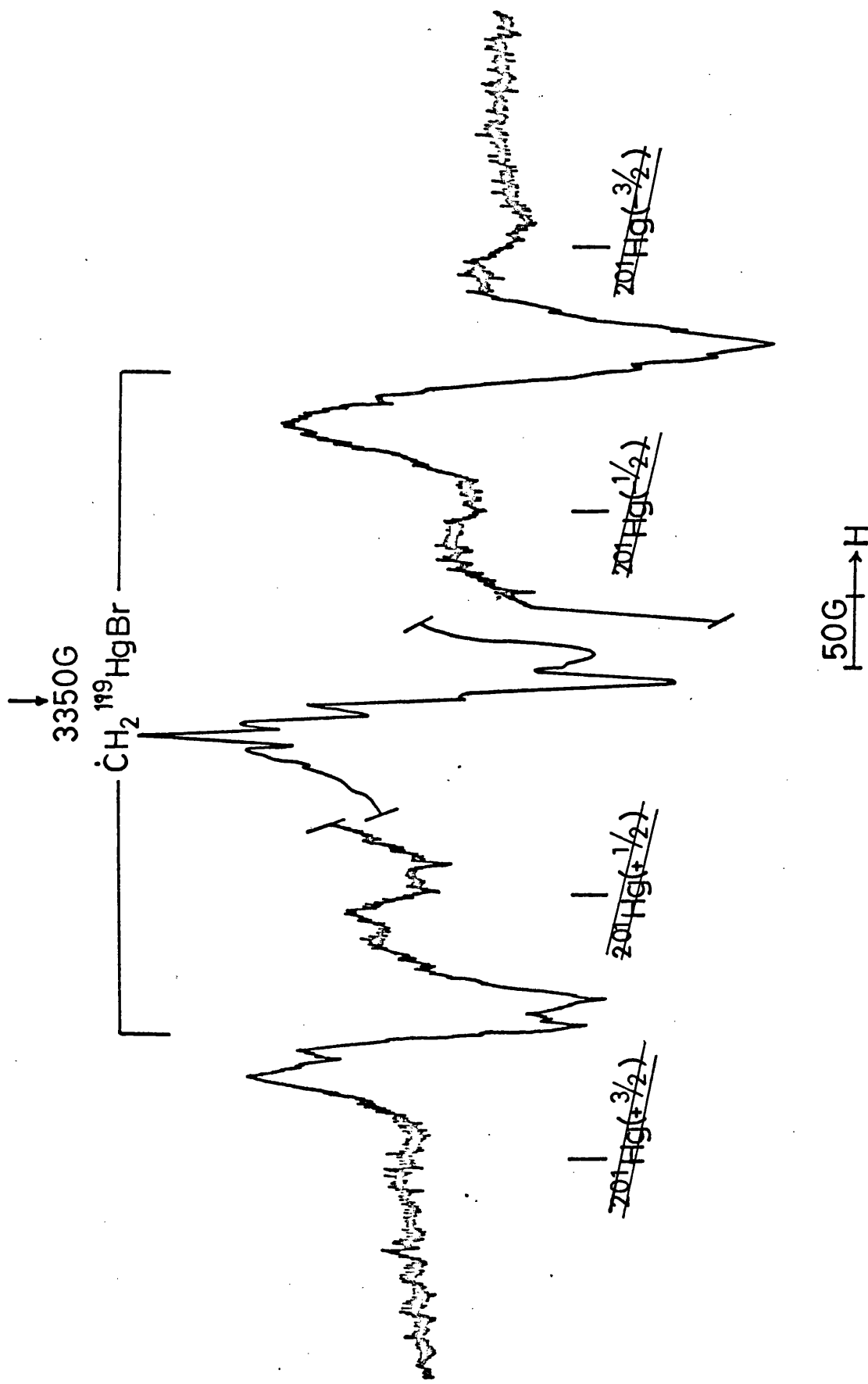
In handling any of the alkyl mercury compounds it is important to bear in mind their extreme toxicity, the alkylated heavy metals being especially easily metabolised. The ethyl mercuric chloride, methyl mercuric bromide and iodide, (Alfa Inorganics), were irradiated at 77 K in small screw - top bottles immersed in a Dewar of liquid nitrogen. These compounds were studied without further purification after it was found that the chloride showed no difference in its spectrum after recrystallisation from hot ethanol. Due to its high volatility and extremely high toxicity, the dimethyl mercury (Pfaltz and Bauer) was handled on a vacuum line where, after thorough degassing by repeated freeze - pump - thaw cycles, it was sealed, under vacuum, into silica tubes. Ethyl mercuric acetate, a less volatile liquid, was frozen to small glassy beads, by dropping into liquid nitrogen. (See Chapter 2), before being placed into small screw top bottles. All samples were irradiated at 77 K in a Vickrad Co source and received doses of ca 3 Mrad h^{-1} for up to 6 hours. The E.S.R. spectra were measured on Varian E3 and V4502/03 X - band spectrometers with a 100KHz field modulation.

3.8 Results.

Typical E.S.R. spectra of irradiated methyl mercuric bromide and iodide, dimethyl mercury and ethyl mercuric chloride are given in Fig.2 for the $g = 2$ region, together with

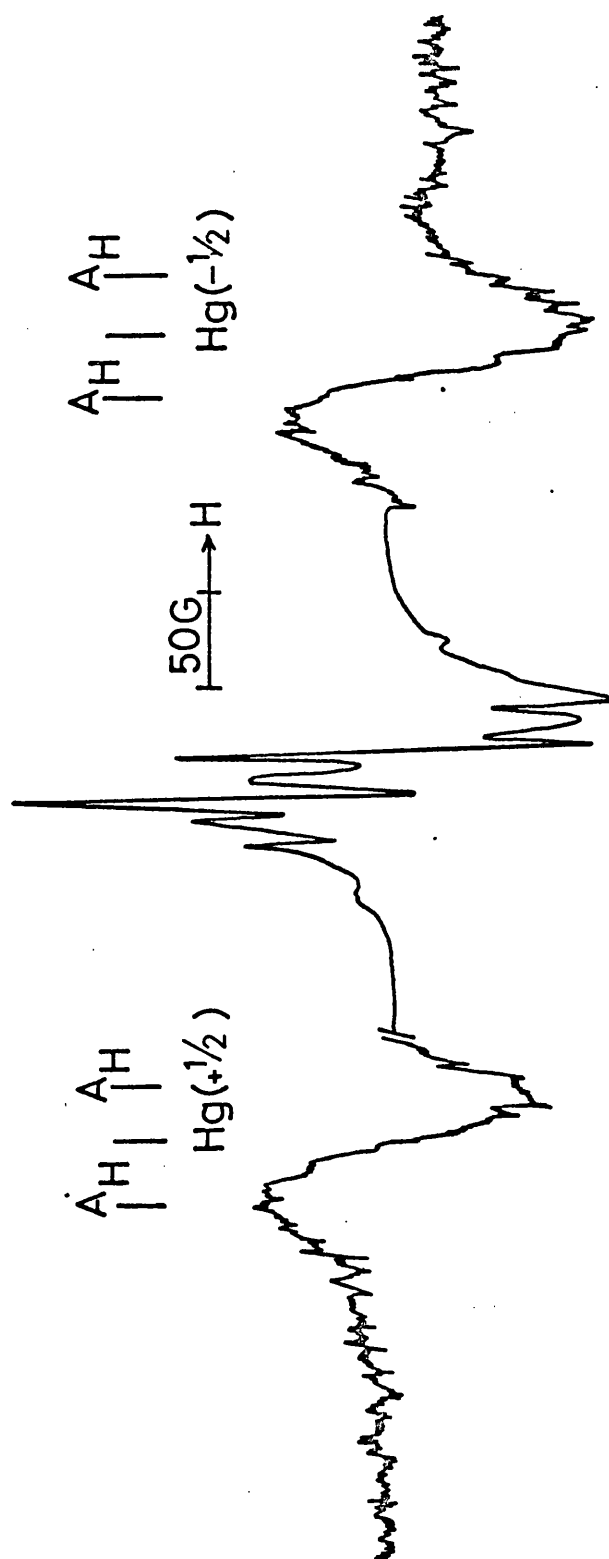
FIGURE 2

a) CH_3HgBr

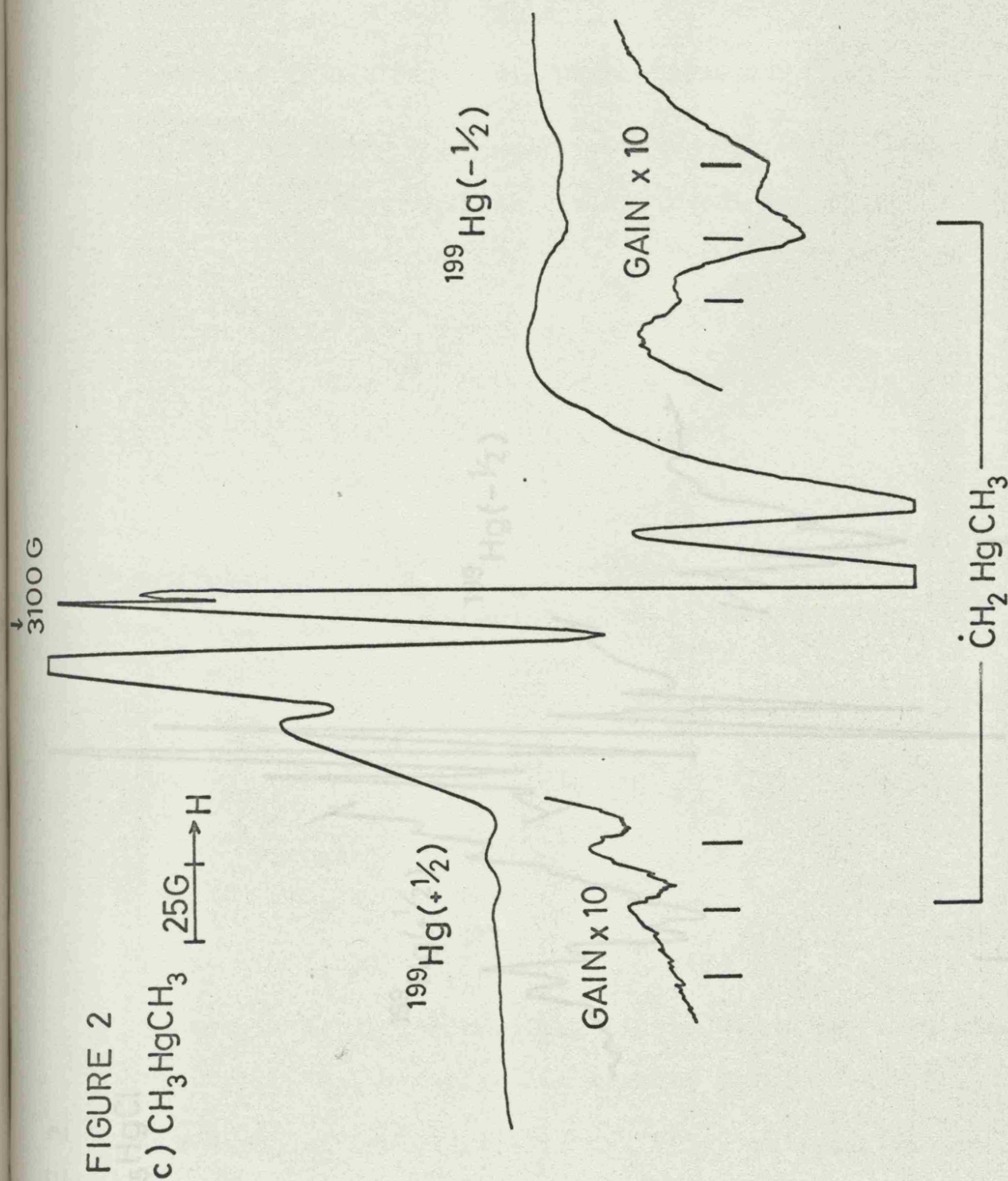


X-band e.s.r. spectrum of irradiated methyl mercuric bromide, at 77K.

FIGURE 2
b) CH_3HgI



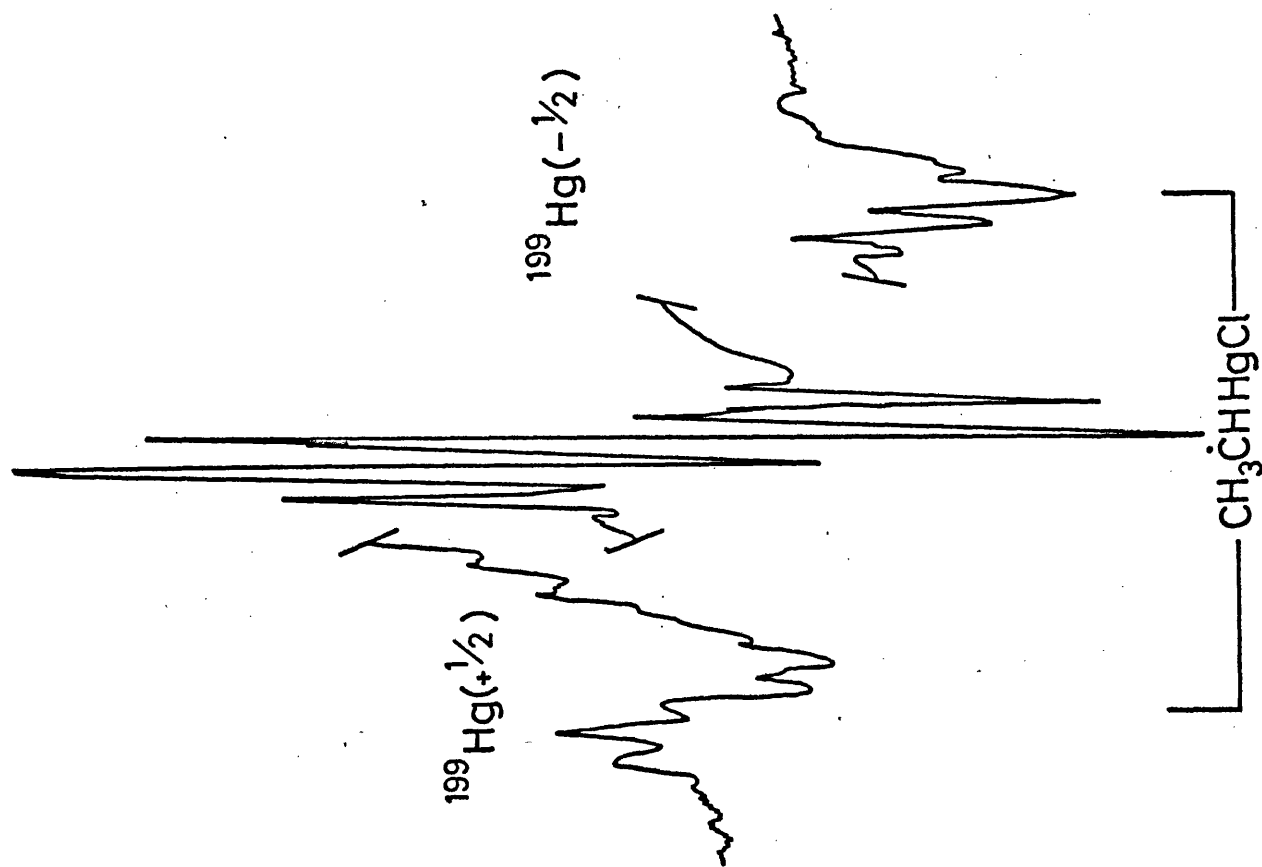
X-band e.s.r. spectrum of irradiated methyl mercuric iodide, at 77K.



X-band e.s.r. spectrum of irradiated dimethyl mercury] at 77K

FIGURE 2

d) $\text{C}_2\text{H}_5\text{HgCl}$



X-band e.s.r. spectrum of irradiated ethyl mercuric chloride, at 77K.

Table 3.

Hyperfine data and orbital populations for EtHg[•], [•]HgCl and Me Hg[•]-. .

Radical	Experimental Field Position (G)	Predicted Field Position (G)	A _{Hg} ^a	%s on Hg.
EtHg ¹⁹⁹ Hg	4392	4392	3693	29.5
²⁰¹ Hg	- <u>b</u>	630		
	2740	2714	1363	
	4860	4911		
	6150	6305		
[•] HgCl ¹⁹⁹ Hg	5200	5200	10595	
(MeHgMe) ¹⁹⁹ Hg	4155	4155	2674	21.7
	- <u>b</u>	920		
¹ H			20	
²⁰¹ Hg	-	1462	987	
	2800	2798		
	4375	4378		
	4500	4494		

a Isotropic hyperfine coupling (A) to ^{199/201} Hg calculated using the Breit-Rabi equation and assumed g-value of 2.00.

b The expected low field line could not be detected because of poor instrument performance in this region.

the suggested analyses. Both the bromide and iodide spectra show evidence of halide coupling though no reliable value for A_{Hal} can be derived. The resulting hyperfine splitting constants and g - values for $\dot{\text{C}}\text{H}_2\text{HgX}$ radicals thought to be responsible, can be found in Table 5.

Both ethyl mercuric chloride and dimethyl mercury had weak lines in their spectra in the 4-6000G region which, as stated above, indicates the presence of radicals in which the unpaired electron is strongly localised on the mercury atom.³⁶ Table 3 gives the actual and predicted field values for these species. The expected line positions were calculated using the full Breit - Rabi equation^{41,42} from which expressions for the line positions can be obtained. (These equations can be found in Appendix 1). The assumption that $g = 2$ was used throughout the calculations and was justified by the close agreement achieved.

3.9 $\text{R}_2\dot{\text{C}}\text{HHgR}$ Radicals.

The form of the proton coupling constants together with the presence of weak satellite lines from the $^{199/201}\text{Hg}$ isotopes strongly supports identification of the major central features in terms of $\text{R}_2\dot{\text{C}}\text{HHgR}$ radicals (where $\text{R} = \text{H}$, Halogen or CH_3). Comparison of the proton hyperfine splittings with those reported for structurally similar radicals^{43,44} shows that there is little or no delocalisation of the unpaired electron. The normal value of ca. 21G for the α -proton hyperfine coupling is maintained. The isotopic coupling to ^{199}Hg can be used in a rough estimate of the % S - character of the unpaired electron on mercury. There is uncertainty relating to the best value to use for the A_{130}^0 figure, and I have used

E.s.r parameters for Hg^+ , HgH^{2+} , HgOH^{2+} , HgOEt^{2+}
and Hg_2^+ or Hg_2^{3+} .

Species	Environment	A-value ^a	Line Positions
		(G)	at X-band.
$^{199}\text{Hg}^+$	$7\text{M}-\text{HClO}_4$	$12,500 \pm 100$	5470
$^{201}\text{Hg}^+$		-4540 ± 50	7350
$^{199}\text{Hg}^+$	EtOH	$11,490 \pm 300$	5410
$^{201}\text{Hg}^+$		-4040 ± 100	7070
$^{199}\text{Hg}^+$	H_2SO_4	$13,860 \pm 100$	5505
$(^{199}\text{Hg}-^{200}\text{Hg})^{+3+}$	H_2SO_4	6900 ± 200	5013
$(^{201}\text{Hg}-^{200}\text{Hg})^{+3+}$	H_2SO_4	-2010 ± 50	5575
			2825
$(^{199}\text{Hg}-^{200}\text{Hg})^{+3+}$	$\text{H}_2\text{SO}_4-\text{EtOH}$	6480 ± 100	4950
$(^{201}\text{Hg}-^{200}\text{Hg})^{+3+}$		-2100 ± 50	5705
			2830
$^{199}\text{HgH}^{2+}$	$7\text{M}-\text{HClO}_4$	$4502 \pm 50(\text{Hg})$	4410
		(ca. 36%spin dens) ^e .	
		$A(\text{H}) = 300 \pm 10$	4710
		(ca. 60%spin dens.) ^f	
$^{199}\text{HgOEt}^{2+}$	EtOH	4525 ± 100	4598
$^{199}\text{HgOH}^{2+}$	$3\text{M}-\text{HClO}_4$	4734 ± 50	4616

^aCalculated assuming $g=2$.

here the "experimental" result for Hg^+ ions as a rough guide. The results show that the % s - character centred on the mercury is larger than that normally found for R_2CAB_3 radicals,⁴³ and they reveal a clear increase in spin - density on mercury as the electronegativity of the ligand increases (Table 5).

Although, in principle, $\text{R}_2\dot{\text{C}} - \text{HgX}$ radicals, which are expected to be linear with respect to the coordination to the mercury and locally planar at the radical centre, could exhibit $p_\pi - p_\pi$ bonding and $p_\pi - d_\pi$ between carbon and mercury, the high value of the α -proton coupling constants seems to rule this out as a major effect. Also, the near - isotropic mercury coupling is not in accord with this. It is therefore suggested that the coupling to $^{199/201}\text{Hg}$ arises primarily from spin - polarization of the carbon mercury σ - electrons. Hunt and Symons⁴⁵ have stressed that the isotropic coupling must reflect the s-p-orbital hybridization on the substituent, and the high value of A_{H_3} for mercury suggests a large s-content in the bonding orbitals, as expected. Indeed if the rough correlation given in the figure of reference 43

is used, it is possible to deduce a 50% bonding orbital s-contribution for $\text{H}_2\dot{\text{C}}\text{HgMe}$ radicals, corresponding to sp-hybridization, rising to ca. 75% s-contribution for $\text{Me}\dot{\text{C}}\text{HHgCl}$.

This increase on replacing methyl by halide, follows on the present argument, the tendency for more electronegative substituents to favour the use of p-orbitals for σ - bonding. Whilst the results here only describe the radical $\text{R}_2\dot{\text{C}}\text{HHgHal}$, it is likely that the degree of perturbation from the undamaged molecule is small. If this is so, the results given here favour a description of bonding in RHgHal molecules in

Table 5.

Hyperfine coupling constants for a range of mercury
and aluminium radicals.

Radical	A_H	$A_{Hg^{199}}$	$A_{Hg^{201}}$	g	% s on Hg
$\dot{C}H_2HgCH_3$	21	220		2.00	1.75 <u>a</u>
$\dot{C}H_2HgI$	21	410		2.0037	3.2 <u>a</u>
$\dot{C}H_2HgBr$	23	439	187	2.0036	3.5 <u>a</u>
$CH_3\dot{C}HHgCl$	27(CH_3) 21(H)	450		2.0035	3.7 <u>a</u>
$\dot{C}H_2Al(Me)_3$	19	(^{27}Al)18.9			(Al)1.93 <u>b</u>
$CH_3\dot{C}HA1CH_3(Cl)_2$	21.2	(^{27}Al)21.2			(Al)2.16 <u>b</u>
$CH_3\dot{C}HA1(Cl)_3$	25.9	(^{27}Al)25.9			(Al)2.64 <u>b</u>

a This work.

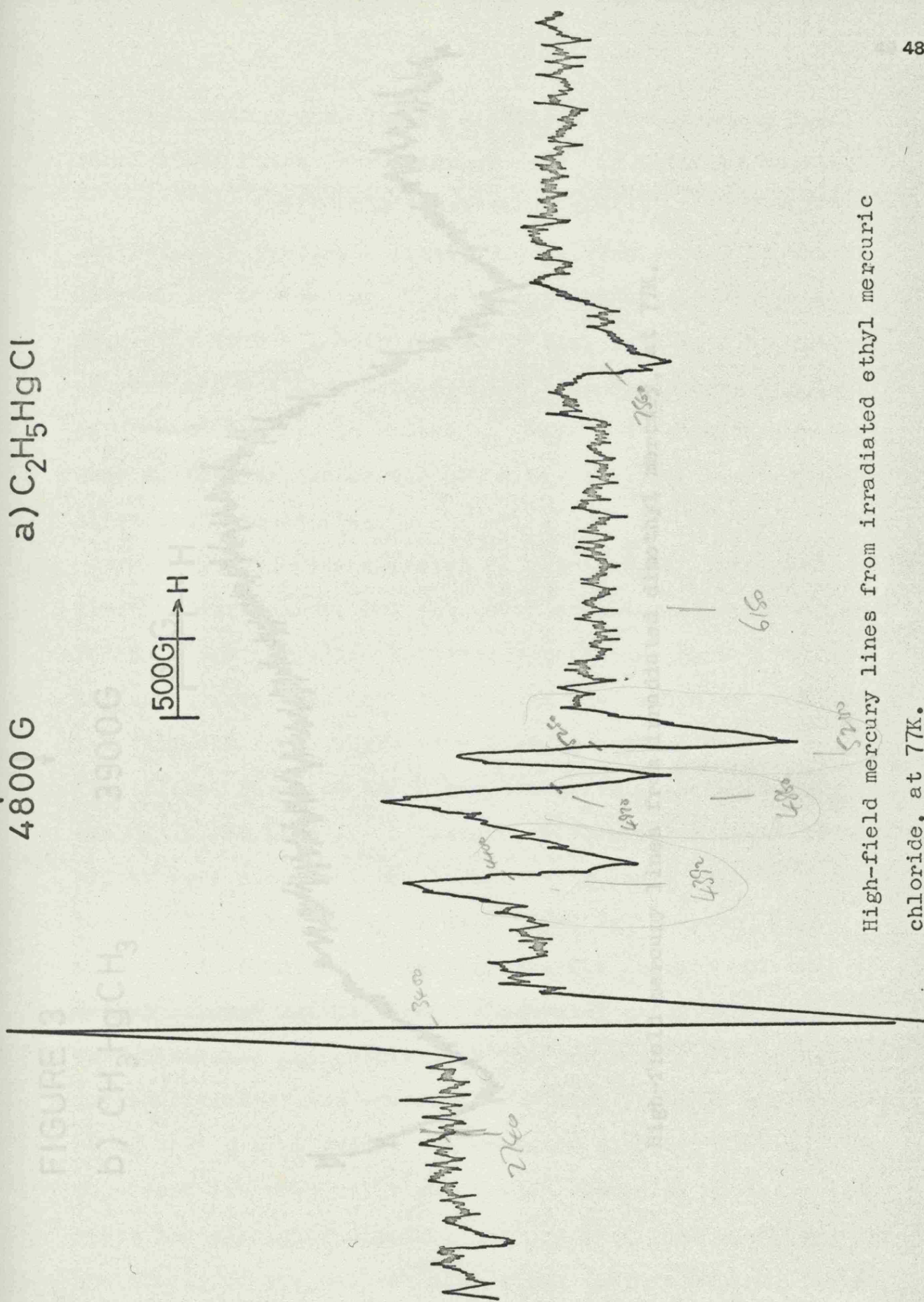
b Reference 47.

which the R-group bonds mainly with the 6s - orbital, and the halide mainly with the 6p_x - orbital on mercury. This is certainly a more realistic analysis of the bonding involved in such compounds than to say that the two covalent bonds involved are simply identical sp-hybrids bonding to the ligands, the high electronegativity of the halogen perturbing the R-Hal bond considerably. This argument was used previously by Symons et al⁴⁶ to explain the changes in the phosphorous coupling constants of the series: PO₄²⁻ (20-30G), O₃PF(39.1G) and O₂PF₂(43.8G), all of which have the unpaired electron largely confined to oxygen. A similar trend has been noted for a range of radicals containing aluminium (R₂C.Al.X₃)⁴⁷ and results are included in Table 5 for comparison purposes.

3.10 Mercury Centred Radicals.

Identification of the species which gives rise to the high field lines for irradiated dimethyl mercury and ethyl mercuric chloride is somewhat tentative because of the lack of any proton hyperfine splitting. Two likely candidates for the latter are $\cdot\text{HgEt}$, produced by the loss of Cl⁻ from the negative ion, and $\dot{\text{HgCl}}$. Since two species are involved we suggest that the species with the lower mercury coupling is $\dot{\text{HgEt}}$ (A (¹⁹⁹Hg) ~ 3693G) and that with the higher coupling is $\dot{\text{HgCl}}$ (A (¹⁹⁹Hg) ~ 10,000G). This is based upon the expectation that $\dot{\text{HgCl}}$ will have considerable ionic character (Hg⁺Cl⁻) and would, therefore, be expected to exhibit a hyperfine coupling close to that for Hg⁺ (ca 10,000 - 12,000G). Clear features from ²⁰¹Hg were only obtained for the $\dot{\text{HgEt}}$ species in these studies. (See Fig. 3). This result accords nicely with the conclusion drawn above, that Cl⁻ will utilise the 6p -

FIGURE 3
a) C_2H_5HgCl



High-field mercury lines from irradiated ethyl mercuric chloride, at 77K.

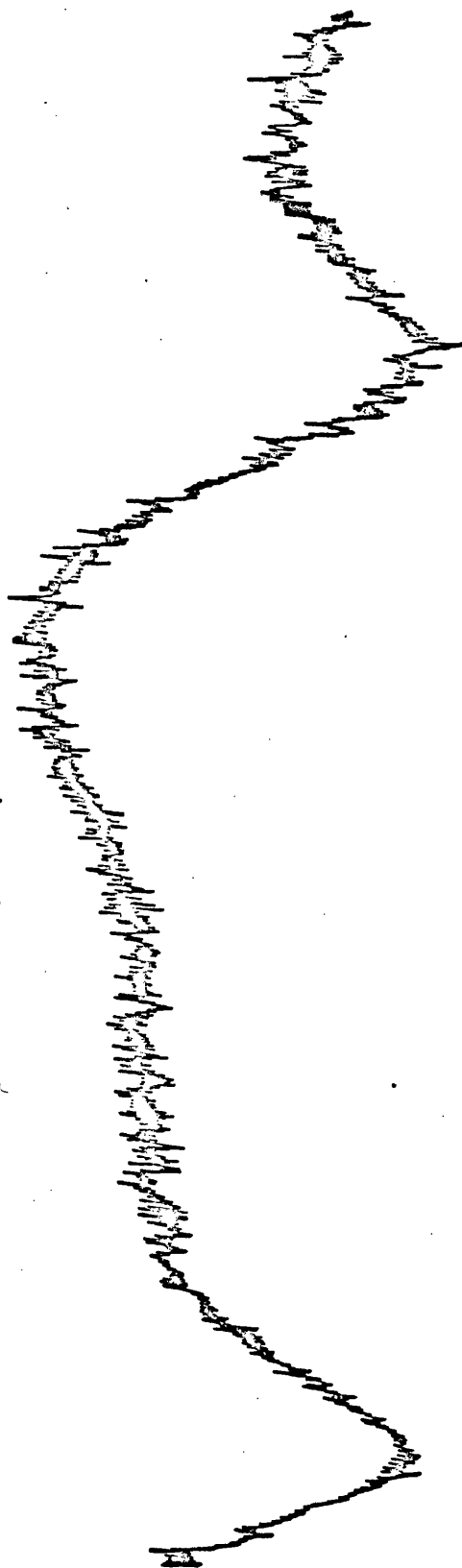
FIGURE 3



b) CH_3HgCH_3

3900 G

50 G $\rightarrow$ H



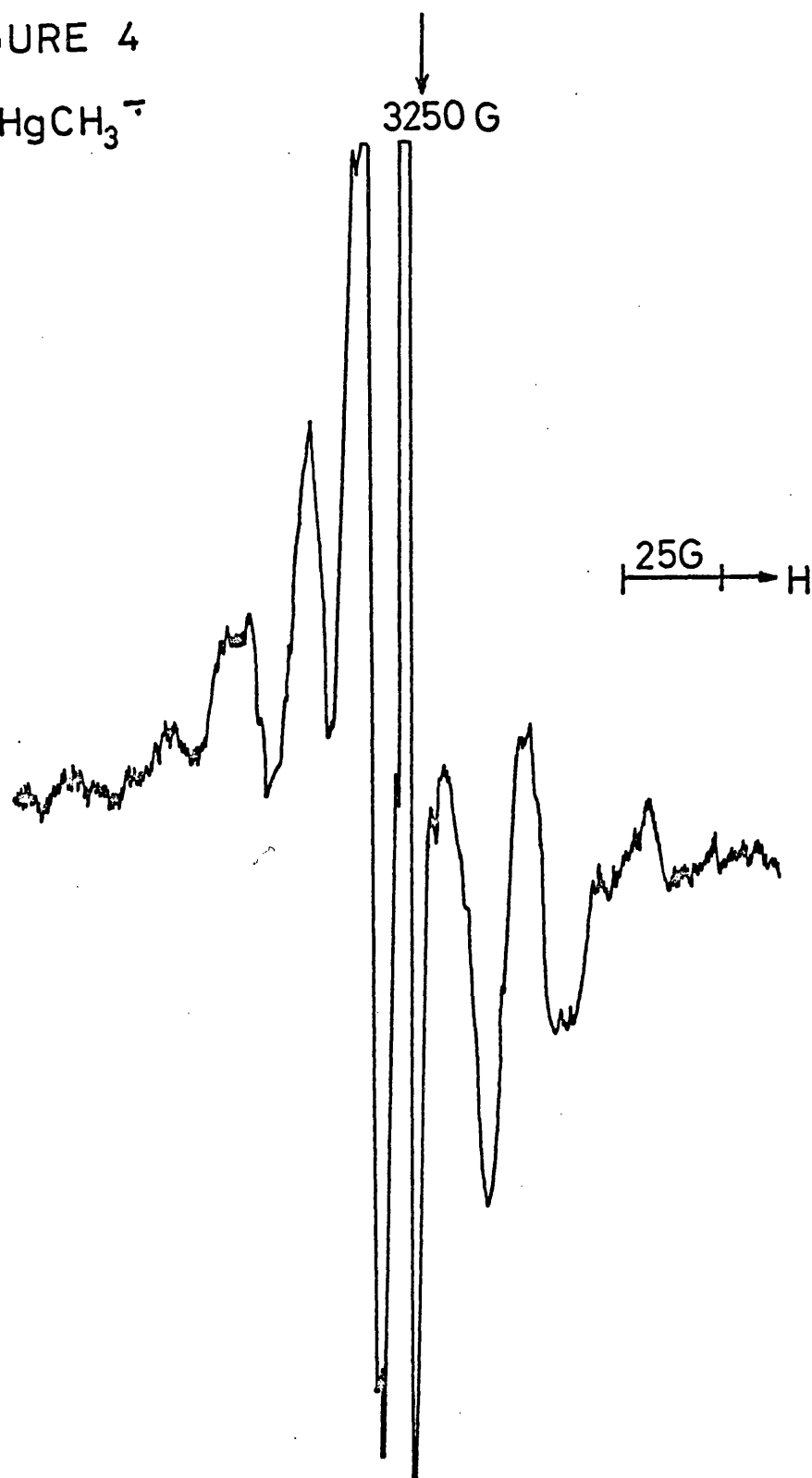
High-field mercury lines from irradiated dimethyl mercury, at 77K.

orbital rather than the 6s - orbital for σ -bonding and is born out by Knight's studies of $\dot{\text{HgCN}}$ ⁴⁰ in an inert matrix.

Similarly, the lower value for A_{150} assigned to $\dot{\text{HgEt}}$ reflects, in part, the presence of a greater use of the 6s - orbital for σ -bonding. This forces the unpaired electron partially into a σ^* -orbital which will have both 6p_z character on mercury, and also considerable ligand character. Both effects will serve to reduce $A_{150}(\text{Hg})$: both should introduce some anisotropy, which was certainly present, but was too ill-defined to utilise.

It had been expected to obtain $\dot{\text{HgMe}}$ from the dimethyl derivative, but the lower coupling constant of ca 2674G (¹⁹⁹Hg) suggests that the species is structurally different from $\dot{\text{HgEt}}$. When the sample was annealed such that the features for $\text{H}_2\dot{\text{C}}\text{HgMe}$ were lost, a central 7-line spectrum (Fig.4) was revealed which was tentatively assigned to $(\text{Me}_2\text{Hg})^\cdot$. The high field features were still present and their widths were such that the 7 components could well be concealed therein. Since radicals of this class are unknown, it is not possible to identify it by analogy. The absence of the methyl mercury radical $\dot{\text{MeHg}}$ is somewhat surprising since it is the postulated intermediate in the gas and liquid phase decomposition of the compound. The most probable explanation being that a cage recombination takes place at 77 K leading to a very low concentration of such radicals. In the solid state photolysis of dimethyl mercury at 4 and 77 K and the photolysis of azo methane⁴⁸ and ethyl acetate⁴⁹ at 4 K, it has been postulated that the $\dot{\text{MeHg}}$ radical was stable enough to undergo a second photolysis reaction leading to the production of hot methyl radicals.

FIGURE 4
 $\text{CH}_3\text{HgCH}_3^-$



X-band e.s.r. spectrum of irradiated dimethyl mercury
after annealing.



If this were to take place in the γ -radiolysis neither of the primary products $(\text{CH}_3\text{Hg})^+$ and $(\text{CH}_3\text{Hg})^-$ would be paramagnetic.

This reaction is probably unlikely.

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CHAPTER 4

Organo-phosphorus Compounds.(I).

4.1 Introduction.

Organophosphorus compounds are amongst the most interesting to be studied by e.s.r., the wide range of compounds available providing an opportunity to study the effect of different ligands on the behaviour of a variety of radicals. Phosphorus-31, with a nuclear spin of $\frac{1}{2}$ and 100% abundance, gives a large hyperfine coupling for phosphorus centred radicals. Because of this it is usually possible to identify phosphorus centred radicals fairly readily, though exact assignment becomes more difficult.

4.2 This Work.

Hyperfine coupling to heavy elements in positions β to the unpaired electron is now well known¹. Conditions controlling the extent of this coupling are still obscure and an attempt to clarify some of these first prompted the study of alkyl thiophosphite radicals.

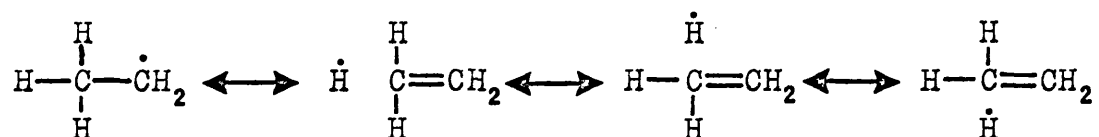
Hyperconjugative β -coupling is very strongly favoured in radicals of the type $\dot{\text{C}}\text{H}_2\text{CH}_2\text{P}$ but has been found not to occur to any significant extent in alkoxy phosphorus compounds, where the radical structure is $\dot{\text{C}}\text{H}_2\text{OP}^2$. This change in behaviour has been attributed to the favouring of C-O conjugative coupling. A paper by Gulick et al³ seemed to indicate that by replacing oxygen by sulphur, in such radicals, this conjugative delocalisation was circumvented, with hyperconjugation again playing a part in the hyperfine coupling.

In an attempt to check and extend this finding trimethyl thiophosphite was irradiated, with the aim of generating $\dot{\text{C}}\text{H}_2\text{SP}(\text{SCH}_3)_2$ radicals. The multiplicity of radicals produced on irradiation led to a widening of the scope of the

study such that a range of phosphorus compounds were considered.

4.3 Hyperconjugation.

The concept of hyperconjugation, as originally stated by Wheland in 1934⁴, was a direct result of the very successful use of valence bond theory to explain conjugation in molecules. Wheland suggested that the weakening of the central C-C bond in ethane, with the substitution of the hydrogen atoms by methyl groups, could be indicative of a mechanism that would stabilise alkyl radicals by the involvement of novel non-bonded structures.

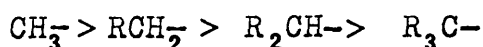


It was then seen that such structures could explain a number of puzzling results, such as the shortening of C-C single bonds adjacent to C-C double bonds. This theory was put onto a firm quantitative base by Mulliken⁵, who examined these interactions using the molecular orbital approach.

Whilst these physico-chemical studies were being pursued, Baker and Nathan⁶, in their kinetic studies, discovered an apparently abnormal order of electron release for alkyl groups, in the reaction of substituted benzyl bromide with pyridine.

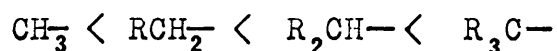


The normal inductive effect expected from alkyl substituents in the para position was,

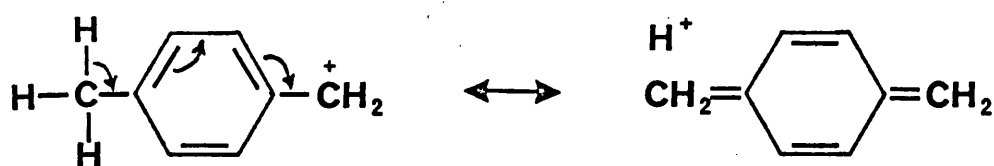


with the t-alkyl substituent showing the greatest electron

releasing effect. The order found in this reaction was the opposite of that above.



This could be explained if the methyl group showed a particularly large stabilising effect on the transition - state of the reaction, in which the methylene group would be expected to have some positive charge, i.e.



This postulate seemed reasonable in resonance terms, though to explain the differences found in the influence of alkyl groups and the methyl group, on the reaction rate, it was necessary to postulate a hyperconjugative effect that was particularly significant for C-H bonds and not for C-C bonds.

After these initial studies a considerable body of chemical and physical evidence appeared that seemed to support the presence of a hyperconjugative effect. Many examples of the Baker-Nathan effect were found^{7,8} (see Table 1) in which reaction rates were apparently increased by the effective delocalisation of positive charge onto methyl groups.

The physical evidence that was considered to support the hyperconjugation effect included the reduction in bond lengths in such compounds as butadiene and methylacetylene, anomalous heats of formation and hydrogenation of double - bonded molecules and the dipole moments, found to be present in simple hydrocarbons. Further evidence was forthcoming from N.Q.R., E.S.R., and N.M.R. measurements. Much of this

Table 1.

Examples of the Baker - Nathan Effect.

<u>Reaction</u>	<u>Rate or Equilibrium Constant Relative to R=H</u>		Effect of Me Rel. to t-Bu
	<u>R=Me</u>	<u>R=t-Bu</u>	
Bromination PhR in AcOH	2420	770	3.14
Benzoylation PhR in PhCOCl	589	430	1.37
Solvolysis of p-RPhCH ₂ Br in wet HCOOH	57.9	28.0	2.07
Solvolysis of p-RPhCHPhCl in 90% aq. EtOH	30.9	19.3	1.59
Solvolysis of RCH=CHCH ₂ Cl in wet HCOOH	3550	2260	1.57
Solvolysis of RC≡CCMe ₂ Cl in 80% EtOH	2160	1180	1.83
p-RC ₆ H ₄ CHO + HCN $\rightleftharpoons$ RC ₆ H ₄ CHOHCN	2.00	1.68	1.19
p-RC ₆ H ₄ CH ₂ Br + I ⁻ in Me ₂ CO	1.46	1.36	1.07
Acid hydrolysis of p-RC ₆ H ₄ SiEt ₃	1.45	1.32	1.10
Alkaline hydrolysis of p-RC ₆ H ₄ COOEt	0.44	0.56	1.27

(For references see Ref. 8).

evidence has been reviewed by Baker.⁷

Whilst, at first sight, the sheer volume of evidence for hyperconjugation was overwhelming a more critical approach⁹ made it clear that most of the results could be explained in more normal terms. Many of the physical results can be explained by invoking changes in bond characteristics with alterations in sp hybridisation of the C-C bonds.⁹ The changes in reaction rates, with differing alkyl substituents, are more convincingly explained by invoking changes in the solvation of the reactants.

The results obtained from magnetic resonance spectroscopy, because these techniques are inherently more sensitive to relatively small changes in molecular structure, provide more convincing evidence for hyperconjugation, and it is the results obtained specifically by e.s.r. methods that will now be discussed.

4.4 E.S.R. Studies of Hyperconjugation.

Early e.s.r. studies of liquid^{10,11} and solid-state^{12,13} alkyl radicals indicated that a large hyperfine coupling could be expected from protons α and β to the unpaired electron. Since, in such radicals, the electron is confined to a p-orbital some mechanism was required to explain these coupling.

Table 2.

Isotropic proton hyperfine coupling constants (G) for Alkyl Radicals.¹⁴

<u>Radical</u>	<u>A_{α}</u>	<u>A_{β}</u>	<u>A_{γ}</u>
Methyl	-23.0	-	-
Ethyl	-22.4	26.9	-
n-propyl	-22.1	33.1	-
n-propyl	-22.1	29.4	-

Table 2(cont).

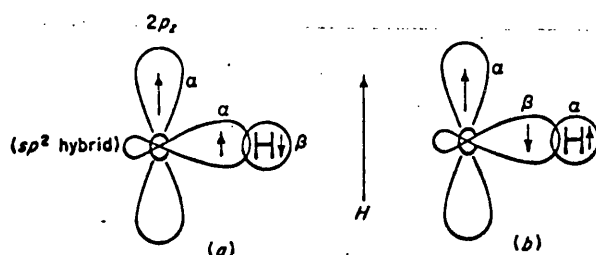
<u>Radical</u>	<u>A_α</u>	<u>A_β</u>	<u>A_γ</u>
i-propyl	-22.2	24.6	-
i-butyl	-22.0	35.1	-
t-butyl	- -	22.7	-
cyclopentyl	-21.6	35.3	0.52
cyclohexyl	-21.0	46.0(2) $\frac{41}{5}$	-
		γ 0.67(2)	-

a. -175 C ; b. -50 C.

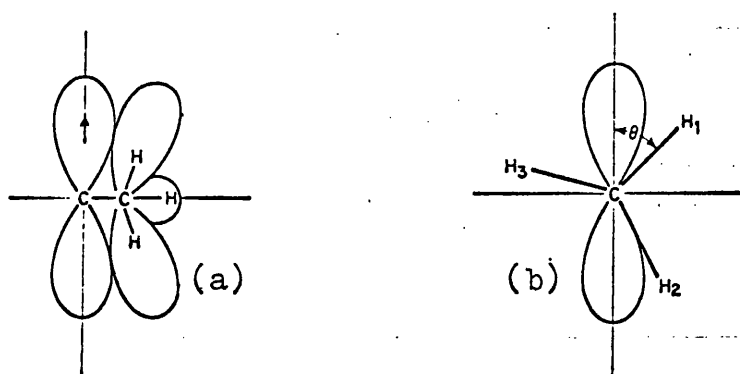
Theory of Hyperfine Coupling to α -Protons. - Consider a C-H fragment of a conjugated system. If the electron in the p_z orbital has a spin α assigned to it then there are two possible assignments for the spins in the C-H σ -bond(Fig 1.). (It is assumed here that the unsaturated carbon has three trigonal sp^2 hybrid orbitals bonding the three ligands and a $2p_z$ orbital perpendicular to the C-H fragment.)

If there were no electron in the p_z orbital then both configurations, (a) and (b), would be equally likely and no spin density would be found on the proton. It has been shown spectroscopically that when two unpaired electrons exist in adjacent orbitals the energetically most favourable configuration is that in which the spins are aligned in the same direction. (one of Hunds' rules) Hence, configuration (a) will be more stable than (b), that is, there will be a net negative spin density (i.e. excess of β spin over α spin) at the proton. It should be noted that this gives a positive spin density at the carbon atom.

This effect, normally called spin-polarisation, was put onto a firm theoretical footing by McConnell and Chestnut.¹⁵

Figure 1.

Possible configurations of electron spin in the orbital bonding the hydrogen atom of a C-H fragment, for spin in the $2p_z$ orbital of carbon. (a) Spins parallel in the bonding orbital and the $2p_z$ orbital of carbon. (b) Corresponding spins antiparallel.

Figure 2.

(a) Overlap of electronic orbitals in a C-CH fragment.

(b) The effect of dihedral angle on overlap of electronic orbitals in a C-CH fragment.

The first experimental confirmation of the negative sign of the α -proton coupling was obtained by an analysis of the splittings obtained for a radical produced by irradiating malonic acid.¹⁶ N.m.r. studies of stable paramagnetic species¹⁷ have also provided evidence for the negative sign of the α -proton coupling.

Theory of Hyperfine Coupling to β -Protons. - The mechanism for coupling to β -protons is not as clearly defined as that which applies to α -coupling. The most successful theory, though one still open to contention, is that of hyperconjugation. The one other theory, of any standing, is an extension of spin-polarisation as found with α -protons.

Consider an ethyl radical. The methyl protons lie in a plane parallel to the axis of the $2p_z$ orbital, containing the unpaired electron. (Fig. 2) This permits a direct overlap between the C-H σ -orbitals and the p_z orbital containing the free spin. This is the hyperconjugative mechanism.

The overlap of orbitals provides the observed positive spin density on the β -proton, since there will be a slight spin-pairing of one electron in the σ C-H bond. A second requirement of any β -coupling mechanism is an explanation of the observed angular dependence. As can be seen in the diagram, the orbital overlap will be at a maximum when the dihedral angle θ equals zero, and at a minimum when the C-H bond lies in the nodal plane of the p_z orbital. The angular dependence is predicted to be of the $\cos^2 \theta$ form, a prediction born out by experiment.

An essential requirement for such a mechanism is that the orbitals of the methyl group must have the same symmetry as the p_z orbital, and be close enough to permit significant

overlap. Molecular orbital treatment of such a situation by Coulson and Crawford¹⁸ has shown that the atomic orbitals of the three hydrogen atoms may be combined to give a molecular orbital of the required symmetry. The combination, given in equation (4.1), is shown schematically in figure 3.

$$\psi = c_1 \phi_1 - c_2 (\phi_2 + \phi_3) \quad (4.1)$$

Results obtained from the study of the radical $\text{HOOC} \cdot \text{CH}_2 \cdot \dot{\text{C}}\text{HCOOH}$, derived from succinic acid,¹⁹ indicate that the true angular dependence of β -coupling follows the equation

$$a_{\beta}^H = B_1 + B_2 \cos^2 \theta \quad (4.2)$$

where $B_1 = 4G$, and is a measure of the residual spin-polarisation present when $\theta = 90$. B_2 ($\approx 50G$) is the maximum coupling, due to hyperconjugation, when orbital overlap is at a maximum. Where the methyl group is free to rotate around the C-C bond, the expected β -coupling can be shown to be of the order of half the maximum value.

Though the hyperconjugative mechanism has successfully explained most of the observed characteristics of β -coupling, it does not fulfill all the requirements. Attempts, therefore, were made to explain β -coupling by a spin-polarisation mechanism, but were not very successful.²⁰ It would appear that a full explanation of β -coupling involves both mechanisms, since hyperconjugation does not explain the lack of any decrease in α -coupling with an increase in the degree of β -coupling. The results in table 2 show how constant the α -couplings are. This would appear to argue for a large component of the β -coupling coming from a spin-polarisation

mechanism.

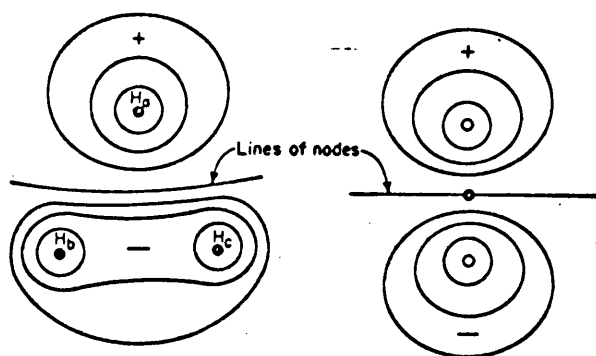
In an attempt to quantify the parts played, in β -coupling, by the two mechanisms, Symons and co-workers²² made a study of the two radicals $\text{H}_2\dot{\text{C}}\text{N}$ and $(\text{CH}_3)_3\dot{\text{N}}^+$. For these radicals it was concluded that spin-polarisation makes about as large a contribution to β -coupling as does hyperconjugation. However, the spin-polarisation occurring in the radical $\text{H}_2\dot{\text{C}}\text{N}$ is of the $\pi-\pi$ type, and not the $\pi-\sigma$ type responsible for α proton coupling. Whether or not this $\pi-\pi$ spin-polarisation is included within the term hyperconjugation is largely a matter of convenience.

4.5 β -Coupling to atoms other than Hydrogen.

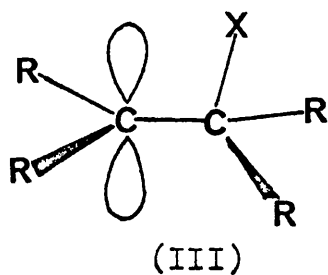
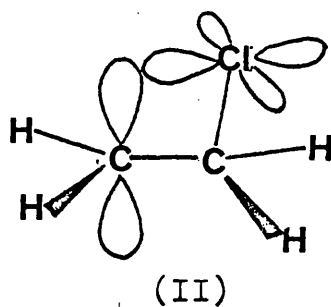
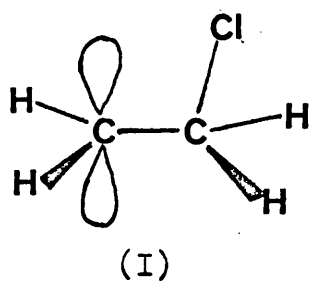
Whilst the kinetic phenomenon originally observed by Baker and Nathan⁶ was explained in terms of a hyperconjugative mechanism confined solely to β -protons, theoretical studies have shown that hyperconjugation to alkyl groups, or for that matter any other group β to the reactive centre, should occur to an equal extent. E.s.r. studies have verified this and have extended the concept of hyperconjugation to cover a range of groups in positions β to the radical centre.

Coupling to β -Halogen Atoms. - Coupling to all the halogen atoms has been reported. However, there is some debate as to the mechanism operative, since p-p homoconjugation, consisting of an interaction between lone-pair electrons on the halogen and the unpaired electron, is also possible.²³

β -Fluorine coupling has been extensively studied in the fluoromethyl nitroxides.^{24,25,26} Addition of perfluoro branches to the trifluoromethyl groups, of such radicals, was found to cause an increase in the remaining β -fluorine splittings. Strom and Bluhm,²⁷ attributing this to the presence of long

Figure 3.

Schematic representation of a three-hydrogen-atom molecular orbital of the same symmetry as the orbitals in a conjugated radical.

Figure 4.

range p-p homoconjugation, since the finding would otherwise require an angular dependence for β -fluorine couplings exactly opposite to that for β -protons. In criticizing this conclusion Jansen *et al*²⁸ argue that the apparently anomolous increase in β -fluorine coupling is due to a different conformational behaviour in these radicals when compared to β -protons.

Both p-p and σ - π overlap has been postulated to explain the β -coupling found with the three other halogens.^{29 30 31} A study of β -chlorine coupling in radicals, produced by γ -irradiation of t-butyl chloride³¹, indicates some contibution from both p-p (II) and hyperconjugative mechanisms (I). (see Fig. 4) The coupling shown in structure II probably induces a slight distortion of the C-C bond, allowing the chlorine atom to be constrained towards the radical centre.³²

Coupling in Radicals containing β -Heavy Atom

Substituents. - Krusic and Kochi³² have shown that radicals of the structure shown in figure 4 (III), where X is $-\text{SiR}_3$, $-\text{SnR}_3$, or $-\text{SR}$, exist in a strongly preferred conformation, such that the group X sits above the radical plane, maximising the overlap between the p_z orbital of the unpaired electron and the C-X σ bond. Lyons and Symons³³, in verifying this finding and extending it to cover other β substituents, suggested that the unusually large isotropic hyperfine couplings to the atom are best understood in terms of a hyperconjugative mechanism. Further work by Kochi *et al*³⁴ was in general agreement with this conclusion but to explain some apparent shifts in g_{av} a d- π delocalisation was postulated. Symons, has effectively argued that such a delocalisation of the unpaired spin into the outer d-orbitals of the metal atom

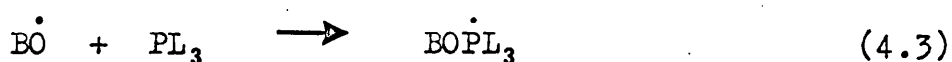
would cause a far greater g-shift than was actually found.

Results obtained by Damerau and co-workers³⁵ show clearly that β -hyperfine coupling to phosphorus, is angularly dependant. The phosphorus coupling of ca. 65G found in this study, whilst being indicative of a hyperconjugative mechanism, is considerably less than that obtained by Lyons and Symons^{30,33} in their study of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{PX}_2$ radicals. In contrast, the coupling obtained for radicals in which the β -carbon had been substituted to oxygen was reduced to ca. 10G². This reduction was attributed to preferential C-O conjugative overlap, which constrains the O-P bond to lie in the nodal plane of the p_z -orbital.

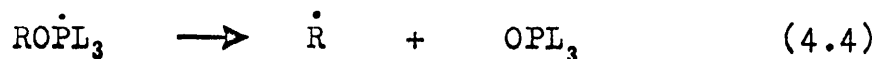
4.6 Irradiation Studies of some Trivalent Phosphorus Compounds.

A variety of phosphorus centred radicals have been characterised by e.s.r. The behaviour of phosphinyl ($\dot{\text{P}}\text{L}_2$)^{36,37} radicals, phosphonyl ($\dot{\text{P}}\text{L}_3$)³⁷⁻⁴⁰ radicals and phosphoranyl ($\dot{\text{P}}\text{L}_4$)⁴¹⁻⁴⁴ radicals is now reasonably well documented, though there still exists some difficulty in distinguishing between the last two species.⁴⁵ Whilst these studies have provided a considerable insight into the free radical chemistry of organo-phosphorus compounds many aspects remain obscure⁴⁶, particularly the radiation mechanisms occurring in the solid state.

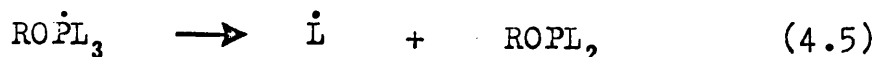
Griller et al,³⁷ in their liquid-phase studies have shown that all three of the above classes of radicals react at or close to, diffusion controlled rates. The radical species considered were generated by photolysis of di-t-butyl peroxide (BOOB) in the presence of a suitable substrate, a method used by themselves and others in a number of studies,^{41,42} e.g.



Secondary processes are often significant, including



and



Photolysis of trimethyl phosphite at 77K, by Terauchi and Sakuri,⁴⁸ produced two phosphorus containing radicals, as well as the ethyl radical. The two phosphorus radicals were identified as $(\text{EtO})_2\dot{\text{P}}\text{O}$ and $(\text{EtO})_2\text{P}\dot{\text{O}}$, but this must now be in doubt. (See Discussion below.)

In extensive studies made on γ -irradiated trialkyl phosphines, both pure and in various solvents,⁴⁹⁻⁵¹ it was not found possible to trap either the primary radical anions or their breakdown products. The cationic radicals were not detected either, though the cationic-dimers, generated by attack of the primary cation on a substrate molecule,



were well characterised in the pure materials.⁵¹

Preliminary studies of γ -irradiated trimethyl phosphite in methanol⁴⁵ indicated that a wide range of radicals are formed for such substrates, and it was therefore decided to extend this work to include several similar compounds in a range of solvents. A number of phosphites (trimethyl phosphite, trimethyl and tri-n-propyl thiophosphite, di-isopropyl phosphinyl chloride, diphenyl phosphinyl chloride and dithioethylphosphinyl chloride) have been exposed, either pure or in a range of solvents, to ^{60}Co γ -rays at 77K.

4.7 Experimental.

Di-isopropyl phosphinyl chloride and dithioethyl

phosphinyl chloride were kindly donated by Professor S. Trippett. Trimethyl thiophosphite and tri-n-propyl thiophosphite were prepared as described in chapter 2. Trimethyl phosphite (B.D.H. Chemicals Ltd.) and diphenyl phosphinyl chloride (Maybridge Chemicals) were used as received. All samples were irradiated in evacuated sealed silica tubes, having been thoroughly degassed by freeze-pump-thaw cycles. Solvents were added by vacuum distillation directly onto the samples and the solutions frozen immediately to prevent any solvolysis. All samples were irradiated at 77K in a Vickrad ^{60}Co γ -source for periods up to 2 hours.

Samples of trimethyl thiophosphite and trimethyl phosphite were frozen to 77K, in silica tubes, under a nitrogen atmosphere before being photolysed, using a Wooten 200w super-high pressure mercury lamp.

E.s.r. spectra were obtained at 77K using a quartz insert dewar in a Varian E3 spectrometer. Annealing studies were carried out either by warming for increasing time intervals followed by quenching and measuring at 77K, or by use of a Varian variable temperature accessory.

4.8 Results and Discussion.

Identification. - The spectra were made up of three generally separate groups of features.

1) The free spin region, consisting of features of alkyl and substituted alkyl radicals, the perpendicular features of the PL_2 radicals and $M_I = 0$ features for the radical dimer-cations.

2) The central region, covering about 300G, dominated by the parallel features for PL_2 radicals.

3) The outer region, covering about 700 -1000G,

which contained the parallel and perpendicular features of $\dot{\text{P}}\text{L}_3$ and $\dot{\text{P}}\text{L}_4$ radicals as well as the $M_I = \pm 1$ features for the dimer cations $(\text{L}_3\text{P}-\dot{\text{P}}\text{L}_3)^+$.

Identification of the species in the inner two regions was generally unambiguous, but for the outer region the presence of overlapping features from a number of radicals made identification more difficult. Assignment of the $M_I = \pm 1$ features due to the dimer-cations was simplified by the noticeable absence of any second-order shifts of the spectral positions. The features for these radicals were symmetrically placed about the free-spin region, whilst those for $\dot{\text{P}}\text{L}_3$ and $\dot{\text{P}}\text{L}_4$ radicals exhibited large second shifts.

Progressive loss of some features could be achieved by annealing of the samples, and in some cases libration and rotation of the radicals, at temperatures above 77K, led to better resolution of the spectra. Thus, for example, revealing superhyperfine coupling to chlorine nuclei. Addition of methyl bromide before irradiation, in some cases, suppressed electron capture by the substrate molecules leaving clearer spectra of the cationic species. An unwanted side effect was to generate methyl adducts, which masked features of other radicals.

A selection of typical spectra are shown in figures 5 - 7, and data relevant to the task of identification, together with brief comments on the basis of the identification, are given in table 3.

Aspects of Mechanism. - No primary anionic PL_3^- radicals were identified in any of the spectra. These species, which can be considered as phosphoranyl radicals with a "lone-pair" of electrons occupying one of the ligands sites, can be

Figure 5. - First derivative X-band e.s.r. spectra for (MeS) P.

- (a) After exposure to ^{60}Co γ -rays at 77K showing features assigned to $\text{Me}\dot{\text{P}}(\text{SMe})_3$ and/or $\text{Me}\dot{\text{P}}\text{S}(\text{SMe})_2^-$ (A) and $(\text{MeS})_4\dot{\text{P}}$ (B) and $(\text{MeS})_2\dot{\text{P}}$ (C)
- (b) After exposure of a dilute solution in methanol to ^{60}Co γ -rays at 77K and slight annealing to remove trapped methyl radicals and some $(\text{MeS})_2\dot{\text{P}}$ radicals, showing features assigned to residual $(\text{MeS})_2\dot{\text{P}}$ (C), $\text{Me}\dot{\text{P}}(\text{SMe})_3$ or $\text{Me}\dot{\text{P}}\text{S}(\text{SMe})_2^-$ (A) together with $(\text{MeS})_2\text{P}-\dot{\text{P}}(\text{SMe})_3$ (D) and $(\text{MeS})_3\text{P}-\text{P}(\text{SMe})_3^+$ radicals (E).
- (c) After exposure to u.v. light showing features assigned to $\text{Me}\dot{\text{P}}(\text{SMe})_3$ or $\text{Me}\dot{\text{P}}\text{S}(\text{SMe})_2^-$ (A) and $(\text{MeS})_4\dot{\text{P}}$ (C) and $\dot{\text{C}}\text{H}_2\text{SP}(\text{SMe})_2$ (F).

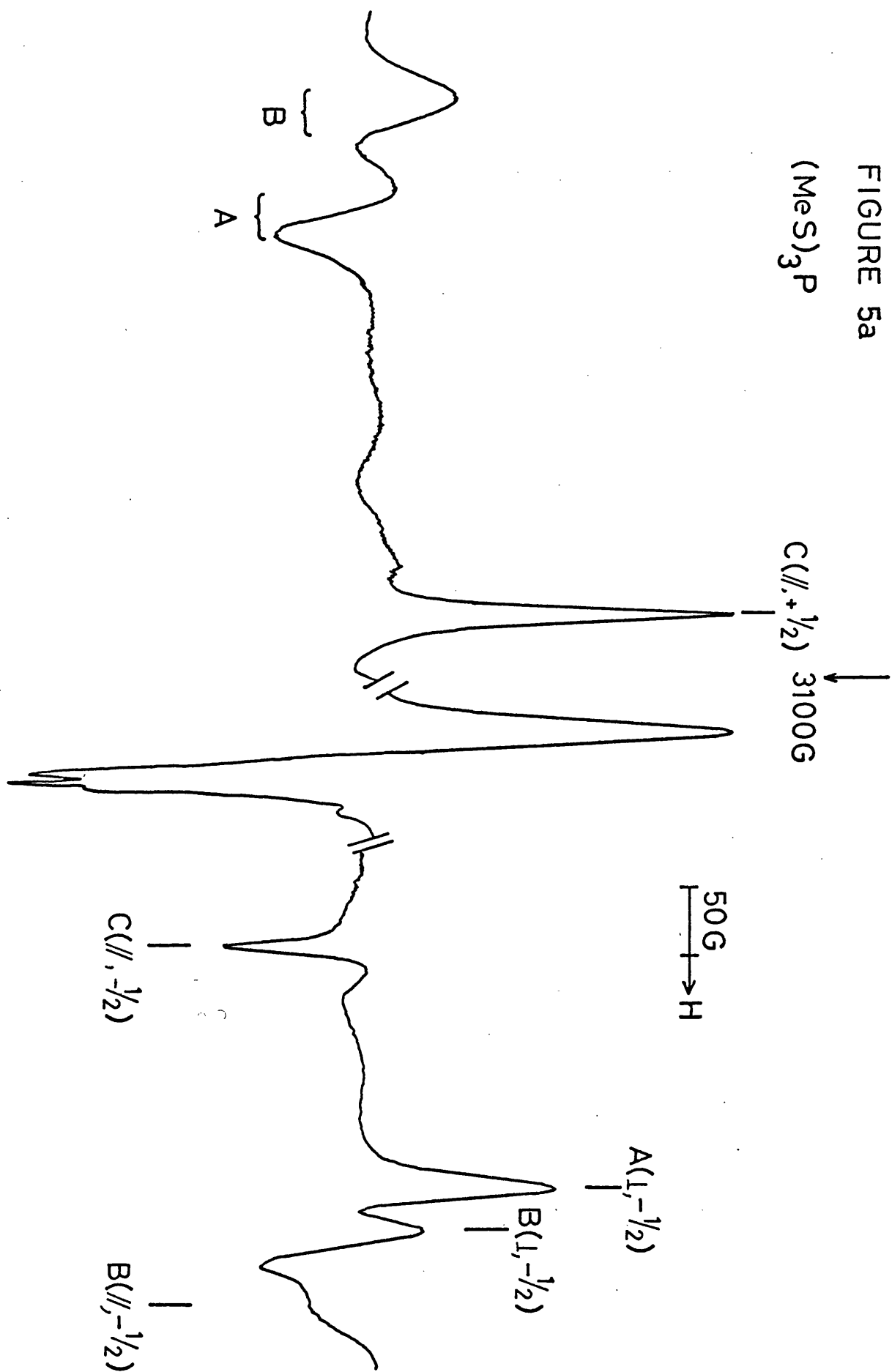
FIGURE 5a
(MeS)₃P

FIGURE 5b
(MeS)₃P

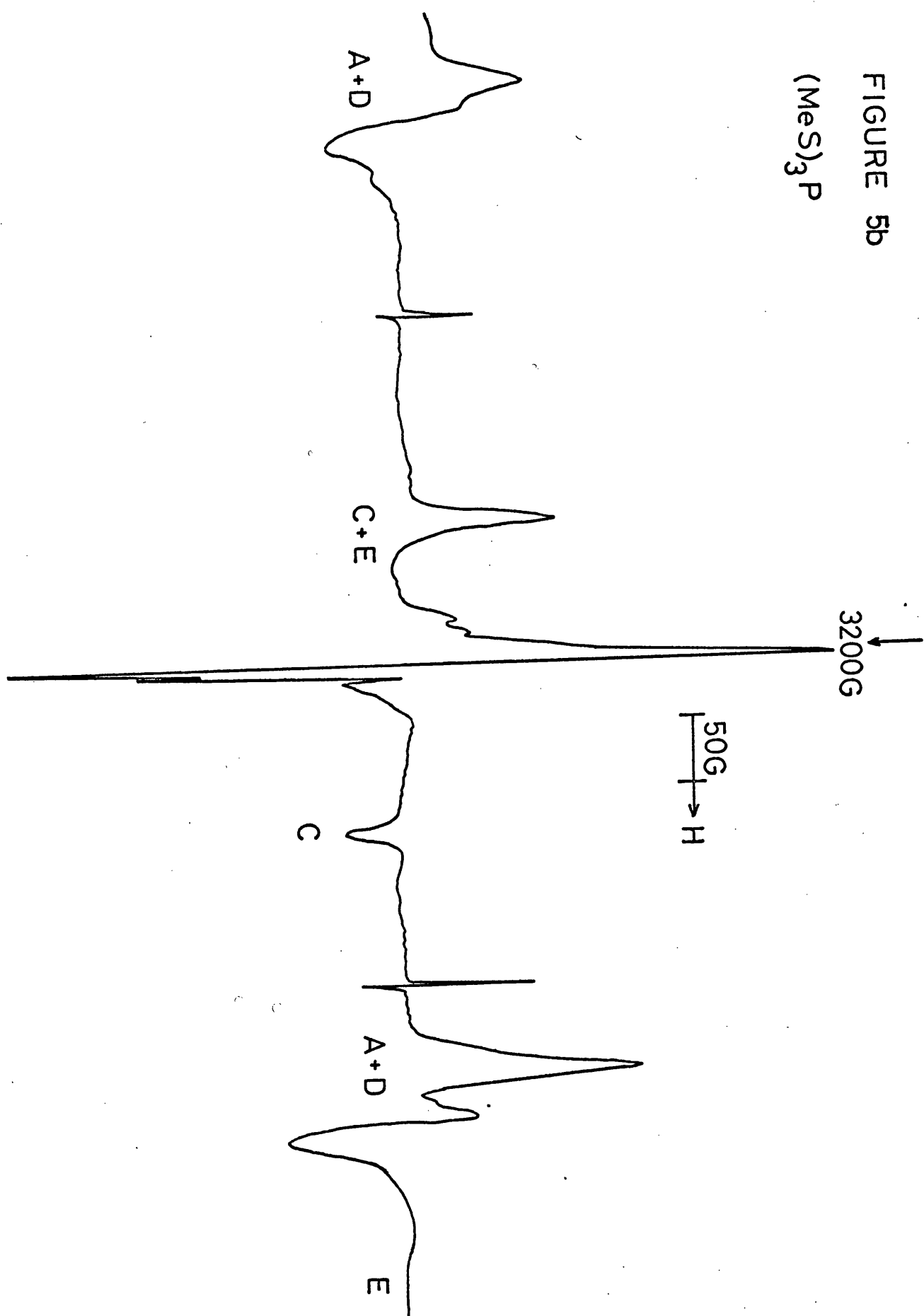


FIGURE 5c
 $(\text{MeS})_3\text{P}$

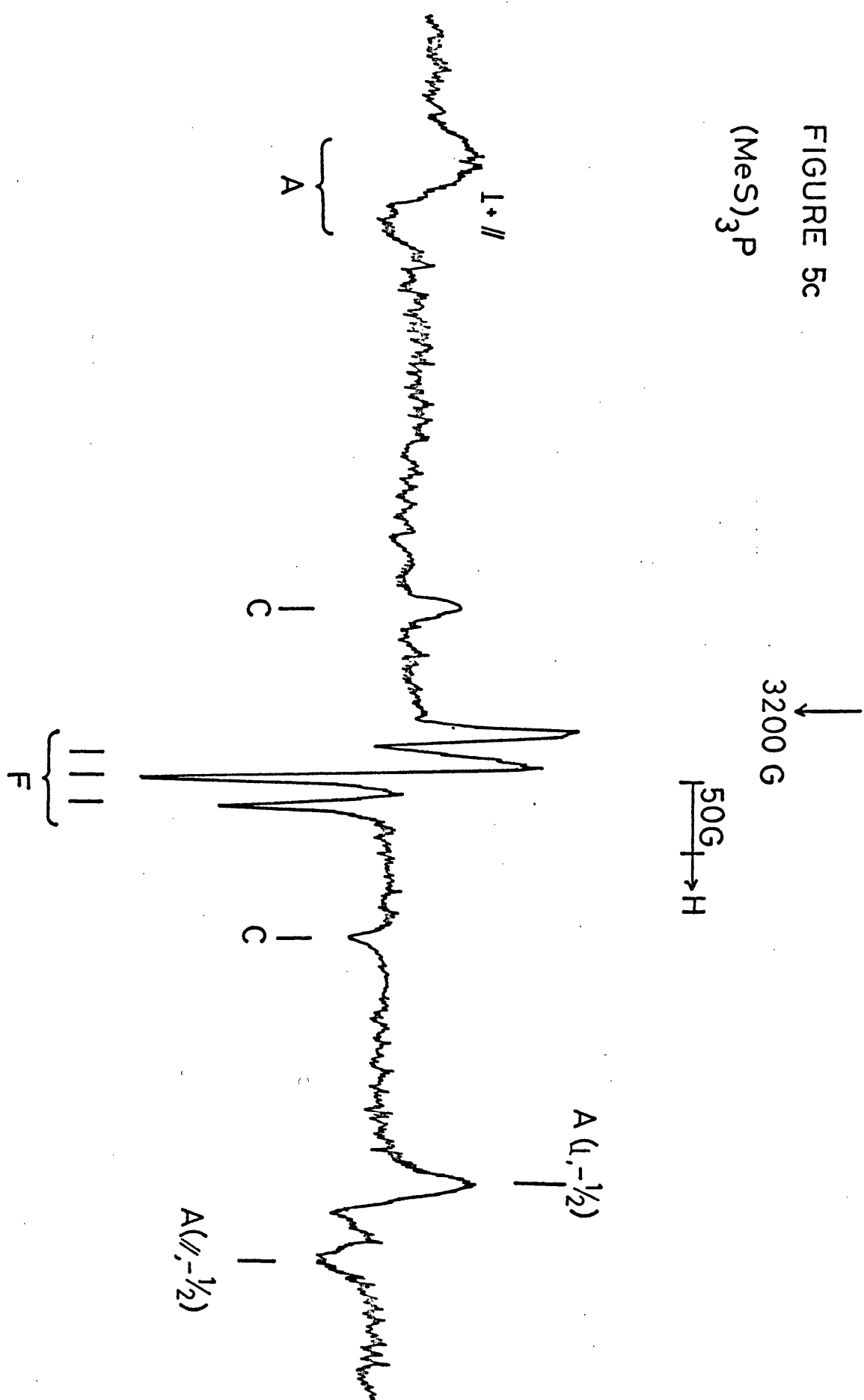


Figure 6. - First derivative X-band e.s.r. spectra for $(\text{PrS})_3\text{P}$ after exposure to Co γ -rays at 77K.

- (a) For the pure material showing features assigned to $(\text{PrS})_2\dot{\text{P}}$ (C), $\text{Pr}\dot{\text{P}}(\text{SPr})_3$ or $\text{Pr}\dot{\text{P}}\text{S}(\text{SPr})_2^-$ (A), $(\text{PrS})_4\dot{\text{P}}$ (B) and $(\text{PrS})_3\text{P}-\text{P}(\text{SPr})_3^+$ (E). In addition, features for trapped $\dot{\text{Pr}}$ radicals, as indicated, in the centre. Other weak features have not been identified, but may include those for $\text{HP}(\text{SPr})_3$, and $\text{SP}(\text{SPr})_2$ radicals.
- (b) For a mixture of $(\text{PrS})_3\text{P}$ and MeBr, after slight annealing, showing, in particular, features assigned to the (1,0) features for $(\text{PrS})_3\text{P}-\text{P}(\text{SPr})_3^+$.
- (c) For a dilute solution in methanol before anneal, showing dominating features for $\dot{\text{Pr}}$ and $\dot{\text{C}}\text{DOD}$ radicals.

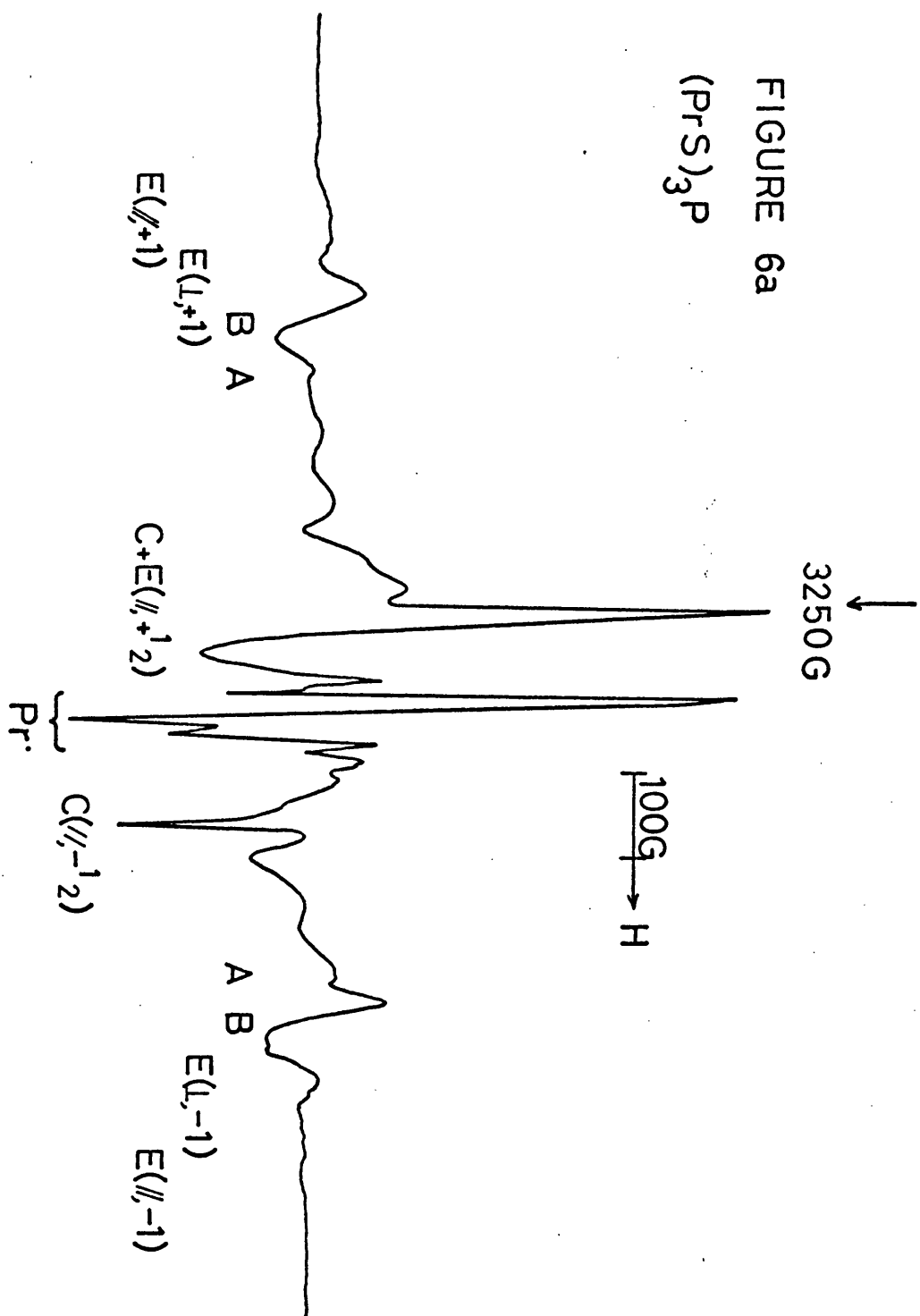


FIGURE 6b
 $(\text{PrS})_3\text{P}$

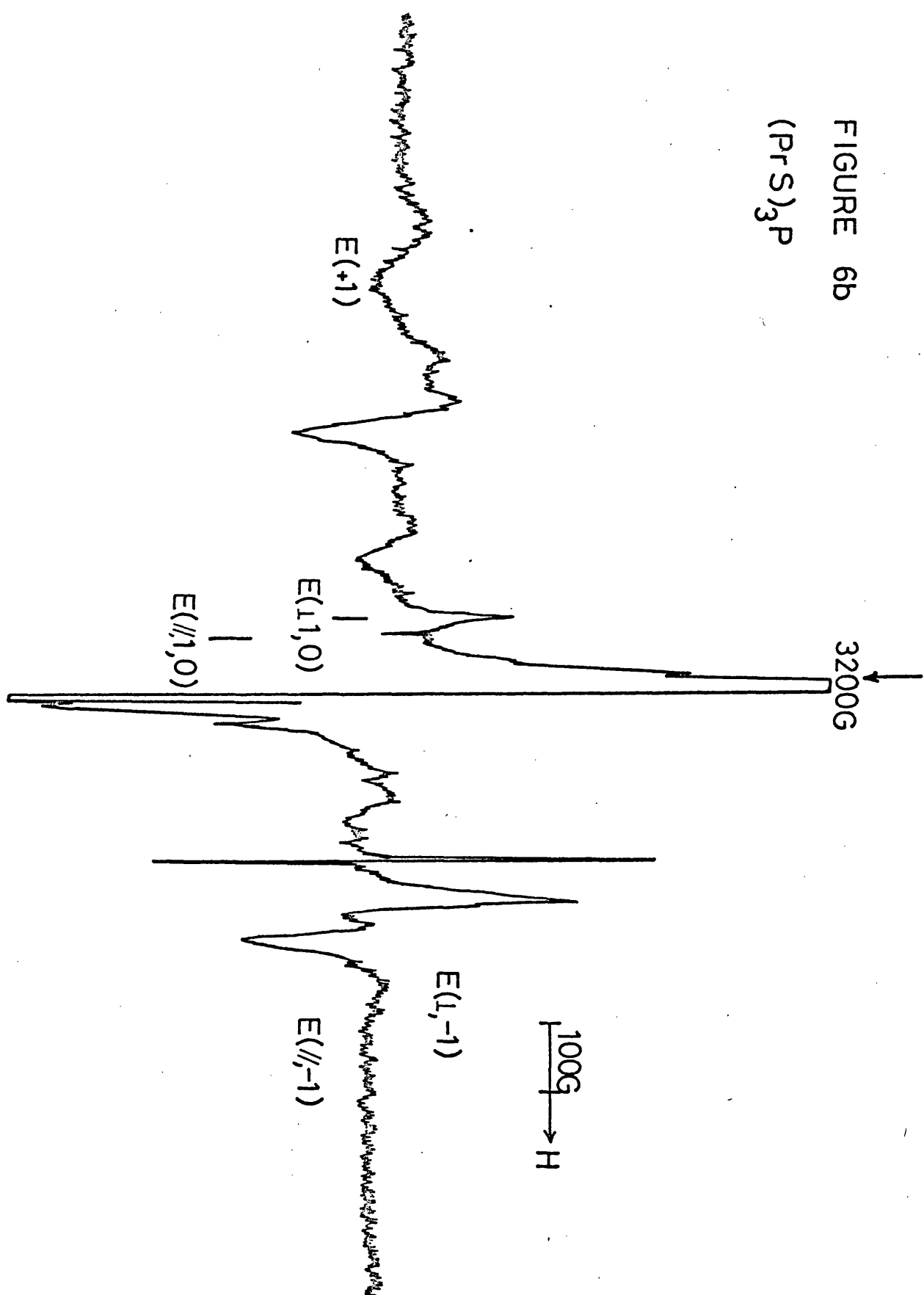


FIGURE 6c
 $(PrS)_3P$

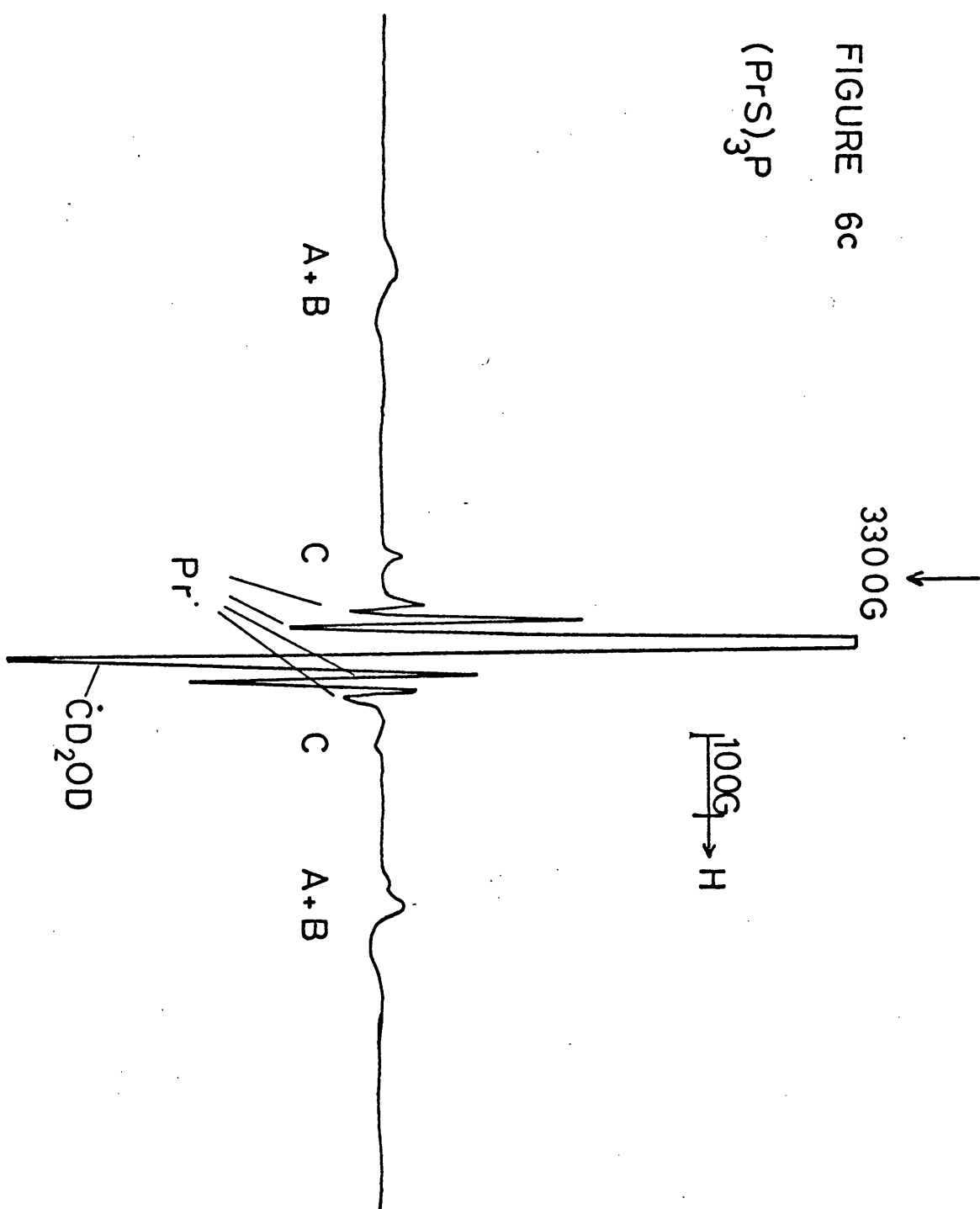


Figure 7. - First derivative X-band e.s.r. spectra for various R PCl derivatives after exposure to Co γ -rays at 77K.

- (a) Pr_2PCl before annealing, showing features assigned to the dimer-cations (E) overlapping those assigned to the dichloride, $\text{Cl}_2\dot{\text{P}}(\text{iPr})_2$, together with those for $(\text{iPr})_2\dot{\text{P}}$ (C) and $\text{iPr}\dot{\text{P}}$ radicals (central lines).
- (b) For Ph_2PCl before annealing, showing features assigned to the dimer-cations (E) which partially obscure those for the dichloride (G). (These were well defined during the annealing process.)
- (c) As b, after annealing, showing features assigned to the monochloride, $\text{Ph}_3\dot{\text{P}}\text{Cl}$ or $\text{Ph}_2\text{P}-\dot{\text{P}}(\text{Ph})_2\text{Cl}$ (I).
- (d) For $(\text{EtS})_2\text{PCl}$ after annealing, showing features assigned to $(\text{EtS})_2\dot{\text{P}}(\text{Et})\text{Cl}$ or $(\text{EtS})_2\text{P}-\dot{\text{P}}(\text{SEt})_2\text{Cl}$ (I) radicals and $(\text{EtS})_2\dot{\text{P}}$ (C) radicals.

FIGURE 7a
 $i\text{Pr}_2\text{PCl}$

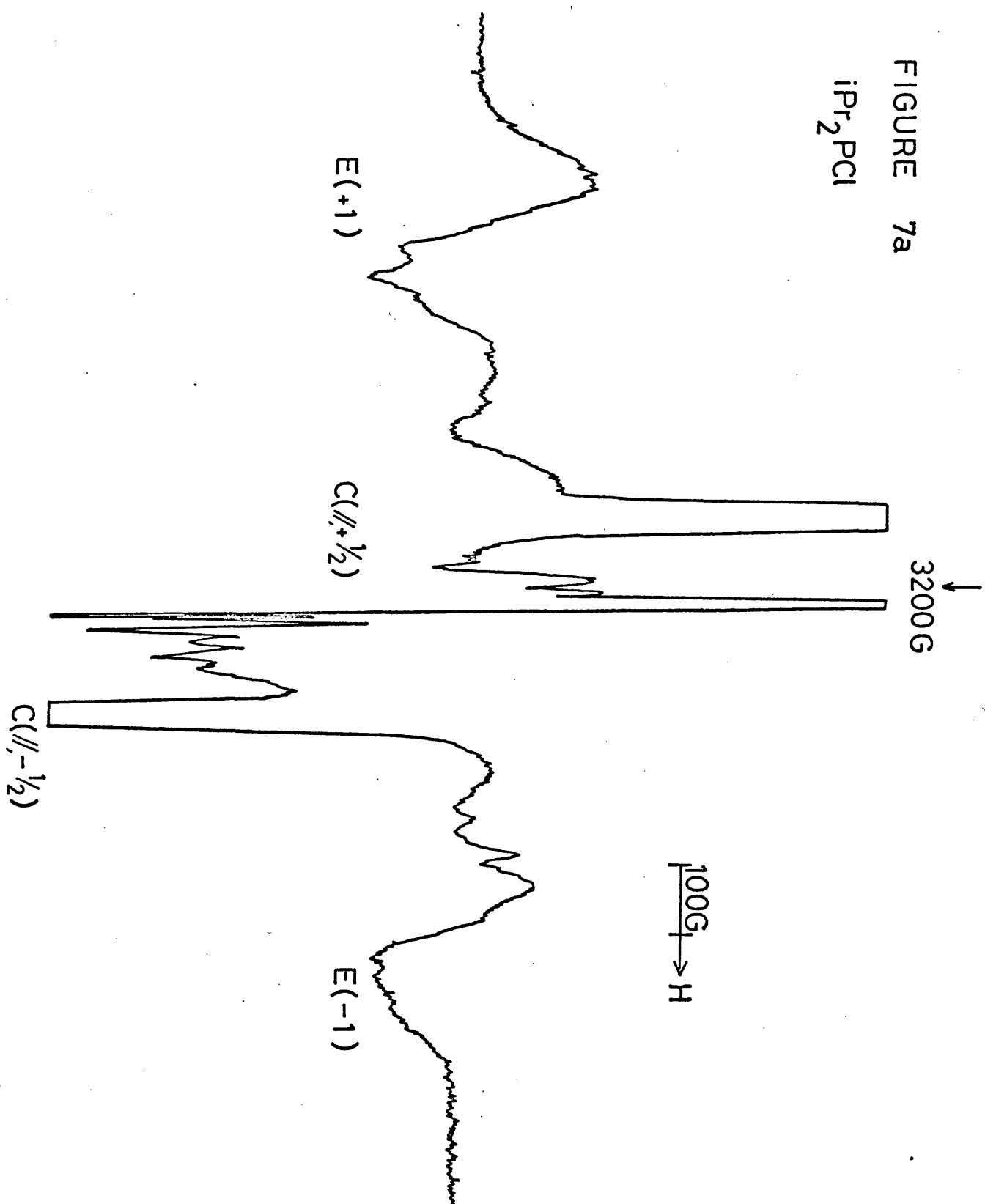


FIGURE 7b

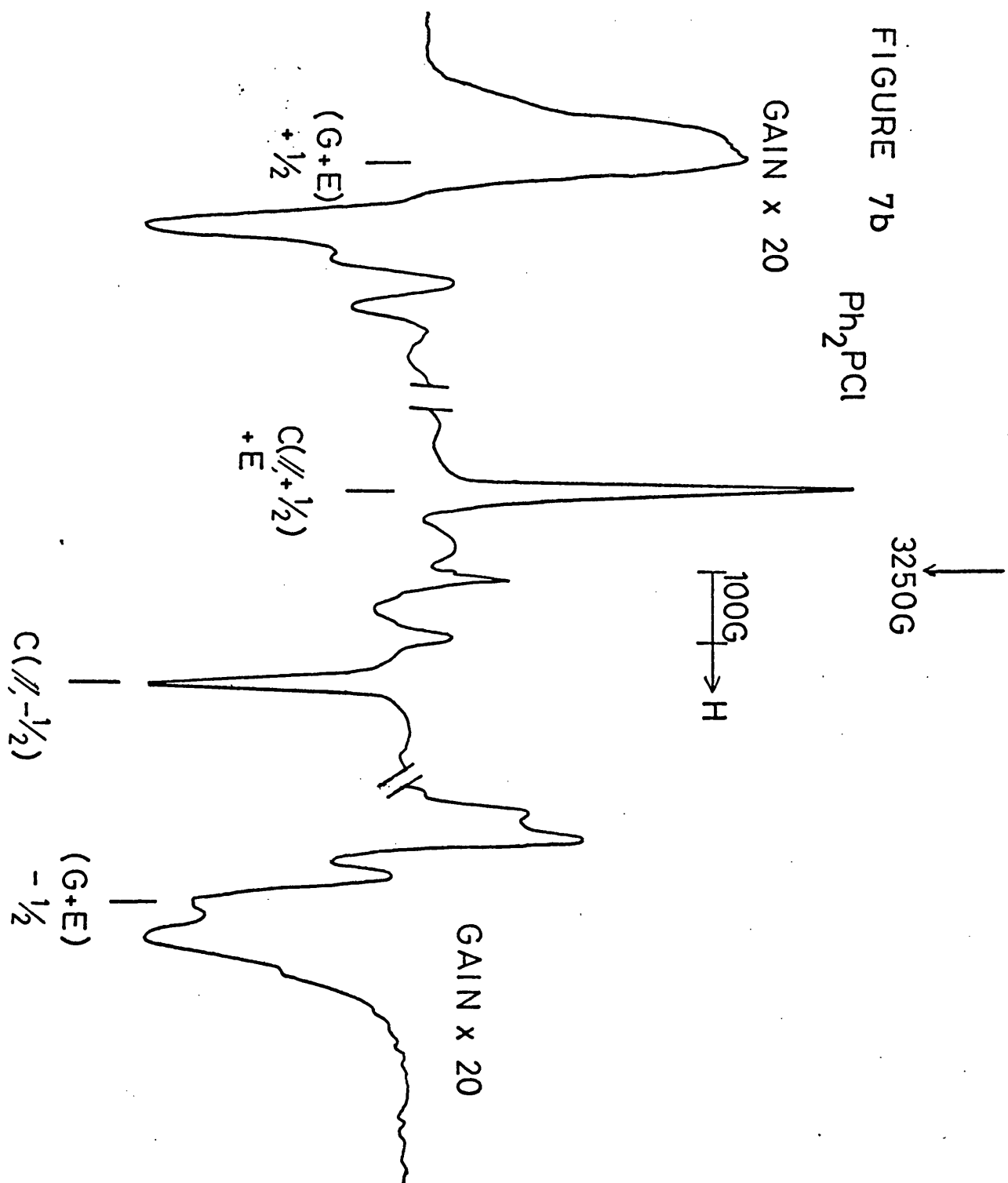


FIGURE 7c
 Ph_2PCl

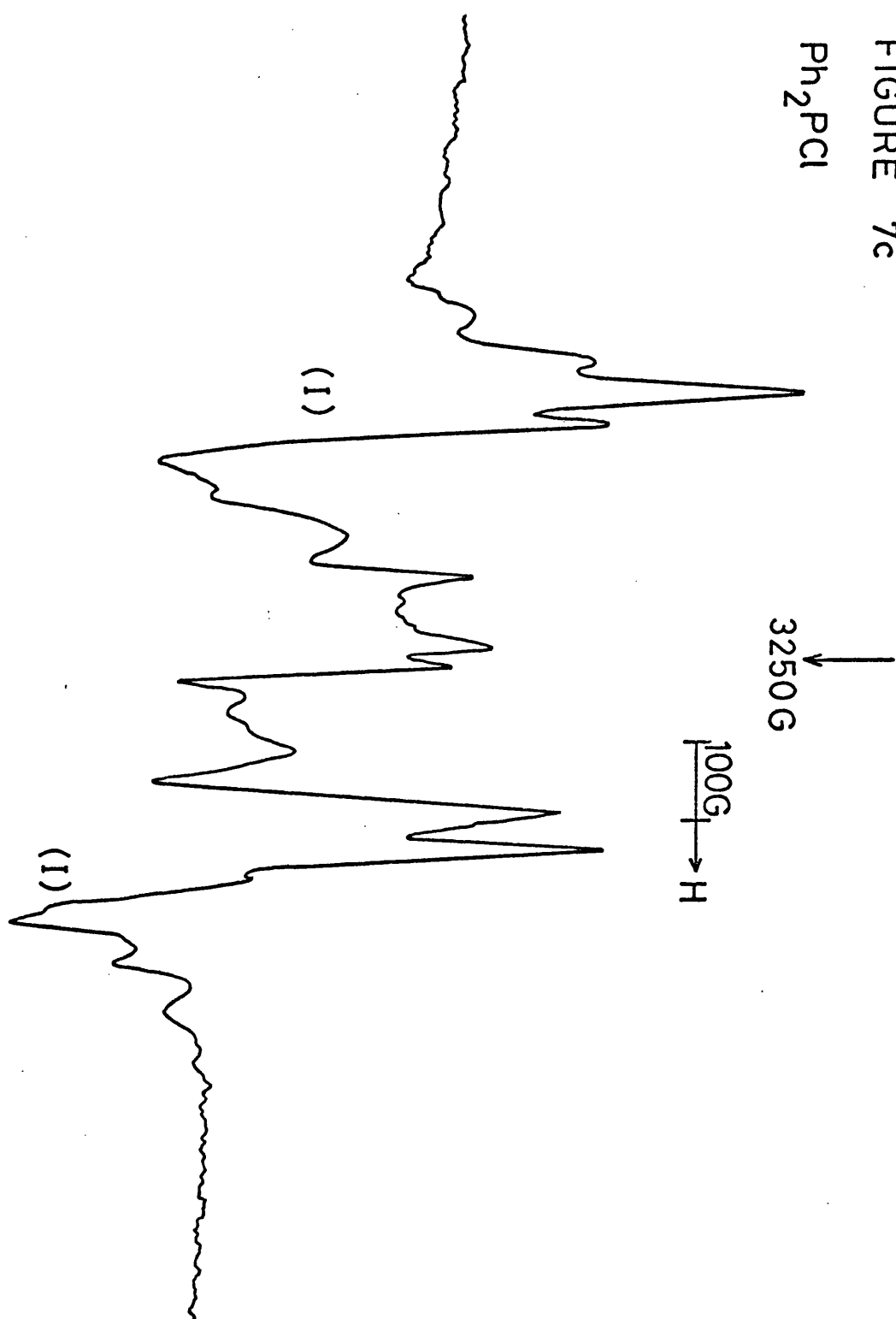
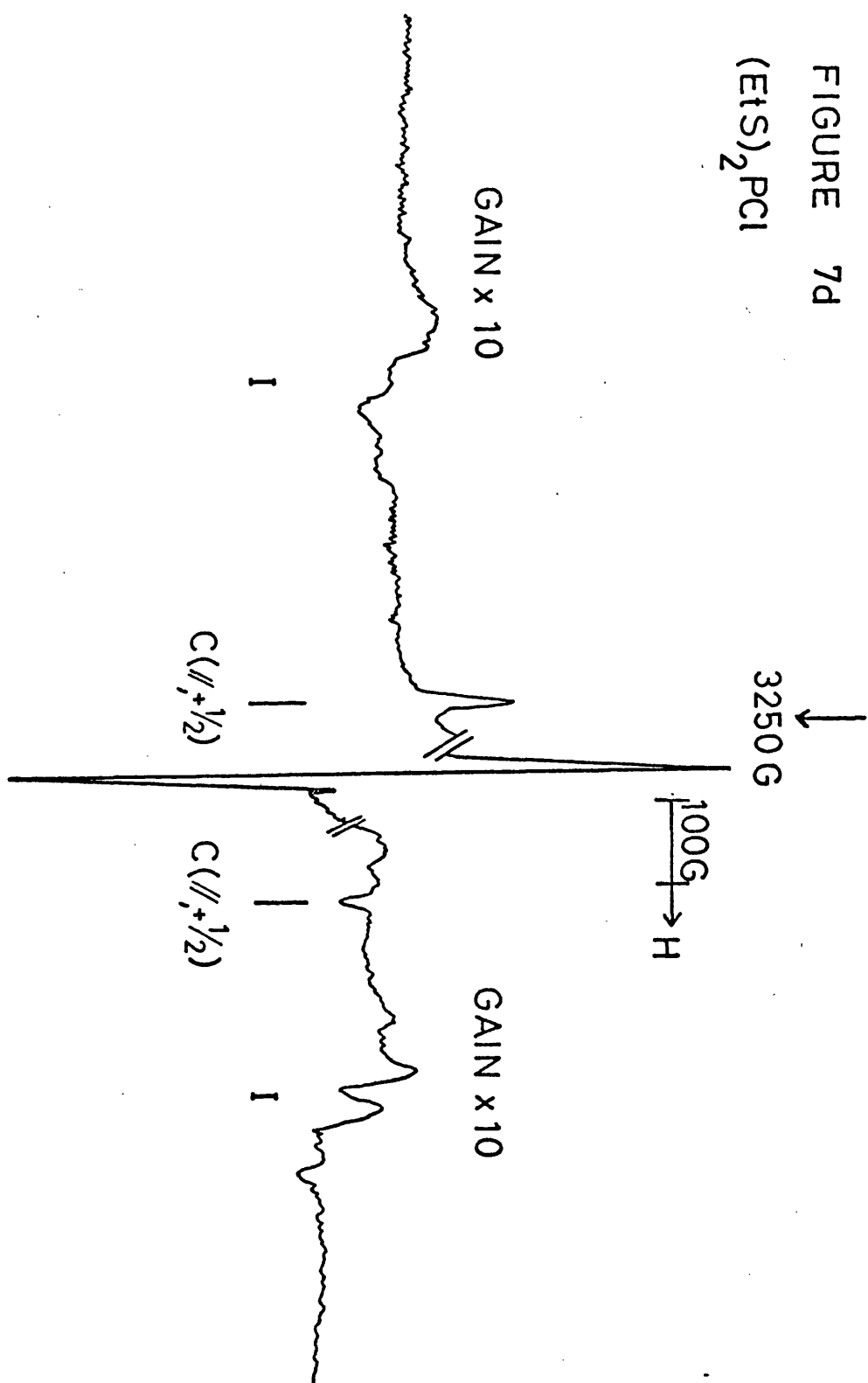
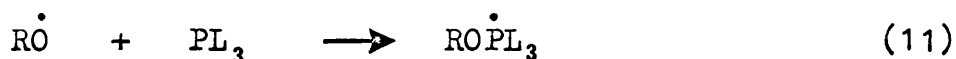


FIGURE 7d
 $(\text{EtS})_2\text{PCl}$

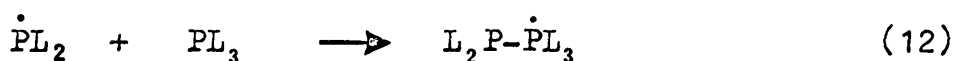


expected, on electronegativity grounds, to have relatively small hyperfine couplings to ^{31}P . Such spectra were not detected and as far as is known no radicals of this type have been reported in the literature.

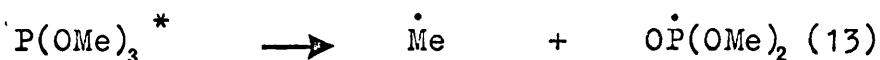
Reaction-scheme 1 summarises the processes which the results appear to require, with additional reactions forming phosphoranyl radicals being



and possible additions of the type

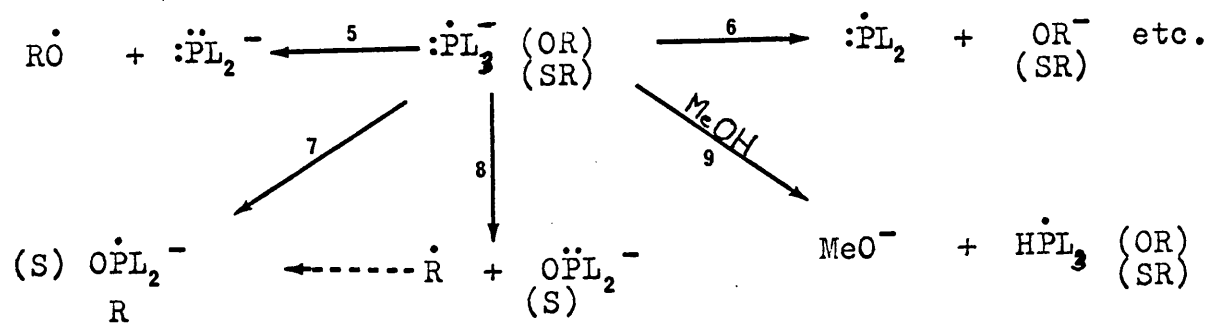


The radical anion of trimethyl phosphite, $\text{P}(\text{OMe})_3^-$, would appear to give $\dot{\text{P}}(\text{OMe})_2$ as a major product. However, methyl radicals, clearly seen in the spectra of this compound, could be produced both by (8) and by dissociation of excited substrate molecules.



Such alkyl radicals would be expected to add efficiently by step (10) to give $\text{Me}\dot{\text{P}}(\text{OMe})_3$ radicals. Step (13) is probably unlikely in a system in which electron trapping is efficient, as in the present study. Certainly, features for $\dot{\text{O}}\text{P}(\text{OMe})_2$ radicals have not been detected in any of the spectra. (However, see below)

In methanol there is some evidence that the anion $\text{P}(\text{OMe})_3^-$ is rapidly protonated, since the $\text{HP}(\text{OMe})_3$ radical is clearly trapped. The proton coupling of 157G indicates that the proton is in an axial position. This can be explained if

Scheme 1.

P(OMe)_3^- , when first formed at 77K, adopts a structure in which the lone-pair is placed axially, a structural change which requires the smallest net ligand movement. Methyl bromide has been found to suppress this species which would suggest that this mechanism is more significant than the previously suggested ³⁵H atom attack on the parent material.

Careful annealing, using the variable-temperature unit, of irradiated $(\text{MeO})_3\text{P}$ in CH_3OH did not lead to the expected rearrangement of the HP(OMe)_3 radical. Since the isomer with H in the axial position is less stable than that with H equatorial it could be expected that rearrangement would occur on heating of the sample. This was not found to occur, the axial isomer remaining until the glass softened, at which point all features rapidly decayed with no new ones developing.

The phosphoranyl radical $\dot{\text{P}}(\text{OMe})_4$ was detected in methanolic solution but not in the pure material, which suggests that (5) is not significant.

Both trimethyl and tri-n-propyl thiophosphite gave anions that readily dissociated to give $\dot{\text{P}}\text{L}_2$ radicals. (See Chapter 5.) In the pure material, the phosphoranyl radicals $\dot{\text{R}}\text{P}(\text{SR})_3$ were produced in good yield, the efficiency of this process being reduced in methanolic solutions, by trapping of the alkyl radicals. In the case of $(\text{PrS})_3\text{P}$ it was possible, in methanol solution during annealing, to notice a parallel loss of features due to the propyl radical and growth of features assigned to $\text{Pr}\dot{\text{P}}(\text{SPr})_3$. The ³¹P coupling for these phosphoranyl radicals clearly indicates that the alkyl group is to be found in an equatorial position. This could occur either by an efficient rearrangement of the axial isomer at

77K or by direct equatorial attack . This latter suggestion is unlikely since it requires far greater ligand rearrangement than does axial attack. These findings are in variance with those for $\text{HP}(\text{OMe})_3$, where axial attack is favoured and isomeric rearrangement does not appear to occur.

In contrast to $\text{P}(\text{OMe})_3$, in methanolic solution, $\text{RO}\dot{\text{P}}$ attack does not occur with the sulphides. Two radicals with very similar ^{31}P couplings are seen, one occurring at 77K, the other as $[\dot{\text{R}}]_t$ falls. It is suggested therefore that the first radical is generated by an efficient internal rearrangement, via (8) and a cage back-reaction to give the radical $\text{SP}(\text{SR})_2 \text{R}^-$. This radical should have magnetic properties similar to $\text{RP}(\text{SR})_3$. Again, the R-group is in an equatorial site. Unfortunately, electron scavenging by MeBr, which might have been expected to clarify the situation, produced a further phosphoranyl radical from attack on a substrate molecule by methyl radicals.

During annealing experiments, loss of $\dot{\text{P}}\text{L}_2$ features was seen to coincide with growth of RPL_3 features, and it is suggested that reaction (12) occurs. Though no clear coupling to a second phosphorus atom could be detected amongst the features due to the various phosphoranyl radicals, in a few instances the high field perpendicular features exhibited a splitting of ca. 35G, which was tentatively assigned to the second phosphorus, probably in an equatorial position.

As was expected, electron capture by the chlorides resulted in dissociation (6) to give $\dot{\text{P}}\text{L}_2$ radicals. Two phosphoranyl radicals were produced in all three chlorides studied, one of which was almost certainly the axial di-chloride, the other the monochloride. The results were obscured

by overlap with the dimer features, but at least five components could be detected for the axial dichloride during the annealing experiments. (Fig.7a) To obtain the dichloride, it would seem that some chlorine atom transfer occurs, the monochloride being formed by alkyl or phenyl radical attack on the parent molecules.

Photolysis. - A brief study was made of the solid-state photolysis of $(\text{MeS})_3\text{P}$ and $(\text{MeO})_3\text{P}$. Both gave clearly defined features due to methyl radicals and features due to two phosphorus containing radicals. One of these was identified as the $\text{Me}\dot{\text{P}}\text{L}_3$ radical, it's parameters being identical to those obtained in the γ -radiolysis studies. The other was assigned to $\dot{\text{P}}\text{L}_2$ radicals, the features being much weaker. Some $\text{H}\dot{\text{C}}\text{SP}(\text{SMe})_2$ radicals were also formed, probably by hydrogen abstraction from substrate molecules by methyl radicals. No clear features were obtained for the radical $\text{S}\dot{\text{P}}(\text{SMe})_2$ unless they fell underneath those for the $\text{Me}\dot{\text{P}}\text{L}_3$ radical, which seems unlikely since the ^{31}P coupling would then be greater than that for $\text{OP}(\text{OMe})_2$ radicals.

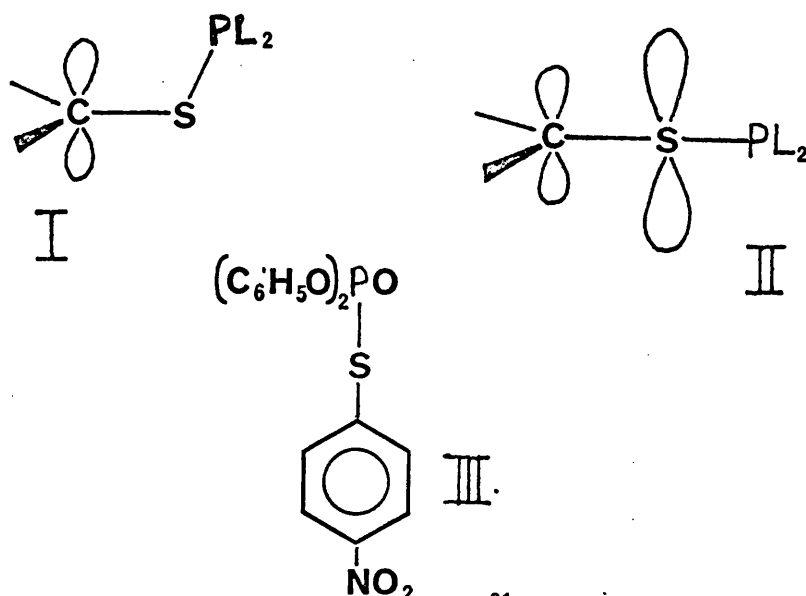
Terauchi and Sakurai, in their study of photolysed $\text{P}(\text{OEt})_3$, identified the two phosphorous containing radicals as $\dot{\text{O}}\text{P}(\text{OEt})_2$ and $\text{OP}(\text{OEt})_2$. It is hardly likely that both these species could co-exist, and a reexamination of their spectra (using the ethyl radical for calibration) suggests that one radical is $\dot{\text{P}}(\text{OEt})_2$, the other being $\text{Et}\dot{\text{P}}(\text{OEt})_2$. With this assignement their results would agree with those obtained here. The absence of $\text{OP}(\text{OMe})_2$ and $\text{S}\dot{\text{P}}(\text{SMe})_2$ can be understood if they add to neighbouring substrate molecules giving phosphoranyl radicals, which as discussed above, would have spectra very similar to those for the alkyl adducts.

Cationic Centres. - In all cases the pure compounds gave no evidence for primary PL_3^+ radicals, but clear outer features for $\text{L}_3\text{P-PL}_3^+$ dimer-cations were obtained. In methanol solution dimer-cation formation for the sulphides was suppressed, with a new pair of asymmetric lines appearing between those for species A and B. These were rapidly lost on annealing, and have been tentatively assigned to the radical cation $\text{P}(\text{SR})_3^+$.

In earlier studies,^{45,51} the $M_I = 0$ components for the dimer-cations could not be detected because of the presence of features due to other radicals. In this study, addition of MeBr led to suppression of some of these radicals with the subsequent clear identification of the low-field (1,0) components. The (0,0) component of the split central line for these radicals was never clearly seen being lost under other features, but the (1,0) parallel and perpendicular lines lie in the correct region, about 135G downfield from the central lines. The splittings ($\delta_{\parallel}$ and $\delta_{\perp}$) between the (1,0) and (0,0) components of the central features can be estimated approximately from the hyperfine parameters ($A_{\parallel}$ and $A_{\perp}$ for ^{31}P), deduced from the $M_I = \pm 1$ using $\delta_{\parallel} \approx A_{\perp}^2/H$ and $\delta_{\perp} \approx (A_{\parallel}^2 + A_{\perp}^2)/2H$.^{52,53} The identification of the central lines for the dimer-cations confirms the original identification^{51,53} and it is concluded that such dimer adducts are likely to be extremely important intermediates in radiolysis involving trivalent phosphorus compounds.

$\text{R}_2\dot{\text{C}}\text{P}(\text{SR})_2$ Species. - In addition to the radicals discussed above, in most cases, weak features were discernable, that were assigned to $\text{R}_2\dot{\text{C}}\text{SPL}_2$ or $\text{R}_2\dot{\text{C}}\text{OPL}_2$ radicals. As previously discussed these are of particular interest

because of the possible configurations that such radicals can take.



Gulik³ observed unusually large ^{31}P isotropic couplings for radical III, but no nearly isotropic coupling to ^{31}P were detected in this study, which would seem to indicate that configuration I is not favoured, the P-S conjugative configuration II being preferred.

Trends in Hyperfine Coupling to ^{31}P . - Assuming the above assignments are correct, it is possible to observe consistent trends in A (^{31}P), similar to those found on replacing -OR groups by -R. An inspection of the data in the table shows that replacing -OR by -SR in phosphoranyl radicals, results in a decrease of ca. 15-25G in A (^{31}P). Replacing -R by -Cl results in an increase of ca. 150-200G. These differences are in good accord with expectations based upon electro - negativity differences.⁴⁶

Such trends are not so obvious with the dimer-cations, though the ^{31}P coupling constants for $(\text{RS})_3\text{P}-\text{P}(\text{SR})_3^+$ cations are appreciably smaller than those for the corresponding oxy-species. It should also be noted that there is considerable

differences between the properties assigned to the "dimers" $R_3P_{(1)}-P_{(2)}R_3^+$ and those for the more tentatively assigned, but apparently similar species $R_2P_{(1)}-\dot{P}_{(2)}R_3$ (Table 3). With the dimer-cations both phosphorus atoms are equivalent, the "excess" electron probably being confined to a σ^* orbital. The $R_2P-\dot{P}R_3$ species are asymmetric in nature, with the unpaired electron being almost completely confined to $P_{(2)}$. This is clearly a phosphoranyl radical the R_2P group acting as an almost non-interacting ligand, and is not structurally equivalent to the dimer with the excess electron being differently distributed.

The dimer-cations could, in principle, also have the asymmetric phosphoranyl radical structure $(R_3P_{(1)})\dot{P}_{(2)}R_3^+$ since distortion at $P_{(2)}$ would trap the electron on this atom. A rapid oscillation of the electron from $P_{(2)}$ to $P_{(1)}$ would then have the effect of making the two phosphorus atoms appear equivalent, but would also require the spectra to be temperature-dependent. This temperature dependence is not seen and the averaged parameters are not in agreement with expectations for phosphoranyl species.

Table 3.

Some Magnetic Data for Various Phosphorus Radicals.

Parent Material	Radical	P and Cl hyperfine coupling constants			Comments
		$A_{\parallel}$	$A_{\perp}$	$A_{\text{iso}}(\text{G})$	
P(OMe) ₃	$\dot{\text{P}}(\text{OMe})_2$	285	0		suppressed by MeBr
	Me $\dot{\text{P}}(\text{OMe})_3$	882	722	775	formed by Me from MeBr
	$\dot{\text{P}}(\text{OMe})_4$	990	840	890	only formed in MeOH
	P ₂ (OMe) ₆ ⁺	720	615	650	suppressed in dil soln
	HP(OMe) ₃	680	535	583	A(¹ H) $\approx$ 157G
P(SMe) ₃	$\dot{\text{P}}(\text{SMe})_2$	237			suppressed by MeBr
	Me $\dot{\text{P}}(\text{SMe})_3$	775	670	705	formed by Me from MeBr
	$\dot{\text{P}}(\text{SMe})_4$	870	770	803	suppressed in solvents
	P ₂ (SMe) ₆ ⁺	595	480	518	
	$\dot{\text{P}}(\text{SMe})_3^+$	785	690	720	only in MeOH
P(SPr) ₃	$\dot{\text{P}}(\text{SPr})_2$	246	-15	71.8	suppressed by MeBr
	Pr $\dot{\text{P}}(\text{SPr})_3$	800	670	713	Me $\dot{\text{P}}(\text{SPr})_3$ formed by MeBr
	$\dot{\text{P}}(\text{SPr})_4$	890	790	823	suppressed in solvents
	P ₂ (SPr) ₆ ⁺	590	480	516	suppressed in solvents
	$\dot{\text{P}}(\text{SPr})_3^+$	785	690	722	only in MeOH
Pr ₂ PCl	$\dot{\text{P}}(\text{Pr})_2$	290	0	96.7	
	Cl ₂ $\dot{\text{P}}(\text{Pr})_2$	850			When coupling to Cl and
	Cl $\dot{\text{P}}(\text{Pr})_3$	650			Cl was detected, and
	Cl ₂ P ₂ (Pr) ₄ ⁺	600			features were not sufficiently resolved to justify precise data extraction

Table 3 cont.

<u>Parent Material</u>	<u>Radical</u>	<u>A_z</u>	<u>A₁</u>	<u>A_{1s}</u>	<u>Comments</u>
Ph ₂ PCl	$\dot{\text{P}}\text{Ph}_2$	268	-13	78.7	
	Cl ₂ $\dot{\text{P}}\text{Ph}_2$	840			For all phosphoranyl
	Cl $\dot{\text{P}}\text{Ph}_3$	690			chlorides A _z (Cl) $\approx$ 40G
	Cl ₂ P ₂ Ph ₄ ⁺	600			and A ₁ (Cl) $\approx$ 50G, $\pm$ <u>ca.</u> 5G
(EtS) ₂ PCl	$\dot{\text{P}}(\text{SEt})_2$	245	-15	71.8	
	Cl ₂ $\dot{\text{P}}(\text{SEt})_2$	1150			All dichlorides lost on
	Cl $\dot{\text{P}}(\text{SEt})_3$	880			anneal but no Cl ₂ ⁻
	Cl ₂ P ₂ (SEt) ₄ ⁺	600			formed.

a. 1G = 10⁻⁴ T ; b. Corrected using the Breit-Rabi equation.;
c. and for Me $\dot{\text{P}}\text{O}(\text{OMe})_2^-$.; d. and for Me $\dot{\text{P}}\text{S}(\text{SMe})_2^-$.; e. The species
 $(\text{MeS})_2\text{P}_{(1)} - \text{P}_{(2)}(\text{SMe})_3$ having A(³¹P₁) $\approx$ 35G is also thought to be
 formed. A(³¹P₂) is approx. as recorded above.; f. and/or
 PrPS(SPr)₂⁻.; g. The species (PrS)₂P_{(1)}} - $\dot{\text{P}}_{(2)}(\text{SPr})_3$ having A(³¹P) $\approx$
 35G is also thought to be formed.; h. and/or (Pr)₂P - $\dot{\text{P}}(\text{Pr})_2\text{Cl}$.;
i. and/or Ph₂P - $\dot{\text{P}}\text{Ph}_2\text{Cl}$.; j. and/or (EtS)₂P - $\dot{\text{P}}(\text{SEt})_2\text{Cl}$.

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CHAPTER 5

Organo-phosphorus Compounds (II).

5.1 Introduction.

As indicated in chapter 4, there is now a considerable body of reported data on phosphorus-centred radicals, obtained from both liquid-phase¹ and solid state studies². Phosphonyl $\dot{\text{P}}\text{L}_3$ and phosphoranyl $\dot{\text{P}}\text{L}_4$ radicals are well known but very few radicals of the type $\dot{\text{P}}\text{L}_2$ have been reported. Of those that have been reported only $\dot{\text{P}}\text{H}_2$ ³, $\dot{\text{P}}\text{F}_2$ ^{4,5} and $\dot{\text{P}}\text{Cl}_2$ ^{6,7} have been unambiguously identified. A six line spectrum, obtained on photolysis of $(\text{Ph}_2\text{P})_2$ in benzene⁸, has been attributed to the $\text{Ph}_2\dot{\text{P}}$ radical, but this result does not agree with those given below. (See discussion section.)

Radicals of the structure $\dot{\text{P}}(\text{OR})_2$ ($\text{R}=\text{H}$ or Me_3C), having $A_{\text{iso}}(^{31}\text{P}) = 83.3\text{G}$, were tentatively identified by Ingold⁹ in his study of the reaction between t-butoxy radicals, photochemically generated, and phosphine. A similar species with $A_{\text{iso}}(^{31}\text{P}) = 78.5\text{G}$, formed during photolysis of tetraethoxy diphosphine in di-t-butyl peroxide at room temperature, was identified as $\dot{\text{P}}(\text{OEt})_2$. The results given here for the radical $\dot{\text{P}}(\text{OMe})_2$, and mentioned previously¹⁰, strongly support this assignment.

5.2 Experimental.

Diphenyl phosphine chloride, di-isopropyl chloride (Maybridge Chemicals) and trimethyl phosphite (B.D.H. Chemicals) were used without further purification, bulb to bulb distillation of the chloride causing no appreciable change in the spectra. Trimethyl thiophosphite and tri-n-propyl thiophosphite were made by the addition of the respective disulphide to powdered white phosphorus in solvent acetone, under a nitrogen atmosphere. (See chapter 2) The resulting thiophosphites were used without further purification, since

their ^{31}P n.m.r. spectra, after removal of acetone, showed the presence of only one phosphorus compound. A purified sample of diethyl thiophosphine chloride was kindly provided by Professor S. Trippett.

5.3 Results and Discussion.

Interpretation of Spectra. - The spectra of all the compounds studied were very similar, being made up of two parallel type features separated by ca. 270G and ill-defined perpendicular features, frequently overlapped by lines from other species. In fact, in many cases $A_{\perp} (^{31}\text{P})$ could only be given the value of zero with the large error of $\pm 5\text{G}$. Extracting the perpendicular (x and y) data was in all instances difficult and where clear $\pm \frac{1}{2}$ features were resolved the g -tensors were usually not quite axial, leading to further interpretative ambiguity.

$\dot{\text{P}}\text{H}_2$ and PR_2 Radicals. - In contrast to Gordy et al, who obtained an isotropic spectrum of $\dot{\text{P}}\text{H}_2$ in a rare-gas matrix at 4.2K, the anisotropic spectrum of this radical has been obtained by irradiation of a sample of phosphine in solution in concentrated sulphuric acid (ca. 90% H_2SO_4). The solvent was cooled during addition of the PH_3 and frozen rapidly to 77K to avoid oxidation. The major reason for using sulphuric acid as a solvent was to anchor the radical ($\dot{\text{P}}\text{H}_2$) by hydrogen bonding and so prevent it tumbling at 77K. Irradiation of the solution gave $\dot{\text{P}}\text{H}_3^+$ as the major radical product, but clear parallel features for the $\dot{\text{P}}\text{H}_2$ radical were discernable on annealing. In a D_2SO_4 solution (D_2O equilibrated to ensure exchange) these became better defined, as did features assignable to $\dot{\text{P}}\text{D}_2$ and $\dot{\text{P}}\text{HD}$. The perpendicular features were not discernable, being concealed by intense lines from SO_4^-

and SO_3^- radicals.

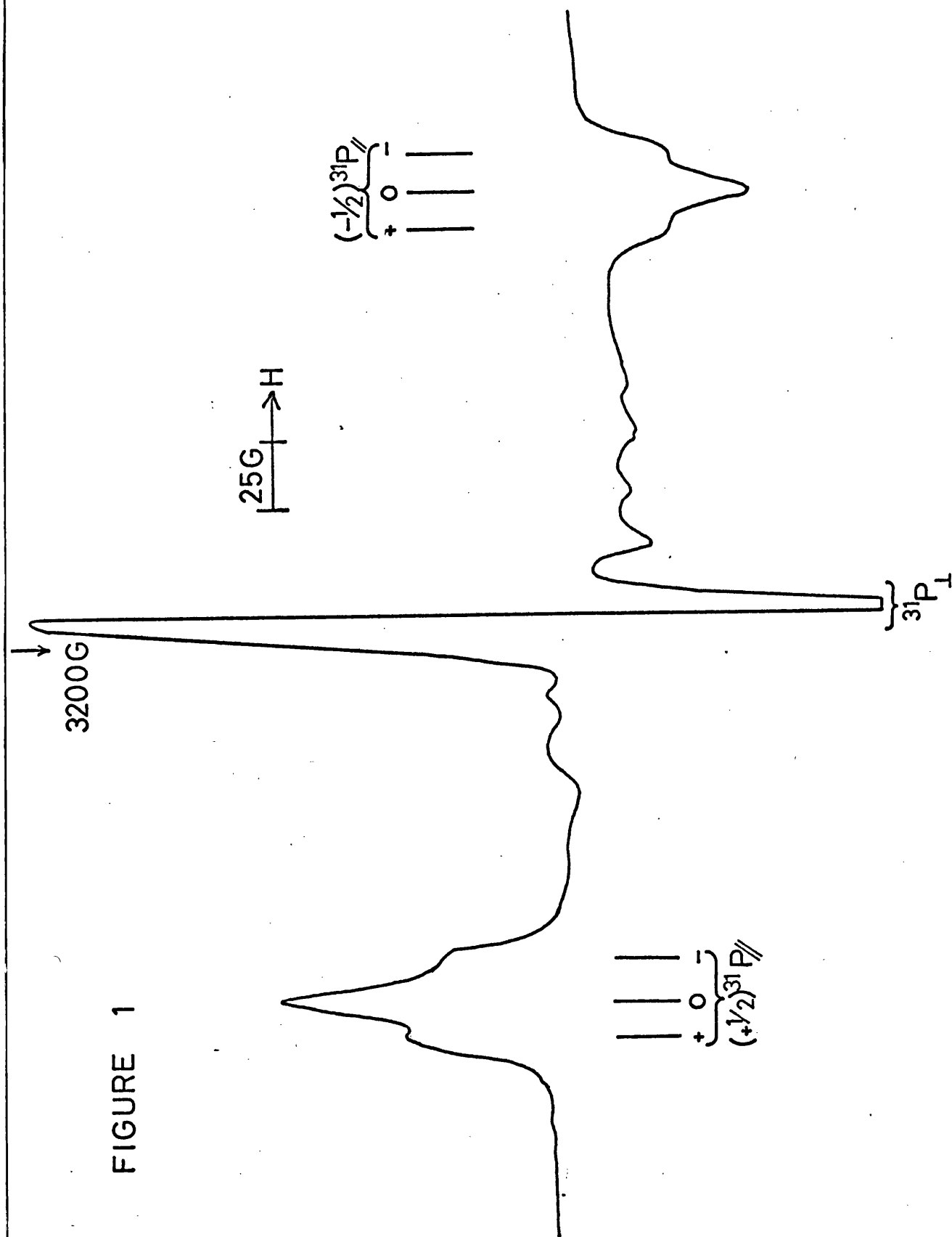
Using the isotropic coupling given in the table, $2B(\text{PH}_2) = 195\text{G}$, which is almost identical with the value for $\dot{\text{P}}(\text{CHMe}_2)_2$ ($2B = 196.5\text{G}$). These values correspond very closely to the phosphorus unit-density values of 206G , previously proposed¹², and 201G calculated from the wavefunctions of Froese¹³. It would appear that the hydrogen-bonding holding the radical is strong enough to prevent the libration usually found in radicals at 77K .

The radical $\dot{\text{P}}(\text{CHMe}_2)_2$, mentioned above, was formed in good yield by dissociative electron capture, at 77K . (Fig. 1)

$\dot{\text{P}}(\text{SR})_2$ Radicals. - Figure 2 gives a typical spectrum for these radicals, which were readily formed by γ -radiolysis of the pure parent materials. The $\dot{\text{P}}(\text{SMe})_2$ radical appears to librate at 77K , the $A_{\parallel}({}^{31}\text{P})$ value being appreciably smaller than that for the diethyl and di-n-propyl derivatives. The monotonic decrease in $A_{\parallel}({}^{31}\text{P})$ for these radicals with increase in temperature is also indicative of libration. This behaviour was not found with the other two radicals, which were temperature insensitive below ca. 140K . Furthermore, $A_{\perp}$ for $\dot{\text{P}}(\text{SMe})_2$ was close to zero at 77K , whereas an appreciable perpendicular coupling was detected for the other two radicals. The negative $A_{\perp}$ values assumed in deriving the A_{iso} values listed in the table, are confirmed by these results.

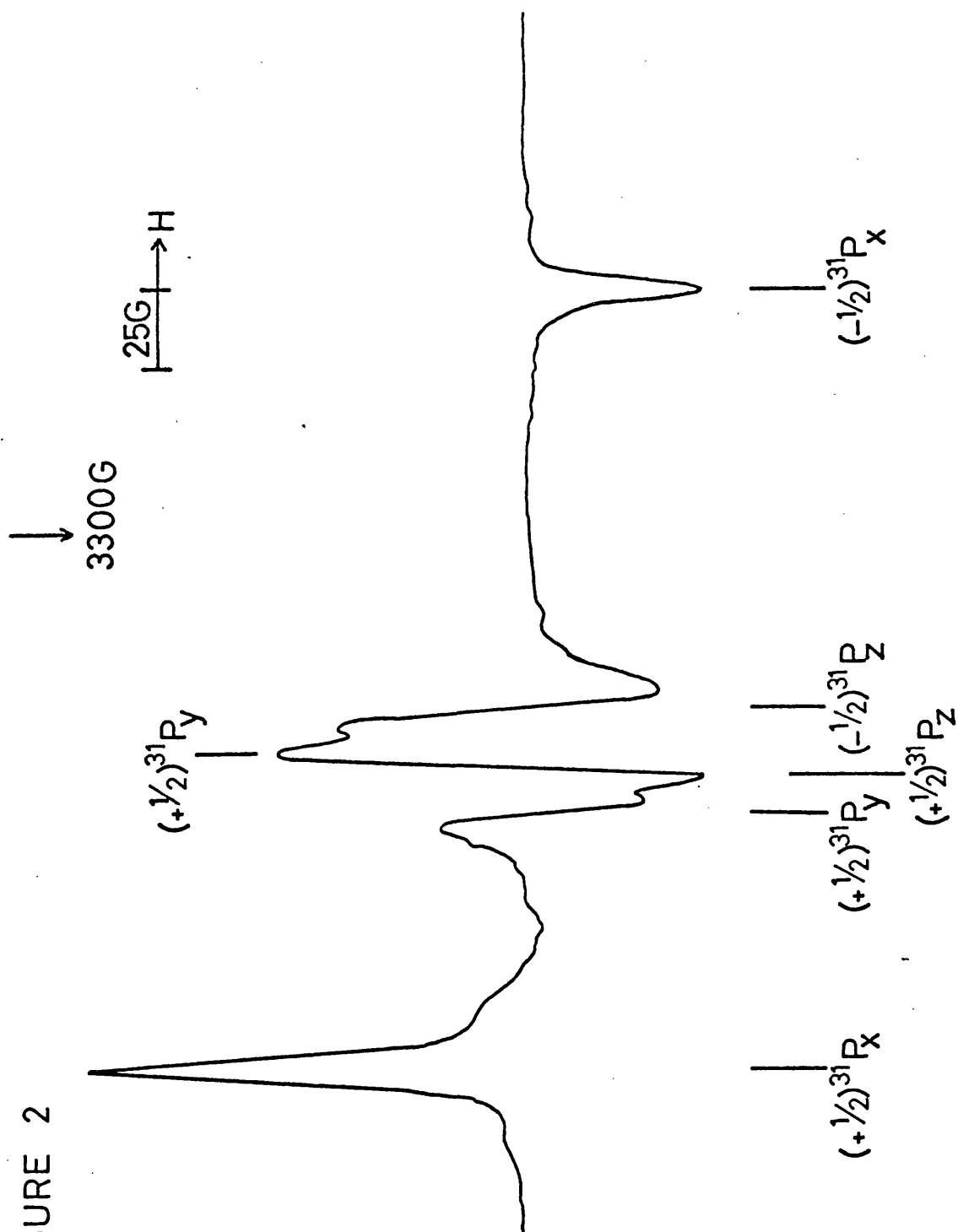
$\text{Ph}_2\dot{\text{P}}$ Radical. - The results obtained for this radical, formed from the chloride Ph_2PCl , indicate that delocalisation of the unpaired electron onto the aromatic π -systems occurs only to a minor extent. This is in accordance with the results the $\text{Ph}_2\dot{\text{P}}\text{O}^-$, $\text{Ph}\dot{\text{P}}\text{O}_2^-$ ¹⁷ and $\text{Ph}_2\dot{\text{A}}\text{s}$ ¹⁸ radicals. These first two radicals, being pyramidal, would not be expected to show marked π -

FIGURE 1



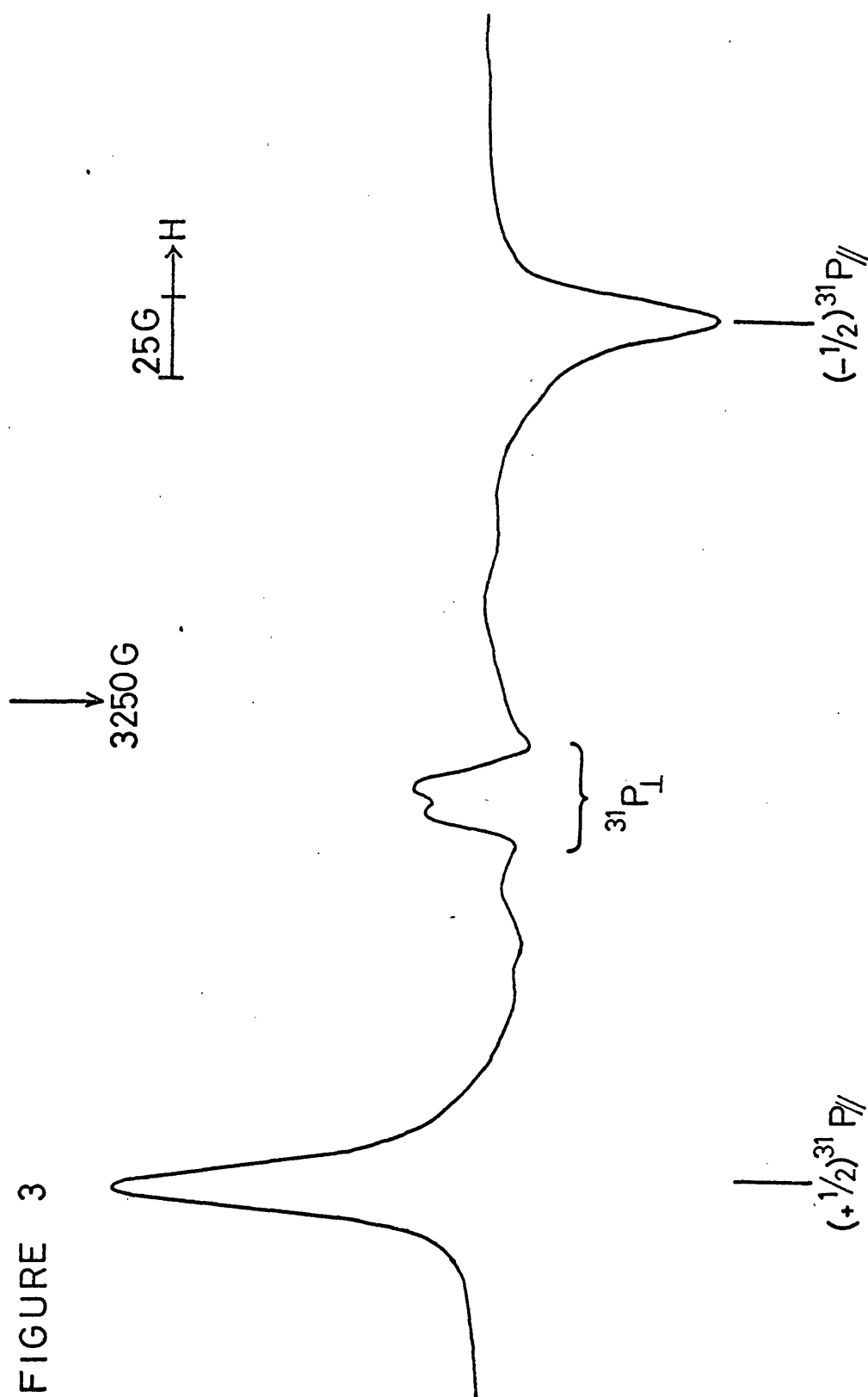
First derivative e.s.r. spectrum for Pr_2Pcl after exposure to ^{60}Co γ -rays at 77K,

FIGURE 2



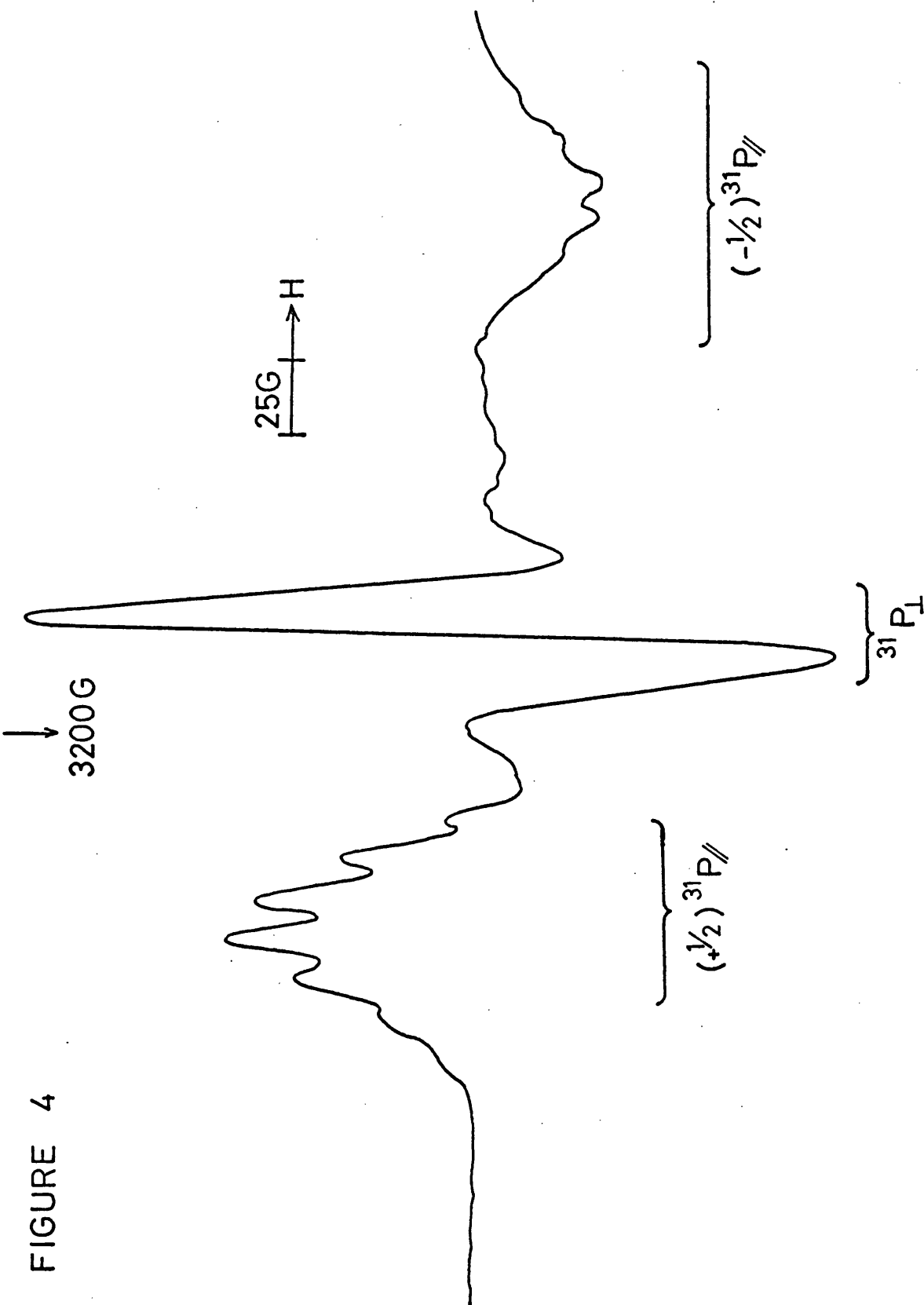
First derivative e.s.r. spectrum for $[\text{PrS}]_3\text{P}$ after exposure to ^{60}Co γ -rays at 77K and partial annealing, showing features assigned to $(\text{PrS})_2\text{P}$ radicals.

FIGURE 3



First derivative e.s.r. spectrum for $\text{Ph}_2\text{P}\cdot$ after exposure ^{60}Co γ -rays at 77K and partial annealing, showing features assigned to Ph_2P radicals.

FIGURE 4



First derivative e.s.r. spectrum for PCl_3 after exposure to ^{60}Co γ -rays at 77K and partial annealing, showing features assigned to PCl_2 radicals.

delocalisation, but the latter species could exhibit such a delocalisation, a result further stressed by Lyons and Symons¹⁷.

The liquid-phase results, previously attributed to the $\text{Ph}_2\dot{\text{P}}$ radical⁸, do not agree with those given above. The six line spectrum is more reminiscent of that normally obtained from five equivalent protons $a(\text{H}) = 6\text{G}$. No explanation can be found for this result.

$\dot{\text{PF}}_2$, $\dot{\text{PCl}}_2$ and related radicals. - A number of differing values have been reported for the $\dot{\text{PF}}_2$ radical. (Table) Gordy et al and Current et al agree on the $A_{\parallel}({}^{31}\text{P})$ value of 307G but differ on their $A_{\perp}$ values. The isotropic phosphorus coupling, obtained by Gordy and co-workers, of 84.6G, fixes the perpendicular value as $(-)\text{27.2G}$. The species with $A_{\text{iso}}({}^{31}\text{P}) = 35\text{G}$ and attributed to $\dot{\text{PF}}_2$ ²⁰ would appear to be incorrectly assigned.

Because of the differences in the assigned g -values for the radical $\dot{\text{PCl}}_2$, in PCl_3 , as studied by ^{Brinckmann} ~~Banckman~~ et al,⁶ Symons et al²⁰ and Wei et al⁷, a further check was made on this radical. (Fig. 4) The A -values assigned to $\dot{\text{PCl}}_2$ in the studies mentioned above are substantially the same, the major area of disagreement being in the relative sizes of $g_{\parallel}$ and $g_{\perp}$. Wei et al⁷, who computer simulated their results, argued that $g_{\perp} < g_{\parallel}$, but a further consideration of their results shows that the computer simulation does not reproduce the experimental spectrum in the vital area of intensities. It would appear, therefore, that the simulation is in error and since the low-field parallel lines in the spectra are clearly more intense than the high-field parallel components it seems more likely that $g_{\perp}$ is $> g_{\parallel}$.

Wei et al⁷ have argued, also, that the experimental spin-densities for the $\dot{\text{PCl}}_2$ radical favour the use of the

Table

E.s.r. data for a range of phosphinyl radicals.

Radical	Source	P Hyperfine Tensor				Other Hyperfine			g-Tensor Components			
		Components (G) ^a				Coupling Data			g_x	g_y	g_z	g_{av}
		$A_{ }$	$A_{\perp}$	A_{iso}	2B	$A_{ }$	$A_{\perp}$	A_{iso}				
PH_2	PH_3	275		80^b	195				2.002			
$P(CHMe_2)_2$	$ClP(CHMe_2)_2$	290	0	96.7	193.3	13		(1H)				
PPh_2	$ClPPh_2$	268	-13	78.7	189.3				2.000	2.005	2.009	2.0047
$P(OMe)_2$ ⁱ	$P(OMe)_2$	285							2.002			
$P(OEt)_2$ ^c	$P(OEt)_2$			78.5								2.002
$P(SMe)_2$	$P(SMe)_2$	237.6							2.002			
$P(SET)_2$	$ClP(SET)_2$	245	-15	71.8	173.7				2.002	2.013	2.021	2.012
$P(S^iPr)_2$	$P(S^iPr)_2$	246	-15	71.8	173.7				2.002	2.018	2.018	2.0127
PF_2 ^d	PF_3	308.1	-27.2	84.6	223.5				2.0027	2.0016	2.0016	
^e	P_2F_4	307	-83	47	260							
^f				35								
PCl_2 ⁱ	PCl_3	272.5	-22.5	75.8	196.7	16.5	0	5.5(^{35}Cl)	1.995	2.0187	2.0187	
^g		269	-28	71.0	198.0	15	0	5.0 "	2.001	2.021	2.021	106
^h		293	-30.5	77.3	215.7	17.5	0.3	5.8 "	2.002	1.999	1.999	

References for table.

- a. $1 \text{ G} = 10^{-4} \text{ T}$
- b. Reference 3.
- c. Reference 9.
- d. Reference 4.
- e. Reference 5.
- f. Reference 20.
- g. Reference 7.
- h. Reference 8.
- i. S.P.Mishra, personal communication.

calculated $2B^0$ values of Hurd and Coodin.¹⁵ The $A_{\parallel}(^{31}\text{P})$ of 293G, obtained by Wei et al , suggests that the radical is librating. Since $A_{\perp}$ is lower for the librating radical and therefore must be negative, it is possible to calculate that $A_{\text{iso}}(^{35}\text{Cl}) = 7\text{G}$ and $2B \approx 216\text{G}$. If the $2B^0$ value of 201.4G ¹³ is used then the spin-density is found to be close to but greater than unity, a problem that does not occur with Hurd and Coodin's value. As stressed above, there are good reasons for favouring the value of ca. 201.4G for neutral radicals. The apparent anomaly in the spin-density can then be explained by considering the high relative electronegativity of the ligands, for $\dot{\text{P}}\text{F}_2$ and $\dot{\text{P}}\text{Cl}_2$. These, it is suggested, confer a small positive change on the phosphorus atom contracting the orbitals close to phosphorus and thereby increasing the ^{31}P coupling, and rendering the calculated $2B^0$ value of 201.4G too small.

There are some difficulties in calculating the π -spin densities on the ligands of $\dot{\text{P}}\text{F}_2$ and $\dot{\text{P}}\text{Cl}_2$ even though the hyperfine coupling constants for ^{19}F and ^{35}Cl are quite normal. The powder spectra used in these studies only provides data along the symmetry g axes and not along the ligand magnetic axes, and since the bond angles are unknown, the principal tensor component values cannot be calculated. With the added complications of spin-polarisation of the P - Hal bond and through-space dipolar interactions it was decided not to make any attempt at these calculations.

Trends in Isotropic Hyperfine Coupling Constants. -

Even though a variety of ligands are present, the $A_{\text{iso}}(\text{P})$ coupling for the $\dot{\text{P}}\text{L}_2$ radicals vary by only a small amount, i.e. from ca. 72 to 97G. This is especially noticeable when compared with similar nitrogen radicals ($\dot{\text{N}}\text{L}_2$) where the ^{14}N coupling vary from ca.

7G ($\text{Ph}\dot{\text{N}}\text{H}$)²² to ca. 17G ($\dot{\text{N}}\text{F}_2$)²³. The nitrogen radicals show considerable delocalisation into the ligands, as typified by the anilino radical $\text{Ph}\dot{\text{N}}\text{H}$ $A_{\text{iso}}(^{14}\text{N}) = 7.77\text{G}$ which shows a relatively large proton hyperfine coupling. This result can be compared with those for the $\dot{\text{N}}\text{H}_2$ radical (10.3 to $\approx 14\text{G}$)^{24,25} and $\dot{\text{N}}\text{Me}_2$ ($\sim 14.8\text{G}$)²⁶ which show a far lower tendency for ligand spin delocalisation. In contrast, $\dot{\text{P}}\text{Ph}_2$ shows no detectable ring-proton hyperfine coupling and there is only a small decrease in 2B (^{31}P) on going from $\dot{\text{P}}(\text{Alk})_2$ to $\dot{\text{P}}\text{Ph}_2$.

The lower value of A_{iso} for $\dot{\text{P}}(\text{SR})_2$ radicals is probably indicative of a greater degree of delocalisation of the spin onto the ligands. Since such a delocalisation requires $2p\pi - 2p\pi$ overlap for the nitrogen radicals and $3p\pi - 2p\pi$ overlap for most of the phosphorus radicals, the favourable size and energy matching in the case of nitrogen and its ligands greatly increases the delocalisation. This then explains the increase in delocalisation to be found with $\dot{\text{P}}(\text{SR})_2$ radicals since delocalisation is again favoured on orbital size and energy grounds, with a $3p - 3p$ interaction occurring.

A tentative explanation can be given for the clear increase in $A_{\text{iso}}(^{31}\text{P})$ on going from $\dot{\text{P}}\text{H}_2$ to $\dot{\text{P}}(\text{Alk})_2$, a similar trend being found in the nitrogen radicals.²⁴⁻²⁶ This latter trend was linked²⁵ to a change in bond angle on replacing H by alkyl,²⁷ and it may well be that a similar increase occurs for the phosphorus radicals. (However, it should be noted that the explanation offered for this link between A_{iso} and θ is quite different in the two cases.)^{25,27}

The orbital-matching argument outlined above also seems to provide an explanation for the downward trend in

$A(^{31}\text{P})$ on going from $\dot{\text{P}}\text{F}_2$ (84.6G) to $\dot{\text{P}}\text{Cl}_2$ (ca. 75G) and the reported upward trend on going from $\dot{\text{N}}\text{F}_2$ (ca 16.8G) to $\dot{\text{N}}\text{Cl}_2$ (20G). Delocalisation would be favoured for $\dot{\text{P}}\text{Cl}_2$ on the one hand and $\dot{\text{N}}\text{F}_2$ on the other. Further consideration of the published data for the $\dot{\text{N}}\text{Cl}_2$ radical casts some doubt on the $A(^{14}\text{N})$ value of 20G. The perpendicular coupling to ^{35}Cl (-17G) would appear to be rather larger than would be predicted from the results of the α -chloro alkyl radicals, and the ^{14}N coupling tensor components (40,14,6) are unusually asymmetric. Consideration of the published spectra seems to indicate that the ^{14}N coupling is better taken as $A_{\parallel} = +40\text{G}$, $A_{\perp} = \pm 5\text{G}$, with $A_{\text{iso}}(^{14}\text{N}) = 16.7$ or 10G. The former value accords well with that for $\dot{\text{N}}\text{F}_2$. It also suggests that there is little difference in delocalisation between the two nitrogen radicals.

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CHAPTER 6

Alkyl Chloro Silanes and Hexamethyl Disilane.

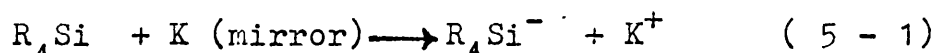
6.1 Introduction.

Silicon, isolated in the middle of the 19th. century, behaves, in many ways, in a similar manner to carbon. The major difference lies in the scarcity of $p\pi - p\pi$ bonded compounds. Whilst formation of such bonds is not impossible, it is, in general, energetically unfavourable. This is especially true for π -bonds formed between carbon and silicon, the result being that the kinetics of the pyrolysis of organosilyl compounds is greatly simplified¹. Most carbon compounds decompose, on pyrolysis, via a free radical mechanism, the kinetics of which is complicated by chain mechanisms propagated through the formation of double bonded compounds. Since this does not take place with silicon compounds the kinetics information obtained gives a direct measure of the bond dissociation energies involved^{1,2}.

A large number of radical reactions have been postulated in silicon chemistry, but until recently very few of the radicals involved had been isolated. The position is slowly being improved, though there still remains a dearth of structural information on the more complex polysilyl radicals.

6.2 Radical Anions of the Phenyl Silanes.

A number of organosilicon radical anions have been characterised using e.s.r. techniques, all of which have one or more aromatic ligands. Most of the radicals have been produced by reduction with an alkali metal³.



The coupling to silicon-29 (^{29}Si , $S_I = \frac{1}{2}$; 4.2%) found in all these radicals is small (5 - 20 G) leading to the conclusion

Table 1

Radical	Matrix	a_{SiH}	a_{CH_3}	a_{X}	a_{Si}	g val.	reference.
$\cdot\text{CH}_3$	Kr	-	23.0	-	-	-	5
$\cdot\text{SiH}_3$	Kr	8.1	-	-	266	2.003 $_{//}$	6,7.
	Xe	-	-	-	199	2.007 $_{\perp}$	
$\cdot\text{SiH}_3$	Soln.	7.84	-	-	-	2.0032	8,9.
		7.96	-	-	-	-	
$\cdot\text{GeH}_3$		15.0	-	-	75	2.003 $_{//}$	6,7.
		-	-	-	-	2.017 $_{\perp}$	
$\cdot\text{SnH}_3$		26.0	-	-	-	2.003 $_{//}$	6
						2.025 $_{\perp}$	
$\cdot\text{SiF}_3$	SF_6	-	-	136.6	498	2.003	10
$\cdot\text{SiCl}_3$	SiCl_4	-	-	13.4	440	-	11
	Cl_3SiCH_3	-	-	12.4	416	-	11
	adamantane	-	-	-	408	-	14
$\cdot\text{GeCl}_3$		-	-	-	220	-	12
$\cdot\text{SiF}_2\text{H}$	SF_6	89.9	-	77.8	-	2.0013	10
$\cdot\text{SiFH}_2$		34.6	-	55.2	-	2.0024	10
$\cdot\text{Si}(\text{CH}_3)_3$	$\text{Si}(\text{CH}_3)_4$		6.32	-	172.5	-	11
	$\text{ClSi}(\text{CH}_3)_3$	-	6.2	-	129	-	11
$\cdot\text{Si}(\text{CH}_3)_3$	Solv.	-	6.34	-	183	2.0031	8,13,9,5
		-	6.28	-	181	-	15
	Solid	-	6.3	-	-	2.0029	15
$\text{Me}_3\dot{\text{Ge}}$		-	5.5	-	-	2.0104	13
$\text{Et}_3\dot{\text{Si}}$		-	5.73	-	-	2.0030	8
		-	0.16	-	-	-	
$\text{Me}_2\dot{\text{Si}}\text{F}$	SF_6	-	4.53	65.21	-	2.0022	10
$\text{Me}_2\dot{\text{Si}}\text{Cl}$	$\text{ClSi}(\text{Me})_3$	-	5.2	-	229	-	4
	$\text{Cl}_2\text{Si}(\text{Me})_2$	-	5.2	-	215	-	11

Table 1 (Continued)

Radical	Matrix	a_{SiH}	a_{CH_3}	a_x	a_{Si}	g val.	Ref.
$Me_2\dot{Si}Cl$	Solid	-	-	-	290//	2.003	15
$Me\dot{Si}Cl_2$	$Cl_2Si(Me)_2$	-	-	10.5	295	-	11
	Cl_3SiMe	-	-	11.4	308	-	11
$Me_2\dot{Si}H$	Soln.	17.3	7.30	-	183	2.0031	8,9
		16.99	7.19	-	-	-	
$Me\dot{Si}H_2$	Soln.	12.11	8.21	-	-	2.0032	8,9
		11.8	7.98	-	-	-	
	Solid	-	8.0	-	181	-	15
$Me_3SiCH_2\dot{Si}Me_2$	Soln.	-	5.56	-	-	2.003	8
		-	6.43	-	-	-	
$Me_3Si\dot{Si}Me_2$	Soln.	-	8.21	-	137	2.0036	8,13
		-	0.47r	-	-	-	
$Me_3Si\dot{Si}MeH$	Soln	16.30	8.15	-	-	2.0037	8,13
		16.50	0.30	-	-		
$(Me_3Si)_3\dot{Si}$	Soln.	-	0.44r	-	-	2.0050	8

that the spin of the unpaired electron is delocalized wholly onto the aromatic ligands. In some cases, interaction of the silicon 3d-orbitals has been postulated⁴.

6.3 Silicon - Centred Radicals.

Data are now available for most of the simple silicon - centred trivalent radicals (Table 1). The silyl radical, $\dot{\text{SiH}}_3$, has been isolated in both krypton and xenon matrices, and though there is some discrepancy between the ^{29}Si coupling constants obtained in the two matrices, the conclusions drawn from the results are similar. Comparison of the results with those for the methyl radical indicate a change in structure. The methyl radical has a planar structure, the free electron occupying a p-orbital lying at right angles to the plane of the C-H bonds. The silicon coupling of 199G, obtained for the silyl radical in a xenon matrix, indicates a degree of s-character in the free spin orbital of $\dot{\text{SiH}}_3$. This requires the radical to have deviated to some extent from the planar. A comparison of the structure of all the Group IV radicals can be found in Table 2.

Table 2.

Radical	s-character of bonding orbitals	$\begin{array}{c} \text{X} \backslash \\ \text{Si} \\ / \text{X} \\ \text{M} \end{array}$ bond angle	pyramidal angle
$\dot{\text{CH}}_3$	0.333	120°	90°
$\dot{\text{SiH}}_3$	0.285	113.5°	74°
$\dot{\text{GeH}}_3$	0.295	115°	76.5°
$\dot{\text{SnH}}_3$	0.31	117°	85°

The difference in structure of these radicals is explained

by considering their varying electronegativities.

Carbon, having a greater electronegativity than hydrogen, polarizes each of the C-H bonds inducing a negative charge to reside on it. This is best stabilized if the 2s-orbital, being of lowest energy, is preferentially filled. Maximization of the s-character in the three C-H bonds, by using sp^2 hybrid orbitals, brings this about, with the unpaired electron remaining in a p-orbital.

Each of the three other Group IV elements have a lower electronegativity than hydrogen and it is therefore more favourable for the M-H bonds to have greater p-character. With this occurring, the bonding involved can be considered as being neither sp^2 or sp^3 but some intermediate, leading to an appreciable bending of the structure.

The decrease in the ^{29}Si hyperfine coupling with substitution of methyl groups for H was initially thought to indicate a change in radical geometry⁸, leading to a near planarity for the trimethylsilyl radical. Sharp and Symons¹⁵ have convincingly argued that this conclusion is in error and that no such change is observed. Comparison of their results with those obtained for the silyl radical in krypton and xenon^{6,7} indicate the krypton value for ^{29}Si (266G) to be incorrect, the xenon result (190G) fitting the expected trends more fully. Further work by Sharp and Symons¹⁶ on the isoelectronic radicals AlR_3^- and PR_3^+ , which might have been expected to further substantiate their conclusions, only provides some unexpected results. Alkyl substitution leads to a greater bending of the aluminium radicals and a flattening in the phosphorus case, both results being explained using a hyperconjugative mechanism.

6.4 This Work.

The work carried out in this study falls into major categories, the effects of γ -radiolysis on silicon compounds and the production of chlorosilyl radicals by liquid-phase photolysis. In general, the amount of information available on the structure of the more complex silyl radicals is relatively small, the only work published to date being that on the γ -radiolysis of the chlorosilanes.¹¹

Roncin et al, in their study¹¹ irradiated a series of chloromethylsilanes, tetramethylsilane and silicon tetrachloride. In each case the predominant radical obtained was the cation product $\dot{\text{C}}\text{H}_2\text{SiX}_3$, the anion product being present in a much lower concentration. In some cases loss of CH_3 was postulated to explain the radical produced. Since the $\dot{\text{C}}\text{H}_2\text{SiX}_3$ signal was so large, identification of the other radicals present was dependant upon the detection of the ^{29}Si hyperfine couplings.

In general, the results obtained for the chlorosilyl radicals were what could be expected from the trends noticeable in previously reported data (Table 1), but in the case of the trimethyl silyl radical the results deviated from those previously obtained. The ^{29}Si hyperfine couplings for this radical, when measured in two different matrices Me_4Si and Me_3SiCl , were found to differ considerably. The value obtained in tetramethyl silane (172.5G) was essentially the same as that found for this radical in solution,^{8,9,13} but the value in trimethylchloro silane (129G) was very much lower. This large change in silicon coupling was attributed to the change in dipole moment found in going from Me_4Si to Me_3SiCl (2.9 debye).

Such a large matrix effect, it was felt, required considerably more study since it cast doubt on previous findings on the $\text{Me}_3\dot{\text{Si}}$ and $\dot{\text{Si}}\text{H}_3$ radical planarities¹⁵, and suggested that inner electron polarization, by the spin of the free electron, played a far greater part in the ^{29}Si coupling constant than that found with ^{13}C .

6.5 Experimental.

Samples of all the silanes used were kindly donated by Dr I.M.T. Davidson. Small quantities of chlorosilane were irradiated at 77 K in sealed silica tubes (chapter 2), the samples having been distilled into the tubes prior to sealing off under vacuum ($< 10^{-3}$ torr).

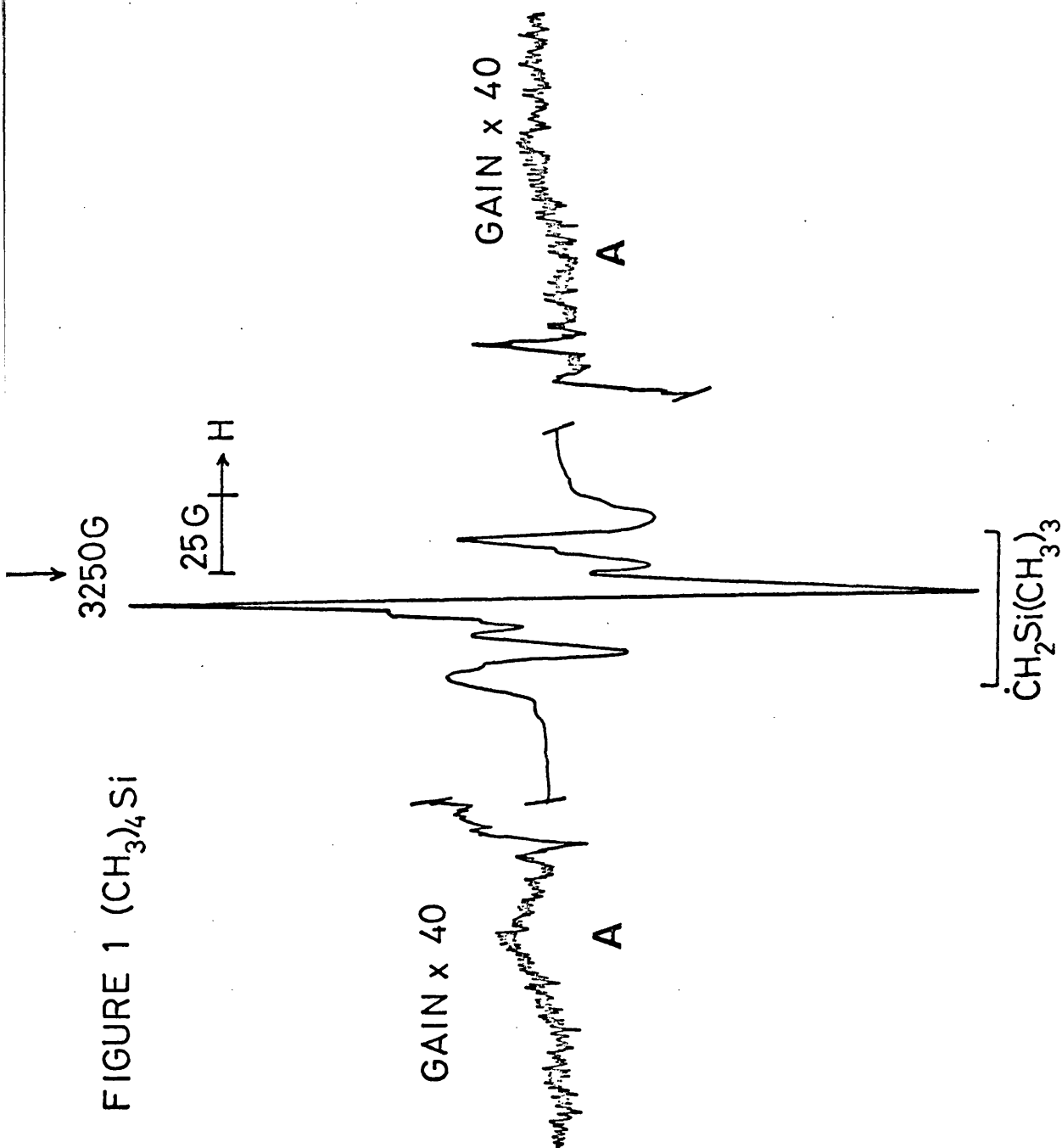
Samples prepared for photolysis experiments consisted of degassed solutions of the silane and t-butyl peroxide (1:1, v:v) in isopentane. The solutions were sealed, under vacuum, in silica tubes. The u.v. source and experimental procedure are described in chapter 2.

6.6 Results.

The γ -irradiated methyl chlorosilanes all gave similar results to those of Roncin¹¹, though the spectra obtained after annealing showed less hyperfine structure.

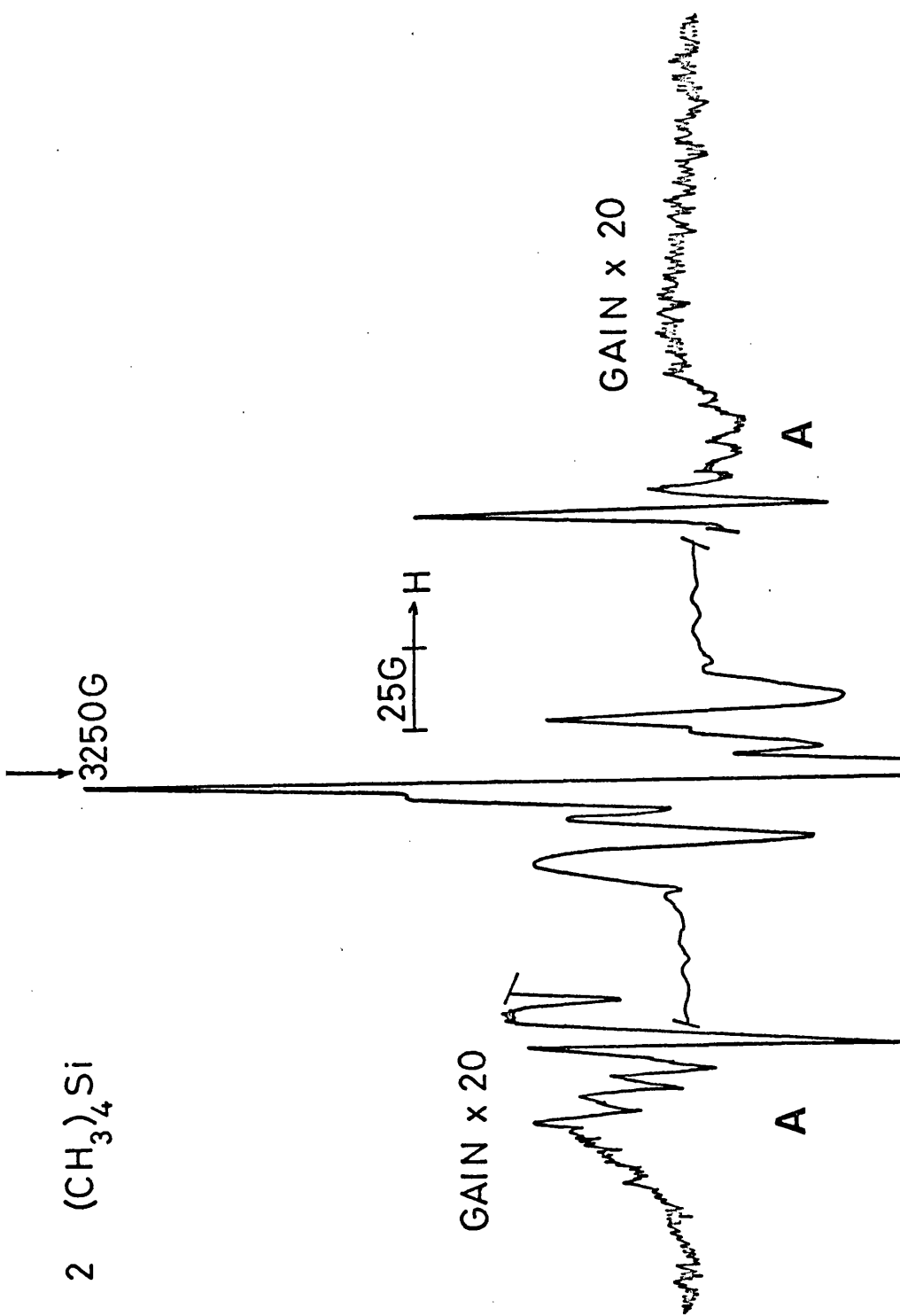
Tetramethylsilane. - The spectrum obtained for tetramethylsilane (Fig. 1) shows the predominant $\dot{\text{C}}\text{H}_2\text{Si}(\text{CH}_3)_3$ radical and, though complicated by the presence of a hydro-carbon impurity, the ^{29}Si satellite lines attributed to the $\text{Me}_3\dot{\text{Si}}$ radical. Controlled annealing of the sample from 77 K to 150 K enabled the proton hyperfine coupling, due to the methyl groups, to be seen clearly (Figs 2 and 3). Attempts to

FIGURE 1 $(\text{CH}_3)_4\text{Si}$



X-Band e.s.r. spectrum for γ -irradiated Me_4Si at 77K, showing features assigned to Me_3Si radicals (A) and CH_2SiMe_3 radicals.

FIGURE 2 $(\text{CH}_3)_4\text{Si}$



X-band e.s.r. spectrum for γ -irradiated Me_4Si after partial annealing, showing features assigned to Me_3Si radicals.

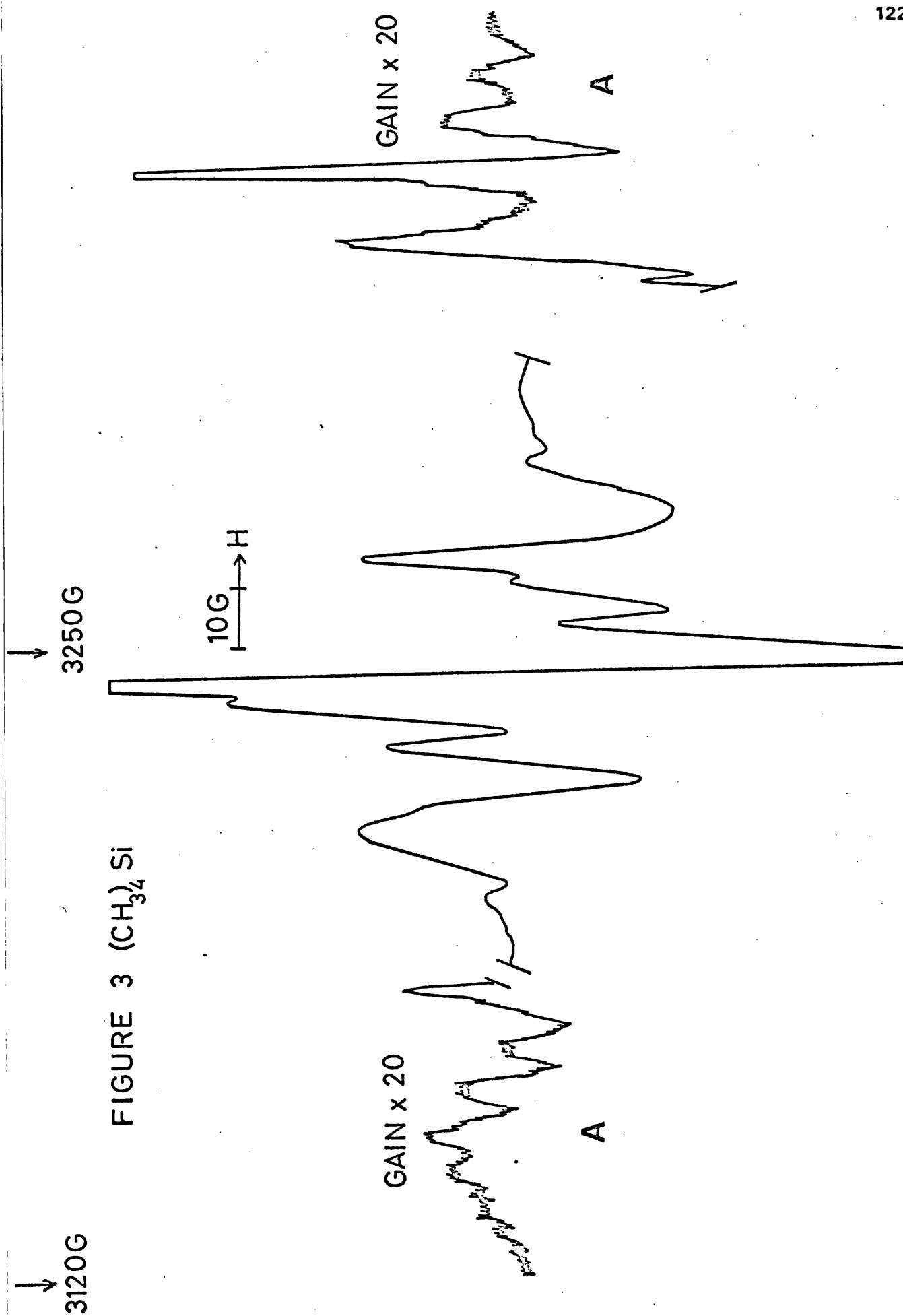


FIGURE 3 $(\text{CH}_3)_3\text{Si}$

X-band e.s.r. spectrum for γ -irradiated Me_4Si after partial annealing.

obtain the $\text{Me}_3\dot{\text{Si}}$ radical by irradiating a solution of tetramethylsilane in CD_3OD proved unsuccessful. Since loss of methyl probably takes place via an excited Me_4Si molecule rather than from the positive or negative ions it seems likely that, in CD_3OD solution, the process leading to molecular excitation could not occur.

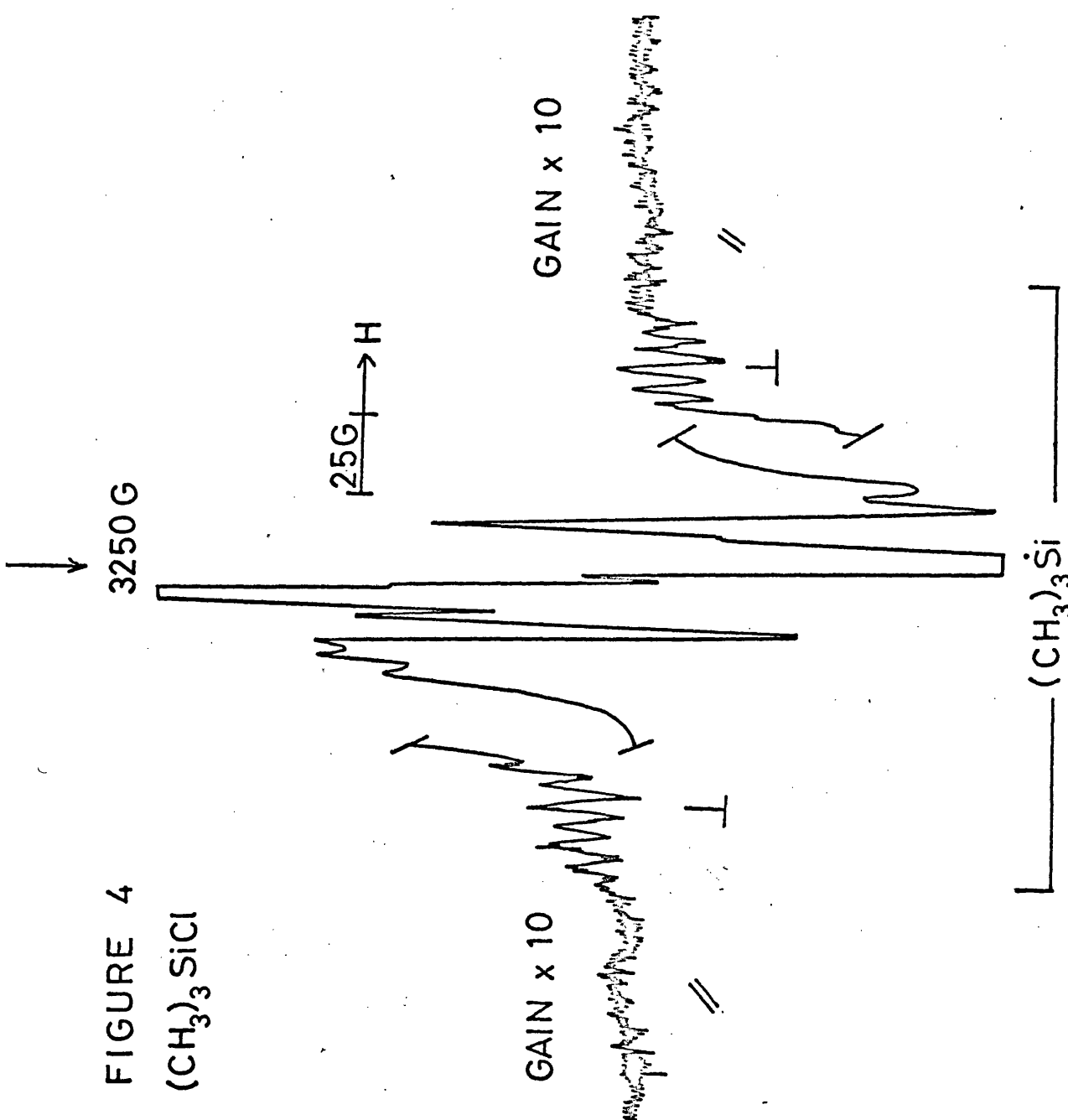
Trimethylsilyl Chloride. - Figure 4 gives the suggested analysis of the spectrum obtained from Me_3SiCl , after annealing to 170 K. At this temperature the trimethylsilyl radical appears to exhibit considerable anisotropy, a fact not recognised by Roncin.

Dimethyl Dichlorosilane. - This silane gave a poorly resolved spectrum even after annealing at 180 K. Though there was some evidence for silicon centred radicals, presumably the radicals $\text{Me}\dot{\text{Si}}\text{Cl}_2$ and $\dot{\text{Si}}\text{Cl}_3$, no accurate data could be obtained.

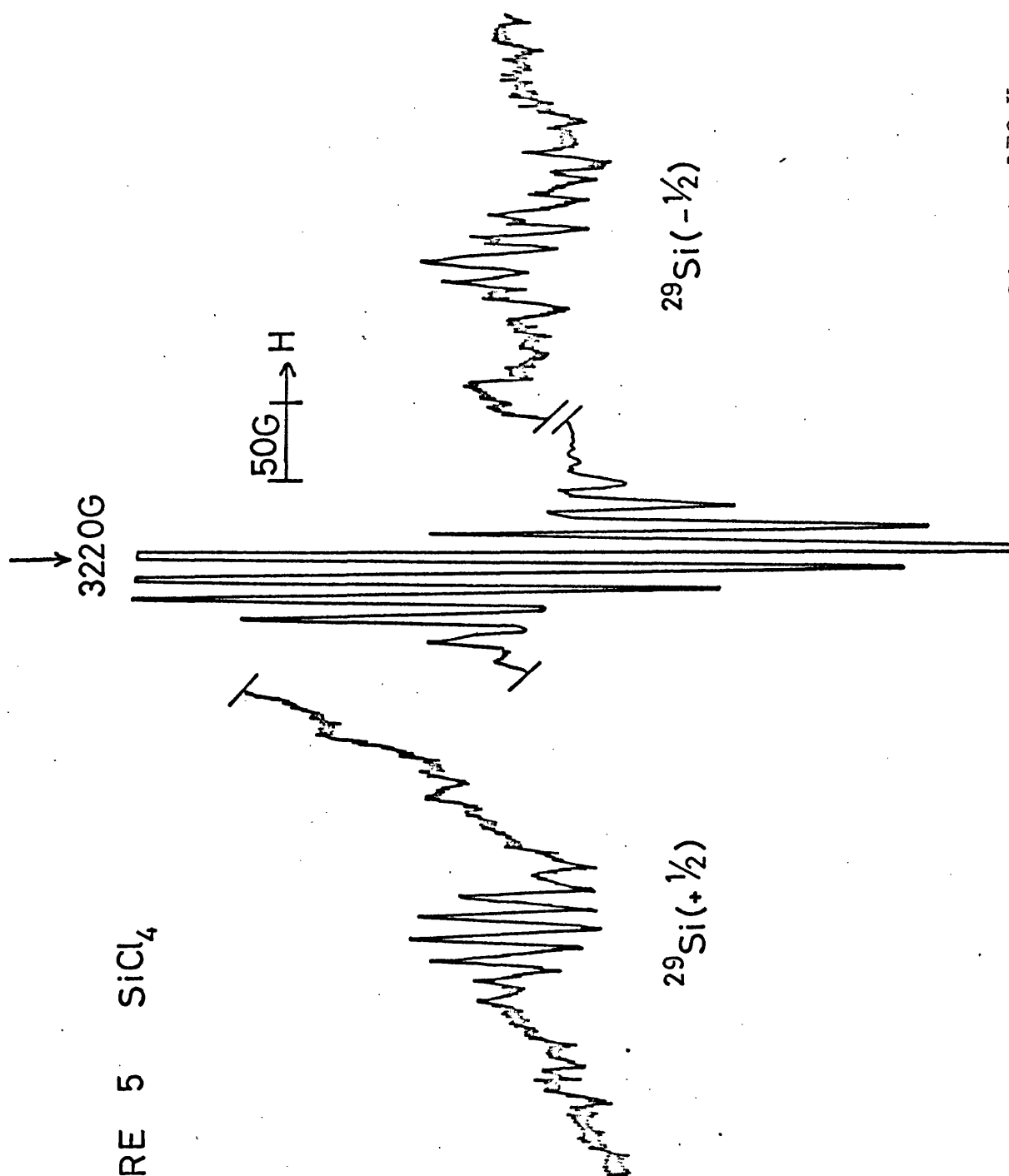
Methyl Trichlorosilane. - The spectrum for this compound was poorly resolved. Irradiation in the presence of finely divided fumed silica led to trapping of methyl radicals on the surface of the SiO_2 , but did not improve the resolution of the spectrum.

Silicon Tetrachloride. - Pure silicon tetrachloride gave a very clear isotropic spectrum of the trichlorosilyl radical, when annealed to 170 K. Irradiation in a matrix of finely divided silica produced a stable anisotropic spectrum of the $\dot{\text{Si}}\text{Cl}_3$ radical, the anisotropy remaining to the softening point of the "solution". (Figs. 5,6,7.).

FIGURE 4

 $(\text{CH}_3)_3\text{SiCl}$ 

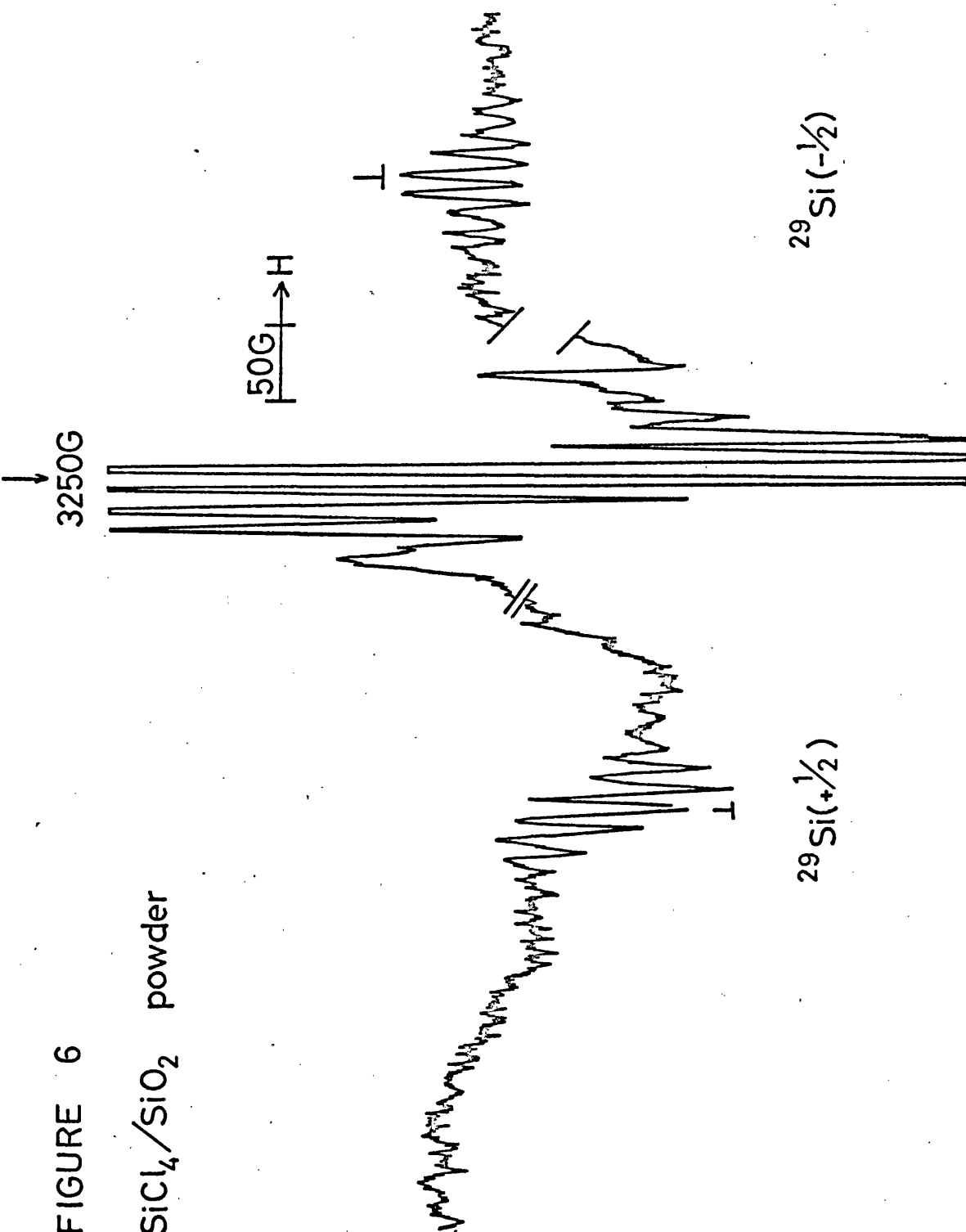
X-band e.s.r. spectrum for γ -irradiated Me_3SiCl after partial annealing, showing the parallel and perpendicular features assigned to Me_3Si radicals

FIGURE 5 SiCl_4 

X-band e.s.r. spectrum for γ -irradiated SiCl_4 after annealing to 170 K, showing features assigned to SiCl_3 radicals.

FIGURE 6

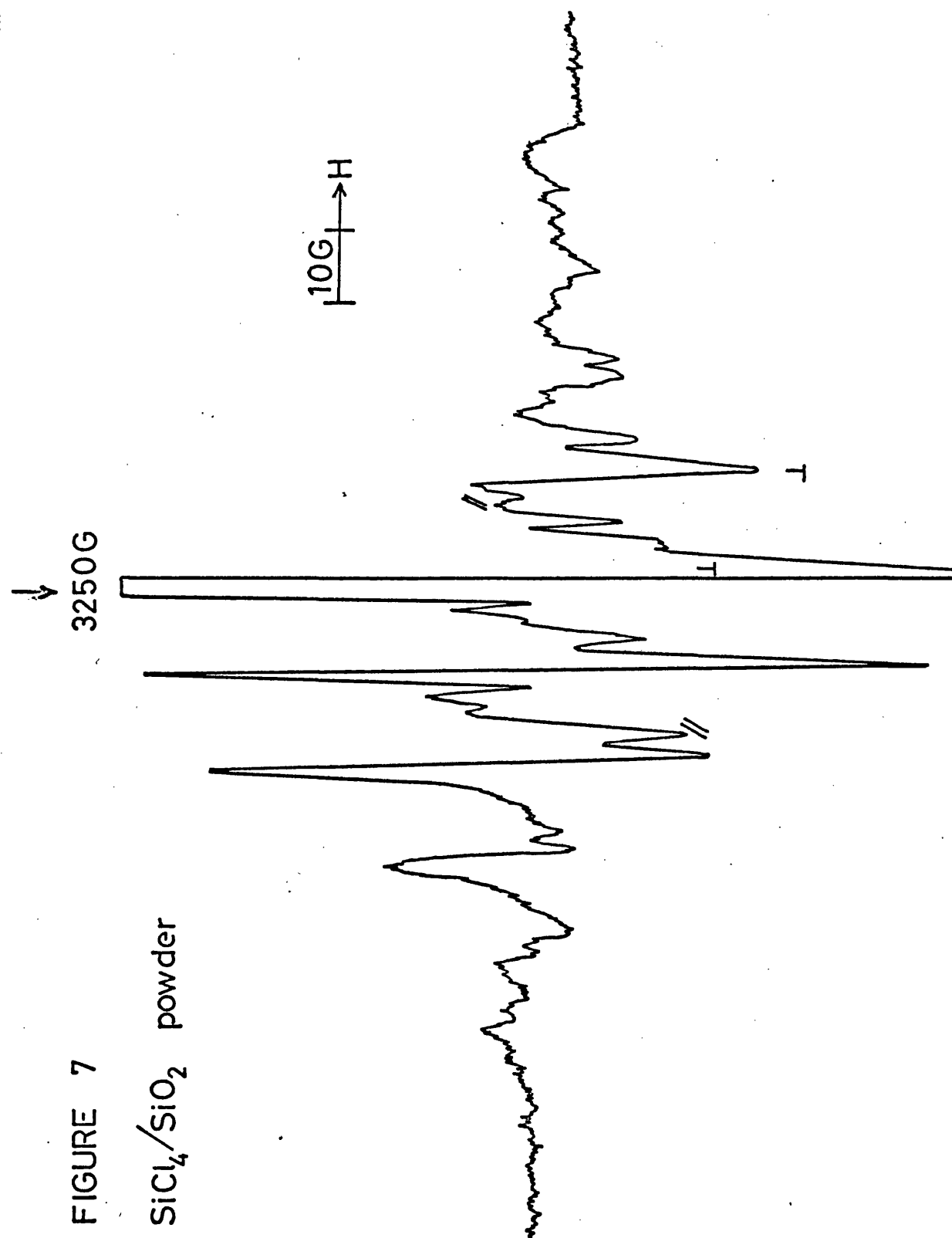
$\text{SiCl}_4/\text{SiO}_2$ powder



X-band e.s.r. spectrum for SiCl_4 γ -irradiated in a fumed silica matrix, showing features assigned to adsorbed SiCl_3 radicals.

FIGURE 7

$\text{SiCl}_4/\text{SiO}_2$ powder



X-band e.s.r. spectrum for SiCl_4 γ -irradiated in a fumed silica matrix, showing features assigned to adsorbed SiCl_3 radicals.

Table 3.

<u>Radical</u>	<u>$a_{//}(\text{Cl})$</u>	<u>$a_{\perp}(\text{Cl})$</u>	<u>$a_{//}(\text{Si})$</u>	<u>$a_{\perp}(\text{Si})$</u>	<u>a_{iso}</u>
$\dot{\text{SiCl}}_3/\text{SiO}_2$	11.5	14.0	490	415	440
$\dot{\text{SiCl}}_3/\text{SiCl}_4$	13.5				430

Presumably the trichlorosilyl radicals were adsorbed onto the powder surface, thereby giving the anisotropic spectrum.

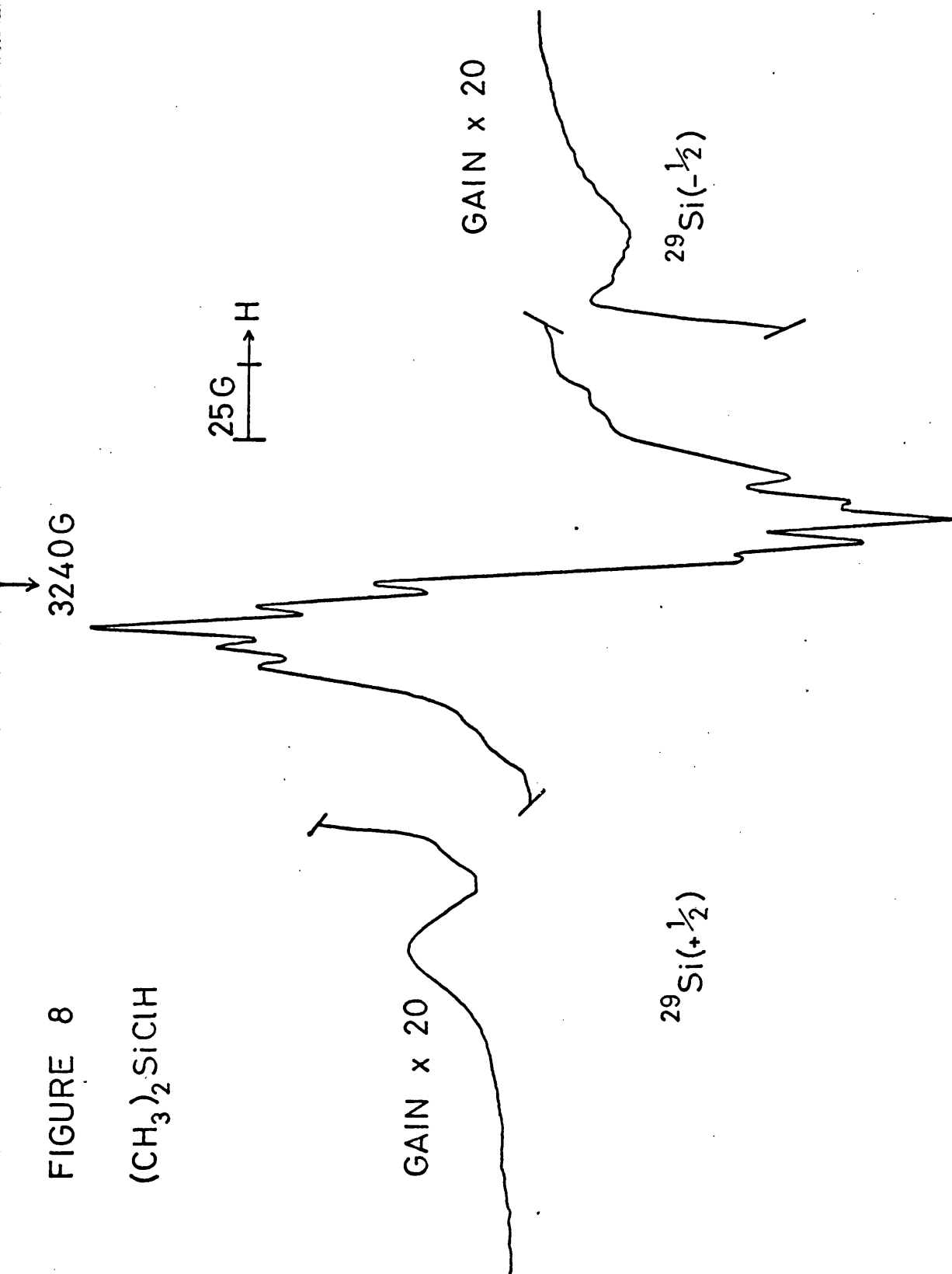
Dimethylchlorosilane. - The major radical trapped in irradiated dimethyl chlorosilane was tentatively identified as $\text{Me}_2\dot{\text{Si}}\text{H}$. The observed hyperfine couplings (Fig. 8) were $a_{//}(\text{Si}) = 245 \text{ G}$; $a_{\perp}(\text{Si}) \approx (159)\text{G}$. $a_{\text{H}} = 17\text{G}$, $a_{\text{CH}_3} = 7\text{G}$. The two possible products of positive ion dissociation, $\text{CH}_2\dot{\text{Si}}\text{MeHCl}$ and $(\text{CH}_3)_2\dot{\text{Si}}\text{Cl}$, could not be identified in the spectra obtained. This is in variance with the findings for the methylchlorosilanes above, where the $\dot{\text{C}}\text{H}_2\text{SiX}_3$ radical constituted the major radical.

Methyldichlorosilane. - Evidence for two silicon-centred radicals was found in the spectrum of this compound but no positive identification could be made for either. The silicon hyperfine couplings obtained were, for one radical in excess of 300G, and for the other approximately 240G. The radical with the large silicon splitting was tentatively assigned to $\text{Me}\dot{\text{Si}}\text{Cl}_2$, the one with the smaller splitting to $\text{Me}\dot{\text{Si}}\text{HCl}$. The spectra were so poorly resolved that no further information could be obtained.

6.7 Discussion.

Table 4 provides a comparison of available data on the trimethylsilyl radical.

FIGURE 8



X-band e.s.r. spectrum for γ -irradiated Me_2SiClH at 77K.

Table 4.

<u>Radical</u>	<u>Matrix</u>	<u>$a_{\parallel}(\text{Si})$</u>	<u>$a_{\perp}(\text{Si})$</u>	<u>a_{iso}/G</u>	<u>Ref.</u>
$\dot{\text{SiMe}}_3$	SiMe_4			172.5	a
	SiMe_3Cl			129	a
	SiMe_4	207	155	172	b
	SiMe_3Cl	239	143	175	b
	$(\text{SiMe}_3)_2$	237	150	179	b
	Soln			183	c
				181	d

a. Ref. 11; b. This work; c. Ref. 8; d. Ref. 9.

From the results obtained in this study it would appear that features assigned, in the Me_3SiCl spectrum¹¹, as isotropic ^{29}Si hyperfine lines were more accurately assigned a perpendicular features. Use of this assignment would remove any apparent anomaly in the results.

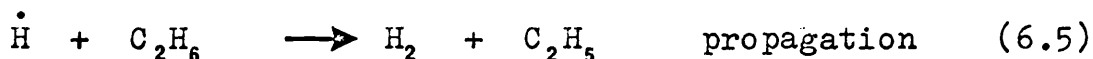
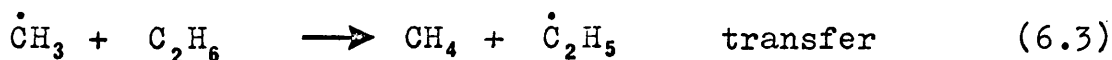
6.8 Photolysis Studies.

Attempts to abstract hydrogen atoms from either methyl dichlorosilane or dimethylchlorosilane, using t-butoxy radicals, met with no success. Neither of the possible radicals, $\dot{\text{CH}}_2\text{SiX}_3$ or $(\text{CH}_3)_n\dot{\text{SiX}}_{3-n}$ could be produced under the conditions used. This is somewhat surprising since tri-alkylsilyl radicals are readily formed using this method⁵. It can only be concluded that some mechanism is operative with the chlorosilanes that either inhibits attack by butoxy radicals or leads to the immediate loss of the silyl radicals produced. At low temperatures (110K) spectra due to hydrogen abstraction from the solvent (isopentane) were obtained.

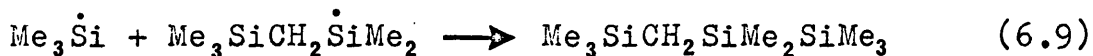
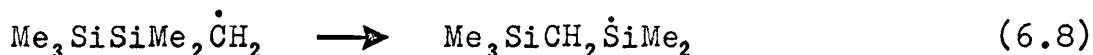
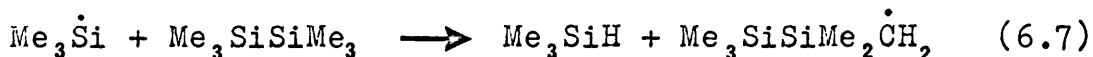
6.9 Hexamethyl Disilane.

This compound has been the subject of considerable kinetic and spectroscopic study. The kinetics of the thermal dissociation are of interest because of the differences to be found in comparing the results with those obtained from analogous carbon compounds.

The dissociation of hydrocarbons usually follows a radical chain-propagation mechanism, the $p\pi$ - $p\pi$ bonding ability of carbon providing the necessary pathways.



This is less likely with silicon compounds and much simpler mechanisms can normally be proposed.¹



Much of the bond dissociation data from silicon compounds has been gained from these studies.

Photo-electron,¹⁷ U.V.¹⁸⁻²⁰ and massspectrometry^{21,22} have provided data on the excited states of hexamethyl disilane and the behaviour of its radical ions. Photo-electron spectra of the polysilanes show that the addition of the trimethyl silyl group to tetramethylsilane, forming hexamethyl disilane introduces very little change into the electronic structure, the two spectra differing only by the addition of a peak due

to ionization of the SiSi bond (Fig. 9). The intense SiC and CH band system of tetramethylsilane, is preceded, in the case of hexamethyl disilane, by an isolated band that has been ascribed to the ionization of a molecular orbital with a preponderant SiSi contribution. The spectra for silanes containing more than one SiSi bond confirm this finding, indicating that the SiC and CH contributions to the SiSi molecular orbitals are negligible.

The results from more complex straight and branched chain polysilanes also indicate that there is little or no contribution by unoccupied silicon orbitals of π - symmetry to the stabilization of the cation. In contrast, the phenyl silanes provide evidence of σ - π interaction between the σ (SiSi) bond and π (C₆H₅) orbitals¹⁸.

6.10 γ - irradiation of Hexamethyl disilane.

Irradiation of the pure compound (in the form of beads) produced two silicon centred radicals (Fig. 10, 11) and a triplet in the free spin region which was assigned to the $\dot{\text{C}}\text{H}_2(\text{Me})_2\text{SiSiMe}_3$ radical. The intensity of the spectrum of this radical masked any central features of other radicals present. Because of this, identification of other radicals could only be based on the data given by the ²⁹Si hyperfine features. Annealing of the sample from 77 K led to a preferential loss of the silicon centred radicals and a slow decay of the $\dot{\text{C}}\text{H}_2\text{SiX}_3$ radical.

The features, marked I in figure 10, have been assigned to the previously unknown positive ion.

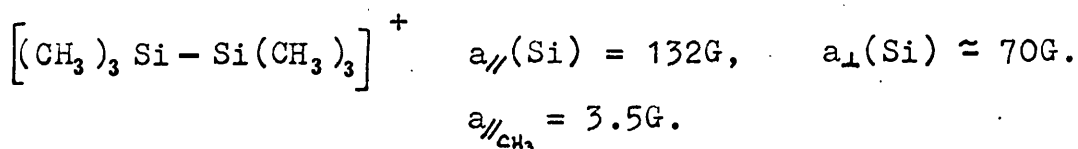


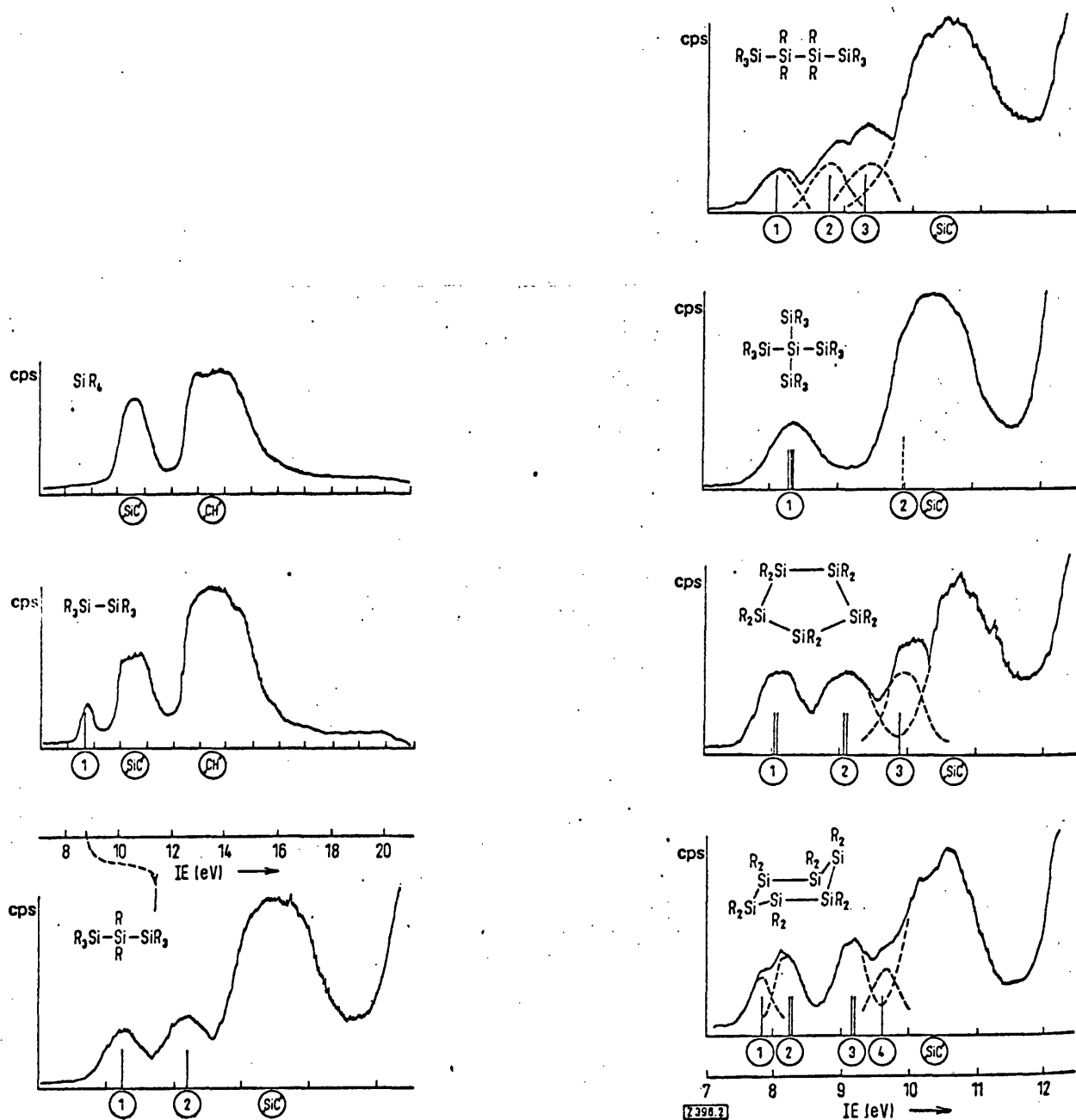
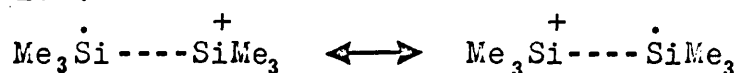
Figure 9.

Photo-electron spectra of linear, branched, and cyclic methylsilanes (R = CH).

The other possible assignment for these features is the radical $\text{Me}_3\dot{\text{Si}}\text{SiMe}_2$. This was rejected on two counts, firstly the proton coupling of 3.5G was considerably less than that obtained previously (8.2G)^{8,13}, and secondly, the general appearance of the spectrum was reminiscent of parallel features. Assuming this assignment is correct one can predict an isotropic splitting of the order of 90G since the positive ion can be considered as a resonance hybrid of the two structures below.



As an intermediate structure between two trimethyl silyl radical / positive ion complexes, one would expect the Si couplings to be half of that for the $\text{Me}_3\dot{\text{Si}}$ radical (180G). This gives an $a_1(\text{Si})$ value of approximately 70G which falls directly underneath the outer features of the $\dot{\text{C}}\text{H}_2\text{SiX}_3$ radical. Occurance of the radical on irradiation in the presence of methyl bromide rules out assignment to the negative ion. (Fig. 12, 13).

The outer features (II) are assigned to the trimethyl silyl radical. The measured hyperfine splittings are very similar to those obtained for the same radical in tetramethyl silane (Table 4). In the presence of methyl bromide there was a slight reduction in the concentration of this radical, but since it is the most likely decomposition product of both the positive and negative ions, no major decrease could be expected.

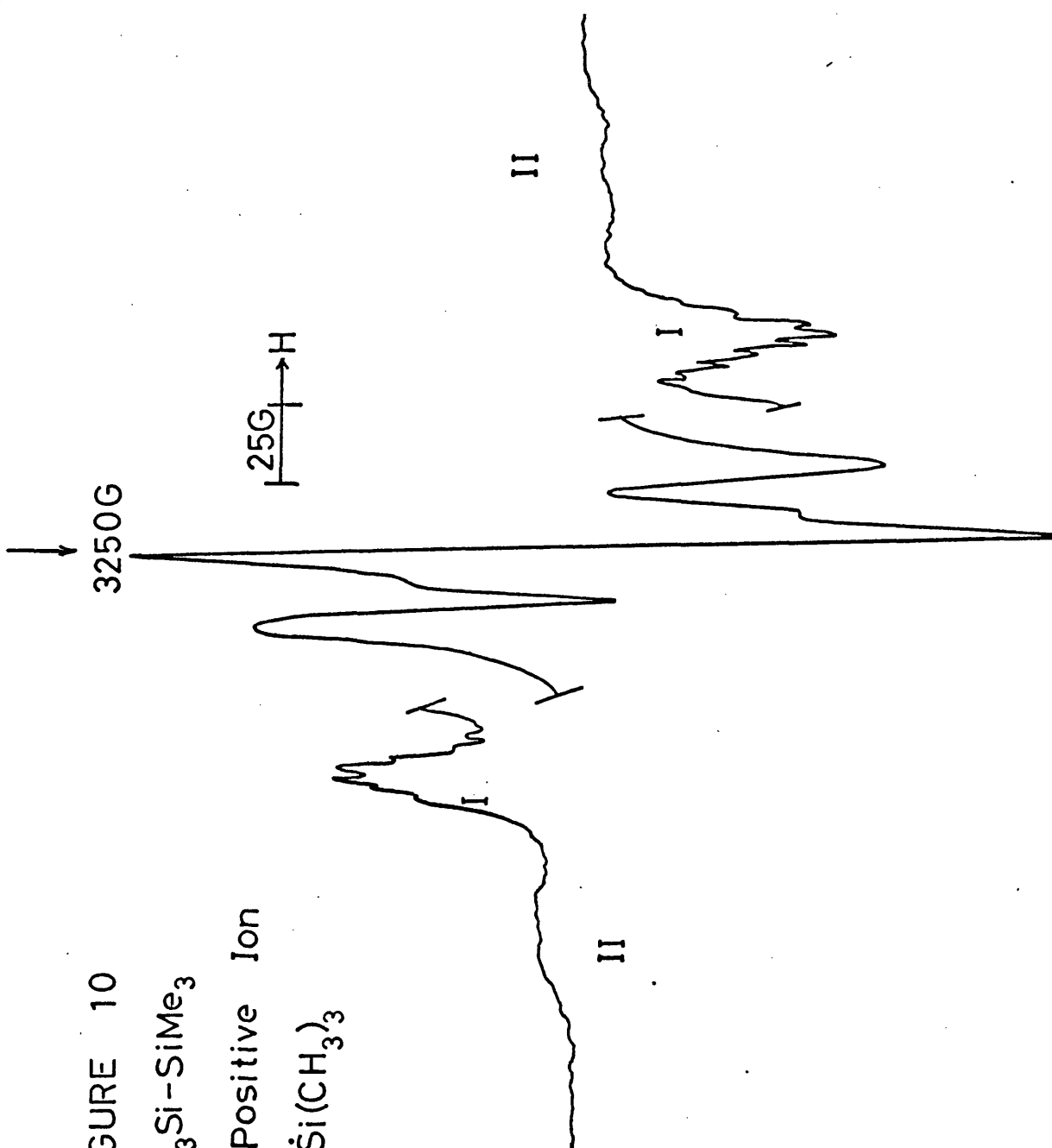
The high concentration of $\dot{\text{C}}\text{H}_2\text{SiX}_3$ radicals is not entirely unexpected since it can be formed by two processes, either dissociation of the positive ion or attack on the parent molecule by $\text{Me}_3\dot{\text{Si}}$ radicals (eq. 6.7). It is noticeable

FIGURE 10

$\text{Me}_3\text{Si-SiMe}_3$

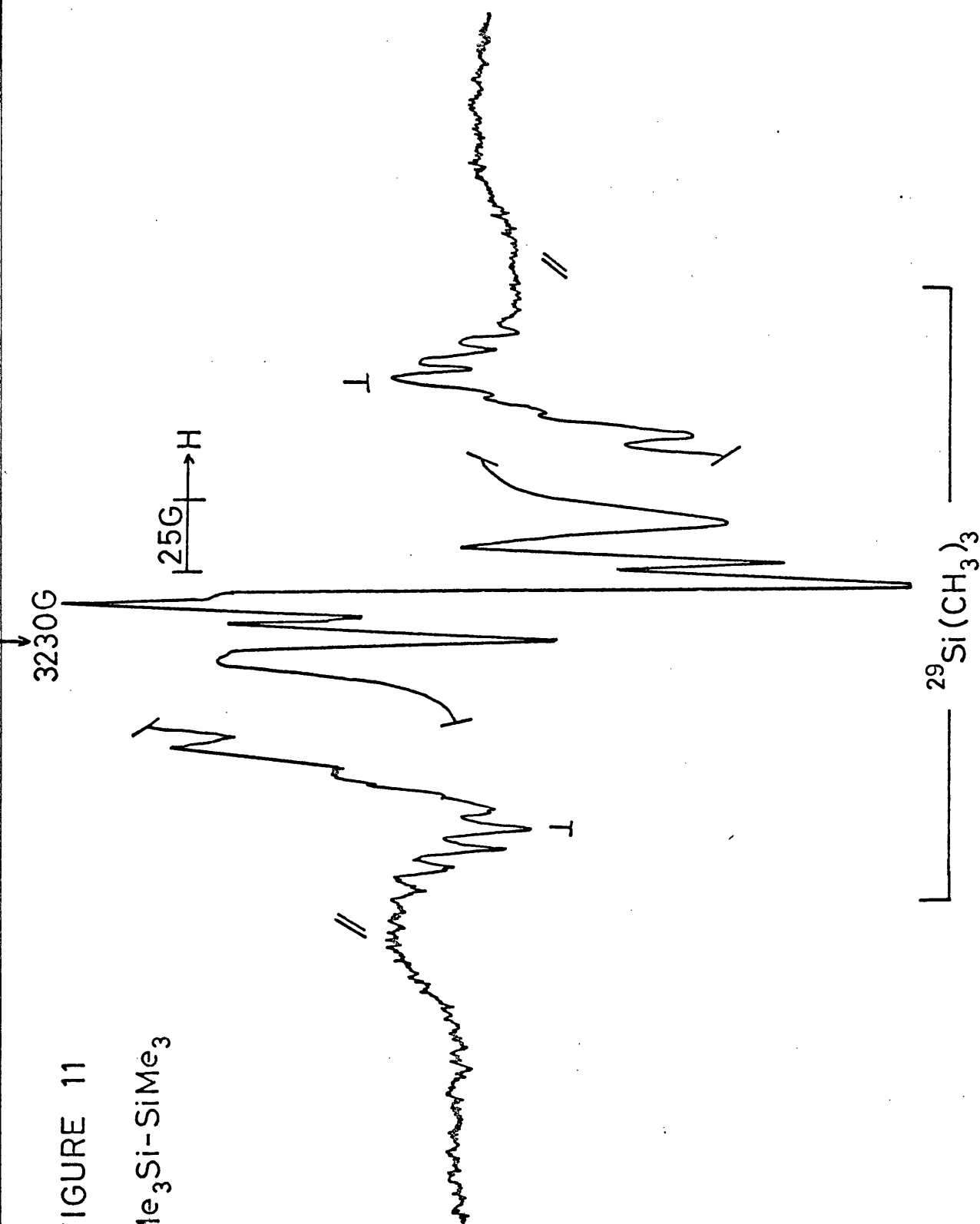
I Positive Ion

II $\dot{\text{Si}}(\text{CH}_3)_3$



X-band e.s.r. spectrum for γ -irradiated $(\text{Me}_3\text{Si})_2$ at 77K, showing features assigned to the positive ion (I) and Me_3Si radicals.

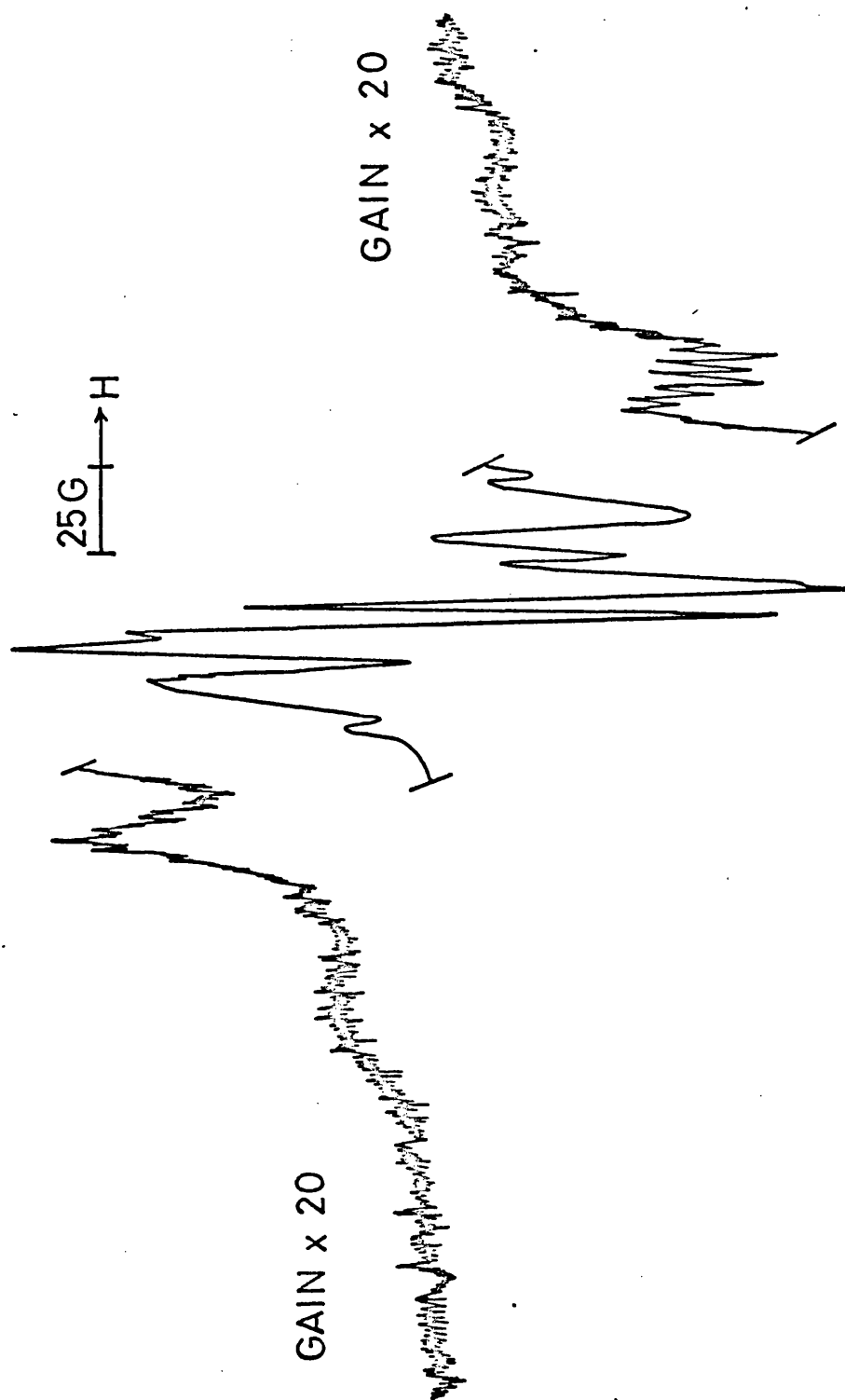
FIGURE 11

 $\text{Me}_3\text{Si-SiMe}_3$ 

X-band e.s.r. spectrum for γ -irradiated $(\text{Me}_3\text{Si})_2$ after partial annealing, showing features assigned to Me_3Si radicals.

FIGURE 12

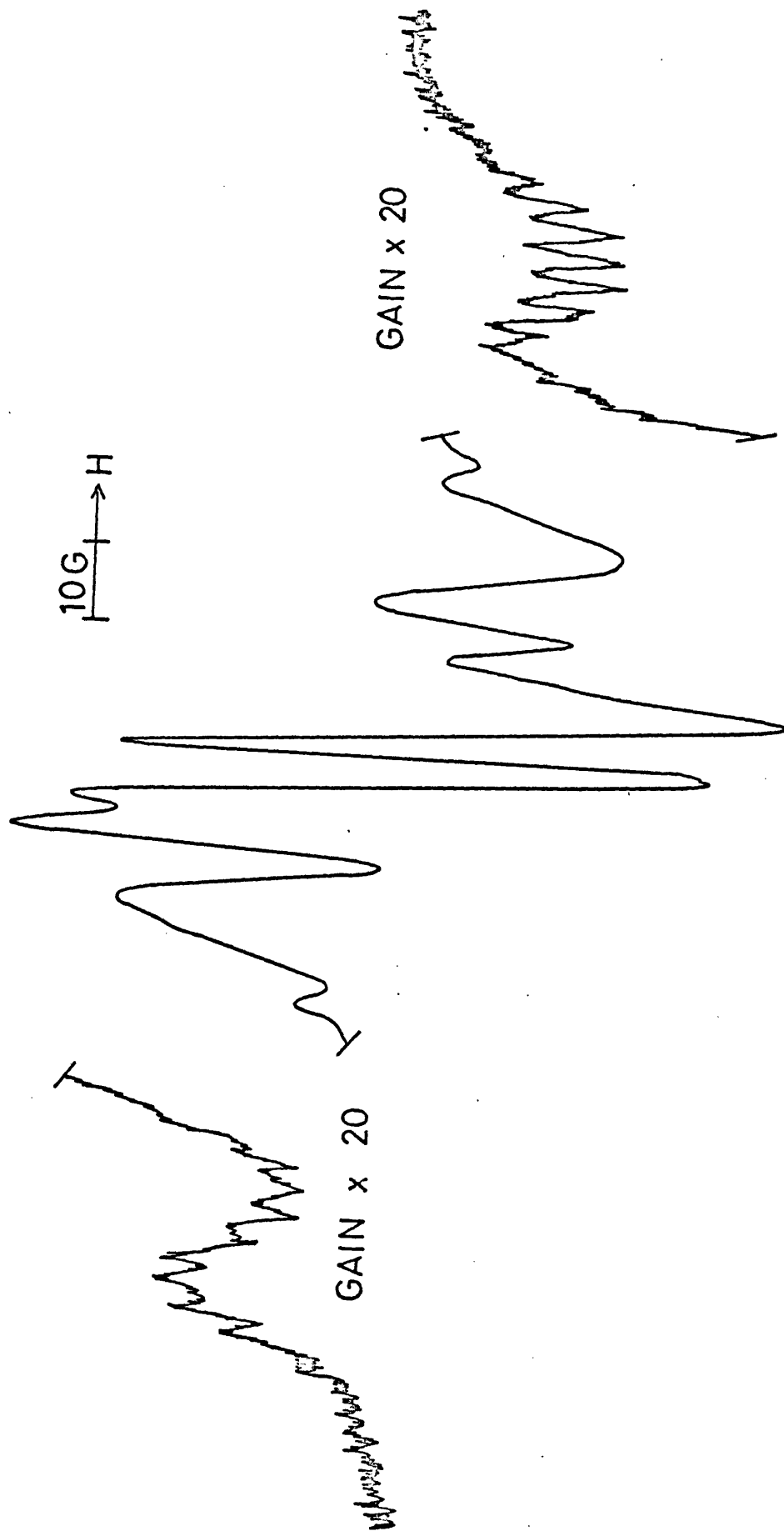
$\text{Me}_3\text{SiSiMe}_3/\text{MeBr}$



X-band e.s.r. spectrum of $(\text{Me}_3\text{Si})_2$ γ -irradiated in the presence of MeBr.

FIGURE 13

$\text{Me}_3\text{SiSiMe}_3/\text{MeBr}$



X-band e.s.r. spectrum of $(\text{Me}_3\text{Si})_2\text{Y}$ -irradiated in the presence of MeBr .

that loss of methyl, which is a favoured decomposition route for the chlorosilanes, does not occur to any major extent with this compound.

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CHAPTER 7

Transition-metal Carbonyls.

7.1 Introduction:

Transition metal ions have played a major part in the development of electron spin resonance theory and techniques. By using stable paramagnetic ions, spectroscopists have gained considerable insight into both the solid and liquid states as well as the complex ligand field interactions found within individual complexes. A number of texts are available covering this aspect of the subject, the best general text probably being that of Abragam and Bleaney¹.

7.2 This Work:

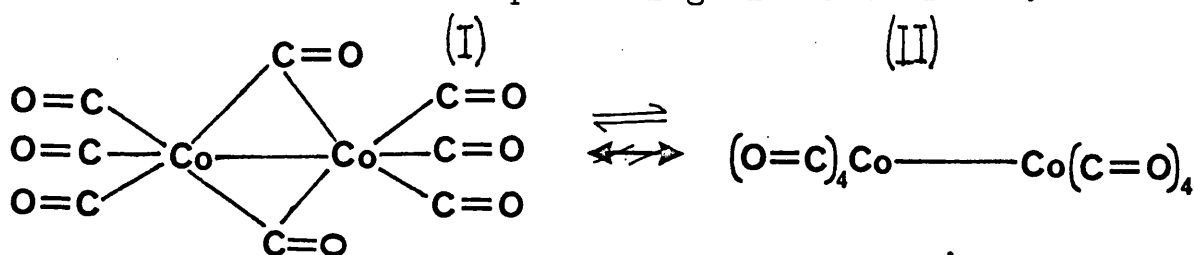
Organometallic transition metal compounds, and in particular the metal carbonyls, have received far less attention than the inorganic complexes. The first part of this work involves the isolation of carbonyl radicals by sublimation of the parent metal-metal bonded dimers. This study was carried out in conjunction with Drs. S.A.Fieldhouse and G.W.Nielson.

The second half of the chapter is given over to preliminary report of some liquid -phase photolysis experiments using metal carbonyls. This last piece of work was pursued in collaboration with Dr. Fieldhouse, and is still continuing. Convincing explanations for many of the effects observed have yet to be found.

7.3 The Reaction of Oxygen with Metal Carbonyls.

Sublimation of some of the first row transition metal carbonyl dimers, containing metal-metal bonds, is

known to take place via the dissociation of the parent compound. Octacarbonyl dicobalt, when sublimed, under vacuum, on to a cold finger (77 K), yields a paramagnetic species, identified² from its e.s.r. spectrum, as the cobalt tetracarbonyl radical $\dot{\text{Co}}(\text{Co})_4$. Since octacarbonyl dicobalt is known to exist in two isomeric forms in solution,³ it is likely that a similar state of affairs occurs in solid state, dissociation of the dimer proceeding via isomer II.



The pentacarbonyl manganese radical, $\text{Mn}(\text{Co})_5$, was reported⁴ to be formed in analogous manner to the cobalt species, though the ^{55}Mn hyperfine couplings reported ($A_{\parallel} = 22.5$ G, $A_{\perp} = 6.75$ G) were low compared with those of other manganese carbonyl radicals. Photolysis of the manganese dimer, $\text{Mn}_2(\text{Co})_{10}$, in a tetrahydrofuran (THF) solution has been purported to give the monomeric radical,⁶ but this finding is now in doubt. (See Section 6.6). Dicyclopentadienylhexacarbonyldichromium sublimes to give a free radical species,⁷ recent N.M.R. data⁸ providing further evidence. The Cr - Cr bond in this compound has been found to be unusually long (3.221 Å) so enabling its ready dissociation. The decacyano dicobalt ion $(\text{Co}_2(\text{CN})_{10})^{6-}$ decomposes in the solid state to give a green paramagnetic monomeric anion.⁹

7.4 Experimental:

Sublimation experiments were performed in the apparatus described in Chapter 2, with the cold finger centred

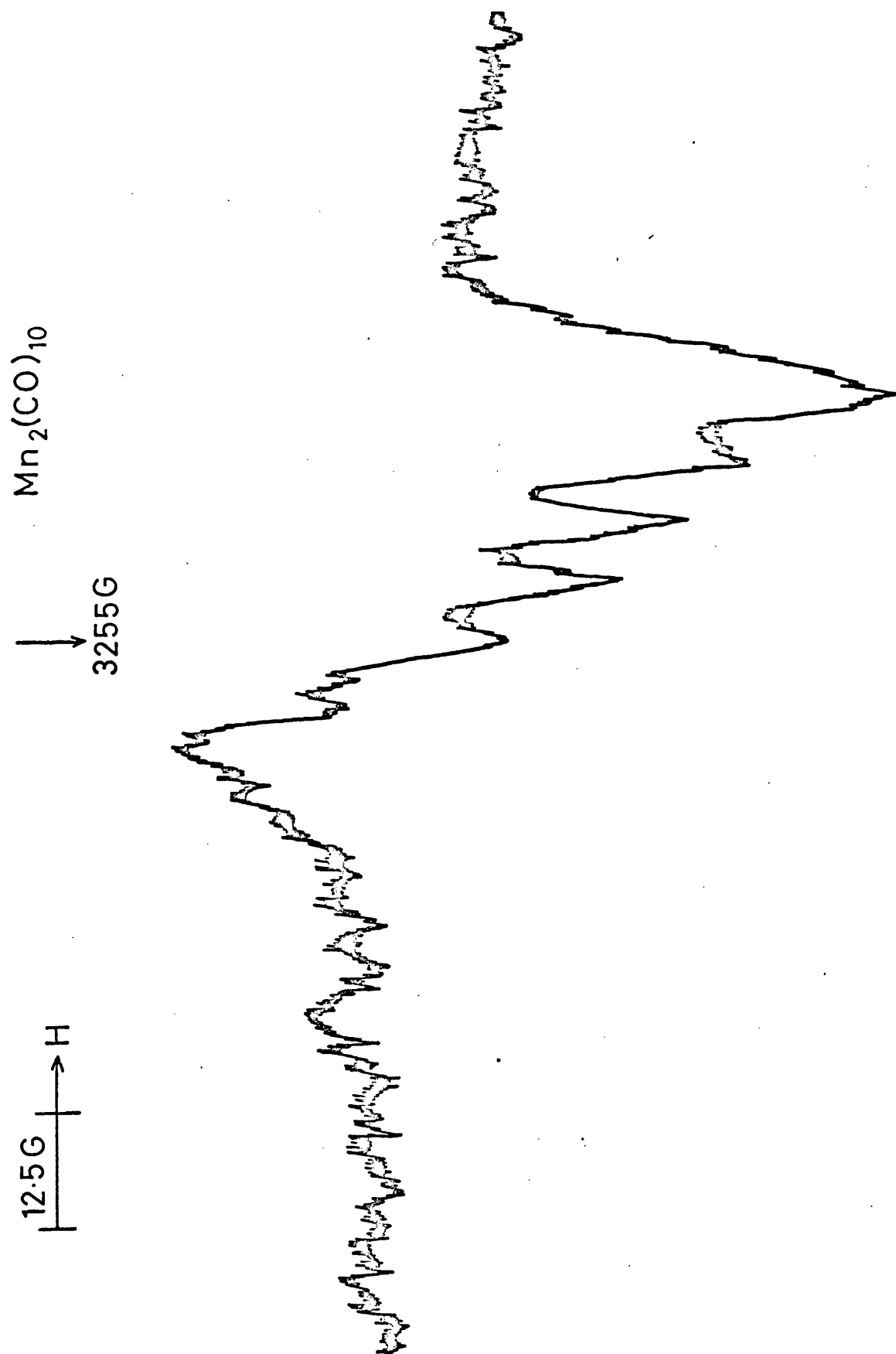
in the cavity of a Varian V4502 e.s.r. spectrometer. For oxygen free experiments the sublimation apparatus was out-gassed for a minimum of 2 hours prior to the introduction of the metal carbonyl samples. Peroxo species were readily obtained when the sublimation apparatus was evacuated for a short period (ca 5 mins.) before introduction of the sample. The spectra were calibrated using DPPH. Identical results were obtained using either the commercial or purified $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$ obtained from Strem Chemicals Inc., Danvers, Mass.

7.5 Results and Discussion:

Decarbonyldimanganese. - The sublimation of $\text{Mn}_2(\text{CO})_{10}$ under conditions previously described (Chapter 2)^{2,4,10} gives no detectable e.s.r. signal in the absence of oxygen. However in the presence of traces of oxygen, a spectrum similar to that originally assigned to $\dot{\text{Mn}}(\text{CO})_5$ was observed. (None of the spectra displayed the weak features taken as parallel shoulders in the previous work⁴). This result suggests that the radical is in fact the peroxo-species $\dot{\text{O}}_2\text{Mn}(\text{CO})_5$ (Fig.1). The results obtained using $\text{Co}_2(\text{CO})_8$ support this assignment.

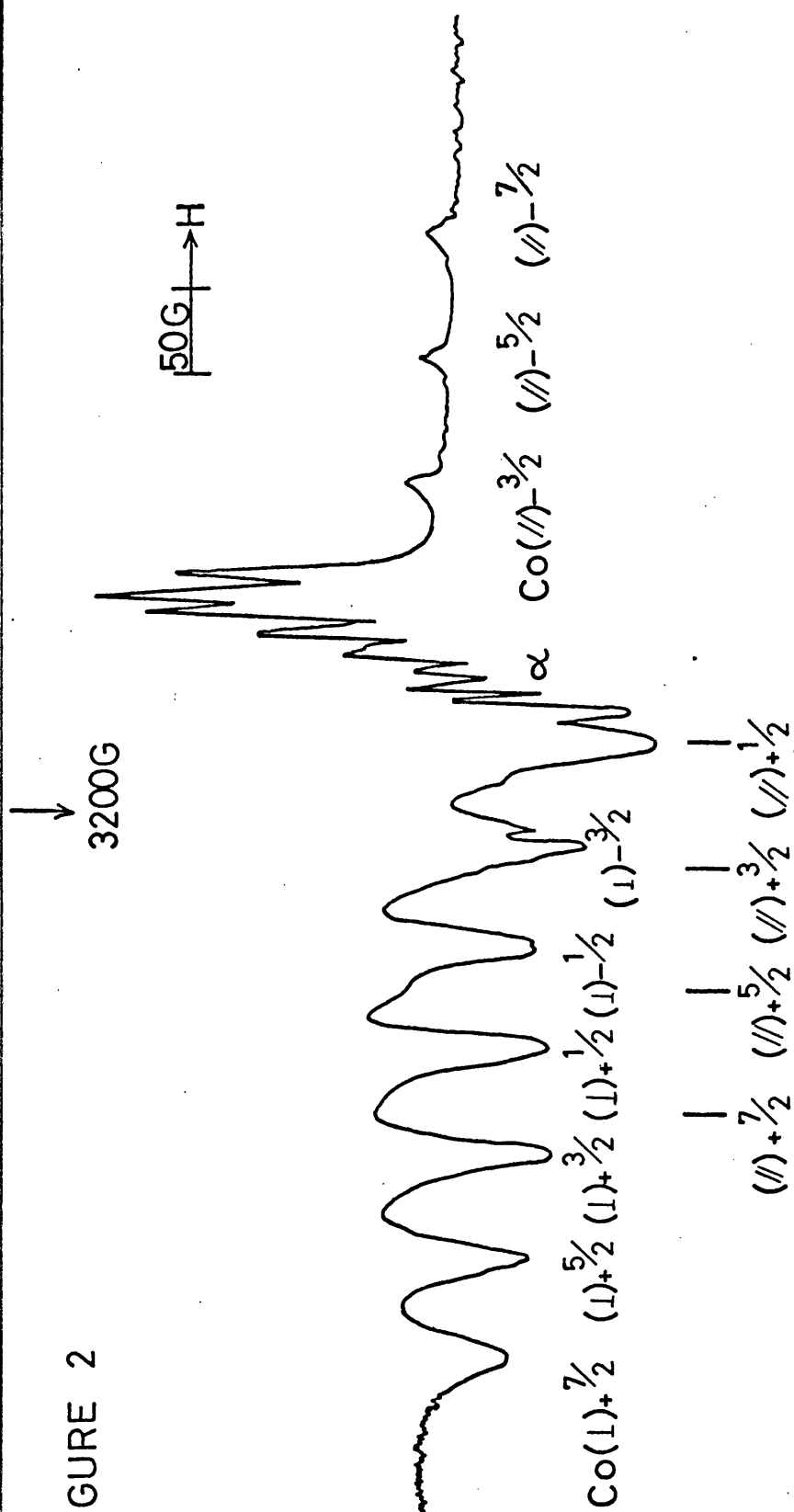
Octacarbonyldicobalt. - Sublimation of $\text{Co}_2(\text{CO})_8$ in the presence of oxygen gives a species identified as $\dot{\text{O}}_2\text{Co}(\text{CO})_4$ whose e.s.r. signal is superimposed upon that of the monomer $\dot{\text{Co}}(\text{CO})_4$ (Figs. 2 & 3). In the absence of oxygen the spectrum due to $\dot{\text{Co}}(\text{CO})_4$ only was obtained.

E.s.r. Spectra. - The results of the analysis of the spectrum of the peroxo cobalt species are given in Table 1



First derivative X-band e.s.r. spectrum for matrix isolated (CO) MnO_2 .

FIGURE 2



First derivative X-band e.s.r. spectrum for matrix isolated $\text{Co}(\text{CO})_4$ (broad spectrum) and $(\text{CO})_4\text{CoO}_2$ (narrow spectrum).

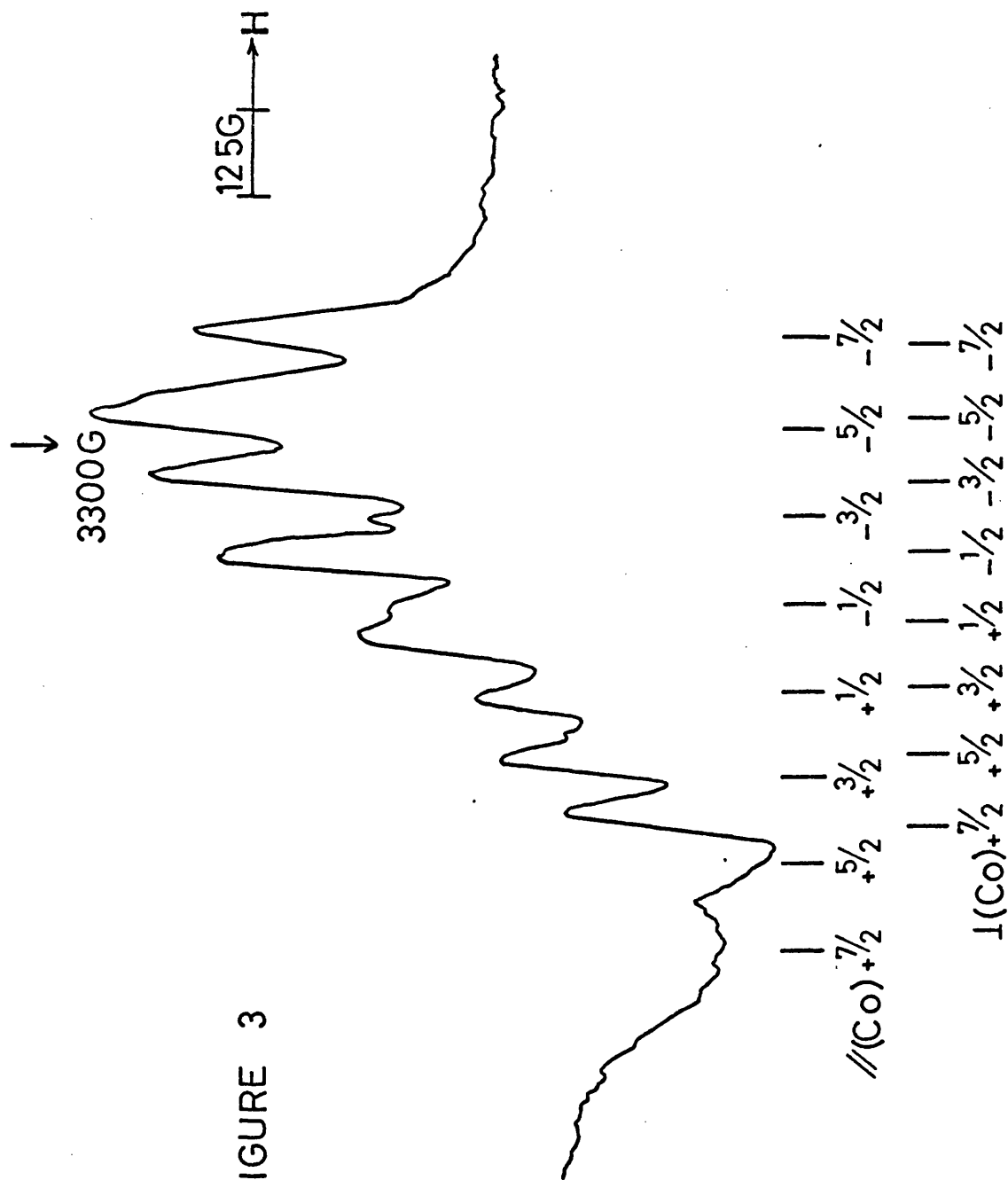


FIGURE 3

First derivative X-band e.s.r. spectrum for matrix isolated $(\text{CO})_4\text{CoO}_2$.

where it can be seen that the values obtained are consistent with those for a variety of other peroxo-complexes of cobalt.¹²

Table 1.

E.s.r. data for various transition metal peroxo-complexes.

<u>Radical</u>	<u>$g_{\parallel}$</u>	<u>$g_{\perp}$</u>	<u>$A_{\parallel}/G$</u>	<u>$A_{\perp}/G$</u>
$(OC)_4Co\dot{O}_2^a$	2.010	2.000	13.5	10.5
$pyCoL_1\dot{O}_2^{b,c}$	2.065	2.000	16	12
$pyCoL_2\dot{O}_2^d$	2.066	2.022	13	12
Vitamin $B_{12}\dot{O}_2^e$ (D.M.F. Soln)	2.069	2.002	16	13
Vitamin $B_{12}\dot{O}_2^e$ (CH OH glass)	2.079	2.003	18	13
$(OC)_5Mn\dot{O}_2^a$	2.007	2.003	8.5	6.3 ^f
$O_3V\dot{O}_2^g$	2.032	2.002	6.6	3.9

a. This work; b. Ref 11; c. py = pyridine, L = bis-dimethylglyoximate; d. py = pyridine, L = bis-diphenylglyoximate; e. Ref 12; f. These values differ from those originally reported in Ref 4; g. Ref 16.

As previously concluded², the species with the large hyperfine coupling to ^{59}Co is $\dot{Co}(CO)_4$. The observed reaction of this species with oxygen at low temperatures, together with the small hyperfine coupling to ^{59}Co of the resulting radical, is indicative of the production of a peroxo-species, in this case $(OC)_4Co\dot{O}_2$. This reduction in the magnitude of the hyperfine coupling is similar to that previously observed for the oxygenation of other cobalt complexes.¹²

Electronic Structure of $\dot{Co}(CO)_4$. - The data for this radical was corrected for zero-field and orbital magnetic contributions. For the former the normal Breit-Rabi equation (Appendix 1) was used and for the latter the second-order

equations¹³

$$A_{\perp}(\text{MHz}) = A_{\text{iso}} - B(1 + \frac{1}{4}\Delta g_{\perp})$$

$$A_{\parallel}(\text{MHz}) = A_{\text{iso}} + 2B(1 - \frac{1}{4}\Delta g_{\parallel})$$

where $\Delta g_{\perp} = g_{\perp} - g_e$

This gives, after reconvertng to gauss,

$$A_{\text{iso}} = -37.4 \text{ G}, \quad 2B = +107.4 \text{ G}.$$

if $A_{\parallel}$ is taken as positive and $A_{\perp}$ as negative. (Any other sign combination gives unacceptable results.) The positive sign of $2B$ unambiguously fixes the orbital of the unpaired electron as d_{z^2} , the magnitude of $2B$ indicating that the electron is not extensively delocalised onto the ligands. In contrast, the isotropic coupling of -37.4G , which is low for cobalt complexes, indicates that there must be some occupancy of the outer $4s$ orbital giving a positive contribution. If a normal (spin-polarisation) value of ca. -90G is assumed and an A_{iso}^0 value of ca. 1320G ¹⁴ it is found that about a 4% occupancy is required to give the observed result. This again is in indicative of systems having a d_{z^2} configuration.¹⁵

Electronic Structure of the Peroxo-species. - Results for the peroxo-species $\text{O}_3\text{VO}\dot{\text{O}}$ show¹⁶ that the electron is strongly localised on the two oxygen atoms despite the possibility of π -delocalisation. A similar conclusion is drawn for the radicals $(\text{OC})_4\text{Co}\dot{\text{O}}_2$ and $(\text{OC})_5\text{Mn}\dot{\text{O}}_2$. Calculation of the approximate $4s$ and $3d_{z^2}$ populations, from the hyper-fine tensor components, gives ca. $(-)$ 1.4% for the d -orbital population, and ca. $(-)$ 1.0% for Co and $(-)$ 0.6% for Mn, values that are close to expectation for simple polarisation.

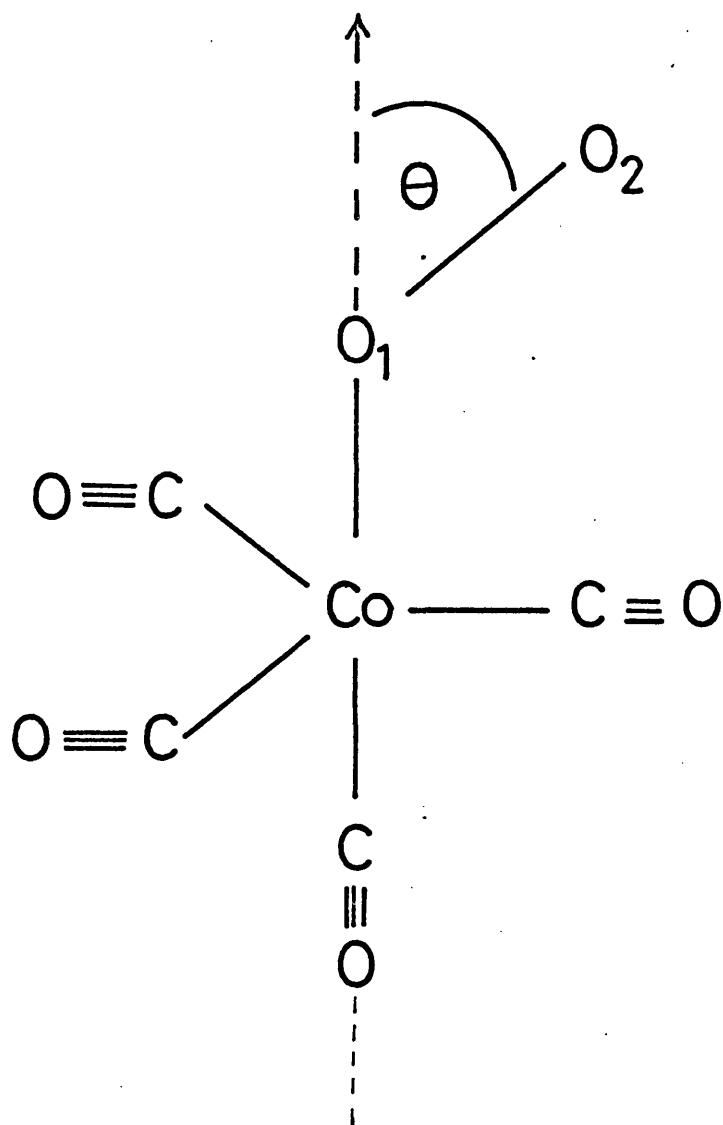
The values for $g_{\parallel}$ are smaller than are usually found for simple peroxo-radicals such as $\text{HO}_2^{\cdot 17}$ (ca. 2.03). Assuming, as argued above, that the delocalisation is trivial, then this reduction in the $g_{\parallel}$ values can be understood in terms of the angle θ , between the $\text{Co} - \text{O}_1$ and $\text{O}_1 - \text{O}_2$ axes (Fig. 4). The smaller the angle θ , the less the degeneracy of the oxygen π -orbitals will be lifted and the greater will be $g_{\parallel}$. It would seem therefore that, for these carbonyls, θ is relatively large, a finding in contrast with those for a range of other cobalt peroxo-complexes which all have $g_{\parallel} \gg 2.03$ (Table 1).

7.6 Photolysis of Metal Carbonyls.

E.s.r. data on metal carbonyls is relatively scarce, the information available falling into two main categories, that for metal-cluster radicals and that for mono-nuclear carbonyl radicals.

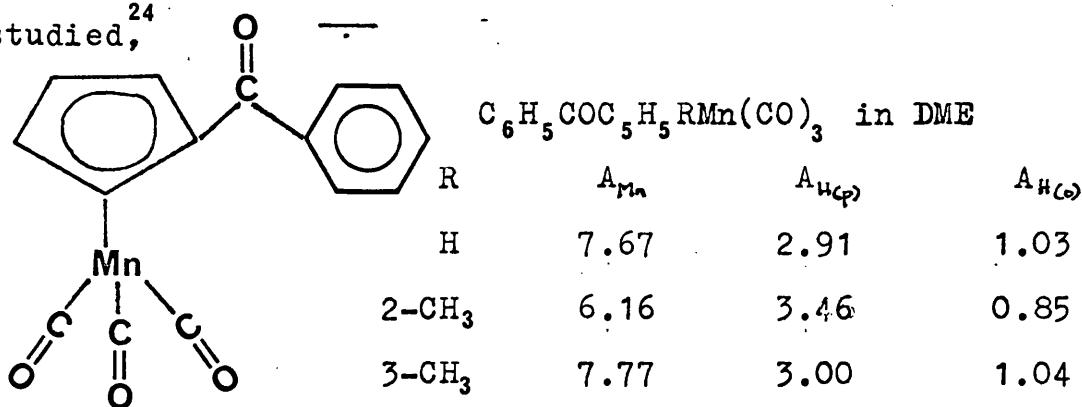
The paramagnetic complex $\text{Co}_3(\text{CO})_9\text{S}$ has been prepared by the reaction of $\text{Co}_2(\text{CO})_8$ with H_2S , in hexane, at 150 C and 100 atmospheres of CO .¹⁸ Diluted single-crystal studies of this radical in the isomorphous diamagnetic $\text{FeCo}_2(\text{CO})_9\text{S}$ reveal that the molecular-orbital containing the unpaired electron must be composed mainly of strong anti-bonding metal atomic orbitals. This can be compared with the findings of Mackay and Schneider¹⁹ who concluded that the unpaired

FIGURE 4.

Structure of $\text{O}_2\text{Co}(\text{CO})_4$.

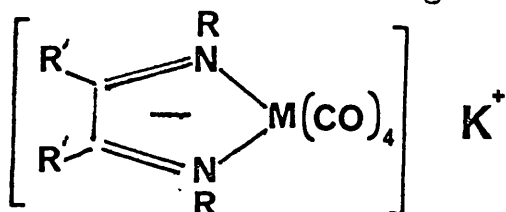
electron in the polynuclear metal halide ion $(\text{Nb}_6\text{Cl}_{12})^{3+}$ was delocalized in a non-degenerate bonding metal d-orbital combination over the entire octahedron of niobium atoms. Further studies by Dahl et al.^{20,21} on the selenide analogue of the sulphur radical bears out the original finding. A cobalt cluster radical characterised by Peake et al.²² is the radical anion $\text{YC Co}_3(\text{CO})_9^-$ (where Y = alkyl, aryl, halogen, SiMe_3). No information is given on the delocalization of the unpaired electron. Non e.s.r. evidence has been published for the methylidyne tricobalt nonacarbonyl radical $\dot{\text{C}}\text{Co}_3(\text{CO})_9$.²³ The addition of the hydride precursor to olefinic compounds is thought to proceed by a radical mechanism.

A number of radical ions have been characterised that contain carbonyl ligands. In each of these cases the free electron is mainly centred on the aromatic ligands present. A range of methyl substituted derivatives of the anion of (benzoylcyclopentadienyl) manganese tricarbonyl have been studied,²⁴



the manganese couplings observed being very small (ca 7). This reflects the spin - polarization mechanism operating.

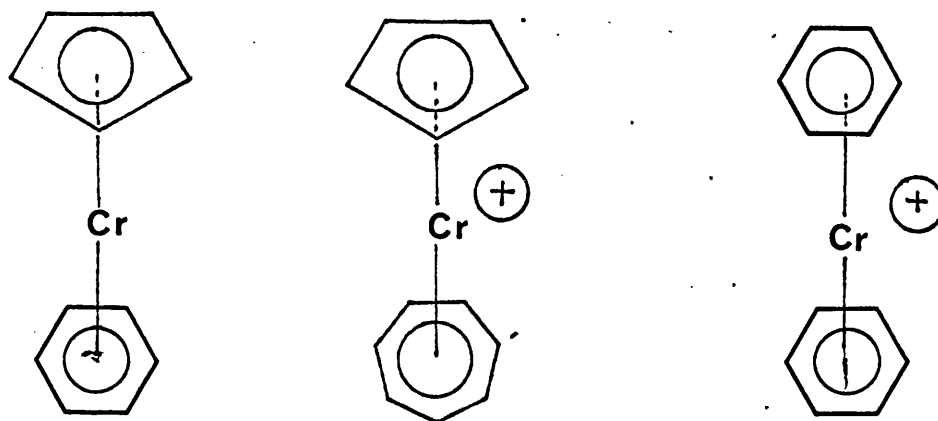
Anions of the general structure



M = Cr, Mo, W

R, R' = H, CH₃, ϕ .

have been prepared,^{25,26} in which the electron is delocalised over the conjugated $N=C-C=N$ group. The coupling to the metal atom remains small $a_{Mn} \approx 3G$, $a_{Cr} \approx 2.8G$, $a_W \approx 5.8G$.²⁵ The di-aromatic radical and radical cations²⁷



show a chromium coupling of the order of 14 - 20G indicating a much greater delocalisation of the unpaired spin onto the metal.

Murdoch and Lucken²⁸ have prepared some paramagnetic π -allyl carbonyl complexes of iron, but no information is available on the coupling to the metal atom.

Vanadium hexacarbonyl, $\dot{V}(CO)_6$, exists in equilibrium with its dimer, in the solid state. At 4.2K only 1% of the free radical monomer is found to be present,²⁹ this proportion increasing with an increase in temperature. Pratt and Myers⁴⁴ observed the e.s.r. spectrum of this radical at 1.3K, finding an unusual change in line shape with microwave power.

Table 2

$\dot{V}(CO)_6$, g values observed at 1.3K.

<u>Sample</u>	<u>$g_{ }$</u>	<u>$g_{\perp}$</u>	<u>g_{iso}</u>	<u>Power Level db.</u>
Pure $\dot{V}(CO)_6$			2.063	-20
$\dot{V}(CO)_6$ - n-pentane			2.079	-30
$\dot{V}(CO)_6$ - n-pentane			2.061	-16
$\dot{V}(CO)_6$ - n-pentane	1.981	2.103	2.062	- 6

Table 2 cont.

<u>Sample</u>	<u>g_x</u>	<u>g_y</u>	<u>g_{iso}</u>	<u>Power Level db.</u>
$\dot{V}(\text{CO})_6$ - benzene	2.023	2.126	2.135	
Pure $\dot{V}(\text{CO})_6$	2.03	2.09	2.07	
<u>a.</u> 4.2K				

The g -values obtained for $V(\text{CO})_6$ in n -pentane were shown to result from a tetragonal distortion of the octahedral structure. Though no ^{51}V hyperfine structure was observed by Pratt and Myers, Keller, et al²⁹ claim a coupling of 39 - 46G at 4.2K, in their single crystal study.

Jong and Wiles³⁰ have used an unusual method of preparation to produce the pentacarbonyl technetium radical. Beta decay of a purified sample of $^{66}\text{Mo}(\text{CO})_6$, prepared by neutron irradiation of normal $\text{Mo}(\text{CO})_6$, led to formation of the metastable $^{99m}\text{Tc}(\text{CO})_5$ species. The small number of molecules formed, 10^5 Tc atoms/mg of $\text{Mo}(\text{CO})_6$, precludes the study of this radical using e.s.r. techniques. Neutron irradiation of $(\text{CpFe}(\text{CO})_2)_2$ produced the radio-active radical $\text{CpFe}^{59}(\text{CO})_2^{31}$.

7.7 Experimental.

Cobalttricarbonylnitrosyl (Strem Chemicals), methyl cyclopentadienylmanganesetricarbonyl (B.D.H. Chemicals Ltd.) and cyclopentadienylvanadiumtetracarbonyl (Strem Chemicals) were each dissolved in a mixture of t -butyl peroxide and isopentane (1:10 v:v), in 4mm O.D. silica tubes. The resulting solutions were thoroughly degassed by repeated freeze-pump-thaw cycles and were sealed under vacuum ($< 10^{-3}$ torr). Cycloheptatrienylmolybdenumtricarbonyl, because of its low solubility in isopentane, was dissolved in a MeTHF/ t -butyl peroxide mixture.

All the samples were photolysed in the microwave cavity, at varying temperatures, using a Wooten 200W super-high pressure (shp) mercury lamp. In one experiment a sample of cyclopentadienylniobiumtricarbonyl was irradiated using a 2KW Xenon lamp fitted with a water-cooled borosilicate filter.

A degassed solution of dimanganesedecacarbonyl in MeTHF was irradiated, at room temperature, using a high pressure mercury lamp, the xenon lamp mentioned above and a 3500A light source (Rayonet Model RPR-100 Photochemical reactor). The sample was then studied using the e.s.r. spectrometer.

7.8 Results and Discussion.

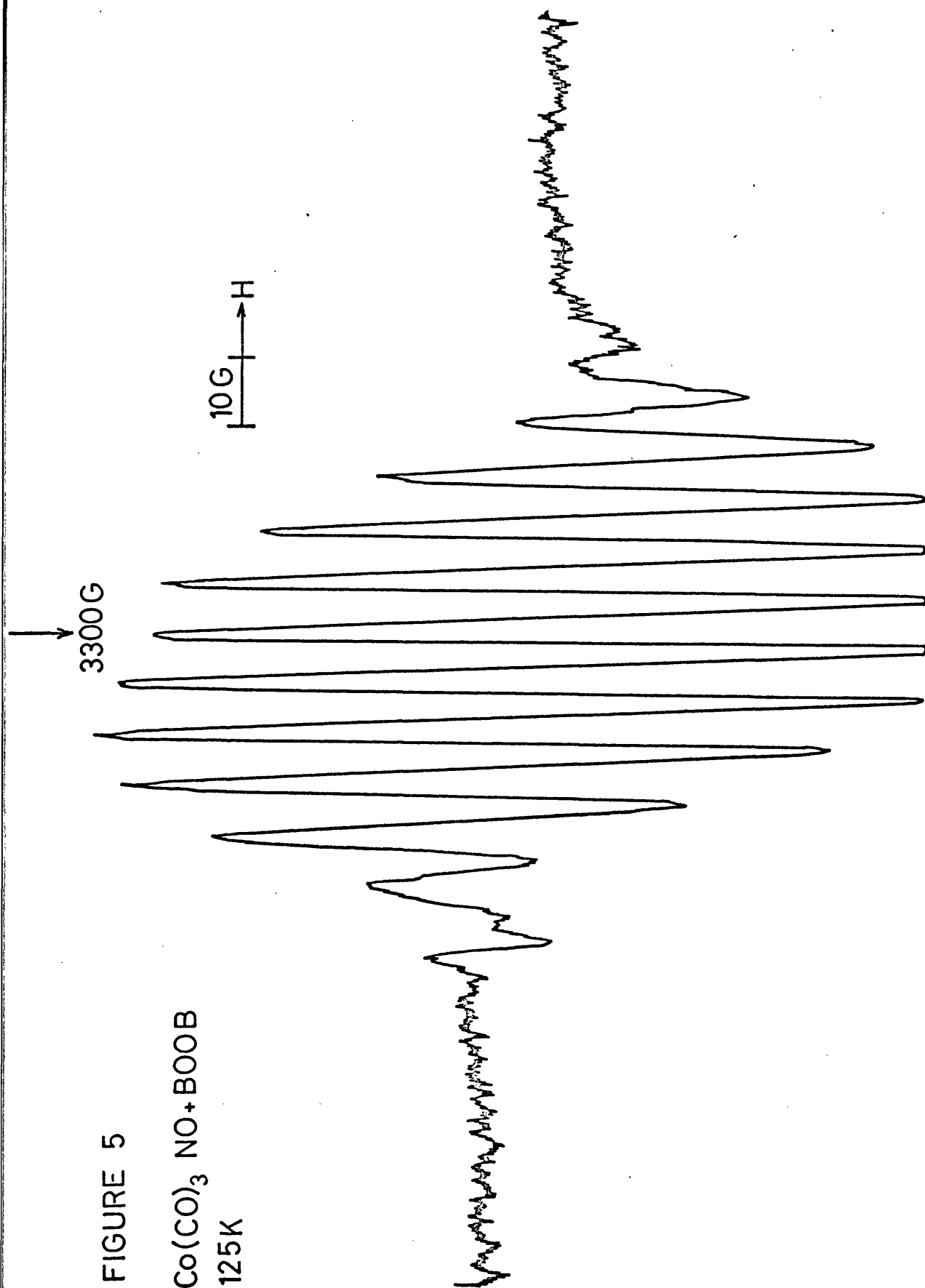
Cobalttricarbonylnitrosyl. -- U.v. photolysis of this carbonyl in the presence of t-butyl peroxide produced two different species, depending upon the temperature of the sample. At ca 125K a strong 12 line isotropic spectrum appeared having a hyperfine splitting of 7.5G (Fig. 5). Lowering the temperature to 85K gave an anisotropic spectrum of much reduced intensity, from which no reliable information could be obtained.

If the sample was studied at higher temperatures (ca 200K) a second species was obtained which gave a 15 line spectrum having a hyperfine coupling of 42G (Fig. 6). On lowering the temperature of the sample from 200K to 125K, whilst continuing the photolysis, the 12 line spectrum was seen to grow in (Fig. 7). Photolysis of samples of the carbonyl without peroxide did not produce either of the two species mentioned above, though a faint spectrum of another dimeric cobalt species was seen.

Hexacarbonyl complexes of chromium, molybdenum and

FIGURE 5

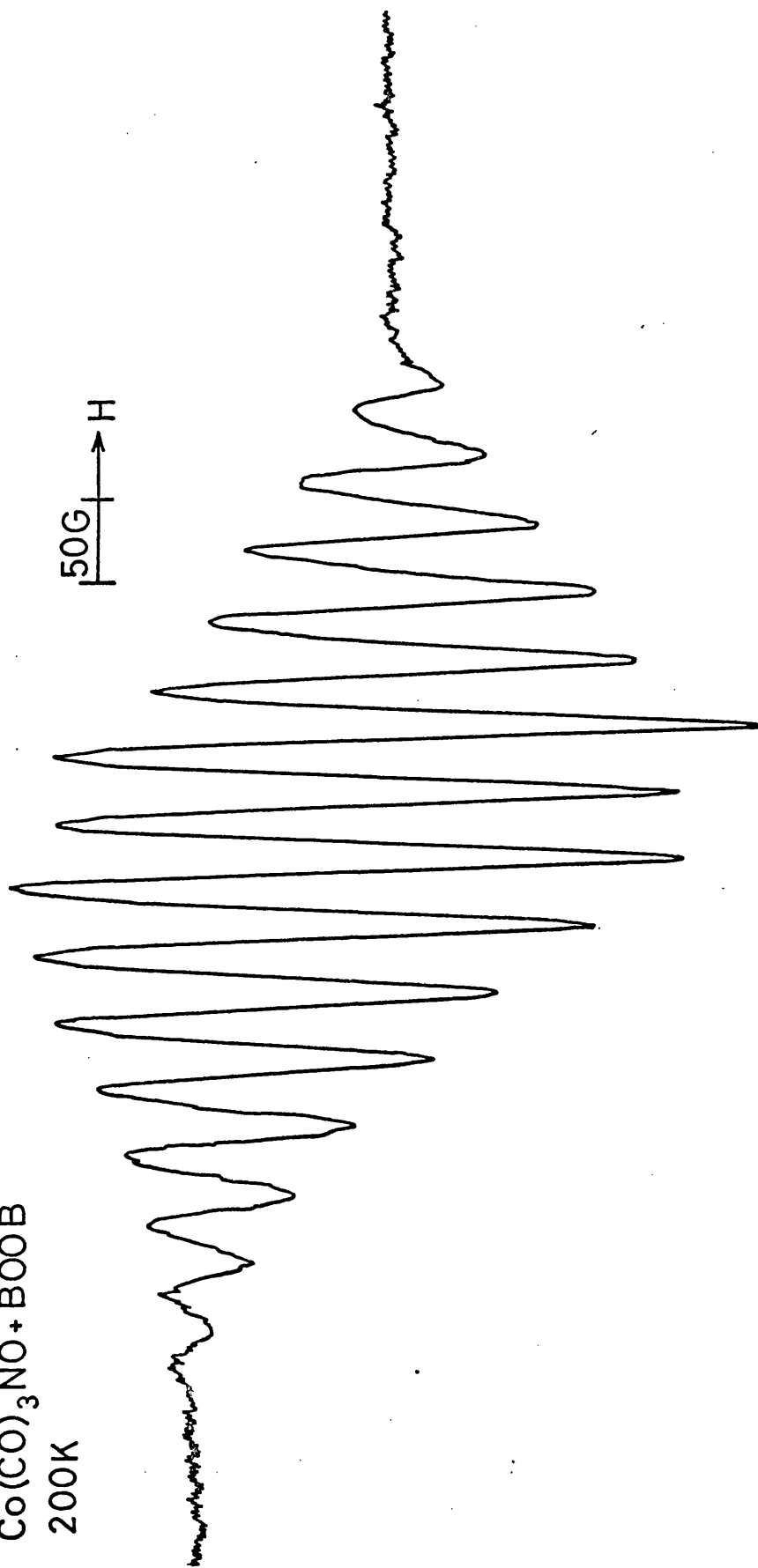
$\text{Co}(\text{CO})_3 \text{ NO} + \text{BOOB}$
125K



First derivative e.s.r. spectrum obtained from a U.V. photolysed solution of $\text{Co}(\text{CO})_3 \text{ NO/t-butyl peroxide}$ in isopentane.

FIGURE 6

$\text{Co}(\text{CO})_3\text{NO} + \text{BOOB}$
200K



First derivative e.s.r. spectrum obtained from a U.V. photolysed solution of $\text{Co}(\text{CO})_3\text{NO}/t\text{-butyl peroxide}$ in isopentane.

FIGURE 7
 $\text{Co}(\text{CO})_3\text{NO} + \text{BOOB}$
125K

↓
 $3200\text{G} \pm 500\text{G}$

50G
→ H



First derivative e.s.r. spectrum obtained from a U.V. photolysed solution of $\text{Co}(\text{CO})_3\text{NO}/t\text{-butyl peroxide}$ in isopentane, showing the growth of the radical in figure 5.

tungsten readily lose carbon monoxide when photolysed in hydrocarbon glasses³² and argon matrices³³, forming the unstable pentacarbonyl species. Photolysis of osmiumpentacarbonyl ($\text{Os}(\text{CO})_5$), in an argon matrix doped with NO, produces the dinitrosyl compound ($\text{Os}(\text{CO})_2(\text{NO})_2$) by loss of CO, the analogous reaction of $\text{Co}(\text{CO})_3\text{NO}$ in a CO doped matrix giving cobalt-tetracarbonyl, following loss of NO .³⁴ These results indicate that, in considering the photolysis of carbonyl/nitrosyl complexes, loss of both NO and CO may be expected. It remains unresolved as to which ligand is lost preferentially. It is most likely ligand loss accompanies attack by butoxy radicals rather than precedes it.

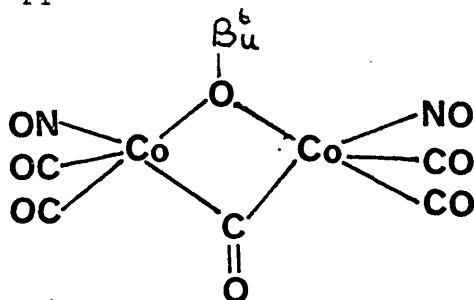
Table 3.

A and g values for radicals obtained on photolysis of $\text{Co}(\text{CO})_3\text{NO}$.

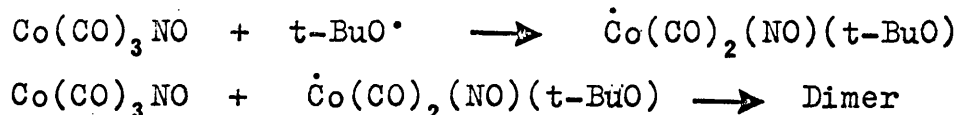
<u>Solution</u>	<u>Temp. (K)</u>	<u>g</u>	<u>a(Co)</u>	<u>a(N)</u>	<u>No. of lines.</u>
Isopentane/BOOB	125	1.97	7.5 G	15 G	12
Isopentane/BOOB	200	2.05	42	-	15
Isopentane	200	2.13	40	-	15

a. t-butyl peroxide.

The high temperature species, obtained in the presence of t-butyl peroxide, giving a 15 line spectrum, can most readily be assigned to a dimeric cobalt complex in which both the cobalt atoms are equivalent. Since t-butyl peroxide is required for the formation of the species the structure given below would appear to fit the limited data available.

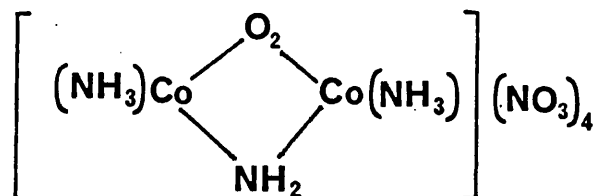


The formation of such a complex would involve loss of CO, addition of a t-butoxy radical and attack of the resulting radical on another substrate molecule.



E.s.r. cannot provide any information on the number of CO molecules lost in the first reaction, it is therefore possible that more than one is lost with the subsequent appearance of two or more bridging ligands. Loss of NO and addition of t-BuO[•] followed by dimerization would lead to a paramagnetic species, since both ligands act as three electron donors.

The lack of any nitrogen hyperfine coupling from the NO groups, at first sight, argues against the above assignment, but dicobalt peroxo radical anions of the structure

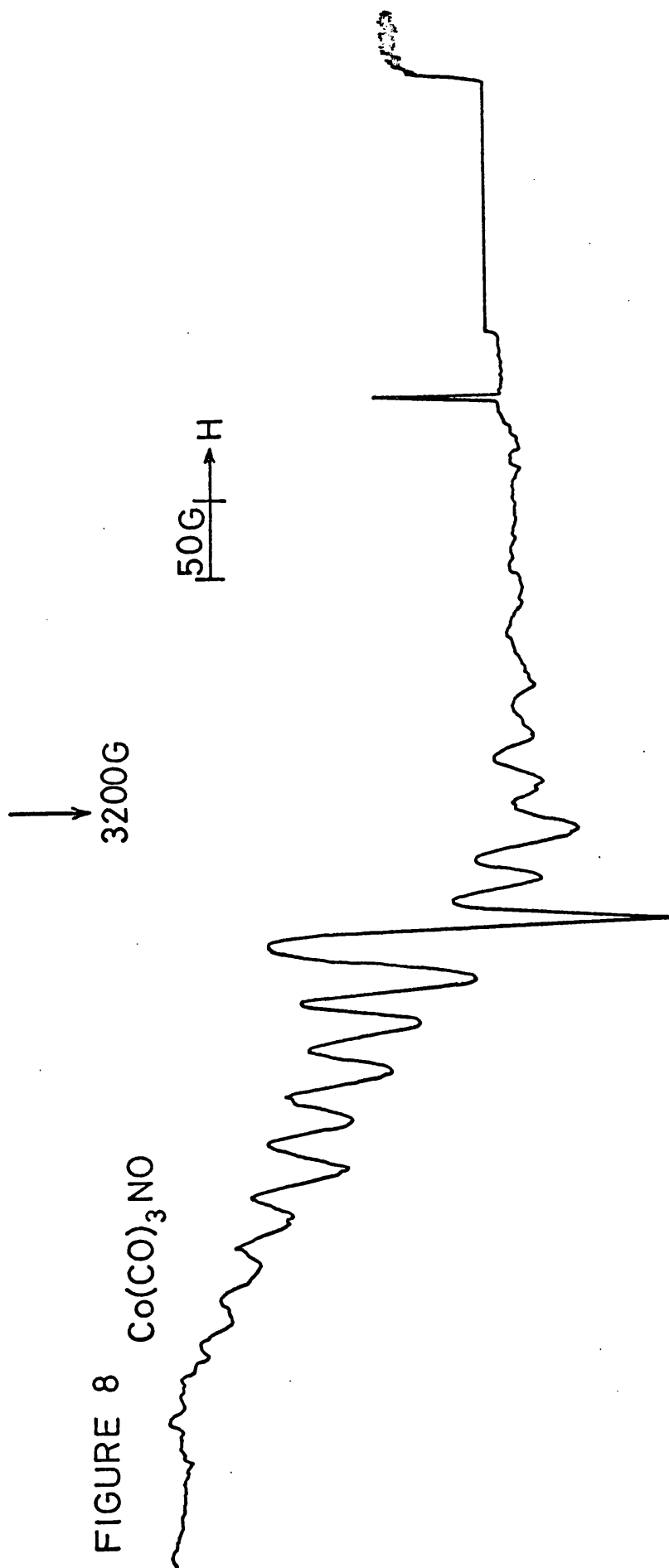


show no such coupling.³⁵ A number of similar compounds have been studied,³⁶ the spectra of which consist solely of 15 equally spaced lines ($a(\text{Co}) \approx 12\text{G}$). If the above assignment is accepted it would indicate that CO is lost preferentially to NO in the presence of t-butoxy radicals.

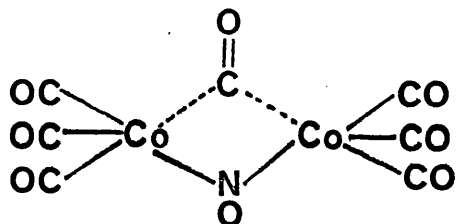
A very faint 15 line spectrum (Fig. 8) generated on photolysis of the carbonyl in the absence of peroxide has been tentatively assigned to the species,

FIGURE 8

$\text{Co}(\text{CO})_3\text{NO}$

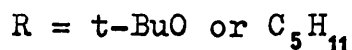
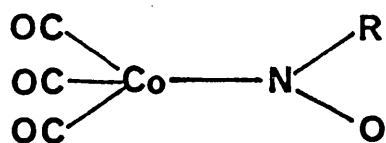


First derivative e.s.r. spectrum of $(\text{CO})_3\text{CoNO}$ U.V. photolysed in the absence of t-butyl peroxide.

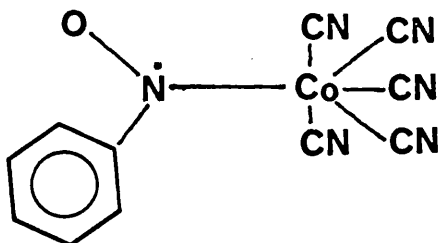


since loss of NO is the most reasonable process which could produce a radical intermediate.

The low temperature species, which also requires the presence of t-butoxy radicals, has been assigned to the radical



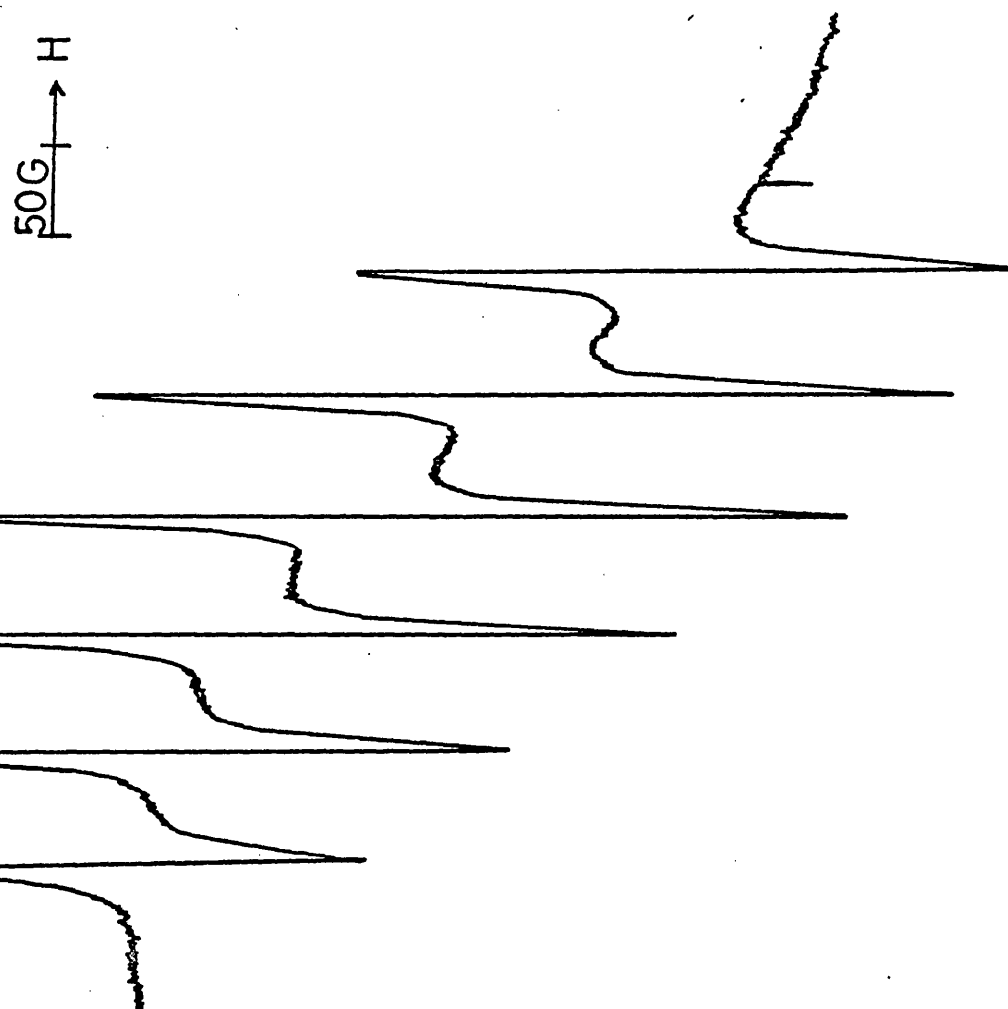
where $a(\text{Co}) = 7.5\text{G}$ and $a(\text{N}) = 15\text{G}$. This is in keeping with the liquid phase results obtained for the pentacyanophenyl - nitroxide ion, which has the structure



with $a(\text{Co}) = 10\text{-}12\text{G}$ and $a(\text{N}) = 13\text{-}15\text{G}$, depending on the phenyl group present.⁴¹ If the R group attached to the nitrogen is t-BuO then the low temperature species could easily undergo an intra-molecular rearrangement leading to the radical precursor of the dimer. Whilst, at first sight, this has much to commend it, providing as it does a link between the two radicals, the nitrogen hyperfine coupling to such a nitroxide species would be much greater than that observed.

Methylcyclopentadienylmanganesetricarbonyl. -- The spectrum obtained on photolysis, at 230K, in the presence of

FIGURE 9
 $\text{MeCpMn}(\text{CO})_3$
+ BOOB



First derivative e.s.r. spectrum of U.V. photolysed $\text{MeCpMn}(\text{CO})_3$ / t-butyl peroxide in isopentane.

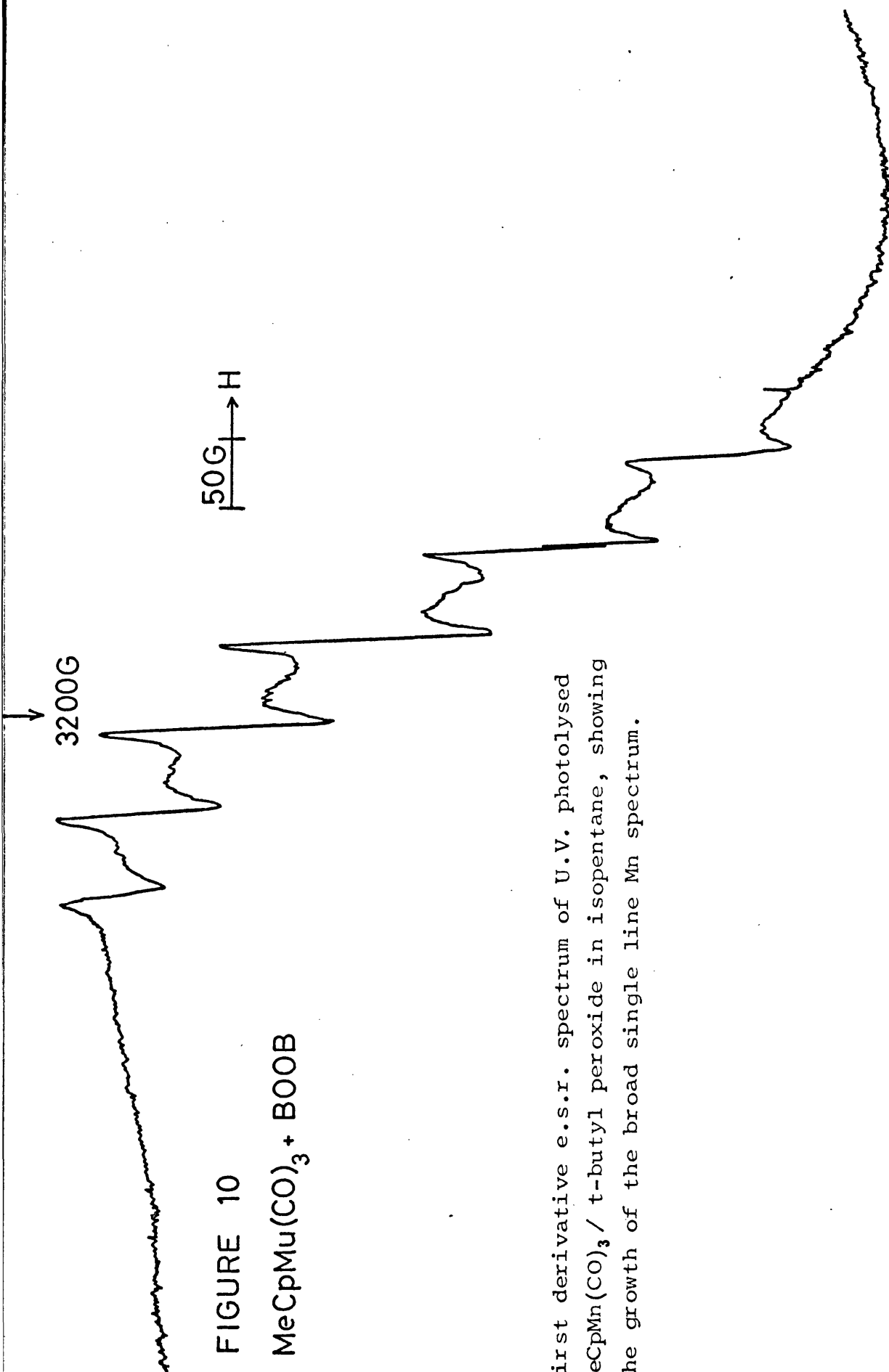
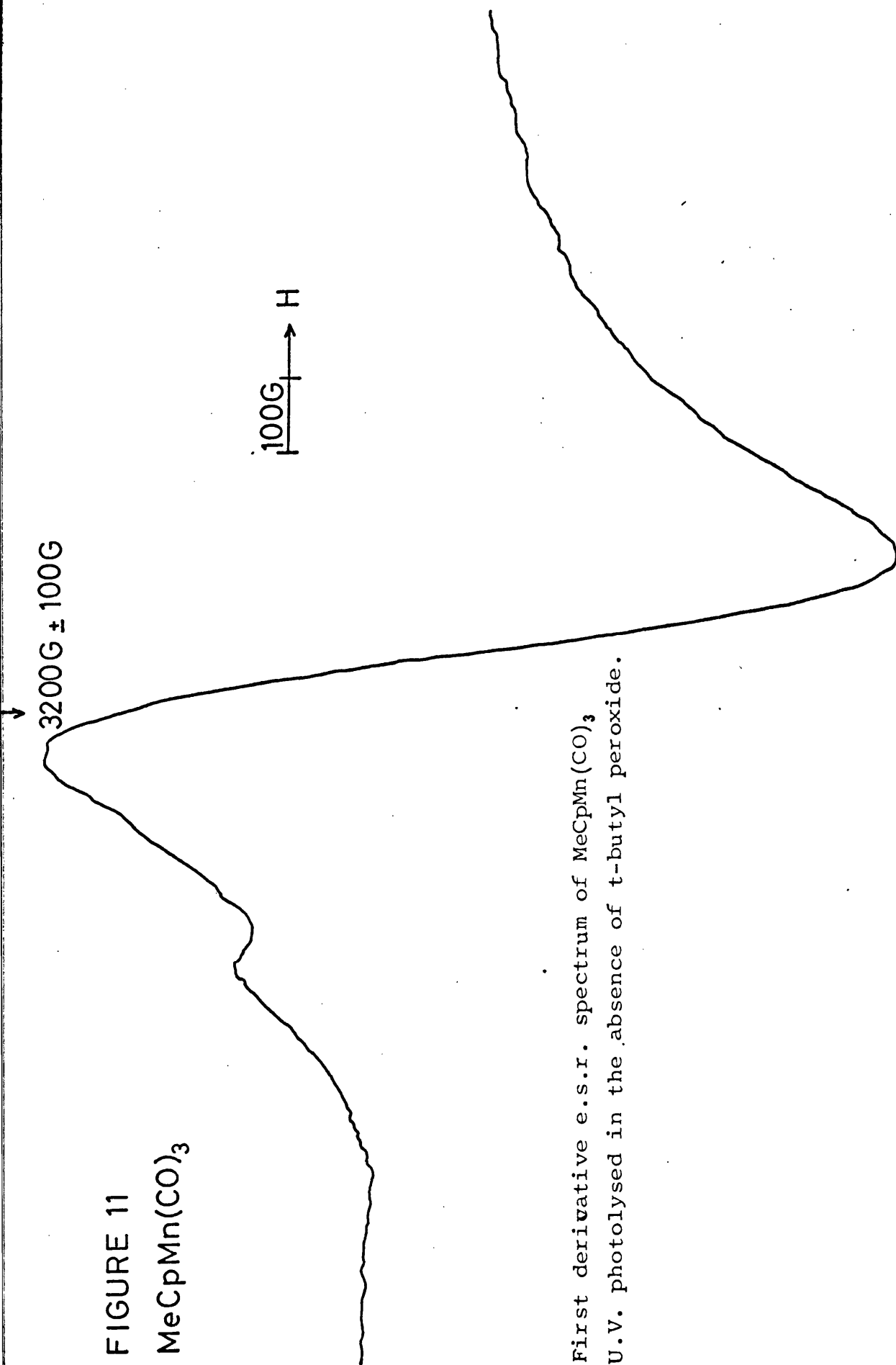


FIGURE 10

$\text{MeCpMn(CO)}_3 + \text{BOOB}$

First derivative e.s.r. spectrum of U.V. photolysed MeCpMn(CO)_3 / t-butyl peroxide in isopentane, showing the growth of the broad single line Mn spectrum.

FIGURE 11
 MeCpMn(CO)_3



First derivative e.s.r. spectrum of MeCpMn(CO)_3
U.V. photolysed in the absence of *t*-butyl peroxide.

peroxide consisted of six isotropic lines $a(\text{Mn}) = 65\text{G}$ (Fig. 9). This species showed considerable stability, removal of the light source leading to a very slow decay of the signal. Cooling of the sample during photolysis led to the growth of a single broad line underneath the six line spectrum and loss of the hyperfine structure (Fig. 10). At 77K only the broad line was present. Photolysis of the complex in the absence of peroxide gave a similar single broad signal, (Fig. 11) both at 77 and 200K.

Table 4.

A and g values obtained on photolysis of $\pi\text{-MeCpMn}(\text{CO})_3$.

<u>Solution</u>	<u>Temp. (K)</u>	<u>a(Mn)</u>	<u>g_{av}</u>	<u>Line width (peak peak)</u>
Isopentane/BOOB	230	65	2.00	-
Isopentane/BOOB	77	-	2.00	290(G)
Isopentane	200	-	2.00	290
Isopentane	77	-	2.00	290

Loss of CO from $\text{CpMn}(\text{CO})_3$ has been reported⁴² upon u.v. ($\lambda = 4545\text{\AA}$) photolysis of a methylcyclohexane/nujol solution. In this case only one CO was lost but complete CO loss can be induced by photolysis in the presence of a tridentate ligand.⁴³ It therefore seems likely that the six line species is either due to addition of a butoxy radical to the manganese atom and loss of one or more CO ligands, or addition of a butoxy radical to one of the carbonyl ligands.

Cyclopentadienylvanadiumtetracarbonyl. -- At 200K, photolysis of the carbonyl, in the presence of peroxide, with the shp. mercury lamp produced a spectrum consisting of 8 evenly spaced lines $a(\text{V}) = 62\text{G}$. (Fig. 12) Warming of the sample to 210K, during the photolysis, gave a very much more

complex spectrum consisting of three species, the original 62G species (A), a second radical with a hyperfine coupling of 66G and a third with a hyperfine coupling of 57G (Fig. 13). Photolysis of the sample, at 250K, with the Xenon lamp, resulted in a further vanadium species with a much smaller coupling of 27G (Fig. 14).

Table 5.

A and g values obtained on photolysis of $\text{CpV}(\text{CO})_4$.

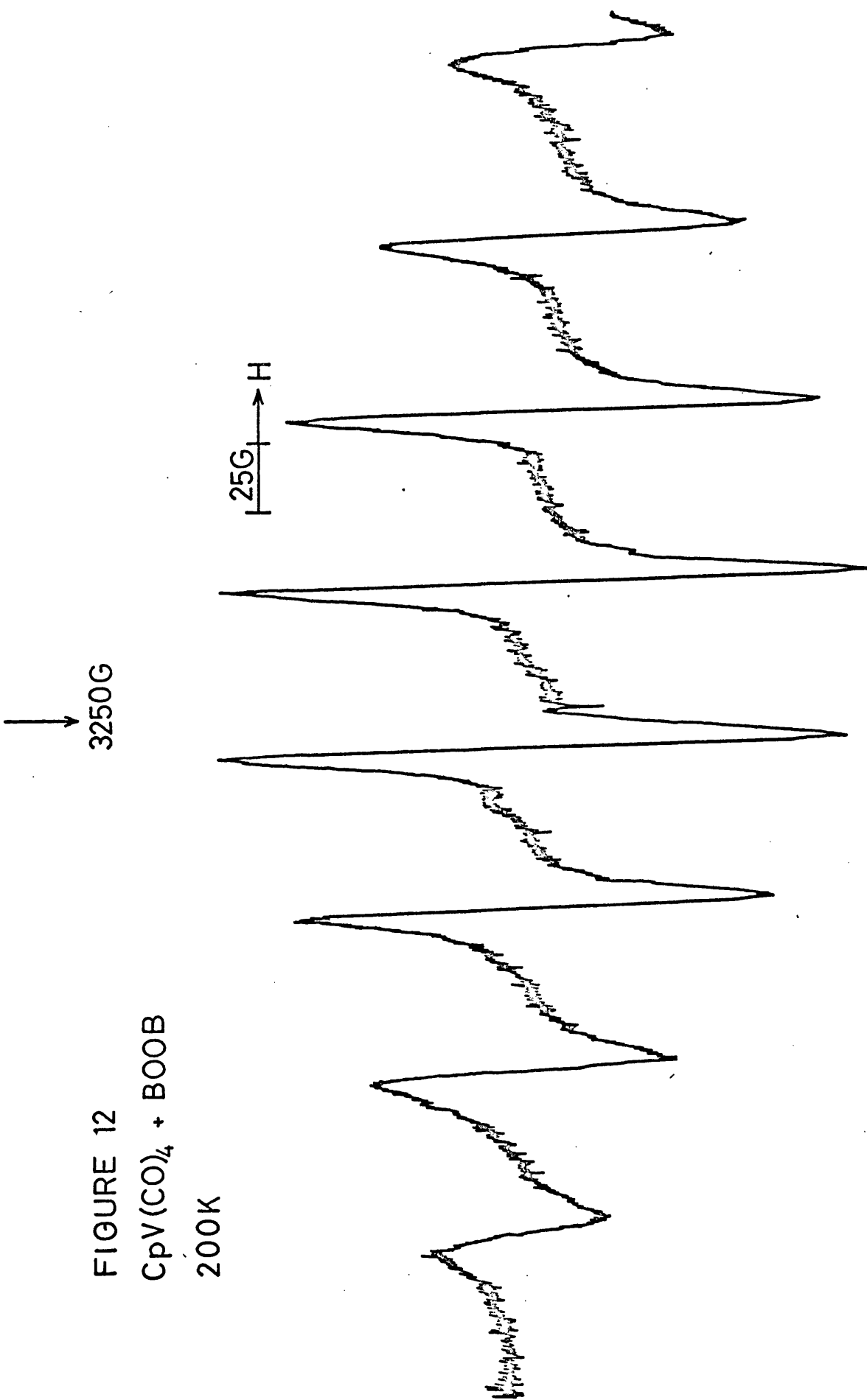
<u>Solution</u>	<u>Temp. (K)</u>	<u>g_{av}</u>	<u>$a(V)$</u>	<u>Species</u>
Isopentane/BOOB	200	1.992	62	A
Isopentane/BOOB	210	1.987	66	B
Isopentane/BOOB	210	2.002	57	C
Isopentane/BOOB	245	2.005	27	
Isopentane/BOOB	77	$g_{ } = 1.976$ $a_{ } = 72$		
		$g_{\perp} = 2.042$ $a_{\perp} = 4.5$		

Rapid cooling of this fourth radical to 77K gave a solid state spectrum showing axial symmetry (Fig. 15). This spectrum shows an $a_{||}(\text{Co}) = 72\text{G}$, which combined with the isotropic hyperfine coupling of 27G, suggests a very small $a_{\perp}$ coupling. This is borne out by the spectrum which provides no clear data for the perpendicular coupling, though consideration of the line shapes fixes the position of $g_{\perp}$.

The spectrum provides no guide as to the sign of the hyperfine couplings, and it is therefore necessary to consider two possible combinations. These are where $a_{||}$ and $a_{\perp}$ are both negative or positive, since any other combination would not provide a small perpendicular coupling.

If $a_{||}$ and $a_{\perp}$ are taken as negative then $2B = -45\text{G}$ indicating that the electron is strongly delocalised into a

FIGURE 12
 $\text{CpV(CO)}_4 + \text{BOOB}$
200K



First derivative e.s.r. spectrum of U.V. photolysed CpV(CO)_4 / t-butyl peroxide in isopentane.

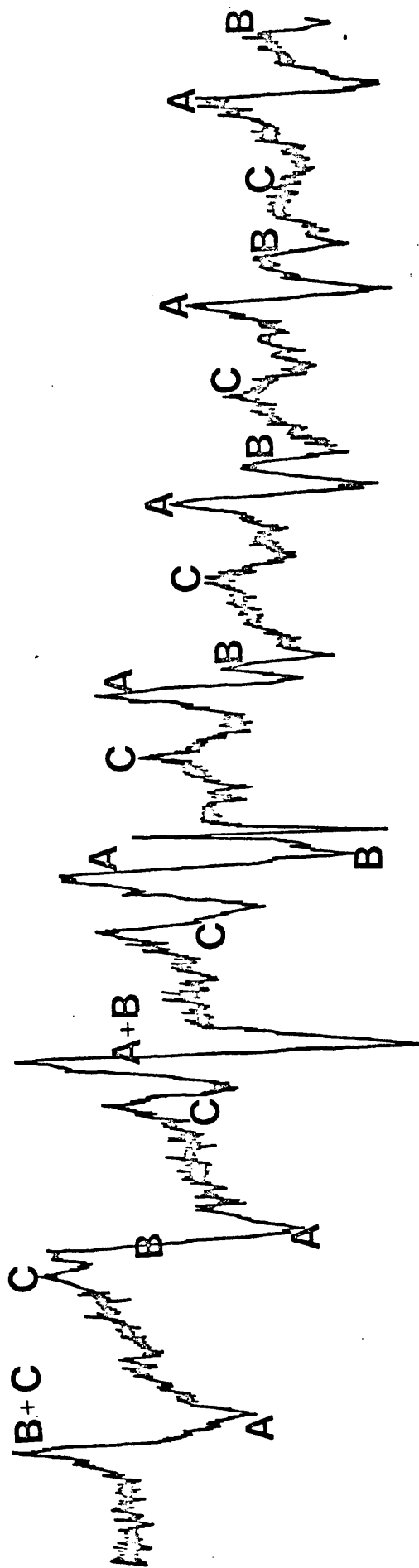
FIGURE 13

$\text{CpV}(\text{CO})_4 + \text{BOOB}$

210 K

↓
3260 G

25G → H

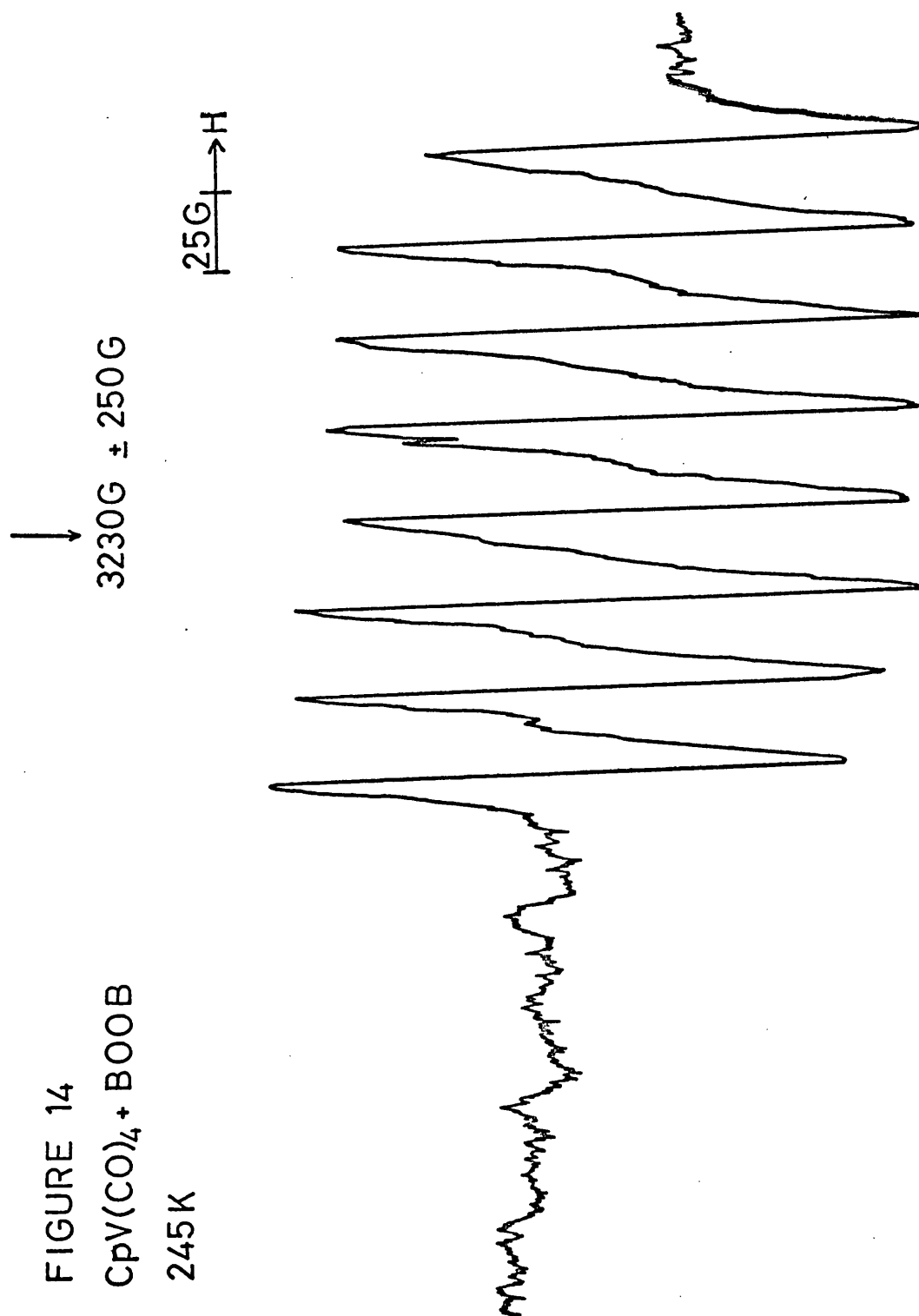


First derivative e.s.r. spectrum of U.V. photolysed $\text{CpV}(\text{CO})_4$ / t-butyl peroxide in isopentane, showing the three vanadium species produced on raising the solution temperature from 200 to 210 K.

FIGURE 14

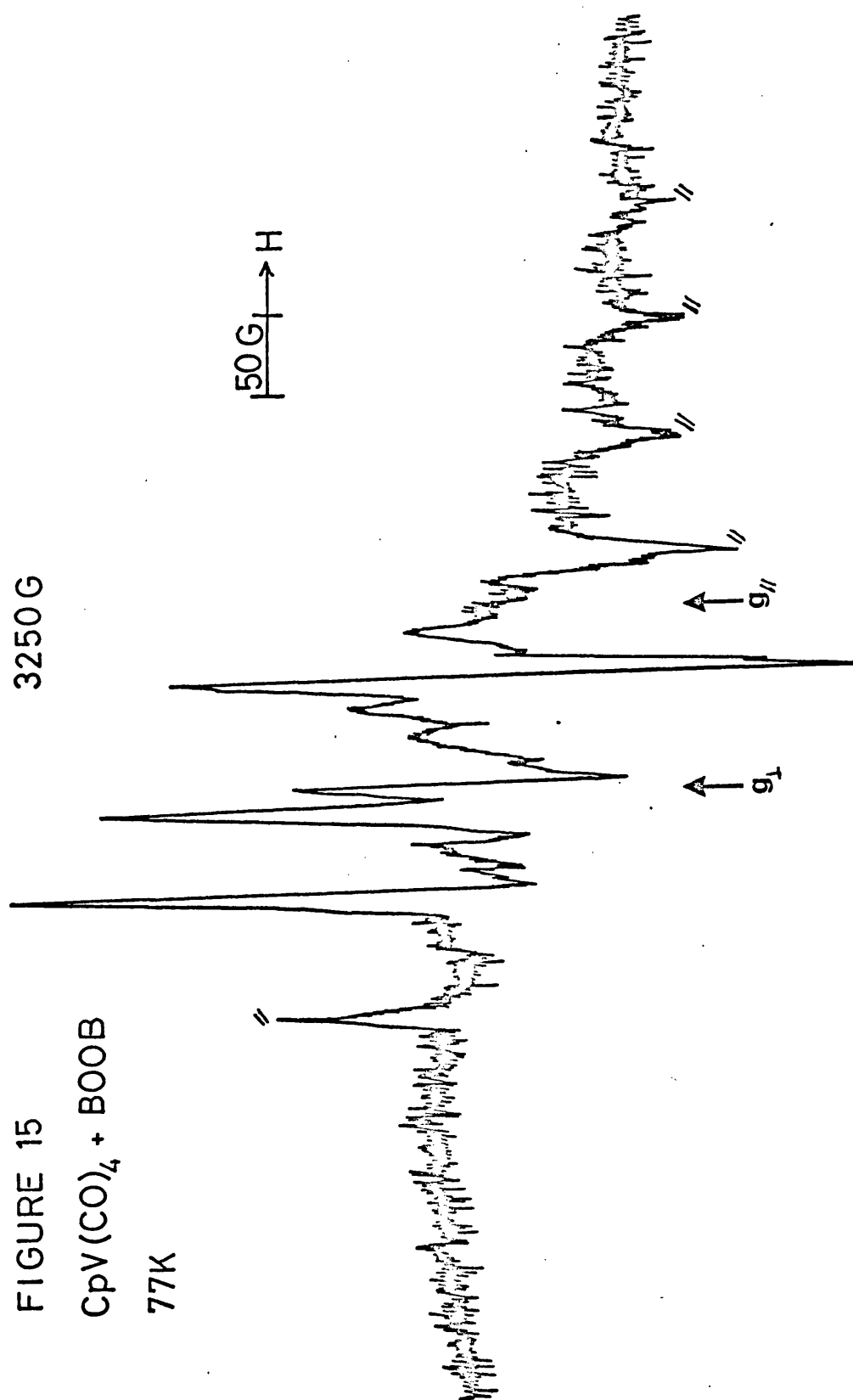
$\text{CpV}(\text{CO})_4 + \text{BOOB}$

245 K



First derivative e.s.r. spectrum of U.V. photolysed $\text{CpV}(\text{CO})_4$ / t-butyl peroxide in isopentane, showing the high temperature spectrum.

FIGURE 15
 $\text{CpV(CO)}_4 + \text{BOOB}$
 77K



First derivative e.s.r. spectrum of U.V. photolysed CpV(CO)_4 / t- butyl peroxide in isopentane, showing the solid-state spectrum of the species shown in figure 14.

d or p - orbital, though not the d_{z^2} - orbital. The low isotropic coupling is indicative of either a small 4s - admixture in the unpaired electron orbital or a small degree of spin polarisation.

When a_{iso} and $a_{//}$ are taken as positive then $2B = +45G$, which immediately requires the unpaired electron to be in an essentially d_{z^2} - orbital. The positive a value now requires a large admixture of 4s character.

Cycloheptatrienylmolybdenumtricarbonyl. -- Photolysis of a MeTHF solution of the compound led to a change of colour (Colourless to yellow) but no e.s.r. spectrum.

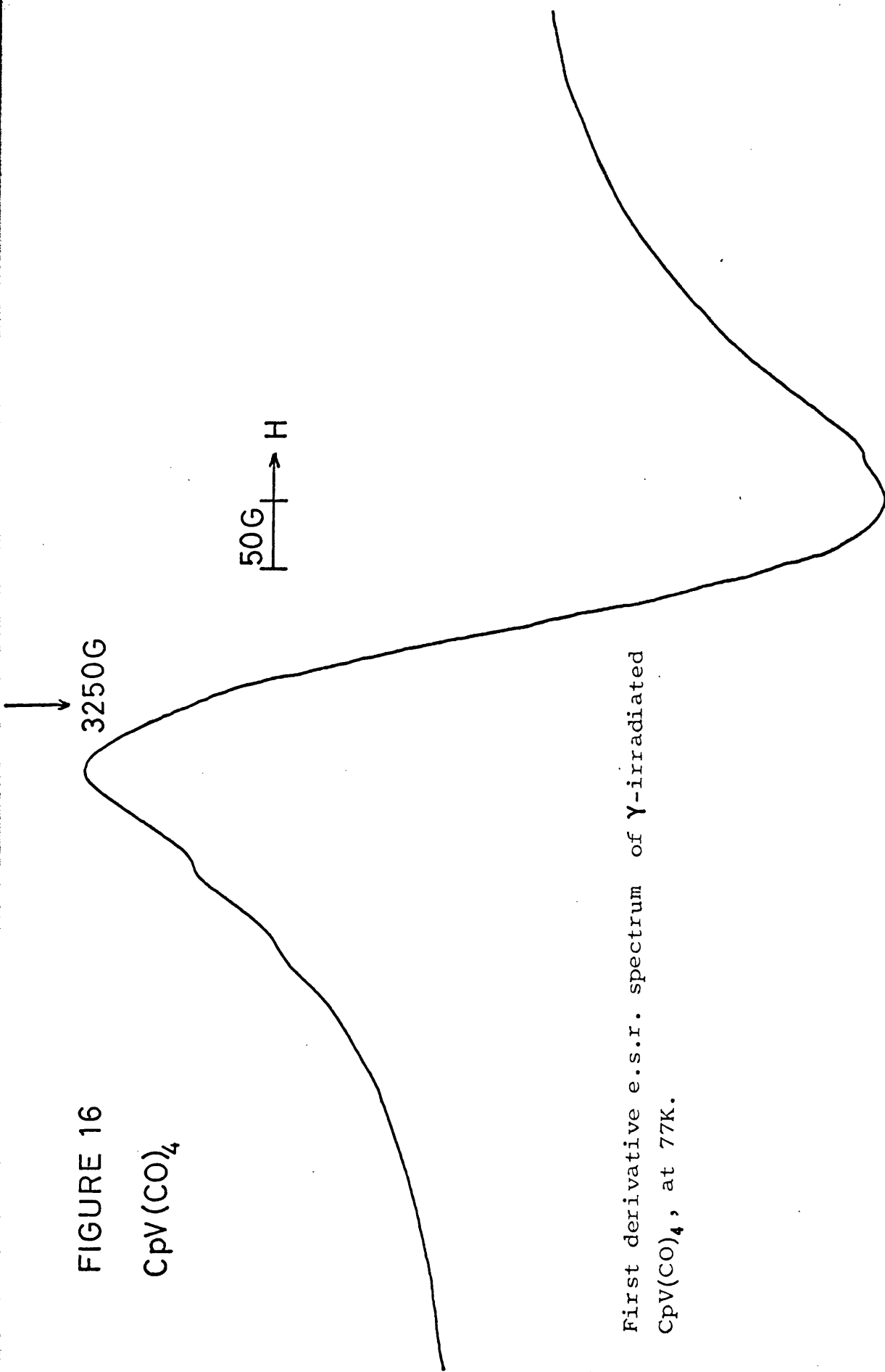
Dimanganesedecacarbonyl. -- Irradiation of the decacarbonyl under exactly the same conditions as Hallock and Wojcicki⁶ did not produce the previously described six line spectrum ($a_{Mn} = 93G$). In all cases the rest of the observed changes were identical, including the decomposition using 3000Å and 2537Å lamps. The only e.s.r. spectrum obtained was a single broad line showing no hyperfine splitting but covering a range of 290G (peak - peak). It can only be concluded that the results reported previously were those of an impurity, present in the starting material. The reported manganese coupling appears very high for $Mn(CO)_5$ and is very similar to that of the Mn^{2+} ion.

7.9 Y- Irradiation of $CpV(CO)_4$.

Irradiation of the powdered solid at 77K produced a single broad isotropic signal (200G peak - peak), showing very slight shoulders indicative of ^{51}V hyperfine coupling ($a(V) = 65G$). Annealing of the sample did not improve the resolution of the hyperfine coupling, (Fig. 16).

FIGURE 16

$\text{CpV}(\text{CO})_4$



First derivative e.s.r. spectrum of γ -irradiated $\text{CpV}(\text{CO})_4$, at 77K.

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Appendix 1.

1.1 Second-order corrections for hyperfine coupling constants g values.

The magnitude of energy for each energy level (arising from the application of the external field) is given by

$$E = E_0 + g(m_s H + m_s m A)$$

where m_s and m are the electronic and nuclear quantum numbers. The transitions between these levels give rise to equally spaced hyperfine lines. This equation is only a valid approximation when the ratio of the external field to hyperfine coupling is large.

When the principal hyperfine coupling constants are of the order of magnitude of the external field, the first order assumption that the nuclear spin is quantized along the external field is no longer true. The direction of quantization of the nucleus will depend on the relative orientations of the external field; and the hyperfine field. This second order field effect introduces an error in the observed coupling which is corrected using a convenient form of the Breit-Rabi¹ equation.

a) Correction for $I = \frac{1}{2}$

If A is the hyperfine coupling constants and H_1 and H_2 are the field at which the resonance lines occur, then the corrected value of A is obtained by solving iteratively the equation

$$A = (H_2 - H_1) - \frac{A^2}{4} \left(\frac{1}{H_1} - \frac{1}{H_2} \right) + \frac{A^4}{16} \left(\frac{1}{H_1^3} - \frac{1}{H_2^3} \right)$$

The third term is neglected for values of $A < 500\text{G}$ and is then written as

$$A^* \simeq (H_2 - H_1) \left(1 - \frac{A^2}{4H_1 H_2} \right)$$

b) Correction for $I = 3/2$.

If a_{ii} , a_{jj} and a_{kk} are the measured hyperfine constants derived from the positions of the extreme lines of the quartet which occur at fields H_1^i and H_4^i etc., then the principal values A_{ii} , A_{jj} and A_{kk} , corrected for second order effects, is given by iteratively solving the three cyclic equations derived from the following:

$$A_{ii} = \left[(H_4^i - H_1^i)/3 - (a_{jj} + a_{kk})^2/16 \right] \left[1/(H_1^i + a_{ii}) - 1/(H_4^i - a_{ii}) \right]$$

similarly, the experimental g-factors can be corrected for second order effects using the three equations derived from:

$$h/g_{ii} = \left[(H_4^i - H_1^i)/2 + \frac{3}{8}(a_{jj} + a_{kk}/2)^2 \right] \left[1/(H_1^i + a_{ii}) + 1/(H_4^i - a_{ii}) \right]$$

Corrections for higher spin systems and systems showing asymmetry involve lengthy iterative procedures. Such calculations in this study have been carried out using a computer program kindly provided by Dr. H.C.Starkie².

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ABSTRACT

A brief account of the principles and experimental techniques of electron spin resonance is given in Chapters 1 and 2.

In Chapter 3, the γ -radiolysis of alkyl mercuric halides and dimethyl mercury is discussed. In the spectra of the first group of compounds two radicals were identified, these being $R_2\dot{C}HgX$ and $Et\dot{H}g$ (or $X\dot{H}g$) species. The negative ion $MeHgMe^-$ was trapped in irradiated Me_2Hg , at 77K.

The mechanisms to be found in the solid state radiolysis of trivalent phosphorus compounds are discussed in Chapter 4. The hyperfine couplings for the radicals generated are tabulated and trends in the ^{31}P couplings discussed with respect to the ligand electronegativities. U.v. photolysis of the phosphites $(MeO)_3P$ and $(MeS)_3P$ is shown to produce two phosphorus centred species, identified as $\dot{P}L_2$ and $Me\dot{P}L_2$ radicals. Production of radicals of the type $H_2\dot{C}SP(SMe)_2$ occurred both on photolysis and γ -irradiation. These radicals did not exhibit the large hyperfine coupling to phosphorus found with $H_2\dot{C}CH_2PR_2$ radicals.

In Chapter 5 a range of previously unknown $\dot{P}L_2$ radicals, produced by γ -radiolysis of PL_3 compounds, is considered. The ^{31}P hyperfine couplings for these radicals are remarkably constant when compared to a similar group of nitrogen-centred radicals, this being taken to show a very small degree of spin-delocalisation onto the ligands.

The radiolytic decomposition of a number of organosilyl compounds is considered in Chapter 6. The trimethylsilyl radical $Me_3\dot{Si}$ is found to behave normally in a range of solvents,

contrary to previously reported results.

Chapter 7 covers firstly the matrix isolation of cobalt and manganese carbonyl peroxo-species, and secondly the u.v. photolysis of transition-metal carbonyls, in the presence of t-butyl peroxide. In this latter section the photolysis of MeCpMn(CO)_4 , $\text{Co(CO)}_3\text{NO}$ and CpV(CO)_4 is discussed. Photolysis of $\text{Mn}_2(\text{CO})_{10}$ in MeTHF is not found to give the $\dot{\text{Mn(CO)}}_5$ radical as reported previously.