

ELECTRON SPIN RESONANCE STUDIES OF
IRRADIATED ALKYL HALIDES

A Thesis presented for the Degree of
Doctor of Philosophy
in the Faculty of Science of Leicester University

by

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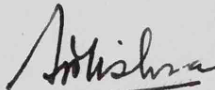
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STATEMENT

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 July 1972 - August 1974. No part of this work is being concurrently submitted for any other degree.


S.P. Mishra.

This work is dedicated to
(the memory of) my late mother.

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CHAPTER ONE

INTRODUCTION ON RADIOLYSIS OF ALKYL HALIDES

The study of the chemical effects caused by ionizing and other nuclear radiations in their passage through matter is generally called radiation chemistry. Such radiation chemical effects are of great practical significance in nuclear-reactor technology and in the interaction of radiations with biological systems. In recent years, considerable research has been carried out for a detailed study of the effects of high-energy radiation on simple molecules, and it has been through the application of techniques for studying fast reactions and for identifying reactive intermediates that a better appreciation of the overall chemical changes involved in radiation chemistry has evolved. Of significant interest has been the electron spin resonance studies of systems irradiated at low temperatures.

I.1 Brief Historical Development of Radiation Chemistry

The earliest studies of the chemical effects of high-energy radiation on matter were concerned mainly with gaseous systems. Bragg (1) pointed out that the ionisation produced in the air surrounding radio-active material was related to the ability of the latter to induce chemical reactions. Curie (2) reasoned that the act of ionisation must precede all chemical processes in a

system undergoing radiation-induced chemical change. At about this time, Lind (3) did a series of experiments on the effect of α -particles on gases in which he measured the number of ion-pairs formed (N) and the number of molecules undergoing chemical change (M) as a result of absorption of radiation. The findings clearly showed that ionisation and chemical action are closely related. Subsequently, based on ion-pair yield (M/N) measurements, the "ion-cluster" theory was proposed (4,5,6) to explain the observations in systems where M/N was found greater than 3. An alternative concept to explain M/N was developed by Eyring, Hirschfelder and Taylor (7) to invoke a free-radical chain mechanism identical with that for the analogous thermal or light-induced reaction. The emphasis on neutral free-radical processes however inadvertently led to an almost total disregard for possible ionic processes in the subsequent treatment of radiation chemical data. It was only in the early 1960's that the importance of the role of ionic processes was re-evaluated, especially in condensed systems.

Several important and interesting researches were carried out during 1930's by Frick and co-workers (8,9) on liquid water and aqueous solutions. A fundamental difference between radiation chemistry and photochemistry was an important finding of these works. In light-induced reactions, energy is generally absorbed by the solute, which subsequently undergoes reaction with the solvent and other solute. Whereas in radiation chemistry, energy

is absorbed by both the solvent and the solute, but if the solution is dilute almost entirely by the solvent. Fricke observed that very little chemical change occurred in the radiolysis of pure water, whereas in aqueous solutions the solute underwent considerable reaction. It was postulated that the water was being converted to a form ("active water") which was chemically reactive but sufficiently long-lived so as to be able to diffuse through the solutions and react with solute molecules. The phenomenon of the transfer of the chemical consequences of energy absorbed by the solvent to dissolved solute introduced the important concept of the 'indirect action' of radiation.

During later stages of the development of radiation chemistry a more logical method of expressing radiation-chemical yield, the 'G value', was introduced by Burton (10) to express the number of molecules undergoing chemical change per 100 ev of energy absorbed by the medium. The advantage of this unit over ion-pair yield (M/N) is that it relates the yield to a quantity which, in principle, can be measured directly. It also has the advantage that it does not imply that chemical action is controlled by the number of ions formed, as does the ion-pair yield. The G value and ion-pair yield are related by the expression : $G = 100 M/WN$, where W is expressed in electron volts.

I.2 Interaction of Radiation with matter

The initial step of the interaction of ionising radiation involves a perturbation of the medium resulting from the passage of radiation. The radiation deposited in the medium is absorbed almost entirely by interaction with the electrons of the constituent molecules (11,12), and the individual acts of energy transfer generally lead to the formation of electronically excited molecules. These processes which occur within about 10^{-17} sec. after the primary radiochemical act, have been described as "physical stage of radiation damage" by Hart and Platzman (11), though from the chemists' point of view there is little detail available for a description of the processes that occur within them (12). The excited molecules do undergo their own characteristic chemical change which not only involves the formation of excited species (13) but also leads to subsequent ionisation with the production of energetic secondary electrons and positive ions. (11,14,15).

Secondary electrons, which arise from ionisation processes caused by the passage of X-rays, γ -rays and radioactive radiations formed by nuclear transformation of nuclei in the medium, are produced from the parent molecule by photoelectric effect, but, when the incident photon energy occurs in the range 0.1 - 2 MeV, their production by concurrent Compton scattering also becomes important (11,14). These ejected electrons may themselves be sufficiently energetic to produce further ionisation and excitation.

The less energetic secondary electrons have short range and produce smaller clusters or spurs of excited and ionised species close to the centre of the original ionisation whereas the more energetic ones (~ 100 eV) in condensed systems form tracks of their own and are, in fact, responsible for a significant proportion of the total number of ions produced in any radiation process. The spurs which contain these clusters of ions and excited species can be considered as the centres of the localised radiation damage and usually occur in discrete little pockets within the medium - typically at intervals of about 10^4 \AA and extending over an area of approximately 500 \AA (11,12,16,17). The immediate surroundings of the species trapped within the spur helps to determine the chemical processes which occur in a system. However, the fate of the ejected electron and the complementary positive hole (or positive ion subsequently formed from it) play an important role in producing reactive intermediates of significance to understand the mechanistic aspects of the overall chemical consequences.

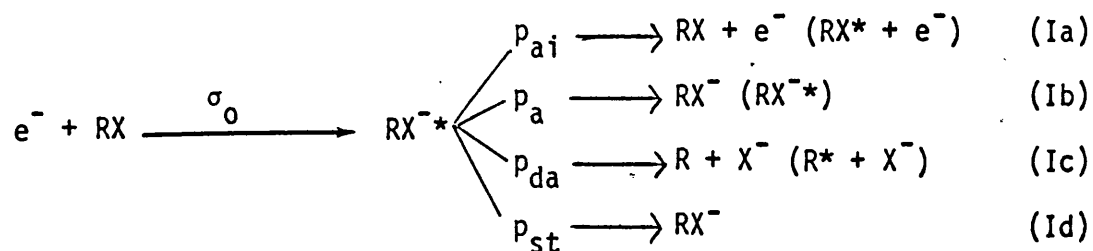
The ejected electron and the secondary electrons rapidly lose their excess energy in condensed phase (within approximately 10^{-10} sec) by collision and then undergo a variety of reactions both by attachment and by dissociative processes. Their fate depends on the nature of the solvent, the extent of hydrogen bonding within the solvent, and the nature of any solute present.

I.3 Radiolysis of Organic halides

Organic halides have acquired a fundamental importance in radiation chemistry, primarily through their often high electron affinities. They are widely used as electron scavengers and preferentially interfere with ionic reactions.

Of all the energies secondary electron attains during the thermalisation process the sub-excitation energy range is one of the most interesting, concerning electron reactions with halocarbons (or any molecule with finite probability for negative ion formation). The scattering processes and the temporary negative ion formation govern the thermalisation process of sub-excited electrons. If the negative ion state decays by auto-ionisation the net result is a loss of energy for the electron evolved. However, if the negative ion state splits into an ionic plus neutral fragment or is itself a long lived anion, the electron is trapped. This process is called electron attachment, being dissociative if fragments are formed immediately.

An electron of energy E_e which is captured by an organic halide molecule will initiate one or several of the reactions (Ia)-(Id). The symbols p_{ai} , p_a , p_{da} and p_{st} represent the probabilities of autoionisation, attachment, dissociative attachment and stabilisation, respectively.



Similarly the reaction cross-sections may be labelled σ_{ai} , σ_a , σ_{da} or σ_{st} , and σ_0 is the cross-section for the formation of the transient negative ion state $(RX^{\cdot-})^*$, normally in some excited state (electronic, vibrational and/or rotational). Decay of $(RX^{\cdot-})^*$ through autoionisation (reaction Ia) corresponds to elastic scattering if RX remains in the ground state, or inelastic scattering if RX is reformed in an excited state. In the dissociative electron attachment (reaction Ic) a chemical bond is broken. For organic halides this is usually the C-X bond. The collisional stabilisation (reaction Id) is characterised by its pressure dependence, in contrast to reaction (Ib) where the anion is stable because of a minimum in the potential energy surface. But with organic halides the dissociative electron attachment and the autoionisation are the most favoured processes. The lifetime of $(RX^{\cdot-})^*$ can be as short as 10^{-14} sec. or more than milliseconds. The anion is somewhat arbitrarily said to be short lived if it cannot be detected in a mass spectrometer ($\tau_{1/2} < \text{microseconds}$) and long lived otherwise ($\tau_{1/2} > \text{microseconds}$).

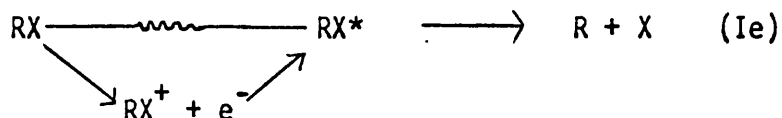
Alkylhalides (fluorides excepted) are among the most radiation-sensitive organic compounds. This sensitivity may be ascribed to the weakness of the C-X bond relative to C-H or C-C.

Thus, the main effect of radiation was found to break a carbon-halogen bond to give alkyl radicals by dissociative electron attachment (reaction 1c). Free halogen atoms show a diminution in reactivity in the series $F^{\cdot} > Cl^{\cdot} > Br^{\cdot} > I^{\cdot}$. Chlorine atoms, for example, can abstract hydrogen atoms from organic molecules, which bromine atoms undergo this reaction less readily, and iodine atoms not at all. Thus the initial products from aliphatic chlorides generally include hydrogen chloride, whereas iodides tend to give iodine, and bromides generally give both hydrogen bromide and bromine.

Early workers in the field of ESR took advantage of the simplicity of the experimental procedure to make very extensive exploratory studies of radiation effects on alkyl halides. γ -irradiation of alkyl halides at 77°K was found to yield parent alkyl radical. Cole, Pritchard, Davidson and McConnel (19) studied the radiolysis of $^{12}CH_3I$ and $^{13}CH_3I$ and gave an early indication of the value of ^{13}C hyperfine splitting for a π -electron radical (41 ± 3 gauss for $^{13}CH_3$ radical). Ayscough and Thomson (20) were able to observe most of the other simple alkyl radicals from irradiated alkyl halides.

Based on various e.s.r. results on irradiated alkyl halides it was concluded that the primary fission process in the radiolysis is the homolytic or heterolytic dissociation of the carbon-halogen

bond (reactions Ic and Ie).



The absence of any detectable signal from trapped halogen atoms did not help to distinguish between the two processes since there is good reason to believe that the spectra of halogen atoms would be broadened beyond detection. The presence of charged species such as RX^- or RX^+ in the irradiated alkyl halide has been of some importance. Some of the most significant information has been provided in papers by Hamill and by Willard who find spectroscopic evidence for the participation of both cationic and anionic species in the radiolysis (21-27). However, e.s.r. evidence has been lacking, though the very curious spectra observed in γ -irradiated polycrystalline alkyl halides and extending over many hundreds of gauss may have great significance. Such a spectrum was first observed in iso-propyl iodide (20) when it was shown that annealing to about 120°K caused the complex broad spectrum to change to the normal simple spectrum in iso-propyl. Since then it has emerged that this behaviour is quite common in the alkyl halides which are prepared in polycrystalline form. Studies using isotopic substitution have shown that proton hyperfine interaction accounts for only part of the structure and g -anisotropy is exceptionally large. Though not fully interpreted, the species responsible were tentatively suggested to be probably ionic, RX^+ or RX^- or

more complex species such as R_2X . Fission processes involving the C-H bond yielding halogen-containing radicals appear to have focussed lesser attention.

I.4 Object of Present Work:

It is clear from the foregoing paragraphs that almost nil or little success was achieved in identifying bromo- and iodo-radicals in irradiated alkyl halides. Possible success in identification of such paramagnetic species along with RX^- , RX^+ greatly helps in the elucidation of radiation damage mechanism by way of participation of free radical species. Also, a large volume of research has been carried out in the past on the 'chemical effects of nuclear transformation' of alkyl halides (28-33) and various workers have tried to explain the observations by participation of free radicals (\dot{R} and halo-radicals) and charged species (RX^- and to a lesser extent RX^+). The most common mode of nuclear activation studies has been the (n, γ) reactions which eventually gives rise, at least qualitatively, to ^{the same} radiolysis products in the medium as one observes during the γ -irradiation. Thus, it was thought desirable to study the identification of the reactive intermediates by e.s.r. spectroscopy during the γ -irradiation of alkyl halides. These findings are incorporated in the proceeding chapters.

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CHAPTER TWO

ELECTRON CAPTURE - FORMATION OF ALKYL RADICALS AND
THEIR HALIDE-ION ADDUCTS

II.1 Introduction

During the course of studies on the acetonitrile dimer radical anion which was produced by γ -irradiation of acetonitrile crystal at 77°K, Williams and co-workers (1) tried to establish the anionic nature of the paramagnetic colour centre. The idea that the formation of the dimer anion may be affected by incorporation of a competitive electron scavenger (such as methyl halides) into the acetonitrile crystal encouraged Sprague and Williams (2) for the e.s.r. studies of ν -irradiated solutions of methyl bromide in methyl cyanide at 77°K. The results showed clear features from two almost equally abundant isotopes of bromine (^{81}Br and ^{79}Br) and were interpreted in terms of four sets of 1:3:3:1 quartets, the quartet splitting of 20.6 G being assigned to the protons of methyl radicals undergoing a weak interaction with bromine. Methyl halides would normally be expected to act as electron scavengers, undergoing dissociative electron attachment to give methyl radicals and halide ions. However, this was the first system in which an interaction from 'ejected' halide ion has been detected.

In the above work on methyl bromide/methyl cyanide system, the authors have reported only the values for A_{\parallel} (Br) and in order to learn more about these paramagnetic centres the work was repeated

under conditions which have enabled us to extract the full hyper-fine tensor components for bromine and hydrogen (3). The interest to repeat the experiment was especially aroused because of an extraordinary contrast between the behaviour of methyl halides on one hand, and of N-halogenoamides on the other. In an interesting work from this laboratory (4), it was found that the latter halides gave stable radical anions when exposed to γ -rays, and that these anions differ markedly from the normal anions of amides or carboxylic acids in having their extra electrons in a σ^* -nitrogen-halogen orbital. Another aspect of the finding was to look for the systems in which the $R\cdots X^-$ species may be obtained without dilution by acetonitrile. Further, there appeared to be a remarkable parallel between the results of Sprague and Williams (2) and the annealing effect described for γ -irradiated crystalline ethyl iodide (5). All these factors encouraged us to do e.s.r. studies of γ -irradiated ethyl and other iodides which resulted in some success in finding $CH_3\dot{C}H_2\cdots I^-$ and $Me_3\dot{C}\cdots I^-$ species (6).

The major aim of the work presented in this chapter was, therefore, to discover reasons for the interesting and unexpected contrast of behaviour between $\dot{R}\cdots X^-$ and N-halogenoamide anions along with the possible identification of species in γ -irradiated ethyl iodide.

II.2 Results and Discussion

The results on methyl bromide in CD_3CN show well resolved parallel and perpendicular features (Figure 1a) from which the data given in the Table^{*} were extracted. The identification of $\dot{\text{C}}\text{H}_3\text{---Br}^-$ species was further confirmed with confidence from the results for CD_3Br (Figure 1b). The spectrum of ethyl bromide/ CD_3CN was similar to methyl bromide but not so well resolved. Also, the spectrum of methyl iodide in CD_3CN (Figure 1c) was remarkably similar, except that the iodine coupling constants were somewhat greater.

γ -irradiation of pure t-butyl iodide at 77°K gave the alkyl radical-halide ion ($\text{Me}_3\dot{\text{C}}\text{---I}^-$) adduct which was similar to species obtained in alkyl halide/ CD_3CN systems. Findings on the irradiated ethyl iodide gave a comparable species with large iodine hyperfine interaction.

Main features of these spectra are: (i) the absence of any significant g -value shift from that of the free-spin and (ii) the absence of any quadrupole shifts even for iodine, despite the very large quadrupole moment of iodine. This was especially surprising for the perpendicular features both for the bromide and iodide, and this certainly means that the electric field gradient is remarkably small. This strongly supports the original description of these paramagnetic species as weak alkyl radical-halide ion adducts, rather than as radical anions. The lack of positive shift for g_\perp also strongly supports this view, since

* See Table on p.26.

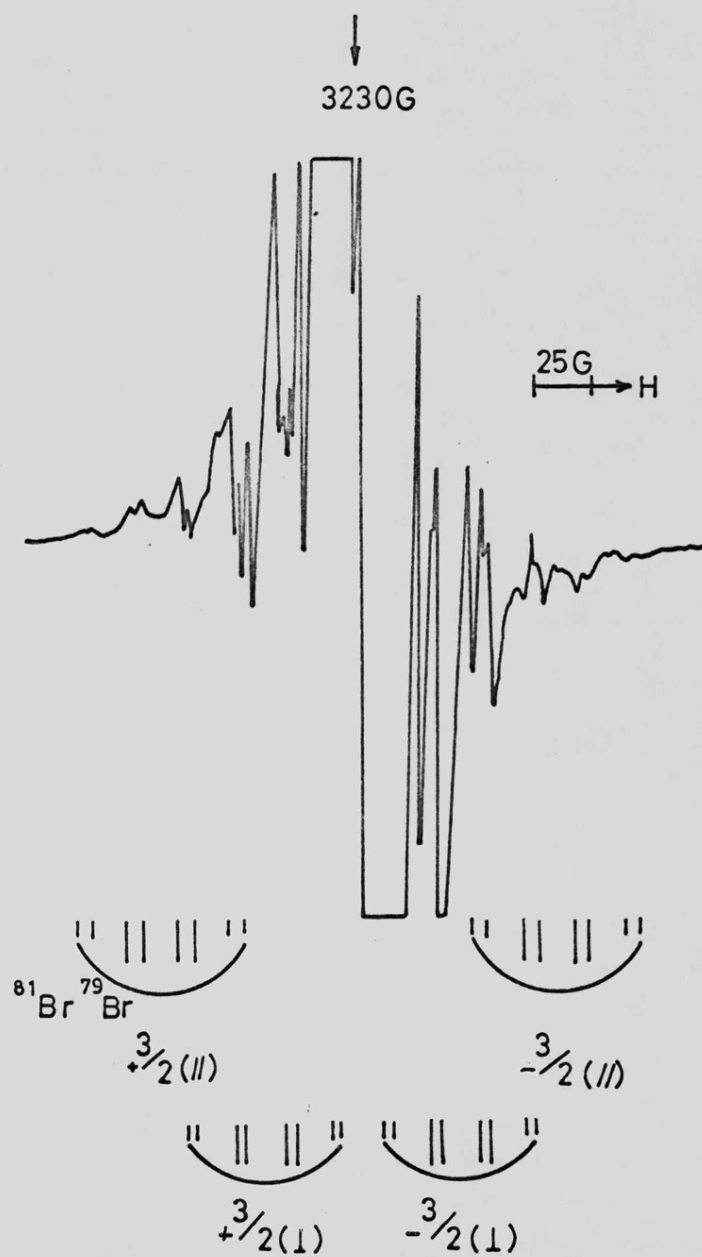


FIGURE 1(a)

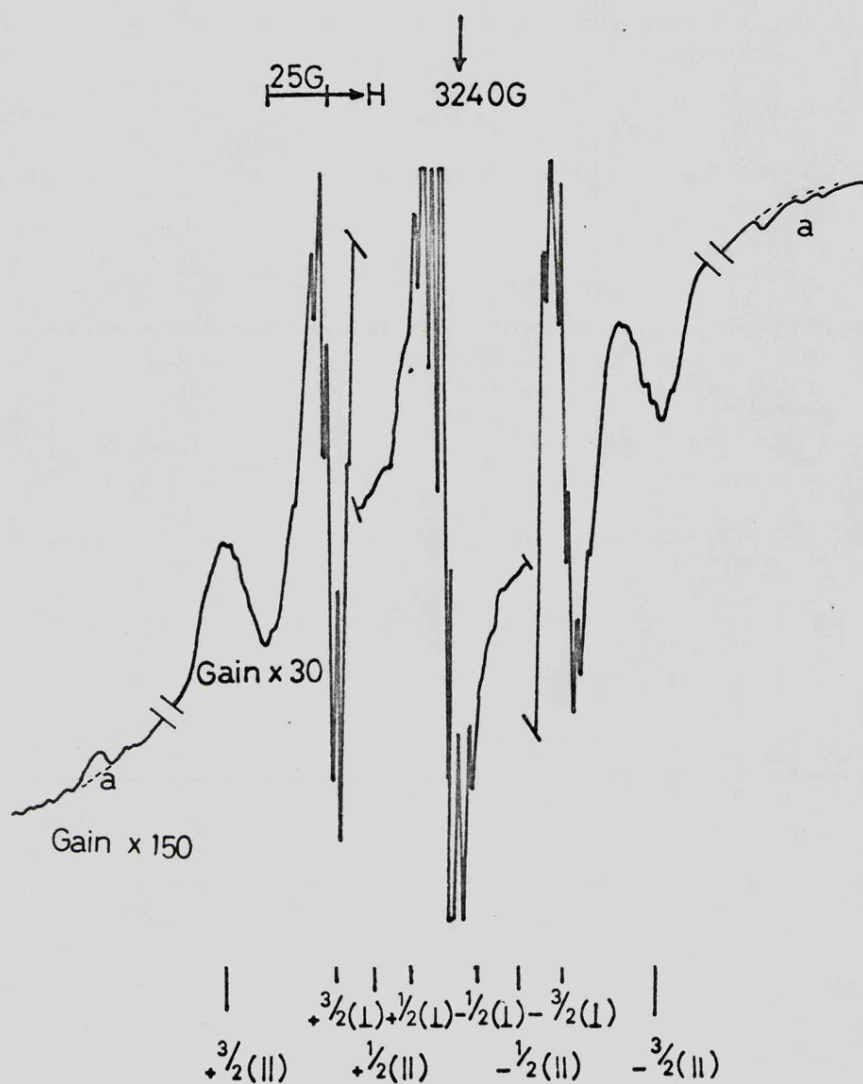


FIGURE 1(b)

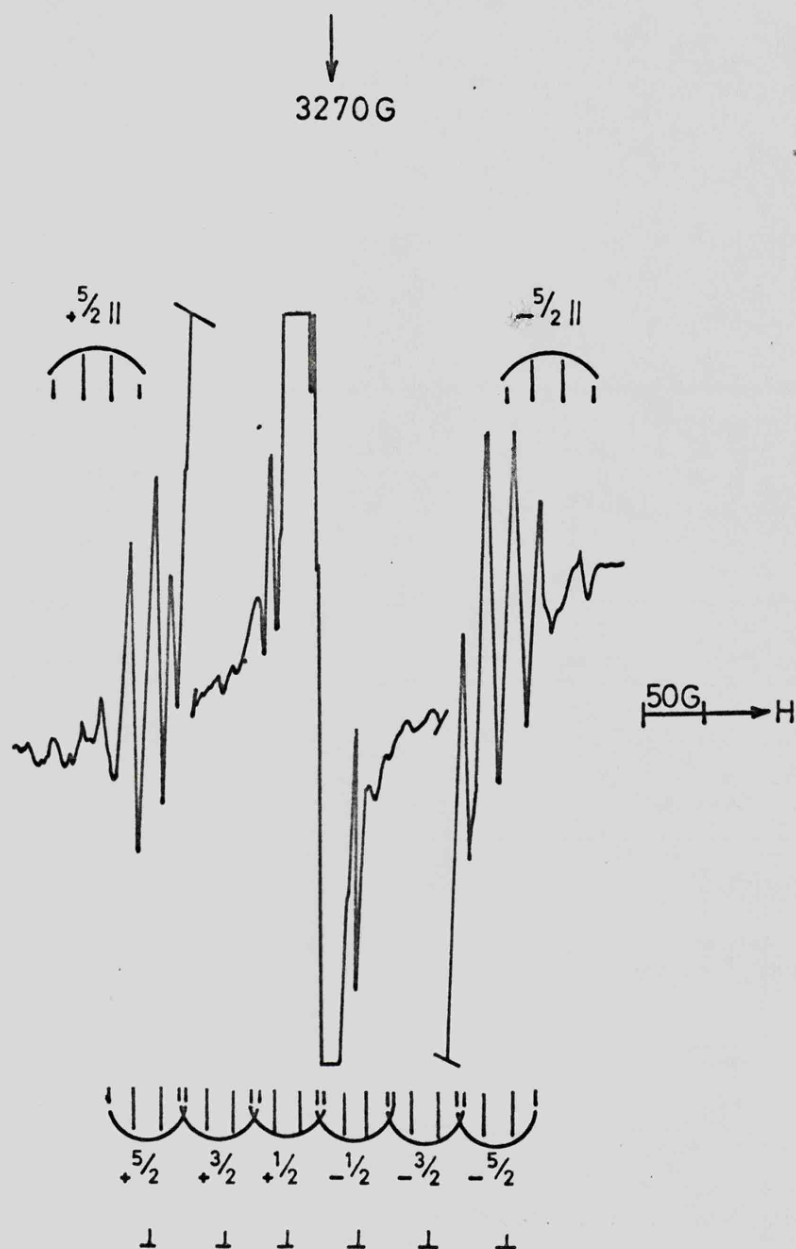


FIGURE 1(c)

Figure 1

First derivative E.S.R. spectra for methyl halides in CD_3CN after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to methyl radical-halide ion adducts: a CH_3Br ; b CD_3Br , including features assigned to ^{13}C (a) despite the noise, these were quite reproducible; and c CH_3I .

large positive shifts are found for the halogenoamide anions (4).

The other interesting aspect of the spectra is the near absence of anisotropy in the proton hyperfine coupling. The anisotropic hyperfine interaction to halogens precludes any major tumbling motion, but for alkyl radicals proton anisotropy can be almost completely removed, by coincidence, if there is free rotation about the C_{3v} (z) axis. This arises because the form of the anisotropic tensor components for each proton (A_x ca. + 10 G, A_y ca. - 10 G, and A_z ca. 0 G) is such that rotation about z-axis leads to a near zero anisotropy overall. The ^{13}C tensor should not be averaged for such a rotation, and in another work from this laboratory (7) it has been explained that the apparent marked change in A_{iso} (^{13}C) for methyl radicals on vicor glass surfaces as the temperature was lowered (8) is in terms of a z-axis rotation, rather than 'free' tumbling. Keeping this in view, a search was made for ^{13}C features, and in fact shoulders in CD_3Br-CD_3CN system were obtained which were not formed for the solvent alone. These shoulders are of about the correct relative intensities for ^{13}C satellites on the $I = \frac{3}{2}$ parallel components (Figure 1b) and yield $A_{//} (^{13}C) =$ ca. 85 G. The correct value of A_{iso} (^{13}C) in this instance is rather uncertain but is probably in the region of +30 G. This gives a 2B term of ca. 55 G which is quite close to the computed value for unit spin density of 66 G (9). This result strongly supports for the alkyl radical-halide ions in which the

alkyl radicals are loosely associated with their parent halide ions.

Halide Spin Densities

The spin densities on halogens (Table)* in the alkyl radical-halide ion adducts have been estimated by the usual procedure (9), and the computed atomic values, $\underline{A}^{\circ} (^{81}\text{Br}) = 8400 \text{ G}$, $\underline{2B}^{\circ} (^{81}\text{Br}) = 564 \text{ G}$, $\underline{A}^{\circ} (^{127}\text{I}) = 7294 \text{ G}$ and $\underline{2B}^{\circ} (^{127}\text{I}) = 453 \text{ G}$, which were derived from the best available Hartree-Fock wave functions (10). The total spin density on halogen in the case of methyl radical-halide (Br or I) ion is found to be of ca. 4% whereas in the case of $\text{C}_2\text{H}_5\text{---I}^-$ is ca. 9.4%. The increase of s orbital contribution for iodine compared to bromine in $\dot{\text{C}}\text{H}_3\text{---X}^-$ adducts may be real, but it must be remembered that the calculated \underline{A}° values for heavy atoms are undoubtedly very poor, and tend to give over-estimates. The large value of total spin density in the case of $\dot{\text{C}}_2\text{H}_5\text{---I}^-$ may indicate that the I^- is relatively closer to the $\dot{\text{C}}_2\text{H}_5$ radical site.

In $\dot{\text{C}}\text{H}_3\text{---X}^-$ systems, a total spin density equivalent to ca. 4% are sufficiently small to be a result of spin polarisation by the methyl electron. Hence, it should be due to a real bonding effect. However, there is a real reduction in $\underline{A}(\text{'H})$ relative to normal methyl radicals of about this degree, which might be taken to favour a delocalisation model.

No bromide ion adduct could be detected in the case of irradiated t-butyl bromide in CD_3CN , but the $\text{Me}_3\dot{\text{C}}$ radical was obtained in good yield. However, t-butyl iodide upon γ -irradiation

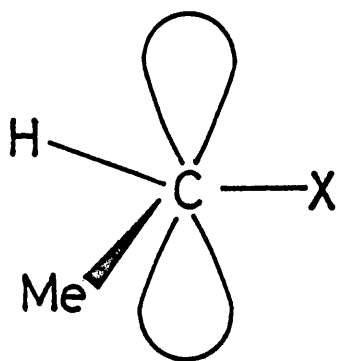
* See Table on p.26.

gave $\dot{R}---X^-$ type species. Non-formation of adduct in the case of bromide may primarily be a steric effect. As the methyl groups move to a planar location they interact with the departing halide ion, thus increasing the carbon-halogen distance to the point where no appreciable orbital overlap occurs.

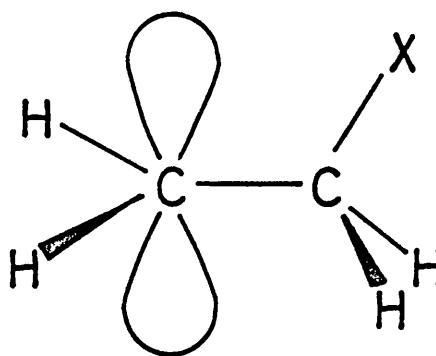
Ethyl halides

The spectra for the ethyl compounds, although sufficiently clear to warrant definite assignment to the halide ion adducts, were nevertheless poorly resolved, especially in the perpendicular regions. The parallel data in the case of C_2H_5Br did not differ significantly from those for the methyl derivatives. The poor resolution almost certainly stems from the inability of the ethyl radical to describe rotations about the carbon-halogen bond for the planar radical adduct, of the type envisaged by methyl. This means that on the perpendicular region the proton couplings vary markedly with orientations, resulting in broad lines.

The possibility of α - or β - halo ethyl radicals, I and II, produced by $C_2H_5X^+ \rightarrow \dot{C}_2H_4X + [H^+]$ or $\dot{C}_2H_5 + C_2H_5X \rightarrow \dot{C}_2H_4X + C_2H_6$ should also be examined.



(I)



(II)

α -halo radical (I) is expected to exhibit a very marked g -value variation which would lead to considerable spectral asymmetry, with strong features in the low field region, and even if these radicals were librating or rotating the resulting g_{av} -value would be $\gg 2.0023$ (11). However, this is not observed as all g -values are close to 2.0023 and hence (I) can be firmly rejected. β -halo radicals (II) are expected to have a far larger hyperfine coupling to halogen (12,13) than is observed in the present studies, and the α -proton coupling should give rise to a triplet having $(a) \leq 20$ G (coupling to the two β -protons should be small). Thus radical (II) should also be rejected. The spectra published by Willard and co-workers (5), and that of the present work for $\text{CH}_3\text{CH}_2\text{I}$ can be quite satisfactorily analysed on the ethyl radical-iodide ion adduct hypothesis, using the parameters given in the Table. In particular, the 22 G sextets having their $-5/2$ components broadened, as is usually the case for ethyl radicals in rigid media, and hence can be mistaken for quartets (1:3:3:1), thus closely resembling the features for $\text{CH}_3\text{CD}_2\text{---I}^-$, as noted by Willard *et al* (5a).

Methanol Solvent

None of the alkyl halides in CD_3OD solvent gave the halide ion adducts on γ -irradiation. This result, which nicely illustrates the subtlety of the effect, can be understood in terms of the far more efficient solvation of the halide ions by alcohol than by

methyl cyanide. This difference has been studied extensively (13) using the u.v. absorption bands of the halide ions to probe solvent interaction and it has been found that methanol and methyl cyanide are almost at opposite ends of the scale of solvents. Thus it appears that as the halogen moves along the reaction coordinate to become halide ion, so the neighbouring alcohol molecules reorient to favour hydrogen bonding to the anion, this helping to stabilise it and reducing any tendency to seek stabilisation by interaction with the liberated alkyl radicals.

Methylene Bromide

In γ -irradiated methylene bromide/ CD_3CN system, no bromide ion adduct was detected. Clear features for the dibromo α -radical, $\text{H}\dot{\text{C}}\text{Br}_2$ were obtained which were identical with those found from solutions in methanol. Also, Br_2^- was formed in γ -irradiated methylene bromide which suggests that the electron capture results in the process $\text{CH}_2\text{Br}_2 + \text{e}^- \rightarrow \text{CH}_2 + \text{Br}_2^-$ rather than the ejection of bromide ion. No features assignable to methylene radical were obtained, but at 77°K this species almost certainly reacts rapidly with the medium.

N-Halogenoamides

Neilson and Symons (4) have obtained the well defined e.s.r. powder spectra of the anions of certain N-halogenoamides. The spectra are analysed in terms of strong hyperfine couplings to



FIGURE 2(a)

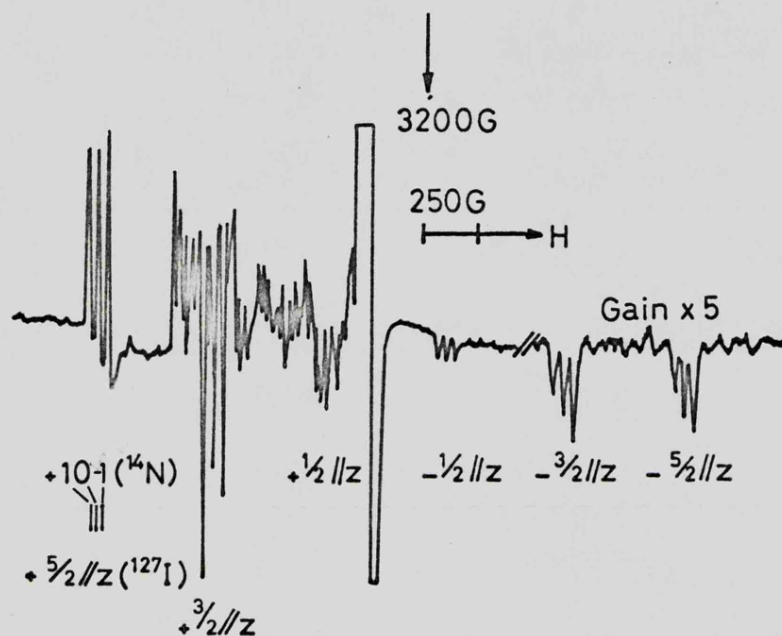


FIGURE 2(b)

First derivative E.S.R. spectrum of N-halosuccinimide in CD_3CN after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to the radical anion: a N-chlorosuccinimide; b N-iodosuccinimide.

^{14}N and to $^{35/37}\text{Cl}$ or $^{81/79}\text{Br}$, and the data show fairly conclusively that these radicals have their extra electrons primarily in the nitrogen-halogen σ^* bonds. Hence they resemble in form the halide ion adducts presently under discussion except with respect to the extent of interaction of the halide ions. (Thus, for example, for $\text{Me}^{\cdot\cdot}\text{---Br}^-$, the spin density on bromine is $\leq 4\%$, whilst for the anion of N-bromoacetoamide it is ca.56%). This difference in the spin densities was further tested by measuring the e.s.r. spectra of N-chloro-, N-bromo-, and N-Iodo- succinimide in methyl cyanide (d_3) and methanol (d_4). Spectra characteristic of the radical anions were obtained (Figure 2), there being only very minor differences between the resulting parameters and those previously reported (4).

Electronic Structures

The contrast between the results of alkyl radical-halide ion adducts and N-halogenoamides may be discussed in terms of the electronic structure. After electron capture by the σ^* carbon-halogen orbital of, say, MeBr , the C-Br bond relaxes in order to lower the anti-bonding character of the extra electron (Figure 3). This results in a flattening of the $\text{H}_3\dot{\text{C}}$ unit, which in turn increases the carbon 2p contribution to the orbital, which raises the energy of the carbon contribution and forces the unpaired electron further onto carbon. This is a continuously adjusting process, with no resulting energy minimum. However, there is little or no tendency for the amide unit to become linear, which

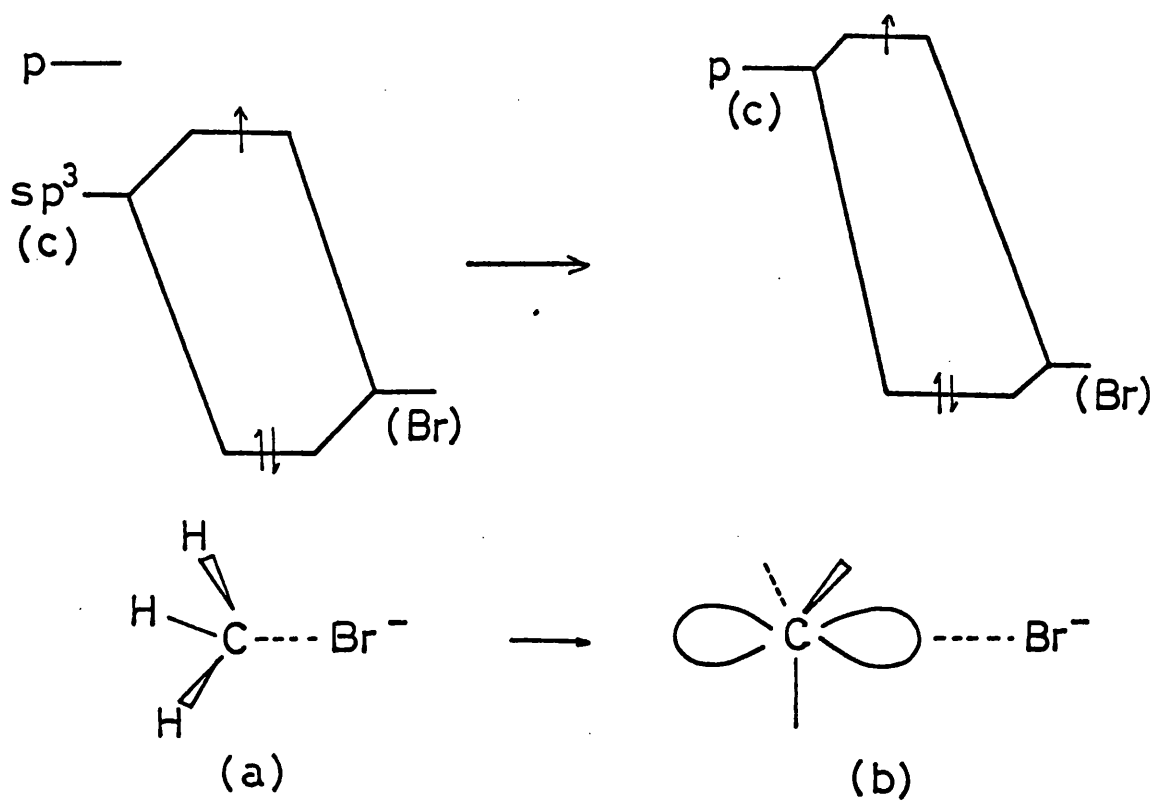


Figure 3 Bonding diagram of MeBr^- (a) and for the methyl radical-bromide ion adduct (b).

would be required if the orbital on nitrogen contributing to the $\text{N-X } \sigma$ bond in N-halogenoamides were to become pure $2p$. In this case, therefore, a new bond length is reached for which a potential minimum exists which is so deep that even the strongly solvating methanol molecules are unable to overcome the nitrogen-halogen interaction. Nevertheless, when halide ion does depart, an electron transfer within the amide radical occurs from the filled $2p(\pi)$ nitrogen orbital into the half-filled σ -nitrogen orbital to give a II -radical (14).

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TABLE: E.s.r. data for alkyl radical-halide ion adducts.

Host	Main Radical	Hyperfine Coupling (G) ^a				Spin density (%) on halogen	
		¹ H	⁸¹ Br (¹²⁷ I)			s	p
			⊥				
CH ₃ Br ^b	$\dot{\text{C}}\text{H}_3\text{---Br}^-$	20.6 ^c		56.7 ^c			
CH ₃ Br ^b	$\dot{\text{C}}\text{H}_3\text{---Br}^-$	21.0	21.5±0.5	58.3	28.3 ± 1.0	0.4	3.3
CD ₃ Br ^b	$\dot{\text{C}}\text{D}_3\text{---Br}^-$	(² H)3.2		58.3	28.3 ± 1.0		
C ₂ H ₅ Br ^b	$\dot{\text{C}}_2\text{H}_5\text{---Br}^-$	ca.23		ca.58	Not resolved		
CH ₃ I ^b	$\dot{\text{C}}\text{H}_3\text{---I}^-$	21.0	20.0±0.5	78.0	56.0 ± 2.0	0.8	3.3
C ₂ H ₅ I	$\dot{\text{C}}_2\text{H}_5\text{---I}^-$	22.0		168.0	126.0	1.83	7.66
Me ₃ CI	$\text{Me}_3\dot{\text{C}}\text{---I}^-$	22.0		>53.5	53.5		

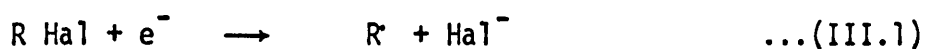
^a All g values close to 2.0023^b in CD₃CN medium^c Ref.2.

CHAPTER THREE

α -Chloro Radicals

III.1 Introduction

Although the α -chloroalkyl radicals, $R_2\dot{C}Cl$, were first observed in γ -irradiated single crystals of chloroacetic acid (1) and chloroacetamide (2), the complete anisotropic ^{35}Cl hyperfine tensor was not evaluated until the late 1960's (3). In the initial studies only two components of the hyperfine tensor were determined, primarily due to complications arising from the chlorine nuclear quadrupole interaction which is comparable in magnitude with the in-plane components of the hyperfine splitting, and the authors were unable to make a complete analysis, concluding that there was little hope of making substantial progress in the immediate future (1). This prognostication was correct, and it was only when isotropic hyperfine coupling constants to chlorine were obtained (4), that further progress was made. Thus, Kohin (3) was able to analyse the results for $H\dot{C}Cl(CONH_2)$ and $H\dot{C}Cl(CO_2H)$ radicals, and Kispert and Myers (5) gave a complete analysis of their results for $F\dot{C}Cl(CONH_2)$ radicals in γ -irradiated $FCCl_2(CONH_2)$ crystals. However, there appears to be no attempt to analyse the powder spectra for α -chloro radicals. Indeed, in work with powders and rigid glassy solutions, it is generally assumed that alkyl halides react solely by dissociative electron attachment (6),



α -Dichloro radicals have received even less attention. Again, no powder spectra seem to have been analysed, and only a partial study of $\text{Cl}_2\dot{\text{C}}(\text{CONH}_2)$ radical in X-irradiated single crystal of 2,2-dichloroacetamide is reported (7). However, several such radicals have been reported in liquid phase studies (8). The tri-chloro radical, $\dot{\text{C}}\text{Cl}_3$, has been more extensively studied largely in irradiated powders, and radicals containing ^{13}C have been formed from $^{13}\text{CCl}_4$ (9) and from $\text{Hg}(^{13}\text{CCl}_3)_2$ (10).

The main objective of the studies reported in the present chapter has been, in the first instance, to obtain authentic powder e.s.r. spectra for $\text{R}_2\dot{\text{C}}\text{Cl}$ and $\text{R}\dot{\text{C}}\text{Cl}_2$ radicals in the hope that these would be of value for diagnostic purposes. Another aspect of the study was to establish the conditions required for the formation of such radicals in the radiolysis, and, using the derived e.s.r. data, to obtain further information regarding the problem of the tendency for such radicals to deviate from the local planarity.

II.2 Results and Discussion

Monochloroacetic acid upon γ -irradiation at room temperature gave the best resolved powder spectra for α -chloro radicals. The s-, x- and Q-band e.s.r. spectra of the resulting $\text{H}\dot{\text{C}}\text{Cl}(\text{CO}_2\text{H})$ radicals are given in Figure 1 and the extracted parameters of this along with other radicals are given in the Table.* In deriving the analyses, assistance from the single crystal data

* See Table on p.40.

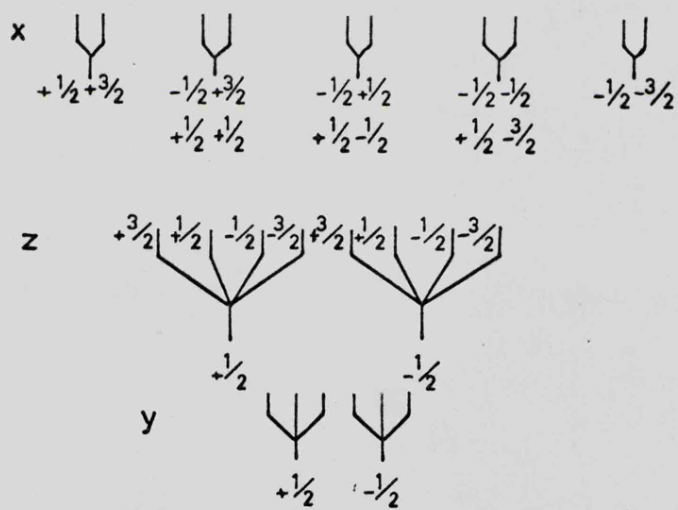
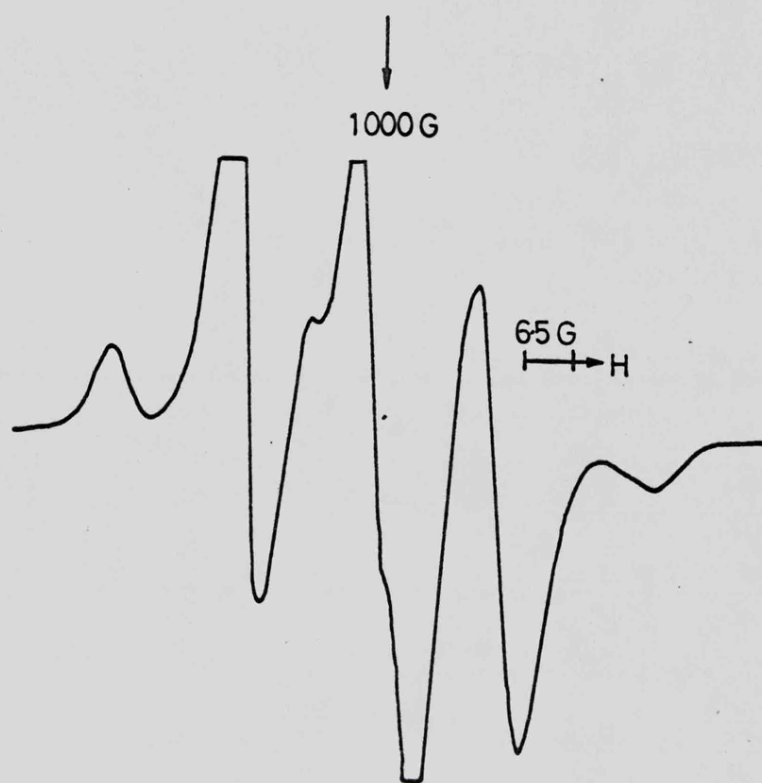


FIGURE 1(a)

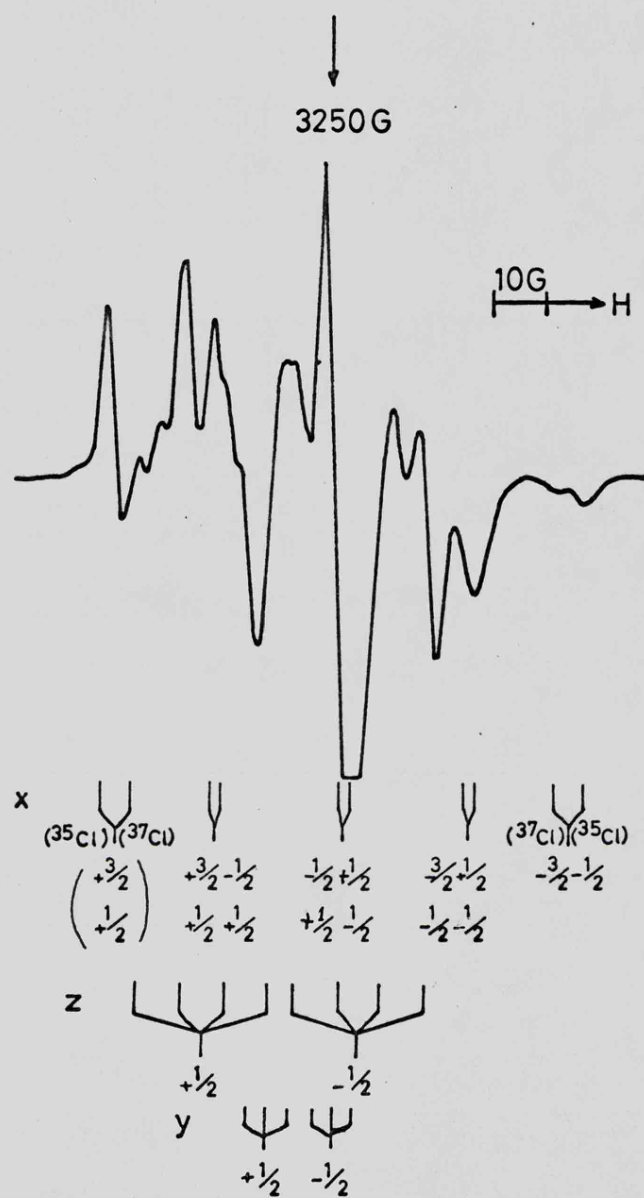


FIGURE 1(b)

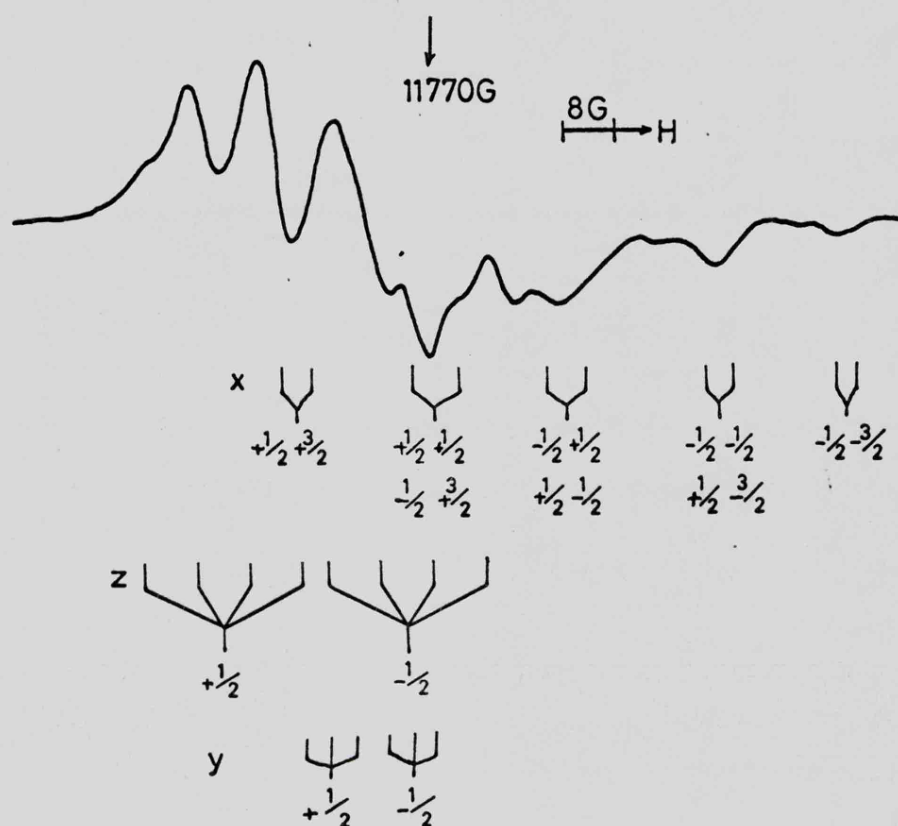
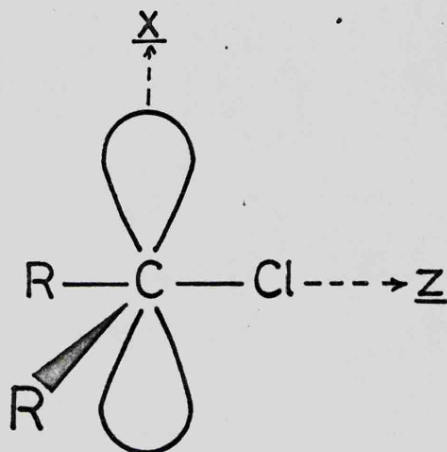


FIGURE 1(c)

First derivative E.S.R. spectra of monochloroacetic acid powder after exposure to ^{60}Co γ -rays at room temperature; (a) at S-band, (b) at X-band and (c) at Q-band. The \underline{x} , \underline{y} and \underline{z} H components are indicated as $M_I = \pm 1/2$, and the chlorine components by four or three vertical lines, designated $+3/2$, $+1/2$, $-1/2$, $-3/2$ when this assignment is valid. Both the S- and Q-band spectra are dominated by the \underline{x} and \underline{z} features: the \underline{y} features indicated are based on the X-band analysis.

previously reported (3,5) together with the results of a calculation reported earlier (11) for the expected form of the powder features for fields along the x, y and z-directions (z- lies along the C-Cl direction and x is normal to the radical plane - see insert 'A') has been taken. It has been concluded (11) that for



Insert 'A'

the field in the z-direction a normal quartet of lines should be obtained, whilst in the x- and y-directions the features dominating the powder spectra should vary strongly as the relative value of the hyperfine coupling to that of $\frac{1}{2}eQq$ varies, as indicated in Figure 2 (a) - (d). The quadrupole effect along H_x should be small, resulting mainly in an increase in the separation between the central pair of chlorine lines. This is indicated in Figure 1. However, along H_y, A_y is small and the dominating lines comprise a triplet, the expected weak wing

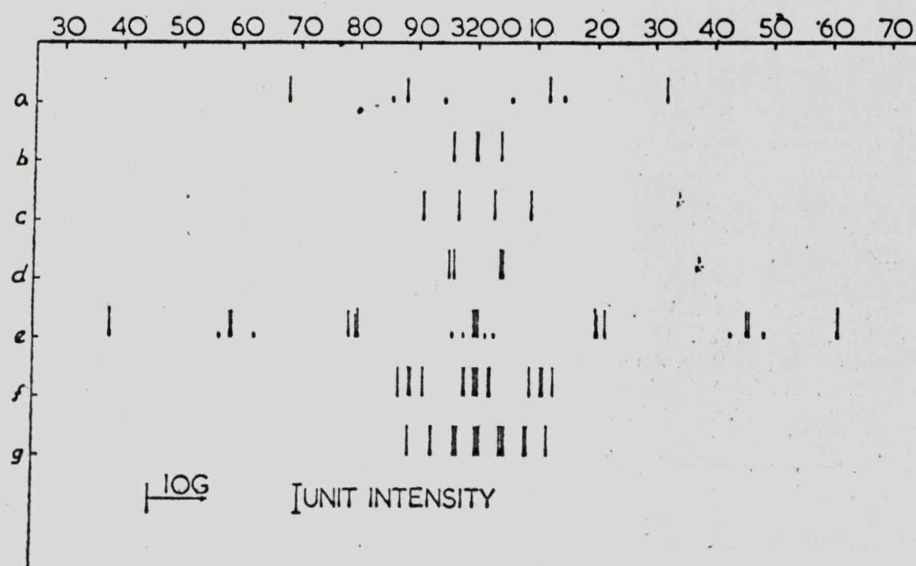


FIG. 2.—Calculated e.s.r. spectra for particular values of Q , A_x , A_y , A_z and $H_0 = (h\nu/g\beta)$ for the radicals $R_2\dot{C}Cl(a)-(d)$ and $R\dot{C}Cl_2(e)-(g)$. In all cases $Q' \sim 5$ G (i.e. $eQg \sim 84$ MHz), and $g = g_e$. (a)-(d) $A_x = 20$ G; $A_y = 4$ G; $A_z = 6$ G. (e)-(g) $A_{x_1x_1} = A_{x_2x_2} = 4$ G; $A_{y_1y_1} = A_{y_2y_2} = 20$ G; $A_{z_1z_1} = A_{z_2z_2} = 6$ G. Specifically (a) $H \parallel \hat{x}$; (b) $H \parallel \hat{y}$; (c) $H \parallel \hat{z}$; (d) H in yz plane; (e) $H \parallel \hat{x}$; (perpendicular to radical plane); (f) $H \parallel \hat{y}$; (g) $H \parallel \hat{z}$.

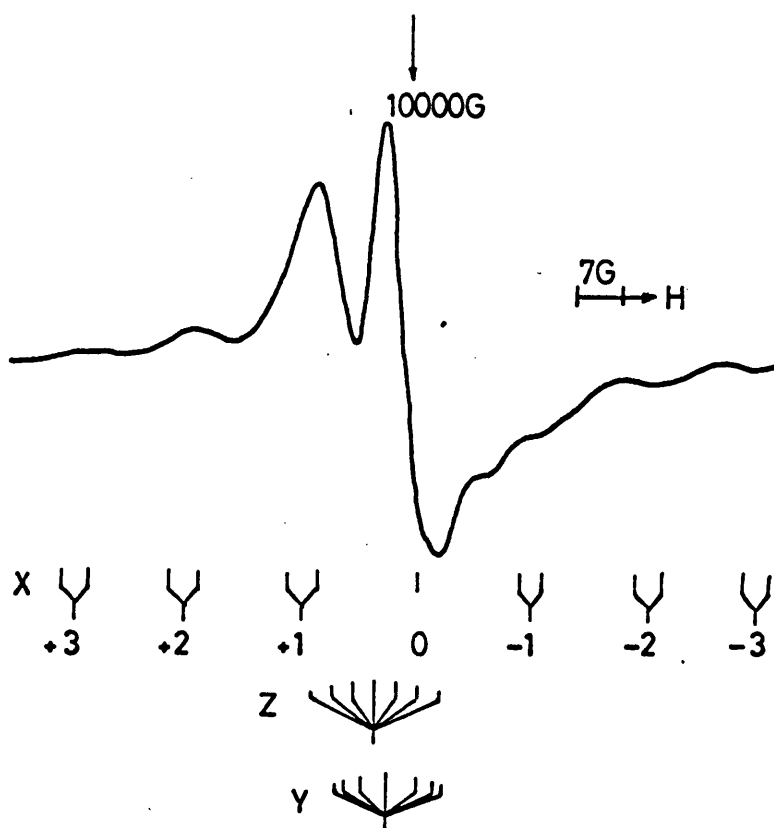


FIGURE 3(a)

First derivative E.S.R. spectra of 2,2-dichloroacetamide after exposure to ^{60}Co γ -rays at room temperature; (a) powder at S-band, (b) powder at X-band, (c) powder at Q-band, (d) spectrum close to the x axis, showing a septet of lines with $A(\text{Cl}) = 13$ G and uneven spacing caused by the quadrupole effect, (e) spectrum close to the z axis showing a marked quadrupole effect with only three well defined transitions giving $A(\text{Cl}) = 4.5$ G, and (f) spectrum close to the y axis, showing only a small quadrupole effect giving $A = 4.1$ G.

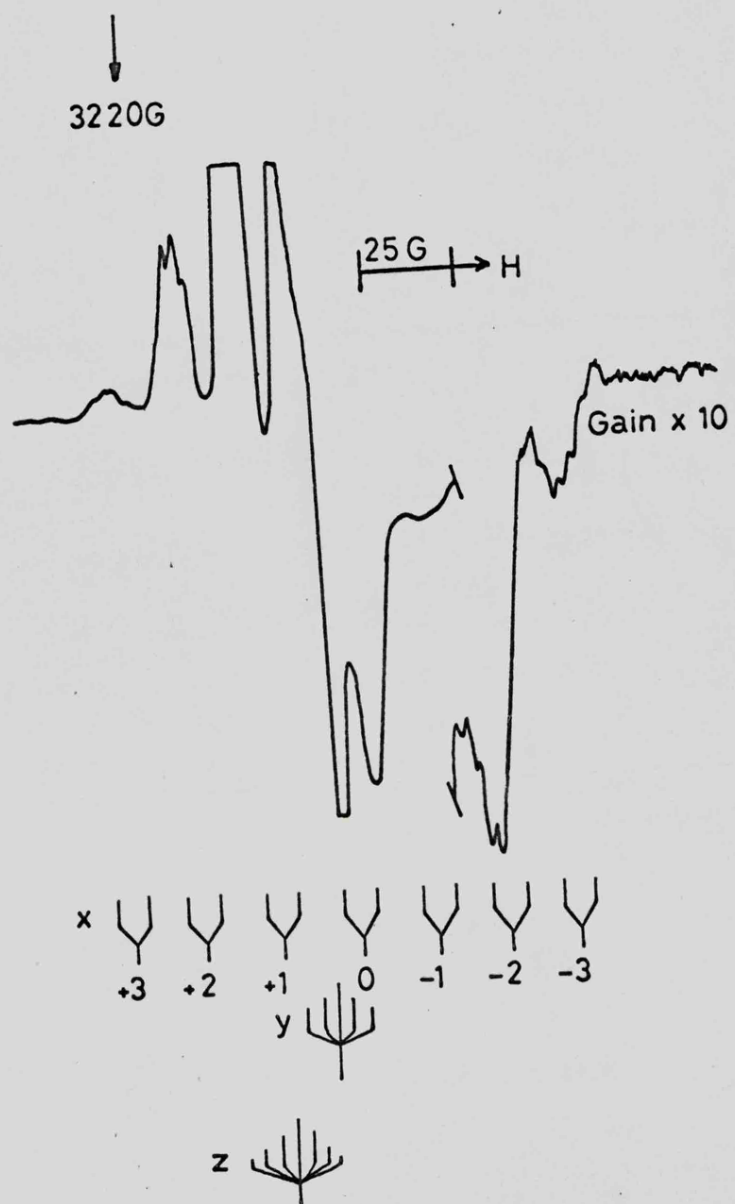


FIGURE 3(b)

FIGURE 3(c)

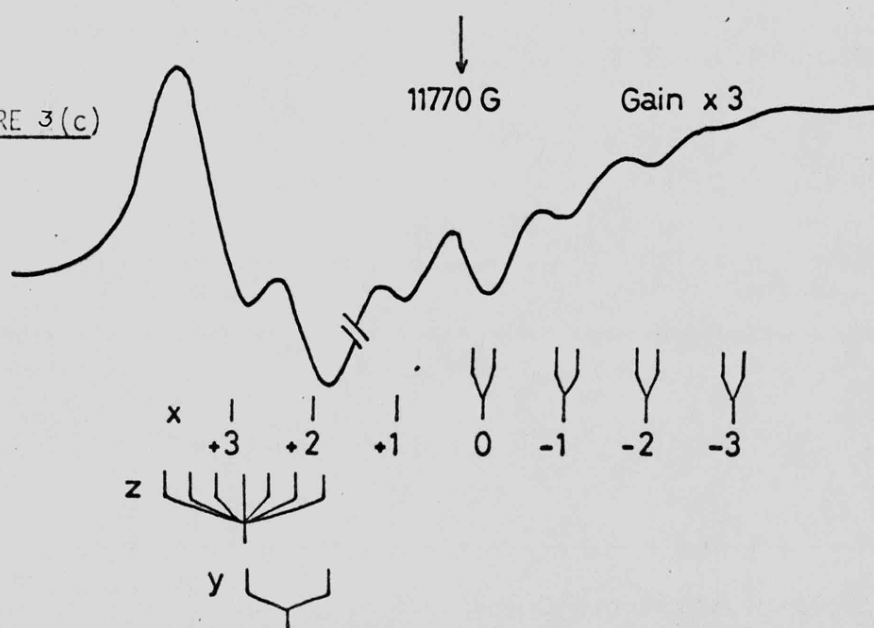


FIGURE 3(d)

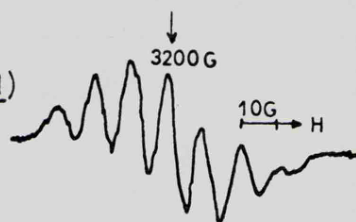


FIGURE 3(f)

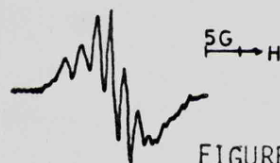


FIGURE 3(e)

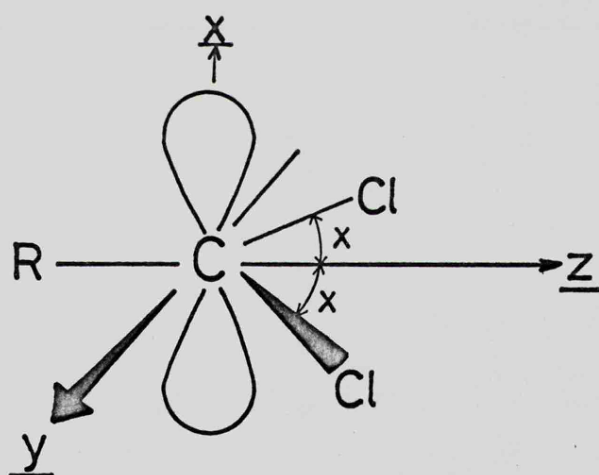


lines being too poorly defined for clear detection. Fortunately, the correct value for A_y is given by the component separations in the triplet. A good agreement for the three spectra in Figure 1 between themselves and with the results from single crystals, encourages us to believe that the present analyses are reasonable. Such spectra can now be taken as diagnostic for $R_2\dot{C}Cl_2$ type radicals and hence an unambiguous detection of radicals listed in the Table.* In all cases, A_x and g_x are reasonable numbers, but in several instances, a clear cut assignment for the y and z features has not been possible.

Methyl chloride gave mainly $H_2\dot{C}Cl$ radicals at 77°K. However, solutions of CH_3Cl in CD_3OD gave mainly $\dot{C}H_3$ with a relatively low yield of $H_2\dot{C}Cl$ radicals. The powder spectrum does not yield the full anisotropic tensor for the two protons, but only the values along the principal axes. The data for $H_2\dot{C}Cl$ radicals in a single crystal of methyl chloride are included in the Table. Ethyl chloride did not give detectable amounts of α -chloro radicals upon γ -irradiation at 77°K. Also, at 77°K α -chloro radicals were not obtained from monochloroacetic acid. But, on partial annealing, spectra for the 1-chloro radicals grew in. On exposure to γ -rays at room temperature, features for the 1-chloro radicals dominated.

* See Table on p.40.

By far the best powder spectra for α -dichloro radicals were obtained from 2,2-dichloroacetamide γ -irradiated at room temperature, typical S-, X- and Q-band spectra being shown in Figure 3. Analyses of these spectra (as indicated in Figure 3) is based upon the results of the α -monochloro radicals. In particular, the dominating X-features can be derived directly from the previous results since the two chlorine atoms are equivalent. The reconstruction pattern is given in Figure 2(e). Selection of the y and z features is more difficult since these directions no longer lie along or at right angles to the C-Cl bond directions



Insert 'B'

The reconstruction patterns for $\underline{H} // \underline{y}$ and $\underline{H} // \underline{z}$ are given in Figure 2 (f) and (g) respectively. The analyses given in the Table are supported by the agreement over a wide frequency range,

and by the good agreement with A_{iso} and g_{av} obtained from liquid phase spectra and are also in accordance with the extrapolated single crystal data of Kashiwagi (7), and the single crystal spectra of present studies. Figure 3 (d), (e) and (f) give the selected single crystal spectra which yield g - and A - values close to those for the x , y and z directions as deduced from the powder spectra. The contrast between (e) and (f) illustrates the effect of quadrupole interaction.

Taking these powder spectra of 2,2-dichloroacetamide as characteristic has helped to detect $\dot{R}CCl_2$ radicals in several γ -irradiated compounds (Table).^{*} Thus, methylene chloride in CD_3OD at $77^\circ K$ gave features assignable to $H\dot{C}Cl_2$ radicals held rigidly in the matrix (Figure 4). Additional weaker features are assigned to $H_2\dot{C}Cl$ radicals. Observations on γ -irradiated methylene chloride (d_2) in CD_3OD has further confirmed these identifications. Dichloroacetic acid upon γ -irradiation at $77^\circ K$ gave spectra which included features for both $Cl_2\dot{C}CO_2H$ and $H\dot{C}Cl(CO_2H)$ radicals. In aqueous (D_2O) and methanolic (CD_3OD) solutions of dichloroacetic acid, the radicals $Cl_2\dot{C}CO_2^-$ and $H\dot{C}Cl(CO_2)^-$ were obtained, but in different proportions in the two solvents, which helped considerably in the analyses. The magnetic parameters of these anions were closely similar to those for the corresponding acids. However, trichloroacetic acid

* See Table on p.40.

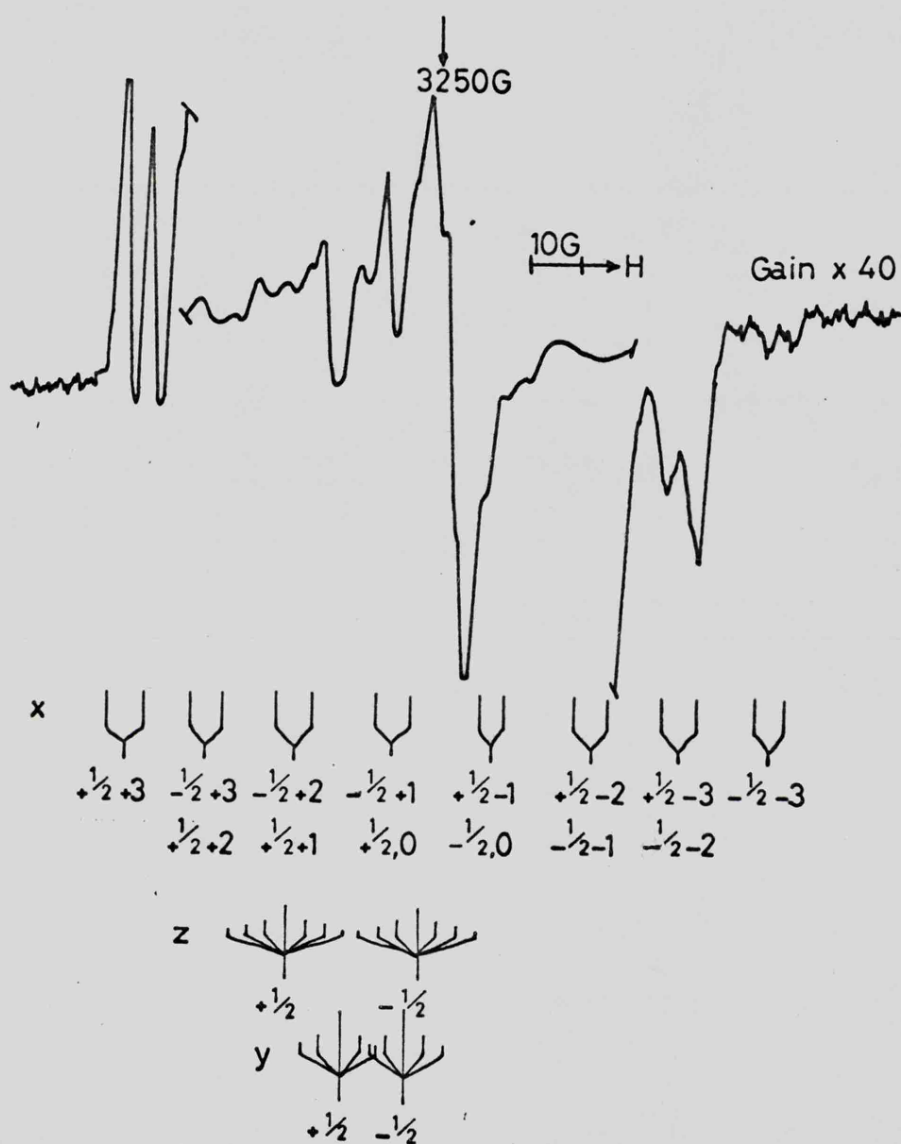


FIGURE 4

First derivative E.S.R. spectrum of methylene chloride in CD_3OD after exposure to ^{60}Co γ -rays at 77 K and slight annealing to remove features of solvent radicals, showing features assigned to $\text{H}\dot{\text{C}}\text{Cl}_2$ radicals. (Weak extra lines are assignable to $\text{H}_2\dot{\text{C}}\text{Cl}$ radicals).

gave mainly $\text{Cl}_2\dot{\text{C}}\text{CO}_2\text{H}$ radicals (or $\text{Cl}_2\dot{\text{C}}\text{CO}_2^-$) both in the pure state and in solvents (Figure 5).

The most distinctive aspect of the results for these α -chloro radicals is that the x -features are always well resolved with A_x close to 20 G, and the low-field components are much more intense than the corresponding high field lines. The x -components always centre on the free-spin ($g \approx 2.0023$) whereas the poorly defined y - and z -components are always displaced to low-field (i.e. higher g -values).

Aspects of Electronic Structure

E.s.r. results for single crystal studies of 1-chloro acids (3,5) establish that these are effectively planar at the radical centre; this being particularly significant for the chloro-fluoro radical $\text{F}\dot{\text{C}}\text{Cl}(\text{CO}_2\text{H})$, since the radical $\text{H}\dot{\text{C}}\text{F}_2$ is pyramidal (12). Radicals $\text{Cl}_2\dot{\text{C}}\text{CO}_2\text{H}$ and $\text{Cl}_2\dot{\text{C}}\text{CONH}_2$ must be planar by an analogy and this would suggest that $\text{H}\dot{\text{C}}\text{Cl}_2$ radicals are close to being planar. A search for the ^{13}C features in the wings of the α -dichloro radicals was made and the findings indicate that the ^{13}C isotropic coupling cannot be much greater than that for planar radicals. Indeed, for the spectra for $\text{Cl}_2\dot{\text{C}}\text{CO}_2\text{H}$ radicals "parallel" features of about the correct intensity were observed from which a tentative value of $A_x(^{13}\text{C}) \approx 75$ G is derived. This value is close to the value expected for A_{\parallel} in planar radicals and thus supporting the above contention about the planarity of these radicals. However, the results for $^{13}\text{C}\text{Cl}_3$

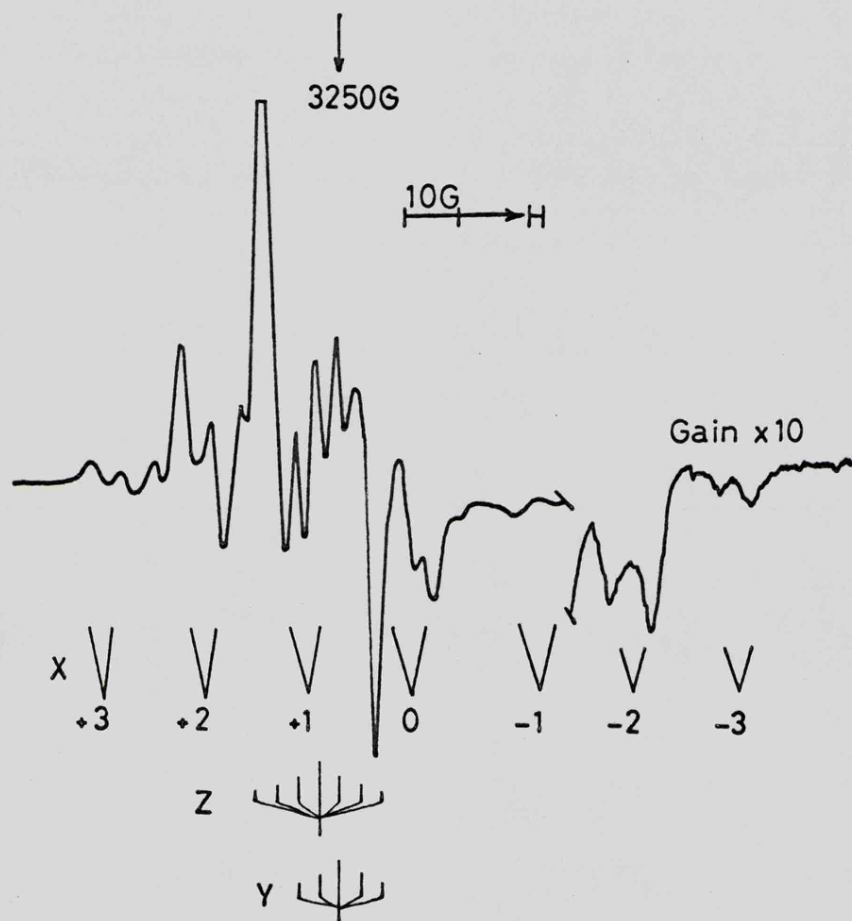


FIGURE 5

First derivative E.S.R. spectrum of trichloroacetic acid in CD_3OD after exposure to ^{60}Co γ -rays at 77 K and annealing to remove solvent radicals, showing features assigned to $\text{Cl}_2\dot{\text{C}}\text{CO}_2^-$ radicals.

radicals (9,10) show conclusively that $A_{iso}(^{13}C)$ is considerably greater than normally found for planar radicals and hence these radicals are surely pyramidal.

^{35}Cl Hyperfine Coupling

A review by Hudson and Root (13) summarises the results for a range of mono- and di-chloro radicals in the liquid phase. The average $A_{iso}(^{35}Cl)$ for mono- and di-chloro radicals is reported as 2.9 ± 0.7 G and 3.5 ± 0.7 G respectively. A clear increase to 6.25 G for $\dot{C}Cl_3$ radical is mentioned (13). The solid state results do not give A_{iso} sufficiently accurately to warrant a distinction between the mono- and di-chloro radicals, but the very slight increase indicated by the liquid phase data may indeed be a consequence of very slight deviation from planarity as suggested by Cooper *et al* (14). The increase for $\dot{C}Cl_3$ strongly implies a non-planar structure, in accord with the results of ^{13}C hyperfine interaction.

The A tensors for many of the 1-chloro radicals are not axially symmetric, but can be arbitrarily decomposed into two axial sets, a major, positive, one symmetrical about x -axis ($2B_x$) and a minor, negative, one symmetrical about z -axis ($2B_z$). These are chosen in this way because delocalisation onto chlorine should give rise to the former, but the major spin-density on carbon results in a considerable spin-polarisation of the C-Cl σ -electrons and hence a negative axial tensor along z -axis.

Typically, for the radical $\dot{\text{C}}\text{HCO}_2\text{H}$, from the data in the Table, one can obtain $2B_x = +16.7$ G and $2B_z = -2.6$ G. Then in the usual manner, using $2B^0 = 100$ G for ^{35}Cl (15), one can find 16.7% as the spin density on chlorine, and ca. -2.6% as the $3p(\sigma)$ -orbital spin-polarisation. In the case of other mono- and di- chloro radicals studied here, the results are quite similar. A spin-polarisation of ca. -2.6% is reasonable for such radicals (16). The small isotropic coupling thus stems from a negative contribution resulting from the σ -polarisation caused by spin on carbon and a positive contribution from polarisation due to spin on chlorine. The finding that the result is positive for a spin-density of only 16% on chlorine suggests that there is a considerable polarisation of "lone pair" electrons (16).

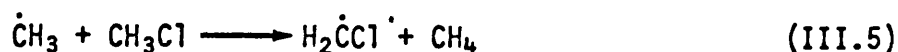
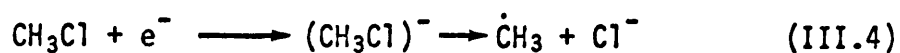
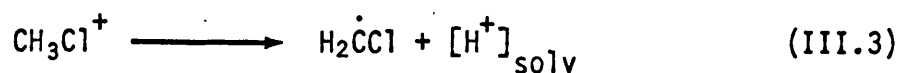
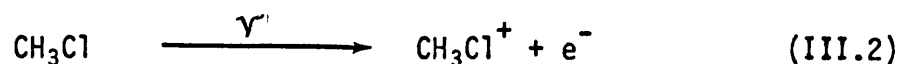
The accurately known values of $A_{\text{iso}}(^1\text{H}) = 16.8$ G (17) for $\dot{\text{H}}\text{CCl}_2$ radicals might be taken to indicate a slight deviation from planarity because of its low magnitude. However, if the present estimate of ca. 15% spin density on each chlorine is correct, then one would predict a value of 16.1 G for $A_{\text{iso}}(^1\text{H})$ which is close to the experimental values. Thus no major deviation from planarity seems to be implied.

Of interest is to compare the results of $\text{R}\dot{\text{C}}\text{Cl}_2$ radicals with those for isostructural $\dot{\text{N}}\text{Cl}_2$ radicals (18). For $\dot{\text{N}}\text{Cl}_2$ radical, the $A_{\text{H}}(^{35}\text{Cl}) = 24$ G is remarkably similar to the corresponding values in $\text{R}\dot{\text{C}}\text{Cl}_2$ radicals, but the value of ± 17 G

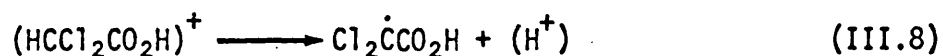
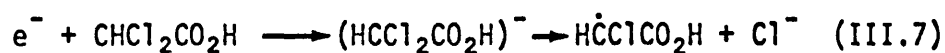
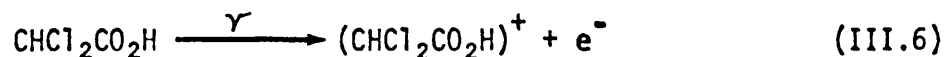
for $A_{\perp} (^{35}\text{Cl})$ seems to be quite out of line and this value is open to doubt. Thus if A_{\perp} is taken to be negative, then $A_{\text{iso}} (\text{Cl})$ is negative. However, since 16% delocalisation gives a positive value for A_{iso} , then the 17% should also. Alternatively, if A_{\perp} is positive, A_{iso} would be large and positive, but the $3p(\pi)$ spin-density is only ca. 4.7%, which is far too low. On the other hand, the results for ^{35}Cl in $\dot{\text{P}}\text{Cl}_2$ (18) agree well with the present results of 1-chloro radicals ($A_{\parallel} (^{35}\text{Cl}) = 17.5 \text{ G}$ and $A_{\perp} \sim 0$).

Aspects of Mechanism

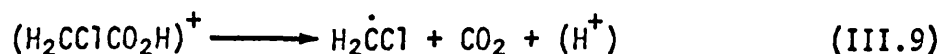
Results of γ -irradiation damage on the various chloro compounds clearly establishes that dissociative electron attachment (Reaction III.1) is not the only significant reaction despite its prevalence in many circumstances. Two reactions can lead to α -chloro radicals, one being loss of protons by the parent radical cation, the other being the secondary attack by alkyl radicals. Thus for methyl chloride:



and for dichloroacetic acid:



For the parent cations of 1-chloro acids, it might be expected that loss of the acidic proton and carbon-dioxide (Reaction III.9) would be more probable than reaction III.3, i.e.,



No clear evidence for $\text{H}_2\dot{\text{C}}\text{Cl}$ radicals could be obtained in the results for monochloroacetic acid, nor for $\text{H}\dot{\text{C}}\text{Cl}_2$ or $\dot{\text{C}}\text{Cl}_3$ radicals from di- and tri-chloroacetic acids. Thus it seems that reaction (III.3) takes precedence over reaction (III.9) for these chloroacids.

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TABLE

Solid-State E.s.r. Data for 1-Chloro Radicals

host	radical	³⁵ Cl hyperfine tensor components/G (ca. +1) ^a			¹ H hyperfine tensor components/G (ca. +1) G			g-tensor components		
		x	y	z	x	y	z	(iso)	(-20.7)	(-20.7)
MeCl ^b (powder)	H ₂ CCl	+21	-4	-8	-20	-16	-26	(-20.7)	2.002 ₀	2.007 ₅ 2.009 ₅
MeCl (crystal) ^h	H ₂ CCl	+20.5	-5.3	-6.9	(+2.8)	-24.9	-9.8	-31.3	(-22)	
ClCH ₂ CO ₂ H ^e	ClCHCO ₂ H	20	-2.5	-6.4	(3.7)					
ClCH ₂ CO ₂ H ^b	ClCHCO ₂ H	21	-4	-8	(3.0)	-21	-12.5	-29	(20.7)	2.002 ₂ 2.007 ₁ 2.009 ₅
ClCH ₂ CONH ₂ ^c	ClCHCONH ₂									
ClCF ₂ CONH ₂ ^f	ClCFCONH ₂	+18	-3.2	-5.8						2.002 ₁ 2.006 ₉ 2.007 ₆
CH ₂ Cl ₂ ^b	CHCl ₂	+20	ca. -4	-4	(ca. 4)	-20	-13	-27	(-20)	2.002 ₃ 2.003 ₄ 2.010 ₀
Cl ₂ CHCO ₂ ^{b, g}	Cl ₂ CCO ₂ ⁻	+21	ca. -4	-4 ^d	(+4.3)					2.002 ₅ ca. 2.009 2.012
Cl ₃ CCO ₂ ^{b, g}	Cl ₂ CCO ₂ ⁻	+21	ca. -4	-4 ^d	(+4.3)					2.002 ₅ 2.009 ₀ 2.013 ₀
Cl ₂ CHCONH ₂ ^b	Cl ₂ CCONH ₂	20	ca. -4	-4	(+4.0)					2.002 ₅ 2.009 ₁ 2.012 ₂

^a 1 G = 10⁻⁴ T; ^b this work; ^c a(N) ≈ a(NH) ÷ 2.5 G; ^d A_x(¹³C) ≈ 75 G, A_y and A_z are not true components;

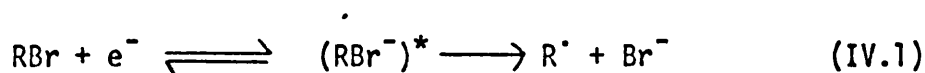
^e ref. (5); ^f ref. (6); ^g in CD₃OD; ^h J.P. Michaut and J. Roncin, Chem. Phys. Letters, 1971, 12, 95.

CHAPTER FOUR

α -Bromo Radicals

IV.1 Introduction

In various studies of the radiolysis of alkyl bromides, only alkyl radicals have been detected, produced by 'dissociative electron attachment' process (IV.1).



However, an exception to this has been the formation of alkyl radical-halide ion adducts (2,3) which have been described in Chapter II. A complex spectrum obtained from irradiated n-propyl bromide and spanning about 1000 G, was assigned to $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HBr}$ radicals (4), but no analysis of the spectrum was offered. An interesting work of Lyons and Symons (5) on this and other related compounds suggest that the β -bromo radical, $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{Br}$ was largely responsible for these features. Also, a complex spectrum which was obtained from irradiated bromoacetic acid but not properly assigned (6), was almost certainly due to α -bromo radicals.

One of the major interpretative difficulties in the analysis of bromine containing radicals has been the large nuclear quadrupole effect exerted by the ^{81}Br and ^{79}Br nuclei, both of which have $I = 3/2$, and large magnetic and quadrupole moments. We have calculated the type of e.s.r. spectra to be expected for various values of the hyperfine coupling energy along the magnetic axes of a typical α -bromo radical (cf. ref.7) which helped considerably in the interpretation of the spectrum of such radicals (8,9).

The aim of the work presented in this chapter is to give all the accumulated evidence in favour of the formation of α -bromo radicals during the radiolysis of a wide range of organic bromides.

IV.2 Results and Discussion

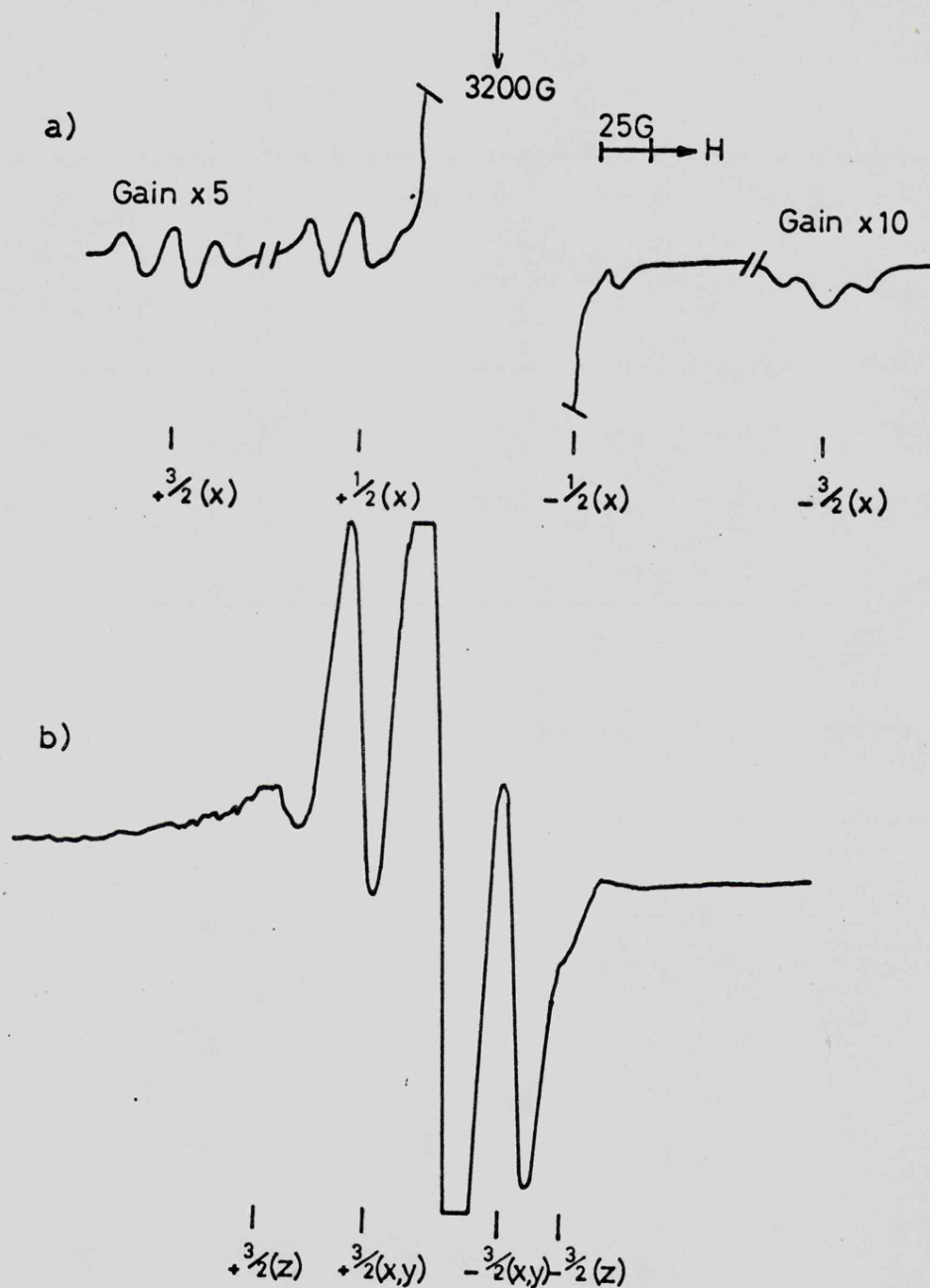
A summary of results is given in the Table and Figures (1)-(3). $M_I = \pm \frac{3}{2}$ features of bromine along the x -direction (largest coupling axis for bromine) were clearly resolved and have been utilised to give $A_x(^1H)$, $A_x(^{81}Br)$ and g_x , which are listed in the table. Provided there are no major libratory or rotary motion in the radical, the $M_I = +\frac{1}{2}$ line is invariably intense because it includes components from all three directions, and those values characterise α -bromo radicals satisfactorily. Libration or rotation in the radical, however, can be eliminated by use of a microscopically-rigid glass such as methanol. For example, for MeBr in CD_3OD a clear α -bromo alkyl radical spectrum was obtained (Figure 1(a)). With this information and using CD_3Br as host, an interpretation of the e.s.r. spectrum from γ -irradiation of the pure material in terms of partially rotating $\dot{C}D_2Br$ radicals is offered. (Figure 1(b)).

Quadrupole Effects

A severe limitation is placed on the interpretation of the powder e.s.r. spectra of α -bromo radicals due to the effect of the relatively large quadrupole moments of ^{81}Br and ^{79}Br nuclei. ($^{79}Br = 0.34 \times 10^{-24} \text{ cm}^2$; $^{81}Br = 0.28 \times 10^{-24} \text{ cm}^2$).

* See Table on p.52.

FIGURE 1



First derivative X-band E.S.R. spectra for methyl bromide after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to $\text{H}_2\dot{\text{C}}\text{Br}$ ($\text{D}_2\dot{\text{C}}\text{Br}$) radicals, a in CD_3OD solvent, b pure CD_3Br ; the $\text{D}_2\dot{\text{C}}\text{Br}$ radicals are thought to be rotating about the z-axis (C-Br direction).

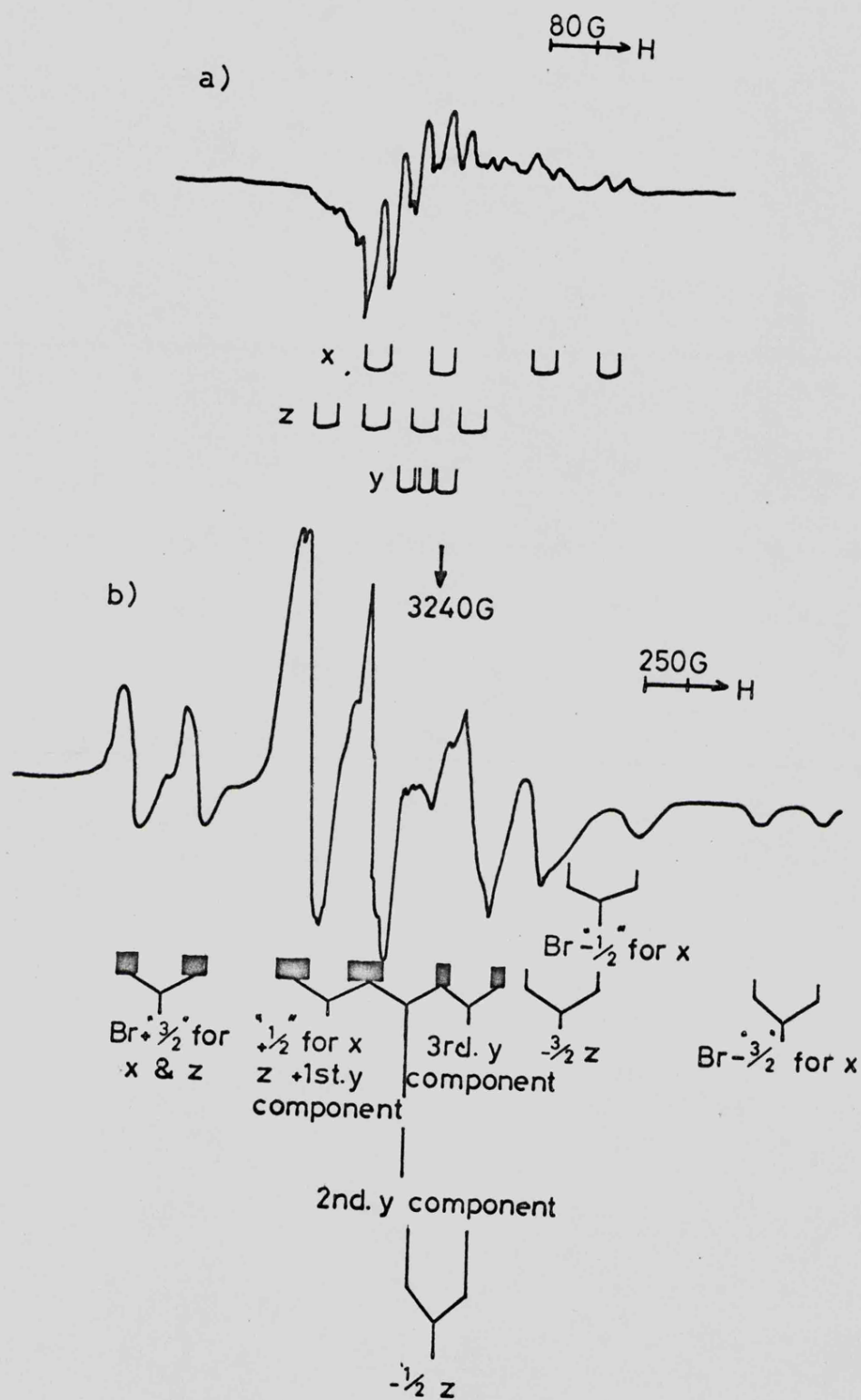


FIGURE 2

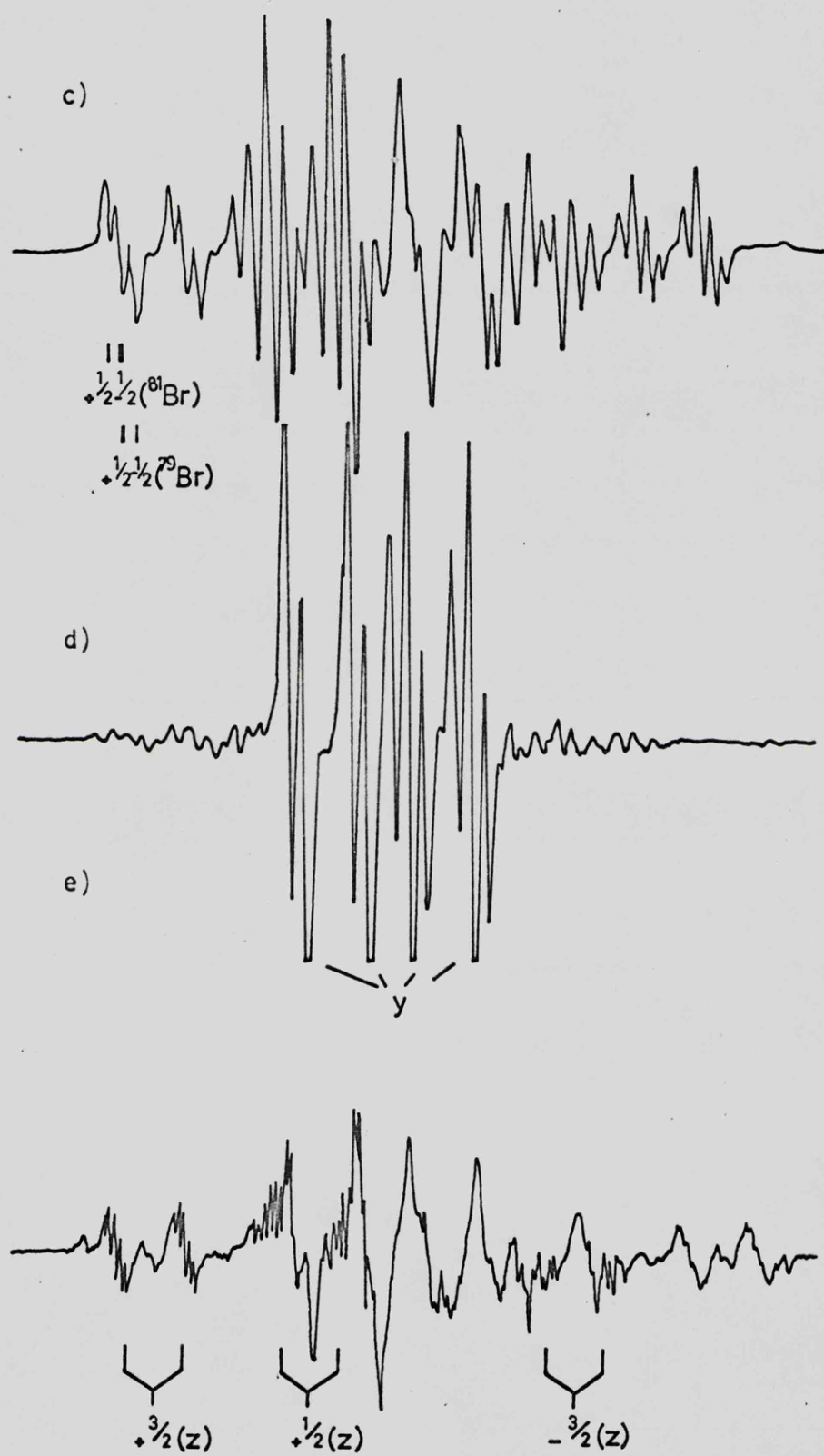


FIGURE 2

CAPTIONS

Figure 2

First derivative e.s.r. spectra for bromomaleic acid after exposure to ^{60}Co γ -rays at room temperature, showing a, powder spectrum at Q-band frequencies; b powder at X-band; and c, d and e selected single crystal spectra, showing c outer features close to x which show a resolved 7 G splitting from another proton together with the ^{81}Br and ^{79}Br features on the low-field components; d, close to the y axis, showing only three main transitions (each subdivided into 40 G and 7 G doublets by proton interaction) together with forbidden outer features; and e, showing well-resolved lines from two almost equivalent radicals near to the z direction. (The poorly-resolved lines are approaching the x direction.)

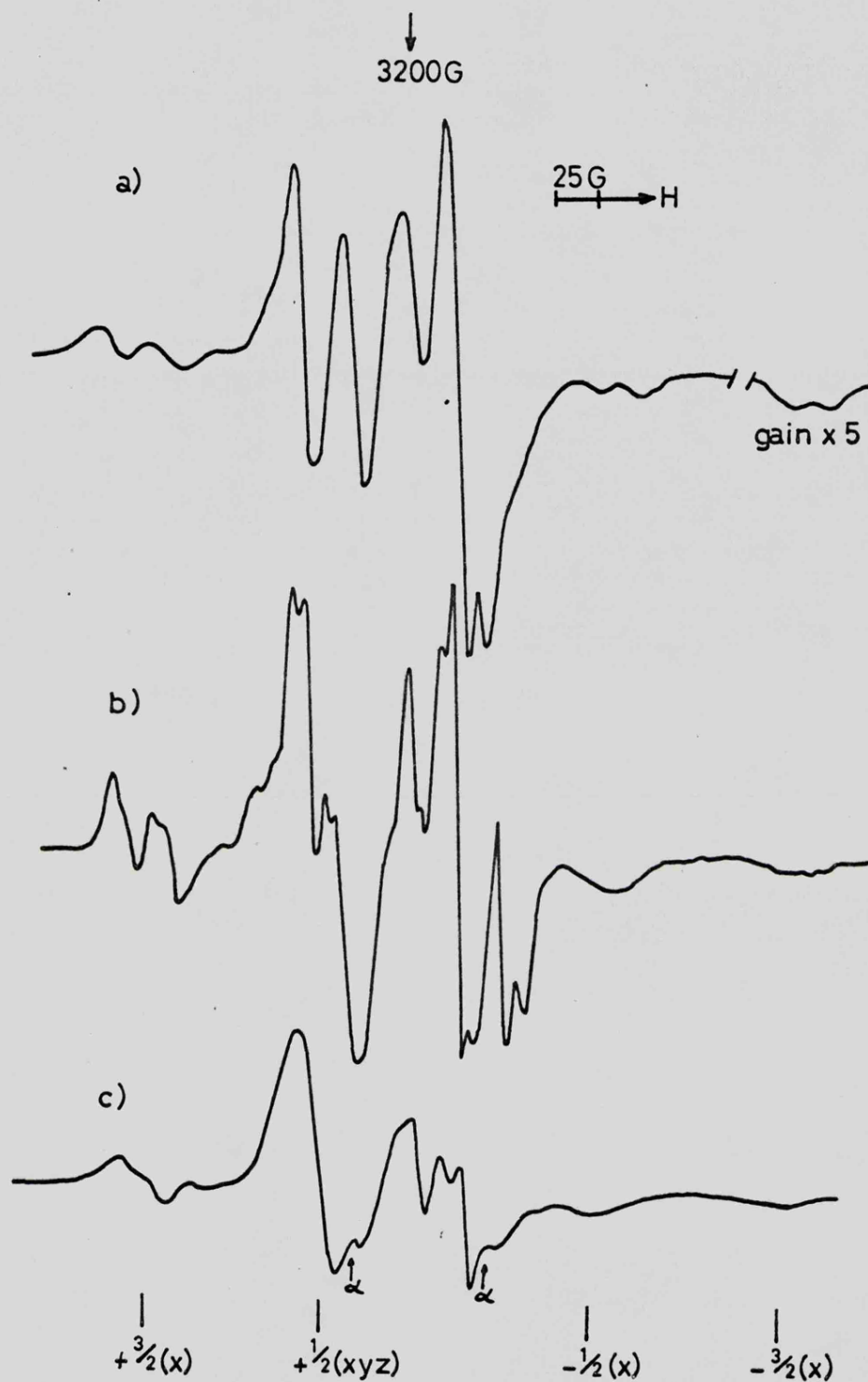
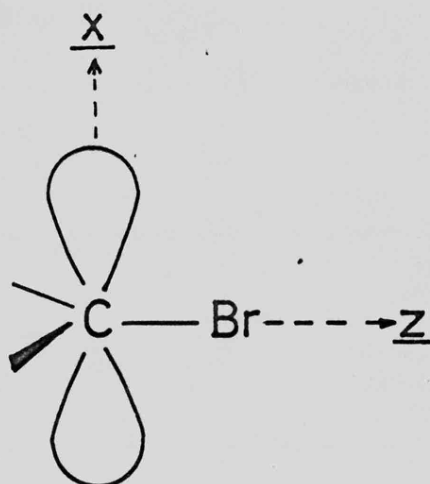


FIGURE 3

First derivative X-band E.S.R. spectra for a, bromomaleic anhydride; b, bromoacetic acid; and c, α -bromoacrylic acid, after exposure to γ -rays at room temperature, showing features assigned to a, $\text{CO} \begin{array}{c} \text{CH}_2 - \dot{\text{C}}\text{Br} \\ \text{O} \end{array} \text{CO}$ radicals; b, $\text{H}\dot{\text{C}}\text{Br}(\text{CO}_2\text{H})$ radicals; and c, $\text{RCH}_2\dot{\text{C}}\text{Br}(\text{CO}_2\text{H})$ radicals (features marked α are assigned to $\text{H}_2\text{O} = \dot{\text{C}}\text{CO}_2\text{H}$ radicals).

Calculations (7) show that, using the axes as indicated in (Insert 'A')



Insert 'A'

for the fields along x and y, the quadrupole effect for large hyperfine energies (ca. 110 G for those radicals along x-axis) is to move the spectrum disproportionately such that the hyperfine splitting A_x is given approximately by the distance between the two strongest low-field lines ("M_I" = +3/2, "M_I" = +1/2) or the two high-field lines ("M_I" = -1/2, "M_I" = -3/2). However, when the hyperfine energy is considerably less than the effective quadrupole energy (ca. 45 G for ⁷⁹Br along A_y) then the quadrupole moment controls alignment, and the spectrum comprises a strong triplet, with weak outer features, the triplet giving the hyperfine coupling constant.

Spectral Interpretation

The interpretation of spectra has been made by reference to the results of α -chloro radicals (7), by comparing powder spectra at S -, X - and Q -band frequencies and by studying single crystal spectra. The conclusion of quadrupole effect outlined in the preceeding paragraph have been verified by single crystal studies, which were particularly clear for γ -irradiated bromo-maleic acid (Figure 2 (c) and (d)). The Z -features comprise an even set of four lines because the z -axis is also the electric field axis for the radical. Also, g_z is expected to be considerably greater than the free spin value since coupling between the bromine $p(\pi)_x$ and p_y non-bonding electrons is maximised for this direction. Hence, g_x should be close to 2.0023 and g_y intermediate between g_x and g_z .

Methylbromide in CD_3OD gives a well resolved spectrum of $H_2\dot{C}Br$ radical from which a clear triplet due to 2 protons is obtained (Figure 1(a)). The quintet features for $Me\dot{C}HBr$ from ν -irradiated $MeCH_2Br$ in CD_3OD support the present identification and so do the clear quartet of lines for $Me\dot{C}Br(CO_2H)$ and $Me\dot{C}Br(COEt)$ radicals. The radical from bromomaleic acid shows coupling to a single proton (38 G) in the powder spectrum (Figure 2(a)) but for certain orientations, a second small splitting (7 G) was clearly resolved in the single crystal spectra (Figure 2(c)). In the case of anhydride, the proton coupling was reduced to ca. 28 G, and the absence of a second proton giving a similar interaction shows that an \dot{R} -radical derived from the anhydride has added, rather than a hydrogen atom. The absence of any resolved proton features

for the radical derived from α -bromoacrylic acid suggests that the species is $\text{RCH}_2\dot{\text{C}}\text{Br}(\text{CO}_2\text{H})$ rather than $\text{Me}\dot{\text{C}}\text{Br}(\text{CO}_2\text{H})$ since the result from the latter radical from α -bromopropionic acid shows well-resolved quartets for the methyl group protons.

Orbital Populations

As a pre-requisite to any theoretical discussion of isotropic hyperfine coupling constants it is necessary to assign the signs of principal \underline{A} -tensors. In the case of α -bromoalkyl radicals there are two reasonable combinations (using, for example, the data from bromomaleic acid), *viz.* +111 G (\underline{X}), +50 G (\underline{Y}), +80 G (\underline{Z}) and +111 G (\underline{X}), -50 G (\underline{Y}), -80 G (\underline{Z}). These non-axially symmetric tensors can be decomposed to give $\underline{A}_{\text{iso}}$ and a pair of axial tensors symmetrical along \underline{x} - and \underline{z} -axes respectively. (These are chosen since π -delocalisation should give a coupling symmetrical along \underline{x} -axis whilst σ -spin-polarisation must be symmetrical along \underline{z} -axis). The former set of \underline{A} -tensors give $2 \underline{B}_{\text{ax}}(\underline{z}) = +20$ G and can be rejected since σ -electron polarisation should make a negative contribution along \underline{z} . The latter set of tensors give $\underline{A}_{\text{iso}} = -6.3$ G, $2 \underline{B}_{\text{ax}}(\underline{x}) = +107.3$ G and $2 \underline{B}_{\text{ax}}(\underline{z}) = -20$ G, which is in good agreement to the expectations. These results are further supported from their similarity to those of α -chloro radicals.

Taking the values $2 \underline{B}_{\text{ax}}(\underline{x}) = +107.3$ G and $2 \underline{B}_{\text{ax}}(\underline{z}) = -20$ G as typical for α -bromoalkyl radicals and using $2 \underline{B}^0(^{81}\text{Br}) = 564$ G, one can find 19% as the spin density on bromine, and -3.5%

as the $3p(\sigma)$ -orbital spin-polarisation of the C-Br σ -electrons. The small negative, isotropic coupling (-6.3 G), corresponding to a net s -orbital character to zero, has two major contributions: a positive one from spin on bromine and a negative one from spin on carbon. Both of these act on the C-Br σ -bonding electrons. The negative contribution is a function of the bromine s -character for the σ -bonding electrons, and the fact that the net value is negative, whilst that for α -chloro radicals is positive, despite the increased delocalisation onto bromine, suggests that this s -contribution to the σ -electrons is greater for bromine than for chlorine.

The g -shifts observed for α -bromoalkyl radicals (see Table)* are large enough to consider the subtraction of 'orbital magnetic contributions' to the hyperfine coupling constants along y - and z - axes. The calculated changes (1-2 G) are of similar magnitude as experimental errors and hence are not incorporated in the computed orbital populations.

Electronic Structure

The results of α -chloro radicals (7,10,11) along with other conclusions based on infra-red studies (12,13) and present results support the implicit assumption that the α -bromoalkyl radicals are planar at the radical centres. The estimated 19% π -delocalisation is larger than that for α -chloro radicals (ca. 16%), which for a π level, accords with the change in electro-

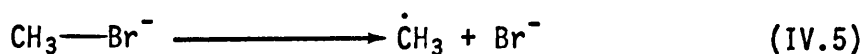
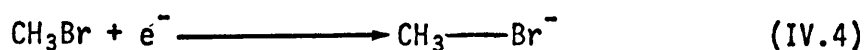
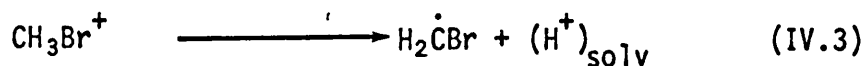
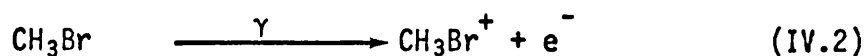
* See Table on p.52.

negativity. This suggests that the large disparity in atomic orbital sizes for carbon and bromine is not seriously inhibiting delocalisation, although it must markedly affect bonding strength.

An interesting result for the radical $\text{H}_2\text{C}=\text{CH}-\dot{\text{C}}\text{HBr}$ derived from allylbromide is the lower bromine coupling constant which suggests only a small contribution from the valence-bond structure $\text{H}_2\dot{\text{C}}-\text{CH}=\text{CHBr}$. This illustrates the significance of the π -contribution from bromine which favours the former structure. Thus, of four possible π -bonds, π_1 is expected to have large bromine character with some C(1) contribution, π_2 will have considerable C(2)-C(3) double bond character and π_3 , the orbital of the unpaired electron, is largely on C(1) with some bromine contribution.

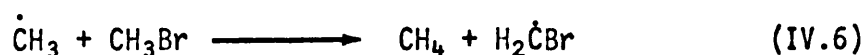
Aspects of Mechanism

Effect of ν -radiolysis and subsequent processes towards productions of paramagnetic species in saturated organic bromides seem to follow the stages as given by reactions IV.(2) - (5).

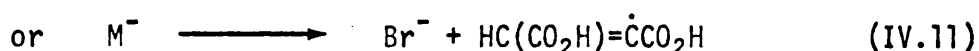
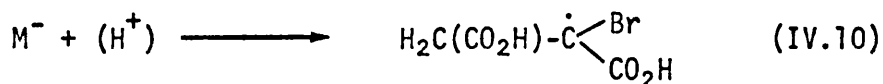
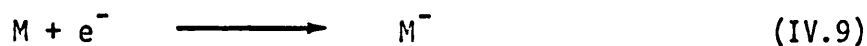
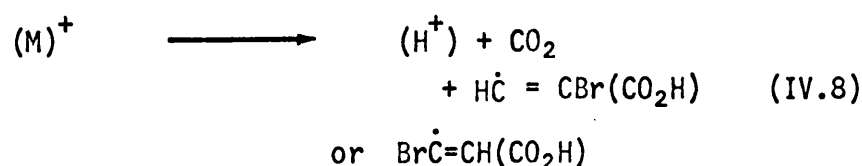
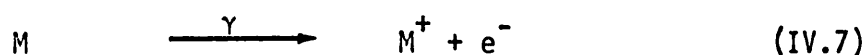


Stage (IV.3) probably involves protonations of methyl bromide, whilst stage (IV.4) accounts for the apparent absence of alkyl radicals in some cases. Methyl bromide in CD_3CN at 77 K gives a

species, $\dot{\text{C}}\text{H}_3\text{---Br}^-$, with a clearly defined hyperfine coupling to bromine (2,3), and various alkyl iodides give similar species even in the absence of methyl cyanide (14). Formation of α -bromo radicals in irradiated organic bromides may be resulted by the (H^+) loss from the parent cation (reaction (IV.3)) or alternatively by the secondary radical attack (reaction (IV.6)).



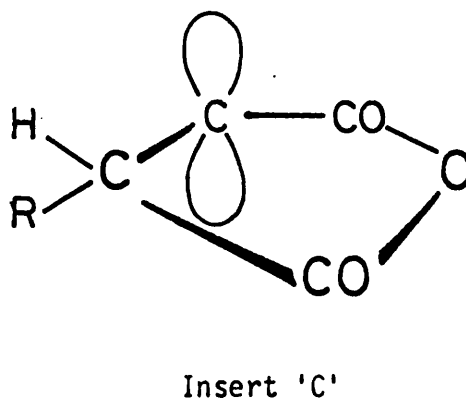
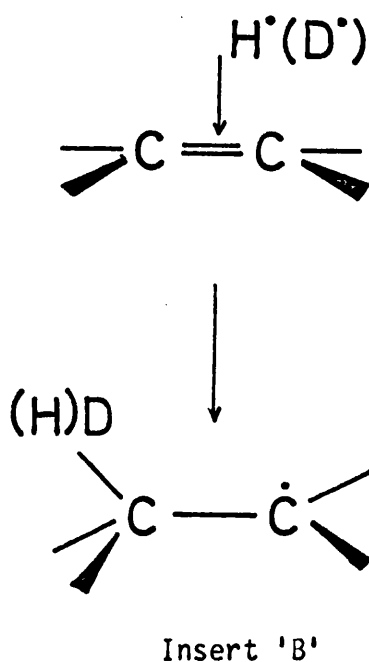
Unsaturated bromides such as bromomaleic acid (M) are expected to react as follows:



Radicals of the type invoked in reaction (IV.8) were not positively detected, but the radical in reaction (IV.10) could be the major species detected, and evidence for the radical in reaction (IV.11) was obtained, especially for $\text{H}_2\text{C}=\dot{\text{C}}\text{CO}_2\text{H}$ from α -bromoacrylic acid and its potassium salt. These radicals are characterised by a nearly isotropic triplet with an overall splitting of ca. 150 G (15,16) and such features are indicated

in Figure 3 (c) for irradiated α -bromoacrylic acid.

The hydrogen atom addition to bromomaleic acid is presumably as indicated in insert 'B' since a near maximum coupling was found for a single hydrogen nucleus, which was lost when ^2H atoms were used. The results for bromomaleic anhydride differ since the relative conformation of the β -groups are now fixed by the 5-membered anhydride ring (insert 'C'). No detectable yields of β -bromo radicals (5) were obtained from bromomaleic or bromoacrylic acids which might have been expected if addition occurred at the bromine side of the olefinic bonds. Such radicals, in their optimised conformation, have large coupling to the bromine nuclei, and would have been clearly detected if formed (5). However, allylbromide gave good yields of $\text{Me}\dot{\text{C}}\text{HCH}_2\text{Br}$. These results indicate that the stability conferred on an alkyl radical by an α -bromine atom is greater than that conferred by a β -bromine atom.



Radical $\text{H}_2\dot{\text{C}}\text{Br}$

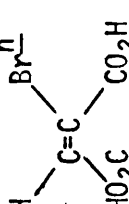
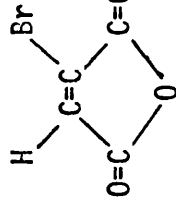
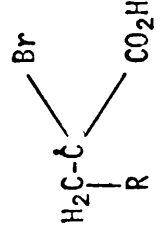
Methyl bromide or CD_3Br upon ν -irradiation at 77°K gave e.s.r. spectra which were too poorly resolved. However, during annealing above 77°K better resolution was obtained (Figure 1(b)), and the spectrum could be interpreted in terms of a rotation about the z -axis together with small librations about the other two axes. Thus, the values of $A_{\text{iso}} = -3$ G and $g_{\text{av}} = 2.018$ are obtained by using the data derived from the spectra (see Table)* which are close to the values for the other α -bromo radicals. Working backwards from the results for, say, the bromomaleic acid radical, for a z -rotation, " A_{\parallel} " (^{81}Br) = -80 G, " A_{\perp} " (^{81}Br) = +31 G, $g_{\parallel} = 2.032$ and $g_{\perp} = 2.010$. A relatively small x and y libration will reduce these to values close to those observed for $\text{H}\dot{\text{C}}\text{Br}$ radical.

* See Table on p.52.

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TABLE: E.s.r. data for a range of α -bromo radicals at 77 K, formed by exposure to γ -radiation at 77 K or at room temperature

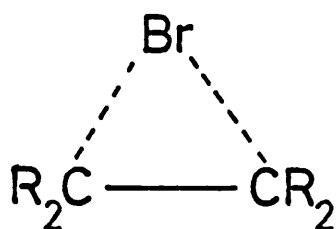
parent/solvent	radical (irradiation temp.)	hyperfine tensor components/G ^a			g-tensor components		
		X	Y	Z	X	Y	Z
CH ₃ Br, CD ₃ Br, CD ₃ OD	H ₂ ĊBr, D ₂ ĊBr (77 K)	-21	-c	-c	85	d	d
CH ₃ Br, CD ₃ Br	H ₂ ĊBr, D ₂ ĊBr (77 K)	-18.5	-18.5 ^f	c	21	21 ^f	-51
BrCH ₂ CO ₂ H ^h +CD ₃ OD	BrĊHCO ₂ H (77 K)	-20	-15	-25	107	-48	-75
BrCHMeCO ₂ H+CD ₃ OD	BrĊMeCO ₂ H (77 K)	22	c	c	95	d	d
		38,7	38,7	38,7	111	-50	-80
CH ₃ CH ₂ Br+CD ₃ OD	MeĊHBr (77 K)	ca.22			85	d	d
H ₂ C=C(Br)CO ₂ H+CD ₃ OD		c	c	c	111	d	d
H ₂ C=CH-CH ₂ Br+CD ₃ CN	H ₂ C=CH-ĊHBr	17g	c	c	93	c	c
HC(Br)(CO ₂ Et) ₂ (77 K)	BrĊ(CO ₂ Et) ₂	-	-	-	114	d	d
MeCH(Br)COEt	BrĊMeCOEt	21	21	21	113	d	d

^a $1 \text{ G} = 10^{-4} \text{ T}$; ^b Identical results were obtained on exposure to H atoms at 77 K, but the 38 G doublets collapsed to broad singlets when D atoms were used; c not clearly resolved; d Ay and Az in the 40-80 G region; e \bar{g}_y and \bar{g}_z in the 2.015-2.035 region; f rotation about z averages x and y components; g one proton only; h single crystals studied as well as powders and rigid solutions.

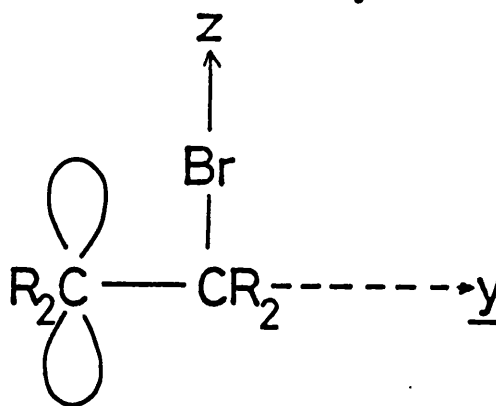
CHAPTER FIVE

β -Bromo RadicalsV.1 Introduction

The mechanism of heavy atom (halogen) addition to olefins has been of great interest to the organic chemists (1). A specific problem related with the radical additions has been the electronic structure and geometry of the intermediate $R_2\dot{C}-CR_2Hal$, which have often been formulated with the cyclic structure I.



(I)



(II)

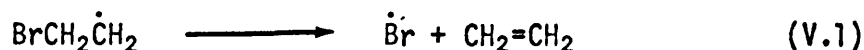
Thus, for example, Korzan et al. (2) favour the symmetrically bridged structure for the intermediate formed by loss of bromide ion from vic-dibromides. The evidence for anchimeric assistance from β -bromine during iodine abstraction from alkyl iodides by radicals (3) and from chlorine in the chlorination of chlorocyclopentane (4) have also been invoked for such intermediates. However, the suggestion that anchimeric assistance from β -bromine in the bromination of butyl bromide is merely an experimental artifact (5) has been firmly refuted by two independent groups (6,7). Most studies have favoured the presence of bridged inter-

mediates, but whether or not these are symmetrical, as in (I), is not established. In a recent study, Skell and co-workers (8), using ^{82}Br as a label, have inferred that, for the radical $\text{CH}_3\overset{\text{Br}}{\text{CH}}-\dot{\text{C}}\text{HCH}_3$, the intermediate must either be symmetrical, or the bromine atom moves from C_2 to C_3 with a frequency greater than 10^{11}sec^{-1} . It is particularly significant that the corresponding chloro-radical is found to be unsymmetrical with migration frequency of less than 10^8sec^{-1} .

Bowles et al. (9) have detected the radical $\dot{\text{C}}\text{H}_2-\text{CH}_2\text{Cl}$ in fluid solution at ca. -60°C and deduced from the small β -proton hyperfine coupling of 11.5 G that the radical is locked in the conformation II which favours p - p -homoconjugation and σ - π -hyperconjugation. Their results show conclusively that the radical has the unsymmetrical structure II, $\text{H}_2\dot{\text{C}}$ -group being normal for an alkyl radical. In a preliminary report, Lyons and Symons (10) have shown that exposure of a range of alkyl halides to γ -irradiation give species which exhibit a large hyperfine interaction with the β -halogen atoms. The most important aspect of their findings was the need to postulate a 1,2 halogen migration for radicals derived from t-butyl chloride and bromide to give $\text{Me}_2\dot{\text{C}}-\text{CH}_2\text{Hal}$, which was rapid at 77 K. (10). This idea of 1,2-halogen migration which was strongly supported in a detailed study of the chloride (11), has now been confirmed by two other groups (12,13). There is extensive chemical evidence for such 1,2-shifts (14), in addition to the recent study of Skell et al. (8).

Other results favouring the asymmetric structure II come from a CIDNP study of the β -bromoethyl radical generated by the thermolysis of benzoyl- β -bromopropionyl peroxide (15). Also a recent INDO M.O. study of the β -chloroethyl radical favours structure II (16). The results suggest that, whereas the $\text{H}_2\dot{\text{C}}$ -fragment is quite normal, the $-\dot{\text{C}}\text{H}_2\text{Cl}$ fragment besides being locked into the conformation II, deviates strongly from a formal tetrahedral arrangement, the chlorine atom being shifted towards the carbon atom of the $-\dot{\text{C}}\text{H}_2$ group, and the protons shifted towards the plane of the $-\dot{\text{C}}\text{H}_2$ group.

The aim of the work incorporated in the present chapter is to give details of the results for radicals containing β -bromine atoms formed by γ -irradiation of various organic bromides. Curiously, it seems that all attempts to detect such radicals by e.s.r. spectroscopy in the liquid-state have failed (17). This was attributed, at least in part, to their unimolecular instability:



However, it is probable that line broadening effects may have been involved for non-detection of such radicals in liquid-state.

V.2 Results and Discussion

The e.s.r. spectra of γ -irradiated alkyl bromides were dominated by features for the alkyl radicals formed by dissociative electron attachment. Thus ethyl bromide gave $\text{CH}_3\dot{\text{C}}\text{H}_2$, n -butyl bromide gave $\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{H}_2$ and t -butyl bromide gave well resolved

features for $\text{Me}_3\dot{\text{C}}$ radicals. In addition, clear features for α -bromo radicals were observed for ethyl bromide ($\text{CH}_3\dot{\text{C}}\text{HBr}$), allyl bromide ($\text{H}_2\text{C}=\text{CH}-\dot{\text{C}}\text{HBr}$) and α -bromo acrylic acid ($\text{Me}\dot{\text{C}}\text{BrCO}_2\text{H}$). Such α -bromo radicals have been discussed in the preceeding chapter. In some cases, weak features assignable to Br_2^- were also observed. These lines overlap seriously with those assigned to β -bromo radicals, but generally, during annealing, the Br_2^- features were lost before those of the β -bromo species. It should be stressed that the features of interest are relatively broad and spread over a range of ca. 1200 G which explains why they have not been detected by previous workers (Figure 1).

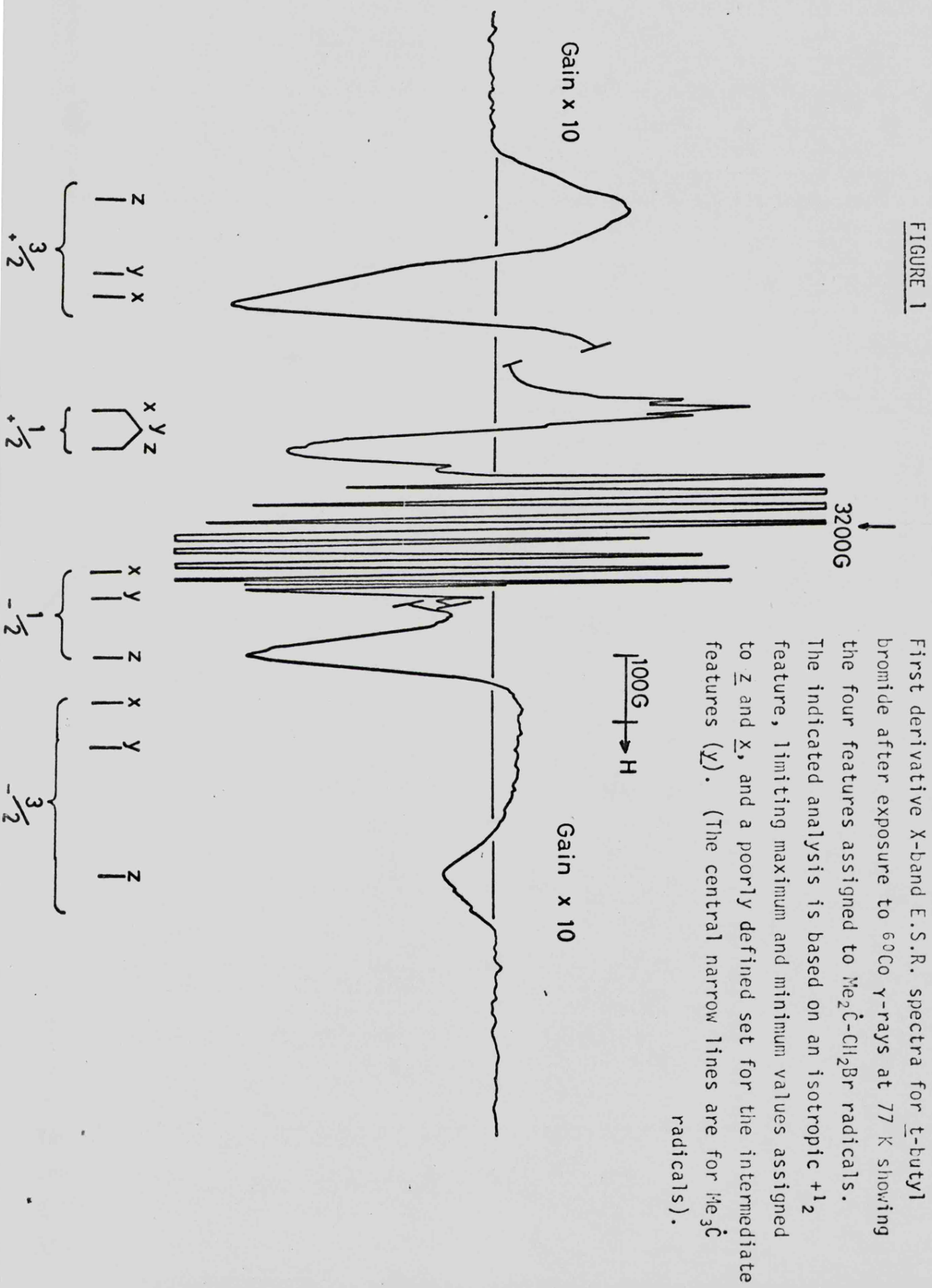
Spectral Analysis

By far the most characteristic feature in the β -bromo radicals is the " $M_I = + \frac{1}{2}$ " line, which is the most intense at X-band and seems to be almost isotropic, displaying characteristic proton hyperfine structure (Figure 2). For t-butyl bromide this gives two sets of several lines (from ^{79}Br and ^{81}Br) with $A(\dot{\text{C}}\text{H}_3) = 13$ G at 77 K and ca. 15 G at about 140 K. For n-butyl bromide a good fit was obtained for one proton, $A = 17$ G and two others having $A = 30$ G (see Table).*

In certain cases, some resolution was also obtained for components of the other three lines assigned to bromine hyperfine coupling and examples are given in Figure 2. These results show conclusively that all four lines belong to the same species, and in the case of t-butyl bromide, that a 1,2-shift has indeed occurred.

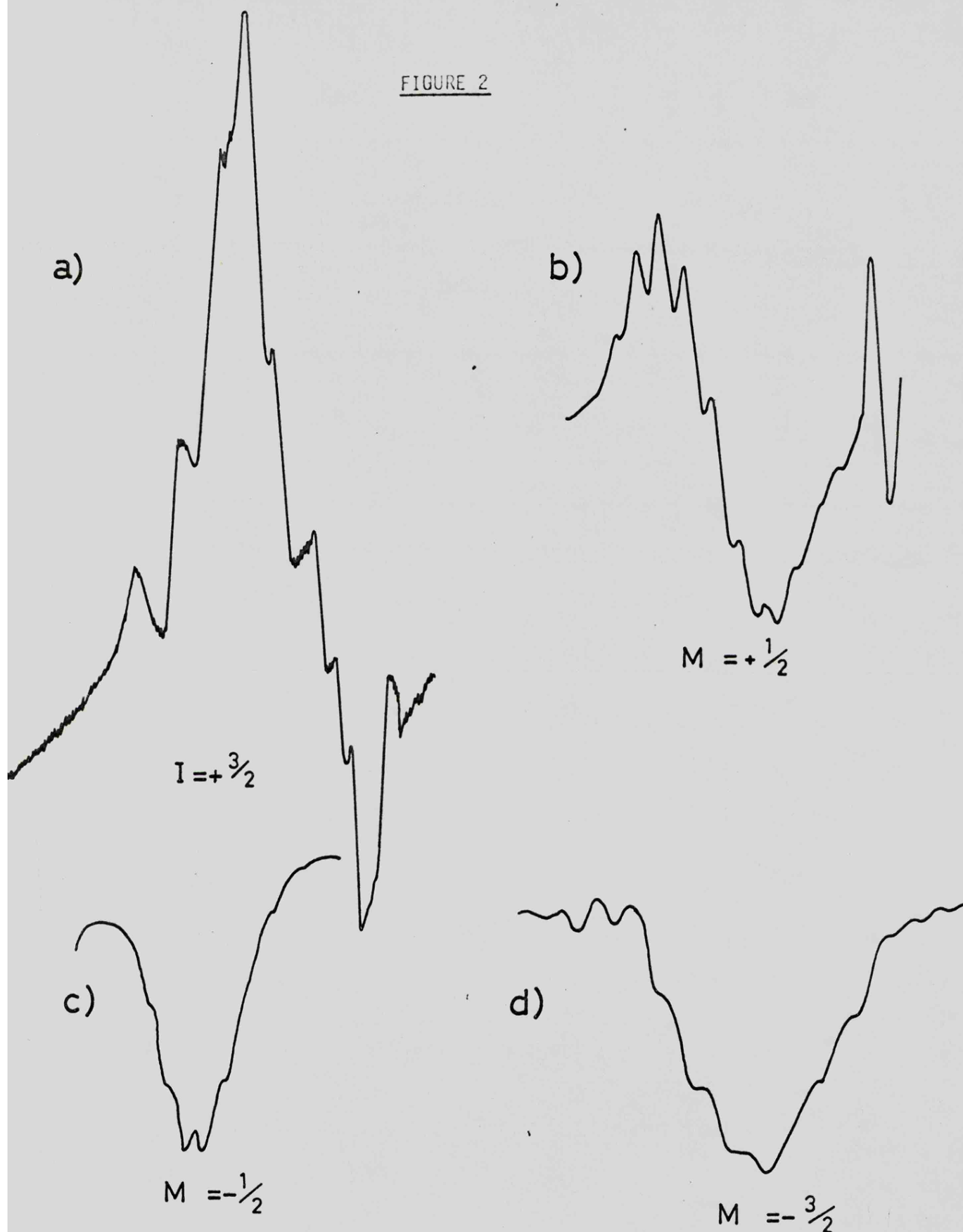
* See Table on p.67.

FIGURE 1



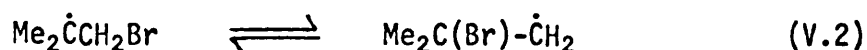
First derivative X-band E.S.R. spectra for t-butyl bromide after exposure to ^{60}Co γ -rays at 77 K showing the four features assigned to $\text{Me}_2\dot{\text{C}}\text{-CH}_2\text{Br}$ radicals. The indicated analysis is based on an isotropic $+^{1}_2$ feature, limiting maximum and minimum values assigned to z and x, and a poorly defined set for the intermediate features (y). (The central narrow lines are for $\text{Me}_3\dot{\text{C}}$ radicals).

FIGURE 2



Various selected features assigned to β -bromo radicals showing resolved proton hyperfine structure. a the " $M_I = +\frac{3}{2}$ " feature for n-butyl bromide. b the " $M_I = +\frac{1}{2}$ " feature for t-butyl bromide. c the " $M_I = -\frac{1}{2}$ " feature for t-butyl bromide. d the " $M_I = -\frac{3}{2}$ " feature for n-butyl bromide.

In contrast with the results of β -chloro radicals (10,11) these features were almost independent of temperature. Thus, cooling to 4.2 K had no noticeable effect, and careful annealing resulted in a very slight increase in $A(^1\text{H})$ and a slight, reversible fall in the overall coupling to bromine. However, during controlled annealing, just prior to complete irreversible loss of these features a very marked reversible broadening was detected for all four lines. This result may give a clue to the inability experienced by other workers to detect β -bromo radicals in the liquid-state. This broadening may have at least three sources. One is the occurrence of a dynamic 1,2-shift:



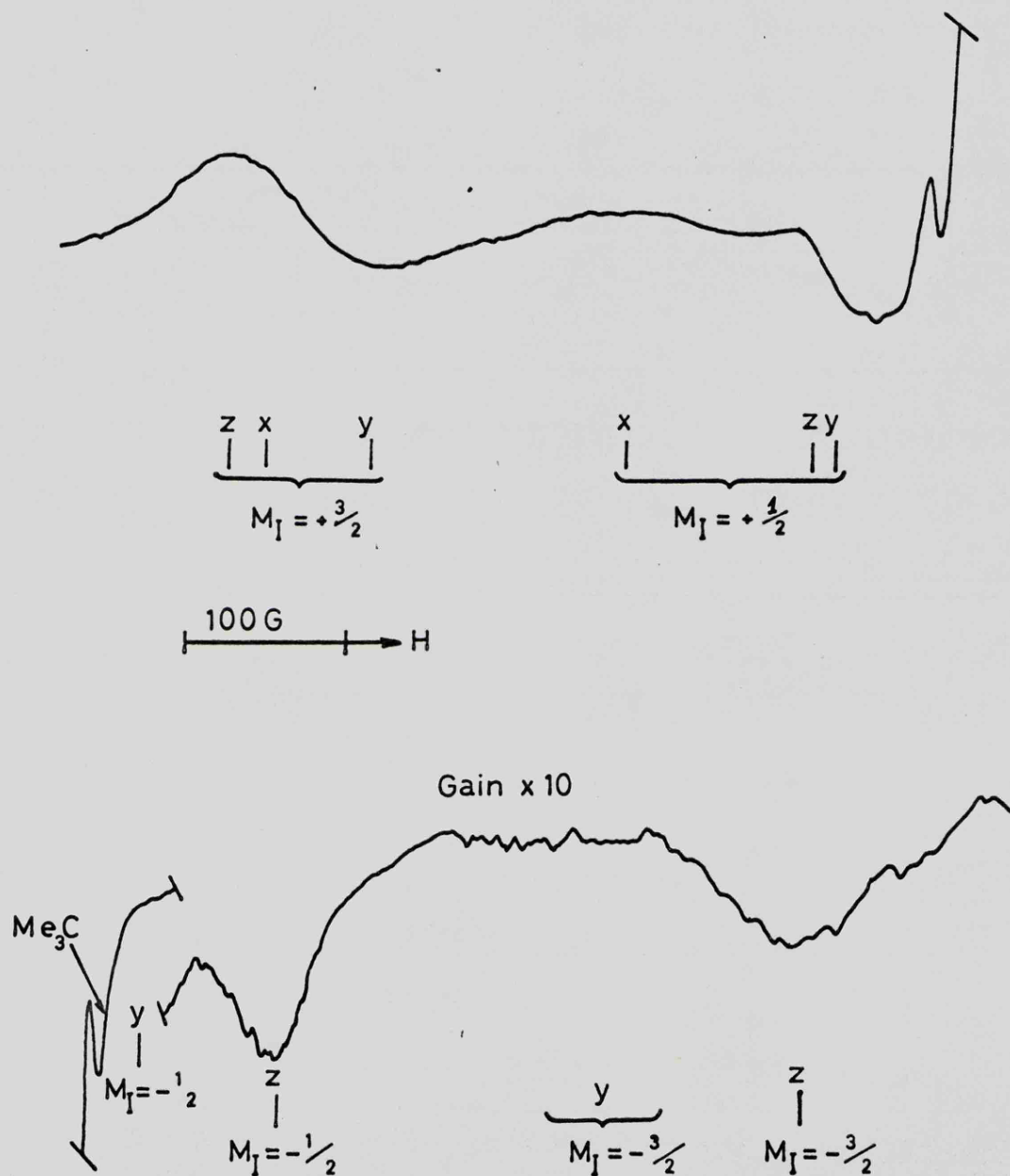
Another is an efficient spin relaxation having its basis in a relatively large g - and hyperfine anisotropy which is modulated as the radicals begin to tumble. The third is a relaxation based upon a modulation of the bond angle between the radical plane and the direction of the C-Br bond. This occurs so rapidly for the corresponding chloride radicals that, on average, temperature dependent coupling to chlorine results. For the bromine radicals the changes in hyperfine coupling could be much larger and hence spin-relaxation more likely. We are inclined to favour the second of these mechanisms, but they could all act in a cumulative way to render liquid-phase spectra too broad to detect.

A study of these radicals in CD_3OD and CD_3CN solvents was made so as to obtain further information about the failure of obtaining such species in liquid-phase. For t-butyl bromide, good β -bromo spectra were obtained with both media, and the results show that there is no major solvation effect. However, the " $M_I = +\frac{1}{2}$ " features were considerably broader than for the pure material and hence the proton structure was not resolved. Once again, annealing resulted in a major reversible broadening prior to radical decay.

Although the different intensities of the four features clearly indicate considerable g - and A -anisotropy, no definite parallel or perpendicular features are apparent. In an attempt to obtain the estimate of the anisotropy, a guidance has been taken from (i) the near isotropy of the " $M_I = +\frac{1}{2}$ " line, (ii) the fact that the relative intensities of the four features at x-band are always $M_I = +\frac{1}{2}$ > $M_I = -\frac{1}{2}$ > $M_I = +\frac{3}{2}$ > $M_I = -\frac{3}{2}$ and (iii) the fact that the only clearly defined part of the $-\frac{3}{2}$ line is a shoulder rather than a cross-over. However, the Q -band modified sequence in which the $M_I = +\frac{3}{2}$ is now more intense than the $M_I = +\frac{1}{2}$ line, and both are much more intense than the $M_I = -\frac{1}{2}$ and $-\frac{3}{2}$ lines.

Taken together, the X - and Q -band spectra define the limits for the anisotropy which are indicated in Figures 1 and 3. We have shown, by trial and error fit to these spectra, that any major

FIGURE 3



First derivative Q-band E.S.R. spectrum for *t*-butyl bromide after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to $\text{Me}_2\dot{\text{C}}\text{-CHBr}$ radicals. The central intense lines are due to $\text{Me}_3\dot{\text{C}}$ radicals.

modification to the resulting \underline{g} - and \underline{A} -tensor components (Table)* yields unacceptable reconstructions for one or other of these spectra. However, despite this agreement, it remains probable that the directions of the \underline{g} - and \underline{A} -tensors are not exactly the same, which lends a further uncertainty to the data. Nevertheless, these approximate results for the $\text{Me}_2\dot{\text{C}}\text{CH}_2\text{Br}$ radical are worth analysing.

Assuming all signs to be positive, for the bromine hyperfine coupling, we get 296 G for $\underline{A}_{\text{iso}}$ and $|-56 \text{ G}, -13 \text{ G}, +70 \text{ G}|$ for the anisotropic coupling. We can decompose the latter into two axial components $|-42, -42, +84|$ and $|-14, +28, -14|$, symmetric about \underline{z} - and \underline{y} -axes respectively. These axes correspond, roughly, to those shown in II, for the following reasons. If, as previously inferred (10,11), σ - π -hyperconjugation is the major mode for hyperfine interaction, we would expect the maximum coupling to occur along the C-Br bond (\underline{Z}). If, however, \underline{p} - \underline{p} -homoconjugation is also significant (17,18), there should be an additional positive component almost at right angles to this, roughly along the C-C bond direction (\underline{Y}). Thus we can, very approximately, associate the axial tensor having $\underline{2B} = 84 \text{ G}$ as a measure of hyperconjugation interaction which corresponds, on the usual approximations (19), to ca. 17% "delocalisation". (This includes spin-polarisation effects (20)). Then the second axial tensor having $\underline{2B} = 28 \text{ G}$ arises from \underline{p} - \underline{p} -homoconjugation, which corresponds

* See Table on p.67.

to ca. 5.7% delocalisation. Since the isotropic coupling of 296 G corresponds to ca. 3.5% delocalisation, the total spin-density on ^{81}Br is then ca. 26%.

If the electron-spin were shared solely between bromine and the trigonal carbon atom, this would lead to a spin-density of 74% on carbon, which in turn leads to a predicted methyl proton coupling of ca. 16.5 G. The observed value of 13 G is appreciably less. This could either mean that there is some spin-density elsewhere, or that the $\text{Me}\dot{\text{C}}\text{-C}$ unit is not locally planar. Slight deviation from the planarity would certainly result in a decrease in the magnitude of the methyl proton coupling. Unfortunately, no coupling to the β -protons of the methylene group could be resolved, but line-widths give an upper limit of ca. 5 G for this coupling. This low value arises in part because of the preferred conformation II, and probably partly because the bromine atom has moved towards the radical centre with a consequent movement of the methylene protons towards the radical "plane".

The bromine isotropic coupling probably arises as a result of hyperconjugation (delocalisation plus spin-polarisation of the C-Br σ -electrons), in which case the derived p/s value of 4.9 is unexpectedly small. This may be a real property of the C-Br bond, but may also be a result of some back-donation of the unpaired electron into the outer, 5s-orbital on bromine.

This would be facilitated by electron-donating methyl groups and may help to explain why the radical $\text{Me}_2\dot{\text{C}}\text{-CH}_2\text{Br}$ has the maximum bromine coupling observed (see Table)*. It is of interest to compare the large isotropic coupling constants for β -bromo radicals with the very small values deduced for α -bromo radicals (21). In addition to $4s$ -delocalisation, which is impossible for the planar α -radicals, there is the fact that spin-polarisation in the $\dot{\text{C}}\text{-Br}$ bond resulting from spin on carbon will contribute a large negative component to the isotropic coupling. This contribution is absent for the β -bromo radicals.

Though the g -values can only be treated as approximate, there is certainly a real positive shift for g_y , where y is thought to be fairly close to the C-C direction (II). For a significant p - p -homoconjugation, we had expected, a maximum positive g -shift along the C-Br direction. However, this was not found. The large g_y shift suggests a relatively large splitting of the $p(\pi)$ -orbitals on bromine, and this may help to explain the zero shift for g_z .

Structural details for this class of radicals have not been forthcoming. We have screened a very wide range of potential sources of β -bromine radicals, but in no other cases have clear features for these radicals been resolved. Single crystal studies of these species are needed, but all our attempts to obtain good crystal spectra have so far failed.

* See Table on p.67.

Comparison with β -Chloro-Radicals

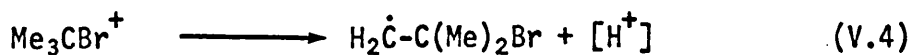
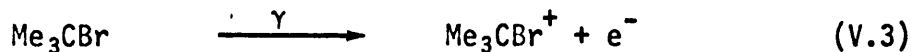
In a previous work on $\text{Me}_2\dot{\text{C}}\text{-CH}_2\text{Cl}$ radicals (11), it was inferred that there must be some g - and A -anisotropy, but this was too poorly defined to be interpretable. Since then, liquid-phase data have become available (12,13), and hence further discussion is warranted. Even if the isotropic chlorine coupling of 21.24 G (^{35}Cl) for $\text{Me}_2\dot{\text{C}}\text{-CH}_2\text{Cl}$ is increased by the ratio of the proton couplings for liquid and solid-states (ca. 1.24), the value, ca. 26 G, remains small compared with the maximum coupling of ca. 45 G obtained at 77 K. (This ratio of 1.24, deduced from $A(\text{Me})$, is assigned to a small libration in the liquid-phase, which is lost on cooling, and it is assumed that the chlorine coupling should roughly increase in the same proportion). Therefore, the difference between 45 G and 26 G must be assigned to anisotropic effects. Taking the chlorine hyperfine coupling as axial, we calculate " A_{\perp} " to be 16.5 G. However, this value is approaching the critical value of ca. 5 G at which major quadrupole effects come into play (22). This has the effect of diminishing the intensity of the outer components and increasing their overall separation. This explains the inability to detect clearly defined "perpendicular" features. The fall on annealing from 45 G to 37 G (11) is then understandable as partial averaging resulting from extensive librational motion in the lattice.

These results correspond to a 2p-orbital population of ca. 19% and a 2s-content of ca. 1.55%. The former is quite comparable with that for the β -bromine radical whilst the latter is considerably smaller. This could mean that p-p-homoconjugation is more important for the chlorine radicals or that the outer s-orbital contributes more for bromine than for chlorine.

Aspects of Mechanism

The results confirm that the protons β to a bromine atom are markedly susceptible to radical attack, but there is, in general, a preference for formation of α -bromo radicals when there is a choice. Thus, the loss of (H^+) from the parent cation generally involves α - rather than β -protons when available. For t-butyl bromide, however, there are no α -protons, and so the β -radical predominates. As with the chloro- compounds, however, the radical $H_2\dot{C}-CMe_2Br$, which is presumably initially formed, readily rearranges to the more stable $Me_2\dot{C}CH_2Br$ species. Since this occurs rapidly at 77 K the activation energy must indeed be small. Our results show that for Me_2CCH_2Br and $Et\dot{C}HCH_2Br$, the 1,2-shift structures $[Me_2C(Br)\dot{C}H_2]$ and $Et\dot{C}H(Br)\dot{C}H_2]$ are, at best, only minor components, and that the intermediates are far from being symmetrical. Results for $H_2\dot{C}CH_2Br$ are similar, but proton structure was not resolved. Since radical $Me\dot{C}HCH(Br)Me$ studied by Skell et al. (8) could not be prepared during the present findings and hence no comment is being made on the possibility that these species have the symmetrical structure, I.

Thus it is to be concluded that the radicals detected are $\text{Me}_2\dot{\text{C}}\text{-CH}_2\text{Br}$ rather than the $\text{H}_2\dot{\text{C}}\text{-C}(\text{Me})_2\text{Br}$ radicals which are, presumably, precursors. A reasonable mechanism is as follows:



The finding for bromo radicals strongly support those of β -chloro radicals, and that they provide a basis for understanding the mechanism of addition reactions to olefins involving bromine. It must be stressed that these results, which establish clearly that structure II is both preferred and long-lived, with a large barrier to rotation about the C-C bond, yield an explanation for the normal trans-mode of radical addition of bromine to olefins.

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TABLE

E.s.r. data assigned to various β -bromo alkyl radicals

Parent	Radical	Hyperfine Coupling Constants (G) ^a				g-values		
		¹ H	⁸¹ Br					
			<u>x</u>	<u>y</u>	<u>z</u>	<u>x</u>	<u>y</u>	<u>z</u>
Me ₃ CBr	Me ₂ \dot{C} CH ₂ Br	13 (15 at 190 K) (2Me)	280	240	366	2.006	2.031	2.000
	H ₂ C=C(Br)CO ₂ H							
	Br H ₂ \dot{C} C(R)CO ₂ H	<u>b</u> 18	<u>d</u>	<u>d</u>	233	<u>d</u>	<u>d</u>	2.000
n-buBr	CH ₃ CH ₂ \dot{C} HCH ₂ Br	$\left\{ \begin{array}{l} 17(H_{\alpha}) \\ 30(2H_{\beta}) \end{array} \right.$	ca. 200	ca. 200	280	ca. 2.01	ca. 2.027	2.000
EtBr	H ₂ \dot{C} CH ₂ Br	<u>c</u>	<u>d</u>	<u>d</u>	250	<u>d</u>	<u>d</u>	2.000
PrBr	H ₃ \dot{C} CHCH ₂ Br	<u>c</u>	<u>d</u>	<u>d</u>	260	<u>d</u>	<u>d</u>	2.000

a 1 G = 10⁻⁴ T. b Only the z components clearly resolved. c Not resolved. d Too poorly resolved for interpretation.

CHAPTER SIX

RADIATION PROCESSES FOR TRICHLOROMETHYL COMPOUNDS:THE $\dot{\text{C}}\text{Cl}_3$ RADICALVI.1 Introduction

A great interest has centred on the E.S.R. spectroscopic study of α -chlororadicals, both in the solid state (1-5) and in solution (6-12), and complete analysis of the powder E.S.R. spectra for $\text{R}_2\dot{\text{C}}\text{Cl}$ and $\text{R}\dot{\text{C}}\text{Cl}_2$ radicals has been described (13) and also presented in Chapter III of the present thesis. The $\dot{\text{C}}\text{Cl}_3$ radical has long been a species of great interest to chemists but its e.s.r. features are not well defined, and interpretations are varied. Hesse et al. (14) studied $^{13}\dot{\text{C}}\text{Cl}_3$ in a matrix of carbon tetrachloride and obtained the isotropic ^{13}C hyperfine coupling. When the present work was almost complete, Maass et al. (15) reported the powder e.s.r. spectrum for this radical in argon and krypton matrices at 4.2 K. Their identification is supported by the present work, but rather different parameters are derived from their spectra.

Studies on the radiolysis of liquid carbon tetrachloride using various scavengers (16) suggest that $\dot{\text{C}}\text{Cl}_3$ radicals and chlorine atoms are the primary neutral products, although low yields of C_2Cl_4 suggest that $\dot{\text{C}}\text{Cl}_2$ molecules may play a minor role. The $\dot{\text{C}}\text{Cl}_3$ radical is also considered to be a primary product in the radiolysis of chloroform (17).

The objective of the present work was to see if a sufficiently distinctive powder spectrum of $\dot{\text{C}}\text{Cl}_3$ could be established so that this radical could be detected by its characteristic e.s.r. spectrum in the presence of other chlorine-containing radical species and also to discover other primary/secondary radical products in the radiolysis of carbon tetrachloride and related compounds.

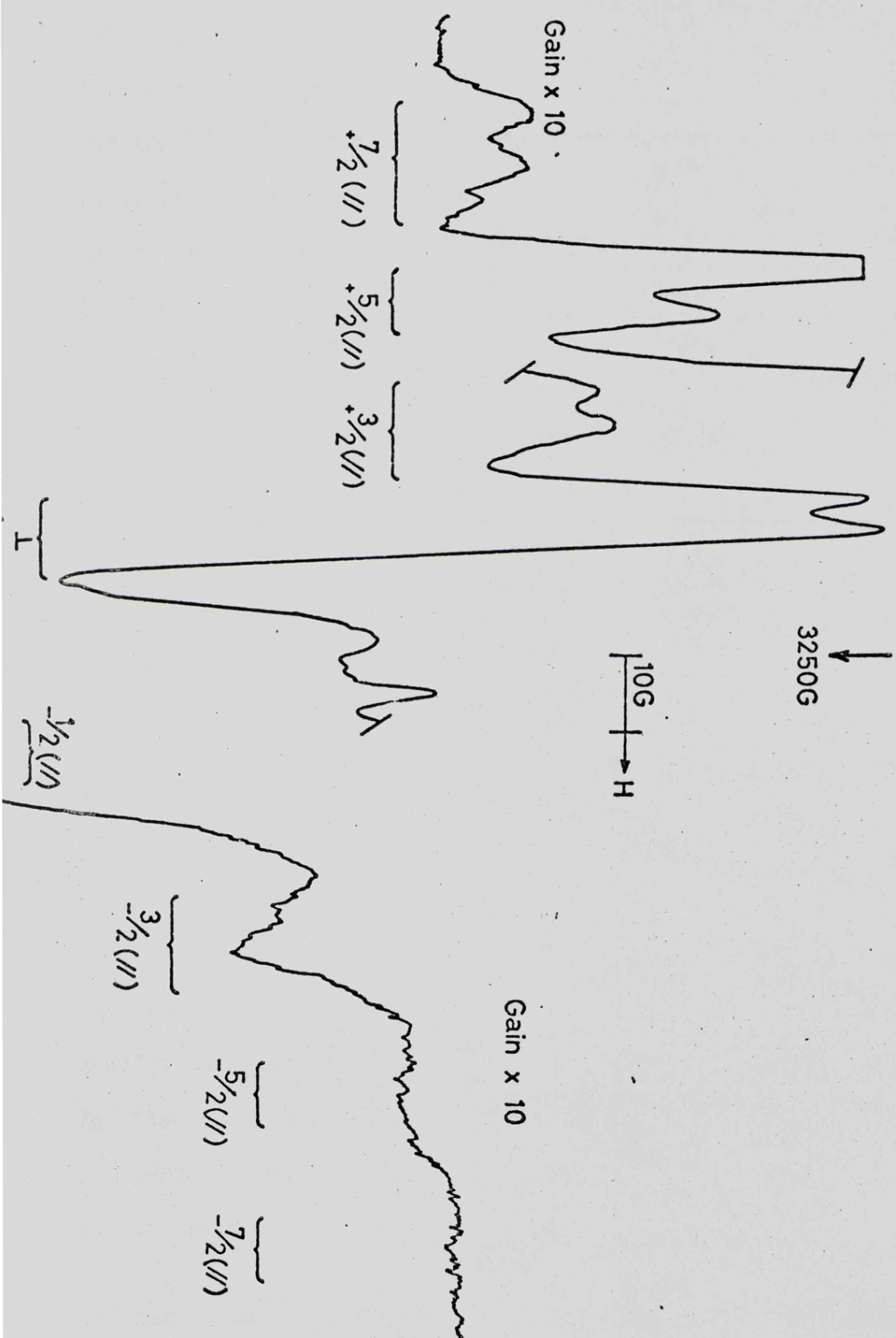
VI.2 Results and Discussion

The $\dot{\text{C}}\text{Cl}_3$ Radical

An e.s.r. spectrum of $\dot{\text{C}}\text{Cl}_3$ radical is shown in Fig.1. A most distinctive feature is a relatively narrow, nearly isotropic line with a peak at $g = 2.0112$. This is flanked on either side by weak "parallel" features separated by ca. 20 G. The $g = 2.0112$ line is assigned to the $M_I = +1/2$ feature, which is fortuitously nearly isotropic at X-band frequencies. This feature is narrow because $A_{\perp}(\text{Cl}) \approx 0$ G. This result differs in two respects from those of mono- and di- α -chloro radicals (13). One is that in these cases, $A_{\perp}(\text{Cl})$ is in the region of -4 to -8 G and the other is that $g_x \neq g_y$. Hence the "perpendicular" region of these radicals is diffuse and multi-featured, and, the $g = 2.0112$ line for $\dot{\text{C}}\text{Cl}_3$ radical stands out clearly in the presence of signals from mono- and/or di-chloro radicals. However, the "parallel" (z) features are very similarly spaced to those for other chloro radicals (13). and cannot be taken as characteristic of $\dot{\text{C}}\text{Cl}_3$ radicals unless they are very well resolved, which is rarely the case. Thus, whilst it is possible to identify $\dot{\text{C}}\text{Cl}_3$ radicals in the presence of other chloro radicals, it may be hard to give a positive identification of the

FIGURE 1

First derivative X-band E.S.R. spectrum from carbon tetrachloride in CD_3OD after exposure to ^{60}Co γ -rays at 77 K after annealing to remove $\dot{\text{C}}\text{D}_2\text{OD}$ radicals, showing features assigned to $\dot{\text{C}}\text{Cl}_3$ radicals.

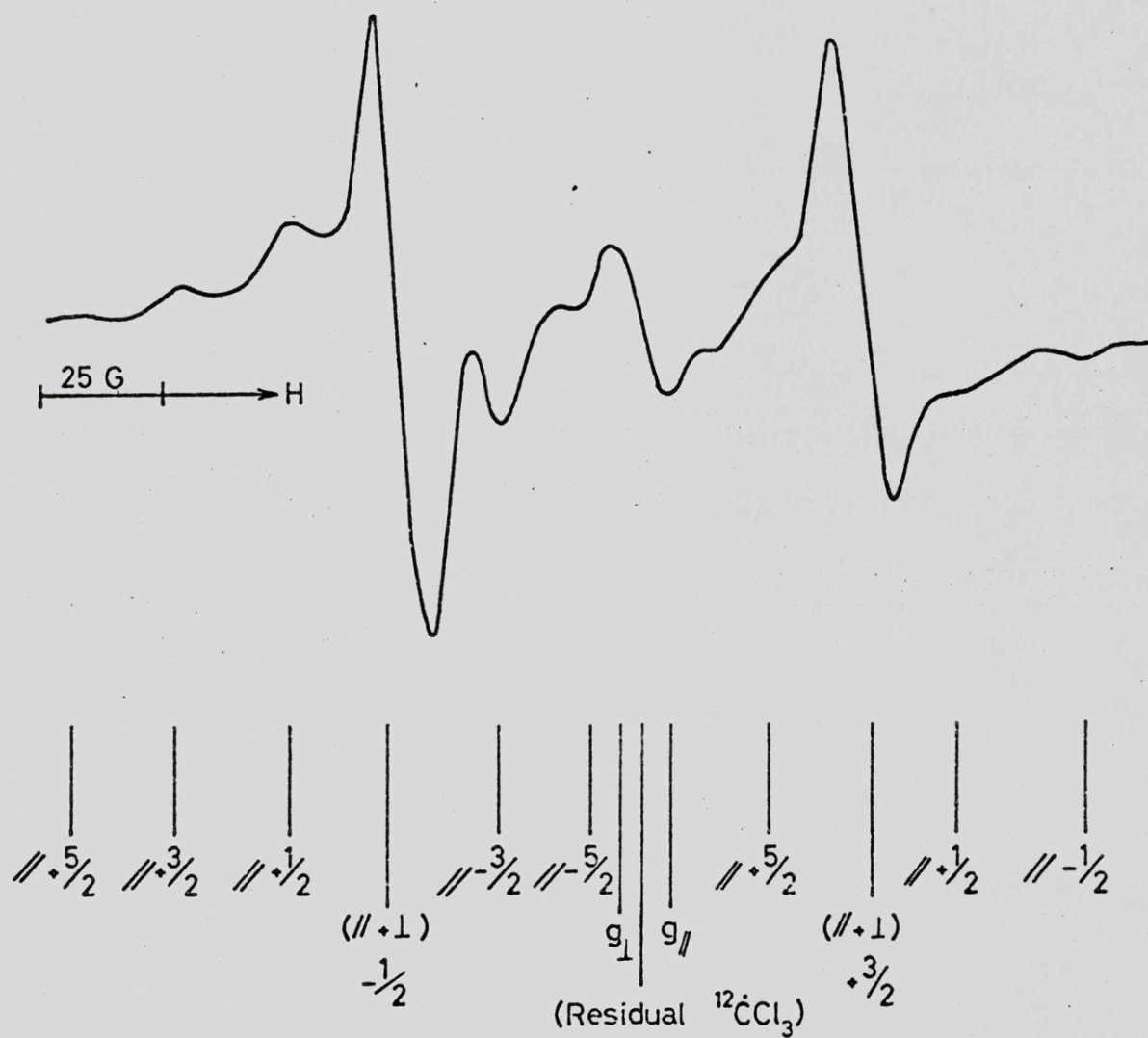


other species since it is the z-feature that provides clear identification in all other cases.

Weak satellite features assignable to ^{13}C nuclei were detected in some cases. However, the spectrum given by Maass et al. (15) for $^{13}\dot{\text{C}}\text{Cl}_3$ radical in a xenon matrix is well defined (Fig.2), and the ^{13}C parameters can be more accurately determined therefrom. Thus, in the light of present analysis as indicated in Fig.2, and hence also the derived parameters (Table)*, are different to those of Maass et al. (15). This is because each half of the spectrum has been interpreted as if it directly related to the $^{12}\dot{\text{C}}\text{Cl}_3$ spectrum, which is not the case. For clarity, this spectrum is reproduced in Fig.2, together with the present analysis. It would appear that the results obtained are in better accord with expectation, since $|A_{||}|(^{13}\text{C})$ is now greater than $|A_{\perp}|$, as required for an s-p hybridized orbital on carbon. This interpretation also gives identical ^{35}Cl hyperfine and g-values for the $^{12}\dot{\text{C}}\text{Cl}_3$ and $^{13}\dot{\text{C}}\text{Cl}_3$ radicals, as required for an axially symmetrical species. Furthermore, $g_{\perp} > g_{||} > \text{free spin (2.0023)}$ and g_{av} calculated from $g_{||}$ and $g_{\perp} \doteq g_{\text{solv}}$ (see Table I). These requirements are not fulfilled by the data of Maass et al. (15). Due to its C_{3v} symmetry, the $\dot{\text{C}}\text{Cl}_3$ radical will have features in the powder spectrum corresponding to values parallel and perpendicular to the symmetry axis. Orbital angular momentum from spin-density on chlorine, which is responsible for the positive g-shifts, will have components in both the parallel and perpendicular directions provided the radical is pyramidal. This is not the case for the mono- and di-chloro radicals, which are

* See Table on p.80.

FIGURE 2



First derivative X-band E.S.R. spectrum for $^{13}\text{CCl}_3$ radicals in a xenon matrix (from ref.15) showing the present analysis into parallel and perpendicular $^{35}/^{37}\text{Cl}$ and ^{13}C hyperfine features.

effectively planar at the carbon centre, and which all display a free-spin g_z -value. For these reasons, the present interpretation of the spectrum assigned to $^{13}\dot{\text{C}}\text{Cl}_3$ radicals is to be considered as correct.

On the basis of above analysis, one can use the ^{13}C hyperfine coupling constants to estimate approximate $2s$ and $2p$ orbital population on carbon (18). Using the atomic wave functions of Froese (19) for ^{13}C ($\underline{A}^0 = 1130 \text{ G}$; $\underline{2B}^0 = 66 \text{ G}$), we find $\underline{a}^2(2s) \doteq 0.103$ and $\underline{a}^2(2p) \doteq 0.50$ whence the total spin-density on carbon is ca. 60.3% and p:s ratio is ca. 4.8. These results imply considerable delocalisation on the chlorine, as expected (ca. 13.3% on each), and also establish unequivocally that the radical is pyramidal, although it is clearly flatter than the $\dot{\text{C}}\text{F}_3$ radical (20).

The present conclusions agree with those of Kispert and Rogers (21) who detected a radical thought to be $\dot{\text{C}}\text{Cl}_3$ in ν -irradiated trichloroacetamide. Their value of $\underline{A}_{//} (^{13}\text{C})$ of 136 G is lower than that used in the present work (150 G) which may mean that the radicals were librating in trichloroacetamide matrix. The spectra were too complex to permit the derivation of further parameters (21).

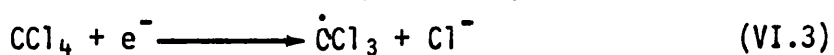
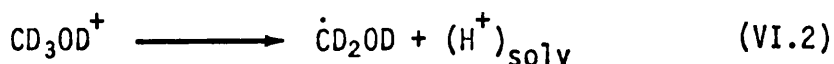
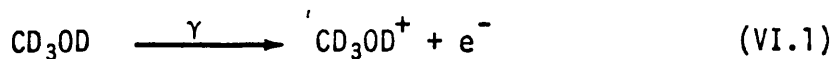
If the $\dot{\text{C}}\text{Cl}_3$ radical was planar, the parallel and perpendicular components of the ^{35}Cl hyperfine tensor could also be used to derive approximate spin-densities on chlorine, but as the radical becomes pyramidal, so the measured $\underline{2B}$ value must fall from the true value. This will not be a major factor for a nearly planar radical, so it is of interest to examine the $\underline{A}_{\text{iso}}$ and $\underline{2B}$ values for ^{35}Cl . These

give apparent spin-densities in the 3s and 3p orbitals on chlorine of ca. 0.4 and ca. 13.3%, respectively, the delocalisation being close to the value estimated from the ^{13}C data of the present work. These suggest that deviation from planarity is not very great. Theoretical studies are in agreement with this conclusion (22, 23).

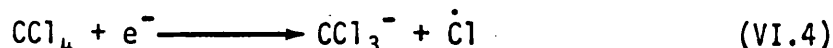
The results of the present study show that the $\dot{\text{C}}\text{Cl}_3$ radicals are stationary at 77 K in carbon tetrachloride matrix, and it is suspected that the apparently rapid increase in A_{iso} value on cooling below 185 K (14) was caused by the onset of hindered movement. This is supported by the fact that A_{iso} at 185 K is close to the value of A_{iso} estimated from the anisotropic data obtained at ca. 15 K. It is usual to find that AB_3 pyramidal radicals have strongly temperature-dependent hyperfine parameters (18).

Radiolysis of Carbon tetrachloride

Radiolysis of carbon tetrachloride solutions in CD_3OD resulted in the formation of $\dot{\text{C}}\text{Cl}_3$ radicals which were the only detectable product other than $\dot{\text{C}}\text{D}_2\text{OD}$. A reasonable mechanism is suggested as follows:



Process (VI.2) is probably not a direct proton loss. Process (VI.3) might be in competition with (VI.4):



But since it has been found that chlorine atoms react in water matrix to give ClOH^- radicals (24), one would expect to observe their analogue (ClOCD_3^-) in the present case. No such features were observed in the E.S.R. spectra, even at very high gain. Also, the chlorine atoms are not expected to give a detectable resonance absorption under the present conditions because of spin-orbit coupling during γ -radiolysis of methanolic solutions of carbon tetrachloride.

This is not necessarily the case for γ -radiolysis of pure carbon tetrachloride, and the formation of chlorine atoms (16) could arise via reaction (VI.4). Alternatively, it could be a consequence of charge recombination between CCl_4^+ and e^- to give an electronically excited molecule (CCl_4^*) which then dissociates



The E.S.R. spectra were examined for the unknown CCl_4^+ radical and some features were detected in the expected regions. These are poorly defined (Fig.3) and cannot be taken as unequivocal proof that CCl_4^+ radicals are formed. Such features were rapidly lost on annealing above 77 K, which would accord with expectation for an electron-transfer mechanism for diffusion. Although some loss of $\dot{\text{CCl}}_3$ radicals was also observed on annealing above 77 K,

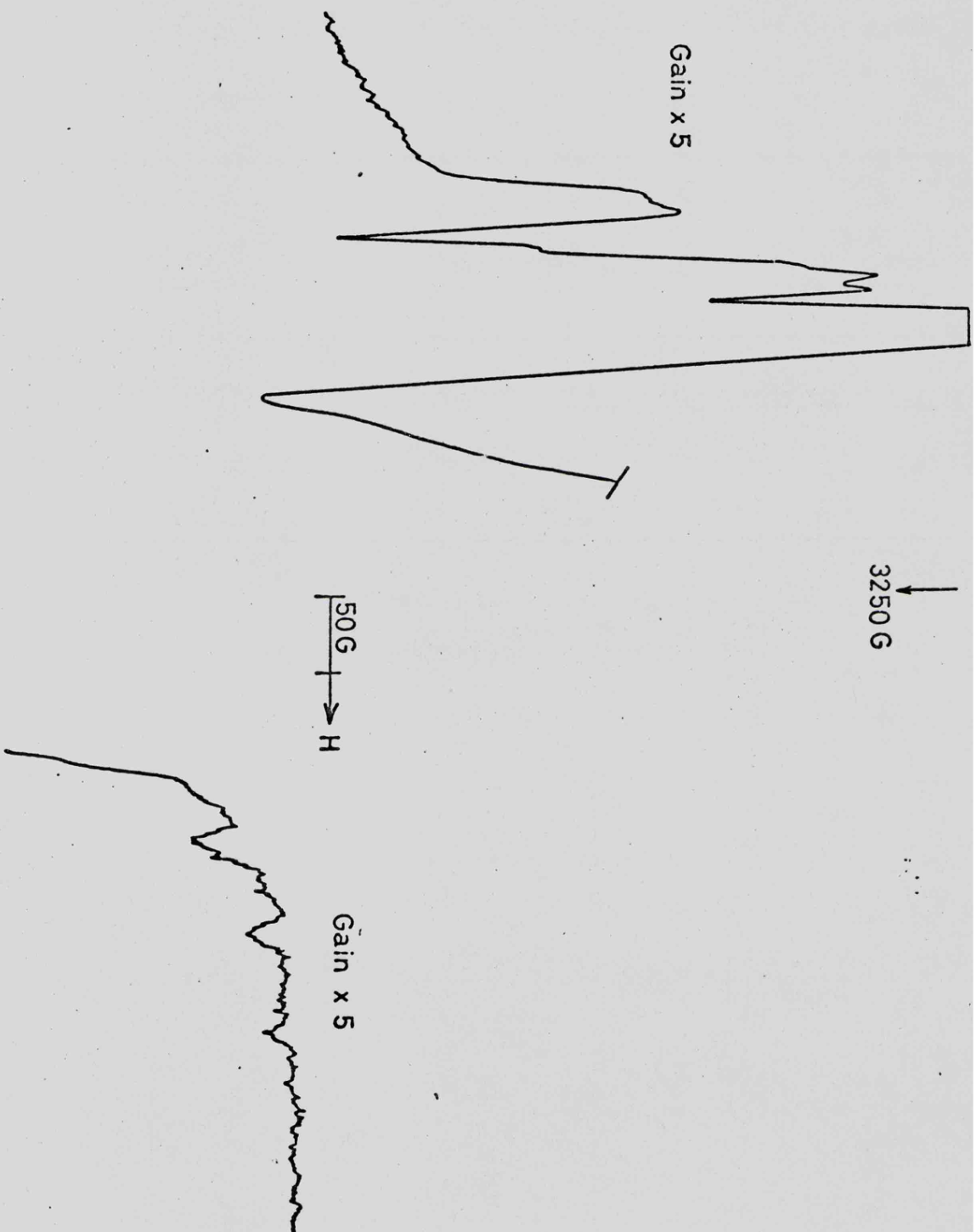
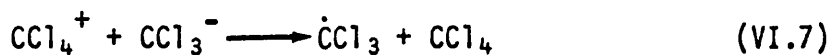
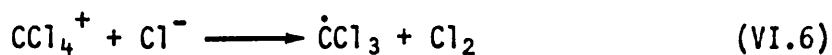


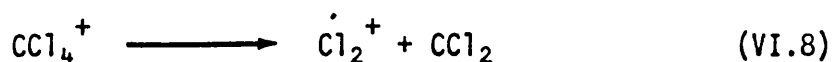
FIGURE 3

First derivative X-band E.S.R. spectrum from pure carbon tetrachloride after exposure to ^{60}Co γ -rays at 77 K at high gain and large sweep, showing features assigned to CCl_4^+ radicals. Central lines assigned to $\dot{\text{C}}\text{Cl}_3$ radicals have been omitted for clarity.

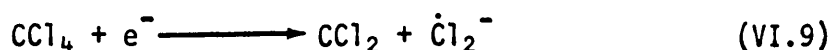
this would not begin to account for the loss of " CCl_4^+ " and it is suggested that process (VI.6) and (VI.7) also contribute:



One alternative is the unimolecular decomposition:



The cation Cl_2^+ might well be undetected under the present conditions (25) and CCl_2 molecules could well be the precursors of C_2Cl_4 (16). In this connection a search for features of the Cl_2^- radical anion was made in the expectation that reaction (VI.9) might occur:



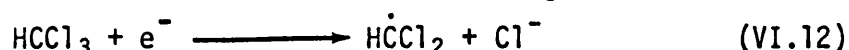
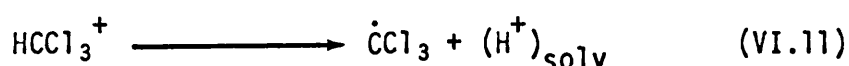
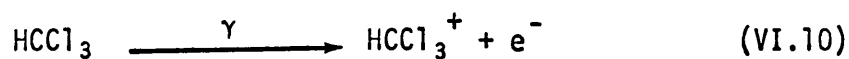
but no such features were detected and hence it is to be concluded that process (VI.9) is not significant.

The CCl_4^+ radical is expected to have the unpaired electron entirely confined to chlorine. In the undistorted tetrahedral ion, this would probably be the t_1 level, but our experience of radicals of this type (18) suggests that various possible types of distortion are to be expected which can confine the electron to one, two or three chlorine atoms only. In the present case, a very tentative interpretation of the E.S.R. spectrum, indicated in Fig.3, would require the presence of three equivalent chlorine atoms. Hence, the measured anisotropy would be far less than the maximum for any one chlorine,

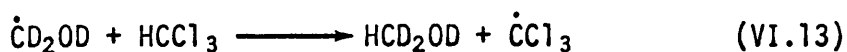
which could indeed accord with the low measured anisotropy. Therefore, it is concluded that this spectrum may well be from CCl_4^+ radicals.

Radiolysis of Chloroform

On γ -radiolysis of pure chloroform at 77 K, a clear $g = 2.0112$ feature was obtained, thus confirming that $\dot{\text{C}}\text{Cl}_3$ radicals are an important primary product. In addition, parallel features assignable to $\text{H}\dot{\text{C}}\text{Cl}_2$ radicals were obtained and hence it is concluded that the overall mechanism is:



In CD_3OD solutions of chloroform γ -radiolysed at 77 K only $\text{H}\dot{\text{C}}\text{Cl}_2$ and $\dot{\text{C}}\text{D}_2\text{OD}$ radicals were formed initially, as expected, but on annealing above 77 K $\dot{\text{C}}\text{D}_2\text{OD}$ radicals were lost, and the $g = 2.0112$ line of $\dot{\text{C}}\text{Cl}_3$ appeared:

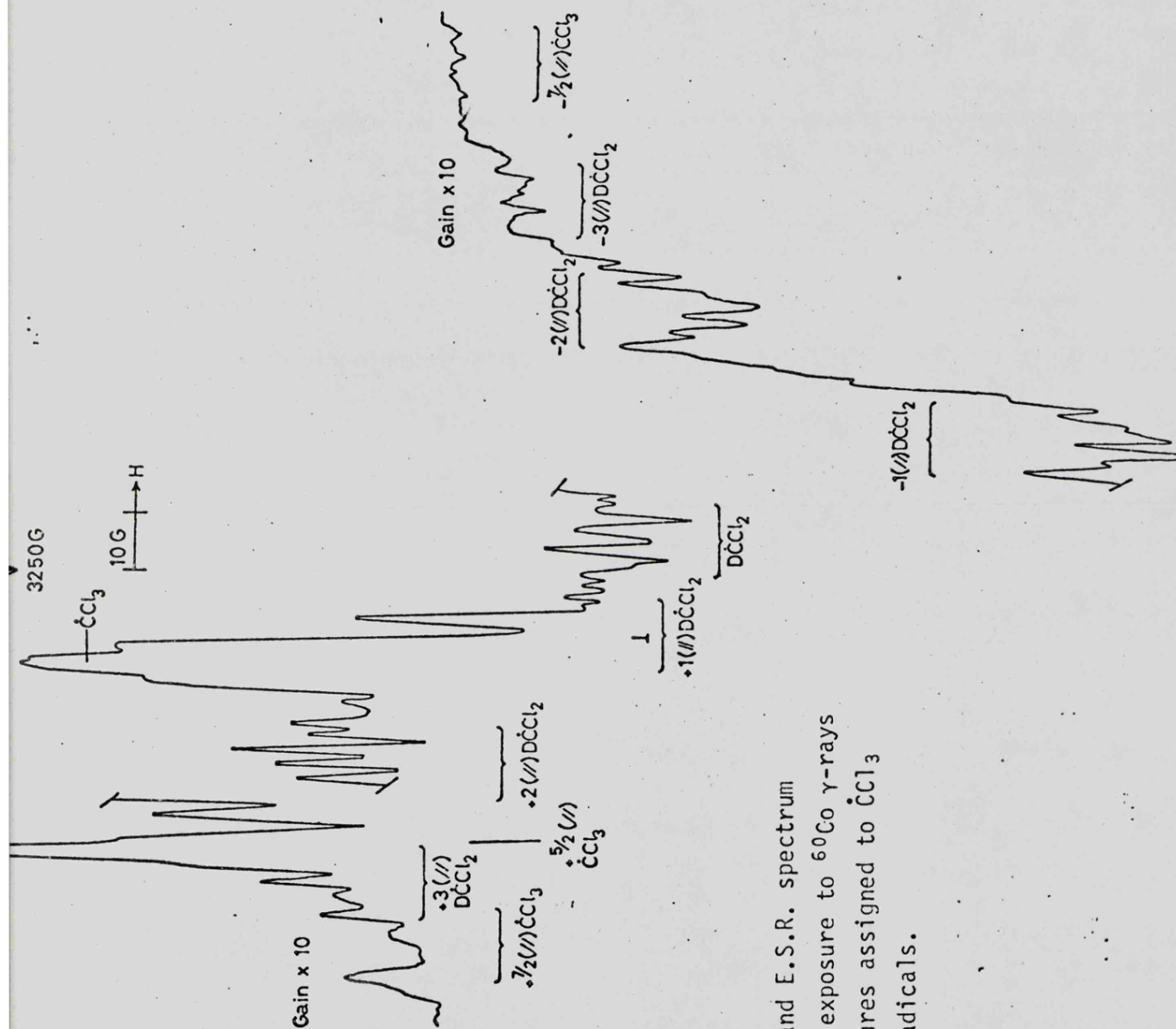


These conclusions were confirmed from the γ -radiolysis of DCCl_3 , which gave well-defined spectra for $\text{D}\dot{\text{C}}\text{Cl}_2$ radicals (Fig.4).

Radiolysis of 1,1,1-trichloroethane

$\text{Cl}_3\text{C}-\text{CH}_3$ and its solutions in CD_3OD gave well defined E.S.R. spectrum of $\text{CH}_3\dot{\text{C}}\text{Cl}_2$ radicals on γ -radiolysis at 77 K. To check this,

FIGURE 4

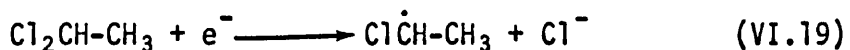
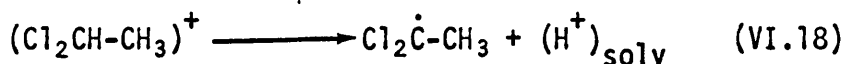
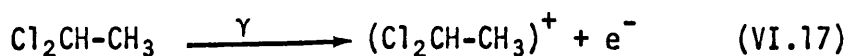
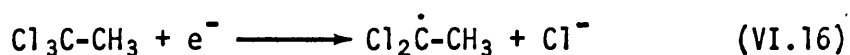
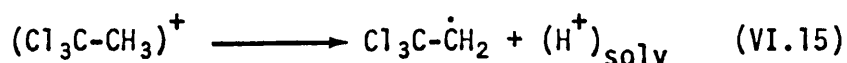
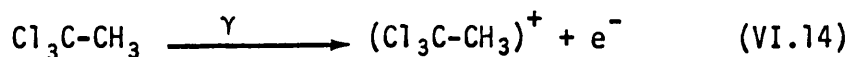


First derivative X-band E.S.R. spectrum for pure DCCl_3 after exposure to ^{60}Co γ -rays at 77 K showing features assigned to $\dot{\text{C}}\text{Cl}_3$ radicals and $\text{D}\dot{\text{C}}\text{Cl}_2$ radicals.

Cl_2CHCH_3 was also irradiated in pure form and in CD_3OD solutions. This gave a mixture of $\text{Cl}_2\dot{\text{C}}\text{-CH}_3$ and $\text{CH}_3\dot{\text{C}}\text{HCl}$ radicals in pure state and the latter only in CD_3OD solutions. On annealing the pure material, $\text{CH}_3\dot{\text{C}}\text{HCl}$ features decayed more rapidly, leaving those for $\text{Cl}_2\dot{\text{C}}\text{-CH}_3$ well defined.

Pure $\text{Cl}_3\text{C-CH}_3$ E.S.R. spectrum displayed weak additional features spread across the spectrum and overlapping with those for $\text{CH}_3\dot{\text{C}}\text{Cl}_2$ radicals. They are probably due to $\text{H}_2\dot{\text{C}}\text{CCl}_3$ radicals. Unfortunately, due to the lack of sufficient resolution of the E.S.R. spectra and other overlapping features, a clear identification of the features for $\text{H}_2\dot{\text{C}}\text{CCl}_3$ radicals was not possible.

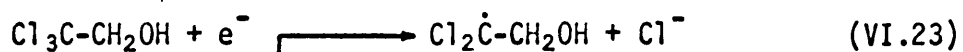
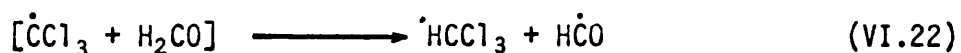
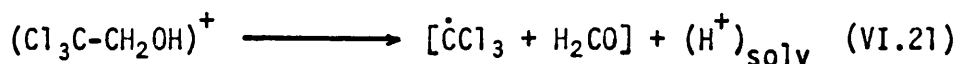
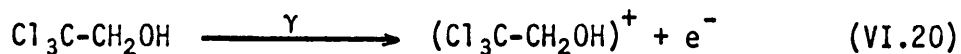
A reasonable mechanism for the formation of various radicals in the radiolysis of 1,1,1-trichloroethane and 1,1-dichloroethane is:



Radiolysis of 1,1,1-trichloroethanol

By their characteristic $g = 2.0112$ feature the $\dot{\text{C}}\text{Cl}_3$ radicals were again recognised as a product of radiolysis of $\text{Cl}_3\text{C-CH}_2\text{OH}$. Also, the $\text{H}\dot{\text{C}}\text{O}$ radical (25) was a major primary

product (Fig.5). The central features probably assignable to $\text{H}_2\dot{\text{C}}\text{OH}$ radicals were also detected. The following reactions are suggested to explain the mechanism of formation of these products:



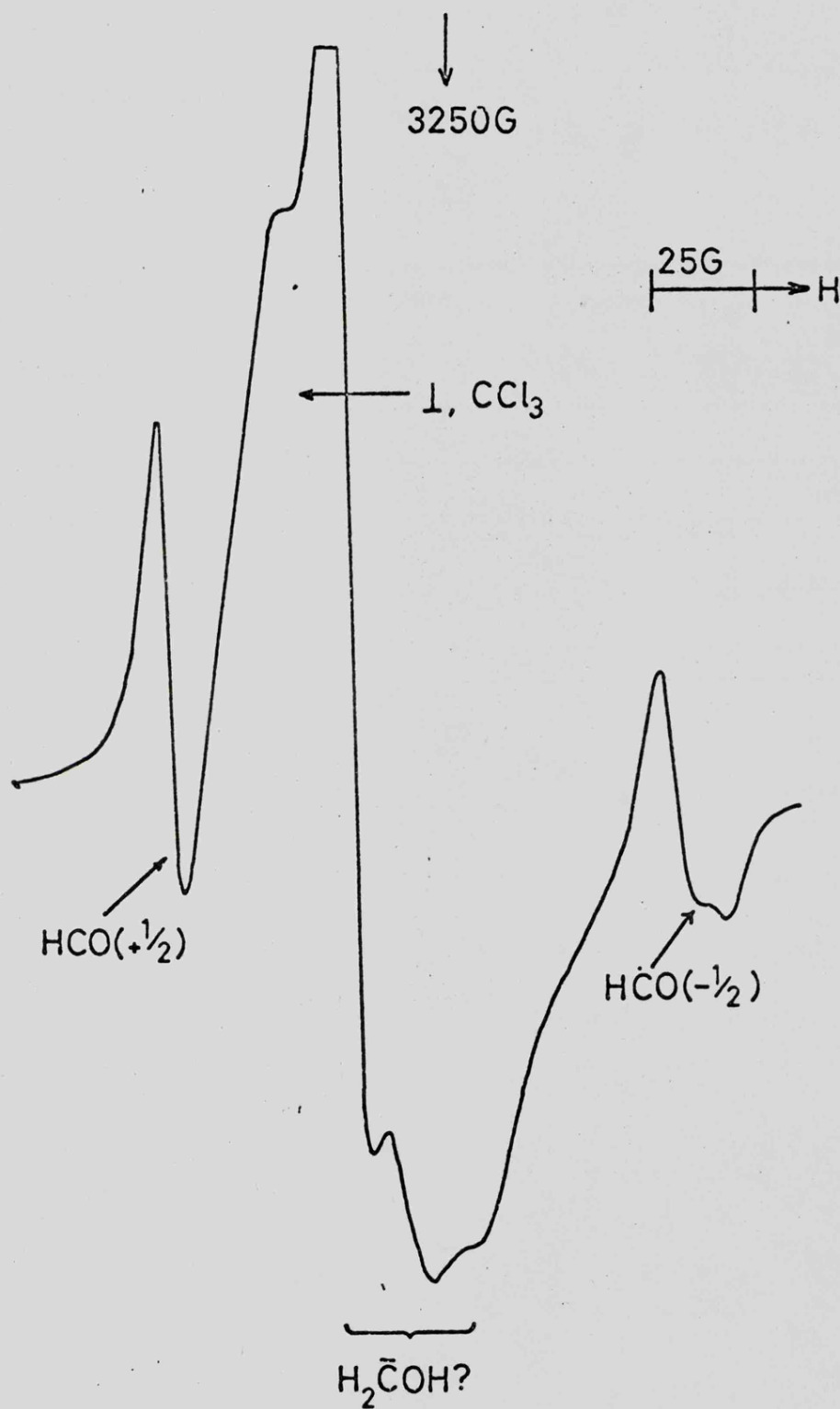
The only radical not clearly observed is $\text{Cl}_2\dot{\text{C}}-\text{CH}_2\text{OH}$. The expected complexity of the E.S.R. spectrum for this radical is such that one cannot rule out its presence in the present spectra, but does not seem to be a major product of radiolysis.

Radiolysis of $\text{Cl}_3\text{C}-\text{COCH}_3$

The only clear species from this material in pure or in solution, was $\text{Cl}_2\dot{\text{C}}-\text{COCH}_3$, having normal parameters for a dichloro radical (13). The $\dot{\text{C}}\text{Cl}_3$ radical was not detected in this case.

Thus it is concluded that 'it is possible to detect the $\dot{\text{C}}\text{Cl}_3$ radical by E.S.R. spectroscopy even when several other radical species are present.

FIGURE 5



First derivative X-band E.S.R. spectrum for pure $\text{Cl}_3\text{CCH}_2\text{OH}$ after exposure to ^{60}Co γ -rays at 77 K showing features assigned to $\dot{\text{C}}\text{Cl}_3$, $\text{H}\dot{\text{C}}\text{O}$ radicals, and possibly, $\text{H}_2\dot{\text{C}}\text{OH}$ radicals.

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TABLE

Magnetic Data for $\dot{\text{C}}\text{Cl}_3$ and Related Radicals

Matrix	Radical	Nucleus	Hyperfine coupling constants (G)			g-values		
			a_{\parallel}	a_{\perp}	Iso	g_{\parallel}	g_{\perp}	Av.
Fluid solution	$\dot{\text{C}}\text{Cl}_3^{\text{b}}$	^{35}Cl	-	-	6.25	-	-	2.0091
	$^{13}\dot{\text{C}}\text{Cl}_3^{\text{c}}$	^{35}Cl	-	-	6.25(7.0)	-	-	2.0093
Xenon	$^{12}\dot{\text{C}}\text{Cl}_3^{\text{d}}$	^{13}C	-	-	114 (117)			
		^{35}Cl	18.9	0	6.3	2.0092	2.0135	2.0113
	$^{13}\dot{\text{C}}\text{Cl}_3^{\text{d}}$	^{35}Cl	23.9	0	8.0	2.0139	2.0137	2.0138
		^{13}C	75.0	100.3	92.0			
$\text{CCl}_4 + \text{CD}_3\text{OD}$	$^{13}\dot{\text{C}}\text{Cl}_3^{\text{e}}$	^{13}C	150	100	116.7	a		
	$\dot{\text{C}}\text{Cl}_3^{\text{f}}$	^{35}Cl	20	0	6.7	2.0072	2.0112	2.0098
CHCl_3	$\text{H}\dot{\text{C}}\text{Cl}_2^{\text{f}}$	^{35}Cl	20	-4	+4	2.003	2.008	
		^1H	-20	-13	-19			2.007
				-24			2.010	

a If g_{\perp} is taken to be 2.0012, then $g_{\parallel} = 2.0072$ and $g_{\text{av}} = 2.0098$. b Ref.10. c Ref.14. d Ref.15.

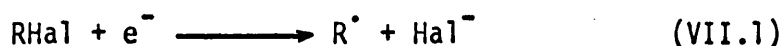
e Present interpretation. f Present work.

CHAPTER SEVEN

DIHALIDE ANIONS AND RELATED SPECIES AS PRODUCTS IN
THE RADIOLYSIS OF ORGANIC HALIDES

VII.1 Introduction

By far the most studied process in the radiation chemistry of organic halides is dissociative electron capture (1) reaction (VII.1),



but a variety of other reactions are now established, which include the formation of α - and β - halogeno-radicals (2-5), and a special type of electron capture in which a weak residual interaction between the alkyl radical and halide ion is detected by E.S.R. spectroscopy (6-8).

During various E.S.R. studies on γ -radiolysed organic chlorides, bromides, and iodides in these laboratories, one of the frequently detected species was comparable to those of Cl_2^- , Br_2^- and I_2^- (9-12) spreading over a wide field range. Similar features were recognised by Willard and his coworkers in their work on alkyl bromides and iodides (13). However, although they drew attention to some similarities with the spectra for Br_2^- and I_2^- , no positive identification was made. Also, Br_2^- has been identified as a radiation product in n-butylbromide (14). The aim of the present work is an attempt to systematise and rationalise these results.

VII.2 Results and Discussion

The central ($g = 2$) part of the E.S.R. spectra of γ -irradiated alkyl halides at 77 K was generally dominated by features from alkyl radicals or their halide ion complexes (8) and by α -halogeno-radicals (5). In some cases features from β -halogeno-radicals (4) were also detected in the wings of the central lines. Many of the features for dihalide anions and related species were well separated on the low-field side of these intense central lines, as shown in Figures 1-3. The most intense lines are found ca. 100 G down-field from the centre for chlorides, and ca. 400 G from the centre for bromides and iodides. Such features can be taken as being diagnostic of dihalogen species. These were absent for most alkyl chlorides except those containing 1,1- or 1,2-dichloro-groups. They were generally present for the bromides and iodides, but except for the 1,2-dihalides, their formation was prevented when glassy solutions in methanol (or CD_3OD) were studied.

Alkyl Chlorides

No low field features were obtained from pure monochlorides or their solutions in methanol (or CD_3OD). 1,1-Dichloroethane (and especially CD_2Cl_2) gave intense features (Fig.1) which were completely suppressed in methanolic solution. These features clearly stem from hyperfine coupling to two equivalent chlorine atoms (both ^{35}Cl and ^{37}Cl have $I = \frac{3}{2}$; ^{37}Cl has an abundance of 24.6% and a smaller magnetic moment than ^{35}Cl). As is often the

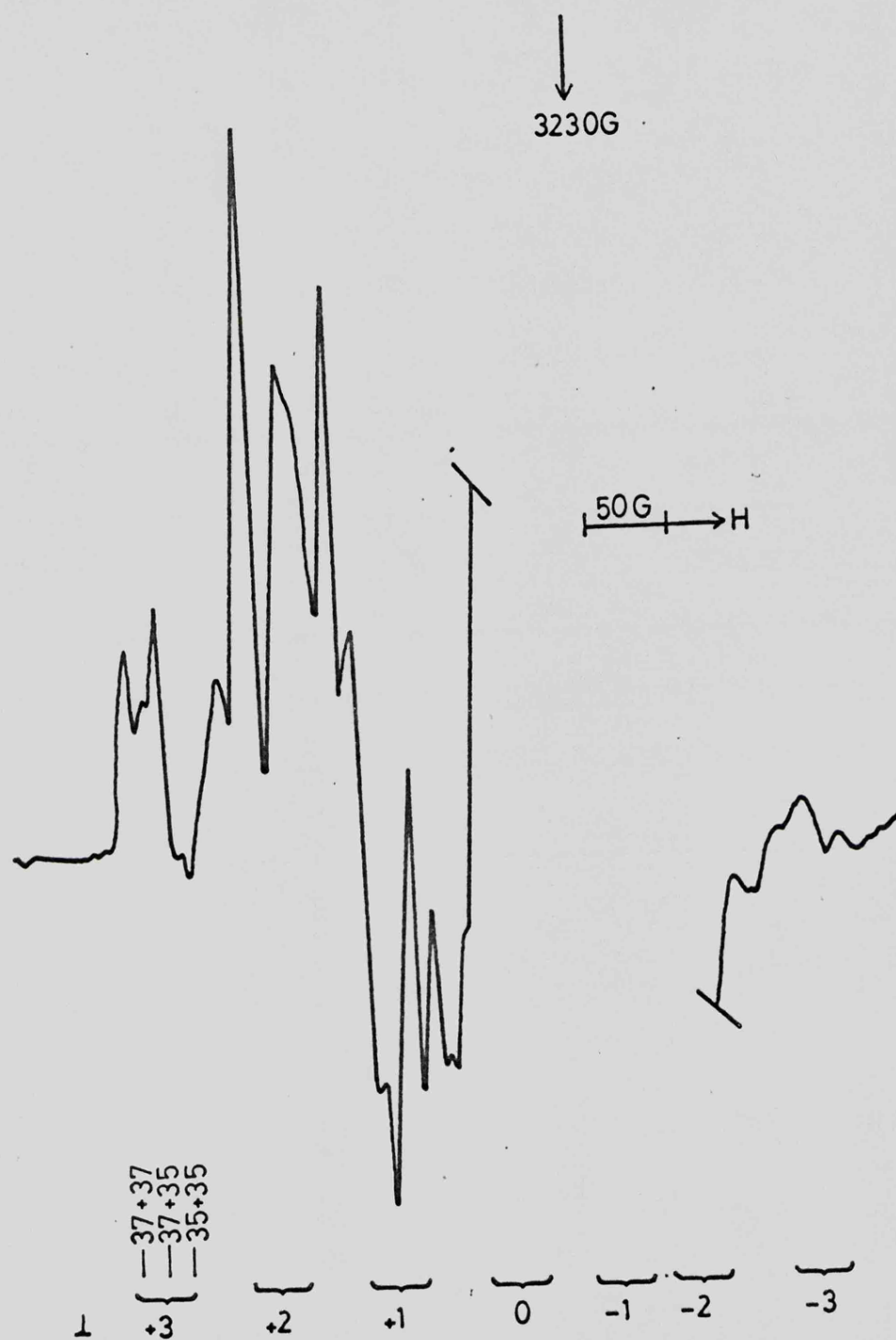


FIGURE 1

First derivative X-band E.S.R. spectrum for methylene chloride after exposure to ^{60}Co γ -rays at 77 K for 0.5 h, showing features assigned to H_2CCl_2^+ radicals.

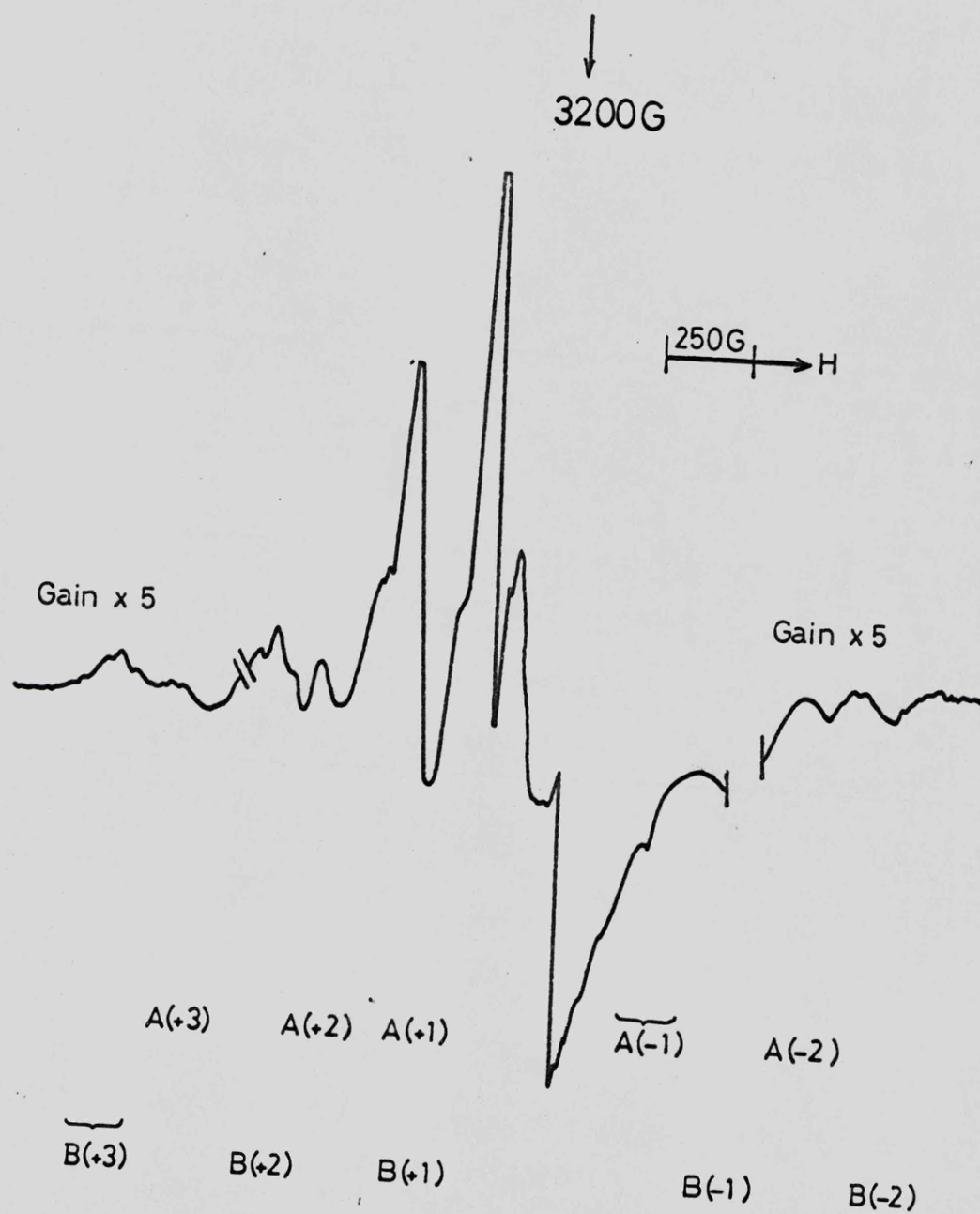


FIGURE 2(a)

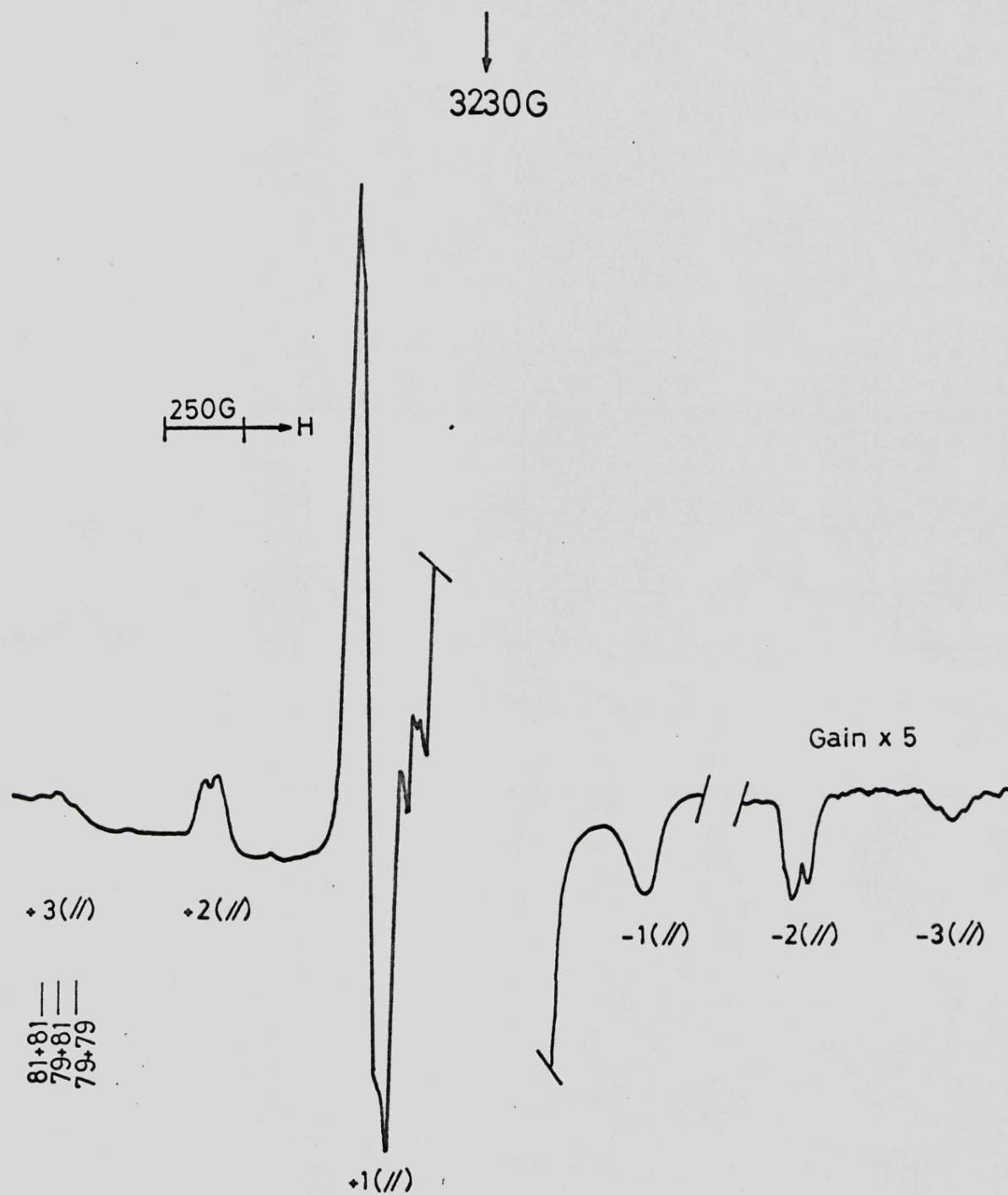


FIGURE 2(b)

First derivative X-band E.S.R. spectra for 2,3-dibromobutane after exposure to ^{60}Co γ -rays at 77 K for 1.0 h, (a) showing features (A) assigned to librating Br_2^- ions and (B) assigned to $[\text{MeCH}(\text{Br})\text{CH}(\text{Br})\text{CHMe}]^+$ cations, and (b) in CD_3OD glass, showing features for non-librating Br_2^- ions.

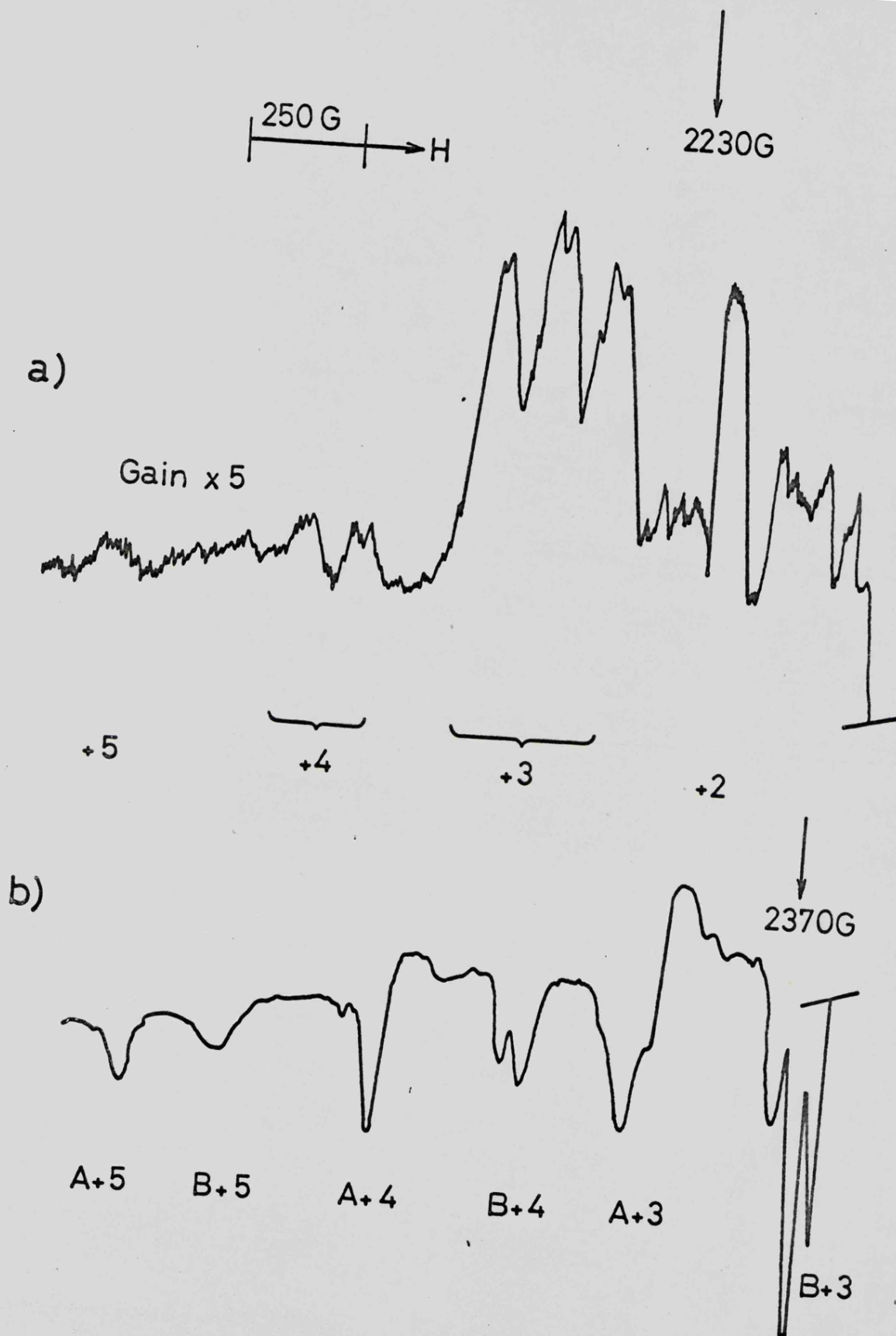


FIGURE 3

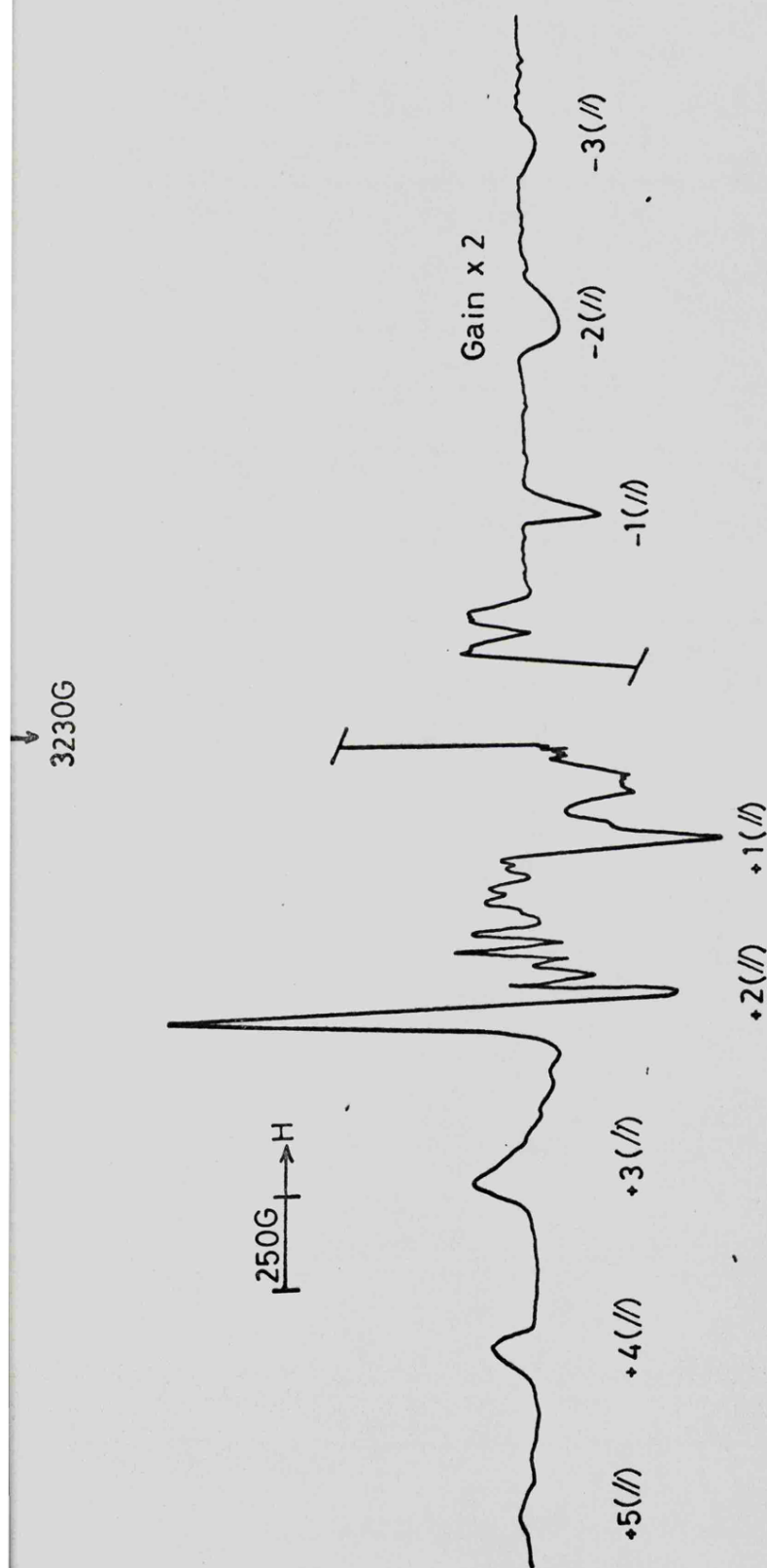
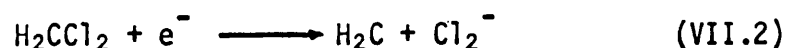


FIGURE 3(c)

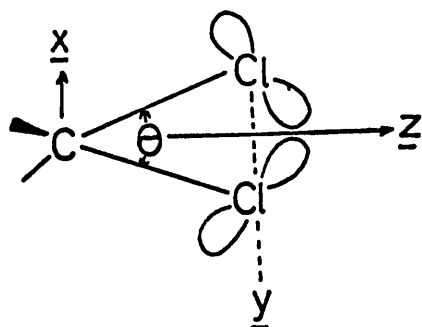
First derivative X-band E.S.R. spectra for (a) methyl iodide glass after exposure to ^{60}Co γ -rays at 77 K for 1.0 h, showing low-field features indicative of two inequivalent iodine atoms, assigned to MeI-I , (b) for ethyl iodide showing similar low-field features assigned to (A) EtI-IEt^+ and (B) EtI-I , and (c) for 1,2-d--iodoethane in CD_3OD after exposure to ^{60}Co γ -rays at 77 K for 1.0 h, showing features for non-liberating I_2^- . (The M_I values for the parallel features are labelled, the -4 and -5 features being too weak to detect).

case for powder spectra dominated by hyperfine coupling to chlorine, bromine, or iodine nuclei, only the largest splitting is readily identifiable. The maximum coupling (65 G, see Table),^{*} is appreciably less than that for Cl_2^- (ca. 100 G) whilst the g -value for these lines ($g = 2.03$) is far greater than that for Cl_2^- ($g = 2.000$). One possible explanation for these features is that Cl_2^- has been formed by dissociative electron capture (VII.2).



However, such an elimination seems rather improbable in view of the high reactivity of methylene. Furthermore, when Hal_2^- ions are formed from 1,2-dihalides by electron capture, methanol does not inhibit their formation as expected, since methanol is a good hole-trap, but a poor electron-trap.

Another explanation is that the cation CH_2Cl_2^+ is responsible for these features. Powder spectra for this cation would show strong features for fields along the symmetry axes (see Insert 'A'). Thus $A_x = A_z$, and $g_x = g_z$ but A_y and g_y fall between



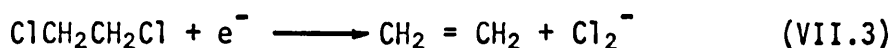
Insert 'A'

* See Table on p.96.

$A_{//}$ and A_{\perp} for a given chlorine atom. For $\theta = 90^\circ$, $A_y = A_z = (A_{//} + A_{\perp})/2$. As weak Cl-Cl bonding can occur, it would appear that the two chlorine atoms will move slightly together on loss of an electron, thus reducing θ to below 109° and making the 90° model a reasonable one. This could account for the 'perpendicular' character exhibited by the outermost features in the spectrum. On this model, and using the relative intensities of the 'perpendicular' features as a gauge for the positioning of the remaining features, the analysis indicated in Figure 1 has been arrived. Using the relationship for $A_y + A_z$ given above, we calculate the 'true' parameters for ^{35}Cl to be $A_{//} \doteq 116$ G and $A_{\perp} \doteq 14$ G. Also $g_{//} \doteq 2.000$, in good accord with expectation.

These hyperfine parameters could be used to derive approximate orbital populations in the usual manner, using $A(^{35}\text{Cl}) \doteq 1680$ G and $2B \doteq 100$ G, whence $a^2(2s) \doteq 2.9\%$ and $a^2(3p) \doteq 68\%$. The s -character is normal for such a system, and the p -character, whilst larger than the expected 50%, is nevertheless reasonable since this method of calculation generally yields an over-estimate of the total spin density on chlorine (9, 12). Hence, the above orbital population calculations support the reasonableness of the derived parameters from the E.S.R. spectra of H_2CCl_2^+ radical.

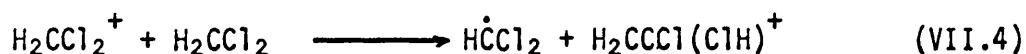
Such considerations lead us to the conclusion that the species formed by methylene chloride is H_2CCl_2^+ rather than liberating Cl_2^- . However, 1,2-dichloroethane yields Cl_2^- in high yield (equation VII.3). The results suggest that Cl_2^- is



librating slightly in the pure material at 77 K but is clearly stationary in a methanol matrix, as expected. The described data are compared with those of Cl_2^- in an alkali chloride crystal in the Table.* (Since the main concern was with the identification of the species rather than with the derivation of accurate parameters, it has not been the aim in general, to attempt the difficult, if not impossible, task of deriving the complete hyperfine and g -tensor components for these radicals. The approximations given for A_\perp and g_\perp in the Table being based upon the overall spread of the perpendicular features. This has been shown to give reasonable results from powder spectra (12), but it is essential to study single crystals in order to obtain accurate perpendicular parameters).

Neither 1,3- or 1,4- dichlorides gave Cl_2^- spectrum. Thus it seems that the electron capture process (VII.3) is efficient because of the stability of the non-radical product. The balance between processes (VII.1) and (VII.3) must be very subtle, as is often found in radiation studies (15). With methylene chloride, process (VII.1) gave $\text{H}_2\dot{\text{C}}\text{Cl}$ ($\text{D}_2\dot{\text{C}}\text{Cl}$) radicals both in the pure material and in methanol. In the pure material clear features for $\text{H}\dot{\text{C}}\text{Cl}_2$ radicals were also detected. This species may well be formed from the primary cation (reaction VII.4) but methanol completely suppresses radical cation formation, by acting as a powerful hole-trap.

* See Table on p.96.



Alkyl Bromides

All monobromides invariably gave broad low-field features in the region expected for dibromo-radicals of the type under consideration but these were generally too broad to permit analysis. However, a fairly clear spectrum for this species is shown in Figure 2a. It is suggested that these species are 'hole-centres' because their formation is suppressed in methol matrices and because the presence of high yields of alkyl radicals or their bromide ion complexes accounts satisfactorily for the reaction of the excess of electrons.

The detection of the parent cation, RBr^+ , would not be expected because the unpaired electron is in a degenerate π -orbital largely confined to bromine, and hence the cation will exhibit orbital magnetism which will depend strongly on the extent to which this is quenched by intra- or inter-molecular interactions. Attempts to detect RBr^+ or RI^+ radicals in rigid inert media such as methyl-cyclohexane failed. However, 1-monobromoadamantane on γ -radiolysis gave clear features of a monobromo radical with the required properties (Figure 4). (^{81}Br and ^{79}Br have approximately equal natural abundances and $I = 3/2$. The magnetic moment for ^{79}Br is slightly smaller than that of ^{81}Br . Two equivalent bromine atoms thus give rise to seven features in the E.S.R. spectrum,

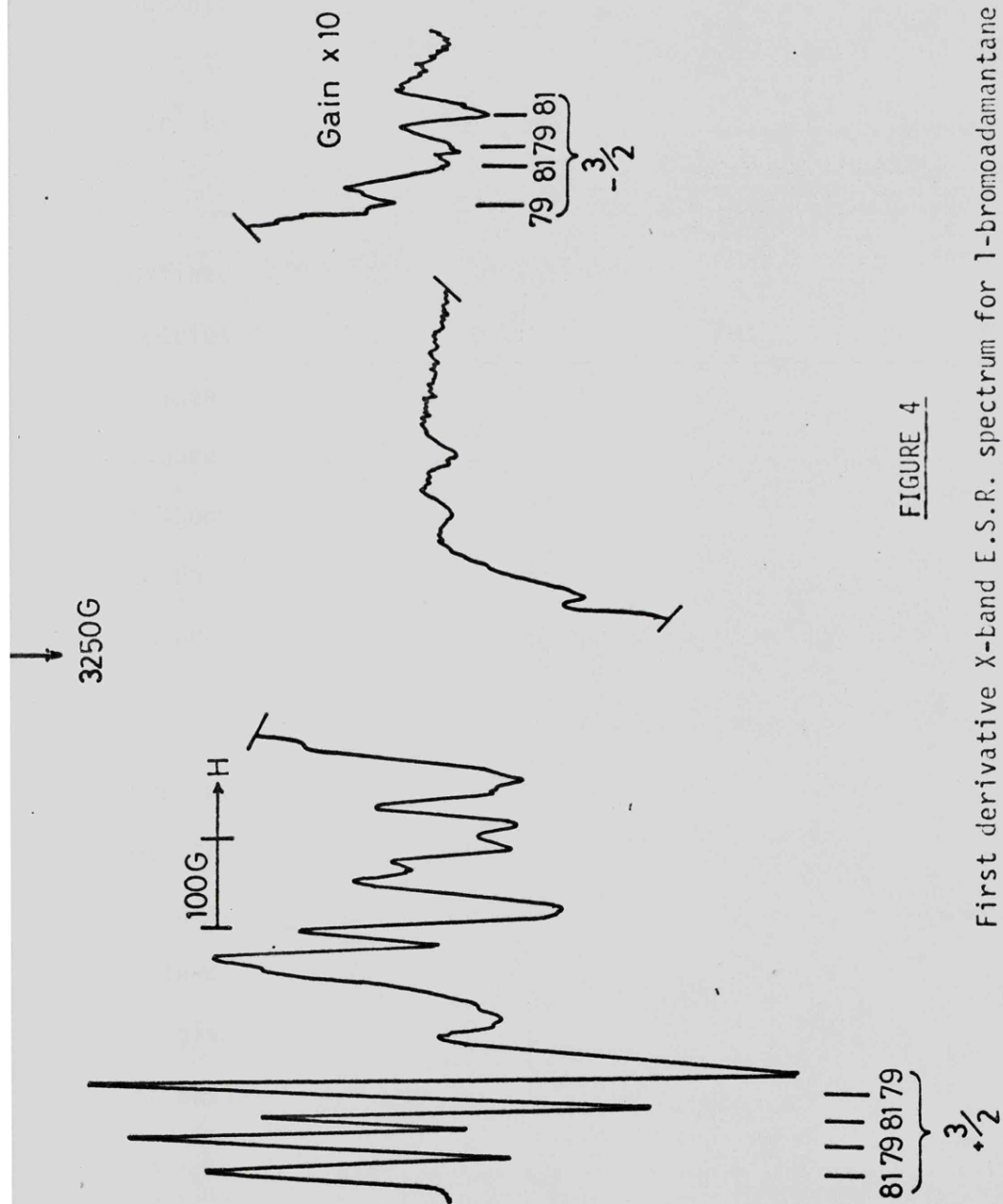


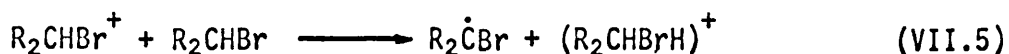
FIGURE 4

First derivative X-band E.S.R. spectrum for 1-bromoadamantane after exposure to ^{60}Co γ -rays at 77 K for 1.0 h, showing features for a monobromo-radical exhibiting an extra doublet of 65 G (see text).

each being sub-divided into multiplets by the different isotopic contributions and by second-order (Breit-Rabi) effects). In contrast with other monobromides, no di-bromo-radicals were obtained from 1-monobromo-admantane. Also, an intense violet colour associated with irradiated bromides whenever low-field dibromo-features were observed was absent, irradiated bromo-admantane being an intense orange colour. Hence, it is suggested that the violet species is $(\text{RBr-BrR})^+$ and that the parent cations RBr^+ have their first electronic transition at higher energies.

Thus two problems arise: what is the source of the well defined quenching of orbital-angular momentum for the admantane species, and what causes the doublet splitting of ca. 65 G, evident in the $M_I = \pm 3_2$ features of the E.S.R. spectrum (see Figure 4)? It could be convenient to suggest that a proton is responsible for both these effects. However, it is not possible to understand how this can arise, and have no reasonable explanation at present.

On chemical grounds we would expect that RBr^+ in the presence of RBr would react and form a $\underline{\sigma}^*$ radical which should be structurally similar to Br_2^- and to the disulphide radical anions, RS-SR^- . Hence, it appears that this is the normal hole-centre for the pure alkyl bromides, although proton loss to give $\underline{\alpha}$ -bromo radicals will compete (especially in the presence of basic solvents) [reaction VII.5].



Both species are generally detectable during γ -radiolysis of alkyl bromides.

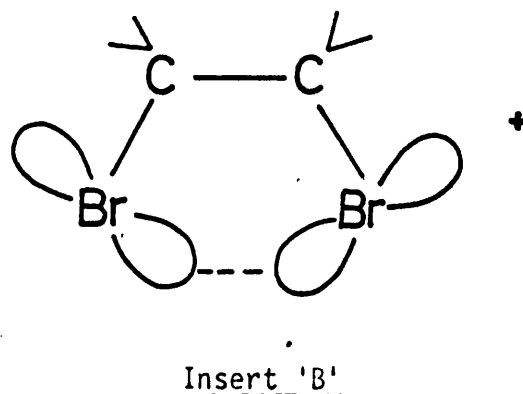
The only reasonable alternative to $(\text{RBr}-\text{BrR})^+$ is Br_2^- . However, it is very difficult to see how these anions can be formed by γ -rays at 77 K. Furthermore, when several of the substrates were doped with bromine (or allowed to stand in daylight prior to irradiation), strong features for Br_2^- were obtained, and these differed from those assigned to the dimer cations in that 'A_{II}' was markedly reduced from the normal values for Br_2^- and 'g_{II}' was shifted well above the normal value of ca. 1.99 (spectra for the two species are shown together in Figure 2). Since the same doped samples in methanol glasses gave good spectra for stationary Br_2^- radicals, it is suggested that Br_2^- radicals are librating in a well defined manner at 77 K in the alkyl bromide matrix. Hence the species formed in the pure bromides cannot be Br_2^- . The other possibility, $\text{RBr}-\text{Br}^\cdot$, can be eliminated at least in those cases in which good spectra were obtained, since the two bromine atoms are equivalent. (If this were not the case, all but the M_I = ± 3 lines would be split to a greater extent than the normal Breit-Rabi splitting, and the 1:2:1 triplet features of the M_I = ± 3 lines would become 1:1:1:1 quartets).

It is surprising that the values of A_{II} found for the dimer cations are so close to those normally found for stationary Br_2^- centres (Table).^{*} It could be anticipated that the presence of the two alkyl groups would result in an increase in the $4s$ contribution to the σ^- and σ^* -orbitals and hence to an increase in A_{II} . But the present results suggest that this is not a very marked effect, since the extent of electron delocalisation onto the alkyl groups is not expected to be very large.

gem-Dibromides - In these cases only very poorly defined low-field features were obtained. Such features span the region predicted for the primary cations $R_2CBr_2^+$, but no firm identification could be drawn. Their formation was completely suppressed using methanolic solutions.

vic-Dibromides - Features for dibromo-radicals were obtained both in pure compounds and methanolic solutions. Thus it is to be concluded that a reaction similar to (VII.3) occurs efficiently. For pure materials the Br_2^- radicals were librating at 77 K, and a second dibromo-species was present (see Figure 2a). This is presumably the cation-dimer, since the intense violet colour, thought to be characteristic of these dimers, was also obtained. This species may possibly have structure as shown in 'Insert B' rather than being formed inter-molecularly, which may account for the relatively well defined nature of the E.S.R. spectrum.

* See Table on p.96.

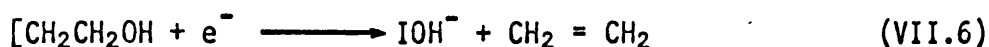


Other dibromides (1,3- and 1,4-) gave low-field spectra similar to those for monobromides with no evident Br_2^- elimination.

Alkyl Iodides

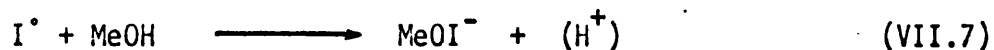
During solid-state radiolysis of alkyl iodides at 77 K, a species containing two equivalent iodine atoms was detected (see Figure 3a) which was in addition to and similar to RI-IR^+ radicals. (^{127}I has $I = 5/2$; two equivalent iodine atoms therefore would give rise to 11 features, which will exhibit a small second-order splitting when well resolved.) These species are thought to be RI-I^{\cdot} , formed by iodine atom addition to the parent molecules. If this identification is correct, then the common description of this species as a 'charge-transfer complex' needs revision. Present results show conclusively that the unpaired electron is fairly evenly distributed between the two iodine atoms, and that a molecular description is required.

In this case again, an elimination analogous to (VII.3) seems to be important for vic-di-iodides; since I_2^- formation was clearly detected by E.S.R. spectroscopy (see Figure 4). The features for mono-iodo σ^* radicals were also found in some iodides, the best being 2-iodo-ethanol (Figure 5). In this instance it is possible that the species is IOH^- , formed by dissociative electron attachment (VII.6).

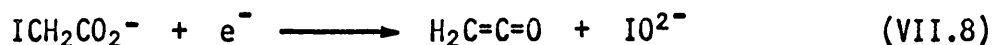


IOH^- species have been detected during the radiolysis of aqueous iodide solutions (12), and the E.S.R. parameters for ^{127}I in the two species are very similar (see Table).

Iodoacetic acid in methanolic glasses upon radiolysis gave a very similar species (Figure 5). It was originally thought that this species was formed from the solvent, by iodine attack (reaction VII.7).



However, since simple alkyl iodides failed to give this species in methanol, we feel that the process is less simple, an alternative possibility being some sort of extrusion process, such as (VII.8).



This is supported by the observation that borad features assign-

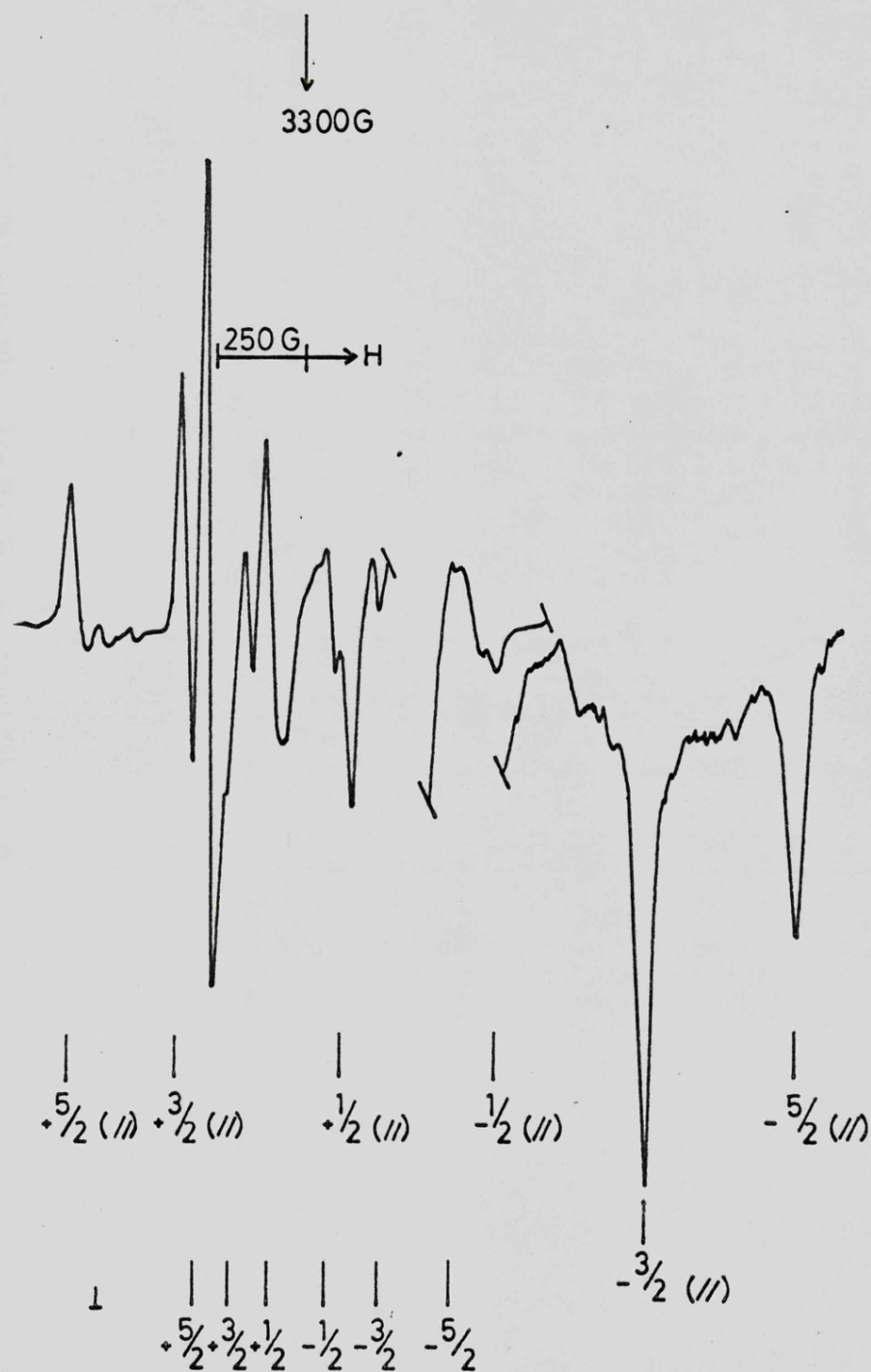


FIGURE 5

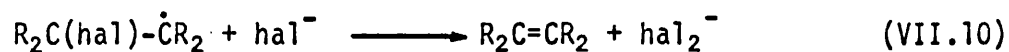
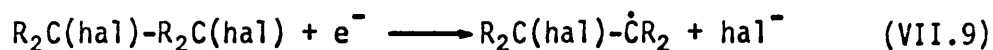
First derivative X-band E.S.R. spectrum for iodoacetic acid in CD_3OD after exposure to ^{60}Co γ -rays at 77 K for 1.0 h, showing features assigned to IO_2^- or IOH^- . (Only the parallel features for ^{127}I are indicated).

able to this species were definitely present in the pure material after irradiation. However, comparable species were not detected in irradiated chloro- or bromo-acetic acid.

Elimination of Hal_2^-

To check the validity of reactions (VII.3) and (VII.6), studies were made on the reactions of methanolic solutions of 1-bromo-2-chloroethane under the same conditions. If the reactions were intermolecular, we would expect to detect some Cl_2^- and Br_2^- in addition to BrCl^- . In fact, however, the sole product was BrCl^- . Furthermore, solutions containing both 1,2-dichloro- and 1,2-dibromo- ethane gave only Cl_2^- and Br_2^- respectively with no trace of BrCl^- .

It is quite likely that processes such as (VII.3) occur in two stages [(VII.9) and (VII.10)]. $\text{R}_2\text{C}(\text{hal})-\dot{\text{C}}\text{R}_2$ radicals are



known to be good halogen atom donors. Nonetheless, they have been detected in several E.S.R. studies (4, 5, 16-18) and it seems unlikely that the β -halo-radicals would react readily with halide ion at 77 K. Hence, the extrusion process (VII.3) is favoured.

Hole Centres

All these hole centres have been previously postulated by Hamill and co-workers (19-21) on the basis of their optical studies on irradiated alkyl iodides and their solutions in hydrocarbon glasses. In dilute solutions, bands at 370 and 440 nm were obtained, which were assigned to the parent cations, RI^+ , whilst the pure compounds gave bands at 540 and 760 nm, assigned to the cation-dimers $RI-IR^+$. The intermediate bands at 390 and 480 nm have been assigned to $RI-I^\bullet$ species (19). Present results confirm the presence of the latter two species. Dimer cations have also been detected by Hamill et al. in their mass-spectrometric studies of alkyl iodides (20, 21), and the neutral species, $RI-I^\bullet$, has also been reported in pulse radiolysis studies (22).

Other Centres

γ -Radiolysis of 1,4-dihalobutanes and 1,3-dihalopropanes gave alkyl radicals ($H_2\dot{C}(CH_2)_3Hal$) and ($H_2\dot{C}CH_2CH_2Hal$) having E.S.R. spectra at 77 K which was identical to those for the corresponding hydrocarbon radicals (terminal halogen couplings were not seen). These results confirm the conclusion of Chen et al. (23) that there is no significant cyclic interaction between the radical centre and remote halogen atoms.

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TABLE

E.S.R. Parameters for Cl_2^- , Br_2^- , I_2^- , and some Related Radicals
Formed in Irradiated Alkyl Halides

Host	Radical	Hyperfine coupling (G) ^a			g Values	
		A_{\parallel}	A_{\perp}	A_{iso}	g_{\parallel}	g_{\perp}
KCl	Cl_2^- ^b	98	9	38.7	2.0010	2.0457
H_2CCl_2	H_2CCl_2^+	14	65	48	2.06	2.03
$\text{ClCH}_2\text{CH}_2\text{Cl}$	Cl_2^- ^c	98			2.0010	
$\text{ClCH}_2\text{CH}_2\text{Cl} + \text{CD}_3\text{OD}$	Cl_2^-	102			2.0010	
$\text{H}_2\text{O} + \text{Br}^-$	Br_2^- ^d	470	85	195	1.98	2.09
$\text{BrCH}_2\text{CH}_2\text{Br}$	Br_2^- ^e	345			2.03	
$\text{BrCH}_2\text{CH}_2\text{Br}$	$(\text{C}_2\text{H}_4\text{Br}_2)^{+e}$	430			2.00	
$\text{BrCH}_2\text{CH}_2\text{Br} + \text{CD}_3\text{OD}$	Br_2^-	480	85	217	1.98	2.11
Bromoadamantane	\underline{g}	380	83	182	2.00	2.154
t-Butyl bromide	$(\text{Me}_3\text{CBr})_2^+$	505			2.00	
$\text{H}_2\text{O} + \text{I}^-$	I_2^- ^d	433	120	193	1.975	2.175
$\text{ICH}_2\text{CH}_2\text{I}$	I_2^- ^e	390			2.00	
$\text{ICH}_2\text{CH}_2\text{I}$	$(\text{C}_2\text{H}_4\text{I}_2)^{+f}$	420			1.99	
$\text{ICH}_2\text{CH}_2\text{I} + \text{CD}_3\text{OD}$	I_2^-	450			1.98	
CH_3I	$(\text{CH}_3\text{I})_2^+$	410			1.98	
CH_3I	CH_3I_2 $\begin{cases} \text{I}_1 430 \\ \text{I}_2 530 \end{cases}$				ca. 1.97	
EtI	$(\text{EtI})_2^+$	400			1.98	
EtI	EtI_2 $\begin{cases} \text{I}_1 420 \\ \text{I}_2 485 \end{cases}$				ca. 1.97	
$\text{H}_2\text{O} + \text{I}^-$	IOH^- ^d	480	70	207	1.98	2.13
$\text{ICH}_2\text{CO}_2\text{H}$	IOH^- or IO_2^-	430	100	210	1.97	2.17
$\text{ICH}_2\text{CH}_2\text{OH}$	IOH^-	420	100	207	1.97	2.16

^a $G = 10^{-4} \text{ T}$. ^b Ref.10 ^c Librating: Hence A and g -values are partially averaged. ^d Ref.12 ^e Or $(\text{C}_2\text{H}_4\text{Br}_2)_2^+$ ^f Or $(\text{C}_2\text{H}_4\text{I}_2)_2^+$

^g See Text $A(^1\text{H}) = 65 \text{ G}$.

CHAPTER EIGHT

EXPERIMENTAL

A good account of experimental techniques, manipulations, etc., related to E.S.R. studies are available in well established texts (1-10) and hence these will not be described here. Only the main features pertaining to the experimental part of the present work will be mentioned.

VIII.1 Materials and Sample Preparation

Most of the alkyl halides and deuterated alkyl halides used were obtained from the suppliers and employed as supplied. In some cases in which impurities were suspected, the halides were purified by recorded analytical procedures. Various solvents used were also obtained from the suppliers. Ethyl bromopropionate was kindly supplied by Dr. R.S. Atkinson of the Chemistry Department, University of Leicester. α -Bromoacrylic acid was prepared from 2,3-dibromopropionic acid by the action of aqueous potassium hydroxide and diethyl α -bromomalonate was prepared from diethylmalonate by interaction with bromine. Beads of liquid samples and their solutions in various solvents were obtained by pipetting directly into liquid nitrogen. For solid materials, well powdered samples were irradiated at 77 K and room temperature.

VIII.2 γ -Source

Samples were irradiated at 77 K and room temperature (in case of solid materials) in a top loading Vickrad ^{60}Co γ -source

at a dose rate of 4 M Rad hr^{-1} . For irradiation at 77 K, the samples were transferred in small glass bottles or sealed tubes, to a metal cased dewar flask containing liquid nitrogen. This dewar was lowered into the irradiation facility of the source for the required period. 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.

VIII.3 Spectral Reading

The E.S.R. spectra of beads, powders and glassy samples were obtained using a commercial X-band Varian E3 spectrometer. The samples to be studied at 77 K were transferred to an un-silvered dewar that narrowed at the bottom to form a long finger, which fitted into the microwave cavity.

Two methods were employed for annealing the samples above 77 K so as to cause a preferential loss of some radicals and enhancement/production of newer species of interest. The first consisted of carefully pouring the liquid nitrogen out of the finger dewar and scanning through the spectrum whilst the sample warmed up. This had the advantage of permitting the anneal to be controlled to a certain extent. The samples being recooled to 77 K by pouring in liquid nitrogen at the required point when marked changes in spectra occurred. The second method involved removing the samples 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 procedure 1.

For a controlled annealing study, a variable-temperature assembly was used in conjunction with the Varian E3 spectrometer. By applying this unit the temperatures between 77 and 270 K were accurately obtained and detailed study could be made at a desired temperature for longer durations. Such an assembly consisted of a vacuum-jacketed tube, which passed through the microwave cavity, and had 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.

E.S.R. spectra of some samples were also recorded at 34 G Hz on a Q-band spectrometer which employed super-heterodyne detection fully described elsewhere (11). The measurements for a few interesting systems were also carried out on an S-band spectrometer (12). These spectrometers were designed in this laboratory.

VIII.4 Single Crystal Spectra

Single crystals of 2,2-dichloroacetamide, bromomaleic acid

and bromoacetic acid were obtained by slow evaporation of aqueous solutions. Slow evaporation of solutions of α -bromoacrylic acid in ethyl acetate gave good single crystals. These single crystals were γ -irradiated at room temperature and quickly transferred to the liquid nitrogen dewar after desired irradiation periods. The E.S.R. spectra were recorded at 77 K and room temperature by placing these irradiated single crystals in the fixed orientations in the small cavity on a rod attached to a scale for reading the angle of rotations which in turn were placed in the finger dewar. Attempts to study single crystal spectra of t -butyl bromide were unsuccessful since they invariably shattered on slow or rapid cooling below room temperature, and irradiation at temperatures above the shattering point (-40°C) did not result in any β -bromo species of interest. Single crystals of n -butyl bromide were also studied, but the β -bromo spectra were no better resolved than for the powder and only slight orientations were observed.

VIII.5 H \cdot and D \cdot Atom Irradiations

Attempts were also made to produce α - and β -halo radicals by adding H \cdot (D \cdot) to the C=C bond of some unsaturated alkyl halides. The H \cdot (D \cdot) were produced by microwave discharge. Generation of α -bromo radicals was particularly successful by this method.

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SUMMARY

The Electron Spin Resonance (E.S.R.) technique has been widely used to detect the reactive intermediates during the radiolysis of condensed systems which provide valuable information about the overall reaction mechanism. The present work is an attempt to identify the varieties of free radical species which are produced in γ -radiolysis of various organic halides and learn more about the radiation damage mechanisms.

As the field of Electron Spin Resonance is now well established, no attempt has been made to review the theory and practice of the technique.

The introductory chapter embodies some brief historical developments in radiation chemistry, interaction of radiation with matter, and relevant descriptions of the radiolysis of alkyl halides.

Chapter II describes the findings of the novel species ($\dot{R}---Hal^-$) in which the halogen ion weakly interacts with the parent alkyl radical. The spin density on halogens in these alkyl radical-halide ion complexes is of smaller order compared to σ radicals of N-halogenoamides.

The detailed aspects of α -mono- and di-chloro radicals as revealed by their powder and single crystal spectra is presented in chapter III. The assignments of the e.s.r. parameters include low but significant 'quadrupole' effects which provide authentic spectral analysis.

There has been a lack of an authentic solid-state spectrum of α -bromo radicals due to spectral complexities caused by multiple features of two magnetic bromine isotopes (^{79}Br and ^{81}Br) and large 'quadrupole moments'. A detailed study of the detection of these radicals in γ -irradiated alkyl bromides was taken and the apparent difficulties were resolved by working on the single crystal spectra in some cases. Details of the findings are given in Chapter IV.

An interesting problem to the organic chemists has been the electronic structure and geometry of the intermediate $\text{R}_2\dot{\text{C}}-\text{CR}_2\text{Hal}$, which has often been formulated with a cyclic structure. Production and identification of such radical intermediates in the radiolysis of alkyl halides was undertaken and the first authentic parameterisation of β -bromo radicals ($\text{R}_2\dot{\text{C}}-\text{CR}_2\text{Br}$) is embodied in Chapter V. The large isotopic coupling due to bromine atoms is explained in the light of a 'hyperconjugative' delocalisation mechanism.

γ -Radiolysis of a series of trichloromethyl compounds was carried in pure materials and in solvents at 77 K and $\dot{\text{C}}\text{Cl}_3$ radicals along with other species were identified by their characteristic e.s.r. spectra. It is of interest to find that $\dot{\text{C}}\text{Cl}_3$ radicals can be reasonably detected in the presence of other chloro radicals produced during irradiation. These findings are reported in Chapter VI.

Several dihalide anions and related species (Hal_2^- , R_2CHal^+ , RHal^+ , RHal-HalR^+ , RHal-Hal^\bullet , ROHal^-) have been recognised as products of radiolysis of organic halides. These species were identified by their characteristic e.s.r. spectra and a full description is

presented in Chapter VII.

The general experimental aspects of Chapters II-VII are presented in Chapter VIII.