Unstable Intermediates. Part 187.[1] The Structure of β-Bromoalkyl Radicals: an Electron Spin Resonance Study of the Radiolysis of Iso- and t-Butyl Bromides

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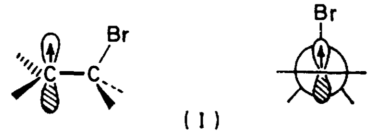
Iso- and t-butyl bromides have been exposed to ^{60}Co γ-rays in a range of matrices at 77 K and the radical products studied by e.s.r. spectroscopy. Two quite different species have previously been detected in such systems. One (species S), having a very large hyperfine coupling to ^{79}Br and ^{81}Br, was identified as $Me_2\dot{C}-CH_2Br$ in which the bromine is out of the radical plane to maximise hyperconjugative overlap. The other (species W), also identified originally as $Me_2\dot{C}-CH_2Br$, had a very small coupling to ^{79}Br and ^{81}Br (*ca.* 6 G) and it was concluded that the bromine atom is twisted *ca.* 75° away from the maximum overlap position and that the radical is strongly pyramidal at trigonal carbon. We find that after radiolysis at 77 K, Me_2CHCH_2Br in adamantane gives a novel species identified as the $Me_2CHCH_2\cdot$ radical interacting weakly with the ejected bromide ion ($Me_2CHCH_2\cdot$, Br^- adduct). On warming to *ca.* 140—170 K this species was lost irreversibly and species W was detected. The spectrum for W comprises a 10 × 4 group of hyperfine features which we assign to the $Me_3C\cdot,Br^-$ adduct. On cooling to 77 K the spectrum for W becomes much more complicated because the protons become inequivalent. At *ca.* 4 K the ^{79}Br and ^{81}Br A values become anisotropic, the data being compatible with those previously assigned to such adduct radicals. Species S is also formed from Me_2CHCH_2Br in adamantane, showing that S and W cannot be the same species, modified by different environments, as has been suggested. Me_3CBr gave species W directly at 77 K, together with species S and a minor production of $Me_3C\cdot$ radicals. Thus W is a primary product in this case. Using tetramethyl-*p*-phenylenediamine to generate photoelectrons we have established that W is formed by electron addition, in accord with the formulation $Me_3C\cdot,Br^-$. By treating Me_3CBr with $Me_3CO\cdot$ radicals formed photochemically, we have shown that species S is formed by hydrogen atom abstraction. We conclude that species S is $Me_2\dot{C}CH_2Br$, and that the structure of this radical is comparable with that of $Me_2\dot{C}CH_2Cl$, the halogen atoms being in the maximum σ–π overlap position.

SOME years ago[2] we reported the detection, by e.s.r. spectroscopy, of a new type of radical derived from alkyl bromides exhibiting a very large hyperfine coupling to bromine (designated hereafter as species S). These radicals were clearly not α-bromo radicals, $R_2\dot{C}Br$, since the hyperfine coupling was considerably greater than that previously observed for α-bromo radicals.[3] Our identification of α-bromo radicals has received strong support and characteristic e.s.r. spectra for such radicals are now well established.[4-6] We originally suggested that these novel radicals (S) were β-bromo radicals having a conformation that maximises σ–π delocalisation (I).

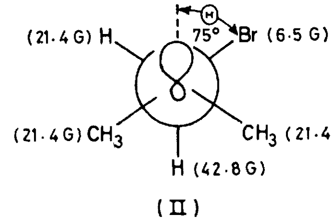


(I)

This seemed to explain the large hyperfine coupling and was in good accord with previous work on β-chloro radicals by ourselves[7] and others.[8,9] These studies[2,10] involved the interpretation of powder e.s.r. spectra and we stress that extraction of the g and A tensor components therefrom is inaccurate. Nevertheless, the maximum coupling is well defined, being in the region of 300 G. Also, the $M_I = +\frac{1}{2}$ feature, at *ca.* g 2.10 is nearly isotropic, and can be used for purposes of identification. Often this feature displays well defined proton hyperfine coupling, and in the particular case of a radical thought to be $Me_2\dot{C}CH_2Br$, a pattern of features assigned to the six methyl protons [$A(^1H)$ *ca.* 13 G] was well defined.[10] This radical was formed from t-butyl bromide, and it was postulated that a 1,2 bromine shift occurred after hydrogen atom loss [reaction (1)].[10]

$$Me_2C(Br)\dot{C}H_2 \longrightarrow Me_2\dot{C}CH_2Br \qquad (1)$$

All attempts to prepare β-bromo radicals in the liquid phase seem to have failed, although there is one suggestion that a radical exhibiting only proton hyperfine coupling might nevertheless be the radical $H_2\dot{C}CH_2Br$.[11] In view of the large magnetic moments for ^{79}Br and ^{81}Br, this suggestion seems improbable to us, and will not be considered further. However, another species, with an isotropic spectrum exhibiting a small (*ca.* 6 G), well defined coupling to ^{79}Br and ^{81}Br has recently been described.[12] This species, designated W herein, was formed from isobutyl bromide in adamantane by ionising radiation. At *ca.* 200 K a well defined isotropic spectrum indicative of a freely rotating radical was obtained. The hyperfine parameters extracted from this spectrum, shown in (II), were assigned to β-bromo radicals having



(II)

the conformation indicated in (II).[12] Thus radicals S and W are contenders for the β-bromo structure: it has been suggested[12] that both species could be β-bromo radicals, different media favouring different conformations, but this seems most improbable to us, and can be eliminated since we have observed both species in the same media. Alternatively, we have tentatively suggested that species W might be the t-butyl radical associated with a bromide ion ($Me_3C\cdot$; Br^-).[13] Species of this type have been observed as products of dissociative electron capture in solid-state radiolyses.[14-16]

However, our suggestion [13] was firmly rejected by Wood and Lloyd.[17]

The case for and against these alternative assignments for species W is rehearsed below. The aim of the present work was to probe these systems more closely in the hope of obtaining more definitive evidence for or against these hypotheses. The controversy is of some significance in view of the mechanistic implications. β-Bromo radicals are undoubtedly intermediates in certain organic reactions,[18] and the steric course of such reactions is thought to require a bridged conformation, not necessarily symmetrical. This requirement might seem to rule out structure (II), but Wood and Lloyd have suggested that, provided these radicals are markedly pyramidal at the radical centre, the steric course of reactions involving radicals having conformation (II) can still be explained,[12,17]

EXPERIMENTAL

t-Butyl bromide (B.D.H.), isobutyl bromide (B.D.H.), tetramethylsilane (TMS) (B.D.H.), and di-t-butyl peroxide (Koch–Light) were purified by distillation, only the middle fractions with acceptable b.p.s being used. Adamantane (Aldrich) was purified by refluxing with activated charcoal in high grade heptane for *ca.* 2 h, followed by recrystallisation. [$^2H_{16}$]Adamantane (Merck, Sharpe and Dohme) and [$^2H_{12}$]TMS (Merck, Sharpe and Dohme) were used as supplied. The purities of the subtrates and matrices were checked using n.m.r. spectroscopy prior to any experimentation.

1% Mole fraction solutions in TMS were pipetted into 4 mm O.D. quartz tubes and degassed *via* the freeze–thaw method. Samples in adamantane were prepared by recrystallising the adamantane from the required substrate, and pressing the solid into a hard pellet. Samples were exposed to ^{60}Co γ-rays at 77 K in a Vickrad cell at a nominal dose rate of 1.7 Mrad h^{-1} for up to 4 h.

Photolysis of tetramethyl-*p*-phenylenediamine (Aldrich) in TMS and adamantane solutions was carried out by exposure at 77 K to radiation from a low pressure mercury lamp through a 253 nm filter. Photolysis of the peroxide mixtures was carried out in the same way.

E.s.r. spectra at all temperatures were recorded using a Varian E 109 spectrometer. Spectra at 4.2 K were obtained using a liquid helium insert, while those at temperatures >77 K were obtained using a variable temperature system. It was appreciated that the spectra of $Me_2\dot{C}CH_2Br$ in a single crystal would shed a great deal of light on the problem. Unfortunately, as previously reported,[10] crystals of Me_3CBr shattered at temperatures <233 K, and irradiation of the crystal above this temperature did not yield the required species.

RESULTS AND DISCUSSION

In view of the complexities of the e.s.r. spectra involved, we start by describing the changes observed after irradiation at 77 K in some detail before discussing the identification of the species involved.

Isobutyl Bromide.—After exposure of solutions in adamantane to ^{60}Co γ-rays followed by slight annealing, the e.s.r. spectrum shown in Figure 1a was obtained (species A). A similar experiment using tetramethylsilane as a matrix gave species B together with $Me_2CH\dot{C}H_2$ radicals (Figure 1b). In the outer regions of both spectra, features characteristic of species S were obtained, similar to those shown in Figure 2a.

On warming the adamantane solutions above 77 K, the features for A became better defined, and then gave way irreversibly to features characteristic of species W (Figure 1c). Features for species S grew and also became better defined under these conditions. On cooling, all but the outermost features for species W broadened reversibly and changed to an unanalysable multiple group of features at 77 K similar to those shown in Figure 2B. For solutions in perdeuterioadamantane, the initial spectra were similar, but better defined. However, at *ca.* 200 K features were detected in between the major lines assigned to species C, marked α in Figure 1c. On annealing above *ca.* 200 K species W was lost irreversibly and features for $Me_3C\cdot$ radicals grew in. The deuteriated solvent gave a mixture of $Me_3C\cdot$ and $Me_2\dot{C}CH_2D$ radicals, as previously reported.

In contrast, on annealing the tetramethylsilane solutions species B was lost and features assigned to $Me_2CHCH_2\cdot$ radicals grew. Some spectra gave weak features due to species W, but these never made more than a minor contribution to the spectra. On further annealing features for $Me_3C\cdot$ radicals grew more intense and those due to $Me_2CH\dot{C}H_2$ radicals were lost. When $(CD_3)_4Si$ was used, species B was not obtained although $Me_2CH\dot{C}H_2$ radicals were formed in good yield. We do not understand this difference. On annealing, $Me_2CH\dot{C}H_2$ radicals were converted into $Me_3C\cdot$ radicals, but there was no intermolecular reaction to give $Me_2\dot{C}CH_2D$ radicals. We suggest that this difference reflects the low reactivity of the primary C–D bonds in $(CD_3)_4Si$.

t-Butyl Bromide.—Wood and Lloyd state that the only product obtained from t-butyl bromide in [$^2H_{16}$]adamantane was $Me_3C\cdot$.[17] We had previously reported the detection of species W after irradiating t-butyl bromide in adamantane, but the features were broad and poorly defined.[13] It was suggested [17] that our samples must have contained some isobutyl bromide. In both studies, we checked the purity of our samples using ^1H n.m.r. spectroscopy, and found no detectable signals from isobutyl bromide. In adamantane at 77 K, t-butyl bromide gave largely species W, characterised by the narrow outermost features (Figure 2b). Broad features for species S were also detected. On annealing the W features changed reversibly to the more characteristic isotropic features for species W. On further annealing species W was lost and, simultaneously, features characteristic of $Me_3C\cdot$ radicals grew in. (This must have been the system studied by Wood and Lloyd.[17]) In perdeuterioadamantane, only species W and $Me_3C\cdot$ radicals were obtained, with no evidence for $Me_2\dot{C}CH_2D$ radicals.

In tetramethylsilane the main initial product at 77 K was $Me_3C\cdot$, but poorly defined features assignable to species W were also detected. These became better

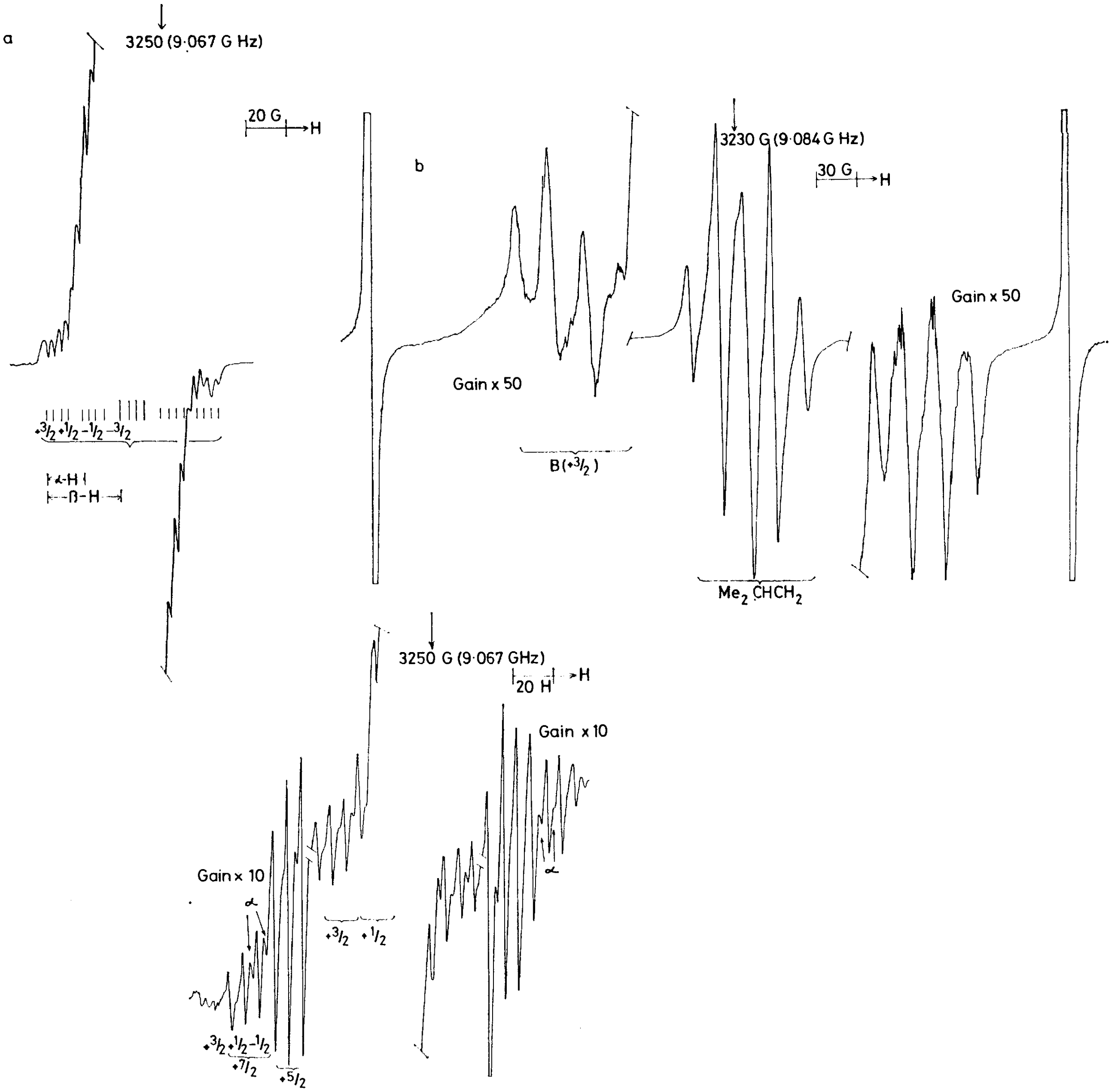


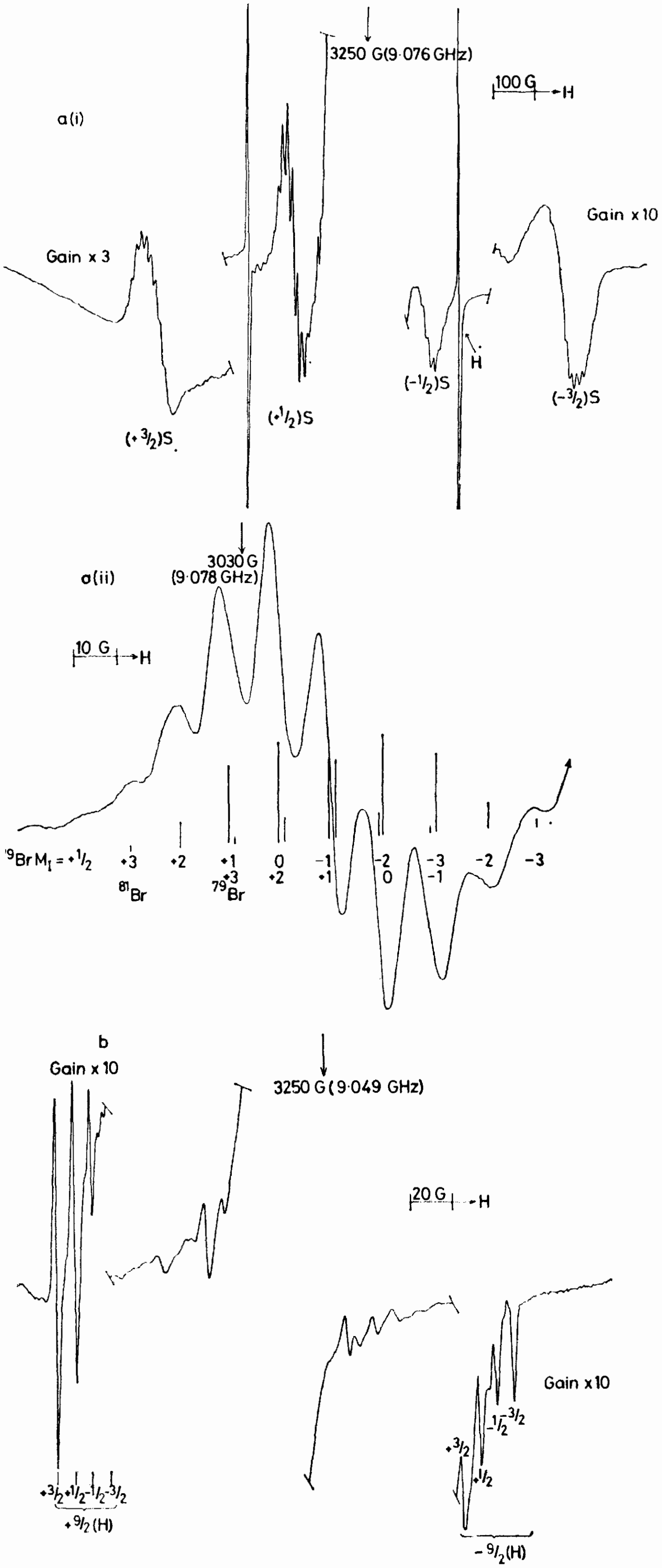
FIGURE 1 First derivative X-band e.s.r. spectra for Me_2CHCH_2Br after exposure to ^{60}Co γ-rays at 77 K: a, in $[^2H_{16}]$adamantane at 94 K showing features for species A; b, in tetramethylsilane showing features assigned to $Me_2CH\dot{C}H_2$ radicals and species B; and c, in $[^2H_{16}]$adamantane at *ca.* 190 K showing features assigned to species W, together with extra features, α, discussed in the text

defined before being lost on annealing. There was a high yield of species S, and the superhyperfine features became relatively well defined on annealing (Figure 2a).

Irradiation of the pure materials gave primarily species S together with $Me_2CH\dot{C}H_2$ and $Me_3C\cdot$ radicals for the iso- and t-butyl bromides respectively. We were not able to detect species A or W in these systems.

Species A and B.—Species A, formed from Me_2CHCH_2-Br in perdeuterioadamantane, is clearly closely related to $Me_2CH\dot{C}H_2$ radicals, but with the proton hyperfine coupling constants slightly reduced (compare Figures 1a and b). Each outer feature comprises a 4 G quartet which we assign to hyperfine coupling to ^{79}Br and ^{81}Br. (Both nuclei have $I = \frac{3}{2}$ and are in nearly 50% abundance: their magnetic moments are 2.099 1 and 2.262 6 respectively: the ^{79}Br and ^{81}Br features almost coincide in Figure 1a: they are responsible for the fact that the $M_I = \pm\frac{3}{2}$ features are somewhat broader than those for $M_I = \pm\frac{1}{2}$.)

Species B in tetramethylsilane also seems to be related to $Me_2CH\dot{C}H_2$ radicals but if this is true, there must be a relatively large extra hyperfine coupling. We postulate that A is the adduct $Me_2CH\dot{C}H_2,Br^-$ with A(α-H) −19.0, A(β-H) 36.2, and A(^{79}Br, ^{81}Br) ±4 G. This species must be undergoing effectively free rotation to give isotropic parameters. Our variable temperature studies show that the onset of this rotation occurs at *ca.* 90 K. The proton hyperfine coupling constants are



slightly less than those for $Me_2CH\dot{C}H_2$ radicals, as found for other complexes of this type.[14,15] The bromine isotropic constant is far smaller than had previously been supposed.[14,15,19] This is because it was assumed that both $A_{\parallel}$ and $A_{\perp}$ (^{79}Br, ^{81}Br) were positive. If $A_{\perp}$ is taken to be negative then the results for A_{iso}, shown in Table 1, are indeed very small, and an isotropic coupling of 4 G is seen to be quite reasonable.

Species B, formed in tetramethylsilane is possibly also the adduct $Me_2CH\dot{C}H_2,Br^-$ but, in this case, it is not freely rotating. If so, the value for $A_{\parallel}$ (^{81}Br) of *ca.* 75 G fits in reasonably well with others (Table 1). Only the $M_I = \pm\frac{3}{2}$ features are defined. Also they comprise quartets rather than the quintets expected for $Me_2CH\dot{C}H_2$ radicals (see centre of Figure 1b). This suggests that the preferred conformation that gives the large β proton coupling of *ca.* 38 G has been lost. This is presumably caused by the bromide ion, but we do not understand why. On annealing, instead of giving the isotropic spectrum, this species decayed, probably to give more $Me_2CH\dot{C}H_2$ radicals together with $Me_3C\cdot$ radicals.

Species W.—Our identification of $Me_2CH\dot{C}H_2,Br^-$ adducts with a small isotropic hyperfine coupling to ^{79}Br and ^{81}Br lends considerable support to our contention that species W is also a bromide ion adduct.[13] This suggestion was dismissed on the grounds that authentic adducts had far larger hyperfine coupling constants to bromine[17] but, provided $A_{\perp}$ is negative, the data in Table 1 show that this is not justified. In view of the importance of this new assignment, we will briefly review the arguments for and against our assignment, and the alternative assignment to $Me_2\dot{C}CH_2Br$ radicals by Wood and Lloyd.[12,17]

The Case for and against W being $Me_2\dot{C}CH_2Br$.—(i) Under the same conditions, Me_2CHCH_2Cl gave $Me_2\dot{C}CH_2Cl$ radicals unambiguously.[12] Thus $Me_2\dot{C}CH_2Br$ should be formed. We agree, and point out that species S is indeed formed in these systems, although this was not appreciated by Wood and Lloyd. If our contention that S is $Me_2\dot{C}CH_2Br$ is accepted, then W must be some other species.

(ii) It is possible to analyse the 10 hyperfine components assigned to ^1H coupling in terms of seven equivalent protons from two methyl groups, one almost equally coupled proton, and one giving twice this coupling. This fits with $Me_2\dot{C}CH_2Br$ radicals provided they have the precise conformation of (II). The intensity distributions are not correct, but by postulating some motional effects linewidths and intensities could be accommodated.[12,17] This concept requires a double coincidence in order that only 10 proton hyperfine components be detected. Only a slight deviation from this precise configuration would generate many more than ten lines. One might have expected that changing the temperature would change

FIGURE 2 First derivative X-band e.s.r. spectra for Me_3CBr after exposure to ^{60}Co γ-rays at 77 K: a(i) and (ii), in tetramethylsilane, showing features assigned to species S; and b, in [$^2H_{16}$]adamantane at 77 K, showing features assigned to species W

TABLE 1

E.s.r. data for alkyl radical–bromide ion adducts, together with results for species A and W

		^{1}H Hyperfine coupling (G) [a]			^{81}Br Hyperfine coupling (G)		
Radical	Medium	$\parallel$	$\perp$	iso	$\parallel$	$\perp$	iso
$Me_3C\cdot,Br^-$ (W)	Adamantane [b] at 209 K			21.4			±6.7
$Me_3C\cdot,Br^-$ (W)	Adamantane at 4 K			*ca.* 21	*ca.* 56 [e]	*ca.* (−) 10	*ca.* 12
$Me\cdot,Br^-$ [c] (C)	CD_3CN	21	21.5	21.5	58.3	(−) 28.3	±1.7
$Me\cdot,Br^-$ [d] (C)	CD_3CN	20.6			56.7		
$Me_2CH\dot{C}H_2,Br^-$ (A)	Adamantane			19.0 (α-H) 36.2 (β-H)			±4
$Me_2CH\dot{C}H_2,Br^-$ (B)	Tetramethylsilane			20 (α- + β-H)	75		
$Me_2CH\dot{C}H_2$	Tetramethylsilane			21.5 (α-H) 38.5 (β-H)			

[a] $G = 10^{-4}$ T. [b] Described as $Me_2\dot{C}CH_2Br$ in ref. 12. [c] Ref. 15. [d] Ref. 14. [e] Estimated from $A_\perp$ and A_{iso}.

the average conformation enough to do this, but no such effect was reported.[12] In fact, the bromine coupling changes considerably on warming (see Table 1) but the 10 proton features are maintained intact. The fact that exactly the same 10 proton features were obtained from the iodine derivative [12] makes these coincidences even more surprising. Since this unusual asymmetric conformation (II) is presumably controlled by steric forces, the change in size on going from Br to I would be expected to change θ enough to induce a splitting of some of the components.

(iii) According to Wood and Lloyd, Me_3C–Br gives only $Me_3C\cdot$ radicals in adamantane.[17] This is given as an argument in favour of the assignment of W to $Me_2\dot{C}HCH_2$-Br radicals. We dispute this argument since it is clear that Me_3C–Cl gives Me_2CCH_2Cl radicals in good yield,[7] and hence Me_3C–Br should give $Me_2\dot{C}HCH_2Br$ on any argument. Our results show that species S is indeed formed at 77 K, but we obtain a far greater yield of W from Me_3C–Br than from Me_2CHCH_2Br. It was suggested [17] that our samples of Me_3C–Br must have contained Me_2CHCH_2Br as an impurity. We could not detect this by ^{1}H n.m.r. spectroscopy, nor could we detect any other impurities likely to be a major source of W.

(iv) A major argument against this assignment is that β-chloroalkyl radicals do strongly favour structure (I), and probably have a weakly bridged structure.[7-9] In view of the usual similarity in behaviour of chlorine, bromine, and iodine, a rejection of this structure by the bromide and iodide would be most remarkable, if it were correct. Steric forces clearly favour (I) over (II), and so do electronic factors *via* σ–π delocalisation. We know of no reason why structure (II) should be favoured. The idea that the radical (II) is significantly non-planar at the radical carbon [17] is controversial.[20,21] In our view [20] the e.s.r. data for the t-butyl radical strongly indicate effective planarity, and this is supported by *ab initio* calculations.[20] Photoelectron spectra for $Me_3C\cdot$ radicals in the gas phase have been interpreted in terms of a major deviation from planarity,[22] but there are, in our view, other possible explanations, and this conclusion cannot be taken as definitive. If $Me_3C\cdot$ radicals are planar, or nearly so, we see no reason why $Me_2\dot{C}CH_2Br$ radicals with the bromine close to the radical ' plane ' should be markedly pyramidal. It is, of course, possible that radicals with structure (I) could deviate slightly from planarity at carbon, especially if these contain a strong bridging element.

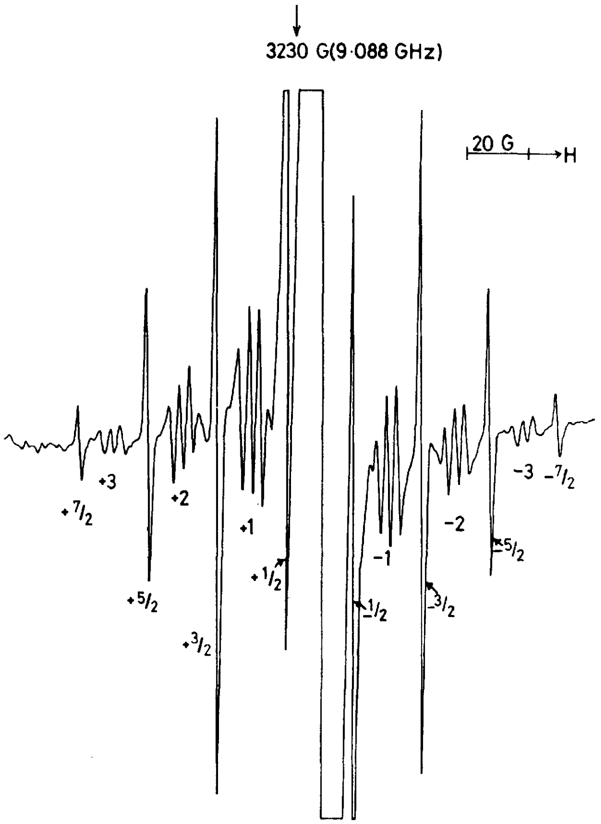


FIGURE 3 First derivative X-band e.s.r. spectrum for $MeCHCH_2$-Br in [$^2H_{16}$]adamantane at *ca.* 210 K, showing features assigned to $Me_3C\cdot$ radicals (β) and $Me_2\dot{C}CH_2D$ radicals (γ)

The Case for and against W being the Adduct $R\cdot,Br^-$.—(i) It is implied that in [$^2H_{16}$]adamantane, when W is lost, the spectrum changes to that of $Me_2\dot{C}CH_2D$.[17] In fact, both $Me_2\dot{C}CH_2D$ and $MeC\cdot$ were detected,[12] $Me_3C\cdot$ being the dominant species (Figure 3). It is not clear how $Me_2\dot{C}CH_2D$ is formed. Since $Me_2C\cdot$, formed, for example, from Me_3CBr, does not exchange in the medium under these conditions, exchange must occur prior to formation of these t-butyl radicals. We suggest that the more reactive primary radicals, $Me_2CH\dot{C}H_2$, can react with the matrix [(2) + (3)] or intramolecularly [(4)].

$$Me_2CH\dot{C}H_2 + Ada\text{-}D \longrightarrow Me_2CHCH_2D + Ada\cdot \quad (2)$$

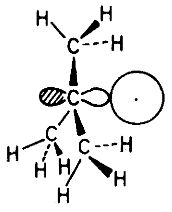
$$Ada\cdot + Me_2CHCH_2D \longrightarrow Me_2\dot{C}CH_2D + Ada\text{-}H \quad (3)$$

$$Me_2CH\dot{C}H_2 \longrightarrow Me_2\dot{C}\text{-}Me \quad (4)$$

That (3) should occur after (2) is reasonable because the two species remain in close proximity, and because of the relative weakness of the tertiary C–H bond. Provided this can also occur for the bromide adduct species, we expect to see $Me_2\dot{C}CH_2D$ radicals after annealing in addition to $Me_3C\cdot$ formed by (4). In view of the extreme weakness of the interaction with Br^- (see below) this seems reasonable. We have found that a second bromine containing species is present together with species W (Figure 1c). This, we suggest, is the adduct $Me_2\dot{C}CH_2D,Br^-$ formed by processes (2) and (3). The discernible features correspond exactly with those predicted for the adduct $Me_2\dot{C}CH_2D,Br^-$ based on the data for species W. We suggest that $Me_2\dot{C}CH_2D$ radicals are formed when this adduct breaks down. One factor that should be stressed is that dissociative electron capture is expected to occur in adamantane and tetramethylsilane solutions. Thus the absence of $Me_2CH\dot{C}H_2$ radicals in the former is curious if bromide ion adduct formation is not accepted. If it is, however, all expectations are fulfilled.

(ii) The second objection raised is that there is no comparison between the hyperfine coupling to ^{79}Br + ^{81}Br in species W and those reported for other Br^- adducts. As stressed above, this difference vanishes if $A_\perp$ is taken to be negative.

(iii) It is claimed that the line intensities are incorrect for the $Me_3C\cdot,Br^-$ adduct. This is indeed the case. In fact, both theories require some form of M_I dependent broadening to explain the observed intensities. In our case, the results between 77 and *ca.* 200 K show clearly that the outermost quartets ($\pm 9/2$ if the species is $Me_3C\cdot,Br^-$) remain narrow whilst the remainder are reversibly broadened and ultimately split into a large number of overlapping features (Figure 2b). This explains why the $\pm 9/2$ features are abnormally intense in the 200 K spectra, but might be taken to favour the β-bromo structure rather than the $Me_3C\cdot,Br^-$ structure. Our opinion is that the evidence in favour of the $Me_3C\cdot,Br^-$ structure is so strong that there must be some reason why $Me_3C\cdot$ should be asymmetric within the adduct. We suggest that methyl group rotation becomes inhibited at low temperatures, and that one specific conformation such as (III) is adopted. This seems to occur before molecular rotation becomes slow. We envisage a migration of the $Me_3C\cdot$ radical within the nearly spherical surface bounded by the surrounding adamantane molecules and the bromide ion. On cooling to *ca.* 4 K all features became very poorly defined. A perpendicular coupling of 10 G was resolved, but only a broad unresolved feature was obtained in the parallel region. Using this value for $A_\perp$ (^{81}Br, ^{79}Br) and an extrapolated isotropic coupling of 12 G gives A 56 G. These values, given in Table 1, are in reasonable accord with those for other such centres. Since the $\pm 9/2$ perpendicular features almost coincide with the isotropic features on this analysis, it is difficult to assess at what stage the radicals actually stop rotating.



(III)

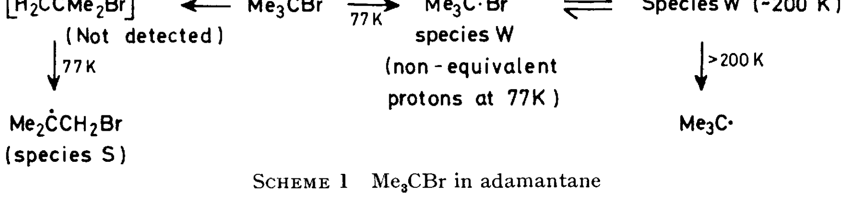
(iv) Wood and Lloyd claim that adding Me_3NBH_3 to adamantane + Me_2CHCH_2Br made no difference to the yield of W and hence W cannot be an electron gain product.[17] In our experience this additive is no more efficient at scavenging holes than electrons,[23] and we have not found that its presence enhances yields in other authentic dissociative electron-capture reactions.

However, in the present study, we found that photolysis of a system containing tetramethylphenylenediamine and Me_3CBr in adamantane gave a clearly detectable yield of species W, establishing that it is indeed formed by electron gain, since photoelectrons are produced in this reaction. Species S was not formed in this photolysis. Also, isobutyl bromide gives a lower, but still detectable yield of W under these conditions.

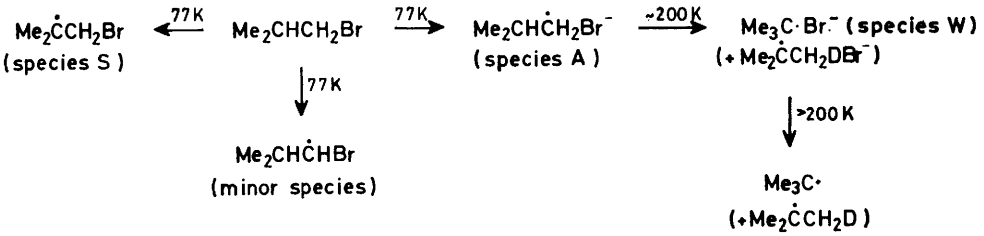
The proposals favoured above are summarised in Schemes 1 and 2.

The Case for Species S being $Me_2\dot{C}CH_2Br$.—So far as we are aware, there are no arguments against this assignment other than that species W is $Me_2\dot{C}CH_2Br$. No alternative structures have been proposed for S by others, but it was suggested that possibly both W and S might be $Me_2\dot{C}CH_2Br$, different conformations being favoured by different media.[12] We find that both species are formed in adamantane and in tetramethylsilane and hence it is most unlikely that they are the same species.

A possible alternative structure is the σ* anion



SCHEME 1 Me_3CBr in adamantane



SCHEME 2 Me_2CHCN_2Br in adamantane

$Me_2CHCH_2{\cdot}Br^-$. Such species do give rise to very large hyperfine coupling to halogen,[24,25] but they have never been detected as intermediates in electron addition to alkyl halides. We have argued that since alkyl halides form stable alkyl radical–halide ion adducts, it is unlikely that they can also form stable σ^* anions.[26] In the present case, species S is not formed by electron addition [see (iv) above].

In favour of our assignment is the fact that seven hyperfine components are often well resolved both for ^{81}Br and ^{79}Br features [Figures 2a(i) and (ii)], indicative of two equivalent methyl groups. The proton hyperfine coupling of *ca.* 13 G is less than that detected for $Me_2\dot{C}CH_2Cl$ at 77 K (17 G),[7] but is reasonable for structure (I) provided σ–π delocalisation is enhanced relative to the chloro derivative. We have not resolved coupling to the methylene protons, but from the linewidths, we conclude that this must be $\leqslant 4$ G. This coupling for the chloro derivative is *ca.* 5 G.

We have not attempted a full analysis of the anisotropic coupling to bromine. In the light of the considerable inaccuracies of our y and z parameters for α-bromo radicals derived from powder spectra,[10,26] we content ourselves with giving an estimate of A_z or $A_{\parallel}$ (^{79}Br, ^{81}Br) (Table 2) and stating that the other components (A_x and A_y) must be $< A_z$ with g_x and $g_y > g_z$ *ca.* 2.00. Thus we cannot compare isotropic coupling constants for chlorine and bromine, but we can compare values for $A_{\parallel}$. Thus, for $Me_2\dot{C}CH_2Cl$, $A_{\parallel}(^{35}Cl)$ 45 G. If this is multiplied by the ratio of the magnetic moments for chlorine and bromine we obtain 225 G which can be compared with our experimental value of *ca.* 350 G. This comparison supports our assignment and the suggestion that delocalisation into the σ-*C–Br bond is enhanced for bromine.

The form of the g tensor components also supports this comparison. Thus g_{av} and $g_{\perp}$ are >2.00 for β-chloro radicals, whilst $g_{\parallel}$ is *ca.* 2.00.[7-9,12] This is true also for radical S, the $g_{\perp}$ shift being clearly greater, as expected in view of the larger spin–orbit coupling constant for bromine. It is noteworthy that g_{av} for species W (Br and I) is less than the free-spin g value. Even if θ is *ca.* 75° [structure (II)] a small positive shift would be expected. However, for the adducts, $g_{\parallel}$ is *ca.* 2.002 3 and $g_{\perp}$ is very slightly less than this, in good accord with the isotropic data. Thus the available e.s.r. data for species S tie in well with those expected for $Me_2\dot{C}CH_2Br$ if this has the same conformation as the β-chloro derivative.

Another result which supports our assignment for species S is that when a solution of di-t-butyl peroxide was photolysed in Me_3C–Br, species S, but not species W, was detected. Since RO· radicals are expected to extract hydrogen atoms under these conditions, this strongly supports our assignment for species S [reactions (5) and (6)]. The 1,2 halogen atom shift (6) is well established

$$RO{\cdot} + Me_3C\text{–}Br \longrightarrow ROH + H_2\dot{C}(Me)_2Br \qquad (5)$$

$$H_2\dot{C}(Me_2)Br \longrightarrow Me_2\dot{C}CH_2Br \qquad (6)$$

for the corresponding chloride.[7] Species S was also formed from Me_2CHCH_2Br under these conditions, but in relatively poor yield.

Mention should be made of a further result reported by Wood and Lloyd. They found that radical W formed from 1-bromo-1,1-dideuterio-2-methylpropane, Me_2CH-CD_2Br, gave a species whose spectrum could be analysed in terms of two inequivalent deuterium atoms having $A(^2H) = 3.28$ and 6.55 G respectively.[12] This species was studied in [$^2H_{16}$]adamantane, so in terms of our theory, there should be two adducts formed, $Me_2\dot{C}CHD_2$,-

TABLE 2

E.s.r. data assigned to β-bromoalkyl radicals (species S), together with some results for β-chloroalkyl radicals

		^1H Hyperfine coupling (G) [a]			^{35}Cl or ^{81}Br hyperfine coupling (G)		
Radical	Medium	$\parallel$	$\perp$	iso	$\parallel$	$\perp$	iso
$Me_2\dot{C}CH_2Br$ (S)	Me_3CBr [b]	13	*ca.* 13	*ca.* 13	*ca.* 366		
$Me_2\dot{C}CH_2Br$ (S)	Adamantane	13	*ca.* 13	*ca.* 13	*ca.* 350		
$Me_2\dot{C}CH_2Br$ (S)	Tetramethylsilane						
$Et\dot{C}HCH_2Br$ [b]	Bu^nBr	*ca.* 17 (α-H) and 30 (2 β-H)			*ca.* 280		
$Me_2\dot{C}CH_2Cl$	Adamantane [c]			21.1			19.5
$Me_2\dot{C}CH_2Cl$	Me_3CCl [d]	17 (2Me) and 5 (CH_2)			*ca.* 45		

[a] G = 10^{-4} T. [b] Ref. 10. [x, y, and z data were reported in ref. 10; we now consider that it is not possible to derive more than $A_{max.}$ (^{79}Br, ^{81}Br) from these powder spectra.] [c] Ref. 7. [d] Ref. 12.

Br^- and $Me_2\dot{C}CD_3,Br^-$. The e.s.r. spectrum,* which was relatively poorly defined, shows that the dominating species comprises a major septet from six equivalent protons, together with the normal bromine quartet and a poorly defined multiplet from deuterium, with *A* 3.28 G. This fits $Me_2\dot{C}CD_3,Br^-$ satisfactorily, and hence we need to postulate that in this experiment, exchange with the matrix was more extensive than usual.

Aspects of Structure.—If these assignments are accepted, then we conclude, as before,[10] that $Me_2\dot{C}CH_2Br$ radicals have the maximum σ–π overlap structure (I). Unfortunately we cannot estimate the spin-density on bromine, but it must be quite high, and by analogy with other structures of this type [27] it is probably *ca.* 15%. If we assume that the methyl proton coupling is reduced solely by delocalisation onto bromine and not because of a deviation from planarity, then the extent of delocalisation is *ca.* $(22 - 13)/22 = 0.4$. This alone will not explain the low value of the CH_2 proton coupling ($\leqslant 4$ G). In a classical system, held rigidly in the preferred conformation (trigonal at C-1 and tetrahedral at C-2) the CH_2 coupling should be *ca.* 13 G.[28] The greatly reduced value for β-chloro radicals has been discussed in terms of a movement of chlorine towards the radical centre, giving what could be described as an asymmetric bridge. This causes a flattening at C-2 and hence a reduced σ–π overlap for the methylene protons.[29] If this is correct, it presumably also applies to the β-bromo radical. An alternative description of this could be that as the unpaired electron becomes delocalised into the C–Br bond, this bond stretches, and there is a concomitant flattening at C-2.

The structure of the halide ion adducts is well described in terms of a planar alkyl radical weakly interacting with a halide ion. Indeed, it seems that the isotropic hyperfine coupling to halogen is close to zero, and we now propose that the anisotropic coupling largely reflects an indirect effect from spin on the alkyl radical. If we use a point-charge model as a rough approximation, we have equation (7) where *r* is the

$$2B = \Delta H_{\|} = 2M_I \cdot g_N \beta_N \cdot r^{-3} \qquad (7)$$

separation between the electron and the nucleus. This gives a separation of *ca.* 2.6 Å for species C, which is reasonable. Any real delocalisation would reduce the contribution to 2B from this dipolar effect, and hence would require a greater separation. Hence we conclude that real delocalisation is small. The fact that the methyl groups adopt a preferred conformation at 77 K suggests that there is a weak attractive force involved, but the ready breakdown of these adducts in media such as cyanomethane [14,15] and tetramethylsilane shows that this force cannot be strong. Clearly for adamantane it must be the rigidity of the medium that inhibits separation. If this is correct, then it is hard to believe that simple monoalkyl halides can form stable σ^* radical anions, $(R\div hal)^-$,[30] since this would require a deep second minimum in the reaction co-ordinate curve. A more detailed argument attempting to establish that such σ^* anions cannot exist for longer than a few vibrational periods has recently been put forward.[31] A key factor governing the stability of such σ^* anions as $[(RCO)_2N\div hal]^-$,[32] $[RC{\equiv}C\div I]^-$,[33] $(C_6F_5I)^-$,[34] and $F_3C\div hal^-$ [35] is thought to be the fact that the potential radical X in $X\div hal^-$ does not significantly change its shape on being formed, whereas alkyl radicals become essentially planar.

Aspects of Mechanism.—Skell *et al.*[36] have concluded, as a result of a thorough mechanistic study, that the 2,3-dibromobutyl radical exists in two symmetrical bridged forms (one optically active), and that these must either be symmetrically bridged, or the bromine must migrate with a frequency greater than 10^{11} s^{-1}. Our results confirm the great ease of migration and show that in our unsymmetrical radical, bridging is clearly asymmetric insofar as it occurs. We stress that this leaves open the question of symmetry in the species studied by Skell *et al.* However, the CIDNP study of Hargis and Shevlin seems to show conclusively that the two methylene groups in the β-bromoethyl radical are inequivalent.[37]

Finally it is interesting to note that well defined features for the α-bromo radical $Me_2CH\dot{C}HBr$ were also obtained after annealing the solutions of Me_2CHCH_2Br in tetramethylsilane. The spectrum was similar to those previously reported.[3] Clearly extraction of an α-hydrogen atom competes with that of the tertiary hydrogen atom.

We thank Drs. D. Nelson and S. P. Mishra for early work in this field, and the S.R.C. for grants.

[9/021 *Received, 5th January,* 1979]

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* A copy of this spectrum was kindly supplied by Professor D. E. Wood.

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