Unstable Intermediates. Part 194.† Alkyl Radical–Halide Ion Adducts: an Electron Spin Resonance Study of the Radiolysis of a Range of Alkyl Bromides and Iodides

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Alkyl radicals formed by dissociative electron capture from alkyl bromides or iodides in solids at low temperatures often remain trapped in the vicinity of the halide ion, their e.s.r. spectra exhibiting hyperfine coupling to the halide ion nuclei. By studying the e.s.r. spectra of a range of such adducts in different media as a function of temperature, we have established that the perpendicular hyperfine coupling to the halogen nuclei is negative, the isotropic coupling being close to zero. The extent of charge transfer, estimated from the dipolar hyperfine coupling to the halogen nuclei or from the ^1H coupling of the radical, is 10—20% and is greater for iodides than from bromides. These results do not support a σ^* structure for electron adducts of alkyl halides, and this is further supported by the absence of a positive shift for $g_\perp$, such as is invariably observed for σ^* radicals. Some iodides were unusual in that species identified as the non-rotating adducts in adamantane co-existed at certain temperatures with the isotropic species. It is suggested that the latter adducts are associated with double vacancies and the former with single vacancies.

EARLY e.s.r. studies of alkyl halides exposed to ionising radiation were entirely concerned with spectra assignable to alkyl radicals formed by dissociative electron capture [equation (1)].[1] Our recent studies have shown

$$\text{R-hal} + e^- \longrightarrow \text{R}\cdot + \text{hal}^- \qquad (1)$$

that many other radicals can be detected under the right conditions.[2-4] Also, it seems that alkyl radicals formed by reaction (1) may remain trapped in the same solvent cavities as the unsolvated halide anions.[5,6] Such centres formed from alkyl bromides and iodides were initially characterised by anisotropic hyperfine coupling to the halogen nuclei, and small reductions in the ^1H hyperfine coupling constants relative to the uncomplexed radicals.

It was assumed that $A_\parallel$ and $A_\perp$ ($^{81/79}Br$ or ^{127}I) were both positive and hence that A_{iso} was relatively large.[5] However, we have recently suggested that $A_\perp$ may be negative and hence that A_{iso} values are close to zero.[7] This suggestion stemmed from a related postulate that radicals detected in adamantane, displaying very small isotropic coupling constants to $^{79/81}Br$ or ^{127}I, were $Me_3C\cdot$–hal^- adducts[7] rather than being $Me_2\dot{C}$–CH_2hal radicals as had previously been suggested.[8]

The aim of the present study was to find less ambiguous examples of R·–hal⁻ adducts having isotropic spectra, which could not be confused with β-halogeno-radicals. We have also sought methods which would unambiguously establish the relative sign of the perpendicular halogen hyperfine coupling constants.

EXPERIMENTAL

[$^2H_3$]Methyl iodide (Merck, Sharpe and Dohme), [$^2H_{16}$]-adamantane (Merck, Sharpe and Dohme), methyl bromide (B.D.H.), methyl iodide (M and B), ethyl bromide (Hopkin and Williams), ethyl iodide (Fisons), n-propyl bromide (Hopkin and Williams), n-propyl iodide (B.D.H.), isopropyl bromide (Hopkin and Williams), isopropyl iodide (Hopkin and Williams), isobutyl iodide (B.D.H.), t-butyl iodide (B.D.H.), and [$^2H_9$]-t-butyl iodide (Merck, Sharpe and Dohme) were all the highest grade available, and were used as supplied.

Liquid samples were used as beads, obtained by pipetting drops of the degassed samples directly into liquid nitrogen. Incorporation of the required alkyl halide into the [$^2H_{16}$]-adamantane matrix was carried out by recrystallising the adamantane from the substrate. The crystals were dried in a vacuum desiccator containing suitable drying agents. Alternatively, adamantane and *ca.* 1 mole % of the substrate were co-sublimed *in vacuo* at *ca.* 180 °C. After 2—3 sublimations, suitably doped samples were obtained. Samples were exposed to ^{60}Co γ-rays at 77 K in a Vickrad cell at a dose rate of *ca.* 1 Mrad h^{-1} for periods of up to 4 h. E.s.r. spectra were recorded on a Varian E109 spectrometer. Temperatures above 77 K were obtained using a Varian variable temperature accessory.

RESULTS AND DISCUSSION

Results are summarised in Tables 1—3. A selection of e.s.r. spectra are given in Figures 1 and 2. Before describing the overall results, we describe some specific results which confirm that $A_\parallel$ and $A_\perp$ have opposite signs.

Relative Signs of $A_\parallel$ *and* $A_\perp$ (hal).—In most cases, when the samples were annealed above 77 K , the e.s.r. spectra changed in a manner characteristic of librating radicals. In general, for nearly isotropic libration and for a given nuclear spin quantum number, if $A_\parallel$ and $A_\perp$ are of like sign, $|A_\parallel|$ will decrease and $|A_\perp|$ will increase with increasing libration. However, if $A_\parallel$ and $A_\perp$ are of opposite sign, both will decrease in magnitude. Our results (Table 3) show clearly that both $|A_\parallel|$ and $|A_\perp|$ decrease with increasing temperature. This proves that $A_\perp$ is opposite in sign to $A_\parallel$, thus confirming our previous assignments.[7]

The actual signs remain undetermined. We had previously thought that a through-space dipolar model was all that was required to explain the experimental anisotropy, but unfortunately our numerical values were in error.[7] In fact a point-charge dipolar model, using a minimum reasonable separation of *ca.* 2.0 Å, leads to a parallel ($2B$) coupling of *ca.* 2 G for ^{81}Br. Hence

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† Part 193 is ref. 12*b*.

TABLE 1

E.s.r. parameters for a range of alkyl radical–bromide ion adducts. Errors ±1 — ±2 G; G = 10^{-4} T. All g values between 2.000 and 2.002

			^{81}Br couplings (G)			% ' p ' orbital population			% drop in $A(^1\text{H})$ from free radical
Adduct	Matrix	T/K	$\parallel$	$\perp$	iso	a	b	$A(^1\text{H})$ for R$\cdot$–Br$^-$ (G)	R$\cdot$
$\cdot$CH$_3$–Br$^-$	CD$_3$CN	77	58	−28	0.7	9	11.5	20.6	10.4
$\cdot$CD$_3$–Br$^-$	CD$_3$CN	77	58	−28	0.7	9	11.5	(^{2}H) 3.2	
$\cdot$CD$_3$–Br$^-$	CD$_3$Br	77	71	−40	−3	11.7	15	(^{2}H) 3.2	
C$_2$H$_5\cdot$–Br$^-$	CD$_3$CN	77	58			9 [c]	11.5 [c]	*ca.* 23	
Bu$^{i}\cdot$–Br$^-$	[^{2}H$_{16}$]Adamantane	94			±4			(α-H) 19, (β-H) 36.2	16
Me$_2\dot{\text{C}}$H–Br$^-$	[^{2}H$_{16}$]Adamantane	187			±4			(α-H) 20.5, (β-H) 24.3	10
Bu$^{i}\cdot$–Br$^-$	Me$_4$Si	77	88.6			14 [c]	18 [c]	(α-H) 21 G	9
Bu$^{t}\cdot$–Br$^-$	[^{2}H$_{16}$]Adamantane	208			±6.7			21.3	5

[a] $2B^\circ$ (^{81}Br) = 630 G.[15] [b] $2B^\circ$ = 494 G.[14] [c] Assuming $A_{\text{iso}} \approx$ zero.

TABLE 2

E.s.r. parameters for a range of alkyl radical–iodide ion adducts. Errors ±1 — ±2 G; g values between 2.000 and 2.002

			^{127}I couplings (G)			% ' p ' orbital population			% drop in $A(^1\text{H})$ from free radical
Adduct	Matrix	T/K	$\parallel$	$\perp$	iso	a	b	$A(^1\text{H})$ for R$\cdot$–I$^-$ (G)	R$\cdot$
$\cdot$CH$_3$–I$^-$	CD$_3$CN	77	108	−60	−4	19	24	20.6	10.4
$\cdot$CD$_3$–I$^-$	CD$_3$CN	77	108	−58	−2.7	19	24		
$\cdot$CD$_3$–I$^-$	CD$_3$I	77	80	−39	0.7	14	17		
Pr$^{i}\cdot$–I$^-$	[^{2}H$_{16}$]Adamantane	77	*ca.* 60			10 [c]	13 [c]	(α H) 21, (β H) 24	9
Pr$^{i}\cdot$–I$^-$	[^{2}H$_{16}$]Adamantane	215			±3.3				
Pr$^{i}\cdot$–I$^-$	Pr^{i}I	77	60			10 [c]	13 [c]		
Bu$\cdot$–I$^-$	[^{2}H$_{16}$]Adamantane	77	99	−47	1.7	17	22	(α-H) 21	9
Bu$^{i}\cdot$–I$^-$	[^{2}H$_{16}$]Adamantane	77	*ca.* 86			15 [c]	19 [c]	(α-H) 21, (β-H) 30	9
Bu$\cdot$–I$^-$	BuI	77		−54		19	24	(α-H) 21	9
Bu$^{i}\cdot$–I$^-$	Bu^{i}I	77	60			10	13	(α-H) 21, (β-H) 30	9
Bu$^{i}\cdot$–I$^-$	[^{2}H$_{16}$]Adamantane	77			±3.3			(α-H) 19.5, (β-H) 23.5	14
[^{2}H$_9$]Bu$^{t}\cdot$–I$^-$	[^{2}H$_{16}$]Adamantane	77	100	−50	0	17	22	21	
Bu$^{t}\cdot$–I$^-$	[^{2}H$_{16}$]Adamantane	77	100	−47	2	17	22		
Bu^{t}]–I$^-$	[^{2}H$_{16}$]Adamantane	215			±7			21.8	5

[a] $2B^\circ$ = 580 G.[15] [b] $2B^\circ$ = 453 G.[14] [c] Assuming $A_{\text{iso}} \approx$ zero.

indirect dipolar coupling does not make a significant contribution. There remain two alternative explanations for the observed anisotropic coupling constants. One is that it is due to spin polarisation of σ-bonding electrons in a system in which the unpaired electron remains effectively localised on carbon. The alternative is that there is a small degree of charge transfer from the halide ion to the radical. We favour the charge-transfer description. Transfers between 10 and 20% are required to produce the observed $2B$ values. We note that for $\text{M}^+\text{A}^{\cdot-}$ ion pairs comparable electron-transfer is observed.[9] We cannot envisage a model in which spin polarisation can occur without delocalisation, and we therefore favour the charge-transfer model. There is always a small reduction in the isotropic proton hyperfine coupling for these adducts relative to the normal radical, from which the degree of electron transfer can also be estimated. Typical values lie in the 5—15% range, and there is fair agreement between the values deduced by the two procedures for specific adducts, as indicated in Tables 1 and 2 although, in general, the halogen data imply greater transfer than the radical data.

TABLE 3

Temperature dependence of the e.s.r. parameters for various adducts

		Hyperfine coupling (G) [a] (^{127}I)		
Adduct	T/K	$\parallel$	$\perp$	iso [b]
CD$_3\cdot$–I$^-$	77	80	−39	0.67
	92	74	−36	0.67
	99	72	−35	0.67
	111	67	−33	0.33
	124	64	−31	0.67
	138	59	−29	0.33
Bu$^{t}\cdot$–I$^-$	4.2	106	50	2
	77	99	47	1.6
	90	97	45.5	2
	100	95	44	2.3
	110	92.5	43	2.2
	120	90	42	2
	140	85	39.5	2
	160	78.5	36.5	1.8
	180	74	34	2
	200	65	31.5	0.7

[a] G = 10^{-4} T. [b] Values calculated from parallel and perpendicular values.

We have previously suggested that these adducts should not be viewed as σ* radicals, and indeed that simple alkyl halides probably cannot form such anions.[10] In view of our present conclusions, we need to reexamine the σ* description. The most significant result is that the alkyl radical fragment is effectively planar at the radical carbon atom as judged from the proton hyperfine coupling and also, for $\cdot{}^{13}CH_3$, from the ^{13}C coupling constant (*ca.* 12% reduction in A_{iso}).[11] Had there been extensive σ-bonding, the alkyl groups should have retained some pyramidal character. The other factor that clearly distinguishes these adducts from σ* anions is the negligibly small *s*-character on halogen. All authentic σ* anions display a relatively large isotropic coupling to the halogen nucleus, the *p*/*s* ratio being *ca.* 17.[12,13] (This is based upon the $2B^\circ$ data quoted by Symons,[14] and the A° data recommended by Morton and Preston.[15]) If the adducts had a similar *p*/*s* ratio, we would expect *s*-characters of *ca.* 0.6% and isotropic coupling constants of *ca.* 100 G for ^{81}Br and ^{127}I, which is far removed from experiment. It seems that the charge-transfer interaction involves only donation from *p*-orbitals, as would be expected if the ground-state structure involves non-bonded halide ions. We conclude that the charge-transfer description is the most satisfactory for these species.

Spectral Characteristics of Adducts.—Because of the complexity of many of the spectra involved, we have developed the following criteria for identifying alkyl radical adducts. (i) All features are centred close to the free-spin *g*-value and are almost symmetrical about this point. If anything, the high-field features are slightly sharper than those at low-field. This is in contrast with results for α- and β-halogeno-radicals, which are markedly asymmetric, the $M_I = +\frac{1}{2}$ features being far more intense than the others.[3,4] (ii) Isotropic spectra (obtained in rotator matrices such as adamantane) exhibit very small halogen (Br, I) splittings ($|A_{iso}| \leqslant 10$ G) which may not always be resolved. (iii) Anisotropic spectra have $|A_\parallel| \approx 2|A_\perp|$, and on annealing, both these values decrease in magnitude. (iv) The spectra exhibit hyperfine coupling to ^1H which is characteristic of the 'free' radicals, R•, in the matrix concerned, although $|A(^1H)|$ values are usually reduced by *ca.* 5—10%. (v) In many cases, warming above 77 K results in dissociation of the adduct to give the uncomplexed radical with its normal e.s.r. spectrum.

These criteria have been largely fulfilled in the assignments made below.

Methyl Halides.—Cyanomethane (CD_3CN) has proven to be the best matrix for preparing $Me{-}Br^-$ and $Me{-}I^-$. The rotator matrices failed to give these adducts or methyl radicals, probably because of their high reactivity towards methyl. Both these adducts displayed libratory changes of type (iii) but isotropic spectra could not be obtained because of dissociation to give methyl radicals. Pure methyl bromide and iodide also failed to give adducts, but CD_3Br and CD_3I gave poorly resolved parallel and perpendicular features characteristic of the librating adducts, which again showed the predicted temperature changes. These results are expected in view of the greater reactivity of CH_3hal than CD_3hal towards attack by methyl radicals to give $\dot{C}H_2hal$ ($\dot{C}D_2hal$) radicals.

Ethyl Derivatives.—Ethyl bromide in adamantane gave a low yield of ethyl radical adducts which had reduced proton hyperfine coupling constants, but no resolved coupling to $^{81/79}Br$. These features were lost at *ca.* 165 K, but normal ethyl radicals were not detected. Again, reaction with the matrix is implicated. Similar results were obtained with ethyl iodide. Well defined adducts were obtained using CD_3CN. Pure ethyl bromide gave broad Et• features which narrowed on annealing and recooling. However, pure ethyl iodide, which has been studied extensively by Willard and his co-workers,[16] gave results that do not accord with the rest of the results given in the Tables. Outer features are indeed obtained, and these have proton hyperfine features characteristic of ethyl radicals. However, if this species is an adduct, the maximum coupling to ^{127}I of *ca.* 150 G is nearly twice that normally observed. Unfortunately, the spectra are so poorly defined in the central region that we cannot be sure that there are six sets of proton lines ($I = 5/2$ for ^{127}I), nor can we pick out clear perpendicular features. Features for irradiated C_2D_5I and CD_3CH_2I confirm the ethyl radical character of this species and the fact that there is a large extra splitting almost certainly due to coupling to ^{127}I. We hope that a single crystal study may help to solve this anomaly.

Propyl Derivatives.—Because of their reduced reactivity, isopropyl radical adducts were relatively stable in adamantane. Well defined e.s.r. spectra for the adducts were obtained using this matrix (Figure 1). Our results showing isotropic spectra clearly establish the postulate that the species involved is closely related to $Me_2\dot{C}H$, since all the expected ^1H hyperfine features for this radical are resolved. This result strongly supports our contention that the species formed from isobutyl bromide and iodide are also adducts[7] rather than being β-halogeno-radicals.[8] However, on further warming, uncomplexed $Me_2\dot{C}H$ radicals were not obtained.

Isopropyl bromide in $[^2H_{16}]$adamantane gave the $Me_2\dot{C}H{-}Br^-$ adduct with a well resolved isotropic spectrum at 187 K (Figure 1). However, n-propyl bromide, on annealing to *ca.* 95 K, had a complex spectrum showing two different components, one of which became isotropic at 187 K whilst the other was lost irreversibly. The isotropic spectrum was identical with that for $Me_2\dot{C}H{-}Br^-$ adducts, and so the $Me_2\dot{C}H$ radical must have been formed. The other species is undoubtedly the $CH_3CH_2\dot{C}H_2{-}Br^-$ adduct. This change, from n-propyl to isopropyl, closely resembles that found for the $Me_2CH\dot{C}H_2{-}Br^-$ adduct,[7] and for $Me_2CH\dot{C}H_2{-}I^-$ described below. However, there was no detectable formation of $CH_3\dot{C}HCH_2D{-}Br^-$ adducts. The possibility that $Me_2\dot{C}H$ radicals were formed from $CH_3CH_2\dot{C}H_2$ by an intramolecular process will be considered elsewhere.

Isopropyl iodide in $[^2H_{16}]$adamantane gave a complex spectrum at 77 K (Figure 2). The outer features are assigned to librating adducts. On annealing there was a reversible decrease in the iodine coupling for this adduct, and at *ca.* 215 K a well resolved isotropic spectrum for the rotating adduct, with $A_{iso}(^{127}I) = \pm 3.3$ G, was obtained. The only certain assignment that can be made for n-propyl iodide is for librating and rotating $Me_2\dot{C}H$–I^- adduct which grew in above *ca.* 150 K. Broad features almost certainly due to $CH_3CH_2\dot{C}H_2$–I^- adducts were detected at 77 K, but were very poorly resolved.

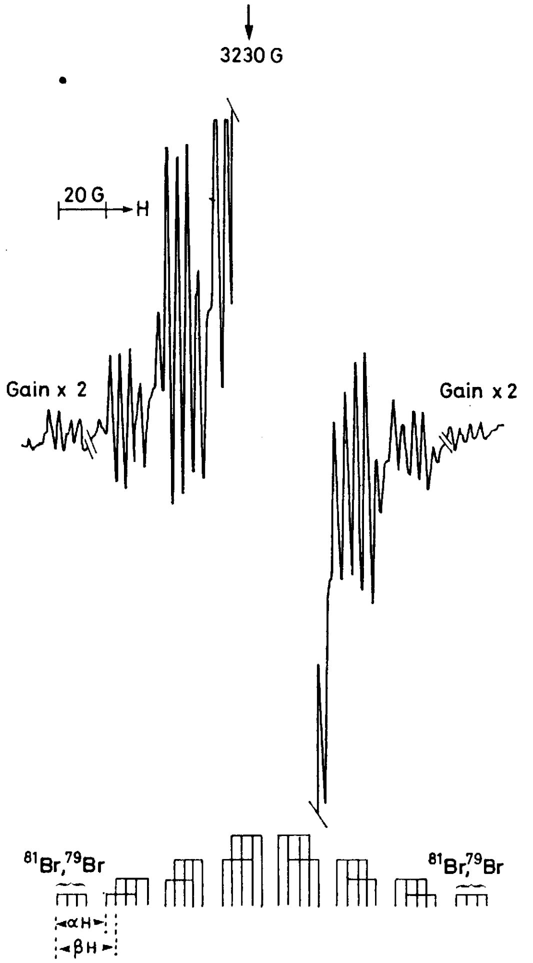

FIGURE 1 First derivative X-band e.s.r. spectrum for a solution of $(CH_3)_2CHBr$ in [$^2H_{16}$]adamantane, after exposure to ^{60}Co γ-rays at 77 K and warming to 187 K, showing features assigned to $(CH_3)_2\dot{C}H$–Br^- adducts

Isobutyl and t-Butyl Halides.—Results for isobutyl bromide and t-butyl bromide in admantane have been previously reported.[7] Results for the iodides were similar, except that two types of adduct were identified, one spanning the field range expected for stationary or librating adducts (Type A) and the other being clearly the rotating adducts (Type B). The situation is not simple, however, since the ' parallel ' features for type A adducts resembled isotropic features rather than shoulders (Figure **3**), and both types A and B co-existed over quite a wide temperature range. We are reasonably satisfied that the outermost type A features are ' parallel ' in the sense that they provide parallel data for the librating radicals. The temperature dependence of all features were quite characteristic of librating adducts (Table 3). Their unusual appearance may be connected with the librational motion of the species, or may indicate slight preferential alignment. If this assignment is accepted, then we must ask why librating and freely rotating radicals can both be detected over a range of temperatures. Dows *et al.*[17] have shown that the two phases of adamantane can co-exist in a 10° temperature range around the phase transition temperature of 208.6 K.

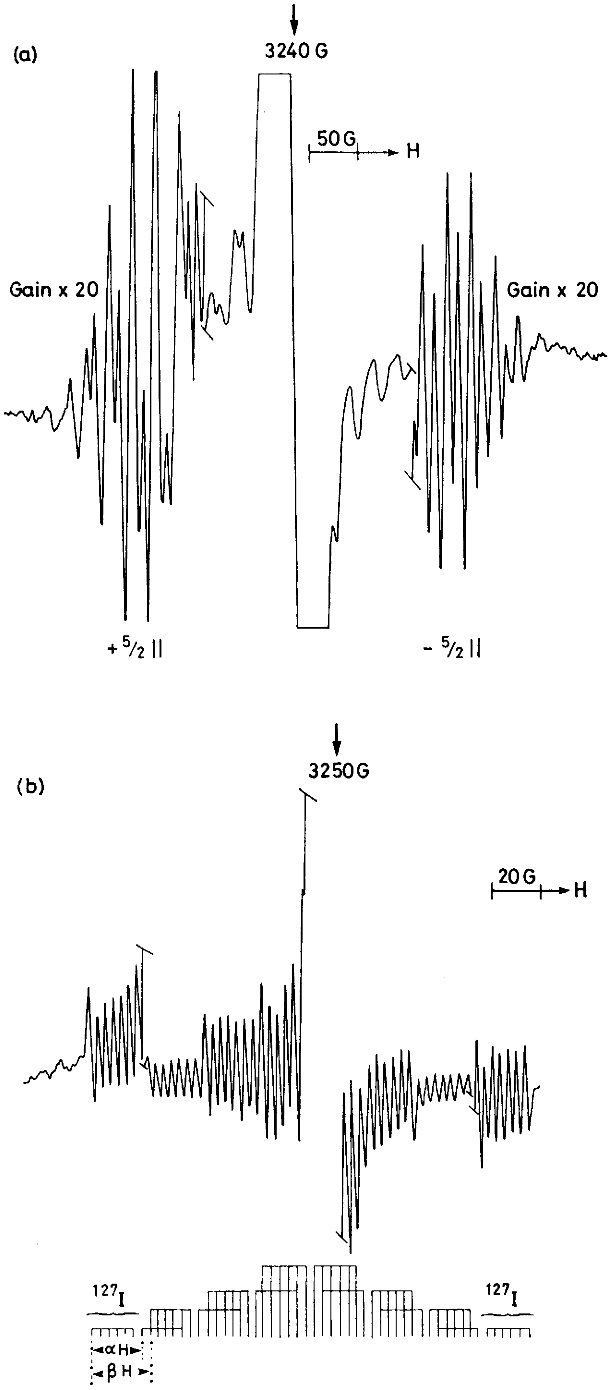

FIGURE 2 First derivative X-band e.s.r. spectra for a solution of $(CH_3)_2CHI$ in [$^2H_{16}$]adamantane, after exposure to ^{60}Co γ-rays at 77 K (*a*) showing anisotropic features assigned to $(CH_3)_2\dot{C}H$–I^- adducts and (*b*) after warming to 215 K, showing isotropic features for these adducts

Also, Bergman *et al.*[18] found it necessary to postulate such co-existence of two types of $R_2\dot{N}O$ radicals in adamantane. Their e.s.r. spectrum at *ca.* 123 K shows clearly the presence of both freely rotating radicals and librating radicals. Since the alkyl bromides did not show this phenomenon, there must be a rather precise size requirement. We suggest that such molecules, when incorporated into adamantane, can occupy single-vacancy sites, only with some difficulty, and that some succeed in occupying double-vacancy sites. The former give the librating species (A), whilst the latter give the isotropic species (B).

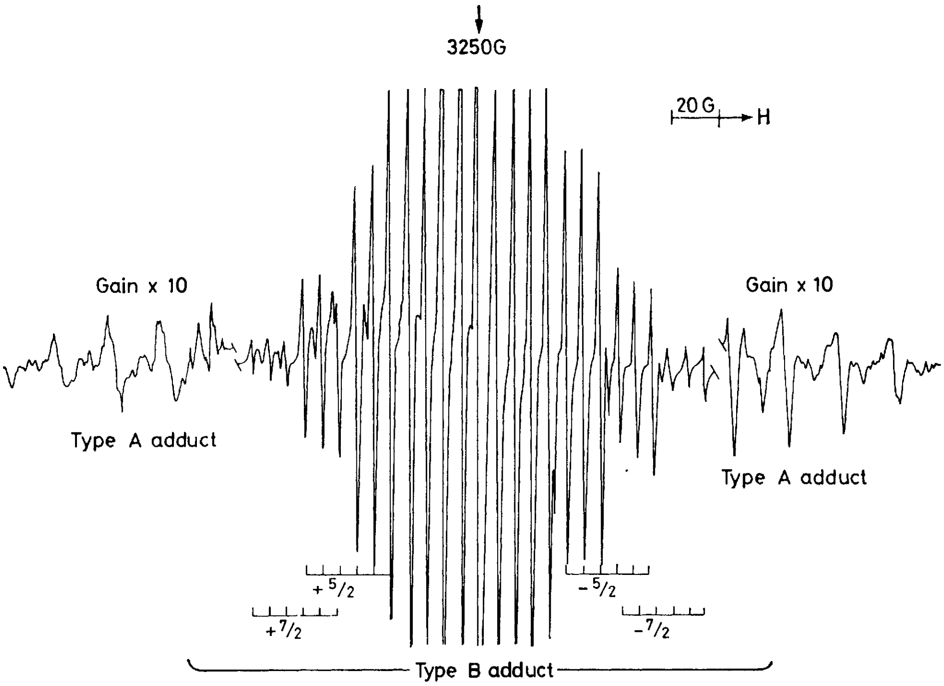

FIGURE 3 First derivative X-band e.s.r. spectrum for a solution of $(CH_3)_2CHCH_2I$ in $[^2H_{16}]$adamantane, after exposure to ^{60}Co γ-rays at 77 K and warming to 215 K, showing outer features for librating adducts, $(CH_3)_3C\cdot$–I^- (Type A) and central features for rotating adducts (Type B)

Spectrum (B) for irradiated Me_2CHCH_2I was previously detected by Wood and Lloyd, but was assigned by them to the β-iodo-radical $Me_2\dot{C}CH_2I$.[8] We feel that our arguments against their identification of the $Me_2\dot{C}CH_2Br$ radical given previously[7] are equally applicable in this case, and need not be rehearsed again here. In our work on Me_3CBr and Me_2CHCH_2Br, we were able to characterise the β-bromo-radicals as well as the bromide ion adduct.[8] However, we have not been able to detect β-iodo-radicals in any of the systems studied herein. This probably means that iodine atoms are lost rapidly even at 77 K [reaction (2)]. Pure t-butyl bromide gave a

$$Me_2\dot{C}CH_2I \longrightarrow Me_2C{=}CH_2 + I\cdot \qquad (2)$$

complex spectrum clearly due to $Me_3C\cdot$–Br^- adducts, but not as well defined as the spectra obtained from adamantane systems. On annealing this gave well resolved features for $Me_3C\cdot$ radicals.

Isobutyl iodide in adamantane, gave results which followed closely those for Me_2CHCH_2Br.[7] The first formed species was the $Me_2CH\dot{C}H_2$–I^- adduct. The outer (‖) features varied with temperature in the normal way. At *ca.* 210 K these features changed irreversibly into those characteristic of $Me_3C\cdot$–I^- (Type B) radicals. Some $Me_2\dot{C}CH_2C$–I^- adducts were also detected.

Pure isobutyl iodide gave outer (parallel) features characteristic of $Me_2CH\dot{C}H_2$–I^-, with $A_{\parallel}(^{127}I) = 86$ G. In this case, to check on the extent of libration at 77 K, we ran a spectrum at 4.2 K. There was no significant change, showing that libration was not significant at 77 K. However, the $Me_3C\cdot$–I^- adduct in adamantane showed a slight increase in $A_{\parallel}$ from 99 G at 77 K to 106 G at 4.2 K.

Magnitude of the Anisotropic Coupling.—Even after allowing for reductions in the measured anisotropy caused by librations, there seems to be considerable variation in coupling from one system to another. For a given alkyl group, the degree of charge-transfer is generally greater for I^- than for Br^-, in accord with the lower ionization potential of iodide ions. It should also depend on the electron affinity of the radical. However, no clear trend with the nature of $R\cdot$ is discernible. This may be because the degree of overlap between the donor and acceptor orbitals must also play an important role. This will be a function of the structure of $R\cdot$, but will also be governed by the local rigidity of the lattice. This will in turn reflect the effective size of the adduct, $R\cdot$–hal$^-$.

Conclusions.—We conclude that simple alkyl halides fail to form σ* radical-anions, electron-addition being purely dissociative. However, in rigid matrices when

R· and hal$^-$ are unable to separate, adducts are formed which exhibit relatively large dipolar hyperfine coupling to the halogen nuclei, but almost zero isotropic coupling. Shifts in g-values are small and slightly negative. These species readily give separate alkyl and hal$^-$ units, and in protic solvents such as methanol they are not detected at 77 K. This is almost certainly due to solvation of hal$^-$, which can occur at 77 K despite the rigidity of the medium.[19]

One problem remains. For some iodide adducts, the dipolar coupling can be large, apparently corresponding to *ca.* 20% charge-transfer (Table 1). However, from the ^{1}H coupling the extent of transfer is only *ca.* 10%. Possibly the whole problem arises because of the inaccuracy of the calculated $2B^\circ$ values. However, these pertain to the iodine atom, and we would expect the $2B^\circ$ value for the iodide anion to be reduced not increased. Furthermore, there is fair agreement between the calculated $2B^\circ$ values and semi-experimental gas-phase values for the atoms.

This difficulty is still more prominent for ethyl iodide, for which, if we assume that the species studied by Willard and his co-workers was indeed the adduct, and if we also assume that $A_{\text{iso}} \approx 0$, we obtain a spin-density of *ca.* 37% on iodine. Since the ^{1}H coupling is close to that for normal ethyl radicals, these adducts are clearly anomalous. We conclude that the species is unlikely to be a normal adduct but have, at present, no alternative identification to offer.

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