# Unstable Intermediates. Part CXXIV.[1] Alkyl Radical–Halide Ion Adducts

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A recent suggestion that methyl bromide in methyl cyanide when exposed to $\gamma$-rays at 77 K gives methyl radicals which are loosely associated with their parent bromide ions has been examined. the previous e.s.r. results have been confirmed. and the bromine hyperfine tensor components obtained. These show that transfer of spin to bromine is small. and indeed it may well be that spin density is acquired mainly by spin polarisation. Similar results were obtained from methyl iodide and ethyl bromide. t-Butyl bromide gave only $Me_3C\cdot$ radicals. The same compounds in methyl alcohol gave only the corresponding alkyl radicals with no halide interaction. This difference is explained in terms of the far greater anion solvating power of the alcohol. Methylene bromide in both solvents gave $Br_2^-$ and $H\dot{C}Br_2$ but no species corresponding to the bromide ion adducts. The pure compounds on irradiation at 77 K gave dihalide anions and other products. but no halide ion adducts. In contrast. *N*-chloro- and *N*-bromo-amides gave $\sigma^*$ radical anions without loss of halide ion. both in methyl cyanide and in methyl alcohol. These differences are explained in terms of the different structures of the organic radicals formed by loss of halide ions.

SPRAGUE and WILLIAMS have reported their studies of solutions of methyl bromide in methyl cyanide after exposure to $^{60}$Co $\gamma$-rays at 77 K.[2] The results showed clear features from the 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 capture to give methyl radicals and halide ions under these conditions, and indeed there is plenty of evidence for such reactions. This is the first system in which an interaction from the 'ejected' halide ion has been detected.

Unfortunately, they only reported values for $A_{\parallel}$(Br), and in order to learn more about these centres, we have repeated their work under conditions which have enabled us to extract the full hyperfine tensor components for bromine and hydrogen. Our interest was especially aroused because of an extraordinary contrast between the behaviour of methyl halides on the one hand, and of *N*-halogenoamides on the other. We have found recently[3] that the latter halides give stable radical anions when exposed to $\gamma$-rays, and that these anions differ markedly from the normal anions of amides or carboxylic acids in having their extra electrons in a $\sigma^*$ nitrogen–halogen orbital.

The major aim of this study was, therefore, to discover reasons for this interesting and unexpected contrast of behaviour.

## EXPERIMENTAL

Methyl bromide (B.D.H.), [$^2H_3$]methyl bromide (Prochem), methyl iodide (Koch–Light), [$^2H_3$]methyl iodide (Merck or Koch–Light), methyl cyanide (Fisons), [$^2H_3$]-methyl cyanide (Prochem), methanol (Koch–Light), [$^2H_4$]methanol (Nuclear Magnetic Resonance Limited, High Wycombe), methylene bromide (Koch–Light), ethyl bromide (Hopkin and Williams), t-butyl bromide (Hopkin and Williams), *N*-chlorosuccinimide (Koch–Light), and *N*-bromosuccinimide (B.D.H.) were used as such without further purification. When preparing samples of halides in methyl cyanide or [$^2H_3$]methyl cyanide care was taken to have halide concentrations as used by Sprague and Williams[2] in their methyl bromide–[$^2H_3$]methyl cyanide system (0·1—0·5M).

In order to avoid the problem of crystal growth encountered by Sprague and Williams,[2] who used solutions frozen in small-bore tubes, we used our normal technique of freezing beads of solution by pipetting directly into liquid nitrogen. In this way, good powder spectra were obtained. Samples were exposed to $^{60}$Co $\gamma$-rays at 77 K in a Vickrad cell at a nominal dose rate of 4 Mrad h$^{-1}$ for periods up to 2 h.

E.s.r. spectra were obtained using a Varian E3 spectrometer. Samples were annealed by allowing to warm in the Dewar flask after the liquid nitrogen had evaporated, and were recooled to 77 K directly any change was observed in the continuously monitored spectra.

## RESULTS AND DISCUSSION

In contrast with those previously reported,[2] our spectra for methyl bromide in $CD_3CN$ show well defined parallel and perpendicular features (Figure 1*a*) from which the data given in the Table were extracted. We confirm[2] that on annealing, these features are lost and strong central lines from methyl radicals are then detected. The central lines derived from radicals formed from the solvent have been discussed prevously.[4,5]

E.s.r. data for alkyl radical halide ion adducts formed in $CD_3CN$

| | | Hyperfine coupling (G)[a] | | | |
|---|---|---|---|---|---|
| Host | Main radical | $^1$H $\parallel$ | $\perp$ | $^{81}$Br ($^{127}$I) $\parallel$ | $\perp$ |
| $CH_3Br$ | $\dot{C}H_3-Br^-$ | 20·6[b] | | 56·7[b] | |
| $CH_3Br$ | $\dot{C}H_3-Br^-$ | 21·0 | 21·5 ± 0·5 | 58·3 | 28·3 ± 1·0 |
| $CD_3Br$ | $CD_3-Br^-$ | ($^2$H) 3·2 | | 58·3 | 28·3 ± 1·0 |
| $CH_3I$ | $CH_3-I^-$ | 21 | 20 ± 0·5 | 78 | 56 ± 2 |
| $C_2H_5Br$ | $C_2H_5-Br^-$ | *ca.* 23 | | *ca.* 58 | |

[a] *g* Values all close to 2·0023. [b] Ref. 2.

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[1] Part CXXIII, K. V. S. Rao and M. C. R. Symons, *J.C.S. Dalton*, 1973, 9.

[2] E. D. Sprague and F. Williams, *J. Chem. Phys.*, 1971, **54**, 5425.

[3] G. W. Neilson and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 1582.

[4] M. A. Bonin, K. Takeda, and F. Williams, *J. Chem. Phys.*, 1969, **50**, 5423.

[5] R. J. Egland and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1326.

Results for $CD_3Br$ confirm our identification and enable us to extract parallel and perpendicular lines with confidence (Figure 1*b*). The spectrum for methyl iodide in $CD_3CN$ (Figure 1*c*) was remarkably similar, except that the coupling constants were somewhat greater.

Notable 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 the iodide, despite the very large quadrupole moment of iodine. This is especially surprising for the perpendicular features both for the bromide and iodide, and must mean that the electric field gradient is remarkably small. This strongly supports the original description of these compounds as weak methyl radical-bromide ion adducts, rather than as radical anions. The lack of a positive shift for $g_\perp$ also strongly supports this view, since large positive shifts were found for the halogeno-amide anions.[3]

Another interesting aspect is the near absence of anisotropy in the proton hyperfine coupling. The anisotropic hyperfine coupling to bromine precludes any major tumbling motion, but for methyl 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 $z$ leads to a near zero anisotropy overall.

The $^{13}C$ tensor should not be averaged for such a rotation, and one of us[6] has previously explained the apparent marked change in $A_{iso}(^{13}C)$ for methyl radicals on Vicor glass surfaces as the temperature was lowered[7] in terms of a $z$-axis rotation, rather than 'free' tumbling. We therefore searched for $^{13}C$ features, and have in fact obtained shoulders from the $CD_3Br$–$CD_3CN$ system that are not formed for the solvent alone, which are of about the correct relative intensities for $^{13}C$ satellites on the $\pm 3/2$ parallel components (Figure 1*b*). From these we obtain $A_\parallel$ ($^{13}C$) = *ca.* 85 G. The correct value for $A_{iso}$ in this instance is uncertain, but it 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.[8] This result strongly supports the present model.

*Halide Spin Densities.*—These have been estimated using the usual procedures,[8] and the computed atomic values, $A^0(^{81}Br) = 8400$ G, $2B^0(^{81}Br) = 564$ G, $A^0(^{127}I) = 7294$ G and $2B^0(^{127}I) = 453$ G, which were derived

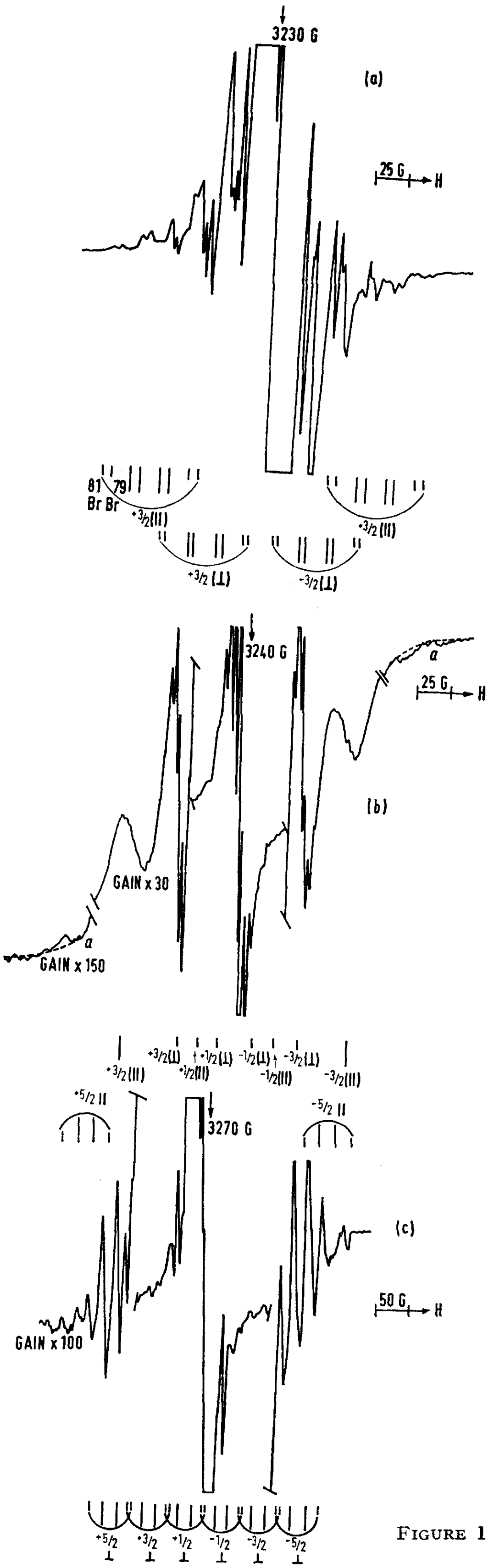

FIGURE 1

FIGURE 1 First derivative e.s.r. spectra for methyl halides in $CD_3CN$ after exposure to $^{60}Co$ $\gamma$-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, $CH_3I$

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[6] M. C. R. Symons, *Ann. Rev. Phys. Chem.*, 1969, **20**, 219.

[7] G. B. Garbutt and H. D. Gesser, *J. Chem. Phys.*, 1968, **48**, 4605.

[8] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

from the best available Hartree–Fock wave functions.[9] We find for bromine, *ca.* 3·3% $p$ character and 0·4% $s$ character, and for iodine, 3·3% $p$ and 0·8% $s$. The increase in $s$ orbital contribution for iodine may be real, but it must be remembered that the calculated $A^0$ values for heavy atoms are undoubtedly very poor, and tend to give over-estimates.

These results, equivalent to *ca.* 4% spin density, are sufficiently small to be a result of spin polarisation by the methyl electron, rather than being a real bonding effect. However, there is a real reduction in $a(^1H)$ relative to normal methyl radicals of about this degree, which might be taken to favour a delocalisation model.

The spectra for the ethyl compounds, although sufficiently clear to warrant definite assignment to the halide ion adducts, were nevertheless so poorly resolved, especially in the perpendicular regions, that we can only report that the parallel data did not differ significantly from those for the methyl derivatives. This 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 orientation, resulting in broad lines.

We were unable to detect the bromide ion adduct with t-butyl bromide in $CD_3CN$, but the $Me_3C\cdot$ radical was obtained in good yield. We think that this is primarily 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.

*Methanol Solvent.*—None of the alkyl halides that gave these halide ion adducts in methyl cyanide gave any such species when $CD_3OD$ was used as solvent, although the corresponding alkyl radicals were clearly detected. This result, which nicely illustrates the subtlety of the effect, can be understood in terms of the far more efficacious solvation of the halide ions by alcohol than by methyl cyanide. This difference has been studied extensively by one of us, using the u.v. absorption bands of the halide ions to probe solvent interaction,[10] and we found that methanol and methyl cyanide were almost at opposite ends of the scale of solvents. This we imagine that as the halogen moves along the reaction co-ordinate 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.*—Again, in contrast with the simple alkyl radicals, no halide ion adducts were formed. Clear features for the radical $H\dot{C}Br_2$ were obtained,* but these were identical with those found from methyl alcohol solutions. We also obtained e.s.r. evidence for the formation of $Br_2^-$ ions, and very tentatively suggest that electron capture results in the process $CH_2Br_2 + e^- \longrightarrow CH_2 + Br_2^-$, rather than the ejection of bromide ion. No features assignable to methylene were obtained, but at 77 K this species almost certainly reacts rapidly with the medium.

We should also stress that irradiation of the pure alkyl halides does not result in the formation of detectable amounts of these halide ion adducts at 77 K. Alkyl radicals and $R_2\dot{C}Hal$ radicals are formed, and also dihalogen anions were generally detected. These systems are being further studied at present.

N-*Halogenoamides.*—We have recently shown that well defined e.s.r. powder spectra of the anions of certain *N*-halogenoamides can be obtained.[3] These were analysed in terms of strong hyperfine couplings to $^{14}N$ and to $^{35/37}Cl$ or $^{81/79}Br$, and the data showed fairly conclusively that these radicals have their extra electrons primarily in the nitrogen–halogen $\sigma^*$ bonds. Thus they resemble in form the halide ion radicals presently under discussion except with respect to the extent of interaction of the halide ions. (Thus for $MeBr^-$, the spin density on bromine is $\leqslant 4\%$, whilst for the anion of *N*-bromoacetamide it is *ca.* 56%.) We tested this difference further by measuring the e.s.r. spectra of *N*-chloro- and *N*-bromo-succinimide in methyl cyanide and methanol. Spectra characteristic of the radical anions were obtained (see Figure 2), there being only very minor differences between the resulting parameters and those previously reported.[3]

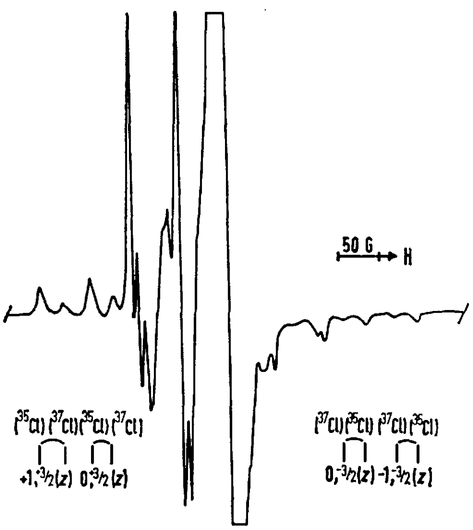

FIGURE 2 First derivative e.s.r. spectra for *N*-chlorosuccinimide in $CD_3CN$ after exposure to $^{60}Co$ $\gamma$-rays at 77 K, showing features assigned to the radical anion

*Electronic Structures.*—We discuss this contrast in terms of the electronic structure of the radicals involved.

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* These results will be reported fully later.

[9] Calculated from the data of C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

[10] M. Smith and M. C. R. Symons, *Trans. Faraday Soc.*, 1958, **54**, 338; M. J. Blandamer, T. R. Griffiths, L. Shields, and M. C. R. Symons, *ibid.*, 1964, **60**, 1524.

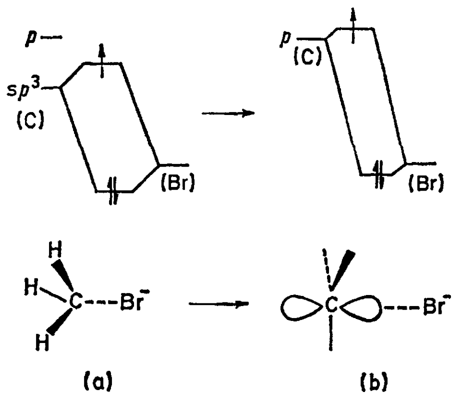

FIGURE 3 Bonding diagram for MeBr⁻ (a) and for the methyl radical bromide ion adduct (b)

After capture of an electron by the σ* carbon–halogen orbital of, say, methyl bromide, the C–Br bond relaxes in order to lower the anti-bonding character of the extra electrons (Figure 3). This results in a flattening of the $H_3C$ 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.

In contrast, there is little or no tendency for the amide unit to become linear, which would be required if the orbital on nitrogen contributing to the N–Br σ bond 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–bromine interaction.

In fact, when the bromide 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 π radical.[11] This reaction was not achieved under the conditions of the present study.

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[11] H. Bower, J. McRae, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2400; M. C. R. Symons, *ibid.*, p. 3205.