Unstable Intermediates. Part CLIX.[1] Dihalide Anions and Related Species as Products in the Radiolysis of Organic Halides

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Electron addition to 1,2-dihalides gave Hal_2^- σ^* radicals, characterised by their e.s.r. spectra. Electron loss often gave a similar species, containing two equivalent halogen atoms, which is identified as the dimer cation, $RHal{-}HalR^+$, isostructural with the well-established disulphide anion, $RS{-}SR^-$. A third species in this class only formed by iodides, containing two different iodine atoms, is thought to be RI–I. Iodoacetic acid and iodoethanol gave a species thought to be IO^{2-} or IOH^-, having e.s.r. spectra characteristic of iodine in σ^* radicals.

By far the most studied process in the radiation chemistry of organic halides is dissociative electron capture (1),[2]

$$RHal + e^- \longrightarrow R\cdot + Hal^- \qquad (1)$$

but a variety of other reactions are now established, which include the formation of α- and β-halogeno-radicals,[3-6] and a special type of electron capture in which a weak residual interaction between the alkyl

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radical and halide ion is detected by e.s.r. spectroscopy.[7-9]

In our work on organic chlorides, bromides, and iodides, we have frequently detected species having e.s.r. features spread over a wide field range, comparable with those of Cl_2^-, Br_2^-, and I_2^-.[10-13] Such features were recognised by Willard and his co-workers in their work on alkyl bromides and iodides.[14] 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-butyl bromide.[15] The present work represents an attempt to systematise and rationalise these results.

EXPERIMENTAL

A wide range of alkyl mono- and di-chlorides, -bromides, and -iodides has been studied. These were the best available commercial samples and were redistilled or crystallised to give acceptable b. or m.p.s. Care was taken to avoid halogen formation prior to irradiation since a trace of dissolved halogen acts as an effective scavenger to give the corresponding dihalide anion. Degassed samples were exposed as fine powders or small beads at 77 K to ^{60}Co γ-rays in a Vickrad source at a dose rate of 1.7 MRad h^{-1} for between 0.2 and 2.0 h.

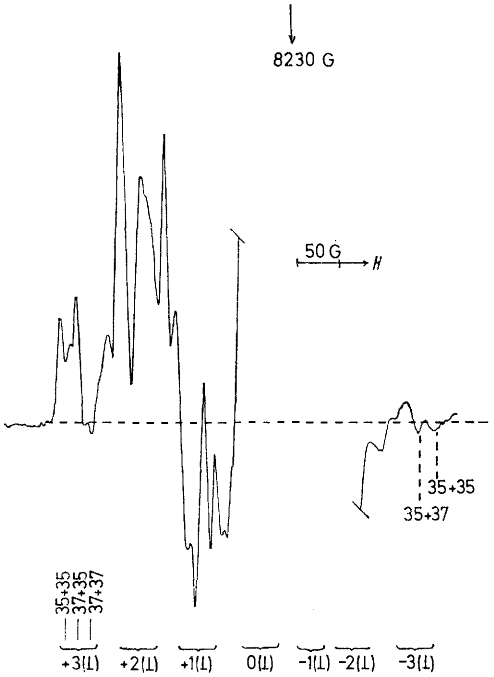

FIGURE 1 First derivative X-band e.s.r. spectrum for methylene chloride after exposure to ^{60}Co γ-rays at 77 K for 0.5 h, showing features assigned to $H_2CCl_2^+$ radicals

E.s.r. spectra were obtained at 77 K directly after exposure, on a Varian E3 spectrometer. Samples were annealed by allowing them to warm above 77 K *in situ* in the empty insert Dewar, and were recooled to 77 K whenever significant spectral changes were detected. When necessary, a Varian variable temperature insert was used in addition to the above procedure.

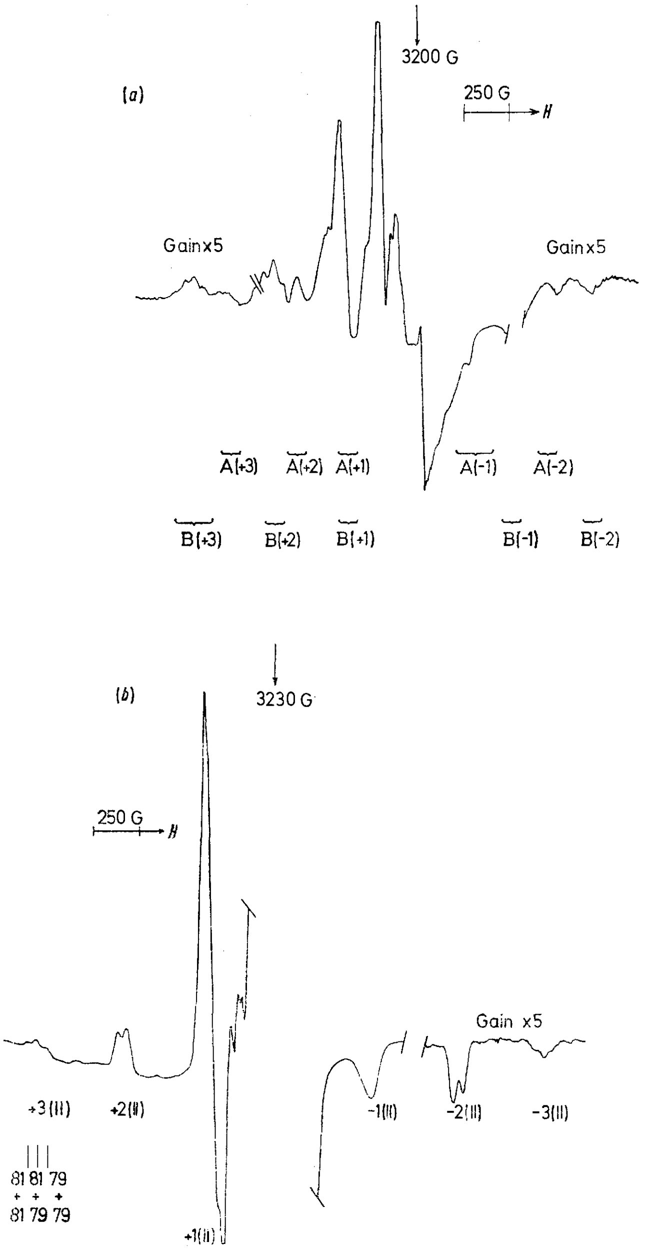

FIGURE 2 First derivative X-band e.s.r. spectra for 2,3-dibromobutane after exposure to ^{60}Co γ-rays at 77 K for 1.0 h, (*a*) showing features (A) assigned to librating Br_2^- ions and (B) assigned to $[MeCH(Br)CH(Br)CHMe]^+$ cations, and (*b*) in CD_3OD glass, showing features for non-librating Br_2^-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

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RESULTS AND DISCUSSION

The central ($g = 2$) spectral region was generally dominated by features from alkyl radicals or their halide ion complexes [9] and by α-halogeno-radicals.[6] In some instances features for β-halogeno-radicals were also detected in the wings of the central lines.[5] Many of the features for dihalide anions and related species were well separated on the low-field side of these intense central signals, as shown in Figure 1—3. The most intense lines are found *ca.* 100 G downfield 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. They 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.

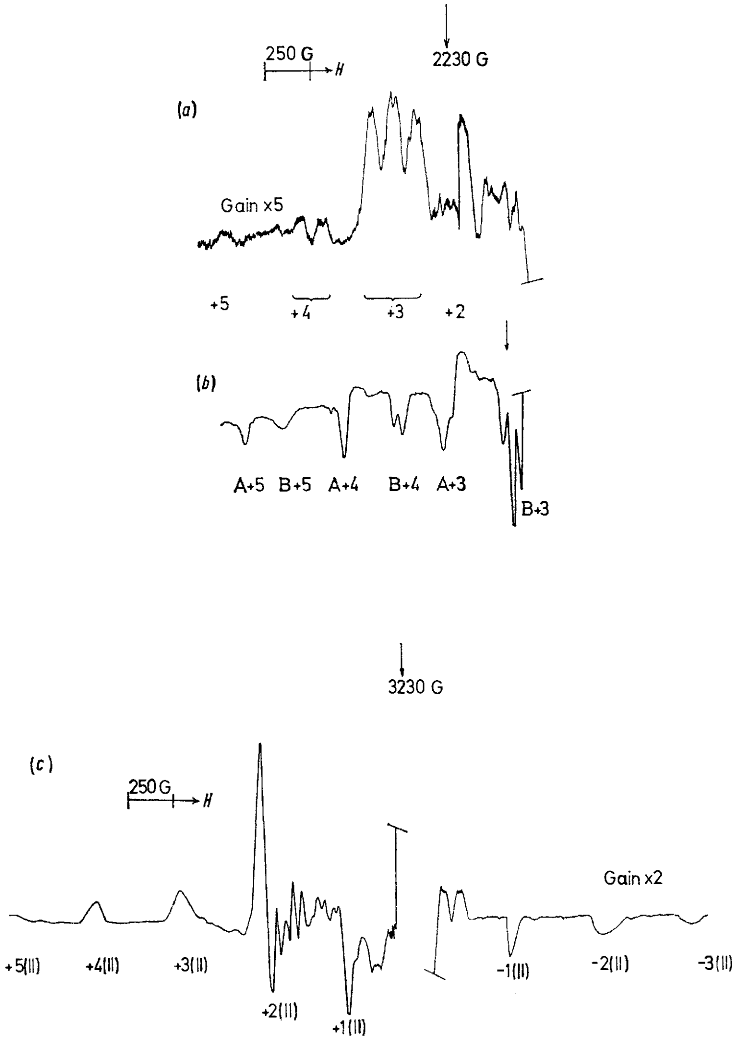

FIGURE 3 First derivative *X*-band e.s.r. spectra for (*a*) methyl iodide glass after exposure to ^{60}Co γ-rays at 77 K for 1.0 h, showing low-field features indicative of two inequivalent iodine atoms, assigned to MeI–I, (*b*) for ethyl iodide showing similar low-field features assigned to (A) $EtI–IEt^+$ and (B) EtI–I, and (*c*) for 1,2-di-iodoethane in CD_3OD after exposure to ^{60}Co γ-rays at 77 K for 1.0 h, showing features for non-librating I_2^-. (The M_I values for the parallel features are labelled, the -4 and -5 features being too weak to detect)

Alkyl Chlorides.—Pure monochlorides or their solutions in methanol (or CD_3OD) gave no low-field features. 1,1-dichloromethane (and especially CD_2Cl_2) gave intense features (Figure 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 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 (2.03) is far greater than that for Cl_2^- ($g \doteqdot 2.000$). One possible explanation for these features is that Cl_2^- has been formed by dissociative electron capture (2). However,

$$H_2CCl_2 + e^- \longrightarrow H_2C + Cl_2^- \qquad (2)$$

such an elimination seems rather improbable in view of the very 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.

An alternative explanation is that the cation $H_2CCl_2^+$ is responsible for these features. Powder spectra for this cation would show strong features for fields along the symmetry axes [see (1)]. Thus $A_x = A_\perp$, and $g_x = g_\perp$ but A_y and A_z fall between $A_\parallel$ and $A_\perp$ for a given chlorine atom. For $\theta = 90°$, $A_y = A_z = (A_\parallel + A_\perp)/2$. Since weak Cl–Cl bonding can occur, we think 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 would 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, we have arrived at the analysis indicated in Figure 1. Using the relationship for $A_y + A_z$ given above, we calculate the 'true' parameters for ^{35}Cl to be $A_\parallel \doteq 116$ and $A_\perp \doteq 14$ G. Also $g_\parallel \doteq 2.000$, in good accord with expectation.

As a check on the reasonableness of these parameters, the hyperfine data have been used to derive approximate orbital populations in the usual manner, using $A°$ (^{35}Cl) $\doteq$ 1 680 and $2B°$ (^{35}Cl) $\doteq$ 100 G, whence $a^2(3s) \doteq 2.9$ 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 overestimate of the total spin density on chlorine.[10,13]

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

$$ClCH_2CH_2Cl + e^- \longrightarrow CH_2{=}CH_2 + Cl_2^- \qquad (3)$$

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 for Cl_2^- in an alkali chloride crystal in the Table. (Since we are concerned with identification of species rather than with the derivation of accurate parameters, we have not, in general, attempted 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,[13] but it is essential to study single crystals in order to obtain reliable perpendicular parameters.)

E.s.r. parameters for Cl_2^-, Br_2^-, I_2^-, and some related radicals formed in irradiated alkyl halides

		Hyperfine coupling (G) [a]			*g* Values	
Host	Radical	$A_\parallel$	$A_\perp$	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
$ClCH_2CH_2Cl$	Cl_2^- [c]	98			2.0010	
$ClCH_2CH_2Cl + CD_3OD$	Cl_2^-	102			2.0010	
$H_2O + Br^-$	Br_2^- [d]	470	85	195	1.98	2.09
$BrCH_2CH_2Br$	Br_2^- [c]	345			2.03	
$BrCH_2CH_2Br$	$(C_2H_4Br_2)^+$ [e]	430			2.00	
$BrCH_2CH_2Br + CD_3OD$	Br_2^-	480	85	217	1.98	2.11
Bromoadamantane	*g*	380	83	182	2.00	2.154
t-Butyl bromide	$(Me_3CBr)_2^+$	505			2.00	
$H_2O + I^-$	I_2^- [d]	433	120	193	1.975	2.175
ICH_2CH_2I	I_2^- [c]	390			2.00	
ICH_2CH_2I	$(C_2H_4I_2)^+$ [f]	420			1.99	
$ICH_2CH_2I + CD_3OD$	I_2^-	450			1.98	
CH_3I	$(CH_3I)_2^+$	410			1.98	
CH_3I	CH_3I_2	I_1 430 I_2 530			*ca.* 1.97	
EtI	$(EtI)_2^+$	400			1.98	
EtI	EtI_2	I_1 420 I_2 485			*ca.* 1.97	
$H_2O + I^-$	IOH^- [d]	480	70	207	1.98	2.13
ICH_2CO_2H	IOH^- or IO^{2-}	430	100	210	1.97	2.17
ICH_2CH_2OH	IOH^-	420	100	207	1.97	2.16

[a] G = 10^{-4} T. [b] Ref. 10. [c] Librating: Hence A and *g*-values are partially averaged. [d] Ref. 13. [e] Or $(C_2H_4Br_2)_2^+$. [f] Or $(C_2H_4I_2)_2^+$. [g] See text. $A(^1H?) = 65$ G.

Neither 1,3- nor 1,4-dichlorides gave Cl_2^-. Thus it seems that the electron capture process (3) is efficient because of the stability of the non-radical product. The balance between processes (1) and (3) must be very subtle, as is often found in radiation studies.[16] With methylene chloride, process (1) gave $H_2\dot{C}Cl$ ($D_2\dot{C}Cl$) both in the pure material and in methanol. In the pure material clear features for $H\dot{C}Cl_2$ radicals were also detected. This species may well be formed from the primary cations [reaction (4)] but methanol completely

$$H_2CCl_2^+ + H_2CCl_2 \longrightarrow H\dot{C}Cl_2 + H_2CCCl(ClH)^+ \qquad (4)$$

suppresses radical cation formation, by acting as a powerful hole-trap.

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[16] S. P. Mishra and M. C. R. Symons, *J.C.S. Chem. Comm.*, 1974, 606.

Alkyl Bromides.—Monobromides invariably gave broad low-field features in the regions expected for dibromo-radicals of the type under consideration but these were generally too broad to permit analysis. (A fairly clear spectrum for this species is shown in Figure 2a.) We suggest that these species are hole-centres, because their formation is suppressed in methanol matrixes 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.

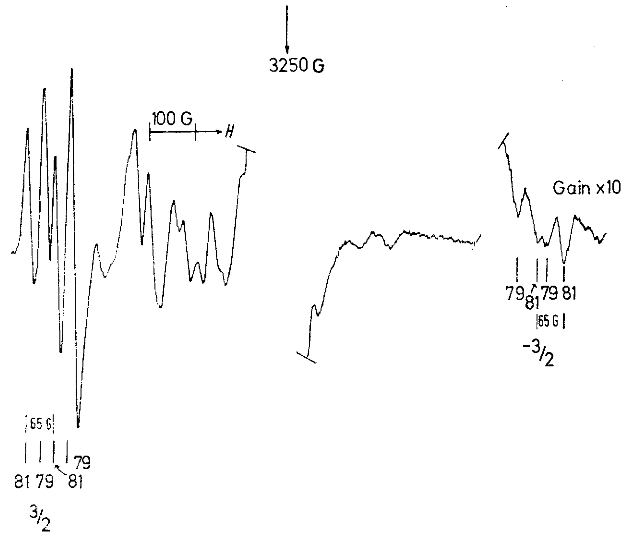


FIGURE 4 First derivative X-band e.s.r. spectrum for 1-bromoadamantane after exposure to ^{60}Co γ-rays at 77 K for 1.0 h, showing features for a monobromo-radical exhibiting an extra doublet splitting of 65 G (see text)

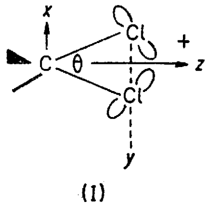
We would not expect to be able to detect the parent cations, RBr^+, because the unpaired electron is in a degenerate π-orbital largely confined to bromine, and hence the cation will exhibit orbital magnetism which will depend strongly on the extent to which this is quenched by intra- or inter-molecular interactions. Attempts to detect RBr^+ or RI^+ radicals in rigid inert media such as methylcyclohexane failed. Only in the case of 1-bromoadamantane were we able to detect a monobromo-radical with the required properties (Figure 4). [^{81}Br and ^{79}Br have approximately equal populations and $I = \frac{3}{2}$. The magnetic moment for ^{79}Br is slightly smaller than that for ^{81}Br. Two equivalent bromine atoms thus give rise to seven features, each being sub-divided into multiplets by the different isotopic contributions and by a second-order (Breit–Rabi) splitting.] This bromide gave no dibromo-radicals, in contrast with the other monobromides. Also, an intense violet colour associated with irradiated bromides whenever low-field dibromo-features were observed was absent, irradiated bromo-adamantane being an intense orange colour after irradiation. We suggest that the violet species is $RBr{-}BrR^+$ and that the parent cations RBr^+ have their first electronic transition at higher energies.

Two problems arise: what is the source of the well defined quenching of orbital angular momentum for the adamantane species, and what causes the doublet splitting of *ca.* 65 G, evident in the first and last features in the e.s.r. spectrum (see Figure 4)? It could be convenient to suggest that a proton is responsible for both these effects, but we are unable to understand how this can arise, and have no reasonable explanation at present.

We would expect, on chemical grounds, that RBr^+ in the presence of RBr would react and form a σ^* radical, structurally similar to Br_2^- and to the disulphide radical anions, $RS{-}SR^-$. We suggest that this is the normal hole-centre for the pure alkyl bromides, although proton loss to give α-bromo radicals will compete (especially in the presence of basic solvents) [reaction (5)]. Both species are generally detectable.

$$R_2CHBr^+ + R_2CHBr \longrightarrow R_2\dot{C}Br + R_2CHBrH^+ \quad (5)$$

The only reasonable alternative to $RBr{-}BrR^+$ 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 use), strong features for Br_2^- were obtained, and these differed from those assigned to the dimer cations in that '$A_\parallel$' was markedly reduced from the normal values for Br_2^- and '$g_\parallel$' 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, we suggest that Br_2^- radicals are librating in a well defined manner at 77 K in the alkyl bromide media. Hence the species formed in the pure bromides cannot be Br_2^-. The other possibility, $RBr{-}Br$, 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 $M_I = \pm 3$ lines would be split to a greater extent than the normal Breit–Rabi splitting, and the 1:2:1 triplet features of the $M_I = \pm 3$ lines would become 1:1:1:1 quartets.]

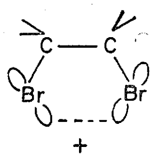


(I)

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

gem-*Dibromides*. Only very poorly defined low-field features were obtained. These 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*. Both in the pure compounds and in methanolic solutions, features for dibromo-radicals were obtained. We conclude that a reaction similar to (3) occurs efficiently. For the pure materials the Br_2^- radicals are librating at 77 K, and a second dibromo-species is 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 (II) rather than being formed intermolecularly, which may account for the relatively well defined nature of the e.s.r. spectrum.



(II)

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

Alkyl Iodides.—In several instances, in addition to the species containing two equivalent iodine atoms which are presumed to be $RI{-}IR^+$, a similar species containing two inequivalent iodine atoms was detected (see Figure 3a). (^{127}I has $I = \frac{5}{2}$; two equivalent iodine atoms therefore give rise to 11 features, which 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. Our results show conclusively that the unpaired electron is fairly evenly distributed between the two iodine atoms, and that a molecular description is required.

Once again, an elimination analogous to (3) seems to be important for *vic*-di-iodides, since I_2^- formation was clearly detected by e.s.r. spectroscopy (see Figure 4). For certain iodides we have detected well-defined mono-iodo σ^* radicals, the best defined being from 2-iodoethanol (Figure 5). In this instance we suggest that the species is IOH^-, formed by dissociative electron capture (7). The IOH^- radical has been detected during the

$$ICH_2CH_2OH + e^- \longrightarrow IOH^- + CH_2 = CH_2 \qquad (6)$$

radiolysis of aqueous iodide solutions,[13] and the e.s.r. parameters for ^{127}I in the two species are very similar (Table).

A very similar species was obtained from iodoacetic acid when in methanolic glasses (Figure 5). We originally thought that this species was formed from the solvent, by iodine atom attack [reaction (7)]. However,

$$I\cdot + MeOH \longrightarrow MeOI^- + (H^+) \qquad (7)$$

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 (8). This is supported by the observation that broad features assignable 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.

$$ICH_2CO_2^- + e^- \longrightarrow H_2C{=}C{=}O + IO^{2-} \qquad (8)$$

Elimination of hal_2^-.—In order to check the validity of reactions such as (3) and (6), we studied 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^- with no trace of $BrCl^-$.

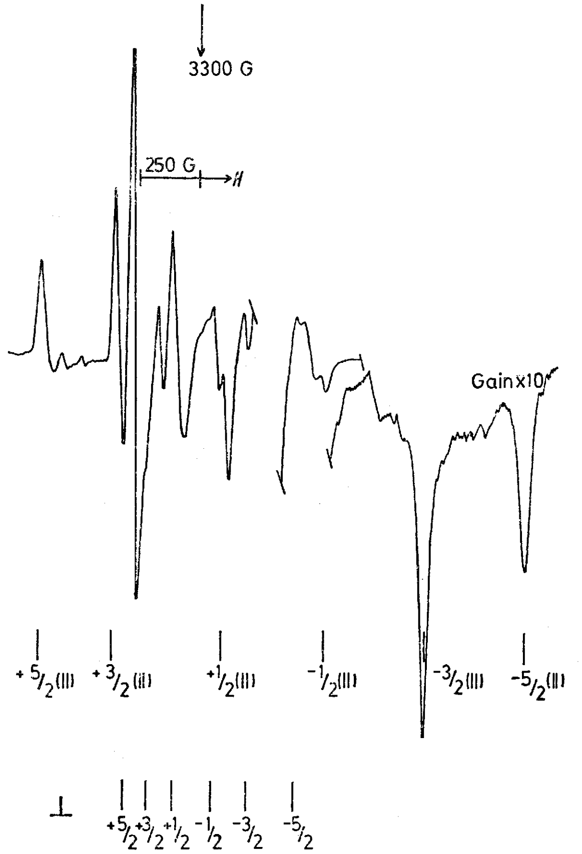


FIGURE 5 First derivative *X*-band e.s.r. spectrum for iodoacetic acid in CD_3OD after exposure to ^{60}Co γ-rays at 77 K for 1.0 h, showing features assigned to IO^{2-} or IOH^-. (Only the parallel features for ^{127}I are indicated)

It is possible that processes such as (3) occur in two stages [(9) and (10)]. Certainly $R_2C(hal){-}\dot{C}R_2$ radicals

$$R_2C(hal){-}R_2C(hal) + e^- \longrightarrow R_2C(hal){-}\dot{C}R_2 + hal^- \quad (9)$$

$$R_2C(hal){-}\dot{C}R_2 + hal^- \longrightarrow R_2C{-}CR_2 + hal_2^- \quad (10)$$

are good halogen atom donors. However, they have been detected in several e.s.r. studies [5,6,17-20] and it seems to us unlikely that the β-chloro-radicals would react readily with chloride ion at 77 K. We, therefore, favour the extrusion process (3).

Hole Centres.—All these hole centres have been postulated by Hamill and his co-workers on the basis of their optical studies of irradiated alkyl iodides and their solutions in hydrocarbon glasses.[21] 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, $RI\text{-}IR^+$. Intermediate bands at 390 and 480 nm were assigned to RI–I.[21] Our results confirm the presence of the latter two species. The dimer cations have also been detected by Hamill *et al.* in their mass-spectrometric studies of alkyl iodides,[22,23] and the neutral species, RI–I, has also been reported in pulse radiolysis studies.[24]

Other Centres.—The 1,3-dihalogenopropanes and 1,4-dihalogenobutanes gave alkyl radicals ($H_2\dot{C}CH_2CH_2Hal$ and $H_2\dot{C}[CH_2]_3Hal$) having e.s.r. spectra at 77 K which was identical with those for the corresponding hydrocarbon radicals. These results confirm the conclusion of Chen *et al.*[25] that there is no significant cyclic interaction between the radical centres and remote halogen atoms.

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