Radiation Mechanisms. Part 21.[1] Electron Spin Resonance Studies of the Effect of Ionising Radiation on Halogenobenzenes: the Formation of σ* Anions and *ipso* Addition Radicals

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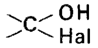
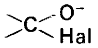
Various chloro-, bromo-, and iodo-benzene derivatives have been exposed to ^{60}Co γ-rays as pure materials and in a range of solvents at 77 K and the radical products have been studied by e.s.r. spectroscopy at this temperature before and after annealing. Two important types of radical have been characterised. Electron addition to certain bromo- and iodo-derivatives gave e.s.r. features characteristic of σ* radicals, the excess electron being largely localised to the C–Hal σ* orbital. It was previously thought that only π* anions of this compound were stable under these conditions. We suggest that the σ* anions are precursors to dissociative electron capture. Competing with σ* anion formation in certain cases was π* anion formation followed by ring protonation. However, the normal substituted cyclohexadienyl radicals with two interacting protons in a $>CH_2$ group were not detected. Instead PhBr and PhI gave radicals containing $>CH{-}Hal$ groups, exhibiting strong hyperfine coupling to one proton and the halogen nucleus. Use of deuteriated compounds and solvents showed complete scrambling of the ring protons, probably induced by migration of the halogen atoms. *para*-Bromo- and -iodo-phenol gave hydrogen atom adducts containing  $>C\begin{smallmatrix}OH\\Hal\end{smallmatrix}$ or  $>C\begin{smallmatrix}O^-\\Hal\end{smallmatrix}$ groups, with no strongly coupled protons. We suggest that halogen atom migration led to their formation and hence that these *ipso*-structures are more stable than the alternative $>CH_2$ or $>CH{-}Hal$ structures. E.s.r. parameters for phenyl radicals having *para*-iodo or *para*–O⁻ substituents were similar to those for normal phenyl radicals.

AROMATIC compounds are usually very resistant to damage by ionizing radiations. This is probably because in the pure state they can transport excess electrons and 'holes' relatively efficiently because of overlap of the π orbitals involved and because neither electron loss nor electron gain results in major changes of geometry for the cyclic systems. This means that deep traps do not form readily and hence electron return is usually favoured.

The radicals most commonly detected by e.s.r. spectroscopy in irradiated aromatic systems are cyclohexadienyl type radicals (I),[2] in which the unpaired electron interacts strongly with the two methylene protons, and phenyl type radicals (II) which exhibit strong interaction with *ortho*-protons, weak coupling to *meta*-protons, and very weak coupling to *para*-protons.[3] Hart and his co-workers[4] showed that electron attachment to benzene in aqueous solution was followed rapidly by protonation [reaction (1)] and it is probable that an

(I)

(II)

$$C_6H_6 + e^- \longrightarrow C_6H_6^- \xrightarrow{H_2O} C_6H_7^{\cdot} + OH^- \quad (1)$$

important route to cyclohexadienyl radicals is anion protonation. However, electron return followed by bond homolysis, hydrogen atom migration and subsequent addition is certainly a major process in many systems [reactions (2)—(4)]. Under these circumstances hydrogen atom capture by neighbouring molecules is to be expected, leading to pair-trapping. Recently Matsuyama and his co-workers[5,6] have established by

$$C_6H_6 \longrightarrow C_6H_6^+ + e^- \quad (2)$$

$$C_6H_6^+ + e^- \longrightarrow (C_6H_6)^* \longrightarrow C_6H_5^{\cdot} + H^{\cdot} \quad (3)$$

$$C_6H_6 + H^{\cdot} \longrightarrow C_6H_7^{\cdot} \quad (4)$$

e.s.r. spectroscopy that such pair trapping is indeed important in many aromatic systems including halogen-substituted aromatic compounds when irradiated in the pure state.

These difficulties can to some extent be avoided by using dilute solutions of the aromatic compounds in certain solvents. Solvents such as methyltetrahydrofuran (MeTHF) or tetramethylsilane (TMS) are useful for the observation of electron addition products by e.s.r. spectroscopy. The solvents themselves readily form and trap electron-loss centres, but do not react with the ejected electrons, which therefore seek out reactive solute molecules. If protic media are used, these may facilitate dissociation rather than electron addition, because of their good anion solvating ability. However, they may also cause protonation of radical anions, as indicated in reaction (1). Since electron return is largely inhibited, radical yields are much higher than for the pure compounds.

In an extensive study of substituted aromatic compounds[7] we have found that for most compounds, π* radical anions, cyclohexadienyl radicals, and phenyl-type radicals dominate the radical products as judged by e.s.r. spectroscopy. However, for certain halogen derivatives, we have detected σ* radicals as primary products. We have also shown that normal cyclohexadienyl radicals (I) containing methylene ($>\!\mathrm{CH_2}$) groups are not formed, radicals (III) containing ($>\!\mathrm{C}<^{\mathrm{R}}_{\mathrm{Hal}}$) units being favoured.[8]

By σ^* radicals, we mean those in which the unpaired electron is accommodated in suitable σ^* orbitals. In the present examples the excess electrons are largely confined to localised carbon–halogen σ^* orbitals, as indicated by the e.s.r. parameters. There are now many examples in which electron capture into σ^* orbitals competes favourably with the more expected capture into suitable π^* orbitals. For example N≡C–Br gave the linear σ^* anion $\mathrm{N{\equiv}C{-}{\cdot}Br^{-}}$[9] and Ph–C≡C–I gives $\mathrm{Ph{-}C{\equiv}C{-}{\cdot}I^{-}}$.[10] *N*-Bromo- and *N*-iodo-amides similarly accept excess electrons into their N-Hal σ^* orbitals.[11,12] Two particularly pertinent examples are the formation of σ^* radicals by bromo- and iodo-uracils, but not by the corresponding chloro- or fluoro-derivatives,[13] and the formation of $\mathrm{C{-}{\cdot}Hal^{-}}$ σ^* anions for C_6F_5I,[14] C_6F_5Br, and related compounds.[15]

Our technique for forming and studying these radicals is a form of matrix isolation in which immobility confers stability. Subsequent reactions of the initially trapped radical products can be studied readily by careful annealing above the temperature of irradiation, which is normally 77 K. This can be described as temperature-resolved spectroscopy and complements the more popular time-resolved techniques. Namiki has used this technique, with optical and e.s.r. spectroscopic detection methods, to study ethanolic solutions of halogenated benzene and naphthalene derivatives irradiated at 4 K.[16] The results are most pertinent to the present study. They are outlined and discussed below. Using pulse radiolysis and conductometric techniques, it was concluded that aqueous solutions of halogenated compounds uniformly react with aquated electrons to give halides ions.[17] Product analysis for *p*-bromophenol led to the same conclusion.[18]

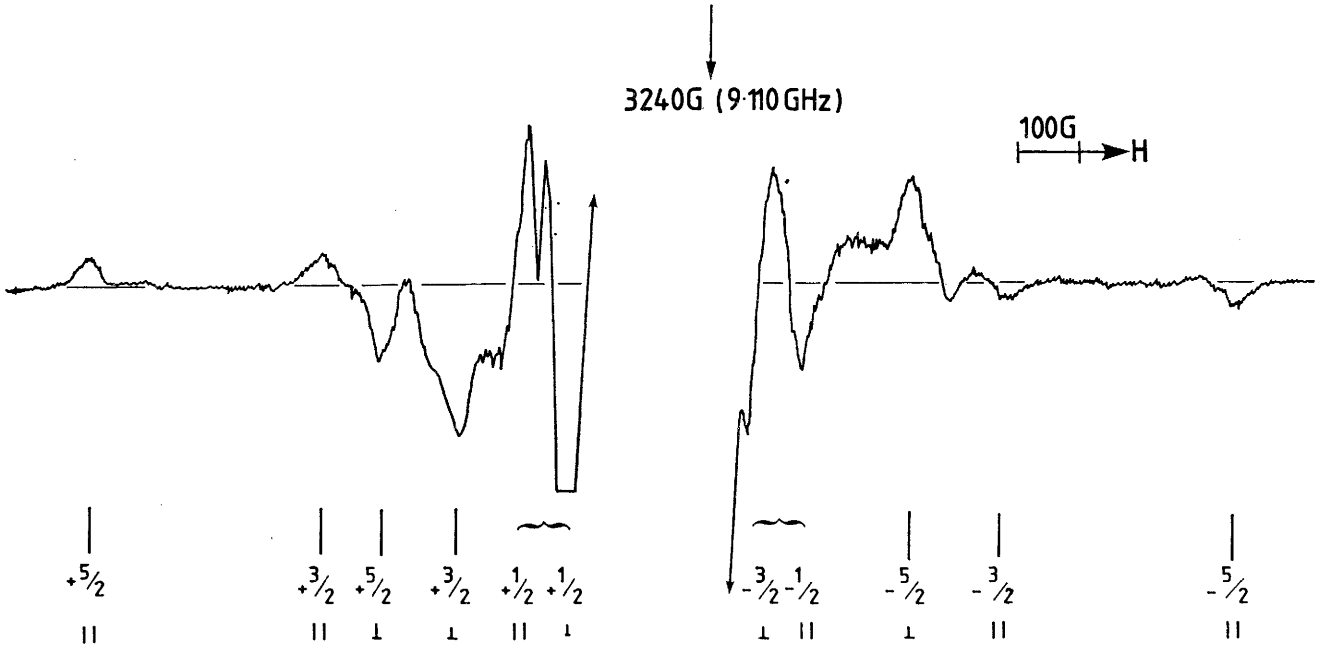


FIGURE 1 First derivative X-band e.s.r. spectrum for *p*-iodophenol after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $\mathrm{HOC_6H_4{-}{\cdot}I^{-}}$ σ^* anions. Intense central features for solvent radicals have been omitted

EXPERIMENTAL

Halogenated benzene derivatives (B.D.H., Aldrich, and Kodak) were the best available grades and were generally used as supplied. Purity was checked by proton resonance measurements. [$^2H_4$]Methanol, [$^2H_3$]cyanomethane, and [$^2H_8$]toluene (NMR Laboratory) were also used as supplied. Adamantane (Aldrich, B.D.H.) was sublimed prior to use.

Dilute solutions of the halogenated derivatives in selected solvents (*ca.* 0.01 mole fraction) were rapidly frozen to 77 K as small glassy beads and exposed to ^{60}Co γ-rays in a Vickrad source with doses up to *ca.* 1 Mrad.

E.s.r. spectra were measured at 77 K on Varian E 3 or E 109 spectrometers.

RESULTS AND DISCUSSION

In all cases, intense, poorly resolved features were obtained in the central (*g* 2) region of the e.s.r. spectra. With the exception of *p*-iodophenol, the pure materials gave no other features. However, *p*-iodophenol (Figure 1) and other bromo- and iodo-derivatives in various solvents exhibited features well removed from the *g* 2 region. As with other halogenated organic systems,[19,20] these outer features seem to have been missed by other workers in the field, probably because they are much weaker than the central features. This weakness arises because of the large anisotropy of the features and their relatively great widths: attempts at assessment of yields, although inaccurate, show that these species are formed in yields comparable with those of other substrate radicals.

Two types of radicals with strongly interacting bromine or iodine nuclei were obtained, which we designate A and B. The A features can be analysed in terms of a maximum hyperfine coupling to bromine nuclei of *ca.* 200 G and to iodine nuclei of *ca.* 340 G. (Table 1). The B features correspond to maximum bromine and iodine coupling constants of *ca.* 100 G (Table 2).

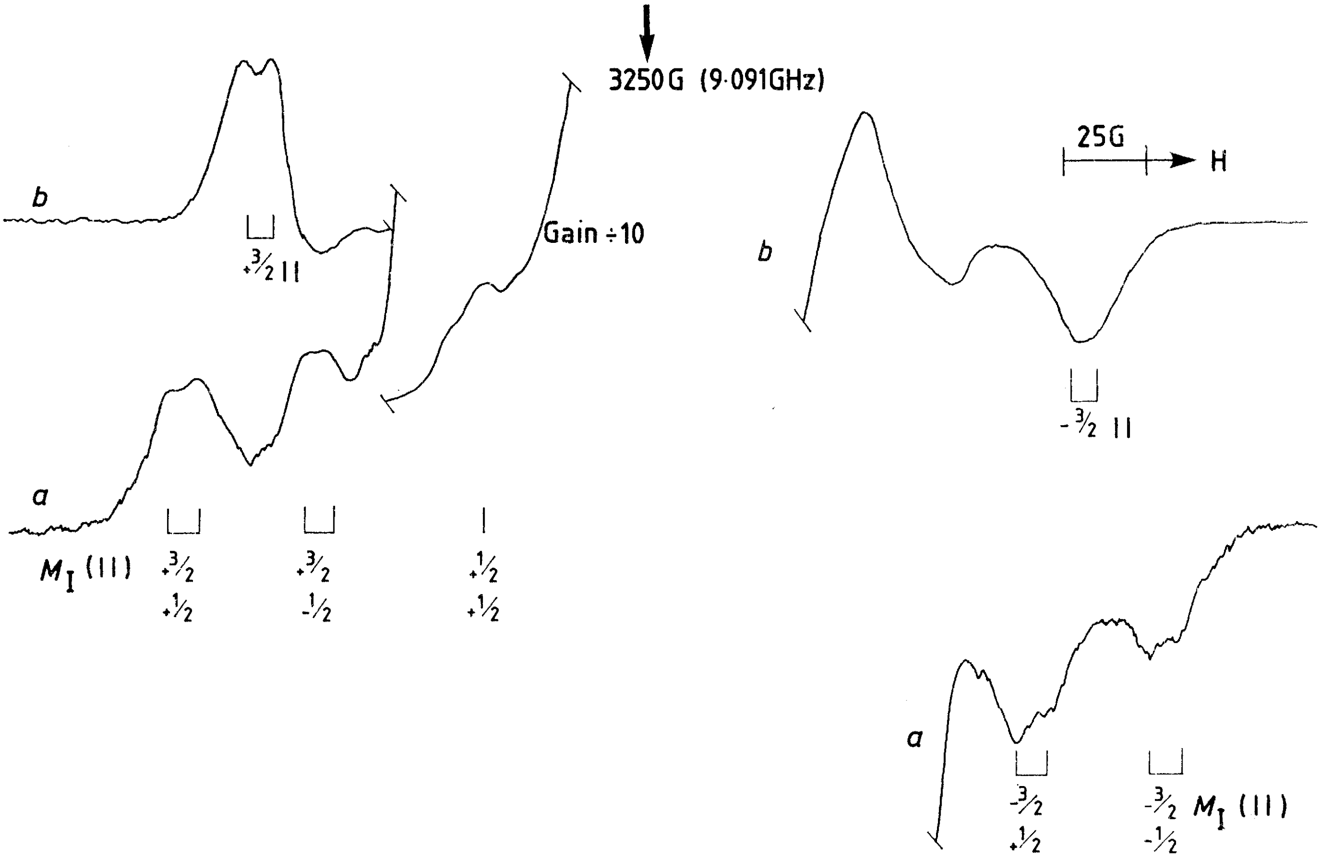


FIGURE 2 First derivative X-band e.s.r. spectra for bromobenzene in methanol after exposure to ^{60}Co γ-rays at 77 K showing features assigned to cyclohexadienyl-type radicals (III): *a*, C_6H_5Br in CD_3OD; *b*, C_6D_5Br in CD_3OD. Spectra for C_6H_5Br in CH_3OH resembled *a*, and those for C_6D_5Br in MeOH resembled *b*

The overall form of the A features is similar to that observed for $F_3C^{-}{\cdot}Hal^{-}$ anions.[21] Analysis leads to the stick diagrams indicated in the Figures and hence to the data in Table 1. The line positions agree well with prediction based on these data, using the Breit–Rabi equation.[22,23] ^{79}Br and ^{81}Br have I 3/2, similar magnetic moments, and almost equal populations: separate components were not resolved in these studies because of the large linewidths. For the same reason ^{1}H superhyperfine splitting was not resolved. The hyperfine interaction is so large that quadrupole effects on the line positions are subtle and could not be detected in the broad powder spectra. Yields for the iodo-derivatives were always greater than those for the bromo-derivatives. It is noteworthy that for the iodo-derivatives, species A gives rise to an intense, almost isotopic feature (M_I +1/2) at *ca.* 200 G downfield from the centre (g 2.002 3).

The B-centres give broad parallel (Z) components but especially for the bromo-derivatives, the x or y components appear as relatively well defined multiplets (Figure 2). Since both the z and the resolved features (Figure 3) have g values close to 2 and since the M_I + features are again the more intense, it seems probable that the x and y components do not coincide. Unfortunately we have not been able to resolve a third set of features, and in subsequent analyses of the data, treat the hyperfine parameters as if they had axial symmetry. We stress that the resulting data are only rough approximations, although they give a reasonable first-order view of the structures of these radicals.

σ^* *Anions.*—We are convinced that species A are σ^* radicals having the excess electron largely confined to localised C–Hal σ^* orbitals. The data given in Table 1 are compared with those for other well established σ^* radicals. The results for the iodo-anions have been corrected for orbital magnetic contributions using the relationships (5) and (6).[12,23] This correction is insignificant for the bromo-radicals.

$$A_{\parallel}(\mathrm{MHz}) = A_{\mathrm{iso.}} + 2B \qquad (5)$$

$$A_{\perp}(\mathrm{MHz}) = A_{\mathrm{iso.}} - B(1 - \tfrac{5}{2}\Delta g_{\perp}) \qquad (6)$$

The data have been converted in the usual way into approximate *s*- and *p*-orbital populations on bromine and iodine. We have used the A° and $2B^{\circ}$ data which are normally accepted,[23] but stress that these parameters are open to question.[24] Using alternative parameters does not affect our qualitative conclusions. The results show that the orbital involved is essentially *p*-type on halogen. The spin densities are remarkably close to those for the $\mathrm{F_3C{-}{\cdot}Br^-}$

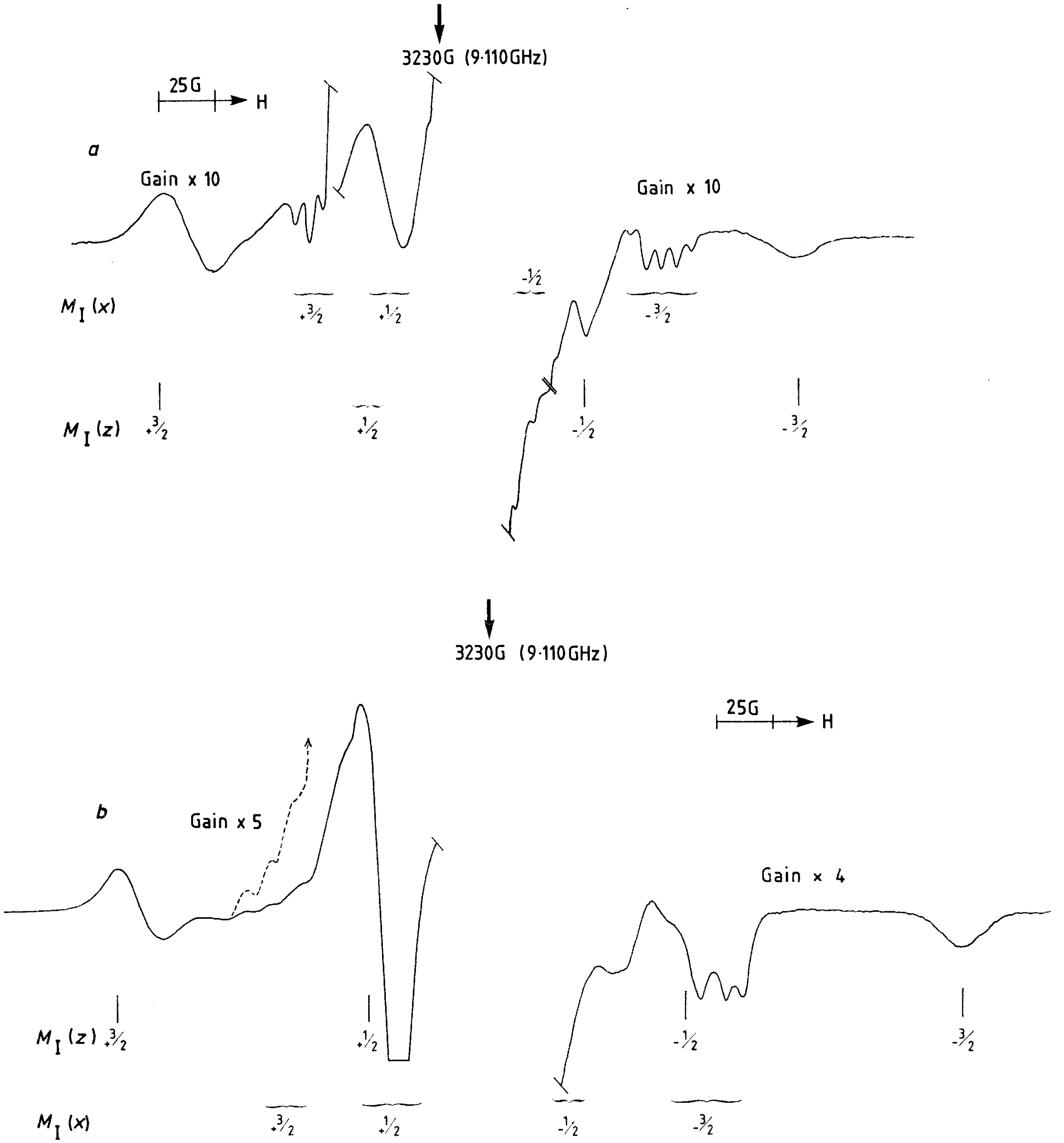


FIGURE 3 First derivative X-band e.s.r. spectra for *p*-bromophenol after exposure to ^{60}Co γ-rays at 77 K: *a*, in NaOD–D$_2$O, showing features assigned to $\mathrm{H_5C_6^{\bullet}}\!<\!\substack{\mathrm{Br}\\ \mathrm{O^-}}$ anions; *b*, in 90% H_2SO_4, showing features assigned to $\mathrm{H_5C_6^{\bullet}}\!<\!\substack{\mathrm{Br}\\ \mathrm{OH}}$ radicals

and $F_3C\text{–}{\cdot}I^-$ anions,[21] and only *ca.* half those for their perfluoro-analogues, $C_6F_5^{-}{\cdot}Br^-$ and $3_6H_5\text{–}{\cdot}I^-$.[14,15] It would be interesting to include the methyl derivatives (Me–Hal⁻) in this comparison, but unfortunately it seems that alkyl halides are unlikely to form σ^* anions as such, forming instead, weak charge-transfer adducts.[20,25–27] The large difference between C_6H_5 and C_6F_5 derivatives must reflect in part the large electronegativity of fluorine. This tends to pull the σ bonding electron pair onto carbon and hence to push the σ^* electron onto halogen. However, the effect is surprisingly large for relatively remote substituents, and we suggest that it may also reflect a smaller ability for the perfluoro ring system to distort as the bond angle θ tries to increase in the unit $\theta(\begin{smallmatrix}C\\C\end{smallmatrix}{>}C\text{–}{\cdot}Hal^-)$. This increase in θ, by analogy with the flattening of methyl radicals, makes the orbital on carbon lose *s* and gain *p* character and this makes the excess electron favour carbon because of the antibonding character of the orbital.

TABLE 1

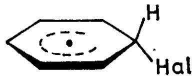
E.s.r. data for some σ^* radicals

Source–solvent	Radical	Halogen hyperfine coupling (G) [a,b] $A_{\parallel}$	$A_{\perp}$	$A_{iso.}$	*g* Values $g_{\parallel}$	$g_{\perp}$	a_s^2 [c] (for halogen)	a_p^2 [d]
PhBr–Toluene MeTHF	$Ph\text{–}{\cdot}Br^-$	193	80	117.7	2.000	2.030	1.4	15.3
HOC_6H_4I	*p*-HOC_6H_4	365	172	236	2.000	2.065	3.2	28
IC_6H_4I–MeTHF	*p*-$IC_6H_4{\cdot}\text{–}I^-$	340	154	216	2.000	2.065	2.9	27
C_6F_5Br [d]–MeTHF	$C_6F_5{\cdot}\text{–}Br^-$	503	180	288	2.000	2.047	3.5	43.6
C_6H_5I [d]–MeTHF	$C_6F_5{\cdot}\text{–}I^-$	540	230	333	2.000	2.10	4.5	45.6
CF_3Br [e]–TMS	$F_3C{\cdot}\text{–}Br^-$	263.6	114.2	164	2.0036	2.0212	1.95	20.1
CF_3I [e]–TMS	$F_3C{\cdot}\text{–}I^-$	373.1	178.8	243.6	2.0002	2.048	3.33	28.5

[a] G = 10^{-4} T. [b] Data derived using the Breit–Rabi equation: results for iodine derivations corrected for orbital magnetism. [c] Calculated using A° = 8 341 G (^{81}Br); 7 295 G (^{127}I). [d] Calculated using $2B^\circ$ = 494 G (^{81}Br); 453 G (^{127}I). [e] Ref. 21.

Cyclohexadienyl Radicals.—Despite their prevalence in other systems, we have never detected the characteristic features for normal cyclohexadienyl-type radicals (I) which comprise a large 45—50 G triplet for the CH_2 protons, further split by the ring protons. We suggest that species B is formed preferentially having structure (III). This accounts for the relatively large coupling to bromine or iodine, and for the *ca.* 40 G coupling to a single proton (Figure 2). These radicals may be formed by direct hydrogen atom addition, but they are major species in protic media, and it is most probable that they are then formed by electron capture followed by protonation.

When C_6H_5Br was irradiated in CD_3OD, the large 40 G splitting was retained, although the resolution was reduced. However, when C_6D_5Br was studied in CD_3OD, these doublet features were replaced by broad singlets (Figure 2b). The small coupling (*ca.* 6 G) expected for ^2H was lost in the linewidths. When C_6D_5Br was studied in CH_3OH, singlet features were again observed, although poorly defined shoulders indicative of a low yield of the 40 G doublet features were detected.



(III)

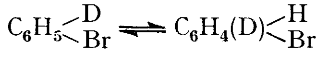
TABLE 2

E.s.r. data for some cyclohexadienyl radicals

Source–solvent	Radical	Hyperfine coupling (G) [a,b] Nucleus	A_z	A_x	*g* Values g_z	g_x	a_s^2 (Halogen)	a_p^2
$PhBr\text{–}CD_3OD$	$H_5C_6{\cdot}{<}\begin{smallmatrix}H\\Br\end{smallmatrix}$	^{81}Br	87	~45				
		^1H	38	38	2.000	2.003	0.7	5.7
		^1H		~7.5				
$HOC_6H_4Br\text{–}CD_3OD$	$H_5C_6{\cdot}{<}\begin{smallmatrix}O^-\\Br\end{smallmatrix}$	^{81}Br	93	50	2.000	2.003	0.8	6.2
		^1H		~7.5				
$HOC_6H_4Br\text{–}H_2SO_4$	$H_5C_6{\cdot}{<}\begin{smallmatrix}OH\\Br\end{smallmatrix}$	^{81}Br	113	63	2.000	2.003	0.9	6.7
		^1H		~7.5				
$PhI\text{–}CD_3OD$	$H_5C_6{\cdot}{<}\begin{smallmatrix}H\\I\end{smallmatrix}$	^{127}I	~80	~35	2.003	2.006	0.7	6.6
		^1H	~40	~40				
$HOC_6H_4I\text{–}CD_3OD$	$H_5C_6{\cdot}{<}\begin{smallmatrix}O^{\cdot}\\I\end{smallmatrix}$	^{127}I	86	40	2.002	2.007	0.7	6.7
$C_6H_4I_2$	$1H_4C_6{\cdot}{<}\begin{smallmatrix}H\\I\end{smallmatrix}$	^{127}I	~80	~35	2.003	2.006	0.7	6.6
		^1H	~40	~40				

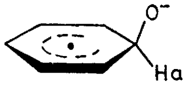
[a] G = 10^{-4} T. [b] Data corrected for zero-field effects. *A* Values *ca.* ±2 G, *g* values ±0.003. [c] Only *x* and *z* parameters obtained from spectra: in deriving a_s^2 and a_p^2 it is assumed that $A_y = A_x$.

The most probable explanation of these results is that the halogen atom is able to migrate around the ring at 77 K. Thus we envisage reactions of type (7). This will lead to a statistical distribution of H and D, and hence the intensity of the doublet feature will be *ca.* 0.1

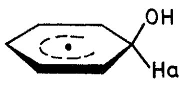


$$C_6H_5\overset{D}{\underset{Br}{<}} \rightleftharpoons C_6H_4(D)\overset{H}{\underset{Br}{<}} \qquad (7)$$

that of the singlet feature in this case. Similarly that of the singlet feature would be *ca.* 0.4 that of the doublet for D addition to C_6H_5Br. (These values will be somewhat increased and decreased respectively by the extra broadening for the unresolved ^2H hyperfine coupling: the point is that $C_6H_5Br + D\cdot$ will give rise to dominating doublets whilst $C_6D_5Br + H\cdot$ will have dominating singlets). Species B was also formed from *p*-bromo- and *p*-iodo-phenol. However, their spectra never showed any 40 G doublet splitting of the type found for the phenyl derivatives (Figure 2). We originally suggested that this implied either a delocalised π-complex structure or, since the halogen coupling constants are so similar, that the halogen atom migration [reaction (7)] was rapid on the e.s.r. time scale.[8] We now think that both these concepts are wrong, and that the true structure is the *ipso*-complex (IVa or b). When D is added these will have a *para*-D substituent. Analysis of the hyperfine features in this case suggests the loss of hyperfine coupling to one ring proton, thus supporting our assignment. Since this species is found in 10M-NaOH glasses as well as in CH_3OH or CD_3OD glasses, we favour structure (IVa). However, even in 6M aqueous H_2SO_4 glasses the spectra were identical. Using *ca.* 90% H_2SO_4 glasses a new spectrum was obtained (Figure 3b) with an increased coupling to $^{79/81}Br$ nuclei. We suggest that this is due to the conjugate acid (IVb). This result shows that (IVb) is a relatively strong acid, which accords well with the suggested structure.

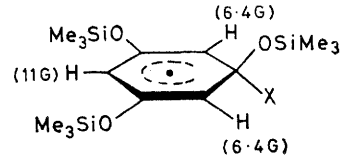


(IVa)



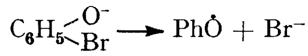
(IVb)

In order to cast light on this surprising preference for the *ipso*-structure, which must have been formed by halogen atom migration, as in (7), but with a clear preference for the *ipso*-site, we have looked for other examples in favour of such stability. It seems that during the past decade, organic chemists have come to realise that *ipso*-attack in aromatic substitution reactions is of considerable importance,[28] both in electrophilic and in homolytic [29] reactions. It seems probable that *ipso*-reactions of radicals are favoured by electronegative groups. Thus OH radicals favour addition to MeO–C sites rather than H–C or ^-O_2C–C sites [30] and Ar–S$^\cdot$ and Ar–$SO_3^\cdot$ radicals displace halogen from Ph–Hal, with F < Cl < Br < I.[31] However, Benati *et al.*[32] claim that aryl radicals will also attack in *ipso*-sites to some extent, with Br < Cl, and even allyl radicals can attack at the *ipso*-site of halogenobenzenes.[33] It is interesting in this context to note that in an e.s.r. study of radical (X) addition to 1,3,5-tristrimethylsiloxybenzene (ArH) Cookson *et al.*[34] suggested that all the radical adducts detected by e.s.r. were of the type $Ar\overset{X}{\underset{H}{<}}$. We suggest that some of the intermediates observed were formed by *ipso*-attack [as in (V): the numbers give the ^1H coupling constants in gauss], since 11 G is a remarkably small coupling for a proton in the $>C\overset{H}{\underset{X}{<}}$ group. If this is the case then alkoxyl radicals favour *ipso*-attack but aryl radicals favour attack on the C–H carbon atoms in this system. We conclude that there is plenty of evidence to support our contention that migrating halogen atoms can favour the *ipso*-site in the halogenated phenols, after the formation of hydrogen atom adducts.



(V)

The most probable subsequent reaction on annealing is (8). We have therefore studied our spectra on annealing above 77 K in the hope of detecting phenoxyl radicals. In our other studies [7] we have often obtained solid-state e.s.r. spectra for PhȮ radicals and hence are familiar with their e.s.r. spectra. Although central features were always complicated by other radical features, extra features in the required positions for PhȮ radicals were detectable in the NaOH glasses and we are reasonably satisfied that this reaction does occur.

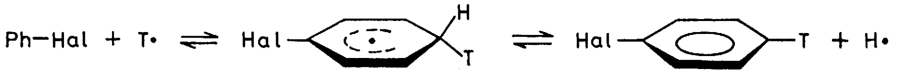


$$C_6H_5\overset{O^-}{\underset{Br}{<}} \longrightarrow Ph\dot{O} + Br^- \qquad (8)$$

This study impinges on the interesting results of Brett and Gold.[35] With respect to work on PhCl, PhBr, and PhI, their results for reactions with tritium atoms are (i) they react at about the same rate as with benzene, (ii) displacement of H by T is purely statistical, and (iii) halogen is also displaced, with I ≫ Br > Cl. They envisage two distinct processes (9) and (10) for displacements. The results are surprising in that some selectivity for hydrogen displacement would have been expected. Our results suggest that the cyclohexadienyl radical in reaction (7) is not formed in detectable amounts for bromo- or iodo-derivatives. We suggest that the only significant intermediate is (III) [*i.e.* that in reaction (10)] and that, because of bromine atom migration, there is a genuinely statistical distribution of H and T in this radical. In that case, the same intermediate can be invoked for loss of halogen or loss of hydrogen, and the observed statistical distribution of T in the halogen-substituted products is predicted.

Our results are also significant with respect to the theory that halogen atoms can form π-complexes with aromatic compounds. Russell [36] has shown that chlorine atom attack becomes much more selective in the presence of aromatic solvents and has suggested that the chlorine atoms form weak π-complexes with the aromatic rings thus becoming less reactive. These 'π-complexes' act as chlorine atom donors. Our results for bromine and iodine containing radicals show that the stable species at low temperature are σ- rather than π-complexes. Although π-complexes are not ruled out, it seems probable that the chlorine atom donor involved is a σ-complex similar to those that we have detected. Unfortunately our studies of chloro-derivatives have not given e.s.r. features for either species.

As we mentioned above, Namiki studied both electronic and e.s.r. spectra of various halogenoaromatic compounds in ethanol, after exposure at 4 K and 77 K.[16]



(9)

(10)

His results for bromo- and chloro-naphthalenes make an interesting contrast. At 4 K, both formed π^* anions. However, on warming to 77 K, the bromo-derivative lost bromide ion whilst the chloro-derivative became protonated. This is exactly the competition that we have been studying: the π^* anion can react in two ways, by protonation or conversion into the σ^* anion. The latter can then lose halide ion by solvation. Both these processes will be promoted by ethanol, but the nature of the halogen will determine the ease of formation of the σ^* anion, with $Cl < Br < I$. Only the π^* anion will undergo ring protonation, and once this has occurred, conversion to the σ^* anion is prevented. We therefore suggest that for the bromo-derivatives, the $\pi^* \longrightarrow \sigma^*$ conversion was favoured over protonation, whereas for the chloro-derivatives the reverse occurred.

The results for the halogenobenzenes are less clear.[16] Solutions of PhCl, PhBr, and PhI in ethanol gave novel electronic spectra at 4 K which were reasonably interpreted as being due to halide ions. In fact, the peaks were only slightly shifted from the gas-phase values, suggesting that the ions are unsolvated at 4 K. Namiki argued that these bands involved charge-transfer to the neighbouring phenyl radical. It is difficult to understand such a process. If $Ph^{\cdot}$–Hal^- systems are really involved, our results show that stable σ^* complexes should be formed therefrom. We suggest either that the spectra actually relate to the σ^* radicals that we detected by e.s.r. spectroscopy, or less probably, that dissociation has already occurred at 4 K to give separated $Ph^{\cdot}$ and Hal^- units, the halide ion remaining unsolvated at 4 K. In the former case loss of the optical bands on warming arises because the solvent extracts the halide ions, whilst in the latter case, solvation develops on warming and this shifts the absorption bands for the halide ions into the 200 nm region.[37] In favour of the latter postulate is the observation that O_2^- ions, generated in ethanol at 4 K, are not solvated, but that solvation reaches the normal level on warming to 77 K.[38] Against this, however, is the fact that ethyl iodide in ethanol at 4 K did not give rise to the expected iodide ion spectrum after irradiation.[16] This is, in fact, quite surprising since extensive solvation of I^- is not really expected to develop at this temperature. Possibly $Et^{\cdot}$–I^- adduct are formed,[20] but they should still exhibit low-energy absorption bands for I^-. Clearly this system should be studied more extensively.

Finally, we should report that we have examined our spectra carefully for other expected products, especially for the π^* anions and for $Ph^{\cdot}$ or substituted phenyl radicals. We expect the π^* orbital to have a node through the halogen substituents and hence to exhibit only small hyperfine coupling to the halogen nuclei. Proton coupling of the order of 5 G is expected for the ring protons, but this coupling should be strongly anisotropic and hence the lines should be broad. No clear features were detected for these anions, because of overlap with feature from radicals. Nevertheless their formation is probable. In several cases, spectra characteristic of $Ph^{\cdot}$ radicals were observed after annealing had destroyed the features from σ^* radicals. In the particular case of *p*-di-iodobenzene in MeTHF, relatively well resolved spectra were obtained (2 H 17 G, 2 H 6 G) and there was no extra coupling from the *p*-iodo-substituent. The coupling to ^{127}I must be very small and hence through-space delocalisation must be small. Similarly the phenyl type radicals formed from *p*-bromophenol in CD_3OD or aqueous NaOH had solid-state spectra very similar to that for unsubstituted phenyl radicals,[3] showing that a *para*-O^- substituent has little effect on the local structure of the radicals.

We have repeatedly studied chloroaromatic systems in the hope of detecting σ^* anions and chlorocyclohexadienyl radicals, but so far we have been unable to produce definitive spectra for either type.

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