# Electron Spin Resonance Study of γ-Ray-induced Reactions of Bromobenzene and *p*-Bromophenol: Bromine Atom–Aromatic Complexes

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*Summary* Radicals exhibiting a large hyperfine interaction with bromine, obtained from solutions of the title compounds by γ-irradiation at 77 K, are identified as cyclohexadienyl radicals with hydrogen added at the bromine site.

BRETT and GOLD[1] have recently studied the reactions of tritium atoms with aqueous bromobenzene (amongst a wide range of aromatic compounds) and demonstrated that in addition to a nearly statistical exchange with *ortho-*, *meta-*, and *para*-hydrogen atoms, there is an extensive displacement of bromine to give tritiated benzene. Similar studies have been reported by Prior *et al.*,[2] although these authors did not report halogen displacement. We have studied some of the radical intermediates involved in these processes by using low temperature glasses exposed to $^{60}$Co γ-rays. Our results shed some light on these reactions and also on the structure of halogen atom aromatic π-complexes that have been invoked to explain aromatic solvent effects on halogen atom reactivities.[3,4]

On irradiation, aqueous or methanolic glasses of the two bromine compounds gave no yield of normal cyclohexadienyl radicals containing a $>CH_2$ group. However, features characteristic of hyperfine coupling to $^{81}$Br and $^{79}$Br were clearly detected (Figure). For bromobenzene in $CH_3OH$ or $CD_3OD$ there was an extra splitting of *ca.* 35 G ($G = 10^{-4}$ T) on each feature which was absent for $C_6D_5Br$ in these solvents. This strongly suggests the adduct (I), the reduction in hyperfine coupling for the out-of-plane proton from the normal value of *ca.* 50 G being quite reasonable for this structure. However, we stress that $C_6D_5Br$ in $CH_3OH$ gave no resolved 35 G doublets, the spectrum being far closer to that in $CD_3OD$ than to that for $C_6H_5Br$. We suggest that this implies a rapid migration (life-time ~ seconds) of the bromine atom from one carbon atom to the next around the benzene ring.[†] Thus H-addition to $C_6D_5Br$ gives 5/6 of species of type (II) with H either *ortho*, *meta*, or *para* to the –CDBr– group and only 1/6 of the initially formed adduct. Indeed, clear evidence for a single *ortho-* or *para*-hydrogen atom can be seen in the e.s.r.

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[†] In principle the hydrogen atom might also migrate to give a methylene group ($>$CHD) with H–D scrambling on return to give (I). However, methylenic cyclohexadienyl radicals were not detected.

spectra. In contrast, D-addition to $C_6H_5Br$ should give 5/6 of the product having a –CHBr–unit, as observed.

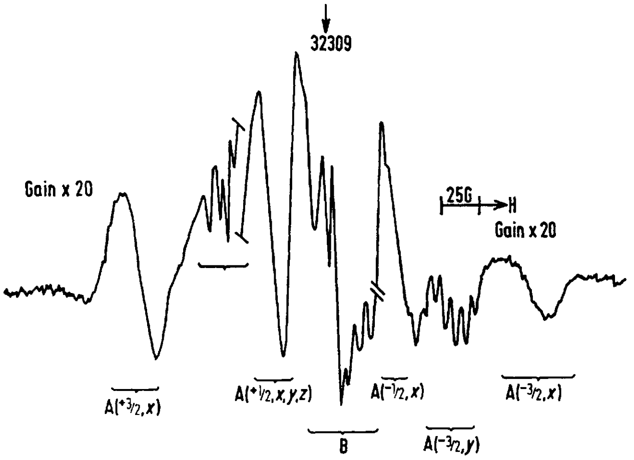
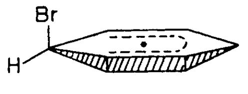


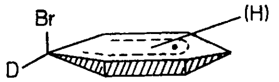
FIGURE. First derivative X-band e.s.r. spectrum for *p*-bromophenol in 6M-aqueous sulphuric acid after exposure to $^{60}$Co $\gamma$-rays at 77 K and slight annealing above this temperature, showing features assigned to the hydrogen atom adduct (A) and the *p*-hydroxyphenyl radical (B).

In addition to this evidence, the pattern of hyperfine coupling to bromine nuclei is similar in form to that observed for $\beta$-bromine radicals, $R_2\dot{C}$–$CH_2Br$, previously described,[5] although the total coupling is reduced by a factor of *ca.* 2·5. [These spectra could also be associated with $\alpha$-bromine type radicals,[6] in which case, for bromophenol, species (III) should be considered. However, the magnitude of the maximum hyperfine coupling of 85 G should be compared with that of *ca.* 120 G found for the maximum coupling in radicals $R_2\dot{C}$–Br having a formal unit spin-density on the $\alpha$-carbon atom. Clearly 85 G is far too high for radicals of structure (III)].

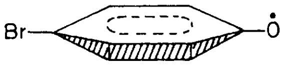
Solutions of bromophenol gave e.s.r. spectra in which the hyperfine coupling to bromine was very similar to that of bromobenzene ($A_{\max}$ *ca.* 93 G), but no large hyperfine coupling to a single proton was exhibited for any solvent. Since hydrogen atoms were efficiently scavenged, this result suggests that the rate at which bromine atoms migrate in this instance is fast, so that only an averaged proton coupling results. (This requires a residence time of < *ca.* $10^{-7}$ s at each site.) Our averaged proton coupling of *ca.* 7 G is quite reasonable and fits the resolved structure on the '*y*' features satisfactorily (Figure).



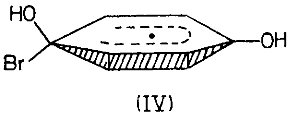
(I)



(II)



(III)



(IV)

Several alternatives should be considered: one is that the complex for bromophenol has a $\pi$-structure of the type postulated by Russell[3] and Walling *et al.*[4] This is certainly possible, but requires the coincidence that the form and magnitude of the hyperfine coupling to bromine be almost identical with that for the $\sigma$-complex formed by bromobenzene. Another possibility is that the hydroxy-adduct (IV) is responsible in this case. There is good evidence for such an intermediate species,[7] but it is not thought to make a major contribution to the overall reactions,[8] and it again requires the coincidence that $A$(Br) be very similar to that for the hydrogen atom adduct. Furthermore, the proton coupling exhibited in the '*y*' features does not fit so satisfactorily and we therefore favour the rapid exchange model.

These considerations suggest a modification to the normal view of hydrogen atom exchange processes for halogenated aromatic compounds. We postulate that, at least for bromine derivatives, addition is predominantly at the halogen site, with consequent rapid movement of bromine around the ring. Extraction of hydrogen will then be statistical, as observed,[1] and loss of bromine atoms, or extraction of bromine will compete with this.

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[1] C. L. Brett and V. Gold, *Chem. Comm.*, 1971, 148; *J.C.S. Perkin II*, 1973, 1437; 1453; C. L. Brett, V. Gold, and G. Perez, *J.C.S. Perkin II*, 1973, 1450.

[2] W. A. Pryor, T. H. Lin, J. P. Stanley, and R. W. Henderson, *J. Amer. Chem. Soc.*, 1973, **95**, 6993.

[3] G. A. Russell, *J. Amer. Chem. Soc.*, 1958, **80**, 4987; 4997.

[4] C. Walling and M. F. Mayahi, *J. Amer. Chem. Soc.*, 1959, **81**, 1485.

[5] A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1971, **93**, 7330.

[6] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1973, **95**, 605.

[7] F. A. Peter and P. Neta, *J. Phys. Chem.*, 1972, **76**, 630.

[8] K. Bhatia and R. H. Schuer, *J. Phys. Chem.*, 1973, **77**, 1356.