CBr_4^- and Related Anions

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Summary On exposure of carbon tetrabromide and various tribromides ($RCBr_3$) to γ-rays at 77 K, species were obtained whose e.s.r. spectra could be analysed in terms of two strongly coupled and two (or one) weakly coupled bromine atoms, which strongly suggests the presence of distorted radical anions CBr_4^- ($RCBr_3^-$).

ALTHOUGH 33 electron penta-atomic ($B_4A\cdot$) radicals, typified by $F_4P\cdot$, are well known and have been extensively studied by e.s.r. spectroscopy, we know of no description of $B_4A\cdot$ radicals in which the central atom, A, is a first-row element. In our extensive studies of the effects of high-energy radiation upon alkyl halides[1,2] we have observed well defined e.s.r. spectra for $R_2BrC\cdot$[2] and $RBr_2C\cdot$ radicals, but compounds expected to give $Br_3C\cdot$ radicals, including CBr_4, Br_3CCO_2H, $HCBr_3$, and Br_3CCH_2OH all gave electron-excess centres which had e.s.r. spectra differing from those expected for $Br_3C\cdot$ radicals in the following ways: (i) the outer features were nearly isotropic, in marked contrast with the results for $R_2BrC\cdot$ and $RBr_2C\cdot$ radicals, (ii) in all cases, there were many more lines all belonging to a single species than expected for $Br_3C\cdot$, (iii) these were centred on the free-spin region, whereas g_{av} values for $R_2BrC\cdot$ and $RBr_2C\cdot$ radicals are $>> 2{\cdot}0$.

The spectra, a typical example of which is given in the Figure, could all be analysed in terms of two strongly coupled bromine nuclei, having $A(Br^1) =$ *ca.* 108 G and one or two (for CBr_4) weakly coupled nuclei, having $A(Br^2) =$ *ca.* 64 G. Although these differences are less extreme, the results are reminiscent of those for $F_4P\cdot$[3] or $Cl_4P\cdot$,[4] both of which show two strongly coupled and two weakly coupled halide ligands. We propose that the present species are the primary radical-anions, in which distortion from local tetrahedral symmetry has occurred in order to relieve the anti-bonding effect of the extra electron. However, probably for steric reasons, this distortion extends less towards the trigonal-bipyramidal limit than is thought to occur for analogous second-row radicals.

We were unable to detect any proton coupling in the radical $(HCBr_3)^-$ and presume that the hydrogen atom is in a near equatorial position with a fortuitously low coupling constant. Also, 1,1-dibromides failed to give similar anions, and Br_3CCO_2H in CD_3OD gave mainly $Br_2\dot{C}CO_2H$ radicals with no detectable radical-anion formation, in contrast with results for the pure material. We presume that the alcohol, being a good anion solvating medium, was able to remove the bromide ion from the anion, as had originally been expected to occur in all cases.

Attempts to obtain similar anionic species from carbon tetrachloride and related species resulted in $Cl_3C\cdot$ formation only. This suggests that there remains considerable σ^* character in the orbital of the unpaired electron, despite the distortion. The C–Br bonds are thus better able to accommodate such an extra electron than are the stronger C–Cl bonds.

In several instances we found that the features associated with these new anionic radicals were reversibly lost on annealing from 77 K to *ca.* 120 K. We suggest that this was due to the onset of 'inversion' in which Br^1 and Br^2 type atoms interconvert. As yet we have been unable to reach temperatures on the fast exchange side, because of the marked thermal instabilities of these species.

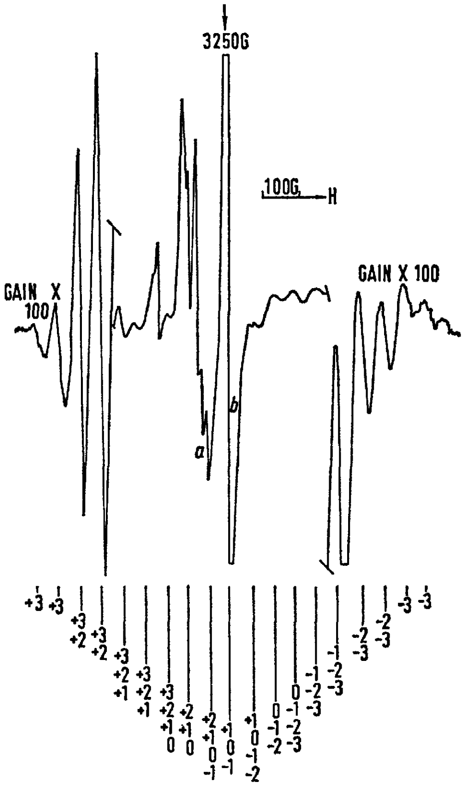

FIGURE. *First derivative* X-*band e.s.r. spectrum for* CBr_4 *in* CD_3OD *after exposure to* Co^{60} γ-rays *at* 77 K, *showing features assigned to* CBr_4^- *radicals. The intense central features are assigned to 'perpendicular' features of* $Br_3C\cdot$ *radicals* (a) *and to* $\cdot CD_2OD$ *radicals* (b).

(*Received, 2nd May* 1973; *Com.* 626.)

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