

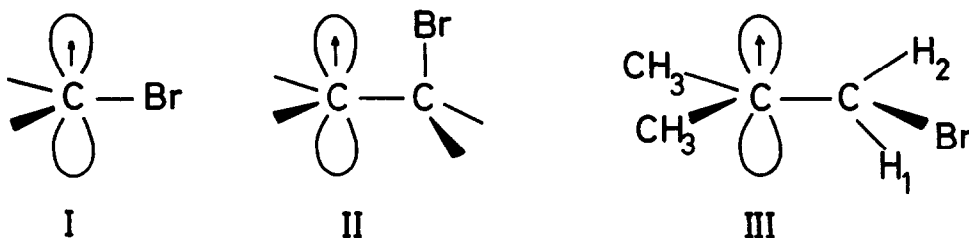
ON THE CONFORMATION OF β -BROMO RADICALS

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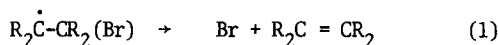
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During the past few years we have assigned e.s.r. spectra to α - and β -bromo-radicals (I and II),^{1,2} but recently both our assignments have been dismissed in favour of others.^{3,4} In the previous letter⁵ a case has been presented in favour of our α -bromo and β -bromo assignments: here we wish to defend our β -bromo assignment and to propose an alternative structure for the species detected by Lloyd *et al.* and assigned structure III.⁴



The species of interest was prepared from isobutyl bromide by X-irradiation of an adamantane "solution".⁴ The resulting narrow-line isotropic spectrum comprised a set of ten quartets, the quartet structure being assigned to hyperfine coupling to bromine ($A_{\text{iso}} = 6.7\text{G}$) because features for ^{81}Br and ^{79}Br were detected. The set of ten lines ($A_{\text{iso}} = 21.4\text{G}$) was analysed in terms of structure III, with $A(\text{Me}) = 21.4\text{G}$, $A(\text{H}_1) = 21.4\text{G} + A(\text{H}_2) = 42.8\text{G}$.

This structure is improbable on chemical grounds: bromine and iodine are expected to resemble chlorine, which certainly adopts conformation II, and mechanistic⁶ and N.M.R.⁷ studies strongly support a symmetric or asymmetric "bridged" structure. Also, β -bromo radicals have never been detected in fluid solution, so why should they give a well-defined e.s.r. spectrum in adamantane at -71°C ? Rapid electron-spin relaxation cannot be the cause, so it is necessary to postulate a high reactivity to explain the negative liquid-phase results. However, it is generally accepted that β -bromo radicals are unimolecularly very unstable:^{8,9}



and this process would not be prevented in adamantane.

Finally, it is a curious coincidence that the preferred staggered conformation is one that accurately results in hyperfine coupling to H(1) + H(2) that produces just ten narrow lines. It seems far more likely that this species contains nine equivalent protons. It is known that $\text{Me}_2\text{CH}-\dot{\text{C}}\text{H}_2$ radicals isomerise to the more stable $\text{Me}_3\text{C}\cdot$ species even at 77 K,¹⁰ and our own studies confirm the formation of $\text{Me}_3\text{C}\cdot$ from isobutyl chloride, bromide and iodide on irradiation at 77 K. This would explain the presence of ten lines. Also we and others have shown^{11,12} that alkyl radicals formed from alkyl bromides and iodides in the solid state by dissociative electron capture often exhibit a small residual hyperfine coupling to halogen, the magnitude of which is a function of the alkyl radical and the solvent. We therefore suggest that the species studied by Lloyd *et al.*⁴ is the radical $\text{Me}_3\dot{\text{C}}\dots\text{Br}^-$. This hypothesis accords with all their data, with $A^1\text{H} = 21.4\text{G}$ and $A(^81\text{Br}) = 6.7\text{G}$. The small reduction in the proton coupling from that for normal $\text{Me}_3\text{C}\cdot$ ($\sim 22.4\text{G}$) is normal for these anion complexes. The relative line intensities are in fair agreement with expectation for $\text{Me}_3\text{C}\cdot$ radicals. If this is correct, *t*-butyl bromide in adamantane should give the same 10-component species, each component comprising four lines separated by ca. 6G. This was indeed detected, in addition to some "free" $(\text{CH}_3)_3\text{C}\cdot$ radicals. On annealing, the bromine splitting was lost, as was observed by Lloyd *et al.*⁴

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