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Bridged Bromine Radicals. An Electron Spin Resonance Study

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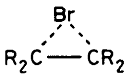
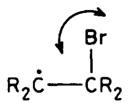
From changes in the e.s.r. spectrum for $Me_2\dot{C}C(Br)Me_2$ radicals, it is deduced that the stable structure is asymmetric, but that the rate of migration of bromine between the two equivalent sites becomes fast on the e.s.r. time-scale at *ca.* 100 K.

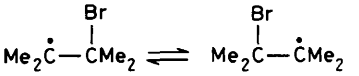
In a series of carefully designed experiments, Skell and his co-workers have presented convincing evidence that β-bromo radicals are either symmetrically bridged (I) or that the bromine atom migrates between two equivalent sites (II) at a frequency $\geqslant 10^{11}$ s^{-1} at room temperature.[1–3] We have obtained e.s.r. evidence in favour of this conclusion, and specifically show that, whilst the favoured structure at 77 K is asymmetric (II), bromine migration is facile.

We have previously suggested that a species formed by the radiolysis of t-butyl bromide at 77 K is the β-bromo radical, $Me_2\dot{C}CH_2(Br)$.[4,5] This species exhibits a very large hyperfine coupling to bromine ($A_{max.} = ca.$ 360 G)† which was explained in terms of strong σ–π conjugation (hyperconjugation). Coupling to the two methylene protons was too small to resolve ($\leqslant$4 G), suggesting that the structure has moved towards the bridging structure, without being symmetrically bridged.

Since symmetrical bridging is unlikely for this asymmetric radical, we have endeavoured to prepare radicals of type $R_2\dot{C}$–$CR_2(Br)$, and have been successful with the tetramethyl derivative. This radical, formed by radiolysis of $Me_2C(Br)$-$CMe_2(Br)$ which loses bromide by dissociative electron capture, has an overall e.s.r. spectrum which closely resembles that assigned to $Me_2\dot{C}CH_2(Br)$ radicals (Figure 1) ($A_{max.}[^{81}Br] = 362$ G). The same radical was formed when dilute solutions of the dibromide in CD_3OD were irradiated, under conditions in which only dissociative electron capture occurs, and the bromide ions are expected to be strongly solvated, and hence unable to perturb the radical strongly.


(I)


(II)



$$Me_2\dot{C}-\overset{Br}{\overset{|}{C}}Me_2 \rightleftharpoons Me_2\overset{Br}{\overset{|}{C}}-\dot{C}Me_2 \quad (1)$$

The outer ($M_I = \pm\ ^3/_2$) lines show the expected 36 G doublet splitting from ^{81}Br and ^{79}Br components at *ca.* 100 K, but no resolution on cooling to 77 K. If the symmetrical structure (I) were correct we would expect to observe 13 binomial components, whereas the asymmetric structure (II) should exhibit strong coupling to 6 protons (7 lines) and very weak coupling to the other six protons. If rapid bromine atom migration occurred, the twelve protons should become equivalent, the hyperfine splitting being *ca.* half that for the slow exchange situation.

Having failed to obtain any ENDOR signals even at 4 K for these radicals, we studied the unresolved $M_I = +\ ^3/_2$ feature using resolution enhancement techniques[6] after signal averaging to reduce the noise level. When this was done for the 77 K spectrum, two sets of features appeared with a splitting of *ca.* 10 G whereas similar treatment of the 100 K doublet revealed a sub-splitting of *ca.* 5.5 G in each component.

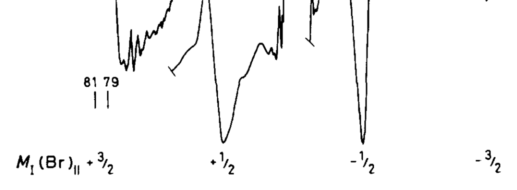


Figure 1. First derivative *X*-band e.s.r. spectrum for $Me_2C(Br)$-$\dot{C}Me_2(Br)$ in CD_3OD after exposure to ^{60}Co γ-rays at 77 K and warming to *ca.* 100 K, showing features assigned to $Me_2CCMe_2(Br)$ radicals. The parallel features for ^{81}Br and ^{79}Br are indicated. The splitting resolved for the $M_I = \pm\ ^3/_2$ lines is lost reversibly on cooling to 77 K. (1 G = 10^{-4} T).

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† 1G = 10^{-4} T.

Simulation of the spectra using these parameters and line-widths just great enough to remove the sub-structure gave good agreement with the experimental spectra.

The results for the 77 K spectra strongly support the asymmetric structure, (II). Thus the overall form of the spectrum is similar to that for the $Me_2\dot{C}CH_2(Br)$ radical, and the methyl proton coupling (10 G) is comparable with, though significantly less than, that for the $\dot{C}CH_2(Br)$ radical (13 G). Resolution enhancement techniques were unable to give a measure of the coupling to the other two methyl groups, but the technique known as CEPSTROM[7] showed that this is $\leqslant$1 G. The simplest explanation of the spectral changes observed in the 80—100 K region is the onset of a rapid equilibrium between the two potential minima for structure (II) (1). Only a small relative movement of the two units is required because of the large size of the bromine atom and we envisage a rocking mode for the organic unit rather than direct migration of the bromine atom. In order to obtain an average coupling of *ca.* 5.5 G we require a coupling of 10 and 1 G for the static radical, which seems to us to be quite reasonable.

In view of the complexities of these spectra and the difficulties associated with the spectral analysis, we have not attempted to estimate line-width enhancements in the intermediate temperature region. However, we can argue firmly that at 77 K the frequency of interchange must be $<$ *ca.* 3×10^7 s^{-1} whilst at 100 K it must be $\gg$ *ca.* 3×10^7 s^{-1}. Thus a value of *ca.* 10^{11} s^{-1} at room temperature, estimated by Skell *et al.*[3] is quite compatible with our results, and we strongly support their conclusions.

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