The $\cdot BH_4$ Radical: an Electron Spin Resonance Study of the Radiolysis of $NaBH_4$

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Exposure of $NaBH_4(NaBD_4)$ to ^{60}Co γ-rays at 77 K gave a species having a large proton hyperfine coupling to two equivalent protons(deuterons), and a small coupling to two other protons(deuterons), together with a strongly anisotropic coupling to ^{11}B.

A recent, exciting development in e.s.r. spectroscopy has been the study of a range of alkane cations.[1,2] Our initial study[1] of $[Me_3C]_2^+$ led to the discovery[2] by Iwasaki and co-workers of $C_2H_6^+$ and a range of other cations. However, no one has yet succeeded in studying CH_4^+ by e.s.r. methods.

We therefore returned to the task of preparing the iso-electronic species $\cdot BH_4$. We originally found that irradiation of KBH_4 at 77 K gave $\cdot BH_3^-$,[3] together with $H\dot{B}O^-$ from sample impurities. The former radicals were subsequently studied in $R_4N^+BH_4^-$ salts.[4] Furthermore, irradiation of solutions of $NaBH_4(NaBD_4)$ in aqueous and methanolic glasses gave $\cdot BH_3^-(\cdot BD_3^-)$ radicals together with another species, very tentatively identified as $\cdot BH_4$:[5] only the outermost features for this species were detected. Very recently, $\cdot BH_3^-$ radicals have been detected in the liquid phase.[6]

We now find that carefully purified $NaBH_4$ and $NaBD_4$ give, on radiolysis at 77 K, novel species having a very large hyperfine coupling to two equivalent protons (Table 1). A typical

Table 1. Observed e.s.r. parameters (A), and calculated spin densities (a_s^2, a_p^2) for $\cdot BH_4$ in irradiated $NaBH_4$.

^1H_a		^1H_b		^{11}B			
$A(^1H)^a$	a_s^2	$A(^1H)^a$	a_s^2	$A_\parallel(^{11}B)^a$	$A_\perp(^{11}B)^a$	a_s^2	a_p^2
104—141[b]	*ca.* 0.25[b]	0—21[b]	*ca.* 0.02[b]	21[b]	0[b]	0.01[b]	0.39[b]
	0.364[c]		−0.017[c]			0.006[c]	0.318[c]
	0.359[d]		−0.013[d]			−0.003[d]	0.355[d]
	0.336[e]		−0.004[e]			−0.001[e]	0.351[e]

[a] A values in Gauss: G = 10^{-4} T. [b] Orbital populations estimated from the e.s.r. parameters using standard methods (ref. 7). Because of ambiguities in interpretation, we have used the average values for $A(^1H_a)$ and $A(^1H_b)$. [c] MNDO values at the optimised MNDO geometry. [d] INDO values at the optimised MNDO geometry. [e] Pure doublet state projected from the wave function used in footnote d, at the MNDO optimised geometry.

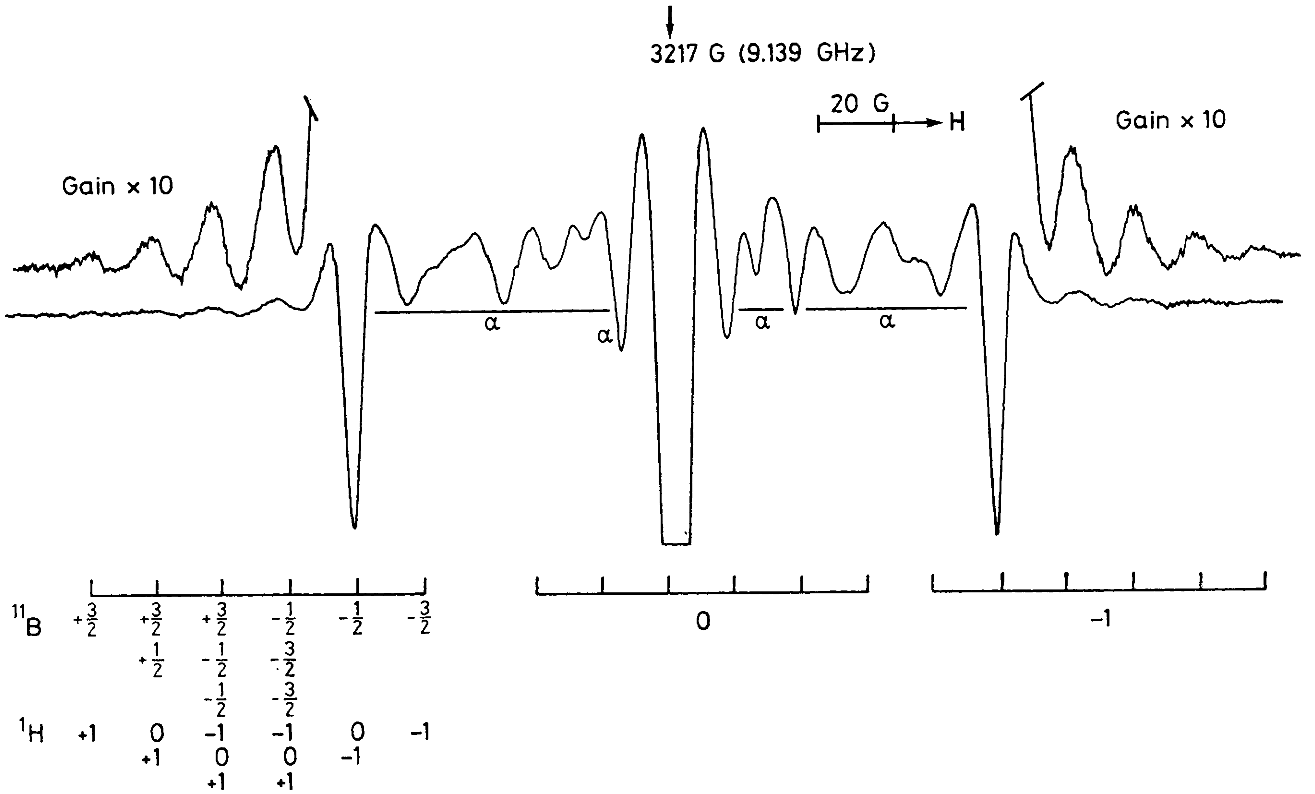

Figure 1. Second derivative X-band e.s.r. spectrum for $NaBH_4$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $\cdot BH_4$ radicals. The features α are assigned to $\cdot BH_3^-$ radicals.

spectrum is shown in Figure 1. There are extra features in the powder spectrum besides the intense triplet, and careful thermal studies suggest that they all belong to the same species. This is supported by results for $NaBD_4$. One possible interpretation of this spectrum is given in Table 1. Although we are not certain that this is the best possible fit, computer simulation accommodates most of the salient features. In effect, the three strong lines may be taken as 'perpendicular' features whilst those indicated on the stick diagram are 'parallel' features. (Extra features marked or in Figure 1 are due to $\cdot BH_3^-$ radicals.)

Since the HOMO for both CH_4 and BH_4^- is triply degenerate (t_2), the radicals CH_4^+ and $\cdot BH_4$ cannot retain T_d symmetry. Our results suggest that, for $\cdot BH_4$, the distortion from T_d is such that the protons stay equivalent in pairs (C_{2v}); the identification of this species as $\cdot BH_4$ seems to be unavoidable, since one ^{11}B nucleus and two pairs of equivalent protons are detected. (The resolution is too poor for us to detect features from ^{10}B.)

Analysis of the e.s.r. data in the usual way[7] shows that the SOMO is confined to a 2p orbital on boron and the 1s orbitals of two hydrogen atoms, with the other pair of hydrogen atoms lying in the nodal plane of the SOMO (Figure 2). It is interesting that this distortion appears to be similar to that in $SiMe_4^+$, where there are two strongly coupled and two weakly coupled sets of methyl protons,[8,9] but different from those in CMe_4^+,[2] and $SnMe_4^+$,[9] which distort to give C_{3v} structures.

Clearly the choice between D_{2d}, C_{3v}, or C_{2v} distortions must be subtle. Experimental and theoretical studies of CH_4^+ all assign D_{2d} symmetry to its ground state,[10–12] and so we have calculated the equilibrium structure of $\cdot BH_4$ using the MNDO-UHF technique.[13,14] The MNDO results (Table 1 and Figure 2) strongly support the e.s.r. interpretation of a C_{2v} radical.

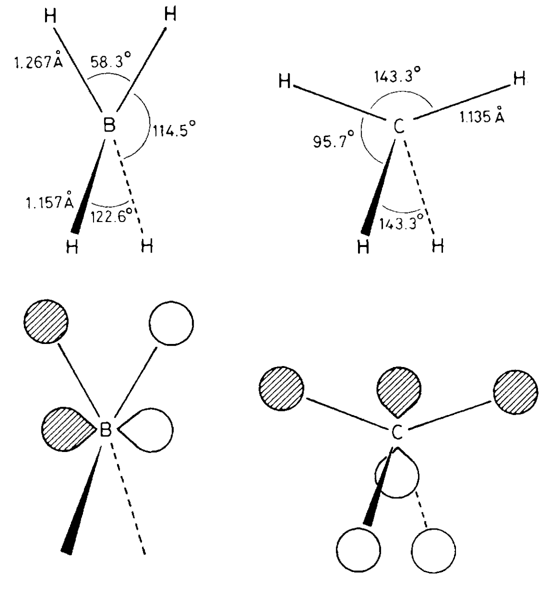

Figure 2. Optimised geometries for $\cdot BH_4$ (C_{2v}, $^2B_1$) and CH_4^+ (D_{2d},$^2B_2$), calculated by MNDO-UHF[13,14] showing geometrical parameters, and schematic forms of the SOMO; ΔH_f° values are: $\cdot BH_4$, $+222.4$ kJ mol^{-1}; CH_4^+, $+1140.8$ kJ mol^{-1}.

The results of a similar calculation for CH_4^+ (D_{2d}) are shown in Figure 2 for comparison. The calculations do not reveal directly the reason for the switch in structural preference from CH_4^+ to $\cdot BH_4$: however, CH_4^+ and $\cdot BH_4$ (and the isoelectronic BeH_4^-) each exhibit two local minima, of D_{2d} and C_{2v} symmetries, and it is the relative energies of these two minima which change with change of radical. Hence the observation of a C_{2v} structure for $\cdot BH_4$ reflects a property intrinsic to this radical rather than one consequent upon the symmetry of the cavities containing the $\cdot BH_4$ radicals.

These results seem to us to be definitive. Other possible species that should display a large hyperfine coupling to two protons are $\cdot BH_2$ and $H_2BO\cdot$. The former should also have a large isotropic component in the ^{11}B hyperfine coupling, since it has a strongly bent ground state, and so it can be ruled out. The latter seems unlikely since we used high grade materials, and the signals for the radical under consideration were lost on exposure to moist air prior to irradiation. Furthermore, the ^1H coupling should be almost completely isotropic (as for $H_2CN\cdot$, for example) and the anisotropic ^{11}B coupling should be small. In fact, a radical thought to be $H_2BO\cdot$ has been studied by Weltner and his co-workers;[15] the isotropic coupling found for ^{11}B, *ca.* 31 G, is far too large for the present species. Of course, neither of these candidates should exhibit coupling to two further protons. We conclude that the species detected is most probably the previously unknown radical $\cdot BH_4$.

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