An E.S.R. Study of the Generation and Reactivity of the Borane Radical Anion ($H_3B\cdot^-$) in Solution

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Summary t-Butoxyl radicals are shown to abstract hydrogen rapidly from H_4B^- and H_3BCN to give $H_3B\cdot^-$ and $H_2\overline{B}CN$, respectively, and the reactions of $H_3B\cdot^-$ with alkyl halides, isocyanides, and azides are reported.

The structures and reactions of carbon-centred radicals ($X_3C\cdot$) have been studied very extensively and the knowledge thus gained has been central to development in the general field of free radical chemistry. By contrast, very little is known about the isoelectronic boron-centred radicals $X_3B\cdot^-$.

The e.s.r. spectra of $H_3B\cdot^-$ [1] and $F_3B\cdot^-$,[2] generated by γ-irradiation of borohydrides and boron trifluoride, respectively, have been observed in rigid matrices. It has been proposed that the reduction of halogeno-benzenes[3] and -cyclopropanes[4] using sodium borohydride proceeds by a radical chain mechanism, the propagation steps of which are shown in equations (1) and (2).

$$H_3B\cdot^- + RBr \longrightarrow H_3\overline{B}Br + R\cdot \quad (1)$$

$$R\cdot + H_4B^- \longrightarrow RH + H_3B\cdot^- \quad (2)$$
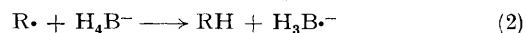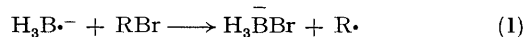
We now report that abstraction of hydrogen from the borohydride anion by photochemically- or thermally-generated t-butoxyl radicals gives rise to the borane
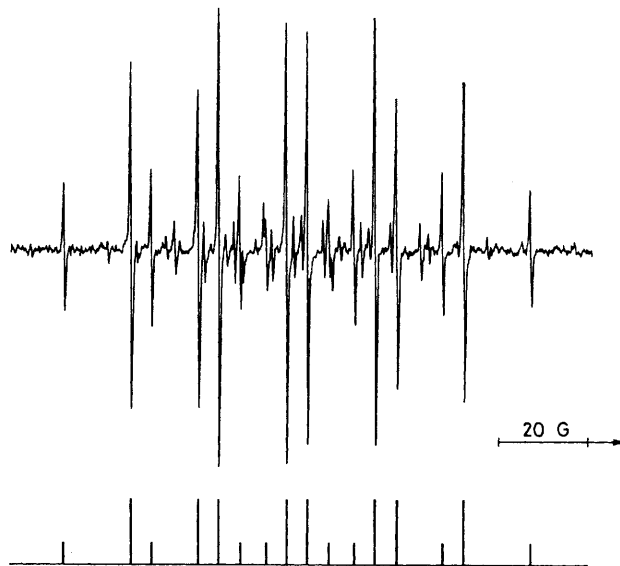

Figure. E.s.r. spectrum of the borane radical anion in dimethyl ether–t-pentyl alcohol (1·3 : 1 v/v) at 260 K. The stick diagram is for $H_3{}^{11}B\cdot^-$, the remaining lines in the spectrum are due to $H_3{}^{10}B\cdot^-$. Some anisotropic broadening of the outer lines is evident and the second-order shifts of $H_3{}^{11}B\cdot^-$ and $H_3{}^{10}B\cdot^-$ are slightly different.

radical anion which can be readily detected in fluid solution by e.s.r. spectroscopy. The Figure shows the spectrum of $H_3B\cdot^-$ observed during continuous photolysis of a solution

$$Bu^tOOBu^t \xrightarrow{h\nu} 2\ Bu^tO\cdot \qquad (3)$$

$$Bu^tO\cdot + H_4B^- \longrightarrow Bu^tOH + H_3B\cdot^- \qquad (4)$$
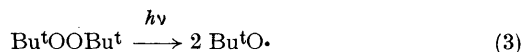
of di-t-butyl peroxide and $Bu_4^nNBH_4$ (ca. 0·3 M) in dimethyl ether–t-pentyl alcohol (1·3 : 1 v/v) [equations (3) and (4)]. The e.s.r. parameters are given in the Table.

TABLE. E.s.r. parameters for borane radical anions in dimethyl ether–t-pentyl alcohol (1·3 : 1 v/v) and for the isoelectronic alkyl radicals.

Radical	T/K	g Factor	Hyperfine splittings/$G^{a,b}$
$H_3B\cdot^-$	253	2·0023	15·3 (3H), 19·9 ($1^{11}B$), 6·7 ($1^{10}B$)
$D_3B\cdot^-$	253	2·0023	2·3 (3D), 18·7 ($1^{11}B$)
$H_2\dot{B}CN$	252	2·0025	15·8 (2H), 14·3 ($1^{11}B$), 3·0 (1N)
$H_3C\cdot^c$	96	2·0026	23·0 (3H), 38·3 ($1^{13}C$)
$H_2\dot{C}CN^d$	306	2·0030	21·0 (2H), 3·5 (1N)

a Numbers of equivalent nuclei shown in parentheses. b The natural abundances of ^{10}B (I 3) and ^{11}B (I 3/2) are 18·8 and 81·2%, respectively: $(\gamma^{10}B/\gamma^{11}B)$ 0·335. c Data from R. W. Fessenden, *J. Phys. Chem.*, 1967, **71**, 74. d Data from R. Livingston and H. Zeldes, *J. Magn. Reson.*, 1969, **1**, 169.

The spectrum of $H_3B\cdot^-$ was also detected when t-butoxyl radicals were generated by thermolysis (at 333 K) of di-t-butyl hyponitrite[5] [equation (5)] in the presence of $Bu_4^nNBH_4$ in t-pentyl alcohol solution.
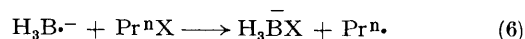
$$Bu^tON=NOBu^t \longrightarrow 2\ Bu^tO\cdot + N_2 \qquad (5)$$

Analogous results have been obtained with substituted borohydrides. For example, an e.s.r. spectrum which we assign to $H_2\dot{B}CN$ was observed when $Bu^tO\cdot$ was generated in the presence of $Bu_4^nN\ H_3BCN$. The spectroscopic parameters are given in the Table, together with those of the isoelectronic carbon-centred radical $H_2\dot{C}CN$.
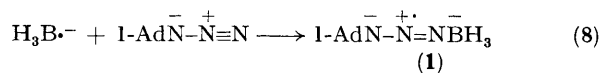
The radical $H_3B\cdot^-$ appears to be essentially planar[1] and the spectroscopic parameters for $H_2\dot{B}CN$ indicate that this species is also planar. The nitrogen splitting for $H_2\dot{B}CN$ is similar to that for $H_2\dot{C}CN$, implying that the extent of

delocalisation of the unpaired electron on to the CN group is similar for both radicals. The larger magnitude of $a(H)$ for $H_2\dot{B}CN$ compared with that for $H_3B\cdot^-$, despite the larger spin population on boron in the latter, is probably a result of the smaller negative charge carried by the hydrogens in $H_2\dot{B}CN$ because of the presence of the charge-withdrawing cyano-substituent. The much smaller value of $a(H)$ for $H_3B\cdot^-$ compared with that for $H_3C\cdot$ has also been attributed to this 'excess charge effect'.[6]

Because of the well-known similarities in the properties of boron and silicon compounds,[7] we anticipated that $X_3B\cdot^-$ and $X_3Si\cdot$ might exhibit similar reactivities. In accord with this expectation, e.s.r. experiments have shown that $H_3B\cdot^-$ abstracts† halogen rapidly from n-propyl halides [equation (6; X = Cl, Br, I)] and displaces alkyl radicals from alkyl isocyanides [equation (7; R = Me, Bu^n, Bu^t)].

$$H_3B\cdot^- + Pr^nX \longrightarrow H_3\bar{B}X + Pr^n\cdot \qquad (6)$$

$$H_3B\cdot^- + RNC \longrightarrow H_3\bar{B}CN + R\cdot \qquad (7)$$

Trialkylsilyl radicals add to alkyl azides to give 1,3-di-substituted triazenyl σ-radicals $R^1N=\dot{N}-NSiR_3$, in which there is appreciable unpaired electron density on the central nitrogen (cf. $O_2N\cdot$).[8] Similarly, thermally- or photochemically-generated $H_3B\cdot^-$ adds to 1-adamantyl azide to give the triazenyl radical (1) [$a(1N')$ 14·3, $a(1N'')$ 6·2, $a(3H)$ 8·1, $a(^{11}B)$ 5·1, and $a(^{10}B)$ 1·7 G, g 2·0014 at 323 K] in t-pentyl alcohol.‡

$$H_3B\cdot^- + 1\text{-}Ad\bar{N}\text{-}\overset{+}{N}\equiv N \longrightarrow 1\text{-}Ad\bar{N}\text{-}\overset{+\cdot}{N}=\bar{N}BH_3 \qquad (8)$$
$$(1)$$

Ad = adamantyl

† The extent of electron transfer from $H_3B\cdot^-$ to the alkyl halide in the transition state remains to be established.

‡ For comparison, the triazenyl radical $MeN=\overset{+\cdot}{N}\text{-}\bar{N}SiEt_3$ shows $a(1N^{central})$ 17·1, $a(1N')$ 3·6, and $a(1N'')$ 1·8 G, g 2·0009 at 260 K (ref. 8).

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