Generation of Borane Radical Anions by Photo-induced Electron Transfer from Hydroborate Anions

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U.v. photolysis of solutions containing H_4B^-, H_3BCN^-, or $(Bu^tO)_3BH^-$ in liquid ammonia results in electron detachment from the anions to give e^-_{amm} and (after proton loss) the appropriate borane radical anion.

In polar solvents, anions with relatively low ionisation energies (*e.g.* I^-, H_2N^-, and CNS^-) exhibit optical absorption in the near ultra-violet region which results from electron transfer to the solvent.[1,2] E.s.r. studies have confirmed the occurrence of electron photo-detachment, for example during photolysis of potassium alkylamides in liquid amines.[3] For a given anion, the wavelength of the charge-transfer-to-solvent (c.t.t.s.) band depends on the temperature and markedly on the nature of the solvent. The c.t.t.s. energies are comparatively small in ammonia, but larger in hydroxylic media (*e.g.* λ_{max} for I^- is 264 nm in NH_3 and 226 nm in H_2O at 293 K; ϵ_{max} *ca.* 1×10^4 l mol^{-1} cm^{-1} in both solvents).

We have reported that the e.s.r. spectrum of the borane radical anion (**1**) may be detected during photochemical generation† of t-butoxyl[4] or bis(trimethylsilyl)aminyl[5] radicals in the presence of tetra-n-butylammonium borohydride in dimethyl ether–t-pentyl alcohol solvent (1.3 : 1 v/v). No e.s.r. signals were detected during photolysis of $Bu^n_4NBH_4$ alone in

$$X^\bullet + H_4B^- \rightarrow XH + \underset{(\mathbf{1})}{H_3B^{\bullet -}} \qquad (1)$$

Me_2O–t-$C_5H_{11}OH$ solvent and (**1**) is produced by abstraction of hydrogen from H_4B^-, as shown in equation (1) [X = Bu^tO or $(Me_3Si)_2N$].

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† Using light from a 500 W high-pressure mercury lamp; most of the incident u.v. radiation is between 240 and 340 nm (ref. 6).

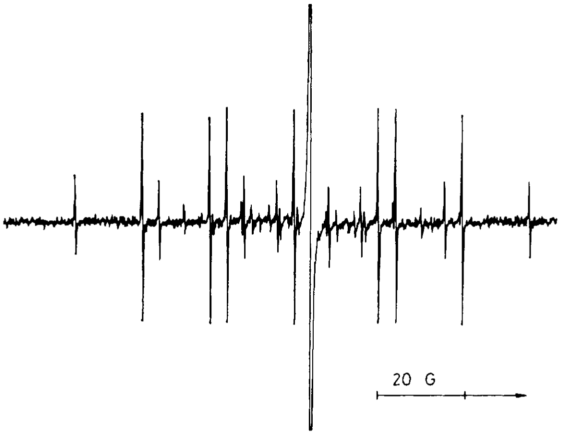

Figure 1. E.s.r. spectra of the borane radical anion and the solvated electron (the strong central line) obtained during photolysis of $Bu^n_4NBH_4$ in NH_3–DME (2:1 v/v) at 276 K.

In contrast, photolysis of $Bu^n_4NBH_4$ in liquid ammonia or in ammonia–1,2-dimethoxyethane (DME) mixtures affords the spectrum of (**1**) along with an intense single line (*g* 2.0012 in neat NH_3) which we assign to the solvated electron[7] (see Figure 1). U.v. absorption induces electron transfer from the borohydride anion to the solvent, presumably to give initially $H_4B^\bullet$ which undergoes rapid proton loss [equation (2)]. Proton loss from $H_4B^\bullet$ also prevents cage electron return which would lead to regeneration of H_4B^-. No signals were obtained when the photolysing beam was filtered through Pyrex glass (with effectively no transmittance below 290 nm) and a preliminary study of the optical spectrum of $Bu^n_4NBH_4$ (0.1 M) in NH_3–DME (2:1 v/v) at 290 K indicated only weak absorption in the 240—280 nm region. Evidently the c.t.t.s. band of H_4B^- in ammonia only tails into the region of u.v. emission from the high-pressure mercury lamp, although other hydroborate anions with lower ionisation energies appear to absorb more strongly in the 240—340 nm region.

$$H_4B^-_{amm} \xrightarrow[-e^-_{amm}]{h\nu} [H_4B^\bullet] \xrightarrow[-NH_4^+]{NH_3} H_3B^{\bullet -}_{amm} \qquad (2)$$

Similar electron detachment was observed during photolysis of $Bu^n_4NBH_4$ in hexamethylphosphoramide (HMPA) or in HMPA–DME mixtures,[1] but no signals were detected in DME alone.

In NH_3–DME during continuous photolysis, the value of $[H_3B^{\bullet -}]/[e^-_{amm}]$ increased with increasing temperature (230—290 K) and as the proportion of DME in the mixed solvent was increased (from neat NH_3 to NH_3–DME 1:4 v/v). These trends probably reflect mainly changes in the rates of removal of $H_3B^{\bullet -}$ and e^-_{amm}, rather than in the rates of their production. When $[Bu^n_4NBH_4]$ was 0.46 M in NH_3–DME (3:2 v/v) at 273 K, decay of both $H_3B^{\bullet -}$ and e^-_{amm} when photolysis was interrupted was approximately first-order, with half-lives of *ca.* 40 and 10 ms, respectively. These half-lives increased to *ca.* 108 and 134 ms at 250 K.

Ammonium ions [see equation (2)] could react with H_4B^- to give ultimately the borane–ammonia adduct $H_3B \leftarrow NH_3$, which might also be formed by other routes.‡ However, at a fixed temperature the value of $[H_3B^{\bullet -}]/[e^-_{amm}]$ did not increase with the extent of sample photolysis, nor in the presence of added $H_3B \leftarrow NH_3$, indicating that reaction (3) is unimportant under our conditions up to 300 K.

$$H_3B \leftarrow NH_3 + e^-_{amm} \rightarrow H_3B^{\bullet -} + NH_3 \qquad (3)$$

Photolysis of lithium, sodium, or potassium borohydride in ammonia gave rise to intense e.s.r. spectra of e^-_{amm}, but $H_3B^{\bullet -}$ was not detected, even when the ammonia was diluted with DME, suggesting that $H_3B^{\bullet -}$ interacts with the alkali metal cations under these conditions.

In the presence of t-butyl chloride at 195 K, photolysis of $Bu^n_4NBH_4$ in NH_3–DME afforded the spectrum of the t-butyl radical and neither $H_3B^{\bullet -}$ nor e^-_{amm} were detected. Evidently both reactions (4) and (5) proceed rapidly under these conditions, since photolysis of Bu^tCl alone or along with trimethylsilane in NH_3–DME solvent did not give detectable concentrations of t-butyl radicals.

$$H_3B^{\bullet -} + Bu^tCl \rightarrow Bu^{t\bullet} + H_3BCl^- \qquad (4)$$

$$e^-_{amm} + Bu^tCl \rightarrow Bu^{t\bullet} + Cl^- \qquad (5)$$

Similarly, photolysis of tetra-n-butylammonium cyanoborohydride or sodium cyanoborohydride in NH_3–DME at 240—300 K afforded spectra of the cyanoborane radical anion ($H_2B^\bullet CN^-$) and e^-_{amm} (the latter spectrum was much weaker than that obtainable from $Bu^n_4NBH_4$ under the same conditions).§ Spectra of $H_2B^\bullet CN^-$ and e^-_{solv} were also observed during photolysis of $Bu^n_4NBH_3CN$ in HMPA or HMPA–DME.

Photolysis of tetrabutylammonium (or potassium) tri-t-butoxyborohydride[8] in NH_3 or NH_3–DME gave rise only to the spectrum of e^-_{amm} and no signal which might be assigned to $(Bu^tO)_3B^{\bullet -}$ was detected. Trialkyl borates are much weaker Lewis acids than H_3B or H_2BCN and, in ammonia, $(Bu^tO)_3B^{\bullet -}$ probably loses an electron rapidly to the solvent.

The exploitation of c.t.t.s. phenomena for the photochemical generation of specific transient free radicals and solvated electrons (the latter could be used for the production of transient radical anions) by electron detachment from stable anions offers many possibilities. Applications in organic synthesis can also be envisaged.

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‡ For example, the reverse of reaction (3).

§ The e.s.r. parameters of $H_3B^{\bullet -}$ and $H_2B^\bullet CN^-$ in ammonia are similar to those reported in Me_2O–t-$C_5H_{11}OH$ (ref. 4). In NH_3–DME (2:1 v/v) at 248 K, $H_3B^{\bullet -}$ shows $a(^{11}B)$ 19.0, a(3H) 15.2 G, *g* 2.0024, and $H_2B^\bullet CN^-$ shows $a(^{11}B)$ 14.4, a(2H) 15.7, a(N) 3.0 G, *g* 2.0025.