Oxidation Intermediates of Borohydride and Tetraphenylborate lons in Aqueous Solutions obtained by Pulse Radiolysis

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Absorption spectra of one-electron oxidized intermediates (the H₄B· and the Ph₄B· radicals) were observed upon the oxidation of H₄B⁻ and Ph₄B⁻ by the azide radical (N₃·), Br₂⁻, or (SCN)₂⁻ in pulse-irradiated solutions; the spectra have absorption maxima at 400 nm, $\varepsilon = 1800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for H₄B· and at 335 nm, $\varepsilon = 8600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for Ph₄B·.

The borohydride ion, H_4B^- , was proposed to be oxidized by OH to yield the H_4B^{\bullet} radical by Baxendale *et al.*¹ The H_4B^{\bullet} radical has also been observed in an e.s.r. study.² An oxidizing radical such as N_3^{\bullet} is a better means for production of the oxidation intermediate, as OH often abstracts an H atom from hydrogen-containing compounds.

The oxidation of tetraphenylborate ion (Ph_4B^-) is also interesting as a comparison with that of H_4B^- . Abley and Halpern³ studied kinetically the oxidation of the tetraphenylborate ion by hexachloroiridate(IV) and proposed an oxidation mechanism including the Ph_4B radical. It has been suggested in the electro-oxidation of the Ph_4B^- ion in acetonitrile⁴ that biphenyl is produced by an intramolecular coupling of two phenyl groups in neutral Ph_4B^+ . The Ph_4B^+ radical has not yet been observed by a direct method as far as we know. We have found that another bulky radical, the tetraphenylphosphoranyl radical (Ph_4P^+) can be produced upon the reduction of Ph_4P^+ by a hydrated electron.⁵

We have studied the oxidation of both H_4B^- and Ph_4B^- in aqueous solutions by the oxidizing azide radical $(N_3 \cdot)$, Br_2^- , or $(SCN)_2^-$, using the pulse radiolysis technique. Pulses of 10 MeV electrons of ~0.5 µs duration were delivered from a linear accelerator to a N₂O saturated solution of 2×10^{-2} M NaN₃ and 3×10^{-4} M NaBH₄ at pH 11.1. Dinitrogen oxide (N_2O) scavenges the hydrated electron (e_{aq}^-) to convert it into the OH radical. Then, most of the radicals react with azide anions (N_3^-) to produce oxidizing radicals $(N_3 \cdot)$. A transient absorption was observed at wavelengths longer (≥ 270 nm) than those at which N₃⁻ absorbs. The optical densities immediately and 100 µs after the pulse were measured at wavelengths 270—500 nm with an average dose of 460 rad (Figure 1). The transient species has an absorption maximum at 400 nm. The absorption coefficient at 400 nm was found to be 1800 dm³ mol⁻¹. The transient absorption is very similar to that¹ generated from the reaction of H₄B⁻ with OH. Hence, the H₄B⁻ ion is most likely to be oxidized by N₃·, equation (1). This fact supports the oxidation¹ of H₄B⁻ through an electron transfer. The rate constant for the reaction of the H₄B⁻ ion with N₃· was obtained as 8×10^8 dm³ mol⁻¹ s⁻¹ from the formation rate of the transient. The transient absorption decays by first-order kinetics ($k = 5.6 \times 10^3$ s⁻¹) at low dose (~250 rad/pulse) and by second-order kinetics ($2k/\epsilon = 1.6 \times 10^6$ cm s⁻¹) at high dose (~900 rad/pulse).

$$H_4B^- + N_3 \cdot \longrightarrow H_4B \cdot + N_3^- \tag{1}$$

On the other hand, a transient absorption was observed in a N₂O-saturated solution of 2×10^{-2} M NaN₃ and 1×10^{-3} M NaBPh₄ at neutral pH \sim 7 at wavelengths longer (\geq 300 nm) than those at which Ph₄B⁻ absorbs. The optical densities immediately, 20, 50, and 400 µs after the pulse were measured at wavelengths 300-370 nm with an average dose of 404 rad (Figure 2). The transient species immediately after the pulse has an absorption maximum at 335 nm, which shifts to 330 nm \sim 50 µs after the pulse. The absorption coefficient at 335 nm was found to be 8600 dm3 mol-1 cm-1. The transient absorption immediately after the pulse decays by first-order kinetics $(k = 2 \times 10^4 \text{ s}^{-1})$ to be converted into another transient absorption which decays more slowly by secondorder kinetics $(2k/\epsilon = 9 \times 10^4 \text{ cm s}^{-1})$. Almost the same spectrum of the transient species was observed in the systems of Br⁻ and SCN⁻. Most of the OH radicals react with N_3^{-} , Br⁻, and SCN⁻ to produce oxidizing azide radicals (N_3) , $Br_2^{\overline{*}}$, and $(SCN)_2^{\overline{*}}$. Hence, the transient species would not be the N_3 , Br_2 , or $(SCN)_2$ adduct of Ph_4B . The azide radical,



Figure 1. Absorption spectra from the pulse radiolysis of a N₂O-saturated solution of NaBH₄ (0.3 mM) and NaN₃ (0.02 M).



Figure 2. Transient spectra from the pulse radiolysis of a N₂Osaturated solution of NaBPh₄ (1 mM) and NaN₃ (0.02 M) at different times after the pulse.

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 Br_{2}^{-} , and $(SCN)_{2}^{-}$ are rather strong oxidants which oxidize triose reductone (2,3-dihydroxyprop-2-enal) to yield the one-electron oxidized radical.⁶ Then, they are most likely to oxidize Ph₄B⁻ to yield the Ph₄B· radical as shown in equation (2).

$$\frac{Ph_4B^- + N_3 \cdot [or Br_2^-, (SCN)_2^-]}{\longrightarrow Ph_4B^+ + N_3^- (or \ 2 \ Br^-, \ 2 \ SCN^-)}$$
(2)

From analyses of formation of the transient and decay of the oxidizing species, the rate constants for the reaction of the Ph₄B⁻ ion with N₃·, Br₂⁻, and (SCN)₂⁻ were obtained as 1.4 $\times 10^9$, 2×10^7 , and 2×10^6 dm³ mol⁻¹ s⁻¹ respectively. The great difference in the rate constant for oxidation of Ph₄B⁻ by N₃· and Br₂⁻ suggests ionic repulsion between Ph₄B⁻ and Br₂⁻. The Ph₄B· radical is suggested to undergo self-decomposition following first-order decay kinetics, equations (3, 4). The phenyl radical (Ph·) has an absorption spectrum ($\lambda_{max.} = 260$ nm) at wavelengths shorter than 280 nm.⁷ Triphenylboron is hydrolysed to yield phenylboric acid or

$$Ph_4B \cdot \longrightarrow Ph_2B \cdot + Ph_2 \tag{3}$$

$$\longrightarrow Ph_3B + Ph$$
 (4)

diphenylboric acid.⁸ Hence, reaction (3) seems more probable for the decay of the Ph_4B · radical, where the secondarilyproduced transient may disappear following second-order kinetics.

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