"one-pot" synthesis of $[B_{11}H_{14}]^-$ from B_5H_9 by altering the ratio of reactants and increasing the reaction temperature. When B_5H_9 and KH were reacted in a 2.4:1 molar ratio (B_5H_9:KH) in glyme at 85 °C, the only nonvolatile boron hydride product was K$[B_{11}H_{14}]$, as indicated from its boron-11 NMR spectrum. A very small amount of B_2H_6 was recovered from the volatile reaction products. Approximately 3.5 equiv of H_2 gas was evolved in the reaction. The use of NaH instead of KH produced similar results. The formation of $[B_{11}H_{14}]^-$ from this reaction is illustrated in eq 2.

$$2.2B_5H_9 + MH \xrightarrow{\text{glyme, 85 °C}} M[B_{11}H_{14}] + 3.4H_2 \qquad (2)$$

In a similar reaction Li$[B_{11}H_{14}]$ was prepared from *t*-BuLi and B_5H_9. When B_5H_9 and *t*-BuLi were reacted in a 2.4:1 molar ratio (B_5H_9:*t*-BuLi) in glyme at 85 °C, the major nonvolatile boron-containing product (>85%) was Li$[B_{11}H_{14}]$, as indicated from its boron-11 NMR spectrum. A small amount of B_2H_6 was identified in the volatile reaction products by IR spectroscopy. Approximately 3.9 equiv of H_2 gas was evolved in the reaction. The formation of Li$[B_{11}H_{14}]$ from this reaction is illustrated in eq 3.

$$2.2B_5H_9 + t\text{-BuLi} \xrightarrow[\text{20 h}]{\text{glyme, 85 °C}} Li[B_{11}H_{14}] + 2.4H_2 + t\text{-BuH} \qquad (3)$$

In addition to the preparative reactions cited above, it was found that 1 equiv of B_2H_6 also reacts with K$[B_9H_{14}]$ under the same conditions to produce $[B_{11}H_{14}]^-$ in essentially quantitative yield based upon analysis of the volatiles and the boron-11 NMR spectrum of the nonvolatile product. Although the reaction of B_5H_9 with Na$[BH_4]$ has been previously shown to produce $[B_{11}H_{14}]^-$, this preparation provides much lower yields of $[B_{11}H_{14}]^-$ along with other anionic species ($[B_3H_8]^-$ and $[B_{12}H_{12}]^{2-}$) and employs the use of high-pressure equipment.[7] The procedure reported here produces pure $[B_{11}H_{14}]^-$ in yields that are in excess of 90% based on B_5H_9 and is carried out in standard Pyrex laboratory apparatus. It is especially attractive in view of the large stockpile of B_5H_9 in government inventories. Other synthetic methods for the preparation of $[B_{11}H_{14}]^-$ not based upon B_5H_9 have also been reported previously.[8-11]

The boron-11 NMR spectrum of $[B_{11}H_{14}]^-$ reported earlier[8] was obtained at 19.1 MHz and does not show resolution of the signals. The boron-11 NMR spectrum shown here (Figure 1), obtained at 96.3 MHz consists of three doublets at −12.5 (J = 146 Hz), −14.1 (J = 156 Hz), and −14.9 ppm (J = 138 Hz), in a ratio of 1:5:5, corresponding to boron atoms 1, 2–6, and 7–11, respectively. The assignments were made by employing 2D ^{11}B–^{11}B NMR spectroscopy. The 2D ^{11}B–^{11}B NMR spectrum clearly shows that there is coupling between the two planes of atoms and that the capping atom is coupled to only one of the planes, allowing the assignment given above. The boron-11-decoupled proton NMR spectrum (300.3 MHz) is in good agreement with the boron-11 NMR spectrum, showing three signals for the terminal hydrogens and a single signal for the bridging hydrogens at 1.93 (1 H, terminal), 1.72 (5 H, terminal), 1.28 (5 H, terminal), −3.67 ppm (3 H, bridge).

Acknowledgment. This work was supported by the Army Research Office through Grant DAAG29-85-K-0187. N.S.H. thanks Southern Methodist University for a sabbatical leave. Z.H. thanks Wuhan University, Wuhan, China, for a sabbatical leave. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center (funded in part by NSF Grant 79-10019 and NIH Grant 1 S10 PRO14058-01A1).

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Peroxoborates. Interaction of Boric Acid and Hydrogen Peroxide in Aqueous Solution

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The interaction of hydrogen peroxide with boric acid has been studied by a wide variety of experimental techniques including conductivity measurements,[1] pH measurements,[2] Raman spectroscopy,[3] and, most recently, ^{11}B NMR spectroscopy.[4] While the crystal structure[5] of sodium peroxoborate shows a cyclic dimeric peroxoborate anion with bridging peroxo groups and two four-coordinate boron atoms ($B_2(O_2)_2(OH)_4^{2-}$), various solution studies have been interpreted in a number of ways ranging from a proposal[3] that one monomeric four-coordinate peroxoborate anion ($(HO)_3BOOH^-$) is the only significant species in solution to the assertion[2] that "...quantitative interpretation of the (pH titration) data requires the postulation of about six peroxyborate species". We have previously used[6] pH methods successfully to determine stability constants for complex formation of boron acids with bidentate chelating ligands. Application of those methods to the study of peroxoboron species permits quantitative evaluation of equilibrium constants for the formation of three peroxoboron species at pH ≤9. High-field ^{11}B NMR spectroscopy was used in conjunction with the pH methods in a qualitative sense in order to determine the minimum number of boron-containing species as a function of pH.

Experimental Section

Boric acid and hydrogen peroxide (Fisher) were used as received. All pH experiments were performed at μ = 0.1 M (KNO_3) and 25 °C. Hydrogen peroxide solutions were freshly prepared just prior to use and standardized[7] by titration with standard $KMnO_4$. Solutions were prepared with freshly boiled water, and titrations were carried out under a N_2 atmosphere. No attempt such as addition[3] of EDTA was made to inhibit the decomposition of H_2O_2. Instead, following each titration the reaction mixture was immediately titrated against standard $KMnO_4$. The peroxide, whether bound or free,[2] is oxidized by $KMnO_4$. In all cases, the decrease in concentration of peroxide during the experiment was less than 1%.

Phenylboronic acid and *tert*-butyl hydroperoxide (Aldrich) were used as received. pH titration experiments were carried out on the $C_6H_5B(OH)_2/H_2O_2$ and the $B(OH)_3/(CH_3)_3COOH$ systems to determine the effect of reactant acidity on the measured equilibrium constants. Standardization of $(CH_3)_3COOH$ solutions was accomplished by titration[8] with standard $S_2O_3^{2-}$ in the presence of excess I^-.

^{11}B NMR spectra were run at a frequency of 128 MHz on a JEOL GX 400-MHz NMR spectrometer. Quartz tubes (10 mm) were used since strong ^{11}B resonances occur in Pyrex.[9] All solutions were 0.1 M KNO_3 with ~25% D_2O used as a frequency lock. All solutions were freshly prepared, and the pH was checked just before running the ex-

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(2) Edwards, J. O. *J. Am. Chem. Soc.* **1953**, *75*, 6154.

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(4) Chernyshov, B. N.; Shchetinina, G. P.; Brovkina, O. V.; Ippolitov, E. G. *Koord. Khim.* **1985**, *11*, 31. In addition, ^{11}B NMR spectroscopy is finding increasing use in the study of both polyborate equilibria (Salentine, C. G. *Inorg. Chem.* **1983**, *22*, 3920) and borate complexation reactions (Van Duin, M.; Peters, J. A.; Kieboom, A. P. G.; Van Bekkum, H. *Tetrahedron* **1984**, *15*, 2901.)

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(6) Pizer, R.; Selzer, R. *Inorg. Chem.* **1984**, *23*, 3023 and earlier references therein.

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(8) Vogel, A. I. *Elementary Practical Organic Chemistry. Part 3. Quantitative Organic Analysis*; Longmans, Green and Co.: London, **1958**; p 836.

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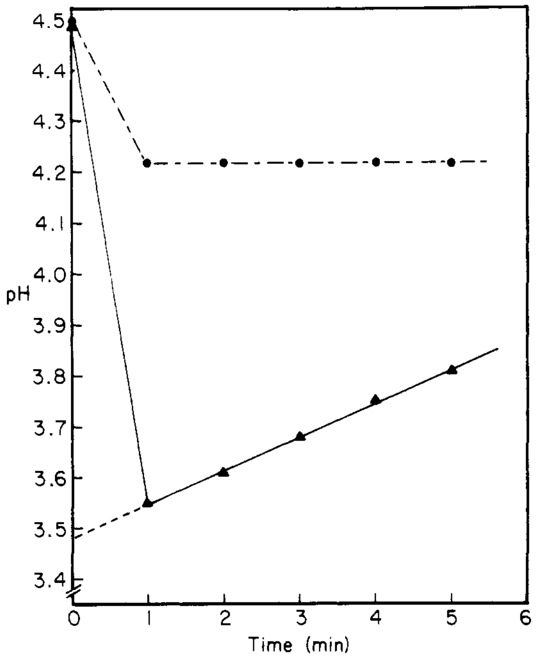

Figure 1. pH mixing experiments: $B(OH)_3/H_2O_2$ system (dashed line), where $[B(OH)_3]_0 = 0.046$ M and $[H_2O_2]_0 = 1.065$ M; $C_6H_5B(OH)_2/H_2O_2$ system (solid line), where $[C_6H_5B(OH)_2]_0 = 0.034$ M and $[H_2O_2]_0 = 1.105$ M.

periment. The ^{11}B NMR signal of a solution of 0.1 M $B(OH)_3$ at pH 6 was set at 0 ppm as a reference. Spectra of solutions which are ~0.1 M $B(OH)_3$ and ~1.0 M H_2O_2 were recorded at several pH values. Spectra at pH ~8 were recorded at different temperatures between 25 and 55 °C. Quantitative evaluation of the spectra was not attempted because of the overlapping of the observed peaks and the uncertainty in hydrogen peroxide concentration due to decomposition of hydrogen peroxide during the experiments. Small bubbles were observed in the NMR tube at higher temperatures, indicating more rapid decomposition of hydrogen peroxide under these conditions.

Stability Constant Determinations

The pK_a of boric acid[10] is 8.98, and that of hydrogen peroxide[11] is 11.6. The interaction of $B(OH)_3$ and H_2O_2 was studied by two independent pH titration methods. In one method a solution of one reactant adjusted to a particular initial pH is titrated with a solution of the second reactant adjusted to the same initial pH. Since hydrogen ion is a product of the reaction, the pH decreases when the solutions are mixed. This method is related to that used by Edwards[2] in his study of peroxoborates. A representative experimental result is shown in Figure 1. The second titration method is the usual one of titrating a $B(OH)_3/H_2O_2$ solution with standard NaOH. The lowest initial pH of these solutions was ca. 5.5, and a small addition of base causes a pH increase of approximately 1 unit. More than 20 titrations of each type were done with reactant concentrations in the ranges 0.01–0.06 M for $B(OH)_3$ and 0.05–1.0 M for H_2O_2.

Analysis of the data from titrations of $B(OH)_3/H_2O_2$ solutions with standard base leads to the conclusion that two peroxoboron species predominate between pH 7 and pH 9. The equilibria are given by eq 1 and 2. The equilibrium constants are accurate to

$$B(OH)_3 + H_2O_2 \rightleftharpoons (HO)_3BOOH^- + H^+ \qquad K_1 = 2.0 \times 10^{-8} \tag{1}$$

$$(HO)_3BOOH^- + H_2O_2 \rightleftharpoons (HO)_2B(OOH)_2^- + H_2O \qquad K_2 = 2.0\ M^{-1} \tag{2}$$

±10%. The first reaction is presented as an addition reaction in which H_2O_2 adds to trigonal boric acid to produce a four-coordinate peroxoborate anion with displacement of one proton from H_2O_2. The second reaction is a substitution reaction in which a OH^- on boron is displaced by a second H_2O_2, again with loss of one proton from H_2O_2.

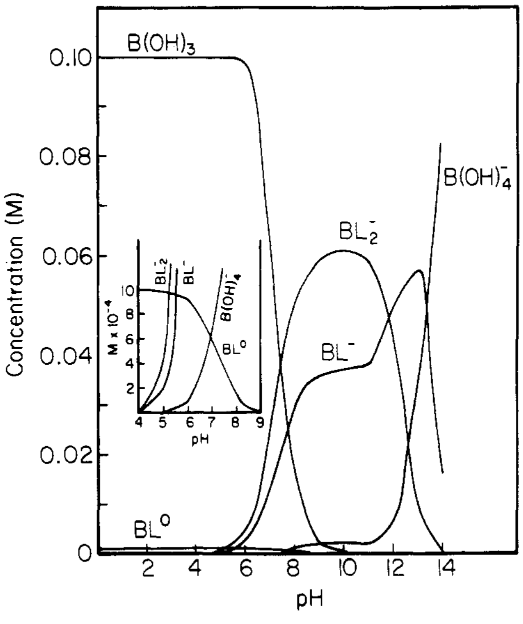

Figure 2. Distribution diagram of 0.10 M $B(OH)_3$/1.00 M H_2O_2 ($BL^0 \equiv (HO)_2BOOH$; $BL^- \equiv (HO)_3BOOH^-$; $BL_2^- \equiv (HO)_2B(OOH)_2^-$).

The usual analysis of data from titrations of this type involves the pairwise selection of points to calculate K_1 and K_2. However, using a large excess of H_2O_2 permits a reliable estimate to be made of β_2 ($=K_1K_2$), which can then be used in analyses of data from other titrations with lower $H_2O_2/B(OH)_3$ concentration ratios to determine K_1.

pH mixing experiments were carried out at lower pH values (Figure 1) and the data could not be fit in terms of eq 1 and 2 alone. Addition of a third reaction

$$B(OH)_3 + H_2O_2 \rightleftharpoons (HO)_2BOOH + H_2O \qquad K_3 = 0.01\ M^{-1} \tag{3}$$

accounts for the observed pH change.[12] This reaction is a substitution reaction in which the product is trigonal peroxoboric acid. A distribution diagram for the system calculated from the determined equilibrium constants is presented in Figure 2.

pH mixing titrations were carried out on two other related systems. In the first case, phenylboronic acid ($C_6H_5B(OH)_2$) was reacted with H_2O_2. The result of one such experiment is presented in Figure 1. Note that, under conditions virtually identical with those for the boric acid reaction, the drop in pH is considerably greater and a subsequent reaction causes an increase in pH. The large drop in pH relative to the boric acid system implies that one or more of the equilibrium constants for the $C_6H_5B(OH)_2/H_2O_2$ system is greater than the comparable constant in the $B(OH)_3/H_2O_2$ system, but the subsequent reaction makes it impossible to determine the equilibrium constants accurately. The kinetics of the overall reaction have been previously studied in detail by Kuivila.[13] The overall reaction is $C_6H_5B(OH)_2 + H_2O_2 \rightarrow C_6H_5OH + B(OH)_3$. The addition of H_2O_2 to $C_6H_5B(OH)_2$ proceeds with proton release from H_2O_2, producing the initial drop in pH as in the $B(OH)_3$ reaction (eq 1). Subsequent reaction of the peroxoborate complex produces the final reaction products.

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(10) Ingri, N. *Acta Chem. Scand.* **1962**, *16*, 439.

(11) Evans, M. G.; Uri, N. *Trans. Faraday Soc.* **1949**, *45*, 224.

(12) Equations that describe the quantitative evaluation of pH mixing experiments when only one complex is present are contained in earlier papers (Friedman, S.; Pace, B.; Pizer, R. *J. Am. Chem. Soc.* **1974**, *96*, 5381. Friedman, S.; Pizer, R. *J. Am. Chem. Soc.* **1975**, *97*, 6059). A minor modification was made to consider the case where the bis complex predominates.[6] In the present case, K_1 and K_2 are known from the previous titration technique, and the pH mixing data can then be used in the determination of K_3.

(13) Kuivila, H. G.; Armour, A. G. *J. Am. Chem. Soc.* **1957**, *79*, 5659 and references therein.

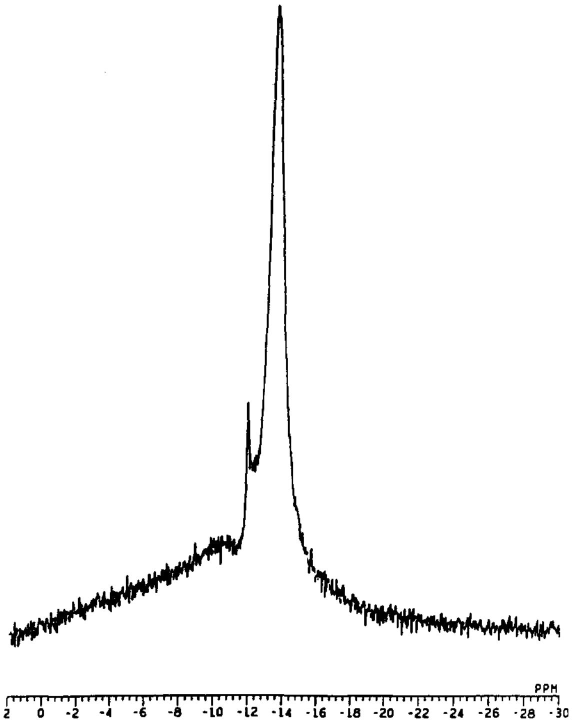

Figure 3. ^{11}B NMR spectrum: $[B(OH)_3]_0 = 0.10$ M; $[H_2O_2]_0 = 1.0$ M; pH = 8.08; $T = 25.5$ °C.

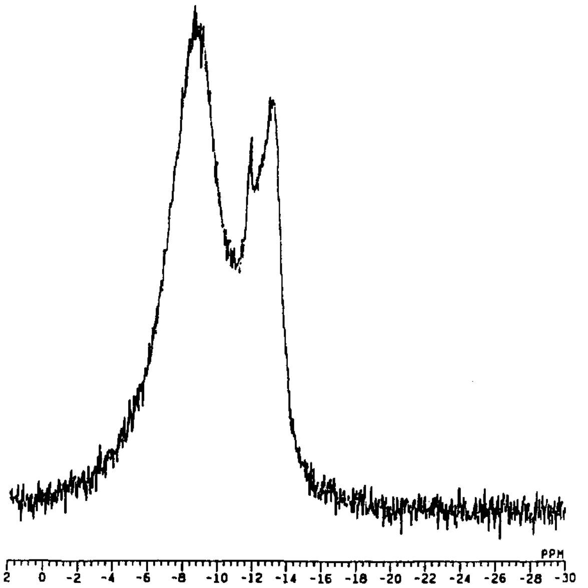

Figure 4. ^{11}B NMR spectrum: $[B(OH)_3]_0 = 0.10$ M; $[H_2O_2]_0 = 1.0$ M; pH = 8.08; $T = 55.5$ °C.

The second pH mixing experiment involved the reaction of $B(OH)_3$ with $(CH_3)_3COOH$. Only a very small drop in pH on mixing occurs in this case, which indicates minimal complex formation.

^{11}B NMR Spectra

The distribution diagram (Figure 2) can be used to determine appropriate pH conditions for carrying out ^{11}B NMR experiments. At pH 6, only one major boron-containing species, $B(OH)_3$, is expected to be present, and in fact, the spectrum of 0.10 M $B(OH)_3$ at pH 6 is identical with a spectrum of a solution that is 0.10 M $B(OH)_3$/1.0 M H_2O_2. Only a single resonance is observed in each case.

However, at pH ~8 three peaks are expected. This spectrum is presented in Figure 3. At 25.5 °C two sharp peaks and one broad peak are observed. Increasing the temperature to 55.5 °C (Figure 4) produces a sharpening of the third resonance, and qualitative agreement with the predictions of the distribution diagram is observed.[14]

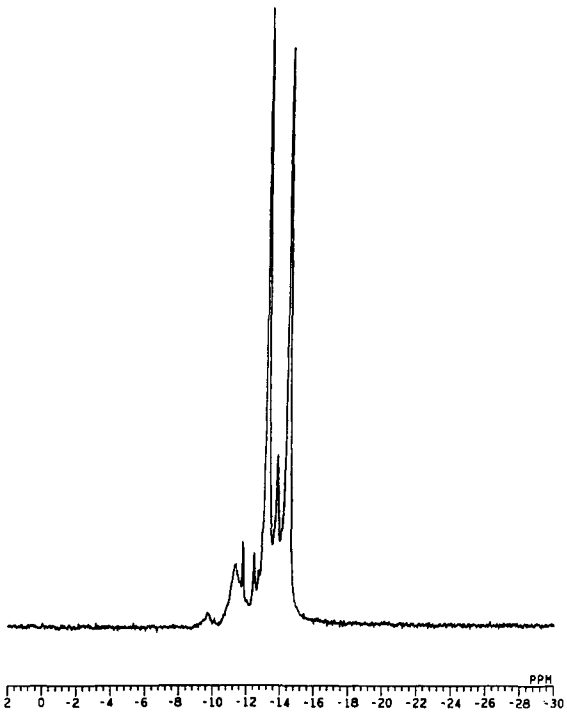

Figure 5. ^{11}B NMR spectrum: $[B(OH)_3]_0 = 0.10$ M; $[H_2O_2]_0 = 1.0$ M; pH = 9.74; $T = 25.5$ °C.

At pH ~10, the concentrations of $B(OH)_3$ and $B(OH)_4^-$ are small and the titration data predict that only the two peroxoborate anions are present. It is clear from Figure 5 that two major complexes do account for a large majority of the boron-containing species, but additional resonances are also observed.

Discussion

The data from our pH titration experiments permit the determination of equilibrium constants for three reactions (eq 1–3) involving boric acid and hydrogen peroxide at pH ≤9. ^{11}B NMR experiments provide qualitative support for this conclusion as noted above. The first point to make is that we are in clear disagreement with the recent Raman study[3] that is interpreted in terms of one peroxoboron species as given by eq 1. Not only does quantitative evaluation of the pH titration data require three peroxoboron species, but it is clear from the ^{11}B NMR spectra at pH ~10 that at least two peroxoborate anions are present in basic solution. The ^{11}B NMR spectrum at pH ~10 even shows a number of minor boron-containing species, which may include the cyclic dimer observed in the solid state[5] as well as other complexes. This result is in agreement with the conclusions[2] of Edwards' pH titration study. The value we obtain for K_1 is in agreement with preliminary results of other workers.[15] The inability to detect peroxoborates in acidic solution by ^{11}B NMR[4] or Raman spectroscopy[3] is simply due to their low concentrations. The pH mixing experiments are a much more sensitive probe of complex formation for reactions of this type. To illustrate the point, the large and easily measurable pH change shown in Figure 1 is produced by formation of peroxoboron species at a total concentration much less than 10^{-3} M.

Peroxoboric acid, $(HO)_2BOOH$, is a species whose presence in acidic aqueous solution is proposed from analysis of the pH titration data. Although the concentration of peroxoboric acid is too small under any of our experimental conditions to be detected independently by ^{11}B NMR spectroscopy, it is possible to determine its acid dissociation constant from the relationship $K_a((HO)_2BOOH) = K_1/K_3 = 2 \times 10^{-6}$. This means that $(HO)_2$-

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(14) The pH reported in Figures 3 and 4 is the initial pH of the solution as prepared. The decomposition of hydrogen peroxide over the course of the NMR measurements causes an increase in pH (eq 1). As the pH increases above pH 8, the concentration of uncomplexed $B(OH)_3$ becomes considerably less than that of either complex, and this accounts for the apparent relative areas in Figures 3 and 4.

(15) Antikainen, P. J. *Suom. Kemistil. B* **1955**, *28B*, 159.

BOOH is a stronger acid than $B(OH)_3$, a result in agreement with earlier work[1] in the area. One possible explanation[15] for the difference in acidity is that the boron–oxygen bond in R_2B–OH has more multiple-bond character than the boron–oxygen bond in R_2B–OOH because of the electron-withdrawing nature of the second oxygen in the –OOH group.

Our previous work on boron acid equilibria shows that the stability constants for boron acid complexation reactions are functions of the acidities of both the boron acid and the ligand. Phenylboronic acid ($pK_a = 8.72$)[12] is more acidic than boric acid, and its complexes with a particular ligand are characterized by stability constants that are greater than those of the analogous boric acid complex by factors of 4–6.[16] Extrapolation of the pH vs time plot in the pH mixing of $C_6H_5B(OH)_2$ and H_2O_2 (Figure 1) shows an initial change in hydrogen ion concentration on mixing that is slightly more than 5 times greater than that observed for $B(OH)_3$ under virtually identical conditions. Although the subsequent oxidation of $C_6H_5B(OH)_2$ by H_2O_2 prohibits accurate determination of the stability constants by this method, the magnitude of the change in pH is in agreement with our expectations. Similarly, since *tert*-butyl hydroperoxide is much less acidic[17] than hydrogen peroxide, the fact that complex formation is minimal when boric acid reacts with $(CH_3)_3COOH$ is in accord with our previous work.

The results of both our pH titration data and ^{11}B NMR experiments are interpreted by us in terms of peroxoboron species in which the hydroperoxo ligand is always unidentate. We have no independent structural data to support this assertion. Since the ligand is bifunctional, the possibilities of bridging peroxo ligands (as are observed in the solid state[5]) or of a peroxo ligand forming a three-membered chelate ring in peroxoboron species must be considered. Our pH titration data can be adequately described in terms of eq 1–3 at pH ≤9. The addition of a dimerization reaction such as $2(HO)_3BOOH^- \rightleftharpoons (B_2(O_2)_2(OH)_4)^{2-} + 2H_2O$ and/or other reactions involving peroxo bridges has an effect on solution pH, and their inclusion is not warranted in our analysis. However, the ^{11}B NMR spectra strongly suggest that such species may be present at higher pH values. The second possibility of peroxoboron species containing triangular bidentate peroxo ligands is more difficult to deal with. For example, whether reaction 1 produces $(HO)_3BOOH^-$ or $(HO)_2B(O_2)^-$ has no effect on solution pH. The latter species also contains a four-coordinate boron and can be thought of as arising from $(HO)_3BOOH^-$ by closure of a peroxo chelate ring with displacement of OH^- from boron and the loss of the hydroperoxide proton: $(HO)_3BOOH^- \rightarrow (HO)_2B(O_2)^- + H_2O$. Such a possibility was briefly considered by the authors[18] of a recent paper that contained an analysis of the infrared spectra of peroxofluoroborate complexes, but structures with no chelate rings were preferred, given the structure of the peroxoborate anion in the solid. We agree that this is the more likely possibility.

Acknowledgment. The support of The Camille and Henry Dreyfus Foundation and the PSC/CUNY Faculty Research Award Program is gratefully acknowledged. The helpful suggestions of Professors P. Gary Mennitt and Herman Zieger concerning the ^{11}B NMR experiments are most appreciated.

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(16) For a related discussion of the acidities of boronic acids, see: Babcock, L.; Pizer, R. *Inorg. Chem.* **1980**, *19*, 56.

(17) Everett, A. J.; Minkoff, G. J. *Trans. Faraday Soc.* **1953**, *49*, 410.

(18) Chandhuri, M. K.; Das, B. *Inorg. Chem.* **1985**, *24*, 2580. The peroxofluoroborate complexes described in this paper were synthesized in basic media (pH ~9). Given the distribution diagram for the $B(OH)_3/H_2O_2$ system presented in Figure 2, the inability to make such complexes in acid media is understandable.

Additions and Corrections

1986, Volume 25

A. Dormond, B. Belkalem, P. Charpin, M. Lance, D. Vigner, G. Folcher, and R. Guilard*: Thorium and Uranium Porphyrins. Synthesis and Crystal Structure of Bis(acetylacetonato)(2,3,7,8,12,13,17,18-octaethylporphyrinato)thorium(IV).

Page 4786. In Table II, the ^1H NMR spectral data for **2b** and **4b** were incorrectly reported. The ^1H NMR data should read as follows (δ in $CDCl_3$). **2b** protons of R^1: s/4[b] (o), 0.32; s/4[b] (o′), 8.00; m/4 (m), 4.36; m/4 (m′), 6.97; m/4 (p), 6.18. **2b** protons of R^2: s/8, 7.48. **4b** protons of R^1: s/4[b] (o), –2.25; s/4[b] (o′), 9.02; m/4 (m), 4.60; m/4 (m′), 6.80; t/4 (p), 6.06. **4b** protons of R^2: s/8, 5.94. **4b** protons of acac: s/2, 13.57; s/12, –5.64.

Page 4787. In the 10th line from the bottom, read "...is located at 7.48 ppm for **2b** and 5.94 ppm for **4b**...".—R. Guilard