Nature of Peroxoborate Species in Aqueous Solution: A Study by Boron-11 Nuclear Magnetic Resonance and Raman Spectroscopy

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The ^{11}B n.m.r. spectra of solutions of $[B(OH)_4]^-$ or $B(OH)_3$ (0.01—4 mol dm^{-3}) with H_2O_2 (0.01—34 mol dm^{-3}) have been studied from pH 14 to 4. A number of peroxoborates have been identified, in particular $[B(O_2H)_n(OH)_{4-n}]^-$ (n = 0—4) and polymeric species including $[B_2(O_2)_2(O_2H)_n(OH)_{4-n}]^{2-}$ n = 0, 2, or 4). Raman spectra have been recorded for concentrated solutions {1—4 mol dm^{-3} $[B(OH)_4]^-$, 1—12 mol dm^{-3} H_2O_2} and partial assignments proposed.

Peroxoborates, particularly the sodium salt $Na_2[B_2(O_2)_2(OH)_4]\cdot 6H_2O$, are important bleaching agents in household detergents.[1] The three published *X*-ray crystal structures of peroxoborates {for $Na_2[B_2(O_2)_2(OH)_4]\cdot 6H_2O$,[2] $Na_2[B_2(O_2)_2(OH)_4]\cdot 4H_2O$,[3] and $Li_2[B_2(O_2)_2(OH)_4]$[4]} show that all these contain a cyclic $B_2(O_2)_2$ ring in the chair conformation in the anions, but there is far less certainty concerning the nature of these species in aqueous solution. There are also reports of solid peroxoborates with peroxide:boron ratios exceeding 1:1;[5—7] it has been suggested that salts containing $[B_2(O_2)_2(O_2H)_2(OH)_2]^{2-}$ and $[B_2(O_2)_2(O_2H)_4]^{2-}$ exist.[6,7] We have studied the i.r. and Raman spectra of the salts $M^I_2[B_2(O_2)_2(O_2H)_2(OH)_2]$ (M = K, Rb, or Cs) in the solid state.[8]

Raman studies on molar solutions of $[B(OH)_4]^-$ in 0.5—2 mol dm^{-3} H_2O_2 (at pH 12.5—8.5) have been interpreted as indicating that in such solutions $[B(O_2H)(OH)_3]^-$ was the only peroxoborate species present,[9] but a recent paper on the pH titration of 0.1 mol dm^{-3} $B(OH)_3$ in 1 mol dm^{-3} H_2O_2 from pH 14 to 2 contradicts this, providing clear evidence for the existence in such solutions of $[B(O_2H)_2(OH)_2]^-$ and $[B(O_2H)(OH)_3]^-$; ^{11}B n.m.r. spectroscopy was used to show that a number of other unspecified species were also present.[10] In this paper we present the results of a systematic study on the ^{11}B n.m.r. and Raman spectra of a series of solutions of $[B(OH)_4]^-$ or $B(OH)_3$ in H_2O_2 with varying B:H_2O_2 ratios and at different pH.

Results and Discussion

^{11}B *N.M.R. Spectroscopy for Borate Equilibria.*—The ^{11}B nucleus (80.42% abundance, $S = \frac{3}{2}$, receptivity 754 times that of ^{13}C) is well suited to the n.m.r. studies; despite the quadrupole moment it gives sharp lines for species of high symmetry, and ^{11}B n.m.r. spectroscopy has been used for a number of studies of borate equilibria[11—13] in aqueous solution. In general, tetrahedrally co-ordinated boron gives sharp resonances in the region δ 0—4 p.p.m. relative to $BF_3\cdot Et_2O$, while trigonal boron gives broader signals in the δ 10—19 p.p.m. region.[11,12] For aqueous solutions the tetrahedral $[B(OH)_4]^-$ species has been identified as a sharp signal at δ 1.53 p.p.m.,[11] and trigonal $B(OH)_3$ gives a broad signal at δ 19.0 p.p.m.[11,12]

Apart from the recent pH titration study of peroxoborates, which made brief use of ^{11}B n.m.r. spectroscopy,[10] published data on the ^{11}B n.m.r. spectra of peroxoborates mainly concern $[BF_n(O_2H)_{4-n}]^-$ [14—17] or peroxoborates in solutions of $B(OH)_3$ in concentrated H_2O_2 at low pH.[16—18] In these studies we have concentrated on solutions of peroxoborates at higher pH (13—9), since it is in the pH range 9—10 that peroxoborate solutions are commonly used, although some data are presented on solutions of lower pH.

Since the ^{11}B n.m.r. spectra are often very complex we use a lettering scheme for each peak for ease of reference (Figures 1—4). All shifts are recorded in p.p.m. relative to $BF_3\cdot Et_2O$ (δ = 0) in diethyl ether and occur downfield of it.

(*a*) *Species Present at Low Boron Concentration* (0.01—0.1 mol dm^{-3}).—We first present data on solutions of low boron concentration in which monomeric species only are likely to predominate. It is generally agreed[19—23] that $[B(O_2H)(OH)_3]^-$ is present in dilute solutions of $[B(OH)_4]^-$ in H_2O_2. This conclusion was reached by Menzel[19] using conductivity and cryoscopy measurements {0.02—0.4 mol dm^{-3} $[B(OH)_4]^-$ in 0.02—0.4 mol dm^{-3} H_2O_2 at pH 8.5—10.5} and by Antikainen[22] using 0.025—0.1 mol dm^{-3} $B(OH)_3$ in 0.1—4 mol dm^{-3} H_2O_2 at pH 5—8 from different pH titration data. Edwards[20] and Pizer and Tihal[10] on the basis of pH titration measurements also conclude that $[B(O_2H)(OH)_3]^-$ predominates at high pH (12—14) but that a number of other species are present at lower pH. Pizer and Tihal[10] and Antikainen[22] have presented evidence for the existence of the $[B(O_2H)_2(OH)_2]^-$ species in solutions of $[B(OH)_4]^-$ in H_2O_2. Chernyshov and co-workers, in studies on solutions containing hydrogen peroxide and metaborate, with and without fluoride, assign ^{11}B resonances to $[F_{4-n}B(O_2H)_n]^-$ [14—17] and $[B(O_2H)_n(OH)_{4-n}]^-$,[16—18] including $[B(O_2H)_4]^-$.[15,17,18]

(*i*) 0.01 mol dm^{-3} B, 0.01 mol dm^{-3} H_2O_2. The lowest total boron concentration at which distinct ^{11}B n.m.r. signals were observed with our systems was 0.01 mol dm^{-3}. In the absence of H_2O_2, a single sharp peak was observed at high pH near δ 1.5 p.p.m., broadening and shifting downfield as the solution pH was reduced, arising from the known $B(OH)_3/[B(OH)_4]^-$ exchanging system. In 0.01 mol dm^{-3} aqueous H_2O_2 similar behaviour was observed, with only one signal (A) discernible (δ + 1.6 p.p.m. at pH 12) (Figure 1); however, this peak is shifted downfield from its position in the absence of H_2O_2, by some 0.5 p.p.m. for pH 11.5—10.0. We suggest that this arises from the three interconverting species $B(OH)_3 \underset{+H^+,\ -H_2O}{\overset{+H_2O,\ -H^+}{\rightleftharpoons}} [B(OH)_4]^- \underset{+H_2O,\ -H_2O_2}{\overset{+H_2O_2,\ -H_2O}{\rightleftharpoons}} [B(O_2H)(OH)_3]^-$ which exchange too fast to be resolved on the n.m.r. time-scale. At lower pH on the trigonal $B(OH)_3$ will predominate, hence the peak broadens.

(*ii*) 0.05 mol dm^{-3} $B(OH)_3$, 8—34 mol dm^{-3} H_2O_2. Chernyshov and co-workers, in studies on solutions containing hydrogen peroxide and metaborate, with and without fluoride, assigned ^{11}B n.m.r. resonances to species such as $[BF_{4-n}(O_2H)]^-$ [14—17] and $[B(O_2H)_n(OH)_{4-n}]^-$,[16—18] including $[B(O_2H)_4]^-$ at δ 8.1 p.p.m. relative to BF_4.[17,18] We have recorded the ^{11}B n.m.r. spectra of a series of solutions in which the boron concentration was kept low (0.05—0.1 mol dm^{-3}) (see

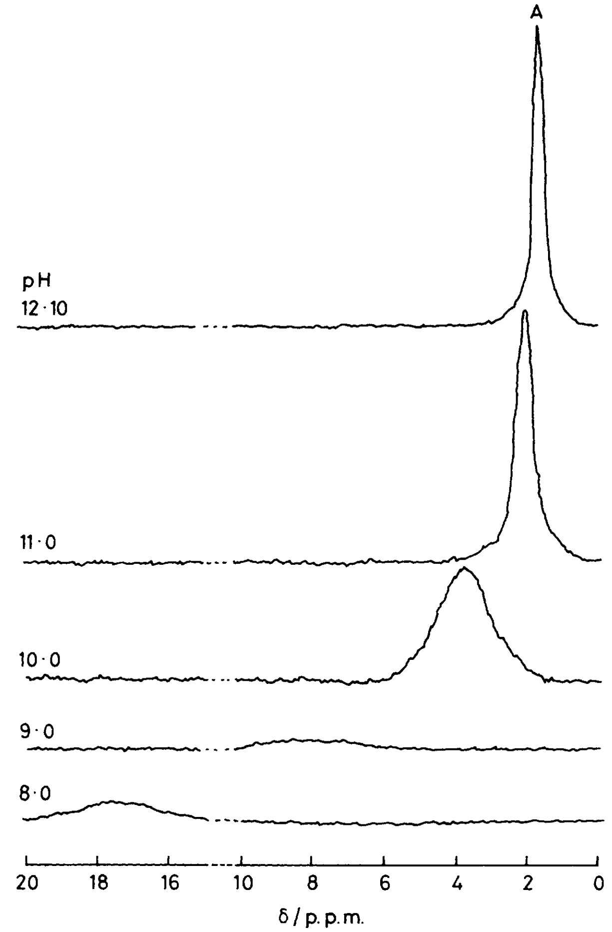

Figure 1. Boron-11 n.m.r. spectra for 0.01 mol dm^{-3} B in aqueous 0.01 mol dm^{-3} H_2O_2 [0.01 mol dm^{-3} $B(OH)_3$, pH adjusted with KOH]

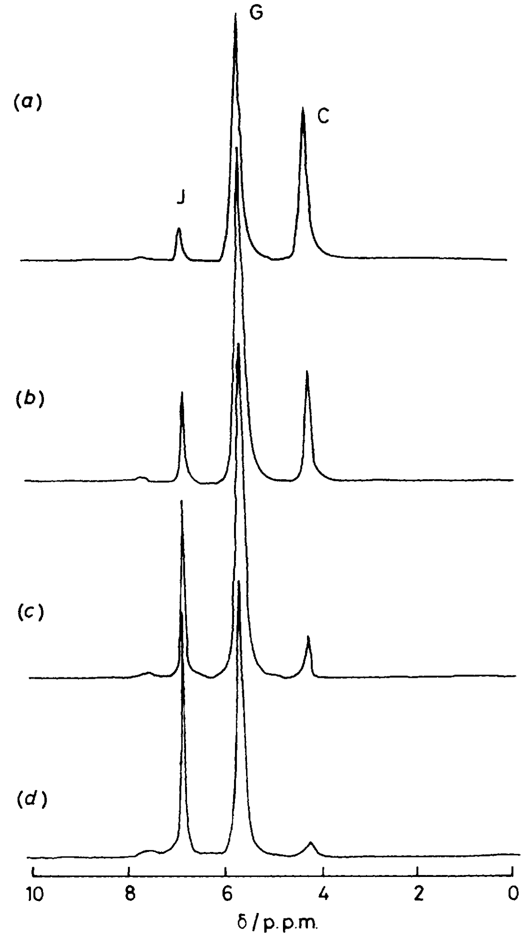

Figure 2. Boron-11 n.m.r. spectra for 0.05 mol dm^{-3} B in large excesses of aqueous hydrogen peroxide: (*a*) 8 mol dm^{-3} H_2O_2, pH 7.3; (*b*) 16 mol dm^{-3} H_2O_2, pH 6.0; (*c*) 24 mol dm^{-3} H_2O_2, pH 5.7; (*d*) 32 mol dm^{-3} H_2O_2, pH 5.3

Figure 2) in order to minimise the concentrations of polymeric species in solution, and the H_2O_2 concentration was varied from 8 to 34 mol dm^{-3}; at such high peroxide concentrations pH adjustment was difficult and inaccurate, but it was kept between 3 and 7, and within this range there was little change in the overall form of the resulting spectra. We have also recorded the ^{11}B n.m.r. spectra of a species of solutions of 0.10 mol dm^{-3} $B(OH)_3$ in 10.0 mol dm^{-3} H_2O_2 from pH 12 to 7 in order to correlate these data with those from previous sections.

All the spectra showed a signal, C, at δ 4.1—4.2 p.p.m., which, together with peak A, was the predominant feature above pH 9. Below pH 9, in addition, two sharp singlets appeared at δ 5.6—5.8 (G) and 6.8—6.9 p.p.m. (J), and at very high peroxide concentrations (20 mol dm^{-3} and above) and below pH 7 these two became the dominant features. A series of spectra showing the effect of increasing peroxide concentration is shown in Figure 2. In view of the low concentration of $[B(OH)_4]^-$ present, it seems reasonable to assume that these arise from monomeric complexes, and also that the ^{11}B resonance will shift to lower field on successive replacement of hydroxo groups by the more electronegative hydrogenperoxo ligands, as suggested by Chernyshov and co-workers.[15,17] In addition, the tetraperoxo species $[B(O_2H)_4]^-$ has tetrahedral symmetry at the boron atom, and should therefore give a very sharp ^{11}B n.m.r. signal. We find that the resonance at δ 6.9 p.p.m. (J) is strongest at maximum peroxide concentration, decreasing as the amount of peroxide present is reduced, while that at δ 5.7 p.p.m. (G) increases slightly relative to it. The *J* signal is also the sharper of the two, and we therefore assign these resonances to $[B(O_2H)_4]^-$ (J) and $[B(O_2H)_3(OH)]^-$ (G) respectively.

It appears that these species are predominant at lower pH, possibly because at higher pH values the OH^- ion is present in significant quantities and competes more effectively with the O_2H^- ion than does H_2O. The major factor in determining the distribution of species at lower pH (7—3) appears to be the ratio of hydrogen peroxide to water.

It is not clear why the species $[B(OH)_4]^-$ and $[B(O_2H)(OH)_3]^-$ should exchange rapidly on the n.m.r. time-scale while more highly peroxidated species do not. However, it is known that trigonal species of the form $B(O_2H)_n(OH)_{3-n}$ do not readily form,[10] although $B(OH)_3$ is stable. This implies that a facile exchange mechanism exists for $[B(OH)_4]^-$ and $[B(O_2H)(OH)_3]^-$, *via* $B(OH)_3$ as intermediate; for more highly peroxidated species such a stable intermediate may not be available, so that the rates of exchange reactions are substantially decreased.

(*iii*) 0.1 mol dm^{-3}, 1.0 mol dm^{-3} H_2O_2. A series of ^{11}B n.m.r. spectra of solutions of these concentrations was recorded from pH 14 to 4 in order to compare our ^{11}B n.m.r. data with the recent pH titration measurements of Pizer and Tihal[10] which also used these concentrations. At pH 13.8 the single peak A predominates at δ 1.7 p.p.m., but at a slightly lower pH (13—11) other features appear near δ 3.7 (B) and 4.2 p.p.m. (C). At still lower pH values weak, broad signals near δ 5.2 (E) and 7.8 p.p.m. (K) appear (see Figure 3). The mole ratio of boron species (obtained by integration of the n.m.r. data) *versus* pH can be

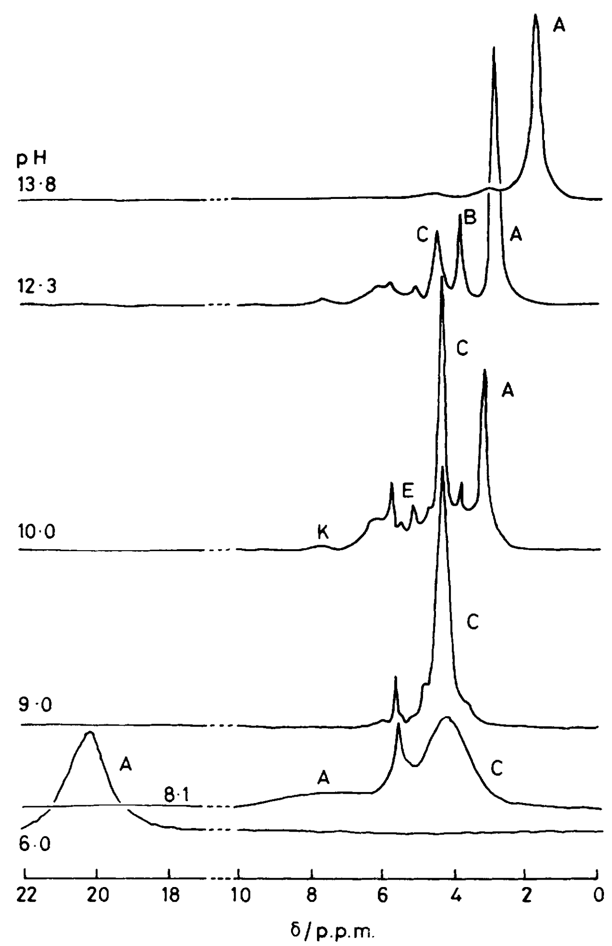

Figure 3. Boron-11 n.m.r. spectra for 0.10 mol dm^{-3} B in aqueous 1.0 mol dm^{-3} H_2O_2 [0.10 mol dm^{-3} $B(OH)_3$, pH adjusted with KOH]

plotted; if peak A is assigned as the sum of the concentrations of $B(OH)_3$, $[B(OH)_4]^-$, and $[B(O_2H)(OH)_3]^-$ and C at δ 4.2 p.p.m. as arising from $[B(O_2H)_2(OH)_2]^-$, the resulting distribution fits the pH titration data[10] diagram very well. The origin of 'B' is discussed below.

Solid $Na_2[B_2(O_2)_2(OH)_4]{\cdot}6H_2O$ has a solubility in water at 25 °C of 0.5 mol dm^{-3},[23] and the natural pH of such a solution is 10.0. At this pH we find that the ^{11}B n.m.r. spectrum of a solution of 0.1 mol dm^{-3} $B(OH)_3$ in 0.1 mol dm^{3} H_2O_2 {*i.e.* simulating $[B_2(O_2)_2(OH)_4]^{2-}$ in terms of $[B]:[H_2O_2]$ ratio} is identical with that of 0.05 mol dm^{-3} $Na_2[B_2(O_2)(OH)_4]{\cdot}6H_2O$. This suggests that identical species are present in solutions of $[B_2(O_2)_2(OH)_4]^{2-}$ and a 1:1 $[B(OH)_3]:[H_2O_2]$ mixture. The A, B, and C peaks are clearly discernible in these spectra.

(*b*) *Species Present at Higher Boron Concentrations* (0.2—1.0 mol dm^{-3}).—We now present data on solutions of higher boron concentration in which binuclear and polynuclear species may be present in significant concentrations; the effect of increasing the boron concentration is shown in Figure 4. Cryoscopic measurements by Koberstein *et al.*[23] on aqueous solutions of $Na_2[B_2(O_2)_2(OH)_4]$ (0.01—0.2 mol dm^{-3} B) suggest that some species in solution retain the dimeric structure at higher concentrations only (0.2 mol dm^{-3}). Chernyshov and co-workers,[16–18] in ^{11}B n.m.r. studies of $[B_2(O_2)_2(OH)_4]^{2-}$ in very concentrated H_2O_2, assigned signals with shifts relative to $[BF_4]^-$ at δ 6.2 p.p.m. to $[B_2(O_2)_2(O_2H)_n(OH)_{4-n}]^{2-}$ and at δ 8.1 p.p.m. to $[B_2(O_2)_2(O_2H)_4]^{2-}$.

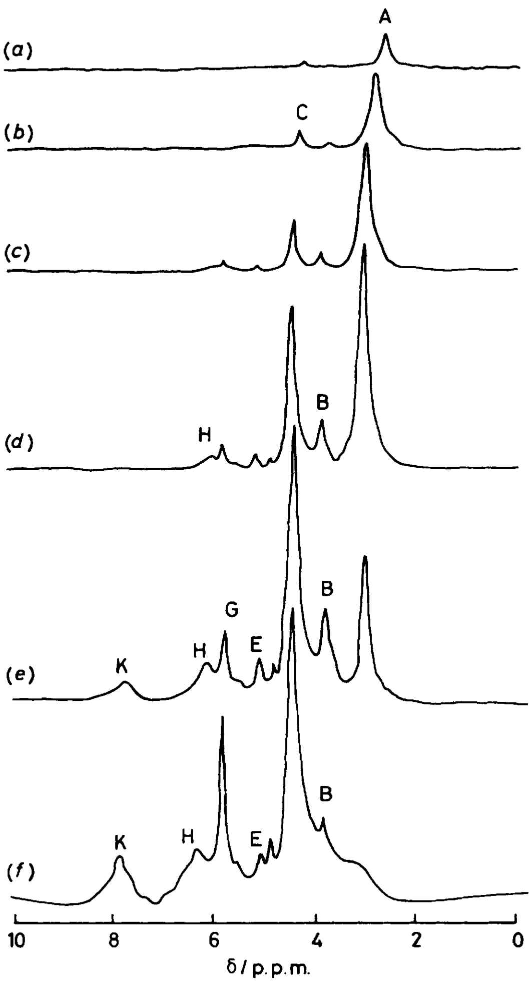

Figure 4. Boron-11 n.m.r. spectra of aqueous solutions with a 10:1 ratio of $[H_2O_2]:[B]$ at pH 10.5. Concentrations (B, H_2O_2) in mol dm^{-3}: (*a*) 0.01, 0.10; (*b*) 0.02, 0.20; (*c*) 0.05, 0.50; (*d*) 0.10, 1.0; (*e*) 0.20, 2.0; (*f*) 0.50, 5.0

We have recorded the ^{11}B n.m.r. spectra of two series of solutions, one in which the ratio of peroxide to boron is kept at 1:1, the other in which a ten-fold excess of H_2O_2 is used, for boron concentrations of 0.2—1.0 and 0.2—0.5 mol dm^{-3} respectively, at high pH (10.5). Examples from the latter series are shown in Figure 4(*e*) and (*f*). We have also studied solutions in which 0.2—0.5 mol dm^{-3} boric acid was dissolved in very concentrated H_2O_2 at lower pH (3—5). By using sodium metaborate rather than the potassium salt, we have been able to obtain up to 4 mol dm^{-3} concentrations of borate in solution, with H_2O_2 up to 12 mol dm^{-3}; in these latter cases, however, pH control was difficult to maintain, and the peaks are broader, perhaps due to the increased viscosity of the solutions.

(*i*) 0.2—1.0 mol dm^{-3} B, 0.2—1.0 mol dm^{-3} H_2O_2. The ^{11}B n.m.r. spectra of a series of equimolar $B:H_2O_2$ solutions were recorded at pH 10.5 for boron concentrations of 0.2, 0.5, and 1.0 mol dm^{-3}. The peaks arising from monomeric species in 0.1 mol dm^{-3} solutions, A and C, were both present, as expected. In addition, there were two new broad features, E and K, at δ 5.2 and 7.8 p.p.m. respectively, which increased in relative intensity as the boron concentration was increased.

(*ii*) 0.2 mol dm^{-3} *and* 2.0 mol dm^{-3} $[H_2O_2]$ *to* 0.5 mol dm^{-3} *and* 5.0 mol dm^{-3} $[H_2O_2]$. In the ^{11}B n.m.r. spectra of these solutions at pH 10.5, we observe, in addition to peaks A, B, and C, that E decreases in intensity relative to K with increasing H_2O_2 concentration. Figure 4 shows a series of spectra from solutions in which a ten-fold excess of peroxide is used where we would expect increased substitution of OH^- by O_2H^-. We tentatively assign peak E to the parent dimer, $[B_2(O_2)_2(OH)_4]^{2-}$, and K to $[B_2(O_2)_2(O_2H)_4]^{2-}$. Both, in particular K, are broader than the peaks (A, C, G, and J) assigned to monomeric species, as might be expected for dimeric complexes in which the geometrical constraints are greater.

(*iii*) 0.2—0.5 mol dm^{-3} B, 30 mol dm^{-3} $[H_2O_2]$. Only a few spectra could be recorded for this series owing to the hazardous nature of the solution, and above pH 4.5 they could not be kept in a sufficiently stable condition for good spectra to be obtained. At pH 4.5, in addition to peaks G and J, we observe K at δ 7.8 p.p.m., which is in reasonable agreement with Chernyshov's assignment of such a peak to $[B(O_2)_2(O_2H)_4]^{2-}$.[18] We also observe a new feature, peak H, at δ 6.4 p.p.m., which, like E and K, is quite broad. It appears as a shoulder to J, which makes the comparison of integrals difficult, but it seems to show a similar variation with H_2O_2 concentration to that of K. We assign this to the dimeric species $[B_2(O_2)_2(O_2H)_2(OH)_2]^{2-}$, which is believed to be present in '$M^IBO_4\cdot H_2O$'.[6,7] In solutions with such high peroxide concentrations it appears that these two species are the only dimeric ones present in detectable quantities. If our assignments of E as $[B_2(O_2)_2(OH)_4]^{2-}$, H as $[B_2(O_2)_2(O_2H)_2(OH)_2]^{2-}$, and K as $[B_2(O_2)_2(O_2H)_4]^{2-}$ are correct, this is in accord with the tendency observed above for monomeric species of the series $[B(O_2H)_n(OH)_{4-n}]^-$ for the ^{11}B resonance to shift to lower field as the replacement of OH^- by O_2H^- groups proceeds. Species such as $[B_2(O_2)_2(O_2H)_n(OH)_{4-n}]^{2-}$ (n = 1 or 3) may of course be formed and may contribute to these signals, but there is definite chemical evidence for the existence of salts with n = 0,[2–4] 2,[5,6] or 4[6,7] in the solid state.

(*iv*) 0.5—4.0 mol dm^{-3} B, 0.5—12.0 mol dm^{-3} H_2O_2. For these very concentrated solutions $Na[B(OH)_4]$ was used as the starting reagent rather than $K[B(OH)_4]$, since it is much more soluble in hydrogen peroxide; the increased viscosity of the solutions however leads to peak broadening. For solutions containing $[B]:[H_2O_2]$ of 1:1 a broad peak was always observed near δ 4.7—5.0 p.p.m., which corresponds to the signal E and supports the assignment of this to $[B_2(O_2)_2(OH)_4]^{2-}$. A shoulder was always present upfield from this, at δ 3.6—4.0 p.p.m., probably B or C, and a further broad signal was always present in the region δ 6.6—7.8 p.p.m., becoming less intense and moving downfield as the ratio of $[B]:[H_2O_2]$ was decreased. For solutions with a 1:1 ratio $[B]:[H_2O_2]$ this was less intense than peak E and had a chemical shift value of 6.6—7.3 p.p.m. For solutions with a 1:3 ratio of boron to peroxide it was of comparable intensity to E and occurred at δ 7.5—7.8 p.p.m.; in this case it corresponds to the signal K in spectra of more dilute solutions. Since the $[B_2(O_2)_2(O_2H)_4]^{2-}$ anion has a 1:3 boron to peroxide ratio it is reasonable to expect that it will be present in substantial concentrations in such solutions, where the contribution of water and hydroxide ion to the reactions taking place will be small compared with that of hydrogen peroxide and the hydrogenperoxo ion. This supports the earlier assignment of K to this ion.

A series of spectra have also been recorded in which the ratio $[B]:[H_2O_2]$ was kept at 2:1 and the concentration of boron was varied from 0.1 to 4.0 mol dm^{-3}. In this case all the spectra showed the same three signals, at δ 2.2, 3.5, and 4.8—5.1 p.p.m. As the concentration of boron was increased the first of these decreased in relative intensity, while the second increased, and the third increased rapidly to become the dominant feature. These correspond to the features A, B, and E respectively, with E being significantly broader than the other two at lower boron concentrations. At higher boron concentrations, above 0.5 mol dm^{-3}, a shoulder is also observed at δ 7.3—7.6 p.p.m.; this again corresponds to the signal K. This supports the assignments given previously, although it is of course possible that higher polymers could be present in such solutions.

(*c*) *Solid-State* ^{11}*B n.m.r. of Peroxoborates.*—We have measured the solid-state ^{11}B n.m.r. spectra under 'magic angle' conditions of $Na[B(OH)_4]$, $Na_2[B_2(O_2)_2(OH)_4]\cdot 6H_2O$ and $M^I_2[B_2(O_2)_2(O_2H)_2(OH)_2]$ (M^I = K, Rb, or Cs), and find ^{11}B chemical shifts (relative to $BF_3\cdot Et_2O$) of 1.34, 3.71, 7.60, 8.05, and 8.03 p.p.m. respectively. These compare with values of 1.5 p.p.m. for $[B(OH)_4]^-$ in solution with our assignment of $[B_2(O_2)_2(OH)_4]^{2-}$ at 5.2 p.p.m. as E, of $[B_2(O_2)_2(O_2H)_2(OH)_2]^{2-}$ at 6.4 p.p.m. as H, and of $[B_2(O_2)_2(O_2H)_4]^{2-}$ as K at 7.8 p.p.m. respectively in solution. From the approximate correlation between the δ values in the solid state and in solution for $[B(OH)_4]^-$ and $[B_2(O_2)_2(O_2H)_2(OH)_2]^{2-}$ it is apparent that our unassigned peak B, at δ 3.6 p.p.m. could be a rival candidate to E at δ 5.2 p.p.m. for $[B_2(O_2)_2(OH)_4]^{2-}$.

(*d*) *Raman Spectra of Peroxoborate Solutions.*—The Raman spectrum of solid $Na_2[B_2(O_2)_2(OH)_4]\cdot 6H_2O$ (**1**) has been reported and in part assigned,[6,9] and the Raman spectrum of $Na[B(OH)_4]$ fully assigned.[24,25] On the basis of differences between the Raman spectra of solid (**1**) and of solutions of $[B(OH)_4]^-$ in H_2O_2 (0.5—1 mol dm^{-3} B, 0.5—2 mol dm^{-3} H_2O_2 at pH 8—11) Adams and Clark[9] concluded that in such solutions there is no $[B_2(O_2)_2(OH)_4]^{2-}$, and that $[B(O_2H)(OH)_3]^-$ is the only peroxo species present. This conflicts with our n.m.r. data and also with Pizer's recent pH titration results,[10] so we have undertaken a Raman study of solutions of $[B(OH)_4]^-$ in H_2O_2 at high concentrations.

From published data on[6,9] the Raman spectrum of $Na_2[B_2(O_2)_2(OH)_4]\cdot 6H_2O$ and our own data on the normal, ^{10}B-, and ^2H-enriched forms of the salt,[8] the bridging O–O stretch in the anion, ν(O–O), is likely to be the strong band at 901 cm^{-1}, close to similar bands observed in the spectra of $K_2[S_2O_8]$[25] and $Li_4[P_2O_8]\cdot 4H_2O$.[26] Other features of $[B_2(O_2)_2(OH)_4]^{2-}$ are a weak band at 711 cm^{-1} due to the asymmetric B–O stretch of the $B(O_2)_2B$ bridge unit, $\nu_{asym}[B(O_2)_2B]$, and a strong band at 968 cm^{-1} assigned to the symmetric stretch of the terminal $B(OH)_2$ unit, $\nu_{sym}[B(OH)_2]$.[9] The salts '$M^IBO_4\cdot H_2O$' (M = K, Rb, or Cs) are likely to contain $[B_2(O_2)_2(OH)_2(O_2H)_2]^{2-}$ ions.[6,7] The Raman spectrum of solid $KBO_4\cdot H_2O$ has strong bands at 935 and 860 cm^{-1}; the former we assign to the $\nu_{sym}[B(O_2)B]$ mode of the peroxide bridges, and the latter to the O–O stretch of co-ordinated hydrogenperoxo ligands {ν(O–O) lies at 837 cm^{-1} for $K[BF_3(O_2H)]$,[27] and at 839 cm^{-1} for $[Co(en)_3][Co(CN)_5(O_2H)]$ (en = ethylenediamine)[28]}. Bands at 740 cm^{-1} are likely to arise from $\nu_{asym}[B(OH)]$ and at 960 cm^{-1} from $\nu_{sym}[B(OH)]$.

According to our n.m.r. data, on the assumption that signal E corresponds to $[B_2(O_2)_2(OH)_4]^{2-}$, a solution of 4 mol dm^{-3} $[B(OH)_4]^-$ in 12 mol dm^{-3} H_2O_2 at pH 6.6 should contain a significant quantity of $[B_2(O_2)_2(OH)_4]^{2-}$ in addition to $[B(OH)_3(O_2H)]^-$. Raman spectra of such solutions show, in addition to the strong O–O stretch of H_2O_2 at 875 cm^{-1},[28] shoulders at 940, 901, and 714 cm^{-1}, which may arise from $\nu_{sym}[B(OH)_2]$, ν(O–O), and $\nu_{asym}[B_2(O_2)_2]$ respectively {observed at 968, 901, and 711 cm^{-1} respectively for solid $Na_2[B_2(O_2)_2(OH)_4]\cdot 6H_2O$}. In more concentrated solutions (4 mol dm^{-3} B and 12 mol dm^{-3} H_2O_2) at pH 8.4 where the n.m.r. data indicate that $[B_2(O_2)_2(O_2H)_2(OH)_2]^{2-}$ is present (peak H), additional bands appear at 690, 855, and 914 cm^{-1}. These may arise from $\nu_{sym}[B\text{–}O(O_2H)]$, the ν_{sym}(O–O) mode of co-ordinated O_2H, and the $\nu_{sym}[O\text{–}O(O_2)]$ mode respectively {observed for solid $K_2[B_2(O_2)_2(O_2H)_2(OH)_2]$ at 678, 862, and 934 cm^{-1} respectively}.[8]

Experimental

All solutions were prepared using water purified by passage through a column of Amberlite MB-3 ion-exchange resin. AnalaR grade boric acid, AristaR grade sodium hydroxide and potassium hydroxide, and 'AristaR grade hydrogen peroxide solution (30% w/w) were used as supplied (BDH Chemicals Ltd.). Potassium and sodium metaborates were prepared *in situ* from these reagents. Where hydrogen peroxide greater than 30% (w/w) was required, 86% (w/w) aqueous hydrogen peroxide supplied by Interox Chemicals Ltd. was used.

Boron-11 n.m.r. spectra were recorded at 80.2 MHz on a Bruker WM-250 NMR instrument, using a sealed 5-mm tube containing 0.1 mol dm^{-3} sodium metaborate at pH 14 in ^2H_2O as a lock and reference. The chemical shift of the signal from this insert was found to be 1.30 p.p.m. relative to $Et_2O{\cdot}BF_3$, and from this the chemical shifts of all the observed signals were referred to $Et_2O{\cdot}BF_3$. The ratio of the sum of the integrals of all the resonances of the sample to the integral of the internal $[B(OH)_4]^-$ reference was directly proportional, within experimental error, to the total boron concentration of the sample for boron concentrations from 0.01 to 0.5 mol dm^{-3}, suggesting that no very broad lines had been missed. All spectra were measured at 300 K, using scans from +100 to −100 p.p.m. relative to $Et_2O{\cdot}BF_3$. 16 K data points were collected, and the free induction decay (F.I.D.) multiplied by an appropriate window function before transformation. The final spectrum had a digital resolution of 2.5 Hz per point.

Solid-state 96.3 MHz ^{11}B n.m.r. spectra were measured on a Bruker MSL-300 instrument with magic angle spinning and proton decoupling. Spinning speeds were 3.6—3.8 kHz in a Bruker single-bearing probe with Delrin rotors. Between 100 and 1 000 transients were acquired using a 5-μs 90° pulse and 2-s recycle time. Spectra were referred to $Et_2O{\cdot}BF_3$ by replacement. The resonances were narrow (<300 Hz) with no resolved second-order quadrupole fine structure, suggesting that the quadrupole interaction is small (<0.5 MHz). Any correction to the chemical shift is therefore likely to be less than 1.0 p.p.m.[29] and no such corrections were applied.

Raman spectra were recorded using a Spex Ramalog V spectrometer operating with an argon-ion laser tuned to the blue line at 488.0 nm, at a power of 200 or 500 mW, and a Spex Datamate data-acquisition unit. Spectra of solids were recorded in sealed glass capillaries, and solutions using a glass spinning cell. All n.m.r. tubes, inserts, and Raman spinning cells were stored in *aqua regia* for at least 48 h, and then left in a solution of Monsanto Dequest 2060 chelating agent for 24 h before use.

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