investigation are indicative of the presence of polyborates, but are not sufficiently detailed to establish molecular formulas.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

Detection of Anionic Complexes by *p*H Measurements. II. Some Evidence for Peroxyborates

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RECEIVED MAY 18, 1953

Studies of the acidity of aqueous solutions containing hydrogen peroxide and boric acid and containing hydrogen peroxide and borates indicate that peroxyborates are present. Quantitative treatment of the results is limited by their complexity. Equilibrium conditions appear to be attained rapidly.

Menzel[1] on the basis of freezing point, distribution and conductivity measurements, concluded that boric acid and hydrogen peroxide (hereafter peroxide) do not form an undissociated peroxyboric acid in measurable quantity in aqueous solution, but that borates and peroxide do combine. He also calculated that peroxyboric acid should be a stronger acid than boric acid.

Chemical evidence for these peroxyborates is, however, scarce and inconclusive.

The present work involves *p*H measurements on solutions containing boric acid and peroxide, and on solutions containing borates and peroxide. The measurements confirm, in part, the conclusions of Menzel[1]; further, the data are considered to be good evidence for the existence of true peroxyborates in aqueous solution.

Experimental

The *p*H measurements were carried out as before.[2]

The temperature was 25.0 ± 0.2°. The K_2SO_4, KNO_3, $NaClO_4$ and $Na_2B_4O_7 \cdot 10H_2O$ were reagent grade materials and were used without purification. The H_3BO_3 was recrystallized from distilled water. The peroxide stock solutions were made by dilution of 90% H_2O_2. Brackets are employed to denote concentrations.

In order to eliminate any possibility that the present phenomenon may be caused by trace impurities, comparable measurements have been made with completely different samples of H_3BO_3, H_2O_2 and distilled water and in a different laboratory. Similar results were obtained in these experiments. Significant differences in the *p*H values of half-neutralization (*pK*'s) of H_3BO_3 solutions in the presence of peroxide are further evidence that the phenomenon cannot be attributed to an impurity. This conclusion is based on the fact that the amount of combined borate must be a significant percentage of the total borate in order to cause the large *p*H differences in some of the experiments.

Treatment of the Data.—The same assumptions will be used here as in the previous article.[2] It is again likely that the first two are good and can only make slight differences at most. The third assumption, which is that all complexes are monoprotic acids under the experimental conditions, may not be completely valid. The complexity of the results obtained in the peroxyborate experiments could be caused in part by successive dissociations of peroxyboric acids. One other assumption will be made. This one, which is that the amount of undissociated peroxyboric acid is small, probably is valid since Menzel[1] could not find any evidence for undissociated peroxyboric acids in the presence of H_3BO_3 and H_2O_2.

If a peroxyborate ion exists in equilibrium with H_2O_2 and H_3BO_3 and only a negligible amount of undissociated peroxyboric acid is present, the equilibrium expression

$$K'_{\mathrm{mn}} = [H^+][B_mP_n^-]/[H_3BO_3]^m[H_2O_2]^n$$

where $B_mP_n^-$ is the symbol for the conjugate base of a peroxyboric acid made up of m molecules of H_3BO_3 and n molecules of H_2O_2, can be added to those already considered in equation II of the previous article.[2] This equation for $[H^+]^2$ has thus become quite complicated for it contains contributions from monomeric boric acid, polyboric acids and peroxyboric acids. The problem of correcting for acidity contributions from the various boric acids has been handled in this study by measuring the *p*H of solutions which contain no H_2O_2 but which are otherwise identical to the measured solutions. The subscript zero refers to these control solutions. This substitution of directly measured values results in the simplified equation

$$[H^+]^2 - [H^+]_0^2 = K'_{mn}[H_3BO_3]^m[H_2O_2]^n$$

Results

In all, nine series of experiments were carried out. The data of two short series, which are presented in Table I, demonstrate the general magnitude of the elaboration of H_3BO_3 ionization by H_2O_2. This elaboration is observed both when electrolyte is present (as K_2SO_4, KNO_3 or $NaClO_4$) and when electrolyte is absent.

TABLE I

THE *p*H OF SOLUTIONS WITH H_2O_2 AND H_3BO_3

$[H_2O_2]$, M	0.732	0.366	0.183	0.0732	None
*p*H[a]	3.83	4.06	4.22	4.36	4.49
*p*H[b]	4.13	4.37	4.57	4.75	4.94

[a] $[H_3BO_3] = 0.301$ M, $[KNO_3] = 0.020$ M. [b] $[H_3BO_3] = 0.151$ M, $[KNO_3] = 0.020$ M.

In Fig. 1, the results of three series in which $[H_2O_2]$ was varied are presented. The curvature of the lines indicates that the number of peroxide groups in complexes is not constant.

Similar series of experiments, in which $[H_3BO_3]$ was varied, were made. The results indicate that analysis on the basis of any single value for m was not possible.

Titrations of H_3BO_3 with KOH when H_2O_2 was present showed that the *pK* of H_3BO_3 is markedly lowered. This effect is illustrated in Table II which gives the *p*H of mixtures of H_2O_2 and borax (which is essentially an equimolar mixture of boric acid and sodium borate). These large *p*H changes have occurred in a buffered solution! The most reasonable explanation for this phenomenon is that reactions of the type

$$B(OH)_4^- + nH_2O_2 \rightleftarrows B(OH)_{4-n}(OOH)_n^- + nH_2O$$

have lowered the concentration of the borate ion to such an extent that the hydrogen ion concentration

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[1] H. Menzel, *Z. physik. Chem.*, **105**, 402 (1923).

[2] J. O. Edwards, THIS JOURNAL, **75**, 6151 (1953).

becomes greater in order to satisfy the known mass action expression

$$K_a = [H^+][B(OH)_4^-]/[H_3BO_3]$$

Any decrease in the borate ion concentration must be accompanied by an increase in the hydrogen ion concentration since the concentration of H_3BO_3 is not changed appreciably. Again, as in the experiments with H_3BO_3, the presence of several complexes is indicated, in this case by the lack of consistency in the values obtained for K_c in Table II.

TABLE II

THE INFLUENCE OF PEROXIDE ON THE pH OF A BORAX SOLUTION

$[Na_2B_4O_7]$ = 0.0500 M,[a] no added salt

$[H_2O_2]$, M	pH	$B(OH)_4^-$ combined,[b] %	K_c[c]
0.000	9.12[d]	0.0	..
.040	8.97	29	37
.080	8.82	50	33
.121	8.68	64	30
.161	8.56	72	29
.201	8.46	78	29
.281	8.25	86	33
.402	8.01	92	38
.603	7.72	96	48
.804	7.49	97.6	58

[a] In solution borax appears to exist as an equimolar mixture of H_3BO_3 and sodium borate. [b] Calculated from the equation $\log [B(OH)_4^-] = \log[H_3BO_3] + pH - pK_a$, which gives the equilibrium concentration of free borate ion. [c] Calculated on the basis of an assumed one-to-one complex ion. [d] This value is the pK_a of H_3BO_3 under these conditions.

Discussion

It is possible to interpret the results of this investigation in three ways. That the phenomenon is caused by impurities is a hypothesis which can be discarded for many reasons; two of the reasons were discussed in the Experimental section. A second interpretation is that the results are caused by "medium effects." This hypothesis can also be discarded, for the results are considerably larger in magnitude than can be explained on such a basis. For example, one solution containing 0.55 M H_2O_2 and 0.329 M H_3BO_3 had a pH of 4.17_5 while the corresponding solution with H_3BO_3 alone had a pH of 4.83. Replacement of 1% of the water molecules by peroxide molecules (which are similar to water molecules in many respects) should not alter the observed acidity of H_3BO_3 by a factor of twenty.

The only interpretation which adequately explains the data is that borate ions combine with H_2O_2 to form peroxyborate ions. The present results coupled with those of Menzel,[1] strongly indicate the existence of peroxyborates in solution.

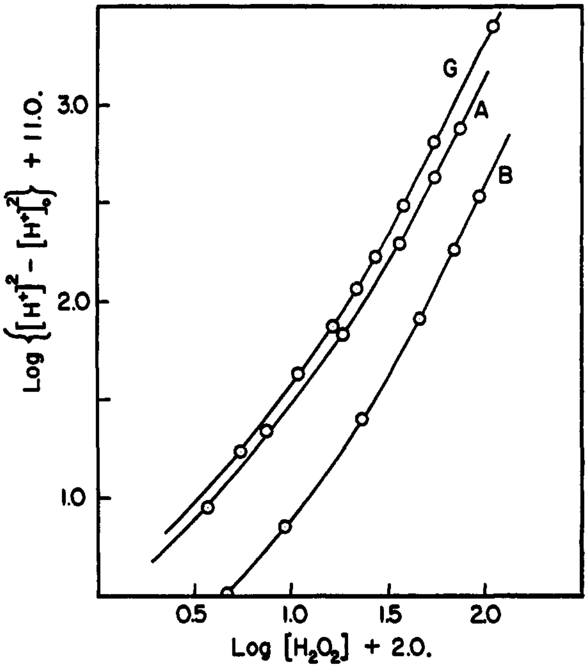

Fig. 1.—Data showing the influence of peroxide concentration on the acidity of boric acid solutions, t = 25.0°: series A, $[H_3BO_3]$ = 0.329 M, $[K_2SO_4]$ = 0.100 M; series B, $[H_3BO_3]$ = 0.1605 M, $[K_2SO_4]$ = 0.100 M; series G, $[H_3BO_3]$ = 0.188 M, $[NaClO_4]$ = 0.100 M.

Any quantitative interpretation of the data requires the postulation of about six peroxyborate species. Such calculations are not conclusive in view of the assumptions and experimental errors involved. It is worth noting, however, that the values obtained from the calculations are in good agreement with those of Menzel[1] for the case of a one-to-one complex.

Both formation and hydrolysis of the peroxyborate ions must be rapid as there was no delay in attaining equilibrium observed in the present study. This attainment of the equilibrium position during the mixing time may explain the lack of chemical evidence for these "bound" peroxides. Most of the chemical methods for distinguishing bound peroxides from H_2O_2 involve a titration procedure such as the permanganate titration. Even if a majority of the peroxide were bound by borate, the peroxide would be released during the titration by the rapid hydrolysis reaction so that all of the peroxide present would show up in this analysis as free H_2O_2. Thus, physical methods which do not alter the equilibrium position should be, and indeed have been, more successful in detecting peroxyborates in solution than have the chemical methods.

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