Obviously, the smallest magnitude of this quantity which can be used is determined by the precision with which the corresponding smallest increment of voltage change throughout the course of the run can be recorded.

The limiting factors in the measurement of fast reactions with the present apparatus are the response times of the electrode system, the amplifier and the recorder. The electrode and recorder characteristics have been discussed above. The frequency response of the amplifier is flat to ten kilocycles, *i.e.*, the amplifier time constant is less than one-tenth of a millisecond. Thus the recorder we used was the factor determining the upper limit of reaction rate that could be measured. The use of oscilloscopic or photographic-galvanometer recorders represents a possible extension of our method for achieving the rates of faster reactions.

For reactions of half-life greater than one hour the glass electrode drift (approximately 0.01 *p*H unit per hour) may become significant. In such cases, however, it is still possible to measure reaction rates during the first few per cent. of reaction providing a sufficient voltage change is obtainable.

Both equations 19 and 20 allow calculation of the v_∞. It should be possible, by utilizing these equations in conjunction with points obtained during the early stages of the reaction before the rate can be appreciably affected by any side or reverse reactions, to calculate equilibrium constants through the v_∞ observed and the v_∞ calculated. For this purpose the following equation can be readily derived. Proceeding on the findings of Hughes[9] that at equilibrium the olefin content is negligible the solvolysis reaction may be written

$$t\text{-BuCl} + H_2O \rightleftharpoons t\text{-BuOH} + H_3O^+ + Cl^-$$

The equilibrium constant for this reaction is then

$$K_{eq} = \frac{[H^+]^2}{[A_0 - H^+]} \qquad (21)$$

Substituting $[H^+] = e^{-2.303a}(e^{2.303bv_\infty} - e^{2.303bV})$ and $[A_0] = e^{-2.303a}(e^{2.303bv_\infty} - e^{2.303bv_0})$, gives

$$K_{eq} = \frac{e^{-2.303a}(e^{2.303bv_\infty} - e^{2.303bv})^2}{(e^{2.303bv} - e^{2.303bv_0})} \qquad (22)$$

where v is the observed voltage at infinite time, v_∞ is the calculated voltage for infinite time and v_0 is the voltage at the arbitrarily chosen time t_0. The value of the constant a is determined by measuring the *p*H of the solution and applying the equation 3.

The close agreement of the v_∞ observed and the v_∞ calculated indicates that the solvolysis of *t*-butyl chloride, under the conditions of this study and to the limit of experimental accuracy is complete.

We are now engaged in extending this method to other electrode systems especially to applications involving halogen ions and oxidation–reduction systems.

NEWARK, DELAWARE

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

Detection of Anionic Complexes by *p*H Measurements. I. Polymeric Borates

BY JOHN O. EDWARDS

RECEIVED MAY 18, 1953

On the basis of acidity data obtained with the glass electrode, it is concluded that concentrated aqueous solutions of boric acid contain two polyborate ions. Calculated values based on the assumption of a singly-dissociated trimer and a singly-dissociated hexamer are in good agreement with the observed acidities. It was found that equilibrium is attained in the time of mixing.

Stetten[1] recently demonstrated by *p*H measurements that polymeric borates must be present in concentrated boric acid solutions, as these solutions are more acidic than can be explained on the basis of monomeric H_3BO_3 alone. He reported that the average degree of polymerization is 3.2, but he made no attempt to determine the exact constitution of the polymer(s).

Previously, Thygesen,[2] on the basis of conductivity measurements, and Owen,[3] on the basis of cell potentials, concluded that polyborates exist in aqueous solutions. Thus, it seems to be reasonably well established from these physical measurements that polyborates do exist in solution.

Studies on the colligative properties of aqueous H_3BO_3 solutions have failed to show the existence of polyborates[4,5]; therefore these polyborates must be present in comparatively minor amounts.

The purpose of this study is to determine the exact degrees of polymerization of the polymer acids in concentrated H_3BO_3 solutions. The results, which are of importance to the aqueous chemistry of boron, are needed as a foundation for the next study which involves similar *p*H measurements designed to detect peroxyboric acids.

Experimental

The *p*H measurements were made with a Beckman model G *p*H meter; the electrodes were checked with commercial standard buffers. All measurements were made at 25.0 ± 0.2°.

The H_3BO_3 employed was reagent grade. It was recrystallized from distilled water three times, as small amounts

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(1) D. Stetten, *Anal. Chem.*, **23**, 1177 (1951).

(2) J. E. Thygesen, *Z. anorg. u. allgem. Chem.*, **237**, 101 (1938).

(3) B. B. Owen, THIS JOURNAL, **56**, 1695 (1934).

(4) L. Kahlenberg and O. Schreiner, *Z. physik. Chem.*, **20**, 547 (1896).

(5) H. Menzel, *Z. anorg. u. allgem. Chem.*, **164**, 1 (1927).

of impurities such as metal borates can cause significant variations in the *p*H values of these non-buffered solutions. Distilled water for stock solutions was freshly boiled before use.

The concentration of H_3BO_3 was determined by titration with standard KOH in the presence of mannitol; the end-point of the titration was detected with the glass electrode. Brackets are employed to denote concentrations.

Treatment of the Data.—In a solution containing only boric acid

$$[H^+] = [B(OH)_4^-] + [B_x^-] \qquad I$$

where $B(OH)_4^-$ represents the conjugate base of monomeric boric acid and B_x^- represents the conjugate base of a polyboric acid containing x boron atoms. Stetten[1] has shown that the *average* value of x is 3.2; this fact plus the present data indicate that more than one polymeric species is present. Thus it is necessary to consider the observed acidity as a sum of contributions from several polymer acids.

Three assumptions, of which two can affect the final results only slightly, will be made. The first, which is that concentrations may be used in place of activities, has been calculated by Stetten[1] to be a good assumption under conditions where no salt is present. The second, which is that the amount of undissociated polyboric acid is small, probably is also a good assumption since these polyborates have not been detected in studies of the colligative properties of H_3BO_3 solutions.[4,5]

The third assumption is that all polyborate complexes contain only a single ionizable proton. Stetten[1] employs this assumption, but Thygesen[2] assumes a doubly-dissociated polymer. Attempts to analyze the present data on the basis of a doubly-dissociated polymer have resulted in a poorer fit of the data; thus it is felt that the assumption of a single ionizable proton is reasonable in polyboric acids.

Upon substitution of the equilibrium expressions

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

and

$$K_x = [H^+][B_x^-]/[H_3BO_3]^x$$

into equation I and rearranging, we have

$$[H^+]^2 = K_a[H_3BO_3] + K_x[H_3BO_3]^x \qquad II$$

or

$$[H^+]^2/[H_3BO_3] = K_a + K_x[H_3BO_3]^{x-1} \qquad III$$

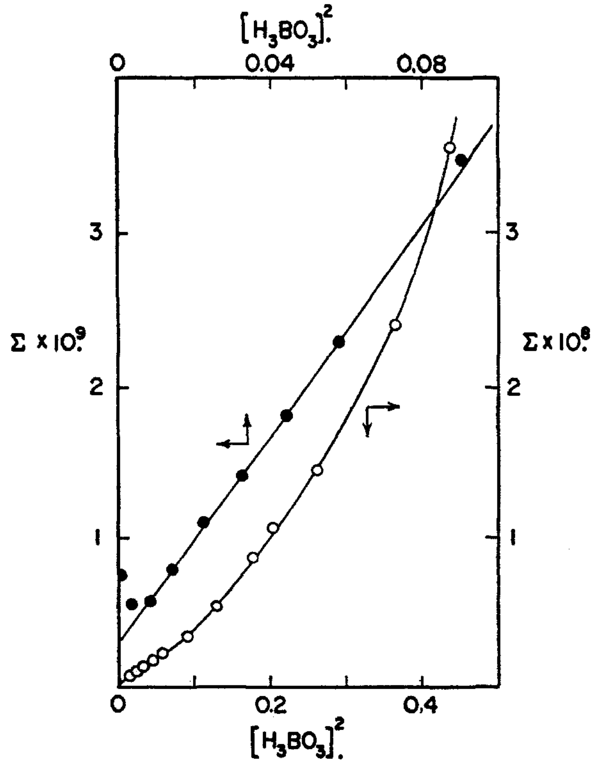


Fig. 1.—Data showing the influence of boric acid concentration on the value of Σ; no added salt, t = 25.0°.

Since the predominant polymeric species seems to be the trimer, the data have been evaluated by means of a plot of the left-hand side of equation III (signified Σ) against the square of the H_3BO_3 concentration. The value of the intercept is equal to K_a under the particular experimental conditions. The plots were found to form straight lines up to 0.3 *M* H_3BO_3, and the values of K_3 (K_x for x = 3) were calculated from the slope of the line. The acidity data for the second polymeric species were obtained by subtracting the contributions of the monomer and the trimer from Σ, and comparing the residual with various powers of H_3BO_3 concentration.

Results

The results of one series of *p*H measurements are presented in Table I. It is apparent that concentrated solutions of boric acid contain at least one acid stronger than monomeric H_3BO_3. The observed values of Σ range over two orders of magnitude; if only a single acid were present, these values would be constant.

TABLE I

THE ACIDITY OF CONCENTRATED H_3BO_3 SOLUTIONS

t = 25.0°; no added salt

$[H_3BO_3]$, *M*	*p*H	$\Sigma_{obsd.} \times 10^{10}$	$\Sigma_{calcd.}$[a] $\times 10^{10}$	Difference,[b] %
0.753	3.69	550	556	+1.1
.663	3.815	355	344	−3.1
.603	3.92	240	244	+1.7
.512	4.065	145	144	−0.7
.452	4.16	107	100.2	−6.4
.422	4.22	87.1	83.0	−4.7
.361	4.35	55.0	56.4	+2.5
.301	4.49	34.7	37.4	+7.8
.241	4.63	22.9	23.9	+4.4
.211	4.71	18.2	18.6	+2.2
.1808	4.795	14.1	14.1	0.0
.1507	4.89	11.0	10.7	−2.7
.1205	5.01	7.9	7.9	0.0
.0904	5.14	5.8	5.7	−1.7
.0603	5.235	(5.6)[c]	4.2	...
.0301	5.32	(7.6)[c]	3.3	...

[a] Calculated from $K_a = 3.0 \times 10^{-10}$, $K_3 = 3.38 \times 10^{-8}$, and $K_6 = 1.49 \times 10^{-7}$. [b] An error of 0.01 *p*H unit would cause a 4.7% deviation. [c] These values may be unduly large as a result of trace acidic impurities.

The data of part of this series are plotted according to equation III (with x = 3) in Fig. 1. The positive intercept and the initial constant slope indicate the presence of monomeric H_3BO_3 and a trimer, respectively. The sharp increase in Σ above 0.3 *M* H_3BO_3 has been found to be well fitted by calculations based on the assumption that the higher polymeric species is a hexamer. Values of the three equilibrium constants in each of three series of measurements are presented in Table II.

TABLE II

VALUES OBTAINED FOR THE EQUILIBRIUM CONSTANTS

Constant	Series "J"[a]	Series "K"[a]	Series "C-D"[b]
K_a	3.0×10^{-10}	2.7×10^{-10}	7×10^{-10}
K_3	3.4×10^{-8}	3.1×10^{-8}	13×10^{-8}
K_6	1.5×10^{-7}	1.4×10^{-7}	$\sim 12 \times 10^{-7}$

[a] No added salt; t = 25.0°. [b] 0.1 *M* K_2SO_4; t = 25.0°; corrected for HSO_4^- using 1.1×10^{-2} as the acid ionization constant for HSO_4^-.

The three values for series "J" have been used to calculate values of Σ to compare with the observed values; the comparative values are presented in Table I. The differences, for the most part, are not greater than could reasonably be expected from variation of ±0.01 pH unit in reading the meter. The observed values of Σ for the two lowest concentrations of H_3BO_3 are much higher than the calculated values; a possible reason for this discrepancy is trace acidic impurities in the water or H_3BO_3.

Equilibrium between boric acid and the polymers is reached during the time of mixing. When 25 ml. of water was added by pipet to 25 ml. of a 0.753 M H_3BO_3 solution, the pH changed from 3.67 to 4.29 during the mixing time of 30 seconds and remained thereafter at the latter value. If equilibrium were reached quite slowly, the pH after mixing would have been 3.97 or less. The rate of depolymerization of the polyboric acids must be extremely rapid, with a half-time of less than 10 seconds. It is probable that the rate of polymerization of H_3BO_3 is also rapid, although this would be difficult to test and it is not necessarily true (since the equilibrium amount of polymer is always small in comparison with the amount of monomeric H_3BO_3).

Discussion

The data obtained in this study are additional evidence that solutions containing H_3BO_3 and/or borates contain polymeric boron species. It is entirely unreasonable to believe that the addition of 0.301 mole of H_3BO_3 to a liter of water could change the medium to such an extent that the resulting solution would be about twelve times as strong as could be expected on the basis of a classical dissociation of H_3BO_3. Further evidence that the phenomenon is a chemical interaction stems from the ability to treat the data quantitatively on the basis of two polymeric species, each with an integral number of boron atoms.

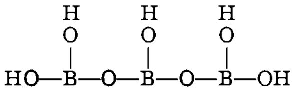
The values observed for K_a in the two series with no added salt are 3.0×10^{-10} and 2.7×10^{-10}. Taking as an average 2.9×10^{-10}, this value is found to be only one-half of the value reported by Owen[3] from cell potential measurements on solutions containing H_3BO_3 and borate ion. This difference seems too great to be explained by an ionic strength effect or a polymerization, since Owen[3] corrected his measurements for both types of error and neither should be significant in the present experiments. The difference is probably too great to be attributed to errors in the extrapolation procedures used in either of the two evaluations. A constant error of 0.15 pH unit in the readings of the pH meter could explain the difference, but an error of this size certainly is outside the experimental error of a calibrated meter. If a tiny amount of borate ion were present in the H_3BO_3, this could cause a significant increase in the observed pH. This explanation seems to be the most reasonable of all those mentioned, particularly in view of the non-buffered nature of the solutions in the present investigation.

The trimeric borate contributes the major part of the observed acidity from approximately 0.06 to 0.6 M H_3BO_3. Consequently, K_3 can be evaluated with reasonable accuracy in any series. In all series, the value observed for K_3 is slightly more than one hundred times that of K_a. If K_3 is considered to be the product of K_a and a complexing constant K_3' for the reaction

$$B(OH)_4^- + 2H_3BO_3 \rightleftharpoons B_3^-$$

the value of K_3' is found to be about 110.

Two structures for a trimer of H_3BO_3 are chemically reasonable. One is a six-membered ring containing alternate boron and oxygen atoms. The second is a chain configuration such as



$$\begin{array}{ccccc} & \overset{\displaystyle H}{\overset{\displaystyle O}{|}} & & \overset{\displaystyle H}{\overset{\displaystyle O}{|}} & & \overset{\displaystyle H}{\overset{\displaystyle O}{|}} \\ HO— & B & —O— & B & —O— & B & —OH \end{array}$$

Although the present data give no implication as to the structure of the trimer, it is noteworthy that the crystals of both potassium and sodium metaborates contain triborate ions with ring structures.[6]

Above 0.6 M H_3BO_3, the hexamer is the largest contributor to the observed acidity. In view of the limited range available (as a result of the low solubility of boric acid) and since the experimental errors accumulate in the hexamer calculations (as a result of the subtraction procedure), the percentage error in K_6 is somewhat larger than that in K_3. However, it is conclusive that the present data are best fitted by the assumption of a hexamer. From the data in Table II, it can be calculated that K_6' has a value of about 500. No reasonable structure for a hexaborate ion suggests itself.

Polyborates, which exist only in small quantities in solution, are known to be plentiful in the solid state.[7] Tetraborates, pentaborates and metaborates are all known. It is interesting to note that no evidence for dimers, tetramers or pentamers was found in the present study.

Chemical evidence for polyborates in solution has not been convincing. This probably is a direct result of the rapid rates of replacement in boron compounds. The present study indicates that depolymerization is a rapid process. It is also known that the oxygen isotope exchange of H_3BO_3 and of borates with the solvent water is rapid,[8,9] as are the reactions of H_3BO_3 with polyhydroxy compounds,[10] with fluoride ion to form fluorohydroxyborates,[11] and with hydrogen peroxide to form peroxyborates.[12] Even the hydrolysis of triesters of H_3BO_3 is rapid.[13]

It is justifiable to conclude that the rapid attainment of equilibrium in H_3BO_3 solutions will necessitate approaches to the study of polymerization different from those used for the polyphosphates, where equilibrium is attained only in times much longer than the time of mixing.

After completion of the manuscript, the work of Kolthoff[14] on conductance and pH of concentrated boric acid solutions was found. The results of his

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[6] W. H. Zachariasen, *J. Chem. Phys.*, **5**, 919 (1937).

[7] A. F. Wells, "Structural Inorganic Chemistry," 2nd Ed., Clarendon Press, Oxford, 1950, pp. 598–600.

[8] N. F. Hall and O. R. Alexander, THIS JOURNAL, **62**, 3455 (1940).

[9] E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *J. Chem. Soc.*, 131 (1940).

[10] See, for example, E. M. Trautner and M. Messer, *Nature*, **169**, 31 (1952).

[11] C. A. Wamser, THIS JOURNAL, **73**, 409 (1951).

[12] J. O. Edwards, *ibid.*, **75**, 6154 (1954).

[13] H. K. Garner and H. J. Lucas, *ibid.*, **72**, 5497 (1950).

[14] I. M. Kolthoff, *Rec. trav. chim.*, **45**, 401 (1926).

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

BY JOHN O. EDWARDS

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

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

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).