

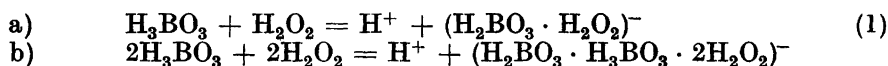
Potentiometric Study on the Formation of Perboric Acids

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The influence of hydrogen peroxide on the ionization of boric acid in aqueous potassium chloride solutions at 25° C has been studied by means of a potentiometric method. Apparently mainly two different peracids exist in solutions of boric acid and hydrogen peroxide. The complex formation constants of these perboric acids in potassium chloride solutions of different concentrations were calculated. The corresponding thermodynamic complex formation constants and the parameters of the Debye-Hückel equation have also been determined.

The formation of perboric acid in solutions containing boric acid and hydrogen peroxide has been the object of only few investigations. According to Menzel¹ conductivity measurements show that the complex acid $\text{H}_3\text{BO}_3 \cdot \text{H}_2\text{O}_2$ or $(\text{H}_3\text{BO}_3 \cdot \text{H}_2\text{O}_2)_2$ exists in solutions of this kind, the equilibrium constants for the reactions



being of the order of 10^{-8} — 10^{-7} . On the other hand, pH measurements carried out by Edwards² do not confirm the assumption that the peroxide complex is a definite compound. The author of this paper has in a recent preliminary study³ reported a potentiometric method and its application to the investigation of perboric acid formation. The object of the investigation to be reported here was to complete this preliminary work.

EXPERIMENTAL

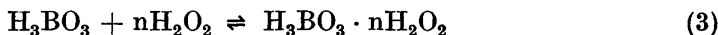
The potentiometric titrations were carried out at 25° C, employing a differential potentiometric method⁴. A tube potentiometer Type PHM 3 manufactured by Radiometer and a Beckmann Glass Electrode Type 4990—83 were used. The reading accuracy of the apparatus was about 0.2 mV. The measurements were carried out in 0.1—1.5 M potassium chloride solutions, the concentrations of boric acid and hydrogen peroxide being varied between 0.025—0.1 M and 0.1—8.0 M, respectively. Other details of apparatus and measurement technique have previously⁵ been described. All reagents used were of reagent grade. The concentration of boric acid stock solutions was determined by titration with sodium hydroxide using mannitol and phenolphthalein⁶. The hydrogen peroxide stock solutions were titrated with permanganate.

THEORY

Recent investigations^{5,7-9} have shown that boric acid in its dilute solutions can be considered as a weak monobasic acid. Since according to cryoscopic measurements carried out by Menzel¹ it is apparent that the amount of any peracid formed is very small, the concentrations of boric acid and hydrogen peroxide in the solutions of boric acid-hydrogen peroxide can be exchanged for the corresponding stoichiometric concentrations C_1 and C_2 , respectively, especially when it is noted that the insignificant ionization of boric acid does not affect conditions. Thus for the apparent ionization constant K^* of boric acid in solutions containing hydrogen peroxide an equation

$$K^* = K_1' \cdot K_k \cdot C_2^n + K_1 = K_m \cdot C_2^n + K_1 \quad (2)$$

can be derived on the basis of the experimental method⁴ and its applications to boric acid⁵ and telluric acid¹⁰⁻¹¹. In this equation K_1' denotes the first ionization constant of perboric acid, here considered as a monobasic acid, and K_k the equilibrium constant of the following assumed reaction:



In addition K_1 is the first ionization constant of orthoboric acid. Further, the value of n is the number of hydrogen peroxide molecules, which combine with each molecule of boric acid. If in this case several complexes occur, n then indicates the average of this number. In such cases it is often possible to calculate the two main complex formation constants using the equation¹²

$$K^* = k_1 \cdot C_2^{n_1} + k_2 \cdot C_2^{n_2} + K_1 \quad (4)$$

where k_1 and k_2 are the complex formation constants corresponding to K_m in eqn. (2), where it is assumed that the value of n is the average of two different values. For the determination of the constants k_1 and k_2 in eqn. (4) it is necessary to know the values of the apparent ionization constants at least two different concentrations of hydrogen peroxide. Further, the most obvious values of n_1 and n_2 should be used in these calculations as shown in a recent investigation¹² concerning the complex formation of boric acid with mannitol.

RESULTS

In Table 1 the values for the apparent ionization constants of boric acid are given at constant ionic strength and different concentrations of hydrogen peroxide. Using these results the average value of n and the complex formation constant K_m can be calculated using eqn. (2). If a complex acid really exists the values of $p(K^* - K_1)$ as a function of $\log C_2$ should lie on a straight line with the slope n . This line should intersect the $p(K^* - K_1)$ -axis at the point pK_m . However, as can be seen from Fig. 1 the linearity is only approximate and two different limiting slopes for this curve can be obtained. Here the value 8×10^{-10} for the constant K_1 has been used when the concentration

Table 1. Potentiometric data for the influence of the concentration of hydrogen peroxide on the apparent ionization constant of boric acid for different concentrations of boric acid in about 0.0996 M potassium chloride solutions at 25° C.

C_1	C_2	$P_m \times 10^4$	pK^*
0.02498	0.09670	4.105	8.409
0.04985	0.09668	5.730	8.510
0.09975	0.2413	1.405	8.032
0.09982	0.4830	1.982	7.750
0.09950	0.7155	2.640	7.483
0.09950	0.9450	3.340	7.279
0.04971	0.9643	2.465	7.242
0.02490	0.9645	1.527	7.357
0.09965	1.446	4.852	6.958
0.02495	2.432	4.021	6.516
0.04991	2.432	5.520	6.542
0.09961	2.425	8.035	6.516
0.009965	3.280	3.721	6.185
0.09943	4.810	18.95	5.731
0.009945	5.730	8.165	5.452
0.009982	6.746	11.99	5.161
0.09802	8.930	43.30	5.034

of potassium chloride is about 0.1 M and that of boric acid ⁵ 0.1 M. Consequently one might assume that mainly two different peracids exist in these solutions. Furthermore, it appears that the most obvious values of n_1 and n_2

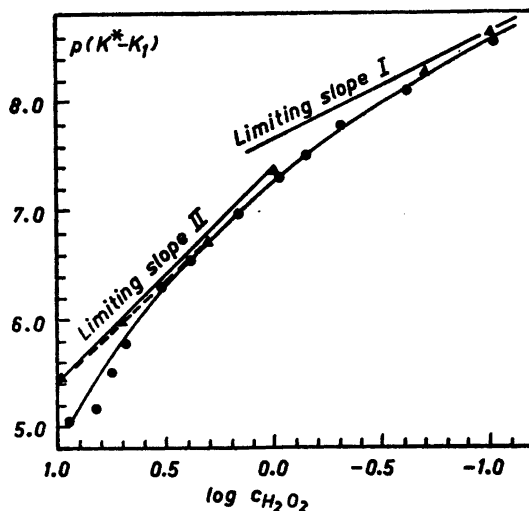


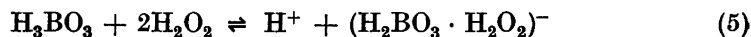
Fig. 1. The dependence of the apparent ionization constant of boric acid^a on the concentrations of hydrogen peroxide in about 0.1 M potassium chloride solutions. ● Experimental results. ▲ Values calculated from the observed values of pk_1 and pk_2 using the theoretical eqn. (4).

Table 2. Determination of the complex formation constants k_1 and k_2 of perboric acids in about 0.0996 M potassium chloride solutions using the interpolated values from Table 1 at 25° C (cf. p. 757 and Eqn. 4).

C_2'	C_2''	$K' \times 10^9$	$K'' \times 10^7$	pk_1
0.2	3.0	6.32	5.02	7.665
0.2	2.0	6.32	2.24	7.644
0.2	1.5	6.32	1.20	7.627
0.2	1.0	6.32	0.632	7.624
0.4	3.0	15.8	5.02	7.703
0.4	2.0	15.8	2.24	7.660
0.4	1.5	15.8	1.20	7.605
0.4	1.0	15.8	0.632	7.624

Average $pk_1 = 7.645 \pm 0.025$
 $pk_2 = 7.40$

in eqn. (4) are 1 and 2, respectively. Using these values it is possible to calculate the corresponding complex formation constants for reactions (1a) and



as already has been stated. The results of these calculations are given in Table 2. Thus the corresponding values for pk_1 and pk_2 are about 7.645 and 7.40, respectively, in about 0.1 M potassium chloride solution. In this connection it should be noted that owing to the slight apparent ionization of boric acid the electrolyte concentration of this acid can be neglected. In Table 3 the values for pk_1 and pk_2 in potassium chloride solutions of different concentrations are calculated using the corresponding values for the apparent ionization constants of boric acid in these solutions. Thus the values 7.914 ± 0.04 and 7.71 ± 0.04 for the thermodynamic complex formation constants $pk_{1,0}$ and

Table 3. Determination of the complex formation constants k_1 and k_2 of perboric acids in different potassium chloride solutions at 25° C (cf. p. 757 and Eqn. 4).

$I^{\frac{1}{2}}$	C_2	pK^*	$(K^* - K_1) \times 10^8$	pk_1	pk_2
0.333	—	—	—	7.645	7.40
0.706	0.0800	8.393	0.305	7.472	7.22
0.705	0.9640	7.059	8.64		
1.181	0.0800	8.378	0.311	7.467	7.28
1.168	0.8802	7.119	7.50		

The average thermodynamic pk -values $pk_{1,0} = 7.914 \pm 0.04$
 $pk_{2,0} = 7.71 \pm 0.04$

$pk_{2,0}$ were obtained. The values for the parameters of the Debye-Hückel equation were also calculated using the values in Table 3, with the following results:

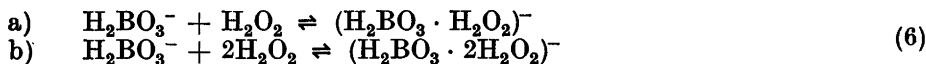
$$pk_1: \alpha = 0.525 \text{ and } B = 0.160$$

$$pk_2: \alpha = 0.450 \text{ and } B = 0.200$$

CONCLUSIONS

It should be noted that the results obtained agree very well with eqns. (1a) and (5). Only the values for the apparent ionization constants measured at high concentrations of hydrogen peroxide differ markedly from the theoretically calculated values. This might be due to the formation of the next complex peracid in very concentrated hydrogen peroxide solutions, but more likely it is caused by the great variations of the dielectric constants of such solutions, which recent investigations have revealed¹³. According to these observations it can be assumed that the variation of the dielectric constants in less than 3 M H_2O_2 solutions is so small that it does not affect results (cf. Tables 2 and 3). On the other hand the existence of a complex acid formed according to eqn. (1b) seems most unlikely, since in this case the values of the apparent ionization constants should vary with the concentration of boric acid (cf. eqn. 2 and Table 1).

Using the above-mentioned values for the complex formation constants the thermodynamic complex formation constants $K_{n,1,0}$ and $K_{n,2,0}$ of the reactions



can also be calculated^{5,10,11}. Thus we get

$$\begin{aligned} \text{a)} \quad & K_{n,1,0} = \frac{c_{(H_2BO_3 \cdot H_2O_2)^-}}{c_{H_2BO_3^-} \cdot c_{H_2O_2}} = \frac{k_{1,0}}{K_{1,0}} = 21.1 \\ \text{b)} \quad & K_{n,2,0} = \frac{c_{(H_2BO_3 \cdot 2H_2O_2)^-}}{c_{H_2BO_3^-} \cdot (c_{H_2O_2})^2} = \frac{k_{2,0}}{K_{1,0}} = 33.6 \end{aligned} \quad (7)$$

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