SUGAR ALCOHOLS. IX

A Physicochemical Study of the Erythritan–Boric Acid Complex

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INTRODUCTION

In previous communications the authors (5, 4) studied the influence of certain of the sugar alcohols and their anhydrides upon the dissociation constant of boric acid. In one study (4) it was demonstrated that erythritan, 1,4-anhydroerythritol, was unique among the compounds investigated, inasmuch as its downward displacement of the titration curve of boric acid was greater than that of any other compound. This interesting property of erythritan prompted the present physicochemical investigation of the erythritan–boric acid complex.

MATERIALS AND METHOD

The boric acid was of buffer quality. The erythritan was prepared from erythritol by dehydration with sulfuric acid (3,1). The calculated values for its composition are as follows: carbon, 46.15 per cent; hydrogen, 7.69 per cent. Analysis gave the following composition: carbon, 46.02 per cent; hydrogen, 7.58 per cent. The levulose employed was Merck's crystals.

The pH was determined electrometrically at 24°C.±1°, using the Wilson-type (7) hydrogen electrode.

EFFECT OF ERYTHRITAN–BORIC ACID RATIO ON pH

In former studies the pH of a 4 per cent erythritan solution in one-tenth molar boric acid was found to be 2.6. The following studies were instituted to determine the influence of varying concentrations of erythritan upon the pH of a solution of boric acid of fixed concentration. The results are set forth in figure 1, curve A.

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EFFECT OF DILUTION UPON THE pH OF THE ERYTHRITAN–BORIC ACID COMPLEX

It is well known that dilution plays an important rôle in the dissociation of polyhydric alcohol–boric acid complexes as evinced by a diminution in the hydrogen-ion concentration upon the addition of water. In order to determine this effect quantitatively with respect to the erythritan–boric acid complex the following experiments were performed, in which a solution of equal quantities of 0.5 molar erythritan and 0.1 molar boric acid was employed. The results are set forth in figure 1, curve B.

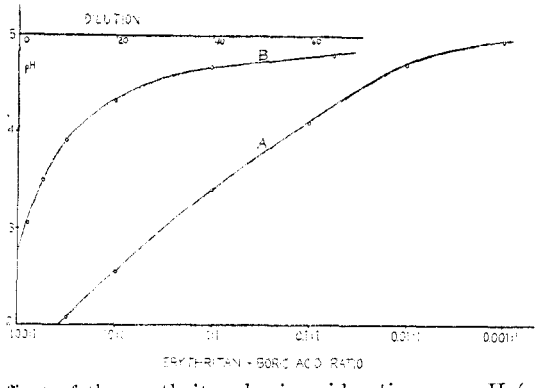

FIG. 1. The effect of the erythritan–boric acid ratio upon pH (curve A) and the effect of dilution upon the pH of the erythritan–boric acid complex (curve B).

EFFECT OF TIME AND TEMPERATURE UPON THE DISSOCIATION OF THE ERYTHRITAN–BORIC ACID COMPLEX

The complex was prepared in 1:1 ratio in 0.1 molar concentrations Portions of the solution were kept at 6°, 25°, and 60°C., respectively, over a period of five hours. During this time the pH was determined hourly, the temperature of the sample for determination having been brought to 25°C. The pH of the complex was 3.01. The fifteen determinations did not vary by more than the error of the experiment, i.e., ± 0.05 pH.

DETERMINATION OF THE NUMBER OF MOLECULES OF ERYTHRITAN COMBINED WITH ONE MOLECULE OF BORIC ACID IN THE COMPLEX

Using the mathematical expression of Böeseken (2) in which D represents the polyalcohol and n the number of moles of it combined with one molecule of boric acid, HB,

$$\log[\mathrm{HB}] + n \log [\mathrm{D}] + K = -2\mathrm{pH}$$

and

$$1/2 \log [\mathrm{HB}] + \frac{n}{2} \log [\mathrm{D}] + K_1 = -\mathrm{pH}$$

Assuming that the polyalcohol–boric acid complex is completely dissociated and, further, that the hydrogen-ion concentration produced by boric acid is negligible compared with the concentration produced by the

TABLE 1

Values of n for polyol–boric acid complexes

RATIO OF POLYOL BORIC ACID	pH	$\frac{a}{b}$	ΔpH	n
A. Levulose (Böeseken)				
4:1	3.01	$\frac{4:1}{3:1}$	0.14	2.3
3:1	3.15	$\frac{3:1}{0.5:1}$	0.79	2.0
1:1	3.60	$\frac{4:1}{0.5:1}$	0.93	2.1
0.5:1	3.94	$\frac{4:1}{1:1}$	0.59	2.0
B. Levulose				
4:1	2.86	$\frac{4:1}{3:1}$	0.09	1.4
3:1	2.95	$\frac{3:1}{0.5:1}$	0.52	1.3
1:1	3.27	$\frac{4:1}{0.5:1}$	0.61	1.4
0.5:1	3.47	$\frac{4:1}{1:1}$	0.41	1.4
		$\frac{3:1}{1:1}$	0.32	1.3
		$\frac{1:1}{0.5:1}$	0.20	1.3
C. Erythritan				
4:1	2.56	$\frac{4:1}{3:1}$	0.08	1.3
3:1	2.64	$\frac{3:1}{0.5:1}$	0.50	1.3
1:1	2.94	$\frac{4:1}{0.5:1}$	0.58	1.3
0.5:1	3.14	$\frac{4:1}{1:1}$	0.38	1.3
		$\frac{3:1}{1:1}$	0.30	1.3
		$\frac{1:1}{0.5:1}$	0.20	1.3

complex, the hydrogen-ion concentration is a measure of the concentration of the complex.

$$[H^+] = [BD'n]$$

In two solutions of different concentrations of the polyalcohol and the same concentration of boric acid, the ratio of the concentrations of the polyalcohol is proportional to the change in pH.

$$\Delta\text{pH} = \frac{n}{2} \log a$$

$$n = \frac{2\,\Delta\text{pH}}{\log a}$$

in which a is the ratio of polyalcohol to boric acid in the two solutions. In accordance with this hypothesis, the authors attempted first to obtain the same value for n found by Böeseken for the levulose–boric acid complex as shown in table 1, A.

Using Merck's crystals of levulose, the values ± 0.02 pH which we obtained, at 22°C. with a hydrogen electrode previously standardized against 0.05 molar potassium acid phthalate, are set forth in table 1, B.

We are unable to account for the differences between the results of our investigations and those of Böeseken. Comparing these with the pH values obtained for the levulose–boric acid complex by Mellon and Morris (6) in 1:4 ratio, we find that our values agree well and show a greater hydrogen-ion concentration of the complex than Böeseken observed.

A similar experiment was made to determine the value of n for the erythritan–boric acid complex. The results are shown in table 1, C.

The fact that n is not an integer points to the likelihood of the presence of more than one complex compound of the polyalcohol in combination with one molecule of boric acid or the presence of a very complex molecule.

CONCLUSIONS

1. Increasing the ratio of erythritan–boric acid potentiates the hydrogen-ion concentration of the complex.
2. The effect of dilution on the hydrogen-ion concentration of the complex has been quantitatively studied.
3. Time and temperature have no permanent effect on the dissociation of the complex.
4. The value of n in the levulose–boric acid complex and for the erythritan–boric acid compound is approximately 1.3.

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