A View on the Formation of Heteroboric Acid.

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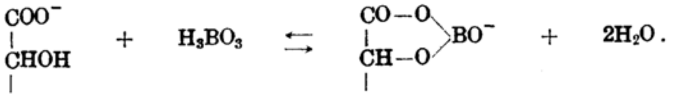
Introduction. It has been shown in previous papers that the so-called heteroboric acid can be favourably formed only when one of the reactants is in ionic state.(1)(2) Thus free boric acid combines only to a small extent with non-disssociable polyoxy compounds such as mannitol(3) and glucose.(4) Hence it is conceivable that boric acid combines only slightly with tartaric esters, but much more freely with tartaric acid and its salts.(2)(5) The authors have undertaken this investigation for the purpose of gaining another evidence for this theory, by dealing with *d*-gluconic and *d*-saccharic acids, whose chemical structures are analogous to that of tartaric acid.

By forming heteroboric acids, polyoxy compounds suffer a great change in chemical constitution, and hence their optical rotation varies to a considerable extent. From this rotational variation we can safely infer that there takes place a certain complex formation, as in the case of tartaric acid.

Comparisons will be made in the following between oxyacids and their esters in the behaviour towards complex formation with boric acid.

The salts of oxy-acids. When free boric acid is added to the salt of gluconic acid, a great increase is observed in its rotation.(2) This is undoubtedly due to the formation of a complex compound, the coo⁻ group of gluconate reacting with boric acid, as shown in the following scheme.



Since a similar complex formation is to be expected, the authors have performed analogous experiments with potassium saccharate, the results being shown in Fig. 1.

As may be seen from Fig. 1 the molecular rotation $[M]_D$ is increased with the increase of the borate concentration and with the decrease of the saccharate concentration. This fact is comprehensible, for there increases the concentration of the complex, whose rotation is very large. It is also seen from Fig. 1 that borax has a remarkable effect. This fact

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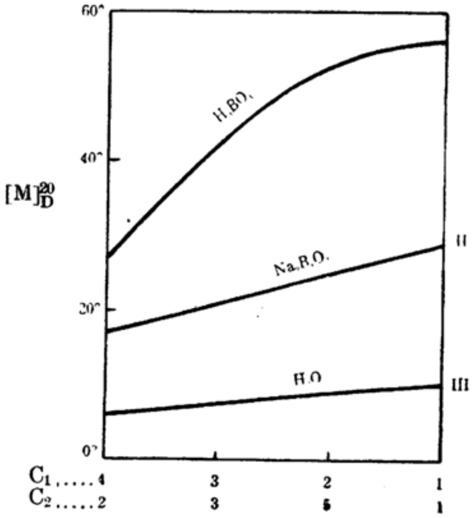
(1) Y. Tsuzuki and Y. Kimura, this Bulletin, **15** (1940), 27; E. Darmois, *J. chim. phys.*, **27** (1930), 179.

(2) Y. Tsuzuki, this Bulletin, **16** (1941), 23.

(3) J. M. Braham, *J. Am. Chem. Soc.*, **41** (1919), 170; F. B. Marti, *Bull. soc. chim. Belg.*, **39** (1930), 590.

(4) E. Darmois and Peyroux, *Compt. rend.*, **193** (1931), 1182.

(5) E. Darmois: *J. chim. phys.*, **23** (1926), 649.



C_1 = The conc. of saccharate $(M/_{24})$

C_2 = The conc. of H_3BO_3 or $\frac{Na_2B_4O_7}{4}$ $(M/_{24})$.

Fig. 1. **The effects of boric acid and borax on the rotation of potassium saccharate.**

can be explained thus: $H_2BO_3^-$, a part of borax, combines with the diol forming a boro-diol as shown in the following scheme:

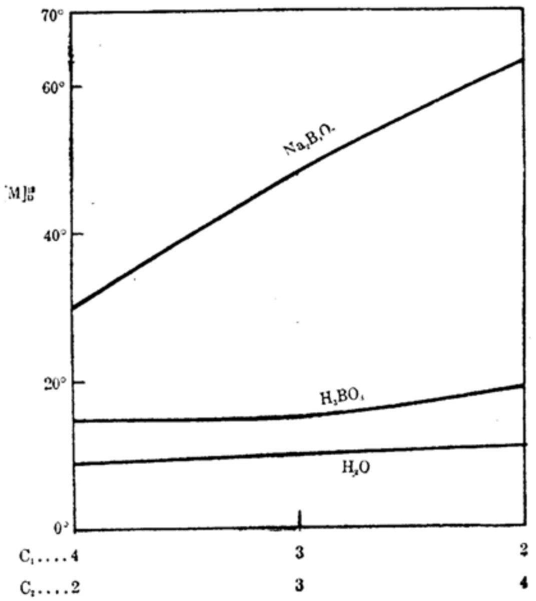
$$\begin{array}{l} >C-OH \\ \quad | \\ >C-OH \end{array} + H_2BO_3^- \rightleftarrows \begin{array}{l} >C-O \\ \quad | \qquad >BO^- \\ >C-O \end{array} + 2\,H_2O\,.$$

But the optical rotation of the boro-diol is not necessarily large, since this complex is different in type from the heteroboric acid produced from ionic oxy-acids.

For comparison's sake we have measured also the rotation of the saccharate in aqueous solutions. (Fig. 1, III). As may be seen from Fig. 1 the optical rotation increases slightly with the decrease of the optically active body, but the effect is far smaller as compared with the case of boric acid and borax.

The esters of oxy-acids. It is expected with the esters of oxy-acids that the effect of free boric acid is not conspicuous, as observed in the case of tartaric esters, and that borate ion exercises a great influence on the optical rotation. The results of our experiments are shown in Fig. 2 and 3. The esters to be investigated are both molecular compounds with calcium chloride. Esters free from this salt can be obtained in pure state only with difficulty, and moreover they are liable to hydrolysis, so that they must rather be regarded as unsuitable materials for the present investigation.

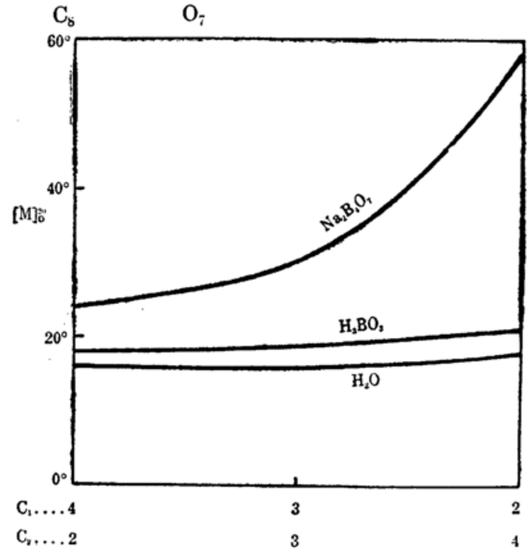
The results show, as may be expected, that the effect of boric acid on the rotation of the esters is remarkably small as compared with that



C_1 = The conc. of the ester ($M/_{24}$)

C_2 = The conc. of H_3BO_3 or $\frac{Na_2B_4O_7}{4}$($M/_{24}$)

Fig. 2. The effects of boric acid and borax on the rotation ethyl *d*-gluconate $C_8H_{16}O_7 \cdot {}^1/_2$ $CaCl_2$.



C_1 = The conc. of the ester ($M/_{24}$)

C_2 = The conc. of H_3BO_3 or $\frac{Na_2B_4O_7}{4}$($M/_{24}$)

Fig. 3. The effects of boric acid and borax on the rotation of ethyl *d*-saccharate $C_{10}H_{18}O_8 \cdot {}^1/_2CaCl_2$.

of borax. It is probably due to the difference of the natures of the medium that the rotation of the esters in aqueous boric acid is somewhat larger than in aqueous solution, but not to the formation of heteroboric acids. If it is due to the complex formation, its effect would be more remarkable than seen from Fig. 2 and 3, and would not be parallel to that of water.

The discussion of the results. From the above considerations we are led to the conclusion that only borate ion forms heteroboric acids, combining with non-dissociable polyvalent alcohols. This fact can be explained as follows: in the first place, let us proceed to analyze the dissociation of boric acid in the presence of polyvalent alcohols. The reaction of polyvalent alcohols with borate ion can be expressed in Equation (1), the polyvalent alcohol being represented by the symbol H_2G. The reaction with free boric acid is expressed by the Equation (2). If we apply the law of mass action to these equilibria, the following relations will be obtained. For simplicity we assume that the polyvalent alcohol is present in large excess, and its concentration is costant. The concentration of water must also be considered as non-variant. In addition to these we must take into consideration the dissociation of heteroboric and boric acids, the equations being shown in the following manners:

$$(1) \qquad H_2G + H_2BO_3^- = GBO^- + 2\,H_2O\,. \qquad K_1 = \frac{[GBO^-]}{[H_2BO_3^-]}$$

$$(2) \qquad H_2G + H_3BO_3 = GBOH + 2\,H_2O\,. \qquad K_2 = \frac{[GBOH]}{[H_3BO_3]}$$

$$GBOH = H^+ + GBO^- \qquad K_3 = \frac{[H^+][GBO^-]}{[GBOH]}$$

$$H_3BO_3 = H^+ + H_2BO_3^- \qquad K = \frac{[H^+][H_2BO_3^-]}{[H_3BO_3]}$$

The observed dissociation constant K_a of boric acid in the presence of a polyalcohol is expressed as follows:

$$K_a = \frac{[H^+]\{[H_2BO_3^-] + [GBO^-]\}}{[H_3BO_3] + [GBOH]}\,.$$

Hence
$$K = K_a \frac{1+K_2}{1+K_1}\,.$$

Now, the dissociation constant of boric acid is as small as 6×10^{-10}, while the dissociation constant of heteroboric acid formed by combining with polyvalent alcohols is far greater, the magnitude of which is comparable to those of organic acids. Thus in mannitolboric acid K is as large as $6.3\sim8.4\times10^{-6}$.(6)

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(6) W. D. Treadwell and L. Weiss, *Helv. Chim. Acta,* **3** (1920), 440.

Hence it follows $K_a \gg K$.

Consequently $K_1 \gg K_2$.

This conclusion signifies that borate ion plays an exceedingly important rôle than free boric acid in the formation of heteroboric acid. It is possible that only borate ion enters into union, but on the contrary undissociated boric acid can not combine with non-dissociable polyoxy organic compounds.

Summary.

By observing the effect of boric acid and borax on the optical rotation of gluconates and saccharates, the authors have demonstrated that heteroboric acid can be favourably formed only when one of the reactants is in ionic state. A rational explanation for this conclusion is also presented.

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