On the Formation of Boro-Diol Complexes.

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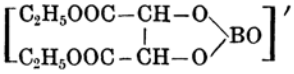
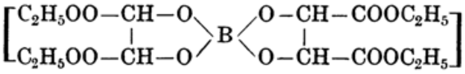
We have shown before some time that borate ion BO'_2 comes into union with ethyl tartrate, while free boric acid H_3BO_3 does not seem to give such boro-diol complexes.⁽¹⁾

In the present paper we will show that this conclusion is confirmed by another different method. Experimental results show that H_3BO_3 is without effect on the rotation of ethyl tartrate in aqueous solution, but BO'_2 diminishes its dextro-rotation to a remarkable degree, and indeed, with the increase in the BO'_2 concentration the dextro-rotation decreases, and even changes the sign. Thus potassium borate KBO_2 shows a much more diminishing effect as compared with borax $Na_2B_4O_7 10H_2O$, when we compare their effects in the same molar concentration of B-atom.

This depressing effect may possibly be due to the formation of the following complex ions (I and II):



I



II

The compound II (potassium salt) has been really isolated and shown to have strong laevo-rotation.⁽²⁾

Results of Experiments. The results of the measurements at 20° are shown in Tables 1–4, and those carried out at 25° in Tables 5–8. The symbol C denotes the concentration of ethyl d-tartrate in mol/24 in the solution.

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(1) Y. Tsuzuki, this Bulletin, **13** (1938), 337.

(2) Lowry, Optical Rotatory Power, 290, London (1935).

Table 1. Effect of KBO_2 on the Rotatory Power of Ethyl Tartrate.

M/4-KBO_2 (c.c.)	M/4-ethyl tartrate (c c.)	C	α	$[\alpha]^{20}_{5461}$
5	10	4	+0.36°	+ 4.8°
15	15	3	−0.71	−12.5
20	10	2	−0.83	−22.0
25	5	1	−0.45	−23.8

Table 2. Effect of Borax on the Rotatory Power of Ethyl Tartrate.

M/16-borax (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]^{20}_{5461}$
10	20	4	+1.44°	+19.1°
15	15	3	+0.45	+ 7.9
20	10	2	−0.26	− 6.9
50	10	1	−0.32	−16.3

Table 3. Rotatory Power of Ethyl Tartrate in Aqueous Solution of Boric Acid.

M/4-H_3BO_3 (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]^{20}_{5461}$
5	10	4	+2.39°	+31.6°
15	15	3	+1.80	+31.8
20	10	2	+1.23	+31.9
25	5	1	+0.66	+34.9

Table 4. Rotatory Power of Ethyl Tartrate in Water.

Water (c.c.)	M/4-ethyl tartrate (c.c)	C	α	$[\alpha]^{20}_{5461}$
5	10	4	+2.34°	+31.0°
15	15	3	+1.79	+31.6
20	10	2	+1.17	+31.0
25	5	1	+0.63	+33.4

Conditions in common for Tables 1–4:
$t = 20^\circ\mathrm{C}$, $l = 2.2$ dm, $\lambda = 5461$ Å.

Table 5. Effect of KBO_2 on the Rotatory Power of Ethyl Tartrate.

M/4-KBO_2 (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]^{20}_{5461}$
10	20	4	+0.57°	+ 7.5°
15	15	3	−0.59	−10.4
20	10	2	−0.75	−19.9
50	10	1	−0.38	−20.1

Table 6. Effect of Borax on the Rotatory Power of Ethyl Tartrate.

M/16 borax (c.c.)	M/4 ethyl tartrate (c.c.)	C	α	$[\alpha]^{25}_{5461}$
5	10	4	+1.43°	+18.9°
15	15	3	+0.43	+ 7.6
22	10	2	−0.21	− 5.0
25	5	1	−0.30	−15.9

Table 7. Rotatory Power of Ethyl Tartrate in Aqueous Solution of Boric Acid.

M/4-H_3BO_3 (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]^{25}_{5461}$
10	20	4	+2.35°	+31.2°
15	15	3	+1.80	+31.7
20	10	2	+1.22	+32.3
25	5	1	+0.64	+33.9

Table 8. Rotatory Power of Ethyl Tartrate in Water.

Water (c.c.)	M/4-ethyl tartrate (c.c.)	C	α	$[\alpha]^{25}_{5461}$
5	10	4	+2.38°	+31.5°
15	15	3	+1.76	+31.1
20	10	2	+1.20	+31.7
25	5	1	+0.62	+32.8

Conditions in common for Tables 5–8:
$t = 25^\circ\mathrm{C}$, $l = 2.2$ dm, $\lambda = 5461$ Å.

The above experimental results (at 25°) are graphically shown in Fig. 1.

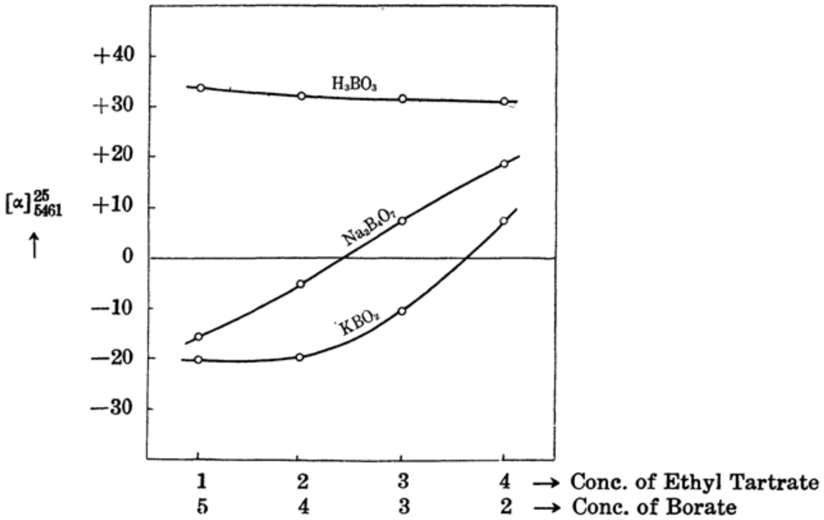
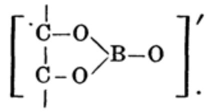


Fig. 1. Effect of Borates on the Rotatory Power of Ethyl *d*-Tartrate at 25°.

Discussion of the Results. The above results indicate that H_3BO_3 exerts only a very little effect on the rotatory power of ethyl tartrate, in sharp contrast to alkali borates. This difference is not due to the change of the acidity of the medium, for the rotation of ethyl tartrate in aqueous solution is not changed by the addition of K_2CO_3: the solution of 10 c.c. M/4-ethyl tartrate and 20 c.c. N/4-K_2CO_3 shows $[\alpha]^{20}_{5461} = +31.0°$ (compare Tables 3 and 4). This fact leads us to conclude that H_3BO_3 does not practically unite with diol, for the combination of H_3BO_3 must result in changing essentially the rotation of the diol, causing the cyclization of the molecule as follows:⁽³⁾



We are, however, imbued with an idea that free boric acid can form complexes with polyalcohols, the extent being considerable. We have had this impression since Magnanini⁽⁴⁾ concluded from the studies of the effect of mannit on the electric conductivity of aqueous boric acid that there exists a mannit-boric acid complex. He thought the composition of this compound to be in the proportions of 3 molecules of acid to 1 of mannit. This conclusion was confirmed later by K. Matsuno and H. Kojima from the measurements of the hydrogen ion concentration and the viscosity of the mannit-boric acid solution. Besides, they showed that a complex of acid: mannit = 1:1 exists.⁽⁵⁾

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(3) van't Hoff, Die Lagerung der Atome in Raume, Braunschweig, 3 Auflage (1908), 90.

(4) G. Magnanini, *Z. physik. Chem.*, **6** (1890), 58; *Gazz. chim. ital.*, **11** (1891), 8.

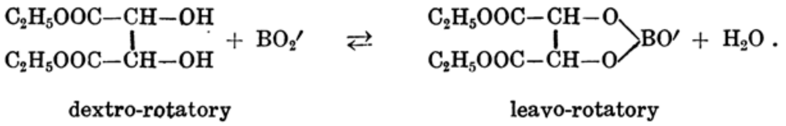
(5) K. Matsuno and H. Kojima, *Bull. Inst. Phys. Chem. Research* (Tokyo), **4** (1925), 45 (in Japanese).

It is, therefore, a somewhat unexpected result that free boric acid gives almost no effect upon the rotatory power of a diol such as ethyl tartrate. This fact can not satisfactorily be explained by the idea of "unfavourable position" of Böeseken,(6) for this diol forms with BO'_2 a certain complex compound. A similar phenomenon can be observed in the case of mannit; it shows a very feeble laevo-rotation,(7) which is scarcely changed by the addition of free boric acid, but in the presence of borate, the solution of mannit shows strong dextro-rotation.(8)

These remarkable facts have not yet been given any explanation. But now it seems to us that free boric acid does not come appreciably into union with polyalcohols, in contrast to borate ion.

Recently Murgier and Darmois expressed as the results of the measurement of rotation that boric acid combines with glucose and xylose only to a slight extent, but $NaBO_2$ gives a well characteristic compound.(9)

The reaction of BO'_2 with ethyl tartrate may be expressed in the following scheme:



Effect of Temperature on the Equilibrium. The author has shown in the distribution experiment(1) that this reaction is exothermic. Thus the equilibrium is shifted to the right when the temperature is lowered, so that the system will be more laevo-rotatory. This supposition has been practically ascertained by experiments. Results are given in Tables 1–4, from which it is evident that the rotation of the system becomes more dextro-rotatory at lower temperature. But in the cases of the solutions containing H_3BO_3 as well as in pure water, where the complex is only scarcely formed, the temperature effect on the totation is neglisibly small, as may be seen by comparing the results of the Tables 3 and 4 with Tables 7 and 8 respectively.

As shown above, free boric acid has no effect on the rotatory power of polyvalent alcohols, but exerts a certain remarkable influence on that of hydroxy-acids, such as tartaric acid, gluconic acid, etc. In these cases, the cause may probably be the interaction between the groups COO′ and H_3BO_3. The experimental results and some considerations on this problem will be published in near future.

The authors desire to thank the Department of Education for a grant.

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(6) Summary of literature, Hermans, *Z. physik. Chem.*, **113** (1924), 338; J. Böeseken, *Bull. soc. chim. Belg.*, **37** (1928), 385.

(7) $[\alpha]^{25}_{E} = -0.24°$ (water), J. M. Braham, *J. Am. Chem. Soc.*, **41** (1919), 1707; $[\alpha]_D = -0.303°$ (without solvent), F. B. Marti, *Bull. soc. chim. Belg.*, **39** (1930), 590.

(8) Vignon, *Compt. rend.*, **77** (1873), 1191; *Ann. chim. phys.*, [5], **2** (1874), 440; E. Fischer, *Ber.*, **23** (1890), 385.

(9) M. Murgier and E. Darmois, X International Congress for Chemistry in Rome, May 1938, Ref. *Angew. Chem.*, **51** (1938), 753.

Summary.

It has been found that free boric acid is without effect on the rotation of ethyl *d*-tartrate but alkali borates have a large effect, and it has been shown that boric acid unites with ethyl *d*-tartrate (dextro-rotatory) to an exceedingly small degree, but borate ion combines with the diol, giving laevo-rotatory boro-diol complex, and with increase of the concentration of borate ion and with fall of temperature the complex formation advances. Thus it has been suggested that only borate ion combines with diol (polyvalent alcohol), but undissociable boric acid does not.

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