CCCLXXXVI.—*The Rotatory Dispersion of Organic Compounds. Part XVIII. Potassium Borotartrate.**

By THOMAS MARTIN LOWRY.

IN the Bakerian Lecture for 1921 (Lowry and Austin, *Phil. Trans.*, 1922, *A*, **222**, 287) it was shown that the rotatory dispersion of an equimolecular mixture of tartaric and boric acids (1 mol. per litre of each acid) no longer exhibited the gross anomalies that had been recorded in aqueous solutions of tartaric acid, but showed a normal rotatory dispersion which could be expressed by the simple formula $[M] = 24{\cdot}835/(\lambda^2 - 0{\cdot}0271)$. A more exact series of observations, including readings for 18 lines in the visual and 5 lines in the photographic region of the spectrum, showed, however, that the simple formula was only an approximation; but since the negative term in the complex formula was very small (only about 1/20 of the positive term) the opinion was expressed that it "would probably disappear altogether if a sufficient quantity of boric acid were used to convert the tartaric acid wholly into borotartaric acid." Justification for this view was found in the fact that the dispersion of a solution of tartaric acid, of half the concentration previously used, but containing $1\frac{1}{2}$ molecular proportions of boric acid, was so nearly simple that the only hint of complexity was that given by a few negative errors in the red and in the extreme violet region of the spectrum. The calculated values for this solution were therefore deduced from a single term of Drude's equation; but these numbers were used in order to demonstrate the presence of systematic deviations, and thus to prove the complexity and not the simplicity of the rotatory dispersion. The excess of boric acid which serves to convert the complex dispersion of tartaric acid into a simple dispersion (see *loc. cit.*, p. 288, § 5 of summary) must therefore be interpreted by means of the preceding text as "a quantity sufficient to convert the tartaric acid wholly into borotartaric acid."

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* Borotartrates of different compositions have been used in pharmacy for nearly a century (Dulk, *Annalen*, 1832, **2**, 39; Soubeiran, *ibid.*, 1839, **31**, 192; Soubeiran and Capitaine, *ibid.*, 1840, **34**, 204, *et seq.*), but there is no evidence to show that any of them are definite chemical compounds. Baudran (*Ann. Chim. Phys.*, 1900, **19**, 559) claimed to have isolated $B(C_4H_5O_6)_3,3H_2O$ and $B(C_4H_4KO_6)_3,\frac{1}{2}H_2O$, but his observations have been called in question by Rosenheim (*Z. anorg. Chem.*, 1906, **48**, 206) and by Darmois (*J. Chim. physique*, 1926, **23**, 671). The existence of a ditartaroboric acid was postulated by Dubrunfaut (*Compt. rend.*, 1856, **42**, 112), by Grossmann and Wieneke (*Z. physikal. Chem.*, 1906, **54**, 385), and finally by Darmois, who mixed equimolecular quantities of potassium tartrate and tartaric acid with 2/3 mol. of boric acid, but obtained in this way a solution which deposited potassium hydrogen tartrate instead of the borotartrate now described.

In view of the definite proof which we gave of the complex character of the rotatory dispersion of our solutions, we regret that a directly opposite opinion has been attributed to us by two writers. Descamps, who devised an apparatus by which he could measure the rotatory power of tartaric acid to 2537 Å.U. (*Compt. rend.*, 1927, **184**, 453) found that the rotatory dispersion of two equimolecular mixtures of boric and tartaric acids was anomalous in the ultra-violet region, and that a maximum could still be observed when 1½ mols. of boric acid were used, although the reversal of sign was now beyond the limits of observation; but he makes the statement that "Lowry and Austin have concluded that the curves of rotatory dispersion of aqueous solutions of tartaric acid containing an equimolecular quantity or a slight excess of boric acid belong to the simple type." Descamps therefore regarded his measurements as correcting an error into which we had fallen as a result of using too narrow a range of wave-lengths, whereas the anomalies which he observed had actually been predicted by us (just as in the case of sodium tartrate, Lowry and Vernon, *Proc. Roy. Soc.*, 1928, *A*, **119**, 706) when we expressed our measurements with the help of a Drude equation with two terms of opposite sign, in which $k_1 > k_2$ whilst $\lambda_2 > \lambda_1$.

A misleading impression is also created by Hunter's statement (*Ann. Reports*, 1928, **25**, 18) that "the validity of the conclusions of Lowry and Austin—that the addition of sufficient boric acid to aqueous solutions of tartaric acid 'fixes' one of its hypothetical dynamic isomerides and thus, by eliminating one component of an alleged mixture of two substances of opposite rotation and unequal simple rotatory dispersion, produces simple rotatory dispersion in the solution—is rendered doubtful by the work of R. Descamps." The true position is that Descamps, using solutions 5—15 times more dilute than ours, was able to demonstrate the anomalous character of the rotatory dispersion of mixtures to which we had already assigned a rotatory dispersion of this type, and that Burgess and Hunter (preceding paper) have obtained independent evidence of the presence in these mixtures of the free tartaric acid to which we had already directed attention. One set of observations therefore explains the other, and both lend support to our conclusion that the complex rotatory dispersion of these solutions is due to uncombined tartaric acid, and would therefore become simple only when this had been converted wholly into borotartaric acid.

This problem has, however, been carried much nearer to a solution by the work described in Descamps's thesis (published early in 1928, but not referred to in the Annual Report for that year), in which it was shown that, when the molecular proportion of tartaric acid at a constant concentration of boric acid was decreased, the maximum was displaced further and further into the ultra-violet as follows :

$H_2(C_4H_4O_6)/H_3BO_3$	4·5	1·8	0·7	0·27	0·14	0·045	0·015
Maximum, Å.U. ...	3300	2925	2830			2760	2700

Finally, at a molecular ratio $H_2(C_4H_4O_6)/H_3BO_3 = 0{\cdot}006$, the maximum was displaced beyond the limit of transmission of light at 2537 Å.U., and the only indication of possible complexity was a doubtful point of inflexion beyond 2753 Å.U. A condition of normal (and perhaps simple) rotatory dispersion was thus realised, right up to the limit at which Drude's formula ceases to be applicable. One must suppose, however, that more precise measurements of optical rotatory power might still reveal the effects of traces of tartaric acid, since these could only be eliminated completely from a reversible system when the boric acid was in infinite excess.

Similar experiments with ammonium tartrate showed a maximum at 3020 Å.U., which was displaced beyond the limit of transmission at 2537 Å.U. even when the molecular ratio was as high as $(NH_4)_2C_4H_4O_6/H_3BO_3 = 3{\cdot}4$, leaving only an inflexion at 2800 Å.U. to mark the complexity of the rotatory dispersion. When the molecular ratio was reduced to 1·4, 0·7, and 0·13, the curves were normal throughout. The addition of borax to a solution of normal sodium tartrate, however, was almost without effect, showing that the two acid radicals do not interact to any marked extent in alkaline solutions.

More remarkable effects were produced by the addition of boric acid to potassium hydrogen tartrate, for a dispersion curve with a maximum at 3650 Å.U. became normal on the addition of only 0·5 mol. of boric acid to each mol. of tartaric acid. Moreover, this curve was not displaced to any important extent when the proportion of boric acid was increased to 1 or to 2 mols. These results show that the product to which the solutions owe their high optical activity is stabilised by the addition of a small proportion of alkali, but destroyed almost completely when alkali is added in sufficient quantity to convert the tartaric acid into a normal tartrate and the boric acid into borax. It is also clear that, when the condition of maximum stability is reached, each molecule of boric acid is capable of transforming *two* molecules of tartaric acid from a low rotatory form with anomalous rotatory dispersion into a high rotatory form with normal rotatory dispersion.

In view of the preceding results, an attempt was made to isolate a complex salt from a mixture of potassium hydrogen tartrate (38 g.; 0·2 mol.) and boric acid (6 g.; 0·1 mol.) in water (100 c.c.); but, since Böeseken's borosalicylates contain only one atom of alkali metal to 2 mols. of salicylic and 1 mol. of boric acid, the precaution was taken of preparing also an equimolecular mixture of potassium hydrogen tartrate (19 g.; 0·1 mol.), tartaric acid (15 g.; 0·1 mol.), and boric acid (6 g.; 0·1 mol.) in water (100 c.c.). In the former case, a large proportion of the cream of tartar remained undissolved, but in the latter case the 40 g. of solid dissolved readily. Further quantities of the mixture were therefore added until a total of 160 g. (including 76 g. of cream of tartar) had been dissolved in 100 c.c. of boiling water. From this liquid, 85 g. of a crystalline salt separated, which had the properties and the approximate composition of a *potassium borotartrate* [Found: K, 12·1; C, 26·2; H, 2·27; equiv., by titration in presence of glycerol, 88·5. $KB(C_4H_4O_6)_2$ requires K, 11·3; C, 27·7; H, 2·31%; equiv., 86·5]. A specimen which had been recrystallised from water and then dried to constant weight gave for the equivalent the value 122 with N/10-sodium hydroxide only, but 88·4 in presence of mannitol.

The molecular rotatory power of the salt in a 5% aqueous solution $[M]_{5780} = 150^\circ(139^\circ), [M]_{5461} = 172\cdot0^\circ(159^\circ), [M]_{4358} = 287^\circ(275^\circ)$ was higher than the highest values observed previously in aqueous solutions of cream of tartar to which boric acid had been added, as recorded by Descamps and shown in parentheses above; but this is natural, in view of the fact that his solutions contained an excess of alkali, which has been shown to diminish the stability of the complex salt. Still higher values were obtained when the recrystallised salt was examined in a nearly saturated solution ($p = 33\cdot54$), *viz.*,

$$[M]_{5893} = 174^\circ, [M]_{5780} = 182^\circ, [M]_{5461} = 206^\circ, [M]_{4358} = 348^\circ.$$

The specific rotations for 14 wave-lengths in the visual region, as measured by Mr. C. B. Allsopp, are shown in Table I.

TABLE I.

Specific rotation of potassium borotartrate at 20°.

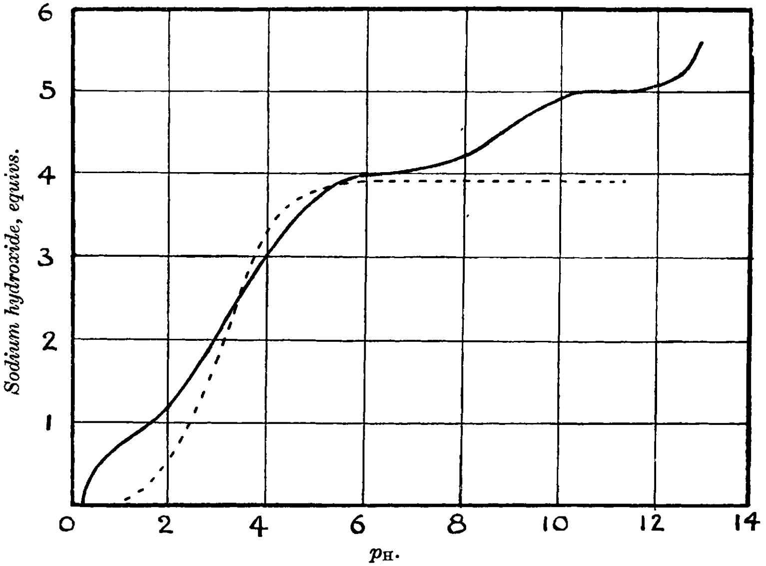
$p = 33\cdot54$; $d_{4^\circ}^{20^\circ} = 1\cdot1864$; $\alpha/\alpha_{5461} = 0\cdot2666/(\lambda^2 - 0\cdot0316)$.

		α/α_{5461},			
Wave-length.	α.	obs.	calc.	1000 (O–C).	$[\alpha]$.
Li 6708·2	30·37°	0·638	0·637	+ 1	38·2°
Cd 6438·7	33·11	0·696	0·696	±	41·6
Zn 6362·6	33·72	0·709	0·714	− 5	42·4
Li 6103·7	37·04	0·779	0·782	− 3	46·5
Na 5893·0	40·08	0·843	0·843	±	50·4
Hg 5780·0	41·84	0·880	0·881	− 1	52·6
Hg 5460·7	47·53	1·000	1·000	±	59·7
Cu 5218·4	52·62	1·107	1·107	±	66·1
Cd 5086·0	55·76	1·173	1·174	− 1	70·1
Zn 4810·7	63·57	1·337	1·334	+ 3	79·9
Cd 4800·0	64·06	1·348	1·342	+ 6	80·5
Zn 4680·3	67·53	1·421	1·422	− 1	84·8
Cd 4678·3	67·73	1·425	1·424	+ 1	87·1
Hg 4358·6	80·06	1·684	1·683	+ 1	100·6

I am indebted to Messrs. W. S. Hughes and T. H. Morton for the electrometric titrations set out in Fig. 1. The broken curve shows the results obtained by titrating $2M$-tartaric acid with $2N$-sodium hydroxide, and the full curve is for a similar titration in presence of M-boric acid. These curves show that a solution containing 1 mol. per litre of borotartaric acid, $HB(C_4H_4O_6)_2$, has $p_H = 0$ approximately, so that the complex acid is comparable in strength with hydrochloric acid. This complex acid is decomposed, however, by excess of alkali, since the full curve for borotartaric acid cuts the broken curve for tartaric acid just beyond the stage at which potassium hydrogen tartrate would be formed, and then shows a neutralisation point at $p_H = 6$ for tartaric acid and $p_H = 11$ for boric acid. In the stages immediately preceding the neutralisation of the tartaric acid, the broken curve rises above the full curve, showing that the acidity of the solution is reduced by the presence of boric acid, as if a little extra work were required to detach the last carboxyl from the boron.

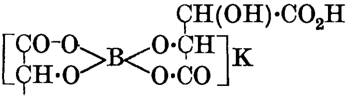
FIG. 1.

Potentiometric titration of borotartaric acid.



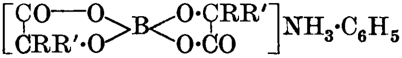
Full curve: $2M$-$C_4H_6O_6$ + M-H_3BO_3. *Broken curve:* $2M$-$C_4H_6O_6$ *alone.*

The new borotartrate evidently contains a quadricovalent complex ion, like the borofluorides; $KB(C_4H_4O_6)_2$: compare KBF_4. Its composition also corresponds precisely with that of the optically active borosalicylates. Professor Böeseken therefore suggests (private communication) that the potassium salt probably has the structure (I), like the asymmetric complexes of boric acid with α-hydroxy-



$$\left[\begin{matrix}\mathrm{CO{\cdot}O} \\ \mathrm{CH{\cdot}O}\end{matrix}\!>\!\mathrm{B}\!<\!\begin{matrix}\mathrm{O{\cdot}CH} \\ \mathrm{O{\cdot}CO}\end{matrix}\right]\mathrm{K}$$ with $\mathrm{CH(OH){\cdot}CO_2H}$ on the upper right CH and $\mathrm{CH(OH){\cdot}CO_2H}$ on the lower left CH

(I.)

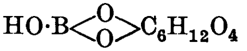


$$\left[\begin{matrix}\mathrm{CO{-}{-}O} \\ \mathrm{CRR'{\cdot}O}\end{matrix}\!>\!\mathrm{B}\!<\!\begin{matrix}\mathrm{O{\cdot}CRR'} \\ \mathrm{O{\cdot}CO}\end{matrix}\right]\mathrm{NH_3{\cdot}C_6H_5}$$

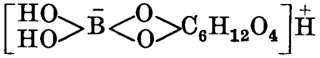
(II.)

*iso*butyric acid (II; R = R′ = Me) and α-hydroxy*iso*valeric acid (II; R = Me, R′ = Et). This structure we have not yet been able to establish, since the complex salt is broken up at once by excess of alkali; but it is confirmed by the fact that ethyl tartrate, which behaves in many respects like a higher homologue of tartaric acid, shows a sharp contrast in its behaviour towards potassium metaborate. We can, however, now explain quite clearly why mannitol and boric acid lose only *one* molecule of water, and not two, in forming mannitoboric acid (Fox and Gauge, J., 1911, **99**, 1075), since the complex is evidently not a tervalent derivative (III) of orthoboric acid, but a quadricovalent complex (IV) of the borofluoride type, which would not readily form the anhydride (III) or (V).

(III.)

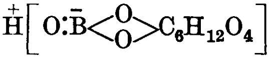


$$\mathrm{HO{\cdot}B}\!<\!\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\!>\!\mathrm{C_6H_{12}O_4}$$



$$\left[\begin{matrix}\mathrm{HO}\\\mathrm{HO}\end{matrix}\!>\!\bar{\mathrm{B}}\!<\!\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\!>\!\mathrm{C_6H_{12}O_4}\right]\overset{+}{\mathrm{H}}$$

(IV.)



$$\overset{+}{\mathrm{H}}\left[\mathrm{O{:}\bar{B}}\!<\!\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\!>\!\mathrm{C_6H_{12}O_4}\right]$$

(V.)

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