CCCLXXXV.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXXIV.** *Borotartaric Acid.*

By STANLEY GROVE BURGESS and HAROLD HUNTER.

THE peculiarities of the rotatory power and rotatory dispersion of tartaric acid and its derivatives have attracted attention ever since they were first observed by Biot, but it cannot be said that a satis-

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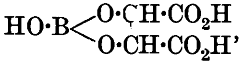
* The previous parts of these investigations to which reference is made in this paper are: Part XXIX, J., 1925, **127**, 2552; Part XXX, J., 1926, 2079; Part XXXI, J., 1927, 188; Part XXXIII, J., 1928, 3000.

factory explanation of them has yet been evolved. Particularly is this the case with the phenomena observed when boric and tartaric acids are mixed in aqueous solution.

The addition of boric acid to aqueous solutions of *d*-tartaric acid produces three obvious effects: (*a*) the solubility of each acid is greater in the presence of the other than when alone (Herz, *Z. anorg. Chem.*, 1903, **34**, 205; 1911, **70**, 70), (*b*) the hydrogen-ion concentrations of solutions of the mixed acids, whether measured colorimetrically, conductimetrically, or potentiometrically, are higher than those due to either acid alone (Böeseken and Van Rossen, *Rec. trav. chim.*, 1911, **30**, 392; Böeseken, *ibid.*, 1921, **40**, 553), and (*c*) a pronounced change of rotatory power occurs, accompanied by a very marked alteration in the character of the rotatory dispersion (Biot, *Ann. Chim. Phys.*, 1844, **11**, 82; Lowry and Austin, *Phil. Trans.*, 1922, *A*, **222**, 249).

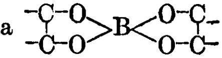
These alterations in physical and chemical properties have usually been ascribed to the formation of molecular complexes, but there is apparently no record of the existence of any such complex in the solid state. It is true that Baudran (*Ann. Chim. Phys.*, 1900, **19**, 559) has described a solid compound, crystallising in large prisms, of the formula $B(C_4H_5O_6)_3,3H_2O$, but, since this was obtained merely by the evaporation of an aqueous solution containing tartaric and boric acids in the molecular proportion 3 : 1, the evidence of its real existence is not at all conclusive. In the absence of a solid phase, the formulation of such a complex is very largely a matter of speculation, and Lowry and Austin (*loc. cit.*), and also others, have tentatively adopted the structure



$HO{\cdot}B{<}\begin{matrix}O{\cdot}CH{\cdot}CO_2H\\ O{\cdot}CH{\cdot}CO_2H\end{matrix}$,

adding that "it is possible that the simple character of its rotatory dispersion may be due to the bridge between the two asymmetric carbon atoms which is shown in this formula." Darmois (*J. Chim. physique*, 1926, **23**, 649) has examined solutions of boric and tartaric acids both polarimetrically and electrometrically and considers that his results are best explained by assuming the formation of a compound of one molecule of boric acid with two molecules of tartaric acid. He was unable, however, to isolate this as a solid, and was equally unsuccessful in his attempts to obtain solid forms of the potassium or ammonium salt.

The electronic theory of valency has been applied by Böeseken and others (Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 97; 1924, **27**, 174; *Rec. trav. chim.*, 1916, **45**, 919; Hermans, *ibid.*, 1926, **46**, 151; *Proc. K. Akad. Wetensch. Amsterdam*, 1923, **26**, 32; Rosenheim and Vermehren, *Ber.*, 1924, **57**, 1337) to explain the formation of boric acid complexes with organic hydroxy-compounds.

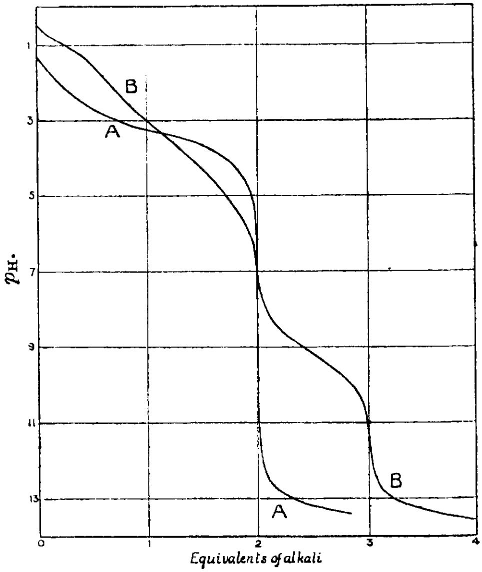
These compounds are given the general formula  $\begin{matrix}-\mathrm{C}-\mathrm{O}\\ |\\ -\mathrm{C}-\mathrm{O}\end{matrix}\!>\!\mathrm{B}\!<\!\begin{matrix}\mathrm{O}-\mathrm{C}-\\ |\\ \mathrm{O}-\mathrm{C}-\end{matrix}$ with the boron atom at the centre of a *spiro*-structure, but again no unequivocal evidence of the structure of a borotartaric complex has been obtained. A formula of this kind is not inconsistent with the experimental observations presented in this paper, except for the very slight indication given by the data represented in Fig. 3 that an equimolecular compound is formed. Nevertheless, although the direct evidence in its favour is slight, an alternative formula for borotartaric acid is here put forward as a possibility, not only because it explains the facts at least as well as any other, but also because the termination of this collaboration renders it improbable that the work will be continued and makes it desirable to place on record that already done.

Any theory of the action of boric acid on tartaric acid must, it would seem, account for the following facts : (*a*) the specific nature of the action of boric acid on organic hydroxy-compounds, (*b*) the large increase of rotatory power produced when boric acid is added to aqueous solutions of *d*-tartaric acid, (*c*) the marked change in the character of the rotatory dispersion of aqueous solutions of *d*-tartaric acid which occurs when boric acid is added, (*d*) the concurrent increase in the acidity and electrical conductivity of such solutions, and (*e*) the difference between the behaviour of tartaric acid as a dibasic acid before and after the addition of boric acid : the dissociation constants of the acidic groups of tartaric acid are sensibly equal ($k_1 : k_2 = 11 : 1$) and this acid accordingly simulates the behaviour of a monobasic acid on titration (see Fig. 1, A); the addition of boric acid, however, changes the form of the titration curve (Fig. 1, B) and causes it to show evidence of dibasic character. It will be seen that the first portion of the titration curve for borotartaric acid lies above, and the second portion below, the corresponding curve for tartaric acid. This must mean that the addition of boric acid to tartaric acid strengthens one of the acid groups of the latter acid and weakens the other.

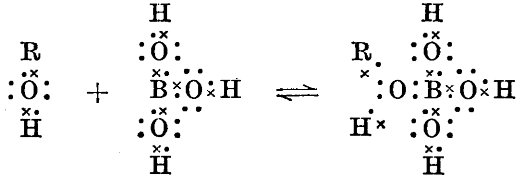
Points (*b*) and (*c*) above are explained by Lowry and Austin (*loc. cit.*) by assuming that the complex rotatory dispersion of *d*-tartaric acid in aqueous solution is due to the presence in such solutions of two labile forms of the acid of different dispersive power, and that the increased rotatory power and close approach to simple rotatory dispersion exhibited by similar solutions to which boric acid has been added are due to the nearly complete combination of one such form of tartaric acid with the boric acid and the almost complete suppression of the other. It must be admitted that the facts are capable of explanation on this hypothesis, but an alternative view is here put forward which accounts for the facts equally well without the necessity of postulating labile forms of tartaric acid

According to the electronic theory of valency, boron is the one element above all others to form stable compounds in which the atom has only a sextet of electrons. These compounds, of which BF_3 may be taken as an example, readily form addition compounds in which the octet of the boron atom is completed by the transfer of electrons from an atom in another compound, as in $H^+BF_4^-$. Since the transfer of electrons must result in the formation of a charged system, the addition of compounds of boron in this manner to other compounds must give rise to a polar bond if the resultant compound is ionised at the boron atom, or to a semipolar double bond if it is not. The main theoretical idea underlying this paper is that *the union of boric acid to tartaric acid, and probably to other organic hydroxy-compounds, occurs by the formation of a semipolar double bond*, thus :

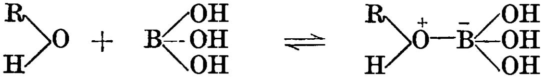
FIG. 1.



A. Titration of M-*tartaric acid with* 2*M*-NaOH.
B. ,, ,, M-*tartaric acid* + M-*boric acid with* 2*M*-NaOH.

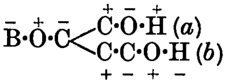


or



This structure for borotartaric acid immediately recalls that assigned to sulphoxides, $^{R'}_{R''}\!>\overset{+}{S}-\overset{-}{O}$, and related compounds by Phillips and his collaborators (Parts XXIX, XXX, XXXI, and XXXIII, *loc. cit.*), and we should expect the positively charged oxygen atom in the borotartaric acid molecule to play somewhat the same part as does the positively charged sulphur atom in the sulphoxide, sulphinic ester, or sulphilimine molecule. Unfortunately, it has so far proved impossible to isolate borotartaric acid in either the optically active or the optically inactive form, so that this view cannot be subjected to the crucial experimental test of direct resolution of the compound into any of its active forms.

It may be argued, however, that, since the union of boric and *d*-tartaric acid takes place under the influence of the dissymmetric carbon system of the latter, it is fair to assume that the latent optical activity associated with the positively charged oxygen atom is thereby developed, and that therefore this union produces a new optically active system about the oxygen atom concerned in the semipolar double bond. If, further, we assume that the rotatory power of this new dissymmetric system is comparable in magnitude with the very large values observed in the structurally similar sulphur compounds of Phillips and his co-workers, we have at once an explanation of the changes in rotatory and dispersive power observed when boric acid is added to solutions of *d*-tartaric acid. The rotatory power of tartaric acid in the visible region of the spectrum is small, and may be represented as the difference of two much larger and nearly equal terms. This accounts for the well-known experimental fact that in this region of the spectrum the rotatory power of tartaric acid varies but little with wave-length. If, therefore, the addition of boric acid to a solution of *d*-tartaric acid results in the addition of at least one more large term to the dispersion equation of the latter to account for the formation of an optically active oxygen atom, then two effects will be expected. There will be, first, a large increase in the magnitude of the rotatory power in the visible region of the spectrum, and secondly, a simulation of simple rotatory dispersion in this region, since the added form will overshadow the others. If the dispersion constant of the added term is smaller than the dispersion constants of the terms in the equation for tartaric acid, then the latter will gain in importance more rapidly than the added term as the region of the spectrum in which the absorption bands of tartaric acid are situated is approached. This will result in an increasingly apparent departure of the dispersion from simplicity, which is precisely the effect actually observed.

The ring condensation formula for borotartaric acid (see p. 2839) offers no explanation of the increased hydrogen-ion concentration caused by the addition of boric acid to aqueous solutions of tartaric acid. Furthermore, from the symmetry of this formula, we should expect that the ionisation constant associated with each acidic group of the tartaric acid would be similarly affected by the addition of boric acid, so that titration curves of tartaric and borotartaric acids would be sensibly parallel. This is far from being the case. The hydrogen-ion concentration of a solution of tartaric acid to which boric acid has been added is higher than that due to tartaric acid alone, but as neutralisation proceeds, the curves cross (see Fig. 1), the second ionisation constant of borotartaric acid being much smaller than the corresponding figure for tartaric acid. This observation can be explained by the addition theory put forward in this paper. The action of induced alternate polarity from the semipolar double bond as indicated in the skeleton formula  $\overset{-}{B}\cdot\overset{+}{O}\cdot\overset{-}{C}\!<\!\begin{matrix}\overset{+}{C}\cdot\overset{-}{O}\cdot\overset{+}{H}\,(a)\\ \underset{+}{C}\cdot\underset{-}{C}\cdot\underset{+}{O}\cdot\underset{-}{H}\,(b)\end{matrix}$ is to favour the ionisation of the hydrogen atom (*a*), but to oppose that of atom (*b*). This effect is observed whichever oxygen atom in the tartaric acid molecule is involved in the semipolar double bond, and is a result of the high degree of structural symmetry possessed by this molecule. It should be borne in mind, too, that the charges involved in a semipolar double bond are perfectly determinate and are not more or less hypothetical tendencies capable of manipulation to suit the purposes of a particular argument, as has unfortunately been the case with some of the applications of the theory of induced alternate polarity.

The Equilibria $H_3BO_3 + C_4H_6O_6 \rightleftharpoons$ *Borotartaric Acid* $\rightleftharpoons$ *Borotartrate Ion* $+ H^+$.

When an infinitely strong (completely ionised*) monobasic acid in aqueous solution is diluted ten-fold, the p_H of the solution rises by one unit. When, on the other hand, an infinitely weak (very feebly ionised) acid is subjected to ten-fold dilution, the p_H

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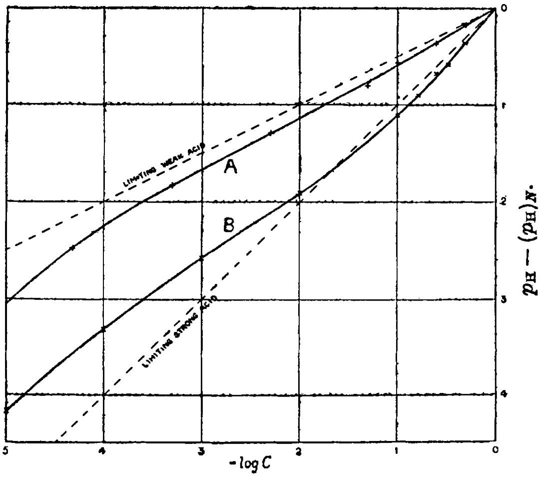
* In this section, the terms " ionised " and " ionisation " will be applied only to the process represented by the second of the above equations, whilst the terms " dissociated " and " dissociation " will be reserved for the process represented by the first equation.

rises by only 0·5 unit.* Normally, all acids show alterations of p_H with dilution which lie between these limits. But a solution which is M with regard both to tartaric and to boric acid, or even one which is $0{\cdot}5M$ with respect to the former and $0{\cdot}75M$ to the latter, shows a more rapid increase of p_H with dilution than would an infinitely strong acid, although the p_H corresponding to the acid concentration indicates incomplete ionisation: hydrogen ions are removed from unit volume more rapidly than can be accounted for by the dilution factor alone. There can be only one explanation of this fact: superposed upon the normal dilution effect is one due to the removal of hydrogen ions from solution by the dissociation of the strong borotartaric acid into the weaker boric and tartaric acids.

FIG. 2.



Variation of p_H *with concentration.*

A. Tartaric acid.
B. Tartaric and boric acids in equimolecular proportion.

This point is illustrated in Fig. 2 where, for convenience, $p_H - (p_H)_N$ is plotted against $-\log C$, p_H being the p_H of a solution containing C mols. of tartaric acid per litre, and $(p_H)_N$ that of a solution of unit acid concentration. It will be observed that the curves

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* Let the degree of ionisation, hydrogen-ion concentration, and p_H at dilutions V_1 and V_2 be α_1, α_2. $[H^{\cdot}]_1, [H^{\cdot}]_2, (p_H)_1$ and $(p_H)_2$, respectively. Then, if K be the ionisation constant, $\alpha_1^2/(1-\alpha_1)V_1 = \alpha_2^2/(1-\alpha_2)V_2 = K$, and, since α_1 and α_2 are negligible compared with unity, $\alpha_1^2 V_2 = \alpha_2^2 V_1$. If $V_2 = 10V_1$, $\alpha_1/\alpha_2 \doteq 1/\sqrt{10}$. But $[H^{\cdot}]_1/[H^{\cdot}]_2 = \alpha_1 V_2/\alpha_2 V_1 \doteq \sqrt{10}$, so that $\log_{10} 1/[H^{\cdot}]_2 - \log_{10} 1/[H^{\cdot}]_1 = \log_{10}\sqrt{10}$ or $(p_H)_2 - (p_H)_1 = 0{\cdot}5$.

become parallel towards the lower left-hand corner of the figure: they would, of course, meet at infinity in this direction but for the fact that the ionisation of the solvent becomes important in the neighbourhood of p_H 7.

It is not possible to treat the equilibrium relations between boric, tartaric, and borotartaric acids and their ions with any considerable degree of rigour, because borotartaric acid is a strong electrolyte and the solutions under consideration are concentrated, but the following treatment is sufficiently accurate to indicate the approximate relations. It is to be observed that the fact that the solutions are concentrated does not debar us from applying the law of mass action to the equilibrium boric acid + tartaric acid $\rightleftharpoons$ borotartaric acid, since this is not an ionic reaction. Furthermore, since we have little information as to the molecular ratio in which boric and tartaric acids combine, the simplest hypothesis of combination, molecule for molecule, is adopted. This hypothesis is supported by the measurements of rotatory power (Table III and Fig. 3).

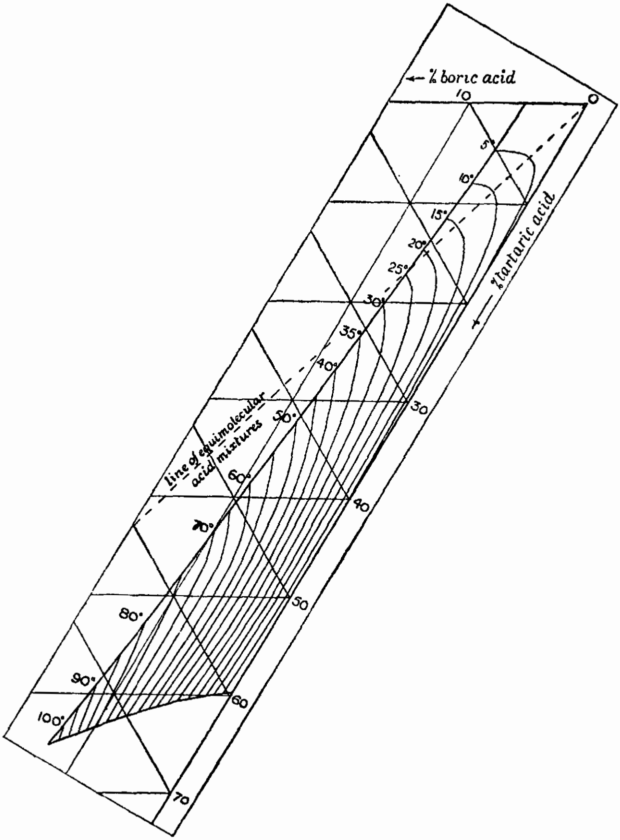
The p_H of a solution molar in both tartaric and boric acids is 0·47 (Table II). The acidity of this solution is so high that borotartaric acid must be comparable in strength with sulphuric acid: if combination between boric and tartaric acids is complete, then borotartaric acid must be at least 34% ionised at this concentration, whilst if it is appreciably dissociated into boric and tartaric acids, it must be a stronger acid still. We may therefore neglect the ionisation of tartaric and boric acids when dealing with solutions of this concentration, and assume that the hydrogen-ion concentration of solutions of borotartaric acid would be proportional, over small ranges of concentration, to the borotartaric acid concentration if no dissociation occurred. The error introduced by this assumption will be in the direction of reducing the calculated value of the equilibrium constant of the above reaction so that the result obtained will be a lower limit for the value of this constant,

$$\frac{[H_3BO_3][C_4H_6O_6]}{[\text{borotartaric acid}]} = K.$$

We may reverse the above argument, and infer that, since the p_H of the above solution is 0·47, at least 34% of the tartaric acid must be combined with boric acid if borotartaric acid is completely ionised in solution, whilst if it is not, then more than this amount of combination must occur. The actual conditions will probably lie between the two extremes. It is now quite a simple matter to obtain, by a process of trial and error, the approximate value of K. The p_H–dilution curves are fitted best by assuming 30% dissociation in a solution molar in tartaric acid and boric acid, giving $K = 0{\cdot}129$.

The proportion of free tartaric acid in a solution 0·5M in tartaric acid and 0·75M in boric acid is then 25% as a lower limit. It follows from this that a molar solution of borotartaric acid, if it could be obtained, would have 50% as the upper limit for its degree of ionisation.

FIG. 3.



*Lines of equal rotatory power for the system boric acid–*d*-tartaric acid–water.*
(l = 200 *mm.*, λ = 5461 Å., t = 25°.)

*The System Boric Acid–*d*-Tartaric Acid–Water at Various Temperatures.*

The case for the postulation of the formation of an additive equimolecular complex of boric and tartaric acids as opposed to a condensation compound, or an additive compound of two molecules of tartaric acid to one of boric, appears sufficiently cogent to warrant an experimental investigation of the question by another method. An application of the principles of the phase theory is one such method of approaching this problem, though it is to be remembered that this theory affords no information as to the structural, as distinct from the ultimate, composition of any phase, and that therefore the method will fail in the event of the non-appearance of a solid phase of borotartaric acid. Apart from this possibility of failure, Schreinemakers's method of intersecting tie-lines should furnish an unequivocal solution to the problem of the ultimate composition of borotartaric acid. In short, should borotartaric acid appear as a solid phase in the system, the conjugation lines running from the solubility curve of borotartaric acid will intersect on the base of the triangle in Fig. 4 if no elimination of water occurs, and beyond the base (outside the triangle) if elimination of water does occur. This method should, if successful, also decide between 1 : 1 and 1 : 2 combination of boric and tartaric acids.

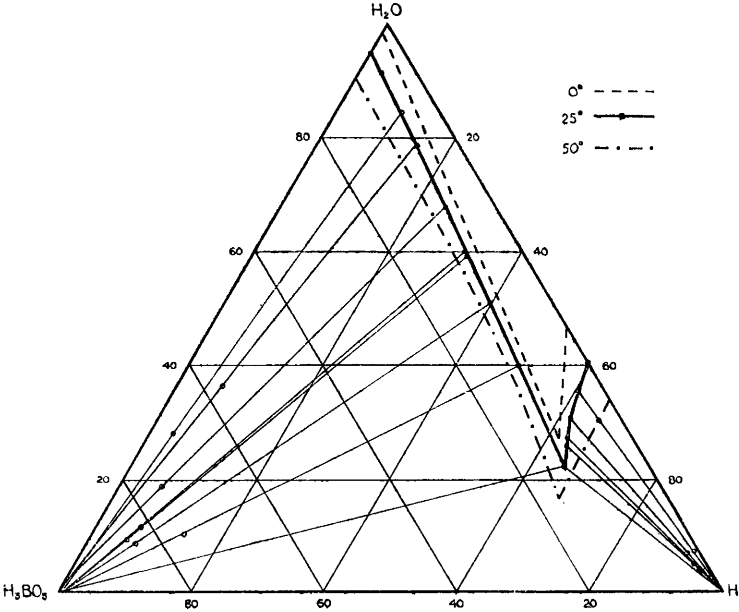
Actually, no evidence of the existence of solid borotartaric acid was obtained at any of the temperatures employed in this investigation. It must be borne in mind, however, that the invariant solutions obtained had very high concentrations of the mixed acids (*e.g.*, at 50°, the water content of the solution saturated with both acids was only 16%) and were very viscous indeed. In view of this fact, and also of the fact that the presence of nuclei of solid borotartaric acid could not be assured, the possibility that the results obtained partly represent metastable equilibrium cannot be overlooked, and it would be rash to assert that solid borotartaric acid cannot exist under some, at least, of the experimental conditions described herein.

Nevertheless, this part of the investigation has not been altogether unfruitful. The slopes of the curves in Fig. 4 afford fresh evidence that some sort of combination of the acids does occur in the liquid phase (compare Koppel, *Z. physikal. Chem.*, 1905, **52**, 385; Caven and Mitchell, J., 1924, **125**, 1428). It may fairly be argued, too, from the fact that the slopes of the solubility curves increase as the temperature is lowered, that combination is more complete at low temperature, and that therefore it occurs with the evolution of heat.

Rotatory Power.

The rotatory powers of solutions in the liquid phase region of the equilibrium diagram at 25° are recorded in Table III and Fig. 3. It will be seen that the lines of equal rotation in this figure are the contour lines of a surface showing the variation of rotatory power with composition, and that they indicate a ridge on this surface running directly over the line representing equimolecular mixtures of the two acids. It is unfortunate that the physical conditions do not allow this ridge to be followed very far, but the curves certainly indicate that, of mixtures containing the same proportion by weight of mixed acids, that containing the acids in equimolecular proportion has the maximum rotatory power, and it is considered fair to infer from this fact that the compound of the two acids contains them in equimolecular proportion.

FIG. 4.



*The system boric acid–*d*-tartaric acid–water.*

EXPERIMENTAL.

Solubility Determinations.—A.R. Boric and tartaric acids were purified by three or four crystallisations, the former from water and the latter from acetone, and suitable quantities were placed with distilled water in closed bottles. These bottles were clamped with their axes horizontal to a horizontal shaft and completely immersed in the water of a thermostat. The shaft was driven by a motor and thus served to agitate thoroughly both the solutions and the water in the thermostat. The temperatures were controlled to ±0·05° by means of a Lowry spiral thermoregulator, except for the measurements at 0°, for which melting ice was used. Preliminary observations showed that equilibrium was attained within 48 hours, and at the end of this time samples of the liquid phase were withdrawn through muslin into a warmed pipette, weighed, and analysed. Samples of the moist solid residues were taken, drained by rapid filtration on Gooch crucibles with mats of fritted glass, and jacketed with water from the thermostat, weighed, and analysed. The results are given in Table I and Fig. 4.

TABLE I.

Solubility data for the condensed isothermal system boric acid–d-tartaric acid–water.

(Compositions given in percentages by weight.)

(*a*) At 0°.

Liquid phase.			Residue.			Solid phase.
$C_4H_6O_6$.	H_3BO_3.	H_2O.	$C_4H_6O_6$.	H_3BO_3.	H_2O.	
53·5	0·0	46·5	—	—	—	$C_4H_6O_6$.
58·6	6·4	35·0	—	—	—	
62·3	11·1	26·6*	—	—	—	$C_4H_6O_6+H_3BO_3$
55·8	10·0	34·2	—	—	—	H_3BO_3
33·1	6·8	60·1	—	—	—	
0·0	1·9	98·1	—	—	—	
(*b*) At 25°.						
59·6	0·0	40·4	—	—	—	$C_4H_6O_6$
60·4	4·2	35·4	92·4	0·6	7·0	
61·6	7·8	30·6	90·7	2·0	7·3	
63·3	9·9	26·8	94·1	1·5	4·4	
63·7	10·7	25·6	92·8	1·8	5·3	
65·1	13·0	21·9*	—	—	—	$C_4H_6O_6+H_3BO_3$
49·1	10·5	40·4	14·2	75·7	10·1	H_3BO_3
39·4	9·6	51·0	7·3	84·2	8·5	
32·0	8·9	59·1	7·1	81·5	11·4	
31·3	8·8	59·9	5·7	85·0	9·3	
24·6	7·3	68·1	6·2	75·1	18·7	
14·9	6·2	78·9	6·6	57·0	36·4	
9·5	5·8	84·7	3·4	68·6	28·0	
2·8	5·3	91·9	—	—	—	
0·0	5·1	94·9	—	—	—	
(*c*) At 50°.						
66·1	0·0	33·9	—	—	—	$C_4H_6O_6$
66·2	5·8	28·0	92·0	1·5	6·5	
66·7	9·3	24·0	89·0	3·0	8·0	
66·9	12·4	20·7	90·0	4·1	5·9	
67·3	16·5	16·2*	—	—	—	$C_4H_6O_6+H_3BO_3$
65·0	15·8	19·2	47·0	37·5	15·5	H_3BO_3
60·1	14·8	25·2	10·5	85·0	4·5	
51·2	12·8	35·0	14·6	76·6	8·8	
37·8	10·7	49·5	9·0	80·1	10·9	
28·6	10·2	61·2	7·2	73·4	19·4	
25·1	10·0	64·9	4·6	79·8	15·6	
19·6	10·0	70·4	5·4	70·9	23·7	
15·2	9·8	75·0	3·1	75·3	21·6	
14·3	9·6	76·1	2·4	80·8	16·8	
4·4	9·5	86·1	1·1	80·9	18·0	
0·0	9·5	90·5	—	—	—	

* Invariant solution obtained from two different initial mixtures in each case.

Method of analysis. It was anticipated that the analysis of the samples would prove to be a matter of some difficulty, but this fear was not realised. Preliminary titrations of solutions of known composition, a hydrogen electrode being used, showed that there was a definite, though small, p_H interval between the end of the neutralisation curve of the tartaric acid and the beginning of that of the boric acid. The analysis of mixtures of these two acids therefore became a matter of suitable choice of indicators, and the following method was devised.

The mixed acids were titrated with caustic soda, bromothymol-blue being used as indicator, until the yellow colour changed to green. This gave the amount of tartaric acid in the solution. Neutral glycerol was then added and, owing to the formation of a boroglycerol complex, the p_H of the solution fell, and the indicator again became yellow. Phenolphthalein was now added and the solution titrated until the colour changed to lilac (compounded of the blue of the first indicator and the red of the second). The additional amount of alkali added gave the amount of boric acid present. The acids should not be more dilute than $0{\cdot}1N$, and the amount of glycerol added should be about one-third of the volume of the solution. The final lilac colour must, of course, persist after the addition of a further quantity of glycerol, and it is advisable although not essential, to have a comparison standard green solution for the first part of the titration, and to work throughout by the light of a " daylight " lamp.

Potentiometric Determinations.—The p_H measurements were made in the usual way. Hydrogen from cylinders was washed with

TABLE II.

Variation with dilution of the p_H of solutions containing tartaric acid.

(v = Dilution of tartaric acid in litres per mol.)

Molecular ratio of tartaric acid to boric acid.

1 : 1.		2 : 3.		1 : 0.	
v.	p_H.	v.	p_H.	v.	p_H.
1·00	0·47	2·00	0·76	1	1·32
1·25	0·58	2·50	0·87	2	1·48
1·50	0·69	3·00	0·94	4	1·69
2·0	0·83	4·0	1·07	10	1·88
2·5	0·94	5·0	1·18	20	2·14
3·0	1·05	6·0	1·28	200	2·62
4·0	1·15	8·0	1·42	2,000	3·15
6·0	1·37	12·0	1·60	20,000	3·8
8·5	1·50	17·0	1·73	200,000	4·6
10	1·58	20	1·81		
100	2·38	200	2·57		
1,000	3·04	2,000	3·27		
10,000	3·8	20,000	4·1		
100,000	4·6	200,000	4·9		

TABLE III.

Observed rotatory powers of solutions of boric and tartaric acids in water at 25° ($l = 200$ mm., $\lambda = 5461$ Å.)

(All ratios and percentages are by weight, and all rotatory powers are positive.)

$C_4H_6O_6 : H_3BO_3$.	H_2O,%.	α.
29·7 : 70·3	93·0	2·10°
	94·3	1·67
	95·7	1·19
50·3 : 48·7	89·8	5·55
	92·2	3·95
	94·3	2·64
70·7 : 29·3	80·2	18·18
	82·4	15·63
	84·4	13·46
	86·0	11·66
	87·7	9·85
	89·6	8·09
	91·3	6·51
	92·6	5·29
	94·6	3·51
83·1 : 16·9	69·1	33·00
	71·8	28·30
	75·1	24·12
	77·1	21·55
	78·9	18·58
	82·0	15·89
	84·2	12·63
	87·7	9·21
	88·5	7·57
	92·1	4·69
	95·8	2·32

$C_4H_6O_6 : H_3BO_3$.	H_2O,%.	α.
85·7 : 14·3	62·8	39·44°
	65·6	35·47
	68·6	31·60
	73·1	25·77
	75·6	22·74
	78·4	19·40
	80·8	16·85
	83·1	14·11
	85·9	11·32
	88·2	9·15
	90·9	6·71
	94·3	3·73
91·9 : 8·1	58·2	33·77
	63·4	28·86
	67·8	24·99
	74·4	19·34
	79·2	14·95
	83·3	11·62
	87·6	8·14
	90·1	6·23
	92·2	4·75
	95·4	2·50
100·0 : 0·0	40·7	10·63
	48·2	10·79
	54·9	10·48
	65·1	9·24
	74·0	7·46
	82·9	5·18
	90·2	3·15
	95·0	1·64

$C_4H_6O_6 : H_2O$.	H_3BO_3,%.	α.
45·1 : 54·9	1·96	25·10°
	3·85	38·38
	5·66	48·98
	7·41	56·88
	9·09	62·45
51·8 : 48·2	1·95	26·30
	3·48	40·70
	5·65	52·85
	7·39	62·87
	9·07	70·25

$C_4H_6O_6 : H_2O$.	H_3BO_3,%.	α.
59·3 : 40·7	1·98	24·38°
	3·84	38·11
	5·66	50·14
	7·41	60·55
	9·09	69·58
65·5 : 34·5	6·99	60·76
	8·07	67·82
	9·11	73·18
	10·13	78·21
	11·13	82·39
	12·11	86·77

alkaline pyrogallol, alkaline permanganate, and two lots of distilled water, and then passed over duplicate electrodes of the Jordan Lloyd type. Any divergence between the readings with the two electrodes led to their immediate rejection and the substitution of two others. The standard half-cell was of the saturated calomel type and was connected to the hydrogen half-cell through saturated potassium chloride solution by means of an agar bridge.

Since these solutions are not buffered, the figures are not trustworthy beyond $v = 1000$.

Polarimetric Determinations.—The rotatory powers of solutions of boric and tartaric acids were observed in a jacketed 200-mm. tube at 25° and are here quoted as read. The illuminant was a mercury arc, and the green line, $\lambda = 5461$ Å., was isolated with the aid of a spectroscopic eyepiece. In order to cover the area of unsaturated solutions on the equilibrium diagram as completely as possible, solutions were made up by taking a series of mixtures of two components and adding to each series successive quantities of the third component and determining the rotatory power after each addition.

Summary.

1. The hypothesis is advanced that the combination of boric acid and organic hydroxy-compounds occurs by the formation of a semipolar double bond between the boron atom and an oxygen atom in the organic molecule. In favourable circumstances this oxygen atom may be a centre of dissymmetry and so give rise to optical activity.

2. This hypothesis explains (i) the specific action of boric acid, (ii) the increase in rotatory power, (iii) the change in the character of the rotatory dispersion, (iv) the increase in the hydrogen-ion concentration, and (v) the change in the shape of the titration curve observed when boric acid is added to aqueous solutions of *d*-tartaric acid.

3. The equilibrium constant of the reaction between boric and tartaric acids in aqueous solution is shown to be approximately 0·129 (concentrations in mols. per litre) at room temperature and to increase as temperature falls. Borotartaric acid is shown to be comparable in strength with sulphuric acid.

4. The system boric acid–*d*-tartaric acid–water has been studied at 0°, 25°, and 50°; no solid phase of borotartaric acid has been isolated, but other evidence of combination has been found.

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