

out by direct comparison of experimental potentials.<sup>2</sup> However, in the series of interest here ligand potential data are uniformly unavailable. The required quinonediimine is too unstable to permit measurement. Dithia-*o*-quinones and thia-*o*-benzoquinoneimine are unknown. The required potentials could also be obtained from oxidation of the anions C<sub>6</sub>H<sub>4</sub>XY<sup>-2</sup> but none of these has been definitely characterized. Thus, a quantitative comparison between ligand and complex potentials appears thwarted.

If comparison of potentials is broadened to include nickel complexes of types **1**, **3**, and **14**, some qualitative conclusions can be reached. Like Ni[C<sub>6</sub>H<sub>4</sub>(NH)<sub>2</sub>]<sub>2</sub><sup>-2</sup>, Ni[(CH<sub>3</sub>CNC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub><sup>-2</sup> is more easily oxidized than Ni[C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>]<sub>2</sub><sup>-2</sup>,<sup>2</sup> both of which are much less oxidatively stable than [NiS<sub>4</sub>C<sub>4</sub>(CN)<sub>4</sub>]<sup>-2</sup>. This is just the order of oxidative stability of the ligands, *viz.*, (CH<sub>3</sub>CNC<sub>6</sub>H<sub>5</sub>)<sub>2</sub><sup>-2</sup> < C<sub>6</sub>H<sub>4</sub>O<sub>2</sub><sup>-2</sup> < (NC)<sub>2</sub>C<sub>2</sub>S<sub>2</sub><sup>-2</sup><sup>38</sup> as measured from half-wave potentials. (Biacetylbenzidine undergoes a two-electron reduction at -1.82 v in acetonitrile *vs.* sce.) This observation, in addition to those already reported,<sup>2</sup> further supports Vlček's ideas and leads to the following general conclusion. Free

(38) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962).

ligands which are most stable in the anionic form tend to stabilize the  $z = -2, -1$ , and (possibly) 0 members of their electron transfer series whereas free ligands most stable in the neutral (oxidized) form tend to stabilize the  $z = 0, +1$ , and  $+2$  members of their series. Thus, the complexes **2** are most stable as mono- and dianions; cationic complexes are relatively unstable due presumably to the instability of the 1,2-dithione structure. Similarly, anions in the [M-N<sub>4</sub>] series can be detected but are extremely oxidatively unstable relative to the  $z = 0, +1, +2$  members; the dianion of *o*-phenylenediamine is undoubtedly quite unstable in an oxidative sense with respect to the quinonediimine. Finally, the [M-N<sub>4</sub>] system obviously benefits at the extremes of its electron transfer series from the generally effective coordinating ability of both imino and amido nitrogen donor atoms, which no doubt enhances the kinetic stability of the terminal and intermediate members.

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## Optical Rotatory Dispersion Studies on the Borotartrate Complexes and Remarks on the Aqueous Chemistry of Boric Acid<sup>1,2</sup>

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**Abstract:** Through precise measurements of the optical rotatory dispersion of solutions of tartaric acid, and its mixtures with boric acid, at controlled pH, apparent Drude parameters for the borotartrate complex and concentrations of free tartrate in the mixtures have been derived. Computations of equilibrium constant indicate the dominant complex to be of 1:1 stoichiometry. The complex is considered to be a chelate of tetrahedrally coordinated B(III) which involves one tartrate hydroxyl and the nearer carboxyl group. The complex's strong acid character is derived through displacement of the hydroxyl proton by boron, as the latter changes its coordination to tetrahedral from the trigonal planar coordination of boric acid. A second stage of acid dissociation occurs above pH 4, and evidence is reported suggesting possible polyborotartrate complexes also.

That the optical rotation of tartaric acid is modified by addition of boric acid has been known since the early work of Biot in 1832.<sup>3</sup> The system has been studied frequently, and it has been generally agreed that some species of complex forms. The stoichiometry of the complex has been suggested variously to be two boric acids per tartrate,<sup>4</sup> one boric acid to one tartarate<sup>5,6</sup> and one boric acid to two tartrates.<sup>7-11</sup>

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

(3) Cf. T. M. Lowry, "Optical Rotatory Power," Longmans, Green and Co., London, 1935; reprinted by Dover Publishers, Inc., New York, N. Y., 1964.

(4) M. Amadori, *Gazz. Chim. Ital.*, **61**, 215 (1931).

(5) T. M. Lowry and P. C. Austin, *Phil. Trans. Roy. Soc. London*, **222A**, 249 (1922).

Evidence presented for the last formulation—an apparent maximum in the rotation at a solution composition corresponding to one mole each of tartrate, bitartrate, and boric acid, and formation (though with difficulties) of a solid phase approximating this formulation—seemed for some time to be most compelling. Analogy to a boric acid-salicylic acid complex of similar stoichiometry<sup>12,13</sup> gave additional support.

After a gap of some 20-odd years, from reinvestiga-

(6) S. G. Burgess and H. Hunter, *J. Chem. Soc.*, 2838 (1929).

(7) T. M. Lowry, *ibid.*, 2853 (1929).

(8) W. D. Bancroft and H. L. Davis, *J. Phys. Chem.*, **34**, 2479 (1930).

(9) B. Jones, *J. Chem. Soc.*, 951 (1933).

(10) I. Jones and F. G. Soper, *ibid.*, 1836 (1934).

(11) H. T. S. Britton and P. Jackson, *ibid.*, 1002 (1934).

(12) E. Johns (1878), cited in ref 13.

(13) A. Rosenheim and H. Vermehren, *Ber.*, **57**, 1337, 1828 (1924).

tions made both by cryoscopic and pH-measurement techniques,<sup>14,15</sup> the conclusions were drawn that a 1:1 boric acid-tartrate complex or complexes dominates, in agreement with the tentative deductions of Burgess and Hunter,<sup>6</sup> rather than with the 1:2 composition which Lowry<sup>7</sup> claimed. Inasmuch as a major portion of Lowry's evidence involved interpretation of his rotatory dispersion data, we investigated this system early in our program of testing the potentialities of precision spectropolarimetry coupled with computer fitting to the Drude equation.<sup>16-18</sup> The results of our studies, presented in this report, confirm the fundamental 1:1 stoichiometry.

### Experimental Section

**Materials.** Tartrate solutions were prepared from sodium *d*-tartrate dihydrate (Fisher Certified reagent), and from reagent grade *d*-tartaric acid which had twice been purified by Soxhlet extraction with ether.<sup>16</sup> Reagent grade boric acid was refluxed for 90 min with 8 *F* HCl (to remove Fe(III) and similar impurities) and left to stand overnight in contact with the acid. The crystals were collected, washed five times with ice-cold distilled water, and dried, first by suction in air and then in a desiccator over Drierite.

Tartrate solution of 0.2 *F* concentration, prepared by dissolving the amounts of sodium tartrate dihydrate and of tartaric acid required to give a solution 0.05 *F* with respect to sodium tartrate and 0.15 *F* with respect to tartaric acid, showed a pH of 2.81. Solution 0.2 *F* in tartrate at pH 4.23 was prepared by diluting 20 ml of 0.500 *F* stock solution (0.375 *F* in sodium tartrate and 0.125 *F* in tartaric acid) plus 1.70 ml of 1 *F* NaOH (prepared from "Acculute" NaOH) to 50.00 ml with water. Sodium tartrate, at 0.200 *F* concentration, showed pH 7.40.

Boric acid-tartaric acid mixtures, 0.200 *F* in tartrate, were prepared by dissolving the required amounts of boric acid in 0.500 *F* tartrate solutions of the composition (as above) appropriate to the desired pH, adding the required amount of NaOH, and making up to volume. All pH measurements were made with the Radiometer Model 4 pH meter, operated to a precision of  $\pm 0.01$  pH unit. Experimental solutions were adjusted to within  $\pm 0.02$  pH unit of target value.

**Polarimetry.** Measurements of optical rotation were made by direct readout on the Rudolph spectropolarimeter Model No. 260/659/810-609, having wavelength calibration in angstroms. The light source was an Osram 150-w xenon lamp.

The wavelength cam of the instrument was calibrated with the mercury lines of a Type S-100 Hanovia quartz mercury lamp, and against the measured rotations of a standard *d*-quartz plate of known thickness, at 50-A intervals, through the nominal wavelength range 6500-2700 Å. The quartz dispersion equation used is from a recalculation<sup>19</sup> of the data of Lowry, *et al.*<sup>20</sup>

Solution temperature was controlled by circulating water at  $25 \pm 0.1^\circ$  through the jacket of a 100-mm polarimeter tube with fused silica end plates. Before each series of measurements, the polarimeter system was allowed to stabilize until both air readings and *d*-quartz readings, at a given wavelength setting, became constant within instrumental precision; 90 min were usually required. Blank readings were made, with water, at 500 Å intervals, which previous experience had shown to be adequate. Generally both the first and final rotation measurements on a given solution were made with the wavelength set at 5461 Å. This served as a check on possible instrumental drift during the course of the measurements, and to guard against possible change in the solution itself (none was ever detected).

The rotation measurements were made generally at 50-Å intervals over the wavelength range 6560-2701 Å. Wavelengths were checked with the *d*-quartz plate at 500-Å intervals during a measurement series, because of a tendency toward drift over a period of time.

(14) M. Lourijsen, *Bull. Soc. Chim. France*, 898 (1956).

(15) V. Frei and A. Šolcová, *Collection Czech. Chem. Commun.*, **30**, 961 (1965).

(16) L. I. Katzin and E. Gulyas, *J. Phys. Chem.*, **66**, 494 (1962).

(17) L. I. Katzin and E. Gulyas, *J. Am. Chem. Soc.*, **86**, 1655 (1964).

(18) A. Singh and L. I. Katzin, *J. Phys. Chem.*, **69**, 3708 (1965).

(19) L. I. Katzin, *ibid.*, **68**, 2367 (1964).

(20) T. M. Lowry and W. R. C. Coode-Adams, *Phil. Trans. Roy. Soc. London*, **A226**, 391 (1927); T. M. Lowry and C. P. Snow, *Proc. Roy. Soc. (London)*, **A127**, 271 (1930).

With these precautions, wavelengths are considered reliable within  $\pm 3$  Å at the longer wavelengths, and to  $\pm 1$  Å at wavelengths below 3000 Å. The precision of the rotation measurements is  $\pm 0.002$ - $0.003^\circ$  at wavelengths above 3000 Å, and  $\pm 0.003$ - $0.008^\circ$  (depending on the steepness of the individual dispersion curve) at shorter wavelengths. For 0.2 *F* tartrate solutions,  $0.003^\circ$  measured rotation in a 100-mm tube corresponds to 0.1 unit in specific rotation.

**Computations.** Preliminary experiments suggested that the rotatory dispersion of the complex (or complexes) formed corresponded to that for a single Drude term. Detailed computations with precise data, based on a single-term Drude equation, revealed deviations which could be ascribed to significant error in this description only for alkaline solutions near pH 9 (see below). Optical rotatory dispersion data for boric acid-tartaric acid mixtures were converted to specific rotation, based on tartrate equivalent. These specific rotation values for (usually) 78 wavelengths, from 6560 to 2700 Å, were then fitted by least-squares criteria to the equation

$$\text{ORD}(\lambda) = (1 - f)(A/(\lambda^2 - B)) + f(\text{ORD}_{\text{tart}}) \quad (1)$$

The parameters optimized were *A* and *B*, the Drude parameters of the complex(es), and *f*, the fraction of free tartrate. The function, ( $\text{ORD}_{\text{tart}}$ ), the rotatory dispersion of free tartrate, was obtained by measuring tartrate alone, at the experimental concentration and pH, and fitting the specific rotations with the five-parameter equation<sup>21</sup>

$$(\text{ORD}_{\text{tart}}) = F/(\lambda^2 - G) + H/(\lambda^2 - J) + K$$

The root-mean-square deviations between experimental and computed specific rotations for the tartrate alone were  $\pm 0.07$ - $0.15$  unit. The data for the mixtures, fitted to eq 1, generally showed root-mean-square deviations of  $\pm 0.10$ - $0.18$  unit, rarely higher. The fraction of free tartrate, *f*, so obtained, was independent of any hypothesis as to the stoichiometric composition of the complex(es), and was probably good to  $\pm 0.01$ , based on reproducibility of results.

### Results

At a fixed pH, because of the concentration-independent equilibrium ratios, it is not necessary to specify which of the three possible species (tartaric acid, bitartrate, tartrate) reacts with the boric acid, in determining the stoichiometry of the complex with tartrate, and the apparent value of its association constant at a given pH. It is therefore permissible to use the formal concentration of the tartaric acid. If a complex is formed which contains the boric acid and tartaric acid moieties in the stoichiometry  $B_aT_b$ , in a solution whose formal composition is  $[T_0]$  in tartaric acid and  $n[T_0]$  in boric acid, and the free tartrate at equilibrium is given by  $f[T_0]$ , the expression for the formation constant *K* becomes

$$K = (1 - f)[T_0]/b(f[T_0])^b(n[T_0] - a(1 - f)[T_0]/b)^a = (1 - f)/bf^b(n - a(1 - f)/b)^a [T_0]^{(a+b-1)} \quad (2)$$

Values for *f* and *n* for a series of solutions, at three pH values, are shown in Table I. In all cases,  $[T_0]$  was 0.200 *F*. Considering only the data for pH 2.81 and 4.23, and assuming a single complex, it is seen that for *n* values of 1.0 and smaller, the quantity  $(1 - f)$  is greater than  $n/2$ . Therefore, of the values for  $a/b$  considered earlier,  $2/1$  is ruled out as it would give negative values for the free boric acid, and one need consider only values  $1/1$  and  $1/2$ . (A complex with more than one boric acid per tartrate might form at high boric acid solution ratios, however.) Of the two remaining stoichiometries, that for the 1:1 complex gave the most consistent values for *K*, and these are shown in Table I. (The values at pH 4.23 for  $n = 0.166$  and  $n = 6.0$  would be more than halved if, in

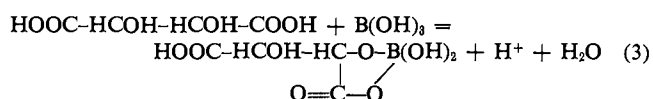
(21) The fifth parameter, *K*, has no theoretical significance, and represents a purely empirical device to obtain maximum match between data and equation.

**Table I.** Borotartrate Complex Formation Constants from Rotatory Dispersion

pH <sup>a</sup>	<i>n</i> <sup>b</sup>	<i>f</i> <sup>c</sup>	<i>A</i> <sup>d</sup>	$\lambda_a^{2d}$	$\Delta(\text{NaOH})_e$ <i>M</i>	<i>K</i> <sub>1:1</sub> <sup>f</sup>
2.81	0.200	0.867	44.41	0.04879	+0.015	11.5
	0.333	0.787	42.46	0.04841	0.024	11.3
	1.000	0.561	39.05	0.04802	0.050	6.98
	3.000	0.305	38.03	0.04768	0.093	4.95
	5.000	0.192	38.98	0.04783	0.128	5.02
4.23	0.1666	0.853	40.93	0.04726	-0.012	29
	0.500	0.681	43.74	0.04798	-0.024	13.0
	1.000	0.488	41.20	0.04781	-0.026	10.8
	2.00	0.275	39.73	0.04787	-0.017	10.3
	4.00	0.117	40.20	0.04833	+0.001	12.0
	6.00	0.018	40.08	0.04825	+0.022	54
7.4	0.200	0.925	32.01	0.04832	+0.001	3.25
	1.000	0.637	31.79	0.04800	0.003	4.47
	3.00	0.305	35.70	0.04849	0.035	4.94
	5.00	0.224	38.02	0.04874	0.11	4.10

<sup>a</sup> Formal concentration of tartaric acid  $[\text{T}_0]$ , 0.200 in all cases. Dispersion formulas for tartrate solutions in absence of boric acid: pH 2.81,  $[\alpha]_\lambda = [342.796/(\lambda^2 - 0.0422478)] - [334.626/(\lambda^2 - 0.0436697)] - 0.387$ ; pH 4.23,  $[\alpha]_\lambda = [423.002/(\lambda^2 - 0.0402962)] - [410.350/(\lambda^2 - 0.0412632)] - 0.059$ ; pH 7.4,  $[\alpha]_\lambda = [536.526/(\lambda^2 - 0.0385688)] - [522.485/(\lambda^2 - 0.0392803)] - 0.841$ . <sup>b</sup> Formal mole ratio of boric acid to  $[\text{T}_0]$ . <sup>c</sup> Fraction of tartaric acid not complexed. <sup>d</sup> Drude parameters for rotatory dispersion of complex,  $R_\lambda = A/(\lambda^2 - \lambda_a^2)$ . <sup>e</sup> Moles per liter of NaOH needed to restore nominal pH of tartaric acid solution after addition of boric acid. <sup>f</sup> Formation constant of 1:1 boric-tartaric complex, based on formal concentration of tartaric acid:  $K_{1:1} = (1 - f)[\text{T}_0]/f[\text{T}_0] (n - 1 + f)[\text{T}_0]$ .

either case, *f* were increased by only 0.02.) It may therefore be assumed, as the basis for further discussion, that in these pH ranges one is dealing primarily with a single complex of 1:1 stoichiometry. The essential constancy of the Drude parameters for the complex (Table I) is consistent with such an interpretation. Titration curves for mixtures of boric and tartaric acids<sup>6,7,10,11</sup> show that the first acid equivalent corresponds to a stronger acid than the first dissociation of tartaric acid, ("...boro-tartaric acid must be comparable in strength with sulfuric acid").<sup>6</sup> The second dissociation stage, however, now behaves like that of an appreciably weaker acid than bitartrate, which has an ionization constant of about  $0.5\text{--}1 \times 10^{-4}$ .<sup>10,22,23</sup> The complexing reaction may be written as



The second proton will then probably come from the remaining carboxyl, now functioning as a weaker acid than in bitartrate ion.

When the complex is formed in a pH region below the *pK* of the second dissociation—say, below pH 5—the net change in proton concentration per mole of complex formed is

$$\Delta(\text{H}^+) = \frac{[1 - K_1K_2/(\text{H}^+)^2]}{[1 + K_1/(\text{H}^+) + K_1K_2/(\text{H}^+)^2]} \quad (4)$$

Assuming values of the tartaric acid dissociation constants, *K*<sub>1</sub> and *K*<sub>2</sub>, of  $1.28 \times 10^{-3}$  and  $3.0 \times 10^{-5}$ , respectively,<sup>23</sup> the value of  $\Delta(\text{H}^+)$  at pH 2.81 is 0.534 mole, and at pH 4.23, -0.297 mole. The corresponding values from Table I, for boric acid concentrations

(22) L. I. Katzin and E. Gulyas, *J. Phys. Chem.*, **64**, 1739 (1960).

(23) V. Frei, *Collection Czech. Chem. Commun.*, **30**, 1402 (1965).

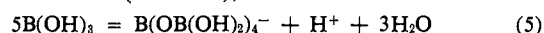
**Table II.** Equilibrium Constant for the Reaction  $5\text{B(OH)}_3 \rightarrow \text{H}^+ + \text{B(OB(OH)}_2)_4^- + 3\text{H}_2\text{O}$ 

Concn of $\text{H}_2\text{BO}_3$ , <i>M</i>	pH (23°)	<i>K</i> <sup>a</sup> $\times 10^7$
0.801	3.697	1.21
0.769	3.737	1.24
0.737	3.778	1.27
0.708	3.824	1.25
0.680	3.861	1.29
0.653	3.915	1.22
0.627	3.949	1.29
0.601	4.002	1.23
0.553	4.092	1.22
0.509	4.165	1.31
0.468	4.240	1.39
0.431	4.336	1.31
0.397	4.415	1.34

<sup>a</sup>  $K = [(\text{H}^+)^2 - K_1B]/B^5$  where *K*<sub>1</sub> is the acid dissociation constant of monomeric boric acid (taken as  $K_1 = 4 \times 10^{-10}$ ) and *B* = concentration of boric acid.

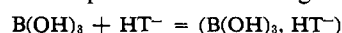
not greater than  $[\text{T}_0]$ , are 0.57 and -0.4 for  $\Delta(\text{NaOH})/(1 - f)[\text{T}_0]$ . The expected  $\Delta(\text{H}^+)$  values are sensitive to the *K*<sub>1,2</sub> values; thus, for constants of  $1.8 \times 10^{-3}$  and  $1.0 \times 10^{-4}$ <sup>22</sup> values of 0.416 and -0.616, respectively, should be obtained at the two pH's. It seems there may possibly be a small excess of acid produced over expectation at pH 2.81. An obvious explanation for this possibility would be attack of a second boric acid on the remaining hydroxyl of the complex, to give a  $\text{B}_2\text{T}^{2-}$  species, in addition to the (BHT)<sup>-</sup> type shown in eq 3.<sup>24</sup> This tendency would be expected to increase with increasing boric acid concentration, and one might even anticipate obtaining a measure for the equilibrium constant, by following the acid release at higher boric acid ratios.

Pursuit of this line of investigation is rendered impractical, however, by the fact that above 0.05–0.1 *M* boric acid forms polymers which are more strongly acidic than the monomer (*pK* 9.0–9.2). Thus, at 0.8 *M* (approximately saturation), boric acid has a pH of about 3.57, corresponding to some ten times the  $(\text{H}_3\text{O})^+$  concentration expected for the monomer. Between 0.8 and 0.4 *M*, the effect goes as the fifth power of the boric acid concentration (Table II), as for



Further, with the measured pH of 0.1 *M* boric acid being 5.2, it takes about 75 ml of 0.1 *N* NaOH per liter to bring 0.8 *M* boric acid to this pH, 14 ml for 0.5 *M* boric acid, and 0.5 ml for 0.2 *M* acid. It therefore becomes impractical to investigate precise acid release values above values of *n* = 1, for our  $[\text{T}_0]$  values of 0.2 *M*.

From the evidence that a monovalent, anionic, 1:1 complex predominates, the variation with pH of the formation constant, *K*<sub>1:1</sub>, computed (Table I) on the formal tartaric acid concentration, may be obtained by considering the complex to form through the reaction



The formation constant for this equilibrium, *K*<sub>HT</sub>, can be shown to be related to *K*<sub>1:1</sub> by

$$K_{\text{HT}} = K_{1:1}/q \quad (6)$$

(24) In this notation,  $\text{H}_2\text{T}$ ,  $\text{HT}^-$ , and  $\text{T}^{2-}$  represent tartaric acid and its ions; *B* represents a moiety, originally boric acid, which may have undergone dehydrative changes, as in eq 3.

where  $q$  is the fraction of free tartaric acid in bitartrate form, namely

$$q = [K_1/(H^+)]/[1 + K_1/(H^+) + K_1K_2/(H^+)^2] \quad (7)$$

$K_{1,2}$  are the tartaric acid ionization constants, as before. Therefore, for two pH values,  $a$  and  $b$ ,  $K_{1:1(a)}/K_{1:1(b)} = q_a/q_b$ . From Table I, in going from pH 2.81 to 4.23,  $K_{1:1}$  increases by a factor of about 2. From the dissociation constants quoted earlier,<sup>23</sup> the predicted factor is 1.44.

## Discussion

So long as only the 1:1 complex is formed, the apparent  $K_{1:1}$  values should follow those of  $q$  (eq 7). They therefore should go through a maximum at the pH giving the maximum value of  $q$  which is determined by

$$(H^+) = (K_1K_2)^{1/2}$$

From the various determinations for the dissociation constants, which individually may still be subject to some uncertainty,<sup>10,22,23</sup> the  $K_1K_2$  product is not likely to be less than  $5 \times 10^{-8}$ , which would correspond to pH 3.65. The concentration of bitartrate by about pH 6 is negligible, and the amount of complex of this composition (eq 3) should thus also be infinitesimal. In contrast, the rotations measured at 300 m $\mu$  for 5:1 boric acid-tartaric acid solutions at various pH's gave a maximum at about pH 4.0 corresponding approximately to Lowry's<sup>7</sup> composition. Most significantly, this maximum is quite flat and falls off *very slowly* on the high pH side, so that whereas at pH 4 [ $\alpha$ ] is 920°, at pH 6 [ $\alpha$ ] has dropped only to about 860° (for tartrate alone, at this wavelength and pH, [ $\alpha$ ] is 129°).

Hence it is certain that at least from pH 4 up an important new complex species is present. The data for pH 7.4 (Table I) show that although at the lower boric acid concentrations the rotation is still well described by a single Drude term, the  $A$  parameter in particular shows a marked change from that which characterizes the complex at low pH's. The obvious conclusion is that under these conditions the complex is the dissociation product, (BT)<sup>2-</sup>, of the weak acid complex (BHT)<sup>-</sup>. At the higher boric acid concentrations, the  $A$  parameter is more like that of the ostensible (BHT)<sup>-</sup> complex, but the high value of the association constant is clearly incompatible. Under these conditions, of high boric acid concentration and relatively high pH, one would anticipate the formation of considerable amounts of polyborate, and possibly, polyboro-tartrate complex(es). These, clearly, do not have rotatory parameters which allow them to be distinguished from the (BHT)<sup>-</sup> of low boric acid, low pH solutions.

At pH 9.1 the rotations for boric-tartaric mixtures are still significantly greater than for tartrate alone, though [ $\alpha$ ] is less than 200° at 300 m $\mu$ . Interestingly, even though these differences from tartrate alone are relatively small, computation indicates that they cannot be satisfactorily matched by the assumption of a single Drude term. This is the only point at which such a finding has been made in our data, and indicates that in this range a new borotartrate complex species is to be considered.

In summary, in the acid region, to about pH 4, the dominant borotartrate complex is a 1:1 species whose composition and probable structure are as indicated in eq 3. Its rotational properties are summarized in the Drude parameters of Table I for the low boric acid, low pH solutions. This complex stoichiometry is in agreement with the deductions of Lourijsen,<sup>14</sup> from cryoscopic investigations, and with the suggestion of Burgess and Hunter.<sup>6</sup> In the more alkaline range, pH 4-8, one finds evidence for probably two more complexes. The one at low boric acid concentrations is almost certainly the acid dissociation product, (BT)<sup>2-</sup>, of the 1:1 complex, (BHT)<sup>-</sup>. The one(s) at high boric acid concentration is probably a polyborate species, perhaps represented also by an acid form at lower pH. Its possible structure is discussed below. Lourijsen too has deduced the existence of (BT)<sup>2-</sup>. She has not investigated the very high boric acid concentration region however. It is also questionable how correct her conclusions as to further ionization states may be, given the tetraborate formation and other polymerizations which become significant in alkaline solution. Our results at pH 9.1 do agree in suggesting that a complex of characteristics different from the 1:1 complexes does exist under these conditions, contrary to Britton and Jackson.<sup>11</sup>

Evidence for a monobasic pentameric boric acid in solution has been adduced by at least one investigator in the early literature,<sup>25</sup> and it is known in some crystalline salts.<sup>26,27</sup> The crystal structures indicate dehydration between neighboring triangular B(OH)<sub>3</sub> units, as well as between these units and the central tetrahedral B(OH)<sub>4</sub><sup>-</sup> structure. Only a trimer has been reported from a relatively recent titration study,<sup>28</sup> but the concentration range used in that study (below 0.6 M) only partly overlaps ours, the technique involved was different, and the solution was 3 M in strong electrolyte. Solid compounds exist in which the corresponding trimeric anion has been identified.<sup>29</sup> Fundamental to all the polyborate units identified is the relation that the anionic charge is equal to the number of tetrahedrally coordinated boron atoms in the unit.<sup>29-31</sup>

In the acid region, at high boric acid concentration, it might be expected that the tetrahedral boron of the 1:1 complex, if it forms polyborates, should give groupings similar to the triborate anion. There is no good evidence from our data of ready formation of a (B<sub>2</sub>T)<sup>2-</sup> type of complex. In the more alkaline solutions, the number of possible polyborate complex species increases. Additional borons may be converted to tetrahedral coordination, and these may facilitate addition of more triangular borons, to increase the number of units in the polymer. Something equivalent to the well-known tetraborate group is a good possibility. In such a group, the presence of two tetrahedral borons suggests the possibility of two sets of chelation bondings. Unless the geometry is accidentally favorable, the most likely bondings would be to two different tartrate residues.

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