Temperature-Jump Study of the Rate and Mechanism of the Boric Acid–Tartaric Acid Complexation[1]

Kenneth Kustin and Richard Pizer

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. *Received July 16, 1968*

Abstract: Temperature-jump studies of the reactions of tartaric acid and bitartrate and tartrate anions with boric acid at three different hydrogen ion concentrations allowed the determination of the rate constants for the reactions of tartaric acid and tartrate anion. The complexation rate constant for tartaric acid is 475 M^{-1} sec^{-1}, which is considerably larger than the rate constant for tartrate anion (215 M^{-1} sec^{-1}). Only a composite rate constant could be determined for the ambident bitartrate anion (430 M^{-1} sec^{-1}), which cannot be experimentally separated into rate constants for the individual reactions. No catalytic effect of acid on the rates of the individual reactions was noted within the limits of the experiments. A concerted mechanism is proposed for the complex formation. The sequence includes attack of a nucleophilic alcoholic oxygen on the electron-deficient boron with concurrent release of water (in the tartaric acid reaction) or hydroxyl (in the bitartrate reaction). The leaving of water is assisted in the former case by the acidic carboxyl proton.

The reactions between boric acid and borates with α-hydroxycarboxylic acids and polyols, respectively, have been known for many years. The stability constants of polyol reactions with borate have been extensively reported in the literature.[2–4] In all cases the data could only be interpreted on the basis of a reaction between borate ion, $B(OH)_4^-$, and the polyol in question, a conclusion supported by nmr work on the boric acid–mannitol system.[5] Both 1:1 and 1:2 borate–polyol complexes have been reported. The fact that boric acid itself, $B(OH)_3$, complexes with tartaric acid has been known since 1940.[6] However, conflicting reports on the stoichiometry of the borotartrate complex have proliferated in the literature up to the present. Under varying conditions and concentration ranges complexes have been reported of 2:1,[7] 1:1,[8,9] and 1:2[9] boric acid:tartaric acid ratios. Most recently, however, an optical rotatory dispersion study on the nature of the complex led to the determination of an over-all stability constant for the formation of a 1:1 complex by means of a computer fitting to the Drude equation.[10] It is probable that both 1:2 and 2:1 complexes do exist in aqueous solution at higher concentration and more extreme ratios of reactants as demonstrated by other work employing different techniques.

That the complexation reactions of boric acid and borate are generally fast has been known for some time. In their study of the stability constants of borate complexes with polyols, Edwards, *et al.*, note that the equilibration of the borate–polyol solutions was complete within the time of mixing.[2] Work by Eyring, *et al.*, on rate studies of polyborate formation in aqueous boric acid by temperature jump has shown these also to be quite facile.[11]

The present investigation was undertaken to determine by temperature-jump methods the rate of the reaction of boric acid with tartaric acid. Particularly, the relative rates of reaction with tartaric acid, bitartrate ion, and tartrate ion are of interest in elucidating probable mechanisms for these reactions. The study was conducted at three different hydrogen ion concentrations in order to study the reaction with each of the forms of the acid and to determine if hydrogen ion catalysis was present.

Experimental Section

The solutions of borotartrate complexes were made from *d*-tartaric acid (Baker Analytical Reagent) and boric acid (Fisher Certified Reagent). Both reagents were used without further purification. All solutions were made up to an ionic strength of 0.15 M by addition of the requisite amount of KNO_3. The indicators used were bromophenol blue (Fisher Scientific Co.) and chlorophenol red (Eastman Organic Chemicals) depending upon the pH. The pH of all solutions was adjusted by dropwise addition of NaOH or HNO_3 and was accurate to ±0.02 pH unit. The temperature was 25 ± 1°.

The temperature-jump instrument itself has been described elsewhere.[12] In order to ascertain whether there were relaxation times in the region of interest which would interfere with the analysis of the relaxation spectra, blank solutions of boric acid with indicator and tartaric acid with indicator were prepared. In the latter case no discernible effect was observed in any time range. In the former case a short effect of very small amplitude appeared reproducibly in the solutions of highest boric acid concentration (0.05 M) at pH 6.00. Because of its small amplitude and short time it did not interfere with the determination of the relaxation times of the experimental solutions whose amplitudes were some ten times greater. This effect did not appear at smaller concentration or at lower pH. Following the work of Eyring, *et al.*,[11] on polyborate formation in aqueous boric acid, this effect is probably due to the formation of the polyborate species $B_3O_3(OH)_4^-$, which is present to a very small extent at pH 6.00.

The relaxation times reported are taken as the average of at least three experimental determinations. The relative error in the measurement of the relaxation spectra is ±10%.

The relaxation curves were measured by semilogarithmic graphical evaluation to ensure greater accuracy and to check on the ex-

---

[1] The authors gratefully acknowledge support from Public Health Service Research Grant GM-08893-07 from the National Institute of General Medical Sciences and an NDEA Title IV graduate fellowship for R. P.

[2] G. L. Roy, A. L. Laferriere, and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **4**, 106 (1957), and earlier literature therein.

[3] P. J. Antikainen, *Suomen Kemistilehti*, **31B**, 255 (1958).

[4] V. Nazarenko and L. Ermak, *Russ. J. Inorg. Chem.*, **3**, 335 (1967).

[5] T. P. Onak, H. L. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

[6] Y. Tzusuki, *Bull. Chem. Soc. Jap.*, **16**, 23 (1941).

[7] M. Amadori, *Gazz. Chim. Ital.*, **61**, 215 (1931).

[8] M. Lourijsen, *Bull. Soc. Chim. Fr.*, 898 (1956).

[9] E. Svartcs and A. Ievins, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, (1) 19, (1961); *Chem. Abstr.*, **57**, 6674*f* (1962).

[10] L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, **88**, 5209 (1966).

[11] J. L. Anderson, E. M. Eyring, and M. P. Whittaker, *J. Phys. Chem.*, **68**, 1128 (1964).

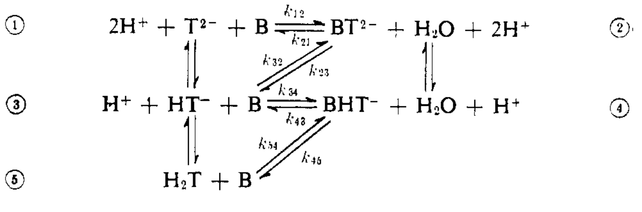
[12] P. Hurwitz and K. Kustin, *Inorg. Chem.*, **3**, 823 (1964).

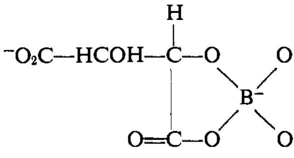
ponential shape of the curves. In all cases the curves were simple exponential.

Equilibrium Quotients

The entire reaction scheme for the borotartrate complexation can be written as shown in Scheme I, where boron is tetrahedrally coordinated in the products. For simplicity, the symbolism ^-O_2C–HCOH–HCOH–CO_2^- = T^{2-}, HOOC–HCOH–HCOH–CO_2^- = HT^-, HOOC–HCOH–HCOH–COOH = H_2T, $B(OH)_3$ = B

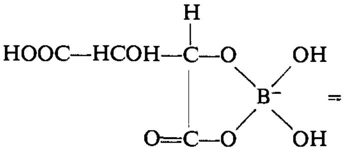
Scheme I





= BT^{2-}

and



= BHT^-

has been, and will be, employed.

Katzin and Gulyas were able to determine an over-all stability constant for the formation of a formal 1:1 complex, by utilizing ORD.[10] The constant is defined as $K_{1:1} = (1 - f)[T]_0/f[T]_0(n - 1 + f)[T]_0$, where $[T]_0$ is the formal concentration of tartaric acid (0.200 *M* in all cases), f is the fraction of tartaric acid not complexed, and n is the formal mole ratio of boric acid to tartaric acid; *i.e.*, $n = [B]_0/[T]_0$, where $[B]_0$ is the formal concentration of boric acid. The over-all stability constant determined can be written in terms of the equilibrium concentrations of the various species as $K_{1:1} = ([\overline{BHT^-}] + [\overline{BT^{2-}}])/[\overline{B}]([\overline{H_2T}] + [\overline{HT^-}] + [\overline{T^{2-}}])$. The constants which must be determined are $K_{12} = [\overline{BT^{2-}}]/[\overline{B}][\overline{T^{2-}}]$; $K_{34} = [\overline{BHT^-}]/[\overline{B}][\overline{HT^-}]$; $K_{32} = [\overline{BT^{2-}}][\overline{H^+}]/[\overline{B}][\overline{HT^-}]$; $K_{54} = [\overline{BHT^-}][\overline{H^+}]/[\overline{B}][\overline{H_2T}]$; and $K_{42} = [\overline{BT^{2-}}][\overline{H^+}]/[\overline{BHT^-}]$, the acid dissociation constant of BHT^-. The values of the acid dissociation constants of tartaric acid to be used are $K_{13} = 3.0 \times 10^{-5}$ and $K_{53} = 1.28 \times 10^{-3}$ [13] (see also Table I).

The rotatory dispersion data were reported at three different hydrogen ion concentrations. At pH 7.40 the only reaction of importance is $B + T^{2-} \rightleftarrows BT^{2-} + H_2O$. The $K_{1:1}$ experimentally determined at this pH corresponds to $K_{1:1} = [\overline{BT^{2-}}]/[\overline{B}][\overline{T^{2-}}]$, where allowance must be made for the fact that not all B exists as $B(OH)_3$, but there are polymeric forms in solution. The following boric acid equilibria as determined by titration studies of boric acid are present.[14]

$$B(OH)_3 + OH^- \rightleftarrows B(OH)_4^- \qquad pK = -5.0$$

$$2B(OH)_3 + B(OH)_4^- \rightleftarrows B_3O_3(OH)_4^- + 3H_2O \qquad pK = -1.71 \pm 0.02$$

$$4B(OH)_3 + B(OH)_4^- \rightleftarrows B_5O_6(OH)_4^- + 6H_2O \qquad pK = -2.23 \pm 0.10$$

Consider, for example, the following data at pH 7.40: $[T]_0 = 0.2\,M, n = 1, f = 0.637, K_{1:1} = 4.47$. At this pH the only complexation step to consider is ① ⇄ ②, as mentioned above. By using the equilibrium constants for polyborate formation, it is found that approximately 8% of the formal boric acid exists either as $B(OH)_4^-$ or in polymeric form. Therefore at this concentration at pH 7.40 $K_{12} = K_{1:1}/0.92 = 1.09K_{1:1} = 4.87$. In view of the uncertainties in the description of polyborate formation, K_{12} is then taken to be approximately 5.

At pH 4.23, the average value of $K_{1:1}$ is 11.5. At this pH virtually all tartrate present is T^{2-} and HT^-; therefore the $K_{1:1}$ experimentally determined can be expressed as $K_{1:1} = ([\overline{BT^{2-}}] + [\overline{BHT^-}])/[\overline{B}]([\overline{HT^-}] + [\overline{T^{2-}}])$. Now $K_{12} = [\overline{BT^{2-}}]/[\overline{B}][\overline{T^{2-}}]$ and $K_{34} = [\overline{BHT^-}]/[\overline{B}][\overline{HT^-}]$. Therefore, $K_{12}[\overline{T^{2-}}] + K_{34}[\overline{HT^-}] = ([\overline{BT^{2-}}] + [\overline{BHT}])/[\overline{B}]$. Dividing through by $[\overline{HT^-}] + [T^{2-}]$, we obtain the following expression for $K_{1:1}$

$$K_{1:1} = K_{12}\Big/\left(1 + \frac{[\overline{HT^-}]}{[\overline{T^{2-}}]}\right) + K_{34}\Big/\left(1 + \frac{[\overline{T^{2-}}]}{[\overline{HT^-}]}\right)$$

Using the experimentally determined $K_{1:1}$, the previously determined K_{12}, and the acid dissociation constants for tartaric acid, K_{34} can be evaluated. It is found that $K_{34} = 15$.

The equilibrium constants K_{24} and K_{32} can be derived from the present ones. Inspection shows that $K_{32} = K_{12}K_{13} = 1.5 \times 10^{-4}$. Similarly, $K_{24} = K_{32}/K_{34} = 1.0 \times 10^{-5}$.

These constants can then be used with the data at pH 2.81 to determine K_{54}. In this case no T^{2-} is present. Therefore, proceeding as in the above case

$$K_{1:1}[\overline{H^+}] = K_{32}\Big/\left(1 + \frac{[\overline{H_2T}]}{[\overline{HT^-}]}\right) + K_{54}\Big/\left(1 + \frac{[\overline{HT^-}]}{[\overline{H_2T}]}\right)$$

Taking $K_{1:1} = 6$ and solving the above equation, $K_{54} = 0.0185$.

These stability constants are probably no better in accuracy than ±15%. They are collected in Table I, along with the more precisely determined tartaric acid dissociation constants.

Table I. Equilibrium Quotients for the Boric Acid–Tartaric Acid System and Dissociation Constants for Tartaric Acid[a]

$K_{12} = [\overline{BT^{2-}}]/[\overline{B}][\overline{T^{2-}}] = 5$

$K_{34} = [\overline{BHT^-}]/[\overline{B}][\overline{HT^-}] = 15$

$K_{32} = [\overline{BT^{2-}}][\overline{H^+}]/[\overline{B}][\overline{HT^-}] = 1.5 \times 10^{-4}$

$K_{54} = [\overline{BHT^-}]\,[\overline{H^+}]/[\overline{B}]\,[\overline{H_2T}] = 0.0185$

$K_{24} = [\overline{BT^{2-}}]\,[\overline{H^+}]/[\overline{BHT^-}] = 1.0 \times 10^{-5}$

$K_{13} = [\overline{T^{2-}}]\,[\overline{H^+}]/[\overline{HT^-}] = 3.0 \times 10^{-5}$

$K_{35} = [\overline{HT^-}][\overline{H^+}]/[\overline{H_2T}] = 1.28 \times 10^{-3}$

[a] The borotartrate equilibrium quotients are derived from over-all stability constants and are applicable under experimental conditions. The more accurately determined tartaric acid dissociation constants are included for completeness.

It is of interest to note that titration curves for mixtures of boric and tartaric acids show that BHT^- functions as a weaker acid than bitartrate. This conclusion

---

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

(14) N. Ingri, *Acta Chem. Scand.*, **16**, 439 (1962).

Table II. Equilibrium Concentrations of Species in Solution

Soln	pH	$[\mathrm{B}]_0$[d]	$[\mathrm{T}]_0$[d]	$[\overline{\mathrm{B}}]$	$[\overline{\mathrm{T}^{2-}}]$	$[\overline{\mathrm{HT}^-}]$	$[\overline{\mathrm{H_2T}}]$	$[\overline{\mathrm{BHT}^-}]$	$[\overline{\mathrm{BT}^{2-}}]$
1	6.00[a]	0.0495	0.0532	0.0403	0.0425	0.0015	0.0000	0.0008	0.0084
2	6.00[a]	0.0297	0.0213	0.0271	0.0181	0.0006	0.0000	0.0002	0.0024
3	6.00[a]	0.0198	0.0213	0.0180	0.0189	0.0006	0.0000	0.0002	0.0016
4	6.00[a]	0.0198	0.0106	0.0189	0.0094	0.0003	0.0000	0.0001	0.0008
5	4.23[b]	0.0498	0.0535	0.0352	0.0128	0.0249	0.0012	0.0125	0.0021
6	4.23[b]	0.0498	0.0214	0.0424	0.0046	0.0090	0.0004	0.0063	0.0011
7	4.23[b]	0.0299	0.0214	0.0255	0.0056	0.0109	0.0005	0.0038	0.0006
8	4.23[b]	0.0199	0.0214	0.0166	0.0060	0.0116	0.0005	0.0028	0.0005
9	3.30[c]	0.0495	0.0510	0.0356	0.0015	0.0256	0.0100	0.0136	0.0003
10	3.30[c]	0.0495	0.0204	0.0431	0.0006	0.0097	0.0038	0.0065	0.0001
11	3.30[c]	0.0197	0.0204	0.0167	0.0007	0.0120	0.0047	0.0029	0.0001

[a] Indicator, chlorophenol red; $K_{\mathrm{HIn}} = 1.25 \times 10^{-6}$; $[\mathrm{HIn}]_0 = 10^{-5}\ M$, $\lambda = 580$ nm, $\gamma = 3.49$ (see Appendix for definition of γ). [b] Indicator, bromophenol blue; $K_{\mathrm{HIn}} = 8 \times 10^{-5}$; $[\mathrm{HIn}]_0 = 10^{-5}\ M$, $\lambda = 580$ nm, $\gamma = 1.04$. [c] Indicator, bromophenol blue, $\lambda = 580$ nm, $\gamma = 1.11$. [d] Subscript denotes initial formal concentration.

is in fact borne out by the lower acid dissociation constant for BHT^- as determined here.

Results and Treatment of Data

The complete reaction (Scheme I) possesses four relaxation times (assuming $\mathrm{B(OH)_4}^-$, polyborates, and indicators to be absent). Of these, only one is characteristic of boric acid complexation. This relaxation time can be calculated quite straightforwardly under the assumption that steps ① ⇄ ③, ③ ⇄ ⑤, ② ⇄ ④, and any indicator equilibria are very fast protolytic reactions.

The rate equation for the disappearance of boric acid is

$$-\frac{\mathrm{d[B]}}{\mathrm{d}t} = k_{12}[\mathrm{B}][\mathrm{T}^{2-}] - k_{21}[\mathrm{BT}^{2-}] + k_{32}[\mathrm{B}][\mathrm{HT}^-] - k_{23}[\mathrm{H}^+][\mathrm{BT}^{2-}] + k_{34}[\mathrm{B}][\mathrm{HT}^-] - k_{43}[\mathrm{BHT}^-] + k_{54}[\mathrm{B}][\mathrm{H_2T}] - k_{45}[\mathrm{H}^+][\mathrm{BHT}^-] \quad (1)$$

To obtain the relaxation time for Scheme I, we insert the definitions (where the "bar" denotes the time-independent equilibrium concentration) and conditions

$$[\mathrm{B}] = [\overline{\mathrm{B}}] + \delta[\mathrm{B}]$$
$$\delta[\mathrm{B}] << [\mathrm{B}], [\overline{\mathrm{B}}] \quad (2)$$

etc. for all other species into eq 1. The result, upon expansion and after neglecting any quadratic terms, is the well-known first-order relaxation expression $\mathrm{d}\delta[\mathrm{B}]/\mathrm{d}t = -\delta[\mathrm{B}]/\tau$, in which

$$\frac{1}{\tau} = k_{12}\left\{\frac{1}{K_{12}\left(1 + \frac{\delta[\mathrm{BHT}^-]}{\delta[\mathrm{BT}^{2-}]}\right)} + [\overline{\mathrm{T}^{2-}}] + \frac{\frac{[\overline{\mathrm{B}}]}{\delta[\mathrm{B}]}}{\delta[\mathrm{T}^{2-}]}\right\} + \vec{k}\left\{\frac{1}{K_{34}\left(1 + \frac{\delta[\mathrm{BT}^{2-}]}{\delta[\mathrm{BHT}^-]}\right)} + [\overline{\mathrm{HT}^-}] + \frac{\frac{[\overline{\mathrm{B}}]}{\delta[\mathrm{B}]}}{\delta[\mathrm{HT}^-]}\right\} + k_{54}\left\{\frac{1}{K_{54}}\left[\frac{[\overline{\mathrm{H}^+}]}{\left(1 + \frac{\delta[\mathrm{BT}^{2-}]}{\delta[\mathrm{BHT}^-]}\right)} + \frac{\frac{[\overline{\mathrm{BHT}^-}]}{-\delta[\mathrm{B}]}}{\delta[\mathrm{H}^+]}\right] + [\overline{\mathrm{H_2T}}] + \frac{\frac{[\overline{\mathrm{B}}]}{\delta[\mathrm{B}]}}{\delta[\mathrm{H_2T}]}\right\} \quad (3)$$

In (3) the over-all forward rate constant for bitartrate reactions is $\vec{k} = k_{32} + k_{34}$. The reverse constant is $\overleftarrow{k} = k_{23}K_{42} + k_{43}$. Since $K_{23} = k_{32}/k_{23}$ and $K_{34} = k_{34}/k_{43}$, this rate constant can be rewritten as

$$(k_{32}K_{42}/K_{23}) + (k_{34}/K_{34}) = (k_{32} + k_{34})/K_{34} = \vec{k}/K_{34} = \overleftarrow{k}$$

The derivation of eq 3 is shown in the Appendix, in which terms such as $\delta[\mathrm{BHT}^-]/\delta[\mathrm{BT}^{2-}]$ are defined. These terms are calculated using the equilibrium concentrations presented in Table II.

These data and the experimental relaxation times are then substituted into eq 3 to solve for k_{12}, $\vec{k}$, and k_{54}. At pH 6.00 a two-parameter equation in k_{12} and $\vec{k}$ is solved, the best fit being obtained with $k_{12} = 215\ M^{-1}\ \mathrm{sec}^{-1}$ and $\vec{k} = 430\ M^{-1}\ \mathrm{sec}^{-1}$. Using the value obtained for k_{12} above and the data for pH 4.23, this value of $\vec{k}$ is corroborated. These two values are used with the data at pH 3.30 to solve for k_{54}, which is found to have the value 475 M^{-1} sec^{-1}. The relative error in the calculated rate constants is ±20%. The experimental relaxation times and results of these calculations are presented in Table III.

Table III. Relaxation Spectra of Borotartrate Complexes[a]

Soln	$1/\tau$, sec^{-1}	k_{12}	$\vec{k}$	k_{54}
1	60.0	211	422	...
2	55.5	228	456	...
3	52.7	225	450	...
4	44.7	198	396	...
5	55.5	215	411	...
6	51.5	215	433	...
7	45.7	215	424	...
8	45.0	215	454	...
9	75.2	215	430	452
10	71.5	215	430	497
11	57.8	215	430	475

[a] All rate constants are expressed in units of M^{-1} sec^{-1}.

Many more experiments were done than are reported in Tables II and III in order to cover the widest possible concentration range. Only those solutions producing the largest effects (hence, greatest certainty in evaluation) are given. At lower total concentrations or higher ratios of tartaric acid to boric acid the effects obtained were of much smaller amplitude.

Experiments were also attempted at higher hydrogen ion concentrations to observe simply the reaction $\mathrm{B} + \mathrm{H_2T} \rightleftarrows \mathrm{BHT}^- + \mathrm{H}^+ + \mathrm{H_2O}$ in the absence of all others.

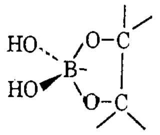
However, in no case were reproducible, measurable effects obtained with indicators.

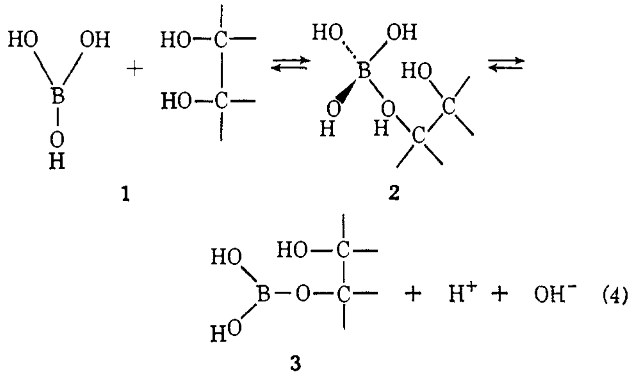
In addition, an attempt was made to measure the activation energy of the reaction $B + T^{2-} \rightleftarrows BT^{2-} + H_2O$ by evaluating the rate constant at different temperatures. Since the stability constants are not known at temperatures other than 25°, the solutions were made with a large excess of boric acid and the tartaric acid concentration was varied. A plot of $1/\tau$ *vs.* the boric acid concentration could then be used to evaluate k_{12} (from the slope). Experiments were run at both 35 and 45°. In both cases relaxation effects were observed. However, at the higher temperatures the boric acid blank itself produced a large measurable effect in the same time range, which made evaluation of the relaxation times of the borotartrate solutions highly uncertain.

Discussion

The conversion of trigonal boric acid[15] to tetrahedrally coordinated borate ion[16] is rapid, as has been shown by nmr[17] and temperature jump.[11] In alcoholic media boric acid reacts with alcohols and diols to produce trigonally coordinated orthoborates and biborates, respectively; however, the equilibrium point of these reactions lies far to the left as the products are readily hydrolyzed. These reactions exhibit no appreciable acid catalysis, acid perhaps being harmful in initiating dehydration of the alcohol.[18] That the esterification and hydrolysis proceed by the breaking of B–O bonds rather than C–O bonds has also been demonstrated.[19]

Reasonable mechanisms for boric acid reactions with oxygen-containing compounds involve as a first step the attack of the nucleophilic oxygen on the electron-deficient boron atom. This being the case, reaction of diols with boric acid is probably not observed because the reaction would produce a readily hydrolyzable orthoborate as a first step as in reaction 4. This mechanism implies that release of a hydroxyl with concerted or subsequent proton release, as shown, occurs instead of release of water by condensation from the adjacent hydroxyls on the diol and boric acid moieties to produce a four-coordinate complex

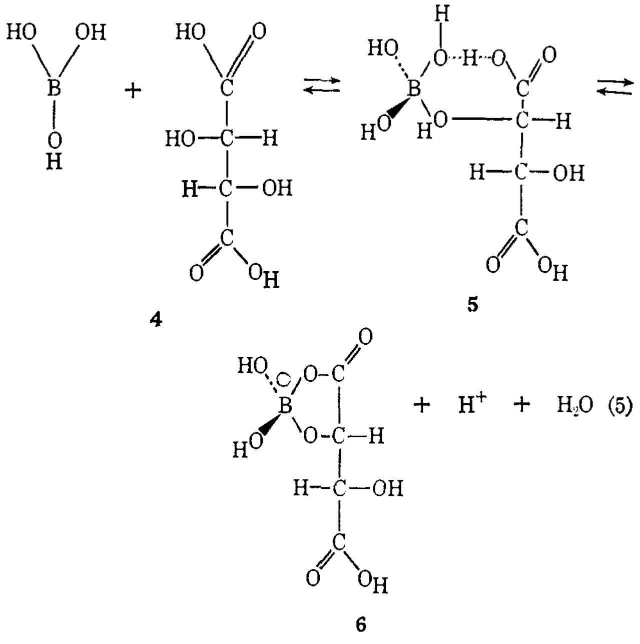




The formation of such a complex in aqueous solution is generally brought about by reaction of diol with borate.[2–5]

The chemistry of aqueous boric acid relevant to the problem at hand has been cited above to help in deducing the mechanism of the reaction of boric acid and tartaric acid. That is, results of the temperature-jump experiments show that the reaction of boric acid with fully protonated tartaric acid is the fastest of these complexation reactions, $k_{54} = 475\ M^{-1}\ \text{sec}^{-1}$. The reaction with tartrate ion is slower, $k_{12} = 215\ M^{-1}\ \text{sec}^{-1}$. The reactions of bitartrate to produce BT^{2-} and BHT^- cannot be measured separately. The only constant which can be determined for the latter reaction by temperature jump is the over-all constant $\vec{k} = k_{32} + k_{34}$, which is, however, intermediate in value with respect to k_{12} and k_{54}.

Because of the ready hydrolysis of the orthoborate structure, a concerted mechanism is proposed for the reaction of tartaric acid with boric acid. The reaction involves attack of a nucleophilic oxygen on the electron-deficient boron with simultaneous release of water, assisted by intramolecular hydrogen bonding (eq 5).



In the reaction of the tartrate ion with boric acid, the reaction would occur in the same way, but the leaving group in this case would be hydroxyl, not water (eq 6). The fact that states **5** and **8** react to form a four-coordinate stable complex and **2** does not, reflects in the former case, the much greater acidity of the tartaric acid proton as opposed to the alcoholic proton of the diol, and, in the latter case, the much greater nucleophilicity of the carboxylate oxygen relative to that of the diol. The rate of the tartaric acid reaction as opposed to the tartrate ion is partially understood in terms of the leaving groups, intramolecular hydrogen bonding assisting

---

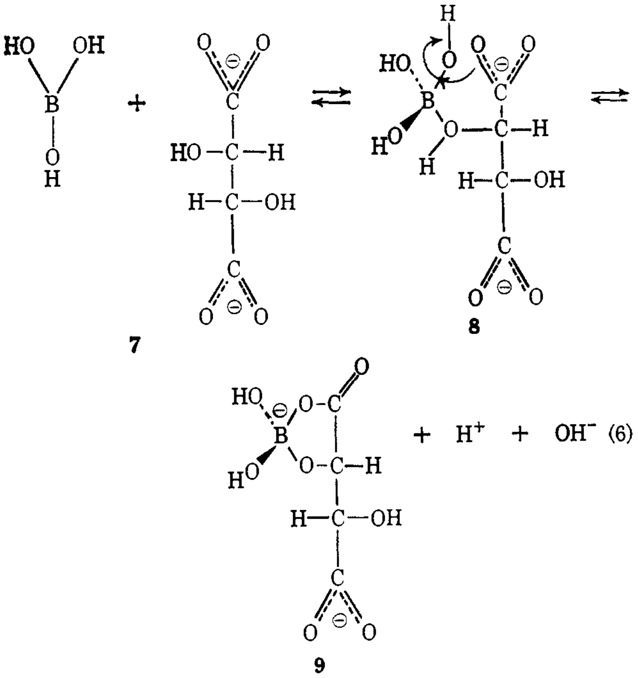
(15) J. H. Hibben, *Amer. J. Sci.*, **35A**, 113 (1938).

(16) J. O. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz, *J. Amer. Chem. Soc.*, **77**, 266 (1955).

(17) R. K. Momii and N. H. Nachtrieb, *Inorg. Chem.*, **6**, 1189 (1967).

(18) (a) H. I. Schlesinger, H. C. Brown, D. L. Mayfield, and J. R. Gilbreath, *J. Amer. Chem. Soc.*, **75**, 213 (1953). (b) A review of these reactions and boron–oxygen chemistry in general is to be found in H. Steinberg, "Organoboron Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964.

(19) H. K. Garner and H. J. Lucas, *J. Amer. Chem. Soc.*, **72**, 5497 (1950).



the leaving of water in the former case as opposed to hydroxyl leaving in the latter. Also to be considered in the case of the tartrate ion are the resonance energy and solvation of the carboxyl group. The loss of resonance energy on reaction and the energy required to break up the solvent cage both tend in general to lead to an increase in activation energy, which is reflected in a decrease in reaction rate.

The data show that no additional, catalytic increase in rate with increasing acid concentration was present within the limits of the experiments. As noted above, esterification of boric acid is not acid catalyzed to a measurable extent either.[18] It would seem that if acid were to assist the leaving of the hydroxyl (as in the removal of -OH and -OR from aliphatic carbon atoms), an sp^2 hybrid would be first formed which would be readily hydrolyzed. In this sense a concerted mechanism seems to be the most probable for this reaction.

The initial attack of the carboxyl end of the molecule on the boron atom must also be considered. In this case, the intermediate would resemble state **2**, with the necessity of removing the not very acidic alcoholic proton *via* a mechanism involving intramolecular hydrogen bonding. That this is not observed in the case of a diol reaction with boric acid negates the presence of this path here. The feasibility of this reaction path depends on the acidity of the proton involved.

Appendix

The complete derivation of the expression for the relaxation time involves first rewriting eq 1 using the conditions (2) and the first-order relaxation expression $-\mathrm{d}\delta[\mathrm{B}]/\mathrm{d}t = \delta[\mathrm{B}]/\tau$ to give

$$\frac{-\mathrm{d}\delta[\mathrm{B}]}{\mathrm{d}t} = \frac{\delta[\mathrm{B}]}{\tau} = k_{12}\,([\overline{\mathrm{B}}]\delta[\mathrm{T}^{2-}] + [\overline{\mathrm{T}}^{2-}]\delta[\mathrm{B}]) - k_{21}\delta[\mathrm{BT}^{2-}] + k_{32}([\overline{\mathrm{B}}]\delta[\mathrm{HT}^-] + [\overline{\mathrm{HT}}^-]\delta[\mathrm{B}]) - k_{23}([\overline{\mathrm{H}}^+]\delta[\mathrm{BT}^{2-}] + [\overline{\mathrm{BT}}^{2-}]\delta[\mathrm{H}^+]) + k_{34}([\overline{\mathrm{B}}]\delta[\mathrm{HT}^-] + [\overline{\mathrm{HT}}^-]\delta[\mathrm{B}]) - k_{43}\delta[\mathrm{BHT}^-] + k_{54}([\overline{\mathrm{B}}]\delta[\mathrm{H_2T}] + [\overline{\mathrm{H_2T}}]\delta[\mathrm{B}]) - k_{45}([\overline{\mathrm{BHT}}^-]\delta[\mathrm{H}^+] + [\overline{\mathrm{H}}^+]\delta[\mathrm{BHT}^-]) \quad \text{(A-1)}$$

Terms such as $\delta[\mathrm{B}]\delta[\mathrm{T}^{2-}]$ approach 0, the perturbation being small, allowing the linearization of the rate equations above. Now $K_{42} = [\mathrm{BT}^{2-}][\mathrm{H}^+]/[\mathrm{BHT}^-] = ([\overline{\mathrm{BT}}^{2-}] + \delta[\mathrm{BT}^{2-}])([\overline{\mathrm{H}}^+] + \delta[\mathrm{H}^+])/([\overline{\mathrm{BHT}}^-] + \delta[\mathrm{BHT}^-])$. Therefore

$$K_{42}[\overline{\mathrm{BHT}}^-] + K_{42}\delta[\mathrm{BHT}^-] = [\overline{\mathrm{BT}}^{2-}][\overline{\mathrm{H}}^+] + [\overline{\mathrm{H}}^+]\delta[\mathrm{BT}^{2-}] + [\overline{\mathrm{BT}}^{2-}]\delta[\mathrm{H}^+]$$

Again the term $\delta[\mathrm{BT}^{2-}]\delta[\mathrm{H}^+]$ is assumed negligible. Since $K_{42} \approx \overline{K}_{42} = [\overline{\mathrm{BT}}^{2-}][\overline{\mathrm{H}}^+]/[\overline{\mathrm{BHT}}^-]$, then the following is obtained

$$K_{42}\delta[\mathrm{BHT}^-] = [\overline{\mathrm{H}}^+]\delta[\mathrm{BT}^{2-}] + [\overline{\mathrm{BT}}^{2-}]\delta[\mathrm{H}^+] \quad \text{(A-2)}$$

Using this relation, eq A-1 can be rewritten

$$\frac{\delta[\mathrm{B}]}{\tau} = k_{12}([\overline{\mathrm{B}}]\delta[\mathrm{T}^{2-}] + [\overline{\mathrm{T}}^{2-}]\delta[\mathrm{B}]) - k_{21}\delta[\mathrm{BT}^{2-}] + (k_{23} + k_{34})([\overline{\mathrm{B}}]\delta[\mathrm{HT}^-] + [\overline{\mathrm{HT}}^-]\delta[\mathrm{B}]) - (k_{23}K_{42} + k_{43})\delta[\mathrm{BHT}^-] + k_{54}([\overline{\mathrm{B}}]\delta[\mathrm{H_2T}] + [\overline{\mathrm{H_2T}}]\delta[\mathrm{B}]) - k_{45}([\overline{\mathrm{BHT}}^-]\delta[\mathrm{H}^+] + [\overline{\mathrm{H}}^+]\delta[\mathrm{BHT}^-] \quad \text{(A-3)}$$

Now $\vec{k} = k_{32} + k_{34}$, $\overleftarrow{k} = k_{23}K_{42} + k_{43}$, and $\overleftarrow{k} = \vec{k}/K_{34}$ as derived in the text. From the conservation of boron, $\delta[\mathrm{B}] + \delta[\mathrm{BT}^{2-}] + \delta[\mathrm{BHT}^-] = 0$, the relation $\delta[\mathrm{B}] = -(\delta[\mathrm{BT}^{2-}] + \delta[\mathrm{BHT}^-])$ is obtained. Using this relation and the above expressions for the over-all forward and reverse rate constants, eq A-3 can finally be written as

$$\frac{1}{\tau} = k_{12}\left\{\frac{1}{K_{12}\left(1 + \dfrac{\delta[\mathrm{BHT}^-]}{\delta[\mathrm{BT}^{2-}]}\right)} + [\overline{\mathrm{T}}^{2-}] + \frac{[\overline{\mathrm{B}}]}{\dfrac{\delta[\mathrm{B}]}{\delta[\mathrm{T}^{2-}]}}\right\} + \vec{k}\left\{\frac{1}{K_{34}\left(1 + \dfrac{\delta[\mathrm{BT}^{2-}]}{\delta[\mathrm{BHT}^-]}\right)} + [\overline{\mathrm{HT}}^-] + \frac{[\overline{\mathrm{B}}]}{\dfrac{\delta[\mathrm{B}]}{\delta[\mathrm{HT}^-]}}\right\} + k_{54}\left\{\frac{1}{K_{54}}\left[\frac{[\overline{\mathrm{H}}^+]}{\left(1 + \dfrac{\delta[\mathrm{BT}^{2-}]}{\delta[\mathrm{BHT}^-]}\right)} + \frac{[\overline{\mathrm{BHT}}^-]}{\dfrac{-\delta[\mathrm{B}]}{\delta[\mathrm{H}^+]}}\right] + [\overline{\mathrm{H_2T}}] + \frac{[\overline{\mathrm{B}}]}{\dfrac{\delta[\mathrm{B}]}{\delta[\mathrm{H_2T}]}}\right\} \quad \text{(A-4)}$$

Also to be considered is the indicator equilibrium used to follow the reaction. In exactly the same manner in which eq A-2 was derived, the following relation is obtained: $K_{\mathrm{HIn}}\delta[\mathrm{HIn}] = [\overline{\mathrm{H}}^+]\delta[\mathrm{In}^-] + [\overline{\mathrm{In}}^-]\delta[\mathrm{H}^+]$. From the conservation of In$^-$, $\delta[\mathrm{HIn}] = -\delta[\mathrm{In}^-]$; therefore

$$\delta[\mathrm{HIn}] = \left(\frac{[\overline{\mathrm{In}}^-]}{K_{\mathrm{HIn}} + [\overline{\mathrm{H}}^+]}\right)\delta[\mathrm{H}^+]$$

Therefore $\delta[\mathrm{H}^+] + \delta[\mathrm{HIn}] = (K_{\mathrm{HIn}} + [\overline{\mathrm{H}}^+] + [\overline{\mathrm{In}}^-])/(K_{\mathrm{HIn}} + [\overline{\mathrm{H}}^+])\delta[\mathrm{H}^+] = \gamma\delta[\mathrm{H}^+]$.

Similarly the following relations can be derived for the fast tartaric acid dissociations.

$$K_{31}\delta[\mathrm{HT}^-] = [\overline{\mathrm{T}}^{2-}]\delta[\mathrm{H}^+] + [\overline{\mathrm{H}}^+]\delta[\mathrm{T}^{2-}]$$

$$K_{53}\delta[\mathrm{H_2T}] = [\overline{\mathrm{H}}^+]\delta[\mathrm{HT}^-] + [\overline{\mathrm{HT}}^-]\delta[\mathrm{H}^+]$$

Using these three equilibrium relations together with the conservation relations for tartrate and proton, the following set of linearly independent equations can be written down in order to evaluate the δ terms in the denominator of the relaxation expression

$$[\overline{\mathrm{H}}^+]\delta[\mathrm{BT}^{2-}] - K_{42}\delta[\mathrm{BHT}^-] + [\overline{\mathrm{BT}}^{2-}]\delta[\mathrm{H}^+] = 0 \qquad \text{(A-5)}$$

$$K_{53}\delta[\mathrm{H_2T}] - [\overline{\mathrm{H}}^+]\delta[\mathrm{HT}^-] - [\overline{\mathrm{HT}}^-]\delta[\mathrm{H}^+] = 0 \qquad \text{(A-6)}$$

$$K_{31}\delta[\mathrm{HT}^-] - [\overline{\mathrm{H}}^+]\delta[\mathrm{T}^{2-}] - [\overline{\mathrm{T}}^{2-}]\delta[\mathrm{H}^+] = 0 \qquad \text{(A-7)}$$

$$\delta[\mathrm{BT}^{2-}] + \delta[\mathrm{BHT}^-] + \delta[\mathrm{H_2T}] + \delta[\mathrm{HT}^-] + \delta[\mathrm{T}^{2-}] = 0 \qquad \text{(A-8)}$$

$$\delta[\mathrm{BHT}^-] + 2\delta[\mathrm{H_2T}] + \delta[\mathrm{HT}^-] - \gamma\delta[\mathrm{H}^+] = 0 \qquad \text{(A-9)}$$

where eq A-8 is the tartrate conservation and eq A-9 is proton conservation. From eq A-8 and boron conservation it is seen that $\delta[\mathrm{B}] = \delta[\mathrm{H_2T}] + \delta[\mathrm{HT}^-] + \delta[\mathrm{T}^{2-}]$. This set of five simultaneous equations can now be solved for the terms in the denominator of the relaxation expression to give the following terms.

$$\frac{\delta[\mathrm{B}]}{\delta[\mathrm{T}^{2-}]} = \frac{\delta[\mathrm{H_2T}] + \delta[\mathrm{HT}^-] + \delta[\mathrm{T}^{2-}]}{\delta[\mathrm{T}^{2-}]}$$

$$\frac{\delta[\mathrm{H_2T}]}{\delta[\mathrm{T}^{2-}]} = \frac{\left([\overline{\mathrm{H}}^+] + \dfrac{B[\overline{\mathrm{H}}^+]}{I} - \dfrac{K_{42}[\overline{\mathrm{HT}}^-]}{I}\right)}{\left(A + \dfrac{K_{42}K_{53}}{[\overline{\mathrm{H}}^+]} - \dfrac{GK_{42}[\overline{\mathrm{HT}}^-]}{[\overline{\mathrm{H}}^+]I} + \dfrac{GB}{I}\right)}$$

$$A = [\overline{\mathrm{H}}^+] + 2K_{42}$$

$$B = \gamma([\overline{\mathrm{H}}^+] + K_{42}) + [\overline{\mathrm{BT}}^{2-}]$$

$$G = K_{53}K_{31}/[\overline{\mathrm{H}}^+]$$

$$I = (K_{31}[\overline{\mathrm{HT}}^-]/[\overline{\mathrm{H}}^+]) + [\overline{\mathrm{T}}^{2-}]$$

$$\frac{\delta[\mathrm{HT}^-]}{\delta[\mathrm{T}^{2-}]} = \frac{\left([\overline{\mathrm{H}}^+] + \dfrac{AD[\overline{\mathrm{HT}}^-]}{K_{53}} + BD\right)}{\left(\dfrac{[\overline{\mathrm{H}}^+]A}{K_{53}} + K_{42} + \dfrac{AC[\overline{\mathrm{HT}}^-]}{K_{53}} + BC\right)}$$

$$C = K_{31}/[\overline{\mathrm{T}}^{2-}]$$

$$D = [\overline{\mathrm{H}}^+]/[\overline{\mathrm{T}}^{2-}]$$

$$\frac{\delta[\mathrm{H_2T}]}{\delta[\mathrm{HT}^-]} = \frac{(BF + [\overline{\mathrm{T}}^{2-}]F + K_{31} - K_{42})}{(A + BE + [\overline{\mathrm{T}}^{2-}]E)}$$

$$E = K_{53}/[\overline{\mathrm{HT}}^-]$$

$$F = [\overline{\mathrm{H}}^+]/[\overline{\mathrm{HT}}^-]$$

$$\frac{\delta[\mathrm{BHT}^-]}{\delta[\mathrm{BT}^{2-}]} = \frac{\left(\dfrac{L[\overline{\mathrm{H}}^+]}{[\overline{\mathrm{BT}}^{2-}]} - [\overline{\mathrm{H}}^+]\right)}{\left(\dfrac{LK_{42}}{[\overline{\mathrm{BT}}^{2-}]} + J[\overline{\mathrm{H}}^+] - K_{31}\right)}$$

$$J = (2K_{31} + [\overline{\mathrm{H}}^+])/(2[\overline{\mathrm{H}}^+] + K_{53})$$

$$L = J\gamma[\overline{\mathrm{H}}^+] - \gamma(K_{31} + [\overline{\mathrm{H}}^+]) - [\overline{\mathrm{T}}^{2-}]$$

$$\frac{\delta[\mathrm{B}]}{\delta[\mathrm{H}^+]} = \frac{\delta[\mathrm{H_2T}] + \delta[\mathrm{HT}^-] + \delta[\mathrm{T}^{2-}]}{\delta[\mathrm{H}^+]}$$

$$\frac{\delta[\mathrm{H_2T}]}{\delta[\mathrm{H}^+]} = \frac{\left([\overline{\mathrm{HT}}^-] - \dfrac{[\overline{\mathrm{H}}^+](B + [\overline{\mathrm{T}}^{2-}])}{(K_{42} - K_{31})}\right)}{\left(K_{53} + \dfrac{A[\overline{\mathrm{H}}^+]}{(K_{42} - K_{31})}\right)}$$

$$\frac{\delta[\mathrm{HT}^-]}{\delta[\mathrm{H}^+]} = -\frac{\left([\overline{\mathrm{HT}}^-] + \dfrac{K_{53}(B + [\overline{\mathrm{T}}^{2-}])}{A}\right)}{\left([\overline{\mathrm{H}}^+] + \dfrac{K_{53}(K_{42} - K_{31})}{A}\right)}$$

$$\frac{\delta[\mathrm{T}^{2-}]}{\delta[\mathrm{H}^+]} = - \left\{\frac{\left(\dfrac{K_{31}}{[\overline{\mathrm{H}}^+] + \dfrac{K_{53}K_{42}}{A}}\right)\left([\overline{\mathrm{HT}}^-] + \dfrac{BK_{53}}{A}\right) + [\overline{\mathrm{T}}^{2-}]}{\left([\overline{\mathrm{H}}^+] - \dfrac{K_{31}}{\dfrac{K_{53}K_{42}}{A} + [\overline{\mathrm{H}}^+]}\right)\left(\dfrac{K_{53}[\overline{\mathrm{H}}^+]}{A}\right)}\right\}$$