

made available to us some unpublished data. Financial support from Ministero della Pubblica Istruzione is gratefully acknowledged.

Appendix

Generally, the diffusion and dissociation rate constants k_d and k_{-d} are obtained from the Debye⁶⁶ and Eigen⁶⁷ equations

$$k_d(\mu = 0) = \frac{8RT}{3000\eta} \frac{b/r}{e^{b/r} - 1} \quad (\text{A1})$$

$$k_{-d} = \frac{2kT}{\pi r^3 \eta} \frac{b/r}{1 - e^{-b/r}} \quad (\text{A2})$$

$$b = \frac{Z_D Z_A e^2}{\epsilon kT} \quad (\text{A3})$$

$$\log k_d(\mu) = \log k_d(\mu = 0) + \frac{1.02 Z_D Z_A \mu^{1/2}}{1 + A r \mu^{1/2}} \quad (\text{A4})$$

where η is the viscosity, r is the encounter distance, e is the electron charge, ϵ is the dielectric constant, $Z_D Z_A$ is the electric charges of the two reactants, and A is $(8\pi N e^2 / 1000 \epsilon k T)^{1/2}$. Equation A4 is usually valid for $r < 5 \text{ \AA}$ and $\mu < 0.1 \text{ M}$.⁶⁸⁻⁷⁰

It should be noted, however, that the values predicted by eq A1, A3, and A4 for larger ions and higher values of ionic strength are always much higher than the values experimentally measured for processes that are believed to be diffusion controlled (Table III). An empirical equation that gives better agreement with the "experimental" values (see Table III) is eq A5, which was previously used in ref 22

$$k_d = \frac{8RT}{3000\eta} \frac{W_r/RT}{e^{W_r/RT} - 1} \quad (\text{A5})$$

where

$$W_r = \frac{Z_D Z_A N e^2}{\epsilon r (1 + A r \mu^{1/2})} \quad (\text{A6})$$

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From the equilibrium constant⁷¹

$$K_0 = \frac{4\pi N r^3}{3000} e^{-W_r/RT} \quad (\text{A7})$$

and eq A5, one gets eq A8 for the dissociation rate constant,²²

$$k_{-d} = \frac{2kT}{\pi r^3 \eta} \frac{W_r/RT}{1 - e^{-W_r/RT}} \quad (\text{A8})$$

which thus is also dependent on the ionic strength. Equations A5 and A8 have been used to evaluate the k_d and k_{-d} values under different experimental conditions. The encounter distance r in the above equations is obtained as the sum of the individual radii of the reactants. The following values have been used for the radii: $M(\text{LL})_3^{n+}$, 7 Å; $\text{Ru}(\text{NH}_3)_6^{n+}$, 3.5 Å; $\text{Ru}(\text{NH}_3)_5\text{py}^{n+}$, 4.5 Å; c - and t - $\text{Co}(\text{en})_2\text{Cl}_2^{n+}$, c - $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{n+}$, and c - $\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}^{n+}$, 3.9 Å; c - and t - $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^{n+}$, 4.4 Å; c - and t - $\text{Co}(\text{en})_2(\text{NCS})_2^{n+}$, 5.0 Å; $\text{Co}(\text{en})_3^{n+}$, 4.3 Å; $\text{Co}(\text{NH}_3)_5(\text{NCS})^{n+}$, 3.6 Å; other Co complexes, 3.2 Å.

Equation 3a of ref 22 was used to homogenize bimolecular electron-transfer rate constants which differ in encounter distance (r), charge product ($Z_D Z_A$), and ionic strength (μ). The method for homogenizing for the different ΔG^\ddagger values of the self-exchange reactions of the reaction partners has been given in Appendix I of ref 22.

Registry No. $\text{Ru}(\text{bpy})_3^{2+}$, 15158-62-0; $\text{Ru}(\text{phen})_3^{2+}$, 22873-66-1; $\text{Ru}(\text{DM-phen})_3^{2+}$, 24414-00-4; $\text{Ru}(\text{DM-bpy})_3^{2+}$, 32881-03-1; $\text{Os}(\text{phen})_3^{2+}$, 31067-98-8; $\text{Co}(\text{NH}_3)_6^{3+}$, 14695-95-5; $\text{Co}(\text{en})_3^{3+}$, 14878-41-2; $\text{Co}(\text{phen})_3^{3+}$, 18581-79-8; $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, 14403-82-8; $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$, 15392-06-0; $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, 14970-14-0; $\text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$, 14970-18-4; $\text{Co}(\text{NH}_3)_5(\text{O}_2\text{CH})^{2+}$, 19173-64-9; $\text{Co}(\text{NH}_3)_5(\text{NO}_2)^{2+}$, 14482-68-9; cis - $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}$, 15693-74-0; cis - $\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}^{2+}$, 15392-82-2; cis - $\text{Co}(\text{en})_2\text{Cl}_2^+$, 14875-15-1; $trans$ - $\text{Co}(\text{en})_2\text{Cl}_2^+$, 14403-91-9; cis - $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$, 24912-92-3; $trans$ - $\text{Co}(\text{en})_2(\text{NCS})\text{Cl}^+$, 16997-24-3; cis - $\text{Co}(\text{en})_2(\text{NCS})_2^+$, 21169-85-7; $trans$ - $\text{Co}(\text{en})_2(\text{NCS})_2^+$, 24988-19-0.

(71) If eq 7a is replaced by the alternative expression

$$K_0 = \frac{4\pi N r^2(\delta r)}{1000} e^{-W_r/RT}$$

with $\delta r = 0.8 \text{ \AA}$,⁷ one obtains for k and ΔG^\ddagger values that are within the uncertainty given in the text.

Contribution from the Department of Chemistry, Brooklyn College, City University of New York, Brooklyn, New York, New York 11210

The Boric Acid/Lactic Acid System. Equilibria and Reaction Mechanism¹

RICHARD PIZER* and RUSSELL SELZER

Received October 12, 1983

Boric acid, $\text{B}(\text{OH})_3$, reacts with lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, to produce anionic complexes of both 1:1 and 1:2 stoichiometries. The boron atom is four-coordinate in the complex ions. The equilibria can be formulated as follows, where H_2L is fully protonated lactic acid: $\text{B}(\text{OH})_3 + \text{H}_2\text{L} \rightleftharpoons 1:1 + \text{H}_3\text{O}^+$, $K_1 = 1.8 \times 10^{-3}$; $1:1^- + \text{H}_2\text{L} \rightleftharpoons 1:2^- + 2\text{H}_2\text{O}$, $K_2 = 6.6 \times 10^{-4}$. The formation of 1:2 complex is strongly favored at low pH. Kinetic studies were carried out by temperature-jump and stopped-flow methods. The forward rate constant for the reaction of the 1:1 complex with lactic acid is 3 orders of magnitude greater than the rate constant for the reaction of trigonal $\text{B}(\text{OH})_3$ with lactic acid. This result is consistent with the previously observed substitution lability of four-coordinate borates.

Bidentate ligands such as polyols,²⁻⁵ 1,2-benzenediols,^{2,3,6,7} and α -hydroxy carboxylic acids^{8,9} form complexes with boric

acid according to eq 1 and 2. The formation of the 1:1 complex is both an addition reaction and a substitution re-

(1) Presented in part at the 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983.

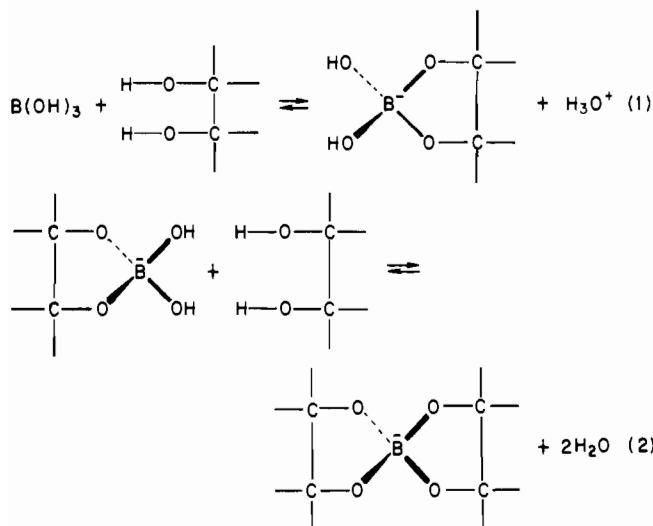
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action. In a continuing study of the reactions of boric acid and substituted boronic acids, RB(OH)_2 , with a large number of ligands varying considerably in acidity, we have shown^{10,11} that the stability constant for complex formation (K_1) is a function of the acidities of both boron acid and ligand, the most stable complexes being formed by the most acidic pair of reactants. The mechanistic pathways include the reaction of fully protonated ligands with boron acids. This mechanism is characterized by a transition state in which proton transfer from the entering ligand to a leaving hydroxide on boron is the most significant and distinctive feature.

The formation of 1:2 complexes (eq 2) involves no change in the coordination number on boron. Although the equilibrium constants for bis complex formation (K_2) show a general increase with increasing ligand acidity,¹² the effect is less pronounced than in the case of the formation of 1:1 complexes. Also, the ratio of successive equilibrium constants implies that, in some cases, a bound ligand has a significant effect on the second complexation step.

The present work concerns the complexation of boric acid and lactic acid [$\text{CH}_3\text{CH(OH)COOH}$]. We have previously studied¹³ the reaction of phenylboronic acid with lactic acid, in which case only formation of the 1:1 complex is possible. While one might expect the formation of the 1:1 boric acid/lactic acid complex to be kinetically similar to that of the previously studied phenylboronic acid system, bis complex formation is a very different type of reaction. The formation of bis complexes is formally analogous to the reactions of tetrahedral borate anions, RB(OH)_3^- , in that both are substitution reactions in which boron retains a coordination number of 4. Our only kinetic results to date on borate complexation reactions suggest that reactions of borates are much faster than reactions of trigonal boron acids. It is not yet known whether the lability of borates extends to the complexation reactions of 1:1 borate complex ions. Another significant question is the effect of an already bound ligand on the thermodynamics and kinetics of the second complexation step.

Experimental Section

Boric acid (Fisher) was used without further purification. Lactic acid (Fisher) was refluxed prior to use as described previously.¹³

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Table I. Equilibrium Constants and Rate Constants for the Complexation of Boric Acid and Lactic Acid

reaction ^a	K_n	k_n	k_{-n}
1	1.8×10^{-3}	$2.5 \text{ M}^{-1} \text{ s}^{-1}$	$1.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$
1'	9.0 M^{-1}	$\leq 9.0 \text{ M}^{-1} \text{ s}^{-1}$	$\leq 1.0 \text{ s}^{-1}$
2	66 M^{-1}	$4.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	61 s^{-1}
2'	3.3×10^5	$< 10^2 \text{ M}^{-1} \text{ s}^{-1}$	

^a The numbers refer to the reaction pathways in the overall mechanism.

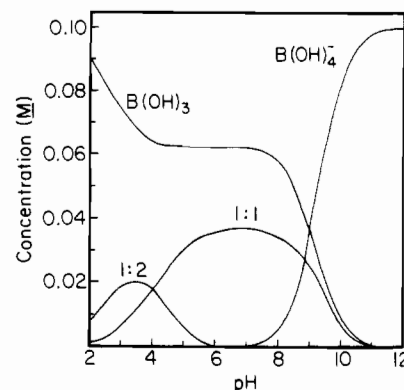


Figure 1. Distribution diagram for the B(OH)_3 /lactic acid system, calculated with 0.10 M concentration for each reactant.

Stability constants were determined by pH-tritration methods. Kinetic studies were performed either by temperature-jump¹³ or by stopped-flow techniques using an Aminco-Morrow instrument. Depending upon the pH at which kinetic measurements were being made, either orange IV, bromophenol blue, or chlorophenol red was used to monitor the reaction. All kinetic measurements were made in acidic solution. Under the conditions of the experiments, the concentrations of borate ion, B(OH)_4^- , and polyborate ions are negligible.¹⁴ Blank solutions of boric acid and lactic acid show no kinetic effect in any time range. All experiments were carried out at 25 °C and 0.1 M (KNO_3) ionic strength. Errors associated with reported rate and equilibrium constants are $\pm 20\%$.

Stability Constants

The $\text{p}K_1$ of lactic acid¹³ is 3.70, and that of boric acid¹⁴ is 8.98. The stability constants for the boric acid/lactic acid complexation reaction (eq 1 and 2) were determined by two independent titration methods. In one method, solutions of one reactant adjusted to a particular pH are titrated with solutions of the other reactant adjusted to the same initial pH. In acidic solution (pH ~ 2), the concentration of lactate anion is small, and mixing boric acid and lactic acid solutions produces a decrease in pH in accord with eq 1. This method has been used extensively by us in the determination of stability constants in borate systems in which only 1:1 complex formation occurs, and equations for data analysis are found in previous papers.^{10,13} The method is applicable to the present case only if conditions can be found in which either 1:1 or 1:2 complex formation is predominant. Attempts to fit data in acidic solution to our previous equation for 1:1 complex formation were not successful. However, it became clear in the course of that analysis that bis complex formation is often predominant in acidic solution. Using an excess of lactic acid at low pH ensures predominance of bis complex, and the titration data can be analyzed to evaluate β_2 directly ($\beta_2 = K_1K_2$).¹⁵

The second pH method involves the titration of solutions of boric acid and lactic acid with standard base. The usual analysis of such data requires pairwise selection of points to determine K_1 and K_2 . In the present case, β_2 was evaluated as described above. Using that value in conjunction with the titration data permits the straightforward calculation of K_1 . The results are presented in Table I.

A distribution diagram for the system was calculated at a concentration of 0.1 M in each reactant as shown in Figure 1. Note

- (14) Ingri, N. *Acta Chem. Scand.* **1962**, *16*, 439.
 (15) This requires a slight modification of the equations in ref 13 in order to account for the fact that 2 mol of lactic acid reacts/mol of H_3O^+ produced.

Scheme I

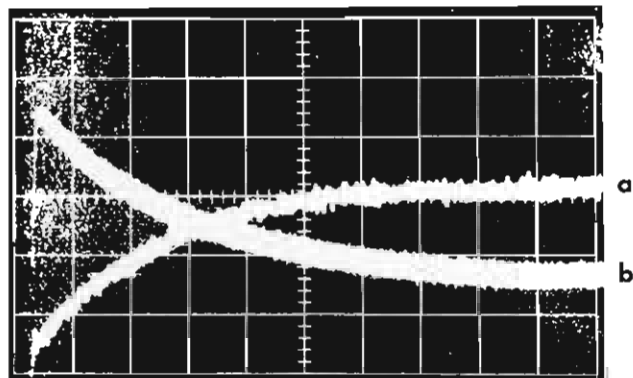
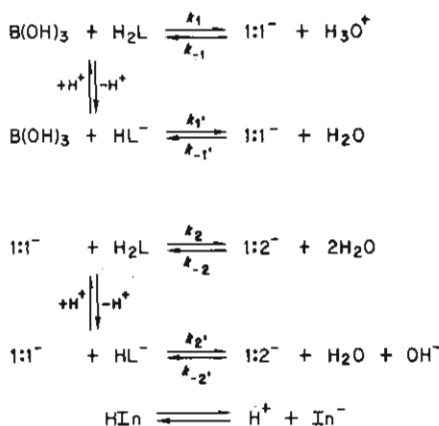


Figure 2. Boric acid/lactic acid temperature-jump relaxation reaction traces ($[\text{B(OH)}_3]_0 = 0.159$ M, $[\text{CH}_3\text{CH(OH)COOH}]_0 = 0.155$ M, $[\text{HIn}]_0 = 3.9 \times 10^{-5}$ M, pH 3.87): (a) 2.0 ms/div, $\tau_{\text{exptl}} = 4.1$ ms, $\tau_{\text{calcd}} = 4.0$ ms; (b) 0.2 s/div, $\tau_{\text{exptl}} = 0.49$ s, $\tau_{\text{calcd}} = 0.47$ s.

that bis complex formation predominates at pH ~ 2 even when the formal concentration ratio of reactants is unity.

Kinetic Results and Treatment of Data

The temperature-jump data were analyzed in terms of the reaction pathways in Scheme I.

The protolytic reactions of lactic acid and indicator are much faster than the complexation reactions. The system is therefore characterized by two relaxation times that are given by the general determinantal equation

$$\begin{vmatrix} a_{11} - 1/\tau & a_{12} \\ a_{21} & a_{22} - 1/\tau \end{vmatrix} = 0$$

The coefficients a_{11} and a_{12} are functions of the rate constants and equilibrium concentrations of reactants and products involved in reaction pathways 1 and 1'. The coefficients a_{21} and a_{22} are functions of the rate constants and equilibrium concentrations of reactants and products involved in reaction pathways 2 and 2'. Under conditions where $a_{11}a_{22} \gg a_{21}a_{12}$, the system is uncoupled and each observed relaxation time is associated with one particular reaction pathway. In the present case, the system is uncoupled at pH ~ 6 and the one relaxation time that is observed¹⁶ depends only on k_1 . The system is coupled at lower pH values. At pH ~ 4 , two well-defined relaxation times are easily measured. At pH ~ 2 , only one relaxation time is observed. The value of k_1 , determined from results at pH ~ 6 was used in the evaluation of k_1 and k_2 at

(16) When fewer than the maximum number of relaxation times are observed experimentally, it can be due either to the time scale of the relaxation effects (either too fast or too slow to be measured) or to factors which affect the amplitudes of the relaxation effects. For a discussion of the latter point, see: Eigen, M.; de Maeyer, L. "Technique of Organic Chemistry"; Weissberger, A., Ed.; Interscience: New York, 1963; Vol. VIII, Part II, pp 928-941.

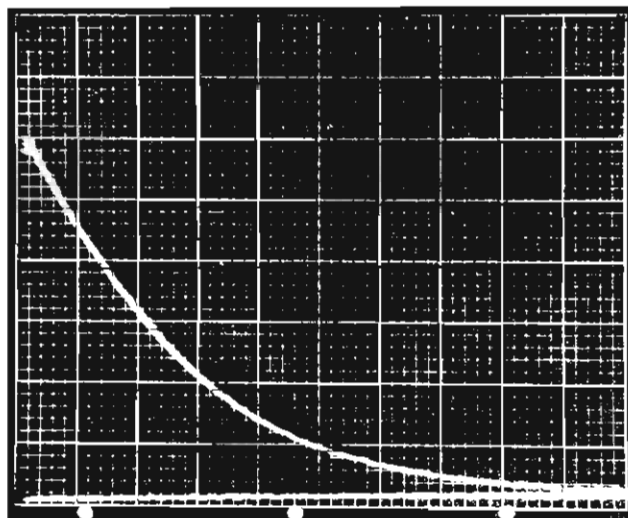


Figure 3. Boric acid/lactic acid stopped-flow reaction trace (50 ms/div, $[\text{B(OH)}_3]_0 = 0.18$ M, $[\text{CH}_3\text{CH(OH)COOH}]_0 = 0.21$ M, $[\text{HIn}]_0 = 3.0 \times 10^{-5}$ M, pH₀ 2.20, pH_f 1.71).

lower pH. The relaxation data could be fit by these three rate constants with k_2 set equal to zero. Once the data were fit, an upper limit for k_2 could be determined. Results are presented in Table I. Representative relaxation traces at pH ~ 4 are presented¹⁷ in Figure 2. Calculated and experimentally determined relaxation times are given.

A simple independent measurement of k_1 is possible by a stopped-flow experiment carried out at pH ~ 2 . A sample trace is presented in Figure 3. Although the overall reaction involves bis complex formation, the data were analyzed simply from the initial rate in order to obtain a rough value of k_1 . The result from a series of experiments ($k_1 = 2.5 \pm 1.0$ M⁻¹ s⁻¹) is in accord with the temperature-jump results.

Discussion

Equilibria. Phenylboronic acid (pK_a = 8.72)¹³ is more acidic than boric acid. Since we have shown¹⁰ that the stability constant for complex formation (K_1) increases with increasing acidity of boron acid, it is not at all surprising to find that the boric acid/lactic acid complexation reaction is characterized by a value of K_1 that is a factor of 2 lower than that observed¹³ for the phenylboronic acid/lactic acid system. The value of K_2 is in accord with early work⁸ on similar systems. Another point to consider is the ratio of successive stability constants. If eq 1 is rewritten to refer to the reaction of tetrahedral borate $[\text{B(OH)}_4]^- + \text{H}_2\text{L} \rightleftharpoons 1:1^- + 2\text{H}_2\text{O}$, then $K_1^* = K_1/K_a(\text{B(OH)}_3)$. K_1^* and K_2 then refer to successive substitution reactions on the tetrahedral borate ion. Although $K_1^*/K_2 = 2.6 \times 10^4$, such unusually large ratios have been previously observed in borate systems with other ligands. We have recently discussed¹² equilibria in systems of this type.

A further unusual feature is the extent to which bis complex formation is favored in acidic media (Figure 1). This result is not unique to borate chemistry as a similar situation obtains in a molybdate chemistry in neutral solution with catechol as the ligand.¹⁸

Formation of 1:1 Complex. Although the stability constant for complex formation is entirely consistent with earlier work,⁸ the rate constants are somewhat unusual. For reactions of fully protonated ligands (pathway 1), the decrease in K_1 as boron

(17) The reaction traces in Figure 2 are the result of two independent temperature-jump experiments monitored at different sweep rates as indicated. Each experiment was conducted by initially applying a bias voltage so that the relaxation trace would appear on the oscilloscope screen. For this reason, the end of reaction trace does not correspond in amplitude to the exact beginning of reaction trace b.

(18) Kustin, K.; Liu, S.-T. *J. Am. Chem. Soc.* **1973**, *95*, 2487.

acid pK_a increases is generally reflected in a decrease in the forward rate constants and an increase in the reverse rate constants. In the present case, both k_1 (by a factor of 56) and k_{-1} (by a factor of 27) are lower than rate constants for the reaction of phenylboronic acid with lactic acid. Since the rate constants are lower than had been expected, an independent kinetic experiment was carried out by stopped-flow techniques, and the results (Figure 3) confirm the analysis of the temperature-jump data. Further, a parallel experiment in which PhB(OH)_2 and lactic acid were reacted was performed, and reaction was found to be complete within the time of mixing, in accord with the previously reported¹³ rate constants for that system.

The rate constants for the reaction of lactate anion (pathway 1') are unexceptional compared with prior results in related systems.¹⁰

Formation of 1:2 Complex. The second complexation step is a substitution reaction of a four-coordinate borate anion. Our only other work¹⁰ in a similar area involved the reactions of $m\text{-NO}_2\text{PhB(OH)}_3^-$ with both mandelic acid and salicylic acid. The rate constants for the complexation of the four-coordinate $m\text{-NO}_2\text{PhB(OH)}_3^-$ anion suggest that this species undergoes substitution more rapidly than trigonal $m\text{-NO}_2\text{PhB(OH)}_2$. This same pattern of reactivity is observed here ($k_2 > k_1$), and the result strongly supports the idea that four-coordinate borates undergo complexation in a more facile manner than trigonal boron acids.¹⁹ The fact that $k_2 > k_1$ may be in part a reflection of electrostatic repulsion between the anionic reactants in the latter case.

A second major point concerning these reactions is whether an already bound ligand has an effect on the rate of the subsequent complexation step. To answer this question requires comparing rate constants for successive substitution on the tetrahedral borate ion. As noted in the discussion of equilibria, K_1^*/K_2 is very large. In terms of the reaction rate constants, $K_1^*/K_2 = k_1^*k_{-2}/k_{-1}^*k_2$. A large value of K_1^*/K_2 may be due to a large value of k_1^* ($k_1^* \gg k_2$), which would mean that B(OH)_4^- undergoes substitution much more easily than the 1:1⁻ complex ion. A second possibility is that 1:2⁻ undergoes hydrolysis much more rapidly than does 1:1⁻ ($k_{-2} \gg k_{-1}^*$). It is also possible that both effects may contribute to produce a ratio of successive stability constants far in excess of that predicted from statistics.

Experimental difficulties prevent making a definitive answer to the question in this system. In particular, since the pathway $\text{B(OH)}_3 + \text{HL}^- \rightleftharpoons 1:1^- + \text{H}_2\text{O}$ is kinetically indistinguishable²⁰ via proton ambiguity from the pathway $\text{B(OH)}_4^- + \text{H}_2\text{L} \rightleftharpoons 1:1^- + 2\text{H}_2\text{O}$, only upper limits can be determined for the various rate constants. From the upper limits of k_1' and k_{-1}' , k_1^* is given by $k_1^* = k_1'K_{\text{H}_2\text{L}}/K_{\text{HB}} \leq 1.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and

$k_{-1}^* \leq 1.0 \text{ s}^{-1}$. Since only an upper limit can be determined for k_1^* , it cannot be concluded that $k_1^* > k_2$. However, it is clear that $k_{-2} > k_{-1}^*$ since k_{-2} exceeds the upper limit of k_{-1}^* . Although k_1^* cannot be determined in the present case, the idea that simple borates may undergo substitution in a more facile manner than 1:1 borate complexes is supported by comparison with results in another system. The reaction of $m\text{-NO}_2\text{PhB(OH)}_3^-$ with mandelate anion¹⁰ is characterized by a forward rate constant of $1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The rate constant for the reaction of the 1:1 complex with lactate anion (k_2) has an upper limit that is more than 2 orders of magnitude lower. If this is indicative of the relative substitution lability of borates and 1:1 complex borate anions, it implies that the large value of K_1^*/K_2 is also due in part to a large value of k_1^*/k_2 . This conclusion implies that a bound ligand inhibits the coordination of a second ligand to a considerable extent. It should be pointed out that this conclusion applies only to α -hydroxy carboxylic acids as ligands. Other borate systems with other classes of ligands are characterized by much lower values of K_1^*/K_2 , and kinetic reasons for the difference are not yet known.

The transition state for the reactions of trigonal boron acids is associative. With fully protonated ligands, it is characterized by proton transfer from the incoming ligand to a leaving hydroxide on boron. This conclusion was reached by examining a wide range of boron acids and ligands varying considerably in acidity. Since only a very few reactions of four-coordinate borate anions have been studied kinetically, it is not yet possible to determine whether proton transfer is significant in the transition state. However, the transition state is likely also to be associative. If dissociation of OH^- from labile four-coordinate borate anions were to precede ligand coordination, one would expect comparable rate constants for the reactions of trigonal boron species and tetrahedral borate anions. Although an associative pathway for borates would involve a five-coordinate boron in the transition state, such a proposal is not without precedent. Five-coordinate boron has been proposed²¹ in the hydrolysis of BH_4^- , and calculations have been done²² on the possible geometries of such species. It may be that the conformational requirements of a bound chelating ligand in a 1:1 borate complex anion inhibit the requisite increase in coordination number and result in lower rate constants compared with reactions of tetrahedral B(OH)_4^- ; that is, $k_1^* > k_2$.

Acknowledgment. The work was supported by a PSC/BHE grant from the Faculty Research Award Program of the City University of New York. We wish to thank Prof. Louis Kirschenbaum for assisting us with the stopped-flow experiments that were conducted in his laboratory.

Registry No. B(OH)_3 , 10043-35-3; lactic acid, 50-21-5.

(19) See ref 10 for further discussion and references.

(20) We are most grateful for the very helpful comments of a reviewer concerning this point. We also mention that this applies to the rate constants denoted k_1' and k_{-1}' collected in ref 10.

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