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Equilibria and Reaction Mechanism of the Complexation of Methylboronic Acid with Polyols

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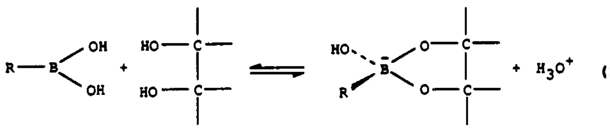
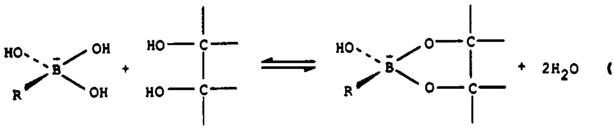
Methylboronic acid, $CH_3B(OH)_2$, forms 1:1 anionic complexes with polyols according to the reaction $CH_3B(OH)_2 + H_2L \rightleftharpoons Cx^- + H_3O^+$. The polyols which were studied are 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, and 1,2,3-propanetriol. Complexes with both five-membered and six-membered chelate rings are formed. Equilibrium constants in the four systems vary between 10^{-9} and 10^{-10}, and they were determined by both pH titration and ^{11}B NMR spectroscopy at 25 °C and $\mu = 0.1$ M (KNO_3). Kinetic studies were carried out by the temperature-jump relaxation method. The most important kinetic result is that trigonal $CH_3B(OH)_2$ is quite unreactive with polyols. Four-coordinate $CH_3B(OH)_3^-$ reacts much more rapidly than trigonal $CH_3B(OH)_2$ by factors which may be $\geq 10^6$ (see Discussion). Forward rate constants for the reactions of the polyols with $CH_3B(OH)_3^-$ vary between 10^2 and 10^3 M^{-1} s^{-1}. The remarkable reactivity of $CH_3B(OH)_3^-$ is discussed in terms of an associative transition state in which proton transfer is important.

Boron acids, $RB(OH)_2$, are weak trigonal Lewis acids which undergo addition of hydroxide ion to produce four-coordinate borates,[1] $RB(OH)_3^-$. Both $RB(OH)_2$ (eq 1) and $RB(OH)_3^-$ (eq 2) can react with bidentate chelating ligands to produce identical complexes. Ligands which undergo these reactions include dicarboxylic acids,[2] α-hydroxy carboxylic acids,[3-6] 1,2-benzenediols,[7-9] and polyols.[7,10,11] Our extensive previous work on these reactions has led us to propose[12] an associative transition state (**1**) for the reaction of trigonal $RB(OH)_2$ with fully protonated ligands in which proton transfer from the entering ligand to a leaving hydroxide on boron is the most significant and distinctive feature. A recent study by Funahashi and co-workers[13] on similar reactions includes both the first observation of a deuterium isotope effect in these reactions and a measurement of reaction activation parameters. The results support the salient features of our proposed transition state, namely that the transition state is associative and that proton transfer in the transition state is significant.


(1)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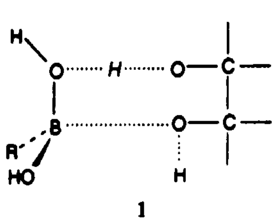
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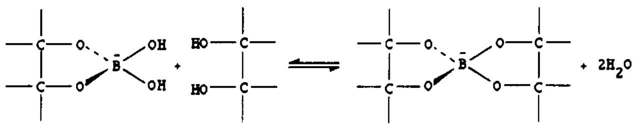
Unsubstituted boric acid, $B(OH)_3$, is capable of forming bis complexes in a second step (eq 3).[6-8,10,11] These reactions are formally analogous to the substitution reactions of borates (eq 2). While the evaluation of rate constants for the substitution reactions of borates with acidic ligands is complicated by reaction pathways which are kinetically indistinguishable via proton ambiguity,[6] no similar problem exists in the formation of bis borate complexes. Our results on one such system[6] support our previous tentative conclusion[12] that complexation reactions of four-coordinate borates are much faster than reactions of trigonal boron acids.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The present work concerns the reactions of methylboronic acid, $CH_3B(OH)_2$, with four different polyol ligands. The ligands are 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, and 1,2,3-propanetriol. Our interest in these particular systems arises mainly from two related mechanistic concerns. First, since the ligands are not acidic, rate constants for the reactions of $RB(OH)_2$ and $RB(OH)_3^-$ can be determined without encountering the problem of proton ambiguity. This study, therefore, allows a direct measurement of the relative substitution lability of $RB(OH)_2$ and $RB(OH)_3^-$. A second, related, point concerns the proposed transition state for the reactions of $RB(OH)_2$ with protonated ligands (**1**). One consequence of the proposed transition state is that trigonal $RB(OH)_2$ may be unreactive if the incoming ligand lacks protons of appreciable acidity. This idea will also be examined.

Experimental Section

Methylboronic acid (Aldrich) was used without further purification. 1,2-Ethanediol, 1,2-propanediol, 1,3-propanediol, and 1,2,3-propanetriol

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were used as received. The stability constants were determined by pH titration (NaOH titration) and also by ^{11}B NMR techniques. pH titration has been used extensively by us and is described elsewhere.[2,6,9,12] ^{11}B NMR spectroscopy has been used in a previous study, and the experimental details are presented there.[14] Kinetic studies were carried out by the temperature-jump method as previously described.[15] All kinetic measurements were made between pH 8 and pH 10 using phenolphthalein to monitor the reactions. Blank solutions of indicator alone, indicator plus methylboronic acid, and indicator plus polyol showed no measurable relaxation effect in any time range accessible to the instrument. All experiments were performed at 25 °C and 0.1 M (KNO_3) ionic strength.

Stability Constants

The overall reaction scheme which describes the various systems studied is presented in Scheme I. The symbol $Cx_{1,2}^-$ refers to a complex with a five-membered chelate ring (1,2-ethanediol and 1,2-propanediol). The symbol $Cx_{1,3}^-$ refers to a six-membered chelate ring (1,3-propanediol). 1,2,3-Propanetriol is capable of forming both five-membered and six-membered chelate rings.

Scheme I

$$CH_3B(OH)_2 + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cx_{1,2}^- + H_3O^+ \qquad K_1$$

$$CH_3B(OH)_3^- + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Cx_{1,2}^- + 2H_2O \qquad K_2 = K_1/K_a$$

$$CH_3B(OH)_2 + H_2L \underset{k_{-1}'}{\overset{k_1'}{\rightleftarrows}} Cx_{1,3}^- + H_3O^+ \qquad K_1'$$

$$CH_3B(OH)_3^- + H_2L \underset{k_{-2}'}{\overset{k_2'}{\rightleftarrows}} Cx_{1,3}^- + 2H_2O \qquad K_2' = K_1'/K_a$$

$$Cx_{1,2}^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Cx_{1,3}^- \qquad K_3 = K_1'/K_1$$

$$CH_3B(OH)_2 + H_2O \rightleftarrows CH_3B(OH)_3^- + H^+ \qquad K_a$$

The pK_a of $CH_3B(OH)_2$ is[12] 10.40. The ligands are much less acidic. For example, the usually cited[16] pK_a of 1,2-ethanediol is 15.4 Since the maximum solution pH in any experiment was 10.5, the ionization of the ligand was not considered in the data analysis.

Although pH titration methods can be used to evaluate all of the stability constants shown in Scheme I, ^{11}B NMR spectroscopy was also used to confirm the results of the pH titrations. The $CH_3B(OH)_2$/1,2,3-propanetriol system is the most complicated of the four systems studied, and it will serve to illustrate the techniques used in the determination of the stability constants. A ^{11}B NMR spectrum is shown in Figure 1 for the $CH_3B(OH)_2$/1,2,3-propanetriol system. The three peaks observed in the spectrum are assigned to $CH_3B(OH)_2/CH_3B(OH)_3^-$, $Cx_{1,2}^-$, and $Cx_{1,3}^-$. The broadest peak observed at 20 ppm is due to the relatively rapid $CH_3B(OH)_2/CH_3B(OH)_3^-$ equilibrium. This is easily verified by running the ^{11}B NMR spectrum of a blank solution of $CH_3B(OH)_2$ at the same pH. Only one ^{11}B NMR resonance is observed which is assigned as described above. The two sharper peaks increasingly upfield are assigned to $Cx_{1,2}^-$ and $Cx_{1,3}^-$, respectively. Integration of these peaks allows a calculation of the equilibrium constants. Note that there is no evidence for a terdentate complex, $Cx_{1,2,3}^-$. This observation and our assignments of observed ^{11}B NMR resonances are in agreement with a recent study[11] of the $B(OH)_3$/1,2,3-propanetriol system.[17] The ^{11}B NMR spectra of each of the other three ligand systems show only two resonances as expected. The equilibrium constants determined by ^{11}B NMR spectroscopy are identical with our values obtained by pH titration. Equilibrium constants for all systems are found in Table I and have errors associated with them of ±10%. The equilibrium constants can be used to calculate distribution diagrams for the various systems. A representative diagram is presented for the $CH_3B(OH)_2$/1,2,3-propanetriol system (Figure 2). Such diagrams are used by us to determine appropriate conditions for carrying out the temperature-jump experiments.

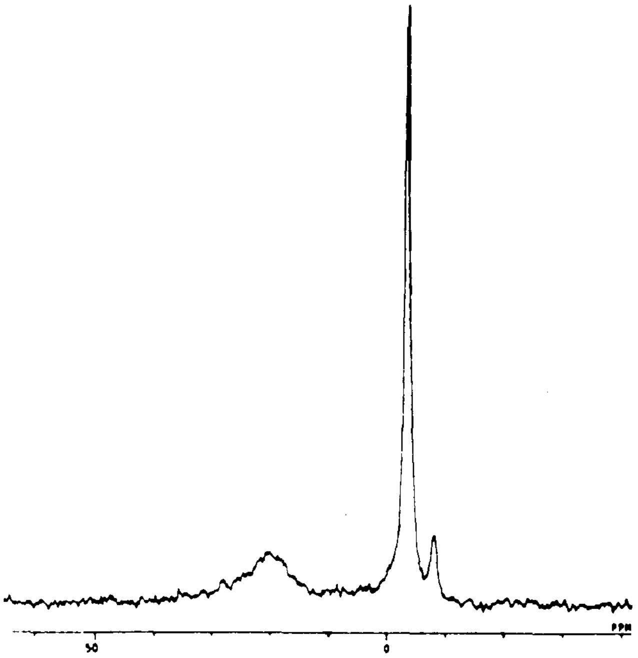

Figure 1. ^{11}B NMR spectrum: $[CH_3B(OH)_2] = 8.73 \times 10^{-3}$ M; $[H_2COHCHOHCH_2OH] = 9.20 \times 10^{-2}$ M; pH = 10.50; $T = 25.0$ °C.

Table I. Stability Constants for Methylboronic Acid/Polyol Complexes

H_2L	K_1	K_2	K_1'	K_2'	K_3
1,2-ethanediol	2.2×10^{-10}	5.5			
1,2-propanediol	2.4×10^{-10}	6.0			
1,3-propanediol			1.0×10^{-10}	2.5	
1,2,3-propanetriol	1.5×10^{-9}	38	1.6×10^{-10}	4.0	0.11

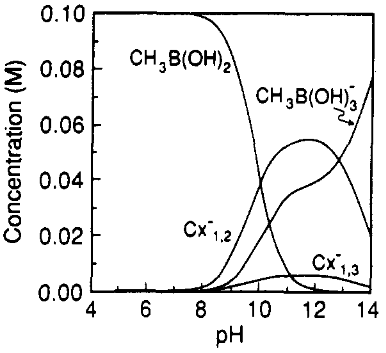

Figure 2. Distribution diagram of 0.10 M $CH_3B(OH)_2$/0.10 M $H_2COHCHOHCH_2OH$.

Kinetic Results and Treatment of Data

The kinetic data were analyzed in terms of the reaction pathways presented in Scheme I. The rapid reversible ionizations

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(17) Terdentate coordination has been noted[11] for polyols such as all-*cis*-1,3,5-cyclohexanetriol, and it has been suggested for pentaerythritol (Lorand, J. P.; Edwards, J. O. *J. Org. Chem.* **1959**, *24*, 769).

Table II. Rate Constants for Methylboronic Acid/Polyol Systems

H_2L	k_1 ($M^{-1}\,s^{-1}$)	k_2 ($M^{-1}\,s^{-1}$)	k_1' ($M^{-1}\,s^{-1}$)	k_2' ($M^{-1}\,s^{-1}$)	k_3 (s^{-1})
1,2-ethanediol	≤0.1	1.1×10^3			
1,2-propanediol	≤0.1	2.8×10^2			
1,3-propanediol			≤0.1	5.2×10^2	
1,2,3-propanetriol	≤0.1	$2.0\ (\pm 1.0) \times 10^2$	≤0.1	$1.5\ (\pm 0.5) \times 10^2$	≤1

H_2L	k_{-2} (s^{-1})	k_{-2}' (s^{-1})	k_{-3} (s^{-1})
1,2-ethanediol	2.0×10^2		
1,2-propanediol	4.7×10		
1,3-propanediol		2.1×10^2	
1,2,3-propanetriol	5.3 (±2.6)	$3.8\ (\pm 1.2) \times 10$	≤10

of both the indicator and $CH_3B(OH)_2$ are included in the expression for the relaxation time in the usual way.[15] The 1,2,3-propanetriol system is one in which all of the reaction pathways in Scheme I must be considered. The other three systems are simpler cases in which at most two of the five reactions in Scheme I may be important. The result of the derivation of the relaxation expression for the 1,2,3-propanetriol system is given below, and it easily reduces to give the relaxation expressions for the other systems. The 1,2,3-propanetriol system is characterized by two relaxation times that are given by the general determinantal equation

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

a_{11} and a_{12} are functions of $Cx_{1,2}^-$ and k_1, k_2, and k_3. The complete expressions are

$$a_{11} = k_1\left(S[\overline{CH_3B(OH)_2}] + R[\overline{H_2L}] + \frac{P[\overline{Cx_{1,2}^-}]}{K_1} + \frac{[\overline{H^+}]}{K_1}\right) + k_2\left(S[\overline{CH_3B(OH)_3^-}] + T[\overline{H_2L}] + \frac{1}{K_2}\right) + k_3$$

$$a_{12} = k_1\left(S[\overline{CH_3B(OH)_2}] + R[\overline{H_2L}] + \frac{P[\overline{Cx_{1,2}^-}]}{K_1}\right) + k_2(S[\overline{CH_3B(OH)_3^-}] + T[\overline{H_2L}]) + k_3\left(-\frac{1}{K_3}\right)$$

All concentrations are equilibrium concentrations, and the various constants are defined in the Appendix. The expressions for a_{21} and a_{22} are identical with the above expressions with the exceptions that $Cx_{1,2}^-$ is replaced by $Cx_{1,3}^-$, k_1 and K_1 are replaced by k_1' and K_1', and k_2 and K_2 are replaced by k_2' and K_2'.

For the 1,2-ethanediol and 1,2-propanediol systems, k_1', k_2', and k_3 are all equal to zero. The expression for the relaxation time for these systems reduces to $1/\tau = a_{11}$. For the 1,3-propanediol system, k_1, k_2, and k_3 are all equal to zero and the relaxation expression reduces the $1/\tau = a_{22}$. Obviously, a_{11} and a_{22} are parallel expressions which independently describe the reactions of $Cx_{1,2}^-$ and $Cx_{1,3}^-$, respectively. The relaxation expressions for the 1,2-ethanediol, 1,2-propanediol, and 1,3-propanediol systems reduce to equations in which the relaxation time is a function of two forward rate constants k_1 and k_2 or k_1' and k_2'. It turns out that k_1 and k_1' are very small and the relaxation expression essentially becomes a function of just one rate constant which is adjusted for the best fit of calculated and experimental relaxation times. Results are presented in Table II. Errors associated with these rate constants are ±20%.

Table III. Kinetic Data for the Methylboronic Acid/1,2,3-Propanetriol System

pH	$[H_2L]_0$ (M)	$[CH_3B(OH)_2]_0$ (M)	$[HIn]_0$ M	τ_{expt} (ms)	τ_{calc}[a] (ms)
9.88	0.136	0.033	6.16×10^{-5}	14	13
9.53	0.136	0.016	9.12×10^{-5}	15	13
9.53	0.055	0.034	9.14×10^{-5}	19	18
9.53	0.027	0.068	9.76×10^{-5}	18	20
9.47	0.136	0.030	6.82×10^{-5}	11	13
9.25	0.027	0.068	9.76×10^{-5}	17	20
9.17	0.137	0.030	9.41×10^{-5}	11	12
9.17	0.136	0.011	9.45×10^{-5}	14	13
9.17	0.033	0.033	8.99×10^{-5}	23	19
9.16	0.137	0.018	9.17×10^{-5}	12	12
9.16	0.055	0.034	9.14×10^{-5}	17	18
8.54	0.137	0.033	2.95×10^{-4}	11	12
8.38	0.137	0.030	3.28×10^{-4}	10	12
8.16	0.136	0.030	4.99×10^{-4}	12	12

[a] Calculated with $k_1 = 0.1\ M^{-1}\,s^{-1}$, $k_2 = 2.0 \times 10^2\ M^{-1}\,s^{-1}$, $k_1' = 0.1\ M^{-1}\,s^{-1}$, $k_2' = 1.5 \times 10^2\ M^{-1}\,s^{-1}$, and $k_3 = 1\ s^{-1}$.

The 1,2,3-propanetriol system is the most complex of the four systems studied, and the complete determinantal equation must be solved to evaluate the rate constants. Not only must all pathways describing the formation of both $Cx_{1,2}^-$ and $Cx_{1,3}^-$ be considered, but a direct interconversion between $Cx_{1,2}^-$ and $Cx_{1,3}^-$ is also included and denoted by k_3. $Cx_{1,2}^-$ and $Cx_{1,3}^-$ can, in fact, interconvert via complete ligand dissociation. What the pathway denoted by k_3 involves is the hydrolysis of a complex at one binding site to produce a unidentate intermediate complex which then, prior to complete ligand dissociation, undergoes ring closure to produce the second possible bidentate chelate complex. Since there is no evidence from our equilibrium studies for unidentate complexes between $CH_3B(OH)_2$ and 1,2,3-propanetriol in measurable concentration, such a reaction intermediate is not explicitly included in the kinetic scheme.

Precise rate constants in this system prove to be difficult to fit mainly because a_{11} and a_{22} have the identical functional form and a_{12} and a_{21} also have the identical functional form. This leads to a situation in which the fit of calculated and experimental relaxation times is quite similar for rather different values of the rate constants. For example, k_2 can be increased from 100 to 300 $M^{-1}\,s^{-1}$ while k_2' is decreased from 200 to 100 $M^{-1}\,s^{-1}$ and fits of calculated and experimental relaxation times are obtained which differ only marginally. Because of this, we have chosen to assign the indicated range for each of the rate constants. A representative fit is shown in Table III. k_3 is a somewhat different case. As the value assigned to k_3 increases, the calculated relaxation time decreases. At a value $k_3 = 10\ s^{-1}$, all calculated relaxation times are too fast, and since the k_3 term in the relaxation term is now dominant, there is very little variation in calculated relaxation time with reactant concentration. A value of $k_3 = 1\ s^{-1}$ produces the fit shown in Table III, but if its value is lowered to 0.1 s^{-1}, all calculated relaxation times increase by less than 10% in most cases. In fact, by varying k_2 and k_2' while leaving k_3 at this lower value, we can again obtain a reasonable fit of calculated and experimental relaxation times. Therefore, we have chosen to assign 1 s^{-1} as the upper limit of k_3.

The 1,2,3-propanetriol system should be characterized by two relaxation times. We have observed only one relaxation time in all experiments, and it turns out to be the positive root of the determinantal equation. From the rate constants used to fit τ_+, the value of τ_- can be calculated. τ_- turns out to be on the order of 0.1 s for all solutions. Although this is a fairly long relaxation time, it is within the time scale accessible to the instrument and we have previously observed[6] relaxation times longer than this in other boron acid systems. It is not unusual to observe fewer

Table IV. Stability Constants and Rate Constants for Methylboronic Acid/Ligand Systems

H_2L	$pK_a(H_2L)$	pK_1	k_1 (M^{-1} s^{-1})	k_{-1} (M^{-1} s^{-1})
salicylic acid[a,c]	2.83	2.35	5.5×10	1.2×10^4
mandelic acid[a]	3.22	2.68		
4-nitrocatechol[a,b]	6.69	4.37	4.5×10	1.0×10^6
catechol[a,b]	9.27	5.80	7.6	4.8×10^6
1,2-ethanediol	15.4	9.66	≤ 0.1	

[a] Reference 12. [b] Reference 9. [c] Salicylic acid forms a complex with a six-membered chelate ring. All of the other ligands form five-membered chelate rings.

than the maximum possible number of relaxation times, and factors which may contribute to this are discussed elsewhere.[6,18]

Discussion

Stability Constants. Boron acid complexation reactions are characterized by stability constants that decrease as the acidities of both the boron acid and the ligand decrease.[12] The present results are in accord with this trend. We have previously studied the reactions of $CH_3B(OH)_2$ with a variety of ligands, all of which are much more acidic than polyols (Table IV). A plot of ligand pK_a vs pK_1 for these reactions is linear, and the stability constants obtained in the present study are entirely consistent with the extrapolation of that line to include the polyols.

The small differences observed among the systems are consistent with expectations. For example, among the five-membered chelate ring systems, 1,2,3-propanetriol is the most acidic ligand,[19] and its five-membered chelate ring complexes are favored by a statistical factor of 2. The value of K_1 for 1,2,3-propanetriol is the largest, and this can be attributed to these two factors. The fact that six-membered rings are somewhat less stable than five-membered rings ($K_1' < K_1$) is unexceptional. Certainly, no particular effects due to ligand conformational equilibria are apparent. If the conformational equilibrium of any polyol favored the anti form, this would be reflected in a lower stability constant. Recent theoretical[20] and experimental[21] studies of 1,2-ethanediol show, however, that both in the gas phase and in solution the gauche O–C–C–O linkage is predominant. Molecular mechanics calculations[22] on other simple vicinal diols also indicate a preference for gauche as opposed to anti conformations in polar protic solvents. While differences among the ligands in the gauche/anti equilibrium certainly exist, the results presented in Table I suggest that they are relatively unimportant.

Rate Constants. (a) Trigonal $CH_3B(OH)_2$. The kinetic data can be fit with essentially no contribution from the pathways describing the reactions of trigonal $CH_3B(OH)_2$. Rate constants for these reactions (k_1, k_1') are, therefore, assigned upper limits of 0.1 M^{-1} s^{-1} (Table II). Further comment on the upper limit for these rate constants is possible, however, by considering the present result in the context of our previous work on similar systems (Table IV). Note that as the ligand becomes less acidic, the stability constant (K_1) decreases and this is reflected in both a decreasing forward rate constant (k_1) and an increasing reverse rate constant (k_{-1}). Although k_{-1} increases as the ligand becomes less acidic, we have also shown that k_{-1} levels off[12] at a maximum value of $\sim 10^7$ M^{-1} s^{-1}. Taking 10^7 M^{-1} s^{-1} as the upper limit for k_{-1} leads to even lower values for the upper limit of k_1. Since $k_1 = K_1k_{-1}$, the upper limit for k_1 ranges from 10^{-2} to 10^{-3} M^{-1} s^{-1}, depending on the particular ligand. Obviously, trigonal $CH_3B(OH)_2$ is quite unreactive with ligands which bear no acidic protons. This conclusion is consistent both with our previous experimental results (Table IV) and with the consequences of the proposed transition state for the reaction (**1**). The polyols do not contain any acidic protons, and the difficulty of chelate ring closure via proton transfer is reflected in the very small value of the rate constants.[23]

(b) Four-Coordinate $CH_3B(OH)_3^-$. The kinetic results (Table II) clearly and unambiguously show that complexation reactions of four-coordinate borates (k_2, k_2') are much faster than complexation reactions of trigonal boron acids. This result is rather surprising considering that kinetic studies[24] on the $B(OH)_3/B(OH)_4^-$ equilibrium show rapid ligand addition to the trigonal boron. So, despite the ease of increase of coordination number on trigonal boron, the more highly substituted four-coordinate borate undergoes reaction much faster. The experimental results in Table II show that borates react more rapidly than trigonal boron acids by factors of at least 10^3–10^4. On the basis of the analysis of upper limits for k_1 in the previous section, this factor could be $\geq 10^6$.

The dramatic difference in the rate constants for the reactions of trigonal and four-coordinate boron is the major kinetic result in Table II. The variation in the rate constants for the reactions of the various ligands with borate is much less pronounced, but some specific results should be mentioned. The lower stability constants for six-membered chelate ring systems compared with five-membered chelate ring systems ($K_2' < K_2$) seem to result mainly from faster opening of the six-membered rings ($k_{-2}' > k_{-2}$). This is readily apparent for the 1,2,3-propanetriol system and also from the comparison of 1,3-propanediol with 1,2-propanediol. In the latter case, it is interesting that the forward rate constant for the reaction of 1,3-propanediol is greater than that for the 1,2-propanediol reaction. Among the six-membered chelate ring systems we have studied to date, the reaction rate constant was found to decrease for dicarboxylic acids of increasing chain length,[2] but no pronounced effect was observed[12] in the case of an *o*-hydroxy carboxylic acid. It seems reasonable that one of the factors that might affect the forward rate constants is the possibility of intramolecular hydrogen bonding in the polyol. If this is more significant for 1,2-diols than for 1,3-diols, it could account for the somewhat faster reaction rates of 1,3-diols. A comparison with the more labile 1,2-ethanediol system, however, indicates that other factors might also be involved, and no definitive explanation can be given as yet to account for the observed differences in the rate constants.

The possibility of isomerization of the 1,2,3-propanetriol complexes via the paths denoted by k_3 and k_{-3} should also be briefly considered. The processes denoted by k_3 and k_{-3} involve ring opening, presumably via hydrolysis, to form a unidentate intermediate complex which then undergoes ring closure. It is interesting to note that the upper limit for k_3 is less than k_{-2} and, similarly, that the upper limit for k_{-3} is less than k_{-2}'. k_{-2} and k_{-2}' refer to reactions which involve the complete hydrolyses of five-membered and six-membered chelate ring complexes, respectively, while k_3 and k_{-3} refer to processes which involve partial hydrolysis followed by chelate ring closure. The kinetic results imply that hydrolysis of a unidentate intermediate may be faster than chelate ring closure.

Although enough is not yet known to propose a transition state

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(18) Eigen, M.; de Maeyer, L. *Technique of Organic Chemistry*; Weissberger, A., Ed.; Interscience: New York, 1963; Vol. VIII, Part II, pp 928–941.

(19) 1,2,3-Propanetriol is approximately twice as acidic as 1,2-ethanediol.

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(23) We have previously done one initial-rate stopped-flow study on a polyol reaction.[9] The data were evaluated in terms of trigonal boron acid being the reactive species. The present results argue against that interpretation. If those data are reevaluated with the assumption that four-coordinate borate is the reactive species, results consistent with the present study are obtained.

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Table V. Rate Constants for the Complexation Reactions of the Boric Acid/Lactic Acid System

reacn[a]	k_n	k_{-n}
1	$2.5\ M^{-1}\ s^{-1}$	$1.4 \times 10^3\ M^{-1}\ s^{-1}$
2	$\leq 1.8 \times 10^6\ M^{-1}\ s^{-1}$	$\leq 1.0\ s^{-1}$
3	$4.0 \times 10^3\ M^{-1}\ s^{-1}$	$6.1 \times 10^1\ s^{-1}$

[a] The numbers refer to the reactions pictured in eqs 1–3 and not to the reaction numbers in ref 6. All data are from ref 6.

for the reactions of four-coordinate borates, we can still say that it is likely to be associative in character and also to involve proton transfer. The assertion that the transition state is probably associative derives from the fact that if dissociation of a hydroxide were to occur prior to ligand coordination, one would expect the rate constants for the reactions of four-coordinate borates to be less than or equal to the rate constants for the reactions of trigonal boron acids. An associative transition state does not necessarily require an increase in coordination number on boron, but a five-coordinate transition state is certainly a possibility. Five-coordinate boron has been proposed[25] in the hydrolysis of BH_4^-, and calculations have been carried out[26] on the geometry of pentacoordinate boron. Hypervalent boron compounds have even been synthesized.[27]

The argument that proton transfer is probably also important arises from a consideration of the difference in reactivity of trigonal and four-coordinate boron species. In trigonal systems, the lack of reactivity of polyols is attributed to the difficulty of chelate ring closure via proton transfer to a leaving hydroxide on boron. In four-coordinate borates, the oxygens on boron are likely to be considerably more basic than the oxygens in trigonal boron acids. This assumption is based on the large difference[28] in boron–oxygen bond length between $B(OH)_3$ (1.37 Å) and $B(OH)_4^-$ (1.48 Å). The longer, weaker boron–oxygen bond in four-coordinate borates means that the hydroxide is both a better proton acceptor and a better leaving group. This facilitates both proton transfer from the ligand and chelate ring closure. It also accounts for the substitution lability of borates relative to trigonal boron acids.

It is useful to compare the present results with our previous work[6] on the boric acid/lactic acid system. Selected rate constants from that study are presented in Table V. Because of proton ambiguity, only upper limits could be determined[6,29] for the rate constant for the reaction of borate with lactic acid (eq 2), but the rate constant for substitution of a second ligand on the four-coordinate borate complex (eq 3) can be directly measured. We have suggested[6] that one effect of a bound ligand in this system may be to inhibit addition of a second ligand. This argument leads to the conclusion that the rate constant for addition of a second ligand (eq 3) may define a lower limit for substitution on borate by lactic acid (eq 2). Therefore, the forward rate constant for reaction of lactic acid with borate may be assumed to be between 4.0×10^3 and $1.8 \times 10^6\ M^{-1}\ s^{-1}$. In either case, the rate constant is at least 3 orders of magnitude greater than the rate constant for the reaction of lactic acid with trigonal boric acid (eq 1). This result is similar to the reactivity pattern observed for the $CH_3B(OH)_2$ and $CH_3B(OH)_3^-$ reactions with polyols. But, more importantly, it is also quite likely that lactic acid reacts much more rapidly than polyols with borates. This conclusion is somewhat uncertain because of the assumptions that must be made in the estimation of a lower limit for the borate/lactic acid rate constant. If it turns out to be generally true that rate constants for complexation reactions of borate increase with increasing ligand acidity, this could be another indication that proton transfer is significant in the transition state for the complexation reactions of borates.

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Appendix

Definitions of the constants used in the derivation of the relaxation expression for the 1,2,3-propanetriol system are as follows:

$$\alpha = 1 + \frac{K_a}{\overline{[H^+]}} \qquad \beta = 1 + \frac{K_{H_2L}}{\overline{[H^+]}}$$

$$\gamma = 1 + \frac{\overline{[OH^-]}}{\overline{[H^+]}} + \frac{\overline{[In^-]}}{K_{HIn} + \overline{[H^+]}}$$

$$P = \frac{\frac{1}{\alpha} + \frac{1}{\beta} - 1}{\alpha + \frac{\overline{[CH_3B(OH)_3^-]}}{\alpha\overline{[H^+]}} + \frac{\overline{[HL^-]}}{\beta\overline{[H^+]}}}$$

$$Q = -\frac{P\overline{[OH^-]}}{\overline{[H^+]}} \qquad R = \frac{1}{\alpha} - \frac{P\overline{[CH_3B(OH)_3^-]}}{\alpha\overline{[H^+]}}$$

$$S = \frac{1}{\beta} - \frac{P\overline{[HL^-]}}{\beta\overline{[H^+]}} \qquad T = 1 - R \qquad V = 1 - S$$

Registry No. Methylboronic acid, 13061-96-6; 1,2-ethanediol, 107-21-1; 1,2-propanediol, 57-55-6; 1,3-propanediol, 504-63-2; 1,2,3-propanetriol, 56-81-5.

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