absence of either $[(CH_3)_3N]_2BH_2^+$ or $[(CH_3)_3NBH_2NC_6H_7]^+$. Furthermore, the presence of more than one $R_3N{\cdot}BH_2CN$ species is indicated by two characteristic cyanide absorptions at 2135 and 2165 cm^{-1}. The assignment of the first one to unreacted $(CH_3)_3N{\cdot}BH_2NC$ suggests that the other band could belong to $C_6H_7N{\cdot}BH_2CN$.

The addition of diborane to the silver cyanide complex of $(CH_3)_3N{\cdot}BH_2NC$ has resulted in the characterization of $(CH_3)_3N{\cdot}BH_2NC{\cdot}AgCN{\cdot}BH_3$. This species could be formally considered to be a complex of the silver cation with the neutral ligand $(CH_3)_3N{\cdot}BH_2NC$ and the anion H_3BNC^-. The ability of H_3BCN^- to form complexes with metal ions,[3] together with the arguments above, suggest that similar complexes for the less stable isomer of the cyanoborohydride, H_3BNC^-, could be prepared by diborane coordination to the corresponding cyano species.

Registry No. $[(CH_3)_3NBH_2NCBH_2NC_6H_7]PF_6$, 62126-26-5; $[(CH_3)_3NBH_2NC)_2BH_2]I$, 62126-27-6; $(CH_3)_3N{\cdot}BH_2NC{\cdot}BCl_3$, 62126-29-8; $(CH_3)_3N{\cdot}BH_2NC{\cdot}BH_3$, 62126-07-2; $(CH_3)_3N{\cdot}BH_2N{=}C(CH_3)OSO_2F$, 62125-79-5; $(CH_3)_3N{\cdot}BH_2N{=}C(Cl)N(CO{-}CH_2)_2$, 62125-81-9; $(CH_3)_3N{\cdot}BH_2NC{\cdot}AgCN{\cdot}BH_3$, 62126-24-3; 4-methylpyridine–iodoborane, 59499-23-9; trimethylamine–isocyanoborane, 60045-36-5; trimethylamine–isocyanoborane–iodoborane, 62126-22-1; boron trichloride, 10294-34-5; diborane, 19287-45-7; methyl iodide, 74-88-4; $[(CH_3)_4N]I$, 75-58-1; methyl fluorosulfate, 421-20-5; *N*-chlorosuccinimide, 128-09-6; $(CH_3)_3N{\cdot}BH_2CN$, 30353-61-8; $(CH_3)_3OBF_4$, 420-37-1; 4-methylpyridine, 108-89-4.

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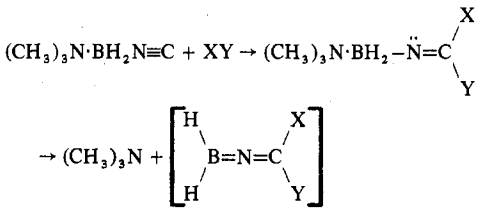
(27) The α-addition reaction of any of these reagents to $(CH_3)_3N{\cdot}BH_2NC$ and the subsequent liberation of trimethylamine could be seen as



The isolation of the intermediate species in the fluorosulfonate case could be caused by the inductive effect of this anion being able to prevent the displacement of trimethylamine by the nitrogen electron pair. Less electronegative anions such as chloride and iodide should be less able to do so.

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Mechanism of the Complexation of Boron Acids with Catechol and Substituted Catechols[1]

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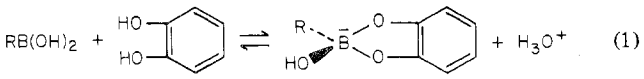
Boron acids form only 1:1 complexes with catechol and catechol derivatives according to the equation $RB(OH)_2 + H_2L \rightleftarrows RB(OH)L^- + H_3O^+$. Both $B(OH)_3$ and phenylboronic acid, $PhB(OH)_2$, were studied with 4-nitrocatechol, catechol, and 4-methylcatechol. Stability constants for the reactions were determined by pH titration methods and kinetics were done by temperature jump at $\mu = 0.1$ M (KNO_3) and 25 °C. The stability constants increase with increasing ligand acidity. Kinetically, this is reflected in both an increased forward rate constant and a decreased reverse rate constant for the more acidic ligands. This is discussed in terms of a mechanism which emphasizes the importance of proton transfer. Complexes of $B(OH)_3$ have smaller stability constants than the analogous $PhB(OH)_2$ complexes; this, too, is reflected in both the forward and reverse processes. 4-Nitrocatechol is sufficiently acidic such that rate constants for the reactions of the 4-nitrocatecholate anion could be determined with both $B(OH)_3$ and $PhB(OH)_2$. The rate constant for this reaction is much greater than previously determined rate constants for reactions of less basic ligand anions. Possible reasons for this are discussed. The reaction of $PhB(OH)_2$ with mannitol was also investigated by pH titration and stopped flow under the same experimental conditions. These results are consistent with those for more acidic ligands and indicate that even weakly acidic ligands can react with trigonal boron acids.

Many kinetics studies involving catechol (1,2-dihydroxybenzene) and substituted catechols have recently appeared in the literature. These have included studies of substitution processes with both transition metal ions[2] and oxy anions.[3,4] Oxidation of catechol or substituted catechols by metal ions,[5] metalloproteins,[6] and molecular oxygen[7] has also been widely investigated. The last process is catalyzed by transition metal ions.[8]

The trigonal boron acids, $RB(OH)_2$, are an additional class of molecule which is capable of forming complexes with catechol and substituted catechols. The overall general reaction is



(1)

The boron is four-coordinate in the complex, the ligand being bidentate. The reaction is both an addition reaction (one ligand donor atom occupying a previously vacant site on boron) and a substitution reaction (the second ligand donor atom displacing an OH^- from boron). Both ligand protons are displaced on reaction.

The present study concerns the reactions of both phenylboronic acid, $PhB(OH)_2$, and boric acid, $B(OH)_3$, with catechol and some substituted catechols. We have previously examined reactions of dicarboxylic acids[9,10] and α-hydroxy acids[11,12] with boron acids. Substituted catechols differ in two important respects from these two classes of ligand—they are considerably less acidic and are rigid. Both of these characteristics are of mechanistic significance.

Experimental Section

Phenylboronic acid (Alfa), boric acid (Fisher), catechol (Fisher), 4-nitrocatechol (Aldrich), mannitol (Fisher), *trans*-1,2-cyclohexanediol (Aldrich), and sodium bisulfite (Baker) were used without further purification. That the ligands required no further purification was determined by titration of the ligand with standard 0.1 N NaOH. In the case of 4-nitrocatechol, mass spectra of the ligand as received and after sublimation were taken and found to be identical. Solid 4-methylcatechol (Aldrich) was vacuum-distilled and the purity of the resultant white crystalline material checked by pH titration.

Acid dissociation constants of the ligands and stability constants for complexation reactions were determined by pH titration methods using a Corning Model 12 research pH meter. The titrations were performed under a nitrogen atmosphere in a double-walled beaker maintained at 25 °C by means of a circulating water bath. All solutions were made up to 0.1 M ionic strength by addition of potassium nitrate, and the hydrogen ion activity coefficient was calculated using the Davies equation.[13]

Kinetic studies of the reactions of phenylboronic and boric acids with catechol, 4-nitrocatechol, and 4-methylcatechol were performed on the temperature-jump instrument described previously.[11] The traces obtained experimentally were plotted semilogarithmically. In all cases, simple exponentials were observed. Relaxation times obtained were averages of at least three traces, and the error is within ±15%.

Kinetic studies of the phenylboronic acid–mannitol system were carried out by stopped flow. The instrument used was an Aminco-Morrow stopped flow which was mounted on a Beckmann DU spectrophotometer. Reactions were monitored spectrophotometrically and the traces recorded on a storage oscilloscope.

Blank solutions of the ligands and of phenylboronic acid were prepared and showed no effect at any pH over the entire time range. The boric acid blank exhibited a relaxation time at pH ~6 which is in the same time range as the relaxation time characteristic of complexation. The effect observed in the boric acid blank at this pH is due to polymerization.[14] However, at pH ~4, the boric acid blank exhibited no relaxation time in any time range in concentrations as high as 0.12 M. Therefore, all boric acid studies have been carried out at pH ~4 with initial boric acid concentration never exceeding 0.1 M.

Depending upon the pH of the solution, either bromophenol blue or chlorophenol red was used to monitor the reaction.

Stability Constants

The pK_as of catechol, 4-nitrocatechol, and 4-methylcatechol at $\mu = 0.1$ M (KNO_3) and 25 °C were determined by titration with standard 0.1 N NaOH. Values of pK_{a_1} are in good agreement with literature values determined under similar conditions; pK_{a_2} values in the literature vary widely. The value of pK_{a_2} is not critical in the evaluation of our stability constant and kinetic data. The results are as follows: 4-nitrocatechol, pK_{a_1} = 6.69, pK_{a_2} = 10.57 (lit.[15] 6.78 and 10.64); catechol, pK_{a_1} = 9.27, pK_{a_2} = 11.49 (lit.[16] 9.25 and 12.37); 4-methylcatechol, pK_{a_1} = 9.39, pK_{a_2} = 11.59. The pK_a of boric acid[17] is 8.98; the pK_a of phenylboronic acid[11] is 8.72.

Table I. Stability Constants of Phenylboronic and Boric Acid Complexes

Ligand	pK_{a_1}	pK_{a_2}	$K(PhB(OH)_2)$	$K(B(OH)_3)$
Mannitol	13.5[a]		5.3×10^{-6}	
4-Methylcatechol	9.39	11.59	3.0×10^{-5}	6.3×10^{-6}
Catechol	9.27	11.49	4.7×10^{-5}	1.1×10^{-5}
4-Nitrocatechol	6.69	10.57	9.5×10^{-4}	1.5×10^{-4}
Lactic acid[11]	3.70		3.7×10^{-3}	
Malonic acid[10]	2.59	5.25	2.6×10^{-2}	
Oxalic acid[9]	1.04	3.78	3.2	
Tartaric acid	2.89[b]	4.52[b]		1.85×10^{-2} [c]

[a] J. Thamsen, *Acta. Chem. Scand.*, 6, 270 (1952). [b] V. Frei, *Collect. Czech. Chem. Commun.*, 30, 1402 (1965). [c] L. I. Katzin and E. Gulyas, *J. Am. Chem. Soc.*, 88, 5209 (1966); see also ref 12.

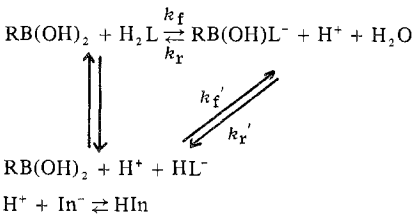
Stability constants for the various complexation reactions (eq 1) were determined by two pH titration methods. One method was the usual one involving titration of a boron acid–ligand solution with standard 0.1 N NaOH. In the second case, boron acid was titrated with ligand (and vice versa) after the two solutions had been adjusted to the same initial pH and ionic strength. In the second method, the decrease in pH upon complexation was monitored. With both techniques, studies were made with varying boron acid and ligand concentrations, and the pH depression data were taken over a wide range of initial pHs. The ionic strength of the solutions in all cases was made up to 0.1 M with KNO_3. Equations for the calculation of stability constants from these data are found in a previous paper.[9]

The reactions of phenylboronic acid with the various ligands produce only 1:1 complexes. In the case of boric acid, titration results consistently show only 1:1 complex formation with catechol, 4-nitrocatechol, and 4-methylcatechol. The conclusion that only 1:1 boric acid–catechol complexes exist was first reported in a stability constant study[18] although a similar previous study had indicated the formation of two complexes.[19] Other stability constant determinations with ligands of this type have also indicated the presence of only 1:1 complexes.[15,20] $B(OH)_3$ and mannitol, however, form a 1:2 complex.[21]

Titrations of phenylboronic acid with *trans*-1,2-cyclohexanediol were also carried out. Over a wide pH range and with varying ratios of phenylboronic acid to diol, our results indicate negligible complex formation. This result is in agreement with a previous study[18] which also concluded that the cis form exhibited minimal complex formation. The results of the stability constant studies for both boric acid and phenylboronic acid are summarized in Table I.

Kinetic Results and Treatment of Data

The complete reaction scheme for the complexation of boron acid with ligand is



The protolytic reactions of the indicator and of the ligand are very fast and, as such, are always in equilibrium with respect to the much slower complexation reactions involving the boron acid. Thus, the observed relaxation time is char-

Table II. Relaxation Spectra of $PhB(OH)_2$/4-Nitrocatechol Solutions

$[PhB(OH)_2]$, M	$[4\text{-}NO_2H_2Cat]$, M	pH[a]	τ, ms Exptl	τ, ms Calcd
0.0396	0.0364	4.33	0.20	0.20
0.0396	0.0364	3.91	0.22	0.27
0.0396	0.0364	3.48	0.41	0.41
0.0163	0.0439	3.90	0.49	0.43
0.0163	0.0439	3.42	0.77	0.80
0.0407	0.0228	4.43	0.25	0.27
0.0407	0.0228	3.97	0.30	0.33
0.0407	0.0228	3.49	0.69	0.64
0.0407[b]	0.0510	4.48	0.25	0.26
0.0407[b]	0.0510	4.05	0.18	0.19
0.0407[b]	0.0510	3.60	0.33	0.28
0.0407[b]	0.0459	6.02	1.97	1.99
0.0407[b]	0.0459	5.59	1.45	1.31

[a] The indicator in all solutions between pH 4.48 and pH 3.42 was bromophenol blue (2.52×10^{-5} M); above pH 5.59 chlorophenol red (2.02×10^{-5} M) was used. All reactions were monitored at λ 580 nm. [b] These solutions contain 0.01 M sodium bisulfite.

acteristic of complex formation.

The relaxation time is given by the two-term expression

$$\frac{1}{\tau} = k_f\left[S[\overline{HB}] + [\overline{H_2L}] + \frac{1}{K}(R[\overline{Cx^-}] + Q[\overline{H^+}])\right] + k_f'\left[(Q-S)[\overline{HB}] + [\overline{HL^-}] + \frac{K_{a_1}}{K}Q\right]$$

where k_f and k_r are the forward and reverse rate constants associated with complex formation via the fully protonated form of the ligand, and k_f' and k_r' are characteristic of the reaction of the anionic form of the ligand. In the pH range examined the concentration of borate anion, $RB(OH)_3^-$, is negligible. Definitions of other terms present in the relaxation expression appear in the Appendix.

Previous studies involving reactions of catechol in neutral and basic solution have been carried out in the presence of sodium bisulfite to inhibit oxidation of the catechol.[3,4] Our studies of catechol and 4-nitrocatechol were carried out at pH ~4 and pH ~6 both with and without bisulfite. The relaxation times at pH ~4 with bisulfite were essentially identical with those obtained without bisulfite, but there was a marked decrease in the amplitude of the effect. At pH ~6 bisulfite had a definite effect on the relaxation time, and studies at this pH must be carried out with bisulfite present. However, because of the decrease in amplitude upon addition of bisulfite, measurements were sometimes impossible. For example, reproducible data were not obtained with catechol at pH ~6.

The relaxation times characteristic of phenylboronic acid and boric acid complexation with catechol and 4-methylcatechol were fit to a one-term kinetic expression. The first term in the relaxation equation is dominant; that is, because of the pK_a of the ligand, the contribution to τ of the reaction of boron acid and ligand anion is negligible. The best fit rate constants for the reactions of phenylboronic acid are $k_f = 110$ M^{-1} s^{-1} with catechol and $k_f = 120$ M^{-1} s^{-1} with 4-methylcatechol. The results for boric acid are $k_f = 60$ M^{-1} s^{-1} for reaction with catechol and $k_f = 54$ M^{-1} s^{-1} for reaction with 4-methylcatechol.

In the case of 4-nitrocatechol, however, the pK_a is lower, and even at pH ~4 there is considerable contribution to the relaxation time of the reaction of boron acid with the anionic form of the ligand. Here k_f and k_f' were determined by fitting the data to the full two-term expression given above. The best fit is $k_f = 650$ M^{-1} s^{-1} and $k_f' = 7.0 \times 10^4$ M^{-1} s^{-1} for phenylboronic acid and $k_f = 250$ M^{-1} s^{-1} and $k_f' = 5.0 \times 10^4$ M^{-1} s^{-1} for boric acid. Table II presents the experimental and calculated relaxation times for one series of solutions. For similar concentrations, the relaxation times characteristic of the other systems were in the same time range. The results of this study as well as pertinent results from previous studies for the reaction of boron acids with various fully protonated ligands are summarized in Table III. Tabulated kinetic results for the complexation reactions of boron acids with the anionic form of the ligands appear in Table IV. The error associated with all of the reported rate constants is ±10%.

Table III. Rate Constants for Boron Acid Reactions with Fully Protonated Ligands

Ligand	K	k_f, M^{-1} s^{-1}	k_r, M^{-1} s^{-1}	log k_r
Phenylboronic Acid Complexes				
Mannitol	5.3×10^{-6}	~50	~10^7	7
4-Methylcatechol	3.0×10^{-5}	120	4.0×10^6	6.6
Catechol	4.7×10^{-5}	110	2.3×10^6	6.4
4-Nitrocatechol	9.5×10^{-4}	650	6.8×10^5	5.8
Lactic acid[11]	3.7×10^{-3}	140	3.8×10^4	4.5
Malonic acid[10]	2.6×10^{-2}	350	1.3×10^4	4.1
Oxalic acid[9]	3.2	2.0×10^3	6.2×10^2	2.8
Boric Acid Complexes				
4-Methylcatechol	6.3×10^{-6}	54	8.6×10^6	6.9
Catechol	1.1×10^{-5}	60	5.4×10^6	6.7
4-Nitrocatechol	1.5×10^{-4}	250	1.7×10^6	6.2
Tartaric acid[12]	1.85×10^{-2}	475	2.6×10^4	4.4

Table IV. Rate Constants for Boron Acid Reactions with the Anionic Form of Various Ligands

Ligand	$K' = K/K_{a_1}$	k'_f, M^{-1} s^{-1}	k'_r, s^{-1}
Phenylboronic Acid Complexes			
4-Nitrocatecholate	4.6×10^3	7.0×10^4	15
Lactate[11]	1.8×10	1500	83
Bimalonate[10]	1.0×10	150	15
Binoxalate[9]	3.3×10	330	10
Boric Acid Complexes			
4-Nitrocatecholate	7.3×10^2	5.0×10^4	68
Tartrate[12]	5	215	43

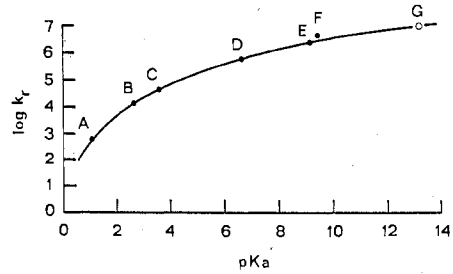
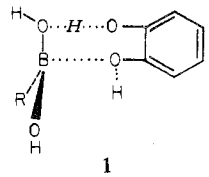


Figure 1. Plot of log k_r vs. ligand pK_{a_1} for various ligands reacting with $PhB(OH)_2$. A–G represent oxalic acid, malonic acid, lactic acid, 4-nitrocatechol, catechol, 4-methylcatechol, and mannitol, respectively. All kinetic experiments were performed by temperature jump except G which was performed by stopped flow.

Discussion

Reactions of the Fully Protonated Form of the Ligands. The stability constants for the formation of boron acid complexes increase with increasing ligand acidity (Table I). That this is reflected in both the forward and reverse rate constants is clear from the kinetic results presented in Table III. Although the forward rate constants generally increase with increasing ligand acidity, the correlation is not precise. For the reverse process, such a correlation does exist. This is displayed in Figure 1 for the reactions of $PhB(OH)_2$.

This plot emphasizes the significance of proton transfer in these reactions and suggests the transition state **1**. The proton



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which is transferred is italic. In the forward direction it is transferred from the fully protonated catechol to a leaving OH^- on boron; in the reverse direction it is transferred from the entering water molecule to the leaving catecholate. The generalization of this transition state to ligands other than catechol is obvious. Since the reaction rate correlates with pK_{a_1} and not pK_{a_2}, it is probable that displacement of the second ligand proton by boron in the forward direction and its subsequent direct protonation in the reverse direction are relatively facile processes. Similarly, the hybridization change of boron ($sp^2 \rightarrow sp^3$) is very fast.[14] In the transition state the boron may be five-coordinate although this is not shown explicitly in **1**. That is, both ligand oxygen donor atoms may be partially coordinated to boron. Five-coordinate boron has been proposed[22] in the hydrolysis of BH_4^-. Calculations have recently been done concerning possible geometries of such species.[23]

The curvature in Figure 1 is consistent with the general mechanism for proton transfer advanced by Eigen.[24] As the leaving ligand becomes more basic, the proton-transfer rate constant increases, leveling off at a maximum value. Less basic acceptors react more slowly. Since both of the oxygens in the donor and acceptor molecules may be partially coordinated to boron, their pK_as are not known. However, since the proton donor is constant, the plot is similar to the typical plot with ΔpK as the abscissa.

There are at least two reasons why the forward rate constants do not display such a precise correlation.[25] One is that the rate constants must be statistically adjusted to reflect the different number of potential donor atoms in the various ligands. These factors are not strictly statistical when all of the donor atoms in a particular ligand are not equivalent. Even considering this factor, the catechols seem to react faster as a class than the results for the more acidic ligands would suggest. For example, 4-nitrocatechol reacts faster with $PhB(OH)_2$ than does lactic acid.

A second difference between the ligands which might account for this is their flexibility. The rigid catechols are properly oriented for reaction while the other ligands (which have an additional rotational degree of freedom) suffer a loss of configurational entropy in the transition state **1**. This factor favors the more rigid ligands and may be responsible for their enhanced reactivity. Since the ligand in the transition state is constrained to the geometry shown, this effect is of minimal importance in the reverse direction.

It is interesting to note that the stability constants for the $PhB(OH)_2$ complexes are generally greater than those for $B(OH)_3$ complexes by factors of 4–6. In kinetic terms, this difference is found in both a larger forward rate constant and a smaller reverse rate constant compared with the analogous $B(OH)_3$ reaction. The difference in the rate constants for the reactions of $B(OH)_3$ and $PhB(OH)_2$ probably reflects differences in the nature of the boron atom in the two boron acids, $PhB(OH)_2$ being more acidic than $B(OH)_3$ by a factor of 2.

Reactions of the Ligand Anions. The reverse rate constants for the reactions involving the ligand anions (Table IV) are remarkably similar, all being about 12 s^{-1} in the case of $PhB(OH)_2$ (with the exception of lactate[26]) and averaging 55 s^{-1} for the two $B(OH)_3$ reactions reported. In this case the incoming ligand is OH^-, not H_2O, and the transition state does not involve proton transfer as shown in **1**. The similar rate constants may indicate that bonds of comparable strength are being broken and formed in the transition states for the various ligands considered.

The forward rate constants show some variation, partly for the reasons mentioned in the previous section. However, the 4-nitrocatecholate reacts much faster than the others and a general increase in rate constant with increasing ligand basicity may exist. A similar result has recently been reported by Kustin[4] in the reactions of catechol and catechol derivatives with octahedral[27] $HMoO_4^-$. Following his argument, highly basic ligands orient several water molecules about them such that the OH^- on boron is protonated by an intervening water molecule, an OH^- being injected into solution at a point removed from the reaction site. One difference between the two systems is that the fully protonated form of the ligand is reported to be unreactive with $HMoO_4^-$. The reactions are not precisely similar, but it is of interest to note that in this case the fully protonated ligand does react but with a considerably lower rate constant than the anion.

Two of our previous studies lend further support to the notion that ligand basicity is significant in determining the rates of reaction of anionic ligands. Both the oxalate[9] and malonate[10] dianions were found to react with very low (or zero) rate constants. These dianions are the least basic ligands we have examined and are not capable of orienting solvent about them as effectively as the catechol anions. In the case of these ligands, donor atom protonation is required for successful chelation. However, the dianions of catechols, which are more basic by several orders of magnitude, might be very reactive with trigonal $RB(OH)_2$ but the experiment would be very difficult to do. At the basic pHs where dianions of catechol exist in reasonable concentration, boron acids exist principally in the form of tetrahedral anions.

Finally, the relative reactivities of $PhB(OH)_2$ and $B(OH)_3$ systems parallel the results obtained in the case of fully protonated ligands. $PhB(OH)_2$ reacts faster with a given ligand anion and the reverse process is slower than the analogous $B(OH)_3$ reaction.

1:2 Boric Acid Complexes. We found no evidence for the formation of 1:2 complexes of boric acid with catechol and the substituted catechols we examined. This is consistent with the results of recent stability constant studies.[15,20] This result is surprising since it is easy to visualize kinetically a condensation between two pairs of adjacent hydroxyls on the 1:1 complex (eq 1, with R = OH) and the incoming catechol ligands although other mechanistic pathways can also be envisioned for this substitution reaction. Our results, both kinetic and thermodynamic, support the conclusion that only 1:1 complexes are formed under the experimental conditions. It is interesting to consider why the reaction to form 1:2 complexes does not occur.

Other 1:2 complexes clearly exist with ligands which are more acidic[28,29] (carboxylic acids) and less acidic[19,21] (mannitol and other polyhydroxy molecules) than catechol. While no definitive explanation is presently possible, once again a major factor may be differences in ligand flexibility and geometry. A rigid ligand is favored in terms of relative rate over a flexible ligand only if it is of precisely the required geometry for reaction. For example, *trans*-1,2-cyclohexanediol does not form complexes with boron acids and other studies indicate that only minimal complex formation may occur[18] with the cis isomer. These ligands do not have rotational freedom about the C–C bonds and the noncoplanarity of the hydroxyls does not facilitate reaction. The geometry of catechol may similarly prohibit formation of a second complex, a reaction for which the stereochemical constraints are surely different from those for the formation of 1:1 complex.

It is interesting to note that this result is also consistent with Kustin's mechanistic study[4] of the reactions of tetrahedral MoO_4^{2-} and octahedral $HMoO_4^-$ with catechol. Fully protonated catechol reacts with tetrahedral MoO_4^{2-} only as an addition reaction and is unreactive with octahedral $HMoO_4^-$, a reaction which bears some similarity to the potential reactions of catechol with tetrahedral boron compounds.

Formation of Polyol Complexes. $PhB(OH)_2$ forms a 1:1 complex with mannitol, a polyol with six hydroxyl groups. The pK_as of aliphatic polyols are in the range 13–14. If our proposed mechanism is correct (Figure 1), the reverse rate constants for all aliphatic polyols would be expected to be quite similar. The wide variation in stability constants for complexes with various polyols[19] should be found in the forward rate constants for the reactions. The forward rate constants will reflect both extensive statistical and stereochemical differences among the ligands.

An initial-rate stopped-flow study was carried out in acid solution on the $PhB(OH)_2$/mannitol system, reaction being monitored by acid–base indicators. Reaction was complete within 50 ms with concentrations as dilute as 0.015 M in each reactant. The forward rate constant determined from the initial slope is 50 M^{-1} s^{-1}. This leads to a reverse rate constant of approximately 10^7 s^{-1}. This initial rate study is subject to considerably larger errors than the temperature-jump kinetic studies on the other ligands. However, the result is of sufficient accuracy to conclude that it is consistent with the general mechanism proposed for these reactions. No temperature-jump studies were successful with this ligand. However, the above rate constants predict very short relaxation times under the experimental conditions.

One reason this study was carried out was to determine whether polyols would complex with trigonal boron acids. Many previous authors have stated that this reaction occurs with the tetrahedral borate ion.[19,21,30] The reasoning in most of these cases was based on thermodynamic arguments and had to do with the interpretation of stability constant data or the dependence of complex concentration on solution acidity. Since our pH depression experiments were carried out in acid solution, we have derived equations[9,11] which express the change in pH in terms of the concentration of the trigonal form and expressed our stability costants in this way. Most other studies of this type were carried out at the pK_a of the boron acid and equations describing the pH change were derived assuming that the tetrahedral form reacts. While this leads, in this case, to a relatively simple expression for concentration of complex produced, it is not sufficient evidence to show that the tetrahedral form is in fact the reactive species. Our more complicated expression[9] for this type of titration can be used and results identical with those reported are obtained.

In our previous work, we have assumed that the hydroxyl oxygen of an α-hydroxycarboxylic acid must attack the boron atom with ring closure occurring via the carboxyl.[11,12] The present result suggests that this is not absolutely true, although ring closure via the carboxyl would be the much faster pathway.

While it is true that polyols react more slowly with trigonal boron acids than do more acidic ligands, they do react. They may even react more rapidly with tetrahedral borate than with trigonal boron acids, but this is not yet known.

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Appendix

The terms appearing in the expression for the relaxation time are defined as

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

$$A = \alpha(K_{a_1} + [\overline{H^+}]) + [\overline{HL^-}]$$

$$Q = \frac{(A/[\overline{B^-}])(K_a + [\overline{H^+}]) + K_{a_1} + [\overline{H^+}]}{A[\overline{H^+}]/[\overline{B^-}] + K_{a_1}}$$

$$R = \frac{[\overline{H^+}] - K_{a_1}K_a/[\overline{H^+}]}{K_{a_1}[\overline{B^-}]/[\overline{H^+}] + A}$$

$$S = \frac{\left\{\dfrac{\alpha[\overline{H^+}] + [\overline{HL^-}]}{[\overline{B^-}] + \alpha[\overline{H^+}]}\right\} K_a + [\overline{H^+}]}{\left\{\dfrac{\alpha[\overline{H^+}] + [\overline{HL^-}]}{[\overline{B^-}] + \alpha[\overline{H^+}]}\right\} [\overline{H^+}] + K_{a_1}}$$

Where all of the concentrations are equilibrium concentrations, HB represents trigonal boron acid, and B^- represents the tetrahedral borate anion. K_{a_1} is the first acid dissociation constant of the ligand and K_a is the acid dissociation constant of boron acid.

Registry No. $PhB(OH)(mannitol)^-$, 62166-61-4; $PhB(OH)(4\text{-methylcatechol})^-$, 62154-36-3; $B(OH)_2(4\text{-methylcatechol})^-$, 62154-37-4; $PhB(OH)(catechol)^-$, 62154-38-5; $B(OH)_2(catechol)^-$, 16986-33-7; $PhB(OH)(4\text{-nitrocatechol})^-$, 62154-39-6; $B(OH)_2(4\text{-nitrocatechol})^-$, 18955-19-6; $PhB(OH)_2$, 98-80-6; $B(OH)_3$, 10043-35-3.

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