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Thermodynamics of Several 1:1 and 1:2 Complexation Reactions of the Borate Ion with Bidentate Ligands. ^{11}B NMR Spectroscopic Studies[1]

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The borate ion, $B(OH)_4^-$, is capable of forming anionic complexes of both 1:1 and 1:2 stoichiometries with bidentate chelating ligands. The reactions are $B(OH)_4^- + H_2X \leftrightarrow BX^- + 2H_2O$ (K_1) and $BX^- + H_2X \leftrightarrow BX_2^- + 2H_2O$ (K_2). Reactions with 1,2-ethanediol, 1,2-propanediol, glycolic acid, lactic acid, and oxalic acid are reported. The successive reactions of the diols with $B(OH)_4^-$ are shown to be thermodynamically similar. In marked contrast, the successive addition of the more acidic α-hydroxy carboxylic acids is characterized by very different thermodynamic parameters for each step. Compared with the first reaction, addition of a second ligand has a much less favorable enthalpy of reaction which is only partially balanced by a much more favorable entropy of reaction. The net result accounts for the experimental observation that the ratio K_1/K_2 is very large for these ligands. The dramatic difference in the thermodynamics of second ligand addition for acidic ligands reaches its limit with oxalic acid, in which case addition of a second ligand does not occur. Thermodynamic results are also presented for several mixed-ligand systems. Thermodynamic parameters were determined from the temperature dependence of K_1 and K_2 as measured by ^{11}B NMR spectroscopy.

The borate ion, $B(OH)_4^-$, can react with bidentate chelating ligands to form anionic complexes of both 1:1 and 1:2 stoichiometries. The overall reactions are shown in (1) and (2). Some ligands which undergo this type of reaction are, in order of increasing acidity, polyols, 1,2-dihydroxybenzenes, α-hydroxy carboxylic acids, and dicarboxylic acids. Stability constants for BX^- complex formation (K_1) increase as the acidity of the ligand increases.[2,3] The ratio of successive stability constants (K_1/K_2) also increases with increasing ligand acidity. For polyols the ratio is close to a purely statistical ratio,[2d,4] but the more acidic ligands have ratios which exceed the statistical ratio by factors which are $\geq 10^3$. Although these results have been in the literature for some time, no complete thermodynamic study has ever been carried out to provide an explanation for the remarkably different behaviors of the various ligands. Those few thermodynamic studies which have been carried out involve only polyols,[5–10] sugars,[6–8,11] and 1,2-dihydroxybenzene.[6,7,12] The results of the earlier thermodynamic studies are, however, quite inconsistent with one another, and we have discussed[13] probable reasons for this difficulty.

We recently established[13] that variable-temperature ^{11}B NMR spectroscopy is a useful and accurate technique for determining stability constants and thermodynamic parameters ($\Delta H°$ and $\Delta S°$) for borate complexation reactions. In that study we were able to show, in contrast to previous reports in the literature, that reactions of 1,2-diols with borate ions (eq 1) are all very similar thermodynamically. Here we considerably extend our application of variable-temperature ^{11}B NMR spectroscopy to include more acidic ligands and BX_2^- complex formation (eq 2).

Experimental Section

Boric acid, 1,2-ethanediol (H_2E), 1,2-propanediol (H_2P), glycolic acid (H_2G), oxalic acid (H_2Ox), potassium nitrate, and deuterium oxide (Aldrich) were all used as received. Lactic acid (H_2L) (Aldrich) was refluxed prior to use as described previously.[14] Acid dissociation constants at 25 °C (μ = 0.10 M (KNO_3)) for oxalic acid[15] and lactic acid[14] have been previously determined by pH titration with standard 0.1 N NaOH. Enthalpies and entropies of dissociation of glycolic acid and lactic acid were determined by measuring K_a as a function of temperature in a thermostated cell under a nitrogen atmosphere using a Fisher Accumet 950 pH meter. The stability constants and thermodynamic parameters for the various borate complexation reactions were determined by variable-temperature ^{11}B NMR spectroscopy as described in detail elsewhere.[13] All solutions were prepared using 20% D_2O in H_2O as the solvent mixture. Boric acid concentrations in various experiments ranged from 0.05 to 0.20 M, and ligand concentrations ranged from 0.10 to 1.0 M. Ionic strength was adjusted by the addition of the requisite amount of KNO_3, and it was maintained at 0.10 M. pH measurements and NMR spectra were recorded over a temperature range from 280 to 330 K. The temperature at the probe given by the variable-temperature unit was checked by a calibration method described in the literature.[16]

Results and Treatment of Data

We have discussed previously[2d] the distribution of species as a function of pH for borate complexation reactions with various ligands. Representative distribution diagrams are contained in that paper. For polyols, the essential results are that borate complex ions are formed only in basic solution and that the ligands must be present in relatively large excess for 1:2 complexes to be present in reasonable concentration. By contrast, large concentrations of 1:2 borate/α-hydroxy carboxylic acid complexes are easily observed, but only in acidic solution. In the case of 1,2-dihydroxybenzene, there is no pH at which the concentration of

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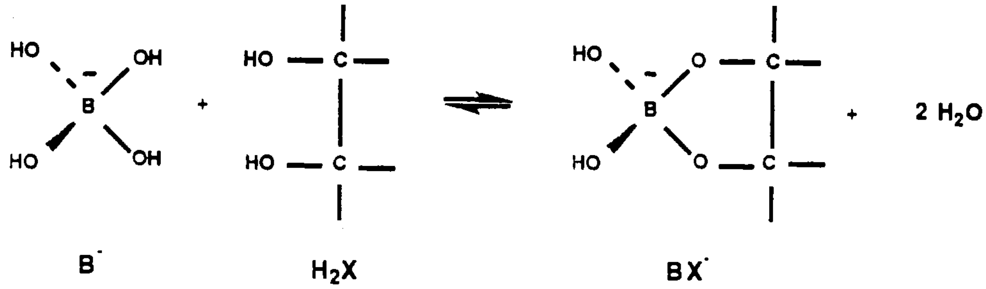

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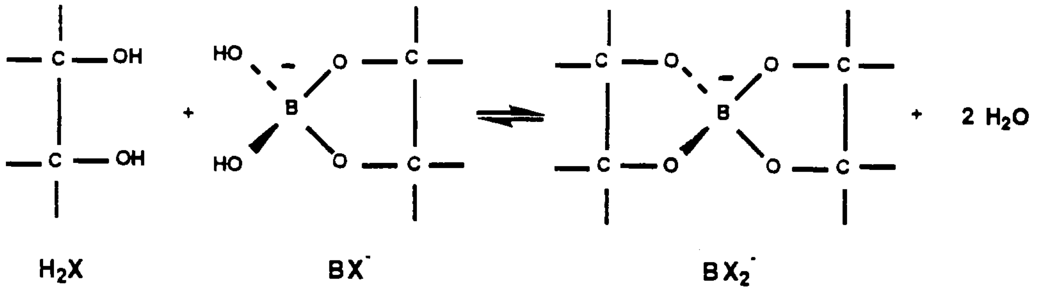

(2)

Table 1. Thermodynamic Parameters for Particular Ligands Reacting with Different Tetrahedral Boron Centers: $H_2X + BY_n^- \leftrightarrow BXY_n^- + 2H_2O$ ($n = 0, 1; X = Y$ or $X \neq Y$)[a]

reaction	K(298 K)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/(mol K))
$H_2E + B^-$	1.4	−18(±2)	−58(±8)
BE^-	0.18	−3(±3)	−24(±10)
BL^-	6.5×10^{-2}	−12(±3)	−63(±7)
$H_2P + B^-$	2.8	−17(±1)	−50(±2)
BP^-	0.82	−15(±3)	−49(±7)
BL^-	0.32	−5(±3)	−27(±8)
$H_2G + B^-$	1.3×10^5	−43(±2)	−46(±6)
BG^-	10	8(±3)	45(±10)
$H_2L + B^-$	7.2×10^5	−51(±2)	−60(±5)
BL^-	61	11(±4)	74(±10)
BE^-	3.1×10^4	−45(±3)	−65(±7)
BP^-	7.8×10^4	−39(±3)	−37(±8)
$H_2Ox + B^-$	1.6×10^8	−46(±2)	4(±5)
BOx^-	0		

[a] H_2E = 1,2-ethanediol, H_2P = 1,2-propanediol, H_2G = glycolic acid, H_2L = lactic acid, and H_2Ox = oxalic acid. Numbers in parentheses denote standard deviations.

1:2 complex is particularly high,[2d] and therefore, that system is not included here.

Diols. At high pH (≥11) it is possible to keep the concentrations of borate (≤0.10 M) and diol (≤0.10 M) sufficiently low so that only 1:1 complex is observed. This was the strategy in our previous study,[13] in which the $B(OH)_4^-$/1,2-ethanediol and $B(OH)_4^-$/1,2-propanediol systems were studied. The pK_a of boric acid is sufficiently low (8.98) that essentially all uncomplexed boron at pH ≥11 is present as the borate ion and integration of the ^{11}B NMR spectra allows the direct calculation of K_1 at each temperature. Results of this previous study are included in Table 1. Extending the technique to measure K_2 and the thermodynamic parameters for 1:2 complex formation is simply a matter of decreasing the concentration of borate ion (~0.05 M) and increasing the diol concentration (~0.40 M). Under these conditions, ^{11}B NMR peaks can be easily integrated for B^-, BX^-, and BX_2^- and all stability constants can be directly measured as a function of temperature (Table 1). K_1 is also redetermined in this experiment, and values identical with those of our previous study[13] are obtained. Since the diol is not acidic, reactant concentrations can be quite high and the ionic strength can still be maintained at 0.10 M. There have been several other ^{11}B NMR spectroscopic studies[17] of equilibrium constants for reactions of diols with $B(OH)_4^-$ at room temperature. Although we are in generally good agreement with van Duin and co-workers,[17a,b] other studies [17d,e] give values for the $B(OH)_4^-/H_2P$ reaction which differ. Experimental conditions in these studies were quite different from ours with ionic strength being as high as 3 M[17a,b,e] and borate concentration being as high as 0.6 M.[17c] The error associated with the stability constants given in Table 1 is ±10%. The errors specifically given in Table 1 for $\Delta H°$ and $\Delta S°$ are the sums of the errors associated with each reaction used in the Hess's law determination of that parameter. Errors associated with thermodynamic parameters derived from variable-temperature ^{11}B NMR experiments were determined from the variances[18] of the slope and intercept of the appropriate van't Hoff plot.

α-Hydroxy Carboxylic Acids. Near neutral pH, only 1:1 borate/α-hydroxy carboxylic acid complexes are observed. Solutions can be prepared with reactant concentrations ≤0.10 M, and K_1 can be measured as a function of temperature. At pH ~7, however, essentially all uncomplexed boron is present as $B(OH)_3$, not as $B(OH)_4^-$. Similarly, since the pK_a values of α-hydroxy carboxylic acids are much less than 7, all uncomplexed H_2X is present as HX^-. Direct integration of the ^{11}B NMR spectrum under these conditions affords the calculation of the equilibrium constant for the reaction $B(OH)_3 + HX^- \leftrightarrow BX^- + H_2O$. We have chosen to express all equilibria and thermodynamic parameters in terms of the reaction of $B(OH)_4^-$ with H_2X (eq 1). In the present example, K_1 can be calculated by multiplying the measured equilibrium constant by $K_a(H_2X)\,/K_a(B(OH)_3)$. We have measured $K_a(H_2X)$ as a function of temperature for lactic acid and glycolic acid, and the thermodynamic parameters are contained in Table 2. The results are in excellent agreement with the literature values.[19] $K_a(B(OH)_3)$ is known[20] as a function of temperature, and the thermodynamic parameters for ionization of $B(OH)_3$ are also included in Table 2.

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(18) Young, H. D. *Statistical Treatment of Experimental Data*; McGraw-Hill: New York, 1962; p 146.

(19) Martell, A. E.; Smith, R. E. *Critical Stability Constants*; Plenum: New York, 1977, 1982, and 1989; Vols. 3, 5, and 6.

(20) Manov, G. G.; DeLollos, N. J.; Acree, S. F. *J. Res. Natl. Bur. Stand.* **1944**, *33*, 287 (μ = 0.1 M (KNO_3)).

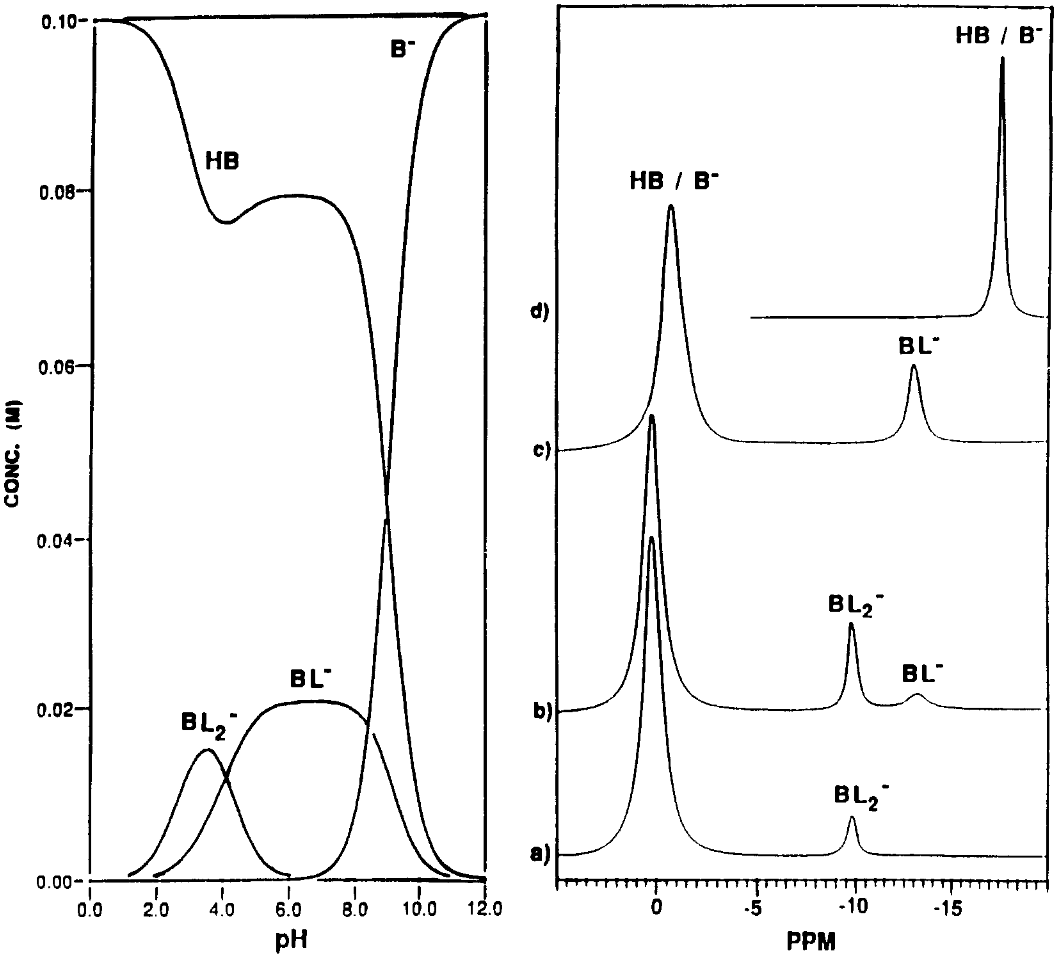

Figure 1. *Left*: Distribution diagram for the boric acid (HB)/lactic acid (H_2L) system, calculated with 0.10 M concentration for each reactant. *Right* ^{11}B NMR spectra for the boric acid ($[HB]_0 = 0.10$ M)/lactic acid ($[H_2L]_0 = 0.11$ M) system at various pH values: (**a**) pH(D) = 2.0; (**b**) pH(D) = 3.3; (**c**) pH(D) = 7.8; (**d**) pH(D) = 11.0. All solutions were prepared in 20% D_2O/H_2O (v/v). $T = 298$ K. Chemical shifts are relative to external 0.15 M boric acid in 20% D_2O/H_2O (v/v) at pH(D) = 2.0.

Table 2. pK_a Values and Thermodynamics of Ionization for Acidic Species Involved in This Study[a]

acid	pK_a(298 K)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/(mol K))
$B(OH)_3$	8.98[b]	12.8[c]	-129[c]
H_2G[d]	3.65	1.5(±1)	-65(±4)
H_2L[d]	3.64	-2.9(±0.2)	-79(±1)
H_2Ox	1.13[e]	-2.9[f]	-31[f]
HOx^- [g]	3.38	-5.4	-96

[a] Numbers in parentheses denote standard deviations. [b] Ingri, N. *Acta Chem. Scand.* **1962**, *16*, 439 ($\mu = 0.1$ M ($NaClO_4$)). [c] Reference 20. [d] This study. [e] Nagata, K.; Umayahara, A.; Tsuchiya, R. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1059 ($\mu = 0.1$ M ($NaClO_4$)). [f] Vasil'ev, V.; Shekhanova, L.; Kochergina, L. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1976**, *46*, 729 (730) ($\mu = 0.15$ M ($NaNO_3$)). [g] Daniele, P.; Rigano, C.; Sammartano, S. *Thermochim. Acta* **1981**, *45*, 103 ($\mu = 0.1$ M ($NaClO_4$)).

The determination of K_2 is facilitated by the fact that formation of BX_2^- is strongly favored in acidic media.[2d,21] At low pH (~2.0) and approximately equimolar reactant concentrations (≤0.10 M), BX_2^- is the only complex species present. Under these conditions, the overall reaction is $B(OH)_3 + 2H_2X \leftrightarrow BX_2^- + H_3O^+ + 2H_2O$. K_2 can be simply calculated from this measured equilibrium constant by dividing it by $[K_a(B(OH)_3)]K_1$. Since there is a small concentration of HX^- at low pH, this must be explicitly taken into account in the mass balance equations which are used in calculating the equilibrium constants. In these particular experiments the correction for HX^- is quite small (≤2% of total free ligand concentration). We have also shown[13] for polyols that equilibrium constants and thermodynamic parameters are independent of solvent composition (D_2O/H_2O) within experimental error. Therefore, in calculations of equilibrium constants and in Hess's law determinations of thermodynamic parameters, we have used the aqueous values[22] of pK_a, $\Delta H°$, and $\Delta S°$ given in Table 2.

Because the concentration dependence as a function of pH is so unusual in these systems, a distribution diagram and representative ^{11}B NMR spectra are presented in Figure 1 for the lactic acid system. The $B(OH)_3/B(OH)_4^-$ interconversion is rapid on the NMR time scale, and as a consequence, only one pH-dependent peak is observed for uncomplexed boron.[23] We have previously determined K_1 and K_2 for H_2L by pH titration methods.[21] While agreement between our two determinations of K_2 is within reported experimental errors, the present study shows that our former value of K_1 was too low. Our values of K_1 and K_2 for H_2G are in excellent agreement with the literature.[17a]

Oxalic Acid. The one dicarboxylic acid included in this study is oxalic acid. By the selection of a pH intermediate between pK_{a1} (1.13) and pK_{a2} (3.38), spectra can be obtained under conditions where HX^- is the predominant species. The data analysis, therefore, conforms exactly to that of α-hydroxy

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(21) Pizer, R.; Selzer, R. *Inorg. Chem.* **1984**, *23*, 3023.

(22) Although acid dissociation constants measured in D_2O are less than those measured in H_2O by approximately a factor of 2, theory (Schaleger, L. L.; Salomaa, P.; Long, F. A. In *Chemical Physics of Ionic Solutions*; Conway, B. E., Barradas, R. G., Eds.; Wiley: New York, 1966; p 237) can accurately describe the dependence of pK_a on solvent composition (D_2O/H_2O). In 20% D_2O, pK_a values are often greater than values in H_2O only by ~0.03 units. This corresponds to an increase in $\Delta G°$ at 298 K of 0.17 kJ/mol. For boric acid in H_2O and D_2O see: Maeda, M.; Sunaoka, Y.; Kakihana, H. *J. Inorg. Nucl. Chem.* **1978**, *40*, 509.

(23) Henderson, W. G.; How, M. J.; Kennedy, G. R.; Mooney, E. F. *Carbohyr. Res.* **1973**, *28*, 1.

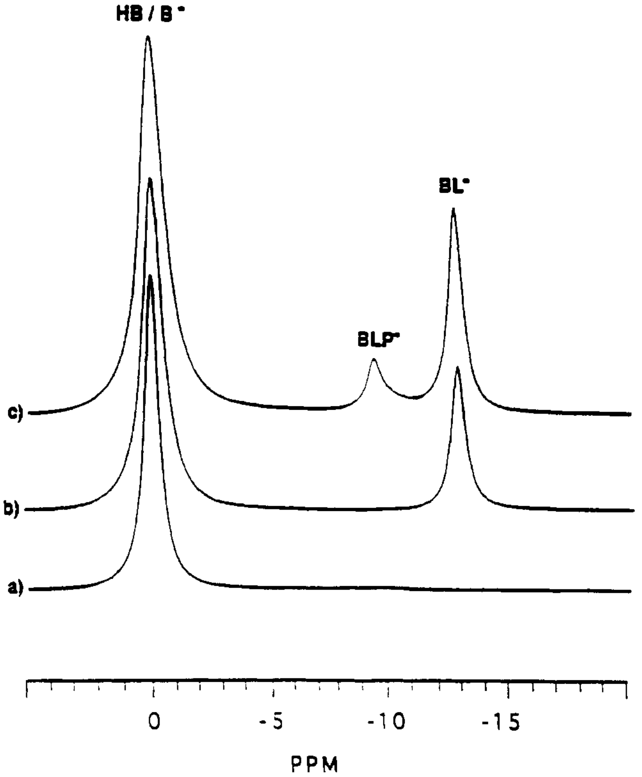

Figure 2. ^{11}B NMR spectra for the mixed-ligand system of boric acid (HB)/lactic acid (H_2L)/1,2-propanediol (H_2P): (**a**) $[HB]_0 = 0.05$ M, $[H_2P]_0 = 0.70$ M, pH(D) = 7.1; (**b**) $[HB]_0 = 0.05$ M, $[H_2L]_0 = 0.10$ M, pH(D) = 7.1; (**c**) $[HB]_0 = 0.05$ M, $[H_2P]_0 = 0.70$ M, $[H_2L]_0 = 0.10$ M, pH(D) = 7.1. All solutions were prepared in 20% D_2O/H_2O (v/v). T = 298 K. Chemical shifts are relative to external 0.15 M boric acid in 20% D_2O/H_2O (v/v) at pH(D) = 2.0.

Table 3. Thermodynamics of Disproportionation

reaction	K(298 K)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/(mol K))
$2BE^- \leftrightarrow BE_2^- + B^-$	0.13	15	34
$2BP^- \leftrightarrow BP_2^- + B^-$	0.29	2	1
$2BG^- \leftrightarrow BG_2^- + B^-$	7.7×10^{-5}	51	91
$2BL^- \leftrightarrow BL_2^- + B^-$	8.5×10^{-5}	62	134
$2BOx^- \leftrightarrow BOx_2^- + B^-$	~0		

carboxylic acids near neutral pH as described above. The relatively small concentrations of H_2X and X^{2-} must, of course, be explicitly taken into account in the relevant mass balance equations. Perhaps the most surprising result in this system is that there is no evidence for BX_2^- complex formation at ligand concentrations as high as 1.0 M. This result is consistent with the literature.[17a]

Mixed Ligand Systems. At pH ~7 there is no measurable concentration of 1:1 borate complexes with diols even at quite high diol concentrations (~0.8 M). There are, however, significant concentrations of BX^- at reactant concentrations ≤0.10 M if X is an α-hydroxy carboxylic acid. By the addition of a diol to a solution which contains boric acid and an α-hydroxy carboxylic acid near neutral pH, an ^{11}B NMR peak for a mixed-ligand complex can easily be assigned and integrated. Stability constants and thermodynamic parameters for the formation of a mixed-ligand complex (BXY^-) from the reaction of a 1:1 α-hydroxy carboxylic acid complex (BX^-) with a polyol (H_2Y) can be calculated directly from the ^{11}B NMR integration and mass balance. Representative spectra are contained in Figure 2.

Disproportionation Reactions. It is useful to look at the thermodynamic data also in terms of disproportionation reactions, which can be written as $2BX^- \leftrightarrow BX_2^- + B^-$. The necessary data can be obtained from Table 1. Table 3 contains results for each system.

Discussion

In all systems, but by very different amounts, formation of BX_2^- from BX^- is characterized by a less favorable enthalpy change and a more favorable entropy change. The differences are relatively small in the case of the 1,2-diols but remarkably large for α-hydroxy carboxylic acids. K_1/K_2 increases dramatically as the ligand becomes more acidic, and a limit is reached in the oxalic acid system in which case a 1:2 complex could not even be observed. It is clear that 1,2-diols, α-hydroxy carboxylic acids, and oxalic acid represent three distinct classes of ligands, and we will discuss each class in turn.

1,2-Diols. We previously studied[13] the thermodynamics of formation of 1:1 borate complexes with H_2P and H_2E as well as the $C_6H_5B(OH)_3^-/H_2E$ and $CH_3B(OH)_3^-/H_2P$ reactions. All four reactions have remarkably similar stability constants and thermodynamic parameters. This result is in contrast to the previous literature in which "the wide variation in...reported thermodynamic parameters...obscured the fact that these reactions are all very similar thermodynamically".[13] There is also a tremendous variation in the literature in reported thermodynamic parameters for BX_2^- complex formation. To cite but one example, the entropy change for the reaction $BP^- + H_2P \leftrightarrow BP_2^- + 2H_2O$ has been independently measured by three groups. The values of $\Delta S°$ are +0.5,[8] −61.5,[7] and −138 J/(mol K).[9,24] Furthermore, all these studies show substantial differences between the thermodynamics of the first and second complexation steps. In contrast to the literature, we show that thermodynamic parameters for the second complexation step are quite similar to those for the first step. Both steps are exothermic, and entropy changes for all reactions are negative. We had attributed[13] the negative entropy change for the first complexation step to a loss of configurational entropy in the ligand on complexation, and this could certainly contribute to the negative entropy change for the second complexation step as well.

On a purely statistical basis,[4] K_1/K_2 for bidentate chelating ligands coordinated to a tetrahedral center should be 12. The 1,2-diols have K_1/K_2 values which are only slightly less than that value. It is interesting to note, however, that while the assumptions of a purely statistical argument attribute the decrease in successive stability constants entirely to a less favorable entropy factor, that is not the case for either diol studied here. For H_2E in particular, addition of a second ligand is considerably more favorable entropically than first ligand addition. The decrease in K_2 relative to K_1 is due to a less favorable standard enthalpy in both cases. Numerically, the ratio of 12 corresponds to an expected entropy decrease caused only by statistical effects of 19.1 J/(mol K) for second ligand addition compared with first ligand addition. The entropy changes observed here ($\Delta S_2° - \Delta S_1°$) are either close to zero (H_2P) or positive (H_2E). This means that there must be a compensating positive contribution to the entropy change which could possibly be related to the release of water of solvation on complexation. Since both complexation reactions (eqs 1 and 2) involve the condensation of two hydroxyl groups on the ligand with two hydroxyl groups on boron, not only are two water molecules formed on each reaction, but any solvent associated with the four reactant hydroxyl groups is also released.

It is useful to reconsider the reaction thermodynamics from the perspective of a disproportionation reaction:2 $BX^- \leftrightarrow BX_2^- + B^-$ (Table 3). Since there is no uncomplexed ligand in the disproportionation reaction, effects caused by ligand solvation and/or a loss of ligand configurational entropy are relatively unimportant. Similarly, the total number of uncoordinated –OH groups available for solvation is the same for reactants and products. Differences in solvation of B^-, BX^-, and BX_2^- are

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[24] Although the ionic strength is not the same in these studies, we have shown[13] that there is essentially no effect of ionic strength at least to μ = 0.6 M on either stability constants or thermodynamic parameters for formation of BP^-.

expected, and it is reasonable to suggest that B^- is better solvated than BX^-, which, in turn, is better solvated than BX_2^-. The small entropy change argues against any significant overall change in solvation on disproportionation. Similarly, the small enthalpy change means that there is no great difference in the B–O bond strength among B^-, BX^-, and BX_2^- for diols.

α-Hydroxy Carboxylic Acids. Compared with that for the diols, K_1 is much greater for α-hydroxy carboxylic acids, and this increase is entirely the result of a much more favorable $\Delta H°$. Entropy changes remain quite negative, and this may again be attributed to a loss of configurational entropy in the ligand on complexation. In marked contrast to that of the diols, the second complexation reaction here is emphatically different from the first. K_2 is much smaller than K_1, and extremely large differences in both $\Delta H°$ and $\Delta S°$ are observed. The second complexation steps for H_2L and H_2G are the only endothermic reactions in the entire set, and the entropy changes are the most positive. For H_2L, the difference in enthalpy change ($\Delta H_2° - \Delta H_1° = +62$ kJ/mol) corresponds to a decrease in stability constant by 11 orders of magnitude. The more favorable entropy change ($\Delta S_2° - \Delta S_1° = +134$ J/(mol K)) corresponds to an increase in stability constant by 7 orders of magnitude. The more favorable entropy change only partially compensates for the much less favorable enthalpy change, and as a consequence, K_2 is 4 orders of magnitude smaller than K_1.

These results can be discussed in terms of the disproportionation reactions. Compared with those for the diols, equilibrium constants are quite small and both $\Delta H°$ and $\Delta S°$ are much more positive. Extending the discussion of the diol disproportionation reactions, it seems that solvation effects cannot explain these data. For example, H_2E differs from H_2G (and H_2P differs from H_2L) only by replacement of two methylene hydrogens by one carbonyl oxygen. While this difference is chemically significant, in terms of the disproportionation reaction the total number of carbonyl groups on each side of the chemical equation is the same and little net effect on overall solvation is expected. If solvation effects are not important, then the endothermic enthalpy value may be interpreted in terms of significant differences in B–O bond strengths in B^-, BX^-, and BX_2^-. In these systems, the strongest B–O bonds may be found in BX^-, with longer, weaker bonds being characteristic of B^- and BX_2^-. This is consistent with the thermodynamics of successive ligand addition (Table 1) and disproportionation (Table 3). Such structural differences would also contribute to the positive entropy of disproportionation. The thermodynamics of bimolecular association reactions were recently studied in detail, and factors which contribute to compensating enthalpy/entropy relations were discussed.[25]

This argument attributes the very different thermodynamic parameters for formation of 1:2 borate/α-hydroxy carboxylic acid complexes to structural differences among the various borate complexes and not to any particular effect of solvation on the reactions. The fact that there may be significant differences in boron–oxygen bonds in various borate complex ions is supported by recent crystal structure determinations[26] of both 1:1 and 1:2 borate complexes of a substituted 1,2-dihydroxybenzene in which there are B–O bond length differences of almost 0.1 Å among the various complexes. When the donor atoms are nonequivalent, as in α-hydroxy carboxylic acids, these differences may be even more substantial.

Oxalic Acid. Oxalic acid is unique among the systems studied in having a much more positive $\Delta S°$ for the first complexation step and not forming a second complex at all. The entropy change is, in fact, comparable to that which we observed previously[13] for a reaction of 1,2-dihydroxybenzene. The unexpectedly large entropy change for the oxalic acid reaction is not without precedent. If one compares the reactions of oxalic acid and 1,2-dihydroxybenzene with Cu^{2+} ($Cu^{2+} + H_2L \leftrightarrow CuL + 2H^+$), the entropy change for the reaction of oxalic acid (–8 J/(mol K))[27] is considerably more positive than the entropy change for the 1,2-dihydroxybenzene reaction (–113 J/(mol K)).[28] The entropy change for the overall ionization of 1,2-dihydroxybenzene (–276 J/(mol K))[19] is much more negative than that for the overall ionization of oxalic acid (–127 J/(mol K)).[29] This accounts in part for the more negative entropy change for the 1,2-dihydroxybenzene reactions with both Cu^{2+} and the borate ion compared with reactions of oxalic acid.

The absence of observable BOx_2^- has been noted previously.[17a] It is of particular interest here because it further supports our contention that there are significant differences in the B–O bond in the various borate species. The hydroxyl groups in BOx^- do not react with H_2Ox to form BOx_2^- whereas B^- reacts easily with H_2Ox. We did several experiments to see if any mixed-ligand complexes could be formed with BOx^-. H_2P at high concentration (~ 1 M) forms a complex with BOx^- whose signal appears in the ^{11}B NMR spectrum only slightly downfield from that of BOx^-. It is of small amplitude and not sufficiently separated from the BOx^- signal to be integrated. It is clear, however, that the equilibrium constant for the reaction is much less than that for the addition of H_2P to any other borate species. Similiar experiments were carried out with H_2G and H_2L. The mixed-ligand complex $BLOx^-$ appears in the NMR as a shoulder on the signal of BL_2^-, but the $BGOx^-$ signal is sufficiently separated from those of other complex ions in the system to permit integration. The approximate value for the equilibrium constant for the reaction $BOx^- + H_2G \leftrightarrow BGOx^- + 2H_2O$ is 4×10^{-2}. This value is less than 1% of the equilibrium constant for the addition of H_2G to BG^-.

It is possible to look at this question from one other point of view. A plot of log K_1 vs. pK_a(ligand) is linear with a large negative slope. A similar plot of log K_2 vs. pK_a(ligand) is also linear with a much smaller negative slope. Extrapolation of this second plot to pK_a ~ 1 allows a prediction to be made for K_2 for the H_2Ox reaction. That value is approximately 100. Using K_1 (Table 1) and this value for K_2, a distribution diagram with initial concentrations of H_2Ox and $B(OH)_3$ both being equal to 0.10 M shows a large excess of BOx_2^- at low pH. This result is similar to that for the lactic acid system (Figure 1). But no such complex can be seen in the NMR at any pH or reactant concentration and the experimental value of K_2 is taken to be zero. It is clear from these results that BOx^- behaves very differently from any other BX^- species and that ligand addition to BOx^- is quite difficult.

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(29) Table 2.