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Boron acid complexation reactions in basic solution

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City University of New York, 1991

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BORON ACID COMPLEXATION REACTIONS IN BASIC SOLUTION

by

Cherryl Ann Tihal

A Dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1991

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Dec. 20, 1990
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Richard Pizer
Chair of Examining Committee

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Date

Richard Pizer
Executive Officer

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Abstract

BORON ACID COMPLEXATION REACTIONS IN BASIC SOLUTION

by

Cherryl Ann Tihal

Adviser: Professor Richard Pizer

Boron acids are Lewis acids and ionize in solution to produce four-coordinate, tetrahedral borate anions. Both the trigonal boron acid and the tetrahedral borate anion can react with bidentate chelating ligands (such as α-hydroxycarboxylic acids) to produce the same four-coordinate chelate complex. For the reactions between the trigonal boron acids and fully protonated ligands, the proposed transition state is characterized by a mechanism which involves proton transfer. The present study was designed to investigate the following: (1) the reactivity of the borate anion towards bidentate ligands, (2) the effect on the reaction mechanism when the ligand contains no acidic protons, (3) the measurement of the enthalpy and entropy changes for borate chelation reactions, and (4) the interaction between boron acids and simple unidentate ligands.

The ligands used are simple polyols such as ethylene glycol, 1,2-propanediol, 1,3-propanediol and glycerol. The kinetic results show that the trigonal boron acids are unreactive toward the polyols while the four-coordinate borate anions are much more reactive. The lability of four -

coordinate borate anions may be a consequence of the longer boron-oxygen bond relative to the trigonal species, but we are unable at this point to propose a transition state for these reactions.

The complexation reactions between the borate anion and the polyols are spontaneous. Therefore, the measurement of the enthalpy and entropy changes allows one to determine whether the driving force for the reactions is enthalpic or entropic in origin. These thermodynamic measurements indicate that the reactions of borate with the polyols are enthalpy driven.

The reactions between boron acids and peroxo ligands produce complexes in which the ligand is unidentate. Boric acid and hydrogen peroxide interact to form the following complexes: $(OH)_3BOOH^-$, $(OH)_2B(OOH)_2^-$ and $(OH)_2BOOH$. Equilibrium constants were determined quantitatively but no kinetic study was possible due to the decomposition of hydrogen peroxide under our experimental conditions. No determination of equilibrium constants was possible in the phenylboronic acid / hydrogen peroxide system because of the oxidation of the boron acid by the ligand. In the boric acid / *tert* - butylhydroperoxide system, complex formation was negligible.

To my parents

ACKNOWLEDGEMENTS

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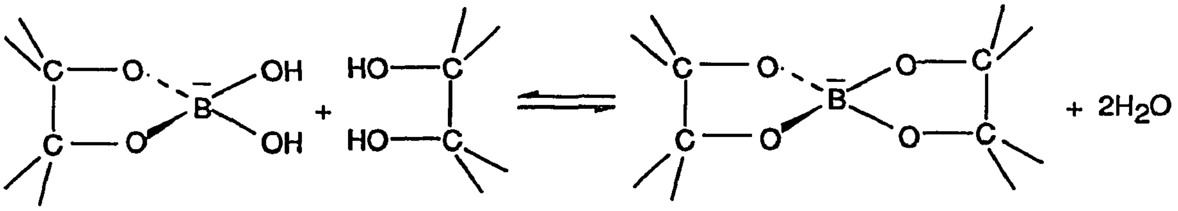
CHAPTER 1

INTRODUCTION TO BORON ACID CHEMISTRY

1.1 Introduction

The interaction between boric acid and hydroxy compounds has been studied for a long time. As early as 1842, Biot [1] reported that a solution of boric acid became acid to litmus upon the addition of sugars. This observation led Thomson [2] to perform a quantitative determination of boric acid in the presence of various hydroxy compounds (such as glycerol) while using phenolphthalein as an indicator. Biot also discovered that the optical rotation of a solution of tartaric acid changed upon the addition of boric acid. Furthermore, Magnanini [3-5] reported that the conductivities of solutions of boric acid and hydroxy compounds were greater than the sum of the individual conductivities. In the late 1800's, van't Hoff [6] proposed complex formation between boric acid and the hydroxy compounds in order to explain the changes in acidity, optical rotation and conductivity. Although the structure of the complex was not clearly defined, many researchers in the early 1900's carried out systematic studies of boric acid reacting with various hydroxy compounds. Investigators who have made major contributions to the understanding of boron acid chemistry include Boeseken [7-14], Hermans [15] and Vermaas [11,13]. Hermans was the first to propose the structures of the complexes which were later proven to be correct and are shown below.

In the above reaction boric acid acts as a Lewis acid to form the 1:1 complex. The 1:1 complex can react further with a second ligand molecule as follows.



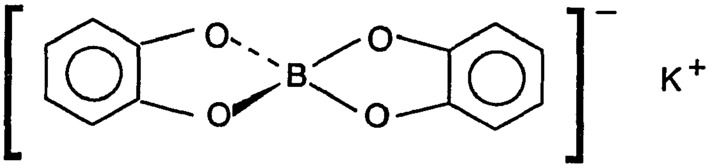
This reaction occurs with the condensation of two water molecules to produce the 1:2 or the bis complex.

The specific configurational requirement of the hydroxy groups which is necessary for successful chelation to boron was demonstrated by Boeseken in the early 1900's. Studies of boric acid reacting with 1,2 -dihydroxybenzene (catechol), 1,2,3-trihydroxybenzene (pyrogallol),1,3-dihydroxybenzene(resorcinol) and1,4-dihydroxybenzene (hydroquinone) were followed by conductivity measurements [7]. Only catechol and pyrogallol caused an increase in the conductivity. This indicated that the hydroxy groups must be adjacent in order for the complex to form. Identical results were obtained with other substituted dihydroxybenzenes and substituted dihydroxynapthalenes. Similarly, conductivity studies were carried out with boric acid reacting with the cis and trans isomers of various substituted cyclic diols such as cyclopentane-1,2-diol [9,12]. In all cases, only the cis isomers produced an increase in the conductivity of the solution.

These studies therefore led to the conclusion that the hydroxy groups must be adjacent and cis in order for complexation to occur. This test of configuration became known as the " Boeseken test " and was applied extensively in the carbohydrate field to determine the nature of the hydroxy groups as well as to distinguish between α and β isomers of various sugars [8,16-18].

Studies were also conducted in which compounds were tested in terms of their ability to decrease the pH of boric acid solutions. In 1942, Boeseken found that α-hydroxycarboxylic acids such as tartaric acid and lactic acid caused a considerable decrease in pH when added to a solution of boric acid. This meant that the complexation reaction produced a proton which was more acidic than boric acid. Since these solutions also exhibited enhanced conductivities, the formation of the protons supported the general belief that the complex was tetrahedral.

Additional proof that certain complexes were involved in these reactions was obtained when solid compounds were isolated from the solution mixtures and studied. From a solution containing boric acid and catechol, Boeseken isolated a compound which was characterized by Hermans [15] as having the following structure:



The anion was characterized as having a four-coordinate boron atom which was connected to two fixed catechol molecules via four oxygen bridges. This was confirmed by Meulenhoff [19] who isolated and characterized a similar bis complex from a solution of boric acid and salicylic acid using an optically active base. Using this technique, Meulenhoff succeeded in resolving several optical isomers.

In 1955, Edwards [20] carried out a Raman study of the borate anion. The spectrum which consisted of four bands resembled that of the tetrahedral BF_4^- ion. The results were also in agreement with the IR spectrum of the teepleite crystal ($NaBO_2.NaCl.\ 2H_2O$) which was known to contain a boron atom tetrahedrally coordinated to four oxygen atoms [21]. However, Edwards decided to calculate the number of Raman active lines expected for the other two possible structures of the borate ion, BO_2^- and $H_2BO_3^-$. The calculated fundamental bands (1 for BO_2^- and 6 for $H_2BO_3^-$) did not agree with the experimental spectrum containing four bands. These results led Edwards to the conclusion that boric acid is a Lewis acid which ionizes in solution as follows.

The fact that the borate anion had been determined to be tetrahedral together with the general agreement that the borate complexes were also tetrahedral led to many quantitative thermodynamic studies of boric acid reacting with various hydroxy compounds. In 1967, Conner and Bulgrin [22] studied the reactions of borate with a series of polyols such as ethylene glycol, glycerol and substituted butanediols. Stability constants as well as enthalpy and entropy changes were reported for both the 1:1 and the 1:2 complexes. Perhaps one of the most intensively studied systems is that of boric acid-borate / mannitol equilibria [22-25]. (Mannitol is a polyhydroxy compound containing six carbon atoms each of which is bonded to a hydroxyl group.) These investigators reported the formation of 1:1 as well as 1:2 complexes, and stability constants which were consistent with previous work. However, in all studies of the boric acid-borate / polyol systems, the authors concluded that it was the borate anion and not the trigonal boric acid which was the complexing species. From thermodynamic studies alone, the authors arrived at this conclusion by considering the magnitude of the stability constants and the variation of the complex concentration with solution pH.

In 1959, Lorand and Edwards [26] carried out a thermodynamic investigation of the phenylboronic acid / polyol system. Phenylboronic acid, $\Phi B(OH)_2$, can form only 1:1 complexes since one of the coordination sites on boron is blocked by the phenyl group. By assuming that the structures of both the phenylboronate anion and the 1:1 complex formed were tetrahedral, these authors also concluded that it was the phenylboronate anion which was the reactive species. In 1961, Edwards and Sederstrom [27] determined that the phenylboronate anion was indeed tetrahedral. They performed pH titrations as a function of the temperature and reported an entropy of ionization of -34 cal / mole - deg for phenylboronic acid. In the case of boric acid, ΔS° was known to be -30.9 cal / mole - deg [28]. The values for the ionization of the two boron acids were seen to be more negative than the average entropy change for the formation of an oxyanion from a neutral acid (ΔS° = -22 cal / mole - deg) [29]. This observation was explained in terms of an increase in coordination number upon ionization of the boron acids. Therefore, the low value of ΔS° for phenylboronic acid and its similarity to that of boric acid which was determined to be tetrahedral, led the authors to conclude that the phenylboronate anion was also tetrahedral.

The first structural study of the chelate complex was carried out in 1970 and 1971 by Larsson and Nunziata [30,31]. They performed IR and Raman studies on solutions of boric acid with salicylic acid and lactic acid. By comparing the boron - oxygen stretching frequencies in the known trigonal boric acid $B(OH)_3$ and the tetrahedral borate $B(OH)_4^-$ with those of the complex, they were able to show that the complexes were tetrahedral. They also reported the presence of both the 1:1 and the 1:2 complexes. In 1972, Oertel [32] carried out a Raman study of boric acid reacting with simple 1,2- and 1,3- diols. The results clearly showed that the 1:1 and the 1:2 complexes were tetrahedral structures as proposed by Hermans [15] in 1925.

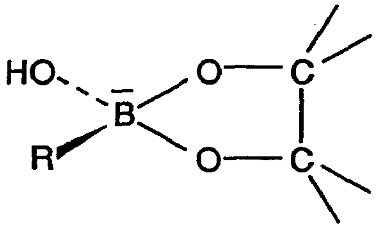
1.2 General Characteristics of Boron Acids

Boron acids are weak acids; they are also Lewis acids and ionize in solution as follows.

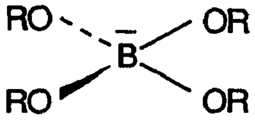
In this reaction boron uses an empty p orbital to accept electrons and form a covalent bond. This interaction is analogous to that which occurs upon complexation. That is, there is nucleophilic attack on the electron deficient boron atom by the oxygen donor atom of the ligand. In the trigonal planar boron acid, boron is sp^2 hybridized with a formal charge of zero; in the tetrahedral borate anion, boron is sp^3 hybridized with a formal charge of negative one.

The acidity of boric acid $B(OH)_3$ has been determined by many investigators. Ingri reported a value of 9.0 for the pK_a of boric acid [33]. In the substituted boron acids $RB(OH)_2$ the variation of the R group can increase or decrease the Lewis acidity and this has been partially explained in terms of backbonding. The existence of multiple bonding in boron compounds is supported by various experimental studies. While compounds of boron can exist as monomers, those of its congeners aluminum and gallium utilize their empty p orbitals in the formation of dimers [34]. This means that backbonding stabilizes the trigonal boron compounds since dimerization would result in a loss of this backbonding interaction. Secondly, force constant calculations from trigonal boron frequencies indicate the presence of multiple bonding [34]. Furthermore, NMR studies report the existence of hindered rotation about the boron - ligand single bond in trigonal boron compounds (such as $(CH_3)_2BOCH_3$) [34,35]. These observations suggest that the degree of backbonding may affect the relative acidity of trigonal boron acids since the loss of this backbonding interaction may oppose the formation of the tetrahedral anion.

Both the trigonal and the tetrahedral forms of a boron acid can react with suitable bidentate compounds to form the same 1:1 anionic complex shown below.



In the case of boric acid the 1:1 complex can react further with a second ligand molecule to form the 1:2 complex. Substituted boron acids do not form 1:2 complexes since one of the coordination sites is blocked by the R group. These complexes are stabilized by the chelate effect and species such as



R ≢ H

are known to rapidly hydrolyze back to boric acid [36]. The tetrahedral nature of the chelate complexes has been determined by structural studies such as IR and Raman techniques [30,31,32]. Finally, experiments with optically active ligands show that it is the boron-oxygen bond which is cleaved upon complexation [37,38].

1.3 Applications of Boron Acid Chemistry

Boric acid and boronic acids find wide use in analytical chemistry, specifically in quantitative analyses, structural studies and separation techniques.

The formation of chelate complexes between dihydroxy compounds and boric acid or borate enables the quantitative determination of boric acid / borate as well as the hydroxy compound. Boric acid is too weak to be determined directly by titration. The acidity of boric acid is known to be enhanced by the addition of compounds such as D-glucitol and D-mannitol [39]. In this manner, direct titrimetric determination of boric acid is possible. It is also known that (catecholato)borate complexes display higher λ_{max} values and larger molar absorptivities than the uncomplexed catechols [40,41]. The chelation process then allows the quantitative assay for catechol and / or borate by spectrophotometric methods. A nondestructive assay for catecholic polymers and catecholic proteins has been developed by the study of the (catecholato)borate complexes using ultraviolet difference spectrophotometry [42].

In the complexation reactions between borate and hydroxy compounds, the specific requirement that the hydroxy groups be adjacent and cis for successful chelation has made these compounds extremely useful in studying structural, configurational and conformational problems. Boeseken and coworkers [43] have applied this principle in the determination of the configuration of polyhydroxy compounds using conductivity and polarimetry methods. From conductivity measurements, these authors were the first to distinguish between the cis and trans isomers of 2-hydroxycyclopentane carboxylic acid. The technique was also applied to the carbohydrate field where it was possible to differentiate between α- and β- lactoses [43].

The selective binding of borates to polyhydroxy compounds forms the basis of separation processes in many analytical techniques such as chromatography. Cellulose columns which were derivatized with boronic acids have been used in the separation of nucleosides as well as various sugars [44]. A method for the separation of a mixture of polyols was developed from the study of the borate / polyol complexes by anion exchange chromatography [45]. The chelation of boronic acids is being exploited in the separation and purification of catecholic compounds by affinity chromatography [46,47] as well as electrophoresis [48,49]. Furthermore, the separation and purification of carbohydrates via distillation or fractional crystallization of boron complexes has been used for a long time [50].

Aside from structural and analytical studies, the complexation reactions between boron acids / borate and hydroxy compounds find increasing applications in other areas of research. It is well established that plants need small amounts of boron. Although boron is present in animals, it is not yet clear whether it is essential. However, there are a few boron - containing antibiotics such as boromycine and aplasmomycine. In addition, many compounds of biological importance such as vitamins, coenzymes, enzymes and polysaccarides contain suitable hydroxy groups which can interact with boron compounds.

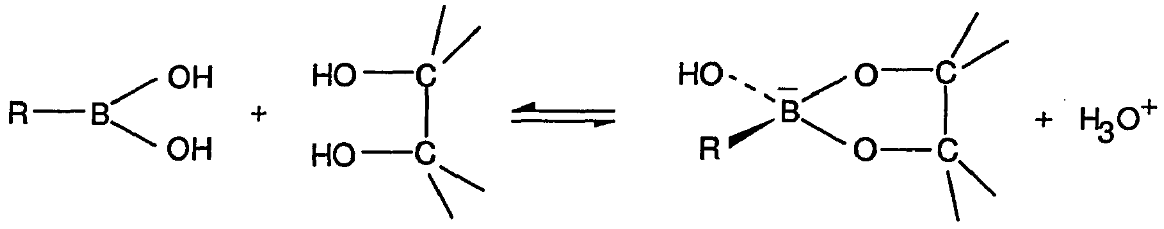
Several enzyme studies have illustrated the use of boron acids as inhibitors and transition - state analogues. A transition - state analogue for an enzyme is a compound which forms a stable complex with the enzyme and which resembles the substrate portion of the transition state in the enzymatic reaction [51,52]. There are some enzyme reactions in which the formation and the breakdown of the anionic tetrahedral enzyme - substrate intermediates occur by proton transfer. Trigonal boron acids are also known to produce anionic tetrahedral borates by proton transfer. In some cases, the enzyme -

boron acid species bear a close resemblance to the enzyme - substrate intermediates in terms of structure and charge. These properties of boron acids have rendered them suitable for study as potential transition - state analogues. In 1971, Koehler and Lienhard reported that 2 - phenylethaneboronic acid inhibited the α - chymotrypsin - catalyzed hydrolysis of methyl hippurate, and was therefore a transition state analogue [53]. Both phenylboronic acid and 2 - phenylethaneboronic acid were found to inhibit subtilisin - catalyzed hydrolyses [54]. Methylboronic acid was not an effective inhibitor which suggests that the aromatic group may be necessary. A further study of 2 - phenylethaneboronic acid acting as an inhibitor for α-chymotrypsin was carried out by the laser - Raman technique [55] and the authors reported that both the trigonal and the tetrahedral forms of the boron acid were involved in the reactions.

An understanding of the kinetics of boron acid complexation reactions would therefore find important applications in mechanistic studies of enzyme reactions.

1.4 Introduction to Boron Acid Kinetics

The complexation reaction between a substituted boron acid and a bidentate hydroxy compound is given below. As mentioned before, the

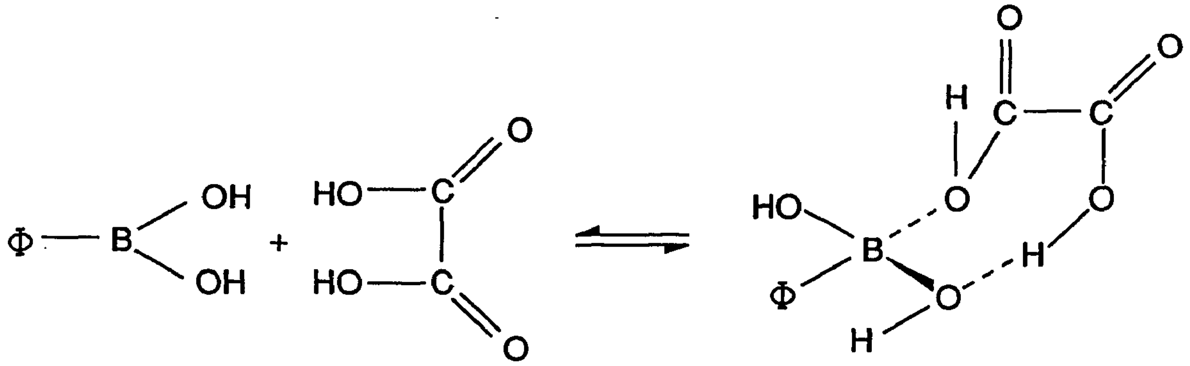


tetrahedral borate anion can also react to form the same chelate complex. Thermodynamically, these reactions have been studied by many experimental techniques and a large amount of quantitative data has been reported in the literature.

The first kinetic investigation of boron acid complexation reactions with bidentate chelating ligands was a temperature-jump study carried out by Kustin and Pizer in 1969 [65]. The reactions of trigonal boric acid with tartaric acid and the tartrate anion to produce the 1:1 complex were studied in acidic solution. For the reaction between boric acid and tartaric acid, it was proposed that the complexation occurred by the attack of the ligand oxygen donor atom on the empty boron p orbital followed by ring closure via loss of a water molecule. Since the tartrate anion reacted slower than tartaric acid, the authors concluded that ligand acidity and donor atom protonation were important factors controlling the reaction rate.

Subsequent kinetic investigations of boron acids with bidentate ligands such as dicarboxylic acids, α-hydroxycarboxylic acids and catechols revealed that the same mechanism was in operation. All of these studies were conducted in acidic solution because the equilibria were such that complex formation occurred only under these pH conditions. In acidic solution the major reactive boron species is the trigonal boron acid. These studies are now described.

Temperature-jump studies were carried out on the complexation reactions of phenylboronic acid with oxalic acid [66] and with malonic acid [67]. Phenylboronic acid has a pK_a of 8.72 while oxalic acid has a value of 1.04 and malonic acid has a value of 2.59. The reaction with oxalic acid was faster than that with malonic acid indicating the importance of ligand acidity. It was also seen that the fully protonated ligands reacted faster than the ligand anions. These strongly acidic ligands afford the possibility of intramolecular hydrogen bonding, as shown below for oxalic acid.



$$\rightleftarrows \quad CX^{-} + H_3O^{+}$$

This hydrogen bonding interaction may be important to aid the leaving of the hydroxyl group and to orient the carboxyl group properly for attack on boron upon loss of the water molecule. In addition, both of the dianions oxalate and malonate failed to react which indicated that donor atom protonation was necessary for successful chelation to boron.

The study of the complexation reactions of phenylboronic acid with salicylic acid (pK_a = 2.83), mandelic acid (pK_a = 3.22) and lactic acid (pK_a = 3.70) in acidic medium yielded similar results [68,69]. In the case of the fully protonated ligands, the magnitude of the rate constants followed the order of ligand acidity. Salicylic acid reacted the fastest while lactic acid reacted the slowest. This result provided additional evidence for the critical role of proton transfer. Analogous to the observation in the dicarboxylic acid systems, salicylate anion reacted slower than salicylic acid. The same trend was seen in the reactions of salicylic acid with both meta-nitrophenylboronic acid (pK_a=6.97) and boric acid (pK_a=8.98). It was suggested that the strong hydrogen bond which is present in the salicylate anion may cause the reaction to be slower. However, both lactate and mandelate reacted with higher rate constants than the fully protonated forms of the ligands by one order of magnitude. The authors explained this result in terms of an attractive interaction between the delocalized π system of the carboxylate group and the phenyl substituent of phenylboronic acid. The subsequent stabilization of the transition state is reflected in the higher rate constants. The identical trend was observed in the meta-nitrophenylboronic acid / mandelic acid system [68] and similar arguments apply.

The last category of ligands to be considered are the catechols and the substituted catechols [68,70]. These ligands are rigid and are considerably less acidic than the dicarboxylic acids and the α-hydroxycarboxylic acids which were described above. The ligands used were 4-nitrocatechol (pK_a = 6.69), catechol (pK_a = 9.27) and 4-methylcatechol (pK_a = 9.39). For the complexation reactions of phenylboronic acid with the fully protonated ligands in acidic solution, the following results were obtained: 4-nitrocatechol, $k_f = 6.5 \times 10^2\ M^{-1}s^{-1}$; catechol, $k_f = 1.1 \times 10^2\ M^{-1}s^{-1}$; 4-methylcatechol, $k_f = 1.2 \times 10^2\ M^{-1}s^{-1}$. The most acidic ligand 4-nitrocatechol reacted the fastest. The reactions with catechol and 4-methylcatechol occur at the same rates in accord with their similar pK_a values. The same reactivity trends were observed for the analogous reactions with boric acid and methylboronic acid (pK_a=10.40) [68].

Up to this point the kinetic studies were performed on systems which produced only 1:1 complexes in acidic solution. The ligands which were used vary in pK_a from 1.04 to 9.39. The studies included four different boron acids in which the pK_a ranges from 6.97 (*meta*-nitrophenylboronic acid) to 10.4 (methylboronic acid). The conclusions from these studies may be summarized as follows. The stability constants and the rate constants depend upon the acidity of both the boron acid and the ligand. For any particular boron acid, the stability constants increase with increasing acidity of the ligand; for any particular ligand, the stability constants increase with increasing acidity of the boron acid. The factors which were responsible for the reaction rates include ligand acidity, donor atom protonation, hydrogen bonding and ligand flexibility. Despite the stereochemical differences among the ligands, the main conclusion was that the addition reaction between the trigonal boron acid and the fully protonated ligand was characterized by a transition state in which proton transfer played a critical role. A detailed description of this transition state is given in Chapter 3.

All of the kinetic studies described so far were concerned with the reactivity of the trigonal boron species and the studies were conducted in acidic solution up to pH 6. However, the pK_a of *meta*-nitrophenylboronic acid being sufficiently low (6.97) caused significant amounts of the tetrahedral *meta*- nitrophenylboronate anion, $m\text{-}NO_2\Phi B(OH)_3^-$, to be present in solution. This made it possible for the authors to determine upper limits of the rate constants for the reactions of the tetrahedral *meta*- nitrophenylboronate anion with both salicylic acid and mandelic acid [68]. Although these rate constants were only estimates, the results indicate that the substitution reactions of the tetrahedral borate anion are 3-4 orders of magnitude faster than the addition reactions of the trigonal *meta*-nitrophenylboronic acid.

The only known kinetic study which includes the formation of the 1:2 (boron acid : ligand) complex was carried out in 1983 by Pizer and Selzer [71]. Experiments consisting of boric acid (HB) coordinating to lactic acid (H_2L) were done under conditions (acidic media) where both the 1:1 and the 1:2 tetrahedral complexes were present. The 1:1 complex is formed by the addition reaction between the trigonal boron acid and lactic acid whereas the 1:2 complex is formed via the substitution reaction between the 1:1 complex and lactic acid. These reactions are shown below.

$$HB + H_2L \rightleftarrows CX_{1:1}^- + H_3O^+$$

$$CX_{1:1}^- + H_2L \rightleftarrows CX_{1:2}^- + 2H_2O$$

The authors discovered that the forward rate constant for the formation of the 1:2 complex was three orders of magnitude greater than that for the formation of the 1:1 complex. This result is analogous to that obtained from the reactions the *meta*-nitrophenylboronate anion. Both studies suggest that the substitution reactions of four-coordinate borates are more labile than the reactions of the trigonal boron species.

1.5 Comparison With Other Kinetic Systems

The complexation reactions of boron acids which were described above are characterized by several distinct features. Among these are a change in coordination number of boron upon complexation, a chelation step which emphasizes the importance of proton transfer and a kinetic requirement that at least one of the ligand donor atoms be protonated. This chemistry is not unique to boron acid reactions but do bear a close resemblance to the reactions of oxyanions.

Although the mechanisms of complexation of aquated metal ions are well understood, those of oxyanions have been less studied. There are various reasons for this. Aside from the fact that the structures of many oxyanions in solution are not clearly defined, there are experimental problems such as hydrolysis and polymerization which occur as conditions are varied [63]. However, the oxyanions molybdate MoO_4^- and tungstate WO_4^- have tetrahedral structures in solution [64]. Upon complexation with bidentate ligands such as catechol and substituted catechols, these oxyanions undergo an expansion of coordination number to form octahedral complexes. It is also known that reactions of unprotonated ligand with unprotonated oxyanion and fully protonated ligand with fully protonated oxyanion do not occur. This suggests a mechanism which involves proton transfer. In fact, studies of molybdate and tungstate complexation reactions show that some degree of protonation of either the ligand or the oxyanion is required [65,66].

The similarities in the chemistry of boron acids and oxyanions are seen in the variable coordination number and a mechanism of complexation which involves proton transfer. Both boron acids and oxyanions also undergo polymerization by the condensation of water molecules. The elucidation of the mechanism in the relatively simpler boron acid systems may therefore prove useful to the understanding of oxyanion complexation reactions.

1.6 Introduction to Peroxoborate Chemistry

All of the chemistry described so far includes boron acids coordinating to oxygen donor atoms of bidentate chelating ligands. However, there are studies in the literature which involve the coordination of unidentate ligands on boron. One such system is the peroxoborate complex $(HO)_3BOOH^-$ which may be formed by either the addition reaction of trigonal boric acid or the substitution reaction of the tetrahedral borate anion when solutions of boric acid are mixed with aqueous hydrogen peroxide. This particular system was chosen for a thermodynamic and kinetic study because it allows the investigation of addition and substitution reactions of a simple unidentate ligand on boron.

Alkali-metal salts of peroxoborates are widely used as bleaching agents in many household detergents. The X-ray crystal structures have been published for the following peroxoborate salts: $Na_2[B_2(O_2)_2(OH)_4].6H_2O$ [67], $Na_2[B_2(O_2)_2(OH)_4].4H_2O$ [68] and $Li_2[B_2(O_2)_2(OH)_4]$ [69]. These studies show that in all cases, the peroxoborate anion exist as a dimer with two tetrahedrally coordinated boron atoms and double peroxo bridges. (The structure of the dimer is given on page 148 .) Although the solid state of peroxoborates has been characterized, the nature of the aqueous species is not well understood.

In aqueous solution, the interaction between boric acid and hydrogen peroxide has been studied by various experimental techniques. As early as 1923, Menzel [70] using conductivity measurements proposed that it was the borate anion and not the trigonal boron acid which reacted with hydrogen peroxide to form a 1:1 peroxoborate complex, as shown below.

$$B(OH)_4^- \quad + \quad H_2O_2 \quad \rightleftarrows \quad (HO)_3BOOH^- \quad + \quad H_2O$$

Thirty years later, Edwards [71] studied the effect of peroxide concentration on the acidity of boric acid solutions. By measuring the decrease in pH of boric acid solutions upon the addition of hydrogen peroxide, Edwards postulated the presence of about six peroxoborate species. Following this work, Antikainen [72] used potentiometric titration in a preliminary study of the boric acid / hydrogen peroxide system and reported the existence of two peroxoborate species, $(HO)_3BOOH^-$ and $(HO)_2B(OOH)_2^-$. From a polarographic study in 1955 by Kern [73], the presence of peroxoborates was demonstrated, but the number and stoichiometry of the complexes was uncertain. In 1983, a Raman study [74] characterized the system as having one peroxoborate complex in solution, formulated as $(HO)_3BOOH^-$. The most recent study of the boric acid / hydrogen peroxide system was a ^{11}B NMR study [75] which reported the absence of any complex in acidic solution.

From the aqueous solution studies summarized above, the attempts to identify and characterize peroxoboron species have been neither successful nor convincing. The proposed number of peroxoboron complexes ranges from one to six. The uncertainty in these results clearly indicates that more work is needed in order to understand the system.

1.7 Experimental Objectives

There are four main objectives for the following experiments. Our first aim was to investigate the reactivity of the tetrahedral borates. This study includes the methylboronic acid / polyol system (Chapter 3) and the phenylboronic acid / polyol system (Chapter 5). Since all previous kinetic studies of complexation reactions between boron acids (pK_a : 6.96-10.4) and bidentate chelating ligands (pK_a : 1.04-9.39) were done in acidic solution, the authors were mainly observing the reactivity of the trigonal boron acid. In order to study the reactivity of the tetrahedral borates, it is necessary to work in basic media where the concentration of borate becomes important. In addition, previous kinetic studies have implied that tetrahedral borates are more labile than trigonal boron acids but there is no direct evidence to support this . The experiments in Chapters 3 and 5 were therefore undertaken to study the reactions of the tetrahedral borates.

Secondly, the boron acid / polyol systems were studied in order to investigate the effect of non - acidic ligands on the reaction mechanism. Recall that previous kinetic studies concluded that the reactions of trigonal boron acids with fully protonated ligands are characterized by a proton transfer transition state. The polyols were therefore used to determine the effect on the proton transfer mechanism when the ligands do no contain any acidic protons.

Thirdly, a thermodynamic study was carried out in order to measure the enthalpy and entropy changes for the substitution reactions of the boronic acid / polyol systems (Chapter 4). The results of Chapters 3 and 5 indicate that these substitution reactions are spontaneous. The measurement of the enthalpy and entropy changes would allow one to determine whether the driving force for the reaction is enthalpic or entropic in origin. Together with the stability constants and rate constants, a knowledge of the enthalpy and entropy changes for the boronic acid / polyol reactions would provide a more complete understanding and characterization of these systems.

Our final goal was to study the interaction between boric acid and hydrogen peroxide in aqueous solution from thermodynamic and kinetic measurements (Chapter 6). Previous thermodynamic studies on aqueous peroxoborates gave inconclusive results where the number of proposed peroxoboron complexes ranges from one to six. The application of the pH techniques used in this Laboratory would allow the characterization of the boric acid / hydrogen peroxide system and the quantitative measurement of the equilibrium constants. Other than the boric acid / hydrogen peroxide system two other systems are included in this study; the phenylboronic acid / hydrogen peroxide system and the boric acid / *tert* - butylhydroperoxide system. For the complexation reactions of boron acids with bidentate chelating ligands, the stability constants are known to increase with increasing acidity of the reactants. Phenylboronic acid is more acidic than boric acid and *tert* - butylhydroperoxide is less acidic than hydrogen peroxide. Therefore, the reason for including the two additional systems was to determine whether the acidity trend could be extended to these peroxoboron systems. In addition, recall that all of the kinetic studies described above contain bidentate chelating ligands. However, the peroxoboron complexes are believed to contain a unidentate hydroperoxo ligand (- OOH). Therefore, a kinetic study of the boron acid / peroxide systems would allow the investigation of addition and substitution reactions of a simple unidentate ligand on boron.

CHAPTER 2

EXPERIMENTAL METHODS AND ANALYSIS OF DATA

2.1 Determination of Stability Constants

The general mechanism for the complexation between a substituted boron acid and a bidentate chelating ligand is given in Scheme 1 below.The stability constants are measured by NaOH titration, pH mixing titrations and ^{11}B NMR experiments. Each method is described below.

Scheme 1

Protolytic equilibria:

$$HB + H_2O \rightleftarrows H^+ + B^- \qquad K_{HB} = [H^+][B^-]/[HB] \qquad (A1)$$

$$H_2L \rightleftarrows H^+ + HL^- \qquad K_{L1} = [H^+][HL^-]/[H_2L] \qquad (A2)$$

$$HL^- \rightleftarrows H^+ + L^{2-} \qquad K_{L2} = [H^+][L^{2-}]/[HL^-] \qquad (A3)$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_W = [H^+][OH^-] \qquad (A4)$$

Complexation equilibria:

$$HB + H_2L \rightleftarrows CX^- + H^+ \qquad K1 \qquad (A5)$$

$$B^- + H_2L \rightleftarrows CX^- + 2H_2O \qquad K2 = K1/K_{HB} \qquad (A6)$$

$$HB + HL^- \rightleftarrows CX^- + H_2O \qquad K3 = K1/K_{L1} \qquad (A7)$$

$$B^- + HL^- \rightleftarrows CX^- + OH^- + H_2O \qquad K4 = (K1{*}K_W)/(K_{L1}{*}K_{HB}) \qquad (A8)$$

2.1.1 NaOH Titration

A solution of known initial concentration of boron acid , ligand and electrolyte is titrated with standard 0.1 M NaOH at 25° C. A stability constant is then calculated for each point in the titration curve.

The derivation of the equations used in the calculation of the stability constant , K1 , for the complexation between the trigonal boron acid and the fully protonated ligand now follows . Once K1 has been determined, the values for K2,K3 and K4 are easily calculated since they are related to K1 by the acid dissociation constants for the boron acid and the ligand, and the ionization constant for water.

Conservation of mass and charge yields the following relationships.

$$B_0 = [HB] + [B^-] + [CX^-] \tag{A9}$$

$$L_0 = [H_2L] + [HL^-] + [L^{2-}] + [CX^-] \tag{A10}$$

$$[Na^+] + [H^+] = [B^-] + [HL^-] + 2[L^{2-}] + [CX^-] + [OH^-] \tag{A11}$$

where the subscript zero (0) refers to the initial concentrations.

From the protolytic equilibrium given by eqn (A1) ,

$$[B^-] = \frac{K_{HB}[HB]}{[H^+]}$$

Substituting this expression for $[B^-]$ into the conservation relationship expressed in eqn (A9) yields

$$B_0 = [HB] + \frac{K_{HB}[HB]}{[H^+]} + [CX^-]$$

$$B_0 = [HB]\left(1 + \frac{K_{HB}}{[H^+]}\right) + [CX^-]$$

Therefore,

$$[HB] = \frac{B_0 - [CX^-]}{\alpha} \qquad \text{(A12)}$$

$$\text{where } \alpha = 1 + \frac{K_{HB}}{[H^+]}$$

Similarly, the protolytic expressions given by eqns (A2) and (A3), are used to solve for the concentrations of $[HL^-]$ and $[L^{2-}]$.

$$[HL^-] = \frac{K_{L1}\,[H_2L]}{[H^+]}$$

$$\text{and } [L^{2-}] = \frac{K_{L2}\,[HL^-]}{[H^+]} = \frac{K_{L1}\,K_{L2}\,[H_2L]}{[H^+]^2} \qquad \text{(A13)}$$

Substituting the expressions for $[HL^-]$ and $[L^{2-}]$ into eqn (A10) yields

$$L_0 = [H_2L] + \frac{K_{L1}\,[H_2L]}{[H^+]} + \frac{K_{L1}\,K_{L2}\,[H_2L]}{[H^+]^2} + [CX^-]$$

$$L_0 = [H_2L]\left(1 + \frac{K_{L1}}{[H^+]} + \frac{K_{L1}\,K_{L2}}{[H^+]^2}\right) + [CX^-]$$

Therefore ,

$$[H_2L] = \frac{L_0 - [CX^-]}{\beta} \qquad \text{(A14)}$$

$$\text{where} \quad \beta = 1 + \frac{K_{L1}}{[H^+]} + \frac{K_{L1}\,K_{L2}}{[H^+]^2}$$

From the conservation relationships expressed by eqns (A9) and (A10) ,

$$[B^-] = B_0 - [HB] - [CX^-] \qquad \text{(A15)}$$

$$[HL^-] = L_0 - [H_2L] - [L^{2-}] - [CX^-] \qquad \text{(A16)}$$

After substituting eqns (A15) and (A16) into eqn (A11) and simplyfying, one obtains

$$[Na^+] + [H^+] = B_0 + L_0 - [HB] - [H_2L] + [L^{2-}] - [CX^-] + [OH^-] \qquad \text{(A17)}$$

Substituting for $[L^{2-}]$ from eqn (A13) and collecting terms ,

$$[Na^+] + [H^+] = B_0 + L_0 - [HB] - \gamma\,[H_2L] - [CX^-] + [OH^-] \qquad \text{(A18)}$$

$$\text{where} \quad \gamma = 1 + \frac{K_{L1}\,K_{L2}}{[H^+]^2}$$

Expressing $[OH^-]$ as $K_w / [H^+]$, $[Na^+]$ as Na_0 , and substituting for [HB] and $[H_2L]$ from eqns (A12) and (A14) yields

$$Na_0 + [H^+] = B_0 + L_0 - \frac{B_0}{\alpha} + \frac{[CX^-]}{\alpha} - \frac{\gamma L_0}{\beta} + \frac{\gamma\,[CX^-]}{\beta} - [CX^-] + \frac{K_w}{[H^+]}$$

Collecting terms,

$$[CX^-]\left(\frac{1}{\alpha}+\frac{\gamma}{\beta}-1\right) = Na_0 + [H^+] + B_0\left(\frac{1}{\alpha}-1\right) + L_0\left(\frac{\gamma}{\beta}-1\right) - \frac{K_w}{[H^+]}$$

One can now solve for $[CX^-]$.

$$[CX^-] = \frac{\left\{ Na_0 + [H^+] + B_0\left(\frac{1}{\alpha}-1\right) + L_0\left(\frac{\gamma}{\beta}-1\right) - \frac{K_w}{[H^+]} \right\}}{\left\{ \frac{1}{\alpha}+\frac{\gamma}{\beta}-1 \right\}} \qquad \text{(A19)}$$

Equation (A19) can be used to calculate $[CX^-]$; inserting this result in eqns (A12) and (A14) allows the evaluation of [HB] and $[H_2L]$, respectively. Knowing the pH from the titration data , K1 can be calculated.

$$K1 = \frac{[H^+]\,[CX^-]}{[HB]\,[H_2L]}$$

2.1.2 The pH Mixing Experiment

When the complexation reaction occurs , there is a readjustment of all the equilibria involved resulting in a pH change. Solutions of known concentration of boron acid and ligand are adjusted separately to the same initial pH. Aliquots of one are then titrated with the other and the pH change is measured.

The equilibria which readjust are as follows:

$$HB + H_2O \rightleftarrows H^+ + B^- \quad (B1)$$

$$H_2L \rightleftarrows H^+ + HL^- \quad (B2)$$

$$HL^- \rightleftarrows H^+ + L^{2-} \quad (B3)$$

The changes in the hydrogen ion concentration due to the shift of reactions (B1) to (B3) are defined below.

ΔH_1^+ = change due to dissociation of HB

ΔH_2^+ = change due to dissociation of H_2L

ΔH_3^+ = change due to dissociation of HL^-

The conservation relationships are as follows:

$$[HB] = [HB]_0 - [CX^-] - \Delta H_1^+ \quad (B4)$$

$$[B^-] = [B^-]_0 + \Delta H_1^+ \quad (B5)$$

$$[H_2L] = [H_2L]_0 - \Delta H_2^+ \quad (B6)$$

$$[HL^-] = [HL^-]_0 - [CX^-] + \Delta H_2^+ - \Delta H_3^+ \quad (B7)$$

$$[L^{2-}] = [L^{2-}]_0 + \Delta H_3^+ \quad (B8)$$

$$\Delta H^+ = \Delta H_1^+ + \Delta H_2^+ + \Delta H_3^+ \quad (B9)$$

In the conservation relationships, the subscript zero refers to the initial concentration before any readjustment , and ΔH^+ represents the measured pH change, that is , $([H_f^+] - [H_i^+])$.

From equations (B1), (B4) and (B5),

$$K_{HB} = \frac{[H_f^+][B^-]}{[HB]}$$

$$K_{HB} = \frac{[H_f^+]\,(\,[B^-]_0 + \Delta H_1^+\,)}{[HB]_0 - [CX^-] - \Delta H_1^+}$$

Solving for ΔH_1^+,

$$\Delta H_1^+ = \alpha - \beta[CX^-] \qquad \text{(B10)}$$

where $\alpha = \dfrac{K_{HB}[HB]_0 - [H_f^+][B^-]_0}{K_{HB} + [H_f^+]}$ and $\beta = \dfrac{K_{HB}}{K_{HB} + [H_f^+]}$

From eqns (B9) and (B10),

$$\Delta H_2^+ = \Delta H - \Delta H_3^+ - \alpha + \beta[CX^-] \qquad \text{(B11)}$$

From eqns (B2) and (B6),

$$K_{L1} = \frac{[H_f^+][HL^-]}{[H_2L]}$$

$$K_{L1} = \frac{[H_f^+]\,(\,[HL^-]_0 - [CX^-] + \Delta H_2^+ - \Delta H_3^+\,)}{[H_2L]_0 - \Delta H_2^+} \qquad \text{(B12)}$$

Using eqns (B11) and (B12), an expression for ΔH_3^+ can be derived in terms of variables except ΔH_1^+ and ΔH_2^+.

This expression is given in eqn (B13).

$$\Delta H_3^+ = \frac{K_{L1}\{[H_2L]_0+\alpha-\Delta H^+\}+[H_f^+]\{\alpha-[HL^-]_0-\Delta H^+\}+[CX^-]\{[H_f^+](1-\beta)-K_{L1}\,\beta\}}{-K_{L1}-2[H_f^+]} \qquad \text{(B13)}$$

From eqns (B3), (B7) and (B8),

$$K_{L2} = \frac{[H_f^+][L^{2-}]}{[HL^-]}$$

$$K_{L2} = \frac{[H_f^+]\{[L^{2-}]_0+\Delta H_3^+\}}{[HL^-]_0-[CX^-]+\Delta H_2^+-\Delta H_3^+} \qquad \text{(B14)}$$

Using eqns (B11) and (B14), an expression for ΔH_3^+ can be derived in terms of variables except ΔH_1^+ and ΔH_2^+.

This expression is given in eqn (B15).

$$\Delta H_3^+ = \frac{K_{L2}\{[HL^-]_0+\Delta H^+-\alpha\}+[H_f^+]\{-[L^{2-}]_0\}+[CX^-]\{K_{L2}(\beta-1)\}}{(2K_{L2}+[H_f^+])} \qquad \text{(B15)}$$

Equating eqns (B13) and (B15) allows one to solve for $[CX^-]$.

The solution is given in eqn (B16).

$$[CX^-] = \frac{P + Q}{R} \qquad \text{(B16)}$$

where

$$P = \frac{K_{L1}\{[H_2L]_0 + \alpha - \Delta H^+\} + [H_f^+]\{\alpha - [HL^-]_0 - \Delta H^+\}}{(K_{L1} + 2[H_f^+])}$$

$$Q = \frac{K_{L2}\{[HL^-]_0 + \Delta H^+ - \alpha\} - [H_f^+][L^{2-}]_0}{(2K_{L2} + [H_f^+])}$$

$$R = \frac{(K_{L2}(1 - \beta))}{(2K_{L2} + [H_f^+])} + \frac{(K_{L1}\beta - [H_f^+](1 - \beta))}{(K_{L1} + 2[H_f^+])}$$

From the above equations, the concentration of the complex can be calculated. Using eqns (B4) and (B10), one can evaluate [HB]. The value for $[H_2L]$ can be calculated from eqns (B6), (B11) and (B13). The stability constant can then be determined.

$$K1 = \frac{[H_f^+][CX^-]}{[HB][H_2L]}$$

Once the stability constants have been determined , they can be used to calculate all equilibrium concentrations from the equations given in each derivation above. The calculated values of the concentrations can then be used to prepare distribution diagrams of all boron-containing species as a function of the pH.

The titrations are carried out at a constant temperature of 25 °C by use of a circulating water bath. Nitrogen gas is bubbled into the solution throughout the titration in order to remove any dissolved carbon dioxide from the atmosphere. The ionic strength is maintained at $\mu = 0.1$ M by the addition of either potassium nitrate or potassium chloride. In order to correct for the hydrogen ion activity , the Davies equation [76] given below was used.

$$\log \gamma_{+,-} = -0.5 \left| z_+ z_- \right| \left\{ \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3 \sqrt{\mu} \right\}$$

The pH measurements were obtained using the following meters;

1. Corning Model 12 Research pH Meter.
2. Fisher Accumet Model 620 pH Meter.
3. Fisher Scientific Accumet Model 950 pH / ion Meter.

2.1.3 The ^{11}B NMR Experiments

The Boric Acid / Hydrogen Peroxide System

Stability constants were determined by both NaOH and pH mixing titrations and were used to calculate a distribution diagram of all boron-containing species as a function of the pH. The distribution diagram was then used to find suitable pH conditions for running the ^{11}B NMR experiments. As a reference, the signal of a 0.1 M $B(OH)_3$ solution at pH 6 was set at 0 ppm and all other spectra were recorded relative to this setting. The spectra of solutions containing both 0.1 M $B(OH)_3$ and 1.0 M H_2O_2 were recorded in a pH range form 6 to 12, and a temperature range from 2.9 °C to 55.5 °C . In all cases, overlapping peaks were observed. Although no quantitative determination of stability constants was possible, the resulting spectra gave qualitative agreement with the predictions from the distribution diagram.

The Methylboronic Acid / Polyol Systems

The ^{11}B NMR spectra of methylboronic acid coordinating to ethylene glycol,1,2-propanediol,1,3-propanediol and glycerol were recorded at 25 °C. As a reference , the signal of a 0.02 M $CH_3B(OH)_2$ solution at pH 11 was set at 0 ppm. Methylboronic acid has a pK_a value of 10.4 ; therefore , the blank solution at pH 11 contained both $CH_3B(OH)_2$ and $CH_3B(OH)_3^-$. Since one peak was observed in the blank solution, this means that the rate of interconversion of the trigonal boron acid and the tetrahedral borate anion is fast on the NMR timescale.

The calculated distribution diagram and a ^{11}B NMR spectrum of methylboronic acid and 1,3-propanediol is given in Figure 2-1. The first peak in the spectrum at approximately 0 ppm is assigned to both methylboronic acid and methylboronate anion; the second, more narrow peak, is assigned to the complex. The calculation of the stability constant from the ^{11}B NMR spectrum now follows.

For methylboronic acid coordinating to ethylene glycol, 1,2-propanediol and 1,3-propanediol, the reaction may be written as

$$B^- + H_2L \rightleftarrows CX^- + 2H_2O \qquad K2$$

From the initial concentrations and the measured pH, the following quantities are known : $[HB]_0$, $[H_2L]_0$ and $[H^+]$ at equilibrium.

The integrated spectra gave :

$$A_{HB+B^-} \quad \text{and} \quad A_{CX^-}$$

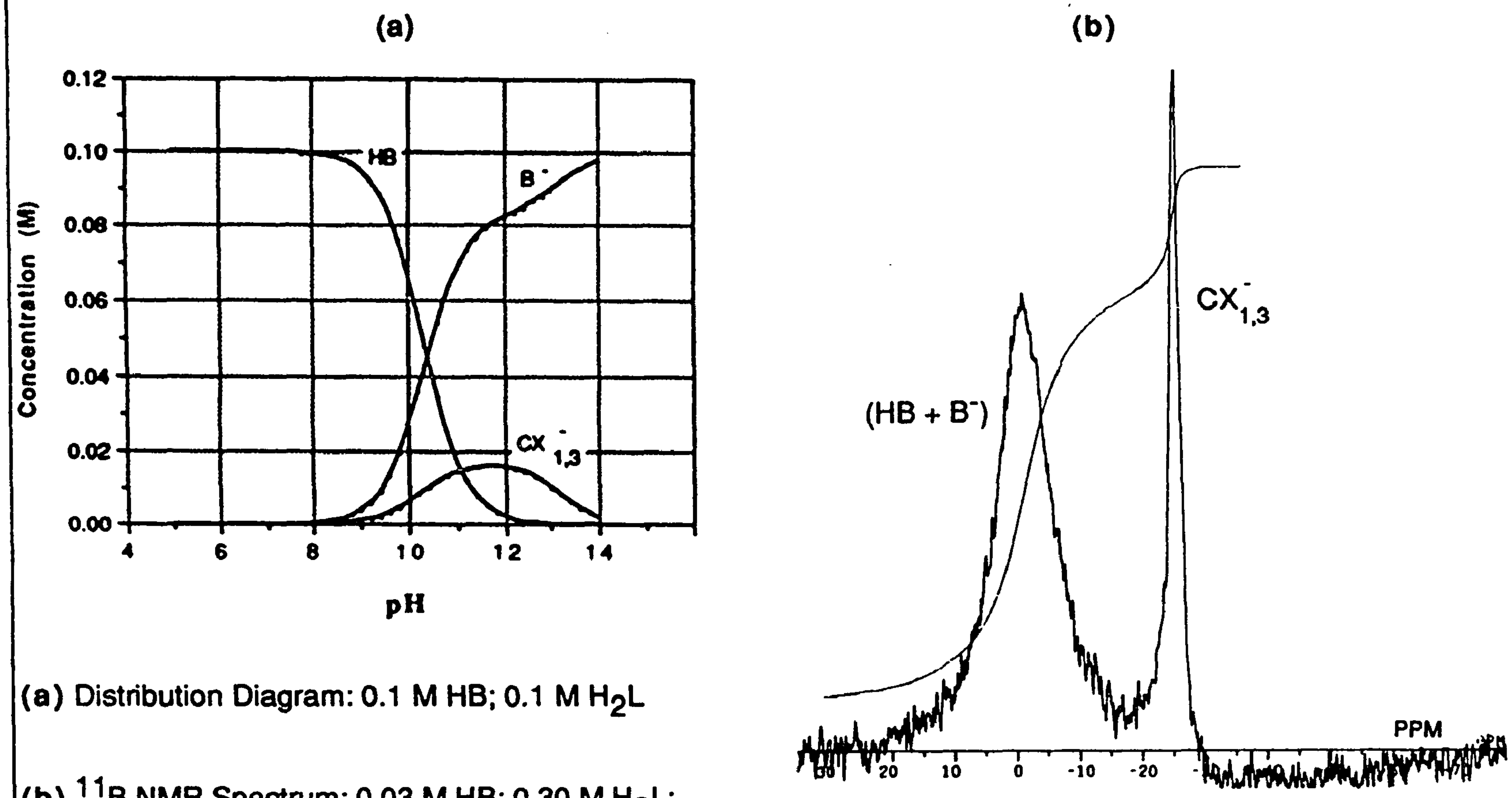
where A refers to the area under the peak.

The conservation relationships are

$$[HB]_0 = [HB] + [B^-] + [CX^-] \qquad (C1)$$

$$[H_2L]_0 = [H_2L] + [CX^-] \qquad (C2)$$

Figure 2-1: Distribution Diagram and ^{11}B NMR Spectrum for Methylboronic Acid / 1,3-propanediol System



(a) Distribution Diagram: 0.1 M HB; 0.1 M H_2L

(b) ^{11}B NMR Spectrum: 0.03 M HB; 0.30 M H_2L;
pH = 10.32

Since the sum of the concentrations of all boron-containing species is equal to $[HB]_0$, the following relationship is true.

$$[CX^-] = \left\{ \frac{A_{CX^-}}{A_{HB+B^-} + A_{CX^-}} \right\} [HB]_0 \qquad \text{(C3)}$$

One can use the known pH and the known ionization constant of the boron acid, K_{HB} , to express [HB] in terms of $[B^-]$. The result is

$$[HB] = \frac{[H^+][B^-]}{K_{HB}}$$

This expression can be substituted into eqn (C1) as follows:

$$[HB]_0 = \frac{[H^+][B^-]}{K_{HB}} + [B^-] + [CX^-]$$

$$[HB]_0 = [B^-]\{1 + \frac{[H^+]}{K_{HB}}\} + [CX^-]$$

Solving for $[B^-]$,

$$[B^-] = \frac{[HB]_0 - [CX^-]}{\alpha} \qquad \text{(C4)}$$

where $\alpha = 1 + \frac{[H^+]}{K_{HB}}$

From eqn (C2),

$$[H_2L] = [H_2L]_0 - [CX^-] \qquad (C5)$$

Knowing the initial concentrations and the pH, the values for $[CX^-]$, $[B^-]$ and $[H_2L]$ can be calculated from eqns (C3) - (C5). The stability constant K2 can then be determined.

$$K2 = \frac{[CX^-]}{[B^-][H_2L]}$$

NMR spectra similar to the one given in Figure 2-1 were obtained for methylboronic acid coordinating to ethylene glycol and 1,2-propanediol. For the methylboronic acid / gylcerol system , an additional peak was observed since this ligand forms two complexes with the boron acid. In all cases, the stability constants from the ^{11}B NMR technique agreed with those obtained by pH titration methods to within ± 20 %.

The ^{11}B NMR spectra were obtained using a JEOL GX 400 - MHz NMR spectrometer operating at a frequency of 128 MHz. Quartz NMR tubes (10 mm) had to be used since strong ^{11}B resonances are known to occur in Pyrex [77]. All solutions were 0.1 M KNO_3 (or KCl), and approximately 25 % in D_2O which was used as a frequency lock. The solutions were freshly prepared , and the pH was measured before and after running the experiment.

2.2 Determination of Rate Constants

2.2.1 The Relaxation Method

For systems in which the reactions are complete within the time of mixing, conventional and flow methods for rate measurements are not suitable. In addition, these classical methods usually determine an overall rate constant which may be composed of equilibrium constants and various rate constants, depending upon the steps prior to the rate determining step. These studies are therefore difficult to analyze in terms of individual elementary reactions. In order to obtain information about the detailed mechanism by which a chemical reaction occurs, methods for studying very fast reactions are needed. The relaxation methods, originally developed by Eigen [78] in the 1950's , spanning a time range between 1 and 10^{-10} seconds, have been proven to be very useful.

All relaxation methods are based on the same principle. Instead of attempting to mix the reactants, a system which is already at equilibrium is perturbed by varying an external parameter (for example, temperature, pressure or electric field), thereby shifting the equilibrium position ; the process by which the system returns to a new equilibrium state is called chemical relaxation and is characterized by a time constant called the relaxation time. An important assumption in relaxation methods is that the perturbations are small and this allows the rate expression to be linearized.

In order to define the relaxation time, consider a species x whose concentration at any time, t, may be expressed as

$$x(t) = (\bar{x}) + \delta x$$

where $(\bar{x})$ = a time independent equilibrium concentration

δx = a time dependent small deviation from equilibrium

For small perturbations, the approach to the new equilibrium state is given by the rate of disappearance of the deviation from equilibrium, and is proportional to the deviation. The first order expression is given by

$$-\frac{d\,\delta x}{dt} = k\,\delta x \qquad (1)$$

where $k = 1/\tau$

τ = the relaxation time

The relaxation time is seen to be the inverse of the observed first order rate constant accompanying the relaxation process.

A second definition of the relaxation time is obtained from the analysis given below. The first order differential equation (1) may be rearranged as follows:

$$\frac{d\,\delta x}{\delta x} = -k\,dt$$

A relationship between concentration change and time may be obtained by integrating from time $t = 0$ ($\delta x = \delta x_0$) to time t ($\delta x = \delta x_t$).

$$\int_{\delta x_0}^{\delta x_t} \left(\frac{1}{\delta x}\right) d\,\delta x = -\int_0^t k\,dt$$

Solving the integral leads to the following:

$$\ln \frac{\delta x_t}{\delta x_o} = -kt$$

or

$$\frac{\delta x_t}{\delta x_o} = e^{-kt}$$

After substituting $k = 1/\tau$ and rearranging , one obtains

$$\delta x_t = e^{-t/\tau}\ \delta x_o$$

when $t = \tau$,

$$\delta x_\tau = \left(\frac{1}{e}\right) \delta x_o \qquad (2)$$

Therefore, the relaxation time is also the time it takes for the time dependent concentration, δx, to decrease to (1 / e) of the initial value. This relationship is illustrated in Figure 2-2.

All that is measured experimentally is the relaxation time ,τ . The expression for the relaxation time is a function of all rate constants and equilibrium constants and depends upon the overall mechanism. Since the system is always close to equilibrium, both the forward and the reverse rate constants will contribute in an additive way to the relaxation time.

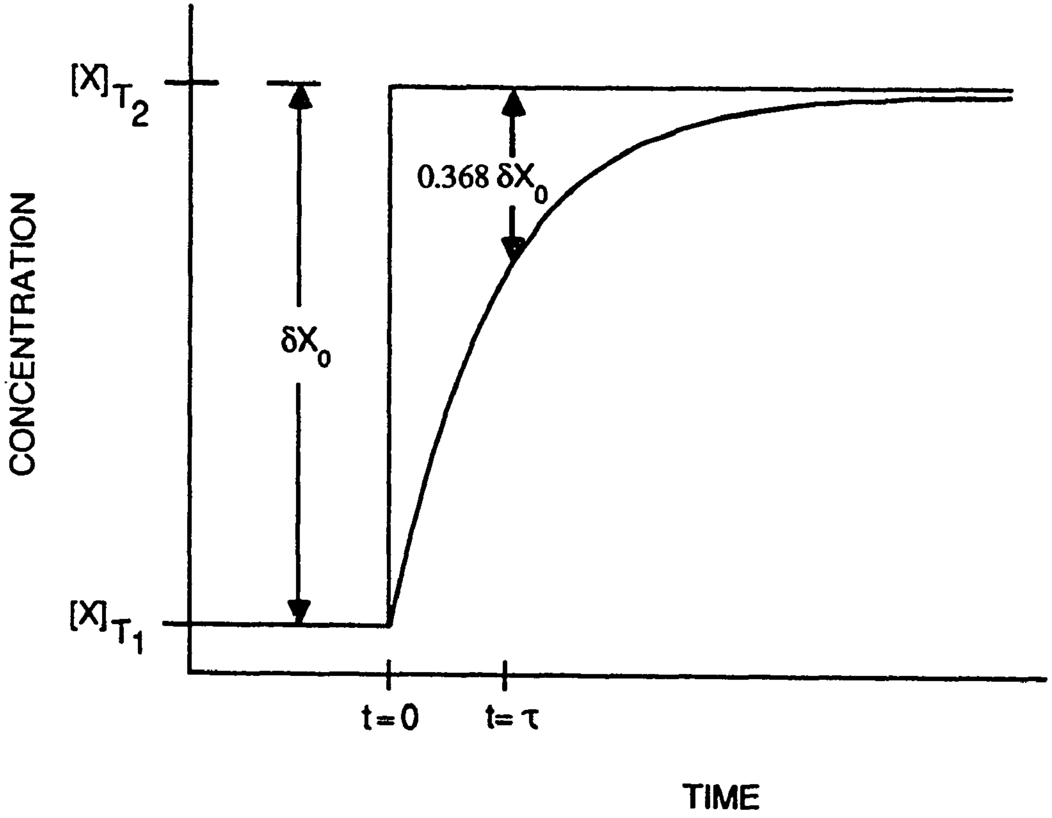


Figure 2-2 : Instantaneous Temperature Displacement Followed by Chemical Relaxation

A simple kinetic derivation of the relaxation time expression for a single-step reaction is now given in order to illustrate the following:

(1) the linearization process

(11) the positive contributions of the forward and reverse rate constants

(111) the dependence of τ upon the overall reaction

Consider the general reaction below with equilibrium constant K.

$$A + B \underset{k_r}{\overset{k_f}{\rightleftarrows}} C \qquad K = \frac{k_f}{k_r} \qquad (3)$$

The rate law is given by

$$-\frac{d(A)}{dt} = k_f (A)(B) - k_r (C)$$

At any time t, the concentration terms may be expanded as the sum of an equilibrium value and a small deviation from equilibrium term.

$$(A) = (\bar{A}) + \delta A$$

$$(B) = (\bar{B}) + \delta B$$

$$(C) = (\bar{C}) + \delta C$$

where

$(\bar{A})$, $(\bar{B})$ and $(\bar{C})$ = time independent equilibrium concentrations

δA, δB and δC = time dependent small deviations from equilibrium

The rate law may be rewritten using the expanded concentration terms.

$$-\frac{d\,((\bar{A})+\delta A)}{dt} = k_f\,((\bar{A})+\delta A)\,((\bar{B})+\delta B) - k_r\,((\bar{C})+\delta C)$$

$$-\frac{d\,(\bar{A})}{dt} - \frac{d\,\delta A}{dt} = k_f\,((\bar{A})(\bar{B}) + (\bar{A})\delta B + (\bar{B})\delta A + \delta A\delta B) - k_r\,((\bar{C})+\delta C) \quad (4)$$

Equation (4) may be simplified by use of the following:

a. Since $(\bar{A})$ does not depend upon time, $\frac{d\,(\bar{A})}{dt} = 0$.

b. At equilibrium, $k_f\,(\bar{A})\,(\bar{B}) - k_r\,(\bar{C}) = 0$.

c. For small perturbations, the deviations from equilibrium are small, that is, $\delta A << (\bar{A})$. Therefore, the crossterms can be neglected or $\delta A\delta B = 0$, and the rate expression is linearized.

After satisfying the above conditions in eqn (4) , one obtains

$$-\frac{d\,\delta A}{dt} = k_f\,((\bar{A})\,\delta B + (\bar{B})\,\delta A) - k_r\,(\delta C)$$

From conservation , $\delta A = \delta B = -\delta C$. Using this relationship leads to

$$-\frac{d\,\delta A}{dt} = \left(k_f\,((\bar{A}) + (\bar{B})) + k_r\right)\delta A \qquad (5)$$

This equation is a first order differential equation and , by definition ,

$$\tau = \left(k_f\,((\bar{A}) + (\bar{B})) + k_r\right)^{-1} \qquad (6)$$

Equation (6) contains two variables , k_f and k_r . Elimination of one of the variables by use of the relationship $k_r = k_f / K$, where K is the equilibrium constant , yields

$$\tau = \left(k_f \left((\bar{A}) + (\bar{B}) \right) + \frac{1}{K} \right)^{-1} \tag{7}$$

These last two equations reveal the dependence of the relaxation time upon equilibrium concentrations, equilibrium constants and the forward and the reverse rate constants.

The kinetic derivation given above was for the case in which a simple reaction occurs in a single step, and is accompanied by one relaxation time. Very often, reactions occur in a series of coupled steps, some of which may be fast diffusion controlled steps (for example, protolytic reactions) , while others may be slower. In the temperature-jump experiments covered in this thesis, the equilibria of protolytic reactions are rapidly established with respect to the timescale of the instrument and are considered to be always in equilibrium.It is then possible to follow the relaxation of the slower steps. For such a multistep mechanism, when there is more than one step exhibiting a relaxation effect , the number of relaxation times expected is given by the equation below [79].

$$n = x - (m + r) \tag{8}$$

where

n = the number of relaxation times expected

x = the number of concentration variables in the equation

m = the number of conservation relationships

r = the number of rapid (protolytic) equilibria

As an example, consider the following reaction mechanism.

$$HA \rightleftarrows H^{+} + A^{-}$$

$$A^{-} + L \rightleftarrows AL^{-}$$

$$AL^{-} + L \rightleftarrows AL_2^{-}$$

The number of relaxation times expected , n , is given by n = 6 - (3 + 1) = 2. This means that there will be two independent rate equations describing the system.

In the general case, for n relaxation times, there are n independent rate equations. At equilibrium, the rate equations are linear first order differential equations of the form

$$-\frac{d\,\delta x_i}{dt} = \sum_{j=1}^{n} a_{ij}\ \delta x_j \qquad (9)$$

where the a_{ij} 's are functions of equilibrium concentrations and rate constants which appear in the rate expression. In order to solve such a system of equations, one can use the matrix method to rewrite the equations in the form

$$-\frac{d\{x\}}{dt} = \{A\}\{x\} \qquad (10)$$

where $\{x\}$ is a column matrix ($\delta x_1, \delta x_2 \ldots \delta x_n$) and $\{A\}$ is an nxn matrix with coefficients a_{ij} .

Solving by integration, the solution defines the elements of the A matrix in terms of $1/\tau_i$ [80]. The relaxation times τ_i are the eigenvalues obtained by solving the determinant

$$\begin{vmatrix} a_{11}-\frac{1}{\tau} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22}-\frac{1}{\tau} & \cdots & a_{2n} \\ - & - & - & - \\ a_{n1} & \cdots & & a_{nn}-\frac{1}{\tau} \end{vmatrix} = 0$$

Since the reactions are all coupled, the relaxation times are not associated with particular steps but are functions of all equilibrium concentrations, equilibrium constants and rate constants in the entire reaction mechanism. The coupling here is analogous to that found in vibrational spectroscopy where the frequency of a normal mode is measured rather than that of a single bond. The relaxation times of coupled reactions are functions of the normal mode coordinates of the system. The normal modes of the reaction are linear combinations of the concentrations of all the species present.

The number of relaxation times calculated from eqn (8) are not always observed experimentally. There are various reasons for this. First, if the amplitude is too small, it may not be seen. Strehlow and Jehn have reported on the difficulty of separating relaxation times of different amplitudes even when the τ's differ by a factor of four [81]. Secondly, if the relaxation process is too fast or too slow with respect to the timescale of the instrument, no exponential is observed. Third, if two relaxation times have the same time constant, only a single relaxation time will be seen [82]. Finally, if a steady state exists for a particular species, no relaxation for that process will be obtained [83].

The relaxation technique has been used successfully in the elucidation of numerous reaction mechanisms. One of the limitations of this technique is that the system must be reasonably reversible so that detectable concentrations of all species are present at equilibrium.

In order to observe a relaxation process, one way to perturb the equilibrium is by a sudden change in the temperature. Most reactions are temperature dependent and from the van't Hoff equation [84],

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} ,$$

a system having a finite ΔH value will experience a shift in equilibrium upon a change in temperature T. When the temperature is the state parameter used to perturb the system, the technique is referred to as the temperature-jump method. It is important to note that one of the requirements for being able to do temperature-jump studies is that at least one step in the mechanism must have a finite ΔH value so that measureable changes are observed.

2.2.2 The Temperature-jump Experiment

The initial equilibrium of the reaction mixture is perturbed by an abrupt increase in the temperature. The most commonly used method for obtaining the temperature rise is by Joule heating in which a high voltage capacitor is rapidly discharged through the solution. The amount of electrical energy which is delivered into the system is given by

$$E = \frac{1}{2} C U^2$$

where C = capacitance (farads)

U = charging voltage (volts)

The temperature rise is an exponential function of time and is characterized by a finite rise time which is given by RC/2 , where R is the resistance (ohms) and C is the capacitance (farads). When the reactions occur in times much longer than RC/2, the temperature rise is close to a step function and the heating process can be considered to occur instantaneously. In this manner, the approach to a new equilibrium state at the final temperature is in accordance with the rate laws governing the system and is first order [78].

To ensure that $\tau >> RC/2$, the resistance of the solution is kept low by the addition of an inert electrolyte (0.1 M KNO_3 or 0.1 M KCl). For a typical experiment, the electrically conducting aqueous solution has a small resistance of about 100 ohms which leads to a fast rise time. The added electrolyte also maintains a constant ionic strength in the reaction mixture.

The electrical energy from the capacitor is discharged through the solution within a very short time. In order to produce a fast homogeneous temperature rise in the system, an energy distribution must take place. For liquids , the energy distribution among translational and rotational modes occur within 10^{-12} seconds. In the case of vibrational modes, the time required for energy transfer is longer than 10^{-12} seconds but is still less than the time required for the temperature rise (10^{-6} sec.). Therefore, for aqueous solutions, a complete equilibration and distribution of energy occurs within the risetime of the temperature.

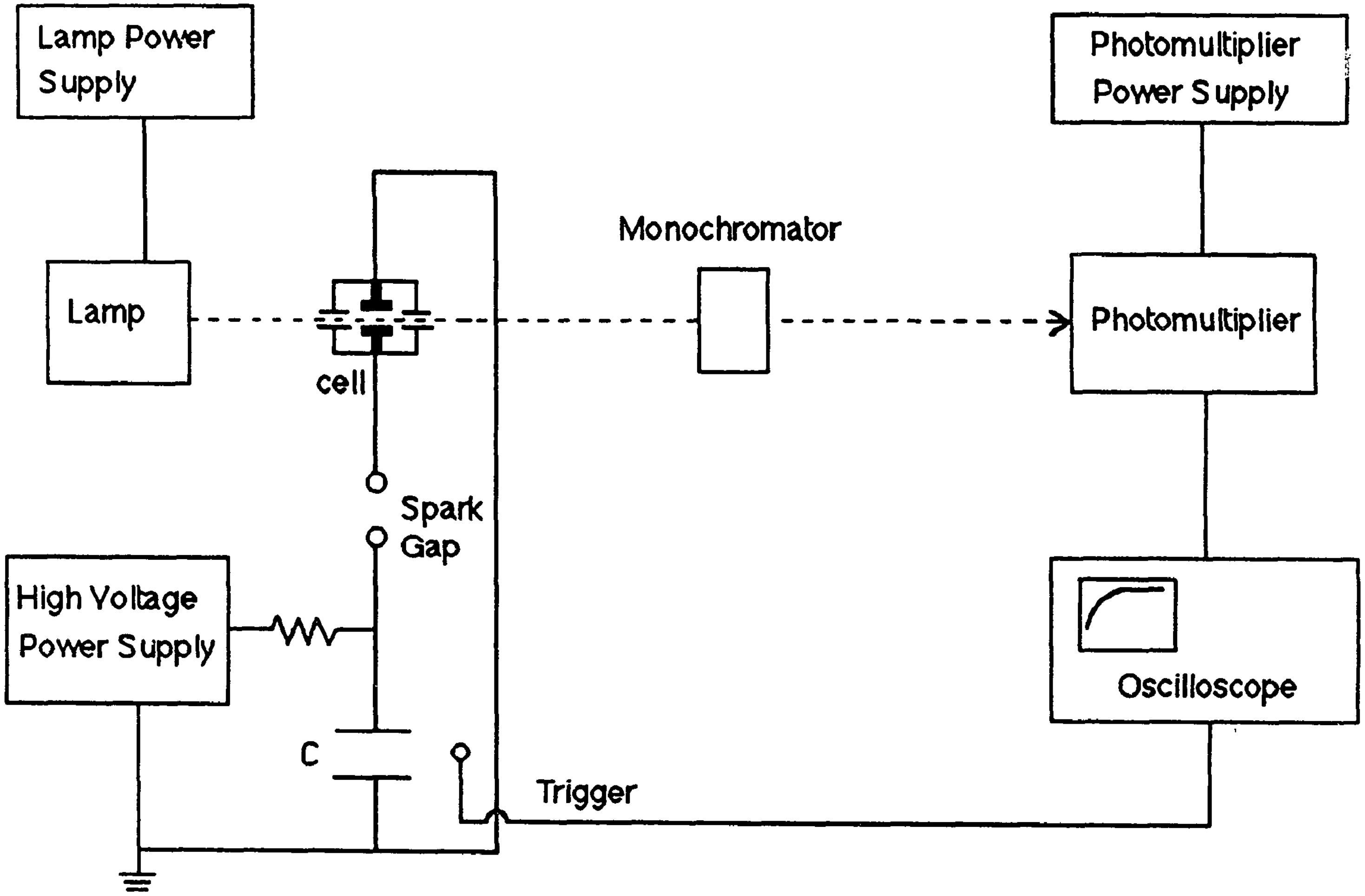
Another point to consider is that of thermal expansion. Since rapid heating of the solution takes place at constant volume, there is a relatively large increase in the pressure (up to 50 atm) which accompanies the temperature change. This pressure increase is propagated through the solution as a shock wave. The reflection of the shock wave by the walls of the sample cell result in cavitation effects which are due to the rise and collapse of the wave. These effects become important if the heating process occurs in less than 10^{-5} seconds and can be avoided by working at lower temperatures [78]. The pressure variation with change in temperature is given by

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T = \frac{\alpha_P}{\kappa_T}$$

At low temperatures, for example at 4 °C, $\alpha_P = 0$ for H_2O and cavitation effects practically disappear. The theory of the relaxation method and the experimental techniques for various applications have been described in many texts [78,80,82,84,85].

A schematic diagram of the temperature-jump apparatus used in this study given in Figure 2 -3.

Figure 2-3 : Schematic Diagram of Temperature-jump Apparatus



In a typical experiment, the reaction mixture is allowed to equilibrate at 15 °C by use of a circulating water bath. A 0.1 µfarad capacitor is then charged to 30,000 volts by a high voltage power supply. Using an external trigger, a variable spark gap completes the circuit and the capacitor discharges 45 Joules of energy into the solution within 10^{-5} to 10^{-6} seconds. The sample cell is designed such that the total volume of solution is 25 ml but the volume between the two stainless steel electrodes is 1 ml. The input of 45 Joules of energy heats the 1 ml of solution by 10 °C. The remaining solution outside of the electrode region acts as a heat sink and after approximately 1 second, convective cooling begins. The upper limit of the time range accessible to the temperature-jump is therefore 1 second. The lower limit is set by the rise time of the instrument which is given by

$$t = \frac{RC}{2}$$

The cell resistance of 100 ohms and the capacitance of 0.1 µfarad leads to rise time of 5 µsec which is well out of the range of any of the relaxation times studied. The 10 °C rise in the temperature is experimentally confirmed by the comparison of the output voltages of an indicator solution at 15°C and 25°C with the change in voltage which is observed when the capacitor is discharged through the solution.

This temperature-jump instrument uses a spectrophotometric method of detection but conductimetric and polarimetric detection systems are also known. Since the reactants are colorless, the system is coupled to an acid - base indicator and the change in absorbance of the indicator is monitored at a suitable wavelength (λ_{max} = 553 nm for phenolphthalein and 596 nm for thymol blue). The proton transfer reaction of the indicator is rapidly established and is therefore always in equilibrium with the slower complexation process. From the coupled reactions the change in concentration of one of the reactants, the hydrogen ion, is monitored as the system approaches the new equilibrium state at 25 °C.

2.3 Relaxation Expressions for Boron Acid Systems

2.3.1 General Boron Acid / Ligand System

The expression for the relaxation time depends upon the overall mechanism. The relaxation time cannot be associated with any particular step but is a function of all rate constants (both forward and reverse), equilibrium concentrations, dissociation constants and stability constants. The equilibria for the formation of a 1:1 complex from a substituted boron acid and a bidentate chelating ligand are presented in Scheme 1. The derivation of the relaxation expression now follows.

Scheme 1

Rapid Protolytic Equilibria:

$$HB + H_2O \rightleftarrows H^+ + B^- \qquad K_{HB} = \frac{[H^+][B^-]}{[HB]} \qquad (D1)$$

$$H_2L \rightleftarrows H^+ + HL^- \qquad K_{L1} = \frac{[H^+][HL^-]}{[H_2L]} \qquad (D2)$$

$$HIn \rightleftarrows H^+ + In^- \qquad K_{In} = \frac{[H^+][In^-]}{[HIn]} \qquad (D3)$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = [H^+][OH^-] \qquad (D4)$$

Complexation equilibria:

$$HB + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CX^- + H^+ \qquad K1 \tag{D5}$$

$$B^- + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CX^- + 2H_2O \qquad K2 \tag{D6}$$

$$HB + HL^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} CX^- + H_2O \qquad K3 \tag{D7}$$

$$B^- + HL^- \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} CX^- + OH^- + H_2O \qquad K4 \tag{D8}$$

The protolytic equilibria of boron acid, ligand and indicator are much faster than, and are always in equilibrium with, the complexation steps. Therefore, it is possible to follow the rate of the slower complexation reaction.

The variables are: HB, B^-, H_2L, HL^-, CX^-, H^+, OH^-, HIn, In^-

The conservation relationships are:

$$0 = \delta HB + \delta B^- + \delta CX^- \tag{D9}$$

$$0 = \delta H_2L + \delta HL^- + \delta CX^- \tag{D10}$$

$$0 = \delta HIn + \delta In^- \tag{D11}$$

$$\delta H^+ = \delta B^- + \delta HL^- + \delta CX^- + \delta OH^- + \delta In^- \tag{D12}$$

The number of relaxation times n is given by the equation, $n = x - (m + r)$, where x = the number of variables, m = the number of conservation relationships and r = the number of rapid protolytic equilibria.

In the present kinetic Scheme, $x = 9$, $m = 4$ and $r = 4$. Therefore, one relaxation time should be seen and the expression for the relaxation time should take the form:

$$-\frac{d\,\delta CX^-}{dt} = \frac{1}{\tau}\,\delta CX^-$$

The complexation pathways given by eqns (D6) and (D7) have the same pH dependence. Due to this " proton ambiguity," the two reactions are kinetically indistinguishable. This means that the values for the rate constants for reactions (D6) and (D7) cannot be determined exactly but upper limits could be set for either one.

From the complexation mechanism (D5) - (D8), the rate law may be described in the usual manner, that is

$$\begin{aligned} +\frac{d[CX^-]}{dt} = \; & k_1[HB][H_2L] - k_{-1}[H^+][CX^-] \\ & + k_2[B^-][H_2L] - k_{-2}[CX^-] \\ & + k_3[HB][HL^-] - k_{-3}[CX^-] \\ & + k_4[B^-][HL^-] - k_{-4}[CX^-][OH^-] \end{aligned} \qquad (D13)$$

Due to the " proton ambiguity " phenomenon, the terms in the rate expression containing k_2, k_{-2}, k_3 and k_{-3} in eqn (D13) may be rewritten as follows:

First, from eqn (D1),

$$[HB] = \frac{[H^+][B^-]}{K_{HB}}$$

and, from eqn (D2),

$$[HL^-] = \frac{K_{L1}\,[H_2L]}{[H^+]}$$

These two expressions may be substituted into the k_2, k_{-2}, k_3 and k_{-3} terms in the rate law, that is,

$$k_2[B^-][H_2L] - k_{-2}[CX^-] + k_3[HB][HL^-] - k_{-3}[CX^-]$$

$$= k_2\,[B^-]\,[H_2L] + k_3\,\frac{[H^+]\,[B^-]}{K_{HB}}\,\frac{K_{L1}\,[H_2L]}{[H^+]} - (k_{-2} + k_{-3})\,[CX^-]$$

$$= (k_2 + k_3\frac{K_{L1}}{K_{HB}})\,[B^-]\,[H_2L] - (k_{-2} + k_{-3})\,[CX^-]$$

$$= k^{/}\,[B^-]\,[H_2L] - k^{//}\,[CX^-]$$

where $k^{/} = k_2 + k_3\,\frac{K_{L1}}{K_{HB}}$ and $k^{//} = k_{-2} + k_{-3}$

The complete rate law in eqn (D13) may now be described as

$$+\frac{d\,[CX^-]}{d\,t} = k_1\,[HB]\,[H_2L] - k_{-1}\,[H^+]\,[CX^-]$$

$$+ k^{/}\,[B^-]\,[H_2L] - k^{//}\,[CX^-]$$

$$+ k_4\,[B^-]\,[HL^-] - k_{-4}\,[CX^-]\,[OH^-]$$

Expressing the concentrations as an equilibrium value plus a small deviation from equilibrium, the rate law becomes

$$+\frac{d\,(\overline{[CX^-]}+\delta CX^-)}{dt} = k_1(\overline{[HB]}+\delta HB)(\overline{[H_2L]}+\delta H_2L) - k_{-1}(\overline{[H^+]}+\delta H^+)(\overline{[CX^-]}+\delta CX^-)$$

$$+\,k^{/}(\overline{[B^-]}+\delta B^-)(\overline{[H_2L]}+\delta H_2L) - k^{//}(\overline{[CX^-]}+\delta CX^-)$$

$$+\,k_4(\overline{[B^-]}+\delta B^-)(\overline{[HL^-]}+\delta HL^-) - k_{-4}(\overline{[CX^-]}+\delta CX^-)(\overline{[OH^-]}+\delta OH^-)$$

This expression may be simplified by use of the following:

(1) the equilibrium concentration $\overline{[CX^-]}$ does not depend upon time;

therefore, $\frac{d\,\overline{[CX^-]}}{dt} = 0$

(2) at equilibrium, $k_1\,\overline{[HB]}\,\overline{[H_2L]} - k_{-1}\,\overline{[H^+]}\,\overline{[CX^-]} = 0$,

$k^{/}\,\overline{[B^-]}\,\overline{[H_2L]} - k^{//}\,\overline{[CX^-]} = 0$

and $k_4\,\overline{[B^-]}\,\overline{[HL^-]} - k_{-4}\,\overline{[CX^-]}\,\overline{[OH^-]} = 0$

(3) Since the perturbation is small the expression can be linearized, that is,

$$\delta HB\,\delta H_2L = \delta H^+\,\delta CX^- = \delta B^-\,\delta H_2L = \delta B^-\,\delta HL^- = \delta CX^-\,\delta OH^- = 0$$

After satisfying the above conditions in the rate law, the resulting expression becomes

$$+\frac{d\,\delta CX^-}{dt} = k_1\left([\overline{HB}]\delta H_2L + [\overline{H_2L}]\delta HB\right) - k_{-1}\left([\overline{H^+}]\delta CX^- + [\overline{CX^-}]\delta H^+\right)$$
$$+ k'\left([\overline{B^-}]\delta H_2L + [\overline{H_2L}]\delta B^-\right) - k''\left(\delta CX^-\right)$$
$$+ k_4\left([\overline{B^-}]\delta HL^- + [\overline{HL^-}]\delta B^-\right) - k_{-4}\left([\overline{CX^-}]\delta OH^- + [\overline{OH^-}]\delta CX^-\right) \qquad \text{(D14)}$$

The expression for the relaxation time was obtained in the following manner. The concentration terms in the protolytic equations (D1) - (D4) are expanded as the sum of equilibrium values plus small deviation terms. The expressions are then linearized in the same manner as before. The resulting equations are then combined with the conservation relationships given by equations (D9) - (D12) in order to express all variables in eqn (D14) in terms of δCX^-. Since $K = k_f / k_r$, the reverse rate constants are rewritten in terms of the stability constants and the forward rate constants. After satisfying all of the above, the rate law takes the form

$$-\frac{d\,\delta CX^-}{dt} = \frac{1}{\tau}\,\delta CX^-$$

where

$$
\begin{aligned}
\frac{1}{\tau} = \; & k_1 \left(S\,[\overline{HB}] + R\,[\overline{H_2L}] + \frac{[\overline{H^+}]}{K1} + \frac{P\,[\overline{CX^-}]}{K1} \right) \\
& + k^{\prime} \left(S\,[\overline{B^-}] + T\,[\overline{H_2L}] \right) + k^{\prime\prime} \\
& + k_4 \left(V\,[\overline{B^-}] + T\,[\overline{HL^-}] + \frac{Q\,[\overline{CX^-}]}{K4} + \frac{[\overline{OH^-}]}{K4} \right)
\end{aligned}
$$

In the above relaxation expressions P, Q, R, S, T and V are complex functions which are composed of equilibrium concentrations, dissociation constants and stability constants. These expressions are known and are defined in Appendix A.

Before carrying out any experiments, blank solutions consisting of indicator alone, indicator plus boron acid and indicator plus ligand are checked to make sure that there is no effect in the time range accessible to the instrument. For each system studied, relaxation times are obtained by varying the concentrations of the boron acid and the ligand at different pH values. By suitable adjustment of the pH, different terms in the above relaxation expression can be made to dominate. For example, phenylboronic acid has a pK_a of 8.72 and if studies are done in the pH range between pH 2 and pH 5, then equations (D6) and (D8) do not exist. The above four - term relaxation expression is therefore simplified to a two - term expression.

For each experiment at least three relaxation traces are recorded on an oscilloscope and photographed. The relaxation times are obtained from semilogarithmic plots of ln δCX^- as a function of time, and τ is the time for the concentration to decrease to 1/e of the initial value. This is shown graphically in Figure 2-4.

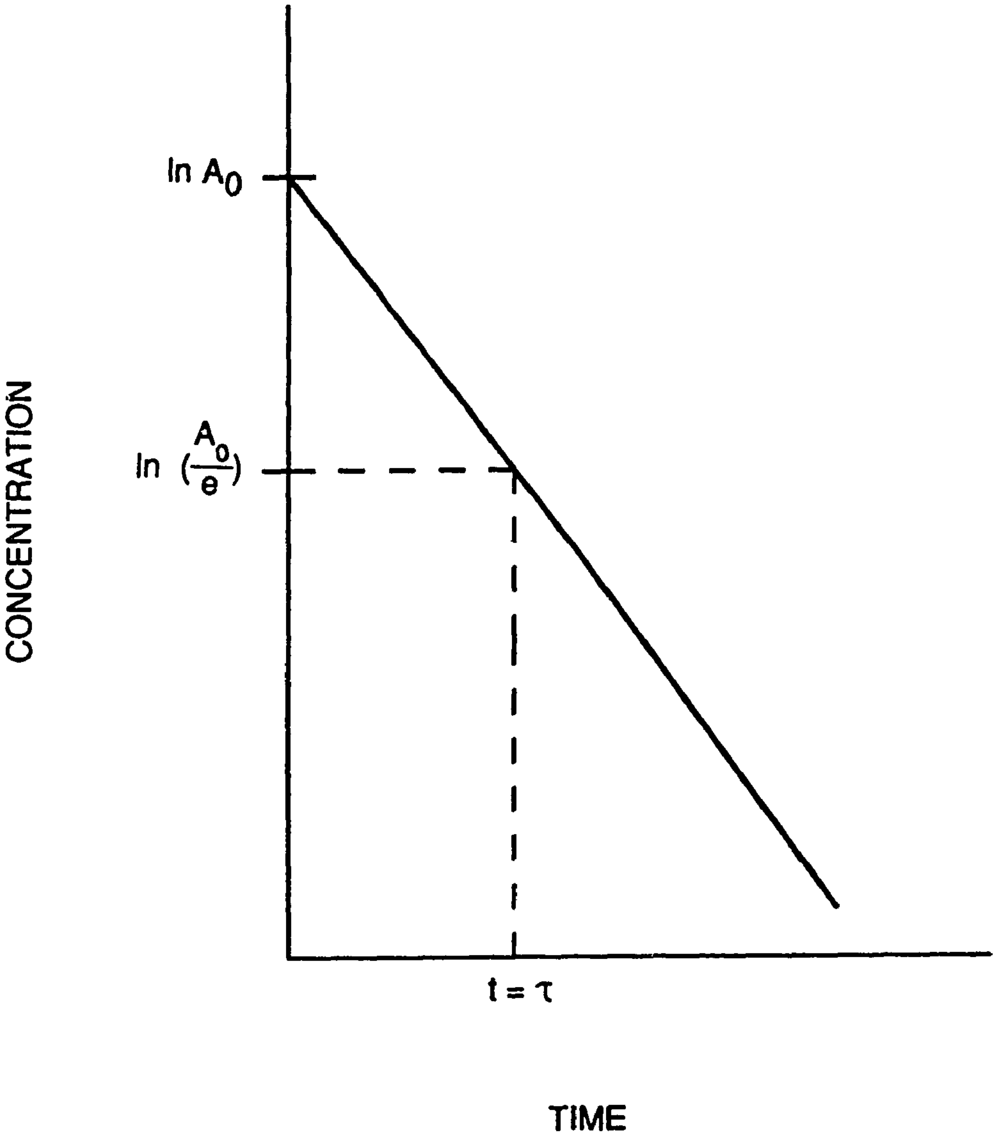


Figure 2-4: Graphical Determination of Relaxation Time

The relaxation times measured at two different sweep speeds generally agree within ± 10 %. The experimentally determined τ then yields the rate of the reaction $1/\tau$ in units of $\sec^{-1}$. From the known dissociation constants and stability constants the concentration coefficients in the relaxation expression are calculated. The rate expression is then fitted with constant values for the k's and the reported rate constants are the ones obtained from the best fit.

2.3.2 The Methylboronic Acid / Diol System

Methylboronic acid, a substituted boron acid with a pK_a of 10.4, forms 1:1 complexes with ethylene glycol, 1,2-propanediol and 1,3-propanediol in aqueous solution. The temperature-jump experiments were done in basic solution between pH 8 and pH 10. Since the pK_a of all of the ligands is 13, the concentration of HL^- is very small in the pH range studied. This means that the pathways to complex formation - $HB + HL^- \rightleftarrows CX^- + H_2O$ and $B^- + HL^- \rightleftarrows CX^- + OH^- + H_2O$, become unimportant. Therefore, for these ligands, the complexation mechanism given in Scheme 1 simplifies to the one given below.

Scheme 2

$$HB + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CX^- + H^+ \qquad K1$$

$$B^- + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CX^- + 2H_2O \qquad K2$$

The rate law is given by

$$+\frac{d[CX^-]}{dt} = k_1[HB][H_2L] - k_{-1}[CX^-][H^+]$$
$$+ k_2[B^-][H_2L] - k_{-2}[CX^-]$$

The conservation relationships remain the same as given in equations (D9) to (D12). The expansion of the concentration terms and the linearization process are done in exactly the same manner as before. The final form of the rate law is given below.

$$-\frac{d\,\delta CX^-}{dt} = k_1\left(S\overline{[HB]} + R\overline{[H_2L]} + \frac{\overline{[H^+]}}{K1} + \frac{P\overline{[CX^-]}}{K1}\right)\delta CX^-$$
$$+ k_2\left(S\overline{[B^-]} + T\overline{[H_2L]} + \frac{1}{K2}\right)\delta CX^-$$

The relaxation expression is then given by

$$\frac{1}{\tau} = k_1\left(S\overline{[HB]} + R\overline{[H_2L]} + \frac{\overline{[H^+]}}{K1} + \frac{P\overline{[CX^-]}}{K1}\right)$$
$$+ k_2\left(S\overline{[B^-]} + T\overline{[H_2L]} + \frac{1}{K2}\right) \qquad \text{(D15)}$$

where P, R, S and T are defined in Appendix A. The above relaxation expression applies to the mechanism given in Scheme 2. For a different mechanism, for instance one which treats the ionization of the boron acid as being non-diffusion controlled, a different relaxation expression is obtained. As mentioned before, τ is the only measurement which is obtained from the kinetic experiment. The value of $1/\tau$ together with the known concentration coefficients are used to determine k_1 and k_2 in equation (D15). The values for k_1 and k_2 can then be used to calculate an expected relaxation time, again by the use of equation (D15). A sample of these data is given in Table 2-1. It is important to note that the independent determination of the stability constant is necessary not only for the calculation of the equilibrium concentrations, but also for rewriting the reverse rate constants in terms of the forward rate constants and the appropiate stability constants.

Table 2-1: Kinetic Data for Methylboronic Acid / 1,2-propanediol System

pH	$[H_2L]_0$	$[HB]_0$	$[HIn]_0$	τ ms (expt)	τ ms (calc)
9.87	0.149	0.049	5.68×10^{-5}	14.1	11.4
9.55	0.149	0.046	7.60×10^{-5}	12.5	11.4
9.21	0.149	0.045	9.49×10^{-5}	10.3	11.4
8.88	0.149	0.046	9.49×10^{-5}	9.9	11.4
8.51	0.149	0.045	9.49×10^{-5}	11.1	11.2
8.38	0.150	0.046	3.17×10^{-4}	9.2	11.3
8.24	0.150	0.046	3.17×10^{-4}	9.1	11.1
9.10	0.217	0.033	9.49×10^{-5}	8.0	9.5
9.06	0.054	0.033	9.51×10^{-5}	14.5	16.2
9.24	0.149	0.023	9.49×10^{-5}	12.2	11.5
8.93	0.122	0.021	2.70×10^{-4}	15.3	12.8
8.70	0.122	0.021	2.70×10^{-4}	15.7	12.8
8.20	0.142	0.044	4.42×10^{-4}	12.0	11.5

HIn = Phenolphthalein

2.3.3 The Methylboronic Acid / Glycerol System

Methylboronic acid reacts with glycerol to form two complexes in solution; a five-membered chelate complex $CX_{1,2}^-$ and a six-membered chelate complex $CX_{1,3}^-$. The pK_a of glycerol is 13 and, as in the case of the methylboronic acid/diol systems, the concentration of HL^- is negligible in the pH range studied (pH 8 - pH 10). The complexation mechanism is given in Scheme 3.

Scheme 3

$$HB + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CX^-_{1,2} + H^+ \qquad K1 \qquad (F1)$$

$$B^- + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CX^-_{1,2} + 2H_2O \qquad K2 \qquad (F2)$$

$$HB + H_2L \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} CX^-_{1,3} + H^+ \qquad K3 \qquad (F3)$$

$$B^- + H_2L \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} CX^-_{1,3} + 2H_2O \qquad K4 \qquad (F4)$$

$$CX^-_{1,2} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} CX^-_{1,3} \qquad K5 \qquad (F5)$$

The derivation of the relaxation expression for methylboronic acid coordinating to glycerol is given below.

The variables are: HB, B^-, H_2L, HL^-, $CX^-_{1,2}$, $CX^-_{1,3}$, H^+, OH^-, HIn, In^-

The conservation relationships are as follows:

$$0 = \delta HB + \delta B^- + \delta CX^-_{1,2} + \delta CX^-_{1,3} \qquad (F6)$$

$$0 = \delta H_2L + \delta HL^- + \delta CX^-_{1,2} + \delta CX^-_{1,3} \qquad (F7)$$

$$0 = \delta HIn + \delta In^- \qquad (F8)$$

$$0 = \delta B^- + \delta HL^- + \delta CX^-_{1,2} + \delta CX^-_{1,3} + \delta OH^- + \delta In^- \qquad (F9)$$

The equilibrium expressions are given by

$$K_{HB} = \frac{[H^+]\,[B^-]}{[HB]} \qquad (F10)$$

$$K_L = \frac{[H^+]\,[HL^-]}{[H_2L]} \qquad (F11)$$

$$K_{In} = \frac{[H^+]\,[In^-]}{[HIn]} \qquad (F12)$$

$$K_w = [H^+]\,[OH^-] \qquad (F13)$$

The number of relaxation times is given by the equation x - (m + r) where x, m and r were defined on page 43. For this system, x=10, m=4 and r=4. This means that two relaxation times are expected; only one is observed. Reasons for observing a number of relaxation times less than the number predicted were presented on page 45.

Since the reaction mechanism is characterized by two relaxation times, there are two linear differential equations which describe the system.

$$+\frac{d\,[CX^-_{1,2}]}{dt} = k_1\,[HB]\,[H_2L] - k_{-1}\,[H^+]\,[CX^-_{1,2}]$$
$$+ k_2\,[B^-]\,[H_2L] - k_{-2}\,[CX^-_{1,2}]$$
$$- k_5\,[CX^-_{1,2}] + k_{-5}\,[CX^-_{1,3}]$$

$$+\frac{d\,[CX^-_{1,3}]}{dt} = k_3\,[HB]\,[H_2L] - k_{-3}\,[H^+]\,[CX^-_{1,3}]$$
$$+ k_4\,[B^-]\,[H_2L] - k_{-4}\,[CX^-_{1,3}]$$
$$+ k_5\,[CX^-_{1,2}] - k_{-5}\,[CX^-_{1,3}]$$

For such a kinetic system, the relaxation times are found by solving the secular determinental equation

$$\begin{vmatrix} a_{11} - \frac{1}{\tau} & a_{12} \\ a_{21} & a_{22} - \frac{1}{\tau} \end{vmatrix} = 0 \qquad \text{(F14)}$$

The two solutions to the resulting quadratic equation are given by

$$\frac{1}{\tau_{+,-}} = \frac{-(a_{11}+a_{22}) \pm ((a_{11}+a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21}))^{0.5}}{2} \qquad \text{(F15)}$$

The coefficients a_{11} and a_{12} are functions of rate constants and equilibrium concentrations associated with the reactions given in equations (F1), (F2) and (F5). The coefficients a_{21} and a_{22} are functions of the rate constants and equilibrium concentrations associated with the reactions given in equations (F3), (F4) and (F5).

The expressions for a_{11}, a_{12}, a_{21} and a_{22} were derived in the following manner. The concentration terms in the equilibrium expressions given by equations (F10) - (F13) were expanded as the sum of equilibrium values plus small deviation terms. The expressions are then linearized in a similar manner as outlined in Section 2.2.1. The resulting equations are combined with the conservation relationships given by equations (F6) - (F9) so that all variables are expressed in terms of $\delta CX_{1,2}^-$ and $\delta CX_{1,3}^-$. Similarly, the concentration terms in the rate law are expanded as the sum of equilibrium values plus small deviations and the rate expression is linearized. The reverse rate constants are rewritten in terms of the forward rate constants and the appropiate stability constants.

After satisfying the above conditions, the final form of the rate law is given by

$$-\frac{d\,\delta CX^-_{1,2}}{dt} = a_{11}\,\delta CX^-_{1,2} + a_{12}\,\delta CX^-_{1,3}$$

$$-\frac{d\,\delta CX^-_{1,3}}{dt} = a_{21}\,\delta CX^-_{1,2} + a_{22}\,\delta CX^-_{1,3}$$

where

$$a_{11} = k_1\left\{S[\overline{HB}] + R[\overline{H_2L}] + \frac{[\overline{H^+}]}{K1} + \frac{P[\overline{CX^-_{1,2}}]}{K1}\right\} + k_2\left\{S[\overline{B^-}] + T\,[\overline{H_2L}] + \frac{1}{K2}\right\} + k_5\{1\}$$

$$a_{12} = k_1\left\{S[\overline{HB}] + R[\overline{H_2L}] + \frac{P[\overline{CX^-_{1,2}}]}{K1}\right\} + k_2\left\{S[\overline{B^-}] + T\,[\overline{H_2L}]\right\} + k_5\left\{-\frac{1}{K5}\right\}$$

$$a_{21} = k_3\left\{S[\overline{HB}] + R[\overline{H_2L}] + \frac{[\overline{H^+}]}{K1} + \frac{P[\overline{CX^-_{1,3}}]}{K1}\right\} + k_4\left\{S[\overline{B^-}] + T\,[\overline{H_2L}] + \frac{1}{K2}\right\} + k_5\{-1\}$$

$$a_{22} = k_3\left\{S[\overline{HB}] + R[\overline{H_2L}] + \frac{P[\overline{CX^-_{1,3}}]}{K1}\right\} + k_4\left\{S[\overline{B^-}] + T\,[\overline{H_2L}]\right\} + k_5\left\{\frac{1}{K5}\right\}$$

P, R, S and T are functions of equilibrium concentrations and equilibrium constants which are all known. These functions are the same as in Appendix A when $K_{L1} = K_L$.

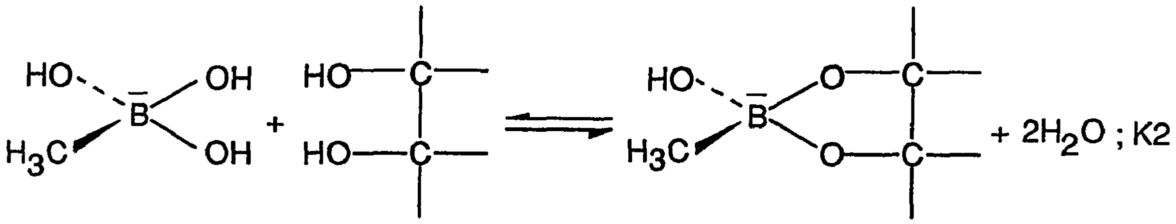
The coefficients a_{11}, a_{12}, a_{21} and a_{22} are seen to be functions of all rate constants, equilibrium concentrations and equilibrium constants, thus depending upon the overall mechanism of the reaction. Putting in values for the rate constants together with the known concentration coefficients, it is then possible to solve the quadratic equation (F15) for the two roots of $1/\tau$. Since only one relaxation time is observed experimentally, the reported rate constants are the ones obtained from the best fit by matching one of the calculated values of $1/\tau$ (+ root) with the experimental values of $1/\tau$. The second calculated relaxation time corresponded to an approximate value of 0.1 sec. This relaxation time was never seen experimentally and reasons for not observing the number of predicted relaxation times were presented before. However, recall that the upper limit of the time range accessible to this temperature-jump instrument is about 1 sec. Perhaps another reason for not observing the second relaxation time may be due to its proximity to the upper time limit of the instrument.

2.4 Determination of ΔG°, ΔH° and ΔS°

2.4.1 The Variable Temperature ^1H NMR Experiment

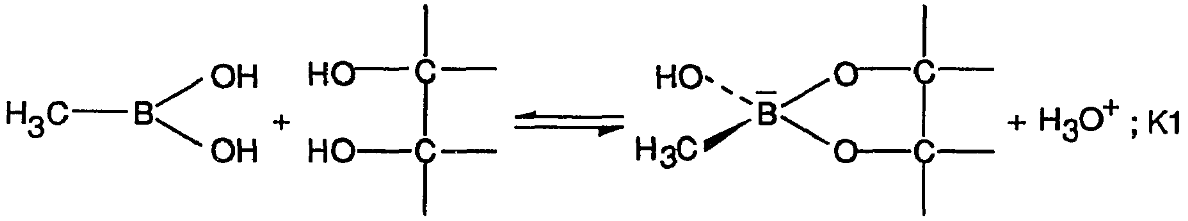
The stability constants are measured as a function of temperature using the proton NMR technique. All solutions are made up in pure D_2O.

For the methylboronic acid / polyol systems the reactions are carried out in basic solution at about pH 12. The complexation reaction is given by



The pH of the solution is adjusted by the addition of solid sodium hydroxide.

For the methylboronic acid / catechol system the reactions are carried out in acidic solution between pH 6 and pH 7. The complexation reaction is given by



Deuterated sodium hydroxide is used to adjust the pH which is measured accurately on the pH meter.

The stability constants K1 and K2 were measured as a function of the temperature. The quantitative integrations were performed on the peaks corresponding to the methyl group in the free and the complexed methylboronic acid / methylboronate species. The temperature range studied was between 276 K and 310 K. Below 276 K, the solution freezes; above 310 K, methylboronic acid decomposes to boric acid and methanol (checked by ^{1}H NMR).

For each experiment, at least five different temperatures were studied. At each temperature, the solutions were allowed to equilibrate for at least fifteen minutes before recording the spectra. The calculations of K1 and K2 from the spectra are similar to the one given in Section 2.1.3 for the ^{11}B NMR experiments.

The methyl group of $CH_3B(OH)_2$ or $CH_3B(OH)_3^-$ occurs upfield and was found to overlap with the TMS peak. The experiments were therefore carried out in pure D_2O without any added TMS. Consequently, no chemical shifts are reported.

The ^1H NMR spectra were obtained using a Bruker IBM 250 MHz FT NMR spectrometer which is equipped with a variable temperature unit (Bruker BVT - 1000). All solutions were freshly prepared prior to use and the pH was measured on a Fisher Scientific Accumet Model 950 pH / ion Meter.

2.4.2 The Variable Temperature pH Experiment

The ionization constant for methylboronic acid was measured as a function of the temperature by pH titration method. The ionization reaction is given below.

$$CH_3B(OH)_2 + H_2O \rightleftarrows CH_3B(OH)_3^- + H^+ \; ; \; K_A$$

A solution of methylboronic acid and electrolyte (KCl) of known concentration was titrated with standard 0.1 M NaOH under a nitrogen atmosphere, at 0.1 M ionic strength and at a constant temperature. An equilibrium constant was calculated for each point in the titration curve. At least five different temperatures were studied in the temperature range 278 - 318 K.

The pH was measured on a Fisher Scientific Accumet Model 950 pH / ion Meter which is equipped with an automatic temperature compensation probe. The measurements on the pH meter are made with accuracies of ± 0.02 pH unit and ± 0.5 K.

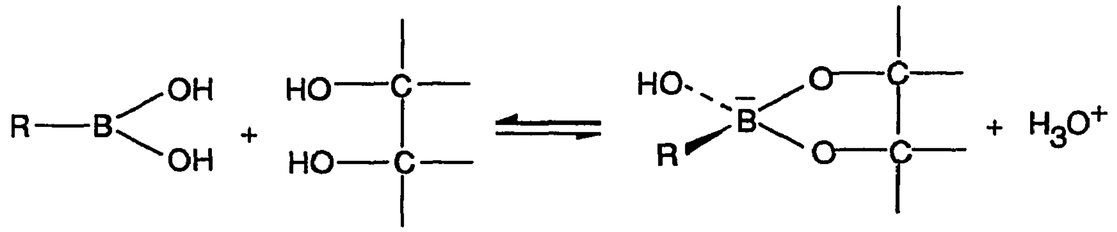
From both methods above, the determination of the thermodynamic parameters ΔG°, ΔH° and ΔS° from the measured equilibrium constants as a function of T is outlined in Chapter 4.

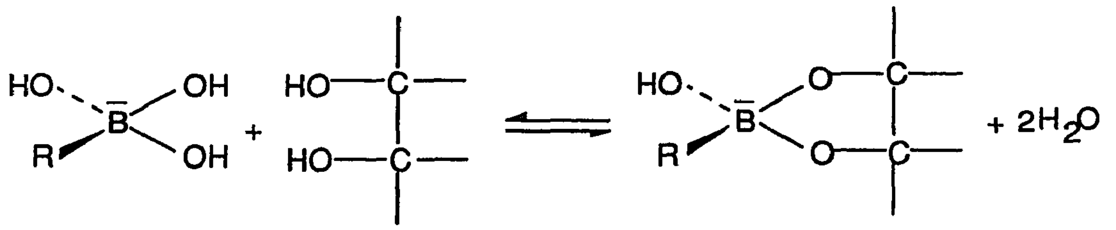
CHAPTER 3

THE METHYLBORONIC ACID / POLYOL SYSTEMS

3.1 Introduction

Both the trigonal and the tetrahedral forms of a substituted boron acid can react with bidentate chelating ligands to form the same anionic tetrahedral complex in solution, as shown below.


(1)


(2)

The reaction given in eqn (1) is an addition, as well as a substitution reaction; the first oxygen donor atom of the ligand adds to the empty p orbital on boron to form a covalent bond; the second donor atom displaces a hydroxyl group on boron to form the chelate ring. Reaction (1) occurs with a change in hybridization from sp^2 to sp^3, and a change in coordination number from three to four. Reaction (2) is a substitution reaction, the hybridization and coordination number of boron remaining unchanged.

The type of ligands which undergo these reactions include polyols [22,25,26,32,86-91], 1,2-benzenediols [92-94], α-hydroxycarboxylic acids [56,60,61,95-98] and dicarboxylic acids [59,62,99]. In these complexation reactions, the ligand donor atoms are oxygen atoms and both protons of the ligand are displaced upon coordination. The resulting complexes are stabilized by the chelate effect, and are known to contain five- and six-membered chelate rings [14,26,96].

The thermodynamics of these complexation reactions have been studied for more than a century and are now firmly established. On the other hand, the kinetics are less well understood. One of the reasons for conducting the experiments in this Chapter was to determine the reactivity of the borate anion. Since previous kinetic studies of boron acids (pK_a ranged from 6.96 to 10.4) coordinating to bidentate chelating ligands (pK_a ranged from 1.04 to 9.39) were done in acidic solution, the main reactions which were being observed were those pertaining to the reactivity of the trigonal boron acid. In order to study the borate anion, the experiments in this Chapter had to be carried out in basic media where the concentration of the tetrahedral borate anion becomes significant. It has been suggested that the tetrahedral borates are more labile than the trigonal boron acids but no kinetic data have been reported to support this claim. The following investigation of the complexation mechanism in basic solution was thus undertaken to determine the lability of the tetrahedral borate anion.

The boron acid chosen is methylboronic acid, a substituted boron acid. This boron acid was an appropiate choice since it can form only 1:1 complexes with bidentate chelating ligands. The resulting kinetic scheme is simpler than in the case of boric acid [62] where both 1:1 and 1:2 complexes are formed in solution.

As mentioned before, previous kinetic studies concluded that ligand acidity played an important role in the complexation mechanism, and that proton transfer was a critical factor in determining the reaction rate. Most of the ligands which were used were acidic and the equilibria were such that complexation occurred mainly in acidic solution. That is, the route to complex formation was predominantly through the fully protonated form of the ligand. The ligand monoanions were found to react slowly while the ligand dianions were seen to be unreactive. Therefore, in basic solution where the concentration of the borate anion becomes significant, it is necessary to use ligands of high pK_a values. The ligands chosen are the simple polyols all of which have pK_a values of 13.

The Methylboronic Acid / Polyol Systems

Methylboronic acid, $CH_3B(OH)_2$,a substituted boron acid has a pK_a value of 10.40 [59] . In its reactions with bidentate chelating ligands, only 1:1 complexes are formed since one of the coordination sites on boron is blocked by the methyl group.

The ligands used in this study are simple polyols; namely, ethylene glycol, 1,2-propanediol, 1,3-propanediol and glycerol. These ligands do not contain any acidic protons, ligand pK_a' s all being 13 [61].

The experiments were conducted in basic solution where the concentration of the borate anion becomes important. The kinetic measurements were made between pH 8 and pH 10. This means that both the trigonal boron acid and the tetrahedral borate anion are present in solution. Also, in this pH range the concentration of the ligand anion, HL^-, is negligible. Therefore the pathways to complex formation involving HL^- which were outlined in the general reaction scheme in Chapter 2 do not exist.

Both ethylene glycol and 1,2-propanediol react with methylboronic acid in aqueous solution to form five-membered chelate complexes, designated as $CX_{1,2}^-$ in Scheme 1 (page 82); therefore, for these ligands, only eqns (3) and (4) apply. With 1,3-propanediol, a six-membered chelate complex is formed, designated as $CX_{1,3}^-$; for this ligand, only eqns (5) and (6) apply. Glycerol forms both five- and six-membered chelate complexes and in this case, the entire mechanism in Scheme 1 applies.

3.2 Experimental

3.2.1 Determination of Stability Constants

Stability constants were determined by two methods; pH titration method and ^{11}B NMR spectroscopy.

For the methylboronic acid / polyol systems, the stability constants were first determined by NaOH titration as described in the experimental Chapter. The values obtained were used to calculate distribution diagrams which were then used to predict suitable conditions for running the ^{11}B NMR experiments.

From the integration of the ^{11}B NMR spectra it was possible to determine the stability constants for the methylboronic acid / polyol systems.

3.2.2 Determination of Rate Constants

The relaxation times were measured by the temperature-jump method between pH 8 and pH 10, as described in the experimental Chapter.

3.3 Results and Treatment of Data

3.3.1 Stability Constants and ^{11}B NMR Spectra

In each of the complexation reactions of methylboronic acid with ethylene glycol, 1,2-propanediol and 1,3-propanediol, only one complex was formed in solution; the five-membered chelate complex $CX_{1,2}^-$ for both ethylene glycol and 1,2-propanediol, and the six-membered chelate complex $CX_{1,3}^-$ for 1,3-propanediol.

For the $CH_3B(OH)_2$ / 1,3-propanediol system, a calculated distribution diagram and a ^{11}B NMR spectrum are presented in Figure 3 -1. The spectrum shows two resonances, one of which is assigned to both the $CH_3B(OH)_2$ and the $CH_3B(OH)_3^-$ species, while the other represents the $CX_{1,3}^-$ species. This assignment was based on the comparison of the spectrum with that of a blank solution of $CH_3B(OH)_2$ (at the same pH) and the implications of the calculated distribution diagram.

Similar spectra were obtained for the $CH_3B(OH)_2$ / ethylene glycol and the $CH_3B(OH)_2$ / 1,2-propanediol systems. Since only one complex was formed in each system, the calculation of K from NaOH titrations and ^{11}B NMR spectra follows directly from the derivations outlined in Chapter 2.

In the case of the $CH_3B(OH)_2$ / glycerol system, two complexes are formed; the five-membered chelate complex $CX_{1,2}^-$ and the six-membered chelate complex $CX_{1,3}^-$. For this system, a distribution diagram and a ^{11}B NMR spectrum are displayed in Figure 3 -2.

The assignment of the peaks in the spectrum shown in Figure 3-2 was done in the following manner. In general, for a particular boron acid coordinating to the same type of ligand, the five-membered chelate complexes formed are more stable than the six-membered analogs. For instance, the stability constant for the formation of the five-membered chelate in the $\Phi B(OH)_2$ / oxalic acid system [57] is greater than that for the formation of the six-membered chelate in the $\Phi B(OH)_2$ / malonic acid system [58] by a factor of 100. Similarly, the stability constant for the formation of the $CX_{1,2}^-$ in the $B(OH)_3$ / 1,2-propanediol system is larger than that for the formation of the $CX_{1,3}^-$ in the $B(OH)_3$ / 1,3-propanediol system, by factors of 2 to 3 [22,93,94(a)]. Furthermore, for boric acid reacting with glycerol, the stability constant of $CX_{1,2}^-$ is greater than that of $CX_{1,3}^-$ by a factor of 7 [94(a)]. The generalization (five-membered boron chelates are more stable than six-membered chelates), together with the spectrum of the blank solution of $CH_3B(OH)_2$, were used to make the assignments illustrated in Figure 3 -2 (b).

The calculations of K1 and K3 from the spectrum in Figure 3-2 were done in a similar manner to that given in Chapter 2, after modifying the derivation to include two complexes in solution. (K1 and K3, or K2 and K4, are the independent stability constants; once they have been determined, the other stability constants are easily calculated (see Scheme 1)).

The analysis of the NaOH titration data for the $CH_3B(OH)_2$ / glycerol system was done as follows. The system is characterized by two independent concentration variables, $CX_{1,2}^-$ and $CX_{1,3}^-$. Therefore, it was necessary to modify the derivation given in Chapter 2. From the integrated ^{11}B NMR spectrum, an independent measurement of K5 was possible.

$$K5 = \frac{[CX^-_{1,3}]}{[CX^-_{1,2}]} \quad \left(= \frac{K3}{K1} \right)$$

The known value of K5 was used in a NaOH derivation to eliminate one of the independent concentration variables. It was then possible to calculate the stability constant K1. From the known values of K1 and K5, a value for K3 was determined.

For methylboronic acid coordinating to each of the polyols, the stability constants obtained by the NaOH titrations and the ^{11}B NMR technique, agreed to within ± 20 %. The resulting stability constants are presented in Table 3-1, and are reported with an accuracy of ± 20 %.

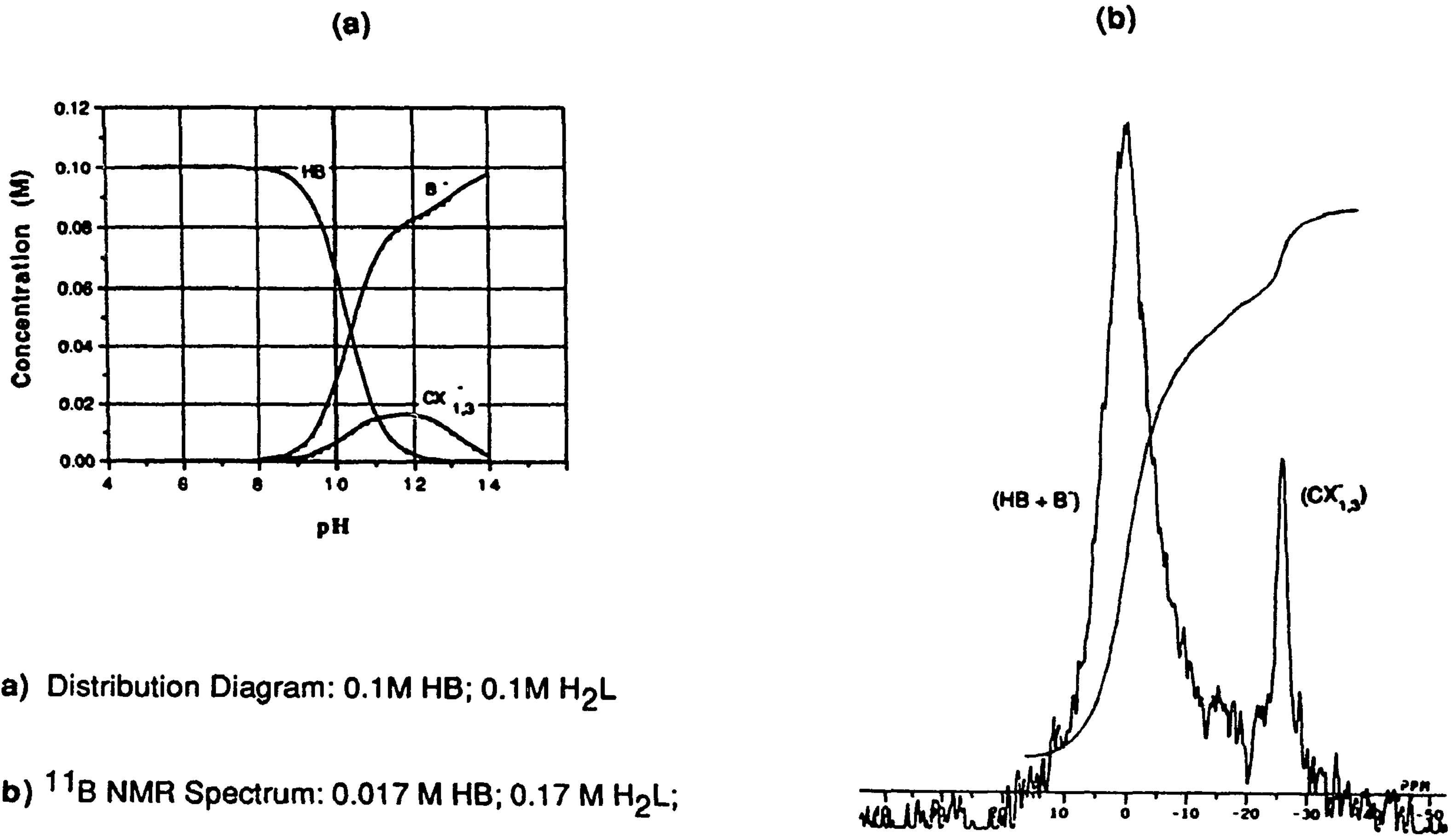
3.3.2 Rate Constants

The detailed kinetic analysis of the mechanism of complexation between methylboronic acid and the simple polyols was outlined in Chapter 2.

Experimental data for two systems, $CH_3B(OH)_2$ / ethylene glycol and $CH_3B(OH)_2$ / glycerol, are given in Tables 3-2 and 3-3, respectively.

The resulting rate constants are reported in Table 3-4. The error associated with these rate constants is ± 20 %.

Figure 3-1: Distribution Diagram and ^{11}B NMR Spectrum for Methylboronic Acid / 1,3-propanediol System



(a) Distribution Diagram: 0.1M HB; 0.1M H_2L

(b) ^{11}B NMR Spectrum: 0.017 M HB; 0.17 M H_2L;

pH = 10.27

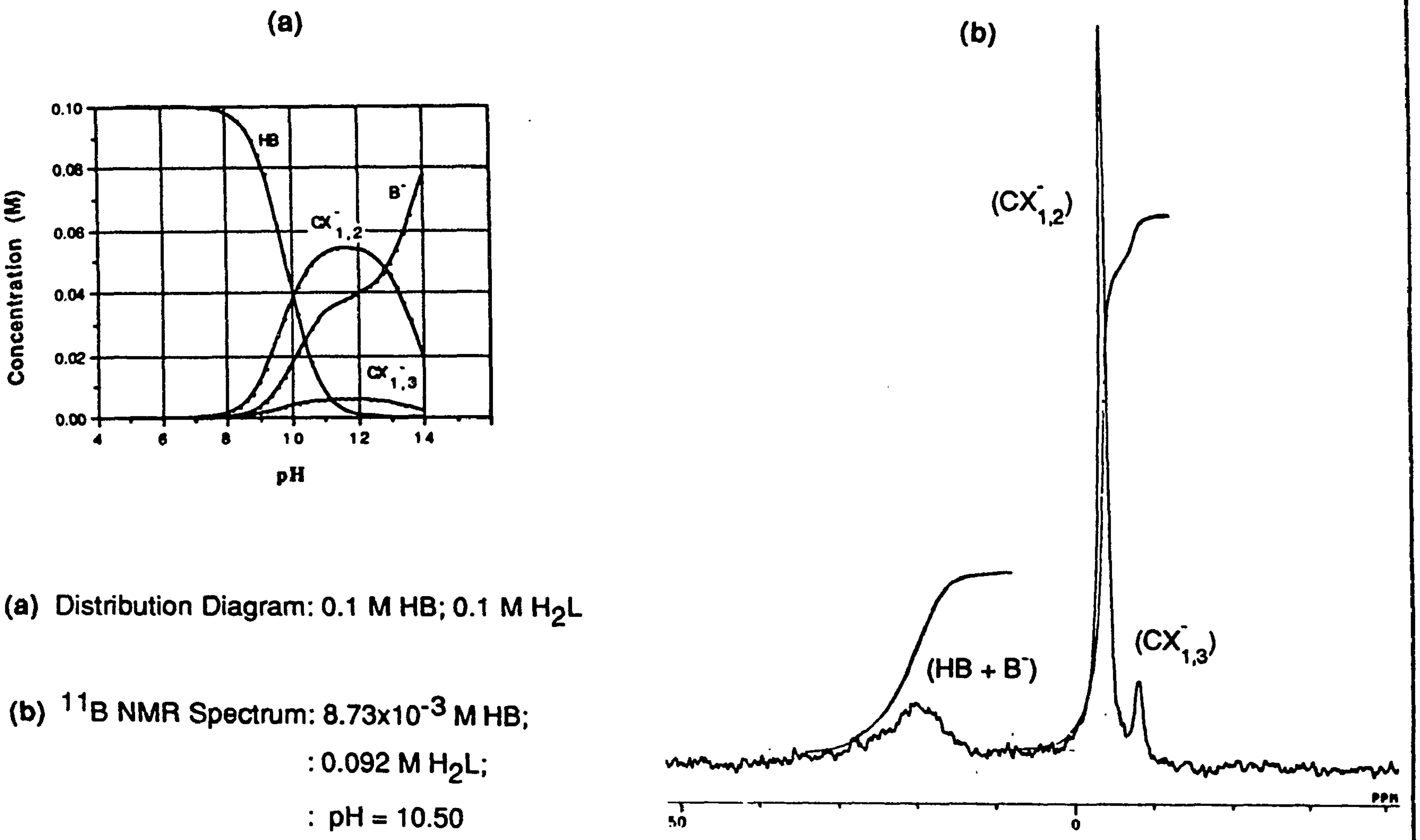


Figure 3-2: Distribution Diagram and ^{11}B NMR Spectrum for Methylboronic Acid / Glycerol System

(a) Distribution Diagram: 0.1 M HB; 0.1 M H_2L

(b) ^{11}B NMR Spectrum: 8.73×10^{-3} M HB;
: 0.092 M H_2L;
: pH = 10.50

3.3 Results

Scheme 1: A General Mechanism for Methylboronic Acid / Polyol Systems

$$\mathrm{HB} + \mathrm{H_2L} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{CX^-_{1,2}} + \mathrm{H^+} \qquad K1 \qquad (3)$$

$$\mathrm{B^-} + \mathrm{H_2L} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{CX^-_{1,2}} + 2\mathrm{H_2O} \qquad K2 = \frac{K1}{K_{HB}} \qquad (4)$$

$$\mathrm{HB} + \mathrm{H_2L} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{CX^-_{1,3}} + \mathrm{H^+} \qquad K3 \qquad (5)$$

$$\mathrm{B^-} + \mathrm{H_2L} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \mathrm{CX^-_{1,3}} + 2\mathrm{H_2O} \qquad K4 = \frac{K3}{K_{HB}} \qquad (6)$$

$$\mathrm{CX^-_{1,2}} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \mathrm{CX^-_{1,3}} \qquad K5 = \frac{K3}{K1} \qquad (7)$$

Table 3-1: Stability Constants for Methylboronic Acid / Polyol Complexes

H_2L	K1	K2	K3	K4	K5
ethylene glycol	2.2×10^{-10}	5.5	-	-	-
1,2-propanediol	2.4×10^{-10}	6.0	-	-	-
1,3-propanediol	-	-	1.0×10^{-10}	2.5	-
glycerol	1.5×10^{-9}	38	1.6×10^{-10}	4.0	0.1

Table 3-2: Kinetic Data for Methylboronic Acid / Ethylene Glycol System

pH	$[H_2L]_0$	$[HB]_0$	$[HIn]_0$	τ (expt) ms	τ (calc) ms
9.80	0.214	0.072	8.66×10^{-5}	2.0	2.4
9.46	0.214	0.072	8.66×10^{-5}	1.9	2.4
9.18	0.214	0.071	8.66×10^{-5}	2.2	2.4
8.91	0.214	0.071	8.66×10^{-5}	2.5	2.4
8.70	0.214	0.070	8.66×10^{-5}	2.5	2.4
8.54	0.214	0.070	8.66×10^{-5}	2.3	2.4
8.34	0.214	0.070	2.60×10^{-4}	2.3	2.4
8.17	0.214	0.070	2.60×10^{-4}	2.5	2.4
9.31	0.500	0.049	8.66×10^{-5}	1.7	1.4
9.29	0.214	0.049	8.68×10^{-5}	3.0	2.4
9.31	0.107	0.048	8.65×10^{-5}	4.1	3.3
9.06	0.053	0.056	8.65×10^{-5}	4.0	4.0
8.51	0.214	0.049	8.66×10^{-5}	3.0	2.4

HIn = Phenolphthalein : $K_{HIn} = 3.98 \times 10^{-10}$

Table 3-3: Kinetic Data for Methylboronic Acid / Glycerol System

pH	$[H_2L]_0$	$[HB]_0$	$[HIn]_0$	τ (expt) ms	τ (calc) ms
9.88	0.136	0.033	6.16×10^{-5}	13.6	13.2
9.47	0.136	0.030	6.82×10^{-5}	11.3	12.9
9.17	0.137	0.030	9.41×10^{-5}	10.6	12.7
8.54	0.137	0.033	2.95×10^{-4}	10.7	12.4
8.38	0.137	0.030	3.28×10^{-4}	10.3	12.3
8.16	0.136	0.030	4.99×10^{-4}	11.8	12.2
9.16	0.137	0.018	9.17×10^{-5}	12.4	12.8
9.17	0.136	0.011	9.45×10^{-5}	14.2	13.0
9.16	0.055	0.034	9.14×10^{-5}	17.0	15.8
9.20	0.136	0.016	9.12×10^{-5}	14.8	12.8
9.25	0.027	0.068	9.76×10^{-5}	17.0	16.5
9.53	0.055	0.034	9.14×10^{-5}	18.8	15.9
9.53	0.027	0.068	9.76×10^{-5}	18.4	17.0
9.53	0.136	0.016	9.12×10^{-5}	15.4	13.0

Table 3-4: Rate Constants for Methylboronic Acid / Polyol Systems

H_2L	k_1, ($M^{-1}s^{-1}$)	k_2, ($M^{-1}s^{-1}$)	k_3, ($M^{-1}s^{-1}$)	k_4, ($M^{-1}s^{-1}$)	k_5, (s^{-1})
ethylene glycol	≤ 1	1.1×10^3	-	-	-
1,2-propanediol	≤ 1	2.8×10^2	-	-	-
1,3-propanediol	-	-	≤ 1	5.2×10^2	-
glycerol	≤ 1	1.0×10^2	≤ 1	1.8×10^2	1

	k_{-1}, ($M^{-1}s^{-1}$)	k_{-2}, (s^{-1})	k_{-3}, ($M^{-1}s^{-1}$)	k_{-4}, (s^{-1})	k_{-5}, (s^{-1})
ethylene glycol	$\leq 4\times10^9$	2.0×10^2	-	-	-
1,2-propanediol	$\leq 4\times10^9$	47	-	-	-
1,3-propanediol	-	-	$\leq 1\times10^{10}$	2.1×10^2	-
glycerol	$\leq 7\times10^8$	2.6	$\leq 6\times10^9$	50	10

3.4 Discussion

3.4.1 Equilibria

From Table 3-1, the stability constants for the complexation reactions between methylboronic acid and the polyols are small. Among the ligands studied, the stability of the five-membered chelate complexes formed by ethylene glycol and 1,2-propanediol are virtually the same. Secondly, the least stable complexes are formed by 1,3-propanediol. That is, the five-membered chelate complexes (H_2L = ethylene glycol and 1,2-propanediol) are more stable than the six-membered chelate complex (H_2L = 1,3-propanediol). Glycerol forms the most stable complexes. The five-membered chelates are formed from the 1,2-diols (ethylene glycol, 1,2-propanediol and glycerol). Since there is more than one way to achieve the 1,2-configuration in glycerol, this statistical factor may be reflected in the relative magnitudes of the stability constants for these ligands. The trends described above are consistent with earlier studies [22,91,93,94(a)] of complex formation between boric acid and the same ligands which were used in this study.

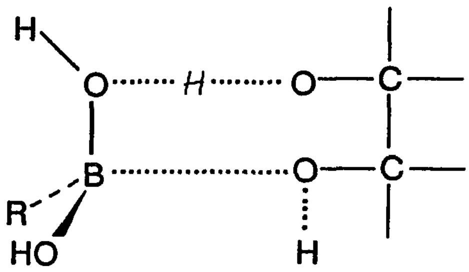
3.4.2 Kinetic Studies

The Trigonal Boron Acid

From the reported rate constants in Table 3-4, the reactions of the trigonal form of the boron acid are seen to be very slow. Trigonal methylboronic acid coordinates to each of the polyols with rate constants which are all less than or equal to one. On the other hand, the tetrahedral methylboronate anion reacts much faster. As mentioned before, these kinetic studies were done in basic solution from pH 8 up to pH 10; the pK_a of methylboronic acid is 10.40. Therefore, the kinetic experiments were done under conditions where the concentration of the trigonal boron acid is greater than that of the tetrahedral borate anion, yet the former species reacts much slower. This result, that is the slowness of the reactions in which the trigonal methylboronic acid coordinates to the polyols, is consistent with conclusions from previous kinetic studies, as explained below.

Previous kinetic studies of different boron acids coordinating to bidentate chelating ligands were done only in acidic solution [56-62]. The boron acids studied were $B(OH)_3$, and the substituted boron acids m-$NO_2\Phi B(OH)_2$, $\Phi B(OH)_2$ and $CH_3B(OH)_2$. Some of the ligands which were used were mandelic acid, salicylic acid, catechol and oxalic acid. In acidic solution the main form of the boron acid is the trigonal species. Since the rate constant was found to increase with increasing ligand acidity, the authors proposed a transition state which was characterized by a proton transfer mechanism.

For the reaction of a trigonal boron acid with a fully protonated ligand in acidic solution, the proposed transition state [59] is given below.



The transition state may be explained as follows. First, nucleophilic attack occurs on the electron deficient boron atom by the oxygen donor atom of the ligand. The formation of a covalent boron - oxygen bond results after the displacement of the less acidic hydroxyl proton; the more acidic proton, *H*, is transferred to the leaving hydroxide on boron, and ring closure occurs. The authors of the kinetic studies in acidic solution found a precise correlation between the rate and pK_{a1} of the ligand; no dependence of the rate on pK_{a2} was found. Therefore, it was assumed that the displacement by boron of the less acidic proton was a facile process. This was followed by the rate determining ring closure step which involves the transfer of the more acidic ligand proton. In the forward direction, the proton is transferred from the ligand to the leaving hydroxide on boron, resulting in the condensation of a water molecule; in the reverse direction, the proton is transferred from an entering water molecule to the leaving ligand anion, and the fully protonated ligand is regenerated.

In the present study of the methylboronic acid / polyol reactions, each of the ligands has a pK_a value of 13. The ligands therefore do not contain any acidic protons. With respect to the above transition state, the proton transfer process is difficult since the ligand protons are not acidic. Ring closure cannot occur unless the ligand proton is transferred. The difficulty of the proton transfer process with these nonacidic ligands causes the rate determining ring closure step to be slow. This is reflected in the very small values of the forward rate constants involving the trigonal methylboronic acid.

As stated earlier, one of the conclusions from previous kinetic studies was that the rate constants for the reactions of the trigonal boron acids increased with increasing ligand acidity [59]. The consistency between this conclusion (acidic media) and the results of the trigonal $CH_3B(OH)_2$ / polyol systems (basic media) is illustrated in Table 3-5. In particular, as the ligand proton becomes more acidic, the forward rate constant increases.

Table 3-5. A Comparison of Rate Constants for the Trigonal Boron Acid Reactions in Methylboronic Acid / Ligand Systems.

H_2L	pK_a (H_2L)	k_1 , $M^{-1}s^{-1}$
salicylic acid [a]	2.83	5.5 x 10
4-nitrocatechol [a]	6.69	4.5 x 10
catechol [a]	9.27	7.6
polyols [b]	13	$\leq$ 1

[a] Ref. 59

[b] polyols = ethylene glycol, 1,2-propanediol, 1,3-propanediol and glycerol.

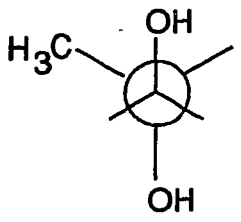
The fact that the trigonal methylboronic acid is unreactive towards the polyols is therefore consistent with previous kinetic studies (done in this Laboratory) from which the proton transfer transition state was proposed. The unreactivity seen here is also in agreement with the assumptions from many other authors who carried out thermodynamic studies on the reactions of boric acid coordinating to a variety of polyols [25,86-89] . Without having done any kinetic studies, these authors arrived at the conclusion that it was only the tetrahedral borate which coordinated to the polyol. Their interpretation was based on the magnitude of the stability constants and the variation of the complex concentration with solution pH.

The Tetrahedral Borate Anion

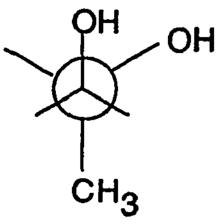
The reported rate constants in Table 3-4 indicate that in all cases, the tetrahedral methylboronate anion reacts much faster than the trigonal methylboronic acid. The values for the rate constants k_2 and k_4 are greater than those for k_1 and k_3 by at least a factor of 100. It was previously suggested that the tetrahedral borates are more labile than the trigonal boron acids [59,61,62]. To our knowledge, the results reported in Table 3-4 are the first direct measurement of the lability of the tetrahedral borate anion relative to the trigonal boron species.

Among the various ligands studied, the differences in reactivity are not dramatic (k_2 and k_4). Ethylene glycol is seen to react the fastest; it reacts faster than 1,2-propanediol by a factor of four. Secondly 1,3-propanediol reacts faster than 1,2-propanediol by a small factor of two. In the case of glycerol, the substitution reactions are the slowest; the fact that the two complexes, $CX_{1,2}^-$ and $CX_{1,3}^-$, are separable in the ^{11}B NMR spectrum means that the exchange between the two complexes is slow on the NMR timescale. Our kinetic analysis leads to a very small rate constant (k_5) for the exchange process.

The difference in reactivity between ethylene glycol and 1,2-propanediol may be explained with the aid of the following diagrams. The Newman projection diagrams for 1,2-propanediol are given below. The equilibrium constant between the anti and the gauche conformations in solution is not known. For successful complexation to occur, it is necessary for the hydroxyl groups to be adjacent and cis. Indeed, this criterion has been used extensively in the configurational analysis of carbohydrates and polyhydroxy compounds [43]. In the diagrams above, in order for (a) to achieve the correct configuration for chelation to boron, there has to be a rotation of the $-CH_3$ group about the carbon - carbon bond. In the case of ethylene glycol, the $-CH_3$ group is replaced by a hydrogen atom. Therefore, one of the reasons why 1,2-propanediol reacts slower than ethylene glycol may be due to hindered rotation of the $-CH_3$ group in the former case. Although molecular mechanics calculations [94 (a)] have been done to determine the steric and electrostatic interactions in the various conformations of these diols, they apply to the gas phase and cannot be compared with the experimental data of this study.



(a) anti



(b) gauche

It is also seen in Table 3-4 that the substitution rate for the reaction between the borate anion and 1,3-propanediol (k_4) is slightly greater than that for 1,2-propanediol (k_2). In other words, the formation of the six-membered complex is more rapid than the formation of the five-membered complex. Similarly, for glycerol which forms both five- and six-membered complexes, the same reactivity pattern is observed (k_2 and k_4). This observation disagrees with previous kinetic studies where the opposite trend was seen. The formation of the six-membered complex in the phenylboronic acid / malonic acid system [58] was slower than the formation of the five-membered complex in the phenylboronic acid / oxalic acid system [58]. Even though these observations may seem to lead to conflicting results of the effect of chelate ring size on reaction rate, the factors involved are very small. Also, other than chelate ring size, there is an additional factor involved in the phenylboronic acid systems, that is ligand acidity. Oxalic acid is more acidic than malonic acid by about 1.6 pK_a unit. Although the two effects cannot be separated, perhaps ligand acidity is more important in the above phenylboronic acid systems.

The investigations of the reactions in this Chapter are the first kinetic studies of boron complexation reactions in basic solution. Therefore, there are no literature values for the rate of substitution of borates in basic media for comparison with the $CH_3B(OH)_2$ / polyol systems. However, there are two previously studied systems [59] which should be mentioned. The *meta*-nitrophenylboronic acid / mandelic acid (pK_a=3.22) system and the *meta*-nitrophenylboronic acid / salicylic acid (pK_a=2.83) system.

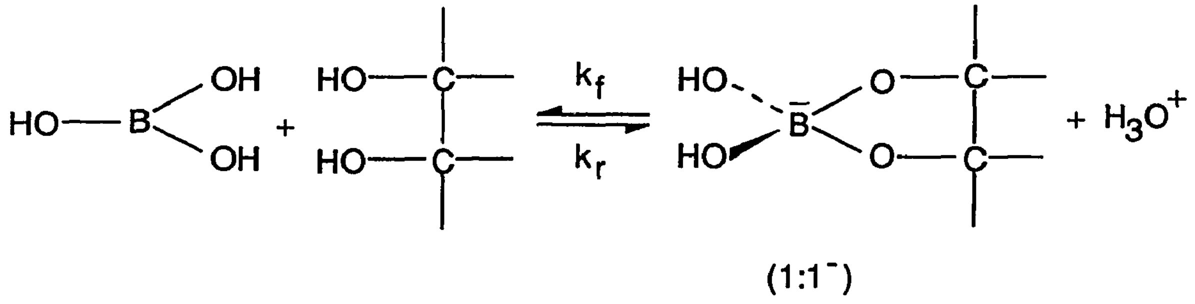
The substitution reaction which is being considered here is given below.

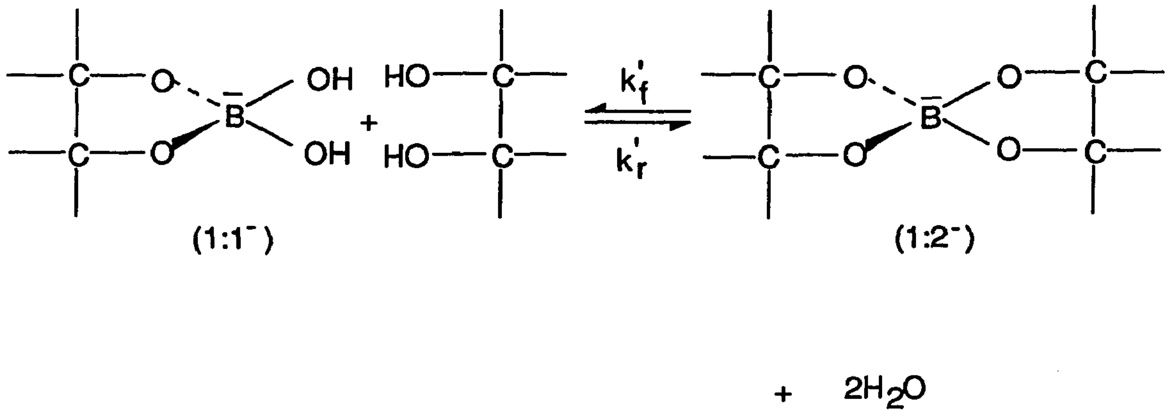
$$B^- + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CX^- + 2H_2O \qquad (8)$$

The complexation reactions of m-$NO_2\Phi B(OH)_2$ were carried out in acidic solution. In the case of mandelic acid, the kinetic experiments were successful up to pH 6. Since the pK_a of the boron acid is 6.96, it was possible to determine the reactivity of the tetrahedral m-$NO_2\Phi B(OH)_3^-$ anion (k_2 in eqn (8)). For salicylic acid, the experiments were done only up to pH 4 because the relaxation times were too long for measurement at a higher pH. In this case, an estimate or an upper limit of the rate constant k_2 was made.

In both cases above, the authors did not take into account the kinetic indistinguishability of the reaction pathways - $HB + HL^- \rightleftarrows CX^- + H_2O$ and $B^- + H_2L \rightleftarrows CX^- + 2H_2O$ (see Chapter 2, page 53). This means that the reported rate constants for the reactivity of the m-$NO_2\Phi B(OH)_3^-$ anion given by eqn (8) are not accurate. However, the relative magnitudes of the rate constants do suggest that the tetrahedral borate species react much faster than the trigonal boron acid. Therefore, these studies gave indirect evidence for the reactivity of the borates. On the other hand, the $CH_3B(OH)_2$ / polyol systems studied in this Chapter provide more conclusive evidence for the lability of the borate anion relative to the trigonal boron acid.

A similar situation where a tetrahedral boron species undergoes substitution more rapidly than a trigonal boron acid is seen in an earlier study of the boric acid (pK_a=8.98) / lactic acid (pK_a=3.70) system [62]. The experiments were done in acidic solution and the complexation pathways being considered here are given below.



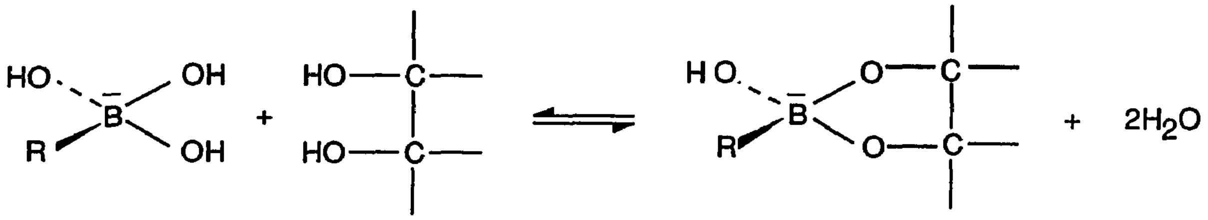


The second reaction given above is similar to the substitution reaction of the tetrahedral methylboronate anion in the sense that both the 1:1⁻ complex and the $CH_3B(OH)_3^-$ anion are four - coordinate boron species which are undergoing substitution reactions. For the boric acid / lactic acid system,

k_f = 2.5 $M^{-1}s^{-1}$ while k_f' = 4.0 x 10^3 $M^{-1}s^{-1}$. These results also reveal the lability of the tetrahedral boron species relative to the trigonal boron acid.

From the systems described above, it is seen that the borate anions react more rapidly than the trigonal boron acids. This difference in reactivity may be explained in terms of the boron - oxygen bond strength. It is known that the boron - oxygen bond is longer in the tetrahedral borate than in the trigonal species. Specifically, for boric acid, the trigonal $B(OH)_3$ species has a boron - oxygen bond length of 1.37 Angstrom units, whereas the tetrahedral $B(OH)_4^-$ anion has a value of 1.48 Angstrom units [100] . This means that the boron - oxygen bond is weaker in the tetrahedral borate anion. Therefore, in this case, the hydroxide may be a better leaving group and the rate determining ring closure may occur more easily. This is reflected in the relative magnitudes of the rate constants k_2 and k_4, compared with those of k_1 and k_3 in Table 3-4.

The results of this study are in no way sufficient to propose a transition state for the substitution reaction of the tetrahedral borate anion. However, there are a few points which can be made concerning a possible transition state. The overall reaction of the borate anion is rewritten below.



The 1,2-diol binds to the boron atom to produce the chelate complex and two condensed water molecules. From this study, since only one type of ligand (non-acidic) was used, it is unclear whether proton transfer is important in the transition state.

One possible route to the transition state is the case where, before the attack of the ligand donor atom, a hydroxide ion dissociates from $RB(OH)_3^-$ as an initial step. As mentioned before, the B - O bond in the borate anion is weaker than in the trigonal boron acid. The dissociation of the hydroxide ion from $RB(OH)_3^-$ would produce the trigonal $RB(OH)_2$ species. Therefore, if this pathway were to exist, it would mean that the trigonal and the tetrahedral species would react with similar rates. This is clearly not the case as seen in Table 3-4.

A second possibility is that perhaps the transition state for the tetrahedral borate anion is an associative one, as in the case of the trigonal boron acid. That is, the oxygen donor atom of the ligand may interact with boron in $RB(OH)_3^-$ to form a pentacoordinate boron species. A coordination number of five for boron is not unknown. In studies [101] of the hydrolysis of BH_4^-, this particular coordination number was proposed, and calculations [102] have been done on the various geometries of the pentacoordinate boron.

The main conclusion from the experiments in this Chapter is that the tetrahedral methylboronate anion reacts much faster than the trigonal methylboronic acid. To our knowledge, this is the first set of reported rate constants for the lability of the tetrahedral borates relative to the trigonal boron acids.

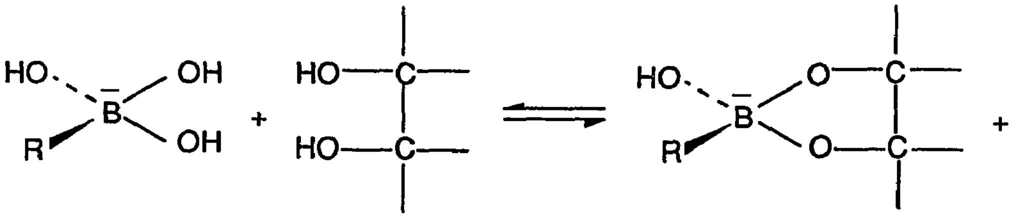
This piece of work certainly does not provide sufficient evidence from which one can propose a possible transition state for the substitution reaction of the tetrahedral borate anion. It is clear that much more studies in basic solution are needed, using different boron acids coordinating to a variety of ligands. This is especially true since the phenylboronic acid / polyol reactions (Chapter 5) failed to follow the same mechanism as the methylboronic acid / polyol systems.

CHAPTER 4

THERMODYNAMIC PARAMETERS ($\Delta G°$, $\Delta H°$ AND $\Delta S°$) FOR BORON ACID / LIGAND SYSTEMS

4.1 Introduction

The reactions between boric acid and polyhydroxy compounds (polyols) which produce chelate complexes in aqueous solution are well established in terms of the stoichiometry and the measured stability constants [22,26,86-91]. The kinetic study presented in Chapter 3 provides the first direct evidence for the unreactivity of the trigonal boron acid and the lability of the tetrahedral borate anion towards the polyol. The only route to the chelate complex is via the more labile borate anion. The reaction between a substituted borate anion and a 1,2-diol is shown in eqn (1).


(1)

The reaction given in equation (1) is a substitution reaction in which the coordination number and the hybridization of boron remain unchanged.

The purpose of the following experiments was to determine the thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the complexation reactions between the methylboronate anion and the simple polyols. A substituted boron acid is chosen since it can form only 1:1 complexes in solution. The reactions are carried out in basic media because the equilibrium is such that complex formation occurs only in basic solution. For these reactions, the stability constants and rate constants were determined and reported in Chapter 3. The present measurement of ΔH° and ΔS° for the complexation step would allow one to determine whether the driving force for the reaction is enthalpic or entropic in origin. A knowledge of the enthalpy and entropy changes accompanying the methylboronic acid / polyol substitution reactions would therefore provide a more complete understanding of the systems.

A second system which was investigated is the methylboronic acid / catechol (1,2-benzenediol) system. The simple polyols and the catechols are similar in the sense that they are both bidentate chelating 1,2-diols. An important difference between the two types of ligands is that the polyols are flexible whereas the catechols are rigid. Recall that the chelate effect is usually attributed to a favorable(+) entropy term. In the case of the polyols, the favorable entropy change upon chelation to boron would be opposed by the negative entropy change which results from the loss in configurational entropy in the free ligand. This is not necessarily true for the analogous catechol system since catechol is a more rigid ligand. Therefore, the reason for including the methylboronic acid / catechol system was to determine the extent to which the flexibility of the free ligand affects the entropy change in the chelation process.

The methylboronate / polyol reactions are studied in basic solution since the complexes are formed only under these pH conditions. The methylboronic acid / catechol reactions are carried out in acidic solution because the ligand undergoes oxidation in basic media. The reactions of methylboronic acid with catechol and methylboronate with catechol are related by the acid dissociation equilibrium of the boron acid. In order to compare the the entropy changes in two systems - methylboronate / 1,2-propanediol and methylboronate / catechol- it was necessary to determine ΔG°, ΔH° and ΔS° for the ionization of methylboronic acid.

4.2 Theory

The determination of ΔG°, ΔH° and ΔS° for the complexation reactions was accomplished by the measurement of the stability constant as a function of the temperature. The theoretical treatment of these measurements is given below.

The van't Hoff equation [103] is given by

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{2}$$

Assuming that ΔH° does not change much with temperature and since $d(1/T) = -1/T^2\, dT$, eqn (2) may be rewritten as

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^\circ}{R} \tag{3}$$

If the enthalpy change is constant over the temperature range studied then a plot of ln K vs 1/T is a straight line with

$$\Delta H^\circ = \text{slope} \times (-R) \tag{4}$$

$$\Delta G^\circ = -RT \ln K \tag{5}$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \tag{6}$$

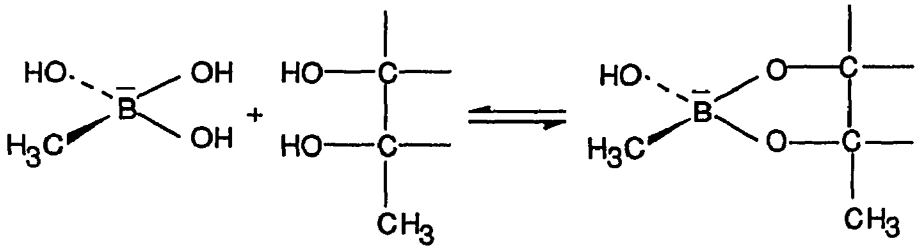
Since the plots of ln K vs 1/T were linear (see Figure 4-3), it is a good approximation to neglect the temperature dependence of ΔH°. From the measurements of the stability constants as a function of the temperature and from eqns (4) - (6), the values for ΔH°, ΔG° and ΔS° were calculated.

4.3 Determination of ΔG°, ΔH° and ΔS°

4.3.1 The Methylboronic Acid / Polyol System

Methylboronic acid has a pK_a value of 10.40 while each of the polyols has a value of 13. For the $CH_3B(OH)_2$ / 1,2-propanediol system, a distribution diagram which was calculated from the known stability constants reported in Chapter 3 is presented in Figure 4-1. At pH 12, the distribution diagram indicates that the concentration of the trigonal boron acid is negligible compared to that of the tetrahedral borate anion. Therefore, at pH 12, the main complexation reaction is between the borate anion and the fully protonated form of the ligand.

The reaction between methylboronate anion and 1,2-propanediol is given below.



$+ 2H_2O$; K2 (7)

The stability constant K2 was measured as a function of the temperature using the ^1H NMR technique as described in Chapter 2. A ^1H NMR spectrum at 25 °C is presented in Figure 4-2. The calculation of the stability constant from the spectrum was outlined in Chapter 2. The stability constant K2 was found to increase with decreasing temperature. For the same spectrum, the plot of ln K2 vs 1/T is given in Figure 4-3.

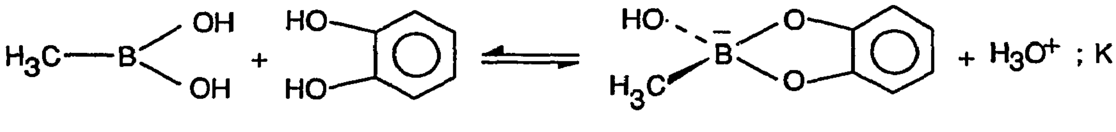
Using several plots together with eqns (4) - (6), the values for ΔG°, ΔH° and ΔS° were calculated and are presented in Table 4-1. The stability constant obtained at 298 K agreed within ± 20 % of the value reported in Chapter 3 which was measured using the pH method and the ^{11}B NMR technique. The reaction is seen to be exothermic and is accompanied by a large and negative entropy change.

The determination of the thermodynamic parameters for the reactions of methylboronic acid with ethylene glycol, 1,3-propanediol and glycerol was not possible by the ^1H NMR technique. In all cases, the resulting spectra were composed of overlapping peaks which did not allow any quantitative determination of the stability constants.

4.3.2 The Methylboronic Acid / Catechol System

From Table 4-1, the entropy change for the chelation of 1,2-propanediol to the methylboronate anion is seen to be negative. It was assumed that the sign of ΔS was perhaps due to the loss of configurational entropy in 1,2-propanediol when it is bound in the complex. This result prompted the investigation of the methylboronic acid /catechol system. Catechol, being more rigid than 1,2-propanediol, was predicted to undergo the analogous substitution reaction with a more positive entropy change.

The thermodynamic experiments with the $CH_3B(OH)_2$ / catechol system had to be conducted in acidic solution because the ligand undergoes oxidation in basic media. Catechol is more acidic than the polyols and is characterized by two pK_a values ; $pK_{a1} = 9.27$ and $pK_{a2} = 11.49$. Using previously determined stability constants [61], a distribution diagram for the $CH_3B(OH)_2$/catechol system was calculated and is presented in Figure 4-4. Since the experiments are being carried out in acidic solution between pH 6 and pH 7, the only complexation pathway is the one between the trigonal boron acid and the fully protonated form of the ligand. The addition reaction between methylboronic acid and catechol is given in eqn (8).

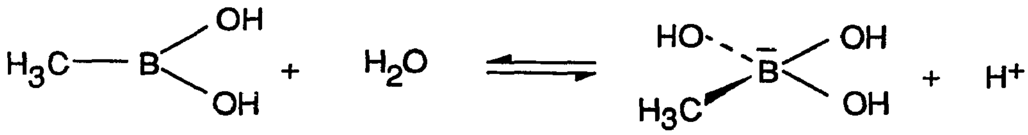


(8)

The stability constant K1 was measured as a function of the temperature by use of the ^{1}H NMR technique. A spectrum at 25 °C is presented in Figure 4-5. Unlike the methylboronate /1,2-propanediol system, the stability constant for the methylboronic acid / catechol system was found to be independent of the temperature. This means that ΔH° for the reaction is close to zero. The approximation $\Delta H^\circ = 0$ was used in the calculation of the entropy change using eqn (6).The results of several experiments are reported in Table 4-2.

4.3.3 The Ionization of Methylboronic Acid

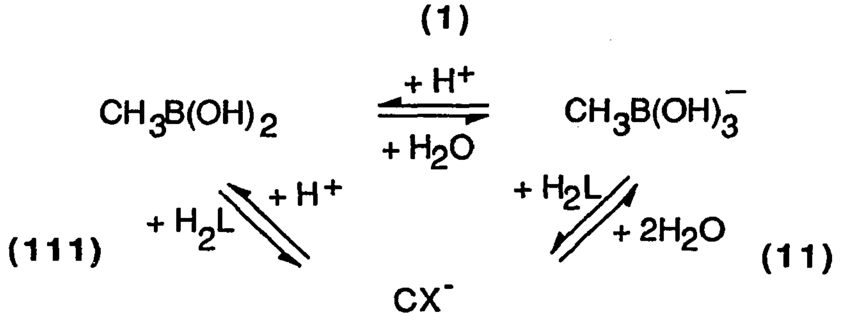
The methylboronate anion /1,2-propanediol system was studied in basic solution while the methylboronic acid / catechol system was studied in acidic solution. In order to compare the entropy changes between the two systems - $CH_3B(OH)_3^-$/1,2-propanediol and $CH_3B(OH)_3^-$/catechol - the determination of ΔG°, ΔH° and ΔS° for the ionization reaction of methylboronic acid was carried out. The ionization reaction is given in eqn (9).



; K_a (9)

The thermodynamic parameters for the equilibrium given in eqn (9) were determined by measuring K_a as a function of the temperature by pH titration method, as described in Chapter 2. A plot of ln K_a vs 1/T is given in Figure 4-6. Several plots together with eqns (4) - (6) were used to calculate ΔG°, ΔH° andΔS° for the ionization of $CH_3B(OH)_2$. The results are presented in Table 4-3.

The comparison of the entropy changes between the systems $CH_3B(OH)_3^-$/1,2-propanediol and $CH_3B(OH)_3^-$/catechol was done in the following manner. Since the reactions with catechol were done in acidic solution, the entropy change for the reaction between $CH_3B(OH)_3^-$ and catechol was calculated using the Born Haber cycle given below.



H_2L = catechol

From the Born Haber cycle, it is readily seen that

$$\Delta S^\circ_{111} = \Delta S^\circ_1 + \Delta S^\circ_{11} \qquad (10)$$

The values for ΔS°_1 and ΔS°_{111} were reported in Tables 4-3 and 4-2, respectively. Therefore, ΔS°_{11} which refers to the substitution reaction of the methylboronate anion with catechol is easily calculated to be 213.1 J/mole-K.

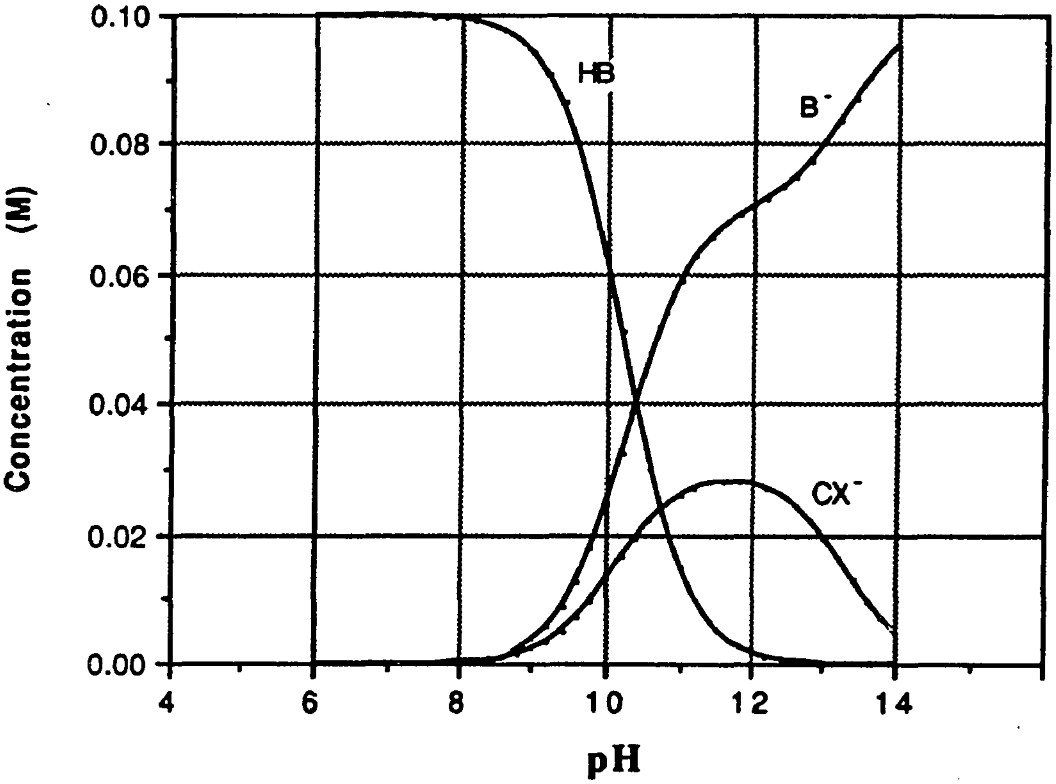


Figure 4-1: Distribution Diagram for Methylboronic Acid (0.1 M) / 1,2-propanediol (0.1 M) System

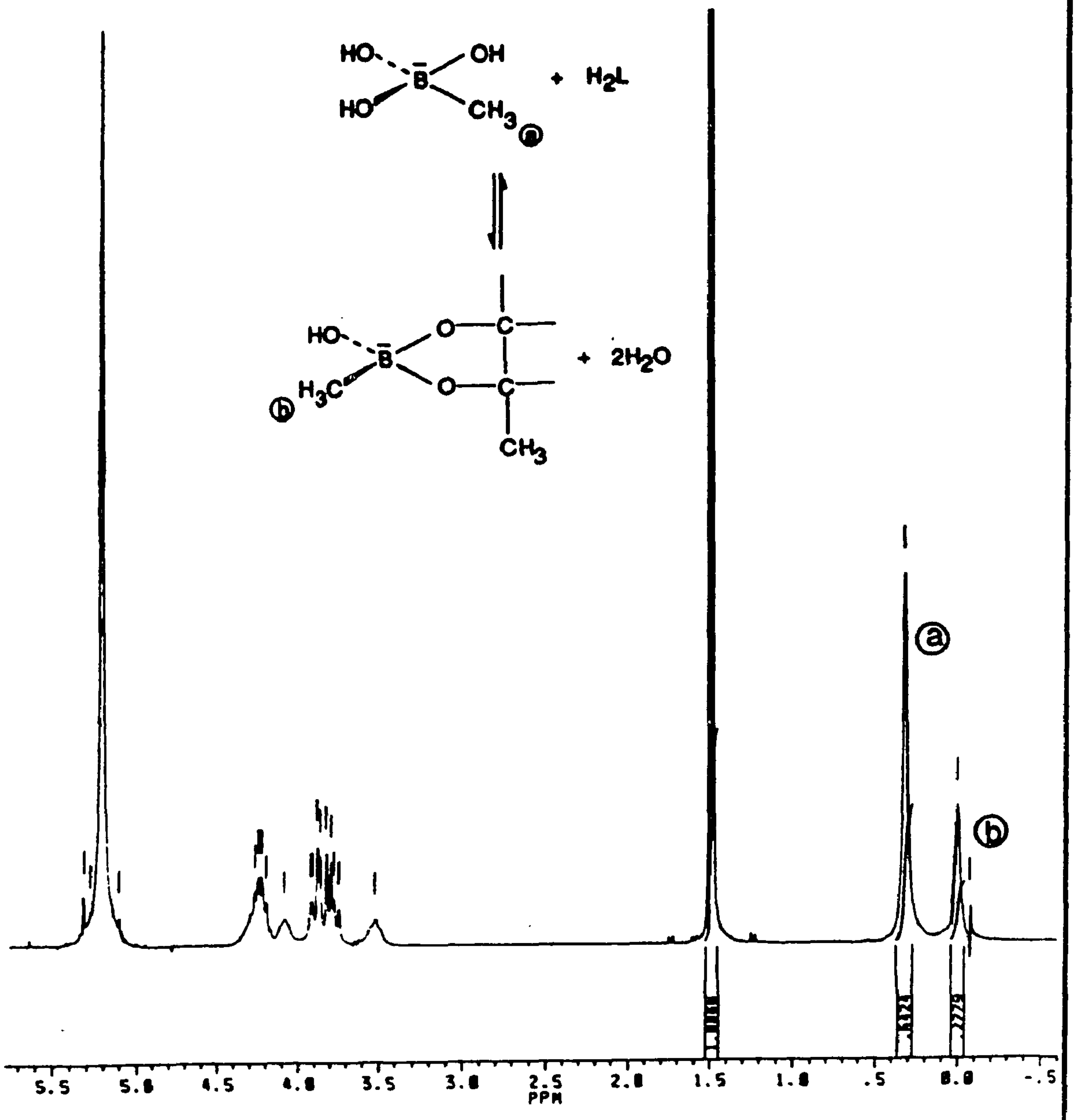


Figure 4-2: ^{1}H NMR Spectrum for Methylboronic Acid (0.165 M) / 1,2-propanediol (0.152 M) System

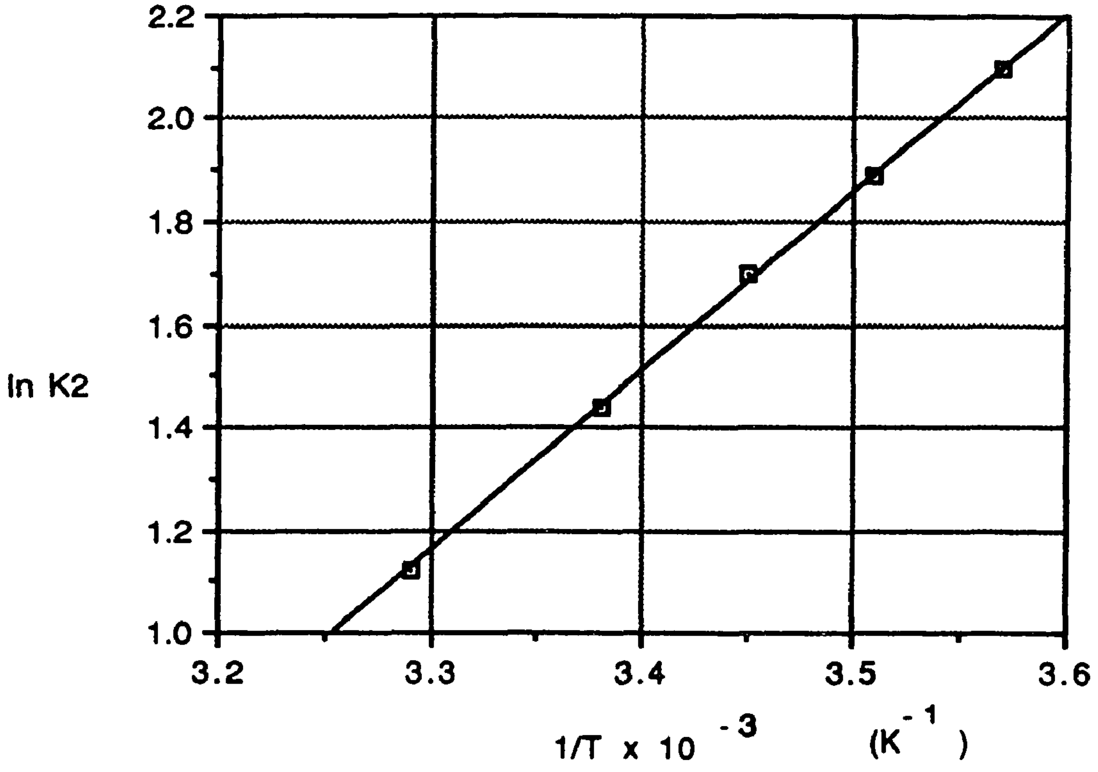


Figure 4-3: Graph of ln K2 vs 1/T for Methylboronic Acid (0.165 M) / 1,2-propanediol (0.152 M) System

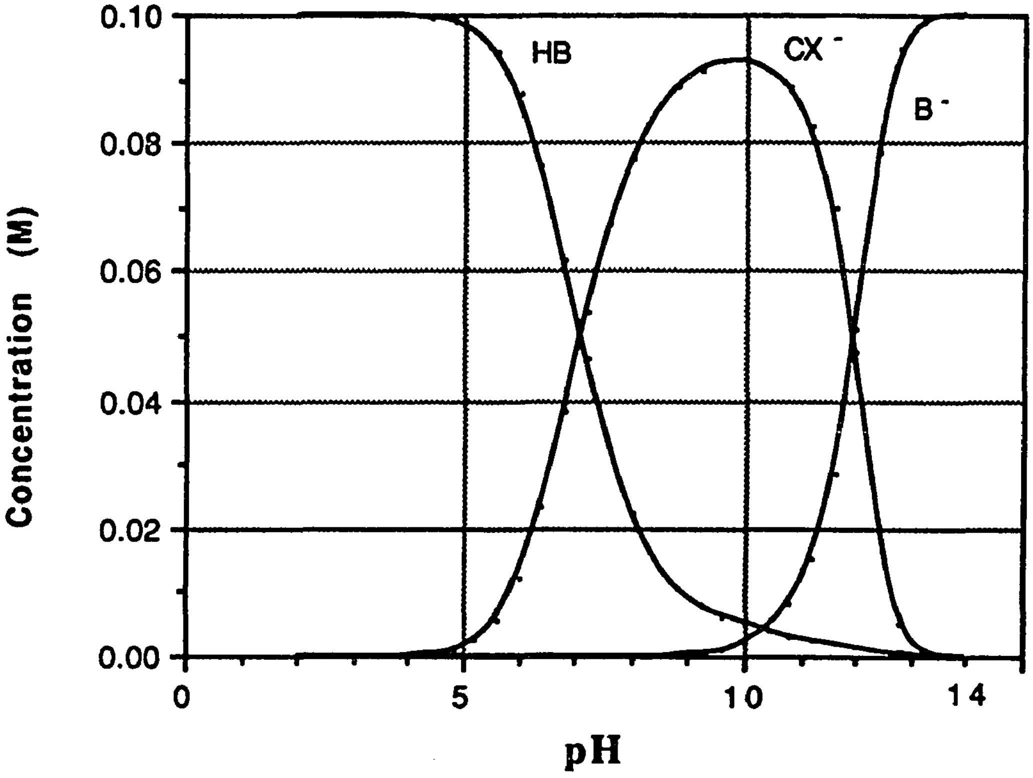


Figure 4-4: Distribution Diagram for Methylboronic Acid (0.1 M) / Catechol (0.1 M) System

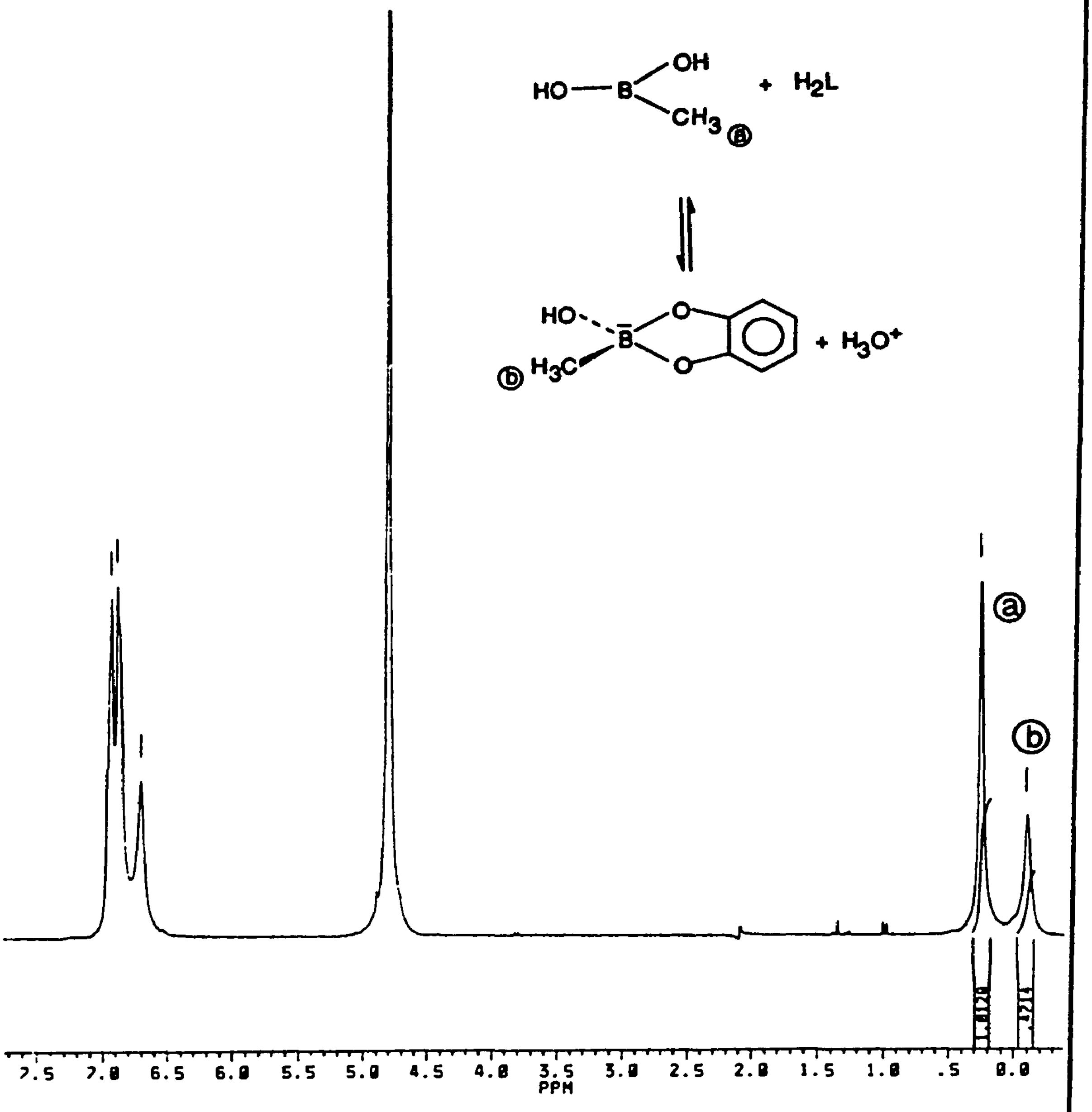


Figure 4-5: ^{1}H NMR Spectrum for Methylboronic Acid (0.118 M) / Catechol (0.164 M) System

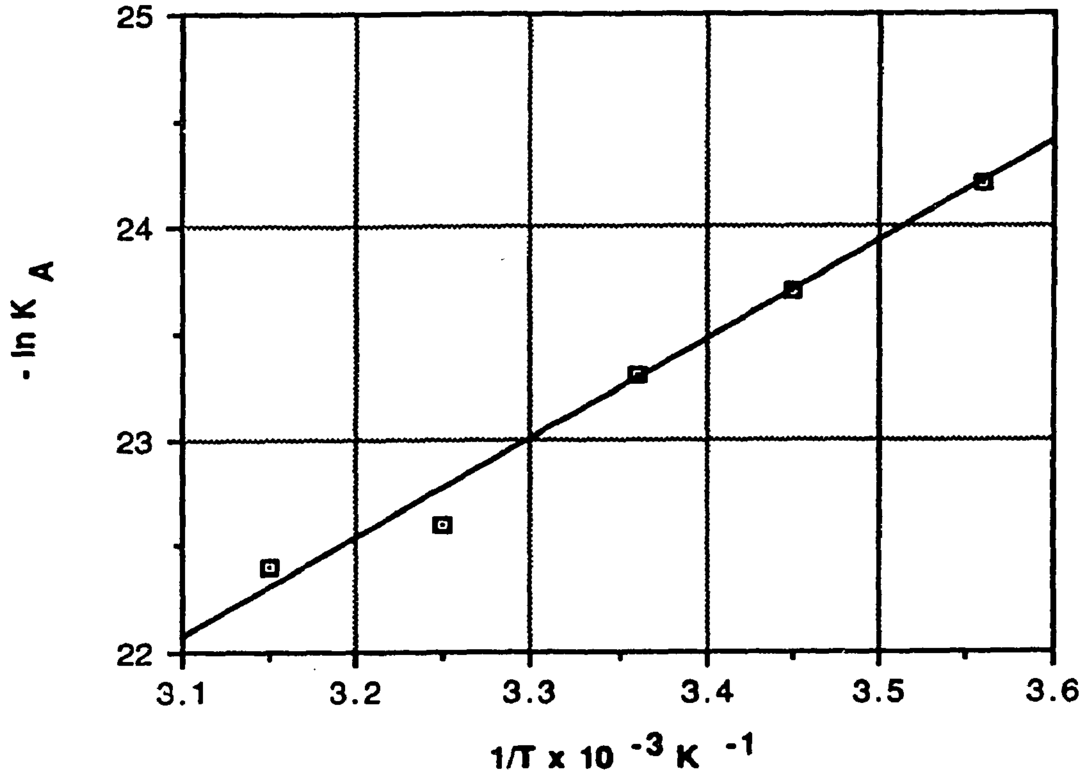


Figure 4-6: Graph of ln K_a vs 1/T for Methylboronic Acid (0.050 M)

4.4 Results

Table 4-1: Thermodynamic Data for Methylboronate Anion / 1,2-propanediol System at 25 °C

ΔG°, kJ / mole	ΔH°, kJ / mole	ΔS°, J / mole-K
- 4.3	- 26.2	- 73.6

Table 4-2: Thermodynamic Data for Methylboronic Acid / Catechol System at 25 °C

ΔG°, kJ / mole	ΔH°, kJ / mole	ΔS°, J / mole-K
33.5	~ 0	112.3

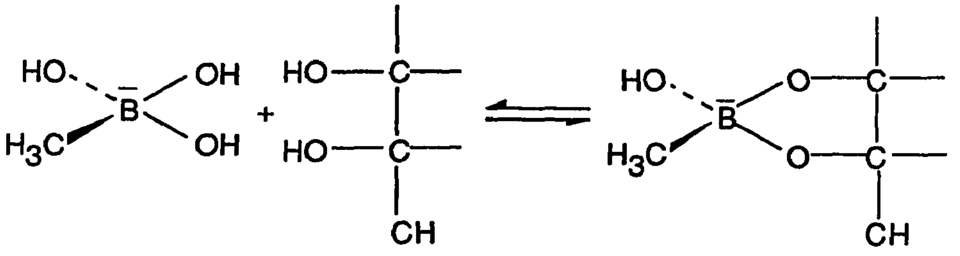
Table 4-3: Thermodynamic Data for the Ionization of Methylboronic Acid at 25 °C

ΔG°, kJ / mole	ΔH°, kJ / mole	ΔS°, J / mole-K
58.0	27.9	- 100.8

4.5 Discussion

The thermodynamic results obtained in this Chapter are the first reported enthalpy and entropy changes for the methylboronic acid / ligand systems. From Table 4-1, the substitution reaction of the methylboronate anion with 1,2-propanediol is exothermic. The chelation reaction is also accompanied by a large and surprisingly negative entropy change. On the other hand, the analogous reaction of the methylboronate anion with the more rigid ligand catechol is characterized by a large and positive entropy change.

The substitution reaction between methylboronate and 1,2-propanediol is rewritten below.



+ $2H_2O$ (11)

The reaction was found to occur with a favorable enthalpy change where $\Delta H^\circ = -26.2$ kJ/mole. For the analogous reaction of borate $B(OH)_4^-$ with 1,2-propanediol, enthalpy changes have been determined by methods such as pH titration [22,104], ^1H NMR technique [105] and calorimetry [106]. In all cases, the reaction was found to be exothermic with ΔH° values ranging from -10 to -21 kJ/mole. The favorable enthalpy changes indicate that relatively strong boron - oxygen bonds are formed in the chelate complexes.

In addition, the substitution reactions of the borate anion $B(OH)_4^-$ with ethylene glycol, glycerol and mannitol are all exothermic [22,104-107].

The entropy change for the chelation of 1,2-propanediol to the methylboronate anion (eqn (11)) is unexpectedly negative. The sign of ΔS° is due to two opposing factors. The favorable entropy change associated with the chelation process is opposed by the loss of rotational freedom in 1,2-propanediol upon coordination to boron. The contribution from the second factor is much greater than that from the first causing the net ΔS° to be negative. It is worth mentioning that negative entropy changes were also observed for the analogous reactions of borate $B(OH)_4^-$ with ethylene glycol, 1,2-propanediol, glycerol and mannitol [22,104-107].

The reaction of the methylboronate anion with 1,2-propanediol occurs with an entropy change of -73.6 J/mole-K. For the analogous reaction of the methylboronate anion with catechol, the entropy change which was calculated from the Born Haber cycle is 213.1 J/mole-K. The difference in these entropy changes is mainly due to the degree of rotational freedom which is present in the free ligands. Catechol being more rigid than 1,2-propanediol does not have much configurational entropy to lose upon chelation. The large and positive ΔS° value for the reaction of methylboronate with catechol is therefore indicative of the entropic origin of the chelate effect.

From Table 4-3, the ionization of methylboronic acid is seen to be endothermic with $\Delta H^\circ = 27.9$ kJ/mole. The ionization of other boron acids are also endothermic . For boric acid , $\Delta H^\circ = 13.8$ kJ / mole [28] and for phenylboronic acid, $\Delta H^\circ = 7.9$ kJ/mole [27].

In the ionization reaction $HB + H_2O \rightleftarrows B^- + H^+$, bonds are being broken and formed while boron undergoes a hybridization change and the above ΔH° values refer to the net enthalpy change. The positive ΔH° indicates that the H - O bond in H_2O is stronger than the B - O bond in $RB(OH)_3^-$. However, it is possible to rewrite the HB/B⁻ equilibrium in the following manner.

$$HB + H_2O \rightleftarrows B^- + H^+ \quad ; \Delta H^\circ_1 \tag{12}$$

$$H^+ + OH^- \rightleftarrows H_2O \quad ; \Delta H^\circ_2 \tag{13}$$

$$HB + OH^- \rightleftarrows B^- \quad ; \Delta H^\circ_3 = \Delta H^\circ_1 + \Delta H^\circ_2 \tag{14}$$

The values for ΔH°_1 were given above. The enthalpy change ΔH°_2 for the neutralization reaction given by eqn (13) has been determined to be - 55.9 kJ/mole [29]. Therefore, the values for ΔH°_3 can be easily calculated. The advantage of writing the HB/B⁻ equilibrium in the form given by eqn (14) is that along with the rehybridization process, this equation describes only the formation of a single covalent bond. The hydroxide ion adds to the empty p orbital on boron in the trigonal species to produce the tetrahedral borate anion. Using the above values for ΔH°_1 and ΔH°_2, the values for ΔH°_3 can be calculated and are presented in Table 4-4.

Table 4-4: Calculated Enthalpy Changes for the Addition of Hydroxide to Trigonal Boron Acids

Boron Acid	ΔH°_3 , kJ/mole
$\Phi B(OH)_2$	- 48.0
$B(OH)_3$	- 42.1
$CH_3B(OH)_2$	- 28.0

The equilibrium given by eqn (14) for the different boron acids describes the formation of boron - oxygen bonds and this is reflected in the sign of ΔH°_3. As mentioned in Chapter 1, multiple bonding is known to exist in the trigonal boron acids and the loss of this backbonding interaction may oppose the formation of the tetrahedral borate anion. Therefore, the fact that ΔH°_3 for $CH_3B(OH)_2$ is the least negative may mean that there is more multiple bonding in $CH_3B(OH)_2$ than in the other boron acids in Table 4-4.

The results in Table 4-3 indicate that the ionization of methylboronic acid is accompanied by a large and negative entropy change where $\Delta S^\circ = - 100.8$ J/mole - K. Similarly, the ionization of boric acid [28] and phenylboronic acid [27] are known to occur with negative entropy changes of -129.3 and -142.2 J/mole-K, respectively. It has been pointed out by Pitzer [29] that the average entropy of ionization of a neutral acid to produce an oxyanion is about -92.0 J/mole-K. The ΔS° values for the ionization of the boron acids are more negative than that for a neutral acid. Edwards [27] explained the lower values of ΔS° for $B(OH)_3$ and $\Phi B(OH)_2$ in terms of the increase in coordination number upon the ionization of the boron acid. It is important to note that while ΔH° and ΔG° values can be determined with fairly good accuracy, the determination of ΔS° is subject to much larger errors. In any case, the negative entropy changes for the ionization of the boron acids reveal that the product side of the reaction is more ordered than the reactant side. Other than the explanation of increasing coordination number which was put forward by Edwards, a second reason for the negative ΔS° may be due to a greater degree of hydrogen bonding which may exist between B^- and H_2O relative to that between HB and H_2O. That is, since multiple bonding is known to exist in HB and not in B^-, the oxygens in the tetrahedral borate anions are likely to be more basic than those in the trigonal boron acids.

In conclusion, the complexation reaction between the methylboronate anion and 1,2-propanediol is exothermic. The reaction is also characterized by a large and negative entropy change. Since the reaction is spontaneous, the chelation reaction is enthalpy driven and not entropy driven. The entropic origin of the chelate effect was demonstrated in the reaction of the methylboronate anion with catechol.

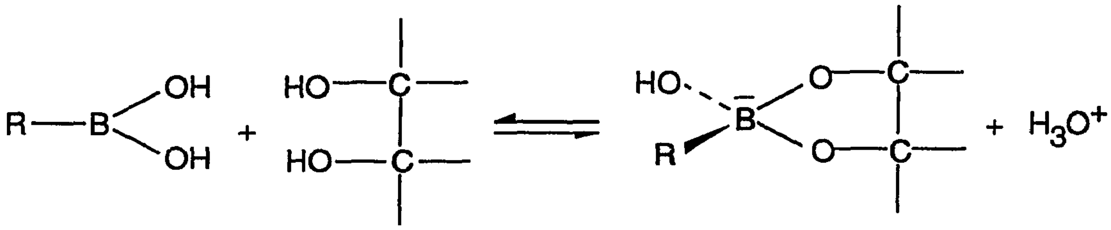
CHAPTER 5

THE PHENYLBORONIC ACID / POLYOL SYSTEM

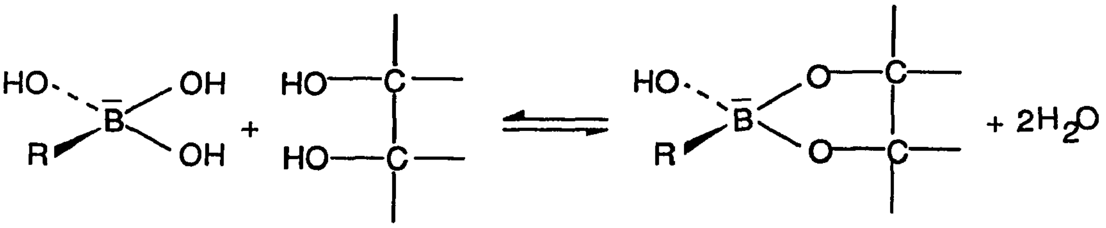
(" An Unsolved Problem")

5.1 Introduction

As seen in the previous two Chapters, both the trigonal and the tetrahedral forms of a substituted boron acid can react with bidentate chelating ligands such as α-hydroxycarboxylic acids and dicarboxylic acids. In both cases, the same anionic tetrahedral 1:1 complex is formed, as shown in eqns (1) and (2).



(1)



(2)

The complexes are stabilized by the chelate effect and are known to contain five- and six-membered rings [30-32].

The present Chapter deals with the complexation reactions between phenylboronic acid and the simple polyols in basic solution. The purpose of the experiments is the same as that which was presented in Chapter 3 for the methylboronic acid / polyol systems; that is, to determine the reactivity of the tetrahedral borate anion. The reactions are carried out in basic solution because the complexes are formed only under these pH conditions. However, phenylboronic acid is more acidic than methylboronic acid. Previous kinetic studies of four different boron acids with a particular ligand indicate a precise correlation between boron acid pK_a and both the forward and the reverse rate constants [59]. Since the studies were performed in acidic solution, the authors were observing only the reactivity of the trigonal boron species. In basic solution, both the trigonal and the tetrahedral forms of the boron acid are present. In addition to studying the reactivity of the borate anion, the phenylboronic acid / polyol reactions are carried out to determine whether a similar acidity correlation exists in these systems.

5.2 Determination of the Stability Constants

Phenylboronic acid has a pK_a value of 8.72 [59]. It is much more acidic than methylboronic acid (pK_a = 10.40). Each of the ligands - ethylene glycol, 1,2-propanediol and 1,3-propanediol - has a pK_a value of 13. The overall complexation reactions are given below.

$$HB + H_2L \rightleftarrows CX^- + H^+ \; ; \; K1 \qquad (3)$$

$$B^- + H_2L \rightleftarrows CX^- + H_2O \; ; \; K2 = K1/K_{HB} \qquad (4)$$

Both ethylene glycol and 1,2-propanediol react with $\Phi B(OH)_2$ to form complexes containing five-membered chelate rings. In the case of 1,3-propanediol, a six-membered chelate complex is formed.

The stability constants were determined by NaOH titrations which were described in Chapter 2. For the $\Phi B(OH)_2$ / ethylene glycol system, the ^{11}B NMR technique was used as well. For all of the complexation reactions only one complex was formed in solution. Therefore the calculation of the stability constants from both methods follows directly from the derivations which were outlined in Chapter 2.

The resulting stability constants are presented in Table 5-1 and are reported with an accuracy of ± 20 %.

For the $\Phi B(OH)_2$ / ethylene glycol system, the stability constants were used to calculate a distribution diagram which is given in Figure 5 -1.

5.3 Kinetic Measurements

The relaxation times were measured by the temperature-jump method which was described in Chapter 2. A sample of the experimental data is given in Table 5-2.

The kinetic data for the reactions of phenylboronic acid with ethylene glycol in Table 5-2 show very unusual behavior. Specifically, the reactivity patterns which are present in the $\Phi B(OH)_2$ / $HOCH_2CH_2OH$ system and which are not seen in the $CH_3B(OH)_2$ / polyol systems are as follows.

(1) At constant concentrations of H_2L and HB, as the pH increases, the relaxation time increases.

(2) At the same pH, with the concentrations of H_2L constant, the relaxation time varies linearly with the concentration of HB.

(3) At the same pH, with the concentration of HB constant, the relaxation time

is independent of the concentration of H_2L.

Since the reactivity trends in the $\Phi B(OH)_2/HOCH_2CH_2OH$ kinetic data were very different from those in the $CH_3B(OH)_2/HOCH_2CH_2OH$ system, several additional tests were carried out with the phenylboronic acid system in order to check the reliability of the kinetic data. These tests are now described.

For the kinetic measurements, all solutions including the indicator are freshly prepared just before use. The boron acid is carefully weighed and the ligand is handled volumetrically. The required aliquots of the electrolyte and the indicator are added and the pH of the solution is adjusted by the dropwise addition of dilute HCl or NaOH.The relaxation times are then measured by the temperature-jump method which has an accuracy of ± 10 %. Only one relaxation time was observed. Immediately following each experiment, the pH of the solution is checked again.

Additional Tests to Check Reliability of the $\Phi B(OH)_2$ / $HOCH_2CH_2OH$ Kinetic Data.

(a) Phenylboronic acid was recrystallized from water and white needle point crystals were obtained. The purity of the recrystallized boron acid was verified by titration with standard 0.1 M NaOH.

(b) An assay for ethylene glycol was carried out and gave satisfactory results.

The method used in the assay was the periodate determination of ethylene glycol [109]. This method is very selective for 1,2-diols; alcohols (such as methanol and ethanol) and 1,3-diols do not react. In the periodate determination, the carbon - carbon bond of ethylene glycol is cleaved by excess periodic acid. The periodate ion is reduced to iodate, and the hydroxyl groups of $HOCH_2CH_2OH$ are oxidized to carbonyl groups in the formation of formaldehyde.

(c) The experiments were repeated several times while varying the concentrations of H^+, H_2L and HB. The reactivity trends remain the same.

The kinetic data in Table 5-2 contain experiments in which the concentrations of the ligand is approximately 0.3 M. This high concentration was necessary in order to vary the pH as much as possible while still maintaining measurable amplitudes in the relaxation traces. When experiments were done in which the concentration of the ligand was 0.1 M, identical reactivity trends were seen.

(d) Experimental results indicate that the rate is independent of the concentration of the indicator, and the type of indicator.

In a set of five experiments, the concentration of phenolphthalein was varied by a factor of ten while the concentrations of H^+, H_2L and HB were kept constant. Among the five measured relaxation times, the values differ by (± 10%) which is within the limits of accuracy of the temperatue-jump method.

In another set of experiments, the type of indicator was varied by using phenolphthalein, thymol blue and cresol red while the concentrations of H^+, H_2L and HB were kept constant. The variation in the measured relaxation times was less than 5 %.

(e) Experiments with constant concentrations of H^+, H_2L, HB and HIn were done in three different electrolytes (KNO_3 , KCl and NaCl). The rate remains the same.

(f) A solution of phenylboronic acid and phenolphthalein was monitored for several hours using the UV - visible spectrometer. No changes in the spectrum were seen.

(g) For a typical reaction mixture, the relaxation time was measured and the solution was covered with parafilm and left to stand overnight. After 24 hours, the identical value of the relaxation time was obtained.

(h) A solution of phenylboronic acid and ethylene glycol in basic medium (pH 11 - 12) was monitored by the ^{1}H NMR technique. There were no changes in the spectrum after several hours. However, after a few days, phenylboronic acid decomposed (in strongly basic solution) to boric acid and phenol, as determined by NMR experiments.

(i) Analogous kinetic experiments with phenylboronic acid and 1,2-propanediol gave the exact trends as observed in Table 5-2 for the phenylboronic acid / ethylene glycol system.

Several reaction mechanisms which were attempted in order to explain the kinetic data in Table 5-2 for the phenylboronic acid / ethylene glycol system are now discussed.

5.4 Results

Table 5-1 : Stability Constants for Phenylboronic Acid / Polyol Complexes

H_2L	K1	K2
ethylene glycol	5.2×10^{-9}	2.7
1,2-propanediol	1.6×10^{-8}	8.7
1,3-propanediol	1.0×10^{-8}	5.3

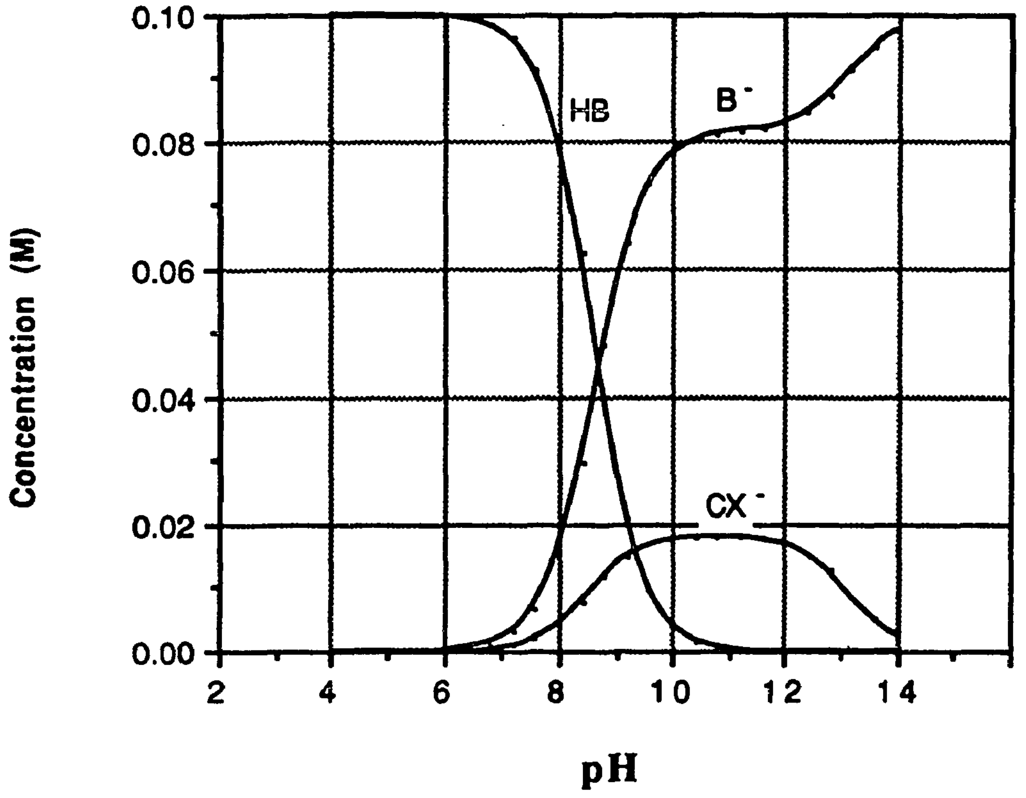


Figure 5-1: Distribution Diagram for Phenylboronic Acid (0.1 M) / Ethylene Glycol (0.1 M) System

Table 5-2 : Kinetic Data for Phenylboronic Acid / Ethylene Glycol System.

H_2L : $HOCH_2CH_2OH$ $K_{H_2L} = 1 \times 10^{-13}$

HB : $\Phi B(OH)_2$ $K_{HB} = 1.9 \times 10^{-9}$

HIn : Phenolphthalein $K_{HIn} = 3.98 \times 10^{-10}$

: Phenol Red * $K_{HIn} = 1.26 \times 10^{-8}$

pH	$[H_2L]_0$	$[HB]_0$	$[HIn]_0$	τ (msec)	$1 / \tau$ (s^{-1})
9.89	0.286	0.078	2.75×10^{-5}	9.83	101.7
9.25	0.286	0.077	2.75×10^{-5}	2.66	375.9
8.67	0.286	0.077	4.58×10^{-5}	1.25	800.0
8.23	0.286	0.077	4.58×10^{-4}	0.92	1081.1
7.97 *	0.286	0.077	1.66×10^{-5}	0.73	1375.5
8.71	0.286	0.081	4.20×10^{-4}	1.22	817.7
8.73	0.286	0.040	4.57×10^{-4}	2.53	395.4
8.60	0.502	0.056	4.23×10^{-4}	1.41	707.7
8.60	0.102	0.057	4.24×10^{-4}	1.58	634.9

5.5 Analysis of Kinetic Data

Mechanism 1

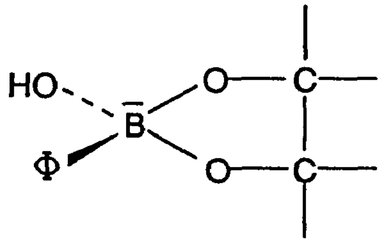
The first mechanism is the one which adequately described the methylboronic acid / polyol reactions in Chapter 3 and is presented in Scheme 1.

Scheme 1

$$HB + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CX^- + H^+ \quad ; K1 \tag{5}$$

$$B^- + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CX^- + 2H_2O \quad ; K2 = \frac{K1}{K_{HB}} \tag{6}$$

where CX^- =



Reaction (5) is an addition reaction in which the ligand adds to the trigonal boron acid to produce the tetrahedral complex, with loss of a ligand proton. Reaction (6) is a substitution reaction. For such a reaction mechanism, the expression for the relaxation time was derived in Chapter 2 and is rewritten below.

$$\frac{1}{\tau} = k_1 \left(S[\overline{HB}] + R[\overline{H_2L}) + \frac{[\overline{H^+}]}{K1} + \frac{P[\overline{CX^-}]}{K1} \right)$$

$$k_2 \left(S[\overline{B^-}] + T[\overline{H_2L}] + \frac{1}{K2} \right) \tag{7}$$

where P, R, S and T are defined in Appendix A.

The coefficients of the rate constants in eqn (7) are functions of equilibrium concentrations and equilibrium constants which are known. The rate constants are usually obtained by fitting the experimentally determined rate, $1/\tau$, to the calculated coefficients given in eqn (7).

A representative sample of the kinetic data for the $\Phi B(OH)_2$ / $HOCH_2CH_2OH$ system is given in Table 5-3. Using the measured stability constants, the coefficients ({ }) were calculated and are also presented in Table 5-3.

Table 5-3 : Data Analysis for Phenylboronic Acid / Ethylene Glycol System Using Mechanism 1.

pH	$[H_2L]_0$	$[HB]_0$	$[HIn]_0$	$1/\tau$ (expt) s^{-1}	k_1 { }	k_2 { }
9.89	0.286	0.078	2.75×10^{-5}	101.7	0.045	0.663
8.80	0.293	0.077	4.58×10^{-5}	555.6	0.555	0.666
8.23	0.286	0.077	4.58×10^{-4}	1081.1	2.03	0.655
8.71	0.286	0.081	4.20×10^{-4}	817.7	0.676	0.659
8.73	0.286	0.040	4.57×10^{-4}	395.4	0.642	0.654
8.60	0.502	0.056	4.23×10^{-4}	707.7	1.139	0.862
8.60	0.102	0.057	4.24×10^{-4}	634.9	0.639	0.484

The three reactivity trends observed experimentally - the decreasing rate with increasing pH, the linear dependence of the rate upon [HB] and the independence of the rate upon [H_2L] - are clearly not seen in the calculated coefficients in Table 5-3. Therefore, the mechanism in Scheme 1 which successfully described the $CH_3B(OH)_2$ / polyol reactions is not adequate for the analogous $\Phi B(OH)_2$ systems.

Mechanism 2

The following mechanism assumes that the complexation reaction occurs in two steps, as shown in Scheme 2. The first step involves the nucleophilic attack of the glycolic oxygen on the trigonal $\Phi B(OH)_2$ to produce a nonchelated intermediate species $C1^-$, with loss of a ligand proton. The second step given by eqn (9) is a substitution reaction which produces the same intermediate species $C1^-$. The final step involves the ring closure process to produce the chelate complex and is accompanied by loss of a water molecule. In the proposal of this mechanism, it was speculated that perhaps the intermediate species $C1^-$ was stable enough so that its formation step can be separated from the ring closure process.

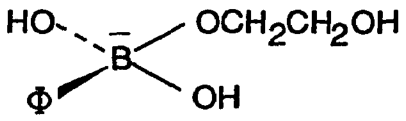
Scheme 2

$$HB + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C1^- + H^+ \;;\; K1 \left(= \frac{K0}{K3}\right) \qquad (8)$$

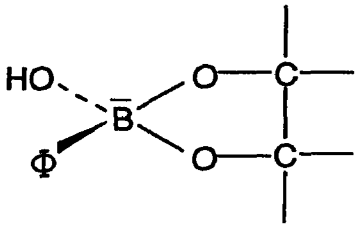
$$B^- + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C1^- + H_2O \;;\; K2 \left(= \frac{K0}{K3\,K_{HB}}\right) \qquad (9)$$

$$C1^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} CX^- + H_2O \;;\; K3 \qquad (10)$$

where $C1^-$ =



and CX^- =



In Scheme 2, K0 refers to the overall stability constant for the equilibrium obtained by adding eqns (8) and (10). This stability constant was measured and is reported in Table 5-1. For K3, guess values were used in the analysis. Once K0 and K3 are defined, the values for K1 and K2 are easily calculated.

The presence of $C1^-$ is being proposed although we have no independent evidence for its existence. The ^{11}B NMR spectrum of the $\Phi B(OH)_2/HOCH_2CH_2OH$ system showed two resonances. One peak was assigned to both the trigonal $\Phi B(OH)_2$ and the tetrahedral $\Phi B(OH)_3^-$, while the other was assigned to the chelate complex CX^-. In the proposal of the formation of $C1^-$, it may be that the chemical shifts of boron in $C1^-$ and CX^- are inseparable or that perhaps the exchange between the two complexes in eqn (10) is too fast for the NMR timescale.

The kinetic analysis was done as follows. Two types of calculations were performed. In the first case, since there are two independent concentration variables $C1^-$ and CX^-, the system is characterized by two relaxation times. (A similar analysis was given in Chapter 2 for the $CH_3B(OH)_2$/glycerol system.) Various values for K3, k_1, k_2 and k_3 were used in order to calculate $1/\tau$. In the second calculation,since one relaxation time is observed experimentally, a variation of the mechanism was done by treating $C1^-$ as a reactive intermediate. The steady state approximation was applied to $C1^-$ and the kinetic derivation was written in terms of one relaxation time. In both types of calculations, the HB dependence on the relaxation time was obtained for some of the data but the other experimental trends were not accounted for.

Mechanism 3

The calculations of the previous mechanism in which a 1:1 unidentate complex $C1^-$ was proposed did account for the HB dependence in some of the data. The pH dependence on the relaxation time was not seen. In Table 5-2, the first set of experiments indicates that the reaction rate is very sensitive to solution pH; a change in pH of approximately two pH units causes the rate to change by a factor which is greater than thirteen. Since the reactions are studied in basic solution, perhaps the hydroxide ion is intimately involved in the reaction mechanism. These observations led to the mechanism in Scheme 3. (The structures of $C1^-$ and CX^- are the same as shown in Scheme 2.) In the proposal of this mechanism it was speculated that perhaps there is a competition between reactions (12) and (13). That is, $C1^-$ can undergo either attack by hydroxide to produce the borate and the ligand anions, or it can undergo ring closure to produce the chelate complex.

Scheme 3

$$\mathrm{HB} + \mathrm{H_2L} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{C1^-} + \mathrm{H^+} \quad ; K1 \qquad \left(= \frac{K0}{K3}\right) \qquad (11)$$

$$\mathrm{C1^-} + \mathrm{OH^-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{B^-} + \mathrm{HL^-} \quad ; K2 \qquad \left(\frac{K_{HB}\, K_{H_2L}}{K1\, K_w}\right) \qquad (12)$$

$$\mathrm{C1^-} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{CX^-} + \mathrm{H_2O} \quad ; K3 \qquad (13)$$

In Scheme 3, K0 and K3 are defined in the same manner as in Mechanism 2. The mechanism given in Scheme 3 is similar to the one given in Scheme 2 with the exception of step (12). The reaction described by eqn (12) is a substitution reaction in which the hydroxide group replaces the ligand in $\mathrm{C1^-}$ to form the borate and the ligand anions.

The kinetic analysis is similar to the one given in Mechanism 2. Guess values for K3 were used in the calculations. Having defined K0 and K3, the other equilibrium constants are known. If the steady state approximation is applied to $\mathrm{C1^-}$, then the kinetic derivation is written in terms of one relaxation time. If both $\mathrm{C1^-}$ and $\mathrm{CX^-}$ are treated as independent variables, then the derivation is written in terms of two relaxation times. In both types of calculations, the HB dependence was obtained for some of the data but the other experimental trends could not be calculated.

Mechanism 4

The following mechanism is based on the results of a temperature-jump relaxation study of the $\mathrm{Zn^{2+}}$ / chlorophenol red system which was carried out by Bidwell and Stuehr in 1987 [110]. The authors were interested in measuring the rate of interconversion between the tetrahedral and the octahedral aquo complexes of the Zn^{2+} ion. The results of the study did not account for the structural change of the aqueous Zn^{2+} ion. In order to explain their kinetic data, these authors proposed a mechanism which included the coupling of the protolytic indicator reaction with that of the aqueous Zn^{2+} ion. A proton transfer process occurred between Zn^{2+} and chlorophenol red. The identical mechanism was proposed for the nucleoside inosine / chlorophenol red system [111]. Despite the differences among Zn^{2+}, inosine and $\Phi B(OH)_2$, these species are similar in their pK_a values. ($Zn^{2+}{}_{(aq)}$, pK_a=9.0; protonated inosine, pK_a=8.96; $\Phi B(OH)_2$, pK_a=8.72 .) These observations led to the following mechanism.

Scheme 4

$$HB + H_2L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CX^- + H^+ \quad ; \quad K1 \tag{14}$$

$$B^- + H_2L \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CX^- + 2H_2O \quad ; \quad K2 \left(= \frac{K1}{K_{HB}}\right) \tag{15}$$

$$HIn \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} H^+ + In^- \quad ; \quad K3 \left(= K_{HIn}\right) \tag{16}$$

$$HB + In^- \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} B^- + HIn \quad ; \quad K4 \left(= \frac{K_{HB}}{K_{HIn}}\right) \tag{17}$$

The reactions given by eqns (14) and (15) are the same as those presented in Mechanism 1. The reaction given by eqn (16) is the ionization step of the indicator. Equation (17) describes the proton transfer process between the indicator and the boron acid.

The kinetic analysis was done in the following manner. The two independent concentration variables, CX^- and In^-, were used to derive the relaxation expression in terms of two relaxation times. In the calculations, all of the equilibrium constants in Scheme 4 are known. Similarly, for the indicator ionization step given in eqn (16), the value for k_{-3} is known to be 10^{10} $M^{-1}s^{-1}$ in the case of phenolphthalein [112]. Since K_{HIn} is 10^{-10} and $k_3 = K_{HIn} \times k_{-3}$, the rate constant k_3 is known. The calculations were therefore carried out with the known value of k_3 while the values for k_1, k_2 and k_4 were varied. The results of the calculations are summarized below.

For the case in which $k_1 = 1$ $M^{-1}s^{-1}$, $k_2 = 100$ $M^{-1}s^{-1}$, $k_3 = 1$ s^{-1} and $k_4 = 10^4$ $M^{-1}s^{-1}$, the following results were obtained.

(1)The pH dependence (increasing τ with increasing pH) was accounted for (± 20 %), with the exception of the experiments which were done at pH > 9.5.

(2) The linear dependence of HB on the measured τ was satisfied (± 20 %).

(3) The independence of H_2L on the measured τ was not obtained.

Since it was impossible to fit all of the data satisfactorily, the mechanism was eliminated.

Mechanism 5

The final mechanism to be considered is given in Scheme 5 and will be discussed in a little more detail than the others. The consideration of our results and those of other authors which eventually led to the proposal of the mechanism in Scheme 5 will be outlined. The analysis of the mechanism is also described.

The simple mechanism in Scheme 1 was successful at explaining the methylboronic acid / polyol kinetic data and not the phenylboronic acid / ethylene glycol data. In Scheme 1, the HB/B^- equilibrium was treated as a fast diffusion controlled process. From a temperature - jump study on the formation of polyborates in aqueous boric acid solutions which was carried out in 1965 by Eyring et al [113], it was assumed that the boric acid trigonal to tetrahedral interconversion step was rapid ($k = 10^{10} - 10^{11}\ M^{-1}s^{-1}$). However, this assumption has been questioned by subsequent kinetic studies using different experimental techniques. Ultrasonic absorption studies of aqueous sodium borate solutions report a rate constant of $10^8\ M^{-1}s^{-1}$ for the interconversion process [114]. Similarly, temperature-jump and sound absorption studies on aqueous boric acid solutions which were carried out in the 1970's and early 1980's concluded that the interconversion rate was slower than the diffusion controlled limit [115-117]. Furthermore, in 1984 Candau et al performed temperature - jump studies with boric acid and reported a rate constant of $1.1\times10^7\ M^{-1}s^{-1}$ for the HB / B^- interconversion process [118].

The kinetic experiments of the complexation reactions between phenylboronic acid and ethylene glycol were done in basic solution.Since the results indicated that the reaction rate was very sensitive to solution pH (Table 5-2), it was postulated that perhaps the hydroxide ion was involved in one of the steps in the reaction sequence. Also, during our continuous search for a reasonable mechanism, the calculations showed that in addition to the reactions in Mechanism 1, whenever a step involving either HB or B^- was included, the HB dependence on the measured relaxation time was obtained. Therefore, the importance of OH^- and HB (or B^-) together with the fact that Candau reported the rate constant for the boric acid HB/B^- interconversion to be three orders of magnitude less than the diffusion controlled limit, led to the proposal of the mechanism in Scheme 5. This mechanism is the same as Mechanism 1 except that the HB/B^- interconversion rate is no longer diffusion controlled.

Scheme 5

$$HB + OH^- \overset{k_f}{\underset{k_r}{\rightleftarrows}} B^- \quad ; \ KK \ \left(= \frac{K_{HB}}{K_w}\right) \tag{18}$$

$$HB + H_2L \overset{k_1}{\underset{k_{-1}}{\rightleftarrows}} CX^- + H^+ \quad ; \ K1 \tag{19}$$

$$B^- + H_2L \overset{k_2}{\underset{k_{-2}}{\rightleftarrows}} CX^- + 2H_2O \quad ; \ K2 \ \left(= \frac{K1}{K_{HB}}\right) \tag{20}$$

The reaction given in eqn (18) is an addition reaction; the hydroxide ion adds to the empty p orbital on boron in the trigonal $\Phi B(OH)_2$ species to produce the tetrahedral $\Phi B(OH)_3^-$ anion. Since the ionization constant for phenylboronic acid is known, the equilibrium constant for reaction (18) is easily calculated to be 1.9x10^5. The complexation reactions given by eqns (19) and (20) are the same as those presented in Mechanism 1 which adequately described the methylboronic acid / polyol reactions in Chapter 3. The stability constants K1 and K2 were reported in Table 5 -1.

The reaction sequence in Scheme 5 contains two independent concentration variables and is therefore characterized by two relaxation times. Recall that only one relaxation time was observed experimentally. In order to explain the kinetic analysis, the relaxation expression for Mechanism 5 is presented below. (The independent variables were chosen to be HB and CX$^-$ and the derivation is very similar to the one outlined in Chapter 2 for the methylboronic acid / glycerol system .)

$$- \frac{d\,\delta HB}{dt} = k_f \Big(\big(Q[\overline{HB}] + [\overline{OH^-}] + \frac{1}{KK} \big) \delta HB + \big(\frac{1}{KK} \big) \delta CX^- \Big)$$
$$+ k_1 \Big(\big([\overline{H_2L}] - \frac{P[\overline{CX^-}]}{K1} \big) \delta HB + \big(-[\overline{HB}] - \frac{[\overline{H^+}]}{K1} \big) \delta CX^- \Big)$$

$$- \frac{d\,\delta CX^-}{dt} = k_1 \Big(\big(-[\overline{H_2L}] + P \frac{[\overline{CX^-}]}{K1} \big) \delta HB + \big([\overline{HB}] + \frac{[\overline{H^+}]}{K1} \big) \delta CX^- \Big)$$
$$+ k_2 \Big(\big([\overline{H_2L}] \big) \delta HB + \big([\overline{B^-}] + [\overline{H_2L}] + \frac{1}{K2} \big) \delta CX^- \Big)$$

where $P = - \dfrac{1}{1 + \dfrac{[\overline{OH^-}]}{[\overline{H^+}]} + \alpha}$ and $Q = -P \left(\dfrac{[\overline{OH^-}]}{[\overline{H^+}]} \right)$

There are two cases to consider. First, when the concentration of the indicator $[HIn] = 0$, $\alpha = 0$. Secondly, when $[HIn] \neq 0$,

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

In order to analyze the relaxation expression , it is necessary to solve the 2x2 determinant given below.

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

where $a_{11} = k_f \{ Q\overline{[HB]} + \overline{[OH^-]} + \frac{1}{KK} \} + k_1 \{ \overline{[H_2L]} - \frac{P\overline{[CX^-]}}{K1} \}$

$$a_{12} = k_f \{ \frac{1}{KK} \} + k_1 \{ - \overline{[HB]} - \frac{\overline{[H^+]}}{K1} \}$$

$$a_{21} = k_1 \{ - \overline{[H_2L]} + \frac{P\overline{[CX^-]}}{K1} \} + k_2 \{ \overline{[H_2L]} \}$$

$$a_{22} = k_1 \{ \overline{[HB]} + \frac{\overline{[H^+]}}{K1} \} + k_2 \{ \overline{[B^-]} + \overline{[H_2L]} + \frac{1}{K2} \}$$

The solution to the resulting quadratic is given below.

$$\frac{1}{\tau}_{(+,-)} = \frac{1}{2} \{ (a_{11} + a_{22}) \pm ((a_{11} + a_{22})^2 - 4 (a_{11}a_{22} - a_{12}a_{21}))^{0.5} \}$$

Since the coefficients (functions of equilibrium concentrations and equilibrium constants) in the above equations are known, values for the rate constants are fed into the calculation to solve for the two roots of $1/\tau$.The usually reported rate constants are the ones obtained from the best fit between the experimental $1/\tau$ and the calculated $1/\tau$ (+ root).

In the present analysis of the phenylboronic acid / ethylene glycol data, various values for the rate constants k_f, k_1 and k_2 were read into the computer program to calculate $1/\tau$. In the cases where $k_f = 10^5 - 10^7\ M^{-1}s^{-1}$, $k_1 = 0.01-1\ M^{-1}s^{-1}$ and $k_2 = 100 - 200\ M^{-1}s^{-1}$, it was found that some of the data were accounted for by this mechanism. In particular, the HB and H_2L dependences on τ were calculated for some of the data, but the pH dependence was only obtained within a smaller pH range than that shown in Table 5 -2. The next step was to calculate each concentration coefficient present in a_{11}, a_{12}, a_{21} and a_{22} , and to check the variation between the experimental and the calculated values of $1/\tau$. In the course of this analysis, it was discovered that the indicator concentration term had a dramatic effect on the calculated rates. For instance, from Table 5-2, as the pH changes from 9.89 to 7.97, the following trends were seen.

	$[HIn] \neq 0$		$[HIn] = 0$	
pH	- P	Q	-P	Q
9.89	1.56×10^{-6}	0.938	1.66×10^{-6}	1.000
7.97	2.10×10^{-3}	0.184	1.14×10^{-2}	0.989

When the indicator concentration term was included, the variations in P and Q were the source of our inability to obtain the pH dependence on the calculated

$1/\tau$. We therefore decided to drop the indicator term from the equations. In our attempts to fit the data, k_f had to be lowered to $2.5\text{x}10^4\ M^{-1}s^{-1}$ while $k_1 = 0.02\ M^{-1}s^{-1}$ and $k_2 = 135\ M^{-1}s^{-1}$. It was then possible to fit all of the phenylboronic acid / ethylene glycol data in the concentration range of $[H_2L]$: 0.1 - 0.3 M and [HB] : 0.02 - 0.08 M, with an accuracy of ± 20 %. A representative sample of the results of the analysis using the above rate constants is given in Table 5-4.

Table 5-4 : Data Analysis for Phenylboronic Acid / Ethylene Glycol System Using Mechanism 5.

pH	$[H_2L]_0$	$[HB]_0$	$[HIn]_0$	$1/\tau$ (expt) s^{-1}	$1/\tau$ (calc)* s^{-1}
9.89	0.286	0.078	$2.75\text{x}10^{-5}$	101.7	90.1
8.80	0.293	0.077	$4.58\text{x}10^{-5}$	555.6	645.0
8.23	0.286	0.077	$4.58\text{x}10^{-4}$	1081.1	1384.5
8.71	0.286	0.081	$4.20\text{x}10^{-4}$	817.7	786.7
8.73	0.286	0.040	$4.57\text{x}10^{-4}$	395.4	373.5
8.95	0.214	0.063	$7.44\text{x}10^{-5}$	400.0	444.2
9.00	0.107	0.063	$7.44\text{x}10^{-5}$	388.3	466.2

* $k_f = 2.5\text{x}10^4\ M^{-1}s^{-1}$; $k_1 = 0.02\ M^{-1}s^{-1}$; $k_2 = 1.4\text{x}10^2\ M^{-1}s^{-1}$

It is important to note that many authors who have used indicators to monitor temperature-jump experiments in basic solution have omitted the indicator concentration term from their equations. In the 1960's, Eyring et al used phenolphthalein, phenol red and cresol red and reported that the indicator concentration term was negligible in order to explain their kinetic data [113,119,120]. In the 1980's, Candau et al carried out temperature-jump studies on boric acid solutions using thymol blue in basic solution [118,121]. Since they found that the reaction rate was independent of the concentration of thymol blue, these authors omitted the indicator concentration term from their equations. Although we have also determined that the reaction rate is independent of the indicator concentration, we do not feel comfortable about excluding [HIn] from the equations. If the indicator term is not important then it should not matter whether it is included or omitted from the calculations. In fact, this was found to be true in the analysis of Mechanism 1 which satisfactorily explained the methylboronic acid / polyol reactions in Chapter 3.

An important result was obtained when the methylboronic acid/ethylene glycol data were subjected to the same calculations as in Mechanism 5. All of the data were accounted for whether or not [HIn] was included. In this case, the same values for k_1 and k_2 which were reported for Mechanism 1 in Chapter 3, were obtained but a low value for k_f (10^3 $M^{-1}s^{-1}$) resulted from the analysis. The results are presented in Table 5-5. The rates which were calculated using Mechanism 1 (1 τ) are included for comparison. (The concentrations of $CH_3B(OH)_2$, $HOCH_2CH_2OH$ and phenolphthalein are similar to those used for the $\Phi B(OH)_2$ system in Table 5-4.)

Table 5-5 : Data Analysis for Methylboronic Acid / Ethylene Glycol System Using Mechanism 1 and Mechanism 5.

		Mechanism 1	Mechanism 5*	
		$[HIn] \not\equiv 0$	$[HIn] \not\equiv 0$	$[HIn] = 0$
pH	$1/\tau$ (expt) s^{-1}	$1/\tau$ (calc) s^{-1}	$1/\tau$ (calc) s^{-1}	$1/\tau$ (calc) s^{-1}
9.80	496.8	416.3	413.3	413.3
8.91	399.4	414.6	414.4	414.4
8.17	395.4	415.7	414.8	414.8
8.54	437.1	416.2	394.9	394.9
8.51	328.7	413.3	395.0	395.0
9.31	599.2	694.0	709.5	709.5
9.31	245.4	304.6	303.9	303.9

* $k_f = 1.0 \times 10^3\ M^{-1}s^{-1}$; $k_1 = 0.01\ M^{-1}s^{-1}$; $k_2 = 1.0 \times 10^3\ M^{-1}s^{-1}$.

The results in Table 5-5 for the methylboronic acid system indicate that the calculated rates are independent of the indicator concentration term. This is not true for the analogous phenylboronic acid systems. One of the reasons for the disagreement between the two boron acid systems is due to the relative magnitudes of k_2. The bimolecular rate constant k_2 is larger for methylboronic acid ($1.0 \times 10^3\ M^{-1}s^{-1}$) than for phenylboronic acid ($1.4 \times 10^2\ M^{-1}s^{-1}$). In both cases, by calculating each of the coefficients a_{11}, a_{12}, a_{21} and a_{22}, it was discovered that the independence of the calculated $1/\tau$ upon [HIn] for the $CH_3B(OH)_2$ data was due to the large value of k_2 relative to that in the $\Phi B(OH)_2$ system. Any attempt to lower k_2 for the $CH_3B(OH)_2$ / $HOCH_2CH_2OH$ reactions resulted in a loss of the experimental $1/\tau$ trends and a dependence upon [HIn]. Alternatively, the attempts to increase k_2 for the $\Phi B(OH)_2$ / $HOCH_2CH_2OH$ reactions resulted in a loss of the experimental $1/\tau$ trends and an independence of [HIn]. Recall that the experimental relaxation trends are very different for the two boron acid systems.

5.6 Discussion

From our analysis, the only mechanism which comes close to explaining the phenylboronic acid / ethylene glycol kinetic data is Mechanism 5 in which the boron acid trigonal to tetrahedral interconversion process is treated as being non-diffusion controlled. More than twenty alternative mechanisms were attempted without any success. However, Mechanism 5 accounted for the phenylboronic acid / ethylene glycol kinetic data only when the indicator concentration term is omitted from the calculations. The system is being presented as an unsolved problem because we believe that k_f is very low (10^4 $M^{-1}s^{-1}$) and that the concentration of the indicator should not affect the calculations.

The results in Table 5-4 indicate that trigonal phenylboronic acid is unreactive toward the polyol. This is consistent with previous kinetic studies in terms of the proton transfer transition state which was described in Chapter 3.

The tetrahedral phenylboronate anion reacts much faster than the trigonal species and possible reasons for this were also presented in Chapter 3. The most surprising and unexplainable results are the low values of the rate constant (k_f) for the addition of hydroxide to the trigonal boron acids.

The methylboronic acid / ethylene glycol kinetic data were adequately accounted for by Mechanism 1 in Chapter 3. The calculations for the system using Mechanism 5 were only carried out for comparison reasons. As mentioned before, the calculated $1/\tau$'s for this system using Mechanism 5 were found to be independent of the indicator concentration term. In addition, the analysis gave the same values for the rate constants k_1 and k_2 as reported in Chapter 3. However, the rate constant obtained for the addition of hydroxide to trigonal methylboronic acid is $1.0\text{x}\ 10^3\ M^{-1}s^{-1}$.

The values obtained for k_f are unexpectedly low (10^3 and $10^4\ M^{-1}s^{-1}$). The magnitudes of these rate constants seem unlikely for the simple addition of hydroxide to the empty p orbital on boron in the trigonal boron acids. In the addition reaction, boron undergoes a rehybridization from sp^2 to sp^3 and some rearrangement must occur. To our knowledge, there are no literature studies on the rate of addition of hydroxide to the substituted boron acids. For boric acid, several attempts have been made and the more recent studies have commented on the complexity of the kinetics.

It has been suggested that the sound absorption in sea water is due to the chemical relaxations involving $MgSO_4$, $B(OH)_3$ and $MgCO_3$. From sound absorption studies in both sea water and aqueous boric acid solutions, Simmons et al [116,117] have proposed a two-step model for the boric acid / borate equilibrium as shown below.

$$B(OH)_3 + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} [B(OH)_3, OH^-] \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} B(OH)_4^-$$

The first step in the formation of the ion-pair was assumed to be fast while the second slow step was believed to be responsible for the low frequency sound absorption. At 25 °C and $\mu = 0.7$ M, the following results were reported: $k_{23} = 2.5 \times 10^4\ s^{-1}$, $k_{32} = 2.4 \times 10^2\ s^{-1}$ and $K_{12} = 2.6 \times 10^2\ M^{-1}$. Additional support for this model was obtained in 1984 in a study concerning the synthesis of artificial sea water. From temperature-jump experiments with aqueous boric acid solutions, Candau et al [121] observed a pH dependence on the measured relaxation times which could only be accounted for by the two-step model. At 20 °C and $\mu = 0.7$ M, they reported the following: $k_{23} = 1.1 \times 10^5\ s^{-1}$, $k_{32} = 80\ s^{-1}$ and $K_{12} = 60\ M^{-1}$. In the same year, further temperature-jump experiments were carried out by Candau et al [118] on aqueous boric acid / sodium bicarbonate solutions. The mechanism they proposed was an acid - base exchange between $B(OH)_3$ / $B(OH)_4^-$ and HCO_3^- / CO_3^{2-} equilibria. In this analysis the authors assumed that the boric acid / borate interconversion process occurred in one step, that is,

$$B(OH)_3 + OH^- \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} B(OH)_4^-$$

The rate constants reported were $k_{12} = 1.1 \times 10^7\ M^{-1}s^{-1}$ and $k_{21} = 91\ s^{-1}$ at 20 °C and $\mu = 0.1$ M. The same mechanism of an acid- base exchange in sea water between $B(OH)_3$ / $B(OH)_4^-$ and HCO_3^- / CO_3^{2-} equilibria was suggested by Yeager [115] several years before Candau's work, but no mechanism was reported for the boric acid - borate reaction. Although these studies did not arrive at the same conclusion regarding the boric acid / borate equilibrium, all of the authors have remarked on the unusual kinetic behavior of boric acid in basic solution.

It is clear that the boric acid / borate interconversion mechanism is not well understood. In our experiments, blank solutions of boron acids and indicator showed no relaxation effect in the time range 10 µsec to 1 sec. In Candau's temperature-jump studies, relaxation times in the microsecond time range were reported. Since we never observed any relaxation time in the µsec region, it is possible that Candau's instrument has a better resolution than ours.

The results of our analysis of the phenylboronic acid / ethylene glycol and methylboronic acid / ethylene glycol data using Mechanism 5 suggest that the addition of hydroxide to boron is not diffusion controlled. We have no explanation for the low values of k_f. However, it is interesting to note that even in the gas phase, in the absence of complicating solvent effects, boron undergoes addition reactions with rates which are less than the collision controlled limit. The chelation reactions of boron trifluoride and silicon tetrafluoride with bidentate ligands such as ethylene glycol, 1,3-propanediol and catechol have been studied in the gas phase using the flowing afterglow technique [122]. The results indicate that while the reactions of SiF_4 occur with rates which are close to the collision controlled limit, those of BF_3 occur with much lower rates (~ 60 % of the collision rate for ethylene glycol and ~ 70 %

of the collision rate for catechol). The author has no explanation for the lower rates observed in the boron trifluoride reactions.

Although we are doubtful about the magnitudes of the rate constants obtained above for the addition of OH^- to the trigonal $\Phi B(OH)_2$ and $CH_3B(OH)_2$ species, a comparison of the two systems yields an important result. Since phenylboronic acid ($pK_a = 8.72$) is a much stronger Lewis acid than methylboronic acid ($pK_a = 10.40$), the relative magnitudes of k_f for the two boron acids are in agreement with the correlation of increasing rate constant with increasing boron acidity for the reactions of trigonal boron acids.

The methylboronic acid / polyol reactions were adequately accounted for by Mechanism 1 in Chapter 3 where the boron acid / boronate equilibrium was assumed to be diffusion controlled. As mentioned before, the application of Mechanism 5 to the kinetic data was done for comparison reasons. On the other hand, the phenylboronic acid / ethylene glycol data can only be accounted for by Mechanism 5 when the boron acid / boronate equilibrium is treated as being non-diffusion controlled and the indicator concentration term is omitted from the calculations. Although the results indicate that the tetrahedral phenylboronate anion reacts much faster than the trigonal phenylboronic acid as expected, the value obtained for k_f is very low. The system is being presented as an unsolved problem because of the magnitude of k_f and the dependence of the calculations upon the indicator concentration term. However, it is possible that the bimolecular rate constant 10^4 $M^{-1}s^{-1}$ may represent a step in the mechanism which, at this moment, is unknown to us.

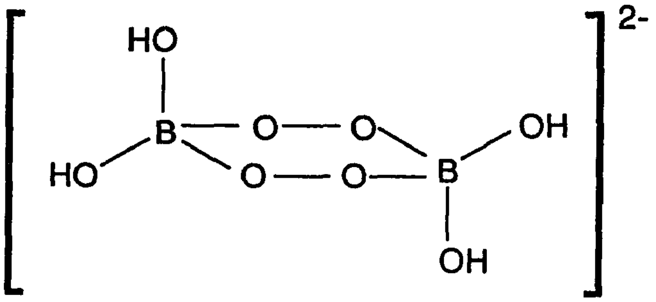
CHAPTER 6

THE BORIC ACID / HYDROGEN PEROXIDE SYSTEM

6.1 Introduction

All of the studies described so far in this thesis were mainly concerned with the reactivity of boron acids / borates towards bidentate chelating ligands, such as the polyols. The results indicate that the substitution reactions of the tetrahedral borates are much faster than the addition reactions of the trigonal boron acids. The present Chapter deals with the coordination of a simple unidentate ligand on boron.

Boric acid and hydrogen peroxide interact to form stable species which are known to exist both in the solid state, and in solution. In the former case, a determination [67] of the crystal structure of sodium peroxoborate indicates that the anion is a cyclic dimer, as shown below. The anion is seen to contain tetrahedrally coordinated boron atoms and double peroxo bridges. Although the solid state of the peroxoborate species has been characterized, the nature of the aqueous species is not well understood.



In aqueous solution, the interaction between boric acid and hydrogen peroxide has been studied by different experimental techniques as described in Chapter 1 [70-75]. Recall that these studies reported inconsistent results where the proposed number of peroxoboron complexes ranges from one to six.

One of the reasons for conducting the following experiments was to investigate the nature of the interaction between boric acid and hydrogen peroxide in aqueous solution. In this Laboratory, pH methods have been successful in determining stability constants for the complexation reactions between boron acids and bidentate chelating ligands [59-62] . The application of these pH techniques would allow the characterization of the boric acid / hydrogen peroxide system, and the quantitative measurement of the equilibrium constant (s). In view of the conflicting results of previous reports on the formation of peroxoborates , another experimental technique, ^{11}B NMR spectroscopy, was used to compare with the pH titration data.

In addition to the boric acid / hydrogen peroxide system, two other systems were investigated; the phenylboronic acid / hydrogen peroxide system and the boric acid / *tert* - butylhydroperoxide system. From previous thermodynamic studies of boron complexation reactions with bidentate chelating ligands (such as α-hydroxycarboxylic acids and dicarboxylic acids), the stability constants are known to be functions of the acidity of both the boron acid and the ligand [59]. In general, the stability constants increase with increasing acidity of the reactants. Phenylboronic acid is more acidic than boric acid, and *tert* - butylhydroperoxide is less acidic than hydrogen peroxide. Therefore, the reason for including the phenylboronic acid / hydrogen peroxide system and the boric acid / *tert* - butylhydroperoxide system was to determine whether the acidity correlation could be extended to these systems containing peroxo ligands.

After having completed the thermodynamic study on the formation of peroxoborates, our next goal was to investigate the mechanism from kinetic measurements, using the temperature - jump method. In the previously mentioned kinetic studies, all of the ligands used were bidentate and formed complexes containing chelate rings. For the reactions of boric acid coordinating to hydrogen peroxide, the resulting complexes are believed to contain a unidentate hydroperoxo ligand (-OOH). Therefore, a kinetic study of the boron acid / hydrogen peroxide systems would allow one to study the addition and substitution reactions of a simple unidentate ligand on boron. Unfortunately, this kinetic study could not be realized since our preliminary experiments indicated the decomposition of hydrogen peroxide under the experimental conditions. A constant stream of small bubbles was observed in the temperature-jump cell during the experiment. The electrodes of the cell are made from stainless steel material, and the decomposition of hydrogen peroxide is known to be catalyzed by metals [123-128].

6.2 Experimental

All pH experiments were done at a constant ionic strength of 0.1 M (KNO_3) , a constant temperature of 25 °C , and under a nitrogen atmosphere. All solutions were prepared with freshly boiled water.

Boric acid and phenylboronic acid (Aldrich) were used without further purification. The purity of these reagents was checked by titrating with standard 0.1 M NaOH.

Hydrogen peroxide (Fisher) was used as received. The solutions were freshly prepared before use, and were standardized [129] by titrating with standard potassium permanganate solution. The $KMnO_4$ solution was standardized [130] against the primary standard $Na_2C_2O_4$. Instead of adding EDTA to inhibit [74] the decomposition of H_2O_2 , the final reaction mixture was analyzed by titrating with the standard KMnO4 solution. The peroxide, whether it is bound in a complex or free in solution, is known to be oxidized [71] by $KMnO_4$. In all cases, the assay for H_2O_2 indicated that the decrease in concentration was less than 1 %.

The *tert* - butylhydroperoxide (Aldrich) was used as received.The solutions were standardized by titrating with standard sodium thiosulfate solution in the presence of excess iodide [131]. The standard $Na_2S_2O_3$ solutions were prepared [132] by titrating against the primary standard $K_2Cr_2O_7$.

The ^{11}B NMR experiment was described in Chapter 2.

6.3 Determination of Stability Constants

6.3.1 The Boric Acid / Hydrogen Peroxide System

Boric acid has a pKa value of 8.98 [33] , while hydrogen peroxide has a value of 11.6 [133]. The interaction between $B(OH)_3$ and H_2O_2 was studied by both NaOH titrations and pH mixing experiments which were described in the experimental chapter. More than twenty titrations of each type were done. The concentration range studied was 0.01 M - 0.06 M for $B(OH)_3$, and 0.05 M - 1.0 M for H_2O_2.

In the NaOH titrations, solutions of known concentrations of $B(OH)_3$ and H_2O_2 were titrated with standard 0.1 M NaOH. Since both $B(OH)_3$ and H_2O_2 are weak acids, the initial pH before any NaOH was added was about 5.5. After the addition of a small amount of 0.1 M NaOH, the pH increased by about one pH unit. Therefore, most of the points in the experimental titration curve were between pH 7 and pH 9.

The pH mixing experiments were carried out in acidic media. Solutions of known concentration of $B(OH)_3$ and H_2O_2 were adjusted, separately, to the same initial pH by the dropwise addition of dilute HCl or NaOH. Aliquots of one solution were then titrated with the other and the change in pH was measured. Since the hydrogen ion is a product of the reaction, the pH decreased. This method is similar to the one used by Edwards [71]. A sample of a pH mixing experiment for the $B(OH)_3$ / H_2O_2 system is shown graphically in Figure 6-1.

6.3.2 The Phenylboronic Acid / Hydrogen Peroxide System

The pKa value of phenylboronic acid , $\Phi B(OH)_2$, is 8.72 [59]. Phenylboronic acid is more acidic than boric acid. A sample of the pH mixing experiment for the $\Phi B(OH)_2$ / H_2O_2 system is also given in Figure 6-1. For the same concentrations of boron acid and hydrogen peroxide, the decrease in pH upon mixing the reactants is larger for the $\Phi B(OH)_2$ / H_2O_2 system than for the $B(OH)_3$ / H_2O_2 system. This means that one (or more) of the equilibrium constants for the $\Phi B(OH)_2$ / H_2O_2 system is greater than that for the $B(OH)_3$ / H_2O_2 system. In the former case, after the initial drop in pH, there is an increase in pH due to a subsequent reaction. The initial drop in pH results from the formation of a peroxoboron complex, that is,

$$\Phi B(OH)_2 + H_2O_2 \rightleftarrows \Phi B(OH)_2(OOH)^- + H^+$$

The subsequent reaction of the peroxoboron complex to give phenol and boric acid accounts for the increase in pH (Figure 6-1). The overall reaction is given below.

$$\Phi B(OH)_2 + H_2O_2 \rightleftarrows \Phi OH + B(OH)_3$$

The kinetics of the overall reaction has been studied by Kuivila [134], who proposed several mechanisms, depending upon the experimental conditions. For the $\Phi B(OH)_2$ / H_2O_2 system, due to the formation of phenol and boric acid in the pH mixing experiment, no determination of the equilibrium constants was possible.

6.3.3 The Boric Acid / *tert*-butylhydroperoxide System

The pKa value of *tert* - butylhydroperoxide is 12.8 [135]. Several pH mixing experiments of various concentrations of $B(OH)_3$ and $(CH_3)_3COOH$ were carried out. Very small pH changes were observed. In all cases, the decrease in pH was close to , or within, the limits of the accuracy of the pH meter (± 0.02). Therefore, for this system as well, no quantitative analysis for the equilibrium constants was possible.

6.3.4 The ^{11}B NMR Experiment

^{11}B NMR experiments were carried out only for the boric acid / hydrogen peroxide system. The experimental details were described in Chapter 2. Several spectra were obtained and, in all cases, overlapping peaks were observed. Therefore, no determination of the equilibrium constants was possible by this technique.

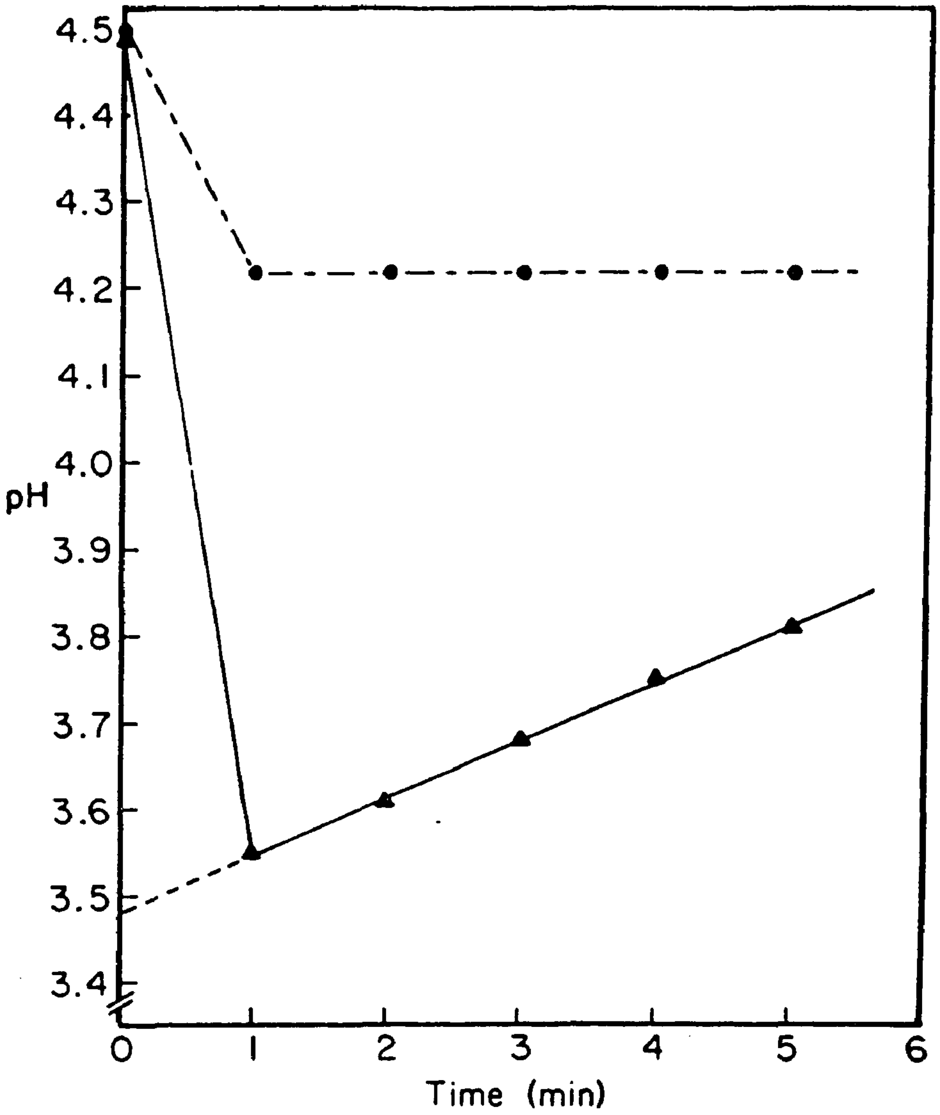


Figure 6-1: pH Mixing Experiments: Boric Acid (0.046 M) / Hydrogen Peroxide (1.065 M) System (dashed line); Phenylboronic Acid (0.034 M) / Hydrogen Peroxide (1.105 M) System (solid line).

6.4 Results

6.4.1 Stability Constants

For the boric acid / hydrogen peroxide system, the analysis of the NaOH titration data led to the conclusion that two peroxoboron complexes are present between pH 7 and pH 9. The equilibria are given in eqns (1) and (2) below. The reaction given in eqn (1) may be described as an addition reaction.

$$B(OH)_3 \quad + \quad H_2O_2 \quad \rightleftarrows \quad (HO)_3BOOH^- \quad + \quad H^+ \quad ; \quad K1=2.0x10^{-8} \quad (1)$$

$$(HO)_3BOOH^- \; + \; H_2O_2 \; \rightleftarrows \; (HO)_2B(OOH)_2^- + H_2O \; ; \quad K2=2.0 \qquad (2)$$

The hydroperoxo ligand adds to the empty p orbital on boron to produce the tetrahedral complex. A ligand proton is also displaced in the reaction.The second reaction is a substitution; a second hydroperoxo ligand replaces a hydroxyl group in the initially formed complex with loss of a ligand proton.

The calculation of the equilibrium constant for the formation of a 1:1 complex by NaOH titration was given in Chapter 2. Equation (2) above contains a complex where the boron acid to ligand ratio is 1:2. Since there are two independent concentration variables, $CX_{1:1}^-$ (BL^-) and $CX_{1:2}^-$ (BL_2^-), the data were analyzed as follows. The concentration of the complex in the conservation relationships of the NaOH derivation was rewritten in terms of $CX_{1:2}^-$ alone. Use of the NaOH titrations where the concentration of H_2O_2 was in large excess allowed a reliable estimate of $\beta 2$ (= K1xK2). With the known value of $\beta 2$, the conservation relationships in the original NaOH derivation were rewritten to include both $CX_{1:1}^-$ and $CX_{1:2}^-$. This modified derivation, along with the NaOH titrations containing lower concentrations of H_2O_2 , was used to calculate K1. From the known values of $\beta 2$ and K1, a value for K2 was determined.

As mentioned before, the pH mixing experiments were done in acidic solution. The analysis of the data using the equilibria described by eqns (1) and (2) did not account for the pH drop seen experimentally. By proposing a third equilibrium given in eqn (3), it was possible to fit the data obtained from pH mixing titrations. The reaction in eqn (3) may be described as a substitution

$$B(OH)_3 + H_2O_2 \rightleftarrows (HO)_2BOOH + H_2O \;; \quad K3 = 0.01 \qquad (3)$$

reaction to produce the neutral peroxoboric acid. In the determination of K3, the conservation relationships of the pH mixing derivation were rewritten to include all of the three complexes. Using the values of K1 and K2 (known from the NaOH titration data analysis), a value of K3 was determined. All of the equilibrium constants are reported with an accuracy of ± 10 %.

6.4.2 ^{11}B NMR Spectra

The equilibrium constants, obtained from pH titration methods, were used to calculate a distribution diagram of all boron - containing species as a function of the pH. This is shown in Figure 6-2. The distribution diagram was then used to determine the conditions for running the NMR spectra. As mentioned before, several experiments were carried out with various concentrations of the reactants. In all cases, overlapping peaks were observed. Therefore, it was not possible to determine the equilibrium constants by this technique. However, qualitative agreement with the pH titration data was obtained, as explained below.

Inspection of the distribution diagram in Figure 6-2 indicates that at pH 6, only one major boron - containing species is present. Agreement with this prediction and the NMR results was seen by comparing the spectrum of a 0.10 M $B(OH)_3$ solution at pH 6, with that of a 0.10 M $B(OH)_3$ / 1.0 M H_2O_2 solution at the same pH. In both cases, only a single resonance was observed.

The distribution diagram also predicts that there are three boron - containing species at pH 8. An NMR spectrum of a solution of the $B(OH)_3$ / H_2O_2 system adjusted to pH 8 was recorded at 25 °C, and is presented in Figure 6-3. The spectrum is composed of two sharp peaks overlapping with one broad peak. It was assumed that one of the reasons for the broadness of the third peak might be due to the slow exchange on the NMR timescale. In order to check this assumption, the spectra of the solution at pH 8 were recorded as a function of increasing temperature with 10 °C increments. The spectrum at 55 °C is presented in Figure 6-4, and shows a sharpening of the third resonance due to the faster exchange at a higher temperature. The number of boron complexes in the spectrum agrees with the number predicted from the calculated distribution diagram.

A comparison of the spectra at pH 8 in Figure 6-3 (25 °C) and Figure 6-4 (55 °C) shows a significant difference in the areas under the peaks. At the higher temperature, the rate of decomposition of hydrogen peroxide is increased (small bubbles were observed in the NMR tube). From the reaction given in eqn (1), as hydrogen peroxide decomposes, the pH increases. When the pH increases above pH 8, the concentration of the free boric acid is much less than that of either complex as seen in Figure 6-3. This may account for the difference in the relative areas in the two spectra.

Figure 6-5 contains a spectrum of the boric acid / hydrogen peroxide system at pH 10. The distribution diagram predicts that there are two major peroxoborate complexes at this pH. The spectrum at pH 10 also shows two major boron species, along with several smaller boron resonances.

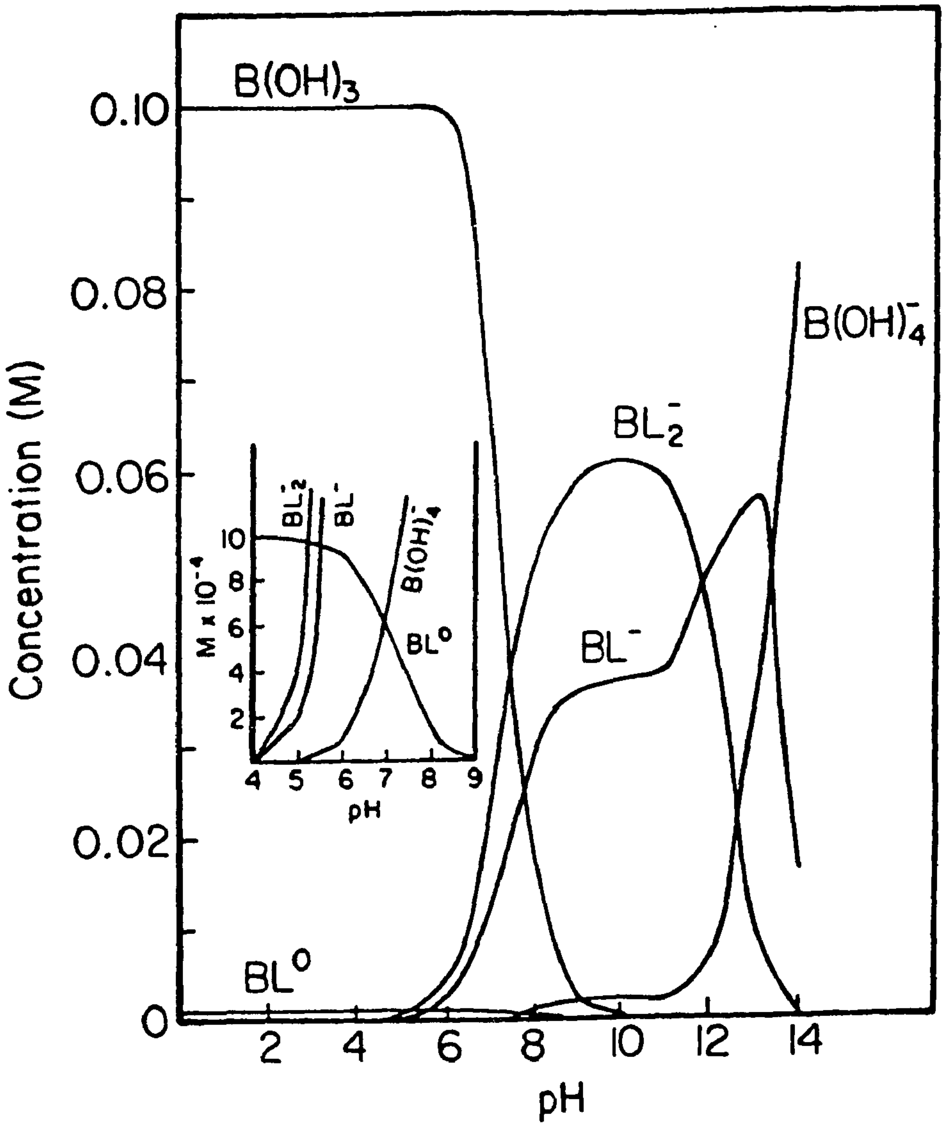


Figure 6-2: Distribution Diagram of the Boric Acid (0.10 M) / Hydrogen Peroxide (1.00 M) System

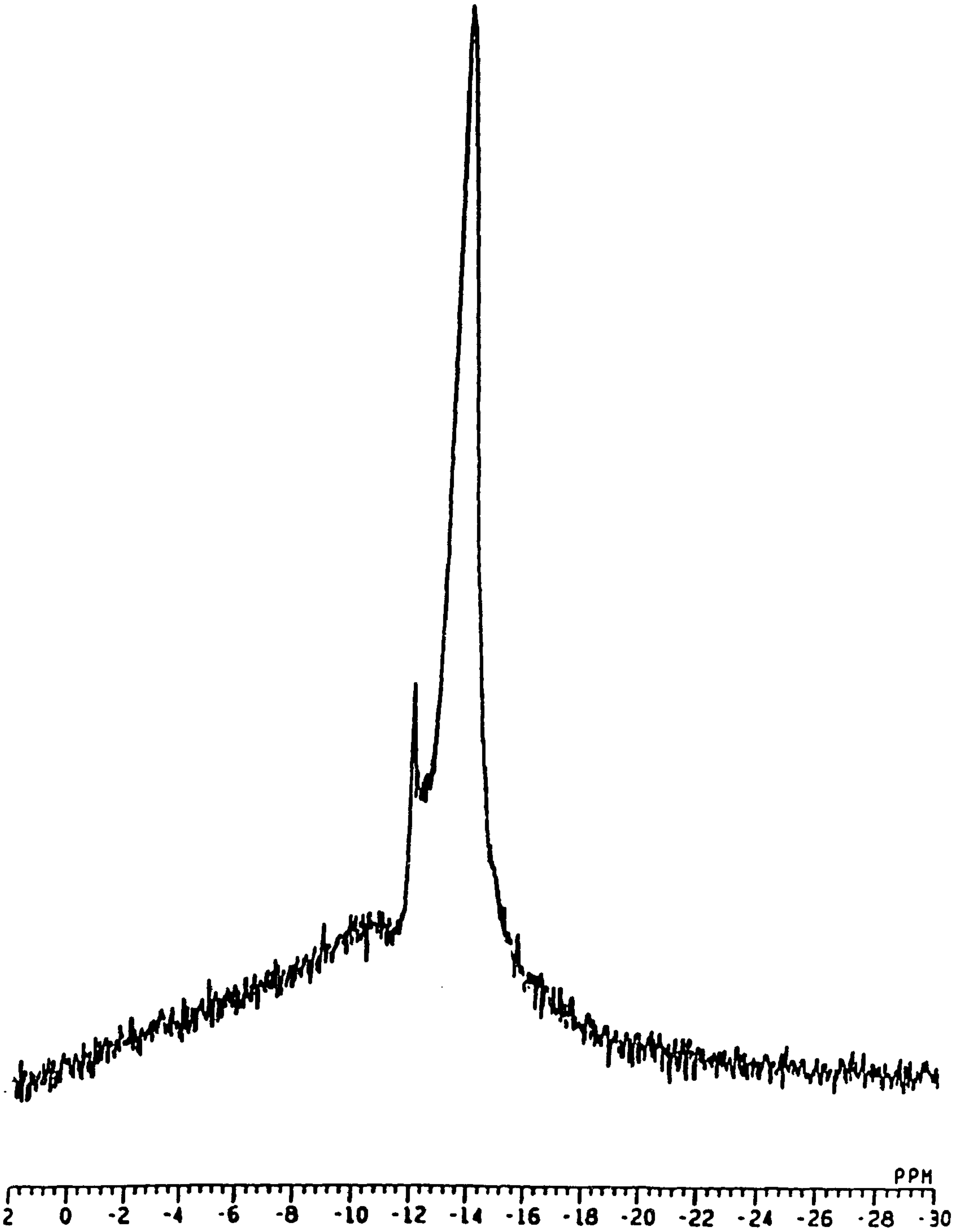


Figure 6-3: ^{11}B NMR Spectrum of the Boric Acid (0.10 M) / Hydrogen Peroxide (1.0 M) System; pH=8.08; T=25.5 °C.

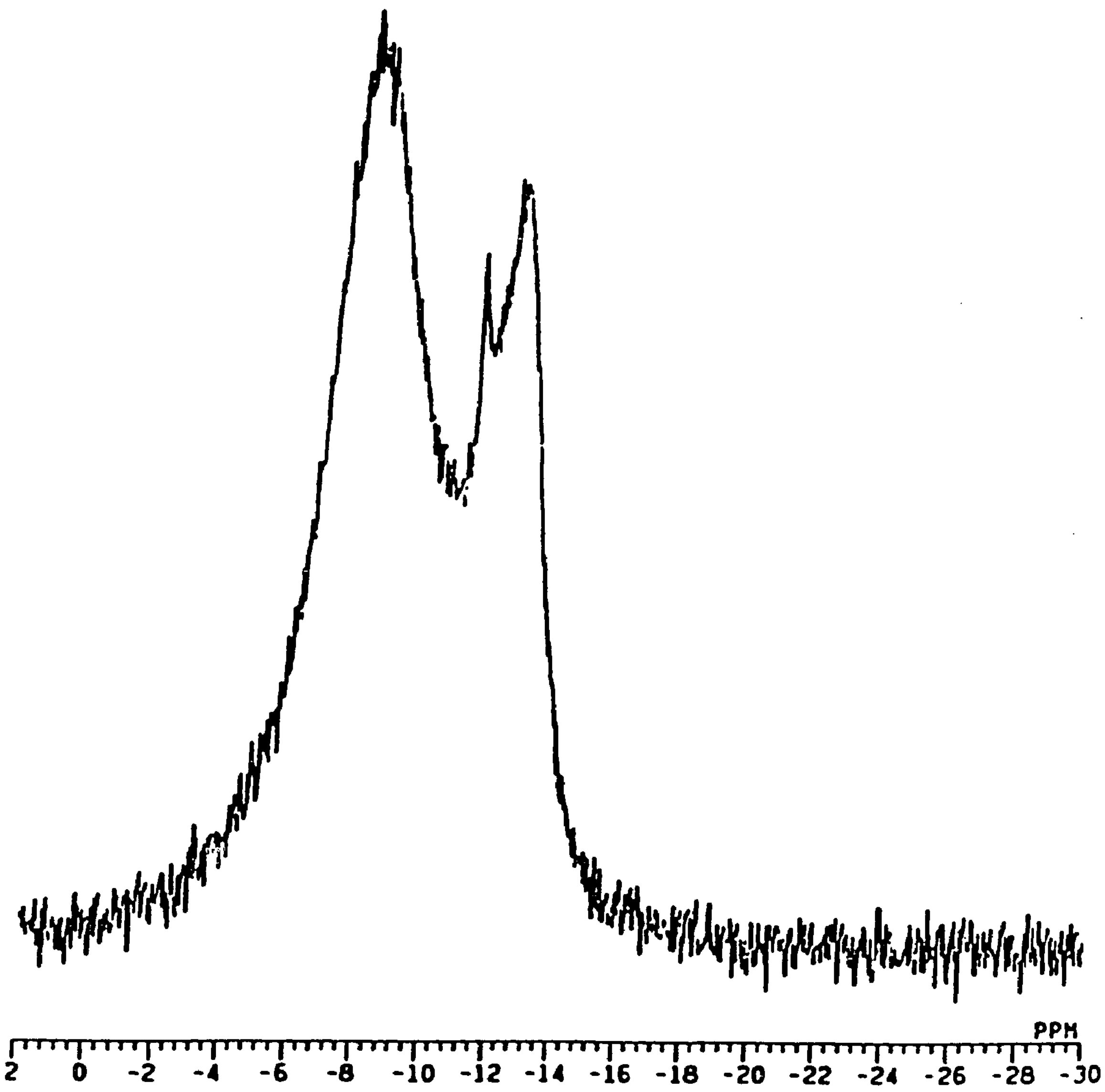


Figure 6-4: ^{11}B NMR Spectrum of the Boric Acid (0.10 M) / Hydrogen Peroxide (1.0 M) System; pH=8.08; T=55.5 °C.

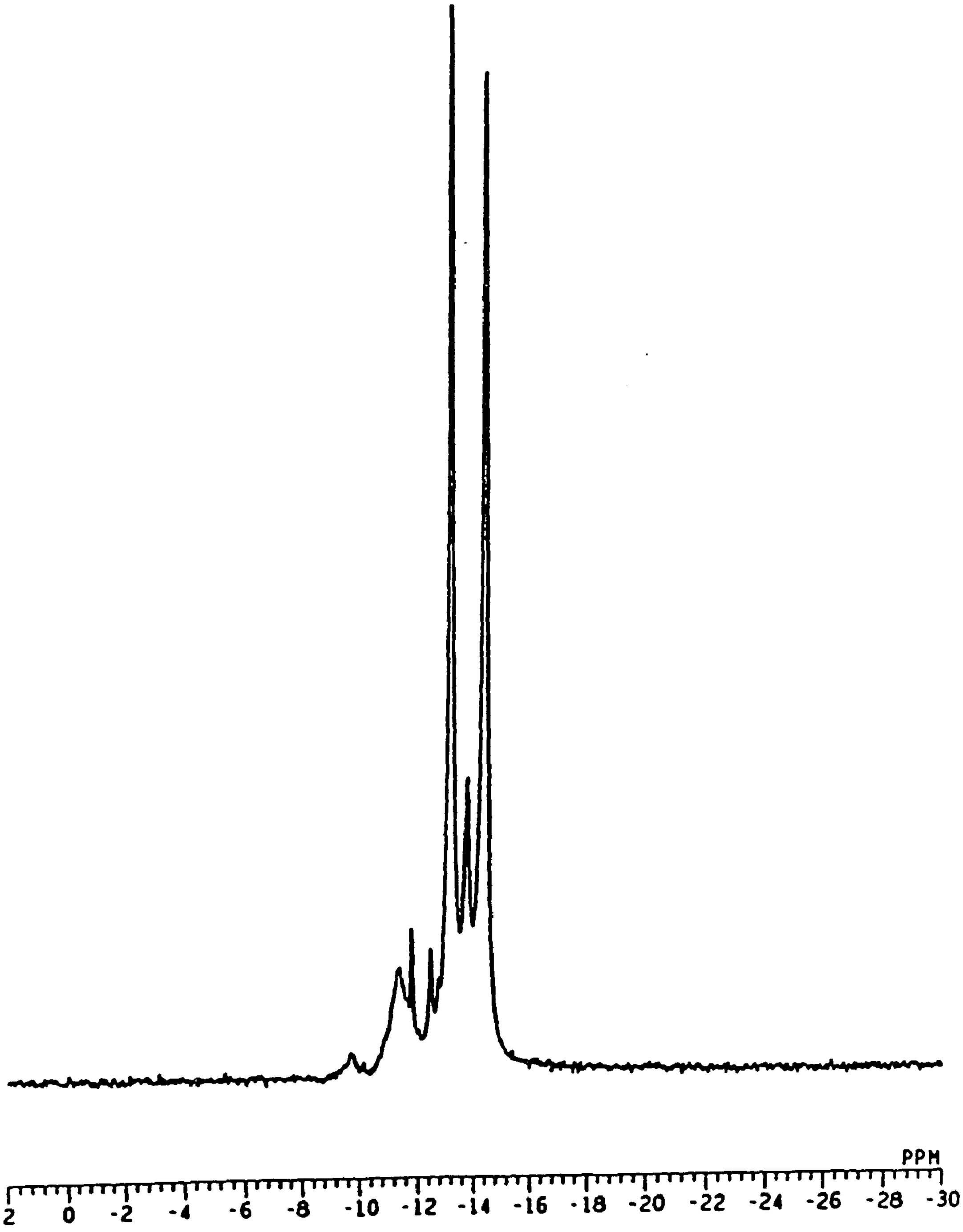
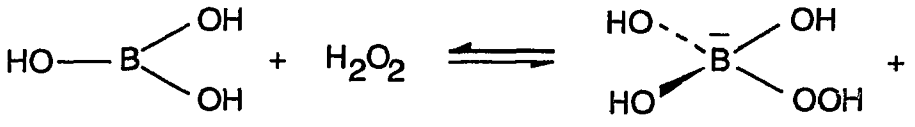


Figure 6-5: ^{11}B NMR Spectrum of the Boric Acid (0.10 M) / Hydrogen Peroxide (1.0 M) System; pH=9.74; T=25.5 °C.

6.5 Discussion

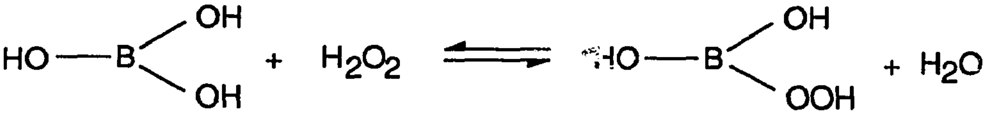
For boric acid interacting with hydrogen peroxide, the quantitative analysis of the pH titration data indicates that there are three peroxoboron species present under conditions where the pH is less than or equal to 9. As seen above, qualitative agreement concerning the number of boron complexes was obtained from the ^{11}B NMR experiments.

The equilibria which emerged from the analysis of the experiments may be summarized as follows.



(BL⁻) ; K1 (4)

(BL_2^-) ; K2 (5)



(BL_0) ; K3 (6)

The reaction given in eqn (4) is an addition reaction. The oxygen donor atom of the hydroperoxo ligand adds to the empty p orbital on boron in the trigonal boric acid to produce the tetrahedral complex and a ligand proton. The boron atom undergoes a change in coordination number from three to four, and a change in hybridization from sp^2 to sp^3. The reaction given in eqn (5) is a substitution reaction; a hydroxyl group in the initially formed complex is replaced by a second hydroperoxo ligand with displacement of a ligand proton. The equilibrium in eqn (6) is a substitution reaction which produces the neutral peroxoboric acid. Both reactions (5) and (6) occur with retention of the coordination number and the hybridization on boron.

The results obtained here are in disagreement with the Raman study which was carried out by Adams and Clark [74]. This Raman study covered the entire pH range and reported that only one peroxoborate species, $(HO)_3BOOH^-$, was formed in solution. The authors interpreted their results in terms of eqn (4) alone. From the experiments done in this Chapter, the quantitative analysis of the pH titration data ($pH \leq 9$) requires the presence of three peroxoboron species. This was confirmed in the ^{11}B NMR spectra given in Figure 6-3 and Figure 6-4. Furthermore, the spectra at pH 10 clearly shows the presence of two major peroxoboron species as well as other smaller boron resonances.

The authors of both the Raman study [74] and the ^{11}B NMR study [75] reported that there was no evidence for the formation of peroxoboric acid, BL_0, at low pH. This is perhaps due to the low concentration. The distribution diagram in Figure 6-2 for 0.10 M $B(OH)_3$ / 0.10 M H_2O_2 predicts the concentration of BL_0 to be approximately 10^{-3} M. This concentration was too small to be detected (in acidic solution) by us, using the 11B NMR technique. A spectrum at pH 6, for the same concentrations of $B(OH)_3$ and H_2O_2 which were used in the calculation of the distribution diagram, indicated only one peak, assigned to the free $B(OH)_3$. This assignment was based on the comparison of the spectrum with that of a blank solution of $B(OH)_3$ at the same pH. The presence of peroxoboric acid, BL_0, was proposed from the analysis of the pH mixing experiments which were carried out at low pH. The pH mixing method is very sensitive for detecting complex formation for reactions of this type. For instance, in Figure 6 -1, the pH changes are seen to be easily measurable eventhough the total concentration of peroxoboron species is less than 10^{-3} M.

As stated earlier, the neutral peroxoboric acid $(HO)_2BOOH$ is a species whose presence was proposed in order to account for the observed pH changes in acidic solution. Under our experimental conditions, the concentration was too small to be detected independently by the ^{11}B NMR technique. However, it is possible to calculate its acid dissociation constant as shown below.

From eqns (4) and (6),

$$K1 = \frac{[(HO)_3BOOH^-]\,[H^+]}{[B(OH)_3]\,[H_2O_2]} \quad \text{and} \quad K3 = \frac{[(OH)_2BOOH]}{[B(OH)_3]\,[H_2O_2]}$$

The acid dissociation equilibrium for peroxoboric acid is given in eqn (7).

$$(HO)_2BOOH \; + \; H_2O \; \rightleftarrows \; (HO)_3BOOH^- \; + \; H^+ \; ; \; K_a \qquad (7)$$

$$\text{where} \quad K_a = \frac{[(HO)_3BOOH^-]\,[H^+]}{[(HO)_2BOOH]}$$

From the above, it is readily seen that

$$K_a = \frac{K1}{K3} = 2 \times 10^{-6}$$

This calculation shows that peroxoboric acid is a stronger acid that boric acid (pKa = 8.98), as suggested by Menzel [70] as early as 1923. One possible reason for the difference in acidity may be related to the electron withdrawing nature of the -OH and the -OOH groups. The boron - oxygen bond in R_2B-OH is known to have more multiple bond character than the boron - oxygen bond in R_2B-OOH due to the electron withdrawing nature of the second oxygen in the -OOH group. This means that the boron atom in R_2B-OOH is more electron deficient than in R_2B-OH and can function as a stronger Lewis acid.

The value obtained for K1 (2.0×10^{-8}) from the analysis of the pH titration data is consistent with that from Antikainen 's measurement (1.6×10^{-8}) using potentiometric methods [72]. As stated earlier, Edwards [71] using pH methods, postulated the presence of at least six peroxoboron species in order to explain his data. Inspection of the ^{11}B NMR spectrum in Figure 6-5 shows an agreement with Edwards' results. This spectrum (at pH 10) also shows the presence of two major peroxoboron complexes, as predicted by the calculated distribution diagram. Furthermore, it is possible that one of the smaller boron resonances in Figure 6-5 may represent the cyclic dimer [67] which was characterized in the solid state.

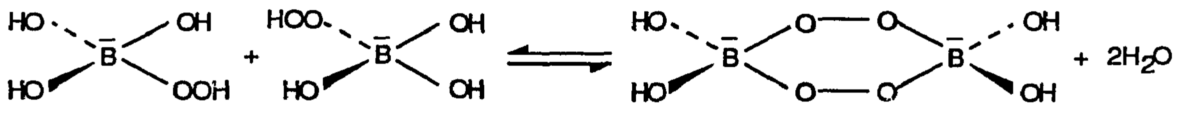
The results of the phenylboronic acid / hydrogen peroxide system are consistent , in part, with conclusions from previous studies. As mentioned before, previous thermodynamic studies on the complexation reactions of boron acids with bidentate chelating ligands indicate that the stability constants increase with increasing acidity of the reactants. Phenylboronic acid (pKa = 8.72) is more acidic acidic than boric acid (pKa = 8.98). It is also known that for a particular ligand H_2L, the stability constants for the $\Phi B(OH)_2$ / H_2L systems are greater than those for the $B(OH)_3$ / H_2L systems by factors of 4 - 6 [59]. In Figure 6 -1, for similar concentrations of the reactants, the initial pH drop in the case of phenylboronic acid is about five times larger than that for boric acid. Although no equilibrium constants could be determined for the phenylboronic acid / hydrogen peroxide system, the relative magnitudes of the pH changes in Figure 6 -1 are in agreement with previous work.

Similarly, the insignificant pH change observed in the boric acid / *tert*-butylhydroperoxide system is also in agreement with previous studies. The magnitude of this pH change indicates that the amount of complex formed is very small. This made it impossible to determine any equilibrium constants for the system. The pK_a value of $(CH_3)_3COOH$ is 12.8, while that for H_2O_2 is 11.6. Since *tert*-butylhydroperoxide is less acidic than hydrogen peroxide, the very small pH change is consistent with the correlation of increasing stability constants with increasing acidity of the reactants.

The analysis of the pH titration data and the ^{11}B NMR spectra led to the conclusion that there are three peroxoboron complexes present in solution for conditions when the pH is less than or equal to 9. The proposed formulation of the complexes are $(HO)_3BOOH^-$, $(HO)_2B(OOH)_2^-$ and $(HO)_2BOOH$. In each of these complexes, it is assumed that the hydroperoxo ligand is unidentate. We have no independent structural data to support this assumption. However, it should be noted that in all of the previous studies on aqueous peroxoborates , the hydroperoxo ligand was always treated as being unidentate.

Since the H_2O_2 ligand is bifunctional, it is possible to form peroxoboron complexes which may contain bridging peroxo ligands, or three - membered chelate rings. Each of these cases is now considered.

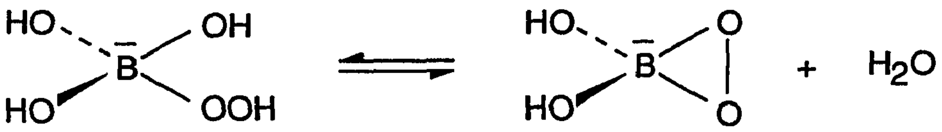
A bridging peroxo ligand was observed in the determination [67] of the crystal structure of sodium peroxoborate. In the solid state, the peroxoborate anion was found to be a cyclic dimer, as shown on page 148. In solution, one possible route to the formation of the dimer is the condensation reaction between two $(HO)_3BOOH^-$ complexes.



The occurence of this dimerization reaction would cause the equilibrium in eqn (4) to be driven more to the right, resulting in a pH change. Since the pH titration data were satisfactorily described by eqns (4) - (6), the dimerization reaction was not considered.

In the second case, it is possible for the initially formed complex, $(HO)_3BOOH^-$, to undergo a further reaction producing a peroxoboron species, $(HO)_2B(O_2)^-$, which contains a three - membered chelate ring.

The reaction is shown below.



This reaction may occur by closure of the peroxoborate ring with displacement of a hydroxyl group from boron, and loss of a ligand proton. The resulting complex, $(HO)_2B(O_2)^-$, contains a triangular bidentate peroxo ligand and it is not certain whether this species is formed instead of the proposed $(HO)_3BOOH^-$. That is, whether reaction (4) from the proposed equilibria (page 164) produces $(HO)_3BOOH^-$ or $(HO)_2B(O_2)^-$ has no effect on solution pH. Therefore, we have no solid evidence to distinguish between the complexes $(HO)_3BOOH^-$ and $(HO)_2B(O_2)^-$.

The choice of the unidentate peroxoboron complex, $(HO)_3BOOH^-$, as being the species formed in solution in our proposed equilibria (page 164) was based, in part, on an infra-red study [136] of peroxofluoroborate complexes. The authors of this infra-red study, taking into account the results of the crystal structure determination [67] of the peroxoborate anion (page 148) ruled out the possibility of having complexes containing the triangular bidentate peroxo ligand. Similarly, the authors of the Raman study [74] of aqueous peroxoborates interpreted their experimental results in terms of the $(HO)_3BOOH^-$ complex ; no complexes containing triangular bidentate peroxo ligands were observed.

There is one further point to be made. In 1985, Chaudhuri and Das [136] synthesized the first known heteroligand peroxoborate complexes. The stable compounds which were made were white, crystalline alkali - metal and ammonium peroxofluoroborates. The attempts to synthesize the compounds in acidic solution (pH 3 - 4) were unsuccessful. The synthesis had to be carried out in basic media, at approximately pH 9. Inspection of the calculated distribution diagram, shows an agreement between our results and the pH conditions which were necessary to carry out the peroxofluoroborate synthesis.

The research described in this Chapter was published in *Inorganic Chemistry* in 1987 [137]. A more extensive study on the nature of peroxoborate species in aqueous solution was carried out in 1989 by Griffith et al [138]. These authors used both ^{11}B NMR and Raman spectroscopy techniques. Their concentrations were 0.01 - 4 M for boric acid and 0.01 - 34 M for hydrogen peroxide, and the experiments were done between pH 14 and pH 4. It is worth mentioning that these authors found good agreement between their results and our distribution diagram which was calculated from the pH titration data.

In conclusion, the interaction between boric acid and hydrogen peroxide in aqueous solution produces three peroxoboron species when the pH is less than or equal to 9. The number of peroxoboron complexes proposed from two different pH titration methods was confirmed by ^{11}B NMR spectroscopy. The equilibrium constants for the formation of the complexes were determined quantitatively and it is assumed that the hydroperoxo ligand is unidentate.

CHAPTER 7

CONCLUSIONS AND FUTURE WORK

The investigation of the boric acid / hydrogen peroxide system demonstrates the addition and the substitution reactions of a simple unidentate ligand on boron. Although no kinetic study was possible by the temperature-jump method, we were able to determine quantitatively the stability constants for the complexes formed in solution.

The kinetic study of the methylboronic acid / polyol systems represent the first known kinetic investigation of boron acid complexation reactions in basic solution. The lability of the tetrahedral methylboronate anion relative to the trigonal boron acid was demonstrated for each of the polyols studied. We do not have enough information in order to propose a possible transition state for the substitution reaction of the borate anion. Since only one type of ligand (non - acidic) was used, it is not clear whether proton transfer is important in the transition state. Much work remains to be done at high pH with a series of ligands varying in pK_a before a plausible transition state can be proposed for the substitution reactions of tetrahedral borates.

The thermodynamic study of the substitution reaction between methylboronate anion and 1,2-propanediol indicates that the reaction is exothermic and is accompanied by an unfavorable entropy change. The complexation reaction is therefore enthalpy driven and not entropy driven. The other polyols could not be studied due to the overlapping resonances in the proton NMR spectra. A future experiment would be to use the ^{11}B NMR technique instead, although the differences among the ligands are expected to be small.

The kinetic behavior of the phenylboronic acid / ethylene glycol system in basic solution is very different from that of the analogous methylboronic acid reactions. At the present time, we have no explanation for this. The $\Phi B(OH)_2$ / $HOCH_2CH_2OH$ kinetic data needs to be re-examined. Mechanism 5 which was proposed in Chapter 5 treated the boron acid trigonal - tetrahedral interconversion process as being non-diffusion controlled. We are not comfortable about the exclusion of the indicator concentration term or about the low value of the rate constant (10^4 $M^{-1}s^{-1}$) obtained for the addition of OH^- to trigonal $\Phi B(OH)_2$. Recall that for $B(OH)_3$, kinetic investigations have been carried out by different experimental techniques on the boric acid / borate equilibrium. Sound absorption studies by Simmons et al [116,117] have proposed the formation of an ion - pair intermediate. The most recent study by Candau et al [118] using the temperature - jump method assumes that the interconversion process occurs in one step. They reported a rate constant of 1.1×10^7 $M^{-1}s^{-1}$ for the addition of hydroxide to trigonal boric acid. These results imply that the boric acid / borate equilibrium is not diffusion controlled. Therefore, a critical experiment which must be done in the future is to independently measure the rate of addition of OH^- to $\Phi B(OH)_2$, preferably in the absence of any indicators. Possible experimental techniques may be the pressure - jump method or even the temperature - jump method which does not utilize a spectrophotometric detection system. Other methods for detection in temperature - jump studies include conductimetric, fluorimetric and polarimetric systems. In fact, it would be worthwhile to repeat the experiments without any indicators in order to confirm the independence of the measured relaxation time upon indicator concentration.

After further analysis of the phenylboronic acid / ethylene glycol system from which one hopes that a satisfactory mechanism may emerge, it would be informative to extend these studies to boric acid. In addition to the 1:1 complexes formed by the substituted boron acids, boric acid can form 1:2 (or bis) complexes as well. The 1:2 complexes are formed via the condensation reaction between the 1:1 complex and a second ligand molecule. These reactions are similar to those of the tetrahedral borates in the sense that both are substitution reactions in which boron retains a coordination number of four. The reactions for the formation of the 1:2 complexes have different geometrical constraints and requirements from those characteristic of the 1:1 complex formation. The investigation of bis complex formation allows one to study the effect of an already bound ligand on the thermodynamics and kinetics of the second chelation step. Thermodynamic studies in the literature have established the presence of bis complexes of boric acid with ligands such as salicylic acid, lactic acid and polyols by pH methods [62], infrared [30,31], Raman [32] and ^{11}B NMR spectroscopy [94,139]. The only kinetic study reported on bis complex formation was for the boric acid / lactic acid system [62]. However, only upper limits were obtained for the various rate constants because of the proton ambiguity phenomenon. The results indicate that the bound α-hydroxycarboxylic acid ligand inhibits the coordination of the second ligand molecule. This is not necessarily true for other types of ligands since the reactions depend upon the nature and the flexibility of the ligands involved. By studying the boric acid / polyol systems, one does not have to deal with the proton ambiguity problem and absolute values for the rate constants can be obtained. In addition, a system such as boric acid reacting with 1,2-propanediol in which both the 1:1 and the 1:2 complexes are known to exist is characterized by two relaxation times. It should be mentioned that preliminary experiments were done on this system and two well separated relaxation times (for example, 2 msec and 20 msec) were observed. This suggests that a kinetic investigation of the boric acid / polyol systems is feasible. A detailed study of these systems would therefore shed further light on the reactions of bis complex formation.

Thermodynamically, the formation of bis complexes between borates and polyols is well understood. For many of these systems, stability constants as well as enthalpy and entropy changes have been reported. The kinetic investigation which was suggested above would provide a more complete understanding of these reactions. As mentioned in the Introductory Chapter, the formation of these complexes finds many applications in analytical techniques, structural problems and enzyme studies. A more recent and equally important application can be found in the area of biological chemistry.

Boron is a trace nutrient and its deficiency in the diet is followed by loss of Ca^{2+} and Mg^{2+} in the urine [140]. These symptons eventually lead to the onset of osteoporosis. The exact function of boron in Ca^{2+} and Mg^{2+} metabolism is not known but it is possible that borate complexes are involved in the binding and transport of Ca^{2+}. Thermodynamic studies in the recent literature show by use of ^{11}B and ^{13}C NMR techniques that borate complexes of polyhydroxycarboxylic acids interact with Ca^{2+} to produce ternary complexes in basic solution [141-143]. Once a good understanding of the reactivity of borates is obtained, it would be useful to extend the kinetic study to include the interaction between borate complexes and Ca^{2+} in basic solution. The study of these ternary complexes would therefore lead to a new and promising area of research in boron acid chemistry.

APPENDIX A

Definition of Symbols

$$\alpha = 1 + \frac{K_{HB}}{\overline{[H^+]}} \qquad\qquad \beta = 1 + \frac{K_{L1}}{\overline{[H^+]}}$$

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

$$P = \frac{\left\{ \frac{1}{\alpha} + \frac{1}{\beta} - 1 \right\}}{\left\{ \gamma + \frac{\overline{[B^-]}}{\alpha \overline{[H^+]}} + \frac{\overline{[HL^-]}}{\beta \overline{[H^+]}} \right\}}$$

$$Q = - \frac{P \overline{[OH^-]}}{\overline{[H^+]}}$$

$$R = \frac{1}{\alpha} - \frac{P \overline{[B^-]}}{\alpha \overline{[H^+]}}$$

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

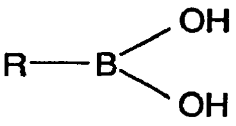
$$T = 1 - R$$

$$V = 1 - S$$

APPENDIX B

STRUCTURES

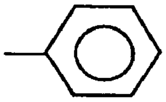
BORON ACIDS



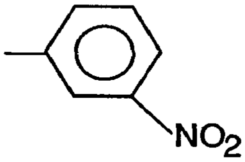
Boric Acid: R = —OH

Methylboronic Acid: R = $—CH_3$

Phenylboronic Acid: R =

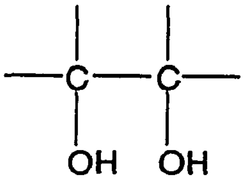


m-nitrophenylboronic acid : R =

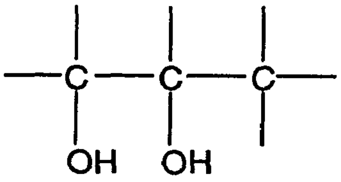


LIGANDS

DIOLS AND POLYOLS

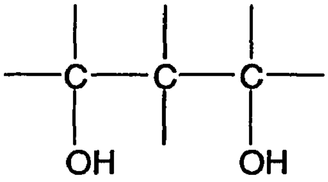


ethylene glycol

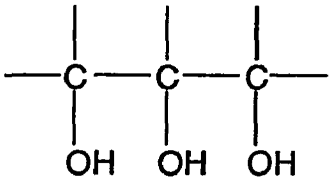


1,2 - propanediol

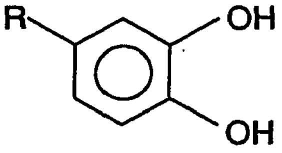
DIOLS AND POLYOLS



1,3 - propanediol



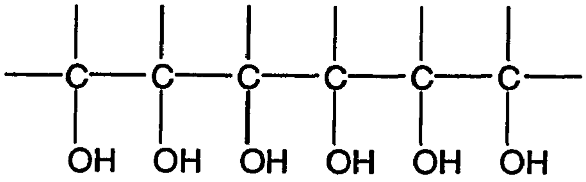
glycerol



catechol : R = H

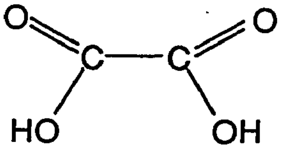
4-nitrocatechol R = NO_2

4-methylcatechol R = CH_3

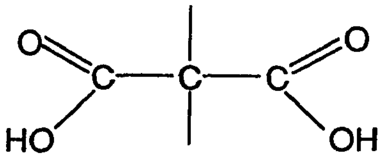


mannitol

DICARBOXYLIC ACIDS

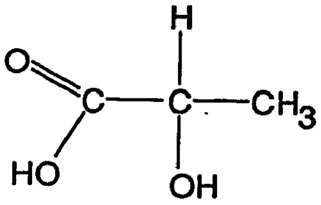


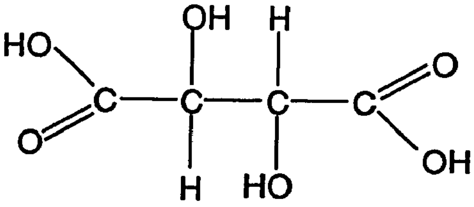
oxalic acid

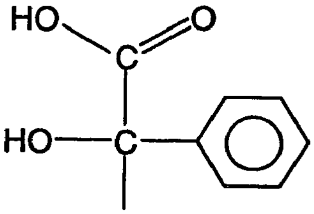


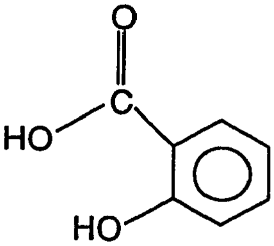
malonic acid

α - HYDROXYCARBOXYLIC ACIDS


lactic acid


tartaric acid


mandelic acid


salicylic acid

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