DALTON
FULL PAPER

Equilibrium and kinetic studies on the complexation of boric acid with chromotropic acid

Chaoying Shao,[a] Shiro Matsuoka,[a] Yoshinobu Miyazaki,[b] Kazuhisa Yoshimura,*[a] Toshishige M. Suzuki[c] and D. A. Pacheco Tanaka[c]

[a] *Department of Chemistry and Physics of Condensed Matter, Graduate School of Sciences, Kyushu University, Ropponmatsu, Fukuoka 810-8560, Japan. E-mail: kazz@rc.kyushu-u.ac.jp*
[b] *Department of Chemistry, Fukuoka University of Education, Akama, Munakata, Fukuoka 811-4192, Japan*
[c] *Tohoku National Industrial Research Institute, 4-2-1, Nigatake, Miyagino-ku, Sendai 983-8551, Japan*

Received 1st June 2000, Accepted 21st July 2000
Published on the Web 23rd August 2000

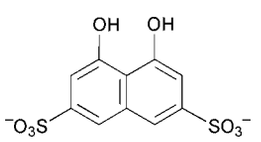
The complexation of boric acid with chromotropic acid in aqueous solution was examined thoroughly by ^{11}B NMR measurements. Two peaks with chemical shift values of δ −17.7 and −18.0 were observed besides the free boric acid/borate peak and ascribed to the 1 : 1 and the 1 : 2 complexes, respectively. The 1 : 2 complex is formed in acidic solution, while the 1 : 1 complex prevails in a higher pH range. The formation constants for these complexes were evaluated based on the signal intensities of ^{11}B NMR spectra to be $\log \beta_1 = -1.57$ and $\log \beta_2 = 2.35$, which are well consistent with those reported previously as well as that (β_2) obtained kinetically in this work. The chromatographic separation of the 1 : 2 complex from the other species enabled a kinetic study of the reaction which revealed that the reaction for 1 : 1 complex formation takes place much faster than that for 1 : 2 complex formation. The pH dependences of the rate constants of the forward and backward reactions of the 1 : 2 complexation could be interpreted by the catalytic role of hydrogen ions in the reactions. Plausible mechanisms for both the reactions of 1 : 2 complex formation and decomposition were proposed. On the basis of the equilibrium and kinetic information on the complexation, the optimum conditions for practical applications of the ligand so far reported could be well understood.

Introduction

It has been confirmed by NMR spectroscopy that boric acid/borate combines with polyhydroxyl compounds to form complexes with 1 : 1 and 1 : 2 stoichiometries.[1–9] Acidic chelate ligands can react directly with trigonal boric acid, whereas for the non-acidic polyols or saccharides the predominant reaction is with tetrahedral borate. Both of the reactions produce tetrahedral anionic complexes.

The equilibrium and kinetics for 1 : 1 complex formation between trigonal boric acid or substituted boronic acid with acidic polyhydroxyl compounds have been studied extensively.[10–14] The reaction pathways, including both an addition reaction and a substitution reaction in which proton transfer is significant for a change in the structure on boron, have generally been accepted, although there are differences in the rate-determining steps and the transition states. For the reaction of tetrahedral borate anion or an analogous 1 : 1 complex which does not involve change in the co-ordination number on boron, however, it is unclear yet whether proton transfer also plays an important role in the mechanism since it has not been studied in detail kinetically.

The formation constants of the complexes increase with increasing acidity of the chelate ligands and reagents having two vicinal phenolic hydroxyl groups are usually thought to form much more stable borate complexes than those of alcohols.[1,15,16] A large number of studies have been carried out on the reaction of boric acid with 4,5-dihydroxy-2,7-naphthalenedisulfonic acid (chromotropic acid), in which the two peri-hydroxyl groups determine the complex-forming properties. Bartusek and Havelkova[17] showed that boric acid reacts with chromotropic acid to form a 1 : 1 complex in extremely dilute solution but a 1 : 2 complex under reagent excess conditions in the pH range 3–6, and determined the formation constants of the complexes by potentiometric titration. On the basis of the boron complex-forming ability in acidic aqueous solutions, many useful methods for determining trace amounts of boron using chromotropic acid were developed by means of solvent extraction, high-performance liquid chromatography (HPLC), flow injection analysis (FIA) and so on.[18–24] It was proposed only later that the maximum sensitivity for boron measurement was obtained at a pH equal to or higher than 7.[25] Among most of the reports, the mechanism of the complexation has rarely been mentioned.



We are interested in boron-selective adsorbents for the concentration and recovery of boron, purification of materials from boron, and isotope separation.[26–29] Recently, an anion exchanger containing chromotropic acid has been developed for removing trace boron from highly purified water for semiconductor manufacture.[30] The adsorption characteristics for boron revealed that the chromotropic acid loaded resin could retain boron over a wide pH range (2–10), unlike that reported previously.[17] Furthermore, it was demonstrated by NMR spectroscopy and acid–base titration that the 1 : 2 complex was formed at pH about 2, and by adsorption capacity measurement that the 1 : 1 complex might be present in a higher pH range.

In order to clarify the mechanism for boric acid reaction with chromotropic acid, we employed ^{11}B NMR spectroscopy to

 DOI: 10.1039/b004399k

examine thoroughly the complex formation behavior in aqueous solution. Ishihara *et al.*[10] studied the kinetics for the 1 : 1 complexation reaction of boric acid with chromotropic acid by using a high-pressure stopped flow apparatus and proposed a two-stage reaction mechanism based on the activation parameters. In the present work, we determined the 1 : 2 complexation reaction rates by separating the complex from chromotropic acid using a HPLC system and discuss the possible reaction mechanism. An overall comprehension about the complexation reaction between boric acid and chromotropic acid could be obtained by combining our ^{11}B NMR and kinetic results with those reported.[10]

Experimental

Chemicals

All chemicals were of analytical grade. Chromotropic acid (disodium salt, dihydrate, Dojindo, Kumamoto, Japan), and boric acid (1000 ppm, Kishida, Osaka, Japan) were used without further purification. The bis complex of boric acid with chromotropic acid was prepared as reported previously.[30] Deionized water prepared with a Milli-Q SP system (Millipore) was used throughout.

^{11}B NMR measurements

^{11}B NMR measurements were performed on a JEOL JNM-GSX 500 spectrometer at a resonance frequency of 160.0 MHz with a 10 mm multinuclear probe at 24 ± 1 °C. Boric acid/borate solutions (ionic strength $I = 0.1$ mol dm^{-3}) containing a known amount of chromotropic acid were prepared. The pH of the solution was adjusted with a small amount of HCl, NH_3 or CH_3CO_2H–CH_3CO_2Na, NaH_2PO_4–Na_2HPO_4, HEPES [*N*′-(2-hydroxyethyl)piperazine-*N*-ethane-2-sulfonic acid] and NH_3–NH_4Cl buffer solution and measured with a Horiba pH meter, model F-22. The solutions were used for NMR measurements after different reaction times. Especially for evaluating the formation constants of the complexes, the solutions were allowed to stand for at least one day before determinations. The standard NMR parameters were selected as previously described[27] and the chemical shifts were reported with respect to 0.1 mol dm^{-3} boric acid solution as external reference.

HPLC measurements

The HPLC system comprised an anion-exchange column (TSK gel IC-Anion-PW, 4.6 mm i.d. × 5 cm, Tosoh)[22] and a SNK DM2M-1024 pump to ensure a constant flow rate of 0.8 cm^3 min^{-1}. The detection was performed using a JASCO U-best 35 UV/vis spectrophotometer with a 17.7 mm^3 flow cell. The sample solution ($I = 0.1$ mol dm^{-3}) was prepared at 25 °C and contained a known amount of chromotropic acid (0.0005–0.0025 mol dm^{-3}) and boric acid (0.0005–0.0025 mol dm^{-3}) in order to give a certain concentration ratio, or 0.002 mol dm^{-3} of the bis complex synthesized by our laboratory.[30] The pH was adjusted using formate or acetate buffer solution. After being kept in a water-bath (thermostatted at 25 °C) for a fixed period, 25.5 mm^3 of the solution was introduced into the HPLC system using a six-way rotary valve, and the absorbance monitored continuously at around 355 nm and recorded with a Pantos U-228 recorder. The eluent consisted of 0.16 mol dm^{-3} sodium perchlorate and 0.001 mol dm^{-3} buffer solution the pH of which was adjusted to be the same as that of the reagent solution.

Results and discussion

Complexation equilibria between boric acid and chromotropic acid

Fig. 1 shows ^{11}B NMR spectra for boric acid solutions with chromotropic acid at different pH values. Without doubt

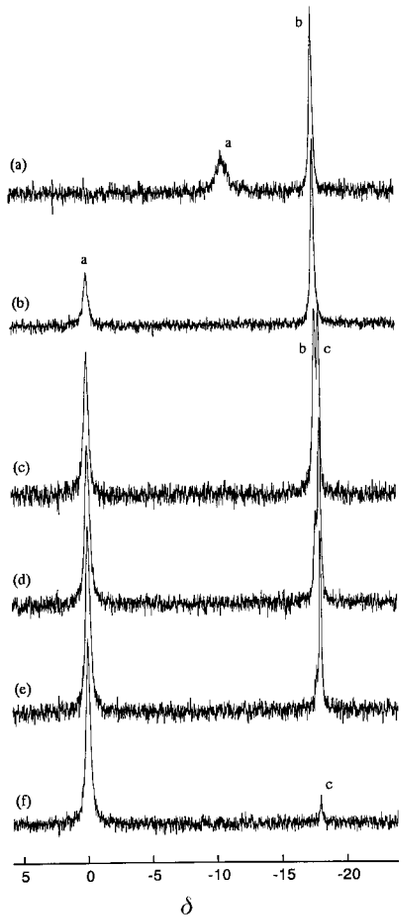


Fig. 1 ^{11}B NMR spectra for boric acid solutions containing chromotropic acid at different pH values. $C_B = C_L = 0.00185$ mol dm^{-3}; $I = 0.1$ mol dm^{-3}. pH (a) 9.46; (b) 6.77; (c) 5.36; (d) 4.54; (e) 3.56; (f) 2.05. a, Boric acid/borate; b, 1 : 1 complex; c, 1 : 2 complex.

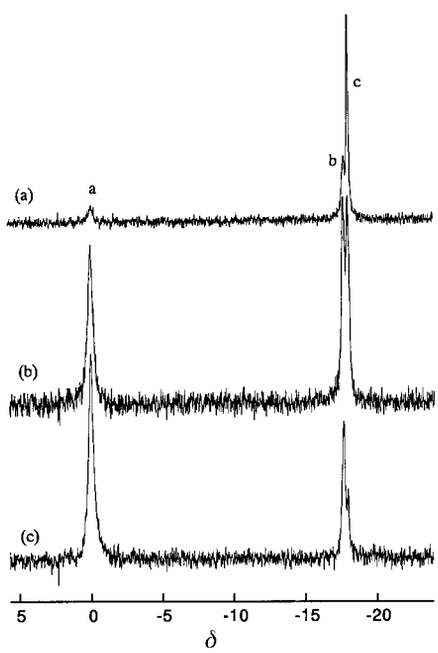


Fig. 2 ^{11}B NMR spectra for solutions containing different concentration ratios of boric acid to chromotropic acid. $C_B = 0.00185$ mol dm^{-3}, $I = 0.1$ mol dm^{-3}, pH = 5.5. $C_B : C_L = 1 : 2$ (a), 1 : 1 (b) or 1 : 0.5 (c). a, Boric acid; b, 1 : 1 complex; c, 1 : 2 complex.

chromotropic acid reacts with boric acid to form complexes in a wide pH range from 2 to 10 because two new signals having chemical shift δ −17.7 and −18.0 are observed besides the signal due to the free boric acid/borate whose chemical shift

Table 1 Formation constants of boric acid complexes with chromotropic acid at 25 °C and $I = 0.1$ mol dm^{-3}

$\log \beta_1$	$\log \beta_2$	Method	Reference
-1.57 ± 0.06	2.35 ± 0.23	^{11}B NMR	This work
	2.06 ± 0.10	Kinetics, HPLC	This work
-1.5 ± 0.04 [a]	2.4 ± 0.2 [a]	Potentiometric titration	17
-1.08 ± 0.05 [b]		Kinetics, UV spectrometry	10

[a] Determined at 20 °C. [b] $I = 1.0$ mol dm^{-3}.

changes with pH in the equilibrated solution ($\delta_{B(OH)_3}$ 0 and $\delta_{B(OH)_4^-}$ −17.7[28]). The chemical shift values for the complexes are in good accordance with those of 6-membered borate complexes with polyhydroxyl compounds reported by van Duin *et al.*[3] In order to identify the complexes, the ^{11}B NMR spectra for solutions containing different concentration ratios of boric acid to chromotropic acid were measured at pH about 5.5 and $I = 0.1$ mol dm^{-3} (Fig. 2). It is obvious that the signal at δ −17.7 is due to the 1 : 1 complex of boric acid with chromotropic acid because its intensity decreases with increasing concentration of chromotropic acid in the solution. Similarly, the signal at δ −18.0 is ascribed to the 1 : 2 stoichiometric complex. Thus, we can conclude that the 1 : 2 complex of boric acid is predominant in acidic solution, while the 1 : 1 complex prevails at a higher pH value. Here is direct evidence of 1 : 1 and 1 : 2 complexes.

The reaction of boric acid with chromotropic acid has an interesting mechanism since the complex formation brings about a change in co-ordination number of boron, *i.e.* in its structure. The complexation equilibria between boric acid and chromotropic acid in solution can be represented by eqns. (1)–(8). Here, H_2chr^{2-}, $B(OH)_2(chr)^{3-}$ and $B(chr)_2^{5-}$

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad (1)$$

$$K_a = [B(OH)_4^-][H^+]/[B(OH)_3] \quad (2)$$

$$H_2chr^{2-} \rightleftharpoons Hchr^{3-} + H^+ \quad (3)$$

$$K_{a1} = [Hchr^{3-}][H^+]/[H_2chr^{2-}] \quad (4)$$

$$B(OH)_3 + H_2chr^{2-} \rightleftharpoons B(OH)_2(chr)^{3-} + H_3O^+ \quad (5)$$

$$\beta_1 = [B(OH)_2(chr)^{3-}][H^+]/[B(OH)_3][H_2chr^{2-}] \quad (6)$$

$$B(OH)_3 + 2H_2chr^{2-} \rightleftharpoons B(chr)_2^{5-} + H_3O^+ + 2H_2O \quad (7)$$

$$\beta_2 = [B(chr)_2^{5-}][H^+]/[B(OH)_3][H_2chr^{2-}]^2 \quad (8)$$

denote chromotropic acid with deprotonated sulfonate and the 1 : 1 and 1 : 2 complexes of boric acid with chromotropic acid, and β_1 and β_2 are the overall formation constants of the 1 : 1 and 1 : 2 complexes, respectively. The acid dissociation constants for boric acid (pK_a) and chromotropic acid (pK_{a1}) are reported as 9.05[27] and 5.35[31] ($I = 0.1$ mol dm^{-3}, 25 °C), respectively.

The formation constants for the 1 : 1 and 1 : 2 complexes were estimated based on the signal intensities of ^{11}B NMR spectra of the boron species. The overlapping NMR signals were resolved into individual peaks by a Lorentzian curve-fitting method and the mole fraction of the total uncomplexed boric acid was calculated from ^{11}B NMR chemical shift of the free boric acid/borate as described previously.[28] The formation constants evaluated are summarized in Table 1 together with those reported using different methods such as potentiometry and spectrophotometry.[10,17] As can be seen, they are in good agreement. In addition, the stepwise 1 : 2 complex formation constant ($10^{3.92}$) is much larger than those of the corresponding complexes with polyhydroxyl compounds.[13,32] The large stability for the 1 : 2 complex is due to the steric bulkiness of the aromatic moiety of chromotropic acid as well as π–π* interaction between boron and phenolic groups enhanced by the sulfonate group acting as a strong electron acceptor for the lone pairs on oxygen.[33]

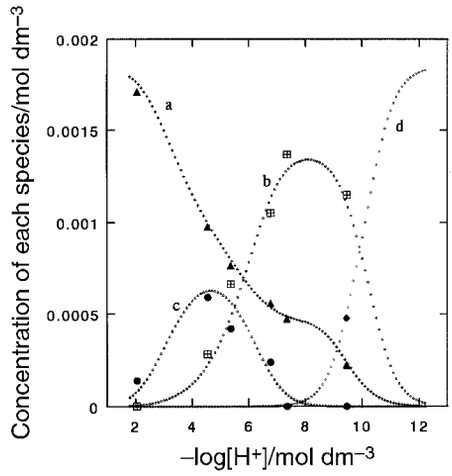


Fig. 3 Concentration of each boron species against pH in the equilibrated solution. Points refer to the experimental results, while the dotted lines are calculated. $C_B = C_L = 0.00185$ mol dm^{-3}, $I = 0.1$ mol dm^{-3}. a, $B(OH)_3$; b, 1 : 1 complex; c, 1 : 2 complex; d, $B(OH)_4^-$.

Based on the formation constants obtained, the molar distribution plot for each boron species against pH in the equilibrated solution is shown in Fig. 3. It is clearly demonstrated under our experimental conditions that the 1 : 2 complex is formed in the pH range from 2 to 7, since the 1 : 2 complexation equilibrium is independent of the hydrogen ion concentration in solution and there exists a much higher concentration of undissociated chromotropic acid in acidic solution. On the other hand, the concentration of the 1 : 1 complex increases with increase in pH of the solution and above pH about 7.5 only it is produced. Thus, in a neutral or alkaline region, the equilibrium reaction of the 1 : 1 complex and the formation constant β_1' may be expressed by eqns. (9) and (10), respectively.

$$B(OH)_3 + Hchr^{3-} \rightleftharpoons B(OH)_2(chr)^{3-} + H_2O \quad (9)$$

$$\beta_1' = [B(OH)_2(chr)^{3-}]/[B(OH)_3][Hchr^{3-}] = \beta_1/K_{a1} \quad (10)$$

As can be seen from eqn. (10), β_1 and β_1' are related to each other.

Kinetics of 1 : 1 and 1 : 2 complexation reactions

Reaction rate measurements. ^{11}B NMR spectra for boric acid solutions ($I = 0.1$ mol dm^{-3}, pH 5.4) with chromotropic acid at different reaction times reveal that the reaction for 1 : 1 complex formation takes place faster than that for 1 : 2 complexation (Fig. 4). By analysing these NMR signals, the formation constant values for the 1 : 1 complexes obtained at different reaction periods are $10^{-1.49}$ (for 0 h), $10^{-1.68}$ (for 4 h) and $10^{-1.61}$ (for 17 h). They are almost identical with those shown in Table 1, even though the relative intensities of the 1 : 1 complex signals decrease with increase in those of the 1 : 2 complex. This result indicates that the 1 : 1 complexation of boric acid with chromotropic acid always reaches equilibrium prior to the 1 : 2 complexation.

Ishihara *et al.*[10] have shown by stopped flow study that the forward and backward reactions for 1 : 1 complex formation are rapid and evaluated the respective rate constants (Table 2), so only the rate for 1 : 2 complexation reaction was investigated in the pH range of 3.5–5.5 where an appreciable amount of 1 : 2 complex could be formed (Fig. 3). It is fairly difficult to express the rate equation for 1 : 2 complexation in the integrated form because of the coexistence of the fast 1 : 1 reaction equilibrium. Thus, the initial rate method was employed. In an early stage

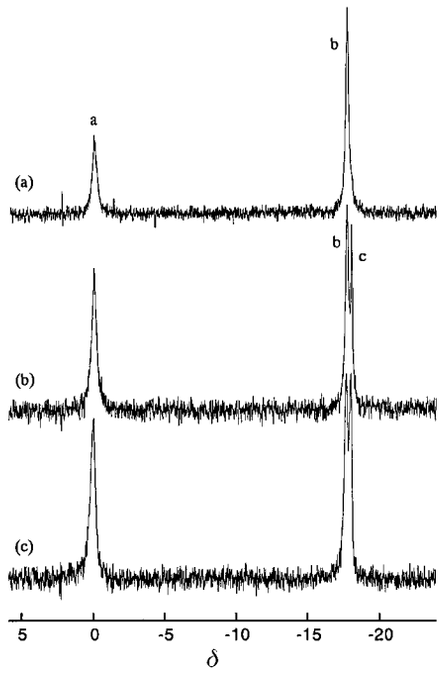


Fig. 4 ^{11}B NMR spectra for boric acid solutions with chromotropic acid at different reaction times. $C_B = C_L = 0.00185$ mol dm^{-3}, $I = 0.1$ mol dm^{-3}, pH 5.4. (a) for 0 h; (b) for 4 h; (c) for 17 h. a, Free boric acid; b, 1 : 1 complex; c, 1 : 2 complex.

Table 2 Rate constants for the reaction of boric acid and chromotropic acid (25 °C, $I = 0.1$ mol dm^{-3})

k_{f1} [a]/ dm^3 mol^{-1} s^{-1}	k_{d1} [a]/ dm^3 mol^{-1} s^{-1}	k_{f2}/ dm^6 mol^{-2} s^{-1}	k_{d2}/ dm^3 mol^{-1} s^{-1}
1.38×10^3	1.61×10^4	$(5.64 \pm 1.01) \times 10^4$	$(1.32 \pm 0.09) \times 10$

[a] k_{f1} and k_{d1} are the forward and backward rate constants for 1 : 1 complexation, respectively.[10]

of the reaction there was a negligible contribution of each opposite direction reaction and the rate equation for 1 : 2 complexation between boric acid and chromotropic acid can be expressed as in eqns. (5), (11) and (12). Here, $d[B(chr)_2^{5-}]/dt$

$$B(OH)_3 + H_2chr^{2-} \overset{\text{fast}}{\rightleftharpoons} B(OH)_2(chr)^{3-} + H_3O^+ \quad (5)$$

$$B(OH)_2(chr)^{3-} + H_2chr^{2-} \underset{k_{d2}}{\overset{k_{f2}}{\rightleftharpoons}} B(chr)_2^{5-} + 2H_2O \quad (11)$$

$$d[B(chr)_2^{5-}]/dt = k_{f2(obs)}[B(OH)_2(chr)^{3-}][H_2chr^{2-}] \quad (12)$$

denotes the rate of the 1 : 2 forward complexation reaction, and $k_{f2(obs)}$ the second-order rate constant observed. The equilibrium concentrations of H_2chr^{2-} and $B(OH)_2(chr)^{3-}$ were estimated by using the 1 : 1 complex formation constant. In a similar way, the backward reaction can be examined by the initial rate method using eqn. (13) where $k_{d2(obs)}$ is the first order rate constant observed for the backward reaction of eqn. (11).

$$-d[B(chr)_2^{5-}]/dt = k_{d2(obs)}[B(chr)_2^{5-}] \quad (13)$$

The reaction rates for 1 : 2 complex formation and its decomposition were examined by monitoring the concentration of the 1 : 2 complex over a certain period of time. Since no absorption spectral changes accompanied the complex formations between boric acid and chromotropic acid, spectrophotometric detection was carried out at around 355 nm by means of the HPLC system, giving two peaks. The 1 : 2 complex was separated satisfactorily from free chromotropic acid under the experimental

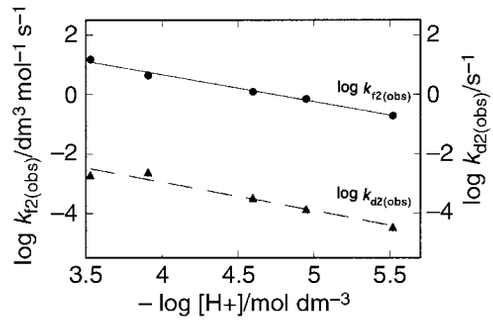


Fig. 5 Second-order forward and the first-order backward rate constants for 1 : 2 complexation reaction of boric acid with chromotropic acid as a function of hydrogen ion concentration in the equilibrated solution. $C_B = C_L = 0.00185$ mol dm^{-3}, $I = 0.1$ mol dm^{-3}, 25 °C.

conditions, while the 1 : 1 complex decomposed on the column because of its lability and lower anionic charges than those of the 1 : 2 complex and was eluted as free chromotropic acid.

The 1 : 2 forward rate constants for solutions of boric acid and chromotropic acid at different concentrations at a constant pH value of 4.7 have been demonstrated to be almost constant by using eqn. (12),[34] indicating that the equation is valid for the reaction system, *i.e.* there is a first order dependence on the concentration of each $B(OH)_2(chr)^{3-}$ or H_2chr^{2-} species. The rate constant for 1 : 2 complexation ($k_{f2(obs)} = 1.37$ dm^3 mol^{-1} s^{-1}) determined under our experimental conditions was about 1/1000th of that for 1 : 1 complexation reported by Ishihara *et al.*,[10] which is acceptable for the results obtained by the ^{11}B NMR measurements shown in Fig. 4.

pH Dependence of the reaction rate for 1 : 2 complexation. Fig. 5 shows that both the forward second-order and the backward first-order reaction rates for 1 : 2 complexation depend on pH in the equilibrated solution. An increase in pH of the equilibrated solution resulted in a decrease in the rate constants and both reactions are first order in the hydrogen ion concentration. That is, one proton appeared to be involved in both the 1 : 2 complex formation and its decomposition. Since no proton transfer is included in the 1 : 2 complexation equilibrium shown in eqn. (11), the pH dependences of the reaction rates could be explained by the proton participating in the reactions as a catalyst. Thus, the effect of hydrogen ion in the solution for the 1 : 2 complexation reaction should also be taken into consideration and the rate constants in eqns. (12) and (13) should be revised as in eqns. (14) and (15). The rate constants for 1 : 2

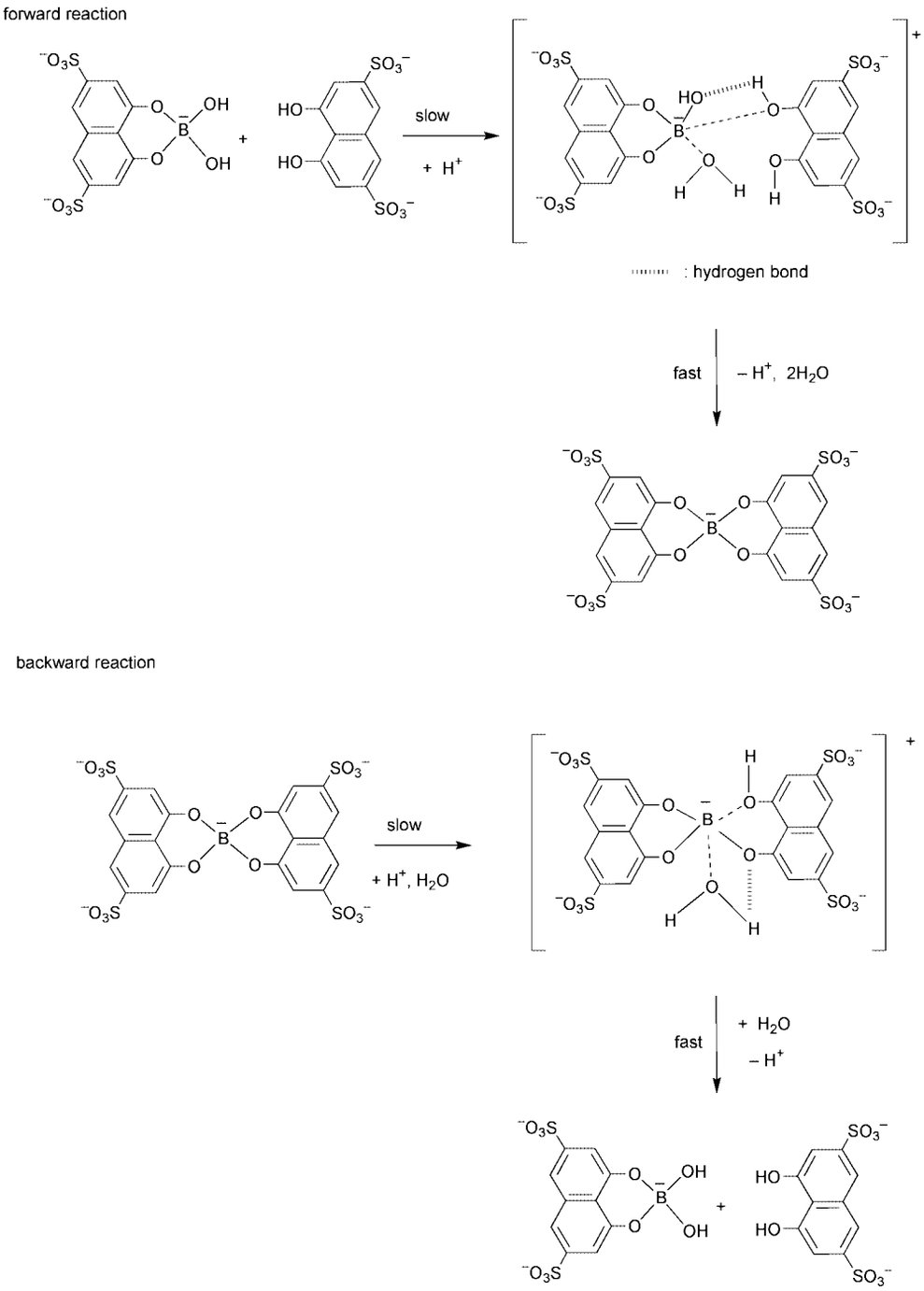
$$k_{f2(obs)} = k_{f2}[H^+] \quad (14)$$

$$k_{d2(obs)} = k_{d2}[H^+] \quad (15)$$

complexation reaction evaluated by eqns. (14) and (15) are listed in Table 2 together with those for the 1 : 1 complexation reaction.[10] By using the k_{f2} and k_{d2} values, the stepwise formation constant of the 1 : 2 complex, which is independent of the hydrogen ion concentration in solution, can be calculated to be $10^{3.63}$. The value is in fairly good accordance with that obtained by NMR measurement (Table 1).

Complexation mechanism. In an acidic pH range where H_2chr^{2-} species participate in the reaction, it is reasonable to consider that the geometry at boron changes from trigonal to tetrahedral and a proton is simultaneously released during 1 : 1 complex formation.

Funahashi *et al.* proposed that trigonal $B(OH)_3$ reacts directly with an acidic chelate ligand *via* a two-step reaction process to produce a 1 : 1 complex.[10,11] The first step, in which nucleophilic attack of the hydroxyl group of the entering ligand by means of hydrogen bonding makes boron change its coordination number from 3 (sp^2) to 4 (sp^3), is considered to be



Scheme 1

rate-determining, while the subsequent chelate-forming ring closure with dissociation of a co-ordinated water molecule is rapid. This reaction pathway is supported by reports that the forward rate constants for the reactions of a series of ligands with different pK_a show an increase with increasing acidity of the ligand.[15,16] The significance of proton transfer for the complexation reaction of boric acid is also demonstrated by Pizer and co-workers[35,36] who studied the reactivities of phenylboronic acid with oxalic acid (H_2ox) and oxalate ions as well as malonic acid (H_2mal) and malonate ions and showed their forward rate constants to be in the following orders: $H_2ox > Hox^-$ and $H_2mal > Hmal^-$, while ox^{2-} and mal^{2-} were unreactive. These facts indicate that at least one proton on the oxygen donor atom is absolutely necessary for the hydroxyl group of boric acid to be released as a water molecule and the second one makes the chelate ring close more rapidly. That is, proton transfer may also play an important role in the leaving of the hydroxyl group from boron as a water molecule.

Our kinetic studies of the 1 : 2 complexation showed that the forward rate constant had a first order dependence on the hydrogen ion concentration in solution (Fig. 5), that is a proton catalyses the process of chelate ring closure with dissociation of two water molecules. As expected from eqn. (11), the decomposition rate for the 1 : 2 complex should also have a first order dependence on the hydrogen ion concentration (Fig. 5). These facts indicate clearly that the catalytic role of proton transfer accelerates both the forward and backward reactions of the 1 : 2 complexation.

As a result, the most plausible reaction mechanism for 1 : 2 complex formation mainly in acidic solution is presented in Scheme 1. During the first step for the forward reaction the hydroxyl group of chromotropic acid co-ordinates directly to boron when a proton supplied from the solution combines with the hydroxyl group of the 1 : 1 complex, and simultaneously the hydroxyl proton in the entering ligand binds with the other hydroxyl group of the 1 : 1 complex to form a five-co-ordinate

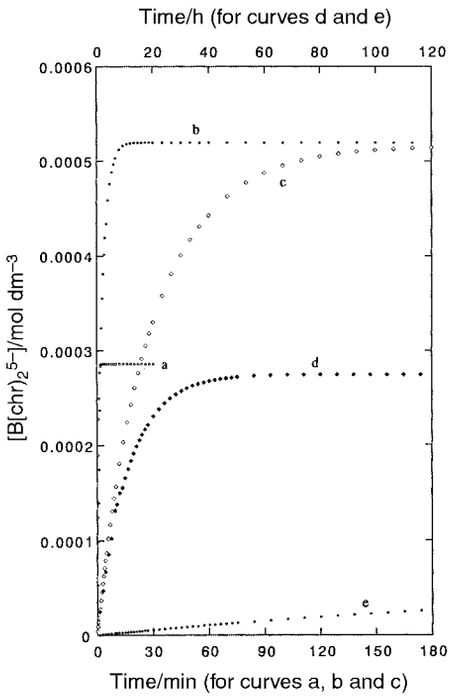


Fig. 6 Simulated concentration change of the bis complex with reaction time under different pH conditions. Initial concentration: $C_B = C_L = 0.00185$ mol dm^{-3}. pH: 3 (a); 4 (b); 5 (c); 6 (d); 7 (e).

transition state. Then, the proton is released together with the hydroxyl group as a water molecule. In the next step the chelate ring is closed to produce a water molecule and a proton from the intermediate.

It is known that the second step of the mechanism for boric acid reaction with chromotropic acid, that is the chelate-forming ring closure, is rapid.[10,11] Thus, the first step, the nucleophilic attack toward the boron atom to form a co-ordination bond, is rate-determining for either the 1 : 1 or the 1 : 2 complexation reaction. The presence of a five-co-ordinate boron has also been proposed in the hydrolysis of BH_4^- and the possible geometries of such species have been calculated.[37,38]

During the 1 : 1 complex formation the nucleophilic attack is completed by introducing the lone electron pair of oxygen into the empty orbital of the central boron atom in boric acid. In the case of the 1 : 2 complex formation, however, the co-ordination to the central boron atom with the sp^3 orbital in the 1 : 1 complex has to proceed by release of the hydroxyl group of the 1 : 1 complex together with hydrogen ion as a water molecule, and it is more difficult than that for 1 : 1 complex formation. This is one of the possible reasons for the lower reaction rate for 1 : 2 complexation in comparison with 1 : 1 complexation. In addition, the electrostatic repulsion between H_2chr^{2-} and $B(OH)_2(chr)^{3-}$ may also be kinetically unfavorable to produce the 1 : 2 complex. As a result, the formation of a five-co-ordinate boron transition state and the electrostatic repulsion between the 1 : 1 complex and free ligand make the 1 : 2 complex formation much slower than that of the 1 : 1 complex formation, unlike tetrahedral borate which should have a larger reaction rate than trigonal boric acid when reacting with the same ligand.[13,16a]

For the backward reaction, the addition of water molecules for the decomposition of the 1 : 2 complex is carried out *via* hydrogen ion binding to a μ-oxo bridge of the complex (Scheme 1). The first proton comes from the solution and the second from the bound water molecule. The addition of the first hydrogen ion is quite difficult since the 1 : 2 complex possesses a structure with high symmetry and there is less electron density on the μ-oxo oxygen atom of the complex due to π–π* interaction of the aromatic moiety; therefore the first proton binding is thought to be the rate-determining step for the decomposition reaction of the 1 : 2 complex. Similar to the forward reaction, the backward reaction rate for the bis complex also depends on the concentration of hydrogen ion in the solution and the first-order backward rate constant is lower than the second-order forward one at the same pH (Fig. 5).

Based on the 1 : 2 forward and backward rate constants together with all equilibrium constants concerned, the concentrations of the bis complex produced over a certain reaction period under different pH conditions were calculated and are shown in Fig. 6. The equilibrium concentration of the 1 : 2 complex species at different pH is in fairly good accordance with that at the corresponding pH in Fig. 3. It is quite evident that the lower the pH value in the equilibrated solution the faster is the reaction. The reaction reaches equilibrium within 3 min at pH 3, after about 50 h at pH 6; when the pH of the solution is 7 the reaction rate is very slow and would take longer than 5 days to reach equilibrium. The fact that the 1 : 2 complex cannot be formed in basic solution may be due to such low reaction rates as well as the thermodynamic difficulty in 1 : 2 complexation under basic conditions.

Conclusion

It has been confirmed by ^{11}B NMR measurements that boric acid reacts with chromotropic acid to form complexes with 1 : 1 and 1 : 2 stoichiometries. The 1 : 2 complex is predominant in acidic solution, while the 1 : 1 complex is mainly distributed over a higher pH range. The kinetic studies revealed that a proton catalyses both the reactions of 1 : 2 complex formation and its decomposition. The mechanism may be generally applicable to reactions between tetrahedral boron and polyhydroxyl compounds.

On the basis of the complexation equilibria of boric acid with chromotropic acid and the pH dependences of the bis-complexation reaction rates, the adsorption properties of boric acid on chromotropic acid resin[30] as well as the optimum conditions for boron determination in acidic aqueous solutions with an excess of chromotropic acid[18–25] can be explained satisfactorily. Chromotropic acid loaded resin, which has been used for the removal of trace amounts of boron from highly purified water, adsorbing boric acid over a wide pH range (2–10), strongly retains boric acid especially in the acidic region (pH 1.8–4.5). This is due to high stability of the 1 : 2 complex of boric acid with chromotropic acid formed under the ligand excess condition in the resin phase and the rapid complexation in this pH region. On the other hand, all of the analytical methods for trace boron involve 1 : 2 complex formation in an acidic or neutral solution with an excess of the ligand. That the 1 : 2 complex can be formed rapidly in acidic solution and hardly decomposed in alkaline solution made it possible to develop a rapid, sensitive detection method for trace boron. Motomizu *et al.*[23] have proposed a highly sensitive FIA system consisting of 1 : 2 complex formation in acidic solution and subsequent fluorimetric determination in alkaline solution to reduce the background fluorescence of the free ligand since the signal belonging to the complex is not changed.

Above all, the complexation of boric acid with chromotropic acid is well understood by combining ^{11}B NMR and kinetic studies. The equilibrium and kinetic information on the complexation will help us to develop further practical applications of the present system.

Acknowledgements

The authors wish to thank Dr Hirofumi Sakashita of the Center of Advanced Instrumental Analysis, Kyushu University, for his help in obtaining ^{11}B NMR data. This work was partially supported by a Research Fund from NEC Corporation, Japan.

References and notes

1 W. G. Henderson, M. J. How, G. R. Kennedy and E. F. Mooney, *Carbohydr. Res.*, 1973, **28**, 1.
2 K. Yoshino, M. Kotaka, M. Okamoto and H. Kakihana, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 3005.
3 (*a*) M. van Duin, J. A. Peters, A. P. G. Kieboom and H. van Bekkum, *Tetrahedron*, 1984, **40**, 2901; (*b*) M. van Duin, J. A. Peters, A. P. G. Kieboom and H. van Bekkum, *Tetrahedron*, 1985, **41**, 3411.
4 C. F. Bell, R. D. Beauchamp and E. L. Short, *Carbohydr. Res.*, 1986, **147**, 191.
5 J. G. Dawber and S. I. E. Green, *J. Chem. Soc.*, *Faraday Trans. 1*, 1986, 3407.
6 J. G. Dawber, S. I. E. Green, J. C. Dawber and S. Gabrail, *J. Chem. Soc.*, *Faraday Trans. 1*, 1988, 41.
7 S. Chapelle and J. F. Verchere, *Tetrahedron*, 1988, **44**, 4469.
8 R. van den Berg, J. A. Peters and H. van Bekkum, *Carbohydr. Res.*, 1994, **253**, 1.
9 M. J. Taylor, J. A. Grigg and I. H. Laban, *Polyhedron*, 1996, **15**, 3261.
10 K. Ishihara, Y. Mouri, S. Funahashi and M. Tanaka, *Inorg. Chem.*, 1991, **30**, 2356.
11 S. Kagawa, K. I. Sugimoto and S. Funahashi, *Inorg. Chim. Acta*, 1995, **231**, 115.
12 K. Kustin and R. Pizer, *J. Am. Chem. Soc.*, 1969, **91**, 317.
13 R. Pizer and R. Selzer, *Inorg. Chem.*, 1984, **23**, 3023.
14 R. D. Pizer and C. A. Tihal, *Polyhedron*, 1996, **15**, 3411.
15 R. Pizer and L. Babcock, *Inorg. Chem.*, 1977, **16**, 1677.
16 (*a*) L. Babcock and R. Pizer, *Inorg. Chem.*, 1980, **19**, 56; (*b*) L. Babcock and R. Pizer, *Inorg. Chem.*, 1983, **22**, 174.
17 M. Bartusek and L. Havelkova, *Collect. Czech. Chem. Commun.*, 1967, **32**, 3853.
18 J. Lapid, S. Farhi and Y. Koresh, *Anal. Lett.*, 1976, **9**, 355.
19 T. Korenaga, S. Motomizu and K. Toei, *Analyst* (*London*), 1978, **103**, 745.
20 S. Motomizu, I. Sawatani, M. Oshima and K. Toei, *Anal. Chem.*, 1983, **55**, 1629.
21 S. Motomizu, M. Oshima and K. Toei, *Bunseki Kagaku*, 1983, **32**, 458.
22 Z. Jun, M. Oshima and S. Motomizu, *Analyst* (*London*), 1988, **113**, 1631.
23 S. Motomizu, M. Oshima and Z. Jun, *Anal. Chim. Acta*, 1991, **251**, 269.
24 F. Capitan, A. Navalon, E. Manzano, L. F. Capitan-Vallvey and J. L. Vilchez, *Fresenius J. Anal. Chem.*, 1991, **340**, 6.
25 T. Lussier and R. Gilbert, *Anal. Chem.*, 1992, **64**, 2201.
26 K. Yoshimura, Y. Miyazaki, S. Sawada and H. Waki, *J. Chem. Soc.*, *Faraday Trans.*, 1996, 651.
27 K. Yoshimura, Y. Miyazaki, F. Ota, S. Matsuoka and H. Sakashita, *J. Chem. Soc.*, *Faraday Trans.*, 1998, 683.
28 C. Shao, Y. Miyazaki, S. Matsuoka, K. Yoshimura and H. Sakashita, *Macromolecules*, 2000, **33**, 19.
29 K. Yoshimura, R. Kariya and T. Tarutani, *Anal. Chim. Acta*, 1979, **109**, 115.
30 T. M. Suzuki, D. A. P. Tanaka, T. Yokoyama, Y. Miyazaki and K. Yoshimura, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1639.
31 P. Letkeman, A. Martell and R. Motekaitis, *J. Coord. Chem.*, 1980, **10**, 47.
32 K. Yoshimura, S. Sawada, Y. Miyazaki and H. Waki, *Proc. 4th Workshop on Boron Chemistry and Boron Neutron Capture Therapy*, Research Reactor Institute, Kyoto University, 1992, 13.
33 A. Pelter and K. Smith, in *Comprehensive Organic Chemistry*, ed. D. N. Jones, Pergamon Press, Oxford, 1979, vol. 3, pp. 915–924.
34 The $k_{f2(obs)}$ value is 1.37 ± 0.22 $dm^3\ mol^{-1}\ s^{-1}$ ($n = 9$) at 25 °C, pH 4.7 and $I = 0.1$ mol dm^{-3}. The concentrations of boric acid and chromotropic acid were changed from 0.0005 to 0.0025 mol dm^{-3}.
35 S. Friedman and R. Pizer, *J. Am. Chem. Soc.*, 1975, **97**, 6059.
36 G. Lorber and R. Pizer, *Inorg. Chem.*, 1976, **15**, 978.
37 I. M. Pepperberg, T. A. Halgren and W. N. Lipscomb, *J. Am. Chem. Soc.*, 1976, **98**, 3442.
38 M. M. Kreevoy and J. E. C. Hutchins, *J. Am. Chem. Soc.*, 1972, **94**, 6371.