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Kinetic study of the complex formation of boric and boronic acids with mono- and diprotonated ligands

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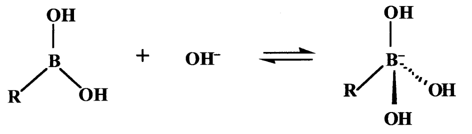
Abstract

The complex formation reactions of boric and boronic acids ($RB(OH)_2$: R = OH, n-Bu, Ph, and *m*-NO_2Ph) with 4-isopropyltropolone (Hipt) and chromotropic acid (H_2cht^{2-}) have been studied kinetically at various pH. The reactions of H_2ipt^+ with boronic acids were faster than those of Hipt by a factor of 1.5–11, and fully deprotonated ipt^- also reacted with *m*-$NO_2PhB(OH)_2$, but slower than Hipt. The tetrahedral *m*-$NO_2PhB(OH)_3^-$ ion did not react with Hipt. Reaction routes for the complexation of boric acid with chromotropic acid could not be specified because of the unexpected problem of proton ambiguity. Mechanism for the reactions of boronic acids with bidentate ligands was discussed in terms of rate determining chelate ring closure. It was concluded that at least one proton is necessary for the OH^- in the tetrahedral intermediates to be eliminated smoothly as water, and a doubly hydrogen-bonded intermediate was proposed for the reactions with diprotic ligands.

Keywords: Boric acid; Boronic acid; Complex formation kinetics

1. Introduction

Boronic acids ($RB(OH)_2$) are weak acids, which produce boronate ions ($RB(OH)_3^-$) in alkaline solution with changes in coordination number (3–4) and in structure (trigonal to tetrahedral, Eq. (1)). Their pK_a values vary with the change of substituent R, e.g. pK_a = 6.96, 8.72, 8.98, 10.40, and 10.74 for R = *m*-nitrophenyl [1], phenyl [2], hydroxyl [3], methyl [1], and n-butyl [4], respectively.



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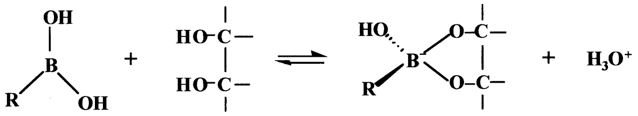

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In general, $RB(OH)_2$ reacts with bidentate ligands, such as dicarboxylic acids, α-hydroxy carboxylic acids, 1,2-benzenediols, polyols, etc. to produce four coordinate complexes (Eq. (2)). Most of these complexation reactions have no spectral changes in the UV–Vis region, so that the reaction rate has been measured by the aid of pH indicator which follows the proton released during the reaction [1,2,5–9]. In previous works, we have used some colorimetric reagents as ligands to follow directly the complexation reactions [10,11]. Reaction 2 consists of the two steps, i.e., the first step corresponding to Eq. (1) at which one of the two donor atoms of bidentate ligand binds to the trigonal boronic acid to form a tetrahedral intermediate, and the second step at which the chelate-ring closure occurs to the intermediate to form the 1:1 complex. We have done

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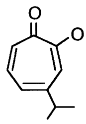
some kinetic measurements to show which of these two steps in reaction 2 is responsible for determining the overall reaction rate. For example, the volumes of activation and the isotope effect on the reaction were measured for the complexation of boric acid [10], and the rate constant for Eq. (1) was also tried to measure by ^{11}B NMR spectrometry to get the information on the first step in Eq. (2). The result was that the measured rate constant was not for Eq. (1) but for the OH^- exchange reaction between $B(OH)_3$ and $B(OH)_4^-$ in Eq. (3) [12], so the conclusive evidence for the rate determining step has not yet been obtained.

$$B(OH)_3 + {}^*B(OH)_4^- = B(OH)_4^- + {}^*B(OH)_3 \tag{3}$$

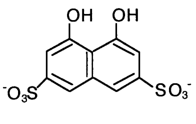
The significance of the proton on the donor atom in the complexation of boronic and boric acids has been demonstrated not only by the reactivity of diprotic acid ligand H_2L decreasing in the order: $H_2L > HL^- \gg L^{2-}$ (unreactive) [5,6], which is in striking contrast with the complexation of metal ions, but also by a deuterium isotope effect in the complexation reactions [10]. On the other hand, it has been shown for some systems that $RB(OH)_3^-$ reacts faster than $RB(OH)_2$ [1], and also shown that the trigonal methyl boronic acid ($MeB(OH)_2$) has been shown to be quite unreactive to polyols without protons of appreciable acidity [13].

The objective of the present work is to reconfirm the significance of the proton to be released during the reactions by comparing the reactivities of H_2L, HL^-, and L^{2-}, to evaluate the relative substitution lability between $RB(OH)_2$ and $RB(OH)_3^-$, and to make sure which of the two steps in reaction 2 is rate determining.

4-Isopropyltropolone (Hipt) and chromotropic acid (H_2cht^{2-}) have been selected as ligands to accomplish the objective. The protonation constant of Hipt and the first acid dissociation constant of H_2cht^{2-} have been reported to be 1.70 M^{-1} ($I = 1.00$ M, 25 °C) [14] and $10^{-5.35}$ ($I = 0.10$ M, 25 °C) [15], respectively, so that kinetic measurements in acidic media may allow us to obtain rate constants for the reactions of $RB(OH)_2$ with H_2ipt^+, Hipt, H_2cht^{2-}, and $Hcht^{3-}$, since the pK_a value of $RB(OH)_2$ ranges 7–11 as mentioned above. In addition, measurements in alkaline media (pH approximately 9) may give us the rate constants for the reactions of $Hcht^{3-}$ with $B(OH)_3$ and $B(OH)_4^-$ without the problem of proton ambiguity, since both the first and second acid dissociation constants for H_2cht^{2-} (pK_{a3} = 5.35, pK_{a4} = 13.0) [15] are far from that of boric acid (pK_a = 8.98).



Hipt



H_2cht^{2-}

2. Experimental

2.1. Materials

4-Isopropyltropolone (Hipt), Chromotropic acid (Na_2H_2cht), and boric acid were purified as described previously [10]. Phenyl boronic acid (Aldrich) was purified by vacuum sublimation. *m*-Nitrophenylboronic acid (m-$NO_2PhB(OH)_2$, Aldrich) and n-butylboronic acid (Aldrich) were recrystallized once from water and $C_6H_5CH_3$, respectively. Perchloric acid (60% UGR for trace analysis, Kanto Chemical Co. Inc., Tokyo) was used as received. A solution of sodium perchlorate was prepared as described previously [16]. Doubly distilled water was used for preparation of all solutions.

2.2. Measurements

The ionic strength was kept at 0.10 M or at 1.00 M with sodium perchlorate and perchloric acid. Reaction rates of the complex formation of the boric and boronic acids were followed at 317 or 330 nm for Hipt reaction and 351 nm for the H_2cht^{2-} reaction by using a stopped-flow spectrophotometer (USP-500, UNISOKU Scientific Instruments, Osaka) and spectrophotometers (UV-160A and UV-2200, Shimadzu, Kyoto). The hydrogen ion concentration ($[H^+]$) in alkaline solution was measured with a pH meter (Model 654, Metrohm) with a flow of nitrogen gas. The 1.00×10^{-2} M perchloric acid solution was used as a standard of the hydrogen ion concentration. The temperature of the solutions was controlled to within ±0.1 °C.

Kinetic measurements were performed under the pseudo first-order conditions. The total concentration of boronic acid or boric acid (C_B) was in large excess over the ligands (C_L): $C_B = 1.3 \times 10^{-3}$–1.0×10^{-2} M, $C_L = 2.5 \times 10^{-5}$ M, and $[H^+] = 6.4 \times 10^{-2}$–$4.8 \times 10^{-1}$ M for the reaction of $B(OH)_3$ with Hipt; $C_B = 1.0 \times 10^{-3}$–1.0×10^{-2} M, $C_L = 1.7 \times 10^{-5}$–1.1×10^{-4} M, and $[H^+] = 1.8 \times 10^{-4}$–$8.6 \times 10^{-1}$ M for the reaction of $PhB(OH)_2$ with Hipt; $C_B = 1.5 \times 10^{-3}$–6.3×10^{-3} M, $C_L = 2.5 \times 10^{-5}$ M, and $[H^+] = 3.4 \times 10^{-8}$ M–9.8×10^{-1} M for the reaction of m-$NO_2PhB(OH)_2$ with Hipt; $C_B = 4.0 \times 10^{-3}$–1.2×10^{-2} M, $C_L = 5.0 \times 10^{-5}$ and $[H^+] = 4.0 \times 10^{-3}$–$2.4 \times 10^{-1}$ M for the reaction of n-$BuB(OH)_2$ with Hipt; $C_B = 3.8 \times 10^{-3}$–8.8×10^{-3} M, $C_L = 2.0 \times 10^{-5}$ M, and $[H^+] = 2.9 \times 10^{-10}$–$6.0 \times 10^{-9}$ M for the reaction of $B(OH)_3$ with H_2cht^{2-}. Under the present experimental conditions, boric and boronic acids exist solely as monomers such as $B(OH)_3$, $B(OH)_4^-$, $RB(OH)_2$, or $RB(OH)_3^-$. All the reaction curves were excellently single exponential, for which conditional pseudo first-order rate constants, k_0, were determined by applying a least-squares fitting.

3. Results and discussion

3.1. Kinetics for the reaction of $RB(OH)_2$ with Hipt in acidic aqueous solution

The reaction of $RB(OH)_2$ ($R = OH$, Ph, and m-NO_2Ph) with Hipt in acidic aqueous solution is expressed by Eq. (4).

$$\mathrm{RB(OH)_2} + \mathrm{Hipt} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{RB(OH)(ipt)} + \mathrm{H_2O} \qquad (4)$$

Formation rate of the 1:1 complex (RB(OH)(ipt)) was first order with respect to the total concentration of the uncomplexed ligand ($[\mathrm{IPT}'] = [\mathrm{Hipt}] + [\mathrm{H_2ipt^+}]$), thus is given by Eq. (5) under the conditions, $C_B \gg C_L$,

$$\mathrm{d[RB(OH)(ipt)]/d}t = k_0[\mathrm{IPT}'] \qquad (5)$$

where k_0 is the conditional pseudo first-order rate constant depending on the total boronic acid concentration, C_B. The rate constant k_0 was linearly dependent on C_B, e.g. as depicted in Fig. 1, hence is expressed by Eq. (6),

$$k_0 = k_f C_B + k_d \qquad (6)$$

where k_f and k_d are the rate constants for the forward and reverse reactions in Eq. (4), respectively.

Under the present experimental conditions, there exist mainly three species, Hipt, H_2ipt^+, and $RB(OH)_2$. Thus, the two reaction paths presented in Scheme 1 should be taken into account. The formation rate of RB(OH)(ipt) is then given by Eq. (7).

$$\mathrm{d[RB(OH)(ipt)]/d}t = k_1[\mathrm{RB(OH)_2}][\mathrm{H_2ipt^+}] + k_2[\mathrm{RB(OH)_2}][\mathrm{Hipt}] - k_{-1}[\mathrm{RB(OH)(ipt)}][\mathrm{H_3O^+}] - k_{-2}[\mathrm{RB(OH)(ipt)}] \qquad (7)$$

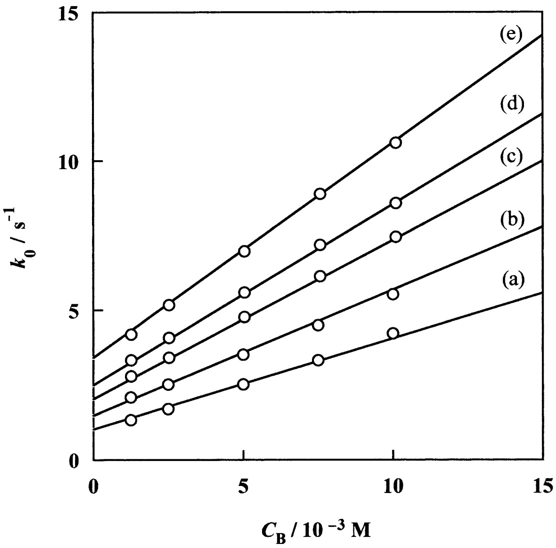
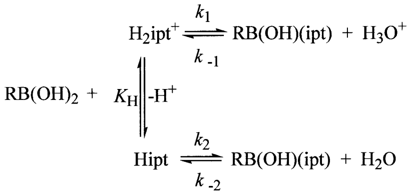


Fig. 1. Dependence of k_0 on C_B for the reaction of $B(OH)_3$ with Hipt. $I = 1.00$ M; $T = 25.0$ °C. $[H^+]$/M = 0.0640 (a), 0.144 (b), 0.240 (c), 0.320 (d), 0.480 (e).



Scheme 1. In strongly acidic aqueous solution for $R = m$-NO_2Ph-$B(OH)_2$, Ph, OH, and n-Bu.

Integration of Eq. (7) gives Eq. (8), since $K_H = [\mathrm{H_2ipt^+}][\mathrm{Hipt}]^{-1}[\mathrm{H^+}]^{-1}$, and $C_B \gg C_L$.

$$k_0 = \frac{k_1K_H[\mathrm{H^+}] + k_2}{1 + K_H[\mathrm{H^+}]}C_B + k_{-1}[\mathrm{H^+}] + k_{-2} \qquad (8)$$

Comparing Eq. (6) with Eq. (8) gives Eqs. (9) and (10).

$$k_f = \frac{k_1K_H[\mathrm{H^+}] + k_2}{1 + K_H[\mathrm{H^+}]} \qquad (9)$$

$$k_d = k_{-1}[\mathrm{H^+}] + k_{-2} \qquad (10)$$

Plots of $(1 + K_H[\mathrm{H^+}])k_f$ against $[\mathrm{H^+}]$ and k_d against $[\mathrm{H^+}]$ were linear for all the systems (e.g., Fig. 2). The values of each rate constant and activation parameter were determined by applying a least-squares fitting to Eq. (8)[1], and are listed in Table 1.

3.2. Kinetics for the reaction of $B(OH)_3$ with H_2cht^{2-} in alkaline solution

The reaction of $B(OH)_3$ with H_2cht^{2-} in alkaline solution is given by Eq. (11).

$$\mathrm{B(OH)_3} + \mathrm{H_2cht^{-2}} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{B(OH)_2(cht)^{3-}} + \mathrm{H_3O^+} \qquad (11)$$

Formation rate of the 1:1 complex ($B(OH)_2(cht)^{3-}$) was first order with respect to the total concentration of the uncomplexed ligand. Conditional pseudo first-order rate constant k_0 was linearly dependent on C_B at a given $[\mathrm{H^+}]$ as shown in Fig. 3, and thus, similarly to the Hipt system in acidic aqueous solutions mentioned above, k_0 is given by Eq. (6).

There are several potential reactants such as $B(OH)_3$, $B(OH)_4^-$, H_2cht^{2-}, and $Hcht^{3-}$ to be considered judging from the pH range employed. Therefore, the four possible reaction paths shown in Scheme 2 should be considered. For Scheme 2, the rate equation and k_0 are given by Eqs. (12) and (13), respectively, where $K_{a3} = [\mathrm{Hcht^{3-}}][\mathrm{H^+}][\mathrm{H_2cht^{2-}}]^{-1}$, $K_a = [\mathrm{B(OH)_4^-}][\mathrm{H^+}]$

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[1] The activation parameters for k_2 and k_{-2} were fixed to those determined previously under more appropriate conditions, because the K_2 (M^{-1}) value calculated from k_2/k_{-2} agreed reasonably to that obtained independently by spectrophotometry (see Table 1).

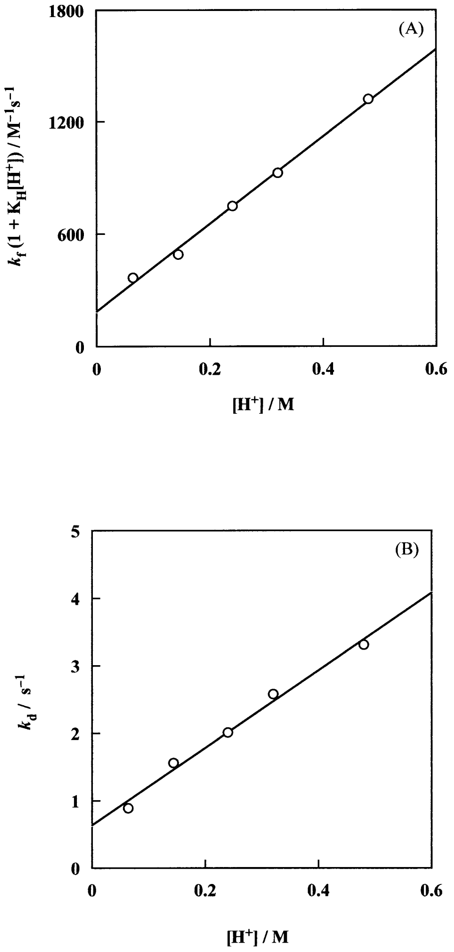


Fig. 2. Dependence of $k_f(1+K_H[H^+])$ (A) and k_d (B) on $[H^+]$ for the reaction of $B(OH)_3$ with Hipt. $I = 1.00$ M. $T = 25.0$ °C.

$[B(OH)_3]^{-1} = K_hK_w$, $K^* = (K_{a3}[H^+]^{-1}+1)(K_a[H^+]^{-1}+1)$, and K_W is ion product of water.

$$\begin{aligned}&d[B(OH)_2(cht)^{3-}]/dt\\&= k_1[B(OH)_3][H_2cht^{2-}] + k_2[B(OH)_3][Hcht^{3-}]\\&+k_3[B(OH)_4^-][H_2cht^{2-}]\\&+k_4[B(OH)_4^-][Hcht^{3-}] - k_{-1}[B(OH)_2(cht)^{3-}][H^+]\\&-k_{-2}[B(OH)_2(cht)^{3-}]\\&-k_{-3}[B(OH)_2(cht)^{3-}] - k_{-4}[B(OH)_2(cht)^{3-}][OH^-]\end{aligned} \quad (12)$$

$$\begin{aligned}k_0 &= (k_1 + k_2K_{a3}[H^+]^{-1} + k_3K_a[H^+]^{-1}\\&+k_4K_{a3}K_a[H^+]^{-2})K^{*-1}C_B\\&+k_{-1}[H^+] + k_{-2} + k_{-3} + k_{-4}K_W[H^+]^{-1}\end{aligned} \quad (13)$$

Both k_1 and k_3 paths may be negligible under the present experimental conditions (pH 8–10), since $pK_{a3} = 5.35$ for H_2cht^{2-}, though the diprotonated ligand (H_2L) is generally more reactive than the monoprotonated ligand (HL) [5,6]. Thus, Eq. (13) is simplified to Eq. (14).

$$\begin{aligned}k_0 &= (k_2K_{a3}[H^+]^{-1} + k_4K_{a3}K_a[H^+]^{-2})K^{*-1}C_B + k_2^-\\&+ k_4^-\ K_W[H^+]^{-1}\end{aligned} \quad (14)$$

The slopes multiplied by K^* and the intercepts in Fig. 3 were linearly dependent on $[H^+]^{-1}$ and $[H^+]$, respectively, as shown in Fig. 4, which disagrees with Eq. (14). Therefore, we must return to Scheme 2 and Eq. (13), where the diprotonated H_2cht^{2-} is involved. The diprotonated H_2cht^{2-} must be much more reactive than we expected.

Comparison of Eq. (6) with Eq. (13) gives Eqs. (15) and (16).

$$\begin{aligned}k_fK^* &= k_1 + (k_2K_{a3} + k_3K_a)[H^+]^{-1}\\&+ k_4K_{a3}K_a[H^+]^{-2}\end{aligned} \quad (15)$$

$$k_d = k_{-1}[H^+] + k_{-2} + k_{-3} + k_{-4}K_W[H^+]^{-1} \quad (16)$$

The straight line in Fig. 4 indicates little participation of the $B(OH)_4^- + Hcht^{3-}$ path (k_4 and k_{-4}) in Scheme 2 under the present conditions. However, k_2 and k_3 are indistinguishable kinetically, owing to so-called proton ambiguity. The upper limits for k_2 and k_3 were calculated by fixing k_1 and k_{-1} values to those determined previously under the more suitable conditions [10], provided that only one of the two paths contributes to the reaction, and are given in Table 2.

3.3. Kinetics for the reaction of *m*-$NO_2PhB(OH)_2$ with Hipt in neutral solution

The reaction of *m*-$NO_2PhB(OH)_2$ with Hipt at pH approximately 7 is expressed by Eq. (4), and the rate law is given by Eq. (5). The relation between k_0 and C_B is shown in Fig. 5(A), which indicates that k_0 is given by Eq. (6). In Fig. 5(A), the slopes vary with $[H^+]$, and the intercepts vary inexplicitly with $[H^+]$. Under the present experimental conditions, there are four possible pathways as given in Scheme 3. For Scheme 3, k_0 is given by Eq. (17), where $K_h = [RB(OH)_3^-][RB(OH)_2]^{-1}[OH^-]^{-1}$ and $K_{a2} = [ipt^-][H^+][Hipt]^{-1} = 10^{-7.01}$ (25 °C and $I = 0.100$ M) [17].

$$\begin{aligned}k_0 &=\\&\frac{k_2 + k_3K_{a2}[H^+]^{-1} + k_4k_hk_W[H^+]^{-1} + k_5k_hk_{a2}K_W[H^+]^{-2}}{(1 + K_hK_W[H^+]^{-1})(1 + K_{a2}[H^+]^{-1})}C_B\\&+k_{-2} + k_{-3}K_W[H^+]^{-1} + k_{-4}K_W[H^+]^{-1} + k_{-5}K_W^2[H^+]^{-2}\end{aligned} \quad (17)$$

The plot of k_f (obtained from the slopes in Fig. 5(A)) × $(1+K_hK_W[H^+]^{-1})(1+K_{a2}[H^+]^{-1})$ versus $1/[H^+]$ was linear within the experimental uncertainties as shown in Fig. 5(B), which denotes that the k_5 path is little relevant to the present reaction. The problem of proton ambiguity arises again, that is, k_3 and k_4 are indistinguishable kinetically. So, the upper limits of k_3

Table 1
Rate constants (25 °C and $I = 1.00$ M) and activation parameters for the reaction of $RB(OH)_2$ with 4-isopropyltropolone (Hipt) in strongly acidic aqueous solution

	pK_a	H_2ipt^+			Hipt		
		k_1 (M^{-1} s^{-1})	k_{-1} (M^{-1} s^{-1})	K_1	k_2 (M^{-1} s^{-1})	k_{-2} (s^{-1})	K_2 (M^{-1})
n-$BuB(OH)_2$	10.74 [a]	1200	4.59	261	156	0.370	422
$B(OH)_3$	8.98 [b]	1340	6.04	222	196	0.588	333
					144 [c]	0.561 [c]	257 [c]
							252 [d]
ΔH^*/kJ mol^{-1}		34.7 ± 1.4	62.2 ± 1.6		22.2 ± 3.6	63.0 ± 3.2	
					26.2 ± 0.7 [c]	68.1 ± 1.2 [c]	
ΔS^*/J $mol^{-1}K^{-1}$		−69 ± 5	−21 ± 5		−126 ± 12	−39 ± 11	
					−116 ± 4 [c]	−21 ± 4 [c]	
$PhB(OH)_2$	8.72 [e]	992	0.564	1771	354	0.120	2950
					350 [f]	0.141 [f]	2480 [f]
							2360 [d]
ΔH^*/kJ mol^{-1}		33.1 ± 1.2	71.7 ± 3.4		25.3 ± 1.2	72.6 ± 6.6	
					25.1 ± 0.3 [f]	69.0 ± 1.7 [f]	
ΔS^*/J $mol^{-1}K^{-1}$		−76.5 ± 8.1	−9.5 ± 4.0		−111 ± 5	−17.7 ± 11.1	
					−111 ± 1 [f]	−29.5 ± 5.8 [f]	
m-$NO_2PhB(OH)_2$	6.96 [g]	1300	0.211	6170	887	0.104	8530
ΔH^*/kJ mol^{-1}		34.4 ± 1.8	40.5 ± 4.8		27.6 ± 2.5	63.7 ± 5.7	
ΔS^*/J $mol^{-1}K^{-1}$		−69.9 ± 6.0	−122 ± 16		−95.9 ± 8.4	−50.1 ± 19.2	

[a] Ref. [4].
[b] Ref. [3].
[c] At $I = 0.100$ M, Ref. [10].
[d] Determined at $I = 0.100$ M by spectrophotometry.
[e] Ref. [2].
[f] Determined at $I = 0.100$ M.
[g] Ref. [1].

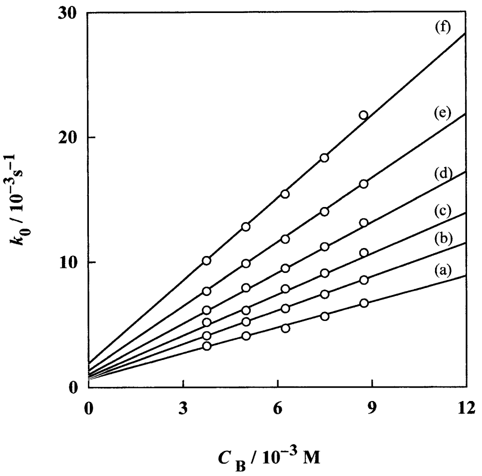
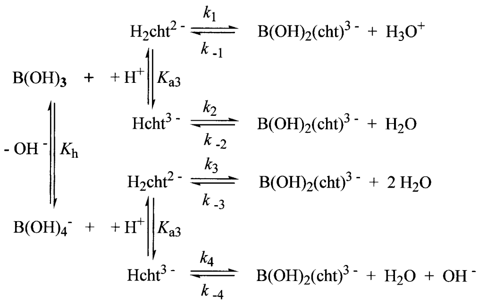


Fig. 3. Dependence of k_0 on C_B for the reaction of $B(OH)_3$ with H_2cht^{2-}. $I = 0.10$ M; $T = 35.0$ °C. $[H^+]/10^{-9}$ M = 0.659 (a), 1.01 (b), 1.42 (c), 2.14 (d), 3.47 (e), 5.79 (f).

and k_4 were calculated as stated in the previous section, and the results were listed in Table 3.

All the numerical values obtained are tabulated in Tables SI–SV (Section 5).



Scheme 2. In alkaline solution.

3.4. *Equilibrium and rate constants for the reactions with Hipt*

Babcock and Pizer reported that complexation reactions of boronic acids are characterized by stability constants that decrease as the acidities of both the boronic acid and the ligand decrease [1], and showed a linear relationship between pK_a of a variety of diprotonated ligands (H_2L) and pK_1 for the reaction of $MeB(OH)_2$ with these ligands [13]. In view of Table 1, both the pK_1 and pK_2 increase almost linearly with increasing pK_a of boronic acids. The decrease in stability constant (K_2) for the reactions of boronic acids with neutral Hipt is reflected in both a decreasing k_2 and an

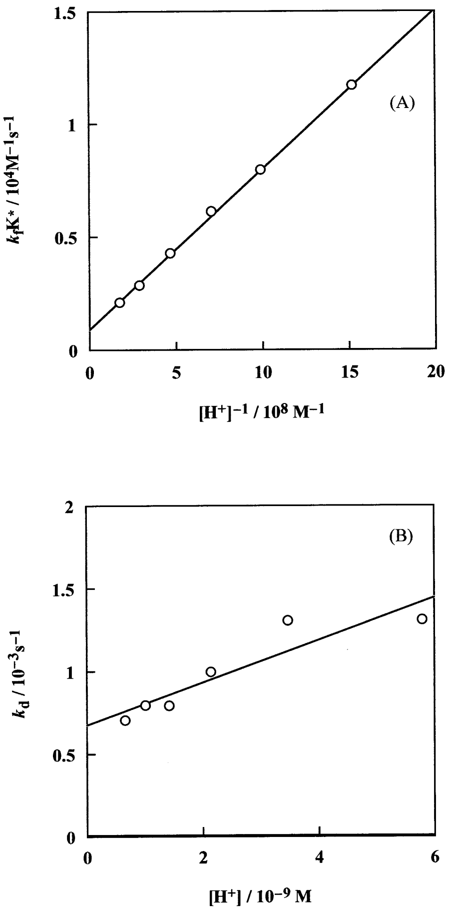


Fig. 4. Dependence of k_fK^* (A) and k_d (B) on [H$^+$] for the reaction of B(OH)$_3$ with H$_2$cht^{2-}. $I = 0.10$ M. $T = 35.0$ °C.

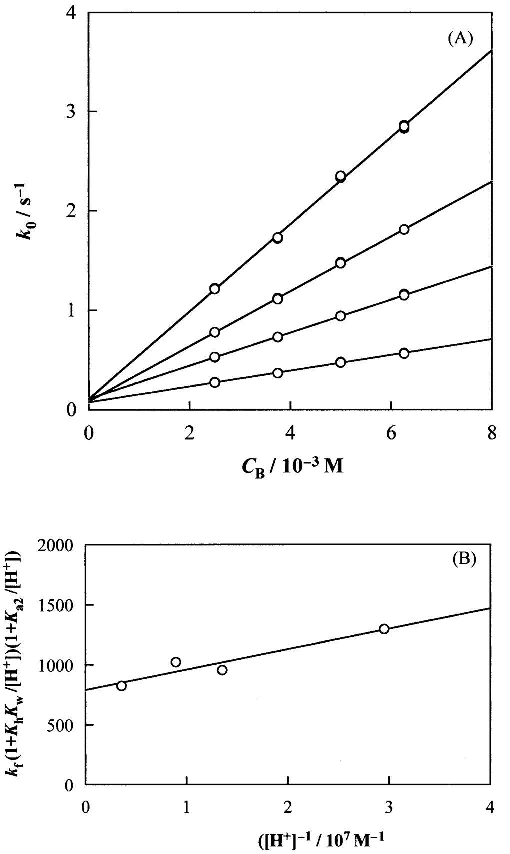


Fig. 5. Dependence of k_0 on C_B (A) and of $k_f(1+K_{a2}[H^+]^{-1})(1+K_hK_w[H^+]^{-1})$ on [H$^+$]$^{-1}$ (B) for the reaction of m-NO$_2$PhB(OH)$_2$ with Hipt. $I = 0.10$ M. $T = 25.0$ °C. [H$^+$]/10^{-7} M = 0.339 (a), 0.741 (b), 1.12 (c), 2.80 (d).

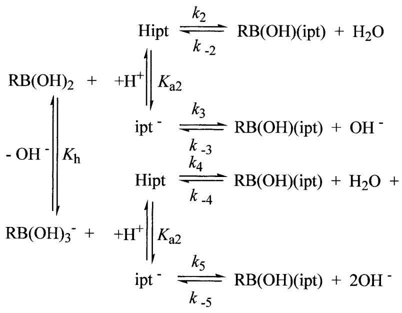
increasing k_{-2}, in accordance with Pizer and Tihal's results [13], whereas the decrease in K_1 for the reactions with cationic ligand H$_2$ipt$^+$ is reflected only in an increasing k_{-1}, since k_1 shows almost no tendency to pK_a. It can also be seen that the relation $K_2 = K_1K_H$ reasonably holds ($K_H = 1.70$ at 25 °C [14]), which supports the validity of Scheme 1.

It is obvious from Table 1 that boronic acids react faster with H$_2$ipt$^+$ than Hipt, i.e. k_1 for H$_2$ipt$^+$ is greater than k_2 for Hipt by a factor of 1.5–6.8. The upper limits of the rate constants estimated above for

Table 2
Rate constants (25 °C and $I = 0.100$ M) [a] and activation parameters for the reaction of B(OH)$_3$ with chromotropic acid (H$_2$cht^{2-}) in alkaline solution

	B(OH)$_3$				B(OH)$_4^-$	
	H$_2$cht^{2-}		Hcht^{3-}		H$_2$cht^{2-}	
	k_1 (M^{-1} s^{-1})	k_{-1} (M^{-1} s^{-1})	k_2 (M^{-1} s^{-1}) [b]	k_{-2} (s^{-1}) [b]	k_3 (M^{-1} s^{-1}) [b]	k_{-3} (s^{-1}) [b]
	1.38×10^3	1.61×10^4	1.2×10^2	3.1×10^{-3}	5.1×10^5	3.1×10^{-3}
ΔH^*/kJ mol^{-1}	12.9 ± 1.5 [c]	45.5 ± 0.6 [c]	20.6 ± 2.5 [d]	29.5 ± 3.6 [d]		
ΔS^*/J mol^{-1} K^{-1}	-141 ± 5 [c]	-12 ± 4 [c]	-136 ± 8 [d]	-194 ± 12 [d]		
ΔV^*/cm^3 mol^{-1}	-14.9 ± 1.9 [e]		-6.7 ± 1.0 [e]			
	15.3 ± 1.9 [c]	-6.3 ± 0.7 [c]				

[a] Rate constants were calculated by using the activation parameters.
[b] Upper limit estimated in the text.
[c] At 20 °C, Ref. [10].
[d] Determined by fixing the activation parameters for k_1 and k_{-1}.
[e] At 16 °C.



Scheme 3. At pH ca. 7 for R = m-$NO_2PhB(OH)_2$.

Table 3
Rate constants (25 °C and $I = 0.100$ M) for the reaction of m-$NO_2PhB(OH)_2$ with 4-isopropyltropolone (Hipt) at pH approximately 7

m-$NO_2PhB(OH)_2$		m-$NO_2PhB(OH)_3{}^-$
Hipt k_2 (M^{-1} s^{-1})	ipt^- k_3 (M^{-1} s^{-1}) [a]	Hipt k_4 (M^{-1} s^{-1}) [a]
790	170	150

[a] Upper limit estimated in the text.

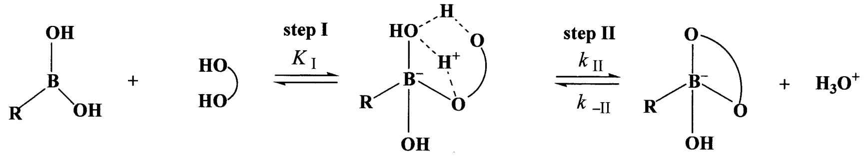
the k_3 and k_4 paths in the m-$NO_2PhB(OH)_2$ reaction are listed in Table 3. It is shown that the reaction of $RB(OH)_3{}^-$ are faster than those of $RB(OH)_2$ with the same ligand [13]. Since the k_2 and k_4 paths in Scheme 3 are for the reactions with the same ligand, Hipt, $k_4 > k_2$ should hold, if the k_4 path is relevant to the present reaction. Thus, only the k_2 and k_3 paths would contribute to the reaction. It is obvious from Table 3 that m-$NO_2PhB(OH)_2$ reacts faster with Hipt than ipt^-. Thus, the reactivity of the fully protonated ligand (H_2ipt^+) is greater than the neutral one (Hipt), and much greater than the deprotonated ligand (ipt^-), (that is, $H_2ipt^+ > Hipt > ipt^-$), which is compatible, except that the fully deprotonated ipt^- was not unreactive, with the results reported previously, i.e. the reactivities with phenylboronic acid are in the order: $k/M^{-1}\ s^{-1} =$ 2000 for H_2Ox, 350 for H_2Mal, 330 for HOx^-, 150 for $HMal^-$, while Ox^{2-} and Mal^{2-} are unreactive, where H_2Ox, HOx^-, Ox^{2-}, H_2Mal, $HMal^-$, and Mal^{2-} are oxalic acid, oxalate ion, oxalate dianion, malonic acid, malonate ion, malonate dianion, respectively [5,6]. Therefore, it can be reemphasized that the proton on the oxygen donor atom plays an important role in the process that the oxygen group in boronic acid is released as a water molecule and the more protonated ligands react more rapidly [10], unlike the complexation of metal ions.

3.5. Rate constants for the reactions with H_2cht^{2-}

For the reaction of boric acid with chromotropic acid (see Scheme 2), contrary to our expectation, k_1 path did contribute to the reaction even in an alkaline solution, although both k_1 and k_3 paths related to H_2cht^{2-} ($pK_{a1} = 5.35$) seemed to be negligible under the present experimental conditions (pH 8–10). As a result, the problem of proton ambiguity emerged between k_2 and k_3 paths. It is claimed that the tetrahedrally coordinated $B(OH)_4{}^-$ reacts much faster than the trigonal $B(OH)_3$ [1]. And as we could see above, the diprotonated species (H_2L) reacts faster than the monoprotonated species (HL). Thus, k_3 path for the reaction between $B(OH)_4{}^-$ and H_2cht^{2-} may be relevant to the present reaction. However, k_4 path for the reaction of $B(OH)_4{}^-$ with $Hcht^{3-}$ was irrelevant to the present reaction, and the monoprotonated Hipt reacted not with m-$NO_2PhB(OH)_3{}^-$ but with m-$NO_2PhB(OH)_2$. Consequently, which of the k_2 and k_3 paths should be relevant is still ambiguous. In Scheme 2, the relationship $K_1 = K_{a3}K_2$ should hold. There is some discrepancy between K_1 ($= k_1/k_{-1} = 0.086$) and $K_{a3}K_2$ ($= K_{a3}k_2/k_{-2} = 0.13$), since the estimated k_2 and k_{-2} values are the upper limits, and the measurements were resultantly performed under the inappropriate conditions.

3.6. Reaction mechanism

Complex formation reaction of boronic acid ($RB(OH)_3$) with a bidentate ligand proceeds through the two steps as shown in Scheme 4. Step I involves changes in structure (trigonal to tetrahedral) and in coordination number (3–4). At step II, the chelate ring closure occurs to the unchelated tetrahedral intermediates. Midgley reported the stability constants for the reaction of boric acid with anionic monodentate ligands: $\log K = -0.49 \pm 0.02$ and -0.43 ± 0.03 at 25 °C for $NO_2{}^-$ and acetate, respectively, where $K = [B(OH)_3(L)^-][B(OH)_3]^{-1}[L^-]^{-1}$ [18]. The stability constants suggest that the addition reaction of step I proceeds without the aid of dissociable proton when the ligand possesses a negative charge, which means that even the fully deprotonated ligands, such as Ox^{2-}, Mal^{2-}, or ipt^- that have no appreciable reactivity towards boronic acids as a bidentate ligand may act as a monodentate ligand to form unchelated tetrahedral complexes of which stability constants are quite small. This denotes that the OH^- in the tetrahedral intermediate is extremely hard to be replaced, whenever no aid of H^+ is available. In other words, at least one proton on a bidentate ligand facilitates chelate-ring formation with liberation of water molecule. If a ligand has no formal charge, it may be required either for the central boron to be more acidic like a boron in the ether adduct such as BF_3OEt_2, or for a ligand to be more basic. In fact, we found that isoquinoline reacts with boronic acids, even with methylboronic acid having lower acidity, to form tetrahedral complexes in acetonitrile.



Scheme 4.

Extensive previous works by Pizer and Hall proposed an associative transition state for the reaction of trigonal $RB(OH)_2$ with fully protonated ligands [19], and we also proposed a similar transition state. That the chelation on the tetrahedral intermediate should not be rate-determining is supported by: (a) the tetrahedral $RB(OH)_3^-$ reacts much faster than the trigonal $RB(OH)_2$ [1,13]; (b) the 1:2 complex formation proceeds much more rapidly that the 1:1 complex formation for the reaction of boric acid with lactic acid [9]; and (c) the very negative entropies of activation (see Table 1). However, it is reported recently by Yoshimura and coworkers that the 1:1 complex formation between boric acid and chromotropic acid takes place much faster than that for 1:2 complex formation [20], and is also stated that the addition of OH^- to phenylboronic acid is much slower than diffusion controlled [19]. These may suggest that the substitution on the tetrahedral complex, whether it is chelated or not, may be slow. We recently studied kinetically the reactions of boronic acids with tridentate ligand H-resorcinol which is used as a colorimetric reagent in boron determination, as shown in Scheme 5 [11]. In this scheme, it was shown that Step 3 (second chelate ring closure) is rate determining, because of strained ring closure, i.e. the observed rate constant k_0 is given by Eq. (18), and that the product of the stability constants, K_1K_2, for the first chelate ring formation decreases as pK_a of the boric acids increases.

$$k_0 = \frac{K_1 K_2 k^* C_B}{1 + K_1 K_2 C_B} \tag{18}$$

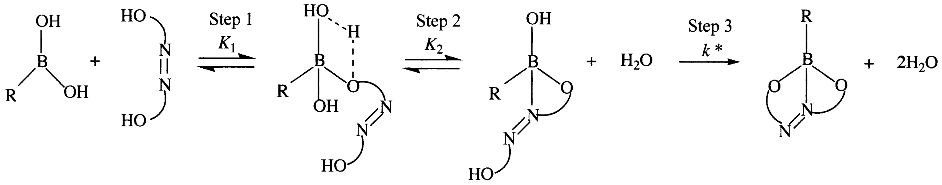
Our following kinetic study on the reaction of the *m*-nitrophenylboronic acid having

$$k_0 \frac{k_1 k_{II} C_B}{1 + K_1 C_B} + k_{-II} \tag{19}$$

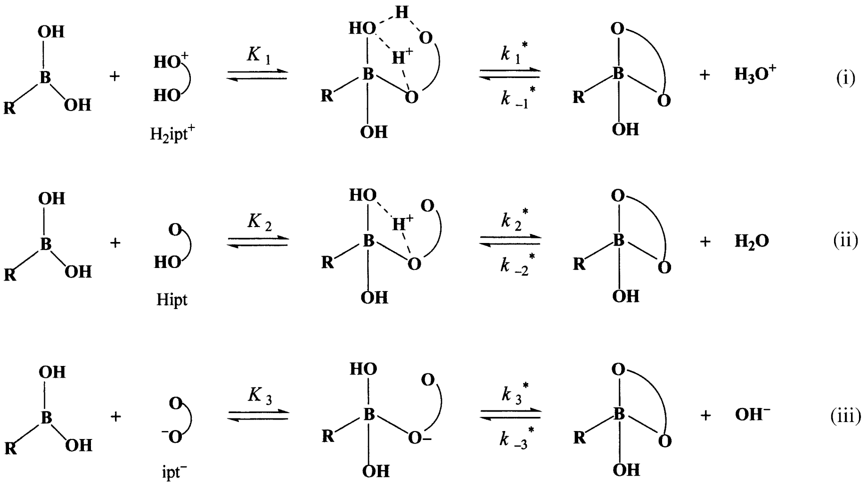
lower pK_a clearly showed that faster step I is followed by rate determining step II in Scheme 4 [21]. Then, similarly to Eq. (18), the observed rate constants, k_0, is expressed as Eq. (19). It follows from this that all the formation rate constants (k_f) reported so far for the boric and boronic acids complexation are composite value of K_I and k_{II}, i.e. $k_f = K_I k_{II}$, since $1 \gg K_I C_B$.

Thus, the formation rate constants, k_1, k_2, and k_3 in Tables 1–3 are equal to the product of the equilibrium constant (K) for the fast unchelated tetrahedral complex formation process and the rate constant (k^*) for the rate determining chelate-ring closure step, and resultantly, the observed volumes of activation are the sum of the reaction volume (ΔV) for K and the activation volume (ΔV^*) for k^*.

Two hydroxy groups in the H_2ipt^+ which is in effect in the form of tropylium ion is non-equivalent, so that it should be mentioned which hydroxy group reacts first. At step I in Scheme 4, the nucleophilic attack of the more acidic hydroxy group to the boron center would be unfavorable, since the group is positively charged. In the same course, the negatively charged oxygen atom in ipt^- is more favorable. The hydroxy group would react first in the Hipt reaction, since reactions with a series of similar ligands would proceed via a common reaction mechanism. Thus, the less acidic hydroxy group or the more basic oxygen atom seems to react first to form an unchelated complex. We observed previously a secondary kinetic isotope effect ($k_H/k_D < 2$) [22] for the reaction of $B(OH)_3$ with Hipt [10], which means that the bond to the isotope atom is not broken in the transition state [22]. As a result, Scheme 6 can be drawn for the H_2ipt^+, Hipt, and ipt^- reactions. Similar reaction scheme (Scheme 4) can be drawn for the reaction of H_2cht^{2-} in which hydroxy groups are equivalent, and also for the $Hcht^{3-}$ reaction, though the latter system is ambiguous in existence. For the reaction of Hipt, the rate constant increased as the acidity of boronic acid increases in accordance with a normal nucleophilic substitution, while for the reaction of H_2ipt^+ there was no such tendency and the reaction is faster than the Hipt reaction as mentioned above. This may be because the extra hydrogen ion on the carbonyl oxygen should participate in the addition reaction before the rate-determining chelation. The extra proton



Scheme 5.



Scheme 6. R = m-NO_2Ph.

on the carbonyl group in H_2ipt^+ or H_2cht^{2-} would accelerate the overall reaction through the second hydrogen bonding to the same hydroxy group having the first hydrogen bonding, assisting the hydroxy group in leaving as H_3O^+.

4. Conclusions

The reactivity of 4-isopropyltropolone (Hipt) towards boronic acid decreases in the order: $H_2ipt^+ > Hipt > ipt^-$. Boronate ion $RB(OH)_3^-$ showed little reactivity to Hipt. The reaction of boric acid with 4-isopropyltropolone consists of two steps, steps I and II. Step I which involves fast nucleophilic attack of the less acidic hydroxy group is followed by rate-determining step II at which chelate ring closure occurs with water molecule liberation. At least one dissociable proton is promotes a chelate ring formation by substituting one of the hydroxy groups in the tetrahedral boronic acid intermediate. Two dissociable protons in the fully protonated ligand may accelerate the overall reaction by forming two hydrogen bondings to the same hydroxy group to be released as H_3O^+ in the boronic acid intermediate. For the reaction between boric acid and chromotropic acid, the problem of proton ambiguity could not be avoided even in alkaline solution.

5. Supplementary material

Numerical values of the observed k_0 under various conditions (Table SI–SV) (21 pages) are available from the authors on request.

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