Mechanistic Study of the Complex Formation of Boric Acid
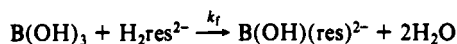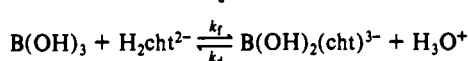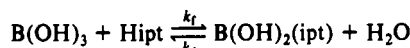
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Trigonal boric acid, $B(OH)_3$, reacts with bidentate ligands like 4-isopropyltropolone (Hipt) and chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonate, H_2cht^{2-}) and a tridentate H-resorcinol (1-((2,4-dihydroxy-1-phenyl)azo)-8-hydroxynaphthalene-3,6-disulfonate, H_2res^{2-}) to form the 1:1 complex. The reactions are represented as follows:

$$B(OH)_3 + Hipt \underset{k_d}{\overset{k_f}{\rightleftharpoons}} B(OH)_2(ipt) + H_2O$$

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

$$B(OH)_3 + H_2res^{2-} \xrightarrow{k_f} B(OH)(res)^{2-} + 2H_2O$$

Kinetic measurements were carried out at various temperatures and pressures by using a high-pressure stopped-flow apparatus with spectrophotometric detection. Rate constants (25 °C) and activation parameters obtained at $I = 0.10$ M ($NaClO_4$) are as follows: $k_f = 144$ M^{-1} s^{-1}, $k_d = 0.561$ s^{-1}, $\Delta H_f^* = 26.2 \pm 0.7$ kJ mol^{-1}, $\Delta H_d^* = 68.1 \pm 1.2$ kJ mol^{-1}, $\Delta S_f^* = -116 \pm 4$ J mol^{-1} K^{-1}, $\Delta S_d^* = -21 \pm 4$ J mol^{-1} K^{-1}, $\Delta V_f^* = -9.9 \pm 0.3$ cm^3 mol^{-1} (25 °C), and $\Delta V_d^* = -7.1 \pm 0.4$ cm^3 mol^{-1} (25 °C) for the Hipt reaction; $k_f = 1.38 \times 10^3$ M^{-1} s^{-1}, $k_d = 1.61 \times 10^4$ M^{-1} s^{-1}, $\Delta H_f^* = 12.9 \pm 1.5$ kJ mol^{-1}, $\Delta H_d^* = 45.5 \pm 0.6$ kJ.mol^{-1}, $\Delta S_f^* = -141 \pm 5$ J mol^{-1} K^{-1}, $\Delta S_d^* = -12 \pm 4$ J mol^{-1} K^{-1}, $\Delta V_f^* = -15.3 \pm 1.9$ cm^3 mol^{-1} (20 °C), and $\Delta V_d^* = -6.3 \pm 0.7$ cm^3 mol^{-1} (20 °C) for the H_2cht^{2-} reaction; $k_f = 1.01$ M^{-1} s^{-1}, $\Delta H_f^* = 45.2 \pm 0.8$ kJ mol^{-1}, $\Delta S_f^* = -93 \pm 4$ J mol^{-1} K^{-1}, and $\Delta V_f^* = 3.9 \pm 0.4$ cm^3 mol^{-1} (25 °C) for the H_2res^{2-} reaction. For the bidentate Hipt and H_2cht^{2-}, the rate-determining step is the change in the coordination environment of boron from trigonal to tetrahedral, while for the tridentate, H_2res^{2-}, the subsequent chelate-ring closure is rate limiting.

Introduction

It has been confirmed by Raman spectroscopy[2] and NMR spectrometry[3-5] that boric acid and the borate ion have trigonal and tetrahedral structures, respectively.[6] Monomeric species can exist under the limited conditions where the total concentration of boron is less than 0.025 M (M = mol dm⁻³), while polymeric ions prevail at higher concentration and at high pH.[7]

Boric acid ($pK_a = 8.98$)[8] reacts with ligands such as polyhydroxy alcohols, 1,2-benzenediols, and α-hydroxy carboxylic acids to form the stable 1:1 and 1:2 complexes, while boronic acid ($RB(OH)_2$), e.g., phenylboronic acid ($pK_a = 8.72$),[9] forms only the 1:1 complex with these ligands. In the course of the complexation, the boron changes coordination number from 3 to 4. The study of the complexation of boric acid is quite attractive mechanistically, because its complexation invokes a change in coordination number and in structure; in the case of multidentate ligands, there are two possible rate-determining steps, i.e., structural change and ring closure.

Since most of the reported complexations of boric and boronic acids are accompanied by no spectral changes in the UV–vis region, the reaction rate has been indirectly followed by monitoring the proton released during the reaction.[9-14] In the present work, we have used 4-isopropyltropolone (Hipt), chromotropic acid (sodium 1,8-dihydroxynaphthalene-3,6-disulfonate, H_2cht^{2-}), and H-resorcinol (sodium 1-((2,4-dihydroxy-1-phenyl)azo)-8-hydroxynaphthalene-3,6-disulfonate, H_2res^{2-}) as ligands, with

Hipt   **H_2cht^{2-}**

H_2res^{2-}
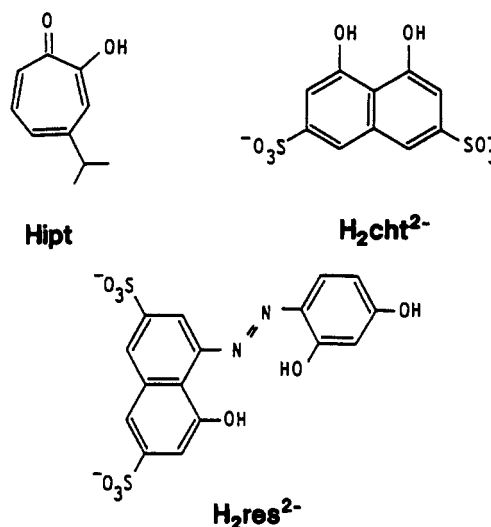
which boric acid reacts to form chelate complexes with measurable changes in the UV–vis absorption spectra. Previously, we have investigated the reaction mechanism for the complexation of Hipt with some metal ions (Fe^{3+}, Al^{3+}, Ga^{3+}, In^{3+}, and Be^{2+}).[15-18] Chromotropic acid and H-resorcinol have been used as reagents for the spectrophotometric determination of boron by means of solvent extraction[19] and flow injection analysis.[20] In the case of the determination of boron using H-resorcinol,[21] the rate of the complexation has been enhanced by heating the sample solution to ca. 100 °C because of its much slower rate in comparison to those of other ligands such as chromotropic acid.

The main objective of this work is to clarify the reaction mechanism of boric acid on the basis of the activation parameters, especially the volume of activation, and to show why the complexation rate of H-resorcinol is lower. This is the first high-

(1) Present address: Department of Chemistry, School of Science and Engineering, Waseda University, Tokyo, 169.
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(21) Toei, K.; Motomizu, S.; Oshima, M.; Onoda, M. *Bunseki Kagaku* 1986, *35*, 344.

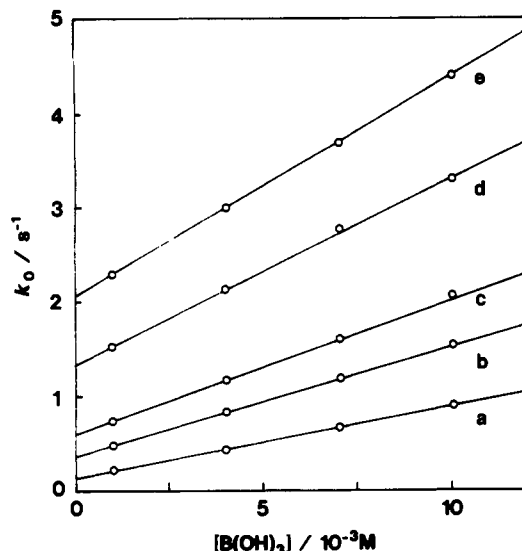**Figure 1.** Conditional first-order rate constants for the Hipt reaction as a function of boric acid concentration at different temperatures. C_{Hipt} = 1.06×10^{-4} M; [H$^+$] = 1.02×10^{-4} M; $T/°C$ = 10.5 (a), 20.2 (b), 25.4 (c), 34.2 (d), 39.1 (e).

pressure study of the complexation of boric acid.

Experimental Section

Materials. 4-Isopropyltropolone (Hipt, Takasago Perfumery Co., Ltd., Tokyo) was purified by vacuum sublimation. Chromotropic acid (Na$_2$H$_2$cht, Wakojunyaku, Osaka) was recrystallized from aqueous ethanol and dried under reduced pressure at room temperature. H-Resorcinol (Na$_2$H$_2$res) was used as donated.[22] Reagent grade boric acid (Wakojunyaku) was recrystallized from distilled water. A solution of sodium perchlorate was prepared as previously described.[23] Perchloric acid-d_1 (Aldrich, Gold Label, 68%), boric acid-d_3 (MSD ISOTOPES, 98%), and deuterium oxide (Merck, 99.8%) were used for the isotopic experiments.

Measurements. The temperature of the reaction solution was maintained to within ±0.1 °C. The ionic strength was kept at 0.10 M with sodium perchlorate. Reaction rates for the complex formation of boric acid were followed at 330 nm for the Hipt reaction, at 351 nm for the H$_2$cht^{2-} reaction, and at 510 nm for the H$_2$res^{2-} reaction by using a stopped-flow spectrophotometer (Type RA401, Union Giken, Osaka), a high-pressure stopped-flow apparatus (Type FIT-3),[24,25] or a standard spectrophotometer (Shimadzu UV 265) with a high-pressure static vessel equipped with a le Noble type quartz cell.[26] The hydrogen ion concentration ([H$^+$]) was measured with a pH meter (Model 605, Metrohm) on the basis of the liquid-junction potential.

In the kinetic experiments, the total concentrations of boric acid, ligands, and hydrogen ion were as follows: $C_{B(OH)_3}$ = 10^{-3}–10^{-2} M, C_{Hipt} = $(1-3) \times 10^{-4}$ M, C_{H_2cht} = 4×10^{-5} M, C_{H_2res} = $(2-3) \times 10^{-5}$ M, and [H$^+$] = $(0.7-7) \times 10^{-4}$ M; for the B(OD)$_3$ + Dipt reaction, $C_{B(OD)_3}$ = $(3.97-9.93) \times 10^{-3}$ M, C_{Na-ipt} = 9.98×10^{-5} M, and [D$^+$] = 10^{-4} M. Under our experimental conditions, boric acid exists as B(OH)$_3$[27,28] and was used in large excess over the ligands to maintain pseudo-first-order conditions. All the reaction curves fell excellently on the single-exponential functions. Conditional pseudo-first-order rate constants, k_0, were determined by a least-squares analysis. Boron-11 NMR spectra were obtained on a Varian XL300 NMR spectrometer.

Results

It is without doubt that Hipt and H$_2$cht^{2-} act as bidentate ligands in the present system. If H$_2$res^{2-} serves as an O,O-bidentate ligand, a proton should be released, but there is no proton release when it operates as an N,O-bidentate ligand or a tridentate
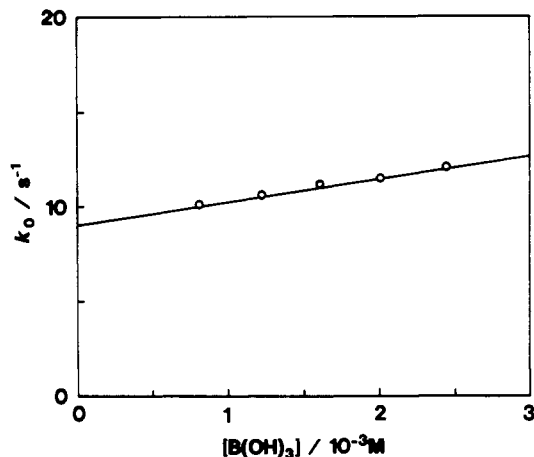
(22) H-Resorcinol was prepared and donated to us by S. Motomizu and M. Oshima at the Department of Chemistry, Faculty of Science, Okayama University, Okayama-shi, 700 Japan.
(23) Funahashi, S.; Haraguchi, K.; Tanaka, M. *Inorg. Chem.* **1977**, *16*, 1349.
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Figure 2. Conditional first-order rate constants for the H$_2$cht^{2-} reaction as a function of boric acid concentration at 20.0 °C. C_{H_2cht} = 5.33×10^{-5} M; [H$^+$] = 7.74×10^{-4} M.

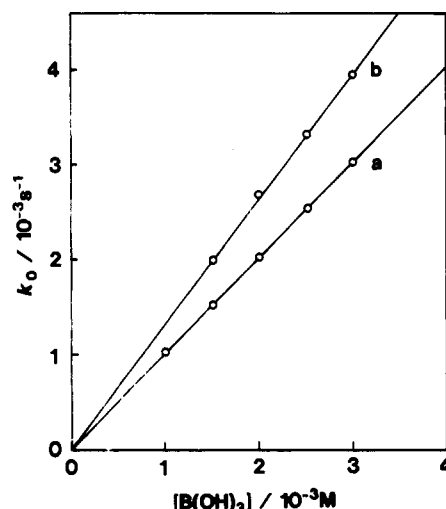**Figure 3.** Conditional first-order rate constants for the H$_2$res^{2-} reaction as a function of boric acid concentration at different temperatures. C_{H_2res} = 2.2×10^{-5} M; [H$^+$] = 1.07×10^{-4} M; $T/°C$ = 25.0 (a), 29.2 (b).
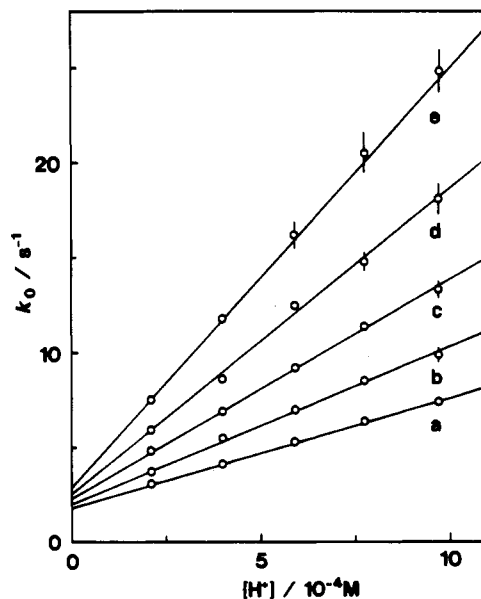

Figure 4. Conditional first-order rate constants for the H$_2$cht^{2-} reaction as a function of hydrogen ion concentration at different temperatures. $C_{B(OH)_3}$ = 1.82×10^{-3} M; C_{H_2cht} = 4.79×10^{-5} M; $T/°C$ = 10.0 (a), 15.0 (b), 20.0 (c), 25.0 (d), 30.0 (e).

ligand. In light of the lower affinity of boron for a nitrogen donor atom than for an oxygen donor atom, the fact that H$_2$res^{2-} reacts
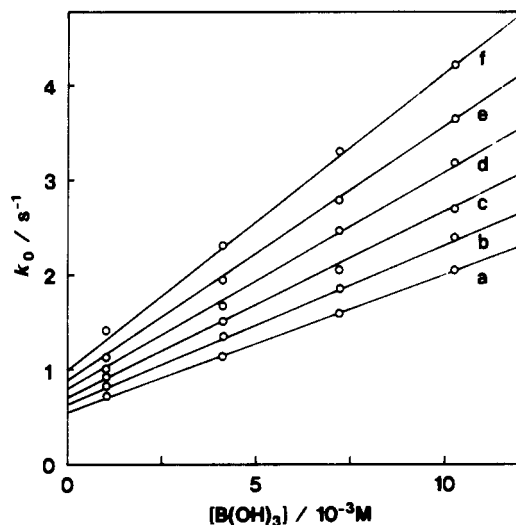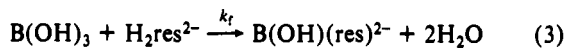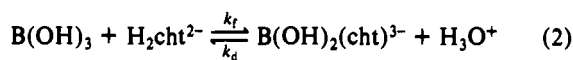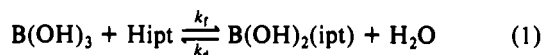
Figure 5. Pressure effect on conditional first-order rate constants for the Hipt reaction as a function of boric acid concentration at 25.0 °C. C_{Hipt} = 1.06 × 10⁻⁴ M; [H⁺] = 1.02 × 10⁻⁴; P/MPa = 0.1 (a), 39.2 (b), 78.5 (c), 118 (d), 157 (e), 196 (f).

with $B(OH)_3$ quantitatively to produce the complex without any proton release strongly indicates that it acts as a tridentate ligand.

Thus, the reactions studied in this work are expressed by eqs 1–3. Plots of the conditional first-order rate constants, k_0, against

$$B(OH)_3 + Hipt \underset{k_d}{\overset{k_f}{\rightleftharpoons}} B(OH)_2(ipt) + H_2O \quad (1)$$

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

$$B(OH)_3 + H_2res^{2-} \overset{k_f}{\longrightarrow} B(OH)(res)^{2-} + 2H_2O \quad (3)$$

the boric acid concentration, $[B(OH)_3]$, are linear (see Figures 1–3). Under the present experimental conditions over the pH range from 3.5 to 4.5, the rates for the Hipt and H_2res^{2-} reactions are independent of the hydrogen ion concentration, while the rate for the H_2cht^{2-} reaction is dependent on the hydrogen ion concentration (see Figure 4). There is negligible contribution of the backward reaction for the H_2res^{2-} reaction, as is obvious from Figure 3. Thus, the conditional first-order rate constants are expressed as follows:

$$Hipt \text{ system:} \quad k_0 = k_f[B(OH)_3] + k_d \quad (4)$$

$$H_2cht^{2-} \text{ system:} \quad k_0 = k_f[B(OH)_3] + k_d[H^+] \quad (5)$$

$$H_2res^{2-} \text{ system:} \quad k_0 = k_f[B(OH)_3] \quad (6)$$

Values of k_f and k_d for each system were determined at various temperatures (Figures 1–4) and pressures (Figure 5 and Tables SI and SII in the supplementary material). The obtained numerical values are tabulated in Tables SIII–SX (supplementary material). The activation parameters were evaluated by applying a least-squares fitting to eqs 4–6 and maintaining relation 7 or 8 for each rate constant, where k^0 represents the rate constant at zero pressure. The parameters obtained are listed in Table I.

$$k = k^0 \exp(-\Delta V^\ddagger / RT) \quad (7)$$

$$k = (\kappa T/h) \exp(-\Delta H^\ddagger / RT) \exp(\Delta S^\ddagger / R) \quad (8)$$
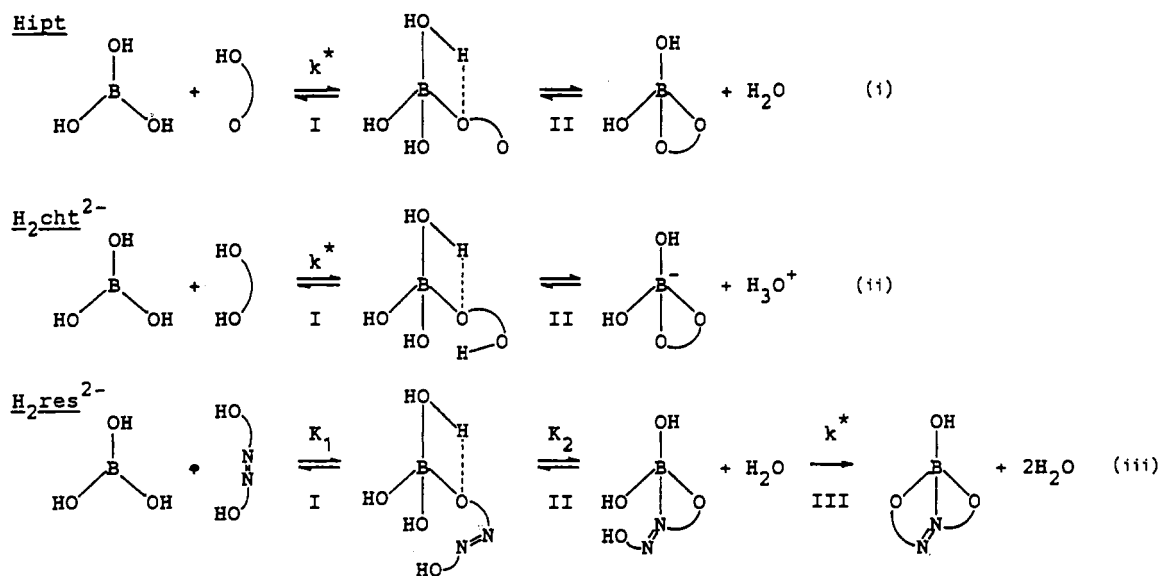
Discussion

Thermodynamic parameters for reactions 1 and 2 were evaluated from the kinetic parameters obtained (see Table I). For validation of the kinetic results, the equilibrium constants for reactions 1 and 2 were determined spectrophotometrically: K_{ipt} = 252 ± 24 M⁻¹ and K_{cht} = (8.4 ± 0.5) × 10⁻² at 25 °C and I = 1.00 M, which are in excellent agreement with those kinetically obtained. Stability constants ($K_{B(OH)_2L}$) for reactions of boric acid with fully protonated neutral ligands (H₂L: 4-methylcatechol,

Table I. Thermodynamic and Kinetic Parameters for the Reaction of Boric Acid with Hipt, H_2cht^{2-}, and H_2res^{2-} at I = 0.10 M (NaClO₄)

	formation reaction				dissociation reaction				equilibrium[a]			
ligand	k_f(25.0 °C)/ M⁻¹ s⁻¹	$\Delta V_f^\ddagger$/ cm³ mol⁻¹	$\Delta H_f^\ddagger$/ kJ mol⁻¹	$\Delta S_f^\ddagger$/ J mol⁻¹ K⁻¹	k_d(25.0 °C)/ s⁻¹	$\Delta V_d^\ddagger$/ cm³ mol⁻¹	$\Delta H_d^\ddagger$/ kJ mol⁻¹	$\Delta S_d^\ddagger$/ J mol⁻¹ K⁻¹	K(25.0 °C)	ΔV/cm³ mol⁻¹	ΔH/kJ mol⁻¹	ΔS/J mol⁻¹ K⁻¹
Hipt	144	−9.9 ± 0.3 (25.0 °C)	26.2 ± 0.7	−116 ± 4	0.561	−7.1 ± 0.4 (25.0 °C)	68.1 ± 1.2	−21 ± 4	2.57 × 10²ᵇ (2.52 ± 0.24) × 10²ᵇ,ᶜ	−2.8	−41.9	−95
Dipt[d]	112 ± 1				0.391 ± 0.009							
H_2cht^{2-}	1.38 × 10³	−15.3 ± 1.9 (20.0 °C)	12.9 ± 1.5	−141 ± 5	1.61 × 10⁴ᵉ	−6.3 ± 0.7 (20.0 °C)	45.5 ± 0.6	−12 ± 4	8.57 × 10⁻² (8.4 ± 0.5) × 10⁻²ᶜ	−9.0	−32.6	−129
H_2res^{2-}	1.01	3.9 ± 0.4 (25.0 °C)	45.2 ± 0.8	−93 ± 4								

[a] Evaluated from the kinetic parameters obtained. [b] In M⁻¹. [c] Determined spectrophotometrically in equilibria. [d] The reaction of B(OD)₃ with Dipt at 24.7 °C (see text). [e] In M⁻¹ s⁻¹.

Scheme I

Hipt

$$\text{I} + \text{(ligand)} \underset{}{\overset{k^*}{\rightleftharpoons}} \text{II} \rightleftharpoons \text{(product)} + H_2O \qquad (i)$$

H_2cht^{2-}

$$\text{I} + \text{(ligand)} \underset{}{\overset{k^*}{\rightleftharpoons}} \text{II} \rightleftharpoons \text{(product)} + H_3O^+ \qquad (ii)$$

H_2res^{2-}

$$\text{I} \cdot \text{(ligand)} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{II} \overset{K_2}{\rightleftharpoons} \text{(product)} + H_2O \overset{k^*}{\longrightarrow} \text{III} + 2H_2O \qquad (iii)$$

catechol, 4-nitrocatechol, tartaric acid, and salicylic acid) have been claimed to increase with increasing ligand acidity.[11] In fact, a plot of log $K_{B(OH)_2L}$ vs pK_{a1} of the ligands shows a nearly linear relationship having a slope of about $-^1/_2$. The stability constant of H_2cht^{2-} is 3 orders of magnitude higher than that expected from the relationship because pK_{a1} of H_2cht^{2-} is 5.56.[29] Furthermore, we measured the chemical shifts of boron-11 in the 1:1 boron complexes.[30] There is no trend in the relation between the chemical shifts and pK_{a1} or log $K_{B(OH)_2L}$. Thus, the stability of the boron complexes should be affected by various factors such as the basicity and charge of the ligand and the size and flexibility of the chelate ring.

Interestingly, large negative values of entropy change (ΔS) imply an increase in the coordination number of the central boron and clearly reflect the change in the boron structure from trigonal to tetrahedral. Similarly, large entropy changes have been demonstrated in the tetrahedral–octahedral interchange.[31]

The most plausible reaction mechanisms are presented in Scheme I. During the first step (I), the hydroxyl group of the entering ligand binds to $B(OH)_3$ to form a tetrahedral intermediate complex; i.e., in this stage boron undergoes a change in coordination number from 3 (sp^2) to 4 (sp^3). The proton in the entering ligand to be released may interact with a hydroxyl group from $B(OH)_3$ via hydrogen bonding in a transition state, and then the proton may move to the hydroxyl group to give a coordinated water molecule in the intermediate. The transition state for step I is the distorted tetrahedron, depicted as
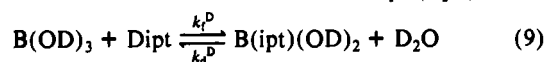
Transition state
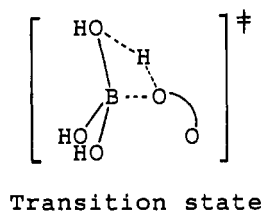
The second step (II) is the chelate-forming ring closure with dissociation of a coordinated water molecule in the intermediate.

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(30) External referencing of the boron-11 spectra was made by taking the signal for H_3BO_3 in water as $\delta = 0.00$ ppm. Chemical shifts (δ, ppm) at 23 °C: Hipt, -10.35; H_2cht^{2-}, -17.95; H_2res^{2-}, -19.13; tartaric acid, -12.96; 4-nitrocatechol, -10.97; lactic acid, -13.13; salicylic acid, -16.51.
(31) (a) Ishiguro, S.; Ozutsumi, K.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 531. (b) Ishiguro, S.; Ozutsumi, K.; Ohtaki, H. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2409. (c) Suzuki, H.; Ishiguro, S.; Ohtaki, H. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2179. (d) Ishiguro, S.; Ozutsumi, K. *Inorg. Chem.* **1990**, *29*, 1117.

Also, in the case of the H_2cht^{2-} ligand with two equivalent hydroxyl groups and in the case of the Hipt ligand, the hydroxyl oxygen instead of the carbonyl oxygen may first bind to the central boron atom. In the case of the H_2res^{2-} ligand with two hydroxyl groups on the ortho position relative to the azo group and on the α-position of naphthalene ring, the latter hydroxyl group with higher basicity may coordinate first. Subsequently step II is not O-coordination but N-coordination, because a five- or six-membered chelate ring is more favorable than the other chelate rings. Finally, the closure of the second chelate ring by the phenolic hydroxyl group is followed by step III.

There are significant data to show that the reactions of (*m*-nitrophenyl)boronate anion $(RB(OH)_3^-)$ with salicylic and mandelic acids are 3–4 orders of magnitude faster than the reactions of (*m*-nitrophenyl)boronic acid $(RB(OH)_2)$.[10] The observed second-order rate constants, k_f, for the $RB(OH)_2$ reaction and for the $RB(OH)_3^-$ reaction are 6.5×10^2 and 1.0×10^6 M^{-1} s^{-1} for salicylic acid and 2.5×10^3 and 2.4×10^7 M^{-1} s^{-1} for mandelic acid, respectively. The fact that the tetrahedral $RB(OH)_3^-$ reacts much faster than the trigonal $RB(OH)_2$ supports the fact that the chelation on the tetrahedral intermediate should not be rate limiting.

The rate constant k_f for the H_2res^{2-} reaction is approximately 2 orders of magnitude smaller than those for the other reactions (see Table I). Moreover, the activation volume for the former is positive, while it is negative for the latter. From these observations it was concluded that for the Hipt and H_2cht^{2-} systems the rate-determining step is step I with rate constant k^*, while step III is rate limiting for the H_2res^{2-} system. Therefore, $k_f = k^*$ for reactions 1 and 2, and $k_0 = K_1K_2k^*[B(OH)_3]/\{1 + K_1[B(OH)_3](1 + K_2)\}$ for reaction 3. Since we have not observed any intermediates using a rapid-scan spectrophotometer under our experimental conditions $(10^{-2}$ mol $dm^{-3} > [B(OH)_3] \gg [H_2res^{2-}])$, K_1 and K_2 should be small. Thus, the forward rate constant for reaction 3 is reduced to the form $k_f = K_1K_2k^*$. Small K_1 and K_2 values are responsible for the much slower overall rate of reaction 3.

According to the literature,[12,13] the reactivities of oxalic acid (H_2Ox), malonic acid (H_2Mal), oxalate ion (HOx^-), malonate ion $(HMal^-)$, oxalate dianion (Ox^{2-}), and malonate dianion (Mal^{2-}) with phenylboronic acid are in the following order: k/M^{-1} $s^{-1} = 2000$ for H_2Ox, 350 for H_2Mal, 330 for HOx^-, 150 for $HMal^-$, while the dianions Ox^{2-} and Mal^{2-} are unreactive. The reactivity underlines the significance of the proton to be released. To confirm this point, we have measured the rate for the reaction of the deuterated boric acid with deuterated Dipt (eq 9). The

$$B(OD)_3 + Dipt \underset{k_d^D}{\overset{k_f^D}{\rightleftharpoons}} B(ipt)(OD)_2 + D_2O \qquad (9)$$

rate constants are reduced by 20–30% when the reactants are deuterated (see Table I). This indicates that the proton on the oxygen donor atom plays an important role in the reaction. At least one proton is absolutely necessary for the hydroxyl group in boric acid to be released as a water molecule and the more protonated ligands react more rapidly. In fact, the difference in reactivity between Hipt and H_2cht^{2-} is significant.

Concerning a number of reaction systems, it has been demonstrated that activation volumes are very useful for diagnosing the reaction mechanism.[32] We shall discuss the pressure effect of the present reactions. The experimentally obtained activation volume, ΔV_f^*, for the forward reaction is given as follows for each respective step: for the Hipt and H_2cht^{2-} systems $\Delta V_f^* = \Delta V^{**}$ and for the H_2res^{2-} system $\Delta V_f^* = \Delta V_1^\circ + \Delta V_2^\circ + \Delta V^{**}$, where ΔV_1° and ΔV_2° are the reaction volumes for step I and step II, respectively, and ΔV^{**} is the activation volume for the rate-determining step.

The fact that the boron–oxygen bond lengths are 137 pm in $B(OH)_3$ and 148 pm in $B(OH)_4^-$, respectively,[33] implies that the structural change from the trigonal boric acid to the tetrahedral unchelated complex causes an increase in the boron–oxygen bond length. On the other hand, the entrance of a hydroxyl group into the inner sphere of boric acid invokes a volume decrease. The latter volume-decreasing effect would prevail, and consequently the volume of activation is negative for the forward reactions of eqs 1 and 2 (see Table I). Furthermore, large negative values of entropy of activation are in accordance with considerably large negative volumes. Thus, the forward reactions of eqs 1 and 2 should proceed by the mechanism with an associative mode.

We can postulate that the sum of volume changes ($\Delta V_1^\circ + \Delta V_2^\circ$) for steps I and II in the H_2res^{2-} reaction is almost equal to the overall reaction volume ($\Delta V^\circ = \Delta V_f^* - \Delta V_d^* = -2.8 \pm 0.7$ cm³ mol⁻¹) for the Hipt reaction because of their similarity (see Scheme I). ΔV^{**} for step III in the H_2res^{2-} reaction should then be equal to $\Delta V_f^* - (\Delta V_1^\circ + \Delta V_2^\circ) = 3.9 - (-2.8) = +6.7$ cm³ mol⁻¹. This second chelate-forming step (III) corresponds to the ring closure of the tetrahedral complex. Therefore, at this stage it is worthwhile to compare step III in Scheme I to the complexation of a tetrahedral metal ion such as the beryllium(II) ion.

The activation volume for the reaction between the tetrahedral beryllium(II) ion and Hipt in aqueous solution is negative (−7.1 cm³ mol⁻¹),[18] while that of the second chelate-ring closure in the H_2res^{2-} reaction is positive (+6.7 cm³ mol⁻¹) as previously estimated. The chelate-forming six-membered-ring closure of the small central atom such as boron is sterically difficult due to strain. This may result in a volume increase of the transition state and is the reason that reaction 3 is much slower compared with reactions 1 and 2.

The volume of activation for the reverse reaction, i.e. the complex dissociation reaction, corresponds to the difference in partial molar volume between a transition state and a final state. The dissociation reaction involves a ring-opening step as a preequilibrium, as shown in Scheme I. In step II for the H_2cht^{2-} system an oxonium ion (H_3O^+) is the entering ligand and the leaving group is the hydroxyl group in H_2cht^{2-}. ΔV_2° for step II of this reaction should then be positive because of charge neutralization during the reaction. Therefore, the activation volume for the activation process should be more negative than the overall activation volume (−6.3 cm³ mol⁻¹) for the dissociation reaction. The difference between the overall reaction volumes for reactions 1 and 2 is −6.2 cm³ mol⁻¹, which may correspond to the electrostriction due to the released proton.[34] Thus, the mechanisms may be substantially the same for both reactions 1 and 2. In conclusion, both the forward and reverse processes for reactions 1 and 2 should be activated via the associative mode.

Registry No. Hipt, 499-44-5; $B(OH)_3$, 10043-35-3; chromotropic acid, 148-25-4; H-resorcinol, 3627-01-8.

Supplementary Material Available: Observed rate constants at various temperatures and pressures (Tables SI–SX) (10 pages). Ordering information is given on any current masthead page.

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Reduction of the Tetrahydroxoargentate(III) Ion by Thiocyanate in Aqueous Alkaline Media

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The reduction of $Ag(OH)_4^-$ by thiocyanate ion in the range $5 \times 10^{-4} \leq [SCN^-] \leq 0.25$ M was studied in aqueous alkaline media at 25 °C and $\mu = 1.2$ M by stopped-flow spectrophotometry. At $[SCN^-] \leq 0.01$ M, the reaction was found to be first-order in each reactant, with an apparent second-order rate constant of 21.7 ± 0.3 M⁻¹ s⁻¹. At higher thiocyanate concentrations, silver(III) disappearance continues to appear pseudo first order, but the thiocyanate dependence becomes complex. Oxidation products are SO_4^{2-}, OCN^-, and (at high SCN^- only) cyanide ion. A mechanism is proposed consisting of a series of two-electron redox steps. Competition between SCN^- and reaction intermediates for remaining silver(III) accounts for changes in both rate and product distribution. The activation enthalpy and entropy for the initial step are 28.3 ± 1.2 kJ mol⁻¹ and -129 ± 7 J mol⁻¹ K⁻¹ respectively. Numerical simulation and reaction with potential intermediates have been used to support the conclusions.

Introduction

The oxidation of thiocyanate is often complicated by the varied oxidation states of sulfur and the relative redox instability of cyanide, which is a potential product. Sulfate and cyanide are often the major products,[1–4] but additional species can be found, including $(SCN)_2$,[5] $S(CN)_2$,[6] and $OSCN^-$,[7] which hydrolyze under relevant conditions to sulfate and cyanide or cyanate. Under

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