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Direct kinetic measurements for the fast interconversion process between trigonal boronic acid and tetragonal boronate ion at low temperatures

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Abstract

The rate constant, k_1 , for the following addition reaction between 4-isopropyltropolonate (ipt⁻) and *meta*-nitrophenylboronic acid (*m*-NO₂PhB(OH)₂) in acetonitrile was measured at various temperatures by using a low-temperature stopped-flow spectrophotometer:

$$m$$
-NO₂PhB(OH)₂ + ipt⁻ $\underset{k=1}{\overset{k_1}{\underset{k=1}{\underset{k=1}{\atop}}}} m$ -NO₂PhB(OH)₂(ipt)⁻;

 $k_1 = 7.9 \times 10^4 \text{M}^{-1} \text{s}^{-1}$ at 25 °C, $\Delta H_1^* = 34.7 \pm 1.0 \text{ kJ mol}^{-1}$, $\Delta S_1^* = -34.8 \pm 3.8 \text{ J mol}^{-1} \text{K}^{-1}$, which indicates that the interconversion between the trigonal boronic acid and the tetrahedral boronate ion is much faster than the chelate formations for the complexation of boronic acid with bidentate ligands, but much slower than the diffusion-controlled reactions. © 2005 Elsevier B.V. All rights reserved.

Keywords: m-Nitrophenylboronic acid; 4-Isopropyltropolonate; Interconversion; Kinetics

Boronic acids (RB(OH)₂) are weak acids, of which $pK_{a}s$ are ranging from 7 to 11 depending on the substituent, R [1–5]. Lewis acid–base reaction of boronic acid is expressed as Eq. (1), in which structural change from trigonal to tetrahedral occurs. We have been interested in the reactivity of boronic acid including boric acid (R = OH in Eq. (1)), especially in the rate of the structural change. Anderson et al. [6] performed kinetic studies on polyborate formation by the temperature jump technique and predicted the second-order rate constant (~10¹⁰ M⁻¹s⁻¹) for the forward reaction of boric acid



Waton et al. [7] reported much faster rate constant $(1.07 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$ for the same reaction which was obtained by the relaxation method with thymol blue as indicator. Pizer and Tihal [8] stated that the addition of OH⁻ to phenylboronic acid (PhB(OH)₂) is much slower than diffusion controlled. In these relaxation studies, pH indicators were used to monitor the reactions indirectly. Recently, we have tried to measure the rate

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constant for the addition reaction of isoquinoline to boric acid (Eq. (2)) in acetonitrile without the aid of pH indicator. The UV-vis spectral change of isoquinoline due to complexation with boric acid was followed as a function of time. We have estimated the forward rate constant to be in the order of $10^4 \text{ M}^{-1} \text{s}^{-1}$ at $-35 \,^{\circ}\text{C}$ for the reaction in Eq. (2) in acetonitrile, but the precise determination could not be done because of interference by water in the acetonitrile solution [5]



In the present study, we studied kinetically the reaction of *meta*-nitrophenylboronic acid (*m*-NO₂PhB(OH)₂) with 4-isopropyltropolonate ion (ipt⁻) (Eq. (3)) in acetonitrile by using a low temperature stopped-flow spectrophotometer. Fully deprotonated bidentate ipt⁻ was used as ligand, because it acts basically as monodentate ligand in acetonitrile and gives rise to very large change in UV–vis spectrum when it reacts with Lewis acid. We have succeeded to determine directly the rate constant and the activation parameters for the interconversion step in the following equation



Sodium 4-isopropyltropolonate (Naipt) was prepared by neutralization of 4-isopropyltropolone (Hipt) which was purified as described previously [9] with equimolar sodium hydroxide. *m*-NO₂PhB(OH)₂ (Aldrich) was recrystallized once from water. Dehydrated acetonitrile (Kanto Chemical Co. Inc., Tokyo) was used as received. Tetra-*n*-butylammonium perchlorate (TBAP, Kanto) was recrystallized twice from ethyl acetate and *n*-hexane, and dried in vacuo.

All the sample solutions were prepared in a dry box. Water contents of sample solutions were measured by an aquacounter (AQ-200, Hiranuma Sangyo. Co. Ltd., Mito, Japan). Purchased dehydrated acetonitrile contained 9.7×10^{-4} M of water. Kinetic measurements were performed with a rapid-scan/stopped-flow spectrophotometer RSP601S with a low temperature mixing unit

(UNISOKU Scientific Instruments, Osaka). Rate constants for the complex formation of m-NO₂PhB(OH)₂ with Naipt in acetonitrile were measured by monitoring the absorbance change at 380 or 400 nm with time under the pseudo first-order conditions that the total concentration of boronic acid (C_B) was in large excess over the ligand (C_L), at -30 to -0 °C and I = 0.10 moldm⁻³ (TBAP). All the reactions were observed as a two-step reaction consisting of two single exponentials. The conditional pseudo first-order rate constants, k_{obs1} and k_{obs2} , were determined by applying a nonlinear least-squares fitting of the equation [10]. The ¹¹B{¹H} NMR spectra were recorded on a Bruker Avance 400 spectrometer. The chemical-shift was referenced to boric acid (B(OH)₃, $\delta_B = 18$ ppm to Et₂O · BF₃ adduct).

Under the pseudo first-order conditions, $C_B \gg C_L$, a two-step reaction was observed for the reaction of m-NO₂PhB(OH)₂ with ipt⁻ in acetonitrile as shown in Figs. S1 and S2, namely, the very fast first-order reaction was followed by the slow first-order reaction. Both the observed pseudo first-order rate constants, k_{obs1} and k_{obs2} , are linearly dependent on C_B as shown in Fig. 1, so they are expressed as Eqs. (4) and (5), respectively, where k_{f1} and k_{f2} are the second-order rate constants [10]

$$k_{\rm obs1} = k_{\rm f1} C_{\rm B},\tag{4}$$

$$k_{\rm obs2} = k_{\rm f2} C_{\rm B}.\tag{5}$$

The ¹¹B{¹H} NMR spectra in Fig. 2 which were acquired under the conditions, $C_{\rm B} > C_{\rm L}$, show that the products of the slower reaction are the equimolar mixture of the chelate complex (B, *m*-NO₂PhB(ipt)(OH)) and *meta*nitrophenylboronate ion (C, *m*-NO₂PhB(OH)₃⁻). The UV-vis spectra of ipt⁻ at various concentrations of boronic acid were measured in acetonitrile, and analyzed successfully into the spectra of the individual species as shown in Fig. S3. So, the observed rapid and slow reactions correspond to steps 1 and 2, respectively, as shown in Scheme 1. Therefore, the rate equations for Scheme 1 are expressed in the following equation:

$$- d[ipt^{-}]/dt = k_{obs1}[ipt^{-}] - k_{-1}[(I)],$$

$$d[(I)]/dt = k_{obs1}[ipt^{-}] - (k_{obs2} + k_{-1})[(I)] + k_{-2}[B][C],$$

$$d[B]/dt = d[C]/dt = k_{obs2}[(I)] - k_{-2}[B][C].$$
(6)

In Scheme 1, the oxygen atom bearing negative charge in ipt⁻ ion attacks the boron center of the boronic acid to form the unchelated complex (I) in the first step. Complex (I) reacts further when $OH^$ acceptor such as boronic acid exists in the reaction solution; the free boronic acid accepts OH^- from complex (I) and becomes boronate ion, concurrently the chelate ring clusure occurs to complex (I) to form chelate complex (B) in the second step. The reaction of complex (I) with the boronic acid would proceed by S_N2 mechanism with Walden inversion, i.e., coordination (chelation) of the uncoordinated oxygen atom in



Fig. 1. Dependences of k_{obs1} (a) and k_{obs2} (b) on C_B for the reaction of m-NO₂PhB(OH)₂ with ipt⁻ in acetonitrile. At I = 0.10 M, $C_L = 1.0 \times 10^{-4}$ M, and $T/^{\circ}C = 0$ (circle), -5 (diamond), -10 (square), -15 (triangle), -20 (inverted triangle), -25 (circle), and -30 (diamond). Data points represented by solid marks were obtained in the presence of excess water ($C_{H_2O} = 7.64 \times 10^{-3}$ M).

the mono-ligated ipt^- to the boron center of complex (I) and dissociation of one of two OH groups in complex (I) occur concertedly with the assistance of free boronic acid.

The ¹H NMR spectra (Fig. S4) were also measured at various $C_{\rm B}/C_{\rm ipt^-}$, which show that step 1 in Scheme 1 is in fast equilibrium.

Eqs. (7) and (8) are derived from the reactions in Scheme 1 under the conditions, $C_{\rm B} \gg C_{\rm L}$, since both the reverse reactions $(k_{-1} \text{ and } k_{-2})$ contribute negligibly to $k_{\rm obs1}$ and $k_{\rm obs2}$, respectively (Fig. 1). Negligible contribution of the reverse reaction (k_{-2}) is also supported by the exact single exponential curve observed for the slower reaction



Fig. 2. ¹¹B{¹H} NMR spectra of the mixture of *m*-NO₂PhB(OH)₂ and (CH₃)₄NOH (TMA-OH) ($C_B/C_{TMA-OH} \sim 3$) (i), the mixture of *m*-NO₂PhB(OH)₂ and Hipt ($C_B/C_{Hipt} \sim 2$) (ii), the mixture of *m*-NO₂PhB(OH)₂ and ipt⁻ ($C_B/C_{ipt^-} \sim 4$) (iii) in CD₃CN at 21 °C.

 $k_{\text{obs1}} = k_1 [m \text{-NO}_2 \text{PhB}(\text{OH})_2], \tag{7}$

$$k_{\text{obs2}} = k_2 [m \text{-} \text{NO}_2 \text{PhB}(\text{OH})_2].$$
(8)

Comparing Eqs. (5) and (6) with Eqs. (7) and (8), respectively, the equations, $k_{f1} = k_1$ and $k_{f2} = k_2$ are obtained, since $C_B \gg C_L$ ($C_B \sim [m\text{-NO}_2\text{PhB}(\text{OH})_2]$). The rate constants, $k_1 = 7.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 100 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, were calculated from the corresponding activation parameters obtained in this study (Table S1).

We obtained previously the forward rate constants, $k_{\rm f} = K_1 k_2 = 144 \text{ M}^{-1} \text{s}^{-1}$ (I = 0.10 M) and 196 M $^{-1} \text{s}^{-1}$ (I = 1.0 M) at 25 °C for the reaction in Eq. (9) in water [9], which is comparable with that in acetonitrile $(171 \pm 2 \text{ kg mol}^{-1} \text{ s}^{-1} \text{ at } I = 0.10 \text{ mol} \text{ kg}^{-1} \text{ and } 25 \text{ °C})$ [11]. This similarity suggests that the second-order rate constants are essentially in the same order in both solvents. The k_1 value (7.9 × 10⁴ M⁻¹s⁻¹ at 25 °C) in acetonitrile obtained in this study is sufficiently greater than the values in water obtained so far for the bidentate reaction systems (the highest value, 1.34×10^3 M⁻¹s⁻¹ at 25 $^{\circ}$ C, are obtained for the B(OH)₃ and H₂ipt⁺ system [9]), though it is substantially smaller than the value for Eq. (1), which clearly indicates that the chelate ring-closure should be rate determining in the bidentate reaction systems

$$B(OH)_3 + HOOO \stackrel{K_1}{\longleftarrow} B(OH)_3(HOO) \stackrel{k_2}{\longleftarrow} (HO)_2BOO + H_2O$$
(9)

The rate-determining step in step 2 in Scheme 1 should not be chelate ring closure but dissociation of OH group in (I), because step 2 is an intermolecular



Scheme 1.

reaction and Lewis acid-base reaction of boronic acid (Eq. (1)) is fast. The k_2 value at 25 °C ($10^2 \text{ M}^{-1}\text{s}^{-1}$) suggests that the ligand substitution on the tetrahedral boron occurs considerably slowly unlike the previous results obtained by relaxation methods [1,2,8].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.inoche.2005.05.011.

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