Substituent and Solvent Effects on the Reactions of Organoboronic Acids with Fluoride

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The introduction of an electron-withdrawing substituent or a substituent protonated to be positively charged and potentially involved in hydrogen bonding enhances the reactivities of phenylboronic acids with fluoride. The use of a 60% aqueous MeOH medium suppresses the formation of the negatively charged species, irrespective of whether their structures are trigonal or tetrahedral, but enhances the overall reactivity because of less solvation of fluoride.

New methods for quantifying fluoride in solution by the use of organoboronic acids have recently been proposed; e. g., voltammetry using ferrocenylboronic acid (FB)[1] and fluorometry using 2-[benzyl(methyl)aminomethyl]phenylboronic acid (AMPB, [ampB(OH)$_2$]),[2] phenylboronic acid (PB, [PhB(OH)$_2$]),[2] and naphthylboronic acid.[3] The relevant reaction equilibria have also been studied at a fixed pH, and the equilibrium constants, conditional upon pH, have been obtained.[1,2] The intrinsic equilibrium constants of PB in water, on the other hand, have been obtained by potentiometry at varying pH values and have afforded a deeper insight into its effective use.[3] In this paper, we extend such studies to 3-nitrophenylboronic (NPB) and methylboronic (MB) acids to examine the electronic effects on boron atoms and also to AMPB to assess the effects of a substituent protonated to be positively charged and potentially involved in hydrogen bonding.[2] Since 60% MeOH is to be used for a potentiometric study of AMPB, the effects of MeOH on the reactivity of PB are also studied for comparison.

Since the acid-base equilibria of hydrogen fluoride and organoboronic acids in water have been well characterized, the protonation constants in the literature were used for subsequent analyses. The corresponding constants in 60% MeOH were determined at an ionic strength of 0.1 mol dm^{-3} KNO$_3$ by pH titration. The addition of MeOH enhances the protonation of fluoride 10 times (K_{HF} = [HF]/[H$^+$][F$^-$] = $10^{3.98}$ compared with $10^{2.97}$), while depressing the formation of HF$_2^-$ (negligible compared with K_{HF2} = [HF$_2^-$]/[HF][F$^-$] = $10^{0.59}$). The protonation constant of [PhB(OH)$_3$]$^-$, yielding [PhB(OH)$_2$], in 60% MeOH ($K_{20}{}^{H} = 10^{9.3}$) is 3 times higher than that in water ($K_{20}{}^{H}$ = $10^{8.8}$).[3] The protonation constant of the amino group of [ampB(OH)$_2$], yielding [$^+$HampB(OH)$_2$] in 60% MeOH, was $10^{5.0}$, which is 3 times lower than that in 50% MeOH ($K_{20}{}^{H}$ = $10^{5.5}$).[2] In any case, the neutral species are relatively stabilized in 60% MeOH compared with those in water and in 50% MeOH.

The UV-spectral change accompanied by the acid-base reaction of PB at 10^{-3} mol dm^{-3} was studied in both water (Fig. 1a) and 60% MeOH (Fig. 1b). Upon deprotonation, both hypsochromic and hypochromic effects were observed; the wavelength for the strongest absorption shifted from 267 to 257 nm and the molar absorption coefficient decreased from 520 to 280 mol^{-1} dm^3 cm^{-1}. Such a change, generally found along with the loss of planarity, is ascribed to a change in coordination number around boron, from three of [PhB(OH)$_2$] to four of [PhB(OH)$_3$]$^-$. The protonation constants obtained from the absorbance change ($K_{20}{}^{H} = 10^{8.6}$ at 1 mol dm^{-3} KCl in water and $10^{9.4}$ at 0.1 mol dm^{-3} KCl in 60% MeOH) were comparable to those given in the literature[3] and by the pH titration described above, respectively.

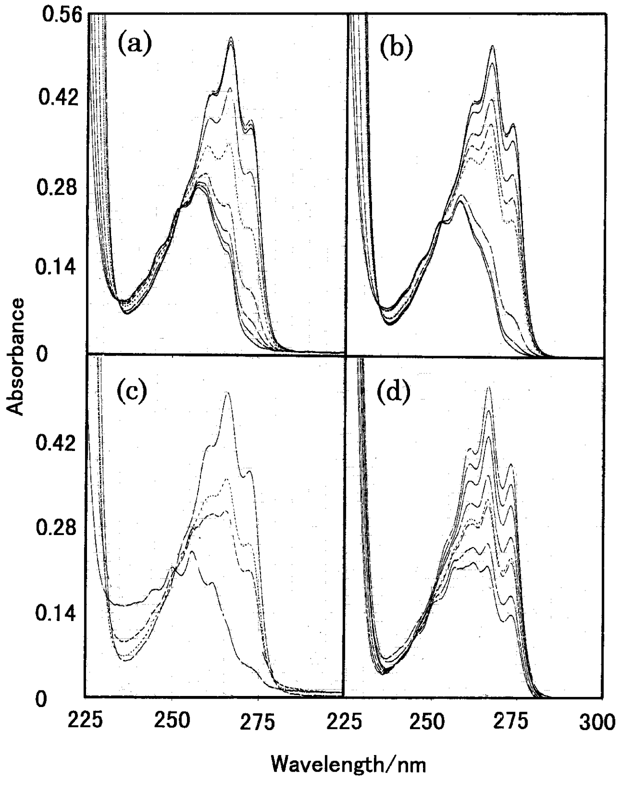

Fig. 1. UV spectral changes by the acid-base reaction of PB (a, b) and by the reaction of PB with F$^-$(c, d) in water (a, c) and in 60% MeOH (b, d). C_{PB} = 10^{-3} mol dm^{-3}. −log [H$^+$] = 6–11 (a, b), 3.0 (c, d). C_F/mol dm^{-3} = 0 (a, b), 0–10^{-2} (c, d).

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The reactions of PB with F^- in water cause a spectral change (Fig. 1c) similar to that produced by the acid-base reaction (Fig. 1a and b). A gradual increase in coordination number along with a reaction giving $[PhBF_3]^-$ is suggested. On the contrary, reactions in 60% MeOH show a simple reduction in intensity without any shift in wavelength at a lower F^- concentration (Fig. 1d); this suggests the prevailing formation of a neutral trigonal species of $[PhBF_2]$. An increase in coordination number from $[PhBF_2]$ occurs discretely at a higher F^- concentration. The chemistry of PhBXY (X, Y = F, Cl, Br, I) in inert solvents has been well characterized by ^{11}B NMR.[4]

The equilibrium constants obtained by potentiometry in water and in 60% MeOH are summarized in Table 1. The reaction of PB with F^- in water yields five species, {(1,1), (2,1), (0,2), (1,2), and (0,3)} : (m,n) indicates the species of $[PhB(OH)_mF_n]$, the electric charge of which is omitted for clarity.[3] MB, which has a lower Brønsted acidity ($K_{20}^{H} = 10^{10.4}$), loses the reactivity to F^- (not included in Table). On the other hand, NPB, which has a higher Brønsted acidity due to a lower electron density on boron, showed a higher affinity to F^- than PB. In this reaction system, only the anionic tetrahedral species of (2,1), (1,2), and (0,3) were formed, and neither neutral trigonal species of (1,1) nor (0,2) was detected because of the higher Brønsted acidities of these species than those of PB.

Table 1. Changes in Charge and Logarithmic Equilibrium Constants on the Reactions of Organoboronic Acids with F^- [a)]

Compound	NPB	PB[b)]	PB	AMPB
Medium	Water	Water	60% MeOH	60% MeOH
	– to 0			0 to +
K_{20}^{H}	7.0	8.8	9.3	5.0[c)]
K_{11}^{H}	—	3.9	—	—
K_{02}^{H}	—	2.1	—	—
	0 to –			+ to 0
K_{21}^{F}	0.9	0.6	—	2.5
K_{12}^{F}	—	2.3	—	—
K_{03}^{F}	—	4.4	4.4	—
	0 to 0			+ to +
$K_{11}^{H,F}$	—	4.5	4.7	—
$K_{02}^{H,F}$	—	4.4	6.7	—
	– to –			0 to 0
$K_{21}^{H,F}$	7.9	9.4	—	7.5
$K_{12}^{H,F}$	6.8	6.2	—	7.9
$K_{03}^{H,F}$	6.1	6.5	—	7.2

a) $K_{mn}^{H} = [ArB(OH)_mF_n]/[ArB(OH)_{m+1}F_n][H^+]$, $K_{mn}^{F} = [ArB(OH)_mF_n]/[ArB(OH)_mF_{n-1}][F^-]$ and $K_{mn}^{H,F} = [ArB(OH)_mF_n]/[ArB(OH)_{m+1}F_{n-1}][H^+][F^-]$ for NPB and PB; Ar to be $^+$Hamp for AMPB. All the constants have ±0.1 error. b) Ref. 3. c) Protonation to the amino group.

As for PB in 60% MeOH, $K_{11}^{H,F}$ and $K_{02}^{H,F}$, which correspond to the reactions keeping the electric neutrality, are increased. Neither anionic tetrahedral species of (2,1) or (1,2) was formed and K_{03}^{F}, which corresponds to the reaction from neutral to minus charge, was not increased. The neutral species were also stabilized in this reaction. The overall reactivity of PB was enhanced in 60% MeOH compared with that in water, because of the less solvation of F^-.

In 60% MeOH, the reactivity of PB was further enhanced by introducing a 2-(benzylmethylaminomethyl) group. The reaction of AMPB with F^- yields only the tetrahedral species of (2,1), (1,2), and (0,3), which are, in contrast to the case of PB, not anionic, but neutral, because of the protonation of an amino group in an acidic medium. Such an enhancement in reactivity is ascribed to an intramolecular electrostatic interaction between the negatively charged boronic and positively charged ammonium moieties.

Experimental

Phenylboronic, 3-nitrophenylboronic, and methylboronic acids(Aldrich) were used as received. 2-(Benzylmethylaminomethyl)phenylboronic acid was synthesized as described previously.[2] The supporting electrolytes used were 1.0 and 0.1 mol dm^{-3} KNO_3 for potentiometry, and 0.1 and 0.1 mol dm^{-3} KCl for spectrophotometry, in water and 60% MeOH, respectively, and the concentration scale was adopted for equilibrium analyses. Potentiometric work was carried out as described previously.[3]

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