

# Thermodynamic Investigations for the Slow Protolysis of Pyridine and 1,10-Phenanthroline

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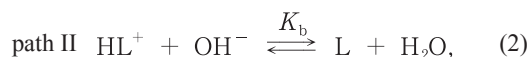
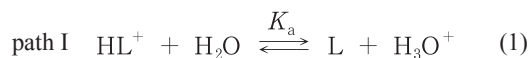
## Abstract

Equilibrium and kinetic measurements were carried out for the protolysis of pyridine, 2,2'-bipyridine, and 1,10-phenanthroline in water and for the protolysis of pyridine and 1,10-phenanthroline in 0.05 mole fraction 1,4-dioxane-water mixture. The thermodynamic and activation parameters for the acid dissociation of their conjugate acids were evaluated from the temperature dependencies of the acid dissociation constants and the deprotonation rate-constants. Their protolysis was discussed thermodynamically. It was suggested that the change in hydration structure significantly affected upon the protolysis.

## Introduction

Proton transfer plays an important role in many chemical and biological processes, and protolysis is an important elementary step for chemical reactions in aqueous solution. Thus, protolysis has so far been studied on a wide variety of compounds.<sup>[1-4]</sup> We have kinetically studied on the protolysis of ligands involved nitrogen atom as a coordination atom, *e.g.* pyridine and 1,10-phenanthroline, paying our attention to the point that the protolysis of a ligand should play an important role in a complex formation.<sup>[5-9]</sup>

We found that the protolysis of pyridine (py), 2,2'-bipyridine (bpy), and 1,10-phenanthroline (phen) proceeded with relatively slow rate through the concurrent paths I and II expressed by Eqs. 1 and 2.<sup>[8,9]</sup>



where L and HL<sup>+</sup> represent the free base form of py or phen and the conjugate acid of them, respectively. A nitrogen acid and an oxygen acid may generally undergo protolysis with fast rates, and there is little instance of slow protolysis of a nitrogen acid such as pyH<sup>+</sup> and phenH<sup>+</sup>. Thus, it is very interested in the mechanism of these slow protolysis, especially in retarding factors operated on their protolysis.

A carbon acid is known to undergo quite slow protolysis. The reasons for the rate retardation in such slow protolysis are considered to be (1) the small hydrogen-bonding

ability of carbon acid with solvent, (2) the electronic and structural reorganization on going from the acid to its conjugate base, and (3) the accompanying reorientation of solvated solvent molecules.<sup>[1,2,4]</sup> The former two reasons are not likely to be the retarding factors in the protolysis of py and phen, because they have relatively strong hydrogen-bonding ability and are rigid molecule.

In our previous work,<sup>[9]</sup> the protolysis of py, phen, and several their derivatives was kinetically investigated in order to elucidate the operated retardation factors in their protolysis. The effect of addition of 1,4-dioxane on their rates was also examined, as 1,4-dioxane is freely miscible with water and has extremely low dielectric constant. We suggested that the change in hydration sphere might participate significantly to retard the protolysis of py and phen. In this study, the temperature dependence of the protolysis of py and phen was examined in water and 0.05 mole fraction 1,4-dioxane-water mixture. Equilibrium and activated state were discussed thermodynamically.

## Experimental

*Materials and Sample Solution.* Pyridine, 2,2'-bipyridine, and 1,10-phenanthroline monohydrate were purchased commercially available and were used without further purification. 1,4-Dioxane was reagent grade for non-aqueous titration and was used without further purification. The water content of this solvent was measured by use of a Mitsubishi CA-02 moisturemeter and was less than 0.2 w/w %. All other reagents were of guaranteed reagent grade and

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were used without further purification.

Stock solutions of py, bpy, and phen were prepared by dissolving a weighed amount of them in water. Sample solutions for measurements were prepared by diluting those stock solutions to the desired concentration with water or the desired amount of 1,4-dioxane. The ionic strength of a sample solution was adjusted to 0.20 mol dm<sup>-3</sup> with sodium chloride and the pH of it was adjusted the desired value as mentioned below. On the kinetic measurements, the pH of a sample was adjusted to the desired value with hydrochloric acid or sodium hydroxide. On the other hand, the buffers, acetate, phosphate, and ammonium buffer systems, were used at the concentration less than 0.02 mol dm<sup>-3</sup> in the pH range of 4 to 10 on the pH adjustment of a sample solution for p*K*<sub>a</sub> measurements.

*Measurements.* Acid dissociation constants were measured by a spectrophotometric pH titration at the wavelength of absorption maximum of pyH<sup>+</sup>, bpyH<sup>+</sup>, and phenH<sup>+</sup>.<sup>[8]</sup> The rate of protolysis were measured at the same

wavelength as those of the measurements of acid dissociation constants by the pH-jump method without buffer solution by use of an Union RA-401 stopped-flow spectrophotometer. The detailed procedures of whole measurements in this study were mentioned in previous work.<sup>[8, 9]</sup> All measurements were carried out at the temperatures controlled within 0.1°C in the range of 15 to 35°C.

The hydrogen-ion concentration in 1,4-dioxane-water mixture was determined by Gran's method.<sup>[10]</sup> The constant appearing in the Nernst equation, *E*<sub>0</sub>, was determined by means of Gran plots and the potential of a sample solution, *E*, was measured under an atmosphere of nitrogen gas saturated with solvent vapor by a TOA HM-6A pH meter equipped with a TOA HGS-2005 glass electrode in combination with a TOA HS-305DS double junction silver-silver chloride electrode as a reference electrode. Then, the hydrogen-ion concentration of a sample solution was calculated by the Nernst equation,

$$E = E_0 + 59.15 \log[H^+].$$

**Table 1** The p*K*<sub>a</sub> values and the number of the transferred proton for conjugate acid of py, bpy, and phen in aqueous solution and 0.05 mole fraction 1,4-dioxane-water mixture.

	<i>t</i> / °C	in aqueous solution		in 1,4-dioxane-water mixture	
		p <i>K</i> <sub>a</sub>	<i>n</i>	p <i>K</i> <sub>a</sub>	<i>n</i>
pyH <sup>+</sup>	15.0	5.48±0.01	1.00±0.01	5.12±0.01	0.96±0.01
	20.0	5.39±0.01	0.96±0.02	5.04±0.01	0.93±0.01
	25.0	5.34±0.01	0.95±0.01	4.97±0.01	0.95±0.01
	30.0	5.29±0.01	0.98±0.01	4.93±0.01	0.95±0.01
	35.0	5.20±0.01	0.96±0.03	4.81±0.01	1.00±0.02
bpy H <sup>+</sup>	15.0	4.61±0.01	0.98±0.01		
	20.0	4.54±0.01	0.99±0.01		
	25.0	4.51±0.01	1.02±0.01		
	30.0	4.48±0.01	0.99±0.01		
	35.0	4.45±0.01	1.00±0.01		
phen H <sup>+</sup>	15.0	5.12±0.01	0.97±0.01	4.72±0.01	0.93±0.01
	20.0	5.08±0.01	0.99±0.01	4.68±0.01	0.94±0.01
	25.0	5.03±0.01	1.00±0.01	4.62±0.01	0.96±0.01
	30.0	4.99±0.01	0.99±0.01	4.55±0.01	0.94±0.01
	35.0	4.94±0.01	1.00±0.01	4.51±0.01	0.99±0.01

These values are shown together with the 0.95 confidence intervals.

## Results and Discussion

**Equilibrium Studies.** The  $pK_a$  values of  $pyH^+$ ,  $bpyH^+$ , and  $phenH^+$  were determined at 15 to 35°C in aqueous solution and 0.05 mole fraction 1,4-dioxane-water mixture. The results are summarized in Table 1. In the temperature range of 15 to 35°C, the number of transferred proton was found to be about unity in both solvents. Therefore, the observed protolysis was one-proton dissociation reaction. The obtained  $K_a$  values at every temperature were larger in 1,4-dioxane-water mixture than those in aqueous solution, *i.e.* those acids easily dissociate in 1,4-dioxane-water mixture. The  $K_a$  values of  $phenH^+$  are of good agreement with those of Ishiguro in both solvents.<sup>[11]</sup> They pointed out that the promotion of acid dissociation of it in mixture solvent was primarily due to the reduction in hydration of proton. All of the van't Hoff plots in Fig. 1 gave a good linearity. This indicates that each compound in this study dissociates through an analogous mechanism in the temperature range of this study.

The relation of Eq. 3 holds between the equilibrium constants of path I and II,  $K_a$  and  $K_b$ ,

$$(K_a / K_b) = K_w \quad (3)$$

where  $K_w$  denotes the ionic product of water. The values of

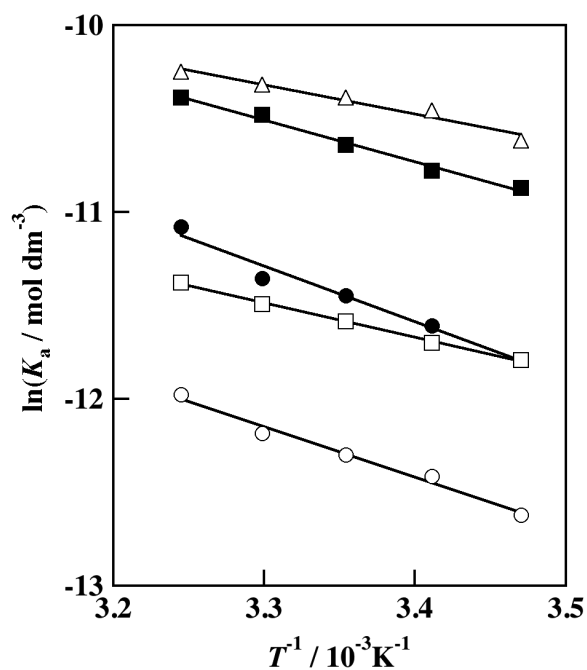


Figure 1 Temperature dependences of the equilibrium constants of deprotonation *via* path I for  $pyH^+$  (○, ●),  $bpyH^+$  (△), and  $phenH^+$  (□, ■). The open and solid symbols represent the data in aqueous solution and in 0.05 mole fraction 1,4-dioxane-water mixture, respectively.

$K_b$  were calculated from the  $K_a$  values obtained in this study and  $K_w$  values in literatures<sup>[12, 13]</sup> using the relation of Eq. 3. Van't Hoff plots for  $K_b$  are shown in Fig. 2 and the van't Hoff plots in Fig. 2 also gave a good linearity. Table 2 summarizes the thermodynamic parameters for the acid dissociation of  $pyH^+$ ,  $bpyH^+$ , and  $phenH^+$  obtained van't Hoff plots

Table 2 Thermodynamic parameters for deprotonation.

		$\Delta G^\circ / \text{kJmol}^{-1}$	$\Delta H^\circ / \text{kJmol}^{-1}$	$\Delta S^\circ / \text{JK}^{-1}\text{mol}^{-1}$
in aqueous solution				
path I	$pyH^+$	30±7	23±5	-27±17
	$bpyH^+$	26±7	13±5	-43±16
	$phenH^+$	29±2	15±2	-45±5
path II	$pyH^+$	-50±7	-34±5	51±17
	$bpyH^+$	-54±5	-44±4	35±12
	$phenH^+$	-51±3	-42±2	33±7
in 0.05 mole fraction 1,4-dioxane-water mixture				
path I	$pyH^+$	28±10	25±7	-12±24
	$phenH^+$	26±5	19±4	-26±12
path II	$pyH^+$	-55±12	-32±9	77±29
	$phenH^+$	-57±8	-38±6	63±19

These values are shown together with the 0.95 confidence intervals.

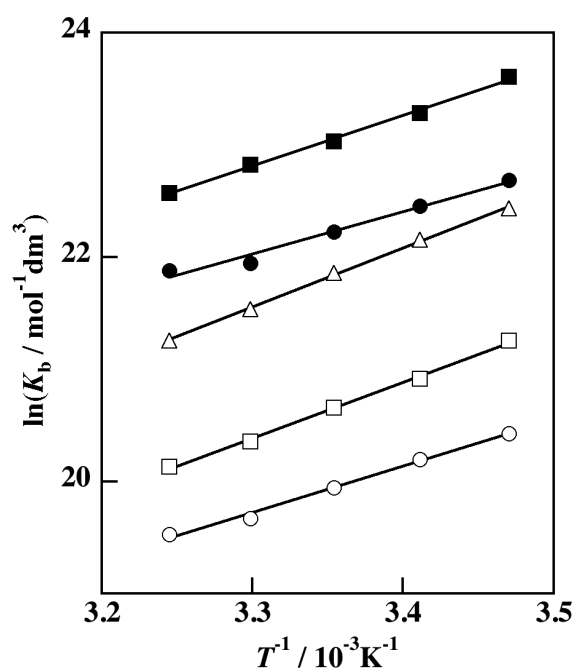


Figure 2 Temperature dependences of the equilibrium constants of deprotonation *via* path II for  $pyH^+$  (○, ●),  $bpyH^+$  (△), and  $phenH^+$  (□, ■). The open and solid symbols represent the data in aqueous solution and in 0.05 mole fraction 1,4-dioxane-water mixture, respectively.

in Figs. 1 and 2. As can be seen in Table 2, the thermodynamic parameters for the acid dissociation of path I are remarkably different from those path II in both aqueous solution and 1,4-dioxane-water mixture. However, they are essentially identical on the deprotonation of all compounds in this study, if taking the thermodynamic parameters for formation of water into account,<sup>[12, 13]</sup>  $\Delta G^\circ = -80 \text{ kJmol}^{-1}$ ,  $\Delta H^\circ = -54 \text{ kJmol}^{-1}$ , and  $\Delta S^\circ = 87 \text{ JK}^{-1}\text{mol}^{-1}$  in aqueous solution, and  $\Delta G^\circ = -83 \text{ kJmol}^{-1}$ ,  $\Delta H^\circ = -58 \text{ kJmol}^{-1}$ , and  $\Delta S^\circ = 85 \text{ JK}^{-1}\text{mol}^{-1}$  in 0.05 mole fraction 1,4-dioxane-water mixture. Hereafter, we shall discuss about the thermodynamic parameter for acid dissociation *via* path I.

The thermodynamic parameters for acid dissociation,  $\Delta X^\circ$  ( $X=G, H, \text{ or } S$ ), is composed of terms ascribed to the bond formation and breaking,  $\Delta X_d$ , and the accompanying the change in hydration,  $\Delta X_h$ .

$$\Delta X^\circ = \Delta X_d + \Delta X_h \quad (4)$$

The  $\Delta X_h$  term is represented by the thermodynamic parameter for the solution of the respective species into the solvents,  $\Delta X_s$ ,

$$\Delta X_h = \Delta X_s(\text{L}) + \Delta X_s(\text{H}^+) - \Delta X_s(\text{HL}^+) \quad (5)$$

and the  $\Delta X_d$  term correspond to the thermodynamic parameter for the acid dissociation in gas phase. Accordingly, the value of  $\Delta X^\circ$  can be calculated if the value of  $\Delta X_d$  and  $\Delta X_s$  on each species participated in the protolysis are known.

For example, the values of  $\Delta X_s(\text{L})$ ,  $\Delta X_s(\text{HL}^+)$ ,  $\Delta X_s(\text{H}^+)$  and  $\Delta X_d$  are reported about pyridine.<sup>[14, 15]</sup> The calculated  $\Delta X_h$  values from them were  $\Delta H_h = -918 \text{ kJmol}^{-1}$  and  $\Delta S_h = -140 \text{ JK}^{-1}\text{mol}^{-1}$ , and the values of  $\Delta X_d$  are  $\Delta H_d = 940 \text{ kJmol}^{-1}$  and  $\Delta S_d = 109 \text{ JK}^{-1}\text{mol}^{-1}$  for the acid dissociation of  $\text{pyH}^+$ . Accordingly, the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the acid dissociation of  $\text{pyH}^+$  were calculated to be  $22 \text{ kJmol}^{-1}$  and  $-31 \text{ JK}^{-1}\text{mol}^{-1}$ , respectively. The  $\Delta H^\circ$  and  $\Delta S^\circ$  values obtained in this study are good agreement with the calculated ones. The positive value of  $\Delta X_d$  reflects the breaking of the N-H<sup>+</sup> bond. Taking the remarkably negative  $\Delta X_s(\text{H}^+)$  value,<sup>[15]</sup> the negative value of  $\Delta X_h$  indicates that the formation of hydration about the dissociated proton contributes to  $\Delta X_h$  in preference to the difference in hydration structure between  $\text{HL}^+$  and L. The thermodynamic parameters can be similarly discussed for the protolysis of bpy and phen. As can be seen in Table 2, the positive values of  $\Delta H^\circ$  for each acid dissociation imply that the  $\Delta H_d$  contributes to  $\Delta H^\circ$  in preference to the  $\Delta H_h$ . However, the difference in  $\Delta H_h$  causes the difference in  $\Delta H^\circ$  among the acid dissociation of  $\text{pyH}^+$ ,  $\text{bpyH}^+$ , and  $\text{phenH}^+$  if the  $\Delta H_d$  corresponding to the breaking energy of the N-H<sup>+</sup>

bond does not differ among them. Furthermore, the negative  $\Delta S^\circ$  is attributed to the contribution of the  $\Delta S_h$  term. The difference in  $\Delta H^\circ$  and the negative  $\Delta S^\circ$  suggested that the change in hydration structure affected significantly upon the acid dissociation of  $\text{pyH}^+$ ,  $\text{bpyH}^+$ , and  $\text{phenH}^+$ .

In 0.05 mole fraction 1,4-dioxane-water mixture, the  $\Delta G^\circ$  for the acid dissociation of  $\text{pyH}^+$  and  $\text{phenH}^+$  are more negative than those in water. This fact implies that the acid dissociation of them is promoted in 1,4-dioxane-water mixture. Although the  $\Delta H^\circ$  in 1,4-dioxane-water mixture is more positive than that in water, the  $\Delta G^\circ$  is more negative than that in water. This indicates that the  $\Delta S^\circ$  term primarily contributes to  $\Delta G^\circ$  in 1,4-dioxane-water mixture. The more positive  $\Delta S^\circ$  is attributable to the fact that the  $\Delta S_h$  term is more positive than that in water, provided that the  $\Delta S_d$  term is similar between in water and in a small mol fraction 1,4-dioxane-water mixture. It is suggested that the main reason for the more negative  $\Delta G^\circ$  is the reduction in hydration in mixture solvent.

*Kinetic Studies.* The rates of protolysis of py, bpy, and phen were measured at 15 to 35°C both in water and in 0.05 mole fraction 1,4-dioxane-water mixture. The apparent first-order rate constants of deprotonation,  $(k_{dp})_0$ , were linearly dependent on hydroxide-ion concentration for all compounds in both solvents. It was obvious that their deprotonation proceeded through the concurrent path I and II in Eqs 1 and 2 in the temperature range of 15 to 35°C, as previous work.<sup>[8]</sup> It was also clarified that in 1,4-dioxane-water mixture their deprotonation was accelerated by two to five times and showed the same behavior as in water.

Figures 3 and 4 show the temperature dependence of the deprotonation rate-constants through path I and II,  $k_{dp}$  and  $k_{OH}$ , which were obtained from the dependence of  $(k_{dp})_0$  on hydroxide-ion concentration. The rate constants of protonation through the path I and II,  $k_p$  and  $k_{H_2O}$ , were calculated by Eq. 6. (Tables 3 and 4) In calculation of

$$K_a = (k_{dp}/k_p) = (k_{OH}K_w/k_{H_2O}[H_2O]) \quad (6)$$

$k_p$  and  $k_{H_2O}$ , the literature values<sup>[12, 13]</sup> were used as the value of  $K_w$ , and 1<sup>[16]</sup> and 0.96<sup>[17]</sup> were used as the activity of water in aqueous solution and 0.05 mole fraction 1,4-dioxane-water mixture, respectively. The activation parameters for deprotonation were obtained from the Arrhenius plots in Figs. 3 and 4, and were summarized in Table 5.

The activation parameters for deprotonation can be similarly discussed to the thermodynamic parameters. With the progress of the deprotonation *via* path I, the N-H<sup>+</sup> bond lengthens and the hydration extends around the N-H<sup>+</sup> bond.

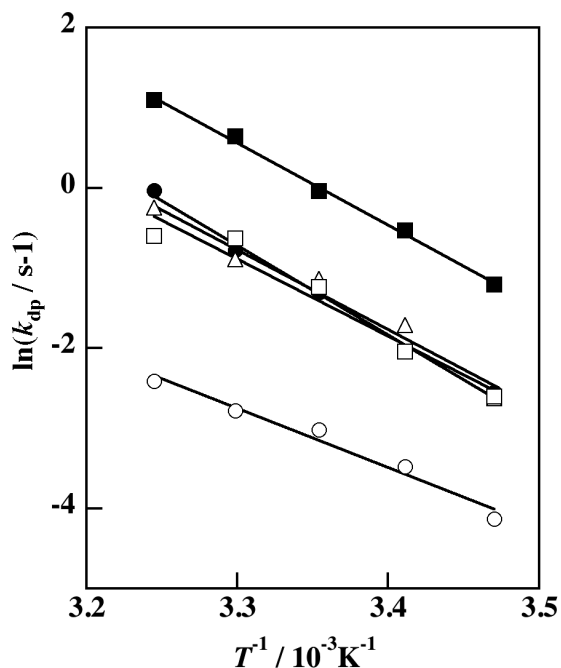


Figure 3 Temperature dependences of the rate constants of deprotonation *via* path I for  $\text{pyH}^+$  ( $\circ$ ,  $\bullet$ ),  $\text{bpyH}^+$  ( $\triangle$ ), and  $\text{phenH}^+$  ( $\square$ ,  $\blacksquare$ ). The open and solid symbols represent the data in aqueous solution and 0.05 mole fraction 1,4-dioxane-water mixture, respectively.

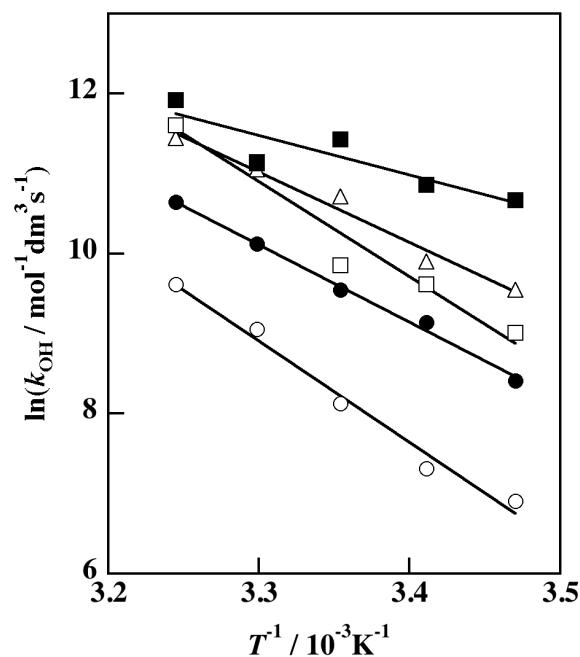


Figure 4 Temperature dependences of the rate constants of deprotonation *via* path II for  $\text{pyH}^+$  ( $\circ$ ,  $\bullet$ ),  $\text{bpyH}^+$  ( $\triangle$ ), and  $\text{phenH}^+$  ( $\square$ ,  $\blacksquare$ ). The open and solid symbols represent the data in aqueous solution and 0.05 mole fraction 1,4-dioxane-water mixture, respectively.

Table 3 The rate constants of the protolysis in aqueous solution.

	$t / ^\circ\text{C}$	$k_{\text{dp}} / \text{s}^{-1}$	$k_{\text{p}} / \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	$k_{\text{OH}} / \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	$k_{\text{H}_2\text{O}} / \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$
py	15.0	$(1.6 \pm 0.4) \times 10^{-2}$	$(4.8 \pm 1.2) \times 10^3$	$(1.0 \pm 0.7) \times 10^3$	$(1.4 \pm 1.0) \times 10^{-6}$
	20.0	$(3.1 \pm 0.7) \times 10^{-2}$	$(7.6 \pm 1.7) \times 10^3$	$(1.5 \pm 0.9) \times 10^3$	$(2.5 \pm 1.5) \times 10^{-6}$
	25.0	$(4.9 \pm 1.0) \times 10^{-2}$	$(1.1 \pm 0.2) \times 10^4$	$(3.4 \pm 1.3) \times 10^3$	$(7.5 \pm 2.9) \times 10^{-6}$
	30.0	$(6.2 \pm 2.4) \times 10^{-2}$	$(1.2 \pm 0.5) \times 10^4$	$(8.6 \pm 3.8) \times 10^3$	$(2.5 \pm 1.1) \times 10^{-5}$
	35.0	$(9.0 \pm 3.4) \times 10^{-2}$	$(1.4 \pm 0.5) \times 10^4$	$(1.5 \pm 0.7) \times 10^4$	$(5.0 \pm 2.3) \times 10^{-5}$
bpy	15.0	$(7.2 \pm 1.5) \times 10^{-2}$	$(3.0 \pm 0.6) \times 10^3$	$(1.4 \pm 0.3) \times 10^4$	$(2.6 \pm 0.6) \times 10^{-6}$
	20.0	$(1.8 \pm 0.3) \times 10^{-1}$	$(6.3 \pm 0.9) \times 10^3$	$(2.0 \pm 0.5) \times 10^4$	$(4.7 \pm 1.3) \times 10^{-6}$
	25.0	$(3.2 \pm 0.5) \times 10^{-1}$	$(1.0 \pm 0.2) \times 10^4$	$(4.5 \pm 1.3) \times 10^4$	$(1.5 \pm 0.4) \times 10^{-5}$
	30.0	$(4.1 \pm 0.7) \times 10^{-1}$	$(1.2 \pm 0.2) \times 10^4$	$(6.3 \pm 2.0) \times 10^4$	$(2.8 \pm 0.9) \times 10^{-5}$
	35.0	$(7.8 \pm 2.0) \times 10^{-1}$	$(2.2 \pm 0.3) \times 10^4$	$(9.3 \pm 3.7) \times 10^4$	$(5.5 \pm 2.2) \times 10^{-5}$
phen	15.0	$(7.4 \pm 1.8) \times 10^{-2}$	$(9.8 \pm 2.4) \times 10^3$	$(8.2 \pm 4.7) \times 10^3$	$(4.9 \pm 2.6) \times 10^{-6}$
	20.0	$(1.3 \pm 0.2) \times 10^{-1}$	$(1.6 \pm 0.2) \times 10^4$	$(1.5 \pm 0.4) \times 10^4$	$(1.2 \pm 0.3) \times 10^{-5}$
	25.0	$(2.9 \pm 0.3) \times 10^{-1}$	$(3.1 \pm 0.3) \times 10^4$	$(1.9 \pm 0.5) \times 10^4$	$(2.1 \pm 0.5) \times 10^{-5}$
	30.0	$(5.3 \pm 1.4) \times 10^{-1}$	$(5.2 \pm 1.4) \times 10^4$	$(6.8 \pm 3.2) \times 10^4$	$(9.8 \pm 4.6) \times 10^{-5}$
	35.0	$(5.5 \pm 1.4) \times 10^{-1}$	$(4.8 \pm 1.2) \times 10^4$	$(1.1 \pm 0.3) \times 10^5$	$(2.0 \pm 0.5) \times 10^{-4}$

These values are shown together with the 0.95 confidence intervals.

Table 4 The rate constants of the protolysis in 0.05 mole fraction 1,4-dioxane-water mixture.

	$t / ^\circ\text{C}$	$k_{\text{dp}} / \text{s}^{-1}$	$k_{\text{p}} / \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	$k_{\text{OH}} / \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	$k_{\text{H}_2\text{O}} / \text{mol}^{-1}\text{dm}^3\text{s}^{-1}$
py	15.0	$(7.8\pm 2.9)\times 10^{-2}$	$(1.0\pm 0.4)\times 10^4$	$(4.5\pm 1.6)\times 10^3$	$(6.5\pm 2.3)\times 10^{-7}$
	20.0	$(1.3\pm 0.2)\times 10^{-1}$	$(1.4\pm 0.2)\times 10^4$	$(9.3\pm 1.1)\times 10^3$	$(1.7\pm 0.2)\times 10^{-6}$
	25.0	$(2.7\pm 0.6)\times 10^{-1}$	$(2.5\pm 0.6)\times 10^4$	$(1.4\pm 0.3)\times 10^4$	$(3.3\pm 0.7)\times 10^{-6}$
	30.0	$(4.6\pm 0.5)\times 10^{-1}$	$(3.9\pm 0.4)\times 10^4$	$(2.5\pm 0.3)\times 10^4$	$(7.7\pm 0.9)\times 10^{-6}$
	35.0	$(9.7\pm 2.1)\times 10^{-1}$	$(6.3\pm 1.4)\times 10^4$	$(4.2\pm 1.2)\times 10^4$	$(1.4\pm 0.4)\times 10^{-5}$
phen	15.0	$(3.0\pm 1.1)\times 10^{-1}$	$(1.6\pm 0.6)\times 10^4$	$(4.3\pm 1.4)\times 10^4$	$(2.5\pm 0.8)\times 10^{-6}$
	20.0	$(5.9\pm 0.8)\times 10^{-1}$	$(2.8\pm 0.4)\times 10^4$	$(5.2\pm 1.1)\times 10^4$	$(4.2\pm 0.9)\times 10^{-6}$
	25.0	$(9.6\pm 1.4)\times 10^{-1}$	$(4.0\pm 0.6)\times 10^4$	$(9.2\pm 2.5)\times 10^4$	$(9.6\pm 2.6)\times 10^{-6}$
	30.0	$1.9\pm 0.2$	$(6.7\pm 0.7)\times 10^4$	$(6.9\pm 3.8)\times 10^4$	$(8.8\pm 4.9)\times 10^{-6}$
	35.0	$3.0\pm 0.4$	$(9.7\pm 1.3)\times 10^4$	$(1.5\pm 0.7)\times 10^5$	$(2.5\pm 1.2)\times 10^{-5}$

These values are shown together with the 0.95 confidence intervals.

Table 5 Activation parameters for deprotonation

		$\Delta G^\ddagger / \text{kJmol}^{-1}$	$\Delta H^\ddagger / \text{kJmol}^{-1}$	$\Delta S^\ddagger / \text{JK}^{-1}\text{mol}^{-1}$
in aqueous solution				
path I	pyH <sup>+</sup>	81±29	60±21	-70± 69
	bpyH <sup>+</sup>	76±27	80±27	14± 5
	phenH <sup>+</sup>	77±48	78±34	4±114
path II	pyH <sup>+</sup>	52±36	102±26	165± 86
	bpyH <sup>+</sup>	47±20	70±19	79± 16
	phenH <sup>+</sup>	48±59	96±42	160±140
in 0.05 mole fraction 1,4-dioxane-water mixture				
path I	pyH <sup>+</sup>	77±19	92±13	49± 45
	phenH <sup>+</sup>	73±13	84± 9	36± 32
path II	pyH <sup>+</sup>	49±14	78±10	97± 33
	phenH <sup>+</sup>	45±55	39±39	-21±132

These values are shown together with 0.95 confidence intervals.

On the other hand, the N-H<sup>+</sup>-OH<sup>-</sup> bond is formed at the same time as the lengthening of the N-H<sup>+</sup> bond with the progress of the deprotonation *via* path II. Accordingly, the hydration structure also changes. Thus, the activation parameters,  $\Delta X^\ddagger$  ( $X=H$  or  $S$ ), are expressed for path I by the summation of the terms of  $\Delta X_{\text{d}}^\ddagger$  and  $\Delta X_{\text{h}}^\ddagger$  and for path II by the summation of the terms of  $\Delta X_{\text{d}}^\ddagger$ ,  $\Delta X_{\text{r}}^\ddagger$ , and  $\Delta X_{\text{h}}^\ddagger$ . The subscripts d and h are the same meaning as mentioned above and  $\Delta X_{\text{r}}^\ddagger$  denotes the change in thermodynamic pa-

rameter due to the formation of the N-H<sup>+</sup>-OH<sup>-</sup> bond at the activation state. Therefore, the  $\Delta X_{\text{d}}^\ddagger$  is positive and  $\Delta X_{\text{r}}^\ddagger$  is negative. On path I, the  $\Delta X_{\text{h}}^\ddagger$  becomes negative because the enhancement of hydration is caused by the charge separation due to the lengthening of the N-H<sup>+</sup> bond. On the other hand, the  $\Delta X_{\text{h}}^\ddagger$  becomes positive on path II because the reduction in hydration is caused by the charge neutralization ascribed to the formation of the N-H<sup>+</sup>-OH<sup>-</sup> bond.

As can be seen from Table 5, the  $\Delta X^\ddagger$  for the deprotonation *via* path I in aqueous solution is positive except the  $\Delta S^\ddagger$  for the deprotonation of pyH<sup>+</sup>. The order of magnitude of  $\Delta H^\ddagger$  is pyH<sup>+</sup> < bpyH<sup>+</sup>  $\cong$  phenH<sup>+</sup> and the difference in  $\Delta S^\ddagger$  is much greater than that in  $\Delta H^\ddagger$ . This fact implies that the difference in  $\Delta S^\ddagger$  term is seriously affected upon  $\Delta G^\ddagger$ , although the  $\Delta X_{\text{d}}^\ddagger$  term is preferred to the  $\Delta X_{\text{h}}^\ddagger$ . Thus, it is suggested that the activation state of deprotonation of pyH<sup>+</sup> is close to the proton dissociated state and has larger increment in hydration around the N-H<sup>+</sup> bond than those of bpyH<sup>+</sup> and phenH<sup>+</sup>. Comparison of  $\Delta X^\ddagger$  for the deprotonation *via* path II to that *via* path I,  $\Delta S^\ddagger$  is remarkably positive more than that *via* path I, and the deprotonation *via* path II becomes more entropic. The positive  $\Delta X_{\text{d}}^\ddagger$  and the negative  $\Delta X_{\text{r}}^\ddagger$  may cancel out each other and summation of them becomes to be nearly equal to zero. On the activation state, however, the hydration around the N-H<sup>+</sup>-OH<sup>-</sup> bond should be reduced because of the charge neutralization due to the formation of the N-H<sup>+</sup>-OH<sup>-</sup> bond. Consequently,  $\Delta S^\ddagger$  becomes markedly positive owing to the contribution of the change in hydration to the  $\Delta S^\ddagger$  term.

Table 6 Difference in activation parameters

		$\delta\Delta G^\ddagger / \text{kJmol}^{-1}$	$\delta\Delta H^\ddagger / \text{kJmol}^{-1}$	$\delta\Delta S^\ddagger / \text{JK}^{-1}\text{mol}^{-1}$
path I	pyH <sup>+</sup>	-4	32	119
	phenH <sup>+</sup>	-4	6	32
path II	pyH <sup>+</sup>	-3	-24	-68
	phenH <sup>+</sup>	-3	-57	-181

$$\delta\Delta X^\ddagger = \Delta X^\ddagger(\text{mix}) - \Delta X^\ddagger(\text{aq})$$

In order to compare the  $\Delta X^\ddagger$  in 0.05 mole fraction 1,4-dioxane-water mixture to that in aqueous solution, the difference in them,  $\delta\Delta X^\ddagger = \Delta X^\ddagger(\text{mix}) - \Delta X^\ddagger(\text{aq})$ , are summarized in Table 6. The values of  $\delta\Delta G^\ddagger$  are -4 to -3 kJmol<sup>-1</sup>. This indicates that the deprotonation should be accelerated in 1,4-dioxane-water mixture. On the deprotonation *via* path I, the magnitude of activation parameters is  $\Delta H^\ddagger(\text{mix}) > \Delta H^\ddagger(\text{aq})$  and  $\Delta S^\ddagger(\text{mix}) > \Delta S^\ddagger(\text{aq})$ , and moreover the difference in  $\Delta S^\ddagger$  is extensively large. If  $\Delta X_d^\ddagger(\text{mix})$  is equal to  $\Delta X_d^\ddagger(\text{aq})$ , the difference in  $\Delta X^\ddagger$  should be the difference in the  $\Delta X_h^\ddagger$  term. It is suggested that the hydrophilic hydration around the N-H<sup>+</sup> bond is not so formed on the activation state of deprotonation *via* path I in 1,4-dioxane-water mixture as in aqueous solution. It is, therefore, concluded that the extent of the newly formed hydration around the N-H<sup>+</sup> bond affects significantly upon the deprotonation rate *via* path I. On the deprotonation *via* path II, the order of magnitude of the activation parameters shows the reverse tendency to that of path I,  $\Delta H^\ddagger(\text{mix}) < \Delta H^\ddagger(\text{aq})$  and  $\Delta S^\ddagger(\text{mix}) < \Delta S^\ddagger(\text{aq})$ . This tendency implies the strong the N-H<sup>+</sup>-OH<sup>-</sup> bond formation at the activation state which arises from the weakly hydrated hydroxide ion in 1,4-dioxane-water mixture. Accordingly, the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  become more negative than those in aqueous solution. It is, therefore, concluded that the deprotonation *via* path II is accelerated by the contribution of the  $\Delta H^\ddagger$  term which is ascribed to the strong the N-H<sup>+</sup>-OH<sup>-</sup> bond formation.

In this study, we found that the acid dissociation of pyH<sup>+</sup> and phenH<sup>+</sup> was promoted and their deprotonation were accelerated in 1,4-dioxane-water mixture. It is suggested that the reduction in pK<sub>a</sub> is caused from the weakened hydrophilic hydration about the solutes in 1,4-dioxane-water mixture. It is also suggested that the deprotonation rate *via* path I is affected by the extent of the newly formed hydro-

philic hydration at the activated state, while the deprotonation rate *via* path II is affected by the strength of the N-H<sup>+</sup>-OH<sup>-</sup> bond formed at the activation state which depends on the extent of hydration about hydroxide ion. In conclusion, the change in hydration accompanied by the protolysis significantly affected the protolysis of py, phen, and their derivatives.

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