The Proton-transfer Reactions of the Univalent Anions of *ortho*-Hydroxy Azo Compounds in Dioxane–Water Media[†]

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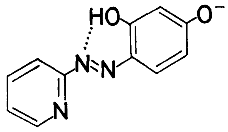
(Received June 13, 1979)

The proton-transfer reactions of the univalent anions of 4-(2-pyridylazo)resorcinol (PAR) and 4-(2-hydroxy-5-ethylphenylazo)benzenesulfonic acid (HEB) with hydroxide ion in dioxane–water media, $HA^- + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^{2-} + H_2O$, were studied by means of temperature-jump method. The dependencies of the rate constants, k_f and k_r, on the solvent compositions were interpreted by a mechanism involving the breaking of an intramolecular hydrogen-bond.

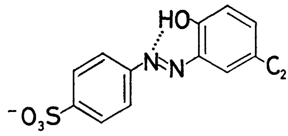
In the previous papers we reported the proton-transfer reactions in mixed solvents of some anionic ortho-hydroxy azo compounds having a strong intramolecular hydrogen-bond.[1,2] These studies have brought us some important informations for the elucidation of mechanisms of proton-transfer reactions of these compounds in aqueous and/or in non-aqueous systems.

Recently Jost *et al.*[3] extensively studied the pressure effects on the proton-transfer reaction of 4-(*p*-nitrophenylazo)resorcinol (MAG) in aqueous solution; they gave the values of activation volumes, $\Delta\overrightarrow{V}^{*} = -(3.9 \pm 0.5)\ \mathrm{cm^3\,mol^{-1}}$ and $\Delta\overleftarrow{V}^{*} = -(3.1 \pm 1)\ \mathrm{cm^3\,mol^{-1}}$ for the forward and the backward reaction, respectively, and supported a mechanism involving the breaking of the intramolecular hydrogen-bond which will be discussed here.

In the present paper we studied the proton-transfer reactions between OH^- ion and the uninegative Brønsted acids, a slightly water-soluble acid PAR and a water-soluble acid HEB, in dioxane–water media by a temperature-jump method in order to clarify the difference of the behavior observed for PAR and HEB of the same charge-type. For kinetics of the proton-transfer reactions in dioxane–water media, the definite difference depending on the water-solubility of the reactant was observed. Although PAR and HEB behave as univalent anions, the dependence of the forward rate constant of PAR on the dielectric constant is considerably different from that of HEB.



PAR: HA^-



HEB: HA^-

Experimental

Measurements. Kinetic measurements were carried out at 25 °C and $I = 0.1\ \mathrm{mol\,dm^{-3}}$ (KNO_3) with a Union Giken co-axial-cable temperature-jump apparatus Model RA-105 equipped with a pressurizing apparatus. The relaxation signal was recorded using a Tektronix oscilloscope Type 545B. The absorption spectra were measured with a Hitachi recording spectrophotometer Model EPS-3T. The pH-measurements in dioxane–water media were reported in a previous paper.[1]

Materials. Water was deionized and distilled. Dioxane was distilled and used without further purification. PAR was synthesized according to the literature[4] and recrystallized from hot ethanol–water. The purity was confirmed by elemental analysis. HEB was synthesized by the azo-coupling of *p*-ethylphenol and sulfanilic acid, and recrystallized from hot ethanol–water. Found: C, 49.31; H, 4.15; N, 8.18; S, 9.74; Na, 6.03%. Calcd for $C_{14}H_{13}N_2O_4SNa \cdot 0.5H_2O$: C, 49.85; H, 4.18; N, 8.30; S, 9.50; Na, 6.82%. Stock solutions of the dyes were prepared by dissolving a desired amount in water.

Results and Discussion

The overall equilibrium for the acid dissociation of the univalent anions of HEB and PAR, HA^-, is represented as follows:

$$HA^- \overset{K_a^c(s)}{\rightleftharpoons} A^{2-} + H^+. \qquad (1)$$

The acid-dissociation constant, $K_a^c(s)$, is determined from the pH-dependence of the absorbance of HEB and PAR in solutions.[1] The values of $K_a^c(s)$ for HEB and PAR in various dioxane-contents are summarized in Table 1. The changes in the values of $pK_a^c(s)$ for

Table 1. Acid-dissociation constants for the reaction of PAR and HEB, $HA^- \rightleftharpoons A^{2-} + H^+$ in dioxane–water media at 25 °C and $I = 0.1\ \mathrm{mol\,dm^{-3}}$ (KNO_3)

x_{diox}	$pK_a^c(s) = -\log(K_a^c(s)/\mathrm{mol\,dm^{-3}})$	
	HEB	PAR
0.000	9.04	12.11 (12.66)[a]
0.023	9.25	12.47 (12.22)
0.050	9.69	12.76 (12.78)
0.083	10.11	13.15 (13.18)
0.123	10.49	13.54 (13.66)
0.174	10.81	13.94 (13.91)

a) The value of pK_a^c in parentheses obtained from the relationship, $pK_a^c = pC_H + \log\{(D_B - D)/(D - D_A)\}$, where D is the absorbance, and A and B is the subscript for the acid and the base form of PAR and HEB, respectively.

[†] Presented in part at the 1977 Winter Meeting in Hokkaido of the Chemical Society of Japan and the Japan Society for Analytical Chemistry, Sapporo, February 2, 1977, Abstract, p. 6.

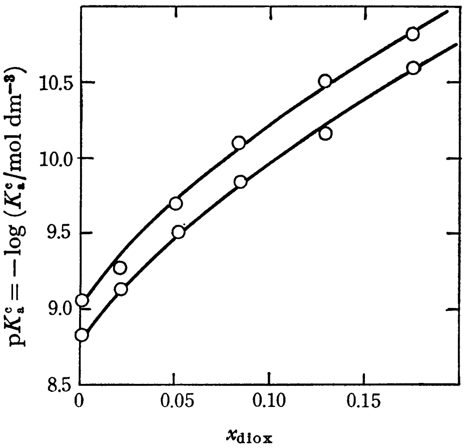


Fig. 1. Dependence of the acid-dissociation comstants, K_a^c, of HEB on the mole fractions of dioxane, x_{diox}. At 25 °C and $I = 0.1\ \mathrm{mol\ dm^{-3}}$ ($\mathrm{KNO_3}$). (a) The plot of $\mathrm{p}K_a^c(\mathrm{s})$ *vs.* x_{diox}. (b) The plot of $\mathrm{p}K_a^c(\mathrm{k})$ *vs.* x_{diox}.

the change in mole fractions of dioxane, x_{diox}, from 0 to 0.174 are evaluated to be +1.77 and +1.83 for HEB and PAR, respectively. The corresponding values for the bivalent anions of *o*-hydroxy azo compounds, 7-hydroxy-8-phenylazo-1,3-naphthalenedisulfonic acid and 4-(2,4-dihydroxyphenylazo)benzenesulfonic acid, were reported to be +2.31 and +2.27, respectively.[2] In Fig. 1, the negative logarithms of the acid-dissociation constants of HEB ($\mathrm{p}K_a^c(\mathrm{s}) = -\log(K_a^c(\mathrm{s})/\mathrm{mol\ dm^{-3}})$) are plotted as a function of x_{diox}. Increasing dioxane content in the medium leads to a decrease in $K_a^c(\mathrm{s})$ of HEB as expected. Similar tendency is observed in the $\mathrm{p}K_a^c(\mathrm{s})$ of PAR.

For the proton-transfer reactions between univalent anions of Brønsted acids and $\mathrm{OH^-}$ ion in dioxane–water media,

$$\mathrm{HA^- + OH^-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{A^{2-} + H_2O}, \qquad (2)$$

with the equilibrium constant $K_b^c = k_f/k'_r = \bar{C}_A/\bar{C}_{HA}\bar{C}_{OH}$, the relaxation time, τ, is expressed by

$$\tau^{-1} = k_f(\bar{C}_{OH} + \bar{C}_{HA}) + k'_r, \qquad (3)$$

where k'_r equals $k_r[\mathrm{H_2O}]$ and the bar over the concentration symbols denotes equilibrium concentrations. Table 2 shows the dependence of the reciprocal relaxation time on the analytical concentrations of HEB and pH*. Figure 2 shows the plots of τ^{-1} *vs.* $\bar{C}_{OH}$, giving k_f and k_r of PAR from the slope and the intercept, respectively. The values of k_f, k'_r, $\mathrm{p}K_a^c(\mathrm{k})$, and K_b^c are summarized in Tables 3 (HEB) and 4 (PAR). In Fig. 1, $\mathrm{p}K_a^c(\mathrm{k})$'s of HEB evaluated as $K_a^c(\mathrm{k}) = K_b^c K_w^c$ from the kinetic data are plotted against x_{diox}, where K_w^c denotes the apparent ionic product

Table 2. The reciprocal relaxation time of the proton-transfer reaction of HEB in aqueous solution at 25 °C and $I = 0.1\ \mathrm{mol\ dm^{-3}}$ ($\mathrm{KNO_3}$)

$C^\circ/10^{-5}\ \mathrm{mol\ dm^{-3}}$ a)	pH* b)	$\tau^{-1}/10^4\ \mathrm{s^{-1}}$
1.81	8.99	6.1
3.62	8.77	8.3
3.76	8.77	9.5
5.77	8.56	12.6
2.68	9.23	9.3

a) C° is the total concentration of HEB. b) pH* denotes the pH-meter readings.

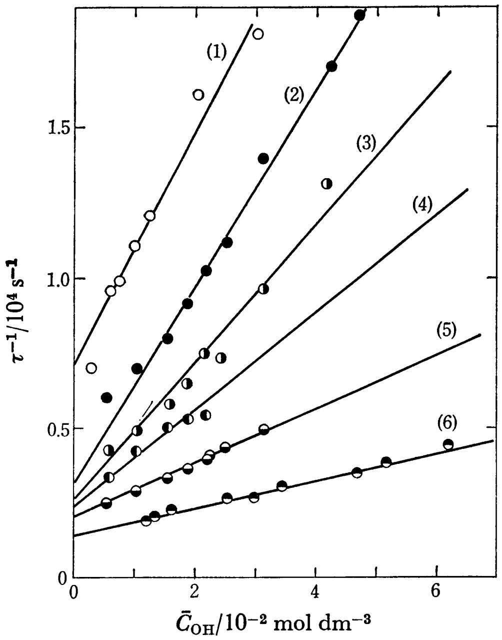


Fig. 2. Plots of reciprocal relaxation time, τ^{-1}, *vs.* $\bar{C}_{OH}$ in dioxane-water media. The mole fraction of dioxane: (1) 0.000, (2) 0.023, (3) 0.050, (4) 0.083, (5) 0.123, and (6) 0.174. At 25 °C and $I = 0.1\ \mathrm{mol\ dm^{-3}}$ ($\mathrm{KNO_3}$).

Table 3. Rate and equilibrium constants for the proton-transfer reaction of HEB, $\mathrm{HA^- + OH^-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{A^{2-} + H_2O}$, in dioxane-water media at 25 °C and $I = 0.1\ \mathrm{mol\ dm^{-3}}$ ($\mathrm{KNO_3}$)

x_{diox}	$k_f/\mathrm{mol^{-1}\ dm^3\ s^{-1}}$	$k'_r/\mathrm{s^{-1}}$	$K_b^c/\mathrm{mol^{-1}\ dm^3}$	$\mathrm{p}K_a^c(\mathrm{k})$
0.000	1.8×10^9	2.0×10^4	9.0×10^4	8.8
0.023	1.6×10^9	2.0×10^4	8.0×10^4	9.1
0.050	1.4×10^9	2.3×10^4	6.1×10^4	9.5
0.083	9.6×10^8	1.7×10^4	5.6×10^4	9.8
0.123	6.9×10^8	1.1×10^4	6.3×10^4	10.2
0.174	6.0×10^8	1.1×10^4	5.5×10^4	10.6

Table 4. Rate and equilibrium constants for the proton-transfer reaction of PAR, $\mathrm{HA^- + OH^-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{A^{2-} + H_2O}$, in dioxane-water media at 25 °C and $I = 0.1\ \mathrm{mol\ dm^{-3}}$ ($\mathrm{KNO_3}$)

x_{diox}	$k_f/\mathrm{mol^{-1}\ dm^3\ s^{-1}}$	$k'_r/\mathrm{s^{-1}}$	$K_b^c/\mathrm{mol^{-1}\ dm^3}$	$\mathrm{p}K_a^c(\mathrm{k})$
0.000	3.8×10^5	7.1×10^3	54	11.99
0.023	3.4×10^5	3.2×10^3	106	12.02
0.050	2.3×10^5	2.7×10^3	85	12.34
0.083	1.6×10^5	2.3×10^3	70	12.69
0.123	8.8×10^4	2.0×10^3	44	13.33
0.174	4.4×10^4	1.4×10^3	31	13.82

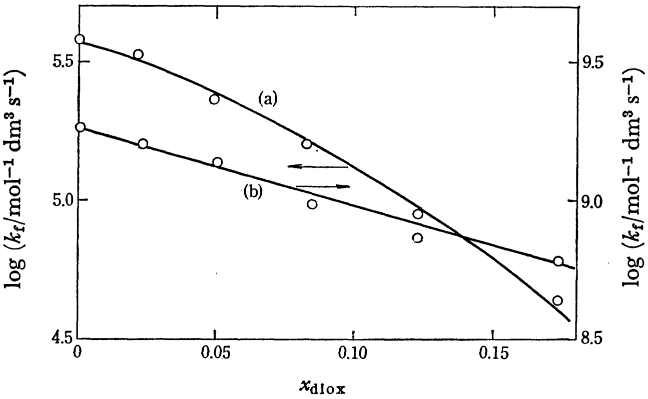


Fig. 3. Dependence of the recombination rate constants k_f on the x_{diox} at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3) for PAR (a) and HEB (b).

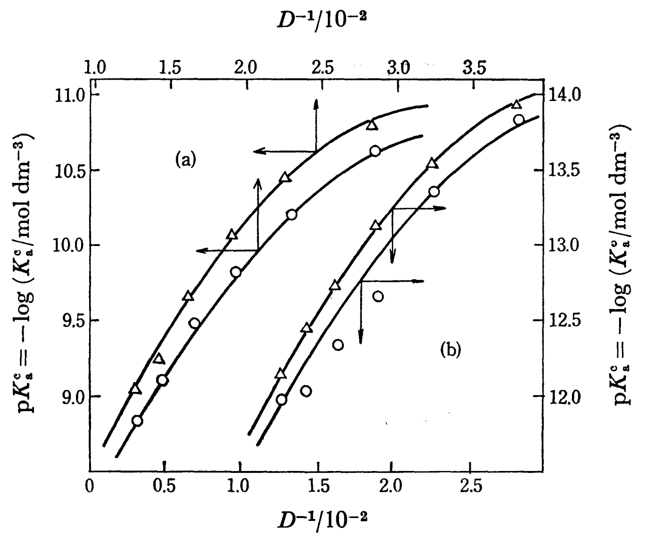


Fig. 4. Dependence of the acid-dissociation constants, K_a^c, of HEB (a) and PAR (b) on the dielectric constant of the medium at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3). ○: The plot of pK_a^c(k) *vs.* D^{-1}. △: The plot of pK_a^c(s) *vs.* D^{-1}.

of water. The differences in values between pK_a^c(k) and pK_a^c(s) of HEB and PAR are found to be small as compared with those of the bivalent anions of azo compounds. Figure 3 shows a dependence of $\log k_f$ on x_{diox}. The recombination rate constants of HEB and PAR with OH$^-$ ion decrease with increasing x_{diox} (Fig. 3).

In Fig. 4 the values of pK_a^c(k) and pK_a^c(s) are plotted against the inverse macroscopic dielectric constant of medium, D^{-1}; the dependence is not linear. The simple electrostatic effect of the Born type is not observed.

The value of pK_a^c of HEB having no para O$^-$-substituent with respect to the azo group is smaller by three orders of magnitude than that of PAR having a para O$^-$-substituent. This is due to the difference in the stabilities of the acid form, HA$^-$, of HEB and PAR.

The recombination of OH$^-$ ion and a univalent anion of HEB was found to proceed with the rate constants in the order of magnitude 10^9 mol^{-1} dm^3 s^{-1} (Table 3). However, the reaction of PAR proceeds considerably slowly, the rate constant k_f being in the order of magnitude 10^5 mol^{-1} dm^3 s^{-1}. These facts would be interpreted by the thermodynamic stability of the intramolecular hydrogen-bond and the increased double-bond character of a C–N bond between an azo nitrogen and the benzene ring owing to the resonance contribution from the para O$^-$-substituent.[1)]

A reaction mechanism

$$HA^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} HA^{*-} \tag{4}$$

$$HA^{*-} + OH^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} HA^{*-}\cdots(H_2O)_n\cdots OH^- \tag{5}$$

$$HA^{*-}\cdots(H_2O)_n\cdots OH^- \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} A^{2-} + H_2O \tag{6}$$

postulated previously[1)] for the proton-transfer reactions in dioxane–water media is applicable also to that of HEB and PAR. Equation 4 suggests the equilibrium between two isomeric species of the acid form of *o*-hydroxy azo compounds, *viz.*, an HA$^-$ species having an intramolecular hydrogen-bond and an intermediate species HA^{*-} having no intramolecular hydrogen-bond. The intermediate species can interact with the surrounding water molecules as the normal Brønsted acids do.

The relaxation time for the above reaction, τ, is given[1)] by

$$\tau^{-1} = K_{12}k_{23}(\bar{C}_{OH} + \bar{C}_{HA}) + k_{32}/K_{34}. \tag{7}$$

The overall rate constants, k_f and k_r', are shown by Eqs. 8 and 9.

$$k_f = K_{12}k_{23} = (k_{12}/k_{21})k_{23} \tag{8}$$

and

$$k_r' = k_{32}/K_{34} = k_{32}/(k_{34}/k_{43}) \tag{9}$$

Although no data on the equilibrium constant, K_{12}= [HA*$^-$]/[HA$^-$], have been reported so far, the values of K_{12} can be estimated to be 10^{-5}—10^{-6} for PAR and 10^{-1}—10^{-2} for HEB provided that the rate constant k_{23} is in the order of magnitude 10^{10} mol^{-1} dm^3 s^{-1} (diffusion-controlled). Since the K_{12} is the equilibrium constant involving the step where HA$^-$ interacts with the surrounding water molecules in the vicinity of reaction site, the larger value of K_{12} in the case of HEB indicates that the HA$^-$ species of HEB can more easily interact with the surrounding water molecules than that of PAR.[5)]

By neglecting the ionic-atmosphere term in Christiansen-Scatchard equation[7,8)] we obtain

$$\ln (k_f/k_f^\circ) = -z_iz_je^2/kTr^*D, \tag{10}$$

where z_i and z_j represent the charge of the reactants, D is the macroscopic dielectric constant of the medium, k the Boltzmann's constant, T the absolute temperature, r^* the reaction distance, e the elementary charge, and k_f° the rate constant at infinite dielectric constant. As shown in Fig. 5, the plot of $\log k_f$ *vs.* D^{-1} is linear. The forward rate constant k_f for the proton-transfer reaction is equal to $K_{12}k_{23}$ (see Eq. 8). Since, in the case of a sparingly water-soluble Brønsted acid, PAR, the value of K_{12} decreases with the decrease of the dielectric constant as observed in the case of 4-(*p*-

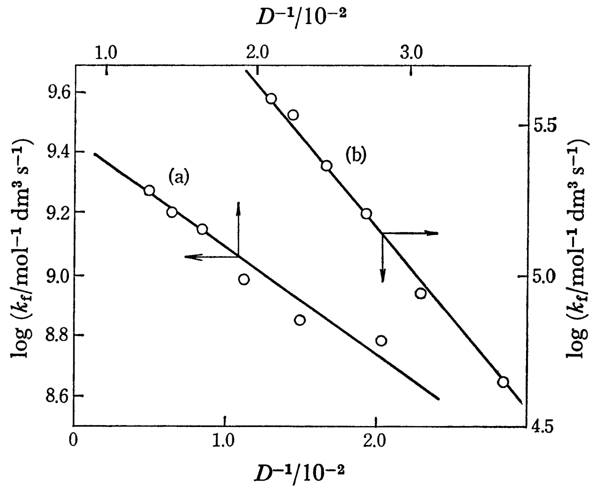


Fig. 5. Dependence of the log k_f of HEB (a) and PAR (b) on the dielectric constant, D, of the medium at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3).

nitrophenylazo)resorcinol,[1] we obtain an expectedly small value for r^* to be 3.8 Å (Fig. 5). Since in the case of a water-soluble Brønsted acid, HEB, the term K_{12} is assumed to be nearly constant, the slope in Fig. 5 is reduced to Eq. 11.

$$\begin{aligned}&\mathrm{d}\log(k_f/\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1})/\mathrm{d}D^{-1}\\&= \mathrm{d}\log(k_{23}/\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1})/\mathrm{d}D^{-1}\\&= -(z_iz_je^2)/(kTr^*). \qquad (11)\end{aligned}$$

From the slope for HEB in Fig. 5, we obtain the value of r^* to be 7.2 Å. The value of r^* was reported to be 8 Å for the neutralization reaction between hydrated proton $H_9O_4^+$ and hydrated hydroxide ion $H_7O_4^-$ in aqueous solution.[9,10] From the data mentioned above the intervening water molecules would be involved in the encounter complex, $HA^{*-}\cdots(H_2O)_n\cdots OH^-$.

Figure 6 leads to the linear relationships between $\log k_f$ and pK_a^c for HEB:

$$\log k_f = -0.27pK_a^c(\text{k}) + 11.65, \qquad (12)$$

and

$$\log k_f = -0.28pK_a^c(\text{s}) + 11.81, \qquad (13)$$

and for PAR;

$$\log k_f = -0.51pK_a^c(\text{k}) + 11.70, \qquad (14)$$

and

$$\log k_f = -0.51pK_a^c(\text{s}) + 11.80. \qquad (15)$$

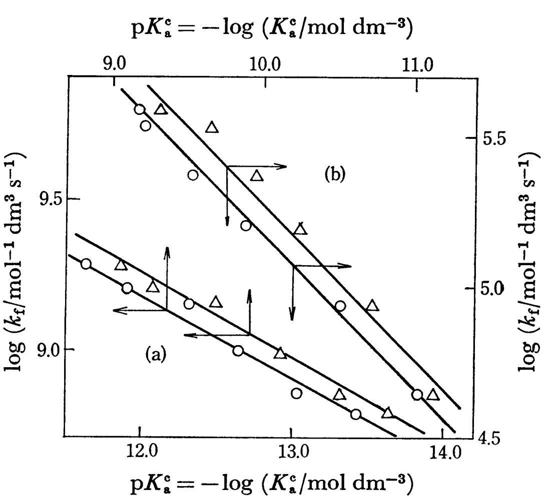


Fig. 6. Dependence of the log k_f on the pK_a^c of HEB (a) and PAR (b) in dioxane-water media at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3). ○: The plot of $\log k_f$ *vs.* $pK_a^c(\text{k})$. △: The plot of $\log k_f$ *vs.* $pK_a^c(\text{s})$.

From the empirical equations 12, 13, 14, and 15, the following Brønsted type relation is found to hold between k_f and K_a^c upon changing the solvent composition:

$$k_f = G(K_a^c)^\alpha \qquad (16)$$

and

$$0<\alpha<1. \qquad (17)$$

Equations 16 and 17 indicates a correlation between the reactivity of HA^- with OH^- ion and the proton-donor strength of HA^- upon changing the solvent composition.

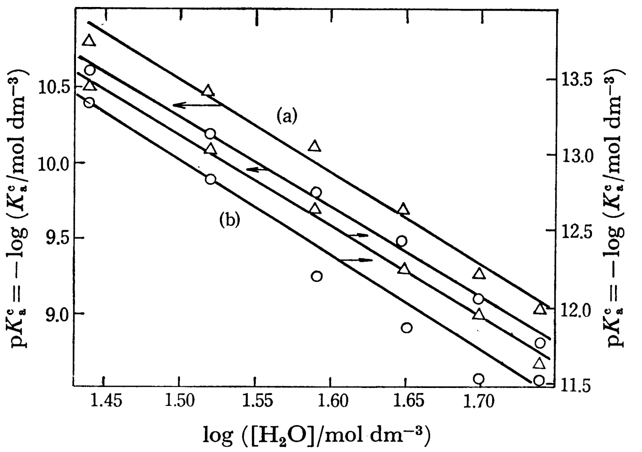


Fig. 7. Dependence of pK_a^c of HEB (a) and PAR (b) on the log $[H_2O]$ in dioxane-water media at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3). △: The plot of $pK_a^c(\text{s})$ *vs.* log $[H_2O]$. ○: The plot of $pK_a^c(\text{k})$ *vs.* log $[H_2O]$.

Figure 7 shows the linear relationship between pK_a^c and the logarithms of the concentrations of water, $\log[H_2O]$, for HEB:

$$pK_a^c(\text{k}) = -5.87\log[H_2O] + 19.08, \qquad (18)$$

and

$$pK_a^c(\text{s}) = -6.13\log[H_2O] + 19.74, \qquad (19)$$

and for PAR:

$$pK_a^c(\text{k}) = -6.27\log[H_2O] + 22.87, \qquad (20)$$

and

$$pK_a^c(\text{s}) = -6.00\log[H_2O] + 22.74. \qquad (21)$$

If the following simple acid dissociation of HA^- is postulated,

$$HA^- + n\,H_2O \overset{K}{\rightleftharpoons} H(H_2O)_x^+ + A(H_2O)_y^{2-} \qquad (22)$$

with the equilibrium constant $K = [H_{aq}^+][A_{aq}^{2-}]/\{[HA^-]\cdot[H_2O]^n\}$, the acid-dissociation constant of HA^-, K_a^c, is defined as

$$K_a^c = [H_{aq}^+][A_{aq}^{2-}]/[HA^-] = K[H_2O]^n. \qquad (23)$$

Therefore the following relationship could be expected:

$$pK_a^c = -n\log[H_2O] + pK. \qquad (24)$$

From the empirical equations 18, 19, 20, and 21, the value of n is estimated to be 6 for the acid dissociation of the univalent anions, HA^-, of HEB and PAR.[11]

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