September, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (9), 2527—2530 (1979) 2527

# Kinetic Studies of the Proton-transfer of the Bivalent Anions of *ortho*-Hydroxy Azo Compounds in Dioxane–Water Media†

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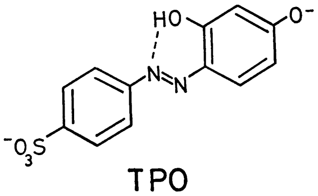
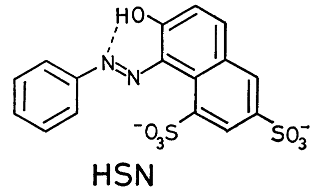
(Received November 13, 1978)

Kinetics of the proton-transfer reactions in dioxane–water media between hydroxide ion and the bivalent anions of 4-(2,4-dihydroxyphenylazo)benzenesulfonic acid (TPO) and 7-hydroxy-8-phenylazo-1,3-naphthalenedisulfonic acid (HPN) were studied by means of the temperature-jump method. For the change in the mole fraction of dioxane from 0 to 0.174, the acid-dissociation constant, $K_a^c(s)$, was found to decrease from $1.07\times10^{-11}$ to $5.25\times10^{-14}$ mol dm$^{-3}$ for HPN and from $1.32\times10^{-12}$ to $7.08\times10^{-15}$ mol dm$^{-3}$ for TPO.

One of the most pronounced and general features in the chemical effects caused by the change in the solvent composition in binary mixed solvents is the change in the degree of ionic dissociation of weak electrolytes. Dependence of the acid-dissociation constants on the solvent composition is explained in terms of both the dielectric constant of the medium and the solute-solvent interactions.[1]

In dioxane–water media the decrease in the acid-dissociation constants of the bivalent anions of *o*-hydroxy azo compounds such as HPN and TPO is mainly due to the decrease in the dielectric constant of the medium.


TPO


HSN

In the present study we have found that the recombination rate constant, $k_f$, for the proton-transfer reaction between hydroxide ion and HPN and TPO

$$\mathrm{HA^{2-} + OH^-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{A^{3-} + H_2O}$$

tion between hydroxide ion and HPN and TPO decreases with decrease in the dielectric constant of the medium, while the backward rate constant, $k_r'$, is influenced only a little by the change in dielectric constant. Based on the kinetic and the equilibrium data in dioxane–water media, the authors aimed to elucidate the solvent effects on the proton-transfer reaction of HPN and TPO.

## Experimental

Water was deionized and distilled. Dioxane was distilled over sodium and used without further purification.[2] HPN and TPO (Wako) were recrystallized from an ethanol–water solution.

Kinetic measurements were carried out at 25 °C; $I=0.1$ mol dm$^{-3}$ (KNO$_3$) with a Union Giken co-axial cable temperature-jump apparatus Model RA-105 under compressed nitrogen gas at *ca.* 2 atm to avoid cavitation upon very fast temperature rise. A Hitachi EPS-3T recording spectrophotometer was used in the equilibrium measurements.

Table 1. Values of $\log U_H$ and $pK_w^c$ at various dioxane contents, 25 °C and $I=0.1$ mol dm$^{-3}$ (KNO$_3$)

| $x_{\text{diox}}$ | $\log U_H$[a] | $pK_w^c = -\log(K_w^c/\text{mol}^2\,\text{dm}^{-6})$ |
|---|---|---|
| 0.000 | −0.07 | 13.73, 13.78[b] |
| 0.023 | −0.06 | 14.05 |
| 0.050 | −0.09 | 14.27 |
| 0.083 | −0.11 | 14.54 |
| 0.128 | −0.13 | 14.97 |
| 0.174 | −0.13 | 15.31, 15.38[c] |

a) $\log U = pC_H - pH^*$, where pH* denotes the pH-meter reading. b) See Ref. 8. c) See Ref. 9.

The measurements of pH in the mixed solvent were reported in the previous paper.[3] The apparent ionic product $K_w^c=[\mathrm{H}]\cdot[\mathrm{OH}]$ of the water in dioxane–water was obtained with a Hitachi-Horiba pH-meter F-7ss equipped with a glass electrode 1026A and Ag–AgCl reference electrode type 2010-05T. The values of $pK_w^c$ are summarized in Table 1. The function $\log U_H$ is defined as $\log U_H = pC_H - pH^*$, where $C_H$ denotes the analytical concentration of proton, and pH* pH-meter readings.

## Results and Discussion

The final step of the acid-dissociation of HPN and TPO can be expressed by

$$\mathrm{HA^{2-}} \overset{K_a^c}{\rightleftharpoons} \mathrm{A^{3-} + H^+}. \qquad (1)$$

The acid-dissociation constant, $K_a^c$, is expressed in terms of the absorbance and the equilibrium concentration of proton, $\bar{C}_H$,

$$C/\Delta A = 1/\Delta\varepsilon + \bar{C}_H/(\Delta\varepsilon\cdot K_a^c) \qquad (2)$$

where $\Delta A = A - A'$, $\Delta\varepsilon = \varepsilon_A - \varepsilon_{HA}$, and $A' = \varepsilon_{HA}C$, $\varepsilon$ is the molar absorption coefficient, $A$ the absorbance at the wavelength of the base form of HPN or TPO, and $C$ the total concentration of the Brønsted acid. The plot of $C/\Delta A$ against $\bar{C}_H$ gives straight lines for each solvent composition, yielding $\Delta\varepsilon$ and $K_a^c(s)$ from the intercept and the slope, respectively. In Fig. 1 the acid-dissociation constants determined spectrophotometrically are plotted against the mole fraction of dioxane, $x_{\text{diox}}$. Increase in the dioxane content in the medium, *viz.*, the decrease in the dielectric constant of the medium leads to a decrease in the dissociation constant of HA$^{2-}$. Such dependency of $K_a^c(s)$ on the solvent composition has also been observed in the case

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† Presented in part at the 26th Annual Meeting on Coordination Chemistry, Sapporo, August 30, 1976, Abstract p. 252 and at the 27th Annual Meeting on Coordination Chemistry, Matsumoto, September 28, 1977, Abstract, p. 233.

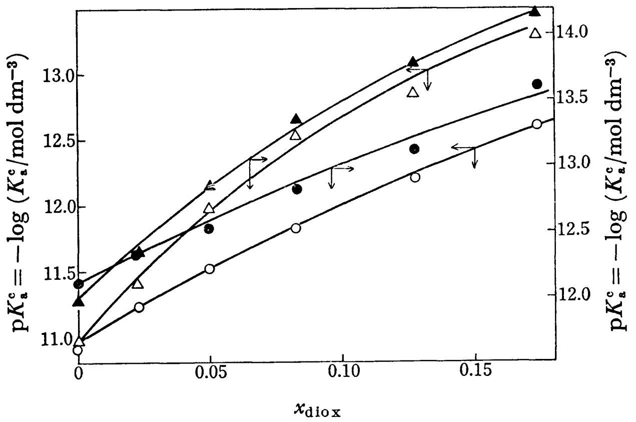

Fig. 1. Dependence of the $pK_a^c$(s) and $pK_a^c$(k) on the mole fraction of dioxane at 25 °C and $I$=0.1 mol dm$^{-3}$ (KNO$_3$). (1) HSN: ○ the plot of $pK_a^c$(k) *vs.* $x_{\text{diox}}$; △ the plot of $pK_a^c$(s) *vs.* $x_{\text{diox}}$. (2) TPO: ● the plot of $pK_a^c$(k) *vs*, $x_{\text{diox}}$; ▲ the plot of p$K$ (s) *vs.* $x_{\text{diox}}$.

of the univalent anion of 4-(*p*-nitrophenylazo)-resorcinol.[3)]

The proton-transfer reaction between hydroxide ion and the bivalent Brønsted acids, HA$^{2-}$, is expressed by

$$\text{HA}^{2-} + \text{OH}^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{A}^{3-} + \text{H}_2\text{O} \qquad (3)$$

with the equilibrium constant $K_b^c = k_f/k'_r = \bar{C}_A/(\bar{C}_{HA}\cdot\bar{C}_{OH})$, where $k'_r = k_r(\text{H}_2\text{O})$. The relaxation time, $\tau$, for Reaction 3 is related to the rate constants as follows.

$$\tau^{-1} = k_f(\bar{C}_{HA}+\bar{C}_{OH}) + k'_r. \qquad (4)$$

If the equilibrium concentration of hydroxide ion is much larger than that of the bivalent anion, Eq. 4 is approximated to $\tau^{-1} = k_f\bar{C}_{OH} + k'_r$ (Fig. 2). The rate constants and equilibrium constants at each solvent composition are summarized in Tables 2 and 3. In

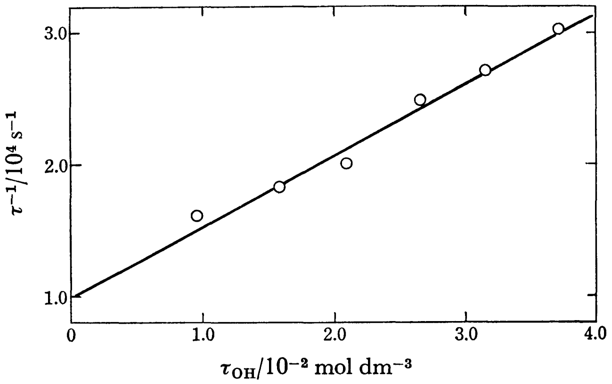

Fig. 2. Plot of the reciprocal relaxation time *vs.* the equilibrium hydroxide ion concentration at $x_{\text{diox}}$= 0.083 (TPO), 25 °C, and $I$=0.1 mol dm$^{-3}$ (KNO$_3$).

Table 2. Rate constants for the proton-transfer reaction of HSN, $\text{HA}^{2-} + \text{OH}^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{A}^{3-} + \text{H}_2\text{O}$, at 25 °C and $I$ = 0.1 mol dm$^{-3}$ (KNO$_3$)

| $x_{\text{diox}}$ | $pK_a^c$(s) | $k_f$ / $10^6$ mol$^{-1}$ dm$^3$ s$^{-1}$ | $k'_r$ / $10^3$ s$^{-1}$ | $K_b^c$ / mol$^{-1}$ dm$^3$ | $pK_a^c$(k) |
|---|---|---|---|---|---|
| 0.000 | 10.97 | 6.3 | 8.5 | 741 | 10.9 |
| 0.023 | 11.40 | 5.8 | 8.5 | 682 | 11.2 |
| 0.050 | 11.98 | 5.4 | 8.5 | 635 | 11.5 |
| 0.083 | 12.52 | 4.9 | 8.0 | 613 | 11.8 |
| 0.128 | 12.82 | 4.7 | 8.5 | 553 | 12.2 |
| 0.174 | 13.28 | 4.2 | 8.5 | 494 | 12.6 |

Table 3. Rate constants for the proton-transfer reaction of TPO, $\text{HA}^{2-} + \text{OH}^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{A}^{3-} + \text{H}_2\text{O}$, at $I$ = 0.1 mol dm$^{-3}$ (KNO$_3$)

| $x_{\text{diox}}$ | $pK_a^c$(s)$^{a)}$ | $k_f$ / $10^5$ mol$^{-1}$ dm$^3$ s$^{-1}$ | $k'_r$ / $10^3$ s$^{-1}$ | $K_b^c$ / mol$^{-1}$ dm$^3$ | $pK_a^c$(k) | $T$ / K | Ref. |
|---|---|---|---|---|---|---|---|
| 0.000 | 11.88 (12.20) | 6.9 | 16 | 43 | 12.1 | 298 | This work |
|  | — | 3.6 | 8 | 45 | — | 285 | 5 |
|  | 12.00 | 8.8 | 6.5 | 135 | — | 288 | 6 |
|  | 12.01$^{b)}$ | 8.6 | — | — | — | 298 | 7 |
| 0.023 | 12.34 (12.24) | 6.4 | 12 | 53 | 12.3 | 298 | This work |
| 0.050 | 12.85 (12.77) | 5.5 | 8.8 | 63 | 12.5 | 298 | This work |
| 0.083 | 13.33 (13.15) | 5.3 | 10 | 53 | 12.8 | 298 | This work |
| 0.128 | 13.77 (13.56) | 4.7 | 6.0 | 78 | 13.1 | 298 | This work |
| 0.174 | 14.15 (14.25) | 3.2 | 5.8 | 55 | 13.6 | 298 | 2 |

a) The values of $pK_a^c$ in parentheses are obtained from the relationship, $pK_a^c = pC_H + \log[(D_B - D)/(D - D_A)]$, where $D$ is the absorbance, subscripts A and B are for the acid and the base form of TPO, respectively. b) $K_a = a_{H^+}\cdot C_A/C_{HA}$, where $a_{H^+}$ is the activity of the proton.

the case of HPN, the value of $k_f$ slightly decreases with increase in the mole fraction of dioxane, $x_{\mathrm{diox}}$, and that of $k_r$ increases from $1.5\times10^2$ mol$^{-1}$ dm$^3$ s$^{-1}$ at $x_{\mathrm{diox}}=0$ to $3.1\times10^2$ mol$^{-1}$ dm$^3$ s$^{-1}$ at $x_{\mathrm{diox}}=0.174$ with increase in $x_{\mathrm{diox}}$. The value of $k_f$ for TPO also gradually decrease with increase in $x_{\mathrm{diox}}$. The value of $k_r'$ for TPO changes quite a little.

The detailed mechanism of the proton-transfer reaction may be written as follows.[2,3]

$$\mathrm{HA^{2-}} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{HA^{*2-}}, \tag{5a}$$

$$\mathrm{HA^{*2-}} + \mathrm{OH^-} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{HA^{*2-}\cdots(H_2O)_\mathit{n}\cdots OH^-} \tag{5b}$$

$$\mathrm{HA^{*2-}\cdots(H_2O)_\mathit{n}\cdots OH^-} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \mathrm{A^{3-}} + \mathrm{H_2O}, \tag{5c}$$

where $\mathrm{HA^{2-}}$ stands for the bivalent anion having an intramolecular hydrogen-bond and $\mathrm{HA^{*2-}}$ an intermediate species without an intramolecular hydrogen-bond. Assuming the steady state for $\mathrm{HA^{*2-}}$ and $\mathrm{HA^{*2-}\cdots(H_2O)_\mathit{n}\cdots OH^-}$ and the relationships $k_{21}\gg k_{23}\overline{C}_{\mathrm{OH}}$ and $k_{34}\gg k_{32}$, the observed rate constants in Eq. 3 are expressed as follows.

$$k_f = K_{12}k_{23} = (k_{12}/k_{21})k_{23} \tag{6}$$

and

$$k_r = k_{32}/K_{34} = k_{32}/(k_{34}/k_{43}). \tag{7}$$

As shown in Fig. 3 the value of $k_f$ decreases with the decrease in the dielectric constant of the solution, while the value of $k_r'=k_r$ ($\mathrm{H_2O}$) varies little with change in the solvent composition particularly in the case of HPN. The decrease in $k_f$ would be mainly due to the dependence of $k_{23}$ on the dielectric constant provided that the change in the value of $K_{12}$ for the intramolecular process is small.[3] By neglecting the ionic-atmosphere term in Brønsted-Christiansen-Scatchard equation,[4] we obtain

$$\mathrm{d}\log(k_f/\mathrm{mol^{-1}\,dm^3\,s^{-1}})/\mathrm{d}\,D^{-1} = \mathrm{d}\log(k_{23}/\mathrm{mol^{-1}\,dm^3\,s^{-1}})/\mathrm{d}\,D^{-1} \tag{8}$$

and

$$\mathrm{d}\log(k_{23}/\mathrm{mol^{-1}\,dm^3\,s^{-1}})/\mathrm{d}\,D^{-1} = -(z_i z_j e^2)/(kTr^*), \tag{9}$$

where $z_i$ and $z_j$ represent the charge of the reactants, $D$ is the dielectric constant of the medium, $k$ Boltzmann's constant, $T$ absolute temperature, $r^*$ the phenomenological reaction distance, and e elementary charge. From the slope in Fig. 3 the value of $r^*$ for TPO is obtained to be 23 Å and that for HPN 26 Å from the plot in lower dioxane content and 66 Å from that in higher dioxane content, respectively. Actually, however, the phenomenological reaction distance $r^*$ should be calculated by considering the ionic strength term, leading to a smaller value for $r^*$. From the value of $r^*$ there would be intervening water molecules in the encounter complex, $\mathrm{HA^{*2-}\cdots(H_2O)_\mathit{n}\cdots OH^-}$.

The kinetic $\mathrm{p}K_a^c(\mathrm{k})$ was derived from the following relation.

$$K_a^c(\mathrm{k}) = K_b^c(\mathrm{k})\cdot K_w^c(\mathrm{s}). \tag{10}$$

In the case of the bivalent anion of a water-soluble Brønsted acid the difference between $\mathrm{p}K_a^c(\mathrm{s})$ and $\mathrm{p}K_a^c(\mathrm{k})$ (Fig. 1) is large, particularly in the higher dioxane content. On the other hand, in the case of the univalent anion of the sparingly water-soluble Brønsted acid such as 4-(*p*-nitrophenylazo)resorcinol (MAG) the difference is small.[3] Such difference in $\mathrm{p}K_a^c(\mathrm{k})$ and $\mathrm{p}K_a^c(\mathrm{s})$ would be ascribed to that in the microscopic environment around the solute such as TPO, HPN, and MAG.

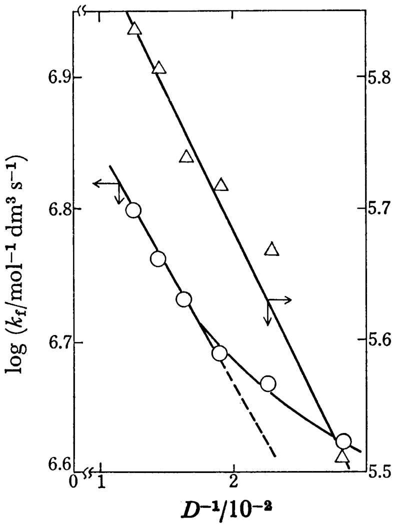

Fig. 3. Dependence of log $k_f$ on the inverse dielectric constant of the medium. ○ The plot for HSN; △ the plot for TPO.

The linear relationship between log ($k_f$/mol$^{-1}$ dm$^3$ s$^{-1}$) and $\mathrm{p}K_a^c$ for HPN is as follows (Fig. 4).

$$\log k_f = -1.1\times10^{-1}\,\mathrm{p}K_a^c(\mathrm{k}) + 8.0 \tag{11}$$

and

$$\log k_f = -7.5\times10^{-2}\,\mathrm{p}K_a^c(\mathrm{s}) + 7.6 \tag{12}$$

On the other hand, the relationship between $\mathrm{p}K_w^c$ and $\mathrm{p}K_a^c$ for HSN is expressed by

$$\mathrm{p}K_a^c = -\log k_f + \log k_r' + \mathrm{p}K_w^c. \tag{13}$$

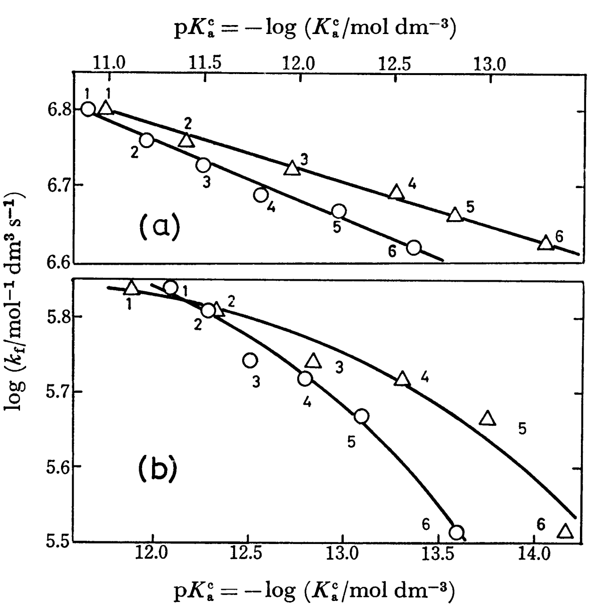

Fig. 4. Dependence of log $k_f$ *vs.* $\mathrm{p}K_a^c(\mathrm{k})$ and $\mathrm{p}K_a^c(\mathrm{s})$ for HSN (a) and TPO (b): ○, log $k_f$ *vs.* $\mathrm{p}K_a^c(\mathrm{K})$. △, log $k_f$ *vs.* $\mathrm{p}K_a^c(\mathrm{s})$. $x_{\mathrm{diox}}$: (1) 0.000, (2) 0.023 (3) 0.050, (4) 0.083, (5) 0.128, and (6) 0.178.

From the plot of $\mathrm{p}K_{\mathrm{w}}^{\mathrm{c}}$ against $\mathrm{p}K_{\mathrm{a}}^{\mathrm{c}}$ for HPN, the following empirical equations are obtained.

$$\mathrm{p}K_{\mathrm{w}}^{\mathrm{c}} = 0.95\,\mathrm{p}K_{\mathrm{a}}^{\mathrm{c}}(\mathrm{k}) + 3.38 \tag{14}$$

$$\mathrm{p}K_{\mathrm{w}}^{\mathrm{c}} = 0.64\,\mathrm{p}K_{\mathrm{a}}^{\mathrm{c}}(\mathrm{s}) + 6.72 \tag{15}$$

Equations 11 and 13 gives the relationship $\mathrm{p}K_{\mathrm{w}}^{\mathrm{c}} = 0.89\,\mathrm{p}K_{\mathrm{a}}^{\mathrm{c}}(\mathrm{k}) + 8.0 - \log k'_{\mathrm{r}}$ which agrees with Eq. 14, since the value of $\log k'_{\mathrm{r}}$ is evaluated to be 3.93 (Table 2). Equations 12 and 13 give the relationship $\mathrm{p}K_{\mathrm{w}}^{\mathrm{c}} = 0.93\,\mathrm{p}K_{\mathrm{a}}^{\mathrm{c}}(\mathrm{s}) + 7.6 - \log k'_{\mathrm{r}}$ which does not agree with Eq. 15. In the case of TPO, no linear relationships are observed (Fig. 4). The linear relationship between $\log k_{\mathrm{f}}$ and $\mathrm{p}K_{\mathrm{a}}^{\mathrm{c}}$ observed for HPN is explained by the constancy of the values of $k'_{\mathrm{r}}$ with variation in solvent composition.

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