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PROTON-TRANSFER REACTION OF 2,4-DIHYDROXYAZOBENZENE IN AQUEOUS SOLUTION

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The recombination reaction of 2,4-dihydroxyazobenzene (DAB; H*HA) with the hydroxide ion is investigated by temperature-jump method in 2%(v/v) ethanol-water solution. The presence of the minimum observed in the τ^{-1} vs. $\bar{C}_{OH}$ plot is interpreted by assuming a pre-equilibrium involving an intermediate H^*A^- with an undissociated para-OH, which has not been pointed out so far.

The rates of recombination with OH^- ion of the Brønsted acids such as ortho-hydroxy-azo compounds having an intramolecular hydrogen-bond are by many orders of magnitude lower than those of the normal Brønsted acids.[1)] Recently the proton-transfer reactions of these compounds were studied in non-aqueous solutions[2)] and in aqueous solutions under pressure.[3)] In the present paper we report an unusual aspect of the kinetics of the proton-transfer reaction with the hydroxide ion of DAB having an intramolecular hydrogen-bond in 2%(v/v) ethanol-water solution.

DAB is a diprotic acid with absorption maxima at $\lambda_{max}^{H^*HA}$ = 378 nm, $\lambda_{max}^{HA^-}$ = 430 nm, and $\lambda_{max}^{A^{2-}}$ = 474 nm for each species, where H* and H denote the proton of the para- and the ortho-hydroxyl group, respectively. H*HA and A^{2-} have also a shoulder around 415 and 410 nm, respectively. The second acid-dissociation constant K_a^c is expressed in terms of the absorbance at 500 nm and the equilibrium concentration of proton, $\bar{C}_H$, as follows,[4)]

$$C/\Delta A_{500} = 1/\Delta\varepsilon + \bar{C}_H/\Delta\varepsilon K_a^c \qquad (1)$$

with $\Delta A_{500} = A_{500} - A'_{500}$, $\Delta\varepsilon = \varepsilon_A - \varepsilon_{HA}$, and $A'_{500} = \varepsilon_{HA}C$, where ε is the molar absorption coefficient, A_{500} the absorbance at 500 nm and C is the total concentration of DAB. Figure 1 shows the relation between $C/\Delta A_{500}$ and $\bar{C}_H$. From the slope and the intercept of the straight line, the value of the K_a^c is obtained. The value of pK_a^c is evaluated to be 11.89. The kinetic study revealed that as for the second acid-dissociation of DAB, the contribution of the species H^*A^- having a para-hydroxyl proton but no ortho-hydroxyl proton can not be neglected (See Scheme I). This was already mentioned by A. Corsini[5)] with respect to the complex formation of some heterocyclic ortho-hydroxy-azo compounds, PAR, PAN, and TAR, but he did not consider the equilibrium I $\rightleftharpoons$ II. The resonance Raman spectral studies of Tropaeolin-O by T. Uno et al.[6)] suggest the contribution of the quinoidal species of HA^- and H^*A^-.[7)] According to the Scheme I, the observed overall acid-

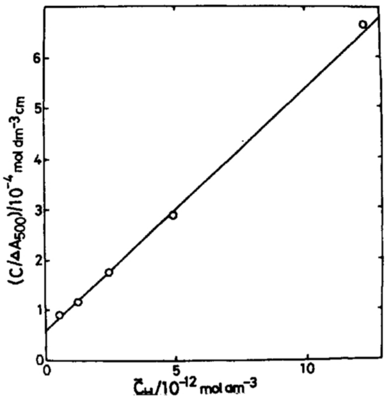


Fig. 1. Plot of $C/\Delta A_{500}$ vs. $\bar{C}_H$ in 2%(v/v) ethanol-water solution. At 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3).

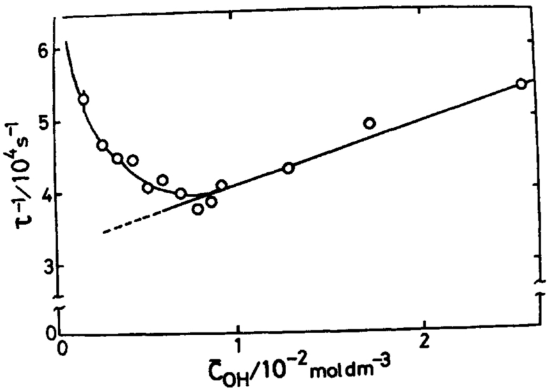
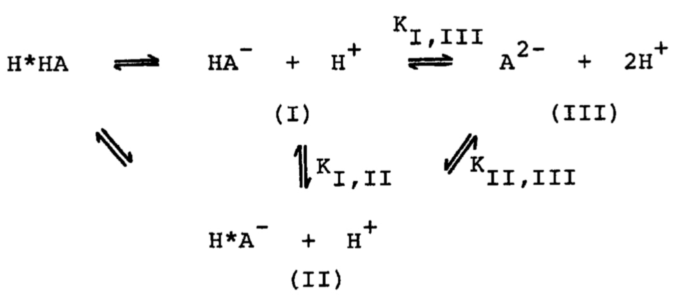


Fig. 3. Dependence of the reciprocal relaxation time on $\bar{C}_{OH}$.



Scheme I

dissociation constant of HA^-, K_a^c, is expressed as follows :

$$K_a^c = (K_{I,III} \times K_{II,III})/(K_{I,III} + K_{II,III}) \qquad (2)$$

Since the acid-dissociation of para-OH group in the species H^*A^- occurs predominantly, the value of $K_{II,III}$ must be larger than that of $K_{I,III}$. Therefore the observed K_a^c is approximately equal to $K_{I,III}$.

The kinetic measurements for the reaction of OH^- ion with DAB were carried out with a Union-Giken co-axial-cable temperature-jump apparatus Model RA-105. Figures 2(a) and 2(b) show the decrease in A_{490} and the corresponding increase in A_{430}, respectively. The log ΔC-time plot at 490 nm yields a straight line but that at 430 nm deviates from the linear relationship. Figure 3 shows the plot of the reciprocal relaxation time τ^{-1} vs. the equilibrium concentration of the hydroxide ion $\bar{C}_{OH}$. The value of τ^{-1} decreases initially with the increase of $\bar{C}_{OH}$, passes through a minimum at $pC_H \simeq 11.6$ and again shows a linear increases.[8] In region $pC_H > 11.6$, the relationship $\tau^{-1} = k_f\bar{C}_{OH} + k_r$ is held, evaluating the values of k_f and k_r to be 8.8×10^5 mol^{-1} dm^3 s^{-1} and 3.2×10^4 s^{-1}, respectively. The concentration-dependence of the reciprocal relaxation time are interpreted by the following Scheme II.

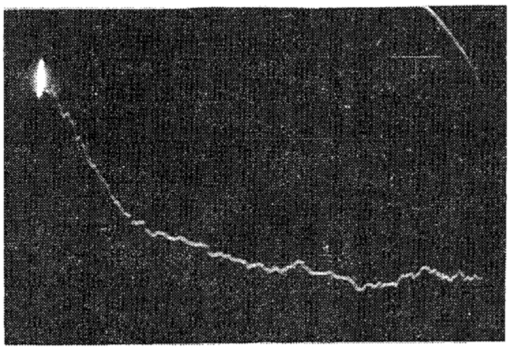


Fig. 2 (a). A temperature-jump signal at 490 nm. $\bar{C}_{OH} = 3.41 \times 10^{-3}$ mol dm^{-3}, $C = 2.92 \times 10^{-5}$ mol dm^{-3}, at 25 °C, and $I = 0.1$ mol dm^{-3}(KNO_3). Abscissa: 10 μs/div. Ordinate: 10 mV/div.

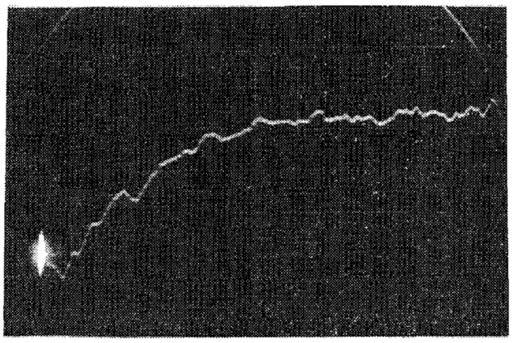
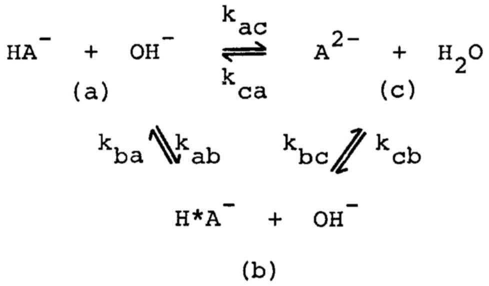


Fig. 2(b). A temperature-jump signal at 430 nm. $\bar{C}_{OH} = 4.26 \times 10^{-3}$ mol dm^{-3}, $C = 2.92 \times 10^{-5}$ mol dm^{-3}, at 25 °C, and $I = 0.1$ mol dm^{-3}(KNO_3). Abscissa: 10 μs/div. Ordinate: 20 mV/div.



$$\begin{tikzcd}[column sep=large]
\underset{(a)}{HA^- + OH^-} \arrow[rr, shift left, "k_{ac}"] \arrow[dr, shift left, "k_{ab}"] & & \underset{(c)}{A^{2-} + H_2O} \arrow[ll, shift left, "k_{ca}"] \arrow[dl, shift left, "k_{cb}"] \\
& \underset{(b)}{H{*}A^- + OH^-} \arrow[ul, shift left, "k_{ba}"] \arrow[ur, shift left, "k_{bc}"] &
\end{tikzcd}$$

Scheme II

For the small perturbation ΔC_i near the equilibrium, the rate equation can be approximated as

$$d\Delta C_A/dt = -a_{11}\Delta C_A - a_{12}\Delta C_{HA} \qquad (3)$$

and

$$d\Delta C_{HA}/dt = -a_{21}\Delta C_A - a_{22}\Delta C_{HA}, \qquad (4)$$

where $a_{11} = k_{cb} + k_{ca} + k_{ac}\bar{C}_{HA} + k_{bc}(\bar{C}_{H*A} + \bar{C}_{OH})$, $a_{12} = (k_{bc} - k_{ac})\bar{C}_{OH}$, $a_{21} = k_{ba} - k_{ca} - k_{ac}\bar{C}_{HA}$, and $a_{22} = k_{ba} + k_{ab} + k_{ac}\bar{C}_{OH}$. The reciprocal relaxation time of this system is derived from the determinant. Since the step b $\rightleftharpoons$ c is assumed to be in pre-equilibrium, the reciprocal relaxation time is given by eq. 5.

$$\begin{aligned}\tau^{-1} = {} & k_{ab} + k_{ba}/(1 + K_{bc}\bar{C}_{OH}) + k_{ca}K_{bc}\bar{C}_{OH}/(1 + K_{bc}\bar{C}_{OH}) \\ & + k_{ac}[\bar{C}_{OH} + \bar{C}_{HA}\bar{C}_{OH}K_{bc}/(K_{bc}\bar{C}_{OH} + 1)] \qquad (5)\end{aligned}$$

where $K_{ac} = k_{ac}/k_{ca}$, $K_{ab} = k_{ab}/k_{ba}$, and $K_{bc} = k_{bc}/k_{cb}$. Since $K_{bc}\bar{C}_{OH} \gg 1$,

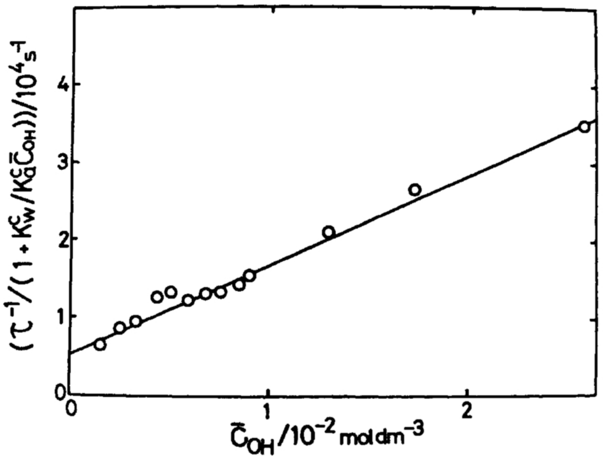


Fig. 4. Plot of Equation 6.

$\bar{C}_{OH} >> \bar{C}_{HA}$ and $K_{ac} = K_{bc}K_{ab}$, eq. 5 is reduced to $\tau^{-1} = k_{ab} + k_{ba}/(K_{bc}\bar{C}_{OH}) + k_{ca} + k_{ac}\bar{C}_{OH}$. Then the eq. 5 is transformed into $\tau^{-1}[1 + 1/(K_{ac}\bar{C}_{OH})]^{-1} = k_{ab} + k_{ac}\bar{C}_{OH}$. In the previous paper[2] we indicated the relation $K_a^c = K_b^c K_w^c$, where $K_w^c = \bar{C}_{OH}\bar{C}_H$ and $K_b^c = \bar{C}_A/(\bar{C}_{H*A} + \bar{C}_{HA})\bar{C}_{OH}$. Using the similar relation in eq. 2, we obtain $K_b^c \simeq K_{ac}$. Therefore eq. 5 is reduced to eq. 6.

$$\tau^{-1}[1 + K_w^c/(K_a^c\bar{C}_{OH})]^{-1} = k_{ab} + k_{ac}\bar{C}_{OH} \qquad (6)$$

From Fig. 4, k_{ab} and k_{ac} are evaluated to be $5.2 \times 10^3\ s^{-1}$ and $1.2 \times 10^6\ mol^{-1}\cdot dm^3\ s^{-1}$, respectively. From the relationship $K_b^c \simeq K_{ac}$, $k_{ca} \simeq 4.2 \times 10^4\ s^{-1}$.

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7) A clear information on the existence of the equilibrium I $\rightleftharpoons$ II involving $H*A^-$ would be obtained by the studies on the pH-dependence of chemical shifts in the carbon-13 NMR spectra.
8) Recently a similar dependence is reported by Perlmutter-Hayman and Schinar, but the mechanism proposed by them differs from that of the Scheme II. See, B. Perlmutter-Hayman and R. Schinar, Int. J. Chem. Kinet., 8, 741 (1976).

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