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Kinetics of the Proton-Transfer Reaction of 4-(2,4-Dihydroxyphenylazo)nitrobenzene in Dioxane–Water Media*

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Kinetics of proton-transfer reactions in 4 to 50%(v/v) dioxane–water media between hydroxide ion and 4-(2,4-dihydroxyphenylazo)nitrobenzene (Magneson; MAG) having a strong OH···N intramolecular hydrogen-bond are studied by means of the temperature-jump method. The forward and the backward rate constants k_f and $k_r[H_2O]$ for the reaction $OH^- + HA^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2O + A^{2-}$ are evaluated to be in the range of 9.2×10^5—1.3×10^5 $mol^{-1}\,dm^3\,s^{-1}$ and 5.5×10^3—$1.8 \times 10^3\,s^{-1}$, respectively. The dependence of the k_f and the acid dissociation constant K_a^c on the dioxane contents of the medium is interpreted on the basis of solute-solvent interactions.

The kinetic studies of proton-transfer reactions in mixed solvents are of particular importance for the interpretation of fast proton-transfer reactions in aqueous solutions, especially from the point of view of solute-solvent interactions.

1,4-Dioxane, a typical water-miscible aprotic solvent, can cover the wide range of dielectric constant of the medium on mixing with water. This characteristic is favorable for evaluating the solvent effects such as electrostatic effect in the fast proton-transfer reactions. Many investigations on the structure of dioxane–water solutions have so far been reported in detail.[1] However, it is necessary to get further information on the liquid structure of dioxane–water system at the periphery of a *bulky* solute molecule such as 4-(2,4-dihydroxyphenylazo)nitrobenzene (Magneson; MAG).

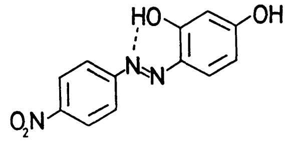
In a previous paper[2] we determined the overall rate constants k_f and k_r for the proton-transfer reactions between hydroxide ion and some *ortho*-hydroxy azo and azomethine compounds HA in 50%(v/v) dioxane–water medium and proposed the following reaction mechanism for this medium;

$$\underset{[1]}{\widehat{HA} + OH^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{[2]}{HA^* + OH^-}$$

$$\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{[3]}{HA^* \cdots (H_2O)_n \cdots OH^-} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{[4]}{A^- + H_2O.}$$

In the step $[1] \rightleftharpoons [2]$, the hydrogen-bonded proton in $\widehat{HA}$ is set free from the azo-nitrogen atom and interacts with solvent *water* molecules to form HA*. Recently Jost and Liphard directly proved the existence of the first elementary step $[1] \rightleftharpoons [2]$ from the activation volume of the overall reaction determined by the temperature-jump study under pressure.[3]

In the present study we found that for the uninegative acid HA^- of MAG the recombination rate constant k_f decreases with increasing dioxane contents in the medium. This dependence in the k_f was attributed to the change of the two terms, $K_{12} = k_{12}/k_{21}$ and k_{23}. From the dependence of $\log k_f$ on the value of the macroscopic dielectric constant of the medium, the number of intervening *water* molecules in the encounter complex, $HA^* \cdots (H_2O)_n \cdots OH^-$, was estimated to be $n = 4$—5.



MAG: $\widehat{H_2A}$

Experimental

Reagents. The water used here was deionized and distilled. Guaranteed grade dioxane (Wako) was distilled and used without further purification.[2] 4-(2,4-Dihydroxyphenylazo)nitrobenzene was purified by repeated recrystallization from methanol. Dioxane solution of the dye (3×10^{-3} mol dm^{-3}) was stored in a well-stoppered bottle to avoid evaporation.

Measurements. *pH in the Mixed Solvent*: We used the following relationship[4] between pH-meter readings (pH*) and values of $-\log(C_H/\text{mol dm}^{-3}) = pC_H$

$$\log U_H = pC_H - pH^*,$$

where C_H denotes the analytical concentration of the solvated proton determined titrimetrically. The plot of pH* *vs.* pC_H shows a good linear relationship for any dioxane content in the medium. The values of $\log U_H$ were evaluated in the range of pH*=3—12 at 25 °C and $I = 0.1$ mol dm^{-3} ($NaClO_4$) to be −0.07, −0.03, −0.06, −0.08, −0.11, and −0.14 for the mixed solvent containing 0, 10, 20, 30, 40, and 50%(v/v) dioxane, respectively. Hitachi-Horiba pH-meters Model P and Model M-7 were used throughout the study.

Equilibria and Kinetics: The acid dissociation constants of MAG were determined spectrophotometrically with a Hitachi recording spectrophotometer Model EPS-3T. The kinetic measurements were carried out with a Union Giken co-axial-cable temperature-jump apparatus Model RA-105. The temperature-jump cell was made of Teflon and equipped with gold electrodes. Temperature-rise was determined for discharge at 25 kV from the calibration curve between the light intensity and the temperature of the sample solution at $I = 0.1$ mol dm^{-3} (KNO_3) to be 4.4 and 3.8 °C in the aqueous and the 50%(v/v) dioxane–water solution, respectively. The rise-time of the temperature in 50%(v/v) dioxane–water solution was *ca.* 5 μs.[5] To avoid partial decomposition of the dye after repeated discharges on the same sample solution, we often renewed the sample solution in the cell. As the

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noise-level in the signal was serious for dioxane–water system, the discharge voltage was carefully controlled below 25 kV. The reaction was followed on the screen of an oscilloscope Tektronix Type 545B at the absorption maximum of the conjugated base of the Brønsted acid. Temperature of the solution was kept constant by circulating the water thermostated with a regulator Lauda Type K2R or Coolnics Model CTR-1B.

Results

Equilibria of the Reaction. The apparent ionic product $K_w^c=[H][OH]$ of the water in dioxane–water mixture at 25 °C and $I=0.1$ mol dm^{-3} (NaClO$_4$) was calculated using the values of log U_H derived from the data of the potentiometric titrations as described in detail in a previous paper.[2] The values of K_w^c thus obtained were used for the evaluation of the acid dissociation constant K_a^c based on the kinetic data, according to the relation $K_a^c=[H][A]/[HA]=(k_f/k'_r)[H][OH]=K_b^cK_w^c$, where K_b^c denotes the ratio k_f/k'_r and $k'_r=k_r\cdot[H_2O]$. Figure 1 shows the dependence of the pK_w^c $(=-\log(K_w^c/\text{mol}^2\,\text{dm}^{-6}))$ on the mole fraction of dioxane in the medium, x_{diox}, indicating the decrease in K_w^c with increasing dioxane content.

The absorption coefficient A of the solution at wavelength where the absorption of an acid form HA$^-$ of MAG can be neglected is given by

$$A = \varepsilon_{HA}\bar{C}_{HA} + \varepsilon_A\bar{C}_A \simeq \varepsilon_A\bar{C}_A, \tag{1}$$

where ε and $\bar{C}$ denote the molar absorption coefficient and the equilibrium concentration, respectively. The acid dissociation constant $K_a^c=[H][A]/[HA]$ is derived from the following equation;

$$C/A_A = 1/\varepsilon_A + \bar{C}_H/\varepsilon_A K_a^c, \tag{2}$$

where C denotes the total concentration, $C = C_{HA} + C_A$, and A_A the absorption coefficient of a basic form A^{2-}. The plot of C/A_A *vs.* $\bar{C}_H$ for each dioxane content of the medium gives a straight line as shown in Fig. 2. From the slope and the intercept of the straight line, the values of the K_a^c and ε_A are obtained, respectively. The acid dissociation constants K_a^c in the medium of varying dioxane content are summarized in Table 1.

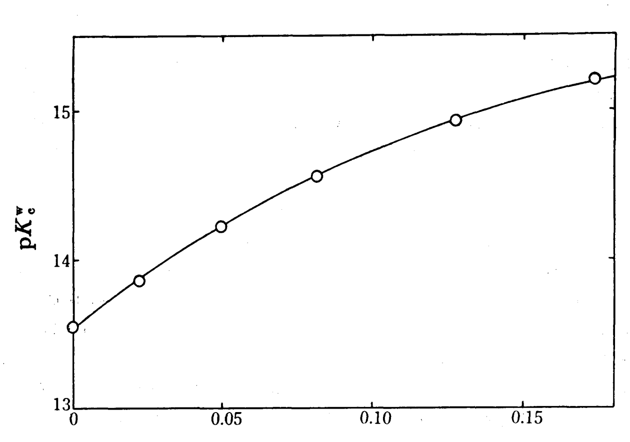

Fig. 1. Dependence of thepK_w^c on the mole fraction of dioxane, x_{diox}. At 25 °C and $I=0.1$ mol dm^{-3} (NaClO$_4$).

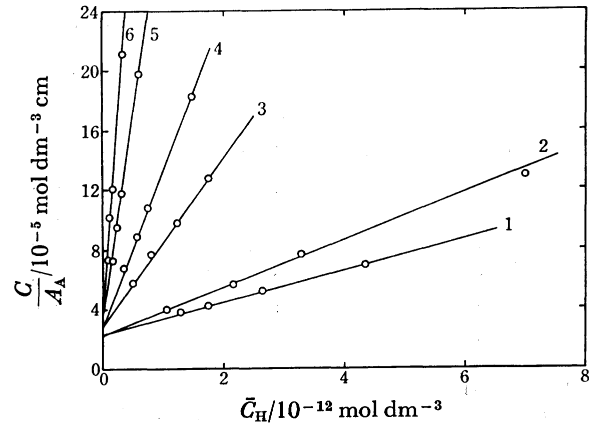

Fig. 2. Plots of C/A_A *vs.* $\bar{C}_H$ in dioxane-water media. Dioxane content: (1) 4, (2) 10, (3) 20, (4) 30, (5) 40, and (6) 50%(v/v). At 25 °C and $I=0.1$ mol dm^{-3} (KNO$_3$).

TABLE 1. ACID DISSOCIATION CONSTANTS K_a^c OF MAGNESON IN DIOXANE–WATER MEDIUM AT 25 °C DETERMINED FROM THE SPECTROPHOTOMETRIC DATA

Dioxane/%(v/v)	pK_a^c $(=-\log(K_a^c/\text{mol dm}^{-3}))$[a]
4	11.66
10	11.88
20	12.26
30	12.60
40	12.98
50	13.23

a) K_a^c = [A] [H]/[HA], I = 0.1 mol dm^{-3} (KNO$_3$).

In Fig. 4(a) the spectrophotometric acid dissociation constants are plotted against the mole fraction of dioxane, x_{diox}. Increasing dioxane content in the medium would lead to a decrease in the acid dissociation constant of HA$^-$. A linear relationship between pK_a^c and x_{diox} is observed in the range of x_{diox} lower than 0.09, while for simple nonaromatic carboxylic acids such as acetic acid Van Uitert and Haas,[4] and Harned and Owen[6] reported the corresponding linear relationship in by far the wider range of the mole fraction of dioxane.

Kinetics. For the proton-transfer reactions of uninegative acid HA$^-$ in the mixed solvent,

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

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

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

where k'_r involves the concentration of the water in the mixed solvent and equal to $k_r[H_2O]$. Figure 3 shows the plots of τ^{-1} *vs.* $\bar{C}_{HA}+\bar{C}_{OH}$, giving k_f and k'_r from the slope and the intercept, respectively. The values of k_f, k'_r, and K_b^c are summarized in Table 2. In Fig. 4, pK_a^c evaluated as $K_a^c=K_b^cK_w^c$ from the kinetic data is plotted against x_{diox} together with the spectrophotometric pK_a^c. Figure 5 shows a dependence of log k_f on x_{diox}. At higher dioxane content, marked deviation from the linear dependence is observed.

TABLE 2. RATE CONSTANTS FOR THE PROTON-TRANSFER REACTION OF MAGNESON $HA^- + OH^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} A^{2-} + H_2O$ IN DIOXANE-WATER MEDIUM AT 25 °C

Dioxane %(v/v)	$\frac{k_f}{10^5\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}}$	$\frac{k'_r}{10^3\ \mathrm{s^{-1}}}$ a)	$\frac{K_b^c}{10^2\ \mathrm{mol\,dm^{-3}}}$	pK_a^c $(=-\log\ (K_a^c/\mathrm{mol\,dm^{-3}}))$ b)
4	9.2	5.5	1.7	11.5
10	6.4	5.2	1.2	11.8
20	4.5	3.8	1.2	12.2
30	2.5	2.5	1.0	12.5
40	1.5	2.4	0.63	13.1
50	1.3	1.8	0.72	13.3

a) $k'_r = k_r[H_2O]$.
b) $K_a^c = K_b^c K_w^c$, $I = 0.1\ \mathrm{mol\,dm^{-3}}$ (KNO_3).

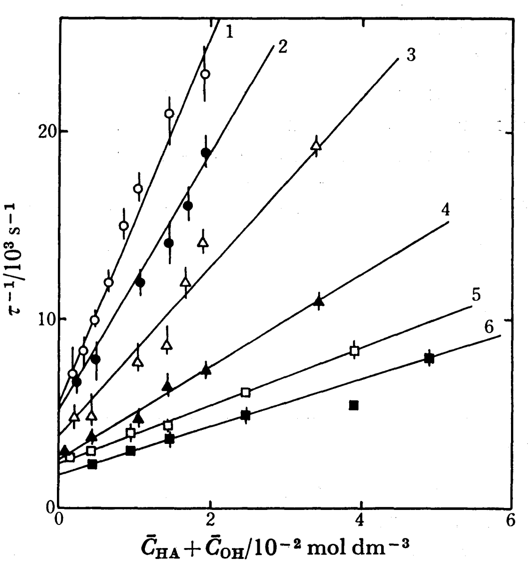

Fig. 3. Plots of the reciprocal relaxation time, τ^{-1}, *vs.* $\bar{C}_{HA}+\bar{C}_{OH}$ in dioxane-water media. Dioxane content: (1) 4, (2) 10, (3) 20, (4) 30, (5) 40, and (6) 50% (v/v). At 25 °C and I=0.1 mol dm^{-3} (KNO_3).

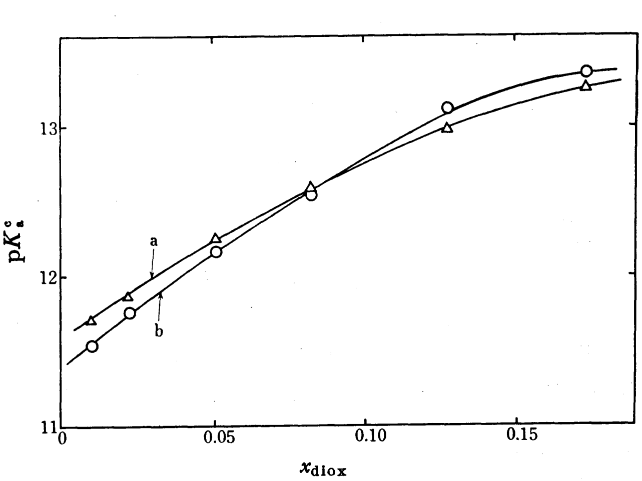

Fig. 4. Dependence of the acid dissociation constants K_a^c of MAG on the mole fraction of dioxane, x_{diox}. At 25 °C and I=0.1 mol dm^{-3} (KNO_3). (a) The plot of the spectrophotometric pK_a^c *vs.* x_{diox}. (b) The plot of the kinetic pK_a^c *vs.* x_{diox}.

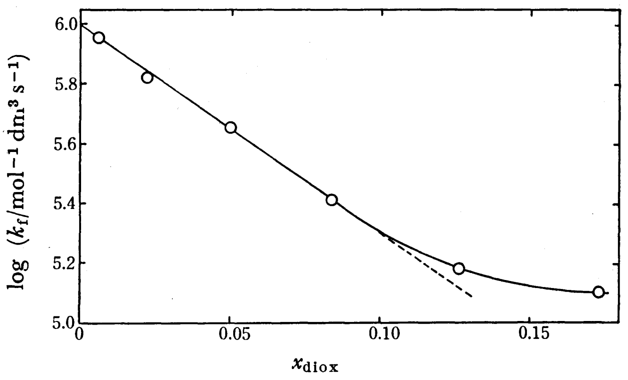

Fig. 5. Dependence of the recombination rate constants k_f on the x_{diox}. At 25 °C and I=0.1 mol dm^{-3} (KNO_3).

Discussion

In Fig. 6 the kinetic and the spectrophotometric pK_a^c are plotted against the inverse macroscopic dielectric constant of the medium.[7] Both pK_a^c's increase with decreasing dielectric constant of the medium, though the linear dependence of pK_a^c on D^{-1} as interpreted by Gilkerson in terms of electrostatic interactions[8] is observed only for the lower dioxane contents. The free energy of the acid dissociation is a sum of the energies required to break the O–H bond, the energies required to break the intramolecular hydrogen-bond, and the hydration energies of various species involved.[9] The decrease of K_a^c with increasing dioxane content in the medium shown in Fig. 6 would partly be ascribed to the difference in the energies of hydration of the reactants.[10]

The recombination of hydroxide ion with a uninegative 4-(2-hydroxy-4-ethylphenylazo)benzenesulfonate ion having no *para*-OH group was found to be almost diffusion-controlled,[11] and the value of pK_a^c for the hydrogen-bonded proton is by two orders of magnitude lower than that of a uninegative ion of 4-(2,4-dihydroxyphenylazo)nitrobenzene having a dissociated *para*-OH group. These facts would lead to the following conclusions: 1. The thermodynamic stability of the intramolecular hydrogen-bond increases mainly due to the presence of a *para*-O$^-$ group which contributes to a resonance quinoidal form and enhances the electron density on the azo-nitrogen. 2. Increased

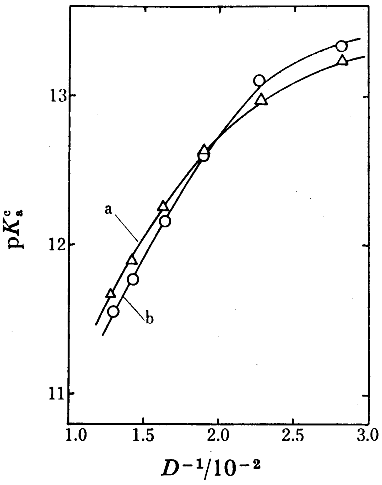

Fig. 6. Dependence of the acid dissociation constant K_a^c of MAG on the dielectric constant of the medium. At 25 °C and I=0.1 mol dm^{-3} (KNO_3). (a) The plot of the spectrophotometric pK_a^c *vs.* the dielectric constant of the medium. (b) The plot of the kinetic pK_a^c *vs.* the dielectric constant of the medium.

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 may restrict the internal rotation about the C–N axis and further enhance the thermodynamic stability of the intramolecular hydrogen-bond. More recently, from the similar point of view Tōei[12] and Johnson and Florence[13] have also explained the stability of the complexes of *o*-hydroxyphenylazo multidentate ligands having a *para*-OH group in terms of a charge-quinone hypothesis.

For the proton-transfer reactions of a uninegative Brønsted acid ion $\widehat{HA}^- + OH^- \rightleftharpoons A^{2-} + H_2O$ in dioxane–water media, we propose the following mechanism which postulates the existence of the first pre-equilibrium between $\widehat{HA}^-$ and HA^{*-};

$$\underset{[1]}{\widehat{HA}^- + OH^-} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{[2]}{HA^{*-} + OH^-}$$

$$\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{[3]}{HA^{*-}\cdots(H_2O)_n\cdots OH^-} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{[4]}{A^{2-} + H_2O,}$$

where $\widehat{HA}^-$ stands for the uninegative species having a *para*-O$^-$ group and an intramolecular hydrogen-bond, and HA^{*-} an intermediate species without an intramolecular hydrogen-bond. The *ortho*-hydroxyl proton in $\widehat{HA}^-$ is set free from the intramolecular hydrogen-bond and associated with surrounding water molecules *via* hydrogen-bond to form HA^{*-}. If a proton-transfer reaction in dioxane-water media proceeds in accordance with the above mechanism, the relations between rate constants of the overall reaction and those for each elementary step are shown by Eqs. 4 and 5.

$$k_f = K_{12}k_{23}\,, \tag{4}$$

and

$$k_r = k_{32}/K_{34}, \tag{5}$$

where $K_{12}=k_{12}/k_{21}$ and $K_{34}=k_{34}/k_{43}$. The equilibrium constant K_{12} is characteristic of the structure of the Brønsted acid and may reflect the liquid structure of the water at the periphery of the reactant, namely, that in the vicinity of the hydroxyl proton. On the other hand, k_{23} is a function of the solvent composition and of the dielectric constant of the medium. Thus the value of K_{12} appears to be one of the measures of the differences in solute-solvent interactions for $\widehat{HA}^-$ and HA^{*-}. The values of k_f and k_r in dioxane–water media are found to be smaller than those in aqueous medium. As discussed above, this decrease in the recombination rate constant in the mixed solvent system is due to two terms K_{12} and k_{23}.

By neglecting the ionic-atmosphere term in Christiansen-Scatchard equation[14] we obtain

$$\ln (k_f/k_f^\circ) = -z_i z_j e^2/kTr^{\ast}D, \tag{6}$$

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 the absolute temperature, $r^{\ast}$ the reaction distance, e the elementary charge, and k_f° the rate constant at infinite dielectric constant. As shown in Fig. 7, the log k_f *vs.* D^{-1}-plot is linear in the region of higher dielectric constant (D=78—52). Since the decrease of log k_f in Fig. 7(a) is due to two terms K_{12} and k_{23}, and the term K_{12} is not constant[15] in this region, we obtain an unexpectedly small value of the reaction distance (2.9 Å) from the slope (a) in Fig. 7. In the region, where the term K_{12} is assumed to be nearly constant,[16] the slope in Fig. 7 is reduced to Eq. 7.

$$\begin{aligned} &\mathrm{d}\log (k_f/\mathrm{mol^{-1}\,dm^3\,s^{-1}})/\mathrm{d}\,D^{-1} \\ &\quad \simeq \mathrm{d}\log (k_{23}/\mathrm{mol^{-1}\,dm^3\,s^{-1}})/\mathrm{d}\,D^{-1}. \end{aligned} \tag{7}$$

From the slope (b) of the log (k_f/mol^{-1} dm^3 s^{-1}) *vs.* D^{-1}-plot we obtain the value of $r^{\ast}$=18 Å as a phenomenological reaction distance. This value of the reaction distance would be reasonable in view of the charge and the size of the reactants, though further investigation is needed with respect to the phenomenological reaction distance derived from the assumption $K_{12} \simeq$ constant. From the value 18 Å for $r^{\ast}$, the number of the inter-

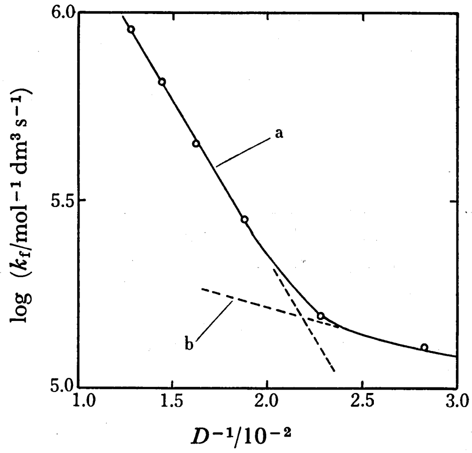

Fig. 7. Dependence of the log k_f on the dielectric constant of the medium. At 25 °C and I=0.1 mol dm^{-3} (KNO_3).

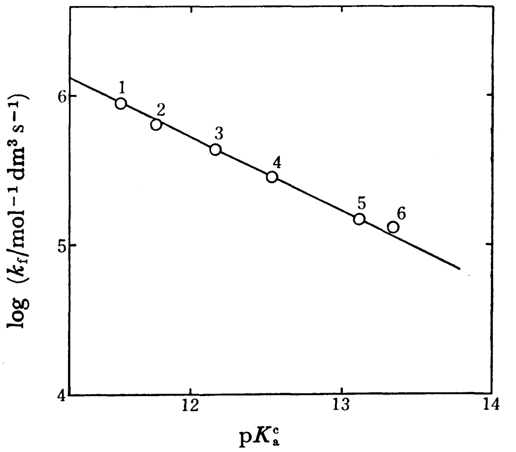

Fig. 8. Dependence of the recombination rate constants k_f on the acid dissociation constants K_a^c of MAG in dioxane-water media. Dioxane content: (1) 4, (2) 10, (3) 20, (4) 30, (5) 40, and (6) 50%(v/v). At 25 °C and I=0.1 mol dm^{-3} (KNO_3).

vening water molecules in the encounter complex, $HA^{*-}\cdots(H_2O)_n\cdots OH^-$ would be estimated to be n=4—5. The value is larger than that (n=2) for the neutralization reaction between the proton H_3O^+ and the hydroxide ion OH^- in aqueous solution.[17]

For a given solvent composition, it was found that the pK_a^c of the Brønsted acids of analogous structures shows a linear dependence on the value of log (k_f/mol^{-1} dm^3 s^{-1}).[2] Figure 8 shows the linear relationship between log (k_f/mol^{-1} dm^3 s^{-1}) and pK_a^c of MAG with respect to the medium effect. Since the variation of k_r' by varying solvent composition is small, the variation of $K_a^c=K_w^c(k_f/k_r')$ depends almost entirely on k_f and K_w^c. The plot of pK_w^c against pK_a^c for varying solvent composition shows a linear relationship, pK_w^c =0.8 pK_a^c+4.3. The plot in Fig. 8 gives a relationship, log (k_f/mol^{-1} dm^3 s^{-1}) = −0.5 pK_a^c + 11.5, or $k_f=G(K_a^c)^\alpha$, where G and α are constants. From Eq. 4 we have a simple relationship, $K_{12}k_{23}=G(K_a^c)^\alpha$. Considering the smaller variation in k_{23} than that in K_{12} we obtain

$$K_{12} = G'(K_a^c)^\alpha, \tag{8}$$

where G' is a constant. Thus, the linear relationship between pK_a^c and log (k_f/mol^{-1} dm^3 s^{-1}) of MAG with respect to the medium effect could be explained by the linear relationship between pK_a^c and log K_{12}.

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5) In the case of 50%(v/v) dioxane-water solution, two relaxation processes were observed in the fast proton-transfer reaction between hydroxide ion and phenolphthalein. From the first relaxation process the rise-time of the temperature in dioxane-water solution was determined to be *ca.* 4—6 μs. In aqueous solution, the rise-time of the temperature was *ca.* 2—5 μs.

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10) In general the solvent effect on the acid-base equilibrium is explained on the basis of the change in the dielectric constant and the acid-base property of the solvent. Furthermore in the case of a bulky organic solute such as Magneson in dioxane-water medium, the preferential solvation by dioxane or water of the various species involved would play a significant role in the acid-base equilibrium.

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14) G. Scatchard, *Chem. Rev.*, **10**, 229 (1932); J. A. Christiansen, *Z. Phys. Chem.*, **113**, 35 (1924).

15) Since K_{12} is the equilibrium constant of the elementary process in which $\widehat{HA}^-$ interacts with surrounding water molecules *via* hydrogen-bond to form HA^{*-}, and since the unimolecular processes inherent to the properties of the reaction site itself, *viz.*, the rupture of the intramolecular hydrogen-bond and the rotation of OH-group around the C–O axis, are almost independent of the solvent composition, the increasing dioxane content of the medium would lead to the decrease in the value of K_{12}.

16) Since the process of dissolution of an ionic crystal is closely related to the process of solvation,[18] the large organic molecule ion $\widehat{HA}^-$ which dissolves readily in dioxane is strongly solvated by dioxane molecules in dioxane-water medium, namely, the preferential solvation of $\widehat{HA}^-$ by dioxane molecules is enhanced when the dioxane content in the medium is increased. The interaction of $\widehat{HA}^-$ with water molecules through hydrogen-bond is considerably restricted when the dioxane content in the medium is increased, and the change in the value of K_{12} due to the solvent composition[14] becomes smaller.

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