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Studies on Coupling Reaction of 1-Naphthol. XI.[1] Effect of Additives on the Dissociation Equilibrium of 4-(4-Nitrophenylazo)-1-naphthol in Pyridine

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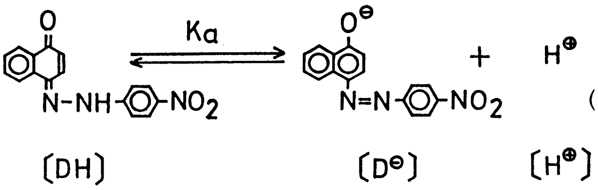
The dissociation of 4-(4-nitrophenylazo)-1-naphthol (azo dye) in pyridine was found to be accelerated by the addition of small amounts of quaternary ammonium compounds, $R_4N^+X^-$. The apparent equilibrium constant of the azo dye was influenced enormously by the species of X^-, but was little affected by the structures of R. The effect increased as the X^- became more basic, $ClO_4^- < I^- < BF_4^- < Br^- < HSO_4^- < Cl^-$, in proportion to the ability of X^- to bind with protons formed by dissociated azo dye. The basicity of the X^-, pK_c, was correlated linearly with the variation of the equilibrium constant, owing to the addition of $R_4N^+X^-$, δpK_a. The dissociation of the azo dye in pyridine-water mixtures was also accelerated upon increasing the amount of water (0—10 vol%), correlating with an increase in the basicity of the solution.

The physical properties of azo dyestuffs (e.g., tone, color, crystal form) have been closely related with their dissociation as well as their tautomerism.

4-(4-Nitrophenylazo)-1-naphthol (azo dye) is particularly interesting as the basic structure of the azo compound. The undissociated form of the azo dye, fortunately, exists entirely as a hydrazone form in a solvent such as pyridine, as described in a previous paper.[2] Therefore, the dissociation of azo dye can be described by the equilibrium between the hydrazone form, DH, and the dissociated form, $D^\ominus$, as shown in Eq. 1.



(1)

In polar aprotic solvents, such as dimethyl sulfoxide and *N,N*-dimethylformamide, azo dye exists partly in the dissociated form.[2] In this paper we report that the dissociation of azo dye in pyridine is accelerated by the addition of small amounts of quaternary ammonium compounds, R_4NX. We also describe the relationship between the variation of the equilibrium constant, owing to the addition of R_4NX, and the basicity of the $X^\ominus$.

Experimental

Material. The azo dye, 4-(4-nitrophenylazo)-1-naphthol, was prepared according to a method described in the literature.[3]

Methods. The spectra of the azo dye were taken on a Shimadzu UV-240 spectrometer in a 1.6×10^{-5} M solution (1 M=1 mol dm^{-3}) with 10 mm cuvettes; Beer's law was shown to be obeyed this concentration. The variation of the equilibrium constant, owing to the addition of R_4NX, δpK_a, of azo dye, was estimated in the following way. The absorption maxima for DH and $D^\ominus$ in pyridine are 472 and 655 nm, respectively. If the molar extinction coefficients of DH (or $D^\ominus$) at 472 and 655 nm in pyridine are expressed by ε_{472}^{DH} and ε_{655}^{DH} (or $\varepsilon_{472}^{D^\ominus}$ and $\varepsilon_{655}^{D^\ominus}$), and the mole fractions of DH and $D^\ominus$ by y and x, respectively, then the ratios of the molar extinction coefficients at 472 and 655 nm ($\varepsilon_{472}/\varepsilon_{655}$) should be

$$\frac{\varepsilon_{472}}{\varepsilon_{655}} = \frac{x\varepsilon_{472}^{D^\ominus} + y\varepsilon_{472}^{DH}}{x\varepsilon_{655}^{D^\ominus} + y\varepsilon_{655}^{DH}} . \tag{2}$$

Figure 1 shows that the ε_{655}^{DH} is almost zero;[2] therefore, Eq. 2 yields

$$\frac{y}{x} = \frac{\varepsilon_{655}^{D^\ominus}}{\varepsilon_{472}^{DH}} \times \left(\frac{\varepsilon_{472}}{\varepsilon_{655}} - \frac{\varepsilon_{472}^{D^\ominus}}{\varepsilon_{655}^{D^\ominus}}\right) . \tag{3}$$

The ratio $\varepsilon_{472}^{D^\ominus}/\varepsilon_{655}^{D^\ominus}$ =2.8/80.3=0.035 was determined by measurements in a pyridine solution saturated with sodium hydroxide; $2.23(=(80.3-4.1)\times10^3/(36.9-2.8)\times10^3)$ for $\varepsilon_{655}^{D^\ominus}/\varepsilon_{472}^{DH}$ was evaluated by the ratio of the difference in the molar extinction coefficients at 655 and 472 nm between solutions of the azo dye in pyridine and pyridine saturated with sodium hydroxide. From these two ratios Eq. 3 yields

$$\frac{y}{x} = 2.23 \times \left(\frac{\varepsilon_{472}}{\varepsilon_{655}} - 0.035\right) . \tag{4}$$

From the y/x value, the proportions (%) and the concentrations ([DH] and $[D^\ominus]$, mol l^{-1}) of DH and $D^\ominus$ can be calculated. When $[H^\oplus]$ is equal to $[D^\ominus]$ in the dissociation constant (pK_a) of Eq. 5 applied in the equilibrium of Eq. 1, the apparent dissociation constant (pK_a') in the individual solutions containing the quaternary ammonium salts can be represented by the form of Eq. 6, and the difference (δpK_a) between the pK_a and the pK_a' may be expressed as in Eq. 7.

$$\mathrm{p}K_a = -\log \frac{[D^\ominus][H^\oplus]}{[DH]} \tag{5}$$

$$\mathrm{p}K_a' = -\log \frac{[D^\ominus]^2}{[DH]} \tag{6}$$

$$\delta \mathrm{p}K_a = \mathrm{p}K_a - \mathrm{p}K_a' \tag{7}$$

If the solution of the azo dye is free from the quaternary ammonium salts pK_a' is equal to pK_a.

The pK_a' values in a pyridine-water solution were also estimated by using the same method.

Results and Discussion

Figure 1 shows the electronic spectrum of the azo dye in pure pyridine or pyridine saturated with sodium hydroxide. The band of the undissociated form (hydrazone form, DH) appeared at 472 nm, and that of the dissociated form (phenolate ion, $D^{\ominus}$) at 655 nm.[2] In pyridine, the addition of quaternary ammonium salts (R_4NX) increased the proportion of $D^{\ominus}$, while that of DH decreased. These two bands gave a well-defined isosbestic point at about 520 nm.

Table 1 exhibits the percentage of DH and $D^{\ominus}$ calculated from y/x (Eq. 4), the pK_a' from Eq. 6 and the δpK_a from Eq. 7 together with the molar extinction coefficients (ε_{472} and ε_{655}) at 472 and 655 nm upon the addition of various concentrations of tetrabutylammonium chloride ($(n\text{-}C_4H_9)_4NCl$). Figure 2 exhibits the relation of the δpK_a to the concentration of $(n\text{-}C_4H_9)_4NCl$. The δpK_a increased with increasing concentration of $(n\text{-}C_4H_9)_4NCl$, with the most dramatic effects observed at lower concentrations. Table 2 shows the result for addition of various quaternary ammonium salts (R_4NX) in 8.0×10^{-5} M solution. In all cases the apparent dissociation constant pK_a' for the addition of R_4NX gave a smaller value than the true dissociation constant pK_a (=7.41). The difference (δpK_a) between pK_a and pK_a' was influenced enormously by the species of anion $X^{\ominus}$ in $R_4N^{\oplus}X^{\ominus}$, but was little affected by the structure of an alkyl group R. Table 3 exhibits the dissociation constant pK_{HX}[4] for the conjugated acid HX of the $X^{\ominus}$ together with the δpK_a, and a plot of δpK_a vs. pK_{HX} is shown in Fig. 3. It is apparent from Fig. 3 that δpK_a increases linearly with increasing basicity of $X^{\ominus}$. These results lead to the following

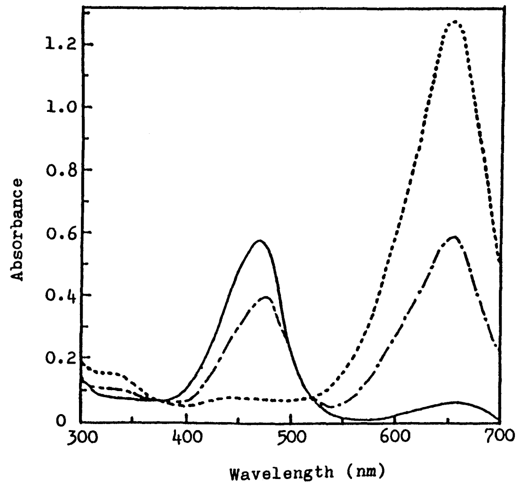


Fig. 1. Absorption spectra of 4-(4-nitrophenylazo)-1-naphthol (1.6×10^{-5} mol l^{-1}).
——: in pyridine. -----: in pyridine saturated with NaOH. —·—·: $+(n\text{-}C_4H_9)_4NCl$ (2.0×10^{-4} mol l^{-1}) in pyridine.

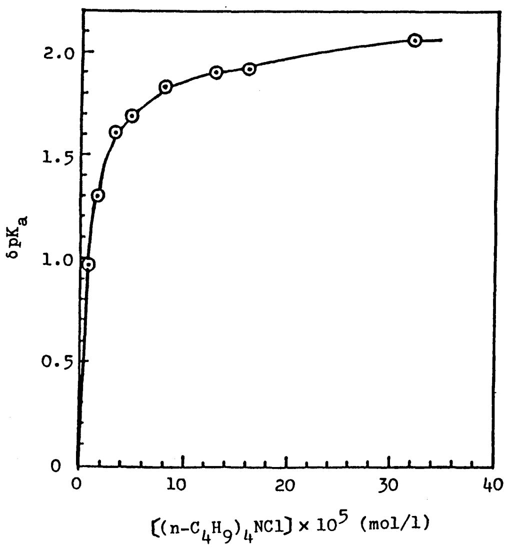


Fig. 2. Plots of δpK_a vs. $[(n\text{-}C_4H_9)_4NCl]$.

Table 1. Molar Extinction Coefficients (ε_{472} and ε_{655}) at the Absorption Maxima of Undissociated and Dissociated Forms (DH and $D^{\ominus}$), Percentage of DH and $D^{\ominus}$, Apparent Dissociation Constant (pK_a') and Difference (δpK_a) between pK_a' and Dissociation Constant (pK_a) on the Addition of Various Concentration of Tetrabutylammonium Chloride ((DH); 4-(4-Nitrophenylazo)-1-naphthol: 1.6×10^{-5} mol l^{-1}. Solvent: Pyridine, T: 25 °C)

No.	$(n\text{-}C_4H_9)_4NCl$ / mol l^{-1}	$\varepsilon_{472}\times10^{-3}$	$\varepsilon_{655}\times10^{-3}$	DH / %	$D^{\ominus}$ / %	pK_a'	δpK_a
1	0	36.9	4.1	95.2	4.8	7.41 (=pK_a)	—
2	8.0×10^{-6}	33.6	12.1	86.0	14.0	6.44	0.97
3	1.6×10^{-5}	31.8	17.2	80.2	19.8	6.11	1.30
4	3.2×10^{-5}	29.2	23.4	73.1	26.9	5.80	1.61
5	4.8×10^{-5}	28.5	25.4	70.8	29.2	5.72	1.69
6	8.0×10^{-5}	27.1	29.0	66.8	33.2	5.58	1.83
7	1.28×10^{-4}	26.7	31.4	64.4	35.4	5.51	1.90
8	1.6×10^{-4}	26.6	32.0	64.0	36.0	5.49	1.92
9	3.2×10^{-4}	25.3	37.5	58.8	41.2	5.34	2.07

Table 2. Molar Extinction Coefficients (ε_{472} and ε_{655}) at the Absorption Maxima of Undissociated and Dissociated Forms (DH and $D^{\ominus}$), Percentage of DH and $D^{\ominus}$, Apparent Dissociation Constant (pK_a') and Difference (δpK_a) between pK_a' and Dissociation Constant (pK_a) on Addition of Various Quaternary Ammonium Compounds ((DH); 4-(4-Nitrophenylazo)-1-naphthol: 1.6×10^{-5} mol l^{-1}, R_4NX: 8.0×10^{-5} mol l^{-1}, Solvent: Pyridine, T: 25 °C)

No.	R_4NX	$\varepsilon_{472}\times10^{-3}$	$\varepsilon_{655}\times10^{-3}$	DH %	$D^{\ominus}$ %	pK_a'	δpK_a
1	—	36.9	4.1	95.2	4.8	7.41 (=pK_a)	—
2	$(CH_3)_4NCl$	28.7	24.9	71.4	28.6	5.74	1.67
3	$(C_2H_5)_4NCl$	28.1	28.1	68.3	31.7	5.63	1.78
4	$(n\text{-}C_4H_9)_4NCl$	27.1	29.0	67.2	32.8	5.58	1.83
5	$[(CH_3)_3NCH_2C_6H_5]Cl$	28.4	24.8	71.3	28.7	5.73	1.68
6	$[(C_2H_5)_3NCH_2C_6H_5]Cl$	27.6	28.6	67.5	32.5	5.60	1.81
7	$[(CH_3)_2C_{16}H_{33}NCH_2C_6H_5]Cl$	29.2	25.3	71.4	28.6	5.74	1.67
8	$(C_2H_5)_4NBr$	32.9	10.6	87.3	12.7	6.53	0.88
9	$[C_5H_5NC_2H_5]Br$	32.7	11.6	86.2	13.8	6.45	0.96
10	$(C_2H_5)_4NI$	34.1	5.0	93.8	6.2	7.19	0.22
11	$(n\text{-}C_3H_7)_4NI$	32.3	5.5	92.9	7.1	7.06	0.35
12	$(n\text{-}C_4H_9)_4NHSO_4$	31.4	14.9	82.2	17.8	6.21	1.20
13	$(n\text{-}C_4H_9)_4NBF_4$	33.9	6.1	92.5	7.5	7.01	0.40
14	$(C_2H_5)_4NClO_4$	34.0	4.9	93.9	6.1	7.19	0.22

Table 3. The Values δpK_a and pK_{HX} to $X^{\ominus}$ in R_4NX ((DH); 4-(4-Nitrophenylazo)-1-naphthol: 1.6×10^{-5}mol l^{-1}, R_4NX: 8.0×10^{-5} mol l^{-1}, Solvent: Pyridine, T: 25 °C)

$X^{\ominus}$	$Cl^{\ominus}$	$HSO_4^{\ominus}$	$Br^{\ominus}$	$BF_4^{\ominus}$	$I^{\ominus}$	$ClO_4^{\ominus}$
δpK_a	1.67—1.83	ca. 1.20	0.96—0.88	ca. 0.40	0.35—0.22	ca. 0.22
pK_{HX}[4]	5.7	—	4.4	—	3.4	3.3

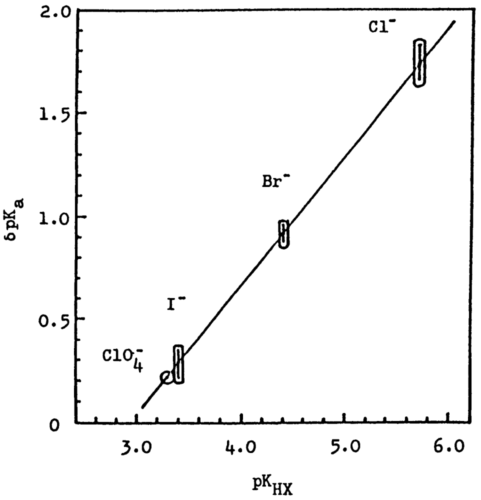


Fig. 3. Relationship between δpK_a and pK_{HX} (pK_a of HX).

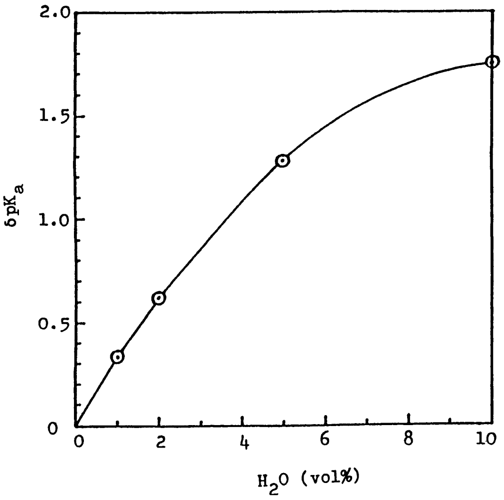


Fig. 4. Plots of δpK_a vs.H_2O (vol%).

discussion. The proton $H^{\oplus}$ formed[5] by the dissociation of azo dye (Eq. 1) reacts with the $X^{\ominus}$ produced in Eq. 8 to give HX (Eq. 9). Therefore, the equilibrium of Eq. 1 is shifted to the right.

$$R_4NX \xrightleftharpoons{K_c} R_4N^{\oplus} + X^{\ominus} \qquad (8)$$

$$HX \xrightleftharpoons{K_{HX}} H^{\oplus} + X^{\ominus} \qquad (9)$$

The above hypothesis can be tested by using the three dissociation constants into Eqs. 1, 8, and 9. Since the pK_a in Eq. 1 is 7.41 ($K_a=3.89\times10^{-8}$), $[H^{\oplus}]$ is equal to 0.077×10^{-5} mol l^{-1} at a total concentration of the azo dye of 1.6×10^{-5} mol l^{-1}; $[X^{\ominus}]$ in Eq. 8 is estimated to be $(7.45—5.25)\times10^{-5}$ mol l^{-1} at an R_4NX concentration of 8×10^{-5} mol l^{-1} because the pK_c[6] is 3—4. Next, we consider the equilibrium of HX, by employing

$[H^{\oplus}]=0.077\times10^{-5}$ and $[X^{\ominus}]=(7.45—5.25)\times10^{-5}$ mol l^{-1} in Eq. 9. If the $X^{\ominus}$ is a strong base, [e.g., the conjugate base of a very weak acid such as HCl in pyridine ($pK_{HCl}=5.7$, $K_{HCl}=2.0\times10^{-6}$)], [HX] becomes $(0.075—0.074)\times10^{-5}$ mol l^{-1}, corresponding to 97—96% of $[H^{\oplus}]=0.077\times10^{-5}$ mol l^{-1}. Therefore, the equilibrium of Eq. 1 may be significantly shifted to the right. On the other hand, if the $X^{\ominus}$ is a weak base [e.g., the conjugate base of a strong acid such as $HClO_4$ in pyridine ($pK_{HClO_4}=3.3$, $K_{HClO_4}=5.0\times10^{-4}$)], [HX] becomes $(0.0100—0.0075)\times10^{-5}$ mol l^{-1}, corresponding to 13—10% of $[H^{\oplus}]$. This means that the equilibrium of Eq. 1 may be only slightly shifted to the right.

The dissociation of azo dye in pyridine is also accelerated by the addition of a large quantity of water. Figure 4 shows the relation of δpK_a to the content of water. The δpK_a for 1 (0.56), 2(1.1), 5(2.8), and 10 vol% (5.6 mol l^{-1}) of water is 0.34, 0.64, 1.28, and 1.75, respectively. This indicates that the hydroxy anion $OH^{\ominus}$ formed in Eq. 10 reacts with a proton $H^{\oplus}$ (in Eq. 1), as shown in Eq. 11, so that the dissociation described in Eq. 1 may be accelerated, and that the basicity in such a solvent system may increase with the water content.

(10)

$$OH^{\ominus} + H^{\oplus} \rightleftharpoons H_2O \qquad (11)$$

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