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Equilibrium and Kinetic Studies on the Formation of Triphenylmethanols from Triphenylmethane Dyes

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For five kinds of triphenylmethane dyes, the rate constants of hydration and dehydration reactions, and equilibrium constants in an aqueous solution were measured by a stopped-flow method. An increase in the number of dialkylamino groups caused a decrease in the rates and the equilibrium constants of the hydration, and the more the electron-donating effect of the dialkylamino groups, the slower the hydration rate became. The more protonated quinonoids were easily converted to the corresponding alcohols. On the basis of the equilibrium constants, Malachite Green was ascertained to be the best reagent of the five dyes for ion association with heteropolyacids in an aqueous medium.

Triphenylmethane dyes have been often used for solvent extraction, precipitation separation, and spectrophotometric determination of various kinds of ionic substances, because they are reactive with bulky counter ions to form ion associates and their molar absorptivities are very large.[1,2] For example, Ethyl Violet (EV) has been used for the solvent extraction-spectrophotometric methods of phosphate and arsenate[3] and anionic surfactants,[4] Malachite Green (MG) and Brilliant Green (BG) being often used for sensitive methods for the measurement of phosphate[5] and silicate,[6] and boric acid,[7] respectively.

We have investigated an ion-association reaction of triphenylmethane dyes with heteropolyacids, such as molybdophosphate and molybdosilicate. The reactivity of MG was found to be the highest of the five dyes, though BG, Crystal Violet (CV), and EV are predicted to have higher reactivity in acidic media with heteropolyacids than MG from the results obtained by solvent extraction. The hydration of the dyes probably causes this result.

Cigén and his co-workers[8—13] measured equilibrium constants (acid dissociation and hydration constants) and rate constants for MG and its halogen derivatives, and discussed the effects of halogen substituents on the reaction rate and equilibrium of the hydration. They reported that the ortho-substituent had marked steric effects on the hydration.

Several kinds of cationic dyes have been often used in analytical chemistry. Of these, only MG and CV have been examined up to now.

In this work, the reliable absorption spectra and the molar absorptivities of various species of the triphenylmethane dyes could be obtained and accurate rate and equilibrium constants were measured by a stopped-flow method using a diode array spectrophotometer.

Experimental

Reagents. **Triphenylmethane Dyes:** MG and BG, having two dialkylamino groups, and Pararosaniline (PR), CV, and EV, having three amino or dialkylamino groups, were investigated. The structural formulas of the dyes are shown in Fig. 1. These dyes (Tokyo Kasei Kogyo Co., Ltd., Ace series) were ones recrystallized from water in the same manner as described previously,[14] except Pararosaniline (Tokyo Kasei Kogyo Co., Ltd., GR grade), and their purity was more than 98%.

pH-Buffer Solutions: Hydrochloric acid (pH<2.5), chloroacetate buffer (pH 2.5—3.5), acetate buffer (pH 3.7—5.7), phosphate buffer (pH 5.8—8.0), borate buffer (pH 9.0—10.5), and sodium hydroxide (pH>11) were used.

Apparatus and Procedure. All the experiments for the measurement of equilibrium and rate constants were done in a temperature-controlled room (25.0±0.1°C). Dye solutions (2×10^{-5} mol dm^{-3}, about pH 5) were mixed with an equal volume of pH-buffer solutions, whose ionic strength were adjusted to 0.2 mol dm^{-3}, by the use of a mixing apparatus (Otsuka Electronics Co., Ltd. MX-7-01). The absorbances of mixed solutions in a quartz flow cell, around which temperature-controlled water (25.0±0.1°C) was circulated through copper tubing, were measured with a Hewlett-Packard 8452A diode array spectrophotometer coupled with an NEC PC-9801 UX21. By this spectrophotometer system, absorbances at six wavelengths can be measured at the same time. The final pHs of the mixed solutions were measured with a Corning 130 pH meter.

Calculations of Equilibrium Constants and Rate Constants. All species of triphenylmethane dyes in aqueous solutions and the equilibria among them are shown in Scheme 1.

The reactions involved and their rate constants are summarized as follows:

$$\mathrm{R^+ + H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HROH^+}$$

$$\mathrm{HROH^+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{ROH + H^+}$$

$$\mathrm{R^+ + OH^-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{ROH}$$

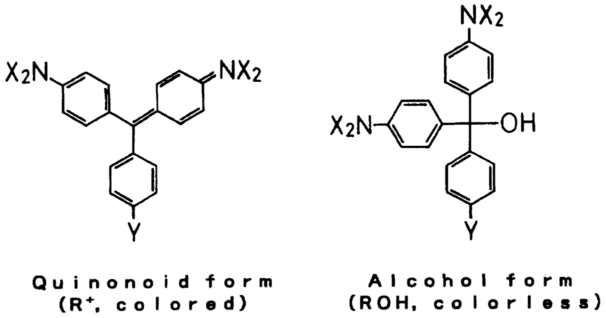
$$\mathrm{HR^{2+}} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{R^+ + H^+}$$

$$\mathrm{HR^{2+} + H_2O} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{H_2ROH^{2+}}$$

$$\mathrm{H_2ROH^{2+}} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{HROH^+ + H^+}$$

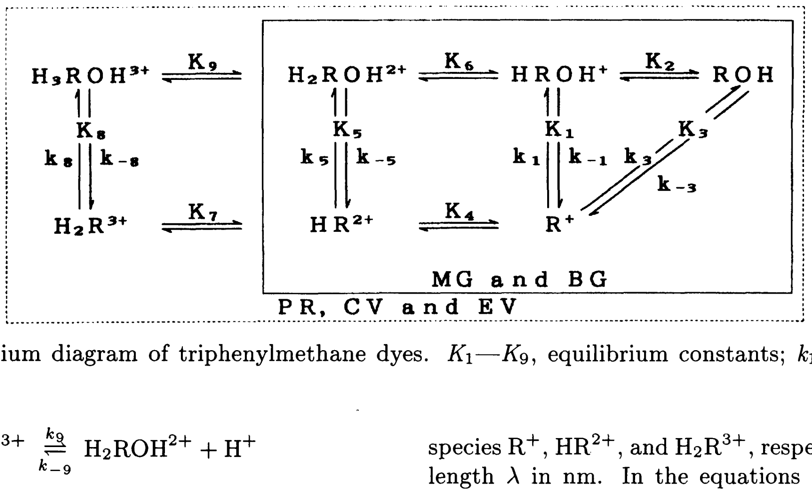
$$\mathrm{H_2R^{3+}} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \mathrm{HR^{2+} + H^+}$$

$$\mathrm{H_2R^{3+} + H_2O} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \mathrm{H_3ROH^{3+}}$$



Y	X	Dye (abbreviation)	
$-H$	$-CH_3$	Malachite Green (oxalate)	(MG)
″	$-C_2H_5$	Brilliant Green (hydrogensulfate)	(BG)
$-NX_2$	$-H$	Pararosaniline (chloride)	(PR)
″	$-CH_3$	Crystal Violet (chloride)	(CV)
″	$-C_2H_5$	Ethyl Violet (chloride)	(EV)

Fig. 1. Triphenylmethane dyes and their alcohols examined in this work.



Scheme 1. Equilibrium diagram of triphenylmethane dyes. K_1—K_9, equilibrium constants; k_1—k_8 and k_{-1}—k_{-8}, rate constants.

$$\mathrm{H_3ROH^{3+}} \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} \mathrm{H_2ROH^{2+}} + \mathrm{H^+}$$

The equilibrium constants K_n are defined as k_n/k_{-n}.

Since the protonation and dissociation reactions are very fast, the rate constants (k_2, k_4, k_6, k_7, and k_9) could not be measured with the apparatus used in this work. However, the hydration and dehydration reactions are much slower than protonation, so there is no problem in the study of hydration reaction.

According to Bodforss et al.,[9] the following expressions for the initial absorbance (A_0), the equilibrium absorbance (A_∞), and the rate constant (k) of the over-all reaction as the function of the hydrogen ion concentration, can be derived for MG and BG:

$$A_0 = \frac{C\{\varepsilon_{\mathrm{R}} + (\varepsilon_{\mathrm{HR}}[\mathrm{H^+}]/K_4)\}}{1 + [\mathrm{H^+}]/K_4}, \tag{1}$$

$$A_\infty = \frac{C\{\varepsilon_{\mathrm{R}} + (\varepsilon_{\mathrm{HR}}[\mathrm{H^+}]/K_4)\}}{1 + K_1 + K_1K_2/[\mathrm{H^+}] + (1+K_5)[\mathrm{H^+}]/K_4}, \tag{2}$$

$$k = \frac{[\mathrm{H^+}]^2k_{-5} + [\mathrm{H^+}]k_{-1}K_6 + k_{-3}K_2K_6}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]K_6 + K_2K_6} + \frac{[\mathrm{H^+}]k_5 + k_1K_4 + k_3K_4[\mathrm{OH^-}]}{[\mathrm{H^+}] + K_4}, \tag{3}$$

where C is the total concentration of the dye in $\mathrm{mol\,dm^{-3}}$, and ε_{R}, $\varepsilon_{\mathrm{HR}}$, and $\varepsilon_{\mathrm{H2R}}$ are the molar absorptivities of the species $\mathrm{R^+}$, $\mathrm{HR^{2+}}$, and $\mathrm{H_2R^{3+}}$, respectively, at a given wavelength λ in nm. In the equations mentioned hereinbefore and hereinafter, $[\mathrm{H^+}]$ and $[\mathrm{OH^-}]$ are defined as the activity of a hydronium and hydroxide ion, respectively, which are calculated from the pH value measured with the pH meter.

For PR, CV, and EV some additional equilibria (K_7, K_8, and K_9) are involved and the following equations are obtained instead of Eqs. 1, 2, and 3.

$$A_0' = \frac{C\{\varepsilon_{\mathrm{R}} + (\varepsilon_{\mathrm{HR}}[\mathrm{H^+}]/K_4) + (\varepsilon_{\mathrm{H2R}}[\mathrm{H^+}]^2/K_4K_7)\}}{1 + ([\mathrm{H^+}]/K_4) + ([\mathrm{H^+}]^2/K_4K_7)}, \tag{4}$$

$$A_\infty' = \frac{C\{\varepsilon_{\mathrm{R}} + (\varepsilon_{\mathrm{HR}}[\mathrm{H^+}]/K_4) + (\varepsilon_{\mathrm{H2R}}[\mathrm{H^+}]^2/K_4K_7)\}}{1+K_1+K_1K_2/[\mathrm{H^+}]+(1+K_5)[\mathrm{H^+}]/K_4+(1+K_8)[\mathrm{H^+}]^2/K_4K_7}, \tag{5}$$

$$k' = \frac{[\mathrm{H^+}]^3k_{-8} + [\mathrm{H^+}]^2k_{-5}K_9 + [\mathrm{H^+}]k_{-1}K_6K_9 + k_{-3}K_2K_6K_9}{[\mathrm{H^+}]^3 + [\mathrm{H^+}]^2K_9 + [\mathrm{H^+}]K_6K_9 + K_2K_6K_9} + \frac{[\mathrm{H^+}]^2k_8 + [\mathrm{H^+}]k_5K_7 + k_1K_4K_7 + k_3K_4K_7[\mathrm{OH^-}]}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]K_7 + K_4K_7}. \tag{6}$$

These equations can be approximated in some pH-ranges, since certain species and reaction steps can then be neglected. These approximations and the transformations of the equations will be shown later in connection with the measurement of the individual constants.

Results

Absorption Spectra and Molar Absorptivities of the Dyes. The absorption spectra of MG and CV obtained under some conditions are shown in Fig. 2. The absorption spectra of BG and those of PR and EV are very similar to those of MG and those of CV, respectively. The wavelengths of the absorption maxima and the molar absorptivities are listed in Table 1.

Measurement of Acid Dissociation Constants. In this work, three equilibrium constants, K_2, K_4, and K_7, could be measured readily in the usual manner by the spectrophotometric method using a general Eq. 7, because the accurate initial absorbance ($t=0$), which was assumed to be practically equal to the value obtained experimentally at $t=0.1$ s, could be measured directly.

$$\mathrm{p}K = \mathrm{pH} + \log\{(\varepsilon_\mathrm{b}C - A_0)/(A_0 - \varepsilon_\mathrm{a}C)\}, \tag{7}$$

where ε denotes a molar absorptivity, and the subscripts a and b denote an acid and a base form, respectively.

According to Eq. 7, the values of $\log\{(\varepsilon_\mathrm{b}C - A_0)/(A_0 - \varepsilon_\mathrm{a}C)\}$ were plotted against pH. Straight lines with a slope of -1 are obtained. The constants K_4 of MG and BG and K_7 of PR, CV, and EV obtained using Eq. 7 are summarized in Table 2.

When $K_7 \gg [\mathrm{H}^+]$ ($\mathrm{p}K_7 \ll \mathrm{pH}$), the value K_4 of PR, CV, and EV could be obtained; they are listed in Table 2.

Cigén et al. obtained a product of K_1 and K_2 experimentally, and predicted the most suitable value for K_2 from the relationships between other equilibrium constants. In this work, however, the initial absorbances could be measured, the value K_2 being measured directly.

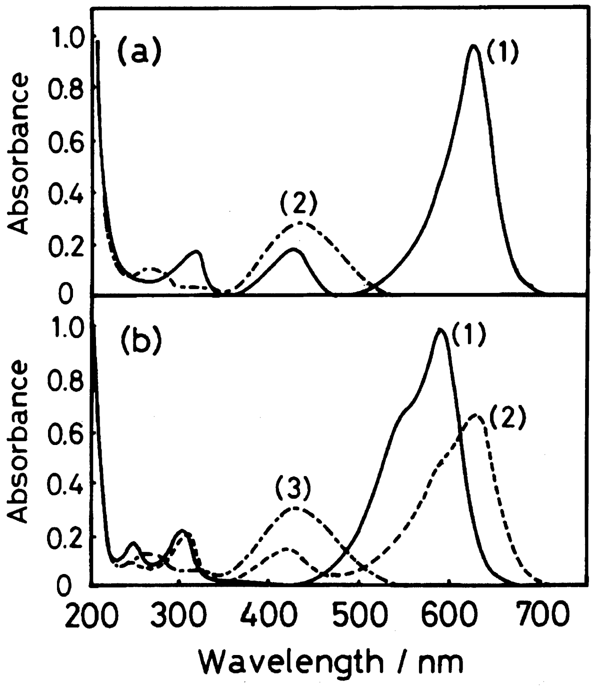


Fig. 2. Absorption spectra in aqueous solution. 1, R^+ (pH 5); 2, HR^{2+} (pH 1.3); 3, H_2R^{3+} (pH 0.3); (a) Malachite Green; (b) Crystal Violet. Dye: 1×10^{-5} mol dm^{-3}.

The dye solutions equilibrated in alkaline solutions (pH>12) were mixed with pH-buffer solutions (pH 4—12), the absorbances being measured at the wavelength of the absorption maximum of ROH, which is listed in Table 1. The equilibrium constants K_2 were calculated according to Eq. 7, and are summarized in Table 2.

At pH around 5, Eq. 3 can be approximated as follows:

$$k = \frac{[\mathrm{H}^+]K_6k_{-1}}{[\mathrm{H}^+]^2 + [\mathrm{H}^+]K_6 + K_2K_6} + k_1. \tag{8}$$

It can be seen from the differential equation of Eq. 8 that the rate constant k has its maximum value at a certain $[\mathrm{H}^+]$, where K_2K_6 is equal to the value of $[\mathrm{H}^+]^2$. Figure 3 shows an example of the plot of the overall rate constant k as a function of pH for MG. From the pH at which k shows the maximum, we can obtain the value of K_2K_6. In pH regions near 5, accurate rate constants can not be obtained in the usual manner, because the changes in absorbances of solutions are too small. Therefore in this study the dye solutions equilibrated and decolorized in an acidic medium (pH≦1) were mixed with pH-buffer solutions, and the absorbances of the species R^+ were measured with progress of time. The value K_6 can be calculated from Eq. 8 using the known value K_2 and $[\mathrm{H}^+]$ near pH 5, and are summarized in Table 2.

The equilibrium constant K_9 could be obtained by the following equation:

$$K_9 = K_5K_7/K_8. \tag{9}$$

Calculation of the Equilibrium Constants of Triphenylmethanol Formation. In alkaline solutions (pH 7—13) where only three species such as R^+, $HROH^+$, and ROH are present, Eq. 2 can be approximated as follows:

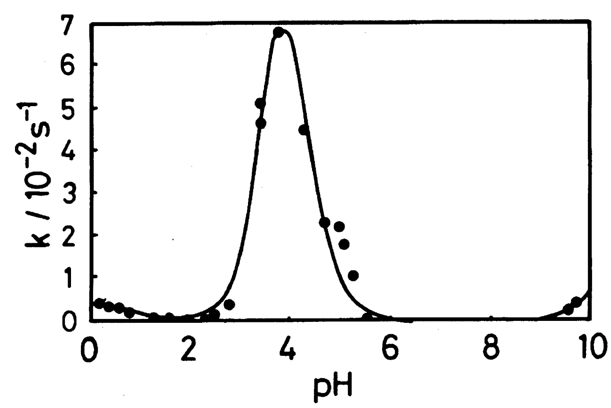


Fig. 3. Rate constants of overall reaction as a function of pH. ●, measured values; solid line, calculated curve using Eq. 8.

Table 1. Absorption Maximum Wavelengths (λ_{max}) and Molar Absorptivities (ε) for Triphenylmethane Dyes and Their Alcohols

	λ_{max}/nm ($\varepsilon/10^5$ dm^3 mol^{-1} cm^{-1})						
Dyes	R^+	HR^{2+}	H_2R^{3+}	ROH	$HROH^+$	H_2ROH^{2+}	H_3ROH^{3+}
MG	618(1.02) 424(0.18)	446(0.35)	—	256(0.25)	256(0.02)[a]	260(0.01)	—
BG	624(1.01) 428(0.18)	450(0.34)	—	284(0.24)	284(0.04)[a]	260(0.01)	—
PR	540(0.61)	568(0.45) 400(0.10)	420(0.20)	244(0.24)	244(0.10)[a]	260(0.01)	260(0.01)
CV	590(1.05)	630(0.79) 424(0.20)	430(0.29)	258(0.33)	258(0.02)[a]	260(0.01)	260(0.01)
EV	596(0.94)	638(0.75) 426(0.20)	434(0.31)	282(0.30)	282(0.04)[a]	260(0.01)	260(0.01)

a) These values were not maximum absorption, and were used for determining the value K_2.

Table 2. Equilibrium Constants[a]

	Triphenylmethane dyes				
Constants	MG	BG	PR	CV	EV
K_1	1.8×10^{-2} (1.5×10^{-2})	2.9×10^{-2}	8.0×10^{-3}	1.5×10^{-4} (1.4×10^{-4})	3.9×10^{-4}
K_2/mol dm^{-3}	4.7×10^{-6} (5.8×10^{-6})	1.7×10^{-6}	7.1×10^{-6}	2.6×10^{-6} (2.5×10^{-6})	1.2×10^{-6}
K_3/dm^3 mol^{-1}	8.4×10^{6}	5.0×10^{6}	5.6×10^{6}	3.7×10^{4}	4.7×10^{4}
K_4/mol dm^{-3}	3.7×10^{-2} (3.6×10^{-2})	8.6×10^{-3}	1.1×10^{-2}	4.8×10^{-3} (4.1×10^{-3})	2.1×10^{-4}
K_5	2.1×10^{1} (2.2×10^{1})	7.5×10^{1}	3.0×10^{-1}	2.7×10^{-2} (3.2×10^{-2})	3.9×10^{-2}
K_6/mol dm^{-3}	3.3×10^{-5} (2.7×10^{-5})	3.3×10^{-6}	2.8×10^{-4}	2.6×10^{-5} (1.8×10^{-5})	2.1×10^{-6}
K_7/mol dm^{-3}	—	—	1.8×10^{-1}	1.4×10^{-1} (1.2×10^{-1})	2.2×10^{-2}
K_8	—	—	2.5×10^{2}	7.5×10^{1} (7.9×10^{1})	3.3×10^{2}
K_9/mol dm^{-3}	—	—	2.2×10^{-4}	5.0×10^{-5} (4.9×10^{-5})	2.6×10^{-6}

a) The figures in parentheses are the constants obtained at 20 °C by Cigén et al. (Refs. 8 and 11).

$$[H^+]/A_\infty = (K_1K_2/\varepsilon_R C) + (1+K_1)([H^+]/\varepsilon_R C). \qquad (10)$$

According to Eq. 10, the values of $[H^+]/A_\infty$ were plotted as a function of $[H^+]$. As shown in Fig. 4, the plots show good linearity. If $1 \gg K_1$, the values of $\varepsilon_R C$ and K_1K_2 can be obtained from the slopes and the intercepts, respectively, and the constants K_1 can be calculated using the value K_2, and are summarized in Table 2.

The equilibrium constants K_3 and K_5 are defined as follows:

$$K_3 = K_1K_2/K_W \quad \text{and} \quad K_5 = (K_1K_4/K_6).$$

Therefore, these constants were calculated from the known values of K_1, K_2, K_4, K_6, and K_W ($=[H^+][OH^-]=1.01\times10^{-14}$ mol dm^{-3}). They are given in Table 2.

In acidic solutions pH below 3, the values of K_1 and $K_1K_2/[H^+]$ are negligibly small in Eq. 5. Further, when the ε_{H2R} can be neglected compared with ε_R or ε_{HR} at a certain wavelength, the following equation can be obtained.

$$K_8 = \frac{\varepsilon_R C + \varepsilon_{HR}C[H^+]/K_4 - A'_\infty\{1+(1+K_5)[H^+]/K_4\}}{A'_\infty[H^+]^2/K_4K_7} - 1 \qquad (11)$$

The values of K_8 were calculated from Eq. 11 by using A'_∞ and the known values of K_4, K_5, and K_7, and are summarized in Table 2.

Calculation of Rate Constants. As the quinonoid species, such as H_2R^{3+} and HR^{2+} of PR, CV, and EV, are mainly present in acidic solutions (pH<3),

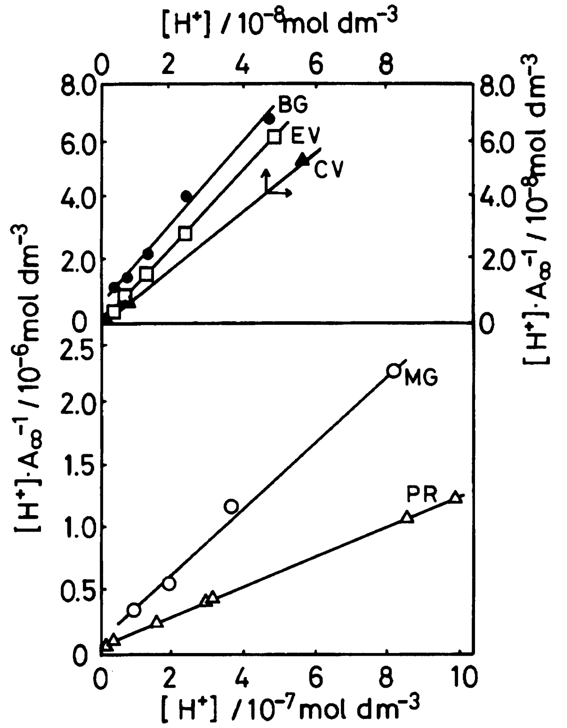


Fig. 4. Plots for calculating product K_1K_2.

Eq. 6 can be approximated as follows:

$$k'(K_7+[\mathrm{H}^+]) = k_5K_7+k_8[\mathrm{H}^+]. \qquad (12)$$

According to Eq. 12, the values of k' $(K_7+[\mathrm{H}^+])$ were plotted as a function of $[\mathrm{H}^+]$, the plots being shown in Fig. 5. From the slopes and the intercepts of these plots, the values of k_8 and k_5 can be obtained using the known values of K_7 and are summarized in Table 3.

In MG and BG, Eq. 13 can be derived from Eq. 3 at pH below 3.

$$k = k_{-5}+k_5\{K_5[\mathrm{H}^+]/(1+K_5[\mathrm{H}^+])\}. \qquad (13)$$

According to Eq. 13, the k values were plotted as a function of $\{K_5[\mathrm{H}^+]/(1+K_5[\mathrm{H}^+])\}$, and the values of k_5 can be obtained from the slopes and are summarized in Table 3.

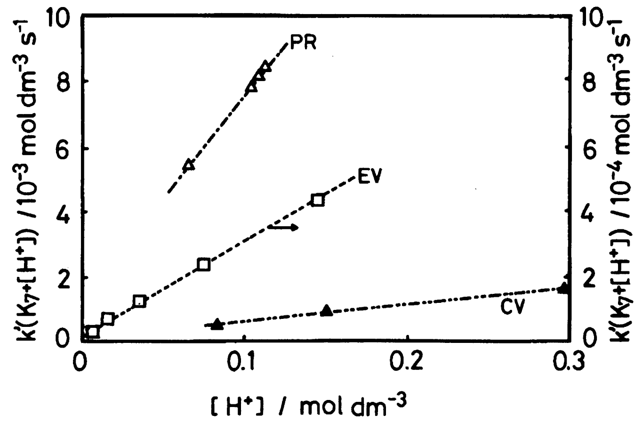


Fig. 5. Plots for calculating rate constants k_5 and k_8.

In the case of alkaline solutions (pH>10), Eq. 3 or Eq. 6 can be approximated as follows:

$$k \text{ or } k' = k_3[\mathrm{OH}^-]+k_1+k_{-3}. \qquad (14)$$

According to Eq. 14, the values k or k' were plotted as a function of $[\mathrm{OH}^-]$ as shown in Fig. 6. The values of k_3 were obtained from the slopes of the lines in Fig. 6.

The rate constant k_{-3} can be calculated from Eq. 15, if the equilibrium constants K_1 and K_2, and the rate constants k_3 are known.

$$k_{-3} = k_3K_\mathrm{W}/K_1K_2. \qquad (15)$$

The calculated values of k_{-3} are summarized in Table 3.

In neutral and weakly alkaline solutions (pH 7—10), Eq. 3, as well as Eq. 6, can be approximated as follows:

$$k \text{ or } k' = k_1\{([\mathrm{H}^+]/K_1K_2)+1\}+k_{-3}+k_3[\mathrm{OH}^-]. \quad (16)$$

From Eq. 16, the rate constant k_1 was obtained, and are summarized in Table 3.

Other constants, such as k_{-1}, k_{-5}, and k_{-8}, could not be experimentally measured, and therefore these were calculated according to the following equations using the known values of concerned constants.

$$k_{-1} = k_1/K_1; \quad k_{-5} = k_5/K_5; \quad k_{-8} = k_8/K_8.$$

These rate constants calculated are summarized in Table 3.

Discussion

Percent Distribution of Different Species of Triphenylmethane Dyes. On the basis of the equilibrium constants obtained in this work, the distribution of different species of triphenylmethane dyes was calculated as a function of pH and is shown in Fig. 7. Even in strongly acidic media below pH 2 more than 80% of the dyes are present in alcohol forms. Since the positive charge of the central carbon atom in more protonated quinonoids is much more than that in less protonated quinonoids, water molecules more easily attack the carbon atom of the dyes in more protonated quinonoids.

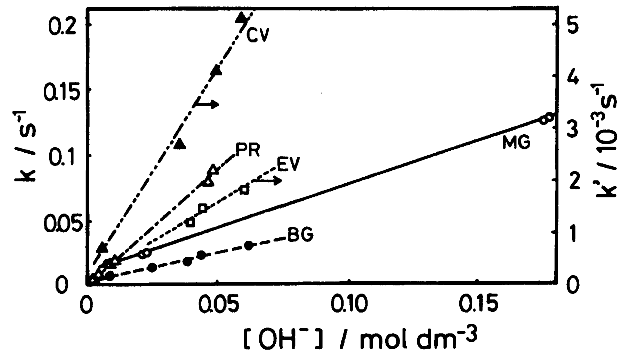


Fig. 6. Plots for calculating a rate constant k_3.

Table 3. Rate Constants of Hydration and Dehydration Reaction[a)]

Constants	Triphenylmethane dyes				
	MG	BG	PR	CV	EV
k_1/s^{-1}	1.6×10^{-4} (1.1×10^{-4})	3.0×10^{-5}	1.2×10^{-3}	1.6×10^{-5} (6.1×10^{-6})	1.1×10^{-5}
k_{-1}/s^{-1}	8.9×10^{-3} (7.3×10^{-3})	1.0×10^{-3}	1.5×10^{-1}	1.1×10^{-1} (4.4×10^{-2})	2.8×10^{-2}
$k_3/\mathrm{mol\,dm^{-3}\,s^{-1}}$	6.8×10^{-1} (5.3×10^{-1})	4.5×10^{-1}	2.1	8.3×10^{-2} (6.9×10^{-2})	2.8×10^{-2}
k_{-3}/s^{-1}	8.1×10^{-8} (7.7×10^{-8})	9.0×10^{-8}	3.7×10^{-7}	2.2×10^{-6} (2.5×10^{-6})	6.0×10^{-7}
k_5/s^{-1}	8.1×10^{-3} (2.8×10^{-3})	3.3×10^{-3}	1.5×10^{-3}	8.3×10^{-4} (1.1×10^{-4})	5.3×10^{-4}
k_{-5}/s^{-1}	3.8×10^{-4} (1.3×10^{-4})	4.4×10^{-5}	5.0×10^{-3}	3.0×10^{-2} (3.5×10^{-3})	1.4×10^{-2}
k_8/s^{-1}	—	—	4.5×10^{-2}	5.1×10^{-3} (2.0×10^{-3})	2.9×10^{-3}
k_{-8}/s^{-1}	—	—	1.8×10^{-4}	6.7×10^{-5} (2.5×10^{-5})	8.8×10^{-6}

a) The figures in parentheses are the constants obtained at 20 °C by Cigén et al. (Refs. 8 and 11).

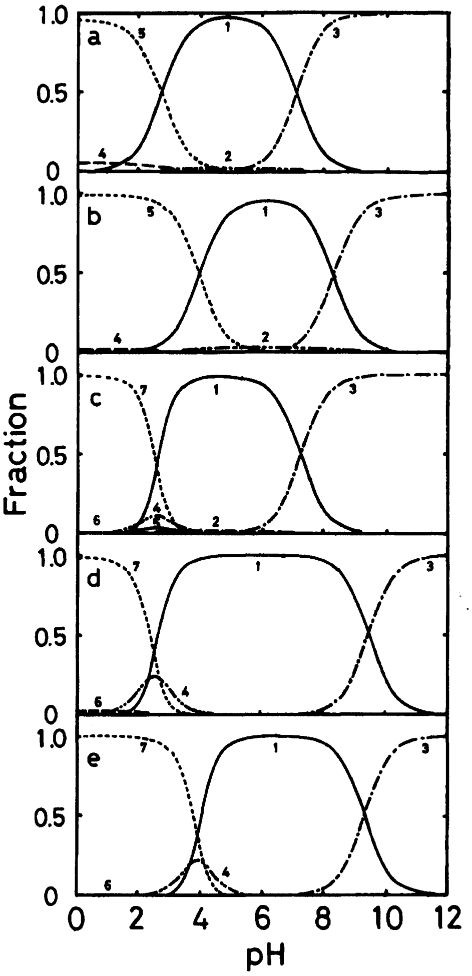


Fig. 7. Fraction of triphenylmethane dyes in various forms as a function of pH at equilibrium. a, MG; b, BG; c, PR; d, CV; e, EV. 1, R^+; 2, $HROH^+$; 3, ROH; 4, HR^{2+}; 5, H_2ROH^{2+}; 6, H_2R^{3+}; 7, H_3ROH^{3+}.

As a result of this the equilibrium constants of the hydration are in this order: $K_1 < K_5 < K_8$.

Figure 7 is very useful for predicting the formation of ion associates at various pHs in an aqueous medium. For example, heteropolyacids such as molybdophosphate and molybdosilicate react in acidic media of pH 0—1 with triphenylmethane dyes to form colored ion associates.[3,6)] In such reactions, MG showed the largest reactivity of the five dyes. This can be well explained from the fraction of quinonoid species in Fig. 7. The ratio of the quinonoid species of MG is the largest of the five dyes in the pH region from 0 to 1, where heteropolyacids, such as molybdophosphate and molybdosilicate, are preferably formed.

Contribution of Amino Groups to Rate and Equilibrium Constants. From Table 3, the hydration rate constants (k_1 and k_5) of dyes with two dialkylamino groups are larger than the corresponding ones with three dialkylamino groups, while the dehydration rate constants (k_{-1} and k_{-5}) of dyes with two dialkylamino groups are smaller than the corresponding ones with three dialkylamino groups. Since the electron density of the central carbon atom of the dye increases with an increase in the number of dialkylamino groups, the addition of a hydroxide ion or a water molecule to the central carbon atom becomes difficult, and the elimination of the hydroxyl group from the central carbon atom becomes easy. Consequently, the equilibrium constants (K_1, K_3, and K_5) for MG and BG are larger than those for CV and EV, respectively.

In strongly acidic solutions, however, the percent distributions of the alcohol species for dyes with three dialkylamino groups were larger than those with two dialkylamino groups, as shown in Fig. 7. Under such conditions, predominant species are, for example, HMG^{2+}

and H_2CV^{3+}. The species H_2CV^{3+} is regarded as a derivative of HMG^{2+} with a substituent group $-NH(CH_3)_2^+$. By adding this electron-withdrawing group to HMG^{2+}, the electron density of the central carbon atom decreases, and then the addition of water molecule becomes easier. Thus, the values K_8 for CV and EV are larger than the values of K_5 for MG and BG, respectively.

Figure 8 shows the plots of $\log K_n$ against the total Hammett's σ values of amino groups. The plots of the acid dissociation constants (K_2, K_4, K_6, K_7, and K_9) show the linear relationship with positive slopes, but in the hydration constants the plots of diethylamino group deviate from the lines. Probably, other factors will affect the hydration and dehydration of the dyes. One possible factor is the hydrophobicity of the dyes. Figure 9 shows the plots of the rate constants of the hydration against π values of amino groups, which are considered to be a hydrophobic parameter.[15] The plots show that the hydration rates decrease with an increase in the value of π; that is, a water molecule has more difficulty in approaching the central carbon atom of a triphenylmethane dye when the dye becomes more hydrophobic. Similarly, hydronium ion has more difficulty in approaching the hydroxyl group of more hydrophobic triphenylmethanol. However, triphenylmethanols are in a tetrahedral structure and less change in the reverse rate constants was found. As a result, the equilibrium constant for the hydration becomes smaller when a dye becomes more hydrophobic.

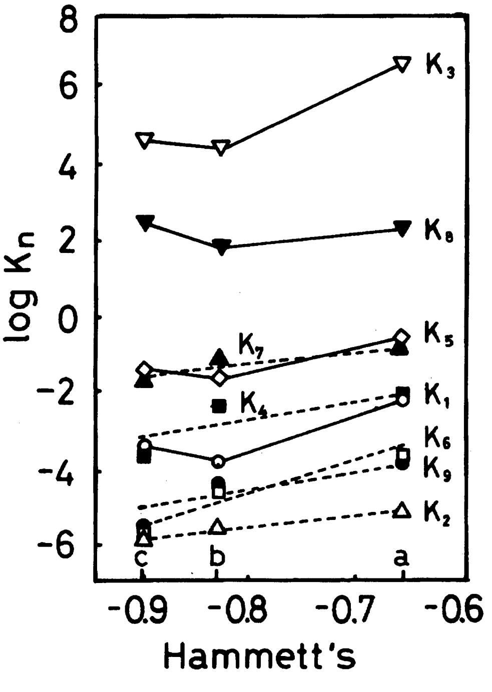


Fig. 8. Relationships between Hammett's σ values and equilibrium constants $\log K_n$. dyes: PR, CV, and EV. Hammett's σ values (σ_P) a: $-NH_2$, −0.66; b: $-N(CH_3)_2$, −0.83; c: $-N(C_2H_5)_2$, −0.90.

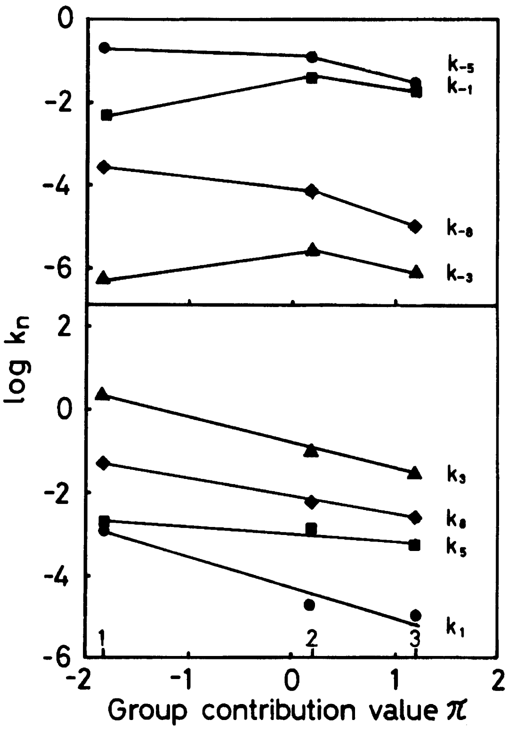


Fig. 9. Relationships between group contribution values (π) and rate constants ($\log k_n$ and $\log k_{-n}$). dyes: PR, CV, and EV. π values 1: $-NH_2$, −1.81; 2: $-N(CH_3)_2$, 0.23; 3: $-N(C_2H_5)_2$, 1.23.

In conclusion, design and synthesis of a new triphenylmethane dye that forms an alcohol with difficulty would be required for the purpose of enhancement of the reactivity in ion association reactions.

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