

Studies on the Pyridine Analogues of Malachite Green.

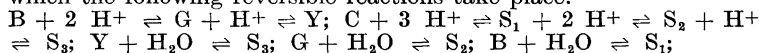
I. Protolytic Equilibria and Reaction Rate Constants of 4-Pyridine Green in Aqueous Solutions

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The protolytic and hydration reactions of 4,4'-bis(dimethylamino-phenyl)-4'-pyridylmethanol, named 4-Pyridine Green (4-PG), have been investigated spectrophotometrically in aqueous solutions with a constant ionic strength 0.5 M at 20.0°C.

The reaction scheme proposed for Crystal Violet has been found valid also for 4-Pyridine Green, which gives seven species, three coloured (B, G, and Y) and four colourless (C, S₁, S₂ and S₃), between which the following reversible reactions take place:

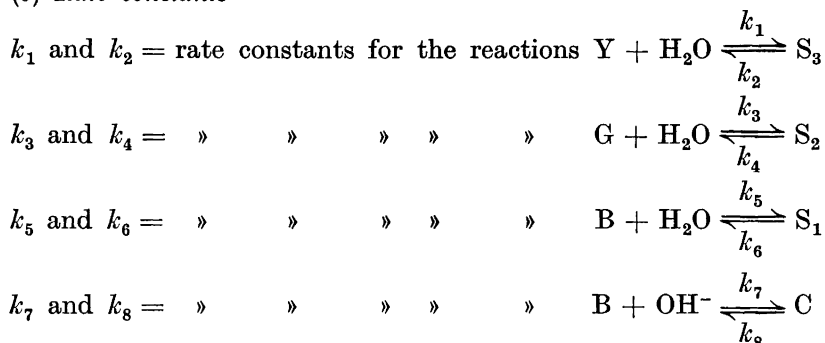


$B + OH^- \rightleftharpoons C$. The equilibria between B, G, and Y and between C, S₁, S₂, and S₃ are reached instantaneously, whereas the other reactions are slow. Five protolytic, three hydration and eight rate constants of the reactions indicated above have been determined, and the results were compared with the results from the corresponding investigation of Crystal Violet.

The existence of pyridine analogues of Malachite Green has been known since the beginning of this century. Harries and Lénart made a report of the preparation of 2-Pyridine Green in 1915¹ and compared the absorption curve of this dye with the absorption curve of Malachite Green, but since then no further attention seems to have been paid to the pyridine analogues of Malachite Green.

As a part of the investigations of triarylmethane dyes in this laboratory²⁻⁷, all three pyridine analogues of Malachite Green have been prepared. In the present investigation protolytic and hydration equilibria and reaction rates of the hydration reactions of 4-Pyridine Green have been studied spectrophotometrically in aqueous solutions with a constant ionic strength 0.49 M at 20.0°C.

(c) Rate constants



k = rate constant for the total reaction

(d) $\epsilon_B, \epsilon_G, \epsilon_Y$ = molar absorbancy coefficients of B, G, and Y.

e_o, e_t, e_∞ = absorbancy per cm of a solution at the times 0 and t and at equilibrium.

E_o, E_t, E_∞ = total absorbancies.

e_B, e_G, e_Y = absorbancy of a solution containing only B, G or Y.

C_M = total concentration of dyestuff.

$h = [H^+]$; $oh = [OH^-]$; $K_w = [H^+][OH^-]$.

The changes in colour nuances and colour intensities that take place, when the pH of an aqueous solution of 4-Pyridine Green is changed, depend on the reactions visualized in the reaction-equilibrium scheme. The values of the constants in the equilibrium scheme can be calculated, if the following quantities are determined for a large number of solutions with varying pH:

1. The absorbancy, e_o , at a moment immediately after the mixing of a stock solution with the appropriate buffer. The dye stock solution is (if possible) prepared in such a way that all of the dye is present as the coloured species B.

2. The absorbancy, e_∞ , when equilibrium is reached.

3. The pH of the solutions.

4. The rate constant, k , of the total reaction that changes the intensity of the colour of the solutions either by the hydration of the coloured species (B, G, and Y) to colourless species (C, S_1 , S_2 , and S_3) or *vice versa*.

EQUATIONS

The following expressions for the initial absorbancy, e_o , the equilibrium absorbancy, e_∞ , and the rate constant of the total reaction, k , as functions of the hydrogen ion concentration can be derived (*cf.* Ref.³)

$$e_o = \frac{K_1 K_2 e_B + h K_1 e_G + h^2 e_Y}{K_1 K_2 + h K_1 + h^2} \quad (1)$$

$$e_\infty = \frac{K_1 K_2 e_B + h K_1 e_G + h^2 e_Y}{K_1 K_2 (1 + K_6 + K_6 K_3' / h) + h K_1 (1 + K_5) + h^2 (1 + K_4)} \quad (2)$$

$$k = \frac{1}{t} \ln \frac{e_0 - e_\infty}{e_t - e_\infty} = \frac{h^3 k_2 + h^2 k_4 K_1' + h k_6 K_1' K_2' + k_8 K_1' K_2' K_3'}{h^3 + h^2 K_1' + h K_1' K_2' + K_1' K_2' K_3'} + \frac{h^2 k_1 + h k_3 K_1 + k_5 K_1 K_2 + k_7 \text{oh} K_1 K_2}{h^2 + h K_1 + K_1 K_2} \quad (3)$$

The eqns. (1–3) can be approximated, since certain species and reaction steps can be neglected in some pH-ranges. These approximations will be further considered in connection with the determination of the individual constants.

EXPERIMENTAL

Preparation of the dyestuff. The leuco base was prepared by the standard procedure of condensing dimethylaniline (0.3 mole) with 4-pyridinealdehyde (0.1 mole) (from L. Light & Co., Colnbrook, England) in a nitrogen atmosphere. Concentrated hydrochloric acid (0.3 mole) was used as a condensing agent. Recrystallization from a mixture of 75 % ethanol-25 % water gave a white powder, m.p. 123–125°C. The leuco base was dissolved in dilute hydrochloric acid and oxidized to dyestuff with lead dioxide.

A perchlorate of the dye was precipitated with sodium perchlorate and recrystallized from 0.2 M acetic acid. Since there are no data available about this dyestuff, its identity is established from: (1) The identity of the initial substances used in the preparation and the method of preparation. (2) The absorption curves of the dye which have the forms that should be expected from a substance of this type. (3) The other two pyridine analogues of Malachite Green, 2- and 3-Pyridine Green, have also been prepared and found to have properties very similar to, but yet in some respects strikingly different from, the present preparation. Furthermore, the leuco base of 2-Pyridine Green was found to have m.p. 110°C, which is exactly the value found by Harries and Lénart. (4) The elementary analyses which are consistent with the mono-perchlorate. (Found: C 61.4; H 5.68; O 14.8; N 9.75; Cl 8.16. Calc. for $C_{22}H_{24}O_4N_3Cl$: C 61.46; H 5.63; O 14.89; N 9.77; Cl 8.25).

A stock solution of the dye was prepared by weighing and dissolving the perchlorate in acetone. A solution was prepared for measurement in the following way. 1 ml of the acetone dye stock solution was added to 49 ml of an appropriate buffer solution, which was well thermostated, and the rate of the change of the colour intensity was measured and the initial and equilibrium absorbancies were determined. The measurements were carried out at the wavelength 639 m μ ; the ionic strength was 0.49 M and the temperature 20.0°C.

The chemicals used for the buffer solutions and the apparatus used for the measurements were the same as in Ref.³ In this paper pH means $-\log[H^+]$ and not $-\log a_{H^+}$.

The dyestuff, in aqueous solutions, is adsorbed on the walls of the vessels and absorption cells used for the measurements. The adsorption phenomena were not, however, so troublesome as in the case of Crystal Violet (Ref.³).

MEASUREMENTS AND RESULTS

Absorption curves. Fig. 1 shows the absorption curves of the three coloured species B, G, and Y. The curve of B was obtained in a phosphate buffer, pH = 6.36, where B proved to be the only coloured species; $[Y] \ll [G] \ll [B]$. $\epsilon_B = e_B/C_M$ was determined by measuring the fading of the colour in phosphate buffers and extrapolating the absorbancy back to $t = 0$. As can be seen from eqn. (1), we have $e_B \approx e_0$ in solutions with $[H^+] \ll K_2$, since $K_2 \ll K_1$ and $e_Y \ll e_G \ll e_B$ at the used wavelength, $\lambda = 639 \text{ m}\mu$.

There is no pH-range, where G is the only coloured species. Therefore, the curve of G was calculated from an absorption curve obtained from the equi-

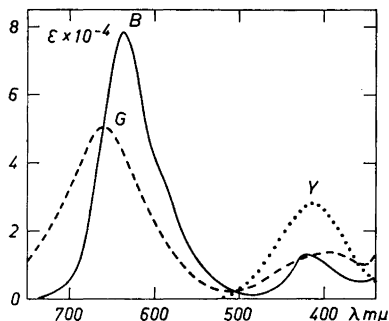


Fig. 1. Absorption curves of 4-Pyridine Green in aqueous solutions. The Curves B, G, and Y are the curves of the blue species B, the green species G, and the yellow species Y, respectively.

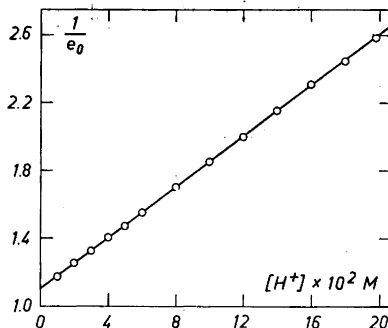


Fig. 2. $1/e_0$ plotted against $[H^+]$ for the determination of K_1 and e_G . $C_M = 2 \times 10^{-5} M$, $d = 1$ cm.

librium absorbancies in an acetate buffer, pH = 3.25, and eqn. (2). At pH = 3.25, B and G are the only coloured species, *i.e.* $[Y] \ll [G] \approx [B]$.

The absorption curve of Y was calculated from eqn. (1) and a number of e_0 -values, measured at different wavelengths, in 0.5 M hydrochloric acid.

The obtained values of λ_{\max} and ϵ_{\max} were

$$\begin{aligned} \lambda_{B \max} &= 636 \text{ and } 420 \text{ m}\mu; & \epsilon_{B \max} &= 7.9 \times 10^4 \text{ and } 1.3 \times 10^4 \text{ respectively} \\ \lambda_{G \max} &= 660 \text{ » } 395 \text{ m}\mu; & \epsilon_{G \max} &= 5.1 \times 10^4 \text{ » } 1.4 \times 10^4 \text{ »} \\ \lambda_{Y \max} &= 413 \text{ m}\mu; & \epsilon_{Y \max} &= 2.8 \times 10^4 \end{aligned}$$

Determination of K_1 and e_G . In HCl + KCl-buffers $[B] \ll [G] + [Y]$ and eqn. (1) can be approximated and written as

$$\frac{1}{e_0} = \frac{1}{e_G} + \frac{h}{K_1 e_G} \quad (4)$$

if the measurements are carried out at a wavelength where $e_Y \ll e_G$. The acetone dye stock solution, in which the dye is present as the coloured species B, was mixed with suitable buffers.

The equilibria $B + 2 H^+ \rightleftharpoons G + H^+ \rightleftharpoons Y$ are then reached instantaneously, whereupon the solutions are decolorized owing to the hydration reactions $G + H_2O \rightleftharpoons S_2$ and $Y + H_2O \rightleftharpoons S_3$. The initial absorbancy, e_0 , was determined by following the fading of the colour and extrapolating the absorbancy to $t = 0$. In Fig. 2 $1/e_0$ is plotted *versus* $[H^+]$, and a straight line is obtained which gives $e_G = 0.907$ and $K_1 = 0.146 M$ ($C_M = 2 \times 10^{-5} M$, $d = 1$ cm).

Determination of K_2 . For acetate buffers, pH = 3.2–4, eqn. (1) can be used in the following approximated form

$$\frac{h}{e_B - e_0} = \frac{K_2}{e_B - e_G} + \frac{h}{e_B - e_G} \quad (5)$$

Table 1. e_o , and k -values for the determination of K_1 , k_1 , and e_G . $\lambda = 639 \text{ m}\mu$, $C_M = 2 \times 10^{-5} \text{ M}$, $d = 1 \text{ cm}$, $T = 20.0^\circ\text{C}$.

[H ⁺] M	e_o	$k \text{ min}^{-1}$	[H ⁺] M	e_o	$k \text{ min}^{-1}$
0.005		0.00573	0.080	0.587	0.0226
0.010	0.852	0.00735	0.100	0.539	0.0255
0.020	0.798	0.01034	0.120	0.500	0.0279
0.030	0.754	0.01297	0.140	0.464	0.0294
0.040	0.711	0.0154	0.160	0.433	0.0309
0.050	0.679	0.0175	0.180	0.409	0.0326
0.060	0.644	0.0193	0.196	0.387	0.0339

Table 2. e_o -Values for the determination of K_2 and e_G in acetate buffers. $\lambda = 639 \text{ m}\mu$, $C_M = 1 \times 10^{-5} \text{ M}$, $d = 1 \text{ cm}$, $e_B = 0.775$, $T = 20.0^\circ\text{C}$.

[H ⁺] $\times 10^7 \text{ M}$	e_o	[H ⁺] $\times 10^4 \text{ M}$	e_o
0.955	0.651	2.23	0.585
1.274	0.628	2.32	0.569
1.50	0.614	3.86	0.546
1.81	0.598	5.69	0.525

The initial absorbancy, e_o , was determined through the extrapolation procedure described above, and $e_B = 0.775$ was determined in a similar way from kinetic measurements in phosphate buffers where $[Y] \ll [G] \ll [B]$ and, therefore, $e_o \approx e_B$. In Fig. 3 $[H^+]/(e_B - e_o)$ is plotted versus $[H^+]$. ($C_M = 1 \times 10^{-5} \text{ M}$, $d = 1 \text{ cm}$, $\lambda = 639 \text{ m}\mu$). From the obtained straight line we get the intercept $y = K_2/(e_B - e_G) = 4.62 \times 10^{-4} \text{ M}$ and the slope $l = 1/(e_B - e_G) = 3.17$. Consequently $K_2 = 1.46 \times 10^{-4} \text{ M}$ and $e_G = 0.459$ are obtained.

Determination of K_6 and K_3' . In phosphate buffers with $\text{pH} \geq 6.3$ the only species of the dye to be considered are B, S₁, and C. Eqn. (2) can be approximated to

$$\frac{h}{e_\infty} = \frac{K_3'K_6}{e_B} + \frac{h(1 + K_6)}{e_B} \quad (6)$$

Table 3. E_{∞} -Values for the determination of K_6 and K_3' in phosphate buffers. $\lambda = 639 \text{ m}\mu$, $C_M = 1 \times 10^{-5} \text{ M}$, $d = 5 \text{ cm}$, $e_B = 0.775$, $T = 20.0^\circ\text{C}$. $E_{\infty \text{ corr.}} = E_{\infty} - 0.007$.

[H ⁺] $\times 10^7 \text{ M}$	$E_{\infty \text{ corr.}}$	[H ⁺] $\times 10^7 \text{ M}$	$E_{\infty \text{ corr.}}$
1.55	0.250	3.56	0.476
1.94	0.298	4.40	0.552
2.37	0.351	5.43	0.637
2.92	0.410		

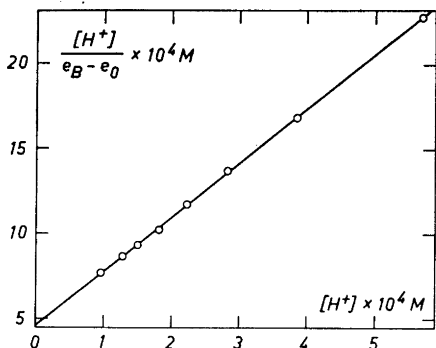


Fig. 3. $[H^+]/(e_B - e_0)$ plotted against $[H^+]$ for the determination of K_2 .
 $C_M = 1 \times 10^{-5}$ M, $d = 1$ cm.

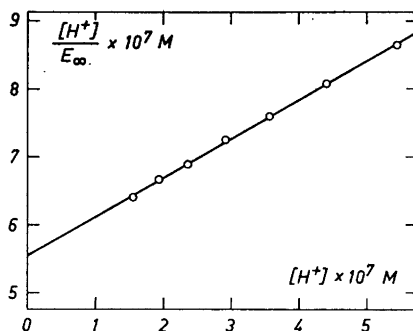


Fig. 4. $[H^+]/E_{\infty}$ corr. plotted against $[H^+]$ for the determination of K_6 and K_3' . $C_M = 1 \times 10^{-5}$ M, $d = 5$ cm.

The equilibrium absorbancies, E_{∞} , were measured 26 h after the mixing of the dye stock solution with appropriate phosphate buffers. No straight line was, however, obtained, when $[H^+]/E_{\infty}$ was plotted against $[H^+]$. The line was curved and the curvature became more pronounced the lower the absorbancies were. The reason for this was the fact that in alkaline solutions, where the dyestuff was assumed to be completely decolourized, a small remaining absorbancy persisted ($E_{\infty} = 0.007$ when $C_M = 1 \times 10^{-5}$ M and $d = 5$ cm). This remaining absorbancy had to be especially considered. If the corrected E_{∞} -values are used, a plotting of $[H^+]/E_{\infty}$ corr. against $[H^+]$ gives a straight line, Fig. 4. The intercept of this line on the ordinate-axis, y , and the slope, l , are: $y = 5.56 \times 10^{-7}$ M, $l = 0.568$. Since $E_B = 5 e_B = 5 \times 0.775$ we obtain, according to eqn. (6), $K_6 = 1.20$ and $K_3' = 1.79 \times 10^{-6}$ M.

Determination of K_4 and K_5 . In the pH-range 3–4 eqn. (2) can be approximated and written as

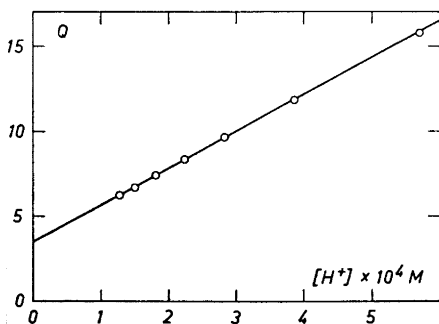


Fig. 5. The right member of eqn. (7), Q , plotted against $[H^+]$ for the determination of K_5 and K_4/K_1 . $C_M = 2 \times 10^{-5}$ M, $d = 1$ cm.

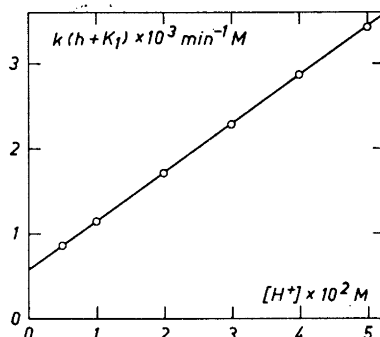


Fig. 6. $k(h + K_1)$ as a function of $[H^+]$ for the determination of k_3 . $[H^+] = 5-50$ mM.

Table 4. E_{∞} -Values for the determination of K_4 and K_5 from equilibrium measurements in HCl + KCl-buffers and acetate buffers. $\lambda = 639 \text{ m}\mu$, $C_M = 2 \times 10^{-5} \text{ M}$, $d = 1$ and 5 cm , $e_B = 1.474$, $e_G = 0.874$.

HCl + KCl-buffers, $d = 5 \text{ cm}$			Acetate buffers, $d = 1 \text{ cm}$			
$[\text{H}^+] \times 10^3 \text{ M}$	$E_{\infty} = 5 e_{\infty}$	$K_4 \times 10^3$	$[\text{H}^+] \times 10^4 \text{ M}$	e_{∞}	$[\text{H}^+] \times 10^4 \text{ M}$	e_{∞}
2.00	0.096	3.37	1.274	0.263	2.82	0.139
3.00	0.066	3.25	1.500	0.233	3.86	0.105
4.00	0.051	3.16	1.81	0.202	5.69	0.0724
5.00	0.041	3.13	2.23	0.170		
Mean value		3.23	$K_{4\text{graph.}} = 3.12 \times 10^3$			
			$K_{5\text{graph.}} = 3.52$			

$$K_5 + \frac{hK_4}{K_1} = \frac{e_G}{e_{\infty}} + \frac{K_2 e_B}{h e_{\infty}} - \frac{K_2(1 + K_6)}{h} - 1 \quad (7)$$

since $K_3' \ll h$ in the actual pH-range and $h^2 e_Y$ in the numerator of eqn. (2) can be neglected at the used wavelength, $\lambda = 639 \text{ m}\mu$, where $e_Y \ll e_G < e_B$. The equilibrium absorbancies were measured in acetate buffers ($C_M = 2 \times 10^{-5} \text{ M}$, $d = 1 \text{ cm}$). The right member of eqn. (7) was calculated, using the already determined values of e_B , e_G , K_2 , and K_6 , and plotted against $[\text{H}^+]$. Fig. 5. A straight line was obtained; $y = 3.52$, $l = 2.14 \times 10^4$. From the values of y and l we get, according to eqn. (7), $K_5 = 3.52$ and $K_4 = 3.12 \times 10^3$, since $K_1 = 0.146$.

The hydration constant K_4 can also be calculated from e_{∞} -values obtained in HCl + KCl-buffers, pH 2.3–2.7. In this pH-range eqn. (2) is approximated to

$$K_4 = \frac{K_1 K_2 e_B + h K_1 e_G}{h e_{\infty}} - \frac{K_1 K_2 (1 + K_6)}{h^2} - \frac{K_1 (K_1 + h) + K_1 K_5}{h} \quad (8)$$

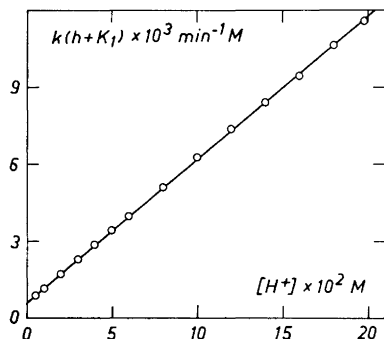


Fig. 7. $k(h + K_1)$ as a function of $[\text{H}^+]$ for the determination of k_1 . $[\text{H}^+] = 5\text{--}200 \text{ mM}$.

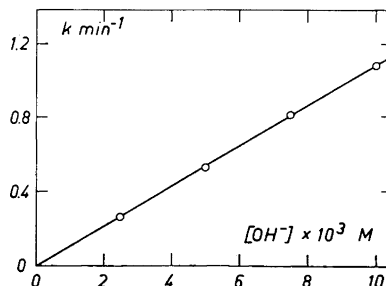


Fig. 8. The rate constant k as a function of $[\text{OH}^-]$ for the determination of k_7 .

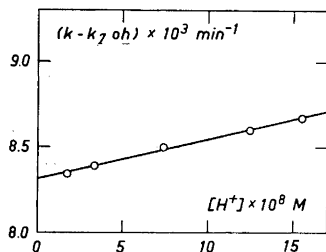


Fig. 9. $(k - k_7 \text{ oh})$ plotted against $[\text{H}^+]$ in the pH-range 6.8–7.8 for the determination of k_5 .

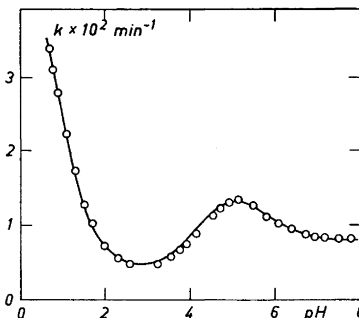


Fig. 10. The rate constant k as a function of pH in the pH-range 0.7–8. The points represented by the symbol O are experimentally obtained. The full-drawn curve is calculated from the non-approximated eqn. (3).

Even a roughly estimated value of K_5 can be used in the calculation of K_4 since the last two terms of eqn. (8) have the character of correction terms, amounting to 1–2 % of K_4 . The calculated values of K_4 are recorded in Table 2 from which the mean value $K_4 = 3.23 \times 10^3$ is obtained. This value of K_4 is not, however, very reliable because of the low absorbancies.

Calculation of K_1' and K_2' . By definitions are

$$K_1' = K_1 K_5 / K_4 \quad (9)$$

and

$$K_2' = K_2 K_6 / K_5 \quad (10)$$

From the values of K_1 , K_2 , K_4 , K_5 , and K_6 , reported above we thus obtain $K_1' = 1.65 \times 10^{-4}$ M and $K_2' = 4.98 \times 10^{-5}$ M.

Determination of k_1 , k_2 , k_3 , and k_4 . For kinetic measurements in HCl + KCl-buffers, pH = 0.7–2.3, eqn. (3) can be approximated to

$$k(K_1 + h) = k_3 K_1 + k_1 h \quad (11)$$

$k(K_1 + h)$ is plotted as a function of $[\text{H}^+]$ in Figs. 6 and 7. Fig. 6, which is an enlargement of the lower, left part of Fig. 7, has the intercept on the ordinate-axis $y = 5.76 \times 10^{-4} \text{ min}^{-1} \text{ M}$ and consequently we get $k_3 = 3.94 \times 10^{-3} \text{ min}^{-1}$, since $K_1 = 0.146$ M. The value of the rate constant $k_4 = 1.12 \times 10^{-3} \text{ min}^{-1}$ is obtained from $k_4 = k_3 / K_5$. The slope of the straight line in Fig. 7 gives $k_1 = 5.57 \times 10^{-2} \text{ min}^{-1}$, and $k_2 = 1.79 \times 10^{-5}$ is then calculated from $k_2 = k_1 / K_4$.

Determination of k_7 and k_8 . For strongly alkaline solutions eqn. (3) is approximated to

$$k = k_5 + k_7 \text{ oh} + k_8 \quad (12)$$

The rate of the decolourization is, however, directly proportional to $[\text{OH}^-]$ as can be seen in Fig. 8, where k is plotted *versus* $[\text{OH}^-]$. In the pH-range used

Table 5. 4-Pyridine Green. A summary of the obtained values of the constants.

Protolytic constants				
K_1 M	$K_2 \times 10^4$ M	$K_1' \times 10^4$ M	$K_2' \times 10^5$ M	$K_3' \times 10^6$ M
0.146 ± 0.05	1.46 ± 0.05	1.65 ± 0.15	5.0 ± 0.5	1.8 ± 0.1
Hydration constants				
$K_4 \times 10^{-3}$	K_5		K_6	
3.12 ± 0.12	3.5 ± 0.2		1.2 ± 0.1	
Rate constants				
$k_1 \times 10^2$ min ⁻¹	$k_3 \times 10^3$ min ⁻¹	$k_5 \times 10^3$ min ⁻¹	k_7 M ⁻¹ min ⁻¹	
5.6 ± 0.1	3.9 ± 0.1	8.3 ± 0.1	107 ± 1	
$k_2 \times 10^5$ min ⁻¹	$k_4 \times 10^3$ min ⁻¹	$k_6 \times 10^3$ min ⁻¹	$k_8 \times 10^5$ min ⁻¹	
1.8 ± 0.6	1.1 ± 0.1	6.9 ± 0.4	6.1 ± 0.4	

in Fig. 8, pH = 11.3–11.9, is thus $k_7\text{oh} \gg k_5 + k_8$ and only k_7 can be obtained from the figure; $k_7 = 107 \text{ min}^{-1} \text{ M}^{-1}$. The rate constant k_8 can be calculated from the expression $k_8 = k_7 K_w / K_3' K_6$, which can be obtained from the definitions of the constants; $k_8 = 6.15 \times 10^{-7} \text{ min}^{-1}$. ($K_w = 1.24 \times 10^{-14} \text{ M}^2$).

Determination of k_5 and k_6 . In neutral and very weakly alkaline solutions eqn. (3) can be approximated to

$$k - k_7\text{oh} = k_5 + \frac{hk_6 + k_8 K_3'}{h + K_3'} \quad (13)$$

In Fig. 9 $k - k_7\text{oh}$ is plotted as a function of $[\text{H}^+]$. $k_7\text{oh}$ is, compared with k in the pH-range used in Fig. 9, pH = 6.8–7.8, a correction term which only amounts to 0.01–0.9 % of k . Extrapolation of the almost straight line to $[\text{H}^+] = 0$ gives an intercept $y = k_5 + k_8 = 8.32 \times 10^{-3} \text{ min}^{-1}$ but $k_8 \ll k_5$ and therefore we obtain $k_5 = 8.32 \times 10^{-3} \text{ min}^{-1}$. The expression $k_6 = k_5 / K_6$ then gives $k_6 = 6.93 \times 10^{-3} \text{ min}^{-1}$.

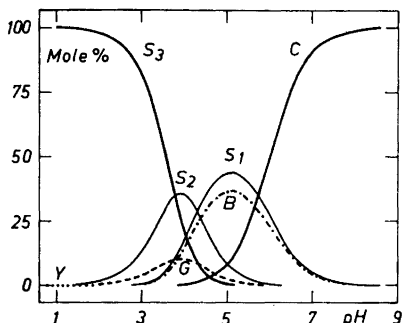


Fig. 11. The distribution of 4-Pyridine Green between the different species as a function of pH. The notations are the same as in the text.

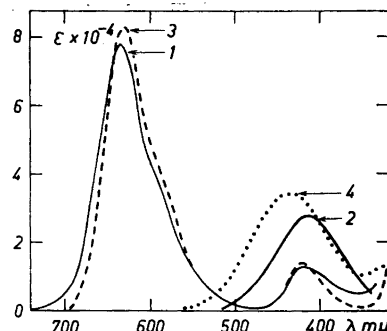


Fig. 12. Absorption curves of 4-Pyridine Green and Crystal Violet. The Curves 1 and 2 are the absorption curves of the blue species B and the yellow species Y, respectively, of 4-Pyridine Green. The Curves 3 and 4 are the absorption curves of the ions $[(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{CC}_6\text{H}_4\text{NHMe}_2]^{2+}$ and $[\text{Me}_2\text{NC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_4\text{NHMe}_2)_2]^{3+}$, respectively, of Crystal Violet.

The determined values of the constants are summarized in Table 5. It is hardly possible to perform an objective estimation of the errors of the values of the constants in such a complicated reaction scheme as the present one and, therefore, the errors given are subjective ones, based on the reproducibility of the measurements and the experience of the reliability of the used method and apparatus.

Fig. 10 shows the rate constant k as a function of pH. The solid curve has been calculated from eqn. (3) using the constants in Table 5. The circles are experimentally found k -values. The agreement between the calculated curve and the experimental points is fairly good, but the curve cannot be used as a control of the obtained values of the constants, since the curve is rather insensitive to variations in these (especially to variations in K_1' , K_2' , and K_3').

Fig. 11 shows the distribution at equilibrium, of the seven species of the dye as a function of pH. The curve of Y is, however, so low that it cannot be drawn apart from the 0 % line.

DISCUSSION

A comparison between the corresponding absorption curves and values of the constants of 4-Pyridine Green and Crystal Violet, $[(\text{Me}_2\text{NC}_6\text{H}_4)_3\text{C}^+] \text{X}^-$ is interesting. The substitution of a $\text{Me}_2\text{NC}_6\text{H}_4$ -group of Crystal Violet for a NC_5H_4 -group has a very marked influence on the hydration reactions and some of the protolytic reactions. The equilibria "Coloured" \rightleftharpoons "Colourless" are strongly displaced towards "Colourless" when we go from Crystal Violet (CV) to 4-Pyridine Green. Compare $K_{4(\text{CV})} = 74$ with $K_{4(4\text{-PG})} = 3120$,

$K_{5(\text{CV})} = 0.0319$ with $K_{5(4\text{-PG})} = 3.5$, and $K_{6(\text{CV})} = 0.00014$ with $K_{6(4\text{-PG})} = 1.2$. There is also a marked difference between $K_{2(\text{CV})} = 0.00406$ and $K_{2(4\text{-PG})} = 0.000146$, whereas the values of the remaining protolytic constants of 4-Pyridine Green are of the same order of magnitude as corresponding values of Crystal Violet.

The great difference between $K_{2(\text{CV})}$ and $K_{2(4\text{-PG})}$ indicates that, as regards the species G, the proton from the reaction $\text{B} + \text{H}^+ \rightleftharpoons \text{G}$ is attached to the pyridine nitrogen as it is shown in the reaction scheme on p. 2252. A further support for this suggestion is given by the absorption curves. Fig. 12. The absorption curve of the species B is very similar to the absorption curve of the ion $[(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{CC}_6\text{H}_4\text{NHMe}_2]^{2+}$ of Crystal Violet. This ion of Crystal Violet has two proton-free amino nitrogens like the species B. The absorption curve of the species Y is very similar to the absorption curve of the ion $[\text{Me}_2\text{NC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_4\text{NHMe}_2)_2]^{3+}$ of Crystal Violet and this ion of Crystal Violet has one proton-free amino nitrogen like the species Y. The species G has an absorption curve which is different from the absorption curves of Malachite Green and derivatives of Malachite Green and, therefore, it is assumed that the protolytic reactions of 4-Pyridine Green proceed according to the reaction scheme. The species B and Y have absorption curves which are of the same type as the absorption curves of Malachite Green and its derivatives. However, it is difficult to decide whether the proton from the reaction $\text{C} + \text{H}^+ \rightleftharpoons \text{S}_1$ is mainly attached to the pyridine nitrogen or to an amino nitrogen.

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