

Studies on a Furane Analogue of Malachite Green. Protolytic Equilibria and Reaction Rate Constants of Furane Green in Aqueous Solutions

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The protolytic equilibria and the reaction rates of a furane analogue of Malachite Green, called Furane Green, have been studied in aqueous solutions with the constant ionic strength 0.49 M and at the temperature 20.0°C.

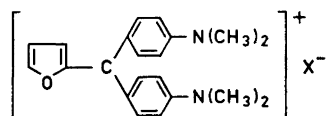
The results of the measurements have been compared with the results of corresponding measurements of Malachite Green and Thiophene Green. Furane Green was found to be very similar to Thiophene Green as regards the hydration equilibria $B + H_2O \rightleftharpoons S'$ and $G + H_2O \rightleftharpoons S''$.

The measurements of Furane Green were complicated by the instability of the dyestuff in aqueous solutions, which necessitated special procedures and made the determination of some of the constants impossible.

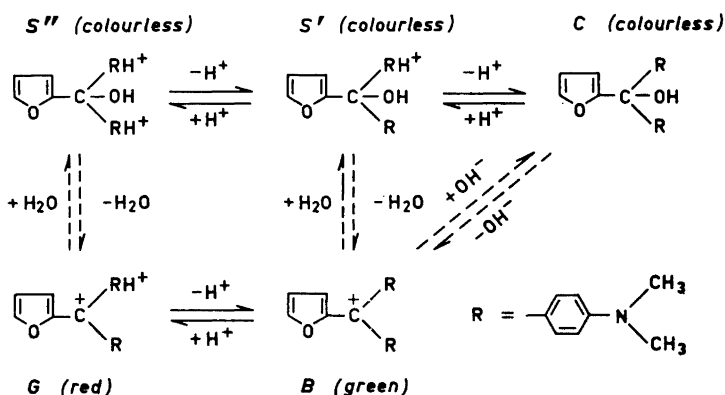
The preparation of a furane analogue of Malachite Green from furfural and *N,N*-dimethylaniline was first described by O. Fischer¹ in 1881. Later on Renshaw and Naylor² have repeated Fischer's synthesis and made some qualitative studies of the dyestuff. There have, however, been no quantitative studies of this dye.

In the course of our investigations of basic triarylmethane dyes Furane Green (FG), a dye salt of bis-(4-dimethylaminophenyl)-furyl-(2)-methanol, has been prepared and its protolytic equilibria and reaction rates in aqueous solutions with the constant ionic strength 0.49 M have been studied spectrophotometrically.

Furane Green can be represented by the following schematic structural formula:



In neutral, weakly alkaline or weakly acid solution FG is green. When such a solution is made strongly acid, it turns immediately red and then the colour intensity rapidly decreases. The reactions of FG can be visualized in the following reaction scheme, which is analogous to the corresponding reaction scheme of Malachite Green (MG).³



The notations B, G, S'' , S' and C are analogous to the notations used with MG. Full drawn arrows denote reactions proceeding at an immeasurable rate and dashed arrows denote reactions proceeding at a measurable rate.

The following constants and notations are defined:

(a) *Equilibrium constants.*

$$K_1 = [G]/[B][H^+]; \quad K_3 = [H^+][S']/[S''];$$

$$K_4 = [H^+][C]/[S']; \quad K_2 = [S']_{\infty}/[G_{\infty}];$$

$$K_6 = [B]_{\infty}/[S']_{\infty}.$$

(b) *Rate constants.*

$$k_1 \text{ rate constant for the reaction } G + H_2O \rightarrow S''$$

$$k_2 \text{ » » » » » } S'' \rightarrow G + H_2O$$

$$k_3 \text{ » » » » » } B + H_2O \rightarrow S'$$

$$k_4 \text{ » » » » » } S' \rightarrow B + H_2O$$

$$k_5 \text{ » » » » » } B + OH^- \rightarrow C$$

$$k_6 \text{ » » » » » } C \rightarrow B + OH^-$$

$$k \text{ » » » » » over-all reaction that changes the colour intensity.}$$

(c) *Notations.*

$$h = [H^+]; \quad oh = [OH^-], \quad K_w = oh \times h$$

$\varepsilon_B, \varepsilon_G$ molar absorptivity coefficient for the species B and G respectively.

e_0, e_t, e_{∞} absorbancy per cm at the times 0 and t and at equilibrium.

E_0, E_t, E_{∞} total absorbancy.

e_B, e_G absorbancy per cm of a solution containing only B or G.

C_M total concentration of the dyestuff.

The constants in the above reaction scheme can be calculated if the following quantities are determined for a great number of solutions with different pH-values:

(1) The absorbancy, e_0 , immediately after the mixing of a dye stock solution with an appropriate buffer solution. The dye solution is, if possible, prepared in such a way that all the dye is present as the species B.

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

(3) The rate constant, k , for the overall reaction that changes the intensity of the colour.

(4) The pH of the solution.

The measurements were complicated by the fact that FG was not stable in aqueous solution but underwent some kind of irreversible reaction (in addition to the reversible reactions indicated in the reaction scheme) that gradually reduced the concentration of the dyestuff. In neutral, weakly alkaline or weakly acid solutions this change was slow, but in strongly alkaline and strongly acid solutions it was rapid and seemed to compete with the decolourizing reactions indicated in the above reaction scheme. Thus, when an acetone stock solution of FG was mixed with water, the colour intensity slowly decreased until the solution after about a week was colourless. The colour of such a decolourized solution could not be restored. When the dye stock solution was mixed with HCl + KCl-buffers or NaOH + KCl-buffers, the solution was rapidly decolourized owing to the reactions indicated in the reaction scheme and to the irreversible process. If such a decolourized solution was mixed with an acetate buffer, so that the resulting pH was approximately 5, the colour was partially restored. The absorbancy of the solution increased rapidly, reached a maximum value and then decreased slowly. The maximum absorbancy was reproducible for a given concentration of acid or hydroxide used for the decolourization. The absorption curves within the wave length range 400–700 $m\mu$ were unchanged after the described operations although they were lower. Around the wave length $\lambda = 380 m\mu$ there was, however, an additional peak that was not present before the decolourization. If a solution had been decolourized with acid, it could not be used for kinetic measurements, since these were disturbed in some way. A detailed examination of the irreversible reaction(s) lay outside the scope of this investigation. For our purpose it was sufficient to make sure that reliable measurements were possible after the dye had been decolourized in strongly alkaline solutions. All of the constants could not, however, be determined.

Equations

The following equations were used for the calculation of the constants:

$$e_0 = \frac{e_B + hK_1e_G}{1 + hK_1} \quad (1)$$

$$e_\infty = \frac{e_B + hK_1e_G}{1 + 1/K_6 + K_4/hK_6 + hK_1(1 + K_2)} \quad (2)$$

$$k = \frac{1}{t} \ln \frac{e_0 - e_\infty}{e_t - e_\infty} = \frac{h^2k_2 + hk_4K_3 + k_6K_3K_4}{h + hK_3 + K_3K_4} + \frac{hk_1K_1 + k_3 + k_5oh}{1 + hK_1} \quad (3)$$

These equations can be approximated in different ways in different pH-ranges. The approximations will be considered further in connection with the determination of the constants.

EXPERIMENTAL

Furane Green Bromide. The leuco base was prepared by the method described by Fischer and Grahl⁴ from furfural and N,N-dimethylaniline. We used, however, concentrated hydrochloric acid and urea instead of zinc chloride. Recrystallization from ethanol gave light yellow crystals with a slightly reddish nuance.

The leuco base was dissolved in 0.01 M sulphuric acid and oxidized at 0°C to dyestuff with lead dioxide. After lead sulphate and remaining dioxide had been filtered off, the dyestuff bromide was precipitated with potassium bromide. The obtained product was filtered off, dissolved in water warmed to 50°C, filtered and reprecipitated at 0°C with potassium bromide. The oxidation and the precipitation procedure had to be made rapidly, otherwise the yield was very poor. The preparation consisted of a light green, felty mass of needle-shaped crystals with a silky lustre. When dried in a desiccator over concentrated sulphuric acid it changed to a dark blue hygroscopic powder. (Found: C 61.7; H 5.79; N 6.86; Br 20.1 %. Calc. for $C_{21}H_{13}ON_2Br$: C 63.2; H 5.81; N 7.01; Br 20.0 %).

A dye stock solution was prepared by weighing and dissolving the dyestuff in acetone. The instability of the dyestuff in aqueous solution necessitated special procedures for the measurements. These will be described in connection with the determination of the constants. Throughout all the kinetic measurements the wave length was 640 μ , the ionic strength 0.49 M, the concentration of the acetone dye stock solution 5×10^{-4} 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 pH means $-\log [H^+]$.

MEASUREMENTS AND RESULTS

Absorption curves. Fig. 1 shows the absorption curves of the green ion B and the red ion G. The curve of B was determined in an acetate buffer with pH = 4.68. Within a broad pH-range around pH = 5, more than 99 % of

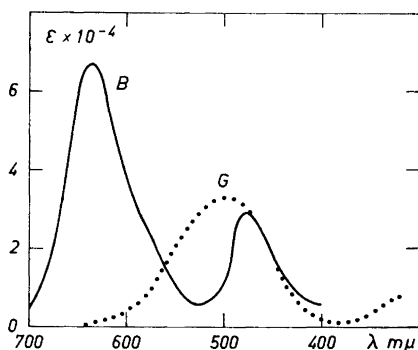
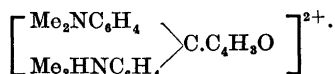


Fig. 1. Absorption curves of the green ion $[(Me_2NC_6H_4)_2.C.C_4H_3O]^+$ and the red ion



the dye is present as the species B and the molar absorptancy coefficients were obtained from the relation $\varepsilon_B = e_B/C_M$. The curve was determined immediately after the mixing of the acetone stock solution with the buffer solution to avoid errors due to the slow decrease in the concentration. $\lambda_{B\max} = 638 \text{ m}\mu$ and $475 \text{ m}\mu$, $\varepsilon_{B\max} = 6.7 \times 10^4$ and 3.0×10^4 , respectively.

The absorption curve of G was calculated from the e_0 -values at different wave lengths in a HCl + KCl-buffer with $[\text{H}^+] = 0.010 \text{ M}$. Eqn. (1) was used then. e_B was obtained from the absorption curve of B, and K_1 was obtained from measurements described below. $\lambda_{G\max} = 496 \text{ m}\mu$, $\varepsilon_{G\max} = 3.4 \times 10^4$.

Determination of K_1 . Eqn. (1) can be transformed to

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

1 ml of the dye stock solution was mixed with 49 ml of different HCl + KCl-buffers. The equilibrium between B and G was reached immediately and then the absorptancy decreased as a result of hydration — and the irreversible change. The extrapolation of the absorptancies to $t = 0$ gave the absorptancies, e_0 , immediately after the mixing. e_B was obtained from the absorption curve of B. Fig. 2 shows $[\text{H}^+]/(e_B - e_0)$ versus $[\text{H}^+]$ within the pH-range 1.3–2.6. From the straight line the intercept on the ordinate-axis $y = 0.0213 \text{ M}$ and the slope $l = 1.54$ are obtained. Hence $K_1 = 72 \pm 2 \text{ M}^{-1}$.

Determination of k_5 . The decolorization in alkaline solution is due to the reversible reaction $\text{B} + \text{OH}^- \xrightarrow{k_5} \text{C}$ and some irreversible reaction $\text{B} + \text{OH}^- \rightarrow \text{X}$ that also seems to have a rate directly proportional to $[\text{OH}^-]$. If the rate constant of the over-all reaction, k , is plotted versus $[\text{OH}^-]$ a straight line is obtained (Fig. 3). The degree of the irreversible reaction was estimated from the part of the colour that was restored when a solution, decolorized with NaOH, was made weakly acid, $\text{pH} \approx 5$. If e_B is the absorptancy of the dye solution, containing only the species B, at the moment of mixing the dye solution with

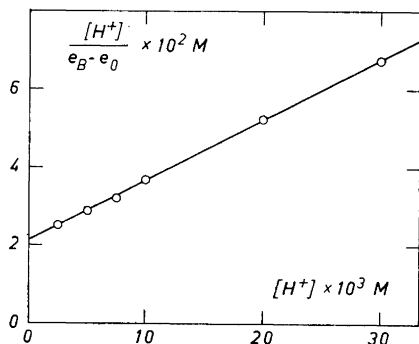


Fig. 2. $[\text{H}^+]/(e_B - e_0)$ versus $[\text{H}^+]$ for the determination of K_1 .

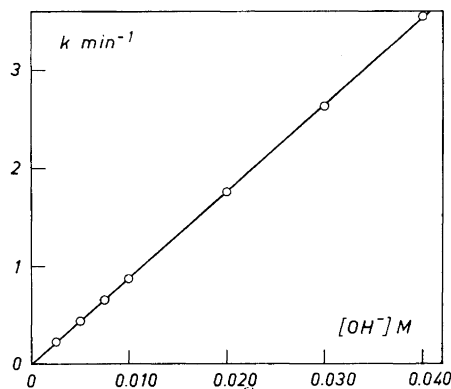
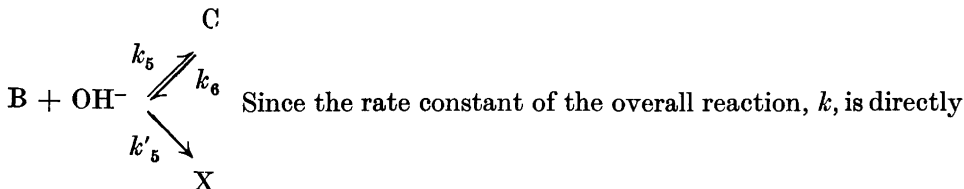


Fig. 3. The over-all rate constant, k , versus $[\text{OH}^-]$ for the determination of k_5 .

NaOH, and e'_B the absorbancy of the dye solution when it has been decolourized with NaOH and carried back to $\text{pH} \approx 5$, where B is the only species if no irreversible reactions occur, e'_B can be used to calculate the constant k_5 .

In alkaline solutions we can write the decolourizing reactions as



proportional to $[\text{OH}^-]$ we get

$$k = (k_5 + k'_5)\text{oh} + k_6 \quad (5)$$

k_6 is very small, however, as can be seen from Fig. 3 where the straight line runs through the origin, and therefore we can neglect the reaction $\text{C} \longrightarrow \text{B} + \text{OH}^-$ and obtain

$$k/\text{oh} = k_5 + k'_5 \quad (6)$$

and at equilibrium we have

$$\frac{k_5}{k'_5} = [\text{C}]/[\text{X}] = \frac{e'_B}{e_B - e'_B} \quad (7)$$

Table 2 shows the results from a great number of measurements. For each $[\text{OH}^-]$ e'_B and k were obtained as mean values from 3–10 kinetic series. The reproducibility was good. Thus we obtain $k_5 + k'_5 = 87.9 \text{ min}^{-1} \text{ M}^{-1}$ and $k_5/k'_5 = 1.367$ giving $k_5 = 50.8 \pm 0.8 \text{ M}^{-1} \text{ min}^{-1}$.

Determination of K_6/K_4 . In phosphate buffers ($\text{pH} = 6.3\text{--}7.6$) eqn. (2) can be approximated and written as

$$\frac{h}{e_\infty} = \frac{1 + K_6}{K_6 e_B} h + \frac{K_4}{K_6 e_B} \quad (8)$$

The equilibrium absorbancies, e_∞ , could not be measured directly because of the irreversible reaction and therefore the following procedure was used: 2 ml of the dye solution was mixed with 48 ml of a solution with the composition 0.001 M NaOH + 0.499 M KCl. The solution was rapidly decolourized. When the decolourization was complete, samples were taken out and mixed with

Table 1. Furane Green. e_0 -values for the determination of K_1 . $C_M = 1 \times 10^{-5} \text{ M}$; $d = 1 \text{ cm}$ $\lambda = 640 \text{ m}\mu$; $e_B = 0.650$; $T = 20.0^\circ\text{C}$.

$[\text{H}^+] \text{ M}$	e_0	$[\text{H}^+] \text{ M}$	e_0
0.0025	0.551	0.0100	0.379
0.0050	0.477	0.0200	0.268
0.0075	0.419	0.0300	0.206

Table 2. Furane Green. Kinetic measurements in alkaline solutions. $C_M = 1 \times 10^{-5}$ M; $d = 1$ cm; $\lambda = 640$ m μ ; $T = 20.0^\circ\text{C}$; $e_B = 0.670$. e_B and e'_B were measured in acetate buffer pH = 4.7.

[OH ⁻] M	$k/[\text{OH}^-]\text{M}^{-1}\text{min}^{-1}$	[OH ⁻] M	e'_B
0.0025	88.4	0.0010	0.389
0.0050	87.8	0.0025	0.384
0.0075	87.5	0.0050	0.388
0.0100	87.5	0.0100	0.390
0.0200	87.8	0.0250	0.384
0.0300	87.8	0.0500	0.386
0.0400	88.8		
Mean	87.9		0.387

equal volumes of suitable phosphate buffers. Part of the colour was then rapidly restored and the absorbancies increased to values that depended on the pH of the solution. These absorbancies, e'_∞ , were reproducible and represented the equilibrium absorbancies since a constant fraction of the dye was destroyed during the decolourization in NaOH (*cf.* above). Because of the slow irreversible reaction in the used pH-range the values of e'_B had to be measured within a few minutes after equilibrium had been reached. The restoration of the colour was too rapid to be appreciably influenced by the irreversible reaction. $[\text{H}^+]/e'_\infty$ versus $[\text{H}^+]$ (Fig. 4) gave a straight line with the intercept on the ordinate-axis $y = 1.09 \times 10^{-7}$ M and the slope $l = 2.74$ from which $(1 + K_6)/K_4 = 2.51 \times 10^7 \text{M}^{-1}$ is obtained. The fact that no rapid decolourization was observed when the acetone dye solution was mixed with an acetate buffer with pH ≈ 5 indicated that $K_6 \gg 1$ and thus $K_6/K_4 = 2.51 \times 10^7 \text{M}^{-1}$. Since $k_6 = k_5 \cdot K_w \cdot K_6/K_4$ we also obtain $k_6 = (1.58 \pm 0.06) \times 10^{-5} \text{min}^{-1}$ ($k_5 = 50.8 \text{min}^{-1} \text{M}^{-1}$ and $K_w = 1.24 \times 10^{-14} \text{M}^2$).

Determination of K_3K_4 . Within a pH-range where [G] and the reactions $\text{B} + \text{OH}^- \rightleftharpoons \text{C}$ are negligible eqn. (3) can be approximated to

$$k = k_4 \frac{hK_3}{h^2 + hK_3 + K_3K_4} + k_3 \quad (9)$$

A differentiation of eqn. (9) with regard to h gives $h_{k_{\max}} = \sqrt{K_3K_4}$. The measurements were carried out in acetate buffers and phosphate buffers (pH = 3.3–7.6) in the same manner as it was described for the determination of K_6/K_4 . The rate of the restoration of the colour was measured instead of e'_∞ . Fig. 5 shows k as a function of pH. $\text{pH}_{k_{\max}} = 4.79 \pm 0.01$ and thus $K_3K_4 = 2.61 \times 10^{-10} \text{M}^2$.

Determination of k_3 . The rate constant k_3 was determined through kinetic measurements in phosphate buffers (pH = 6.7–7.5). Within this pH-range eqn. (3) is approximated to

$$k - k_5\text{oh} = k_4 \frac{h}{h + K_4} + k_3 + k_6 \quad (10)$$

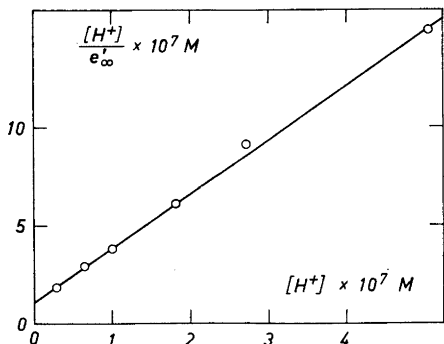


Fig. 4. $[H^+]/e'_\infty$ versus $[H^+]$ for the determination of K_6/K_4 .

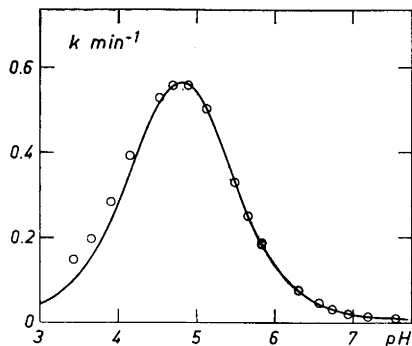


Fig. 5. The over-all rate constant, k , as a function of pH. The circles represent experimental values, the full drawn curve is calculated from eqn. (9).

If $k - k_5\text{oh}$ is plotted against h an almost straight line is obtained. This line can be extrapolated to $[H^+] = 0$ and the intercept on the ordinate-axis gives $k_3 + k_6 = 6.0 \times 10^{-3} \text{ min}^{-1}$. $k_6 \ll k_3$ and accordingly $k_3 = (6.0 \pm 0.2) \times 10^{-3} \text{ min}^{-1}$.

Determination of K_3 , K_4 , K_6 and k_4 . From eqn. (9) the following expression can be derived:

$$k_{\max} = \left(\frac{K_6}{K_4} \cdot \frac{K_3 K_4}{K_3 + 2\sqrt{K_3 K_4}} + 1 \right) k_3 \quad (11)$$

since $k_4 = k_3 K_6$. Fig. 5 gives $k_{\max} = 0.564 \text{ min}^{-1}$ and, since $K_6/K_4 = 2.51 \times 10^7 \text{ M}^{-1}$, $K_3 K_4 = 2.61 \times 10^{-10} \text{ M}^2$, $k_3 = 6.0 \times 10^{-3} \text{ min}^{-1}$ are known, the following values are obtained:

$K_3 = (3.8 \pm 0.2) \times 10^{-5} \text{ M}$; $K_4 = (6.9 \pm 0.4) \times 10^{-6} \text{ M}$; $K_6 = 172 \pm 8$ and $k_4 = 1.03 \pm 0.07 \text{ min}^{-1}$.

When K_4 is known, a control of the value of K_6/K_4 determined through equilibrium measurements can be obtained from the kinetic measurements in phosphate buffers (pH = 6.7–7.5). Eqn. (10) can be rewritten as

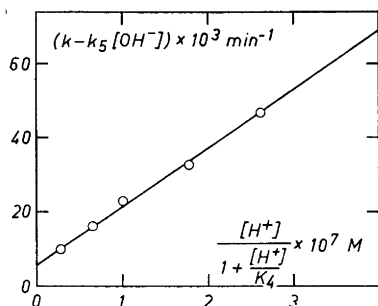


Fig. 6. $k - k_5[OH^-]$ versus $[H^+]/(1 + [H^+]/K_4)$ for the determination of K_6/K_4 .

Table 3. Furane Green. e'_{∞} -values for the determination of K_6/K_4 . $C_M = 1 \times 10^{-5}$ M; $d = 1$ cm; $\lambda = 640$ m μ ; $T = 20.0^\circ\text{C}$.

$[\text{H}^+] \times 10^7$ M	e'_{∞}	$[\text{H}^+] \times 10^7$ M	e'_{∞}
0.284	0.154	1.820	0.296
0.658	0.226	2.716	0.296
1.014	0.263	5.07	0.338

Table 4. Furane Green. Kinetic measurements in acetate buffers. Experimentally determined k -values and k -values calculated from eqn. (9) for the determination of k_1 from eqn. (13). $C_M = 1 \times 10^{-5}$ M; $d = 1$ cm; $\lambda = 640$ m μ ; $T = 20.0^\circ\text{C}$.

$[\text{H}^+] \times 10^5$ M	$k_{\text{exp}} \text{ min}^{-1}$	$[\text{H}^+] \times 10^4$ M	$k_{\text{exp}} \text{ min}^{-1}$	$k_{\text{calc}} \text{ min}^{-1}$	$k_1 \text{ min}^{-1}$
0.324	0.332	0.716	0.394		
0.740	0.505	1.242	0.286	0.246	0.11
1.288	0.560	2.178	0.198	0.159	0.10
2.046	0.560	3.74	0.150	0.101	0.11
3.04	0.530				
Mean					0.11

Table 5. Comparison between corresponding constants of Malachite Green, Thiophene Green and Furane Green.

	$1/K_1$ M	$K_3 \times 10^5$ M	$K_4 \times 10^6$ M	K_2	$1/K_6$	
Malachite Green	0.036	2.7	5.8	22	0.0147	
Thiophene Green	0.036	4.4	5.9	3.96	0.0048	
Furane Green	0.014	3.8	6.9	(2)	0.0058	
	$k_1 \text{ min}^{-1}$	$k_2 \text{ min}^{-1}$	$k_3 \text{ min}^{-1}$	$k_4 \text{ min}^{-1}$	$k_5 \text{ min}^{-1}\text{M}^{-1}$	$k_6 \text{ min}^{-1}$
Malachite Green	0.168	0.0078	0.00647	0.44	31.7	4.6×10^{-6}
Thiophene Green	0.056	0.0141	0.00221	0.46	32.7	1.44×10^{-5}
Furane Green	(0.11)	(0.05)	0.0060	1.03	50.8	1.58×10^{-5}

$$k - k_5\text{oh} = k_3 + k_3 \cdot \frac{K_6}{K_4} \cdot \frac{h}{1 + h/K_4} \quad (12)$$

since k_6 can be neglected. In this equation h/K_4 in $(1 + h/K_4)$ is only a correction term which amounts to 0.004—0.04 within the used pH-range and therefore the used value of K_4 does not appreciably influence the results. Fig. 6 shows $k - k_5\text{oh}$ versus $h/(1 + h/K_4)$, a straight line, the intercept on the ordinate-axis $y = 6.0 \times 10^{-3} \text{ min}^{-1}$ and the slope $l = 1.566 \times 10^5 \text{ min}^{-1} \text{ M}^{-1}$ of which give $k_3 = 6.0 \times 10^{-3} \text{ min}^{-1}$ and $K_6/K_4 = 2.61 \times 10^7 \text{ M}^{-1}$ in fair agreement with the values obtained earlier.

The hydration equilibrium constant K_2 could not be determined but the definitions give $K_1K_2K_3K_6 = 1$ and consequently $K_2 = 2.1$.

Determination of k_1 . In Fig. 5 the circles represent experimental values and the full drawn curve has been calculated from eqn. (9) using the values of k_3 , k_4 , K_3 , and K_4 already determined. The discrepancies between the experimental values and the calculated values on the left side of the maximum arise because the reactions $G + H_2O \rightleftharpoons S''$ are not quite negligible within the pH-range 3.3–4.6. These discrepancies provide a means to obtain a rough determination of the rate constant k_1 (the reactions $B + OH^- \rightleftharpoons C$ are negligible). Table 4 shows the experimental k -values and the k -values calculated from eqn. (9) and the k_1 -values calculated from the expression

$$k_{\text{exp}} - k_{\text{calc}} = \frac{h^2k_1}{K_2(h^2 + hK_3 + K_3K_4)} + \frac{hK_1(k_1 - k_3)}{1 + hK_1} \quad (13)$$

derived from eqns. (3) and (9) and using the relation $k_2 = k_1/K_2$. The mean values $k_1 = 0.11 \text{ min}^{-1}$ and $k_2 = 0.05 \text{ min}^{-1}$ are obtained.

DISCUSSION

Table 5 shows a comparison between the corresponding constants of Malachite Green (MG), Thiophene Green (TG)⁵ and Furane Green (FG). It can be seen that the substitution of the phenyl group of MG for a furane group has about the same effect on the hydration equilibria $B + H_2O \rightleftharpoons S'$ and $G + H_2O \rightleftharpoons S''$ as the substitution for a thiophene group. Both the 2-furane group and the 2-thiophene group have a strong electro-positive character and increase the electron-density of the central methane carbon atom as compared with MG. The addition of a polarized water molecule to TG and FG is then more difficult than the addition to MG and there is a displacement of the hydration equilibria towards the coloured, unhydrated species B and G.

Whether the rate constant k_1 of FG increased with the hydrogen ion concentration in strongly acid solutions in the same manner as it was observed with TG (*cf.* Ref.⁵) or not, could not be established. Kinetic measurements in HCl + KCl-buffers indicated, however, such a behaviour.

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