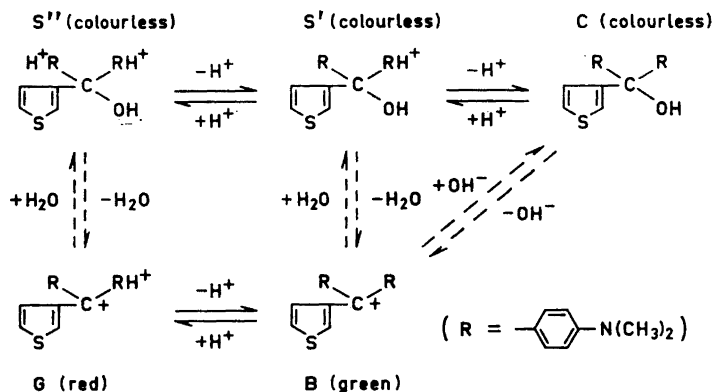


has been prepared and investigated correspondingly.

To distinguish these two thiophene analogues from each other analogue I will be called 2-Thiophene Green (2-TG) and analogue II will be called 3-Thiophene Green (3-TG).

The reactions of 3-TG in aqueous solutions are quite analogous to the reactions of Malachite Green (MG) and most of its derivatives.² There could not, however, be found any reactions corresponding to the reactions of 2-TG in strongly acid solutions. The reactions of 3-TG in aqueous solutions can be visualized in the following reaction-equilibrium scheme:



The scheme is exactly analogous to scheme I of 2-TG (*cf.* Ref.¹). The definitions of the constants and the used symbols are the same as in Ref.¹

The three fundamental equations that can be derived

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

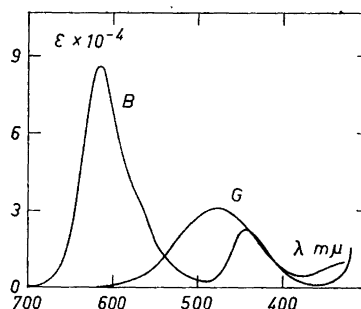
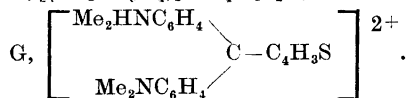
$$e_\infty = \frac{e_B + hK_1 e_G}{1 + 1/K_6 + K_4/hK_6 + hK_1(1 + K_2)} \quad (2)$$

$$k = \frac{h^2 k_2 + h k_4 K_3 + k_6 K_3 K_4}{h^2 + h K_3 + K_3 K_4} + \frac{h k_1 K_1 + k_3 + o h k_5}{1 + h K_1} \quad (3)$$

are also analogous to the equations used for 2-TG. It was not, however, possible to make an aqueous dye stock solution, which contained all of the dyestuff, as the coloured species (B or G) and, therefore, e_B and e_G in eqn. (1) are replaced by e'_B and e'_G , respectively. The following relation exists:

$$\frac{e'_B}{e_B} = \frac{e'_G}{e_G} = \frac{[\text{B}]_0 + [\text{G}]_0}{C_M} \quad (4)$$

Fig. 1. Absorption curves of the green ion B, $[(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{C}\cdot\text{C}_4\text{H}_3\text{S}]^+$, and the red ion G,



EXPERIMENTAL

3-Thiophene Green. The leuco base and the dyestuff perchlorate were prepared in exactly the same manner as it was described for 2-TG. The leuco base was obtained as a white powder, m.p. 105–107°C; the dyestuff perchlorate consisted of small green crystals with a reddish lustre. (Found: C 58.5; H 5.22; N 6.37; Cl 7.89; S 7.10. Calc. for $\text{C}_{21}\text{H}_{23}\text{O}_4\text{N}_2$ ClS: C 58.0; H 5.33; N 6.44; Cl 8.15; S 7.37).

The chemicals used for the buffer solutions and the apparatus used for the measurements were the same as in Refs.¹⁻²

The experimental conditions of temperature and ionic strength were also the same as in Ref.¹

MEASUREMENTS AND RESULTS

Absorption curves. In a neutral aqueous solution 3-TG is green and in a strongly acid solution it is deep red. In a pH-range around pH = 5 about 97 % of the dye is present as the ion B. The remainder is distributed between the species S'', S' and C. The concentration of G is negligible.

The absorption curve of B shown in Fig. 1 was determined in the following manner: The equilibrium absorbancies within the wave length range 320–700 μm were measured in an acetate buffer with pH = 4.68. $e_B = C_M \epsilon_B$ at the wave length 615 μm was determined by the mixing of 1 ml of an acetone dye stock solution with 49 ml of a series of suitable phosphate buffers. The solutions were partly decolourized at a measurable rate and e_0 was determined through the extrapolation of the absorbancies to a moment immediately after the mixing. $e_B \approx e_0$ in a pH-range where $[\text{H}^+] \ll 1/K_1$. Table 1 shows the

Table 1. *3-Thiophene Green.* e_0 , e_∞ and k -values for the determination of e_B , K_6/K_4 and k_3 . $C_M = 1 \times 10^{-5}$ M; $d = 1$ cm; $\lambda = 615$ μm ; $T = 20.0^\circ\text{C}$.

$[\text{H}^+] \times 10^7$ M	e_0	e_∞	$k \text{ min}^{-1}$	$[\text{H}^+] \times 10^7$ M	e_∞
0.0705	0.862	0.084	0.01178	1.641	0.619
0.1274	0.856	0.145	0.01262	2.44	0.682
0.275	0.861	0.258	0.01487	3.72	0.733
0.431	0.858	0.350	0.01716	5.92	0.771
0.608	0.864	0.423	0.0201		
1.050	0.858	0.538	0.0273		

Mean value e_0 0.860

obtained values of e_B ($C_M = 1 \times 10^{-5}$ M; $d = 1$ cm; $\lambda = 615$ m μ). Mean value $e_B = 0.860$.

The absorption curve of the red ion G is also shown in Fig. 1. It was calculated from the equilibrium absorbancies in a HCl + KCl-buffer with $[H^+] = 0.040$ M. $e_G = C_M \epsilon_G$ was calculated from eqn. (2). K_1 , K_2 , K_4 and K_6 were known from measurements described below and e_B was obtained from the absorption curve of B.

An absorption curve of G calculated from the equilibrium absorbancies in 2.50 M HCl agreed within very narrow limits with the curve obtained above.

The following results were obtained:

	λ_x max	ϵ_x max	λ_y max	ϵ_y max
B	615 m μ	8.6×10^4	443 m μ	2.3×10^4
G	477 m μ	3.1×10^4		

The notations of the absorption bands are the same as those, which were used by Tolbert, Branch and Berlenbach³ for triphenylmethane dyes.

The determination of the constants in the reaction-equilibrium scheme on p. 2166 was carried out in essentially the same manner as it was described for 2-TG. *Determination of K_1* . Eqn. (1) can be rearranged to

$$\frac{h}{e'_B - e_0} = \frac{h}{e'_B - e'_G} + \frac{1}{(e'_B - e'_G)K_1} \quad (5)$$

The measurements were carried out at two wave lengths, $\lambda = 615$ m μ and 480 m μ . $C_M = 1 \times 10^{-5}$ M; $d = 1$ and 2 cm; $e'_B = 0.822$ and $E'_B = 2 e'_B = 0.066$, respectively. Fig. 2 shows $[H^+]/(E'_B - E_0)$ versus $[H^+]$ in HCl + KCl-buffers ($[H^+] = 0.010$ – 0.100 M). The following results are obtained:

$\lambda = 615$ m μ : The intercept on the ordinate-axis $y = 0.0417$ M and the slope $l = 1.260$. $K_1 = 30.2$ M⁻¹ and $e'_G = 0.028$. $\lambda = 480$ m μ : $y = -0.062$ M; $l = -1.91$; $K_1 = 30.8$ M⁻¹ and $E'_G = 2 e'_G = 0.590$. The measurements at $\lambda = 480$ m μ were, however, less reliable because of the low absorbancies at this wave length. Accordingly $K_1 = 30.2 \pm 0.8$ M⁻¹.

Determination of K_6/K_4 . Fig. 3 shows the linear relationship between $[H^+]/e_\infty$ and $[H^+]$ in phosphate buffers (pH = 6.2–8.2) according to the expression

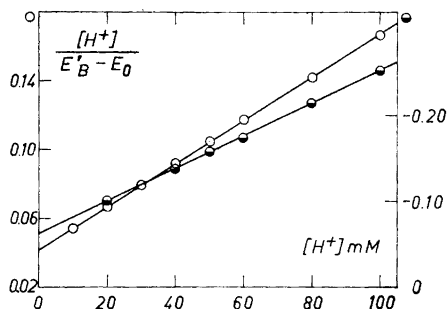


Fig. 2. $[H^+]/(E'_B - E_0)$ versus $[H^+]$ for the determination of K_1 . \circ $\lambda = 615$ m μ ; \bullet $\lambda = 480$ m μ .

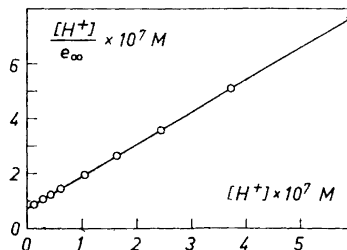


Fig. 3. $[H^+]/e_\infty$ versus $[H^+]$ for the determination of K_6/K_4 .

$$\frac{h}{e_{\infty}} = h \frac{1+K_6}{K_6 e_B} + \frac{K_4}{K_6 e_B} \quad (6)$$

which is valid within a pH-range, where B, S' and C are the only species to be considered. $C_M = 1 \times 10^{-5}$ M; $d = 1$ cm; $\lambda = 615$ m μ . The intercept on the ordinate-axis $y = 0.72 \times 10^{-7}$ M and the slope $l = 1.170$ give $(1 + K_6)/K_4 = 1.62(4) \times 10^7$ M $^{-1}$ and, since $e_B = 0.860$, $K_6/K_4 = 1.61(5) \times 10^7$ M $^{-1}$. The fact that $(1 + K_6)/K_6 \approx 1$ indicates that $K_6 \gg 1$.

Determination of k_5 and k_6 . In strongly alkaline solutions the overall rate constant, k , increases linearly with $[\text{OH}^-]$ according to the equation

$$k = k_3 + k_6 + k_5 \text{oh} \quad (7)$$

In Fig. 4 k is plotted *versus* $[\text{OH}^-]$ in NaOH + KCl-buffers with $[\text{OH}^-] = 0.0025-0.0100$ M. The straight line passes almost through the origin and only k_5 can be determined from the measurements in this pH-range. The slope $l = 64.5$ min $^{-1}$ M $^{-1}$ gives $k_5 = 64.5 \pm 1$ min $^{-1}$ M $^{-1}$. $k_6 = k_5 K_w K_6 / K_4$ and, since $K_w = 1.24 \times 10^{-14}$ M 2 and $K_6/K_4 = 1.61 \times 10^7$ M $^{-1}$ $k_6 = (1.29 \pm 0.05) \times 10^{-5}$ min $^{-1}$ is obtained.

Determination of k_3 . In phosphate buffers (pH = 7.0–8.2) eqn. (3) is approximated to

$$k - k_5 \text{oh} = k_3 + k_6 + \frac{hk_4 K_3}{h^2 + hK_3 + K_3 K_4} \quad (8)$$

An extrapolation to $[\text{H}^+] = 0$ (Fig. 5) of the almost straight line that is obtained if $k - k_5 \text{oh}$ is plotted as a function $[\text{H}^+]$ gives $k_3 + k_5 = 0.0106$ min $^{-1}$. $k_6 \ll k_3$ and thus $k_3 = 0.0106 \pm 0.0003$ min $^{-1}$.

Determination of K_3 , K_4 , K_6 and k_4 .

Eqn. (3) is written:

$$k' = \frac{hk_4 K_3}{h^2 + hK_3 + K_3 K_4} \quad (9)$$

$$\text{where } k' = k - \frac{h^2 k_2 + k_6 K_3 K_4}{h^2 + hK_3 + K_3 K_4} - \frac{hk_1 K_1 + k_3 + k_5 \text{oh}}{1 + hK_1} \quad (10)$$

A differentiation of eqn. (9) with regard to $[\text{H}^+]$ shows that k' has a maximum when $[\text{H}^+] = \sqrt{K_3 K_4}$ and hence

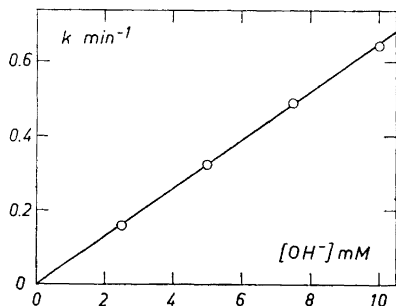


Fig. 4. The over-all rate constant, k , versus $[\text{OH}^-]$ for the determination of k_5 .

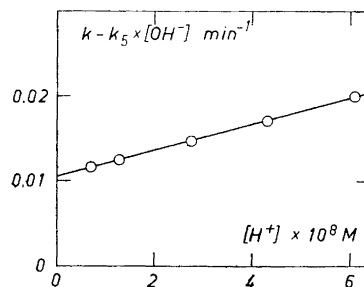


Fig. 5. $k - k_5 [\text{OH}^-]$ as a function of $[\text{H}^+]$ for the determination of k_3 .

$$k'_{\max} = k_3 \frac{K_6}{K_4} \frac{K_3 K_4}{K_3 + 2\sqrt{K_3 K_4}} \quad (11)$$

since $k_4 = k_3 K_6$.

The values of k were determined within the pH-range 3.2–6.5 in the following manner: The dye solution was partly decolourized in a HCl + KCl-buffer ($[H^+] = 0.010$ M) and then mixed with equal volumes of suitable acetate buffers or phosphate buffers. The intensity of the colour then rapidly increased and the rate of this increase was measured.

For the calculation of k' in eqn. (9) it is necessary to know k_1 , k_2 , k_3 , K_1 , K_3 , and K_4 . (The reaction path $B + OH^- \rightleftharpoons C$ can be neglected for $pH \leq 6.5$). The second and third terms in eqn. (10) are within the pH-range 4.5–5.5 correction terms which amount to 4.4–3.4 % of k and therefore it is not necessary to know the constants in these terms with any higher degree of accuracy. K_1 and k_3 are known from measurements described above. Approximate values of k_1 and $k_2 = k_1/K_2$ were obtained from measurements in HCl + KCl-buffers described below. The reactions $B + H_2O \rightleftharpoons S'$ were then disregarded and it was assumed that $K_6 \gg 1$. The approximate values $K_2 \approx 13$, $k_1 \approx 0.30$ min⁻¹, and $k_2 \approx 0.023$ min⁻¹ were used. For the estimation of K_3 k'_{\max} is put equal to k_{\max} as a first approximation. $pH_{k'_{\max}} = 4.897$ and $k'_{\max} = 0.503$ are obtained from Fig. 6 and, since $k_3 = 0.0106$ min⁻¹ and $K_6/K_4 = 1.61 \times 10^7$ M⁻¹ we can calculate $K_3 \approx 3 \times 10^{-5}$ M from eqn. (11). Then the following refined values were obtained: $pH_{k'_{\max}} = 4.907 \pm 0.005$, $k'_{\max} = 0.487$ min⁻¹ and hence $K_3 = (2.9 \pm 0.1) \times 10^{-5}$ M, $K_4 = (5.3 \pm 0.2) \times 10^{-6}$ M, $K_6 = 85 \pm 2$ and $k_4 = k_3 K_6 = 0.91 \pm 0.03$ min⁻¹.

Determination of K_2 . This constant was calculated from the equilibrium absorbancies in HCl + KCl-buffers, $pH = 1-2$, using the expression

$$K_2 = \frac{e_G}{e_\infty} + \frac{e_B - e_\infty (1 + hK_1 + 1/K_6)}{e_\infty hK_1} \quad (12)$$

Table 2 shows the results ($C_M = 1 \times 10^{-5}$ M; $d = 5$ cm; $\lambda = 615$ m μ ; $E_G = 5 e_G = 5 \times 0.029$; $E_B = 5 e_B = 5 \times 0.860$; $K_1 = 30.2$ M⁻¹; $K_6 = 85$). The mean value $K_2 = 12.9 \pm 0.3$ was obtained.

Determination of k_1 and k_2 . These constants were determined through kinetic measurements in HCl + KCl-buffers ($pH = 1-2$). In this pH-range eqn. (3) can be written

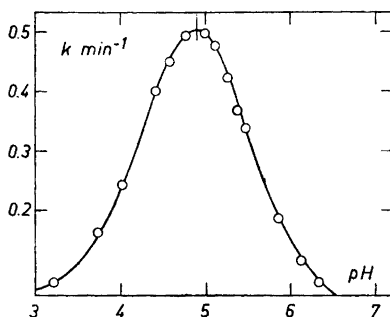


Fig. 6. The over-all rate constant, k , as a function of pH. The symbols O are experimentally found values, the full drawn curve is calculated from eqn. (3).

Table 2. 3-Thiophene Green. e_0 -, e_{∞} -, and k -values for the determination of K_1 , K_2 and k_1 .
 $C_M = 1 \times 10^{-5}$ M; $d = 1$ cm; $\lambda = 615$ m μ ; $T = 20.0^\circ\text{C}$; $e'_B = 0.822$; $K_6 = 85$.

[H ⁺] M	e_0	e_{∞}	K_2	k min ⁻¹	k_1 min ⁻¹
0.010	0.638	0.1664	13.0	0.0928	0.290
0.020	0.523	0.0922	13.1	0.1345	0.293
0.030	0.443	0.0650	13.0	0.1642	0.295
0.040	0.388	0.0500	13.0	0.1826	0.291
0.050	0.346	0.0410	12.9	0.202	0.295
0.060	0.312	0.0356	12.6	0.210	0.291
0.080	0.259	0.0271	12.8	0.231	0.294
0.100	0.222	0.0226	12.6	0.248	0.299
Mean value			12.9		0.294

Table 3. 3-Thiophene Green. e_0 - and k -values for the determination of K_1 and k_1 at the wave length $\lambda = 480$ m μ . $C_M = 1 \times 10^{-5}$ M; $d = 2$ cm; $T = 20.0^\circ\text{C}$; $E'_B = 0.066$.

[H ⁺] M	e_0	k min ⁻¹	k_1 min ⁻¹
0.020	0.262		
0.040	0.356	0.1853	0.295
0.050	0.382	0.202	0.297
0.060	0.411	0.214	0.295
0.080	0.440	0.234	0.298
0.100	0.461	0.251	0.303
Mean value			0.298

$$k_1 = \frac{k - hk_4K_3 - k_3/(1 + hK_1)}{1/K_2 + hK_1/(1 + hK_1)} \quad (13)$$

The term $(hk_4K_3 + k_3/(1 + hK_1))$ is a correction term, which amounts to 0.1–2.5 % of k in the used pH-range. Tables 2 and 3 show the obtained results, $k_1 = 0.296 \pm 0.006$ min⁻¹ and $k_2 = k_1/K_2 = 0.023 \pm 0.001$ min⁻¹.

In Fig. 6 the full drawn curve is calculated from the non-approximated eqn. (3). The obtained values of the constants have then been used. The circles represent experimentally found k -values.

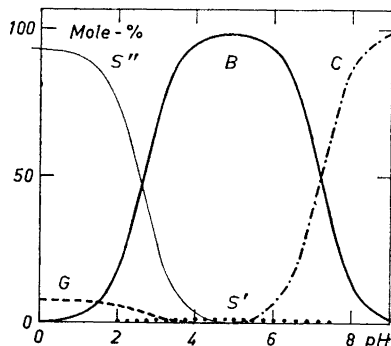


Fig. 7. The distribution of the dyestuff between the species B, G, S'', S' and C at equilibrium.

Table 4. 3-Thiophene Green. Comparison between the values of corresponding constants of 2-Thiophene Green, 3-Thiophene Green and Malachite Green.

	K_1	K_2	$K_3 \times 10^5$	$K_4 \times 10^6$	$1/K_6$
2-Thiophene Green	28	3.96	4.4	5.9	0.0048
3-Thiophene Green	30	12.9	2.9	5.3	0.0117
Malachite Green	28	22	2.7	5.8	0.0147

	k_1	k_2	k_3	k_4	k_5	k_6
2-Thiophene Green	0.056	0.014	0.0022	0.46	32.7	1.4×10^{-5}
3-Thiophene Green	0.296	0.023	0.0106	0.91	54.5	1.3×10^{-5}
Malachite Green	0.168	0.0078	0.0065	0.44	31.7	4.6×10^{-6}

Fig. 7 shows the distribution at equilibrium of the dyestuff between the species B, G, S'', S' and C as a function of pH.

DISCUSSION

Table 4 shows a comparison between the corresponding constants of 2-TG, 3-TG and MG. The chief differences between these dyestuffs concern the hydration equilibria and the rates of hydration. The substitution of the phenyl group in MG for a 3-thiophene group has a marked influence on the hydration equilibria $G + H_2O \rightleftharpoons S''$ and $B + H_2O \rightleftharpoons S'$. The effect is, however, less pronounced than the corresponding effect of a 2-thiophene group. The values of the hydration-equilibrium constants K_2 and $1/K_6$ decrease in the order $MG > 3-TG > 2-TG$. This decrease depends on the electro-positive character of the aryl group, which increases in the order phenyl < 3-thiophene < 2-thiophene. The electron-donating power of the 2-thiophene group is so great that 2-TG can bind a second proton in strongly acid solutions (*cf.* Ref.¹). A similar addition of a second proton was not observed with MG and 3-TG for $pH \geq 1$.

The rate constants of the reactions described above in the direction (\rightarrow) do not show the same trend as the hydration-equilibrium constants. The hydration reactions of 3-TG proceed much faster than the corresponding reactions of 2-TG and MG. The factors that determine the rates of the hydration reactions cannot, however, be established as yet.

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