

## Polarographic Studies of Basic Triarylmethane Dyes

### I. Kinetics, Equilibria, and Polarographic Behaviour of Methyl Green in Aqueous Solutions

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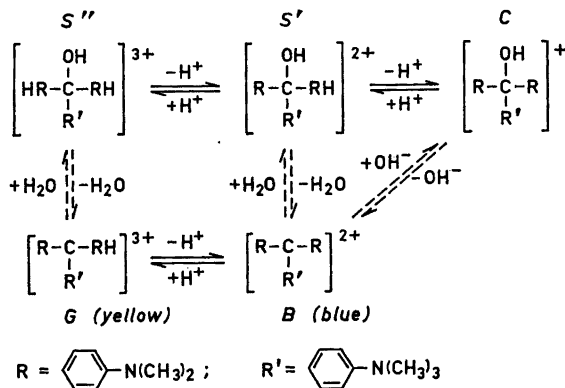
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The chemical equilibria, reaction rates, and polarographic behaviour of Methyl Green have been studied in aqueous solutions with the ionic strength 0.50 M and the temperature 20.0°C. Five equilibrium constants and six rate constants have been determined. The values of these are compared with the corresponding values obtained from spectrophotometric measurements by Cigén.<sup>2,3</sup>

At concentrations below about  $2 \times 10^{-5}$  M Methyl Green is reduced at the dropping mercury electrode yielding one two-electron wave. At greater dyestuff concentrations the polarograms are complicated due to the adsorption of the depolarizer and the reduction product.

In a previous paper<sup>1</sup> a polarographic investigation of the reactions of Methyl Green in aqueous solutions has been briefly reported. The present paper is devoted to a detailed description of a study of the chemical reactions and the polarographic behaviour of this dyestuff in aqueous solutions with the ionic strength 0.50 M and the temperature 20.0°C.

The reactions of this type of dyestuffs in aqueous solutions are fairly well understood, and the reactions of Methyl Green can be visualized by the following reaction-equilibrium scheme:<sup>2,3</sup>



The dyestuff is present in the solution as five species, two coloured carbonium ions (B and G), and three colourless carbinolic species (C, S', and S''). The carbonium ions on one hand, and the carbinolic species on the other hand are related by instantaneously reached protolytic equilibria (full drawn arrows). Transitions from carbonium species to carbinolic species occur by reactions with water or hydroxide ions proceeding at a measurable rate (dashed arrows). These reactions can be observed by the gradual change of the colour intensity of the solution. The reactions are reversible and the colour intensity reaches an equilibrium value. At sufficiently high or low pH-values the solutions are almost completely decolourized at equilibrium. The reaction  $B + H^+ \rightleftharpoons G$  can be observed by the immediate change of colour from blue to yellow, when a neutral dye solution is made strongly acid. The reactions  $S'' \rightarrow G + H_2O$ ,  $S' \rightarrow B + H_2O$ , and  $C \rightarrow B + OH^-$  are first order, the hydration reactions  $G + H_2O \rightarrow S''$  and  $B + H_2O \rightarrow S'$  are pseudo-first order, and the reaction  $B + OH^- \rightarrow C$  is second order.

The equilibria and the reaction rates can be described by a set of constants, which are defined as follows:

a) Protolytic constants:  $K_1 = \frac{[G]}{[B][H^+]}$ ;  $K_3 = \frac{[S''][H^+]}{[S']}$ ;  $K_4 = \frac{[C][H^+]}{[S']}$

b) Hydration equilibrium constants:  $K_2 = \frac{[S'']_\infty}{[G]_\infty}$ ;  $K_6 = \frac{[B]_\infty}{[S']_\infty}$

c) Rate constants:

$k_1$	rate constant for the reaction	$G + H_2O \rightarrow S''$
$k_2$	»	$S'' \rightarrow G + H_2O$
$k_3$	»	$B + H_2O \rightarrow S'$
$k_4$	»	$S' \rightarrow B + H_2O$
$k_5$	»	$B + OH^- \rightarrow C$
$k_6$	»	$C \rightarrow B + OH^-$
$k$	»	over-all reaction, that occurs when the pH of a dye solution is changed, <i>i.e.</i> for the over-all reaction colourless $\rightarrow$ coloured or coloured $\rightarrow$ colourless.

The values of these constants can be calculated, if the following quantities are determined for a large number of solutions with different pH-values over a sufficiently wide pH-range:

1, The concentration at equilibrium of the species B or G, or the sum of these concentrations, often represented by a quantity that is proportional to them; 2, The pH of the solution; 3, The rate constant  $k$ .

The papers dealing with polarographic studies of triarylmethane dyes<sup>4-10</sup> have been concerned mainly with the electrode processes and have paid but little attention to the chemical reactions of these dyestuffs and the use of polarography for analysis. Refs. 4-5 consider the use of polarography for a study of the rates of reaction between Methyl Green and Crystal Violet and a few solvents. No thorough study has, however, been carried out either of the chemical reactions or of the electrode processes.

Preliminary investigations showed that Methyl Green is reduced at the dropping mercury electrode yielding one wave within the investigated pH-

range (0.3–12.4). Above the dyestuff concentration  $C \approx 2 \times 10^{-5}$  M the wave becomes somewhat extended and splits up into two adjacent waves when  $\text{pH} \gtrsim 4$ . This splitting up is, however, due to adsorption, as will be discussed later in this paper. A necessary condition for polarography to be useful as an analytical tool for the determination of the constants was that the wave heights were proportional to the concentration of the carbonium species. An aqueous solution of Methyl Green contains less than about 85 % of the dye as coloured species, and therefore no calibration curve representing the wave height as a function of the concentrations ( $[B] + [G]$ ) could be determined before the equilibrium constants had been determined. It was, however, possible to determine the wave heights at equilibrium for a definite buffer composition. The differences of pH due to differences of the dyestuff concentrations were small and fell within the normal experimental error. Fig. 1 shows five such calibration curves at  $\text{pH} = 2.82, 3.75, 4.68, 5.89,$  and  $6.32$ . The proportionality between wave height and dye concentration (and thus  $[B] + [G]$ ) is a good approximation only at sufficiently high dyestuff concentrations. The deviations from the proportionality at low dyestuff concentrations are probably due to the formation of polarographic maxima, which are more conspicuous at low dyestuff concentrations and low pH-values. At  $C \lesssim 2 \times 10^{-5}$  M no maxima could be detected.

The dyestuff concentration  $C = 75 \times 10^{-5}$  M was chosen for the measurements, from which the constants were evaluated. This value is a compromise between the solubility of Methyl Green Perchlorate, which was estimated to about  $2 \times 10^{-3}$  M in 0.50 M KCl at  $20.0^\circ\text{C}$ , and a reasonable precision of the measurements, since it demands a  $1.5 \times 10^{-3}$  M dye stock solution. Some measurements were also carried out at the dyestuff concentration  $C = 10 \times 10^{-5}$  M. The results agreed with the results obtained at the greater dyestuff concentration, but the precision was less good.

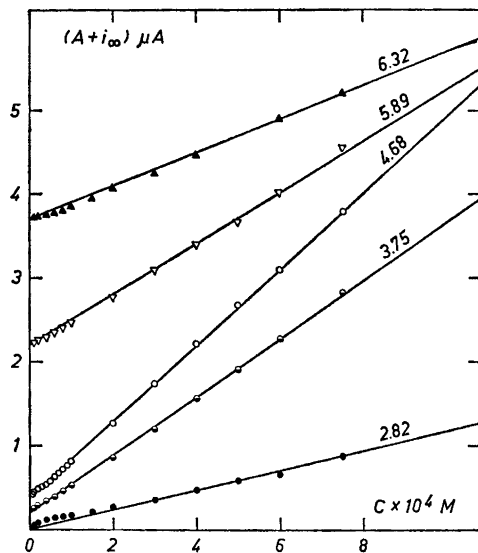


Fig. 1. Calibration curves at  $\text{pH} = 2.82, 3.75, 4.68, 5.89,$  and  $6.32$ .  $A$  is 0, 0.2, 0.4, 2.2, and 3.7  $\mu A$ , respectively.

## EXPERIMENTAL

*Methyl Green Perchlorate.* Commercial Methyl Green (Merck's "Methylgrün für Mikroskopie und Bakteriologie") was converted into the perchlorate, which was recrystallized three times from water. Optical constancy was attained thereby. The product consisted of green crystal needles with a bronzy lustre. The absorption curve of the preparation in an aqueous solution with pH = 4.68, the ionic strength 0.50 M, and the temperature 20.0°C had the following characteristics within the wave length range 320–750 m $\mu$ :  $\lambda_{\max} = 633$  and 422 m $\mu$ ;  $\epsilon_{\max} = 7.6 \times 10^4$  and  $1.3 \times 10^4$ , respectively (*cf.* Ref. 2).

Hydrochloric acid, citric acid and disodium hydrogen phosphate, sodium acetate and acetic acid, disodium hydrogen phosphate and potassium dihydrogen phosphate, boric acid and sodium hydroxide, were used for the buffer solutions. The buffer concentrations were 0.030–0.250 M, 0.030 M, 0.100 M, 0.030 M, and 0.050 M, respectively, in the final solutions. The effect of the buffer concentrations on the polarograms was studied for the citric acid-disodium hydrogen phosphate buffers and the phosphate buffers. The polarograms at equilibrium were recorded for a number of solutions with the buffer concentrations 0.060 M, 0.030 M, 0.015 M, and 0.0075 M. The buffers were prepared by diluting stock buffer solutions. Besides differences due to differences of pH the polarograms were similar and the wave heights and half-wave potentials fitted into the same graph irrespective of the buffer concentration.

Potassium chloride was used to keep the ionic strength constant (0.50 M). All chemicals were of analytical grade.

A conventional dropping mercury electrode was used for the polarographic measurements. An external saturated calomel electrode was used as a reference electrode. Two different capillaries were used:

Capillary 1:  $m = 2.22$  mg.sec<sup>-1</sup>;  $t_1 = 3.50$  seconds.

Capillary 2:  $m = 1.92$  mg.sec<sup>-1</sup>;  $t_1 = 4.18$  seconds.

$m$  is the rate of mercury flow.  $t_1$  is the drop-time, determined in 0.50 M KCl at the potential of the reference electrode. The polarographic cell was thermostated to  $20.0 \pm 0.1^\circ\text{C}$ . The solutions were deaerated by a stream of commercial nitrogen, which was passed through three gas washing bottles containing 0.50 M KCl before entering the polarographic cell. The polarograms were recorded by a PO4 Radiometer Polarograph.

The determination of the wave heights at equilibrium was carried out in the following manner: Equal volumes of buffer solution and dye stock solution were mixed and equilibrated in a thermostat at 20.0°C. After equilibration (24–40 h) the solutions were deaerated for 15 min before the recording of the polarograms. 6–10 polarograms were recorded for each solution. The mean value of the wave heights was accepted as the wave height at equilibrium. The wave heights were evaluated by the graphical subtraction of the extrapolated residual current from the extrapolated limiting current at the half-wave potential. For pH < 3 the wave heights were small, and maxima decreased the precision of the measurements markedly. Therefore the values obtained within this pH-range were not used for the calculation of the constants.

The kinetic measurements were carried out by recording polarograms at suitable time intervals and by recording the over-all current at a constant potential corresponding to the limiting current. Before the measurement both buffer solution and dye stock solution were deaerated for 15 min and then equal volumes were mixed. For rapid reactions the solutions were allowed to reach equilibrium in the polarographic cell. For slow reactions the solutions were transferred to flasks and equilibrated in a thermostat. When both recording of polarograms and recording of the over-all current at a constant potential

were used, the results agreed equally well as two measurements with the same method. Within the pH-ranges 0.6–3.1 and 6.1–12.2 a dye stock solution in 0.50 M KCl was used, within the pH-range 3.1–6.1 a partially decolourized stock solution in 0.01 M HCl + 0.49 M KCl.

The carbinol C is only slightly soluble in water and the solutions were supersaturated with regard to carbinol during a great part of the kinetic measurements in NaOH + KCl (pH = 11.6–12.4). The reactions proceeded, however, so rapidly that no precipitation occurred until after equilibrium had been reached. Furthermore  $([B] + [G]) \approx 0$  at equilibrium within this pH-range, and the current at a given potential is equal to the current in the absence of dyestuff *i.e.* to the residual current.

The hydrogen ion concentrations were determined titrimetrically and potentiometrically. Within the pH-range 2–8 the electromotive force ( $E'$  mV) for the following element was measured:

Pt	Quinhydrone Dye solution $[H^+] = x M$	Saturated KCl-solu- tion	Quinhydrone $C_{HCl} = 0.0100 M$ $C_{KCl} = 0.49 M$	Pt
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$$pH = \frac{E' + 116.3}{58.16} \quad (1)$$

For  $8 < pH < 10$  a glass electrode and a Radiometer pHM 4 pH-meter was used. The potentiometric determinations of pH were carried out in the dye solutions at equilibrium. The titrimetric determinations were carried out in the pure buffer solutions (NaOH + KCl or HCl + KCl). The change of pH due to the presence of 0.75 mM dyestuff was negligible at the hydrogen ion and hydroxide ion concentrations used. pH means  $-\log[H^+]$  and not  $-\log a_{H^+}$ .

#### EQUATIONS, CALCULATIONS, AND RESULTS

The following symbols and notations are defined:

- $i_B$  the wave height in a solution, where the dyestuff is present only as carbonium species (B and G).
- $i_0$  the wave height at a moment immediately after mixing a dye stock solution and a buffer solution.
- $i_t$  the wave height at the time  $t$ .
- $i_\infty$  the wave height at equilibrium.
- $h = [H^+]$ ;  $oh = [OH^-]$ ;  $K_w = h \cdot oh = 1.24 \times 10^{-14} M^2$ .

Two non-approximated equations can be derived for the wave height at equilibrium and the over-all rate constant as functions of the hydrogen ion concentration:

$$i_\infty = \frac{i_B(1 + hK_1)}{1 + 1/K_6 + hK_1(1 + K_2) + K_4/K_6h} \quad (2)$$

$$k = \frac{1}{t} \ln \frac{i_0 - i_\infty}{i_t - i_\infty} = \frac{h^2k_2 + hk_4K_3 + k_6K_3K_4}{h^2 + hK_3 + K_3K_4} + \frac{hk_1K_1 + k_3 + k_5oh}{1 + hK_1} \quad (3)$$

Table 1. Obtained values of  $i_0$ .  $C = 75 \times 10^{-5}$  M; Capillary 1.

pH	$i_0$ $\mu$ A	pH	$i_0$ $\mu$ A
1.00	3.21	6.13	3.13
1.52	3.33	6.50	3.17
2.23	3.19	7.10	3.15
2.58	3.22	7.71	3.16
3.05	3.17	9.82	3.10

These two equations are analogous to the equations used for the calculations of the constants from spectrophotometric measurements. G and B give, however, equal contributions to the wave height, and therefore  $i_0$  is independent of the hydrogen ion concentration. This was confirmed experimentally by extrapolating the lines, from which the values of  $k$  were determined ( $\ln(i_t - i_\infty)$  versus  $t$ ; polarograms recorded) to  $t = 0$ . The results are shown in Table 1.

Eqns. (2) and (3) can be approximated, since certain concentrations and reaction paths can be neglected within some pH-ranges. When the approximations, that would give simple relations, are too rough, more accurate values of the constants can be calculated by a series of successive approximations.

When  $h \ll 1/K_1$  and  $1/K_1K_2$ ,  $[G]$ , and  $[S'']$  are negligible compared to  $[B]$ , and eqn. (2) is approximated and transformed to

$$\frac{h}{i_\infty} = \frac{K_4}{K_6 i_B} + \frac{1 + 1/K_6}{i_B} h \quad (4)$$

From the straight line, that is obtained, when  $h/i_\infty$  is plotted *versus*  $h$ ,  $K_4/(1 + K_6)$  and  $i_B/(1 + 1/K_6)$  are evaluated.

Eqn. (3) can be rewritten as

$$k = \frac{k_1 h K_1}{1 + h K_1} + \frac{k_2 h^2}{h^2 + h K_3 + K_3 K_4} + \frac{k_3}{1 + h K_1} + \frac{k_4 h K_3}{h^2 + h K_3 + K_3 K_4} + \frac{k_5 o h}{1 + h K_1} + \frac{k_6 K_3 K_4}{h^2 + h K_3 + K_3 K_4} \quad (5)$$

or

$$k = \sum_{i=1}^6 f_i \quad (6)$$

where

$$f_1 = \frac{k_1 h K_1}{1 + h K_1}; f_2 = \frac{k_2 h^2}{h^2 + h K_3 + K_3 K_4} \quad \text{etc.}$$

In strongly acid solutions ( $\text{pH} \leq 2$ )  $f_1$  and  $f_2$  dominate. The equilibria within this pH-range are strongly displaced towards the colourless species. Thus  $k_2 = k_1/K_2$  and consequently  $f_2$  are much less than  $f_1$ . We can therefore as a first rough approximation put  $k \approx f_1$  and obtain

$$\frac{h}{k} = \frac{1}{k_1 K_1} + \frac{h}{k_1} \quad (7)$$

Approximate values of  $k_1$  and  $K_1$  are obtained from a plot of  $h/k$  versus  $h$ . In strongly alkaline solutions eqn. (3) can be approximated to

$$k = k_3 + k_6 + k_5 \text{oh} \quad (8)$$

and  $k_5$  is equal to the slope of the line  $k$  versus  $oh$ .

Within the pH-range 3–8  $f_3$  and  $f_4$  dominate, and we can write

$$k = \frac{k_4 h K_3}{h^2 + h K_3 + K_3 K_4} + k_3 \quad (9)$$

Within the pH-range 6–8  $k$  changes almost linearly with  $h$ . Extrapolation of the approximately straight line, that is obtained, when  $k$  is plotted as a function of  $h$ , to  $h = 0$  gives  $k_3$  as the intercept on the ordinate-axis.

Derivation of eqn. (9) with regard to  $h$  shows that  $k$  has a maximum, when  $h = \sqrt{K_3 K_4}$  with

$$k_{\max} = k_3 + \frac{k_3 \sqrt{K_3 K_4}}{2 \cdot \frac{K_4}{K_6} + \frac{\sqrt{K_3 K_4}}{K_6}} \quad (10)$$

Of the quantities in eqn. (10), pH at  $k_{\max}$  and  $k_{\max}$  can be determined graphically from  $k$  as a function of pH;  $k_3$  is determined as described above. As a first approximation we also put  $K_4/K_6 \approx K_4/(1 + K_6)$ , which is obtained from equilibrium measurements. An approximate value of  $K_6$  is calculated, which in its turn gives approximate values of  $K_4$ ,  $K_3$ , and  $k_4 = k_3 K_6$ . The obtained value of  $K_4/K_6$  is inserted into eqn. (10) and the calculations are repeated. This procedure is repeated until further recalculations do not change the obtained value of  $K_6$  noticeably.

In solutions with  $h \gg K_4$ ,  $[C]$  can be neglected and eqn. (2) be written

$$\frac{1 + h K_1}{i_{\infty}} = \frac{1 + 1/K_6}{i_B} + \frac{K_1(1 + K_2)}{i_B} h \quad (11)$$

For  $\text{pH} \geq 2$   $h K_1$  is only a correction term and therefore the approximate value of  $K_1$ , obtained as described above, can be used for the calculation  $(1 + h K_1)/i_{\infty}$ . From  $(1 + h K_1)/i_{\infty}$  versus  $h$  approximate values of  $K_2$  and  $k_2 = k_1/K_2$  are obtained.

The value of  $k_6$  is calculated by the relation

$$k_6 = k_5 K_w K_6 / K_4 \quad (12)$$

When values of all the constants are known, at least approximately, the calculations are repeated, beginning with the calculation of  $f_1$ . The previously obtained constants are used in the correction terms. The iterations are repeated until the values of the constants do not change noticeably.

Figs. 2–6 show  $h/i_{\infty}$  versus  $h$  within the pH-range 5.8–7.4,  $h/f_1$  versus  $h$  within the pH-range 0.6–1.3,  $k$  versus  $oh$  within the pH-range 11.6–12.2,  $k$  versus  $h$  within the pH-range 6.5–7.7, and  $(1 + h K_1)/i_{\infty}$  versus  $h$  within the pH-range 3.1–4.5. The circles represent the final, corrected values. The experimental values of  $i_{\infty}$  and  $k$  are shown in Tables 2–3.

Table 2. Obtained values of the equilibrium wave heights,  $i_{\infty}$ , in citric acid- $\text{Na}_2\text{HPO}_4$ , acetate and phosphate buffers.  $C = 75 \times 10^{-5}$  M; Capillary 1.

pH	$i_{\infty}$ $\mu\text{A}$	pH	$i_{\infty}$ $\mu\text{A}$
2.22	0.348	4.49	3.098
2.38	0.428	4.68	3.160
2.58	0.583	4.88	3.238
2.82	0.855	5.11	3.156
3.12	1.375	5.47	2.854
3.54	2.200	5.80	2.472
4.16	3.048		
5.12	3.086	5.54	2.808
6.13	1.825	5.89	2.309
6.81	0.668	6.13	1.918
		6.32	1.504
3.10	1.299	6.50	1.171
3.29	1.698	6.67	0.884
3.31	1.713	6.87	0.603
3.44	2.000	7.10	0.382
3.57	2.240	7.44	0.190
3.75	2.528	7.71	0.109
3.89	2.724	8.04	0.058
4.12	2.957		

Table 3. Obtained values of the over-all rate constant  $k$ .  $C = 75 \times 10^{-5}$  M.

pH	$k$ $\text{min}^{-1}$	pH	$k$ $\text{min}^{-1}$
0.60	0.0992	4.42	0.0342
0.70	0.0951	4.50	0.0356
0.82	0.0894	4.62	0.0376
1.00	0.0790	4.67	0.0383
1.10	0.0718	4.78	0.0387
1.16	0.0689	4.89	0.0387
1.22	0.0632	4.99	0.0372
1.30	0.0589	5.11	0.0354
1.52	0.0441	5.27	0.0317
2.23	0.0176	5.38	0.0274
2.38	0.0145	5.47	0.0248
2.58	0.0124	5.62	0.0203
2.82	0.0103	5.94	0.0143
3.05	0.0104	6.13	0.0111
3.13	0.0110	6.33	0.0101
3.31	0.0110	6.50	0.00926
3.57	0.0142	6.67	0.00857
3.78	0.0180	6.81	0.00760
3.89	0.0206	6.87	0.00768
4.03	0.0245	7.10	0.00698
4.14	0.0267	7.44	0.00659
4.33	0.0319	7.71	0.00645



Table 4. Obtained values of the constants compared to the spectrophotometrically determined values.  $T = 20.0^\circ\text{C}$ . Ionic strength = 0.50 M.

	Polarographically $C = 75 \times 10^{-5} \text{ M}$	Spectrophotometrically $C = 1 \times 10^{-5} \text{ M}$
$1/K_1 \text{ M}$	$0.061 \pm 0.002$	$0.060 \pm 0.001$
$K_2$	$133 \pm 11$	$132 \pm 5$
$K_3 \times 10^5 \text{ M}$	$4.3 \pm 0.5$	$5.2 \pm 0.2$
$K_4 \times 10^6 \text{ M}$	$6.3 \pm 0.3$	$6.5 \pm 0.2$
$1/K_6$	$0.110 \pm 0.006$	$0.108 \pm 0.002$
$k_1 \text{ min}^{-1}$	$0.122 \pm 0.003$	$0.123 \pm 0.001$
$k_2 \times 10^4 \text{ min}^{-1}$	$9.2 \pm 1.2$	$9.4 \pm 0.5$
$k_3 \times 10^3 \text{ min}^{-1}$	$6.3 \pm 0.1$	$6.2 \pm 0.1$
$k_4 \times 10^2 \text{ min}^{-1}$	$5.8 \pm 0.5$	$5.8 \pm 0.2$
$k_5 \text{ min}^{-1} \text{ M}^{-1}$	79	87
$k_6 \times 10^6 \text{ min}^{-1}$	1.6	1.5

Table 4 shows the obtained values of the constants compared with the values obtained by Cigén<sup>2</sup> from spectrophotometric measurements. Figs. 7 and 8 show  $i_\infty$  as a function of pH and  $k$  as a function of pH, respectively. The circles represent experimental values (different symbols denote different buffer systems), and the full drawn curves are calculated by the use of eqns. (2) and (3), and the constants in Table 4. It should be emphasized that because of the difficulty to determine pH at  $k_{\text{max}}$  accurately the obtained values of  $K_6$ ,  $K_4$ ,  $K_3$ , and  $k_4$  should be accepted only if there is good agreement between the experimental values of  $k$  and the calculated ones. Slightly different values of these constants were tried, but the agreement was less good than with the values of Table 4. The errors in Table 4 are the maximum random errors estimated from the reproducibility of different series of measurements, and from the errors of the graphical evaluations.

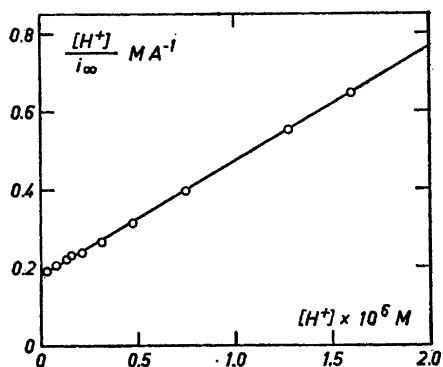


Fig. 2.  $[\text{H}^+]/i_\infty$  versus  $[\text{H}^+]$  for the determination of  $K_4/(1 + K_6)$  and  $i_B/(1 + 1/K_6)$ .

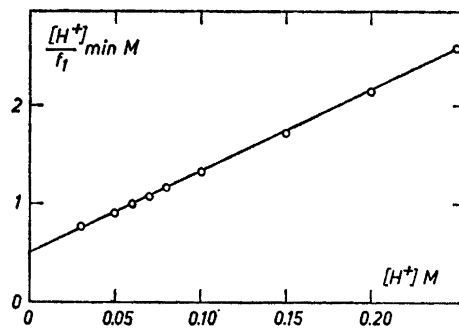


Fig. 3.  $[\text{H}^+]/f_1$  versus  $[\text{H}^+]$  for the determination of  $k_1$  and  $K_1$ .

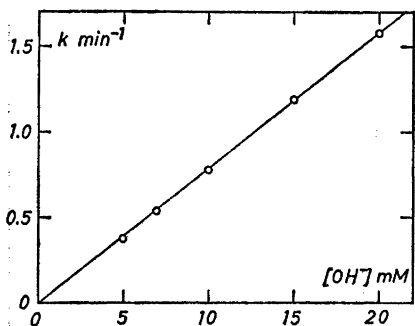


Fig. 4.  $k$  versus  $[\text{OH}^-]$  for the determination of  $k_5$ .

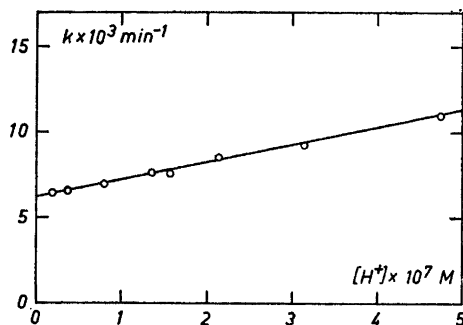


Fig. 5.  $k$  versus  $[\text{H}^+]$  for the determination of  $k_3$ .

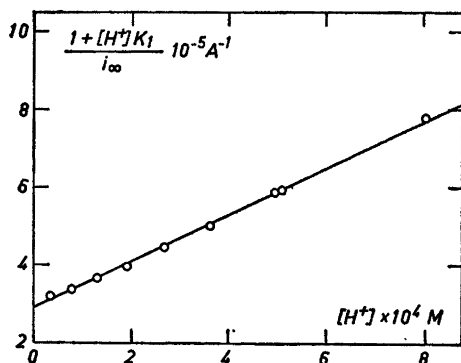


Fig. 6.  $(1 + [\text{H}^+]K_1)/i_\infty$  versus  $[\text{H}^+]$  for the determination of  $K_1$ .

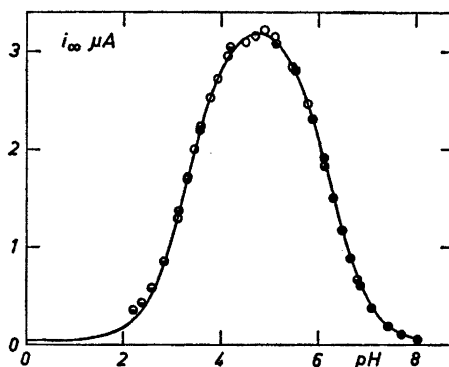


Fig. 7.  $i_\infty$  as a function of pH. The full drawn curve has been calculated by eqn. (2).  $i_B = 3.76 \mu\text{A}$ . Capillary 1. The different symbols denote different buffer systems.

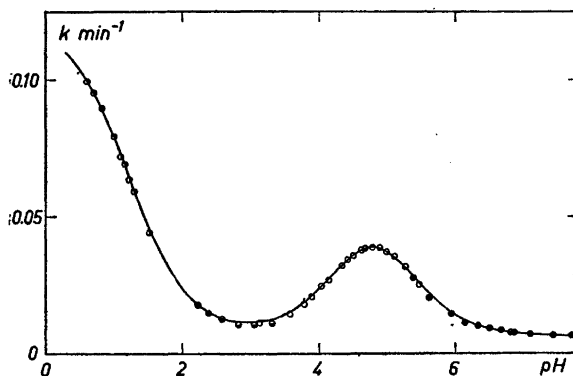


Fig. 8. The over-all rate constant  $k$  as a function of pH. The full drawn curve has been calculated by eqn. (3). The different symbols denote different buffer systems.

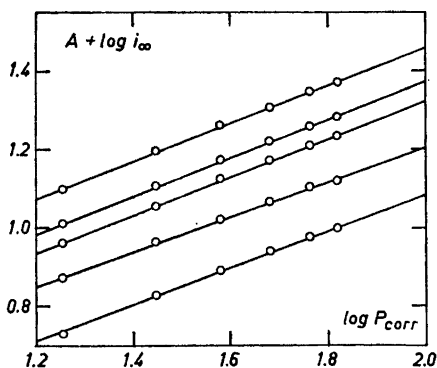


Fig. 9.  $A + \log i_{\infty}$  versus  $\log P_{\text{corr}}$  at pH = 2.82, 6.32, 5.89, 3.75, and 4.68 from below.  $A$  is 7.0, 6.9, 6.8, 6.8, and 6.8, respectively.

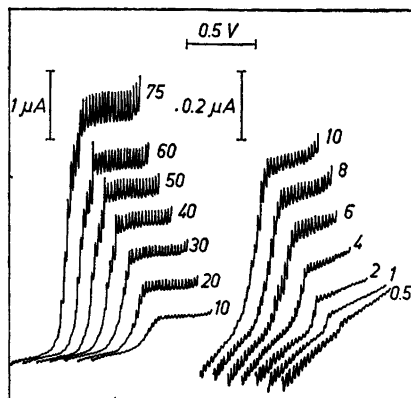


Fig. 10. Polarograms recorded at equilibrium for different dyestuff concentrations. All the polarograms start at  $E = -0.2$  V vs. SCE. pH = 4.68; Capillary 1.

#### POLAROGRAPHIC BEHAVIOUR

The wave heights are approximately proportional to the concentration of the depolarizer (*cf.* Fig. 1). They are also proportional to the square root of the height of the mercury column, as can be seen from Fig. 9. The slopes of  $\log i_{\infty}$  versus  $\log P_{\text{corr}}$  ( $P_{\text{corr}}$  = the mercury pressure in cm mercury, corrected for the back pressure) at the five pH-values represented in this figure are

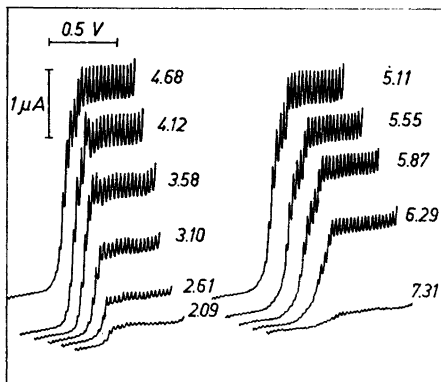


Fig. 11. Polarograms recorded at equilibrium for different pH-values. All the polarograms start at  $E = -0.2$  V vs. SCE.  $C = 75 \times 10^{-5}$  M; Capillary 1.

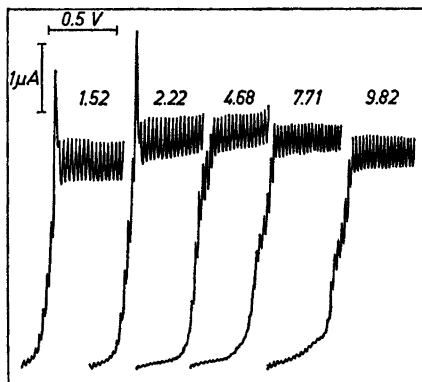


Fig. 12. Polarograms at different pH-values but comparable depolarizer concentrations, recorded 1 min after mixing equal volumes of a dye stock solution and buffer solution. All the polarograms start at  $E = -0.2$  V vs. SCE.  $C = 75 \times 10^{-5}$  M; Capillary 1.

approximately 0.5. These properties classify the limiting current as a diffusion current.

Two electrons are transferred in the reduction process as estimated from the Ilkovič equation,  $i_{\infty} = 0.607 n D^{1/2} m^{2/3} t_1^{1/6} ([B] + [G])$ .  $m = 1.92 \text{ mg}\cdot\text{sec}^{-1}$ ;  $t_1 = 4.10 \text{ sec}$ ;  $([B] + [G]) = 0.844 \times 75 \times 10^{-5} \text{ M} = 6.33 \times 10^{-4} \text{ M}$  (pH = 4.68,  $C = 75 \times 10^{-5} \text{ M}$ );  $i_{\infty} = 2.98 \times 10^{-6} \text{ A}$ ;  $D = 5.2 \times 10^{-6} \text{ cm}^2\cdot\text{sec}^{-1}$  give  $n = 1.75$ . The value of the drop-time  $t_1$  was determined in the dye solution at the half-wave potential. The value of the diffusion coefficient,  $D$ , is the value of phenolphthalein in water at 25°C determined by Kolthoff and Lehmicke.<sup>9</sup> This value was used, since phenolphthalein has about the same shape and size as Methyl Green.

As can be seen from Figs. 10, 11, and 12 the polarograms change their general appearance with pH and with the concentration of the depolarizer. At concentrations below about  $2 \times 10^{-5} \text{ M}$  the polarograms are regular within the investigated pH-range and have slopes roughly corresponding to those of a reversible two-electron wave. At greater concentrations, however, maxima and other kinds of irregularities occur. Electrocapillary curves (Figs. 13 and 14) indicate that these irregularities are adsorption phenomena. The surface tension of the mercury, represented by the drop-time, is lower in a dye solution than in the pure buffer solution already at the potential  $E = 0 \text{ V vs. SCE}$ . It can therefore be assumed that the dyestuff is adsorbed on the surface of the mercury drop and decreases the surface tension. Since the depolarizer (which might be the species B or G) is positively charged, it is reasonable to believe that the adsorption increases with increasing negative potential of the dropping mercury electrode and the electrocapillary curves pass through a maximum. At potentials corresponding to the rise of the wave the electrocapillary curves have a minimum followed by another maximum at still more negative potentials. The heights of both maxima depend on the concentration of the dyestuff and the pH of the solution. At pH > 7 the

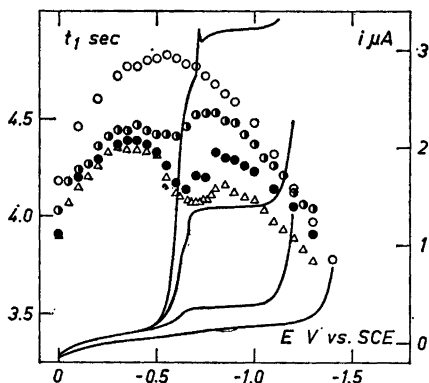


Fig. 13. Electrocapillary curves and the corresponding polarograms at different dyestuff concentrations.  $\circ$  Buffer solution;  $\bullet$   $5 \times 10^{-5} \text{ M}$ ;  $\bullet$   $30 \times 10^{-5} \text{ M}$ ;  $\triangle$   $75 \times 10^{-5} \text{ M}$ . pH = 4.68; Capillary 2.

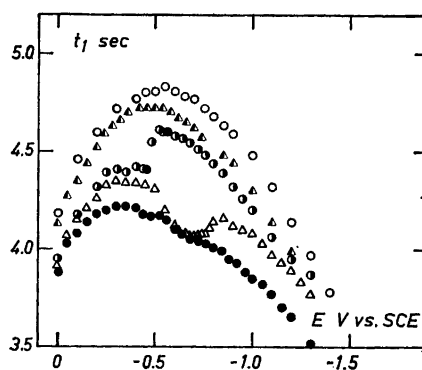


Fig. 14. Electrocapillary curves at different pH-values.  $C = 75 \times 10^{-5} \text{ M}$ ; Capillary 2.  $\circ$  0.50 M KCl;  $\triangle$  pH = 1.00;  $\triangle$  pH = 2.53;  $\triangle$  pH = 4.68;  $\bullet$  pH = 7.31.

latter maximum is hardly observable and the minimum is only an inflexion point on the curves (*cf.* Fig. 14). These observations might be interpreted as follows: When the potential of the dropping mercury electrode has reached the value at which Methyl Green is reduced, the adsorbed layer of the dyestuff disappears and the surface tension increases. The fact that the surface tension of the mercury depends on the concentration of the dyestuff at potentials corresponding to the limiting current, where virtually no dyestuff is present at the surface of the drop, indicates that also the reduction product is adsorbed on the mercury. The occurrence of a pre-wave at concentrations greater than about  $2 \times 10^{-5}$  M and  $\text{pH} \gtrsim 4$  supports this conclusion. The pre-wave is ill-defined and disappears at still greater concentrations. The splitting of the wave into two waves at  $\text{pH} \gtrsim 4$  and so great concentrations that no pre-wave can be detected might also be explained by adsorption of the reduction product, if it is assumed that the adsorbed reduction product inhibits the electroreduction. In strongly acid solutions ( $\text{pH} \leq 1$ ) the electrocapillary curves differ but little from the curves for the pure buffer solutions. This might be due to the low concentration of the depolarizer at equilibrium and the greater solubility of the dyestuff and its reduction product in strongly acid solutions.

Fig. 15 shows the half-wave potentials as a function of pH within the pH-range 0.6–7.9. The determinations were carried out in  $1 \times 10^{-5}$  M dyestuff solutions, for at this low concentration no adsorption phenomena could be detected neither on the polarograms, nor on the electrocapillary curves. The half-wave potential for each pH-value represents the mean value obtained by slow recording of the polarograms in two directions, *i.e.* from less negative potentials to more negative ones and then back, starting at negative potentials. Thereby the inertia of the recording system was eliminated as far as possible. The polarograms were recorded as soon as possible after the mixing of equal volumes of a definite dye stock solution and buffer solution in order to secure as nearly as possible equal depolarizer concentrations. The half-wave potentials decrease with pH within the pH-range 0.6–6.6 and become independent of pH for  $\text{pH} > 6.6$ . These general features of the  $E_{1/2}$ -pH-plots are found also at greater dyestuff concentrations. There are, however, some anomalies such as an increase of  $E_{1/2}$  with pH at  $\text{pH} > 6.5$  for  $C = 75 \times 10^{-5}$  M, probably due to the adsorption.

The steep rise of the polarograms, when adsorption phenomena are absent, indicates a reversible electrode reaction. Reduction of the dyestuff with

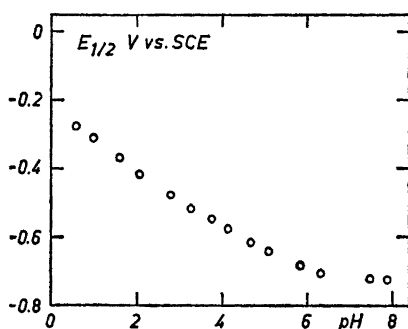


Fig. 15.  $E_{1/2}$  as a function of pH.  
 $C = 1 \times 10^{-5}$  M.

sodium sulphite did not, however, give rise to any anodic wave on the polarograms within the available potential range.

#### DISCUSSION

An investigation of the polarographic behaviour of the basic triarylmethane dyes requires a thorough knowledge of the chemical behaviour of these substances. The equilibria between coloured, electroactive species and colourless, electroinactive species with slow transitions between them might otherwise lead to erroneous interpretations of the obtained results. Information about these reactions can be obtained from spectrophotometric measurements (*cf.* Refs. 2, 3, 11). The present investigation shows that this information can be obtained also from polarographic measurements, although the precision is less good than the precision of spectrophotometric measurements (Table 4). The agreement between the two methods is excellent, despite the difference of the overall concentration of Methyl Green ( $75 \times 10^{-5}$  M *contra*  $1 \times 10^{-5}$  M). The precision of the polarographic measurements decreased markedly with decreasing concentration of the dyestuff, but even at  $C = 10 \times 10^{-5}$  M reliable results could be obtained, which agreed with the results obtained at the greater concentration. In spite of the fact that polarographic measurements are more laborious and less accurate than spectrophotometric measurements, they have the advantage that the chemical reactions are studied under exactly the same conditions that the polarographic behaviour is studied, and by the same apparatus.

A detailed discussion of the polarographic behaviour of Methyl Green will be postponed until the corresponding studies of a few other triarylmethane dyes with slightly different chemical properties, which are now in progress, have been completed. The obtained results can, however, be briefly summarized as follows: Of the five species present at equilibrium in an aqueous solution of Methyl Green only the carbonium species B or G is reducible at the dropping mercury electrode within the available potential range. The fact that the half-wave potentials become more negative with increasing pH within the pH-range 0.6–6.6 might indicate that the species G is the electro-active species. Within the pH-range 0.3–9.8 the polarographic reduction occurs by the transfer of two electrons in one step. At  $\text{pH} \gtrsim 4$  and  $C > 2 \times 10^{-5}$  M irregularities caused by the adsorption of the depolarizer and the reduction product on the mercury drops can be observed. At a sufficiently great dyestuff concentration the adsorption of the reduction product inhibits the electroreduction, and the wave is split into two adjacent waves, when pH is greater than about 4. The adsorption increases with increasing pH, and the depolarizer concentration, at which the inhibition starts, decreases with increasing pH. The slope of the polarographic wave, when adsorption phenomena are absent, indicates a reversible electrode process, but the absence of an anodic wave, when the dyestuff in solution has been partly reduced to the leuco compound by chemical means, indicates either that the electrode process is irreversible in spite of the theoretical slope of the wave, or that the immediate reduction product is not Leuko-Methyl Green.

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