

## Polarographic Studies of Basic Triarylmethane Dyes

### III. Kinetics, Equilibria, and Polarographic Behaviour of 3-Thiophene Green in Aqueous Solutions

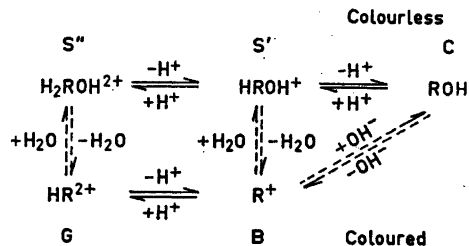
GÖSTA BENGTSSON and MAGNUS ARONSSON

*Division of Inorganic Chemistry, Chemical Centre, University of Lund, Lund, Sweden*

The kinetics and equilibria of 3-Thiophene Green in aqueous solutions, previously studied by a spectrophotometric method,<sup>4</sup> have been studied by classical polarography. The results of the two methods agree fairly well, as it was found also for Methyl Green<sup>1,2</sup> and Malachite Green,<sup>3</sup> despite the greater concentrations used in the polarographic studies. The precision of the polarographic measurements is discussed.

The polarographic behaviour of 3-Thiophene Green has also been studied. It was found to be similar to that of Malachite Green.

The polarographic studies of basic triarylmethane dyes described in previous papers<sup>1-3</sup> have been continued by a study of the kinetics, equilibria, and polarographic behaviour of the Thiophene analogue of Malachite Green (MG) called 3-Thiophene Green (3-TG)<sup>4</sup> in aqueous solutions with the ionic strength 0.49 M at the temperature 20.0°C. This dyestuff has been studied previously by a spectrophotometric method<sup>4</sup> and it was found to be very similar to MG chemically. The chemical reactions in aqueous solutions can be visualized in the following simplified manner<sup>4,5</sup>: R represents the dyestuff



nucleus, *i.e.*  $C_4H_3S \cdot [C_6H_4 \cdot N(CH_3)_2]_2$ . Full drawn arrows denote very rapid (*i.e.* momentaneous) protolytic reactions, whereas dashed arrows denote rather slow reactions with water or hydroxide ions.

The reaction rates and the equilibria can be described by a set of rate constants and equilibrium constants which were defined in Ref. 2 (*cf.* also Ref. 5).

The following two non-approximated equations, showing the dependence of the over-all wave height at equilibrium,  $i_\infty$ , and the over-all rate constant  $k$ , respectively, on the hydrogen ion concentration, can be derived:

$$i_\infty = \frac{i_B}{1 + 1/K_6 + hK_1(1 + K_2) + K_4/hK_6} \quad (1)$$

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

The notations are the same as were used in Refs. 2 and 3. In the deduction of eqn. (1) it is assumed that the over-all wave height represents the sum of the concentrations ( $[B] + [G]$ ). Eqn. (2) can be rewritten as <sup>6</sup>

$$k = \sum_{i=1}^6 f_i \quad (3)$$

where

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

Thus every  $f_i$  represents the contribution to the over-all rate constant from the reaction path in question. These non-approximated equations can be approximated, since the concentrations of some of the species and the contributions to the over-all reaction rate from some reaction paths can be neglected within some pH-ranges. From the experimentally determined values of  $i_\infty$  and  $k$  for a great number of different pH-values it is then possible to calculate the constants.

### EXPERIMENTAL

The 3-Thiophene Green Perchlorate preparation used for the spectrophotometric study <sup>4</sup> was used also for the polarographic study. Dye stock solutions were prepared by dissolving a weighed amount of the dyestuff perchlorate in acetone and then diluting with 0.50 M KCl or 0.010 M HCl + 0.49 M KCl to the final volume of the solution. In this manner it was possible to prepare aqueous dye stock solutions with the over-all dyestuff concentration  $C = 40 \times 10^{-6}$  M which were stable for a few weeks and contained more than 98 % of the dyestuff as coloured species. When the solutions were diluted and prepared for the measurements, the amount of acetone was adjusted so that the final solutions contained 2 % by volume of acetone.

Dye solutions with  $C$  as great as  $50 \times 10^{-6}$  M were prepared for one pH-value (4.68) only. This solution was stable for only a few hours, and then a precipitate was formed. It is thus evident that at this high concentration the solution was supersaturated with regard to the dyestuff perchlorate. Equilibrium was, however, established before the precipitation occurred and it was possible to record the polarogram. The obtained values of the wave heights fitted into the calibration curves (*cf.* Fig. 3). The determination of the equilibrium constants and the rate constants was carried out at the over-all dyestuff concentration  $C = 9.26 \times 10^{-6}$  M.

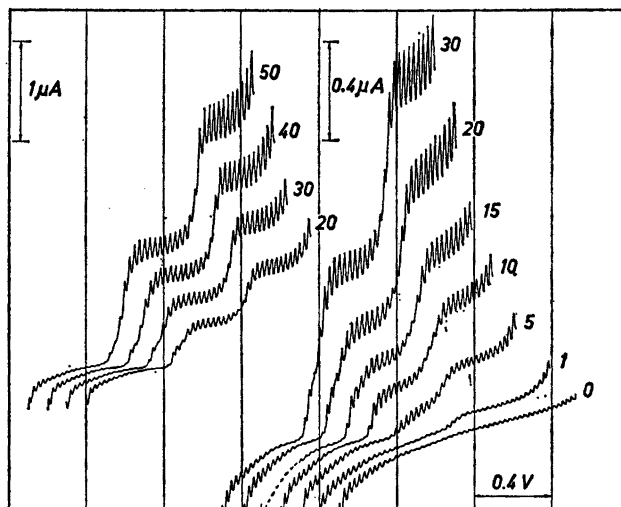


Fig. 1. Polarograms recorded at equilibrium for different over-all dyestuff concentrations at a constant pH-value. The curves start at 0 V vs. SCE. pH = 4.68. The figures beside the polarograms denote  $C \times 10^5$  M.

The composition of the buffer solutions, the apparatus, and the experimental procedure were the same as they were described in Ref. 3. Polarographic maxima appeared and were suppressed by the addition of 0.05 % of gelatine. The capillary had the following characteristics: Mercury flow rate,  $m = 2.18 \text{ mg}\cdot\text{s}^{-1}$ ; drop-time in 0.50 M KCl at the potential of the SCE,  $t_1 = 3.75 \text{ s}$ .

The polarographic behaviour of 3-TG is similar to the polarographic behaviour of MG and will be discussed more fully later in this paper. The change of the polarograms with  $C$  at a constant pH-value is shown in Fig. 1. The reduction of 3-TG gives rise to one polarographic wave, when  $C \leq 2 \times 10^{-5} \text{ M}$ . At greater concentrations there is a splitting of the polarographic curve into three waves at the pH-value (4.68) represented in the figure. For pH > 6 there are two waves on the polarographic curves at the concentration  $C = 1 \times 10^{-5} \text{ M}$  in contrast to MG. The wave heights were evaluated in the manner shown in Fig. 2. The over-all wave height at equilibrium,  $i_\infty$ , is approximately proportional to the over-all dyestuff concentration at a constant pH-value (Fig. 3) and represents the sum of the concentrations of the carbonium species B and G within the pH-range 1–5. The latter is shown by Table 1 which shows the over-all wave height,

Table 1. Experimental values of  $i_0$ .  $C = 10 \times 10^{-5} \text{ M}$ .

pH	$i_0 \mu\text{A}$	pH	$i_0 \mu\text{A}$
1.00	0.38	4.13	0.37
1.60	0.35	4.68	0.35
2.13	0.39	5.12	0.35
2.85	0.41	5.97	0.35
3.33	0.40	6.39	0.33
3.80	0.39	7.42	0.32

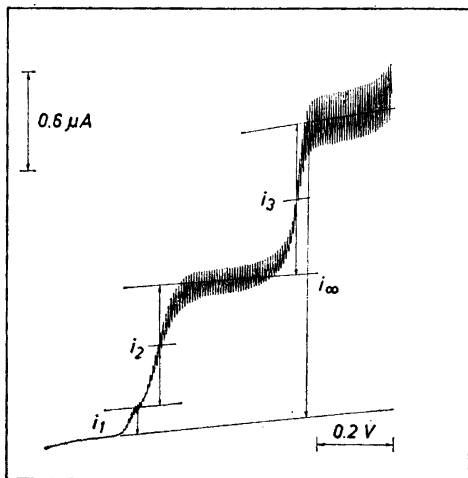


Fig. 2. Evaluation of the wave heights.

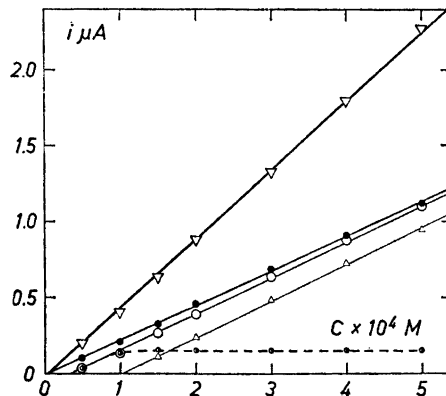


Fig. 3. The wave heights  $i_1$ ,  $i_2$ ,  $(i_1 + i_2)$ ,  $i_3$ , and  $i_\infty$  as functions of  $C$ . pH = 4.68. ●  $i_1$ ; △  $i_2$ ; ○  $(i_1 + i_2)$ ; ●  $i_3$ ; ▽  $i_\infty$ .

$i_0$ , immediately after the mixing of a definite dye stock solution (slightly buffered to pH  $\approx 4.7$ ) and a few suitable buffer solutions. For greater pH-values there is a slight decrease of  $i_0$  which might be an adsorption phenomenon, possibly due to the presence of gelatine.

#### EQUILIBRIA AND REACTION RATES

The chemical equilibria and reaction rates of 3-TG in aqueous solutions were studied as it was described for MG. The similarity between the chemical properties of 3-TG and MG made it possible to carry out the calculation of the equilibrium constants and rate constants in the same manner as was used for

Table 2. Experimental values of  $i_\infty$  in citric acid— $\text{Na}_2\text{HPO}_4$ , acetate, and phosphate buffers.  $C = 9.26 \times 10^{-5}$  M.

pH	$i_\infty$ $\mu\text{A}$	pH	$i_\infty$ $\mu\text{A}$
2.12	0.118	4.51	0.359
2.33	0.155	4.69	0.359
2.56	0.206	4.88	0.359
2.82	0.265	5.11	0.354
3.13	0.326	5.25	0.360
3.60	0.370	5.46	0.325
		5.82	0.309
3.12	0.325	5.56	0.349
3.30	0.348	5.95	0.339
3.46	0.358	6.16	0.328
3.57	0.354	6.38	0.306
3.68	0.366	6.54	0.278
3.75	0.361	6.72	0.230
3.93	0.368	6.91	0.168
4.14	0.371		

MG. With 3-TG it was, however, possible to carry out reliable kinetic measurements, starting with a partially decolourized dye stock solution, to a higher pH-value than could be done with MG. This fact made possible a more reliable determination of the equilibrium constant  $K_4 = [H^+][C]/[S']$ . The value of the rate constant  $k_3$  for the reaction  $B + H_2O \longrightarrow S'$ , obtained from kinetic measurements in phosphate buffers (pH = 6.7–7.3), is very unreliable also with 3-TG due to the precipitation of the carbinol. The rate constants  $k_5$  and  $k_6$  for the reactions  $B + OH^- \rightleftharpoons C$  could not be determined for the same reason.

Table 3. Experimental values of the over-all rate constant  $k$ .  $C = 9.26 \times 10^{-5}$  M.

pH	$k \text{ min}^{-1}$	pH	$k \text{ min}^{-1}$
0.82	0.255	4.51	0.481
0.90	0.252	4.60	0.525
1.00	0.240	4.79	0.569
1.22	0.234	4.98	0.580
1.30	0.203	5.11	0.541
1.60	0.156	5.19	0.497
		5.26	0.468
2.13	0.088	5.36	0.424
2.85	0.076	5.49	0.325
3.56	0.121	6.74	0.0196
3.76	0.173	6.93	0.0136
4.03	0.278	7.01	0.0134
4.24	0.368	7.15	0.0126
4.41	0.410	7.31	0.0131

The experimental values of  $i_\infty$  and  $k$  at different pH-values are shown in Tables 2 and 3, respectively. Figs. 4–7 show  $h/f_1$  versus  $h$  (pH = 0.8–1.6)

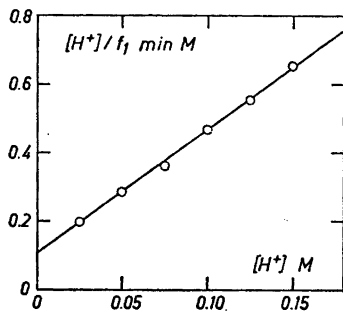


Fig. 4.  $h/f_1$  versus  $h$  for the determination of  $k_1$  and  $K_1$ .

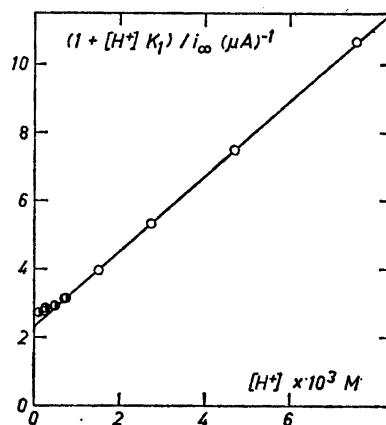


Fig. 5.  $(1 + hK_1)/i_\infty$  versus  $h$  for the determination of  $K_2$ .  $\circ$  Citric acid– $Na_2HPO_4$ ;  $\bullet$  Acetate buffers.

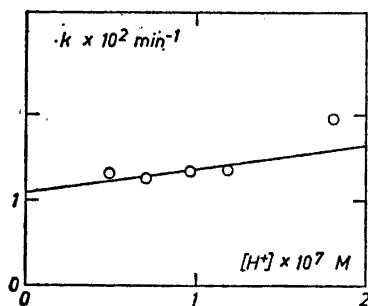


Fig. 6.  $k$  versus  $h$  for the determination of  $k_3$ .

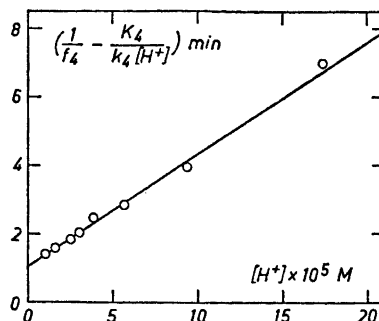


Fig. 7.  $(1/f_4 - K_4/k_4[h+])$  versus  $h$  for the determination of  $k_4$  and  $K_3$ .

for the determination of  $k_1$  and  $K_1$ ;  $(1 + hK_1)/i_\infty$  versus  $h$  (pH = 2.1–3.9) for the determination of  $K_2$ ;  $k$  versus  $h$  (pH = 6.7–7.3) for the estimation of  $k_3$ ;  $(1/f_4 - K_4/k_4h)$  versus  $h$  (pH = 3.8–5.0) for the determination of  $k_4$  and  $K_3$ , respectively (cf. Ref. 3). The obtained values of the constants are shown in Table 4 together with the corresponding values obtained from the spectrophotometric measurements.<sup>4</sup> The errors of the table are the maximum random errors estimated from the reproducibility of different series of measurements and from the estimated errors of the graphical evaluations. Fig. 8 shows  $k$  as a function of pH within the pH-range 0.3–7. The full drawn curve has been calculated with eqn. (2) using the polarographically determined values of the constants, shown in Table 4. The symbols denote experimental values.

#### POLAROGRAPHIC BEHAVIOUR

The polarographic behaviour of 3-TG is very similar to that of MG. The dyestuff is reduced at the dropping mercury electrode within the whole investigated pH-range (0.3–7.9), the carbonium species being the electroactive species. Within the pH-range 0.3–6 the polarographic curves show

Table 4. Comparison between spectrophotometrically and polarographically determined values of the equilibrium and rate constants.

	Polarographically	Spectrophotometrically
$1/K_1$ M	$0.029 \pm 0.005$	$0.033 \pm 0.001$
$K_2$	$13 \pm 2$	$12.9 \pm 0.3$
$K_3 \times 10^5$ M	$3.0 \pm 0.7$	$2.9 \pm 0.1$
$K_4 \times 10^6$ M	$6 \pm 1$	$5.3 \pm 0.2$
$1/K_5$	$0.014$	$0.0117 \pm 0.0002$
$k_1$ min <sup>-1</sup>	$0.28 \pm 0.02$	$0.296 \pm 0.006$
$k_2$ min <sup>-1</sup>	$0.021 \pm 0.006$	$0.023 \pm 0.001$
$k_3$ min <sup>-1</sup>	$0.011$	$0.0106 \pm 0.0003$
$k_4$ min <sup>-1</sup>	$1.0 \pm 0.2$	$0.91 \pm 0.03$
$k_5$ min <sup>-1</sup> M <sup>-1</sup>	—	$64.5 \pm 1$
$k_6$ min <sup>-1</sup>	—	$(1.29 \pm 0.05) \times 10^{-5}$

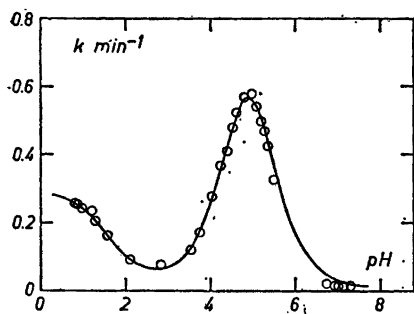


Fig. 8. The over-all rate constant  $k$  as a function of pH.

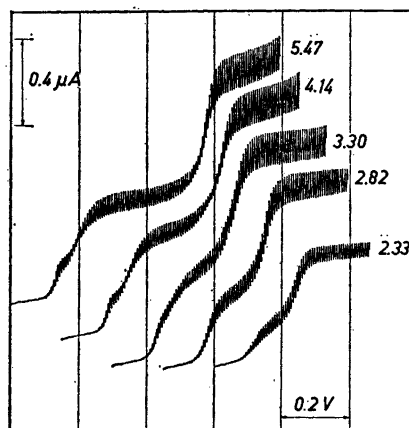


Fig. 9. Polarograms recorded at equilibrium for different pH-values. The polarograms start at  $-0.3$  V vs. SCE.  $C = 20 \times 10^{-5}$  M.

one wave, when the depolarizer concentration is below about  $2 \times 10^{-5}$  M. With increasing depolarizer concentrations two, and within some pH-ranges, three waves appear (cf. Fig. 1). In the most acid solutions only two waves can be observed. For pH-values above about 6 two waves were obtained on the polarographic curves also for  $C = 1 \times 10^{-5}$  M which was the lowest over-all dyestuff concentration for which polarograms were recorded. Within

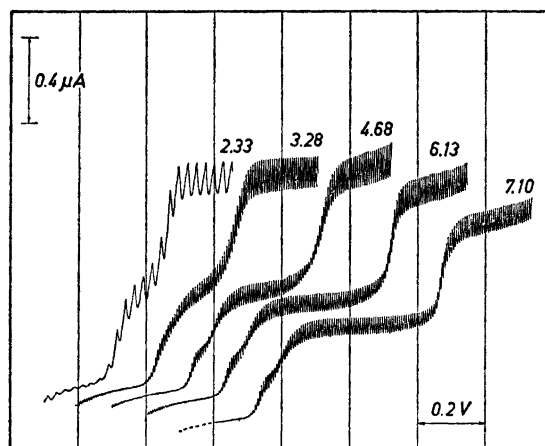


Fig. 10. Polarograms recorded as soon as possible after the mixing of a dye stock solution and buffer solutions. The polarograms start at  $-0.2$  V vs. SCE.  $C = 20 \times 10^{-5}$  M. The curve at pH = 2.33 has been recorded at a greater (4 times) scanning rate than the others.

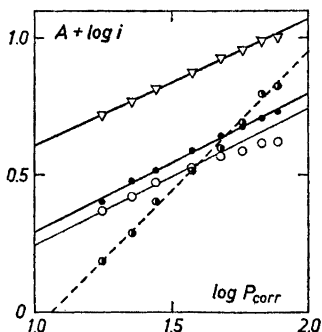


Fig. 11.  $A + \log i$  versus  $\log P_{\text{corr}}$  for the wave heights  $i_1$  (●),  $(i_1 + i_2)$  (○),  $i_3$  (●), and  $i_\infty$  (▽).  $C = 20 \times 10^{-5}$  M; pH = 4.68;  $A = 1.40, 1.00, 1.00,$  and  $1.00$ , respectively.

the whole investigated pH-range there was a spreading out of the waves over a wider potential range with increasing dyestuff concentration at a constant pH-value, and also with increasing values of pH (cf. Ref. 3). This is illustrated by Figs. 1, 9, 10, 13, and 14. Fig. 9 shows a few polarograms recorded at equilibrium for different pH-values ( $C = 20 \times 10^{-5}$  M). Fig. 10 shows a few polarograms recorded at comparable depolarizer concentrations *i.e.* as soon as possible after the mixing of equal volumes of a certain dye stock solution and a number of buffer solutions ( $C = 20 \times 10^{-5}$  M).

The three waves found within some concentration ranges and pH-ranges are numbered in the order of increasing negative potentials as waves number 1, 2, and 3 with the wave heights  $i_1$ ,  $i_2$ , and  $i_3$ , respectively, evaluated as shown in Fig. 2.

The over-all wave height at equilibrium,  $i_\infty$ , is proportional to the depolarizer concentration (Fig. 3). It is also proportional to the square root of the height of the mercury reservoir,  $P_{\text{corr}}$ , corrected for the back pressure (Fig. 11).

The wave height  $i_1$  at first increases with  $C$  and then attains an approximately constant value. In the most acid solutions wave 1 could not be recognized.  $i_1$  is approximately proportional to  $P_{\text{corr}}$ .

The sum of the wave heights ( $i_1 + i_2$ ) represents the first one of two "main waves" of approximately equal heights, which are found, when the depolarizer concentration is sufficiently great, whereas  $i_3$  represents the second. ( $i_1 + i_2$ ) increases linearly with  $C$  at a constant pH-value (and thus with the depolarizer concentration). The line cuts, however, the  $C$ -axis to the right of the origin.  $i_3$  is approximately proportional to  $C$ .  $\log (i_1 + i_2)$  versus  $\log P_{\text{corr}}$  for  $C = 20 \times 10^{-5}$  M, pH = 4.68, is not quite straight (cf. Fig. 11). Its approximately linear part has, however, a slope that is almost 0.5.  $\log i_3$  versus  $\log P_{\text{corr}}$  is a straight line with the slope 0.5.

The electrocapillary curves in Fig. 12 have been determined in acetate buffers with pH = 3.28 and 4.68. They show a close resemblance to the electrocapillary curves of MG determined under comparable conditions. The corresponding polarograms are also shown.

Fig. 13 shows the half-wave potentials  $(E_{1/2})_1$ ,  $(E_{1/2})_2$ , and  $(E_{1/2})_3$  as functions of the over-all dyestuff concentration  $C$  for pH = 4.68. These



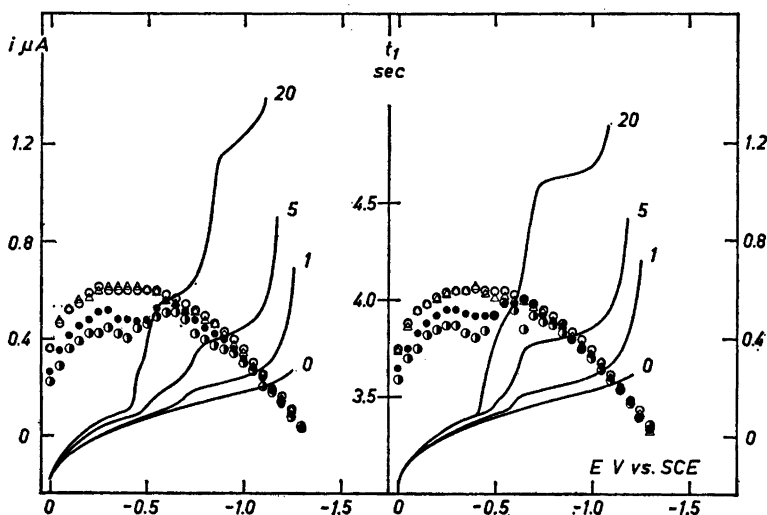


Fig. 12. Electrocapillary curves for different values of  $C$  at the pH-values 4.68 (left) and 3.28 (right).  $\circ$  0;  $\triangle$   $1 \times 10^{-5}$  M;  $\bullet$   $5 \times 10^{-5}$  M;  $\bullet$   $20 \times 10^{-5}$  M.

half-wave potentials were determined, when the solutions had reached chemical equilibrium.

Fig. 14 shows the half-wave potential of the single wave found for  $C = 1 \times 10^{-5}$  M within the pH-range 0.6–6 as a function of pH. These half-wave potentials were determined both with and without added gelatine. Fig. 14 also shows the half-wave potentials  $(E_{1/2})_1$ ,  $(E_{1/2})_2$ , and  $(E_{1/2})_3$  of waves

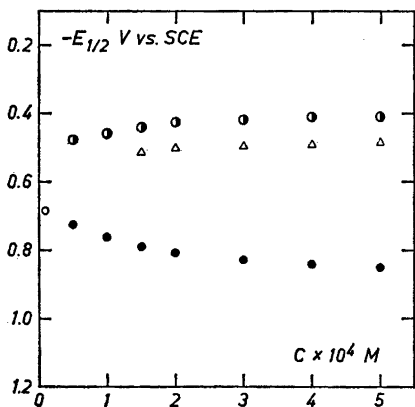


Fig. 13. The half-wave potentials as functions of  $C$ . 0.05 % gelatine. pH = 4.68.  $\bullet$   $(E_{1/2})_1$ ;  $\triangle$   $(E_{1/2})_2$ ;  $\bullet$   $(E_{1/2})_3$ ;  $\circ$   $E_{1/2}$  for the single wave found at  $C < 2 \times 10^{-5}$  M.

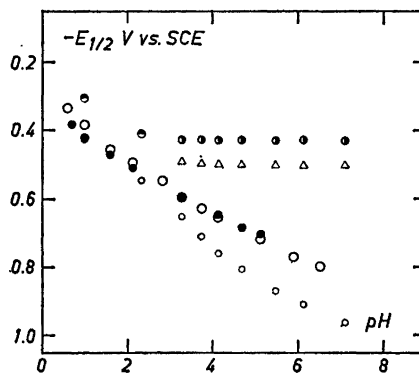


Fig. 14. The half-wave potentials versus pH.  $C = 1 \times 10^{-5}$  M:  $\circ$  without gelatine;  $\bullet$  0.05 % gelatine.  $C = 20 \times 10^{-5}$  M, 0.05 % gelatine:  $\bullet$   $(E_{1/2})_1$ ;  $\triangle$   $(E_{1/2})_2$ ;  $\circ$   $(E_{1/2})_3$ ;  $\bullet$   $(E_{1/2})_{12}$ .

number 1, 2, and 3 as functions of pH at  $C = 20 \times 10^{-5}$  M. For this concentration 0.05 % of gelatine was added. Since the half-wave potentials change with the depolarizer concentration, the polarograms from which all these half-wave potentials were evaluated, were recorded as soon as possible after the mixing of a dye stock solution (slightly buffered to  $\text{pH} \approx 4.7$ ) and buffer solution.

#### DISCUSSION

The comparison between the values of the equilibrium constants and rate constants of 3-TG determined by spectrophotometry and polarography (Table 4) shows a fairly good agreement between the two methods. The observed differences might be explained by the fact that different experimental methods have been used, and by the lower precision of the polarographic measurements.

For all three dyestuffs hitherto studied both polarographically and spectrophotometrically the results have agreed in spite of the greater dyestuff concentration used in the polarographic studies. The over-all dyestuff concentrations have been 10–75 times greater in the polarographic studies of the equilibria and reaction rates than in the spectrophotometric studies. Since this kind of dyestuffs tend to aggregate<sup>7</sup> already at rather low concentrations, it might be expected that this aggregation should influence the equilibria and the reaction rates, especially as some of the measurements have been carried out near the solubility limit of the dyestuff salt (Methyl Green). The results of the studies of Methyl Green, MG, and 3-TG do not, however, show any such influence. Thus it seems possible to use the information obtained from spectrophotometric measurements to interpret the polarographic behaviour of these dyestuffs despite the greater dyestuff concentrations generally used.

It is now also possible to make a few general remarks on the polarographic method of studying the equilibria and reaction rates of these dyestuffs. As a general rule the precision of the polarographic measurements is lower than the precision of the spectrophotometric measurements. This is especially true, when the polarograms are complicated such as with MG and 3-TG. The precision decreases markedly with decreasing depolarizer concentrations. An over-all dyestuff concentration equal to about  $5 \times 10^{-5}$  M might be regarded as the lowest practical value at which measurements can be carried out and give meaningful results. At this depolarizer concentration the experimental error, as estimated from the reproducibility, amounts to about 5 %, whereas it is below about 1 % at the depolarizer concentration  $50 \times 10^{-5}$  M. The precision of the measurements of Methyl Green was slightly better due to the less complicated polarograms. Since the polarograms change with pH and there is a decrease of  $i_0$  for MG and 3-TG at greater pH-values (*cf.* Table 1), the results obtained from equilibrium measurements seem to be less reliable than the results obtained from kinetic measurements.

The great concentrations used in the polarographic studies limit the available pH-range, since the carbinol base of most of these dyestuffs is only slightly soluble in water and precipitates at greater pH-values. For this reason the rate constants  $k_5$  and  $k_6$  could not be determined with MG and 3-TG, and the obtained values of  $k_3$  are very unreliable. For MG the equilibrium constant  $K_4$  is also very unreliable for the same reason.

The polarographic behaviour of 3-TG is very similar to that of MG. A few marked differences can, however, be noted, such as 1) the absence of the ill-defined wave 2 found with MG, 2) the absence of any post-wave, and 3) the occurrence of two waves already at  $C = 1 \times 10^{-5}$  M and  $\text{pH} > 6$  with 3-TG. It should, however, be noted that the significance of wave 2 with MG is very questionable.

## REFERENCES

1. Bengtsson, G. *Acta Chem. Scand.* **20** (1966) 1176.
2. Bengtsson, G. *Acta Chem. Scand.* **21** (1967) 1138.
3. Bengtsson, G. *Acta Chem. Scand.* **21** (1967) 2544.
4. Bengtsson, G. *Acta Chem. Scand.* **17** (1963) 2165.
5. Cigén, R. *Protolysengleichgewichte und Reaktionsgeschwindigkeiten einiger basischer Triphenylmethanfarbstoffe*, (Diss.), University, Lund 1956.
6. Ekström, C.-G. *Acta Chem. Scand.* **20** (1966) 444.
7. Hillson, P. J. and McKay, R. B. *Trans. Faraday Soc.* **61** (1965) 374.

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