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Polarographic Studies of Basic Triarylmethane Dyes

VI. The Polarographic Behaviour of Three Pyridine Analogues of Malachite Green

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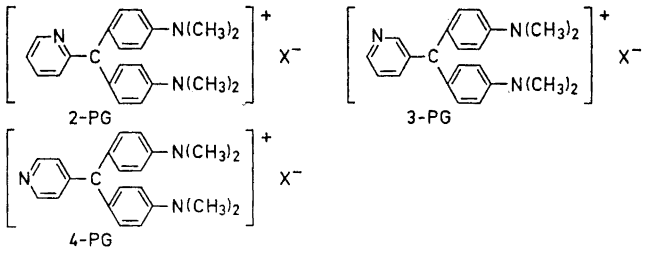
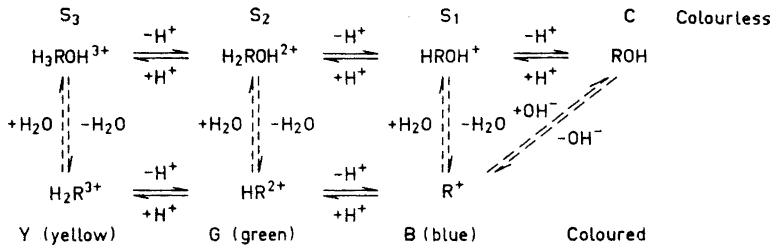
The polarographic behaviour of the pyridine analogues of Malachite Green called 2-Pyridine Green,[6] 3-Pyridine Green,[7] and 4-Pyridine Green [8] has been studied at the dropping mercury electrode and the mercury pool electrode. The behaviour of these dyestuffs is compared to the behaviour of the dyestuffs studied previously,[1–5] a reaction mechanism is discussed, and a few general remarks are made concerning the influence of the third aryl group (*i.e.* the aryl group that is different for the different dyestuffs) on the polarographic behaviour.

The polarographic studies of some basic triarylmethane dyes reported previously [1–5] have been continued by a corresponding study of three pyridine analogues of Malachite Green (MG) called 2-Pyridine Green (2-PG),[6] 3-Pyridine Green (3-PG),[7] and 4-Pyridine Green (4-PG).[8] These dyestuffs have been prepared and their protolytic equilibria, hydration equilibria, and rates of reaction with water or hydroxide ions have been studied in aqueous solutions in this laboratory by a spectrophotometric method.[6–8] They may be represented by the following schematic structural formulae:



The reactions of these dyestuffs in aqueous solutions may be written schematically in the following way:



R denotes the dyestuff nucleus shown within the brackets of the structural formulae above. Full drawn arrows denote very rapid (instantaneous) reactions whereas dasted arrows denote rather slow reactions. This reaction-equilibrium scheme is analogous to the one proposed by Cigén for Crystal Violet (CV).[9]

The pyridine group is strongly electron-attracting and causes a decrease of the electron density at the central methane carbon atom with all three dyestuffs, thus stabilizing the colourless carbinolic species as compared to MG.

EXPERIMENTAL

Dyestuff preparations. The 2-Pyridine Green Carbinol and 3-Pyridine Green Perchlorate preparations used in the spectrophotometric studies [6,7] were used also in the polarographic studies. 2-Pyridine Green Carbinol: (Found: C 75.7; H 6.91; N 12.1; O 4.56. Calc. for $C_{22}H_{25}N_3O$: C 76.0; H 7.25; N 12.1; O 4.61). 3-Pyridine Green Perchlorate:

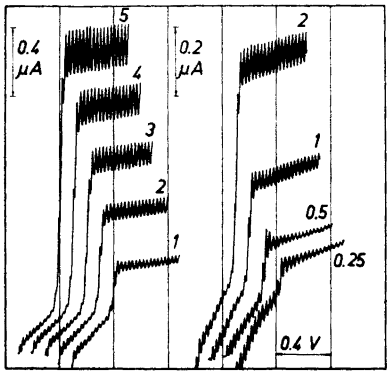


Fig. 1. 2-Pyridine Green. Polarograms recorded at equilibrium for different overall dyestuff concentrations. pH=4.68. All the polarograms start at 0 V *vs.* SCE. The figures beside the polarograms denote $C \times 10^4$ M.

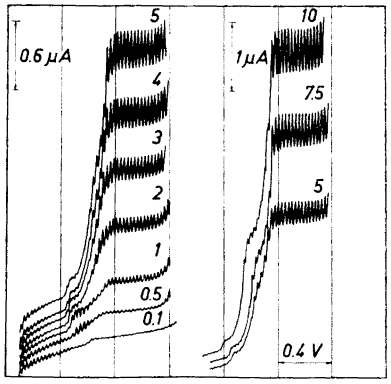


Fig. 2. 3-Pyridine Green. Polarograms recorded at equilibrium for different overall dyestuff concentrations. pH=4.68. All the polarograms on the left side start at 0 V *vs.* SCE. The figures beside the polarograms denote $C \times 10^4$ M.

(Found: C 60.0; H 5.76; N 9.23; O 15.0; Cl 9.44. Calc. for $C_{22}H_{24}N_3O_4Cl$: C 61.5; H 5.63; N 9.77; O 14.9; Cl 8.25).

The 4-Pyridine Green Perchlorate preparation used in the spectrophotometric study gave rise to two small additional waves which were probably due to impurities. When a 4-Pyridine Green Carbinol preparation was used these additional waves were absent, so this preparation was used for the polarographic studies. (Found: C 75.8; H 7.00; N 12.0; O 4.77. Calc. for $C_{22}H_{25}N_3O$: C 76.0; H 7.25; N 12.1; O 4.61).

Dyestuff solutions were prepared by dissolving a weighed amount of the dyestuff preparation in acetone and then mixing the acetone solution with the appropriate buffer solutions or with 0.50 M KCl. The solutions for which polarograms were recorded contained 2 % by volume of acetone. The composition of the buffer solutions, the apparatus, and the essential features of the experimental procedure were the same as in Ref. 2. The capillary had the following characteristics: Mercury flow, $m = 2.18$ mg $\times$ sec^{-1}; drop-time, $t_1 = 3.86$ sec, determined in 0.50 M KCl with short circuited cell.

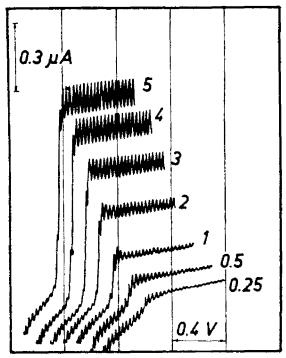


Fig. 3. 4-Pyridine Green. Polarograms recorded at equilibrium for different over-alldyes tuff concentrations. pH = 4.68. All the polarograms start at 0 V *vs.* SCE. The figures beside the polarograms denote $C \times 10^4$ M.

MEASUREMENTS AND RESULTS

A few polarograms recorded for different over-all dyestuff concentrations, C, at equilibrium at a constant pH-value (4.68) are shown in Figs. 1—3. The polarograms of 2-PG and 4-PG show one polarographic wave within the whole concentration range studied. The polarograms of 3-PG change, however, with increasing values of C in a manner analogous to that observed with many of the dyestuffs studied previously. There is an increase of the number of waves and a spreading out of the over-all polarographic curve over a wider potential range with increasing over-all dyestuff concentration. The solutions of 4-PG with $C \geq 20 \times 10^{-5}$ M were probably supersaturated with regard to the carbinol at pH = 4.68, for when the solutions were allowed to stand for a few days a white precipitate was formed. This precipitate could be dissolved in dilute hydrochloric acid. When pH of this solution was increased to about 5 by the addition of an acetate buffer, the solution turned blue.

The over-all wave heights are approximately proportional to the over-all dyestuff concentration at a constant pH-value as can be seen from Figs. 4 and 5.

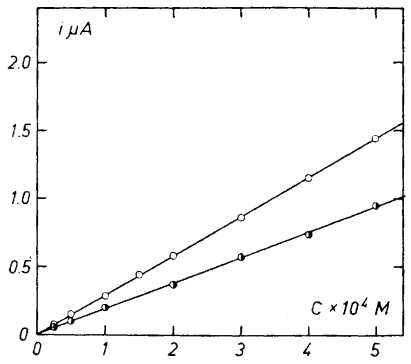


Fig. 4. 2-Pyridine Green and 4-Pyridine Green. The wave height at equilibrium, i_∞, *versus* the over-all dyestuff concentration C. pH = 4.68.

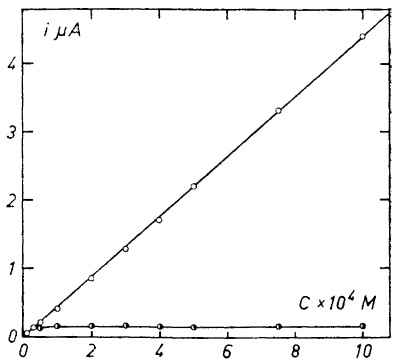


Fig. 5. 3-Pyridine Green. The over-all wave height at equilibrium (○) and the height of the pre-wave (◑) *versus* C. pH = 4.68.

The general shapes of the polarograms of 2-PG and 4-PG are independent of pH whereas the shapes of the polarograms of 3-PG change considerably with pH. A few polarograms of 3-PG recorded at different pH-values as soon as possible after the mixing of equal volumes of a 100×10^{-5} M dye stock solution in 0.48 M KCl + 4 % acetone and suitable buffer solutions are shown in Fig. 6. The change of the polarograms with pH is analogous to the change

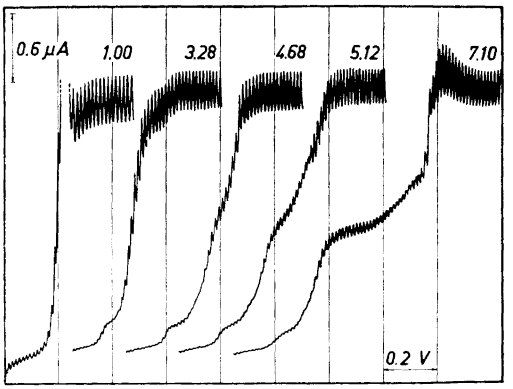


Fig. 6. 3-Pyridine Green. Polarograms recorded at comparable depolarizer concentrations. $C = 50 \times 10^{-5}$ M. All the polarograms start at −0.20 V *vs.* SCE. The figures above the polarograms denote the pH-values.

observed with MG, 3-Thiophene Green (3-TG), and *p*-Methoxy Malachite Green (*p*-MeOMG).

The over-all wave heights at equilibrium were determined for all three dyestuffs at a series of pH-values. The results are shown in Table 1 together

Table 1. A comparison between the over-all wave heights at equilibrium and the mole-% carbonium ions (B+G+Y) at equilibrium calculated from the results of spectrophotometric studies.

2-Pyridine Green

pH	i_∞ μA $C=20\times10^{-5}$ M	i_∞ μA $C=50\times10^{-5}$ M	Mole-% B + G + Y
3.28	0.09	0.30	10.4
3.75	0.30	0.75	25.5
4.14	0.47	1.15	42.0
4.40	—	1.36	50.3
4.58	—	1.43	54.1
4.68	0.60	1.45	55.6
4.78	—	1.42	56.3
4.99	0.59	—	56.5
5.12	0.53	—	55.4

3-Pyridine Green

pH	i_∞ μA $C=20\times10^{-5}$ M	i_∞ μA $C=50\times10^{-5}$ M	i_∞ μA $C=100\times10^{-5}$ M	Mole-% B + G + Y
2.28	—	0.07	—	2.5
3.28	0.29	0.74	1.50	24.0
3.75	—	1.38	—	51.3
4.14	—	1.81	3.84	72.1
4.68	0.84	2.16	4.40	84.5
5.12	—	2.11	(3.69)	85.0
5.47	0.81	2.09	(2.93)	81.3
5.80	—	1.63	—	72.7
6.13	—	1.01	—	59.0

4-Pyridine Green

pH	i_∞ μA $C=50\times10^{-5}$ M	Mole-% B + G + Y
3.28	0.14	8
3.75	0.40	19
4.14	0.66	28
4.62	0.94	36
4.68	0.95	37

with the mole-% B+G+Y calculated by the equilibrium constants determined spectrophotometrically. The available pH-range was limited by the low solubility of the carbinols which were precipitated at greater pH-values. The figures of Table 1 show a parallelism between the two sets of values which might

Table 2. A comparison between the over-all wave heights of Phenolphthalein, Methyl Green, 2-Pyridine Green, 3-Pyridine Green, and 4-Pyridine Green. Depolarizer concentration $=20\times10^{-5}$ M; pH = 4.68.

Dyestuff	i μA
Phenolphthalein	0.93
Methyl Green	1.00
2-Pyridine Green	1.06
3-Pyridine Green	1.00
4-Pyridine Green	1.04

justify the use of spectrophotometrically determined values of the equilibrium constants for the calculation of the concentrations at equilibrium of the different species. This is further supported by the results of a few kinetic measurements carried out polarographically with 3-PG and 4-PG. The obtained values of the over-all rate constants, k, for the reaction carbonium species $\rightleftharpoons$ carbinolic species are shown in Table 3 compared to the corresponding constants obtained by spectrophotometric measurements.[7,8] Table 2 shows

Table 3. A comparison between polarographically and spectrophotometrically determined over-all rate constants of 3-Pyridine Green and 4-Pyridine Green

	3-Pyridine Green Spectrophot.	Polarogr.
pH	k min^{-1}	k min^{-1}
1.00	0.0226	0.0228
2.28	0.0051	0.0050
3.28	0.0059	0.0056
	4-Pyridine Green	
	Spectrophot.	**Polarogr.**
pH	k min^{-1}	k min^{-1}
2.10	0.0068	0.0076
3.28	0.0055	0.0051
4.03	0.0089	0.0077
4.99	0.013	0.016

the over-all wave heights of the three dyestuffs which would be obtained for $([B]+[G]+[Y])=20\times10^{-5}$ M compared to the wave heights of Methyl Green (MeG) and Phenolphthalein at the same depolarizer concentration and pH-value (4.68). The value of Phenolphthalein was determined in the presence of 0.05 % gelatine. The agreement between the values indicate that two electrons are consumed for the over-all reduction of these dyestuffs.

The over-all wave heights of all three dyestuffs are approximately proportional to the square root of the mercury pressure (corrected for the back pressure). The total limiting currents are thus diffusion controlled. The depend-

Table 4. 3-Pyridine Green. The exponent b in the expression $i \propto P_{corr}{}^{b}$. $C=50\times10^{-5}$ M; pH=5.12.

Wave height	b
i_1	1.1
i_1+i_2	0.7
$i_1+i_2+i_3$	0.5
$i_1+i_2+i_3+i_4$	0.5

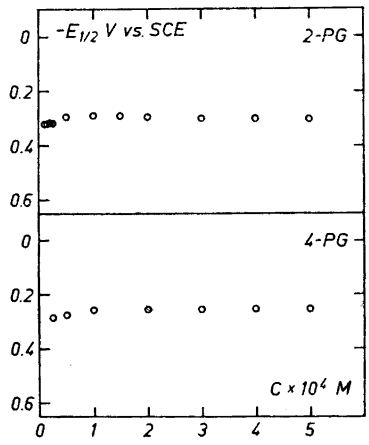


Fig. 7. 2-Pyridine Green and 4-Pyridine Green. The half-wave potential $E_{\frac{1}{2}}$ *versus* C at a constant pH-value (4.68).

ence of the different limiting currents of 3-PG is rather complicated. At pH = 5.12 four different waves can be recognized (*cf.* Fig. 6). The exponents b in the relation $i \propto P_{corr}{}^{b}$, where i represents the different sums of wave heights and P_{corr} the mercury pressure corrected for the back pressure, are shown in Table 4. The waves are numbered in the order of increasing negative potential.

The half-wave potentials of the sole wave found with 2-PG and 4-PG change somewhat with the over-all dyestuff concentration at a constant pH-value as can be seen from Fig. 7. The complicated behaviour of 3-PG does not make a corresponding figure justified for this dyestuff. The half-wave potentials *versus* pH shown in Fig. 8 were determined at the depolarizer concentration 1×10^{-5} M. With 3-PG and 4-PG the determinations were carried out as soon as possible after the mixing of an acetone stock solution of the dyestuff perchlorate (containing all of the dyestuff as carbonium species) with the buffer solution in question. Thus a depolarizer concentration as

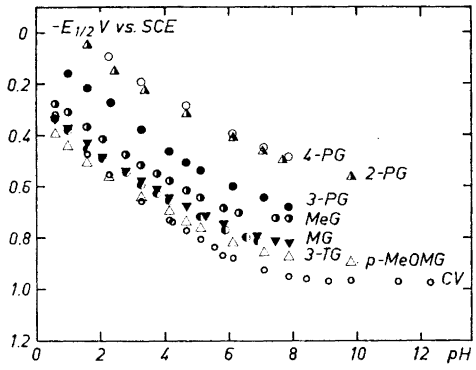


Fig. 8. $E_{\frac{1}{2}}$ as a function of pH. Depolarizer concentration = 1×10^{-5} M.

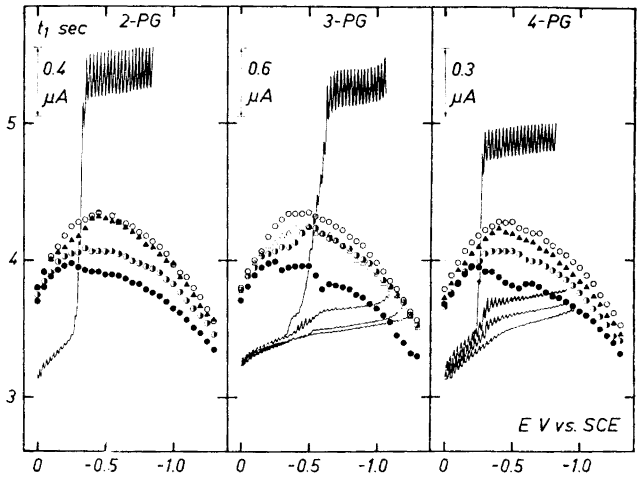


Fig. 9. Electrocapillary curves and some of the corresponding polarograms. pH = 4.68. Different symbols denote different over-all dyestuff concentrations: ○ 0; △ 1×10^{-5} M; ▲ 2.5×10^{-5} M; ◑ 5×10^{-5} M; ● 50×10^{-5} M.

near 1×10^{-5} M as possible was ascertained. With 2-PG a perchlorate preparation was not available so this procedure could not be applied. Instead a 3.6×10^{-5} M dye stock solution in 0.48 M KCl + 4 % acetone, slightly buffered to pH = 5, was prepared. In this solution the depolarizer concentration ([B]+[G]+[Y]) is equal to 2.0×10^{-5} M according to the spectrophotometric studies.[6] Samples of this stock solution were then mixed with equal volumes of suitable buffer solutions, and the half-wave potentials were determined as soon as possible after the mixing.

The electrocapillary curves shown in Fig. 9 together with some of the corresponding polarograms show that the reduction products are adsorbed on the mercury, causing a decrease of the drop-times as compared to the pure buffer solution. These curves also indicate a less marked adsorption of the depolarizer than was observed with the dyestuffs previously studied.[1-4]

3-PG and 4-PG were studied also at the mercury pool electrode.[5,9,10] The current-voltage curves show one (irreversible) cathodic maximum which checks well with the rise of the polarographic wave.

DISCUSSION

Since now a number of basic triarylmethane dyes have been studied at the dropping mercury electrode (and the mercury pool electrode), it seems possible to make a fuller discussion of the polarographic behaviour of these dyestuffs, and also to make some general remarks on the influence of the nature of the third aryl group.

The polarographic properties common to all these dyestuffs might be summarized as follows:

a) All the dyestuffs are reducible at the dropping mercury electrode and the mercury pool electrode; the carbonium species being the electro-active species as shown by the dependence of the over-all wave height at equilibrium on pH. The species B seems to be the species that is reduced (*cf.* below). The fact that the over-all wave height is proportional to the sum of the concentrations of the carbonium species seems to be due to the existence of a mobile equilibrium between these species.

b) Two electrons are consumed for the full reduction of the dyestuff. The uptake of the electrons proceeds in one or two steps depending on the nature of the dyestuff, on the concentration of it, and on the pH-value of the solution. At sufficiently low concentrations, and at low pH-values, all the dyestuffs studied, except 2-TG, yield one polarographic wave.

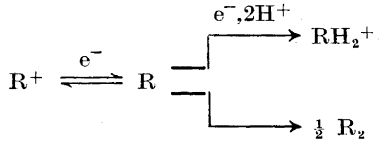
c) When the reduction proceeds in one step, the half-wave potential of the corresponding polarographic wave depends on pH in acid solutions, becoming more negative with increasing values of pH. In neutral and alkaline solutions it tends to become independent of pH. The precision of the determinations of the half-wave potentials generally decreases, however, at greater pH-values for the waves become more drawn out. This behaviour limits the available pH-range within which determinations of half-wave potentials can be carried out with a reasonable precision and might be due to a beginning splitting of the sole wave found at lower pH-values.

When two main waves are obtained the position of the first of these on the potential axis is independent of pH, except in the most acid solutions. The second main wave is, however, displaced towards more negative potentials with increasing values of pH within the pH-ranges studied.

d) The total limiting current is diffusion controlled as can be seen from the dependence of the over-all wave heights on the depolarizer concentration and on the mercury pressure.

e) Adsorption of the depolarizer or/and the reduction products occurs with all the dyestuffs studied. The adsorption of the semiquinone formed as an intermediate generally manifests itself by the appearance of a pre-wave with adsorption wave characteristics (MeG, MG, 3-TG, 2-TG, CV, and 3-PG). The adsorption is also apparent on the electrocapillary curves and on the current-voltage curves obtained at the mercury pool electrode. The adsorption of the semiquinone or the final reduction product seems to be the cause of some inhibition phenomena.

A schematic reaction mechanism has been outlined in Refs. 2—5 for those dyestuffs which are reduced at the dropping mercury electrode yielding two main waves on the polarographic curves at sufficiently great depolarizer concentrations and pH-values. For pH greater than about 2 it might be represented as follows:



R^+ denotes the carbonium ion B (*cf.* page 456).

According to this scheme the semiquinone R formed in the first step can react in two ways, either being reduced further to the final reduction product or being dimerized. The assumption of this competition between two reactions is supported by the displacement of the second main wave towards more negative potentials with increasing depolarizer concentration at a constant pH-value, and the displacement of the first main wave towards less negative potentials at the same time. The latter displacement is, however, small and also obscured by the appearance of adsorption waves, so its significance is uncertain. Furthermore, the displacement of the second main wave is too great to be ascribed solely to the competition between reduction and dimerization, and indicates an inhibition mechanism. The strongest support for the proposed reduction mechanism seems to be the appearance of two adjacent anodic minima on the current-voltage curves obtained at the mercury pool electrode (*cf.* Ref. 5).

The number of protons participating in the second reduction step was estimated from the slope of the curve obtained, when the index potential $E_{3/4}$ is plotted *versus* pH. For $C=20\times10^{-5}$ M this quantity ranges between about -0.08 V and -0.09 V. This is a quite reasonable value for an irreversible reduction involving two protons, but hardly for one involving only one proton.

For 2-PG and 4-PG the reduction process within the pH-range 2-8 can be represented by the simplified formula:

$$R^+ + 2e^- + 2H^+ \longrightarrow RH_2^+$$

The polarographic behaviour of each of the dyestuffs has been described previously, and it seems obvious that the nature of the third aryl group (*i.e.* the aryl group being different for the different dyestuffs) influences the polarographic behaviour as well as the chemical equilibria and reaction rates. The influence on the polarographic behaviour is, however, rather complicated, since the nature of the aryl group might influence many of the processes that determine the general shapes of the polarographic curves. In spite of this fact a few general remarks on the influence of the electron-attracting and electron-repelling properties of the third aryl group on the polarographic behaviour can be made.

4-PG and 2-PG contain the strongly electron-attracting 4-pyridine and 2-pyridine groups, respectively. With these two dyestuffs the full reduction proceeds in one step within the whole concentration and pH-range studied. With 3-PG and MeG, containing the electron-attracting 3-pyridine group and *p*-trimethylanilinium group, respectively, there is a tendency towards a splitting of the sole wave found at lower depolarizer concentrations into two main waves at greater depolarizer concentrations and greater pH-values. This tendency seems to be most pronounced with 3-PG. MG and 3-TG have very similar polarographic properties and contain each a weakly electron-donating aryl group. With these two dyestuffs there is a distinct splitting of the polarographic curve into two main waves at sufficiently great depolarizer concentrations and pH-values. The general trend observed when going from 4-PG

to MG is an increasing tendency towards a splitting of the over-all reduction process into two steps with decreasing electronegativity of the third aryl group. This trend seems to be continued with 2-TG containing the strongly electron-donating 2-thiophene group. *p*-MeOMG and CV, both with strongly electron-donating aryl groups fall, however, a little outside this general trend, but there is a two-step reduction also with these dyestuffs at sufficiently great depolarizer concentrations and pH-values.

The half-wave potentials of all the dyestuffs studied have been determined at different pH-values at the depolarizer concentration 1×10^{-5} M in the presence of 2% by volume of acetone. At this low depolarizer concentration there is only one polarographic wave on the polarograms, except with 2-TG and also 3-TG at greater pH-values, and no adsorption phenomena can be noticed, either on the polarograms or on the electrocapillary curves. In spite of these facts indicating that the adsorption is of minor importance it is not certain that the polarograms represent the pure reduction process without the complications observed at greater depolarizer concentrations, and the results should be treated with some care. That complications are present also at this low depolarizer concentration is indicated by the decrease of the slopes of the waves observed at greater pH-values with most of the dyestuffs. The experimental curves are summarized in Fig. 8. The curve of 2-TG has been omitted in this figure, since only the half-wave potential of the second wave could be determined with a reasonable precision. It is seen that the curve of CV has a slope in strongly acid solutions that differs significantly from the curves of the other dyestuffs which are else roughly parallel to each other. This fact indicates a different mechanism for the reduction of CV within this pH-range.

The half-wave potentials follow approximately the order of decreasing electro-negativity of the third aryl group and thus run parallel to the hydration equilibria. The spectrophotometric studies indicated that the non-protonated 2-pyridine group is less electro-negative than the 4-pyridine group whereas the protonated 2-pyridinium group is more electro-negative than the corresponding 4-pyridinium group. Thus there is a change of the relative magnitudes of the hydration-equilibrium constants K_4, K_5, and K_6 for the reactions $Y + H_2O \rightleftharpoons S_3$, $G + H_2O \rightleftharpoons S_2$, and $B + H_2O \rightleftharpoons S_1$, respectively. We have $K_{6(4-PG)} > K_{6(2-PG)}$, but $K_{5(2-PG)} > K_{5(4-PG)}$ and $K_{4(2-PG)} > K_{4(4-PG)}$. Fig. 8 shows that $E_{\frac{1}{2}(4-PG)} > E_{\frac{1}{2}(2-PG)}$. This fact indicates that the carbonium ion B probably is the species undergoing reduction at the electrode.

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