

Polarographic Studies of Basic Triarylmethane Dyes

V. The Reduction of Methyl Green, Malachite Green, *p*-Methoxy Malachite Green, and Crystal Violet at a Stationary Mercury Electrode

GÖSTA BENGTSSON

Division of Inorganic Chemistry, Chemical Centre, Box 740, University of Lund, S-220 07 Lund 7, Sweden

In order to obtain some further information about the processes occurring, when the basic triarylmethane dyes, previously studied by classical polarography,¹⁻⁴ are reduced at a mercury electrode, these dyestuffs have been studied at a stationary mercury electrode (mercury pool electrode). The results agree with the results obtained at the dropping mercury electrode although a few differences can be noted, probably due to the different nature of the two electrodes. The current-voltage curves recorded indicate that the formation of a semiquinone in the first step is a reversible process whereas the further reduction seems to be irreversible. When the reduction proceeds in only one step or when the two steps are not well separated, the overall reduction is irreversible. The appearance of the anodic branch of the current-voltage curves of Malachite Green, *p*-Methoxy Malachite Green, and Crystal Violet has been interpreted as due to a dimerization of the semiquinone. The thiophene analogues of Malachite Green could not be studied at the mercury pool electrode since the first cathodic runs poisoned the electrode surface.

In order to obtain some further information about the reaction mechanism of the reduction of some basic triarylmethane dyes previously studied¹⁻⁴ by classical polarography, these dyestuffs were studied also at a stationary mercury electrode (mercury pool electrode). The results obtained at this electrode are in the essential parts in good agreement with the results of the studies carried out by classical polarography although a few differences can be noted, which may be attributed to the different properties of the two electrodes.

EXPERIMENTAL

The mercury pool electrode consisted of an electrode vessel designed for an amalgam electrode with a cylindrical lower part of about 1 cm diameter into which an amount of mercury was poured. A platinum wire fused into a glass tube served as the electrical

lead to the mercury pool. The contact between mercury and platinum was improved by plating the part of the platinum wire protruding from the glass tube, and being immersed in the mercury pool, with mercury. If this plating was not carried out, or if the mercury layer was damaged, disturbances appeared on the current-voltage curves.

An external saturated calomel electrode served as a reference electrode. Electrical conductance between the half-cells was secured by means of an agar-agar bridge containing potassium chloride.

The current-voltage curves were recorded by a Radiometer PO 4 Polariter. The voltage scanning rate was 0.8 V/min. The mercury pool electrode was first polarized continuously from 0 V vs. SCE towards negative potentials (cathodic run) and then the change was interrupted at a suitable potential. The reversal of the direction of the polarization (anodic run) was either carried out immediately or after the electrolysis had been continued for some time at the constant potential. Several current-voltage curves could generally be recorded with the same mercury pool electrode. If the solution was stirred between the recording of successive curves the reproducibility was good. The stirring was carried out by bubbling nitrogen gas through the solution for one half to one minute.

The dyestuff preparations, the preparation of the dye solutions and the experimental procedure were else the same as those used in the classical polarographic studies.¹⁻⁴ Unless it is stated otherwise, the measurements were carried out in solutions which had reached chemical equilibrium. Some of the curves of Malachite Green (MG), *p*-Methoxy Malachite Green (*p*-MeOMG), and Crystal Violet (CV) were recorded both with and without added gelatine.

RESULTS

The results of the studies at the stationary mercury electrode are summarized in Figs. 1–8.

Methyl Green. Fig. 1 shows the current-voltage curves of Methyl Green obtained for $C=1, 5,$ and 20×10^{-5} M at pH=4.68, and for $C=20 \times 10^{-5}$ M at pH=3.28 and 7.71. The corresponding polarograms are also shown. These curves were recorded as soon as possible after the mixing of a dye stock solution in 0.50 M KCl and the buffer solution in question. Fig. 2 shows the

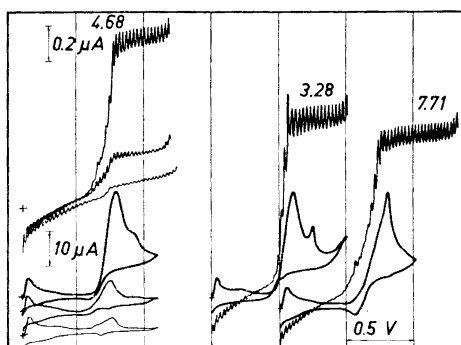


Fig. 1. Methyl Green. Current-voltage curves obtained at the mercury pool electrode compared to the corresponding polarograms obtained at the dropping mercury electrode. pH=4.68: $C=1, 5,$ and 20×10^{-5} M; pH=3.28 and 7.71: $C=20 \times 10^{-5}$ M.

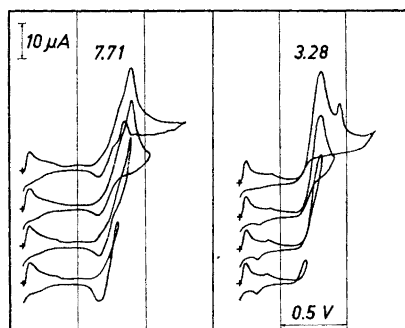


Fig. 2. Methyl Green. Current-voltage curves with the voltage scanning direction reversed at different potentials. pH=7.71 (left) and 3.28 (right); $C=20 \times 10^{-5}$ M.

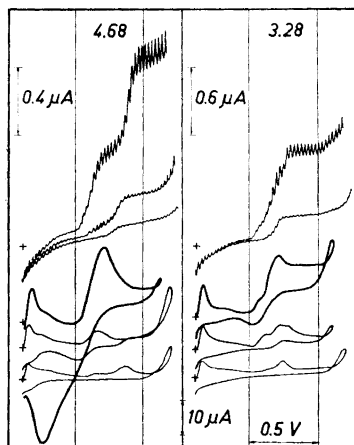


Fig. 3. Malachite Green. Current-voltage curves obtained at the mercury pool electrode compared to the corresponding polarograms obtained at the dropping mercury electrode. pH=4.68 (left) and 3.28 (right); 0.05 % gelatine; $C=1, 5,$ and 20×10^{-5} M. The polarogram at pH=3.28, $C=1 \times 10^{-5}$ M has, however, been omitted.

curves obtained at the latter two pH-values by reversing the scanning direction at different potentials. The current-voltage curves obtained at the mercury pool electrode all have a cathodic maximum immediately after the start of the cathodic run. This maximum was obtained also for the pure buffer solutions and will not be considered further. All the curves in Figs. 1 and 2 have a high cathodic maximum which checks very well with the polarographic wave obtained with the dropping mercury electrode.

Malachite Green. Fig. 3 shows the current-voltage curves of MG recorded at two pH-values (3.28 and 4.68) in the presence of 0.03 % gelatine and with $C=1, 5,$ and 20×10^{-5} M. The corresponding polarograms recorded with the dropping mercury electrode are also shown. At the lowest concentrations there are two cathodic maxima which check well with the two polarographic main waves obtained at greater depolarizer concentrations under

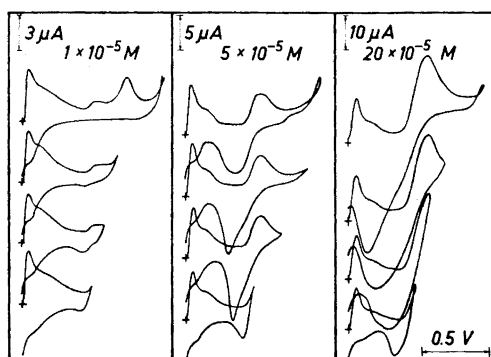


Fig. 4. Malachite Green. Current-voltage curves with the voltage scanning direction reversed at different potentials. pH=4.68; 0.05 % gelatine; $C=1$ (left), 5 (middle), and 20×10^{-5} M (right).

ordinary polarographic conditions. At greater depolarizer concentrations the curves at pH=3.28 resemble the polarographic curves. At pH=4.68 the second cathodic maximum disappears, when the depolarizer concentration is increased. The shape of the anodic branch of the current-voltage curves depended on the potential at which the cathodic run was interrupted (Fig. 4) and also on the time of electrolysis at potentials more negative than those corresponding to the first cathodic maximum. For short times of electrolysis only one sharp anodic minimum was obtained corresponding to the first cathodic maximum (or the sole cathodic maximum at greater depolarizer concentrations). With increasing time of electrolysis the anodic minimum became broader and deeper, and finally a second minimum appeared at less negative potentials. The depth of this latter anodic minimum increased with the time of electrolysis whereas the depth of the other minimum remained approximately constant.

If the voltage scanning at pH=4.68 and $C=1 \times 10^{-5}$ M was continued to potentials more negative than those corresponding to the second cathodic maximum, no anodic minima were obtained on the anodic run. At pH=3.28 the two cathodic maxima lay very close together at this dyestuff concentration and no anodic minima were obtained, irrespective of how far the cathodic run had been continued.

The curves recorded without added gelatine did not differ much from those recorded in the presence of 0.03 % gelatine. The current-voltage curves obtained at pH=7.71 agreed with those obtained at pH=4.68.

p-Methoxy Malachite Green. The current-voltage curves obtained for *p*-MeOMG at $C=1, 5,$ and 20×10^{-5} M and pH=4.68 are shown in Fig. 5 together

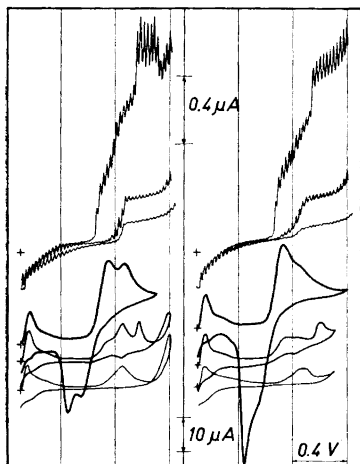


Fig. 5. *p*-Methoxy Malachite Green. Current-voltage curves obtained at the mercury pool electrode compared to the polarograms obtained at the dropping mercury electrode. pH=4.68; $C=1, 5,$ and 20×10^{-5} M; Left: No added gelatine; Right: 0.05 % gelatine.

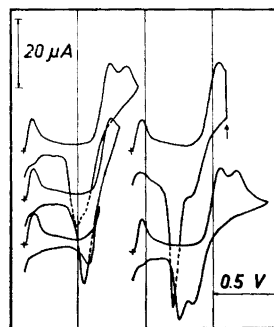


Fig. 6. *p*-Methoxy Malachite Green. Current-voltage curves with the voltage scanning direction reversed at different potentials. The vertical arrow denotes 1.00 min electrolysis at this potential. pH=4.68; $C=20 \times 10^{-5}$ M; No added gelatine.

with the polarograms obtained under ordinary polarographic conditions for the same solutions. The curves were recorded both with and without added gelatine (0.05 %). Fig. 6 shows a few current-voltage curves where the cathodic run has been interrupted at different potentials. The curves show the same general features as the corresponding curves of MG. A few marked differences can, however, be noted. Thus there is a second cathodic maximum also at $C=20 \times 10^{-5}$ roughly corresponding to the rise of the second polarographic main wave (*cf.* Fig. 5). At $C=5 \times 10^{-5}$ M the cathodic branch of the curve has a complicated shape, resembling the polarogram obtained at greater concentrations. At $C=1 \times 10^{-5}$ M there is only one irreversible cathodic maximum which, however, might actually be two overlapping maxima.

Current-voltage curves with the mercury pool electrode were recorded also at pH=3.28 and 7.10 for $C=20 \times 10^{-5}$ M in the presence of gelatine. The curve obtained at the greater pH-value agreed with that obtained at pH=4.68. The curve obtained at pH=3.28 was, however, different. The cathodic run gave rise to one high and sharp cathodic maximum with an inflexion a little above the midpoint of the rising part. The anodic branch showed one anodic minimum at the potential $E=-0.7$ V *vs.* SCE, when the scanning was continued to potentials more negative than about -0.8 V *vs.* SCE. If the cathodic scanning was interrupted and reversed within the narrow potential range -0.58 to -0.62 V *vs.* SCE a very small anodic minimum was obtained, corresponding to the rise of the cathodic maximum.

The effect of gelatine is demonstrated by Fig. 5. The addition of gelatine decreased the height of the sole maximum at $C=1 \times 10^{-5}$ M, the intermediate

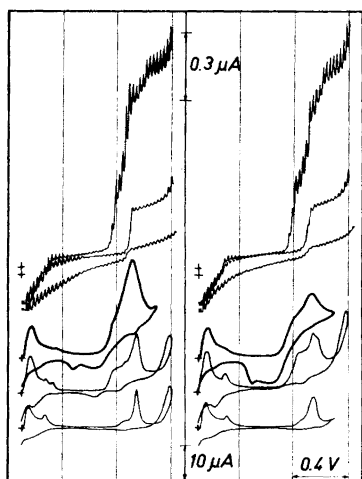


Fig. 7. Crystal Violet. Current-voltage curves obtained at the mercury pool electrode compared to the polarograms obtained at the dropping mercury electrode. pH=4.68; $C=1, 5,$ and 20×10^{-5} M; Left: No added gelatine; Right: 0.05 % gelatine.

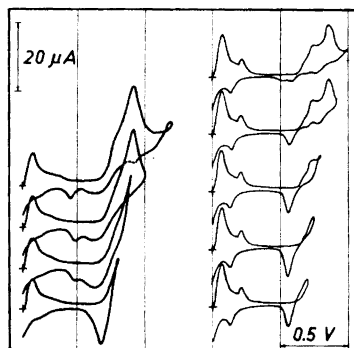


Fig. 8. Crystal Violet. Current-voltage curves with the voltage scanning direction reversed at different potentials. pH=4.68. Left: $C=20 \times 10^{-5}$ M; No added gelatine. Right: $C=5 \times 10^{-5}$ M; 0.05 % gelatine.

maximum at $C=5 \times 10^{-5}$ M, and the second maximum at $C=20 \times 10^{-5}$ M. The position of these maxima at approximately the same potential indicates a common origin.

Crystal Violet. The behaviour of CV at the mercury pool electrode was in the essential parts analogous to the behaviour of *p*-MeOMG. Figs. 7 and 8 show some of the current-voltage curves recorded at pH=4.68.

2-Thiophene Green and 3-Thiophene Green. Attempts were made to study also 2-Thiophene Green (2-TG) and 3-Thiophene Green (3-TG) at the mercury pool electrode. These were, however, unsuccessful due to the fact that the first few cathodic runs poisoned the electrode.

DISCUSSION

The studies at the mercury pool electrode support in the essential parts the conclusions drawn from the results of the classical polarographic studies, although some differences may be noted.

The obtained current-voltage curves show that the reduction corresponding to the first main wave obtained under ordinary polarographic conditions (and the first cathodic maximum) is reversible, for an anodic minimum is obtained at approximately the same potential provided the cathodic run is not continued to too negative potentials. The appearance of the first cathodic maximum at potentials which check very well with the potentials of the first polarographic main wave indicates a common reaction mechanism of the reduction process at the two electrodes.

When two well separated main waves are obtained at the dropping mercury electrode, there are generally also two cathodic maxima on the current-voltage curves obtained at the mercury pool electrode. The second maximum checks well with the second polarographic main wave and probably corresponds to the reduction of the semiquinone formed in the first step to the final reduction product. This reduction seems to be irreversible. The second cathodic maximum appears at depolarizer concentrations much lower than those at which two main waves are obtained on the classical polarograms. As a general rule the cathodic runs of the current-voltage curves obtained at the mercury pool electrode are analogous to the classical polarograms obtained at much greater depolarizer concentrations. This behaviour is probably due to the greater currents obtained at the mercury pool electrode which produce amounts of the reduction products comparable to the amounts formed at the dropping mercury electrode at much greater depolarizer concentrations. Furthermore the reduction products can accumulate at the stationary electrode whereas they are removed by the falling drops from the dropping mercury electrode.

The possibility of a dimerization of the semiquinone formed in the first reduction step has been considered in Refs. 2 and 3 on the basis of the change from one polarographic wave to two with increasing depolarizer concentration,⁵ and in Ref. 4 on the basis of the change of the "halfwave potentials" of the two main waves with increasing depolarizer concentration.^{6,7} The displacement of the first main wave is rather small and might be of the ex-

pected order of magnitude, whereas the displacement of the second main wave seems to be much greater than theory predicts.⁷

The appearance of a second anodic minimum with MG, *p*-MeOMG, and CV at less negative potentials than the minimum corresponding to the first cathodic maximum might be interpreted as a support of this view. This minimum might then be ascribed to the oxidation of the dimerized semiquinone, an oxidation which would require a more positive potential than the reoxidation of the monomer. The increase of the depth of this less negative anodic minimum with increasing time of electrolysis indicates the accumulation of great amounts of the dimer in the vicinity of the electrode surface, in the adsorbed state or as a precipitate. This view is in the essential parts identical with the conclusions drawn by Kemula and Axt-Zak⁸ from their studies of CV at the hanging mercury drop electrode. These authors could not, however, find any analogies between the curves obtained at the latter electrode and the dropping mercury electrode. The assumption that both the semiquinone and its dimer are adsorbed on the mercury seems to be verified by the present studies, at least for most of the dyestuffs studied. The appearance of a pre-wave to the first main wave with adsorption characteristics indicates the adsorption of the semiquinone. The adsorbed layer of the semiquinone and its dimer might also cause the great displacement of the second polarographic main wave by inhibiting the further reduction.⁹ This assumption is also supported by the total suppression of the second cathodic maximum with MG at greater depolarizer concentrations. With this dyestuff a corresponding inhibition was found also at the dropping mercury electrode at greater dyestuff concentrations and greater pH-values (*cf.* Ref. 2).

REFERENCES

1. Bengtsson, G. *Acta Chem. Scand.* **21** (1967) 1138.
2. Bengtsson, G. *Acta Chem. Scand.* **21** (1967) 2544.
3. Bengtsson, G. and Aronsson, M. *Acta Chem. Scand.* **22** (1968) 1241.
4. Bengtsson, G. *Acta Chem. Scand.* **23** (1969) 435.
5. Brdička, R. *Z. Elektrochem.* **47** (1941) 314.
6. Mairanovskii, S. G. *J. Electroanal. Chem.* **4** (1962) 166.
7. Mairanovskii, S. G. *Izv. Akad. Nauk. SSSR., Otd. Khim. Nauk.* **1961** 2140.
8. Kemula, W. and Axt-Zak, A. *Roczniki Chem.* **36** (1962) 737.
9. Laviron, E. and Degrand, C. *Bull. Soc. Chim. France* **1966** 2194.

Received June 21, 1968.