

## Equilibrium and Kinetic Studies on Derivatives of Malachite Green. *o*-, *m*-, and *p*-Methyl Malachite Green

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The series of investigations concerning the protolytic and hydration equilibria and the reaction rates of basic triphenylmethane dyes has been extended to cover the systems *o*-, *m*-, and *p*-Methyl Malachite Green.

Three protolytic, two hydration, and six rate constants for each dye have been determined at 20.0°C by spectrophotometric measurements in aqueous solutions of ionic strength 0.5 M.

A comparison with the values of the corresponding constants for Malachite Green shows that there is no great difference between Malachite Green and its *m*- and *p*-Methyl derivatives, whereas in the case of *o*-Methyl Malachite Green there is a very strong steric hindrance of the hydration reactions.

The *m*- and *p*-Methyl derivatives (*m*-Me-MG and *p*-Me-MG, resp.) react in a similar manner to Malachite Green (MG), and their carbinols are sufficiently soluble to allow reliable measurements to be made in phosphate buffers (pH < 8). In contrast, *o*-Methyl Malachite Green (*o*-Me-MG) behaves like the *o*-Bromo and *o*-Iodo derivatives,<sup>5</sup> *i.e.* it is decolourized at a higher pH-value than MG in alkaline solutions and at a lower pH-value than MG in acid solutions. The fading rates are much lower than for MG, and the carbinol does not permit measurements to be made in solutions with a pH-value higher than ~6. Neutral, aqueous solutions of the dyestuffs now investigated are blue (*o*-Me-MG) and blue-green (*m*- and *p*-Me-MG). In strongly acid solution they turn yellow at first and are then more or less decolourized. In alkaline solutions they are colourless. The reactions may be written schematically as in Fig. 1. Definitions of constants and symbols are the same as those reported previously.<sup>5</sup>

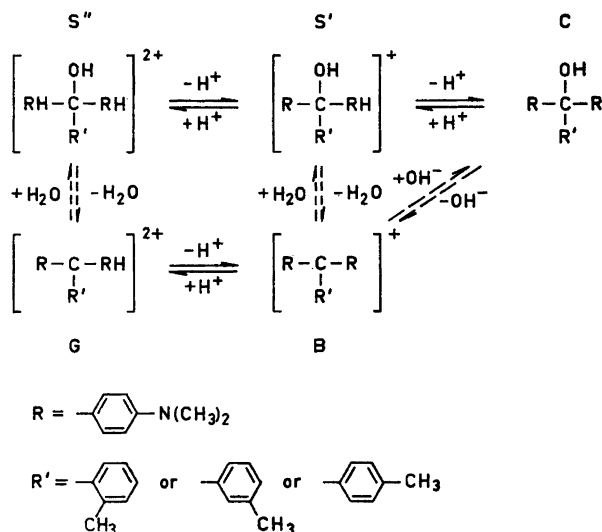


Fig. 1. Reaction scheme.

## EQUATIONS

The following expressions for  $e_0$ ,  $e_\infty$ , and  $k$  can be derived:<sup>2,3</sup>

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

$$e_\infty = \frac{e_B}{K_4/K_6 h + 1 + 1/K_6 + K_1(1 + K_2)h} \quad (2)$$

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

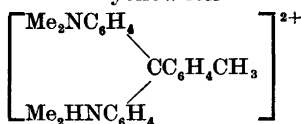
The term  $K_1 h e_C$  has been omitted in the numerators of eqns. (1) and (2) since the absorption of the species G was found to be negligible at the wavelengths where the measurements were carried out, *i.e.* at the wavelengths where the species B have their principal absorption maxima.

## EXPERIMENTAL

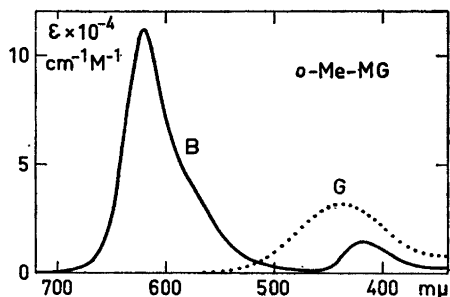
*Preparation of the dyestuffs. o-Me-MG.* The leuco compound was prepared in a nitrogen atmosphere, by condensation of 0.04 mole *o*-toluylaldehyde (Fluka) with 0.12 mole freshly distilled N,N-dimethylaniline in 10 ml conc. hydrochloric acid, 0.04 mole urea, and 50 ml ethanol. After refluxing the mixture for 20 h, a yellowish oil settled out on adding dilute ammonia. The leuco base was then purified by steam distillation, washed with hot ethanol (the oil crystallized after cooling), and recrystallized from ethanol. White needles, m.p. 86–87°C were obtained; *c.f.* Ref. 1. (Found: C 83.9; H 8.2; N 8.1. Calc. for  $\text{C}_{24}\text{H}_{28}\text{N}_2$ : C 83.68; H 8.19; N 8.13).

Fig. 2. *o*-Me-MG

Absorption curves. *B* is the curve for the blue-green ion  $[(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{CC}_6\text{H}_4\text{CH}_3]^+$  in acetate buffer. *G* is the curve for the yellow ion



in dilute hydrochloric acid.



The dyestuff was prepared by oxidizing 0.01 mole of the leuco base dissolved in 5 ml of 5 M hydrochloric acid and diluted with 500 ml of 10 % acetic acid. For the oxidizing agent, 0.01 mole of lead dioxide was used. From the oxidized product a perchlorate was prepared, and was obtained as very well crystallized gleaming golden needles after repeated recrystallization from water. (Found: C 66.7; H 6.3; N 6.0; O 14.1; Cl 8.0. Calc. for  $\text{C}_{24}\text{H}_{27}\text{N}_3\text{O}_4\text{Cl}$ : C 65.07; H 6.14; N 6.32; O 14.45; Cl 8.02).

*m*-Me-MG and *p*-Me-MG were prepared in the same manner as *o*-Me-MG. The leuco bases were obtained as white needles, m.p. 87–88°C and 73–74°C, respectively, and the dyestuffs were produced as redbrown and brownblack powders. (Found: *m*-Me-MG: C 65.7; H 6.3; N 6.2; O 14.0; Cl 7.6. *p*-Me-MG: C 64.1; H 6.1; N 6.4; O 16.0; Cl 7.8).

Stock solutions of the dyes were prepared by weighing and dissolving the perchlorates in acetone which was then diluted with potassium chloride solution, and very weakly buffered with an acetate buffer to give a final solution with ionic strength 0.5 M, pH  $\approx$  5, and containing 4 % v/v acetone. The chemicals used for the buffer solutions and the apparatus used for the measurements were the same as in Ref. 4.

### MEASUREMENTS, CALCULATIONS, AND RESULTS

The absorption curves for the three dyestuffs *o*-, *m*-, and *p*-Me-MG, have very similar shapes. For this reason, curves for only the *o*-Me-MG have been drawn (Fig. 2). The wavelengths at the absorption maxima and the molecular extinction coefficients at these wavelengths have been determined and the results are tabulated in Table 1.

Table 1. The wavelengths and the molecular extinction coefficients at the absorption maxima of the absorption curves of *o*-, *m*-, and *p*-Me-MG.

Dyestuff	Species B		Species G	
	$\lambda$ m $\mu$	$\epsilon \times 10^{-4}$ cm $^{-1}$ M $^{-1}$	$\lambda$ m $\mu$	$\epsilon \times 10^{-4}$ cm $^{-1}$ M $^{-1}$
<i>o</i> -Me-MG	418	1.5	437	3.2
	621	11.3		
<i>m</i> -Me-MG	429	2.0	456	3.5
	618	9.6		
<i>p</i> -Me-MG	430	2.2	461	3.6
	618	9.4		

Table 2. Obtained values of the initial absorbancy,  $e_0$ , in HCl-KCl buffers.  $C_M = 1.0 \times 10^{-5}$  M;  $d = 1$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 621$  m $\mu$  (*o*-Me) and 618 m $\mu$  (*m*- and *p*-Me).

[H <sup>+</sup> ] M	$e_0$		
	<i>o</i> -Me-MG	<i>m</i> -Me-MG	<i>p</i> -Me-MG
0.01	—	0.714	0.681
0.02	0.783	0.601	0.572
0.03	0.676	0.519	0.498
0.04	—	0.451	0.436
0.05	0.542	0.401	0.388
0.06	0.492	0.364	0.353
0.07	—	0.333	0.321
0.08	0.407	0.298	0.290
0.09	0.383	0.283	0.269
0.10	0.358	0.265	0.256
0.12	0.318	—	—
0.14	0.283	—	—

Table 3. Obtained values of the equilibrium absorbancy,  $e_\infty$ , in HCl-KCl buffers.  $C_M = 1.0 \times 10^{-5}$  M;  $d = 1$  cm (*o*-Me) and 5 cm (*m*- and *p*-Me);  $T = 20.0^\circ\text{C}$ ;  $\lambda = 621$  m $\mu$  (*o*-Me) and 618 m $\mu$  (*m*- and *p*-Me).

[H <sup>+</sup> ] M	$e_\infty$		
	<i>o</i> -Me-MG	<i>m</i> -Me-MG	<i>p</i> -Me-MG
$2 \times 10^{-5}$	1.105	0.905	0.870
0.01	—	0.1666	0.1866
0.02	0.692	0.0922	0.1060
0.03	0.586	0.0636	0.0742
0.04	—	0.0482	0.0566
0.05	0.450	0.0396	0.0468
0.06	0.404	0.0336	0.0398
0.07	—	0.0288	0.0346
0.08	0.328	0.0246	0.0296
0.09	0.308	0.0226	0.0270
0.10	0.285	0.0206	0.0250
0.12	0.250	—	—
0.14	0.221	—	—

*Measurements of  $e_0$  and  $e_\infty$ .* The dye stock solutions were mixed with an equal volume of a suitable buffer (HCl-KCl, acetate, or phosphate) and  $e_0$  was determined by extrapolation of the absorbancies to  $t = 0$  (Table 2);  $e_\infty$  was determined by measuring the absorbancies after at least ten half-time periods (Tables 3 and 4).

*Measurements of  $k$ .* The change in concentration of the species B was followed by spectrophotometric measurements of the absorbancies at the wavelengths where the species B have their maximum extinction. To determine the over-all rate constants in the acid region for *o*-Me-MG, it was necessary

Table 4. Obtained values of the equilibrium absorbancy,  $e_{\infty}$ , in acetate and phosphate buffers.  $C_M = 0.2 \times 10^{-5}$  M;  $d = 5$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 618$  m $\mu$ .

pH	$e_{\infty}$	
	m-Me-MG	p-Me-MG
3.42	0.788	0.769
3.65	0.832	0.812
3.89	0.862	0.832
4.13	0.875	0.842
4.50	0.894	0.862
4.78	0.892	0.857
4.98	0.892	0.852
5.26	0.885	0.847
5.46	0.879	0.847
5.81	0.862	0.835
6.04	0.837	0.815
6.43	0.762	0.749
6.79	0.639	0.640
7.00	0.542	0.554
7.26	0.402	0.426
7.44	0.310	0.344
7.55	0.261	0.292
7.70	0.203	0.230
7.83	0.157	0.179

Table 5. Obtained values of the rate constant of the over-all reaction,  $k$ , in HCl-KCl buffers.  $C_M = 0.3 - 0.8 \times 10^{-5}$  M (*o*-Me) and  $1.0 \times 10^{-5}$  M (*m*- and *p*-Me);  $d = 3-5$  cm (*o*-Me) and 1 cm (*m*- and *p*-Me);  $T = 20.0^\circ\text{C}$ ;  $\lambda = 621$  m $\mu$  (*o*-Me) and 618 m $\mu$  (*m*- and *p*-Me).

[H <sup>+</sup> ] mM	$k \times 10^2 \text{ min}^{-1}$		
	<i>o</i> -Me-MG	<i>m</i> -Me-MG	<i>p</i> -Me-MG
10	—	4.81	5.01
13.3	0.748	—	—
20	—	6.96	7.02
23.3	0.739	—	—
30	—	8.31	8.48
33.3	0.744	—	—
40	—	9.76	9.76
50	—	10.09	10.42
56	0.762	—	—
60	—	11.13	11.37
70	—	11.50	11.87
76	0.782	—	—
80	—	12.35	12.27
90	—	12.40	12.71
96	0.792	—	—
100	—	13.05	13.35
115	0.809	—	—
118	0.808	—	—
138	0.819	—	—

Table 6. Obtained values of the rate constant of the overall reaction,  $k$ , in acetate and phosphate buffers.  $C_M = 1.0 \times 10^{-5}$  M;  $d = 1$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 621$  m $\mu$  (*o*-Me) and 618 m $\mu$  (*m*- and *p*-Me).

pH	$k \times 10^2 \text{ min}^{-1}$		
	<i>o</i> -Me-MG	<i>m</i> -Me-MG	<i>p</i> -Me-MG
3.25	—	4.11	4.70
3.55	4.94	6.40	7.24
3.65	5.94	—	—
3.75	6.96	8.74	9.79
3.90	8.88	—	—
4.03	11.24	13.09	15.12
4.23	15.15	17.76	20.5
4.42	20.6	21.8	25.3
4.50	23.1	24.2	—
4.60	25.3	26.0	28.9
4.69	26.5	26.0	30.4
4.78	28.3	28.4	32.4
4.88	28.9	28.7	32.4
4.99	29.0	29.1	31.9
5.06	—	27.2	33.5
5.13	27.9	28.0	31.9
5.21	27.2	26.6	29.2
5.31	24.7	25.3	28.3
5.41	22.8	21.3	25.3
5.53	20.1	19.79	23.4
5.61	17.59	16.47	19.50
5.70	16.25	14.52	16.82
5.80	—	12.34	14.67
7.01	—	1.465	1.612
7.27	—	1.055	1.116
7.45	—	0.928	0.966
7.56	—	0.845	0.854
7.69	—	0.767	0.792
7.85	—	0.717	0.736

Table 7. Obtained values of the rate constant of the over-all reaction,  $k$ , in NaOH—KCl buffers.  $C_M = 1.0 \times 10^{-5}$  M;  $d = 1$  cm;  $T = 20.0^\circ\text{C}$ ;  $\lambda = 621$  m $\mu$  (*o*-Me) and 618 m $\mu$  (*m*- and *p*-Me).

[OH <sup>-</sup> ] mM	$k \times 10^2 \text{ min}^{-1}$		
	<i>o</i> -Me-MG	<i>m</i> -Me-MG	<i>p</i> -Me-MG
2.31	—	5.41	5.75
4.63	—	11.85	10.59
5.79	—	15.55	13.90
6.94	—	16.61	17.03
9.26	—	22.6	23.1
11.57	—	29.7	29.6
17.36	—	43.9	42.1
48.3	3.36	—	—
96.6	6.99	—	—
144.9	10.64	—	—
193.2	14.81	—	—
242	18.10	—	—

to decolourize the dye stock solution at a high pH ( $\sim 12$ ) and then make it acid (pH  $\sim 2$ ) with HCl to dissolve possible precipitated carbinol, before mixing it with suitable HCl-KCl or acetate buffers. Corresponding constants for *m*- and *p*-Me-MG were determined either directly from the dye stock solution and suitable HCl-KCl buffers or, in the acetate buffer region, from a dye stock solution, decolourized with acid, and equal volume of buffers.

In the pH-range 7–8 it was possible to perform measurements with the *m*- and *p*-Me-MG dyes: equal volumes of dye stock solution and phosphate buffers were mixed (Tables 5 and 6). In alkaline solutions the fading rates were measured after mixing dye stock solution and NaOH-KCl buffers (Table 7). The total concentration of dye used for the measurements, was 0.003–0.010 mM and the optical length of the absorption cell was 1–5 cm.

The calculations of the sought constants and their error limits were carried out as in Ref. 6. To get more reliable values of the error limits of the rate constants  $k_1$  and  $k_2$  when the equilibrium constant  $K_2$  is less than 4, the computation scheme has been modified to include a new way of computation (Fig. 3). The obtained values are collected in Table 8 together with the corresponding values of the constants for MG to serve as a convenient comparison. The rate constant of the over-all reaction and the distribution of the different species as functions of pH have been drawn in Figs. 4, 5, 6, and 7 for *o*- and *m*-Me-MG.

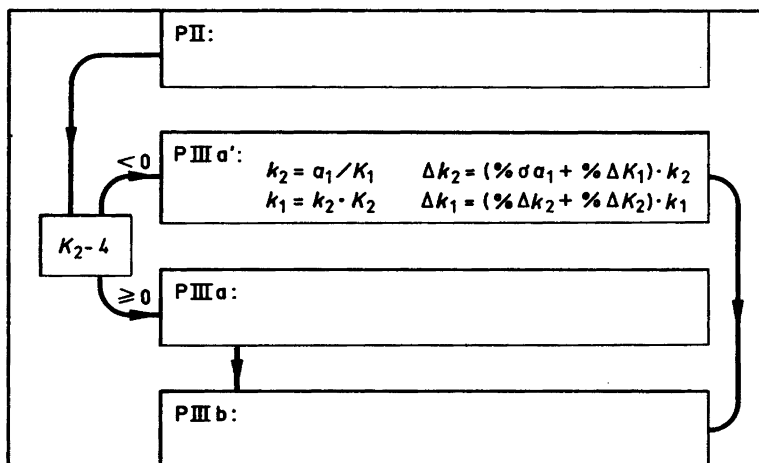
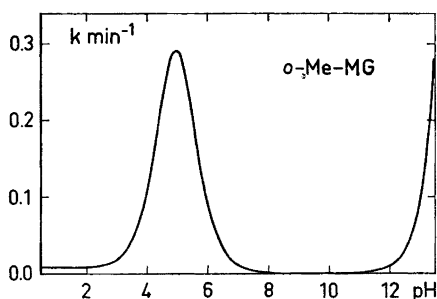
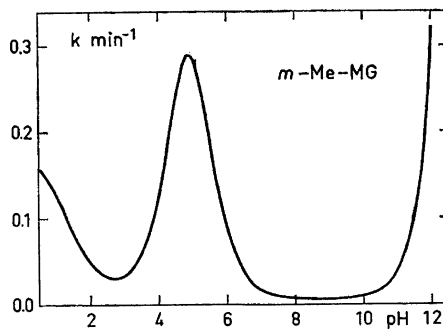
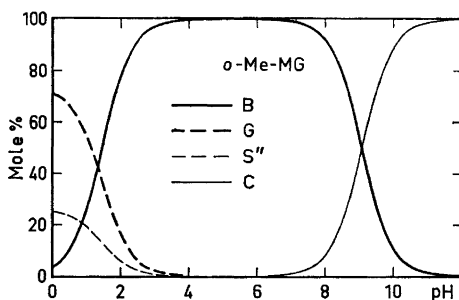
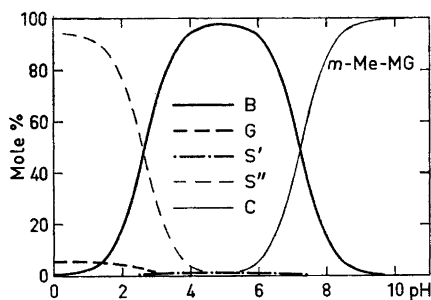


Fig. 3. Modification of the block scheme of the computation. If  $K_2$  is less than 4 the polynomial PIIIa is transformed to PIIIa' and, from the constant  $a_1$  of the latter, the rate constant  $k_2$  is computed. The relation between the polynomials is: PIIIa' = PIII/K<sub>2</sub> with

$$y = \frac{k}{\frac{K_2}{1 + K_1 h} + \frac{K_2}{K_1 K_2 h + 1/K_2}}; \quad x = h, \quad a_0 = k_3/K_2, \text{ and } a_1 = k_2 K_1.$$

Fig. 4. *o*-Me-MG.Fig. 5. *m*-Me-MG.

The rate constant of the over-all reaction,  $k$ , as a function of pH.

Fig. 6. *o*-Me-MG.Fig. 7. *m*-Me-MG.

The distribution of the dye between the different species as a function of pH at equilibrium.

## DISCUSSION

From a comparison of the constants for the methyl derivatives now investigated with those for MG it can be seen that on the amino-free phenyl ring a methyl group in the *m*- or *p*-position has a very minor influence on all of the reactions.

The small effects that can be discovered (facilitating of the dehydration reactions and hindering of the hydration reactions) are in agreement with the electron donating character of the methyl group, *i.e.* the electron density on the central methane carbon atom is a little higher in the methyl derivatives than in the unsubstituted MG. When the methyl group is in the *o*-position the hydration reactions are strongly hindered, obviously mainly due to steric hindrance ( $k_1$ ,  $k_3$ , and  $k_5$  for *o*-Me-MG have values that are only *ca.* 2 % of the values of the corresponding constants for MG), whereas the other reactions are but little influenced.



Table 8. Obtained values of the constants and their error limits of *o*-, *m*-, and *p*-Me-MG together with the values of the constants of MG. Equilibrium constants

	protolytic			hydration	
	$10^2 \times 1/K_1$ M	$K_3 \times 10^5$ M	$K_4 \times 10^6$ M	$K_2$	$10^3 \times 1/K_6$
MG	3.6	2.7	5.8	22	14.7
<i>o</i> -Me-MG	$4.8 \pm 0.1$	$2.3 \pm 0.1$	$5.0 \pm 0.2$	$0.35 \pm 0.05$	$0.17 \pm 0.03$
<i>m</i> -Me-MG	$4.2 \pm 0.1$	$2.8 \pm 0.1$	$5.3 \pm 0.3$	$17.8 \pm 0.5$	$11.1 \pm 0.5$
<i>p</i> -Me-MG	$4.3 \pm 0.1$	$2.9 \pm 0.1$	$4.9 \pm 0.3$	$14.4 \pm 0.3$	$9.7 \pm 0.5$

Rate constants

	coloured $\rightarrow$ colourless			colourless $\rightarrow$ coloured		
	$k_1 \times 10^2$ min <sup>-1</sup>	$k_3 \times 10^3$ min <sup>-1</sup>	$k_5$ M <sup>-1</sup> min <sup>-1</sup>	$k_2 \times 10^3$ min <sup>-1</sup>	$k_4 \times 10$ min <sup>-1</sup>	$k_6 \times 10^6$ min <sup>-1</sup>
MG	16.8	6.5	31.7	7.8	4.4	4.6
<i>o</i> -Me-MG	$0.23 \pm 0.04$	$0.10 \pm 0.01$	$0.77 \pm 0.01$	$6.4 \pm 0.2$	$5.6 \pm 0.1$	$11 \pm 2$
<i>m</i> -Me-MG	$16.7 \pm 0.5$	$5.9 \pm 0.1$	$25.5 \pm 0.5$	$9.4 \pm 0.5$	$5.3 \pm 0.2$	$5.4 \pm 0.7$
<i>p</i> -Me-MG	$16.9 \pm 0.4$	$5.7 \pm 0.1$	$24.5 \pm 0.7$	$11.7 \pm 0.5$	$5.9 \pm 0.2$	$6.4 \pm 0.8$

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