

Studies on Derivatives of Malachite Green. Protolytic Equilibria and Reaction Rate Constants of *o*-Methoxy Malachite Green

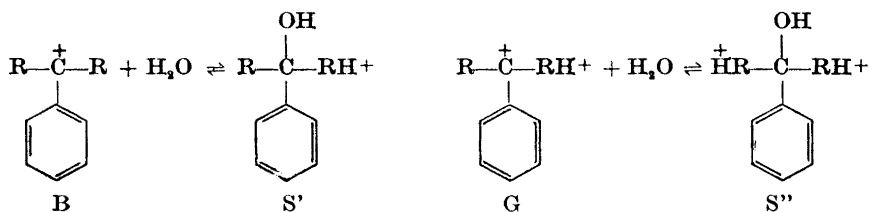
RUNE CIGÉN

*Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund,
Lund, Sweden*

Previous investigations on protolytic and hydration equilibria and reaction rates of basic triphenylmethane dyes have been continued with the investigations of *o*-methoxy Malachite Green.

Three protolytic, two hydration, and six reaction rate constants have been determined by spectrophotometric measurements in aqueous solutions with the ionic strength 0.5 M at 20.0°C.

In earlier investigations on derivatives of Malachite Green¹, with the substituent *ortho* or *para* to the central carbon atom, electrostatic and steric effects were observed in the hydration reactions similar to those shown below for Malachite Green ($R = C_6H_4-NMe_2$)



In comparison with Malachite Green, the dyes with the electron attracting substituents $-Cl$ and $-NO_2$ in the *para* position increases the tendency of the central carbon atom to bond a polarized water molecule which then splits off a proton by an intermolecular proton transfer.

With the same substituents in the *ortho* position the adding of a water molecule is made more difficult. Thus the rate constants of the reactions from left to right, stated above, are 30-50 times smaller for the *ortho* than for the *para* derivatives in adding a water molecule to the ion B, with one positive charge, and 70-300 times smaller in adding to the ion G, with two positive

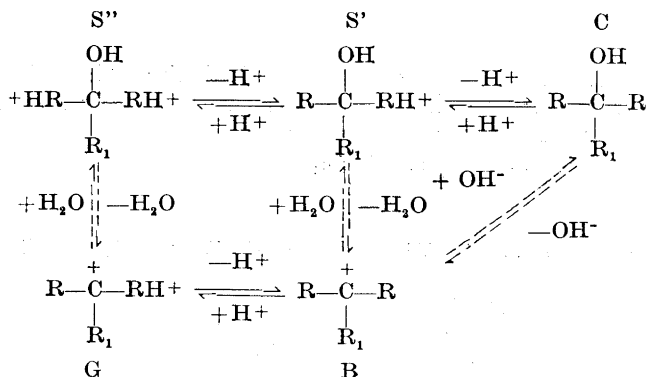
charges. At the same time the equilibria are displaced towards the coloured species B and G. This indicates a strong steric hinderance. The conditions are analogous to the previously investigated sulfonated dyestuffs of the Malachite Green type ², "Lichtgrün SF" and its *o*-chloro-derivative, "Brillantsäuregrün 6B".

Two *m*-derivatives, *m*-hydroxy MG and *m*-methoxy MG have been investigated up to the present time ³. The effect of a substituent in the *m*-position is, as a rule, small and this proved to be true for the two investigated *m*-derivatives. Rate constants as well as dissociation and hydration constants differ only 0–30 per cent from the corresponding constants of Malachite Green.

Previous investigations (Ref.¹) on *p*-hydroxy MG and *p*-methoxy MG have been continued now with investigations on *o*-methoxy MG. (The corresponding *o*-hydroxy-derivative has also been investigated and the results will be published soon.)

The "ortho"-effect of the group $-\text{OCH}_3$ (and $-\text{OH}$) is marked but not as pronounced as the effect of the groups $-\text{Cl}$ and $-\text{NO}_2$. The rate constants of the hydration and dehydration reactions of the *ortho*-methoxy- and *ortho*-hydroxyderivatives are only about a third of those of the corresponding *para*-derivatives.

o-Methoxy MG is beautifully blue-green in neutral water solutions, becomes yellow in strongly acid solutions and is colourless in alkaline solutions. The reactions which take place when the pH of a solution of *o*-methoxy MG is changed can be indicated schematically in the following manner, where $\text{R} = \text{C}_6\text{H}_4\text{NMe}_2$ and $\text{R}_1 = \text{C}_6\text{H}_4\text{OCH}_3$



Definitions of constants and symbols, *cf.* a previous article by the author (*Acta Chem. Scand.* **15** (1961) 1892).

The constants in the equilibrium scheme can be calculated if the following data are determined for a large number of solutions with varying pH: (1) The absorbance, e_0 , at the moment of mixing a dye stock solution with the appropriate buffers; (2) The absorbance, e_∞ , when equilibrium is reached; (3) The pH of the solutions; (4) The total rate constant, k , for the reactions that change the intensity of the colour of the solutions either by hydration of the coloured forms (B and G) to colourless (C, S', and S'') or *vice versa*.

EQUATIONS

The following equation for e_0 can be derived

$$e_0 = \frac{e_B + hK_1e_G}{1 + hK_1} \quad (1)$$

Eqn. (1) requires that the dyestuff is present only as the coloured form B (or G) when it is mixed with the buffer solutions. This can be realized in a dye stock solution that is buffered very weakly with acetate buffer, $\text{pH} \approx 5$. In such a stock solution the dyestuff is present to $\gg 99\%$ as the ion B.

Determination of K_1 . Eqn. (1) is transformed to

$$\frac{h}{e_B - e_0} = \frac{h}{e_B - e_G} + \frac{1}{K_1(e_B - e_G)} \quad (2)$$

The terms K_1 and e_G can be obtained from eqn. (2) by a graphical method when h , e_0 , and e_B have been determined.

The following equation for the equilibrium absorbance, e_∞ , can be derived

$$e_\infty = \frac{e_B + hK_1e_G}{1 + 1/K_6 + K_4/hK_6 + hK_1(1 + K_2)} \quad (3)$$

In acid solutions, $\text{pH} \leq 2$, eqn. (3) can be approximated and written

$$K_2 = \frac{e_G}{e_\infty} + \frac{e_B - e_\infty(1 + hK_1 + 1/K_6)}{hK_1e_\infty} \quad (4)$$

The constant K_2 can be determined from eqn. (4) when e_B , e_G and an approximate value of K_6 ($K_6 \gg 1$) are known.

In very weakly alkaline solutions eqn. (3) is approximated and transformed to

$$\frac{h}{e_\infty} = \frac{h(1 + K_6)}{K_6e_B} + \frac{K_4}{K_6e_B} \quad (5)$$

Eqn. (5) gives a straight line from which e_B and $(1 + K_6)/K_4$ are obtained.

KINETIC MEASUREMENTS

The equilibrium between the two coloured forms B and G is reached instantaneously. The same is true for the equilibrium between the colourless forms C, S', and S''. The hydration equilibrium between a coloured and a corresponding colourless form and the equilibrium $B + \text{OH}^- \rightleftharpoons C$, on the other hand, are reached only after a measurable time. The following rate expression can be derived (*cf.* Ref.^{1,4}).

$$k = \frac{k_2h^2 + k_4hK_3 + k_6K_3K_4}{h^2 + hK_3 + K_3K_4} + \frac{k_1hK_1 + k_3 + k_5\text{oh}}{hK_1 + 1} = \frac{1}{t} \ln \frac{e_0 - e_\infty}{e_t - e_\infty} \quad (6)$$

In strongly acid solutions eqn. (6) is approximated to

$$k = k_2 + \frac{k_1 h K_1 + k_3}{h K_1 + 1} \quad (7)$$

and in strongly alkaline solutions to

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

Between these two extreme approximations we can make a smaller approximation of eqn. (6) in the pH-range 4–8.

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

When pH = 7–8 eqn. (9) can be simplified further to

$$k = k_4 h / K_4 + k_3 \quad (10)$$

Approximate values of k_1 , k_2 , and k_4 can be determined from eqns. (7) and (9) while eqns. (8) and (10) give exact values of k_3 and k_5 but not of k_6 since $k_6 \ll k_3$. Then non-approximated values of k_1 , k_2 , and k_4 can be calculated from eqn. (6) when K_3 and K_4 have been determined. The rate constant k_6 is obtained from the expression $k_6 = k_5 K_w K_6 / K_4$.

The constants K_3 , K_4 , and K_6 are obtained from eqns. (9) and (5) in the following way. If k is differentiated with respect to $[H^+]$ in eqn. (9), k is found to have a maximum when $[H^+] = \sqrt{K_3 K_4}$

$$k_{\max} = \frac{k_4 K_3}{K_3 + 2\sqrt{K_3 K_4}} + k_3 \quad (11)$$

Eqn. (11) can be written

$$k_{\max} = \left(\frac{K_6}{K_4} \cdot \frac{K_4 K_3}{K_3 + 2\sqrt{K_3 K_4}} + 1 \right) k_3 \quad (12)$$

since $k_4 = k_3 K_6$. From eqn. (5) $(K_6 + 1)/K_4$ is obtained. But since $K_6 \gg 1$ for *o*-methoxy MG the expression $(1 + K_6)/K_4 \approx K_6/K_4$ can be used with sufficient accuracy. In eqn. (12) K_6/K_4 , $K_3 K_4$, k_{\max} , and k_3 are known and therefore K_3 can be calculated.

The K_4 is obtained from $\sqrt{K_3 K_4} = [H^+]_{k_{\max}}$ and K_6 from eqn. (5).

As a control of the correctness of the approximations undertaken the k -values can be calculated from the non-approximated eqn. (6), using values of the constants obtained, and the calculated results compared with those experimentally found. Further, by definition, $K_1 K_2 K_3 K_6 = 1$ which gives another possibility of control.

EXPERIMENTAL

Chemicals and solutions. *o*-Methoxy Malachite Green. The leuco compound was prepared in a nitrogen atmosphere by refluxing for 18 h *o*-methoxybenzaldehyde, (0.1 mole), *p*-dimethylaniline (0.3 mole), conc. hydrochloric acid (0.3 mole), and urea (0.1 mole). The leuco compound was recrystallized from benzene-ethanol. White needles, m.p. 152°C, were obtained. The dyestuff was prepared by oxidizing 3.6 g of the leuco compound dissolved in 5 ml of 5 M hydrochloric acid and diluted with 500 ml of 10 % acetic acid.

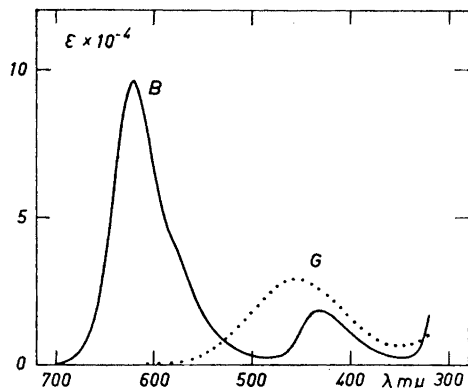


Fig. 1. *o*-Methoxy Malachite Green. Absorption curves: B is the curve for the blue-green ion $[(\text{Me}_2\text{NC}_6\text{H}_4)_2\text{CC}_6\text{H}_4\text{OMe}]^+$ in acetate buffer, G is the curve for the yellow ion $\left[\begin{array}{l} \text{Me}_2\text{NC}_6\text{H}_4 \\ \text{Me}_2\text{HNC}_6\text{H}_4 \end{array} \right] \text{CC}_6\text{H}_4\text{OMe}^{2+}$ in dilute hydrochloric acid.

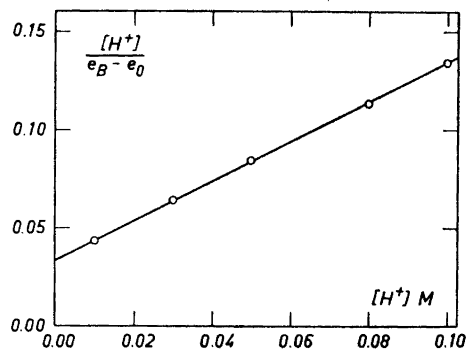


Fig. 2. $[\text{H}^+]/(\epsilon_B - \epsilon_0)$ plotted against $[\text{H}^+]$ for the determination of K_1 .

For an oxidizing agent 3.0 g of lead dioxide was used. From the oxidized product a perchlorate was prepared that was obtained as small green balls of needle-like crystals. (Found: C 62.7; H 6.01; O 17.45; N 5.89; Cl 7.51. Calc. for $\text{C}_{24}\text{H}_{27}\text{O}_6\text{N}_2\text{Cl}$: C 62.8; H 5.93; O 17.43; N 6.11; Cl 7.72).

Stock solutions of the dye were prepared in the same manner as in Ref.³ Chemicals used for the buffer solutions and apparatus used for the measurements were the same as in Ref.³

MEASUREMENTS AND RESULTS

In Fig. 1 the absorption curves are seen for the blue-green ion B in acetate buffer and for the yellow ion G in dilute hydrochloric acid. The molecular extinction coefficients were calculated from the experimentally obtained absorption curves and eqn. (3) ($\epsilon_B = C_M \cdot \epsilon_B$ and $\epsilon_G = C_M \cdot \epsilon_G$). The following values were obtained: $\lambda_{B \text{ max}} = 624 \text{ m}\mu$ and $435 \text{ m}\mu$; $\epsilon_{B \text{ max}} = 1.02 \times 10^5$ and 1.20×10^4 , resp. $\lambda_{G \text{ max}} = 452 \text{ m}\mu$; $\epsilon_{G \text{ max}} = 2.75 \times 10^4$.

Determination of K_1 . The dye stock solution was mixed with an equivalent volume of suitable HCl + KCl-buffers and ϵ_0 was determined by extrapolation of the absorbancies to $t = 0$. The measurements were carried out at the wavelength $\lambda = 620 \text{ m}\mu$, where $\epsilon_B = 9.80 \times 10^4$. In Fig. 2 $[\text{H}^+]/(\epsilon_B - \epsilon_0)$ is plotted against $[\text{H}^+]$. A straight line is obtained. The slope l and the intercept y on the y -axis of this line and eqn. (2) give ($\epsilon_B = 0.980$): $y = 0.0335 \text{ M}$; $l = 1.015$; $K_1 = 30.3 \pm 0.5 \text{ M}^{-1}$.

Determination of K_2 . The dye stock solution was mixed with HCl + KCl-buffers and the equilibrium absorbancies, ϵ_∞ , were measured in 1 and 5 cm absorption cells. K_2 was calculated from eqn. (4) where $K_1 = 30.3$ is known and $K_6 \gg 1$. $\epsilon_B = 0.980$ and $\epsilon_G \approx 0$ at the wavelength used, $620 \text{ m}\mu$. The

Table 1. *o*-Methoxy Malachite Green $\lambda = 620 \text{ m}\mu$; $\epsilon_B = 0.980$; $T = 20.0^\circ\text{C}$. Determination of K_1 , K_2 , and k_1 .

[H ⁺] M	e_∞	K_2	e_0	$k \text{ min}^{-1}$	$k_1 \text{ min}^{-1}$
0.010	0.359	4.71	0.748	0.0248	0.0487
0.020	0.220	4.70			
0.030	0.159	4.67	0.512	0.0361	0.0491
0.040	0.124	4.70			
0.050	0.1026	4.65	0.385	0.0426	0.0497
0.060	0.0878	4.59			
0.080	0.0674	4.58	0.272	0.0477	0.0496
0.100	0.0546	4.59	0.232	0.0516	0.0514

Mean

 $K_2 = 4.65$ $k_1 = 0.0497$ $k_2 = 0.0107$

Table 2. *o*-Methoxy Malachite Green. E_∞ -values for determination of $K_4/(K_4 + 1)$. $\lambda = 624 \text{ m}\mu$; $C_M = 2.5 \times 10^{-6} \text{ M}$; $d = 2 \text{ cm}$; $T = 20.0^\circ\text{C}$.

[H ⁺] $\times 10^8 \text{ M}$	E_∞
14.00	0.453
8.24	0.427
3.72	0.360
1.844	0.280
0.774	0.168

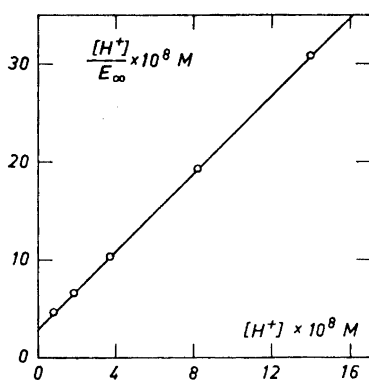


Fig. 3. $[\text{H}^+]/E_\infty$ plotted against $[\text{H}^+]$ for the determination of $K_4/(K_4 + 1)$.

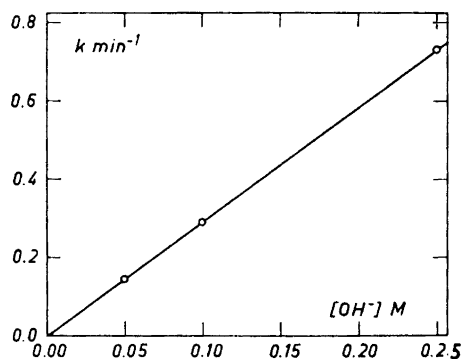


Fig. 4. The total rate constant k plotted against $[\text{OH}^-]$ for the determination of k_5 .

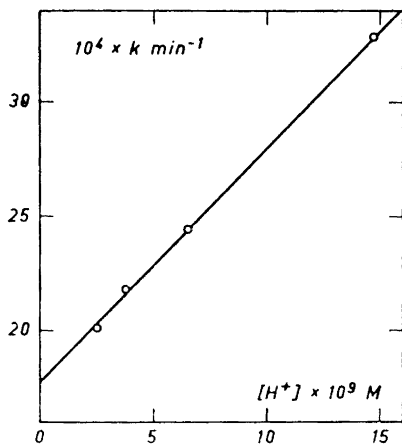


Fig. 5. The total rate constant k as a function of $[H^+]$ for the determination of k_3 .

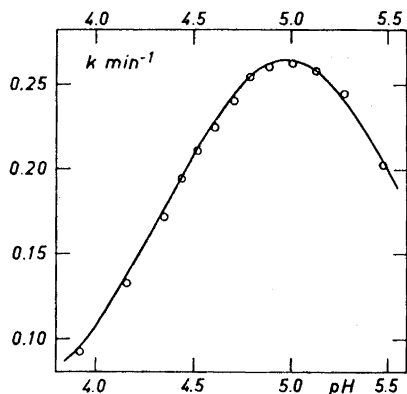


Fig. 6. The total rate constant k as a function of pH. The points represented by the symbols, O, are obtained experimentally; the full drawn curve is calculated from the non-approximated eqn. (6).

results are recorded in Table 1. From this table the mean value $K_2 = 4.65 \pm 0.10$ is obtained.

Determination of $K_4/(K_6 + 1)$. The dye stock solution was mixed with appropriate phosphate buffers and the equilibrium absorbancies, E_∞ , (Table 2) were read off after 42 h. $C_M = 2.5 \times 10^{-6} \text{ M}$, $d = 2 \text{ cm}$, $\lambda = 624 \text{ m}\mu$, $T = 20.0^\circ \text{C}$. In Fig 3 $[H^+]/E_\infty$ is plotted as a function of $[H^+]$. A straight line is obtained which gives $l = 1.988$, $y = 2.90 \times 10^{-8} \text{ M}$ and from eqn. (5) $K_4/(K_6 + 1) = 1.46 \times 10^{-8} \text{ M}$ is obtained.

Kinetic measurements. If the dye stock solution is mixed with NaOH + KCl-buffers, the solutions are decolorized with a rate that is directly proportional to $[\text{OH}^-]$. In Fig. 4 the rate constants of the decolorization are plotted against $[\text{OH}^-]$. A straight line is obtained which passes almost through the origin. This means that in this pH-range $k_3 + k_6 \ll k_5 \cdot \text{oh}$. Therefore, only k_5 can be determined from Fig. 4; $k_5 = 2.90 + 0.03 \text{ min}^{-1} \text{ M}^{-1}$.

The rate constant k_3 was determined from kinetic measurements in borate buffers, pH = 7.8–8.6. The approximate eqn. (10) can be used since $k_6 + k_5 \text{oh} \ll k_3$ in this pH range. In Fig. 5 k is plotted as a function of $[H^+]$. From the straight line $k_3 = 0.00177 \pm 0.00002 \text{ min}^{-1}$ is obtained.

Determination of k_1 and k_2 . These rate constants were determined by kinetic measurements on the fading which is caused by the reactions $G + \text{H}_2\text{O} \rightleftharpoons \text{S}''$ and $B + \text{H}_2\text{O} \rightleftharpoons \text{S}'$ in HCl + KCl-buffers. Table 1 contains k -values experimentally found and values of k_1 and k_2 calculated from eqn. (6) (Approximate values of k_1 and k_2 were calculated initially from eqn. (7).) The following values were obtained: $k_1 = 0.0497 \pm 0.0010 \text{ min}^{-1}$ and $k_2 = 0.0107 \pm 0.0003 \text{ min}^{-1}$.

Determination of k_4 , K_3 , K_4 , and K_6 . The dye stock solution was partially decolorized by making it 0.02 M with respect to hydrochloric acid. The following reactions then occur in the forward direction (\rightarrow):

$B + H^+ + H_2O \rightleftharpoons G + H_2O \rightleftharpoons S''$ and $B + H^+ + H_2O \rightleftharpoons S' + H^+ \rightleftharpoons S''$. This partially decolorized dye solution was then quickly mixed with acetate buffers and the colour was more or less restored owing to the reactions above in the reverse direction. The rate constants for the restoring of the colour were determined.

In Fig. 6 k is plotted as a function of pH. The following values are obtained: $k_{\max} = 0.263 \text{ min}^{-1}$ when $\text{pH} = 4.99$ which gives $\sqrt{K_3 K_4} = 1.024 \times 10^{-5} \text{ M}$ since k has a maximum when $[H^+] = \sqrt{K_3 K_4}$. Then $K_3 = (2.83 \pm 0.04) \cdot 10^{-5} \text{ M}$ is obtained from eqn. (12) since $K_4/(K_6 + 1) = 1.46 \times 10^{-8} \text{ M}$ and $K_6 + 1 \approx K_6$. The expression $K_3 K_4 = 1.05 \times 10^{-10}$ gives $K_4 = (3.71 \pm 0.05) \times 10^{-6} \text{ M}$ and K_6 is calculated from the determined value of $K_4/(K_6 + 1)$; $K_6 = 253 \pm 4$.

The remaining rate constants k_4 and k_6 are calculated from $k_4 = k_3 K_6$ which gives $k_4 = 0.448 \pm 0.010 \text{ min}^{-1}$ and from $k_6 = k_5 K_w K_6 / K_4$ which gives $k_6 = (2.45 \pm 0.10) \times 10^{-6} \text{ min}^{-1}$.

As can be seen in Fig. 6 the agreement between the experimentally determined k -values and those calculated from the non-approximated eqn. (6) is good. By definition, $K_1 K_2 K_3 K_6 = 1$. The determined values of these constants give $K_1 K_2 K_3 K_6 = 1.01$.

The author is indebted to Mr Olle Nilsson for valuable help in preparing the dye and to Fil.Mag. Gösta Bengtsson for assistance in some of the kinetic measurements.

The English has been revised by Dr D. Karipides (USA).

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Received June 5, 1961.